

Geochemical background heavy metal concentrations of stream sediments at mineralized areas of NE Chalkidiki*

Efstratios Kelepertzis¹, Ariadne Argyraki¹, Emmanouil I. Daftsis² & Dimitrios Ballas²

¹Department of Economic Geology and Geochemistry, Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistimiopolis Zographou 157 85, Athens

e-mail: kelepert@geol.uoa.gr, argyraki@geol.uoa.gr,

²Hellas Gold S.A., Stratoni 630 82, Chalkidiki

e-mail: edaftsis@hellas-gold.gr, dballas@hellas-gold.gr

ABSTRACT: Heavy metal concentrations in upland stream sediments from Kerasia and the adjacent Piavitsa hydrological catchments, an area of Tertiary mineralization within metamorphic amphibolite terrain located west of Stratoni village (NE Chalkidiki), were determined to evaluate the geochemical distribution of selected elements prior to any proposed new mining activities and to identify possible factors that can explain their spatial distribution. A total of 14 stream sediment samples were collected and analysed for Cu, Pb, Zn, Mn, Ni, Cr, Co, As, Sb, Cd and Fe. Results showed that the majority of stream sediments have high concentration loads of Zn, Mn, As and Sb, whereas certain specific sampling sites showed additionally elevated concentrations of Pb and Cd. On the contrary, Cu, Co, Cr and Ni concentrations are similar to both the world average range of soil composition and the median values of soils reported for the wider area of Stratoni. The results reflect the elevated geochemical background of the wider area due to the presence of various types of mineralization in this old metallogenic province. The application of R-mode factor analysis explained 88% of the total variability by grouping the elements according to their geogenic origin.

Key-words: stream sediments, heavy metals, mineralization, NE Chalkidiki.

ΠΕΡΙΛΗΨΗ: Στην εργασία αυτή προσδιορίστηκαν οι περιεκτικότητες βαρέων μετάλλων σε ιζήματα ρεμάτων από τις υδρολογικές λεκάνες Κερασιάς και Πιάβιτσας, μια περιοχή όπου απαντά Τριτογενούς περιόδου μεταλλοφορία εντός ενός μεταμορφωμένου πεδίου αμφιβολιτών και η οποία βρίσκεται δυτικά του χωριού Στρατωνίου (ΒΑ Χαλκιδική). Σκοπός της έρευνας αυτής ήταν η εκτίμηση της γεωχημικής κατανομής επιλεγμένων στοιχείων πριν από οποιοδήποτε προταθείσες νέες μεταλλευτικές δραστηριότητες και η αναγνώριση πιθανών παραγόντων που μπορεί να εξηγήσουν τη χωρική κατανομή τους. Συλλέχθηκαν 14 δείγματα ιζήματος ρέματος και αναλύθηκαν για τα στοιχεία Cu, Pb, Zn, Mn, Ni, Cr, Co, As, Sb, Cd και Fe. Τα αποτελέσματα έδειξαν ότι η πλειονότητα των ιζημάτων ρεμάτων παρουσιάζει υψηλές συγκεντρώσεις Zn, Mn, As και Sb, ενώ ορισμένες ειδικές θέσεις δειγματοληψίας έδειξαν επιπρόσθετα υψηλές περιεκτικότητες Pb και Cd. Αντίθετα, οι περιεκτικότητες Cu, Co, Cr και Ni εμπίπτουν στο παγκόσμιο μέσο εύρος της σύστασης εδαφών και είναι όμοιες με τις διάμεσες τιμές εδαφών που αναφέρονται για την ευρύτερη περιοχή του Στρατωνίου. Τα αποτελέσματα αντανακλούν το υψηλό γεωχημικό ανάγλυφο της ευρύτερης περιοχής λόγω της παρουσίας διαφόρων τύπων μεταλλοφορίας σε αυτή τη παλιά μεταλλογενετική επαρχία. Η εφαρμογή της μεθόδου της παραγοντικής R-mode ανάλυσης εξηγεί το 88% της συνολικής διακύμανσης με την ομαδοποίηση των στοιχείων σύμφωνα με τη γεωγενή τους προέλευση.

Λέξεις κλειδιά: ιζήματα ρεμάτων, βαρέα μέταλλα, μεταλλοφορία, ΒΑ Χαλκιδική.

INTRODUCTION

Sediments constitute an integral and dynamic part of stream basins, originating from the weathering of minerals and soils upstream. Natural concentrations of heavy metals as a result of the weathering processes of mineral deposits can be quite high in stream sediments close to the deposit, but decrease with increasing distance downstream, due to dissipating energy and dilution of sediments from other unpolluting sources (PLUMLEE, 1999). The premining geochemical signature for areas around mineral deposits, known as a geochemical background in pristine areas, or a geochemical baseline in areas that have experienced anthropogenic activity, is essential to know for setting realistic reclamation goals after mining at any proposed or abandoned mines (RUNNELS *et al.*, 1998).

Kerasia and Piavitsa hydrological catchments are adjacent basins in the “metallogenic province” of N.E. Chalkidiki peninsula, west of Stratoni village (Fig. 1), which has a his-

tory of intense mining of sulphide deposits that started around 600 BC and continues today (PERANTONIS, 1994). One of the future mine development plans in the area is the Skouries project located some 35 km by road west of Stratoni village. Skouries is a typical gold-copper porphyry deposit that forms a near-vertical pipe. The porphyry outcrop is located on a high plateau about 500 m ASL with no habitation in the immediate vicinity (Fig. 1). Currently, in the wider area only the Mavres Petres deposit is mined (Fig. 1), since the Madem Lakkos ore deposit has been exhausted.

