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## ALKALIES IN THE GRANITOID ROCKS OF THE MALÉ KARPATY MTS.

(Tabs. 9, Figs. 12)



Abstract: The authors have evaluated the contents of alkalies in the Variscan granitoids and metamorphites (phyllites, gneisses) of the Malé Karpaty Mts. Analytical data were obtained by method of flame photometry at the Institute of Geochemistry and Physics of Minerals in Kiev, U.S.S.R. (A. I. Samchuk, T. K. Bondar) and checked by means of AAS method in the Geological Institute of the Slovak Academy of Sciences in Bratislava. The paper reports on the correlations of alkalic elements, their contents in dependence on the rock type, and on the conclusions deduced from geochemical studies. The granitoid and metamorphic rocks of the Malé Karpaty region (periplutonic granite metamorphism) show low Li, Rb and Cs contents, which are considerably lower in granodiorite than in granite. The biotite granodiorite of Modra is most impoverished in alkalies. In schistose metamorphites the contents of Li, Rb, Cs are only slightly increased as a result of metamorphism. Low contents of alkalies range most of the granitoid rocks of the region studied, particularly those of the Modra massif, to the "I" type of Chappell - White's classification (1974). The granitoids of the Bratislava massif, the major part of which were formed by anatexis of sedimentary rocks, devoid of or poor in basaltoids, belong to the mixed ("I" and "S") types. They have higher alkali contents. There is a minimum potentiality of mineralization of granitoids, especially as concerns Sn. W and Li.

Резюме: Авторы оценивают содержания щелочей в варийских гранитоидах и метаморфитах (филлиты, гнейсы) из Малых Карпат. Аналитические данные, полученны методом пламенной фотометрии на Инститыте геохимии и физики минералов в г. Киев, СССР (А. И. Самчук, к. х. н., Т. К. Бондарь, инж.) и проверенны при помощи ААС метода на Геологическом институте Словацкой академии наук в Братиславе. Статья разбирает взаимозависимости щелочных элементов, их содержания в зависимости от типа породы и также результаты, происходящие из геохимических исследований. Гранитоидные и метаморфические породы из области Малых Карпат (периплутонический гранитовый метаморфизм) показывают понижене Li, Rb и Cs содержаний, которые значительно низшие в гранодиоритах чем в граните. Биотитический гранодиорит. Модра наиболее обнищен щелочами. В сланцевых мегаморфитах содержания Li, Rb, Cs только немножко повышенные наследствием метаморфизма. Низкие содержания щелочей присоединяют большинство гранитоидных пород исследуемой области и в частности из области Модранского массива к "І" типу для классификации Чапела — Вайта (1974). Гранитоиды Братиславского массива, которых превосходящая часть возникла анатексисом осадочных пород обнищенных базальтоидами, принадлежат к смешанным ("I" и "S") типам, имеющим повышенные содержания щелочей. Существует минимальная потенциальность минерализации гланитоидов, главным образом касающаяся Sn. W и Li.

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In connection with the integrated geochemical investigation of the granitoids of the West Carpathians the authors have studied in great detail the alkalies of the granitoids and metamorphites in the region of the Malé Karpaty Mts. Within the scope of cooperation with B. F. Mickievič, the analyses of alkalies were performed in the IGFM laboratories in Kiev, U.S.S.R. The statistical evaluation of analytical data and correlative analysis was done by V. E. Tepikin. Using the AAS method, the results were simultaneously verified in the Geological Inst. of the Slovak Academy of Sciences (by Ing. E. Martíny, CSc.) in Bratislava. Several samples were analysed by INAA method in the laboratories of the Czechoslovak Uranium Industry at Stráž pod Ralskem (anal. Ing. P. Kotas, CSc.). In this way appropriate conditions were created for the correlation of analytical results obtained in different laboratories and using different methods.

The alkalies Li, Rb and Cs are of great geochemical importance as indicators of the genesis of rocks, since they make it possible to characterize the rocks under study and help to recognize the geological history of the area. The contents of Li, Rb, Cs provide relevant discrimination and correlation signals which enable the granitoids of different genetic types and different degrees of fractional crystallization to be correlated. The alkalies together with Ba, Sr, Ca, Pb, Mg and Fe elements may indicate the affinity of later dyke derivates to the parental magmatic rock in which they occur.

## The contents of Li, Rb and Cs in granitoids

The contents of all these microelements in granitoid rocks and their minerals are highly variable (Tables 1,2).

Lithium forms separate Li minerals in alkalic pegmatites and, besides, concentrates particularly in tourmaline, phlogopite, biotite and muscovite. According to Solodov et al. (1980), it covers 0.61 to 0.67 % in these minerals. It forms an isomorphous admixture in mineral lattices with coordination numbers 8—12, more rarely 6. It chiefly substitutes for Mg, Fe and Al; formerly isomorphous substitution of Li for Na was also presumed. According to Taylor (1965) a high lithium is distinctive of the sedimentary origin of granitoids. Stavrov (1978) ascribed high Li contents to intrusive differentiation complexes of the granodiorite-granite-permatite series. In some cases high lithium contents indicate a high differentiation of magma and appear in some pegmatites.

Rubidium is characterized by a complete isomorphism with potassium. Their ionic radii, electronegative values and ionization potentials are very similar [Taylor, 1965]. Barneckaja, 1975, (in Solodov et al., 1980] prepared rubidium microcline which had no more than 0.2 % Cs. From this it follows that cesium need not be isomorphically closely related to rubidium. The K/Rb ratio is highly variable; the variability does not depend only on isomorphism [diadochy] but also on the different conditions of the origin of the rocks analysed which, when correctly interpreted, can be deciphered.

The rubidium contents in granitoids range from a few tens of ppm to more than 1 %, depending on the Rb, Li and Cs contents in rock minerals. Potassium feldspars, for example, can have as much as 3.1 % Rb<sub>2</sub>O. More numerical data are given in the work of Ljachovič [1972]. Micas usually

have the highest Rb contents. On the entry of rubidium into micas the feldsparquartz residual melt may be relatively impoverished in Rb, Li and/or Ba, all of which concentrate in biotite. This may be the cause of relatively low rubidium contents in K-feldspars of the pegmatites in the Malé Karpaty Mts.

Table 1

Contents of alkalic trace metals in granitoid formations (Solodov et. al., 1980 — Table 10, modified)

	In structures w	ith predominant			
Formation and genetic	Magma n	novement			
group of granites	primary autochthonous type	derived intru- sive type	Average values		
	L i t h i u r	n			
1. Ganbro-granite Basaltoid granites 2. Granodiorite 3. Granite 4. Leucogranite-alaskite 5. Lithium-granite 6. Sialic granites 7. All granites	4.3 (14;63) 19 (24;137) 18 (51;500) 24 (24;179) — 18.5 (99;816) 17 (113;879)	122 (3;37) 73 (33;490) 81 (29;138) 261 (17;110) 76 (82;775) 76 (82;775)	4.3 (14;63) 33 (27;174) 27 (84;990) 55 (53;317) 261 (17;110) 38 (181;1591) 36 (195;1654)		
	Rubidiu	m			
Gabbro-granite Basaltoid granites Granodiorite Granite Leucogranite-alaskite Li-granite Sialic granites All granites	85 (16;140) 103 (24;139) 183 (54;834) 221 (27;272) — 164 (105;1245) 156 (121;1385)	260 (3;37) 251 (35;601) 292 (32;217) 686 (18;190) 254 (70;855) 254 (70;855)	85 [16;140] 120 [27;186] 209 [89;1435] 260 [59;489] 683 [18;190] 193 [175;2100] 186 [191;2240]		
	Cesiun	n			
Gabbro-granite Basaltoid granites Granodiorite Granite Leucogranite-alaskite Lithium-granite Sialic granites All granites	1.1 (15;97)  3 (24;115) 3 (53;768) 2.8 (27;313)  3 (104;1136) 2.8 (119;1233)	45 (3;37) 11 (36;535) 25 (34;140) 66 (17;170) 15 (93;882) 15 (90;882)	1.1 (15;97)  8 (27;152) 6 (89;1243) 15 (61;453) 66 (17;170) 8 (194;2018) 7.4 (209;2115)		

Explanation: In the sense of Tichomirova (in Solodov et al., 1980) five granitoid formations divided into two genetic groups are listed in the Table. The first group is represented by the gabbro—granitoid formation associated with basaltoid magma; the other four formations are associated with crustal sialic magmatism. The first vertical column of number relates to the primary rocks, the second to the rocks altered by differentiation or contamination, and the third gives average values. The first number in bracket is the number of sampled massifs and the second the number of samples analysed.

