

**Geodynamic Evolution of the Aegean Back-arc
and its Implication for
Associated Precious and Base Metal Mineralization**

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Abstract

The exposed metamorphic core complexes in the Cyclades continental back-arc of south-east Greece host a range of base and precious metal deposits. Shallow crustal mineral deposits that formed since the late Miocene to active seafloor hydrothermal systems occur in the footwall and hanging wall of the major detachment systems and within all tectono-stratigraphic units. The carbonate-replacement, vein-type, intermediate-sulfidation epithermal, and skarn deposits tapped different sources of metals and fluids along the major low-angle detachment systems and steep normal faults. This study links the regional metallogenic diversity to fluid and crustal sources, within a framework of the evolving geodynamic context and complex basement structure.

Over 30 mineral occurrences, from Lavrion of Attica on the Greek mainland across the Cycladic archipelago to Milos and Santorini on the active South Aegean volcanic arc, were investigated, encompassing $\sim 40,000$ km² of the arc- to backarc system. Petrographic observations are combined with mineralogical, geochemical, and isotopic analyses (Pb, Sr, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) of galena (PbS) and ore-associated hydrothermal barite (BaSO₄).

New galena Pb isotope data complemented by Pb isotope data of galena from the literature exhibit a range of isotopic ratios, with a resolvable geologic pattern. Galena from deposits in the north-central Cyclades has low $^{206}\text{Pb}/^{204}\text{Pb} \leq 18.84$, while galena from the west Cyclades has higher $^{206}\text{Pb}/^{204}\text{Pb} \geq 18.84$. This distinct regional pattern is further

supported by the Sr isotope signature of hydrothermal barite, with $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.711$ in the north-central Cyclades and $^{87}\text{Sr}/^{86}\text{Sr} \leq 0.711$ in the west Cyclades. When considered together with compiled Pb and Sr isotope data of potential source rocks, large-scale regional patterns in the isotopic signatures are recognized, suggesting two distinct sources of lead and strontium in the underlying basement of the core complexes. These two sources (Lower Cycladic Blueschist Nappe and Upper Cycladic Blueschist Nappe including the Cycladic Basement) correspond to known tectono-stratigraphic units of different provenance and age and help to correlate the basement over considerable distances, even where exposures are limited.

Sulfur and oxygen isotope data of barite indicate variable contributions of sulfur from seawater and magmatic fluids among the range of deposit types. This indicates that different fluid generations evolved and tapped the basement, likely along the major detachment faults. The $\delta^{34}\text{S}$ values of barite indicate that mineral deposits in the Cyclades can be clearly distinguished.

Compiled whole-rock isotopic and geochemical data of the basement lithologies exhibit a broad dispersion. Miocene to recent mineralization in the Cyclades caused homogenization of the crustal sources and indicate regional lithological differences in the architecture of the exposed metamorphic core complexes. This thesis demonstrates that regional studies of the geochemical and isotopic composition of mineral deposits can provide additional constraints for the paleogeographic reconstruction of juxtaposed tectono-stratigraphic units across the Cyclades and other complex continental back-arc systems.

Résumé

Les dômes métamorphiques cycladiques en Grèce, qui se développent au sein d'un système d'arrière-arc continental, contiennent une grande diversité de gisements de métaux communs et précieux. Des gisements peu profonds de minerais, formés depuis le Miocène supérieur jusqu'à des systèmes hydrothermaux océaniques, ont été découverts d'une part aussi bien dans le mur que dans le toit des systèmes de détachement et d'autre part dans l'ensemble des unités tectoni-stratigraphiques impliqués dans les dômes métamorphiques. Les métaux et les fluides des gisements épithermaux de type substitution de carbonates, filoniens et de sulfuration modérée ainsi que ceux des gisements de type skarn occurring dans les failles de détachement et dans les failles normales proviennent de différentes sources. L'objectif de ce travail est d'étudier les liens entre la diversité métallogénique régionale et les sources des fluides et des métaux dans un contexte géodynamique changeant et au sein d'une structure crustale complexe.

Plus de 30 occurrences de gisements de minerais affleurant depuis Lavrio, en Attique en Grèce continentale jusqu'à Milos et Santorin, en passant par l'archipel des Cyclades, ont été étudiés, ce qui représente environ 40,000 km² de surface d'un système arc/arrière-arc. Des observations pétrographiques ainsi que des analyses minéralogiques, géochimiques et isotopiques (Pb, Sr, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) ont été effectuées sur de la galène (PbS) et de la barytine (BaSO₄) hydrothermale associée aux minerais.

Les nouvelles données isotopiques du Pb sur la galène, complétées par des données de la littérature, montrent une variation des rapports isotopiques en fonction de leur répartition géographique. Ainsi la galène, issue des gisements des Cyclades septentrionales, a de faibles rapports $^{206}\text{Pb}/^{204}\text{Pb}$, inférieur à 18.84, tandis que la galène, provenant des Cyclades occidentales, a des rapports $^{206}\text{Pb}/^{204}\text{Pb}$ plus élevés, supérieurs à 18.84. Ces variations géographiques régionales sont également observées dans la signature isotopique du Sr de la barytine hydrothermale, avec des rapports $^{87}\text{Sr}/^{86}\text{Sr}$ supérieurs à 0.711 dans la région septentrionale et des rapports $^{87}\text{Sr}/^{86}\text{Sr}$ inférieurs à 0.711 dans la région occidentale des Cyclades. En associant les données isotopiques du Pb avec celles du Sr des roches mères potentielles, des variations régionales à grande échelle des signatures isotopiques sont mises en évidence et suggèrent des sources crustales en plomb et en strontium différentes. Ces deux sources correspondent à des unités tectono-stratigraphiques connues, d'origine et d'âge différents, et permettent d'avoir une meilleure connaissance de la nature du socle sous-jacent sur de grandes distances, en particulier quand son exposition à la surface est limitée.

Les données sur les isotopes du soufre et de l'oxygène de la barytine montrent des contributions variables du soufre provenant de l'eau de mer et des fluides magmatiques au sein des différents types de gisements. Cela semble indiquer que les différentes générations de fluides ont évolué et ont contaminé le socle probablement au sein des failles de détachement majeures. Les valeurs de $\delta^{34}\text{S}$ de la barytine révèlent que les gisements de minerais dans les Cyclades peuvent être clairement différenciés par les signatures isotopiques des barytines.

Une compilation des données isotopiques et géochimiques des roches totales des lithologies du socle montre une grande dispersion des valeurs. Les minéralisations du Miocène à l'actuel dans les Cyclades provoquent une homogénéisation des différentes sources crustales et indiquent des différences lithologiques régionales au sein de la structure des dômes mé-

tamorphiques à l’affleurement. Les résultats de cette thèse démontrent que des études, à l’échelle régionale, des compositions géochimique et isotopique des gisements minéralisés peuvent fournir un nouvel outil pour les reconstructions paléogéographiques des différentes unités tectono-stratigraphiques des Cyclades ou d’autres systèmes d’arrière-arcs continentaux complexes.

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Contents

Abstract	ii
Résumé	iv
Acknowledgements	vii
Contents	ix
List of Figures	xiv
List of Tables	xviii
Abbreviations	xix
1 Introduction	2
1.1 Geodynamic evolution of the Aegean continental back-arc	3
1.2 Cycladic metamorphic core complex	5
1.3 The Cyclades Mineral District	6
1.3.1 Importance of the Cyclades Mineral District	6
1.3.2 Geological setting and deposit styles	7
1.4 Research objective and relevance	13
1.5 Thesis outline	15

1.6	Statement of original contribution	16
2	Regional similarities in lead isotopes and trace elements in galena of the Cyclades Mineral District, Greece with implications for the underlying basement	20
	Abstract	20
2.1	Introduction	21
2.2	Geological setting	24
2.2.1	Cycladic islands	24
2.2.2	Cyclades Mineral District	30
2.3	Previous Pb-isotope studies	38
2.4	Methodology	41
2.4.1	Sampling approach	41
2.4.2	LA-Q-ICP-MS Pb-isotope analysis	46
2.4.3	LA-Q-ICP-MS trace element analysis	47
2.5	Field observations and mineral paragenesis	48
2.6	Results	57
2.6.1	Galena Pb-isotopes	57
2.6.2	Galena trace element geochemistry	61
2.7	Discussion	70
2.7.1	Variation in the Pb isotope signature of the Cyclades Mineral District	70
2.7.2	Implications for the underlying basement	73
2.7.3	Trace element variations in galena and implication for base and precious metal-rich deposits	80
2.8	Conclusions	83

2.A	Supplementary information for Chapter 2	86
2.A.1	Cyclades Mineral District	86
3	Origin of hydrothermal barite in polymetallic veins and carbonate-hosted deposits of the Cyclades continental back-arc	91
	Abstract	91
3.1	Introduction	92
3.2	Regional geology	103
3.2.1	Regional metallogeny	107
3.3	Samples and methodology	114
3.4	Mineral paragenesis	117
3.5	Results	125
3.5.1	Geochemistry of barite	125
3.5.2	Stable isotope data of mineral separates	130
3.5.3	LA-MC-ICP-MS data	134
3.6	Discussion	136
3.6.1	Sulfur sources in Cycladic barite	137
3.6.2	Sulfide-sulfate relationships	141
3.6.3	Oxygen isotopes in barite	144
3.6.4	Strontium isotopes and crustal sources	147
3.6.5	Geochemical and isotopic zoning in barite	152
3.7	Summary and conclusions	156
3.A	Supplementary information for Chapter 3	163
3.A.1	Analytical methodology	163
3.A.2	Compilation of Sr isotope data	168

3.A.3 Additional figures	169
4 Geochemical and isotopic composition of the metamorphic basement in the Cyclades, Greece: Source rocks of the Cyclades Mineral District	174
Abstract	174
4.1 Introduction	175
4.2 Regional geology	177
4.2.1 Regional metallogeny	185
4.3 Isotopic signature of the mineralization and basement	187
4.4 Whole-rock compilation	190
4.5 Whole-rock composition	191
4.5.1 Felsic meta-igneous rocks of the Cycladic Basement and CBU . . .	191
4.5.2 Metabasites of the CBU	193
4.6 Interpretation and discussion	195
4.6.1 Sources of metals	195
4.6.2 Preconcentration of metals in the CBU	198
4.6.3 Limitations in the interpretation of the compiled data	201
4.6.4 Implications for the basement structure	202
4.7 Conclusions	204
5 Synthesis, conclusions, and outlook	206
5.1 Mineralization in the Cyclades Mineral District	210
5.1.1 Lavrion	210
5.1.2 Serifos	212
5.1.3 Tinos	212
5.1.4 Mykonos	212

5.1.5	Antiparos	213
5.1.6	Milos	214
5.2	Perspectives and outlook	214
	References	216

List of Figures

1.1	Simplified map of the Aegean and the Cyclades metamorphic core complex	4
1.2	Stratigraphic columns illustrating the position of the investigated mineral- izing systems in the Cyclades Mineral District	9
2.1	Simplified geological map of the Cyclades Mineral District, Greece	27
2.2	Schematic tectono-stratigraphic sequences of the west Cyclades and north- central Cyclades	29
2.3	Compiled Pb-isotope data of Cycladic galena	40
2.4	Field and sample photos of representative deposit types in the Cyclades Mineral District	49
2.5	Reflected light microphotographs of representative samples from the major deposit types in the Cyclades Mineral District	52
2.6	Representative backscattered-electronmicroscopy images of galena	55
2.7	LA-Q-ICP-MS $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot of galena	58
2.8	Silver, antimony, copper, bismuth, cadmium and thallium concentrations in galena	62

2.9	Comparison of new LA-Q-ICP-MS Pb-isotope ratios in galena with compiled data for galena from previous studies and whole-rock data of potential source rocks	72
2.10	Simplified geological map of the Cyclades Mineral District highlighting lead sources and enrichment in trace elements in galena	78
2.11	Schematic representation of major sources of base and precious metals for the different deposit types in the Cyclades Mineral District, Greece	81
3.1	Simplified geological map of the Cyclades Mineral District, Greece, highlighting locations of barite occurrences	104
3.2	Simplified model summarizing the main characteristics of hydrothermal barite in the Cyclades linked to the different fluid and crustal sources	108
3.3	Field photographs of representative hydrothermal barite occurrences in the Cyclades Mineral District	116
3.4	Representative photographs of the investigated barite samples	118
3.5	Photomicrographs and backscattered-electron microscopy images of characteristic mineral assemblages and crystal shapes of barite	121
3.6	Compositional zoning in barite recorded by variations in Sr concentration .	126
3.7	Variation in Sr concentration in barite detected by electron microprobe analyses	128
3.8	Sulfur isotope compositions from EA-IRMS and LA-MC-ICP-MS spot analyses of Cycladic barite and galena	131
3.9	$\delta^{34}\text{S}$ values vs. $\delta^{18}\text{O}$ values of Cycladic barite obtained by mineral separate analyses (EA-IRMS)	133

3.10 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and $\delta^{34}\text{S}$ values of barite obtained by LA-MC-ICP-MS spot analyses	135
3.11 Strontium isotope ratios of barite from different mineral deposit types from this study compared to published ratios and selected reservoirs of Sr	148
3.12 Zoned barite crystal from the Panormos Bay vein-type mineralization, Mykonos, with constant Sr isotope ratios and a positive correlation between the $\delta^{34}\text{S}$ values and Sr concentration	153
3.13 Geochemical and isotopic zoning in barite crystals of the sample 17L145_1 of the carbonate-hosted mineralization at Plaka, Lavrion	155
3.14 Flow chart illustrating the potential fluid and crustal sources in the Cyclades	159
3.A.1 Internal variation in $\delta^{34}\text{S}$ values obtained by LA-MC-ICP-MS analyses of crystal 17L145_3B_n (Plaka, Lavrion).	168
3.A.2 Backscattered-electron microscopy image and EMPA traverse of a zoned barite crystal	170
3.A.3 Backscattered-electron microscopy image and $\delta^{34}\text{S}$ values vs. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and Sr intensity (cps) vs. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of the sample 17AP13 (Agios Georgios, Antiparos)	171
3.A.4 Backscattered-electron microscopy images of analyzed barite crystals . . .	172
4.1 Simplified geological map of the Attic-Cycladic Crystalline Belt	179
4.2 Sr-isotopes vs. Pb-isotopes for the mineralization and different lithologies .	188
4.3 $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr content (ppm) for the Miocene intrusions and exposed rock types	189
4.4 Major element diagrams of the different basement rock types	192

4.5	Major and trace element plots for the felsic and mafic rocks of the Cycladic Basement and Cycladic Blueschist Unit	194
4.6	Primitive mantle-normalized trace element plots for the felsic and mafic rocks of the Cycladic Basement and the Cycladic Blueschist Unit	196
4.7	Box and whisker plots showing the barium, strontium, and rubidium content in the different rock types of the metamorphic basement	199
4.8	Box and whisker plots showing the lead, zinc, and copper content in the different rock types of the metamorphic basement	200
4.9	Schematic paleogeographic reconstruction of the protoliths for the Upper and Lower Cycladic Blueschist Nappe.	203
5.1	Map of the Cyclades Mineral District highlighting the different crustal sources of lead and strontium.	208
5.2	Simplified model summarizing the main characteristics of the hydrothermal mineral deposits in the Cyclades	211

List of Tables

2.1	Characteristics of the different deposit types in the Cyclades Mineral District in Greece	32
2.2	Coordinates and geological details of galena samples, Cyclades, Greece . .	43
2.3	Weighted mean of Pb-isotope ratios of galena, Cyclades, Greece	60
2.4	LA-Q-ICP-MS minor and trace element concentrations in galena, Cyclades, Greece	66
3.1	Literature summary of investigated deposits in the Cyclades Mineral District in Greece.	97
3.2	Results of geochemical and S, O, and Sr isotope analyses of barite and S isotope analyses of galena, Cyclades, Greece.	129
3.3	Characteristics of potential hydrothermal fluids and source rocks in the Cy- clades, Greece	157

Abbreviations

Geological terms

ACCB: Attic-Cycladic Crystalline Belt
BSR: bacterial sulfate reduction
CBU: Cycladic Blueschist Unit
CR: carbonate-replacement mineralization
FDS: Folegandros Detachment System
HS: high-sulfidation
IS: intermediate-sulfidation
LCBN: Lower Cycladic Blueschist Nappe
LS: low-sulfidation
MLD: Meghalo Livadi Detachment
NCDS: North Cycladic Detachment System
NPDS: Naxos-Paros Detachment System
REE: rare earth elements
SAVA: South Aegean Volcanic Arc
SDS: Santorini Detachment System
TCT: Trans-Cycladic Thrust
UCBN: Upper Cycladic Blueschist Nappe
VMS: volcanogenic massive sulfide
WCDS: West Cycladic Detachment System

Analytical terms

AAS: Atomic adsorption spectroscopy
BSE: Backscattered-electron microscopy
EA: Elemental analyzer
EDS: Energy-dispersive X-ray spectrometry
EMPA: Electron microprobe analyzer
INAA: Instrumental neutron activation analysis
IRMS: Isotope ratio mass spectrometer
LA-ICP-MS: Laser ablation inductively-coupled plasma mass spectrometer

LA-MC-ICP-MS: Laser ablation multi-collector inductively-coupled plasma mass spectrometer

LA-Q-ICP-MS: Laser ablation quadrupole inductively-coupled plasma mass spectrometer

MSWD: Mean square weighted deviations

PPL: Transmitted plain polarized light

REF: Reflected light

SEM: Scanning electron microscopy

TIMS: Thermal ionization mass spectrometer

XPL: Transmitted cross-polarized light

VCDT: Vienna Cañon Diablo Troilite standard

VSMOW: Vienna Standard Mean Ocean Water

Chapter 1

1 Introduction

Continental back-arc settings contain significant resources of Pb and Zn. The Cyclades back-arc in Greece, which forms a part of the Hellenides and largely consists of islands between Greece and Turkey in the Aegean Sea, presents an opportunity to understand how different metal and fluid sources are involved in a wide range of mineral systems in a rapidly evolving geodynamic framework. The back-arc setting is well-endowed with base and precious metal occurrences on nearly all Cycladic islands. Mineral deposits that form in the shallow crust of back-arc regions can tap a variety of different sources of metals and fluids along major low-angle detachment systems and normal faults. Although many of the deposits have been studied in isolation, no regional model has been proposed that links the wide range of mineralization styles in this tectonic environment to underlying crustal sources. This project attempts to link the regional metallogenic diversity to fluid and crustal sources in an evolving geodynamic context and basement structure using isotopic and geochemical data, emphasizing lead and strontium. This chapter introduces the geological setting and evolution of the area and the importance of the Cyclades Mineral District.

1.1 Geodynamic evolution of the Aegean continental back-arc

Closure of the Vardar ocean, a small back-arc basin of the Neotethyn ocean, during the Cretaceous resulted in the convergence of Adria (Hellenides) and Eurasia (Rhodope; [Grasemann et al., 2022](#) and references therein). Cenozoic subduction of the African plate beneath Eurasia caused accretion of successive oceanic and continental fragments since the Mesozoic and led to the formation of the Hellenides, an orogenic belt which forms part of the Alpine-Himalaya belt located in Greece ([Jolivet et al., 2010](#); [Menant et al., 2016](#); [Papanikolaou, 2021](#); [Pe-Piper & Piper, 2002](#) and references therein). The Hellenides are divided into Internal and External Hellenides. The External Hellenides are characterized by a preserved stratigraphy, consisting of the Phyllite-Quartzite, Ionian, Gavrovo-Tripolitza, and Pindos thrust units. These units were affected by Eocene-Miocene tectonism ([Papanikolaou, 2021](#) and references therein). The Internal Hellenides, including the Axios-Vardar oceanic unit and the Pelagonian, Serbo-Macedonian and Rhodope continental blocks, are characterized by two orogenic periods (Late Jurassic-Early Cretaceous and Eocene-Oligocene; [Papanikolaou, 2021](#) and references therein). Extension in the Aegean was caused by trench retreat and slab rollback, beginning in the Rhodope Massif during the Eocene and which migrated south in the Aegean Sea and Menderes Massif after the late Eocene ([Jolivet et al., 2018, 2010](#); [Ring et al., 2010](#); [Brun et al., 2016](#)). Widespread mineralization along the Tethyan orogen is related to the long-lived geodynamic evolution of subduction and collisional processes ([Richards, 2015](#)). [Menant et al. \(2018\)](#) highlighted different stages of mineralization in the Aegean, with a Cretaceous Cu-rich metallogenic period in the Balkans and Pontides followed by a late Eocene-Miocene Pb-Zn period in the Rhodopes and a Au-rich metallogenic period with generally smaller deposits spread over the back-arc basin.

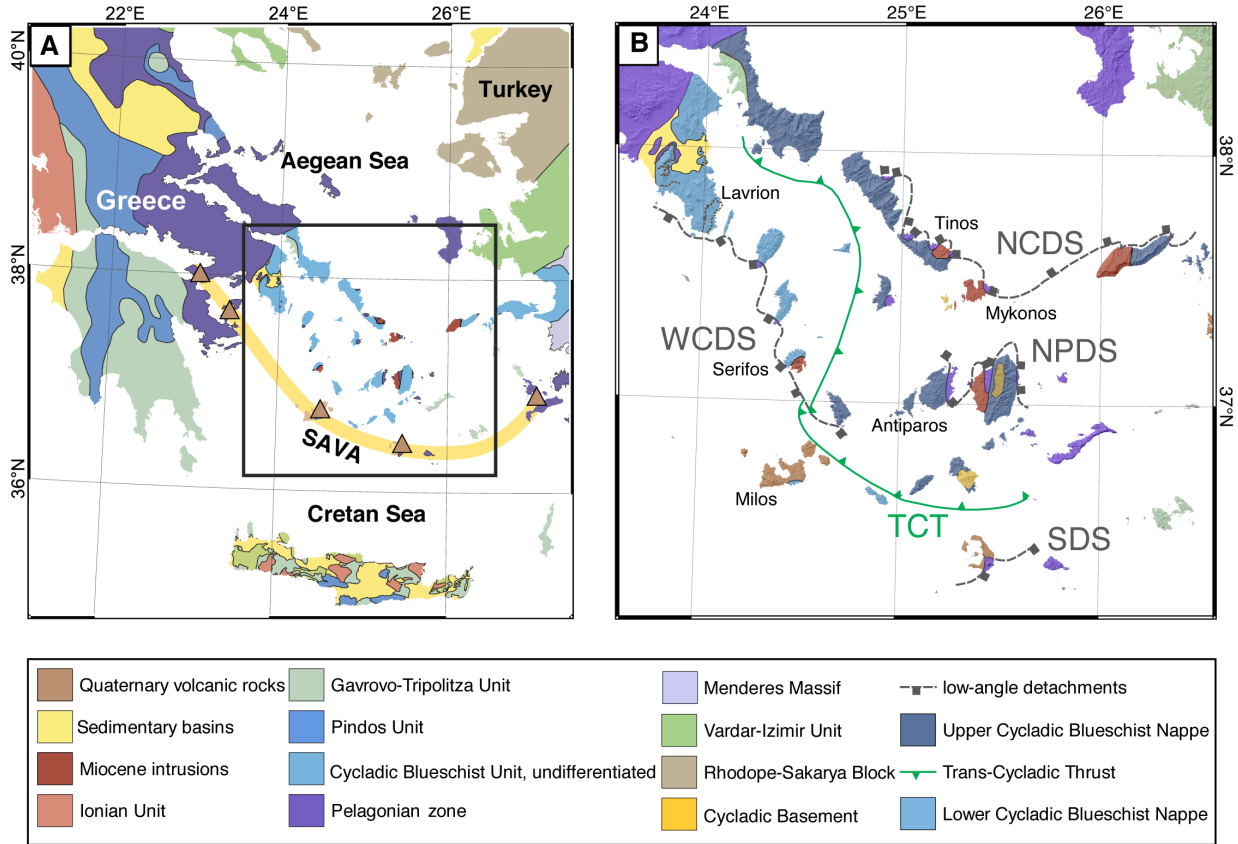


Fig. 1.1: A: Simplified bedrock geological map of the Hellenides (modified after Coleman et al., 2019). The Hellenides are a series of nappes recording the accretion of oceanic basins and microcontinents to the European continental margin. Shown in yellow is the active South Aegean Volcanic Arc (SAVA) with the volcanic fields (from west to east) of Sousaki, Aegina-Poros-Methana, Milos, Santorini-Kolumbo, and Kos-Nisyros-Yali. B: Simplified geological map of the Cycladic metamorphic core complex. WCDS: West Cycladic Detachment System, NCDS: North Cycladic Detachment System, NPDS: Naxos Paros Detachment System, SDS: Santorini Detachment System, SAVA: South Aegean Volcanic Arc, TCT: Trans-Cycladic Thrust

1.2 Cycladic metamorphic core complex

The Attic-Cycladic Crystalline Belt (ACCB) or Cycladic metamorphic core complex are terms that are used interchangeably for the area and will be used here. The ACCB forms a major tectono-stratigraphic unit of the Hellenides. Accelerated slab retreat and rapid southward migration of the Hellenic trench since the Eocene-Oligocene caused extension and thinning of the back-arc domain, manifested in the southward migration of arc magmatism (Pe-Piper & Piper, 2002; Schaarschmidt et al., 2021b and references therein). Final exhumation of middle and lower crustal material as metamorphic core complexes (e.g., Lister et al., 1984; Gautier & Brun, 1994; Jolivet et al., 2004, 2015; Ring et al., 2010) was facilitated by a series of low-angle, crustal-scale detachment systems (Fig. 1.1).

Major tectono-stratigraphic units exposed on the Cycladic islands are the mostly unmetamorphosed and undifferentiated Pelagonian zone in the hanging wall of the major detachment systems, the metamorphosed Cycladic Blueschist Unit, and Cycladic Basement in the footwall (Fig. 1.1, e.g., Bonneau, 1984; Flansburg et al., 2019; Grasemann et al., 2018; Jolivet et al., 2015). In this study, the term metamorphic basement is commonly used and refers to the units in the footwall of the major detachment systems; the Cycladic Basement and the undifferentiated Cycladic Blueschist Unit. The Cycladic Basement (s.s.) consists of gneisses with intercalated metabasites as well as metapelites and marbles with a pre-Alpine history and is exposed in the central and southern part of the Cyclades (e.g., Ios, Naxos, Paros, Serifos; Henjes-Kunst & Kreuzer, 1982; Keay & Lister, 2002; Jolivet et al., 2010; McGrath et al., 2017; Flansburg et al., 2019). The Cycladic Blueschist Unit (CBU), the primary unit in the Cyclades and exposed on most of the Cycladic islands, is a volcano-sedimentary sequence with clastic metasedimentary rocks and marbles. These rocks recorded two stages of metamorphism: a high-pressure metamorphism under eclog-

ite to blueschist facies conditions at 52–43 Ma and a younger greenschist facies overprint caused by the exhumation of the CBU which started at ca. 30 Ma (e.g., Jolivet et al., 2010; Grasemann et al., 2018). Grasemann et al. (2018) proposed a division of the CBU into the Upper Cycladic Blueschist Nappe (UCBN) and Lower Cycladic Blueschist Nappe (LCBN) based on peak metamorphic conditions (Fig. 1.1). These nappes are divided by the predicted Trans-Cycladic Thrust (TCT), which has not been mapped nor imaged in the field. The Pelagonian zone consists of klippen of unmetamorphosed Late Permian to Jurassic volcanoclastic rocks with ophiolite sequences and carbonates (e.g., Bonneau, 1984; Schenker et al., 2014). Generation of the Cycladic granitoids started ca. 17 Ma, when the southward migrating arc reached the Cyclades, leading to the emplacement of a suite of syntectonic intrusions within the extending upper crust (e.g., Pe-Piper & Piper, 2002; Altherr & Siebel, 2002; Stouraiti et al., 2010; Schaarschmidt et al., 2021a). Since the Pliocene, the South Aegean volcanic arc has extended from Sousaki in the northwest, across Milos and Santorini towards Nisyros in the southeast (Fig. 1.1; Innocenti et al., 1981; Francalanci et al., 2005; Francalanci & Zellmer, 2019).

1.3 The Cyclades Mineral District

1.3.1 Importance of the Cyclades Mineral District

Mining in the Cyclades Mineral District started during the antiquity (Gale & Stos-Gale, 1981; Aulsebrook, 2022), and experienced a rebirth during the 19th and 20th century. Especially the presence of argentiferous galena in the Cyclades Mineral District contributed to wealth of the ancient Greeks (Gale & Stos-Gale, 1981). The Rhodopes in northern Greece and the Cyclades are the most promising targets for future exploration and discovery of precious, rare, and critical metals in Greece (Melfos & Voudouris, 2017). The importance

of this area as part of the metal endowment of Europe has also been highlighted by the extensive research over the past half dozen years (e.g., [Smith et al., 2018](#); [Ivarsson et al., 2019](#); [Scheffer et al., 2019](#); [Kilias et al., 2020](#); [Schaarschmidt et al., 2021a](#); [Grosche et al., 2023](#); [Hector et al., 2022](#); [Miles, 2021](#)) with a focus on the mineralization at Lavrion, Milos, and Kolumbo. Recent reviews include those by [Melfos & Voudouris \(2017\)](#); [Menant et al. \(2018\)](#) and [Voudouris et al. \(2019\)](#).

A rebirth in mining activity during the late 19th to the early 20th century occurred in the area, including Pb-Zn-Ag (Lavrion), Fe (Serifos), Ba±Pb-Ag (Mykonos), and Ba, Pb-Zn-Ag-(Au) and Mn (Milos). Some portions of these historically important deposits are not accessible anymore due to a higher water table (e.g., Sifnos) or a repurposing of the deposits as dump sites (e.g., Sifnos, Mykonos), whereas on Milos deposits are preserved as geoheritage sites. Consequently, historical important deposits in this area are often not included in recent studies; however, good descriptions are available by [Fiedler \(1841\)](#) and [Ardaillon \(1897\)](#), as well as [Gale & Stos-Gale \(1981\)](#), [Lahti & Govett \(1981\)](#), and [Vavelidis et al. \(1985\)](#), which describe the deposits before modern mining activities or repurposing of the deposits in the 20th century.

1.3.2 Geological setting and deposit styles

Deposits in the Cyclades Mineral District formed during accelerated slab retreat and back-arc extension in the Miocene, with largely Pb-Zn detachment-related deposits and low-to intermediate-sulfidation epithermal Au±Cu deposits as part of the Miocene metallogenic episode ([Menant et al., 2018](#)). The Cyclades Mineral District includes a range of mineralization styles ([Kilias et al., 2001](#); [Liakopoulos et al., 2001](#); [Skarpelis, 2002](#); [Kilias et al., 2013](#); [Melfos & Voudouris, 2017](#); [Menant et al., 2018](#); [Voudouris et al., 2019](#); [Wind et al., 2020](#) and references therein). These include low-grade porphyry Mo, carbonate-

hosted replacement, vein and breccia Pb-Zn-Ag-Au, intermediate-sulfidation epithermal base and precious metal veins, Cu-Fe and Fe skarn ore deposits, Fe- and Zn-rich gossan, breccia-hosted Ag-Pb-Zn-Ba(-Au) ore deposits of possible epithermal affinity, iron and barite (Fe-Ba) veins, sediment-hosted Mn oxide ores and polymetallic seafloor massive sulfide (SMS) deposits. These deposits occur in all tectono-stratigraphic units in the hanging and footwall of the major detachment systems (Fig. 1.2). Ore deposits are generally temporally and spatially linked to the major detachment systems or the emplacement of the Miocene granitoids. However, on Syros and Sifnos, mineralization occurs without a spatial link to intrusions nor major faults or detachment systems.

The deposits in the Lavrion District, mainland Greece, and on the Cycladic islands, north to south, of Tinos, Mykonos, Serifos, Antiparos, and Milos are the focus of this thesis. This range of deposit types, formed over the last 10 Myr, occur along the two major detachment systems, the North Cycladic Detachment System (NCDS) and West Cycladic Detachment System (WCDS).

Lavrion District

In the Lavrion District a range of mineralization styles are present, including multiple stages of mineralization and formation of supergene ore (e.g., [Berger et al., 2013](#); [Bonsall et al., 2011](#); [Skarpelis & Argyraki, 2009](#); [Scheffer et al., 2017, 2019](#); [Spry et al., 2014](#); [Voudouris et al., 2008a,b, 2019](#)): carbonate-replacement Pb-Zn-Ag ore (Kamariza-Sounio-Plaka, Megala Pefka, Villia), Cu-Fe skarn and porphyry Mo mineralization (Plaka), vein- and breccia-style mineralization (Vein 80, Plaka-Kamariza), and Fe- and Zn-rich gossan (Plaka-Kamariza). Porphyry and skarn mineralization occur within or adjacent to the Plaka granodiorite ([Leleu et al., 1973](#); [Voudouris et al., 2008a](#)). By contrast, the Pb-Zn-Ag replacement ores occur within the lower and upper marble of the Lower Unit (Basal

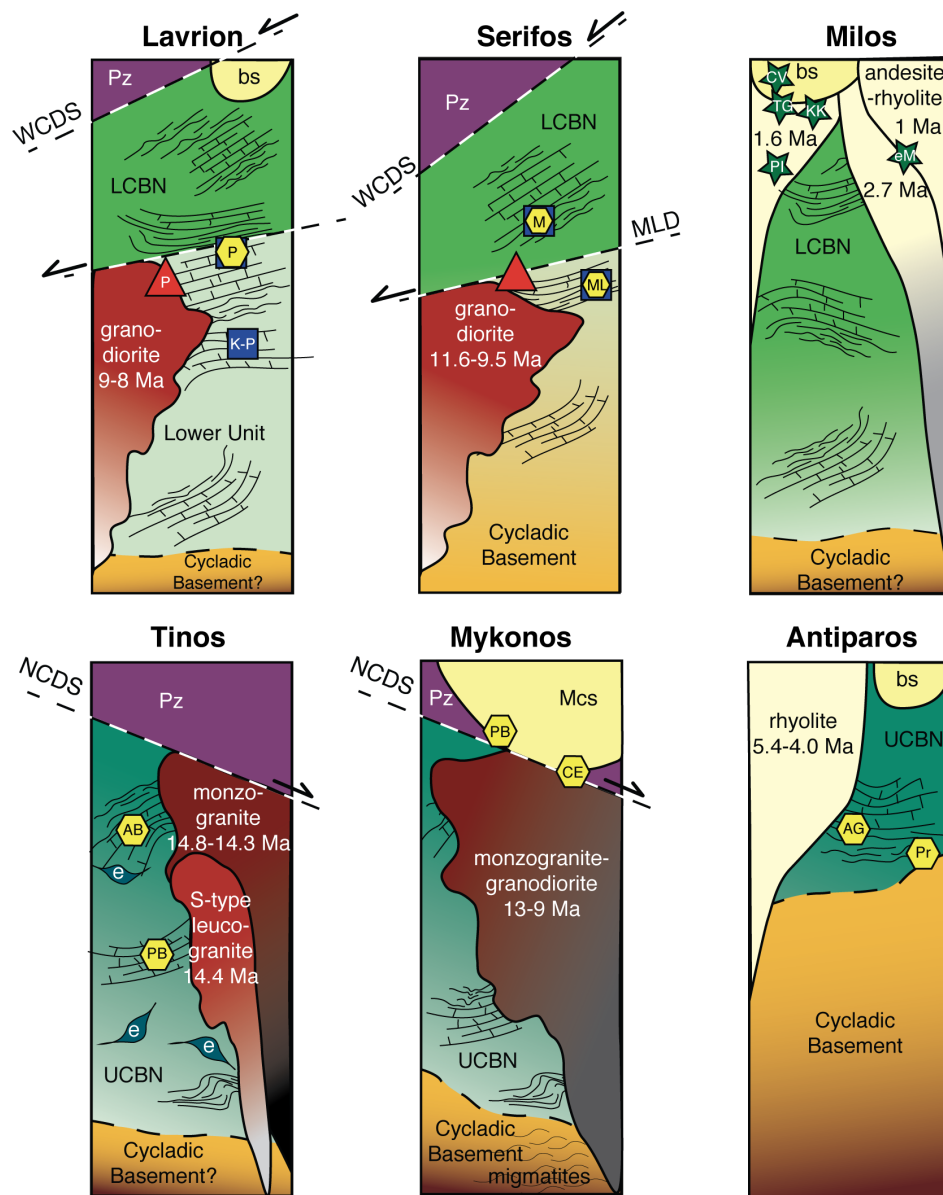


Fig. 1.2: Schematic tectono-stratigraphic sequences of the west Cyclades (along the WCDS) and north-central Cyclades (along the NCDS), showing the main correlations between the stratigraphic units. Placement of the deposits are at relative structural levels. Carbonate-replacement (blue square), vein-type (yellow hexagon), epithermal mineralization (green star) and skarn and porphyry deposits (red triangle) are hosted in all tectono-stratigraphic units. AB: Apigania Bay, AG: Agios Georgios, bs: basin sediments (Miocene to Neogene), CV: Cape Vani, CE: Cape Evros, e: eclogite, eM: eastern Milos, KK: Kondaros-Katsimouti, K-P: Kamariza-Plaka, LCBN: Lower Cycladic Blueschist Nappe, M: Moutoulas, Mcs: Miocene conglomeratic sequence, ML: Mega Livadi, NCDS: North Cycladic Detachment System, PB: Panormos Bay, Pr: Prassovounia, Pz: Pelagonian zone, TG: Triades-Galana, UCBN: Upper Cycladic Blueschist Nappe, WCDS: West Cycladic Detachment System.

Unit) and along the marble-schist contact of the local low-angle detachment (Fig. 1.2; e.g., Voudouris et al., 2008b; Berger et al., 2013; Scheffer et al., 2017). A magmatic origin for the fluids related to the formation of the porphyry, skarn and carbonate-replacement deposits has been widely accepted (e.g., Bonsall et al., 2011; Spry et al., 2014; Voudouris et al., 2008a,b), whereas mixed seawater and meteoric fluids were proposed for the formation of the late vein and breccia-style mineralization (Bonsall et al., 2011; Scheffer et al., 2019).

Tinos

Multiple stages of precious metal mineralization are present on Tinos in stockworks of subvertical quartz veins. Mineralized quartz veins at Panormos Bay occur exclusively in the marble of the UCBN; however, veins crosscut marbles and schists of the UCBN at Apigania Bay (Tombros et al., 2008). Tombros et al. (2007, 2008) proposed that the Au-Ag vein system at Panormos Bay pre-dates the vein system at Apigania Bay. The source fluids for the mineralization at Panormos Bay have been interpreted as a mix of magmatic fluids from the Tinos leucogranite and meteoric water, with metal leached from the surrounding UCBN and Pelagonian zone rocks (Tombros et al., 2008).

Mykonos

On Mykonos, subvertical banded barite veins, up to 10 m wide, are spatially related to extensional faults and the local low-angle detachment system (Menant et al., 2013; Skarpelis, 2002; Tombros et al., 2015). At Panormos Bay, north-central Mykonos, these veins crosscut the exposed Miocene conglomeratic sequence (Menant et al., 2013; Sánchez-Gómez et al., 2002; Skarpelis, 2002). In the eastern part of the island at Cape Evros, subvertical NW-SE-trending barite and Fe-oxide/oxyhydroxide veins cut the upper part of the Mykonos laccolith, the metabasites of the Pelagonian zone and the Miocene conglomeratic sequence

(Lecomte et al., 2010; Menant et al., 2013; Skarpelis, 2002). In addition, sub-economic Au enrichment was reported within the siliceous cap and silicified breccia at Profitis Elias and Mavro Vouno (Skarpelis, 2002). Tombros et al. (2015) proposed that magmatic fluids derived from the Miocene intrusion mixed with Miocene seawater to produce the barite and sulfide mineralization on Mykonos, whereas Skarpelis & Gilg (2006) suggested a two-stage hydrothermal event, with epithermal-style Au-quartz deposition followed by brittle faulting and barite-sulfide deposition from basinal brines.

Serifos

On Serifos island, numerous magnetite-rich exo- and endoskarns and iron and barite (Fe-Ba) orebodies occur mainly in Cycladic Basement marbles in the footwall of the local detachment and are related to the Serifos granodioritic pluton (Salemink, 1985; Ducoux et al., 2017). Ducoux et al. (2017) suggested that Fe-Ba veins formed by surface-derived (meteoric) fluids causing remobilization of the Fe from the Fe-rich skarns. More distal to the intrusion, polymetallic mineralization occurs in small lenses in the Moutoulas prospect, where mineralization has been variably interpreted as skarn, retrograde skarn, metamorphosed exhalite or low-temperature vein and carbonate-replacement ore (e.g., Fitros et al., 2017; Salemink, 1985; St. Seymour et al., 2009b). Fitros et al. (2017) proposed that ore fluids derived from the Serifos pluton mixed with meteoric waters and interacted with the wall-rock.

Antiparos

On Antiparos, base metal mineralization occurs in subvertical quartz and minor barite veins, which cut the Cycladic Basement and marbles and schists of the UCBN, in the south of the island at Agios Georgios and in the western part of the island near Prassovounia

([Gale & Stos-Gale, 1981](#); [Kevrekidis et al., 2015](#); [Skarpelis, 2002](#)). [Kevrekidis et al. \(2015\)](#) proposed that the Agios Georgios argentiferous galena deposit is related to magmatic fluids from the leucogranitic Paros pluton that mixed with meteoric water.

Milos

On Milos, economic mineralization formed in the western part of the island in the Quaternary calc-alkaline submarine and submarine to subaerial volcanic rocks. Mineralization includes sediment-hosted exhalative Mn, Fe and barite (Cape Vani; [Hein et al., 2000](#); [Liakopoulos et al., 2001](#); [Ivarsson et al., 2019](#)), epithermal Pb-Zn-Ag veins (Kondaros-Katsimouti, [Papavasiliou et al., 2016b](#); [Schaarschmidt et al., 2021a](#)), epithermal-like barite-quartz breccia Zn-Pb-(Ag-Au) sulfide (Triades-Galana; [Marschik et al., 2010](#); [Alfieris et al., 2013](#); [Papavasiliou et al., 2016a](#); [Vavelidis & Melfos, 1998](#); [Smith et al., 2018](#)), and epithermal Au-Ag-Te vein-type (Profitis Ilias-Chondro Vouno; [Kilias et al., 2001](#); [Naden et al., 2005](#); [Alfieris et al., 2013](#); [Grosche et al., 2023](#)) deposits. In addition, abundant barite occurs in the eastern part of the island which is mostly barren in metal anomalies (Kastanas, Kavos, Picridou, Fourkovouni; [Hauck, 1984](#)). Mineralization on western Milos formed by a mix of fluid sources including magmatic, meteoric, and seawater derived fluids, with metals thought to be derived from the interaction of the hydrothermal fluid with the Quaternary volcanic rocks and metamorphic basement ([Kilias et al., 2001](#); [Naden et al., 2005](#); [Marschik et al., 2010](#); [Schaarschmidt et al., 2021a](#); [Grosche et al., 2023](#)).

1.4 Research objective and relevance

Despite the recent geological interest in this area, no study has so far addressed the regional metallogenic context with a systematic study of comparable isotopic or geochemical signatures. This project attempts to constrain and better understand the rapidly evolved geodynamics and basement structure through a study of the regional metallogeny, including examination of the fluid and crustal sources of ore components. This was achieved through petrologic, isotopic, and geochemical studies, with an emphasis on determining the lead and strontium provenance. The Cyclades back-arc system is one of the few easily accessible continental margin arc systems in the world and presents a good opportunity to understand how various metal sources interact with different mineral systems within such a rapidly evolving geodynamic setting. Understanding the structural, tectonic, and volcanic controls on ore deposit formation and hydrothermal activity are crucial for guiding future exploration activities. Better understanding of these processes in relatively young environments can improve understanding of a wide range of mineralization styles in older volcanic arc terranes.

The range of deposit types in the Cyclades Mineral District in Greece reflects fluids interacting with different types of underlying rock types (e.g., metapelites, marbles and crystalline rocks); fluid migration is related to the southward slab retreat and resulting rapidly extending continental back-arc setting. Changes in the regional geodynamics led to multiple metal sources and fluid pathways, as recorded in polyphase precious and base-metal mineral occurrences. In addition, the trace element and isotopic signature of minerals provide additional constraints on the nature of these hydrothermal systems. Two common mineral phases in the Cyclades Mineral District, galena (PbS) and barite (BaSO₄), were selected for a regional study of their isotopic and trace element signature, to provide

fingerprints of the mineral systems and their crustal roots. This study also examined the mineralized systems on Antiparos and Mykonos, with few recent studies.

Analytical results were obtained by LA-Q-ICP-MS and LA-MC-ICP-MS, supplemented by a compilation of previous isotopic studies. LA-Q-ICP-MS and LA-MC-ICP-MS analyses for sulfates and sulfides are still novel (e.g., [George et al., 2015, 2016](#); [McFarlane et al., 2016](#); [Jamieson et al., 2016](#)) but in combination with the compilation and comparison of different methodologies, this study demonstrates the robustness with regard to the accuracy of these methods. This study also shows that a careful analytical protocol and data acquisition can produce accurate and precise Pb isotope measurements in galena by LA-Q-ICP-MS with results comparable to the standard techniques (double spike TIMS or MC-ICP-MS). In addition, this study produced the first sequential measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ on the same ablation spot in barite and showed the efficacy of LA-MC-ICP-MS for these isotopic systems. Furthermore, results of this study demonstrated the usefulness of LA-MC-ICP-MS to track changes in the isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$) of barite that are not resolvable by the standard techniques of stable isotope analyses (isotope ratio mass spectrometry, IRMS).

Due to the importance of this area on the metallurgy of the Bronze Age (~ 3300 to 1200 B.C.E.), large data sets of Pb isotopes of galena exist, although typically without much geological context. The geological and isotopic compilation of the deposits in the Cyclades will also be of use to archeometallurgical research in the Aegean (e.g., [Aulsebrook, 2022](#)), and the data generated has been included in the new GlobalID - Global Lead Isotope Database (<https://globalid.dmt-lb.de/>; [Westner et al., 2021](#)). This thesis also provides a review on existing Pb and Sr isotope data and whole-rock geochemistry across the Attic-Cycladic Crystalline Belt, and highlights where open questions remain.

1.5 Thesis outline

This thesis is divided into five chapters and presents a collection of three scientific articles. Two are published in peer-reviewed journals *Lithos* and *Economic Geology*. The third article is in preparation at the time of this thesis submission. Supplementary tables for Chapters 2, 3 and 4 are included as digital supplements.

Chapter 1 is an introduction to this thesis and provides an overview of the existing literature and the main questions of this research.

Chapter 2 presents a detailed study of the Pb isotope and trace element signature of galena by LA-Q-ICP-MS analyses. Results of this study highlight that mineralization in the Cyclades is strongly influenced by the underlying basement and that inclusions and trace elements in galena are dependent on the physico-chemical conditions of ore formation and are distinct for the different deposit types. Results of this study have been published in *Lithos* (Wind et al., 2020) and were presented at international conferences (*Goldschmidt-2018*, *EGU-2019*). Aspects of the trace element study were also published as extended abstract (Wind et al., 2019) and presented orally at *SGA Biennial Meeting 2019*.

Chapter 3 presents a multi-isotope ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$) study of Cycladic barite to trace the fluid and metal sources of hydrothermal barite. Comparing the isotopic composition of hydrothermal barite obtained by IRMS and LA-MC-ICP-MS analyses reveal that laser ablation analyses are a useful tool to trace the different fluid and crustal sources. Isotopic variations (Pb isotopes) in the underlying basement could be confirmed by the Sr isotope composition of barite. Differences in the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values suggest that Cycladic barite formed from a mixture of fluid sources, mainly seawater and magmatic derived fluids. Results of this study are published in *Economic Geology* (Wind et al., 2023) and were presented orally at *GEOMünster-2019* and *GSA-2021*.

Chapter 4 examines the isotopic and geochemical composition of the underlying basement in the Cyclades. Regional variations observed in the Pb and Sr isotope composition of the polymetallic ore deposits were further used to constrain the different crustal units exposed in the Cyclades. Aspects of this work were published in an abstract and presented orally at *GSA-2021* (invited speaker).

Chapter 5 provides an overview and conclusions of the different mineral occurrences examined in this study and their respective metal and fluid sources, discusses the implications of this work, and makes recommendations for future research.

1.6 Statement of original contribution

This thesis presents original research conducted by Sandra C. Wind under the co-supervision of Professor David Schneider and Professor Mark Hannington at the University of Ottawa. Funding for this research was provided from NSERC Discovery grants awarded to David Schneider and Mark Hannington. Additional funding was received from two student research grants of the Society of Economic Geologists Canada Foundation awarded to Sandra Wind. This section outlines the contribution of the co-authors and collaborators to each chapter.

Chapter 1: Introduction

Written by Sandra C. Wind with editorial corrections by D.A. Schneider and M.D. Hannington.

Chapter 2: Regional similarities in lead isotopes and trace elements in galena of the Cyclades Mineral District, Greece with implications for the underlying basement

This chapter is based on fieldwork in the Cyclades Mineral District carried out by the author, with assistance from Gabriela Marshy, M.D. Hannington, D.A. Schneider, J.B.

Gemmell, and S.P. Kiliass. Sample description and thin-section petrography were performed by S.C. Wind. Renelle Dubosq and Anna Jegen assisted with sample preparation for galena grain mounts. Galena grain mounts were prepared by S.C. Wind. Imaging of the grain mounts by SEM and selection of ablation spots was carried out by the author. Brandon Boucher (UNB) conducted the Pb isotope analyses of galena by LA-Q-ICP-MS under the supervision of S.C. Wind and Chris McFarlane (UNB) processed the isotope data. Trace element data of galena was conducted and processed by Brandon Boucher. Data analysis and interpretation by S.C. Wind. S.C. Wind produced the figures and wrote the initial manuscript for this chapter with editorial corrections by D.A. Schneider, M.D. Hannington and C.R.M. McFarlane. Reviews and comments by Panagiotis Voudouris, Armel Menant and Michael Roden were incorporated into the manuscript.

Chapter 3: Origin of hydrothermal barite in polymetallic veins and carbonate-hosted deposits of the Cyclades continental back-arc

This chapter is based on fieldwork in the Cyclades Mineral District carried out by the author, with assistance from Gabriela Marshy, M.D. Hannington, D.A. Schneider, J.B. Gemmell, and S.P. Kiliass. Parts of the barite geochemistry work was conducted by Joëlle Dufour under the supervision of S.C. Wind as part of her honours thesis. Joëlle Dufour conducted SEM and EMPA analyses at the University of Ottawa under the guidance of S.C. Wind and assistance of Renelle Dubosq and Glenn Poirier. Reduction of the EMPA data was conducted by Glenn Poirier. Barite grain mount *SWV* was prepared by Joëlle Dufour. As part of her thesis, Joëlle Dufour produced the original SrO vs. BaO plot (Fig. 3.7) which was later modified by S.C. Wind. Additional barite grain mounts were prepared by S.C. Wind and imaged and analyzed by SEM. Selection of ablation spots by S.C. Wind, and conduction and data processing of laser ablation data by Jan Fietzke (GEOMAR). Pure galena and barite crystals were handpicked by S.C. Wind and further

processed for IRMS analysis. The team from the Ján Veizer Stable Isotope Laboratory performed the IRMS analyses and Paul Middlestead the data reduction. Data analysis and interpretation by S.C. Wind. S.C. Wind produced the figures and tables and wrote the initial manuscript for this chapter with editorial corrections by D.A. Schneider and M.D. Hannington. Additional comments by S.P. Kiliyas, J.B. Gemmell and J. Fietzke were incorporated into the manuscript. This manuscript was reviewed by two anonymous referees and edited accordingly.

Chapter 4: Geochemical and isotopic composition of the metamorphic basement in the Cyclades, Greece: Source rocks of the Cyclades Mineral District

Data from the literature was compiled, processed and interpreted by S.C. Wind. This chapter benefited from discussions with Mark Coleman. Marc Fassbender assisted with the initial data presentation by ioGas for the following Figures [4.5](#) and [4.6](#). This chapter was written by the author with editorial corrections by D.A. Schneider and M.D. Hannington.

Chapter 5: Summary and Conclusions

Written by Sandra C. Wind with editorial corrections by D.A. Schneider and M.D. Hannington.

Chapter 2

Published as:

Wind, S.C., Schneider, D.A., Hannington, M.D., and McFarlane, C.R.M. (2020), Regional similarities in lead isotopes and trace elements in galena of the Cyclades Mineral District, Greece with implications for the underlying basement. *Lithos*, 366–367, 105559.

2 Regional similarities in lead isotopes and trace elements in galena of the Cyclades Mineral District, Greece with implications for the underlying basement

Abstract

Polymetallic ore deposits of the Aegean Sea, Greece, are temporally and spatially associated with the emplacement of Miocene granitoids and Pliocene to Quaternary volcanic units along the active volcanic arc and occur adjacent to the crustal-scale detachment systems. A variety of mineral deposits (e.g., carbonate-replacement, skarn, porphyry, vein-type, and low- to high-sulfidation epithermal deposits) formed during different stages of back-arc evolution and can be found in the footwall and hanging wall of the major detachment systems and all tectono-stratigraphic units. New galena Pb-isotope data collected by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis exhibit a range of isotopic ratios: $^{206}\text{Pb}/^{204}\text{Pb}$: 18.68–18.91, $^{207}\text{Pb}/^{204}\text{Pb}$: 15.67–15.75 and $^{208}\text{Pb}/^{204}\text{Pb}$: 38.83–39.18, with a resolvable geographic pattern. Together with compiled Pb-isotope data of Cycladic galena, large-scale regional similarities in the Pb-isotope signatures are recognized, suggesting distinct sources of lead in the underlying basement. Base metal-rich deposits in the west Cyclades have a common lead source with a more radiogenic signature, whereas lead in the deposits in the north-central Cyclades was derived from a less

radiogenic source. Similarities between the Pb-isotopic signature of galena and regional host rocks suggest, that the pre-Alpine Cycladic Basement was the main source of lead for the deposits in the north and central, and the metamorphosed volcano-sedimentary Lower Cycladic Blueschist Nappe was the source of lead for the deposits in the west. Moreover, there is a close spatial relationship of the $^{206}\text{Pb}/^{204}\text{Pb}$ 18.84 line and trace of the proposed Trans-Cycladic Thrust. Regional trends were also observed in the new LA-ICP-MS trace element analysis in galena. Galena in carbonate-replacement and skarn deposits in the west is enriched in base metals and silver, whereas galena in vein-type deposits in the north and low- to high-sulfidation epithermal deposits along the active volcanic arc is enriched in gold, tellurides and selenium. Combined trace element and isotopic data of galena indicate distinct metal sources in the Cyclades. Heterogenous rock assemblages of mixed provenance and age account for the differences in lead isotopes. Whereas the base metals and silver are ultimately sourced from the basement, the precious metals might be derived from the metasomatized lithospheric mantle.

2.1 Introduction

The Cyclades Mineral District in Greece hosts a variety of precious and base metal-rich mineral deposits that formed by a complex interplay of multiple metal and fluid sources (e.g., metal source: crustal, mantle; fluid source: magmatic, seawater, and meteoric; e.g., Tombros et al., 2007; Bonsall et al., 2011; Alfieris et al., 2013; Kevrekidis et al., 2015; Menant et al., 2018). The geodynamic evolution of the region is dominated by subduction of the African plate beneath Eurasia, which has created an extensional back-arc setting in the Aegean Sea where metamorphic core complexes are exhumed along low-angle, crustal-scale detachments (Jolivet & Brun, 2010; Grasemann et al., 2012; Jolivet et al., 2015).

Carbonate-replacement, skarn, vein-type, porphyry, low- to high-sulfidation epithermal and volcanic-hosted massive sulfide deposits variably occur in the metamorphosed footwall and unmetamorphosed hanging wall of the major detachment systems as well as in Quaternary volcanic units (e.g., [Skarpelis, 2002](#); [Melfos & Voudouris, 2017](#); [Menant et al., 2018](#); [Voudouris et al., 2019](#) and references therein). The deposits are spatially associated with Miocene granitoids and Quaternary volcanic units along the active volcanic arc, including the modern seafloor, where back-arc extension continues (e.g., [Skarpelis, 2002](#); [Nomikou et al., 2012](#); [Menant et al., 2018](#); [Voudouris et al., 2019](#)). Widespread circulation of ore-forming fluid is facilitated by both high- and low-angle crustal-scale fault systems (e.g., [Berger et al., 2013](#); [Menant et al., 2013](#); [Ducoux et al., 2017](#); [Scheffer et al., 2017](#)). The temporal change in mineralization styles and ore genesis in response to the subduction dynamics was highlighted by [Menant et al. \(2018\)](#) and [Voudouris et al. \(2019\)](#).

These deposits, which led to the wealth of the ancient Greeks, were partly reopened and mined until the 19th century and were further developed for future mining although this was stopped for economic, social and environmental reasons (e.g., [Melfos & Voudouris, 2017](#) and references therein). Here, we focus on the Cyclades, where regional variations in the tectono-metamorphic and magmatic evolution are well documented (e.g., [Altherr et al., 1982](#); [Bonneau, 1984](#); [Pe-Piper & Piper, 2001](#); [Klaver et al., 2016a](#); [Grasemann et al., 2018](#); [Schneider et al., 2018](#); [Flansburg et al., 2019](#)). These variations have been widely considered to be a major control on the regional metallogeny, with lithological differences and distinct metamorphic histories of the upper crust influencing the metal endowment of the Cyclades Mineral District (e.g., [Scheffer et al., 2017](#); [Menant et al., 2018](#)). In particular, the complexity of the regional detachment systems accommodating extension, which tap highly variable basement lithologies, presents challenges to decipher the primary sources of metals for the ore deposits. We investigate the metal sources in a range of carbonate-

replacement, vein-type, low- to high-sulfidation epithermal, and skarn deposits along the major detachment systems and encompassing $\sim 40,000$ km² of the arc-backarc system.

The dominant ore minerals of the deposits are galena, sphalerite, pyrite and sulfosalts together with the gangue minerals quartz, barite and carbonates. We use lead isotopes in galena as robust indicators of metal source that are largely unaffected by metamorphism or deformation. Technical development in the last decades has allowed for precise measurements of lead isotopes in minerals by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS; [McFarlane et al., 2016](#)), and the results are comparable to TIMS lead isotope measurements on galena reported in the literature (e.g., [Vavelidis et al., 1985](#); [Gülen, 1990](#); [Stos-Gale & Gale, 2009](#); [Marschik et al., 2010](#); [Klaver, 2016](#); [Klaver et al., 2016a](#)). High spatial resolution methods such as LA-ICP-MS methods ([George et al., 2015, 2016](#)) have confirmed a long-standing observation that galena is a preferred host for trace metals and metalloids (e.g., Ag, Bi, Se, Sb, Cd, Tl, Te) which are highly sensitive to source rocks, magmatic-hydrothermal processes, and conditions of mineralization (e.g., [Huston et al., 1996](#); [Chutas et al., 2008](#)). These studies highlight the potential of combining isotope and trace element geochemistry of galena as an indicator of the metallogenic evolution throughout the Cyclades Mineral District. Lead isotopes in galena from the Cyclades can be separated into two distinct regional metal sources, which correspond with known and proposed tectono-metamorphic units and can be used as a tracer of the underlying basement in the Cyclades. The unique crustal exposures of the region provide an important opportunity to understand metal sources and metal endowment in other continental margin arc-backarc systems.

2.2 Geological setting

2.2.1 Cycladic islands

The geodynamic evolution of the Mediterranean region was mainly controlled by the behavior of the subducting African slab beneath continental Europe (Jolivet & Faccenna, 2000; Jolivet et al., 2015; Grasemann et al., 2018; Rabillard et al., 2018; Roche et al., 2018 and reference therein). Northward subduction of the African plate underneath Eurasia since the Mesozoic led to the subduction and accretion of successive oceanic and continental fragments (e.g., Jolivet & Brun, 2010; Menant et al., 2016 and references therein). Accelerated slab retreat and rapid southward migration of the Hellenic trench started ca. 35-30 Ma (Jolivet & Faccenna, 2000), although a Miocene age for the slab retreat has also been proposed (e.g., Ring et al., 2010). In the middle Miocene, slab tearing below western Turkey further accelerated the slab retreat (Menant et al., 2016 and references therein), causing extension and thinning of the back-arc domain and led to the exhumation of middle and lower crustal material as metamorphic core complexes from north to south along ductile to brittle detachment systems (e.g., Gautier & Brun, 1994; Jolivet et al., 2004, 2015; Ring et al., 2010). Final exhumation of footwall rocks was facilitated by bivergent major low-angle, crustal-scale detachment systems (Fig. 2.1): the top-to-NE North Cycladic Detachment System (NCDS, Jolivet et al., 2010), the top-to-N Naxos-Paros Detachment System (NPDS, Gautier et al., 1993), the top-to-SSW West Cycladic Detachment System (WCDS, Grasemann et al., 2012) and the top-to-SSE Santorini Detachment System (SDS, Schneider et al., 2018). Rocks that occur in the footwall of the major detachment systems record at least two major Cenozoic metamorphic events: 1) Eocene subduction-related high-pressure/low-temperature blueschist to eclogite facies metamorphism, and 2) Oligocene-Miocene extension related retrograde greenschist to amphibolite facies metamor-

phism (e.g., Altherr et al., 1982; Coleman et al., 2019; Grasemann et al., 2018; Jolivet & Brun, 2010; Schliestedt et al., 1987; Schneider et al., 2011).

Three major tectono-metamorphic units have been identified in the Cyclades: the Cycladic Basement and the Cycladic Blueschist Unit in the footwall, and the Pelagonian zone in the hanging wall (Fig. 2.1, e.g., Bonneau, 1984; Flansburg et al., 2019; Jolivet et al., 2015; Grasemann et al., 2018; Rabillard et al., 2018). The Cycladic Basement (Flansburg et al., 2019; Jolivet et al., 2010; Poulaki et al., 2019; Henjes-Kunst & Kreuzer, 1982; Zlatkin et al., 2018), also referred to as the Basal Unit (but not the Basal Unit in Attica and Evia: Figure 2.1A; e.g., Gerogiannis et al., 2019; Ring et al., 2007) and Cycladic Continental Basement Unit, is exposed in the central and southern part of the Cyclades (e.g., on Antiparos, Delos, Ios, Naxos, Mykonos, Paros, Sikinos, Serifos, and Syros) and consists of orthogneisses, paragneisses and mica-schists with a pre-Alpine history (e.g., Augier et al., 2015; Flansburg et al., 2019; Keay & Lister, 2002; McGrath et al., 2017; Philippon et al., 2012; Poulaki et al., 2019). Detrital zircon U-Pb geochronology and geochemical studies of the Cycladic Basement have shown the heterogeneous nature of the pre-Alpine basement (e.g., Flansburg et al., 2019; Keay & Lister, 2002; McGrath et al., 2017; Poulaki et al., 2019; Seman et al., 2017; Stouraiti et al., 2010). The protracted and punctuated metamorphic history of the Cycladic Basement, including late stage high-temperature/low-pressure metamorphism with migmatization during the Miocene (e.g., Rabillard et al., 2018), makes correlating the limited exposures of pre-Alpine Cycladic Basement difficult. The Cycladic Basement is probably best represented by the orthogneiss dome on Ios (330–303 Ma: Flansburg et al., 2019), with Carboniferous magmatism related to the Paleo-Tethys subduction that intruded into pre- to syn-intrusive metasedimentary rocks that has been metamorphosed to amphibolite facies during the Variscan orogeny (Henjes-Kunst & Kreuzer, 1982). Jolivet et al. (2004) suggested that the majority of the basement rocks of this age were

subducted, and the metamorphic core complexes were mostly built of a stack of cover units, leading to limited outcrops of basement rocks.

The Cycladic Blueschist Unit (CBU), the dominant unit in the Cyclades and exposed on most of the islands, is a metamorphosed volcano-sedimentary sequence with metabasites, clastic metasedimentary rocks and marbles. Paleogeographically, the CBU has been considered to be derived from the subducted Pindos oceanic domain and Adria (Apulia) continental block with its sedimentary cover (Bonneau, 1984; Fu et al., 2015; Jolivet & Brun, 2010; Pe-Piper, 1998; Philippon et al., 2012). Detrital zircon data from the CBU along the WCDS indicate that the Cycladic Basement rocks have not been exposed during the Triassic and that the majority of clastic sediments of the CBU were derived from the recycled northern margin of Gondwana (e.g., Seman et al., 2017). This is in contrast to the interpretations of rocks in the central Cyclades (Sikinos and Ios; Flansburg et al., 2019; Poulaki et al., 2019), that suggest a continuous stratigraphic record and provenance evolution from the Cycladic Basement into the CBU.

The CBU records a tectonic evolution from the subduction of the Paleo-Tethys to Permo-Triassic rifted margin with syn-rift bimodal volcanism towards Mesozoic passive continental margin sedimentation and subduction of the Neo-Tethyan Pindos basin (e.g., Bonneau, 1984; Bröcker & Pidgeon, 2007; Fu et al., 2015; Pe-Piper, 1998; Poulaki et al., 2019; Seman et al., 2017). The CBU has been divided into the Upper and Lower Cycladic Blueschist Nappe (Grasemann et al., 2018), based on differences in peak high-pressure/low-temperature metamorphic conditions that were attained during Eocene subduction (Fig. 2.1B-C). The Upper Cycladic Blueschist Nappe (UCBN) exposed in the north and central Cyclades consists of high-pressure/low-temperature metamorphic rocks, which experienced eclogite facies metamorphism. These rocks occur in the hanging wall of a proposed syn-orogenic Trans-Cycladic Thrust (TCT, Fig. 2.1) that separates the two nappe structures

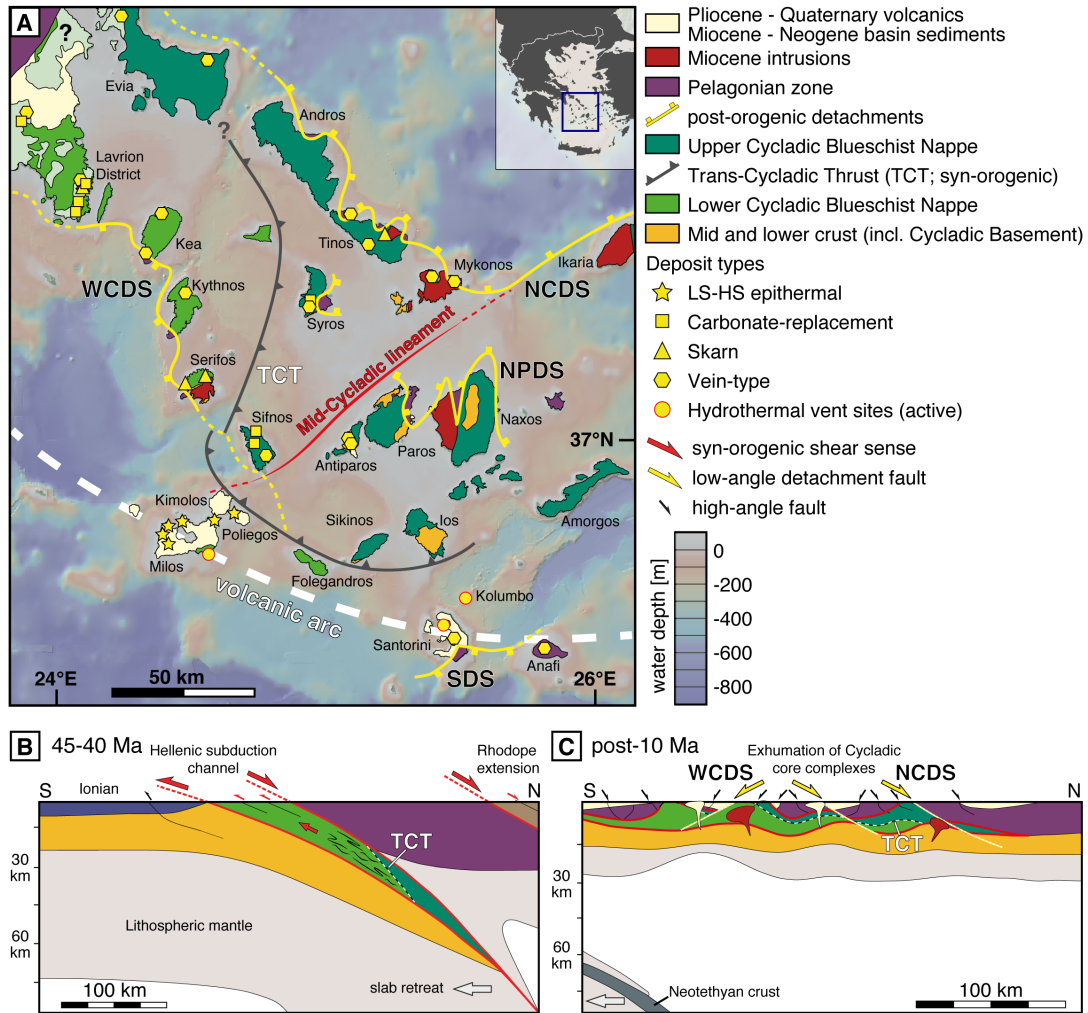


Fig. 2.1: A. Simplified geological map of the Cyclades Mineral District, Greece (modified after Grasmann et al., 2018; Schneider et al., 2018), highlighting locations of ore deposits included in this study. Unit in grey-green represents the Basal Unit in Attica and Evia (e.g., Gerogiannis et al., 2019; Ring et al., 2007) and Lower Unit in Lavrion (e.g., Coleman et al., 2019; Scheffer et al., 2017). Blue square in the inset shows the location of the study area in the Aegean Sea. Background bathymetry map made with GeoMapApp (www.geomapp.org) and CC BY (Ryan et al., 2009). B. and C. Cross-sections of the Aegean from ca. 45–40 Ma and post-10 Ma, respectively (simplified after Grasmann et al., 2018; Roche et al., 2016). Colors on map are the same as the cross-sections, which are drawn to illustrate the Cyclades have evolved as a back-arc setting due to slab retreat. LS-HS: Low- to high-sulfidation, NCDS: North Cycladic Detachment System, NPDS: Naxos-Paros Detachment System, SDS: Santorini Detachment System, WCDS: West Cycladic Detachment System.

