New Insights into the Mineralogy and Geochemistry of Sb Ores from Greece

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Abstract: Antimony is a common metalloid occurring in the form of Sb-sulfides and sulfosalts, in various base and noble metal deposits. It is also present in corresponding metallurgical products (concentrates) and, although antimony has been considered a penalty element in the past, recently it has gained interest due to its classification as a critical raw material (CRM) by the European Union (EU). In the frame of the present paper, representative ore samples from the main Sb-bearing deposits of Greece (Kilkis prefecture, Chalkidiki prefecture (Kassandra Mines), and Chios Isl.) have been investigated. According to optical microscopy and electron probe microanalysis (EPMA) data, the Greek ores contain stibnite (Sb$_2$S$_3$), boulangerite (Pb$_5$Sb$_4$S$_{11}$), bournonite (PbCuSbS$_3$), bertherite (FeSbS$_4$), and valentinite (Sb$_2$O$_3$). Bulk analyses by inductively coupled plasma mass spectrometry (ICP-MS) confirmed, for the first time published, the presence of a significant Hg content in the Kilkis Sb-ore. Furthermore, Kassandra Mines ores are found to contain remarkable amounts of Bi, As, Sn, Tl, and Se (excluding Ag, which is a bonus element). The above findings could contribute to potential future exploration and exploitation of Sb ores in Greece.

Keywords: antimony ore; critical raw materials; ore mineralogy; ore geochemistry

1. Introduction

Antimony has been recently included in the so-called critical raw materials (CRMs) list, which are economically and strategically important for the global and European economy and have a high risk associated with their supply. It is important to note that these materials are classified as “critical” because (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 CRM in all relevant official European Union (EU) reports [1]. Applications of Sb include flame-retardants, alloys, pigments, semiconductors, and pharmaceuticals [2], 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 (Light REEs and Heavy REEs). Sb metal is recovered from ore primarily by pyrometallurgical techniques. Hydrometallurgical processing is suitable for some ores containing precious metals [2]. According to Klocho [3], worldwide reserves are 1,500,000 tones (rounded). Major Sb deposits are found in 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) [3]. China is the main global supplier, with a share of 87% of the world production [1].

In northern Greece, there are many Pb-, Zn-, and Cu-sulfide deposits, where often Mo, Sb, Bi, W, Ag, Au, and other metals are also present in elevated concentrations. Except stibnite, Sb occurs in many sulfosalts, which are common in porphyry-, epithermal-, and intrusion-related systems in the Rhodope Massif. In some cases, samples contain up to 0.2 wt. % Sb ([4] and references therein). The Rizana/Lachanas porphyry-epithermal deposit is considered the most significant source of stibnite ore in Greece [5]. This deposit is related to sheeted quartz veins, usually of small dimensions, that crosscut Paleozoic metamorphic rocks such as gneisses and amphibolites. The paragenesis of the ore comprises gangue minerals (quartz, calcite, dolomite, sericite, and chlorite), together with pyrite, stibnite, and wolframite. During the period 1930–1950, about 9000 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 wt. % for half of the total production. The mineralization is spread over an area of 50 km long and 30 km wide. The proven reserves of stibnite are 5000 t (av. Sb = 0.3 wt. %), and its indicated reserves are 50,000–100,000 t with the same Sb concentration. The proven reserves of wolframite are 1000 tonnes [6]. Later studies have suggested the utilization of the ore as flux agent in the production of cement [7]. A promising Sb occurrence in Greece occurs in the mixed sulphide ore deposits of Kassandra mining district (NE Chalkidiki), currently operated by Hellas Gold S.A./Eldorado Gold (https://www.eldoradogold.com/assets/operations-and-projects/europe/default.aspx). Sb mainly occurs in the galena concentrate, which also hosts a significant amount of Ag (LEAD/SILVER CON. in Figure 1). This is clearly depicted in the amount of Sb in the concentrates, produced by hydrometallurgy (Flotation; Figure 1) from these mines: Sb has an average concentration of 713 ppm in the Py-AsPy concentrate from Olympias, 748 ppm in the ZnS concentrate from Stratoni, and >2000 ppm in the PbS concentrate from Stratoni ([8] and references therein).