 $T\,a\,b\,l\,e\,\,2$  Contents of Li, Rb and Cs in rock-forming minerals of the granitoids [Solodov et al., 1980, selected parts from Table 3]

Mineral and its genetic type	Li ppm	Rb ppm	Cs ppm	K/Rb	K/Cs	Rb/Cs
Quartz of	3.2—20	7.5-40	25-40		_	11.0
intrusive granite	13.2(40)	33(19)	3[17]			
Quartz of granodiorite	11.(4)	16(4)	25(3)	-	-	0.6
Microcline	4-60	340-1090	5.1 - 12			
of intrusive granitoids	18(20)	550(28)	6.9(141)	-	l	8.00
Microcline of pegmatite	11.7(12)	568(12)	46(12)	-	<u></u>	12.3
Microcline	ND-5	200-480	20-60	400.0	3180.0	8.0
of micaceous pegmatite	2(11)	270(11)	B4(11)			
Plagioclase of intrusive granitoids	24.7(36)	107(68)	15(2)	-	_	7.1
Plagioclase of autochthon. granites	24.8[9]	,152(4)	7(1)	_	_	21.7
Oligoclase of	5-22	-50	10 - 40	_	-	0.8
micaceous pegmatite	12(27)	24(27)	30(27)			
Albite of peg- matite with rare metals	3-280	10-130	- 80	58.0	90.0	1.6
Tourmaline	50-200	10-70	-30	- 1	<u></u>	4.0
of granite	100(10)	40(10)	10(10)			
Common amphi-	7-68	3-28	4-17	33.0	300.0	9.0
bole of granite	32(9)	9(9)	10(9)			
Alk. amphibole	1000-1900	20-73	50-329	-	_	0.5
of alkaline granitoids	1340	52	96			
Biotite of	900-6100	590-8300	40-520	330.0	30.0	11.0
granite	2500(24)	2530(24)	230[24]			
Biotite of	280-600	340-700	5-70	152.8	2650.0	17.3
micaceous pegmatite	480(16)	520[16]	30(14)			
Biotite of	2200-4900	2800-4000	250-420	<i>y</i> —	-	_
granite with rare metals	4300(8)	3000(8)	350(8)			
Phlogopite of	760-4060	1070-4180	190 - 820	32.0	195.0	6.3
oligoclase- phlog. veins	2430(5)	2270(5)	360(5)			

Table 2, continued

Mineral and its genetic type	Li ppm	Rb ppm	Cs ppm	K/Rb	K/Cs	Rb/Cs
Muscovite of	40-400	310—1100	10-30	100.9	3622.7	27.2
micaceous pegmatite	210(100)	820[100]	22(200)		78 may 2 m 22 . 7 % a 1	
Muscovite of	100-210	200-4100	210-300	30.3	346.4	11.2
microcline- albite pegmatite	140(80)	2800(80)	250(80)			
Hydromuscovite	6-50	290—380	32-50	169.1	1607.5	9.5
from low-temp. deposits	10(25)	330(25)	40(25)			

Explanation: Limit values in numerator, average contents in denominator, and the number of samples analysed in brackets.

Table 3

Contents of alkalic metals in minerals of micaceous pegmatites [Solodov et al., 1980, selected data from Table 6]

Minoral	Conten	ts (%)	Dh/Ga	IZ/DI-	12/0-		
Mineral	Rb	Cs	Rb/Cs	K/Rb	K/Cs		
microcline	0.027	0.0034	8	400	3180		
muscovite	0.057	0.0058	16	132	2080		
biotite	0.066	0.0058	11.4	118	1330		

In view of genetic interpretations and correlations the K/Rb ratio is of much importance. It varies between 1.5 and 24.100. These concentrations of rubidium in potassium minerals are a result of the fact that the other elements having similar ionic radii, i.e. Tl, Ba and Pb, are not able to bind rubidium and disperse it for crystallo-chemical reasons.

Taylor (1965) estimates the rubidium content in the earth's crust at 90 ppm and the K/Rb ratio as varying between 150 and 300. The K/Rb changes even within one granitoid massif and in dependence on individual generations (populations) of minerals. A ratio below 150 may indicate a supply of differentiated rest magma or, alternatively, a mere mobilization of pegmatitic feldspar-quartz mass from the country rocks. Using the K/Rb ratio, the crystallization stages or, better to say, stages of fractional crystallization can be determined.

The K/Cs and Rb/Cs ratios are also of diagnostic significance. There is mostly a direct interrelationship between these elements. Similarly as rubidium, cesium concentrates in micas (< 0.2 to 1 %), in K-feldspars of pegmatites, and in beryl (up to 2.68 %). Late microclines (Solodov et al., 1980) may contain up to 0.233 — 0.269 % Cs (Table 3). Solodov et al. (1980) give the Rb and Cs contents in the minerals of micaceous pegmatites (Table 3).

Table 4

Contents of microelements in granitoids according to geochemical classification of Tauson (1977b) and their correlation with the values for the rock of the Malé Karpaty Mts.

Element	1	2	3	4	5(24)	6(11)
% K	3.5	3.3	4.6	3.9	2.99	2.09
Na	3.4	2.8	2.3	2.8	2.45	2.86
F'	0.06	80.0	0.018	0.27	0.03	0.03
g/t Li	21	50	11	180	27	17.6
Rb	125	175	140	440	94	58.2
Cs	_	_		17.5	1.4	1.4
Sr	700	330	280	70	181	681.4
Ba	1700	833	2800	175	920	1126.4
K/Rb	280	200	140	90	322	363
Ba/Rb	14	5	1.9	0.4	10	19.7

Explanation: 1 — granite of latite type (basaltoid). 2 — palingenic calc-alkaline granitoids, 3 — ultrametamorphosed granitoids, 4 — plumasite-leucogranite with TR content, 5 — two-mica monzogranite of the Bratislava massif (Malé Karpaty), 6 — biotite granediorite of the Modra massif (Malé Karpaty).

For comparison we give here the average contents of Rb (270 ppm) and Li (2.8 ppm) from 15 specimens of microcline and micaceous pegmatites from the Malé Karpaty Mts. (according to Dávidová and Dávid, 1981). Tauson (1977a) assigns great importance to the K/Rb and Ba/Rb ratios. It Tauson's geochemical classification scheme based on the contents of some microelements the granitoids possess values that are given in Table 4. From this Table it is apparent that according to the content of alkalies the granitoids of the Malé Karpaty region approach only broadly the groups as given by Tauson. They are nearest to them in the values of K/Rb and Ba/Rb ratios. This fact suggests that the Malé Karpaty granitoids are rocks of mixed chemical properties produced by anatexis of crustal clayey-siliceous complexes containing rocks of tholeitic (metabasite) nature. They are neither a sort of differentiates of basic rocks of a "pure line" nor anatexites of "pure sediments" devoid of magmatites and their tuffs.

