Special Session S15

Tertiary potassic and ultrapotassic magmatism along the Carpathian- Balkan-Dinaride chain: petrological processes and geodynamics

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.

MINERALOGY OF THE PLIOCENE TRACHYTE AND ITS CARBONATITIC MINETTE INCLUSIONS IN OSTRVICA, F.Y.R. OF MACEDONIA

Yanev Y.¹, Boev B.², Iliev Tz.¹, Pecskay Z.³, Karadjov M.¹ and Boev I.²

¹Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; yotzo@geology.bas.bg; metodi@geology.bas.bg ²University "Goce Delčev", Štip, F.Y.R. of Macedonia; blazo.boev@ugd.edu.mk ³ATOMKI, Hungarian Academy of Sciences, 4001 Debrecen, Hungary; pecskay@namafia.atomki.hu

Abstract: The trachyte at Ostrvica hill (age 3.21±0.10 Ma) in Vardar zone is the most evolved volcanics of the ultrapotassic Pliocene-Quaternary series in F.Y.R. of Macedonia. It is aphyric, with clinopyroxene and phlogopite microphenocrysts within a sanidine-anorthoclase groundmass. It contains inclusions of carbonatitic minette ranging in size from several mm to 6-7 cm. They are light coloured porphyric rocks, rich in vacuoles, composed of phlogopite and completely altered olivine(?) phenocrysts amongst acicular clinopyroxenes within a feldspar-calcite groundmass with abundant Fe-oxides and acicular apatite microlites. The inclusions are rimmed by a mm thick mixing zone composed of the same minerals but with intermediate composition between that of minette and trachyte. The clinopyroxenes are mainly diopside-augite with low Ti and Al content (with ⁶Al only in the minette). Positive correlations are observed between Na and Fe³⁺, Al and Ti, and negative one – between Al and Si. In the inclusions phlogopites the negative correlation between Mg# and ⁴Al is found. The feldspars in the trachyte and minette inclusions are Ca-sanidine to Ca-anorthoclase, in the mixing zone - sanidine only. In the inclusions two plagioclase generations (An_{41} and An_{25}) exist. The estimated crystallization temperature of the minette clinopyroxenes is $1280-1180^{\circ}$ C, of plagioclase (An₄₁) – 1130° C and in the hosting trachyte - 1080°C, at the pressures 6.9 and 7.7 kbar, respectively. The temperature of the feldspars crystallization (K-Na-feldspars and Pl₂₄) in the minette groundmass is 809–878°C. By analogy with other ultrapotassic volcanics from F.Y.R Macedonia it is suggested, that the discussed volcanics originated from phlogopite-bearing metasomatised mantle.

Key words: F.Y.R. of Macedonia, ultra-K series, trachyte, carbonatitic minette, magma mixing

1. Introduction

In the Northern Mediterranean domain of the Alpine orogen, from Spain to Syria, Cenozoic ultrapotassic (UK) volcanics, accompanied by rocks of the shoshonitic series, are widespread (review in Prelević et al., 2007). The UK volcanics in F.Y.R. of Macedonia (Yanev et al. 2003, 2008a,b; Altherr et al., 2004) belong to this series. They form the southern part of a NNW-SSE belt extended from Southern Hungary and across Serbia ends in F.Y.R. of Macedonia (in Vardar zone). The rocks are phonotephrites to ultra-K shoshonites (Mlado Nagorichane, Ejevo Brdo, Kureshnichka Krasta, Malino and Kishino), ultra-K latite (Gradishte) and high-Mg latite (Djurishte) dated from 3.24 to 1.47 Ma (Yanev et al., 2008a). The most evolved rocks are the trachytes at Nikushtak and Ostrvica hill (Fig. 1 and 2a). The latter contains inclusions of carbonatitic lamprophyre from several mm to 6–7 cm in size. The petrography and mineralogy of these inclusions and the hosting trachyte, as well as their age, are the subjects of the present communication. It is believed that it will complete the picture of the UK series in F.Y.R. of Macedonia and it will contribute to the clarification of their origin.

2. Methods

The petrographic studies of the rocks were performed by the classical methods, and the analyses of rock-forming minerals – by the Jeol 733 Superprobe at the Geological Institute, Sofia (analyst Tz. Ilyev) equipped with EDS (with ZAF corrections) at the following conditions: 15 kV, 1 nA beam current and 5 μ m beam (standards: in Yanev et al., 2008b). To calculate Fe³⁺ in pyroxenes, a modified version of the Papike et al. (1974) program was used on a charge-balance basis (kindly provided by P. Nimis, Padova University, Italy). The pyroxene components were calculated using the scheme of Yoder and Tilley (1962) complemented by White (1964) to divide the acmite and jadeite components. The pyroxene and plagioclase temperatures and pressures ware determined using the programs of Putirka et al. (2003) and Putirka (2005). The temperatures of groundmass feldspars were calculated using the geothermometer of Fuhrman and Lindsley (1988) at 1 kbar taking the values with difference between each equation <80°C.