Finally, significant Sb mineralization occurs in northern Chios Isl. (Keramos). These ores are hosted into Paleozoic sedimentary rocks and volcanics. Exploitation of these ores took part in the past; the ore was mined in small scale in the mid-19th century, but is not clear if it was for metal ore or just the surrounding rock. Nevertheless, the mines were systematically used in the 1890s when French scientists assayed the metal ore. The mining and exploration activities of French and Greek companies ended in 1954. Later, the Greek government decided the exception of mining in all Chios with a 1987 law. There are some studies about Sb in the groundwater and thermal springs of the area [9,10], since particularly high concentrations of Sb may occur in water draining abandoned mining sites [11–16], but no publications about the Sb-ore.

It is evident that although Sb is a CRM present in many localities from Greece, detailed publications regarding the mineralogy and geochemistry of Sb minerals and ores have not yet been presented in the literature. Moreover, concerning the final metallurgical products, it is generally measured as a penalty element because it reduces the quality of the concentrates produced from ore and delivered to the smelters ([17] and references therein). However, since Sb has been recently classified as a CRM, it is now considered to be separated from massive sulphide ores. In this case, the knowledge of the mineralogy and geochemistry of this metalloid in the ores is critical. Thus, the scope of the present study is to provide new insights into the chemical and mineralogical compositions of ore samples from the main Sb deposits of Greece (Kilkis prefecture, Chalkidiki prefecture, Chios Isl.).
2. Materials and Methods

For the present study, Sb ore samples from the main Sb deposits of Greece (Kilkis prefecture, namely Rizana/Lachanas (abandoned) mines; Chalkidiki prefecture, i.e., Kassandra Mines, namely, Stratoni/M. Lakkos and Olympiada (active) mines; Chios Isl., namely, Keramos (abandoned) mines) were collected and subsequently examined using optical microscopy and electron microscopy. In particular, the samples included (i) macroscopically “pure” stibnite ore from Kilkis, (ii) macroscopically “pure” stibnite and boulangerite from Stratoni/M. Lakkos and Olympiada, and (iii) oxidized/altered Sb-ore from Chios Isl. (Figures 2 and 3).

Polished sections and powdered material were prepared for each sample. The mounted polished sections were examined in optical microscope. Scanning electron microscopy (SEM) images and microprobe analyses (EPMA) were conducted with a JEOL 8200 (JEOL Ltd., Akishima, Japan) equipped with a wavelength dispersive system (WDS) at the Earth Sciences Department of the University of Milan. The microprobe system operated using an accelerating voltage of 15 kV, a sample current on brass of 15 nA, 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. A series of X-Ray lines from natural and synthetic standards were used for analyzing the following elements: Sb, S, As, W, Pb, Zn, Se, Hg, Ag, Ni, Fe, Mn, Cu, Mg, Co, Bi, and Ca. EPMA data was corrected for matrix effects by applying the PRZ algorithm included in JEOL software.
Major and trace elements in the powdered concentrates were analyzed using a Perkin Elmer ICP-OES (Medtech, Waltham, MA, USA) and a Perkin Elmer Sciex Elan 9000 ICP-MS (Medtech, Waltham, MA, USA) following LiBO$_2$/LiB$_4$O$_7$ fusion and HNO$_3$ digestion of the fused solid sample at external collaborating laboratories (Bureau Veritas Commodities Canada Ltd., Vancouver, BC, Canada). Quality control report of these analyses is given in Appendix A (Figure A1.).

Figure 2. Stibnite onto calcite and quartz from Stratoni/Mantem Lakkos (a); and boulangerite, also onto calcite and quartz, from Olympiada (b); Stibnite ore from Kilkis (c).

Figure 3. Cont.
3. Results

According to the optical microscopy and EPMA data, the Sb minerals, detected in the examined Greek ores, are identified as stibnite (Sb$_2$S$_3$), boulangerite (Pb$_5$Sb$_4$S$_{11}$), bournonite (PbCuSbS$_3$), bertherite (FeSbS$_4$), and valentinite (Sb$_2$O$_3$).

Particularly, in Kassandra Mines samples from Stratoni/Mantem Lakkos locality, the presence of stibnite and boulangerite was observed along with galena and pyrite (Figure 4a–d). In Olympiada samples (Figure 4e,f), along with stibnite and boulangerite, bournonite also occurs, and it is associated with seligmannite (PbCuAsS$_3$).

