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Compositional Zoning in Amphibole from Amphibole Bearing Parageneses of West Psunj (Croatia): Evidence for Progressive Metamorphism?

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Abstract

Amphibole bearing parageneses from the western part of Mt. Psunj (Croatia) record evidence of prograding metamorphism. Optical and microprobe analyses, together with thermobarometric evaluations on amphibole bearing parageneses, show a zonation with Si- and Mg-concentrations decreasing from core to rim along with increasing Al-, Na-, and Ti-content. Changes in the chemical composition of amphibole grains are interpreted through coupled substitutions, and reactions with co-existing minerals during an increase in metamorphic conditions from greenschist to amphibolite facies. The change in P-T conditions recorded in the growth of amphibole grains (general prograding pattern) together with changes in the modal compositions in related parageneses could be interpreted in a model of a subduction zone.

1. INTRODUCTION

Minerals of the amphibole group are common rock-forming minerals in metamorphic rocks. They are stable over a wide range of pressures and temperatures i.e. in various grades of metamorphism. The associations of amphibole with plagioclase, epidote, clinozoisite, chlorite, sphene, etc. are common in metamorphosed mafic rocks of the greenschist facies, epidote-amphibolite facies and amphibolite facies.

Many authors recognize similar assemblages, usually called "common assemblages" (LAIRD & ALBEE, 1981) for mafic schists of greenschist to amphibolite facies all over the world. In contrast to mafic schists, in metapelitic rocks even small incremental changes in pressure and temperature can be determined by the simple recognition of key minerals. Changes of metamorphic grade in mafic schists are less obvious. Differences between metamorphic facies may be recorded through continuous reactions which produce "fingerprints" in the chemical composition of phases and the modal composition of minerals. These, less obvious changes may be followed through changes in optical properties and the information recorded in the zone of growth. In general the appearance or disappearance of phases (i.e. first appearance of hornblende in epidote-amphibolite) are only revealed when great changes in P-T conditions occur and small changes of P-T conditions is easy to overlook, especially in the field.

The assemblage stable in the greenschist zone consists of albite + epidote + chlorite + actinolite + quartz + sphene (temperature below 370°C). In the transition zone an assemblage appears which includes peristerite pairs + epidote + chlorite + Ca-amphibole (usually both actinolite and hornblende) + quartz + sphene and the temperature varies between 370-420°C. The amphibolite facies is characterized by Ca-plagioclase (An_{20-50}) + Ca-amphibole (usually hornblende) + chlorite + sphene + ilmenite (MARUYAMA et al., 1982).

Geologic evidence suggests that the transition from the greenschist to the epidote-amphibolite facies and from the epidote-amphibolite to amphibolite facies may represent a P-T field in which a number of the critical equilibrium curves are closely spaced and intersect each other (APTED & LIOU, 1983). Therefore the recognition of P-T conditions in mafic schists is a difficult task but in favorable circumstances oscillations of metamorphism could be recorded and the quantitative value of metamorphic variables could be approximated.

Petrological study of the ultramafic rocks together with known data from associated amphibolites in the area of the Slavonian mountains suggests that the investigated rocks belong to an ophiolite complex (PAMIĆ & MARCI, 1990; PAMIĆ & LANPHERE, 1991)

The purpose of this study is to determine the mineral assemblages that coexist in equilibrium, and to estimate (through chemical data of the amphiboles) the limits of temperature and pressure during metamorphism of the amphibole-bearing rocks of western Psunj. The growth of amphibole under changing P-T conditions may serve as an indicator of the geotectonic evolution of the investigated area.

2. HISTORICAL REVIEW

There are numerous papers published on the crystalline rocks from the Slavonian mountains (for a comprehensive list of references see PAMIĆ & LANPHERE, 1991). KIŠPATIĆ (1892) produced the first petrographic and geologic data for various metamorphic