(Grasemann et al., 2018). In the footwall of the TCT are the rocks of the Lower Cycladic Blueschist Nappe (LCBN) that reached peak blueschist facies metamorphic conditions and underwent Paleocene-Eocene pervasive ductile deformation.

The Pelagonian zone, also referred to as Upper Cycladic Unit, records a polymagmatic and polyorogenic history and consists of klippen of a Palaeozoic basement with Late Permian to Jurassic volcanoclastic rocks and carbonate cover overlain by ophiolite sequences that were thrust onto the Cycladic Blueschist Nappes between 25 and 20 Ma (Bonneau, 1984; Jolivet et al., 2004; Jolivet & Brun, 2010; Schenker et al., 2014). The uppermost unit consists of Miocene to Pliocene marine to continental sediments deposited in the supradetachment basins that are preserved on Mykonos, Paros, Naxos and Lavrion (e.g., Bargnesi et al., 2013; Krohe et al., 2010; Sánchez-Gómez et al., 2002). The lack of clasts from the UCBN, LCBN and Cycladic Basement in the Miocene conglomeratic sequence indicate that the deeper metamorphic units were not exposed until 8 Ma (Sánchez-Gómez et al., 2002).

In the early Miocene, the southward migrating volcanic arc reached the Cyclades, introducing a suite of syn-tectonic intrusions within the deformed upper crust (Fig. 2.1 and 2.2; e.g., Tinos, Mykonos, Serifos, Naxos, Thera: Altherr et al., 1982; Altherr & Siebel, 2002; Bolhar et al., 2010; Iglseder et al., 2009; Jolivet et al., 2015; Rabillard et al., 2018; Schneider et al., 2018). Magmatism in the east started at ca. 17 Ma (e.g., Ikaria, Tinos; Bolhar et al., 2010), whereas in the west it started only after 10 Ma (e.g., Lavrion, Serifos; Iglseder et al., 2009; Liati et al., 2009). Metaluminous to slightly peraluminous I-type intrusive bodies show a systematic regional variation in their compositions with increasing distance from the trench: medium- to high-K granodiorites in the west (Lavrion, Serifos), high-K, low-silica granites in the central region (Tinos, Mykonos, Naxos, Thera) and high-K, high-silica granites (Ikaria), monzonites, monzogranites and composite lamprophyric-monzonitic dikes

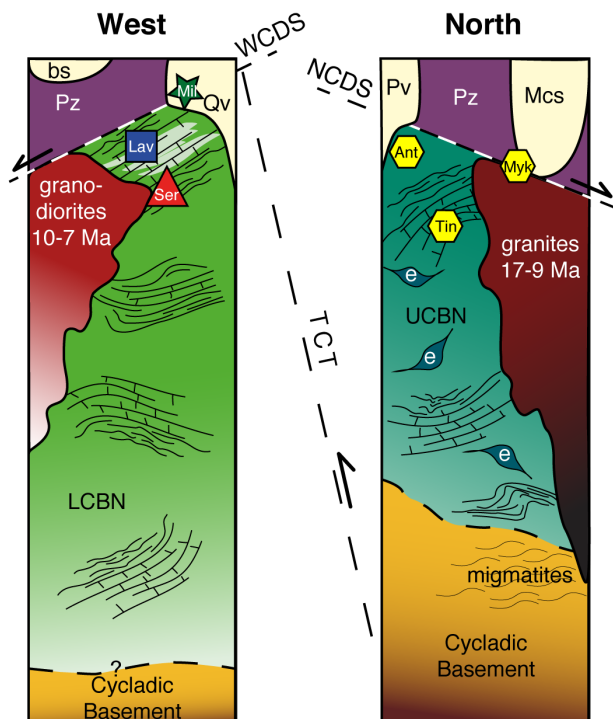


Fig. 2.2: Schematic tectono-stratigraphic sequences of the west Cyclades (along the WCDS) and north-central Cyclades (along the NCDS, including NPDS), showing the main correlations between the stratigraphic units. Placement of the deposits are at relative structural levels. Carbonate-replacement and vein-type deposits in Lavrion mainly occur along detachment fault contact of the marbles and schists of the Basal Unit and LCBN. Note that deposits on Antiparos are temporally related to the Pliocene volcanic sequences in the hanging wall, but quartz and barite veins cut the schists and marbles of the UCBN and gneiss units of the Cycladic Basement. Ant: Antiparos, bs: basin sediments (Miocene to Neogene), e: eclogite, Lav: Lavrion District, LCBN: Lower Cycladic Blueschist Nappe, Mcs: Miocene conglomeratic sequence, Mil: Milos, Myk: Mykonos, NCDS: North Cycladic Detachment System, Pv: Pliocene volcanics, Pz: Pelagian zone, Qv: Quaternary volcanics, Ser: Serifos, TCT: Trans-Cycladic Thrust, Tin: Tinos, UCBN: Upper Cycladic Blueschist Nappe, WCDS: West Cycladic Detachment System.

in the east (Kos, Samos; [Altherr et al., 1982](#); [Altherr & Siebel, 2002](#); [Schliestedt et al., 1987](#)). In addition to the I-type intrusions, smaller S-type intrusive bodies occur on Serifos, Tinos, Paros and Naxos ([Altherr et al., 1982](#); [Altherr & Siebel, 2002](#) and references therein), which pre-date the I-type intrusions ([Bolhar et al., 2010](#)). Geochemistry and isotopic composition of the Cycladic granitoids are typical for crustal-derived magmas (e.g., [Stouraiti et al., 2010](#)), whereas Miocene to Quaternary volcanics are indicative of mantle-derived magmas with variable degrees of metasomatism and crustal contamination (e.g., [Francalanci & Zellmer, 2019](#); [Ersoy & Palmer, 2013](#); [Pe-Piper, 1994](#)). Moreover, an influence of subducted carbonate-rich and Nile-derived terrigenous sediments on the magmatism of the active Aegean arc has been suggested (e.g., [Francalanci & Zellmer, 2019](#); [Klaver et al., 2015, 2016a](#); [Pe-Piper & Piper, 2001](#); [Woelki et al., 2018](#)). The present-day south Aegean volcanic arc extends from Sousaki in the northwest, across Milos and Santorini towards

Nisyros in the southeast where it has been located since the Pliocene (e.g., [Francalanci et al., 2005](#); [Francalanci & Zellmer, 2019](#); [Innocenti et al., 1981](#)).

2.2.2 Cyclades Mineral District

The metallogenic evolution of the eastern Mediterranean was strongly influenced by the geodynamic evolution of the subduction zone. According to [Menant et al. \(2018\)](#) large Cu deposits, including porphyry Cu(-Mo-Au) deposits and associated epithermal and skarn mineralization in the Balkans and Pontides, formed during the late Cretaceous above a stable subduction zone that produced large amounts of potentially fertile magmas. Large Pb-Zn(-Ag) deposits formed in the Rhodope Massif during the late Eocene-Miocene in response to mobilization of Pb and Zn by crustal melts during back-arc extension, followed by Au-rich deposits in western Turkey in response to rapid retreat of subduction and slab tearing ([Menant et al., 2018](#)). The latter is thought to have favored the mobilization of Au from the metasomatized lithospheric mantle and the ascent of magmatic and hydrothermal fluids through the brittle crust ([Menant et al., 2018](#)). During accelerated slab retreat and back-arc extension, the deposits of the Cyclades Mineral District formed as part of the Miocene metallogenic episode, dominated by Pb-Zn detachment-related deposits and low sulfidation epithermal Au $\pm$ Cu deposits ([Menant et al., 2018](#)). Here, economic mineral deposits occur in all tectono-stratigraphic units (Fig. 2.1 and 2.2) and are temporally and spatially associated with the detachments and Miocene granitoids, as well as Pliocene-Quaternary volcanic rocks along the active volcanic arc.

The Cyclades Mineral District extends from the Attica Peninsula in the north to the active volcanic arc in the south and includes the transition from mid-Miocene shallow crustal magmatism to modern seafloor hydrothermal systems (Fig. 2.1). The mineral deposits are temporally associated with different stages of the geodynamic evolution of the Aegean arc-

to backarc (e.g., [Skarpelis, 2002](#); [Menant et al., 2018](#)). Although geochronological data for the deposits are lacking, the spatial association with dated Miocene intrusions (e.g., [Altherr et al., 1982](#); [Bolhar et al., 2010](#); [Iglseder et al., 2009](#); [Liati et al., 2009](#)) throughout the district and Pliocene to Quaternary volcanism along the active arc suggests that magmatic-hydrothermal activity was older in the east and north of the district and younger in the west and south. [Menant et al. \(2018\)](#) highlighted that all the deposits formed during transtension or extension where crustal-scale detachments and associated high-angle normal faults facilitated the final exhumation of the metamorphic core complexes, and further fostered the ascent of metal-bearing fluids. This is supported by the involvement of seawater and/or meteoric fluid components in the hydrothermal systems, as described for the majority of precious and base metal-rich deposits in the Cyclades (e.g., Milos, Serifos, Lavrion District, Antiparos, Mykonos, Tinos; [Alfieris et al., 2013](#); [Bonsall et al., 2011](#); [Fitros et al., 2017](#); [Kevrekidis et al., 2015](#); [Kilias et al., 2001](#); [Tombros et al., 2007, 2015](#)).

Table 2.1: Characteristics of the different deposit types in the Cyclades Mineral District in Greece.

Deposit style	Location	Deposit or district name	Ore minerals	Gangue minerals	Mineralization style	Morphology of orebodies	Main rock	Age	References
<i>Porphyry</i>									
Porphyry	Lavrio	Plaka	Py, Ccp, Mol, Po, Sch	Qz, Ser	Alkaline Cu-Mo porphyry	Sheeted quartz veins, stockwork	Granodiorite	Miocene (HR: 8.3 Ma)	Altherr et al. (1982); Bon-sall et al. (2011); Liati et al. (2009); Voudouris et al. (2008a, 2019)
<i>Epithermal deposits</i>									
Epithermal Type	Milos	Profitis Ilias	Stage I: Py, Gn, Sp, Ccp, Hs, Alt, Pz, Col, Au, Ag; Stage II: Bn, Cv, Cc, Gn, Sp, Au	Stage I: Qz, Brt, Adl, Ser; Stage II: Qz, Brt, Adl, Ilt	LS-IS	Massive to semi-massive ore, veins	Rhyolite-rhyodacite, pyroclastic rocks	Pliocene-Pleistocene (HR: 2.7 Ma)	Alfieris et al. (2013); Kilias et al. (2001); Naden et al. (2005)
Epithermal Type	Milos	Chondro Vouno	Py, Gn, Sp, Ccp, Td, Au, Ag	Qz, Brt, Adl, Ilt	LS-IS	Veins	Dacite, rhyodacite, pyroclastic rocks	Pliocene-Pleistocene (HR: 2.7 Ma)	Alfieris et al. (2013); Kilias et al. (2001); Naden et al. (2005)
Epithermal Type	Milos	Triades-Galana	Py, Gn, Sp, Ccp, Apy, Cv, Td, Th, Prg, Eng, Fam, Prs, Prc, Au	Qz, Brt, Adl, Ser	IS-HS	Veins, stockworks, breccia bodies	Andesite-dacite, pyroclastic, and volcanic sedimentary rocks	Pliocene-Pleistocene (HR: 2.2–1.5 Ma)	Alfieris et al. (2013); Marschik et al. (2010); Stewart & McPhie (2006)
Epithermal Type	Milos	Kondaros-Katsimouti-Vani	Py, Gn, Sp, Ccp, Td, Plb, Hem, Ag, Arg, Pyr	Qz, Brt, Cal, Zeo	LS-IS epithermal style	Massive to semi-massive ore, veins, stratabound and stratiform layers	Dacite-andesite, pyroclastic, and volcanic sedimentary rocks	Pliocene-Pleistocene (HR: 2.5–1.4 Ma)	Alfieris et al. (2013); Pavasilou et al. (2016b); Pavasilou et al. (2017)
<i>Vein-type deposits</i>									
Vein-type (intrusion related)	Anafi	Langada	Py, Gn, Sp, Ccp	Qz, Ser, Cal	IS sub-epithermal	Banded and brecciated veins	Granodiorite	Miocene?	Voudouris et al. (2019)
Vein-type (intrusion related)	Anafi	Stavros, Dumbaria	Gn, Sp	/	IS sub-epithermal	Banded and brecciated veins	Granodiorite	Miocene?	Gale & Stos-Gale (1981)

Table 2.1: (continued)

Deposit style	Location	Deposit or district name	Ore minerals	Gangue minerals	Mineralization style	Morphology of orebodies	Main host rock	Age	References
Vein-type (intrusion related)	Antiparos	Agios Georgios, Prassovounia	Py, Po, Mag, Sp, Gn, Ccp, Bn, Td, Arg, Au, Ag	Qz, Ser, Chl, Cal, Brt, Fl	Vein-type	Veins, stockworks	UCBN: marble, schist	5–4 Ma (intrusion related)	Innocenti et al. (1982); Kevrekidis et al. (2015); this study
Vein-type (intrusion related)	Evia	Kallianou	Py, Gn, Ccp, Td, Hs, Styl, Col, Pz, Stz, Te, Te-Plb, El	Qz, Chl, Ser, Ab, Cb	IS sub-epithermal	Veins, dissemination	UCBN: schist, marble	Miocene	Voudouris et al. (2011, 2019)
Vein-type	Kea	Faros, Nikolieri, Petrousa, Schoinos	Gn	/	/	/	LCBN	Miocene?	Gale & Stos-Gale (1981); Stos-Gale et al. (1996)
Vein-type (intrusion related)	Kythnos	Agios Dimitrios	Gn, Hem	Brt	/	Vein	LCBN: metabasites?	Miocene?	Gale & Stos-Gale (1981); Laner (2009)
Vein-type	Lavriion	Vein 80	Gn, Sp, Po, Py, Apy, Ccp, Lo, Td, Bnn, Mia, Prg, Lil	Qz, Sd, Fl, Cal	LS-IS epithermal-style	Banded and brecciated Qz-Sd-Fl vein	LCBN?: hornfels, marble, schist	<8.3 Ma (structural evidences)	Scheffer et al. (2017, 2019); Voudouris et al. (2008a, 2019)
Vein-type	Lavriion	Kamariza (Clenence)	Py, Sp, Apy, Gn, Eng, Ccp, Th/Td, Grf, Stn, Au, Bmt, Mia, Sb, Bnn	Qz, Fl, Cal, Brt	IS-HS epithermal-style	Banded and brecciated Qz-Fl vein, open space filling	LCBN?: marble, schist	<8.3 Ma (structural evidences)	Scheffer et al. (2017, 2019); Voudouris et al. (2019)
Vein-type (intrusion related)	Mykonos	Panormos Bay	Gn, Td, Ccp, Sp, Bnn, Fam, Plb, Py, Fbg	Brt, Qz	Vein (IS?)	Brt veins, stockworks	Miocene conglomeratic sequence	11–8 Ma (structural evidences)	Menant et al. (2013); Sánchez-Gómez et al. (2002); Tombros et al. (2015); this study
Vein-type (intrusion and detachment related)	Mykonos	Cape Evros, Profitis Ilias	Py, Sp, Gn, Ccp, Apy, Bn, Hs, Prg, Alt, Arg, Ag, Au, Prg, Jrd, Gen, Blg	Qz, Brt, Chl, Ser, Cal, Sd	Detachment related IS epithermal?	Banded veins and stockworks	Monzogranite and Pelagian zone	11–8 Ma (structural evidences)	Menant et al. (2013, 2018); Skarpelis (2002); Tombros et al. (2015); this study

Table 2.1: (continued)

Deposit style	Location	Deposit or district name	Ore minerals	Gangue minerals	Mineralization style	Morphology of orebodies	Main host rock	Age	References
Vein-type (intrusion related)	Santorini	Cape Athinios	Gn, Py	Qz	Vein-type	Veins and stockworks	LCBN: phyllitic schist	Miocene	Gale & Stos-Gale (1981)
Vein-type (fault-related)	Sifnos	Faros, Platy Gialos	Py, Ccp, Po, Ag, Au	Qz	Fault-related	Subvertical Au-Qz veins	UCBN: greenschist-gneiss	13–10 Ma (structural evidences)	Menant et al. (2018); Neubauer (2005)
Vein-type (fault-related)	Sifnos	Cape Sostis	Td, Ag-Sb-S, Gn, Au, Ag	Sd, Ank, Cer, Ang, Sm	Fault-related	Lenses and layers, breccias, massive bodies	UCBN: marble	13–6 Ma (structural evidences)	Gale & Stos-Gale (1981); Neubauer (2005); Vavidis et al. (1985)
Vein-type	Syros	Azolimnos	Gn, Td, Fam, Bm, Sp	Qz, Cal	LS epithermal style	Veins and breccias	LCBN: marble	10–8 Ma (structural evidences)	Voudouris et al. (2014)
Vein-type	Syros	Tourlos	Gn, Py, Ccp	Qz, Chd, Cal	LS epithermal style	Qz-Chd-Cal veins	LCBN: schist, marble	10–8 Ma (structural evidences)	Voudouris et al. (2014)
Vein-type (intrusion related)	Tinos	Apigania Bay	Stage I: Py, Sp, Po, Apy, Mag, Arg, El, Stage II: Td, Fam, Ccp, Stage III: Gn, Plb, El	Qz, Ep, Chl	Fault-related LS?	Qz veins	UCBN: marble, schist, amphibolites	15–13 Ma (intrusion related)	Tombros et al. (2007, 2008)
Vein-type (intrusion related)	Tinos	Panormos Bay	Py, Td, Th, Gf, Ccp, Bn, Stn, Blg, Alt, Hs, Syl, Gn, Arg, Sp, Au, Ag, Prg	Qz, Cal, Chl, Ser	Detachment-related LS?	Qz veins	UCBN: marble	15–13 Ma (intrusion related)	Menant et al. (2018); Tombros et al. (2007, 2008, 2010)
<i>Volcanic hosted massive sulfide</i>									
Volcanic hosted massive sulfide	Kolumbo	Kolumbo	Py, Mrc, Sp, Gn, Ccp, Sb-Pb-S, As-S	Brt, Anh	Hydrothermal vent site	Chimneys, vertical spires, pinnacles, mounds	Rhyolite, basalts-andesites	Active	Kilias et al. (2013, 2016); Nomikou et al. (2012); Ahmad (2018)
<i>Carbonate-replacement deposits</i>									

Table 2.1: (continued)

Deposit style	Location	Deposit or district name	Ore minerals	Gangue minerals	Mineralization style	Morphology of orebodies	Main host rock	Age	References
Carbonate-replacement	Attica/Hymittos Mt.	Agios Ioannis Kynigos	Gn, As-Py, Td, Bnn, Ccp, Cv, Sp	Dol, Cal, Qz	Carbonate-replacement, vein	Open-space filling, disseminated, veinlets	LCBN?: mylonitic marbles (upper marble), schists	Miocene	Stouraiti et al. (2019)
Carbonate-replacement	Lavrion	Lavrion district: Kamariza-Sounio-Plaka	Py, Ccp, Po, Gn, Sp, Apy, Td-Tn, Bnn, Eng, Prg, Cv	Cal, Dol, Fl, Qz, Brt, Ser	Carbonate-replacement, vein	Massive, disseminated, layers, veins	LCBN?: marble-schist contact (lower and upper marble)	11.9-8.3 Ma (detachment and intrusion related)	Berger et al. (2013); Bonsall et al. (2011); Liati et al. (2009); Scheffer et al. (2019); Voudouris et al. (2008b)
Carbonate-replacement	Sifnos	Faros, Platy Gialos	Hem, Goe, Td, Py, Ccp, Gn, Sp, Ag	Cal, Dol, Cer, Sm, Brt, Qz	Shear zone and detachment fault related	Massive orebodies and lenses	UCBN: gneiss, schist, marble	Miocene	Neubauer (2005); Vavelidis et al. (1985)
Carbonate-replacement	Syros	Rozos, Tourlos	Py, Sp, Gn, Po, Stn, Apy, Mol	Qz	Carbonate replacement, vein	Dissemination, massive bodies	UCBN: marble, schist, gneiss	10-8 Ma (structural evidences)	Voudouris et al. (2014)
Skarn mineralization	Lavrion	Adami	Mag, Po, Py, Sch, Apy, Sp, Ccp, Gn, Bmt, Ttd	Qz, Cal	Magnetite Ca-Fe-exo- and endo-skarn	Lenses and layers	LCBN?: schist, marble (lower and upper)	8.3 Ma (intrusion related)	Altherr et al. (1982); Leleu et al. (1973); Scheffer et al. (2019); Voudouris et al. (2008a)
Skarn	Serifos	Moutoulas	Py, Apy, Sp, Ccp, Po, Gn, Bmt, Td-Tn, Ttd, Hs, Bi	Qz, Brt, Cal, Fl	Skarn, carbonate-replacement	Massive ore, pods, breccia, veins	LCBN: marble, schist, amphibolite	11.6-9.5 Ma (intrusion related)	Ducoux et al. (2017); Fitros et al. (2017); Salemink (1985); St. Seymour et al. (2009b); this study
Skarn	Serifos	Mega Chorio Megalo Livadi	Mag, late: Hem, Goe	Qz, late: Brt, Cal	Mag Ca-Fe-exo- and endo-skarn	Massive ore, banded veins	LCBN: marble, schist, amphibolite	10-8 Ma (intrusion and detachment related)	Ducoux et al. (2017); Salemink (1985)

Table 2.1: (continued)

Deposit style	Location	Deposit or district name	Ore minerals	Gangue minerals	Mineralization style	Morphology of orebodies	Main host rock	Age	References
Skarn	Tinos	Volax - Li-vadas Bay	Sch, Mag, Ccp, Po, Py, Sp	Grt, Px, Qz, Cal	Garnet-pyroxene skarn, horn-felses	Pods, veinlets	LCBN: marble, schist	14 (intrusion related)	Altherr et al. (1982); Seymour et al. (2009a)
/: No data available. HR: host rock, HS: high-sulfidation, IS: intermediate-sulfidation, LS: low-sulfidation. Mineral abbreviations: Ab: albite, Adl: adularia, Ag: native silver, Ag-Sb-S: Ag-Sb-rich sulfosalt, Alt: altaite, Anl: anhydrite, Ang: anglesite, Ank: ankerite, Apy: arsenopyrite, Arg: argentite, As-Py: arsenian pyrite, As-S: As-sulfides, Au: native gold, Bi: native bismuth, Blg: boulangerite, Bmt: bismuthinite, Bn: bornite, Bnn: bournonite, Brt: barite, Cal: calcite, Cb: carbonate minerals, Cc: chalcocite, Ccp: chalcopyrite, Cer: cerussite, Chd: chalcedony, Chl: chlorite, Col: coloradoite, Cv: covellite, Dol: dolomite, El: electrum, Eng: enargite, Ep: epidote, Fam: famatinite, Fl: fluorite, Gen: geoninite, Glf: goldfieldite, Gn: galena, Goe: goethite, Grf: gersdorffite, Grt: garnet, Hem: hematite, Hs: hessite, Ill: illite, Jrd: jordanite, Lil: lillianite, Lo: löllingite, Mag: magnetite, Mol: molybdenite, Mia: miargyrite, Mrc: marcasite, Po: pyrrhotite, Plb: polybasite, Prc: pearcette, Prg: pyrrargyrite, Prs: proustite, Py: pyrite, Pyr: pyrolusite, Px: pyroxene, Pz: petzite, Qz: quartz, Sb: native antimony, Sb-Pb-S: Sb-Pb-rich sulfosalts, Sch: scheelite, Ser: sericite, Sd: siderite, Sm: smithsonite, Sp: sphalerite, Stn: stannite, Stz: stützite, Syl: sylvanite, Td: tetrahedrite, Te: native tellurium, Te-Plb: tellurium-rich polybasite, Tn: tennantite, Ttd: tetradyomite, Zeo: zeolite.									

Variable exchange of the hydrothermal fluids with the metasedimentary host rocks also has been proposed as an important mechanism of ore formation (e.g., Lavrion District, Tinos, Serifos; [Berger et al., 2013](#); [Bonsall et al., 2011](#); [Fitros et al., 2017](#); [Scheffer et al., 2017](#); [Tombros et al., 2007](#)).

The deposits have been classified as manto-type carbonate-replacement Pb-Zn-Ag(-Au), low- to high-sulfidation epithermal, polymetallic and precious metal vein, skarn and porphyry systems (Table 2.1; see also summaries by [Melfos & Voudouris, 2017](#); [Menant et al., 2018](#); [Voudouris et al., 2019](#)). Carbonate-hosted replacement Pb-Zn-Ag mineralization in the Lavrion District and on the islands of Syros, Serifos and Sifnos is commonly spatially related to major detachment faults (e.g., [Berger et al., 2013](#); [Bonsall et al., 2011](#); [Fitros et al., 2017](#); [Scheffer et al., 2017](#)). Magnetite, Ca-Fe exo- and endo-skarns occur on Serifos and Lavrion ([Bonsall et al., 2011](#); [Ducoux et al., 2017](#); [Fitros et al., 2017](#); [Salemink, 1985](#); [Voudouris et al., 2008a](#)). Low- to high-sulfidation epithermal Au deposits and detachment- and fault-related base and precious metal vein mineralization are found on Evia, Tinos, Kythnos, Mykonos, Sifnos, Antiparos, Milos, and Anafi islands (e.g., [Alfieris et al., 2013](#); [Kevrekidis et al., 2015](#); [Menant et al., 2013](#); [Tombros et al., 2007, 2015](#); [Voudouris et al., 2019](#)). Although several of these deposits have been studied in isolation, no regional model has been proposed which links the wide range in mineralization to the accessible underlying crustal sources. The main focus of this study are the deposits of the Lavrion District, and the islands of Milos, Serifos, Mykonos, Tinos and Antiparos; a literature review of the mineralization styles on these islands is included in the Supplementary Information 2.A.

Argentiferous galena was one of the major mining products in the Cyclades Mineral District. Silver concentrations in galena up to a few weight percent have been reported from Agios Georgios on Antiparos (0.2–2.9 wt% Ag: [Kevrekidis et al., 2015](#)), Panormos Bay on Tinos (0.0–1.3 wt% Ag: [Tombros et al., 2010](#)) and Cape Evros on Mykonos (7.3

wt% Ag: Tombros et al., 2015). However, Gale & Stos-Gale (1981) reported highly variable Ag concentrations in galena throughout the Cyclades: <100 ppm in samples from Anafi, Naxos, Milos and Poliegos; 300–1000 ppm from Antiparos, Kythnos, Lavrion, Santorini, Serifos and Syros; >3000 ppm in one sample from Serifos and another sample south of Plaka (Lavrion). Voudouris et al. (2008a) compared trace element concentrations in galena in different styles of mineralization in the Lavrion District, where Ag concentrations in skarn-associated galena were the highest (~0.5 wt%).

2.3 Previous Pb-isotope studies

Lead isotopes of the mineral deposits in the Cyclades Mineral District have been studied previously to fingerprint the sources of metals and materials in archeological artefacts and the results are compiled in the Oxford Lead Isotope Database, OXALID (<http://oxalid.arch.ox.ac.uk>). Data were obtained from 1975 to 1998 at the Isotrace Laboratory in Oxford (UK) using thermal ionization mass spectrometer (TIMS) techniques. Due to technical advances over the years, samples have been analyzed multiple times and data have been continuously updated in OXALID. Details of the analytical methods and rationale of OXALID are described in Stos-Gale et al. (1995, 1996) and Stos-Gale & Gale (2009). The database includes $^{208}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ measurements, from which we have calculated values of $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$. Despite the large number of measurements, there is a lack of precise information on the sample localities, mineralization types and data quality. Although deposit names as well as mine sites are in most cases indicated, the majority of samples were collected from slag piles (e.g., Gale & Stos-Gale, 1981). The database does not provide a specific error for each measurement, but an overall accuracy better than 0.1% was achieved (Stos-Gale & Gale, 2009). In addition, a run

quality for each measurement is provided (e.g., excellent, very good, good, fair, poor, and very poor). Our studies of the OXALID database have shown that samples analyzed from, for example, Lavrion with an "excellent" data quality show a very narrow range in Pb-isotopes of galena ($^{206}\text{Pb}/^{204}\text{Pb}$: 18.84–18.89; $^{207}\text{Pb}/^{204}\text{Pb}$: 15.68–15.70), whereas the entire data set of Lavrion across the spectrum of quality shows a wide range in Pb-isotope ratios of galena ($^{206}\text{Pb}/^{204}\text{Pb}$: 18.79–18.96; $^{207}\text{Pb}/^{204}\text{Pb}$: 15.63–15.75). For these reasons, data with a run quality of "very poor," "poor" and "fair" have been excluded. In the case of multiple analyses of the same sample, the more recent analytical results were included. In addition to the OXALID database, Pb-isotope data have been compiled for Evia, Kolumbo, Milos, Serifos and Sifnos from published literature ([Ahmad, 2018](#); [Chalkias & Vavelidis, 1988](#); [Gale & Stos-Gale, 1981](#); [Fitros et al., 2017](#); [Marschik et al., 2010](#); [Vavelidis et al., 1985](#)). However, mineral occurrences in the central Cyclades and along the active volcanic arc are underrepresented in the compiled data set, often with samples from only one deposit on each island. In the case of Sifnos only few data were obtained on galena where the majority are from litharge. In all other cases only data obtained on galena has been selected for better comparison with our new results; data obtained on other mineral phases and material (e.g. pyrite, sphalerite, sulfosalts, cerussite, malachite, azurite, litharge and lead slag) have been excluded as they often show a larger range in Pb-isotope ratios. This is especially true for data obtained on pyrite and sulfosalts that have significantly lower Pb-isotope ratios (e.g., [Fitros et al., 2017](#); [Ahmad, 2018](#)) than co-genetic galena. Assuming that the galena, pyrite and sulfosalts formed from the same metal-bearing fluid, the apparent variation might occur due to isobaric interferences or lower accuracy because of low lead concentrations, as it is assumed that no isotopic fractionation occurs during mineralization. Taken together, the existing Pb-isotope data covers over 25 occurrences of galena on 14 Cycladic islands, and indicate a range of different regional lead sources in the

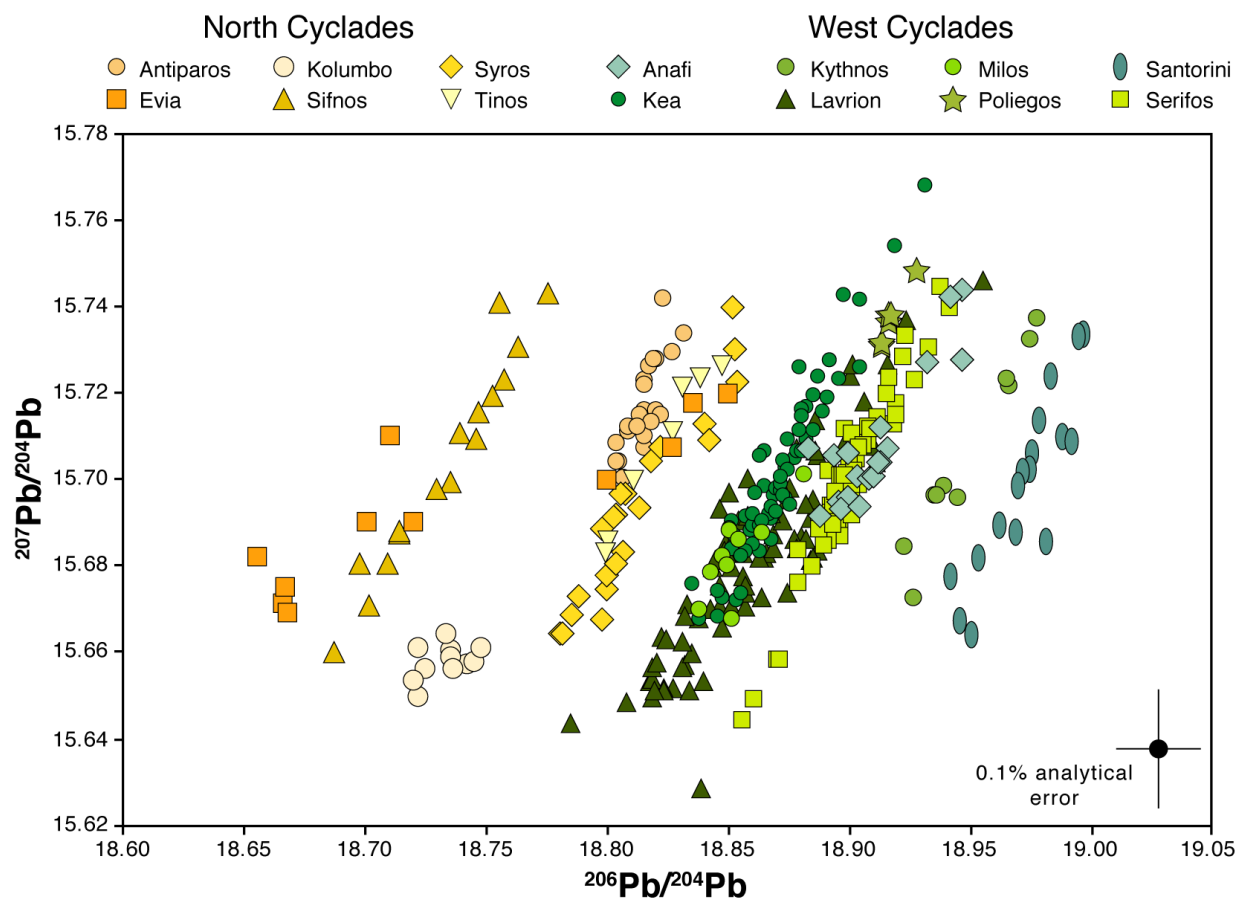


Fig. 2.3: Compiled Pb-isotope data of galena from the north-central Cyclades and west Cyclades from archaeometry studies involving TIMS analyses (OXALID database, e.g., [Gale & Stos-Gale, 1981](#); [Stos-Gale & Gale, 2009](#)) as well as [Ahmad \(2018\)](#); [Chalkias & Vavelidis \(1988\)](#); [Fitros et al. \(2017\)](#); [Marschik et al. \(2010\)](#) and [Vavelidis et al. \(1985\)](#). A 0.1% analytical error scale is drawn for reference.

Cyclades Mineral District (Fig. 2.3). Galena from mineral occurrences in the north-central Cyclades have low $^{206}\text{Pb}/^{204}\text{Pb}$ values (e.g., <18.84 : Evia, Tinos, Syros, Sifnos, Antiparos, Kolumbo), and galena from Kallianou (Evia) shows the lowest ratios (~ 18.68). Galena from mineral occurrences in the west Cyclades have generally higher $^{206}\text{Pb}/^{204}\text{Pb}$ values (e.g., ≥ 18.84 : Lavrion, Kea, Kythnos, Serifos, Milos, Poliegos, Anafi, Santorini). Galena from Santorini, along the active volcanic arc, has the highest $^{206}\text{Pb}/^{204}\text{Pb}$ values (~ 18.97). These examples indicate potentially highly variable lead sources in the Cyclades, which seem to be unrelated to the style or timing of mineralization.

2.4 Methodology

2.4.1 Sampling approach

Sampling for this study was focused on two traverses, one along the NCDS and one along the WCDS, as well as mineral occurrences on islands (e.g., Milos, Tinos, Mykonos) that are underrepresented in the OXALID Pb-isotope data for galena. Deposits on multiple islands were sampled to test the hypothesis of regional variations and the possible influence of mineralization style and immediate country rock. Samples were taken over $\sim 40,000 \text{ km}^2$ of the arc-backarc system, covering deposits of late Miocene to early Pleistocene Epoch, in an attempt to understand the role of the geodynamic setting on the sources of lead.

On each island several prospects were targeted. The sample locations and characteristics are listed in Table 2.2 and described in more detail in Section 2.5. Sampling along the WCDS was carried out on the mainland at Lavrion and on the islands of Serifos and Milos. At Lavrion samples were collected in the Kamariza area, near Plaka and Soureza. These carbonate-replacement deposits occur mainly in the carbonate horizons of the Basal Unit (Fig. 2.1). On Serifos, polymetallic veins and sulfide-rich horizons were sampled in

Moutoulas, where mineralization is also concentrated in the carbonate-rich layers of the LCBN. Quaternary epithermal deposits were sampled on Milos, including sulfide-rich low- to high-sulfidation mineralization in the western part of the island at Kondaros-Katsimouti, Triades-Galana and Profitis Ilias.

Along the NCDS and NPDS, samples were taken on Tinos, Mykonos and Antiparos, where steeply-dipping quartz and barite veins occur along major fault systems that cut the metamorphic basement (Upper Cycladic Blueschist Nappe, UCBN) and Pelagonian zone rocks in the hanging wall of the detachments. On Tinos, sulfide-bearing quartz veins were sampled at Panormos Bay and Apaginia Bay (the latter were free of galena). Sampling at Mykonos targeted sulfide-bearing barite veins in Cape Evros, Cape Charos and Panormos Bay (none previously sampled for galena). However, samples from Cape Charos were free of galena. Two sets of sub-vertical quartz veins were sampled in the Prassovounia area on Antiparos. No samples of galena were recovered from Kimolos, Sifnos, and Santorini.

Table 2.2: Coordinates and geological details of galena samples, Cyclades, Greece.

Sample	UTM (N)	UTM (E)	Region/Deposit	Mineralization	Host rock (unit)	Ore phases	Gangue minerals	Inclusions in Gn
17L145_1 "	4183242	238695	Lavrion/ Plaka (Adit No. 145)	breccia	marble-schist contact (LCBN?)	Fe-Sp, Py, Gn, Po	Cb, Brt	Cer, Cb
17L145_2 "	4183242	238695	Lavrion/ Plaka (Adit No. 145)	carbonate- replacement	marble (LCBN?)	Fe-Sp, Gn, Py, Ccp, Apy, Po, Sm	Cb, Brt, Ap, Ttn, Fl, Rt	Sp, Py, Po, Ccp, Ank, Dol, Fl
17L145_3 "	4183242	238695	Lavrion/ Plaka (Adit No. 145)	carbonate- replacement	marble (LCBN?)	Py, Gn, Fe-Sp, Ccp, Po	Dol, Ank, Brt, Ser	inclusion-rich: Sp, Py, Ccp, Fe-Mn-Dol
17L145_4 "	4183242	238695	Lavrion/ Plaka (Adit No. 145)	breccia	marble-schist contact (LCBN?)	Py, Gn, Fe-Sp, Ccp, Apy, Td	Cb, Ser, Cer, Ang	Sp, Py, Ccp, Td, Ang
17LK1	4177323	237207	Lavrion/ Kamariza	carbonate- replacement, breccia, vein	marble (LCBN?)	Gn, Fe-Sp, Py	Qz, Cb	Sp, Py, Cb
17LK3	4177539	237207	Lavrion/ Kamariza	carbonate- replacement	silicified (LCBN?)	Gn, relicts of Py, Ccp replaced by Fe-oxide	Ank, Qz	Cer, Ang, Qz
17LK4	4177539	237207	Lavrion/ Kamariza	carbonate- replacement	marble-schist contact (LCBN?)	Gn, Sp, sec- ondary Fe-oxide	Qz, Cb	inclusion-rich: Sp, Cb, Qz, Cer
17LK6	4175196	236728	Lavrion/ Kamariza	carbonate- replacement	marble (LCBN?)	Gn, Sp, relicts of Py replaced by Fe-oxide	Qz, Ank	Sp, Py, Cv, Fe- oxides
17LS2*	4176225	237010	Lavrion/ Soureza (Gallery No. 2)	carbonate- replacement, vein	marble (LCBN?)	Gn, Td, Sp, Py, Ccp	Cb, Qz, Ser	inclusion-rich: Sp, Td, Po, Py, Cb, Qz, Cer
17SG1**	4118528	278253	Serifos/ Moutoulas	skarn, carbonate- replacement	marble (LCBN)	Gn, Py	Cb, Qz	rare
17SG2**	4118502	278244	Serifos/ Moutoulas	skarn, carbonate- replacement	marble (LCBN)	Fe-Sp, Gn, Py, Ccp, Po, Fe- oxides	Cb, Ser, Ang	rare: Sp, Py, Po, Ang
17SG6**	4118495	278230	Serifos/ Moutoulas	skarn, carbonate- replacement	marble (LCBN)	Gn	Cb	/
17MK1	4068624	264878	Milos/ Kondaros- Katsimouti	Qz veins	pyroclastic and volcano-sedimentary (dacitic Quaternary volcanics)	Gn, Sp, Py	Qz, Ser, Ep, Ang, Jrs	Sp, Ag-Td, Plb, Fbg, Ang

Table 2.2: (continued)

Sample	UTM (N)	UTM (E)	Region/Deposit	Mineralization	Host rock (unit)	Ore phases	Gangue minerals	Inclusions in Gn
17MK2_1	4068624	264878	Milos/ Kondaros- Katsimouti	Qz veins	pyroclastic and volcano-sedimentary (dacitic Quaternary volcanics)	Sp, Gn, Py, Ccp, Td	Qz	Py, Sp, Plb
17MK5	4068624	264878	Milos/ Kondaros- Katsimouti	Qz-Brt veins	pyroclastic and volcano-sedimentary (dacitic Quaternary volcanics)	Sp, Py, Gn	Qz, Brt, Jrs	Sp
17MGA03	4066365	262890	Milos/ Galana	breccia bodies	volcano-sedimentary (andesitic-dacitic Quaternary volcanics)	Sp, Gn, Tn, Py, Ccp, Eng, Td- Tn	Qz, Brt, Ser	rare: Sp, Ccp, Tn
17MGA04	4066365	262890	Milos/ Galana	breccia bodies	volcano-sedimentary (andesitic-dacitic Quaternary volcanics)	Gn, Sp, Td-Tn, Py, Ccp	Qz, Brt, Ser, Ep, Anh, Jrs, Pb-Cl, Anh	Td-Tn, Py, Cd- Hg-S, Qz
17MGA05	4066365	262890	Milos/ Galana	breccia bodies	volcano-sedimentary (andesitic-dacitic Quaternary volcanics)	Gn, Sp, Ccp	Qz, Brt, Ser	Sp, Ccp
17MGA07	4066344	262852	Milos/ Galana	breccia bodies	volcano-sedimentary (andesitic-dacitic Quaternary volcanics)	Sp, Py, Ccp, Gn, Td-Tn	Qz, Ser	inclusion-rich: Sp, Py, Qz
17MT02	4065598	262992	Milos/ Triades	breccia bodies	volcano-sedimentary (andesitic-dacitic Quaternary volcanics)	Py, Sp, Gn, Ccp, Td-Tn	Qz, Brt, Ser	Py, Sp, Qz
17MT03	4065598	262992	Milos/ Triades	breccia bodies	volcano-sedimentary (andesitic-dacitic Quaternary volcanics)	Sp, Py, Gn, Ccp, Td-Tn, Plb	Qz, Brt, Ser	inclusion-rich: Sp, Py, Ccp, Td-Tn, Qz
17MT04	4065598	262992	Milos/ Triades	breccia bod- ies, veins	volcano-sedimentary (andesitic-dacitic Quaternary volcanics)	Sp, Gn, Py, Ccp, Td	Qz, Brt, Ser	
PD012***	4062073	265678	Milos/ Profitis Ilias	Qz vein	pyroclastics (rhyolite- rhyodacite Quater- nary volcanics)	Sp, Py, Gn, Ccp, Td	Qz	Sp, Py, Hs, Pz, Ag-Alt, Ag-Col
17TP1	4168661	327338	Tinos/ Panormos Bay	Qz vein	marble (UCBN)	Gn, Py	Qz	/
17MYP1	4149176	355219	Mykonos/ Panormos Bay	Brt vein	Miocene conglomer- atic sequence	Gn, Td, Ag-Td, Ccp, Py, Plb, Fam, Bnn, Sp, Fbg	Brt, Qz, Cer	Ccp, Td, Qz, Brt
17MYP3	4149176	355219	Mykonos/ Panormos Bay	Brt vein	Miocene conglomer- atic sequence	Gn, Hem	Brt, Qz	Hem, Qz
17MYP4	4149176	355219	Mykonos/ Panormos Bay	Brt vein	Miocene conglomer- atic sequence	Gn, Ccp, Td-Tn, Hem	Brt, Qz	Sp, Ccp, Plb, Qz, Brt

Table 2.2: (continued)

Sample	UTM (N)	UTM (E)	Region/Deposit	Mineralization	Host rock (unit)	Ore phases	Gangue minerals	Inclusions in Gn
17MYV2_1	4147638	363342	Mykonos/ Cape Evros (Vein2)	Brt vein	silica (Miocene intrusion)	Gn, Sp, Ccp, Py, Tdt-Tn, Bn, Hem	Qz, Brt, Ms	Py, Ccp, oxide, Sp, Qz, Mck
17MYV2_1B	4147638	363342	Mykonos/ Cape Evros (Vein2)	Brt vein	silica (Miocene intrusion)	Gn, Ccp, Py	Qz, Brt, Ms	rare: Qz
17AP2	4096444	325429	Antiparos/ Prassovounia	Qz-Brt veins	schist, (UCBN)	Gn, Py, Sp, Hem, Sm	Qz, Brt, Cer	rare: Sp
17AP6	4097196	325108	Antiparos/ Prassovounia	Qz vein	schist (UCBN), gneiss (CB)	Sp, Py, Gn	Qz, Ser	rare: Sp, Py
Notes: *Archival sample of Hercules Katsaros. **Archival sample. *** Archival sample of Stephanos Kilias. "Coordinates of adit entrance. Abbreviation: Ag-Alt: Ag-rich altaite, Ag-Col: Ag-rich coloradoite, Ag-Td: Ag-rich tetrahedrite, Ang: anglesite, Anh: anhydrite, Ank: ankerite, Ap: apatite, Apy: arsenopyrite, Bn: bornite, Bnn: bournonite, Brt: barite, Cb: carbonate minerals, Ccp: chalcopyrite, Cd-Hg-S: Cd-Hg-sulfosalt, Cer: cerrusite, Cv: covellite, Dol: dolomite, Eng: enargite, Ep: epidote, Fam: famatinite, Fbg: freibergite, Fe-Sp: Fe-rich sphalerite, Fl: fluorite, Gn: galena, Hem: hematite, Hs: hessite, Jrs: jarosite, Mck: mckinstyrite, Ms: muscovite, Pb-Cl: Pb-chloride, Plb: polybasite, Po: pyrrhotite, Py: pyrite, Pz: petzite, Rt: rutile, Ser: sericite, Sm: smithsonite, Sp: sphalerite, Tdt: tetrahedrite, Tn: tennantite, Ttn: titanite								

Notes: *Archival sample of Hercules Katsaros. **Archival sample. *** Archival sample of Stephanos Kilias. *Coordinates of adit entrance.

Abbreviation: Ag-Alt: Ag-rich altaite, Ag-Col: Ag-rich coloradoite, Ag-Td: Ag-rich tetrahedrite, Ang: anglesite, Anh: anhydrite, Ank: ankerite, Ap: apatite, Apy: arsenopyrite, Bn: bornite, Bm: bourmonite, Brt: barite, Cb: carbonate minerals, Ccp: chalcopyrite, Cd-Hg-S: Cd-Hg-sulfosalt, Cer: cerrusite, Cv: covellite, Dol: dolomite, Eng: enargite, Ep: epidote, Fam: famatinite, Fbg: freibergite, Fe-Sp: Fe-rich sphalerite, Fl: fluorite, Gn: galena, Hem: hematite, Hs: hessite, Jrs: jarosite, Mck: mckinstyrite, Ms: muscovite, Pb-Cl: Pb-chloride, Plb: polybasite, Po: pyrrhotite, Py: pyrite, Pz: petzite, Rt: rutile, Ser: sericite, Sm: smithsonite, Sp: sphalerite, Td: tetrahedrite, Tn: tennantite, Ttn: titanite

2.4.2 LA-Q-ICP-MS Pb-isotope analysis

Galena mineral separates were prepared from 31 samples collected at twelve deposits on six islands (from north to south: Lavrion-9, Tinos-1, Mykonos-5, Serifos-3, Antiparos-2, Milos-11). For all samples, detailed field and petrographic descriptions were recorded with an emphasis on different generations of galena, if present. Samples were crushed, and single galena crystals were handpicked. Epoxy grain mounts were prepared and imaged under the reflected light microscope and with the scanning electron microscope (SEM) to target inclusion-free areas within the galena crystals for analysis.

Lead-isotope analyses were carried out at the University of New Brunswick (Fredericton, Canada) on a Resonetics S-155-LR 193 nm Excimer laser ablation system coupled to an Agilent 7700x quadrupole inductively coupled plasma mass spectrometer (LA-Q-ICP-MS) following the method of [McFarlane et al. \(2016\)](#). Data were collected in five analytical sessions over two consecutive days, and the detector pulse/analog (P/A) factors were calibrated between each analytical session. Ablations were 25 s with a laser pulse rate of 2.5 Hz and a fluence of $\sim 2 \text{ J/cm}^2$ with 25 s of background collection and washout time. For 29 of the samples a spot diameter of $82 \text{ }\mu\text{m}$ was used, and two smaller sample populations were analyzed with $60 \text{ }\mu\text{m}$ diameter spot. For each sample, 20 ablations on a minimum of twelve grains were obtained. The following isotopes have been analyzed: ^{107}Ag , ^{111}Cd , ^{202}Hg , $^{204}(\text{Pb}+\text{Hg})$, ^{205}Tl , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , and ^{238}U . To correct for instrument drift and mass bias in-house galena reference materials from Broken Hill Australia ([Stacey et al., 1969](#)) and Jubilee Nova Scotia ([Sangster et al., 1998](#)) were interspersed with the unknowns. Long-term (3-year) repeated measurements (n: 22) of Pb-isotope ratios of Jubilee galena yielded an accuracy (measured as percent relative standard deviation: %RSD), which is better than 0.10% for all ratios compared to the least-radiogenic value of [Sangster](#)

et al. (1998). However, external error associated with the choice of Broken Hill galena reference values (only bulk values are available) are expected to expand this error envelope by 0.02%. Table 2.3 shows weighted means for 20 individual measurements with errors reported at 2 S.E. (95% confidence interval); a table including results for all spot analyses (n: 620) is included in the Appendix Table (2.A.1.), together with reference values for Jubilee galena (2.A.2.).

2.4.3 LA-Q-ICP-MS trace element analysis

The same galena grains that were analyzed for Pb-isotopes were then analyzed for trace element concentrations by LA-Q-ICP-MS (Agilent 7700x), also at the University of New Brunswick. Grains were selected based on the results of the Pb-isotope analyses (e.g., Ag, Cd, Hg, and Tl). For each sample at least ten ablations on a minimum of seven grains were obtained. The laser was set to an on-sample fluence of ~ 1.75 J/cm² with a laser pulse rate of 3 Hz. All samples were analyzed using a 45 μ m diameter crater size and 30 s ablation time, with a gas blank and washout time of 30 s between each ablation. Gas flow rates were kept constant through all runs at 930 ml/min of argon, 300 ml/min of ultra-pure helium, and 2 ml/min of ultra-pure nitrogen. The in-line signal smoothing device was used between the laser cell and the ICP-MS. Tuning of the ICP-MS was performed using NIST610 glass, with a constant gas rate, similar fluence and spot size, to maximize sensitivity of medium and heavy masses. To ensure mitigation of oxide and doubly charged ion interference, $^{232}\text{Th}^{16}\text{O}^+ / ^{232}\text{Th}^+$ and $^{44}\text{Ca}^{++} / ^{44}\text{Ca}^+$ ratios were kept $< 0.1\%$ and $< 0.2\%$ respectively. The secondary rotary pump was turned on, to ensure maximum sensitivity. In addition to the spot analyses two traverses have been carried out, using the same analytical setting to check for internal-zoning within the galena crystals. The following isotopes were analyzed: ^{34}S , ^{51}V , ^{55}Mn , ^{56}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{71}Ga , ^{72}Ge , ^{75}As , ^{78}Se , ^{95}Mo , ^{107}Ag ,

^{111}Cd , ^{115}In , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{182}W , ^{185}Re , ^{189}Os , ^{197}Au , ^{201}Hg , ^{205}Tl , ^{208}Pb , and ^{209}Bi . The limit of detection (LOD) for each element in each sample is given in the Appendix Table (2.A.3.). Standards used were NIST610 and GSE-1G glass, MASS-1 sulfide reference material, and in-house Broken Hill galena. Data reduction was performed using Igor Pro with the Iolite software package with reference to the MASS-1 sulfide reference material (formerly PSD-1; [Wilson et al., 2002](#)). Relative deviation of cross-calibrated trace-element standards (MASS-1, GSE-1G, NIST610) was typically <10%. The minor and trace element data (mean, standard deviations, minimum and maximum concentrations) are summarized in Table 2.4, which includes data for 14 elements present at measurable concentrations in one or more samples. A table including all analyzed elements is provided in the Appendix Table (2.A.3.).

2.5 Field observations and mineral paragenesis

Investigated mineral deposits along the WCDS (e.g., Lavrion District, Serifos) and the active volcanic arc (Milos) are mostly polymetallic replacement deposits and epithermal systems that share a common low-temperature, base metal-rich mineral assemblage dominated by sphalerite (Fe-rich to Fe-poor), pyrite, galena and minor chalcopyrite and sulfosalts. In contrast, the deposits associated with the NCDS and NPDS (e.g., Tinos, Mykonos, Antiparos) are mostly precious metal-rich vein-type deposits characterized by chalcopyrite, pyrite, galena and sulfosalts with minor sphalerite and tellurides. The following is a detailed description of the investigated sample sites highlighting the different mineralization styles.

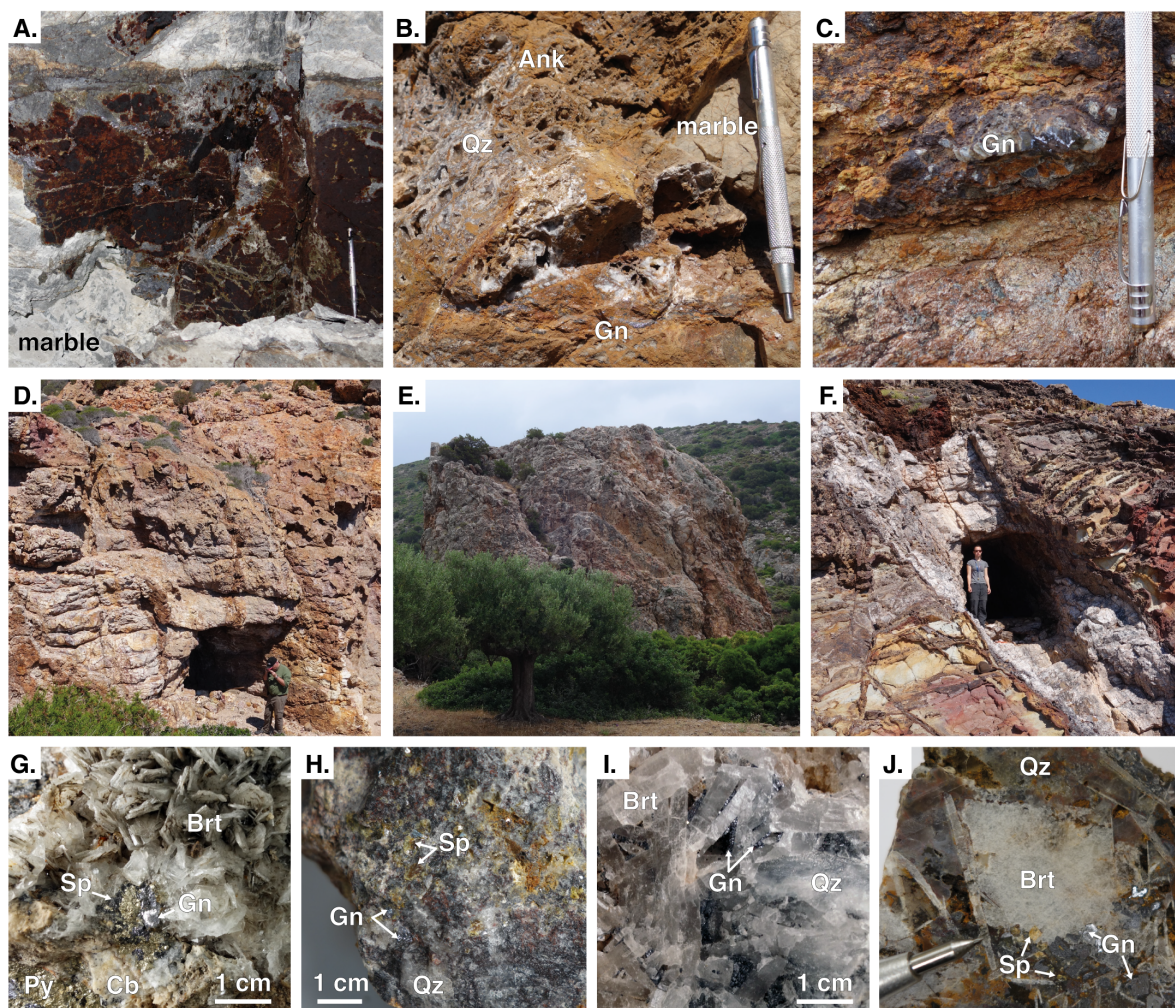


Fig. 2.4: Field and sample photos of representative deposit types in the Cyclades Mineral District. A. Detachment fault-related carbonate-replacement deposit with brecciated and massive orebodies hosted by marbles of the Basal Unit (underground, Adit No. 145, Plaka, Lavrion District). B. Carbonate-replacement deposit (Kamariza, Lavrion) with mineralized zones of galena, ankerite and quartz. C. Sulfide-rich pods (mainly galena) in marble and schist of the Lower Cycladic Blueschist Nappe (Moutoulas, Serifos). D. Steeply-dipping quartz and barite veins of an intermediate-sulfidation epithermal deposit, cutting Quaternary volcanic units on Milos Island (Kondaros-Katsimouti). E. Quartz-barite breccia body exposed at surface as a ~12 m-high mound. Mineralization occurs in veins and are preserved in distinct mineralized horizons of replaced volcanoclastic units (Triades, Milos). F. Several meter-wide banded barite vein cutting the Miocene conglomeratic sequence (Panormos Bay, Mykonos). G. Sample photo of 17L145_1 (Adit No. 145, Plaka, Lavrion District) with galena, Fe-sphalerite, pyrite and chalcopyrite replacing carbonate minerals. Late crystallization of barite in cavities. H. Galena and Fe-poor sphalerite in sampled quartz vein (17MK2_1, Kondaros, Milos). I. Late interstitial polymetallic sulfides filling open spaces in between large euhedral barite crystals (Panormos Bay, Mykonos). J. Sample photo of 17AP2 (Prassovounia, Antiparos) with galena, Fe-poor sphalerite and barite in silicified matrix. Mineral abbreviations: Ank: ankerite, Brt: barite, Cb: carbonate minerals, Gn: galena, Py: pyrite, Qz: quartz, Sp: sphalerite.

Carbonate-replacement deposits

In Lavrion, samples were taken underground from Adit No. 145 near Plaka, from several locations near Kamariza and one sample underground from Soureza. The mineralization is spatially related to the local detachment faults and occurs in the marble horizons near the marble-schist contact. Carbonate-replacement, as well as brecciated and massive orebodies (Fig. 2.4A) occur in the marbles of the Basal Unit. In the Plaka mine, a first generation of mineralization with generally smaller grains of disseminated sulfides replacing carbonate minerals was sampled (17L145_2 and 17L145_3). Massive to brecciated orebodies have an ore-mineral assemblage with brecciated pyrite, plastically deformed galena, Fe-rich sphalerites, one generation with up to 12.3 wt% Fe and a second generation with pervasive chalcopyrite disease and <10 wt% Fe, and minor chalcopyrite replacing the carbonate minerals (17L145_1 and 17L145_4; Fig. 2.4G, 2.5A). Two types of galena were identified: 1) disseminated galena with generally smaller grains and other sulfides (e.g., Fe-rich sphalerite, pyrite and arsenopyrite), as well as apatite and titanite within the carbonate matrix; 2) massive galena (Fig. 2.4A) with mm-scale cubic grains and bent crystal faces (Fig. 2.5A). The disseminated galena is inclusion-rich (Fig. 2.6A), with sphalerite, ankerite, and minor fluorite, pyrite and chalcopyrite and often intergrown with other mineral phases. The massive galena is generally inclusion free but can contain inclusions of Mn-bearing ankerite and cerussite.

In Kamariza, samples were collected from three different sites in the 5 km between Kamariza in the north and Megala Pefka in the south. Sulfides occur in open spaces created by carbonate dissolution (Fig. 2.4B) and include mostly galena, minor Fe-poor to Fe-rich sphalerite and pyrite. Supergene Fe-oxides have widely replaced hypogene sulfides and are commonly coating galena grains. Galena occurs as granular aggregates to single

cubic crystals, commonly with deformed grain boundaries (Fig. 2.6B). Cerussite, together with other carbonate minerals, quartz, sphalerite, and pyrite occur as micro-inclusions in galena.

At Soureza, galena, Fe-poor to Fe-bearing sphalerite, together with minor tetrahedrite, chalcopyrite, and pyrite and recrystallized, zoned carbonates (Pb-Mn-rich siderite) occur in distinctive bands (Fig. 2.5B) and surround fragments of altered quartz-rich micaceous host rock. Here, two generations of galena are observed: 1) larger, up to several mm-scale, crystals and 2) inclusion-rich galena containing sphalerite, pyrrhotite, tetrahedrite, minor pyrite (small aggregates) and chalcopyrite. Galena also contains many Sb-(Ag)-rich and Sb-Cu-rich micro-inclusions (Fig. 2.6C). Inclusions of galena were also observed in the core of Fe-poor sphalerite (Fig. 2.5B).

Skarn mineralization

On Serifos exo- and endo-skarn deposits occur peripheral to the 11.6 to 9.5 Ma granodioritic intrusion (Ducoux et al., 2017; Fitros et al., 2017; Iglseder et al., 2009; Salemink, 1985). At Moutoulas, sulfide-rich lenses and pods are intercalated with marble horizons within the greenschist and metabasites of the LCBN. The mineralized zone extends ~20 m horizontally and over 40 m in the vertical direction, and samples come from the upper, middle and lower part of the abandoned mine. Sulfide-rich pods (mainly galena) are up to several cm-wide (Fig. 2.4C) and replace the marble host rock. All of the sulfide phases replace carbonate minerals, including galena, pyrite, Fe-sphalerite and minor chalcopyrite and pyrrhotite (Fig. 2.5C). One generation of sphalerite contains inclusions of galena, pyrite, carbonates and sericite, and another consists of larger crystals with pervasive chalcopyrite disease. Galena occurs as large euhedral, mm- to several cm-scale crystals, which are mostly inclusion free (Fig. 2.6D).

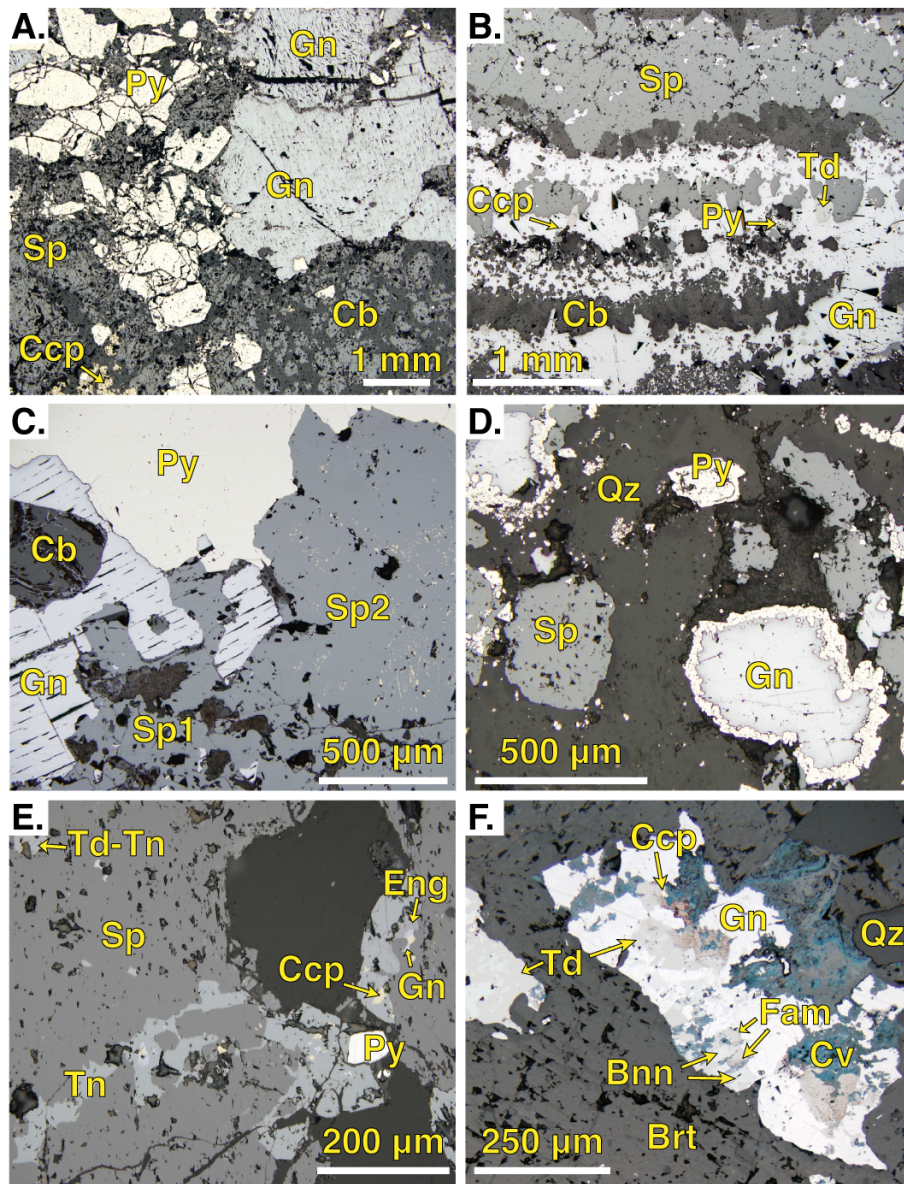


Fig. 2.5: Reflected light microphotographs of representative samples from the major deposit types in the Cyclades Mineral District. A. Ore-mineral assemblage with brecciated pyrite, plastically deformed galena, Fe-rich sphalerite and minor chalcopyrite, which are replacing carbonate minerals (Adit No. 145, Plaka, Lavrion District). B. Alternating mineralized bands of sphalerite, galena and carbonate minerals (Soureza, Lavrion District). C. Replacement of carbonate minerals by galena, pyrite and two generations of inclusion-rich Fe-sphalerite: Sp1 with inclusions of galena, pyrite and carbonate minerals, and zoned Sp2 with pervasive chalcopyrite disease (Moutoulas, Serifos). D. Fe-poor sphalerite and galena with pyrite corona in the matrix of silicified breccia (Triades, Milos). E. Polymetallic ore-mineral assemblage of tennantite, galena, pyrite, chalcopyrite and enargite in Fe-poor sphalerite (Galana, Milos). F. Late interstitial polymetallic sulfides (galena, chalcopyrite, tetrahedrite, bournonite, famatinite, covellite) and quartz filling open spaces between large euhedral barite crystals (Panormos Bay, Mykonos). Mineral abbreviations: Bnn: bournonite, Brt: barite, Cb: carbonate minerals, Ccp: chalcopyrite, Cv: covellite, Eng: enargite, Fam: famatinite, Gn: galena, Py: pyrite, Qz: quartz, Sp: sphalerite, Td: tetrahedrite, Tn: tennantite.

