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Article

Investigation of trace and critical elements (including actinides) in flotation sulphide concentrates of Kassandra mines (Chalkidiki, Greece)

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Abstract: Pyrite/As-pyrite/arsenopyrite (Py-(As)Py-AsPy), galena (PbS) and sphalerite (ZnS) concentrates from the flotation plants of Olympiada and Stratoni (Kassandra mines, Chalkidiki, N. Greece) have been investigated for their trace and critical element content, including actinides associated to natural radioactivity. It has been revealed that except Pb, Zn, Ag, and Au, being exploited by Hellas Gold S.A., there are also significant concentrations of Sb and Ga (Sb: >0.2 wt.% in PbS concentrate; Ga: 25 ppm in ZnS concentrate), but no considerable contents of Bi, Co, V, and REE. Concerning other elements, As is found in elevated concentrations (> 1 wt.% in Py-(As)Py-AsPy Olympiada concentrate and almost 1 wt.% in Stratoni PbS and ZnS concentrates) together with Cd (specifically in ZnS concentrate). However, it has been postulated, for first time in the literature, that actinides occur in very low concentrations (U<2 ppm and Th<0.5 ppm in all examined concentrates), eliminating the possibility of natural radioactivity in the Hellas Gold S.A. products. The concentrations of the natural radionuclides (^{238}U, ^{232}Th and ^{40}K) are much lower compared to commercial granitic rocks. Thus, the associated radioactive dose is insignificant and it can be assumed that no risk concerning natural radionuclides contamination of surface and underground waters is present.

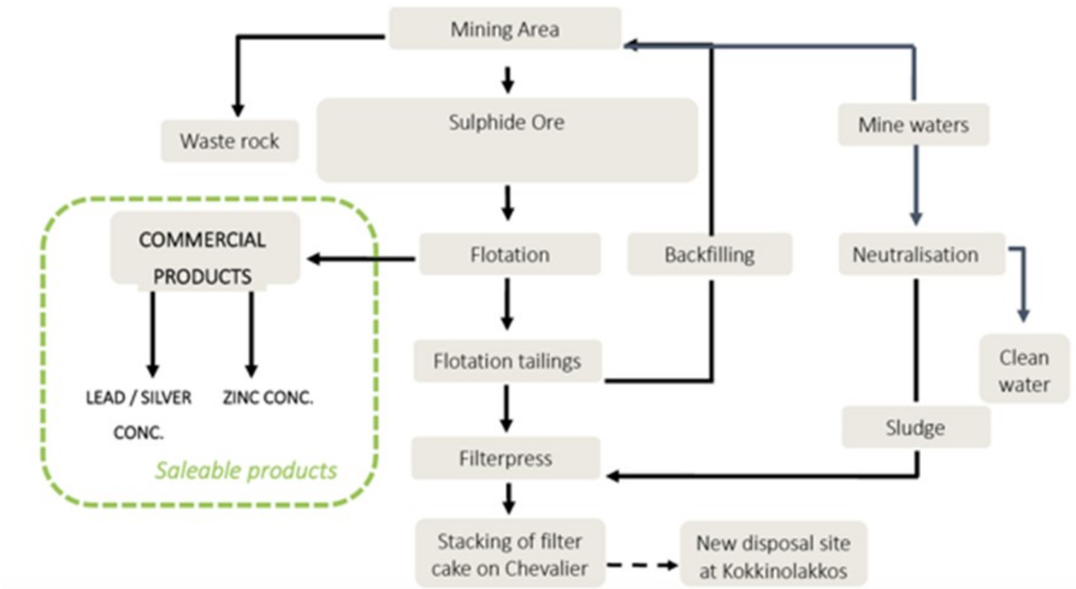
Keywords: Kassandra mines; Chalkidiki; sulphide ores; flotation concentrates; critical elements; actinides

1. Introduction

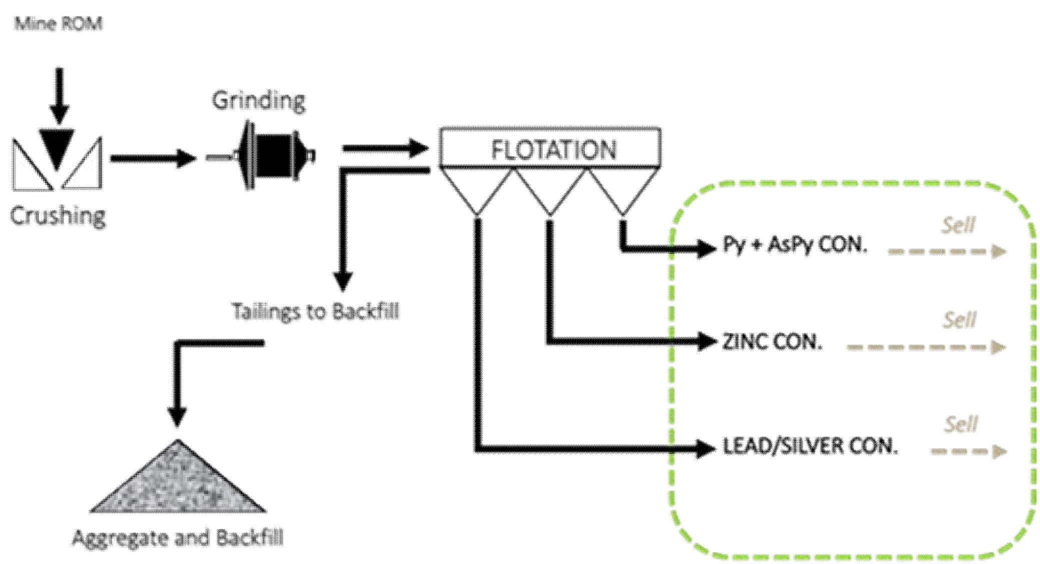
1.1 Kassandra mines flotation concentrates

The Kassandra mines are located in the Chalkidiki peninsula, Northern Greece. Presently production is being held in Olympiada mine and Stratoni mines comprising of two deposits; MademLakkos and MavresPetres. There is a long history of mining in the Kassandra area. It has been estimated, from the volume of ancient slags, that about 1 million tons of ore were extracted during the classical Greek period and that the Stratoni mine continued in production through the

Roman, Byzantine and Turkish periods. Currently, the Kassandra mines are operated by Hellenic Gold S.A. [1] and produce PbS (galena), ZnS (sphalerite) and Fe-As-S (pyrite/As-pyrite/arsenopyrite) concentrates in two flotation plants, constructed during 70s, at Stratoni and Olympiada areas (Figure 1). Recently (2018), Olympiada mine has started again the production of concentrates containing Pb, Zn, Ag and Au.



