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BIOTITES FROM GRANITOID ROCKS OF THE WEST CARPATHIANS AND THEIR PETROGENETIC IMPORTANCE

(Figs. 1—7)

Abstract: The individual mountain ranges of the east Carpathians are subdivided on the basis of different Fe/Fe+Mg ratio in biotite. Main attention is paid to two, from this standpoint extreme mountain ranges, the Malé Karpaty and Tribeč mts. On the basis of comparison of chemical analyses of biotite, modal analyses and successive relations in rocks with existing experimental data, the attempt to derive temperature of biotite crystallization and to valuate the studied rocks from the standpoint of water content was carried out.

Резюме: Отдельные горные массивы Западных Карпат подразделены на основании разного отношения Fe/Fe+Mg в биотите. Двум с этой точки зрения крайним горным массивам, Малым Карпатам и Трибечу уделено главное внимание. На основании сравнения химических анализов биотита, модальных анализов и последующих отношений в породе с существующими экспериментальными данными, сделана попытка вывести температуру кристаллизации биотита и оценить изучаемые породы с точки зрения содержания воды.

In postkinematic granitoids of the West Carpathians biotite forms an essential component. In this article 32 original chemical analyses of biotite practically from all core mountains are mentioned. As the Malé Karpaty and Tribeč mts., with regard to Fe/Fe+Mg ratio in biotite, display extreme values, main attention is paid to them. Fundamental information about chemical composition of West Carpathian biotites was presented by J. Ďurkovičová (1966, 1967). Her study shows that biotite from more acid rocks is richer in iron than biotite from more basic types, the varieties with most iron come from Hrončok granite and Gemeride granites. J. Ďurkovičová (1967) expressed the assumption that it is connected with their Neoid age. On the whole biotites are characteristic in having relatively monotonous composition.

In this work, mainly dealing with postkinematic granitoids, besides the original analyses, three analyses of biotite from tonalite of Tribeč (52 B, 53 B, 54 B) are used from the work by J. Ďurkovičová.

Analytical methods

Biotite concentrate was obtained from crushed rock (about 10 kg) by separation: flotation, magnetically and in heavy liquids. The achieved purity was 95 to 99 %. The concentrate was analysed by classical chemical analysis by Ing. E. Walzel from the Geological Institute of the Slovak Academy of Sciences. The chemical analysis obtained this way represents average composition of biotite grains within one sample. Chemical analyses and structural formulas are mentioned in Tab. 1. The studied biotites come from samples

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"ZK" determined for complex mineralogical-geochemical investigation. In this work only localities of biotites from the Malé Karpaty and Tribeč mts. are mentioned, location of other samples is given in the work by J. Macek et.al. (1979).

Chemical composition of studied biotites

The ration of the two main cations Fe/Mg in the octahedral layer of biotite is the fundamental characteristic of this mineral. Composition of the studied biotites is shown in Fig. 1 in the triangle: $Mg—Fe^{2}+Mn—Al^{VI}+Fe^{3}+Ti$, according to M. Foster (1960). As visible from the position of the individual samples, iron biotites slightly predominate. The terminal members-phlogopites and lepidomelanes are missing. Regional dependence is shown quite distinctly. Mg—rich biotites are from the mountain ranges of Tribeč, part of the Nízke Tatry, Malá Fatra and Kráľova hoľa zone of the Veporides. Fe—rich biotites come from the Malé Karpaty, Považský Inovec, Kohút zone, Veľká Fatra and part of the Nízke Tatry. Subdivision of the individual massifs according to increasing iron content is shown in histograms of Fig. 2. In the histograms also all analyses of J. Ďurkovičová (1967) are used.

Biotites from two mountain ranges, the Malé Karpaty and Tribeč, form in Fig. 1 relatively closed and from each other most distant fields. As the ratio Fe/Fe+ Mg is of genetic importance, it is possible at least to a certain extent to extrapolate the conclusions made on the basis of these two mountain ranges on granitoids of the whole West Carpathian crystalline.

The fundamental trend appearing in chemical composition of biotite, described by many authors (S. R. Nockolds, 1947; E. W. Heinrich, 1946; F. C. W. Dodge — V. C. Smith — R. E. Mays, 1969) lies in increasing iron content to the detriment of magnesium in biotites from more differentiated, acid rocks. More basic rocks, on the contrary, contain biotite with higher magnesium content. Such a trend is also evident from chemical composition of biotites from granitoids of the West Carpathians. The composition of biotite therefore is not only a simple reflex of chemical composition of magma but depends on temperature and oxygen fugacity in the course of cooling of magma so that Mg—richer biotites are more stable at higher temperature and higher oxygen fugacity (D. R. Wones — H. P. Eugster, 1965).

Petrogenetic interpretations

The temperature and succession of crystallization of magma is influenced mainly by total pressure, content (or fugacity) of water or other volatile components and oxygen fugacity. For melts of granitic and tonalitic composition with various content of water a lot of experimental data exist. In order to obtain an idea about the succession of crystallization of the Malé Karpaty granodiorite and Tribeč tonalite, we recorded the selected samples into Ab — Or — An — Q — H_2O, system, Fig. 3. The composition of melt existing at isobaric cotectic surface of quartz + plagioclase + liquidus + vapour at 5 kilobars of total pressure and excess water is according to the works by H. G. F. Winkler (1976), H. G. F. Winkler et al. (1975, 1977). The modal composition of samples (ZK— 1, 50, 51, 54), which was prefered to more often

Table 1

Chemical analyses and structural formulae+ of biotites from granitoid rocks of the West Carpathians