Low- to high-sulfidation epithermal deposits

On Milos, polymetallic mineralization occurs in steeply-dipping quartz and barite veins and breccia bodies. We sampled at four different sites: the Kondaros-Katsimouti deposit in the north-west, Triades and Galana in the west, and a sample from the drill core 12 on Profitis Ilias. At Kondaros-Katsimouti several steeply-dipping, 10 to 30 cm-wide, NE-SW-trending quartz and barite veins crosscut the Quaternary dacitic volcanoclastic host rocks (Fig. 2.4D). Whereas veins near the coastline show a high degree of silicification, veins further inland are dominated by barite. Ore mineral paragenesis is dominated by Fe-poor sphalerite, galena, and minor pyrite and tetrahedrite with pervasive silicification (Fig. 2.4H). Silicified samples show quartz and chalcedony after barite. Inclusions, up to 25 μm in length, of Ag-rich tetrahedrite, polybasite and freibergite are common in galena in samples from Kondaros-Katsimouti (Papavasiliou et al., 2016b). In surface samples, the galena crystals are corroded and partly replaced by anglesite.

At Triades and Galana silicified breccia bodies form distinctive mounds at the surface with mineralized veins and replacement zones. At Galana, variably silicified and weathered samples were collected from dump sites, in front of mined breccia bodies. The sulfide mineral assemblage is dominated by Fe-poor sphalerite, galena, tennantite, tetrahedrite-tennantite, pyrite, chalcopyrite and minor enargite (Fig. 2.5E). Galena contains inclusions of tetrahedrite-tennantite, Fe-poor sphalerite, pyrite, and chalcopyrite and is commonly fractured and partly replaced by anglesite. At Triades samples were taken from mineralized veins and horizons exposed at the surface of a breccia mound (Fig. 2.4E). The ore mineral assemblage consists of mm-scale, Fe-poor sphalerite, intergrown with tetrahedrite-tennantite, galena and pyrite (Fig. 2.5D). Aggregates of Fe-poor sphalerite, galena, pyrite, chalcopyrite, tetrahedrite-tennantite, and polybasite, with secondary covellite, occur in a

siliceous matrix, together with corroded bladed barite. The galena is inclusion-rich and commonly intergrown with other sulfides and quartz (Fig. 2.6E).

At Profitis Ilias, steeply-dipping, NW-SE and NE-SW-trending, quartz and barite veins are exposed at the surface at an elevation of more than 600 m above sea level. Galena from drill core 12 (PD012 from the 1995 drilling campaign; Alfieris, 2006; Kiliyas et al., 2001), collared at an elevation of ~ 515 m of the Profitis Ilias mountain and sampled at a depth of 317.8 m, contains massive quartz-sulfide ore with galena, pyrite, Fe-poor sphalerite and minor chalcopyrite. Cubic galena crystals, up to several millimeter in size and partly deformed, contain 5-60 μm rounded inclusions of tellurides (mostly hessite, minor petzite, Ag-rich altaite and an Ag-Hg-telluride, likely Ag-rich coloradorite; Fig. 2.6F). Initial entrapment of hessite-forming droplets in galena and sphalerite at Profitis Ilias was previously described by Alfieris et al. (2013) at a temperature of $\sim 250^\circ\text{C}$ constraint by fluid inclusion homogenization temperatures of Kiliyas et al. (2001). Inclusions of quartz, pyrite, and Fe-poor sphalerite (with up to 0.35 wt% Cd) are also common in the galena.

Vein-type deposits

Vein-type deposits with steeply-dipping quartz and barite veins occur in the north and central Cyclades and have been sampled on Mykonos, Tinos and Antiparos. On Mykonos, several m-wide barite veins occur in Cape Evros, Panormos Bay and Cape Charos. At Panormos Bay, WNW-ESE trending banded barite veins cut Miocene clastic sediments of the Pelagonian zone rocks (Fig. 2.4F). The mother lode is ~ 10 m wide, contains several zones, and is intersected by smaller up to a few cm-wide veinlets, with no preferred orientation. Late interstitial polymetallic sulfides and quartz fill voids between large euhedral barite crystals in the center of the vein (Fig. 2.4I, 2.5F). Major sulfides and sulfosalts are galena and Ag-rich tetrahedrite-(tennantite), with up to 10 wt% of Ag, with minor

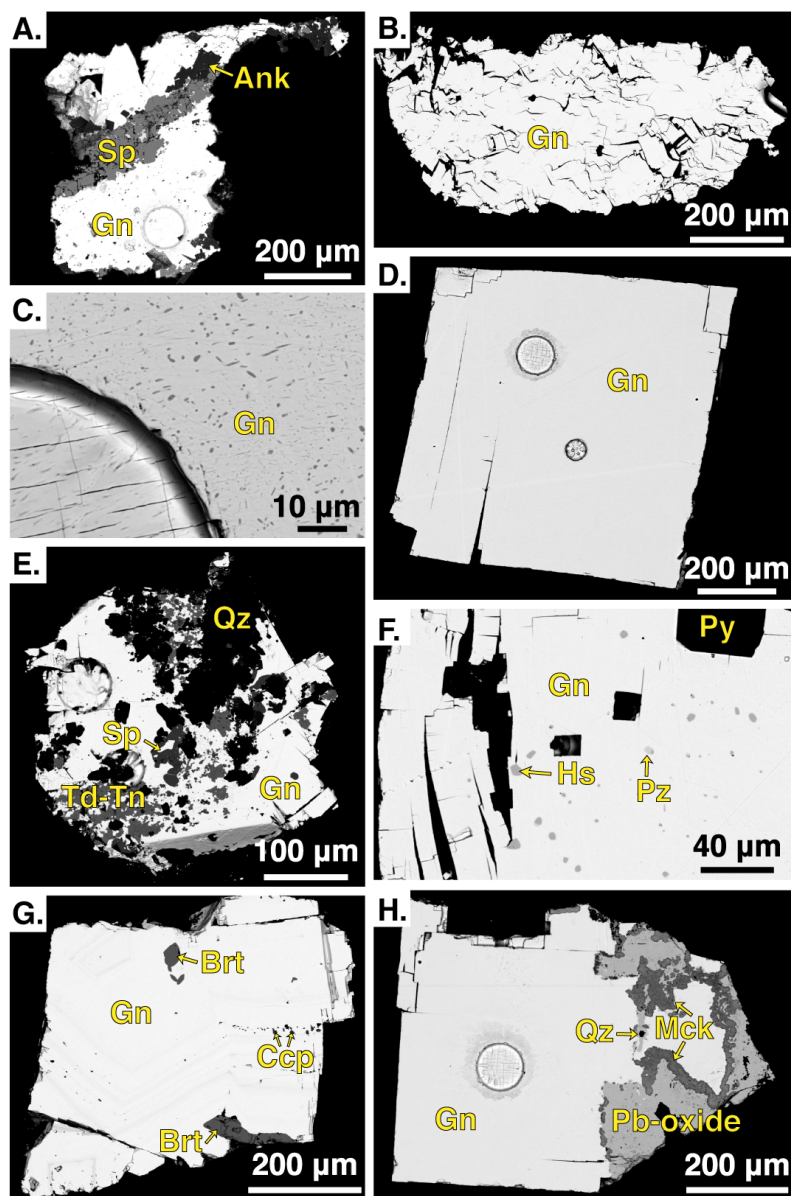


Fig. 2.6: Representative backscattered-electron microscopy images of galena. A. Inclusion-rich anhedral galena from the carbonate-replacement deposit in Lavrion (Plaka) with inclusions of ankerite and Fe-rich sphalerite. B. Aggregate of galena grains (Kamariza, Lavrion District). C. Micro-inclusions of Sb-Cu-rich and Sb-(Ag)-rich galena in galena (Soureza, Lavrion District). D. Euhedral, galena showing ablation craters for Pb-isotope analyses (82 μm) and trace element analyses (45 μm) (Moutoulas, Serifos). E. Inclusion-rich galena from Triades (Milos) with inclusions of tetrahedrite-tennantite, Fe-poor sphalerite and quartz. F. Inclusions of tellurides (mainly hessite, minor petzite and coloradoite) in galena from the Profitis Ilias drill core sample (Milos). G. Zoned galena with growth zones enriched in antimony and silver (up to 4 wt%: Panormos Bay, Mykonos). Chalcopyrite inclusions are concentrated along growth zones. Inclusions of barite occur inside the crystal and at the crystal rims. H. Mckinstryite and Pb-oxide rim around subhedral galena from Cape Evros (Mykonos). Mineral abbreviations: Ank: ankerite, Brt: barite, Ccp: chalcopyrite, Gn: galena, Hs: hessite, Mck: mckinstryite, Py: pyrite, Pz: petzite, Qz: quartz, Sp: sphalerite, Td: tetrahedrite, Tn: tennantite.

chalcopyrite, famatinite, bournonite, polybasite (~ 60 wt% Ag), Cd-rich Fe-poor sphalerite, Cd-freibergite and an Hg-bearing sulfosalt, likely Ag-Hg-rich tetrahedrite (Fig. 2.5F). Supergene covellite, hematite, anglesite and phosgenite were identified via SEM analyses. Late Fe-hydroxide fill voids and rim quartz veinlets, which cut the barite veins and contain minor galena. The galena has subhedral, triangular form and contains inclusions of barite, quartz, chalcopyrite, and an Hg-bearing sulfosalt. Galena from the center of the vein (17MYP1, 17MYP4) shows growth zones with elevated Ag and Sb in different zones (Fig. 2.6G; Wind et al., 2019); growth zones were not observed in galena from the quartz veinlets (17MYP3).

At Cape Evros, the wall rocks of the Miocene laccolith and Pelagonian zone are highly silicified, and sulfides occur within several m-wide, NW-SE-trending barite veins. A polymetallic mineral assemblage with galena, cubic pyrite replaced by chalcopyrite and bornite, and Fe-poor sphalerite (< 2.5 wt% Fe) is found in the quartz and barite veins. Supergene covellite, Zn-Cu-sulfides, hematite, anglesite and two Pb-phosphates were also identified via SEM analyses. Small crystals of disseminated pyrite, sphalerite and chalcopyrite occur in the silicified host rock. The galena have leached rims and inclusions of chalcopyrite, pyrite, sphalerite and quartz. In some cases, a corona of mckinstryite, a low-temperature ($< 100^\circ\text{C}$) Ag-Cu-sulfide (Kolitsch, 2010), together with Pb-oxide was observed around galena crystals (Fig. 2.6H). At Cape Charos, samples from m-wide barite veins were free of galena but had more abundant chalcopyrite than in the other localities, perhaps reflecting higher temperatures that prevented galena deposition.

At Agios Georgios on Antiparos two sets of steeply-dipping quartz veins were described (Kevrekidis et al., 2015): one older generation of NE-SW-trending milky quartz veins and a younger set of clear quartz veins, which is trending NW-SE. We sampled NE-SW-trending milky to clear, up to 40 cm-wide, quartz veins near Prassovounia that cut the gneisses and

schists of the UCBN and have low concentrations of pyrite, Fe-poor sphalerite, chalcopyrite and galena (17AP6). A second sample from an abandoned mine site in the Prassovounia area, contains bladed barite intergrown with Fe-poor sphalerite and galena within recrystallized quartz (17AP2; Fig. 2.4J). Supergene hematite, cerussite and smithsonite were also identified. The galena consists of pristine euhedral to subhedral cubes, which are mostly inclusion free, rarely with small inclusions of Fe-poor sphalerite and pyrite.

On Tinos a stockwork of several NW-SE-trending, cm-wide quartz veins was sampled near Panormos Bay that cut the marbles of the UCBN. Galena occurred mostly in clusters within the clear quartz vein, and the grains were pristine euhedral to subhedral cubes. Small, oxidized grains of cubic pyrite occur at the rim of the vein.

2.6 Results

2.6.1 Galena Pb-isotopes

The lead isotope compositions of 31 galena samples (n: 620 analyses) from the Cyclades Mineral District are summarized in Table 2.3, and the entire dataset is reported in the Appendix Table (2.A.1.), including reference values for Jubilee galena (2.A.2.). For each sample, 20 ablations on a minimum of twelve grains were carried out, and weighted means for the 20 ablations were calculated using Isoplot 3.75 (Ludwig, 2003) for the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios. The reported data are drift and externally corrected values relative to the Broken Hill galena (Stacey et al., 1969) and with fully propagated 2 S.E. (95% confidence interval) errors on weighted means. Mean square weighted deviations (MSWD) on the weighted average remained for most samples <1.3. Multiple spot analyses on one grain returned the same isotopic ratios within the analytical error and based on the Pb-isotope ratios no variation could be observed between

different generations of galena from the same deposit (e.g., Plaka and Soureza, Lavrion and Panormos Bay, Mykonos).

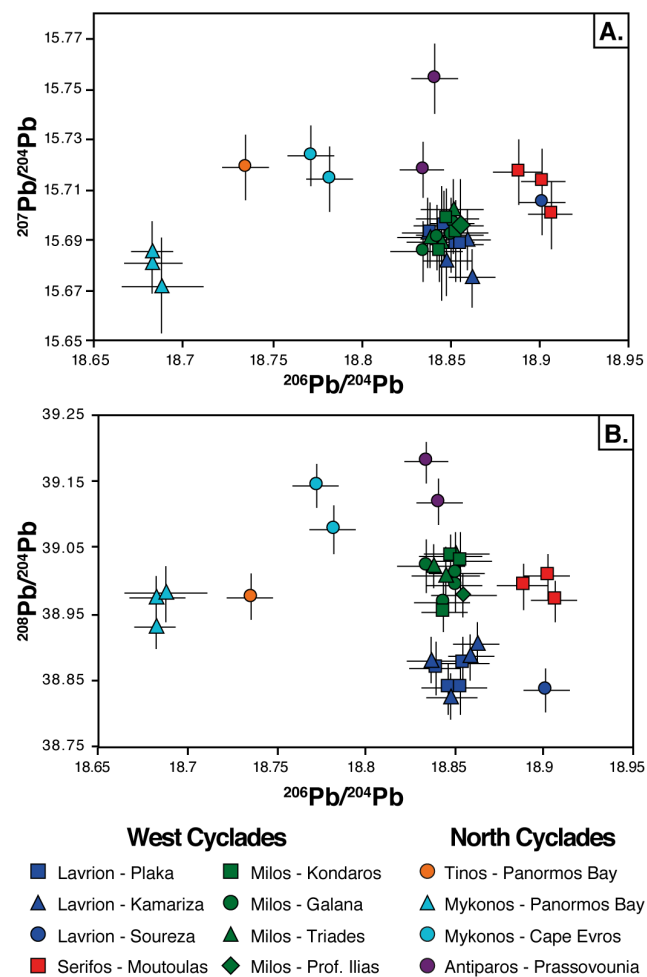


Fig. 2.7: A. and B. LA-Q-ICP-MS $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot and $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ plot of galena, respectively, from mineral deposits in the Cyclades Mineral District. Each data point is the weighted mean for 20 individual measurements per sample with errors reported at 2 S.E..

The calculated weighted means for the lead isotope ratios of galena samples are plotted on conventional $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams (Fig. 2.7). Galena samples from throughout the Cyclades Mineral District exhibit a range of isotopic ratios: $^{206}\text{Pb}/^{204}\text{Pb}$: 18.68–18.91, $^{207}\text{Pb}/^{204}\text{Pb}$: 15.67–15.75 and $^{208}\text{Pb}/^{204}\text{Pb}$: 38.83–39.18, with resolvable isotopic differences among the deposits. Lead isotope analyses of galena from the same deposit exhibit only minor variations and are generally within error, and the isotopic composition of lead in deposits from the same islands are remarkably homogeneous (Fig. 2.7).

Galena from the various deposits (e.g., Kondaros-Katsimouti, Triades,

Galana, Profitis Ilias on Milos) have very similar lead isotope ratios. Likewise, galena from different samples of the same deposits (e.g., carbonate-replacement deposits in the Lavrion

district at Plaka and Kamariza) have very similar lead isotope ratios. Of the samples from Lavrion, only sample 17LS2 from Soureza has higher $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values than the other deposits, which is within the range of measured lead isotope ratios in galena from Moutoulas (Serifos). Only the galena samples from Mykonos show significant differences between the mineral occurrences on the same island: galena from a banded barite vein at Panormos Bay has low $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values (18.68–18.69 and 15.67–15.69, respectively), whereas galena from Cape Evros (Mykonos) has distinctly higher $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ (18.77–18.78 and 15.71–15.72, respectively). The highest $^{207}\text{Pb}/^{204}\text{Pb}$ values of ~ 15.75 have been measured in galena from Antiparos in the central Cyclades together with intermediate $^{206}\text{Pb}/^{204}\text{Pb}$ values of ~ 18.84 .

More generally, galena from the different deposit types in the west Cyclades (carbonate-replacement, skarn and low- to high-sulfidation epithermal) has very uniform and high $^{206}\text{Pb}/^{204}\text{Pb}$ values (≥ 18.84) and show little variation in the $^{207}\text{Pb}/^{204}\text{Pb}$ values (15.68–15.72). These comparisons suggest that the major differences in lead isotope ratios throughout the Cyclades Mineral District are, for the most part, not directly related to the style of mineralization. The major differences in the lead isotope ratios of galena are found between deposits in disparate regional parts of the Cyclades Mineral District. Whereas galena from the deposits in the north-central Cyclades (Antiparos, Mykonos, Tinos) has low $^{206}\text{Pb}/^{204}\text{Pb}$ values (≤ 18.84), galena from the deposits in the west Cyclades (Lavrion, Milos, Serifos) have uniform and higher $^{206}\text{Pb}/^{204}\text{Pb}$ values (≥ 18.84 , noted above). These data tentatively suggest that there are major regional differences in the sources of lead in the basement, which are reflected in the deposits irrespective of the style of mineralization.

Table 2.3: Weighted mean of Pb-isotope ratios of galena, Cyclades, Greece.

Sample	$^{207}\text{Pb}/^{206}\text{Pb}$	2SE	$^{206}\text{Pb}/^{208}\text{Pb}$	2SE	$^{206}\text{Pb}/^{204}\text{Pb}$	2SE	$^{207}\text{Pb}/^{204}\text{Pb}$	2SE	$^{208}\text{Pb}/^{204}\text{Pb}$	2SE
<i>Lavriton</i>										
17L145_1	0.8320	0.0009	0.4850	0.0004	18.853	0.014	15.688	0.014	38.84	0.04
17L145_2	0.8325	0.0006	0.4840	0.0004	18.839	0.013	15.693	0.012	38.87	0.03
17L145_3	0.8317	0.0009	0.4850	0.0004	18.855	0.014	15.688	0.014	38.87	0.04
17L145_4	0.8325	0.0009	0.4850	0.0004	18.846	0.017	15.696	0.014	38.84	0.03
17LK1	0.8313	0.0007	0.4846	0.0004	18.862	0.013	15.675	0.012	38.91	0.03
17LK3	0.8328	0.0009	0.4845	0.0005	18.837	0.014	15.693	0.014	38.88	0.04
17LK4	0.8317	0.0010	0.4855	0.0004	18.848	0.014	15.682	0.014	38.83	0.03
17LK6	0.8318	0.0006	0.4847	0.0005	18.859	0.013	15.690	0.012	38.89	0.03
17LS2	0.8307	0.0009	0.4862	0.0004	18.901	0.013	15.705	0.013	38.83	0.03
<i>Serifos</i>										
17SG1	0.8314	0.0006	0.4843	0.0004	18.902	0.013	15.713	0.013	39.01	0.04
17SG2	0.8317	0.0007	0.4840	0.0004	18.888	0.014	15.717	0.013	38.99	0.04
17SG6	0.8306	0.0006	0.4847	0.0004	18.906	0.013	15.700	0.013	38.97	0.03
<i>Milos</i>										
17MK1	0.8327	0.0007	0.4825	0.0004	18.848	0.018	15.699	0.012	39.04	0.03
17MK2_1	0.8316	0.0007	0.4830	0.0004	18.853	0.018	15.693	0.013	39.03	0.04
17MK5	0.8319	0.0006	0.4834	0.0005	18.844	0.013	15.686	0.012	38.95	0.03
17MGA03	0.8320	0.0008	0.4836	0.0004	18.843	0.018	15.691	0.013	38.97	0.04
17MGA04	0.8324	0.0007	0.4826	0.0004	18.834	0.018	15.686	0.012	39.02	0.03
17MGA05	0.8328	0.0006	0.4825	0.0004	18.851	0.013	15.697	0.012	39.01	0.03
17MGA07	0.8327	0.0008	0.4827	0.0006	18.850	0.019	15.692	0.015	38.99	0.04
17MT02	0.8329	0.0007	0.4827	0.0004	18.838	0.018	15.692	0.012	39.02	0.03
17MT03	0.8331	0.0009	0.4829	0.0011	18.845	0.019	15.689	0.023	39.01	0.04
17MT04	0.8328	0.0007	0.4822	0.0005	18.851	0.018	15.702	0.012	39.04	0.03
PD012	0.8317	0.0007	0.4837	0.0004	18.855	0.018	15.696	0.013	38.98	0.03
<i>Tinos</i>										
17TP1	0.8386	0.0007	0.4804	0.0004	18.735	0.013	15.719	0.013	38.98	0.03
<i>Mykonos</i>										
17MYP1	0.8385	0.0006	0.4797	0.0004	18.683	0.016	15.681	0.012	38.97	0.03
17MYP3	0.8381	0.0013	0.4792	0.0007	18.688	0.023	15.672	0.019	38.98	0.04
17MYP4	0.8392	0.0007	0.4798	0.0004	18.682	0.012	15.686	0.012	38.93	0.03
17MYV2_1	0.8376	0.0006	0.4794	0.0004	18.772	0.013	15.724	0.012	39.14	0.03
17MYV2_1B	0.8366	0.0007	0.4802	0.0004	18.782	0.013	15.714	0.013	39.08	0.04
<i>Antiparos</i>										
17AP2	0.8360	0.0009	0.4809	0.0004	18.841	0.013	15.754	0.014	39.12	0.04
17AP6	0.8342	0.0006	0.4804	0.0004	18.834	0.012	15.718	0.011	39.18	0.03

Notes: Weighted means are calculated for each sample based on 20 spot analyses.

2.6.2 Galena trace element geochemistry

To test whether these differences in the sources of lead are similarly reflected in the trace element signature of the galena, the grains were analyzed by LA-Q-ICP-MS methods for their geochemistry. An overview of the minor and trace element data is summarized in Table 2.4. Although the galena targets were carefully studied prior to the analyses in order to analyze only those areas that are free of inclusion, some results (e.g., elevated Cu, Zn, As or Fe) are likely due to mineral inclusions (e.g., Triades, Milos) and were not included in the calculated mean concentration and standard deviation, but are included in the maximum and minimum values and shown in Figure 2.8. In contrast to the very uniform Pb-isotope signatures among the galena samples, significant variations in trace element concentrations were found between samples from different deposits on the same island (e.g., Mykonos, Lavrion, Milos; Fig. 2.8), and samples from the same deposit have generally similar geochemical patterns.

Traces of Ag, Sb, Cu, Bi, Cd, and Tl were detected in all analyses of galena. Silver and Sb have the highest concentrations (>100 ppm in most deposits) and are commonly correlated with each other. Solely galena from Panormos Bay (Tinos) and Profitis Ilias (Milos) show higher concentrations of Se (~806 ppm) and Te (~438 ppm), respectively. Ratios of Sb/Ag range from 0.06 to 9.8 but are between 0.6 and 1.1 for the majority of analyses. In samples with mean concentrations of Sb and Ag >1000 ppm (e.g., at Soureza, Lavrion and Panormos Bay, Mykonos), Sb concentrations exceed Ag concentrations. Cadmium concentrations in galena are rather uniform in all samples and vary between 20 and 30 ppm, except in samples from Panormos Bay on Tinos and Mykonos, which have significantly higher and lower values (~120 ppm and <14 ppm, respectively; Fig. 2.8). Thallium concentrations are <10 ppm. Mean concentrations of Bi in galena are generally <10

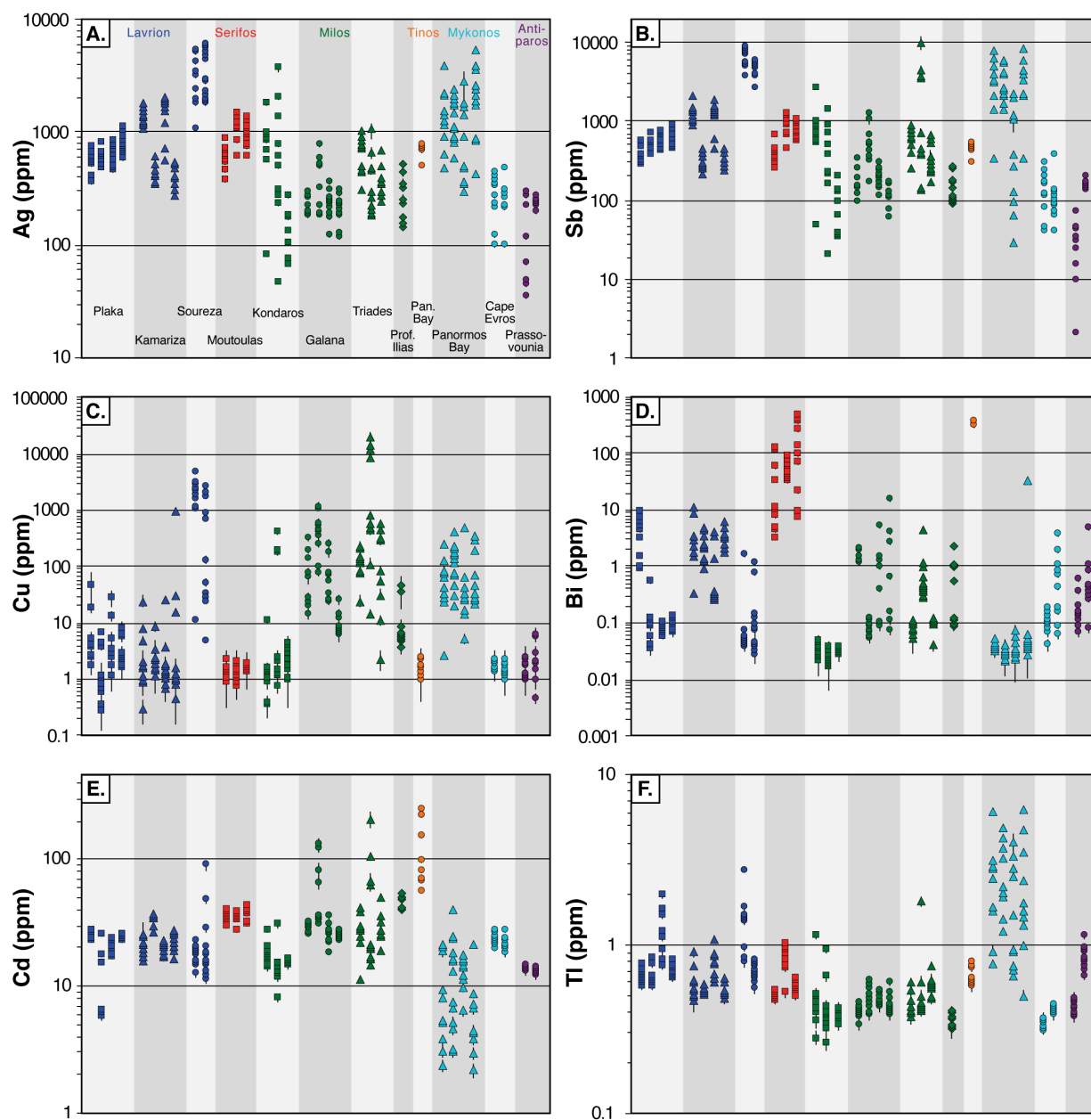


Fig. 2.8: A.-F. Silver, antimony, copper, bismuth, cadmium and thallium concentrations, respectively, in parts per million (ppm) in galena displayed on a logarithmic scale. For each sample the individual spot analyses (N: 10–14) are shown with their respective errors (in certain cases errors are smaller than the symbol). Samples are displayed in the same order as in Table 2.4.

ppm, except for the skarn deposit on Serifos and vein-type deposit on Tinos, where Bi concentrations of a few 100 ppm were measured. Copper concentrations vary significantly from <0.5 ppm to 5030 ppm between deposits but also within a sample (Table 2.4, Fig. 2.8). Samples with high concentrations of Sb and Ag also commonly have elevated concentrations in Cu (e.g., Soureza, Lavrion and Panormos Bay, Mykonos), which is linked to zoning and micro-inclusions in galena (Fig. 2.6C, G). Except for traces of Ag, Sb, Cu, Cd, Tl, and Bi that were detected in all galena analyses, significant concentrations of Hg were detected in galena from Panormos Bay on Mykonos, with a mean value of ~ 100 ppm; low Hg concentrations of a few parts per million were also detected in galena from Triades and Galana (Milos). The same analyses record a few parts per million of As (and Zn, Appendix Table 2.A.3), and some spot analyses with up to 6000 ppm of As likely indicate the presence of As-rich inclusions such as tennantite (Fig. 2.6E). Tellurium concentrations of several 100 ppm were measured in galena from the vein-type deposit on Tinos (Panormos Bay) and from the intermediate-sulfidation epithermal deposit on Milos (Profitis Ilias). Low concentrations of Te were also detected in galena from Triades and Galana on Milos, but galena from Kondaros-Katsimouti is free of Te. Similar for Au, which was detected in most galena samples from Milos (average 0.59 ppm at Triades, 0.05 ppm at Galana, and 5.46 ppm at Profitis Ilias), but have not been detected in samples from Kondaros-Katsimouti. Gold concentrations can reach up to 100 ppm in galena from the Profitis Ilias drill core sample, where Au occurs likely in notable petzite-inclusions (Fig. 2.6F). Galena from carbonate-replacement deposits in Plaka (Lavrion), skarn deposit at Moutoulas (Serifos), epithermal deposits at Triades, Galana, and Profitis Ilias (Milos) all have low concentrations of Mn, with a mean concentration of ~ 4 ppm. Galena from most deposits also has low concentrations of In (below 1 ppm). Tin concentrations in galena are generally low, but galena in the carbonate-replacement deposits at Lavrion has mean

concentrations of ~ 20 ppm.

These data confirm that trace element concentrations in galena throughout the Cyclades Mineral District are highly variable (e.g., [Gale & Stos-Gale, 1981](#); [Voudouris et al., 2008a](#)) and representative of the different deposit types and observed mineral assemblages. The highest precious metal concentrations were detected in galena from a vein-type deposit at Panormos Bay (Tinos) with 707 ppm Ag and 0.04 ppm Au, together with >300 ppm of Se, Sb, Te, and Bi (Fig. 2.8), the low standard deviations suggest these elements are present in solid solution. The abundance of precious metals in galena from Tinos is in good agreement with previously described Au-Ag-Te-rich mineral assemblages ([Tombros et al., 2007](#)), although the presence of Bi minerals was not noted. High Bi concentrations in galena from a skarn deposit at Moutoulas (Serifos) are in good agreement with the presence of native Bi reported by [Fitros et al. \(2017\)](#) and elevated Bi concentrations in galena for skarn deposits ([George et al., 2015](#)). In general galena from Moutoulas is more enriched in trace elements than previously reported by [St. Seymour et al. \(2009b\)](#), however, elevated concentrations of As in galena (>262 ppm) reported by [Gale & Stos-Gale \(1981\)](#) are not detected. On Mykonos galena has been analyzed from the polymetallic barite vein deposits at Cape Evros and Panormos Bay, where generally low concentrations of trace elements have been detected for galena from the former (Table 2.4). Galena from the latter exhibits high mean concentrations in Ag (~ 1500 ppm) and Sb (~ 3000 ppm), as well as up to a few 100 ppm for As, Cu, and Hg in notable growth zones (Table 2.4; [Wind et al., 2019](#)). Low concentration of Cd in galena (<14 ppm) from Panormos Bay, Mykonos, is in strong contrast to high Cd concentrations in co-genetic sphalerite and Cd-freibergite inclusions in galena. Galena from the vein-type deposits at Prassovounia on Antiparos has the lowest analyzed concentrations of trace elements, with a mean Ag concentration of <250 ppm. This contrasts with data reported from Agios Georgios on Antiparos, where

microprobe analyses of [Kevrekidis et al. \(2015\)](#) showed 0.17–2.90 wt% Ag in galena, as well as trace element concentrations from [Gale & Stos-Gale \(1981\)](#) with Ag (>300 ppm) and Sb (>135 ppm) and elevated concentrations of Cu (>400 ppm) in galena. In the case of sample 17AP2, the lower concentrations of Ag are likely related to metal leaching, whereas sample 17AP6 is likely related to the first generation of hydrothermal veins, which were described as poor in argentiferous galena ([Kevrekidis et al., 2015](#)). Trace element concentrations in galena from Milos are overall low (Fig. 2.8), which was previously noted by [Alferis \(2006\)](#), however, some analyses with elevated concentrations can be linked to notable micro-inclusions within galena (e.g. tellurides, sulfosalts; Fig. 2.6E, F).

Table 2.4: LA-Q-ICP-MS minor and trace element concentrations in galena, Cyclades, Greece (data in parts per million).

Sample	Mn	Cu	As	Se	Ag	Cd	In	Sn	Sb	Te	Au	Hg	Tl	Bi
<i>Lavrion</i>														
17L145_1 (10)														
Mean	6.2	9.3	-	-	549	26.2	0.082	26.3	370	0.68	<0.013	-	0.66	3.91
S.D.	2.5	14.2	-	-	112	1.7	0.016	5.04	96	0.32	-	-	0.06	2.94
Min.	1.6	1.7	-	-	358	22.6	0.063	21.3	290	0.38	<0.013	-	0.57	0.91
Max.	9.6	47.0	<0.51	<11	747	27.4	0.106	34.2	590	1.44	0.015	<0.46	0.77	9.35
17L145_2 (10)														
Mean	<12.8	2.0	<0.6	<10.1	612	12.1	0.068	19.9	532	<0.28	<0.006	-	0.65	0.12
S.D.	19.6	2.2	-	-	89	8.3	0.031	9.31	84	0.38	0.003	-	0.08	0.14
Min.	0.8	0.3	<0.44	<9.1	480	5.8	0.037	12.1	395	<0.03	<0.007	-	0.58	0.04
Max.	208	6.8	0.6	10.1	813	25.9	0.135	40.5	704	1.12	0.012	<0.45	0.83	0.51
17L145_3 (10)														
Mean	3.2	<4.1	-	<11.8	635	20.8	0.055	17.3	602	0.26	<0.006	-	1.20	0.08
S.D.	2.0	3.6	-	-	136	2.3	0.005	0.56	123	0.17	-	-	0.40	0.01
Min.	0.8	1.1	-	<11	453	17.0	0.049	16.4	443	0.07	<0.012	-	0.76	0.06
Max.	7.7	29.2	<0.53	11.8	821	23.8	0.066	18.3	756	0.59	0.008	<0.44	1.98	0.10
17L145_4 (10)														
Mean	8.5	4.1	-	-	798	24.2	0.093	23.6	613	<0.08	<0.016	-	0.70	0.09
S.D.	1.1	2.4	-	-	168	0.8	0.052	1.15	158	0.03	0.001	-	0.06	0.02
Min.	7.1	1.7	-	-	579	22.8	0.063	21.9	454	<0.04	<0.014	-	0.65	0.06
Max.	10.1	8.1	<0.54	<11.8	1120	25.3	0.240	25.2	899	0.12	0.017	<0.48	0.82	0.13
17LK1 (10)														
Mean	<7.5	4.8	-	-	1360	20.4	0.167	47.4	1260	<0.21	<0.004	<1.18	0.60	3.75
S.D.	-	7.6	-	-	235	3.0	0.202	56.1	358	0.14	0.001	-	0.14	3.30
Min.	<0.5	0.3	-	-	1080	15.6	0.048	14.3	933	<0.04	<0.005	<0.45	0.47	0.32
Max.	7.5	25.2	<0.45	<13.6	1793	25.0	0.713	199	2120	0.41	0.007	1.18	0.91	10.9
17LK3 (10)														
Mean	6.6	2.6	-	-	453	34.5	0.038	7.27	316	2.23	<0.010	-	0.54	2.42
S.D.	2.6	2.2	-	-	83	3.5	0.037	11.1	74	1.11	0.003	-	0.02	1.27
Min.	1.0	1.2	-	-	338	26.9	0.016	1.26	215	0.76	<0.011	-	0.51	0.90
Max.	9.3	8.7	<0.47	<10.7	612	37.3	0.119	33.4	455	4.33	0.013	<0.45	0.59	4.59
17LK4 (10)														
Mean	<5.1	4.2	-	-	1478	19.5	0.114	27.7	1303	0.25	<0.006	<1.92	0.76	1.08
S.D.	-	8.1	-	-	510	2.0	0.098	10.8	451	0.23	-	-	0.15	1.37
Min.	<0.7	0.7	-	-	559	16.6	0.045	12.2	465	0.10	<0.010	<0.47	0.61	0.25
Max.	9.3	27.0	<0.49	<10.9	2020	22.5	0.383	44.0	1911	0.85	0.009	1.92	1.08	3.82
17LK6 (10)														
Mean	<1.2	<6.0	-	<15.3	414	23.0	0.074	5.74	362	4.70	<0.021	<0.93	0.53	3.67
S.D.	-	10.5	-	4.0	92	3.8	0.047	0.49	84	0.84	0.005	-	0.05	1.57
Min.	<0.5	0.5	-	<9.9	271	16.3	0.026	5.02	246	3.70	<0.015	<0.63	0.48	1.78
Max.	1.4	1040	<0.41	21.4	534	27.7	0.148	6.39	470	6.22	0.026	1.31	0.64	6.24
17LS2 (10)*														
Mean	-	2206	<7.6	-	3019	17.6	0.023	5.20	6821	<0.09	<0.028	<0.63	1.43	0.20
S.D.	-	1378	-	-	1468	3.1	0.017	3.69	1718	-	0.010	-	0.56	0.47

Table 2.4: (continued)

Sample	Mn	Cu	As	Se	Ag	Cd	In	Sn	Sb	Te	Au	Hg	Tl	Bi
Min.	-	11.5	<0.54	-	1054	12.5	0.006	0.54	3727	<0.05	<0.015	<0.49	0.79	0.04
Max.	<0.7	5030	7.6	<11.7	5390	22.9	0.065	13.6	9230	0.11	0.039	0.63	2.77	1.54
17LS2-T (14)*														
Mean	<1.3	779	<1.0	-	3783	23.9	<0.151	1.99	5133	<0.08	<0.016	-	0.71	0.19
S.D.	-	995	-	-	1678	21.1	0.273	2.36	964	-	0.014	-	0.08	0.32
Min.	<0.5	5.0	<0.42	-	1781	11.3	<0.009	0.23	2723	<0.06	<0.003	-	0.55	0.03
Max.	1.3	2703	1.1	<15.6	5902	89.7	0.729	9.37	6057	0.12	0.043	<0.77	0.83	1.12
Serifos														
17SG1 (10)														
Mean	2.4	1.5	-	<30	606	35.6	<0.005	0.34	404	<0.55	<0.020	-	0.51	36.4
S.D.	0.8	0.4	-	13.6	142	2.8	0.002	0.11	119	0.53	0.002	-	0.02	45.8
Min.	0.9	0.9	-	<12	366	29.9	<0.002	0.19	259	<0.06	<0.017	-	0.47	3.12
Max.	3.7	2.3	<0.53	47.1	871	40.1	0.008	0.46	694	1.37	0.025	<0.48	0.54	121
17SG2 (10)														
Mean	4.9	1.5	-	-	1095	34.8	<0.020	0.28	934	0.24	<0.014	-	0.83	52.9
S.D.	1.0	0.5	-	-	266	3.0	0.044	0.03	258	0.11	0.004	-	0.15	18.3
Min.	2.9	0.8	-	-	612	27.2	<0.003	0.23	454	0.08	<0.016	-	0.53	32.4
Max.	5.8	2.1	<0.52	<11.6	1446	37.7	0.130	0.32	1251	0.37	0.017	<0.48	1.01	87.5
17SG6 (10)														
Mean	2.2	1.7	-	<15.6	968	37.1	0.008	0.47	800	0.30	<0.020	-	0.58	179
S.D.	0.8	0.2	-	1.7	231	4.2	0.003	0.10	173	0.18	0.002	-	0.05	171
Min.	1.2	1.4	-	<13	614	30.8	0.004	0.38	565	0.06	<0.018	-	0.51	7.28
Max.	3.1	1.9	<0.54	17.4	1330	42.7	0.011	0.73	1074	0.59	0.023	<0.47	0.64	448
Milos														
17MK1 (10)														
Mean	-	2.0	-	-	850	18.3	<0.009	<0.06	886	<0.09	<0.016	-	0.49	0.03
S.D.	-	3.3	-	-	425	3.9	-	-	676	0.03	0.024	-	0.24	0.01
Min.	-	0.4	-	-	82	14.1	<0.007	<0.04	49	<0.07	<0.003	-	0.28	0.02
Max.	<0.5	11.2	<0.68	<12.2	1794	27.8	0.009	0.06	2650	0.13	0.072	<1.41	1.15	0.05
17MK2_1 (10)														
Mean	-	81.4	-	-	985	14.2	<0.008	<0.04	607	<0.10	<0.053	-	0.45	0.02
S.D.	-	143	-	-	1136	6.0	0.002	-	522	-	0.067	-	0.20	0.01
Min.	-	0.8	-	-	46	8.0	<0.007	<0.03	21	<0.09	<0.003	-	0.27	0.02
Max.	<0.5	424	<0.61	<12.6	3730	30.3	0.010	0.04	1478	0.13	0.169	<1.21	0.94	0.04
17MK5 (10)														
Mean	<0.7	2.8	-	-	143	15.3	<0.002	<0.01	100	<0.07	<0.009	-	0.38	0.03
S.D.	-	1.4	-	-	67	0.7	0.001	0.001	56	-	0.004	-	0.03	0.003
Min.	<0.4	1.0	-	-	66	14.5	<0.001	<0.01	35	<0.02	<0.009	-	0.34	0.03
Max.	0.8	4.6	<0.38	<9.0	272	16.4	0.005	0.01	205	0.10	0.014	<0.46	0.43	0.04
17MGA03 (10)														
Mean	4.1	97.1	<3.36	<17.9	227	28.3	<0.003	<0.02	199	0.35	0.08	<0.95	0.41	1.52
S.D.	1.2	98.2	3.4	-	45	2.3	0.002	-	88	0.20	0.03	0.40	0.03	0.41
Min.	2.1	15.3	<0.39	<9.7	181	25.3	<0.002	<0.02	95	0.12	0.03	<0.36	0.34	1.10
Max.	6.7	320	10.9	17.9	291	31.3	0.007	0.02	342	0.75	0.15	1.48	0.46	2.09

Table 2.4: (continued)

Sample	Mn	Cu	As	Se	Ag	Cd	In	Sn	Sb	Te	Au	Hg	Tl	Bi
17MGA04 (10)														
Mean	22.4	514	4.8	-	366	59.6	0.004	<0.03	663	0.79	0.05	5.13	0.49	0.08
S.D.	25.0	380	4.3	-	205	38.0	0.001	0.01	397	0.30	0.01	5.76	0.08	0.03
Min.	4.3	76.5	0.7	-	183	30.5	0.002	<0.01	173	0.40	0.03	0.61	0.39	0.05
Max.	68.1	1210	12.6	<9.7	756	130	0.006	0.04	1274	1.22	0.06	16.6	0.63	0.12
17MGA05 (10)														
Mean	2.2	90.5	<4.45	<15.2	233	26.1	<0.002	<0.04	202	1.28	0.03	<1.38	0.48	1.18
S.D.	0.3	77.6	-	4.5	66	4.7	0.001	0.06	60	0.92	0.01	0.52	0.04	1.44
Min.	1.6	24.7	<0.39	<9.6	122	18.4	<0.001	<0.02	113	0.04	0.02	<0.50	0.43	0.08
Max.	2.6	267	7.1	22.9	351	35.8	0.005	0.17	313	3.64	0.05	2.07	0.54	5.05
17MGA07 (10)														
Mean	3.1	11.3	-	<20.7	209	25.1	<0.006	<0.03	125	0.33	0.05	<0.51	0.45	2.55
S.D.	1.0	6.2	-	1.4	60	1.3	0.003	0.03	37	0.12	0.02	0.13	0.07	4.61
Min.	1.9	6.4	-	<9.5	114	22.9	<0.004	0.02	62	0.06	0.03	<0.33	0.39	0.07
Max.	4.4	26.2	<0.36	22.0	308	27.0	0.011	0.07	175	0.48	0.10	0.67	0.61	15.1
17MT02 (10)														
Mean	<2.0	137	2.5	-	670	27.8	<0.008	<0.17	614	<0.10	0.22	<1.64	0.44	0.08
S.D.	1.0	65.2	1.9	-	233	8.2	-	-	197	0.04	0.11	1.06	0.08	0.02
Min.	<0.6	25.1	0.9	-	304	11.2	<0.008	<0.05	261	<0.08	0.09	<2.26	0.38	0.05
Max.	3.7	247	6.9	<17.8	1033	40.6	0.012	0.38	922	0.14	0.47	3.40	0.60	0.11
17MT03 (11)														
Mean	12.9	<3977	1696	<16.9	385	51.7	<0.088	<0.04	2228	0.73	1.29	<4.23	0.59	0.89
S.D.	23.5	5848	2455	7.3	267	59.5	0.252	0.02	3044	1.44	1.49	4.10	0.41	1.19
Min.	1.6	15	5.3	<10.2	181	14.3	<0.002	<0.01	138	0.04	0.21	<0.68	0.41	0.28
Max.	81.2	21000	6670	26.7	1050	207	0.761	8.12	9900	5.00	5.09	11.7	1.82	4.38
17MT04 (10)														
Mean	3.5	195	6.2	-	378	29.1	<0.009	<0.02	372	0.26	0.28	<1.33	0.59	0.10
S.D.	2.3	219	7.3	-	132	8.7	0.004	-	177	0.21	0.12	0.87	0.08	0.03
Min.	1.2	24	0.5	-	241	19.2	<0.001	<0.02	174	0.04	0.14	<0.53	0.48	0.04
Max.	9.1	597	20.0	<11.7	695	50.5	0.014	0.03	690	0.72	0.47	3.26	0.76	0.12
PD012 (10)														
Mean	4.0	13.5	-	<19.8	280	47.7	<0.002	<0.03	154	438	5.46	<1.83	0.36	0.57
S.D.	1.5	15.8	-	9.3	122	4.5	0.001	0.01	65	103	6.95	-	0.03	0.67
Min.	0.7	4.0	-	<10.0	142	39.2	<0.004	<0.01	92	287	0.08	<0.42	0.32	0.08
Max.	5.8	48.0	<0.49	28.5	508	53.7	0.005	0.05	266	607	21.3	3.20	0.41	2.18
Tinos														
17TP1 (10)														
Mean	-	1.6	-	806	707	124	0.041	0.51	480	312	0.04	1.01	0.65	312
S.D.	-	0.5	-	36	78	66.0	0.042	0.19	71	30.8	0.01	0.14	0.08	14.6
Min.	-	1.0	-	750	504	56.4	0.024	0.31	300	247	0.02	0.81	0.57	302
Max.	<0.6	2.5	<0.51	875	779	245	0.160	1.00	544	350	0.06	1.28	0.80	352
Mykonos														
17MYP1 (10)*														
Mean	<0.5	75.1	132	-	1541	9.8	0.035	0.33	3796	<0.07	<0.018	99.4	2.58	0.04

Table 2.4: (continued)

Sample	Mn	Cu	As	Se	Ag	Cd	In	Sn	Sb	Te	Au	Hg	Tl	Bi
S.D.	-	71.9	199	-	976	7.6	0.062	0.60	2263	0.03	0.003	73.1	1.56	0.01
Min.	<0.5	2.9	0.8	-	472	2.4	0.002	0.01	353	<0.06	<0.012	9.22	0.77	0.03
Max.	0.5	250	629	<10.1	3830	21.5	0.193	1.79	7840	0.11	0.021	198	6.20	0.05
17MYP1-T (13)*														
Mean	-	154	65.1	-	1349	13.9	<0.029	<0.18	3228	<0.07	-	142	2.66	0.03
S.D.	-	115	108	-	570	10.8	0.039	0.13	1531	0.03	-	117	1.20	0.01
Min.	-	20.0	1.0	-	570	3.1	<0.002	<0.03	1455	<0.04	-	12.9	1.20	0.02
Max.	<0.5	441	300	<8.8	2330	40.1	0.116	0.43	6040	0.14	<0.002	426	4.91	0.04
17MYP3 (10)														
Mean	<2.3	74.5	684	-	1057	13.1	0.139	1.57	752	<0.19	<0.003	157	1.83	0.04
S.D.	-	147	536	-	836	3.4	0.072	0.81	843	0.13	0.001	313	1.25	0.02
Min.	<0.5	5.3	42.6	-	294	6.3	0.044	0.76	29	<0.10	<0.003	<0.60	0.66	<0.03
Max.	2.8	491	1540	<12.7	2780	17.5	0.292	3.43	2263	0.44	0.005	1037	4.01	0.07
17MYP4 (11)*														
Mean	-	104	272	-	2325	6.0	0.010	<1.30	3721	<0.13	<0.019	127	2.38	2.87
S.D.	-	123	599	-	1487	5.6	0.009	2.77	2152	0.07	-	214	1.77	9.39
Min.	-	21.7	<0.30	-	427	2.2	<0.003	<0.03	346	<0.05	<0.012	2.20	0.50	0.03
Max.	<0.5	348	1634	<11.7	5380	21.5	0.028	8.32	8380	0.21	0.020	685	6.24	31.2
17MYV2_1 (10)														
Mean	<0.5	1.9	-	-	284	23.5	0.500	0.09	149	<0.05	<0.017	-	0.34	0.10
S.D.	-	0.3	-	-	117	2.3	0.100	0.02	84	-	0.003	-	0.02	0.04
Min.	<0.4	1.5	-	-	97	19.9	0.355	0.06	42	<0.03	<0.015	-	0.32	0.04
Max.	0.6	2.4	<0.40	<9.5	444	27.1	0.653	0.11	301	0.08	0.019	<0.39	0.37	0.18
17MYV2_1B (10)														
Mean	<0.8	1.6	-	-	266	21.4	0.422	0.08	123	<0.09	<0.021	-	0.41	0.88
S.D.	-	0.5	-	-	97	2.8	0.071	0.01	95	0.03	0.003	-	0.02	1.09
Min.	<0.6	1.0	-	-	97	17.9	0.291	0.06	41	<0.06	<0.016	-	0.39	0.06
Max.	0.8	2.4	<0.58	<12	478	27.4	0.505	0.10	378	0.13	0.026	<0.45	0.45	3.56
<i>Antiparos</i>														
17AP2 (10)														
Mean	-	1.6	-	-	163	13.8	<0.002	0.02	31	<0.06	<0.012	-	0.42	0.20
S.D.	-	0.5	-	-	110	0.7	0.001	0.01	20	-	0.004	-	0.04	0.16
Min.	-	1.0	-	-	34	13.0	<0.001	0.01	2	<0.04	<0.011	-	0.38	0.07
Max.	<0.7	2.5	<0.48	<11	296	14.8	0.004	0.04	73	0.08	0.016	<0.47	0.49	0.59
17AP6 (10)														
Mean	0.9	2.7	-	<14.8	231	12.9	0.012	<0.04	164	0.21	<0.011	-	0.85	0.86
S.D.	0.3	2.0	-	-	24	0.5	0.004	0.02	18	0.12	0.005	-	0.14	1.36
Min.	0.5	0.5	-	<8.9	193	12.0	0.005	<0.02	139	0.08	<0.010	-	0.66	0.08
Max.	1.7	6.2	<0.66	16.8	273	13.8	0.018	0.07	206	0.46	0.017	<0.43	1.13	4.64

Notes: * Zoned galena grains. (X) Number of individual spot analyses per sample. (-T) Traverse through one galena grain. (-) All values below LOD. The given max. value is the average LOD within this population. <mean: Values below LOD or inclusions were excluded from the mean calculation. <min: Spot analyses with numbers less than LOD. The number given is the average LOD within that population.

2.7 Discussion

2.7.1 Variation in the Pb isotope signature of the Cyclades Mineral District

These new data show that the main controls on lead in the Cyclades Mineral District are deep sources contributing to the magmatic and hydrothermal systems. Lead isotope analyses of galena from the same deposit exhibit only minor variations and are generally within error, and the isotopic composition of lead in deposits from the same islands are in most cases remarkably homogeneous, including deposits of different types or with different upper crustal fluid pathways (Fig. 2.7). An exception is Mykonos, where variances were found in the isotopic composition of lead at Panormos Bay and Cape Evros. At Mykonos, the variations are observed mainly in $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ values (Fig. 2.7), which could be due to isobaric interferences with ^{204}Hg within the LA-ICP-MS system, although these interferences were explicitly examined and corrected. There is no disparity in the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values (Fig. 2.9). Galena from the four Quaternary deposits (Kondaros-Katsimouti, Triades, Galana, and Profitis Ilias) on Milos have nearly identical $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ values (Fig. 2.7), but the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ values vary within the deposits and between deposit types (Fig. 2.9A). Based on the sample location, petrological description, and potential age of mineralization there is currently no meaningful geological explanation for the lower $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in certain samples from Milos: 17MK2_1, 17MK5, 17MGA03, PD012.

Our results are comparable to data for the same locations from the OXALID archaeometry database and overlap within analytical error with modern published data (Fig. 2.9A; Ahmad, 2018; Chalkias & Vavelidis, 1988; Fitros et al., 2017; Marschik et al., 2010; Vavelidis et al., 1985), despite the different analytical methods used for the analyses (e.g., Baker et al., 2006; McFarlane et al., 2016). Discrepancy between lead ratios from the same island,

were observed for Tinos and Antiparos, with higher $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ values in galena from Panormos Bay on Tinos than those in the OXALID database reported for Apigania Bay on Tinos. Tombros et al. (2007, 2008) suggested that Apigania Bay represents the most recent phase of hydrothermal activity on the island and that metals were derived from volcano-metasedimentary units of the CBU and the leucogranite, whereas at Panormos Bay a combination of the former and the Cycladic Basement and Pelagonian zone were suggested as likely sources. The less radiogenic Pb-isotope signature at Panormos Bay would suggest that lead is primarily derived from the Cycladic Basement, rather than from a more radiogenic source, such as the Tinos intrusion, as suggested by Tombros et al. (2007). The data in OXALID for Antiparos are from the St. Helen's Mine dump (Agios Georgios) and are somewhat similar to our samples (Fig. 2.9A, B), which are from the Prassovounia area in the western part of the island. Kevrekidis et al. (2015) described two generations of mineralization at Agios Georgios and reported an increase in whole-rock Pb-isotope ratios from the first stage of milky quartz veins to the second stage with clear quartz. $^{206}\text{Pb}/^{204}\text{Pb}$ values are within the range of values for galena, but $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values are significantly lower (Kevrekidis et al., 2015). Variation in the Pb-isotope ratios of the two generations of quartz veins at the deposits scale at Agios Georgios (Kevrekidis et al., 2015) might also be responsible for the range of Pb-isotope ratios of galena from the Prassovounia area. Described variances in the Pb-isotopic signature of galena from Kamariza and Plaka (Lavrion) and Soureza can also be observed in the compiled data set, potentially related to the heterogeneity in the local host rocks (namely the LCBN and Basal Unit; e.g., Scheffer et al., 2017). Additional Pb-isotope ratio variations in galena from Evia (Fig. 2.9A, B; Kallianou and Almyropotamos, $^{206}\text{Pb}/^{204}\text{Pb}$: 18.65–18.72 and 18.80–18.85, respectively) are likely ascribed to different lead reservoirs (Ring et al., 2007) as further discussed in Section 2.7.2.

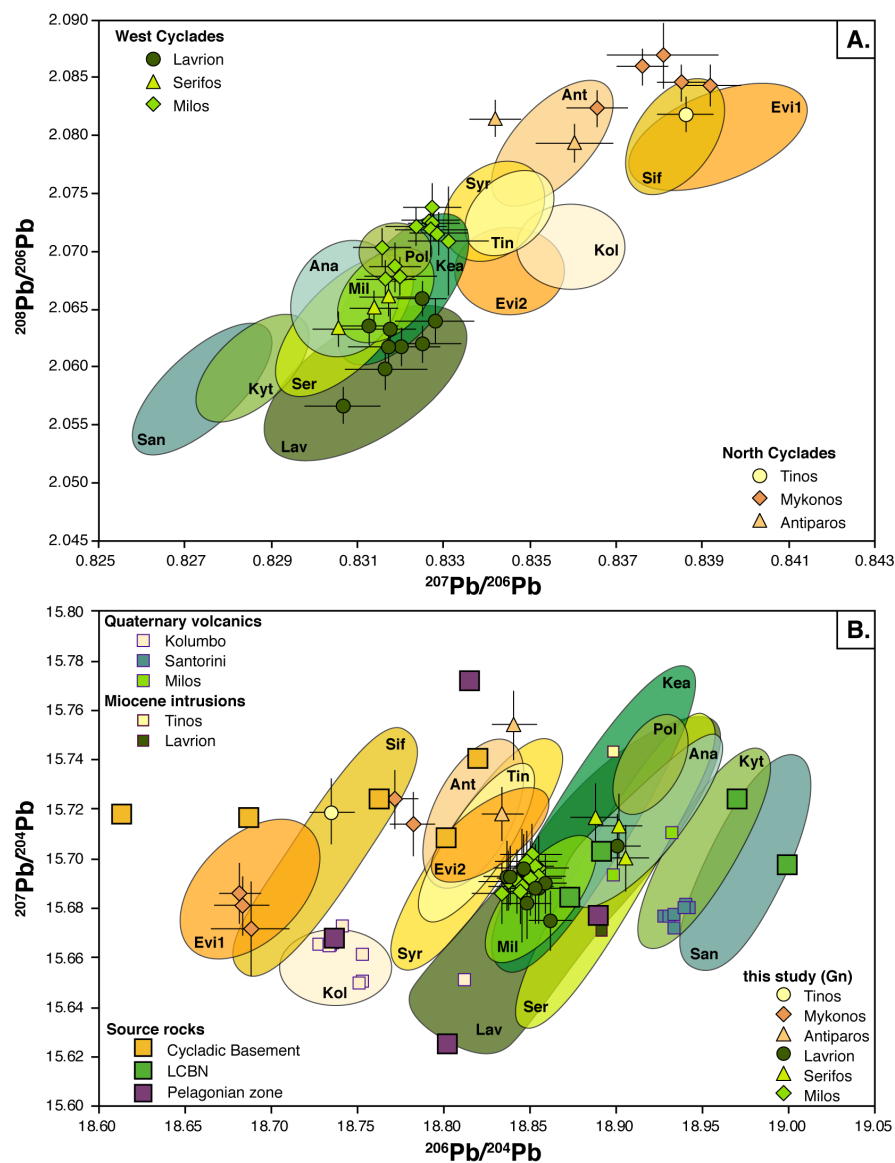


Fig. 2.9: A. Comparison of new LA-Q-ICP-MS Pb-isotope ratios in galena (symbols in legend and at 2 S.E.) with compiled data for galena from previous TIMS studies (shaded ellipses). Published Pb-isotope data are from archaeometry studies (OXALID database, e.g. Gale & Stos-Gale, 1981 and Stos-Gale & Gale, 2009) as well as Ahmad (2018); Chalkias & Vavelidis (1988); Fitros et al. (2017); Marschik et al. (2010) and Vavelidis et al. (1985). Pb-isotope signatures in galena from deposits in the north-central Cyclades (yellow-orange) have higher $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios than galena from the deposits in the west Cyclades (green). B. Compiled whole-rock Pb-isotope data of representative Quaternary volcanic rocks (Gülen, 1990; Klaver et al., 2016a), Miocene intrusions (Juteau et al., 1986), Cycladic Basement on Ios (Buettner et al., 2005; Klaver, 2016), Lower Cycladic Blueschist Nappe on Santorini (Klaver, 2016) and Pelagonian zone on Santorini and Naxos (Klaver, 2016; Stouraiti et al., 2017) in the Cyclades (squares, error bars are smaller than shown symbols). New Pb-isotope ratios and compiled Pb-isotope data on galena are shown in the same colour code as in Fig. 2.9A. Ana: Anafi, Ant: Antiparos, Evi1: Evia (Kallianou), Evi2: Evia (Almyropotamos), Kea: Kea, Kol: Kolumbo, Kyt: Kythnos, Lav: Lavrion, Mil: Milos, Pol: Poliegos, San: Santorini, Ser: Serifos, Sif: Sifnos, Syr: Syros, Tin: Tinos.

These variations in the Pb-isotopic signatures of different deposits on the same island might indicate a change in the source of fluids during the evolution of the hydrothermal system. However, we have observed that galena from mineral deposits that formed as much as 10 m.y. apart, such as at Lavrion (Plaka and Kamariza) and Milos, have similar $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ values and therefore probably a similar source of lead. Disparities in the $^{208}\text{Pb}/^{204}\text{Pb}$ values between Milos and Lavrion suggest lower Th/U concentrations in the source for the carbonate-replacement deposits at Lavrion (Fig. 2.7, 2.9A). This is in agreement with reported values of Th and U in marbles from Lavrion (Scheffer et al., 2017), with Th/U <1 for most marble units, which is significantly lower than for the continental crust (Th/U $\geq$ 3.8: Rudnick & Gao, 2003).

Galena samples from mineral deposits in the north-central Cyclades (Antiparos, Evia, Kolumbo, Mykonos, Sifnos, Syros, Tinos; Fig. 2.9A) have higher $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ values than galena from deposits in the west Cyclades (Anafi, Kea, Kythnos, Lavrion, Milos, Poliegos, Santorini, Serifos; Fig. 2.9A). This strongly suggests that there is a common underlying basement source of lead for the base metal-rich carbonate-replacement, vein-type, low- to high-sulfidation epithermal, and skarn deposits in the west Cyclades, and a distinctive source of lead for the vein-type, carbonate-replacement and volcanic-hosted massive sulfide deposits in the north-central Cyclades. The results suggest two dominant sources: a primitive (less radiogenic) and, in general, more heterogeneous source in the north and central Cyclades and an evolved (more radiogenic) and homogeneous source in the west.

2.7.2 Implications for the underlying basement

To track the possible sources of lead within the Cyclades, whole-rock Pb-isotope data of representative Quaternary volcanic units (Gülen, 1990; Klaver et al., 2016a), Miocene

intrusions (Juteau et al., 1986), as well as Cycladic Basement, LCBN and Pelagonian zone rocks (Buettner et al., 2005; Klaver, 2016; Stouraiti et al., 2017) have been compiled and are shown in Figure 2.9B together with the Pb-isotope data on galena. Deposits in the Cyclades Mineral District, but also related magmatic and volcanic rocks, inherit the Pb-isotopic signature of the underlying basement, which is the primary source of lead.

Galena from the submarine massive sulfides at Kolumbo (Ahmad, 2018) has the same Pb-isotopic signature as the volcanic material from the volcano (Klaver et al., 2016a), and the primitive values have been interpreted to reflect a mantle component (Rizzo et al., 2016; Klaver et al., 2016a,b), supported by the high $^3\text{He}/^4\text{He}$ values of gases discharged at the volcano (7.0–7.1 Ra: Rizzo et al., 2016). However, even the least radiogenic lead from Kolumbo is too evolved for a pure mantle source and must be explained by a mixture of lead from the Cycladic Basement and a minor mantle component (Klaver et al., 2016b). Volcanic rocks from Santorini (Gülen, 1990; Klaver et al., 2016a) have Pb-isotope signatures similar to associated galena, which is hosted in mineralized veins within the LCBN, indicating a common lead source for mineralization and magmatism. Compared to the Pb-isotopic signature at Kolumbo, volcanic rocks and galena from Santorini are more evolved, which has been previously related to distinctive mantle sources at Kolumbo and Santorini and pronounced crustal contamination at Santorini (Klaver et al., 2016a; Rizzo et al., 2015, 2016), consistent with lower $^3\text{He}/^4\text{He}$ values of gases and mafic cumulate enclaves in dacitic lavas (3–4 Ra: Rizzo et al., 2015).

Subtle variations were observed between the Pb-isotopic signature of the Quaternary volcanic units from Milos and associated galena and also between Miocene intrusions from Lavrion and Tinos and associated galena. For example, potassium feldspar of Miocene intrusive rocks from Lavrion and Tinos (Juteau et al., 1986) have slightly more evolved $^{206}\text{Pb}/^{204}\text{Pb}$ values than galena from the associated mineral deposits (Fig. 2.9B). Whole-

rock Pb-isotope data of the Quaternary volcanic rocks from Milos ([Gülen, 1990](#)) have slightly more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ values than galena from the different mineral deposits on Milos. [Marschik et al. \(2010\)](#) proposed a seawater-dominated hydrothermal system with country rock interaction as the dominant source of metals at Triades-Galana and suggested an igneous source of lead based on the similar Pb-isotope signatures of galena, sphalerite, and local volcanic rocks. Despite these small variations, there is overall a good agreement between the Pb-isotope signature of the intrusive and extrusive rocks and the associated galena, which was also noted by [Pe-Piper \(1994\)](#). Previous studies (e.g., [Ersoy & Palmer, 2013](#); [Francalanci et al., 2005](#); [Francalanci & Zellmer, 2019](#); [Klaver et al., 2015, 2016b](#); [Woelki et al., 2018](#)) highlighted that the Miocene to Quaternary volcanics in the Cyclades are dominated by a mantle-derived composition, with variable degree of crustal contamination, and addition of melts from subducted sediments. Crustal contamination or addition of melt from subducted sediments, which some studies concluded to be difficult to distinct, would dominate the Pb-isotopic composition of the mantle-derived magma due to the low lead content in the depleted mantle (e.g., [Francalanci & Zellmer, 2019](#); [Klaver et al., 2016a](#); [Pe-Piper, 1994](#); [Pe-Piper & Piper, 2001](#); [Woelki et al., 2018](#)). The regional similarities in the Pb-isotopic signature of galena from the upper crustal hydrothermal systems considered in this study, emphasize that local basement rocks were the dominant source of lead.

Whole-rock Pb-isotope ratios of upper crust calc-silicates ([Klaver, 2016](#)) have been reinterpreted based on [Schneider et al. \(2018\)](#), which subdivided the exposed pre-volcanic basement rocks of Santorini into the LCBN and the Pelagonian zone, separated by the newly defined Santorini Detachment System. Based on their structural position, we correlate the whole-rock data of the metapelites and marbles near Athinios to the LCBN, and phyllites of the metaflysch series near Mt. Mesa Vouno to the Pelagonian zone. In contrast

to the galena Pb-isotopes within the island groups, whole-rock lead isotope signatures from the Cycladic Basement and LCBN vary significantly across the region (e.g., $^{206}\text{Pb}/^{204}\text{Pb}$: 18.54–18.80 for the Ios gneiss compared to 18.87–19.00 for LCBN on Santorini), reflecting the heterogeneous nature of the Cycladic Basement and Cycladic Blueschist Unit (e.g., Bröcker & Pidgeon, 2007; Flansburg et al., 2019; Poulaki et al., 2019; Seman et al., 2017). The lead isotope signature of galena from deposits occurring in the north-central Cyclades is in good agreement with the whole-rock isotopic composition of the Ios gneiss (Buettner et al., 2005; Klaver, 2016) consistent with a source of lead in the Cycladic Basement. In contrast, the array of Pb-isotope ratios obtained for galena from the diverse deposit types in the west Cyclades corresponds closely to the Pb-isotope values from the LCBN from Santorini (Klaver, 2016). Whole-rock Pb-isotope analyses of the Pelagonian zone rocks, represented by the metaflysch series on Santorini (Klaver, 2016) and the metaophiolitic rocks on Naxos (Stouraiti et al., 2017), plot in the center of these two distinct groups. Migmatites in the north-central Cyclades, related to the hot asthenospheric flow triggered by slab tearing under West Anatolia (Jolivet et al., 2015; Rabillard et al., 2018), originate from the Cycladic Basement, and would therefore have the same Pb-isotopic signature. Since whole-rock Pb-isotope data of basement units are limited, additional analyses of the Pb-isotopic composition of the Cycladic Basement, including exposures in the west Cyclades, and of the metamorphic basement, the LCBN in the west and UCBN in the north-central Cyclades, are needed to confirm the relationship between the two distinct lead sources. In particular, Flansburg et al. (2019) argued for exhumation of the Cycladic Basement prior to the deposition of the CBU, based on detrital zircon populations from Ios (central Cyclades). This is in contrast to Seman et al. (2017), who concluded that the Cycladic Basement was not exposed during the Triassic in the west Cyclades. Flansburg et al. (2019) proposed that the central Cyclades were part of the proximal continental mar-

gin by the earliest Mesozoic, in contrast to the hyperextended margin in the west Cyclades. Because of the lack of Pb-isotope data of the UCBN, it cannot be excluded that the UCBN is a potential source of lead for the different deposit types in the north-central Cyclades. Moreover, the Pb-isotopic signature of potassium feldspar from the Miocene intrusion on Tinos plots in the array of data for the LCBN, indicating that the UCBN might plot in the center of the two arrays similar to the Pelagonian zone.

