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GRANITOIDS OF THE MALÉ KARPATY MTS.: MAJOR ELEMENT CHEMISTRY AND ITS CONTRIBUTION TO PETROGENESIS

(Figs. 9)

Abstract: The petrochemical evaluation of chemical analyses of the Malé Karpaty granitoid rocks has shown a peraluminous character, trends of differentiation and secondary alteration of the granitoids of the Bratislava massif, and a more basic metaluminous-peraluminous character of the granitoids of the Modra massif. Fractional crystallization of amphibole was not a process that caused the peraluminous character of the Bratislava granitoids. The primary petrochemical features of the granitoids in the massifs studied are inherited from the sources. It appears that the granitoids of the Bratislava and Modra massifs had crystallized from two separate portions of the magma.

Резюме: Петрохимическая оценка химических анализов гранитоидных пород Малых Карпат показала высокоглиноземистый характер, тенденции дифференциации и вторичного изменения гранитоидов братиславского массива и более основный, металюминиево-пералюминиевый характер гранитоидов модранского массива. Фракционная кристаллизация амфибола не являлась тем процессом, который вызвал высокоглиноземистый характер гранитоидов братиславского массива. Первичные петрохимические черты гранитоидов исследованных массивов унаследованы от источника. Кажется, что гранитоиды братиславского и модранского массивов кристаллизовали из двух отдельных порций магмы.

Introduction

Variscan granitoids of the Bratislava and Modra Massifs constitute a substantial part of the Malé Karpaty Mts. crystalline complex. The granitoids of the Malé Karpaty Mts. were studied in detail particularly by J. Koutek — V. Zoubek (1936) and B. Cambel — J. Valach (1956), who also evaluated the results of the earlier studies. The geological position of the two granitoid massifs and their relations to the adjacent rocks were characterized chiefly by B. Cambel — J. Valach (1956) and B. Cambel in M. Mahel' (1972). Recently, M. Mahel' (1980), S. Polák — D. Rak (1980) and F. Hrouda (1981) expressed the idea that the granitoid massifs of the Malé Karpaty might be parts of a nappe.

The modern petrology cannot dispense with information stemming from the chemical composition of the whole rock. Petrochemistry was, especially in the past, a means of determining the differentiation trends, distinguishing the genetic rock types, and providing a basis for correlation and classification, etc.

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The appraisal of chemical analyses of the rocks always formed a foundation of more detailed investigations. In order to create these possibilities we have evaluated 255 chemical analyses of the Malé Karpaty granitoids, 198 of which were granitoids of the Bratislava massif and 57 of the Modra massif. Additionally, also some dioritic rocks (33 samples) were examined, which make up small bodies in both massifs, recently studied by B. Cambel et al. (1981 a). The analyses were performed by M. Vondrovic of the Geological Institute of the Slovakian Academy of Sciences in Bratislava, with the use of the X-ray fluorescence method. The set of analyses also comprises those given in B. Cambel – J. Valach (1956) and D. Bodiš (1977). The sampling localities are listed in B. Cambel et al. (1980).

The granitoids have been divided into groups according to their chemical composition, using the Q'-ANOR diagram (A. Streckeisen – R. W. Le Maitre, 1979) and mesonormative minerals Qz, Or, Ab, An (P. Mielke – H. G. F. Winkler, 1979). It should be mentioned that I. Petrík – V. Vilinovič (1981) and V. Vilinovič – I. Petrík (1982) have shown, on the example of granitoid samples from the West Carpathians, a relatively good agreement between the mesonormative and modal classification of the granitoids. As the mesonormative classification has been published in the paper of V. Vilinovič (1981), it is not given here.

Petrochemistry of the Malé Karpaty granitoids

The correlation of the major element contents in granitoids of the massifs studied (Fig. 1 a, b, c) has shown a known fact, viz. a more basic character of the Modra massif, which has lower average contents of SiO_2, K_2O and higher TiO_2, Al_2O_3, (Fe_2O_3, FeO), MgO, CaO and Na_2O. In the Bratislava massif granitoids rich in quartz and with $Na_2O \leqq 1$ wt. %, mineralogically related to greisens, have been established at the localities Svätý vrch, Kňažný vrch, Kráľova búda and the Horvátka gamekeeper's lodge. H. De la Roche et al. (1980) give a value of $Na_2O \leqq 0.5$ wt. % as a characteristic feature of such granitoids.

The question whether the AFM and CaO – Na_2O – K_2O diagrams are suitable for assessing the differentiation trends and/or assigning the granitoids to some of the magmatic series has recently been studied by J. C. Butler (1979). The AFM diagram for the granitoids of the Bratislava massif (Fig. 2 a) shows a relatively small range of differentiation and, moreover, tonalites are virtually lacking (only 4 samples); according to B. Cambel et al. (1981 a) diorites are not in a direct comagmatic relation with granitoids. The field of granitoid varieties of the Modra massif (Fig. 2 b) overlap considerably one another and the granitoids of the Bratislava massif as well. The studied sets of samples suggest that the two massifs are actually formed only by the end members of the CA-series (V. Vilinovič, 1981). In the series of granodiorite – monzogranite – syenogranite – alkali-feldspar granite of the Bratislava massif (Fig.

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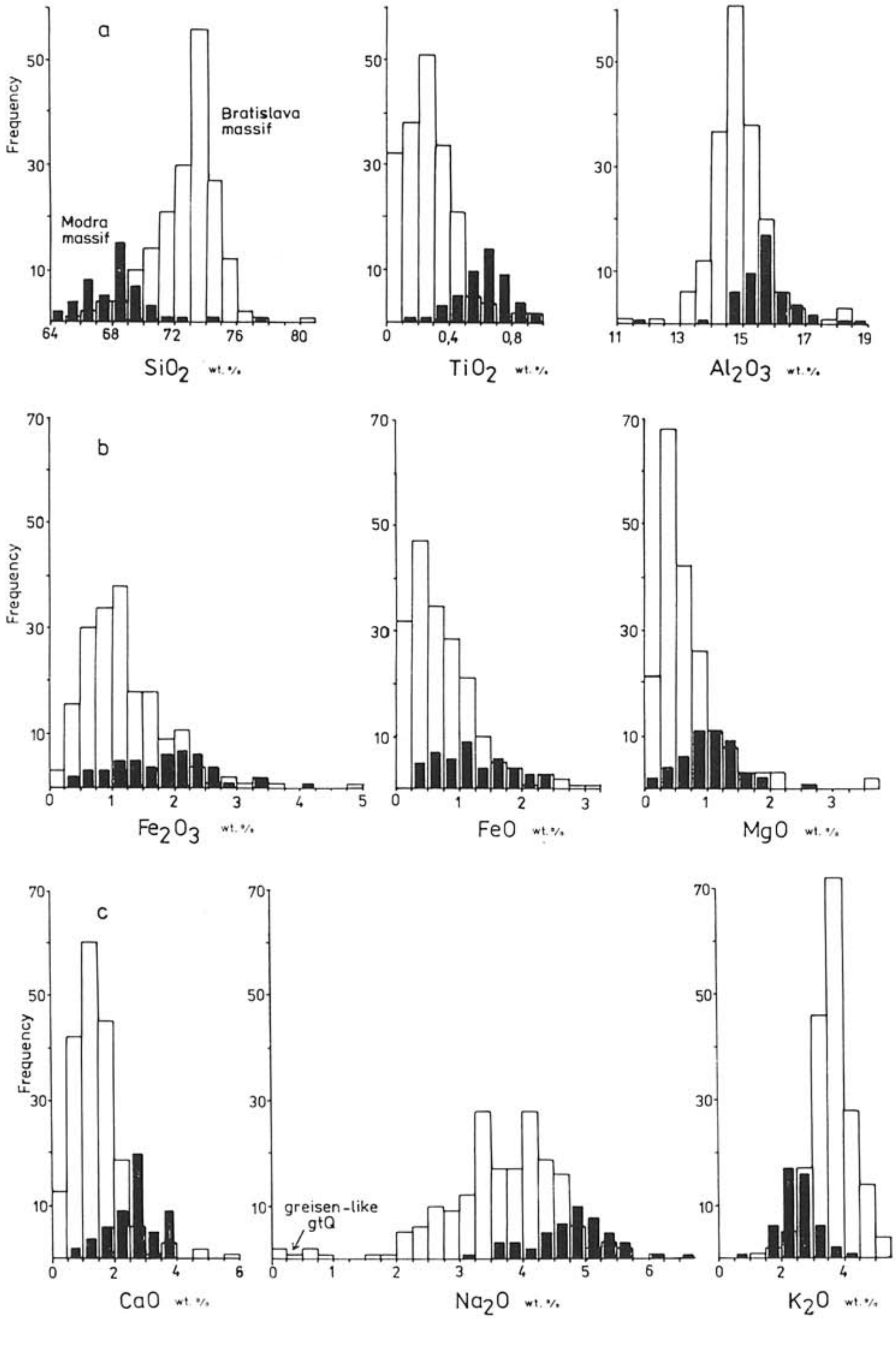
Fig. 1 a, b, c. Histograms showing the contents of petrogenic oxides from chemical analyses of the granitoid rocks of the Bratislava (blank column) and Modra massifs (black columns).


