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# Mineralogical and Geochemical Investigation of Sb-bearing minerals from Greek ores

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Critical Raw Materials (CRMs) are those raw materials that are economically and strategically important for the European economy, but have a high-risk associated with their supply. It is important to note that these materials are not classified as 'critical' because these materials are considered scarce, rather they are classified as 'critical' because (http://criticalrawmaterials.org/critical-raw-materials) : (1) they have a significant economic importance for key sectors in the European economy, such as consumer electronics, environmental technologies, automotive, aerospace, defense, health and steel, (2) they have a high-supply risk due to the very-high import dependence and high level of concentration of set critical raw materials in particular countries and (3) there is a lack of (viable) substitutes, due to the very unique and reliable properties of these materials for existing, as well as future applications.

Sb is classified as a Critical Raw Material (CRM) in all relevant official EU reports (e.g. European Commission, 2017). Applications of Sb include flame-retardants, alloys, pigments, semiconductors, pharmaceuticals etc. (e.g. Grund *et al.*, 2006) and according to the latest EC report (2017), Sb has the third highest supply risk for the EU industry after the two categories of rare earth elements (LREEs and HREEs). Sb metal is recovered from ore primarily by pyrometallurgical techniques. Hydrometallurgical processing is suitable for some ores containing precious metals (Grund *et al.*, 2006).

According to Arvanitidis (2011) Sb ores in Greece are formed and found in veins at various areas of Rhodope, Thessaloniki and Chios Isl.. The concentration of Sb in these veins varies between 1 and 2.5wt.% and secondary mineral phases occurring with Sb minerals include Pb, Fe, Cu, Ag and Au sulphides. The indicative reserves of Sb from these areas are 2,400 tones and further research is required at these occurrences for the determination of their potential. According to Klocho (2019), worldwide reserves are 1,500,000 tones (rounded). Major Sb deposits are found China (reserves 480,000 tones), Russia (350,000 recoverable tones), Bolivia (reserves 310,000 tones), Australia (reserves 140,000 tones) and Turkey (reserves 100,000 tones) (Klocho, 2019). China is the main global supplier with a share of 87% of the world production (European Commission, 2017).

The most promising Sb occurrence in Greece is found in the mixed sulphide ore deposits of Kassandra mining district (NE Chalkidiki). This is clearly depicted in the concentration of Sb in the concentrates produced from these mines: Sb is found having a concentration of 712.9 ppm in the Py-AsPy concentrate from Olympias, 748.2 ppm in the ZnS concentrate from Stratoni and >2000 ppm in the PbS concentrate from Stratoni (Tzamos *et al.*, 2019).

Although Sb is a CRM present in many localities from Greece, detailed studies regarding the mineralogy and geochemistry of Sb minerals and ores of Greece have not yet been made. Thus, the scope of the present study is to report new results concerning the mineralogy and the chemistry of these minerals from different Greek localities.

For the present study, twelve (12) Sb-bearing ore samples from Lachanas (Thessaloniki), Chios Isl., Kassandra mining district (Olympias and Stratoni, Chalkidiki) were concerned. Polished sections were mounted from each sample and were examined in optical microscope (Fig. 1). After examination in optical microscope, scanning electron microscopy (SEM) images and microprobe analyses (EPMA) were obtained using a JEOL 8200 electron probe micro-analyzer equipped with a wavelength dispersive spectrometer (WDS). Analytical conditions were: 15kV accelerating voltage, 15 nA beam current, 2 μm beam diameter with a counting time of 20 s on the peaks and 10 s on the background. The approximate detection limit was 0.01 wt.% for each element.Also, four (4) representative samples were analyzed for their concentration in trace elements using Perkin Elmer ICP-OES/MS after standard fusion and acid-digestion.

Microscopic study of polished sections under the optical microscope and SEM, revealed the presence of stibnite in Olympias (sample O1), stibnite (sample M1) and boulangerite along with galena, pyrite and sphalerite (sample M2) in Stratoni, boulangerite in Lachanas (sample K1), stibnite (sample C4) and valentinite (sample C5) in Chios. Microprobe analyses showed that all Sb-bearing minerals have typical concentration regarding their content in major elements.

Table 1 presents the results of the chemical analyses for some trace elements analyzed. Elevated concentrations of samples of samples M1, M2 and O1 in Ag, Mn, Cd and Sn is attributed to the presence other mineral phases (e.g. galena) micro-inclusions and impurities, along with Sb minerals.

