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ALKALIC METALS IN GRANODIORITES OF THE MODRA MASSIF ALTERED BY ALKALIC METASOMATISM (MALÉ KARPATY Mts.)

(Figs. 10, Tabs. 5)



Abstract: In the presented work on the basis of representation of alkalic elements and elements of alkalic earths in granodiorites of Modra type, in vein aplites and pegmatites or in pegmatoid granodiorites from the area of mount Dolínovský vrch near the village Harmónia (Modra-Harmónia) the authors trace correlation relations of the individual alkalic elements and elements of alkalic earths mutually, or their correlations with alkalic elements. These investigations confirmed the genetic dependence of aplite rocks on rocks of the Modra granitoids as well as the presumption of genetic dependence of pegmatoid rocks on derivatives altered by K⁻ metasomatism. The determined concentrations of alkalic elements in the studied rocks are in agreement with the content limits of Variscan granitoid rocks from the Malé Karpaty Mts. and West Carpathian regions. Concerned are mainly relatively little contents of Rb and Cs and prevalence of Na over K in granodiorites and aplite granitoids.

Резюме: В настоящей работе авторы на основе замещения щелочных элементов и элементов щелочных земель в гранодиоритах модранского типа, в жильных аплитах и пегматитах, или в пегматоидных гранодиоритах из области Долинковской горы у с. Гармония (Модра-Гармония) изучают корреляционные отношения отдельных щелочных элементов и элементов щелочных земель или их корреляции с щелочными элементами. Эти исследования подтвердили генетическую зависимость аплитовидных пород от пород модранских гранитоидов, а также предположение генетической зависимости пегматоидных пород от дериватов измененных К-метасоматизмом. Определенные концентрации щелочных элементов в исследованных породах в соответствии с лимитами содержания варисийских гранитоидных пород из района Малых и Западных Карпат. Это, главным образом, низкие содержания Rb и Cs, и преимущество Na перед K в гранодиоритах и аплитовидных гранитоидах.

In the geological bulletin "Geologica Carpathica", (33, 6, p. 697—728 an article was published by the authors Camel, Veselský and Miklós (1982 a), which solved the problem of alkalic metasomatism of granitoid rocks of the Modra granitoid massif. The contents of Li, Rb, Cs, however, were not published and correlation relations of alkalic elements mutually as well as their ratios to further elements mentioned in the tables were not studied. It is necessary to call attention to the fact that this article completes in a suitable way the data already published in numerous works, which refer to granitoids as well as also their minerals on the basis of contents of alkalic elements: Camel—Martiny—Pitoňák (1983); Camel—Mickievič—Veselský—Vilínovič (1981 a); Camel—Veselský—Vilínovič (1982 b); Cam-

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bel—Vilinovičová (1981 b); Dávidová (1970); Dávidová—Dávid (1981). In the presented article we publish evaluation of alkalic elements in unaltered granitoids as well as altered by metasomatism to a various degree. In addition, the authors have at disposal the contents of alkalic elements of leucocratic vein differentiates of granitoids. Essentially there are the same samples of rocks, which were studied in the above cited article Cambel et al. (1982 a). Therefore the reader can obtain further necessary information about these samples only after studying of the quoted article from the year 1982 a, in which are the data of silicate and planimetric analyses, classification of studied rocks and their petrometric valuation and contents of trace elements besides Li, Rb and Cs. Here also the interpretation of conditions of metasomatism, dependence of contents of macro-microelements on the intensity of rock alteration etc. were established.

In the presented work we use the same division of rocks and the same legend in graphs for individual types and groups of rocks so that the contribution clearing up the role of alkalic elements (Li, Na, K, Rb, Cs) in primary granodiorites and altered rocks could be considered as complement to the article from the year 1982 a.

Concerned are potassium metasomatites of the Modra massif, which are found in the Malé Karpaty Mts. in the area of Mt. Dolinkovský vrch near the town of Modra-Harmónia. At the territory of the villages Pila and Častá not far from the ruins of the forester's house Kobylé altered granodiorites albized even into albitites and haematite-albitites are found (Cambel—Valach, 1956).

