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TRACE ELEMENTS IN BASALTS OF SLOVAKIA

(Fig. 1—15)

Abstract: Basalts are found in Slovakia in the region of central and southeastern Slovakia. In this paper I present average contents of trace elements, their distribution and mutual relations of macro- to microelements and between microelements. I also show dependence of the content of microelements on the amount of olivine und pyroxenes indicating different sings in the content of some microelements in minerals of basalts in central and southeastern Slovakia.

Резюме: Базальты развиты на территории Словакии в области средней и юговосточной Словакии. В статье приведятся среднее содержание редких элементов, их расширение и взаимные связи макроэлементов с микроэлементами и связь микроэлементов друг с другом. Далее подается зависимость содержания микроэлементов от количества оливина и пироксена с указанием на отличительные знаки в содержании некоторых микроэлементов в минералах в базальтах средней и юговосточной Словакии.

Introduction

Basalts in Slovakia fall in its origin into the final stage of the development of the Carpathian orogene. They are found in the region of central and southeastern Slovakia in numerous bodies, predominantly in the form of lava streams and less as dykes. Pyroclastic material is represented by tuffs, tuffites and shreds. Basalts are mostly spread by us in southeastern Slovakia (Fig. 1), where they are found in the Upland of Fiľakovo and at the margins of the Rimava and Lučenec Basin. In the time of their origin they fall into the Upper Pliocene to Lower Pleistocene (O. Fejfar, 1957; V. Čechovič 1959). In central Slovakia basalts are spread considerably less. They are found in the Mountains of Štiavnica and Javorie (Fig. 2). For determination of the age of basalts from central Slovakia there are no evidences by fauna and stating their age as Pliocene to Pleistocene is relative, derived from superposition to the underlying andesite and rhyolite complexes and compared to basalts of southeastern Slovakia.

As to their petrography basalts were treated by F. Fiala (1938, 1952) and recently their detailed petrographic-petrochemic characterization from central Slovakia was presented by M. Šímová (1965) and from southeastern Slovakia by A. Miháliková (1966). They distinguished several petrographic types of basalts like basanitoids, limburgitoid basanites, basanites, amphibole and plagioklase basalts. All the distinguished types include olivine. Their chemism and petrographic composition are given in tab. 1, 2. The basalts of southeastern Slovakia are designated by A. Miháliková (1966) as exclusively alkaline while these from central Slovakia are not exclusively alkaline, they acquired the more alkaline character by magma differentiation (M. Šímová 1965). Both the authors agree that basalts originated from magma of alkaline-calcareous character and as a consequence of differentiation the magma has acquired a more alkaline character, getting graduały poorer in silicon.

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The goal of the presented paper is to continue in the foregoing works, to record and clear up distribution of microelements and their relation to macroelements and mineralogical composition of basalts.

Methods of Investigation

The study of trace elements was performed at eighteen localities. For determination of trace elements the same samples were used as for chemical silicate analyses and petrographic analyses as mentioned in the works by A. Miháliková (1966), M. Šímová (1965). The samples for quantitative spectral analysis were diluted after homogenization in the ratio 1 : 1 with garphic powder, into which inner standards were admixed, and that Pd and In in concentration of hundredths. The analyses were performed on spectrograph E 492, exposure 60 seconds at 6 amperes and after a pause of 15 seconds 45 seconds at 9 amperes. The spectra were registered on photographic plate Agfa Blau Extrahart. Rb and Li were ascertained particularly on spectrograph ISP 51, dilution of homogenized samples 1 : 1 with NaCl and scintillation was carried

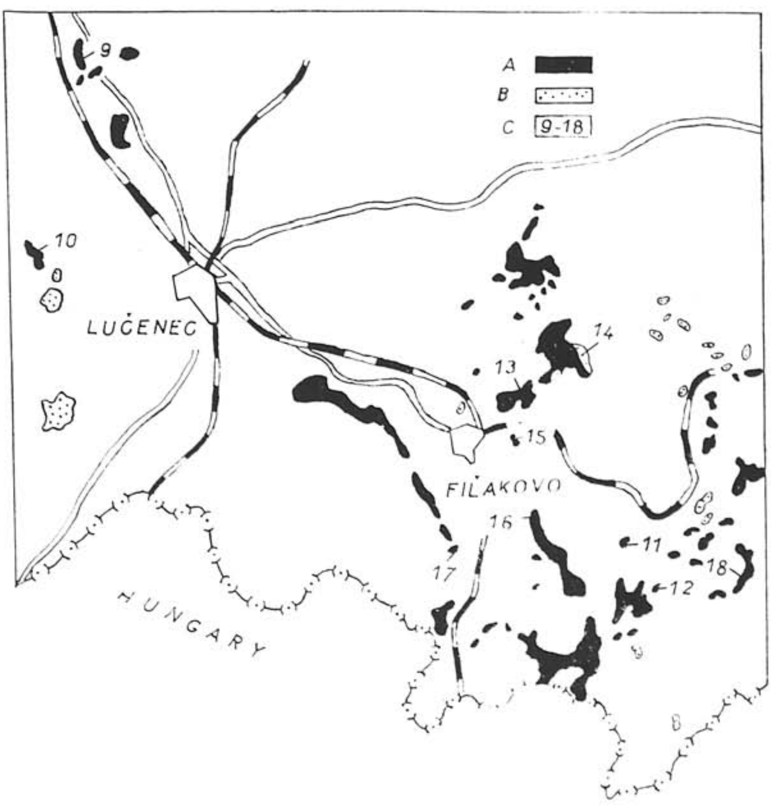

Fig. 1. Scheme of extension of basalts in southeastern Slovakia. A — basalts, B — pyroclastic material of basalts, C — places of sampling. Explanations numbers 1—8 are with table 1.)

out at 6 amperes in one minute. The spectra were registered on photographic plate I 850. The details about the applied methods are in the work by G. K u p č o (1963). The samples were analysed by M. K l i n č e k o v á in the laboratory of the Dionýz Štúr Institute of Geology.

From each studied locality the same sample was analyzed five times by quantitative spectral analysis in order to exclude accidental error and form these results the average was made for each locality mentioned in tables.

When the amount of the microelement was below the sensitivity minimum of the picture, it was taken as zero in determination of average values. In compiling distribution curves all determinations of microelements were applied (5 times from each locality) in order to catch all the width of their distribution and dispersion. In further evaluation, I only apply average values for each locality.

Differentiation of Magma

Following crystallization of the magma, from which the discussed basalts were formed, I set out from reaction series found out in petrographic study (M. Š í m o v á 1965, A. M i h á l i k o v á 1966), for dark-coloured minerals — olivine-pyroxene-biotite and for light-coloured minerals — Ca plagiklase-Na plagioklase-nepheline and from chemical composition of basalts. I also set out from the fact that olivine and pyroxene crystallizing from the magma as early minerals under higher temperatures include more magnesium than iron in structural lattices (T. B a r t h 1956), whereby in the melt the content of iron relatively increases and the ratio of magnesium to iron is changing. On the other hand in initial stages of magma crystallization plagioklases richer in

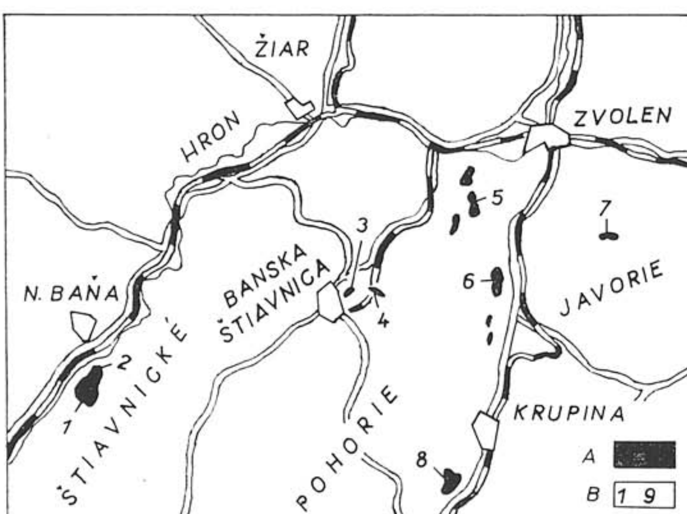

Fig. 2. Scheme of extension of basalts in central Slovakia. A — basalts, B — places of sampling. (Explanations to numbers 9 to 18 are with table 2.)