The present survey was conducted in collaboration with Hellenic Gold S.A. with the following objectives: a) to determine the mineralogical and heavy metal composition of stream sediments within the catchment basins of Kerasia and Piavitsa prior to any kind of new mining activities, b) to assess the levels of heavy metal stream sediment contamination in comparison to world average ranges in soil composition and published median values for soils reported

* Το γεωχημικό ανάγλυφο βαρέων μετάλλων σε ιζήματα ρεμάτων μεταλλοφόρων περιοχών της ΒΑ Χαλκιδικής

for the wider mined area of Stratoní and c) to identify possible factors that can explain the geochemical element variability within the study area.

ability within the study area.

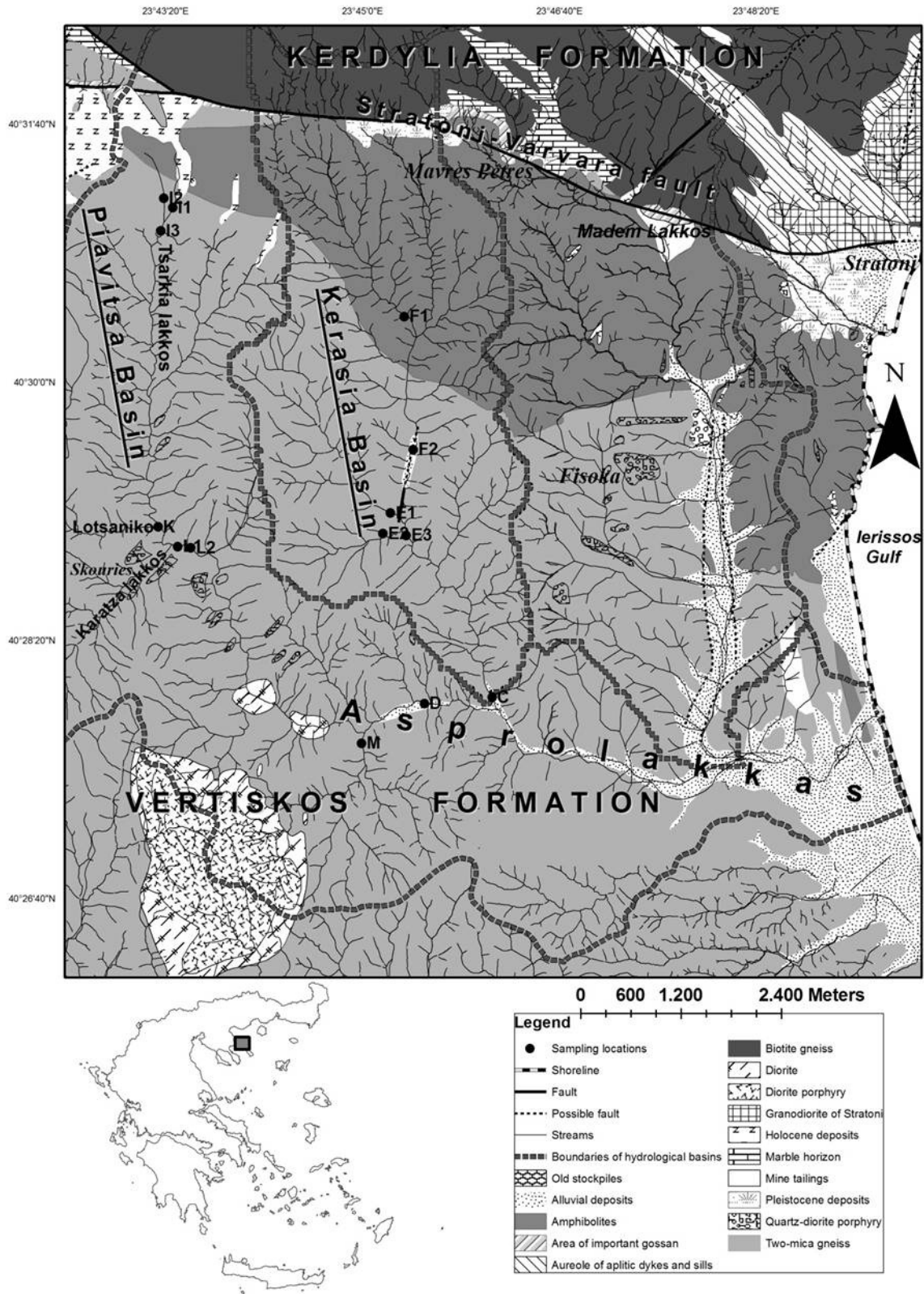


Fig. 1. Geological map of the studied area, indicating sampling locations and hydrological catchments (after KOCKEL *et al.*, 1977).

DESCRIPTION OF THE STUDIED AREA

Geological setting

The studied area is located in the eastern Chalkidiki peninsula within the Greek part of the 'Serbo-Macedonian Massif', a series of metamorphic rocks that extend northward into Bulgaria and eastern Yugoslavia. The crystalline basement of the Serbo-Macedonian massif comprises two lithostratigraphic-tectonic units (KOCKEL *et al.*, 1977): the lower Kerdylia formation and the upper Vertiskos formation, separated by the NW-striking Stratonii-Varvara fault (Fig. 1), a major structural feature that dominates the area.

The Kerdylia formation mainly consists of migmatitic biotite gneiss interlayered with several marble horizons, amphibolites and hornblende gneiss, whereas the Vertiskos sequence, outcropping in the studied area, largely includes biotite-muscovite gneiss and amphibolites with hornblende amphibolite intercalation (KOCKEL *et al.*, 1977). The regional metamorphic grade of rocks of the Kerdylia formation falls within the amphibolite facies (DIXON & DIMITRIADIS, 1984) while the Vertiskos sequence is at lower metamorphic grade and has suffered retrograde metamorphism to the greenschist facies (SAKELLARIOU, 1989).

