

PGE MINERALIZATION RELATED TO ALBANIAN OPHIOLITIC COMPLEX

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Four types of PGE mineralization related to the Jurassic ophiolitic complex of Albania are distinguished. They belong to different lithotypes of the petrologic section and are characterized by their proper elementary and mineral assemblages. A fractionation of PGE from mantle to cumulates is evidenced which is explained by the evolution of the mineralizing system from the mantle to cumulates under different conditions of fO_2 and fS_2 .

INTRODUCTION

The ophiolitic complex of Albania lies between the western and eastern mediterranean segments of ophiolites. Outstanding features are its complete lithological sequences and related metallogeny especially the high chrom-bearing potential. Some PGE mineralizations related to chromitites and the other types as well are discovered too.

The concentration of PGE varies from 250 ppb, sometimes reaches 11100 ppb. PGM grains have usual sizes 3-10 microns, to uncommon 50-100 microns. The different types of PGE mineralizations are characterized by various $Pt/(Pt+Pd)=0.26$ to 0.92 and $(Pt+Pd)/(Ru+Os+Ir)=0.07$ to 0.8 ratios (Çina, 1989; Ohnenstetter et al., 1991; Neziraj 1992; Karaj 1992; Çina et al., 1995). The normalized models of PGE versus chondrites show different trends being similar to the ophiolitic chromitites as well as of the stratiform complexes. The numerous phases of nativ elements and PGE, BME alloys and their sulphides, sulphoarsenides, arsenides and in some cases telurides of PGE are present.