At Chios island, oxidized samples bertherite and valentinite occur, together with primary stibnite (Figure 4g–j).

Finally, the main mineral Sb phase found at Kilkis samples is boulangerite (Figure 4k,l).

According to the EPMA results (Table 2), the following mineral formulae were calculated for the identified minerals in the samples from Greek Sb ores:

- Stibnite from Olympiada locality: Sb$_{2.02}$As$_{0.01}$S$_{3.00}$
- Stibnite from Stratoni/Mantem Lakkos locality: Sb$_{2.06}$As$_{0.01}$S$_{3.00}$
- Stibnite from Chios locality: Sb$_{2.03}$As$_{0.01}$S$_{3.00}$
- Boulangerite from Olympiada locality: Pb$_{5.02}$Zn$_{0.02}$Cu$_{0.01}$Fe$_{0.01}$Ni$_{0.01}$W$_{0.01}$Se$_{0.01}$Sb$_{4.09}$As$_{0.30}$S$_{11.00}$
- Boulangerite from Kilkis area: Pb$_{5.16}$Zn$_{0.01}$Cu$_{0.01}$Ni$_{0.01}$W$_{0.01}$Hg$_{0.01}$Mn$_{0.01}$Sb$_{4.03}$As$_{0.09}$S$_{11.00}$
- Bournonite from Olympiada locality: Pb$_{1.00}$Cu$_{1.00}$Sb$_{0.68}$As$_{0.36}$S$_{3.00}$
- Bertherite from Chios island: Fe$_{1.00}$Sb$_{2.14}$As$_{0.01}$S$_{4.00}$

The bulk chemical composition of the examined ores is given in Table 3. According to the results, there is a significant variation concerning particular metals and metalloids. Regarding trace elements:

- The boulangerite sample from Kassandra Mines (Olympiada locality) shows unusual high concentrations in Bi (1610 ppm), Ag (>200 ppm), and Tl (92 ppm), and is particularly enriched in Cd (22 ppm) and Sn (70 ppm).
- The stibnite sample from Kassandra Mines (Stratoni/Mantem Lakkos locality) has an elevated concentration of Se (10 ppm) and Ag (27 ppm).
- The stibnite sample from Kassandra Mines (Olympiada locality) is enriched in As (157 ppm), Sn (83 ppm), Ag (70 ppm), and Tl (15 ppm).
- The stibnite sample from the Kilkis area (Lachanas/Rizana locality) contains a significant amount of Hg (10.08 ppm).
Figure 4. Cont.
Figure 4. Optical microscopic (reflected light) and SEM images of typical Sb-minerals from Greek Sb ores. (a) Stibnite from Stratoni/Mantem Lakkos locality, Nicols; (b) Stibnite from Stratoni/Mantem Lakkos locality, Nicols +; (c) Boulangerite (Boul) with galena (Ga) from Stratoni/Mantem Lakkos locality, Nicols; (d) Boulangerite (Boul) with pyrite (Py) from Stratoni/Mantem Lakkos locality, Nicols; (e) Boulangerite from Olympiada locality, Nicols; (f) backscattered electron (BSE) image from Olympiada locality; (g) Stibnite from Chios island, Nicols; (h) Stibnite from Chios island, Nicols +; (i) Stibnite from Chios island, Nicols; (j) Stibnite from Chios island, Nicols +; (k) BSE image of boulangerite (white "needles") from Kilkis; and (l) (BSE) image of boulangerite from Kilkis.
Table 1. EMPA point analyses of Sb minerals from Greece.

