

## REGIONAL VARIATIONS IN COMPOSITION OF THE NEOGENE–QUATERNARY ALKALINE BASALTS IN CENTRAL EUROPE

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**Abstract:** Neogene–Quaternary alkaline basalts in Central Europe are joined with two types of geotectonic structures: *a*) rift zones in Hercynian platform, *b*) hinterland of the Alpine folded system. *a*) Rift volcanism (Hessian Depression – F.R.G., Lower Silesia – Poland) represents a great variety of alkaline ultrabasic, alkaline basic rocks and their differentiates with higher content of  $\text{TiO}_2$  (2.5%), lower content of  $\text{SiO}_2$  and relatively higher values of F/K, P/Zr, L/La, Ca/Na, Ti/Sc. The ratio  $\text{Ti/V} = 63–74$  is characteristic of continental basalts. *b*) Volcanism in hinterland of Alpine folded system (Slovakia, Romania, Yugoslavia) is characterized by rather limited petrographic composition with dominancy of basanites and subalkaline olivine basalts, lower content of  $\text{TiO}_2$  (2%), higher content of  $\text{SiO}_2$ . The ratio  $\text{Ti/V}$  50 is close to the oceanic islands. Basalts of Persani Mts. (Romania) with low content of  $\text{TiO}_2$  (1.6%), higher content of  $\text{SiO}_2$  (48%) and lower content of incompatible elements show specific character. Comparative analysis reveals different conditions of magma-forming processes controlled by partial melting, crystallization differentiation with eventual contamination of crustal material.

**Key words:** alkaline basalts, Central Europe, rift zones, hinterland of Alpine folded belt, major and trace elements.

In the Cenozoic time the basalt volcanism proceeded practically on all continents. Volcanic products of the Neotectonic period show extremely variable alkali contents (from normal to alkaline series with highly alkaline rocks predominant) and basicity (basic rocks prevailing over ultrabasic and intermediary rocks). In Central Europe the alkaline basalts formed many volcanic fields in the hinterland of the Alpine orogenic belt and in its marginal platforms in the Neogene–Quaternary time.

This article is linked up to former papers (Kononova et al. 1985) concerning the Neogene–Quaternary basalts in the eastern and central parts of the Alpine system and its marginal platforms. Geochemistry is paid most attention and the research has been performed on original sample collections representative of the Neogene–Quaternary volcanism in Lower Silesia (Dziedzić), Slovakia (Konečný, Kononova, Andreyeva), Romania (Peltz), Yugoslavia (Kononova). Data on the Hessian Depression were used for comparative purposes (Wedepohl 1985).

A variety of inclusions of depth xenoliths with the peridotite composition, poor differentiation of rocks and high MgO-contents are particular characteristics of volcanics of the Neotectonic period. This is why they are regarded as products of mantle melts extraction. Their petrological and geochemi-

cal features are indicative of composition, physical and chemical regimes of deep parts of the lithosphere and of the character of magma-forming processes.

### Geology and petrography of the objects under study, methods of investigations

Numerous products of Neogene–Quaternary alkali-basalt volcanism in Central Europe generally can be joined with two types of structures;

1 – with the system of NNE rifts on the Hercynian platform (Hessian Depression etc. in the Rhine Graben, the Ohře rift in the Bohemian Massif, Lower Silesia etc.);

2 – with the hinterland of the Alpine folded system (the area of back-arc basins) in Slovakia, Hungary, Romania, Yugoslavia.

### Rift volcanism

*a* – Volcanic products of the Hessian Depression (in the Rhine Graben) were studied in detail by Wedepohl (1985). About two thousands of outcrops in the area of more than

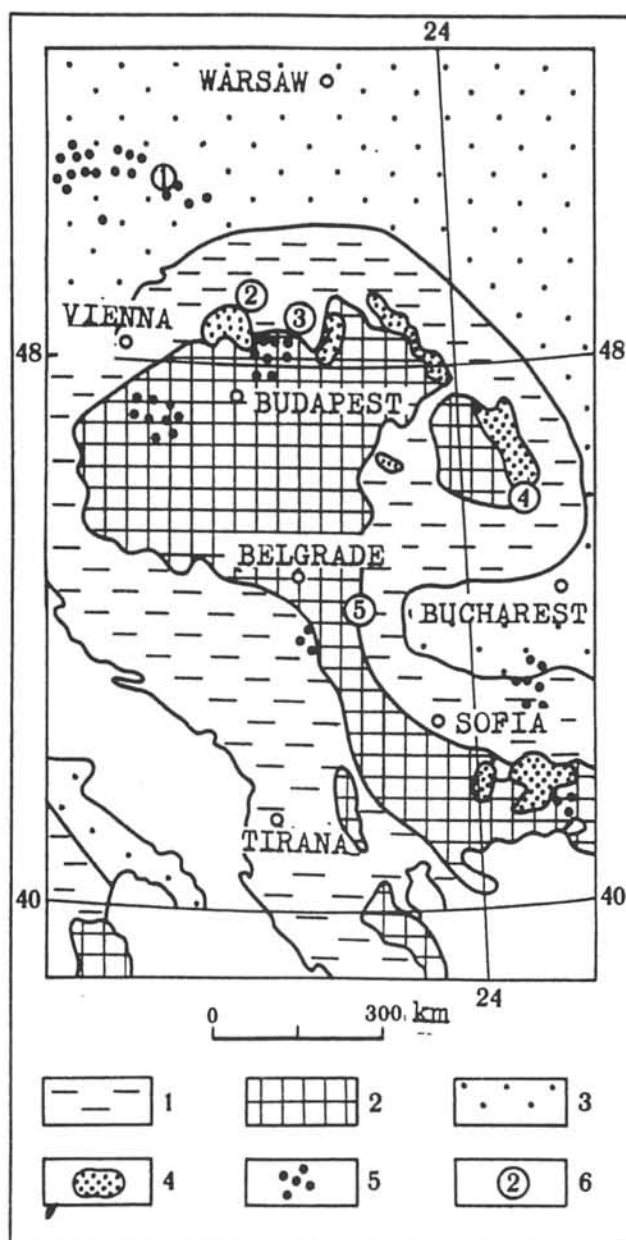


Fig. 1. Scheme of occurrences of Neogene–Quaternary alkaline magmatism in Central Europe (a tectonic scheme according to Tectonic map..., 1979).

