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GARNET GROUP MINERALS FROM THE AMPHIBOLITE FACIES METAMORPHIC ROCKS OF KRIVAJA-KONJUH ULTRAMAFIC MASSIF IN BOSNIA AND HERZEGOVINA

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ABSTRACT

In Bosnia and Herzegovina's ophiolitic zone there are six different ophiolitic complexes including Krivaja-Konjuh ultramafic massif. In the south-eastern parts of the massif, the basement is built of different varieties of amphibolites with subordinate occurrence of metamorphic rocks that don't contain amphiboles. Locality NE of Vareš near the village of Vijaka is generally the best outcrop of amphibolites rocks. The results of petrologic studies indicate that the analyzed rocks can be divided into several groups like garnet-diopside amphibolites, garnet-diopside-hypersthenes amphibolites, plagioclase-garnet rocks, garnet-pyroxene-plagioclase schist; plagioclase-garnet-hornblende - diopside schist and porphyryblastic hornblende and garnet bearing schist.

The garnets show wide variation in chemical composition with prevalance of almandine and pyrope component in all of analyzed samples. The differences in the composition profile through the garnets are attributed to changes in the metamorphic conditions during the growth of minerals. Abrupt changes in distribution of elements were observed in a thin zone on the very edge of the garnet grains which is interpreted as a result of the retrograde phase of metamorphism and rapid cooling.

Keywords: minerals, chemical composition, garnet, metamorphic rocks, amphibolites, pyrope, almandine, grossular, andradite.

INTRODUCTION

Krivajska - konjuški ultramafic massif and associated ophiolite from the amphibolites have an area of about 500 km^2, massif izrasjedanu a plate thickness of about 2000 m, embedded in the ophiolite mélange (Figure-1). In the south-eastern parts of Krivajska-konjuški massif, in the basement, is built of different varieties of amphibolites. Best discovered amphibolites belt located in the village of bolts, about 18 miles NE of Vares. It is the largest mass in amphibolites ophiolite zone in Bosnia, the provision can be traced about 15 km and maximum width is about 4 km. Entire complex is characterized by the presence of rocks of different metamorphic grade and facies greenschist with rocks in their lowest parts whose degree grows amphibolite epidote facies, facies to the rocks amphibolite granulite amphibolites facies.

Amphibolites Vijaka areas were studied for many years, starting from Kišpatićeva (1897) and researchers included on mapping the (Basic Geological Map SFRY, Sheet of Vareš, 1968) were noted decorative green pargasite-bearing amphibolites. To date it have been published many research papers (Pamić, J. *et al*., 1971, 1973, 2000, 2002) that were based on the available laboratory documentation. Today's sophisticated analytical methods allow obtaining new data that will significantly expand our knowledge in these rocks. In addition, one of the main goals of petrology of metamorphic rocks is to determine the P-T evolution of metamorphic rocks. There are many ways for establishing P - T conditions. One of them is studying the structures and inclusions, which can outline a part of the P - T conditions before reaching the maximum conditions, and yet studying the zones occurred during the growth of minerals provides the insight into the events that preceded the maximum in the process of metamorphosis (Triboulet and Andreu, 1988). Differences in the distribution of elements in mineral grains are the result of changes in conditions during the growth of minerals (Spear, 1981a, b, Tracy, 1982).

Data on the conditions of formation may be collected through the study on the chemical composition, variations and optical properties of amphiboles, garnets and other minerals (ilmenite, titanite, and plagioclase).

Since the recording of the garnet grains through dot method (with the electronic microprobe) can give us the information on changes in metamorphic conditions during the growth of minerals, in this paper for the first time were presented the results of chemical researches of garnets from garnet varieties of metamorphic rocks in the southern rim of Krivaja-Konjuh massif (in the amphibolite zone of Duboštica-Vijaka). By these researches in all the analyzed varieties, we tried to gain an insight into the processes that occurred during the genesis, since variations in chemical composition of the garnets, and variations in the optical characteristics of the garnets allow the establishment of processes that occurred in the geological past.

