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The Results of Chemical Researches on Mineral Phases in Metamorphic Rocks of The Krivaja – Konjuh Ophiolite Complex (Bosnia and Herzegovina)

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ABSTRACT

The Vijaka amphibolites complex is situated in the south rim of the Krivaja – Konjuh ophiolite complex in Bosnia and Herzegovina. Amphibolites rocks are in association with various types of tectonic peridotites, cumulative peridotites, gabbros and rocks of Jurassic volcanogenic-sediment formation. Frequent layering of amphibolites rocks with ultramafic rocks points on their genetically mutual relations, and that was proved also by P-T estimations as well as radiometric determinations, which are in accordance to regional termobarometric calculations for the metamorphic rocks determined the following sorts of amphibolite rocks: classical amphibolite, monomineralic amphibolite schists, diopside amphibolite schists, garnet-diopside amphibolite schists, bimineral amphibolite schists, and rarely corundum-bearing amphibolites. Within these sorts, appears amphibolities association, pyroxene and garnet association. Amphibolites properties vary from the association to the association, depending on rock hemisam and metamorphic conditions, and once appear mainly in Mg-hornblende fields, tschermakite, and subordered by pargasite and edenite.. The paper shows the results on the optical examinations, x-ray fluorescence spectroscopy and examinations with electronic microsonde of the main ingredients of amphibolites rocks in the south rim of the Krivaja – Konjuh ophiolite complex. The accent in this paper was on the results of chemical researches of mineral phases that are results on dotted analyses of amphiboles, plagioclases, pyroxenes and garnets. Researching the amphiboles in all rock varieties was an attempt to get insight into processes that had been developing during the genesis. During those researches, chemical variations in plagioclase structure were established, starting from plagioclase (oligoclase – andesine) up to plagioclase (bytownite – anorthite). It was confirmed that garnets as well as amphiboles showed great variations in chemical composition.
The results of the garnet grains' screening in all varieties of garnet rocks shown deviations on the rims and core.
KEY WORDS: Bosnia and Herzegovina, The Krivaja-Konjuh ophiolites complex, metamorphic rocks, amphibole, plagioclase, pyroxene, garnets, chemical examinations, optical analyses, x-ray fluorescence spectroscopy, electronic microsonde analyses.

INTRODUCTION

Ophiolite zone of the Internal Dinarides is the special geotectonic unit and is spread from Banija in Croatia, through Bosnia and west Serbia, all to Kosovo in the southeast and further more to Helenides. The greatest spreading of amphibolites in the Internal Dinarides is found in the south rim of the Krivaja – Konjuh ultramafic massif which covers the area of 500 km^2 (Pamić, 1978).

In the south rim of the Krivaja – Konjuh massif, amphibolites have significant spreading in the zone which stretches between the villages of Vijaka and Duboštica, but the greatest masses were localized in wider area of the Vijaka village, where they cover the area of 20 km^2 and over.

For many years amphibolites of the Vijaka region have been researched, started from Kišpatić (1897) all to 1968, during the work on the Main geological map of Vareš when there were noticed decorative green pargasite amphibolites. In that period many scientific papers were published, based on disposal laboratory documentation.

Present sophisticated analytical methods enable getting new data which will significantly spread our knowledge on those rocks. Besides that, conducting detailed research works in the year 1990 and in period 1996 – 2000, there were found out new profiles and borders among some varieties of amphiboles, what enabled optimal sampling. Sampled were 150 specimens of amphibolites and amphibolites slates along the most opened and the most favorable profiles in the region of Stupčić, Selišta, Pobilje – Šarena kuća, Donja Vijaka – Podlazine and Duboki potok. All the samples were processed in detail by microscope, and on the base of microscope treatment were chosen 26 representative samples, which then were detailed and systematically examined.

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The paper shows the results on laboratory examinations (optical examinations, x-ray, and examinations with electronic microsonde) of the main ingredients of amphibolites rocks in the south rim of the Krivaja – Konjuh ophiolite complex. There were analyzed in detail the results of chemical researches on mineral phases, means the results of dotted analyses on amphiboles, plagioclases, pyroxenes and garnets.

Characteristics of ophiolite and amphibolites

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

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.

Krivaja-Konjuh ultramafic massif and joined ophiolite with amphibolite covers area of about 500 km^2 and it represents faulted plate that is thick about 2000 m, which overlaps ophiolite melange. In its most part, it is composed of moderately seprentinised porphyroblast lersolite tectonic rocks. In its southeast parts, in the floor, they are composed of different varieties of amphibolite (Fig. 1.). The most exposed and the greatest belt of amphibolite is located in the area of village Vijaka, about 18 km in the northeast of Vareš.

Foliation in amphibolite is parallel foliation of lersolite tectonites.

Contact between amphibolite and ophiolite melange is tectonic.

