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PENTLANDITE MINERALIZATION RELATED TO ALBANIAN OPHIOLITES

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Abstract: The Jurassic ophiolites in Albania are characterized by several mineralization types including chromites, Fe-Ni-Cu sulfides and arsenides, Fe-Ti-minerals and minerals of the Platinum Group Elements (PGE). Pentlandite-bearing mineralization is related to upper mantle serpentinized harzburgites, chromitite deposits associated with upper mantle dunites, dunites of the supra-Moho zone, ultramafic-mafic intrusions (wehrlites, lherzolites, pyroxenites and gabbros) and to cumulate layered sequences of olivine-gabbros and gabbronorites. Pentlandite occurs in several mineral associations including Ni-bearing sulfides, Fe-Ni-Cu-Co-PGE-bearing sulfides and chromite + Ni-bearing sulfides + PGM. It accompanies chromite, olivine, pyrrhotite, chalcopyrite, cubanite, magnetite, native copper, valleriite, mackinawite, heazlewodite, millerite and PGM. The chemical composition of pentlandite (metal:sulfur ratios, Fe:Ni ratios and Co and PGE contents) is variable depending on the geological setting, mineral associations and textural relationships. It is suggested that the pentlandite-bearing mineralization hosted within chromitite deposits, related to upper mantle dunites and dunites of the supra-Moho zone, is of primary magmatic origin, but the one hosted within upper mantle serpentinized harzburgites, ultramafic-mafic intrusions and to cumulate layered sequences of olivine-gabbros and gabbronorites is genetically related to hydrothermal activity combined with serpentinization processes, which played an essential role for the remobilization of some elements from the host rocks and the transformation of primary sulfides and PGM.

Keywords: Albania, ophiolites, pentlandite, serpentinization, remobilization.

1. Introduction

Albania represents the connecting segment between the Dinarides and the Hellenides. The principal feature of Albanian geology is the presence of a widespread ophiolitic complex, related to important mineral deposits. This ophiolitic complex covers an area of about 4200km^2, representing one of the biggest exposures of oceanic lithosphere in the Mediterranean area. Triassic rifting was followed by intensive development of ophiolitic magmatism during the Middle Jurassic. The ophiolitic complex is partly covered by Cretaceous, Paleogene and Neogene sedimentary rocks. The Albanian ophiolitic complex is composed of two ophiolitic belts, a western and an eastern one, with a transitional zone displaying mixed petrologic features. The western ophiolite belt is characterized by the presence of high-Ti basaltic pillow lavas and corresponds to Jurassic oceanic lithosphere, constructed along a mid-ocean ridge (MORB ophiolite type). The ophiolites of the eastern belt include low-Ti volcanic rocks with geochemical features typical of Island Arc Tholeiites (IAT). The eastern ophiolite belt is considered to have been formed in a supra subduction zone (SSZ) (Shallo et al. 1995) by a high percentage of partial melting in the mantle source. This ophiolite belt is characterized by harzburgites-dunites (enriched in Mg and depleted in Si, Ca and Al as a result of a strong partial melting of the upper mantle), by the presence of supra-Moho dunites (some hundred meters thick), and finally the presence of a zone with ultramafic-mafic intrusions. In addition, in the two ophiolitic belts of the northern part of Albania, cumulate sequences of gabbroic rocks, quartz diorites, diorites and plagiogranites, as well as sheeted dykes and basaltic pillow lavas occur.

