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Tabula materiae

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Chemical composition of the actinolite-hornblende assemblage as indicator for the P-T metamorphic conditions in chlorite-amphibole schists and metadiabases, Vrteška, Plačkovica Mt., Eastern Macedonia

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В. Мирчовски, Бл. Боев, Г. Петров, О. Спасовски — Химический состав актинолитово-роговообманковой ассоциации как индикатор P-T условий метаморфизма хлорит-амфиболовых сланцев и метадиабазов (Вртечшка, гора Плачковица, Восточная Македония). Микроскопическими и электрон-микроскопическими исследованиями в хлоритово-амфиболовых сланцах и метадиабазах окрестностей деревни Вртешка выявлена ассоциация следующих минералов: актинолит, Mg-роговая обманка, биотит, эпидот, хлорит, альбит, кальцит, кварц и ильменит. Эта ассоциация в сочетании с текстурно-структурной характеристикой пород указывают на их образование при региональном динамотермальном метаморфизме в условиях фации, принадлежащей к сериям типа Барроу. По степени метаморфизма эта фация соответствует переходу между кварц-альбит-эпидот-биотитовой и альбит-эпидот-альмандиновой субфациями. Химический состав актинолита и роговой обманки показывает, что иседованные породы образовались в условиях повышающегося метаморфизма при T= 400-500°C и P= 2—3 kbar.

Abstract. Microscopic and electronic microprobe studies carried out on the chlorite-amphibole schists and the metadiabases from the vicinity of Vrteška determined an actinolite, Mg-hornblende, biotite, epidote, chorite, albite, calcite, quartz, and ilmenite assemblage. The metamorphic mineral assemblage and structural-textural characteristics indicate that these rocks metamorphosed in conditions of regional dynamothermal metamorphism in a Barovian type series of facies which, according to the degree of metamorphism, corresponds to the transition from quartz-albite-epidote-biotite to quartz-albite-epidote-almnadine subfacies. The chemical composition of actinolite and hornblende indicate that the rocks under investigation metamorphosed in conditions of prograde metamorphism at T = 400-500°C and P = 2-5 kbar.

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Key words: Actinolite, Mg-hornblende, chlorite, regional prograde metamorphism.

Introduction

The village of Vrteška is situated in the central western slopes of Plačkovica Mt., 25 km east of the town of Stip (Fig. 1). Plačkovica Mt., is built up of a complex of Precambrian-Early Paleozoic metamorphic rocks. The complex of the Early Paleozoic schists also contains elongated stripes of chlorite-amphibole schists hosting also small masses of metadiabases. Chlorite-amphibole schists and metadiabases made it possible to determine the degree of metamorphism,