1, 2 – Alpine folded system: epigeosynclinal folded zone (1), median massifs (2); 3 – marginal platforms and massifs; 4 – Paleogene–Neogene orogenic volcanism; 5 – Neogene–Quaternary alkaline volcanism; 6 – regions under study: 1. Lower Silesia, Poland, 2. N. Baňa, Banská Štiavnica, Central Slovakia, 3. Filakovo, South Slovakia, 4. Persani Mts., Romania, 5. Carpathian–Balkanides, Yugoslavia.

$0.02 \text{ km}^2$  are described in this area. The largest outcrop occupies about  $125 \text{ km}^2$ . It is much smaller than the neighbouring volcanic field of Vogelsberg where basalts occupy about  $2500 \text{ km}^2$ . The map of the Moho surface (Prodehl 1981) shows that the crust/mantle boundary is lifted under the Central European rift system up to the level of  $28 \text{ km}$  (the minimum of the Moho boundary is about  $24\text{--}25 \text{ km}$ ). According to K–Ar data volcanism in the Upper Rhine Graben started  $100 \text{ Ma}$  ago in the pre-rift stage. In the

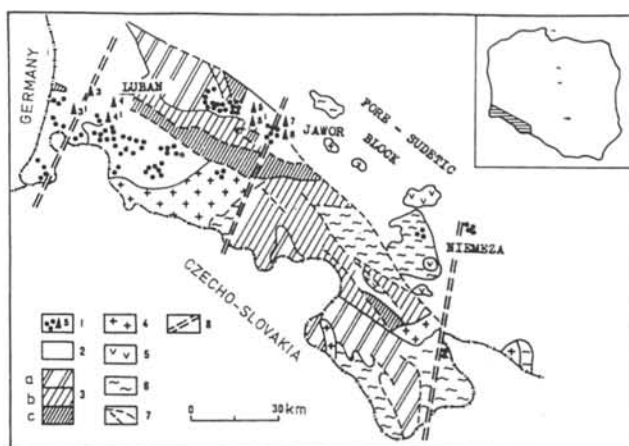


Fig. 2. Geological scheme of Tertiary alkaline volcanism from Lower Silesia (by K. Dziedzić).

1 – Tertiary alkaline volcanics and sampled regions (number of points in the scheme correspond to analyses number in Tables 1, 2); 2 – Cenozoic sediments; 3 – Paleozoic rift depressions including Epihercynian platform cover (a), Hercynian molasses (b), premolasse (Precambrian) metamorphic rocks of greenschists facies (c); 4 – Hercynian granitoids; 5 – basic and ultrabasic rocks; 6 – metamorphic rocks of amphibolite facies; 7 – fractures, 8 – fracture zones.

Neogene–Quaternary period at least 3 stages of volcanism can be distinguished. The composition of volcanic products changed in these stages: 1)  $20\text{--}10 \text{ Ma}$  – erupted quartz tholeiite; 2)  $12\text{--}13 \text{ Ma}$  – mostly subalkaline olivine basalts; 3)  $14\text{--}17 \text{ Ma}$  – ultrabasic and basic rocks containing nepheline (olivine nephelinites, olivine tephrites, a.o.).

b – In Lower Silesia (SW Poland) the alkali-basalt volcanism is concentrated over a  $230 \text{ km}$  long belt regarded as the extension of the Central European rift system (Fig. 1, Pt. 1). K–Ar age of volcanics is  $28\text{--}15 \text{ Ma}$ . They are distributed in submeridian systems of transform fractures in the areas of Luban, Jawor, Niemeza (Fig. 2) and particularly in the southwestern part of the country (Alibert et al. 1987). Alkaline and subalkaline ultrabasic and basic rocks like olivine nephelinites, alkaline picrites, subalkaline olivine basalts are predominant. Limburgites are infrequent. Other differentiated varieties up to trachytes are known, as well as xenoliths of peridotite composition, mainly harzburgites, lherzolites, dunites and wehrlites (Smulikowski et al. 1984).

#### Volcanism in hinterland of Alpine folded system (back-arc basins)

Alkali basalt volcanism in Slovakia is situated in the hinterland of the western branch of the Carpathian orogenic arc, near the western margins of the Pannonian Basin (Fig. 1, Pt. 2). Volcanic activity followed immediately the Neogene andesite volcanism of the molasse stage. Several volcanic bodies are known in the Central Slovakian Neogene volcanic field. A small scoria cone is preserved at Nová Baňa with several lava flows, lava necks and dykes at B. Štiavnica and a lava flow near Zvolen. The time of volcanic activity varies from  $7.29 \pm 0.41 \text{ Ma}$  (lava neck Banská Štiavnica) to  $0.53 \pm 0.16 \text{ Ma}$  (lava flow near Nová Baňa).

More intensive volcanic activity proceeded in Southern Slovakia (Lučenec–Filakovo; Fig. 1, Pt. 3). There it is

represented by scoria cones (Bučoni, Ragáč), numerous lava flows, dikes, necks, maars and diatremes (Hajnačka, Šurice). Two stages of volcanic activity have been distinguished by K/Ar dating: the older Podrečany formation (4.9–7.15 Ma) with subalkaline olivine basalts and the younger Cerová formation (1.35–2.75 Ma) with dominant nepheline basanites and olivine basanites. Some lava flows contain kersutite, pyroxene megacrysts and spinel ilherzolite xenocrysts.

In Romania (Fig. 1, Pt. 4) in the region of Lucarets (Banat), in the northern part of the Poiana Rusca in the Persani Mts. lava flows and pyroclastic complexes of subalkaline and alkaline compositions were formed in the Pleistocene time. The Pleistocene volcanism was the most intensive in the inner part of the Eastern Carpathians in the Persani Mts. The effusive activity in the Persani Mts. is K-Ar dated to 1.39–1.23 Ma and the terminal phase of volcanic activity is dated as far back as 0.5 Ma (Ghenea et al. 1981). Volcanics are mainly represented by subalkaline olivine basalts, although more alkaline varieties and peridotite inclusions have also been found.

