Доклади на Българската академия на науките
Comptes rendus de l'Académie bulgare des Sciences
Tome 56, No 4, 2003

GEOLOGIE
Pétrologie

NEOGENE ULTRAPOTASSIC-POTASSIC VOLCANIC ASSOCIATION IN THE VARDAR ZONE (MACEDONIA)

Y. Yanev, B. Boev*, C. Doglioni, F. Innocenti***, P. Manetti****, S. Lepitkova***

(*Submitted by Corresponding Member I. Velinov on January 24, 2003*)

Abstract

The studied volcanic rocks in Kumanovo, Sveti Nikole, Shtip and Demir Kapia areas are of Late Miocene – Pliocene age and potassic to ultrapotassic character (Romanian type). They have been classified as phonotephrites, shoshonites and latites with high Mg# (> 70) and high Ni and Cr contents indicative of their primitive nature. The volcanics contain phenocrists of Fo-rich olivine, diopside to augite, phlogopite to Ba- and Ti-rich biotite (close to a kinoshitalite) in a groundmass consisting of microlites of the same minerals + leucite, Ti-magnetite ± ilmenite enclosed by Na-sanidine and/or anorthose. The rocks are significantly enriched in LILE and show negative Ta, Nb, Ti and positive Pb anomalies. The trace elements distribution for ultrapotassic varieties indicates a process of crystal fractionation while this pattern for latites might have resulted from mixing of ultrapotassic and latite melts. Although Sr isotope ratios are relatively high (0.7081-0.7104) and Nd – low (0.5121-0.5124) a minor role of the crustal contamination has been supposed assuming the relatively high Sr and Nd contents in Mg-rich rocks. Isotope and trace elements features define the studied volcanics as derived from metasomatized mantle resulted from subduction-collision processes.

Key words: Macedonia, Vardar zone, ultrapotassic rocks, petrological characteristic, isotopes

Introduction. The central and northern part of the Balkan Peninsula was affected since Cretaceous by NE-directed subduction, with both SW (Hellenides-Dinarides) and NE (Balkans) migration of the orogenic conjugate fronts and intervening later extension. As a result an intricate geotectonic evolution developed, associated with a magmatism with varying petrogenetic affinity ranging from calc-alkaline to alkaline either potassic or sodic. In particular, the Hellenides-Dinarides system was characterized by the occurrence of the Late Eocene – Early Miocene magmatic belt, expression of the Adria subduction under the Euro-Asia margin. After a time gap of 10-12 Ma [1,2], the eruptive activity resumed in Late Miocene – Pliocene which produced scattered volcanic centres. They are located within the Vardar zone between Northwestern Greece and Southern Serbia through Macedonia (Fig. 1) and form a K-rich alkaline association [1,4,5]. In this paper we present new geological, petrological and geochemical data on these rocks from Macedonia (KMR, K-rich Macedonia Rocks) that constitute the most widespread products of the late Tertiary alkaline association and on which only scattered data are available [6-8]; finally, the obtained results will be used in order to constrain the geodynamic evolution of the area.

Space-time distribution. On the territory of Macedonia these volcanics are found within 4 volcanic areas [8,4]. Only some bodies of these areas have been studied in the present paper. From north to south they are: Malo Nagorichane (Kumanovo area), Djurishte, Gradishte, and Kishino (Sveti Nikole area), Ejovo Brdo (Shtip area), and Koreshnichka Krsta (Demir Kapia area) (Fig. 1). The volume of emitted products is always limited; they generally form small and thin lava flows in some cases connected with the feeder dykes as in Koreshnichka Krsta and Ejovo Brdo where erosional remnants of a vent (necks) are also present. In Kumanovo area (Malo Nagorichane) the volcanic cover with a thickness ranging from 10 to 30 m, displays the greatest extension; it is constituted by several superimposed lava flows separated by thin scoria levels which extend on an area of about 15 km^2. In some places as Malo Nagorichane, Kishino and Trstnik (Sveti Nikole area), the volcanic products cut or overlie Pliocene sediments. A Late Miocene – Pliocene age is suggested by the few K-Ar dating available [7] for Ejovo Brdo (5.5 Ma) and Koreshnichka Krsta volcanics (9.5 Ma).

