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Sb- Bi-BEARING METALLOGENY OF THE SERBOMACEDONIAN-RHODOPE METALLOGENIC BELT (SRMB)

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Abstract

Various types of deposits such as carbonate-replacement Pb-Zn-Ag-Au, porphyry Cu-Mo-Au, stratiform volcano-sedimentary, isolated magmatic-hydrothermal and skarns compose the Serbomacedonian-Rhodope Metallogenic Belt (SRMB), which intersects with a NNW-SSE trend the Balkan Peninsula. This arcuate belt is about 500 km long and 130-180 km wide. Sb-Bi alloys and Ag-Cu-Pb-Sb-Bi sulfosalts have been discovered in some metal assemblages in the SRMB. The European Union (EU) is highly dependent on critical and rare metals, such as Sb and Bi, which are very important for a sustainable development. Greece is one of the EU countries with the most potential for supplying the strategic metal Sb in the future, since it hosts a significant ore deposit at Rizana/Lachanas (central Macedonia). Here, the stibnite reserves are 5,000 t (proven) and 50,000-100,000 t (indicated). Both have average Sb=0.3 wt%. In addition, at the same district, there are 1000 t (proven) of wolframite. Another promising Sb-bearing mineral assemblage exists at Alshar (North Macedonia). Here, the stibnite reserves are >20,000 t (indicated) with average Sb=0.5 wt%. At both mineralization districts further investigations are needed to determine the grade and the proven reserves of the critical metal Sb. Until today none encouraging site has been located in the SRMB for remarkable Bi-bearing ore.

Keywords: *Sb- and Bi-bearing minerals, metal concentrations, reserves, SR Metallogenic Belt.*

Περίληψη

Διάφοροι τύποι κοιτασμάτων όπως ανθρακικής αντικατάστασης Pb-Zn-Ag-Au, πορφυριτικά Cu-Mo-Au, στρωματόμορφα ηφαιστειο-ιζηματογενή, απομονωμένα μαγματο-υδροθερμικά και σκαρνς συνθέτουν τη Σερβομακεδονική-Ροδοπική Μεταλλογενετική Ζώνη (ΣΡΜΖ), η οποία διατέμνει με ΒΒΔ-ΝΝΑ κατεύθυνση τη Βαλκανική Χερσόνησο. Αυτή η τοξοειδής ζώνη έχει μήκος περίπου 500 km και πλάτος 130-180 km. Κράματα Sb-Bi και θειοάλατα Ag-Cu-Pb-Sb-Bi έχουν ανακαλυφθεί σε μερικές μεταλλικές συγκεντρώσεις στη ΣΡΜΖ. Η Ευρωπαϊκή Ένωση (ΕΕ) εξαρτάται σε μεγάλο βαθμό από κρίσιμα και σπάνια μέταλλα, όπως το αντιμόνιο και το βισμούθιο, τα οποία είναι πολύ σημαντικά για μια βιώσιμη ανάπτυξη. Η Ελλάδα είναι μία από τις χώρες της ΕΕ με το μεγαλύτερο δυναμικό για προμήθεια του στρατηγικού μετάλλου Sb στο μέλλον, καθώς φιλοξενεί ένα σημαντικό κοίτασμα στα Ριζανά / Λαχανά (κεντρική Μακεδονία). Εδώ, τα αποθέματα αντιμονίτη είναι 5.000 t (βέβαια) και 50.000-100.000 t (ενδεικτικά). Και τα δύο έχουν μέση περιεκτικότητα Sb = 0,3% κατά βάρος. Επιπλέον, στην ίδια περιοχή, υπάρχουν 1000 t (βέβαια αποθέματα) βολφραμίτη. Μια άλλη πολλά υποσχόμενη συγκέντρωση ορυκτών που περιέχει Sb υπάρχει στο Alshar (Βόρεια Μακεδονία). Εδώ, τα αποθέματα αντιμονίτη είναι > 20.000 t (ενδεικτικά) με μέση περιεκτικότητα Sb = 0,5% κατά βάρος. Και στις δύο μεταλλοφόρες περιοχές χρειάζονται επιπλέον έρευνες για τον προσδιορισμό της ποιότητας και των βέβαιων αποθεμάτων του κρίσιμου μετάλλου Sb. Μέχρι σήμερα δεν έχει εντοπιστεί καμία ενθαρρυντική περιοχή στη ΣΡΜΖ με αξιοσημείωτο κοίτασμα Bi.

Λέξεις-κλειδιά: *ορυκτά πού περιέχουν Sb και Bi, συγκεντρώσεις μετάλλων, αποθέματα, ΣΡ Μεταλλογενετική Ζώνη*

1. INTRODUCTION

The Alpine-Balkan-Carpathian-Dinaride (ABCD) metallogenic and geodynamic belt is considered Europe’s premier Pb-Zn-Cu (-Mo-Sb-Ag-Au) province. It is divided into three spatially and temporally distinct tectonic and metallogenic belts (Heinrich and Neubauer, 2002). One of them is the Serbomacedonian-Rhodope Metallogenic Belt (SRMB), which intersects with a NNW-SSE trend south-western Serbia, Kosovo, North Macedonia, north-eastern Greece and south Bulgaria. This arcuate belt is about 500 km long and 130-180 km wide (Fig. 1). Carbonate-replacement Pb-Zn-Ag-Au deposits, porphyry Cu-Mo-Au deposits, stratiform volcano-sedimentary deposits, skarns, and various isolated magmatic-hydrothermal deposits compose the SRMB. All are genetically related to Oligocene-Miocene post-subduction magmatism (Kalogeropoulos et al., 1989; Frei, 1995; Mitchell, 1996; Kroll et al., 2002; Serafimovski et al., 2010). Several other types of gold mineralization (e.g., intrusion-related, epithermal, Carlin-type), are, in general, genetically related to arc- magmatic rocks, and, in part, are controlled by exhumation structures in this belt (Melfos et al., 2002; Marchev et al., 2005; Eliopoulos and Kilias, 2011; Fornadel et al., 2011).

Although native Bi is a relatively common mineral, native Sb is less abundant, and Sb-Bi alloys are relatively rare phases in nature. Sb-Bi alloys and Ag-Cu-Pb-Sb-Bi sulfosalts have been discovered in some metal assemblages in the SRMB as well as in other continental areas. Stibnite (Sb_2S_3) is the predominant ore mineral of Sb. The most important ores of Bi are bismuthinite (Bi_2S_3) and bismite (Bi_2O_3). Trace metallic minerals like Bi-sulfosalts and Bi- sulfotellurides, precious- and base metal tellurides are usually associated with Au-bearing ores and can be considered as pathfinder minerals for Au.

Elements, such as Ag, As, Au and Sb, have been concentrated in massive sulphide deposits that have undergone metamorphism at or above the middle amphibolite facies. A polymetallic melt may form at temperatures as low as 300°C, where orpiment and realgar melt. However, for many ore deposits, the first melting reaction would be at 500°C, where arsenopyrite and pyrite react to form pyrrhotite and an As–S melt. A melt with temperature 500°C to 600°C will be enriched in Ag, As, Au, Bi, Hg, Sb, Se, Sn, Tl, and Te (low-melting point chalcophile metals). Progressive melting to higher temperatures (600-700°C) will enrich the polymetallic melt in Cu and Pb. The highest-T melt (in the upper amphibolite and granulite facies) usually contain substantial Fe, Mn, Zn, as well as Si, H_2O, and F (Frost et al., 2002).

Various types of ore deposits, such as orogenic Au, skarn, VMS, intrusion-related, and epithermal deposits, usually contain Bi-sulfosalts and Bi-tellurides. Although they are present as minor constituents in most of these deposit types, they are of major importance, since they usually accompany native Au. These Bi- minerals may provide physicochemical means towards the formation of precious metals and help to understand the trace element distribution within the deposit (Cook, 1997; Ciobanu and Cook, 2000; Cook et al., 2009).

