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Alexandre Tarantola, Christophe Scheffer, Olivier Vanderhaeghe, Panagiotis Voudouris, Adonis Photiades, Denis Morin

Geologic and metallogenic overview of the Lavrion mining district: A guide for archaeological exploration

ABSTRACT: *The Lavrion mining district (SE Attica, Greece) comprises ore deposits of (1) low-grade Mo-Cu porphyry style, (2) Cu-Fe skarn, (3) high-temperature carbonate replacement Pb-Zn-Ag-(Au), and (4) vein and breccia Pb-Zn-Ag mineralizations. These are the result of the transport and deposition of economic elements from fluids that circulated from the construction to the gravitational collapse of the Hellenides-Aegean Domain along the Africa-Eurasia convergent plate boundary active for the last 80 Ma. Oceanic and continental rocks of the African plate were buried to high pressure conditions in the subduction zone. Progressive southward slab retreat was accompanied by magmatism and exhumation of metamorphic rocks along high- and low-angle detachment systems, with associated mineralized systems. The porphyry and skarn deposits are spatially and genetically related to the Plaka magmatic intrusion dated 12 – 8 Ma. Carbonate replacement is associated with decarbonation and the liberation of* CO_2 *during exhumation at the ductile to brittle transition. Fluorite and calcite gangue minerals enclosing the vein and breccia Pb-Zn-Ag mineralization were precipitated during brittle deformation from a fluid resulting from mixing of meteoric water with evaporated seawater closer to the surface. Base and precious metals were exploited since the Bronze Age to the late 20th century. As such, the Lavrion area represents an exceptional site to study the evolution of mining technologies through history.*

KEYWORDS: LAVRION, DETACHMENT, GEOLOGICAL FLUIDS, ORE DEPOSITS, MINING ARCHAEOLOGY

Introduction

The Lavrion mining district (SE Attica, Greece) is known at least since 3000 BC for its Pb-Zn-Ag deposits, among others. It was intensively mined during the 5th – 4th centuries BC, corresponding to the so-called Classical Hellenic period, where it was an essential piece for the development of Athens. It continued to be exploited over historical times until the late 20th century by the Compagnie Française des Mines du Laurion (CFML) (Conophagos, 1980). To understand how the metals were deposited at this specific place is of key importance to better apprehend how they were mined during history. Why are these deposits here and not somewhere else? When and how did they form? These are questions of major importance to understanding the Aegean world during the past centuries and also to bring keys for the discovery of other such deposits. The purpose of this paper is to situate the deposits of the Lavrion mining district in their geological dynamic framework with a particular interest in geological fluids based on the latest published papers. Moreover, this contribution aims to be understandable by a large audience of readers who are not familiar with the geological jargon.

During geodynamic evolution, rocks are modified (formation of metamorphic rocks through recrystallization processes, which include deformation and apparition of new minerals) due to changes of tectonic stress and of pressure (*P*) and temperature (*T*) conditions. In active tectonic settings rocks experience burial and exhumation. During this cycle, temperature and pressure vary within the Earth's crust. The rocks are then deformed and their minerals thus recrystallize through metamorphic transformations. During exhumation, metamorphic rocks evolve from elevated *PT* conditions with a ductile rheologic behaviour (plastical deformation with no rupture in the structure, the result is stretched deformed rocks showing intense dynamic recristallisation named mylonites) to more superficial low-temperature (L*T*) and low-pressure (L*P*) conditions where deformation is brittle and localized along fractures or faults. The resulting cohesive brittle fractured rocks are named cataclasite, the fragments of which are cemented thanks to interactions with fluids (hydrothermal breccia). The ductile to brittle transition was thus demonstrated to be a structural, rheological, and thermal boundary separating an upper crust dominated by the percolation of meteoric, marine, and basinal fluids and a lower crust marked by the circulation of magmatic and metamorphic fluids (e.g. Ingebritsen and Manning, 1999; Siebenaller, et al., 2013). Therefore, many case studies reported that the mylonitic-cataclastic transition is pivotal for ore deposition, as it corresponds to preferential zones of fluid circulation and possible mixing of reservoirs associated with fluctuations in the pressure regime (e.g. Lindsay, et al., 1995; Baker and Laing, 1998; Boiron, et al., 2003; Moritz, et al., 2006). This transition occurs during exhumation along low-angle detachments that correspond to regional scale normal faults formed in extensional tectonic regime (Jolivet, et al., 1998; Jolivet and Faccenna, 2000; Scheffer, et al., 2016).

Fluids carry heat and matter under the form of dissolved elements within the Earth's crust (Fyfe, et al., 1978; Etheridge and Wall, 1983; Thompson and Connolly, 1992). Geological fluids of various nature have been demonstrated to flow within the Earth's crust, including magmatic (metal- and salt-rich aqueous solutions, and vapour exsolved from magma), metamorphic (issued from dehydration [water] or decarbonation [carbon dioxide] reactions), connate (water-dominated aqueous solutions contained in pores of sedimentary rocks), marine (aqueous solutions containing salts; the concentration of standard seawater is of around 3.5 wt.% $NaCl_{eq}$, this value increases with evaporation), or meteoric (water derived from the atmosphere by precipitation or condensation, i.e. rain water) origin (Taylor, 1974, 1997; Arndt and Ganino, 2012). The geochemistry of geological fluids is dominated by water and salts (with NaCl, $CaCl_2$ and KCl as the predominant species), but they may also contain gases, where CO_2, N_2 and CH_4 are the most commonly found. Their characterization is a central part of the study of mineralized systems as hydrothermal fluid circulation permits leaching, mobilization, transport, and deposition of elements of economic interest at the crustal scale. It is thus of major interest to constrain the source of ore-forming fluids and associated fluid-fluid and fluid-rock interactions to characterize the mode and conditions of formation of metal deposits. Indirect evidence of hydrothermal fluid circulation within the Earth's crust are mineralized veins and alteration minerals. Geological fluids may also be trapped in micrometric tiny pockets within minerals called fluid inclusions. Fluid inclusions (FIs) trapped a fluid (water, dissolved salts, gases) circulating during rock history. The physical and geochemical properties of FIs thus directly witness the conditions of paleofluid circulation. Inclusions may be found as isolated FIs or aligned underlining crystal growth zones thus suggesting entrapment during mineral growth (primary FIs). Inclusions may also have trapped a fluid present in a fracture formed during (pseudo-secondary FIs) or after (secondary FIs) crystal growth (Roedder, 1984). The analysis of fluid inclusions in the laboratory by specific techniques like microthermometry, Raman spectrometry and Laser Ablation ICP-MS permit the composition (*X*) and density or molar volume (*V*) of individual FIs to be quantified. These information are key constraints to the discussion of element transport and *PT* conditions of formation of a hydrothermal deposit. Stable isotope signatures ($\delta^{13}C$, δD, $\delta^{18}O$, $\delta^{34}S$) of host-minerals and FIs complement *VX* data and provide information regarding the temperature and the source of the fluid and possible fluid-rock interactions. The integration of fluid inclusion petrography and their *VX* properties in their tectonic and petrographic context provides a dynamic view of mineralization evolution through time.

The Lavrion Pb-Zn-Ag mining district (Greece), located along the western boundary of the Attico-Cycladic Metamorphic Complex in the internal zone of the Hellenic-Aegean orogenic belt, is an illustrative and emblematic example of the involvement of multiple ore fluid systems in the formation of various ore type deposits. We will show in this paper the particular geological context of the Lavrion area and its location in the Attico-Cycladic system, the main lithologies and tectonic units, the types of ore deposits and their link with the circulation of geological fluids. The Lavrion mining district is the result of favourable geological conditions that permitted deposition of exceptional base metal content over a small area. Consequently, metal exploration lasted over centuries, making this place a reference case study for mining archaeology and the evolution of mining technologies over History.