a
b
c
Frequency
Bratislava massif
Modra massif
greisen-like gtQ
SiO2 wt.%
TiO2 wt.%
Al2O3 wt.%
Fe2O3 wt.%
FeO wt.%
MgO wt.%
CaO wt.%
Na2O wt.%
K2O wt.%

3 a) the CaO content decreases and the Na_2O/K_2O ratio only slowly develops on behalf of K_2O. Some samples of monzogranite and alkali-feldspar granite displayed higher K_2O contents as a result of intensive sericitization of feldspars and of other secondary alterations. The Modra granodiorites – tonalites (Fig. 3 b) are characterized by a uniform ratio of $Na_2O/K_2O > 1$.

Niggli's differentiation diagram and Zavarickij's diagram have been constructed in addition, in order to present a complete picture of the granitoid composition and to enable the correlation of the Malé Karpaty granitoids with those of other West Carpathian ranges, which were evaluated from this aspect by B. Cambel – Ľ. Vilinovičová (1981). Each of the rock groups of the Modra massif is more basic than the corresponding group in the Bratislava massif (Fig. 4). The normal differentiation trend of the Bratislava granitoids was disturbed in the group of quartz-rich granitoids, whose composition resulted from subsolidus alterations. In both massifs there is a gap between the composition of the diorites and granitoids. In the sense of A. N. Zavarickij (1955), the granitoids of the Bratislava massif (Fig. 5 a, b, c, d) usually belong to the rocks oversaturated with respect to aluminium (up to 94 % of samples) and quite

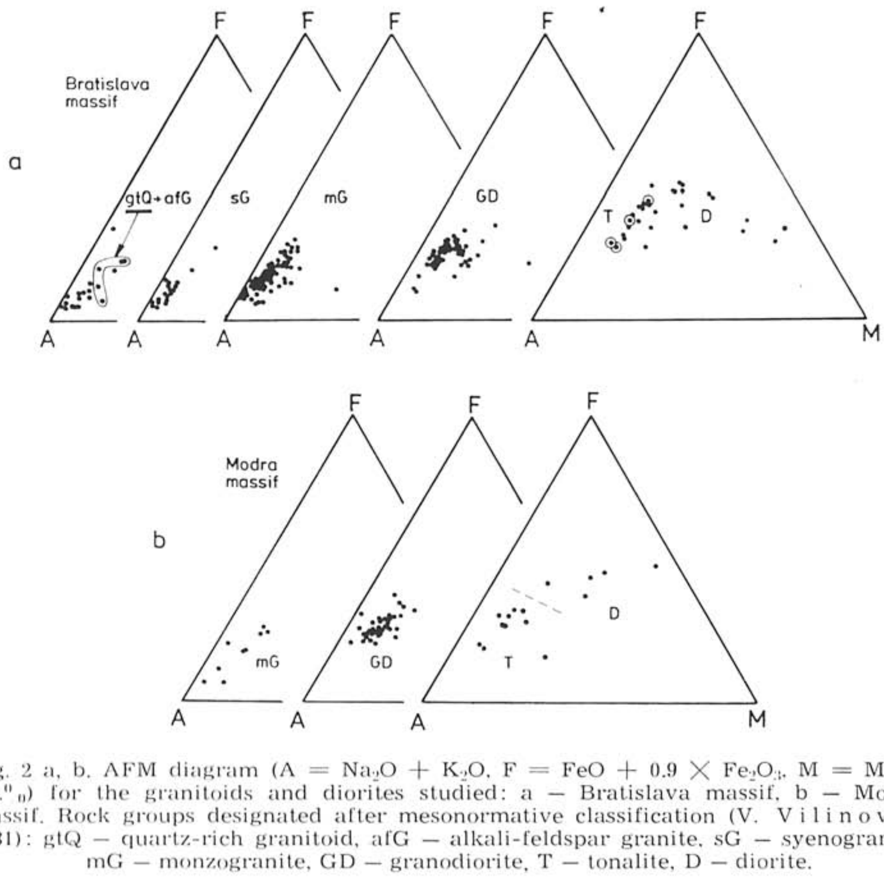


Fig. 2 a, b. AFM diagram ($A = Na_2O + K_2O$, $F = FeO + 0.9 \times Fe_2O_3$, $M = MgO$; wt. %) for the granitoids and diorites studied: a – Bratislava massif, b – Modra massif. Rock groups designated after mesonormative classification (V. Vilinovič, 1981): gtQ – quartz-rich granitoid, afG – alkali-feldspar granite, sG – syenogranite, mG – monzogranite, GD – granodiorite, T – tonalite, D – diorite.

rarely to normal rocks (6 % of samples); the granitoids of the Modra massif (Fig. 5 e) are represented almost equally by Al-oversaturated rocks (56 % of samples) and by normal rocks (44 % of samples), as is indicated by the SAB

