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Interpretation of the Metamorphic Processes in Various Rock Types Using the Chemistry of Garnets (Selečka Mountain, Macedonia)

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Ključne riječi: granati, metamorfizam, Selečka planina, Makedonija

Abstract

The garnets from the complex of Selečka Mountain could be divided in two groups on the basis of their chemical composition and zoning.

The garnets from muscovite-schist and amphibole-schist show characteristics typical for a growth in prograde metamorphic conditions up to the medium metamorphic grade.

Characteristics of the other garnets (from aplite granite, aplite veins and metabasite) suggest their formation in anatectic or highly metasomatic conditions. The inversion in chemical zoning, observed in some of them, is discussed and related to possible processes of growth.

Sažetak

Granati sa Selečke planine mogu se podijeliti u dvije grupe na temelju njihovog kemijskog sastava i zoniranja.

Granati iz tinjčevih i amfibolskih škriljavaca imaju značajke tipične za rast tijekom progresivne metamorfoze, do srednje metamorfnih uvjeta. Značajke ostalih granata (iz aplitskih granita, aplitskih žica i metabazita) sugeriraju nastanak u anatektičkim ili metasomatskim uvijetima. Ovdje se diskutira zoniranje kemijskog sastava, opaženo u nekima od njih i o mogućim procesima tijekom njihovog rasta.

1. INTRODUCTION

The garnets investigated in this study originate from rock samples collected in various parts of the Selečka mountain, near Prilep, Macedonia. In this part of the Pelagon Massif, garnet crystals are present in many types of metamorphic and granitic rocks. The garnets were separated from muscovite schist, amphibole schist, metabasite, aplitic granite and aplite.

The central part of the Pelagonian Massif was petrologically investigated by TUĆAN (1926), MARIĆ (1940), STOJANOV (1958) and many other authors.

According to STOJANOV (1958), whose paper we have used as the geological basis of our work, the Pelagonian Massif represents horst anticlinorium formed from various metamorphic rocks and a large granitic pluton.

It is possible to divide all metamorphic rocks into upper and lower series. The lower series is represented by gneisses and micaschists. This part of the complex is strongly folded. The upper series is represented by a "mixed-series" and marbles. Aplite veins are very abundant in the gneisses and in the "mixed-series" and are probably of anatectic origin. All metamorphic rocks were prograde metamorphosed up to the amphibolite facies (STOJANOV, 1958).

2. EXPERIMENTAL

Garnet crystals were separated from specimens of rocks by hand picking (when large enough) or using a binocular microscope, and combining heavy liquids and a Frantz isodynamic magnetic separator (when crystals were smaller).

The separated garnet specimens were analyzed by powder x-ray diffraction to determine the unit cell parameters of the garnet crystals. A Seeman-Bohlin automated diffractometer (Ital Structures) was used, applying the symmetrical transmission technique (Cu $K_{\alpha 1}$ radiation, l=1.54051 Å) and with ZnO as its internal standard. Diffraction maxima in the range $15° < \theta < 30°$ were measured and the value of the unit cell parameter (a_o) was determined applying least-square refinements (LCLSQ program, BURNHAM, 1962).

Chemical composition was determined by microprobe analyses (Table 1). An energy-dispersive spectrometer (EDS EG&G) was used on an SEM electron microscope (Autoscan) operating at 15 kV. X-ray counts were converted into oxide weight percentages using the MAGIC program (COLBY, 1972), version ORTEC MAGIC IV. The quantities of SiO_2, Al_2O_3, FeO, MgO, MnO and CaO were determined at four or more points in each crystal, scanning from the center to the edge of a grain.

