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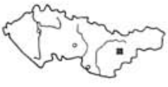
CHEMICAL STUDY OF BIOTITES FROM SOME VEPORIDE GRANITOIDE ROCKS

(Figs. 2)



Abstract: Electron microprobe analyses of biotites from veporide granitoides have been carried out. On the basis of octahedral layer charge balance computations, biotites from Sihľa and Sinec granitoide types are oxidized relics of original biotite grains in the process of antexy. Biotites from Ipeľ and Vepor type granitoides are new—formed in the course of anatexy within the region 660 — 675°C and 186 — 245 MPa of f_{H_2O}.

Резюме: Исследование химического состава биотитов при помощи электронного микрозонда показало возможность интерпретировать генетические условия его формирования с частным обобщениим на установление генезиса гранитоидных пород вепоридного кристаллиника. Судя по химическом составу биотитов, кристаллизация гранитоидов изученных типов протекала при фунгитивности воды 186 — 245 MPa в температурном интервале 650 — 675 °C.

Introduction

Detailed study of chemical composition of biotites as possible genetic information source has not been dealt with to a large extent in the petrological studies of the West Carpathian rock complexes. With two exceptions (J. Ďurkovičová, 1966; 1967), all studies were reduced to state just the presence of biotite and/or their chemical composition is given without any rigorous interpretation. The work of I. Petrík (1980), recently published is the first one which deals wits biotites study from the point of view of their petrological significance.

Petrography

Localisation and petrographic characteristics of biotite host rocks have been done by E. Krist (1979). Genesis and age of the granitoids rocks have not been precisely fixed so far. Details of rock description are given in Table 1.

Biotites from all rock types mentioned above are of irregular shape with green (V-10 to V-14) to redish brown and brown colour. The sagenite lamellae are absent in samples V-10 to V-14, in all other samples they are relatively well supplied. In all samples, existence of phase equilibrium mineral assemblage biotite-magnetite-K-feldspar has been observed.

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Table 1

Petrographic types of biotite host rocks

Sample label	Rock type
V—10, V—11, V—13	biotite trondhjemite
V—12	leukogranite
V—14, V—18, V—25, V—26	biotite granodiorite
V—15	granodiorite
V—16	granite
V—17	muscovite melanogranitoide
V—19, V—20, V—23, V—27	biotite granite

samples V—10 — V—14 belong to the Sihľa type
samples V—15 — V—18 belong to the Vepor type
samples V—19, V—20 belong to the Ipeľ type
samples V—23 — V—27 belong to the granitoide body Sinec
Numbering of samples according to E. Krist (1979).

Experimental

Analyses of biotites have been carried out using the CAMECA MS 60 electron microprobe. Instrumental setting included an accelerating potential of 15 KV and sample current 50nA. Natural biotite (standard for K, Na, Al, Fe, Mg, Ti and Si) and hypersthene (Ca, Mn) served for calibration. Raw data were corrected for drift, background, generation factor, absorption and characteristic fluorescence, using the computer program EMPADR VII (J. Rucklidge — E. L. Gasparini, 1969).

Chemical composition of biotites

The point microprobe analyses are given in Table 2. With respect to the analytical procedures and their disadvantages (all Fe analysed as Fe^{+2}, non analysed H_2O and F), the cation contents were computed on the basis of 22 oxygen atoms (e. g. on 44 cationic charges) and following assumptions have been made:

a) tetrahedral layer of biotites is fully occupied (Σ Si + Al = 8)
b) all Ti is placed in the octahedral layer

In most analyses sum of large cations (K^+, Na^+, Ca^{2+}) is close to theoretical value 2,000, deviations from it are due to experimental difficulties of measurement (low concentration of Na and Ca and instability of alkalies beneath an electron beam, respectively). If other cations are present (Cs^+, Rb^+, Ba^{2+}), they are under the microprobe limit of detection.

Octahedral layer is occupied also by trivalent cation Al^{3+} and/or Fe^{3+} (for the latter see next section) and sum of cations varies from 5,273 to 5,843.

Relatively large part of Si^{4+} is substituted by Al^{3+} in tetrahedral layer (from 1,984 to 2,554) to compensate additional charges due to the presence of Al^{3+}, Fe^{3+} and Ti^{4+} in the octahedral layer.

In spite of the principal shortcomings of the used analytical method mentioned above we consider presented analyses to be the representative ones.