The Lavrion area in the Attico-Cycladic system

Attica is part of the Alpine belt, which extends from Morocco to extreme SE Asia and which results from the closure of the Tethys Ocean since Mesozoic times (Fig. 1a). During Jurassic (Lias and Dogger), the region was situated at tropical latitudes and was subjected to alternating sedimentation of limestones and marls. Since 80 Ma, due to Atlantic opening, Africa slowly rotated anticlockwise towards the north and Eurasian continent. The result is the Hellenides domain formed during subduction at this convergent plate boundary, with a slab (portion of the African tectonic plate that is being subducted) oriented to the North, including several oceanic and continental fragments (Aubouin, 1973; 1976; Dewey and Sengör, 1979). During the subduction stage, oceanic rocks (ophiolitic rocks made of gabbros and basalts often altered to serpentinites, also referred to as green rocks) and rocks deposited on the continental shelf (limestones and marls) were submitted to elevated *P* conditions. Rocks were deformed and new minerals witnessing these *PT* conditions appeared through recrystallization and metamorphic reactions. Limestones and marls became marbles and schists, respectively. The subduction zone with the Aegean slab progressively retreated from Rhodopes massif (since around 30 Ma) to the currently active Santorini Island as indicated by the migration of calc-alkaline arc magmatism (Fytikas, et al., 1984). The metamorphic rocks formed in this subduction zone were then exhumed due to the southward retreat of the slab beneath the Aegean domain and the associated Metamorphic Core Complex (MCC) (Dürr, et al., 1978; Jacobshagen, et al., 1978; Jacobshagen, 1986). The present situation of the Aegean slab and the lithospheric structure was shown by

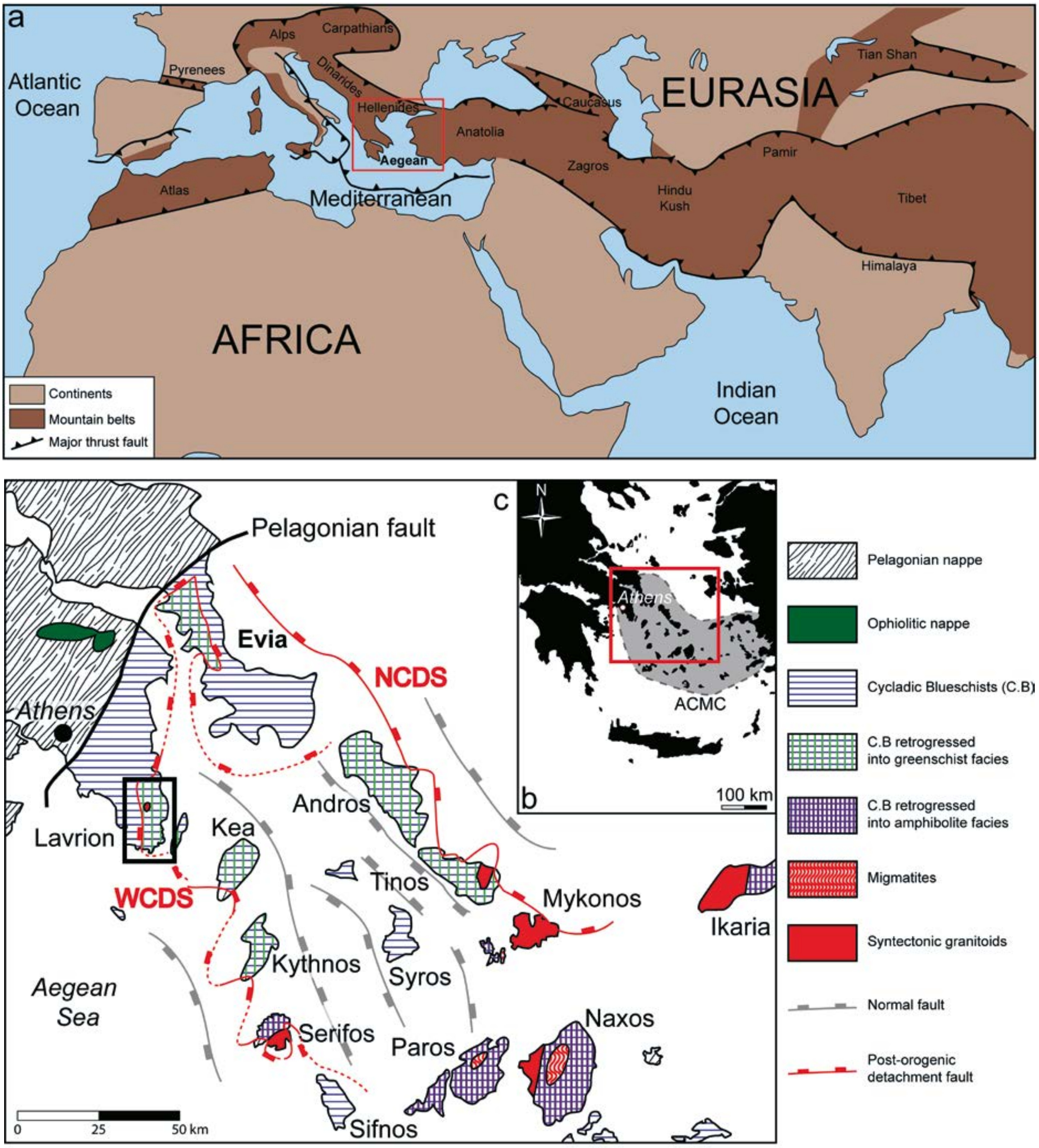

Fig. 1: a. Location of the Hellenic domain within the Alpine orogenic system (modified after Vanderhaeghe, et al., 2007). – b. Attico-Cycladic Metamorphic Complex (ACMC) and location of map c in red. – c. Tectono-metamorphic map of the ACMC with syntectonic magmatic rocks and position of the Western and Northern Cycladic Detachment Systems (WCDS and NCDS, respectively) low-angle faults accommodating post-orogenic exhumation. The black rectangle area corresponds to the location of the Lavrion map of Fig. 2.

seismic tomography with the subduction trench that now lies beneath south of Creta Island (Spakman, et al., 1988; Bijwaard et al., 1998).

The Attico-Cycladic MCC (Fig. 1b,c) is composed mainly of the Cycladic Blueschists. These H*P* rocks were partially or totally retromorphosed by retrograde greenschist to amphibolite H*T* metamorphism during their exhumation along the low-angle North and West Cycladic detachment systems. The extensional phase of the Aegean domain occurred during Oligocene-Miocene (Lister, et al., 1984; Gautier and Brun, 1994a, b; Jolivet, et al., 2010; Grasemann, et al., 2012). Naxos, Paros, Mykonos and Ikaria islands exposed the core of the Attico-Cycladic MCC where high-temperature rocks showing