|            | Sb        | Stibnite (Olympiada) | Stibnite (Stratoni/M.Lakkos) | Stibnite (Chios) |
|------------|-----------|----------------------|------------------------------|------------------|
|            | wt. %     | Average, \( n = 31 \) | Average, \( n = 15 \)       | Average, \( n = 9 \) |
| Sb         | 71.833    | 71.784               | 71.694                       |                  |
| S          | 28.049    | 27.543               | 27.928                       |                  |
| As         | 0.261     | 0.215                | 0.183                        |                  |
| W          | 0.080     | 0.074                | 0.030                        |                  |
| Pb         | 0.054     | 0.050                | 0.059                        |                  |
| Zn         | 0.053     | 0.076                | 0.045                        |                  |
| Se         | 0.025     | 0.040                | 0.019                        |                  |
| Hg         | 0.021     | 0.038                | 0.036                        |                  |
| Ag         | 0.020     | 0.009                | 0.014                        |                  |
| Ni         | 0.017     | 0.017                | 0.015                        |                  |
| Fe         | 0.015     | 0.015                | 0.012                        |                  |
| Mn         | 0.015     | 0.010                | 0.005                        |                  |
| Cu         | 0.011     | 0.023                | 0.037                        |                  |
| Mg         | 0.009     | 0.010                | 0.010                        |                  |
| Co         | 0.009     | 0.016                | 0.021                        |                  |
| Bi         | 0.000     | 0.000                | 0.000                        |                  |
| Ca         | 0.000     | 0.000                | 0.000                        |                  |
| Total      | 100.472   | 99.919               | 100.107                      |                  |
| Atom       |           |                      |                              |                  |
| S          | 3.000     | 3.000                | 3.000                        |                  |
| Sb         | 2.024     | 2.059                | 2.028                        |                  |
| As         | 0.012     | 0.010                | 0.008                        |                  |
| Zn         | 0.003     | 0.004                | 0.002                        |                  |
| W          | 0.001     | 0.001                | 0.001                        |                  |
| Mg         | 0.001     | 0.001                | 0.001                        |                  |
| Se         | 0.001     | 0.002                | 0.001                        |                  |
| Ni         | 0.001     | 0.001                | 0.001                        |                  |
| Fe         | 0.001     | 0.001                | 0.001                        |                  |
| Mn         | 0.001     | 0.001                | 0.000                        |                  |
| Pb         | 0.001     | 0.001                | 0.001                        |                  |
| Ag         | 0.001     | 0.000                | 0.000                        |                  |
| Cu         | 0.001     | 0.001                | 0.002                        |                  |
| Co         | 0.000     | 0.001                | 0.001                        |                  |
| Hg         | 0.000     | 0.001                | 0.001                        |                  |
| Bi         | 0.000     | 0.000                | 0.000                        |                  |
| Ca         | 0.000     | 0.000                | 0.000                        |                  |
| Total      | 5.048     | 5.085                | 5.049                        |                  |

|            | Boulangerite (Olympiada) | Boulangerite (Kilkis) |
|------------|--------------------------|-----------------------|
|            | Average, \( n = 13 \)   | Average, \( n = 10 \)  |
| Pb         | 54.468                   | 55.932                |
| Sb         | 26.090                   | 25.701                |
| S          | 18.465                   | 18.474                |
| As         | 1.161                    | 0.338                 |
| Zn         | 0.057                    | 0.027                 |
| W          | 0.053                    | 0.093                 |
| Hg         | 0.033                    | 0.094                 |
| Bi         | 0.026                    | 0.000                 |
| Cu         | 0.024                    | 0.033                 |
| Fe         | 0.020                    | 0.011                 |
| Se         | 0.020                    | 0.010                 |
| Ni         | 0.017                    | 0.026                 |
| Co         | 0.011                    | 0.006                 |
| Ag         | 0.007                    | 0.000                 |
| Mn         | 0.003                    | 0.038                 |
| Mg         | 0.000                    | 0.000                 |
| Ca         | 0.000                    | 0.000                 |
| Total      | 100.454                  | 100.784               |
Table 2. Cont.

| Atom       | Boulangerite (Olympiada) Average, $n = 13$ | Boulangerite (Kilkis) Average, $n = 10$ |
|------------|------------------------------------------|----------------------------------------|
|            | wt. %                                    | wt. %                                  |
| S          | 11.000                                   | 11.000                                 |
| Pb         | 5.022                                    | 5.155                                  |
| Sb         | 4.094                                    | 4.031                                  |
| As         | 0.295                                    | 0.086                                  |
| Zn         | 0.017                                    | 0.008                                  |
| Cu         | 0.007                                    | 0.010                                  |
| Fe         | 0.007                                    | 0.004                                  |
| Ni         | 0.006                                    | 0.008                                  |
| W          | 0.005                                    | 0.010                                  |
| Se         | 0.005                                    | 0.003                                  |
| Co         | 0.004                                    | 0.002                                  |
| Hg         | 0.003                                    | 0.009                                  |
| Bi         | 0.002                                    | 0.000                                  |
| Ag         | 0.001                                    | 0.000                                  |
| Mn         | 0.001                                    | 0.013                                  |
| Mg         | 0.000                                    | 0.000                                  |
| Ca         | 0.000                                    | 0.000                                  |
| Total      | 20.470                                   | 20.338                                 |