The chemical compositions of the trachyte and inclusions was determined by X-ray fluorescence at the Geological Institute (SRM-25, analyst S. Danev), and the carbonate content in minette – by gas sorption (analyst T. Popova, Niproruda Ltd, Sofia). The chemical composition of a powder sample (melted in Spectromelt-4 Merck) from the inclusions peripheral zone was analyzed by scanning of 5 areas (size 100x100 μ m). The trachyte K–Ar age is determined on whole rock sample by Z. Pecskay. The analytical procedure is described in many papers (e.g. Yanev et al., 2008a).

3. Petrography

The Ostrvica trachyte (age 3.21 ± 0.10 Ma) forms an elliptical body (100x150 m) cutting Eocene flysch sediments 15 km NNW of Sveti Nikole town (Fig. 1). The trachyte is a grey aphyric rock, locally containing phlogopite phenocrysts up to 1.5x0.075 mm in size. Microphenocrysts of phlogopite and clinopyroxene are present in a dense groundmass made by microlites of the same minerals plus feldspars and accessories. The feldspar and phlogopite microlites are commonly oriented giving the rock trachytic texture. Phlogopite forms fine flakes, locally opacitized, with most common dimensions 0.2-0.4x0.02-0.045 mm. Clinopyroxene microphenocrysts are mostly acicular, up to 0.45-0.75x0.075-0.1 in size and the microlites are fine-acicular or isometric. The rock contains rounded quartz xenocrystals with diameter up to 1.5 mm, surrounded by a 0.15 mm reaction rim of fine acicular clinopyroxene. Some of them are entirely resorbed and only small lenses of pyroxene needles remain. Accessory minerals are magnetite, apatite and titanite, the latter reaching 0.6x0.225 mm in size.

The trachyte contains mm to 6-7 cm rounded inclusions of light-rusty to grey-brown rocks with

rounded aggregates (diameter from 50 to 230 µm), probably of olivine completely replaced by alteration products and phlogopite flakes usually up to 0.75x0.075 mm (some to 4-5 mm). They are strongly opacitized, randomly oriented, forming a polygonal grid (Fig. 3a,b). In this grid are observed radial, rarely isometric aggregates of clinopyroxene microphenocrysts (up to 0.97x0.105 mm). Between them occur xenomorphic feldspars, skeletal clinopyroxene (diameter 20-40 μm) and phlogopite microlites. Some parts of the groundmass are rich in cryptocrystalline carbonate appearing together with the feldspars. We suppose that this carbonate is primary because it contains very small pyroxene microlites. The inclusions are very rich in vacuoles (from 50x50 to $240x120 \mu m$), partly filled with secondary minerals. Skeletal apatite needles (up to 430x8 µm), "crosscutting" the clinopyroxene microphenocrysts and some alternation products (Fig. 3c), Ti-magmetite (with hercynite molecule) and ilmenite are accessories.



Fig. 1. Location map, after Yanev et al. 2008a. of the ultra- and high-potassic volcanic rocks in F.Y.R. of Macedonia and their K-Ar age in Ma (in parentheses).

Comparing the chemical compositions of the inclusions and their minerals (Tabl. 1-4), the quantities of latter can be estimated by a sample arithmetic procedure (alteration products excluding) as: clinopyroxene 42%, phlogopite+magnetite 25%, feldspars 21% (the carbonate quantity is 12% determined by a gas sorption). According to this mineral composition (Mitchell, 1995; Woolley et al., 1996) and the presence of carbonate >10% this is carbonatitic minette (Woolley and Kempe 1989). Such rocks have been described, among others, in Dubawnt (Canada, Peterson et al., 2002), in Jarangdihi with ~35% carbonate (India, Gupta et al., 2002).



Fig. 2. a- TAS diagram (crosses, F.Y.R. of Macedonian UK volcanics and filed circles, Djurishte latites, after Yanev et al., 2008a); b- comparison between some oxides in studied volcanics; c and d – clinopyroxene diagrams (the fields are after Aoki and Kushiro, 1968; clinopyroxenes of Djurishte latites are after Yanev et al., 2008b); e- phlogopite diagram (Djurishte latites phlogopites are after Yanev et al., 2008b); f- Si/Al vs. Ba feldspar diagram.

