

Sb- Bi-Bearing Metallogeny of the Serbomacedonian-Rhodope Metallogenic Belt (SRMB)

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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 in three spatially and temporally distinct tectonic and metallogenic belts. One of them, the Serbomacedonian-Rhodope Metallogenic Belt (SRMB), intersects with a NNW-SSE trend south-western Serbia, Kosovo, F.Y.R.O.M., north-eastern Greece and south Bulgaria. This arcuate belt is about 500 km long and 130-180 km wide. Deposits of carbonate-replacement Pb-Zn-Ag-Au, of porphyry Cu-Mo-Au, of stratiform volcano-sedimentary, of isolated magmatic-hydrothermal and skarns, as well as intrusion-related, epithermal and Carlin-type, compose this belt. All are genetically related to Oligocene-Miocene post-subduction magmatism (Kalogeropoulos et al., 1989; Marchev et al., 2005; Serafimovski et al., 2010; Tsirambides & Filippidis, 2016; Voudouris et al., 2018).

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. Stibnite (Sb₂S₃) is the predominant ore mineral of Sb. The most important ores of Bi are bismuthinite (Bi₂S₃) and bismite (Bi₂O₃). 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 (Melfos & Voudouris, 2012).

The European Union (EU) is highly dependent on critical and rare metals which are very important for a sustainable development. However, European industry is not able to cover its demands from native sources and it imports commodities from third countries. The various types of deposits of the SRMB are promising targets for future exploration and exploitation in Sb, Te, Mo, Re, Ga, In, REE and PGE. Therefore, the mineral wealth of this belt can contribute significantly to a sustainable and a competitive economy of Europe (Tsirambides & Filippidis, 2012, 2016).

Results and discussion

The Au-As-Sb-Tl Alshar deposit of Carlin type in F.Y.R.O.M. 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-F.Y.R.O.M. border. The deposit is composed of several ore deposits and 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. The ore field covers an area of 21 km². It is considered a very significant deposit containing economic grades of Sb (up to 2.5 wt%), As (up to 1.5 wt%), Tl (up to 0.5 wt%) and Au (about 1 g/t). The indicated stibnite reserves exceed 20,000 t (av. Sb=0.5 wt%) (Volkov et al., 2006).

In the regions of Macedonia and Thrace in Greece 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. Except stibnite, antimony is also contained in many sulfosalts which are common in porphyry-, epithermal- and intrusion-related systems at the Rhodope Massif. In some cases samples contain up to 0.2 wt% Sb (Voudouris et al., 2011; Melfos & Voudouris, 2012; Tsirambides & Filippidis, 2016).

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. 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 (Rodonas) ore type occurrences (Stergiou et al., 2018).

The most important porphyry-epithermal ore occurrences in the Regional Unit of Kilkis are (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, 9-156 ppm Zn, up to 341 ppm Mo, up to 239 ppm Bi, up to 11 ppm Sb and up to 4.6 ppm Ag.
- 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.
- 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 0.2 ppm Au.
- The Rizana/Lachanas porphyry-epithermal deposit 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 at 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 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%) and its indicated reserves are 50,000-100,000 t of the same Sb concentration. The proven reserves of wolframite are 1000 t (Liatsikas *et al.*, 1947).

- The Kimmeria Xanthi intrusion-related Mo-Cu-W-Bi-Au deposit is associated with an Oligocene (25-30 My) 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. The intrusion-related polymetallic system includes sheeted quartz veins and stockworks crosscutting the granitic pluton. Bulk chemical analyses of vein-type mineralization resulted in the following composition: ~1 wt% Cu, ~0.2 wt% Mo, up to 2.7 g/t Au, up to 80 g/t W, up to 457 g/t Bi, and up to 4 g/t Te (Theodoridou *et al.*, 2016).

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 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, Greece). 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 (F.Y.R.O.M.). 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 sites.

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