| Atom       | Boumonite-Seligmannite (Olympiada) Average, $n = 5$ | Bertherite (Chios) Average, $n = 6$ |
|------------|----------------------------------------------------|-------------------------------------|
|            | wt. %                                              | wt. %                               |
| Pb         | 43.132                                             | 57.982                              |
| S          | 20.134                                             | 28.615                              |
| Sb         | 17.244                                             | 12.415                              |
| Cu         | 13.242                                             | 0.237                               |
| As         | 5.620                                              | 1.135                               |
| Se         | 0.053                                              | 0.072                               |
| Zn         | 0.049                                              | 0.065                               |
| Hg         | 0.042                                              | 0.051                               |
| Ni         | 0.034                                              | 0.048                               |
| Fe         | 0.018                                              | 0.041                               |
| W          | 0.018                                              | 0.037                               |
| Mn         | 0.014                                              | 0.019                               |
| Co         | 0.010                                              | 0.013                               |
| Mg         | 0.000                                              | 0.011                               |
| Bi         | 0.000                                              | 0.003                               |
| Ag         | 0.000                                              | 0.000                               |
| Ca         | 0.000                                              | 0.000                               |
| Total      | 99.610                                             | 99.745                              |

| Atom       | wt. %                                              |
|------------|----------------------------------------------------|
| S          | 3.000                                              |
| Cu         | 0.996                                              |
| Pb         | 0.995                                              |
| Sb         | 0.677                                              |
| As         | 0.358                                              |
| Zn         | 0.004                                              |
| Se         | 0.003                                              |
| Ni         | 0.003                                              |
| Fe         | 0.002                                              |
| Mn         | 0.001                                              |
| Hg         | 0.001                                              |
| Co         | 0.001                                              |
| W          | 0.000                                              |
| Mg         | 0.000                                              |
| Bi         | 0.000                                              |
| Ag         | 0.000                                              |
| Ca         | 0.000                                              |
| Total      | 6.040                                              |

Total 20.470 20.338

Total 99.610 99.745

Table 2. Cont.
Table 3. Trace element chemical composition (ppm) of Sb minerals from Greek ores.

| Locality                  | Main Phase | Kilkis (Lachanas/Rizana) | Kassandra Mines (Olympiada) | Kassandra Mines (Olympiada) | Kassandra Mines (Stratoni/M.Lakkos) |
|---------------------------|------------|--------------------------|-----------------------------|----------------------------|---------------------------------------|
|                           |            | Stibnite (Sb$_2$S$_3$)   | Stibnite (Sb$_2$S$_3$)      | Stibunate (Pb$_5$Sb$_4$S$_{11}$) | Stibnite (Sb$_2$S$_3$)              |
| Fe                        | 100        | 100                      | 300                         | 3200                        |                                       |
| Ba                        | 89         | 158                      | 34                          | 115                         |                                       |
| Zn                        | 33         | 20999                    | 64                          | 3                           |                                       |
| Cu                        | 19         | 242                      | 190                         | 43                          |                                       |
| Hg                        | 10.08      | 0.01                     | 0.22                        | 0.37                        |                                       |
| Tl                        | 8.8        | 15.1                     | 92.0                        | 0.6                         |                                       |
| Pb                        | 7          | >10,000                  | >10,000                     | 1                           |                                       |
| Bi                        | 6.7        | 4.2                      | 1609.7                      | 0.7                         |                                       |
| Mn                        | 3          | 3074                     | 428                         | 63                          |                                       |
| Ag                        | 1.4        | 70                       | >200                        | 26.8                        |                                       |
| *ΣREE + Y + Sc            | <2         | <6                      | <3                          | <2                          |                                       |
| Ni                        | 1.2        | 8.5                      | 0.1                         | 0.2                         |                                       |
| V                         | 1.0        | 3.0                      | 1.0                         | 1.0                         |                                       |
| As                        | 1          | 157                      | 105                         | 0                           |                                       |
| Cd                        | 0.7        | 8.2                      | 21.9                        | 0.9                         |                                       |
| Se                        | 0.30       | 0.70                     | 0.80                        | 10.00                       |                                       |
| Sn                        | 0.2        | 83.7                     | 69.7                        | 15.7                        |                                       |
| U + Th                    | <0.2       | <1                      | <0.7                        | <0.2                        |                                       |
| W                         | 0.10       | 0.10                     | 0.10                        | 0.10                        |                                       |
| Ta                        | 0.10       | 0.10                     | 0.10                        | 0.10                        |                                       |
| Ga                        | 0.07       | 1.28                     | 0.27                        | 0.20                        |                                       |
| Mo                        | 0.05       | 0.29                     | 0.12                        | 0.05                        |                                       |
| Te                        | 0.05       | 0.17                     | 2.74                        | 0.05                        |                                       |
| Nb                        | 0.04       | 0.04                     | 0.04                        | 0.04                        |                                       |
| In                        | <0.01      | 0.02                     | 0.16                        | <0.01                       |                                       |

