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## GEOCHEMISTRY OF Cu, Pb, Zn, Ag IN NEOVOLCANICS OF SLOVAKIA

(Fig. 1—7)

**Abstract:** The phroducts of Neogene to Quaternary volcanic activity are found in the region of central and aestern Slovakia. In the paper the distribution of Cu, Pb, Zn, Ag in the main rocks types as rhyolites, andesites, basalts is shown. Mutual relation of microelements as well as their relation to Fe, Mg, K, Na is solved. Indicated are the differences in concentration of Cu, Pb, Zn, Ag in other volcanic regions and world standards.

**Резюме:** Продукты неогенного и четвертичного вулканизма развиты в среднесловацкой и восточнословацкой неовулканической областях. В этих породах изучалась дистрибуция меди, свинца, олова и серебра в главных типах пород — риолитах, андезитах, базальтах, с указанием на разницу между среднесловацкой и восточнословацкой областями. Далее решается взаимоотношение вышеупомянутых микроэлементов, а также и их отношение к железу, магнию, калию и натрию. В статье отмечена и разница в концентрации меди, свинца, олова и серебра в других вулканических областях и в мировом масштабе. Анализированы были те же образцы, описанные уже в трудах И. Форгача (1970a, 1970) и Й. Форгача — Г. Купчо (1974).

*Introduction*

The study of quantitative representation of trace elements in neovolcanics of Slovakia has not a long tradition. The first investigations were mainly focused on their distribution in alluvial and deluvial weathering products (F. Fiala — Z. Pácl 1955, M. Böhmer — E. Mecháček, 1966; J. Valach 1955; J. Forgáč 1970 a. o.). Another group of specialists traced the problem of primary aureoles regarding to the course of ore veins (J. Forgáč, 1966; J. Forgáč — E. Mecháček — J. Kováčik, 1969) or the concentration of trace elements in minerals of ore veins was observed (M. Koďera, 1964 a. o.). These works are in their extent of more or less local character. Only in the last years attention is devoted to the study of trace elements in neovolcanics of Slovakia from the regional viewpoint (J. Forgáč, 1970a, 1970b; J. Forgáč — G. Kupčo, 1974). With valuation of the distribution of some trace elements in the foregoing years in neovolcanics of Slovakia from the regional standpoint attention was called to considerable differences in the concentration of some elements in other volcanic regions with regard to their content in neovolcanic regions of Slovakia. Differences in the concentration of some elements between individual neovolcanic regions have also been shown within Slovakia. The requirement has been evident from that to found out in a regional scale also the distribution of other trace elements as copper, lead, zinc, silver, because the data on their concentration in neovolcanics of Slovakia are missing or sporadic and from local section only. Therefore we have proceeded to the study of the mentioned elements from regional standpoint and present the results achieved in further part of the work.

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*Methods of work*

The work presented continues from the papers by J. Forgáč (1970a, 1970b), J. Forgáč – G. Kupčo (1974). Samples were analysed from the same localities as in the papers mentioned. The studied localities are selected in a way to include the areal extension of neovolcanic rocks of Slovakia and their age scale. In the analyses we were mainly focused on establishing the concentration of Cu, Zn, Ag. The data on concentration of lead were adopted from the above mentioned works and some localities with a low concentration of lead were reevaluated.

The preceding spectrochemical methods did not provide more precise values or did not display the necessary sensitivities, mainly in zinc. Precision of determining in copper and silver was limited by flatness of analytical curves and in copper also a certain content of this element in electrodes contributed to inaccuracy. This fact has shown very unfavourably mainly at the values from 1 to 30 ppm, where the majority of copper and mainly silver contents occur.

Establishing of Cu and Zn by the method of AAS: Into a Pt-dish 1 g sample is weighed. 10 ml. HF are added, intermixed and still 2 ml HClO<sub>4</sub> are given. The mixture is left evaporating on sand bath until the first smokes of HClO<sub>4</sub>. Afterwards 5 ml HF are added and evaporate to dry state. The dry evaporation remain we leach with 15–25 ml warm distilled water and is left to digest 10–20 min. Then 5 ml HCl are added for dissolution and filled up to 100 ml distilled water. From this solution Cu and Zn are determined.

Determination of Ag by means of AAS: 1 g sample is dissolved in 5 ml conc. HNO<sub>3</sub>. To the mixture is still added 1 drop of pure mercury. The mixture is heated with intense stirring to the boiling point. The solution is left to cool down and 5 ml H<sub>2</sub>O are added. 10 ml are poured over to a volumetric flask and filled up to the mark with conc. HNO<sub>3</sub>. The solution we filter or centrifuge and measure on AAS photometer. Zero value is set up on solution of conc. HNO<sub>3</sub> with water in the ratio 1 : 1.

The rocks were analysed by M. Klinčeková, Dionýz Štúr Institute of Geology, Bratislava.

*Petrographical character of the investigated rocks.*

The investigated rocks are a product of long-lasting volcanic activity, which started in the Eggenburgian and terminated in the Pliocene to Quaternary. The mentioned range of time was characterized by vigorous volcanic activity. In the course of volcanic activity its alternation with interperiods of calming and quiescence was evident. In the time of long-lasting volcanic activity a wide variability of rocks of the order rhyolite-andesite-basalt originated. This fundamental order of rocks is locally completed with transitional types of the differentiation order, which were manifested in mineralogical-petrographical and chemical composition of rocks.

The most acid investigated rocks are rhyolites. They are rocks of greyishwhite, grey to pinkish colour, of porphyritic texture. The ratio of porphyritic phenocrysts and groundmass is variable. The majority of rhyolites are formed by groundmass. Porphyritic phenocrysts take up prevalingly 3 to 19 % of total

rocks volume and seldom attain around 30 % of total rock only. Porphyritic phenocrysts are formed by feldspars, quartz and biotite. According to representation of feldspars sanidine rhyolites (feldspars formed by sanidine and plagioclase) and plagioclase rhyolites (feldspars formed by plagioclase, without sanidine) are present. The groundmass is mostly vitrophyric, cryptocrystalline to spherulitic.

In neovolcanic regions of Slovakia are of largest extension andesites and their eruptions took place in the Badenian, Sarmatian to Pliocene. Andesites have a variable mineralogical-petrographical composition. They are of porphyritic texture. On the whole, the groundmass is prevailing over porphyritic phenocrysts in them. The mostly spread type are pyroxenic andesites. Porphyritic phenocrysts are formed by plagioclase and pyroxenes, hypersthene generally prevails over augite. As accessories they contain amphibole and biotite. Of less extension are pyroxene-amphibolic andesites. A distinct petrographic type represent coarse-porphyritic-biotite-amphibolic andesites with sporadic pyroxenes and quartz and amphibolic andesites, which as accessories contain pyroxene and biotite. In general of little extension are basaltoid andesites. Essentially they are olivine-pyroxenic andesites.

The latest volcanism of Pliocene-Quaternary age is represented by basalts. In basalts as fundamental types are distinguished plagioclase basalts, amphibolic basalts and basanites or basanitoids. A common feature of basalts is their content of olivine, nepheline, alkalic pyroxenes and amphiboles in variable ratio and amount.

According to petrographical and chemical composition rhyolite-andesite order rocks display an alkalic-calcareous character and the basalts and alkalic character.

The samples taken from the rocks types mentioned and given to chemical analyses are fresh rocks, modal composition of which is mentioned in the preceding works by J. Forgáč (1970a, 1970b), J. Forgáč — G. Kupčo (1974).

### *Distribution of elements*

In this chapter distribution of copper, zinc, silver and lead is mentioned for volcanics as a whole and also for main groups of rocks as rhyolites, andesites and basalts. The average contents of elements from the main groups of rocks, standard deviations, dispersion are also present and the differences in distribution of elements between the volcanic regions of central and eastern Slovakia are indicated.

#### *Zinc*

In neovolcanics of Slovakia zinc is distributed within the range from 13 to 120 ppm. From the rocks studied poorest in zinc are rhyolites. In rhyolites of central Slovakia it is found in the range from 19 to 47 ppm, with most frequent concentration from 30 to 40 ppm. Average concentration of zinc in rhyolites of central Slovakia is 32,94 ppm, dispersion 59,26 with standard deviation 7,69. In rhyolites from eastern Slovakia zinc is distributed from 13 to 58 ppm, with an average content of 32,22 ppm, dispersion 206,45 and standard deviation 16,13.

Higher concentration of zinc have been found in andesites. In andesites from central Slovakia zinc is distributed from 58 to 104 ppm and most often found in concentration from 75 to 85 ppm. Its average concentration attains the value 82,06 ppm, dispersion 147,77 and standard deviation 12,6. In andesites from eastern Slovakia zinc is distributed within the range from 57 to 104 ppm, with most abundant concentration from 75 to 85 ppm, with average concentration 80,68 ppm, standard deviation 11,71 and dispersion 137,08. The information obtained shows that there are no essential differences in distribution of zinc in andesites from central and eastern Slovakia.