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		SiO_2	Al_2O_3	FeO	MnO	CaO	MgO
	1	37.81	20.98	28.90	4.00	8.11	0.12
Muscovite	2	37.51	20.90	28.84	3.92	8.83	0.00
schist	3	37.78	21.64	34.37	2.79	2.50	0.92
	4	37.66	21.75	36.11	0.74	1.15	2.58
	5	38.23	21.73	33.49	0.08	0.74	5.74
	1	37.33	22.29	25.68	3.55	9.43	1.72
Amphibole	2	38.40	21.39	27.14	1.14	8.48	3.45
schist	3	38.51	22.13	27.23	3.38	7.47	3.28
	4	38.61	22.11	26.69	0.85	7.35	4.39
	1	37.41	21.23	26.63	1.83	12.27	0.62
Granite	2	37.14	20.98	27.70	1.52	12.52	0.13
aplite	3	37.60	21.18	28.28	1.21	11.13	0.59
	4	37.86	20.48	27.76	0.89	11.38	1.62
	5	36.87	21.28	29.93	0.79	10.29	0.85
	1	37.49	20.75	27.38	1.27	13.10	0.00
Aplite	2	36.72	21.12	27.46	1.40	13.30	0.00
vein	3	37.74	21.03	28.03	0.73	12.47	0.00
	4	37.03	20.95	25.96	0.98	14.92	0.16
	5	37.96	20.70	22.30	1.24	17.80	0.00
	1	39.05	21.51	23.21	1.73	13.78	0.73
Metabasite	2	39.16	21.69	20.28	2.80	15.95	0.13
(large grain)	3	37.94	20.94	21.65	2.65	16.81	0.00
	4	38.30	22.15	22.93	1.97	13.76	0.89
Metabasite	1	38.32	21.24	21.62	2.42	14.75	0.65
(small grain)	2	37.14	21.29	24.18	1.94	13.82	0.83

Table 1. Chemical composition of garnets (wt.%) along traverse.

The chemical formulas were calculated from the analyses using the MINFILE program (AFIFI & ESSENE, 1988).

3. RESULTS

In Table 2 the average chemical compositions and formulas of garnets from various rock types are presented, together with calculated molecular percentages of almandine, andradite, spessartine, pyrope and grossular end members and crystal lattice parameters.

The calculated chemical formulas indicate that in the crystal structures of the analyzed garnets the tetrahedral (T) sites are fully occupied by Si, the octahedral (O) sites are practically fully occupied by Al (over 95%), while Fe^{2+} and Ca^{2+} dominate in the eight-coordinated (A) sites. The observed crystal lattice parameters are in good accordance with the parameters calculated from the chemical composition, assuming the formula proposed by Novak and Colville (MEAGHER, 1980). Based on the bulk chemical composition, the two groups can be recognized. The garnets from amphibole schist and muscovite schist represent the first group in which an almandine component dominates, with a relatively small amount of grossular component and a significant content of pyrope component. The a_o values are, accordingly, equal to or lower than 11.6 Å. The garnets from aplite veins and metabasite belong to the second group in which the content of the grossular component almost equals that of almandine, while the pyrope component almost disappears. The a_o values, accordingly, approach 11.7 Å. The chemical composition of garnets from aplitic granite is intermediate between these two groups.

The observations of chemical zoning in various specimens can be summarized as follows:

Characteristic of the garnets from muscovite schist (Fig. 1) is that the crystal core is about ten times richer in Ca than the rim in which Fe and Mg increase. Mg is especially enriched on the very edge, even at the expense of Fe.

Characteristic of the garnet from amphibole schist (Fig. 2) is a significantly higher Mg content, matched only by the outer zone of the garnet from muscovite-schist. A fairly constant Fe content and a decrease in Ca and Mn going from the core to the rim can also be observed.

In the garnets from aplitic granite (Fig. 3), a small increase in Fe and Mg, as well as a depletion of Ca and Mn can be observed from the core to the rim.

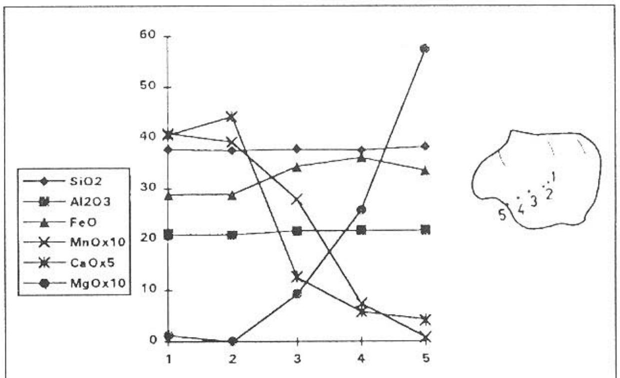

Fig. 1. The zoning of Si, Al, Fe, Mn, Mg and Ca (as oxide percentages) in investigated garnets from muscovite schist.