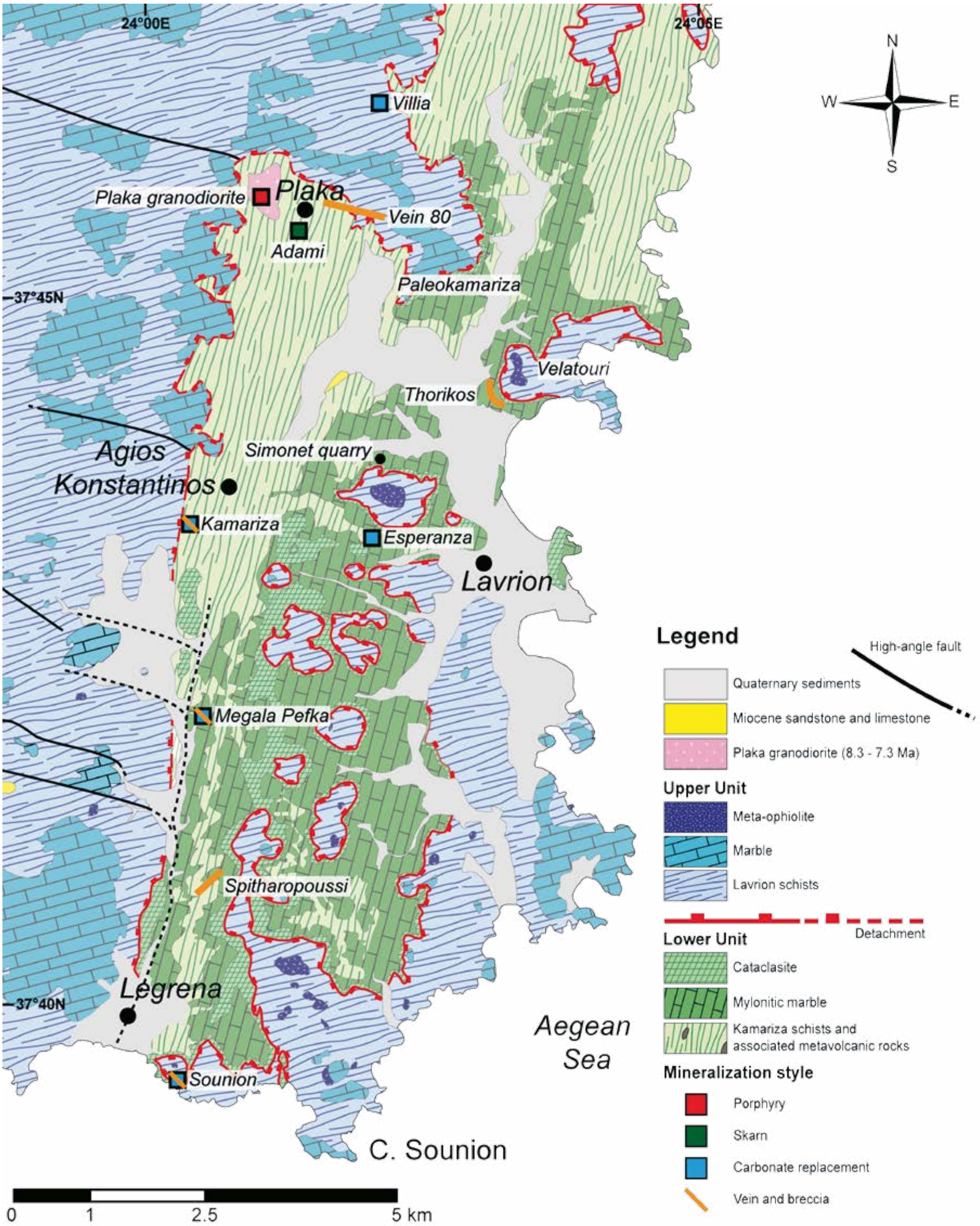

Fig. 2: Geological map of the Lavrion Peninsula and SE Attica with main types of ore deposits (modified after Scheffer, et al., 2016).

partial melting (migmatites) are observed (Fig. 1c; Keay, et al., 2001; Vanderhaeghe, 2004; Martin, et al., 2006; Ring, 2007; Kruckenberg, et al., 2011).

The Lavrion Peninsula, located some 40 km SE of Athens, represents the southern part of Attica and marks the western boundary of the Attico-Cycladic MCC. As such, the Lavrion area represents a highly strategic place from a geological point of view, where intensely deformed and metamorphosed oceanic (green metabasalts and serpentinites) and sedimentary (schists

Fig. 3: Typical landscape of the Lavrion Peninsula (Legrena Valley) showing the superposition of the Lower marble, Kamariza schists and Upper marble of the Lower unit (photo: A. Tarantola).

and marbles) are exposed (Fig. 2). The area is marked by the West Cycladic detachment, which localizes deformation and fluid circulation during exhumation of the rocks. Moreover, the extension phase is associated with magmatic intrusions.

Lithologies and tectonic units of the Lavrion area

The geology of the Lavrion area is marked by the low-angle post-orogenic West Cycladic detachment fault system that separates the Lower and Upper units in the extension regime during exhumation (Grasemann, et al., 2012; Scheffer, et al., 2016). The area is dominated by the Lower unit (also referred to as the Kamariza unit) composed of alternating folded marbles (Lower and Upper marbles) and the Kamariza schists (Fig. 3), which host boudins of metavolcanic basic rocks. The Lower and Upper marbles are generally white or blue as a function of the amount of detrital materials in them (Fig. 4a,b). These rocks are strongly deformed with intense mylonitization (ductile deformation). Towards the top of the Upper marble, the metamorphic marbles show cataclastic texture resulting from brittle deformation (Fig. 4c). The last meters of the Lower unit is composed of an orange dolomitic hydrothermal breccia suggesting intense fluid circulation (Scheffer, et al., 2017b; Fig. 4d). This shallow dipping mylonitic to cataclastic transitional shear zone marks the location of the detachment fault over the Lavrion area (Scheffer, et al., 2016; 2017b). This low-angle detachment, which was active during the Miocene, lies within the metamorphic nappe stack and localizes the deformation during orogenic gravitational collapse with a transition from ductile to brittle conditions (Scheffer, et al., 2016).

The Upper unit (also named the Lavrion unit), above the detachment fault, (also referred to in the literature as the phyllite nappe or the Lavrion Blueschists tectonic unit), exposes alternating marbles and schists (Lavrion schists; Fig. 4e) with small lenses of metabasic rocks. The whole area is marked with magmatic activity as evidenced by the Plaka granodiorite, which represents the exposed part of a larger batholith at depth (Marinos and Makris, 1975; Tsokas; et al., 1998) dated 12-8 Ma by U-Pb on zircon (Liati; et al., 2009) and several felsic and mafic dykes (Fig. 4f) that intruded the metamorphic nappe stack (Skarpelis, et al., 2008; Voudouris, et al., 2008a,b; Liati, et al., 2009; Bonsall, et al., 2011; Coleman, et al., 2019). The structural distribution of the dykes witnesses their continuous emplacement at the ductile to brittle transition. Some of the dykes are boudinaged and partially transposed within the mylonitic structures of the lower unit and some of the dykes are purely brittle and crosscut the rock units and the detachment shear zone (Liati, et al., 2009). The upper part of the Upper unit shows green meta-ophiolitic rocks (metamorphosed basalts and serpentinites of the oceanic domain) (Fig. 4g,h).

Tectonic phases and deformation of metamorphic rocks

Two main successive stages of metamorphism were noticed at the scale of the Cycladic system. The Cycladic blueschists underwent a first event to the blueschist (H*P*) facies (up to 1.2 – 2.2 GPa and 450 to 550 °C) during Eocene subduction phase (50 – 40 Ma; e.g. Altherr, et al., 1982; Buick and Holland, 1989; Bröcker, et al., 1993; Avigad, 1998; Groppo, et al., 2009). The second event was recorded during exhumation of the Cycladic Blueschist unit and is characterized by medium-pressure and temperature conditions between 25 and 15 Ma at ~0.9 GPa and 550 to 570 °C (Andriessen, et al., 1979; Altherr, et al., 1982; Ring, et al., 2001; Parra, et al., 2002; Bröcker, et al., 2004; Duchêne, et al., 2006; Seward, et al., 2009).