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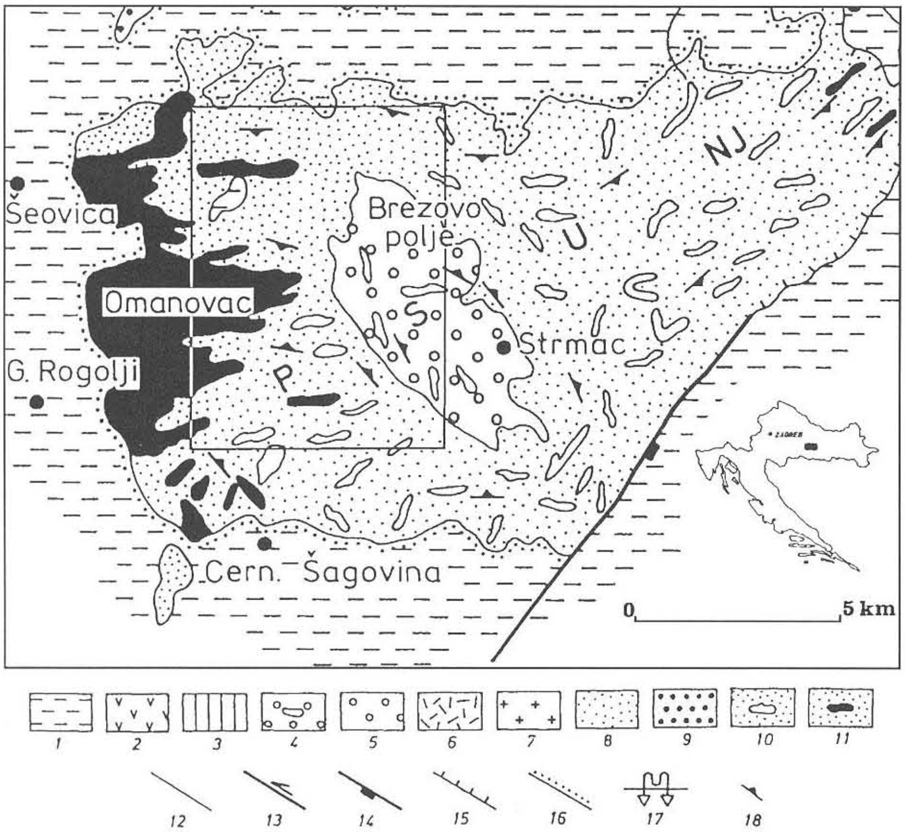

Fig. 1 Generalized geological map of Mt. Psunj from PAMIĆ & LANPHERE (1991). Legend: □ - study area; 1) Tertiary and Quaternary sediments; 2) Tertiary volcanic rocks; 3) Mesozoic sediments; 4) metamorphic complex with metabasites; 5) metamorphic complex without metabasites; 6) migmatites; 7) S-type granitoids; 8) amphibolite facies; 9) greenschist facies; 10) amphibolite interlayers; 11) I-type granites; 12) contact line; 13) horizontal fault; 14) normal fault; 15) reverse fault; 16) unconformity; 17) isoclinal folds; 18) foliation.

rocks and indicated the importance of index minerals and assemblages. MARCI (1965) and TAJDER (1969) focused their attention on the western part of Mt. Psunj and on the mineralogical composition of amphibole-bearing rocks. Recently PAMIĆ & MARCI (1990) and PAMIĆ & LANPHERE (1991) examined the amphibolites petrographically and showed that the amphibolite of the Slavonian mountains is regular member of the Hercynian progressive metamorphic complex. The chemical composition of the amphibolitic rocks correlates with oceanic tholeiite. Nevertheless, the geotectonic setting is not reliably determined.

3. STUDY AREA

The study area is delimited by the creeks Rašaška and Jezerica to the south, Šumetljica to the north, Brezovo Polje peak in the east, and the granite body of Omanovac to the west (Fig. 1).

Amphibolite and amphibole schists of west Psunj occur as lenses up to 10-20 m in size. There are also occurrences of small bodies of metagabbro in the study area. The investigated rocks (amphibolite, amphibole schist, metagabbro) occur in discordant position to the surrounding rocks (granite, sediments), and are probably Precambrian in age (JAMIČIĆ et al., 1989). Later intrusion of the granite body resulted in retrograde alteration of the amphibole bearing rocks.

4. MATERIALS AND METHODS

The mineral parageneses of amphibole bearing schists, metagabbro and amphibolite were examined by standard polarizing microscope and detailed optical measurements were made using a Carl Zeiss Jena microscope equipped with a five axes universal stage and conoscopic illumination.

Selected grains were chemically analyzed by electron microprobe at the University of Bern. The electron microprobe used was a CAMECA SX 50 instrument equipped with WDS spectrometers with LiF, PET and TAP diffraction crystals. A beam current of 20 nA, accelerating voltage 15 kV, peak counting 20 sec, and beam diameter less than 1 μm were the operating conditions. Synthetic standards used included fayalite (Fe), spinel (Mg), tephroite (Mn), ilmenite (Ti), eskolaite (Cr) together with natural standards: orthochlase (Si, K), albite (Na), anorthite (Ca, Al). Instrument control and on-line data reduction were performed using the CAMECA version of the PAP procedure (POUCHOU & PICHOIR, 1984).

The amphibole formulae were generated with the MINFILE software (AFIFI & ESSENE, 1988) on the basis of 23 O and 13 cations + Ca + Na + K.