In the area of Mt. Dolinkovský vrch, where K-metasomatism of granodiorites was manifested, are also leucocratic differentiates of granodiorites, aplites with prevalence of Na- over K-feldspars as well as veiny granitoid rocks, mainly pegmatites and pegmatitoid granitoids with prevalence of K-feldspars are found. The contents of alkalic elements in these rocks are mutually correlated.

The up to present investigations have confirmed that K-metasomatism in the area of Mt. Dolinkovský vrch represents a highthermal process connected with the last phase of crystallization of granitoid magma, mainly of pegmatitoid character. The albitization in the area of the forester's house Kobylé ruin is considered as a product of low-thermal to hydrothermal alteration.

From Figs. 1 to 10 is possible to trace the histograms resp. correlation relations of the contents of the pursued elements, the values or relations of values of which are mentioned in Tables 1 to 5 (K, Na, Mg in specif. grav. ‰, Li, Rb, Cs, Sr and Ba in gt^{-1}).

From histograms (Fig. 1) is clearly to be seen, which elements in which intervals are mostly wide-spread. The highest contents of Li are in unaltered granodiorites and partly also in aplitoid rocks with prevalence of sodium over potassium and minimum contents of Li are in Na-metasomatites (albitites). Most cesium contain potassium pegmatitoid rocks, most rubidium is in K-metasomatites. The histograms of other microelements are mentioned in the work of Cambel—Veselský—Mikláš (1982 a).

It is visible from the correlation graphs (Figs. 2–9) that sodium leucocratic vein rocks have a dispersion mainly of trace alkalic elements similar as at the fundamental types of rocks of the Modra granodiorite. Albitites occur in corre-

Table 1

Table of contents of alkalic elements Sr, Ba and Mg and some ratios in unaltered fundamental rock types of the Modra granitoid massif (K, Na, Mg — specif. grav. $\%$, Li, Rb, Cs, Sr, Ba — gt^{-1})

Sample No.	K	Na	Mg	Li	Rb	Cs	Sr	Ba	K/Rb	Ba/Rb	Rb/Sr
M — 3	2.91	3.62	0.25	43.2	150	—	135	830	194.0	5.5	1.11
M — 7	2.52	3.56	0.43	24.6	78	—	425	1150	323.1	14.7	0.18
M — 18	2.19	3.85	0.95	31	69	3.1	310	1320	317.4	19.1	0.22
M — 19	2.52	3.86	0.92	31.5	55	1.3	285	890	458.2	16.1	0.19
M — 20	2.16	4.05	1.08	54	74	2.0	196	710	291.9	9.6	0.38
R — 18	2.55	4.47	0.28	32.5	73	1.6	178	1820	349.3	24.9	0.41

Localization of samples: M — 3 biotite granodiorite, at the margin of vineyard, SE slope of Mt. Dolinkovský vrch, elev. point 392, village Modra-Harmónia; M — 7 underlying granodiorite of transversal vein in limestones of the Harmónia Group, margin of vineyard, SE of elev. p. 392, Mt. Dolinkovský vrch, village Modra-Harmónia; M — 18 granodiorite, medium-grained, weakly albitized, Pailanská dolina-valley, to W of the forester's house Kobylé, NW of elev. p., village Pila; M — 19; 23/63/JV biotite tonalite to leucotonalite, NE of the town Modra, abandoned quarry in the valley of the Žliabok brook, below elev. p. 477.7 m 292°/800 m of the village Harmónia; M — 20; 25/63/JV biotite tonalite, middle part of the Veľký lom quarry at the N-slope not far from the way to the settlement Piesky, village Modra-Harmónia; R — 18 fundamental Modra type of granodiorite, 8m in the southern arm of the groove, Mt. Dolinkovský vrch, village Modra-Harmónia.