2. Mineralization

Harzburgites and dunites in the eastern ophiolite belt display a high chromite-bearing potential, whereas the mafic volcanic sequences include abundant copper-bearing mineralization. Pentlandite-bearing mineralization within various associations of Fe-Ni-sulfides/arsenides, Fe-Ni-Cu-bearing sulfides and PGM is hosted either within upper mantle ultramafic rocks, or within ultramafic-mafic intrusions at the mantle-crust transition zone. The sulfide minerals occur as interstitial grains in chromitites of both upper mantle ultramafic intrusions and supra-Moho dunites and as Fe-Ni-Cu-mineralizations related to troctolite-gabbro sequences. The Fe-Ni- and Fe-Ni-Cu mineralization associated with PGM is situated mainly in the eastern ophiolite belt of Albania, particularly in Bulqiza and Kom-Tropoja ultramafic massifs. In the southern part of Bulqiza massif, pentlandite mineralization related to the supra-Moho dunites is composed of disseminated sulfides (1-5 vol. %) associated with disseminations and bands of chromite (Fig. 1). A similar PGE-bearing mineralization of disseminated Ni-sulfides is related to "black dunites" at the northwestern part of this massif, as well as with spatially associated ultramafic-mafic intrusions, such as plagioclase harzburgites, lherzolites, wehrlites and even gabbros. Within veins of gabbros crosscuting chromitite bodies, disseminations of Ni-Cu sulfides and native copper occur. At the Kom-Tropoja ultramafic massif pentlandite-

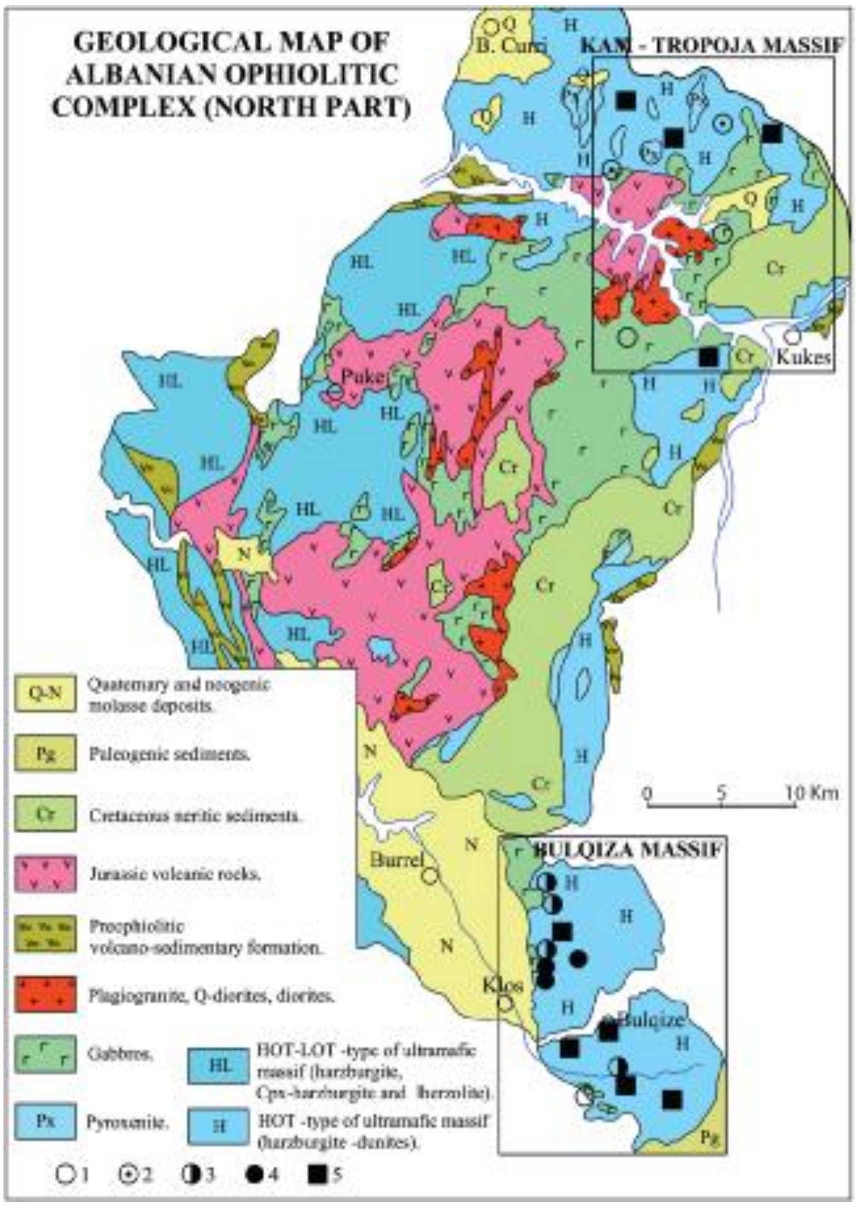

Fig. 1. Geological map of the ophiolitic complex of Albania, northern part. 1: Fe-Ni-Cu mineralization related to gabbro-troctolites; 2: Fe-Ni-Cu mineralization related to serpentinites; 3: Fe-Ni-Cu-PGE mineralizetion related to supra-Moho dunites; 4: Fe-Ni-Cu-PGE mineralization related to chromitites; 5: Chro-