(**a**)



(**b**)

Figure 1. The current flotation plant scheme in Stratoni(**a**) and Olympiada (**b**).

1.2 Kassandra deposits and previous work on mineralogy and geochemistry of the concentrates

The Kassandra mining district (Figure 2) contains porphyry Au-Cu and Au-Ag-Pb-Zn-Cu carbonate replacement deposits that are associated with Oligocene-Miocene intrusions emplaced into poly-deformed metamorphic basement rocks belonging to the Permo-Carboniferous to Late Jurassic Kerdilion unit and the Ordovician–Silurian Vertiskos unit. Regional extensional tectonics active since the middle Eocene resulted in the development of widespread normal and transtensional faults, including the Stratoni fault zone that hosts carbonate replacement sulfide ore bodies [2]. More particularly, Stratoni (MademLakkos, MavresPetres) and Olympiada are the two main carbonate-replacement massive sulphidePb-Zn (Ag-Au) deposits of the district; they are located on the footwall of the Tertiary Stratoni-Varvara fault. Both deposits are interpreted to form the proximal and distal part of a fault-controlled exoskarn-type ore system triggered by nearby small-scale intrusions close to the fault system [3] Sulphide mineralization occurs within amphibolite grade metamorphic rocks of the Kerdylia assemblage. The assemblage represents ametamorphosed marine sedimentary-volcanic sequence of probable Mesozoic or older age. Eocene and Oligocene age granitic intrusions occur throughout the Kerdylia sequence, mainly as pegmatite and granite dykes of several generations that range from syn- to post-metamorphic in age. The sequence is affected by syn-peak metamorphic penetrative deformation that is manifested by adominant, shallow dipping layer-parallel foliation. At least two other foliation-forming events affect the sequence with progressively less strain, as well as significant late extensional faulting.

Previous workers [4-8] have interpreted the area to lie at the southwestern margin of the Rhodope complex, and that the shallow dipping foliations which are present formed in response to Tertiary unroofing of the Rhodope Complex as a metamorphic core complex. In such an interpretation, the Stratoni Fault has been interpreted as the principal detachment fault forming the southern major bounding structure between the Rhodope complex, represented locally by the Kerdylia sequence, and the Vertiskos Formation to the south.

Other interpretations suggest that the fabrics are contractional and that the fault may remobilize a major reverse structure that superimposed the Vertiskos sequence against the Kerdylia. Geological relationships suggest that the metamorphic fabrics represent contractional rather than extensional fabrics, and the Stratoni Fault as is currently manifested is dominantly a later, lower greenschist grade extensional structure that is superimposed onto the amphibolite grade fabrics.

Mineralization at Olympiada and Stratoni (M. Lakkos-MavresPetres) is of carbonate replacement. It occurs in association with a marble horizon. Mineralization is structurally late in timing and is superimposed on the metamorphic fabrics in the area and in association with an extensional, brittle to semi-brittle fault network that was likely active coevally with the ore-hosting Stratoni Fault to the south.