Richest in zinc are basalts from the observed rocks. Zinc in them is distributed within the range from 82 to 120 ppm and most often concentration of zinc varies within the range of 85 to 100 ppm. Basalts contain zinc 97,89 ppm on an average, with dispersion 119,75 and standart deviation 10,94.

### Lead

In the rocks investigated lead is distributed within the range 3 to 66 ppm. Richest in lead are rhyolites. In rhyolites from central Slovakia lead is distributed from 23 to 57 ppm, with most frequent concentration from 30 to 50 ppm and its average content is 43,31 ppm. The dispersion of lead in rhyolites of central Slovakia is 77,96 and standard deviation 8,82. Rhyolites from eastern Slovakia have lead distributed within the range from 20 to 66 ppm with the most frequent occurrence from 35 to 50 ppm. Its average content is 46,2 ppm, standard deviation attains the value 13,06 and dispersion 170,70.

Lesser concentration of lead is in intermediate rocks. Considerable differences in distribution of lead are evident in andesites. In andesites from central Slovakia lead is distributed from 7 to 44 ppm with most frequent concentration within the range from 10 to 35 ppm. The average concentration of lead in andesites from central Slovakia is 20,78 ppm, dispersion 104,81 and standard deviation 10,24. Largely different are the contents of lead in andesites from eastern Slovakia. In 22 samples from andesites of eastern Slovakia the presence of lead has been found in concentration higher than 3 ppm, i. e. above the detection limit of the applied method in 12 samples only. Following from the data obtained it may be stated that the concentration of lead in andesites from eastern Slovakia has been found within the range from 3 to 20 ppm with an average content of 6,18 ppm, dispersion reaching the value 52,73 and standard deviation 7,26. The data on concentration of lead from andesites of eastern Slovakia should be considered as informative. It may be stated, however, that concentration of lead in andesites of central Slovakia is more than three times higher than in andesites from eastern Slovakia.

Poorest in lead from the studied rocks are basalts. From 18 samples subjected to investigation a concentration of lead higher than 3 ppm has been observed only in four samples within the range 3 to 10 ppm.

### Copper

In neovolcanic rocks of the order rhyolite-andesite-basalt copper is distributed within the range from 4 to 66 ppm (Tab. 1., 2.). Rhyolites are poorest in copper from the studied rocks groups. Rhyolites from central Slovakia have contents

Table 2. Contents of elements in rhyolites, andesites and basalts from central and southeastern Slovakia in ppm. and ‰

	Zn ppm	Pb ppm	Cu ppm	Ag ppm	Fe <sup>+2</sup> ‰	Fe <sup>+3</sup> ‰	Mg ‰	K ‰	Na ‰
1	30	40	7	0,12	1,10	1,00	0,40	3,70	1,70
2	47	37	8	0,18	0,40	1,80	0,40	3,10	1,80
3	32	35	8	0,08	0,30	0,30	0,50	2,00	2,80
4	34	40	4	0,08	0,70	1,30	0,30	3,40	2,20
5	40	46	5	0,08	0,80	1,30	0,80	2,40	2,90
6	38	52	5	0,14	0,70	2,00	0,30	3,30	1,50
7	31	54	10	0,06	0,60	2,50	0,30	2,90	1,50
8	35	37	7	0,15	0,60	0,60	0,06	3,50	1,80
9	30	38	9	0,12	0,70	0,60	0,10	3,80	1,20
10	42	23	10	0,18	1,70	1,50	0,70	3,10	2,00
11	23	45	4	0,08	0,70	0,40	0,03	2,60	1,80
12	19	39	9	0,10	1,30	0,05	0,30	3,90	2,20
13	37	57	12	0,12	1,20	2,20	0,50	3,30	1,80
14	20	53	9	0,08	0,10	1,20	0,20	3,40	2,90
15	38	50	10	0,04	0,50	1,80	0,06	2,00	1,80
16	31	47	7	0,10	0,50	1,60	0,70	3,40	1,80
17	80	18	33	0,50	2,35	2,69	1,11	1,91	2,37
18	66	12	37	0,95	3,21	1,73	1,62	1,66	1,56
19	78	32	26	0,50	1,69	3,03	0,88	1,28	1,78
20	84	37	23	0,25	1,58	3,49	0,55	1,20	1,87
21	76	33	27	0,25	2,21	3,15	0,64	1,78	1,94
22	76	28	42	0,50	1,58	2,23	1,51	1,58	1,94
23	70	7	30	0,15	1,86	3,21	1,39	1,36	1,96
24	88	15	18	0,50	2,69	4,08	1,18	1,19	2,02
25	88	18	34	0,50	3,96	2,52	1,66	1,39	1,93
26	84	26	25	0,50	3,35	2,79	1,97	1,28	1,85
27	100	15	60	0,40	3,89	1,40	1,69	0,93	2,05
28	94	19	37	0,50	3,51	3,54	1,50	1,57	1,84
29	66	23	35	0,25	2,94	2,41	1,98	1,92	2,22
30	100	44	39	0,50	2,91	2,22	2,14	1,31	1,87
31	96	16	43	0,30	3,35	3,35	3,02	1,00	1,33
32	70	10	36	0,85	3,91	2,23	2,07	1,38	2,05
33	94	22	53	0,45	0,32	2,62	2,15	1,38	1,66
34	98	32	52	0,50	2,39	2,44	1,91	1,94	2,05
35	104	24	30	0,55	3,85	2,93	1,12	1,83	1,87
36	82	14	18	0,30	3,85	0,66	0,96	1,14	2,19
37	60	32	25	0,20	0,46	2,34	0,95	1,56	2,22
38	74	26	43	0,30	3,12	3,02	1,63	1,49	1,79
39	100	29	30	0,30	2,84	2,14	2,76	1,56	1,84
40	84	14	14	0,70	2,11	2,61	1,44	1,45	2,00
41	82	13	47	1,00	3,35	2,52	2,05	1,08	1,85
42	70	17	24	0,40	2,25	2,10	0,75	2,16	2,56
43	82	26	31	0,45	2,66	2,99	1,40	1,53	1,94
44	74	21	40	0,40	2,17	0,19	1,22	1,57	1,99
45	53	15	21	0,25	1,79	2,96	1,27	1,83	2,37
46	64	12	19	0,25	0,79	4,01	0,90	1,63	1,84
47	80	22	40	0,20	3,46	2,12	1,97	2,24	2,05
48	94	42	30	0,20	0,36	2,62	2,15	2,00	2,27
49	90	15	30	0,50	5,22	2,29	2,71	1,33	2,11
50	84	—	55	0,60	4,14	3,35	3,99	1,10	2,17
51	90	—	39	0,45	5,41	0,44	3,93	1,85	1,52
52	120	—	60	0,75	6,29	5,15	2,86	1,89	3,02
53	100	—	60	0,65	3,78	3,23	3,87	1,05	2,49
54	84	3	38	0,15	2,88	2,96	2,73	2,32	3,06
55	100	—	30	0,50	5,32	2,95	2,58	1,49	3,01

	Zn ppm	Pb ppm	Cu ppm	Ag ppm	Fe <sup>2+</sup> ‰	Fe <sup>3+</sup> ‰	Mg ‰	K ‰	Na ‰
56	110	10	25	0,45	4,31	3,09	2,67	1,74	4,23
57	98	—	32	0,45	4,41	2,91	3,01	1,41	3,26
58	98	—	48	0,70	4,79	3,20	2,83	1,41	2,37
59	98	—	34	0,70	5,10	4,86	2,75	1,51	2,80
60	82	—	59	0,85	4,07	2,83	4,74	1,30	1,86
61	96	3	54	1,25	4,35	2,78	4,69	2,09	2,43
62	90	—	48	1,00	5,21	4,69	5,19	1,52	2,34
63	88	—	54	0,90	4,91	2,40	5,45	1,74	2,64
64	86	—	48	0,95	4,50	3,50	4,35	1,08	2,34
65	102	—	60	0,50	6,27	1,85	4,42	1,13	2,70
66	88	4	45	1,00	4,00	2,25	3,82	2,40	3,78
67	98	—	45	0,85	4,09	6,01	3,00	2,05	2,93
68	120	—	66	0,50	6,49	2,49	7,21	1,09	2,08
69	104	—	38	0,85	6,27	2,96	8,12	0,88	2,18