*ΣREE = Sum of Rare Earth Elements.
4. Discussion

The Olympiada samples are rich in Bi, Ag, As, Sn, and Tl. Bismuth can be attributed to the potential presence of bismuthinite (Bi$_2$S$_3$), whereas Ag could also be related to minor Pb–Sb–Ag sulfosalts (e.g., diaphorite Ag$_3$Pb$_2$Sb$_2$S$_6$; [18]) and associated galena (PbS). Tin is most probably related to traces of stannite (Cu$_2$FeSnS$_4$), while Tl could be due to a variety of unidentified Sb–Tl sulfosalts, such as weissbergite (TlSb$_2$S$_2$). There is also a possibility that boulangerite and bournonite contain traces of Tl [13].

Moreover, As, except minor arsenopyrite (FeAsS), can be related to traces of tetrahedrite-tennantite series phases (Cu$_{12}$As$_4$S$_{13}$). On the other hand, it is known that Sn, Bi, and Se can also be incorporated into stibnite and boulangerite [19]. According to Sejkora et al. [20], Sn-bearing stibnite, Sb$_{2.00}$Sn$_{0.01}$S$_{2.99}$, has been found in Pernek, Slovak Republic. Moreover, Mumme [15] reported Bi- and Se-bearing boulangerite, exhibiting the formula Pb$_{5.05}$(Sb$_{3.75}$Bi$_{0.28}$)$_\Sigma$ = 4.03(S$_{10.72}$Se$_{0.28}$)$_\Sigma$ = 11, while Zhang et al. [21] and Sheng et al. [22] mentioned As-, Bi-boulangerite (Pb$_{5.18}$(Sb, Bi, As)$_{3.88}$S$_{12.30}$), and As- and Cd-bearing boulangerite.

Bournonite may also contain As and Cd [23]. The heterogeneity of the macroscopically “pure” Olympiada samples is illustrated in the EPMA elemental maps on the micrometer scale (Figure 5). On the other hand, the Kilkis Sb ore is the only one enriched in Hg, and that could be a subject of future interesting research using complementary microscopic and analytical/spectroscopic techniques. According to Martinez-Friaz [24] and Li et al. [25], boulangerite may contain traces of Hg. However, it should be noted that the literature concerning Hg-bearing stibnite, as far as we know, is rather limited, and this leads to the presumption that perhaps Hg (due to the absence of boulangerite in the Kilkis ore) is contained in separate unidentified phases, including cinnabar (HgS), and not in stibnite itself.

Remarkably, all samples are very low in lanthanides (REE + Y + Sc) and actinides (U + Th). Finally, it should be mentioned again that, in contrast to Kilkis and Chalkidiki ores, the Chios Isl. materials are rather oxidized/alterred, and that is why they were not subjected to detailed geochemical investigation. This fact is also clear in the corresponding EPMA elemental maps (Figure 5).