In comparison to other deposits in the Mediterranean (e.g., Chalkidiki, Crete, Peloponnese, Rhodope Massif; OXALID database; [Frei, 1995](#); [Kalogeropoulos et al., 1989](#); [Marchev et al., 2005](#)) lead in the deposits of the west Cyclades is the most radiogenic, whereas these mostly plot in the field defined by the Cycladic Basement. [Kalogeropoulos et al. \(1989\)](#) pointed out that the uniformity of the Pb-isotopic signature of Chalkidiki ore sulfides and Tertiary magmas likely indicate a crustal inheritance of lead. In the Rhodope Massif, [Marchev et al. \(2005\)](#) described an east-west trend based on Pb- and Sr-isotope ratios and suggested a stronger input of crustal versus mantle material, with a magmatic origin of lead or lead being derived from the metamorphic basement. Similarities between the Pb-isotope ratios of the deposits in the north-central Cyclades and deposits in northern Greece, supported by similar ages for the orthogneiss units (Late Carboniferous, e.g., [Flensburg et al., 2019](#); [Schenker et al., 2014](#)) throughout the Mediterranean region might indicate that many of the ore deposits have inherited the Pb-isotopic signature of a similar Pre-Alpine crystalline basement.

In the Cyclades lead isotope ratios reflect two distinctive basement sources, where the orthogneiss on Ios (Cycladic Basement) and metapelites and marbles on Santorini (LCBN) represent two end-member sources of lead. The lack of Pb-isotope data of the Cycladic Basement in the west Cyclades or the UCBN in the north-central Cyclades do not allow elimination of regional variances in the Cycladic Basement and CBU (UCBN and LCBN)

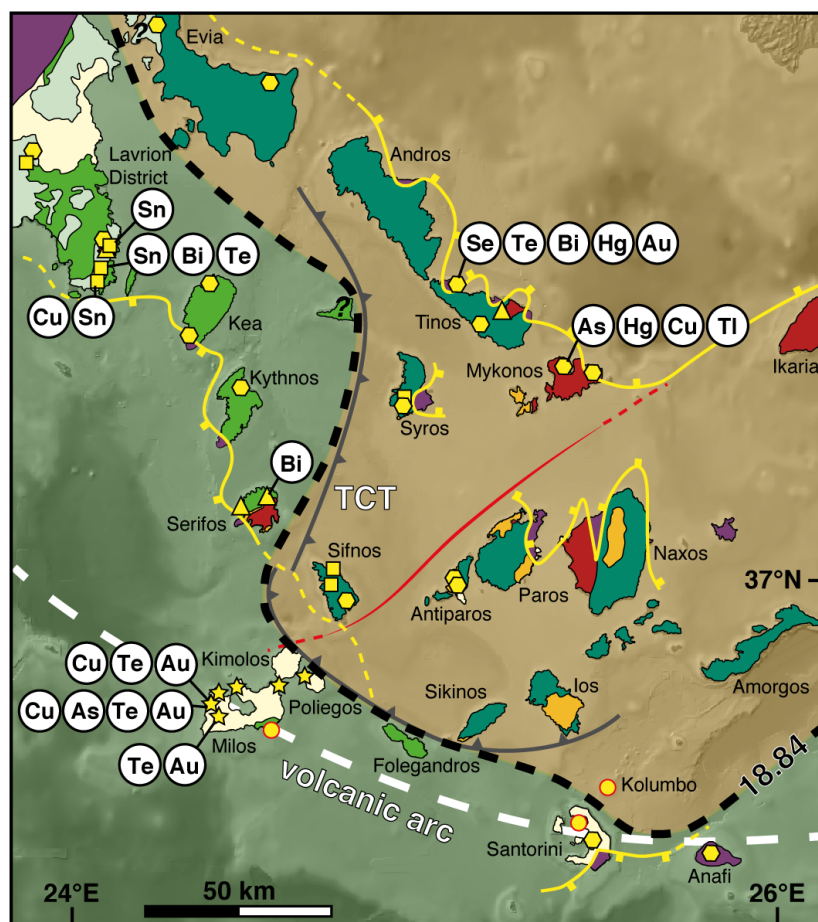


Fig. 2.10: Simplified geological map of the Cyclades Mineral District, Greece, modified after Fig. 2.1 and using the same legend. Based on the Pb-isotope signature of galena from the Cyclades Mineral District, metal sources can be divided into two regions: a less radiogenic base metal source for the deposits in the north-central Cyclades, reaching the Cycladic Basement, and a more radiogenic source for the deposits in the west Cyclades, tapping the Lower Cycladic Blueschist Nappe. Notably, these two regions are separated by the $^{206}\text{Pb}/^{204}\text{Pb}$ 18.84 line, which is parallel to the proposed trace of the Trans-Cycladic Thrust (TCT). White circle summarizes LA-Q-ICP-MS trace element data in galena, showing the enrichment of base and precious metals in galena from the Cyclades Mineral District. Not included are Ag, Sb and Cd which were detected in all analyzed galena (Fig. 2.8). Silver and Sb are the most abundant trace elements in galena, except for Panormos Bay (Tinos) and Profitis Ilias (Milos), where Se and Te concentrations exceed Ag and Sb, respectively. Metals are sorted from the most to the least abundant.

as potential precursor of the described Pb-isotope trends. The new and compiled data define a $^{206}\text{Pb}/^{204}\text{Pb}$ line (Fig. 2.10) that closely follows the trace of the proposed TCT (Grasemann et al., 2018), which is based on peak metamorphic conditions recorded in the Cycladic Blueschist Unit, dividing the CBU into discrete nappe structures (UCBN and LCBN). A difference in the metamorphic grade alone should not cause a change in the Pb-isotopic signature; however, distinct detrital zircon populations in the UCBN and LCBN suggest mixed provenance and age that could account for the variations in Pb-isotopes (e.g., Bröcker & Pidgeon, 2007; Flensburg et al., 2019; Seman et al., 2017; Poulaki et al., 2019). Changes in the geochemistry of the intrusive rocks in the west and north-central Cyclades also have been proposed by Altherr et al. (1982). These regional variations are traceable in the Pb-isotopic signature of the shallow crustal deposits throughout the Cyclades Mineral District. Our data indicate that the $^{206}\text{Pb}/^{204}\text{Pb}$ line passes between Santorini and Kolumbo, which have been proposed to possess distinct mantle sources with more pronounced crustal contamination at Santorini based on whole-rock Pb-isotope ratios of the volcanic rocks (Klaver et al., 2016a). Significant variations in the Pb-isotope signature of the deposits on Evia (Kallianou and Almyropotamos) might indicate a continuation of the $^{206}\text{Pb}/^{204}\text{Pb}$ line northwards, following the trace of the proposed thrust separating the Almyropotamos Nappe from the UCBN (Ring et al., 2007). This would imply that the Pb-isotopic signature of the Basal Unit in Attica and Evia is closer to the observed array of Pb-isotopic ratios from the LCBN, supported by the striking similarity of the Pb-isotope ratios in galena from Lavrion and Milos.

Figure 2.11 schematically illustrates the inferred sources of the base and precious metals for the diverse deposit types in the Cyclades Mineral District from the late Miocene and into the Quaternary. Homogeneous Pb-isotope ratios for the shallow crustal deposits in the west Cyclades suggest a common lead source in the LCBN, which was accessible since the

late Miocene and is still accessible today to the young epithermal deposits on Milos. The less radiogenic and heterogeneous Pb-isotope signature for the different deposit types in the north-central Cyclades indicate a mixture of lead sources, mainly the Cycladic Basement (including the migmatites), with minor contributions from the UCBN and Pelagonian zone.

2.7.3 Trace element variations in galena and implication for base and precious metal-rich deposits

Unlike the lead isotopes, which mainly reflect the deep sources of lead and its signature inherited in the supracrustal rocks, the concentrations of trace elements in galena are strongly influenced by the compositions of the local host rocks, the conditions of mineralization (e.g., temperature and redox: e.g., [Chutas et al., 2008](#); [George et al., 2016](#); [Grant et al., 2015](#); [Huston et al., 1996](#)), and partitioning of trace elements into co-crystallized mineral phases (e.g., [George et al., 2016](#)). Galena trace elements in some deposits in the Cyclades also show evidence of remobilization during mineralization. Galena from Cape Evros (Mykonos) is mostly inclusion free and has low concentrations of trace elements, but rims of Ag-rich mckinstryite were observed (Fig. 2.6H) suggesting that later recrystallization of galena, linked to silicification, caused leaching of Ag and remobilization to the rims, with a decrease in the precious metal concentrations in the crystal lattice.

Galena from the Panormos Bay vein-type deposit on Tinos, which is characterized by high Se, Te, and Bi, indicates higher mineralization temperatures (e.g., 200–300°C: [Tombros et al., 2007](#)) than for most deposits in the Cyclades Mineral District, supported by the estimated minimum depth of formation of 1 km. Similar, high Te concentrations (~438 ppm) and Au (~5.5 ppm) at Profitis Ilias, compared to other deposits on Milos ([Kilias et al., 2001](#)), imply higher temperatures and pressures of mineralization for the precious metal-rich deposits. The differences between the precious metal-rich system (Profitis Ilias)

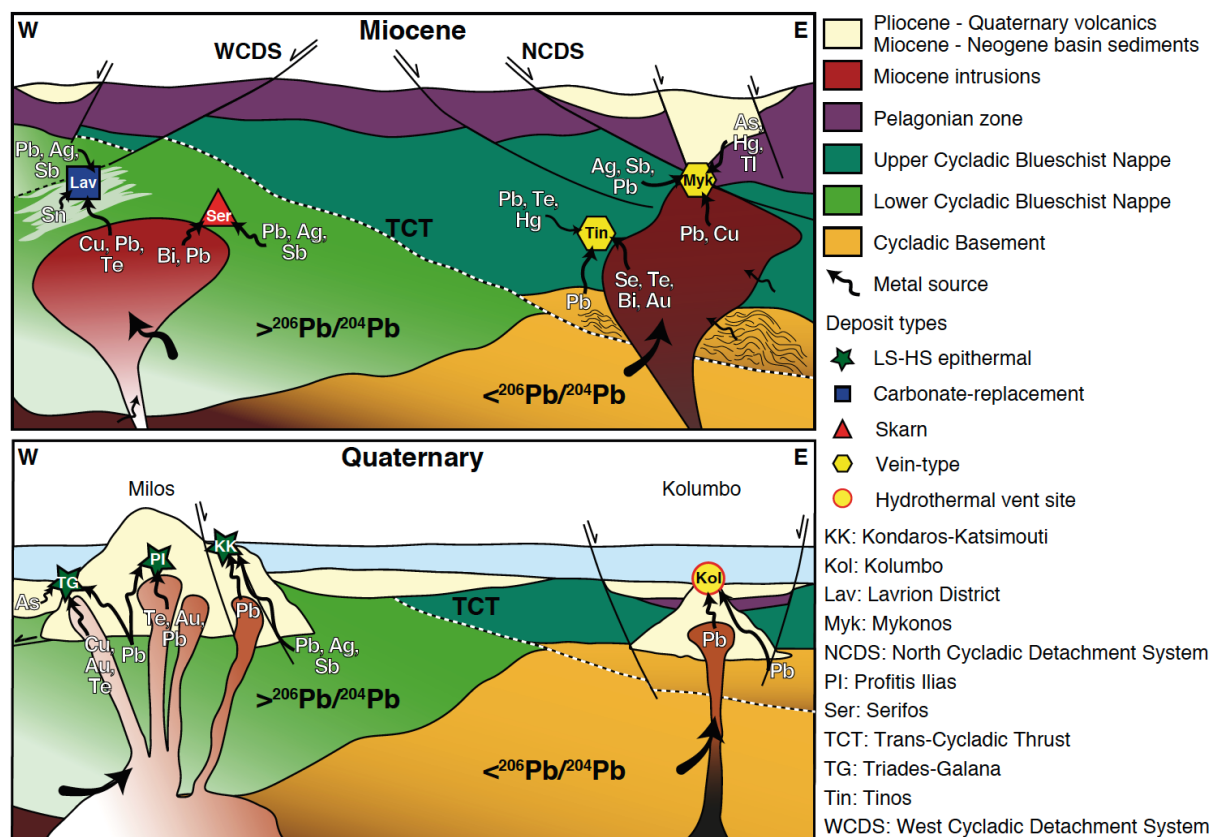


Fig. 2.11: Schematic representation of major sources of base and precious metals for the different deposit types in the Cyclades Mineral District, Greece. Regional similarities in the Pb-isotopic signature of galena, but also related magmatic and volcanic rocks, indicate that these inherit the Pb-isotopic signature of the underlying basement, which is the primary source of lead. Homogeneous Pb-isotope ratios for the shallow crustal deposits in the west Cyclades suggest a common base metal source in the Lower Cycladic Blueschist Nappe, which was accessible since the Late Miocene. The major lead (and base metal) source for the deposits in the north-central Cyclades is the Cycladic Basement (including migmatites) and potentially the Upper Cycladic Blueschist Nappe. Major detachments and fault planes were favorable paths-ways for the metal-bearing fluids. Different fluid-rock interactions and variable contributions from magmatic fluid components led to the metal enrichment in the Cyclades Mineral District (see text for discussion).

and the base metal-rich system (Kondaros-Katsimouti-Vani) on Milos have been noted by [Alfieris et al. \(2013\)](#). However, the Pb-isotope compositions of the different mineral occurrences on Milos are very uniform, reflecting the deep sources and inheritance by the more local intrusive, volcanic and sedimentary sources.

Bismuth is particularly abundant in galena from skarn deposits (Fig. 2.8, 2.10; Serifos: [Fitros et al., 2017](#), this study; Plaka, Lavrion: [Voudouris et al., 2008a](#)) and from the vein-type deposit at Panormos Bay on Tinos; which likely indicates a magmatic input and higher mineralization temperatures (e.g., [Grant et al., 2015](#); [Chutas et al., 2008](#)). Enrichment in As, Tl, and Hg in galena has been observed for the deposits occurring in the hanging wall of the major detachment systems (Fig. 2.10, Tab. 2.4; e.g., Mykonos, Milos, and Kolumbo: [Ahmad, 2018](#)) and are generally associated with a shallow depth and lower temperatures of mineralization. In particular, elevated concentrations of As, Hg, and Tl in galena from Mykonos might be explained by leaching from the surrounding supradetachment sediments of the Miocene conglomeratic sequence. Base metal and Ag enrichment in Zn-Pb-Fe-Ag deposits in the west Cyclades are likely related to remobilization of metals by magmatic-hydrothermal fluids from an enriched metamorphic basement (LCBN). Galena from the deposits in the Lavrion District is enriched in Sn, with a potential source of Sn within the marbles of the Basal Unit (Fig. 2.10 and 2.11). Precious metal enrichment in the north-central Cyclades, is possibly related to remobilization from the metasomatized lower crust or mantle or partitioning of Au in back-arc, primary magmas ([Menant et al., 2018](#)). An enrichment in precious metals in the low- to high-sulfidation epithermal deposits along the present-day volcanic arc, is linked to the significant mantle contribution in the magmatic-hydrothermal systems, which differs from the signature of the Miocene back-arc magmatism in the Cyclades ([Ersoy & Palmer, 2013](#); [Francalanci & Zellmer, 2019](#)). Regional variations in the trace element geochemistry of galena indi-

cate multiple metal sources, mainly the underlying LCBN in the west Cyclades and minor UCBN in the north-central Cyclades, with magmatic contributions in the north-central Cyclades and along the present-day volcanic arc causing an enrichment in precious metals, as well as variable contributions for the Pelagonian zone and Miocene to Pliocene basin sediments in the hanging wall (Fig. 2.11). Major detachments, as well as late brittle faults, were favorable pathways for the metal-bearing fluids and enhanced fluid-rock interaction with the surrounding host rocks, which is reflected in the trace element geochemistry.

2.8 Conclusions

The presented study provides the first comprehensive overview of the geochemistry and isotopic compositions of galena in a variety of mineral deposit types of the Cyclades Mineral District, including over 30 mineral occurrences on 15 Cycladic islands. Lead-isotope ratios and trace elements in galena indicate significant regional variances in the source of metals that contributed to the metal endowment of the district. Base and precious metal-rich deposits in the Cyclades Mineral District inherited the Pb-isotopic signature of the primary source of lead, and regional similarities indicate two lead sources: a less radiogenic source in the north-central Cyclades ($^{206}\text{Pb}/^{204}\text{Pb} \leq 18.84$) and a more radiogenic source in the west Cyclades ($^{206}\text{Pb}/^{204}\text{Pb} \geq 18.84$). Constrained by the similarity to existing whole-rock Pb-isotope values of potential source rocks, two major primary lead sources could be identified: the pre-Alpine Cycladic Basement, for the deposits in the north-central Cyclades, and the metamorphosed volcano-sedimentary Lower Cycladic Blueschist Nappe for the deposits in the west Cyclades. However, because of the lack of Pb-isotope ratios of the Upper Cycladic Blueschist Nappe and the close spatial relationship of the $^{206}\text{Pb}/^{204}\text{Pb}$ 18.84 line and the trace of the proposed Trans-Cycladic Thrust (Grasemann et al., 2018), the Upper

Cycladic Blueschist Nappe cannot be excluded as a potential source of lead for the deposits in the north-central Cyclades. The distinct sources of lead also correlate with the mineral assemblages of the deposits and trace elements in the galena. Deposits in the west Cyclades are mainly enriched in Ag and base metals (e.g., Zn, Pb, Fe), which are likely derived from the upper crust, the Lower Cycladic Blueschist Nappe, as previously proposed by [Menant et al. \(2018\)](#). Mineral occurrences in the north-central are generally more enriched in Pb and Cu as well as Te±Se, Ag, and Au. Precious metal enrichment (Au, Te) is also evident in the Quaternary epithermal vein deposits on Milos. The enrichment of precious metals may be linked to fast subduction retreat and slab tearing, which mobilized Au from the metasomatized lithospheric mantle ([Menant et al., 2018](#)).

Trace metal signatures of the deposits reflect a complex interplay of distinct metal sources, including not only the Cycladic Basement and Cycladic Blueschist Unit but also contributions of the metasomatized lithospheric mantle and leaching of the adjacent sedimentary host rocks. These data confirm that lead isotopes in galena, combined with trace element fingerprints, are a reliable archive and powerful tool for identifying metal sources in complex tectono-stratigraphic assemblages.

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2.A Supplementary information for Chapter 2

Supplementary information for:

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2.A.1 Cyclades Mineral District

The following is an overview of the mineralization styles in the Lavrion District, and the islands of Milos, Serifos, Mykonos, Tinos and Antiparos, which are the focus of the accompanied paper. In the Lavrion District, the mineralization has been variably described as carbonate-replacement stratabound Pb-Zn-Ag ore (manto-chimney type), veins, skarn, porphyry-style mineralization, five-element veins, and breccia style, commonly with supergene oxidation (e.g., [Berger et al., 2013](#); [Bonsall et al., 2011](#); [Skarpelis & Argyraki, 2009](#); [Scheffer et al., 2017, 2019](#); [Spry et al., 2014](#); [Voudouris et al., 2008a,b, 2019](#)). Multiple stages of polymetallic mineralization were identified where remobilization and deposition of pre-concentrated ore favored an increase in the metal grade (e.g., [Bonsall et al., 2011](#); [Scheffer et al., 2017](#); [Skarpelis & Argyraki, 2009](#)). Porphyry and breccia-style mineralization, as well as skarn mineralization, are within or adjacent to the Plaka granodiorite ([Leleu et al., 1973](#); [Voudouris et al., 2008a](#)). Whereas the Pb-Zn-Ag replacement ores occur within the lower and upper marble of the Basal Unit and along the marble-schist contact (Fig. 2.1; e.g., [Scheffer et al., 2017](#); [Voudouris et al., 2008b](#)), and are more closely spatially related to the local low-angle detachment system ([Berger et al., 2013](#)). Recently, [Scheffer et al. \(2017\)](#) suggested that brecciation and epithermal ore deposition postdates the

carbonate-replacement deposits. A magmatic origin for the fluids related to the formation of the porphyry, skarn and carbonate-replacement deposits has been widely accepted (e.g., [Bonsall et al., 2011](#); [Spry et al., 2014](#); [Voudouris et al., 2008a,b](#)), whereas mixed seawater and meteoric fluids were proposed for the formation of the late vein and breccia-style mineralization ([Scheffer et al., 2019](#)).

On Milos, low- to high-sulfidation epithermal deposits occur primarily in the Quaternary calc-alkaline volcanic rocks in the western part of Milos (e.g., [Alfieris et al., 2013](#); [Kilias et al., 2001](#); [Marschik et al., 2010](#)). Because of the densely mineralized area, polymetallic mineralization on Milos has been investigated extensively. Base and precious metal-rich mineralization have been classified as Kuroko-type seafloor massive sulfide (e.g., [Hauck, 1984](#); [Smith et al., 2018](#); [Vavelidis & Melfos, 1998](#)), seawater-dominated epithermal ([Kilias et al., 2001](#); [Liakopoulos et al., 2001](#); [Marschik et al., 2010](#)), shallow submarine epithermal ([Alfieris et al., 2013](#); [Stewart & McPhie, 2006](#)), and deposits that are transitional between volcanic-hosted massive sulfide and epithermal ([Naden et al., 2005](#)). The active shallow submarine hydrothermal vent field located in the crater of the Kolumbo volcano northeast of Santorini is a modern analogue for the massive sulfide mineralization in western Milos ([Alfieris et al., 2013](#); [Kilias et al., 2013](#)). Three successive magmatic events have been correlated to the polymetallic mineralization on Milos: 1) felsic volcanism from 3.5–2.7 Ma with subseafloor Pb-Zn-Cu-Ag-Te mineralization in steep interconnected quartz veins at Profitis Ilias and Chondro Vouno ([Alfieris et al., 2013](#); [Kilias et al., 2001](#)); 2) a second stage of Pb-Zn-Cu-As-Sb-Ba-Ag-Au mineralization in submarine andesitic to dacitic domes and lava from 2.7–1.5 Ma at Triades-Galana ([Alfieris et al., 2013](#); [Marschik et al., 2010](#); [Smith et al., 2018](#)) and late deposition of Pb-Zn-Ag-Sb-Mn along the NW-SE-trending Kondaros-Katsimouti-Vani fault during the transition from submarine to subaerial conditions ([Alfieris et al., 2013](#); [Papavasiliou et al., 2016b](#); [Papavassiliou et al., 2017](#)); and 3) continuous

injection of dacitic to rhyolitic magma in a submarine to subaerial environment in the eastern and central parts of Milos together with geothermal-hydrothermal activity since 1.5 Ma ([Alfieris et al., 2013](#); [Liakopoulos et al., 1991](#)). [Marschik et al. \(2010\)](#) proposed a seawater-dominated hydrothermal system with country rock interaction as the dominant source of metals at Triades-Galana and suggested a magmatic source of lead. At Kondaros-Katsimouti bulk ore analysis indicate enrichment in W and Mo, which evince a dominantly magmatic-hydrothermal contribution to the ore fluids ([Papavasiliou et al., 2016b](#)).

Less research has been conducted on the vein-type, skarn and carbonate-replacement deposits on the exhumed metamorphic core complexes. Multiple stages of precious metal mineralization occur on Tinos in stockworks of steeply-dipping quartz veins. Mineralized quartz veins at Panormos Bay occur exclusively in the marble of the UCBN; however, at Apigania Bay veins crosscut the marble and schist units of the UCBN ([Tombros et al., 2008](#)). The Au-Ag vein system at Panormos Bay contains abundant telluride minerals, whereas the vein system at Apigania Bay lacks tellurides and likely represents a later stage of mineralization ([Tombros et al., 2007, 2008](#)). Homogenization temperatures of fluid inclusions at Panormos Bay suggest mineralization from 200°C to 300°C, and precipitation of telluride ores from 230°C to 260°C, in contrast to the mineralization at Apigania Bay, which occurred between 150°C and 195°C. The source fluids for the mineralization at Panormos Bay have been interpreted as a mix of magmatic fluids from the Tinos leucogranite and meteoric water with metal leached from the surrounding UCBN and Pelagonian zone rocks ([Tombros et al., 2008](#)).

On Mykonos, subvertical extensional veins, over 15 meters wide are spatially related to extensional faults and the local low-angle detachment system and are filled by banded barite ([Menant et al., 2013](#); [Skarpelis, 2002](#); [Tombros et al., 2015](#)). At Panormos Bay, these veins crosscut the exposed Miocene conglomeratic sequence ([Menant et al., 2013](#);

[Sánchez-Gómez et al., 2002](#); [Skarpelis, 2002](#)). In the eastern part of the island at Cape Evros, subvertical NW-SE trending barite and Fe-hydroxide veins cut the upper part of the Mykonos laccolith, the metabasites of the Pelagonian zone and the Miocene conglomeratic sequence ([Lecomte et al., 2010](#); [Menant et al., 2013](#); [Skarpelis, 2002](#)), and sub-economic Au enrichment was reported within the silica-cap and silica-breccia at Profitis Elias and Mavro Vouno ([Skarpelis, 2002](#)). [Tombros et al. \(2015\)](#) proposed that magmatic fluids derived from the Miocene intrusion mixed with Miocene seawater to produce the barite and sulfide mineralization on Mykonos.

Magnetite, Ca-exo- and endo-skarns are associated with the Miocene pluton on Serifos ([Ducoux et al., 2017](#); [Salemink, 1985](#)). More distal to the intrusion, polymetallic mineralization occurs in small lenses in the Moutoulas prospect, where mineralization has been variably interpreted as skarn, retrograde skarn, metamorphosed exhalite or low-temperature vein and carbonate-replacement ore (e.g., [Fitros et al., 2017](#); [Salemink, 1985](#); [St. Seymour et al., 2009b](#)). [Fitros et al. \(2017\)](#) proposed that ore fluids derived from the Serifos pluton interacted with the wall-rock and, after mixing with meteoric water, deposited the bismuth minerals at Moutoulas.

On Antiparos base metal mineralization occurs in subvertical quartz and minor barite veins, which cut the Cycladic Basement and UCBN, in the south of the island at Agios Georgios and in the western part of the island near Prassovounia ([Gale & Stos-Gale, 1981](#); [Kevrekidis et al., 2015](#); [Skarpelis, 2002](#)). [Kevrekidis et al. \(2015\)](#) proposed that the Agios Georgios argentiferous galena deposit on Antiparos is genetically related to the leucogranitic Paros pluton, yet as pointed out by [Voudouris et al. \(2019\)](#) a connection to the Pliocene rhyolites (5–4 Ma: [Innocenti et al., 1982](#)) on Antiparos seems more likely.

Chapter 3

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3 Origin of hydrothermal barite in polymetallic veins and carbonate-hosted deposits of the Cyclades continental back-arc

Abstract

Polymetallic veins and breccias and carbonate-replacement ore-deposits in the Cyclades continental back-arc, Greece, formed from a range of fluid and metal sources strongly influenced by the dynamics of the late Mesozoic–Cenozoic Hellenic subduction system. These complexities are recorded in the isotopic signatures of hydrothermal barite. We investigated 17 mineral occurrences on four Cycladic islands and from Lavrion on the mainland. Here, barite occurs in almost all deposit types of Miocene to Quaternary age. We used a multiple isotope and geochemical approach to characterize the barite in each deposit, including mineral separate analysis of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ and laser ablation inductively-coupled plasma mass spectrometry of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$. Barite from carbonate-hosted vein and breccia Pb-Zn-Ag mineralization on Lavrion has a wide range of $\delta^{34}\text{S}$ (2–20‰) and $\delta^{18}\text{O}$ (10–15‰) values, reflecting a mix of magmatic and surface-derived fluids that have exchanged with isotopically heavy oxygen in the carbonate host rock. Sulfur ($\delta^{34}\text{S}$: 10–13‰) and oxygen ($\delta^{18}\text{O}$: 9–13‰) values of barite from the carbonate-hosted vein iron and barite mineralization on Serifos are permissive of a magmatic sulfate component. Barite from epithermal base and/or precious metal deposits on Milos has $\delta^{34}\text{S}$ (17–28‰) and $\delta^{18}\text{O}$ (9–11‰) values that are similar to the modern seawater. In contrast, barite from vein-

type deposits on Antiparos and Mykonos has a wide range of $\delta^{34}\text{S}$ (16–37‰) and $\delta^{18}\text{O}$ (4–12‰) values, indicating a seawater sulfate source modified by mixing or equilibration of the hydrothermal fluids with the host rocks. Strontium isotope ratios of barite vary regionally, with $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.711$ in the central Cyclades and $^{87}\text{Sr}/^{86}\text{Sr} \leq 0.711$ in the west Cyclades confirming the strong influence of the upper crustal rocks on the sources of fluids, Sr, and Ba in the formation of ore.

3.1 Introduction

The metamorphic core complexes of southern Greece host a wide range of base and precious metal deposit types throughout the Cycladic islands from Attica, on the mainland, to the active volcanic arc in the south. Polymetallic mineralization in the Cycladic metallogenic belt (hereafter Cyclades Mineral District) is strongly influenced by the dynamics of the subduction zone and regional variations in the underlying basement ([Menant et al., 2018](#); [Wind et al., 2020](#)). Major detachment faults have been active in the region since at least the early Miocene, accommodating some of the most rapid extension of continental crust in the world ([Pe-Piper & Piper, 2002](#)), and created widespread fluid pathways in the brittle upper crust. The Cyclades Mineral District includes several mineralization styles, such as low-grade porphyry Mo, carbonate-hosted replacement, vein and breccia Pb-Zn-Ag-Au, low- and intermediate-sulfidation (LS and IS) epithermal veins, Cu-Fe and Fe skarn, Fe- and Zn-rich gossan, epithermal-like Ag-Pb-Zn-Ba(-Au) ore, iron and barite veins, sediment-hosted Mn oxide ores and polymetallic seafloor massive sulfide deposits ([Skarpeilis, 2002](#); [Kiliyas et al., 2013](#); [Melfos & Voudouris, 2017](#); [Menant et al., 2018](#); [Voudouris et al., 2019](#); [Wind et al., 2020](#) and references therein). In addition, well-known non-metallic deposits of bentonite, perlite and kaolinite occur on Milos ([Plimer, 2000](#)).

Low-angle detachments formed at the ductile-brittle transition, where deep fluids (magmatic, metamorphic) have extensively mixed with surface-derived seawater and meteoric water (e.g., [Marchev et al., 2005](#); [Moritz et al., 2006](#); [Menant et al., 2018](#); [Scheffer et al., 2019](#)). Polymetallic veins and replacement deposits occur in the metamorphosed footwall and unmetamorphosed hanging wall of the major detachment systems as well as in overlying Quaternary volcanic units ([Berger et al., 2013](#); [Menant et al., 2013](#); [Ducoux et al., 2017](#); [Menant et al., 2018](#); [Wind et al., 2020](#)). However, the relative importance of magmatic, meteoric, and seawater-derived fluids and their complex interplay is widely debated (e.g., [Naden et al., 2005](#); [Tombros et al., 2007](#); [Bonsall et al., 2011](#); [Alfieris et al., 2013](#); [Spry et al., 2014](#); [Kevrekidis et al., 2015](#); [Scheffer et al., 2017](#)). This is partly due to the wide range of mineral and isotopic systems and various paragenetic stages that have been studied in different deposits. In this paper, we examine the possible sources of fluids and their interaction with host rocks using hydrothermal barite, which occurs in the majority of deposits ([Hauck, 1984](#); [Salemink, 1985](#); [Skarpelis, 2002](#); [Bonsall et al., 2011](#); [Tombros et al., 2015](#); [Schaarschmidt et al., 2021a](#)). This approach allows a comparison of the same or similar mineralizing processes across the region because of the very restricted paragenesis and conditions of barite mineralization in each of the deposits.

Mining in the Cyclades Mineral District probably started as early as the eighth to fourth millennia B.C. ([Gale & Stos-Gale, 1981](#)), but it remains a promising region for exploration of precious, rare, and critical metals ([Melfos & Voudouris, 2017](#)). The carbonate-replacement, vein- and breccia-style Pb-Zn-Ag ore deposits (Lavrion District) were mined in antiquity until the late 20th century and played a major role in the economic development of the region. The most important deposits in the Lavrion District are thought to have produced 13 million tonnes (Mt) of ore at 400 g/t Ag and 20% Pb, with resources of 4 Mt at 7% Pb-Zn remaining ([Melfos & Voudouris, 2017](#)). The Fe skarns and Fe-Ba vein

mineralization on Serifos produced ~ 6.6 Mt of Fe ore ([Salemink, 1985](#)). On Antiparos, argentiferous galena was mined from polymetallic quartz-sulfide veins at Agios Georgios. Barite was exploited on Milos and Mykonos islands until the mid-1980s. Mining activity on the island of Mykonos involved barite exploitation and processing until 1984, and older small-scale occasional mining for argentiferous galena, cerussite, anglesite, and Fe-hydroxides ([Skarpelis, 2002](#)). The barite vein ores on Mykonos produced ~ 2.3 Mt of barite with reserves of ~ 1 Mt ([Tombros et al., 2015](#)). The sulfide-sulfate deposits of Milos contained ~ 2 Mt of barite ([Hauck, 1984](#)). Barite-quartz veins on Milos are widely associated with epithermal systems, including the Au-Ag-Te mineralization at Profitis Ilias (current reserves of 5 Mt at 4.4 g/t Au, 43 g/t Ag) and Chondro Vouno (3.3 Mt at 4.2 g/t Au: [Kilias et al., 2001](#); [Alfieris et al., 2013](#)). Breccia-style Ag-Pb-Zn-Ba(-Au) ores were mined at Triades-Galana on Milos, from the late 19th to the early 20th century, firstly for Pb and Zn, and later for Ag, when reserves were estimated at 10 Mt ore at 500 g/t Ag ([Liakopoulos et al., 2001](#)). Reported resources at Triades-Galana are 1.2 Mt at 1 g/t Au and 124 g/t Ag ([Stewart & McPhie, 2003](#)). The Cape Vani deposit on Milos operated as Mn mine from 1886 to 1909 and from 1916 to 1928 producing 0.22 Mt of Mn ([Plimer, 2000](#)).

The deposits of the Cyclades Mineral District have been extensively studied to determine the origin of metals and ore-forming fluids, with variable contributions inferred from magmatic, meteoric, and modified seawater sources ([Kilias et al., 2001](#); [Naden et al., 2005](#); [Bonsall et al., 2011](#); [Alfieris et al., 2013](#); [Kevrekidis et al., 2015](#); [Tombros et al., 2015](#); [Scheffer et al., 2017, 2019](#); [Wind et al., 2020](#)). A wide range of investigations, mainly involving isotopic studies of sulfides, whole-rock geochemistry, and fluid inclusion microthermometry have been carried out (Table 3.1). Part of the challenge of determining the dominant fluid sources is the complex paragenesis of the studied minerals and the lack of a common mineral or isotopic system to compare between the different deposits across the region. We

previously demonstrated the use of Pb isotopes in identifying metal sources, taking advantage of the nearly ubiquitous presence of galena in all deposits, and showed the regional differences in the underlying basement in the north-central and western Cyclades (Wind et al., 2020). Herein, we explore the geochemical and isotopic signatures of barite, which is also present in nearly all of the deposits.

The properties of barite, especially its low solubility and the possibility of analyzing multiple isotope systems, make it an excellent geochemical archive for ore-forming processes. It is also an important proxy for different mineralizing systems involving diverse fluid types almost always involving mixing of reduced and oxidized fluids (Hanor, 2000; Griffith et al., 2018). In this study, we used a multi-isotope approach to investigate the composition of Cycladic barite from 17 mineral occurrences on four islands and from Lavrion on the mainland, spanning $\sim 40,000$ km² of the Mineral District and arc-backarc system. We also demonstrate the value of combining isotopic studies of barite with analyses of trace elements, especially the Sr content and spatially resolved analyses of mineral zonation, as also shown in studies from other mineral systems (e.g., Jamieson et al., 2016; Magnall et al., 2016). In particular, we combined analyses of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ by isotope ratio mass spectrometry (IRMS) with analyses of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{34}\text{S}$ values by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) to trace the fluid and crustal sources in a range of mineralization styles. The combination of isotopic systems indicates that different fluids were tapped along the major detachment faults where highly variable basement rock types are exposed.

Cycladic barite can be grouped into two end-member systems: (1) seawater-dominated systems, with high $\delta^{34}\text{S}$ values, low $\delta^{18}\text{O}$ values, and radiogenic Sr with variations in the isotopic signatures and Sr content likely influenced by the underlying basement, and (2) magmatic-dominated systems, with low $\delta^{34}\text{S}$ values, high $\delta^{18}\text{O}$ values, and Sr derived from

the Miocene intrusions. Figure 3.1 and Table 3.1 present an overview of the investigated mineral occurrences and their characteristics, and our interpretation is summarized in Figure 3.2 and in the following sections. We show that different mineral deposits in the region can be clearly distinguished by the isotopic signatures of their barite, providing a useful guide in future exploration for these types of deposits in Greece and in other continental arc-backarc systems.

Table 3.1: Literature summary of investigated deposits in the Cyclades Mineral District in Greece.

Location/ Deposit/ district name	Ore min- erals	Gangue minerals	Mineral- ization style	Morphology of ore- bodies	Main host rock	$\delta^{34}\text{S}$ (‰ VCDT)	$\delta^{18}\text{O}$ (‰ VSMOW)	δD (‰ VSMOW)	Fluid salinity (wt% NaCl eq)	Tempera- ture (°C)	Fluid sources and process of ore deposition	References
<i>Porphyry</i> Lavrio/ Plaka	Py, Ccp, Mol, Po, Sch	Qz, Ser	Alkaline Cu-Mo porphyry	Sheeted Qz veins, stock- work	Granodiorite /		FI in Qz: 10.6–11.0 ¹	/	FI in Qz (23–24) ² ; FI in Qz (10.4–54.5) ³	FI in Qz (220–437, peak ~330) ² ; FI in Qz (268–460) ³	Magmatic, highly saline, boiling fluids	Voudouris et al. (2008a, 2019) Bon- sall et al. (2011); Scheffer et al. (2019)
<i>Epithermal deposits</i> Milos / Cape Vani	Pyr, Ram, Hol, Cor, Hem, Goe, Gn, Py, Sp	Qz, Brt, K-fsp, Zeo, Anh, Sme	IS epithermal- style, seafloor exhalite	Massive to semi- massive ore, veins, strata- bound and strat- iform layers	Dacite- andesite, pyroclas- tic, and volcano- sedimentary rocks	Brt: 19.6–21.6 (mean 20.8) ⁴ ; Brt: 21.2–21.4 ⁵ ; Brt: 19.8–24.2 ⁶ ; Brt: 21.4–21.6 ⁷	Brt: 9.7–14.7 ⁶	/	FI in Brt+Qz (0.1–17.0) ⁸ ; FI in Brt+Qz (0.3–16.3; median 10.6) ⁶	FI in Brt+Qz (95–297) ⁸ ; FI in Brt+Qz (95–297; median 148) ⁶	Seawater, met- als leached from basalt and volcanic rocks ⁵ ; shallow marine setting, hydrother- mal fluids leached metals from schist basement ⁹ ; boiling and vaporization of seawater ⁸ ; mixing of deep hydrothermal fluids and sea- water modified by BSR ⁶	Hauck (1984); Hein et al. (2000); Liakopoulos et al. (2001); Kiliass et al. (2007); Al- fieris et al. (2013); Ivarsson et al. (2019); Schaarschmidt et al. (2021a)
Milos/ Kondaros- Katsimouti	Py, Gn, Sp, Ccp, Td, Plb, Hem, Ag, Arg	Qz, Brt, Cal, Zeo	IS epithermal- style	Massive to semi- massive ore, veins	Dacite- andesite lavas and volcano- sedimentary rocks	Brt: 16.1–19.0, Gn: - 0.3–2.9, Sp: 2.9–3.9, Py: 4.7–7.4, in-situ Py: -6.3 to 5.2 ⁷	/	/	/	/	Magmatic- hydrothermal system, mixing of magmatic fluids and seawater, boil- ing, buried granitoid at depth ¹⁰ ; seawater- dominated hydrothermal fluid, exten- sive boiling, metals and S leached from metamorphic and volcanic host rocks ⁷	Alfieris et al. (2013); Papavasiliou et al. (2016b); Pa- pavasiliou et al. (2017); Wind et al. (2020); Schaarschmidt et al. (2021a)

Table 3.1: (continued)

Location/ Deposit/ district name	Ore min- erals	Gangue minerals	Mineral- ization style	Morphology of ore- bodies	Main host rock	$\delta^{34}\text{S}$ (‰ VCDT)	$\delta^{18}\text{O}$ (‰ VSMOW)	δD (‰ VSMOW)	Fluid salinity (wt% NaCl eq)	Tempera- ture (°C)	Fluid sources and process of ore deposition	References
Milos/ Galana	Py, Gn, Sp, Ccp, Apy, Td, Cv, Prg, Eng, Fam, Prc, Au	Qz, Brt, Adl, Ser	IS	Veins, stock- works, breccia bodies	Andesite- dacite, pyroclas- tic, and volcano- sedimentary rocks	Gn: 1.0–1.5, Brt: 24.1 ¹¹	Brt: 10.5 ¹¹	/	/	/	Magmatic fluids mixed with seawater, boiling ¹² ; seawater with high fluid-rock interaction ¹¹	Vavelidis & Melfos (1998); Stewart & McPhie (2006); Marschik et al. (2010); Alfieris et al. (2013)
Milos/ ades	Py, Gn, Sp, Ccp, Apy, Td, Cv, Prg, Eng, Fam, Prc, Au	Qz, Brt, Chd, Ser, Adl, Ser, Sm, Cer	Hybrid epi- thermal to VMS	Veins, stock- works, breccia bodies	Andesite- dacite, pyroclas- tic, and volcano- sedimentary rocks	Brt: 20.7–27.3 (mean 23.0), sulphides: 1.4–5.5 ⁴ ; Sp: 2.7–3.0, Gn: 2.2–3.6, Brt: 22.8–24.4 ¹¹ ; Brt: 23.5, Sp: 1.9–2.2 ⁷	Brt: 9.5–11.0 ¹¹	/	FI in Brt (2.1–5.6) ¹² ; FI in Brt, Qz, Sp (0.4–8.1, median 5.1) ¹³	FI in Brt (135–380, majority 280–340); FI in Sp (160–260) ¹² ; interaction ¹¹ ; FI in Brt, boiling of Qz, Sp (110–250, median 202) ¹³	Magmatic flu- ids mixed with seawater ¹² ; seawater with high fluid-rock interaction ¹¹ ; boiling of hydrother- mal fluids in open system, mixing with seawater ¹³	Hauck (1984); Vavelidis & Melfos (1998); Stewart & McPhie (2006); Marschik et al. (2010); Alfieris et al. (2013); Smith et al. (2018); Schaarschmidt et al. (2021a)
Milos/Chon- dro Vouvo	Py, Gn, Sp, Ccp, Td, Au, Ag	Qz, Brt, Adl, Ilr	Hybrid IS epi- thermal to VMS	Veins	Dacite, rhyo- dacite, pyro- clastic rocks	/	/	/	FI in Qz (0.5–14.7), FI in Brt (4.9–13.0) ¹⁴	FI in Qz (155–238) ¹⁴	Seawater + meteoric water	Kilias et al. (2001); Naden et al. (2005); Al- fieris et al. (2013)
Milos / Prof- itis Ilias	Stage I: Py, Gn, Sp, Ccp, Hs, Alt, Pz, Col, Au, Ag; Stage II: Bn, Cv, Cc, Gn, Sp, Au	Stage I: Qz, Brt, Adl, Ser; Stage II: Qz, Brt, Adl, Ilr	Hybrid IS epi- thermal to VMS	Massive to semi- massive ore, veins	Rhyolite- rhyodacite, pyroclas- tic rocks	/	FI in Qz: -7.8 to -0.3, Qz: 13.4–15.9 ¹⁵	FI in Qz: -68.0 to 23.8 ¹⁵	FI in Stage I (0.0–15.5), FI in Stage II (3.0–8.5) ¹⁶	FI in Stage I (145–400) and Sp (290–295), FI in Stage II (110–330) ¹⁶	Seawater, and boiling vaporization ¹⁶ ; seawater + me- teoric water ¹⁵	Kilias et al. (2001); Naden et al. (2003, 2005); Alfieris et al. (2013)
Milos / East- ern Milos: Kastana, Pieridou, Kavos	Ang, Py, Gn	Brt, Qz, Kln, Alu, Jrs	Epithermal- type	Impregna- tion of volcanic material, veins, lenses	Felsic pumice breccia to pyro- clastic material	Brt: 6.4–25.4 (mean 17.3), Anh: 2.3–8.9, Alu: 2.3–6.9 ⁴	/	/	/	/	Hydrothermal fluids mixed with seawater	(Hauck, 1984; Stew- art & Mc- Phie, 2006)

Vein-type deposits

Table 3.1: (continued)

Location/ Deposit or district name	Ore min- erals	Gangue minerals	Mineral- ization style	Morphology of ore- bodies	Main host rock	$\delta^{34}\text{S}$ (‰ VCDT)	$\delta^{18}\text{O}$ (‰ VSMOW)	δD (‰ VSMOW)	Fluid salinity (wt% NaCl eq)	Tempera- ture (°C)	Fluid sources and process of ore deposition	References
Antiparos/ Agios Geor- gios	Stage I: Py, Po, Mag, Sp, Ccp, Bn, Td, Arg; Stage II: Gn, Au, Ag, Cv	Stage I: milky Qz, Ser, Chl, Cal, Ank; Stage II: clear Qz, Sm, Brt, Fl	Vein- type	Veins, stock- works	Gneiss, marble, schist	/	Stage I Qz: 7.7–9.3, Stage II Qz: 6.5–12.1	Stage I Qz: -71.8 to -64.4, Stage II Qz: -73.2 to -57.2	FI in Qz, Stage I: (5.4–15.7, outlier 30.5), Stage II: (4.8–12.2)	FI in Qz, Stage I: (270–408), Stage II: (131–245)	Magmatic fluids with contribution of meteoric water, boiling	Kevrekidis et al. (2015)
Antiparos/ Prassovounia	Py, Po, Mag, Sp, Gn, Ccp, Bn, Td, Arg, Au, Ag	Qz, Ser, Chl, Cal, Brt, Fl	Vein- type	Veins, stock- works	Marble, schist	/	/	/	/	/	/	Kevrekidis et al. (2015); Wind et al. (2020)
Lavriou/ Vein 80	Gn, Sp, Py, Apy, Ccp, Lo, Td, Bnn, Mia, Prg, Lil	Qz, Sd, Fl, Cal	IS epithermal- style	Banded and brec- ciated Qz-Sd-Fl vein	Hornfels, marble, schist	Py: -1.1, Gn: -3.2 to 2.0 ³	Cal: 16.1–21.4 ³ , FI in Fl: -6.1 to -5.1 ¹	FI in Fl: -51.0 to - 47.7 ¹	FI in Fl (14–18) ² , FI in Fl (13.6–16.1) ³ , FI in Fl (5.7–8.1) ¹	FI in Fl (130–228, peak ~200), FI in Cal (196–218) ² , FI in Fl (158–221) ³ , FI in Fl (131–154) ¹	Magmatic and meteoric fluids with minor seawater component, water-rock interaction ³ , non-magmatic hydrothermal system (me- teoric water + evaporated seawater) ¹	Voudouris et al. (2008a, 2019); Bon- sall et al. (2011); Scheffer et al. (2019)
Lavriou/ Kamariza (Clemence, Ilarion), Thorikos, Megala Pefka	Py, Sp, Apy, Gn, Eng, Ccp, Th-Td, Grf, Sn, Au, Bmt, Mia, Sb, Bnn	Qz, Fl, Cal, Brt	Pb-Zn- Ag vein and brec- cia, IS epithermal- style	Banded and brec- ciated Qz-Fl open space filling	Marble, schist	/	FI in Fl: -10.4 to -6.7, Qz: 10.6–11.0 ₁	FI in Fl: -82.1 to - 53.4 ¹	FI in Fl (1.6–19.8) ¹	FI in Fl (105–207) ¹	Magmatic ± meteoric fluids with minor seawater con- ponent, high water-rock interaction ³ , hydrother- mal system dominated by evapo- rated seawater and meteoric fluids ¹	Bonsall et al. (2011); Scheffer et al. (2017, 2019); Voudouris et al. (2019)
Mykonos/ Profitis Ilias, Mavro Vouno	Gn, Py, Sp, Ccp, Td-Tn, Au, Goe	Qz, Brt, Chl, Ser, Cal, Sd	Epithermal- type	Silica cap and silica breccia	Silicified molasse: Miocene conglom- eratic sequence	Brt: 25.5–26.0 ¹⁷	Brt: 4.8, Qz: 7.7 ¹⁷	Brt: -34 Qz: -75 ¹⁷	FI in Qz (3–4) ^{18,19}	FI in Qz (220– 230) ^{18,19}	Early precious epithermal Au-silica mineraliza- tion <1km, boiling ^{18,19} , magmatic flu- ids, boiling ¹⁷	Skarpelis (2002); Skarpelis & Gilig (2006); Menant et al. (2013, 2018); Tombros et al. (2015)

Table 3.1: (continued)

Location/ Deposit or district name	Ore min- erals	Gangue minerals	Mineral- ization style	Morphology of ore- bodies	Main host rock	$\delta^{34}\text{S}$ (‰ VCDT)	$\delta^{18}\text{O}$ (‰ VSMOW)	δD (‰ VSMOW)	Fluid salinity (wt% NaCl eq)	Tempera- ture (°C)	Fluid sources and process of ore deposition	References
Mykonos/ Cape Evros, Cape Charos	Py, Mrc, Sp, Gn, Ccp, Bn, Apy, Bn, Hs, Prg, Alt, Arg, Ag, Au, Prg, Jrd, Gen, Blg	Qz, Brt, Chl, Ser, Cal, Sd	Detachment related IS ep- ither- mal?	Banded veins and stock- works	Monzo- granite and Pelag- onian zone	Brt: 21.4–23.5, Gn: 13.7, Py: 5.1–22.5, Mrc: 25.1, Ccp: 4–24.8, Sp: 4.3–22.8 ¹⁷	Brt: 0.6–4.1 ¹⁷	Brt: -61 to -54 ¹⁷	FI in Brt (4–15) ¹⁷	Chl Up- per Unit (250– 282), Chl cat- aclasites (203–258) ²⁰ ; boiling sulfide pairs + FI (275–320), FI in Brt (226–335) ¹⁷	Basinal brines ^{18,19} ; of mixing and magmatic and seawater de- rived fluids, boiling ¹⁷	Skarpelis (2002); Skarpelis & Gilg (2006); Menant et al. (2013, 2018); Tombros et al. (2015); Wind et al. (2020)
Mykonos/ Panormos Bay	Gn, Td, Ag-Td, Td-Tn, Ccp, Sp, Bn, Fam, Py, Plb, Py, Fbg, Hem, Goe	Brt, Qz, Cer	Vein (IS?)	Brt veins, stock- works	Miocene conglom- eratic sequence	/	/	/	/	/	/	Sánchez- Gómez et al. (2002); Menant et al. (2013); Tombros et al. (2015); Wind et al. (2020)
Tinos/ Panormos Bay	Py, Td, Tn, Glf, Ccp, Bn, Stn, Blg, Alt, Hs, Syl, Gn, Arg, Sp, Au, Ag, Prg	Qz, Cal, Chl, Ser	Detachment related epither- mal	Qz veins	Marble	Py: 1.9–2.0, Td: -12.5 to -9.3, Ccp: -12.4 to -9.1, Bn: -11.6 to -3.4, Gn: -14.6 to -8.6, Sp: -12.9 to -9.6 ²¹	Qz: 6.6–17.9, Ms: 12.4–16.2, Cal: 13.3–18.8 ²¹	Ms: -99 to -39 ²¹	FI in Qz (0.6–13.3) ²¹	FI in Qz (198–290), FI in smoky Qz (280–320) ²¹	Magmatic fluid + meteoric hydrother- mal fluid with wall-rock interaction	Tombros et al. (2007, 2008, 2010); Menant et al. (2018)

Carbonate-replacement deposits

Table 3.1: (continued)

Location/ Deposit/ district name	Ore min- erals	Gangue minerals	Mineral- ization style	Morphology of ore- bodies	Main host rock	$\delta^{34}\text{S}$ (‰ VCDT)	$\delta^{18}\text{O}$ (‰ VSMOW)	δD (‰ VSMOW)	Fluid salinity (wt% NaCl eq)	Tempera- ture (°C)	Fluid sources and process of ore deposition	References
Lavrio/ Lavrio District: Kamariza- Sounio- Plaka-Villia	Py, Ccp, Po, Gn, Sp, Apv, Tt-Tn, Bnt, Eng, Cv Prg	Cal, Dol, Fl, Qz, Brt, Sd, Gp, Ser	Carbonate- replacement, vein (mantos, chim- neys)	Massive, dissemi- nated layers, lenses, and veins contact	Marble (lower and up- per) and marble- schist	Gn+Sp+Py: Cal: -4.8 to 4.0 ²² ; Py: -3.4 to 5.3; Sp: -3.6 to 9.4; Gn: - 4.9 to 4.2, Gp: -0.9 to -0.8, Bnt: 17.2-23.7 ³	2.7-24.9 (mainly <15) ³ ; Cal: 23.5, 13.0-23.5, Dol: 13.2-15.5 ²³	/	FI in sulphides (14-17), FI in Qz+FI (125- 250) ²² ; stage I: FI in Qz (12.3-14.4), stage II: FI in Cal+FI (12.0-17.9), stage III: FI in FI (2-15) ²⁴ ; FI in Sp (3.5-18.8), FI in FI (4.2-21.5) ³	FI in sulphides (280), FI in Qz+FI (125- 250) ²² ; stage I: FI in Qz (312-399), stage II: FI in Cal+FI (214-282), stage III: FI in FI (100-200) ²⁴ ; FI in Sp (178-282), FI in FI (130-237) ³	Magmatic S and metal source with seawater component, high water- rock ratio ³ ; magmatic- hydrothermal fluids (Miocene intrusion) and high water- rock ratios ²³ ; magmatic and metamorphic (decarbona- tion) fluids + surface-derived fluids ¹	Skarpelis et al. (2007); Voudouris et al. (2008b); Bonsall et al. (2011); Berger et al. (2013); Scheffer et al. (2019)
<i>Skarn mineralization</i>												
Lavrio/ Adami (Plaka)	Mag, Po, Py, Sch, Apv, Sp, Ccp, Gn, Bmt, Ttd	Qz, Cal	Mag Fe exco- and en- dorskarn	Lenses and layers	Schist, marble and (lower upper)	Apv: 7.3 ³	/	/	/	/	Magmatic flu- ids	Lelen et al. (1973); Voudouris et al. (2008a); Bonsall et al. (2011); Scheffer et al. (2019)
Serifos/ Moutoulas	Py, Apv, Sp, Ccp, Po, Gn, Bmt, Td- Tn, Ttd, Hs, Bi	Qz, Bnt, Cal, Fl	Skarn, carbonate- replacement, volcano- sedimentary veins origin	Massive ore, pods, breccia, veins	Marble, schist, amphibo- lite	Sp: 3.4-4.7, Py: 3.0-4.3, Gn: 1.6-4.6 ²⁵ ; Stage I: Py (3.8-4.8), Sp (2.7-3.7), Ccp (5.1), Stage II: Sp (3.5), Stage III: Gn (5.0-5.6) ²⁶	Qz: 11.6-13.8 ²⁷	/	Stage I: Qz (4-5.3), Sp (4.8-5.7), Stage II: Qz (3.4-5.4), Sp (3.7-3.9), Stage III: Qz (3.4-4.8), Stage IV: Qz (1.3-4.9) ²⁶	FI in Qz ₂₇ ; (280-350) ²⁷ ; Sp-Gn pairs (255) ²⁵ ; FI in Qz+Sp: Stage I: Qz (229-251), Sp (239- 245), Stage II: Qz (220- 227), Sp (218- 226), Stage III: Qz (203-214), Stage IV: Qz (190-197) ²⁶	Exhalite gen- esis with later meta- somatism/ metamorphism ²⁵ ; magmatic + meteoric wa- ters with wall-rock interaction ²⁶	Saleminik (1985); St. Sey- mour et al. (2009b); Ducoux et al. (2017); Fitros et al. (2017); Wind et al. (2020)

Table 3.1: (continued)

Location/ Deposit or district name	Ore min- erals	Gangue minerals	Mineral- ization style	Morphology of ore- bodies	Main host rock	$\delta^{34}\text{S}$ (‰ VCDT)	$\delta^{18}\text{O}$ (‰ VSMOW)	δD (‰ VSMOW)	Fluid salinity (wt% NaCl eq)	Tempera- ture (°C)	Fluid sources and process of ore deposition	References
Serifos/ Mega Chorio, Megalio Li- vadi	Stage I (MT): Mag, Py; Stage II (LT): Hem, Goe	Stage I (MT): Qz, Ep, Cal; Stage II (LT): Brt, Cal, Qz	Mag Fe exo- and en- doskarms	Massive ore, banded veins	Marble, granodi- orite	/	MT: Mag: -4.9 to 0.5, Qz: 11.6-16.6, LT: Brt: 8.8-10.5, Qz: 22.0, Cal: 18.8 ²⁷	/	FI in Brt (10-20) ²⁷	MT: Mag- Qz pairs (410-260), LT: FI in Brt (210-100), Qz-Cal pair (125) ²⁷	Magmatic fluid with exter- nally derived material at late stages ²⁷ ; oceanic or me- teoric waters remobilized Fe from MT and HT skarns ²⁸	Salemink (1985); Ducoux et al. (2017)

Notes: /: no data available, BSR: bacterial sulfate reduction, FI: fluid inclusions, HT: high temperature, IS: intermediate-sulfidation, LT: low temperature, MT: medium temperature, VCDT: Vienna Canyon Diablo Troilite, VMS: volcanogenic massive sulfide, VSMOW: Vienna standard mean ocean water

Data sources: ¹Scheffer et al. (2019), ²Voudouris et al. (2008a), ³Bonsall et al. (2011), ⁴Hauck (1984), ⁵Hein et al. (2000), ⁶Ivarsson et al. (2019), ⁷Schaarschmidt et al. (2021a), ⁸Kiliass et al. (2007), ⁹Liakopoulos et al. (2001), ¹⁰Papavasiliou et al. (2016b), ¹¹Marschik et al. (2010), ¹²Vavelidis & Melfos (1998), ¹³Smith et al. (2018), ¹⁴Naden et al. (2005), ¹⁵Naden et al. (2003), ¹⁶Kiliass et al. (2001), ¹⁷Tombros et al. (2015), ¹⁸Skarpelis (2002), ¹⁹Skarpelis & Gilg (2006), ²⁰Menant et al. (2013), ²¹Tombros et al. (2007), ²²Skarpelis et al. (2007), ²³Berger et al. (2013), ²⁴Voudouris et al. (2008b), ²⁵St. Seymour et al. (2009b), ²⁶Fitros et al. (2017), ²⁷Salemink (1985), ²⁸Ducoux et al. (2017)

Mineral abbreviations: Adl: adularia, Ag: native silver, Alt: altaite, Alu: alunite, Ang: anglesite, Anh: anhydrite, Ank: ankerite, Apy: arsenopyrite, Arg: argentite, Au: native gold, Bi: native bismuth, Blg: boulangerite, Bmt: bismuthinite, Bn: bornite, Bnn: bornonite, Brt: barite, Cal: calcite, Cc: chalcocite, Ccp: chalcopyrite, Cer: cerussite, Chd: chalcedony, Chl: chlorite, Col: coloradoite, Cor: coronadite, Cv: covellite, Dol: dolomite, Eng: enargite, Ep: epidote, Fam: famatinite, Fbg: Freibergite, Fl: fluorite, Gen: geocronite, Gfl: goldfieldite, Gn: galena, Goe: goethite, Gp: gypsum, Grf: gersdorffite, Hem: hematite, Hs: hessite, Hol: hollandite, Ilr: illite, Jrd: jordanite, Jrs: jarosite, K-fsp: K-feldspar, Klin: kaolinite, Lil: lillanite, Lo: löllingite, Mag: magnetite, Mol: molybdenite, Mia: miargyrite, Mrc: marcasite, Ms: muscovite, Pbl: pyrrhotite, Prc: pearceite, Prg: pyrrargyrite, Prs: proustite, Py: pyrite, Pyr: pyrolusite, Pz: petzite, Qz: quartz, Ram: ramsdellite, Sb: native antimony, Sch: scheelite, Ser: sericite, Sd: siderite, Sm: smithsonite, Sme: smectite, Sp: sphalerite, Stn: stannite, Syl: sylvanite, Td: tetrahedrite, Tn: tennantite, Ttd: tetradymite, Zeo: zeolite.

3.2 Regional geology

The extended continental back-arc domain in the Aegean formed by the northward subduction of the African plate underneath Eurasia, where subduction and accretion of successive oceanic and continental fragments occurred since the Mesozoic (Jolivet et al., 2010; Papanikolaou, 2013; Menant et al., 2016 and references therein). Accelerated slab retreat and rapid southward migration of the Hellenic trench since the Eocene-Oligocene caused extension and thinning of the back-arc domain, manifested in the southward migration of arc magmatism (Fytikas et al., 1984; Pe-Piper & Piper, 2002). Miocene exhumation of middle and lower crustal material as metamorphic core complexes (Gautier & Brun, 1994; Jolivet et al., 2004; Ring et al., 2010; Jolivet et al., 2015) occurred along four major low-angle, crustal-scale detachment systems (Fig. 3.1): the North Cycladic Detachment System (NCDS, top to-NE: Jolivet et al., 2010), the Naxos-Paros Detachment System (NPDS, top-to-N: Gautier et al., 1993), the West Cycladic Detachment System (WCDS, top-to-SSW: Grasemann et al., 2012) and the Santorini Detachment System (SDS, top-to-SSE: Schneider et al., 2018). Three major tectono-stratigraphic units have been identified: the undifferentiated and (mostly) unmetamorphosed Pelagonian zone in the hanging wall of the major detachment systems, and the metamorphosed Cycladic Basement and the Cycladic Blueschist Unit in the footwall (Fig. 3.1; Bonneau, 1984; Jolivet et al., 2015; Grasemann et al., 2018; Flansburg et al., 2019).

As the structurally lowest unit, the Cycladic Basement is exposed in the central part of the Cyclades (e.g., Antiparos, Delos, Ios, Naxos, Mykonos, Paros, Sikinos, Serifos, and Syros) and consists of Carboniferous orthogneisses, as well as paragneisses and mica-schists with a pre-Alpine history and peri-Gondwanan affinity (Henjes-Kunst & Kreuzer, 1982; Keay & Lister, 2002; Jolivet et al., 2010; McGrath et al., 2017; Flansburg et al., 2019). The

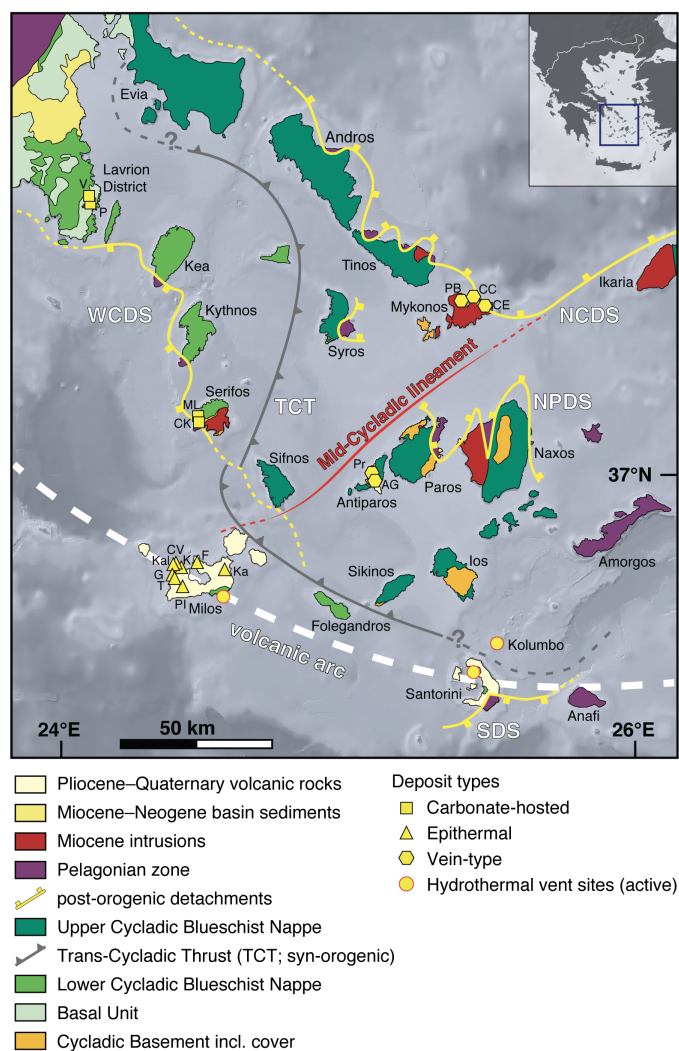


Fig. 3.1: Simplified geological map of the Cyclades Mineral District, Greece (modified after Wind et al., 2020; Laskari et al., 2022), highlighting locations of barite occurrences included in this study. Deposits in the west Cyclades include Villia and Plaka at Lavrion on the mainland, Cape Kaparia and Mega Livadi on Serifos, Cape Vani, Kalogries, Katsimouti, Galana, Triades, Profitis Ilias, Fourkovounia, and Kastana on Milos. These islands together with Kea, Kythnos, Folgeandros, Santorini and Anafi are along the WCDS and include the main exposures of the LCBN. The deposits in the central Cyclades highlighted in this study include Cape Charos, Cape Evros, and Panormos Bay on Mykonos and Agios Georgios and Prassovounia on Antiparos which are located along the NCDS and NPDS. These islands together with Evia, Andros, Tinos, Syros, Sifnos, Paros, Naxos, Sikinos, and Ios, include the main exposures of the UCBN. Bathymetry map in the background, where darker colors correspond to a greater water depth. Blue square in the inset shows the location of the study area in the Aegean Sea. NCDS: North Cycladic Detachment System, NPDS: Naxos-Paros Detachment System, SDS: Santorini Detachment System, TCT: Trans-Cycladic Thrust, WCDS: West Cycladic Detachment System. Sample locations: Antiparos: AG: Agios Georgios, Pr: Prassovounia; Lavrion: P: Plaka Adit No. 145, V: Villia; Milos: CV: Cape Vani, F: Fourkovounia, G: Galana, K: Katsimouti, Ka: Kastana, Kal: Kalogries, PI: Profitis Ilias, T: Triades; Mykonos: CC: Cape Charos, CE: Cape Evros, PB: Panormos Bay; Serifos: CK: Cape Kaparia, ML: Mega Livadi.

nature of the contact between the Cycladic Basement and overlying Cycladic Blueschist Unit is debated (local detachment planes, thrust faults or reactivated detachment faults: e.g., [Huet et al., 2009](#); [Schneider et al., 2011](#); [Grasemann et al., 2012](#); [Augier et al., 2015](#); [Ducoux et al., 2017](#)), and recently a para-autochthonous origin has been suggested ([Poulaki et al., 2019](#)). Regionally, carbonate platform sediments, which are variably described in the literature as Lower, Basal or Gavrovo-Tripolitza units ([Chatzaras et al., 2011](#); [Schneider et al., 2011](#); [Grasemann et al., 2018](#); [Gerogiannis et al., 2019](#)), occur stratigraphically below the Cycladic Blueschist Unit (CBU) on the mainland in Lavrion as well as on Evia, Andros, Serifos, and Amorgos.