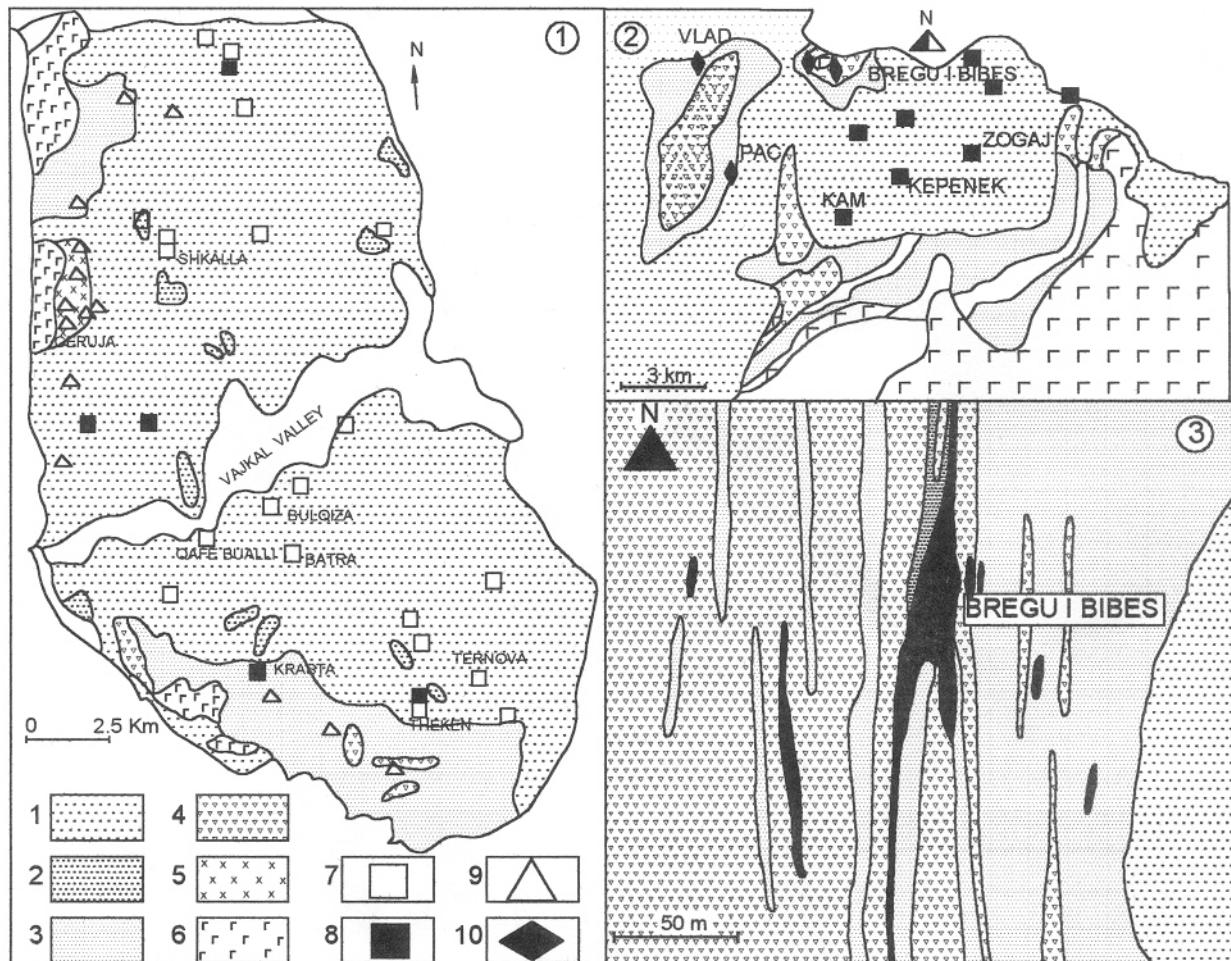
GEOLOGICAL SITUATION OF PGE MINERALIZATION TYPES

Two ophiolite belt are well distinguished in Albania: The eastern one and the western one, showing petrological and metallogenic differences. The eastern belt has a depleted mantle with harzburgite and dunite having undergone high-grade partial melting, a high chrome-bearing potential mainly of the Cr-rich metallurgical type. The ultramafics of the western belt are less depleted, being composed of harzburgites and lherzolites affected by a low-grade partial melting of the upper mantle (5 to 7 %) (Çina, 1987). The metallogenic potential of this belt is very limited and the chromitites are mainly of the Al-rich refractory type. Regarding the PGE-bearing the Bulqiza and Tropoja massifs are the most important. Bulqiza massif is of harzburgite-dunite type. Its main part, the eastern and central ones consist of mantle harzburgite with dunite intercalations, and southern and western parts consist of dunites, wherlites, pyroxenites and gabbros (fig.1).

Tropoja massif is of harzburgite-dunite type where besides these mantle rocks, the transition dunites and the cumulates-represented of dunites, plagioclase harzburgites, pyroxenites, wherlites, lherzolites and gabbros are also present (Fig.2). Just related to cumulate sequence the typical Pt-mineralization of Bregu i Bibes occurs (Fig.3) (Ohnenstetter et al., Neziraj, 1992). Frequently the PGE-bearing rocks and chromitite have a breccias-magmatic view due to the presence of numerous veins of pyroxenites and gabbros.

Different mineralogical-geochemical features and relation with specific ultramafic sequence permit to distinguish some PGE mineralization types (Çina 1989, Ohnenstetter et al., 1991, Çina et al., 1995):

I- (Ru+Os+Ir) related to the mantle chromitites; II- (Pt + Ru+Os+Ir) related to the upper mantle chromitites; III- Pd related to BMS (pentlandite) - dunite of supra Moho; IV- Pt related to the interface chromitite-dunite-pyroxenite cumulates.



Geological map of Bulqiza (1) and Tropoja (2) ultramafic massifs and Bregu i Bibes PGE mineralization (3).

1- Mantle harzburgites; 2 - Mantle dunites; 3 - Transition zone dunites; 4 - Pyroxenite; 5 - PI - harzburgites, lherzolites, wherlites; 6 - Gabbro rocks; 7 - PGE - mineralization type I; 8 - PGE - mineralization type II; 9 - PGE - mineralization type III; 10 - PGE - mineralization type IV. (Çina, 1989; Neziraj, 1992; Karaj 1992; Çina et al., 1995).