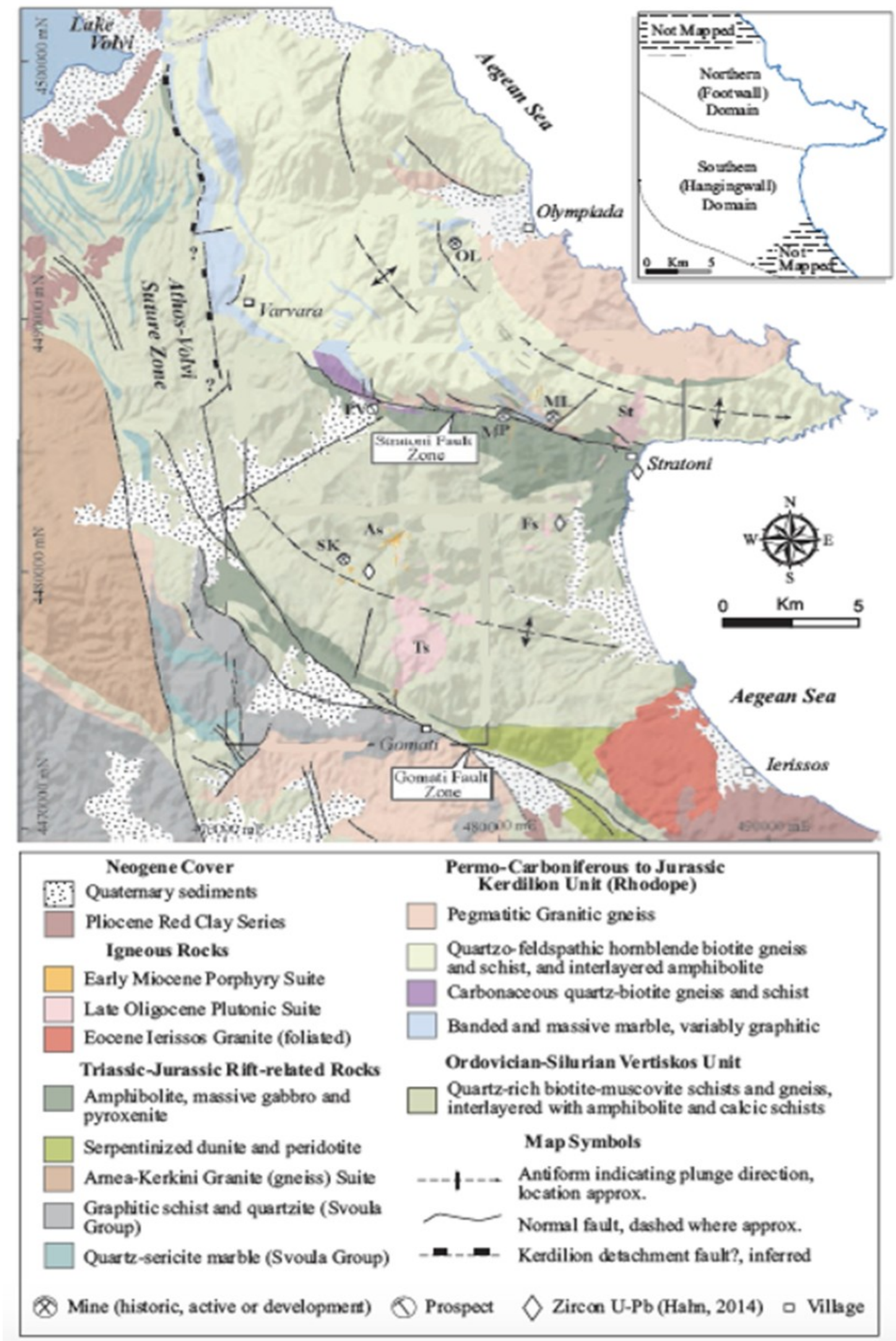


Figure 2. Geological map of the area of NE Calkidiki [2 and references therein] .

Previous works on mineralogy and geochemistry of ores, derived from both Stratoni (MademLakkos-Mavres Peters) and Olympias mines, have been presented in the literature (e.g [2, 3, 9-15]). However, there is very limited literature about the flotation concentrates (e.g. [-20]) and particularly with respect to their mineral chemistry issues and moreover trace and critical element content.

1.3 Scope of the present study

As mentioned above, there are few published works about the concentrates, produced by Kassandra mines since 70s. Additionally, on the best of our knowledge, there are no published data about trace and critical elements in these hydrometallurgy (flotation) products. Thus, the scope of the present study, was to demonstrate new results concerning: i) the mineral chemistry and the formulae of the sulfide minerals into the concentrates, ii) the trace and critical element content, specifically REE, Sb, Bi, Ge, V, Ga, Co (e.g. BGS), iii) the actinide element content (U, Th) as well as their natural radioactivity. Radioisotopes present in the environment can be classified as naturally occurring and are components of the earth's crust since its formation (e.g. ^{238}U, ^{235}U, ^{232}Th and their decay products as well as ^{40}K), cosmogenic radioisotopes (radioisotopes that are produced by the interaction between cosmic radiation and the atmosphere (e.g. ^{14}C, ^{10}Be, ^{44}Ti and ^{22}Na) and finally artificially produced radionuclides that are produced in nuclear reactors (e.g. ^{90}Sr and ^{137}Cs). Natural radionuclides can be found in soil, rocks, water, air, food, building materials, etc. The study of natural radioactivity present in geological materials and ores is an important subject in environmental radiological protection as it provides the possibility to assess any associated health hazard. In this paper, the products of the Kassandra mines are studied for their natural radioactivity. This involves not only the products themselves, but the associated risk from mine tailings (surface water) and dissolution from underground water. Moreover, the results are explained by bulk geochemistry of the samples.

2. Materials and Methods

2.1 Samples

Representative composite pyrite/As-pyrite/arsenopyrite (Py-(As)Py-AsPy), galena (PbS) and sphalerite (ZnS) concentrates -in powdered form-, from the flotation plants of Olympiada and Stratoni (Kassandra mines, Chalkidiki, N. Greece), were supplied by Hellas Gold S.A.

2.2 Point analyses

Scanning electron microscopy (SEM) images of free mineral grains and microprobe analyses (EPMA) on polished mineral grains (after examination in optical microscope -see Figure 3-) were obtained using a J EOL 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.

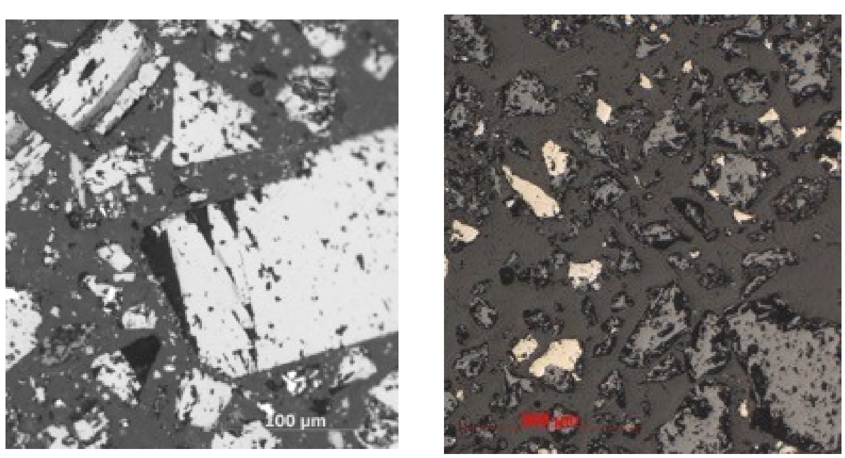


Figure 3. Optical images (reflected light) of polished minerals grains in Stratoni PbS and ZnS concentrates.

2.3 Bulk analyses

Major and trace elements, in the powdered concentrates, were analyzed using a Perkin Elmer ICP-OES and a Perkin Elmer Sciex Elan 9000 ICP-MS following a $LiBO_2/LiB_4O_7$ fusion and HNO_3 digestion of the fused solid sample.