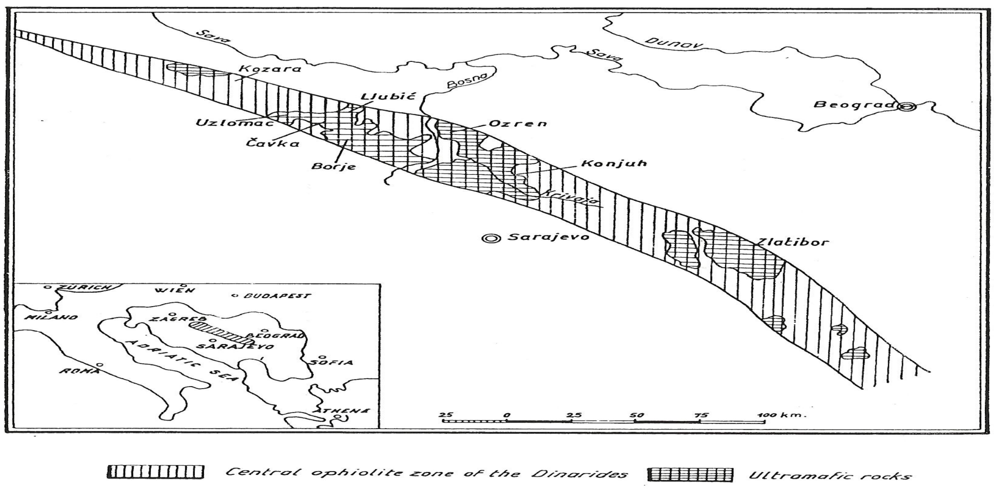

Fig.1 Simplified geological map of Central ophiolite zone of the Dinaride with index map (Petković,1961).

In Vijaka amphibolite complex, the following varieties of the rocks are confirmed: bimineral amphibolite schist, diopside amphibolite schist, garnet-diopside amphibolite schist, mono mineral amphibolite schist and rarely corundum amphibolite schist. Complete amphibolite complex is characterized with presence of the rocks of different metamorphic level together with rocks of green schist facies in their lowest parts which level increases towards epidote amphibolite facies, amphibolite facies to the boundary of granulite amphibolite facies (Pamić et al., 1977; 2001). Zone division from rocks of green schist facies to rocks of granulite-amphibolite facies also indicates variation in composition from potassium plagioclase to anorthite, hornblende to actinolite-tschermakite-edenite to pargasite and garnets enriched with pyrope and almandine component.

Corundum amphibolite occurs only in parts of Vijaka's amphibolite of the greatest range of metamorphism. They are unevenly divided within the zone of emerald green pargasite and edenite-pargasite amphibolite, in over 10 mainly narrow zones that could hardly be represented in the map. Exceptions are localities of Donja Vijaka, Stupčić and Crni potok, where thickness of those zones is exceeding 100 m.

As a rule, amphibolites are similar in space and they are connected to narrow and lengthen zones of greatly or completely seprentinised ultramafic accumulations that have bands of inserted amphibolite (Fig. 2).

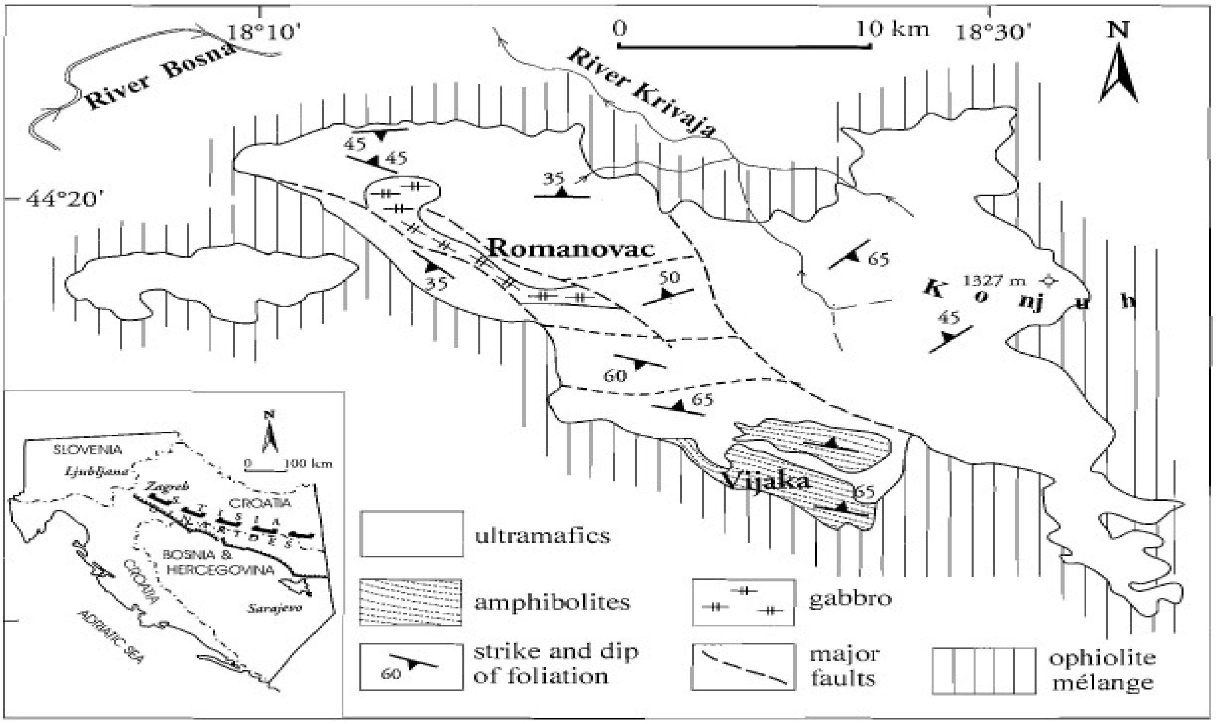

Fig. 2. Schematic structural map Krivajsko-konjuškog massif (Pamić *et al.*, 1977).