The inclusions are rimmed by a dark grey zone up to 4–5 mm thick composed of clinopyroxene and rare phlogopite microlites in a sanidine groundmass. Sanidine in the darker part of the zone contains higher quantity of Fe, Mn and Mg (Tabl. 4). The clinopyroxene microlites are isometric (up to 0.18x0.12 mm) or short-prismatic (0.18x0.045 mm), commonly skeletal, with a central vacuole. Phlogopite forms microlites (from 0.15×0.015 to 0.3×0.1 mm) or rare microphenocrysts ($0.8 - 0.9 \times 0.1$ mm).

4. Chemical composition

The trachyte is normative nepheline-bearing rock

(18.66% wt) containing equal quantity of Na₂O and K₂O (Tabl. 1). The inclusions are characterized by their low alkalis content, due to the almost

complete decomposition of phlogopite. Because of this alteration and their specific lamprophyre mineral composition, it must not be classified accord-



Fig. 3. Minette inclusions in the trachyte (Tr) – a and b, photomicrographs (plane-polarized light); c and d, back-scattered electron images. Phl, strongly altered phlogopite; Cpx, clinopyroxenes (in c and d, zoned and partly resorbed; the composition of Cpx-3 is presented in the table 2); Ap, skeletal apatite; Kf, K-Na-feldspars with different Ba content (in a an b – the white crystals in the groundmass); Ol?, completely altered olivine(?); Car, cryptocrystalline carbonate; Vd, voids (in c and d – the black spots).

Ψηφιακή Βιβλιοθήκη Θεόφβαστος - Τμήμα Γεωλογίας. Α.Π.Θ.

ing to the TAS diagram (Woolley et al., 1996); however we plotted inclusions in such a diagram just for comparison with other volcanics from F.Y.R Macedonia (Fig. 2a). The composition of the zone, surrounding the inclusions, is transitional between trachyte and minette (Fig. 2b) and may be considered as product of mixing between the still liquid inclusions and the hosting trachytic magma. The mixing is suggested also by the rounded form of the inclusions and the absence of the sharp contact. This zone has a composition similar to the Djurishte latite (Yanev et al. 2008a), which is the only rock of shoshonitic affinity accompanied the UK volcanics from F.Y.R Macedonia. This latite has similar age (3.19 Ma, Yanev et al., 2008a) and it is exposed in the same region as the Ostrvica trachyte (Fig. 1).

Table 1. Whole-rock analyses

Poals	Minette	Trachuta	Mixing
ROCKS	inclus.	Tractifyte	zone
SiO ₂	51,27	60,92	56,06
TiO ₂	0,99	0,53	0,58
Al_2O_3	11,51	14,43	13,93
Fe ₂ O ₃	7,03	4,05	7,01
MnO	0,24	0,07	0,09
MgO	6,56	3,69	5,72
CaO	12,61	4,18	8,09
Na ₂ O	1,36	5,70	3,68
K ₂ O	2,50	5,14	3,89
CO_2	5,57	n.d.	n.d.
Total	99,64	98,71	99,05

The studied minette inclusions actually are not UK rock, probably due to the alteration of the phlogopite. The majority of the minettes described in the literature are UK rocks excepting some minettes as those in Mexico (dykes in the Colima volcano, Luhr and Carmicael, 1981, in the volcanic fields of Ayutla and Tapalpa, Righter and Rosas–Elguera, 2001, of Mascota, Ownby at al., 2008 and Los Volcanos, Wallace and Carmichael, 1989), in Shahewen monzonitic pluton, Chine (Wang et al., 2007), in Qulitat Suweidi in Oman (Worthing and Nasir, 2008).

5. Mineral chemistry

5.1. *Clinopyroxenes* (Tabl. 2). They have a similar composition (diopside-augite) in all described rocks but those from the mixing zone occupy an intermediate position between the trachyte and inclusions pyroxenes. The more magnesian are the trachyte clinopyroxenes. In many crystals a zoning

with respect to the Mg \leftrightarrow Fe²⁺ substitution is observed, the periphery being richer in Fe component due to the decreasing crystallization temperature. There are, however, crystals with oscillatory zoning (Fig. 3d). The other elements as Ti and Mn do not reveal definite variations.