	1	2	3	4	5
SiO_2	37.67	37.87	37.26	36.29	36.97
Al_2O_3	21.56	21.65	20.79	20.25	20.76
FeO	34.37	26.55	28.42	24.38	21.17
MnO	1.01	1.17	0.94	1.02	2.36
MgO	3.23	3.61	1.12	0.07	0.34
CaO	1.63	7.48	10.98	14.93	15.04
Total	99.47	98.33	99.51	96.94	96.64
Si IV	6.04	6.03	5.98	5.96	6.03
Al IV	0.03	0.03	0.02	0.04	-
T site	6.07	6.06	6.00	6.00	6.03
Al VI	4.08	4.07	3.91	3.88	3.99
Fe^{+3}	-	-	0.09	0.13	0.03
O site	4.08	4.07	4.00	4.01	4.02
Fe^{+2}	4.61	3.54	3.72	3.22	2.86
Mn^{+2}	0.14	0.16	0.13	0.14	0.33
Mg	0.77	0.86	0.27	0.02	0.08
Ca	0.28	1.28	1.89	2.63	2.63
A site	5.80	5.83	6.00	6.01	5.90
al	79	61	62	54	48
an	-	-	2	3	1
sp	2	3	2	2	6
py	13	15	5	0	1
gr	5	22	29	41	44
a_o (Å)	11.537(2)	11.600(3)	11.668(1)	11.678(4)	11.691(1)
calc.	11.535	11.595	11.632	11.681	11.678

1 garnet from muscovite schist
2 garnet from amphibole schist
3 garnet from granite
4 garnet from aplite veins
5 garnet from metabasite

The bulk chemical composition calculated from microprobe measurements, averaged taking into account volume contributions. a_o is the value observed, calc. is calculated assuming the following formula:

$a_o = 8.44 + 1.71\langle r_A\rangle + 1.78\langle r_O\rangle + 2.17\langle r_T\rangle$

r represents the average ionic radii for the appropriate site (MEAGHER,1980).

Table 2. The average chemical composition, calculated formulas (on the basis of 24 oxygens), molecular percentages of end members and the lattice parameters (a_o) of garnets from various rock types of Selečka mountain.

Garnets from aplite veins (Fig. 4) are characterized by a negligible Mg content and a very small Mn content, which, however, shows an increase in the mantle, in contrast with the other analyzed garnets. Reversal zoning can also be observed, but in the opposite sense than in garnets from metabasite. Going from core to rim, the first trend is an increase in Fe, Ca and Mn which reverses in the mantle. Between the two zones characterized by opposite trends, an inclusion of epidote was observed.

The garnets from metabasite (Fig. 5) show reversal zoning. Going from core to rim, the first trend in zoning is a decrease of Fe and Mg, and an increase in Ca which reverses in the rim. Fe content here is lower than in all the other analyzed garnets.

4. DISCUSSION

In all cases, the investigated specimens are predominantly almandine garnets. In aplitic granite, aplite veins and metabasite, the content of grossular amounts is unusual for dominantly almandine garnets. In addition, the content of pyrope is very low in these cases. Especially in aplite veins, with MnO and MgO contents of only about 1%, the garnet could be described as a practically pure mixture of almandine and grossulare in a proportion very close to 1:1.

As proven by the chemical composition of garnets, a clear distinction in composition and/or process of formation exist between the schists and the aplitic rocks (to these we can account aplite veins, aplitic granite and metabasite - see below). Garnets from amphibole schist and muscovite schist can be regarded as almandine garnets formed in prograde metamorphic conditions, while

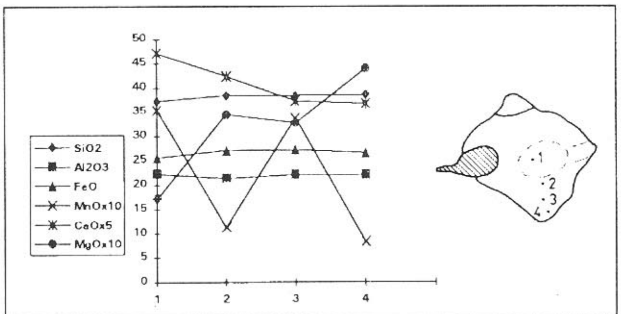

Fig. 2. The zoning of Si, Al, Fe, Mn, Mg and Ca (as oxide percentages) in investigated garnets from amphibole schist.