5. RESULTS

5.1. PETROGRAPHY

Four rock types were recognized in the amphibole bearing rocks of western Mt. Psunj on the basis of microscopic study, mineral content and textural features, and are listed as follows:

A) epidote-amphibole schist:

amphibole (actinolite and hornblende), epidote, quartz, oligoclase, albite ± ilmenite, sphene, chlorite;

B) amphibolite:

amphibole (hornblende), oligoclase ± clinozoisite, chlorite, ilmenite, sphene, quartz;

C) metagabbro:

amphibole (hornblende), oligoclase, clinozoisite, ilmenite, sphene ± epidote, chlorite, clinopyroxene, quartz;

D) "granitized" amphibolite:

amphibole (hornblende), oligoclase, clinozoisite, biotite, ilmenite, sphene ± quartz, epidote, microcline.

The minerals are listed in order of abundance.

Some minerals (chlorite, clinozoisite, ...) which are common in the rock types are products of later retrograde metamorphism and do not represent an equilibrium state with the other minerals. Also, clinopyroxene-amphibole-chlorite+clinozoisite alterations imply a retrograde trend. These retrograde changes are attributed to changes of the metamorphic conditions during intrusion of the granite body.

Amphibole

Amphibole occurs as xenoblasts in all the parageneses. In assemblage A it also occurs as needle like aggregates with weak green-yellow pleochroism. During growth, amphibole replaced pyroxene and encompassed other mineral grains (plagioclase, ilmenite, sphene). Within the cracks inside the amphibole grains aggregates of chlorite and clinozoisite were formed. Amphiboles in epidote-amphibole schists of the neighbouring granite body often show alteration to biotite. This is characterized by the change from a green coloured amphibole at one end of a grain toward the brown colour of biotite at the other end of the same grain (in sections parallel to the c-axis of amphibole).

Measurements of the optical parameters of selected grains of amphibole indicated six different types of amphibole:

a) Needle like actinolite with a maximum extinction angle Z^c = 12° and optical axial angle 2V = -74°; pale pleochroism: X = Y = yellow, Z = green. It was observed in type A assemblage.

b) Hornblende with a maximum extinction angle Z^c = 19° and optical axial angle 2V = -64°; pleochroism: X = yellow, Y = green, Z = bluish-green, observed in type A and B assemblages.

c) Hornblende with a maximum extinction angle Z^c = 16° and optical axial angle 2V = -72°; pleochroism: X = yellow, Y = green, Z = dark green, observed in type C assemblage.

d) Hornblende with maximum extinction angle Z^c = 30° and optical axial angle 2V = +87°; pleochroism: X = yellow, Y = green, Z = dark green, observed in type C assemblage.

e) Hornblende with maximum extinction angle Z^c = 18° and optical axial angle 2V = -89°; pleochroism: X = yellow, Y = green, Z = dark green, observed in type C assemblage.

f) Hornblende with maximum extinction angle Z^c = 8° and optical axial angle 2V = -85°; pleochroism: X = brown, Y = yellowish-green, Z = green, observed in type D assemblage.

Plagioclase (oligoclase)

Plagioclase occurs as hipidiomorphic elongated grains and alotriomorphic equidimensional grains. Usually, the hipidiomorphic grains display polysynthetic twin lamellae according to albite law $B_{1/2} = \perp(010)$. Metamorphic processes caused intensive sericitization and saussuritization. The Michel-Levy method and U-stage measurements using the Fedorov method determined the plagioclase as oligoclase with a composition of An 26-30 mol. %. Oligoclase appears in all assemblages.

Albite and microcline

Albite occurs as fresh xenoblasts, obviously as a late mineral in the assemblage. It occurs in assemblage A. Microcline is observed in the type D assemblage and is a product of metasomatic reactions caused by the later intrusion of the granite body.

Epidote

Epidote is common in type A assemblage and a minor component in both C and D assemblages. It appears as irregular, weakly pleochroic grains, pale yellow to yellow colors; 2V = -75° (pistacite) and is often associated with needle like actinolite.

Clinozoisite

Clinozoisite appears as irregular grains, which originated from primary basic plagioclases; 2V = +85°. It occurs in the B, C and D assemblages.

Quartz

Quartz is present in all assemblage types and often shows evidence of cataclastic processes.