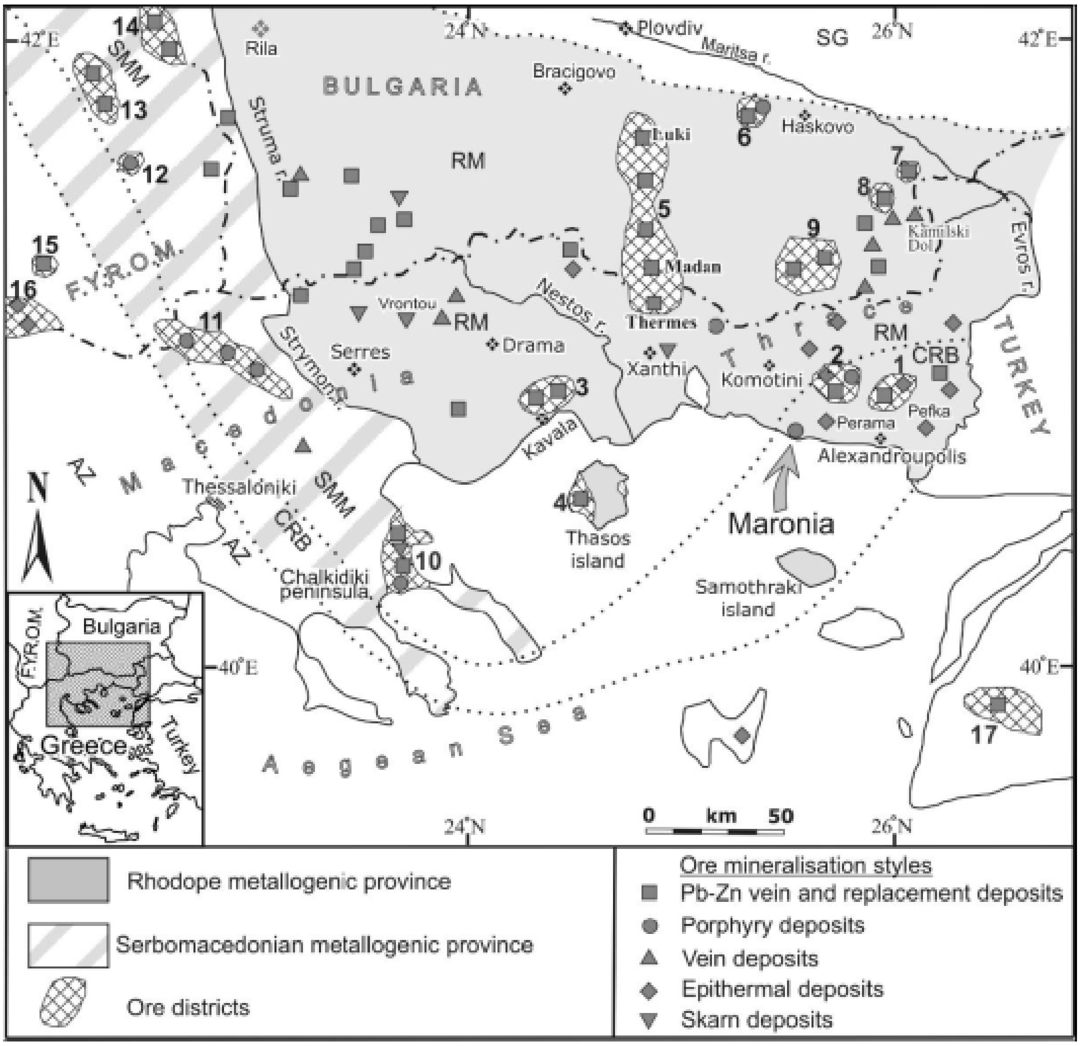

Fig. 1: Geologic map showing the metallogeny centers of the Serbomacedonian-Rhodope Metallogenic Belt (SRMB). AZ=Axios (Vardar) Zone, CRB=Circum Rhodope Zone, SMM=Serbomacedonian Massif, RM=Rhodope Massif, SG=Srednogorie Zone. 1. Esymi, 2. Kirki-Sapes, 3. Palea Kavala, 4. Thasos, 5. Thermes-Madan-Luki, 6. Spahievo, 7. Lozen, 8. Madjarovo, 9. Zvezdel, 10. Chalkidiki (Olympias-Stratoni-Skouries), 11. Kilkis (Gerakario-Vathi-Pontokerasia), 12. Buchim, 13. Kratovo-Zletovo, 14. Osogovo-Sasa-Toranica, 15. Borov Dol, 16. Aridea-Kozuf, 17. Balikesir (Melfos et al., 2002).

At the Ohori base metal deposit of NE Japan some Pb-Bi-S minerals have been discovered in the chalcopyrite-rich ores of the area. In minor amounts they contain Cu and Ag, cosalite, krupkaite and Bi-bearing galena. This ore has higher homogenization temperatures (>300°C) of fluid inclusions, and higher FeS contents in sphalerite compared to the Bi-free ores. Most of these Bi-bearing deposits are referred to as xenothermal (Yokoro and Nakashima, 2010).

Bismuth-sulfosalts and tellurides are present in many hydrothermal gold deposits and can provide important genetic and physicochemical means on the metallogeny. Bismuth-sulfosalts are characterized by replacement textures resulting from changes in the composition of the fluids. They mainly include bismuthinite and cuprobismutite derivatives. These Bi-sulfosalts and tellurides are usually related to native Au (Zhou et al., 2018).

The rich in Sb- and Bi-sulfosalts deposit of Jialong at south China, is hosted by schist within the contact zone of a Neoproterozoic granite. Cooling temperatures of 270-400°C and decreasing sulfur fugacity promoted the precipitation of Sb- Bi-alloys and sulfosalts during the late stage of an incursion of Sb- and Bi-bearing hydrothermal fluids (Liu et al., 2018).

The European Union (EU) is highly dependent on critical and rare metals which are very important for sustainable development. However, the European industry is not able to cover its demands from native sources and it imports commodities from third countries. Greece is one of the EU countries with the most potential for supplying certain strategic metallic raw materials in the future, since it hosts some significant ore deposits. The epithermal- and porphyry-type deposits and the intrusion related deposits of the SRMB are promising targets for future exploration and exploitation in Sb, Te, Mo, Re, Ga, In, REE, and PGE. REE are found in high contents at the placer deposits between Chalkidiki and Kavala (Macedonia, Greece). Therefore, the mineral wealth of this belt can contribute significantly to a sustainable and competitive economy of Europe (Tsirambides and Filippidis, 2012).

Some metal reserves in the SRMB are 24 t Au, 14 t Ag, and >100 Mt (Pb+Zn) ore in Bulgaria, 743 t Au, 4100 t Ag, 5345 th.t Cu, and 3125 th.t (Pb+Zn) in Greece, 106 t Au, 96 t Ag, and 834 th.t Cu in North Macedonia, >150 Mt (Pb+Zn) ore in Kosovo, 118 t Au and 1270 th.t Cu in Serbia (Tsirambides and Filippidis, 2016).

The Sb- Bi-bearing metallogeny of the Serbomacedonian-Rhodope Metallogenic Belt (SRMB) in the Balkan Peninsula is the focus of this paper.

2. SERBIA

The most important metallic mineral resources of Serbia are Cu, Pb-Zn, Au, Ag, Sn, Mn, U, Mo, Ti, W, Co, Sb, and Fe (Jelenkovic et al., 2008).

The Serbo-Macedonian Metallogenetic Province (SMMP) hosts several ore deposits in three geotectonic units: the Vardar Zone, the Serbomacedonian massif, and to a lesser extent the Dinarides. This metallogenic province includes the most significant Pb-Zn and Sb deposits in Serbia, as well as smaller Bi, Mo, Cu, Fe, Sn, Au, U, W, and Hg deposits, which are genetically associated to emplacement of granitic rocks (Radosavljević et al., 2013).

The Podrinje Metallogenic District belongs to the SMMP and includes several smaller ore fields: Cer (Northwest Serbia), Boranja (West Serbia), and Srebrenica (East Bosnia and Herzegovina).

The Boranja ore field (Fig. 2, Table 1) contains a large number of sulphide deposits with Pb-Zn, and Sb with small amounts of Cu, As, Bi, and Ag. Galena was found to contain varying amounts of Ag, Bi, and Sb (0-0.94, 0-3.34, and 0.01-0.51 wt%, respectively) (Radosavljević et al., 2013). The sulfosalts of the Boranja ore field are divided into four main groups: (i) Pb-Sb(As)-S with ±Fe and ±Cu; (ii) Cu(Ag)-Fe(Zn)-Sb(As)-S; (iii) Ag(Pb)-Bi(Sb)-S; (iv) Pb-Bi-S(Te). The most abundant of these are found in the following polymetallic deposits and ore zones: Cu(Bi)-FeS Kram-Mlakva; Pb(Ag)-Zn-FeS_2 Veliki Majdan; Sb-Zn-Pb-As Rujevac; and Pb-Zn-FeS_2-$BaSO_4$ Bobija (Radosavljevic et al., 2016).

