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STRUCTURAL STATE AND CHEMICAL COMPOSITION OF K-FELDSPARS FROM THE GRANITOID ROCKS OF THE MALE KARPATY MTS.

(Figs. 9, Tabs. 3)



Abstract: K-feldspars of granodiorites from the Malé Karpaty Mts. may be characterized on the basis of microscopic observations. X-ray diffraction study and chemical composition as follows: in the Bratislava massif they are represented by poikilitic as well as interstitial grains having a structural state of maximum microcline or they are created by a mixture of monoclinic and triclinic modifications. They may be characterized by the following average contents of major elements (wt. $\frac{0}{0}$): K = 11.5, Na = 1.00, Ca = 0.102 and trace elements (ppm): Rb = 260, Sr = 292, Ba = 3698. Their K--phase with average mol. $^{0}/_{0}$ Or = 96.34 \pm 3.02 is very pure. In contrast to it, structural state of oikocrysts of K-feldspars from the Modra massif corresponds to intermediate — low orthoclase till high microcline. Further on, they differ from K-feldspars of the Bratislava massif by lattice strain (Δa up to 0.016 nm), by higher content of non-unmixed (Ab + An)-component in K-phase having 88.94 \pm 4.86 mol. $\frac{0}{0}$ Or and by higher average contents of Na = 1.40, Ca = 0.194 wt. 0 and Sr = 501, Ba = 4559 ppm and by lower contents of K = 10.8 wt. 0 /₀ and Rb = 140 ppm. Established characteristics of K-feldspars indicate different conditions of formation of granodiorites from the Bratislava and Modra massifs.

Р езюме: На основе микроскопических исследований, рентген-диффракци онного изучения и химического состава можно характеризовать калиевые полевые шпаты гранодиоритов Малых Карпат следующим образом: в братиславском массиве они представлены пойкилитовыми и интерстициальными зернами, которые имеют, стурктурное состояние максимального микроклина или они образованы смесью моноклинной и триклинной модификации. Они характерны следующими средними содержаниями главных элементов (вес. %): K = 11.5; Na = 1.00; Ca = 0.102 и следов (ppm): Rb = 260, Sr = 292, Ba = 3698. Их K-фаза с средним мол. % $Or = 96.34 \pm 100$ ± 3,02 очень чистая. Наоборот, структурное состояние ойкокристов калиевых полевых шпатов модранского массива отвечает переходному низкому ортоклазу вплоть до высокого микроклина. Кроме того они отличаются от калиевых полевых шпатов братиславского массива напряжением в решетке (Да до 0,016 нм), высшим содержанием неотмешанного (Ab + An)-компонента в К-фазе, у которой 88,94 \pm 4,86 мол. % Or, и высшими средними содержаниями Na = 1,40; Ca = 0,194 вес. % и Sr = 501, Ba = 4559 ppm и низшими содержаниями K = 10,8 вес. % и Rb = 140 ppm. Установленные характеристики калиевых полевых шпатов намечают разные условия образования гранодиоритов братиславского и модранского массивов.

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Introduction

Structural state and composition of K-feldspars are often used as petrogenetic indicators and it should be stressed that not only in the study of granitoids in which K-feldspar has a key position. Discussion on formation of K-feldspars in granitoids continues also today, it is aimed especially at megacrysts of K-feldspars (Senderovetal, 1978; Hibbard, 1979; Eggleton, 1979; Mehnert—Büsch, 1981; Winkler—Schultes, 1982). Though various methods are used in the study of K-feldspars (Smith, 1974), interpretation of various degrees of their ordering is not simple even nowadays (Senderov—Byčkov, 1979; Ferguson, 1979). Since X-ray diffraction analysis represents a widely used method of K-feldspars study, some authors have lately proposed new ways of presentation of its results in order to determine Al-contents in tetrahedral positions and structural state of K-feldspars (Blasi, 1977, 1982; Afonina et al., 1978, 1979; Kumejev, 1982).

In spite of considerable attention paid up to now in our literature to post-kinematic granitoids of the Bratislava and Modra massifs of the Malé Karpaty Mts. (the West Carpathians), a detailed information on K-feldspars from these rocks is still missing. K-feldspars of pegmatites from the Bratislava massif form an exception. They were characterized by Dávidová (1970 a, b: 1978 a) as micro- to macroperthitic maximum microclines, whose triclinity ($\Delta r = 0.85$ —1.00) is the highest from all core mountain ranges of Tatrides. Though Sr and Ba contents in these K-feldspars are not the lowest, anyhow they contain the most Rb in comparison with the other core mountains (Dávidová, 1978 b). According to Dávidová—Dávid (1981) the following average contents are typical of K-feldspars of pegmatites from the Malé Karpaty Mts.: Sr = 463 ppm, Ba = 1372 ppm and Rb = 270 ppm.

Practically an only information on K-feldspars of fundamental rock types of the Bratislava and Modra massifs was given by Cambel—Valach (1956): in the Bratislava two-mica granites to granodiorites, perthitic K-feldspars (18—33 vol. 0 /0) are present in form of microcline and orthoclase in variable proportions, they often enclose plagioclase, biotite and quartz, and in contrast to plagioclases they are not intensively sericitized. The quoted authors established that K-feldspar (13—26 vol. 0 /0) is represented in the Modra biotite granodiorites almost exclusively by orthoclase.

Difference of massifs and a certain independence of their formation resulted from the present studies of granitoids from the Bratislava and Modra massifs concerning major elements (Cambel et al., 1982), relation of granitoids to metamorphism of surrounding crystalline rocks (Korikovskij et al., 1984) and distribution of trace elements during the processes of crystallization (Vilinovič—Petrík, 1984). As far as various magmatic series usually converge in the region of the most acid derivates, study of their more basic members from the beginning of differentiation trend is more informative. Therefore the main task of the present work was to examine differences in evolution of the Bratislava and Modra massifs by means of the study of K-feldspars from the granodiorites and granodiorites — tonalites, respectively.