	ZK-1	ZK-2	ZK-3	ZK-10	ZK-11	ZK-12	ZK-15
SiO_2	35.31	33.90	34.22	35.23	34.63	34.42	34.97
TiO_2	1.89	2.47	2.70	2.41	3.52	3.34	2.59
Al_2O_3	17.66	17.25	17.88	15.55	13.80	16.24	18.28
Fe_2O_3	7.06	2.79	2.12	6.32	6.22	5.72	5.44
FeO	12.29	16.96	17.99	14.75	18.01	15.26	19.13
MnO	0.24	0.20	0.15	0.37	0.08	0.07	0.21
CaO	4.14	1.38	0.46	0.82	0.74	0.74	0.34
MgO	11.44	9.43	9.14	11.05	9.41	11.91	6.83
K_2O	4.11	6.96	8.88	9.20	8.20	6.70	7.12
Na_2O	0.34	0.15	0.18	0.13	1.64	1.21	1.15
H_2O^-	0.24	0.23	0.14	0.06	0.47	0.58	0.42
H_2O^+	4.44	3.27	2.56	1.70	3.09	3.67	3.29
P_2O_5	0.02	0.03	0.02	0.00	0.14	0.16	0.17
Total	99.18	95.02	96.44	97.59	99.95	100.02	99.94
Si	2.62	2.67	2.66	2.68	2.67	2.59	2.66
Al^{IV}	1.38	1.33	1.34	1.32	1.25	1.41	1.34
Fe^{3+}	0.00	0.00	0.00	0.00	0.08	0.00	0.00
Z	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al^{VI}	0.16	0.26	0.29	0.07	0.00	0.04	0.30
Fe^{3+}	0.39	0.16	0.12	0.36	0.28	0.32	0.31
Fe^{2+}	0.76	1.11	1.17	0.94	1.16	0.96	1.22
Mg	1.26	1.10	1.06	1.25	1.08	1.34	0.77
Mn	0.02	0.01	0.01	0.02	0.01	0.00	0.01
Ti	0.11	0.15	0.16	0.14	0.20	0.19	0.15
Y	2.69	2.81	2.81	2.77	2.73	2.85	2.76
Ca	0.40	0.14	0.05	0.08	0.07	0.07	0.03
Na	0.05	0.02	0.03	0.02	0.24	0.18	0.17
K	0.39	0.70	0.88	0.89	0.80	0.64	0.69
X	0.84	0.86	0.96	0.99	1.12	0.89	0.89
Fe/Fe + Mg	0.67	0.71	0.72	0.70	0.75	0.68	0.81

used normative composition because of the presence of muscovite is adopted from the work by J. Macek et al. (1979) and the information about basicity of plagioclases from the work by J. Macek (1975).

From Fig. 3 and Tab. 2 results that the samples from two-mica granodiorite of the Malé Karpaty mts. are in close proximity of the cotectic surface of plagioclase + quartz + liquidus + vapour between isotherms 685—700°C. The succession of crystallization is as follows: plagioclase — quartz — K-feldspar. The position of tonalite is shifted more to the area poorer in Or between isotherms 680—740°C, in the field of plagioclase. The succession of crystallization is: plagioclase—quartz. The such derived succession agrees also in the case of two minca granodiorite and biotic tonalite very well with optical observation of thin sections, according to which the succession for two-mica graniodiorites is: biotite, muscovite — plagioclase — quartz — K-feldspar and for tonalite: biotite, plagioclase—quartz. The placing of biotite in this succession is very important in order to obtain the total picture about the temperature of crystallization, fugacity of H_2O and fugacite of O_2 of the magma. The influence of the content of water on phase and temperature

Continuation of Table 1

	ZK-19	ZK-20	ZK-21	ZK-24	ZK-25	ZK-26	ZK-28
SiO_2	37.87	34.86	30.67	33.80	35.29	34.47	36.87
TiO_2	3,02	3.17	2.45	3.78	3.41	2.40	2.35
Al_2O_3	15.84	16.15	17.54	16.57	15.01	15.64	15.89
Fe_2O_3	8.12	4.34	6.51	8.80	4.60	8.34	4.13
FeO	14.82	16.40	18.69	12.52	15.48	18.23	13.67
MnO	0.11	0.29	0.40	0.52	0.32	0.50	0.17
CaO	1.08	0.84	1.12	1.75	0.77	1.97	0.53
MgO	6.91	9.45	9.63	8.45	10.74	6.02	11.46
K_2O	7.83	7.84	5.78	8.70	9.66	8.30	9.90
Na_2O	1.19	0.40	0.13	0.14	0.12	0.16	0.18
H_2O^-	0.52	0.13	0.06	0.06	0.12	0.22	0.15
H_2O^+	2.60	2.72	4.12	1.72	1.96	1.68	2.34
P_2O_5	0.14	0.04	0.00	0.00	0.04	0.07	0.04
Total	100.15	96.63	97.10	96.81	97.52	98.00	97.68
Si	2.82	2.69	2.43	2.58	2.70	2.67	2.78
Al^{IV}	1.18	1.31	1.57	1.42	1.30	1.33	1.22
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Z	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al^{VI}	0.21	0.16	0.06	0.07	0.05	0.09	0.19
Fe^{3+}	0.45	0.25	0.39	0.51	0.26	0.49	0.23
Fe^{2+}	0.92	1.06	1.24	0.80	0.99	1.18	0.86
Mg	0.77	1.09	1.14	0.96	1.22	0.69	1.29
Mn	0.01	0.02	0.03	0.03	0.02	0.03	0.01
Ti	0.17	0.18	0.15	0.22	0.20	0.14	0.13
Y	2.53	2.76	3.00	2.59	2.74	2.62	2.72
Ca	0.10	0.08	0.12	0.17	0.08	0.20	0.05
Na	0.17	0.06	0.02	0.02	0.02	0.02	0.03
K	0.74	0.77	0.58	0.85	0.94	0.82	0.95
X	1.01	0.91	0.72	1.04	1.04	1.04	1.03
Fe/Fe+Mg	0.80	0.72	0.76	0.75	0.69	0.84	0.65

relations is so essential that its estimation belongs to the most important characteristics of natural systems.