As in the rest of the volcanics of this series (Yanev et al., 2008b), the Al content in the described clinopyroxenes is likewise low (up to 0.1 apfu), slightly higher in the inclusions (up to 0.135 apfu), whereas in the mixing zone the values are intermediate. The lowest Al contents and respectively highest of Si are observed in the reaction pyroxenes around quartz xenocrystals. However, due to the high Si content, only in single cases there is an Al deficiency in the Si-Al tetrahedrons (mainly in the trachyte), which is compensated by Fe^{3+} (Hartman, 1969). In the inclusions and the mixing zone ⁶Al is present (up to 0.059 *apfu*), in some cases even ${}^{6}Al > {}^{4}Al$. Experiments prove that the ${}^{6}Al / {}^{4}Al$ ratio in silicate melts (in the crystallizing from them clinopyroxenes, respectively) increases with increasing pressure due to the increasing coordination of Al in the melt (Velde and Kushiro, 1978). In the inclusions clinopyroxenes (Tabl. 2) small quantities of jadeite component are formed, which is typical high-pressure molecule. Therefore, they plot in the field defined by Aoki and Kushiro (1968) for pyroxenes from mafic inclusions in basalts (Fig. 2c), where plot also the Djurishte latite pyroxenes. The pyroxenes from all UK volcanics cropping out in the F.Y.R. of Macedonia (Yanev et al., 2008b) and the studied trachyte are without or with low ⁶Al content and they plot in the igneous rocks field.

The highest Na contain is found in low-Mg core (often resorbed – fig. 3d) of some zonal pyroxenes in the inclusions (up to 0.092 *apfu*, J/J+Q = 0.05). Na always participates in the clinopyroxene structure manly as acmite and in some cases as jadeite components. A weakly expressed positive correlation exists between Na and Fe^{3+} . The TiO₂ content is likewise relatively low without some regularity in its distribution in the individual pyroxene zones. Ti connects with Al in TAL (CaTiAl₂O₆) and rarely in NATAL components (NaTiSiAlO₆, Papike et al. 1974) determining the classical positive Al-Ti correlation related to the most important nonquadrilateral substitution in the pyroxene structure. The observed negative Al–Si correlation (Fig. 2d) resulted of $TiAl_2 \leftrightarrow MgSi_2$ exchange reaction.

Table 2. Microprobe analyses of clinopyroxenes

Rock					ľ	Minette i	nclusions					
	needle	needle	core-1	rim	core-2	rim	core-3*	interm.	interm.	interm.	rim*	core-4
SiO ₂	50,46	52,47	51,41	50,43	51,83	54,21	50,45	53,88	51,66	54,73	51,92	53,07
TiO ₂	0,97	0,59	0,85	1,09	0,90	0,46	0,63	0,66	1,04	0,28	0,73	0,61
Al_2O_3	2,63	1,04	2,54	3,10	2,50	1,05	3,50	1,94	3,45	1,19	2,38	1,33
FeO _{tot}	6,01	7,67	5,07	6,59	5,49	4,22	8,13	3,82	6,30	3,41	8,39	4,83
MnO	0,23	0,04	0,00	0,00	0,14	0,21	0,55	0,21	0,23	0,09	0,09	0,05
MgO	14,64	14,08	15,47	13,67	14,82	16,65	12,33	16,36	13,38	16,91	12,65	18,24
CaO	23,32	22,91	23,37	23,69	22,54	22,69	22,63	22,74	22,99	22,44	22,88	20,95
Na ₂ O	0,76	0,30	0,47	0,63	0,73	0,59	1,28	0,32	0,78	0,69	0,91	0,19
K ₂ O	0,18	0,55	0,17	0,18	0,05	0,05	0,15	0,03	0,09	0,10	0,01	0,10
Cr ₂ O ₃	n.d.	n.d.	n.d.	n.d.	0,01	n.d.	n.d.	0,04	0,07	0,16	0,06	n.d.
Total	99,20	99,65	99,35	99,38	99,01	100,13	99,65	100,00	99,99	100,00	100,02	99,37
Mg#	0,92	0,78	0,92	0,87	0,86	0,89	0,82	0,88	0,81	0,90	0,76	0,90
Wo	48,4	47,2	47,8	49,5	47,4	46,0	48,6	46,7	49,2	46,1	48,6	41,8
Jd comp	onent				0,022	0,019		0,024	0,043	0,039	0,028	

*Cpx-3 on the fig. 3d (interm., intermediate zone)

Table 2 (continued)