bearing mineralization of the Fe-Ni-sulfide type is related to serpentinites. The lenticular ore bodies are composed of massive sulfide minerals, mainly pyrrhotite and pentlandite. These are the product of hydrothermal activity and serpentinization processes resulting of remobilization and modification of magmatic sulfides. Lenticular- to vein-shaped ore bodies, composed of Fe-Cu- Ni-rich massive sulfides are hosted within troctolite-gabbros in proximity to the ultramafic rocks.

Sulfides hosted within the dunites from the supra-Moho zone display the highest PGE contents ranging from 650-690 ppb to 2410 ppb and even 8400 ppb (Ohnenstetter et al. 1991; Karaj 1992; Burgath et al. 2002), with Pt/Pd ratios at 0.33. The Au content varies from 680 to 1600ppb. The chromite + sulfide ores are distinguished by the presence of low PGE contents (up to 820 ppb), higher Pt/Pd ratios (1.5 to 6), and very low Au contents. The Cu/(Cu+Ni)- and Ni/Co ratios for the Ni-sulfide ores from the supra-Moho dunites vary within values from 0.1 to 0.15, and from 20 to 25 respectively. These values are clearly distinct from similar mineralization in other Mediterranean regions (e.g. Tsangli/Eretria, Greece and Pevkos and Laxia to Mavrou/Limassol Forest, Cyprus). In contrast, the massive Fe-Ni-Cu sulfide mineralization related to serpentinites and troctolite-gabbro sequence displays intermediate Cu/(Cu+Ni) ratios (0.4 to 0.5), and high Ni/Co ratio (15 to 20), similarly to those from Cyprus and Greece ores, where later hydrothermal-serpentinization processes played a major role.

Table 1. Electron microprobe analyses of pentlandite and some other minerals from the ophiolitic complex of Albania (in wt. %, atoms).

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13
	41C	215K	195K	279K	266K	993C	991C	992C	60C	997C	42C	46C	64C
S	30.87	32.12	32.19	33.44	30.67	33.50	32.40	32.40	32.70	35.90	0.39	34.84	26.42
As	0.12	-	0.11	0.03	0.06	0.01	0.02	0.02	-	-	-	0.06	0.26
Fe	38.14	44.09	39.53	21.97	19.48	40.90	34.90	37.70	24.60	58.30	26.41	1.06	0.30
Ni	27.86	22.42	26.15	44.69	31.86	22.40	18.70	19.90	19.50	3.85	72.10	56.83	71.03
Co	0.34	0.43	0.37	0.51	2.53	3.16	13.60	8.60	23.00	1.02	0.06	0.07	-
Cu	-	0.21	0.02	0.36	0.04	0.01	0.04	0.02	0.02	0.08	0.53	0.08	-
Os	-	0.04	-	0.41	0.14	-	-	-	-	-	-	0.19	-
Ir	0.15	-	0.29	-	13.12	-	-	-	-	-	-	-	-
Ru	0.07	-	-	-	0.42	-	-	-	-	-	-	-	-
Pt		0.51	0.11	-	-	-	-	-	-	-	-	-	-
Pd	0.03	-	-	0.12	0.33	-	-	-	-	-	-	0.22	-
Total	97.58	99.82	98.77	101.50	98.65	99.98	99.66	98.64	99.82	99.15	99.49	96.78*	99.55*
S	7.681	7.793	7.881	7.99	7.997	8.041	7.870	7.888	7.956	0.996		1.036	2.015
As	0.012		0.012		0.018							0.001	0.009
Fe	5.447	6.131	5.56	3.09	2.929	5.627	4.861	5.27	3.434	0.93	1.106	0.018	0.013
Ni	3.785	2.969	3.497	5.83	4.619	2.924	2.452	2.652	2.584	0.058	2.873	0.923	2.959
Co	0.046	0.057	0.049	0.062	0.357	0.411	1.802	1.19	3.026	0.015	0.002		
Cu		0.026	0.002	0.01	0.06					0.001	0.019	0.001	
Os		0.002		0.007	0.008							0.001	
Ir	0.006		0.012		1.034								
Ru	0.005				0.019								
Pt		0.02	0.04										
Pd	0.018			0.007	0.002							0.02	0.003
Atoms	17	17	17	17	17	17	17	17	17	2	4	2	5
M/S	1.21	1.186	1.152	1.109	1.12	1.115	1.162	1.135					
Fe/Ni	1.439	2.065	1.585	0.529	0.634	1.924	1.959	1.989	1.329				
Fe_9S_8	58.7	67.23	60.99	34.57	44.3	62.81	53.18	57.84	37.98				
Ni_9S_8	40.8	32.47	38.47	65.25	51.73	32.64	27.12	29.1	28.56				
Co_9S_8	0.5	0.3	0.54	0.18	3.97	4.55	19.7	13.06	33.46				