The melting experiments of H. G. F. Winkler et. al. (1975, 1977) are carried out with presence of excess water, where $P_t = P_{H_2O}$. Actually the prevailing majority of experiment determinations of liquid-solid equilibria was carried out in the presence of a free vapour phase and many times such conditions are supposed also for natural, mainly anatectic systems. The works of several authors (W. C. Luth, 1969; G. C. Brown — W. S. Fyfe, 1970; A. J. Piwinskij — P. J. Wylie, 1970; J. K. Robertson — P. J. Wyllie, 1971), however, relatively unambiguously demonstrate that natural granitic systems are in the major part of their history water-undersaturated. The content of water according to various authors does not exceed 2 to 5 %. Only under certain circumstances — by gradual crystallization and by rising of magma the content of water increases so much that in apical and marginal parts of magma chambers conditions of water-saturated magma can originate.

The difference in phase and thermal relations between „dry" and „wet" melts (of intermediate composition) is clearly illustrated in Fig. 4 according to J. K. Robertson — P. J. Wyllie (1971). The curve of solid in Fig. 4 A has a negative slope and with rising temperature sinks to 650°C whereas

Continuation of Tab. 1

	ZK-29	ZK-30	ZK-38	ZK-40	ZK-42	ZK-46	ZK-47
SiO_2	35.38	33,06	31.56	33,14	37.39	32.33	30.06
TiO_2	2.31	3.50	3.54	3,52	2.40	3.49	3.40
Al_2O_3	17.49	16.26	16.90	17,77	16.96	14.97	15.94
Fe_2O_3	3.06	7.54	3,60	1,28	11.47	9.50	10.48
FeO	16.87	14.22	17.96	18,59	10.68	15.67	12.56
MnO	0.25	0.43	0.20	0,15	0.43	1.64	0.40
CaO	0,68	2.20	1.70	0.95	0.67	0.41	3,35
MgO	8.68	8.75	10.58	8,95	7.36	9.85	9.79
K_2O	9.12	6.93	4.65	7.92	7.80	6.12	4.43
Na_2O	0.14	0.50	0.22	0,21	0.22	0.28	0.50
H_2O^-	0.40	0.06	0.38	0.30	0.16	0.30	0.18
H_2O^+	2.38	2.34	4.73	2.97	2.58	3.65	3.98
P_2O_5	0.02	0.00	0.02	0.04	0.00	0.04	0.00
Total	97.78	95.79	96.04	95.79	98.12	98.25	95.07
Si	2.73	2.57	2.50	2.61	2.79	2.51	2.39
Al^{IV}	1.27	1.43	1.50	1.39	1.21	1.37	1.49
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.12	0.12
Z	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al^{VI}	0.32	0.05	0.08	0.25	0.28	0.00	0.00
Fe^{3+}	0.18	0.44	0.21	0.08	0.64	0.44	0.51
Fe^{2+}	1.09	0.92	1.19	1.22	0.67	1.02	0.83
Mg	1.00	1.01	1.25	1.05	0.82	1.14	1.16
Mn	0.02	0.03	0.01	0.01	0.03	0.03	0.03
Ti	0.13	0.20	0.21	0.21	0.13	0.20	0.20
Y	2.73	2.66	2.96	2.82	2.56	2.83	2.73
Ca	0.07	0.22	0.18	0.10	0.07	0.17	0.35
Na	0.02	0.08	0.03	0.03	0.03	0.04	0.08
K	0.90	0.69	0.47	0.79	0.74	0.61	0.45
X	0.99	0.98	0.68	0.92	0.84	0.81	0.87
Fe/Fe + Mg	0.73	0.75	0.71	0.72	0.79	0.76	0.74

the curve of liquidus, represented partly by clinopyroxene (cpx) and partly by hornoblende (hb), exceeds 1000°C. In the dry system, Fig. 4 B, the solid has positive slope from 950—1000°C.

The presence of hydrous minerals, biotite, muscovite and amphibole excludes the possibility of anhydrous conditions for two-mica granodiorite, also biotitic tonalite, even when it does not proof the presence of free water phase.

From the viewpoint of water content or water vapour in crystallizing magma it is important to mention some pecularities of the Bratislava massif of the Malé Karpaty. It is mainly the fact that the SW part of the massif is very rich is pegmatites. Their amount is greater than in the other core mountains. The western part of the massif does not contain so much pegmatites, is, however, more acid on the whole. B. Cambel — J. Valach (1956) admit the following conception: whereas in the highest part of the domed body acid and supercritical agent (mainly water) made possible the origin of many pegmatites, in somewhat more basic rock, in relatively deeper position they remained in dissipation state and gave rise to rock of acid character with less pegmatites. The deeper relief more uncovered by erosion, of the western part of the massif is testified by lacking gneiss remnants, which are abundant in the eastern part.

Table 1 (cont.)