GEOCHEMICAL - MINERALOGICAL FEATURES OF THE PGE MINERALIZATION

The four types of PGE mineralization are distinguished due to elementary and mineral composition. The PGE values become higher from the deep mantle chromitites to the ones of uppermost levels and specially for BMS and the IVth type of the cumulate sequences, respectively from 160-350 ppb, 580-2050 ppb, 2195-8820 ppb to 1943-9730 ppb. For the type I Ru, Os and Ir are predominant, up to 90 %; in the II one, Ru, Os, Ir and Pt are main constituent; in the III one Pd predominates, more than 90 % and in the IV one Pt is more frequent, up to 80 %.

For the type I PGE mineralization, the I-PGE subgroup predominates clearly versus P-PGE subgroup: $(Pt+Pd)/(Ru+Os+Ir)$ ratio is less than 0.10. In the I-PGE subgroup the Ru is predominant: $Ru/Ir=2.8$ and $Ru/Os=3.2$. Similarity in the subgroup P-PGE, Pt predominates versus Pd: $Pt/(Pt+Pd) = 0.65$ up to 0.75.

For the type II P-PGE predominates, but the I-PGE subgroup is present too. Pt predominates over Pd, like for the type I ($Pt/(Pt+Pd) = 0.65$ up to 0.75). In the type III the P-PGE predominates over I-PGE subgroup as is shown by the high $(Pt+Pd)/(Ru+Os+Ir)$ ratio of 50 to 80. In the P-PGE subgroup, Pd predominates over Pt, to give $Pt/(Pt+Pd)$ ratio = 0.26 to 0.32 .

	Pt/ (Pt+Pd)	(Pt+Pd)/ Ru+Os+Ir	Cr/ (Cr+Al)	PGE CHARACTERISTICS	MINERAL ASSEMBLAGES
CUMUL. SEQUENC. TROCTOL. OL-GABB.					
PYROX. DUNIT CHROM. TYPE IV	0.82-0.92	14-16	0.78	P-PGE Pt SIMILAR WITH Pt- ENRICHED CHROMITITES FROM SHETLAND, QUEBEC, NORWAY, URALS	ISO FERROPLATINUM TETRA FERROPLAT. ALLOYS OF Pt,Pd,Rh, Fe,Ni,Cu, SULPHIDES AND ARSENIDES
MASSIVE DUNIT BMS TYPE III	0.26-0.32	50-80	0.82	P-PGE Pd SIMILAR WITH BUSHVELD AND STILLWATER STRATIFORM COMPLEX	Pd-PENTLANDITES
UPPER MANTL CHROM. BMS TYPE II	0.60-0.75	0.3-0.7	0.80	P-PGE AND I-PGE Pt and Ru, Os, Ir TRANZITORY TYPE BETWEEN TYPES I AND IV	SULPHIDES AND ARSENIDES OF Pt; PGE ALLOYS
MIDDLE MANTLE CHROMIT. TYPE I	0.65-0.75	0.07	0.78	I-PGE Ru,Os,Ir SIMILAR WITH GREECE, TURKEY AND OMAN CHROMITITES	ALLOYS OF Ru, Os, Ir; SULPHIDES OF Ru
DEEP MANTLE CHROM.					

Fig. 4 - Elementary and mineral assemblage evolution through ophiolitic column, Albanian ophiolitic complex.