1-3: Pentlandite from sulfide mineralization related to supra-Moho dunites; 4, 5: Pentlandite from sulfide mineralization related to upper mantle chromitites; 6-8: Pentlandite from sulfide mineralization related to serpentinites; 9: Pentlandite from sulfide mineralization related to gabbro-troctolite; 10: Mackinawite from transformed pentlandite; 11: Awaruite; 12: Millerite; 13: Heazlewoodite. * The sample nr. 12 contains 3.52% Cr_2O_3 whereas sample nr. 13 contains 1.34% Cr_2O_3 which are excluded from the calculation of the analysis considered as contamination mixtures.

2. Mineral associations and textural features

According to the geological setting of the mineralization, pentlandite is associated to a large group of minerals, (e.g. chromite, magnetite, delafosite, pyrrhotite, chalcopyrite, cubanite, digenite, millerite, heazlewoodite, mackinawite, valleriite, native copper, awaruite, ferrite and PGM). Pentlandite from the Ni-sulfide mineralization related to the supra-Moho dunites is associated with chromite, magnetite, awaruite and native copper. It occurs, as interstitial, irregular shaped grains surrounding the chromite and olivine grains (Fig. 2a). In some cases, minute pentlandite grains are enclosed within chromite grains. Usually, the pentlandite grains are crosscut along cleavage planes by magnetite and ferrite veinlets and are surrounded by thin awaruite rims (Fig. 2b). Some native copper and delafosite grains occur in a serpentine groundmass, whereas fibrous aggregates of valleriite occur within pentlandite grains (Fig. 2c). The Fe-Ni-Cu-PGE sulfide mineralization related to the "black dunites" and ultramafic/mafic intrusions is composed of pyrrhotite, chalcopyrite, pentlandite, heazlewoodite, magnetite, native copper and PGM. Pentlandite is interstitial to chromitite surrounding and cementing chromite grains (Fig. 2d). Both minerals are crosscut by pyrrhotite and magnetite veinlets (Fig. 2e). Some composite pentlandite und sperrylite inclusions (Fig. 2f) occur within chromite grains. Minute pentlandite inclusions occur within laurite grains or the opposite (Fig 3a). The pyrrhotite,