Methodology of study and analytical methods

15 samples of granitoids from the Bratislava massif and 20 samples of granitoids from the Modra massif were chosen for a detailed study after microscopic observations of thin sections. K-feldspars were separated from quartz--feldspar fraction of grinded rock by gravimetric method of separation in bromoform (Macek et al., 1980). X-ray-diffraction analysis of K-feldspars was performed in the Geological Institute of the Slovak Academy of Sciences by means of Philips PW 1150 appliance under the following conditions: Cu radiation, Ni-filter, 40 kV, 25 mA, diaphragms 1° — 0.2° — 1°, 10³ impulses/sec. T=2, shift of paper 600 mm/hour, rate of goniometer 0.5° 2θ /min, measurements were carried out in the direction of $52^{\circ} - 20^{\circ} 2\theta$. Observance of the conditions of measurement was controlled by KBrO3 measurement, which was not, however, used as an internal standard, since it overlaps with 131 reflex of K-feldspar by one of its reflexes, by this way it impedes identification of structural state of K-feldspars. After evaluation of diffraction patterns by means of the tables (Borg-Smith, 1969) the values of triclinity Ar, monoclinic order Δz and Al contents in tetrahedral sites T₁O, T₁m, T₂O, T₂m were calculated using 131, 131, 204 and 060 reflexes (Afonina et al., 1978, 1979):

$$\begin{split} \Delta \mathbf{r} &= 1.264 \cdot \delta \ 2\theta \ _{131-131}, \\ \Delta z &= 1.47 \cdot (9.38 - \delta \ 2\theta \ _{204-060}), \\ \mathrm{Al}_{\mathrm{T_{I}O}} &= \frac{1 + \Delta z + 2\Delta \mathbf{r}}{4} \ , \qquad \mathrm{Al}_{\mathrm{T_{I}m}} \ = \frac{1 + \Delta z - 2\Delta \mathbf{r}}{4} \ , \\ \mathrm{Al}_{\mathrm{T_{2}O}} &= \mathrm{Al}_{\mathrm{T_{2}m}} \ = \frac{1 - \Delta z}{4} \end{split}$$

In the case of presence of only one wider and lowered 131 reflex, $\delta\,2\theta\,_{131}\,_{-131}$ value equals to the half of angle width of this reflex in the half of its height (Afonina et al., 1978; Jiránek, 1982). Since heterogeneous alkali feldspars — perthites are concerned, what indicates the presence of 201 reflexes of the K-phase and the Na-phase, their total composition was calculated using the relation proposed by Kuellmer (1960):

$$\log \left(I_{O} \; I_{A} \right) = -0.0026 + 1.0628 \cdot \log \left(\frac{Or}{Ab + An} \right),$$

where I_O and I_A are intensities of 201 reflex of the K-phase and the Na-phase. The area of $\overline{201}$ reflex equaling to the product of height and width in the half of height was considered for intensity of 201 reflex. However, these estimations of total composition of K-feldspars are considered only for approximate owing to overlapping of 100 reflex of quartz with $\overline{201}$ reflex of K-phase (it is the case of some hardly separable K-feldspars from the Modra massif)

or overlapping of 111 reflex with 201 reflex of Na-phase (in the case of maximum microclines from the Bratislava massif).

Unit cell parameters of the studied K-feldspars, but only those with univocally identifiable 130, 130, 131 and 131 reflexes, were calculated and refined by POWDER program using Siemens 4004/151 computer in the Institute of Computing Technique of the Colleges at the Comenius University. Composition of the K-phase was then established from the volume of unit cell according to the relation given by Stewart—Wright (1974):

$$\mathrm{mol.} \ ^{0}/_{0} \ \mathrm{Or} = \frac{0.2962 - \sqrt{0.953131} - 0.0013 \ . \ \mathrm{V}}{0.0018062}.$$

K, Na, Ca, Rb and Sr contents in K-feldspars were determined from the chloride medium after decomposition of the samples with fluorhydric and chlorine acids by atomic absorption spectrometry method. Ionization interferences in K, Na, and Rb determination were removed by additive solution of caesium chloride (in K and Na) or potassium chloride (Rb). In Ca and Sr determination, disturbing moments caused by production of little volatile compounds were removed by addition of lanthanum-oxine solution. The mentioned elements were determined in acetylene-air flame by means of atomic absorption spectrometer Perking-Elmer 2380. Measurements were carried out in the most intensive resonant curves using discharge lamps with hollow cathode. Extrapure chemicals from the firm Johnson—Mathey were used for preparation of calibration and additive solutions.

Ba was established spectrochemically in K-feldspars using unidirectional current with intensity of 6 A in visible area (455.4 nm). Eu was used as an internal reference element. Spectra were taken on spectrograph PGS-2 of the firm Karl-Zeiss Jena.

Correctness of determinations was verified by means of reference standard materials G-2 (USGS), GSP-1 (USGS) and GM (ZGI).

Petrographic characteristics of the studied rocks

Two-mica granodiorites—monzogranites of the Bratislava massif

In the sense of Streckeisen's (1976) terminology, 11 of 15 studied samples belong to granodiorites and 4 of them to monzogranites (VK-25, VK-105, VK-112, VK-182). The studied granitoids are predominantly medium-grained and equigranular, sometimes they contain small feldspar phenocrysts. K-feldspar occurs in them in two forms:

1. It forms perthitic (spindle-shaped or spotted type of perthite) poikilitic grains with inclusions of plagioclases, biotite, quartz, myrmekite, accessories and also another K-feldspar. Inclusions are dislocated mostly accidentally, but they may be oriented along the growth zones of host K-feldspar (Fig. 1 a, b, c). Margins of these poikilitic grains are usually irregular. Grid-twinning is observable either locally near the margins and inclusions or on the whole area (Fig. 2 a). Twinning according to the Carlsbad law is frequent;

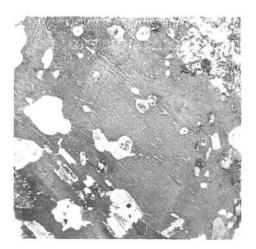


Fig. 1 a. Perthitic character of poikilitic K-feldspar from the biotite granodiorite (JV-37/63), Bratislava massif. XN, magn. $\times 21$; photo: L. Osvald.