2.4 Gamma-ray spectroscopy

The samples after oven-dried at 60°C to constant weight, were measured using two high-resolution gamma ray spectrometry systems. The first one consisted of an HPGe coaxial detector with 42% efficiency and 2.0 keVresolution at 1.33 MeV photons, shielded by 4″ Pb, 1mm Cd and 1mm Cu and the second one consisted of a LEGe planar detector with 0.7 keV resolution at 122 keV photons, shielded by 3.3″ Fe-Pb, 1mm Cd and 1mm Cu. The first spectrometry system with the High Purity Ge detector was used to measure the majority of the natural radionuclides examined in this study, except ^{238}U. The second one with the Low Energy planar Ge detector was used so as to determine only the concentration of ^{238}U, considering the low energy γ-ray of 63 keV emitted by its daughter ^{234}Th.

The ^{40}K content was obtained using its 1461 keV γ-ray. The ^{232}Th content was calculated as the weighted mean value of ^{228}Ra concentration (measured as ^{228}Ac, using 911, 968 and 338 keV γ-rays) and ^{228}Th concentration (measured as decay products in equilibrium, i.e. ^{212}Pb, using 238 and 300 keV γ-rays, ^{212}Bi, using 727 keV γ-ray and ^{208}Tl, using 2614, 583 and 860 keV γ-rays). The determination of ^{226}Ra content was based on measurement of ^{222}Rn decay products being in equilibrium. The measurement of ^{226}Ra from its own γ-ray at 186.25 keV introduces some problems because of the adjacent photo peak of 235U at 185.75 keV, so that the isotopic ratio between ^{235}U and ^{238}U was considered being the natural one, i.e. 0.0072 and secular equilibrium between ^{238}U and ^{226}Ra had to be assumed. Accuracy in the measurements of ^{226}Ra concentrations by ^{222}Rn decay products depended on the integral trapping of radon gas in the sample volume, so a small addition (~2%) of charcoal in powder form (less than 400 μm in size) was mixed with the sample before sealing it hermetically and storing it in a freezer during ^{222}Rn in-growth period [21] . The efficiency calibration of the gamma spectrometry systems was performed with the radionuclide specific efficiency method in order to avoid any uncertainty in gamma ray intensities as well as the influence of coincidence summation and self-absorption effects of the emitting gamma photons. A set of high quality certified reference materials (RGU-1, RGTh-1, RGK-1) [22] was used, with densities similar to the average beach sands measured after pulverization. Cylindrical geometry was used assuming that the radioactivity is homogenously distributed in the measuring samples. The samples were measured up to 200.000 s in order to achieve a Minimum Detectable Activity of 12 Bq kg^{-1} for ^{40}K, 4 Bq kg^{-1} for ^{232}Th, 2 Bq kg^{-1} for ^{228}Th, 2 Bq kg^{-1} for ^{226}Ra and 21 Bq kg^{-1} for ^{238}U, with 33% uncertainty. The total uncertainty of the radioactivity levels was calculated by propagation of the systematic and random errors of measurements. The systematic errors in the efficiency calibration ranges from 0.3–2% and the random errors of the radioactivity measurements extend up to 19 %, except in the ^{238}U measurement, where the error extends up to 50% for activities measured lower 10 Bq kg^{-1}.

3. Results and Discussion

3.1 Mineral chemistry

The SEM and EPMA data, concerning the mineral chemistry of the sulfide minerals (major phases) into the concentrates from the flotation plants of Stratoni and Olympiada mines, are given in Figures 4-6 and Tables 1-3.

The chemical formulae of the major sulfide minerals were calculated as following:

- Galena (Stratoni): $Pb_{0.98\text{-}0.99}S$
- Sphalerite (Stratoni): $Zn_{0.79\text{-}0.85}Fe_{0.12\text{-}0.17}Mn_{0.00\text{-}0.01}S$
- Pyrite (Olympiada): $Fe_{1.02\text{-}1.05}As_{0.00\text{-}0.03}S_2$
- Arsenopyrite (Olympiada): $FeAs_{0.85\text{-}0.88}S_{1.07\text{-}1.13}$

In addition, the frequent presence of boulangerite was confirmed in the Olympiada concentrate. The EPMA revealed the following chemical formula:

- Boulangerite (Olympiada): $Pb_{5.18-5.25}Sb_{4.21-4.45}As_{0.06-0.15}Fe_{0.04-0.15}Zn_{0.00-0.06}Mn_{0.01-0.02}S_{11}$

All sulfide minerals studied were found to exhibit typical/expected chemical compositions in major elements. Ongoing research on these samples is also targeting the characterization of noble metals [19, 23] .

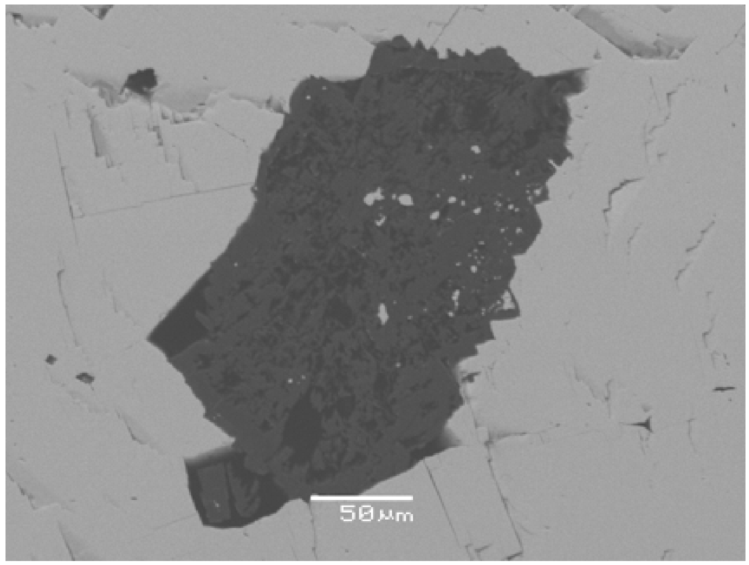


Figure 4. BSE image of polished galena, with carbonate mineral inclusions, in Stratoni PbS concentrate.