In East Yugoslavia within the Carpathian-Balkan arc there are many outcrops of Cenozoic volcanic rocks (Fig. 1, Pt. 5). They form dykes, small flows located in sublatitudinal and submeridian fractures. It can be assumed that this volcanism is of Miocene age. As regards composition melanocratic rocks like olivine nephelinites, olivine tephrites prevail. Subalkaline varieties belonging to subalkaline olivine basalts are also present.

To reveal regional variations of Neogene–Quaternary volcanics from Central Europe the authors selected representative samples from lava flows and volcanic cones (not less than 10 from each volcanic areal). Considering the fact, that criteria of comparison of rare element concentration determined by different analytical methods are not sufficiently worked out, the majority of analytical data were obtained with one and the same set of methods and laboratories guided by V. A. Kononova. The main rock-forming elements were analysed by the X-ray fluorescent method (VIMS, Ministry of Geology of the U.S.S.R.; University of Freiburg, F.R.G.) as well as by a classic method (IGEM of the U.S.S.R. Academy of Sciences). The latter was used in all cases to determine FeO, H<sub>2</sub>O, F, Cl, S, CO<sub>2</sub>. To study rare elements behaviour flame photometry methods and RFA were used. In IGEM of the U.S.S.R. Academy of Sciences by means of flame photometry Ni, Co, Cr, V, Ba, Sr, Li, Rb, Cs were determined. Zr, Nb, Y, Sr, Rb were determined by the RFA method in IGEM too. In the University of Freiburg (F.R.G.) V, Sc, Ni, Cr, Co, Rb, Sr, Ba, Pb, La, Ce, Nd, Y, Nb, Zr were determined by the RFA method. This very set of elements was also determined by the RFA method in VIMS, Ministry of Geology of the U.S.S.R. In the course of analytical work a control over the comparison of results was exercised using the alkaline basaltoid rock samples. They were studied in F.R.G. by 2 methods in parallel: in the University of Freiburg by REA method and in Mainz- by the neutron-activation method (Max Plank Institute of Geochemistry and Cosmochemistry). Partially data from literature were used (Alibert et al. 1987; Forgáč 1970; Wedepohl 1985). Because CO<sub>2</sub> content is not higher than 0.3%, Cl content is not higher than 0.02–0.06%, S – 0–0.3%, Pb not more than 15 ppm, the information is not given in the table.

This paper is based on a comparative analysis of petrochemical data from 5 regions under investigation (Hessian Depression, F.R.G.; Lower Silesia, Poland; Central and South

Slovakia; Persani Mountains, Romania; Carpathian-Balkan area in Yugoslavia). From the total number of the analysed samples (about 70) the analyses were selected according to less differentiated rock varieties where MgO content coefficient ( $K_{Mg}$ )<sup>\*</sup> is usually more than 65. To the selection of analysis in each region, besides MgO-content in rocks a special attention was paid to the contents of SiO<sub>2</sub> and alkalines. For comparison the most primitive varieties of the following types of rocks were selected: olivine nephelinites (sometimes alkaline picrites), olivine tephrites (basanites), subalkaline olivine basalts (sometimes hawaiiites). The average composition of each type of rock was calculated (the composition was recalculated to 100%). The data as well as some analyses with ( $K_{Mg}$ )<sup>\*</sup> coefficient calculations, nepheline contents in norm, Na<sub>2</sub>O/K<sub>2</sub>O ratio are given in Tabs. 1, 2.

### Petrochemical regional variations

Neogene–Quaternary volcanic products of volcanic fields under study, are characterized by high contents of MgO (usually more than 8% for poorly differentiated varieties) and by SiO<sub>2</sub> undersaturation (the normative nepheline is always present on recalculation according to CIPW system). Poorly differentiated rock varieties with  $K_{Mg}$  coefficient lower than 65 are quite frequent in the volcanic fields under study. In relation to mantle material the volcanic rocks are regularly enriched with rare elements. A comparison of volcanics (of primitive composition) from different areas revealed their variable composition in relation to both the rock-forming and minor elements which seems to result from regional magma-generating processes.

First of all such differences are revealed when comparing two distinguished types of Cenozoic volcanism; rift volcanism in Epihercynian platform, and volcanism in hinterland of Alpine orogenic belt. Principal tendencies of regional variations of composition should be considered using data from Tabs. 1, 2. Among petrochemical peculiarities of volcanic rocks the following are most interesting:

– Variations of set of rocks at the variety of volcanism products in rift structures. In the Hessian Depression (Wedepohl 1985) primitive rocks corresponding to olivine nephelinites, melilite-bearing olivine nephelinites, nepheline basanite, subalkaline olivine basalts except for products with markedly different composition which differ in composition very much. Neogene–Quaternary volcanism in hinterland of Alpine folded region is more limited as regards the composition variations. Olivine tephrite (basanites) and subalkaline olivine basalts are predominant. Apart from it quite often one type of rocks dominates within a concrete volcanic field. Thus subalkaline olivine basalts are mostly well developed in Persani Mts. and olivine tephrite in Slovakia.

– Extensive distribution of alkaline ultrabasic rocks including melilite-bearing and olivine-bearing foidite in volcanic fields of Central European rift system, for example Hessian Depression (Wedepohl 1985; Tab. 1, an. 1) Lower Silesia (Tab. 1, an. 3–6). These ultrabasic rocks are scarce in

<sup>\*</sup>  $K_{Mg} = 100 \text{ Mg} / (\text{Mg} + \text{Fe}^{2+})$ , where  $\text{Fe}^{2+}$  was received while measuring total Fe contents, considering the ratio of  $\text{Fe}_2\text{O}_3/\text{FeO} = 0.15$ .

**Table 1.** Representative analyses and average compositions (wt. %) of Neogene–Quaternary volcanites of Central Europe.