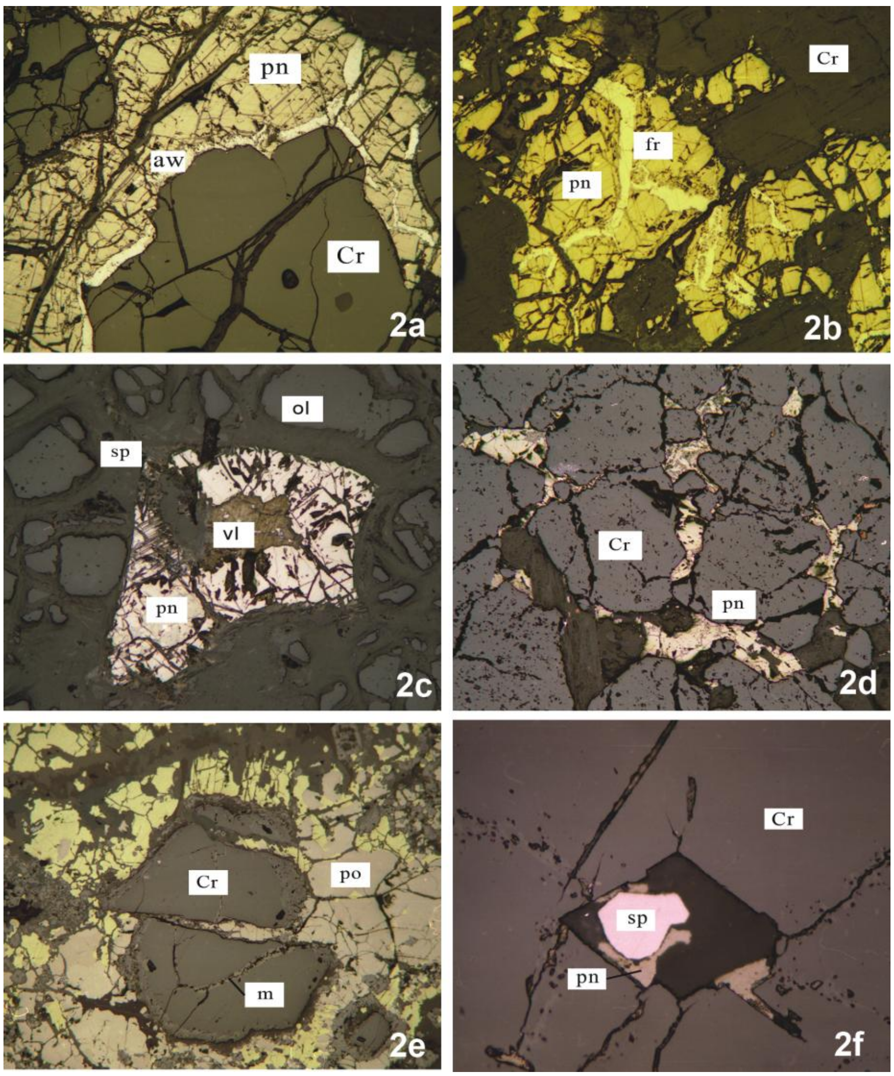

Fig. 2. (a) Intergranular pentlandite (pn) and chromite grains (cr) surrounded by awaruite rim (aw); (b) Ferrite veinlet (fr) crosscuting pentlandite grain (pn); (c) Pentlandite grain (pn) replaced by valleriite (vl).; (d) Pentlandite (pn) interstitial between chromite grains (cr); (e) Chromite grain (cr) intersected by pyrrhotite (po) and magnetite (m); (f) Composite inclusion of pentlandite (pn) and sperrylite (sp) included in chromite (Cr).

chalcopyrite and native copper occur within gabbro veins crosscutting chromitite ore. Pentlandite from the serpentinite-hosted sulfide mineralization is associated with hexagonal pyrrhotite, magnetite, native copper and mackinawite, valleriite. The groundmass is composed of pyrrhotite, whereas exsolved euhedral pentlandite grains occur as fine lenticular inclusions. The pentlandite grains are surrounded and intersected by magnetite and native copper (Fig. 3b). Usually, pentlandite is transformed partialy, into mackinawite (Fig. 3c, d).