The CBU, exposed on the majority of the Cycladic islands, is a metamorphosed Triassic to Cretaceous volcano-sedimentary sequence with clastic metasedimentary rocks, marbles, and metabasites ([Gärtner et al., 2011](#); [Seman et al., 2017](#); [Poulaki et al., 2019](#)). Paleogeographically, the CBU has been considered to be derived from the subducted Pindos oceanic domain ([Bonneau & Kienast, 1982](#); [Pe-Piper, 1998](#); [Jolivet et al., 2010](#); [Fu et al., 2015](#)). It has been divided into an Upper Cycladic Blueschist Nappe (UCBN) and Lower Cycladic Blueschist Nappe (LCBN), based on their peak metamorphic conditions, which are separated by the Trans-Cycladic Thrust (TCT; [Grasemann et al., 2018](#)). Differences between the UCBN and LCBN also have been identified by the distinct Pb isotope compositions of galena in the west and north-central Cyclades mineral deposits ([Wind et al., 2020](#)). Deposits in the west Cyclades highlighted in this study include Villia, Plaka, Cape Kaparia, Mega Livadi, Cape Vani, Kalogries, Katsimouti, Galana, Triades, Profitis Ilias, Fourkovounia, and Kastana, which are located on islands along the WCDS (Serifos, Milos), and Lavrion on the mainland. These islands together with Kea, Kythnos, Folgeandros, Santorini, and Anafi include the main exposures of the LCBN. The deposits in the central Cyclades highlighted in this study include Cape Charos, Cape Evros, Panormos Bay,

Agios Georgios, and Prassovounia, which are located on the islands along the NCDS and NPDS (Mykonos, Antiparos). These islands together with Evia, Andros, Tinos, Syros, Sifnos, Paros, Naxos, Sikinos, and Ios include the main exposures of the UCBN. The investigated deposits in the central Cyclades, in the center of the metamorphic core complex, are proximal to exposures of the Cycladic Basement (on Ios, Antiparos, Paros, Naxos, and Mykonos).

The Pelagonian zone in the hanging wall of the major detachment systems consists of klippen of Paleozoic basement and Late Permian to Jurassic volcanoclastic rocks with ophiolite sequences and carbonates (e.g., [Bonneau, 1984](#); [Schenker et al., 2014](#)). Rock types of the Pelagonian zone have a complex tectonomagmatic history and are thought to comprise mostly remnants of the Vardar ocean and continental Pelagonian terrane ([Schenker et al., 2014](#); [Lamont et al., 2020a](#)).

The uppermost unit in the Cyclades consists of Miocene to Pliocene marine to continental sediments deposited in the supradetachment basins that are preserved on Mykonos, Paros, and Naxos, chiefly in the hanging wall of the local detachments (e.g., [Sánchez-Gómez et al., 2002](#); [Bargnesi et al., 2013](#)). Marine to continental sediments on Attica and Milos unconformably overlie the CBU ([Stewart & McPhie, 2006](#); [Krohe et al., 2010](#)).

In the Cyclades, the southward-migrating volcanic arc was active since the early Miocene as a suite of syntectonic intrusions, the Cycladic granitoids, emplaced within the deformed upper crust (Fig. 3.1; [Altherr et al., 1982](#); [Altherr & Siebel, 2002](#); [Iglseider et al., 2009](#); [Bolhar et al., 2010](#); [Schneider et al., 2018](#)). Emplacement of Cycladic granitoids in the northeast started at ca. 17 Ma (e.g., at Ikaria and Tinos; [Altherr et al., 1982](#); [Bolhar et al., 2010](#)), whereas in the northwest it started only after 10 Ma (e.g., at Lavrion and Serifos; [Iglseider et al., 2009](#); [Liati et al., 2009](#)). Metaluminous to slightly peraluminous I-type intrusive bodies show a systematic regional variation in their composition with in-

creasing distance from the trench (Altherr et al., 1982; Schliestedt et al., 1987; Altherr & Siebel, 2002). In addition to the I-type intrusions, smaller S-type intrusive bodies occur on Serifos, Tinos, Paros, Naxos, and Ikaria (Altherr et al., 1982; Altherr & Siebel, 2002 and references therein), which generally pre-date the I-type intrusions (Altherr et al., 1982; Bolhar et al., 2010). Mafic to felsic dikes of Miocene age occur in Lavrion and on Serifos (Altherr et al., 1982; Skarpelis et al., 2008). At the Miocene-Pliocene boundary, bimodal volcanism occurred in the central Cyclades (e.g., rhyolites in the south of Antiparos; Innocenti et al., 1982). The initiation of bimodal magmatism is thought to be related to thinning and melting of the continental crust above a slab tear (Pe-Piper & Piper, 2007). The geochemistry and isotopic compositions of the Miocene Cycladic granitoids are typical for crustal-derived magmas. Strontium and Nd isotopes indicate a mix of a radiogenic metapelitic greywacke-type paragneiss and a less radiogenic mafic component as melt sources (Stouraiti et al., 2010; McGrath et al., 2017). In contrast, Miocene to Quaternary volcanism of the volcanic arc is indicative of mantle-derived magmas with variable degrees of metasomatism and crustal contamination (Pe-Piper, 1994; Ersoy & Palmer, 2013; Francalanci & Zellmer, 2019). Since the Pliocene, the modern Aegean volcanic arc lies from Sousaki in the northwest, across Milos and Santorini towards Nisyros in the southeast (Innocenti et al., 1981; Francalanci et al., 2005; Francalanci & Zellmer, 2019).

3.2.1 Regional metallogeny

High heat flow and a permeable brittle upper crust promoted a wide range of magmatic-hydrothermal activity throughout the Cyclades. Some workers have linked the mineralization in the Aegean to regional transtension or extension where crustal-scale detachments and associated high-angle normal faults facilitated the ascent of metal-bearing fluids

(Berger et al., 2013; Menant et al., 2013; Ducoux et al., 2017; Menant et al., 2018). Both seawater and meteoric water, as well as direct magmatic contributions, have been implicated in the formation of the majority of precious and base metal-rich deposits in the Cyclades (Table 3.1).

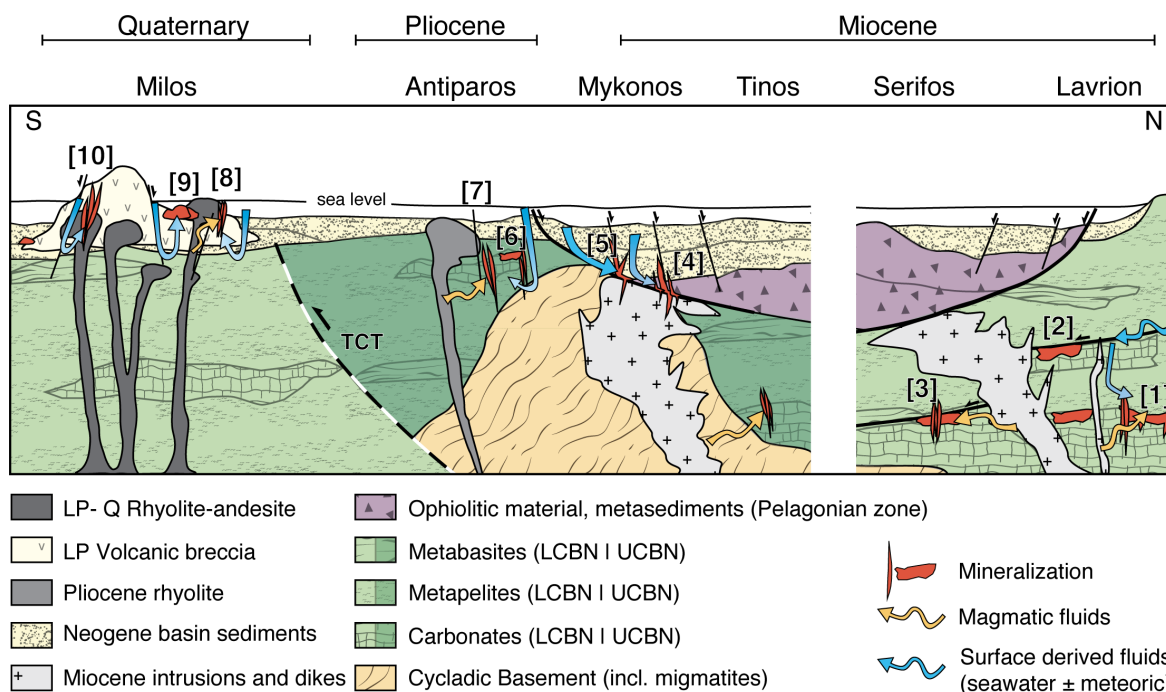


Fig. 3.2: Simplified model summarizing the main characteristics of hydrothermal barite in the Cyclades linked to the different fluid and crustal sources. The model is not to scale and focuses on the upper 5 km of the crust during ore mineralization from the late Miocene and into the Quaternary. Different fluid-rock interactions and variable contributions from surface-derived (seawater $\pm$ meteoric) and magmatic fluid components led to the formation of hydrothermal barite. Numbers correspond to the following deposits: [1] Plaka and [2] Villia at Lavrion, [3] Mega Livadi and Cape Kaparia on Serifos, [4] Cape Charos, Cape Evros, and [5] Panormos Bay on Mykonos, [6] Prassovounia and [7] Agios Georgios on Antiparos, [8] Katsimouti, [9] Cape Vani, Kalogries, Triades, Galana and [10] Profitis Ilias, Fourkovouni and Kastana on Milos. See 3.6 Discussion and 3.7 Summary and Conclusion for further explanation. LCBN: Lower Cycladic Blueschist Nappe, LP: late Pliocene, Q: Quaternary, TCT: Trans-Cycladic Thrust, UCBN: Upper Cycladic Blueschist Nappe.

In the Lavrion District, mineralization occurs principally in marbles of the LCBN (Fig. 3.1) and Upper and Lower marbles of the Basal Unit that define the footwall of the local Lavrion detachment which is part of the WCDS (Fig. 3.1). This district comprises porphyry Mo style, Cu-Fe skarn, strata-bound high-temperature carbonate-replacement (mantos and chimneys), vein- and breccia-style Pb-Zn-Ag mineralization (i.e., high-grade Ag in base metal sulfides that are cemented by fluorite and carbonate gangue) and Fe- and Zn-rich gossan (Voudouris et al., 2008a,b; Skarpelis & Argyraki, 2009; Bonsall et al., 2011; Berger et al., 2013; Spry et al., 2014; Scheffer et al., 2017, 2019; Voudouris et al., 2019). The carbonate-replacement Pb-Zn-Ag mineralization is temporally and spatially associated with the emplacement of the Plaka granodiorite at 8.3 Ma (Altherr et al., 1982) and several mafic and felsic dikes at 9.4 Ma (Skarpelis et al., 2008). Multiple stages of mineralization have been identified throughout, including a late-stage remobilization of the Pb-Ag-Zn deposits resulting in the formation of supergene iron ore (Skarpelis & Argyraki, 2009; Bonsall et al., 2011; Scheffer et al., 2017). Porphyry and sulfide breccia porphyry-style mineralization, as well as skarn mineralization, occur within or adjacent to the Plaka granodiorite (Leleu et al., 1973; Voudouris et al., 2008a), whereas carbonate-replacement deposits, and vein- and breccia-style mineralization are confined to a zone structurally below the Lavrion detachment (Berger et al., 2013; Scheffer et al., 2017, 2019). A magmatic origin for the fluids that formed the porphyry, skarn and high-temperature carbonate-replacement deposits has been well established (e.g., Voudouris et al., 2008a,b; Bonsall et al., 2011; Spry et al., 2014). However, Scheffer et al. (2019) argued that the polymetallic vein- and breccia-style mineralization was related to mixing of meteoric water with evaporated seawater and concluded that two different and independent hydrothermal systems caused ore deposition in the Lavrion District. Barite, although not abundant at Lavrion, occurs in several deposits as open-space filling (Bonsall et al., 2011; Scheffer et al.,

2019; Wind et al., 2020). Bonsall et al. (2011) and Scheffer et al. (2019) suggested that barite formation in the Lavrion District occurred late in the hypogene paragenesis during veining, brecciation, and carbonate-replacement Pb-Zn-Ag mineralization, post-dating the higher-temperature porphyry-style, skarn- and carbonate-replacement-forming events. Based on the S isotope composition of carbonate-replacement-associated barite, Bonsall et al. (2011) suggested a Miocene seawater source of sulfate.

On Serifos island, numerous magnetite-rich exo- and endoskarns and iron and barite (Fe-Ba) orebodies occur predominantly in Cycladic Basement marbles in the footwall of the Meghalo Livadi Detachment (MLD; Salemink, 1985; Ducoux et al., 2017). The formation of the Serifos skarn was associated with the intrusion of the 11.6 to 9.5 Ma syn-tectonic Serifos granodioritic pluton and extensional deformation along the WCDS (Fig. 3.1; Salemink, 1985; Iglseder et al., 2009; Ducoux et al., 2017). Most of the mined Fe came from the hydrothermal Fe-Ba mineralization, which occurs in late, banded veins consisting of hematite-limonite and barite, with minor fluorite and calcite, and hematite-barite breccias. These mined Fe-Ba veins abound in the western part of the island chiefly within calcitic-marbles; however, they cut across all lithologies of the island above and below the MLD and clearly postdate the skarns (Salemink, 1985; Ducoux et al., 2017). Based on fluid inclusion studies, Salemink (1985) estimated that deposition of the Fe-Ba veins occurred at temperatures of 210 to 100°C. Ducoux et al. (2017) suggested that these veins were deposited late in the evolution of the detachment system by surface-derived (meteoric) fluids causing remobilization of the Fe from the Fe-rich skarns. Distal skarn and polymetallic (including native Bi) marble-replacement mineralization occurs in small lenses in the Moutoulas prospect in the north; polymetallic sulfide-bearing quartz veins (up to 100 m long and 0.5 m wide) also cross-cut the schists and marbles of the Moutoulas prospect (Salemink, 1985; St. Seymour et al., 2009b; Fitros et al., 2017; Wind et al., 2020).

[Fitros et al. \(2017\)](#) suggested that native Bi mineralization at Moutoulas was a product of Bi-bearing magmatic fluids interacting with the wall rock and mixing with meteoric water.

On Milos, a recently emergent volcanic island (<2 Ma), economic mineralization occurs in the western part of the island in the Quaternary calc-alkaline submarine and submarine-to-subaerial volcanic rocks. Mineralization includes sediment-hosted exhalative Mn, Fe and barite (Cape Vani), epithermal Pb-Zn-Ag veins (Kondaros-Katsimouti), epithermal-like barite-quartz breccia Zn-Pb-(Ag-Au) sulfide (Triades-Galana), and epithermal Au-Ag-Te vein-type (Profitis Ilias-Chondro Vouno) deposits. The deposits in this densely mineralized area have been investigated extensively ([Hauck, 1984, 1988](#); [Hein et al., 2000](#); [Kilias et al., 2001](#); [Liakopoulos et al., 2001](#); [Stewart & McPhie, 2003](#); [Naden et al., 2005](#); [Marschik et al., 2010](#); [Alferis et al., 2013](#); [Papavassiliou et al., 2017](#); [Chi Fru et al., 2018](#); [Smith et al., 2018](#); [Kilias et al., 2020](#); [Miles, 2021](#); [Schaarschmidt et al., 2021a](#)). Manganese oxide and barite deposits at the abandoned Cape Vani Mn mine, and the area around it, formed in a shallow-water paleohydrothermal system predominantly from modified seawater and leaching of the metamorphic and volcanic host rocks ([Hein et al., 2000](#); [Liakopoulos et al., 2001](#)). [Ivarsson et al. \(2019\)](#) confirmed barite formation from seawater sulfate that was isotopically modified through bacterial sulfate reduction (BSR). [Kilias \(2012\)](#) and [Kilias et al. \(2020\)](#) further suggested that biologically mediated Mn^{2+} oxidation played a significant role in Mn deposition. The polymetallic epithermal-type vein mineralization at Kondaros-Katsimouti crosscuts the dacitic lavas and volcanoclastics and is thought to be related to a buried granite at depth ([Papavasiliou et al., 2016b](#)), although evidence of this model is not obvious. [Schaarschmidt et al. \(2021a\)](#) proposed that the NNW-SSE trending Kondaros-Vani fault zone represents a vertical profile through the boiling zone of a shallow-submarine hydrothermal system. Mineralization at Kondaros-Katsimouti as well as Triades and Galana are spatially related to the NE-SW trending Kontaro fault.

Mineralization at Triades-Galana has been identified as either Kuroko-type volcanogenic massive sulfide (VMS; [Hauck, 1984, 1988](#); [Vavelidis & Melfos, 1998](#)) or seawater-dominated, intermediate- to high-sulfidation epithermal mineralization ([Alfieris et al., 2013](#); [Marschik et al., 2010](#)). [Smith et al. \(2018\)](#) present a hybrid model with an epithermal-like vein system superimposed on a shallow-seafloor sulfide-sulfate deposit whose development was limited by mass wasting events. Barite, as well as sulfides, at Triades are thought to be a result of rapid precipitation at the hydrothermal-seawater interface by boiling hydrothermal fluids ([Christanis & St. Seymour, 1995](#); [Smith et al., 2018](#); [Schaarschmidt et al., 2021a](#)). At Triades and Galana, barite formed continuously over multiple stages including pre-, syn- and post-ore ([Smith et al., 2018](#)). The vein mineralization at Profitis Ilias-Chondro Vouno is also interpreted to be the product of a hybrid VMS-continental epithermal system with mixing of meteoric water, seawater and volcanic gases as volcanism changed from submarine to subaerial ([Naden et al., 2005](#); [Kilias et al., 2001](#)). Post-ore-stage barite occurs in the veins together with quartz and rarely fine pyrite, sphalerite, chalcopyrite, and galena ([Kilias et al., 2001](#)). Epithermal Au mineralization at Profitis Ilias is concentrated above the base-metal zone and spatially related to boiling ([Kilias et al., 2001](#)). Mining of barite during the 20th century was concentrated in the east of Milos in the area around Kastana, and the different occurrences have been described in detail by [Hauck \(1984\)](#). In addition, small occurrences of barite mineralization can be found at Fourkovouni in the central north of the island. The widespread barite occurrences on Milos have been studied by [Hauck \(1984, 1988\)](#), [Hein et al. \(2000\)](#), [Naden et al. \(2005\)](#), [Marschik et al. \(2010\)](#), [Ivarsson et al. \(2019\)](#), and [Schaarschmidt et al. \(2021a\)](#). These authors all suggested a seawater sulfate source with Sr derived from the country rocks. In the western part of the island, the barite occurs in association with abundant sulfides, but in the east of the island the barite veins are mainly barren of sulfides.

On Mykonos, the mined barite mineralization occurs in sub-vertical NW–SE-trending, extensional, polymetallic banded veins that are concentrated in the northeastern part of the island (Cape Evros and Cape Charos). The veins cut the upper part of the Mykonos monzogranitic laccolith, the metabasites of the Pelagonian zone, and the Miocene sediments and are associated with the Livada and Mykonos detachments that belong to the NCDS (Fig. 3.1; [Lahti & Govett, 1981](#); [Skarpelis, 2002](#); [Lecomte et al., 2010](#); [Menant et al., 2013](#)). The mined veins are >3 m wide, can be traced for 5 km, and consist dominantly of barite, with Fe-hydroxide, argentiferous galena, pyrite, sphalerite, chalcopyrite and quartz ([Skarpelis, 2002](#); [Menant et al., 2013](#); [Tombros et al., 2015](#); [Wind et al., 2020](#)). At Panormos Bay, in north Mykonos, the banded veins cut the exposed marine to terrestrial Miocene conglomeratic sequence ([Sánchez-Gómez et al., 2002](#); [Menant et al., 2013](#); [Wind et al., 2020](#)). [Menant et al. \(2013\)](#) have shown that the barite vein mineralization was formed from 11 to 10 Ma when the Mykonos monzogranite was exhumed and crossed the ductile-to-brittle transition below the NCDS. [Tombros et al. \(2015\)](#) proposed that magmatic Ba-rich fluids derived through hydrothermal alteration of the Mykonos monzogranite mixed with sulfate-rich Miocene seawater to produce the barite and sulfide veins. Brittle deformation, including fault zones and cataclasites adjacent to the Mykonos detachment, is thought to have allowed incursion of sulfate-rich Miocene seawater into the pluton. Sub-economic Au-bearing (1 g/t) mineralized siliceous caps and silicified breccias occur within the monzogranitic cupola along the Mykonos detachment at Cape Evros, Profitis Ilias, and Mavro Vouno in the northeasternmost part of the island ([Skarpelis, 2002](#); [Skarpelis & Gilg, 2006](#)). The breccias are cemented by hydrothermal minerals, including epithermal-style quartz and barite, and relics of primary sulfides (pyrite, chalcopyrite, sphalerite, galena) now oxidized to hematite and goethite. The breccias are cut by north-trending normal faults that are filled with barite $\pm$ fluorite and marcasite ([Tombros et al., 2015](#)).

[Skarpelis \(2002\)](#) suggested that the siliceous cap and silicified breccia are remnants of a deeply eroded precious metal epithermal system, and [Skarpelis & Gilg \(2006\)](#) suggested a two-stage hydrothermal event, with epithermal-style Au-quartz deposition followed by brittle faulting and barite-sulfide deposition from basinal brines.

On Antiparos, subvertical, epithermal-style crustiform quartz veins, up to 80 cm wide, occur in the gneiss and schist of the Cycladic Basement and marble of the UCBN at Agios Georgios in the south of the island and in the western part near Prassovounia ([Gale & Stos-Gale, 1981](#); [Skarpelis, 2002](#); [Kevrekidis et al., 2015](#); [Wind et al., 2020](#)). Barite has been described in crustiform banded quartz veins with smithsonite and fluorite at Agios Georgios ([Kevrekidis et al., 2015](#)) and with galena and Fe-poor sphalerite in the Prassovounia area ([Wind et al., 2020](#)). Argentiferous galena (containing 800–2000 ppm Ag: [Kevrekidis et al., 2015](#)), sphalerite, pyrite and chalcopyrite occur in the veins. [Kevrekidis et al. \(2015\)](#) proposed that the mineralization is related to magmatic fluids from the leucogranitic Paros pluton that mixed with meteoric water. However, [Voudouris et al. \(2019\)](#) and [Wind et al. \(2020\)](#) suggested that a connection to the Pliocene rhyolites (5–4 Ma: [Innocenti et al., 1982](#)) exposed in the south of Antiparos is more likely.

3.3 Samples and methodology

We sampled 17 mineral occurrences from Miocene to early Pleistocene age throughout the Cyclades Mineral District. Despite the wide range of mineralization styles, barite occurs as an abundant mineral in all of the deposits. On each island several prospects were sampled (App. Table 3.A1). In the western Cyclades, samples were taken from the Lavrion District on the mainland and on Serifos and Milos islands. In Lavrion, barite samples were collected underground near Plaka (Fig. [3.3A](#)), and one sample was taken from the Villia adit in

the northern part of the district, where barite occurs as late stage open-space filling of the carbonate-replacement deposits. On Serifos, hematite-barite (Fe-Ba) mineralization was sampled from Mega Livadi (Fig. 3.3B) and near Cape Kaparia (Fig. 3.3C). Sampling on Milos included the range of deposit styles in the western part of the island at Cape Vani, Kalogries, Katsimouti (Fig. 3.3D), Galana and Triades (Fig. 3.3E-F), and on top of Profitis Ilias, as well as Fourkovouni (Fig. 3.3G) and Kastana (Fig. 3.3H) in the eastern part of the island. In the central Cyclades samples were taken from the vein-style mineralization at Cape Evros (Fig. 3.3I), Cape Charos (Fig. 3.3J) and Panormos Bay (Fig. 3.3K-L) on Mykonos and at Prassovounia and Agios Georgios on Antiparos. Sampling of galena at a number of these sites (Lavrion, Serifos, Milos, Tinos, Mykonos, and Antiparos) was previously reported in Wind et al. (2020). Mineral paragenesis was investigated in thin sections using reflected and transmitted light microscopy and is described below.

Selected samples were imaged, and the compositions of barite determined, with a JEOL 6610LV Scanning Electron Microscope (SEM) and JEOL JXA-8230 electron microprobe (EMPA) at the University of Ottawa, Canada. Twelve samples were analyzed for the following elements by EMPA: S, Ba, Al, Sr, Ca, K, Pb, Fe, and Si. The analytical detection limits ranged from <0.01 wt% for Al, Ca, K, and Si to ≤ 0.04 wt% for Sr and Pb. For mineral separate analyses, samples were crushed, and single barite crystals were carefully selected under a binocular microscope. Fine powder of barite was analyzed for S and O isotopes using a Elementar Isotope Cube elemental analyzer (EA) interfaced to a Thermo Finnigan DeltaPlusXP isotope ratio mass spectrometer (IRMS) at the Ján Veizer Stable Isotope Laboratory at the University of Ottawa. Epoxy grain mounts of barite from 21 samples were also prepared for analysis using a New Wave UP193 laser, attached to an AXIOM multi-collector inductively coupled plasma mass spectrometer (LA-MC-ICP-MS) at GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany. Prior to the LA-



Fig. 3.3: Field photographs of representative hydrothermal barite occurrences in the Cyclades Mineral District. The coordinates of the sample locations are included in the Appendix Table 3.A1. A: Late-stage barite as open-space filling in the breccia-style mineralization. Pb-Zn(-Ag) sulfides of the brecciated carbonate-replacement mineralization (CR) are cemented by carbonate (Cb) gangue (Plaka, Lavrion). B: Carbonate-hosted barite, with banded hematite/limonite and barite vein; note late open-space infill texture with blade-shaped, euhedral tabular barite and late open-space carbonates (Mega Livadi, Serifos). C: Carbonate-hosted barite, with hematite-limonite/barite breccia with barite open-space infilling and late carbonates in marble (Cape Kaparia, Serifos). D: Several cm-wide barite vein in hydrothermally altered dacitic lava (Katsimouti, Milos). E: Quartz-barite breccia body with distinct mineralized horizons of replaced volcanoclastic units (Triades, Milos). F: Sulfide pods decorated by late bladed barite at the base of a barite-quartz breccia mound (Triades, Milos). G: Barite as veins and open-space filling in altered and silicified tuffaceous rock (Fourkovouni, Milos). H: Impregnation of volcaniclastic material by bladed barite and quartz (Kastana, Milos). I: Veins and veinlets of barite and Fe-oxide/hydroxide intersecting silicified siliciclastic sediments (Cape Evros, Mykonos). J: Huge barite crystals at the edge of a massive barite and Fe-oxide/hydroxide (oxidized sulfides) breccia (Cape Charos, Mykonos). K: Several m-wide banded barite vein with a pronounced alteration halo cutting the Miocene conglomeratic sequence (Panormos Bay, Mykonos). L: Plan view of the banded barite vein with sample locations (Panormos Bay, Mykonos). Mineral abbreviations: Brt: barite, Cb: carbonate minerals, FeO: Fe-oxide/hydroxide.

MC-ICP-MS analysis, individual crystals were imaged under transmitted and reflected light and with the SEM to identify inclusion-free areas for analysis of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{34}\text{S}$. Analyses and data reduction of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{34}\text{S}$ followed the approach described by [Fietzke et al. \(2008\)](#) and [Jamieson et al. \(2016\)](#). Concentrations of a suite of 54 elements in four barite crystals were measured using an Excimer laser ablation system (GeoLasPro, Coherent) coupled to a double-focusing, high-resolution magnetic sector mass spectrometer (AttoM, Nu Instruments) at GEOMAR following the method of [Fietzke & Frische \(2016\)](#). Selected samples were also processed for measurement of S isotopes by EA-IRMS in coexisting galena. A detailed description of the analytical methods is provided in the Supplementary Information [3.A](#) together with the complete data sets in Appendix Tables 3.A2 and 3.A3.

3.4 Mineral paragenesis

Following is a brief description of the main characteristics of Cycladic barite. A complete list of the sample locations and paragenesis is included in the Appendix Table 3.A1.

Carbonate-hosted barite, Lavrion and Serifos

Two carbonate-hosted Pb-Zn-Ag orebodies of the Lavrion District were sampled for this study. In the Villia deposit (Adit No. 123), in the north of Lavrion, several cm-scale, bladed, clear barite crystals occur as open-space filling in carbonate-replacement mineralization (mantos and chimneys). At the Plaka deposit (Adit No. 145), massive barite and barite flakes occur as open-space filling in the breccia-style mineralization (Figs. [3.3A](#), [3.4A](#)). The analyzed barite in this study was deposited during a late stage (stage II) that followed the main carbonate-replacement and breccia ore formation (stage I). At the Plaka

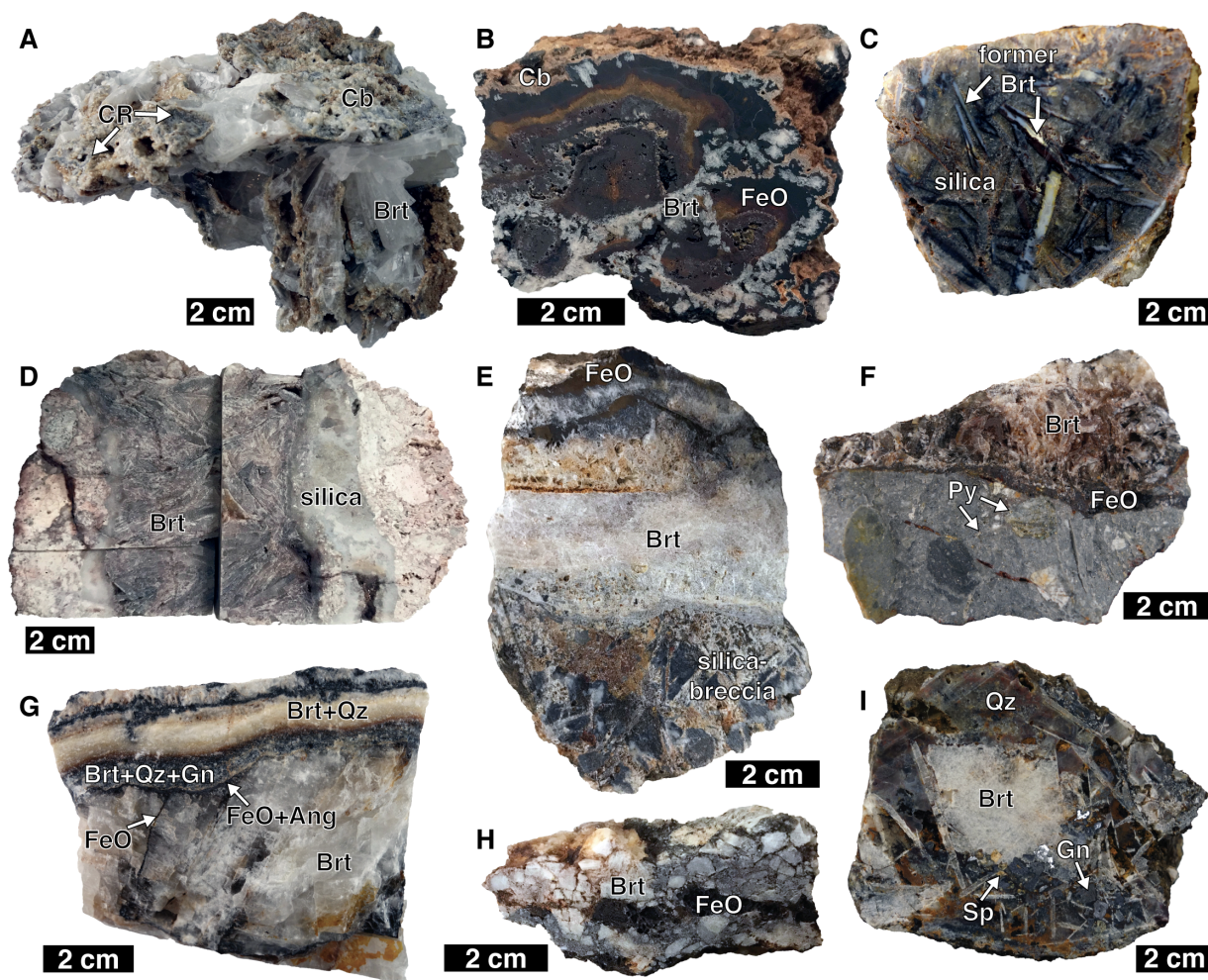


Fig. 3.4: Representative photographs of the investigated barite samples. A: Clear large barite laths (Brt) filling open spaces in the breccia-style mineralization where Pb-Zn-(Ag) sulfides of the carbonate-replacement mineralization (CR) are cemented by carbonate gangue (Cb) (17L145_3, Plaka, Lavrion). B: Radial and snowflake barite followed by Fe-oxide/hydroxide and carbonates, which are infilling the framework of preexisting barite (17SCK1, Cape Kaparia, Serifos). C: Silica pseudomorphs after barite (17MK4, Katsimouti, Milos). D: Altered volcanic host rock cut by a banded vein with marginal, early formed, microcrystalline, and colloform quartz and coarse-grained, bladed barite occupying the central portion of the veins (17MP2, Profitis Ilias, Milos). E: Barite vein in a silica breccia (17MYE8, Cape Evros, Mykonos). F: Silicified and mineralized host rock in contact with barite vein and Fe-oxide/hydroxide rim (17MYV3_3, Cape Evros, Mykonos). G: Coarse tabular barite intersected by a fine-grained veinlet of barite, quartz, and minor galena. Fe-oxides, anglesite and Pb-oxides occur at rims and between large barite laths (17MYP3, Panormos Bay, Mykonos). H: Brecciated barite in a fine matrix of Fe-oxide/hydroxide (17AP13, Agios Georgios, Antiparos). I: Barite, galena, and Fe-poor sphalerite in silicified matrix (17AP2, Prassovounia, Antiparos). Mineral abbreviations: Ang: anglesite, Brt: barite, Cb: carbonate minerals, CR: carbonate-replacement, FeO: Fe-oxide/hydroxide, Gn: galena, Py: pyrite, Qz: quartz, Sp: sphalerite.

deposit, stage I consists mainly of pyrite, Fe-sphalerite, galena, chalcopyrite, and minor arsenopyrite and pyrrhotite with carbonate gangue (Wind et al., 2020). The barite associated with the stage II Pb-Zn-Ag mineralization occurs with carbonates, Fe-poor sphalerite, pyrite, and minor galena (Fig. 3.5A). We interpret the late barite-rich open-space filling and the main carbonate-replacement (Villia), and breccia-style (Plaka) Pb-Zn-Ag mineralization as having formed during the same event. Cavities filled by euhedral barite, indicating open-space crystallization and growth, contain similar sulfide minerals as the main ore-forming stages (Fig. 3.5A), consistent with formation at the same time during ongoing regional deformation. Coarse barite, intergrown with calcite and Fe-oxides, was also observed in gossanous material close to the mine entrance (Fig. 3.5B). On a crystal scale, multiple growth zones are visible in the barite (Fig. 3.6B).

In the southwestern part of Serifos, carbonate-hosted barite was sampled from the mined Fe-Ba mineralization that occurs as veins, open-space fillings, and breccia lenses (Fig. 3.3B-C). At Mega Livadi, the veins are concentrated in marbles and schists in the footwall of the Meghalo Livadi Detachment (MLD; Salemink, 1985; Ducoux et al., 2017). Euhedral barite flakes (up to 3 cm in length) occur in crustiform-banded veins a few tens of meters in length, consisting of subparallel layers ($\leq 2-3$ cm wide) of carbonate, hematite, and rarely magnetite, limonite, and barite, with barite infilling open spaces in the veins (Fig. 3.3B). Although sulfides are mostly absent in the veins, fine pyrite and minor pyrrhotite inclusions are found in the barite (Fig. 3.5C). Similarly at Cape Kaparia, breccia veins and lenses several meters-wide occur in marbles in the footwall of the MLD. Euhedral bladed barite crystals (up to 1 cm in length) with radial growth or snowflake structures fill the open spaces between colloform-crustiform-banded clasts of hematite and limonite breccia lenses (Figs. 3.3C, 3.4B). Late calcite often forms a corona around barite. Small inclusions of Fe-oxides (Fig. 3.5D) and minor pyrite occur in the barite, which also shows very fine

growth-zoning patterns (Fig. 3.6C).

Epithermal, seafloor and sub-seafloor barite mineralization, Milos

In the different deposits on Milos, hydrothermal barite occurs in veins crosscutting altered lava domes and pyroclastic/volcaniclastic sequences (Fig. 3.3D), in horizons within the volcanic and sedimentary strata (Fig. 3.3E), and as pods and impregnations in altered volcaniclastic sediments (Fig. 3.3F-H).

At Cape Vani, previous work cited above combined with observations in this study indicate barite was deposited throughout the paragenesis of Mn-oxide mineralization. It occurs as disseminated crystals or cement, and in pervasive hydrothermal alteration (barite, quartz, K-feldspar, illite) of the volcaniclastic sandstone that hosts the Mn ore, as well as in subvertical quartz-barite (Mn-oxide, chalcedony, chert, K-feldspar) hydrothermal veins and stockworks in the andesites/dacites and overlying Mn-mineralized sediments. Quartz-barite veins are a few cm-wide and contain barite crystals, which vary from a few mm to 3 cm in length. In places quartz-barite veins that crosscut Mn-oxide mineralization contain minor sulfides (pyrite, galena). Barite also occurs as bedding-conformable layers, underlain by mineralogically similar discordant pipe-like bodies. These layers contain small (<5 mm), acicular and milky barite crystals, with Mn-oxides $\pm$ Fe-hydroxides (oxidized sulfides) and chert that fill open spaces and relicts of K-feldspar crystals (Fig. 3.5E-F). SEM-EDS analyses indicate that Mn-oxide minerals associated with pyrite in barite belong to the hollandite supergroup. Mn-oxide minerals identified within the Vani Mn-oxide deposit include todorokite, manjiroite, vernadite, and ramsdellite (Liakopoulos et al., 2001; Kiliyas et al., 2020). Rarely small inclusions of oxidized pyrite, galena, and (Pb-)Mn-oxides were observed in barite.

Mineralization near Kalogries formed contemporaneously with the Cape Vani deposit and

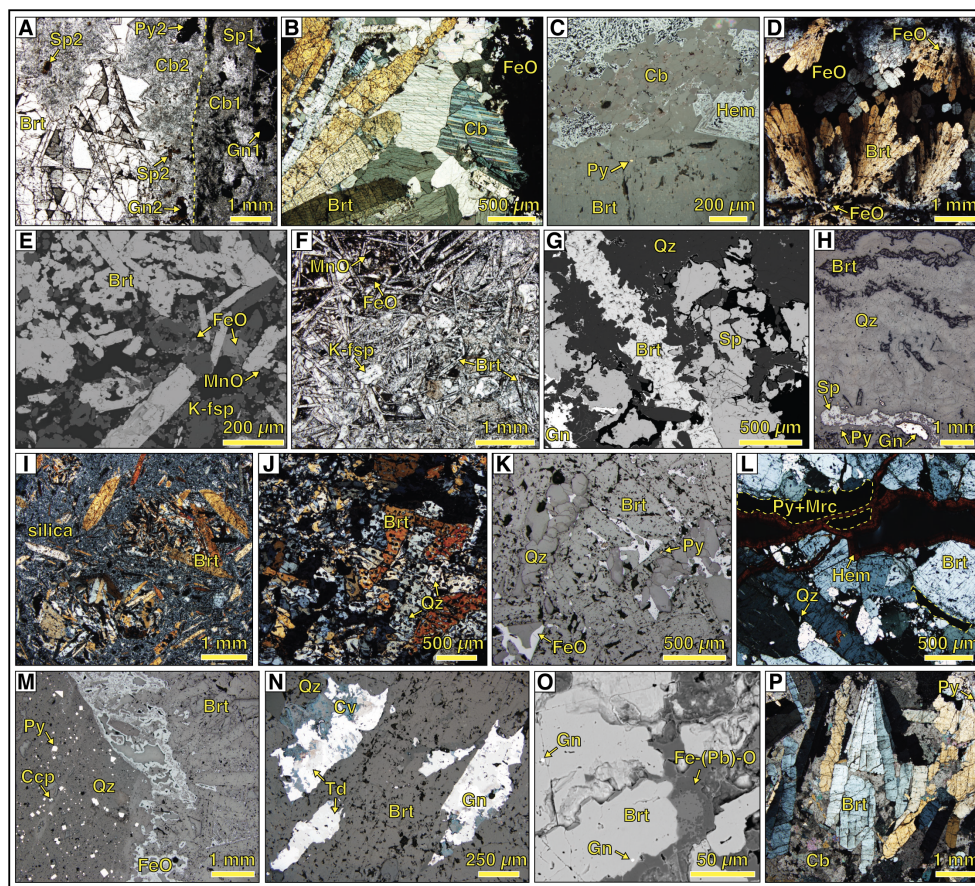


Fig. 3.5: Photomicrographs and backscattered-electron microscopy images of characteristic mineral assemblages and crystal shapes of barite. A: Transmitted light image (PPL) of stage I carbonate-replacement mineralization (Sp1, Gn1, Cb1) transected (dotted line) by stage II mineralization with barite (Brt), low Fe-sphalerite (Sp2), and minor pyrite (Py2) and galena (Gn2) (17L145_3, Plaka). B: Cross-polarized light image (XPL) of coarse bladed barite, carbonates, and oxidized sulfides (Fe-oxides of gossanous material: 17L145_6, Plaka). C: Reflected light image (REF) showing pyrite inclusion in barite (17SML1, Mega Li-vadi). D: XPL image of snowflake barite (17SCK3, Cape Kaparia). E: Backscattered-electron microscopy image (BSE) of relict K-feldspar with barite laths in a matrix of Fe-oxide and spherical Mn-Fe-oxides (17MV2, Cape Vani). F: PPL image of barite sand (17MV7, Cape Vani). G: BSE image of tabular barite and Fe-poor sphalerite replaced by quartz (17MGA04, Galana). H: REF image of layered silica, barite, and sulfides from mineralized breccia mound (17MT03, Triades). I: XPL image of barite clasts and barite laths in a matrix of microcrystalline quartz (17MKA2, Kastana). J: XPL image of granular barite with quartz inclusions (17MKA5, Kastana). K: REF image of coarse bladed barite with pyrite inclusion. Quartz and Fe-oxides/hydroxides fill voids between barite crystals (17MYE1, Cape Evros). L: XPL image of pyrite + marcasite veinlets oxidized at the rim to hematite intersecting a barite vein (17MYV2_2, Vein 2 Cape Evros). M: REF image of mineralized, silicified host rock in contact with a barite vein with Fe-oxides/hydroxides along the contact (17MYV3_3, Vein 3 Cape Evros). N: REF image showing open spaces between coarse, bladed barite filled by polymetallic sulfides and quartz (17MYP1, Panormos Bay). O: BSE image of fine galena inclusions in barite in a matrix of Pb-(Mn)-bearing Fe-oxides/hydroxides (17AP13, Agios Georgios). P: XPL image of fractured radial barite crystals in carbonate matrix (17AP1, Prassovounia). Mineral abbreviations: Brt: barite, Cb: carbonate minerals, Ccp: chalcopyrite, Cv: covellite, FeO: Fe-oxide/hydroxide, Gn: galena, Hem: hematite, K-fsp: K-feldspar, MnO: Mn-oxide, Mrc: marcasite, Py: pyrite, Qz: quartz, Sp: sphalerite, Td: tetrahedrite.

has a similar mineralogy and paragenesis. Quartz-barite veins hosted by manganiferous glauconitic volcanoclastic sandstone/sandy tuff were sampled for this work. The veins, which trend north-northeast to south-southwest, vary in thickness from a few cm to 10 cm and consist predominantly of barite, quartz, and minor Mn-oxides, with relict K-feldspar crystals and glauconite clasts. Barite crystals preserve radial growth, with primary growth zones in the core and diffuse secondary zones at the rim and in smaller crystals (Fig. 3.6D).

At Kondaros-Katsimouti, samples were obtained from polymetallic epithermal quartz and barite veins that cut the dacitic lavas and overlying volcanoclastic sandstone. The veins are steeply dipping, subparallel, northeast-southwest trending and up to 20 cm wide and extend over several tens of meters at Katsimouti (Fig. 3.3D). Barite occurs together with galena, pyrite, Fe-poor sphalerite, and minor tetrahedrite. Late-stage silicification, including quartz or chalcedony pseudomorphs after barite (Fig. 3.4C), has significantly reduced the sulfide and barite content of the veins.

At Galana and Triades, samples were taken from multiple, barite- and quartz-cemented breccia domes and pod-like veins and lenses at the base of the breccia domes. Quartz and barite gangue are associated with galena, Fe-poor sphalerite, pyrite, and minor chalcopyrite, tetrahedrite-tennantite, and enargite (Fig. 3.5G); rare covellite and bornite of probable supergene origin also occur. Samples from the barite-filled pods contain euhedral bladed barite showing void-filling textures (Fig. 3.3E-F). Vein barite is massive to bladed and commonly has corroded rims due to silicification (Fig. 3.5G-H). Inclusions of galena, sphalerite, Pb-oxides, and euhedral quartz were observed in barite (Fig. 3.5G).

At Profitis Ilias, barite was sampled from subvertical interconnected quartz veins that are up to 3 m wide and extend to a depth of at least 300 m (Kiliyas et al., 2001). Veins at the surface cut silicified rhyolitic tuffs and are several centimeters wide, banded, and composed mainly of quartz and barite; sulfides were not observed in the studied samples,

but small inclusions of Fe-oxides were observed. Coarse-grained bladed barite occupies the central portions of the veins (Fig. 3.4D); the early formed margins of the veins are mainly colloform with microcrystalline quartz belonging to the Au-bearing ore stage (Kilias et al., 2001).

Samples of barite from Fourkovouni, in the northeast of Milos, were collected from veins and open-space fillings that occur in the altered and silicified tuffaceous rock (Fig. 3.3G). Here, the volcanoclastic host rock is highly silicified and stained red, possibly indicating oxidized pyrite. Barite crystals are acicular to tabular and milky and show pronounced growth zoning (Fig. 3.6E).

At Kastana, also in the east of Milos, we sampled barite veins up to 5 cm wide and stockworks, as well as barite $\pm$ quartz impregnations in the volcanoclastic material (Fig. 3.3H). Here, massive to tabular barite occurs together with quartz, as well as barite clasts and barite laths in a matrix of microcrystalline quartz (Fig. 3.5I) and granular barite with abundant quartz inclusions (Fig. 3.5J). Rarely fine inclusions of K-feldspar, muscovite, and oxidized pyrite were also observed in barite.

Vein barite, Mykonos and Antiparos

At Cape Evros and Cape Charos on Mykonos, samples were collected from subvertical barite veins, up to 10 m wide and over kilometers long, which cut the metabasites of the Pelagonian zone and Miocene conglomeratic sequence in the hanging wall as well as the monzogranite in the footwall of the local detachment systems. Barite veins and stockworks (Fig. 3.3I-J) crosscut and postdate silicified breccias, which have been previously described by Skarpelis (2002) and Skarpelis & Gilg (2006). Samples of the silicified breccia from this study contain euhedral pyrite, minor chalcopyrite, and covellite (Figs. 3.4E-F, 3.5M). Banded barite veins, which crosscut the siliceous breccia, consist mainly of barite and

Fe-oxides/hydroxides. Barite samples include massive to bladed barite crystals, ranging in size up to 7 cm (Fig. 3.3J). Sulfides (e.g., galena, Fe-poor sphalerite, pyrite, chalcopyrite: Wind et al., 2020) occur often interstitially between large barite laths but also as micro-inclusions, with pyrite and chalcopyrite as well as supergene covellite being the most common inclusions (Fig. 3.5K). Veinlets of pyrite and marcasite, at rims often oxidized to hematite, are intersecting barite veins and occur also between large barite laths (Fig. 3.5L). Late-stage quartz and hematite, as well as goethite of probable supergene origin, were observed in all studied samples. At Panormos Bay on Mykonos, banded veins consisting of massive and bladed barite (Fig. 3.3K-L) cut the clastic sediments of the Miocene conglomeratic sequence. Barite crystals vary in size from <1 cm to 5 cm in the different bands of the vein, whereas veinlets of fine-grained barite occur in the later stages of vein formation intergrown with quartz and galena with late supergene hematite $\pm$ anglesite at rims (17MYP3 in Figs. 3.3L, 3.4G top). In the center of the banded veins, polymetallic sulfides, including galena, tetrahedrite(-tennantite), chalcopyrite, and supergene covellite (Wind et al., 2020), together with quartz $\pm$ carbonates, fill spaces between large barite crystals (Fig. 3.5N), which show distinctive growth zoning (Fig. 3.6F).

At Agios Georgios on Antiparos, the vein system consists of two generations of steeply dipping quartz veins: an older NE-SW-trending generation filled with milky quartz and a younger NW-SE-trending set with clear quartz (Kevrekidis et al., 2015). Previous work and our own observations show barite occurs together with clear quartz, smithsonite, fluorite, argentiferous galena, and minor native Au and Ag, and covellite. We sampled milky, commonly broken, and brecciated blades of barite in a vein surrounded in a matrix of Pb- and Mn-bearing Fe-oxides/hydroxides, Pb-Mn-oxides, and minor quartz (Fig. 3.4H), although small inclusions of galena, a few μm in size, are still preserved in the barite (Fig. 3.5O). At Prassovounia, NE-SW-trending milky to clear quartz veins cut the gneisses and

schists of the UCBN and contain low concentrations of base metal sulfides. We sampled bladed barite in association with Fe-poor sphalerite, galena, and minor pyrite in a matrix of microcrystalline quartz (Fig. 3.4I), where the sulfides are commonly oxidized and barite has partially replaced crystal rims, likely related to the late-stage silicification. We also sampled NE-SW-trending barite-carbonate veinlets that cut the marble of the UCBN. Barite crystals are up to 4 cm in length, show radial growth, and are intergrown with coarse carbonates and Fe-oxides (Fig. 3.5P). Inclusions of pyrite, now mostly oxidized, were observed in both samples of barite from Prassovounia.

3.5 Results

3.5.1 Geochemistry of barite

Results of the semi-quantitative analysis by SEM in energy-dispersive mode (EDS), and analyses by EMPA and LA-ICP-MS are provided in the Appendix Tables 3.A2 and 3.A3 and summarized in Table 3.2. Compositional zoning in barite was observed in samples from all of the investigated deposits, mainly recorded by variations in the amount of Sr in the crystal lattice (Figs. 3.6, 3.7). In backscattered-electron microscopy (BSE) images, the brightness of the zones is correlated with the Sr content, which ranges from below detection limit of the SEM-EDS and EMPA (<0.04 wt%) to 5.2 wt% (Fig. 3.6A; Table 3.2). The lowest concentration of Sr measured by LA-ICP-MS is 435 ppm in sample 17L145_1 (crystal b analysis 3 (rim): Fig. 3.13A) from Lavrion. The strong negative correlation between BaO and SrO (Fig. 3.7) reflects the complete solid solution between barite and celestine (Hanor, 2000). These variations are linked to primary growth zones and secondary depletions often at the crystal rim (Fig. 3.6B-F). The majority of samples analyzed by SEM-EDS are from Milos, which also records the highest Sr concentrations

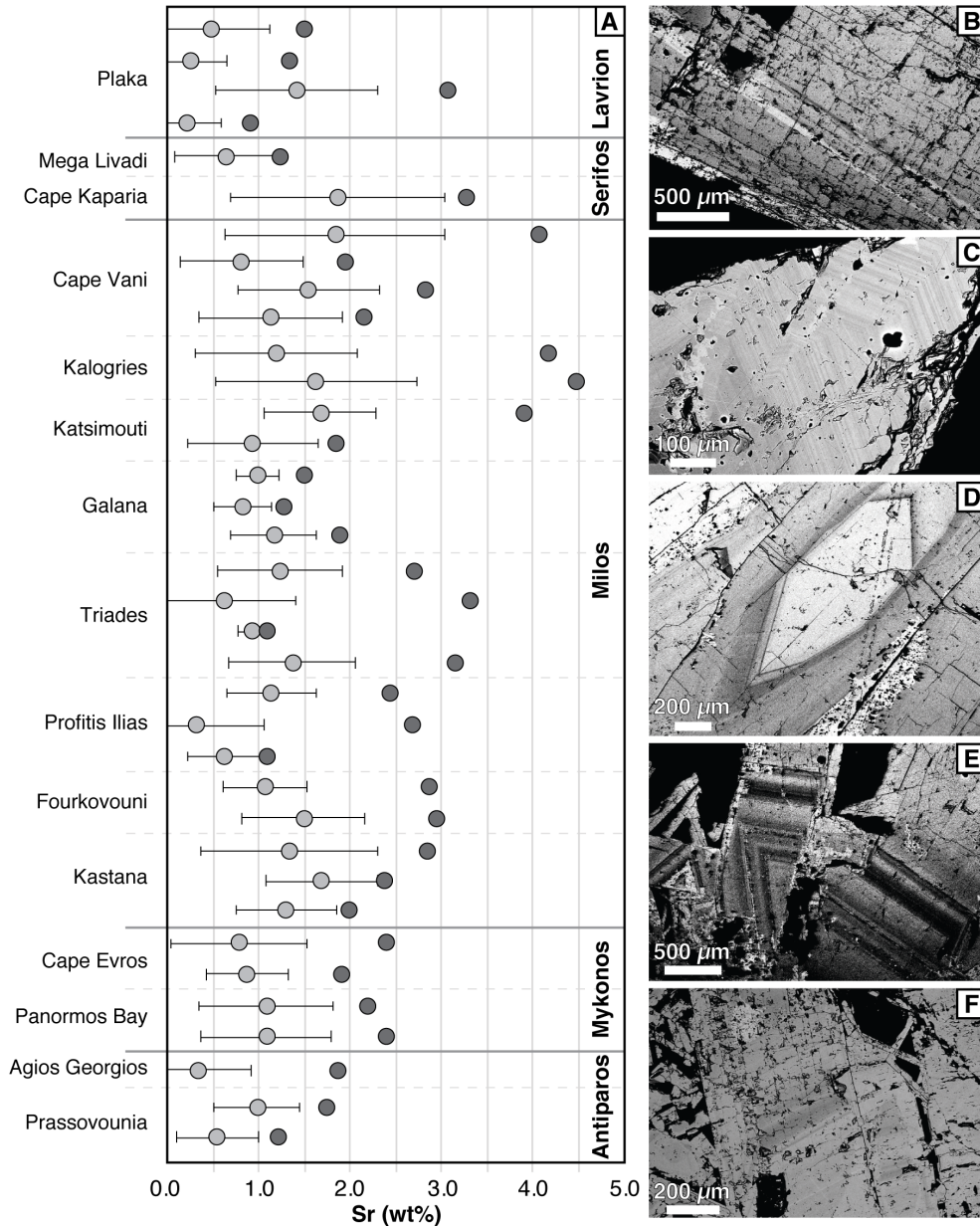


Fig. 3.6: A: Variations in Sr concentration detected by scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) analyses. Each row represents one sample with average and standard deviation in light grey and maximum Sr content in dark grey. B-F: Representative backscattered-electron microscopy images of zoned Cycladic barite. Dark zones correspond to elevated concentrations of Sr. B: Alternating Sr-rich and Sr-poor zones, with an overall decrease in Sr towards the rim of barite laths (Plaka, Lavrion). C: Very fine growth zones in bladed barite. Bent and fractured crystal faces with diffusive patterns (Cape Kaparia, Serifos). D: Strong primary growth zones of bladed barite, with Sr-poor core followed by a Sr-rich thin margin and Sr loss at barite rims (Kalogries, Milos). E: Tabular barite with pronounced primary growth zones, offset in the center. Later overgrowth with low Sr and Sr loss at rims (Fourkovouni, Milos). F: Massive to bladed barite with primary cyclic growth zones and diffusive patterns (Panormos Bay, Mykonos).

(Fig. 3.6: Cape Vani, Kalogries, Katsimouti). However, barite from Cape Kaparia, Serifos, has higher average Sr contents than almost all barite samples from Milos (Fig. 3.6A) and the range of the sample is also greater than that at any individual deposit on Milos. The highest concentrations of Sr were measured by EMPA in two samples from Kalogries and Fourkovouni, Milos (Fig. 3.7; Table 3.2) with concentrations of 4.2 and 5.2 wt%, respectively. Overall, barite from barren submarine volcanic breccias shows a broad range and high concentrations of Sr (e.g., Figs. 3.6D-E, 3.7), whereas barite in association with sulfides from Milos, Lavrion, Mykonos, and Antiparos has a narrower range of Sr concentrations (0.8 to 2.7 wt%: Fig. 3.7).

The following elements were detected by LA-ICP-MS in nearly all analyzed samples: S, Ca, Zn, Cu, Sr, Ba, La, Ce, Pr, Gd, and Hf. However, it should be noted that because of unavoidable interferences (e.g., Sr^{2+} on Ca, S-O cluster on Zn and Cu, or BaH on La) concentrations of some trace elements may be overestimated. In samples associated with galena mineralization (e.g., Plaka, Lavrion; Katsimouti, Triades, and Galana, Milos; Cape Evros and Panormos Bay, Mykonos; Agios Georgios, Antiparos), Pb was detected by SEM-EDS analysis and concentrations of up to 0.64 wt% were measured by EMPA. In contrast, LA-ICP-MS analyses showed low concentrations of a few parts per million up to 20 ppm in samples lacking any association with galena mineralization (e.g., Mega Livadi, Serifos). Barite from Plaka, Lavrion, contains elevated Ca and Pb, which likely represent carbonate and galena inclusions, respectively. Rarely, increased Ca correlates with Sr-rich growth zones (e.g., traverse 17MAR2 from Fourkovouni, Milos: App. Fig. 3.A.2). Sodium concentrations were measured by SEM in barite grain mounts, and concentrations of a few parts per million up to 52 ppm were found by LA-ICP-MS in the samples 17MAR3 (Milos) and 17MYP1 (Mykonos), potentially related to Na-rich fluid inclusions. Concentrations of other trace elements and rare earth elements (REEs) are generally at or below detection

limits of EMPA and LA-ICP-MS (Appendix Tables 3.A2 and 3.A3).

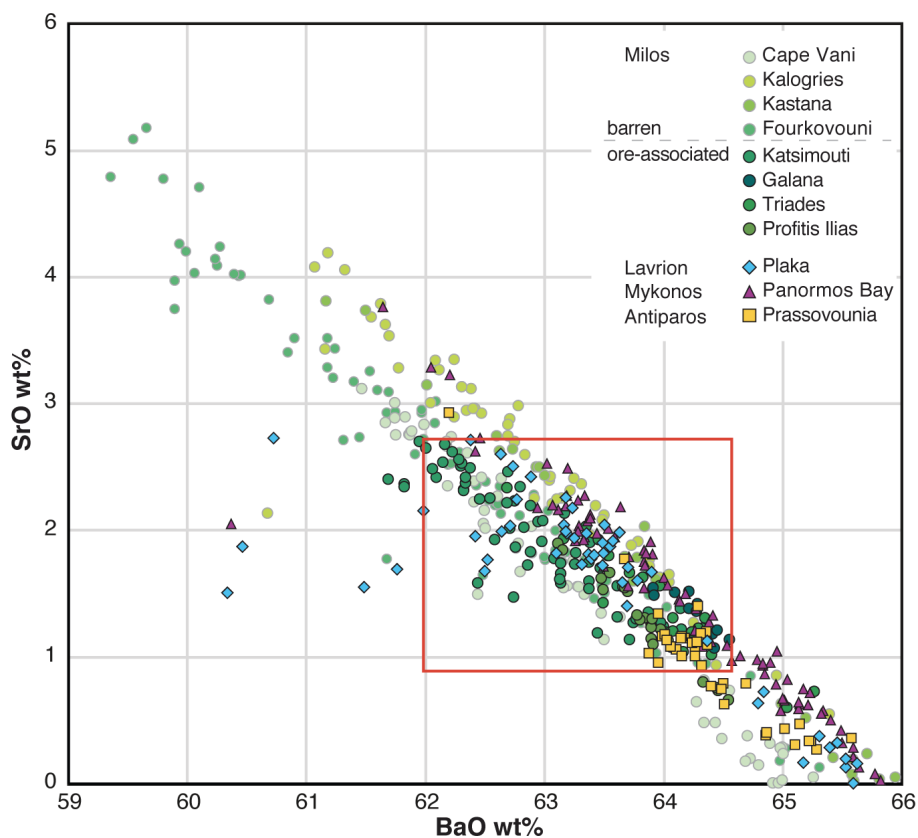


Fig. 3.7: Variation in Sr concentration detected by electron microprobe analyses of barite from Milos, as well as Lavrios, Mykonos, and Antiparos. There is a strong negative correlation between SrO and BaO in barite. Barite in association with sulfides plots mostly within the red rectangle and has a narrow range in SrO (0.8–2.7 wt%) and BaO (62.0–64.5 wt%).

Table 3.2: Results of geochemical and S, O, and Sr isotope analyses of barite and S isotope analyses of galena, Cyclades, Greece. $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ relative to the VCDT and VSMOW standards, respectively.

Location	Deposit	Sample	IRMS			LA-MC-ICP-MS		IRMS		EMPA			SEM			LA-MC-ICP-MS	
			Galena	Barite		Min	Max			SrO min	SrO max	SrO avg	Sr max	Sr avg	Min	Max	
Lavרון	Villia	17LV1	/	18.3	/	/	/	15.3	/	/	/	/	/	/	/	/	
Lavרון	Plaka	17L145_1	3.6	9.3	2.1	20.4	15.0	/	/	/	/	1.50	0.48	0.7092	0.7101	/	
Lavרון	Plaka	17L145_3	3.3	19.5	18.3	24.5	11.9	bdl	/	2.73	1.61	3.07	1.41	0.7097	0.7108	/	
Lavרון	Plaka	17L145_3B	/	11.7	3.5	11.6	13.2	/	/	/	/	0.90	0.21	(0.7080);	0.7104	/	
Lavרון	Plaka	17L145_6	/	19.8	/	/	10.5	/	/	/	/	/	/	/	/	/	
Serifos	Mega Livadi	17SML1	/	11.6	10.0	11.8	8.7	/	/	/	/	1.22	0.64	(0.7078);	0.7101;	(0.7112)	
Serifos	Mega Livadi	17SML2	/	10.9	/	/	9.0	/	/	/	/	/	/	/	/	/	
Serifos	Cape Kaparia	17SCK1	/	12.3	10.8	12.8	10.7	/	/	/	/	3.27	1.86	0.7097	0.7100	/	
Serifos	Cape Kaparia	17SCK2	/	13.5	/	/	12.8	/	/	/	/	/	/	/	/	/	
Milos	Cape Vani	17MV2	/	22.9	22.6	24.6	10.8	bdl	3.11	1.54	1.95	1.95	0.81	0.7096	0.7099	/	
Milos	Cape Vani	17MV7	/	21.2	/	/	10.4	/	/	/	2.14	2.14	1.13	/	/	/	
Milos	Kalogries	17MKAL1	/	22.5	/	/	10.5	/	/	/	4.16	4.16	1.19	/	/	/	
Milos	Katsimouti	17MK3	/	17.8	16.5	18.2	10.3	1.08	2.70	1.98	3.91	3.91	1.67	0.7096	0.7098	/	
Milos	Katsimouti	17MK5	/	18.5	17.2	22.6	/	1.19	2.07	1.53	1.84	1.93	0.93	0.7097	0.7100	/	
Milos	Galana	17MGA02	/	/	24.5	25.9	9.7	1.07	1.55	1.35	1.49	1.49	0.98	0.7091	0.7094	/	
Milos	Galana	17MGA03	-1.1	24.6	22.9	27.1	9.7	0.60	2.33	1.42	2.69	2.69	0.81	0.7096	0.7102	/	
Milos	Triades	17MT03	-0.9	22.8	21.0	25.9	9.7	0.66	2.33	1.42	2.69	2.69	1.22	0.7093	0.7098	/	
Milos	Profitis Ilias	17MP2A	/	21.8	23.4	26.8	11.3	0.13	5.18	1.89	2.67	2.67	0.31	0.7099	0.7104	/	
Milos	Fourkovouni	17MAR2	/	22.9	22.9	25.0	10.5	0.13	5.18	2.60	2.86	2.86	1.07	0.7095	0.7101	/	
Milos	Fourkovouni	17MAR3	/	21.8	21.9	25.6	10.1	bdl	3.81	1.62	2.94	2.94	1.48	0.7094	0.7104	/	
Milos	Kastana	17MKA2	/	22.7	(12.4); 25.2	27.7	10.4	bdl	3.81	1.62	2.84	2.84	1.33	0.7101	0.7104	/	
Mykonos	Cape Evros	17MYE1	/	31.5	/	/	4.4	/	/	/	/	/	/	/	/	/	
Mykonos	Cape Evros	17MYE7	/	27.6	25.9	27.4	8.3	/	/	/	2.40	2.40	0.77	0.7139	0.7143	/	
Mykonos	Cape Evros	17MYE8	/	27.9	/	/	/	/	/	/	/	/	/	/	/	/	
Mykonos	Cape Evros	17MYV2_1	3.9	30.8	28.1	37.2	5.6	/	/	/	1.90	1.90	0.86	0.7139	0.7144	/	
Mykonos	Cape Evros	17MYV2_2	/	25.2	/	/	8.3	/	/	/	/	/	/	/	/	/	
Mykonos	Cape Evros	17MYV3_3	/	25.4	/	/	9.1	/	/	/	/	/	/	/	/	/	
Mykonos	Cape Choros	17MYC1	/	25.4	/	/	11.9	/	/	/	/	/	/	/	/	/	
Mykonos	Panormos	17MYP1	-1.1	25.8	20.3	27.8	8.8	/	/	/	2.19	2.19	1.08	(0.7114);	0.7124;	(0.7130)	
Mykonos	Bay	17MYP3	/	26.2	24.4	25.5	10.2	bdl	3.76	1.46	2.40	2.40	1.08	0.7120	(0.7130)	0.7125	
Mykonos	Bay	17MYP4	-1.7	26.1	/	/	9.2	/	/	/	/	/	/	/	/	/	
Antiparos	Agios Georgios	17AP13	/	19.6	15.4	22.4	13.8	/	/	/	1.87	1.87	0.33	0.7110	0.7126	/	
Antiparos	Prassovounia	17AP1	/	21.3	/	/	7.5	/	/	/	1.73	1.73	0.97	/	/	/	
Antiparos	Prassovounia	17AP2	-1.7	23.5	20.3	26.3	4.6	0.28	2.93	0.95	1.20	1.20	0.54	0.7122	0.7124	/	

Notes: Table contains data of barite samples analyzed for their isotopic composition; additional geochemical data of barite and S isotope analyses of galena are included in the Appendix Tables 3.A2 and 3.A3; outliers are shown in brackets; minimum Sr concentration detected by SEM was generally below detection limit (bdl); / indicates not analyzed. Abbreviations: EMPA: electron microprobe analysis, IRMS: isotope ratio mass spectrometry, LA-MC-ICP-MS: laser ablation multi-collector inductively coupled plasma mass spectrometry, SEM: scanning electron microscopy, VCDT: Vienna Canyon Diablo Troilite, VSMOW: Vienna standard mean ocean water

3.5.2 Stable isotope data of mineral separates

Sulfur isotopes were determined by elemental analyzer-isotope ratio mass spectrometry (EA-IRMS) in 33 representative samples of barite and 24 samples of galena coexisting with barite or in associated veins. The results are reported in standard δ notation as per mil (‰) relative to the VCDT (Vienna Cañon Diablo Troilite) standard. Barite has a wide range of $\delta^{34}\text{S}$ values, between 9.3 and 31.5‰ (Table 3.2 and Appendix Table 3.A2; Fig. 3.8). Significant variation in $\delta^{34}\text{S}$ values was observed between the different mineralization styles. Barite from the carbonate-hosted mineralization at Lavrion has $\delta^{34}\text{S}$ values from 9.3 to 19.8‰. At Plaka, two samples taken underground from Adit No. 145 with coarse tabular barite have the lowest $\delta^{34}\text{S}$ values (9.3 and 11.7‰), whereas a sample with small barite flakes and barite associated with carbonate in gossan material near the mine entrance has higher values (19.5 and 19.8‰, respectively). Barite from Serifos has a narrow range of $\delta^{34}\text{S}$ values from 10.8 to 13.5‰, with slightly higher $\delta^{34}\text{S}$ values at Cape Kaparia (mean: ~ 12.9 ‰) than at Mega Livadi (mean: ~ 11.1 ‰). Barite from the different deposits on Milos has $\delta^{34}\text{S}$ values of 21.2 to 24.6‰, except for two samples of vein barite from Katsimouti, which have lower $\delta^{34}\text{S}$ values of 17.9 and 18.5‰. High $\delta^{34}\text{S}$ values were measured in vein barite from Mykonos; barite from Cape Evros has $\delta^{34}\text{S}$ values between 25.2 and 31.5‰ and shows three clusters around ~ 25.3 ‰, ~ 27.8 ‰, and ~ 31.1 ‰. Vein barite from Cape Charos has $\delta^{34}\text{S}$ values of 25.4‰, and barite from Panormos Bay has values between 25.7 and 26.2‰. The $\delta^{34}\text{S}$ values for barite from Antiparos vary between 19.6 and 23.5‰, with barite from Prassovounia (mean: 22.4‰) having higher values than barite from Agios Georgios (19.6‰).

