

## GEOCHEMICAL CHARACTERISTICS OF SULFIDE MINERALIZATIONS FROM THE PINDOS OPHIOLITE COMPLEX: PRELIMINARY DATA

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### ABSTRACT

In the Pindos ophiolite complex three types of sulfide mineralization can be distinguished: (a) sulfide mineralization of Cyprus type, in the Kondro hill, (b) the Fe-Cu-Ni-Co type, in the Tsoumes hill, consisting of pyrrhotite, chalcopyrite, Co-pentlandite, pyrite and magnetite and (c) disseminated pyrite within a diabase breccia pipe, in the area of Neropriona (Aspropotamos).

The sulfide massive mineralization from Kondro and Tsoumes Hills exhibits significant Au, Cu, Zn, Mo, Sb, Hg and Se, and low Pt, Pd contents, which point to precipitation from a circulating hydrothermal system. A significant Pt-enrichment (160 to 1000 ppb) in the brecciated diabase, is probably derived by leaching from a rock-source with initially much lower Pt content, and may reflect heterogeneity in the permeability of the hydrothermal circulation zones and/or variable water/rock proportion.

**KEY WORDS:** Pindos, ophiolite, breccia, sulfides, mineralization, platinum, palladium, selenium.

### 1. INTRODUCTION

Based on the mineralogical and chemical composition of sulfide mineralization and host rocks in the Pindos ophiolite complex the following types can be distinguished: (a) sulfide mineralization of Cyprus type, containing variable proportions of pyrite, chalcopyrite, bornite and sphalerite (b) the Fe-Cu-Ni-Co type consisting of pyrrhotite, chalcopyrite, Co-pentlandite, pyrite and magnetite and (c) disseminated pyrite mineralization within a diabase breccia pipe.

Some mineralogical and geochemical data have been published in previous studies (Skounakis et al., 1980, 1981; Sideris et al., 1984; Robertson and Varnavas, 1993; Economou-Eliopoulos and Eliopoulos, 1996). In the present study representative samples of the above three types of the sulfide mineralization were analyzed for minor and trace elements, including Pt, Pd and Au. These results are given and their implication to the metallogenetic processes, along with comments on their influence to the environment are briefly discussed.

### 2. DESCRIPTION OF THE SULFIDE MINERALIZATION

The Pindos ophiolite complex of NW Greece, is part of a nappe which is tectonically overthrust on the Eocene flysch of the Pindos zone. It constitutes a complete complex, although it is mainly comprised of large harzburgite-dunite masses. The magmatic sequence of the complex includes ultramafic rocks, gabbros, diabase and a spectrum from MORB through IAT to BSV, suggesting more than one eruptive settings (Pearce et al., 1984). The structure of the Pindos ophiolite is complex, in particular in the regions of Perivoli (Kondro and Tsoumes) and Aspropotamos (Neropriona) where sulfide mineralizations have

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been described (Skounakis et al., 1980, 1981; Sideris et al., 1984). According to Jones and Robertson (1991) the Aspropotamos dismembered ophiolite consists of thrust slices of geochemically and lithologically complicated ophiolitic cumulate, intrusive and extrusive rocks, formed by supra-subduction zone spreading. Also the Perivoli ophiolite is incorporated in the Avdella melange, including dismembered Triassic-Jurassic extrusives (MORB to transitional MORB) and sedimentary rocks, which underlies the Aspropotamos unit. Based on the mineralogical and chemical composition and host rocks three types can be distinguished in the Pindos ophiolite complex: the Cyprous type, Fe-Cu-Ni-Co type and disseminated pyrite.

## 2.1. Cyprus type copper mineralization - Kondro hill

At the Kondro hill, SE slopes of the mountain Smolicas, close to the villages of Perivoli and Avdella (Fig. 1) massive sulfide mineralization hosted in diabase (in tectonic contact with serpentinitized peridotite), occurs in the form of lenses (maximum 4m x 40m, with an estimated ore potential about 10.000 tons). Pervasive shearing trending E-NE over host ophiolitic rocks, with limestone tectonic inclusions, continues into the adjacent area of Perivoli (Tsoumes). The whole ophiolite unit has been thrust over the Eocene Pindos flysch. The sulfide ore is composed mainly of pyrite, chalcopyrite, bornite, sphalerite, marcasite and chalcocite. Pyrite occurs either in framboidal forms or as euhedral crystals (Skounakis et al., 1981, 1982). The occurrence of bornite in association with chalcopyrite penetrating earlier pyrite and chalcopyrite seems to be common in the studied samples of massive ore.