Data about the geological structure of the

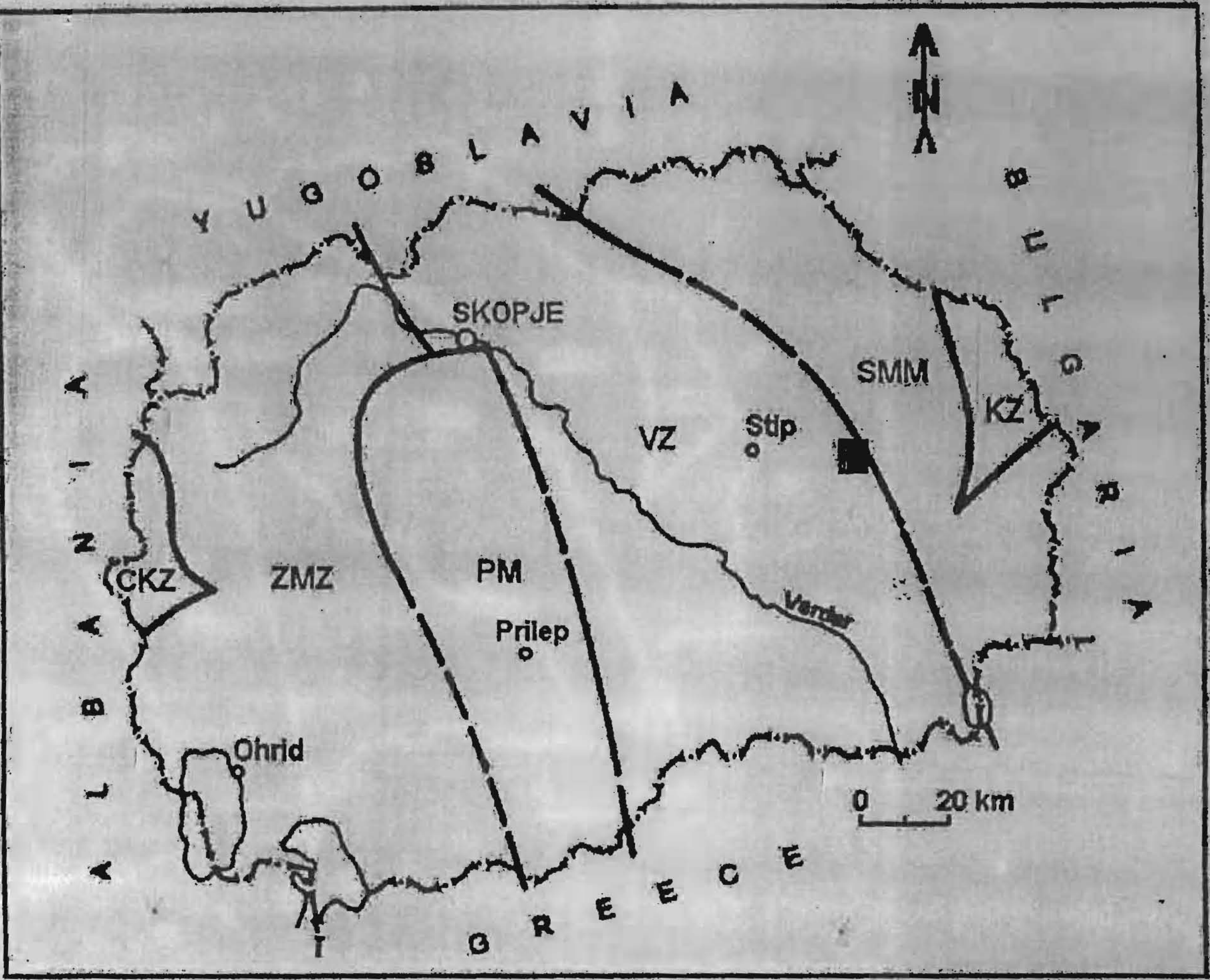

Fig. 1. Location of the area and regional tectonic setting of the Republic of Macedonia (Arsovski, 1997). Tectonic units: CKZ — Cukali Krasta zone; ZMZ — western Macedonian zone; PM — Pelagonian massif; VZ — Vardar zone; SMM — Serbo-Macedonian massif; KZ — Kraishtide zone

terrain and the degree of metamorphism may be found in the geological map and explanations of the sheet Stip (Rakicevic et al., 1976).

Geological setting

The wider vicinity of Vrteška, with regard to its tectonics, belongs to two large geotectonic units: the Vardar zone (which embraces most of the terrain including the Radoviš-Teranci-Nivičanski graben and the Bučim block) and the Serbo-Macedonian mass (which embraces the most north-easterly part or parts of the Zrnovci anticline) (Fig. 1).

The vicinity of Vrteška is built up of Precambrian high-grade metamorphic rocks Riphean-Cambrian albite-quartz-muscovite-chlorite schists, Early Paleozoic schists and Jurassic rocks (Ракичевич, 1976).

The Precambrian metamorphic rocks in the south-western part of the terrain are the oldest rocks and tectonically belong to the Bučim block. In the north-east they are tectonically related to Early Paleozoic schists. Micaschists, leptinolites and muscovite gneisses of a general north-west — south-east trend can be distinguished based on the mineralogical-structural characteristics of the complex.

The Riphean-Cambrian is present in the northeasternmost sector. The exposures belong to the Serbo-Macedonian mass and the Zrnovci anticline. In the south-west Riphean-Cambrian is tectonically related to the Early Paleozoic schists. The Riphean-Cambrian is present as albite-quartz-muscovite-chlorite schists of north-west — south-east strike.

Early Paleozoic metamorphic schists comprise a graben structure (Radoviš — Teranci — Nivičanski graben) in the north-eastern sector of the Vardar zone at the contact with the Serbo-Macedonian mass. Chlorite-quartz-sericite schists, marbles, graphite schists and phyllites, metasandstones and marbles, marbles and carbonate schists, chlorite-amphibolite schists and metadiabases have been distinguished based on the lithological composition of the Early Paleozoic complex. The complex is estimated to be about 2900 meters thick.