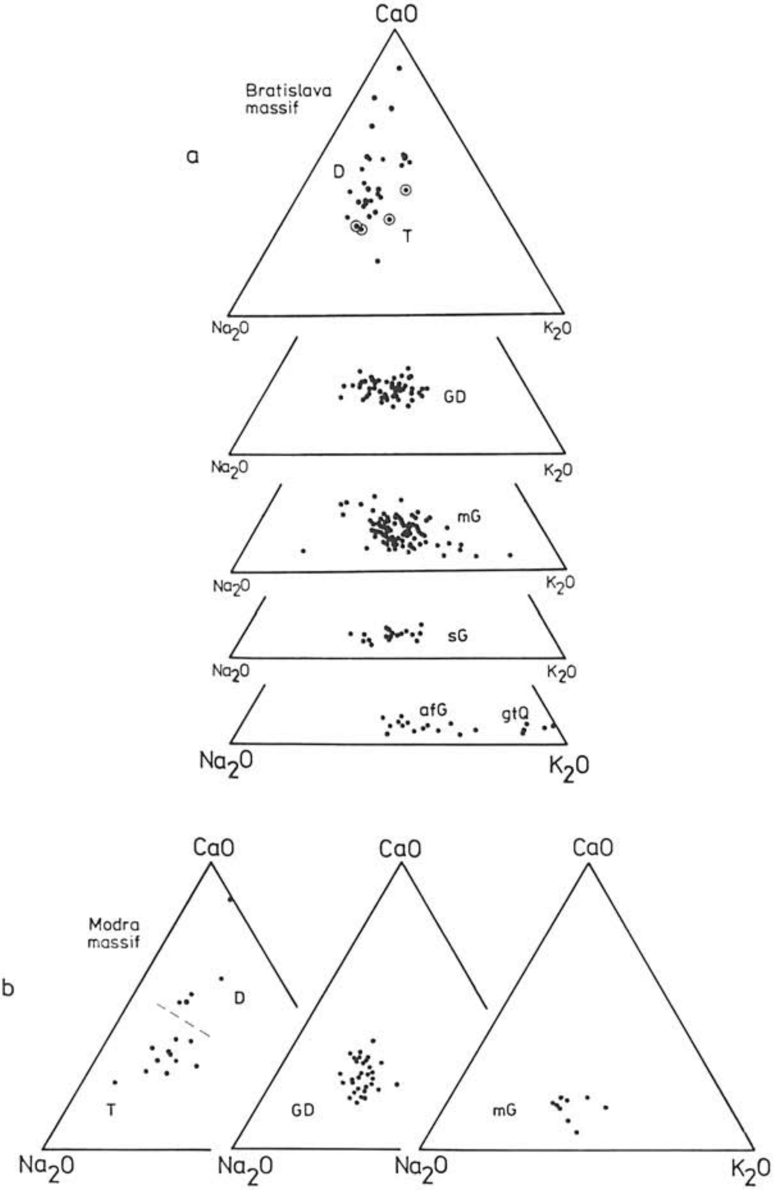


Fig. 3 a, b. CaO — Na_2O — K_2O (wt.%) diagram for the granitoids and diorites studied: a — Bratislava massif, b — Modra massif. For abbreviations of rock names see Fig. 2.

projection. From the SCB projection (Fig. 5) the same conclusions can be inferred for the granitoids studied as from the CaO – Na_2O – K_2O diagram.

According to the CIPW classification (not published here) the composition of the Bratislava granitoids can be generally expressed by the following symbols: I.4.2.4 – 30 % of samples, I.3.2.3. – 23 %, I.4.2.3. – 13 %, I.3.1.3. – 13 %, and invariably less than 5 % of samples are to be denoted by other symbols. The Modra granitoids in 82 % of samples correspond to symbol I.4.2.4, and in less than 5 % of samples to other symbols. This implies that in both cases the mineral composition of the granitoids is dominated by quartz and feldspar, the weight amount of normative quartz being smaller than or equal to that of

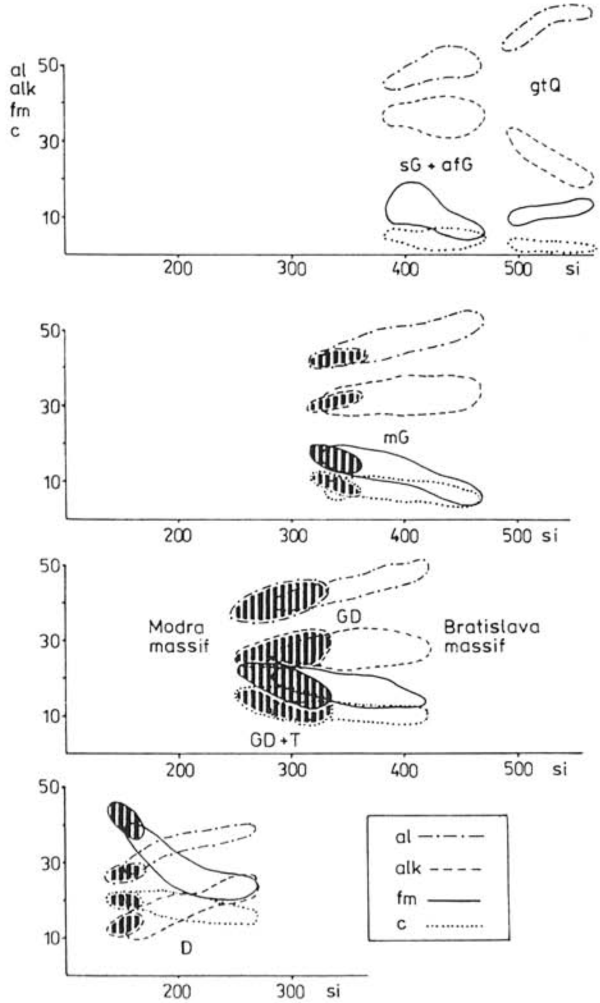


Fig. 4. Niggli's differentiation diagram for Malé Karpaty granitoids and diorites. Fields with hachure – the Modra massif. For abbreviations of rock names see Fig. 2.

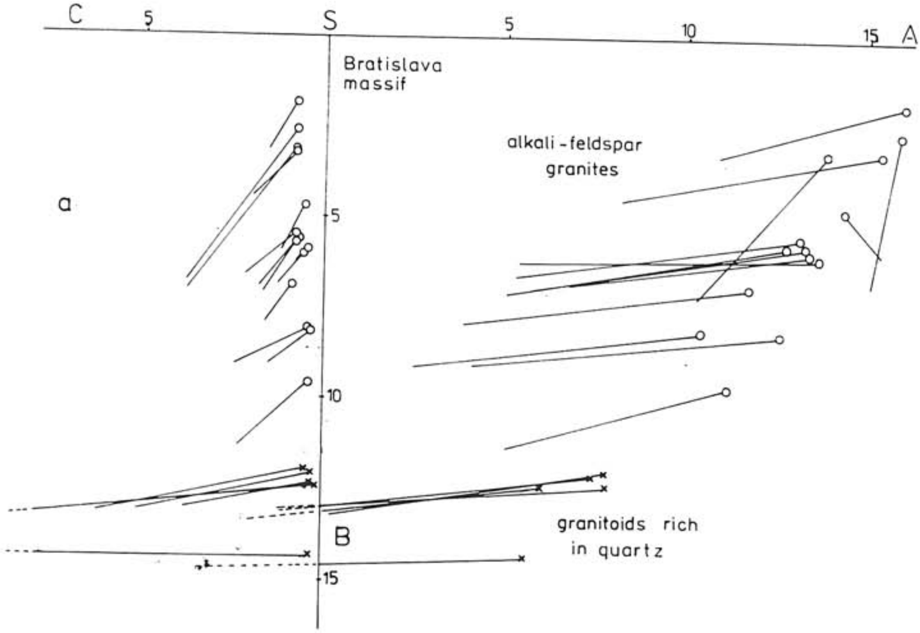


Fig. 5 a.

