

Geochemically anomalous olivine-poor nephelinite of Říp Hill, Czech Republic

Geochemicky anomální olivínem chudý nefelinit z Řípu (Czech summary)

(9 text - figs.)

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Dedicated to the memory of Professor František Ulrich

Sodalite olivine-poor nephelinite of Říp Hill substantially differs both from olivine nephelinite and olivine-free nephelinite of the Cenozoic volcanic province of the Bohemian Massif. Říp Hill represents an erosion-resistant neck 25.6 Ma in age located in the Teplá-Barrandian terrane block in contrast to the České středohoří Mts. volcanic complex in the Saxothuringian terrane. The very low Mg-value (48.5), low contents of compatible elements as Cr (79 ppm), Ni (31), Co (32), Sc (21) and lack of mantle-type xenoliths gives evidence of differentiation of primary mantle magma. Anomalous enrichment in incompatible elements particularly in Σ REE (650 ppm), U (3.6), Th (15.6), Nb (154), Ta (12.1), is associated with late magmatic crystallization (mostly of apatite, Ti-magnetite \pm hauyne). $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7036–0.7038) and $^{143}\text{Nd}/^{144}\text{Nd}$ (0.51278) ratios of the olivine-poor nephelinite are consistent with HIMU OIB from a sublithospheric source; ϵ_{Nd}^t (+3.4) value implies an depleted mantle source. Olivine-poor nephelinite could be derived from carbonated nephelinite magma with high $\text{CO}_2/\text{H}_2\text{O} + \text{CO}_2$ volatile fraction resulting in high viscosity and thus stopping of magma associated with differentiation and contamination in crustal reservoir during its ascent to the surface. Such magma could be associated with high explosive pyroclast-rich volcano of maar or stratovolcano type. The olivine-poor nephelinite of Říp Hill reveals common features in mineral paragenesis and chemical composition of minerals such as clinopyroxene, (Mg, Al, Ti)-magnetite, barite, ankerite with carbonate-bearing alkaline ultramafic lamprophyres in the vicinity. This fact suggests their mutual genetic association within the Říp Hill volcanic centre.

Key words: Bohemian Massif, Říp Hill, olivine-poor nephelinite, geochemistry, age, Sr, Nd isotopes

Introduction

Říp Hill is situated in the Labe river lowland of central Bohemia. It represents an eroded volcanic neck (459 m a.s.l.) rising up to 240 m above the surrounding plain (220–280 m a.s.l.). This plain is formed by sediments of the Bohemian Cretaceous Basin covering the epi-Variscan platform of the Bohemian Massif. The Cretaceous sediments are underlain by claystones of the Carboniferous Roudnice Basin. There are many publications dealing with the interpretation of volcanological position of Říp Hill (Zahálka 1923, Ulrich 1941, Žeberská – Mikula 1982, Kašpar in Škoda 1983, Kopecký 1983, 1987–1988), however, only scarce relevant geochemical data exist on volcanic rocks forming the hill.

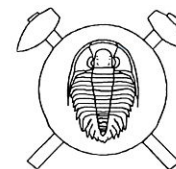
Geological setting

The origin of Říp Hill neck is associated with the activity of the young (Upper Cretaceous–Quaternary) volcanism of the Bohemian Massif, forming the young Central European volcanic province (Wimmenauer 1974). Kopecký (1987–1988) supposed immediate association of Říp Hill with the southern marginal fault of the Labe tectono-volcanic zone (NW–SE), near its intersection with the deep-seated Litoměřice Fault – master fault of the

Ohře Rift (ENE–WSW), see Fig. 1. Detailed local tectonic information on Říp Hill was given by Zahálka (1923) and Ulrich (1941). These authors linked structural position of Říp Hill with the crossing of fault systems WNW–ESE and NNE–SSW, forming the narrow „Rovné grove block“ with vertical displacement about 13 m. Three problematic occurrences of volcanic products including volcanoclastic material described by Zahálka (1923) within 1 km of Říp Hill, are no more accessible. Petrologically similar olivine-free nephelinitic to olivine-poor nephelinitic rocks occur in the central Bohemian region primarily at Kopeč Hill near Odolena Voda, Chloumek Hill near Chloumek, Špičák Hill near Štětí, Slánská hora Hill at Slaný (Fig. 1), Vinařická hora Hill near Kladno, Horní Zimov, Šibenec Hill near Mšeno etc., though only single olivine nephelinite – Jenišovická hůrka Hill at Jenišovice, cf. Fig. 1.

Olivine-poor nephelinites (and analcimites), frequently containing minerals of the sodalite group \pm amphibole and/or biotite are typically developed in the central part (between Mělník and Doksy) of the Bohemian Cretaceous Basin (Šrbený 1992). Analcimites originated mostly by late magmatic alteration of primary foiditic rocks.

The southern marginal fault of the Labe tectono-volcanic zone is accompanied by several mineral springs (e.g. Roudnice nad Labem). The long fibrous calcite sin-



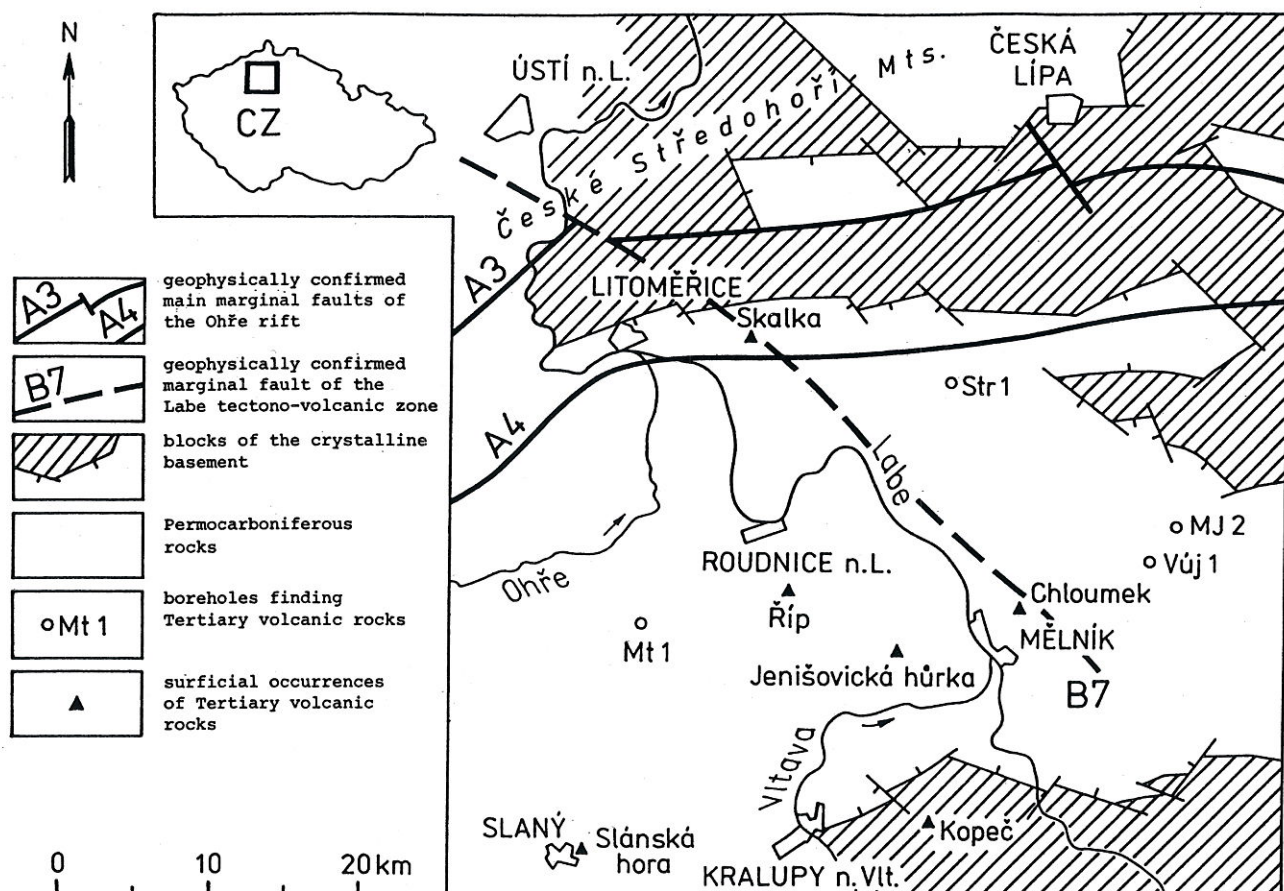


Fig. 1. Geological sketch of pre-Cretaceous formations of Říp surrounding and main occurrences of Cenozoic volcanic rocks; tectonic data compiled from Pokorný et al. (1985) and Ulrych et al. (1993).

ter, cementing the Plio–Pleistocene debris formed mostly by massive blocks of volcanic material at the foot of Říp Hill (exposure Hýkovina near Ctiněves), may represent precipitation product of subsurface water circulation (Ložek 1971). Impressive talus aprons around Říp Hill neck form the bell-shaped form of Říp Hill. The exposed neck is strongly influenced by atmospheric disintegration disturbing primary columnar jointing.