# Evaluation of alkali contents in granitoids of the Malé Karpaty region

Our conclusions are based on the analyses of samples of the granitoids and crystalline schists, listed in Tables 5, 6, 7, 8. These samples representing the principal types of rocks of the mountain range have been for several years the subject of integrated geochemical study. The granitoids were divided into groups using the mesonormative classification because there is not a sufficient number of reliable planimetric analyses available from the region under study. The division was performed by Vilinovič (1981) according to the mesonormative classification diagram Q'-ANOR (A. Streckeisen — Le Maitre, 1979), which is appropriate for the classification proposed by the IUGS Subcommission 1973. For the classification of granitoids nor-

and representation of other elements Contents of alkalies in the granitoids of the Maié Karpaty Mts. and The Brutislava Massif Table 5

ratios

	20	24	40	200	2 2	99	22	26	42	28	32	37	28	33	35	38	38	43	82	35	82	40	64	34	33	54	69	14	20	59	55	37	1
Rb/Sr	12.	6	i -	ic		. c	. o	0.26	0.	0	0.	0	0.	0.	0	0.	0.	0	11.	0.	0	0.	0.	0	0	0.	0	H	0.	0.	0.	0	0
Ba/Rb	0.3	-	5.6	i (*)	4.00	2.8	7.9	12.5	8.9	11.6	11.7	10,3	20.5	21.9	15.7	9.1	7.0	5.6	2.7	6.3	15.1	19.2	11.5	15.6	18.5	7.3	8.9	6.5	11.1	10.9	7.3	10.9	0 0
K/Cs	22 941	15,923	33 231	16 632	24 333	28 077	15 154	19 700	21 538	13 529	13 529	21 185	22 000	16 937	17 176	29 556	17 533	15 667	32 917	20 143	30 857	32 778	23 000	14 200	7 939	25 364	25 454	28 600	18 438	16 571	30 909	34 000	000 20
K/Rb	195	246	288	226	474	265	290	323	280	256	274	365	418	327	295	391	296	188	304	303	441	410	351	296	312	313	475	315	307	281	382	392	000
Li/Mg	0.012	0.032	0.010	0.000	0.005	0.011	0.003	0.003	0.007	0.097	0.003	0.005	0.007	0.009	0.003	900.0	0.017	0.014	0.033	0.005	0.006	0.034	900.0	0.002	0.007	0.005	0.008	0.004	0.004	0.015	0.010	0.017	+000
Na/Li	200	996	1930	770	2123	1333	1882	1738	1535	684	816	869	406	839	2154	27.83	808	458	1 045	1 267	1 583	2 700	1 021	2 138	650	1 182	940	1 830	674	408	948	1 444	000
Ba	69	16	350	440	650	870	540	760	890	1949	980	955	1620	1823	1550	620	620	260	355	590	1480	1380	1020	1120	1550	650	525	575	1070	1350	650	820	000
Sr	16	37	101	148	91	151	329	234	239	316	263	251	282	251	285	178	234	234	Ξ	269	120	178	138	209	257	166	82	78	191	209	162	239	1111
Cs	1.7	1.3	1.3	1 9	1.5	1.3	1.3	1.0	1.3	1.7	1.7	1.6	1.5	1.6	1.7	0.9	1.5	1.2	2.5	1.4	1.4	0.9	1.2	1.5	3.3	1.1	1.1	1.0	1.6	2.1	1:1	0.9	4 0
Rb	200	84	150	140	77	100	89	19	100	06	82	93	79	83	66	89	83	100	130	93	200	72	89	72	84	83	29	83	93	124	83	78	107
Γį	32	29	13	28	13	18	17	16	17	38	32	32	64	31	13	12	36	31	20	21	12	6	23	13	32	22	22	15	31	49	27	18	200
Mg	0.27	0.10	0.13	0.33	0.25	0.16	0.50	0.49	0.24	0.56	1.05	0.65	0.89	0.34	0.49	0.21	0.21	0.23	90.0	0.42	0.19	0.22	0.53	0.70	0.49	0.45	0.31	0.40	0.86	0.33	0.27	0.10	010
Ñ	1.60	2.8	2.47	2.18	2.76	2.40	3.2	2.78	2.61	2.60	2.61	2.78	2.60	2.60	2.83	2.50	2.9	1.42	2.09	2.66	1.90	2.43	2.96	2.78	2.08	2.60	2.35	2.70	2.09	2.00	2.56	2.60	2 46
М	3.93	2.07	4.32	3.16	3.65	3.65	1.97	1.97	2.80	2.30	2.30	3.39	3.30	2.71	2.92	2.63	2.63	1.88	3.95	2.82	4.32	2.95	3.12	2.13	2.62	2.79	2.80	2.80	2.95	3.48	3.40	3.06	0.10
Sample	afG C—83	G VK-34	G VK-41	G C-84	G VK-123	G VK-145	D VK-25	iD VK—102	10 VK 107	0 VN - 100	10 VK 134	127 VN -124	12 VA - 127	0 VN 130	10 VN 153	CD2-NV CD	10 VN -30a	1G VN - 33	10 C 00	10 C - 08	TOT - MA DE	20 VN -133	IG VK-111	IG VN-113	TO VA-III	16 VA-118	1G VK—119	1G VK-123	1G VK-121	1G VK-144	1G VK-152	1G VK-159	16: VK-168

Continuation of Tab. 5

Rb/Sr	0.46	0.64	0.43	0.77	0.65	0.87	0.23	-	0.15	0.13	0.08	0.06	0.05	0.10	0.09	0.12	0.08	0.10	0.07	0.11	0.15
Ba/Rb	18.4	11.8	14.4	6.8	5.5	4.3	9.8		6.3	17.8	10.3	15.9	12.2	29.0	16.1	21.8	29.6	27.2	15.6	14.1	24.7
K/Cs	27 273	28 364	23 333	28 182	19 400	22 286	14 550		21 429	35 000	16 071	22 182	14 462	11 600	6 118	14 375	15 833	18 571	13 750	16 533	.16 923
K/Rb	333	286	298	279	291	284	300		375	560	326	478	356	348	170	338	388	426	386	376	386
Li/Mg	0.009	0.015	0.008	0.014	0.009	0.018	0.008		0.002	0.003	0.003	0.003	0.008	0.003	0.003	0.003	0.013	0.003	0.003	0.004	0.002
Na/Li	897	753	929	970	644	933	706	<u></u>	333	3 450	1 330	1 528	2 533	1 412	652	1 429	2 053	1 867	1 812	1 675	1 700
Ва	1660	1290	1350	760	550	470	955	The Modra Massif	200	890	710	810	620	1450	980	1480	1450	1660	68	930	1410
Sr	195	170	219	145	155	126	420	ne Modi	525	380	830	890	1010	200	099	560	630	630	830	575	380
CS	1:1	T	1.2	11	1.5	1.4	2.0		1.4	80	1.4	-	1.3	1.5	1.7	1.6	1.2	1.4	1.6	1.5	1.3
RD	06	109	94	111	100	110	97		83	202	69	25	51	20	61	89	.49	61	57	99	57
Ξ	29	38	28	27	17	27	35		40	φ	20	2 = 2	12	17	23	21	1 1 1	2 1	17	16	16
Mg	0.31	0.26	0.33	0.20	0.43	0.15	0.43		0.81	0.24	0.60	0.00	0.20	0.56	0.71	0.75	0.12	2 2 2	0.57	0.45	0.73
Na	2.60	2.86	2.60	2.62	2.64	2 52	2.47		1 33	276	0 88	27.0	3.80	2 40	1.50	3.00	3 08	2.80	30.8	2,68	2.72
:\foots	3.00	3.12	2.80	3 10	2 91	3 12	2.91		3 00	2.80	20.0	2 44	188	1 74	1.04	2.30	1 90	2.50	2000	2 48	2.20
Sample	VK	VKI	C. S.	X	DRI	DB	mG DB-8		6 6-79	G VK_210	D VK-46	D VK 47	C - 85	VK	VK	VK	C S	VK	VK	VK	GD VK-212

Explanation: Classification symbols, classification of rocks according to the mesonorm. afG — alkali-feldspar granite (dyke aplite granite); sG — syenogranite (leucocratic muscovite granite); mG — monzogranite (muscovite-biotite granite); GD — Numers behind classification symbols are working number of geologists and laboratory numbers. Sampling localities are listed in separate supplement. The K, Na, Mg contents are given in %, the remaining elements in ppm. granodiorite (two-mica or biotite granodiorite); Bm - Bratislava massif; Mm - Modra massif.