anorthite constituent originate and increasingly with magma crystallization the ratio of albite and anorthite constituent is changing relatively as it is evident from the petrographic studies of the foregoing authors. Expressing the succession of crystallizing differentiation. I chose the ratio of iron to magnesium as $\frac{Fe^{3+} + Fe^{2+} + Mn}{Mg + Fe^{3+} + Fe^{2+} + Mn}$ against the ratio of albite to anorthite calculated from chemical analyses. Since the prevailing part of the studied rocks includes nepheline. I added it to albite as $\frac{\text{norm. alb} + \text{neph.}}{\text{norm. anor.} + \text{alb.} + \text{neph.}}$. It is evident from graphic presentation of the ratio of iron to magnesium against that of albite to anorthite (fig. 3) that basalts are forming a relatively continuous scale of crystallizational differentiation of the magma with linear trend of succession. As it is evident from the distribution of the points of projecitons. basalts from central and south-eastern Slovakia are mutually overalapping in direction of the linear trend of magma differentiation. With increasing magma differentiation representation of magnesium lowers distinctly (fig. 4), what roughly corresponds to the amount of olivine in rocks (tab. 1. 2), similarly as at megnesium also representation of calcium decreases. The content of sodium an silicon increases

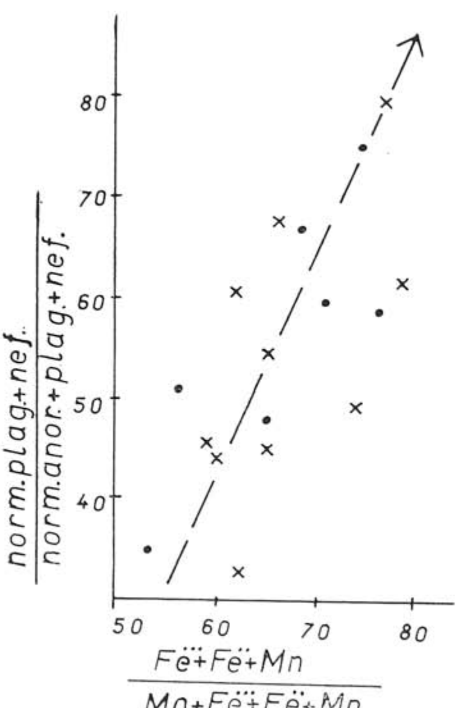

Fig. 3. Graphic presentation of magma crystallization.

with gradual crystallization of magma in the melt (fig. 4) while representation of aluminium and potasium does not show any marked changes. This succession of magma crystallization is also confirmed by representation of chromium. nickel. cobalt and lithium showing a tendency of accumulation in iron-magnesium minerals in the first stages of crystallization. Their representation in basalts corresponds to the ratio of iron to magnesium (fig. 5). The mentioned analysis shows that the basalts of Slovakia originated. from one mother rock. from which different petrographic rock types have formed by almost continuous differentiations. It is to remark that with increasing differentiation a tendency of magma enrichment in silicon and sodium appears indicating the succession of differentiation of this basic magma towards more acid members. As most basic in the region of central Slovakia appeared the rocks from Banská Belá and Banská

Štiavnica and the most acid ones the basalts from Bacúrov and Lomno. In southeastern Slovakia the most basic rocks are found in Hajnačka and Šurica and almost acid the basalts from the locality Borkul — Ragáč were proved.

Distribution of Trace Elements and Their Binding to Minerals

In this chapter I present distribution of trace elements, their mutual relations as well as relations of micro- to macroelements and different relations of microelements to some minerals in basalts of central and southeastern Slovakia.

Chromium is distributed in basalts in a relatively wide scale. In the region of central Slovakia its content varies within the range of 20 to 500 ppm. The curve of arithmetic frequency of chromium (fig. 6d) is articulated with several peaks. The most distinct peak is between 0 and 50 ppm, where basalts from the localities of Devičie and

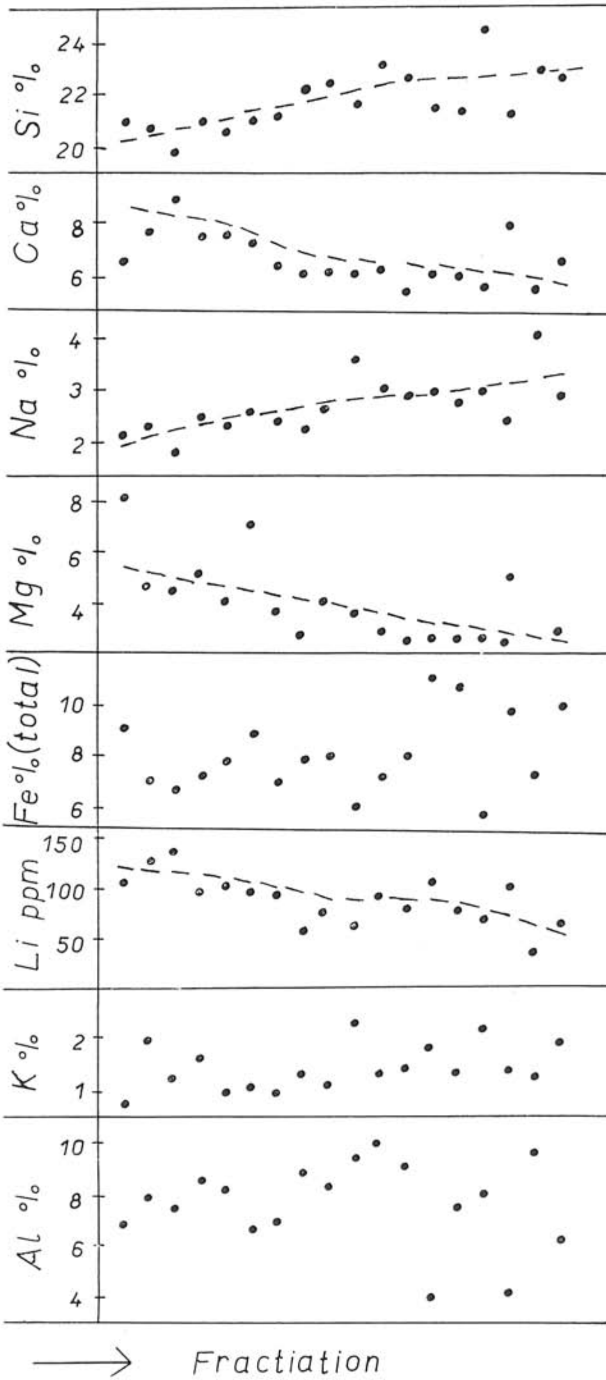

Fig. 4. Graphic presentation of the change of the content of element in direction of magma crystallization.

Table 1. Chemical and Mineralogical Composition of Basalts from Central Slovakia

Weight %

	Basanites				Amphibole basalts	Plagioklase basalts		
	1	2	3	4	5	6	7	8
SiO_2	46.17	45.31	45.21	45.21	53.27	48.83	49.02	50.40
TiO_2	1.72	1.88	1.71	1.00	1.60	1.98	1.89	1.00
Al_2O_3	15.14	13.17	17.38	13.10	15.41	17.59	16.90	17.69
Fe_2O_3	7.36	3.56	4.62	4.22	4.22	4.22	4.43	4.16
FeO	8.09	8.39	4.86	8.07	3.72	6.85	5.55	5.67
MnO	0.14	0.17	0.19	0.17	0.21	0.19	0.63	0.22
MgO	4.74	11.96	6.41	13.47	4.53	4.27	4.42	4.99
CaO	8.80	10.39	9.10	9.21	8.26	7.94	6.90	8.84
Na_2O	4.16	2.80	3.35	2.94	4.13	4.06	5.70	4.40
K_2O	2.28	1.32	1.27	1.06	2.80	1.80	2.10	1.70
P_2O_5	0.94	0.57	0.36	0.41	0.23	0.39	0.60	0.63
H_2O^+	0.06	0.12	3.18	0.11	0.29	0.43	0.55	1.14
H_2O^-	0.38	0.04	1.62	0.21	0.17	0.86	0.75	0.46
Sum:	99.98	99.69	99.60	99.18	99.34	99.41	99.44	100.30

Modal Composition

	1	2	3	4	5	6	7	8
Plagioklase	40.12	10.30	30.90	28.20	36.07	59.10	69.60	59.70
Olivine	4.05	22.10	29.30	31.50	9.30	15.00	5.60	13.00
Nepheline	8.64	7.40	3.50	7.20	—	—	—	1.40
Amphibole	—	—	—	—	27.60	—	—	1.40
Ti-augite	31.93	55.00	28.80	—	—	—	—	—
Ca-augite	3.11	—	—	—	—	—	—	—
Aegirine	3.31	—	—	—	—	—	—	—
Pyroxene	—	—	—	24.90	11.70	16.70	14.00	20.40
Anarthoclase	—	—	—	—	—	—	—	2.00
Rhönite	—	—	—	—	7.30	—	—	—
Accessories	—	—	7.50	—	—	—	—	—
Amphibole (needles) + Apatite + Nepheline etc.	3.00	—	—	8.50	—	1.52	1.80	—
Magnetite and ore min.	6.35	5.10	—	—	—	5.40	6.90	3.10
Nepheline + Zeolites etc.	—	—	—	—	7.60	—	2.10	—
Analcime	—	—	—	—	—	2.30	—	—
Groundmass + Accessories + Zeolites	—	—	—	—	—	—	—	4.80
Sum:	99.51	99.90	100.00	100.30	99.57	100.02	98.00	99.80

Compiled according to the work by M. Šimová (1965). Localities: 1. Tekovská Breznica, 2. Brehy, 3. Banská Štiavnica — Kalvária, 4. Banská Belá, 5. Bacúrov, 6. Dobrá Niva, 7. Lomno, 8. Devičie.