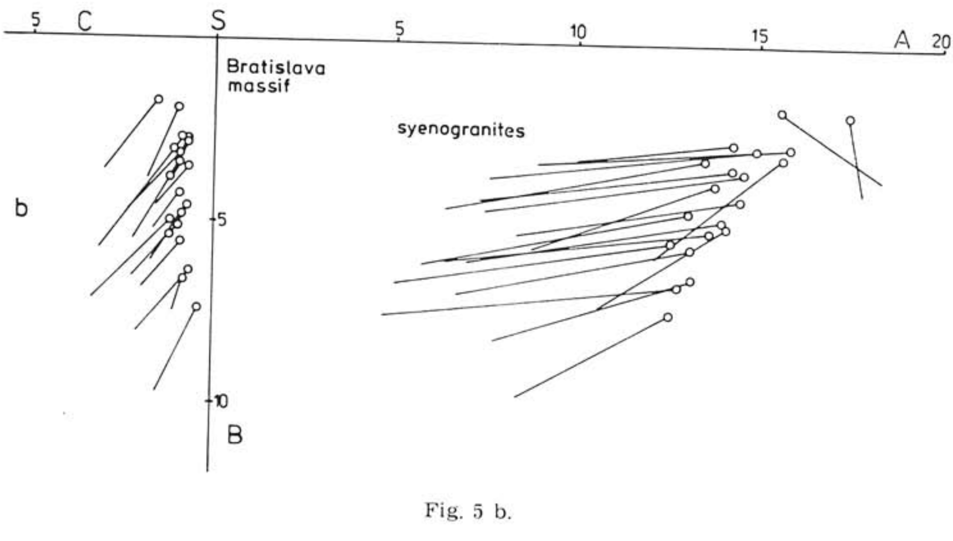


Fig. 5 b.

normative feldspars. The molar amount of alkalies in these feldspars is greater than CaO and $Na_2O \geq K_2O$.

The granitoids of the two massifs undoubtedly belong in V. A. Kutolin's (1964) field II: "granitoids of batholiths of the orogenic regions (Fig. 6 a, b, c, d). The projections of the Modra granitoids into the field of metaluminous rocks,

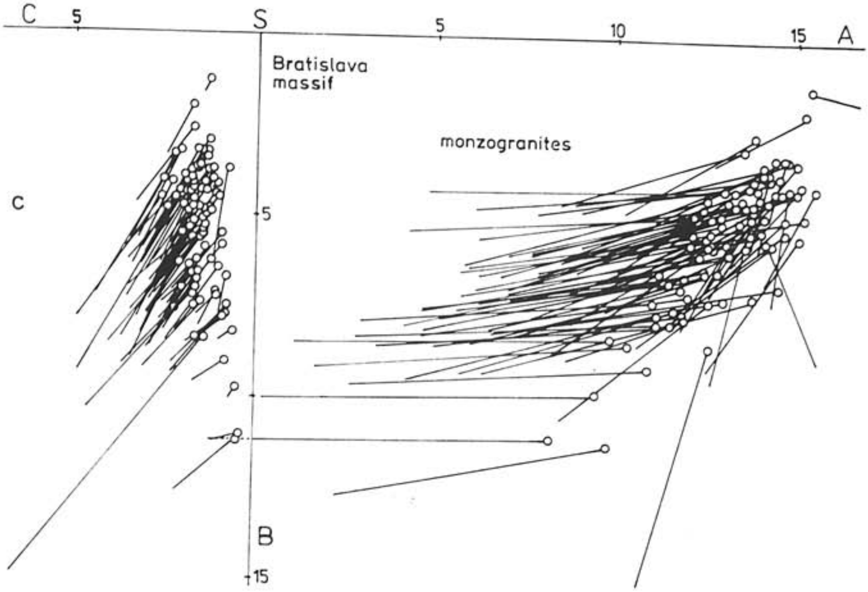

C
5
S
5
10
15
A
Bratislava
massif
monzogranites
c
5
B
15

Fig. 5 c.

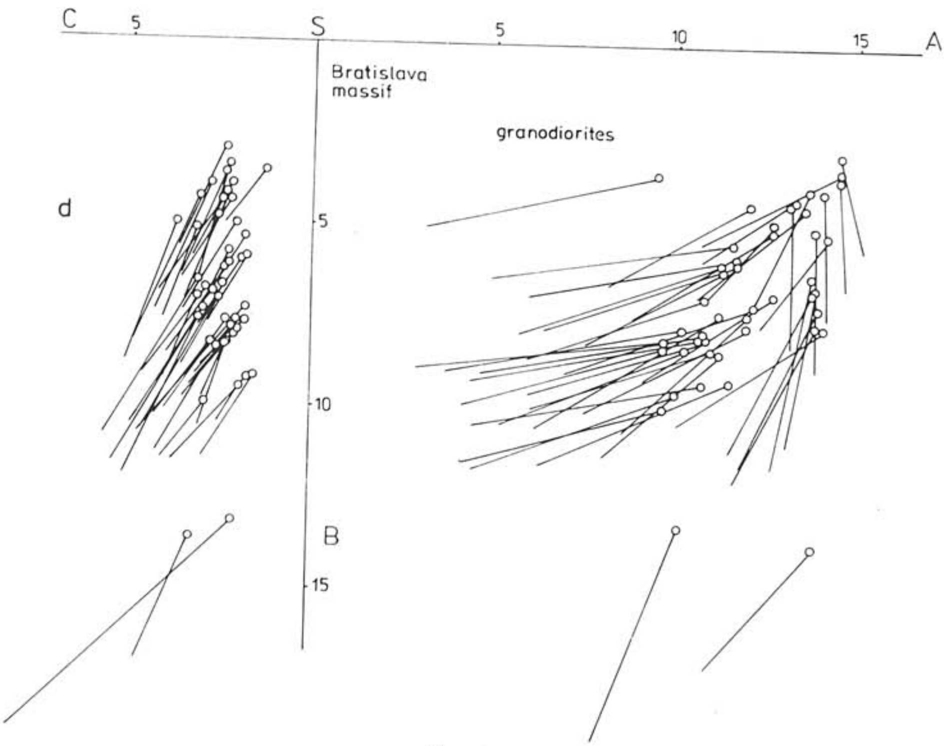

C
5
S
5
10
15
A
Bratislava
massif
granodiorites
d
5
10
B
15

Fig. 5 d.