GEOLOGICAL CHARACTERISTICS OF OPHIOLITE AND AMPHIBOLITE

Dinaric ophiolite zone extends from Zagreb up to the northwest and across the Bani and Bosnia to Serbia, where it runs continuously in Hellenides. Ofiolitnog rock

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complexes are related to the internal Dinarides and represent a very complex association of rocks among which are the most characteristic rocks associated with different varieties of gabbros, Dolerite, diabase, amphibolite and spilite and united in the so-called. Diabase - hornfels formation or Jurassic - magmatic - sedimentary formation (Katzer 1906, Ćirić 1954; Pamić, 1964).

In some parts Dinaric ophiolite zoneis camouflaged with pulled Mesozoic, mainly carbonate rocks and Palaeozoic semimethamorphic rocks. In the ophiolite zone of Dinarides predominate ultramafic rocks (lerzolites, harzburgites, and serpentinites), with subordinate gabbroes, diabases, basalts and spilites. Very rarely one could meet completely preserved ophiolite profiles (Pamić and Desmons, 1989), and more often chaotic relationships, i.e., ophiolite mélange (Dimitrijević, 1973).

Ophiolite mélange is made of shale-silt matrix in which predominate smaller or larger fragments of greywacke and ophiolites, and occasionally arise cherts, sediments and limestone blocks of Tithonian age. As the most predominant rocks in the ophiolite mélange there are peridotite fragments and blocks which represent fault blocks, thickness of a few hundred meters up to 2000 m, drawn to the ophiolite mélange (Pamić and Desmons, 1989). So far in the ophiolite mélange and in its matrix have not been found typical fossil remains. On the base of non-typicalfossils it is presumed Jurassic age, which is consistent with available data on the isotopic age, 189-136 Ma (Lanphere *et al*., 1975; Majer *et al*., 1979; Lugović *et al*., 1991). Over Dinaride ophiolite melange zone lie transgressive lower Cretaceous formations of the Pogari formation in which ophiolite rocks are redeposited. In this way, stratigraphically is defined upper limit of the ophiolite mélange.