## 2.2. Fe-Cu-Ni-Co sulfide type - Tsoumes hill

Irregular to lens-like masses (about 4m x 1.5m) of massive sulfide mineralization, associated with magnetite are found in the area of Perivoli (Tsoumes hill), hosted within gabbros, close to the

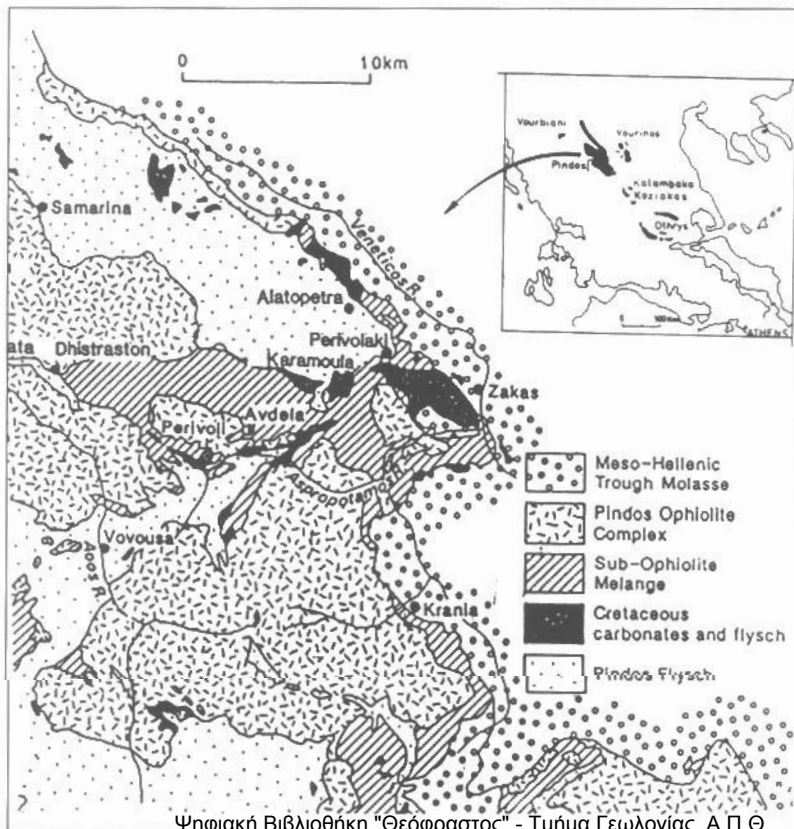


Fig. 1: Simplified geological map of the northern Pindos region showing the Perivoli-Aspropotamos area (after Jones and Robertson, 1991)

retoniccontact with serpentized harzburgite. The most abundant minerals are pyrrhotite and pyrite. Troilite, Co-pentlandite (as inclusions within pyrrhotite), mackinawite and chalcopyrite occur in lesser amounts. Malachite and azurite are also present. Magnetite associated with sulfides occurs as massive ore with inclusions of sulfides and shows a network texture with occasionally deformed crystals (Economou et al., 1980; Skounakis et al., 1982).

### 2.3. Disseminated pyrite within diabase breccia - Aspropotamos (Neropriona)

A brecciated pipeform diabase is found in the ophiolitic unit of the Aspropotamos (Neropriona), about 600 m NE of Perivoli. It has a surface area of approximately 200 m by 50 m and extends over a vertical distance of about 150 m. The brecciation is restricted entirely into the diabase. Although relics of subophitic texture are observed it is characterized by a strong pervasive silicification and chloritization. The mineral assemblage found in the brecciated diabase includes plagioclase (partly altered) + clinopyroxene (altered) + penninite + kaolinite + quartz + epidote + calcite and disseminated mineralization (Sideris et al., 1984). Disseminated pyrite mineralization is widespread, while vesicles filled by pyrite, quartz, kaolinite and epidote are less common.