Galena $\delta^{34}\text{S}$ values range between -13.9 and 4.3‰ (Table 3.2; Appendix Table 3.A2; Fig. 3.8). The majority of $\delta^{34}\text{S}$ values are between -1.8 and 4.3‰, except for galena from

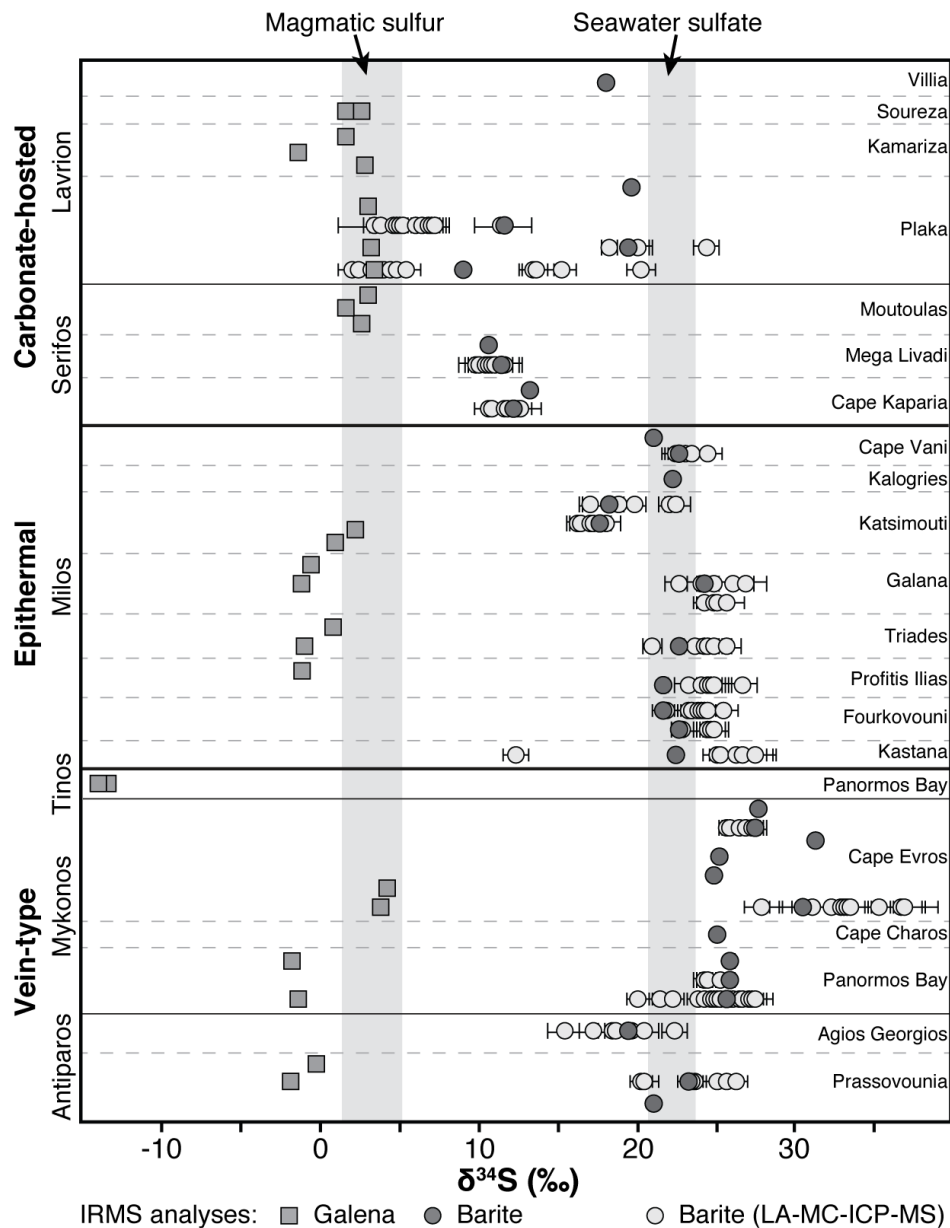


Fig. 3.8: Sulfur isotope compositions from EA-IRMS and LA-MC-ICP-MS spot analyses of Cycladic barite and galena. All values are reported relative to the Vienna Cañon Diablo Troilite (VCDT). For duplicate analyses of the same sample by IRMS the average is plotted. Also shown are the isotopic range of Miocene to present Mediterranean seawater (Burdett et al., 1989; Böttcher et al., 1998; Paytan et al., 1998; Markovic et al., 2016), and arc-related magmatic S (e.g., Hauck, 1984; Marini et al., 2002). Values plotted along one line are from the same sample. Note that in the case of galena and barite from Plaka, Lavrion, the analyzed galena and barite are not in textural equilibrium (Fig. 3.5A).

Panormos Bay on Tinos, which has significantly lower values of -13.9 and -13.1‰. Galena from Plaka, Lavrion, has a narrow range of $\delta^{34}\text{S}$ values from 3.0 to 3.6‰, contrasting with the wide range of $\delta^{34}\text{S}$ values of barite (9.3–19.8‰) from the same site. Galena from Kamariza and Soureza at Lavrion has slightly lower $\delta^{34}\text{S}$ values of -1.2 to 2.9‰ and 1.8 to 2.6‰, respectively. On Serifos, galena from the polymetallic mineralization at Moutoulas has $\delta^{34}\text{S}$ values between 1.7 and 3.0‰. Galena from the epithermal deposits at Katsimouti, Galana, Triades, and Profitis Ilias on Milos has $\delta^{34}\text{S}$ values between -1.1 and 2.2‰, where $\delta^{34}\text{S}$ values of galena from Katsimouti are only positive. Galena from Mykonos has distinct $\delta^{34}\text{S}$ values for the vein systems at Cape Evros and Panormos Bay. Galena from Cape Evros has $\delta^{34}\text{S}$ values of 3.9 and 4.3‰ from the same samples where barite has high $\delta^{34}\text{S}$ values (~ 31.1 ‰). Galena from Panormos Bay has $\delta^{34}\text{S}$ values of -1.7 to -1.0 compared to 25.7 to 26.2‰ in the coexisting barite. Galena from Prassovounia on Antiparos has $\delta^{34}\text{S}$ values between -1.8 and -0.2‰ compared to 23.5‰ in the coexisting barite.

Oxygen isotope ratios were determined by EA-IRMS in barite from 31 samples and are reported in δ notation as per mil (‰) relative to the VSMOW (Vienna Standard Mean Ocean Water) standard in Table 3.2 and Figure 3.9, and the complete data set is reported in the Appendix Table 3.A2. The $\delta^{18}\text{O}$ values range between 3.7 and 15.3‰, with significant variation between the different deposit types. Barite from the carbonate-hosted deposits at Lavrion has high $\delta^{18}\text{O}$ values between 10.5 and 15.3‰, where lower $\delta^{18}\text{O}$ values correlate with higher $\delta^{34}\text{S}$ values. Barite from Serifos has $\delta^{18}\text{O}$ values between 8.8 and 12.8‰. Here, $\delta^{18}\text{O}$ values of barite from Cape Kaparia are higher than $\delta^{18}\text{O}$ values of barite from Mega Livadi. Barite from the different deposits on Milos has a narrow range of $\delta^{18}\text{O}$ values from 9.7 to 11.3‰. Barite from Triades-Galana on Milos has the lowest $\delta^{18}\text{O}$ values, and barite from Profitis Ilias has the highest. Samples of vein barite on Mykonos and Antiparos have the widest range of $\delta^{18}\text{O}$ values, from 4.4 to 11.9‰ and 3.7 to 13.8‰, respectively. In

general, we observed a negative covariation between the $\delta^{34}\text{S}$ values and $\delta^{18}\text{O}$ values of barite (Fig. 3.9), which is further discussed below.

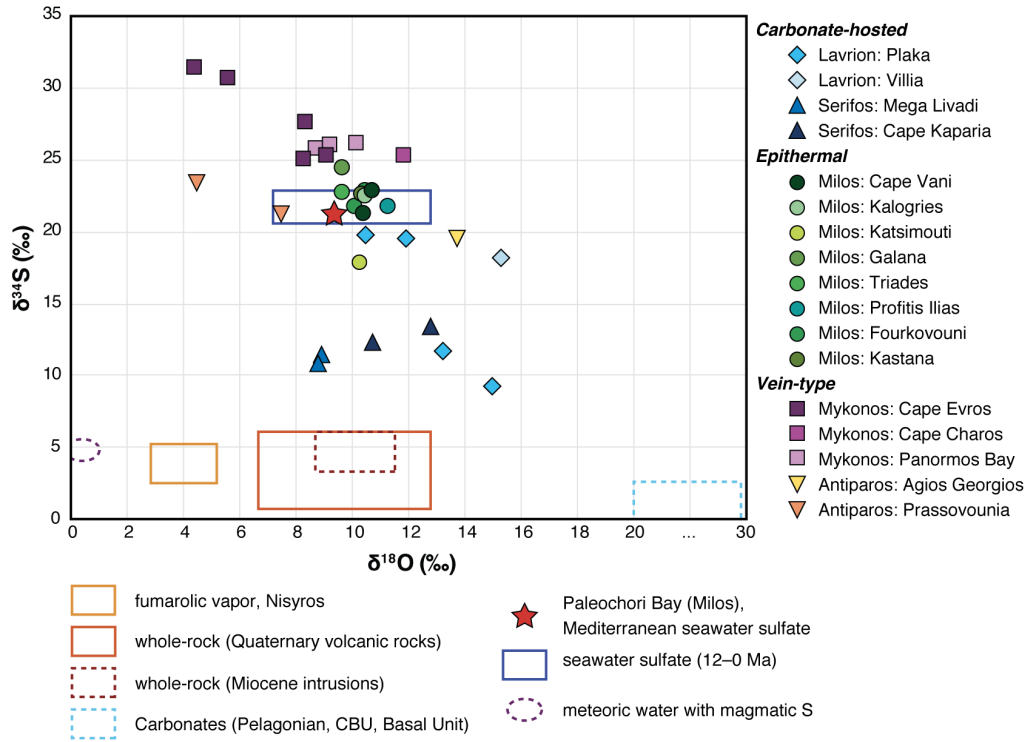


Fig. 3.9: $\delta^{34}\text{S}$ values vs. $\delta^{18}\text{O}$ values of Cycladic barite obtained by mineral separate analyses (EA-IRMS) of Cycladic barite. All isotope values are reported relative to the Vienna Cañon Diablo Troilite (VCDT) and Vienna Standard Mean Ocean Water (VSMOW). In the case of duplicates, the average of the two analyses was plotted. Errors for EA-IRMS analyses are generally smaller than the shown symbol. Dashed boxes represent uncertain $\delta^{34}\text{S}$ values. Purple circle represents meteoric water with a magmatic S source. For data sources refer to the Discussion and Table 3.3.

3.5.3 LA-MC-ICP-MS data

In this study, we were able to make sequential measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ on the same ablation spot in barite by LA-MC-ICP-MS. In total 165 ablations were performed on 51 barite crystals from 21 samples. The results are summarized in Table 3.2 and shown in Figure 3.10, and the complete data set is reported in the Appendix Table 3.A3. For samples with replicate analyses, $\delta^{34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ were reproduced within analytical error, except in Sr-poor barite zones ($<7 \times 10^7$ cps, <0.2 wt% Sr). Ablations in Sr-poor barite zones (light colors on Fig. 3.10) often yielded Sr isotope ratios outside the range of values obtained on Sr-rich zones of the same sample and crystal.

Strontium isotope ratios vary significantly from 0.7089 to 0.7144 (n: 155), but samples from the same deposit commonly show only minor variations, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are remarkably homogeneous among all occurrences on one island (Fig. 3.10A-B). Except for a sample from Agios Georgios on Antiparos (App. Fig. 3.A.3), no significant correlation between the Sr concentration and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio could be found (Fig. 3.10B). The carbonate-hosted barite at Lavrion has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.7093 to 0.7107, and that on Serifos from 0.7089 to 0.7112, though the majority of analyzed barite from Serifos has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7099 ± 0.0002 (Fig. 3.10A). Barite from seven mineral occurrences sampled on Milos has a narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7091 to 0.7104, with the least radiogenic barite from Galana and the most radiogenic from Kastana (Figs. 3.10, 3.11). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of vein barite from Mykonos fall into two distinct groups (Figs. 3.10, 3.11), with more radiogenic Sr in barite from Cape Evros than in barite from Panormos Bay (0.7139–0.7144 and 0.7120–0.7125, respectively). Vein barite from Antiparos has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7110 to 0.7124, with generally higher and more homogeneous values from Prassovounia than from Agios Georgios (Fig. 3.11).

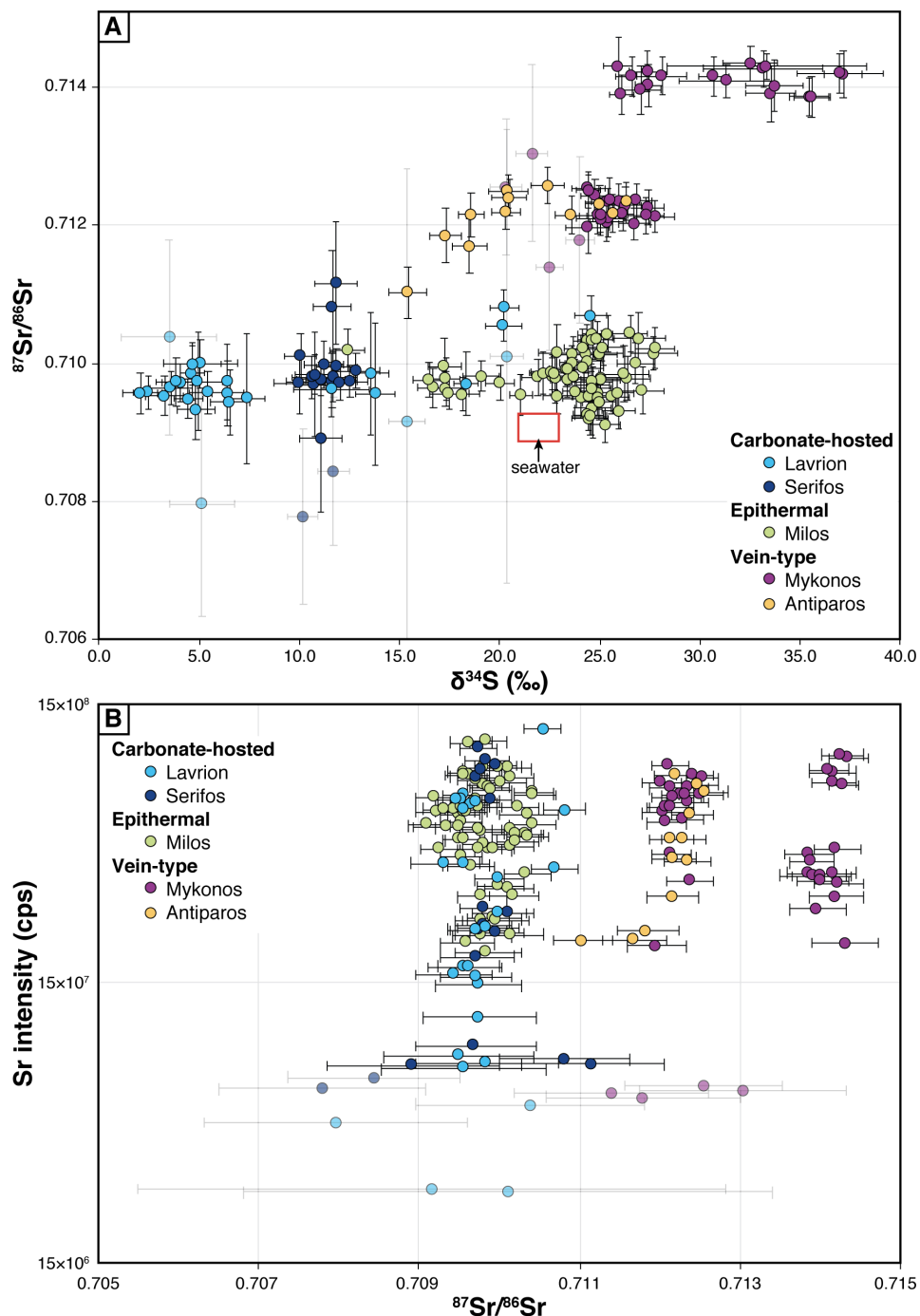


Fig. 3.10: $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios vs. $\delta^{34}\text{S}$ values (A) and Sr intensity vs. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios (B) of Cycladic barite obtained by LA-MC-ICP-MS spot analyses. Each data point is one individual measurement with errors reported at 1 standard error (S.E.); spot analyses within Sr-poor barite zones ($<7 \times 10^7$ cps, <0.2 wt% Sr) are represented by light colors, with error bars in light grey. The red box shows the range of composition for the Miocene to present Mediterranean seawater (e.g., [Burdett et al., 1989](#); [Hodell et al., 1991](#); [Farrell et al., 1995](#); [Böttcher et al., 1998](#); [Markovic et al., 2016](#)).

Barite $\delta^{34}\text{S}$ values from mineral separates (EA-IRMS) and from LA-MC-ICP-MS spot analyses are very similar with a somewhat larger range for spot analyses of single crystals (Fig. 3.8). Sulfur isotope compositions obtained by LA-MC-ICP-MS spot analyses vary from 2.1 to 37.2‰ (Table 3.2), emphasizing a strong zoning in $\delta^{34}\text{S}$ values at the crystal scale (e.g., Lavrion and Mykonos). In some cases, lower $\delta^{34}\text{S}$ values might be related to micro-inclusions of sulfides in barite, often at the crystal rim (App. Fig. 3.A.4). Significant zoning in $\delta^{34}\text{S}$ often correlates with a variation in the Sr concentration (Figs. 3.10, 3.12, 3.13); however, for most crystals the Sr isotope ratios did not vary.

3.6 Discussion

The isotopic compositions ($\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$) of barite vary distinctly between the different deposit types across the Cyclades and allow us to compare the source of barite-forming fluids, where a wide range of fluid sources has been previously suggested. In the extensively studied Lavrion District and on Milos, a range of mineral and fluid inclusion assemblages have been analyzed (Table 3.1) corresponding to multiple stages of mineralization (e.g., Naden et al., 2005; Bonsall et al., 2011; Scheffer et al., 2019) and different fluid sources (magmatic, meteoric, and seawater). Fluid mixing has been widely interpreted as a fundamental control on the mineralization in many of the hydrothermal systems (Table 3.1), but the nature of the fluids involved has been difficult to determine. We have examined this record in hydrothermal barite, which occurs in all of the deposits and almost always reflects different mixing processes. The results are discussed in the following sections according to the regional patterns of S sources, sulfide-sulfate relationships, O isotopes and Sr isotopes. For details of the individual deposits, readers are referred to the summaries provided in Tables 3.1, 3.2, and 3.3 and in the synoptic Figures 3.2 and 3.14.

3.6.1 Sulfur sources in Cycladic barite

It is well established from experimental results that there is no isotopic fractionation of S between barite and dissolved sulfate at temperatures of 110 to 350°C (Kusakabe & Robinson, 1977); thus, the composition of barite can be used to trace the isotopic composition of sulfate from the parent fluid. Sulfur isotope compositions of barite in the Cyclades Mineral District vary significantly between the different deposit types (Table 3.2, Fig. 3.8). In general, we observed that barite samples from the same deposit have only small variations in $\delta^{34}\text{S}$ values, except for carbonate-hosted barite from Lavrion (2.1–24.5‰; Fig. 3.8). High $\delta^{34}\text{S}$ values from analyses of mineral separates of barite from Plaka and Villia at Lavrion are similar to those previously reported (17.2–23.7‰ at Villia, Kamariza, Kiafa Mariza, and Megala Pefka: Bonsall et al., 2011). However, two samples from Plaka yielded low $\delta^{34}\text{S}$ values (9.3–11.7‰), and by LA-MC-ICP-MS spot analyses we found significant variability in $\delta^{34}\text{S}$ of individual barite crystals ranging from 2.4 to 20.4‰ (Fig. 3.13, further discussed below). These strong variations in S isotope ratios of barite in our samples from Plaka suggest that sulfate was derived from at least two distinct S sources, most probably magmatic and seawater-derived sulfate. High $\delta^{34}\text{S}$ values (18.2–24.6‰) of barite at Lavrion have been interpreted as evidence of the involvement of Miocene seawater sulfate (Bonsall et al., 2011); however, lower values (2.1–7.4‰) reported in this study are more consistent with a magmatic source for sulfate or remobilization of S from stage I of ore mineralization (Figs. 3.8, 3.9). Our findings support the observations by Bonsall et al. (2011) and Scheffer et al. (2019) that barite formed late in the paragenetic sequence, and further suggest a shift in the dominant sources from magmatic to seawater-derived fluids, which is recorded in barite and is further supported by the $\delta^{18}\text{O}$ values.

The small variation in S isotope values for the Fe-Ba mineralization at Serifos (10.0–13.5‰)

likely indicates that sulfate is derived from one dominant sulfate source. Since the S is significantly lighter than Miocene seawater sulfate (Fig. 3.8; $\delta^{34}\text{S}_{\text{SO}_4}$: 21.2–22.6‰: [Burdett et al., 1989](#); [Paytan et al., 1998](#)), magmatic sulfate might be the source of sulfate for the barite-hematite deposits on Serifos. In a few barite crystals, we observed small inclusions of pyrite (Fig. 3.4C), which are often oxidized to hematite, suggesting that lower $\delta^{34}\text{S}$ values might also have been produced by the oxidation of reduced magmatic S. [Ducoux et al. \(2017\)](#) suggested that surface waters (oceanic or meteoric) circulated along the detachment and penetrated into the footwall, leading to remobilization of Fe from high-temperature magnetite-skarns providing an alternative (i.e., leached magmatic) source of S. However, the spatial relationship of the Fe-Ba deposits to the high-temperature skarns and rather homogeneous $\delta^{34}\text{S}$ values of barite support a juvenile S source for barite mineralization.

The $\delta^{34}\text{S}$ values of barite from the epithermal veins on Milos tend to overlap with the present Mediterranean seawater value ($\delta^{34}\text{S}_{\text{SO}_4}$: 20.7‰: [Böttcher et al., 1998](#)) and the isotopic composition of coastal seawater in the Palaeochori Bay ($\delta^{34}\text{S}_{\text{SO}_4}$: 21.2‰: [Gilhooly et al., 2014](#)). Our S isotope values of barite from Milos are similar to the values from [Hauck \(1984\)](#); [Hein et al. \(2000\)](#); [Marschik et al. \(2010\)](#); [Ivarsson et al. \(2019\)](#) and [Schaarschmidt et al. \(2021a\)](#), and all authors proposed a seawater-dominated hydrothermal system for the mineralization (Table 3.1). Whereas $\delta^{34}\text{S}$ values obtained by IRMS analysis for the different deposits on Milos are generally within the range of seawater sulfate, LA-MC-ICP-MS spot analyses yielded $\delta^{34}\text{S}$ values of up 27‰ within individual barite crystals (e.g., Galana and Kastana; Fig. 3.8; Table 3.2). One explanation for the high $\delta^{34}\text{S}$ values might be that sulfate was shifted isotopically in response to bacterial sulfate reduction (BSR), as previously suggested by [Ivarsson et al. \(2019\)](#) for the Cape Vani deposit. However, for most barite occurrences on Milos, BSR seems unlikely because of the high fluid temperatures of 100 to 300°C estimated by fluid inclusion work (Table 3.1) and calculated temperatures for

barite-galena equilibrium (this study). These high $\delta^{34}\text{S}$ values of barite might also reflect a mixture of seawater sulfate and sulfate leached by interaction with the wall rock, as indicated by the Sr isotope ratios. Although, whole-rock $\delta^{34}\text{S}$ values of the basement rock types on Milos are lacking, whole-rock $\delta^{34}\text{S}$ values of the metamorphic basement (phyllites, CBU) from Santorini are generally low (0.5–18.2‰, majority <2.5‰: [Hubberten et al., 1976](#)). A similar range was reported for whole-rock $\delta^{34}\text{S}$ values of total S in Santorini lavas (0.1–17.5‰, majority ≤ 6 ‰: [Hubberten et al., 1975](#)). The absence of a source of high $\delta^{34}\text{S}$ values makes the interpretation of $\delta^{34}\text{S}$ values in barite that are higher than that of Mediterranean seawater uncertain. We found significantly lower $\delta^{34}\text{S}$ values of 16.5 to 22.6‰ in vein barite from Katsimouti, similar to the values reported by [Schaarschmidt et al. \(2021a\)](#), indicating either oxidation of reduced S in the hydrothermal fluids or a direct contribution of oxidized magmatic S to the hydrothermal system. [Schaarschmidt et al. \(2021a\)](#) suggested that boiling caused the lower $\delta^{34}\text{S}$ values at Katsimouti; however, boiling was an important process at most mineral occurrences on Milos (Table 3.1; e.g., [Christanis & St. Seymour, 1995](#); [Kilias et al., 2001](#); [Papavasiliou et al., 2016b](#); [Smith et al., 2018](#); [Schaarschmidt et al., 2021a](#)) without significantly influencing the $\delta^{34}\text{S}$ values of barite. Similar, low $\delta^{34}\text{S}$ values (~ 17 ‰) have been reported from pore water sulfate at hydrothermal vents in Palaeochori Bay, where an input of secondary sulfate from sulfide oxidation was suggested ([Gilhooly et al., 2014](#)). [Miles \(2021\)](#) reported low $\delta^{34}\text{S}$ values of jarosite (-7.6 to 9‰) from Triades, and alunite (5.9‰) and jarosite (6.9‰) from Katsimouti and linked these to steam-heated alteration above the groundwater table. In general, however, S isotope values of barite from Milos indicate seawater-dominated hydrothermal fluid sources for the past 3 Myr ([Hein et al., 2000](#); [Marschik et al., 2010](#); [Ivarsson et al., 2019](#)). Sulfide S in galena from the Milos deposits has $\delta^{34}\text{S}$ values closer to H_2S in the free vent gases and pore waters (~ 2.5 and 2.7‰, respectively: [Gilhooly et al., 2014](#)) col-

lected from Palaeochori Bay. These are at the low end of $\delta^{34}\text{S}$ values reported for native S and fumarolic vapor from Nisyros and Milos (1.0–6.7‰: [Hauck, 1984](#); [Marini et al., 2002](#)) and elemental S of Nea Kameni, Santorini (0.0–10.0‰: [Hubberten et al., 1975](#)), and are discussed in more detail in the following section.

High $\delta^{34}\text{S}$ values of barite were found in the veins from Mykonos. All of the $\delta^{34}\text{S}$ values are higher than that of Miocene seawater sulfate and higher than values reported by [Tombros et al. \(2015\)](#). Pronounced variations were observed in individual barite crystals from Cape Evros on Mykonos (28.1–37.2‰, sample 17MYV2_1), with higher $\delta^{34}\text{S}$ values corresponding to lower Sr concentrations. In the barite from Cape Evros, we observed three clusters of $\delta^{34}\text{S}$ values: $\delta^{34}\text{S}$ values >30 ‰ in coarse bladed barite associated with sulfides that occur as inclusions (Fig. 3.5K) or interstitially; $\delta^{34}\text{S}$ values ~ 28 ‰ in finer-grained barite (<1 cm) together with quartz (Fig. 3.4E barite vein in the center); and $\delta^{34}\text{S}$ values ~ 25 ‰ in fine to coarse bladed barite rich in Fe-oxides/hydroxides (Figs. 3.4F, 3.5L-M). In contrast, mineral separates of barite from the different zones of the vein at Panormos Bay have uniform $\delta^{34}\text{S}$ values and are similar to those from Cape Charos and the lowest $\delta^{34}\text{S}$ values of barite from Cape Evros (25–26‰). However, on the crystal scale the $\delta^{34}\text{S}$ values of barite from Panormos Bay vary from lower than Miocene seawater sulfate to 27.8‰ (Fig. 3.12). This was most likely due to preferential reduction of $^{32}\text{SO}_4$ in pore fluids, leading to residual enrichment of ^{34}S in sulfate. Partial reduction of the porewater sulfate might have been caused by ferrous Fe in the hydrothermal fluid ([Chiba et al., 1998](#); e.g., as suggested for the barite-gold orebodies on Wetar island, Indonesia: [Scotney et al., 2005](#)). In the absence of a reservoir of high $\delta^{34}\text{S}$ values, $\delta^{34}\text{S}$ values in barite that are higher than that of Miocene seawater might also imply a source in the wall rocks that was oxidized and leached, but this source has not been identified. Variation in the $\delta^{34}\text{S}$ values of barite on the crystal scale might also be an indication of local isotopic fractionation of S during

precipitation (e.g., during boiling, which has been suggested for several deposits: Table 3.1). Isotopic fractionation of S at the crystal scale during boiling has been documented in sulfide minerals in other epithermal vein systems (e.g., McKibben & Eldridge, 1990; Arehart et al., 1993).

Vein barite from Antiparos also has a range of $\delta^{34}\text{S}$ values from higher than that of Miocene seawater sulfate (20.3–26.3‰ at Prassovounia) to significantly lower (15.4–22.4‰ at Agios Georgios). The heavier S in barite from Prassovounia can be best explained by a modified seawater sulfate source or leaching of heavy S from the wall rocks, whereas at Agios Georgios a mix of seawater sulfate and sulfate derived from magmatic fluids is also possible. This is in contrast to the model by Kevrekidis et al. (2015), who proposed a mix of magmatic and meteoric fluid sources. The fluid inclusion work of Kevrekidis et al. (2015) showed large temperature and salinity variations (130–400°C, 4.8–15.7 wt% NaCl equiv.) in ore-stage vein quartz, which they considered to be evidence of dominantly magmatic fluids. However, we note that $\delta^{34}\text{S}$ values of barite are more indicative of a dominantly seawater-related system. These data suggest mixing of two fluid sources or possibly that barite postdates the main ore-forming event and records a shift in the dominant fluid source of the system.

3.6.2 Sulfide-sulfate relationships

The $\delta^{34}\text{S}$ values of galena coexisting with barite in the different deposits plot close to magmatic S values from the Aegean arc (Fig. 3.8). Galena was analyzed in the same samples as barite from Plaka at Lavrion, Galana and Triades on Milos, Cape Evros and Panormos Bay on Mykonos, and Prassovounia on Antiparos (Table 3.2). Galena and barite from Katsimouti and Profitis Ilias on Milos are from different samples but collected at the same site and therefore temperatures for the barite-galena equilibrium were not calculated

for these samples.

At Lavrion, S isotope values of galena are mostly positive in the carbonate-replacement mineralization at Plaka and Soureza and range from negative to positive values at Kamariza, similar to previously reported values (Table 3.1; Skarpelis et al., 2007; Bonsall et al., 2011). Bonsall et al. (2011) reported slightly lower $\delta^{34}\text{S}$ values for sulfides from Kamariza, possibly reflecting a temperature-dependent fractionation or disproportionation of magmatic SO_2 . Our $\delta^{34}\text{S}$ values of galena from Plaka show almost no variation (3.0–3.6‰), in contrast to the $\delta^{34}\text{S}$ values of barite from the same samples, which range between 2.1 and 24.5‰ (Fig. 3.8), demonstrating that much of the barite and galena analyzed in this study were not in isotopic equilibrium. $\delta^{34}\text{S}$ values of galena are similar to the lowest $\delta^{34}\text{S}$ values of barite, indicating a similar source of S for those samples (e.g., from a magmatic contribution or remobilization and inherited from stage I sulfides during barite formation). Skarn-associated galena from the polymetallic mineralization at Moutoulas on Serifos similarly shows only minor variations in $\delta^{34}\text{S}$ values (1.7–3.0‰), consistent with values for pyrite and sphalerite reported by St. Seymour et al. (2009b) but slightly lower than the values reported by Fitros et al. (2017). Those studies suggested a dominantly magmatic source for the S. Galena from the epithermal mineralization on Milos has $\delta^{34}\text{S}$ values from -1.1 to 2.2‰, whereas galena from epithermal veins at Katsimouti has only positive $\delta^{34}\text{S}$ values, and galena from Triades, Galana, and a drill core sample from Profitis Ilias has mainly negative values. Our $\delta^{34}\text{S}$ values for galena from Triades and Galana are slightly lower than the values obtained for sulfides by Hauck (1984); Marschik et al. (2010), and Schaarschmidt et al. (2021a) (Table 3.1). Marschik et al. (2010) suggested that the $\Delta^{34}\text{S}$ (sulfate-sulfide) between sulfide and barite at Triades and Galana was due to sulfate reduction from a seawater-dominated fluid under conditions of isotopic equilibrium. Galena from vein-type mineralization at Panormos Bay on Tinos was previously reported

to have strongly negative $\delta^{34}\text{S}$ values (Table 3.1; Tombros et al., 2007) that were explained by leaching of S from the underlying basement by a hydrothermal fluid derived from meteoric water. The low $\delta^{34}\text{S}$ values were attributed to metamorphic pyrite with $\delta^{34}\text{S}$ of -11.4‰ from a schist in the CBU (Table 3.3). Our sample of galena from a quartz vein at Panormos Bay on Tinos confirms the low $\delta^{34}\text{S}$ values, but there are no data for coexisting barite. At Cape Evros on Mykonos, Tombros et al. (2015) reported a wide range of $\delta^{34}\text{S}$ values for sulfides from 4.0 to 25.1‰, but the high $\delta^{34}\text{S}$ values of the sulfides were not found in our study. Galena in our study shows significant local variations with positive $\delta^{34}\text{S}$ values (3.9–4.3‰) at Cape Evros, similar to the magmatic S values, and negative $\delta^{34}\text{S}$ values (-1.7 to -1.0‰) at Panormos Bay. The range of values closely match the variation in $\delta^{34}\text{S}$ values of barite for the two locations with a consistent $\delta^{34}\text{S}$ of ~ 27 ‰. Tombros et al. (2015) proposed an early magmatic fluid source and later seawater-dominated system, whereas Skarpelis & Gilg (2006) suggested that the barite veins were related to basinal brines. Our data suggest a seawater-dominated fluid that interacted extensively with the basement, based on Sr isotopes of the whole-rock and veins leading to important local isotopic variations on Mykonos. Galena from two vein systems at Prassovounia on Antiparos has slightly negative $\delta^{34}\text{S}$ values (-1.8 to -0.2‰). Kevrekidis et al. (2015) proposed a link between the Miocene intrusion on Paros and the ore mineralization based on O and H isotopes from vein quartz, and a magmatic S component is supported by the low $\delta^{34}\text{S}$ values of barite from Agios Georgios in this study.

Temperatures were calculated for barite-galena equilibrium using fractionation factors from Ohmoto & Rye (1979) reported in Seal (2006) and S isotope data from the different deposits of the Cyclades. Some authors have suggested that sulfide and sulfate minerals were coprecipitated under conditions of isotopic equilibrium (e.g., Triades and Galana on Milos; Marschik et al., 2010). Calculated temperatures for barite-galena equilibrium in

these deposits vary between 259 and 281°C (samples 17MGA03 and 17MT03) and are slightly higher than temperatures estimated by [Smith et al. \(2018\)](#) from fluid inclusion studies in barite, quartz, and sphalerite but within the range of values of [Vavelidis & Melfos \(1998\)](#) from fluid inclusion data in barite of Triades (Table 3.1). In barite veins from Mykonos, inclusions of galena in barite, and vice versa, indicate these phases were in equilibrium in 17MYP1 and 17MYP4 from Panormos Bay and 17MYV2_1 from Cape Evros. Our data give equilibrium temperatures of 237 to 246°C at Panormos Bay and 246°C at Cape Evros. These are within the range of formation temperatures of hydrothermal chlorite in the cataclasites of the local detachment (203–258°C: [Menant et al., 2013](#)) and within error of the fluid inclusion trapping temperatures in quartz of the mineralized breccia (~230°C: [Skarpelis & Gilg, 2006](#)). Intergrowths of barite and galena in sample 17AP2 from Prassovounia on Antiparos also suggest coprecipitation (Fig. 3.4I). The calculated temperature for barite-galena equilibrium in this sample is 263°C, which is within the range of temperatures reported from fluid inclusion microthermometry in vein quartz from Agios Georgios on Antiparos (130–400°C: [Kevrekidis et al., 2015](#)). For the carbonate-hosted deposits (Lavriion) barite-galena pairs give unreasonably high temperatures, indicating that sulfide and sulfate minerals were not precipitated under equilibrium conditions and consistent with reversed fractionations calculated from previously published isotopic data ([Skarpelis et al., 2007](#); [Bonsall et al., 2011](#)).

3.6.3 Oxygen isotopes in barite

At hydrothermal temperatures, the O isotope composition of sulfate in barite equilibrates with water according to experimentally determined isotopic fractionation (e.g., [Kusakabe & Robinson, 1977](#); [Chiba & Sakai, 1985](#); [Seal et al., 2000](#)). However, the O isotope exchange rate of dissolved sulfate and water depends strongly on the temperature and pH of the

solution, with small fractionation factors at temperatures $>200^{\circ}\text{C}$ (Seal et al., 2000).

We observe a negative correlation between the $\delta^{18}\text{O}$ values and $\delta^{34}\text{S}$ values of barite, in general, and within individual deposit clusters (e.g., Mykonos and Antiparos: Fig. 3.9) that reflects the range of end-member fluids involved in the different mineralizing systems. Ore-forming fluids for the Cyclades mineral deposits acquired distinct O isotope signatures depending on the fluid source and the extent of interaction with wall rocks of different compositions ($\delta^{18}\text{O}$: 10–30‰; Figs. 3.9, 3.14; Table 3.3), which we define in the following. Although Turchyn & Schrag (2004) have documented marine barite $\delta^{18}\text{O}_{\text{SO}_4}$ excursions in the past 10 Myr (8–13‰), Markovic et al. (2016) suggest a more steady $\delta^{18}\text{O}_{\text{SO}_4}$ of 7 to 6‰ since 4 Ma. The present-day $\delta^{18}\text{O}_{\text{SO}_4}$ of surface seawater from Palaeochori Bay on Milos is 9‰ (Gilhooly et al., 2014). The O isotope compositions in Cycladic barite are distinguishable from a pure meteoric water source (-8 ± 7 ‰; Table 3.3). Fumarolic vapors from Nisyros island have low $\delta^{18}\text{O}$ values from 3.0 to 4.9‰ (Marini et al., 2002). The majority of whole-rock $\delta^{18}\text{O}$ values of the Miocene intrusions on Serifos and Mykonos are between 9.2 and 11.5‰ (Altherr et al., 1988; Altherr & Siebel, 2002), and whole-rock $\delta^{18}\text{O}$ values of Quaternary volcanic rocks from Milos are generally between 8.0 to 9.5‰, with values up to 11.6‰ in glass (Briqueu et al., 1986). The basement lithologies in the Cyclades have whole-rock $\delta^{18}\text{O}$ values that are generally higher than for magmatic rocks, although the data are limited (Table 3.3).

The $\delta^{18}\text{O}$ values of barite from the carbonate-replacement and breccia-style deposits at Lavrion and carbonate-hosted vein-type deposits of Serifos range from 8 to 16‰, consistent with fluid-rock interaction with an isotopically heavy source like the carbonate host rocks. Unaltered carbonates in the Cyclades have $\delta^{18}\text{O}$ values of >20 ‰ (Table 3.3), whereas calcite and dolomite from the deposits have $\delta^{18}\text{O}$ values of ~ 15 ‰ (Bonsall et al., 2011; Berger et al., 2013), consistent with mixing of heavy O from the carbonaceous wall rocks

with lighter O in a magmatic fluid and/or surface-derived water (seawater $\pm$ meteoric). The $\delta^{18}\text{O}$ values of barite from Serifos are within the range of values reported by [Salemink \(1985\)](#) who also proposed a magmatic fluid source with wall-rock interaction. The $\delta^{18}\text{O}$ values of barite from the epithermal deposits on Milos range from 9 to 11‰ and are similar to the values reported by [Marschik et al. \(2010\)](#) of barite from Triades and Galana. [Ivarsson et al. \(2019\)](#) reported a broader range of $\delta^{18}\text{O}$ values of barite from Vani and linked these to a seawater sulfate source modified through BSR. The narrow range of $\delta^{18}\text{O}$ values of barite from this study are close to the values of modern marine sulfate of the Palaeochori Bay on southern Milos (Fig. 3.9). In contrast to the $\delta^{34}\text{S}$ values, $\delta^{18}\text{O}$ values of barite from Katsimouti are not distinguishable from those of barite at other occurrences on Milos, although variable degrees of boiling between the deposits should have resulted in differences in the $\delta^{18}\text{O}$ values of barite ([Huston, 1997](#)). Similarities in the O isotope composition of barite and Quaternary volcanic rocks indicate that magmatic fluids could also have played a role in ore formation at Katsimouti. The polymetallic veins on Mykonos and Antiparos have $\delta^{18}\text{O}$ values of barite that range from 4 up to 12‰. High $\delta^{18}\text{O}$ values are consistent with a mix of seawater $\pm$ magmatic-hydrothermal fluids. Low $\delta^{18}\text{O}$ values from our study (Cape Evros, Mykonos) are higher than the $\delta^{18}\text{O}$ values of barite reported by [Tombros et al. \(2015\)](#). [Tombros et al. \(2015\)](#) reported low $\delta^{18}\text{O}$ values ($<4\text{‰}$) for vein barite and slightly higher values for silica-cap barite ($\sim 5\text{‰}$) and vein quartz (6.4–9.5‰) at Cape Evros. Whole-rock $\delta^{18}\text{O}$ values of the Miocene intrusion from Mykonos vary between 4 to 11.5‰ ([Altherr et al., 1988](#)), with the lowest values in altered rocks near the contact with metapelites and gneisses of the CBU and Cycladic Basement, which could explain the low values from our study and those reported by [Tombros et al. \(2015\)](#). Low $\delta^{18}\text{O}$ values ($<6\text{‰}$) for some barite on Mykonos and Antiparos might also be related to a meteoric water component or basinal brines as suggested by [Skarpelis & Gilg \(2006\)](#). However,

this contrasts with the observations based on the $\delta^{34}\text{S}$ values, which indicate a modified seawater source with wall-rock equilibration. This is further supported by the data on Sr isotopes in barite, discussed below.

3.6.4 Strontium isotopes and crustal sources

In Figure 3.11 we compiled the Sr isotope compositions of potential source rocks in the Cyclades, as well as the composition of Miocene to present-day seawater. Since 12 Ma, the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of seawater has increased from 0.7088 to 0.7092 (e.g., [Veizer, 1989](#); [Hodell et al., 1991](#); [Farrell et al., 1995](#)). Values for the intrusions and volcanic rocks are recalculated to their initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios based on their reported ages, which are further described in the Supplementary Information (3.A.2). Miocene Cycladic granitoids have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.709 to 0.712. [Stouraiti et al. \(2010\)](#) suggested a crustal source for Sr in the intrusions, derived from a mix of radiogenic gneisses and less radiogenic metabasites and marbles. The underlying Carboniferous to Cretaceous basement rocks across the Cyclades also have a wide range of Sr isotope ratios, with generally low $^{87}\text{Sr}/^{86}\text{Sr}$ in metabasites and marbles (≤ 0.709), high $^{87}\text{Sr}/^{86}\text{Sr}$ (0.716–0.766) in the gneisses of the Cycladic Basement, and intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ (0.708–0.739) in clastic metapelites of the CBU. Quaternary volcanic rocks along the active volcanic arc, in contrast, have low $^{87}\text{Sr}/^{86}\text{Sr}$ consistent with a mantle source at Milos and neighboring Santorini and Kolumbo (0.704–0.707).

The range of Sr isotope ratios of barite from carbonate-hosted deposits at Plaka, Lavrion (0.7092–0.7108) indicates a mix of different upper crustal Sr sources. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Plaka granodiorite ([Altherr et al., 1988](#); [Stouraiti et al., 2010](#)) and barite overlap, indicating that they could be a source of Sr for the associated barite (Fig. 3.11). However, a spatial relationship to pegmatitic dikes, which are enriched in Ba and Sr (>700 ppm and >250 ppm, respectively; [Skarpelis et al., 2008](#); [Bonsall et al., 2011](#); [Berger et al., 2013](#))

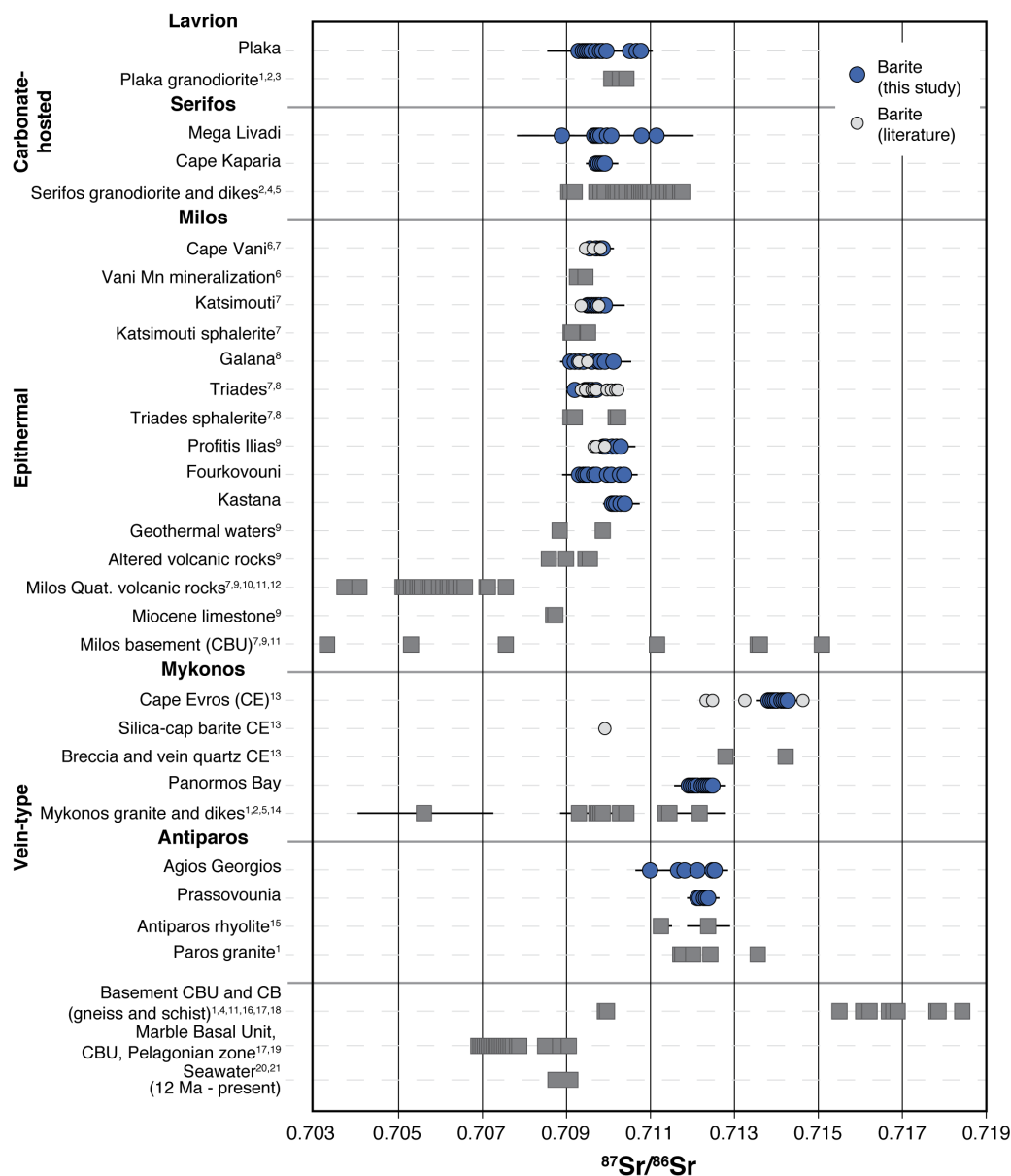


Fig. 3.11: Strontium isotope ratios of barite from different mineral deposit types in the Cyclades Mineral District from this study (blue) compared to published ratios (grey) and selected reservoirs of Sr (squares). Values for the intrusions and volcanic rocks are represented by their initial $^{87}\text{Sr}/^{86}\text{Sr}$ composition (Paros: 11.5 Ma, Mykonos: 10 Ma, Serifos: 9.5 Ma, Lavrion: 8.3 Ma, Antiparos: 4.3 Ma), as explained in the Appendix 3.A.2. CB: Cycladic Basement, CBU: Cycladic Blueschist Unit, CE: Cape Evros. Data sources: ¹Stouraiti et al. (2010), ²Altherr & Siebel (2002), ³Juteau et al. (1986), ⁴Stouraiti et al. (2018), ⁵Altherr et al. (1988), ⁶Hein et al. (2000), ⁷Schaarschmidt et al. (2021a), ⁸Marschik et al. (2010), ⁹Naden et al. (2005), ¹⁰Barton et al. (1983), ¹¹Briqueu et al. (1986), ¹²Gülen (1990), ¹³Tombros et al. (2015), ¹⁴Altherr et al. (1982), ¹⁵Innocenti et al. (1982), ¹⁶McGrath et al. (2017), ¹⁷Klaver (2016), ¹⁸Buettner et al. (2005), ¹⁹Gärtner et al. (2011). Strontium ratios for seawater are from ²⁰Hodell et al. (1991) and ²¹Farrell et al. (1995).

suggests that they may have been a more likely source, although no Sr isotope data are available for these rocks. Barite with $^{87}\text{Sr}/^{86}\text{Sr}$ lower than the Plaka granodiorite could be explained by Miocene seawater mixing with the barite-forming fluids or interactions with the immediate carbonate host rock (marble, Fig. 3.11), which is supported by the $\delta^{18}\text{O}$ values of barite, whereas higher $^{87}\text{Sr}/^{86}\text{Sr}$ values are indicative of an interaction of the hydrothermal fluid with the radiogenic metapelites of the CBU. Barite from the carbonate-hosted deposits on Serifos has a narrow range of Sr isotope ratios (0.7097–0.7108), except for some outliers. The $^{87}\text{Sr}/^{86}\text{Sr}$ compositions are close to those of the nearby granitoid intrusions (Serifos granodiorite and dikes in Fig. 3.11; Altherr et al., 1988; Altherr & Siebel, 2002; Stouraiti et al., 2010, 2018), suggesting little or no input from the immediate carbonate host rock.

The range of Sr isotope ratios of barite in epithermal deposits on Milos can be explained by a mixture of a seawater source and an upper crustal source of radiogenic Sr (e.g., Hein et al., 2000; Naden et al., 2005; Marschik et al., 2010; Schaarschmidt et al., 2021a). Quaternary volcanic rocks and Neogene sediments from Milos have much lower whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ values than barite (Fig. 3.11). Altered volcanic rocks show a significant shift in $^{87}\text{Sr}/^{86}\text{Sr}$ closer to the values for local geothermal waters (Naden et al., 2005). Schists, glaucophane schists, and eclogites of the crystalline metamorphic basement (CBU) on Milos have a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7033–0.7151; Briquieu et al., 1986; Naden et al., 2005; Schaarschmidt et al., 2021a). We observed small variations in Sr isotope ratios of the different barite occurrences on Milos. These are potentially related to the amount of mixing between seawater and this type of hydrothermal fluid or the degree of interaction of the hydrothermal fluid with different basement rock types. Local variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of barite can also be caused by reaction of the hydrothermal fluid with different proportions of the metamorphic basement and the Quaternary volcanic

rocks as proposed by [Schaarschmidt et al. \(2021a\)](#). Lower $^{87}\text{Sr}/^{86}\text{Sr}$ values of sphalerite from Milos (Fig. 3.11; [Marschik et al., 2010](#); [Schaarschmidt et al., 2021a](#)) compared to barite support the interaction of the hydrothermal fluid with the metamorphic basement and Quaternary lavas. Strontium isotope ratios of barite at Galana, and to a lesser extent at Triades, are permissive of Sr being partially derived from the volcanic rocks and the metamorphic basement, whereas other barite occurrences on Milos (e.g., barite from Profitis Ilias, Fourkovouni, and Kastana) require a more radiogenic crustal source in the crystalline metamorphic rocks.

The Sr isotope ratios of vein barite from Mykonos and Antiparos are completely different from Milos, Serifos, and Lavrion (Fig. 3.11). Barite from Cape Evros on Mykonos is isotopically homogeneous, with $^{87}\text{Sr}/^{86}\text{Sr}$ values averaging ~ 0.7141 . [Tombros et al. \(2015\)](#) reported a wider range of $^{87}\text{Sr}/^{86}\text{Sr}$ for barite from a banded barite vein at Cape Evros (0.7124–0.7146) and one sample from the siliceous cap with 0.7095. Barite from Panormos Bay, with $^{87}\text{Sr}/^{86}\text{Sr}$ values averaging ~ 0.7122 , has distinctly less radiogenic Sr than barite from Cape Evros (Fig. 3.11). Significant local variations in the isotopic composition of the mineralization at Panormos Bay and Cape Evros were previously reported by [Wind et al. \(2020\)](#), based on the Pb isotope composition of galena. In general, however, the Sr in barite from Mykonos is too radiogenic to have been derived from the local Miocene granitoid (Mykonos granite and dikes in Fig. 3.11). [Altherr et al. \(1988\)](#) suggested metapelites and gneisses of the basement were a likely source of radiogenic Sr for the granitoid. In contrast to the values from [Altherr et al. \(1988\)](#), [Tombros et al. \(2015\)](#) reported significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for a sample of a K-feldspar-biotite monzogranite and silicified monzogranite (0.7303 and 0.7138, respectively) from Cape Evros. The possible role of basement rocks, as well as metabasites, and Miocene conglomeratic sequences in the hanging wall cannot be assessed owing to the lack of whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ measurements of those rocks.

The Sr isotope ratios of vein barite from Antiparos similarly indicate a radiogenic source with some variations between the different deposits on the same island. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of barite from Agios Georgios and Prassovounia are within the range of values for the Pliocene rhyolite on Antiparos (Fig. 3.11; Innocenti et al., 1982). However, a trend towards more radiogenic Sr in barite, which is accompanied by an increase in Sr content and $\delta^{34}\text{S}$ values at Agios Georgios (App. Fig. 3.A.3), likely points to a change in fluid composition related to leaching of Sr from the radiogenic basement. In general, the Sr concentrations of the basement lithologies (8–246 ppm: gneiss and schist; Table 3.3) are higher than in the Pliocene rhyolite (≤ 10 ppm: Innocenti et al., 1982), although S-type intrusions on Paros have Sr isotope ratios similar to those of the Pliocene rhyolite and higher concentrations of Sr and Ba (42–383 ppm and 87–992 ppm, respectively: Stouraiti et al., 2010). Kevrekidis et al. (2015) have suggested that these intrusions were a potential source of the mineralizing fluids for the polymetallic veins on Antiparos. However, no age data exist to link the mineralization to the intrusions. Therefore, the Pliocene rhyolites that are spatially related to the veins appear to be a more likely source of Sr and S.

To summarize, for barite with a dominant seawater source (e.g., Milos, Mykonos, and Antiparos) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are homogeneous within deposits but vary between the different deposits on the same island, suggesting interaction of the hydrothermal fluid with the immediate host rock. However, in general, the broadly similar Sr isotope composition of Cycladic barite across the sampled region suggests that the basement may have a larger influence than the immediate host rocks as the dominant source of Sr. Strontium isotope ratios of barite define different crustal sources for the central Cyclades ($^{87}\text{Sr}/^{86}\text{Sr} \geq 0.711$) and the western Cyclades ($^{87}\text{Sr}/^{86}\text{Sr} \leq 0.711$) consistent with the regional basement influence described in Wind et al. (2020), and the isotopic signatures of the mineral occurrences in the west Cyclades are more homogeneous than in the central Cyclades.

3.6.5 Geochemical and isotopic zoning in barite

Strontium concentrations in Cycladic barite are high in comparison to ore-associated barite in many other deposit types (e.g., [Griffith et al., 2018](#)), although barite in VMS deposits has similar concentrations of Sr (e.g., [Jamieson et al., 2016](#); [Lajoie et al., 2020](#)). In general, higher concentrations of Sr are found in barite from deposits with an obvious seawater component in the hydrothermal fluids (e.g., Milos). However, isotopic data suggest that most of the Sr was leached from the basement rocks and not derived solely from seawater. The narrow range of SrO (<1–3 wt%: Fig. 3.7) in barite associated with sulfides indicates mostly uniform hydrothermal fluid concentrations of Sr during barite formation. Variations in Sr content in individual barite crystals are either due to small changes in the fluid compositions, mixing of fluids, or the temperature dependence of Ba-Sr partitioning ([Hanor, 2000](#) and references therein). Later silicification and/or circulation of post-ore hydrothermal fluids also can cause a decrease in Sr concentrations, which is often observed at the crystal rims (Fig. 3.6D-E). Concentrations of other trace elements are generally very low, similar to values reported for barite from ancient and modern hydrothermal vents (e.g., [Hanor, 2000](#); [Jamieson et al., 2016](#); [Lajoie et al., 2020](#)).

On a sample and crystal scale we commonly observed geochemical and isotopic variations that indicate a change in fluid composition during barite precipitation. Variations in the isotopic composition of Cycladic barite are often accompanied by changes in the Sr concentration. Barite from vein systems at Panormos Bay on Mykonos shows geochemical variations that can be best explained by fluctuations in temperature. In single crystals from these samples, a positive correlation between the Sr content and $\delta^{34}\text{S}$ values was observed (Fig. 3.12B), while the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remained constant (Fig. 3.12C). One possible explanation is crystallization in a closed system with a decrease in temperature.

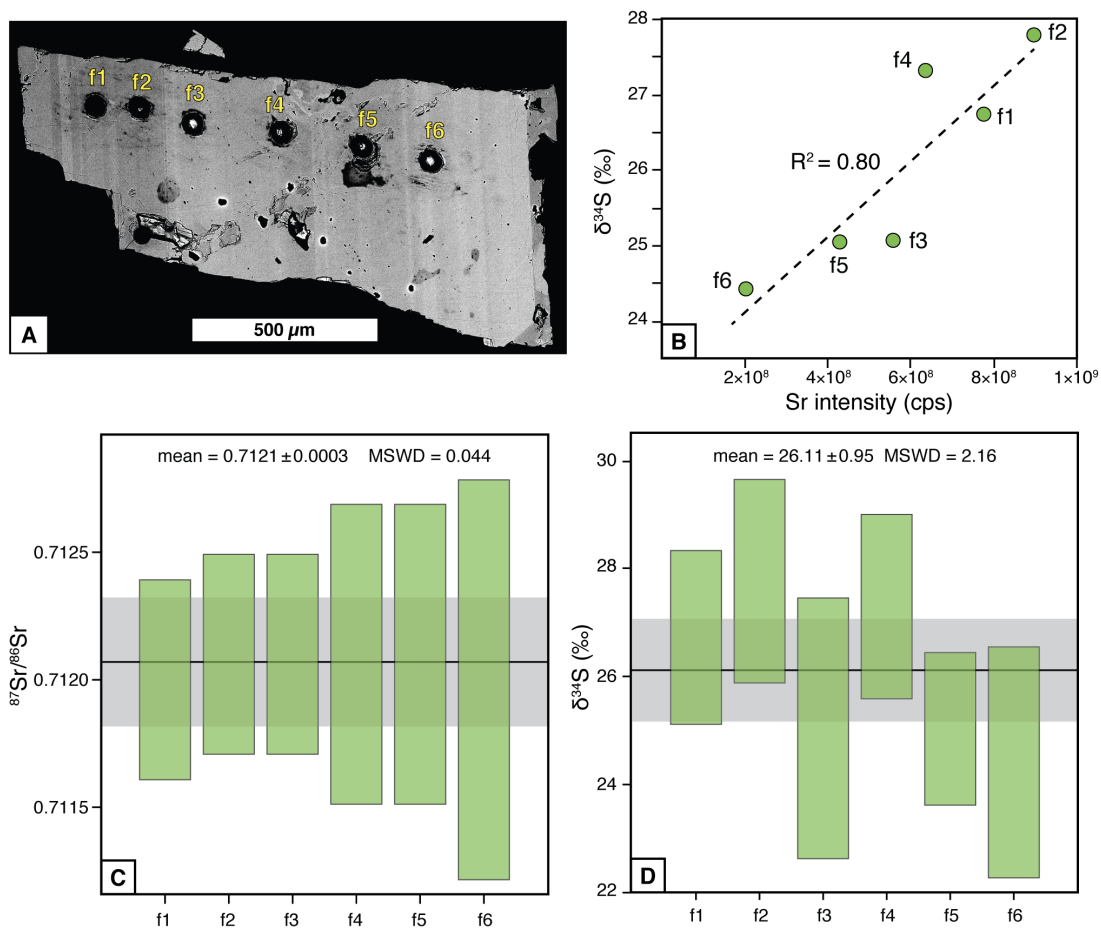


Fig. 3.12: A: Backscattered-electron microscopy image of a zoned barite crystal (sample 17MYP1, grain f) with the analytical spots from the Panormos Bay vein-type mineralization, Mykonos. B: $\delta^{34}\text{S}$ values vs. Sr content (approx. 0.6–2.4 wt% Sr) for the six ablations across the crystal, with a positive correlation between $\delta^{34}\text{S}$ values and Sr content. C-D: Variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{34}\text{S}$ values, respectively, for the six ablations. C and D plotted using IsoplotR software (Vermeesch, 2018) where MSWD is the mean square weighted deviations. Despite constant Sr isotope ratios, a positive correlation between the $\delta^{34}\text{S}$ values and Sr concentration indicates a change in fluid composition and/or temperature.

Temperature-controlled variations in the Sr content of barite were previously suggested by [Jamieson et al. \(2016\)](#) and [Lajoie et al. \(2020\)](#). Another possible explanation is that hotter hydrothermal fluids have the ability to leach more Sr out of the surrounding host rock, potentially modifying the fluid composition.

In barite samples from the carbonate-hosted deposits at Plaka, Lavrion, we observed an increase in $\delta^{34}\text{S}$ values with a strong decrease in the Sr content (Fig. 3.13C) and an increase in $^{87}\text{Sr}/^{86}\text{Sr}$. The pronounced zoning is indicative of a change in fluid sources, consistent with models of the mineralization at Lavrion (e.g., [Bonsall et al., 2011](#); [Scheffer et al., 2017, 2019](#)). We propose that the low $\delta^{34}\text{S}$ values and less radiogenic Sr observed in barite cores (Fig. 3.13A-E) point to a magmatic-dominated fluid with interaction with the carbonaceous wall rock, whereas the high $\delta^{34}\text{S}$ values and higher $^{87}\text{Sr}/^{86}\text{Sr}$ in the rims point to a fluid dominated by seawater and modified by additional leaching of Sr from a radiogenic basement source. A comparison of all samples from Plaka, Lavrion (Fig. 3.13E), also supports the suggestion of a positive correlation between $\delta^{34}\text{S}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ highlighting a shift in the dominant fluid source.

We also observed the reverse trend in some barite (e.g., Agios Georgios on Antiparos: App. Fig. 3.A.3) where $\delta^{34}\text{S}$ values decrease with decreasing Sr content and decreasing $^{87}\text{Sr}/^{86}\text{Sr}$. Changes in both isotopic systems and Sr concentrations are recorded at the mineral scale in response to episodic mixing of end-member fluids. In some cases, the transition from coarse barren barite to smaller ore-associated barite crystals (e.g., Galana on Milos) shows decreasing Sr from >1.5 wt% to <1 wt% with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.7092 to 0.7099 but constant $\delta^{34}\text{S}$. As suggested above, the low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios could be explained by Sr from present seawater or the Quaternary volcanic rocks, whereas the more radiogenic values imply mixing with a fluid that had equilibrated with Sr from the basement.

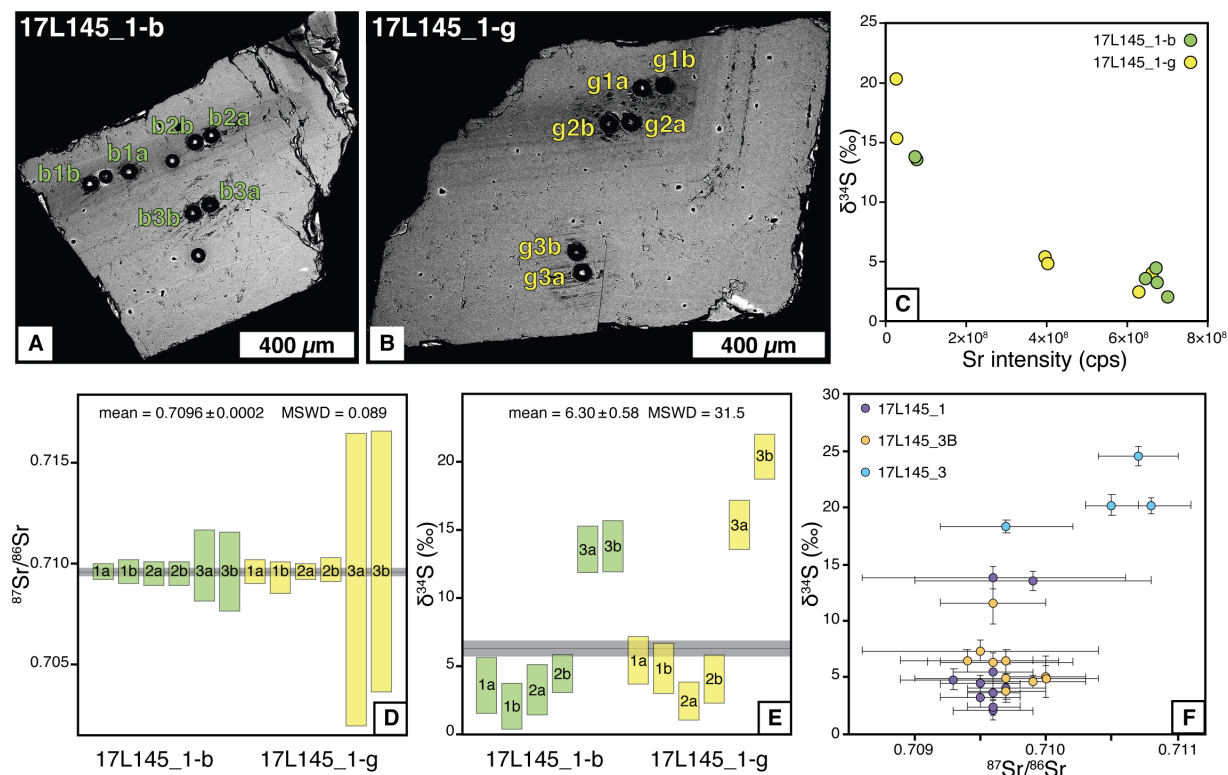


Fig. 3.13: A-B: Backscattered-electron microscopy images of two zoned barite crystals of the sample 17L145_1 from the carbonate-hosted mineralization at Plaka, Lavrion. Shown are the ablation craters of 50 μm of the repeated sequential $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ analyses and the 44 μm ablation craters of the trace element analyses. C: $\delta^{34}\text{S}$ values vs. Sr content (approx. 0.1–2.1 wt% Sr) for the twelve ablations across the grains, with a negative correlation between $\delta^{34}\text{S}$ values and Sr content. D-E: Variation in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{34}\text{S}$ values for the twelve ablations. Results of crystal b are shown in green and for crystal g in yellow. Significant increase in $\delta^{34}\text{S}$ values towards the rim correlates with low concentrations in Sr and consequently larger errors in the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. D and E plotted using IsoplotR software Vermeesch (2018), where MSWD is the mean square weighted deviations. F: $\delta^{34}\text{S}$ values vs. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for all samples from Plaka (Adit No. 145) analyzed by LA-MC-ICP-MS methods. Ablations within zones of low Sr concentrations ($n: 4; <7 \times 10^7$ cps) are not included. High $\delta^{34}\text{S}$ values correlate with more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting a change from a magmatic-hydrothermal fluid to a modified seawater-dominated fluid with host rock interaction.

3.7 Summary and conclusions

Fluid mixing is a fundamental process in many hydrothermal ore deposits, including the spectrum of mineral deposit types in the Cyclades Mineral District (Table 3.1). However, it is challenging to draw a comparison of fluid mixing processes between the broad range of deposit types because of the variety of styles of mineralization, complicating the interpretations of their origins. In this study, we examined one mineral, hydrothermal barite, which occurs in all of the deposits and records mixing of different magmatic to surface-derived (seawater $\pm$ meteoric) fluids. In most cases, barite precipitation was close to the terminal stage of mineralization, where mixing was coincident with (or caused) the end of base metal deposition, whereas in others (e.g., Lavrion District) barite formation occurred over multiple stages and involved more diverse fluid sources (Bonsall et al., 2011; Scheffer et al., 2017, 2019), including magmatic, meteoric, and seawater-derived fluids. The distinct isotopic signatures of barite can be used to trace this complex interplay of different fluid and crustal sources. In particular, the geochemical and isotopic compositions reveal that seawater was a source of sulfate in many of the deposits, but magmatic and meteoric fluids also played a role.