Volcanic region	Hessian Depression F. R. G.		Lower Silesia Poland							Lower Silesia Poland, No. 3	
	1(9)	2(13)	3	4	5	6(5)	7	8	9(3)	10	11(2)
SiO <sub>2</sub>	40.26±0.95	45.18±1.13	40.21	41.18	40.80	41.75±1.40	46.18	44.97	46.00±0.58	39.12	39.01±0.16
TiO <sub>2</sub>	2.73±0.25	2.23±0.12	3.30	2.87	3.19	3.02±0.25	2.34	2.50	2.48±0.08	3.13	2.95±0.17
Al <sub>2</sub> O <sub>3</sub>	11.41±0.78	12.47±0.95	12.21	11.53	12.30	12.39±0.79	13.94	14.22	14.27±0.14	11.11	10.84±0.29
Fe <sub>2</sub> O <sub>3</sub>	4.06±0.59	3.00±0.54	6.63	5.21	3.82	5.05±1.40	4.69	4.80	4.46±0.26	12.81t	12.80±0.02t
FeO	6.78±0.46	7.49±0.59	6.28	6.70	8.02	7.30±0.87	7.0	6.88	7.06±0.09	–	–
MnO	0.19±0.01	0.18±0.02	0.17	0.17	0.16	0.17±0.01	0.16	0.18	0.17±0.01	0.22	0.22±0.01
MgO	12.22±2.06	10.95±2.45	11.39	13.33	11.30	12.27±1.01	9.79	9.48	9.64±0.21	12.23	13.47±1.22
CaO	12.55±0.77	10.18±0.59	13.03	12.05	12.32	12.30±1.27	9.79	10.24	10.09±0.22	13.83	13.22±0.62
Na <sub>2</sub> O	3.34±0.65	2.88±0.57	3.80	3.30	3.80	3.64±0.25	3.50	3.79	3.77±0.20	3.09	2.95±0.15
K <sub>2</sub> O	1.70±0.49	1.89±0.15	0.77	0.36	1.10	0.94±0.39	0.84	1.01	0.97±0.12	1.12	0.89±0.23
H <sub>2</sub> O	2.71±1.07	2.06±0.33	0.30	1.08	0.04	0.41±0.52	0.30	0.30	0.30±0.10	2.64	2.68±0.03
P <sub>2</sub> O <sub>5</sub>	1.14±0.20	0.73±0.16	1.01	0.78	1.05	0.86±0.24	0.48	0.66	0.61±0.09	1.03	0.97±0.06
Na <sub>2</sub> O/K <sub>2</sub> O	1.9	1.5	4.9	9.2	3.4	4.3	4.2	3.7	3.9	2.7	3.3
K <sub>Mg</sub>	75	72	65	70	67	67	64	63	63	–	–
Ne <sub>(CIPW)</sub>	15	6	17	12	17	13	3	7	6	–	–

Continuation of Tab. 1.

Volcanic region	Central Slovakia C.S.F.R.				South Slovakia C. S. F. R.					Persani Mountains Romania				Carpathian-Balkan zone Yugoslavia	
	12	13	14(4)	15(8) /5/	16/5/	17	18	19	20(12)	21	22	23	24(11)	25(6)	26
SiO <sub>2</sub>	45.22	45.00	45.26±0.38	45.34±0.10	42.75	45.83	45.43	46.34	45.54±0.63	45.88	46.94	48.39	47.96±1.47	43.76±0.55	47.54
TiO <sub>2</sub>	2.39	2.50	2.47±0.14	1.87(1)	1.93	2.11	2.20	2.07	2.17±0.18	1.81	1.78	1.55	1.61±0.20	2.14±0.09	1.82
Al <sub>2</sub> O <sub>3</sub>	13.33	12.69	13.10±0.37	13.15±0.07	14.42	16.89	16.49	16.97	16.32±0.56	15.33	16.51	16.04	16.06±0.59	14.50±0.38	15.53
Fe <sub>2</sub> O <sub>3</sub>	4.46	4.82	4.39±0.37	3.89±0.33	4.05	2.94	2.90	2.81	3.26±0.31	7.24	3.09	3.12	3.97±2.61	5.42±0.66	3.45
FeO	6.42	7.09	7.03±0.66	8.24±0.16	5.19	5.35	5.57	5.50	5.54±0.43	2.63	5.87	5.72	5.07±2.12	5.69±0.45	6.34
MnO	0.18	0.18	0.18±0.01	0.17±0.0	0.32	0.16	0.15	0.16	0.17±0.03	0.17	0.18	0.17	0.17±0.01	0.09±0.01	0.18
MgO	10.58	10.60	10.50±0.12	12.70±0.92	7.86	8.60	8.87	8.32	8.60±0.74	9.98	9.27	8.95	9.64±1.69	10.42±0.50	8.43
CaO	10.12	9.33	10.04±0.09	9.82±0.59	12.79	10.02	10.77	10.04	10.40±0.48	9.48	9.03	9.70	9.56±0.15	11.94±0.53	9.92
Na <sub>2</sub> O	4.01	4.07	4.11±0.06	2.88±0.07	2.51	4.01	4.20	4.21	4.08±0.28	3.00	2.82	3.55	3.13±1.58	3.26±0.53	3.36
K <sub>2</sub> O	1.71	1.62	1.68±0.03	1.20±0.13	1.57	2.26	2.25	2.42	2.27±0.14	1.39	1.08	1.11	1.39±0.52	1.17±0.18	1.97
H <sub>2</sub> O	0.44	0.57	0.46±0.08	0.24±0.08	3.90	1.72	0.95	0.65	1.14±0.67	1.71	1.80	0.96	0.97±0.79	0.84±0.31	0.91
P <sub>2</sub> O <sub>5</sub>	0.77	0.70	0.78±0.05	0.49±0.07	0.26	0.64	0.53	0.64	0.51±0.15	0.59	0.50	0.51	0.47±0.11	0.67±0.07	0.55
Na <sub>2</sub> /K <sub>2</sub> O	2.3	2.5	2.4	2.4	1.6	1.8	1.9	1.7	1.8	2.1	2.6	3.2	2.2	2.8	1.7
K <sub>Mg</sub>	67	69	—	69	62	69	69	68	—	—	—	—	—	—	64
Ne <sub>(CIPW)</sub>	11	—	11	—	—	13	16	14	—	—	—	—	—	—	5.1

Note: In Table 1, 2, 3, an. 1, 3–6, 10–11, 16, 25 – olivine nephelinites, alkaline picrites; an. 12–14, 17–20 – alkaline basaltoids, mostly olivine tephrites; an. 2, 7–9, 15, 21–24, 26 – hawaiites, subalkaline olivine basalts. In brackets a number of analyses used to calculate an average one. Fe<sub>2</sub>O<sub>3</sub> value marked „t“ is a general iron in Fe<sub>2</sub>O<sub>3</sub>.