The Rudnik ore field is a skarn-replacement and high-temperature hydrothermal Pb-Zn-Cu-Ag-Bi-W polymetallic sulphide deposit (Fig. 2, Table 1). The pseudostratified and plate like ore bodies contain valuable metals the content of which varies widely: Pb (0.94-5.66 wt%), Zn (0.49-4.49 wt%), Cu (0.08-2.18 wt%), Ag (50-297 ppm), Bi (100-150 ppm), and Cd (100-150 ppm). Copper, Pb, Ag, Sb- and Bi-sulfosalts have been found in noticeable amounts. The presence of Bi-sulfosalts and argentopentlandite suggests formation temperatures >350°C and <445°C, respectively. Therefore, the assemblage of these minerals was formed in the temperature range 350-445°C. The enrichment of the deposit in Bi and Ag indicates a magmatic origin (Stojanovic et al., 2018).

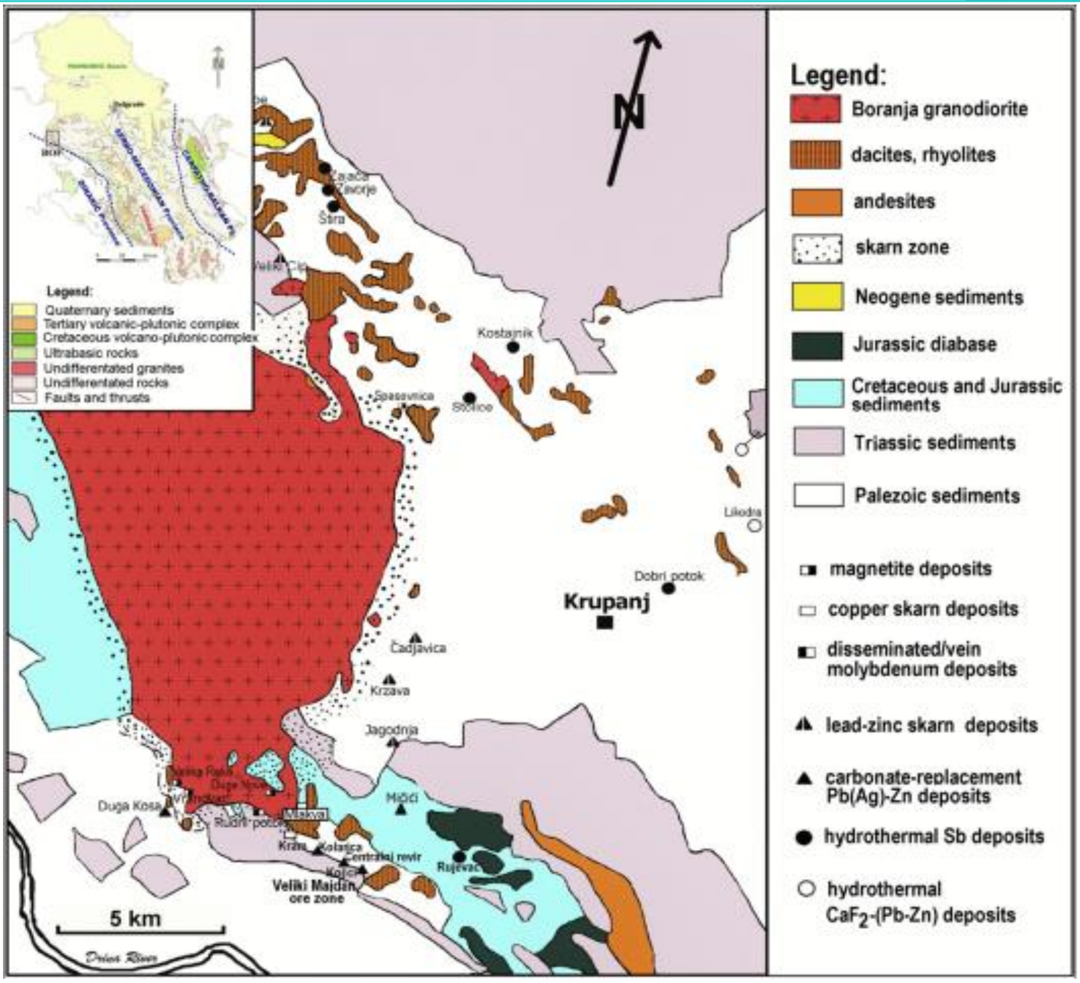

Fig. 2: Geologic and metallogenic map of the Boranja Ore Field (BOF) and sites of mineral assemblages (Radosavljević-Mihajlović et al., 2016). Upper left corner shows the location of the BOF.

Rujevac (Fig. 2, Table 1) is a low-temperature hydrothermal polymetallic Sb-Pb-Zn-As vein ore deposit, hosted within a volcanogenic-sedimentary suite situated in the Diabase-Chert Formation (DCF) of the Podrinje Metallogenic District (PMD). The mineral association of this deposit consists of sulphides, Pb- Sb(As)-sulfosalts, native metals, oxides, hydroxides and gangue minerals. The ore contains valuable metals such as: Sb (0.17-24.31 wt%), Zn (0.21-6.29 wt%), Pb (0.15-6.33 wt%), As (0.06-1.28 wt%), Cd (25-747 ppm), Ag (7-408 ppm), Hg (13-473 ppm), and Tl (1-29 ppm) (Radosavljević et al., 2014).

The Mlakva skarn-replacement polymetallic deposit (Fig. 2, Table 1), includes the phases: β-domeykite, Ni-bearing koutekite, and (Ni-Sb)-bearing α-domeykite. These arsenides are associated with nickeline, chalcocite, native Ag, native Pb, and litharge. Pyrrhotite, pyrite, chalcopyrite, cubanite, bismuthinite, molybdenite, sphalerite, galena, and native Bi are associated with the sulphide paragenesis (Table 1) (Radosavljević-Mihajlović et al., 2016).

Table 1. Characteristics of the Sb- Bi-bearing metallogeny districts from Serbia, Kosovo, North Macedonia and Bulgaria of the Serbomacedonian-Rhodope Metallogenic Belt (SRMB)[1].

Country	Region/Site	Type	Metals, concentrations (in wt% or ppm), reserves
Serbia	Boranja	P-E	Pb, Zn, Cu, Fe, Ag (0-0.94 wt%), **Sb** (0.01-0.51 wt%), **Bi** (0-3.34 wt%), Te, As
	Rudnik	RBMS	Pb (0.9-5.7 wt%), Zn (0.5-4.5 wt%), Cu (0.1-2.2 wt%)
	Rujevac	P-E	Ag (50-297 ppm), **Bi** (100-150 ppm), Cd (100-150 ppm), **Sb**, W
	Mlakva	RBMS	Pb (0.2-6.3 wt%), Zn (0.2-6.3 wt%), **Sb** (0.2-24.3 wt%), As (0.1-1.3 wt%)
Kosovo	Stan Terg	RBMS	Pb (6 wt%), Zn (4 wt%), Cu, Ag, Au, **Bi**, **Sb**, Te (probable + indicated) reserves of (Pb+Zn) ore: >150 Mt
North Macedonia	Buchim	P-E	Cu (0.3 wt%), **Bi**, Se, Te, As, Au (0.3 g/t), Ag (0.8 g/t), Pd (probable + indicated) reserves: Cu=360 th.t, Au=36 t, Ag=96 t
	Alshar	Carlin	**Sb** (<2.5 wt%), As (<1.5 wt%), Tl (<0.5 wt%), Au (~1 g/t) Stibnite reserves >20,000 t (indicated) (av. Sb=0.5 wt%)
Bulgaria	Madan	E-V	Pb (2.5 wt%), Zn (2.1 wt%), Ag (300-1200 ppm), **Sb** (130-1410 ppm), **Bi** (0-2300 ppm) (probable + indicated) reserves of (Pb+Zn) ore: 95 Mt
	Madjarovo	E-V	Pb, Zn, **Bi, Sb**, As, Au (3.9 g/t), Ag, Se (probable + indicated) reserves of (Pb+Zn) ore: 8.5 Mt
	Chelopech	E-V	Pb, Zn, Cu (1.14 wt%), Au (3.73 g/t), Ag (9.27 g/t), **Sb**, **Bi**, As (probable + indicated) reserves of ore: 31.4 Mt
	Elshitsa	E-V	Pb, Zn, Cu, Au, Ag, **Sb, Bi**, Se, Te
	Krassen	HSE	Pb, Zn, Cu, Fe, Au, **Sb, Bi**, Hg, As, Te, Se

[1]references are presented in the text, P-E=Porphyry-Epithermal, RBMS=Replacement Base Metal Sulphide, E-V=Epithermal Vein, HSE=High Sulfidation Epithermal.