METHODS OF INVESTIGATIONS

On nineteen selected samples of amphibolite rocks from amphibolite zone Duboštica-Vijaka in the south edge of Krivaja-Konjuh massif, detailed optical analyses were done with use of polarisation microscope, chemical analyses of microelements, also microelements of rare grounds, x-ray-florescent spectroscopic analyses, and chemical analyses of minerals (amphibole, garnet, plagioclase, pyroxene, corundum, spinel, chlorite, magnetite, titanite, ilmenite, zeolitic minerals, prehnite, rutile, serpentine, olivine, apatite, analcime) with electronic micro sonde. Samples are optically analysed with standard polarisation microscope of brand Leitz, when determined were structural-texture characteristics and mineral composition. Mineral composition of the samples was checked with x-ray analyses with instrument of brand Philips with CuKα rays with graphite monochromator.
Noted analyses were completed in Institute for Mineralogy and Petrography in Innsbruck

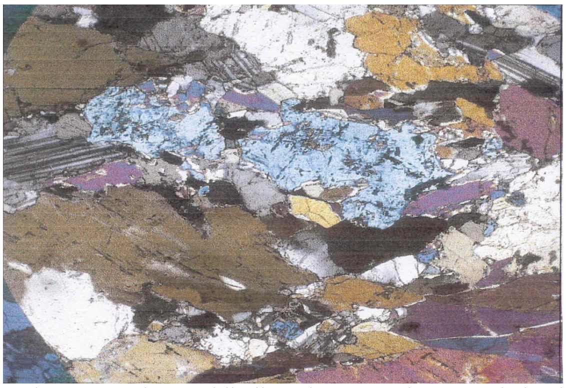

Fig. 3 Pargasite amphibolites slate, Stupčić I, association inside amphibolites schists, 27x, N+.

Fig. 4: Hornblende porphyroblasts and garnets in pargasite the small-grain plagioclase's mass.

Fig. 5: Plagioclases as root minerals in garnet-diopside amphibolites joined schists.

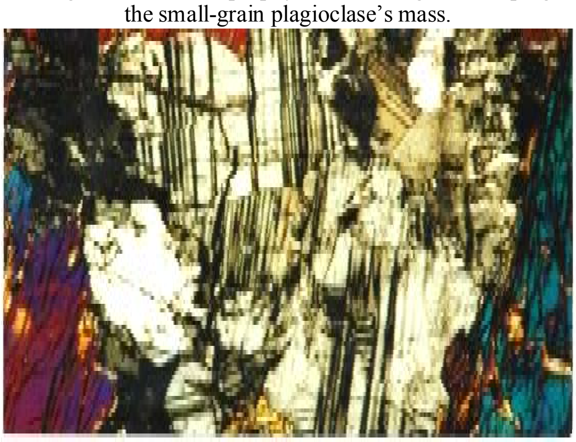

Fig. 6: Basic plagioclases with expressive lamellas in diopside amphibolites schists.

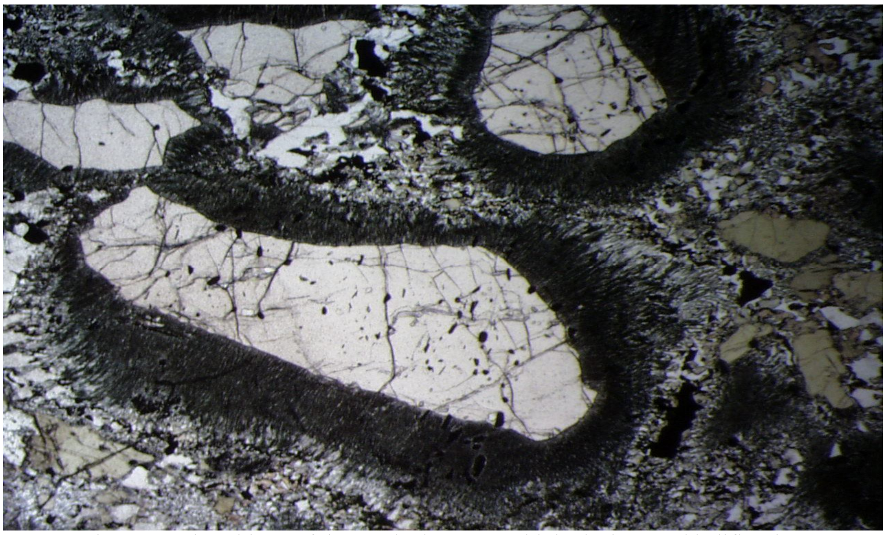

Fig. 7: Porphyroblasts of the cracked garnets with inclusions and kelifite rim. Kelifit's cover was made of chlorite, amphibole, clinopyroxene, ortho-pyroxene, plagioclase, magnetite, pirite, spinel and rutile, 110x, N-.

Results of chemical researches on mineral phases

RESULTS OF DOTTED ANALYSES

Amphibole

The results of the chosen chemical analyses of amphiboles, along with calculated formulas were shown in table 1. Analyses were processed by the computer program according to IMA recommendation (AMPH – IMA 1997, A. Moggesie, K. Ettinger, B. E. Leake & R. Tessadri) on 23 O and 13 eCNK and on mol parts of components in amphiboles.

The greatest part of analyses of amphiboles in the Vijaka region (deposits of Pobilje, Stupčić I, Stupčić II, Selište, Donja Rijeka and contact zone of amphibolites with mélange-Jurassic-volcanogenic-sediment formation as well as from amphibolites of Jurassic volcanogenic-sediment formation) are projected to fields of magnesium-hornblende and in tchermakite field, and less part of analyses are projected to actinole field (Pobilje deposit). The part of the analyses from deposits of Stupčić I, Stupčić II, Duboki potok, Pobilje, Donja Vijaka, Selište, and from contact zone of amphibolites with mélange-Jurassic-volcanogenic-sediment formation as well as from amphibolites of Jurassic volcanogenic-sediment formation is projected on fields of pargasite/magnesium-hastingsite that is edenite (depends on content of Al^{VI} : Fe^{3+}). This refers to variety in the structure of amphiboles what can be the consequence of the metamorphic condition's change in the geological past.