Needle-like aggregates of valleriite fill cleavage planes of silicates (Fig. 3e). Pentlandite from the sulfide mineralization related to gabbro-troctolites is accompanied by pyrrhotite, cubanite, chalcopyrite, magnetite and mackinawite. Some small pentlandite grains included in pyrrhotite have an intensive pink color and higher reflectance index in comparison to usual pentlandite, being the result of its high Co content (up to 23 wt. %). Composite pentlandite and pyrrhotite lamellae are interpreted as exsolution products. Two types of pyrrhotite are distinguished, the first as groundmass and the second in the form of lamellae. Twinned chalcopyrite includes lamellae of cubanite and pyrrhotite as exsolution products (Fig. 3f).

3. The chemical composition of pentlandite

The chemical composition of pentlandite (met-

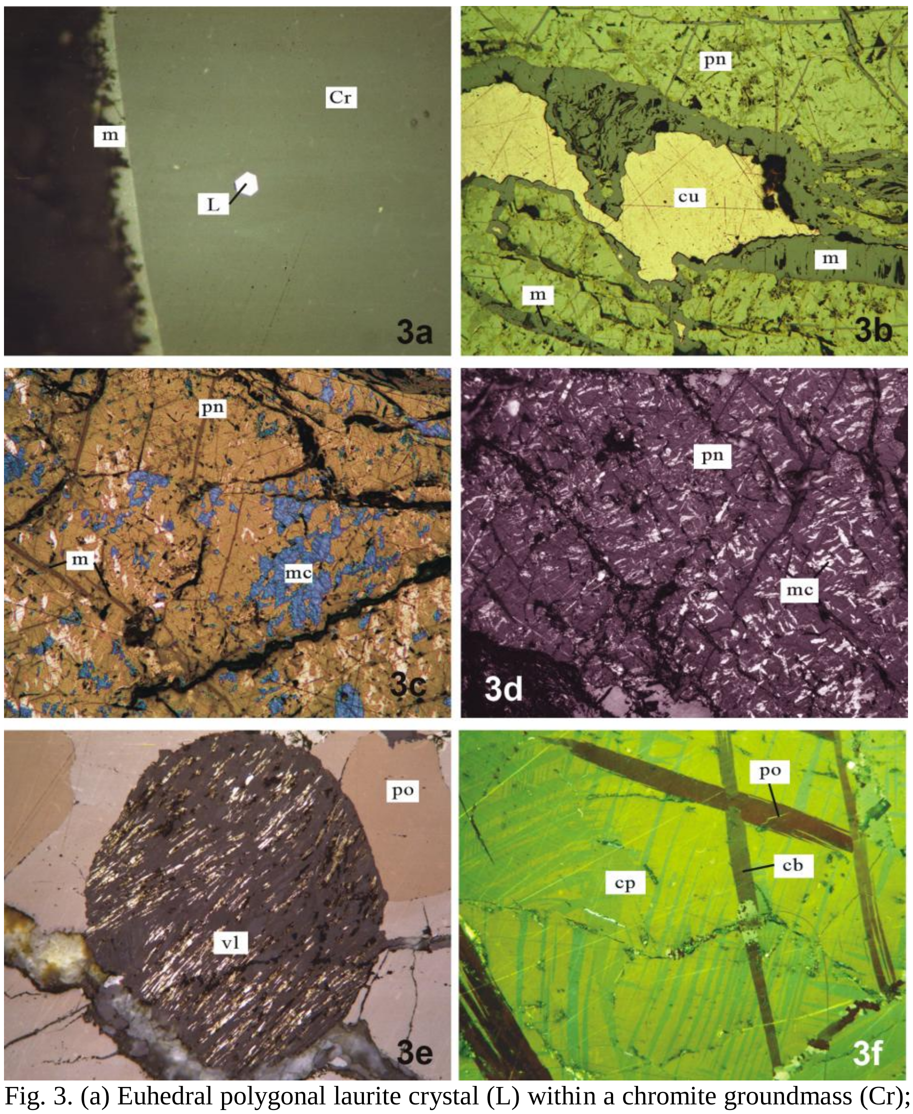

Fig. 3. (a) Euhedral polygonal laurite crystal (L) within a chromite groundmass (Cr); (b) Native copper (cu) surrounded by magnetite rim (m) within pentlandite (pn); (c) Pentlandite (pn) partially transformed into mackinawite (mc) (crossed nicols); (d) Pentlandite (pn) replaced along octahedral cleavage planes by mackinawite (mc) (crossed nicols); (e) Needles of valleriite (vl) along cleavage planes of silicate grain within coarse-grained pyrrhotite (po) (crossed nicols); (f) Pyrrhotite (po) and cubanite (cb) lamellae within twinned chalcopyrite groundmass (cp) (crossed nicols).