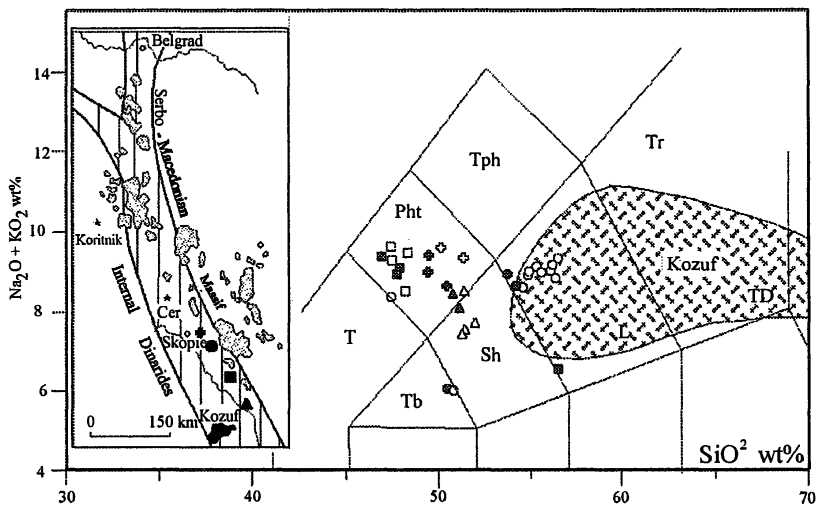

Fig. 1. TAS classification diagram after [3] for KMR and, in the left, the geological sketch map of Macedonia and surrounding region [1,2] showing the location of Late Miocene-Pliocene ultrapotassic-potassic volcanic association in Macedonia (cross, Malo Nagorichane; circle, Sv. Nikole area; square, Ejovo Brdo; triangle, Koreshnichka Krsta; filled symbols: data from [8]) and in Serbia (stars); black area: Late Miocene – Pliocene subduction-related [4,5] Kozuf volcano; dotted area: Late Eocene – Early Miocene magmatic rocks. Shaded area is Vardar zone. T, tephrite; Pht, phonotephrite; Tph, tephriphonolite; Tb, trachybasalt; Sh, shoshonite; L, latite; Tr, trachyte; Td, trachydacite

Petrography and geochemistry. Based of TAS diagram (Fig. 1), the studied samples of KMR can be classified as shoshonites, latites and phonotephrites. They are relatively primitive as evidenced by the high Mg# (generally > 70) and the high content of Ni (100-250 ppm) and Cr (170-420 ppm).

KMR are generally undersaturated (Table 1) with nepheline (0.6-11%) in the norm. The Ejovo Brdo and Kishino rocks contain also normative leucite (0.9-6.6%); only the latites from Djuriste are saturated. All the rocks show a marked alkaline potassic character with a consistent group of samples falling in the ultrapotassic (UK) field as defined by [9] (Fig. 2). The ultrapotassic rocks exhibit a Roman-type affinity according to their CaO/Al_2O_3 ratio.

Major element distribution allows recognition of two distinct groups. The first one includes the latites from Djurishte (LG) with K_2O/Na_2O ratio between 1.42 and

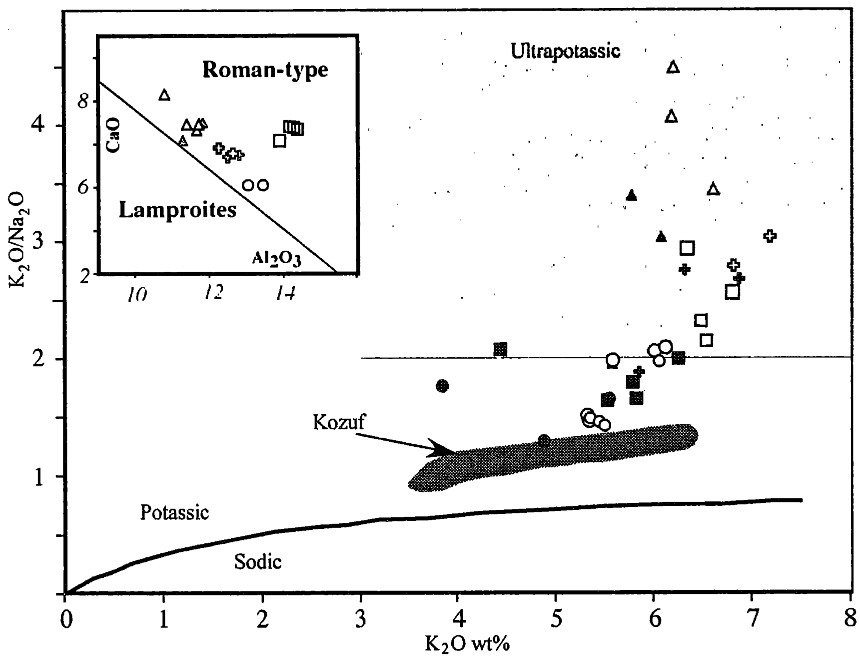

Fig.2. K_2O/Na_2O vs. K_2O classification diagram for KMR. The line between sodic and potassic rocks was drawn after [3]. Inset: CaO vs. Al_2O_3 diagram for ultrapotassic rocks. Dividing line between lamproites and Roman-type rocks drawn according to [9]. The symbols are the same as Fig. 1

1.51, whereas the second comprises UK-shoshonites (K_2O/Na_2O ratio between 3.44 and 5.5) from Demir Kapia, UK-latites (K_2O/Na_2O ratio between 1.97 and 2.09) from Gradishte and phonotephrites (UK-SLP with K_2O/Na_2O ratio between 1.98 and 3.04) from the other areas. The latites show a relatively homogeneous composition and are characterized by higher SiO_2, Al_2O_3 and Na_2O and lower MgO, CaO, FeO_{tot}, TiO_2 and K_2O contents in respect to ultrapotassic rocks. The latter exhibit a good negative correlation between MgO and Al_2O_3 and positive between FeO_{tot} and CaO. Alkalis display a different behaviour in the plot MgO vs. alkali element: in fact Na_2O shows a fairly good negative correlation (r=0.74), whereas K_2O is poorly positively correlated.