As concerns the volcanic position of Říp Hill, the following interpretations have been formulated:

- (i) volcanic dome (Zahálka 1923, Špaček – Zahálka 1930, Kettner 1956) – without further specification as to originally extrusive or intrusive character?,
- (ii) relict of a feeding channel of a stratovolcano (Žebera – Mikula 1982),
- (iii) magnetically homogeneous intrusive volcanic form (Kašpar in Škoda 1983),
- (iv) relict of compact filling of a diatreme (maar-type) (Kopecký 1983).

With respect to the fact that Cretaceous sediments min. 200 m in thickness were removed including any possible Tertiary volcanoclastic products, interpretations sub (ii) and (iv) cannot be either confirmed or refused. However, Zahálka (1923) reported two occurrences of tuffaceous breccias at the foot of Říp Hill. Říp Hill (Špaček

– Zahálka 1930) may actually represent, as many other volcanic hills of the České středohoří Mts. (e.g. Radobýl, Lovoš, Raná, Milá, Ronov, Tlustec Hills), neck associated with significant faults. However, its chemical composition (olivine-poor nephelinite) is substantially different from the main basaltic rocks (basanite to olivine nephelinite) prevailing in the České středohoří Mts. Olivine-free and olivine-poor nephelinites, however, with very high contents of TiO_2 (up to 5.8 wt.%), are concentrated in the Krušné hory Mts. (Šrbený 1980).

Sampling and analytical procedures

The following basaltic rock samples from natural outcrops and large free massive blocks of Říp Hill were studied:

- R-1 – northern foot of the hill
- R-2 – central part of the hill (NE hillside)
- R-3 – top of the hill
- R-4 – central part of the hill (E hillside, Šrbený 1992)
- R-5 – shaft in abandoned brickworks pit, 1.5 km NW of Ctiněves (debris with altered basaltic boulders cemented by massive fibrous calcite aggregates, possibly representing a formerly exposed uppermost part of Říp Hill neck).

Chemical investigation of the rock samples was performed using wet chemical analyses (V. Chaloupský, Institute of Geology, Academy of Sciences of the Czech Republic), XRF analyses (V. Macháček, Geoindustria Laboratory, Černošice) and INAA (Institute of Raw Materials, Kutná Hora). For detailed analytical conditions see Ulrych et al. (1993).

The Sr isotope analyses (samples R-1, 2, 3) were done in the Isotope Laboratory of the Czech Geological Survey, Praha. Samples of 10 kg weight were homogenized to powder and the aliquot part dissolved in a mixture of HF and HNO₃. Sr was isolated on ion-exchange column. Sr isotope ratios were determined on a Finnigan MAT 262 mass spectrometer. Measured Sr^{87/86}Sr ratios were normalized to the value 0.1194 for ⁸⁶Sr/⁸⁸Sr. The NBS SRM 987 standard repeatedly yielded an average ratio of 0.71025(4).

Nd isotope study was performed from the aliquot of sample R-2 in the Federal Institute for Geosciences and Natural Resources, Hannover, Germany. 20 mg of the sample material was spiked with a mixed ¹⁴⁷Sm – ¹⁴⁸Nd tracer and decomposed with HF–HNO₃ by microwave treatment in a Teflon screw-top vessel at 150–200 degree centigrade. Lanthanides were separated by conventional cation-exchange chromatography with 6.1 N HCl. Sm and Nd were isolated from each other and adjacent lanthanides in separate columns using HDEHP-coated teflon powder (Ceraí – Testa, 1963). Isotopic analyses of Sm and Nd were performed on a Finnigan MAT 261 multicollector mass spectrometer in static mode. The La Jolla isotopic standard yielded ¹⁴³Nd/¹⁴⁴Nd = 0.511847 ± 0.000010 (standard deviation, n = 24). Error estimates for the isotopic ratios were derived from repeated analyses of standard samples (South African Reference Ma-

Table 1. Chemical analyses (wt.%) and CIPW norms of rock samples from Říp Hill

Nos.	R-1	R-2	R-3	R-4	x ₄	s	R-5	R-6	OFN	ON
SiO ₂	40.11	40.71	40.22	40.29	40.33	0.26	40.58	40.16	38.48	40.91
TiO ₂	3.44	3.03	2.92	2.51	2.98	0.38	2.60	3.10	4.36	2.99
Al ₂ O ₃	11.53	11.51	11.68	11.95	11.67	0.20	11.73	11.26	11.41	11.70
Fe ₂ O ₃	12.47	10.10	12.11	8.28	10.74	1.94	14.94	7.53	7.30	5.12
FeO	3.36	5.08	3.90	7.77	5.03	1.96	0.86	7.73	7.10	6.90
MnO	0.53	0.41	0.44	0.36	0.44	0.07	0.27	0.35	0.25	0.20
MgO	6.87	6.62	6.15	6.71	6.59	0.31	6.99	6.87	7.04	11.12
CaO	12.05	11.89	11.91	11.99	11.96	0.07	11.91	12.49	14.50	12.45
Na ₂ O	4.50	4.64	4.90	4.84	4.72	0.18	1.63	4.24	2.96	3.06
K ₂ O	1.31	1.49	2.04	1.31	1.54	0.35	1.25	0.96	1.21	1.09
P ₂ O ₅	1.53	1.60	1.44	1.43	1.50	0.08	0.15	1.69	1.26	0.83
H ₂ O+	1.11	1.71	1.35	2.12	1.57	0.44	4.87	1.17	2.24	2.27
H ₂ O-	0.70	0.78	0.28	0.31	0.52	0.26	1.44	0.72	0.76	0.58
CO ₂	0.08	0.12	0.27	0.18	0.16	0.08	0.20	1.06	0.65	0.50
C			0.03	0.03						
F			0.12	0.12				0.13	0.10	
S			0.07	0.07				0.07	0.04	
-O=2F, S, C			100.27	99.96				99.72	99.86	
				-0.08	-0.08				-0.07	-0.05
Total	99.77	99.69	99.61	100.19	99.88		99.42	99.33	99.68	99.81
Or	7.92	9.07	12.32	7.94			7.94	5.83	7.42	6.66
Ab	9.25	10.27	6.28	6.80			14.80	14.98	3.76	5.80
An	7.54	6.34	3.91	7.16			22.52	9.07	14.76	15.43
Ne	16.07	16.30	19.50	19.03			0.00	11.81	12.01	11.33
Di	34.13	34.14	33.89	34.98	30.50		29.72	37.28	31.58	
Hy	0.00	0.00	0.00	0.00			1.35	0.00	0.00	0.00
Ol	1.23	0.85	0.00	3.29	2.45		5.09	0.85	12.64	
Mt	2.64	9.18	5.65	12.30			3.92	11.21	10.97	7.66
Hm	10.93	4.06	8.46	0.00			13.34	0.00	0.00	0.00
Il	6.68	5.92	5.66	4.89	0.00		6.04	8.58	5.86	
Ap	3.42	3.59	3.21	3.20			0.35	3.79	2.85	1.87
Mg#	49.70	49.49	46.57	48.04	48.46		50.61	49.83	51.92	66.96
C.I.	44.69	50.10	45.21	55.46			37.78	52.06	57.68	57.75
D.I.	33.24	35.64	38.10	33.76			22.74	32.62	23.18	23.78
⁸⁷ Sr/ ⁸⁶ Sr	0.703798	0.703563	0.703635							
±2σ	12	8	9							
¹⁴³ Nd/ ¹⁴⁴ Nd		0.512794								
±2σ		10								
ε _{Nd} ^t		+3.4								
K/Ar (Ma)		25.57								
±2σ		1.02								

Nos. R-1 foot of Říp Hill, R-2 central part of the western slope, R-3 top of the hill, R-4 central part of the eastern slope (Shrbený 1992), s – standard deviation, x – arithmetic mean of R-1, 2, 3, 4, R-5 foot of the hill, brickwork pit at Ctíněves, R-6 Říp Hill, (Vaněčková et al. 1993), OFN – olivine-free nephelinite, ON – olivine nephelinite – average data on volcanic rocks of the Cenozoic Volcanic Province of the Bohemian Massif (Shrbený 1995), 2σ – standard deviation (internal precision), λ = 1.42 × 10⁻¹¹ year⁻¹.