The rocks of the Serbo-Macedonian massif have been intruded by various post-orogenic granitoids of Tertiary age, which have not been affected by regional metamorphism and none show any relationship to the regional schistosity (KOCKEL *et al.*, 1975). In the wider studied area, the earliest post-tectonic intrusion is represented by the Stratonii granodiorite (27.9±1.2 Ma) (GILG & FREI, 1994), followed by porphyritic stocks and dikes of granodioritic to quartz dioritic composition, mainly in the area between Fisoka and Stratonii.

The latest magmatic phase is the Skouries porphyry, which has been dated at 19.1±0.6 Ma according to FREI, 1995, belonging to a series of dominantly dioritic to andesitic porphyritic dikes and stocks.

Mineralization

Various ore deposits in the area are strongly related to the Tertiary intrusive bodies. The Madem Lakkos and Mavres Petres (Fig. 1) orebodies occur near or within the Stratonii-Varvara fault and are classified as Pb-Zn-Ag carbonate replacement type mineralization. The former, mainly develops along the contact between the lower marble horizon and the biotite gneiss of Kerdylia formation, whereas the latter develops along the tectonic contact between the biotite gneiss of Kerdylia formation and the amphibolites of Vertiskos formation (KALOGEROPOULOS *et al.*, 1989). The major ore sulphide minerals are pyrite, sphalerite, galena, arsenopyrite, and chalcocite, with quartz, rhodochrosite and calcite representing the gangue minerals (NICOLAOU & KOKONIS, 1980; KALOGEROPOULOS *et al.*, 1989). Based on ore mineralogy, textures and geochemistry, mineralization at Madem Lakkos consists of massive sulphide ore, disseminated sulphide ore

and skarn ore (NEBEL *et al.*, 1991). In addition, the porphyry Cu-Au deposits in Skouries and Fisoka areas represent another ore type. Mineralization of the porphyry Cu-Au has been studied by ELIOPOULOS & ECONOMOU-ELIOPOULOS (1991). They reported that ore minerals mainly include pyrite, bornite, chalcocite and magnetite in the form of veins, stockwork and disseminations. Finally, a manganese oxide mineralization occurs along the Stratonii-Varvara fault, following the same marble horizon with the Mavres Petres and Madem Lakkos ore bodies. Ore bodies of this type are located west of Mavres Petres and represent the final products of the hydrothermal fluids activity.

Hydrological and water quality characteristics

The hydrological characteristics of the region are typical of a Mediterranean type climate, with cool, rainy winters and long, dry, warm summers. Flow rates of the streams are rapidly affected by episodic rainfall and present strong variations according to the pluviometric regime. The studied area is characterized by mountainous relief, typically around 300 m ASL, and by a well developed dendritic style drainage network with streams originating from the Stratonikon Mountain and flowing within the sub-basins of Piavitsa and Kerasia (Fig. 1). Both of them discharge their water in Asprolakkas which has an W-E direction flowing towards the Gulf of Ierissos. KELEPERTZIS *et al.*, 2010 studied the surface water chemistry of Asprolakkas watershed throughout an hydrologic year and reported that each of the studied basin presents its own water quality characteristics, being influenced by metal release from outcrops of the sulphide mineralization occurring in the wider area. In general, water samples from Piavitsa present higher concentrations of SO₄, Zn, Mn and As in relation with the stream water from Kerasia catchment. The latter shows a more uniform chemical composition whereas water samples at Piavitsa are characterized by extended variability in the concentrations of their constituents due to different kind of mineralization occurring upstream and downstream of this sub-basin. Stream water pH for all the sampling points is around 8.

Regarding the EU Council Directive 98/83/EEC, Pb, Mn and As concentrations in Piavitsa basin usually exceed the parametric values of 10 µg/l, 50 µg/l and 10 µg/l respectively. Concentrations of all the other elements are lower than the regulatory limits. Kerasia shows a similar pattern for all the studied elements, except for the fact that Mn levels are always below the drinking quality standards.

MATERIALS AND METHODS

Collecting and processing samples

During April 2008, a total of 14 samples of active stream sediment were collected by using a hand trowel, preferably near stream confluences, in order to cover the whole drainage network within Piavitsa and Kerasia catchments. The upper

layer of bottom sediment was sampled, by collecting material to make a composite sample over a stream stretch of about 100 m at each sampling location and the samples were put in clean polyethylene bags for transport. Sampling locations are depicted in Fig. 1. Specifically, samples F1, F2, E1, E2, E3 and C were collected from Kerasia whereas samples I1, I2, I3 (Tsarkia Lakkos sampling site), K (Lotsaniko stream), L1 (Karatzá Lakkos stream), L2, M and D from Piavitsa catchment basin. Over 1kg of bulk active sediment sample was collected at each sampling site in order to ensure that sufficient fine-grained material would be available for analysis. The sample preparation was carried out at the Laboratory of Economic Geology and Geochemistry, National and Kapodistrian University of Athens. Samples were oven-dried at a constant temperature of 45 °C for 3 days, sieved to < 2.00 mm fraction representing about 50% of the bulk sample, then pulverized in an agate mortar to < 0.075mm and stored in polyethylene bags for routine mineralogical and chemical analyses.