The Jurassic is represented by serpentinites which, as a 800 meters long and 100-150 meters wide lens-like body, are tectonically emplaced along the fault structure that separates the Precambrian metamorphic rocks and the Early Paleozoic schists.

Petrographic features

Chlorite-amphibole schists

Chlorite-amphibole schists occur as an elongated stripe in the top most parts within the Early Paleozoic complex. The schists are 500 meters thick (Fig. 2). They are light to dark green fine-grained rocks. Their structure is granoblastic, lepidoblastic and nematoblastic. Their texture is schistose. They are composed of amphibole, chlorite, epidote, albite, quartz and ilmenite.

Amphiboles occur as individual elongated rod-like to fibre-like crystals up to 0,5-1 mm long and 0.1 mm thick. It is clear that crystals are always paralelly oriented. They comprise 20-30 % of the mass.

Chlorite occurs as small leaf-like aggregates of the same orientation as the amphibole. Leaves are 0.1 to 0.3 mm long. It amounts to 10 % of the rock mass.

Epidote occurs as rounded xenomorphic grains regularly distributed in the mass. Grains are 0.1 to 0.5 mm in size. Epidote comprises 10 to 15 % of the rock mass.

Albite occurs as small xenomorphic grains regularly distributed in the rock. The grains are from 0.1 to 0.3 mm in size. It amounts to 20% of the total mass.

Quartz occurs in xenomorphic grains of 0.1 to 0.3 mm, rarely of 0.5 mm in size. It sometimes occurs as millimetre size thin veinlets. It amounts to 25% of the rock mass.

Ilmenite is often found as xenomorphic shapes, seldom as hypidiomorphic grains. It is evenly distributed in the rock mass. The grain size is within 0.8 mm.

Metadiabases

Metadiabase occur as lens-like bodies in the lower level of the series of graphite schists and phylites. They can be found as 200 to 300 meters long and maximum 100 meters thick bodies (Fig. 2). They are dark green to light green in colour. Their texture is massive to slightly schistose. The structure is nematoblastic, lepidoblastic and granoblastic and relicts of blastoophitic structure can also be found. Metadiabases are composed of amphibole, biotite, chlorite, albite, calcite, quartz and ilmenite.

Amphiboles occur as elongated rod-like 0.3 to 0.8 mm and rarely 1 to 5 mm long and 0.1 to 0.2 mm thick crystals. Crystals are not always clearly oriented in one direction. They amount to 20% of the rock mass.

Biotite commonly occurs in individual xenomorphic elongated leaves reaching 1.5 mm in length and rarely in association with other leaves. The leaves are of the same orientation as amphiboles. In some cases they do not exhibit any orientation. Biotite amounts to 10% of the mass.

Epidote occurs as xenomorphic grains distributed in albite, and also in coarser individual xenomorphic grains of 0.5 mm in size. Its mass amounts to 15 %.

Albite fills the space between the coloured minerals. It occurs as xenomorphic to hypidiomoprhic rod-like crystals. The crystals are 0.5 to 0.8 mm, rarely 1 mm, long and 0.3 to 0.5 mm wide. A large number of grains enclose fine epidote grains and zoisite with xenomorphic clacite grains along the periphery. This is probably due to the saussuritization process of basic plagioclases from basic diabases that transformed to albite, epidote, zoisite and calcite. Relicts of primary plagioclases have not been found in the samples studied. In individual albite grains amphibole, epidote and calcite fine amphibole grains can be noticed as enclosures indicating that albite is the final mineral fomed in this assemblage. It amounts to 35% of the rock mass.

Calcite is a common mineral in metadiabases, but rare in chlorite-amphibolite schists. In metadiabases it occurs as alotriomorphic grains ranging from 0.1 to 0.2 mm in size. The grains occur individually or as clusters of grains with regual distribution in the rock. Calcite also occurs in small grains as products of saussuritized plagioclases.

Quartz occurs as fine individual xenomoprhic grains of 0.1 to 0.3 mm in size.

Ilmenite is present as individual xenomorphic and hypidiomorphic shapes of 0.3 to 0.8 mm in size.