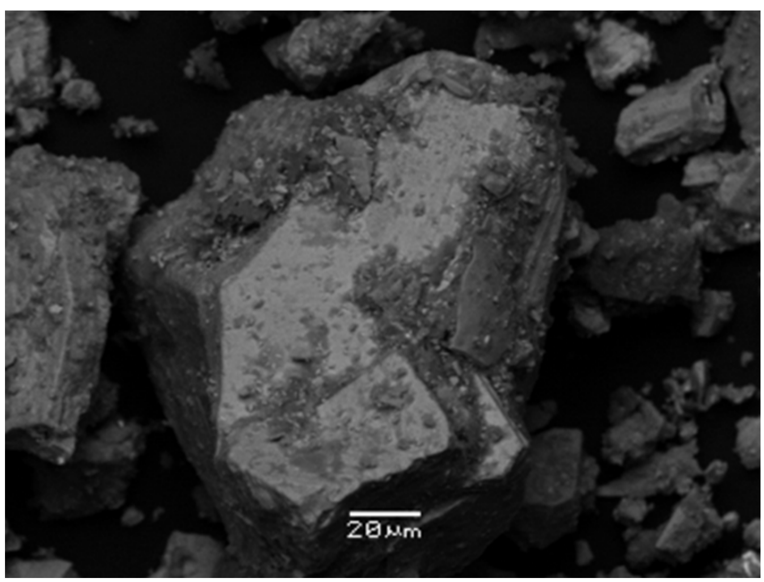


Figure 5.BSE image of free pyrite grain (darker), including arsenopyrite (brighter), in Olympiada Py-(As)Py-AsPy concentrate.

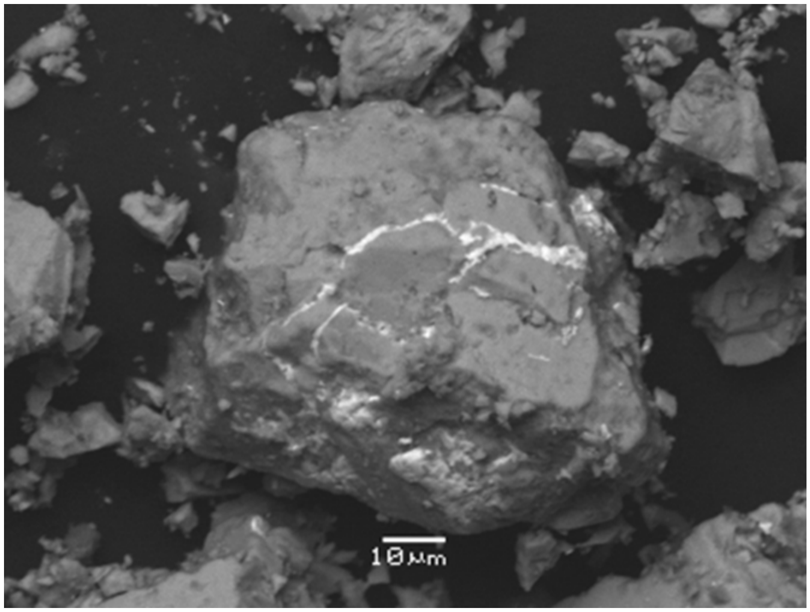


Figure 6.BSE image of free sphalerite grain, with galena veins, in Stratoni ZnS concentrate.

Table 1. EPMA analyses of mineral phases present in Stratoni ZnS concentrate.

Phase	**Sphalerite**						**Galena**		**Arsenopyrite**	**Pyrite**		
Endmember	**(Zn,Fe)S**						**PbS**		**FeAsS**	**FeS_2**		
AnalysisNo.	**2**	**3**	**4**	**15**	**16**	**17**	**10**	**11**	**1**	**5**	**6**	**7**
As	0.03	0.00	0.00	0.00	0.01	0.02	0.00	0.01	42.08	1.08	1.40	1.24
Fe	8.35	7.05	10.07	8.37	8.22	7.48	0.46	0.08	36.07	47.54	47.56	47.12
Mn	0.58	0.61	0.38	0.43	0.57	0.49	0.00	0.00	0.00	0.06	0.00	0.02
Pb	0.00	0.06	0.14	0.05	0.08	0.02	85.91	84.86	0.08	0.12	0.02	0.16
S	34.37	34.33	34.59	34.52	34.42	34.53	13.33	13.38	22.37	52.76	52.58	53.12
Zn	56.84	59.13	55.58	57.04	57.71	58.24	0.79	0.28	1.33	0.07	0.53	0.28
Total	100.18	101.18	100.75	100.41	101.01	100.79	100.48	98.61	101.94	101.63	102.09	101.95
Ionsbasedon:	1 (S)						1 (S)		1 (Fe)	2 (S)		
As	---	---	---	---	---	---	---	---	0.87	0.02	0.02	0.02
Fe	0.14	0.12	0.17	0.14	0.14	0.12	0.02	---	1.00	1.03	1.04	1.02
Mn	0.01	0.01	0.01	0.01	0.01	0.01	---	---	---	---	---	---
Pb	---	---	---	---	---	---	1.00	0.98	---	---	---	---
S	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.08	2.00	2.00	2.00
Zn	0.81	0.84	0.79	0.81	0.82	0.83	0.03	0.01	0.03	---	0.01	0.01

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189 **Table 2.** EPMA analyses of mineral phases present in Stratoni PbS concentrate