Table 6

Jo Contents of alkalies in metamorphites of the schistose crystalline complex of the Malé Karpaty, and representation cher elements and ratios. For explanation see Table 5

Rb/Sr	0.32 0.21 0.23 0.17 0.32	0.13° 0.17 3.00 0.56 0.70	0.46 0.50 0.30 0.38 0.62 0.62 0.48 0.16 1.39
Ba/Rb	8.2 12.7 14.9 10.7 3.2	17.3 6.3 10.3 14.9 15.7	7.4 5.7 7.4 8.1 6.0 5.5 11.3 8,0 6,3
K/Cs	10 000 9 400 10 286 10 550 8 941	12 071 8 100 9 941 14 000 13 714	8 621 10 714 9 240 4 518 11 778 10 800 8 684 7 333 9 636
K/Rb	289 320 318 358 310	352 261 282 328 262	250 300 229 298 290 327 311 300 312
Li/Mg	0.002 0.001 0.002 0.002 0.002	0.003 0.002 0.004 0.002 0.002	0.003 0.004 0.002 0.002 0.002 0.002 0.002
Na/Li	814 1 494 1 018 1 026 512	1 623 904 213 1 138 1 529	608 611 543 780 832 655 632 771
Ва	690 560 1 010 630 390	830 390 1 230 955 830	740 425 590 690 690 440 860 600 625 430
Sr	257 214 295 355 309	360 360 40 115 76	219 148 269 98 191 107 110 420
Cs	2.4 2.1 2.0 3.4	1.4 3.4 1.5 1.4	2.9 2.1 2.5 5.6 5.6 1.9 2.7 2.7
Rb	83 44 68 59 98	48 62 120 64 53	100 75 80 85 73 66 53 66
ΙΊ	21 16 21 23 33	13 26 40 16 14	35 35 35 31 29 33 31 17
Mg	1.26 1.52 1.26 1.39 1.86	0.51 1.20 0.91 0.75 0.83	1.44 0.97 1.44 0.30 1.27 1.19 1.77 1.10
Na	1.71 2.39 2.16 2.36 1.69	2.11 2.35 0.85 1.82 2.14	2.37 2.14 1.90 1.95 2.58 1.90 2.40 2.39 2.19
М	2.40 1.41 2.16 2.11 3.04	1.69 1.62 3.28 2.10 1.92	2.50 2.25 2.31 2.53 2.12 2.12 2.16 1.98 2.12
Sample	11/63—JV 14/63—JV 131/63"—JV 44/63—JV 49/63—JV	12/63—JV 21/63—JV 2 24/63—JV 30/63—JV 53/63—JV	3/63-1V 5/63-1V 6/63-1V 13/63-1V 3 20/63-1V 29/63-1V 38/63-1V 43/63-1V 44/63-1V 45/63-1V

gneiss (biotite-garnet gneiss 1 3 slates of the Harmónia Formation; garnet]; 2 Explanation: 1 - biotite phyllite ( $\pm$   $\pm$  muscovite, sillimanite, staurolite).

Table 7

granitoids of the Bratislava and the Modra massifs Average centents of alkalic elements in individual groups of

Rb/Sr		1.24	0.56	5.32		0.14
Ba/Rb		4.7	TO	13		12.1
K/Cs		23 640	23 583	17 678		28 215 15 129
K/Rb		320	322	322		468
Li/Mg		0.013	0.011	0.005		0.004
Na/Li		1420	1066	1302		1892
Ba	Bratislava massi	489.2	620	1578	Modra massif	695
SL		105.6	181	261	The Modr	453
Cs	The	1.4	1.4	1.4	I	1.1
Rb		110.2	94	82.5		65
Γ		20.2	27	27.2		24
Mg		0.19	0.33	0.54		0.53
ВN		2.52	2.45	2.71		2.02
×		3.37	2.99	2.63		2.90
Rock type				GD (10)		mG (2)

For explanation see Table 5.

Table 8

Mts. groups according to the intensity of meta-Average contents of alkalies in the metasadiments of the Malé Karpaty morabism

Rb/Sr	0.25 0.39 0.57
Ba/Rb	9.9 13.6 7.3
K Cs	9 835 11 971 9 036
K/Rb	319 301 291
Li/Mg	0.002
Na/Li	973 1 299 747
Вз	656 751 533
Sr	286 228 179
Cs	2.3
RD	70 57 74
Ē	23
Mg	1.46
Na	2.06
Ж	2.22 1.83
	1 (5) 2 (5) 3 (9)

For explanation see Table 6.

mative minerals were calculated according to the procedure recommended by Mielke — Winkler (1979).

The analysed samples were divided into groups as is seen from Table 5 and Figs, 1, 2. The rocks were studied separately in the Bratislava massif and in the Modra massif.

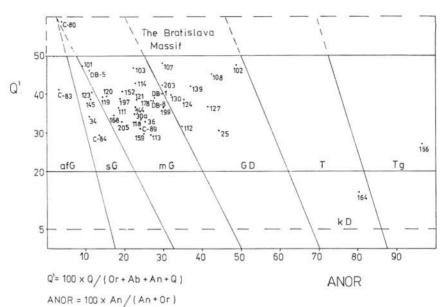


Fig. 1. Division of granitoid rocks of the Bratislava massif, Malé Karpaty Mts., based on the mesonorm of Mielke — Winkler (1979). Division proposed by Vilinovič (1981).

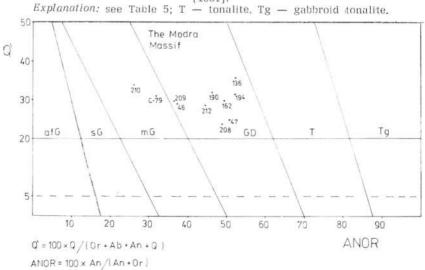


Fig. 2. Ditto as Fig. 1 — Modra massif

The group of metamorphites was divided into phyllitoid rocks on the basis of metamorphic grade. It involves biotite phyllites and transitional rocks to gneisses and biotite—granitoid gneisses (± staurolite, sillimanite, muscovite). The rocks of the Harmónia Formation (denoted by H) form a separate group.

The discussion and interpretation of results the same as the genetic conclusions are based on the data contained in the Tables and Figures. Explanations of Tables 5 and 6 (localization of samples and their brief designations) are given in a separate appendix.

#### Discussion

1. The comparison of the contents of alkalic elements in the granitoids of the Malé Karpaty Mts. has shown that they are low relative to those of granitoids of sialic origin (see Fig. 3a, b, c). This fact confirms the opinion that the rocks of so-called "I" type (Chappell and White, 1974) corresponding to the criteria given by these authors occur in the Malé Karpaty Mts., but the granitoids of the entire West Carpathians show similar features. The finding also agrees to a certain degree with the classification of Tauson (1977 b) based on the microelement contents. (This concerns particularly the affinity with the group of latite series derived from tholeitic basalts). It is also consistent with the results of Solodov et al. (1980), Table 1, since the contents of microelements of alkalies in some samples agree with the gabbro-granitoid formation and with the group of basaltoid granitic rocks, which can be regarded as a primary derivative of basaltoid rocks. However, the I/S classification in the sense of Chappell and White (1974) is most appropriate; according to it the granitoids of the Malé Karpaty Mts.

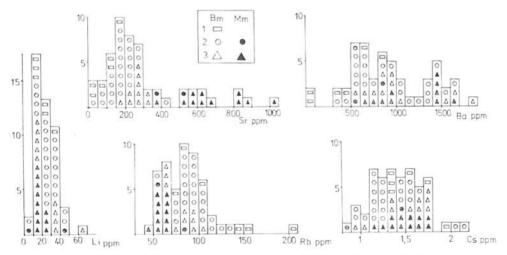


Fig. 3 a. Histogram of Rb, Li, Cs, Sr and Ba contents in the granitoid rocks of the Malé Karpaty Mts.

Expanation: 1 — alkali — feldspar granite + syenogranite (muscovite aplite-granite);
 2 — monzogranite (muscovite-biotite granite);
 3 — granodiorite (muscovite-biotite or biotite granodiorite);
 Bm — Bratislava massif;
 Mm — Modra massif.

can be considered as sedimentary and magmatic rocks altered by anatexis process. Geochemically, the rocks are genetically mixed types, because the alkali contents vary between the values of "basaltoid granitic rocks" and those of the granodiorite-granite group and the leucogranite—alaskite group [Solodov et al., 1980]. The last group already belongs to the granites of the formation of crustal sialic palingenic granitoids [Table 1]. In contrast to the typical palingenic granitoids, the major part of samples have reduced contents of alkalies.