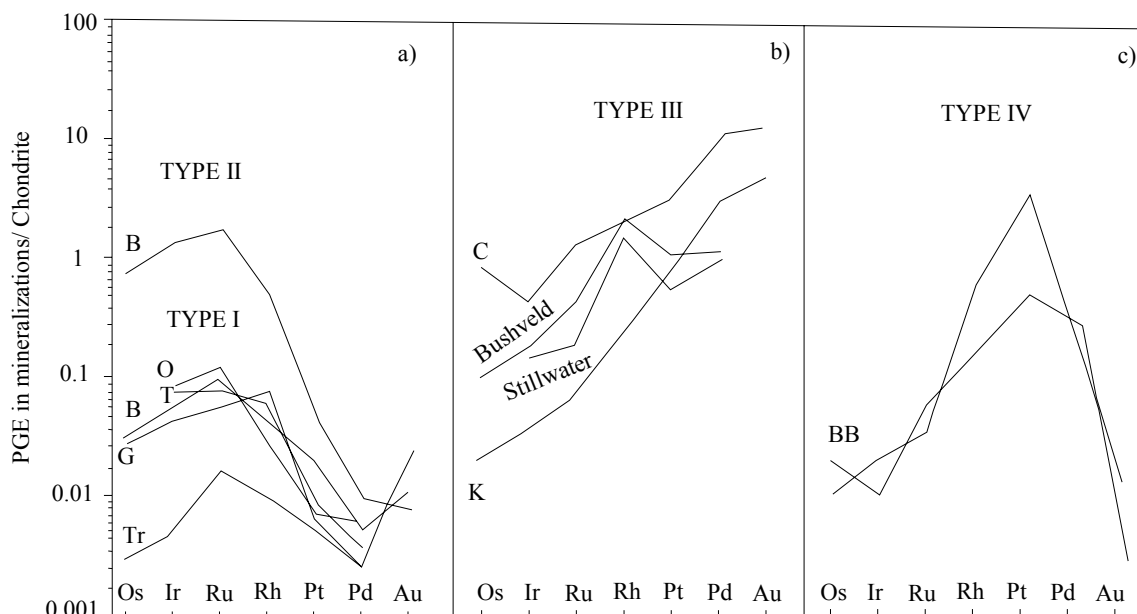


Fig. 5. Average chondrite normalized PGE concentrations from ophiolite complex of Albania (Çina, 1989; Ohnenstetter et al., 1991; Neziraj, 1992; Karaj, 1992) compared with other ophiolite complexes of Greece (G); Turkey (T) and Oman (O) as well with stratiform ones of Bushveld and Stillwater (after Page et al., 1982; 1984; Economou, 1984). a) Type I; B - Bulqiza, T - Tropoja; Type II, B - Bulqiza massif; b) Type III Krasta mineralization (K) and Cerruja one (C), Bulqiza massif; c) Type IV Bregu i Bibes mineralization (BB), Tropoja massif.

In the last, type IV the P-PGE subgroup again predominates, giving $(Pt+Pd)/(Ru+Os+Ir) = 14$ to 16, but Pt predominates over as is shown by the high Pd : Pt/(Pt + Pd) ratio 0.8 to 0.9, similar to the two first types of mantle chromitites (Fig.4).

Figure 5 shows the similarities and differences between the PGE mineralization of the Albanian ophiolitic complex and that of other ones. So, evident similarity can be seen between the mineralization related to the mantle chromitites of Bulqiza and Tropoja and that of Greece, Turkey and Oman with a negative trend for Pt and Pd reflecting the high consumption of upper mantle in these elements. The PGE occurrences of the second type have the same trend although with a higher content of I-PGE subgroup. The third type of Pd-mineralization related to BMS shows a similar trend to the stratiform complexes of Bushveld and Stillwater, i.e. an enrichment in P-PGE subgroup for the dunites with a positive trend for Rh, Pt and Pd. The fourth type is marked by a strong positive Pt anomaly due to high Pt and low Pd and Au contents.

A large group of PGM, especially those related to Type II and Type IV mineralization, is present in the Albanian ophiolitic complex. Different mineral phases are examined by scanning electron microscopy and analysed by microprobe analysis (Çina, 1989, Neziraj 1992, Karaj 1992, Çina et al., 1995). The main minerals are alloys, but some sulphide, sulphoarsenide, arsenide and teluride minerals of PGE+BME are also present:

Irid osmium	Os, Ir	Os0.463 Ir0.336.....
Rutheniridosmine	Ir, Os, Ru	Os0.375 Ir0.430 Ru0.174..
Ruthenium	Ru	Ru0.643 Os0.095 Ir0.071..
Platinum	Pt	Pt0.805 Rh0.042 Fe0.088...
Isoferroplatinum	Pt3Fe	Pt2.700 Rh0.180 Fe0.180 Cu0.068..
Unnamed	Pt2Fe	Pt1.790 Fe0.830 Rh0.216 Cu0.061..
Tetraferroplatinum	PtFe	Pt0.979 Fe0.867 Cu0.055 Ni0.036..
Unnamed	RhFe	Rh0.778 Fe0.770 Pt0.246 Pd0.084 Cu0.100..
Unnamed	Rh,Pt,Fe,Cu	Rh0.355 Pt0.324 Fe0.0627 Cu0.463..
Unnamed	PtCu2	Pt0.894 Cu1.785 Pd0.084....
Unnamed	PtCu3	Pt0.819 Pd0.095 Cu2.972....
Unnamed	Pt,Pd,Cu3	Pt0.533 Cu2.909 Pd0.467....

Unnamed	Pd2Cu	Pd1.750 Cu0.709 Au0.254 Pt0.166...
Unnamed	PdCu2	Pd0.866 Cu2.091 Pt0.040...
Unnamed	PdCu3	Pd0.515 Cu2.777 Os0.331 Pt0.277 Fe0.087...
Unnamed	(Pd,Rh),(Cu,Fe)2	Pd0.453 Rh0.373 Cu1.499 Fe0.478 Pt0.188...
Ni-Tulameenite	Pt2Fe(CuNi)	Pt1.953 Fe1.015 Cu0.648 Ni0.288....
Unnamed	PtNi2Fe	Pt1.037 Ni1.824 Fe0.974....
Unnamed	RuS	Ru0.717 Ir0.220 S1.017....
Unnamed	Ru(Fe,Cu)S	Ru1.018 Fe0.252 Cu0.489..S0.954....
Cuproiridsite	Ir2CuS4	Ir1.532 Rh0.384 Cu0.831 S3.959
Ni- Cuproiridsite	(IrNi,Cu)3S4	Ni1.079 Cu0.620 Ir1.089 Rh0.222..)S3.944
Kashinite	(Ir,Cu..)2S3	Ir0.900 Rh0.250 (Ru0.150 Cu0.450 Fe0.150...)S3.000
Cuprorhod-mallan.	(Cu,Pt,Rh)3S4	(Cu0.987 Pt0.917 Rh0.854...)S4.004
Bowieite	(Pt,Rh,Cu)3S4	(Pt0.690 Rh0.672 Cu0.668..)S2.928
Cooperite	PtS	(Pt0.684 Pd0.259..)S1.034
Ruarsite	RuAsS	(Ru0.733 Os0.208..) (S1.004 As1.007)
Irarsite	IrAsS	(Ir0.829...)(S0.996 As0.927)
Ru-platarsite	(Pt,Ru)AsS	(Pt0.431 Ru0.387 Rh0.153..)(S0.875 As1.058)
Ir-hollingworthite	(Rh, Ir)AsS	(Rh0.504 Ir0.400...)(S1.090 As0.923)
Unnamed	(Rh,Ni,Pd)3(AsS)4	(Rh1.185 Ni0.842 Pd0.664..)(S1.635 As2.265)
Unnamed	Ir(AsS)	(Ir0.628 Os0.252..)(S0.506 As0.554)
Anduoite	RuAs2	(Ru0.789 Os0.114..)As1.975
Unnamed	(Rh,Ni..)2As	(Rh1.102 Ni1.006 Cu0.513..)(As0.927 Te0.105)
Unnamed	Ir3Os2As	(Ir2.744Os2.079..)(As0.927 S0.021)
Unnamed	(Pd,Ni..)2As	(Pd1.080 Ni0.417 Ru0.240 Os0.105..)As0.960
Keithconnite	Pd3Te	(Pd2.900..)Te1.048
Unnamed	RhTe	(Rh0.747 Pd0.113 Cu0.135 Hg0.024..)Te0.952

The PGM usually occur as fine inclusions in host chromite grains. They were trapped during the chromite crystallisation. Only in a few cases are they observed at interstices between chromite and silicate mineral aggregates. The PGM grains are of various sizes: this the grains of PGM related to mantle chromitites are the finest with an average size of 2 to 5 microns. The size of PGM grains from Pt- mineralization related to the dunite-pyroxenite interface are extremely large, reaching 80 microns.