Mineralogical analysis

Methods used to determine the mineralogical composition of the stream sediment samples included X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Diffraction spectra were obtained by using a Siemens D5005 Diffractometer with Cu-K α radiation, operating at 40 kV and 40 mA. Each powdered sample was scanned from 3^o to 65^o 2 θ with a one counting time per step. X-Ray power diffraction patterns were evaluated for the total of pulverized stream sediment samples, using the software EVA 2.2. SEM was performed on a Jeol JSM-5600 instrument, equipped with an energy dispersive X-Ray spectrometer for microanalysis (EDS, Oxford Link ISIS 300). Six representative carbon coated metallographic sections were prepared by mixing the powdered material with an appropriate resin and were studied with operating conditions being: acceleration voltage 20 kV, beam current 0.5 nA, beam diameter 2 μ m and acquisition time 80 sec. The studied samples were F1, E3 and C from Kerasia, and I2, I3 and D from Piavitsa basin.

Chemical analysis and quality control

Multi-element analysis using Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) was performed at the accredited ACME Analytical Laboratories, Canada. A 0.5 g portion of each pulverized sample was digested into hot (95 °C) aqua regia (HCl-HNO₃-H₂O) for 1h. After dilution to 10ml with water, solutions were analyzed for a series of 33 elements. In this study, emphasis was given to the following chemical elements: Cu, Pb, Zn, Mn, Ni, Cr, Co, As, Sb, and Fe. The instrumental detection limits reported by the analytical laboratory are presented in Table 1.

Generally, the digestion by modified aqua regia extracts only a proportion of the major elements (pseudo-total analysis), being suitable for the dissolution of metals bound as

TABLE 1

Instrument detection limits for the measured elements (values are in mg kg⁻¹ for all the elements, except for Fe that is presented in %).

Chemical element	Detection limit
Cu	1
Pb	3
Zn	1
Mn	2
Ni	1
Cr	1
Co	1
As	2
Sb	3
Cd	0,5
Fe	0,01

TABLE 2

Measured concentrations and certified median values for the analyzed metals (certified median values refer to median leach data from various cooperating laboratories using ICP-OES method).

Element	SRM 2709 (mg kg ⁻¹)		SRM 2710 (mg kg ⁻¹)		SRM 2711 (mg kg ⁻¹)	
	Measured value	Certified Median	Measured value	Certified Median	Measured value	Certified Median
Cu	29	32	2769	2700	107	100
Pb	16	13	5104	5100	1090	1100
Zn	93	100	6053	5900	312	310
Ni	69	78	10	10	16	16
Co	11	12	7,5	8,2	8	8,2
Mn	469	470	7764	7700	502	490
As	13	<20	581	590	94	90
Cd	<0,5	<1	19	20	38	40
Sb	<3	<10	13	7,9	7,5	<10
Cr	63	79	17	19	21	20
Fe	28100	30000	26050	27000	21700	22000

water-soluble salts, in cation-exchange sites, statically bound to clay particles, in organic chelates, in amorphous oxides and hydroxides of Mn and Fe, in carbonates, in sulphides and some sulphates. It also partially solubilizes metal in some silicates (the darker colored ferromagnesian-rich silicates) and some crystalline oxides of Fe, Ti and Cr (ALBANESE *et al.*, 2007; MLAYAH *et al.*, 2009).

Analytical precision was determined by duplicate analysis of 3 random samples, being in all cases lower than 10% for all the analyzed elements (in most cases lower than 5%), while blanks prepared by the ACME Analytical Laboratories were always below the instrumental detection limits. Accuracy was checked by the submission from the authors of 3 standard soil certified reference materials: SRM 2709 San Joaquin soil, SRM 2710 Montana Soil and SRM 2711 Mon-

tana Soil, covering low, middle and high concentrations of heavy metals (Table 2).

The obtained results indicate a good agreement between our data and the reference values, with the percent difference being lower than 10% for 80% of the cases.

RESULTS AND DISCUSSION

XRD and SEM-EDS results

According to the XRD results, all collected stream sediment samples present similar mineralogical composition consisting of quartz, albite/anorthite and actinolite as the major minerals, and clinocllore, illite and montmorillonite as minor clay minerals. The existence of montmorillonite was confirmed by 2 representative oriented samples (one per each hydrological basin) treated with glucose. This observation has significant implications for the present study because montmorillonite shows high Cation Exchange Capacity (CEC) values (800-1200 meq/kg) and acts as a metal adsor-

ber (APPELO & POSTMA, 2005).

Sulphide minerals were not detected by XRD but were identified by SEM-EDS semiquantitative chemical analyses (Fig. 2). Results revealed the presence of pyrite, arsenopyrite, sphalerite and chalcocopyrite in the studied stream sediments samples from Tsarkia Lakkos (sampling sites I1, I2 and I3). All the studied samples are dominated by grains of rhodochrosite often containing various amounts of Pb, Sb and Zn. In addition, Fe-oxides are present in the majority of the samples, often containing traces of Pb, Cu, As and Zn.

Metal content evaluation

Results of chemical analyses

The results of the ICP-OES chemical analysis for the collected stream sediments samples are presented in Table 3, together with the world average abundance of selected metals in soils (data from TAYLOR, 1966, SAXBY, 1969) and the median values for soils of the wider area of Stratoní reported in