Explanations to Table 1., localities 1–69

1 — Rhyolite, West of Nová Lehota and SW of Handlová. 2 — Rhyolite. Pokutský potok brook north of Hrabíčov. 3 — Rhyolite Nová Baňa, western slope of elev. p. Háj. 4 — Rhyolite. East of Trubín, near the Lutilský potok brook. 5 — Rhyolite. Central part of the Poľana Mts. 6 — Rhyolite. Southwestern margin of Stará Kremnička. 7 — Rhyolite. Southwest of Bartošová Lehôtka. 8 — Rhyolite. 2 km northeast of Banská Belá. 9 — Rhyolite. South of Horné Opatovce. 10 — Rhyolite. Voznická skala rocks, cutting of the state road southwest of Voznica. 11 — Rhyolite. Rudno n/Hronom. 12 — Rhyolite. Sabová skala rocks, southeast of Hliník n/Hronom. 13 — Rhyolite. West of Horné Opatovce. 14 — Rhyolite. East of the village Ilija. 15 — Rhyolite. Northeast of Banský Studenec. 16 — Rhyolite. North of Turčok. 17 — Pyroxenic andesite. Machulince, quarry. 18 — Pyroxenic andesite. Stará Huta near Nová Baňa, quarry. 19 — Pyroxenic andesite. Gondovo, north of the community. 20 — Pyroxenic andesite. Ladzany–Žemberovce, quarry at the state road. 21 — Pyroxenic andesite. Bohunice, north of the community. 22 — Pyroxenic andesite. South of the community Uhlišká. 23 — Pyroxenic andesite. Hronská Dúbrava, quarry west of the railway station. 24 — Pyroxenic andesite. West of the community Krnišov. 25 — Pyroxenic andesite. North of Beluža. 26 — Pyroxenic andesite. North of Hontianske Nemce, quarry above the state road. 27 — Pyroxenic andesite. North of the community Šášovské Podhradie. 28 — Pyroxenic andesite. North of Krupina quarry Hanišberg. 29 — Pyroxenic andesite with amphibole. Tlmače, quarry. 30 — Amphibole-pyroxenic andesite. Prochot, northern margin of the community. 31 — Pyroxenic andesite. East of Kremnica. 32 — Pyroxenic andesite. Northern margin of Kremnica, quarry. 33 — Pyroxenic andesite. Turčok, west of the railway station. 34 — Pyroxenic andesite. Víglaš, west of the railway station. 35 — Pyroxenic andesite. North of Maďačka, quarry south of the state road Podkriváň–Stará Huta. 36 — Pyroxenic andesite. Ladomer, quarry. 37 — Amphibolepyroxenic andesite. Southeast of the village Preňčov. 38 — Amphibole-pyroxenic andesite Hrabíčov, quarry. 39 — Pyroxene-amphibolic andesite. Cut of the road Kremnica–Skalka. 40 — Pyroxenic andesite. East of Krahule. 41 — Amphibolic andesite with pyroxene and garnet. Breziny, quarry south of Zvolen. 42 — Amphibolic andesite with pyroxene and garnet. Šiatroš, quarry. 43 — Biotite-amphibolic andesite. Dekýš, near the old mill. 44 — Biotite-amphibolic andesite. Southwest of Sitno, cut of the forest path. 45 — Biotite-amphibolic andesite. Banský Studenec, quarry north of the village. 46 — Biotite-amphibole andesite. Trnavá Hora. 47 — Biotite-amphibolic andesite. Krahufe. 48 — Biotite-amphibolic andesite. East of Turčok. 49 — Pyroxene-olivine andesite. Skalka, northeast of Kremnica. 50 — Pyroxene-olivine andesite. Pitelová, Ostrý vrch. 51 — Pyroxene-olivine andesite. Bartošová Lehôtka, railway cut. 52 — Basanite. Tekovská Breznica. 53 —



Basanite. Banská Niva. 56 — Plagioclase basalt. Lomo. 57 — Plagioclase basalt. Nevičie. 58 — Basanitoid. Podrečany. 59 — Basanitoid. Mášková. 60 — Limburgitoid basanite. 61 — Limburgitoid basanite. 62 — Nepheline basanite. Radzovce. 63 — Nepheline basanite. Konrádovce. 64 — Nepheline basanite. Filakovo. 65 — Nepheline basanite. Beľina. 66 — Nepheline basanite. Rodrovce. 67 — Nepheline basanite. Borkul-Ragáč. 68 — Basanite. Brehy, quarry. 69 — Basanite. Banská Belá, railway cut.

Table 2. Content elements in rhyolites and andesites from eastern Slovakia

	Pb ppm	Zn ppm	Cu ppm	Ag ppm	Fe <sup>+2</sup> ‰	Fe <sup>+3</sup> ‰	Mg ‰	K ‰	Na ‰
1	50	34	4	0,06	0,40	0,80	0,80	2,40	2,30
2	46	18	7	0,04	0,30	1,90	0,10	2,50	1,80
3	38	33	12	0,14	0,50	0,70	0,07	2,20	1,70
4	43	35	15	0,10	0,50	1,40	0,40	3,00	1,70
5	45	56	7	0,10	0,30	1,00	0,30	3,10	2,00
6	48	26	6	0,01	0,60	0,90	0,40	2,50	1,80
7	66	13	5	0,08	0,90	0,04	0,20	2,10	1,60
8	60	17	8	0,12	0,30	0,20	0,10	2,50	1,40
9	20	58	7	0,08	0,60	2,50	0,30	2,20	1,90
10	13	84	32	0,35	3,96	1,06	1,53	1,53	1,76
11	9	75	36	0,55	3,57	2,01	2,44	0,97	1,85
12	3	81	27	0,70	4,47	0,83	1,62	0,97	1,85
13	3	85	18	0,50	3,24	1,64	1,36	1,66	2,15
14	—	65	27	0,70	3,68	1,20	2,40	0,91	1,48
15	10	70	29	0,60	3,10	2,25	2,51	1,01	1,47
16	—	74	38	0,60	1,35	5,28	4,52	0,53	1,23
17	—	80	35	0,30	3,74	1,87	1,13	1,59	1,85
18	17	104	30	0,55	4,43	1,61	2,45	1,16	1,51
19	4	101	36	0,50	5,29	2,18	2,07	0,73	1,75
20	—	87	30	0,50	3,55	3,22	1,88	1,06	1,57
21	—	77	38	0,45	5,18	1,15	1,69	1,23	1,81
22	—	72	49	0,85	2,60	2,76	2,07	0,85	1,28
23	9	94	26	0,60	2,65	1,30	1,82	1,44	1,51
24	12	99	24	0,60	3,10	2,67	2,68	1,18	1,35
25	—	80	34	0,75	3,97	1,06	1,89	1,29	1,54
26	—	70	23	0,45	3,40	1,78	1,47	1,34	1,54
27	—	84	17	0,45	2,99	2,18	1,34	1,46	1,69
28	—	70	17	0,35	2,18	2,99	0,50	1,53	2,02
29	20	82	23	0,35	2,19	2,04	1,51	1,53	2,17
30	19	57	19	0,50	2,01	1,44	1,12	1,33	1,75
31	17	84	27	0,60	3,51	1,66	2,17	1,03	1,77

## Explanations to Table 2., localities 1—31

1 — Rhyolite. North of Komárany, below elev. p. Lipovo. 2 — Rhyolite. South of Hrčel. 3 — Rhyolite. Kašov, quarry in the community. 4 — Rhyolite. West of the village Byšta. 5 — Rhyolite. South of the lake Izra 6 — Rhyolite. East of the village Beňatina. 7 — Rhyolite. Lesné, elev. p. Hôrka. 8 — Rhyolite. Michalovce. Hrádok. 9 — Rhyolite. Malý Kamenec, southeast of Streda nad Bodrogom. 10 — Pyroxenic andesite. Skároš, quarry. 11 — Pyroxenic andesite, Rákoš, quarry. 12 — Pyroxenic andesite. Ruskov, quarry. 13 — Pyroxenic andesite with amphibole. Northern foothill of the Malý Milič. 14 — Pyroxenic andesite with amphibole. Southern slope of elev. p. Dobrák, west of Slanská Huta. 15 — Pyroxenic andesite. Elev. p. Garaboš, southeast of Slanská Huta. 16 — Pyroxenic andesite. Kalša, quarry. 17 — Pyroxenic andesite. Dargov quarry near the state road east of the Dargov saddle. 18 — Pyroxenic andesite.

Vehec-quarry at the state road Vehec–Banské. 19 – Pyroxene-andesite. Kamenný potok, quarry northeast of Kokošovce. 20 – Pyroxenic andesite. Streda nad Bodrogom. 21 – Pyroxenic andesite. Imreg, quarry. 22 – Pyroxenic andesite. East of the village Koromľa. 23 – Pyroxenic andesite. Elev. p. Veža near the Morské Oko lake in the Vihorlat Mts. 24 – Pyroxenic andesite, Sninský kameň. 25 – Pyroxenic andesite. Quarry north of the village Klokočov. 26 – Pyroxenic andesite. Vinné, quarry at the southeastern margin of the village. 27 – Pyroxene-amphibolic andesite. Northern margin of the Zemplínska Šírava lake. 28 – Amphibole-pyroxenic andesite. Vinné, castle. 29 – Amphibole-pyroxenic andesite with garnet. Brestov, quarry northeast of the village. 30 – Amphibole-pyroxenic andesite with garnet. Fintice quarry. 31 – Amphibole-pyroxenic andesite with garnet-Záhradné quarry.

of copper ranging from 4 to 12 ppm, most often its concentration is from 6 to 10 ppm. Average concentration of copper is 7,75 ppm, dispersion 5,53 and standard deviation 2,35. A very similar concentration of copper is also in rhyolites from eastern Slovakia, where copper is distributed within the range of 4 to 15 ppm with most frequent concentration from 6 to 8 ppm. Its average content in rhyolites from eastern Slovakia is 7,89 ppm with a dispersion of 12,11 and standard deviation 3,48.