Phase	Galena						Arsenopyrite				Pyrite			
Endmember	PbS						FeAsS				FeS_2			
AnalysisNo.	1	4	5	6	13	14	2	7	8	9	3	10	11	12
As	0.04	0.01	0.03	0.03	0.03	0.02	41.53	42.43	41.60	43.41	1.03	0.11	2.03	1.92
Fe	0.00	0.00	0.00	0.00	0.00	0.00	36.52	36.22	36.55	36.04	47.12	47.71	47.19	47.03
Mn	0.02	0.02	0.00	0.04	0.03	0.01	0.01	0.02	0.04	0.00	0.03	0.04	0.00	0.05
Pb	86.33	85.87	85.66	85.76	85.92	86.12	0.17	0.10	0.16	0.00	0.16	0.14	0.15	0.21
S	13.61	13.42	13.56	13.54	13.52	13.67	23.72	22.46	23.02	22.05	53.15	53.69	52.04	52.67
Zn	0.00	0.02	0.12	0.00	0.08	0.00	0.18	0.06	0.08	0.00	0.02	0.08	0.00	0.05
Total	100.01	99.33	99.37	99.37	99.58	99.82	102.13	101.29	101.45	101.50	101.50	101.76	101.41	101.93
Ionsbasedon:	1 (S)						1 (Fe)				2 (S)			
As	---	---	---	---	---	---	0.85	0.87	0.85	0.90	0.02	---	0.03	0.03
Fe	---	---	---	---	---	---	1.00	1.00	1.00	1.00	1.02	1.02	1.04	1.03
Mn	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Pb	0.98	0.99	0.98	0.98	0.98	0.98	---	---	---	---	---	---	---	---
S	1.00	1.00	1.00	1.00	1.00	1.00	1.13	1.08	1.10	1.07	2.00	2.00	2.00	2.00
Zn	---	---	---	---	---	---	---	---	---	---	---	---	---	---

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Table 3. EPMA analyses of mineral phases present in Olympiada Py-(As)Py-AsPy concentrate

Phase	**Sphalerite**	**Boulangerite**			**Arsenopyrite**						**Pyrite**					
Endmember	**(Zn,Fe)S**	**$Pb_5Sb_4S_{11}$**			**FeAsS**						**FeS_2**					
AnalysisNo.	**1**	**13**	**14**	**15**	**2**	**3**	**16**	**17**	**18**	**20**	**5**	**6**	**7**	**19**	**21**	**22**
As	0.00	0.22	0.58	0.35	41.02	41.35	41.07	41.22	41.43	41.18	2.03	0.02	1.43	0.89	1.68	1.24
Fe	11.28	0.11	0.43	0.15	36.41	36.77	36.52	36.55	36.85	36.57	47.42	47.82	47.25	47.55	47.74	47.33
Mn	0.61	0.03	0.06	0.06	0.03	0.02	0.03	0.03	0.22	0.23	0.00	0.00	0.00	0.00	0.00	0.00
Pb	0.10	54.76	54.38	56.25	0.04	0.07	0.05	0.06	0.05	0.04	0.17	0.14	0.12	0.15	0.13	0.16
S	34.55	17.99	17.66	18.23	23.47	22.73	22.84	23.15	22.36	22.94	52.03	53.90	52.45	53.11	52.17	52.41
Zn	53.64	0.21	0.05	0.00	0.10	0.16	0.13	0.15	0.17	0.15	0.00	0.04	0.00	0.03	0.00	0.02
Sb	n/a[1]	27.08	27.12	26.51	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Total	100.17	100.40	100.27	101.55	101.07	101.10	100.64	101.16	101.08	101.10	101.65	101.92	101.25	101.74	101.72	101.16
Ionsbasedon:	1 (S)		11 (S)				1 (Fe)						2 (S)			
As	---	0.06	0.15	0.09	0.84	0.84	0.84	0.84	0.84	0.84	0.03	---	0.02	0.01	0.03	0.02
Fe	0.19	0.04	0.15	0.05	1.00	1.00	1.00	1.00	1.00	1.00	1.05	1.02	1.03	1.03	1.05	1.04
Mn	0.01	0.01	0.02	0.02	---	---	---	0.00	0.01	0.01	---	---	---	---	---	---
Pb	---	5.18	5.24	5.25	---	---	---	---	---	---	---	---	---	---	---	---
S	1.00	11.00	11.00	11.00	1.12	1.08	1.09	1.10	1.06	1.09	2.00	2.00	2.00	2.00	2.00	2.00
Zn	0.76	0.06	0.01	---	---	---	---	---	---	---	---	---	---	---	---	---
Sb	n/a	4.36	4.45	4.21	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

[1]n/a=not analyzed.

3.2 Geochemistry

The bulk chemical compositions (ICP-OES & MS) of the studied Kassandra mines concentrates are given in Table 4. It is obvious that basic and noble metals (Pb, Zn, Ag, and Au) being exploited by Hellas Gold S.A., show high concentrations, as well as Sb and Ga (Sb: >0.2 wt.% in PbS concentrate; Ga: 25 ppm in ZnS concentrate). On the other hand, there are no considerable contents of Bi, Co, V, and REE. Considering other elements, As is found in elevated concentrations (>1 wt.% in Py-(As)Py-AsPyOlympiada concentrate and almost 1 wt.% in StratoniPbS and ZnS concentrates) along with Cd (specifically in ZnS concentrate). Moreover, actinides occur in very low concentrations (U <2 ppm and Th<0.5 ppm in all concentrates).

The enrichment and depletion of the elements studied can be revealed form the normalization to the Upper Crust (UCC) (Figure 7), the Primitive Mantle (Figure 8) and the Chondrite (Figure 9). REE's and other elements like Cs, Rb, Co, Ni, Ba and V are depleted. As expected, major elements like Pb, Zn and Cu are enriched, as well as other trace elements like Mo, As, Sb, Se, Sn, Cd, Hg, Rb and U. It should be noted that the enrichment in these trace elements, relative to UCC, Primitive Mantle and Chondrite, is strictly geochemical and it is not associated to practical mining and metallurgical issues. For instance, if we consider U, the bulk natural radioactivity of the samples is negligible, as discussed below.

Table 4. Trace and critical elements concentration of the studied Kassandra mines concentrates.