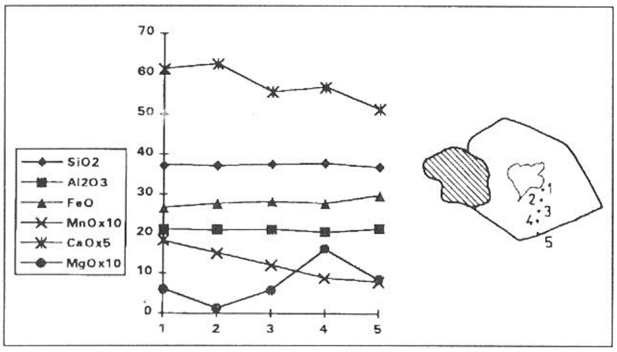

Fig. 3. The zoning of Si, Al, Fe, Mn, Mg and Ca (as oxide percentages) in investigated garnets from aplitic granite.

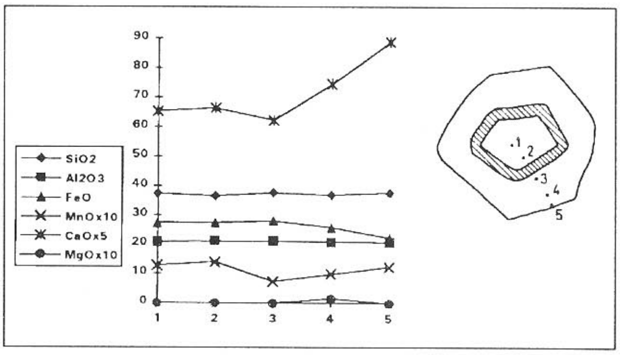

Fig. 4. The zoning of Si, Al, Fe, Mn, Mg and Ca (as oxide percentages) in investigated garnets from aplite veins.

for the others, specific conditions of formation must be considered.

1. Garnets from the muscovite schist (Fig. 1). Muscovite schists belong to the upper part of the lower metamorphic series of the Pelagonian Massif. The typical mineral assemblage is muscovite+garnet+kyanite, with or without staurolite. Garnet represents one of the main minerals in the paragenesis and it can be concluded that it grew continuously during a prograde metamorphic event. The size of the individual crystals varies from approximately 1 mm to 1 cm, and the largest ones were chosen for the analysis.

The composition and zoning are typical for prograde metamorphic growth of garnet up to the medium metamorphic grade (kyanite grade). The only specific feature is the relatively low content of Mg (especially in the core). Garnet is the main mafic mineral, which probably reflects a very low Mg content in the original pelitic rock.

Fig. 1 illustrates the SiO_2, Al_2O_3, CaO, FeO, MnO and MgO variations (in the traverse) from the core to the rim of the (large) garnets. It is obvious that the Fe and Mg contents increase continuously from the core to the rim of the crystal, but Mn and Ca increase in the opposite direction. All chemical investigations of garnets in such regionally metamorphosed terrains reveal the same trend, the well-known bell-shaped distribution (ATHERTON, 1968; HOLLISTER, 1966; De BETHUNE et al., 1975; CYGAN & LASAGA, 1982). This means that the distribution of Fe, Ca, Mn and Mg obviously suggest prograde regional metamorphic development of muscovite schists.

2. Garnets from the amphibole schist (Fig. 2). Amphibole schists are mainly found as intercalations in gneiss series. Their common assemblage is: green hornblende, feldspar, some quartz and garnet. In the thin section, two optical zones are visible in the garnet crystals. The overall trend of chemical zoning is very similar to that in garnet from muscovite-schist, signifying a prograde metamorphic growth up to the medium grade in this case as well. The Mg and Mn contents here are more typical for the metamorphic almandine garnets, which could be attributed to differences in the bulk chemical compositions of the two rocks. The observed optical zoning and the observed kink in chemical zoning probably show that the garnet grew in two cycles of different gradients. A more systematic petrological investigation is necessary to show the significance of this observation and relate it to reactions during the metamorphic event.