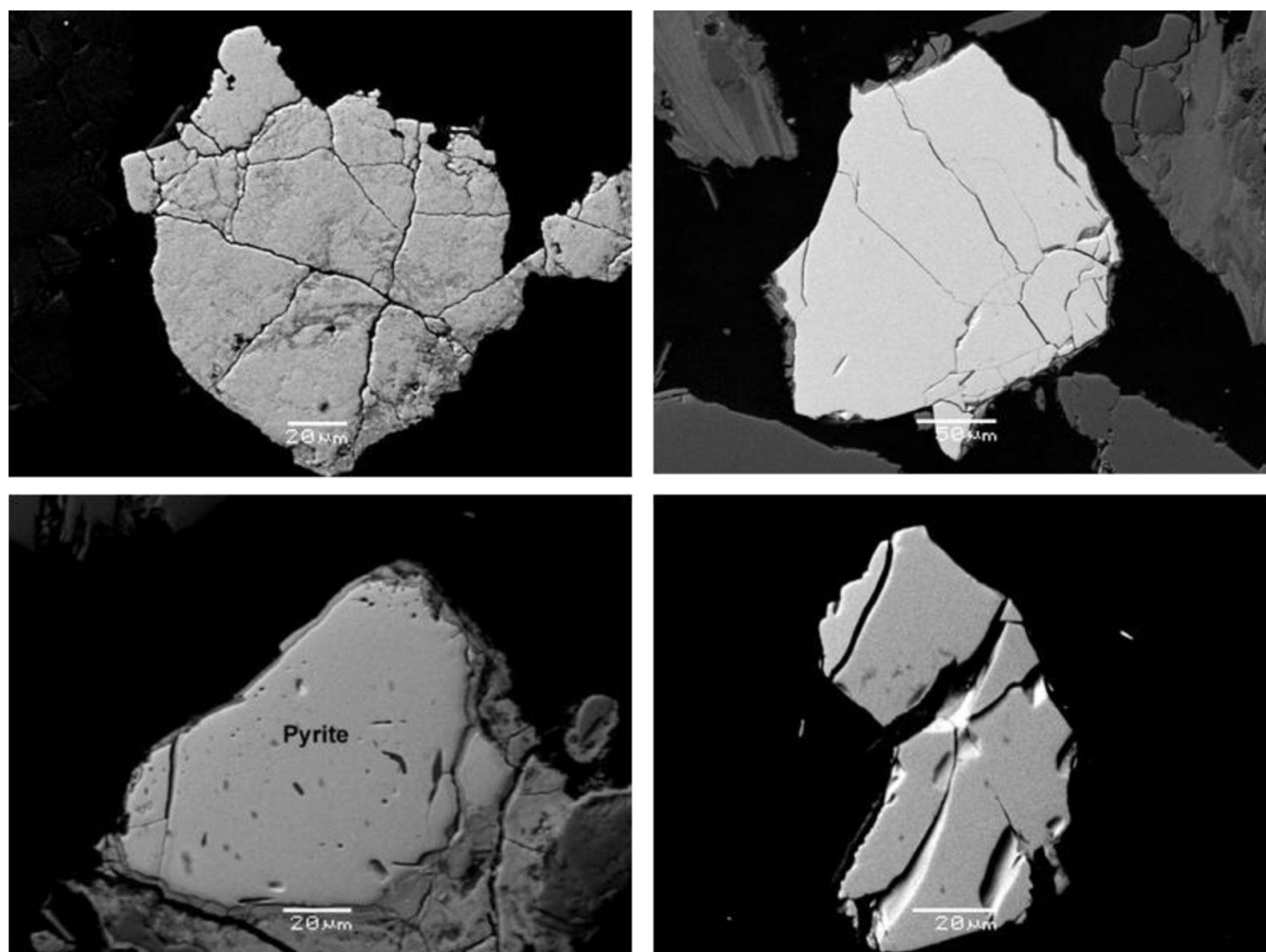


Fig. 2. Selected back-scattered image SEM photomicrographs of samples from Piavitsa and Kerasia catchments. Top left: rhodochrosite grain with traces of Si and Ca from sampling site I3. Top right: chalcocopyrite grain from sampling site I2. Bottom left: pyrite from sampling site I2. Bottom right: Fe-oxide grain from sampling site F1.

the study by KELEPERTSIS *et al.* (2006) and the intervention limits for stream sediments fixed by Dutch legislation (VROM, 2000).

A comparison of the metal concentrations with the global average range of soil composition reveals that the studied samples present Cu, Co, Cr and Ni concentrations lower than the average reported values, indicating that there are no significant sources for these elements. Only sample L1 (Karatza Lakkos) has a notable Cu concentration (349 mg/kg) higher than both the average range in soils and the median value of 104 mg/kg reported for the Stratoni area, probably being influenced by the porphyry copper mineralization occurring in nearby Skouries. The highest Cr and Ni concentrations were also measured for Karatza Lakkos sampling site. However,

the majority of the samples are significantly contaminated by Zn, Mn, As and Sb, showing concentrations, in most cases, higher than the average range in both soil composition and the median values that have been published for the adjacent area of Stratoni. Regarding Cd and Pb concentrations, only samples I1, I2, and I3 exceed the median values of 1,3 mg/kg and 325 mg/kg respectively. These samples also show high levels of Zn, Mn, As and Sb. Iron concentration is always lower than the local soil median value of 5,95%, but this could be due to the different method of digestion applied to the samples.

Since there are no guidelines for stream sediment quality in Greece, metal contents were compared to quality criteria derived from the Netherlands. All the studied samples except

TABLE 3

Concentrations of the analyzed elements in the studied stream sediments (values in mg kg⁻¹ for all the elements, except for Fe that is presented in %).