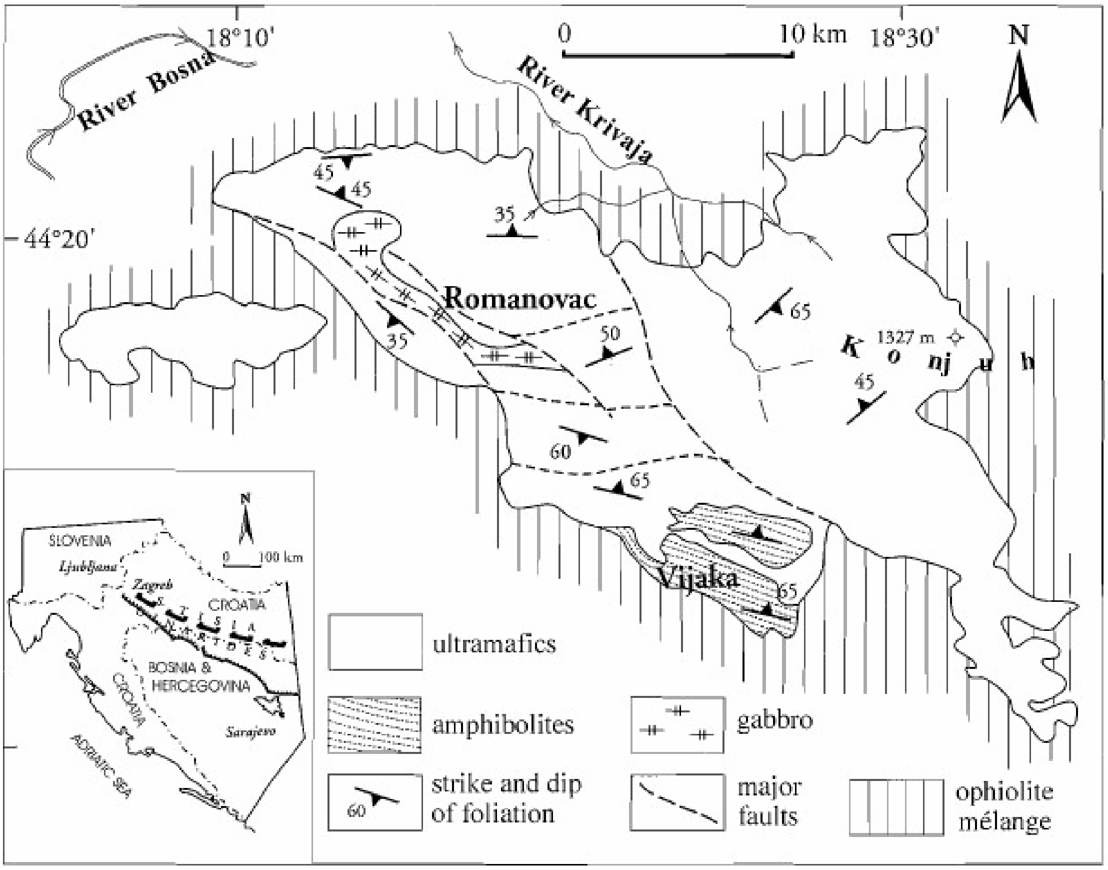

Figure-1. Schematic structural map Krivajska-konjuškog massif (Pamić *et al*., 1977).

Amphibolite complex has been made of rocks with various metamorphic grades - it means with greenshist facies rocks in the lowest parts whose degree grows towards epidot amphibolites facies, amphibolites facies and to granulite amphibolites facies.

Typical amphibolite rock is consisted of amphiboles and plagioclases with different amounts of the subordinate minerals: pyroxene, garnet, quartz, corundum, magnetite, ilmenite, titanite, rutile, spinel, chlorite, zeolitic minerals, prehnite, epidote-clinozoisite, zircon, biotite, apatite and phlogopite.

RESEARCH METHODS

The paper examined in detail the six samples of metamorphic rocks taken from the shoots, cuttings-storey and exploration wells in the amphibolite's area of Duboštica-Vijaka (locality Pobilje, Stupčić II and Duboki potok) on the southern edge of the Krivaja-Konjuh ultramafic massif. The samples were geologically mapped in detail and laboratory tested. In optical determinations were used a polarizing microscope (Reichart with an increase range of 25-630 x) in the Faculty of Science in Zagreb and a polarizing microscope (Olympus PX 40) at the Institute of Mineralogy and Petrography in Innsbruck.

Selected representative rock samples were chemically tested by X-ray fluorescence spectroscopy method using wave-dispersion instrument and SRS 3000 analysis. Ferrous iron content in the samples was determined by volumetric method. The water in the samples was determined gravimetrically, a four-hours drying at 110° C (H_2O-) and subsequent two-hours anneal the sample at 1025°C to determine H_2O+. The content of macro elements and trace elements were determined by the quantitative chemical method. The chemical composition of minerals in the rocks was determined by the electronic microprobe (ARL-SEMQ).

Both analyses were performed at the Institute of Mineralogy and Petrography in Innsbruck. Garnets are recalculated on the basis of 12O and on the mole fractions of uvarovite, andradite, grossularite, pyrope, spessartine and almandine components

RESULTS

By the optical examination using polarizing microscope representative samples of metamorphic rocks according to their textural-structural characteristics and mineral composition, the following varieties were selected:

- garnet-diopside amphibolite;
- garnet-diopside-hypersthene amphibolite;
- plagioclase-garnet rock;
- garnet-pyroxene plagioclase schist;
- plagioclase-garnet-hornblende-diopside schist; and
- porphyryblastic hornblende granatites.

Figure-2a. Garnet-diopside amphibolite schist (garnet porphyroblasts size of 2.5 cm with kelifitskim one around the garnets).

Figure-2b. Garnet-diopside amphibolite slate with banded of fresh plagioclase.

In addition to garnet varieties of the amphibolite schists, optical examinations included also varieties that do not contain amphiboles (plagioclase-garnet rocks and garnet plagioclase pyroxene schist's).

By the optical determinations it was found that researched garnet varieties of metamorphic rocks had granoblastic, nematoblastic to porphyroblastic structures, and massive, banded up to modal band texture (Figures 2 and 3).