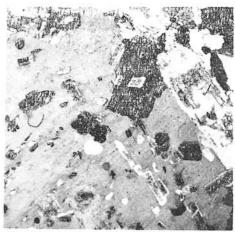


Fig. 1 b. Poikilitic K-feldspar enclosing another K-feldspar with different orientation of inclusions. Muscovite-biotite monzogranite (VK-205), Bratislava massif. XN, magn. \times 21; photo: L. O s v a l d.

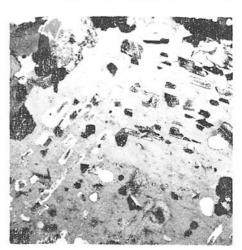


Fig. 1 c. Oriented inclusions in K-feldspar phenocryst. Muscovite-biotite monzogranite (VK-205), Bratislava massif. XN, magn. × 21; photo: O s v a l d.

2. K-feldspar forms minute interstitial grains with well-developed gridding.

Replacement of K-feldspars by albite may be observed, whereby chess-board albite is formed, and replacement of plagioclase by K-feldspar is sporadically observed too (VK-185). Quartz has sometimes idiomorphic forms against K-feldspar (Fig. 2 b). Presence of the so-called ovoids, oval formations of 2 cm size, whose core formed by plagioclase and quartz is covered by rim from several K-feldspar grains, is quite exceptional (VK-112). In general, amount of K-feldspar in the studied samples established by planimetric analysis by



Fig. 2 a. Development of twinning in poikilitic K-feldspar. Biotite leucomonzogranite (VK-147), Bratislava massif. XN, magn. × 21; photo: L. Osvald. K--feldspars from the samples JV-37/63, VK-205 (Fig. 1) and VK-147 were not studied in more detail.



Fig. 2 b. Quartz enclosing biotite with euhedral limitation against K-feldspar. Biotite granodiorite (VK-127), Bratislava massif. XN, magn. × 22; photo: L. Osvald.

means of apparatus Eltinor 4 varies from 9.5 to 29.4 vol. 0 $_{0}$ (average content is 18 vol. 0 $_{0}$).

In plagioclases with basicity An₂₅₋₁₆ (Cambel-Valach, 1956) normal zoning may be observed, though they are considerably sericitized or even epidotized. They have also developed albite rims. They are often overfilled with lamellae of secondary muscovite. Biotite and oval quartz are the most frequent inclusions in plagioclase. Quartz forming mosaic aggregates under a stronger pressure influence is abundant in these rocks. The only substantial dark mineral of the Bratislava granitoids is brown biotite, enclosing apatite and zircon. which can be fresh, but mostly it is altered, whereby muscovite or chlorite and epidote are formed. Sagenite is present in some samples. Sometimes it looks as if biotite is overgrown with muscovite or as if it encloses muscovite, whereby there are no Fe-Ti oxides present, which would indicate a secondary character of muscovite. From the above-mentioned it comes out that muscovite in these rocks may be considered for the primary, as well as for the secondary mineral. From the accessories, apatite, zircon and small amounts of ore minerals should be mentioned. Myrmekite is very typical of the Bratislava granitoids.

Biotite granodiorites — tonalites of the Modra massif

20 granitoid samples from the Modra massif, out of them 17 granodiorites and 3 tonalites (VK-45, VK-50, VK-212) in the sense of Streckeisen (1976) were chosen for the study of K-feldspars; they may be characterized as medium-grained and equigranular rocks. In the case that they are porphyric, phe-







Fig. 3 b. Albite rims of plagioclases on contact with K-feldspar. Biotite granodiorite (VK-193), Modra massif. XN, magn. × 32; photo: L. Osvald.

nocrysts are formed by plagioclases. K-feldspar is interstitial in these rocks, in the case of greater contents it forms usually perthitic oikocrysts, which appear in thin section as optically continuous areas between the laths of plagioclases and biotites without any regular limitation (Fig. 3 a). From the point of view of succession, such K-feldspar appears as the latest. Grid-twinning in K-feldspar is usually not manifested, or just in a small degree (VK-208, VK-209, VK-211, VK-212). In some samples chess-board albite (VK-136, VK-190) is frequent. Contents of K-feldspar vary from 0.5 to 17.0 vol. $\frac{9}{10}$ (average content is 9 vol. $\frac{9}{10}$). Sericitized plagioclases are predominantly idiomorphic, sometimes with complicated lamellae and they show a normal zoning from the core with basicity An_{20-29} to the margin with An_{17-20} (Macek, 1971). Albite rims on the contact with K-feldspar are not always developed (Fig. 3 b). In contrast to K-feldspar, plagioclases represent the earliest phase, because they are enclosed in biotite, or biotite is interstitial among plagioclases. Relatively frequent brown biotite is often chloritized and epidotized, whereby ore minerals and titanite are formed. Quartz is present in form of coarse, often undulatory grains, especially in tonalites it takes over the role of K-feldspar and it fills interstices. In Modra granodiorites — tonalites, hornblende or muscovite occur sporadically; from accessories, apatite, ore minerals, zircon, zonal allanite usually surrounded with epidote and titanite should be mentioned. Though myrmekite occurs less frequently in the Modra granitoids than in the Bratislava ones, nice typical examples may be observed in several samples on the contact of K-feldspar and plagioclase (VK-46, VK-196, VK-208). It should be mentioned that some samples of the studied Modra granitoids show signs of strong cataclasis (VK-136, VK-162, VK-188). Just one sample (VK-210) differs considerably from the others by complicated relations of feldspars and quartz (simultaneous crystallization ?), by expressive hydrothermal alteration and chemical composition of acid granite.