3. Garnets from aplitic granite (Fig. 3). Garnet-containing aplitic granite was injected in the form of granitic infiltrations in the granito-metamorphic complex. Some authors described these rocks as granulites (STOJANOV, 1958). However, the texture and mineral composition do not show the characteristic features for the metamorphic rock of a granulite facies. A relatively high Ca content and a very low Mn and Mg content speak in favour of anatectic origin. Compositional zoning could be attributed to crystallization from infiltrat-

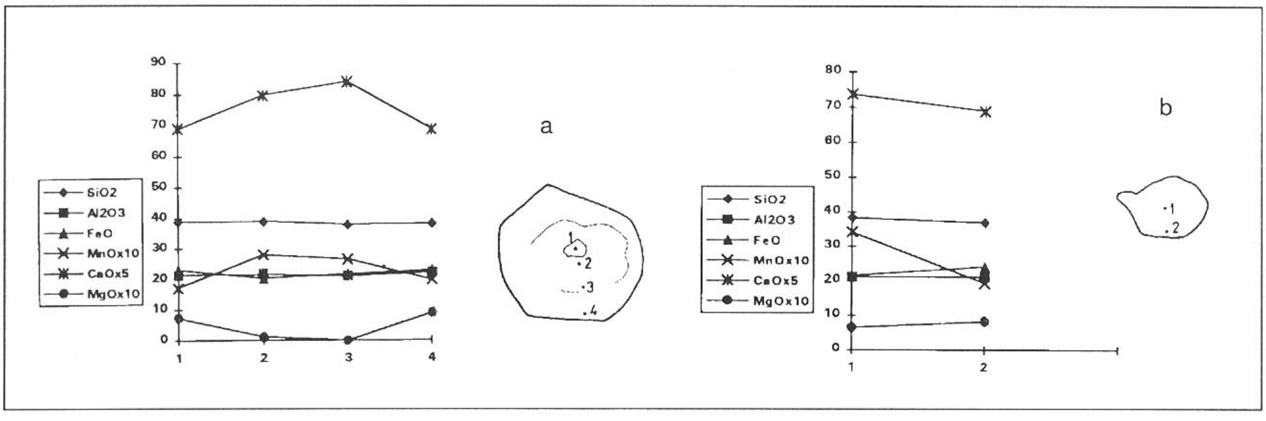

Fig. 5. The zoning of Si, Al, Fe, Mn, Mg and Ca (as oxide percentages) in investigated garnets from metabasite: a) large grain; b) small grain.

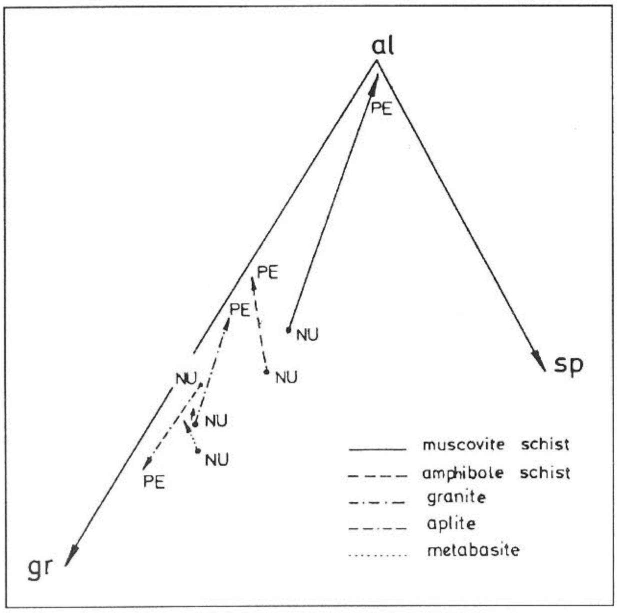

Fig. 6. Ternary molecule percent plots showing chemical trend of zoning in garnets of investigated rock types. Garnets from aplite veins have an reversed trend in comparison to the garnets from other rocks.