Three successive stages of deformation (D) and metamorphism (M) were identified within the rock units

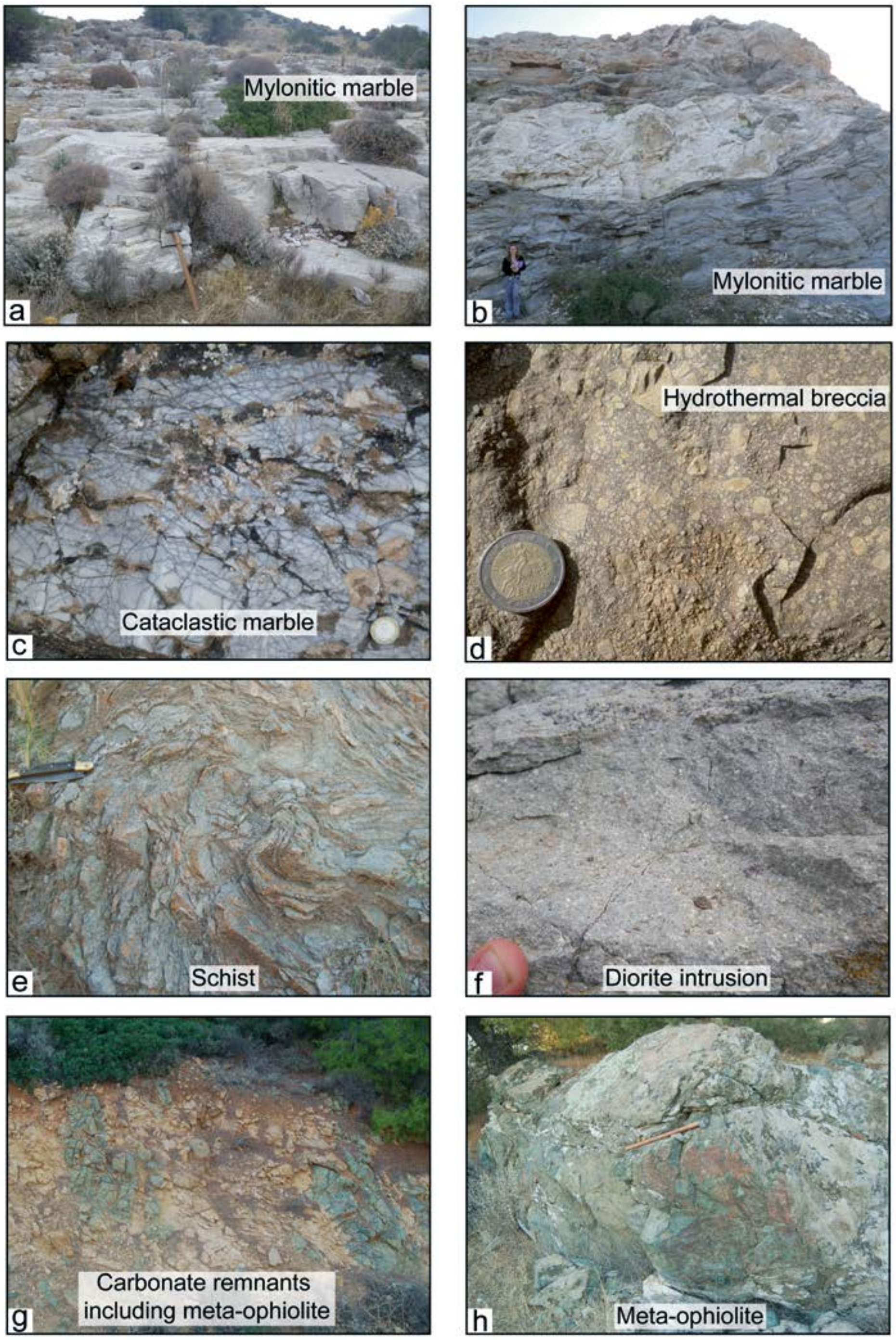

Fig. 4: Field photographs showing main lithologies at the scale of the Lavrion Peninsula. – a. Upper mylonitic white marble transposed into S_3 shallow-dipping schistosity (Velatouri hill). – b. General view of the Simonet quarry showing boudins of white pure marble wrapped within foliated impure blue marble. – c. Brittle fractures within marble superimposing over the mylonitic fabric. – d. Hydrothermal cataclastic dolomitic level marking the detachment. – e. Deformed and folded blue schist of the Upper unit. – f. Dyke of dioritic/ andesitic composition intruding marbles of the Lower Unit and blue schists of the Upper Unit (W Velatouri hill). White minerals are plagioclase; black minerals are amphibole. – g. Carbonate and green serpentinite within the upper part of the Upper unit. – h. Green metabasalts of the upper part of the Upper unit (photos a, b, c, d: Scheffer, et al., 2017b; photos e, f, g, h: C. Scheffer).

of the Lavrion area with (i) burial of the rocks during subduction (D_1M_1), (ii) syn-orogenic exhumation (D_2M_2) during collision stage and (iii) post-orogenic exhumation along the low-angle detachment fault system (D_3M_3) accommodating orogenic collapse. The rocks of the Lavrion nappe stack reached D_1M_1 pressure and temperature conditions of 0.9–1.3 GPa and 315 ±30 °C during the subduction stage (Scheffer, et al., 2016). The D_2M_2 syn-orogenic exhumation stage recorded *PT*-conditions of 0.6–0.9 GPa and 300 ±30 °C (Scheffer, et al., 2016) between 32 and 23 Ma, based on $^{40}Ar/^{39}Ar$ ages of white mica (Coleman, et al., 2019). The D_3M_3 post-orogenic exhumation phase is associated with the formation of the Western Cycladic and Northern Cycladic detachment systems, in relation to orogenic gravitational collapse induced by slab retreat during the Miocene (Gautier, et al., 1999; Vanderhaeghe and Teyssier, 2001; Vanderhaeghe, et al., 2007; Jolivet, et al., 2010; Grasemann, et al., 2012; Scheffer, et al., 2016). The D_3M_3 post-orogenic exhumation event was accompanied by isothermal decompression that resulted in H*T* metamorphism, as evidenced by the occurrence of migmatite (rocks showing partial melting) in the Nax-

Fig. 5. Folded schist layer in a mylonitic blue marble of the Upper unit mainly characterized by a shallow-dipping schistosity S_3 (Velatouri hill) (photo: A. Tarantola).