Analyst: V. Macháček, Geoindustria Laboratory Praha (XRF method).

terial) which yielded standard deviations of $\pm 0.4\%$ for $^{147}\text{Sm}/^{144}\text{Nd}$ and ± 30 ppm for $^{143}\text{Nd}/^{144}\text{Nd}$.

Determination of K/Ar age of the same sample was performed in the Institute of Nuclear Research, Hungarian Academy of Sciences, Debrecen, using isotope dilution method. For analytical condition see Balogh (1985) and Odin et al. (1982).

Rock-forming minerals were analyzed using an electron microprobe JEOL XA-50A equipped with EDAX 711 under standard conditions (Hulínský et al. 1972) in polished section.

Petrographic characteristics

Homogeneous dark grey basaltic rocks with inexpressive (micro)porphyritic texture occur at Říp Hill. Rare eu-

hedral to subhedral microphenocrysts are formed dominantly by clinopyroxene and rare olivine (0.5–2 mm). Hemicrystalline matrix is formed mostly by anhedral grains of nepheline and by decomposed glass, both strongly analcimized. However, rounded pseudomorphs after mineral of the sodalite group and numerous magnetite grains are present in the matrix, too. Other minerals of matrix such as anorthoclase, apatite, biotite, carbonates and barite are more rare.

Conspicuous magnetic (Špaček – Zahálka 1930, Ulrich 1941, Kropáček 1985) and gamma-radiation properties (Chlupáčová 1977) of Říp Hill are well-known. Strong magnetism of the rock samples from Říp Hill is linked with very high magnetite contents (about 10 vol.%). The rock of Říp Hill was described by different authors under different names, as a consequence of

Table 2. Minor and trace element contents (ppm) in rock samples from Říp Hill

Nos.	R-1	R-1A	R-2	R-3	x_4	s	R-4	R-5	R-6	OFN	ON
Cr	93	79	74	71	79.3	9.7	31	81	52	54	377
Ni	31	45	26	23	31.3	9.7	27	22	22	36	218
Co	37	37	28	26	32.0	5.8		25	39	54	59
Sc	22	23	21	19	21.3	1.7		18	23	31	31
Cu*	46		32	32	36.7	8.1		30		131	80
Zn	180	213	197	187	194.3	14.3		131	151	95	87
Pb	20				20.0				8		
Mo*	19		15	14	16.0	2.6		15			
As*									6		
V	200				200.0				209		
Rb	63	46	57	46	53.0	8.4	50	44	75	41	42
Cs	1.3	1.4	1.9	1.3	1.5	0.3		1			1.1
Ba	1023	1020	1199	1180	1105.5	97.3	608	1100	1206	806	806
Sr	1249	1802	1704	1367	1530.5	264.4	1510	1950	1677	1094	956
Ga*	19		17	20	18.7	1.5		17	26		
Ta	11.9	12.1	12.2	12.3	12.1	0.2		13.9		7.4	4.9
Nb*	153		150	158	153.7	4.0	206	180	198	131	95
Hf	15.4	18.2	15.9	16.2	16.4	1.2		19.3		11	6.5
Zr	527		505	533	521.7	14.7	812	571	700	486	271
Y*	40		42	41	41.0	1.0		41	49	33	25
Th	14.5	17.2	15.1	15.6	15.6	1.2		17.7	18	10.2	8.4
U	2.6	4.1	3.6	3.9	3.6	0.7		4.1	1	3.2	2.7
La	130	148	138	140	139.0	7.4		157	151	105	78
Ce	274	318	282	291	291.3	19.1		351	287	186	134
Nd	119	126	116	126	121.8	5.1		131			
Sm	19.6	21	20.5	20.6	20.4	0.6		22		13.5	8.9
Eu	5.5	6.1	5.7	5.8	5.8	0.2		6.4		4.1	2.9
Gd	20.1	17.7	22	19	19.7	1.8		23.1			
Tb	1.3	1.4	1.4	2.2	1.6	0.4		2.2		1.6	1.0
Tm	0.88	1.1	1.2	1.4	1.1	0.2		1.4			
Yb	3.7	3.8	3.9	4.1	3.9	0.2		4.3		3.9	2.6
Lu	0.61	0.52	0.66	0.68	0.62	0.07		0.71		0.33	0.27
K/Rb	172.6		217.0	368.2	241.2		217.5	235.9		245.0	215.5
Rb/Sr.10 ³	50.4	25.5	33.5	33.7	30.3		33.1	22.6		37.5	43.9
Σ REE	574.7	643.6	591.4	610.8	605.1			699.1		314.4	227.6
(La/Yb) _N	25.2	27.9	25.4	24.5	25.6			26.2		19.3	21.5
Eu/Eu*	0.84	0.94	0.82	0.88	0.87			0.86			
Th/U	5.6	4.2	4.2	4.0	4.4			4.3		3.2	3.1
Zr/Hf	34.2		31.8	32.9	31.8			29.6		44.2	41.7
Nb/Ta	12.9		12.3	12.8	12.7			12.9		17.7	19.4

For explanation of sample signature see Table 1. R-1A schlieren in R-1, x – arithmetic mean of R-1, 1A, 2, 3; s – standard deviation. Analyst: V. Macháček, Geoindustria Laboratory, Praha – XRF (designated by asterisk) and INNA methods.

difficulties associated with optical determination of foids and of unusual low content of olivine. Bořický (1873) used in the first petrographic description of the rock the term noseanite. Hoffman (1896) named the rock sodalite olivine hauynite, Kopecký in Horný ed. (1963) nepheline hauynite and Shrbený (1992) sodalite nephelinite with olivine admixture. The modal composition of the rock (lack of plagioclase and presence of minor anorthoclase) corresponds to nephelinite with transitions to phonolitic nephelinite in the IUGS quantitative mineralogical classification (Le Maitre ed. 1989).

The bulk chemical and CIPW normative compositions of the Říp samples are presented in Table 1; for minor and trace elements see Table 2. In the chemical classification of Le Maitre ed. (1989) the rock plots to the foidite field at the boundary with tephrite field, Fig. 2. According to the special terminology of foiditic (nephelinitic rocks) of Le Bas (1989) the rock from Říp Hill can be specified as nephelinite with transitions to melanephelinite (sub-root), and nephelinite to pyroxene melanephelinite (species), i.e., olivine-poor nephelinite or nephelinite (Group II sensu Le Bas 1978, 1987). Position of rock from Říp Hill in CaO–MgO plot (Fig. 3) illustrates its character and affinity to nephelinites in the sense of Le Bas et al. (1987). The whole sample set reveals a homogeneous character with the exception of partly altered sample R-5 from boulder of cemented debris, substantially low in Na₂O content. In comparison to the average contents in young olivine nephelinite–ON and olivine-free nephelinite–OFN (both about 4.2 wt.%) in the Bohemian Massif (Shrbený 1995), the Říp samples show substantially higher total alkali contents (up to 6.9 wt.%). All samples are Ne-normative with the exception of al-

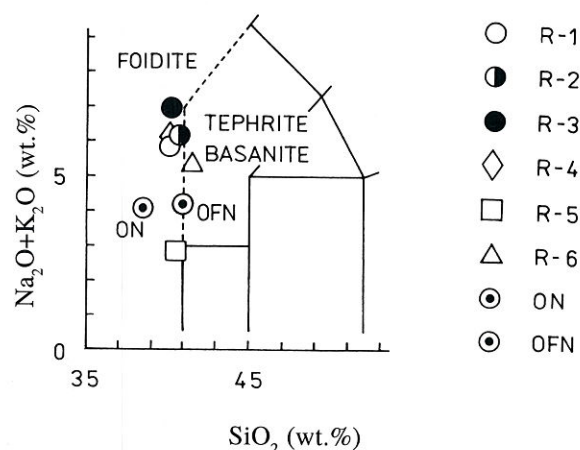


Fig. 2. Position of olivine-poor nephelinite from Říp Hill in the TAS diagram (Le Maitre ed. 1989).