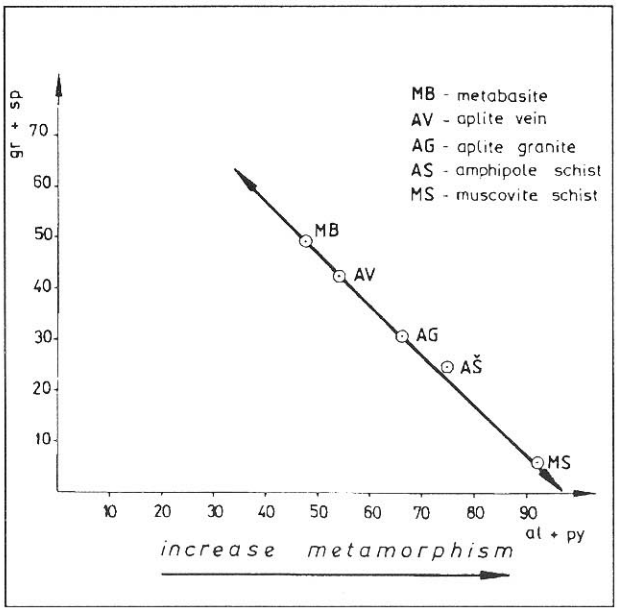

Fig. 7. Relation between almandine-pyrope and grossulare-spessartite garnets and metamorphic conditions.

ing fluid granitic material, which would produce a Mn-richer core and an Fe and Mg-richer rim of the garnet grain. It is interesting to note that this garnet, which appears in relatively small grains, has a composition which is very similar to that of the cores of the much larger garnets from the aplite vein.

4. Garnets from the aplite vein (Fig. 4). Aplite veins are abundant in granite body and in metamorphic rocks, especially in gneiss. The form of the aplite veins, their texture and mineral paragenesis point to their anatectic origin. Large garnet crystals (1.5-2 cm) originating from such a vein, were analyzed in this work. Crystals are usually poikiloblastic porphyroblasts. In the thin section, two optical zones can be observed, separated by a narrow belt containing inclusions. As stated earlier, the trend of chemical zoning is reversed in the grain, and this change could be correlated with the optical zoning. The core has composition and zoning similar to those of garnet from granite. Therefore, the same mechanism for the initial formation of these garnets could be suspected. In the mantle, reversed zoning is found, i.e. an increase in Ca and Mn, and a decrease in Fe and Mg. Various reactions could be proposed as being responsible for this change in zoning: the subsequent growth of previously crystallized garnets in retrograde metamorphic conditions, pressure changes (TRACY et al., 1976), the consumption of some calcic mineral from the surrounding assemblage (epidote?), or the Ostwald ripening of the garnet crystals in a relatively low heating gradient. The last process (the growth of the large grains at the expense of the small ones) would imply that the already anatectically-formed garnet remained for a longer period in an environment with high intergranular diffusion and a low heating gradient, as could be expected for the veins. During this period, the smaller grains dissolved, giving material in order for the larger ones to grow in accordance with the rules governing Ostwald ripening. This would explain both the presence of exclusively large garnet crystals in the veins and the inversion of the zoning trend in their mantles (LOOMIS, 1975, 1982; LOOMIS & NIMICK, 1982). The formation of the mantle of the large crystals by the deposition of material supplied by the progressive dissolution of smaller ones would, evidently, produce a constant increase in Ca and Mn content. Ostwald ripening for some metamorphic garnets has been documented by MIYAZAKI (1991) on the basis of crystal size distribution and chemical zoning in the coexisting small and large grains.

5. Garnets from metabasite (Fig. 5). These metamorphosed basic rocks were described as metamorphosed sills or dykes (STOJANOV, 1958).

The garnet crystals were separated from a small laccolith body of a metabasic rock. The rock texture is well layered, at higher levels of intruded body, due to multiple intercalations of material with granitic composition, where small garnet crystals are also concentrated. Garnet is in the association with pyroxene, hornblende, zoisite, albite and biotite. As stated earlier, the trend of zoning in garnet reverses from an initial decrease in Fe and Mg to an increase in the rim. The zoning of Mg and Ca show an opposite trend through the entire profile. The zoning of Mn shows a constant depletion of this element from core to rim, which suggests a continuous prograde metamorphic growth of garnet. The zoning of other elements could be highly influenced by the metasomatic processes connected with the vicinity of granitic melts, as shown by the rock texture. The garnet is generally very high in grossular component, which is characteristic of aplite garnets from Selečka Mountain. Thus, we can conclude that the first part of the curves refer to a growth period, probably of metasomatic exchange between the granitic melt and the primary mineral assemblage. The outer part continued the growth under conditions of regional metamorphism.