Considerably higher contents of copper have been observed in intermediate and basic rocks. In andesites from the volcanic region of central Slovakia its distribution varies from 14 to 60 ppm. Most often it is found within the range 20 to 40 ppm and the average concentration is 34,36 ppm, with dispersion 129,09 and standard deviation 11,36. Lesser concentration of copper is in andesites from eastern Slovakia, where its distribution is 17 to 49 ppm. The average content of copper in andesites from eastern Slovakia is 28,86 ppm, dispersion 64,69 and standard deviation 8,04.

In basalts a concentration of copper 25 to 66 ppm with average concentration 46,89 ppm. The dispersion attains the value 144,10 and standard deviation 12,00.

### Silver

Silver is present in least concentration from the elements traced in neovolcanics of Slovakia. In rocks of the rhyolite-andesite-basalt order it is distributed from 0,01 to 1,25 ppm. Rhyolites in central Slovakia have a content of silver from 0,04 to 0,18 ppm. Most often it is in concentration from 0,06 to 0,12 ppm and its average content is 0,11 ppm. The standard deviation of silver in rhyolites of central Slovakia is 0,034 and its dispersion 0,0012. Rhyolites in eastern Slovakia have silver from 0,01 to 0,14 ppm. Most often the concentration of 0,6 to 0,8 ppm has been found, its average content is 0,08 ppm and dispersion is of the value 0,0026, standard deviation 0,05.

A higher concentration of silver is in andesites. In andesites of central Slovakia silver is distributed within the range 0,15 to 1,00 ppm, with most frequent concentration 0,40–0,55 ppm. The average content is 0,45 ppm, dispersion attains the value 0,04 and standard deviation 0,20. Andesites of eastern Slovakia have silver from 0,30 to 0,75 ppm and its average content is 0,54 ppm. Dispersion is of the value 0,02 and standard deviation 0,14.

Highest concentration of silver have been found in basalts. In basalts the content of silver is 0,15 to 1,25 ppm. Most often it is found concentration from 0,69 to 0,98 ppm (Tab. 1., 2.). Its average concentration in basalts is 0,45 ppm. The dispersion attains the value 0,07 and standard deviation 0,27.



In general it may be said that the rocks most potential in lead are rhyolites and with increasing basicity of rocks its concentration diminishes. In rocks of the rhyolite-andesite order in the neovolcanic regions of central and eastern Slovakia are the following differences in distribution of the observed elements. In concentration of copper andesites from eastern Slovakia show the tendency towards a smaller content of copper than andesites from central Slovakia, with the exception of lead, the content of which is in andesites from central Slovakia more than from eastern Slovakia and in andesites it is the contrary. Andesites from eastern Slovakia show the tendency to a higher content of silver than andesites from central Slovakia. In concentration of zinc between the neovolcanic regions of central and eastern Slovakia no essential differences have been evinced. The mentioned differences in concentration of elements between the neovolcanic regions of central and eastern Slovakia complete up to present

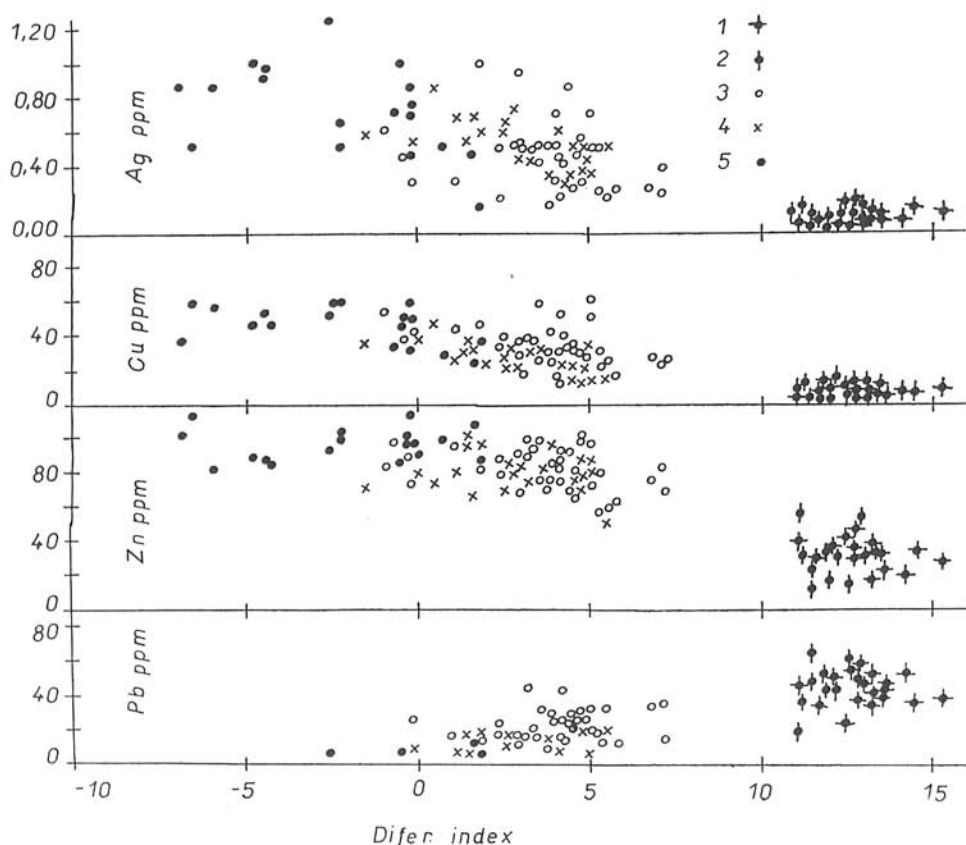


Fig. 1 — Relation of the differentiation index to Pb, Zn, Cu, Ag. 1 — Rhyolites from central Slovakia, 2 — rhyolites from eastern Slovakia, 3 — andesites from central Slovakia, 4 — andesites from eastern Slovakia, 5 — basalts.

knowledge on the differences in chemical characteristics of volcanic rocks of these regions and together with they indicate that volcanic rocks of these regions originated from different magma chambers.

### *Mutal relations of elements*

In this chapter mutal correlation of the traced microelements as well as their correlation with some macroelements in volcanic rocks as a whole and in the groups of rocks (andesites, rhyolites, basalts) are presented and the differences between rocks from central and eastern Slovakia are indicated.

### *Zinc*

Zinc displays the tendency to accumulate in basic and intermediate rocks. It may be supposed that the content of zinc gradually decreases with the trend of magma differentiation. In correlation of zinc to the differentiation index  $1/3 \cdot \text{Si} + \text{K} - (\text{Ca} + \text{Mg})$  projection points are distributed in three fields (Fig. 1). In one field are distributed rhyolites, in the second andesites and in the third basalts. On the whole it may be said that in correlation of zinc to the differentiation index signs of negative correlation appear, i. e. with increasing degree of magma differentiation representation of zinc lowers in rocks. Zinc in rocks of the rhyolite-andesite-basalt order with the studied trace elements has a variable degree of dependence. A distinct degree of positive dependence displays zinc with silver in rhyolites from central and eastern Slovakia only. With lead and copper it shows a low degree of dependence, except andesites from central Slovakia. In andesites from central Slovakia zinc shows the lower boundary of moderate degree of dependence with copper (Tab. 3.). A more distinct correlation dependence is evident between zinc and macroelements. Positive dependence is evident between zinc and bivalent iron in basalts and andesites from eastern Slovakia and in rhyolites with trivalent iron, where correlation reaches a distinct degree of dependence (Fig. 3) while in andesites from eastern Slovakia the relation lowers to a moderate degree of dependence and in andesites from central Slovakia to a low degree of dependence. In andesites zinc has a moderate degree of positive dependence with magnesium (Tab. 3.). A moderate negative degree of dependence has been evident between zinc and alkalies (Na, K), however, only in rhyolites from eastern Slovakia while in other studied groups of rocks is a low degree of dependence between zinc and alkalies (Fig. 2).

In general it may be said that zinc displays a low correlation relation to the no essential differences evident in rhyolites. A similar case is also concentration of microelements, except its relation to silver in rhyolites. The relation of zinc to macroelements and to iron and magnesium alternately in the whole scale of the studied rocks (rhyolite-andesite-basalt) shows a moderate to distinct positive degree of dependence. We suppose that one part of zinc is bound in Fe, Mg minerals (biotite, pyroxene, olivine).

Fig. 2 — Relation of Zn to Cu, Ag, K, Na. I Region of central Slovakia, II — region of eastern Slovakia, 1 — rhyolites, 2 — andesites, 3 — basalts, 4 — line for rhyolites, 5 — line for andesites, 6 — line for basalts.