	ZK-48	ZK-50	ZK-51	ZK-53	ZK-56	ZK-57	ZK-60
SiO_2	35.77	36.02	34.89	36.18	35.92	35.94	33.55
TiO_2	3.49	2.16	3.26	3.12	2.68	2.05	3.16
Al_2O_3	16.55	18.76	17.92	12.45	14.37	17.88	17.70
Fe_2O_3	6.91	8.71	6.76	4.88	5.50	3.05	7.55
FeO	16.49	13.30	15.92	16.49	18.66	15.40	17.20
MnO	0.48	0.54	0.46	0.51	0.15	0.11	0.51
CaO	0.89	0.86	1.94	0.78	1.05	0.88	1.19
MgO	6.98	6.42	6.79	7.06	8.69	9.55	6.42
K_2O	8.30	8.60	7.52	8.70	8.70	9.24	5.78
Na_2O	0.31	0.25	0.30	0.40	0.19	0.14	0.25
H_8O^-	0.18	0.10	0.08	0.06	0.12	0.28	0.12
H_2O^+	1.28	2.26	2.36	1.74	2.02	2.04	4.20
P_2O_5	0.12	0.00	0.08	0.19	0.02	0.03	0.04
Total	97.75	97.98	98.28	92.56	98.07	96.59	97.67
Si	2.71	2.71	2.64	2.92	2.76	2.74	2.66
Al^{IV}	1.29	1.29	1.36	1.08	1.24	1.26	1.34
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Z	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al^{VI}	0.19	0.37	0.24	0.11	0.06	0.34	0.23
Fe^{3+}	0.39	0.49	0.38	0.30	0.32	0.17	0.44
Fe^{2+}	1.04	0.84	1.01	1.11	1.20	0.98	1.12
Mg	0.79	0.72	0.76	0.85	0.99	1.08	0.74
Mn	0.03	0.03	0.03	0.03	0.01	0.01	0.03
Ti	0.20	0.12	0.19	0.19	0.15	0.12	0.18
Y	2.64	2.58	2.61	2.59	2.73	2.70	2.74
Ca	0.09	0.08	0.19	0.08	0.11	0.09	0.03
Na	0.05	0.04	0.04	0.06	0.03	0.02	0.17
K	0.80	0.82	0.73	0.90	0.85	0.90	0.69
X	0.94	0.95	0.96	1.04	0.99	1.01	0.89
Fe/Fe+Mg	0.80	0.81	0.80	0.78	0.77	0.70	0.81

For the so characterized magma water saturated conditions are not excluded. The lower temperature of intruding magma is indicated also by its low metamorphic capacity (little thickness or even missing isomorphic zones of deep contact metamorphism, rare occurrence of migmatites, B. Cambel — J. Valach, 1956).

From the viewpoint of water regime it is more difficult to characterize the tonalite magma of the Tribeč mts. According to E. Krist (1960) this magma was characterized by little differentiation. Besides the generally more basic character it is also attested by lacking aplitoid and pegmatitoid differentiates. The contact effect of magma cannot be valuated because the crystalline schists in contact with granitoids in the present-day relief are missing. It appears, however, that for water saturated conditions are not sufficient preconditions. From optical observation the succession of minerals is not completely unambiguous. The biotite and plagioclase were the first but their mutual relation is not clear. When we admit that biotite is at least partly of relict character (H. G. F. Winkler — R. Breitbart, 1978), the question arises, to what an extent its composition can be influenced by chemical composition of surrounding melt because the high magnesiality of the Tribeč biotite is connected with more basic character of tonalite magma.

Continuation of Tab. 1

	ZK-82	ZK-86	ZK-92	ZK-100	B	53 B	54 B
SiO_2	39.90	39.62	37.11	37.52	36.72	36.60	34.25
TiO_2	2.06	2.34	2.47	2.32	2.47	2.05	3.80
Al_2O_3	14.91	15.29	17.65	16.79	15.77	15.80	13.25
Fe_2O_3	7.84	6.50	9.82	12.64	5.25	5.68	7.18
FeO	11.63	15.08	13.85	8.74	14.74	11.80	15.09
MnO	0.19	0.26	0.02	0.15	0.32	0.22	0.20
CaO	0.24	0.48	0.24	0.32	1.81	1.65	0.93
MgO	12.02	9.15	8.29	8.69	11.02	14.19	12.07
K_2O	9.71	9.08	3.24	8.46	10.07	9.20	9.30
Na_2O	0.16	0.17	0.12	0.18	0.12	0.16	0.16
H_2O^-	0.32	0.26	0.24	0.44	0.05	0.29	0.26
H_2O^+	1.02	1.70	6.90	3.72	1.26	1.86	3.03
P_2O_5	0.06	0.05	0.08	0.06	0.00	0.00	0.00
Total	100.06	100.00	100.03	100.03	99.60	99.50	99.52
Si	2.88	2.90	2.78	2.77	2.71	2.68	2.62
Al^{IV}	1.12	1.10	1.22	1.23	1.29	1.32	1.19
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.19
Z	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al^{VI}	0.14	0.22	0.34	0.24	0.09	0.05	0.00
Fe^{3+}	0.43	0.36	0.55	0.70	0.29	0.31	0.22
Fe^{2+}	0.70	0.92	0.87	0.54	0.91	0.72	0.96
Mg	1.29	1.00	0.93	0.96	1.21	1.55	1.38
Mn	0.01	0.02	0.00	0.01	0.02	0.01	0.01
Ti	0.11	0.13	0.14	0.13	0.14	0.11	0.22
Y	2.68	2.65	2.83	2.58	2.66	2.75	2.79
Ca	0.02	0.05	0.02	0.03	0.17	0.16	0.09
Na	0.02	0.02	0.02	0.03	0.02	0.02	0.02
K	0.89	0.85	0.31	0.80	0.95	0.86	0.91
X	0.94	0.92	0.35	0.85	1.14	1.04	1.02
Fe/Fe+Mg++	0.66	0.74	0.78	0.75	0.68	0.60	0.69

+Structural formulae were calculated on the basis of 44 cationic and anionic valencies per unit cell. To write the half-cell formula, the values for the cations per unit cell are halved.

++ Fe/Fe+Mg rations were calculated on the basis of FeO,Fe_2O_3 Mg O oxides.

Analyses 53 B, 54 B, 55 B are from J. Ďurkovičová (1967).