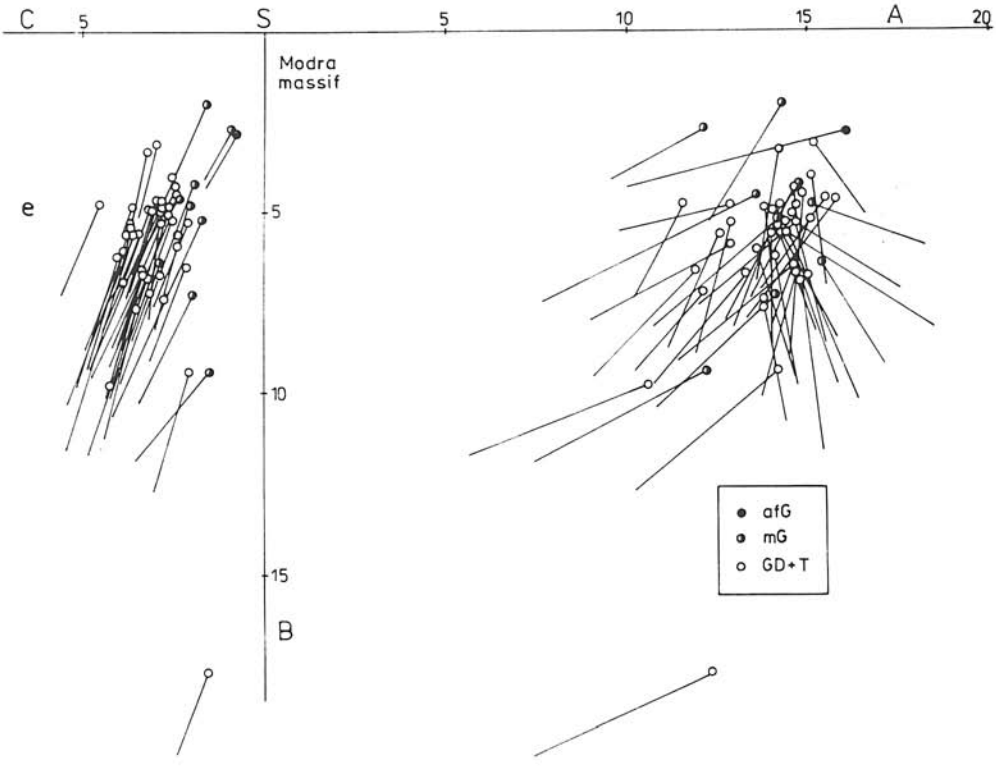


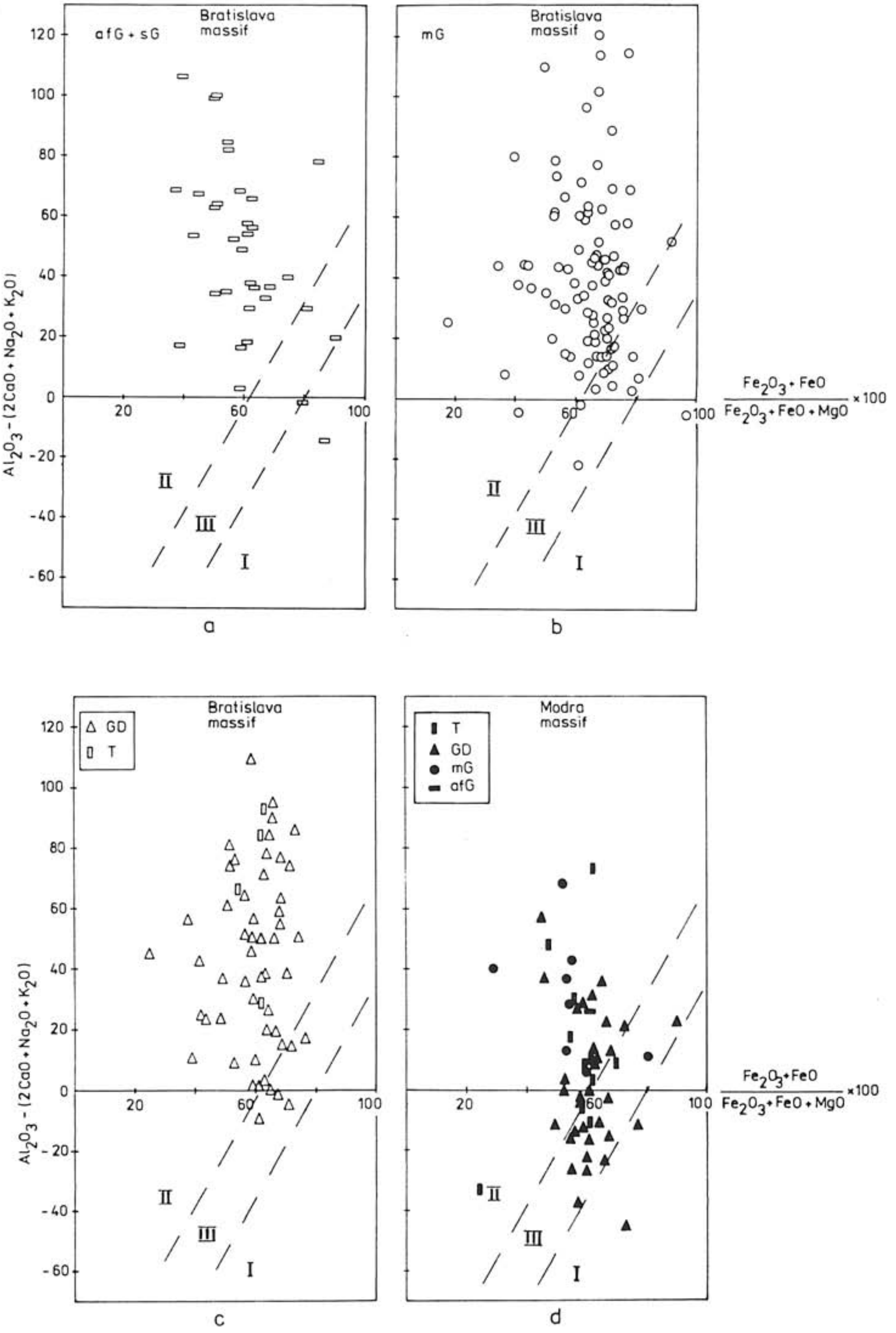
Fig. 5 a, b, c, d, e. Zavarickij's diagrams for different granitoid groups of the Bratislava (a, b, c, d) and Modra (e) massifs: afG — alkali-feldspar granite, mG — monzogranite, GD + T — granodiorite and tonalite.

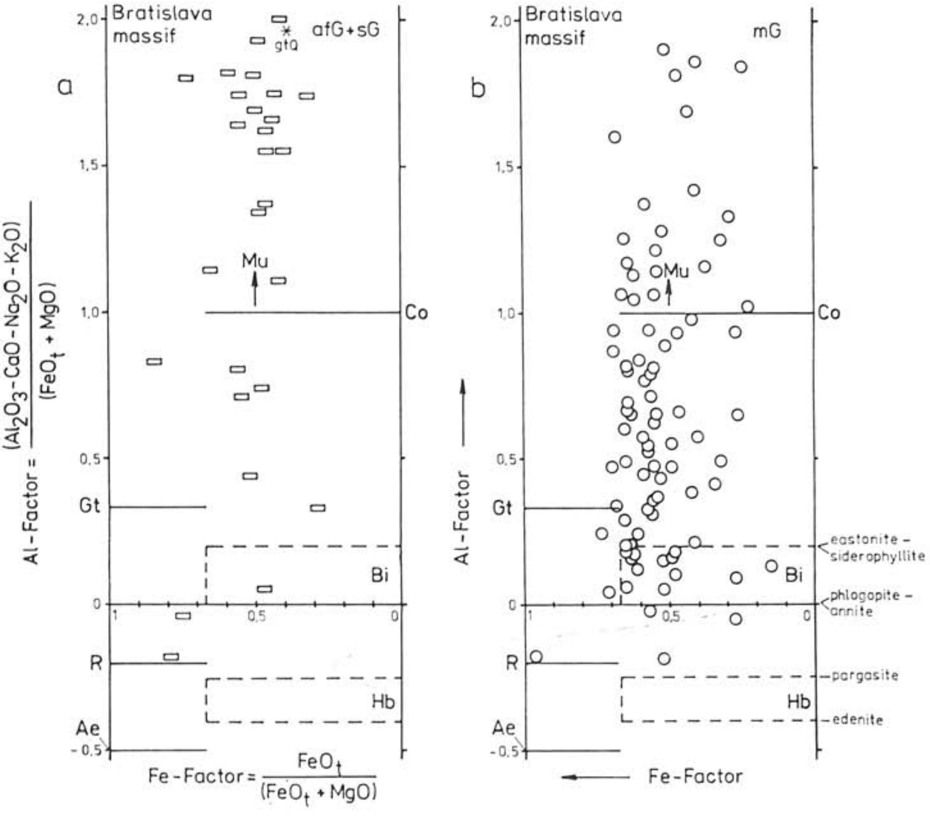
where $Al_2O_3 - (2\,CaO + Na_2O + K_2O) < 0$, i.e. in fields III and I, can be interpreted in terms of a somewhat different source material from that of the Bratislava granitoids. The value of the ratio of $(Fe_2O_3 + FeO) \times 100$ to $(Fe_2O_3 + FeO + MgO)$ varies about 60 for all granitoids studied. into in the monzogranites of the Bratislava massif within the range of 60—70. In the secondarily altered granites the Al-oversaturation exceeds 90, and the greisen-like quartz-rich granitoids are beyond the range of the diagram in this respect.