Olivine-poor nephelinite: R-1 northern foot of the hill; R-2 central part of the hill (NE hill-side); R-3 top of the hill; R-4 central part of the hill (E hill-side, Shrbený 1992); R-5 brickwork pit, 1.5 km NW of Ctíněves (boulders in debris); R-6 unspecified (Vaněčková et al. 1993); ON and OFN – average chemical composition of the olivine nephelinite and olivine-free nephelinite of the Bohemian Massif (Shrbený 1995).

tered sample R-5 (Hy-normative!). Normative Ol contents (0.0–3.4, average = 1.1) correspond to the average value of OFN of the Bohemian Massif (Shrbený 1995). High normative magnetite is a specific feature of the rock (2.6–12.0 vol.%); hematite (0.0–10.7 vol.%) contents are strongly depending on the oxidation degree (alteration).

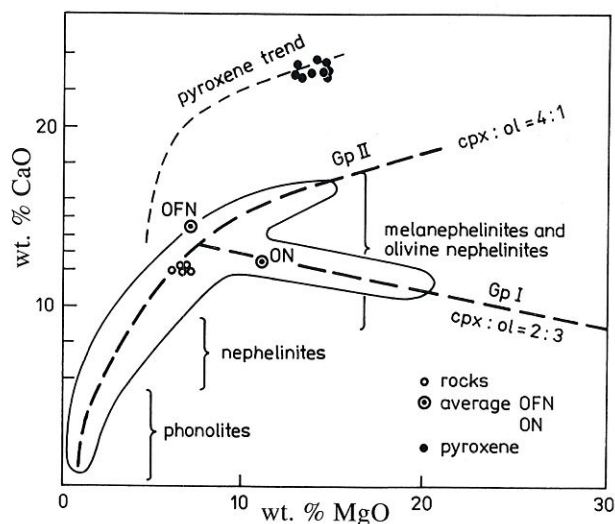


Fig. 3. Olivine-poor nephelinite from Říp Hill in CaO–MgO plot (Le Bas 1987).

Chemical mineralogy

Olivine

occurs in rare microphenocrysts (about 2 vol.%), often exhibiting magmatic corrosion, irregularly dispersed in matrix. It is relatively homogeneous in composition and characterized by low Fo₇₂, high Fa₂₆ and Te₂ contents, see Table 4. Its high Fa content corresponds to rare olivine of phonotephritic rocks known from the České středohoří Mts.

Clinopyroxene

is the most abundant constituent of the rock. Subhedral to anhedral columnar microphenocrysts (about 9 vol.%) are greenish to pale brown in colour and very often twinned. Neither sector, nor concentric zoning are optically distinguishable. However, contents of Ti, Al, Fe tot and Na systematically increase from the centre (pyramidal sector?) to margin (prismatic sector?) of the grain. Si, Mn and Mg contents reveal an opposite tendency (Table 3, Fig. 5). Low contents of Ti and Al are most characteristic of olivine-poor nephelinites (Le Bas 1987). Clinopyroxene grains in matrix, often in association with Ti-magnetite, are characteristic by lower Al and Ti and by partly higher Na contents in comparison to clinopyroxenes of nephelinites reported by Le Bas (1987). Such chemical composition of clinopyroxene may indicate higher T of crystallization

Table 3. Representative analyses of clinopyroxenes

Nos.	R1c	R1r	R1m	R2c	R2r	R3c	R3r
SiO ₂	51.30	47.34	50.98	50.19	47.36	50.56	47.52
TiO ₂	1.35	2.46	0.82	1.69	2.77	1.70	2.75
Al ₂ O ₃	3.08	5.25	2.75	2.66	5.06	3.06	5.11
FeO _{tot}	5.99	7.50	7.90	7.75	7.79	7.10	7.98
MnO	0.30	0.12	0.08	0.21	0.17	0.14	0.10
MgO	14.83	13.14	14.45	14.57	12.97	14.68	13.07
CaO	23.37	22.06	22.49	22.84	22.80	22.78	22.50
Na ₂ O	0.46	0.70	0.85	0.45	0.62	0.39	0.58
K ₂ O	0.02	0.01					
Total	100.70	98.58	100.32	100.36	99.54	100.41	99.61
Si ^{IV}	1.889	1.798	1.898	1.871	1.789	1.875	1.792
Al ^{IV}	0.111	0.202	0.102	0.117	0.211	0.125	0.208
Al ^{VI}	0.023	0.033	0.018	—	0.014	0.008	0.019
Ti	0.037	0.037	0.023	0.047	0.079	0.047	0.078
Fe	0.184	0.238	0.246	0.242	0.246	0.220	0.252
Mn	0.009	0.004	0.003	0.007	0.005	0.004	0.003
Mg	0.814	0.744	0.802	0.810	0.730	0.811	0.735
Ca	0.922	0.898	0.897	0.912	0.923	0.905	0.909
Na	0.033	0.052	0.061	0.033	0.045	0.028	0.042
K	0.001	0.000	—	—	—	—	—
O	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Wo	47.8	47.7	46.1	46.3	48.4	46.6	47.9
En	42.2	39.5	41.2	41.1	38.3	41.8	38.7
Fs	10.0	12.9	12.8	12.6	13.2	11.6	13.4

c – core, r – rim of phenocryst, m – matrix; for explanation see Table 1

Table 4. Representative analyses of olivine, biotite and titanian magnetite

Nos.	R1c	R1r	R3	R1	R3
SiO ₂	38.17	38.27	42.17	0.05	0.07
TiO ₂			0.68	17.66	15.43
Al ₂ O ₃	0.07	0.06	26.74	2.57	3.42
FeO _{tot}	23.64	23.86	9.28	70.20	71.67
MnO	1.38	1.60	0.05	1.40	1.25
MgO	36.80	36.35	7.58	4.34	3.85
CaO	0.38	0.36	0.37	0.02	0.04
Na ₂ O			0.16		
K ₂ O			7.00		
H ₂ O*			4.35		
Total	100.44	100.50	94.03	99.63	99.40
Si ^{IV}	2.000	2.007	5.918	0.015	0.020
Al ^{IV}			2.082		
Al ^{VI}	0.004	0.004	2.341	0.879	1.173
Ti			0.072	3.852	3.376
Fe ⁺³	1.097	1.118	1.089	*7.388	*8.034
Fe ⁺²				*9.640	*9.406
Mn			0.006	0.344	0.308
Mg	2.875	2.842	1.586	1.877	1.670
Ca	0.021	0.020	0.056	0.006	0.012
Na			0.044		
K			1.253		
O	8.000	8.000	24.000	24.000	24.000
cations				18.000	18.000
	Fo 72.1	71.8	X 8.000	Usp 47.8	47.1
	Fa 26.3	26.4	Y 5.083	Hcn 6.1	8.8
	Te 1.6	1.8	Z 1.369	Jcb 4.2	5.1
				Mgf 22.6	24.5
				Mgt 19.3	14.5

For explanation see Table 1.

*calculated according to stoichiometry

(Thompson 1974). Chemical composition of the matrix clinopyroxene is not similar to that of marginal zones of phenocrysts, crystallizing probably later. Clinopyroxenes plot along the boundary between diopside and augite fields (Fig. 4), marginal zones mostly reveal an augite affinity (Morimoto ed. 1988 classification).

Foids (nepheline, sodalite, hauyne)

are present in rounded pseudomorphs, locally resembling hexagonal crystal habit of nepheline (pseudomorphs?) or as individual grains of nepheline preserved in newly formed analcime. For chemical analyses see Table 5. Complex forms (about 0.3 mm in size) are composed of aggregates of nepheline and calcite cemented by a foid of transitional compositions of the sodalite-hauyne-hauyne series (Table 5, Fig. 5). With regard to the exceptional mixing ability among members of the sodalite-hauyne group (Tröger 1969) inclusive of S and Cl contents even within single grain (Fig. 6), together with the textural evidence, the secondary origin of these foids at the expense of primary nepheline is most probable. Conversion of nepheline to sodalite during the subsolidus reaction is known from nepheline syenites (Finch 1991). Secondary origin of sodalite follows also from experimental studies of Barker (1976) and Sharp et al. (1983). Similar zonal development of minerals of the sodalite-hauyne group was described from young olivine melilititic and nephelinitic rocks in northern Bohemia (Pivec et al. 1990) and carbonate-bearing alkaline lamprophyres from central Bohemia (Ulrych et al. 1993).