Table 2

Aplittoid vein derivatives of Modra granodiorites with prevalence of sodium over potassium, area of Mt. Dolinkovský vrch, Modra-Harmónia

Sample No.	K	Na	Mg	Li	Rb	Cs	Sr	Ba	K Rb	Ba Rb	Rb Sr
M — 1	4.05	4.01	0.07	2.9	78	—	158	2510	519.2	32.2	0.49
M — 2	0.66	4.45	0.39	5.3	22	2.5	433	620	300.0	28.2	0.05
M — 6	3.03	3.52	0.27	50.2	148	1.3	140	760	206.8	5.1	1.06
M — 8	1.12	4.48	0.27	28.5	114	3.1	79	460	98.3	4.0	1.44
M — 12	1.69	3.98	0.45	8.2	55	1.9	450	830	307.3	15.1	0.12
M — 17	3.20	4.45	0.19	12.5	95	2.8	103	955	336.8	10.1	0.92
R — 7	3.46	3.89	0.34	32	83	2.0	123	710	415.9	8.5	0.67

Localization of samples: M — 1 aplite vein granitoid passing through limestones of the Harmónia Group, SE of elev. p. 392 of the Mt. Dolinkovský vrch, Modra-Harmónia; M — 2 vein granitoid rock at contact with limestones of the Harmónia Group, SE of the elev. p. 392 Mt. Dolinkovský vrch, village Modra-Harmónia; M — 6 aplittoid granitoid transversal vein in limestones of the Harmónia Group in SE of the locality of lime-silicate-hornstones, margin of vineyard SE of the elev. p. 392 Mt. Dolinkovský vrch, village Modra-Harmónia; M — 12 vein leucocratic granitoid rock with amphiboles, locality of lime-silicate-hornstones, SE of the elev. p. 392 Mt. Dolinkovský vrch, village Modra-Harmónia; M — 17 aplittoid granodiorites, transversal vein in limestones of the Harmónia Group, limestone quarry S of the Mt. Dolinkovský vrch, village Modra-Harmónia; R — 7 aplittoid mica-free granodiorite, 81 m in NE — arm of the groove dug on the ridge of the Mt. Dolinkovský vrch elev. p. 392, village Modra-Harmónia.

Table 3

Vein pegmatitoid granitoid rocks to pegmatites with prevalence of potassium over sodium, region Mt. Dolinkovský vrch, Modra-Harmónia

Sample No.	K	Na	Mg	Li	Rb	Cs	Sr	Ba	K/Rb	Ba/Rb	Rb/Sr
M - 4	4.73	3.31	0.06	2.1	50	1.3	243	1200	946.0	24.0	0.21
M - 5	3.99	3.56	0.31	16.5	117	1.4	380	2750	341.0	23.5	0.31
M - 9	5.58	3.68	0.48	4.0	137	5.6	373	2390	407.3	17.2	0.37
R - 21	4.99	2.98	0.20	14.5	53	2.5	108	2880	941.5	54.3	0.49
R - 24	5.23	1.87	0.25	8.5	106	1.3	105	3800	493.4	35.8	1.01
R - 27	4.88	2.93	0.01	5.5	92	4.4	70	1700	530.4	18.5	1.31
R - 39	5.72	1.94	0.51	5.0	80	4.4	80	1740	715.0	21.8	1.00

Localization of samples: M - 4 aplitoid part of the pegmatite vein with amphiboles breaking through limestones of the Harmónia Group, SE of the slope of the Mt. Dolinkovský vrch, margin of the vineyard, locality of lime-silicate-hornstones, village Modra-Harmónia; M - 5 leucocratic chamber of muscovite-biotitic granodiorite in the subjacent granodiorite, locality of lime-silicate-hornstones, elev. p. 392 Mt. Dolinkovský vrch, village Modra-Harmónia; M - 9 leucocratic vein granodiorite from the contact with erlan, at the border of the forest and vineyards, locality of lime-silicate-hornstones, SE of the elev. p. 392 Mt. Dolinkovský vrch, village Modra-Harmónia; R - 21 pegmatitoid granitoid rock, at the groove, ridge of the Mt. Dolinkovský vrch elev. p. 392, village Modra-Harmónia; R - 24 pegmatitoid granitoid rock at the groove dug at the ridge of the Mt. Dolinkovský vrch elev. p. 392, village Modra-Harmónia; R - 37 pegmatitoid granitoid rocks, at the ridge on dug groove elev. p. 392 Mt. Dolinkovský vrch, village Modra-Harmónia; R - 39 pegmatitoid granitoid rocks at the ridge from dug groove elev. p. 392 Mt. Dolinkovský vrch, village Modra-Harmónia.