3. KOSOVO

The Stan Terg deposit (Trepca ore district) comprises Bi-sulfotellurides, chalcogenides, ikunolite, cosalite, Sb-lillianite, and babkinite and may be considered as a skarn-replacement deposit (Fig. 3, Table 1). Phase relationships among the minerals in the system Bi-Te-Pb-Ag-Cu indicate that they were formed at different times with successive replacement of one mineral assemblage by the next. Other identified Bi-bearing minerals include cannizzarite, native Bi, and bismuthinite. All described minerals are associated with galena rich in Bi and Ag contents (0.02 Bi+Ag apfu). Native Au is spatially related to Bi mineralization. The Bi-bearing phases were formed during the retrograde evolution of the hydrothermal deposit under generally low-sulfidation and the action of fluids in the temperature range 250-350°C (Kołodziejczyk et al., 2015). Compositional trends of the Bi-sulfotellurides suggest lattice-scale incorporation of Bi-(Pb)-rich module and/or admixture with submicroscopic PbS layers in modulated structures, or complicated Bi-Te substitution. The low contents of Au, Ag, Ag in Bi-sulfosalts, together with the lack of Au- Ag-bearing phases in the ore deposit, indicate either ore deposition from fluid(s) depleted in precious metals, or physico-chemical conditions of ore formation preventing Au and Ag precipitation at the deposit site. The temperature of the initial mineralization may have exceeded 400ºC. Non-stoichiometric phases among the Bi-sulfosalts and sulfotellurides studied at Stan Terg reflect modulated growth processes in a metasomatic environment (Kolodziejczyk et al., 2017). Trepca has >150 Mt of probable / indicated reserves of ores containing by average 6% Pb and 4% Zn (Tsirambides and Filippidis, 2016).

4. NORTH MACEDONIA

In the Buchim (Figs. 1, 3) porphyry-epithermal deposit several representative and rare mineral phases, from the Au-Pd- group as well as from the Cu-Bi-Se-Te-As group have been identified. Its Cu mineralization covers an area of 0.5 km^2 and is traced to a depth of 300 m. The probable and indicated reserves are 120 Mt of ore with an average grade of 0.3 wt% Cu (~360 th.t Cu), 0.3 g/t Au (~36 t Au), and 0.8 g/t Ag (~96 t Ag) (Table 1). From the Bi- Se-minerals bismuthinite, krupkaite, emplectite, and native bismuth were found. In addition, the presence of Au and Pd in mixtures was confirmed, too. It should be emphasized that both types of rare mineral phases were determined in the pyrite and chalcopyrite of this deposit. The Bi-Se- mineral phases are related to the major quartz-pyrite-chalcopyrite paragenesis, while Au-Pd mineral phases are related to oxido-sulphide paragenesis (Serafimovski et al., 2010, 2013).

The Au-As-Sb-Tl Alshar of Carlin-type deposit is unique in its mineral composition. It is located at the intersection of the Axios (Vardar) and Aridea-Kozuf metallogenic zones at the western side of the Vardar Graben and the Pelagonian crystalline massif, approximately 3 km from the Greek-North Macedonia border (Fig. 1). The Alshar deposit is composed of several ore bodies and ore occurrences, which are characterized by specific assemblages of elements and minerals. More than 40 minerals have been identified in this ore deposit. Stibnite occurs in the form of crystals up to 2 × 5 mm in size and frequently cements quartz and marcasite grains, indicating its younger age in comparison to pyrite–marcasite assemblage. A probable temperature of about 200°C is accepted for the formation of the main Au-ore.

The Alshar deposit is undoubtedly related to the action of post-volcanic hydrothermal fluids and represents an epithermal type of mineralization. The ore field covers an area of 21 km^2. It is considered a very significant deposit containing economic grades of Sb (<2.5 wt%), As (<1.5 wt%), Tl (<0.5 wt%), and Au (about 1 g/t) (Table 1). The indicated stibnite reserves exceed 20,000 t (av. Sb=0.5 wt%) (Volkov et al., 2006).

5. BULGARIA

Contents of Ag, Bi, Sb, Te, and Tl in galena crystals selected from different Pb-Zn ore deposits of Bulgaria have been determined. Silver and Sb were found in all samples in variable amounts in the ranges 10-1000 ppm for Ag and 70-600 ppm for Sb. Bismuth is nearly completely absent in some deposits, but it is of significant content in some of them in the range of 100-2500 ppm. All crystals of octahedral and cubic-octahedral habit belong to the early generation of galena, deposited at a rather high temperature (>300°C). They contain increased amounts of Bi and Ag (+Sb), most likely in solid solution, which suggests that Bi plays an important role in stabilizing the octahedral faces. The crystals of cubic habit contain Ag, Sb, and traces of Bi (Bonev, 2007).

Antimony and bismuth bearing minerals have been identified in some hydrothermal ore deposits of the SRMB crosscutting the south-eastern part of Bulgaria (e.g., Madan, Spahievo, Zvezdel, and Madjarovo).

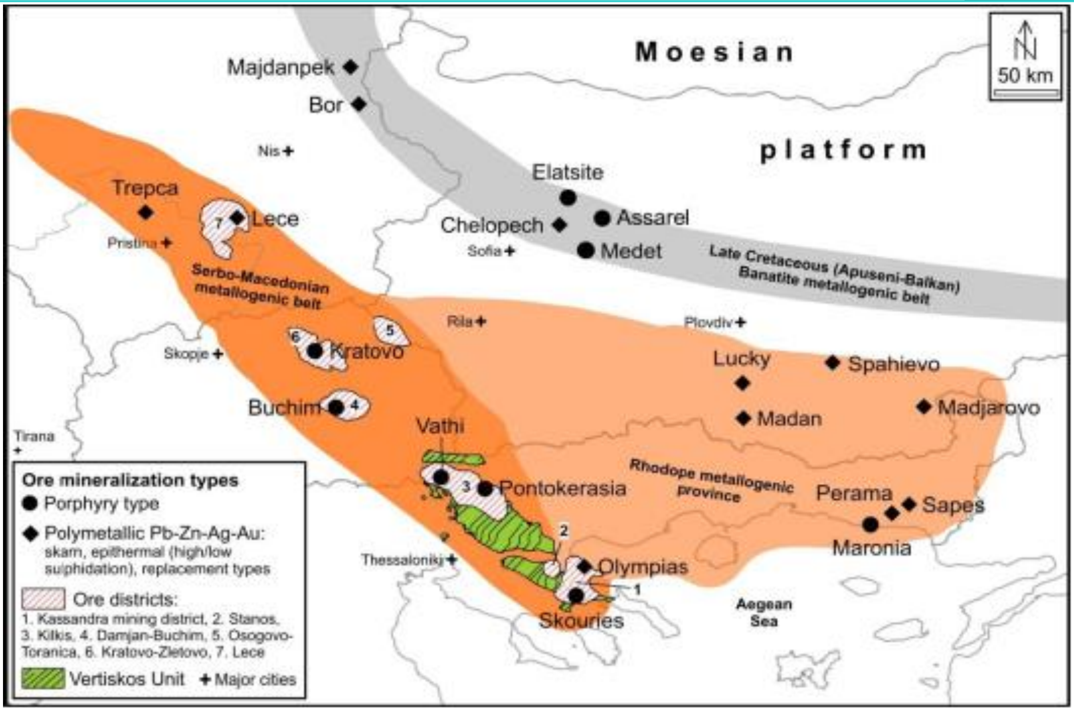

Fig. 3: Geologic map showing the spatial development of the SRMB across the SE Balkan Peninsula. Major ore districts are highlighted (Stergiou et al., 2018).

The Madan vein- and skarn-type deposit (Figs. 1, 3) comprises the largest and richest Pb-Zn ore accumulation of the Rhodope Massif. During the second half of 20th century, the extensive underground mining in more than 50 deposits in this area led to a production of more than 100 Mt of ores with a mean content of 2.5% Pb and 2.1% Zn. Large ore reserves are still available and some mines have a potential for development (Marchev et al., 2005; Bonev, 2007; Vassileva et al., 2009). Hundreds of analyses of galena from the main deposits in this district are given by Kolkovski and Dobrev (2000). The most important elements contained in galena crystals are Ag, Sb, and Bi, in the ranges: 300-1200 ppm, 130-1410 ppm, 0-2300 ppm, respectively (Table 1). Silver and Sb exist uniformly in all deposits and their average contents are about the same (660 ppm). However, the distribution of Bi in galena crystals is rather irregular and concentrated only in some deposits. The probable and indicated reserves of (Pb+Zn) ore are about 95 Mt (Marchev et al., 2005).