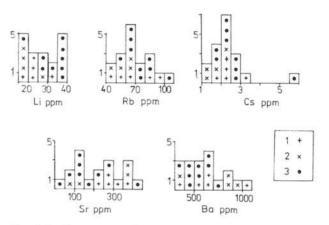


Fig. 3 b. Histograms of microelements in metapelites. Explanation: 1 — phyllite; 2 — slates of the Harmónia Formation; 3 — gneiss.

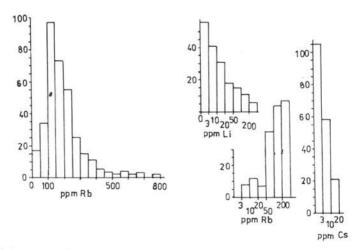


Fig. 3 c. Histograms of Li, Rb, Cs contents in granitoids, selected from the paper of Heier — Adams (1964, Fig. 7, pp. 288, 289). Graph 3a shows much lower Li and Rb and higher Sr contents in the Modra granitoid massif than in the Bratislava massif, which indicates different petrology of the two bodies. From Fig. 3 a, c, it is evident that in the Malé Karpaty granitoids compared with the granitoids studied by Heier—Adams most of the Rb values are low, falling in the interval of 50—100 ppm.

As the two genetic types mentioned above combine, the granitoid rocks of the Malé Karpaty Mts. show in places the features of "I" types and in places those of "S" types (the "I" types predominate in the Modra massif and the "S" types in the Bratislava massif). Under the assumption that in the Malé Karpaty region as well as in other mountain ranges of the West Carpathians the anatectic remelting of sedimentary and magmatic rocks occurred simultaneously, it is obvious that it geve rise to mixed transitional rock types. Compared with the "pure" sialic clayey-siliceous anatectites these show atypical decreased contents of individual components of the alkalic elements.

- 2. Impoverishment of granitoids in micro-alkalies (Table 5) is associated with the overall deficiency in potassium; this would suggest a geochemical primitiveness of granitoids, which could be interpreted in terms of a great age of the initial material (substrate). However, the interpretation given sub (1), the radiometric geochronological dating of the schistose crystalline complex of the West Carpathian Mts., and palaeontological and palynological data as well speak against this contention.
- 3. On the basis of the determination of alkali contents in metapelites of the Malé Karpaty crystalline complex, and also in the amphibolites of the Malé Karpaty region, it may be said (Table 6) that the Palaeozoic metapelites (gneisses and phyllites) including those of the Harmónia Formation, provide a similar geochemical pattern impoverished in alkalies, the content or which increases only slightly with the intensity of metamorphism (Table 8). The Li contents vary between 10 and 40 ppm (x 26 ppm), the Rb content ranges from 44 to 120 ppm ( $\bar{x}$  73) and Cs from 1.7 to 5.6 ppm ( $\bar{x}$  2.4 ppm). The average contents of these elements in the West Carpathian metabasites are : Li - 24.02 ppm, Rb - 22.88 ppm and Cs - 0.96 ppm [Cambel et al., 1979). This fact may be regarded as evidence that a similar type of sedimentary and igneous rocks may have been the initial material for the formation of anatectic magma. It is possible that the Palaeozoic sediments developed from Precambrian clastic material and the submarine volcanites were emplaced syngenetically with them. Consequently, the Malé Karpaty rocks display a geochemistry with a small content of macro- and microalkalies, and these low background values of alkalies were evident even after the anatectic reworking of the rocks during these formation of the Variscan granitoid magma. The impoverishment in alkalies has also been established in the Upper Devonian-Lower Carboniferous slates of the Harmónia Formation, which had presumably derived from a similar terrigenous material as its basement. Low contents of light rare earths (La, Ce, etc.) have also been proved preliminarily in metapelites of the Malé Karpaty Mts. and similarly in the granitoids of the whole West Carpathian mountain range.
- 4. To verify the results of chemical-analytical determinations of these low alkali contents, some samples were analysed using three methods (AAS, SPA, INAA) at the Geological Institute of the Slovak Academy of Sciences in Bratislava, at the IGFM AN in Kiev, U.S.S.R. and in the laboratories of the Czechoslovak Uranium Industry at Stráž pod Ralskem. Since the results fairly agree, particularly Rb determinations are very close, we believe that the relatively low contents of Li, Rb, Cs can be regarded as well established.
- 5. The feldspars of the West Carpathian pegmatites and their contents of alkalies have been studied by Dávidová and Dávid (1981). Their results

also confirm relatively lower Li, Rb and Cs contents in relation to literary records. The authors give the following microelement contents from the K-feldspars of the Malé Karpaty pegmatites [in ppm]: Pb 47.8, Sr 462.51, Fe 321, Ba 1372, Li 2.8, Rb 270, and Ba/Rb 5.03. These values are the highest of all obtained for other mountain ranges of the West Carpathians. The lowest Rb values, for example, have been determined in the West Tatra Mts. (Rb = 178)

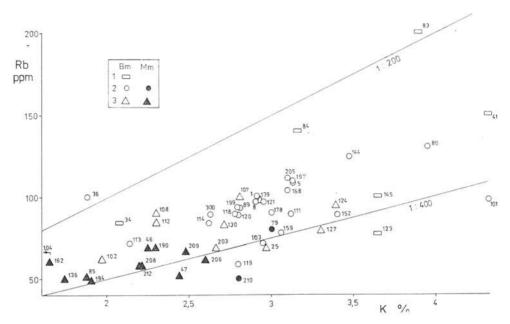


Fig. 4. Graph showing the relationship between K and Rb: a direct dependence of Rb on K is distinct. Most points in the graph occur between the K/Rb ratio values of 1:300 and 1:400. For explanation see Fig. 3.

ppm). Dávidová and Dávid therefore consider the Malé Karpaty pegmatites to be most differentiated. High Ba, Sr and Fe contents and low Li, Cs, Pb and Rb contents are also characteristic of feldspars in the pegmatites of other mountain ranges. This shows that not only feldspars of the fundamental granitoid types but also K-feldspars of pegmatites have a geochemical composition poor in alkalic microelements, which provides evidence that the pegmatites are a genetic component of the Variscan granitoids.

It schould be noted, however, that according to the analyses performed in the Geological Institute, Slovak Acad. Sci. [Ing. E. Martíny, CSc.] the K-feldspars of granitoids have higher Rb relative to potassium content: 250 ppm Rb [N=40] in the Tatride granitoids and 245 ppm Rb in the Veporide granitoids. This finding is at variance with the expectation that the feldspars of pegmatites, as the products of rest magma, will show a more conspicuous increase in rubidium content. We may explain it tentatively so that the rest magma, on the entry of rubidium into the already crystallizing biotite and/or

plagioclases, was enriched in Rb only very slightly. It has been reliably proved that the biotites of granitoids have high rubidium contents.

6. From the comparison of the contents of alkalies in the granitoids and metapelites of the Malé Karpaty Mts. and from the conclusions derived from the works of Stavrov (1978) and Solodov et al. (1980) the following statements can be made: Stavrov points out that the granitoids of intrusive

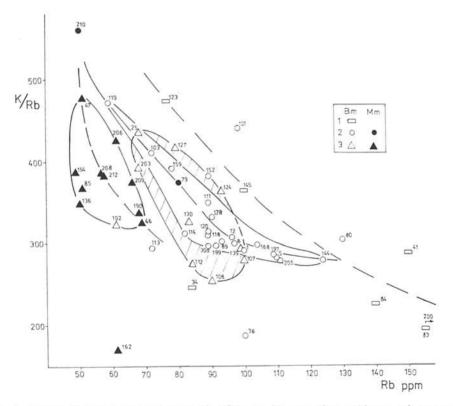


Fig. 5. Graph showing the relation of K/Rb to Rb provides evidence of separate positions of the Modra granodiorite and leucocratic granitoids. On the contrary the fields of rock types 2 and 3 of the Bratislava massif overlap. For explanation see Fig. 3 a.