Table 4

Granitoids metasomatically altered by K-metasomatism in three degrees of alteration, region of Mt. Dolinkovský vrch, Modra-Harmónia

Sample No.	K	Na	Mg	Li	Rb	Cs	Sr	Ba	K/Rb	Ba/Rb	Rb/Sr
M — 11	3.45	4.45	0.15	22.1	145	1.9	153	510	237.9	3.5	0.95
M — 16	4.98	3.41	0.78	11.6	120	1.3	450	1590	415.0	13.3	0.27
R — 13	5.28	3.07	0.25	17.5	98	1.6	128	3500	538.8	35.7	0.77
R — 23	6.78	3.03	0.32	16.0	144	3.8	239	4100	470.8	28.5	0.60
R — 29	6.67	1.45	0.34	10.0	132	3.1	319	4000	505.3	30.3	0.41
R — 13	8.34	2.72	0.53	7.4	198	3.1	480	2340	421.2	11.8	0.41
R — 23	7.41	3.16	0.60	12.1	167	2.5	623	1740	443.7	10.4	0.27
R — 29	8.20	2.71	0.67	10.0	201	1.3	488	6300	408.0	31.3	0.41
R — 32	7.82	3.42	0.58	15.5	128	2.8	263	4100	610.9	32.0	0.49

Localization of samples: M — 11 granodiorite metasomatically altered (degree 1), at the margin of the forest and vineyards, SE of the elev. p. 392 Dolinkovský vrch, village Modra-Harmónia; M — 16 granodiorite metasomatically altered (degree 1), the ridge of the hill, NE of the elev. p. 392 Mt. Dolinkovský vrch, village Harmónia; R — 13 granodiorite metasomatically altered (degree 1), 76 m in the northern arm of the groove dug at the ridge, elev. p. 392 Mt. Dolinkovský vrch, village Harmónia; R — 23 granodiorite metasomatically altered (degree 2), from the groove at the ridge of the hill, elev. p. 392 Mt. Dolinkovský vrch, village Harmónia; R — 29 granodiorite metasomatically altered (degree 2), ridge of the hill, elev. p. 392 Mt. Dolinkovský vrch, village Harmónia; M — 13 granodiorite metasomatically altered (degree 3), ridge of the hill, NE of the elev. p. 392 Mt. Dolinkovský vrch, village Modra-Harmónia; M — 14 granodiorite metasomatically altered (degree 3), at the same place; M — 15 granodiorite metasomatically altered (degree 3), at the same place; R — 32 granodiorite metasomatically altered (degree 3), at the same place.

Table 5

Granitoids altered by Na-metasomatism W of the village Píla and to the S of the ruin "Kobylé"

Sample No.	K	Na	Mg	Li	Rb	Cs	Sr	Ba	K/Rb	Ba/Rb	Rb/Sr
M — 21	2.08	6.71	0.15	9.5	61	1.9	141	540	341.0	8.9	0.43
M — 22	1.81	6.86	0.20	9.0	46	1.9	143	680	393.5	14.8	0.32
M — 23	1.91	6.26	0.27	13.5	41	3.9	120	630	465.9	15.4	0.34

Localization of samples: M — 21 granodiorite metasomatically altered in to albite, hill-side of the Pailanská dolina valley, S of the ruin of forester's house "Kobylé", to the W of the village Píla; M — 22 granodiorite metasomatically altered, at the same place; M — 23 granodiorite metasomatically altered, at the same place.

lation graphs with little dispersion in the field of the fundamental Modra granodiorite and aplittoid rocks. It is to be seen from the dependence of contents Sr — Ba (Fig. 2), Rb — K/Rb (Fig. 3) and Rb — K (Fig. 5). Independently, outside this field the fields of albitites are found in correlation graphs Na — K (Fig. 4), Rb — Ba (Fig. 6) and Rb — Sr (Fig. 7).