Oxides	A1	A2	B1	C1	C2	C3	C4	D1	D2
SiO_2	45.71 (1.43)	50.84	44.54 (0.33)	42.96 (0.74)	46.74	46.12 (0.24)	49.33 (0.57)	47.52 (0.80)	45.63 (0.71)
TiO_2	1.09 (0.32)	0.04	0.95 (0.04)	2.73 (0.46)	1.86	0.95 (0.14	0.66 (0.05)	0.98 (0.22)	0.55 (0.08)
Al_2O_3	7.31 (0.97)	2.34	10.32 (0.28)	11.53 (1.02)	9.19	8.99 (0.19)	6.44 (0.19)	7.77 (0.54)	14.43 (0.77)
$Fe_2O_3^*$	3.27 (0.39)	1.38	4.41 (0.22)	6.51 (1.97)	2.49	3.30 (0.50)	4.34 (0.58)	3.55 (0.74)	3.70 (0.86)
FeO	15.39 (0.76)	16.40	12.69 (0.16)	8.45 (1.74)	9.54	12.16 (0.40)	10.88 (0.55)	13.17 (0.85)	9.51 (1.18)
MnO	0.42 (0.04)	0.25	0.29 (0.03)	0.21 (0.03)	0.27	0.22 (0.03)	0.23 (0.04)	0.40 (0.09)	0.22 (0.08)
MgO	10.12 (0.78)	11.75	10.90 (0.14)	11.70 (0.44)	13.66	11.79 (0.16)	13.28 (0.29)	11.59 (0.60)	11.12 (0.58)
CaO	11.85 (0.16)	12.29	12.02 (0.12)	10.93 (0.47)	12.27	12.02 0.10)	12.02 (0.19)	11.88 (0.20)	10.51 (0.44)
Na_2O	0.91 0.13)	0.24	1.44 (0.08)	1.61 (0.29)	1.00	1.05 (0.02)	0.81 (0.09)	1.10 (0.09)	2.20 (0.24)
K_2O	0.71 (0.18)	0.11	0.47 (0.06)	0.49 (0.14)	0.27	0.47 (0.02)	0.24 (0.03)	0.44 (0.08)	0.51 (0.07)
H_2O^*	1.98 (0.02)	1.99	2.02 (0.01)	2.03 (0.00)	2.06	2.03 (0.00)	2.07(0.01)	2.04 (0.02)	2.09 (0.01)
Sum	98.75 (0.62)	97.62	100.05 (0.59)	99.15 (0.07)	99.35	99.11 (0.17)	100.30 (0.71)	100.44 (0.62)	100.47 (0.39)
$\#Si^{IV}$	6.91	7.68	6.59	6.33	6.80	6.83	7.14	6.97	6.55
$\#Al^{IV}$	1.09	0.32	1.41	1.67	1.20	1.17	0.86	1.03	1.45
T site	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
$\#Al^{VI}$	0.22	0.09	0.39	0.34	0.37	0.39	0.24	0.30	0.99
$\#Fe^{3+}$	0.37	0.16	0.49	0.72	0.27	0.37	0.47	0.39	0.40
#Ti	0.12	0.00	0.11	0.30	0.20	0.11	0.07	0.10	0.06
#Mg	2.28	2.64	2.40	2.57	2.96	2.60	2.87	2.53	2.38
$\#Fe^{2+}$	1.95	2.07	1.57	1.04	1.16	1.50	1.32	1.62	1.14
#Mn	0.05	0.03	0.04	0.03	0.03	0.03	0.03	0.05	0.03
$M_{1,2,3}$	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
#Ca	1.92	1.99	1.91	1.72	1.91	1.90	1.86	1.86	1.62
#Na	0.08	0.01	0.09	0.28	0.09	0.10	0.14	0.14	0.38
M_4 site	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
#Na	0.19	0.06	0.32	0.18	0.19	0.21	0.09	0.18	0.23
#K	0.14	0.02	0.09	0.09	0.05	0.09	0.05	0.08	0.09
A site	0.33	0.08	0.41	0.27	0.24	0.30	0.14	0.26	0.32
#O	22	22	22	22	22	22	22	22	22
#OH	2	2	2	2	2	2	2	2	2
No anal.	9	1	5	6	1	5	4	8	10

Table 1 Representative microprobe analyses of amphiboles and formulae calculated on the basis of 23 O and 13 cations +Ca+Na+K.

Ilmenite

Ilmenite shows alteration to sphene in all assemblages.

Clinopyroxene

This is a primary magmatic mineral which appears as a relict. The contact of pyroxene and plagioclase is rimmed by very fine needles of amphibole. Within the grains of plagioclase, clinozoisite and other alteration products such as saussirite can be observed.

According to optical examinations combined with microprobe data, this pyroxene could be characterized as diopside. It is observed in type C assemblage.

Biotite

Biotite is often replaced by chlorite, and near the granite body it replaces amphibole due to metasomatic processes. It occurs in type D assemblage.