Ongoing and future research on this subject, including detailed investigation of the mineralogical and geochemical characteristics of the minerals present with Sb phases, is needed in order to definitely identify the sources of particular trace elements with elevated concentrations in Sb ores.

5. Conclusions

The results of the present study can be summarized as follows:

- Greek Sb-ores are identified as stibnite, boulangerite, bournonite, bertherite, and valentinite. Bournonite is associated with seligmannite, and bertherite and valentinite occur together with primary stibnite.
- Significant amounts of trace elements can be found in Sb minerals Bi, Ag, Tl, Cd, and Sn in boulangerite from Olympiada mine; Ag and Se in stibnite from Olympiada mine; As, Sn, Ag, and Tl in stibnite from Olympiada mine; and Hg in stibinite from Lachanas/Rizana mine.
- The presence of trace elements in elevated concentrations in Greek Sb minerals is mainly attributed to the co-presence of mineral phases rich in these elements.
Figure 5. Cont.
Figure 5. EPMA elemental maps for the Olympiada Sb minerals (unit of scale bar: um = μm).
**Author Contributions:** Conceptualization, E.T. and A.G.; methodology, E.T., G.G., A.X., and A.Z.; software, E.T. and M.B.; validation, G.G., A.X., A.Z., D.D. and Y.P.; investigation, E.T., P.N.G., G.G., and M.B.; resources, E.T. and G.G.; data curation, E.T., P.N.G., and A.G.; writing—original draft preparation, E.T., P.N.G., and A.G.; writing—review and editing, E.T., P.N.G., G.G., M.B., and A.Z.; supervision, A.G.; project administration, D.D.; funding acquisition, E.T. All authors have read and agreed to the published version of the manuscript.