H. W. Nesbitt — J. J. Cramer (1981) have recently compiled a diagram, which resembles that of Kutolin and can be applied to the study of mineral equilibrium, mass balance, differentiation trends, and mixing of source materials of the magmatites (Fig. 7 a, b, c, d). In this modified "Thompson projection" with mineral background, the considerable scatter of the Al-factor clearly shows the two-mica character of the Bratislava granodiorites and monzogranites and the predominantly muscovitic character of syenogranites and alkali-feldspar granites (aplites, pegmatites and muscovite leucogranites). The high values of Al-factor cannot be ascribed to cordierite as it is absent from the Bratislava granitoids. A major amount of garnet occurs mainly in aplites and pegmatites. From the slightly lower average Fe-factir of granodiorites in relation to this factor in monzogranites it could be inferred that fractional crystallization of biotite contributed to the origin of these two varieties. The biotitic character of the Modra granitoids is well documented by their position near the composition field of biotite Fig. 7 d). The samples that are projected into the metaluminous region of the diagram, and according to the lever rule should also contain amphibole are actually lacking this mineral. The problem of biotite being the only mafic mineral in granitoids was discussed by R. N. Abbott, Jr. (1981); the case of the Modra granitoids can be, in our opinion, best explained by crystallization at increased pH_2O, which extends the range of primary crystallization of biotite into the metaluminous region of the AFM diagram ($A = Al_2O_3 - K_2O - Na_2O - CaO$, $F = FeO$, $M = MgO$). The position of diorites of both the massifs (Fig. 7 c, d) between the composition fields of biotite and amphibole well corresponds to their modal composition.

One of the processes leading to the generation of peraluminous granitoids is the fractional crystallization of amphibole from the metaluminous diopside-normative magmas (R. G. Cawthorn – P. A. Brown, 1976, 1978; R. N. Abbott, Jr., 1981). On the basis of the diagram: mesonormative amphibole or corundum vs. SiO_2 (Fig. 8), which is a modification of the diagram: CIPW diopside or corundum vs. SiO_2 (R. G. Cawthorn – P. A. Brown, 1976) we have arrived to the following views: Diorites are the only rock type under study that contains both the normative and modal amphibole in large amounts. The minor representation of diorites and other established characteristics (B. Cambel et al., 1981 a) exclude the generation of peraluminous granitoids (e. g. of the Bratislava massif) from the diorite magma in the manner, as suggested by R. G. Cawthorn – P. A. Brown (1976). Mesonormative amphibole is typical of some granodiorites and tonalites of the Modra massif, but modal amphibole is present only in accessory amounts (B. Cambel – J. Valach, 1956; M. Dyda, 1975; J. Veselský – J. Gbelský, 1978). The granitoids of the Modra massif are often peraluminous with 0 – 3 wt.% of normative corundum. Their differentiation trend is difficult to determine because of a small number of samples of tonalites and of granites with which the predominating granodiorites constitute essentially one field in the diagram. Moreover, some of the mesonormative monzogranites are petrographically in fact epimylonites of granodiorites. It is of importance that all granitoid groups of the Bratislava massif are characterized by an equal oversaturation with respect to aluminium, demonstrated by the contents of normative corundum of 0 – 5 wt.%. This indicates that the peraluminous character within the scope of the small but discrete differentiation trend of the Bratislava granitoids remained practically unchanged. Only the secondary alteration caused an increase in normative corundum content (C = 5 – 8 wt.%), and sporadically produced greisen-like quartz-rich granitoids (C = 8 – 10 wt.%). Although the fractional crystallization of amphibole is evidently a process that produces peraluminous

Fig. 6 a, b, c, d. The $Al_2O_3 - (2\,CaO + Na_2O + K_2O)$ vs. $(Fe_2O_3 + FeO) \times 100/(Fe_2O_3 + FeO + MgO)$ diagram, in which V. A. Kutolin (1964) distinguished three fields: I – granites, derivatives of basaltoid magma, II – granitoids of batholiths of the orogenic regions, III – field of uncertainty. Coefficients are calculated from atomic amounts. For abbrevations of rock names see Fig. 2.


Bratislava massif
afG + sG
Bratislava massif
mG
Bratislava massif
GD
T
Modra massif
T
GD
mG
afG
I
II
III
a
b
c
d
$Al_2O_3 - (2CaO + Na_2O + K_2O)$
$\frac{Fe_2O_3 + FeO}{Fe_2O_3 + FeO + MgO} \times 100$



granitoids in many CA-series of the world's occurrences, it is not appticable to the Malé Karpaty granitoids known at the present erosion level. Maybe, because the typical CA-series of granitoids actually does not exist in the region under study. As already hinted at by R. Hine et al. (1978), it is problematical to rank among granitoids of CA-series also those whose SiO_2 contents vary within a relatively small range of high values (e. g. granitoids of the Bratislava massif).