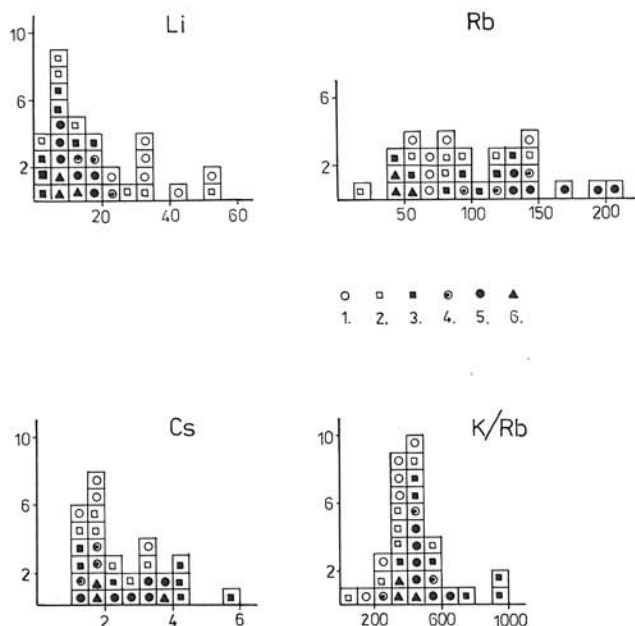


Fig. 1. Histogram of Li, Rb, Cs contents in gt^{-1} (in ppm) and K/Rb ratio in fundamental and unaltered vein types of rocks and in rocks altered by metasomatism. *Explanations:* 1 — fundamental types of granodiorites of the Modra granitoid massif, unaltered by metasomatism; 2 — aplittoid vein derivatives with prevalence of sodium over potassium; 3 — vein pegmatitoid granitoid rocks to pegmatites with prevalence of potassium over sodium; 4 — granodiorites metasomatically altered by K-metasomatism in the 1-st grade of alteration; 5 — granodiorites metasomatically altered by K-metasomatism in the 2nd and 3rd grade of alteration; 6 — granodiorites altered by Na metasomatism.

The distribution of alkalic elements as well as also the elements Sr and Ba in pegmatitoid granitoids and pegmatites with prevalence of potassium over sodium records the highest dispersion. It is mainly to be seen from the correlation graphs Sr — Ba (Fig. 2), Rb — Ba (Fig. 6). But sometimes the pegmatites form a common field with K-metasomatites, for example in Rb — Sr (Fig. 7), or another time the fields of K-metasomatites and K-pegmatites are more or less independent e. g. Rb — K/Rb (Fig. 3), Na — K (Fig. 4) and Rb — K (Fig. 5).

It is visible from the graph of Li — Mg dependence (Fig. 8) that the fundamental granodiorites and a part of aplitoid Na-types have the highest level of Li content, on the contrary to K-pegmatites and K-metasomatites, which have lower Li contents. A direct dependence of Li on Mg is not obvious.

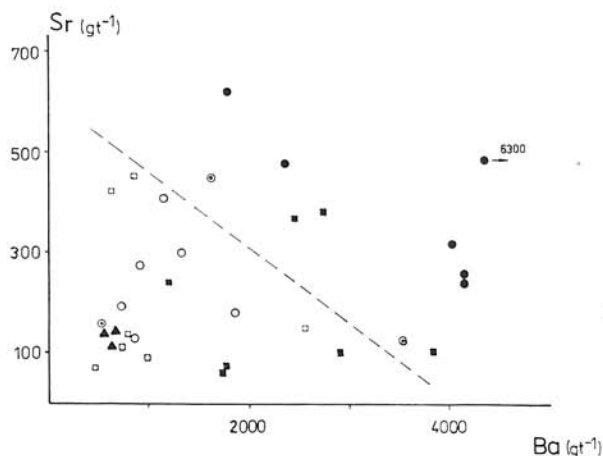


Fig. 2. Graph of Sr — Ba dependence. The interrupted line delimits the levels of maximum occurrence of K-metasomatites and partly also the K-pegmatites from other types of rocks with lower content of elements (Explanations see Fig. 1).