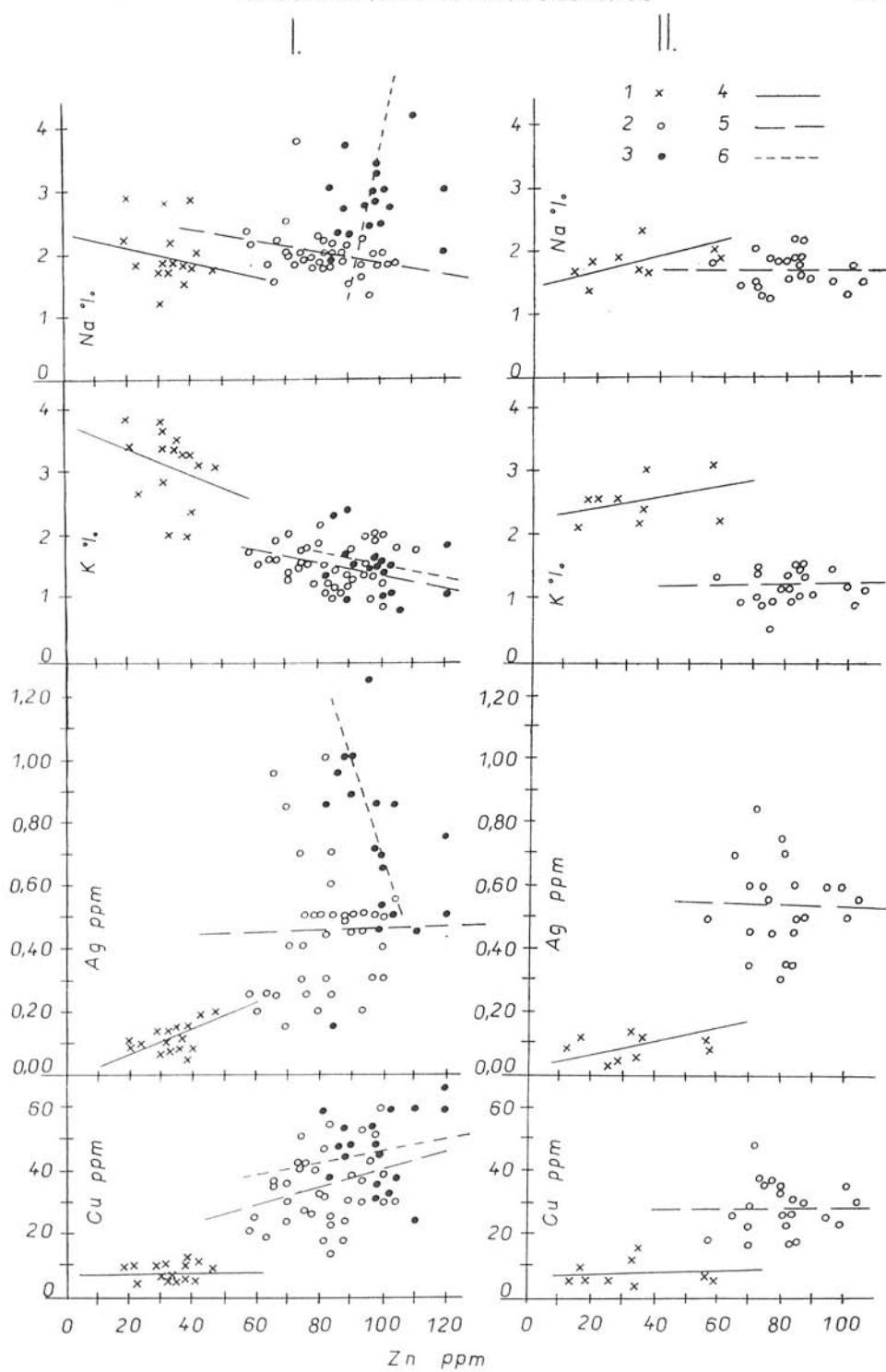


Table 3. Correlation coefficients  
Rhyolite from central Slovakia

	Pb	Cu	Ag	Fe <sup>+2</sup>	Fe <sup>+3</sup>	Mg	K	Na
Zn	-0,21	-0,05	0,68	0,12	0,55	0,38	-0,30	-0,17
Pb	—	-0,01	-0,05	0,08	0,51	-0,17	-0,09	0,01
Cu	—	—	0,14	0,22	0,29	0,03	0,05	-0,13
Ag	—	—	—	0,06	0,01	0,20	0,05	-0,35

## Rhyolites from eastern Slovakia

	Pb	Cu	Ag	Fe <sup>+2</sup>	Fe <sup>+3</sup>	Mg	K	Na
Zn	-0,78	0,14	0,51	-0,22	0,57	0,27	0,34	0,39
Pb	—	-0,29	0,07	0,15	-0,85	-0,04	-0,01	-0,05
Cu	—	—	0,88	-0,01	0,14	-0,26	0,55	-0,54
Ag	—	—	—	-0,09	-0,02	-0,40	-0,45	-0,23

## Andesites from central Slovakia

	Pb	Cu	Ag	Fe <sup>+3</sup>	Fe <sup>+2</sup>	Mg	K	Na
Zn	0,21	0,31	0,07	0,28	-0,05	0,40	-0,25	-0,28
Pb	—	-0,11	-0,32	-0,49	-0,13	-0,35	0,18	0,01
Cu	—	—	0,28	0,30	-0,19	0,46	-0,12	0,05
Ag	—	—	—	0,39	-0,09	0,14	-0,23	0,04

## Andesites from eastern Slovakia

	Pb	Cu	Ag	Fe <sup>+2</sup>	Fe <sup>+3</sup>	Mg	K	Na
Zn	0,20	0,05	-0,06	0,43	-0,04	0,14	0,03	-0,03
Pb	—	-0,25	-0,15	-0,14	-0,24	0,02	0,15	0,19
Cu	—	—	0,40	0,28	0,19	0,47	-0,58	-0,44
Ag	—	—	—	0,01	-0,01	0,48	-0,61	-0,61

## Basalts

	Zn	Cu	Ag	Fe <sup>+2</sup>	Fe <sup>+3</sup>	Mg	K	Na
Zn	—	0,13	-0,26	0,67	0,15	0,11	-0,23	0,13
Cu	—	—	0,31	0,28	-0,12	0,42	-0,24	-0,61
Ag	—	—	—	0,05	0,18	0,33	0,09	-0,32

## Lead

Lead shows the tendency to accumulate in acid lavas. Highest concentrations of lead are in rhyolites, lesser in andesites and in basalts. Its content was detectable only in four samples as in basalts lead is prevailingly below detection limit of the applied method. In relation on the differentiation index lead has positive correlation. Relations of lead to the observed elements are very variable. Its relation to microelements (Cu, Zn, Ag) shows a low degree of dependence. More distinct is relation of lead to macroelements. A significant positive correlative

relation display lead to trivalent iron only in rhyolites from central Slovakia while in rhyolites from eastern Slovakia lead shows a high negative correlative relation. Moderate negative relation is between lead, bivalent iron and magnesium in andesites from central Slovakia. Sodium and potassium show a low correlative réelation to lead.

Lead appears as the most dispersed element since it does not form more distinct correlative relations with regard to the observed microelements and even to the macroelements except rhyolites from central Slovakia, where in shows dictinct relation to iron. The posibility cannot be excluded that in rhyolites of central Slovakia it partly enters biotite. Reading to the low degree of dependence of lead to alkalis its bond in plagioclases and potassium feldspars cannot be supposed (Tab. 3. Fig. 6.).