The conception of two contrasting granite types of B. W. Chappell – A. J. R. White (1974), included in his multicationic diagrams by H. De la Roche (1980) has also been applied to the study of the Malé Karpaty granitoids. The $Q_3B_3F_3$ diagram (Fig. 9) enables us to deduce the plausible source materials and characterize the differentiation trends and secondary alteration of the rocks. The Modra granodiorites – tonalites are of a biotitic character. It cannot yet be said with certainty whether the differentiation trend of the Modra massif coincides with the extension of its projection field in Fig. 9. However, a substantial contribution of the primary magmatites to the composition of the melt of the Modra granitoids is evident; this, together with other characteristics, makes it possible to range them chiefly to the I-type of B. W. Chappell – A. J. R. White (1974). The different position of the two-mica

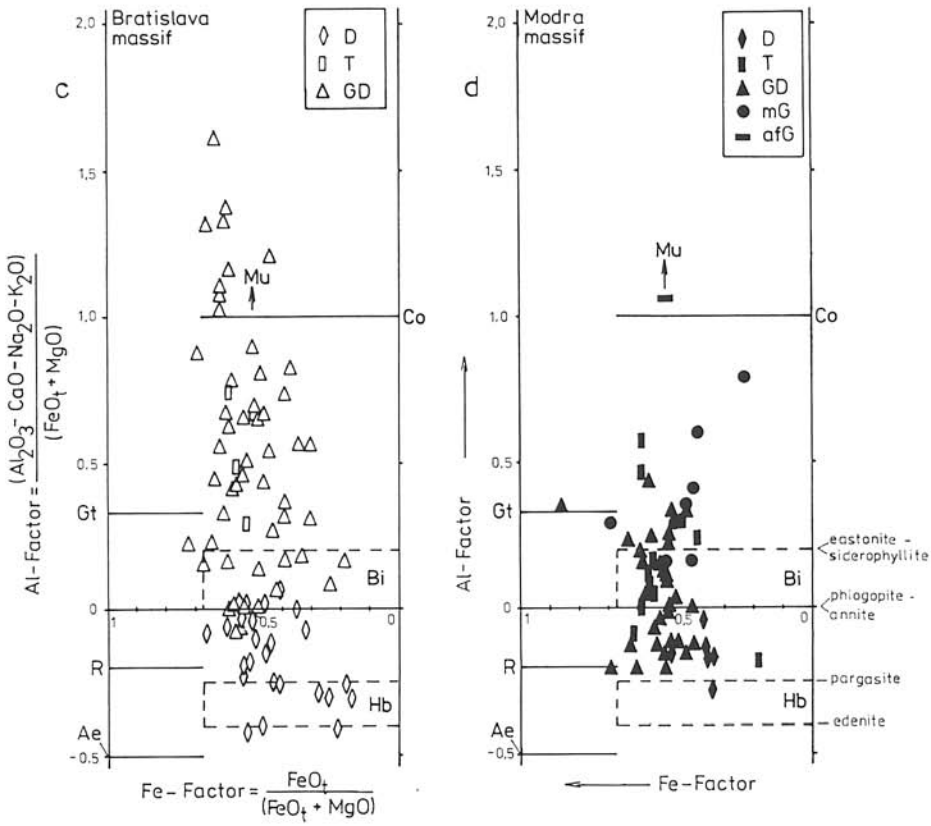


Fig. 7 a, b, c, d. "Thompson projection" (H. W. Nesbitt — J. J. Cramer, 1981) showing the whole-rock chemistry of the Malé Karpaty granitoids and diorites on the background of mafic minerals. Without correction of FeO_t for ilmenite and CaO for apatite. Four samples of quartz-rich granitoids, 8 samples of alkali-feldspar granite and syenogranite and 12 samples of monzogranite of the Bratislava massif that have Al-factor > 2 are not plotted. Factors are calculated from molar amounts. Mu — muscovite, Co — cordierite, Gt — garnet, Bi — biotite, Hb — amphibole (hornblende), R — riebeckite, Ae — aegirine. For abbreviations of rock names see Fig. 2.

Bratislava granitoids in the $Q_3B_3F_3$ diagram can be explained in terms of anatexis of a crustal source, predominatly of sedimentary nature (thus S-type). The differentiation trend is perpendicular to the extension of the projection fields of the individual rock groups of the Bratislava massif. It can also be assumed that the source rocks were of gneiss and metagreywacke character and the melts had left a residuum of R_3 and R_4 types from them at the site of their origin. The nature of the source rocks of the Modra and Bratislava massifs cannot be characterized in detail without a thorough study of their xenoliths and of the country rocks. Not even H. De la Roche (1980) recommends to use the $Q_3B_3F_3$ diagram for making direct petrological conclusions. The trend of the secondary hydrothermal alteration of the Bratislava granitoids did not reach the stage of the true greisens (point G).

Discussion and conclusions

The character of the source rocks of the Malé Karpaty granitoids is indicated by the criteria of B. W. Chappell – A. J. R. White (1974). However, the chemical criteria cannot be applied indiscriminately, because the rock need not have the Na_2O and K_2O contents equal to those given by the above authors for the S-type granitoids of the Berridale batholith in order to possess the molar ratio of Al_2O_3 to $(CaO + Na_2O + K_2O)$ above 1.1 (in further text only A/CNK ratio). The granitoids of the Bratislava massif, for example, with a predominant ratio A/CNK > 1.1 and a peraluminous mineral composition (muscovite, garnet) should be assigned according to Na_2O and K_2O contents to the I-type of B. W. Chappell – A. J. R. White (1974), which we cannot accept. R. Hine et al. (1978) have also pointed out that the Na_2O and K_2O contents are often a local feature of the granitoids and need not have a discrimination importance see G. K. Czamanske et al., 1981).

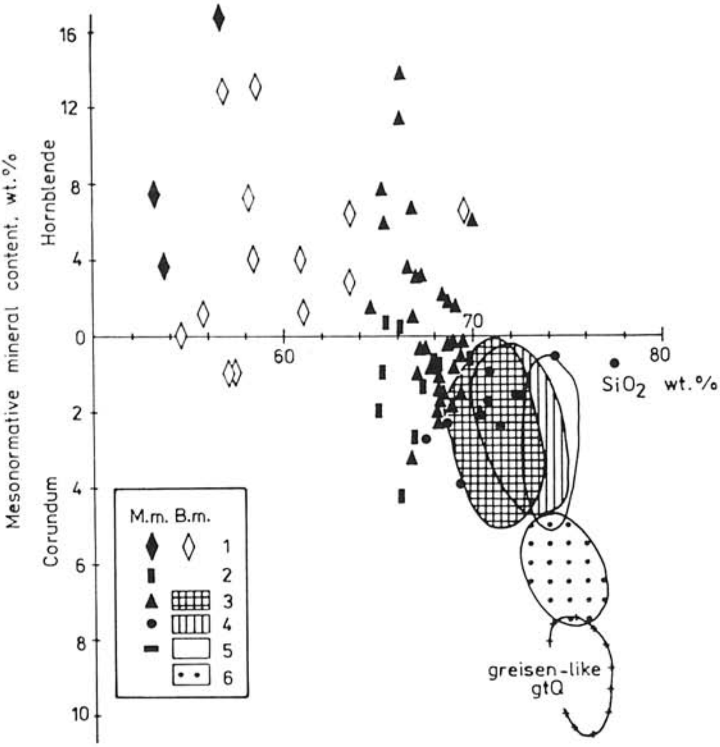
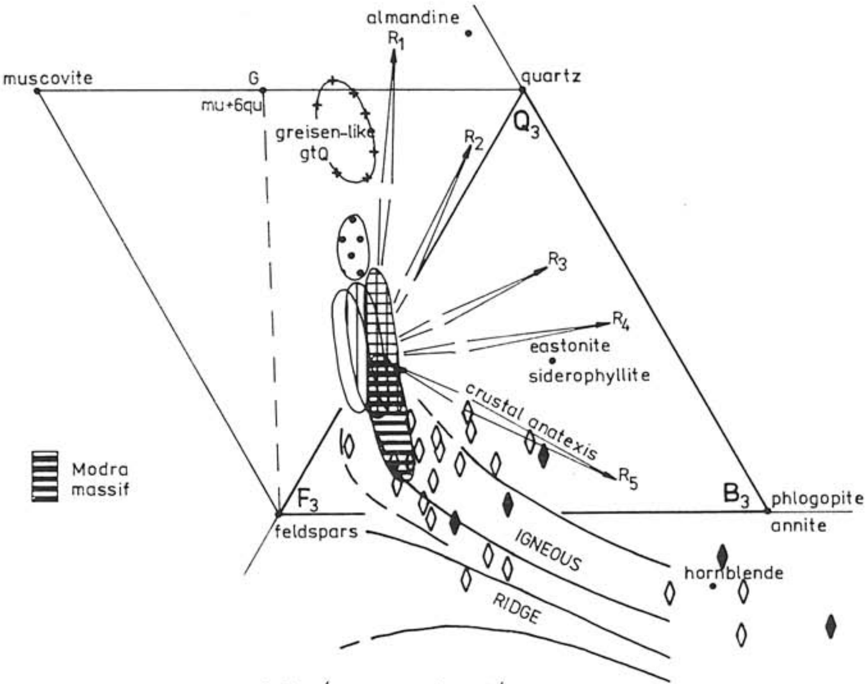