Stream site	Basin	Cu	Pb	Zn	Mn	Ni	Cr	Co	As	Sb	Cd	Fe (%)
F1	Kerasia	52	153	223	1215	67	98	17	70	4	0,7	2,93
F2	Kerasia	46	243	273	1849	72	101	18	130	6	0,9	2,96
E1	Kerasia	45	76	101	1086	84	94	18	117	<3	<0,5	3,43
E2	Kerasia	38	97	107	1509	160	163	20	153	4	<0,5	3,43
E3	Kerasia	40	313	370	1547	71	91	16	143	8	0,8	2,82
C	Kerasia	46	320	330	1986	78	93	17	185	9	1,2	2,91
I1	Piavitsa	89	1812	2090	>10000	59	38	9	964	40	8,4	2,5
I2	Piavitsa	52	1165	1368	>10000	160	98	15	1098	39	3,8	3
I3	Piavitsa	70	1716	1621	>10000	121	63	11	1136	51	6,5	2,75
K	Piavitsa	30	68	137	1079	110	134	15	43	<3	<0,5	2,8
L1	Piavitsa	349	208	390	679	242	319	25	70	<3	1,4	2,92
L2	Piavitsa	47	271	476	7252	92	107	15	220	8	1,4	2,87
M	Piavitsa	111	39	73	861	57	50	23	63	<3	0,6	3,83
D	Piavitsa	86	245	405	7400	134	144	18	195	10	1	3,02
Average range in soil composition (Taylor, 1966, Saxby, 1969)												
		2-100	2-200	10-300	850	5-500	5-1000	1-40	1-50	5	1	*
Median value of soils reported for the adjacent area of Stratoni (Kelepertsis et al, 2006)												
		104	325	240	1501	69	178	32	119	*	1,3	5,95
Intervention limits, established by Dutch law (VROM, 2000)												
		190	530	720	*	210	380	240	55	15	12	*

* Not available

for Lotsaniko site (sample K) have As concentrations that exceed the corresponding value of 55 mg/kg whereas only the stream sediment sample L1 surpasses both Cu and Ni intervention limits. Furthermore, Pb, Zn and Sb values for Tsarkia Lakkos sampling site are significantly higher than the limits of 530 mg/kg, 720 mg/kg and 15 mg/kg respectively. Regarding Cr, Co and Cd concentrations, stream sediments samples are characterized by values lower than the Dutch regulatory limits.

A distinction seems necessary to be made for metals that show a different distribution in some sampling sites. Lead, Zn, Mn, As, Sb and Cd concentrations are considerably higher in stream sediments from Tsarkia Lakkos, (I1, I2 & I3), located upstream in Piavitsa catchment, when compared to the corresponding concentrations from the other studied locations. This could be explained by the hypothesis that Tsarkia Lakkos site is influenced by the nearby metalliferous Stratoni-Varvara fault and its associated ore metals. Elevated concentrations of Zn, Mn and As were also found in L2 and D stream sediment samples, downstream in Piavitsa, as well as in all the sampling locations from Kerasia catchment, although to a lesser extent. Lotsaniko site (sample K), Karatza Lakkos site (L1) and sample M, present the lowest concentrations for Pb, Zn, Mn, As and Sb regarding the Piavitsa basin.

The overall results are expected if we bear in mind that the studied area is located within the “metallogenic province” of NE Chalkidiki, and the minerals involved contain high concentrations of these metals. Additionally, the concentrations of the analyzed elements are similar to the results of chemical analyses for soils within Piavitsa basin of a previous unpublished study, conducted by ARGYRAKI (2006). Furthermore, the fact that the downstream evolution of the measured element concentrations, for each of the studied catchments, does not show a general decrease certifies the variability of the geological and mineralogical characteristics, resulting in the spatial variation of the analyzed chemi-

cal elements throughout the studied area. The stream sediment chemistry is also in spatial accordance with surface water quality characteristics at the same stream sites (KELEPERTZIS *et al.*, 2010).

Data Processing

All studied elements presented positively skewed distributions, since the arithmetic mean was always higher than the median value. For this reason a normal score transformation was applied to the data before performing the parametric statistical tests described below. Pearson correlation coefficients are shown in Table 4. Concentrations of Pb, Zn, Mn, Sb, As and Cd display strong positive inter-correlation between each other. Also, a strong positive correlation is observed between Ni and Cr, indicating common sources for these metals. Further, R-mode factor analysis was applied to the data. This is a statistical method that characterizes different groups of chemical elements with approximately similar geochemical patterns, naming as factors. Rotated factor loadings, communalities and the proportion of the variance explained by three factors are presented in Table 5.

The three-factor model, accounting for 88,2% of the data variability, was deemed appropriate for the stream sediment data of the studied area. Factor 1 includes Pb, Zn, Mn, As, Sb and Cd showing high positive loadings whereas Fe and Co are included with negative loadings. Factor 2 comprises Ni and Cr with high positive loadings while Factor 3 consists of Cu with also high positive loading.

Specifically, Factor 1, accounting for 56% of the total variance, reflects the signature of the massive sulphide mineralization of the area on the data since it includes all the chemical elements that are abundant in this type of ore deposits. Same high factor loadings for these elements were reported after the application of factor analysis in soil data, deriving from the wider area of Stratoni village, in the study

TABLE 4
Pearson correlation coefficient for stream sediment data after normal score transformation.

	Cu	Pb	Zn	Mn	Ni	Cr	Co	As	Sb	Cd	Fe
Cu	1										
Pb	0,21	1,00									
Zn	0,33	0,93	1,00								
Mn	0,00	0,83	0,75	1,00							
Ni	-0,03	0,09	0,23	-0,01	1,00						
Cr	-0,14	-0,35	-0,18	-0,40	0,78	1,00					
Co	0,20	-0,68	-0,67	-0,76	0,22	0,55	1,00				
As	0,20	0,86	0,78	0,90	0,22	-0,28	-0,56	1,00			
Sb	0,18	0,91	0,83	0,94	0,03	-0,42	-0,71	0,92	1,00		
Cd	0,60	0,87	0,91	0,66	0,06	-0,34	-0,53	0,74	0,78	1,00	
Fe	0,05	-0,68	-0,74	-0,43	0,03	0,27	0,76	-0,34	-0,53	-0,59	1,00

by KELEPERTSIS *et al.* (2006). The second factor, explaining 18% of the total variance, is controlled by Ni and Cr and indicates the influence of amphibolite rocks present in the whole studied area, on the chemistry of the collected stream sediments. Finally, the third factor accounting for 14% of the total variability, contains positive factor loadings for Cu and is possibly related with the porphyry copper mineralization occurring in Skouries.