Localities of all studied samples are given in the Appendix.

Results and discussion

In introduction it should be mentioned that owing to the way of separation of K-feldspars from the rock samples, the obtained results are considered for average ones, representing all K-feldspars from the rock. This statement is especially valid for the Bratislava granitoids from which it is practically im-

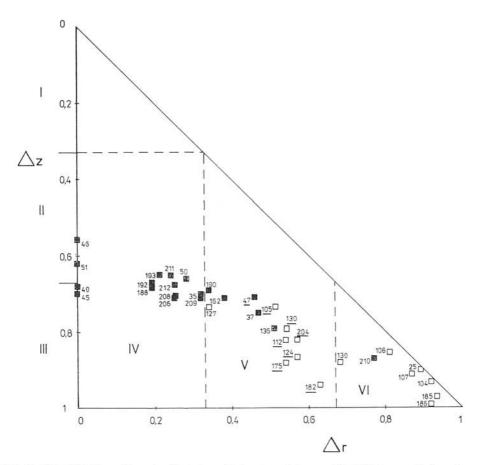


Fig. 4. Classification $\Delta z - \Delta r$ diagram of structural types of K-feldspar (A fonina et al., 1978).

 $\label{eq:explanations: I - high orthoclase (sanidine); II - intermediate orthoclase; III - low orthoclase; IV - high microcline; V - intermediate microcline; VI - maximum microcline. Full square - Modra massif, open square - Bratislava massif. In some samples (their numbers are underlined) monoclinic, as well as triclinic modification of K-feldspar is present.$

possible to separate interstitial K-feldspars from the K-feldspars forming small poikilitic phenocrysts. It is clear that these two forms of K-feldspar differ from each other by their history.

Already in classification of structural state of K-feldspars (Fig. 4) an expressive separation of samples from two studied massifs occurred. There are only intermediate to maximum microclines in the Bratislava massif. Not even one

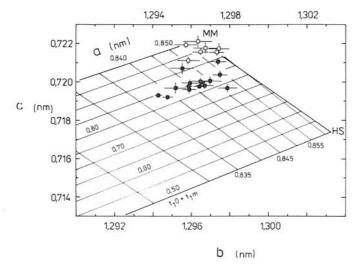


Fig. 5. Unit cell parameters of the studied K-feldspars represented in b—c diagram of Stewart—Wright (1974). Explanations: MM — maximum microcline, HS — high sanidine. Low albite and high albite, end members of the series low albite — maximum microcline and high albite — high sanidine, are outside the figure. Full square — Modra massif, open square — Bratislava massif. Also \pm one standard deviation for the both parameters is plotted there. One sample from the Modra massif is missing, because it is overlapped.

high microcline or purely monoclinic K-feldspar was established here. However, in 7 samples monoclinic and triclinic modifications are present simultaneously in comparable amounts. Low, spread and diffuse 131 reflex in diffraction patterns of these samples (three peaks are often present in 131 area) proves their mixture character. They may be compared with artificial mixtures of Steiger—Hart (1967). Since the interstitial K-feldspars of the Bratislava granitoids are as a rule grid-twinned and their quantity is low when compared with the poikilitic ones, imperfectly triclinized poikilitic phenocrysts are the contributors of monoclinic modification into these mixtures. In the Modra massif K-feldspar reached a structural state of maximum microcline just in one sample (VK-210). Majority of samples are orthoclases to high microclines, the other ones with lowered and spread 131 reflex should be marked as intermediate microclines in the sense of Afonina et al. (1978). Result of classification of structural states of K-feldspars from the Malé Karpaty Mts. granitoids is given in Tab. 1 a, b. From the tables it follows that ranges of

Table 1a

Triclinity, monoclinic ordering, Al-contents in tetrahedral sites T_1O , T_1m , T_2O , T_2m , content of free (Ab + An)-component and structural state of K-feldspars, Bratislava massif

Sample	Δ^{r}	Δ^z	TIO	T_1 m	$T_2O=T_2m$	Ab + An	Structural state
X-25	0.89	0.897	0.9193	0.0293	0.0258	16.1	maximum microcline
VK-104	0.92	0.933	0.9448	0.0218	0.0168	29.7	maximum microcline
K-105	0.51	0.735	0.6868	0.1807	0.0662	5.2	intermediate microcline
2-106	0.81	0.853	0.8678	0.0588	0.0363	17.5	maximum microcline
2-107	0.87	0.911	0.9108	0.0448	0.0223	15.8	maximum microcline
5-112	0.54	0.823	0.7258	0.1858	0.0442	13.0	intermediate microcline
5-124	0.57	0.867	0.7518	0.1818	0.0332	14.8	intermediate microcline
5-127	0.34	0.735	0.6038	0.2638	0.0663	11.2	intermediate microcline
ζ-130	0.54	0.794	0.7170	0.1800	0.0515	7.0	intermediate microcline
ζ-139	0.68	0.882	0.8085	0.1325	0.0295	13.3	maximum microcline
Z-175	0.54	0.882	0.7405	0.2005	0.0295	9.5	intermediate microcline
ζ-182	0.63	0.941	0.8003	0.1703	0.0147	20.0	intermediate microcline
K-185	0.93	0.970	0.9570	0.0280	0.0075	16.3	maximum microcline
ζ-186	0.32	0.990	0.9575	0.0375	0.0025	28.8	maximum microcline
₹-204	0.57	0.823	0.7408	0.1708	0.0442	8.7	intermediate microcline

Triclinity, monoclinic ordering, Al-contents in tetrahedral sites T₁O, T₁m, T₂O, T₂m, content of free (Ab + An)-component and structural state of K-feldspars, Modra massif Table 1b