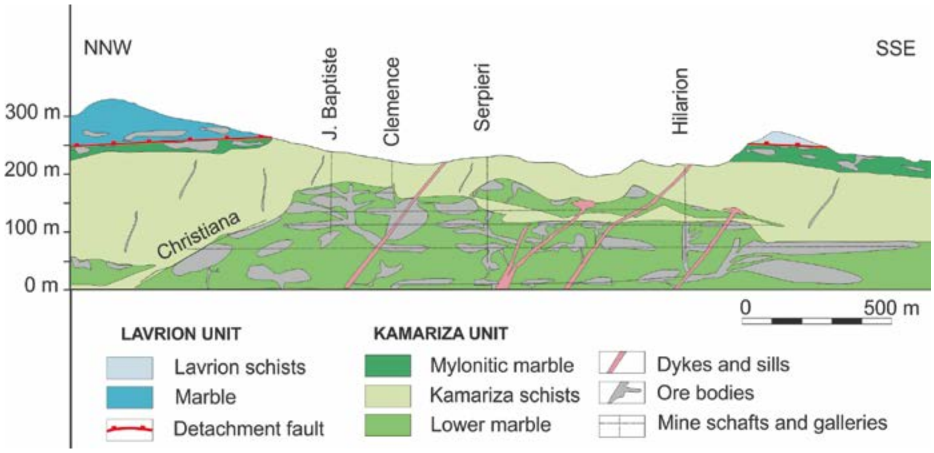

Fig. 6. Geological location of main ore bodies in the area of Kamariza with the mine shafts and galleries. Figure modified after Ottens and Voudouris (2018), and references therein.

os, Paros, Mykonos, and Ikaria islands (Keay, et al., 2001; Vanderhaeghe, 2004; Martin, et al., 2006; Ring, 2007; Kruckenberg, et al., 2011). In the Lavrion area, the D_3M_3 post-orogenic exhumation event was marked by an increase in temperature that reached 350 ±30 °C at a pressure of 0.50 to 0.85 GPa (Scheffer, et al., 2016). The main location of the D_3 deformation is at the contact between the Lower and Upper units, which marks the location of the West Cycladic detachment system with a transition from mylonitic to cataclastic deformation (Lekkas, et al., 2011; Berger, et al., 2013; Scheffer, et al., 2016; 2017b).

Relics of steep-deeping and folded structure related to early D_1 and D_2 deformation stages may be observed in the rocks of the Lavrion Peninsula (Fig. 5). However, the dominant feature is the subhorizontal D_3 feature observed at all scales of observation from the foliation of the rocks of the Lower unit (Fig. 5) to the landscape outcrops (Fig. 3,4a,b).

Main characteristics of metal deposits in the Lavrion mining district

Metal deposition in the Lavrion mining district is subdivided in hypogene and supergene stages (i.e. primary and secondary mineralizations), whether it refers to the Miocene original mineralization associated with the D_3M_3 event or to later remobilization. The hypogene stage itself is divided into four styles of mineralization with their particular structural setting and mineral paragenesis or association: (i) Mo-Cu porphyry, (ii) Cu-Fe skarn, (iii) Pb-Zn-Ag-(Au) carbonate replacement (non-skarn) and (iv) Pb-Zn-Ag epithermal veins and breccias (Leleu, et al., 1973; Skarpelis, 2002; Voudouris, et al., 2008a, b; Tombros, et al., 2010; Bonsall, et al., 2011; Scheffer, et al., 2019). The supergene mineralization consists of

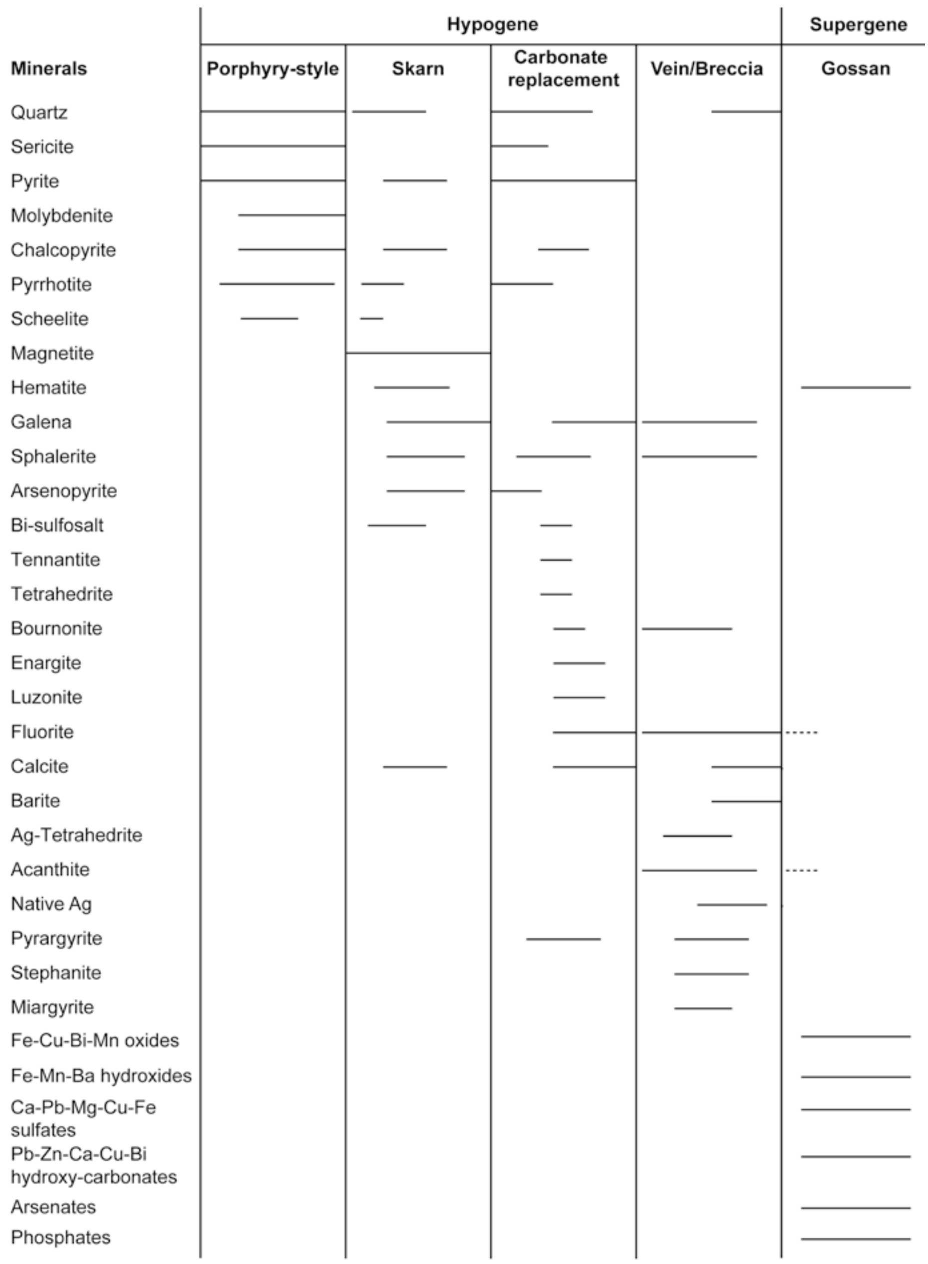

Fig. 7: Paragenetic sequence of the Lavrion district for porphyry-style, skarn, carbonate replacement, vein and breccia, and gossan/supergene ore (modified after Voudouris, et al., 2008a,b; Skarpelis and Argyraki, 2009; Bonsall, et al., 2011; Scheffer, et al., 2019).

late oxidation essentially found under Fe-(hydr-)oxides (gossan) (Skarpelis and Argyraki, 2009). The geological location of main ore bodies, corresponding to carbonate replacement, epithermal veins and breccias and supergene oxidation, is represented in the cross-section of Fig. 6 drawn in the area of Kamariza. In Fig. 7 only the main features of each mineralization style are presented.

Mo-Cu porphyry style of mineralization

This low-grade, sub-economic, porphyry-style mineralization is localized and restricted within the Plaka granodiorite. It occurs predominantly as discrete pyrite (FeS_2)-molybdenite (MoS_2) sheeted decimetric quartz veins trending northwest-southeast (Fig. 8a), with minor pyrrhotite ($Fe_{1-x}S$) and chalcopyrite ($CuFeS_2$) (Voudouris, et al., 2008a). Associated potassic alteration is suggested by the presence of hydrothermal centimetric biotite in subvertical quartz veins within the altered granodiorite (Fig. 8b).