According to Hawthorn (1983), amphiboles from the analyzed samples are mostly projected to the fields of tchermakite, tchermakite hornblendes and magnesium-hornblendes.

Since the greatest number of samples were taken from localities of Stupčić II and from the contact zone of amphibolites with Jurassic-volcanogenic sediment formation, from those localities were also analyzed the chemical composition of amphiboles and were shown mol percentage of some outermost amphiboles' members.

Such estimation was done with help of the program CLASAMPH (Currie, 1991 a) .

Diversity of substitutions in that mineral group makes difficult the considerations about the genesis conditions, however in suitable cases can be noticed conditions on which substitution reactions were developed.

In the structure of amphiboles in garnet-diopside amphibolites slates (Duboki potok) and in amphiboles slates (Donja Vijaka) one can notice:

- Increase of tchermakite and edenite components in compare to hornblende component looking from the core towards the rim of the same mineral, what points to prograde character of metamorphism, means the increase of P-T conditions inside the area of P-T value which characterize the amphibolites facies. The prograde character of metamorphism is not the same in all grains, but in some grains the retrograde metamorphism were also noticed.

Garnet diopside amphibolites schists (Stupčić II) show the decrease of the hornblende component from rim towards the core, with increase of pargasite component. The part of pargasite component grows with the increase of metamorphism conditions.

Researching the amphibolites rocks (garnet-diopside amphibolites schists, garnet-diopside hyphestene amphibolites schists, plagioclase-garnet-hornblende-diopside schists, pargasite amphibolites schists, actinolite and amphibolites schists) in the Vijaka region it was confirmed the possible coexistence of two and more amphiboles.

In hornblende granitite and edenite amphibolites schists prevail edenite and tchermakite hornblende what is typical for lower boundary of the amphibolites facies (Leake, 1965 and Spear, 1981 b) .

In pargasite amphibolites schists prevails pargasite component pointing on increase of metamorphism conditions, and in hornblende granitite prevails tchermakite component, which is stable at significantly lower temperatures.

With the increase of metamorphism conditions, grows the participation of pargasite component, and with that grows the content of Na and Al in samples linked with increase of PT conditions, especially P conditions when the content of Na grows on position A and the content of Al in T position and $M_{1,2,3}$ position. Transition of actinolite into hornblende (in actinolite schists from the Pobilje locality) is the result of two main substitutions (edenite and tchermakite substitution) inside the tremolite-actinolite structure.

Combining the edenite and tchermakite substances with the increase of metamorphic level arises the ideal, pargasite. (Grapes and Graham, 1978). Such combinations of edenite and tchermakite hornblende appear in transit zone between the green slates' facies and amphibolites facies.

Due to dependence of aluminum content in Ca-amphiboles on plagioclase structure, it will come to "rapid" change in the structure of amphibole at the same time with sudden changes in the structure of plagioclase. It will happen when amphibole is in co-existence with plagioclase which participation of anorthite component suddenly changes in certain structure areas (miscibility gap).

Generally more basic structure of plagioclase increases the content of Na and Al in amphibole with the increase of metamorphic level. (Robinson et al., 1969; 1982 and Spear, 1980 and 1981 a).

Plagioclase

The results of chosen chemical analyses with appropriate calculated formulas were given in table 2. The structure of plagioclase in amphibolites rocks in the Vijaka region significantly varies 22, 7-98,00 % An, and in some samples (plagioclase garnet rock from the Pobilje locality) appears pure albite. Plagioclase variations in amphibolites rocks in the region of Vijaka are the followings:

Gr-di-hi amphibolites schists 43, 65-96,33 % An
Gr-di amphibolites schists 43, 33-97,30 % An
Di amphibolites schists 97, 60-97,7 % An
Amphibolites schists 45, 31-96,02 % An
Pargasite amphibolites schists 89, 00 % An (plagioclase inclusions in corundum are of content 93,4-98,00 % An)
Amphibolites bimineral 22, 7-28, 9 % An

The structure of plagioclase in amphibolites rocks in the region of Vijaka varies from 22, 68-97,72 % An in contact with amphibole (rocks from the localities of Duboki potok, Stupčić II, Stupčić I and Selište), in contact with clinopyroxenes 88,40 % An, in contact with ortopyroxenes 48,7-54,09 % An (rocks from the locality of Stupčić II), in contact with garnets 32,34-81,66% An (rocks from the localities of Stupčić II and Pobilje) and in contact with spinels 97,30 % An (rock from the locality of Stupčić II).

Pyroxenes

Results of the chemical examinations on mineral phases of pyroxene from amphibolites rocks in the region of Vijaka were presented on three-component diagram according to Morimoto, 1988 (Table 2). Analyses of clinopyroxenes and orthopyroxenes from amphibolites and ultramafic rocks were calculated according to recommendation of Norm (Wood & Banno) on 6 O and on mol participation of components in pyroxenes (Table 2).

Diagram represents pyroxenes analyzed from different rock varieties from the localities of Duboki potok, Stupčić II, Stupčić I and Selište (garnet-diopside-hypersthenes amphibolites schists, garnet-diopside amphibolites schists, garnet-plagioclase-pyroxene schists, pargasite amphibolites schists and edenit amphibolites schists). This analysis included orto and clinopyroxenes which appeared as synmorphes in garnets and in kelyphitic rim around garnet's porphyroblast. Clinopyroxenes from garnet-diopside of amphibolites schists, locality of Duboki potok, and from edenite amphibolites schists from the locality of Stupčić I, are projected close to the diopside field. On the base of classification diagram used by Hess, clinopyroxenes from analyzed rocks in the region of Vijaka should belong then to diopside and salite.