Precise location of samples: an. 3, 4 – region of the town Luban: Granowskie hills (an. 3), Ksieginki (an. 4); an. 4, 7, 8 – region of the town Jawor: Kozia (an. 5), Mecinka (an. 7), Wennica (an. 8); an. 10 – region of Bogatynia; an. 12–14 – N. Baňa; an. 15 – Banská Štiavnica (Kysyhýbel); an. 17 – Fífakovo the village Bulhary; an. 18 – Konrádovce; an. 19 – Fífakovo (the village Hodejov); an. 21–22 – Racosul de Jos; an. 23 – Bogata.

hinterland of the Alpine folded system. These rare representatives of an ultrabasic group of rocks are visibly enriched with SiO<sub>2</sub> (42–43%). This corresponds to intermediate differences between rocks of ultrabasic and basic groups of rocks (Tab. 1, an. 16, 23). This tendency is characteristic of subalkaline basaltic rocks from the Persani Mts. (Romania) and Carpathian-Balkanides of Yugoslavia. They most of all are enriched with SiO<sub>2</sub> (about 48%, Tab. 1, an. 21–24, 26) despite their rather primitive composition. Fig. 3 quite distinctly shows a sharp dislocation to the right of the volcanic

products in the hinterland of the Alpine orogenic belt. Their SiO<sub>2</sub> content is higher (conventional symbols 3–6).

– Differences in SiO<sub>2</sub> content are in a reverse correlation with TiO<sub>2</sub>, i.e. TiO<sub>2</sub> 2% is characteristic of rift volcanism in the Hessian Depression and in Lower Silesia. In volcanic products from the Alpine folded system TiO<sub>2</sub> 2% is more typical (see Fig. 3). Extremely low values of TiO<sub>2</sub> (closer to 1.6%) were noted in volcanic rocks from the Persani Mts. (Romania). They are also characterized by higher concentrations of SiO<sub>2</sub>.



**Table 2.** Representative analyses and average compositions (ppm) of Neogene–Quaternary volcanites of Central Europe.

	1			2			3	4	5	6			7	8	9			10	11			12	13
	<sup>x</sup> N	<sup>±</sup> S	N	<sup>x</sup> N	<sup>±</sup> S	N				<sup>x</sup> N	<sup>±</sup> S	N			<sup>x</sup> N	<sup>±</sup> S	N		<sup>x</sup> N	<sup>±</sup> S	N		
Li	4.0	–	3	5.8	0.9	8	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	4
F	924	184	6	853	46	6	1000	870	950	864	175	5	430	450	466	45	3	–	–	–	–	–	700
P	4970	870	9	3190	670	13	4408	3404	4582	3709	1037	5	2095	2880	2618	392	3	–	4233	260	2	3360	3055
Sc	21	1.7	3	19.9	0.6	10	26	14	12	17	7	5	16	23	21	3	3	–	–	–	–	17	–
V	220	23	8	187	13	13	310	230	230	256	45	5	210	170	203	30	3	298	280	18	2	218	336
Cr	371	100	7	395	206	10	300 <sup>x</sup>	400 <sup>x</sup>	100 <sup>x</sup>	300	200	5	200 <sup>x</sup>	100 <sup>x</sup>	150	50	3	446	472	26	2	281	144
Co	49	5	8	49	7.3	14	65	48	44	51	21	5	49	43	44	4	3	–	–	–	–	50	42
Ni	329	220	8	301	242	13	220	340	170	296	165	5	130	110	112	16	3	262	328	66	2	184	181
Rb	57	8	8	55	14	14	81	40	28	40	31	5	22	28	23	5	3	39	48	9	2	48	42
Sr	1450	374	7	1020	113	13	931	721	932	817	173	5	425	579	580	155	3	1206	1086	120	2	869	845
Y	27.5	5	4	23	4.3	7	32	17	24	26	4	5	24	30	23	7	3	–	–	–	–	23	–
Zr	287	44	3	218	55	4	299	268	271	264	36	5	207	251	218	26	3	–	–	–	–	260	–
Nb	–	–	–	–	–	–	82	62	75	71	16	5	33	55	39	13	3	–	–	–	–	74	–
Cs	1.1	0.3	5	0.73	0.22	10	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.5	–
Ba	890	240	8	780	89	14	500 <sup>x</sup>	700 <sup>x</sup>	800 <sup>x</sup>	700	150	5	400 <sup>x</sup>	800 <sup>x</sup>	667	180	3	971	847	123	2	549	610
La	112	11	5	63	13	10	73	59	85	65	25	5	28	39	39	10	3	97	86	10	2	57	–
Ce	217	21	5	135	24	10	110	120	140	116	32	5	40	100	80	30	3	166	156	10	3	79	–
Nd	79	29	4	60	21	7	70	50	60	54	20	5	30	30	30	–	3	72	67	3	3	38	–
Yb	2.0	0.65	5	1.9	0.35	11	2	3	2	2	1	5	4	2	3	1	3	1.87	1.96	0.07	3	–	–
La/Nb	–	–	–	–	–	–	0.9	0.09	1.1	0.9	–	–	0.8	0.7	1	–	–	–	–	–	–	0.8	–

Continuation of Tab. 2.