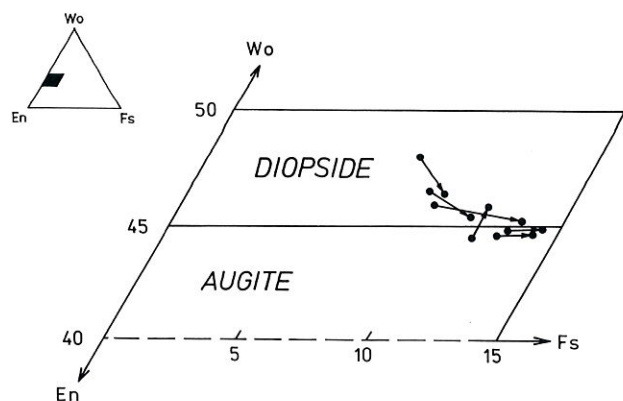


Fig. 4. Plot of clinopyroxenes in Morimoto et al. (1988) classification diagram. Arrow indicates core-rim relations.

Analcime

occurs as individual anhedral grains replacing foids (mostly nepheline), anorthoclase and glass in matrix, rarely forming crystals (pseudomorphs?). Chemical analyses are presented in Table 5. Its origin is associated with the analcimization of the rock caused by late magmatic crystallization and redistribution of Na from decompo-

sed nepheline and soda-rich glass (Na_2O contents up to 10 wt.%).

Anorthoclase

was found as primary, relatively abundant anhedral grains in matrix. Chemical analysis is given in Table 5. (Na, K)-alkali feldspars of similar chemical composition are known from trachybasaltic (essexitic) rocks in the České středohoří Mts. (Ulrych et al. 1983).

Titanian magnetite

is widely distributed within the rock (about 13 vol.%). It occurs in rare unzoned microphenocrysts (up to 0.2 mm) passing into the average grain size of matrix (0.04 mm). The chemical composition (Table 4) of grains is largely uniform and characterized by high contents of ulvöspinel (47–48 mol.%) and magnesioferrite (23–25 mol.%) components. Primary homogeneous titanium-rich magnetite dissolved into two phases with different titanium contents and deuterio oxidation state. Exsolved submicroscopic titanium-rich lamellae of ulvöspinel phase are in the titanium-poor magnetite matrix. Bulk

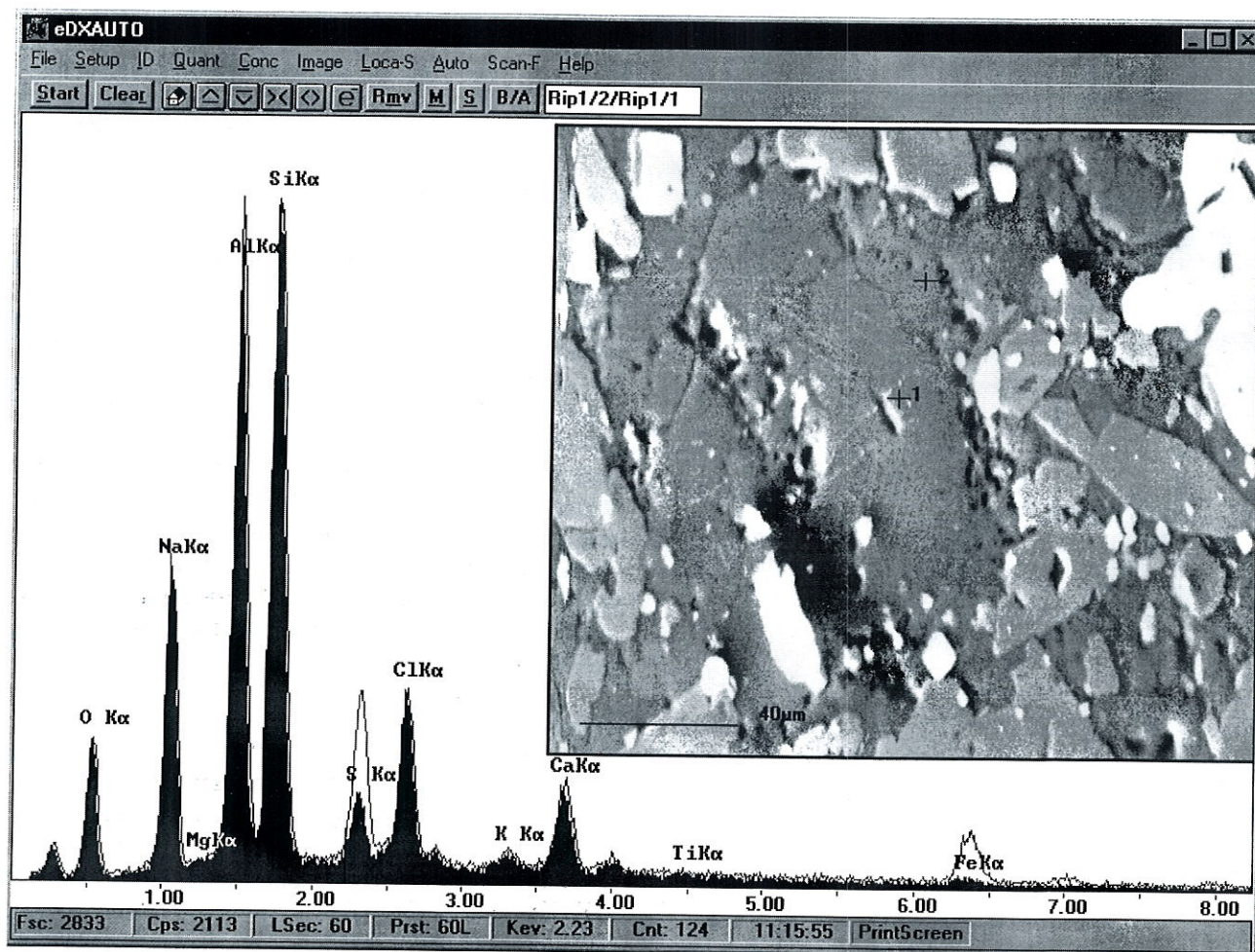


Fig. 5. Secondary electron image with comparing spectra of zoned foid from the olivine-poor nephelinite of Říp Hill. 1 – hauyne (central part rich in S, and Fe); 2 – sodalite (marginal part with opposite trends).

Table 5. Representative analyses of K-Na feldspar, nepheline, sodalite, hauyne, analcime and ankerite

Nos.	R-1	R-2	R-2	R-2	R-1m	R-1p	R-1
SiO ₂	61.40	43.41	36.43	34.76	54.75	55.01	
TiO ₂	0.19	0.05					
Al ₂ O ₃	20.68	32.04	30.15	27.84	23.95	23.31	
Fe ₂ O ₃		0.58	1.12	1.05	0.46	0.48	
FeO0.31							33.76
MnO							2.61
MgO							2.22
CaO	0.69	1.13	3.52	3.66	0.05	0.08	21.32
Na ₂ O	7.06	17.31	20.69	18.50	12.74	12.80	
K ₂ O	8.12	4.88	1.30	0.67	0.30	0.11	
Cl		5.64	1.54				
SO ₃		1.88	11.40				
	98.45	99.40	100.73	99.42	92.25	91.79	59.91
-O=2Cl			-1.27	-0.35			
Total	98.45	99.40	99.46	99.07	92.25	91.79	59.91
Si ^{IV}	11.379	8.404	6.004	6.087	1.991	2.006	
Al ^{IV}	4.543	7.311	5.856	5.746	1.027	1.001	
Ti	0.007						
Fe ⁺²	0.048						1.995
Mn						0.156	
Mg						0.234	
Ca	0.137	0.234	0.622	0.687	0.002	0.003	1.614
Na	2.537	6.497	6.611	6.281	0.898	0.905	
K	1.92	1.205	0.273	0.15	0.014	0.005	
Cl		1.875	0.457				
S		0.232	1.498				
O cations	32.000	32.000	21.000	21.000	6.000	6.000	
	An 3.0					4.000	
	Ab 55.2						Ca 42.0
	Or 41.8						Fe 51.9
							Mg 6.1

For explanation see Table 1; m – matrix, p – pseudo-morph

composition data of titanian magnetite (oxidation # = 0.42; $a = 8.427 \pm 0.002$ Å) are highly non-stoichiometric with high proportion of vacancies (Kropáček 1985). The completely prevailing crystal phase with higher value of parameter a is characterized by low temperature ($\Theta = 340$ °C) whereas the less abundant phase with lower value of parameter a has a higher temperature of Curie point ($\Theta = 450$ °C). High degree of deuteric oxidation of titanian magnetite is typical for near-surface conditions of crystallization.