Sample	Δr	Δz	T_1O	T_1m	$T_2O = T_2m$	Ab + An	Structural state
VK-35	0.32	0.698	0.5845	0.2645	0.0755	11.4	high microcline
VK-37	0.47	0.750	0.6725	0.2025	0.0625	9.7	intermediate microcline
53	0	0.698	0.4245	0.4245	0.0755	17.9	low orthoclase
91	0	0.559	0.3897	0.3897	0.1104	5.2	intermediate orthoclase
1.1	0.46	0.710	0.6575	0.1975	0.0725	8.2	intermediate microcline
61	0	0.676	0.4190	0.4190	0.0810	4.7	low orthoclase
VK-50	0.23	0.660	0.5572	0.2728	0.0850	9.8	high microcline
51	0	0.617	0.4044	0.4044	0.0957	20.1	intermediate orthoclase
.36	0.51	0.790	0.7025	0.1925	0.0525	23.9	intermediate microcline
.62	0.38	0.710	0.6175	0.2375	0.0725	21.7	intermediate microcline
881	0.19	0.684	0.5160	0.3260	0.0750	16.7	high microcline
06	0.34	0.691	0.5934	0.2521	0.0773	36.5	intermediate microcline
92	0.19	0.669	0.5121	0.3225	0.0828	14.2	high microcline
93	0.21	0.650	0.5175	0.3075	0.0875	23.3	high microcline
907	0.25	0.710	0.5525	0.3025	0.0725	1.7	high microcline
803	0.25	0.706	0.5515	0.3015	0.0735	13.0	high microcline
VK-209	0.32	0.710	0.5875	0.2675	0.0725	24.3	high microcline
VK-210	7.77	0.870	0.8525	0.0825	0.0325	20.1	maximum microcline
VK-211	0.24	0.650	0.5325	0.2925	0.0875	23.2	high microcline
VK-212	0.25	0.676	0.5440	0.2940	0.0810	10.6	high microcline

Unit cell parameters, composition of the K-phase and lattice strain of K-feldspars, Bratislava massif Table

Number of re- flexes used	18	19	12	12	11	20	11
Δ^{a}	-0.003	0.001	0	0.002	0.006	0.001	0.003
Or (mol. ⁰ / ₀)	95.86	95.60	98.49	97.43	90.11	98.88	98.03
V (A³)	721.53	721.44	722.41	722.06	719.48	722.54	722.26
, , , , , , , , , , , , , , , , , , ,	87.91	87.81	88.06	87.95	88.10	87.77	87.84
8, (6)	115.96	116.04	116.00	115.89	115.99	115.90	115.85
(_o)	90.60	90.62	90.55	90.59	90.72	29.06	19.06
c (nm)	0.7217(2)	0.7218(3)	0.7216(1)	0.7216(1)	0.7211(2)	0.7221(3)	0.7219(2)
b (mm)	1.2974(6)	1.2967(7)	1.2973(4)	1.2964(4)	1.2958(6)	1.2963(8)	1.2957(6)
a (nm)	0.8575(11)	0.8585(12)	0.8590(8)	0.8584(10)	0.8571(17)	0.8586(11)	0.8585(16)
Sample	VK-25	VK-104	VK-106	VK-107	VK-139	VK-185	VK-186

Note: Errors in the last decimal places are given in parentheses after the a, b, c parameters values.

Table 2b

Unit cell parameters, composition of the K-phase and lattice strain of K-feldspars, Modra massif

Number Δa of re- (nm) flexes used	.012	.008	0.005	.015	600.	600.	600.	.012	.004	800.	.001	.014	.016	.010	.012	.007
Or (mol. ⁰ ₀) (89.55		90.87			(T)		920				1952)			· 650	//20
V (A ³)	719.27	719.13	719.76	715.67	718.43	719.16	719.35	718.54	721.50	718.51	722.31	718.01	715.15	720.77	718.06	720.14
\(()	90	06	06	06	06	06	90	06	06	06	06	06	90	88.42	06	90
£.(°)	115.96	115.89	115.99	116.02	115.87	116.00	115.99	116.03	115.95	115.99	115.98	115.92	116.01	115.90	116.02	115.93
α (۵)	90	06	06	06	06	06	06	06	06	06	06	06	06	90.29	06	06
c (nm)	0.7199(2)	0.7200(2)	0.7196(2)	0.7192(1)	0.7197(1)	0.7198(1)	0.7200(0)	0.7198(0)	0.7204(1)	0.7198(0)	0.7210(1)	0.7196(2)	0.7192(1)	0.7207(2)	0.7195(1)	0.7201(2)
b (mm)	1.2959(4)	1.2964(5)	1.2979(5)	1.2948(3)	1.2964(3)	1.2966(5)	1.2966(1)	1.2959(1)	1.2975(3)	1.2967(2)	1.2974(4)	1.2952(6)	1.2943(2)	1.2955(6)	1.2959(3)	1.2969(5)
a (nm)	0.8574(11)	0.8562(8)	0.8573(8)	0.8550(7)	0.8556(7)	0.8572(5)	0.8572(4)	0.8572(4)	0.8583(8)	0.8563(5)	0.8588(7)	0.8564(14)	0.8548(6)	0.8584(16)	0.8569(8)	0.8573(14)
Sample	VK-35	VK-45	VK-46	VK-49	VK-50	VK-51	VK-188	VK-190	VK-192	VK-193	VK-206	VK-208	VK-209	VK-210	VK-211	VK-212

c parameters values. þ, a, Note: Errors in the last decimal places are given in parentheses after

 $$\operatorname{\mathtt{Table}}\ 3$\,a$$ Contents of alkalies and alkaline earths in K-feldspars, Bratislava massif