Chlorite

Chlorite occurs in type A, B and C assemblages, in

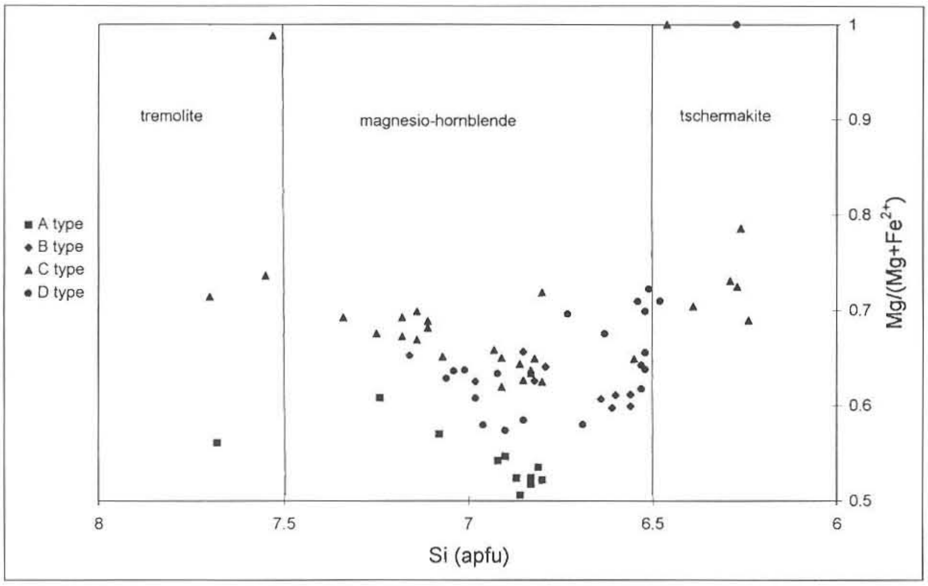

Fig. 2 Classification of calcic amphibole (modified after LEAKE, 1978; HAWTHORNE, 1983; ROCK & LEAKE, 1984 according to International Mineralogical Association Commission on New Minerals and Mineral Names (IMA CNMMN) Nomenclature of Amphiboles (Draft 5, 1995)). Diagram parameters: $Ca_B \geq 1.50$; $(Na + K)_A < 0.50$; $Ca_A < 0.50$.

the cleavage cracks of amphibole as alterations and as individual grains in the matrix.

Additional minerals

Garnet occurs as grains in type D assemblage. Calcite is a secondary mineral. Apatite and zircon are very rare, and are observed as solid inclusions in both amphibole and plagioclase.

5.2. MINERAL CHEMISTRY

Amphibole

A representative chemical analysis of selected amphibole samples and their chemical formulae are presented in Table 1. The Fe^{2+} and Fe^{3+} contents were estimated from the total of cations (excluding Na, K and Ca) normalized to 13.

Assumption of normalizing cations to 13 + Ca + Na + K excludes Mn, Fe^{2+} and Mg from the M_4 site in the formulae (ROBINSON et al., 1982) and produces fairly reasonable estimates of FeO and Fe_2O_3. This normalization procedure is also favored by the International Mineralogical Association (IMA) amphibole nomenclature scheme (LEAKE, 1978; HAWTHORNE, 1983; ROCK & LEAKE, 1984). In this work, the original classification scheme after Leake was modified according to the Commission on New Minerals and Mineral Names (CNMMN IMA) Nomenclature of Amphiboles (Draft 5, 1995). Modifications are basically changes in the values of diagram parameters which result in the disappearance of the fields of tchermakitic and actinolitic hornblende.

All the analyzed amphibole grains have $(Ca+Na)_B > 1.0$ and $Na_B < 0.5$, so they are calcic amphiboles. A graphical presentation of the analyses is given in Fig. 2.

Further subdivision of the amphiboles on the basis of the plot $Mg/(Mg+Fe^{2+})$ against Si shows that most of the analyzed samples occur in the field of magnesio-hornblende (type A, B and D). Amphiboles of C type show a high degree of variability and project into the fields of tschermakite and magnesio-hornblende. The actinolite of type A project into the "tremolite" field.

The tetrahedral values of Si are restricted between 6.33 and 7.14 apfu with the exception of actinolite (7.68 apfu Si).

The octahedral aluminum ranges between 0.22 and 0.39 apfu with the exception of actinolite (0.99). According to ROBINSON et al. (1982), the total Al^{VI} should not exceed 1.4 and averages around 0.4 apfu. Titanium in the octahedral sites varies from 0.06 to 0.30 apfu (it is not detected in actinolite).

The contents of Mg and Fe^{2+} in the $M_{1,2,3}$ sites are complementary because these are two essential cations in the amphiboles. Variation of these two cations in the amphiboles reflects the chemistry of their host rocks. Mn is a minor element in the $M_{1,2,3}$ site.

Calcium is concentrated in the M_4 site and varies from 1.62 to 1.99 apfu. Sodium partially fills the M_4 site to 2.00 apfu and the remaining Na with K is assigned to the A site. The total Na in both sites in amphiboles from type D assemblage can reach 0.62 apfu which is an elevated concentration in comparison with other amphiboles. Potassium is restricted to the A site from 0.02 to 0.14, averaged 0.08 apfu.

5.3. THERMOBAROMETRIC EVALUATION OF METAMORPHISM

Recent studies indicate rules which govern changes in the composition of amphiboles and plagioclases as a response to progressive alteration of the metamorphic conditions (HOLLAND & RICHARDSON, 1979; SPEAR, 1980, 1981a, b; HYNES, 1982; MARUYAMA et al., 1982, 1983; BLUNDY & HOLLAND, 1990).