	14			15			16	17	18	19	20			21	22	23	24			25			26
	<sup>x</sup> N	<sup>±</sup> S	N	<sup>x</sup> N	<sup>±</sup> S	N					<sup>x</sup> N	<sup>±</sup> S	N				<sup>x</sup> N	<sup>±</sup> S	N	<sup>x</sup> N	<sup>±</sup> S	N	
Li	5.0	1	2	–	–	–	–	–	–	–	4.0	1.0	5	7	7	–	7	1	4	5	2	6	4
F	765	65	2	–	–	–	–	–	–	–	774	59	5	500	500	–	500	–	4	–	–	–	–
P	3404	327	4	2092	296	3	1135	2793	2313	2793	2002	766	12	2574	2182	2226	2051	523	9	2916	296	6	2356
Sc	18	1	2	–	–	–	–	13	20	18	18	2	5	10	10	21	18	10	9	–	–	–	–
V	274	53	4	263	58	2	312	195	224	196	255	60	10	225	220	210	185	80	9	231	20	6	235
Cr	234	60	3	274	47	2	246	158	197	173	190	20	8	383	315	–	314	78	4	240	38	6	200
Co	44	2	4	48	16	2	42	37	42	36	36	3	12	39	39	42	38	16	9	40	3	6	73
Ni	183	2	4	–	–	–	–	126	143	126	126	13	10	196	181	–	200	55	4	182	22	6	149
Rb	46	3	4	50	12	2	119	70	67	71	80	8	12	20	18	48	28	9	9	28	6	12	36
Sr	856	10	4	755	110	2	603	859	789	840	833	28	11	465	685	710	602	55	4	1063	213	12	761
Y	24	1	2	–	–	–	–	25	25	26	25	1	5	14	18	19	18	5	9	23	1	6	25
Zr	261	1	2	270	55	2	253	215	193	216	220	7	7	141	148	185	156	30	9	157	16	6	165
Nb	74	–	2	–	–	–	–	79	75	79	78	2	5	35	14	24	28	10	9	48	9	6	52
Cs	0.5	–	2	–	–	–	–	–	–	–	1	–	5	0.5	0.5	–	0.5	–	4	2	1	6	1
Ba	570	26	4	469	61	2	677	738	711	748	811	68	12	987	690	800	816	205	9	758	37	6	801
La	65	8	2	–	–	–	–	59	53	63	55	5	5	56	39	36	40	12	9	–	–	–	–
Ce	78	2	2	–	–	–	–	77	67	81	72	9	5	70	50	25	40	18	9	–	–	–	–
Nd	38	–	2	–	–	–	–	35	40	35	36	3	5	47	23	–	31	14	4	–	–	–	–
Yb	–	–	–	–	–	–	–	–	–	–	–	–	–	3.0	2.0	2.1	1.8	0.3	8	–	–	–	–
La/Nb	0.9	–	–	–	–	–	–	0.7	0.7	0.8	0.7	–	–	1.6	2.8	1.5	1.4	–	–	–	–	–	–

Note: Elements marked with × are measured by spectrochemical method;

Zr, Nb, V, Sr, Ba – by an X-ray fluorescent analysis in IGEM of the U.S.S.R. Acad. of Sci; La, Ce, Nd, Sc, Ni, Co, V, Nb, Y – by an X-ray fluorescent analyses in VIMS of the U.S.S.R. Ministry of Geology. In an. 10, 11 Rb and Sr, REE were measured by the method of isotope dissolving.

Additional determinations: in an. 1, 2 consequently Hf – 7.0, 4.8; Ta – 7.1, 4.6; Th – 13.3, 7.9; Tb – 1.6, 0.98; in an. 10 and 11 consequently Sm – 12.3, 11.5; Eu – 3.54, 3.40; Gd – 9.62, 9.30; Dy – 6.09, 6.90; Er – 2.57, 2.55; an. 23 Sm – 2.2, Eu – 1.15; an. 24 Tb – 0.43.

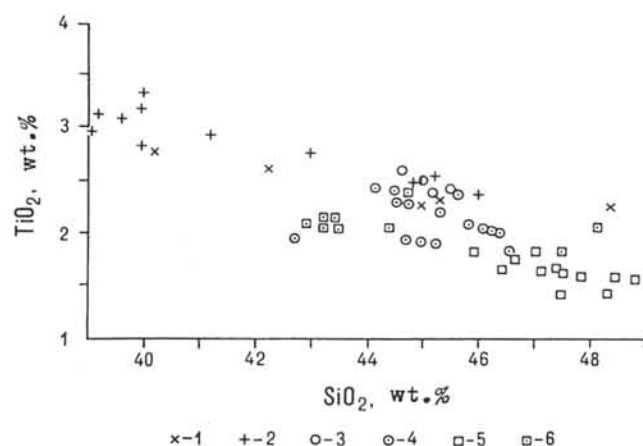


Fig. 3.  $\text{SiO}_2$ - $\text{TiO}_2$  correlation in Neogene-Quaternary continental alkaline volcanism of Central Europe.

1 - Hessian Depression, F.R.G.; 2 - Lower Silesia, Poland; 3 - Central Slovakia, C.S.F.R.; 4 - South Slovakia, C.S.F.R.; 5 - Persani Mts., Romania; 6 - Carpathian-Balkanides, Yugoslavia.

- Alkaline ratio ( $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ) is rather stable in all volcanic fields studied irrespective of basicity, general alkalinity and geologic-tectonic position. Following are  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios in the respective fields: 1.5-1.9 in Hessian Depression; 1.6-1.9 in South Slovakia; 2.7-4.9 (up to 9.2) in Lower Silesia and 2.1-3.2 in the Persani Mts. Only in the Carpathian-Balkanides (Yugoslavia) the values of  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  are different (2.3-3.7, occasionally 1.5-4.3) and in subalkaline olivine basalt 1.4-1.7.

As for peculiarities in geochemistry, it is to be noticed, that there are evident variations in the rare elements distribution, in spite of the selection of primitive rocks ( $K_{\text{Mg}} > 65$ ,  $\text{MgO}$  9-13%). In the analysis we have applied the element ratios suggested by Wedepohl (1985) and diagrams of elements distribution according to Thompson et al. (1983).

Indicative element ratios were calculated for the average compositions of Neogene-Quaternary volcanics in Central

Europe (Tab. 3) and data by Wedepohl (1985) on cosmic material (Tab. 3, an. 28) and on tholeiite basalts of middle oceanic ridges (Tab. 3, an. 27) were used for a comparison. The analysis of these data revealed many geochemical peculiarities of volcanics studied.

Several element ratios ( $\text{Li}/\text{Al}$ ,  $\text{F}/\text{K}$ ,  $\text{Na}/\text{Al}$ ,  $\text{Ba}/\text{La}$ ) in volcanic fields with a rare exception vary slightly and less than twice differ from chondrites. This behaviour is indicative of a close crystallochemical interrelation between element couples, and of the absence of their distinct fractionation in the Earth in comparison with chondrites.