## 3. GEOCHEMICAL CHARACTERISTICS

Some mineralogical and mineral chemistry data concerning sulfide occurrences hosted in the Pindos complex have been published by Economou et al., (1981); Sideris et al., (1984); Skounakis et al., (1980; 1982); Robertson and Varnavas (1993). The sulfide ores described above were further studied and analyzed for minor and trace elements, including platinum, palladium and gold. In addition, representative samples from the brecciated diabase were analyzed for major and trace elements. Samples were analyzed for oxides at the Athens University by A.A.S., minor elements by neutron activation analysis and Pt, Pd and Au by the lead fire -assay technique, at the XRAL Laboratories, Ontario, Canada. The detection limit is 10ppb for Pt, 1 ppb for Pd and 5 ppb for Au. These results are given in the Tables 1 & 2 and provide a preliminary characterization of the mineralizations, since the present study is in progress.

The analyzed samples of massive sulfide mineralization from the Kondro exploration gallery are characterized by significant contents of Au (up to 3.2 ppm), Zn (up to 8.3 wt%), Mo (up to 120 ppm), As (up to 150 ppm) and Sb (up to 10ppm), Hg (up to 280 ppm), while the copper content in those samples ranges between 4.8 and 21.6 wt% Cu (Table 1). Also, in some samples the highest values of selenium (average 1400 ppm Se), in particular, in Cu - rich portions were recorded. In contrast, pyrite-rich samples, having lesser amount of chalcopyrite exhibit the lower Se content. The selenium content in the sulfide mineralization of the Fe-Cu-Ni-Co type, which is exposed at the neighboring area of Perivoli (Tsoumes) is lower (130-350 ppm Se) compared to that in the Kondro. A common feature of these two types of sulfides is the significant concentration of Se, Au, As, Zn, Mo and Sb, although the level of all elements is lower in the latter.

The concentrations of elements which are generally considered to be immobile during hydrothermal alteration (Ti, Zr, Y Nb, Cr, Ni) (Table 1), may provide evidence for the formation of the diabase breccia within an environment influenced by subduction processes (Pearce et al., 1984). The strongly altered samples (yellow colored fragments) are characterized by a depletion in Na<sub>2</sub>O, CaO and an enrichment in silica, and platinum, ranging from 160 to 1000 ppb while Pd and Au content ranges from 9 to 27 ppb, and 1 to 25 ppb respectively (Tables 1 & 2). The less altered samples show a small noble metal content, while all analyzed samples of brecciated diabase are rare earth element (REE) depleted. Finally, the selenium content in the brecciated pipeform diabase is less than 5 ppm, except the highly altered sample (36 ppm), which is also characterized by an enrichment in platinum (1 ppm).

Although the selenium values in the analyzed mineralizations are scattered in a wide range assuming that Cu forms stoichiometric chalcopyrite and bornite, which are the main collectors of Se, when calculating the average selenium content in these minerals reaches a level of >2500 ppm Se, which is much

Table 1. Trace element data on sulfide mineralization from the Pindos ophiolite complex.