	Mixing zone								Trachyte								
Rocks	ocks microphenocryst skelet		etal		core interm.		rim	rim around guartz		microphenocryst							
SiO ₂	53,02	51,86	51,23	52,56	51,86	51,39	50,02	52,94	52,87	53,69	52,47	54,84	52,59	50,46	53,46	50,96	52,36
TiO ₂	0,45	0,82	0,56	0,32	0,62	0,37	0,74	0,41	0,12	0,23	0,34	0,23	0,43	0,97	0,28	0,76	0,41
Al_2O_3	1,61	2,68	2,49	1,27	2,62	2,69	3,65	1,64	0,42	0,47	1,31	0,28	1,61	2,36	0,81	2,03	1,85
FeO _{tot}	4,13	6,94	6,56	4,32	7,26	9,95	11,08	6,57	8,60	7,29	7,01	4,17	4,28	6,01	5,27	8,80	4,30
MnO	0,16	0,40	0,28	0,32	0,11	0,74	0,59	0,43	0,74	0,33	0,17	0,25	0,05	0,23	0,33	0,37	0,27
MgO	17,25	16,42	15,41	18,28	14,68	12,36	11,57	16,79	15,2	16,01	15,27	18,79	17,19	14,64	15,47	12,96	17,26
CaO	22,39	20,40	20,79	21,39	22,11	22,48	21,51	20,66	21,15	22,16	21,51	21,84	21,79	23,32	23,19	23,04	22,93
Na ₂ O	0,52	0,69	0,74	0,55	0,63	0,88	0,89	0,51	0,68	0,60	0,84	0,43	0,68	0,76	0,76	0,65	0,67
K ₂ O	0,01	0,15	0,07	0,03	0,00	0,06	0,02	0,05	0,00	0,06	0,03	0,18	0,05	0,18	0,11	0,15	0,02
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,16	n.d.	0,12	n.d.	n.d.	n.d.	n.d.
Total	99,54	100,36	98,13	99,04	99,89	101,35	100,46	100,24	99,78	100,84	99,11	101,01	98,79	98,93	99,68	99,72	100,07
Mg#	0,90	0,90	0,88	0,95	0,84	0,78	0,73	0,87	0,80	0,84	0,91	0,87	0,95	0,91	0,90	0,80	0,97
Wo	45,0	41,6	43,7	42,9	45,8	46,8	46,0	41,7	43,1	44,4	42,9	44,5	44,4	48,6	47,2	47,9	45,9

5.2. *Phlogopite* (Tabl. 3). It shows low Ba and Ti contents. A negative correlation between Mg# and ⁴Al is observed in the inclusions only (Fig. 2e); such a finding is found also in the Djurishte latite phlogopites. This correlation reflects the Ti+2Al=Mg+2Si substitution occurring at high temperature and pressure (Guo and Green 1990).

The inclusions phlogopites are almost completely opacitized (Fig. 3c) and their composition has been analysed only in the rare relics among magnetite crystals and the different alteration products.

5.3. *Feldspars* (Tabl. 4). They are Ca-sanidine to Ca-anorthoclase (according to the diagram of Smith and Brown 1988) in the trachyte and inclusions, and sanidine only in the mixing zone. The Ba content in sanidines is low whereas in the anorthoclases it reaches 0.55 *apfu* where a negative correlation between Ba and Si/Al ratio is observed (Fig. 2f). It is explained by Ba²⁺Al³⁺ \leftrightarrow K⁺Si⁴⁺ substitution (Afonina et al., 1978). In the inclusions

two plagioclase generations $(An_{41} \text{ and } An_{25})$ also exist crystallizing at different temperatures (see below).

5.4. *Carbonates*. They are irregularly distributed in the minette groundmass. Most of them are calcite (average of 9 analyses: CaCO₃ 95.18, MgCO₃ 4.10, BaCO₃ 0.18, MnCO₃ 0.12, FeCO₃ 0.10 wt%) to high Mg calcite (CaCO₃ 69.75, MgCO₃ 29.00, MnCO₃ 1.85 wt%). Calcite sporadically appears also in other UK volcanics from F.Y.R Macedonia (in Ejevo Brdo and Kishino phonotephrites, Yanev et al., 2008b).

6. Crystallization parameters

The estimated crystallization temperature and pressure (Tabl. 5) of minette pyroxenes is 1280– 1180°C (pressure 6.9 kbar), of plagiocalse (Pl_{41}) – 1130°C and of trachyte pyroxenes – 1080°C (pressure 7.7 kbar). This pressure explains the absence of orthopyroxene, which crystallizes at pressure