Like in rock-forming elements, differences in geochemical peculiarities were also determined in volcanic products from rift zones and from the hinterland of the Alpine orogenic belt. There are some variations in slightly fractionated elements whose ratios almost do not differ from those of chondrites. The  $\text{F}/\text{K}$  ratio in products of the rift volcanism is constantly higher. Other ratios also show conspicuous differences, for example  $\text{P}/\text{Zr}$ ,  $\text{P}/\text{La}$ ,  $\text{Ca}/\text{Na}$ ,  $\text{Ti}/\text{Sc}$ ,  $\text{Ti}/\text{V}$ . Their values in products of the rift volcanism (Hessian Depression, Lower Silesia) are always higher. As regards the association of  $\text{Ti}/\text{V}$  ratio in basaltic rocks with tectonic conditions (Thompson et al. 1983), it is evident that the  $\text{Ti}/\text{V} = 63-74$  in the samples from the Hessian Depression and Lower Silesia is characteristic of continental basalts (61-90 according to Wass 1980). The  $\text{Ti}/\text{V} \approx 50$  in rocks from hinterland of the Alpine orogenic belt corresponds to the values characteristic of oceanic islands ( $\text{Ti}/\text{V} = 47-57$  according to Wass 1980). Many ratios like  $\text{P}/\text{Zr}$ ,  $\text{P}/\text{Ta}$ ,  $\text{Ti}/\text{Cs}$ ,  $\text{Ti}/\text{V}$ ,  $\text{Cr}/\text{Ni}$  show that the continental alkaline volcanic rocks differ markedly from tholeiite basalts of middle oceanic ridges (Tab. 3, an. 27). It is possible that the revealed variations of element ratios as well as the correlation of these ratios with rock composition, geotectonic position of objects are the consequence of differences in processes of element fractionation in various magmatic systems under different geotectonic regimes.

Geochemical differences in volcanic fields under study mainly in relation to incompatible elements are visible in diagrams of element distributions (Fig. 4 A, B). The diagrams are based on Thompson's principles and coefficients (Thomp-

Table 3. Indicating element ratios (ppm) in average composition of Neogene-Quaternary volcanites of Central Europe.

	1	2	6	9	11	14	20	24	25	26	27	28
$10^4 \times \text{Li}/\text{Al}$	0.66	0.88	-	-	-	0.72	0.42	-	0.65	0.49	1.06	1.5
$10 \times \text{F}/\text{K}$	0.65	0.54	1.24	0.58	-	0.55	0.38	0.43	-	-	-	0.44
$\text{Na}/\text{Al}$	0.41	0.32	0.40	0.37	0.38	0.44	0.33	0.27	0.31	0.30	0.21	0.58
$\text{P}/\text{Sr}$	3.4	3.1	4.5	4.5	3.9	4.0	1.8	3.4	2.7	3.1	3.9	97
$10^{-1} \times \text{P}/\text{Zr}$	1.7	1.5	1.4	1.2	-	1.3	0.6	1.3	1.8	1.4	0.6	17
$10^{-2} \times \text{P}/\text{La}$	0.44	0.51	0.57	0.67	0.49	0.23	0.27	0.51	-	-	0.95	32
$10^{-1} \times \text{P}/\text{Ce}$	2.3	2.4	3.2	3.3	2.7	4.4	2.1	5.1	-	-	3.3	117
$10^{-2} \times \text{K}/\text{Rb}$	2.5	2.9	1.7	3.5	1.5	3.0	1.9	4.1	3.5	4.5	3.4	2.8
$10^{-1} \times \text{K}/\text{Ba}$	1.6	2.0	1.0	1.2	0.9	2.4	2.5	1.4	1.3	2.0	3.4	21
$\text{Ca}/\text{Na}$	3.6	3.4	3.3	2.6	4.3	2.4	2.3	3.0	3.5	2.9	4.8	2.0
$10^{-2} \times \text{Ti}/\text{Sc}$	7.8	6.7	10.5	7.0	-	6.4	6.4	5.3	-	-	1.7	0.81
$10^{-2} \times \text{Ti}/\text{V}$	0.75	0.72	0.70	0.72	0.63	0.54	0.51	0.52	0.55	0.46	0.28	0.10
$\text{Cr}/\text{Ni}$	1.1	1.3	1.0	1.3	1.4	1.3	1.7	1.6	1.3	1.3	2.2	0.24
$10^{-3} \times \text{Ni}/\text{Mg}$	4.4	4.6	4.0	1.9	4.0	2.9	2.3	3.4	2.9	2.9	3.4	102
$\text{Ni}/\text{Co}$	6.7	6.1	5.8	2.5	-	4.1	3.0	5.3	4.5	2.0	3.2	21.4
$10^{-1} \times \text{Ba}/\text{La}$	0.79	1.2	1.1	1.7	1.0	0.88	1.5	2.0	-	-	0.9	1.2

Note: an. 1-26 - according to Tables 1,2; an. 27 - tholeiitic basalt of the middle oceanic ridges (11); an. 28 - chondrite (6).

son et al. 1983). The diagrams mainly show average compositions of the rocks under investigation. Thus Fig. 4A contains data on rift magmatism (Hessian Depression, Lower Silesia), Fig. 4B contains data from hinterland of Alpine folded belt (Slovakia, Romania, Yugoslavia).

As expected, volcanic rocks from the Rhine Graben, primitive ( $\text{Mg}=10-12\%$ ,  $\text{Ni}=300 \text{ ppm}$ ) lavas from the Hessian Depression (Fig. 4A, an. 1, 2) are most enriched with incompatible elements. Nephelinites (Fig. 4A, an. 6) and subalkaline olivine basalts (Fig. 4B, an. 9) from Lower Silesia are poorer in incompatible elements and the respective lines of element distribution are therefore placed lower than the lines concerning samples from the Hessian Depression. In respect of the element distribution, Slovak basanites (Fig. 4B, an. 14, 20) are rather close to samples from Lower Silesia. Subalkaline olivine basalts from the Persani Mts. (Romania), show marked differences in geochemical characteristics (Fig. 4B, an. 24).

Besides incompatible elements in lower concentrations and indicative elements (in ppm) like Ni – 200, Co – 38, Cr

– 314, V – 185, the prominent minima of Rb and Nb-concentrations should be noticed, being characteristic of rocks whose formation was associated with the process of crustal contamination. The minimum of Sr in the analysis 9 (Fig. 4A) may be indicative of the influence of a similar process upon the formation of subalkaline olivine basalts in Lower Silesia. It should be emphasized that nephelinites in this region (Fig. 4A, an. 6) show the element distribution line typical of continental mantle basalts. A definite role of contamination processes in basalt formation in the Persani Mts. is also proved by La/Nb values. According to published information (Thompson et al. 1983) this ratio in chondrites is equal to 0.94, in oceanic island basalts it is 0.2–1.2, in continental basalts it is 0.4–1.6. But in island arc basalts, where the influence of contamination processes is proved by isotope methods, La/Nb value varies from 0.5 to 1.5.