The dependence of crystallization succession and the width of crystallization interval on the water content in the melt were shown clearly by the melting experiments of J. A. Whitney (1975), W. L. Huang — P. J. Wyllie (1973) or S. Maaløe — P. J. Wyllie (1975). In Fig. 5 is the crystallization interval of biotitic granite (modal composition: pl—28,4 %, af—39,1 %, qz—26 %, bi—5,2 %), as function of the water content at pressure 2 kbar, according to S. Maaløe — P. J. Wyllie (1975). The picture shows how the crystallization interval expands from the water saturated to water undersaturated area. The liquidus represented by plagioclase attains almost 1200°C under anhydrous conditions. From phase relations an important fact results: the upper limit of biotite stability changes with the change of the water content at constant fugacity of oxygen and constant total pressure very little only — from 840°C in water saturated conditions to 875°C when traces of water are present only. The phase boundary of biotite thus sharply intersects the phase boundaries of anhydrous minerals and the position of biotite in crystallization succession is essentially influenced by the water content in magma. Similar relations are also valid for further hydrous mineral—muscovite (W. L. Huang — P. J. Wyllie, 1973). In the case of granite MG—1 S. Maaløe — P. J. Wyllie (1975) it was derived from the petrographically confirmed crystallization succession: plagioclase—microcline—quartz—biotite that the content of water in crystallizing magma was less than 1,2 %.

In the case of the two-mica Bratislava granodiorite a different situation arises. Petrographic observation has shown the succession: biotite — quartz — plagioclase — alkalic feldspar. Anhydrous minerals — quartz and feldspars thus crystallized at lower temperature than biotite and the total scheme rather corresponds to water saturated conditions in the right part of Fig. 5. In the case of granite MG—1 such conditions were attained at water content greater than 6,5 %.

The data about stability of the system biotite — K—feldspar magnetite (D. R. Wones — H. P. Eugster, 1965), which is common for Malé Kar-

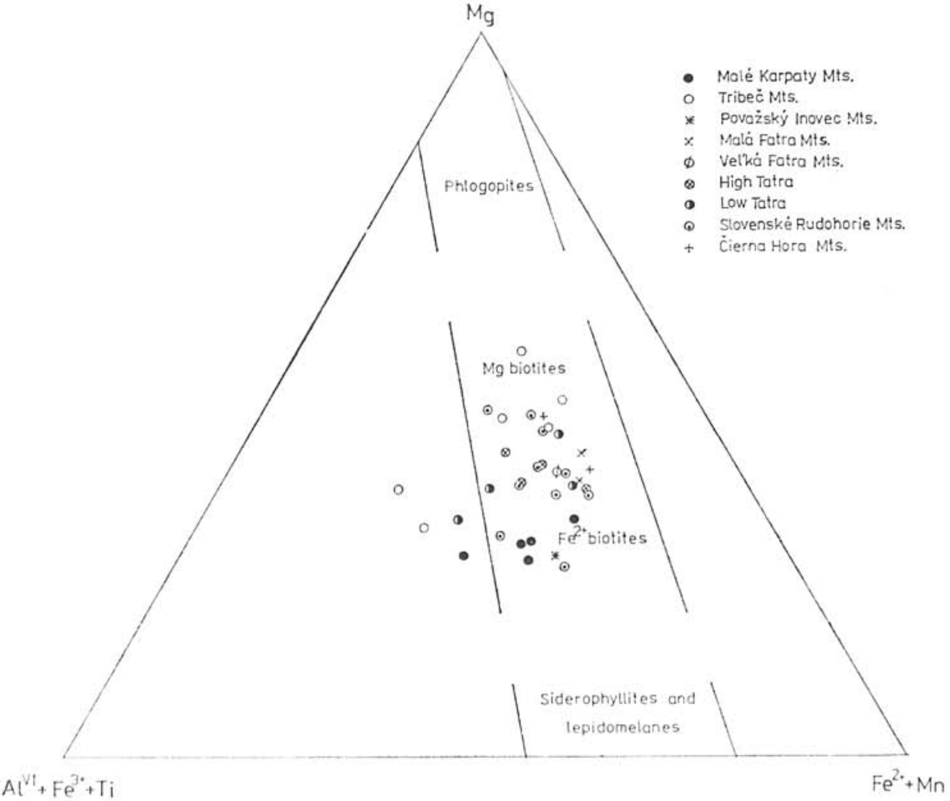

Fig. 1. Relations between octaheral cations of biotites from West Carpathian granitoid rocks. Composition fields according to M. Foster (1960).

paty as well as Tribeč granitoids, can provide fundamental information about T, f_{O_2}, f_{H_2O} conditions for both magmas. D. R. Wones (1972) proposed a model of ideal solution for biotites in the chain phlogopite-annite. For equilibrious system of biotite—K-feldspar—magnetite is valid the equation $\log f_{H_2O} = 7409/T + 4{,}25 + 1/2 \log f_{O_2} + 3 \log x - \log a_{KAlS_3O_8} - \log a_{Fe_3O_4}$ (1.) where T is temperature in °K, x is molar fraction Fe^{2+} in octahedral layer of biotite, "a" is activity of K-feldspar and magnetite.

From the ternary system $Fe^{2+} - Fe^{3+} - Mg$ according to D. R. Wones — H. P. Eugster (1965), Fig. 6 an approximate estimation of oxygen fugacity in comparison with Fe_2O_3—Fe_3O_4 buffer and Ni—NiO is possible. The fugacity of oxygen for biotites of the Malé Karpaty and Tribeč is higher than Ni—NiO buffer. The conditions of Fe_2O_3—Fe_3O_4 buffer for some of the samples (leucocratic granite from the Tribeč ZK—42) appear very high and a secondary oxidation of Fe^{2+} from octahedral layer is not excluded. The absence of primary haematite in granodiorite, also tonalite confirms it.