Table 3. Microprobe analyses of phlogopites

Rocks		Mine	tte inclus	sions		Μ	lixing zoi	ne		Г	Trachyte		
SiO ₂	39,37	39,79	40,43	41,87	39,96	38,75	40,00	40,05	40,62	40,56	40,02	40,40	40,62
TiO ₂	1,48	1,83	2,11	1,60	1,50	1,90	1,99	1,48	1,60	1,64	1,76	1,52	1,78
Al_2O_3	13,43	13,35	13,30	14,21	14,70	13,59	14,08	14,32	14,20	14,66	14,33	14,38	13,69
FeO	6,37	6,97	5,84	5,56	4,80	6,74	4,19	6,50	4,41	4,26	4,41	4,64	5,02
MnO	0,00	0,18	0,11	0,28	0,00	0,05	0,05	0,00	0,00	0,11	0,00	0,00	0,00
MgO	22,28	22,42	22,89	22,55	24,31	22,63	25,14	24,46	25,18	24,83	24,76	24,60	24,37
CaO	0,04	0,10	0,07	0,24	0,20	0,26	0,22	0,00	0,04	0,25	0,19	0,29	0,54
Na ₂ O	1,11	1,00	0,88	0,45	0,73	0,64	1,06	0,61	0,94	0,75	0,81	0,51	0,62
K_2O	9,69	10,02	9,86	9,48	10,08	9,73	9,32	9,84	9,78	9,68	9,99	9,61	9,00
Cr_2O_3	n.d.	n.d.	n.d.	0,39	0,43	n.d.	n.d.	n.d.	0,17	0,41	0,49	0,40	0,11
BaO	0,35	0,10	0,04	1,06	0,46	0,47	0,01	0,38	0,41	0,18	0,18	0,43	0,31
LOI	5,87	4,25	4,47	2,31	2,82	5,26	3,95	2,34	2,64	2,68	3,05	3,24	3,94
Total	99,99	100,01	100,00	100,00	99,99	100,02	100,01	99,98	99,99	100,01	99,99	100,02	100,00
Mg#	0,86	0,85	0,87	0,88	0,90	0,86	0,91	0,87	0,91	0,91	0,91	0,90	0,90

Dooka				Min	atta ina	luciona			Μ	ixing z	one	Trachuta						
RUCKS				IVIII	lette me	lusions				clear part darl				Tacilyte				
												Na-						
Minera	l	Ca-anorthoclase					sanidine	plagioclase		sanidine		sani-	Ca- anorthoclase		Ca-sanidine			
												dine						
SiO ₂	62,58	63,12	59,76	59,81	63,53	60,93	64,49	57,17	61,27	65,57	65,60	64,75	61,49	64,06	62,34	65,19	65,83	
Al_2O_3	21,35	21,22	23,95	22,92	20,94	22,37	19,35	27,64	23,55	18,99	19,07	19,49	22,26	19,69	22,81	20,15	18,54	
Fe_2O_3	0,12	1,06	0,34	0,52	0,16	1,08	0,70	0,40	0,64	0,52	0,38	0,49	0,48	0,84	0,62	0,21	0,56	
CaO	1,72	4,19	2,90	2,38	2,02	4,34	0,77	8,63	4,86	0,38	0,87	1,44	2,21	1,31	3,38	0,89	1,13	
Na ₂ O	5,26	5,98	6,32	4,71	5,42	6,40	4,89	6,30	7,22	4,74	4,95	5,63	6,68	6,24	7,43	5,80	4,65	
K_2O	6,69	3,93	4,40	6,15	7,30	3,05	8,78	0,78	1,57	9,94	8,66	7,03	4,63	6,07	2,87	7,52	8,48	
BaO	1,58	1,21	2,09	3,05	0,64	0,70	0,47	0,27	0,10	0,18	0,28	0,60	2,30	0,36	0,56	0,43	0,42	
Total	99,30	100,71	99,76	99,54	100,01	98,87	99,45	101,19	99,21	100,32	99,81	99,43	100,05	98,57	100,01	100,19	99,61	
An	9,0	21,3	14,8	13,1	9,8	22,2	3,8	41,2	24,6	1,8	4,3	7,2	11,2	6,6	16,7	4,4	5,8	
Ab	49,5	55,0	58,4	46,7	47,8	59,2	44,1	54,4	66,0	41,3	44,5	50,9	61,0	57,0	66,4	51,6	42,8	
Or	41,5	23,8	26,8	40,2	42,4	18,6	52,1	4,4	9,4	56,9	51,2	41,9	27,8	36,5	16,9	44,0	51,4	
											*MnO	0,18						
											MgO	0,25						

more than 10 kbar (Barton and Hamilton 1982). The obtained data are comparable with the crystallization parameters of pyroxenes in the UK volcanics from F.Y.R Macedonia: temperature 1300– 1150°C at pressure 6–8 kbar (Yanev et al., 2008a). The temperature of the feldspars crystallization in the minette groundmass (K-Na-feldspars and Pl₂₄) is 809–878°C. The carbonates crystallize between 650 and 1050°C when X_{CO2} in the remaining liquid of the SiO₂–CO₂ system reaches 0.83 (Otto and Wyllie, 1993).