Chemical composition of the minerals

The chemical composition of the mineral

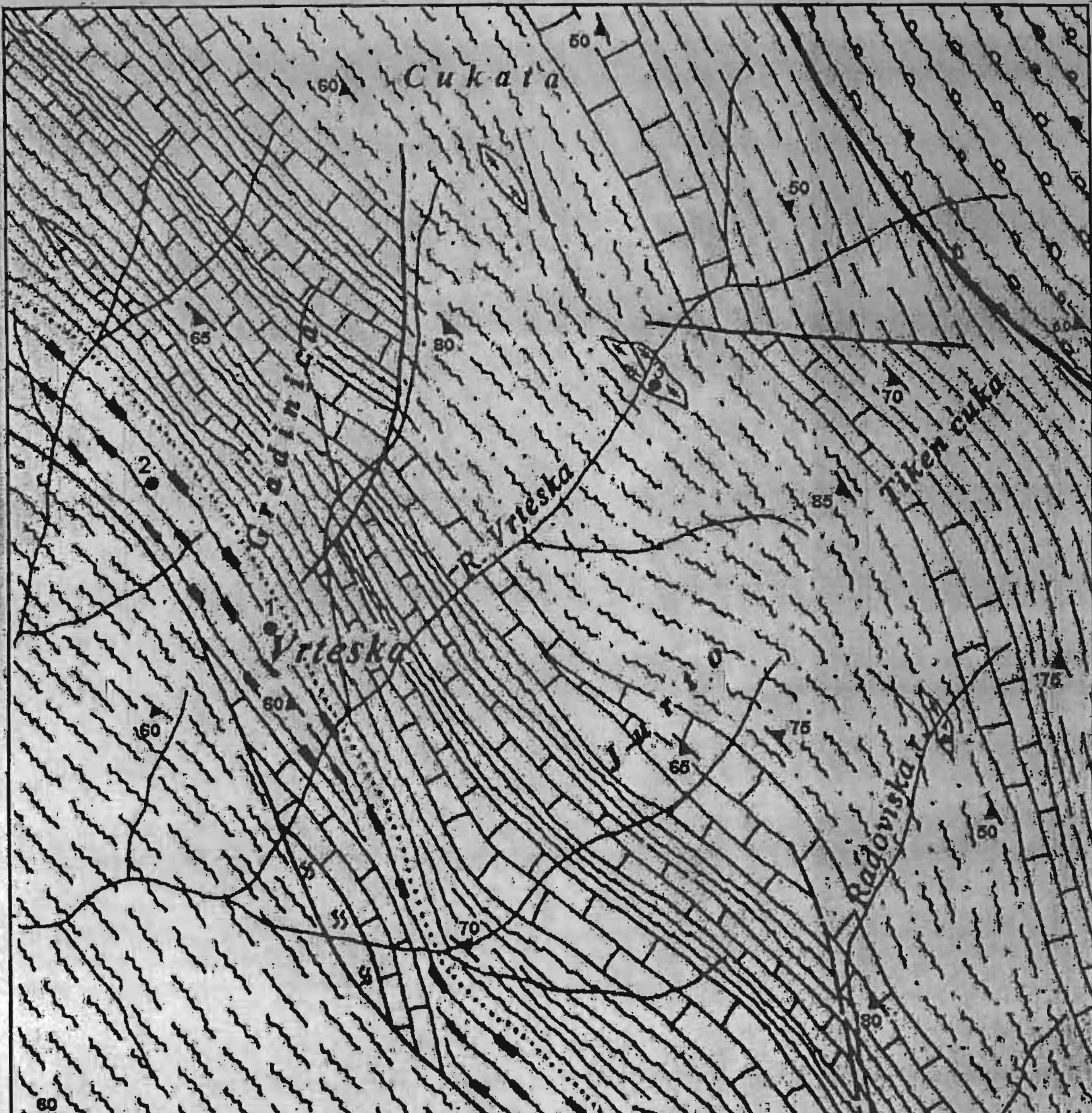

Fig. 2. Geological map of the vicinity of Vrteška
1 — Serpentinites; 2 — chlorite-amphibole schists, 3 — phyllites, metasandstones and marbles, 4 — marbles and carbonate schists, 5. metadiabases, 6. graphite schists and phyllites, 7 — marbles, 8 — chlorite-quartz-sericite schists, 9 — albite-quartz-sericite-chlorite schists, 10 — muscovite gneisses, 11 — micashists and leptinolite, 12 — boundary between the Vardar zone and the Serbo-Macedonian massif, •1-2. sampling sites