differentiates strikingly differ in their alkali content from the anatectic granites, even when occurring in one and the same region. Anatectic granites are characterized by a decrease in lithium and cesium contents in the order of phyllite-gneiss-granodiorite-granite and the increase in the K/Rb ratio. This regularity is not generally valid for the metamorphites and granitoids of the Malé Karpaty region; these show manifestations of trace alkalies, which are partly characteristic of the intrusive differentiated complexes. In intrusive differentiated complexes an enrichment in lithium and cesium should proceed in the order: granodiorite-granite-pegmatite, and the K/Rb

ratio should diminish. Solodov et al. (1980) explain these changes in the following way:

With respect to trace metals the regional metamorphism shows two stages: isochemical and allochemical. Isochemical metamorphism is represented by the greenschist and epidote-amphibolite facies, partly also by the amphibolite facies, whilst the amphibolite and granulite facies are representative of the

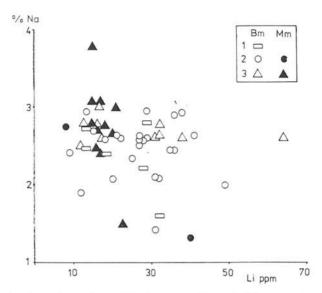


Fig. 6. Graph showing the relationship between Ba and Rb contents (no correlation is indicated). For explanation see Fig. 3 a.

allochemical metamorphism. The reduced content of Li, Rb, Cs in the two last facies is explained as due to that in allochemical metamorphism the alkalies-bearing minerals (chiefly micas) disappear and the minerals having considerable low contents of alkalies (pyroxene, garnet, etc.) are formed.

The analysis of the data on the contents of trace alkalic metals thus does not allow to draw unambiguous conclusions on the genesis of the granites of the Malé Karpaty region conformable with the above conceptions (the reason has already been given under points 1, 2, 3). The difference relates to the decrease of the average cesium content, which should proceed in the order: phyllite-gneiss-granodiorite-granite. On the other hand, the increase in lithium and the K/Rb ratio indicates an intrusive plutonic origin of granitoid rocks (Table 1). If we consider them to be the "I" types of Chappell and White, we can assume an anatectic derivation of granitoids from the rocks of a sedimentary complex containing layers of basic volcanites and/or their metatuffs.

7. The differentiation of the granitoid magma in the region of the Malé Karpaty Mts. can also be attested by the change in the potassium and rubi-

dium contents proceeding in the succession: granodiorite-granite, muscovite-biotite granite and leucocratic granite.

Stavrov (1978) has demonstrated that in the given series of differentiated massifs the increase of rubidium content and the reduction of K/Rb ratio do occur. These changes are particularly conspicuous with metasomatic alteration of granites in the apical parts of the massifs (Beus, Ojzerman,

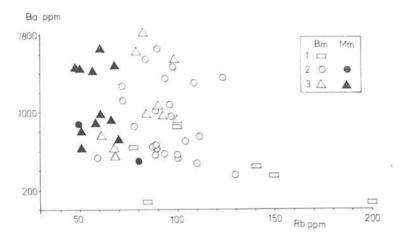


Fig. 7: Graph showing the relationship between Na and Li contents (the interdependence is not confirmed). For explanation see Fig. 3 a.

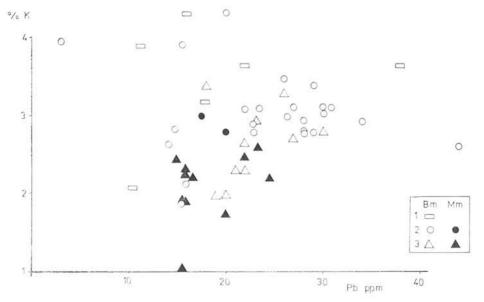


Fig. 8, Graph showing a discrete relationship between K and Pb. For explanation see Fig. 3 a.

1965). In the Malé Karpaty Mts. the evidently metasomatic postmagmatic alterations are only of local extent and do not show a greisenization character. They result in the formation of muscovite in the final crystallization phase (autometasomatism) or of a high-temperature alkalic K-metasomatism of granitoids (orthoclasites) and Na-metasomatism (albitites).

The data given in Tables 5 and 7 point to the existence of differentiation

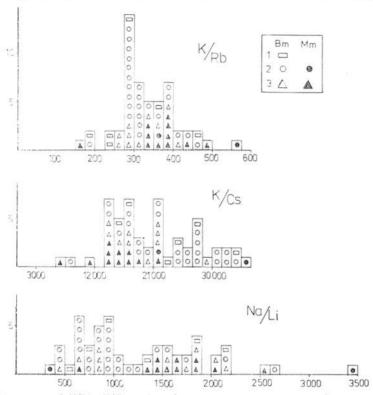


Fig. 9. Histograms of K/Rb, K/Cs and Na/Li ratios. The scatter of K/Cs ratios is great, and their values from 12,200 to 30,600 (according to Solodov et al., 1980) indicate a low potential mineralization of granitoids, chiefly as concerns Sn, W and Li metals. For explanation see Fig. 3 a.

of the palingenic magma that formed the Malé Karpaty granite massifs; the increase in Rb content and reduction of the K/Rb ratio from the granodiorites towards the aplitic and leucocratic granites is particularly well expressed. The same conclusion can be derived from the graph showing the K/Rb ratio and rubidium content (Fig. 5). In the graph, the fields of muscovite-biotite granitoids and biotite granodiorite of the Bratislava massif overlap each other. The biotite granodiorite of the Modra massif has a quite separate position in the graph similarly as the leucocratic granitoids.

This and other graphs draw attention to the differences between the granodicrites of the Bratislava massif and those of the Modra massif, which was already referred to by B. Cambeland J. Valach (1956).

8. Of importance is the histogram of the K/Rb ratio values (Fig. 9), similarly as the histogram of Ba/Rb ratio (Fig. 10), for the classification purposes. It was used, for example, by Tauson (1977 b) in his division of the geochemical rock types. The K/Rb values ranging from 200 to 300 correspond, e.g., to Tauson's types nos. 3.5 and 9 in Table 1, op. cit. 1977 b. In general, some ratios of K/Rb established for the rocks of the Malé Karpaty region are

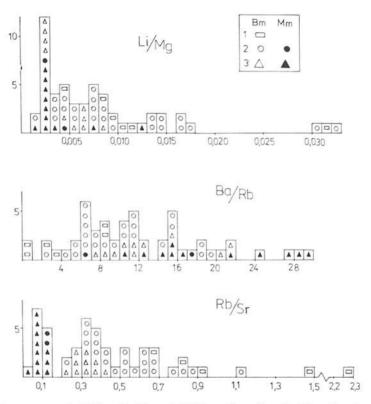


Fig. 10. Histograms of Li/Mg, Ba/Rb and Rb/Sr ratios. The Ba/Rb ratio does not suggest a regular grouping of samples according to the types of granitoid rocks; Li/Mg and Rb/Sr histograms clearly separate the rocks of the Modra massif from those of the Bratislava massif, which has a discrimination significance.

somewhat higher than those defined by the classification [Fig. 4], which follows from their lower rubidium content (Table 4). Analogously, the Ba/Rb ratios in Variscan granitoids of this mountain range vary within the limits corresponding to Tauson's type 3 = granite of latite type, type 5 — palingenic granitoids of calc-alkaline series, and type 9 = ultrametamorphic granitoids.

9. The differentiation of the Malé Karpaty granites being confirmed, the question arises whether they can be regarded as potentially ore-bearing on the basis of the contents of trace alkaline elements. A characteristic feature

of potential mineralization, (particularly Sn and W) are decreased values of K/Cs, Rb/Cs and Rb/Li ratios. Stavrov [1978] gave average values for these ratios in ore-bearing complexes as 3000, 17 and 2.5. In the Malé Karpaty Mts. the granites possess appreciably higher values, i.e. 22,000 — 24,000, 71—77 and 4.0 — 5.1. The mineralization associated with trace alkalic metals thus appears little prospective. In individual samples, however, the ratio

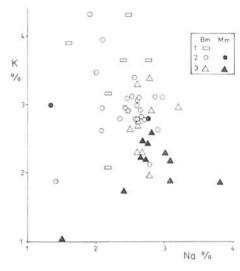


Fig. 11. Correlation K-Na graph. The elements show a negative relation and great scatter which is characteristic of the granitoids formed by remelting of inhomogeneous substrate.