Amphiboles of assemblage D have the largest amounts of Na, K and Al. In amphiboles of assemblage C concentrations of Ti are higher but this is probably due to the high content of Ti in the protholite (gabbro).

Sample	SPEAR (1980)	BLUNDY & HOLLAND (1990) 26% An	BLUNDY & HOLLAND (1990) 30% An
	T/°C		
A1	500	666	675
A2	350	478	484
B1	500	730	740
C1	530	783	795
C2	500	688	697
C3	490	682	691
C4	510	618	626
D1	510	654	662
D2	530	738	749

Table 2 Temperature of metamorphosis on the basis of the SPEAR (1980) and BLUNDY & HOLLAND (1990) geothermometers.

A high content of Ti is also found in type D amphiboles. The lowest Si contents are found in amphiboles of type C and D assemblages. In amphiboles from A assemblage the distribution of Ti, Na, K, Al and Si have an opposite trend to those amphiboles of assemblage D. Amphiboles from assemblage A have the lowest content of Ti, Na, K and Al and largest amounts of Si.

Therefore it can be stated that the highest temperatures occurred during growth of amphiboles in assemblage D, were lower in assemblages B and C and lowest in the assemblage A.

Equilibrium on the scale of the hand-specimen is assumed between observed amphibole-plagioclase pairs. Because plagioclase grains were not measured by microprobe the whole range of plagioclase compositions obtained by optical measurements were used for geothermobarometry calculations.

Temperatures of metamorphism were outlined with graphical solution on the basis of SPEAR's (1980) geothermometer, and calculated from the equation from the BLUNDY & HOLLAND (1990) geothermometer, with an assumed pressure of 5 kbars ($5 \cdot 10^8$ Pa) and plagioclase composition range between 26% An and 30% An (determined by U-stage measurements). The results are shown in Table 2.

There are differences between the results obtained using these two approaches. The "semiquantitative" numerical solution (because the chemistry of plagioclase had not been determined by electron microprobe) obtained from the BLUNDY & HOLLAND (1990) geothermometer shows a similar trend in temperature distribution for all amphibole bearing parageneses, but the values seem to be too high for the observed parageneses. This geothermometer is very sensitive for cation content and due to the "semiquantitative approach", a possible disequilibrium (amphibole rim - plagioclase core), and metasomatic effects from intrusion of granite body, exact values of the thermometric evaluation should not be accepted.

Temperatures obtained on the basis of the diagram proposed by PLYUSNINA (1982) are in the range of 520-550 C for the non-actinolite assemblages (B, C and D). Geothermometry evaluations are in agreement with the SPEAR (1980) empirical geothermometer.

Estimation of pressures was performed with the aid of a diagram proposed by PLYUSNINA (1982). The calibration of this diagram produced a wide range of pressures (depending on the Al content in the amphibole) where amphiboles occur in the range from 2 kbars to 5 kbars (2 to $5 \cdot 10^8$ Pa) with the exception of one specimen in assemblage D. This specimen has a P value of 7 kbars ($7 \cdot 10^8$ Pa).

According to temperatures stated in the introduction (MARUYAMA et al., 1982) amphiboles from assemblage A belong to the greenschist facies, while amphiboles from assemblages B, C and D are of the amphibolite facies.

Zonal growth of amphibole grains is a result of multiple periods of mineral growth. The cores appear to be relics, preserved because of incomplete equilibrium. Assuming that the cores grew before the rims, amphiboles can be used as an relative time indicator. Moreover, the distinct compositions of core and rim, indicate different metamorphic conditions. Each growth event can be characterized by a different metamorphic grade. Partial reequilibration will prevent the determination of the core composition at the peak of metamorphism. It is also very probable that the mineral assemblage was slightly different when the core crystallized. Of course, only larger grains have different cores from rims, because the core in the smaller grains was completely consumed. Elements necessary to make new rims come from alteration of other phases (change in modal and chemical compositions).

Information about the metamorphic conditions during crystal growth of amphiboles from type C assemblage are recorded in Fig. 3. As minerals are buffered by the whole assemblage, the composition of individual minerals can be mutually compared, and variations in mineral chemistry can be related to differences in metamorphic grade or facies series rather than bulk rock composition.

Profiles show the differences in the distribution of cations. These differences are due to changes in metamorphic conditions during the mineral growth. The cores of amphiboles have higher amounts of Si and Mg and lower amounts of Al, Ti, Na, K and Fe than the rim of same grain. Increasing of Fe, Na, Fe/Mg ratio and decreasing of Mg and Si from cores to rims of the grains also indicates rising pressure. According to SPEAR (1981b) this suggests that the temperature increased during mineral growth.

Therefore we can suggest conditions of relative prograding metamorphism.