The Madjarovo epithermal vein deposit is located within the synonymous volcanic center at the eastern Rhodope Massif (Figs. 1, 3). The polymetallic ore deposit is closely related to Paleogene magmatism represented by sub-volcanic and volcanic rocks. Six stages of vein type mineralization have been established: 1. quartz-pyrite-chalcopyrite with Bi-sulfosalts; 2. quartz-hematite-chlorite with Au; 3. quartz-galena-sphalerite; 4. quartz-barite-chalcedony with Sb-sulfosalts; 5. quartz-arsenic sulfosalts; 6. calcite-siderite. Silver-bearing galena and Fe-poor sphalerite are the main minerals. Galena of early formation contains Bi, while in late stages it carries more Sb. Three groups of sulfosalts were established: Se-bearing Bi-sulfosalts; Sb-sulfosalts, and As-sulfosalts with more or less Ag (Table 1). Fluid inclusion data obtained in quartz, amethyst, sphalerite, and barite from several ore veins indicated formation temperatures in the range of 150°C to 370°C. Analyses of fluids indicate pressures of 70 bars to 180 bars which correspond to an average depth of mineralization of 1.000 m. The low salinities of the fluids (av. 3.5 wt% NaCI equiv.) indicate an influx of meteoric waters during mineralization (Breskovska and Tarkian, 1993). The probable and indicated reserves of (Pb+Zn) ore are about 8.5 Mt grading at 3.9 g/t Au (Marchev et al., 2005).

The following three mineralization districts belong to the adjacent Srednogorie Zone that crosscuts central Bulgaria in a W-E trend.

The largest epithermal vein deposit in the Panagyurishte mineral district is exploited since 1954 at the Chelopech underground mine, which currently has 31.4 Mt of probable and indicated resources at an average grade of 1.14% Cu, 3.73 g/t Au, and 9.27 g/t Ag (Fig. 3, Table 1) (Marton et al., 2016). The widespread pyrite in the ore bodies of the area is associated mainly with enargite and sphalerite. It forms veinlets crosscutting massive enargite or occurs as disseminated small grains in the groundmass, together with other sulphides and gangue minerals. An important characteristic of this pyrite is its increased content in Cu (134-1746 ppm) and As (3-914 ppm). Other significant elements are: Sb (3-927 ppm), Bi (2-164 ppm), Pb (14-4294 ppm), Zn (2-476 ppm), Ga (1-843 ppm), and Ag (2-50 ppm). Their wide variation probably is owed to micro-inclusions in the ore minerals. Significant amounts of Sb (0.002-1.3 wt%) and Bi (0.007-7 wt%), have been detected in the enargites from different mine levels (Vassileva et al., 2016) .

The Elshitsa Pb- Zn- Cu- Au-bearing sulphide is a volcanic hosted deposit of epithermal vein-type. It is considered a product of an island arc volcano-plutonic process and hydrothermal activity that took place during Late Cretaceous. In addition to the major Au-hosted opaque minerals such as pyrite, chalcopyrite, sphalerite and galena there are minor amounts of tennantite, goldfieldite, Se-bearing aikinite, native silver, and bornite in the massive sulphide lenses and stringer zones. Pyrite deformation and recrystallization in the temperature range 250–160°C has led to Au and Ag migration to cracks and grain boundaries of the sulphide minerals. Antimony, Bi, and Te (Table 1) are the most common trace-elements in gold and electrum (Bogdanov et al., 1997).

Part of the Au in the early massive pyrite dominated Krassen high-sulfidation epithermal deposit is sub-microscopic in size (<0.1 μm) and could be attached to the so-called "invisible" gold. Later fracturing of the early massive pyrite followed the deposition of Cu-pyrite ore bodies enriched in chalcopyrite, enargite, bornite, galena, and sphalerite. The electrum fineness in individual grains varies between 882‰ and 998‰. Most common trace elements in the native gold, electrum grains and gold hosting sulphide minerals are: Hg, Sb, Te, Bi, As, and Se (Table 1). The Au content in pyrite and chalcopyrite varies from 0.4 ppm to 7.8 ppm. Bi-Te-Se and Ga-Ge-In trace elements are considered indicators of Au enrichment in many ore minerals of this district (Bogdanov and Kuncheva, 2017).

6. GREECE

In northern Greece (Regions of Macedonia and Thrace) there is a large number of occurrences and ores of Pb, Zn, and Cu, which are often accompanied by Mo, Sb, Bi, W, Ag, Au, and other metals. Some of these ores are economically very significant (Liatsikas et al., 1947; Maben and Zigdis, 1947; Filippidis et al., 1986; Kalogeropoulos et al., 1989; Melfos et al., 1993; Michailidis et al., 1993; Michael, 2004; Shawh and Constantinides, 2001; Vasilatos et al., 2001; Voudouris et al., 2011; Tsirambides and Filippidis, 2012).

Except for stibnite, Sb is also contained in numerous sulfosalts (e.g., tetrahedrite, famatinite, chalcostibite, zinkenite, bournonite, boulangerite) which are common in porphyry-, epithermal- and intrusion-related systems at the Rhodope Massif, such as in Maronia, Pagoni Rachi/Kirki, St. Philippos/Kirki, Mavrokoryfi, Pefka, Perama Hill, Sapes, and Thassos (Michailidis et al., 1989; Vavelidis et al., 1989; Melfos et al., 1991; Filippidis, 1992; Filippidis et al., 1993, 2012). In some cases, samples contain up to 0.2 wt% Sb (Voudouris et al., 2005; Melfos and Voudouris, 2012).

Copper-Au-Bi-Te-bearing porphyry-epithermal deposits (e.g., Pagoni Rachi, Maronia, Stypsi, Perama Hill), sheeted veins (e.g., Xanthi), carbonate replacements (e.g., Madem Lakkos), and shear-zone hosted deposits (e.g., Stanos) have been examined by Voudouris et al. (2007).

Porphyry Cu-Mo-Au, high- and intermediate-sulfidation epithermal Au-Ag deposits and other intrusion-related deposits are characterized by enrichment of trace metallic minerals like Bi-sulfosalts and Bi-sulfotellurides, precious- and base metal tellurides and Se-bearing phases, which can be considered as pathfinder minerals for gold (Voudouris et al., 2018).

The Vertiskos Unit of the Serbomacedonian massif (SMM) hosts several Oligocene-Miocene ore deposits and mineralization occurrences. Some of these contain significant amounts of metals such as Sb, Bi, Te, Co, REEs and PGMs (Stergiou et al., 2018). At the northern part of the SMM there are porphyry-epithermal (Vathi, Palatiano, Gerakario, Pontokerasia, Doirani), skarn/carbonate replacement (Myriofyto, Petrades, Monolithi) and epithermal vein-ore-type (Rodonas) occurrences (Figs. 1, 3, 4). The most important porphyry-epithermal ore occurrences in the Regional Unit of Kilkis are (Veranis and Tsamantouridis, 1991; Stergiou, 2016):

The Vathi Cu- Au- U±Mo deposit is associated with a high-K calc-alkaline monzonite intrusion. Its probable and indicated reserves are 0.15 Mt ore with up to 0.3 wt% Cu and up to 0.8 ppm Au. Other constituents of this deposit are: 20-977 ppm Pb, 9.0-156 ppm Zn, 0-341 ppm Mo, 0.4-239 ppm Bi, 0.1-11 ppm Sb, 0.1-4.6 ppm Ag (Table 2).

The Gerakario Cu- Au-deposit is hosted in a calc-alkaline syenite and granodiorite intrusion. Its probable and indicated reserves are 0.13 Mt ore with up to 0.3 wt% Cu and up to 1.4 ppm Au (Table 2).

The Pontokerasia Cu- Mo- Au-deposit is associated with a calc-alkaline syenite intrusion. It contains up to 0.3 wt% Cu and up to 0.16 ppm Au (Table 2).