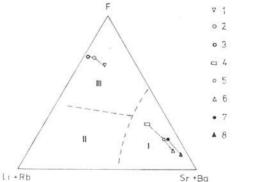


Fig. 12. Graph showing potential mineralization of the granitoids (especially for Sn, W and Li); according to Tauson — Kozlov et al. (1977). The granitoids of the Malé Karpaty region fall in the field of the least potential mineralization. Explanation: I — barren granitoids; II — granitoids showing limited potentiality for

mineralization; III — ore-bearing granitoids.

Granitoids of the Hnilec massif in the Spišsko-gemerské rudohorie Mts: 1 — biotite granite; 2 — biotite-muscovite granite; 3 — ore-bearing granite.

Malé Karpaty, Bratislava massif: 4 — muscovite leucogranitoids (alkali-feldspar granite, syenogranite); 5 — muscovite-biotite granite (monzogranite); 6 — muscovite-biotite granodiorite.

Malé Karpaty, Modra massif: 7 — biotite granite (monzogranite); 8 — biotite granodiorite.

values are near to those of ore-bearing granites, which indicates a need for further investigation and verification of feasibilities. A low mineralization grade is also inferable from the ternary graph F—Li+Rb—Sr+Ba (Tauson et al., 1977).

10. Rich graphic representation of the data is based on the analyses of the contents of alkalies in individual groups of the rocks in the Malé Karpaty Mts., which have been differentiated according to petrochemical properties of the rocks. Numerous graphs, histograms, tables and correlations [Figs. 3—12] indicate isomorphism and other interrelationships of the alkalic metals, present the contents of the elements in the individual rock groups and make possible their correlation. As a result of this graphic evaluation, genetic conclusions can be made on the association or, on the other hand, phasal independence of the separate types of the granitoid complexes. For example, the muscovite-biotite monzogranite and granodiorites of the Bratislava massif are closely associated, as is seen from the partly coincident position of the

Correlation matrices of alkalic metals and zinc arranged according to principal rock types

Table 9

1	Na	Li	Rb	Сз	Zn	2	Na	Li	Rb	Cs	Zn
K Na Li Rb Cs	-0.57	-0.33 -0.58	10.000	0.32 -0.62 0.40 0.66	-0.75 -0.02 0.75 0.15 0.35	K Na Li Rb Cs	0.01	0.03 -0.31	0.31 -0.15 0.65		-0.11 0.29
3	Na	Li	Rb	Cs	Zn	4	Na	Li	Rb	Cs	Zn
K Na Li Rb Cs	0.21	0.33 -0.30	0.35 -0.24 0.11		-0.17 -0.03 0.25 0.35 0.34	K Na Li Rb Cs	0.79	-0.45 -0.63	0.22 -0.09 0.53		
5	Na	Li	Rb	Cs	Zn	6	Na	Li	Rb	Cs	Zn
K Na Li Rb Cs	-0.32	0.07 0.15	0.92 -0.03 0.30	- 0.53 0.06 0.22 0.66	-0.26 0.46 0.51 0 -0.13	K Na Li Rb Cs	-0.50	0.82 -0.67	0.72 -0.90 0.88		-0.68 0.66

Explanation: 1 — syenogranite (aplite, pegmatite, leucogranite); 2 — muscovite-botite monzorganite (Bratislava massif); 3 — muscovite-biotite granodiorite (Bratislava massif); 4 — biotite granodiorite (Modra massif); 5 — gnaiss; 6 — phyllite.

projection points in the graphs. The granodiorites of the Modra massif, in contrast, show a separate and isolated pattern, which can be accounted for by the specific conditions of their origin (Fig. 5). The K/Rb compiled for the leucocratic granitoids also shows a different line of the development of changes in this relation. The evaluation of the graphs is not dealt with in the text as it follows directly from the figures.

11. The statistics compiled for individual elements has shown that between the average contents of alkalies in the established groups there are no statistical differences. Inside the groups, however, the contents of alkalies differ in individual samples and their relationships change, particularly in the granodiorite group. All this suggests that by means of detailed geochemical investigation the granitoids of the Malé Karpaty Mts. can be subdivided into minor groups which would reflect their genetic and facies differences.

The results of correlation analysis deserve particular attention (Table 9). It is well known that the unaltered granites are distinguished by a high positive correlation between Rb and K, and the late-magmatic microclinization is characterized by a reversed value (Beus, Ojzerman, 1965). In the Malé Karpaty granitoids a significant and unambiguous close relation between rubidium and potassium does not exist in all samples, which is indicative of the peculiarity of their origin.

### Conclusion

- 1. The authors performed analyses for alkali metals on 53 samples of the granitoid rocks of the Malé Karpaty Mts. and 19 samples of clayey-siliceous metamorphites (phyllites, gneisses and slates of the Harmónia Formation). Analyses were made at the Institute of Geochemistry and Physics of Minerals (IGFM) in Kiev (AN U.S.S.R.), using the method of flame photometry.
- 2. The analytical results have shown a relatively low content of alkalies in the rocks under study and a particularly small amount of microalkalies (Li, Rb and Cs). The authors derive these conditions from the mode of genesis of the granitoids, which they believe to be products of anatexis of the clayey-siliceous sediments containing different portions of metabasites (tholeiites). The features of the "I" rock type (Chappell, White, 1974) are marked in the Modra granodiorite, whereas the Bratislava granitoids are predominantly a "S" rock type; granitoids showing features both of "I" and "S" types also occur in the latter massif.
- 3. Similarly low contents of alkalies have been established in crystalline schists (biotite phyllites and gneisses). The material from which the Palaeozoic shales had derived should thus have been analogous to that from which granitoids were formed by anatexis during the Variscan orogeny. The clastic material of the Palaeozoic clayey-siliceous shales may have derived from the decomposed Precambrian rocks with admixed, probably Palaeozoic or earlier hasic volcanites. The investigation of metamorphic rocks based on the study of alkalies has shown a nearly isochemical metamorphism of schists in the Malé Karpaty region.
- 4. The microelemer's of alkalies and their and other elements' ratios provide evidence for the fractional crystallization of the palingenic magma formed as a result of anatexis, and for the aplites and pegmatites being deriva-

tes of the fundamental granitoid types of the Malé Karpaty region. This can be inferred from the relatively high Ba and Sr contents in aplites and leucogranite dykes, which are also characteristic of the main granitoid types of this region. According to Stavrov (1978), the fractional crystallization is demonstrated by the systematic reduction of the K/Rb ratio and increase in Rb content of more leucocratic differentiates.

5. On the basis of the higher K/Cs, Rb/Cs and Rb/Li ratios [Stavrov, 1978] the mineralization (chiefly in Sn and W) of the Malé Karpaty granitoids seems little promising. The same follows from the ternary diagram F-RB+Li-Sr+Ba (Fig. 12), which was used by Tauson et al. (1977) to determine a potential ore content in the rock.

From the preliminary comparison of the contents of alkalies in the granitoids of the Tatro—Veporides the authors conclude that the contents of alkalies of the Malé Karpaty granitoids do not differ substantially from those in the granitoids of the other West Carpathian mountain ranges.

6. Correlations, distribution of elements caused by isomorphism and other factors, and the overall geochemical characteristics of the individual rock types are apparent from the numerous graphs presented in the paper. From these graphs it is possible to draw conclusions on the genetic association of the single rock types, or on their separate, at least relatively independent genetic position. The graphs reveal that the granodiorites of the Modra massif differ geochemically and petrochemically from the granitoids of the Bratislava massif. They have to be considered as genetically different, even if the field investigations did not prove that they represent a separate phase of the Malé Karpaty plutonic granitoids on the basis of their mode of occurrence, sharp contacts or other features.

Translated by H. Zárubová.