Implications for future mining activities

In general, stream sediment samples from Piavitsa catchment are enriched in metals compared with the samples from Kerasia catchment. This observation has implications for any future mining development at Skouries. Specifically, the higher metallic load already present in Piavitsa justifies the positioning of any future mining waste treatment facility in this catchment rather than the adjacent Kerasia where the geochemical background is relatively lower i.e. is a more pristine area.

However, the absence of minerals with high neutralization capacity, such as calcite, dolomite, and magnesite from the sediments implies that special care should be taken for preventing acid mine drainage and its well-documented deleterious consequences for the environment (GRAY, 1997, SÁNCHEZ-ESPAÑA *et al.*, 2005), since rhodochrosite detected by SEM-EDS methods is much less effective acid-consuming mineral (PLUMLEE, 1999, HAMMARSTROM & SMITH, 2002). Despite the absence of calcite, stream waters are characterized by alkaline pH values (KELEPERTZIS *et al.*, 2010).

CONCLUSIONS

A stream sediment survey was undertaken in Piavitsa and the adjacent Kerasia catchments of Chalkidiki peninsula, north-east Greece. The collected stream sediment samples present a uniform mineralogical composition of quartz, albite/anorthite, actinolite, clinocllore, illite and montmorillonite reflecting the lithological composition of the area comprising amphibolite metamorphic rocks. The absence of calcite or other effective acid-consuming minerals is noteworthy because it signifies the poor neutralizing capacity of the natural lithologic components. SEM-EDS analyses of representative samples revealed the presence of sulphide minerals including pyrite, arsenopyrite, chalcopyrite and sphalerite, mainly in Tsarkia Lakkos sampling site, located upstream in Piavitsa, near to the large Stratoni-Varvara fault.

Regarding chemical analyses, Mn Zn, As and Sb are present in most of the collected stream sediments in concentrations both above the world average range of soil composition and the reported median values for soils in the wider area of Stratoni village, whereas Cd and Pb are only significantly enriched in Tsarkia Lakkos sampling location. On the contrary, Co, Cu, Cr and Ni values are similar to the average range, indicating that there are no significant sources of contamination for these elements. The highest concentrations of Pb, Zn, Mn, As, Cd and Sb were measured at the upstream sampling sites I1, I2 and I3 from Piavitsa, possibly being influenced by the metalliferous Stratoni-Varvara fault and the associated metal ores. The spatial variability of the studied elements, especially within Piavitsa basin, indicates the influence of different kind of mineralization that control stream sediment chemistry. Bearing in mind that in Greece there are not any legal standards for soil and stream sediment chem-

TABLE 5
Varimax component loadings of three factors, communality and percentage of variance explained for the studied elements.

Variable	Factor 1	Factor 2	Factor 3	Communality
Cu	0,074	-0,058	0,977	0,964
Pb	0,952	-0,042	0,169	0,937
Zn	0,932	0,107	0,239	0,938
Mn	0,902	-0,129	-0,034	0,832
Ni	0,145	0,962	0,008	0,947
Cr	-0,311	0,910	-0,087	0,931
Co	-0,812	0,375	0,337	0,913
As	0,875	0,077	0,196	0,811
Sb	0,935	-0,109	0,130	0,903
Cd	0,813	-0,061	0,535	0,95
Fe	-0,721	0,136	0,194	0,576
% Variance	0,563	0,179	0,140	0,882

istry evaluation, these results may assist legislators to establish intervention values for Chalkidiki prefecture in accordance to the local geochemical baseline levels.

The application of R-mode factor analysis grouped the measured elements in three groups according to their geogenic origin, explaining 88% of the data variability. The most significant factor comprises Pb, Zn, Mn, As, Cd and Sb, i.e. the elements that are abundant in the sulphide minerals occurring in the wider studied area. The second factor includes Ni and Cr, reflecting the natural levels derived from amphibolite metamorphic rocks whereas the third factor comprises Cu and could be related with the porphyry copper mineralization occurring in Skouries area.

ACKNOWLEDGMENTS

The authors wish to express their great appreciation to N. Adam of Hellas Gold S.A. for his invaluable help during fieldwork and Dr. I. Mitsis for his considerable assistance with the evaluation of XRD patterns.