Sample	$K_{(0)}$	Na (0 0)	Ca (" 0)	Rb (ppm)	Sr (ppm)	Ba (ppm
VK-25	11.2	0.84	0.081	200	330	4600
VK-104	10.7	1.28	0.076	200	230	3600
VK-105	12.0	0.88	0.094	265	330	3680
VK-106	11.4	1.10	0.179	235	310	3530
VK-107	11.8	0.92	0.070	245	280	3170
VK-112	11.6	0.94	0.122	300	315	3450
VK-124	11.4	1.22	0.078	270	324	3900
VK-127	11.9	0.96	0.095	260	340	4000
VK-130	11.8	0.98	0.070	305	250	2760
VK-139	11.9	0.82	0.070	285	295	3450
VK-175	12.0	0.86	0.085	320	305	3680
VK-182	10.4	1.46	0.259	290	265	3300
VK-185	11.6	0.92	0.096	285	250	3700
VK-186	11.4	1.04	0.080	175	260	4400
VK-204	12.0	0.82	0.069	270	300	4250
$\overline{\mathbf{x}}$	11.5	1.00	0.102	260	292	3698
S	± 0.5	± 0.19	± 0.052	± 42	± 34	± 480

Explanations: $\overline{x} \pm s$: arithmetical mean \pm standard deviation.

triclinity and of monoclinic ordering of K-feldspars from the Bratislava and Modra massifs are overlapping just a little.

Evident absence of "actual" intermediate microclines with clear and well distinguishable 131 and 131 relfexes in the studied sets of samples caused that it was not possible to obtain unit cell parameters of some K-feldspars — the very mentioned mixtures in which Wright—Stewart (1968) do not recommend refining of parameters. All K-feldspars whose parameters were not obtained upon expectation are intermediate microclines according to Δz — Δr diagram. Therefore only 16 samples from the Modra massif and only 7 samples from the Bratislava massif are plotted in b—c diagram (Fig. 5). Majority of K-feldspars (in fact the K-phases of perthites) from the Modra granodiorites — tonalites shows a small variability of Al-contents in tetrahedral sites ($T_1O + T_1m = 0.80 - 0.85$), but a considerable variation in the content of non-unmixed (Ab + An)-component. Mol. 0 0 Or in the K-phase (Tab. 2 b) ranges from 79.23 to 95.77 and it has an average value of 88.94 \pm 4.86. Variable portion of free (Ab \pm An)-component in the Modra K-feldspars results from

 $$\operatorname{Table}\ 3$\ b$$ Contents of alkalies and alkaline earths in K-feldspars, Modra massif

Sample	K (0/0)	Na (" 0)	Ca (0 0)	Rb (ppm)	Sr (ppm)	Ba (ppm
VK-37	10.1	1.29	0.134	175	730	5300
VK-45	10.7	1.80	0.338	90	770	5250
VK-46	11.8	1.04	0.104	160	515	3600
VK-47	11.6	1.45	0.185	135	560	4950
VK-49	12.6	0.92	0.164	125	665	5350
VK-51	11.9	1.58	0.192	175	545	4400
VK-162	9.5	1.54	0.198	125	335	3700
VK-188	11.6	1.30	0.104	135	370	4100
VK-192	11.6	1.54	0.131	145	365	4000
VK-193	9.9	1.86	0.207	139	375	5000
VK-206	11.9	0.75	0.087	145	575	5550
VK-209	9.0	1.80	0.324	130	495	4750
VK-210	10.6	1.18	0.164	170	295	3200
VK-211	9.6	1.48	0.315	150	420	3940
VK-212	9.6	1.54	0.265	115	500	5300
$\overline{\mathbf{x}}$	10.8	1.40	0.194	140	501	4559
S	± 1.1	± 0.33	± 0.082	± 23	± 144	± 756

Explanations: $\overline{x} \pm s$: arithmetical mean \pm standard deviation.

the intensities of 201 reflex of the K-phase and Na-phase (Tab. 1 b), so that X-ray-diffraction data show that (Na, Ca)-component of K-feldspars of the Modra granitoids cannot be neglected in interpretations. On the contrary, one of the main reasons of lattice strain in these K-feldspars manifested by "anomalous character" expressed by $\Delta a = a_{\rm established} - a_{\rm estimated\ from\ b-c}$ (S te wart — Wright, 1974) lies in the quality of unmixing of the Na-phase. According to the quoted authors, K-feldspars whose $\Delta a > 0.005$ nm are anomalous. From Tab. 2 bit follows for K-feldspars of the Modra granitoids that they are all, but 3, anomalous. In contrast to it, maximum microclines from the granitoids of the Bratislava massif have (Ab + An)-component almost totally unmixed, because their K-phase with average mol. $^0/_0$ Or = 96.34 \pm 3.02 is very pure. Their lattices are (perhaps excluding sample VK-139) practically without any strain (Tab. 2 a).

K, Na, Ca, Rb and Sr contents (determined by AAS-method) and Ba (determined by OES-method) in K-feldspars of the studied rocks give a further information on environment of their formation. It is evident that study of

distribution of e. g. Ba within K-feldspar grains by means of electron microanalyser may give more information on crystallization processes than a total Ba content, but it turned out that differences between granodiorites of the Bratislava and Modra massifs are apparent already from the total contents of trace (and major) elements in K-feldspars (Tab. 3 a, b). K-feldspars of the Modra granitoids are characterized by higher variability of contents of the

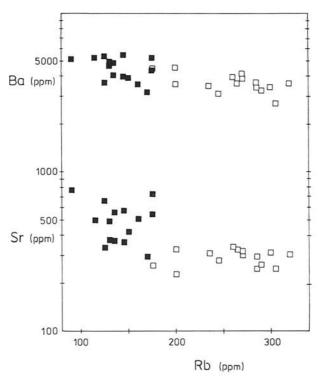


Fig. 6. Dependence of Rb—Sr, Ba in K-feldspars of the Modra (full square) and Bratislava (open square) massifs.