Orthopyroxenes from garnet varieties of amphibolites rocks from the locality of Stupčić II are projected to the clinoenstatite field and close to clinoenstatite field i.e. into boundary area between clinoenstatite and clinoferosilite (according to Hess, those pyroxenes should belong to hyperstenes and ferohyperstene). Orthopyroxenes from edenite amphibolites schists from the locality of Selište are projected into clinoenstatite field (according to Hess, into the field of bronzite).

Table 1: Selected chemical analyses of amphiboles from amphibolites rocks in the Vijaka region (on localities Duboki potok, Selište, Donja Vijaka, Stupčić II, Pobilje).

Locality	Duboki	potok	Selište	Donja	Vijaka	Stupčić	I	Stupčić	II	Pobilje	
	1-rub	1-jezgro	2-jezgro	3-rub	3-jezgro	4-rub	4-jezgro	5-rub	5-jezgro	6	6-1
SiO_2	43, 63	44, 92	47, 55	45, 53	47, 00	44, 33	44, 31	40, 60	41, 87	45, 67	52, 38
TiO_2	0, 98	1,09	0, 22	0, 00	0,00	0, 24	0, 34	0, 77	2, 58	0, 58	0, 00
Al_2O_3	14, 66	12, 86	10, 81	15,64	13, 62	13, 40	13, 43	14, 93	12, 76	9, 53	2, 67
Cr_2O_3	0, 11	0, 26	0, 19	0, 79	0, 04	0, 25	0, 35	0, 04	0, 12	0, 17	0, 10
Fe_2O_3	2, 65	3, 39	2, 11	0, 84	2, 45	2, 41	3, 13	12, 90	6, 49	5, 83	0, 68
FeO	7, 16	6, 28	2, 87	3, 76	2, 91	5, 28	4, 59	1, 91	6, 09	9, 67	15, 20
MnO	0, 22	0, 05	0, 18	0, 05	0, 12	0, 29	0, 02	0, 52	0, 12	0, 31	0, 06
MgO	13, 78	14, 46	20, 08	16, 55	17, 33	15, 78	16, 07	12, 72	13, 31	12, 49	13, 68
CaO	12,56	11, 96	11, 58	12, 30	12, 95	12, 75	12, 67	10, 52	11, 16	11, 99	13, 15
Na_2O	1, 99	21,46	2, 16	1, 24	1, 48	2, 37	2, 44	2, 79	2, 57	1, 45	0, 25
K_2O	0, 33	0,07	0, 10	0, 13	0, 12	0, 18	0, 22	0, 05	0, 09	0, 13	0, 13
ZnO	0,00	0,44	0, 00	0, 00	0 55	0, 00	0, 00	0, 00	0, 04	0, 00	0, 00
H_2O	2, 068	2, 07	2, 141	2, 125	2, 147	2, 087	2, 095	2, 064	2, 050	2, 05	2, 059
TOTAL:	**99, 53**	**99, 31**	**99,99**	**99, 02**	**100, 17**	**99, 55**	**99, 67**	**99, 82**	**99, 25**	**99, 86**	**100, 36**
Si IV	6, 324	6, 507	6, 660	6, 424	6, 565	6, 368	6, 341	5, 896	6, 125	6, 684	7, 628
Al IV	1, 6776	1, 493	1, 340	1, 576	1, 435	1, 632	1, 659	2, 104	1, 875	1, 316	0, 372
T site	**8, 000**	**8, 000**	**8, 000**	**8, 000**	**8, 000**	**8, 000**	**8, 000**	**8, 000**	**8, 000**	**8, 000**	**8, 000**
Al VI	0, 794	0, 668	0, 444	1, 025	0, 807	0, 636	0, 606	0, 452	0, 325	0, 328	0, 086
F^{+3}	0, 278	0, 359	0, 223	0,089	0, 257	0,261	0, 338	1, 410	0, 714	0, 642	0, 074
Ti	0, 107	0, 118	0, 024	0, 008	0, 001	0, 026	0, 037	0, 084	0, 284	0, 064	0, 000
Cr	0, 012	0, 030	0, 021	0, 088	0, 004	0, 028	0, 040	0, 005	0, 014	0, 019	0, 011
Mg	2, 914	3, 058	4, 193	3, 481	3, 609	3, 379	3, 428	2, 754	2, 902	2,725	2, 970
Fe^{+2}	0,868	0, 762	0, 095	0,309	0, 322	0, 634	0, 549	0, 232	0, 745	1, 138	1, 852
Mn	0, 027	0, 005	0, 000	0, 000	0, 000	0, 035	0, 002	0, 064	0, 015	0, 039	0, 007
$M_{1, 2, 3}$	**5, 000**	**5, 000**	**5, 000**	**5, 000**	**5, 000**	**5, 000**	**5. 000**	**5, 000**	**5, 000**	**5, 000**	**5, 000**
Ca	1, 904	1, 834	1, 705	1, 839	1, 933	1, 960	1, 943	1, 637	1, 749	1, 880	2, 000
Na	0, 096	0, 166	0, 295	0, 161	0, 067	0, 040	0, 057	0, 363	0, 251	0, 120	0, 000
M_4 site	**2,000**	**2, 000**	2, 000	**2, 000**	**2, 000**	**2, 000**	**2, 000**	**2, 000**	**2, 000**	**2, 000**	**2, 000**
Na	0, 463	0, 299	0, 587	0, 338	0, 371	0, 641	0, 062	0, 422	0, 481	0, 292	0, 071
K	0, 005	0, 013	0, 018	0, 024	0, 021	0, 033	0, 040	0, 010	0, 017	0, 025	0, 024
A site	**0, 468**	**0, 312**	**0, 605**	**0, 362**	**0, 392**	**0,674**	**0, 660**	**0, 432**	**0, 498**	**0, 317**	**0, 147**

Legend: 1-amphibolites; 2-pargazite amphibolites schists; 3-amphibolites schists; 4-garnet-diopside amphibolits schists; 5-garnet diopside hyperstene amphibolites schists

Table 2. Selected chemical analyses of plagioclases and pyroxenes from amphibolites in the Vijaka region.