Titanian magnetites with similar properties are known from carbonate-bearing alkaline lamprophyres of central Bohemia (Ulrych et al. 1993).

Biotite

is a fairly rare phase in the studied rock. It was found in anhedral form exclusively in association with the late magmatic minerals (ankerite, barite). The low Ti and Mg contents prove the low-temperature origin of biotite (Table 4).

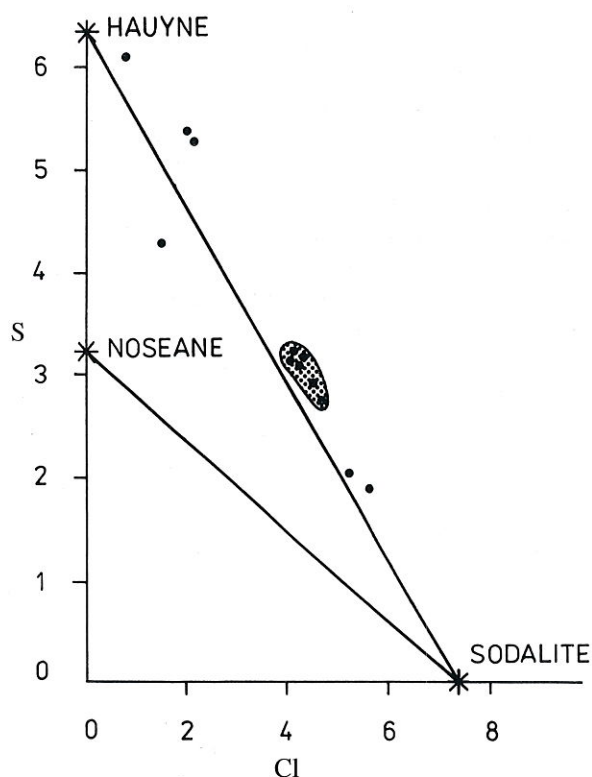


Fig. 6. Sodalite group minerals from the olivine-poor nephelinite of Říp Hill plotted in S vs Cl diagram.

Carbonates and sulphates

are seldom present in the studied rocks. Ankerite was analyzed in young veinlets (0.05–0.2 mm) penetrating the rock. The chemical analysis (Table 5) indicates the mineral belongs to complex carbonates of ankerite type (cf. similar composition of young carbonates from lamprophyres of central Bohemia, Ulrych et al. 1993). Pure calcite occurs in minute grains and aggregates in partly altered rock. Together with barite grains of the same size it can be interpreted as a product of late magmatic activity (cf. presence of barite in lamprophyres of central Bohemia, Ulrych et al. 1983). The textural position of rare calcite inclusions in the rock-forming minerals (clinopyroxene), however, resembles the primary crystallization.

Petrology and geochemistry

Olivine-poor nephelinites (Group II sensu Le Bas 1989) are characterized by the presence of clinopyroxene (+) and rarely of olivine phenocrysts (+), low contents of MgO (about 9.5 wt.%), low Mg-number (48.5) and high 100K/Na + K ratio (26.8), absence of associated basalts (+) and mantle-type xenoliths (+), strong fractionation (+), presence of phonolite derivatives (+), formation of large volcanic structures (feeding channel?), presence of

pyroclastic material (?) and plutonic equivalents (?). These features are perceptible to various degrees in the olivine-poor nephelinite of Říp Hill (data in parentheses). The nearest phonolitic intrusions, only 15 km of Říp Hill, are represented by the Skalka Group Hills near Encovany. Mantle magma of olivine-poor nephelinite volcanoes apparently stopped in a high-level magma reservoir during its ascent. This is corroborated by the lower Mg-number (48.5, *sensu* Frey et al. 1978) and lower contents of compatible elements including Cr (80 ppm), Ni (26), Co (31), Sc (21) in the samples studied. The reason for the stopping is probably the mechanical behaviour of magma. Nephelinites associated with carbonatites due to liquid immiscibility represent products of carbonated nephelinite magma and hence have a high $\text{CO}_2/\text{H}_2\text{O}+\text{CO}_2$ volatile fraction resulting in high viscosity that causes stopping of magma in crustal reservoir during its ascent to the surface (Le Bas 1987). Pyroclastic products of such magma are naturally of frequent occurrence.

K/Ar age of 25.6 ± 1.0 Ma (sample R-2) links the volcanism of Říp Hill with the main episode (42–16 Ma) of the Cenozoic activity within the Bohemian Massif, which is characteristically developed in the near České středohoří Mts.

The first $^{87}\text{Sr}/^{86}\text{Sr}$ isotope data (0.70364)_{meas.} on olivine-poor nephelinite of Říp Hill were already published by Vokurka – Bendl (1992). However, an array (cf. Table 2) of Sr ratios in three samples (0.70363 – 0.70380)_{init.} is broader. In comparison with $^{87}\text{Sr}/^{86}\text{Sr}$ data on primitive young alkali basaltic rocks of the Bohemian Massif (0.7031 – 0.7037 , Bendl et al. 1993) and (0.7032 – 0.7037 , Wilson et al. 1994) the ratios of rocks from Říp Hill plot at the upper limit or even exceed it. In a plot of $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ the Říp Hill sample R-2 (0.51278 vs. 0.70367) plot to the field of Tertiary volcanites of the Bohemian Massif established by Wilson et al. (1994), corresponding to the melt originating by mixture of HIMU-DM and EM in the sense of Zindler – Hart (1986). The positive ϵ_{Nd}^t (+3.4) value implies a magma derived from a source with a greater Sm/Nd than CHUR, i.e. a depleted mantle source region.

The considerable heterogeneity of the lithospheric part of upper mantle (*sensu* Wilson – Downes 1991) beneath the Bohemian Massif is highly probable as a consequence of partly preserved relicts of Hercynian fabrics or of ancient subduction zone associated with the Hercynian orogeny (Hoernle et al. 1995). Data available at present give support to the model of melt generation preferentially in a heterogeneous mantle rather than to selective magma contamination by crustal-derived components. Brooks et al. (1976 a, b) and Brooks – Hart (1978) argue that high and variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of most continental volcanics are result of heterogeneities of the mantle. However, Le Bas (1987) mentioned that indistinctly differing contents of trace elements in nephelinites and olivine nephelinites do not support the argument of expressive mantle chemical heterogeneity. No substantial lateral variation

of the lithosphere is apparent in any of the provinces and therefore the answer may be in the different volatile content of both magmas, especially in the $\text{CO}_2/\text{H}_2\text{O}+\text{CO}_2$ ratio (Le Bas 1987). The Litoměřice Fault represents the most substantial discontinuity in the Bohemian Massif limiting the Teplá-Barrandian terrane block with the scarce volcanism (e.g., of the Říp Hill volcanic centre) and the Saxothuringian terrane with the Ohře Rift and numerous volcanic products e.g., of the České středohoří Mts. (terrane boundaries *sensu* Franke 1989). Hoernle et al. (1995) proved the existence of a large, sheet-like region of upwelling in the upper mantle in Europe. A low S-wave velocity anomaly (LVA), where the LVA intersects the base of the lithosphere, it covers an area of 2,500 by 4,000 km, extending from the Eastern Atlantic volcanic province (EAVP) to northern Africa, the Western Mediterranean volcanic province (WMVP) and the Central European volcanic province (CEVP). Nevertheless, Sr and Nd isotope data for all three main young volcanic regions in Europe, converge on a restricted composition, inferred to be that of the upwelling mantle.