7. Discussion on the rock genesis

The age of the Ostrvica trachyte and its major and trace elements composition (Altherr et al., 2004) define it as part of the UK volcanic series form F.Y.R of Macedonia. It is the most evolved member (with the trachyte from Nikushtak), but its composition is not ultrapotassic. It is assumed that this series originated from phlogopite-containing

metasomatized mantle (Yanev et al., 2003, 2008a, b; Altherr et al., 2004) based on the hypothesis of Foley (1992) and others for the origin of high-K magmas.

Rocks	T°C	P kbar				
	Cpx/	melt ¹				
Minette:						
core	1282	7,7				
rim	1272	6,9				
Mixing zone:						
core	1186	7,3				
Trachyte:	1082	7,4				
	Pl/n	nelt ²				
Minette:						
An ₄₁	1132	n.d.				
C D 1 (0000)	2 c D (1)	(2005)				

¹after Putirka et al. (2003), ²after Putirka (2005)

The present study suggested the presence of another type of magma in this series – that of the minette as in the Serbian Tertiary UK volcanics (Prelević et al., 2004). The minette, irrespective of its minor quantities, commonly accompanies shoshonitic and UK magmas. Here it is characterised by high amount of volatile components (particularly CO_2), which make it very mobile and enabled mixing with the trachytic magma. The mixing zone around the minette inclusions is similar in chemical and mineral composition to the Djurishte latite, which is also not UK. It is possible that the latter originated from this mixing of these two magmas.

The lack of trace elements and isotopes data in the studied rocks does not allow to discuss the depth and processes of magma generation. Geobaro-tehrmometric data suggest that they began to crys-tallize into the crust at a depth of 20–22 km and at the above mentioned temperatures. The minette groundmass crystallizes at lower pressure and at about 250°C lower temperature.

References

- Afonina G.G., Makagon V.M. and Shmakin B.M., 1978. Barium and Rubidium Bearing Potassic Feldspars. Nauka, Novosibirsk, 112p. (in Russian).
- Altherr R., Meyer H.-P., Holl A., Volker F., Alibert C., McCulloch M.T. and Majer V., 2004. Geochemical and Sr-Nd-Pb isotopic characteristics of Late Cenozoic leucite lamproites from the East European Alpine belt (Macedonia and Yugoslavia). Contribution to Mineralogy and Petrology, 147, 58-73.
- Aoki K. and Kushiro I., 1968. Some clinopyroxenes from ultramafic inclusions in Dreiser Weiher, Eifel. Contribution to Mineralogy and Petrology, 18, 326-337.
- Barton M. and Hamilton D.L., 1982. Water-satured melting experiments bearing upon the origin of potassium-rich magmas. Mineralogical Magazine, 45, 267-278.
- Foley S., 1992. Vein-plus-wall-rock melting mechanisms in the lithosphere and the origin of potassic alkaline magmas. Lithos, 28, 435–453.
- Fuhrman M. and Lindsley P., 1988. Ternary feldspar modeling and thermometry. American Mineralogist, 73, 201-215.
- Guo J. and Green T.H., 1990. Experimental study of Ba partitioning between phlogopite and silicate liquid at upper mantle pressure and temperature. Lithos, 24, 83-95.
- Gupta A.K., Chathopadhyay B., Fyfe W.S. and Powell M., 2002. Experimental study on three potassiumrich ultramafic rocks from Damodar Valley, East India. Mineralogy and Petrology, 74, 343-360.
- Hartman P., 1969. Can Ti⁴⁺ replace Si⁴⁺ in silicates? Mineralogical Magazine, 37, 366-369.
- Luhr J.E. and Carmichael I.S.E., 1981. The Colima volcanic complex: Part II. Late Quaternary cinder cones. Contribution to Mineralogy and Petrology, 76, 127-147.