	1-Pl	2-PL	4-Pl	5-Pl	4-Cpx	5-Cpx	5-Opx
	rub	rub		rub	rub	rub	
SiO_2	60, 99	45, 43	42, 23	55, 84	49, 53	50, 73	44, 47
TiO_2	0, 00	0, 00	0, 00	0, 00	0, 27	0, 60	0, 15
Al_2O_3	23, 85	34, 67	35, 83	27, 63	3, 72	3, 71	9, 01
Cr_2O_3	0, 00	0, 04	0, 09		0, 33	0, 08	0, 18
Fe_2O_3					2, 00	2, 03	0, 00
FeO	0, 24	0, 34	0, 88	0, 32	6, 79	7, 28	24, 49
MnO	0, 23	0, 00	0, 05		0, 10	0, 12	0, 80
MgO	0, 00	0, 06	0, 00		13, 32	12, 91	20, 75
CaO	5, 88	18, 33	19, 84	9, 81	22, 42	21, 00	0, 23
Na_2O	8, 24	1, 39	0, 25	5, 79	0, 59	0, 71	0, 06
K_2O	0, 17	0, 00	0, 11	0, 02	0, 00	0, 00	0, 00
NiO			0, 05	0, 02		0, 37	
ZnO	0, 00	0, 00	0, 24	0, 44	0, 000		0, 00
H_2O	0, 00	0, 00					
TOTAL:	**99, 60**	**100, 26**	**99, 56**	**99, 87**	**99, 07**	**99, 61**	**100, 14**
Si	2, 737	2, 094	1, 982	2, 520	1, 877	1, 907	1, 692
Al	1, 253	1, 883	1, 981	1, 469	0, 166	0, 164	0, 404
Ti	0, 000	0, 000	0, 000		0, 008	0, 002	0, 004
Cr	0, 000	0, 001	0, 003		0, 100	0, 002	0, 005
F^{+3}					0, 056	0, 059	0, 000
Mg	0, 000	0, 004	0, 000		0, 752	0, 723	1, 176
Fe^{+2}	0, 009	0, 013	0, 000		0, 223	0, 233	0, 779
Mn	0, 009		0, 018	0, 012	0, 003	0, 003	0, 025
Ca	0, 274	0, 905	0, 475	0, 474	0, 910	0, 845	0, 009
Na	0, 700	0, 124	0, 528	0, 507	0, 043	0, 051	0, 004
K	0, 010		0, 005	0, 001	0, 000	0, 000	0, 000
Ni			0, 003	0, 001		0, 011	
Zn				0, 015			
Total:	**4, 991**	**5, 026**	**5, 014**	**4, 999**	**4, 148**	**4, 000**	**4, 098**

Legend: Pl-plagioclase, Cpx-clinopyroxene, Opx-Orthopyroxene

Garnets

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). 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. 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 3).

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

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. 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 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.

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 porphyroblast 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.

Matrix of the plagioclase garnet rock is made of plagioclase (albite to andesine) in which is immersed garnet porphyry blasts with - inclusions of epidote clinozoisite and zircon. Synmorphes of clinozoisite-epidote in the garnets point to prograde sequence to amphibolite 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.

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.

Table 3. Selected chemical analysis of garnets in the Vareš area (Vijake) - wt. % and calculation formula based on 12 O, the mol % component

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
Grossular	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

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 component.

Dependence of chemical variations in mineral structure on changes of metamorphism's conditions

Plagioclases, pyroxenes, garnets and amphiboles were analyzed by microsonde in order to determine P-T conditions that had been during the metamorphism. Pressure could be estimated from the structure of pyroxene balanced with quartz in quartz-enriched amphibolites. Plagioclase-amphibole pairs were used for identification of the balance's conditions, and at the end, chemism of amphiboles for estimation of P-T conditions.

Zoned amphiboles and garnets were analyzed in order to establish P-T variations during metamorphism, and that from the same type of rock in order to keep the structure variable being constant. Analyzed rocks have partially equalized structure and variations in the structure of amphiboles what can be imputed to changes in P-T conditions. Change in amphibole's color is in connection with the structure of amphiboles, what then reflects the dependence on temperature: yellow green→dark green→brown. Change in amphibole's colour from green to brown roughly coincides with the appearance of diopside and later titanite, and with instability of ilmenite. That change happened due to change in content of Ti in amphiboles, but there are also variations of other elements in the structure of amphiboles.

MgO/ (MgO+FeO $_{tot}$) proportion in amphibole is in relation with the proportion in the whole rock what points out to balance. That relation in itself is clear, if observing the association Hbl+Pl, however it is the same if there are also pyroxene, epidote and Fe-oxides. At some part of the Vijaka's amphibolites there is strictly linear dependence of An content in plagioclase and Mg/ (Mg+Fe $^{2+}$+Fe $^{3+}$+Mn) proportion in coexistent amphibole with increase of Na and Fe in accordance with increase of metamorphic conditions.