Regarding other trace elements, sample M2 shows an unusual high concentration in Bi (1610 ppm), sample M1 has an elevated concentration of Se (10 ppm) and sample K1 contains significant amount of Hg (10.08 ppm). Moreover, Tl shows enrichment in three out of the four analyzed samples: 92 ppm in sample M2, 15.12 ppm in sample O1 and 8.80 ppm in sample K1. Elevated concentrations in Bi, Se, Hg, and –especially- Tl and their geochemical significance are part of our ongoing research concerning the Sb ores of Greece along with research on the development of methods for the extraction of Sb from mixed sulphide concentrates.

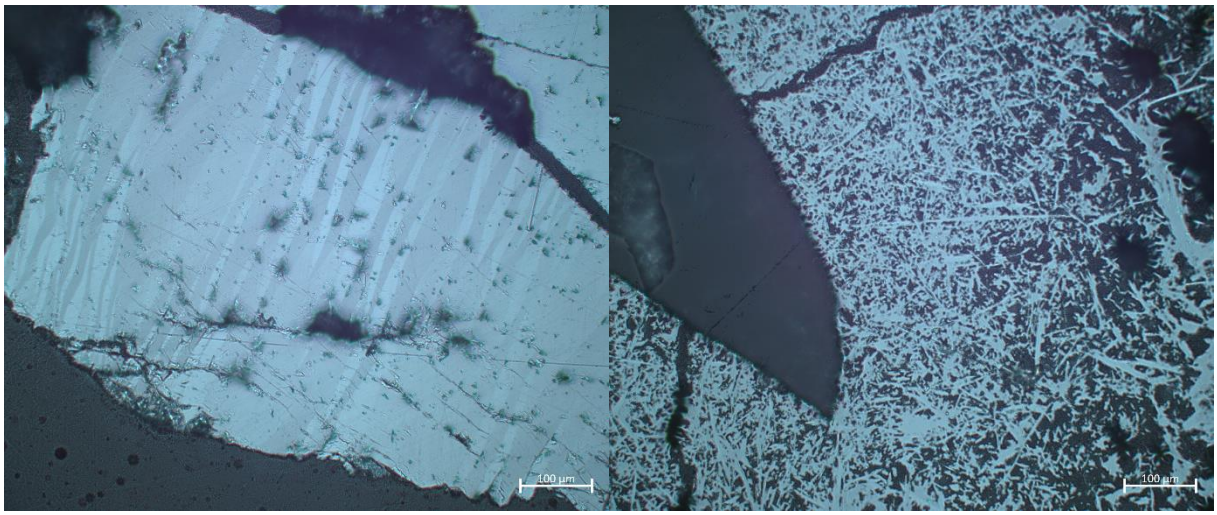


**Figure 1. Stibnite (left-sample M1) and boulangerite (right-sample M2) from Stratoni, reflected light (N //).**

**Table 1. Trace element concentrations of the studied samples.**

| Element | Mo | Ag | Mn | Cd | Bi | Sn | Se | Te | Tl | Hg |
|---|---|---|---|---|---|---|---|---|---|---|
| Unit | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| Detectionlimit | 0.05 | 20 | 1 | 0.02 | 0.04 | 0.1 | 0.3 | 0.05 | 0.05 | 0.01 |
| Sample M1 (Stratoni) | <0.05 | 26759 | 63 | 0.94 | 0.69 | 15.7 | 10.0 | 0.05 | 0.58 | 0.37 |
| Sample M2 (Stratoni) | 0.12 | >200000 | 428 | 21.85 | 1609.67 | 69.7 | 0.8 | 2.74 | 92.00 | 0.22 |
| Sample K1 (Lachanas) | <0.05 | 1391 | 3 | 0.74 | 6.73 | 0.2 | <0.3 | <0.05 | 8.80 | 10.08 |
| Sample O1 (Olympias) | 0.29 | 70047 | 3074 | 8.17 | 4.20 | 83.7 | 0.7 | 0.17 | 15.12 | n/a[1] |

1: n/a = not analyzed

## Conclusions

- Sb (considered as a Critical Raw Material) is reported to have potential for exploitation from Greek ores, especially from the Kassandra mining district were new methods for its extraction from the mixed sulphide concentrates must be developed
- Sb-bearing minerals found in Greek relevant ores are antimonite, stibnite, boulangerite and valentinite with typical chemical composition in major elements.
- Mineral samples hand-picked and analyzed with ICP-ES/MS were found to have elevated concentrations in various trace elements (Bi, Se, Hg and Tl) with ongoing research aiming to reveal the significance of this fact.

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