Element	MDL (ppm)	Py-(As)Py-AsPy Conc. OLYMPIADA	PbS Conc. STRATONI	ZnS Conc. STRATONI
Pb	0.1	5235.9	>10000.0	>10000.0
Zn	1	>10000	>10000	>10000
Ag	0.1	22.5	>100.0	>100.0
Au	0.0005	16.9	1.1	1.0
Cu	0.1	710.8	1035.9	2191.1
As	0.5	>10000.0	>10000.0	9476.9
Sb	0.1	712.9	>2000.0	748.2
Bi	0.1	0.1	2.0	0.2
Cd	0.1	54.5	77.7	>2000.0
Ni	0.1	9.3	6.6	3.1
Co	0.2	1.7	0.5	0.2
Hg	0.01	0.15	0.49	10.98
Tl	0.1	1.2	37.2	3.4
Se	0.5	2.7	8.3	<0.5
Be	1	<1	<1	<1
Th	0.2	0.5	<0.2	<0.2
U	0.1	1.4	2.0	1.1
Sn	1	43	131	218
Mo	0.1	2.6	29.9	5.7
Ga	0.5	4.5	1.5	25.4
V	8	12	9	<8
Nb	0.1	1.0	<0.1	<0.1
Ta	0.1	<0.1	<0.1	<0.1

W	0.5	1.8	1.0	0.7
Ba	1	15	8	2
Cs	0.1	0.4	0.2	0.3
Hf	0.1	0.2	<0.1	<0.1
Rb	0.1	6.9	2.1	3.1
Sr	0.5	7.1	1.5	1.9
Zr	0.1	3.9	2.0	1.9
Y	0.1	0.5	0.2	0.1
La	0.1	1.2	<0.1	0.4
Ce	0.1	2.0	0.8	1.1
Pr	0.02	0.20	0.09	0.10
Nd	0.3	0.8	<0.3	<0.3
Sm	0.05	0.12	<0.05	<0.05
Eu	0.02	0.03	<0.02	<0.02
Gd	0.05	0.16	<0.05	0.08
Tb	0.01	0.02	<0.01	<0.01
Dy	0.05	0.10	<0.05	<0.05
Ho	0.02	<0.02	<0.02	<0.02
Er	0.03	0.04	<0.03	<0.03
Tm	0.01	0.01	<0.01	<0.01
Yb	0.05	<0.05	<0.05	<0.05
Lu	0.01	0.01	<0.01	<0.01

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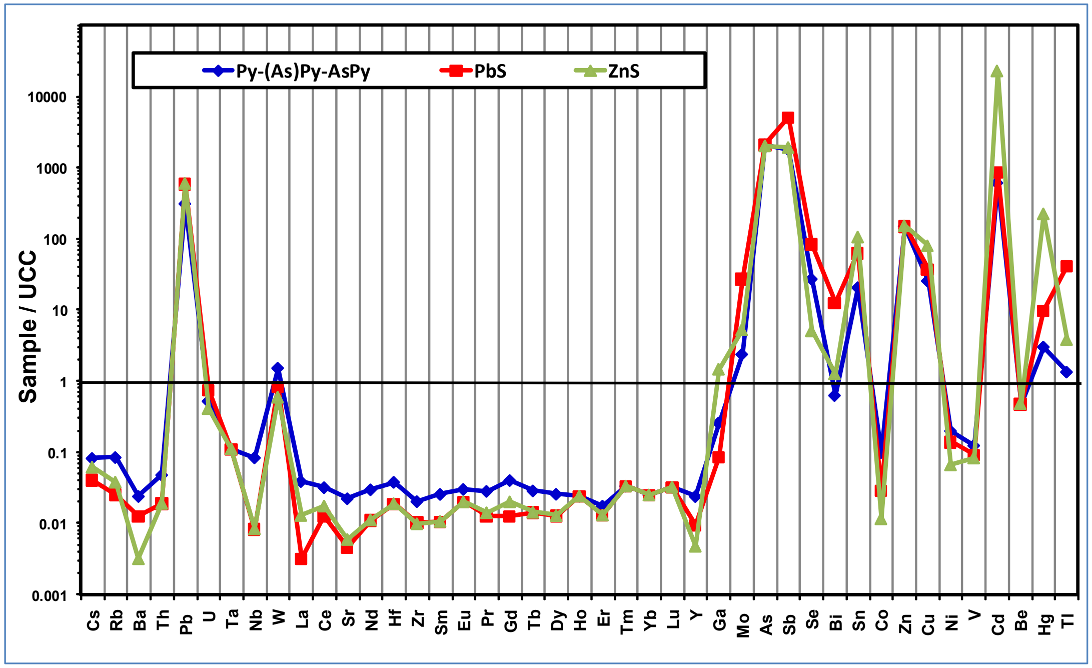
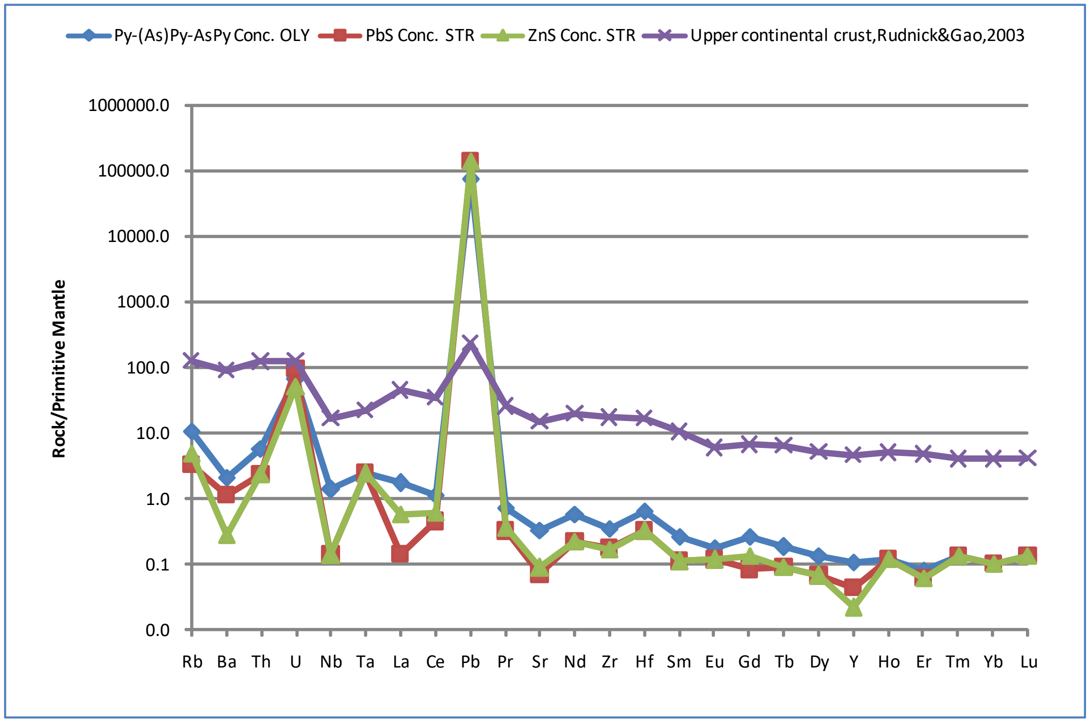
210



211 **Figure 7.**Spider diagram of Sample/Upper Continental Crust (UCC).