Figure 3.14 is a summary of the inferred fluid and wall-rock sources for the different deposit types in the Cyclades Mineral District. They include (1) a direct magmatic source (e.g., in carbonate-hosted deposits at Mega Livadi, Serifos), (2) magmatic fluids that have reacted with the carbonates (marble) of the Basal Unit and/or CBU (Cape Kaparia, Serifos; Stage I of Plaka, Lavrion), (3) magmatic fluids that have mixed with seawater and reacted with the carbonates (marble) of the Basal Unit and/or metapelites of the CBU (Stage II of Plaka and Villia, Lavrion), (4) magmatic (likely Pliocene) and seawater fluids that have reacted with the basement gneisses or schists of the CBU (Agios Georgios,

Table 3.3: Characteristics of potential hydrothermal fluids and source rocks in the Cyclades, Greece.

	$\delta^{34}\text{S}_{VCDT}$ ‰	$\delta^{18}\text{O}_{VSMOW}$ ‰	δD_{VSMOW} ‰	Sr content (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>Fluids</i>					
Magmatic (Miocene intrusions)	/	4–11.5 ^{1,2}	-112 to -105 ^{1,2}	200–520 ^{3,4,5}	0.7086–0.7116 ^{1,2,3,4,5,6}
Magmatic (Quaternary volcanic rocks)	0.1–17.5 ⁷ , 2.5–5.1 ^{8,*}	6.5–12.7 ⁹ , 3.0–4.9 ^{8,*}	-12.9 to -8.4 ^{8,*}	50–650 ^{9,10,11,12}	0.7038–0.7071 ^{9,10,11,12,13}
Seawater (late Miocene-Pliocene)	21.2–22.6 ^{14,15}	7–13 ^{14,15,16}	/	/	0.7088–0.7091 ^{17,18}
Modern Mediterranean seawater (Palaeochori Bay)	20.7–21.2 ^{19,20}	9–9.4 ^{19,20} , 1.1 ^{21,**}	7.2 ^{21,**}	~8–10 ²¹	0.7091–0.7092 ¹⁷
Meteoric	/	-8 ± 7 ^{22,23}	-50 ± 20 ^{22,23}	/	/
Metamorphic	-7.4 to 3.3 ²⁴	/	-65 to -56 ²⁵	/	/
<i>Crustal sources</i>					
Schists and metapelites (CBU)	-11.4 ^{26,***} , 0.5–18.2 ⁷	18.8 ^{26,***}	-56 ^{26,***}	29–246 ^{9,12,27}	0.7076–0.7392 ^{9,12,27,28}
Metabasites (Pelagionian zone, CBU)	/	5.2–9.0 ²⁹	-64 to -33 ²⁹	1–425 ^{4,5,9,29,30}	0.7051–0.7105 ^{4,5,9,30}
Carbonates (Pelagionian zone, CBU, Basal Unit)	/	20–29 ^{31,32}	/	50–650 ^{9,27,32}	0.7069–0.7091 ^{9,27,32}
Gneiss (Cycladic Basement)	/	10–12.7 ^{5,33}	/	8–186 ^{5,27,33,34}	0.7155–0.7663 ^{5,27,33,34}

Note: Oxygen and S values are reported for seawater sulfate if not indicated otherwise; / indicates no data available
Abbreviations: CBU: Cycladic Blueschist Unit, VCDT: Vienna Cañon Diablo Troilite, VSMOW: Vienna standard mean ocean water

* $\delta^{34}\text{S}$ of fumarolic H_2S , and $\delta^{18}\text{O}$ and δD of fumarolic vapors from Nisyros.

** $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ from Milos seawater.

*** $\delta^{34}\text{S}$ from a metamorphic pyrite in a schist of the CBU; $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ for metamorphic muscovite at 400°C

Data sources: ¹Altherr et al. (1982), ²Altherr et al. (1988), ³Altherr & Siebel (2002), ⁴Stouraiti et al. (2010), ⁵Stouraiti et al. (2018), ⁶Juteau et al. (1986), ⁷Hubberten et al. (1976), ⁸Marini et al. (2002), ⁹Briqueu et al. (1986), ¹⁰Barton et al. (1983), ¹¹Gülen (1990), ¹²Naden et al. (2005), ¹³Innocenti et al. (1982), ¹⁴Burdett et al. (1989), ¹⁵Markovic et al. (2016), ¹⁶Turchyn & Schrag (2004), ¹⁷Farrell et al. (1995), ¹⁸Hodell et al. (1991), ¹⁹Böttcher et al. (1998), ²⁰Gilhooly et al. (2014), ²¹Price et al. (2013), ²²Craig (1961), ²³Dotsika et al. (2010), ²⁴Walters et al. (2019), ²⁵Siebenaller et al. (2013), ²⁶Tombros et al. (2007), ²⁷Klaver (2016), ²⁸Schaarschmidt et al. (2021a), ²⁹Cooperdock et al. (2018), ³⁰Stouraiti et al. (2017), ³¹Berger et al. (2013), ³²Gärtner et al. (2011), ³³McGrath et al. (2017), ³⁴Buettner et al. (2005).

Antiparos), (5) seawater-dominated fluids with magmatic $\pm$ meteoric contributions that reacted with the basement gneisses/metapelites and/or rock types in the hanging wall (Prassovounia, Antiparos; Cape Evros, Cape Charos and Panormos Bay, Mykonos), (6) seawater-dominated fluids that have reacted with metapelites of the CBU and Quaternary volcanic rocks (Cape Vani, Kalogries, Galana-Triades, Profitis Ilias, Fourkovouni, and Kastana, Milos), (7) seawater-dominated fluids with Quaternary magmatic contributions that have reacted with metapelites of the CBU (Katsimouti, Milos).

Strontium isotope ratios support the strong influence of the underlying basement in the source of labile elements (e.g., Ba and Sr) in barite and correlate with the regional trends in Pb isotope composition observed in Cycladic galena by [Wind et al. \(2020\)](#). We show a clear division between $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.711$ values in barite from Antiparos and Mykonos in the central Cyclades and $^{87}\text{Sr}/^{86}\text{Sr} \leq 0.711$ in barite from Lavrion, Serifos, and Milos in the west Cyclades, separated by the Trans-Cycladic Thrust (Fig. 3.1). This division tracks the exposures of the LCBN and UCBN.

Figure 3.2 schematically illustrates the inferred fluid and crustal sources of the different barite occurrences in the Cyclades from the late Miocene into the Quaternary. At Lavrion [1–2], Serifos [3], and Mykonos [4–5] regional detachment faults provided pathways for the deep circulation of the hydrothermal fluids. On Antiparos [6–7] and Milos [8–10] mixing of surface-derived fluids, predominately seawater, and magmatic fluids was facilitated by normal faults. In the following, the numbers in brackets correspond to the numbers in Figure 3.2.

Stage II barite mineralization at Plaka [1] and Villia [2] at Lavrion has a wide range of $\delta^{34}\text{S}$ values, consistent with a range of S sources. Individual crystals of barite show strong zoning in $\delta^{34}\text{S}$, Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, with low $\delta^{34}\text{S}$ close to magmatic values in the core and high $\delta^{34}\text{S}$ close to seawater sulfate at the rim. Barite with low $\delta^{34}\text{S}$

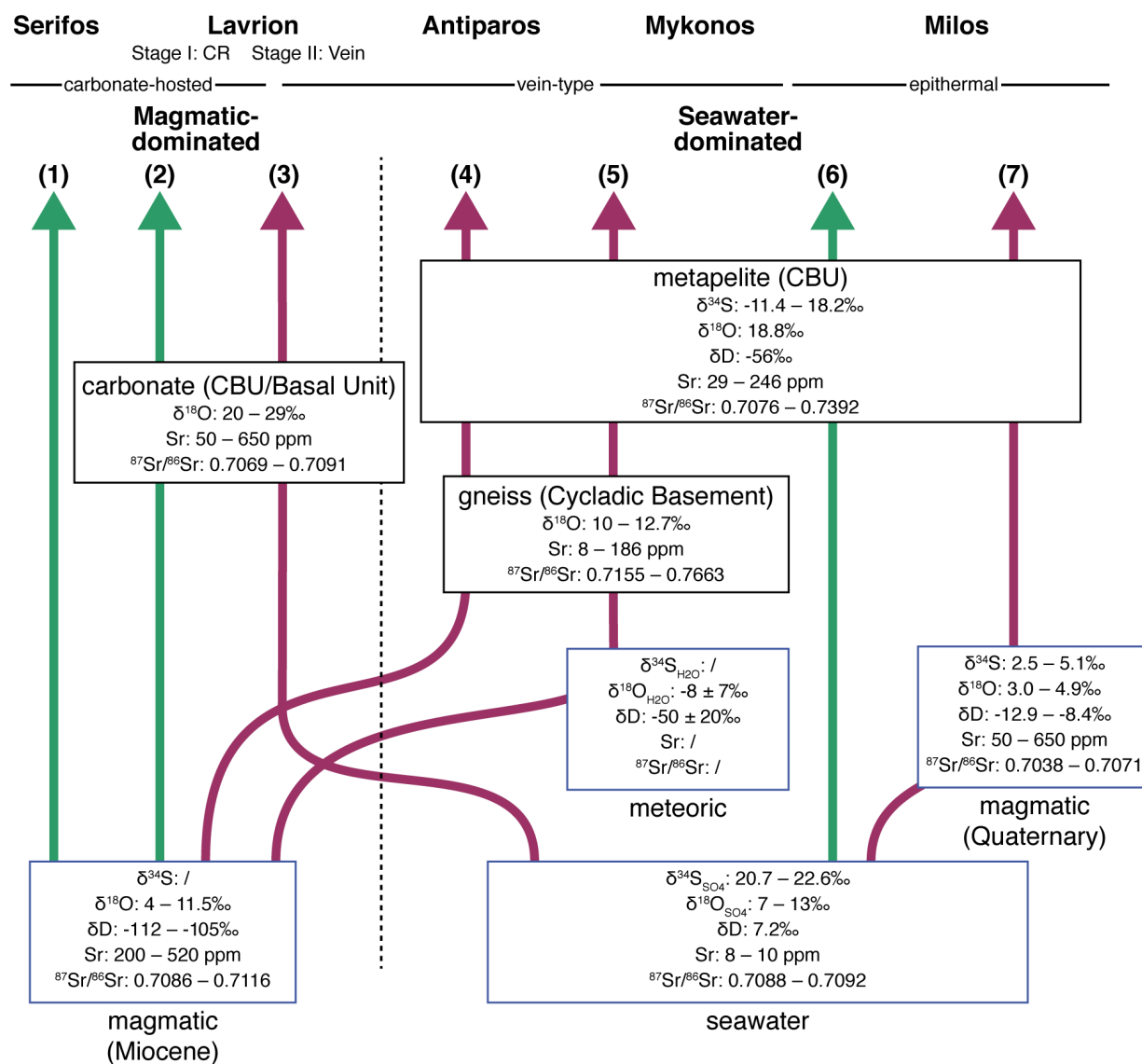


Fig. 3.14: Flow chart illustrating the potential fluid and crustal sources in the Cyclades. Green arrows indicate pure magmatic or seawater sources with wall rock interaction; purple arrows indicate mixed fluid sources with wall rock interaction. Numbers correspond to those listed in the Summary and Conclusion 3.7; see text for further discussion. Data sources are included in Table 3.3. CBU: Cycladic Blueschist Unit, CR: carbonate-replacement.

values but high $\delta^{18}\text{O}$ values, similar to the ore-hosting carbonates (Bonsall et al., 2011; Berger et al., 2013), indicates that the magmatic fluids likely exchanged with the carbonate wall rocks, whereas a shift to high $\delta^{34}\text{S}$ values and intermediate $\delta^{18}\text{O}$ values is permissive of a seawater-dominated fluid. Strontium isotope ratios are similar to the Miocene intrusions and interpreted to record dominantly magmatic hydrothermal fluids, where small variations are likely related to the interaction of the hydrothermal fluids with the wall rocks (e.g., marbles and/or metapelites of the CBU). Scheffer et al. (2017, 2019) observed similar variations in their study of carbonates from Lavrion, which were interpreted to have formed in a magmatic-dominated system that evolved to later-stage breccia and vein mineralization involving meteoric water and evaporated seawater.

Barite from carbonate-hosted, intrusion-related veins at Serifos [3] has a very narrow range of $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ values, suggesting that mixing of fluids was limited. As observed at Lavrion, the low $\delta^{34}\text{S}$ and intermediate to high $\delta^{18}\text{O}$, as well as $^{87}\text{Sr}/^{86}\text{Sr}$ values similar to the granitoid intrusion, suggest a magmatic fluid with minor interaction with the carbonate wall rocks. These relationships are similar to the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ systematics of barite in other well-known high-temperature carbonate-replacement and skarn deposits, such as in the Colorado Mineral Belt and in Peru (e.g., Stegen et al., 1990; Thompson & Beatty, 1990; Baumgartner et al., 2008).

On Mykonos, the isotopic signatures of barite from Cape Charos and Cape Evros [4] are distinct from those at Panormos Bay [5]. At Cape Evros, high $\delta^{34}\text{S}$ values of barite are consistent with a fractionated Miocene seawater-dominated fluid source. To explain the range of O isotope values, especially low $\delta^{18}\text{O}$ values of barite from Cape Evros close to the values from meteoric water, basinal brines are a possible source, but also interaction with the immediate host rock could cause the low $\delta^{18}\text{O}$ values. Local variations in Sr isotope ratios suggest distinct sources of Sr, such as leaching of the basement gneisses or

the Miocene conglomeratic sequence (Neogene basin sediments in Fig. 3.2), as observed at Panormos Bay. Differences in the metal sources at Panormos Bay and Cape Evros were previously reported by Wind et al. (2020) based on the Pb isotope ratios and trace element concentrations of galena. Also, Lahti & Govett (1981) observed local variations in the geochemistry of whole-rock samples, with an enrichment in Cu, potentially related to the metabasites of the Pelagonian zone in the hanging wall of the local detachments. These isotopic and geochemical differences between Cape Evros and Panormos Bay correlate with the position of an inferred N-S-trending normal fault in the center of the island (Lecomte et al., 2010; Denèle et al., 2011).

On Antiparos, specifically Agios Georgios [7], a mixture of magmatic and seawater-derived fluids is suggested to explain the $\delta^{34}\text{S}$ values of barite, whereas at Prassovounia [6] seawater was dominant. Low $\delta^{18}\text{O}$ values of barite from Prassovounia, similar to the values of barite from Cape Evros on Mykonos, might suggest a contribution of meteoric water or indicate interaction of the hydrothermal fluid with the host rock. The nearby Pliocene rhyolite intrusion (Fig. 3.2) is a probable source of the magmatic fluid components at Agios Georgios, although Sr and Ba probably were also derived by leaching of the radiogenic underlying basement.

On Milos, the isotopic signatures of barite among the different deposits are remarkably similar, despite the different styles of mineralization from seafloor massive sulfide [9] (hybrid epithermal-to-VMS) to subaerial epithermal [10]. Barite occurrences on Milos formed mainly from a seawater-dominated fluid with small variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ related to variable fluid-rock interaction or mixing of seawater and hydrothermal fluids that equilibrated with different source rocks (metapelites of the CBU and Quaternary volcanic rocks). The vein mineralization at Katsimouti [8] is the only location where the S isotopes in barite indicate a significant magmatic fluid component.

The abundance of barite in the different deposit types of the Cyclades Mineral District highlights a range of enriched sources for Ba (and Sr) and the presence of chloride-rich seawater in many of the hydrothermal systems capable of leaching Ba from the basement. As in other continental back-arc settings, the basement rock types are accessible through large-scale detachments and high-angle normal faults that provide pathways for leaching of crustal source rocks. Mixing of fluids from magmatic to surface-derived (seawater $\pm$ meteoric), highlighted by the strong isotopic and compositional zoning, was responsible for the widespread formation of barite in the different mineralizing systems.

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We thank two anonymous reviewers for their helpful comments that have greatly improved the manuscript, and Sarah Gleeson and Larry Meinert for efficient editorial management. Financial support for this work was provided by Natural Sciences and Engineering Research Council (NSERC) Discovery grants to MDH and DAS, a Society of Economic Geologists Canada Foundation Student Research Grant to SCW, and additional support from the Helmholtz Centre for Ocean Research Kiel (GEOMAR). This project was also supported by the NSERC Collaborative Research and Training Experience program (iIMAGE-CREATE) on Marine Geodynamics and Georesources. We thank Hercules Katsaros and Nikos Leloudas for their assistance with underground sampling in Lavrion. Gabriela Marshy is thanked for her great help as field assistant and Joëlle Dufour for SEM analysis and EMPA as part of her honors thesis. Glenn Poirier is thanked for his assistance with SEM analysis and EMPA, and Paul Middlestead and the team from the Ján Veizer Stable Isotope Laboratory for IRMS analyses and data reduction. SCW thanks Jeffrey Hedenquist for discussions about the fractionation of S isotopes in hydrothermal systems.

3.A Supplementary information for Chapter 3

Supplementary information for:

Wind, S. C., Hannington, M. D., Schneider, D. A., Fietzke, J., Kiliyas, S. P., Gemmell, J. B. (2023), Origin of Hydrothermal Barite in Polymetallic Veins and Carbonate-Hosted Deposits of the Cyclades Continental Back-Arc. *Economic Geology*

3.A.1 Analytical methodology

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) imaging and energy dispersive (EDS) analyses were performed on a JEOL 6610LV at the University of Ottawa, Canada, on carbon coated thin sections and barite grain mounts. The majority of analyses were conducted at 20 kV acceleration voltage with a spot size of 56 (no unit) at a working distance of 10 mm and a beam current of 1 μ A. For some grain mounts an acceleration voltage of 15 kV and a spot size of 57 (no unit) was used. X-ray intensity and energy were measured on an Oxford INCA 30 mm² SD detector. Data was processed with the INCAEnergy software in the mode “Oxygen by stoichiometry (normalized),” except for the samples 17L145_2, 17MT03, 17MP2A, 17MP2B, and 17AP13, for which “All elements analyzed (normalized)” was used. Barite samples processed in “All elements analyzed (normalized)” mode have elevated O concentration and lower Ba, S, and Sr concentration. Analytical results (n: 967) are summarized in the Appendix Table 3.A2.

Electron Microprobe Analyzer (EMPA)

Quantitative mineral chemical composition of twelve barite samples were determined in thin sections using the JEOL JXA-8230 SuperProbe electron microprobe analyzer (EMPA) at the University of Ottawa, Canada. The following suite of elements were analyzed: S, Ba, Al, Sr, Ca, K, Pb, Fe, and Si. Analyses were conducted with a beam energy of 20 kV and beam current of 40 nA, and a beam diameter of 10 μm . The X-ray takeoff angle was 40°. Count times and off-peak count times were for all elements at 20 s. The following standards and lines were used: Barite ($\text{SK}\alpha$ on PETJ and $\text{BaL}\alpha$ on PETL), Celestine ($\text{SrL}\alpha$ on PETJ), Diopside #1 ($\text{CaK}\alpha$ on PETJ), Sanidine ($\text{SiK}\alpha$, and $\text{AlK}\alpha$ on TAP and $\text{KK}\alpha$ on PETJ), Hematite ($\text{FeK}\alpha$ on LIFL), and Galena ($\text{PbM}\alpha$ on PETL). Interference corrections were applied to Al for interference by Ba ([Donovan et al., 1993](#)). Achieved analytical detection limits were <0.01 wt% for Al, Ca, K, and Si, between 0.012 and 0.026 wt% for S, Ba, and Fe and ≤ 0.042 wt% for Sr and Pb. A total of 1–8 barite crystals per polished thin section were analyzed by probing 3–15 points per single barite crystal to explore possible chemical variations within the crystals and between barite types. In addition to electron microprobe spot analyses, chemical traverses of barite, with visible zoning in backscattered-electron images, have been produced to assess any spatial chemical variation within individual barite crystals. These traverses were conducted under the same analytical conditions than the described spot analyses. Analytical results (n: 504) are summarized in the Appendix Table 3.A2.

Isotope Ratio Mass Spectrometer (IRMS)

The $\delta^{34}\text{S}$ isotope analyses of barite and galena and $\delta^{18}\text{O}$ isotope analyses of barite were conducted at the Ján Veizer Stable Isotope Laboratory, University of Ottawa, Canada.

Fine powder of barite and galena was weighed into tin capsules for $\delta^{34}\text{S}$ analyses. Samples were loaded into the Elementar Isotope Cube elemental analyzer (EA) which was flash combusted at 1800°C using the method of [Grassineau et al. \(2001\)](#). Ultra-pure He is used to carry the resulting gases into the Thermo Finnigan DeltaPlusXP isotope ratio mass spectrometer (IRMS) for analyses. Stable S isotope data are reported in standard δ notation as per mil (‰) relative to the VCDT (Vienna Cañon Diablo Troilite) standard, with an analytical precision of $\pm 0.3\text{‰}$. For S isotope values of barite, a total of 33 samples were analyzed in two sessions. The following standards were used: IAEA-NBS-127, T-123, and HAS-1. Duplicate analyses indicate a maximum internal variation of $< 0.3\text{‰}$.

A total of 24 galena samples, previously described in [Wind et al. \(2020\)](#), were analyzed for their S isotope geochemistry by EA-IRMS. Standards IAEA-S1, IAEA-S2 and AG-6 were used for data normalization and repeated measurements (n: 5) of the blind standard AG-6 returned an average value of $-0.70 \pm 0.14\text{‰}$ (current known value -0.63‰). Duplicate analyses during the analytical session indicate a maximum internal variation of $< 0.3\text{‰}$.

For $\delta^{18}\text{O}$ measurements in barite, dry, powdered samples were weighed into silver capsules, and analyzed with a Thermo Finnigan DeltaPlusXP continuous-flow IRMS coupled with a Thermo Scientific thermal conversion elemental analyzer (TC/EA) via a ConFlo IV. For $\delta^{18}\text{O}$ measurements, the method of [Coplen & Qi \(2012\)](#) was used. Standards IAEA-SO-6, IAEA-NBS-127, G-741 and G-743 were used for data normalization and repeated measurements (n: 3) of the blind standard G-741 returned an average value of $20.6 \pm 0.4\text{‰}$ (current known value 21.0‰). Oxygen isotopic data are reported in δ notation as per mil (‰) relative to the VSMOW (Vienna Standard Mean Ocean Water) standard with an analytical precision of $\pm 0.3\text{‰}$. For the majority of barite samples duplicate analyses indicate a maximum internal variation of $< 0.3\text{‰}$, solely duplicate analyses of sample 17AP2 showed a significant larger spread for $\delta^{18}\text{O}$ from 3.6 to 5.5‰.

The results of the $\delta^{34}\text{S}$ isotope analyses of barite and galena and $\delta^{18}\text{O}$ isotope analyses of barite are presented in the Appendix Table 3.A2.

Laser Ablation Analysis

Four barite crystals from Lavrion, Mykonos, Serifos, and Milos were analyzed for the concentrations of a suite of 54 elements using a 193 nm Excimer laser ablation system (GeoLasPro, Coherent) coupled to a double-focusing, high-resolution magnetic sector mass spectrometer (AttoM, Nu Instruments) at GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany. The following isotopes were analyzed: ^7Li , ^{23}Na , ^{24}Mg , ^{27}Al , ^{33}S , ^{34}S , ^{35}Cl , ^{39}K , ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{55}Mn , ^{56}Fe , ^{57}Fe , ^{63}Cu , ^{64}Zn , ^{65}Cu , ^{66}Zn , ^{71}Ga , ^{72}Ge , ^{73}Ge , ^{75}As , ^{77}Se , ^{79}Br , ^{85}Rb , ^{86}Sr , ^{88}Sr , ^{89}Y , ^{107}Ag , ^{109}Ag , ^{111}Cd , ^{115}In , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{126}Te , ^{127}I , ^{128}Te , ^{132}Ba , ^{133}Cs , ^{134}Ba , ^{135}Ba , ^{136}Ba , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{143}Nd , ^{145}Nd , ^{146}Nd , ^{147}Sm , ^{149}Sm , ^{151}Eu , ^{153}Eu , ^{155}Gd , ^{157}Gd , ^{159}Tb , ^{161}Dy , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{167}Er , ^{169}Tm , ^{171}Yb , ^{172}Yb , ^{173}Yb , ^{175}Lu , ^{178}Hf , ^{179}Hf , ^{181}Ta , ^{182}W , ^{185}Re , ^{188}Os , ^{189}Os , ^{197}Au , ^{202}Hg , ^{205}Tl , ^{208}Pb , ^{209}Bi , ^{232}Th , and ^{238}U . Instrument tuning was optimized for hot plasma conditions with a normalized Ar index (NAI) of ~ 30 following the method of [Fietzke & Frische \(2016\)](#). For each sample three ablations were obtained. Individual analyses on the crystal surface consisted of a pre-ablation to remove surface contaminations with a $60\text{ }\mu\text{m}$ beam width and a fluence of 1 J/cm^2 at a repetition rate of 5 Hz, followed by measurements of the suite of elements at a $44\text{ }\mu\text{m}$ beam width and a fluence of 3 J/cm^2 at a repetition rate of 5 Hz. Ablation spots were chosen on the basis of the transmitted light, and SEM images in order to avoid fractures or areas with abundant fluid inclusions. Two standard reference glasses (NIST-SRM 612 and 610) were used for calibration. The mean detection limits were >100 ppm for S, Cl, Ca, Fe, and Ba, between 10 and 100 ppm for Na, K, Fe, Zn, Ge, Se, Br, Sr, and I, between 1 and 10 ppm for Li, Mg, Al, Mn, Cu, Ga, Ge, As, Rb, Y, Cd, Sn, Te, Gd,

Au, and Hg and ≤ 1 ppm for all other elements.

A New Wave UP193 laser, attached to an AXIOM multi-collector inductively-coupled plasma mass spectrometer (LA-MC-ICP-MS) at GEOMAR, Germany, was used to measure the $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ composition of individual barite crystals from 21 samples (from north to south: Lavrion-3, Mykonos-4, Serifos-2, Antiparos-2, Milos-10). For each sample at least four ablations on a minimum of two grains were obtained, with a sequential measurement of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{34}\text{S}$ values on the same ablation spot. Analyses and data reduction using a LRS (linear regression slope) method followed the approach described by [Fietzke et al. \(2008\)](#) and [Jamieson et al. \(2016\)](#). Instrumental settings were tuned for hot plasma conditions (NAI ~ 9) to optimize a maximum ion transmission and low polyatomic cluster production according to the method of [Fietzke & Frische \(2016\)](#). The laser was set to an on-sample fluence of ~ 0.9 J/cm² with a laser pulse rate of 10 Hz. All samples were analyzed using a 50 μm diameter crater size and 30 s ablation time, with a gas blank and washout time of 30 s between each ablation. For the first session analyses were repeated close to the previous spot to check for reproducibility. Precision and accuracy of the measurements was evaluated by repeated duplicate analysis of a modern marine carbonate coral (*Desmophyllum dianthus*), representing modern seawater $^{87}\text{Sr}/^{86}\text{Sr}$, and reference standard MASS-1 (using $\delta^{34}\text{S}$: 5.7‰ as reference value; [Chen et al., 2017](#); [Fu et al., 2017](#)) before and after the analytical suite, as well as grain 17L145_3B_n after every 15 analysis. Data reduction of the natural coral (*Desmophyllum dianthus*) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, includes rubidium and mass fractionation (exponential law) corrections, but no drift or offset corrections. Rb concentrations are generally at or below detection limit. It yielded a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70917 ± 0.0003 (2 S.E., n: 12), being indistinguishable from the expected result for modern seawater. Small variation in the $\delta^{34}\text{S}$ values is likely related to the selection of standards, where repeated measurement of 17L145_3B_n showed an internal variation in

$\delta^{34}\text{S}$ values from 4.6 to 7.4‰ with an average value of 6.3 ± 0.8 ‰ (n: 15, App. Fig. 3.A.1 and Appendix Table 3.A3). For $\delta^{34}\text{S}$ values a minimum analytical uncertainty of ± 1 ‰ for 1 S.E. should be assumed for all individual spot analyses. The results of the laser ablation analysis are included in the Appendix Table 3.A3.

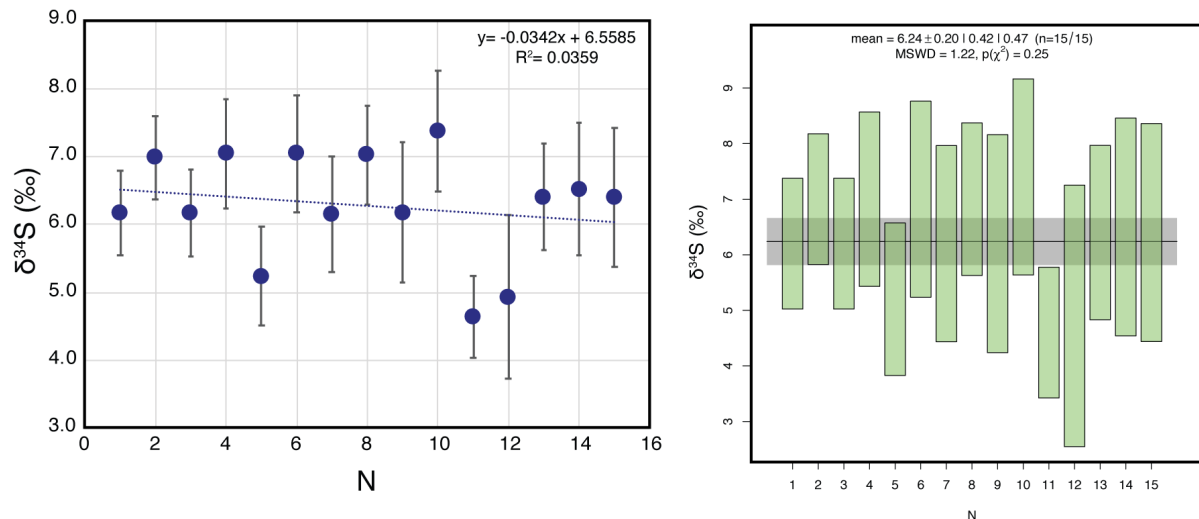


Fig. 3.A.1: Internal variation in $\delta^{34}\text{S}$ values obtained by LA-MC-ICP-MS analyses of crystal 17L145_3B_n (Plaka, Lavrion). Crystal 17L145_3B_n was repeated measured after every 15 analysis to evaluate precision and accuracy of the S measurements. Left figure plotted using the IsoplotR software (Vermeesch, 2018) where MSWD is the mean square weighted deviation.

3.A.2 Compilation of Sr isotope data

Strontium isotope ratios were compiled from the literature. For samples that have been analyzed multiple times we included the most recent analytical results. Compiled Sr isotope data of the Miocene intrusions and the Pliocene rhyolite on Antiparos show significant variations in the measured Sr isotope ratios due to the variability in the Rb and Sr concentrations. To better compare values compiled from different publications, and because mineralization occurred likely shortly after the emplacement of the granitoids, we recalculated the values for the intrusions and volcanic rocks to their initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

based on their reported emplacement ages. Data for the Lavrion granodiorite ([Juteau et al., 1986](#); [Altherr & Siebel, 2002](#); [Stouraiti et al., 2010](#)) has been recalculated for i: 8.3 Ma ([Altherr et al., 1982](#)). For the granodiorite and dikes from Serifos ([Altherr et al., 1988](#); [Altherr & Siebel, 2002](#); [Stouraiti et al., 2018](#)) an intrusion age of 9.5 Ma ([Iglseider et al., 2009](#)) has been used. Initial Sr ratios from the granite and dikes from Mykonos ([Altherr et al., 1982, 1988](#); [Altherr & Siebel, 2002](#); [Stouraiti et al., 2010](#); [Tombros et al., 2015](#)) are calculated for i: 10 Ma. Here, we used the estimated mineralization age of the barite veins of 11-10 Ma ([Menant et al., 2013](#)), although the emplacement of the Mykonos laccolith is dated at 13.5 Ma ([Brichau et al., 2008](#)). For the Paros granite ([Stouraiti et al., 2010](#)) an initial Sr value for 11.5 Ma ([Altherr et al., 1982](#)) has been calculated and for Antiparos we used the reported initial Sr data for 4.3 Ma from [Innocenti et al. \(1982\)](#).

3.A.3 Additional figures

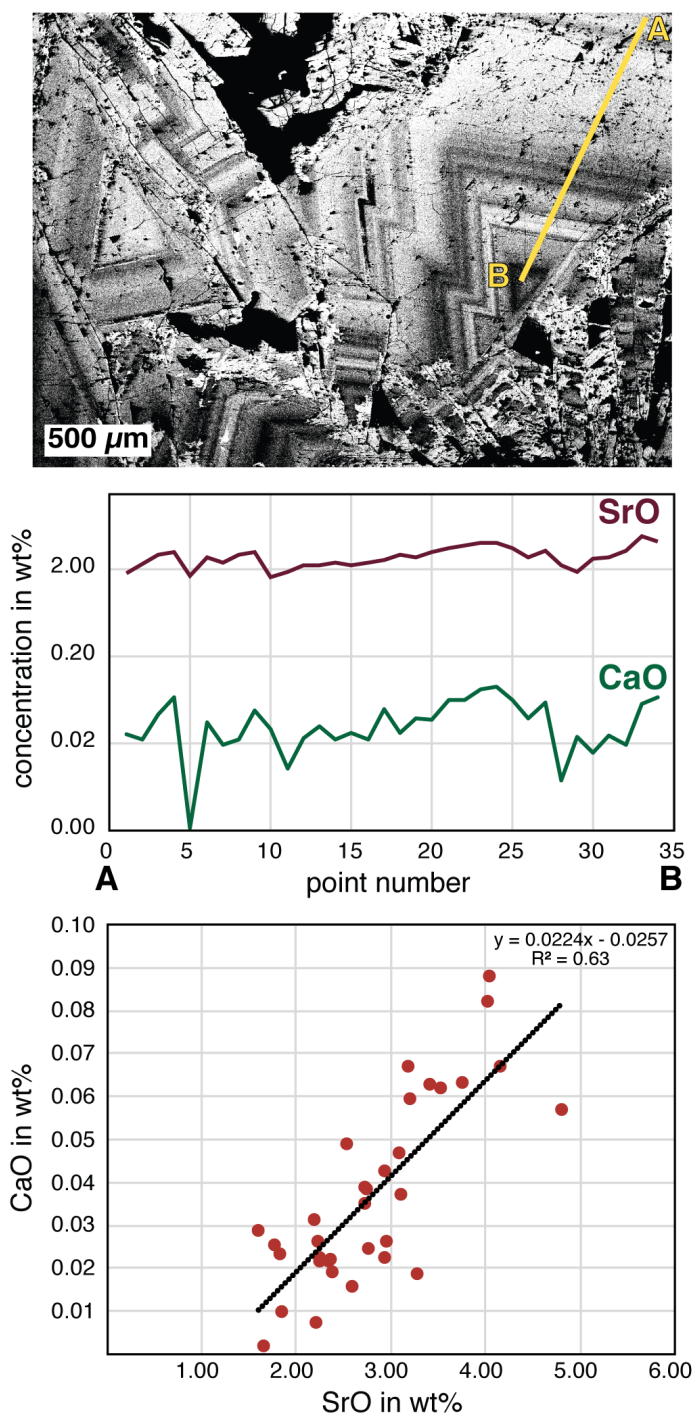


Fig. 3.A.2: Backscattered-electron microscopy image illustrating an EMPA traverse through a zoned barite crystal from Fourkovouni, Milos (sample 17MAR2). There is a positive correlation between the concentration of SrO and CaO in barite. Darker zones correspond to higher SrO concentrations with up to 4.8 wt% in the core of the crystal.

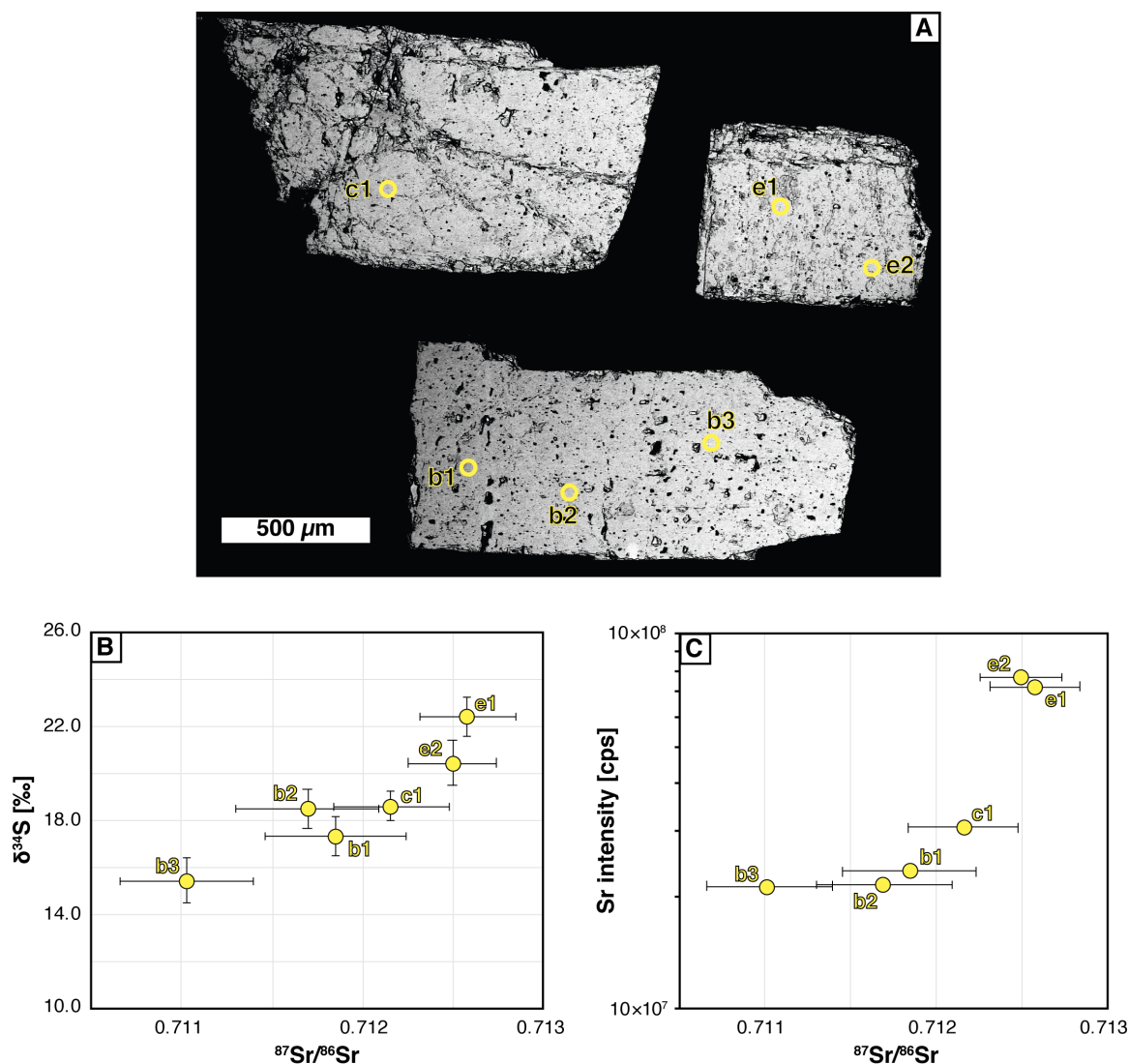


Fig. 3.A.3: Backscattered-electron microscopy image of analyzed barite crystals from the sample 17AP13 of the brecciated vein mineralization at Agios Georgios, Antiparos. Barite crystals are rich in fluid inclusions. Yellow circles highlight the ablation spots of 50 μm . $\delta^{34}\text{S}$ values vs. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios (B) and Sr intensity (cps) vs. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios (C) of barite obtained by LA-MC-ICP-MS spot analyses. The Sr intensity (cps) is displayed on a logarithmic scale where the range in Sr intensity corresponds to a variation of approximately 0.6 to 2.3 wt% of Sr. Each data point is one individual measurement with errors reported at 1 S.E. A positive correlation can be observed between $\delta^{34}\text{S}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, as well as for the Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting a change in fluid composition and potentially fluid sources during barite formation.

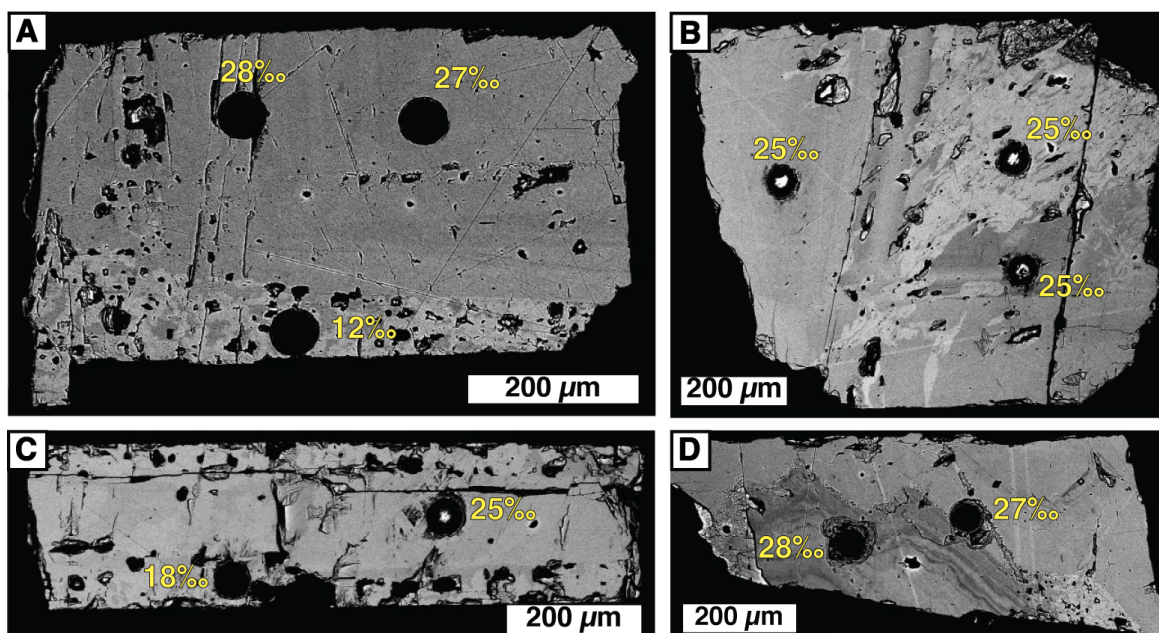


Fig. 3.A.4: Backscattered-electron microscopy images of analyzed barite crystals with the 50 μm ablation crater, illustrating the variation of $\delta^{34}\text{S}$ values on a crystal scale. $\delta^{34}\text{S}$ values were determined by LA-MC-ICP-MS spot analyses and are reported relative to the VCDT standard. A: Kastana, Milos, B: Fourkovouni, Milos, C: Plaka, Lavrion, D: Kastana, Milos.

Chapter 4

4 Geochemical and isotopic composition of the metamorphic basement in the Cyclades, Greece: Source rocks of the Cyclades Mineral District

Abstract

The lithological heterogeneity and complex structural framework of the Cyclades, south-east Greece, is a consequence of nappe stacking, exhumation within the subduction channel, rapid extension along low-angle detachment systems, as well as erosion. This makes correlation between scattered exposures of basement rocks across the Cycladic islands a challenge. Mid-Miocene to active seafloor hydrothermal mineralization in the upper crust records one of the latest events in the geodynamic evolution of the Cyclades. Lead isotope ratios of galena (PbS) and Sr isotope ratios of barite (BaSO₄) indicate distinct regional patterns in the isotopic signature of these hydrothermal minerals. The west Cyclades and the north-central Cyclades exhibit resolvable isotopic patterns that follow the trace of the Trans-Cycladic Thrust and largely correlate with the exposures of the Upper and Lower Cycladic Blueschist Nappe. Here, we present a comprehensive compilation of whole-rock geochemical data from the literature to further explore the crustal sources that led to the wide range of different styles of mineralization in the Cyclades. This compilation includes data from the exposed basement lithologies, including Carboniferous gneisses of the Cy-

cladic Basement and the range of rock types of the Cycladic Blueschist Unit (metabasites, marbles, metapelites, ultramafites, and felsic metavolcanic rocks). Whole-rock geochemical data confirm that the Cycladic Basement is a probable source of Ba, Rb, and Pb. Although Sr concentrations are highest in metabasites and marble, the more radiogenic Sr of barite suggest that it was also sourced from the Cycladic Basement or metapelites of the Cycladic Blueschist Unit. There is no clear geochemical difference between the exposed units in the hanging and footwall of the Trans-Cycladic-Thrust. However, isotopic data strongly suggest that the Cycladic Basement and its inherited signature in the Upper Cycladic Blueschist Nappe has a more pronounced influence on the metal sources in the north-central Cyclades than in the west Cyclades, where metals are mainly derived from the Lower Cycladic Blueschist Unit. Furthermore, we propose that the Upper Cycladic Blueschist Nappe and Lower Cycladic Blueschist Nappe represent different segments of a hyper-extended continental margin sequence.

4.1 Introduction

The Attic-Cycladic Crystalline Belt is one of the most rapidly extending areas of continental crust in the world (Pe-Piper & Piper, 2002; Jolivet et al., 2010). In the past decade extensive research has improved our understanding of the subduction processes and exhumation of the Cyclades (e.g., Menant et al., 2016; Grasemann et al., 2018; Glodny & Ring, 2022; Kotowski et al., 2022). However, less is known about the bulk geochemical composition of the metamorphic basement, which makes correlating scattered exposures of basement rocks across the Cyclades challenging. This is partly due to the heterogeneity and complex architecture of the basement resulting from nappe stacking, exhumation within the subduction channel and rapid extension, as well as erosion. High heat flow

and a permeable upper crust, resulting from numerous low-angle and steep normal faults, fostered a diversity of polymetallic ore deposits on the majority of the Cycladic islands. Porphyry, skarn, vein-type, VMS, carbonate-replacement, and epithermal and breccia deposits occur on the mainland and the Cycladic islands (e.g., [Skarpelis, 2002](#); [Menant et al., 2018](#); [Voudouris et al., 2019](#); [Wind et al., 2020](#) and references therein). The majority of these deposits did not experience tectonic overprinting or metamorphism. We have already demonstrated the inherited isotopic signatures of the crustal sources in galena (PbS) and barite (BaSO₄; [Wind et al., 2020, 2023](#)). In this chapter, we present a compilation of published geochemical data of the dominant crustal rocks exposed in the Cycladic metamorphic core complex and use the isotopic and geochemical signature of the basement lithologies to characterize the sources of metals and correlate the scattered exposures of the metamorphic basement.

An east-west trend in the isotopic signatures of galena and barite is apparent, which largely corresponds to the exposures of the metamorphic basement lithologies and coincides spatially with the proposed Trans-Cycladic Thrust (TCT). The TCT separates the Upper Cycladic Blueschist Nappe from the Lower Cycladic Blueschist Nappe, based on the peak metamorphic conditions. The regional isotopic pattern is preserved despite the wide range of mineralization ages over the past 10 Myr and the different structural levels of the mineral deposits. The magmatic processes and their geochemical signature have been studied in detail (e.g., [Pe-Piper & Piper, 2002](#); [Altherr & Siebel, 2002](#); [Stouraiti et al., 2010](#); [Schaarschmidt et al., 2021b](#)) but are not of focus of this work. Minor variations in the geochemical and isotopic compositions of the Miocene intrusions, which are an important source of fluids and metals for the Cyclades Mineral District, are not the source of the observed regional pattern in the isotopic signature of the mineralization. Instead, they show generally a north-south oriented pattern in their isotopic signature, which has

been related to the nature of the subducting slab (e.g., [Schaarschmidt et al., 2021b](#)). Granodiorites predominate in the west Cyclades and granites in the north-central Cyclades (Tinos, Mykonos, Delos, Naxos, and Ikaria), related to crustal assimilation and mixing of mafic and felsic magmas ([Stouraiti et al., 2010](#)), but this does not appear to be reflected in any mineral deposits. Instead, regional trends in the isotopic composition of hydrothermal minerals indicate a relatively stronger influence of the Carboniferous Cycladic Basement in the north-central Cyclades than in the west Cyclades. Another explanation might be that the lithologies of the Cycladic Blueschist Unit, occurring in the hanging and footwall of the TCT, are of different origins or at least from different parts of the same oceanic basin.

This chapter addresses two major questions: (1) which lithologies are the major sources of metals; and (2) is the pronounced regional pattern recorded by the isotopic composition of Cycladic galena and barite also recognizable in the whole-rock geochemistry of the metamorphic basement?

4.2 Regional geology

Northward subduction of the African plate underneath Eurasia, where subduction, rifting, and accretion of successive oceanic and continental fragments occurred since the Mesozoic, led to the formation of the Hellenides (e.g., [Jolivet et al., 2010](#); [Menant et al., 2016](#); [Schmid et al., 2020](#); [Papanikolaou, 2021](#); [van Hinsbergen et al., 2020](#) and references therein). The Hellenides are divided into the Internal and External Hellenides, where the latter is characterized by continuous stratigraphy, consisting of the Phyllite-Quartzite, Ionian, Gavrovo-Tripolitza, and Pindos thrust units. These units were dominantly affected by the Eocene-Miocene tectonism ([Papanikolaou, 2021](#) and references therein). The Internal Hellenides, with the Axios-Vardar oceanic unit and the Pelagonian, Serbo-Macedonian

and Rhodope continental blocks, are characterized by two orogenic periods: Late Jurassic-Early Cretaceous and Eocene-Oligocene (Papanikolaou, 2021 and references therein). The Attic-Cycladic Crystalline Belt forms a major tectono-stratigraphic unit of the Hellenides. Accelerated slab retreat and rapid southward migration of the Hellenic trench since the Eocene-Oligocene caused extension and thinning of the back-arc domain, manifested in the southward migration of arc-magmatism (Pe-Piper & Piper, 2002; Schaarschmidt et al., 2021b and references therein). Here, exhumation of middle and lower crustal material as metamorphic core complexes (e.g., Lister et al., 1984; Gautier & Brun, 1994; Jolivet et al., 2004, 2015) was facilitated by major low-angle, crustal-scale detachment systems (Fig. 4.1). In the Cyclades, major detachment systems were recognized: the top to-NE North Cycladic Detachment System (NCDS, Jolivet et al., 2010), the top-to-N Naxos-Paros Detachment System (NPDS, Gautier et al., 1993), the top-to-SSW West Cycladic Detachment System (WCDS, Grasemann et al., 2012), the top-to-SSE Santorini Detachment System (SDS, Schneider et al., 2018), and the recently discovered top-to-S Folegandros Detachment System (FDS, Bakowsky et al., 2023). On the Cycladic islands three major tectono-stratigraphic units are exposed: (1) the unmetamorphosed to low-grade metamorphosed Pelagonian zone in the hanging wall of the major detachment systems and (2) the high pressure metamorphosed Cycladic Blueschist Unit overlying (3) the Cycladic Basement in the footwall (Fig. 4.1, e.g., Bonneau, 1984; Flansburg et al., 2019; Grasemann et al., 2018; Jolivet et al., 2015). The following presents a description of the tectonic units exposed in the Cyclades, with a focus on the Cycladic Basement and Cycladic Blueschist Unit.

Cycladic Basement

Limited exposures of the lowermost unit, the Variscan Cycladic (continental) Basement, occur in the central part of the Cyclades (e.g., Antiparos, Delos, Ios, Naxos, Mykonos,

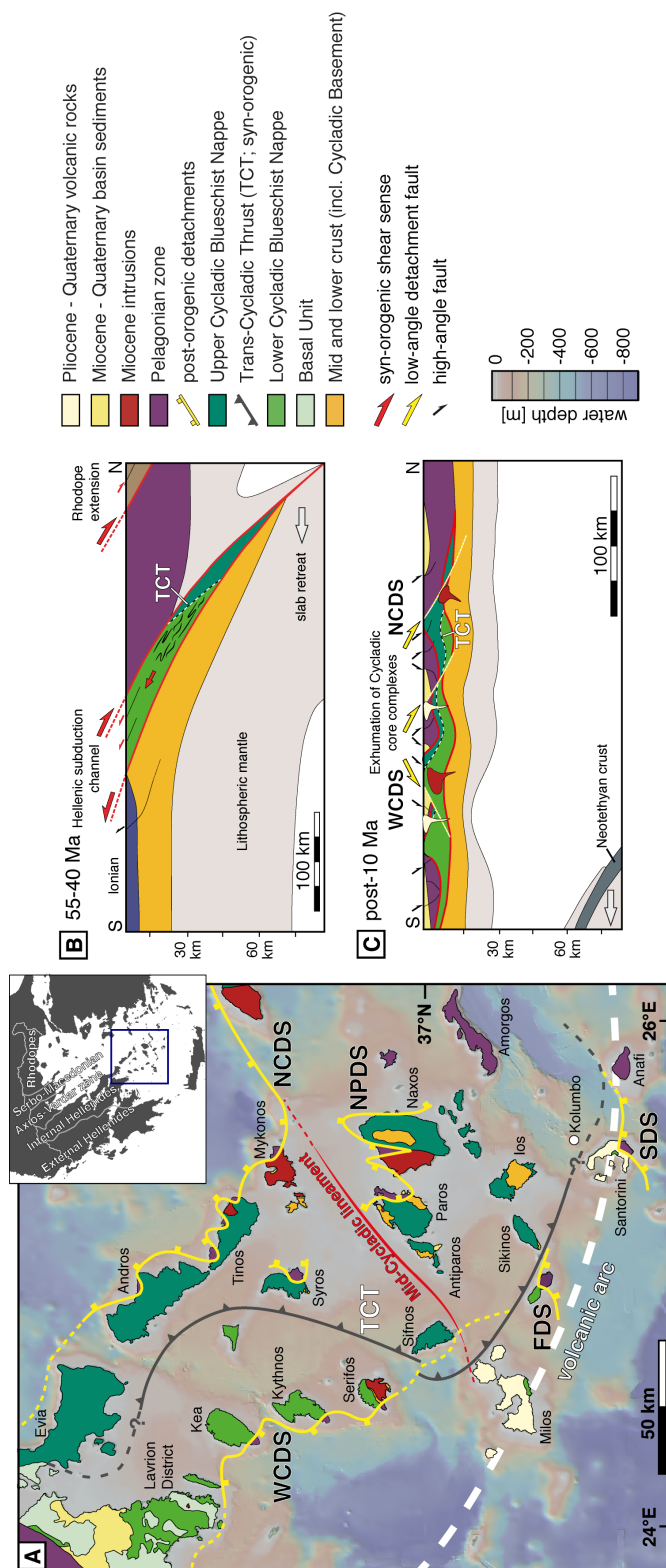


Fig. 4.1: A. Simplified geological map of the Attic-Cycladic Crystalline Belt, Greece (modified after Wind et al., 2020, 2023). Blue square in the inset shows the location of the study area within the Hellenides and Aegean Sea. B. and C. Cross-sections of the Aegean from ca. 55–40 Ma and post-10 Ma, respectively (simplified after Grasemann et al., 2018; Roche et al., 2016). Colors on map are the same as the cross-sections, which are drawn to illustrate the Cyclades have evolved as a back-arc setting due to slab retreat and following extension. FDS: Folegandros Detachment System, NCDS: North Cycladic Detachment System, NPDS: Naxos-Paros Detachment System, SDS: Santorini Detachment System, TCT: Trans-Cycladic Thrust, WCDS: West Cycladic Detachment System.

Paros, Sikinos, Serifos, Syros). The origin of the Cycladic Basement is still debated but likely corresponds to a sliver of the Pelagonian continental block that was detached during Triassic back-arc rifting due to rollback of the Paleotethyan subduction zone (e.g., [Grasemann et al., 2022](#)); a link to the continental margin of Apulia, a promontory of Gondwana, has also been suggested ([Flansburg et al., 2019](#); [Poulaki et al., 2019](#)). The Cycladic Basement consists of Carboniferous intrusive rocks (orthogneisses, aplites and metabasite dikes) that were emplaced into a pre-Variscan Neoproterozoic to Carboniferous metasedimentary (mica-schists, paragneisses) basement with a pre-Alpine history and peri-Gondwanan affinity ([Henjes-Kunst & Kreuzer, 1982](#); [Keay & Lister, 2002](#); [Jolivet et al., 2010](#); [McGrath et al., 2017](#); [Zlatkin et al., 2018](#); [Flansburg et al., 2019](#)). The nature of the contact between the Cycladic Basement and Cycladic Blueschist Unit is debated as either local detachment planes, thrust faults or reactivated detachment faults ([Huet et al., 2009](#); [Schneider et al., 2011](#); [Grasemann et al., 2012](#); [Augier et al., 2015](#); [Ducoux et al., 2017](#)), and an original para-autochthonous contact has been proposed ([Poulaki et al., 2019](#)).

Regionally, Triassic to Upper Eocene carbonate platform and flysch sediments, which are variably described in the literature as Lower Unit, Basal Unit or Gavrovo-Tripolitza Unit ([Chatzaras et al., 2011](#); [Schneider et al., 2011](#); [Grasemann et al., 2018](#); [Gerogiannis et al., 2019](#); [Ducharme et al., 2022](#)), occur stratigraphically below the Cycladic Blueschist Unit (e.g., Lavrion, Evia, Andros, Serifos, Amorgos). These thick marble sequences are considered to be the lateral equivalent of the Gavrovo-Tripolitza Unit of the External Hellenides on the mainland ([Fleury, 1980](#); [Grasemann et al., 2022](#)). Rarely, Triassic (~240 Ma) orthogneisses are present within the Basal Unit (e.g., Lavrion; [Liati et al., 2009](#)).

Cycladic Blueschist Unit

The Cycladic Blueschist Unit (CBU) is exposed on the majority of the Cycladic islands and occurs in the footwall of the detachment systems. Paleogeographically, the CBU has been considered to represent the metamorphosed equivalent of the Pindos oceanic domain (e.g., [Bonneau & Kienast, 1982](#); [Pe-Piper, 1998](#); [Jolivet et al., 2010](#); [Fu et al., 2015](#)). However, some authors also suggested a connection to the Vardar Ocean (e.g., [Chatzaras et al., 2013](#); [Zlatkin et al., 2018](#); [Gerogiannis et al., 2019](#)). Recently, the Pindos oceanic domain has been reinterpreted as an extended and thinned continental crust with a narrow oceanic basin ([Kotowski et al., 2022](#); [Schmid et al., 2020](#)) due to limited exposures of ophiolitic sequences (Syros, Evia; [Katzir et al., 2000](#); [Cooperdock et al., 2018](#)) and a general association of the CBU with continental crust (e.g., [Keay & Lister, 2002](#); [Zlatkin et al., 2018](#)). The CBU is a metamorphosed Triassic to Cretaceous volcano-sedimentary sequence with clastic metasedimentary rocks, marbles, and metabasites (e.g., [Bonneau, 1984](#); [Gärtner et al., 2011](#); [Seman et al., 2017](#); [Poulaki et al., 2019](#)). Locally Carboniferous orthogneisses are preserved within the CBU (~ 315 Ma orthogneiss on Syros: [Tomaschek et al., 2008](#)). Metavolcanic rocks of the widespread rift-related volcanic activity during the Triassic (~ 235 – 245 Ma) are intercalated within metasediments on several Cycladic islands (Lavris, Evia, Andros, Tinos, Sifnos, Ios, Syros, Santorini; [Pe-Piper, 1998](#); [Bröcker & Pidgeon, 2007](#); [Chatzaras et al., 2013](#); [Fu et al., 2015](#); [Löwen et al., 2015](#); [Lion, 2018](#); [Mocek, 2001](#); [Koutsovitis et al., 2020](#)). In addition to the Triassic meta-igneous rocks, Jurassic meta-gabbros and felsic gneisses are preserved on Andros ([Fu et al., 2015](#)). Triassic rifting was largely followed by passive margin sedimentation until the late Cretaceous (e.g., [Löwen et al., 2015](#); [Seman et al., 2017](#); [Poulaki et al., 2019](#)). In the Cretaceous (~ 80 Ma), continued rifting dissected the hyper-extended basement and passive margin

sequences and formed a small basin with oceanic affinity (Bonneau, 1984; Keiter et al., 2011; Fu et al., 2015; Cooperdock et al., 2018; Kotowski et al., 2022). High pressure ophiolitic mélanges with meta-igneous and metasedimentary Cretaceous rocks with a back-arc affinity are persevered on Tinos, Syros, and potentially Evia (Bulle et al., 2010). Based on differences in peak metamorphic conditions, the CBU has been divided into an Upper Cycladic Blueschist Nappe (UCBN) and Lower Cycladic Blueschist Nappe (LCBN), which are separated by the Eocene, syn-orogenic Trans-Cycladic Thrust (TCT; Grasemann et al., 2018). Differences between the UCBN and LCBN have also been identified by the distinct Pb and Sr isotopic compositions in the west and north-central Cyclades mineral deposits (Wind et al., 2020, 2023). Depending on the authors, a further division of the CBU into multiple thrusts of coherent tectonic slices including domains of oceanic, passive margin and continental provenance has been proposed (e.g., Kotowski et al., 2022; Uunk et al., 2022). Furthermore, Papanikolaou (2021) summarized that the northern Cyclades unit has pelagic features with volcano-sedimentary sequences, whereas the southern Cyclades unit comprises more quartzitic and conglomeratic lithotypes and metamorphosed shallow water carbonate platform with meta-bauxites.

Pelagonian zone

Small remnants of the Pelagonian zone also described as Cycladic Upper Unit, which were not buried during the Hellenic subduction, occur in the hanging wall of the major detachment systems. These exposures present a composite unit, equivalent to the continental Pelagonian zone on mainland Greece, which is the westernmost unit of the Internal Hellenides (Bonneau, 1984; Schenker et al., 2014) overlain by Jurassic ophiolites of the Vardar oceanic unit (Lamont et al., 2020a). Lithologies of the Pelagonian zone have a complex magmatic and orogenic history and consist of a Permian-Triassic continental margin of

volcano-sedimentary rocks, Triassic-Jurassic carbonates and Cretaceous magmatic rocks (Bonneau, 1984; Jacobshagen, 1986; Schenker et al., 2014; Papanikolaou, 2021; Koutsovitis et al., 2022). These rocks overlie a crystalline basement of Variscan orthogneisses that intruded the Neoproterozoic amphibolites and metapelites.

Miocene to Quaternary basin sediments

Neogene syn-extensional basin sediments form the uppermost unit in the Cyclades and consist of Miocene to Pliocene marine to continental sediments. These sediments are preserved in the hanging wall of the local detachments on Mykonos, Paros, and Naxos, and represent inverted unroofing sequences that were deposited in supradetachment basins (e.g., Sánchez-Gómez et al., 2002; Bargnesi et al., 2013). On Attica and Milos, Miocene to Quaternary marine to continental sediments unconformably overlie the CBU (Stewart & McPhie, 2006; Krohe et al., 2010).

Miocene intrusions

In the early Miocene, extension-related exhumation of the Cycladic metamorphic core complex produced a suite of syntectonic intrusions (Cycladic granitoids) within the upper crust (Fig. 4.1; Altherr et al., 1982; Pe-Piper & Piper, 2001; Altherr & Siebel, 2002; Iglseder et al., 2009; Bolhar et al., 2010; Schneider et al., 2018; Rabillard et al., 2018). Schaarschmidt et al. (2021b) proposed that variation in the magma composition of the Aegean is related to the changes in the subduction history including subduction of oceanic lithosphere with a thick sediment cover and continental blocks in the past 30 Myr. The geochemistry and isotopic composition of the Miocene Cycladic granitoids are typical for crustal derived magmas; granodiorites predominate on Serifos and at Lavrion and granites in the central Cyclades (Tinos, Mykonos, Delos, Naxos, and Ikaria; Pe-Piper & Piper,

2002; Stouraiti et al., 2010 and references therein). Emplacement of Cycladic granitoids started earlier in the northeast (~ 17 Ma at Ikaria and Tinos: Altherr et al., 1982; Bolhar et al., 2010), whereas in the northwest it started at 10 Ma (e.g., at Lavrion and Serifos: Iglseder et al., 2009; Liati et al., 2009). Minor peraluminous intrusions and dikes, with S-type characteristics, occur on Serifos, Tinos, Paros, Naxos, and Ikaria (Altherr et al., 1982; Pe-Piper & Piper, 2002; Altherr & Siebel, 2002 and references therein). The S-type intrusive bodies generally pre-date the I-type intrusions (Altherr et al., 1982; Bolhar et al., 2010). Additionally, undeformed mafic to felsic dikes of Miocene age (~ 10 Ma) occur in Lavrion and on Serifos, Tinos, and Delos (Altherr et al., 1982; Pe-Piper & Piper, 2002; Skarpelis et al., 2008). Local eruptions of felsic volcanic rocks occurred at the Miocene-Pliocene boundary and are preserved in the central Cyclades (e.g., rhyolites in the south of Antiparos; Innocenti et al., 1982).

Pliocene-Quaternary volcanic unit

Since the Pliocene, the active south Aegean volcanic arc (SAVA) extends from Sousaki in the northwest, across Milos and Santorini towards Nisyros in the southeast (e.g., Francalanci et al., 2005; Francalanci & Zellmer, 2019; Innocenti et al., 1981). The Pliocene-Quaternary volcanism is related to the release of hydrous fluids from the subducting slab and the chemical compositions are typical for mantle-derived magmas with variable degrees of metasomatism and crustal contamination (e.g., Pe-Piper, 1994; Ersoy & Palmer, 2013; Francalanci & Zellmer, 2019; Pe-Piper & Piper, 2005). Various authors proposed an influence of subducted carbonate-rich and Nile-derived terrigenous sediments on the magmatism of the SAVA (e.g., Pe-Piper & Piper, 2001; Klaver et al., 2015, 2016a; Woelki et al., 2018; Francalanci & Zellmer, 2019; Schaarschmidt et al., 2021b). In addition, changes in the tectonics during the evolution of the arc caused regional variations in the composition

and age of the arc with generally older volcanism ($\sim$ Pliocene) and an andesitic to dacitic composition in the western arc and younger volcanism (mid to late Quaternary) and a tholeiitic and calc-alkaline basaltic to andesitic composition in the central and eastern arc (Pe-Piper & Piper, 2005).

4.2.1 Regional metallogeny

Mineralization in the Cyclades occurred during transtension or extension, and forms one of the most recent developments in the geodynamic evolution of the Cycladic continental back-arc. Crustal-scale detachments and associated high-angle normal faults facilitated the ascent of metal-bearing fluids within a permeable brittle upper crust (Menant et al., 2018). Mineralization resulted by a mixture of hot metal-bearing deep fluids (magmatic and minor metamorphic) and cold surface-derived fluids (seawater or meteoric; Tombros et al., 2007; Kevrekidis et al., 2015; Scheffer et al., 2019; Schaarschmidt et al., 2021a; Frenzel et al., 2022; Wind et al., 2023). A late and shallow crustal mineralization is supported by the involvement of seawater and/or meteoric fluid components in the hydrothermal systems, as described for many precious and base metal-rich deposits in the Cyclades (e.g., Milos, Serifos, Lavrion District, Antiparos, Mykonos, Tinos; Alfieris et al., 2013; Bonsall et al., 2011; Fitros et al., 2017; Kevrekidis et al., 2015; Kiliyas et al., 2001; Tombros et al., 2007, 2015; Wind et al., 2023). Mineralization in the Cyclades likely started about 10 Ma and continued until today (e.g., hydrothermal venting in the crater of the shallow-submarine arc-volcano, Kolumbo, and Palaeochori and Spathi Bay, Milos; Kiliyas et al., 2013; Price et al., 2013; Houghton et al., 2019; Voudouris et al., 2021). The spatial association with Miocene intrusions (e.g., Altherr et al., 1982; Bolhar et al., 2010; Iglseder et al., 2009; Liati et al., 2009) and Pliocene to Quaternary volcanism along the active volcanic arc, suggests that magmatic-hydrothermal activity was older in the east and north of the district

and younger in the west and south. In addition to the recent mineralization (Miocene and younger), some authors argue that an enrichment of base and precious metals in the Cyclades might also be related to hydrothermal venting during Triassic and Cretaceous back-arc rifting preserved in the volcanoclastic sequences of the CBU ([Katzir et al., 2000](#); [Stouraiti et al., 2022](#)).