Co-existing amphiboles have $(Na_A+K) \leq 0.25$, $Na_{M4} \leq 0.2$, $0.6 \leq Al^{IV} \leq 1.2$ and $0.6 \leq (Al^{VI}+Fe^{3+}+Ti) \leq 1.2$ in low-pressure samples. Alternatively co-existing amphibole have $0.2 \leq (Na_A+K) \leq 0.5$, $0.2 \leq Na_{M4} \leq 0.5$, $1.2 \leq$

	rim		core		rim
SiO_2	46.74	49.70	50.19	48.99	46.61
TiO_2	0.86	0.54	0.49	0.70	0.95
Al_2O_3	8.68	5.80	5.41	6.28	8.51
Fe_2O_3	2.33	2.67	2.41	2.99	4.00
FeO	2.92	11.63	11.06	11.50	11.84
MnO	0.20	0.27	0.29	0.19	0.22
MgO	11.82	13.54	13.89	13.22	11.98
CaO	12.08	12.21	12.11	12.12	11.94
Na_2O	1.08	0.81	0.71	0.71	1.06
K_2O	0.47	0.21	0.17	0.28	0.42
H_2O	2.03	2.05	2.05	2.04	2.04
Total	99.21	99.43	98.78	99.02	99.57
$\#Si^{IV}$	6.91	7.25	7.34	7.18	6.86
$\#Al^{IV}$	1.09	0.75	0.66	0.82	1.14
T pos.	8.00	8.00	8.00	8.00	8.00
$\#Al^{VI}$	0.42	0.25	0.27	0.27	0.34
$\#Fe^{3+}$	0.26	0.29	0.26	0.33	0.44
#Ti	0.10	0.06	0.05	0.08	0.11
#Mg	2.60	2.95	3.03	2.89	2.63
$\#Fe^{2+}$	1.60	1.42	1.35	1.41	1.46
#Mn	0.03	0.03	0.04	0.02	0.03
$M_{1,2,3}$	5.00	5.00	5.00	5.00	5.00
#Ca	1.91	1.91	1.90	1.90	1.88
#Na	0.09	0.09	0.10	0.10	0.12
M_4pos	2.00	2.00	2.00	2.00	2.00
#Na	0.22	0.14	0.10	0.11	0.19
#K	0.09	0.04	0.03	0.05	0.08
A pos.	0.31	0.18	0.13	0.16	0.26
#O	22.00	22.00	22.00	22.00	22.00
#OH	2.00	2.00	2.00	2.00	2.00

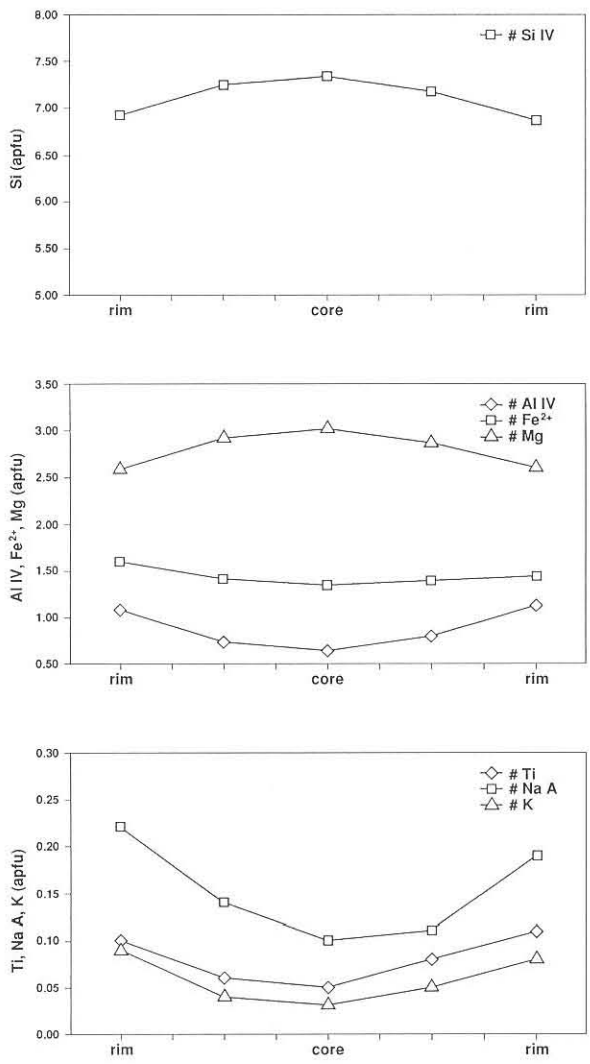

Fig. 3 Comparison of chemical compositions in core and rims from type C amphibole.

$Al^{IV} \leq 1.8$ and $1.2 \leq (Al^{VI}+Fe^{3+}+Ti) \leq 1.8$ in medium-pressure samples (LAIRD & ALBEE, 1981). In the west Psunj region there are low-pressure amphiboles but samples of types C and D were probably stabilized at medium-pressure. Accurate estimation of pressure is difficult and the broad conclusion of pressure estimates is that pressures in parageneses from B, C and D assemblages were higher (in respective order) than in assemblage A.