- Mitchell R.H., 1995. Kimberlites, Orangeites and Related Rocks. Plenum Press, New York.
- Otto J.W. and Wyllie P.J. 1993. Relationships between silicate melts and CaO–MgO–SiO₂–CO₂–H₂O at 2 kbar. Mineralogy and Petrology, 48, 343-365.
- Ownby S.E., Lange R.A. and Hall Ch.M., 2008. The eruptive history of the Mascota volcanic field, western Mexico: Age and volume constraints on the origin of andesite among a diverse suite of lamprophyric and calc-alkaline lavas. Journal of Volcanology and Geothermal Research, 177, 1077-1091.
- Papike J.J., Cameron K.L. and Balfwin K., 1974. Amphiboles and pyroxenes: characterization of other than quadrilateral component and estimates of ferric iron from microprobe data. Geological Society of America. Abstracts with programs, 6, 1053-1054.
- Peterson T.D., Van Breemen O., Sandeman H. and Cousens B., 2002. Proterozoic (1.85-1.75 Ga) igneous suites of the Western Churchill Province: granitoid and ultrapotassic magmatism in a reworked Archean hinterland. Precambrian Research, 119, 73-100.
- Prelević D., Foley S.F., Cvetković V. and Romer R.L., 2004. Origin of minette by mixing of lamproite and dacite magmas in Veliki Majdan, Serbia. Journal of Petrology, 45, 759-792.
- Prelević D., Foley S.F. and Cvetković V., 2007. A review of petrogenesis of Mediterranean Tertiary lamproites: A perspective from the Serbian ultrapotassic province. Geological Society of America. Special Paper, 418, 113-129.
- Putirka K., 2005. Igneous thermometers and barometers based on plagioclase + liquid equilibria: Test of some existing models and new calibrations. American Mineralogist, 90, 336-346.
- Putirka K., Mikaelian H., Ryerson F.J. and Shaw H., 2003. New clinopyroxene–liquid thermobarometers for mafic, evolved and volatile-bearing lava compositions, with applications to lavas from Tibet and the Snake River Plain, ID. American Mineralogist, 88, 1542-1554.
- Righter K. and Rosas–Elguera J., 2001. Alkaline lavas in volcanic front of the Western Mexican Volcanic Belt: Geology and petrology of the Ayutla and Tapalpa volcanic fields. Journal of Petrology, 42, 2333-2361.
- Smith J.V. and Brown W.S., 1988. Feldspar Minerals. Crystal Structure, Physical, Chemical and Microtextural Properties, v. 1. 2nd ed. Springer Verlag, N. York.
- Velde B. and Kushiro I., 1978. Structure of sodium alumino-silica melts quenched at high pressure; infrared and aluminum K-radiation data. Earth and Planetary Science Letters, 40, 137-140.
- Wallace P. and Carmichael I.S.E., 1989. Minette lavas and associated leucitites from the Western Front of the Mexican Volcanic Belt: petrology, chemistry, and origin. Contribution to Mineralogy and Petrology, 103, 470-492.

- Wang F., Lu X.-X., Lo C.-H., Wu F.-Y., He H.-Y., Yang L.-K. and Zhu R.-X., 2007. Post-collisional, potassic monzonite–minette complex (Shahewan) in the Qinling Mountains (central China): 40Ar/39Ar thermochronology, petrogenesis, and implications for the dynamic setting of the Qinling orogen. Journal of Asian Earth Sciences, 31, 153–166.
- White A.J.R., 1964. Clinopyroxenes from eclogites and basic granulites. American Mineralogist, 49, 883-888.
- Woolley A.R. and Kempe D.R.C., 1989. Carbonatites: nomenclature, average chemical compositions and element distribution. In: Carbonatite Genesis and Evolution, Bell, K. (ed.), Unwin Hyman, London.
- Woolley A.R., Bergman S.C., Edgar A.D, Le Bas M.J., Mitchell R.H., Rock N.M.S. and Scott Smith B.H., 1996. Classification of lamprophyres, lamproites, kimberlites, and the kalsilitic, melilitic, and leucitic rocks. Journal of the Mineralogical Association of Canada, 34, part 2.
- Worthing M.A. and Nasir S., 2008. Cambro-Ordovician potassic (alkaline) magmatism in Central Oman: Petrological and geochemical constraints on petrogenesis. Lithos, 106, 25-38.

- Yanev Y., Boev B., Doglioni C., Innocenti F., Manetti P. and Lepitkova S., 2003. Neogene ultrapotassicpotassic volcanic association in the Vardar zone (Macedonia). Comptes-rendus de l'Académie bulgare des Sciences, 56 (4), 53-58.
- Yanev Y., Boev B., Doglioni C., Innocenti F., Manetti P., Pecskay Z., Tonarini S. and D'Orazio M., 2008a. Late Miocene to Pleistocene potassic volcanism in the Republic of Macedonia. Mineralogy and Petrology, 94, 45-60.
- Yanev Y., Boev B., Manetti P., Ivanova R., D'Orazio M. and Innocenti F., 2008b. Mineralogy of the Plio-Pleistocene ultra- and high potassic volcanic rocks in Republic of Macedonia. Geochemistry, Mineralogy and Petrology, 46, Sofia, 35-67.
- Yoder H.S.jr. and Tilley C.E., 1962. Origin of basalt magmas: An experimental study of natural and synthetic rock systems. Journal of Petrology, 3, 342-532.

Ψηφιακή Βιβλιοθήκη Θεόφραστος - Τμήμα Γεωλογίας. Α.Π.Θ.