Primitive mantle and olivine-free nephelinite-normalized contents of incompatible elements in samples from Říp Hill are presented in spidergrams, see Fig. 7A and 7B, respectively. These diagrams suggest a compositional homogeneity of the rock. Depletion of the olivine-poor nephelinite in Rb and K can be explained by the presence of residual phlogopite in the mantle source. Troughs of Sr and Ti are probably associated with fractionation of plagioclase and titanian magnetite (Ti-rich clinopyroxene?).

Enrichment in phosphorus is characteristic for the whole petrographically distinctive group of olivine-poor nephelinites from central Bohemia (Štrbený 1992). Nevertheless, more than 10 vol.% of normative apatite (up to 4.52 wt.% P_2O_5) in olivine-poor nephelinite from Slánská hora Hill has rare analogues among basaltic rocks. Alkaline lamprophyres of the teschenite rock association represent the differentiates richest in phosphorus (> 5 wt.% P_2O_5 , Kudělášková 1987). According to Exley – Smith (1982), generation of P-anomalous magmas is probably associated with clinopyroxene fractionation producing P-enriched liquids which might subsequently crystallize as amphibole- and apatite-rich cumulates. During generation of later primary magma, apatite-rich materials might preferentially contaminate the liquids to yield positive P-anomalies. The proposed model requires that magmas undergo prolonged fractionation at a considerable depth (about 100 km). This process is apparently most probable in subcontinental environments (Exley – Smith 1982). The presence of the P-rich olivine-poor nephelinites in central Bohemia thus might reflect a presence of metasomatized upper mantle (cf. Lloyd – Bailey 1975, Wass – Rogers 1980). The progressive fractionation and/or liquation (Ulrych et al. *in press*) rather than contamination (Vaněčková et al. 1993) may be responsible for this trend.

However, both ON, as well as OFN (average data from the Bohemian Massif by Shrbený 1994) in Fig. 7A show lower concentrations of incompatible elements. Using the average OFN of Shrbený (1992) representing mostly the titanium-rich olivine-free nephelinites of the Krušné hory Mts., as a normalizing factor, the olivine-poor nephelinite of Říp Hill reveals typical depletion in Ti only, see Fig. 7B. Lower concentrations of compatible elements in the olivine-poor nephelinite of Říp Hill fit well with characteristics of compared average composition of OFN presented by Shrbený (1992), cf. Table 2.

K/Rb ratios range between 173–368 with the average value of 241. Shrbený (1994) gives the average values 216 for ON and 245 for OFN of the Bohemian Massif. However, these values may be partly affected by late magmatic processes. Relatively low Rb/Sr ratios ($2.6\text{--}5.0 \cdot 10^3$) probably reflect the presence of primary magma from the mantle source.

Contents of U (2.6–3.9 ppm) and Th (14.5–17.2 ppm) are considerably high (Table 2) and comparable with those of olivine nephelinitic and melilititic rocks from the Osečná Complex (Ulrych et al. 1988) and ultramafic al-

kaline lamprophyres from boreholes in broader neighbourhood of Říp Hill (Ulrych et al. 1993). The Th/U ratios of Říp Hill rocks display range between 3.1–5.6 (3.0–5.7 by Chlupáčová 1977) corresponding to the developed continental alkali basalts (Lutic 1975), see Fig. 8. However, in contrast to the above mentioned volcanites with perovskite and apatite, the last mineral represents the solitary host mineral concentrating incompatible elements (REE, Nb, Ta, U, Th) in the rocks of Říp Hill. From the geochemical point of view (based among others on distribution of REE, U, Th etc.) the cognate rocks probably represent carbonate-bearing alkaline lamprophyres of central Bohemia (Ulrych et al. 1993) associated with the Říp Hill volcanic centre.

REE contents and $(\text{La/Yb})_N$ are fairly high (cf. Table 2). It seems that the contents of REE, U, Th, Nb, Ta a.o. incompatible elements are associated with magmatic crystallization (apatite \pm Ti-magnetite and hauyne?). Source of these elements is linked with metasomatized mantle material. Hanson (1977) suggested small-scale veining of the upper mantle by material enriched in LILE. Enrichment of the lithosphere by diapiric addition of material from an enriched mesosphere was proposed, e.g., by Brooks et al. (1976 b).

He presumed plumes of depleted mantle from the mesosphere mixing with fertile asthenosphere material. High contents of REE are comparable with those of olivine melilitic rocks of the Osečná Complex (Ulrych et al. 1988), where they were associated with late magmatic fluids. Chondrite-normalized REE patterns with characteristic dominance of LREE are presented in Fig. 9. The omnipresent low negative Eu/Eu* anomaly (0.8–0.9) is associated with fractionation of plagioclase. Partly altered (argillized and dealcalized) sample R-5 reveals a tendency to concentrate REE, as well as other incompatible elements (Nb, Th etc.).

Conclusions

Říp Hill is a resistant erosional neck representing either a relict of feeding channel of a stratovolcano (cf. Le Bas 1987 and Žeberská – Mikuláš 1982) or a compact filling of diatreme (maar-type) in sense

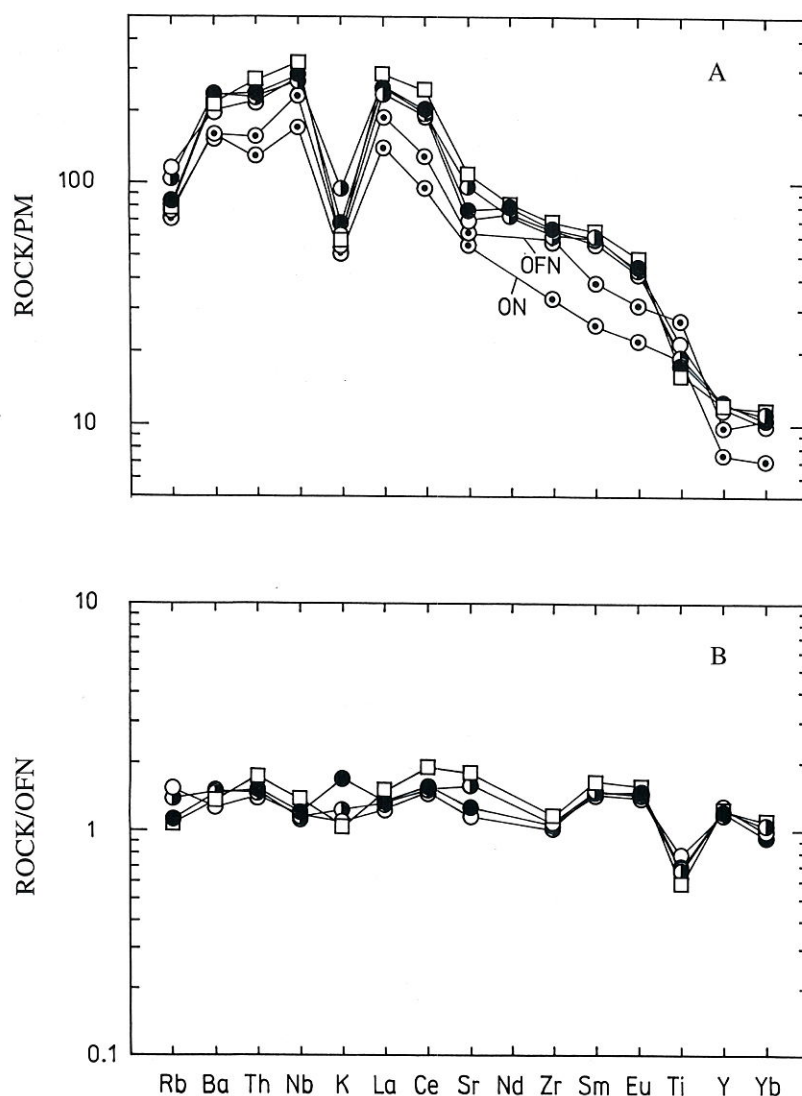


Fig. 7. Spidergrams of the olivine-poor nephelinite from Říp Hill. Average olivine nephelinite (ON) and olivine-free nephelinite (OFN) of the young volcanism of the Bohemian Massif (Shrbený 1995). 7A – Normalization constants of PM from Sun – Mc Donough (1989), 7B – Normalization constants of OFN from Shrbený (1995).