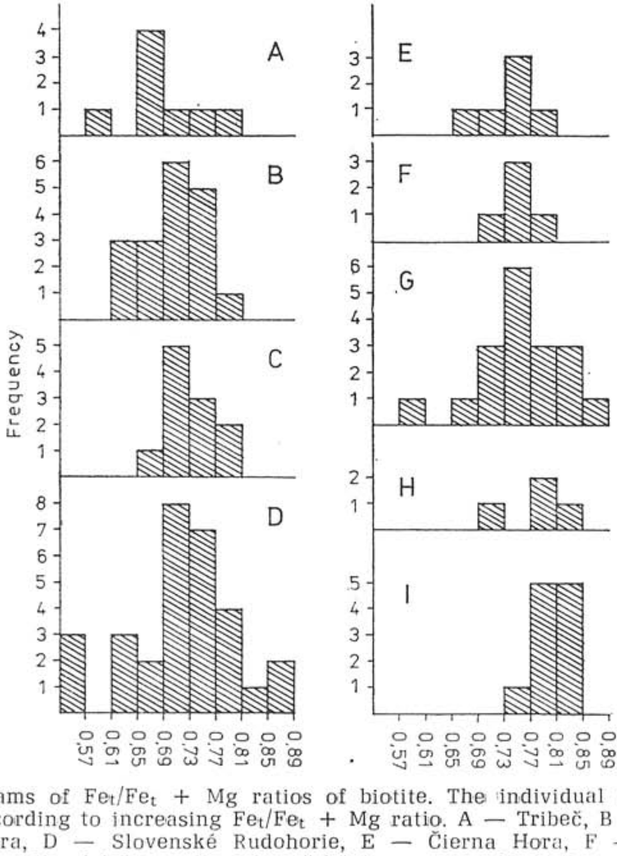

Fig. 2. Histograms of $Fe_t/Fe_t + Mg$ ratios of biotite. The individual montain ranges are ordered according to increasing $Fe_t/Fe_t + Mg$ ratio. A — Tribeč, B — Nízke Tatry, C — Malá Fatra, D — Slovenské Rudohorie, E — Čierna Hora, F — Veľká Fatra, G — Vysoké Tatry, H — Považský Inovec, I — Malé Karpaty.

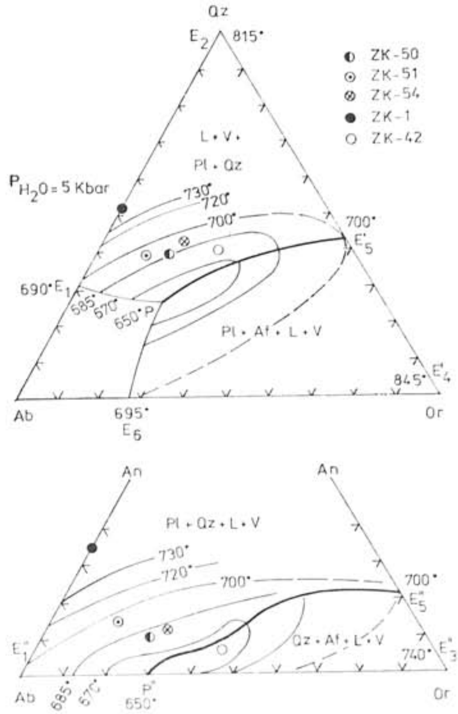

Fig. 3. Projection of isobaric cotectic lines and isotherms on three cotectic surfaces of Qz—Ab—Or—An—H_2O system at pressure P_{H_2O} = 5 kb, according to H. G. F. Winkler et al. (1977). Shown are compositions of five studied samples from the Malé Karpaty and Tribeč, other data see Tab. 2.

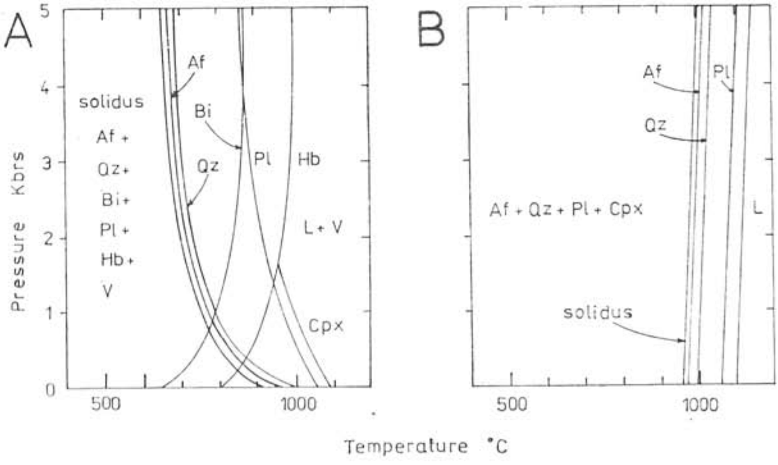

Fig. 4. Phase relationships of melt of granodioritic composition with excess water (A) and dry melt (B) in projection pressure temperature, according to J. K. Robertson — P. J. Wyllie (1971). Abbreviations: Af — alkalic feldspar, Qz — quartz, Bi — biotite, Pl — plagioclase, Hb — hornblende, Cpx — clinopyroxene, L — liquid, V — vapour.

Table 2

Sample	Qz	Ab	Or	An	Remarks
Malé Karpaty Mts.					
ZK—50	37.0	40.8	15.9	6.2	in qz space; 2.8 % An below cotectic surface: plag + qz
ZK—51	36.0	44.6	10.0	9.3	on surface: plag + qz
ZK—54	39.8	35.8	17.0	7.4	in qz space; 3.6 % An below cotectic surface: plag + qz
ZK—1	41.0	38.6	—	20.4	in plag space; 6.4 % An over cotectic surface: plag + qz
ZK—42	39.1	29.8	26.8	4.2	in qz space; 5.8 % An below cotectic surface: plag + qz