In all the analyzed samples optical studies have shown that garnets occur as partially or totally broken grains rarely with kelyphitic rims and worm-like myrmekite made of amphibole, chlorite and magnetite (in garnet-diopside hypersthene amphibolite schists) - Figures 4a and 4b. In the massive and compact varieties of metamorphic rocks, garnets are fine grained, but also appear in the form of porphyryblasts size 1 to 2.5 cm.

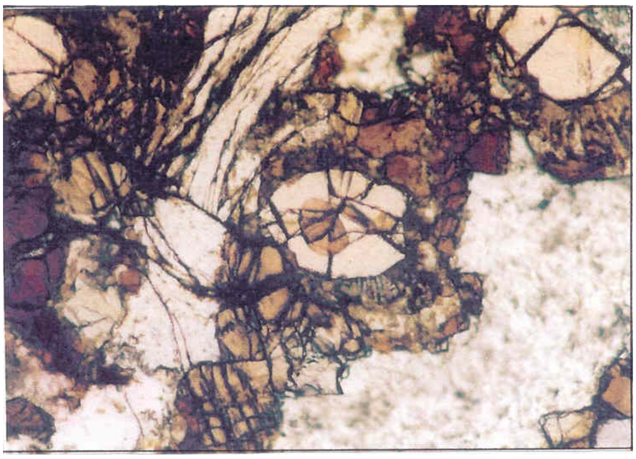

Figure-3. Grano to porphyroblastic structure in the garnet-diopside amphibolite, arnet porphyrooblast postkinematically enclose small diopside grain.

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Figure-4a. Garnet-dopsid-hiperstenski amphibolite slate. Garnet completely suppressed myrmekite worm made of amphibole, chlorite and magnetite, 110 x, N.

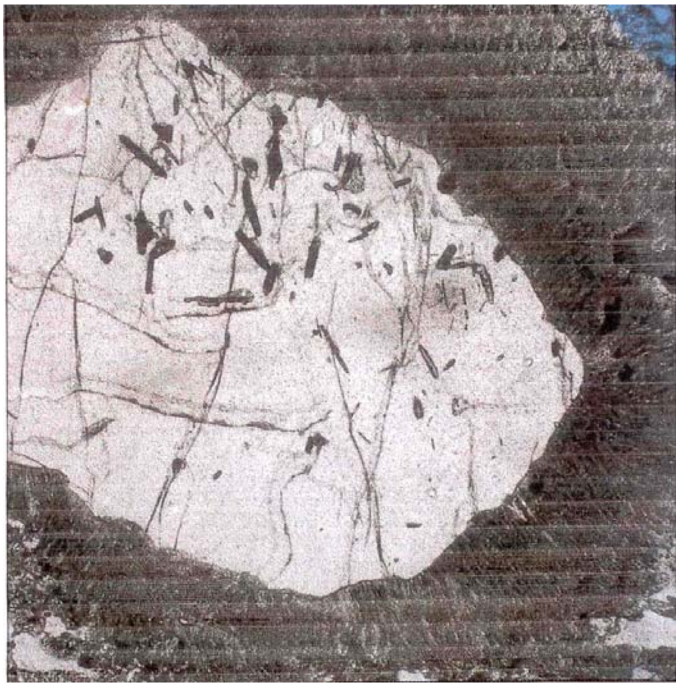

Figure-4b. Kelyphitic halo or rim around the garnets was made of chlorite, amphibole, clinopyroxene, orthopyroxene, plagioclase, magnetite, pyrite, spinel and rutile, 110 x, N N.

The chemical composition of garnets in garnet varieties of metamorphic rocks from the area of Vareš-Vijaka is determined by electronic microprobe, in the way that in plagioclase-garnet-hornblende-diopside and porphyryblastic hornblende granatites, garnet's share is determined by optical methods (idiomorphic characteristic forms, zonal structure, brownish color, prominent relief, with typical shagreen rough surface). Analysis of garnets were calculated by the computer program Garnet Norm on 12 O and on the mole fractions of uvarovite, andradite, grossularite, pyrope, spessartite and almandite components (Table-1).