Table 2. Chemical and Mineralogical Composition of Basalts from Southeastern Slovakia

Weight %

	Basanitoids		Limburgitoid basanites		Nepheline basanites					
	9	10	11	12	13	14	15	16	17	18
SiO_2	48,28	46,10	42,75	44,69	45,53	44,92	44,23	48,53	46,53	42,75
TiO_2	2,33	2,55	1,93	1,90	2,70	1,88	2,66	1,88	1,71	1,93
Al_2O_3	17,22	14,71	14,42	15,15	10,76	16,59	15,87	16,03	18,21	14,42
Fe_2O_3	4,58	6,95	4,05	3,98	6,70	3,43	5,01	2,65	3,21	4,05
FeO	6,17	6,56	5,19	5,60	6,70	6,32	5,79	8,07	5,15	5,19
MnO	0,22	0,18	0,32	0,27	0,20	0,24	0,17	0,26	0,32	0,32
MgO	4,69	4,69	7,86	7,78	8,60	9,03	7,21	7,32	6,34	7,86
CaO	8,68	8,89	12,79	11,07	11,43	10,70	11,01	9,04	8,69	12,79
Na_2O	3,19	3,78	2,51	3,27	3,15	3,56	3,15	3,64	5,09	2,51
K_2O	1,70	1,30	1,57	2,52	1,83	2,10	1,30	1,36	2,90	1,57
P_2O_5	0,19	0,55	0,26	0,22	tr.	0,12	tr.	0,17	0,51	0,26
CO_2	0,16	2,74	2,18	1,12	0,34	0,41	0,10	0,30	0,11	2,18
H_2O	0,29	0,33	1,71	0,83	1,28	0,38	0,50	0,32	0,29	1,71
H_2O^-	2,35	0,88	2,19	1,58	0,78	0,86	2,87	0,92	0,94	0,19
Sum:	100,05	100,21	99,73	99,98	100,00	100,54	99,87	100,49	100,00	99,73

Modal Composition

	9	10	11	12	13	14	15	16	17	18
Plagioklase	60,02	20,20	19,86	10,57	10,58	19,05	11,23	27,69	35,96	23,09
Olivine	8,40	2,81	13,25	18,57	26,95	31,02	14,39	23,87	11,08	5,26
Nepheline	0,80	3,48	—	—	16,61	8,81	34,13	19,66	12,51	21,61
Amphibole	—	2,44	—	0,69	—	—	—	—	—	—
Pyroxene	—	7,13	5,43	15,13	35,72	—	5,49	10,18	—	24,94
Ti-augite	—	—	—	—	0,46	18,93	—	—	—	—
Augite	6,66	—	4,31	11,85	—	29,83	—	6,31	12,32	8,55
Aegirine	—	—	—	0,57	—	0,34	2,00	—	—	0,32
Klinoenstatite	0,07	0,73	—	6,15	—	—	4,72	0,78	0,32	2,18
Opacite min. (amph. pyr.)										
Palag.	2,10	—	0,62	0,18	—	—	—	—	—	—
Parg.	—	—	0,17	9,94	1,11	—	2	0,66	—	0,47
Groundmass	6,48	29,29	26,93	22,09	—	3,48	—	—	16,08	—
Arag. + calcite	—	9,72	7,27	—	—	0,40	—	—	0,64	—
Quartz	—	—	0,19	0,59	—	—	—	—	—	—
Zeolite/Magnetite	15,47	14,20	16,70	10,67	8,45	6,55	6,86	10,59	10,81	12,58
Apatite	—	—	—	—	—	—	—	0,26	—	—
Rhönite	—	—	5,27	—	0,56	—	0,25	—	—	—
Sum:	100,00	90,00	100,00	90,00	90,00	99,94	100,00	100,00	100,00	100,00

Compiled according to the work by A. Miháliková (1966). Localities: 9. Podrečany, 10. Mášková, 11. Šurice, 12. Hajnáčka, 13. Bulhary, 14. Konrádovce, 15. Fiľakovo, 16. Belina, 17. Radzovce, 18. Borkul-Ragáč.

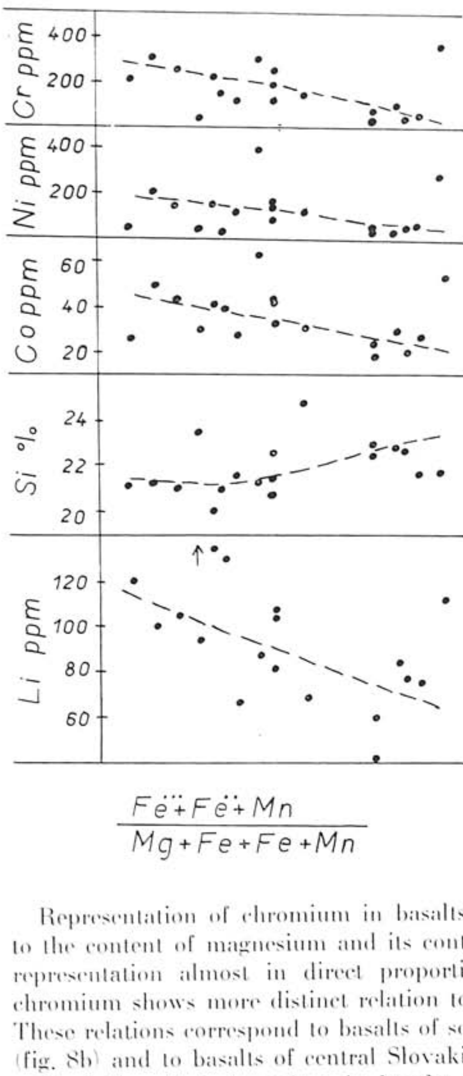

Fig. 5 Graphic presentation of the change in content of Ni, Co, Si, Li, to relation of Fe and Mg.

Lomno belong. The second peak is from 150 to 200 ppm. with basalts from Bacúrovo and towards higher concentrations the curve is slightly falling and includes basalts from other localities. According to average analyses (tab. 3) concentration of chromium varies in basalts of central Slovakia from 30 to 380 ppm and the average value of chromium for this region is 200 ppm. Smaller dispersion of chromium concentration is present in basalts of southeastern Slovakia (from 20 to 350 ppm). The curve of arithmetic frequency does not form any distinct peak of culmination (fig. 6d) but is flat in shape. According to average analyses (tab. 4) representation of chromium varies from 39 to 249 ppm. The average value of chromium content for basalts of southeastern Slovakia is 153 ppm (tab. 5).

Representation of chromium in basalts of southeastern Slovakia is in direct relation to the content of magnesium and its content decreases with the decrease of magnesium representation almost in direct proportion (fig. 7a). In basalts of central Slovakia chromium shows more distinct relation to bivalent iron than to magnesium (fig. 7a, b). These relations correspond to basalts of southeastern Slovakia with the content of olivine (fig. 8b) and to basalts of central Slovakia with the content of pyroxenes (fig. 9a). It is evident then that chromium in basalts of southeastern Slovakia is bound to olivine, where it substitutes magnesium, while in basalts of central Slovakia it substitutes iron in pyroxenes.