The PGM grains also have different shapes. They may be euhedral or subhedral usually with rounded angles. Some inclusions, and in particular laurite, erlichmanite, as well as Ru, Os, Ir and Pt, Fe alloys are monophasic grains, whereas others, such as sulphide, sulphoarsenide, arsenide minerals and complex alloys of PGE+BME, are polyphase aggregates. The textural relationships between mineral grains indicate the existence of mineral phase equilibrium; some compound aggregates are observed as the consequence of exsolution of the complex alloys; some sulphoarsenide and arsenide minerals underwent a late decomposition and have been transformed to secondary phases under new hydrothermal conditions (Neziraj, 1992; Karaj, 1992) (Plate I).

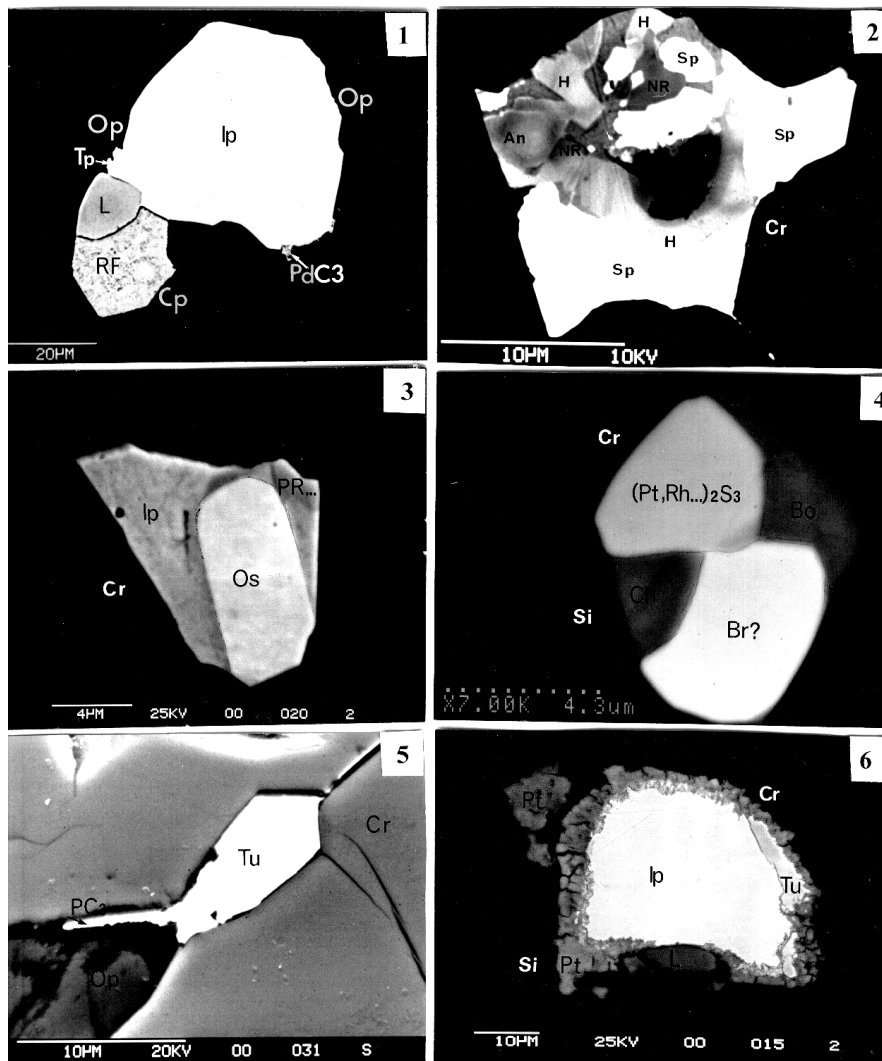


Plate I - SEM photomicrographs of PGM, Albanian ophiolitic complex:

1. Euhedral crystal of isoferroplatinum (Ip), (Rh, Pt, Fe, Cu) alloy (RF), laurite (L), tetraferroplatinum (Tp) and (Pd,Cu) alloy (PdC3). 2. Arsenide and sulphoarsenide PGM assemblage within host chromite (Cr): sperilyte (Sp), Ir-hollingworthite (H), anduite (An) and Ni-rhodesite (NR). 3. Osmium grain (Os) surrounded by isoferroplatinum (Ip) and complex alloy of Pt, Rh, Ru....(PR) trapped within host chromite (Cr). 4. Polyphase PGM and BMS aggregate composed of (Pt,Rh....)2S3, braggite (Br), chalcopyrite (Ch) and bornite (Bo). 5. Interstitial tulameenite (Tu) between chromite grains and a like vein alloy of PtCu3 (PC3). 6. Isoferroplatinum (Ip) grain rimmed by tulameenite (Tu) and platinum (Pt).

CONCLUSIONS

Four mineralization types, well distinguished on the basis of their PGE content and PGM assemblage, occur in specific ultramafic lithotypes of Albanian ophiolitic complex.

A clear PGE-fractionation and consequently fractionation of mineral phases and paragenetic associations, are evidenced for these four mineralization types: predomination of I-PGE subgroup for the mantle chromitites, of IPGE-PPGE for the upper mantle chromitites, of BMS-PPGE with high Pd for the supra-Moho dunites+pentlandite and of PPGE with high Pt for the mineralization related to dunite-pyroxenite cumulate interface.

The four mineralization types reflect the evolution of the mineral-forming system related to chromitites and BMS from mantle sequence to the cumulate sequence under different fO_2 and fS_2 conditions.

References

- Çina A. (1989)** - Mineralizime te EGP ne kompleksin ofiolitik te Albanideve. Buletini i Shkenc. Gjeol. 4, 125-139.
- Çina A., Neziraj A., Karaj N., Ostrosi B., Boshnjaku B. (1995)** -PGE mineralization related to the Tropoja and Bulqiza massifs, Albanian ophiolitic complex. Workshop on Albanian ophiolites and related mineralization. Documents du BRGM 244, France.
- Economou, M. (1983)** - Platinum group metals in chromite ores from the Vourinos ophiolite complex, Greece, Ofioliti, 8(3), 339-356.
- Karaj N. (1992)** - Repartition des platinoïdes, chromites et sulphures dans le massif de Bulqiza, Albanie. Thèse, Univ. d'Orléans, France, 364.
- Legendre, O. (1982)** - Minéralogie et géochimie des platinoïdes dans chromitites ophiolitiques. Comparaison avec d'autres types de concentrations en platinoïdes. Thèse de troisième cycle, Univ. Paris VI. France.
- Neziraj A. (1992)** - Etude pétrologique et métallogénique du massif ophiolitique de Tropoja, Albanie. Référence particulière aux gisements de chromite et éléments du groupe du platine. Thèse Univ. d'Orléans, France. 544.
- Ohnenstetter, M., Karaj N., Neziraj A., Johan Z., Çina A. (1991)** - Le potentiel platinifère des ophiolites : minéralisations en éléments du groupe du platine (PGE) dans les massifs de Tropoja et Bulqiza, Albania.C.R.Acad. Sci. Paris, t. 313, serie II, 201-208.
- Page N.J., Pallister J.S., Brown M.A., Smewing J., Haftty J. (1982)** - Palladium, platinum, rhodium, iridium and ruthenium in chromite-rich rocks from the Semail ophiolite, Oman. Can. Mineral. 20, 537-548.
- Prichard, H.M., Potss, P.J., Neary, C.R. (1988)** - Platinum-group-minerals in ophiolites complexes: an example from Shetland. Can. Mineral., 23, 311-320.