The increase of Si activity is seen in the increase of Na content in plagioclase. Relative quantities of Al_2O_3, CaO and Na_2O are controlled by the structure of plagioclase in greater measure than by the structure of amphiboles. TiO_2 content of amphibole is strictly temperature dependent, but direct correlation of Ti in amphibole with temperatures can be doubtful in paragenesis which contains Fe-Ti oxides. At higher f_{O2} increases the participation of Fe-Ti oxide and decreases Ti content in amphibole. It means that during the increase of the brown zone, the instable one must be ilmenite, which decay brought Ti being built in amphibole's bars, and with the temperature's fall (development of actinolites on the rim of zonal amphiboles) at high f_{O2} and pressures originated leucoxene and titanite. Changing the conditions (higher f_{O2}) brings to ending of Ti being built in amphibole and to increase of participation of Fe-Ti oxide.

Zonal increase of amphibole's grains is the result of several episodes in mineral's growing. It seems that the mineral's core is relict kept due to unreachment of the complete balance. Concerning that the core grew before the rim, amphiboles can be considered as the time's relative indicator. Furthermore, various structures of the core and rim points out to several of metamorphic conditions. Each of the growth's event could (or could has been) characterized by its specific metamorphic conditions. Partially balance will keep the core's structure at the top of metamorphic conditions. However, it is likely that mineral paragenesis was different (if not in phase and modal structure then sure in chemical phase structure) while the core was in process of crystallization. Of course, in that case only larger grains would have their cores kept, because smaller grains would then be totally changed (over-crystallized). Elements necessary for making new rims come from alterations (changes) in other phases (changes in modal and chemical structure).

DISCUSSION

By chemical analysis of macro elements, microelements and rare lands and by chemical analyses with microsonde, it was established that analyzed rocks probably originated from magmatic rock of toleit structure (gabbros, diabase-dolerite) which gave ortho-varieties.

Amphiboles, plagioclases, pyroxenes, garnets and corundum were analyzed by electronic microsonde in order to establish P-T conditions which had ruled during the metamorphism. Plagioclase-amphibole pairs were used for identification of the balance conditions and at the end, chemism for estimation of P-T conditions.

Zoned amphiboles and garnets were analyzed in order to establish P-T variations during the metamorphism, and that is from the same type of rock in order to keep the variable of the structure being constant. Analyzed rocks have partially equalized structure and variations in the structure of amphiboles what can be imputed to P-T conditions.

Researching amphiboles in all rock varieties was an attempt to get insight in processes which had been developed during the genesis. Understanding the type of amphibole and variations in its chemical structure, and by that, the variations in optical characteristics, it enables the establishment of processes which had been developed in geological past.

According to classification diagram (Leake et al., 1997) the greatest part of the analysis of amphibole in the region of Vijaka, are projected in the field of magnesium hornblende and tchermakite, and significantly smaller part is projected in the field of pargasite/magnesium-hastingsite, edenite and in the field of actinolite. Dividing the structure of amphiboles into some outermost members in a great number of samples from deposit Stupčić II and from the contact zone of amphibolites with mélange-Jurassic volcanogenic sediment formation, it was established that in complex structure prevail tchermakite and edenite in the contact zone. Mutually comparing direction's inclines of certain substitutions, i.e. comparing Δ (Mg + Fe $^{2+}$)/ΔSi and Δ(Na + K) $_A$ /ΔSi it was shown that tchermakit's substitution in all analyzed amphibolites rocks in the region of Vijaka, has approximately 8 times more importance than the edenite's one.

In some samples of garnet-diopside amphibolites slates and amphibolites schists it was noticed the insignificant growth of the tchermakit's component in compare to hornblende's component looking from the core towards the rim of the same mineral what points to prograde character of metamorphism, means growth of P-T conditions inside the region of P-T values which characterize the amphibolites facies. Prograde metamorphism character is not the same in all grains, but in some grains the retrograde trend was also noticed. On the base of screening the amphibole's grains by dotted method with microsonde in zonal amphibole of the actinolit's schists, were shown the differences in distribution of elements (greater concentration of Si, Fe and Mg in the core and smaller quantity of Al, Na, K and Ti) what is the consequence of the condition's change during the growth of minerals, what points to prograde character of the reactions that caused the change of the structure of amphiboles from actinolite towards magnesium hornblende.

The results on examination of amphibole grains showed that the amphibole's core contain larger quantity of Si and larger quantity of Fe and Mg. Concentrations of Al, Na and K show, though at some elements slight expressed, quite opposite distribution, means richer grain rims than it is the core of mineral.

The same distribution applies also for Ti at which the enrichment towards the grain rims is much expressed. According to Spear (1981) it means that during the core's growth the temperature was lower than during the rim's growth of the same amphibole.

With less increase of Na content and with the fall of Si, Fe and Mg towards the rim of a grain, one can assume that the pressure of fluids grew. The conclusion on pressure of fluids, drawn from available data, cannot be unanimously brought because the distribution of elements, beside dependence on fluid's pressure, also depends on the structure's oxidation state and on the activities of some ions. The fact given above, points out to prograde character of reactions which caused the change in the structure of amphiboles from tchermakite towards classic hornblende.

Researching the amphiboles in amphiboles rocks in the region of Vijaka, it was proved the possible coexistence of two and more amphiboles. In the hornblende granitite and edenite amphibolites schists prevail edenite and tchermakite hornblende, what is typical for lower border of amphibolites facies. Combining edenite and tchermakite substance with increase of metamorphic grade, appears ideal pargasite hornblende as in pargasite amphibolites schists (from the Stupčić I locality) and by that, also grows the content of Na on the position A and the content Al in T position and $M_{1,2,3}$ position. The increase of Na and Ti brings to increase of taramite component (in samples from the locality of Stupčić II) what is also linked to increase of P-T conditions. Due to aluminum content's dependence, in Ca amphiboles, on the structure of plagioclase, comes to changes in a structure of amphiboles at the same time with sudden changes in the structure of plagioclase.