N i c k e l shows in basalts of central Slovakia similar dispersion of concentrations as cobalt, and that within the range of 14 to 500 ppm. The curve of arithmetic frequency for nickel (fig. 6g) shows distinct peak of culmination between 0 and 50 ppm, where basalts from the localities of Banská Belá, Dobrá Niva, Lomno and Devičie belong. Towards higher concentrations the curve acquires a slightly falling course with several little distinct peaks. The concentration of nickel varies from 22 to 295 ppm (tab. 3) at the studied localities of central Slovakia according the average contents. The average content of nickel is 143 ppm for this region. Nickel shows narrower dispersion of concentration in basalts of southeastern Slovakia, 20 to 200 ppm. Its frequency curve

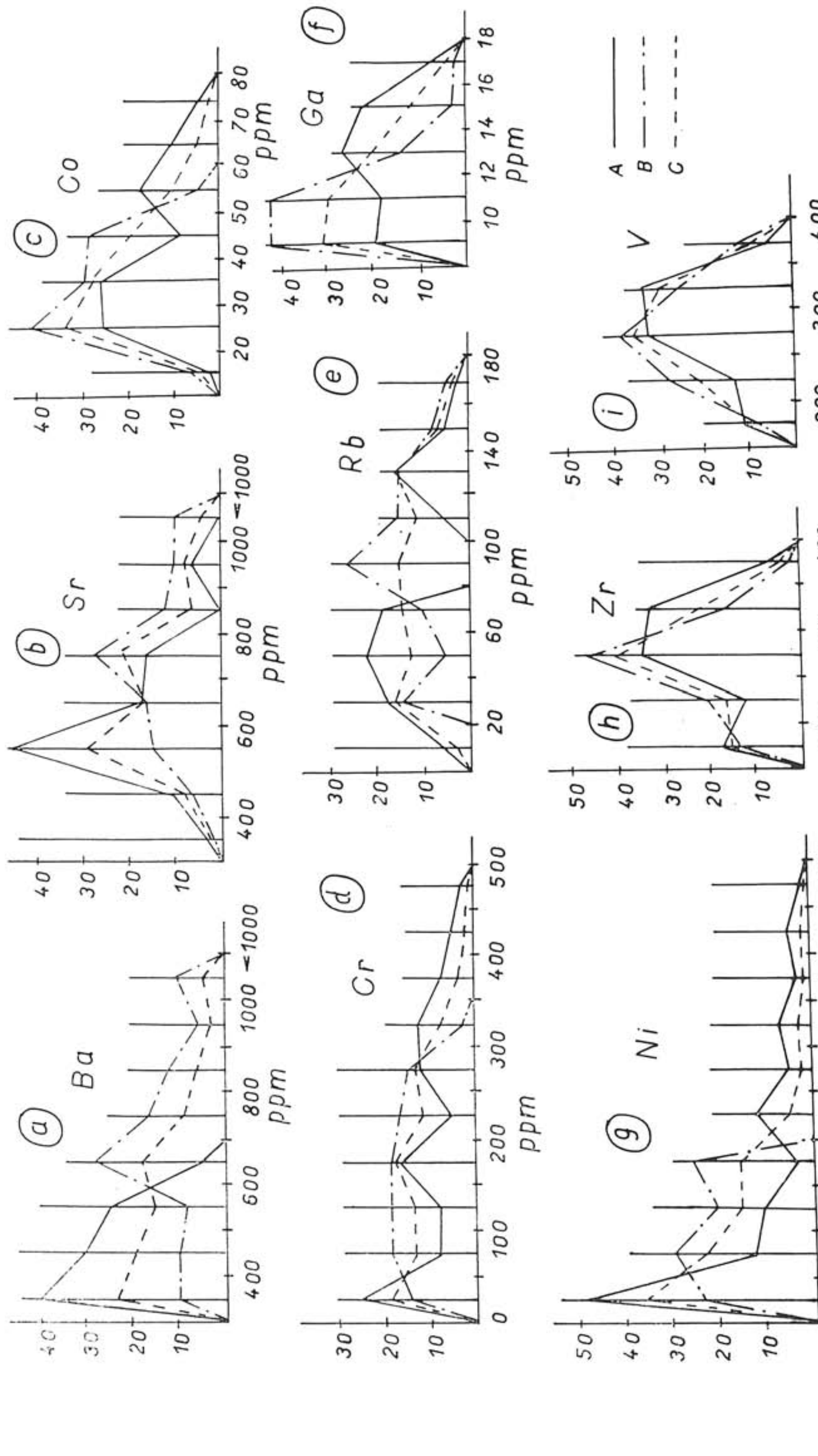

Fig. 6. Curves of relative frequency for Ba, Sr, Co, Cr, Rb, Ga, Ni, Zr and V. A — basalts from the region of central Slovakia, B — basalts from the region of southeastern Slovakia, C — basalts from Slovakia on the whole.

does not form any distinct peak, but two smaller peaks, the first between 50 and 100 ppm, where the basalts from Podrečany, Mášková and Fiľakovo belong. The second peak is between 150 and 200 ppm, where the basalts from Bulhary, Konrádov-

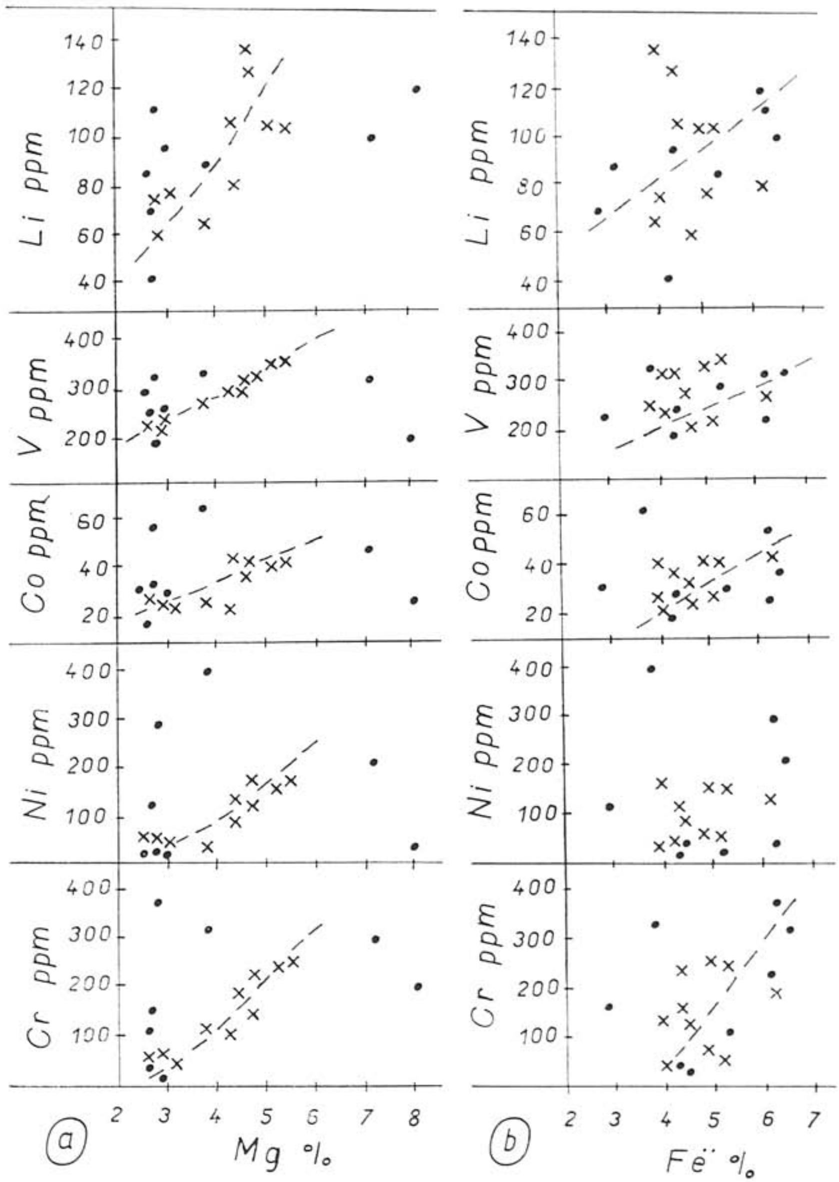

Fig. 7. Relation of Cr, Ni, Co, V and Li to Mg and Fe^{+2}. ● — basalts from the region of central Slovakia, x — basalts from the region of southeastern Slovakia.

Table 3. Content of Elements in Basalt from Central Slovakia in % and ppm (Trace Elements — Average of 5 Analyses)

	1	2	3	4	5	6	7	8
	Basanites				Amphibole basalts	Plagioklase basalts		
	%							
Si	21,58	21,18	21,29	21,13	24,90	22,83	22,91	23,56
Ti	1,03	1,13	1,03	0,60	0,96	1,19	1,13	0,60
Al	4,00	6,97	9,19	6,93	8,16	9,31	8,94	10,29
Fe^{3+}	5,15	2,49	3,23	2,95	2,95	2,95	3,09	2,91
Fe^{2+}	6,29	6,49	3,78	6,27	2,88	5,32	4,31	4,41
Mn	0,10	0,13	0,15	0,13	0,18	0,15	0,49	0,17
Mg	2,86	7,21	3,87	8,12	2,73	2,58	2,67	3,01
Ca	6,29	7,43	6,50	6,58	5,90	5,67	4,93	6,32
Na	3,03	2,08	2,49	2,18	3,06	3,01	4,23	3,26
K	1,89	1,09	1,05	0,88	2,32	1,49	1,74	1,41
P	0,41	0,49	0,16	0,18	0,10	0,17	0,26	0,27
	ppm							
Pb	—	—	10	—	10	10	10	10
Ga	13	14	11	12	14	14	14	13
Cu	20	27	21	20	12	10	11	10
Ag	10	10	10	10	10	10	10	10
V	322	321	329	205	237	289	194	254
Zr	250	326	256	215	301	390	238	270
Ni	295	213	401	38	122	22	23	30
Co	57	65	26	32	32	32	19	30
Cr	380	321	332	227	159	110	38	30
Ba	372	531	352	408	534	439	525	352
Sr	526	865	526	646	581	670	529	536
Rb	48	63	32	38	137	49	104	123
Li	113	101	88	120	70	85	40	96

ce and Šurica belong. The average content of nickel in basalts of southeastern Slovakia is 103 ppm (tab. 4).