studied elements (except Rb), higher average contents of Na, Ca, Sr, Ba and lower K and Rb contents in comparison with K-feldspars of the Bratislava granitoids. From Fig. 6 it follows that two studied sets of K-feldspars do not practically overlap at all by their Rb and Sr contents. Rb—Sr correlation is absent and slight negative Rb—Ba correlation within the individual massifs is present. In the both massifs Ba contents are in one order higher than Sr contents. It should be pointed out that differences in Rb, Sr, Ba contents between K-feldspars from the both massifs are analogous to the differences between granodiorites themselves (C a m b e l et al., 1981). From Fig. 7 it is evident that there is a positive Ba—Sr and Ca—Sr correlation in K-feldspars, but these dependences are less striking within the individual massifs. After all, no more

significant correlations can be expected within one petrographic type of rocks — granodiorites.

As far as established structural states of K-feldspars are concerned, it may be stated that their ordering path follows a two-stage process. It is documented by Al-occupations of tetrahedral sites (Tab. 1 a, b) represented in trapezium diagram (Fig. 8). But it is not an ideal two-stage process during

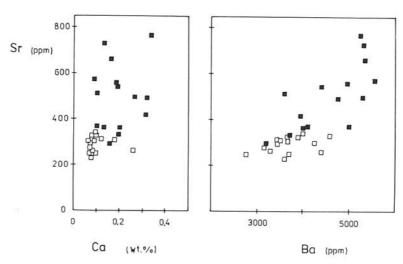


Fig. 7. Dependence of Ca—Sr and Ba—Sr in K-feldspars of the Modra (full square) and Bratislava (open square) massifs.

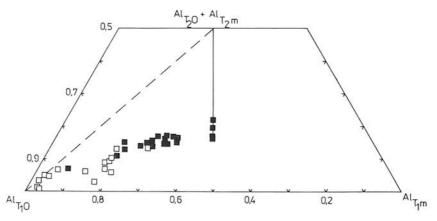


Fig. 8. Diagram of Al-contents in tetrahedral sites (Stewart-Wright, 1974) in which the studied K-feldspars follow two-stage process of ordering.
 Explanations: Dashed line — one-stage process of ordering of albites; monoclinic K-feldspars are projected on vertical straight line. Full square — Modra massif, open square — Bratislava massif.

which Al $_{T_1O}=$ Al $_{T_1m}=$ 0.50 occurs by monoclinic ordering and only after that monoclinic — triclinic transformation and subsequent triclinic ordering take place, whereby Al is transferred from T_1m to T_1O . Monoclinic — triclinic transformation in the Modra massif occurred sooner, about around Al $_{T_1O}=$ Al $_{T_1m}=$ 0.42, since K-feldspars with higher monoclinic ordering were not established. Stewart—Wright (1974) state that ordering of mono-

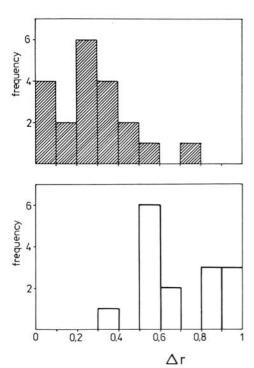


Fig. 9. Frequencies of triclinity of K-feldspars in granitoids of the Modra massif (hatched columns) and the Bratislava massif (white columns).

clinic and triclinic K-feldspar is a continuous process, but monoclinic - triclinic transformation is discontinuous. It was proved also by Cherry--Trembath (1979 a, b) who consider lack of intermediate microclines in nature (the most rapid event is ordering of triclinic K-feldspar) and presence of monoclinic and triclinic modifications in the same K-feldspar for a manifestation of discontinuous transformation. Besides the sample VK-210 (or VK-37) which is a more acid differentiate with manifestations of H₂O-activity and samples VK-136 and VK-162 in which the higher triclinity is caused by stress effects, in K--feldspars of the Modra massif just a slight triclinization occurred after monoclinic - triclinic transformation. what proves the application of some impeding factors. But presence of Ba is not considered for such factor, because its contents are < 100 and A f onina et al. (1978) do not ascribe an impeding influence in ordering to such contents. Preservation of orthoclases and impeding to further ordering of high microclines in the Modra granodiorites - tonalites enabled strain in their lattice caused by micro-(crypto ?)-perthitic character in the sense of

Stewart—Wright (1974), as well as strain caused by domain structure, as characterized by Eggleton—Buseck (1980). There are no doubts that relatively quicker cooling of the Modra massif and a weaker manifestation of H₂O fluids co-acted here in comparison with the Bratislava massif. Slower cooling of the Bratislava massif is suggested by its greater depth of emplacement (Korikovskijetal., 1984). Relics of monoclinic symmetry in K-feld-spars of this massif prove that process of ordering terminated in formation of maximum microclines started also from monoclinic state. Though petrographic observations of rocks and petrogenetic modelling of fractional crystallization processes of magmas from the both massifs (Vilinovič—Petrik.

1984) evidence the magmatic origin of K-feldspars, after Senderov—By č-kov (1979) or Senderov et al. (1981) orthoclases with Al $_{T_1O}$ + Al $_{T_1m}$ =

0.80 have no their field of stability at magmatic temperatures, but they are formed under metastable conditions at $\leq 500~\pm~50~^{\circ}\text{C}$ in the field of microcline stability. Statements contradictory at first sight do not exclude each other, if we admit that life of granite does not end by magma solidification and that established structural states of K-feldspars reflect the above-mentioned subsolidus conditions.

Interpretation of triclinity of K-feldspars is not always simple (Jiránek, 1979), but difference between granodiorites of the Bratislava and Modra massifs expressed by triclinity (Fig. 9) and other established properties of K-feldspars give evidence undoubtedly in favour of different conditions of their formation. Our data do not allow, for the time being, to quantify a temperature history and besides it, number of the studied samples is too small to establish any regularity in areal distribution of structural states of K-feldspars in the both massifs of the Malé Karpaty Mts.