From all nephelinite samples under study subalkaline olivine basalts and basanites from Lower Silesia and Slovakia have ratio values varying from 0.7 to 1.1, that means that they correspond to values of volcanics of mantle origin. But still in subalkaline olivine basalts from the Persani Mts. the values vary from 1.4 to 2.8 and indicate the contamination by crust material in the object.

Sr minima in some samples could be related to low fractionation of melilite in nephelinite, plagioclase in subalkaline olivine basalts but this process is likely to be insignificant.

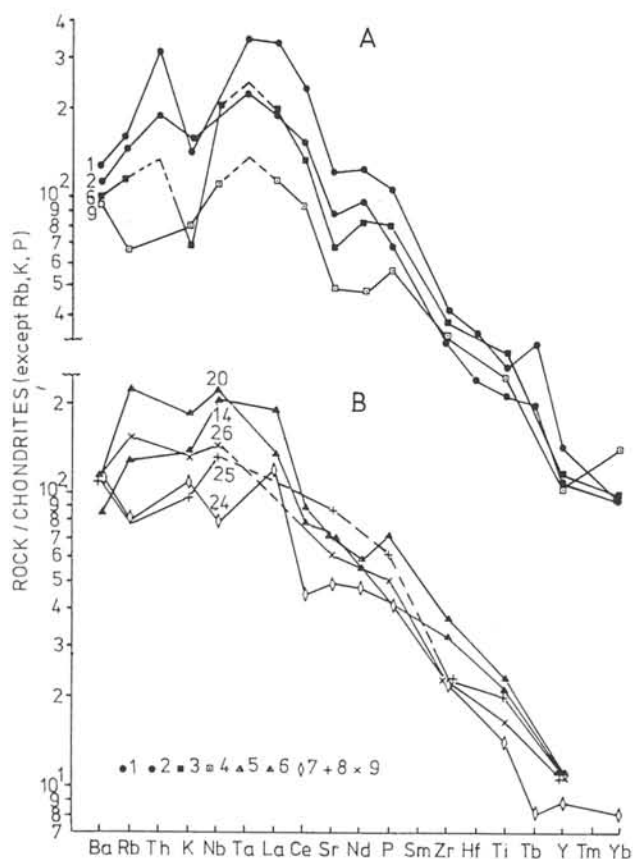
## Conclusions

A comparative analysis of Neogene–Quaternary volcanism of Central Europe (Hessian Depression, F.R.G.; Lower Silesia, Poland; Central and South Slovakia, Czechoslovakia; Persani Mts., Romania; Carpathian-Balkanides, Yugoslavia) enables the determination of the number of general peculiarities and regional variations in their composition and the expression of some ideas about their possible reasons.

1. Among general petrogeochemical features of the volcanic rocks under study interesting are high contents of  $\text{MgO}$  (9–13%) and undersaturation in  $\text{SiO}_2$  (the constant presence of normative nepheline during recalculations according to CIPW system). Poorly differentiated varieties of rocks with  $K_{\text{Mg}}$  higher than 65 are rather wide-spread and sometimes even dominant. A regular enrichment with incompatible and other rare elements is noted in relation to chondrite material.

2. With respect to geotectonic position and forms of Neogene–Quaternary volcanism, two types have been distinguished: the volcanism ranged to new-formed rift structures on the Epihercynian platform, and the volcanism related to hinterland of Alpine folded belt. Each type of volcanism has specific petrochemical features.

3. The rift volcanism (Hessian Depression, Lower Silesia) is characterized by a great variety of volcanic products, a wide-spread occurrence of alkaline ultrabasic rocks, alkaline basic rocks and their differentiated products. Besides low concentrations of  $\text{SiO}_2$ , high concentrations of  $\text{TiO}_2$  are typical of their composition ( $\text{TiO}_2 > 2.5\%$ ). Among significant geochemical features the increased values of ratios F/K, P/Zr, P/La, Ca/Na, Ti/Sc, Ti/V should be noticed. The character of incompatible element distribution mainly reproduces specific features of continental basalts of the mantle origin.



**Fig. 4.** Rare elements distribution in Neogene–Quaternary continental alkaline volcanics of Central Europe in relation to mantle (recalculating factors according to Thompson et al. 1983).

1, 2 – Hessian Depression, F.R.G.: olivine nephelinite (1), subalkaline olivine basalt (2); 3, 4 – Lower Silesia, Poland: olivine nephelinite (3), subalkaline olivine basalt (4); 5 – basanite, Central Slovakia, C.S.F.R.; 6 – basanite, South Slovakia, C.S.F.R.; 7 – subalkaline olivine basalt, Persani Mts., Romania; 8, 9 – Carpathian-Balkanides, Yugoslavia: olivine nephelinite (8), subalkaline olivine basalt (9). Numbers on the diagram are numbers of analyses in Tab. 2.



4. The dispersed volcanism in hinterland or Alpine folded belt (Slovakia, Romania, Carpathian-Balkanides) is rather limited in its petrographic composition. Olivine tephrites (basanites) and subalkaline olivine basalts prevail. In some volcanic fields one type of rocks is markedly predominant. Rocks of the ultrabasic group rarely show the maximum content of  $\text{SiO}_2$  (42–43%). Enrichment with  $\text{SiO}_2$  and rather low  $\text{TiO}_2$  concentrations ( $\text{TiO}_2$  2%), are characteristic features.

5. In the studied areas of volcanism from hinterland of Alpine folded belt subalkaline olivine basalts of Persani Mts. (Romania) show the most specific petrochemical characteristics. Their composition comprises higher  $\text{SiO}_2$  (concentrations up to 48%), lower  $\text{TiO}_2$  concentrations (1.6%), low concentrations of rare elements. Diagrams of incompatible elements distribution show minimum Rb and Nb- concentrations and the La/Nb ratio (1.4–2.8) ranges to the maximum value of all values from the studied objects. According to Thompson et al. (1983) a similar distribution of incompatible elements and their interrelations are characteristic of the objects whose genesis was controlled by crustal contamination processes.

Translated by E. Jassingerová

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