Fig. 8. Relationship between mesonormative corundum or amphibole and SiO_2, which is a modification of the CIPW corundum or diopside vs. SiO_2 diagram (R. G. Cawthorn – P. A. Brown, 1976). M. m. – Modra massif, B. m. – Bratislava massif. Labelling of rocks: 1 – diorite, 2 – tonalite, 3 – granodiorite, 4 – monzogranite, 5 – syenogranite + alkali-feldspar granite, 6 – sericitized rocks. The number of projection points of diorites is lower than in Fig. 7 c, d, because the mesonorm could not be calculated for some samples.



$$Q_3 = Si + 7\,Al/2 - 9\,Ca - 13\,(Na+K)/2$$
$$B_3 = -7\,Al/2 + 7\,Ca + 7\,(Na+K)/2 + 8\,(Mg+Fe+Ti)/3$$
$$F_3 = +\,Al + 3\,Ca + 4\,(Na+K) - 5\,(Mg+Fe+Ti)/3$$
$$\Sigma = Si + Al + Ca + (Na+K) + (Mg+Fe+Ti)$$

in milications

Fig. 9. Position of the Malé Karpaty granitoids and diorites in the multicationic diagram $Q_3B_3F_3$, after H. De la Roche (1980). R_1 to R_5 — different types of residues after melting of argillaceous shales, arkoses, gneisses and greywackes. For designation of fields of the Bratislava granitoids see Fig. 8, field with horizontal lining — Modra massif, diamond symbol — diorites.

The division of various granitoids into I- and S-types can also be impeded by that the A/CNK > 1.1 criterion and the content of CIPW-corundum > 1 are not strictly equivalent. In other words, there are granitoids that have A/CNK < < 1.1 but the content of corundum above 1, which makes them unclassifiable according to these criteria.

The SiO_2 contents are relatively high in the Bratislava granitoids, which is typical of the S-type, but according to the set of samples studied, the Modra massif does not show such a wide range of composition as would agree with the I-type character. On the other hand, the Modra granitoids have a high average Al_2O_3 content (Fig. 1 a), regarded by A. J. R. White et al. (1977) as distinctive of the I-type.

The most recent investigations (M. L. Coleman, 1979) have shown that the earlier applied analogy between S-type vs. I-type and the ilmenite series vs. magnetite series cannot be used unconditionally either. The granitoids of the Japanese magnetite series, for example, are considered to be of the I-type but those of the ilmenite series belong to both types, although prevalently to the I-type (G. K. Czamanske et al., 1981). Irrespective of this, the established antagonism between magnetite and ilmenite in the Malé Karpaty granitoids (J. Veselský – J. Gbelský, 1978) indicates a difference in the oxidation states of magmas from which the granitoids of the Modra and Bratislava massifs had crystallized.

Of the isotopic characterics that are applied to the distinction between two contrasting granitoid types, the first data on the initial $^{87}Sr/^{86}Sr$ ratio are available. The $\delta^{18}O$ and $\delta^{34}S$ values have not yet been obtained. G. P. Bagdasarjan et al. (1982) using the Rb/Sr method determined the age of the Bratislava granitoid massif as 347 ± 4 Ma with $(^{87}Sr/^{86}Sr)_0 = 0.7076 \pm 0.0013$, and the age of the Modra granitoids as 324 ± 18 Ma with $(^{87}Sr/^{86}Sr)_0 = 0.7075 \pm 0.00032$. G. P. Bagdasarjan et al. (l. c.) interpret the relatively coincident age and initial $^{87}Sr/^{86}Sr$ ratio of the two massifs as a manifestation of their time and genetic continuity. They assume that the source was probably common to both the massifs, and that the more basic character of the Modra granitoids may reflect the differences in the lithofacies of the volcano-sedimentary series, which was the source of the anatectic granitoid magma.

The initial $^{87}Sr/^{86}Sr$ ratios for the Malé Karpaty granitoids established by the above authors are at the very boundary between the ratios characteristic of the I- and S-types in the sense of B. W. Chappell – A. J. R. White (1974). The most plausible explanation of this fact is that the Malé Karpaty granitoids are a product of melting of a mixed source, as is also indicated by the contents of Li, Rb and Cs (B. Cambel et al., 1981 b). In this context it should be mentioned that according to W. S. Pitcher (1979) the Hercyno-type orogeny produces either S-type or mixed S- and I-types of granitoids with the initial $^{87}Sr/^{86}Sr$ ratio > 0.706.

Although the characteristic features of both the I- and S-type could have been produced in three to four ways (W. S. Pitcher, 1979; D. B. Clarke, 1981), we maintain that the peraluminous character of the Bratislava granitoids (Figs. 5, 6, 7, 8) is inherited from the source rocks and is not derived from the magmas of the diorites or Modra granitoids by fractional crystallization of amphibole. An appreciable increase in the oversaturation with respect to aluminium in the secondarily altered granitoids, particularly in the quartz-rich granitoids similar to greisens, with low Na_2O lends support to the opinion of W. C. Luth et al. (1964) that the peraluminous character may be caused (in our case only increased) by the removal of alkalies.

The discussed petrochemical differences between the granitoids of the Bratislava massif and those of the Modra massif are observable in almost all graphs. Only the commonly used AFM diagram (Fig. 2 a, b) is the least informative in this respect. B. Cambel (1980) was the first who questioned the close connection of the granitoids of the Bratislava massif with those of the Modra massif. On the basis of the geology, petrography and mineral composition of the two massifs and of the petrochemical data here presented we assume that the two granitoid massifs crystallized from two separate portions of magma. In case they had a source in common, the more basic character of the Modra massif can be explained in terms proposed by B. Cambel et al. (1981 b) and G. P. Bagdasarjan et al. (1982), or by higher P–T conditions of melting of the source material in relation to the Bratislava massif, consistently with the hypotheses of G. C. Brown – W. S. Fyfe (1970) and J. D. Clemens – V. J. Wall (1981).

In conclusion we point out that we kept intentionally in the examined set of samples those showing subsolidus alterations in order to establish the trends of these conversions in the petrochemical diagrams. We are well aware that all information obtained by petrochemical analyses should be substantiated by a detailed petrographic-mineralogical investigation and by the study of trace-element contents, which is the object of present research.

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