Location	Sample	ppb			ppm							wt%		
		Au	Pt	Pd	Se	As	Mo	Sb	Hg	Zn	Co	Cu	Fe	
<b>Pondro: massive mineralization consisting of pyrite, chalcopyrite, bornite and sphalerite</b>														
	Ko.A	1390	<10	3	950	25	78	1.7	94	9550	1590	21.6	11	
	Ko.B	3000	<10	4	350	140	90	6.6	36	22000	910	5.4	20.8	
	Ko.C	3200	<10	3	170	130	90	9.5	48	29000	1500	7.6	26.5	
	KoAD	1900	<10	4	1900	60	40	10	280	83000	280	17	26.4	
	Ko.E	2900	<10	5	410	160	165	7.5	97	28000	1000	4.2	21.8	
<b>Lsoumes: massive mineralization consisting of pyrrhotite, pyrite, pentlandite, chalcopyrite &amp; magnetite</b>														
	Ts.1	150	<10	15	130	19	80	0.9	10	4400	580	1.8	49.8	
	Ts.4	140	20	3	350	27	150	0.9	29	1200	1500	2.5	33.4	
	Ts.5	44	<10	10	95	20	70	0.8	11	1100	540	1.4	31.2	
	Ts.6	33	<10	12	40	11	57	0.4	14	1200	530	1.6	30.3	
<b>Neropotamos (Neropriona): disseminated mineralization in diabase breccia</b>														
	N.Br.3	1	440	20	<5	26	<5	<0.2	<1	80	27	0.004	6.2	
	N.Br4	8	<10	9	<5	22	<5	0.4	<1	40	20	0.003	7.1	
	N.Br5	7	284	16	36	31	<5	0.9	<1	50	10	0.007	8.7	
	N.Br7	25	1000	27	<5	25	<5	0.6	<1	90	15	0.007	6.9	
	N.Br8	15	160	13	<5	18	<5	0.3	<1	80	22	0.005	6.7	
	N.Br9	12	<10	10	<5	4	<5	0.2	<1	110	37	0.006	6.4	
	N.Br10	15	200	20	<5	10	<5	0.2	<1	60	14	0.007	7.4	

**Table 2. Representative chemical analyses (by XRF) of mineralized diabase breccia**

Samples	N.Br4	N.Br5	N.Br3	N.Br7	N.Br8
<b>Wt%</b>					
SiO <sub>2</sub>	62.0	56.95	64.0	66.0	58.0
Al <sub>2</sub> O <sub>3</sub>	15.5	16.3	14.1	15.2	15.9
FeO <sub>t</sub>	9.2	7.25	8.8	11.3	13.9
MgO	11.25	7.9	8.5	5.01	2.4
CaO	0.28	9.8	3.5	0.24	0.3
MnO	0.11	0.14	0.15	0.04	0.04
TiO <sub>2</sub>	0.6	0.4	0.41	0.49	0.65
Na <sub>2</sub> O	1.8	0.9	1.85	1.2	1.75
K <sub>2</sub> O	0.62	0.3	0.15	1.28	1.52
P <sub>2</sub> O <sub>5</sub>	0.03	0.02	0.05	0.02	0.03
<b>ppm</b>					
Cr	200	30	24	72	98
Ni	43	25	16	10	13
V	250	240	230	300	300
Zr	28	22	21	31	35
Y	4	8	8	8	9
Nb	1	2	2	2	2
Sc	38	35	38	39	37
Ba	80	60	48	94	100
Σ REE	<10	<10	<10	<10	<10

higher than that of the porphyry - Cu deposit of the Skouries (average 250 ppm Se, calculated from data reported by Eliopoulos and Economou-Eliopoulos, 1991).

#### 4. DISCUSSION AND CONCLUSIONS

An important class of sulfide deposits is thought to have been formed at or near the discharge vents of submarine hydrothermal systems. The result of the heating and interaction of solutions with the rocks is a reduced, slightly acid saline solution that contains ore metals, as it is rising along a zone of high permeability. Physicochemical changes to the hydrothermal solutions, near to the surface, included their mixing with sea or pore water, caused precipitation of sulfide mineralization and gangue minerals. Among the main factors controlling the trace element content in sulfide mineralization is considered to be temperature, redox and/or pH conditions (Scott et al., 1990).

Auclair et al., (1987) based on the Se distribution in different mineral assemblages, components of Fe-Cu-rich massive sulfides, at NE Pacific Rise, concluded that relatively high temperature, low  $fO_2$  and low pH during precipitation of chalcopyrite and Zn-sulfides are optimal for Se incorporation in the structure of sulfides. Huston et al., (1995) suggest that differences in the Se content between Cu-rich and Cu-poor zones of those sulfide deposits can be caused by variation in the degree of the fluid evolution rather than temperature changes. More specifically, the lower Se content in the Cu-poor sulfides has been attributed to more evolved seawater, with a minimal magmatic input of Se and S, either from magmatic volatiles or

from leached volcanic rocks. In addition, they suggest that sulfides deposited from oxidized fluids should have high and variable Se content.