Table 1

Microanalyses of amphiboles of chlorite-amphibole schists

Sample	Pl-1			Pl-2			
Mineral	Act	Mg-Hbl	Mg-Hbl	Mg-Hbl	Mg-Hbl	Act	Par-Hbl
Point	core →	rim	rim	core →	rim	core →	rim
SiO_2	52.53	45.92	47.26	50.52	48.15	55.57	43.89
TiO_2	-	0.25	0.28	0.12	0.04	0.02	-
Al_2O_3	2.51	9.35	8.24	9.07	11.56	3.43	15.22
FeO	17.13	21.74	20.75	6.77	7.27	4.95	8.25
MnO	0.30	0.20	0.40	0.09	0.12	0.06	0.13
MgO	12.81	8.29	9.19	17.57	16.08	20.26	14.82
CaO	11.56	9.68	9.03	12.29	12.37	12.53	12.73
Na_2O	0.77	2.27	2.69	1.69	1.83	0.94	2.29
K_2O	0.08	0.37	0.38	0.21	0.28	-	0.29
Total	97.69	98.07	98.22	98.33	97.70	97.76	97.62
O=23							
Si	7.659	6.797	6.937	7.045	6.808	7.684	6.276
Al^{IV}	0.341	1.203	1.063	0.955	1.192	0.316	1.724
T-site	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al^{VI}	0.090	0.427	0.361	0.535	0.733	0.242	0.839
Ti	-	0.028	0.031	0.013	0.004	0.002	0.000
Fe^{2+}	1.682	1.762	1.584	0.561	0.708	0.467	0.689
Fe^{3+}	0.407	0.929	0.963	0.228	0.151	0.105	0.297
Mn	0.037	0.025	0.050	0.011	0.014	0.007	0.016
Mg	2.784	1.829	2.011	3.653	3.389	4.176	3.159
C-site	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Ca	1.806	1.535	1.420	1.836	1.874	1.856	1.950
Na	0.194	0.465	0.580	0.164	0.126	0.144	0.050
B-site	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.024	0.187	0.186	0.293	0.376	0.108	0.638
K	0.015	0.070	0.071	0.037	0.051	0.000	0.053
A-site	0.038	0.257	0.257	0.331	0.426	0.108	0.638
Sum cat	15.038	15.257	15.257	15.331	15.426	15.108	15.638

Fe^{3+} Is the value calculated.

phases was analyzed in order to find out the degree of metamorphism and carry out a precise determination of minerals. This was performed in the IGEM Institute (Russian Academy of Sciences, Moscow, Russia).

Amphiboles

The chemical composition of amphiboles was analyzed with 13 samples (Tables 1 and 2). The determination of the homogeneity of amphiboles was carried out for the periphery and the middle parts of the crystals. Analyses indicated that amphiboles are homogenous in composition or show prograde zonation. According to Leakes's classification (1978) the middle parts of some of the amphiboles analyzed in chlorite amphibole schists indicate actinolite composition and the periphery consists of magnesite hornblende except for one analysis which indicated pargasite hornblende. In metadiabases all amphiboles anlayzed are actinolite both in the middle part and in the periphery (Fig. 3).

Homogenous ampbibioles are actinolite or magnesite hornblende in composition.

Chlorites

The chemical composition of the chlorites is shown in Table 3. Chlorites, like amphibolites, show a nonhomogenous composition from one to another leaf.

The difference in the chemical composition is probably due to the prograde metamorphism that metamorphosed the schists and also due to the chemical composition of the primary rocks. According to Hey's classification (1954) (Fig. 4) the chlorite of sample PL-I was determined as ripidolite, samples Pl-2 and Pl-4 indicated ripidolite- pycnochlorite compositions and sample Pl-3, sheridanite-clinochlore.