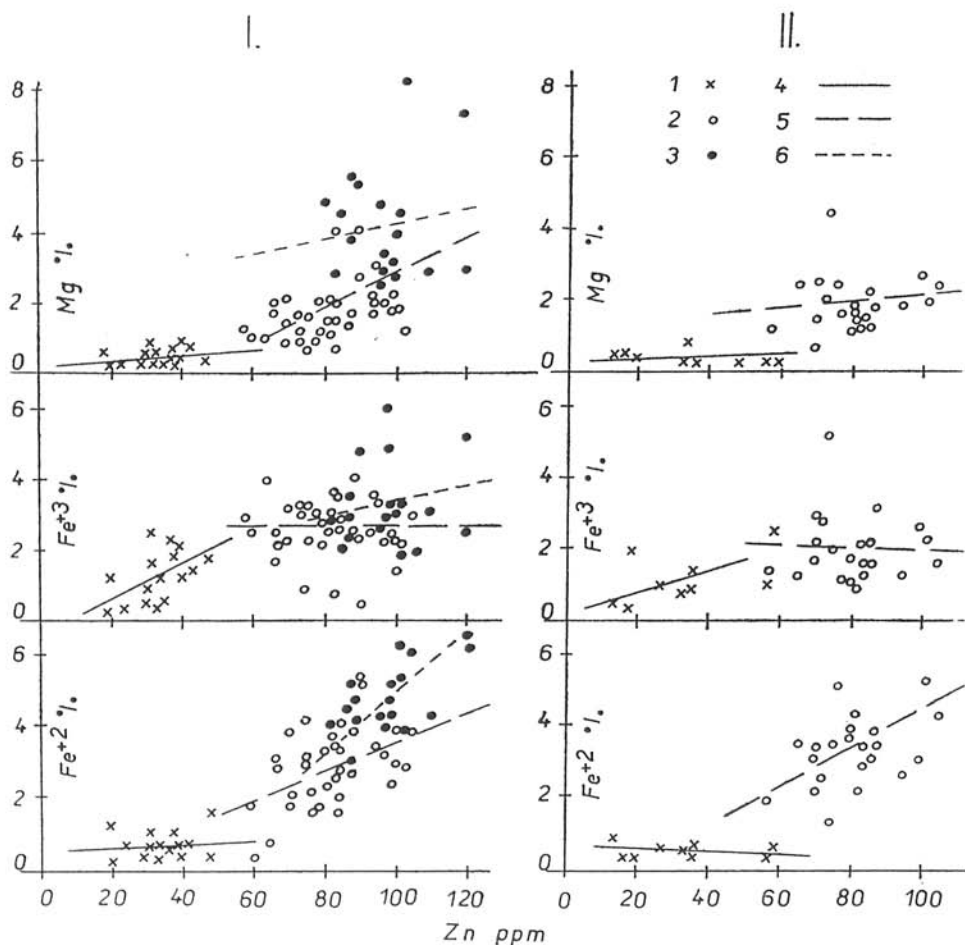


Fig. 3 — Relation of Zn to Fe, Mg. I — Region of central Slovakia, II — region of eastern Slovakia, 1 — rhyolites, 2 — andesites, 3 — basalts, 4 — line for rhyolites, 5 — line for andesites, 6 — line for nasalts.

## Copper

Copper has the tendency to accumulate in basic magmas. In correlative relation of copper to differentiation index a gradual trend to negative correlation has been shown, in which with increasing basicity of rocks content of copper is higher (Fig. 1). In copper a high and moderate positive degree of dependence to silver was evident in rhyolites and andesites from eastern Slovakia while in rocks of the rhyolite-andesite order in central Slovakia is a low degree of dependence between copper and silver. In relation of copper to macroelements

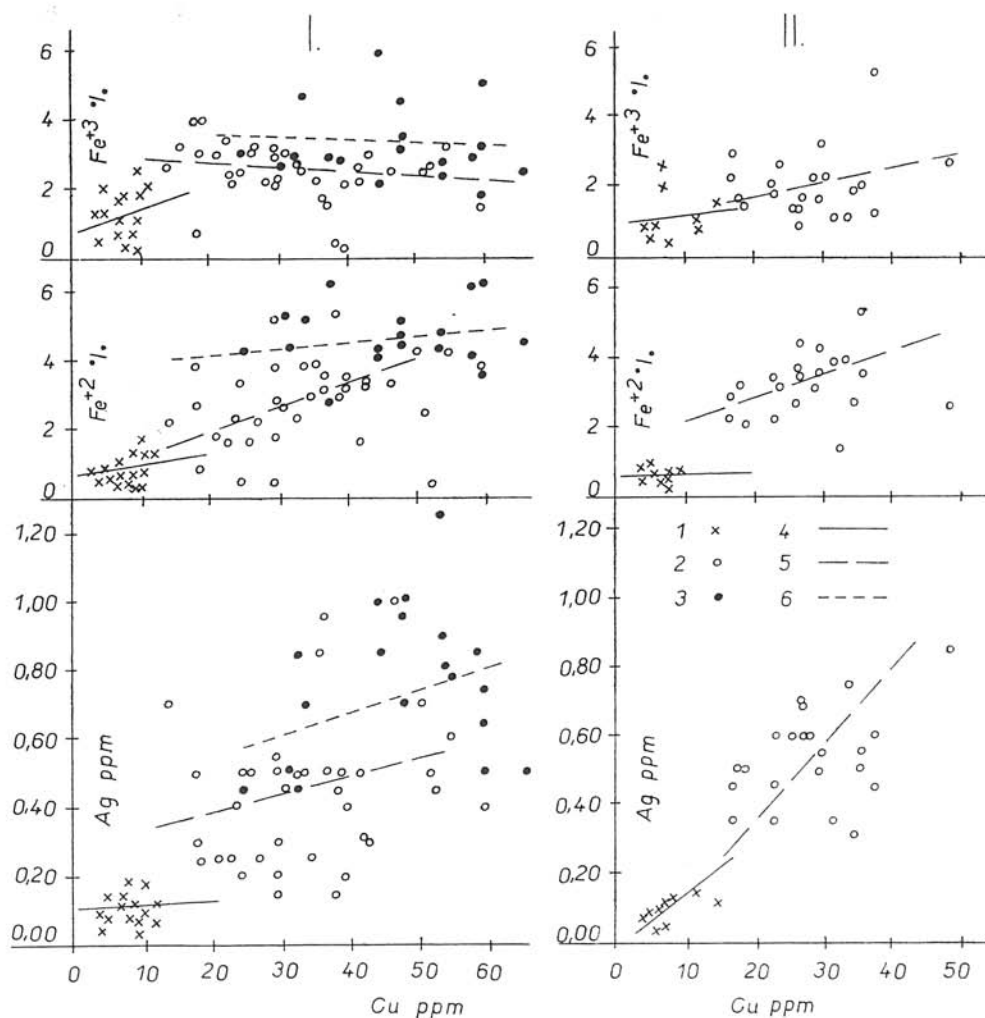


Fig. 4 — Relation of Cu to Ag, Fe. I — Region of central Slovakia, II — region of eastern Slovakia, 1 — rhyolites, 2 — andesites, 3 — basalts, 4 — line for rhyolites, 5 — line for andesites, 6 — line for basalts.



copper is in moderate positive relation to magnesium in intermediate and basic rocks while in acid rocks this relation is low. A distinct correlative relation has been evident between copper and potassium, however, in rhyolites from eastern Slovakia only (Fig. 4, 5).

Copper, on the whole, displays more distinct correlative relation to macroelements than to the observed microelements except rhyolites from eastern Slovakia. As a consequence, we suppose that copper participates in the structure of Fe, Mg, minerals in intermediate and basic rocks while in rhyolites of eastern Slovakia its partial bond in feldspars may be supposed.

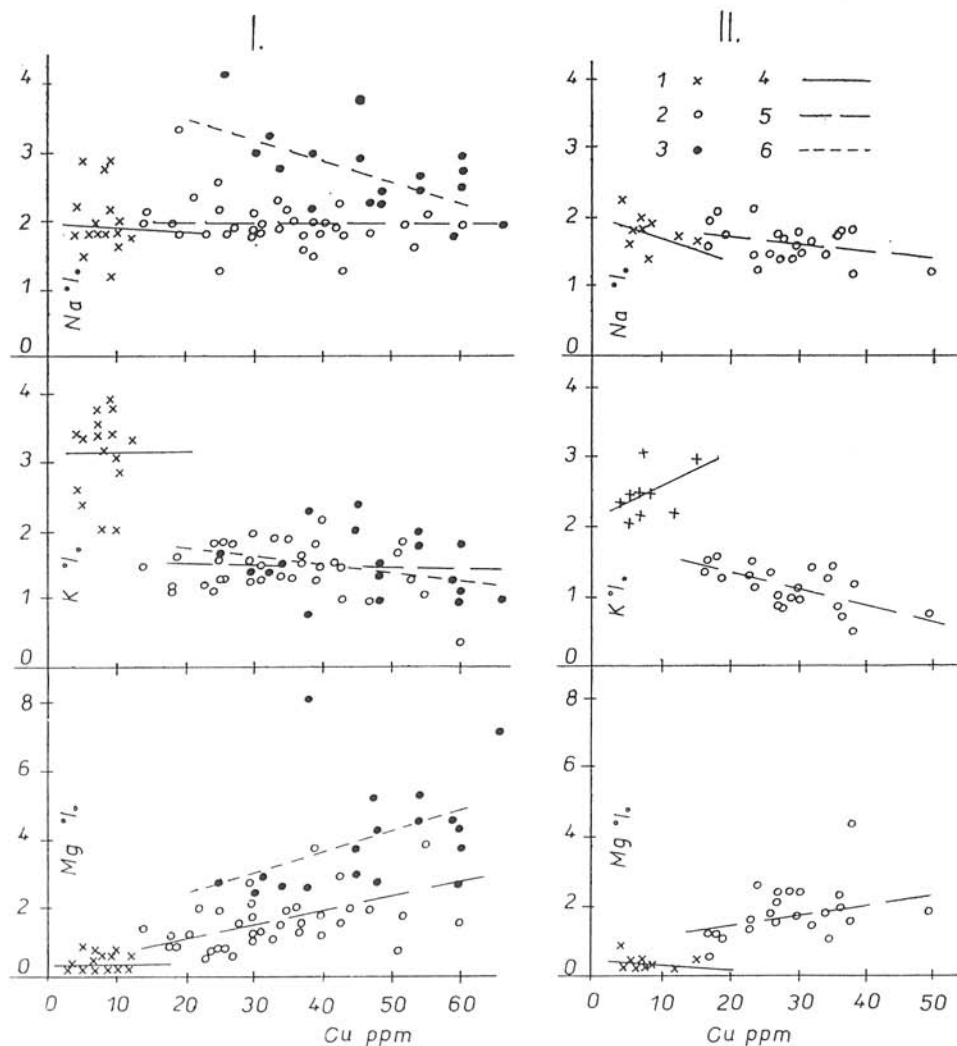


Fig. 5 — Relation of Cu to Mg, K, Na. I — Region of central Slovakia, II — region of eastern Slovakia, 1 — rhyolites, 2 — andesites, 3 — basalts, 4 — line for rhyolites, 5 — line for andesites, 6 — line for basalts.