Antimony bearing minerals (e.g., bournonite, boulangerite, jamesonite, andorite, etc.) have been detected inside a complex of small veins at Pontokerasia Kilkis (Figs. 1, 3, 4). Usually rounded tiny crystals of bournonite occur inside larger euhedral galena crystals. In addition, jamesonite and boulangerite occur in the form of felt aggregations composed of numerous needle crystals. The above Sb-minerals were formed under hydrothermal processes. Bournonite was formed under hypothermal (500-300°C) conditions, boulangerite under mesothermal (300-200°C) conditions and jamesonite under epithermal (200-50°C) low depth (1000 m) conditions. The ore mineralization of Pontokerasia belongs to the porphyry-epithermal deposit type (Melidonis, 1973).

The Cu-Au porphyry-epithermal deposits of Vathi – Gerakario - Pontokerasia Kilkis may be considered the second most important center for gold in Macedonia Greece. The probable / indicated reserves are about 258 Mt of ore grading up to 0.4% Cu (~1140 th.t Cu) and up to 0.9 g/t Au (~237 t Au) (Tsirambides and Filippidis, 2016).

The Rizana/Lachanas porphyry-epithermal deposit (Fig. 4) is considered the most important stibnite ore in Greece. It is related to sheeted quartz veins, usually of small dimensions, that crosscut Paleozoic metamorphic rocks such as gneisses and amphibolites. Many occurrences of minerals of antimony and some of tungsten exist in the broader area. These sheeted veins are the most spread type of ore mineralization. The paragenesis minerals of the ore are quartz, pyrite, calcite, dolomite, sericite, chlorite, stibnite, and wolframite. This mineral assemblage reinforces the aspect that this ore has an epithermal hydrothermal origin. The difficulty in the dissolution of the hosted rocks by the thermal solutions prevented the creation of extended stibnite and wolframite ore (Paraskevopoulos, 1958). However, he suggested by that time that additional research is needed at the broader area for the evolution of Sb- W-metallogeny in deeper horizons. In the period of 1930-50 about 9,000 tons of stibnite ore and some tons of wolframite ore have been extracted from rough tunnels of 350 m total length. The Sb concentration reached 40% for half of the total production. The mineralization is spread over an area of 50 km long and 30 km wide, and today presents high potential for future exploitation (Paraskevopoulos, 1958). The proven reserves of stibnite are 5000 t (av. Sb=0.3 wt%), its indicated reserves are 50,000-100,000 t of the same Sb concentration and the proven reserves of wolframite are 1000 t (Liatsikas et al., 1947).

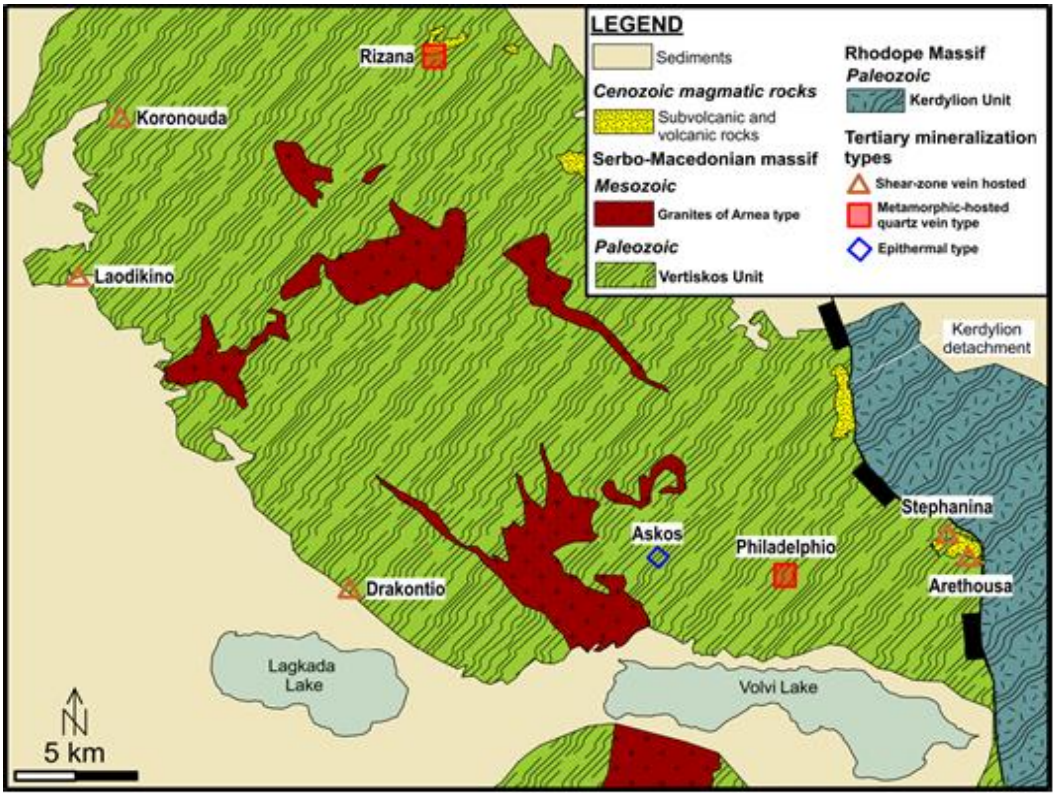

Fig. 4: Geologic map of the central part of the Serbo-Macedonian Massif in North Greece, with the major ore deposits and occurrences (Stergiou, 2016).

Table 2. Characteristics of the Sb- Bi-bearing metallogeny districts from Greece of the Serbomacedonian-Rhodope Metallogenic Belt (SRMB)*.

Region/Site	Type	Metals, concentrations (in wt% or ppm), reserves
Macedonia/Rizana-Lachanas	P-E	**Sb**, W. Wolframite reserves: 1000 t (proven) Stibnite reserves: 5,000 t (proven), 50,000-100,000 t (indicated) (av. Sb=0.3 wt%)
Macedonia/Vathi	P-E	(probable + indicated) reserves: 0.15 Mt of ore with Cu (up to 0.3 wt%), Au (up to 0.8 ppm), Ag (up to 4.6 ppm), Pb (20-977 ppm), Zn (9-156 ppm), Mo (up to 341 ppm), **Bi** (up to 239 ppm), **Sb** (up to 11 ppm), W, Te, U
Macedonia/Gerakario	P-E	(probable + indicated) reserves: 0.13 Mt of ore with Cu (up to 0.3 wt%), Au (up to 1.4 ppm), **Sb**
Macedonia/Pontokerasia	P-E	**Sb**, Pb, Zn, Cu (up to 0.3 wt%), Au (up to 0.16 ppm)
Macedonia/Stanos	I-R	Pb, Zn, Cu, Au, Ag, Mo, **Bi**, Te
Macedonia/Skouries	I-R	Cu (0.5 wt%, 1205 th.t), Au (0.7 g/t, 166 t), Ag, Mo, **Bi,** Co, Se, Te, Pd, Pt, Ru
Macedonia/Kavala	I-R	Pb, Zn, Cu, Fe, Mn, Au, Ag, **Bi, Sb**, Te, W, As
Thrace/Kimmeria	I-R	Pb (0.03 wt%), Zn (0.74 wt%), Cu (1 wt%), Mo (0.2 wt%), Au (<2.7 g/t) Sb (<332 ppm), W (<80 ppm), As (<76 ppm), Sn (<50 ppm), Bi (457 g/t)
Thrace/Neo Kallyntirio	P-E	Pb, Zn, Cu, **Sb**, Ag, Au, Te, As
Thrace/Sapes	P-E	Cu (0.3 wt%, 3000 th. t), Au (av. 15.1 g/t, 16 t), Ag (av. 8.2 g/t, 8 t), Mo, **Bi**, Te (proven/probable) reserves 1.32 Mt of ore
Thrace/Perama Hill	HSE	**Bi**, Au (3.1-3.5 g/t, 74 t), Ag (2.8-4.2 g/t, 62 t), Sn, Te, Se (probable / indicated) reserves 11.7 Mt of ore
Thrace/Maronia	P-E	Mo (7,600 ppm), Cu (5,460 ppm), Au (1 g/t), **Bi**
Thrace/Konos Hill	P-E	Cu, Mo, Re, Au, Se, **Bi**
Thrace/Pagoni Rachi	P-E	Pb, Cu, Fe, Mo, Te, Se, Ag, Au, Sn, **Bi**
Thrace/Esymi-Leptokarya	P-E	Mo (<215 ppm), Se (<29 ppm), **Bi** (<8 ppm), Sn (<14 ppm)

*references are presented in the text, P-E=Porphyry-Epithermal, I-R=Intrusion-Related, HSE=High Sulfidation Epithermal.