REFERENCES

- ALBANESE, S., DE VIRO, B., LIMA, A. & D. CICHELLA (2007). Geochemical background and baseline values of toxic elements in stream sediments of Campania region (Italy). *Journal of Geochemical Exploration*, 93, 21-34.
- APPELO, C.A.J. & D. POSTMA (2005). *Geochemistry, groundwater and pollution*. 2nd edition. A.A. Balkema Publishers, The Netherlands.
- ARGYRAKI, A. (2006). Preliminary geochemical study of soils of Pivavitsa basin. *unpublished Technical Report, University of Athens*.
- DIXON, J.E. & S. DIMITRIADIS (1984). Metamorphosed ophiolitic rocks from the Serbo-Macedonian massif, near lake Volvi, north-east Greece. *Geological Society, London, Special Publications*, 17, 603-618.
- ELIOPOULOS, D.G. & M. ECONOMOU-ELIOPOULOS (1991). Platinum-group element and gold contents in the Skouries porphyry copper deposit, Chalkidiki peninsula, northern Greece. *Economic Geology*, 86, 740-749.
- European Union Council, 1998. 'Council Directive on the quality of water intended for human consumption, 98/83/EC', *Official Journal of the European Communities*, 330, 32-54.
- FREI, R. (1995). Evolution of mineralizing fluid in the porphyry copper system of the Skouries deposit, northeast Chalkidiki (Greece): Evidence from combined Pb-Sr and stable isotope data. *Economic Geology*, 90, 746-762.
- GILG, H.A. & R. FREI (1994). Chronology of magmatism and mineralization in the Kassandra mining area, Greece: The potentials and limitations of dating hydrothermal illites. *Geochimica et Cosmochimica Acta*, 58, 2107-2122.
- GRAY, N.F. (1997). Environmental impact and remediation of acid mine drainage: a management problem. *Environmental Geology*, 30, 62-71.
- HAMMARSTROM, J.M., & SMITH, K.S. (2002). Geochemical and mineralogic characterization of solids and their effects on waters in metal-mining environments. In: SEAL II, R.R., FOLEY, N.K. (Eds), *Progress on Geoenvironmental Models for Selected Mineral Deposit Types*, US Geol. Surv. Open file Rep.02-195.
- KALOGEROPOULOS, S.I., KILIAS, S.P., BITZIOS, D.C., NICOLAOU, M. & R.A. BOTH (1989). Genesis of the Olympias carbonate-hosted Pb-Zn(Au,Ag) sulfide ore deposit, eastern Chalkidiki peninsula, northern Greece. *Economic Geology*, 84, 1210-1234.
- KELEPERTSIS, A., ARGYRAKI, A. & D. ALEXAKIS (2006). Multivariate statistics and spatial interpretation of geochemical data for assessing soil contamination by potentially toxic elements in the mining area of Stratonis, north Greece. *Geochemistry: Exploration, Environment, Analysis*, 6, 349-355.
- KELEPERTZIS, E., ARGYRAKI, A., DAFTSIS, E. & D. BALLAS (2010). Quality characteristics of surface waters at Asprolakkas river basin, N.E. Chalkidiki, Greece. *Bulletin of the Geological Society of Greece, Proceedings of the 12th International Congress*, Patra p. 1737-1746.
- KOCKEL, F., MOLLAT, H. & H. GUNDLACH (1975). Hydrothermally altered and (copper) mineralized porphyritic intrusions in the Serbo-Macedonian Massif (Greece). *Mineralium Deposita*, 10, 195-204.
- KOCKEL, F., MOLLAT, H. & H.W. WALTHER (1977). Erläuterungen zur geologischen Karte der Chalkidiki und angrenzender Gebiete 1:100000 (Nord-Griechenland): *Hannover, Bundesanstalt für Geowissenschaften und Rohstoffe*, p. 119.
- MLAYAH, A., FERREIRA DA SILVA, E., ROCHA, F., BEN HAMZA, CH., CHAREF, A. & F. NORONHA (2009). The Oued Mellègue: Mining activity, stream sediments and dispersion of base metals in natural environments, North-western Tynisia. *Journal of Geochemical Exploration*, 102, 27-36.
- NEBEL, M.L., HUTCHINSON, R.W. & R.E. ZARTMAN (1991). Metamorphism and polygenesis of the Madem Lakkos poly-metallic sulfide deposit, Chalkidiki, Greece. *Economic Geology*, 86, 81-105.
- NICOLAOU, M. & D. KOKONIS (1980). Geology and development of Olympias mine, eastern Chalkidiki, Macedonia, Greece; In: JONES, J.M. (Ed.), *Complex sulfide ores, Instit. Mining Metallurgy*, London, pp. 260-270.
- PERANTONIS, G. (1994). Mixed sulphide deposits of M. Lakkos and Olympiada mines in Kassandra. In: Dabitzias, S. (Ed), *Proceedings of One-Day Symposium on Mineral Wealth of Chalkidiki and the Environment*, Gerakina Beach Hotel, Chalkidiki, Greece, May 1994, 113-126.
- PLUMLEE, G.S. (1999). The environmental geology of mineral deposits. In: PLUMLEE, G.S. & M.J. LOGSDON (Eds), *The Environmental Geochemistry of Mineral Deposits, Part A. Processes, Techniques, and Health Issues*, Society of Economic Geologists, Reviews in Economic Geology, 6A, 71-116.
- RUNNELS, D.D., DUPON, D.P., JONES, R.L. & D.J. CLINE (1998). Determination of natural background concentrations of dissolved components in water at mining, milling and smelting sites, *Mining Engineering*, 50 (2), 65-71.
- SAKELLARIOU, D. (1989). Geologie des Serbomazedonischen Massivs in der nordöstlichen Chalkidiki, N-Griechenland – Deformation and Metamorphose. *PhD thesis*, Univ. Johannes Gutenberg, Mainz, Germany.
- SAXBY, J.D. (1969). Metal-organic chemistry of the geochemical cycle. *Rev. Pure Appl. Chem*, 19, 131-150.
- SÁNCHEZ-ESPAÑA, J., LÓPEZ PAMO, E., SANTOFIMIA, E., ADUVIRE, O., REYES, J., and BARETTINO, D. (2005). Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications, *Applied Geochemistry*, 20, 1320-1356.
- TAYLOR, S.R. (1966). The application of trace element data to problems in petrology. *Physics and Chem. of the Earth*, 6, 135-213.
- VROM (Ministry of Housing, Spatial Planning and the Environment, the Netherlands), 2000. Circular on target and intervention values for soil remediation. *Netherlands Government Gazette of the 24th February 2000*, no. 39.