Data obtained on the content of Se and associated metals on the sulfide samples collected for this study, in combination with data from the literature (Hawley and Nichol, 1959; Scott et al., 1990; Huston et al., 1995), indicate that values for Cu, Zn and Se in the Kondro sulfides are considerably higher than the ones found in other sea floor sulfide deposits (Table 1; Scott et al., 1990). On the basis of factor analysis of selected geochemical data, a positive interelement correlation ( $r > 0.78$ ) between Se and Cu and Zn, coupled with its association with chalcopyrite, bornite and to a lesser extent with sphalerite, which mainly occurs as mass cutting a matrix of pyrite-chalcopyrite, appears to support a correlation of Se with temperature, which may be related with a later stage of mineralization penetrating earlier minerals (pyrite). The presence of chalcopyrite exsolutions in bornite, and the low content of iron (0.2 wt % Fe) in the associated sphalerite are considered to indicate a low temperature, around 220 °C (Skounakis et al., 1980). However, the observed wide variation in the Se level in the area of Kondro and the presence of sulfide mineralization which are also of low temperature (about 150°C), like those in Ermioni (Sideris and Skounakis, 1987) which have much lower Se content (Economic-Eliopoulos and Eliopoulos, 1996), may indicate that such variation cannot be caused only by temperature changes. Although more geochemical research is required to define the Se level in each mineral phase and factors controlling the distribution of selenium in sulfide mineralizations related with ophiolites, the present geochemical characteristics, may suggest that chalcopyrite and bornite are the main collectors of Se and that the Se level in sulfide mineralizations depends mainly on the composition of the hydrothermal fluids. Also, the presence of significant concentrations of Se and other trace elements (Au, As, Mo, Sb, Hg, Zn), and the low Pt-Pd concentrations in both areas Perivoli and Kondro (Table 1), point to their common origin, e.g. precipitation from a circulating hydrothermal system.

Considering the chemical composition of the brecciated diabase, with the disseminated pyrite mineralization, formed by the circulation of a hydrothermal system, given the low Pt (and Pd, Au) content of that rock type in ophiolite complexes, the Pt-enrichment is probably derived by leaching from a rock-source with initially much lower Pt content. In addition, the observed variation in the Pt content in the analyzed samples may reflect heterogeneity in the permeability of the hydrothermal circulation zones and/or variable water/rock proportion. Moreover, the enrichment in the more altered samples of the Pt only may indicate a redistribution and precipitation of Pt under different conditions than those favorable for Au, Pd and REE, during a multistage evolution of the breccia pipe.

The significant Se content in the sulfide ores of Cyprus type, may indicate that Se could influence on the environment around, the mining areas and exploration galleries.

The presence of sulfide ore within and around exploitation galleries in several places and their oxidation still remains a source of pollution. Heavy metals such as Cu, Zn, Co, Cd, Mn, Hg, As, V and Fe are transferred into stream sediments, soils, beach sands, surface waters and subsurface waters causing a significant pollution. More specifically, the waters coming throughout the galleries are characterized by a strong acid and oxidizing feature and a high concentration in Cu, Zn, Fe, Mn and sulphate ions. The contamination along rivers, in the alluvial deposits their close vicinity are probable.

Besides the pollution of the environment by heavy metals around exploration and exploitation galleries, the significant Se content in the Cyprus-type sulfides may effect positively the environment. Such a high content of Se in concentrates of chalcopyrite (2500 ppm) seems to be an encouraging economic factor for that type of mineralization, taking into consideration that it may be recovered along with other trace elements (Au) as a by-product although the main economic product is still copper. Therefore, the significant Se concentrations in this type of sulfide deposits may contribute to the reduction of the Se deficiency in agricultural regions, either in the immediate vicinity of oxidized sulfide deposits or/and by the addition of commercial fertilizers in order to increase the Se concentrations in plants.

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