The Skouries porphyry intrusion (Figs. 1, 3) and the surrounding rocks are strongly fractured and intensely altered by hydrothermal fluids. Mineralization mainly includes chalcopyrite, pyrite, bornite, chalcocite, and magnetite in the form of veins, stockworks, and disseminations. Native gold and electrum are commonly present as small inclusions in chalcopyrite. The deposit exhibits high levels of Cu, Au, Ag, B, Bi, Co, Se, and Te (Eliopoulos and Economou-Eliopoulos, 1991). The measured / indicated reserves of this deposit are 246 Mt of ore grading by average at 0.49% Cu (~1205 th.t Cu) and 0.7 g/t Au (~166 t Au) (Tsirambides and Filippidis, 2016).

Shear-zone hosted deposits in the Vertiskos Unit (Serbomacedonian massif) occur in four areas: 1. Pravita-Stanos; 2. Stanos-Nea Madytos; 3. Askos-Drakontio; 4. Paliomylos-Laodikino-Koronouda.

The Stanos area of the Chalkidiki includes several porphyry Cu-Au-Mo-Bi, skarn- and carbonate-replacement deposits, which are genetically related to Oligocene-Miocene post-subduction magmatism (Kalogeropoulos et al., 1989; Frei, 1995). The area hosts several metallic prospects (Paliomylos, Chalkoma, and Karambogia), which are dissimilar to other porphyry Cu-Au-Mo and carbonate-replacement Pb-Zn-Au-Ag deposits of Chalkidiki, since the Stanos ores are syn-deformational and related to major shear zones (Kalogeropoulos et al., 1991; Hellingwerf et al., 1994).

The Stanos mineralization is emplaced within a shear zone hosted in two-mica gneisses. Detailed textural studies of the ore assemblages revealed two stages of hydrothermal mineralization. Initially, Fe-bearing sulphides (pyrite, arsenopyrite, and pyrrhotite) were introduced and followed by a Cu-bearing association that included chalcopyrite and minor amounts of galena, sphalerite, molybdenite, and Bi-Au-Te minerals (Table 2). The last mineral association consists mainly of Bi-sulfosalts (bismuthinite derivatives, lillianite homologs, and ikunolite), native elements, and bismuth sulfotellurides. Ikunolite corresponds to the formula Bi_4S_3 and is reported here for first time in Greece (Voudouris and Sakellaris, 2008; Voudouris et al., 2010a, b). The observed association suggests an evolution of the system towards more reducing conditions and that precious metals may have been scavenged by composite Bi-Te-Pb-S melts in a manner proposed by Ciobanu et al. (2005). The Cu-Bi-Au-Te-mineralization is spatially scattered in the Stanos area. Metallic minerals occur as disseminated or massive aggregates along foliation planes and in boudinaged quartz veins. Fluid inclusion homogenization temperatures range from 170°C to 350°C. The mineralization in the Stanos area derived from magmatic rocks at a shallow depth that intruded an extensional shear environment about 19 Ma. The porphyry system of Stanos was formed by successive hydrothermal pulses from fluids that penetrated the shear zone at different times. This system developed under fluctuating $f(S_2)$ and $f(O_2)$ conditions and precious metals may have been scavenged at temperatures >350ºC (Voudouris et al., 2013a; Bristol et al., 2015).

Stibnite from Mavres Petres Chalkidiki has been investigated in detail. Its chemical composition is 67.48 wt% Sb, 4.72 wt% Bi and 27.74 wt% S, while its chemical formula is $Sb_{1.92}Bi_{0.08}S_3$. Antimonite unit cell dimensions are: a-axis = 11.236(2) Å, b-axis = 11.311(2) Å, c-axis = 3.830(1) Å and cell volume = 487.74 Å^3 (Livas et al., 2015).

The Kavala pluton in eastern Macedonia, Greece (Fig. 1), intrudes gneisses and marbles of the Rhodope Massif. An extensive magmatic hydrothermal system rich in Au, Ag, Cu, Pb and Zn is associated with this pluton (Table 2). A new intrusion-related Bi-Te-Pb-Sb±Au deposit was found in quartz veins crosscutting the magmatic and metamorphic rocks. U-Pb dating showed that the magmatic rock was emplaced at about 21 Ma (Early Miocene). The veins consist of quartz, K-feldspar, plagioclase, and muscovite which are mainly altered to sericite. The Bi-Te-Pb-Sb sulphide mineralization forms <5% of these veins (Melfos et al., 2008).

Intrusion-related gold systems are generally characterized by Au-Bi-Te±Sn-W metal assemblages genetically associated with the emplacement of granitic rocks. The Kavala ore system consists of about 150 minor metal assemblages such as Fe–Mn (Pb±Zn±Ag), Fe-Mn-Au, Fe-As-Au, Fe-Cu-Au, and Bi-Te-Au that exist in quartz-calcite-sulphide veins (hypogene mineralization), or as supergene bodies. A sheeted quartz vein system of Bi-Te-Pb-Sb±Au assemblage, ~4 km long and with E-W trend, crosscuts the adjacent schists and gneisses. Pyrite (~5% of vein volume) contains inclusions of tetradymite (some Au-bearing), bismuthinite, and cosalite. Homogenization temperatures (Th) of type I (two-phase aqueous liquid-vapour) and type II (three-phase, H_2O-CO_2-rich) fluid inclusions in quartz from the Kavala and Chalkero veins range from 216°C to 420°C and 256° to 414°C, respectively. The salinities of type I and type II inclusions range from 15.9 wt% NaCl equiv. to 22.6 wt% NaCl equiv. and from 5.5 wt% NaCl equiv. to 11.2 wt% NaCl equiv., respectively (Fornadel et al., 2011).

Several magmatic-hydrothermal systems in Thrace are highly enriched in tellurides which represent major carriers of precious metals. Deposition near the porphyry-epithermal transition for several systems is indicated by field relations and by the presence of characteristic minerals such as Pb- and Ag-rich tellurides, Bi-sulfosalts, and Bi-tellurides.

The presence of hessite, goldfieldite, native gold, and enargite suggests deposition at a high sulfidation state. The main stage of telluride deposition took place at about 275°C, log fTe_2 values of -8.5 to -7.1 and log fS_2 values of -10.8 to -9.0. The close spatial association of telluride mineralization with intrusive centers of intermediate composition, the base metal enrichment and the presence in minor amounts of the trace elements Au, Ag, Te, Bi, Sn, and Mo, suggest that such ores were introduced at the porphyry-epithermal transition stage (Voudouris et al., 2006).

The Kimmeria-Xanthi intrusion-related Mo-Cu-W-Bi-Au deposit is associated with an Oligocene (25-30 Ma) pluton, which consists of granodiorite and minor outcrops of tonalite, quartz-diorite, monzonite, and gabbroic rocks. The pluton intruded gneiss, mica schist, amphibolite and marble of the Rhodope Massif. Two different ore types are genetically connected with the magmatic intrusion: 1. Massive Au-bearing skarn-type mineralization and 2. Mo-Cu-Bi-W quartz vein mineralization. An extensive skarn formation outcrops 2-3 km NNE of Kimmeria consisting mainly of garnet, epidote, hematite, wollastonite, vesuvianite, and secondary amphibole, quartz, and calcite. A magnetite ore deposit accompanied by pyrrhotite, chalcopyrite, pyrite, sphalerite, molybdenite, native gold, and galena is hosted in this skarn formation (Vavelidis et al., 1990). Native gold was found in pyrite and chalcopyrite in the form of irregular grains of 5 μm to 450 μm in size. The intrusion-related polymetallic system includes sheeted quartz veins and stockworks crosscutting the granitic pluton. Bi-sulfosalts bearing up to 6.65 wt% Se are included in pyrite, and Se-bearing galena (up to 3.2 wt% Se and 1.5 wt% Bi). Bulk chemical analyses of vein-type mineralization contains ~1 wt% Cu, ~0.2 wt% Mo, up to 2.7 g/t Au, up to 79.5 g/t W, up to 456.6 g/t Bi, and up to 4 g/t Te (Table 2) (Theodoridou et al., 2016). The Kimmeria-Xanthi intrusion-related ore presents many characteristics of Au-Bi granite-related deposits, with the ore being mostly enriched in Cu, Mo, and W, and, to a lesser extent, in Au, Bi, and Te (Voudouris et al., 2017).