## Silver

Silver displays a tendency of accumulating in basic rocks. In relation of silver to the differentiation index a negative correlation has been evident. In Fig. 1 it may be observed that from acid rocks towards basic ones the field of projection point extends as a consequence of larger distribution scale of copper in basic rocks than in acid ones. Correlative relations of silver to zinc, lead

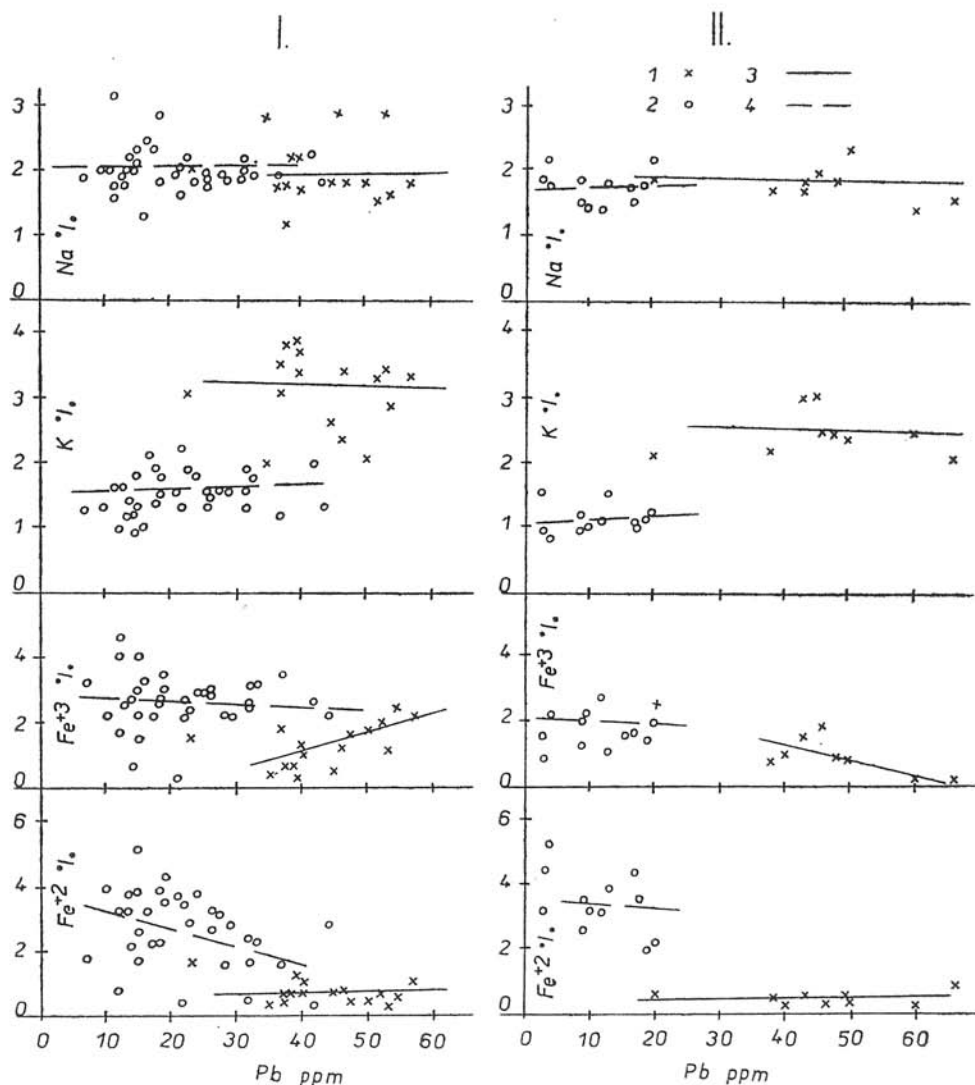


Fig. 6 — Relation of Pb to Fe, K, Na. I — Region of central Slovakia, II — region of eastern Slovakia, 1 — rhyolites, 2 — andesites, 3 — basalts, 4 — line for rhyolites, 5 — line for andesites, 6 — line for basalts.

and copper are mentioned above in connection with relations of these elements. Silver shows a low degree of dependence to the macroelements in general (Fig. also differences between rocks from central and eastern Slovakia. Rhyolites from three times higher than in andesites from eastern Slovakia. In rhyolites are no essential differences in concentration of lead. In concentration of silver are 7). A moderate positive degree of dependence has been evident between silver and magnesium in andesites of eastern Slovakia and in basalts while in andesites from central Slovakia is a moderate positive degree of dependence between silver and bivalent iron. On the basis of the mentioned facts we suppose that in intermediate and basic rocks silver can be partly bound in Fe, Mg minerals.

### *Contents of elements in other volcanic regions*

The concentrations of zinc, copper, silver and lead are not equal in volcanic rocks of various regions, whether with related or different association of rocks. Therefore we present in this chapter a brief comparison of average contents of the mentioned elements from volcanic rocks of same regions with the average content according to A. P. Vinogradov (1962) as well as to the international standards for andesites-AVG-1 and basalts-BCR-1. The data on the standards from rhyolites have not been available to us so far (Tab. 4.).

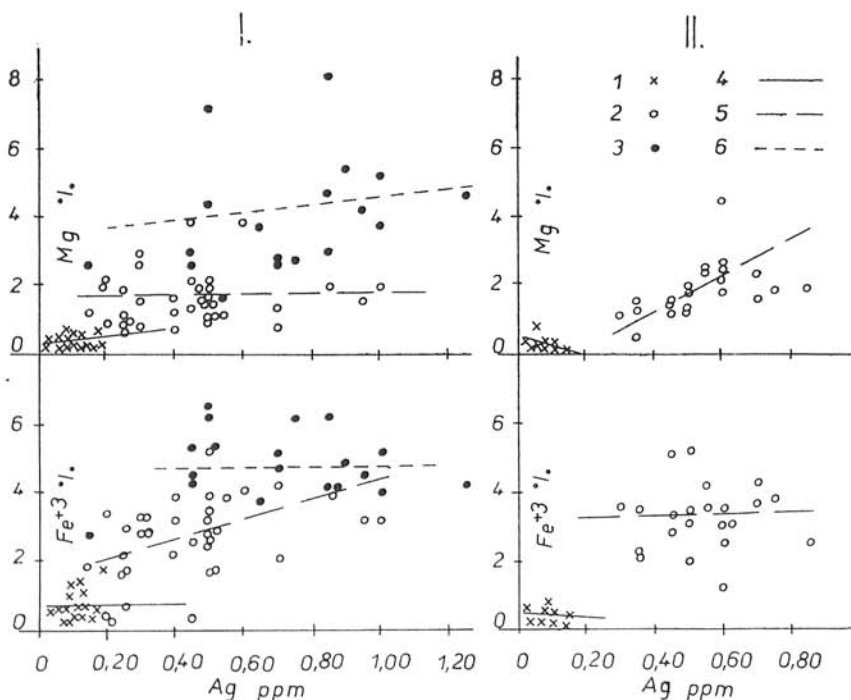


Fig. 7 — Relation of Ag to Fe, Mg. I — Region of central Slovakia, II — region of eastern Slovakia, 1 — rhyolites, 2 — andesites, 3 — basalts, 4 — line for rhyolites, 5 — line for andesites, 6 — line for basalts.

Table 4. Average contents elements from other regions in ppm.