Table 2
Microanalyses of chlorite, biotite and alblite

Mineral	Chl				Ilm	Bt	Ab	
Sample	PI-1	PI-2	PI-3	PI-4	PI-1	PI-3	PI-1	PI-3
SiO_2	26.27	29.40	27.54	27.34	0.10	38.35	68.14	68.02
TiO_2	–	–	0.07	0.04	48.95	1.34	–	–
Al_2O_3	19.95	23.07	21.09	19.66	–	15.36	19.55	19.65
FeO^*	30.05	9.18	21.08	23.26	–	17.99	–	–
MnO	0.32	0.16	0.17	0.23	2.45	0.11	–	–
MgO	12.45	26.73	19.06	18.03	0.26	13.73	–	–
CaO	0.14	0.16	0.16	0.32	0.01	–	0.15	0.16
Na_2O	0.26	–	–	–	–	0.16	11.73	11.58
K_2O	–	–	–	0.05	–	9.15	0.08	–
Total	89.44	88.70	89.17	99.93	99.79	96.19	99.65	99.41
	O = 36					O = 24	O = 8	
Si	5.565	5.584	5.554	5.612		5.981	11.952	11.947
Al^{IV}	2.435	2.416	2.446	2.388		2.019	4.038	4.065
Al^{VI}	2.542	2.744	2.563	2.365		0.802	–	–
Ti	–	–	0.011	0.06		0.157	–	–
Fe^{2+}	5.323	1.458	3.555	3.993		2.346	–	–
Mn	0.057	0.026	0.029	0.040		0.015	–	–
Mg	3.932	7.568	5.730	5.515		3.192	–	–
Ca	0.032	0.033	0.035	0.070		–	0.028	0.030
Na	0.107	–	–	–		0.048	3.990	3.944
K	–	–	–	0.013		1.821	0.018	–
Cations	19.993	19.829	19.923	20.004		16.381	20.026	19.986
Fe/Fe + Mg	0.58	0.16	0.38	0.42		0.42		
Ab							98.90	99.20
An							0.70	0.80
Or							0.40	–

*FeO calculated as Fe^{2+}
Samples; PI-1 and PI-2 — chlorite-amphibole schists; PI-3 and PI-4- metadiabases

Albite, biotite and ilmenite
Minerals found in the schists and analyzed included albite (0.70-0.80 An), biotite and ilmenite. The results obtained are shown in Table 3.

Metamorphism

The metamorphic mineral assemblage of actinolite, magnesium hornblende, chlorite, epidote and albite as well as structural-textural characteristics of rocks investigated indicate that they metamorphosed in conditions of regional dynamo-thermal metamorphism in Barovian series of facies.

Many authors use the variations of the chemical composition as an indicator for the determination of the pressure and temperature of metamorphism (Miyashiro, 1961; Leake, 1965; Raase, 1974; Holland and Richardson, 1979; Brown, 1977; Laird and Albee, 1981a).

The Laird and Albee's diagrams for the chemical composition of amphiboles were used to determinate the degree of metamorphism (Laird and Albee, 1981a). In diagrams A, B and C (Fig. 5) most of the data project in the field of biotite zone or close to it, whereas some data (magnesite hornblende only) fall in the field of garnet zone or close to it. Diagram B does not provide good data because of the very low NaM4 values. These data lead to the conclusion that metamorphism occurred in prograde conditions.

The mineral assemblage of low aluminium actinolite, biotite, chlorite, epidote, and albite is a characteristic facies of greenschists.

The occurrence of magnesite chlorite and albite containing 7% anortitic component and magnesite hornblende in individual crystals in the periphery of actinolite are indicators that metamorphism was prograde and the degree of metamorphism corresponds to the transition from quartz-albite-epidote-biotite to quartz-albite-epidote-almandine subfacies (Winckler, 1969).

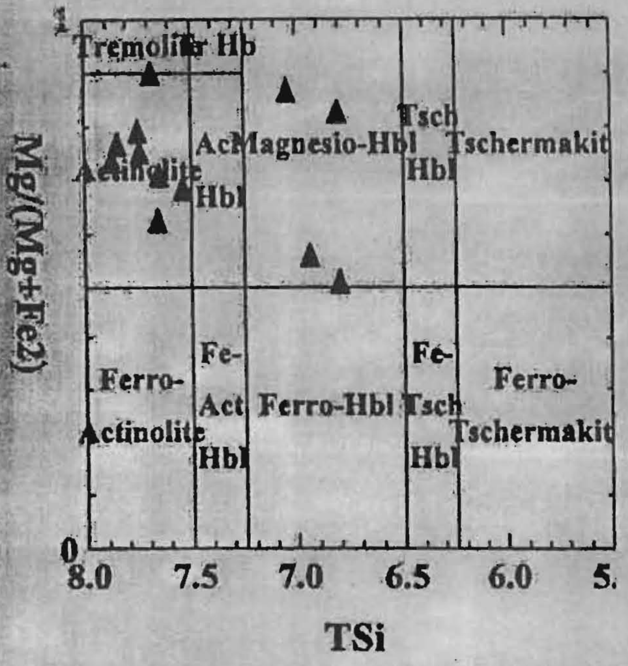

Fig. 3. Amphibole classification after B. Leake (1978)