Representation of nickel in basalt of southeastern Slovakia corresponds to magnesium. With increasing content of magnesium also the content of nickel increases (fig. 7a). In basalts of central Slovakia relation of nickel to bivalent iron is more distinct than to magnesium (fig. 7). These relations correspond differently in both the regions with the content of olivine and pyroxenes in basalts (fig. 8, 9). In basalts of southestern Slovakia nickel is probably bound in olivines, where it substitutes magnesium, and in basalt of central Slovakia it is bound in pyroxenes, probably substituting bivalent iron.

Cobalt is scattered in the range of 10 to 8 ppm, what corresponds to its dispersion of concentration for basalts of central Slovakia, where the curve of relative frequency (fig. 6e) shows two distinct peaks. The first peak is in lower concentration, where average values of cobalt of the predominating part of basalts belong (Banská Belá, Bacúrov, Dobrá Niva, Lomno, Devičie) with Co content of 19 to 32 ppm and the smaller part of basalts (Tekovská Breznica, Brehy, Banská Štiavnica) falls into the second peak of the frequency curve with the content of average analyses 79 to 65 ppm. Cobalt in

Table 4. Content of Elements in Basalts from Southeastern Slovakia
(Trace Elements — Average of 5 Analyses)

	Basanitoids		Limburgitoid basanites		Nepheline basanites					
	9	10	11	12	13	14	15	16	17	18
					%					
Si	22.57	21.55	19.98	20.89	21.28	21.03	20.68	22.69	21.75	22.73
Ti	1.40	1.53	1.16	1.14	1.62	1.13	1.59	1.13	1.03	1.29
Al	9.11	7.78	7.63	8.02	4.18	8.78	8.40	8.48	9.64	6.40
Fe^3	3.20	4.86	2.83	2.78	4.69	2.40	3.50	1.85	2.25	6.01
Fe^2	4.79	5.10	4.03	4.35	5.21	4.91	4.50	6.27	4.00	4.09
Mn	0.17	0.14	0.25	0.21	0.15	0.19	0.13	0.20	0.25	0.12
Mg	2.83	2.75	4.74	4.69	5.19	5.45	4.35	4.42	3.82	3.00
Ca	6.20	6.35	9.14	7.91	8.17	7.65	7.87	6.46	6.21	6.40
Na	2.37	2.80	1.86	2.43	2.34	2.64	2.34	2.70	3.78	2.93
K	1.41	1.51	1.30	2.09	1.52	1.74	1.08	1.13	2.40	2.05
P	0.08	0.24	0.11	0.09	traces	0.06	traces	0.07	0.22	0.19
					ppm					
Pb	—	—	—	10	10	10	10	10	10	10
Ga	12	11	10	11	10	12	12	11	10	11
Cu	13	13	16	12	11	15	19	23	12	18
Ag	10	10	10	10	10	10	10	10	10	10
V	216	224	312	326	349	353	286	288	261	242
Zr	346	291	253	248	30	233	244	215	252	245
Ni	57	58	173	121	160	159	87	129	43	39
Co	26	29	42	39	42	44	34	45	28	23
Cr	68	57	246	160	249	265	117	199	133	39
Ba	661	476	667	948	671	652	709	383	1000	888
Sr	709	79	603	867	705	687	740	486	1000	767
Rb	124	29	119	104	78	96	101	40	149	121
Li	61	48	147	129	105	105	103	82	66	77

basalts of southeastern Slovakia is distributed in the range of 10 to 60 ppm and has a distinct amplitude of the curve of relative frequency (fig. 6a) in the range of 20 to 50 ppm, where all basalts of this region belong with representation of cobalt in the range of 23 to 45 ppm according to average contents (tab. 4). The average content of cobalts in basalts of southeastern Slovakia is 35 ppm (tab. 5).

Representation of cobalt in basalts shows dependence on the content of magnesium (fig. 7a), which is more distinct for basalts of southeastern Slovakia than for those of central Slovakia, where relation of cobalt to bivalent iron is more distinct (fig. 7b). These deviations are also manifested in the content of olivine and pyroxenes. The content of cobalt in basalts of southeastern Slovakia corresponds to the content of olivine (fig. 8), where it is probably bound to magnesium, while in basalts of central Slovakia its concent corresponds more distinctly to the amount of pyroxenes (fig. 9), in which it probably substitutes bivalent iron and perhaps also in olivine as this relation is little distinct. The increase of the content of cobalt is accompanied by the increase of the content of nickel almost in direct proportion as presented in fig. 10.

Vanadium is represented in concentration from 150 to 400 ppm and its representation in basalts of central and southeastern Slovakia does not show any essential differences. The curve of arithmetic frequency for vanadium (fig. 6j) is nearly regular. Its content in basalts of central Slovakia varies from 194 to 329 ppm (tab. 3) and the total average for central Slovakia is 269 ppm (tab. 5). In basalts of southeastern Slovakia the content of vanadium varies from 216 to 353 ppm (tab. 4). The total average for basalts of southeastern Slovakia is 286 ppm.

Representation of vanadium corresponds to the content of magnesium. With in-

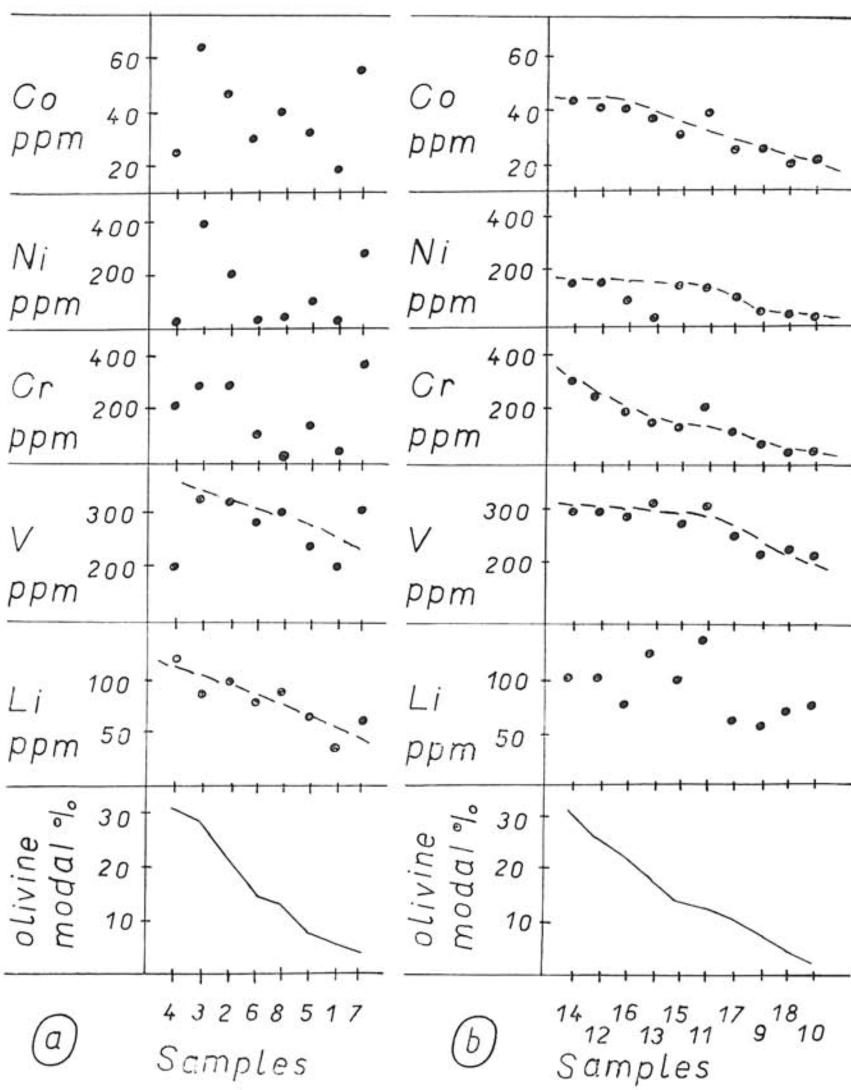

Fig. 8. Comparison of the content of Co, Ni, Cr, V, Li and the amount of olivine. a — basalts from the region of central Slovakia, b — basalts from the region of southeastern Slovakia.

creasing content of magnesium also vanadium content increases (fig. 7a). Relation of vanadium and magnesium is more distinct in basalts of southeastern Slovakia than in the region of central Slovakia, where its relation to bivalent iron is more distinct (fig. 7b) and with increasing content of bivalent iron also that of vanadium increases.