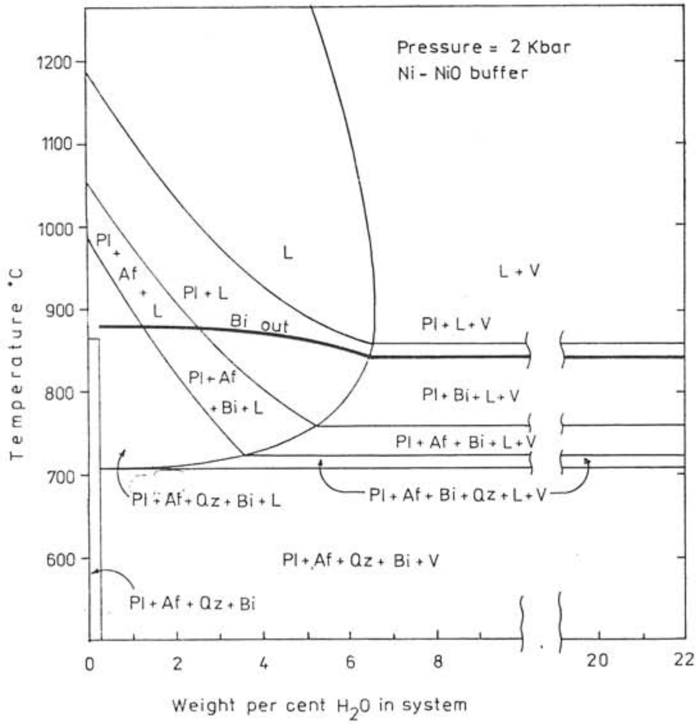

Fig. 5. Crystallization interval of biotitic granite as function of water content at pressure 2 kb, according to S. Maaløe — P. J. Wyllie (1975). The heavy line is the upper boundary of biotite stability. In the vapour-absent region it sharply intersects the phase boundaries of quartz and feldspare. Abbreviations see Fig. 4.

On the graph — f_{H_2O} vs T, Fig. 7 the curves of biotites stability of the Malé Karpaty and Tribeč are calculated according to equation (1). Ni—NiO buffer according to J. S. Huebner — M. Sato (1970) was used as the lower boundary of fugacity O_2. As molar fraction (x) for biotite of two-mica Bratislava granodiorite was used the value x = 0,39, i.e. average from five analyses (ZK—48 ZK—50, ZK—51, ZK—53, ZK—60) and for biotite from Tribeč tonalite the value x = 0,30, i.e. average from four samples (ZK—1, 52 B, 53 B, 54 B), Table 1. According to D. R. Waldbaum — J. B. Thompson (1969) the activity from definity solid solution of alkalic feldspars is not ideal, at temperatures between 600—800°C, in composition: molar fraction $KAlSi_3O_8$ = 0,25—0,75 the activity of $KAlSi_3O_8$ is approximately 0,6. The activity of magnetite was supposed as unit one.

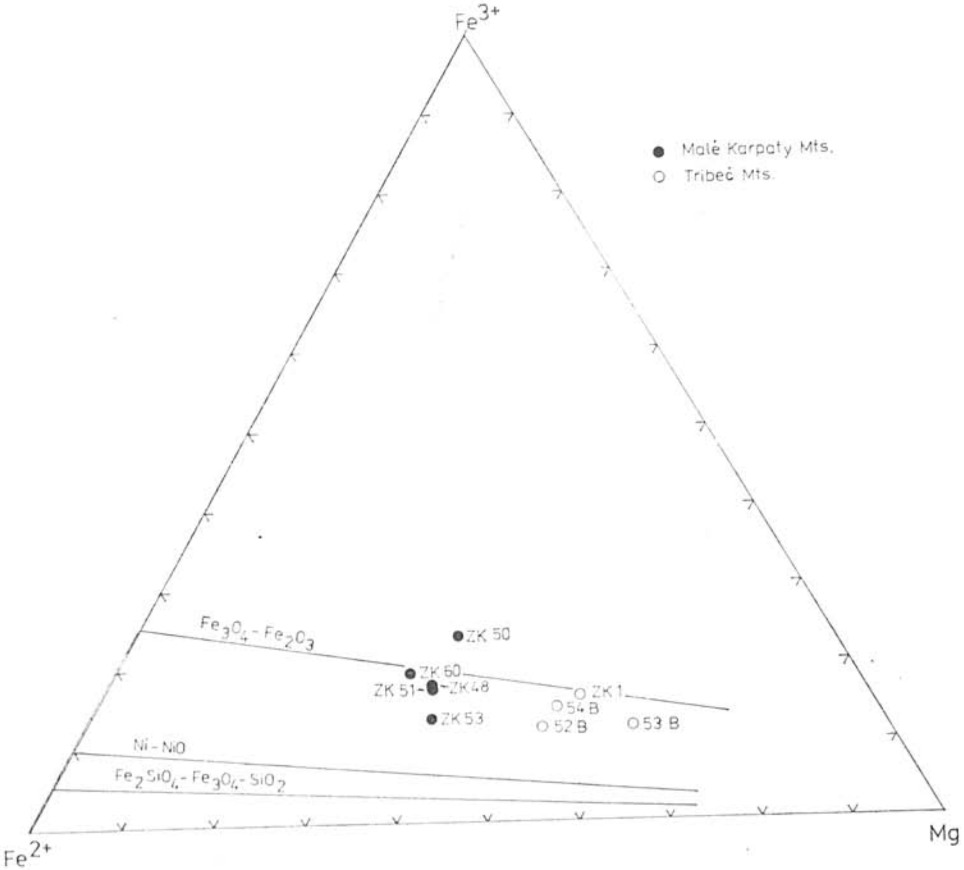

Fig. 6. Relationships of Fe^{2+} – Fe^{3+} – Mg contents of biotites in the Malé Karpaty and Tribeč mts. The lines represent approximate composition of biotites buffered by haematite-magnetite, nickel-nickel, oxide, fayalite-magnetite-quartz, according to D. R, Wones — H. P. Eugster (1965). Samples 52 B, 53 B, 54 B are from J. Ďurkovičová (1967).