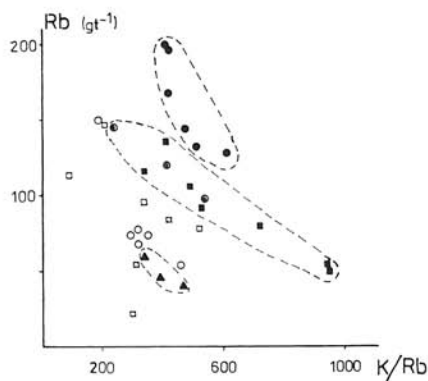


Fig. 3. Graph of Rb — K/Rb dependence. (Explanations in Fig. 1).

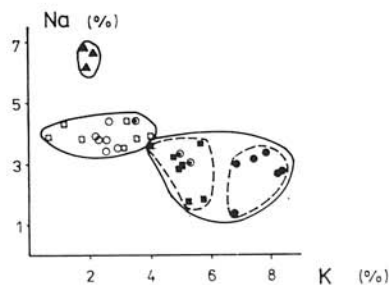


Fig. 4. Graph of Na — K dependence. (Explanations in Fig. 1).

The graph of Cs — K dependence (Fig. 9) indicates that the fundamental granodiorites and Na-aplitoid types have lower Cs contents, but a greater part of K-pegmatites and K-metasomatites have a similar level of Cs content independently on the K content.

From some graphs at potassium metasomatites positive a correlation of elements is recognizable. They are graphs of Rb — K (Fig. 5) and Rb — Sr

(Fig. 7). Negative correlation is in the graphs Sr — Ba (Fig. 2), weak at Rb — K/Rb (Fig. 3) and Na — K (Fig. 4). In fundamental metasomatically unaltered granodiorites and sodium aplite vein rocks is a negative correlation in the graphs of Rb — Sr (Fig. 7), whilst the K-metasomatites and K-pegmatites have a positive correlation.

Fig. 5. Graph of Rb — K dependence. (The dashed fields are partial fields of a larger common area with points of metasomatites and K-pegmatites). (Explanations in Fig. 1).

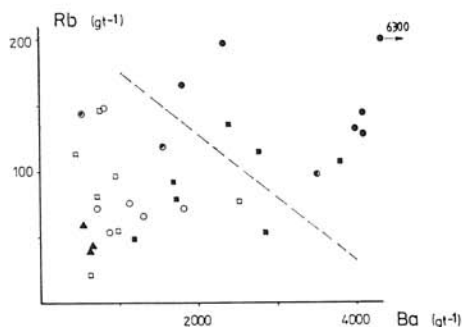
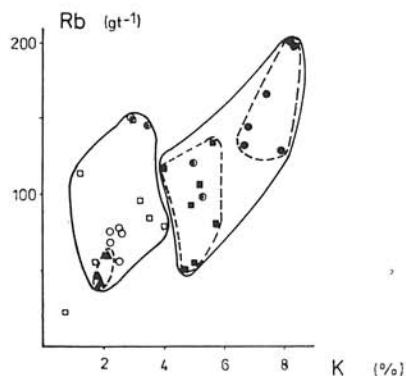


Fig. 6. Graph of Rb — Ba dependence. (The interrupted line delimits the levels of maximum occurrence of K-metasomatites and partly also K-pegmatites from further types of rocks with lower content of elements). (Explanations in Fig. 1).

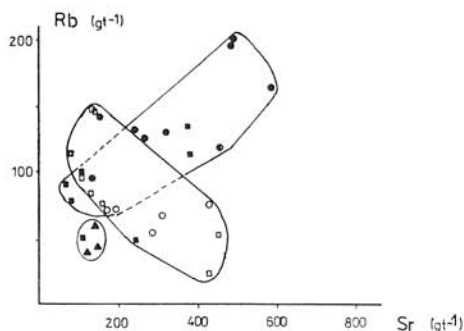


Fig. 7. Graph of Rb — Sr dependence. (The field of K-metasomatites and K-pegmatites has a positive trend, however, of aplites and fundamental types of granodiorite a negative trend). (Explanations in Fig. 1).