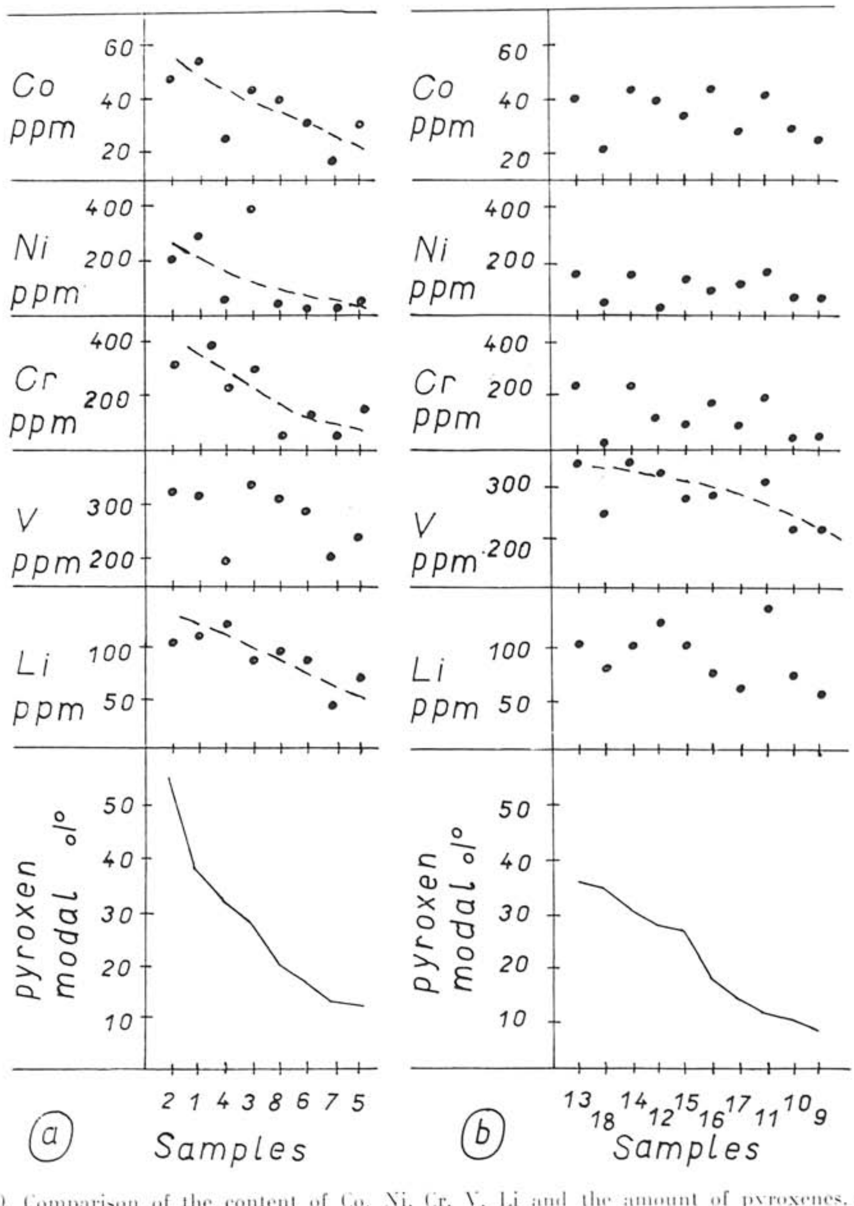

Fig. 9. Comparison of the content of Co, Ni, Cr, V, Li and the amount of pyroxenes. a — basalts from the region of central Slovakia, b — basalts from the region of southeastern Slovakia.

These relations correspond to the amount of olivine and pyroxenes in basalts. With decreasing content of olivine in basalts vanadium shows the tendency of smaller representation, distinct for the region of central Slovakia (fig. 8). In the region of southeastern Slovakia it shows also relation to the content of pyroxenes (fig. 9) while in basalts of central Slovakia this relation of vanadium to the amount of pyroxenes was not evident. Vanadium probably substitutes iron and magnesium in pyroxenes as well as in olivines, in basalts of central Slovakia it corresponds more to the amount of olivine and in southeastern Slovakia its concentration is more distinct in dependence on the amount of olivine.

Strontium is distributed in the range of 300 to 1000 ppm and only at the locality of Radzovce its content attains > 1000 ppm. The curve of arithmetic frequency (fig. 6b) for central Slovakia has a distinct peak between 400 and 700 ppm, where according to the average contents all localities of this region belong besides Brehy with higher strontium content (865 ppm). The average content of strontium in basalts of central Slovakia is 610 ppm. The curve of arithmetic frequency from basalts of southeastern Slovakia reaches a distinct peak between 700 and 800 ppm, including the localities of Podrečany, Bulhary, Fiľakovo and Borkul — Ragáč. The basalts in southeastern Slovakia are richer in strontium than those of central Slovakia and the average content of strontium is 664 ppm.

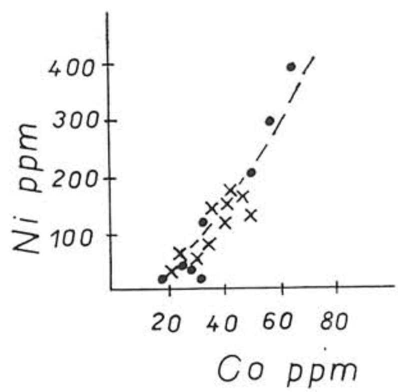

Fig. 10. Relation of Ni, to Co. ● — basalts from the region of central Slovakia, x — basalts from the region of southeastern Slovakia.

Strontium displays distinct relation to barium. With increasing representation of strontium the content of barium increases. Points of projekction in fig. 11a are distributed in two lines. Near the upper line basalts from southeastern Slovakia and two localities of central Slovakia (Bacúrov, Lomno) are placed, with higher content of barium. At the lower line basalts from central Slovakia are placed, characterized by lower content of barium. Strontium shows also distinct relation to calcium, mainly in basalts from central Slovakia, while the projection points of basalts from southeastern Slovakia are almost irregularly dispersed (fig. 11a). Representation of strontium in basalts of southeastern Slovakia corresponds to the content of potassium (fig. 11b).

Barium is represented in the range of 300 to 1000 ppm, only at the locality of Radzovce it attains > 1000 ppm. The differences in distribution of barium in basalts of central and southeastern Slovakia are conspicuous. In central Slovakia barium is present in the range of 300 to 700 ppm. The point of culmination of the curve of arithmetic frequency (fig. 6a) falls into the concentration of 300 to 500 ppm, including the predominating part of basalts. The average values from the localities vary from 352 to 354 ppm and the average content of barium for this region is 414 ppm. In basalts of southeastern Slovakia the range of barium distribution is larger, from 300 to 1000 ppm. The point of culmination of the curve of arithmetic frequency is in the range of 600 to 700 ppm, where the half of studied basalts belongs. The average value of barium concentration for basalts of southeastern Slovakia is 705 ppm (fig. 12).

Barium shows relation to potassium and sodium differently in basalts of central and southeastern Slovakia. The content of barium increases with increasing content of potassium in the region of southeastern Slovakia (fig. 11b) and in central Slovakia relation of barium to calcium is more distinct (fig. 11a).

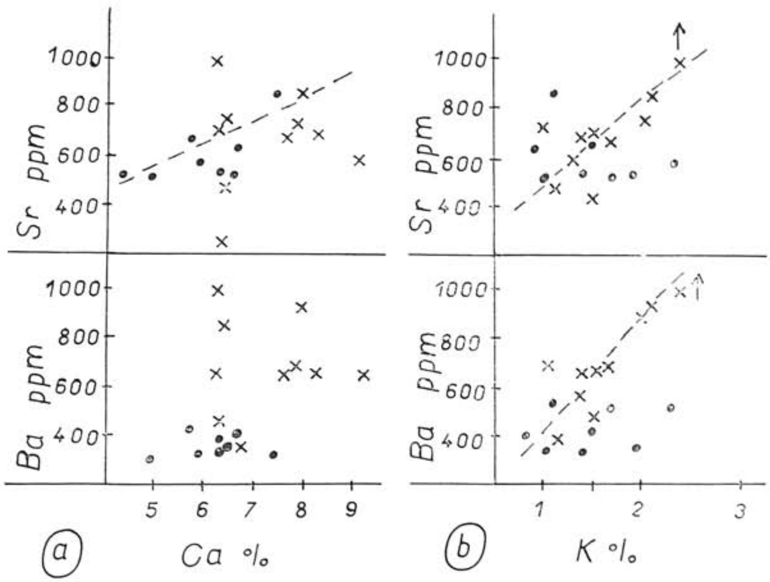

Fig. 11. Relation of Sr and Ba to Ca and K. ● — basalts from the region of central Slovakia, x — basalts from the region of southeastern Slovakia.