Table 2

Chemical composition of biotites (wt. %)

	V—10	V—11	V—12	V—13	V—14	V—15	V—16	V—17	V—18	V—19	V—20	V—23	V—25	V—26	V—27
SiO_2	39,96	37,47	39,75	39,50	38,94	38,56	38,35	36,67	38,67	38,25	35,98	37,77	37,81	37,21	37,97
Al_2O_3	15,19	16,71	16,09	17,20	17,92	18,64	19,94	19,30	18,19	19,62	19,13	18,58	17,95	17,71	16,55
FeO	17,57	18,34	18,17	17,13	16,24	19,95	19,10	21,81	19,05	19,87	20,21	21,82	22,03	25,10	24,29
MgO	9,96	8,09	10,11	8,73	9,84	8,91	6,55	6,60	8,16	7,41	8,81	6,04	5,92	6,00	4,55
TiO_2	1,94	1,97	1,69	1,64	1,49	1,34	2,57	1,25	2,10	1,67	1,36	2,62	1,76	1,70	1,26
MnO	0,37	0,37	0,31	0,20	0,18	0,30	0,32	0,39	0,29	0,31	0,31	0,40	0,39	0,29	0,34
K_2O	10,03	11,55	10,56	10,91	10,89	9,84	10,16	9,26	9,42	9,84	10,84	9,93	9,91	9,25	9,29
Na_2O	0,18	0,29	0,12	0,29	0,27	0,29	0,26	0,31	0,29	0,25	0,26	0,38	0,33	0,36	0,38
CaO	—	—	—	0,01	0,03	0,08	0,06	0,07	0,09	0,27	0,05	—	—	0,06	0,73
Σ	95,20	94,81	96,80	95,60	95,79	97,91	97,31	95,64	96,27	97,49	96,94	97,55	96,10	96,97	95,36
Cation content (based on 22 oxygen atoms)															
Si	6,016	5,772	5,913	5,917	5,811	5,686	5,667	5,596	5,761	5,653	5,446	5,650	5,749	5,752	5,888
Al^{IV}	1,934	2,228	2,087	2,081	2,189	2,314	2,333	2,404	2,239	2,342	2,554	2,350	2,251	2,248	2,112
Al^{IV}	0,712	0,806	0,735	0,959	0,963	0,927	1,142	1,070	0,955	1,081	0,860	0,929	0,968	0,979	0,912
Fe	2,212	2,363	2,261	2,150	2,026	2,461	2,361	2,787	2,374	2,460	2,559	2,732	2,803	3,245	3,151
Mg	2,235	1,858	2,242	1,953	2,188	1,959	1,444	1,511	1,813	1,636	1,988	1,348	1,343	1,384	1,051
Ti	0,220	0,228	0,189	0,185	0,167	0,148	0,286	0,144	0,236	0,186	0,155	0,295	0,202	0,198	0,148
Mn	0,047	0,048	0,039	0,026	0,023	0,037	0,040	0,050	0,036	0,039	0,039	0,049	0,050	0,037	0,044
Σ	5,426	5,303	5,466	5,273	5,367	5,532	5,273	5,562	5,414	5,402	5,601	5,353	5,366	5,843	5,306
K	1,927	2,243	2,004	2,088	2,073	1,853	1,916	1,806	1,792	1,292	2,093	1,897	1,924	1,826	1,839
Na	0,053	0,085	0,034	0,033	0,078	0,085	0,073	0,092	0,086	0,074	0,077	0,110	0,095	0,109	0,114
Ca	—	—	—	0,001	0,005	0,013	0,008	0,011	0,013	0,042	0,008	—	—	0,009	0,121
Σ	1,980	2,328	2,038	2,171	2,156	1,951	1,997	1,909	1,891	1,975	2,178	2,007	2,019	1,944	2,074
Σ total	15,406	15,631	15,504	15,444	15,523	15,483	15,270	15,471	15,305	15,377	15,779	15,360	15,385	15,767	15,380

Note: total iron as FeO; roman numerals indicate coordination of cation

Charge balance of octahedral layer

The ideal trioctahedral mica formula

$$K_2(Mg,Fe^{2+})_6\ (Si_6Al_2)O_{20}\ (OH)_4$$

suggests that the octahedral group is neutral and all the inherent layer charge is on the tetrahedral layer. This ideal formula must be modified when Ti^{4+}, Al^{3+}, and/or Fe^{3+} enter the octahedral layer. M. D. Foster (1960) showed that biotite can accomodate the positive charge excess introduced either through increased substitution of Al for Si (resulting in an increase in the negative charge on the tetrahedral layer) or by development of octahedral vacancies. Relationship between biotite octahedral occupancy (Σ X) and the number of additional positive charges for biotites studied is on the Fig. 1.

For our purposes the charge balance computations allow to estimate the presence and evaluate approximately the quantity of Fe^{3+}.

Discussion

Chemical composition of biotites studied shows the dependence on granitoide rock type (Fig. 1). On the basis of charge balance there are clear differencies between biotites from granitoides of Sihľa and Sinec type and biotites from Vepor and Ipeľ type granitoides respectively.