Conclusion

The following knowledge resulted from the study of K-feldspars of granitoid rocks from the Malé Karpaty Mts.: K-feldspars of two-mica granodiorites — monzogranites of the Bratislava massif represented by poikilitic and interstitial grains have structural state of maximum microcline or monoclinic as well as triclinic modifications occur in them simultaneously.

K-feldspars of biotite granodiorites — tonalites of the Modra massif forming oikocrysts have a structural state of intermediate — low orthoclase to high microcline. They differ from K-feldspars of the Bratislava massif by strained lattices, higher content of non-unmixed (Ab + An)-component in the K-phase, higher average Na, Ca, Sr, Ba and lower K and Rb contents. Established characteristics of K-feldspars suggest different conditions of formation of granodiorites from the Bratislava and Modra massifs.

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Translated by O. Mišániová

APPENDIX: LOCALITIES OF THE STUDIED SAMPLES

Bratislava massif

- VK-25 Muscovite-biotite leucomonzogranite, road Jur Myslenice, exposure in bend near railway viaduct.
- VK-104 Muscovite-biotite leucogranodiorite, N end of the village Neštich, exposure at the road in direction to Šenkárka.
- VK-105 Biotite monzogranite, about 600 m NW of elev. point Veľký Javorník (593.5), road Biely Kríž – village Jur.
- VK-106 Biotite granodiorite, 400 m SE of observatory in Malý Javorník, road to Biely Kríž.
- VK-107 Muscovite-biotite leucogranodiorite, W of the village Jur pri Bratislave, valley above the farmyard, 500 m from the edge of forest.
- VK-112 Biotite monzogranite, elev. point Malý Javorník (588.6), excavation below observatory.

- VK-124 Biotite granodiorite, Bratislava, quarry near railway station Červený most.
- VK-127 Biotite granodiorite, valley of Bystrica brook, about 400 m NW of sanatory, 600 m NE of elev. point Hrubý Drinovec (396.6).
- VK-130 Biotite granodiorite, Bratislava—Krasňany, Pekná cesta, about 800 m from the forest Krasňany in direction to Čierny vrch hill.
- VK-139 Biotite granodiorite, region of Malý Javorník, Červený potok brook, road from gamekeeper's cottage Medené Hámre, small quarry NW of elev. point 553.0.
- VK-175 Muscovite-biotite granodiorite, the village Myslenice, elev. point Krkavec (349.8).
- VK-182 Muscovite-biotite leucomonzogranite, Myslenice, region of Ostrý vrch hill, 250 m W of elev. point Jurské hory (350.6), artificial exposure.
- VK-185 Muscovite-biotite leucogranodiorite, Myslenice, region of Staré hory, 250 m SE of elev. point 212.3.
- VK-186 Biotite leucogranodiorite, W of Myslenice, 300 m N of elev. point 214.9; reservoir.
- VK-204 Biotite granodiorite, the village Rača, Dvornická dolina valley, 600 m SE of elev. point 320.9.

Modra massif

- VK-35 Biotite granodiorite, region of Peterklín Skalnatá, about 300 m W of elev. point Peterklín (584.2).
- VK-37 Biotite granodiorite, region of Peterklín Skalnatá, about 300 m N of elev. point Peterklín (584.2).
- VK-45 Biotite tonalite, NW of the village Píla, valley of Kamenný potok brook, gamekeeper's cottage Pri Rybníčku, road cutting on the right slope of a dam.
- VK-46 Biotite granodiorite, the village Castá, about 600 m E of elev. point Jelenec (694.6), road at elev. point 356.
- VK-47 Biotite granodiorite, upper part of the valley of Kamenný potok brook, 500 m SE of elev. point Krvavý buk.
- VK-49 Biotite granodiorite, valley of Kamenný potok brook, 500 m W of gamekeeper's cottage Pri Rybníčku, natural exposure at the road.
- VK-50 Biotite tonalite, Castá, below the peak of elev. point Prostredník (414.6), 700 m S of reservation.
- VK-51 Biotite granodiorite, Častá, Jánova dolina valley, 300 m N of elev. point 365, about 1 km from gamekeeper's cottage Kobylé.
- VK-136 Biotite granodiorite, exposure in road cutting between Modra and Kráľová (against the house No. 34/220).
- VK-162 Biotite granodiorite, the village Dolany, 50 m NW of gamekeeper's cottage in Dolanská dolina valley, excavation on fork of roads.
- VK-188 Biotite granodiorite, Modra, Popelárová, 100 m S of cross-roads of road and brook, 250 m W of elev. point 361.
- VK-190 Bjotite granodiorite, Modra Harmónia, gamekeeper's cottage Hrnčiar, about 600 m NNE of elev. point Šárka (330.2).
- VK-192 Biotite granodiorite, Modra Harmónia, cross-roads 300 m E of elev. point Peprovec (491.0).
- VK-193 Biotite granodiorite (ditto as VK-192).
- VK-206 Biotite granodiorite, region Piesok, 400 m NW of gamekeeper's cottage Panský dom, road to Kuchynská Baba.
- VK-208 Biotite granodiorite, region Piesok, about 2 km N of Panský dom.
- VK-209 Biotite granodiorite, 700 m NNE of elev. point Skalnatá (704.1) in the valley at the road.
- VK-210 Biotite leucogranodiorite (apophysis in amphibolites), depression between Kuchynská Baba and Gajdoš, 250 m SE of elev. point Gajdoš (650.4).
- VK-211 Biotite granodiorite, S of Kuchynská Baba, 500 N of elev. point Tri kopce (661.7).
- VK-212 Biotite leucotonalite, region Piesok, road cutting 300 m E of Zochova chata.

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