Studies with electronic microprobe have shown that garnets show a large variation in chemical composition. In all analyzed samples dominated almandine and pyrope component (Tables 1 and 2).

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Table-1. Selected chemical analysis of garnets in the Vareš area (Vijake) - wt. % and calculation formula Based on 12 O, the mol % components.

Sample	Rim	Core	Rim	Core	Rim	Core	Rim	Core	Rim
Point	1	1	2	2	3	3	4	4	5
SiO_2	38,56	38,82	37,86	39,09	38,91	38,98	38,62	38,77	37,55
TiO_2	0,00	0,00	0,00	0,04	0,00	0,03	0,00	0,00	0,15
Al_2O_3	22,04	21,98	21,82	22,28	22,09	21,67	21,35	21,78	20,99
Cr_2O_3	0,09	0,07	0,00	0,00	0,05	0,16	0,00	0,00	0,10
Fe_2O_3	2,04	1,38	2,40	1,71	2,46	2,33	2,92	2,72	0,47
FeO	21,70	22,70	23,06	20,81	17,68	16,44	20,74	21,27	28,46
MnO	1,19	1,44	2,15	0,96	0,90	0,54	0,61	0,70	1,40
MgO	9,62	9,26	8,65	11,10	9,56	10,20	8,93	8,93	3,54
CaO	4,44	4,20	3,27	3,92	8,12	8,93	6,64	6,61	6,87
Na_2O	0,08	0,08	0,06	0,04	0,10	0,00	0,00	0,00	0,05
K_2O	0,00	0,00	0,05	0,00	0,01	0,00	0,11	0,00	0,00
TOTAL	99,75	99,94	99,32	99,95	99,88	99,31	99,91	100,77	99,58
Uvarovite	0,300	0,200	0,000	0,000	0,200	0,500	0.000	0,000	0,300
Andradite	6,000	4,100	7,200	4,900	7,200	6,700	8,600	7,900	1,400
Grossuluni	6,100	7,400	2,100	5,700	15,200	17,200	10,000	10,400	17,300
Pyrope	37,500	35,800	34,400	42,400	37, 000	39,000	34,900	34,300	14,100
Spessartite	2,600	3,200	4,900	2,100	2,000	1,200	1,300	1,500	3,200
Almandine	47,400	49,300	51,400	44,600	38,400	35,300	45,200	45,900	62,800
Na-Ti grt				0,200					0,800
Ti-Al grt						0,100			0,100

In the garnets from the garnet- pyroxene-plagioclase schists, the participation of spessartine and pyrope (Prp 34.6%, Sps 1.4%) is less than in the garnet-diopside amphibolites (Prp 36.6%, Sps 3.06%) and garnet-diopside-hypersthene amphibolite (Prp 47.5%, Sps 1.9%), while the content of almandine and grossularite components (Alm 45.5%, 10.2% Grs) is higher than in the garnet-diopside-hypersthene amphibolites (Alm 33.7%, Grs 9.85%) and garnet-diopside amphibolites (Alm 44.6%, 8.69% Grs). In the plagioclase garnet rocks, participation of pyrope and andradite (Prp 14.1 to 14.6%, and 5.55%) is significantly less than in mentioned varieties of rocks while the participation of almandine, and grossularite components is (Alm 62.8 to 67.6%, Grs 12.3%) higher (Table-2).

Variations of the end-members are more expressive in the garnet rims than in the cores. Variations of the outermost members both in the rim and garnet core of all the garnet varieties in amphibolite rocks are:

- pyrope (34-50%)
- almandine (31 - 51%)
- grossular (3 - 17%)
- andradite (4 - 12%)
- spessartine (1 - 5%)
- uvarovite (0.0 to 0.7).