212
213 **Figure 8.**Spider diagram of Sample/Primitive Mantle.

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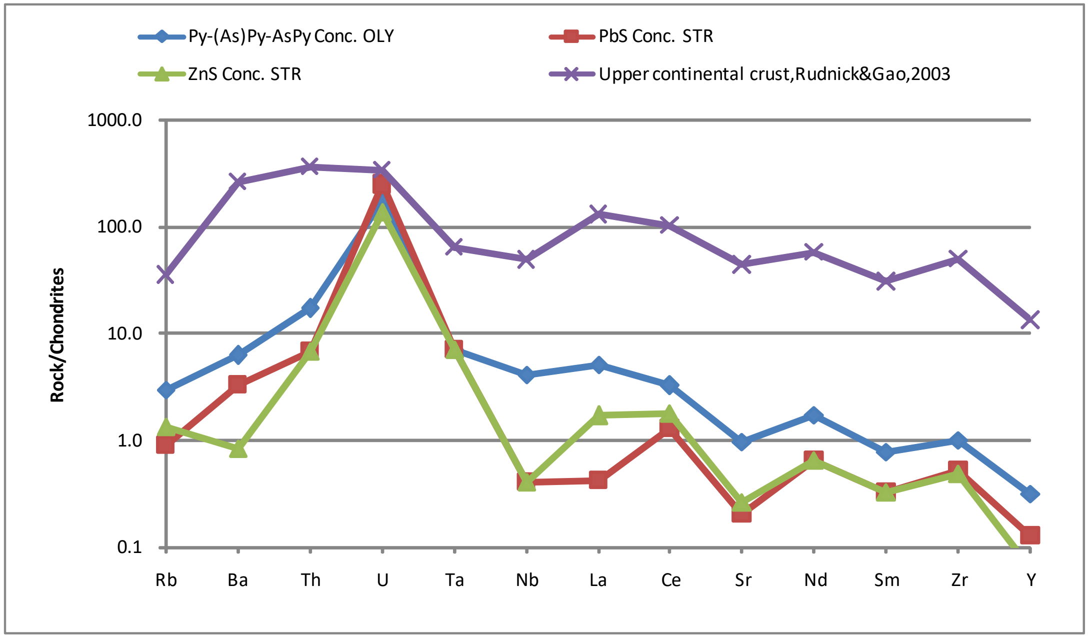
214



215 **Figure 9.**Spider diagram of Sample/Chondrite.

3.3 Actinide elements and natural radioactivity

The concentrations of the natural radionuclides, detected by gamma-ray spectroscopy, are given in Table 5.

Table 5. Activity concentrations of ^{238}U, ^{226}Ra, ^{232}Th, ^{228}Th and ^{40}K (Bq.kg^{-1}), along with the respective standard errors (±σ).

Sample	^{238}U-series				^{232}Th-series							
	^{238}U		^{226}Ra		^{232}Th		^{228}Th		^{40}K		^{226}Ra	^{232}Th
	Bq.kg^{-1}	±σ	Bq.kg^{-1}	±σ	Bq.kg^{-1}	±σ	Bq.kg^{-1}	±σ	Bq.kg^{-1}	±σ	ppm	ppm
OLY-C-(FeAsS)	B.D.L.	-	24.8	0.3	4.1	0.7	3.3	0.2	51.5	2.9	2.0	1.0
STR-(PbS)	B.D.L.	-	22.0	0.3	1.0	0.5	B.D.L.	-	10.8	2.1	1.8	0.2
STR-(ZnS)	B.D.L.	-	19.1	0.4	1.3	0.8	B.D.L.	-	18.2	2.8	1.5	0.3

The concentrations of the radionuclides of ^{238}U, ^{232}Th-series and ^{40}K are small and close to the detection limit of gamma-ray spectroscopy. These small concentrations are mainly due to the small ability of the chemical components of the sulphides to be substituted by the measured radionuclides. Moreover, low concentrations of these radionuclides have been detected in the Stratoni granitic bodies [24]. Similar conclusions on the U content of sulphides have been previously reported by [25, 26]. However, the previous researchers mention that high U concentrations may be present in the late accessory mineral phases deposited in microfissures.

These values are by far lower than a typical granitic rock used as building material [26]. Therefore, the radioactive dose to humans from these materials is insignificant.

4. Conclusions

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

- Except basic (Pb, Zn, and potentially Cu) and noble (Ag, Au) elements in Kassandra mines concentrates, being exploited and commercialized by Hellas Gold S.A., it can be argued that there are also significant concentrations of Sb and Ga (Sb: >0.2 wt.% in PbS concentrate; Ga: 25 ppm in ZnS concentrate), but no substantial contents of Bi, Co, V, and REE.
- Concerning other elements, of course it well-known that As occurs in rather high concentrations (>1 wt.% in Py-(As)Py-AsPy Olympias concentrate and almost 1 wt.% in Stratoni PbS and ZnS concentrates), as well as Cd (specifically in ZnS concentrate).
- There are negligible concentrations of actinides (U <2 ppm and Th<0.5 ppm in all concentrates), minimizing the possibility of increased natural radioactivity. The concentrations of natural radionuclides are by far lower than a typical granitic rock used as building material (Papadopoulos et al. 2013). Therefore, the radioactive dose to humans from these materials is insignificant.

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