Cu-Fe skarn style of mineralization

A skarn corresponds to the development of a contact metamorphic and metasomatic aureole within calcareous rocks during the intrusion of a magmatic body. In the case of the Lavrion area, skarn developed at the vicinity of the Plaka granodiorite intruding marbles and schists of the

Lower and Upper units. The rocks are green and dominated by minerals of the epidote-, pyroxene-, amphibole- and garnet-groups with additional feldspar, chlorite, calcite, titanite, scapolite, magnetite, pyrrhotite and marcasite. They were estimated to be formed at 440–600 °C and 1.0–1.5 kbars (Leleu, et al., 1973; Baltatzis, 1981). Magnetite and magnetite-hematite are found close to the granodiorite within the Upper Marble, whereas the assemblages composed of pyrite-pyrrhotite and sphalerite-pyrite-galena are present within the Kamariza schists, farther away from the Plaka granodiorite (Leleu, et al., 1973).

Pb-Zn-Ag-(Au) carbonate replacement

These deposits together with epithermal veins and breccias were the most economically significant ore types in the Lavrion district with dominating galena, sphalerite, pyrite and chalcopyrite. They are found along the low-angle detachment fault and at the contact between marbles and schists of the Lower units forming several parallel mineralized levels. Their location is thus both structurally and lithologically controlled and results in sub-horizontal deposits (Fig. 6; Fig. 8d,e). The carbonate-replacement deposits occur as centimeter-scale lenses to bedded replacement and chimneys that are up to tens of meters in length (Fig. 6; Bonsall, et al., 2011). Base metal mineralization along the detachment fault was mentioned by Skarpelis (2007). The sulfides occur as massive pods and veins along shear bands in marble (Fig. 6).

Pb-Zn-Ag epithermal veins and breccias

Pb-Zn-Ag vein and breccia deposits are generally localized below, but also above, the Lavrion detachment (1) within the marbles of the Lavrion unit, (2) within the Upper marble, (3) within the Kamariza schists, and (4) at the interface between the Kamariza schists and the Lower marble (Fig. 6; Scheffer, et al., 2019). The crosscutting relationship between the vein and breccia ore deposits and the S_3 mylonitic deformation suggests deposition in a purely brittle regime. The deposits are mainly characterized by fluorite and carbonate gangue minerals enclosing Pb-Zn-Ag sulfides and/or oxides (Voudouris, et al., 2008a,b; Scheffer, et al., 2019).

Supergene alteration

Subsequent alteration of the primary sulfides resulted in an extensive and deep oxidation zone (up to 270 m thick) from which about 600 mineral species of oxides, hydroxides, carbonates, sulfates, arsenates, native metals, etc, have been described (Skarpelis and Argyraki, 2009; Ottens and Voudouris, 2018). Supergene oxidation resulted among others in replacement of pyrite by goethite and limonite, of sphalerite by smithsonite and of galena by cerussite and anglesite and secondary deposition of the silver-bearing sulfide acanthite. According to Marinos and Petrascheck (1956) and Conophagos (1980), cerussite in addition to galena is a major carrier of silver in Lavrion deposit.

Fluid circulation and ore deposition in a dynamic setting

Earlier published data based on fluid inclusion investigations showed the existence and possible interaction of several fluid reservoirs associated with ore deposition in the Lavrion mining district. Two dominant fluid systems were described with high-temperature magmatic-hydrothermal fluids associated with the Plaka granodiorite intrusion and related magmatism and low-temperature surface derived fluids circulating in the last stages of exhumation in the brittle domain.

Bonsall, et al. (2011) observed the presence at room temperature of salt-poor vapor-rich (VL) and aqueous dominated halite-saturated (LVH) fluid inclusions in quartz veins associated with porphyry style mineralization within the Plaka granodiorite (Fig. 9a,b). Their coexistence within single fluid inclusion assemblages (FIAs) and their similar temperatures of homogenization (T_h), temperature at which one single phase is present during microthermometric experiments, are evidence of fluid boiling. This process is generally observed in magmatic-hydrothermal environments resulting in porphyry-style deposits where high-temperature fluids exsolved at shallow depths, and thus at low pressure conditions. Boiling is an efficient process for phase and metal separation between an aqueous liquid salt-rich phase and a salt-depleted vapor phase (e.g. Roedder, 1984). During boiling, metallic elements also partition into one or the other phase leading to supersaturation and metal precipitation under the form of oxide and/or sulphide. For instance, Bonsall, et al. (2011) suggested the presence of chalcopyrite within LVH inclusions. Another particularity of these systems is that, because VL and LVH FIs are demonstrated to have been trapped contemporaneously, their entrapment *PT* conditions must be similar. This is shown by their behaviour during microthermometric experiments with the similar homogenization temperatures. In such systems, the *PT* conditions at homogenization reflect directly the conditions of entrapment without any pressure correction (e.g. Diamond, 2001). In the Lavrion district, the formation of porphyry-style mineralization was thus estimated to take place at 300–400 °C after FI measurements in quartz veins for a pressure below 300 bars, reflecting the shallow environment during magmatic intrusion (Voudouris, et al., 2008a,b; Bonsall, et al., 2011).

The emplacement of the porphyry system in Plaka is also responsible for decarbonation of carbonate rocks, as demonstrated by the presence of CO_2-rich fluid inclusions (Fig. 9c,d) (i) dismembered and deformed along subgrain boundaries, (ii) within deformation lamellae and (iii) in planes crosscutting subgrains. Microstructural