According to the classification of Shand (1927) the rocks studied in the work (Fig. 10) were divided into two groups: peraluminous and metaluminous. Metasomatites prevailingly belong to the metaluminous group. We ask to consider Fig. 10 as correct when compared with Fig. 15 b in the work by Campbell et al. (1982 a) into which it came by mistake.

On the basis of the analytical-geochemical and petrographical study as well as statistical evaluation of quantitative representation of the elements pursued in the investigation rocks the more or less distinctly known correlation are confirmed, which result from the regularities of isomorphous replacement of

elements. Further is confirmed that sodium vein apliteoid granodiorites and unaltered granodiorites of the Modra massif have as to the content of alkalis and elements Sr, Ba a similar geochemical picture, from what their mutual geochemical linking can be explained. On the other hand, pegmatitoid vein

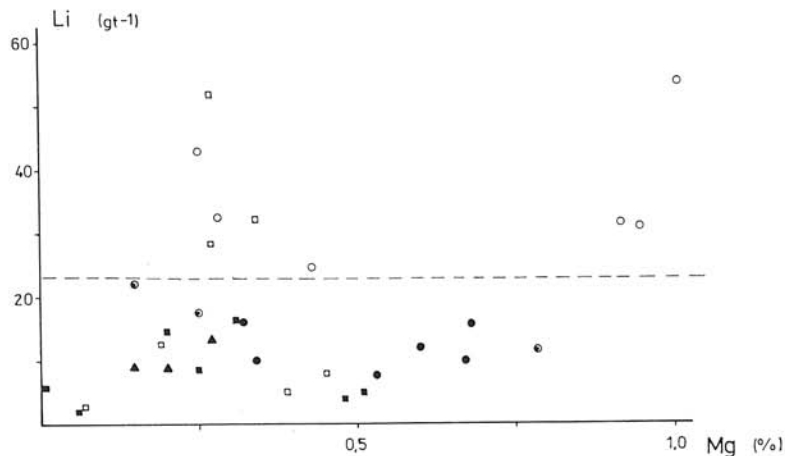


Fig. 8. Graph of Li — Mg dependence. (The interrupted line delimits the levels of maximum content of Li in the fundamental types of granodiorite and partly also of aplites in contrast to other types of rocks with lower content of Li). (Explanations in Fig. 1.).

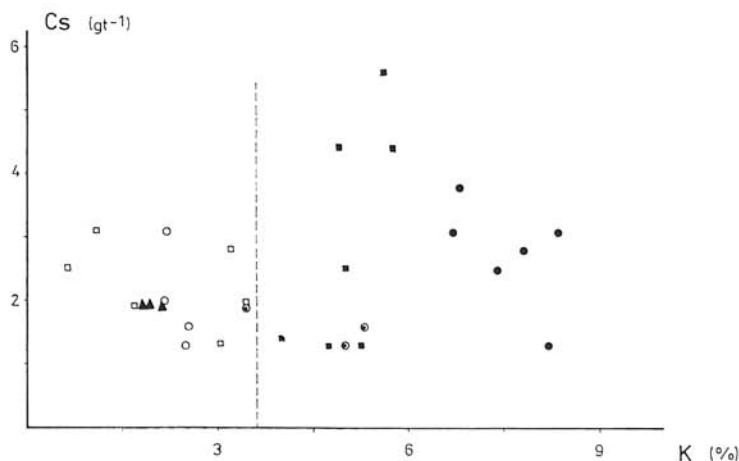


Fig. 9. Graph of Cs — K dependence. (The interrupted line delimits the levels of Cs content in dependence on K, which is higher in K-metasomatites and K-pegmatites in contrast to other types of rocks). (Explanations in Fig. 1.).

granitoids and pegmatites with prevalence of potassium over sodium on the basis of distribution of alkalic elements show analogous dependence as K-metasomatites, confirming the already expressed opinion, that K-metasomatism is a process bound to the high-thermal phase, connected with the pegmatite process.