	Zn			Cu			Ag			Pb		
	R	A	B	R	A	B	R	A	B	R	A	B
1	—	112	132	—	63,7	22,4	—	0,097	0,044	—	35,4	18
2	60	72	130	20	35	100	0,05	0,07	0,10	20	15	8
3	—	46,9	—	—	54,4	—	—	—	—	—	9,85	—
4	—	—	—	—	42	—	—	—	—	—	—	—
5	—	66,5	—	—	39,5	—	—	—	—	—	15,4	—
6	—	74,2	—	—	44,2	—	—	—	—	—	12,5	—
7	—	—	—	—	68	—	—	—	—	—	10,6	—
8	—	—	—	—	35	—	—	—	—	—	8,6	—
9	—	—	—	66	—	400	—	—	—	43	—	20
10	—	—	—	33	34	63	—	—	—	—	—	—
11	—	—	—	—	—	43	—	—	—	—	—	—
12	—	—	—	—	—	—	—	—	—	13	—	—
13	38	—	—	—	—	—	—	—	—	—	—	—
14	—	—	107	—	—	—	—	—	—	—	—	—
15	—	—	57	—	—	—	—	—	—	—	—	—
16	—	—	—	—	—	—	0,049	0,080	0,100	—	—	—
17	57,5	58,8	—	16,5	52,04	—	—	—	—	—	—	—

R — Rhyolites, A — Andesites, B — Basalts. 1 — International standards, andesite AVG-1, basalt BCR-1, Oregon (from the work by Flanagan J. E. 1969). 2 — Clark contents of elements (from the work by Vinogradov A. P. 1962). 3 — Andesites from the Gutii mountains, Galimani, Gurgiu, Hargita mountains (from the work by Ianovici V., Moldarescu I. — David B. — Bratosin I. 1068). 4 — Andesites of Badenian age from the Cserhat mountains, Hungary (from the work by Arkai P. 1973). 5 — Pyroxenic andesites of Pliocene age from the Gutii mountains, Rumania (from the work by Lang B. — Midroiu V. — Udrescu C. 1973). 6 — Pyroxenic andesites of Sarmatian age from the Gutii mountains, Rumania (from the work by Lang B. — Midroiu V. — Udrescu C. 1973). 7 — Andesites from Japan (from the work by Taylor S. R. — White A. J. R. 1966). 8 — Andesites from New Zealand (from the work by Taylor S. R. — White A. J. R. 1966). 9 — Tertiary volcanics from Northern Ireland (from the work by Patterson E. M. 1952). 10 — Volcanics from Kamchatka (from the work by Marchinin E. K. — Sapožnikova A. M. 1962). 11 — Basalts from Siberian traps (from the work by Nesterenko V. G. — Ovilova N. S. — Smirnova N. P. 1964). 12 — Medicine Lake Highlands (from the work by Nockolds S. E. and Allen R. 1954). 13 — Central Honshu, Japan (from the work by Morita Y. 1955). 14 — Hawaii islands (from the work by Wedepohl K. H. 1972). 15 — Iceland (from the work by Wedepohl K. H. 1972). 16 — Volcanics from Japan (from the work by Hamaduchi H. — Kuroda R. 1959). 17 — Neogene subvolcanic zone, Rumania (from work by Peltz S. — Vasilin C. — Undrescu C. 1972).

Rhyolites from Slovakia have a content of zinc very near to rhyolites from Japan, however, the rhyolites from the subvolcanic zone of Rumania contain nearly twice as much zinc as our rhyolites. Similarly also the average value (A. P. Vinogradov, 1962) for zinc from rhyolites is nearly twice as high as the concentration of zinc in rhyolites from Slovakia. Considerable differences

in the concentration of zinc are also in andesites. Andesites of the subvolcanic zone in Rumania are almost by one third poorer than our andesites and the average content of zinc in andesites from the major volcanic mountain ranges of Rumania is almost by one half lesser than by us. Only a somewhat less zinc than our andesites contain andesites from the Gutii mountains in Romania. The average value of zinc for andesites (A. P. Vinogradov 1962) is a little lesser than content of zinc in our andesites. Our andesites, however, are by one third poorer in zinc than andesite AVG-1 from Oregon, which is mentioned as world standard. The basalts of Slovakia are in their content of zinc very close to to tholeiitic basalts from the Hawaii islands and nearly twice richer in zinc than basalts from Iceland. Our basalts are by one third poorer in zinc than the average value of zinc for basalts, also with regard to the content of zinc in the international standard of basalt—BCR-1.

Distinct differences are in concentration of copper. Rhyolites from Slovakia, compared with other regions, are largely poorer in copper. Rhyolites from the Neogene subvolcanic zone of Rumania contain as much as twice copper than our rhyolites. The average value of copper (A. P. Vinogradov, 1962) for rhyolites is nearly three times higher than the content by us and rhyolites from Kamchatka contain as much as four times of it than our rhyolites. Tertiary rhyolites from Ireland, compared to our ones, are very rich in copper they contain eight times more copper than its concentration in rhyolites of Slovakia. A great inhomogeneity in concentration of copper is also in andesites. In concentration of copper andesites from Kamchatka, New Zealand as well as the average value of copper for andesites are very close to our andesites. Moderately higher contents are in andesites from the Cserhát mountains in Hungary and in andesites from the Gutii mountains in Rumania. Almost by one third higher is the concentration in andesites from the subvolcanic Neogene zone in Rumania as well as the average concentration of copper in andesites from the main volcanic mountain ranges in Rumania. Almost as much as twice copper than in our andesites is in andesites from Japan. The international standard AVG-1 contains nearly twice as much copper as our andesites. Contrary is the situation in concentration of copper in the international standard for basalt. Basalt from Slovakia contain nearly twice as much copper as its concentration in the international standard for basalt. In the content of copper are very close to our basalts those from Siberian traps. Basalts from Kamchatka are nearly by one third richer in copper than our basalts and the average value for copper in basalts exceeds twice the concentration of copper in our basalts.

Neovolcanic rocks of Slovakia, with regard to the compared regions, are distinctly richer in silver. Rhyolites from Slovakia contain twice as much silver as its average value according to A. P. Vinogradov (1962). Rhyolites from Japan also contain by one half less silver than its concentration in rhyolites by us. More distinct differences are in andesites. Concentration of silver in the international standard for andesite is six times less than its content in andesites from Slovakia. The average content is also seven times lesser than its concentration by us. Andesites from Japan are six times poorer in silver than our andesites. Great differences are also in concentration of silver in basalts. Our basalts are seven times richer in silver than basalts from Japan. Very distinct

differences are in the international standard for basalt, which contains almost six times less silver than our basalts.

Considerable differences according to data from literature are also in concentration of lead. Rhyolites from Medicine Lake, compared to our rhyolites, have only one third of the lead content for our rhyolites. According to A. P. Vinogradov (1962) the average content of lead for rhyolites is by one half lesser than its average content by us. Our rhyolites are close to rhyolites from the subvolcanic zone in Rumania and to rhyolites from Northern Ireland. In andesites a lesser concentration of lead is mentioned from New Zealand, by one third lesser than in our andesites. Andesites from Japan contain by one half less lead. A concentration of lead very close to our andesites is the subvolcanic zone of Rumania. The international standard for andesites, compared to our andesites, is by one third richer in lead.

In basalts from Slovakia concentration of lead is less than 3 ppm in the most studied samples. The average value of lead for basalts is 8 ppm and the international standard for basalts contains 18 ppm lead.

The total analysis of the content of zinc, copper, silver and lead in various volcanic regions makes clear that in works concerning the contents of the mentioned elements it is necessary to set out from their concentrations within each volcanic region, especially with regard to the character of volcanic association and in studies of various character it is not possible to adopt data from literature generally.

### *Conclusion*

The young volcanic rocks in Slovakia are producers of long-dated volcanic activity taking place from the Eggenburgian to the Pliocene, even Quaternary. The rocks of the rhyolite-andesite order are of alkalic-calcareous character and extended in the neovolcanic regions of central and eastern Slovakia. Basalts are of alkalic character and developed in central and southeastern Slovakia, are the youngest volcanic rocks in Slovakia.

For the total investigation of the concentration of zinc, lead, silver and copper in these rocks is evident as follows:

1. Rocks most potential in lead are rhyolites. With increasing basicity of rocks concentration of lead lowers in them. Most potential in copper, zinc and silver are andesites and basalts and with increasing acidity of rocks their concentration decreases.

2. In rocks of the rhyolite-andesite order of the neovolcanic regions of central and eastern Slovakia are the following differences in the concentration of the traced elements. In the content of copper andesites from eastern Slovakia show a tendency towards a lesser content of copper than in andesites from central Slovakia, in rhyolites no essential changes have been evident. Differences are also in the content of lead. In andesites from central Slovakia is three times as much lead as in andesites from eastern Slovakia. In rhyolites are no essential differences in the concentration of lead. In concentration of silver rhyolites from eastern Slovakia display the tendency towards a lower content than rhyolites from central Slovakia. In andesites it is the contrary. Andesites from eastern Slovakia display a tendency towards a higher content of silver than andesites from central Slovakia. In concentration of zinc no essential changes have been evident. These data complete preceding knowledge on the differences



in chemical characteristics in the Middle and East Slovakian regions, indicating that volcanic rocks of these regions originated from different magmatic chambers.

3. Mutual relations of elements have shown wider correlative relations of the observed microelements to macroelements, of copper, zinc and silver to iron and magnesium as between microelements to one another. We suppose that copper, zinc and silver are partly bound in Fe, Mg minerals of the studied rocks. Lead appears to be the most dispersed element, however, its partial bond to biotite cannot be excluded and also it is not possible to suppose its bond in plagioclases and potassium feldspars.

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