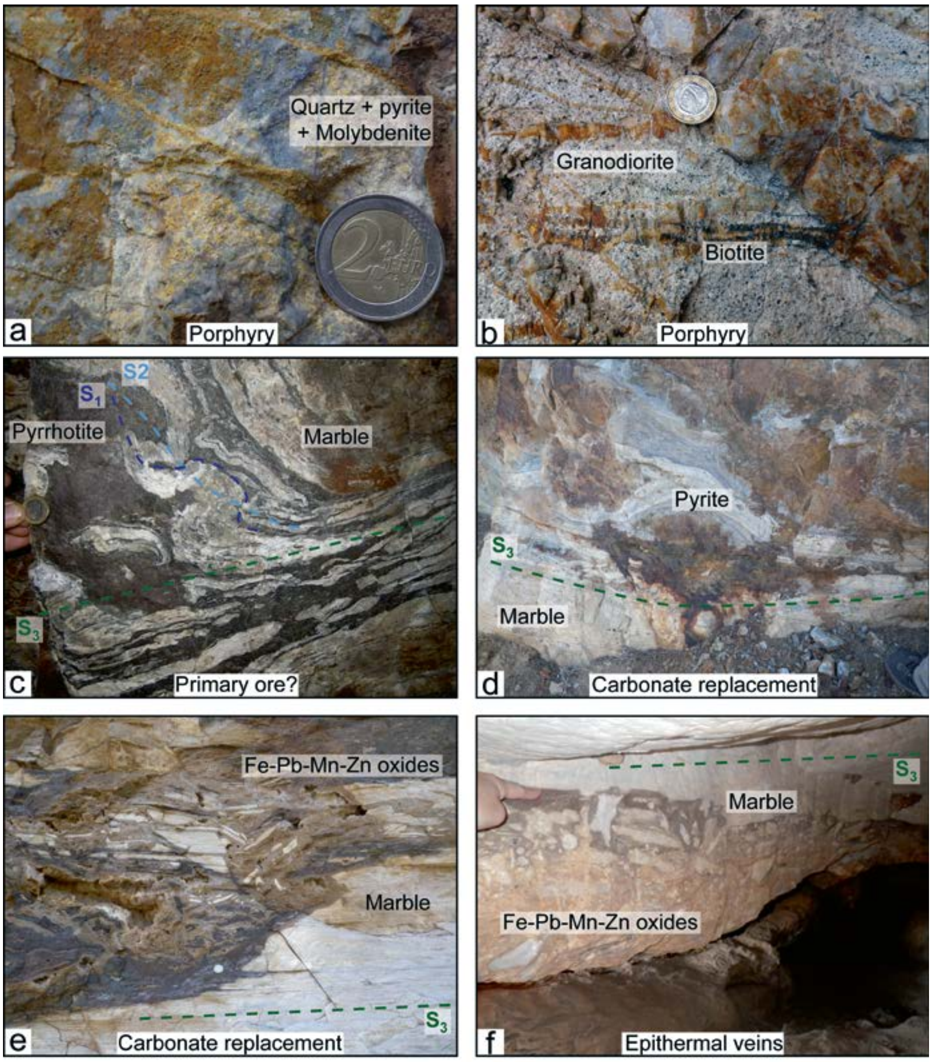

Fig. 8: Photographs illustrating the structural position of the main ore type deposits in the Lavrion mining district. – a. Quartz-pyrite veins with molybdenite coating within Plaka granodiorite. – b. Evidence of potassic alteration by strongly altered granodiorite and crosscutting veins containing centimetric hydrothermal biotite crystals. – c. Interstratified massive pyrrhotite layers folded with marbles suggest primary ore probably related to the sedimentary sequence before subduction (ante-S1). – d. The carbonate replacement deposits associated with the emplacement of the Plaka granodiorite attest to a set-up during ductile deformation of the marble. – e. The carbonate replacement deposits also point to an entrapment at the ductile-brittle transition as evidenced by ore deposits found both concordant and discordant to the S3 mylonitic foliation. Deposits are nowadays strongly altered by supergene alteration. – f. The more surficial Pb-Zn-Ag ore deposits are localised within marble breccia parallel to the low-angle detachment in agreement with a late brittle deformation event (photos a,b: A. Tarantola; photos c,d,e,f: Scheffer, et al, 2017b).

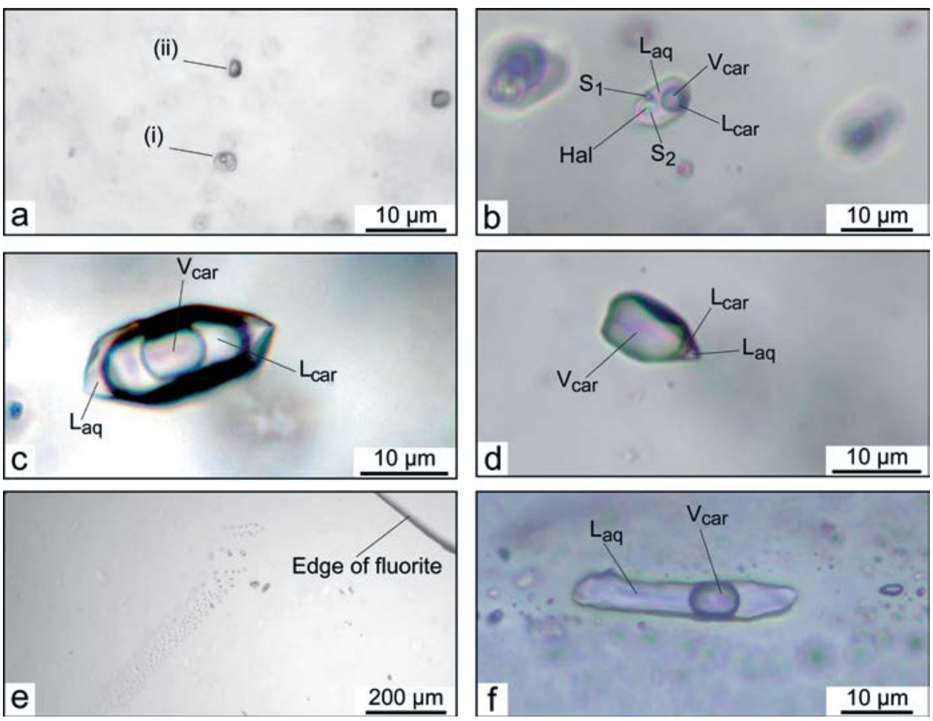

Fig. 9: Microphotographs showing the phase state at room temperature of the main types of fluid inclusions found in the Lavrion mining district. – a. Coexisting halite-saturated liquid-rich (i) and vapor dominated (ii) fluid inclusions. – b. Multiphase halite saturated aqueous-carbonic fluid inclusion. – c. Three-phase CO_2-rich fluid inclusion dominated by carbonic liquid. – d. Three-phase CO_2-rich fluid inclusion dominated by carbonic vapor. – e. Pseudo-secondary plane of two-phase liquid-vapor fluid inclusions within fluorite. – f. Two-phase aqueous fluid inclusion. Hal.: halite, L_{aq}: aqueous liquid, L_{car}: carbonic liquid, V_{car}: carbonic vapor, S_1 and S_2: unidentified solids (photos a, e: A. Tarantola; photos b,c,d,f: Scheffer, et al., 2017a).

analysis, stable isotope equilibrium and *VX* properties showed that CO_2 release took place under a heat flow with a thermal gradient of 70–115 °C·km^{-1} at the ductile to brittle transition, during exhumation accommodated by regional NNE-SSW extension. The $\delta^{18}O$ signatures of the marble enclosing the carbonate replacement deposits (Scheffer, et al., 2017a) indicate that deposits are related to this decarbonation process with implication of magmatic fluids. The contribution of Miocene seawater was also invoked in the deposition of the carbonate replacement mineralization and is supported by $\delta^{34}S$ values of sphalerite and galena (Bonsall, et al., 2011). In the same way, $\delta^{13}C$ pointed to interaction with organic matter during sulfide precipitation of the carbonate replacement deposits (Scheffer, et al., 2017a; 2017b).

The low-angle detachment fault is marked by a transition from mylonitic to cataclastic deformation, demonstrating the evolution from ductile to brittle behaviour of carbonate rocks during exhumation. For example, a cataclastic sub-horizontal zone of some 1–2 meters thick is visible all around the western side of the Velatouri hill (Scheffer, et al., 2017b; 2018). This zone is formed by cataclastic calcitic marble with lower $\delta^{18}O$ values, which is overlain by dolomitic breccia (Fig. 4d), thus suggesting the localisation of fluid circulation at the detachment fault during exhumation (Scheffer, et al., 2017b). It is interesting to note that ore deposition is not strictly located at the detachment fault but a few meters lower as shown in the Velatouri hill and Simonet quarry. This indicates multiple domains of preferential fluid circulation during transition from ductile to brittle deformation, likely due to a strong local lithological control marked by micaceous lenses in the calcitic marble (Scheffer, et al., 2017b).

The analyses of fluid inclusions found in fluorite, sphalerite and calcite from vein and breccia deposits with lower T_h have suggested an ongoing dilution and mixing of magmatic-hydrothermal fluids by surficial fluids in the purely brittle stage (Bonsall, et al., 2011). However, Scheffer, et al. (2019) suggested the existence of two independent fluid systems (magmatic-hydrothermal and surficial) without mixing and interactions in the more superficial mineralizing stages. Primary and pseudo secondary fluid inclusions (Fig. 9e,f) in fluorite and calcite are characterized by a wide range of T_h (92–207 °C) and salinity of up to 17.1 wt.% $NaCl_{eq.}$. The stable isotope signatures ($\delta^{18}O$ and δD) and low Cl/Br ratios of water extracted from fluid inclusions are compatible with a surficial fluid being the result of mixing of meteoric water with evaporated seawater.