R u b i d i u m is considerably irregularly distributed. It is distributed in the range of 5 to 180 ppm. According to average analyses its content varies from 32 to 137 ppm in basalts of central Slovakia (tab. 3). Great variability in reprentation of rubidium is also manifested on the curves of arithmetic frequency. The curve for basalts of central Slovakia consists of two parts. The first part is up to 80 ppm, with flat and almost regular course, including plagioklase basalts from Dobrá Niva and basanites (tab. 3). The second part of the curve lies in the range of 100 to 180 ppm with the peak between 120 to 140 ppm (fig. 6e), what corresponds to average contents of rubidium in plagioklase basalts from Devičie and Lomno and in amphibole basalts. The average content of rubidium in basalts of central Slovakia is 74 ppm. The frequency curve for basalts of southeastern Slovakia forms two distinct peaks, one between 20 and 40 ppm, corresponding to average values of rubidium in basanitoid from Šurica and nepheline basanitoid from Belina. The second peak is between 60 and 140 ppm, where the predominating part of basalts belong. According to average analyses its concentration varies from 29 to 149 ppm and the average value is 96 ppm in southeastern Slovakia. In representation of rubidium relation to potassium was evident. With increasing content of potassium also that of Rb increases (fig. 13) and similarly as potassium also rubidium does not shows distinct relations to other elements, not even to representation of minerals in basalts, but is manifesting as element considerably scattered.

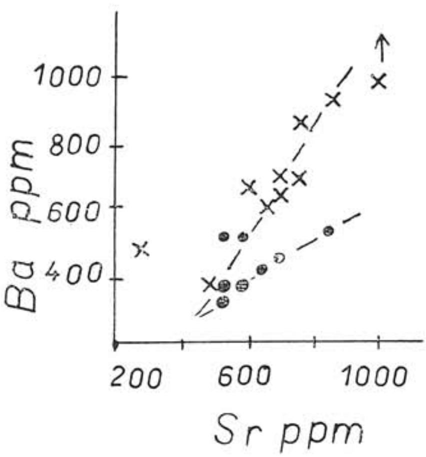

Fig. 12. Relation of Ba to Sr. ⊛ — basalts from the region of central Slovakia, x — basalts from the region of southeastern Slovakia.

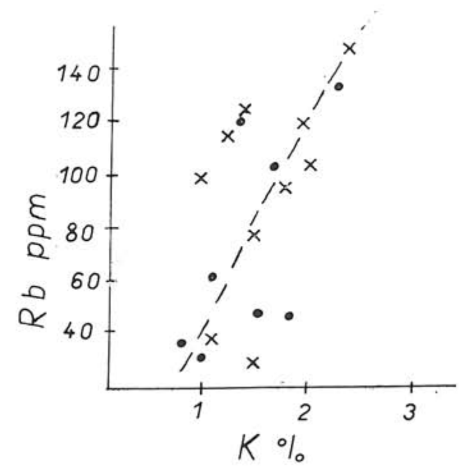

Fig. 13. Relation of Rb to K. ● — basalts from the region of central Slovakia, x — basalts from the region of southeastern Slovakia.

L i t h i u m is distributed in basalts in the range of 15 to 200 ppm. The curve of arithmetic frequency (fig. 14a) for basalts of central Slovakia forms a flat peak between 80 and 120 ppm, where average contents of lithium from the predominating part of localities of basalts belong. Average contents of Li vary from 40 to 120 ppm in basalts of central Slovakia (tab. 3). Basalts from southeastern Slovakia shows two distinct peaks at the curve of arithmetic frequency. One is from 60 to 100 ppm, includings the half of the studied basalts and the second from 120 to 140 ppm, closest to the content of lithium in limburgitoid basanites.

Representation of lithium increases in rocks with increasing content of calcium (fig. 15). It also shows distinct tendency of decreasing content with the increase of the vaule of the ratio of iron magnesium (fig. 5). Dependence of lithium on magnesium is more distinct in basalts of southeastern Slovakia (fig. 7a) than in the region of central Slovakia, where lithium shows more distinct, relation to bivalent iron (fig. 7b). These dependences are also manifested in relation to Fe-Mg minerals. In basalts of central Slovakia the content of lithium increases with increasing content of olivine and pyroxenes, in which it probably substitutes more iron than magnesium. In basalts from southeastern Slovakia relation of lithium to the content of olivine is more distinct (fig. 8, 9) than to the content of pyroxenes. It is evident from relation of lithium to magnesium as well as to the content of olivine that Li substitutes magnesium in olivines in basalts of southeastern Slovakia.

C o p p e r is represented in the range of 4 to 35 ppm. The peak of the curve of arithmetic frequency (fig. 14b) for central Slovakia falls into the concentration of 4 to 20 ppm and according to average contents at the mentioned localities its concentration varies from 10 to 27 ppm and the total average for central Slovakia is 16 ppm. The curve of arithmetic frequency for basalts of southeastern Slovakia has a distinct peak between 10 and 15 ppm. The average concentration of copper for this region is 15 ppm. In its representation copper does not shows more distinct relations to other elements, even not to minerals but it is found in basalts as an element considerably dispersed.

Zirconium is scattered in concentrations of 150 to 400 ppm in basalts (fig. 6b). Its concentrat varies frequently in the range of 250 to 300 ppm, including culmination points of the curves of arithmetic frequency. The average values of zirconium content vary from 215 to 301 ppm at the studied localities of basalts from central Slovakia and the average concentration for this region is 268 ppm. In the region of southeastern Slovakia average values of zirconium vary from 215 to 346 ppm at the studied localities of basalts, an anomalous low concentration was recorded at the locality of Bulhary (30 ppm). The average concentration of zirconium for the whole region of basalts of southeastern Slovakia is 237 ppm.

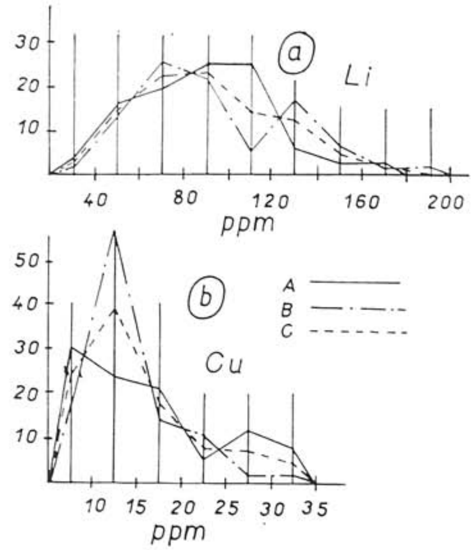

Fig. 14. Curves of arithmetic frequency for Li and Cu. A — basalts from the region of central Slovakia, B — basalts from the region of southeastern Slovakia.

Gallium is dispersed in the range of 8 to 18 ppm (fig. 6f). According to average contents at the localities in basalts of central Slovakia its concentration varies within the limits from 11 to 14 ppm and the culmination point of the curve of relative frequency falls into concentration 12 to 14 ppm. The average value of gallium repre-

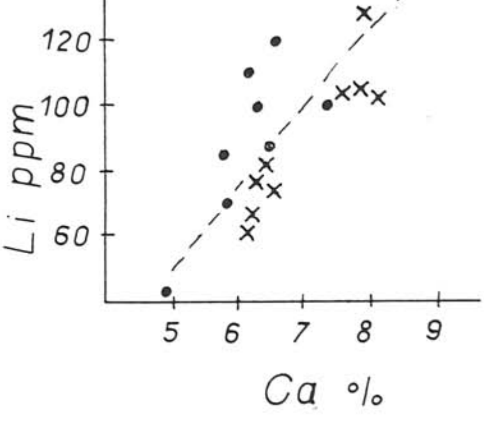

Fig. 15. Relation of Li to Ca. ● — basalts from the region of central Slovakia, x — basalts from the region of southeastern Slovakia.

sentation for basalts of central Slovakia is 13 ppm on the whole. Lower concentrations of gallium are found in southern Slovakia. where the culmination point of the curve of arithmetic frequency lies between 10 and 12 ppm and the average values of the studied localities are included there. Average concentration of gallium for basalts of southeastern Slovakia is 11 ppm on the whole and for basalts of whole Slovakia 12 ppm.

Comparison of Basalts from Slovakia with Basalts of Other Regions

Volcanites of the Carpathian orogene are in petrochemical studies mostly compared with the association of volcanites of oceanic islands. the chemism of which has been applied as comparing standards up to present. I chose from this region for comparison olivine basalts from Ireland and Hawaian tholeite basalts. I also mention predominantly olivine basalts from the region of Hakome. average values of elements of basalts from Kamèatka and the Kuril Islands and from platform basalts Siberian traps as also the clarks according to A. F. V i n o g r a d o v (1962).