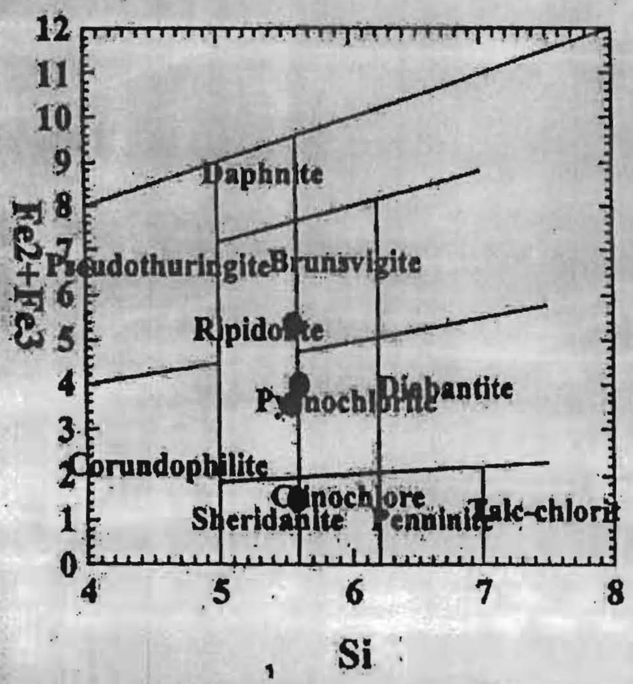

Fig. 4. Classification of chlorite after Hey (1954)

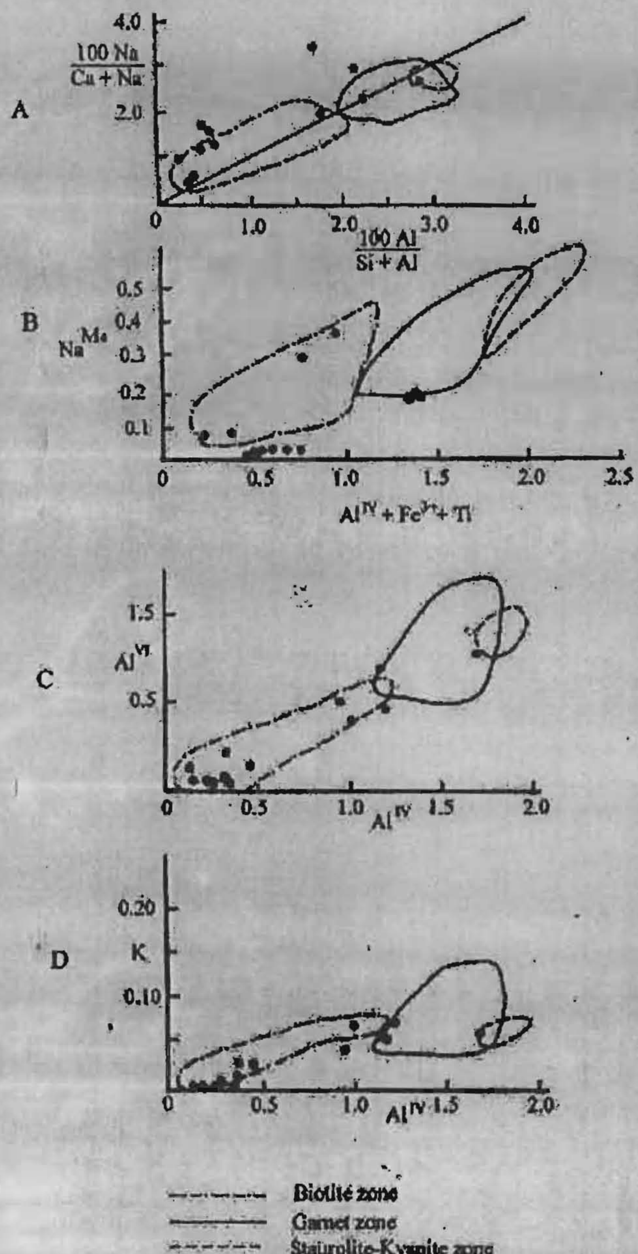

Fig. 5. Projection of the chemical composition of amphiboles from the chlorite-amphibole schists and metadiabases of the diagrams after Laird, Albee (1981a)

Estimation of P and T

The chemical composition of amphiboles and plagioclases were used for the estimation of P and T. P for magnesium hornblende was determined with the Raase geobarometer (1974). Data project below or above the line denoting approximately 5 kbar and yield the peak of metamorphism. The Brown geobarometer (1977) yields P for magnesium hornblende from 4 to 5 kbars, whereas data obtained for actinolite indicate 2 kbar.