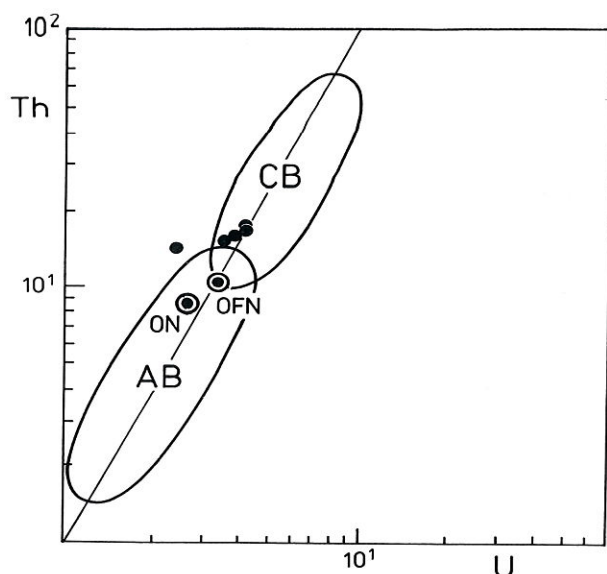


Fig. 8. Olivine-poor nephelinite from Říp Hill in Th vs U plot. Fields AB – alkali basalts, CB – continental basalts (Lutic 1975).

of Kopecký (1985), exhumed from sediments of the Bohemian Cretaceous Basin. However, no relicts of surficial volcanic products were preserved.

According to Le Maitre *et al.* (1989) classification, the rock of Říp Hill corresponds to nephelinite, however, in a special nephelinitic rocks classification of Le Bas (1989) it belongs to nephelinite with transitions to melanephelinite. Olivine-poor to olivine-free nephelinites with specific chemical composition represent a rare group among the Cenozoic volcanics in the Bohemian Massif, characteristic of the central part of the Bohemian Cretaceous Basin.

The rock from Říp Hill reveals a typical polyphase crystallization. Phenocrysts of clinopyroxene \pm olivine belong to the early magmatic generation. The main magmatic phase comprise crystallization of nepheline, anorthoclase, clinopyroxene, Ti-magnetite (\pm calcite?) in matrix. Products of the late magmatic activity include minerals of the sodalite group, analcime, ankerite, biotite, apatite and Ti-magnetite(?).

The low Mg-value (48.5), low contents of compatible elements i.e. Cr (79 ppm), Ni (31), Co (32), Sc (21) and lack of any mantle-type xenoliths give evidence of Říp Hill rock development by differentiation of primary

magma. Clinopyroxene phenocrysts are abundant, while those of olivine are rare (max. 5 vol.%). The mantle-derived magma of Říp Hill probably exhibits fractionation up to phonolitic rocks (Skalka Group phonolites outside the Ohře Rift). The olivine-poor nephelinite of Říp Hill is geochemically anomalous with distinct high REE contents (Σ 650 ppm) and significant domination of LREE, very high U (2.6–3.9 ppm), Th (14.5–17.2 ppm), Nb (150–180 ppm) and Ta (11.9–12.3 ppm) contents and very high Th/U, Nb/Ta, Zr/Hf ratios. These elements are fixed into the late magmatic minerals (mostly apatite).

Taking the geochemical character of the Říp Hill magma into account it corresponds to a typical olivine-poor nephelinite type (Group II *sensu* Le Bas 1989). Genetic association with carbonatitic and phonolitic derivatives and formation of large volcanic structures with frequent pyroclastic products are characteristic features of these rocks. Nephelinites of the Group II are characterized by a high $\text{CO}_2/\text{H}_2\text{O}+\text{CO}_2$ volatile fraction resulting in high viscosity. Their possible association with highly explosive central stratovolcano cannot be neglected. Mantle magma of such volcanoes apparently stopped in a crustal magma reservoir during its ascent and differentiated. The reason of the stopping is in mechanical behaviour of the nephelinitic highly viscous magma.

Both geochemical character and mineral association [clinopyroxene, (Mg, Al, Ti)-magnetite, barite, ankerite] of the olivine-poor nephelinite from Říp Hill reveal some common features with carbonate-bearing ultramafic alkaline lamprophyres from deep boreholes in the vicinity of Říp Hill (Ulrych *et al.* 1993). This fact may indicate a role of comagmatic Říp volcanic centre. Říp Hill volcanic centre with olivine-poor nephelinites is situated outside the Ohře Rift in the Teplá-Barrandian terrane block as opposed to the olivine nephelinites of the České středohoří Mts. with the Saxothuringian basement.

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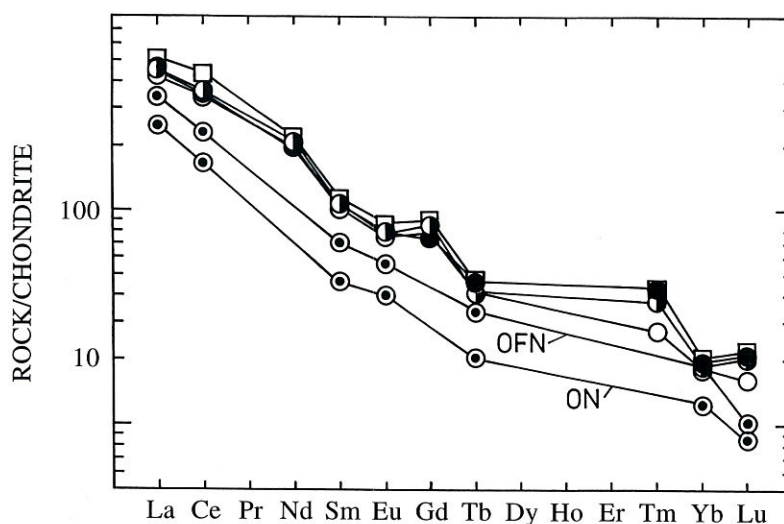


Fig. 9. Chondrite-normalized REE contents of the olivine-poor nephelinite from Říp Hill. Average olivine nephelinite (OF) and olivine-free nephelinite (OFN) of the young volcanism of the Bohemian Massif (Štrbený 1994). Normalization constants from Sun – Mc Donough (1989).

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Geochemicky anomální olivínem chudý nefelinit z Řípu

Sodalitický olivínem chudý nefelinit Řípu se liší jak od olivínických nefelinitů, tak bezolivínických nefelinitů kenozoické vulkanické provincie Českého masivu. Říp vystupuje v terénu jako vypreparovaný sopouch, 25,6 mil. let starý, v bloku tepelsko–barrandienském, na rozdíl od vulkanitů blízkého Českého středohoří v terénu sasko–durynském. Velmi nízké hodnoty Mg # (48.5), nízké obsahy kompatibilních prvků (v ppm) jako Cr (79), Ni (31), Co (32), Sc (21) a nepřítomnost xenolitů plášťového typu poskytují důkazy o jeho vzniku diferenciací primárního plášťového magmatu. Anomální nabohacení inkompatibilními prvky (v ppm) jako U (3,6), Th (15,6), Nb (154), Ta (12,1) a SREE (650) je spjato s pozdní magmatickou krystalizací (převážně apatitu, Ti–magnetitu ± hauynu). Izotopické poměry $^{87}\text{Sr}/^{86}\text{Sr}$ (0,7036–0,7038) and $^{143}\text{Nd}/^{144}\text{Nd}$ (0,51278) horniny Řípu odpovídají složením HIMU OIB ze sublitosferického zdroje; z hodnoty ϵ_{Nd}^t (+3.4) vyplývá ochuzený plášťový materiál. Olivínem chudý nefelinit může být odvozen z karbonatického nefelinitického magmatu s vysokým poměrem $\text{CO}_2/\text{H}_2\text{O}+\text{CO}_2$ ve volatilní frakci vyvolávajícím vysokou viskozitu magmatu, která způsobila přerušování jeho výstupu spolu s následnou diferenciací a kontaminací v korovém rezervoáru. Lze předpokládat, že toto magma bylo příčinou vysoce explozivní vulkanické činnosti maarového či stratovulkánového typu. Olivínem chudý nefelinit Řípu projevuje některé obecné rysy v minerální paragenézi a chemickém složení minerálů – klinopyroxenu, (Mg, Al, Ti)–magnetitu, barytu, ankeritu ap. s karbonatickými alkalickými ultramafickými lamprofyry v jeho okolí. Tato skutečnost dává předpoklad jejich vzájemného genetického sepětí v rámci řípského vulkanického centra.

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