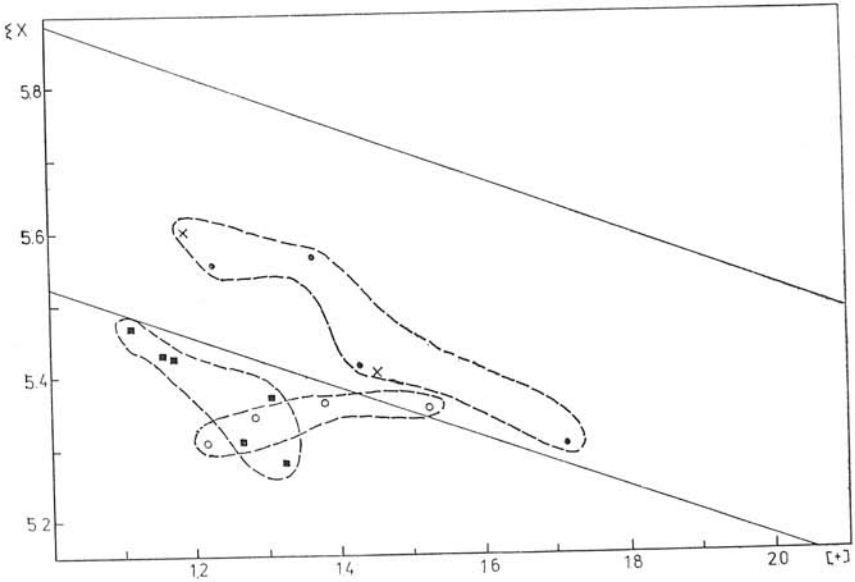

Fig. 1. Relationship between biotite octahedral occupancy (Σ X) and the number of additional positive charges (+). Solid lines represent biotite field presented by M. D. Foster (1960). Squares — biotites from Sihľa, open circles — Sinec, solid circles — Vepor and crosses — Ipeľ type granitoides.

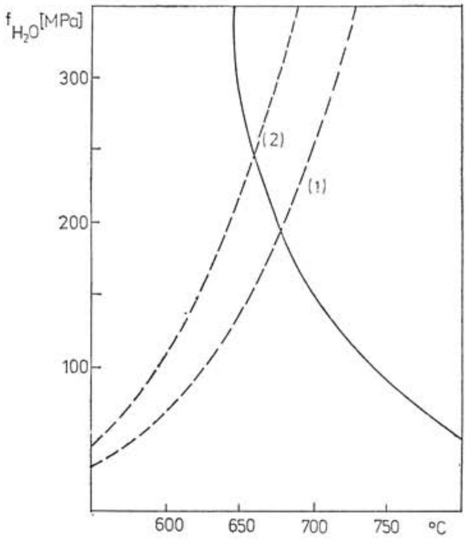

Fig. 2. Calculated biotite stability curves (dashed lines) for the Ipeľ (1) and Vepor (2) type granitoides and the granitic minimum melting curve (solid line) on an f_{H_2O} versus T plot.

As follows from the charge balance analyses, a part of iron is in the form fo Fe^{3+} for certain only in samples from Sihľa and Sinec type granitoides (additional charges on the Fig. 1 computed supposing all Fe as Fe^{2+}). The mean ammount of Fe^{3+} graphically interpolated from the Fig. 1 is 0,238/22 oxygens, which corresponds approximately to 10 % of total Fe being Fe^{3+}. The presence of ferric iron in the biotites from Ipeľ and Vepor type granitoides seems to be improbable.

The process of $Fe^{+2} \rightarrow Fe^{3+}$ oxidization in biotites has been experimentaly studied by A. I. Cvetkov — E. P. Valjašichina (1956), J. Rimsaite (1970) and reaction scheme

$$4\ Fe^{2+} + 4\ OH^- \rightarrow 4\ Fe^{3+} + 4\ O^{2-} + 2\ H_2O$$

at temperatures of 500 — 900°C has been suggested by the authors. The biotite oxidization results in the change of Fe^{3+} coordination octahedron, where, to retain the structure charge equilibrium, OH^- is replaced by O^{2-}.

According to the results, we conclude that biotites from Sihľa and Sinec type granitoides represent the relics of original biotites oxidized during the process of anatexy. On the other hand, biotites from Vepor and Ipeľ type granitoides are new-formed by the anatexy of rock complexes.

The ideal biotite stability equation suggested by D. R. Wones (1972) for biotite — K-feldpar — magnetite mineral assemblage $\log f_{H_2O} = (7409/T) + 4{,}25 + 1/2 \log f_{O_2} + 3 \log x - \log a_{KAlSi_3O_8} - \log a_{Fe_3O_4}$ (T— temperature in °K, x — molar fraction of annite molecule in octahedral layer, a — activity of subscripted phase[1]) was used to compute the phase equilibria conditions of Ipeľ and Vepor type biotites. The equation is not suitable for oxidized biotites from Sihľa and Sinec type granitoides. Intersection points of biotite stability curves with granitic minimum melting curve (O. F. Tuttle — N. L. Bowen, 1958) indicated (Fig. 2) the minimum forming conditions of Vepor and Ipeľ granitoides to be very similar, lying in the range of 660—675°C and 245—186 MPa of f_{H_2O} respectively. These values are slightly different from those published for granitoides of Malé Karpaty and Tríbeč Mts.

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[1] f_{O_2} determined according to J. Haas (in G. K. Czamanske — D. R. Wones, 1973); $a_{KAlSi_3O_8} = 0{,}6$ and $a_{Fe_3O_4} = 1$

(I. Petrík, 1980). Relatively higher f_{H_2O} values can be considered as confirming the hypothesis of anatectic origin of biotite host rocks, according to E. Krist (1979).

We note that the verification of results presented above seems to be necessary by Mössbauer spectrometry.

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