During the researches, chemical variations were established in the structure of plagioclase (oligoclase-andesine) up to plagioclases (bytownite-anorthite). Generally, the more basic structure the greater content of Na and Al in amphibole with the increase of metamorphic grade.

Appearances of albite as cut mineral are established only in garnet diopside amphibolites schists. The structure of plagioclase in all analyzed amphibolites rocks in the Vijaka region vary from 22, 00 up to 98, 00 % An, while in a contact with amphiboles the structure of plagioclase vary from 22, 68 up to 97, 72 % An. The most basic plagioclases, bytownite-anorthite partially is retrograde changed into andesine and oligoclase or transformed into prehnite.

The results of chemical examination on mineral phases of pyroxene, from all varieties in amphibolites rocks, are projected into fields of diopside, the field of clinoenstatite and close to field of clinoenstatite, i.e. in border area between clinoenstatite and clinoferosilite.

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

Conclusion

Our researches confirmed that the complete Vijaka amphibolites complex is characterized with the presence of rocks of various metamorphic grades that is from rocks of grinschist facies in their lower parts which grade grows towards epidote amphibolites facies, amphibolites facies to the border of granulite amphibolites facies. Amphibolites rocks come in community with heterogeneous types of tectonic peridotites, cumulative peridotites, gabbros and rocks with Jurassic volcanogenic-sediment formation. Frequent layering of amphibolites rocks with ultramafic rocks points to their genetically close mutual relations, what was also confirmed by P-T estimations as well as radiometric determinations, which were in accordance to regional termobarometric estimations for metamorphic DOZ rocks.

Researched amphibolites rocks have equalized petrographic characteristics with certain structural – texture variations and variations in chemical and modular mineral structure.

On the base of texture and structure data can be extracted three groups of rocks: group with a much expressed strip texture and nematoblastic up to lepidooblastic structure; group with good expressed strip texture and porphyroblastic structure and a group of massive texture and granoblastic up to porphyroblastic structure.

Detail classification of amphibolites rocks concerning the mineral structure includes five subgroups: monomineral amphibolites schists and rarely corundum amphibolites schist's, then amphibolites bimineral, diopside amphibolites schists, garnet diopside amphibolites schists and bimineral amphibolites schist's.

Inside the stated varieties of amphibolites rocks, there are amphibole association, pyroxene association and garnet mineral association. There are also rocks at which amphiboles are not dominant kind such are plagioclase garnet rocks, garnet-plagioclase of pyroxene schists and gabbros-peridotites. The structure of amphiboles vary from association to association, depends on chemism of the rock and metamorphic conditions, and which are usually in fields of Mg-hornblende and tchermakite, and subordinate of pargasite and edenite.

Changes in PT conditions were registered in growth of amphiboles' grains (prograde row of metamorphism, but local and retrograde) and in changes in modal structure of rocks and minerals in paragenesis. Changes in P-T conditions at genesis of amphibole's rocks were registered in growth of amphiboles' grains and changes in modal structure of minerals in paragenesis.

The evolution of metamorphic conditions can be followed by the growth of zonal amphiboles, and which is reflected in reducing the concentration of Si, Fe and Mg parallel with increase of Al, Na and Ti from the core up to the rim of grain. The changes in structure of amphiboles can be described by the following substitutions: pargasite substitutions, edenite substitution, tchermakite, titan-tchermakite substitution.

The results of chemical analyses put on TAS diagram, without taking into account mineral composition, structure, texture and the way of rock's appearing, showed that the analyzed samples represent basaltic association of rocks.

Heterogeneous in types of amphibolites can be described by characteristics of initial rocks with the impact of many subsequent processes. By testing the chemical variations in compound of amphibolites rocks based on simple processes of magmatic fractionation, one can conclude that proportions of immobile elements point out that the system in the beginning behaved as closed, and they also point to non-homogeneity in compound of the initial rocks.

Distribution of amphibolites' analyses doesn't show trend, typical for magmatic rocks, what brings us to conclusion that those chemical variations didn't appear due to magmatic processes. If there was chemically homogeny magmatic rock, then heterogeneous presented today (especially at garnet varieteties of amphibolites rocks and at rocks with parallel-stripped textures) cannot directly points to original structure. The structure is closed on Al, Ti and P what exclude then fractionation and accumulation of feldspaths and Fe-Ti oxides and assimilation of surrounding rocks as the cause for variations. Furthermore, fractionation and accumulation of olivine and pyroxene was excluded because of lack of coherent trend with proportion of 1:1 defined by the proportion of elements which represented that process. That's why the chemical variation which appears as consequence of metamorphic processes, of which the last event is the final grade of consolidation associated with low-pressured and low-temperature flow of fluids – metasomatism in period when the structure is opening. Those flow processes had significant role in layering of gabbros' mass. The structure during the metamorphism didn't stay completely closed, but was opening during genesis of rocks with parallel-stripped textures and during intrude of basical magmas in already formed peridotites-amphibolite-gabbros process, as well as in surrounding Jurassic sediments. In fact, in higher hypabisal levels comes to strengthening of dolerite and diabases which stand in intrusive contact also towards peridotites, amphibolites and gabbros, from one side and towards Jurassic sediments, from the other side.

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