### Supplement to Tables 5 and 6; list of localities

#### Granitoids: Bratislava massif

- C 83: alkali-feldspar granite; Marianka village, Malinský vrch Hill, 300 m W of El. 400,
- VK 34: syenogranite (apophysis in amphibolite); valley of the Bystrica brook, 2 km from the sanatorium.
- VK 41: syenogranite (granite dyke in gneiss); Limbach village, Slnečné údolie, El. 306.
- C 84: syenogranite; village Jur pri Bratislave, Kráľova búda, 1 km S of El. Malý Javorník (588).
- VK 123: syenogranite (aplitic dykes); Bratislava, quarry near the Červený most railway station.
- VK 145: syenogranite; Bratislava Kamzík, excavation for the television transmitter.
- VK 30 a: monzogranite; Limbach village, brook Rakový potok, branch road to Kr-kavec [forester's lodge], 300 SW of the valley.
- VK 36: monzogranite; Limbach, Slnečné údolie, 500 m N of the village. C 80: monzogranite; Rača village, 500 m NE of El. Veľká Baňa (443.7).
- C 89: monzogranite; Jur pri Bratislave, El. 480, 750 m SE of El. Veľký Javorník (593.6), on the road between Biely Kríž Modrý Kríž.
- VK 101: monzogranite; Jur pri Bratislave, Sviní les Hill, El. 250, reclaimed vineyards.

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  m VK-103:}$  monzogranite; Jur pri Bratislave, Sviní les Hill, El. 250, reclaimed vineyards.
- VK 111: monzogranite; Rača, boulders at the road to Biely Kríž, some 250 m from the crossrcads below Dobrá voda, 350 m SW of El. Piesky (446.5).
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  m VK-113:}$  monzogranite; Malý Javorník village excavation below the observatory.
- VK 114: monzogranite; Jur pri Bratislave road to Šenkárka ca. 450 m SE of El. Šenkárka (519.7).
- VK 118: monzogranite; Bratislava—Železná studnička restaurant at the crossroads, parking lot opposite the branch-road to Kačín, 100 SE, in the slope.
- VK-119: monzogranite; Bratislava-Železná studnička (= VK-118).
- VK 120: monzogranite; Bratislava—Železná studnička (= VK—118).
- VK 121: monzogranite; Bratislava, valley of the Bystrica brook, 200 m uphill from the upper amphibolite quarry, 750 SE of El. Hrabovina (433.8).
- VK 144: monzogranite; Marianka village, in the valley, ca. 700 m from the quarry. VK 152: monzogranite; Bratislava—Kramáre, excavation for the State sanatorium,
- transformer.
- VK 159: monzogranite; Jur pri Bratislave, abandoned quarry between Rača and Jur, NW of Šurské jazero.
- VK 168: monzogranite; Limbach, forester's longe Šenkýrka, El. 448.3, some 750 m NE of El. Tri kamenné kopce (583.5).
- VK 178: monzogranite; Limbach, about 1 km from El. Bradovice (406), 500 m NE of El. 536.5, crossroads.
- VK 197: monzogranite; Limbach, forester's lcdge Slnečné údolie, recreation area in the valley turning westwards from Slnečné údolie.
- VK 199: monzogranite; Rača, Dvornická dolina, 1 km SE of El. 320.5, at the roadside along the margin of the wood.
- VK 205: monzogranite; Limbach, Slnečné údolie, road digressing to the SW of Slnečné údolie, road-cutting close below the recreation camp.
- DB 1: monzogranite; Bratislava, rock below the castle, 50 m from the new bridge.
- ${\tt DB-5}$ : monzogranite; Bratislava, W of the castle, quarry above the bathing pool.
- DB 8: monzogranite; Bratislava, Mlynská dolina, abandoned quarry 80 m beyond the crossroads near the Botanical garden.
- VK 25: granodiorite; Jur pri Bratislave, road between Jur and Myslenice, exposure in the bend near the railway overbridge.
- VK 102: granodiorite; Jur pri Bratislave, Svini les Hill, El. 250 m, reclaimed vineyards.
- VK 107: granodiorite; Jur pri Bratislave, W of the village, valley above the cooperative farm, 500 m from the margin of the wood.
- VK 108: granodiorite; Jur pri Bratislave, some 500 m NE of El. Veľký Javorník [593.5], road from Biely Kríž to Jur.
- VK 112: granodiorite; Jur pri Bratislave, El. Malý Javorník (588.6), excavation below the observatory.
- VK 124: granodiorite; Bratislava, quarry at the Červený most railway station.
- VK 127: granodiorite; Bratislava, valley of the Bystrica brook, ca. 400 m NW of the sanatorium, 600 m NE of El. Hrubý Drinovec [396.6].
- VK 130: granodiorite; Bratislava—Krasňany, Pekná cesta, some 800 m from the Krasňany wood district, towards Čierny vrch.
- VK 139: granodiorite; Jur pri Bratislave, Malý Javorník area, Červený potok, a small quarry NW of El. 553.
- VK 203: granodiorite; Rača, Dvornická dolina, 200 m SE of El. 218.2.

### Granitoids: Modra massif

- C 79: monzogranite; Piesky village, 350 m SE of El. 356, rocky outcrop in the brook.
- VK 210: monzogranite (apophyses in amphibolite); Modra village, depression between Baba Hill and Gajdoš Hill, 250 m SE of El, Gajdoš (650.4).
- VK 46: granodiorite; Castá village, ca. 600 m E of El. Jelenec (694.6), road near El. 356.

VK - 47: granodiorite: Píla village, upper part of the Kamenný brook vallev, 500 m SE of El. Krvavý buk.

C - 85: granodicrite (mylonitized); Modra, quarry in the valley 250 m W of El. Barvinek (390.7).

VK - 136: granodiorite; road cutting between Modra and Králova villages, opposite the house No. 34/220,

VK - 162: granodiorite; Dolany village, 50 m NW of forester's lodge in Dolanská dolina, excavation at the crossroads.

VK - 190: granodicrite; Modra-Harmónia, forester's lodge Hrnčiar, about 600 m NNE of El. Sárka [330.2].

VK — 194: granodjorite [mylonitized]; Modra, m N of El. Srnčí vrch [375.8].

VK - 206: granodiorite: Piesky area, 400 m NW of the forester's lodge Panský dom, road to Kuchynská Baba Hill.

VK - 208: granodicrite: Piesky area, N of Panský dom, boulders at the roadside, VK - 209: granodiorite; 700 m NNE of Skalnatá Hill [704.1 m], at the roadside in the valley.

VK - 212: granodiorite; Piesky area, road cutting 300 m E of the Zochova chalet.

## Metamorphic rocks of the Malé Karpaty Mis.

11/63 - IV: biotite phyllite: Horné Orešany village, abandoned quarry on the SW. margin of the village, near the chapel.

14/63 - IV: biotite gneiss; Častá village, a large quarry in the Častianska dolina.

31/63 - [V: biotite schist; Pezinok-Cajla, road cutting above hospital.

14/63 - [V: biotite gneiss; Častá village, a large quarry in the Častianska dolina. leading to the glass-works,

49/63 - JV: phyllite; Devin village, rock below the castle, last house on the Danube bank.

12/63 - [V: biotite gneiss; Dolany village, abandoned quarry at the margin of the village,

21/63 - IV: Harmónia slate; Častá, quarry S of Predný vršek Hill,

24/63 — JV: gneiss; Harmónia village, a large quarry in the Kamenný brook valley. 30/63 — IV: Harmónia slate; Častá, pit heap of the Sivá Mine.

53/63 — JV: gneiss; Častá, above the large quarry in the Častianska dolina.

3/63 - JV: piotite gneiss; Bratislava-Červený Kríž, terminal station of trolleybus No. 17.

5/63 — IV: biotite gneiss; Bratislava—Železná Studnička, pit heap near the restaurant.

6/63 - IV: gneiss: Bratislava-Zelezná Studnička, 400 m SE of the bridge.

13/63 - IV: biotite gneiss; Limbach, Limbašská dolina, road to old mines, Slnečné údolie.

20/63 - JV: gneiss; Píla village, water reservoirs, 200 m SW of El. 313 in the Kamenný brook vallev.

29/63 - IV: biotite gneiss; Lamač village, valley N of the village.

38/63 - IV: paragneiss; Pezinok-Baba township.

43/63 - IV: biotite gneiss; Dúbrayka, saddle between Dúbrayská Hlavica and Brižitie.

45/63 - JV: gneiss, Záhorská Bystrica village, gully above the shooting range.

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