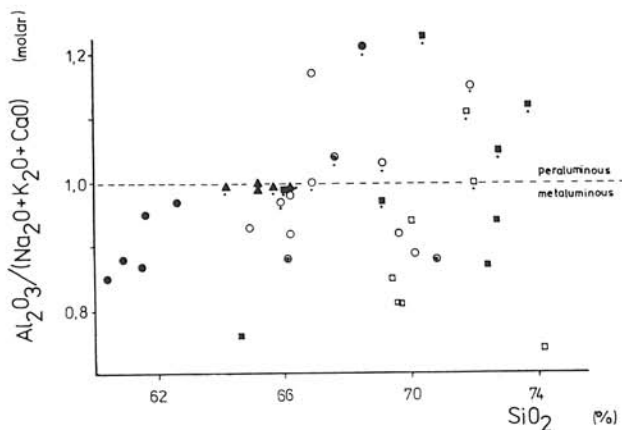


Fig. 10. The classification graph of rocks according to Shand (1927).

Note: We call attention that this graph is right to the contrary to the analogous graph in the work of Cambel et al. (1982 a), which came into the work by mistake. The point under the sign of rock expresses the presence of normative corundum according to calculation of CIPW. (Explanations in Fig. 1.).

The established concentrations of alkalic elements in all the above mentioned rocks fall into the content limits of Variscan granitoid rocks in the Malé Karpaty and West Carpathian region (Cambel et al. 1981 a, 1983). There are relatively little contents of Rb and Cs and prevalence of Na over K in granodiorites and aplittoid granodiorites.

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REFERENCES

- CAMBEL, B. — MARTINY, E. — PITOŇÁK, P., 1983: Alkalies in the granitoids of the West Carpathian. *Geol. Zbor. Geol. carpath.* (Bratislava), 34, 1, pp. 15—44.
- CAMBEL, B. — MICKIEVIČ, B. I. — VESELSKÝ, J. — VILINOVIC, V., 1981 a: Alkalies in the granitoids rocks of the Malé Karpaty Mts. *Geol. Zbor. Geol. carpath.* (Bratislava), 32, 6, pp. 643—669.
- CAMBEL, B. — VALACH, J., 1956: Granitoidné horniny v Malých Karpatoch, ich geológia, petrografia a petrochémia. *Geol. Práce, Zoš.* 42, (Bratislava), pp. 113—268.
- CAMBEL, B. — VESELSKÝ, J. — MIKLÓŠ, J., 1982 a: The Malé Karpaty rocks altered by metasomatism. *Geol. Zbor. Geol. carpath.* (Bratislava), 33, 6, pp. 697—728.
- CAMBEL, B. — VESELSKÝ, J. — VILINOVIC, V., 1982 b: Granitoids of the Malé Karpaty Mts.: Major elements chemistry and its contribution to petrogenesis. *Geol. Zbor. Geol. carpath.* (Bratislava), 33, 6, pp. 679—696.
- CAMBEL, B. — VILINOVICOVÁ, L., 1981 b: Petrochemistry and geochemistry of selected granitoid samples from the West Carpathian region. *Geol. Zbor. Geol. carpath.* (Bratislava), 32, 5, pp. 517—546.

- DAVIDOVA, S., 1970: Charakteristik der Pegmatite der Kleinen Karpaten. Geol. Zbor. Geol. carpath. (Bratislava), 21, 1, pp. 115–137.
- DAVIDOVA, S. — DAVID, A., 1981: Distribution of some trace elements in feldspars from pegmetites of the Tatrides. Geol. Zbor. Geol. carpath. (Bratislava), 32, 1, pp. 35–54.
- SHAND, S. J., 1927: Eruptive rocks, their genesis composition, clasification and their relation to the deposits. London—New York, 225 pp.

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