Spear, F. S. (1993) showed that replacement of pyrope with almandine was more the function of pressure than that of temperature. It could be estimated from their data that if the garnet contains approximately 50% of pyrope and 50% of almandine then it is stable at temperature of 920 º C and pressure of 10 kbar. Recording the garnet's grain by dot method with electronic microprobe it was observed, that all analyzed garnets from metamorphic rocks garnet varieties from the area of Vijaka represent almost continuous series in which the changes in the proportions of almandine and pyrope are particularly interesting. Increasing the participation of almandite and pyrope components in the garnet rims brings to reduction of grossular and spessartine. Increase in grossular content in the garnet core is followed by the increase in spessartine while almandine and pyrope content decreases. Reduce of grossularite, spessartine components and Fe / Fe + Mg ratio, and increase of pyrope and almandite components towards the rim suggests prograde metamorphism conditions. However, it could be identified minor deviations in the distribution of these components at the rims and the grain nucleus. Changes at the rims of garnets are small-sized and are

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manifested in the impoverishment of the Mg (pyrope) and the enrichment of Mn (spessartine). Although changes at the garnet rims are insignificant by volume they can be attributed to retrograde metamorphism.

Table-2. Variations of the end-members (in mol. %) in garnets for single garnet rocks varietes.

End members	Grt-di-hi amphibolite schist	Grt-di amphibolite schist	Grt-pl-px schist	Pl-grt rocks
Uvarovite	0,1-0,4	0,2-0,6	0,0-0,7	0,0-0,3
Andradite	6,0-8,6	2,8-11,8	7,7-8,6	1,4-9,7
Grossulunite	8,8-10,4	2,1-17,2	8,6-10,4	7,3-17,3
Pyrope	41,3-50,5	34,4-42,4	33,7-34,9	14,1-14,6
Spessartite	1,0-2,4	1,2-4,9	1,3-2	0,7-3,2
Almandine	30,5-40,8	35,3-51,4	45,2-47,1	62,8-67,6

Samples of garnet-diopside amphibolite are associated with garnet-amphibole edenit, clinopyroxene and plagioclase-diopside rocks.

In kelyphitic rim around the garnet there are amphiboles (ferric tschermakite, magnesium hastingsite) and plagioclase (bytownite). Garnet with kelyphitic rim has been enriched with pyrope component (39%). Garnet is enriched with pyrope which is associated with ferri-tchermakite hornblende when plagioclases are more calcium-bytownite. Amphiboles, which occur as torn pieces in kelyphitic rim have less of SiO_2, FeO and more of Al_2O_3, K_2O, Na_2O and TiO_2 compared to amphiboles that are integrated into the garnets. Edge of the garnets around which is kelyphitic rim has more of MgO content and less of MnO, CaO and Fe / Fe + Mg comparing to garnets' cores

As synmorphes, four parageneses occur in the garnets:

- Amphibole (tchermakite, edenite and pargasite), plagioclase (andesine-labrador), clinopyroxene (diopside) with veins of albite.
  The appearance of albites indicates the retrograde stage of metamorphism. The impact of higher SiO_2, at constant alkali content lies in the fact that the composition of amphibole departs from pargasite components (Na, Al-rich) and amphibole occurs with less pargasite components and albite (Spear, 1981 b).
- Amphibole (magnesium hornblende), clinopyroxene (diopside) and zeolite minerals (mesolite). Mesolite is incorporated between clinopyroxene and amphibole as a product of alteration.
- Amphibole (pargazite and ferric magnesium hornblende), clinopyroxene and chlorite (ripidolite). Chlorites occur in the form of halo around amphibole and clinopyroxene. In contact with clinopyroxenes amphibole is pargasite and in contact with chlorites is ferric magnesium hornblende.
  The participation of pyrope component in the garnet porphyroblasts is higher (50.4 to 50.5) than in the others.
- Amphibole (gedrite), plagioclase (anorthite), spinel and zircon-hercinite. The garnet enriched with almandine component (43.7 to 45.0%) is associated with amphiboles which are enriched with edenite and pargasite and plagioclase (andesine).
  Analyzing the spinel grains from the core to the rim, the share of SiO_2, Cr_2O_3, FeO, CaO, K_2O and ZnO increases and the content of Al_2O_3, TiO_2, MnO and MgO decreases.

To form gedrites characterized are lower temperatures and higher pressures (Hietanen, 1974) and they can arise by transformation of general hornblende at which arises also plagioclase, they represent the latest stage in the process of magnesium metasomatism. According to Hietanen (1974), appearances of gedrites and garnets indicate late stage in crystallization of gedrites and garnets.