The Cyclades Mineral District contains a wide range of mineralization styles that occur in all tectono-stratigraphic units in the hanging and footwall of the major detachment systems (e.g., [Skarpelis, 2002](#); [Menant et al., 2018](#); [Voudouris et al., 2019](#); [Wind et al., 2020](#) and references therein). Carbonate-hosted replacement Pb-Zn-Ag mineralization occurs in the Lavrion District and on the islands of Syros, Serifos and Sifnos, and is commonly spatially related to major detachment faults (e.g., [Bonsall et al., 2011](#); [Berger et al., 2013](#); [Fitros et al., 2017](#); [Scheffer et al., 2017, 2019](#)). Intermediate- to high-sulfidation epithermal Au deposits and detachment and fault-related base and precious metal vein and breccia mineralization are found in the Lavrion District, and on Evia, Tinos, Kythnos, Mykonos, Sifnos, Serifos, Antiparos, Milos, and Anafi islands (e.g., [Voudouris et al., 2011](#); [Alfieris et al., 2013](#); [Kevrekidis et al., 2015](#); [Menant et al., 2013](#); [Tombros et al., 2007, 2015](#); [Voudouris et al., 2019](#); [Tombros et al., 2021](#)). Small occurrences of porphyry style mineralization have been identified in the Lavrion District ([Voudouris et al., 2008a, 2019](#)). Magnetite, Ca-Fe exo- and endoskarns occur on Serifos and Lavrion ([Bonsall et al., 2011](#); [Ducoux et al., 2017](#); [Fitros et al., 2017](#); [Salemink, 1985](#); [Voudouris et al., 2008a](#)) and Mn skarns on Paros ([Tombros et al., 2023](#)). Seafloor massive sulfide mineralization occurs in the crater of the shallow-submarine arc-volcano, Kolumbo ([Kilias et al., 2013](#)). Often multiple phases of mineralization have been identified throughout the district which are commonly genetically linked (e.g., Lavrion, Milos).

4.3 Isotopic signature of the mineralization and basement

Lead and Sr isotope ratios of the Cycladic mineralization and exposed lithologies in the Cyclades have been compiled by [Wind et al. \(2020, 2023\)](#) and were expanded with data from recent publications (e.g., [Tombros et al., 2021](#)). Rock units occurring in the footwall of the TCT have generally higher $^{206}\text{Pb}/^{204}\text{Pb}$ ratios than the rock units in the hanging wall of the TCT, while Sr-isotope ratios depend highly on the rock type (Fig. 4.2). Regional variations in the Pb isotope ratios of galena and Sr isotope ratios of barite have been discussed in more detail in [Wind et al. \(2020, 2023\)](#) and are summarized herein. The Pb and Sr isotope ratios of barite and galena show an intermediate composition respectively, suggesting they formed by a mixture of different sources of Pb and Sr, mainly magmatic and crustal derived metal sources. Galena and barite from the western Cyclades have $^{206}\text{Pb}/^{204}\text{Pb} \geq 18.84$ and $^{87}\text{Sr}/^{86}\text{Sr} \leq 0.711$, respectively. Here, the isotopic signatures of the galena and barite are more homogenous despite the different styles and ages of mineralization. In the north-central Cyclades isotope ratios of galena and barite are more heterogenous, generally $^{206}\text{Pb}/^{204}\text{Pb} \leq 18.84$ and $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.711$, respectively. This regional homogenization of the Pb isotope composition in sulfides, despite the occurrences within different host rocks, has also been observed in other continental arc-type mineral districts (e.g., the Guerro composite terrane in Mexico: [Potra & Macfarlane, 2014](#); the Rhodope Massif: [Marchev et al., 2005](#)). The isotopic signature of minerals and rocks in the hanging wall of the TCT are intermediate between the Cycladic Basement and Pelagonian zone and are distinct from the isotopic signature of minerals and rocks in the footwall of the TCT. The isotopic compositions of rocks from the LCBN and UCBN suggest that they are sourced from different sub-basins or different parts of the same sub-basin. Furthermore, isotope data from the mineralization suggests the Cycladic Basement underlies the CBU in the north-

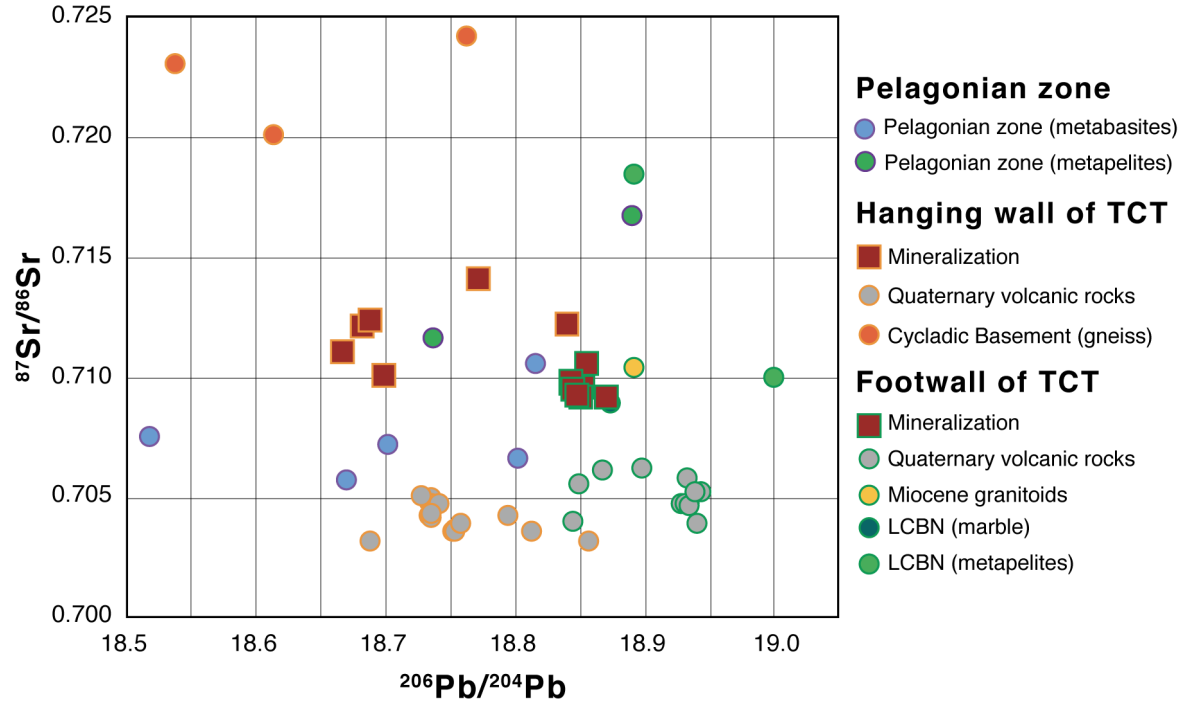


Fig. 4.2: $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the mineralization, magmatic intrusions and host rocks in the Cyclades.

central Cyclades, but was likely not or less accessible in the western Cyclades (Wind et al., 2020, 2023).

The Miocene magmatic intrusions have overall high Sr isotope ratios with no pronounced regional pattern (Altherr & Siebel, 2002; Stouraiti et al., 2010; Schaarschmidt et al., 2021b). Contrary to the geochemical variations between the Cycladic granitoids, where granodiorites predominate in the west Cyclades (Serifos, Lavrion) and granites in the central Cyclades (Tinos, Mykonos, Delos, Naxos, and Ikaria; Pe-Piper & Piper, 2002; Stouraiti et al., 2010 and references therein). The overall more homogenous Sr isotopic compositions of the Miocene intrusions, in contrast to the basement, is potentially related to a common lower-to-mid crustal signature inherited by the Miocene intrusions.

Comparing the Sr isotope ratios and Sr content of the different rock types (Fig. 4.3A)

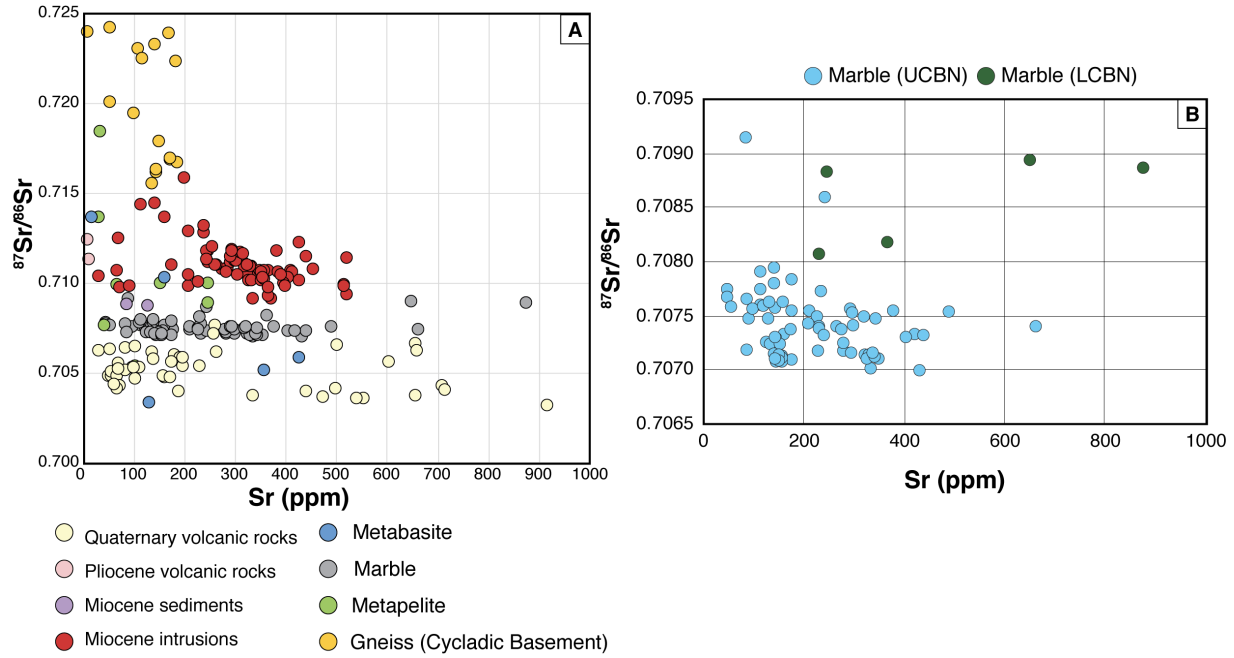


Fig. 4.3: A: $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr content (ppm) for the Miocene intrusions and exposed rock types. B: Sr isotopes versus Sr content (ppm) for marble units in the Upper and Lower Cycladic Blueschist Nappe.

highlights that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios depend highly on the rock type and show a large dispersion from 0.703 (metabasites of the CBU) to 0.766 (gneiss of the Cycladic Basement). The Sr content, however, seems to be independent of the rock type and in certain cases potentially reflects the grade of metasomatism as discussed below. In general, schists (metapelites) and gneisses have a wide range of Sr isotope ratios, whereas marbles and metabasites have a narrow range and low Sr-isotope ratios. Despite limited data of marble from the LCBN, a regional pattern based on the Sr content and Sr isotope ratios (Fig. 4.3B) is apparent for the occurrences of marble in the UCBN and LCBN. Marble derived from the UCBN has generally lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr contents than marble from the LCBN.

4.4 Whole-rock compilation

Based on the findings of the Pb and Sr isotope studies (Wind et al., 2020, 2023), whole-rock geochemical data of potential source rocks have been compiled covering the range of metamorphic basement lithologies exposed in the Cyclades. For this study, we focused on the units in the footwall of the detachments (CBU and Cycladic Basement). Rock units occurring in the hanging wall of the major detachment systems (e.g., limited exposures of the Pelagonian zone) are generally excluded, as they are not the major source of metals for most of the mineral occurrences in the Cyclades Mineral District. In addition, samples with pronounced metasomatism or mineralization have been excluded from the database (e.g., Kleine et al., 2014; Gyomlai et al., 2021). The final database includes whole-rock geochemical data of 328 rock samples. The data sources have been cited in the text, Figure 4.4 and can also be found in the Appendix Table 4.A.

The compilation contains 50 samples of the potential Carboniferous Cycladic Basement (gneiss, augengneiss, mylonitic orthogneiss) from Ios, Serifos, Naxos, and Paros. In addition, 29 samples come from the felsic metavolcanic rocks which occur generally within the CBU and are mostly Triassic in age. The database also contains 78 marble samples from rock units occurring in the hanging wall of the TCT (UCBN). The limited data for metasedimentary rocks (21 metapelites) is not representative of the large number of exposures within the CBU. Data of the limited exposures of ultramafites (N: 16) within the CBU are from Syros and Evia. The majority of samples in the database (N: 134) are of Triassic to Cretaceous metabasites from the exposed Cycladic Blueschist Unit on Andros, Attica, Evia, Lavrion, Milos, Naxos, Serifos, Sifnos, Syros, and Tinos. These samples provide the largest data set for a comparison of the subducted and exhumed oceanic crust in the Cyclades. Where available the metamorphic grade and crystallization ages of the

metabasites and meta-igneous rocks were considered. However, the interpretation of the different units (e.g., Basal Unit, Cycladic Basement) is ambiguous in the literature and makes the classification of the different lithologies challenging.

4.5 Whole-rock composition

Results of the whole-rock compilation are summarized in Figure 4.4. Within each group of rock types (Carboniferous gneiss, Permian to Jurassic felsic metavolcanic rocks, Triassic to Cretaceous metapelites, Triassic to Cretaceous metabasites, meta-ultramafites, marbles), we observe large variability in the trace element concentration, whereas major elements are generally characteristic for the specific lithology. Data of the carbonates are restricted to the UCBN, and marble is rather pure and does not contain notable concentrations of SiO_2 , Al_2O_3 , Na_2O and K_2O . Ultramafic rocks have low Al_2O_3 , SiO_2 and alkali concentrations, while being enriched in MgO . Whole-rock data of the metapelites are limited and scattered with a large variability in the major element concentrations representing a range of clastic sediments including quartzites and volcano-clastic sediments with similar major element compositions as the felsic and mafic meta-igneous rocks. In the following we describe in more detail the geochemistry of the felsic and mafic rocks of the Cycladic Basement and CBU.

4.5.1 Felsic meta-igneous rocks of the Cycladic Basement and CBU

The major element composition of the Carboniferous Cycladic Basement and the meta-granitoids (felsic metavolcanic rocks) of the CBU and Basal Unit are similar (Figs. 4.4, 4.5A-B). However, except for a few outliers, the felsic metavolcanic rocks have generally lower Al_2O_3 and alkali contents. Of the Cycladic Basement, 50 whole-rock geochemical

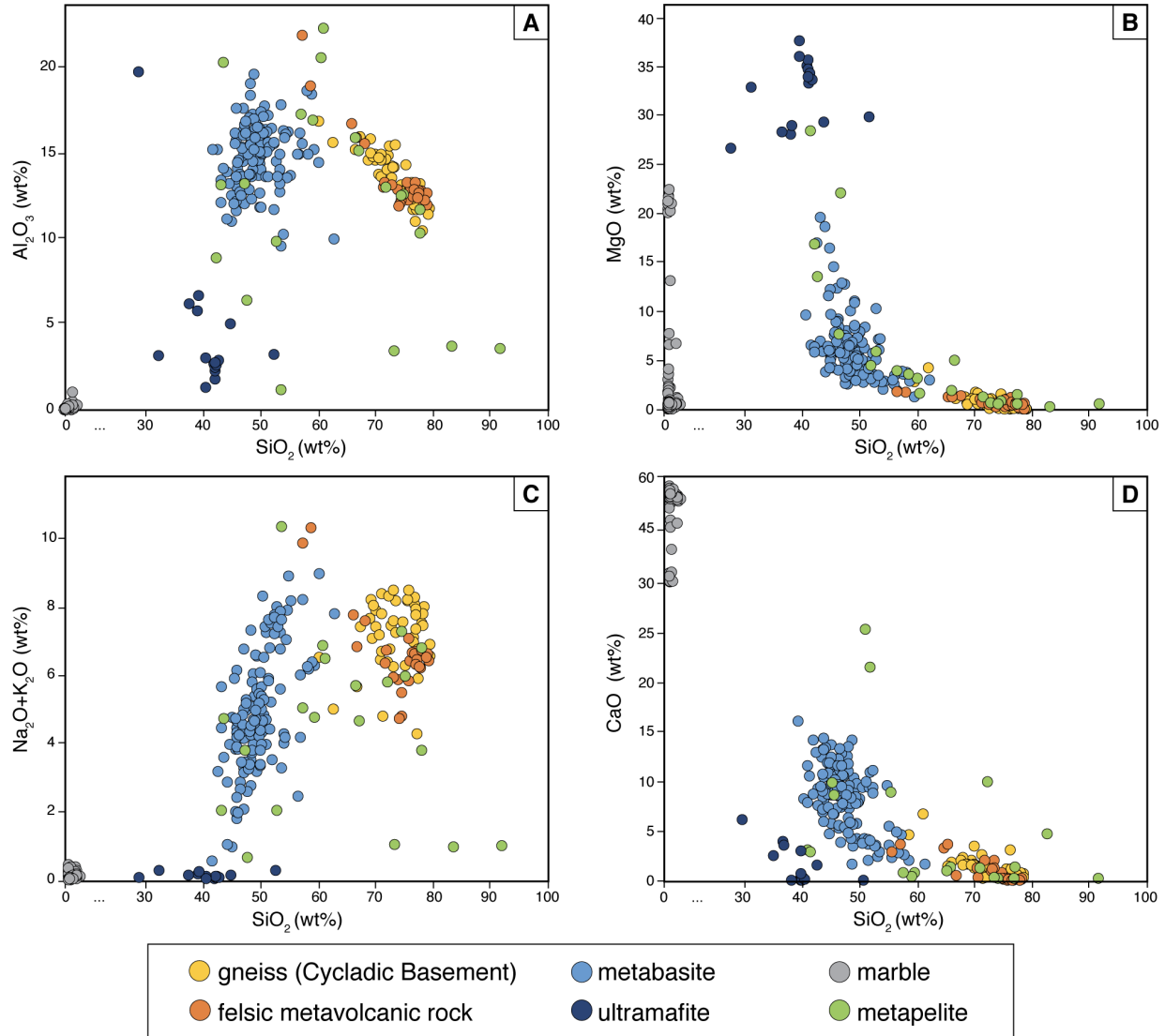


Fig. 4.4: Major element diagrams with (A) Al_2O_3 versus SiO_2 , (B) MgO versus SiO_2 , (C) $\text{Na}_2\text{O} + \text{K}_2\text{O}$ versus SiO_2 , and (D) CaO versus SiO_2 displaying characteristic trends for each rock type. Data sources: Baziotis & Mposkos (2011); Berger et al. (2013); Bolhar et al. (2017); Buettner et al. (2005); Bulle et al. (2010); Chatzaras et al. (2013); Cooperdock et al. (2018); Ducharme et al. (2022); Gärtner et al. (2011); Grosche et al. (2023); Gyomlai et al. (2021); Iglseder et al. (2009); Katzir et al. (2000); Klaver (2016); Kleine et al. (2014); Kornprobst et al. (1979); Koutsovitis et al. (2020); Lion (2018); McGrath et al. (2017); Mocek (2001); Pe-Piper et al. (1997); Pe-Piper (2000); Stouraiti et al. (2010); Tombros et al. (2007).

analyses of meta-igneous rocks from Ios, Serifos, Paros, and Naxos have been examined. These show high SiO_2 concentrations (average >70 wt%), and low CaO and MgO concentrations. Samples of the Cycladic Basement show a covariance between the Al_2O_3 and SiO_2 content (Fig. 4.4A). Na_2O and K_2O concentrations are slightly enriched with an alkali content between 5–8.2 wt%. Samples of the Cycladic Basement are enriched in Rb (average 124 ppm) but depleted in Sr (average 104 ppm, Fig. 4.7). Gneisses show a wide range in Ba concentrations from 30 to 1973 ppm with an average of 604 ppm (Fig. 4.7). Rubidium concentrations in the Cycladic Basement are significantly higher than for the felsic metavolcanic rocks (Fig. 4.7C). The gneisses and felsic metavolcanic rocks have a granitic to granodioritic composition (Fig. 4.5B) similar to the Miocene granitoids and show a strong enrichment in fluid mobile elements (Fig. 4.6A).

4.5.2 Metabasites of the CBU

There is a significant variability of major and trace elements for metabasites from the Cycladic islands (Andros, Evia, Lavrion, Milos, Naxos, Serifos, Sifnos, Syros, Tinos). We observe a large spread in the concentration of SiO_2 (40–63 wt%) and Al_2O_3 (10–20 wt%). In contrast to the whole-rock composition of the Cycladic Basement (Fig. 4.4), no covariance between SiO_2 and Al_2O_3 could be observed. Likewise, for the major elements no clear difference between the metabasites of the UCBN and LCBN is obvious (Fig. 4.5C-D). Rubidium concentrations are low (0.04–147 ppm; average 25 ppm), whereas Sr concentrations vary from 0.5 to 1690 ppm (average 210 ppm; Fig. 4.7). Strontium concentrations for samples from the LCBN are lower than for the UCBN (Fig. 4.6B-C), likely related to the higher metamorphic grade as discussed below. Barium concentrations vary from 0 to 400 ppm, except for samples from Sifnos, where several samples (7 of 29 samples) had Ba concentrations >1000 ppm; those samples have been characterized as eclogites. Based on

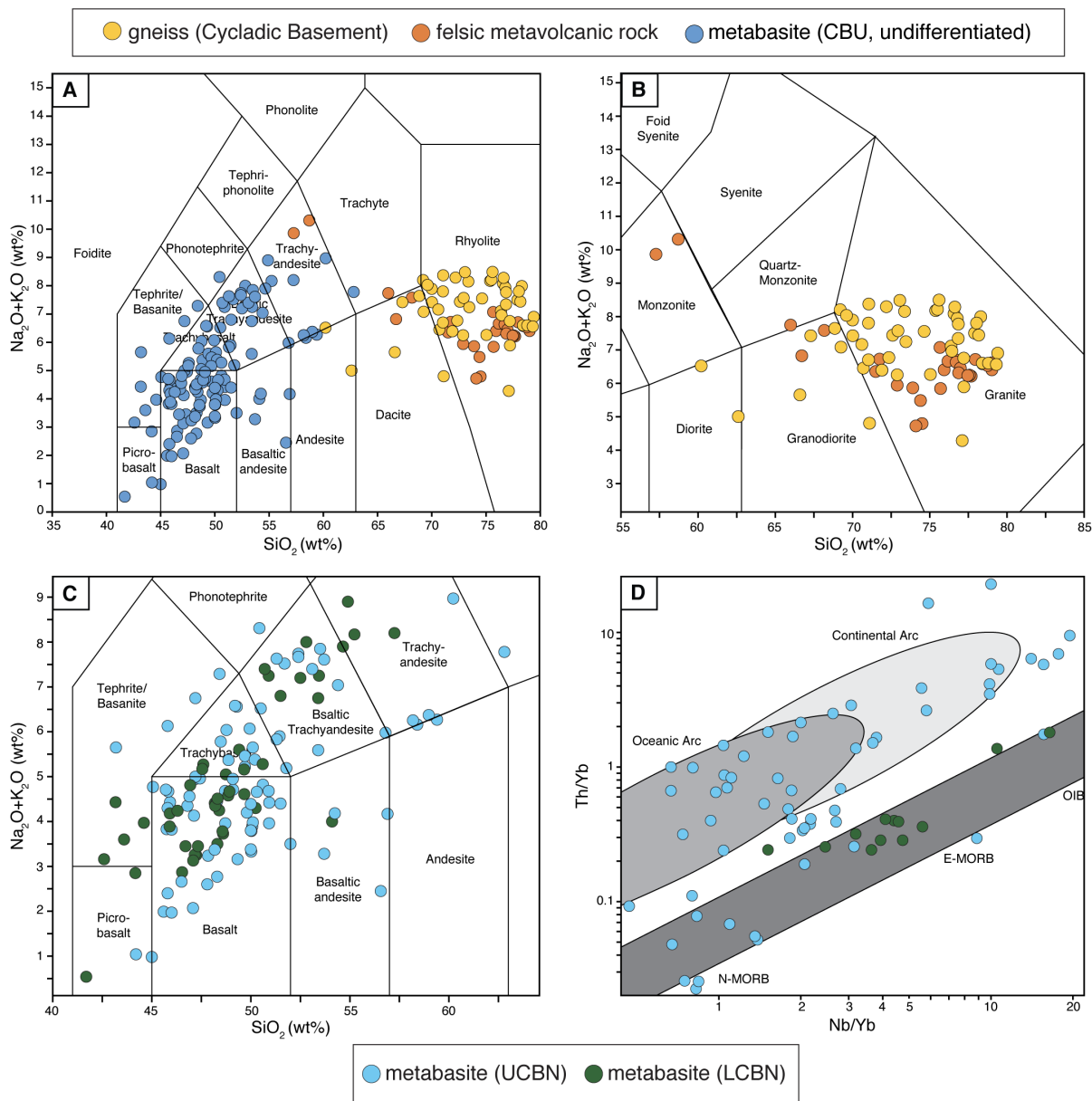


Fig. 4.5: Major and trace element plots for the felsic and mafic rocks of the Cycladic Basement and Cycladic Blueschist Unit (CBU). A: Total-alkali silica plot (after [Le Maitre, 1989](#)) showing the distribution of gneiss (Cycladic Basement), and felsic metavolcanic rocks and metabasites of the CBU. B: Total-alkali silica plot for the Carboniferous to Triassic felsic rocks in the Cyclades (after [Middlemost, 1994](#)). C: Total-alkali silica plot for the metabasites classified by the occurrences in the Upper Cycladic Blueschist Nappe (UCBN) and Lower Cycladic Blueschist Nappe (LCBN). D: Trace element data of metabasites in the lithotectonic discrimination plot of [Pearce \(2014\)](#). Samples are classified based on their occurrences in the hanging wall (UCBN) or footwall (LCBN) of the TCT.

the Th/Yb versus Nb/Yb lithotectonic discrimination plot of [Pearce \(2014\)](#) metabasites show continental arc, E-MORB and N-MORB affinity (Fig. 4.5D), highlighting the range of tectonic settings that led to the formation of metabasites during the Triassic and Cretaceous. Here, a broader dispersion occurs in the trace element data of the metabasites within the UCBN, which is potentially related to the different rock types (Fig. 4.6C).

4.6 Interpretation and discussion

Exposures of ore mineralization on nearly all Cycladic islands highlight the enrichment of metals in the continental crust in Attic-Cycladic Crystalline Belt. The metal endowment (Pb, Zn, Sr, Ba) in the Cycladic Mineral District is typical of a continental source of these elements. In the following we discuss the source of metals for the deposits, the potential limitations in the interpretation of the geochemical data, and implications for the basement structure.

4.6.1 Sources of metals

Elemental concentrations vary significantly for the different lithologies in the metamorphic basement (Figs. 4.7, 4.8). Barium is enriched in rocks from the Cycladic Basement and felsic metavolcanic rocks and metapelites of the CBU (Fig. 4.7A). Although Sr concentrations are high in marble and metabasites (Fig. 4.7B), high Sr isotope ratios observed in hydrothermal barite ([Wind et al., 2023](#)) suggest that Sr is derived from the Cycladic Basement or the metapelites of the CBU.

Base metal concentrations (Pb, Zn, Cu; Fig. 4.8) are high but reflect characteristic trends for the different lithologies ([Barrie & Hannington, 1997](#)). Lead concentrations are high in gneisses of the Cycladic Basement and metapelites of the CBU (Fig. 4.8A) and

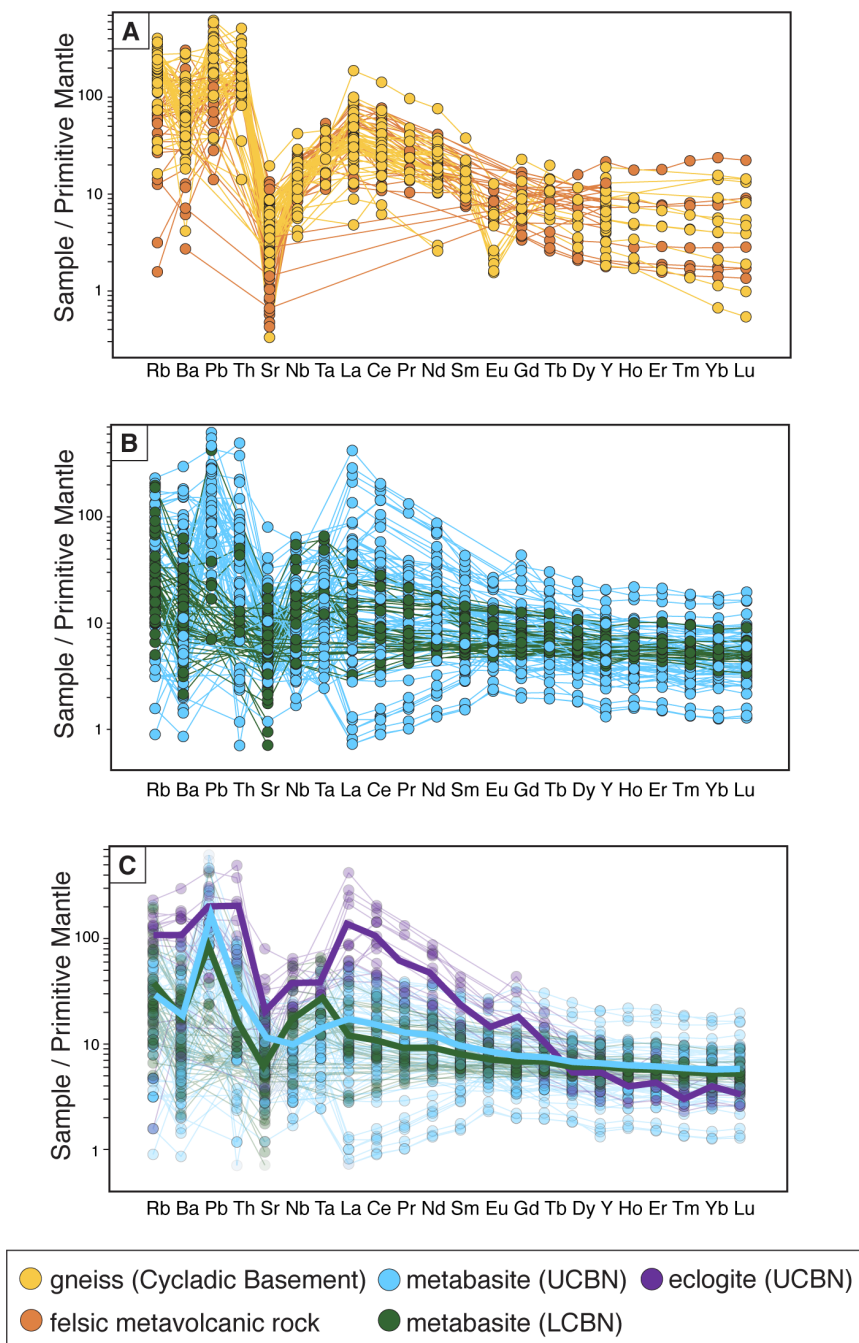


Fig. 4.6: Primitive mantle-normalized trace element plots for the felsic (A) and mafic (B) rocks of the Cycladic Basement and the Cycladic Blueschist Unit. C: Primitive mantle-normalized trace element plot for the metabasites of the Upper Cycladic Blueschist Nappe (UCBN) and Lower Cycladic Blueschist Nappe (LCBN), and eclogites of the UCBN. The bold lines highlight the average compositions.

confirm that these are the major sources of Pb for the mineralization. In contrast, Zn and Cu concentrations are highest in the metabasites of the CBU (Fig. 4.8B-C). This suggests that the Cycladic Basement and metapelites of the CBU are most reasonably the main sources of Pb, Ba, and Sr because of the high concentrations of these elements in these rock types. While the carbonate horizons of the CBU are an excellent host for the mineralization in the Cyclades (e.g., Lavrion District, Serifos, Syros, Tinos, Antiparos) they are not a major source of metals nor fluids. Metals in the polymetallic deposits of the Cyclades Mineral District are likely derived from a mix of different sources the Miocene granitoids and the metamorphic basement, including gneisses, metapelites, and minor metabasites.

Combined with the observations from the the Pb and Sr isotope data, galena and barite had a mix of Pb and Sr sources in the magmatic and volcanic rocks and the basement lithologies in the footwall of the major detachment systems. In the western Cyclades the metasedimentary rocks of the LCBN are likely the dominant source of metals, whereas in the north-central Cyclades the source was a mix of rocks within the Cycladic Basement, UCBN, and Pelagonian zone. For the Kolumbo seafloor massive sulfides, [Hector et al. \(2022\)](#) concluded that the basement is likely the main source of base metals (Cu, Zn, Pb), whereas the epithermal suite of metals (As, Ag, Sn, Sb, Tl) is derived from a combination of leaching of the basement and direct magmatic contributions. [Hector et al. \(2022\)](#) highlighted an enrichment of metals in the Pelagonian zone (Tertiary flysch exposed on Santorini) that also underlies the caldera of Kolumbo and presents a potential metal source. Also, for the mineralization on Milos a mix of sources of metals has been proposed from the Quaternary volcanic units and the metamorphic basement ([Schaarschmidt et al., 2021a](#)). The inferred source lithologies of the majority of the mineral occurrences are in the footwall of the major detachment systems. An influence of the Pelagonian zone for certain

deposits (e.g., Panormos Bay, Mykonos) in the north-central Cyclades could explain the more heterogeneous isotopic composition of galena and barite in these deposits (Wind et al., 2020, 2023).

4.6.2 Preconcentration of metals in the CBU

An enrichment of metals within the footwall of the metamorphic core complexes is likely due to the complex geotectonic evolution of the area. Moreover, the amount of residual sulfide phases in these rocks may influence the metal ratios in the Cyclades Mineral District (Richards, 2015). Several authors have described metamorphic sulfides in the Cyclades and their importance in the metal endowment of the Cyclades Mineral District. Stouraiti et al. (2022) proposed that Mn-oxide accumulation within the volcanoclastic sequences of the CBU is genetically related to hydrothermal venting in a Triassic back-arc rift setting that also led to an enrichment in As and Ba in these layers. On Evia, Katzir et al. (2000) described occurrences of pyrite in the rims of metapillows together with an enrichment in alkali and Fe and depletion in Ca in the metabasalts, likely linked to hydrothermal sub-seafloor alteration. Scheffer et al. (2017) proposed that a pre-concentration of metals occurred before deformation, subduction, and burial of carbonates during the Cenozoic, as attested by preserved relics of folded pyrrhotite layers in the Lavrion District. At Panormos Bay on Tinos, metamorphic pyrite was described in schists of the CBU (Tombros et al., 2007). In addition, metamorphic sulfides (pyrite in garnet, and pyrite and chalcopyrite in omphacite) were described in the metabasites (blackwall zone) and matrix sulfides in a metagabbroic eclogites from Syros (Walters et al., 2019). Walters et al. (2019) suggested a hypothetical reactive transport model in which fluids migrate along the slab mantle interface and precipitate sulfide minerals in the exhuming high-grade blocks and mélange matrix. These examples illustrate that a pre-enrichment in metals could have occurred dur-

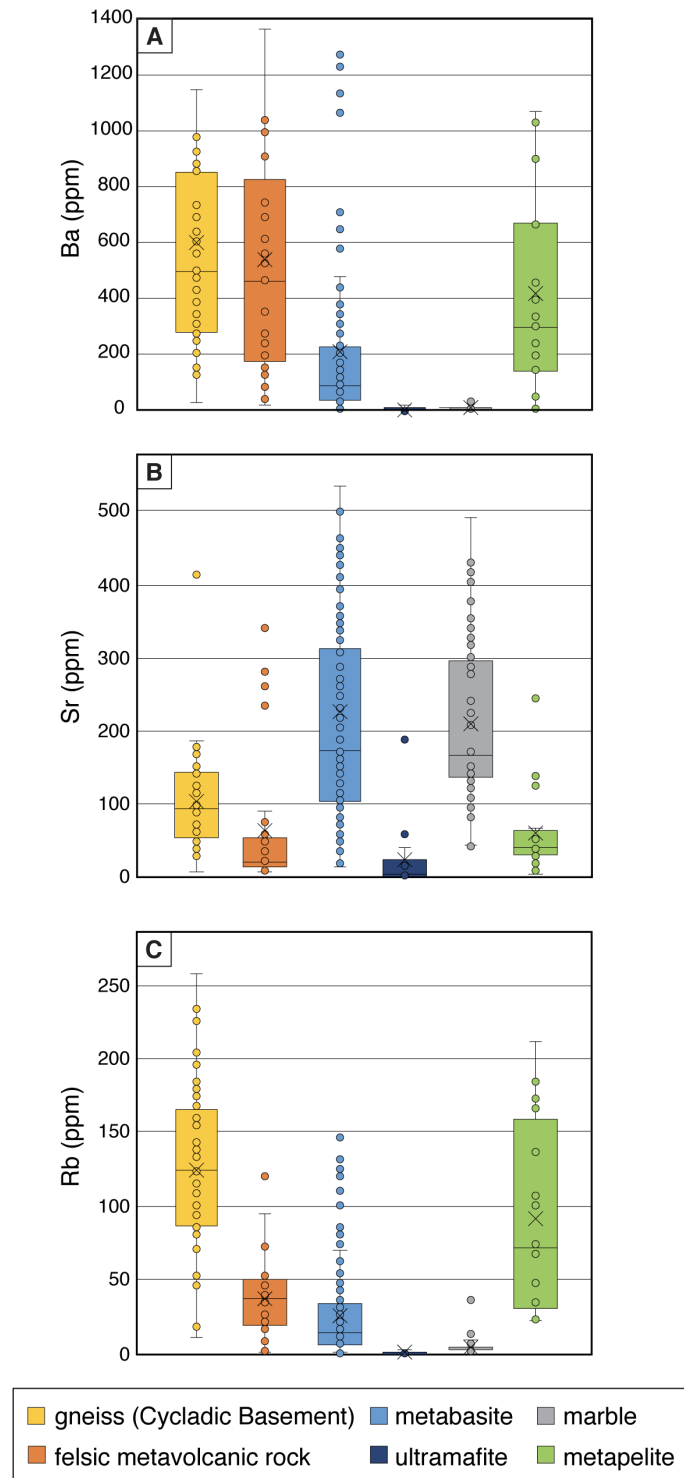


Fig. 4.7: Box and whisker plots showing the barium (A), strontium (B), and rubidium (C) content in the gneisses of the Cycladic Basement and the different rock types of the Cycladic Blueschist Unit.

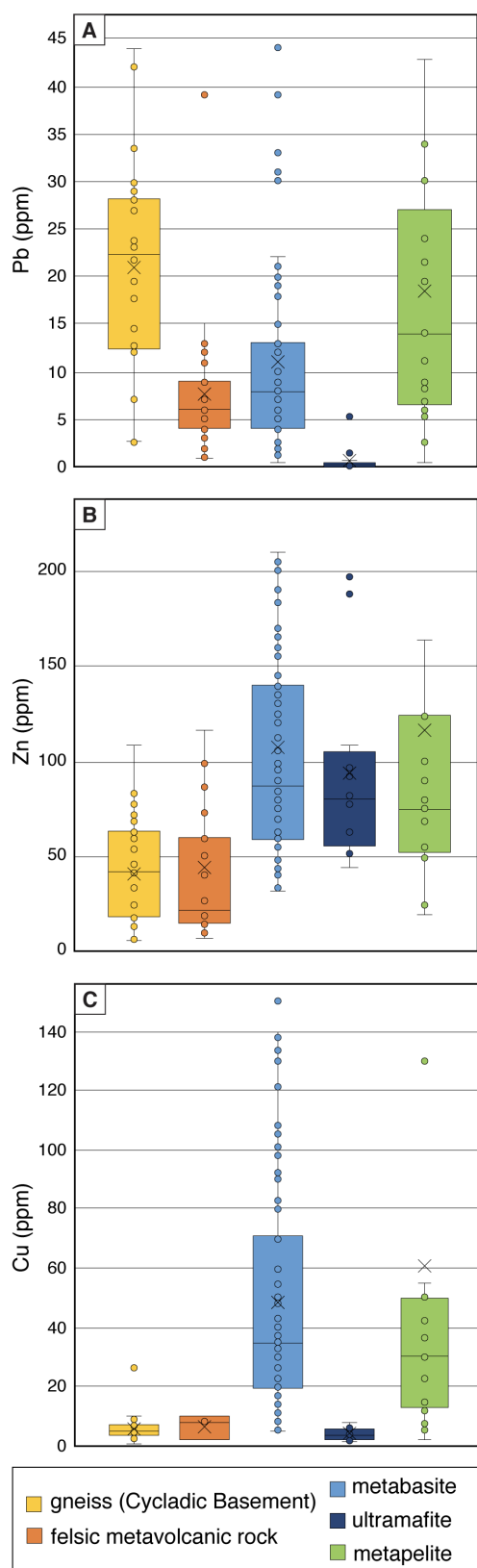


Fig. 4.8: Box and whisker plots showing the lead (A), zinc (B), and copper (C) content in the gneisses of the Cycladic Basement and the different rock types of the Cycladic Blueschist Unit.

ing back-arc rifting in the Triassic or Cretaceous but might also be related to metamorphic fluids of the Mediterranean subduction zone.

4.6.3 Limitations in the interpretation of the compiled data

Lead and Sr isotope data of potential source rocks from the literature are limited and often do not cover both sides of the TCT. Similarly, the compilation of the whole-rock data often shows a focused sampling along a traverse of islands which causes a biased interpretation of the data. In addition, the interpretation of the geochemistry of metamorphic rocks is often challenging due to the pronounced metasomatism and hydrothermal alteration. These processes generally add Na_2O , SiO_2 , K_2O and large ion lithophile elements (LILE: K, Rb, Sr, Cs, Ba, Eu), but remove CaO , Al_2O_3 and MnO (e.g., [Kleine et al., 2014](#)). This can also be observed for the gneisses of the Cycladic Basement (Fig. 4.4), which are enriched in SiO_2 , Na_2O , and K_2O but depleted in CaO and MgO . The strong covariance between SiO_2 and Al_2O_3 might also be related to metasomatism. Studies in the Otago Schist Belt, New Zealand, highlighted the influence of the metamorphic grade on the element mobility ([Pitcairn et al., 2006](#)). Consequently, variations observed in the geochemistry of the blueschists and greenschists (metabasites) of the LCBN at Lavrion might not be related to variations in the ocean basin ([Baziotis & Mposkos, 2011](#)), but rather be linked to the element mobility based on the metamorphic grade. This is highlighted by the abundance of fluid mobile elements (e.g., Sr, Rb, Ba, K) in the eclogites of the CBU (Fig. 4.6C). While the initial purpose of this study was to identify regional scale geochemical patterns in the basement lithologies it highlighted the necessity of a better classification for the exposed metabasites in the Cyclades. Previous studies of the metabasites explained the broad range in the geochemical composition by a multi-tectonic environment, where the protoliths of the metabasites formed at oceanic spreading centers, in a back-arc setting or

in an island-arc setting (e.g., Baziotis & Mposkos, 2011; Mocek, 2001; Cooperdock et al., 2018; Bulle et al., 2010). This re-classification of the metabasites needs to consider the potential ages of the protoliths constraint by new geochronological data from the literature and the metamorphic grade.

4.6.4 Implications for the basement structure

Based on the metal endowment of the Cyclades we conclude that continental derived lithologies are dominant (e.g., as a source of Pb, Sr, Ba). Comparison of the whole-rock geochemistry of metabasites of the CBU and gneisses of the Cycladic Basement and felsic metavolcanic rocks show no pronounced regional pattern (Fig. 4.6). However, marble and metapelites are more abundant in the west Cyclades than in the north-central Cyclades, and metabasic and ophiolitic rocks are more abundant in the north-central Cyclades than in the west Cyclades. We propose that these regional patterns are linked to differences within the CBU itself and that inheritance of the pre-Alpine architecture influenced the geochemistry and isotopic signature preserved in the lithologies and Miocene to recent mineralization. While a higher metamorphic grade and metasomatism in the north-central Cyclades influences the whole-rock geochemistry (Fig. 4.6C) it should not influence the isotopic composition of the lithologies.

The isotopic compositions of rocks from the LCBN and UCBN suggest that they are sourced from different sub-basins or different parts of the same sub-basin. Furthermore, the geochemical and isotopic composition of the metamorphic basement and exposures of the lithologies support the hyper-extended continental margin model for the CBU. [Seaman \(2016\)](#) originally proposed a hyper-extended continental margin model for the CBU based on detrital zircon studies in the western Cyclades in comparison with observed hyper-extended margin sequences elsewhere (e.g., between Iberia and Newfoundland in the North

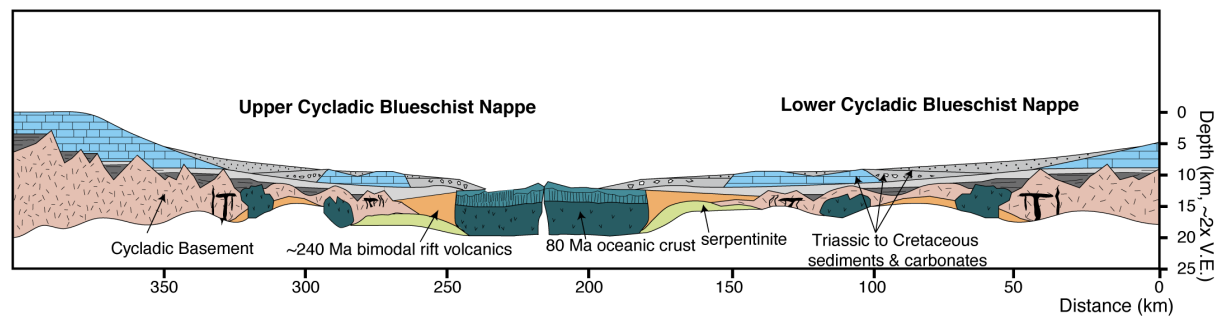


Fig. 4.9: Schematic paleogeographic reconstruction of the protoliths for the Upper and Lower Cycladic Blueschist Nappe (modified from Kotowski et al. (2022)).

Atlantic: Sutra et al., 2013; Chenin et al., 2015). Kotowski et al. (2022) further developed this model for the CBU based on the exposed lithologies on Syros and concluded that Syros comprises three coherent tectonic slices. Figure 4.9 shows a simplified sketch of the proposed hyper-extended margin illustrating a schematic paleogeographic reconstruction of the protoliths of the CBU during the Cretaceous prior to the Cenozoic subduction. Rock units exposed in the north of the UCBN are derived from segments of the margin (exhumation domain: Chenin et al., 2015) closer to the ongoing rifting in the Cretaceous (oceanic domain), while the central Cyclades corresponds to the necking domain, with a thick underlying continental basement. The LCBN represents a section of the passive continental margin of the hyperextended domain with a thinned underlying Cycladic Basement at greater depth.

Based on the peak metamorphic conditions, Evia has been correlated to the LCBN (Grasemann et al., 2018; Ducharme et al., 2022), however, based on the Pb isotope composition of galena, Wind et al. (2020) correlated Evia with the UCBN. Also, the exposures of ophiolitic mélanges on Evia (Katzir et al., 2000) support a correlation with the UCBN where mafic and ultramafic occurrences are generally more abundant than in the LCBN. Furthermore, the heterogenic nature of the exposed Basal Unit and Cycladic Basement

might potentially be related to the architecture of the margin prior to the Cenozoic geodynamics including subduction and exhumation.

4.7 Conclusions

This compilation and review of the basement lithologies provides a first step in the reconstruction of the architecture of the metamorphic basement. Characteristic trends observed in the whole-rock geochemistry reflect the range of different lithologies exposed in the Cyclades. In addition, variations observed in the geochemical composition of the metabasites across the Cyclades is partly also related to variances in the metamorphic grade. Although the whole-rock isotopic composition shows a broad dispersion, Miocene to recent mineralization in the Cyclades causes homogenization of different metal/crustal sources leading to the observed regional pattern in the isotopic signature. The isotopic composition of the hydrothermal minerals indicate that the Cycladic Basement has a stronger influence on the metal sources in the north-central Cyclades than in the west Cyclades. This is most likely influenced by the inheritance of the pre-Alpine architecture and its influence on the geochemistry and isotopic signature preserved in the lithologies and Miocene and younger mineralization. In complex continental back-arc settings, mineralization can provide information about past tectonic events and provides information on the geologic history from unobservable depths to the surface.

Chapter 5

5 Synthesis, conclusions, and outlook

This thesis provides a comprehensive view of the metal and fluid sources of the different mineralizing systems in the Cyclades Mineral District, Greece. The widespread mineralization in this continental back-arc system is strongly influenced by the host rocks of the metamorphic core complexes. Major detachment systems played a significant role in the circulation of ore-forming fluids, with mixing of surface-derived fluids (seawater $\pm$ meteoric water) and magmatic fluids. Base and precious metal-rich deposits in the Cyclades Mineral District all contain galena and barite, which record the fluid sources. Combining multiple isotope systems in these minerals allows them to provide a tracer of the fluid and crustal sources. This thesis provides the first regional overview of their isotopic and geochemical compositions.

The regional pattern observed in the Pb isotopes of Cycladic galena discussed in Chapter 2 correlates well with the Sr isotopes in barite outlined in Chapter 3. These results support the strong influence of the underlying basement in the source of labile elements (e.g., Pb, Sr, Ba) in the hydrothermal fluids. There is a clear division between $^{206}\text{Pb}/^{204}\text{Pb} \leq 18.84$ and $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.711$ in the north-central Cyclades and $^{206}\text{Pb}/^{204}\text{Pb} \geq 18.84$ and $^{87}\text{Sr}/^{86}\text{Sr} \leq 0.711$ in the west Cyclades (Fig. 5.1). This correlates with the exposures of the Lower Cycladic Blueschist Nappe (LCBN) and Upper Cycladic Blueschist Nappe (UCBN) and follows the trace of the synorogenic Trans-Cycladic Thrust (TCT). The regional patterns

in the isotopic and geochemical signature of the galena and barite highlight the differences in lithologies between the hanging wall and the footwall of the TCT, which include not only differences in metamorphic grade ([Grasemann et al., 2018](#)) but also different parts of the pre-Alpine extended continental margin sequence. Regional heterogeneities in the composition of the metamorphic basement (Chapter 4) reflect a crustal inheritance of the pre-Alpine basement, consistent with the UCBN and LCBN representing different parts of the extended continental margin. [Kotowski et al. \(2022\)](#) and [Seman \(2016\)](#) previously proposed a hyper-extended continental margin model for the Cycladic Blueschist Unit based on the exposed lithologies on Syros and detrital zircon studies in the western Cyclades. Results of this thesis include the first regional isotopic and geochemical evidence for this model. Moreover, the isotopic composition of the barite and galena provide an additional tool for the paleogeographic reconstruction of juxtaposed tectono-stratigraphic units across the Cyclades and other complex continental back-arc systems.

This study also shows a strong variation in the isotopic composition and trace element concentrations of galena and barite among deposits on the same island in the north-central Cyclades, which is not observed in the west Cyclades. This suggests that the intrusion-related vein-type deposits in the north-central Cyclades tap a mixture of magmatic and crustal sources, whereas metals in the deposits in the west Cyclades are mainly sourced from the LCBN. For the majority of the deposits in the north-central Cyclades the Cycladic Basement is the main source of metals causing the observed regional pattern. However, leaching of metals from the Paleogonian zone and Neogene basin sediments in the hanging wall is also possible for some deposits, as seen at Panormos Bay, Mykonos ([Wind et al., 2023](#)) and Kolumbo ([Hector et al., 2022](#)).

Results of this study demonstrated the usefulness of LA-ICP-MS to track the isotopic and trace element compositions of barite and galena. Such studies are still novel (e.g., [George](#)

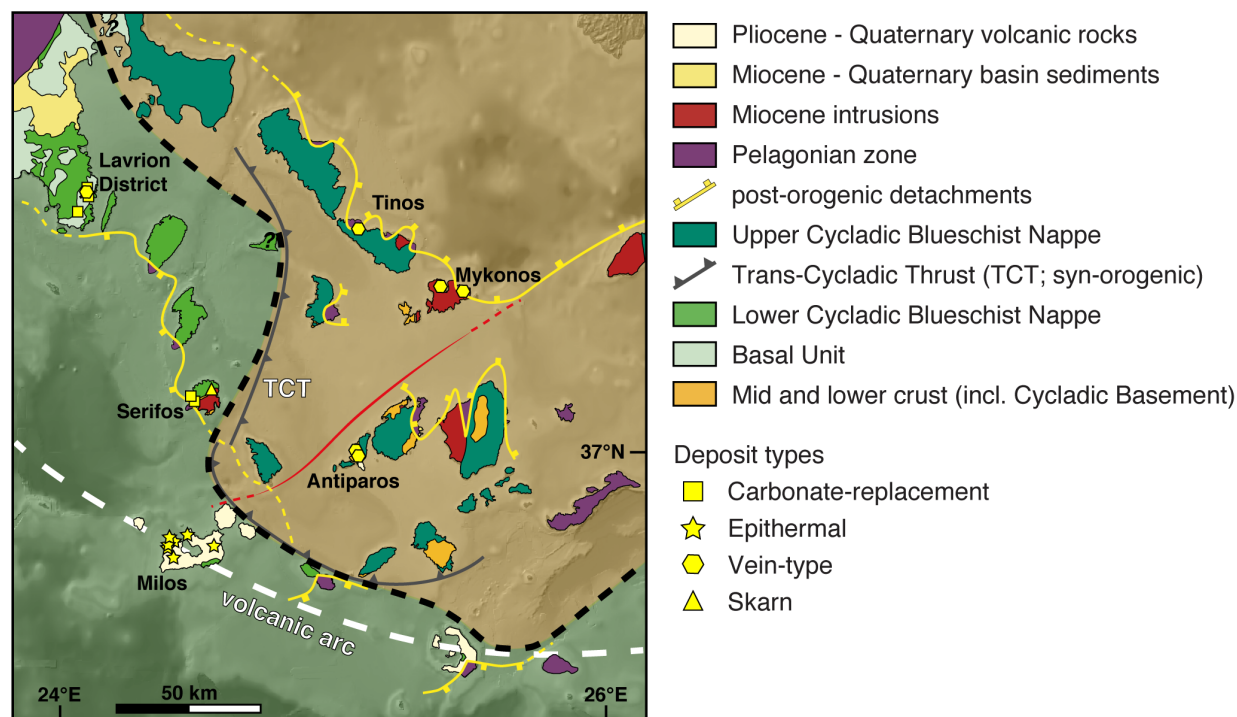


Fig. 5.1: Simplified geological map of the Cyclades Mineral District, Greece, slightly modified after Wind et al. (2020). Based on the Pb isotope ratios of galena and Sr isotope signature of barite from the Cyclades Mineral District, metal sources can be divided into two regions: $^{206}\text{Pb}/^{204}\text{Pb} \leq 18.84$ and $^{87}\text{Sr}/^{86}\text{Sr} \geq 0.711$ in the north-central Cyclades, reaching the Cycladic Basement and Upper Cycladic Blueschist Nappe, and $^{206}\text{Pb}/^{204}\text{Pb} \geq 18.84$ and $^{87}\text{Sr}/^{86}\text{Sr} \leq 0.711$ for the deposits in the west Cyclades, tapping the Lower Cycladic Blueschist Nappe. Notably, these two regions are separated by the $^{206}\text{Pb}/^{204}\text{Pb}$ 18.84 and $^{87}\text{Sr}/^{86}\text{Sr}$ 0.711 line (bold dashed line) which is parallel to the proposed trace of the Trans-Cycladic Thrust (TCT).

et al., 2015, 2016; McFarlane et al., 2016) but became more of a focus recently (e.g., Hu et al., 2021; Aldis et al., 2022). This study shows that a careful analytical protocol and data acquisition can produce accurate and precise Pb isotope measurements in galena by LA-Q-ICP-MS with results comparable to the standard techniques (double spike TIMS or MC-ICP-MS). In combination with the extensive compilation of previously published Pb isotope data of galena, these data can be used to map regional variations throughout the Cyclades (Chapter 2). In addition, sequential measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ on the same ablation spot in barite showed the efficacy of LA-MC-ICP-MS for these isotopic systems (Chapter 3). The results showed that combining $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{34}\text{S}$ analyses by LA-MC-ICP-MS is a powerful tool to monitor the changes in the ore-forming system that are preserved by isotopic and compositional zoning in barite.

The LA-ICP-MS data showed that galena is also enriched in certain trace elements and their concentrations vary depending on the mineralization style and the physico-chemical conditions of ore formations (Chapter 2). For example, Bi concentrations in galena are high in deposits formed by magmatic fluids (e.g., Moutoulas, Serifos; Panormos Bay, Tinos). Similarly, elevated Te concentrations are also likely related to contributions from magmatic fluids as seen at Panormos Bay (Tinos) and Profitis Ilias (Milos). Low standard deviations for Se and Te in galena from Panormos Bay (Tinos) suggest that these elements are present in solid solution, whereas enrichment in Te is likely partly due to micro-inclusions in galena from Profitis Ilias, Milos. However, a model that explains the occurrences of Te within the crystal lattice in galena is still lacking (George et al., 2015).

Strong isotopic and compositional variances in barite from polymetallic veins and carbonate-hosted deposits showed a range of fluid sources and mixing of fluids from magmatic to surface-derived. Barite from the Cyclades can be grouped into two end-member systems; a seawater-dominated system with high $\delta^{34}\text{S}$ values, low $\delta^{18}\text{O}$ values, and radio-

genic Sr derived from the metamorphic basement, and a magmatic-dominated system with low $\delta^{34}\text{S}$ values, high $\delta^{18}\text{O}$ values, and Sr derived from the Miocene intrusions. This shows that different mineral deposits in the Cyclades can be clearly distinguished by the isotopic signatures of their barite, providing a useful guide in future exploration for these types of deposits in Greece and in other continental arc-backarc systems.

5.1 Mineralization in the Cyclades Mineral District

Figure 5.2 summarizes the fluid and crustal sources for the different deposit types in the Cyclades Mineral District. The following provides a summary of the major findings for the investigated deposits at Lavrion, mainland Greece, and the Cycladic islands. The numbers in brackets correspond to the numbers in Figure 5.2.

5.1.1 Lavrion

At Lavrion on the Attica Peninsula, mainland Greece, carbonate-replacement and late vein- and breccia style mineralization has been studied at Plaka, Kamariza, Soureza [1] and Villia [2]. Sulfur and oxygen isotopes in barite of the late vein- and breccia-style mineralization record the shift from a magmatic dominated fluid source to a seawater derived fluid source. Pb isotope ratios of galena and Sr isotope ratios of barite show small variations depending on the interaction with various host rocks. Trace element concentrations in galena from Kamariza and Plaka are similar but distinct from Soureza, where galena is notably enriched in Ag, Sb, and Cu. Samples from Lavrion show low concentrations of Sn in galena, which was not observed in other samples of galena from the Cyclades.

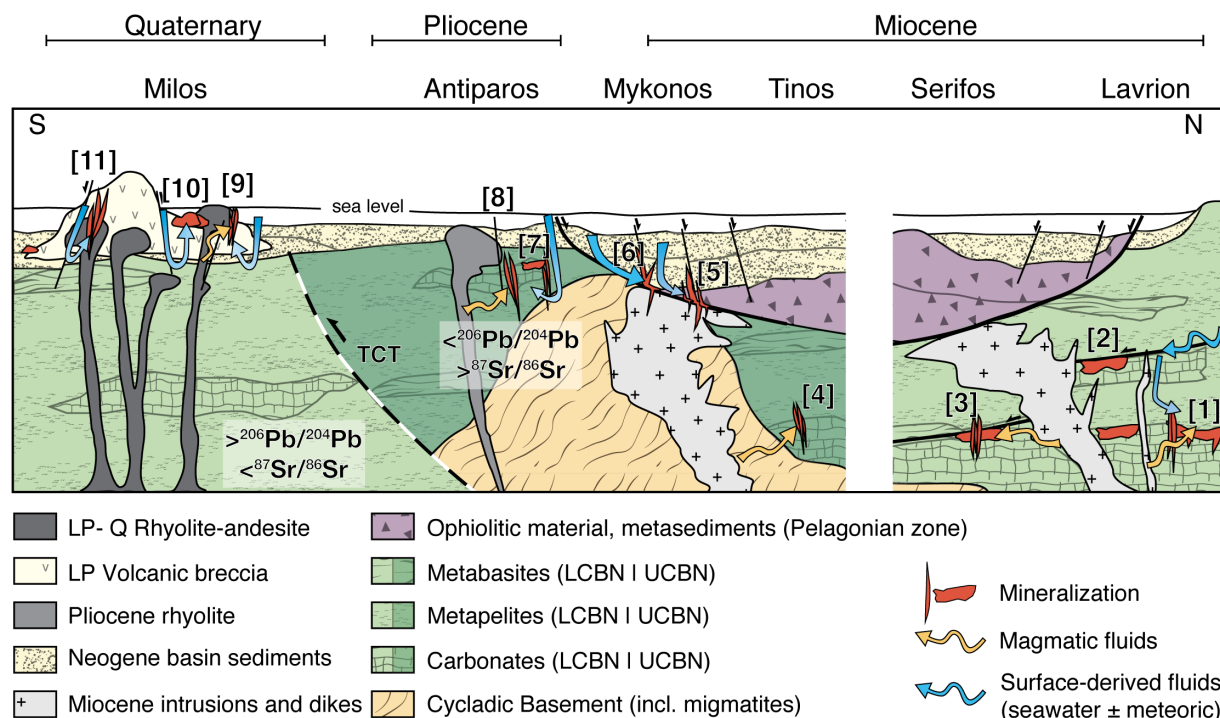


Fig. 5.2: Simplified model summarizing the main characteristics of the hydrothermal mineral deposits in the Cyclades (modified after Wind et al. (2023)). The model is not to scale and focuses on the upper 5 km of the crust during ore mineralization from the late Miocene and into the Quaternary. Numbers correspond to the following deposits: [1] Plaka, Kamariza and [2] Villia at Lavrion; [3] Mega Livadi and Cape Kaparia on Serifos; [4] Panormos Bay on Tinos; [5] Cape Charos, Cape Evros, and [6] Panormos Bay on Mykonos; [7] Prassovounia and [8] Agios Georgios on Antiparos; [9] Katsimouti, [10] Cape Vani, Kalogries, Triades, Galana, and [11] Profitis Ilias, Fourkovouni, and Kastana on Milos. LCBU = Lower Cycladic Blueschist Nappe, LP = late Pliocene, LP-Q = late Pliocene-Quaternary, TCT: Trans-Cycladic Thrust, UCBN: Upper Cycladic Blueschist Nappe.

5.1.2 Serifos

On Serifos, carbonate-hosted Fe-Ba mineralization has been studied at Mega Livadi and Cape Evros [3] in the west of the island. In addition, galena has been investigated from the polymetallic skarn and vein-type mineralization at Moutoulas in the north of the island. At all deposits fluid sources are mostly of magmatic origin. Galena from Moutoulas is notably enriched in Bi, supporting the formation at higher temperatures and by magmatic derived fluids.

5.1.3 Tinos

Sampling on Tinos returned appropriate galena samples from Panormos Bay [4] while samples from Apigania Bay were not suitable for this regional study. Galena from the vein-type mineralization at Panormos Bay has a lower $^{206}\text{Pb}/^{204}\text{Pb}$ composition than galena from Apigania Bay (OXALID database) highlighting the variations observed in the isotopic signature for different mineral occurrences on the north-central Cycladic islands. Galena from Panormos Bay has the highest average concentrations in Se (800 ppm), Te (300 ppm), and Bi (300 ppm) likely related to magmatic fluids. Barite crystals of a few micrometer were observed in the mineralization from Apigania Bay while barite is absent in the samples from Panormos Bay.

5.1.4 Mykonos

In comparison to other areas in the Cyclades the mineralization on Mykonos is not well studied and results of this study highlighted significant differences in the sources of metals and fluids among the different deposits (Panormos Bay, Cape Evros, Cape Charos). Lead and Sr isotope ratios and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of barite and galena of Cape Evros [5] differ

significantly from those at Panormos Bay [6]. These isotopic and geochemical differences between Cape Evros and Panormos Bay correlate with the position of an inferred N-S trending normal fault in the center of the island (Lecomte et al., 2010; Denèle et al., 2011). A large fault which bisects the island has previously been proposed by Lahti (1978) based on anomalous base metal values in a rock chip survey covering Mykonos island. However, leaching of the Miocene conglomeratic sequence which is evident by the pronounced alteration halo observed at Panormos Bay (Fig. 3.3K) could also have influenced the observed geochemical and isotopic variances. This is supported by high Sb and Ag concentrations, together with elevated concentrations of a few 100 ppm of As, Cu, and Hg in combination with oscillatory zoning. Oscillatory zoning in galena (Fig. 2.6G) might also be related to pulses of mineralization with crystallization in a locally closed system as previously proposed for galena from epithermal veins (George et al., 2015). This process could also explain the observed positive correlation between $\delta^{34}\text{S}$ and Sr content in barite from Panormos Bay (Fig. 3.12). These observations highlight potential questions for future research on Mykonos.

5.1.5 Antiparos

On Antiparos vein-type mineralization at Prassovounia [7] and Agios Georgios [8] has been studied. At Agios Georgios barite records a shift in the dominant fluid sources, from magmatic to seawater dominated. The nearby Pliocene rhyolite intrusion is a probable source of the magmatic fluid components at Agios Georgios. Barite from Prassovounia records a seawater dominant fluid source. Low $\delta^{18}\text{O}$ values of barite from Prassovounia, might suggest a contribution of meteoric water or indicate an interaction of the hydrothermal fluid with the host rock. Trace element concentrations of galena from Prassovounia are low and contrast with previously reported trace element concentrations from Agios Georgios (e.g.,

[Kevrekidis et al., 2015](#); [Gale & Stos-Gale, 1981](#)). This might suggest that mineralization at Agios Georgios and Prassovounia formed by two independent mineralizing systems.

5.1.6 Milos

Variations in the Sr and Pb isotope composition for the deposits on Milos are small and depend on the interaction of the hydrothermal fluids with the underlying metamorphic basement (LCBN) and Quaternary volcanic rocks. Significant variations among the deposits on Milos were only observed in the $\delta^{34}\text{S}$ values of barite of the polymetallic mineralization at Kondaros-Katsimouti [9], suggesting contribution of a magmatic fluid source to the generally seawater-dominated hydrothermal fluids for the hybrid intermediate sulfidation epithermal-to-VMS [10] to subaerial epithermal systems [11]. Galena at Profitis Ilias is enriched in $\text{Te} \pm \text{Au}$ while the highest concentrations in Ag were measured in galena from Kondaros-Katsimouti. Recent studies of the mineralization on western Milos suggested that mineralization occurred temporally unrelated to each other from 2.8–1.5 Ma ([Miles, 2021](#)). However, as shown in this study and by [Schaarschmidt et al. \(2021a\)](#) and [Grosche et al. \(2023\)](#), the different mineralizing systems on Milos have similar metal and fluid sources that are potentially accessed by a large-scale fault network as proposed by [Grosche et al. \(2023\)](#).

5.2 Perspectives and outlook

In this study, analyses of the isotopic and geochemical composition of hydrothermal galena and barite were carried out by LA-Q-ICP-MS and LA-MC-ICP-MS on handpicked mineral separates from a range of deposits in the Cyclades Mineral District. It was shown that this approach is useful for documenting regional changes in fluids and in crustal sources of

metals and other elements during deposit formation. Isotopic and geochemical zoning occurs in both galena and barite from several of the investigated deposits, recording multiple stages of mineralization (e.g., Lavrion). Documenting these changes during mineralization requires in-situ high-resolution analyses in polished thin sections.

Limited and widely-spaced isotope analyses of the whole-rocks, such as the underlying metamorphic basement (Cycladic Basement, CBU), make comparisons between mineral deposits difficult. An expanded Pb and Sr isotope study of the basement lithologies is needed to fully reconstruct the role of the metamorphic basement in the metallogeny of the region. Because most studies have focused either on the west Cyclades or north-central Cyclades, more closely spaced sampling across the TCT would be useful. The particular role of the different nappes of the Cycladic Blueschist Unit could be better resolved with more data on the Sr isotopes of marble units with a focus on the west Cyclades.

The timing of ore mineralization with respect to the intrusions and activity of the detachment systems still needs to be resolved. Due to the lack of dating, the age of mineralization is only indirectly linked to the emplacement of the intrusions and transition of the detachments from ductile to brittle conditions. However, gaps in the geological record need to be filled, for example, where a 5 Myr pause in the Cycladic mineralization was proposed between Miocene and Pliocene events (Antiparos, [Melfos & Voudouris, 2017](#)). Constraining the ages of mineralization would also help to better reconstruct the past 10 Myr of exhumation. Exhumation rates in the Cyclades vary significantly (0.5–6 km/Ma; [Ring et al., 2007](#); [Lecomte et al., 2010](#); [Kotowski et al., 2022](#); [Lamont et al., 2020b](#)) with little data after 10 Ma. What happened in the past 10 Ma, during ore mineralization, is still poorly constrained. A better estimation of the ages and depth of ore formation would be a first step in closing this gap in the geodynamic evolution of the Cycladic metamorphic core complex.

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