The Neo Kallyntirio porphyry-epithermal deposit of the Rhodope Massif is a Sb- Pb- Zn- Ag- Au- Te-occurrence (Table 2) deposited within and above a low-angle shear zone. It is hosted within silicified marbles and schists and occurs in the form of dissemination, high-angle quartz-barite-carbonate veins, and breccias. The ore developed from early pyrite, followed by low-iron sphalerite, galena, chalcopyrite, and bournonite group minerals, and then by antimonite, arsenopyrite, and realgar. The deposit presents features similar with the detachment related sedimentary rock-hosted low-sulfidation mineralization in Bulgaria. For both sites, the magmatic contribution is supported because of the presence of tellurides in both systems (Kanellopoulos et al., 2014).

The Sapes (Figs. 1, 3) ore in the Circum Rhodope Belt represents a multi-centered, porphyry-epithermal system developed during the Oligocene to Miocene at a calc-alkaline to a high-K calc-alkaline suite of volcanic rocks. The ore mineralization includes hessite, altaite, stützite, and tetradymite in close relation to a high-sulfidation assemblage of enargite, chalcopyrite, goldfieldite, and native Au. The ore is characterized by Au, Ag, Te, Bi, and Mo (Table 2), which suggests a magmatic contribution to the mineralizing fluids. Ore-forming constituents were derived from the porphyritic rocks (Voudouris et al., 2006). The proven / probable reserves are 1.32 Mt of ore at an average grade of 15.1 g/t Au (~16 t Au), 8.2 g/t Ag (~8 t Ag), and 0.3% Cu (~3000 th.t Cu) (Tsirambides and Filippidis, 2016).

The Perama Hill deposit (Figs. 1, 3) is a high-sulfidation Bi-Au-Ag-Te-Se epithermal system (Table 2) hosted at its deeper levels in silicic- and argillic-altered andesitic rocks. The deposit evolved from an early stage silica-pyrite rock and was followed by the formation of sulphide- sulfosalt- and telluride-bearing quartz-barite veins and stockworks. Early ore formation is characterized by a high-sulfidation-type enargite-galena-bearing ore assemblage. Fluid inclusion data demonstrate that the ore evolved from an initial high temperature of 330°C and low salinity fluid of 4.9 wt% NaCl equiv. towards a cooler (200°C) and very low salinity (0.7 wt% NaCl equiv.) hydrothermal fluid suggesting progressive cooling and dilution of the ore fluid. Variable fS_2 and fTe_2 conditions during base and precious metal deposition prevailed. Early ore deposition took place at ~300°C, at $\log fS_2$ values between -8.2 and -5.5, and $\log fTe_2$ between -11.8 and -7.8. Late ore deposition occurred at $\log fS_2$=-11.8 to -9.8 and $\log fTe_2$ of -9.2 to -7.8. The presence of tellurides and Bi- and Sn-bearing minerals in the ore means direct deposition of metals from the vapour phase of a degassing magmatic body (Voudouris et al., 2007, 2011). The probable / indicated reserves of this deposit are ~11.7 Mt of ore at an average grade of 3.1-3.5 g/t Au (~74 t Au) and 2.8-4.2 g/t Ag (~62 t Ag) (Tsirambides and Filippidis, 2016).

The Maronia Cu- Mo-porphyry-epithermal deposit (Figs. 1, 3, Table 2) is hosted by a porphyritic microgranite. The area is dominated by metamorphosed Mesozoic sedimentary and volcanic rocks, and Tertiary plutonic and sub-volcanic intrusions. The rocks mainly consist of marbles and schists and belong to the Makri Unit of the Circum

Rhodope Zone. Three hydrothermal alteration zones have been recognized: an argillic zone, a phyllic zone, and a propylitic zone. Additionally, three highly silicified zones crop out at the north-eastern, south-eastern and southern parts of the microgranite. Chalcopyrite-pyrite-molybdenite mineralization occurs as disseminations, veinlets and segregations. Surface samples contain as much as 7,600 ppm Mo, 5,460 ppm Cu, and 1 ppm Au. The ore-related mineral assemblage consists of sulphides (pyrite, chalcopyrite, cubanite, pentlandite, molybdenite, sphalerite, galena, and bismuthinite), sulfosalts (tetrahedrite, tennantite, zinkenite, bournonite, boulangerite) and oxides. Microthermometry investigation of fluid inclusions in quartz revealed salinities from 5 wt% NaCl equiv. to 55 wt% NaCl equiv., with homogenization temperatures varying from 280°C to 460°C. The estimated trapping pressures of the ore-forming fluids range from 150 bars to 510 bars (Melfos et al., 1991, 2002).

The Konos Hill prospect represents a telescoped Mo–Cu–Re–Au porphyry-epithermal occurrence (Table 2) characterized by deep-level high-sulfidation mineralization. Ore minerals include pyrite, molybdenite, chalcopyrite, and rheniite. Bulk ore analyses show enrichment in elements such as Se, Mo, and Bi, which supports a genetic link between the lithocap and the underlying porphyry. The occurrence of advanced argillic alteration along the faults in the region suggests that highly acidic hydrothermal fluids ascended into the lithocap (Mavrogonatos et al., 2018).

The Pagoni Rachi Mo- Cu- Te- Ag- Au-prospect is a porphyry-epithermal system hosted by dacite porphyry and quartz–feldspar porphyry dikes. Molybdenite (with contents of Re up to 4.7 wt%), occurs in quartz veins along with Fe-Cu sulphides, Pb-Sn- and Cl-bearing oxides, hematite, ilmenite, and tellurides of Bi (Table 2). The fluid inclusions in quartz show that they homogenize by either the liquid or vapour phases (354°C to 428°C) or by halite dissolution at 317°C to 585°C, which equates to salinities of 40 wt% NaCl equiv. to 59 wt% NaCl equiv. (Voudouris et al., 2009). The mineralization may be divided into four paragenetic stages (early to late): (1) sodic/potassic-calcic alteration with quartz- and magnetite-bearing veins (A- and M-type), (2) sodic/potassic alteration with quartz-pyrite-chalcopyrite-molybdenite veins (B-type), (3) sericitic alteration with “transitional” porphyry to epithermal pyrite-chalcopyrite-molybdenite veins (D-type), and (4) argillic alteration with quartz-calcite base metal and precious metal-rich veins (E-type) with epithermal affinity. The D-type veins contain the highest Au grades (up to 5 g/t), as well as Ag- Bi- Te- and Se-bearing minerals indicating a possible genetic relationship with E-type epithermal veins. Fluid inclusion data indicate that A- and B-type veins were deposited at 360-510°C and at pressures up to 690 bars (<2 km depth) in A-veins and up to 360 bars (<1.5 km depth) in B-veins, from boiling hydrothermal fluids. This process produced low to moderate saline (1.7-10.7 wt% NaCl equiv.) and high saline (36-74 wt% NaCl equiv.) fluids (Voudouris et al., 2013b).

A new porphyry-epithermal Mo mineralization has been discovered at Esymi-Leptokarya (Regional Unit of Evros) (Fig.1). The area is dominated by an Oligocene felsic dyke complex, which hosts the Mo mineralization and intrudes Upper Eocene sandstones, marls, and a monzodiorite. The main ore minerals are pyrite, molybdenite, magnetite, bismuthinite, kesterite, galena, and sphalerite. Bulk ore analysis showed enrichment in Mo (up to 215 ppm), Se (up to 29 ppm), Bi (up to 8 ppm), and Sn (up to 14 ppm) in the quartz veins (Table 2). The Mo-ore has affinities to the "arc-related" class of porphyry Mo-deposits. Magmatism played a major role in the metal concentration in the area (Galanopoulos et al., 2018).

7. CONCLUSIONS

- Antimony-bismuth alloys and Ag-Cu-Pb-Sb-Bi sulfosalts have been discovered in some metal assemblages in the SRMB.
- The European Union (EU) is highly dependent on critical and rare metals, such as Sb and Bi, which are very important for sustainable development.
- Greece is one of the EU countries with the most potential for supplying the strategic metal Sb in the future, since it hosts a significant ore deposit at Rizana/Lachanas.
- Here, the stibnite reserves (proven + indicated) are 50,000-100,000 t with average Sb=0.3 wt% and the wolframite reserves (proven) are 1000 t.
- Another promising Sb-bearing mineral assemblage exists at Alshar (North Macedonia). Here, the stibnite indicated reserves are >20,000 t with average Sb=0.5 wt%.
- At both mineralization districts further investigations are needed to determine the grade and the proven reserves of the critical metal Sb.
- Until today none encouraging site has been located in the SRMB for remarkable Bi-bearing ore.

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