6. DISCUSSION AND CONCLUSIONS

Investigated amphiboles can be regarded as a solid solution consisting of

tremolite	$(Ca_2Mg_5Si_8O_{22}(OH)_2)$,
pargasite	$(NaCa_2Mg_4AlSi_6Al_2O_{22}(OH)_2)$,
edenite	$(NaCa_2Mg_5Si_7AlO_{22}(OH)_2)$, and
tchermakite	$(Ca_2Mg_3Al_2Si_6Al_2O_{22}(OH)_2)$

components. The tremolite-actinolite molecule is stable in the greenschist field while the tschermakite molecule is stable in the amphibolite facies, and the edenite molecule in the epidote-amphibolite facies (HOLLAND & RICHARDSON, 1979). Recalculations of the amphibole compositions to the mole fractions (CURRIE, 1991) shows that the tremolite-actinolite and edenite mole fractions prevail in amphiboles of assemblage A, while tschermakite and edenite are dominant in the other assemblages (Table 3).

Amphiboles from assemblage A belong to the greenschist facies or to the albite-epidote zone. With a rise of P-T conditions, the tschermakite mole-fractions also increase, so the amphiboles of assemblages B, C and D belong to the transition zone and lower amphibolite facies.

In this range of P-T conditions a change in the composition of amphiboles leads to the transition from actinolite into hornblende through coupled substitutions:

$\square$ (A) + Si(IV) = Na(A) + Al(IV) edenite substitution

Mg(VI) + Si(IV) = Al(VI) + Al(IV) tschermakite substitution

	A1	A2	B1	C1	C2	C3	C4	D1	D2
hornblende	51.3	23.3	9.1		46.5	43.6	58.4	56.9	
barroisite	7.5	1.2	9.0	15.6	8.1	9.0	13.3	13.1	30.4
tchermakite	8.2		40.6	55.2	20.0	17.3		3.5	37.1
edenite	32.8	7.9	41.1	18.1	25.0	30.0	13.8	26.3	24.7
gedrite				0.3	0.2				
taramite				10.8					7.7
tremolite		37.6					9.8		
actinolite		29.5					4.5		

Table 3 Mole fractions of amphibole end-members calculated with software after CURRIE (1991).

which together gave

□ (A) + Mg(VI) + 2Si(IV) = Na(A) + Al(VI) + 2Al(IV) pargasite substitution

and numerous other reactions with co-existing minerals. During reactions there are changes in the chemical compositions of minerals (continuous reactions) and in the modal composition of minerals, resulting in formation of new minerals and the detriment or expiration of pre-existing minerals (discontinuous reactions). So, parallel with the transition of actinolite into hornblende, albite disappears, the composition of chlorite changes (increasing Mg component, detrimental to the chlorite modal composition, and finally disappearance of chlorite from the assemblage). Parallel to this process is an increase in the Al component in epidote, detrimental of the modal composition and the final disappearance of epidote. With the changes of modal composition of chlorite and epidote, the Al content in the plagioclase and the Fe content in amphiboles increases. Also with more basic plagioclase the Al and Na content in the amphiboles increases. These changes are discontinuous.

The studied material has consistent petrographic features with certain structural, textural, compositional and mineralogical variations. Differences between the amphibole bearing parageneses of west Psunj are mainly the modal composition of minerals, and variations in the chemical compositions which have only been investigated in detail in the amphiboles. All parageneses have in common amphibole and plagioclase with minor amounts of quartz and ilmenite or sphene.

Chemical investigations of the amphiboles indicate variations in the features which enable deduction of genetic conditions and processes. Temperature of formation is set to between 490 and 550°C (350°C for actinolites) and pressure between 2 and 5 kbars (2 and $5 \cdot 10^8$ Pa). One specimen (type D) has a P value of 7 kbars ($7 \cdot 10^8$ Pa).

Geochemical investigations (PAMIĆ & MARCI, 1990) suggest that there is no radical change in the protholite composition (protholite is tholeiitic basalt) and that these metamorphic processes can occur in the ophiolite zone (PAMIĆ & LANPHERE, 1991). Differences in assemblages may be attributed to changes in P-T conditions.

Changes in P-T conditions are recorded in the growth of the amphibole grains (general prograding metamorphism) and changes in modal compositions in related parageneses indicate that the study area has undergone geotectonic change during its evolution. A model which may explain the change of conditions from greenschist to amphibolite facies as recorded in the amphibole of west Psunj, may be that of a subduction zone. However to thoroughly validate this model more data are required to confirm especially the relationship between the P-T increments and the time scale.

Furthermore, differences between assemblage A and B, C and D could be explained by varying chemical composition of original protholite (for instance tuffitic sediments). The protholite composition of assemblage A has not yet been reliably determined.

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