Figure-5. The distribution of minerals in blast garnets (garnet-diopside schist amphibolite).

Matrix of the plagioclase garnet rock is made of plagioclase (albite to andesine) in which is immersed garnet porphyryblasts with - inclusions of epidote clinozoisite and zircon. Synmorphes of clinozoisite-epidote in the garnets point to prograde sequence to amfibolite facies.In plagioclases occur synmorphes of ripidolite-chlorite, ilmenite and titanite.

Analyzing the garnets from the core to the rim, it was observed decrease in concentration of MnO, CaO and increase in concentration of MgO, which is consistent with the content of these elements in garnet-diopside amphibolites. Not often was observed that the garnet grains at the rims of the plagioclase garnets rocks had higher spessartine and less of pyrope components.

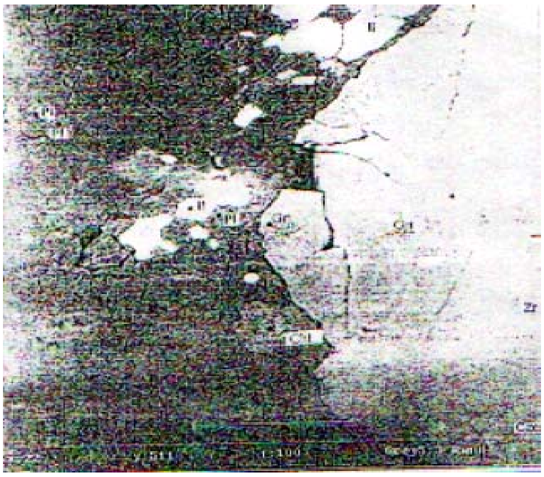

Figure-6. The distribution of minerals in garnet plagioclase rocks.

Legend: Amp-amphibole, Pl-plagioclase, Czo-clinozoisite, Zr-zircon, Sp-spinel, IL-ilmenite, Chl-chlorite

In kelyphitic rim of the garnet-diopside-hypersthene amphibolite there are plagioclases in contact with spinels, orthopyroxene, magnetite and pyrites. In the contact zones of plagioclases with spinels occur rutile and orthopyroxenes. Amphiboles are in contact with clinopyroxene and plagioclase-diopside-anorthite-bytownite. In contact with spinel-magnesium hercinite and orthopyroxenes, plagioclase is anorthite, and in contact with garnets and orthopyroxenes, plagioclase is bytownite. Amphiboles are rich in ferri-tchermakite, ferric magnesiumhornblende as end-members who are associated with more basic plagioclase-anorthite-bytownite.

As synmorphes in garnets two parageneses occur:

- Amphibole (pargasite and magnesiumhornblende), clinopyroxene-diopside.
- Amphibole (pargasite hornblende and magnesium hastingsite), Orthopyroxene, clinopyroxene, plagioclase (andesine) and chlorite. On plagioclase- andesine is associated with amphibole rich in pargazite molecules.

Likely that andesine has been produced by retrograde metamorphosis of the more basic plagioclases.

In the garnet - plagioclase schist, around garnet porphyryblasts there are kelyphitic halo which contain plagioclase (labrador - bytownite) orthopyroxene, magnetite, ilmenite, zeolite mineral - tomsonite and teared parts of the garnets.

Magnetite is incorporated in the orthopyroxenes. The presence of ilmenite indicates that the hornblende has been saturated with titanium oxide. Excess of titanium oxide that cannot be incorporated into hornblende, crystallizes as ilmenite, titanium magnetite andrutile. Ilmenite is typical at higher degree of metamorphism.

The distribution of Si in the garnet-pyroxene plagioclase schist indicates the maximum concentration in orthopyroxene, less in plagioclase and garnets and very small concentrations in titanite and ilmenite. The amount of Si in orthopyroxene and garnet in the core is larger than at the rim.

The Na distribution indicates that plagioclase is the richest phase in the paragenesis, followed by magnetite, orthopyroxene, and in the lowest concentrations at garnets and ilmenites.