Diversity of the chemistry of garnets is shown on Fig. 6. The common end-member components almandine (alm), grossulare (gro) and spessartine (sp) change from nucleus (NU) to rim (PE) in garnets of muscovite schist, amphibole schist, aplitic granite and metabasic rocks. The trend of chemical changes in all of these rocks is the same except in aplite, where it is reversed.

5. CONCLUSION

We have made an attempt to explain the diversity of the metamorphic processes which affect the growth of garnets in the various rock types.

The change in chemistry was influenced not only by pressure and temperature changes, but also by changes of metasomatic processes. It is well known that by an increase of PT conditions a garnet is enriched with almandine and pyrope molecule. From Fig. 7 it is obvious that garnets in muscovite schist were created under highest metamorphic conditions. Metamorphic processes in metabasite and aplite belong to some lower PT event.

6. REFERENCES

AFIFI, A.M. & ESSENE, E.J. (1988): Minfile.- University of Michigan, Ann Arbor.

ATHERTON, M.P. (1968): The variation in garnet, biotite and chlorite composition in medium grade pelitic rocks from Dalradian, Scotland, with particular reference to the zonation in garnet.- Contrib. Mineral. Petrol., 18, 347-371.

BURNHAM, C.W. (1962): Lattice constant refinement.- Carnegie Institution of Washington Yearbook, 61, 132-135.

COLBY, J.W. (1972): MAGIC IV, a computer program for quantitative electron microprobe analysis.- Bell Telephone Laboratories Inc., Allentown, Pennsylvania.

CYGAN, R.T. & LASAGA, A.C. (1982): Crystal growth and the formation of chemical zoning in garnets.- Contrib. Mineral. Petrol., 79, 187-200.

De BETHUNE, P., LADURON, D. & BOCQUET, J. (1975): Diffusion processes in resorbed garnets.- Contrib. Mineral. Petrol., 50, 197-204.

HOLLISTER, L.S. (1966): Garnet zoning: An interpretation based on the Rayleigh fractionation model.- Science, 154, 1647-1651.

LOOMIS, T.P. (1975): Reaction of zoning of garnet.- Contrib. Mineral. Petrol., 52, 285-305.

LOOMIS, T.P. (1982): Numerical simulation of the disequilibrium growth of garnet in chlorite-bearing aluminous pelitic rocks.- Can. Mineral., 20, 411-423.

LOOMIS, T.P. & NIMICK, F.B. (1982): Equilibrium in Mn-Fe-Mg aluminous pelitic compositions and the equilibrium growth of garnet.- Can. Mineral., 20, 393-410.

MARIĆ, L. (1940): Petrografska i geološka građa okoline Prilepa u južnoj Srbiji.- Vesn. Geol. inst. Kr. Jug., VIII, Beograd.

MEAGHER, E.P. (1980): Silicate garnets.- In: RIBBE, P.H. (ed.): Ortho-silicates. Mineralogical Society of America, Reviews in Mineralogy, 5, Washington D.C.

MIYAZAKI, K. (1991): Ostwald ripening of garnet in high P/T metamorphic rocks.- Contrib. Mineral. Petrol., 108, 118-128.

STOJANOV, R. (1958): Prethodni rezultati od geološkite i petrografskite istražuvanja na Selečka planina.- Trudovi geol. inst. NRM, Skopje, 6, 127-182.

TRACY, R.J.(1982): Compositional zoning and inclusions in metamorphic minerals.- In: FERRY, J.M. (ed.): Characterisation of metamorphism through mineral equilibria. Mineralogical Society of America, Reviews in Mineralogy, 10, Washington, D.C.

TRACY, R.J., ROBINSON, P. & THOMPSON, A.B.(1976): Garnet composition and zoning in the determination of temperature and pressure of metamorphism, central Massachusetts.- Am. Mineral., 61, 762-775.

TUĆAN, F. (1926): Mineraloško-petrografska proučavanja u kristalnom masivu između Prilepa i Kajmakčalana.- Glasnik Sk. Nauč. društva, Skopje, II/1,2.

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