Geology and mining archaeology

Mining is essentially a full destructive and irreversible process and the geologist generally can only deal with partial remnants of original rocks to reconstruct the conditions of formation of ore deposition. Mining areas are however key in the technological development of past and present civilization and are thus of particular interest for archaeologists to better understand past history thanks to human and mechanical traces left by mining activities. At Lavrion, the extraction of base metal resources has had a profound impact on the landscapes (Morin-Hamon and Morin, 2006).

The rise of metallurgy in mainland Greece is observed in Early Helladic II, between 2900 and 2400 BC (Cosmopoulos, 1991; Coleman, 1992). At Lavrion, the exploitation of mineral veins probably began in Early Helladic period as evidenced by the presence of ceramic and stone mining tools (hammerstones), which corresponds roughly to the 3rd millennium BC (Bourhis, et al., 1981; Spitaels, 1981; McGeehan Liritzis, 1996, p.176; Kayafa, et al., 2000). At this time, metal exploitation was generally confined to relatively restricted working areas unlike the subsequent extensive surface and underground working at Thorikos and in some areas on the Spitharopoussi plateau. The Classical Hellenic period is shown by pluridecimetric (usually 80 cm) squared galleries and plurimetric (up to 100 m) vertical shafts that allowed ventilation and access to deep levels. The Roman-Byzantine period is evidenced through the discovery of artifacts (lamps, pottery) and charcoal ^{14}C-dating found by firesetting mining. Technological advances that are known to have taken place during the Classical and Late Roman period, provided greater opportunities for mineral exploitation and ore-dressing activities (Morin and Photiades, 2012a; Morin, et al., 2013). It was not until the Industrial Age that the metal mining industry began to have a more profound and visible impact upon the landscape. The increasing demand for raw materials during the 19th century led to rapid expansion of mining activities all over the Lavrion district. Extensive workings were focused on the already known mineralized veins and levels that were exploited during the past centuries. However, with time, new mineralized levels were needed to be found at increasingly deeper locations (Levat, 1885). The result was the three horizontal levels that were exploited at Kamariza and below the Spitharopoussi plateau. Some places like Thorikos were not, or only to small extent, exploited during the Industrial era and are thus unique places to describe mining archaeology in ancient times.

The subsequent decline of mining activities during the 20th century has left a rich legacy of abandoned metal mining landscapes. They represent a dialogue with the landscape and its resources that lasted for almost 5,000 years from the Early Helladic period (Spitaels, 1984; Treuil, et al., 2008; Gale and Stos-Gale, 1982; Stos-Gale and Gale, 1982) to the late 20th century. Archaeological investigations are therefore needed to unravel the meaning of mining landscapes, to understand what is still visible from the past history and from technological developments. In this way, it is necessary to make mental associations between what might appear to be a confusing array of waste tips and bumps, discarded ruins, trackways, washeries, cisterns and buildings that remain scattered widely across the plateau and the mountainside, to provide an interpretation of the technologies involved in the winning and processing of ores, and to assess how these may have changed through time.

Today, archaeology focuses on the physical remains of mining and metallurgical activities and on interpretation of mining landscape evidences that were created by the metallurgical process (Morin-Hamon, 2013a; 2013b). The particular value of a mining landscape is that it can provide a clear illustration of the inter-relationship of the orebody itself, the various structures to be found within an entire mining complex, and of the developments that were made in extraction and processing techniques over the course of time.

Underground mining archaeology, through survey representation of the works, leads to an exhaustive knowledge of the general architecture of the orebody, i.e. remnants of the veins or layers that were exploited, including the gangue and the mineralized part, both in terms of direction and inclination (Ancel, 2001). Thus, the topographical representation of an underground network can reveal the main architecture of the mineralization and its volume. Geology defines history: as a potential natural heritage, geology governs the economic prosperity of a site. As a science, geology enlightens the whole history of a mining district as Lavrion (Morin and Photiades, 2012b). Beyond its architecture and volume, the mineral content of the site is another element in the foreground, including: (i) portions of bedrock like breccias, (ii) gangue made of non-metallic substances such as quartz, calcite and fluorite, (iii) minerals not useful at the time like zinc sulphide rejected on waste tips, and (iv) the ore itself. The morphology of the ore deposit conditions the organization of the mining works. Within the framework of the structurally and lithologically controlled shallowly dipping mineralized clusters of the Lavrion area, exploration will take the form of low-cut mining works according to the main concentrations. Finally, geology conditions mining technologies, i.e. the organisation and technology of driving galleries, shafts, stopping areas, ore dressing workshops and buildings.

Conclusions

The area of Lavrion was the largest mining site of Antiquity that contributed to the economic growth of the City of Athens. This exceptional ore deposit is the result of a long geologic and geodynamic evolution. The most recent interpretations point to metal deposition in a very active dynamic setting during the last stages of exhumation of the Attico-Cycladic Metamorphic Core Complex. The associated tectonic extension led to emplacement of magmatic bodies such as the Plaka granodiorite and numerous felsic/mafic dykes all over the peninsula at the ductile to brittle transition, associated with Mo-Cu porphyry style and Cu-Fe skarn deposits where magmatic-hydrothermal fluids are observed. This change in the deformation dynamics is demonstrated by the sub-horizontal detachment marked by cataclastic rocks at the contact between the Lower and Upper units of the Lavrion area. High-temperature Pb-Zn-Ag carbonate replacements and late veins and breccias were the most economic deposits over time. The different mineralization styles are the results of two hydrothermal systems, magmatic and meteoric water mixed with evaporated seawater where the detachment fault plays as a hydrogeological barrier at the ductile to brittle transition. Although the geodynamic setting of the Lavrion mining district seems to be constrained, some questions remain regarding (i) the absolute age of magmatism and ores at all scales, (ii) the provenance of the metals and (ii) the role of organic compounds, as a reducing agent, during ore deposition.

The geologic and particular metallogenic environment of the Lavrion area resulted in an exceptional district that was mined for their base and precious metals over centuries since the Early Helladic/Early Bronze Age periods.

Although the Industrial era and the extensive mining works of the French Mining Company (Compagnie Française des Mines du Laurion—CFML) destroyed much of the ancient archaeological mining evidence, it also opened access to antic galleries as is the case at Ari or at Spitharopoussi. Overall, the Lavrion district is an exceptional site, where geology and archaeology meet and allow us to understand the evolution of mining and metallurgical technologies over the past 5,000 years.

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Authors

Alexandre Tarantola – Université de Lorraine, Centre National de la Recherche Scientifique (CNRS), GeoRessources, BP 70239, F-54506 Vandœuvre-lès-Nancy, France
Christophe Scheffer – Université de Lorraine, Centre National de la Recherche Scientifique (CNRS), Centre de Recherches Pétrographiques et Géochimiques (CRPG), UMR 7358, Nancy, France
Panagiotis Voudouris – National and Kapodistrian University of Athens, Faculty of Geology and Geoenvironment, University Campus-Zografou 15784, Athens, Greece
Olivier Vanderhaeghe – Géosciences Environnement Toulouse (GET), Université de Toulouse, CNRS, IRD, CNES, 14 avenue Edouard Belin, Toulouse, F-31400, France
Adonis Photiades – Institute of Geology and Mineral Exploration (IGME), 1st Spirou Louis St., Olympic Village, Acharnae 13677, Greece
Denis Morin – Université de Lorraine, EA1132-HisCAnt-MA Lab., Pôle Archéologique Universitaire,
BP 13 397 – F-54 015 Nancy Cedex, France

Correspondence and material requests should be addressed to: alexandre.tarantola@univ-lorraine.fr