According to the average contents of macroelements basalts from Slovakia are close to basalts from Kamèatka and the Kuril Islands. from which they differ in lower content of silicon and aluminium and somewhat higher representation of magnesium (tab. 5). Higher content of silicon and aluminium is found in basalts from the region of Hakome compared to basalts of Slovakia. Average contents of chemical elements according to A. F. V i n o g r a d o v as well as tholeite basalts from the Hawaian Islands shows smaller representation of Al. In basalts of Ireland and tholeite basalts from the Hawaian Islands representation of Mg is higher. Basalts from the islands of Oceania. Siberian traps and also the average values of A. F. V i n o g r a d o v have less alkalii than basalts from Slovakia. In the content of alkalii our basalts are very close to basalts from Kamèatka and the Kuril Islands.

Essentially greater differences than in macroelements are evident in microelements of the mentioned regions (tab. 5). Representation of gallium is almost three times higher in basalts from Ireland and almost twice higher in the region of Hakome and in tholeite basalts than in basalts from Slovakia with the content of gallium close to the clarks of A. F. V i n o g r a d o v. Basalts from Ireland shows enormously high representation of copper. twenty-six times more than our basalts while those from Kamèatka have four times more copper. The average values of A. F. V i n o g r a d o v are by one third lower and in Siberian traps the content of copper is roughly by one fourth smaller than in basalts of Slovakia. Basalts from Kamèatka and the Kuril Islands, Ireland and the region of Hakome are twice to three times richer in vanadium than our ones and tholeite basalts from the Hawaian Islands shows content of vanadium very close to our. The clarks according to A. P. V i n o g r a d o v are by about one fourth lower. Enormously low content of vanadium is mentioned from Siberian traps. Our basalts are richer in zirconium. nearly by 50 % in contrast to tholeite basalts from the Hawaian Islands and the basalts from Ireland. The content of zirconium from Kamèatka and the Kuril Islands as well as from the clark of A. P. V i n o g r a d o v are by three fifths lower and from the region of Hakome by four fifths. Basalts from Ireland show a content of nickel nearly eight times higher and tholeite basalts almost three times higher than our basalts. Basalts from the region of Kamèatka, to the contrary. show the content of nickel by one half and basalts from Hakome by six times lower than in Slovakia. The average content of Ni mentioned by A. P. V i n o g r a d o v is six times and in Siberian traps nine times lower than in basalts of Slovakia. Richest in cobalt are

Table 5. Average Contents of Elements in Basalts from Various Regions

	1	2	3	4	5	6	7	8	9
					%				
Si	22,42	21,51	21,96	23,62	22,76	21,10	24,04	24,01	23,63
Ti	0,96	1,3	1,13	0,57	0,81	0,70	0,48	0,9	1,57
Al	7,97	7,81	7,10	9,12	7,83	7,77	8,73	8,76	6,84
Fe^{3+}	3,46	3,44	3,45	3,68	2,31	1,90	2,16	8,56	1,70
Fe^{2+}	4,97	4,73	4,85	4,53	5,65	6,68	6,65		6,91
Mn	0,18	0,18	0,18	0,11	0,13	0,13	1,65	0,20	0,81
Mg	4,13	4,12	4,12	3,29	4,40	6,75	3,41	4,5	5,89
Ca	6,20	7,24	6,72	6,68	6,91	7,14	7,75	6,72	6,83
Na	2,92	2,62	2,77	2,15	1,75	1,52	1,36	1,94	1,75
K	1,48	1,62	1,55	1,16	0,70	0,18	0,39	0,83	0,38
P	0,25	0,19	0,22	—	0,04	0,09	0,04	0,14	1,38
					ppm				
Pb	10	10	10	—	—	20	—	8	—
Ga	13	11	12	—	—	33	23,33	18	21,61
Cu	16	15	15	63	4,3	400	—	10	—
Ag	10	10	10	—	—	—	415,28	—	—
V	269	286	277	520	17	630		200	247,61
Zr	268	237	252	100	—	180	53,06	100	125,43
Ni	143	103	123	61	13	900	23,00	16	398,48
Co	39	35	37	56	2,5	140	32,78	45	59,57
Cr	200	153	167	89	16	1600	62,94	200	500,0
Ba	414	705	558	130	40	310	118,06	300	83,26
Sr	609	664	636	—	43	680	265,28	440	377,17
Li	89	96	92	—	—	8	7,39	15	7,17
Rb	74	96	85	—	—	3	0,83	45	0,87

1. Basalts from central Slovakia (macroelements — average of 8 analyses, microelements — average of 4 analyses). 2. Basalts from southeastern Slovakia (macroelements — average of 10 analyses, microelements — average of 50 analyses). 3. Basalts from Slovakia on the whole (macroelements — average of 18 analyses, microelements — average of 90 analyses). 4. Basalts from Kamčatka and the Kuril Islands (according to the work by E. K. Marchinin, A. M. Sapožnikova 1962a, b; 1964). 5. Basalts of the Siberian traps (according to the work by G. V. Nesterenko, N. P. Smirnova 1964). 6. Olivine basalts from northeastern Ireland (according to the work by E. M. Patterson 1962). 7. Predominantly olivine basalts from the region of Hakome (from the work by S. R. Nockolds, R. Nockolds, R. Allen 1956). 8. Clarks according to A. P. Vinogradov (1962) for diorites and basalts. 9. Tholerite basalts from the Hawaian Islands (from the work by S. R. Nockolds, R. Allen 1956).

basalts from Ireland, almost four times richer than our and by about 6 % richer are basalts from Kamčatka and tholeite basalts from the Hawaian Islands. Smaller differences are in the clarks of A. P. Vinogradov. Co content closest to our basalts is present in basalts from the region of Hakome and enormously low representation of cobalt in basalts of the Siberian traps. Great differences in the individual regions are also in representation of chromium. Uncommonly high content of chromium is mentioned from basalts in Ireland and tholeite basalts have cobalt three times more than basalts in Slovakia. The clark of A. P. Vinogradov is very close to tohe amount of Cr in our rocks (tab. 5). Lower content of chromium is present in basalts from the region of Hakome and Kamčatka and ten times less Cr in the Siberian traps.

Basalts of Slovakia show highest representation of barium from the compared regions. The contents mentioned by A. P. Vinogradov as also the contents in basalts from Ireland are almost by one half lower and in the region of Kamčatka and Hakome the amount of Ba is only nearly one fifth of the content in our rocks and in Siberian traps it is fourteen times lower. In representation of strontium basalt from Ireland are closest to our basalts and in all the compared regions its contents are lower, uncommonly low content of Sr is present in the traps of Siberia with Sr nearly fifteen times less than in our basalts. In contrast to the compared regions basalts from Slovakia are richer in lithium and rubidium. Basalts from Ireland, the region of Hakome and tholeite basalts from the Hawaian Islands include 11 to 13 less lithium and the average content mentioned by A. P. Vinogradov is six times smaller than the content of Li in basalts from Slovakia. Greater differences are in representation of rubidium. Basalts from Ireland, the region of Hakome as well as tholeite basalts from the Hawaian Islands show very low content of Rb in contrast to its content in our basalts. The clark value of Rb is almost by a half less than the value of Rb in basalts from Slovakia.

It is evident from the mentioned discussion about the average representation of trace elements in basalts from various regions that they are very variable in equal or allied rocks and these data cannot be applied in comparative studies without thorough analysis.

Conclusion

Basalts found in Slovakia represent a relatively continuous scale of differentiation of the magma with linear trend of succession. With gradual differentiation of the magma the content of sodium and silicon was increasing, the magma was getting poorer in calcium and magnesium. The changes in representation of magnesium correspond roughly to the content of olivine in basalts. Chromium, nickel, cobalt and lithium are bound to iron-magnesium minerals formed in the first stages of magma crystallization and with gradual crystallizational differentiation they show the tendency of smaller representation in rocks. The basalts from Slovakia are derived from one mother magma coming from great depth. Differentiation of the magma was taking place in partial reservoirs independent for the regions of central Slovakia and southeastern Slovakia. Partial reservoirs were situated nearer to the surface than original mother magma. Crystallization of magma was taking part in these partial reservoirs partly under different conditions, manifested by entering of chromium, nickel and cobalt in basalts of southeastern Slovakia into structure lattice of olivine, where they are substituting Mg, and in basalts of central Sovakia these elements entered into structure lattice of pyroxenes, where they are substituting iron. Different conditions of magma differentiation for basalts of central Slovakia are also indicated by binding of vanadium and lithium to olivines more marked this region than in basalts of southeastern Slovakia.

Translated by J. Pevný.

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Review by B. Cambel.