al/sulfur ratios, Fe/Ni ratios and Co, PGE contents) from various geological settings, associations and textural relationships, was examined by electron microprobe analyses at the MGA Department of B.R.G.M-Orleans and presented in Table 1. The metal/sulfur ratios vary from 1.115 to 1.210 (ideal ratio is 9/8 = 1.125). The Fe/Ni ratios are usually > 1 and reach values up to 2.065. In two samples the Fe/Ni ratios are <1 (0.529 to 0.634). According to the Co content pentlandite is characterized as low-Co (up to 0.5wt. %), medium-Co (from 2.53 wt. % to 3.16. %) and high- to very high-Co (from 8.5 wt. % to 23 wt. %) (Tab. 1). Another feature of pentlantide is the presence of PGE mainly Ir (up to 13.12 wt % according to Karaj 1992). Mackinawite derived from transformation of pentlantide, contains abundant Ni and Co (3.85 and 1.0 wt. % respectively, Tab. 1). Awaruite rimming pentlandite grains has Ni/Fe ratios 3:1. Millerite and heazlewoodite that associates the pentlandite have low PGE contents (Tab. 1).

There is a relationship between pentlandite composition and geological setting: The pentlandite related to supra Moho dunite + sulfide mineralization is Fe-rich containing up to 44.09 wt. % Fe (Tab. 1, analyses Nr 1-3, Fig. 4). The Ni content reaches values up to 27.86 wt. % and the Co content is very low (< 0.43 wt. %). Pentlandite from the massive pyrrhotite-pentlandite mineralization hosted within serpentinites, displays a similar to the above Fe and Ni contents. However, it is distinguished by higher Co contents ranging from 3.16-8.6 wt. % for granular pentlandite (Tab. 1, analyses 6 and 8), up to 13.6 wt. % for the fine lenticular exsolved inclusions of pentlandite hosted within pyrrhotite (Tab.1, analysis 7). Integranular pentlandite related to upper mantle chromitites displays the highest Ni contents (up to 44.09 wt. %), whereas the Fe contents are very low (up to 21.97 wt. %) (Tab. 1, analyses 4 and 5). Finally, the pentlantide from the pyrrhotite-cubanite-chalcopyrite association, related to gabbro-troctolites close to ultramafic rocks, is characterized by very high Co contents (up to 23 wt.%) and low Fe and Ni contents (Tab. 1, analysis 9, Fig. 4).

The following is a comparison of pentlandite compositions from the Albanian ophiolitic complex with those from ophiolites in other Mediterranean regions: Pentlandite of Tsangli/Eretria, Greece contains variable amounts of Co (from 2.8 wt. % to 28 wt. %), depending on its associations with chromite, magnetite or pyrrhotite (Economou and Naldrett 1984). The pentlantide from the Fe-Ni-Cu-Co mineralization of Pevkos/Limassol Forest, Cyprus contains relatively low Co abundances, whereas the Fe content predominates over Ni (Panayiotou 1980; Foose et al.1985; Thalhammer et al. 1986). These contents are almost similar to those from pentlandite related to chromitites and sulfides of serpentinites from Albania. The pentlandite of the Laxia to Mavrou, Cyprus sulfide mineralization is characterized by the highest Co contents (23.24 wt. %) and low Fe and Ni abundances (Thalhammer el al., 1986), similarly to pentlandite of massive sulfide mineralization related to gabbro-troctolites of Albania. It must be noted that pentlandite of Ivrea-Verbano (Italy) related to stratiform intrusions, has very low Co contents (0.6 to 1 wt. %) and is Fe-rich (Garuti et al. 1986), similar with pentlandite related to dunite + sulfide mineralization of Albania.