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**Appendix A**

**Table A1.** Quality control report of the bulk analyses.

| Analyte | Unit | MDL | STD | STD | STD | STD | BLK | BLK |
|---------|------|-----|-----|-----|-----|-----|-----|-----|
| Mo | ppm | 0.05 | 2.23 | 2.49 | 2.4 | 2.55 | <0.05 |
| Ca | ppm | 0.1 | 779.3 | 36.2 | 780 | 33.0 | 0.1 |
| Pb | ppm | 0.02 | 17.49 | 23.72 | 18.2 | 25.2 | 0.99 |
| Zn | ppm | 0.05 | 41.1 | 41.3 | 41.7 | 44.4 | <0.2 |
| Ag | PBP | 20 | 20.7 | 20.7 | 311 | 70 | <20 |
| Ni | ppm | 0.1 | 406.0 | 49.0 | 454 | 45.8 | 0.1 |
| Co | ppm | 0.2 | 57.2 | 8.0 | 57 | 8.2 | <2 |
| Mn | ppm | 1 | 602 | 504 | 570 | 470 | <1 |
| Fe | % | 0.01 | 23.30 | 6.61 | 24.12 | 6.6 | <0.01 |
| Au | ppm | 0.1 | 17.4 | 10.6 | 16.3 | 9.94 | 0.0 |
| U | ppm | 0.1 | 2.4 | 2.8 | 2.41 | 2.94 | <0.1 |
| Th | ppm | 0.1 | 13.2 | 15.8 | 12.9 | 15.8 | <0.1 |
| Sr | ppm | 1 | 16 | 48 | 15.9 | 48.5 | <1 |
| Cd | ppm | 0.02 | 0.02 | 0.02 | 0.06 | 0.06 | <0.02 |
| Sb | ppm | 0.02 | 1.06 | 0.62 | 1 | 0.67 | 20.91 |
| Bi | ppm | 0.06 | 0.32 | 0.32 | 0.28 | 0.25 | <0.04 |
| V | ppm | 1 | 340 | 156 | 322 | 157 | <1 |
| Ca | % | 0.1 | 0.17 | 0.17 | 0.165 | 0.39 | <0.01 |
| P | % | 0.01 | 0.033 | 0.040 | 0.034 | 0.048 | <0.001 |
| La | ppm | 0.1 | 11.4 | 23.8 | 11 | 23.8 | <1 |
| Cr | ppm | 1 | 932 | 122 | 939 | 113 | <1 |
| Mg | % | 0.01 | 0.16 | 0.54 | 0.156 | 0.527 | <0.005 |
| Ba | ppm | 1 | 299 | 153 | 292 | 147 | <1 |
| Li | % | 0.001 | 0.017 | 0.091 | 0.059 | 0.077 | <0.001 |
| Al | % | 0.01 | 0.087 | 0.032 | 0.079 | 0.087 | <0.001 |
| Na | % | 0.001 | 0.036 | 0.123 | 0.059 | 0.134 | 0.005 |
| K | % | 0.01 | 0.24 | 0.48 | 0.624 | 0.482 | <0.01 |
| Fe | ppm | 0.1 | 1.1 | 2.0 | 1.07 | 2 | <1 |
| Zr | ppm | 0.2 | 98.1 | 152.0 | 97 | 155 | <2 |
| Sn | ppm | 0.1 | 1.5 | 3.7 | 1.32 | 4.06 | <0.1 |
| Re | ppm | 0.1 | 0.1 | 1 | 0.69 | 0.1 | <0.1 |
| Sc | ppm | 0.1 | 88.8 | 12.5 | 95 | 13.7 | <1 |
| Cu | ppm | 0.06 | 0.04 | 0.04 | 0.046 | 0.047 | <0.01 |
| V | ppm | 0.1 | 7.9 | 11.0 | 8.26 | 10.5 | <1 |
| Ce | ppm | 0.02 | 24.34 | 50.08 | 23.5 | 48.9 | <0.02 |
| Pr | ppm | 0.1 | 2.6 | 5.6 | 2.47 | 5.11 | <1 |
| Nd | ppm | 0.1 | 8.2 | 19.2 | 9.57 | 18.2 | <1 |
| Sm | ppm | 0.1 | 2.3 | 3.3 | 2.28 | 3.35 | <1 |
| Eu | ppm | 0.1 | 0.4 | 0.7 | 0.52 | 0.69 | <1 |
| Gd | ppm | 0.1 | 1.9 | 2.3 | 1.99 | 2.68 | <1 |
| Tb | ppm | 0.1 | 0.2 | 0.3 | 0.33 | 0.34 | <1 |
| Dy | ppm | 0.1 | 1.7 | 2.1 | 2.07 | 2.23 | <1 |
| Ho | ppm | 0.1 | 0.4 | 0.4 | 0.39 | 0.43 | <1 |
| Er | ppm | 0.1 | 1.1 | 1.1 | 1.2 | 1.23 | <1 |
| Tm | ppm | 0.1 | 0.2 | 0.2 | 0.17 | 0.19 | <1 |
| Yb | ppm | 0.1 | 1.1 | 1.2 | 1.19 | 1.3 | <1 |
| Lu | ppm | 0.1 | 0.2 | 0.2 | 0.175 | 0.2 | <1 |
| Hf | ppm | 0.02 | 3.06 | 4.25 | 3.11 | 4.28 | <0.02 |
| Nb | ppm | 0.1 | 6.9 | 36.0 | 6.38 | 36.7 | <1 |
| Ta | ppm | 0.1 | 21.1 | 62.8 | 21.2 | 6.1 | <1 |
| Nb | ppm | 0.1 | 0.3 | 0.4 | 0.54 | 1.5 | <1 |
| Cs | ppm | 0.1 | 1.3 | 3.3 | 1.26 | 3 | <1 |
| Ca | ppm | 0.02 | 16.10 | 24.02 | 15.7 | 25.9 | <0.02 |
| In | ppm | 0.01 | 0.11 | 0.09 | 0.099 | 0.099 | <0.01 |
| Bi | ppm | 0.002 | 0.002 | 0.002 | 0.002 | 0.002 | <0.01 |
| Sr | ppm | 0.3 | 2.6 | 2.7 | 2.97 | 2.5 | <1 |
| Ta | ppm | 0.05 | 0.15 | 0.07 | 0.13 | 0.15 | <0.01 |
| TI | ppm | 0.05 | 0.17 | 0.35 | 0.15 | 0.35 | <0.01 |
| Ag | ppb | 0.01 | <0.01 | 0.01 | 0.01 | 0.01 | <0.01 |

**Figure A1.** Quality control report of the bulk analyses.
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