Participation of pyrope and andradite components increases towards the rim; the opposite is trend of distribution of spessartine and almandine components.

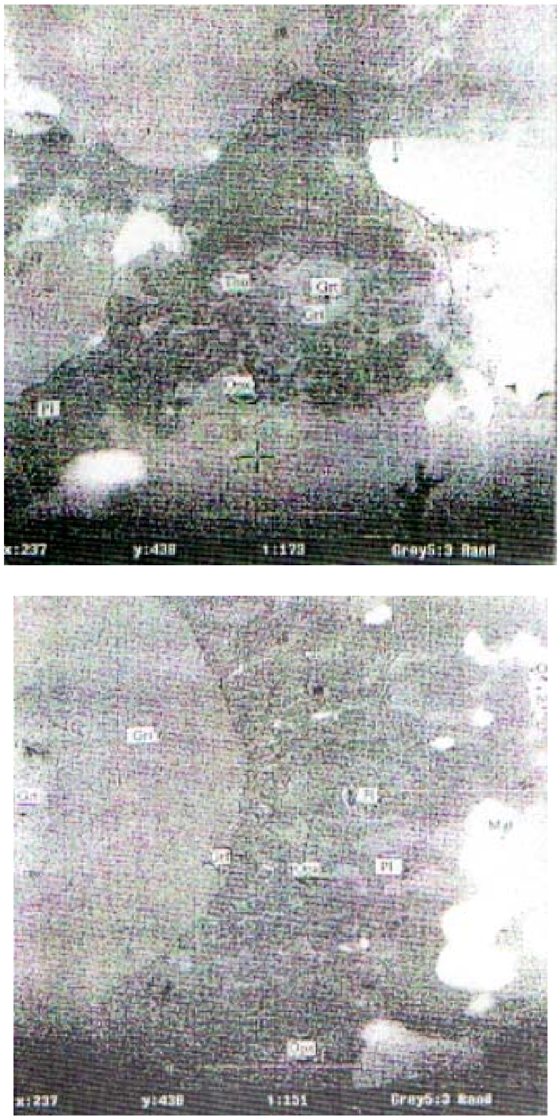

Figure-7. The distribution of minerals in kelyphitic around garnet's porphyroblasts (garnet-pyroxene-plagioclase schists).

CONCLUSIONS

Selected representative samples of garnet-bearing varieties of metamorphic rocks from amphibolite zone of Duboštica-Vijaka (locality Pobilje, Stupčić II and Duboki potok) on the southern edge of Krivaja-Konjuh ultramafic massif were examined optically and chemically by X-ray fluorescence spectroscopy.

Beside garnets varieties of amphibolite, optically were examined also varieties that do not contain amphiboles (plagioclase-garnet rocks and garnet plagioclase pyroxene schist's).

Analysed garnet-bearing varieties of metamorphic rocks are granoblastic, nematoblastic to porphyroblast structures, and massive, banded to banded modal textures.

In all the analyzed samples optical studies showed that garnets occur as partially or completely altered grains, often with kelyphitic rims around porphyryblasts and rarely with presence of worm-like myrmekite. The chemical composition of garnets in garnet varieties of metamorphic rocks from the area ofVijaka has been determined by the electronic microprobe, and that in the plagioclase garnet hornblende schist and diopside porphyryblastic hornblende garnets the share of garnets isdetermined by optical methods.

Recording the garnet grains by dot method with electronic microprobe it was noted those garnets shown large variations in chemical composition as well as their associated amphiboles.

Dismantling band garnets on the end-members in the core and rims, it is evident that all garnets represent almost continuous series in which the changes in the proportions of almandine and pyrope are particularly interesting. Variations of the end-members are more expressive in the rim than in the core.

Trend of growth of almandine and pyrope components to the rim and reducing the concentration of spessartine and grossularite component indicates prograde metamorphism. Sporadically are noticed also changes at the rims of grains, which are manifested in the growth of spessartine components (the enrichment of the Mn) and reducing the concentration of pyrope components (impoverishment in Mg).

Trend of growth of the spessartite components towards the rimshowes slightly indicated trend of retrograde metamorphism as well as rapid cooling.

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