Both curves of stability in Fig. 7 intersect with the curve „granite minimum" of O. F. Tuttle — N. L. Bowen (1958). For Malé Karpaty biotite the estimation of the minimum temperature of crystallization is 740°C at f_{H2O} = 770 bars, for Tribeč biotite is the minimum temperature 775°C at f_{H2O} = 590 bars. Regarding to the used buffer Ni—NiO the estimated values of water fugacity can be also considered as minimum.

When we also take into consideration the assumption that the Malé Karpaty magma, at least in the upper part of the magmatic chamber, attained conditions of water saturation, the actual temperature of crystallization of biotite must have been higher, because biotite, if crystallized first, formed the first solid phase, (however, with the exception of some accessory and ore minerals), consequently liquidus and not solidus, compare Fig. 4A. The real liquidus could be possibly by 100 — 200°C higher as the experiments of S. Maaløe — P. J. Wyllie (1975), Fig. 5 or A. J. Piwinski (1968) illustrate. As the lower boundary of the crystallization interval, consequently as solidus temperature we may suppose the value of 650°C, i.e. minimum melting temperature (O. F. Tuttle — N. L. Bowen, 1958; W. C. Luth et al., 1964).

The attempt to derive similar temperature limitation for the Tribeč tonalite is rendered more difficult by unclear relation of biotite and plagioclase in crystallization succession. It can be concluded from Fig. 7, however, that crystallization took place at higher temperature and lower H_2O fugacity in comparison with the Malé Karpaty granodiorite, what to a certain extent supports the assumption of water undersaturated conditions for tonalite magma.

The biotites from postkinematic granitoids of the West Carpathians can be characterized as relative monotonous according to the ratio Fe/Fe Mg, with more ferrous varieties slightly predominating A higher portion of Fe^{3+} in the octahedral layer of biotite (f.g. in leucocratic granites of Tribeč) can be

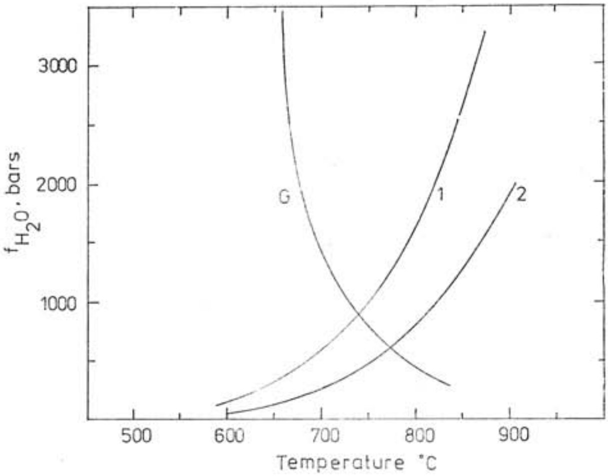

Fig. 7. Stability curves of biotites from the Malé Karpaty (1) and Tribeč mts. (2), calculated according to D. R. Wones (1972), intersecting Ab—Or—Qz minimum melting curve O. F. Tuttle — N. L. Bowen (1958) on diagram f_{H2O} versus T.

connected with secondary circumstances, e.g. subsequent processes, rather than with increased O_2 fugacity in magma.

Comparison of the results of melting experiments with mineral succession of Malé Karpaty and Tribeč granitoids has shown that the position of biotite in these succession can be an important indicator in valuation of the water regime (expressed by the content or water fugacity) of magma.

In valuation of the obtained data about crystallization temperature (740°C for the Malé Karpaty biotite and 775°C for Tribeč biotite) it is necessary to realize that minimum values are concerned. Similarly the idea of water saturated Malé Karpaty magma and, vice versa, water undersaturate Tribeč magma will have to be confronted with the other Core mountains and possibly revaluated.

Translated by J. Pevný

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Location of samples

ZK— 1 Biotitic tonalite, Tribeč, northern slope of the valley near foresters' house house in the road cut. Area of the village Jánova Ves, 183 °/5 km of V. Klíže, E of Topoľčany.

ZK— 42 Biotitic granite, Tribeč, quarry at the N slope of the valley Uhrovská dolinna, 133 °/km of V. Klíža, E of Topoľčany.

ZK— 48 Fine-grained biotitic granodiorite, Rössler's quarry on the hill Briežky, Bratislava, 86 °/1 km of Kamzík (elev.p. 440 m), NE of Bratislava, Malé Karpaty mts.

ZK— 50 Biotitic-muscovite granodiorite, Malé Karpaty, granite quarry Železná studnička, 16 °/1,8 km of Kamzík (elev. p. 440 m), NE of Bratislava.

ZK— 51 Biotitic-muscovite granodiorite, Malé Karpaty, termination of the valley below the castle, Jur —Neštych, 130 °/2,2 km of V. Javorník (elev.p.524 m) SW of Pezinok.

ZK— 53 Biotitic granite, Malé Karpaty, big quarry below the slope, road to Králová Ves, Bratislava, 251 °/7 km of Kamzík (elev.p.440 m), NE of Bratislava.

ZK— 54 Biotitic-muscovite granodiorite, Malé Karpaty, quarry near the chapel, road Karlová Ves — Devín, 230 °/5 km of Kamzík (elev.p.440 m), NE of Bratislava.

ZK— 60 Biotitic-muscovite leucogranite, Malé Karpaty, N slope of elev.p.511, 4, Prepadlé valley, Borinka near Bratislava, 83 °/4,2 km o. Marianka, SE of Stupava.

ZK—100 Aplitoid leucogranodiorite, Tribeč, road Topoľčianky—Skýcov, 1,5 km S of Skýcov, 210 °/1,5 km of Skýcov.

52 B Biotitic tonalite, Tribeč, massif of Veľký Tribeč
53 B Biotitic granodiorite, Tribeč, W of Skýcov
54 B Biotitic tonalite, Tribeč, Zobor — Jazierko

The locations of the other samples „ZK" were published in the work by J. Macek et al. 1979). The location of samples „B" is form the work by J. Ďurkovičová (1967).