Estimation of P and T was carried out with the Plyusnina hornblende — plagioclase geothermobarometer (1982). Pressures of 5-6 kbars were obtained for magnesium hornblende and P below 2 kbars for actinolite. T was found to be around 450°C.

Based on experimental data of Plyusnina (1986) the greenschist facies starts with the occurrence of actinolite-epidote assemblage

Table 3
Microanalyses of amphiboles of metadiabases

Sample	Pl-3				Pl-4	
Mineral	Act	Act	Act	Act	Act	Act
Point	core →	rim	core →	rim	core →	rim
SiO_2	55.36	55.68	54.28	55.03	53.62	52.20
TiO_2	–	0.01	–	0.11	0.03	0.01
Al_2O_3	1.60	1.24	1.88	1.91	2.50	3.57
FeO	11.00	12.62	12.45	12.02	15.19	15.81
MnO	0.21	0.16	0.19	0.27	0.28	0.27
MgO	16.59	16.37	16.12	16.52	14.44	13.51
CaO	12.22	11.77	12.05	11.72	10.74	10.75
Na_2O	0.74	0.38	0.50	0.41	1.35	1.38
K_2O	–	–	0.07	0.04	0.21	0.13
Total	97.72	98.23	97.54	98.03	98.36	97.63
O = 23						
Si	7.746	7.753	7.878	7.847	7.655	7,540
Al^{IV}	0.254	0.247	0.122	0.153	0.345	0.460
T - site	8.000	8.000	8.000	8.000	8.000	8.000
Al^{VI}	0.062	0.070	0.146	0.053	0.076	0.147
Ti	–	0.012	–	0.001	0.003	0.001
Fe^{2+}	1.130	0.920	1.264	1.048	1.249	1.336
Fe^{3+}	0.356	0.496	0.045	0.439	0.565	0.573
Mn	0.023	0.032	0.025	0.019	0.034	0.033
Mg	3.429	3.470	3.519	3,439	3.073	2.909
C - site	5.000	5.000	5.000	5.000	5.000	5.000
Ca	1.842	1.769	1.863	1.777	1,643	1.664
Na	0.138	0.112	1.137	0.104	0.357	0.336
B - site	2.000	2.000	2.000	2.000	2,000	2,000
Na	–	–	0.067	–	0.038	0.024
K	0.013	0.007	–	–	0.038	0.024
A - site	0.013	0.007	0.067	–	0.038	0.024
Sum cat	14.993	14.888	15.067	14.881	15.055	15.074

Fe^{3+} is the value calculated.

at T from 350 to 430°C at $XCO_2 = 0.1$ and $P_{fluid} = 2$ kbar. An increase of fluid pressure resulted in the increases the temperature limit to 520°C at fluid pressure of 6 kbar.

Based on data obtained it can be inferred that these rocks metamorphosed in conditions of prograde metamorphism at T = 400-500°C and P = 2-5 kbar.

Conclusion

Investigations carried out made it possible to draw the the conclusions as follows:

— Chlorite-amphibole schists are composed of actinolite, Mg-hornblende, epidote, chlorite, albite, quartz and ilmenite. The metadiabases are composed of actinolite, biotite, epidote, chlorite, albite, calcite, quartz and ilmenite.

— The rocks metamorphosed in regional metamorphism in Barovian series of facies that, due to their degree of metamorphism, correspond to the transition from quartz-albite-epidote-biotite to quartz-albite-epidote-almandine subfacies.

— Geothermometers and geothermobarometers used in the study of the chemical composition of actinolite and hornblende revealed that the rocks metamorphosed at T = 400-500°C and P = 2-5 kbar.

— The zonal composition of actinolite from the centre to the periphery and the occurrence of Mg-hornblende and that of Mg-hornblende in individual crystals indicate prograde metamorphism.

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