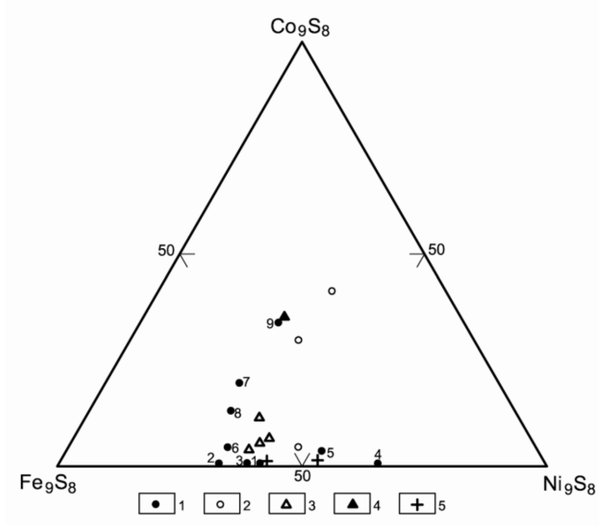

Fig. 4. Ternary Fe_9S_8-Ni_9S_8-Co_9S_8 plot of pentlandite compositions (in At. %) in Albanian and other Mediterranean ophiolites. 1. Pentlandite-bearing mineralization of Albania (dots 1-9); 2. Tsangli/Eretria, Greece (Economou and Naldrett 1984); 3. Pevkos/Limassol Forest, Cyprus (Panayiotou 1980; Foose et al., 1985; Thalhammer et al., 1986); 4. Laxia to Mavrou/Limassol Forest, Cyprus (Thalhammer et al., 1986); 5. Ivrea Verbano, West Alps, Italy (Garuti 1986).

4. Discussion

On the basis of the geological setting, ore body morphology, mineral associations, mineralogy and textural relationships, it can be concluded that the Ni-sulfide mineralization of the Albanian ophiolitic complex is not only the consequence of primary magmatic mineral-forming processes, but it is also related to processes of deformation, hydrothermal alteration and serpentinization. The later processes caused remobilization of elements and transformation of primary minerals as a result of hydrothermal fluid circulation through the host rocks. The pentlandite-bearing mineralization from the Albanian ophiolitic complex can be subdivided into two types: (1) the Ni-sulfide mineralization related to chromite bands and disseminations hosted within supra Moho dunites, contain pentlandite grains are interstitial between chromite and olivine and are crosscut by magnetite, awaruite and ferrite veinlets. Pentlandite contains substantial amounts of Fe, resulting in very high Fe/Ni ratios (1.44 to 2.07 apfu) and it is characterized by remarkable low contents of Co (less than 1.0 wt. %). The ore is characterized by quite low Cu/(Cu+Ni) ratios (from 0.1 to 0.15), very high Ni/Co ratios (from 20 to 25) and high PGE contents (from 2410 ppb to 8400 ppb), with Pt/Pd ratios at 0.33 (Ohnenstetter et al. 1991; Karaj 1992). These geological-mineralogical features of Ni-sulfide mineralization related to supra-Moho dunites are indicative of a magmatic origin (Naldrett 1981). Similarly, the Ni-sulfide mineralization related to upper mantle chromitites is also suggested to be of primary magmatic origin. It is characterized by a predominance of Ni over Fe (Fe/Ni ratios from 0.53 to 0.63) and by high Ni/Co ratios in pentlandite. (2) The other type of pentlandite-bearing mineralization is represented by lenticular and vein ore bodies related to serpentinites along faults and troctolite-gabbro crustal sequences. The massive sulfide ores are composed of pyrrhotite and pentlandite, as well as pyrrhotite, cubanite, chalcopyrite associated with magnetite, mackinawite, valleriite and native copper, as secondary minerals. Based on the Cu/(Cu+Ni) ratios (0.4 to 0.5) and the Ni/Co ratio (~2), this mineralization is considered to be of a hydrothermal origin, as suggested for similar mineralization in other ophiolitic complexes in the Mediterranean region (Çina 1981, 1990; Foose et al. 1985; Thalhammer et al., 1986).

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