Petrographically (Table 1) the studied rocks exhibit a texture ranging from slightly porphyritic to subaphyric with a phenocryst assemblage constituted by Mg-rich olivine (up to Fo_{93}) and clinopyroxene of diopside or augite composition in variable amount, associated with minor phlogopite or Mg-rich biotite (f.i. in Ejovo Brdo). The olivine is normally zoned, sometimes with relatively large difference in FeO content of the crystal core and periphery as in UK-shoshonites and UK-latites (Table 1). The clinopyroxene have low Na_2O, Al_2O_3 and TiO_2 contents typical of orogenic volcanics [10]. The micas are largely opacitized. They are locally Ba and Ti-rich and Si-poor with a composition close to the kinoshitalite end-member, as in Ejovo Brdo (BaO~8.2%; TiO_2 ~11.4%) which is typical of the lamproites [11] and kimberlites [12,13]. Generally, the micas display tetrahedral site deficiency also typical of the mica of lamproites [14]. The groundmass of latites is microlitic with microlites of Na-sanidine, clinopyroxene and phlogopite; the groundmass of UK rocks consists in poikilitic sanidine (Or~98) or Na-sanidine and/or anorthose with microlites of the same phases present as phenocrysts + apatite, and Ti-magnetite. Carbonates with clinopyroxene microlites are also observed in some phonotephrites (Ejovo Brdo and Kishino). Leucite is sporadically present in microphenocrysts or more often in the groundmass mainly of the shoshonites and phonotephrites. The microphenocrysts often contain rings of fluid inclusions; in some cases they are deeply transformed in analcime as in Kishino sample. The phonotephrites of Ejovo Brdo are cut by pegmatitic veins (large up to 5-6 mm), constituted by olivine, alkali feldspars with Fe-dendrites, mica, apatite and Ti-magnetite.

Trace element abundance (Fig. 3) of 7 selected samples has been performed by ICP-MS analysis. The two groups distinguished on the basis of major elements, and they exhibit divergent trends: in fact, the UK-SLP and LG rocks show negative and positive trends, respectively, for La, Sr, Rb and Ba. Nb and Ta define a negative correlation in both groups, with a significantly better marked slope in UK-SLP rocks. The trace element variations observed in the latter group may be ascribed mainly to crystal fractionation process involving the phases present as phenocrysts (olivine and clinopyroxene) as supported also by Ni and Cr decreasing with evolution degree and by major element distribution. The trend observed in latites

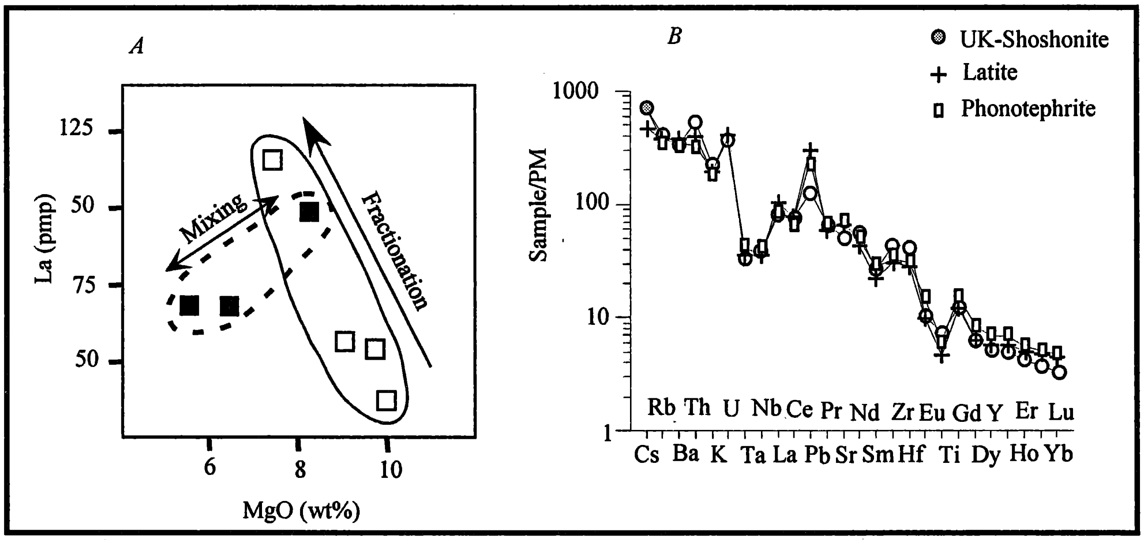

Fig. 3. *A*: La vs. MgO diagram for selected KMR samples. Filled and open symbols represent UK-SLP and LG rocks, respectively. *B*: Primordial mantle (PM [15]) normalized trace element concentration of selected KMR samples

is more difficult to be explained. The general decrease of all incompatible elements, both LILE and HFSE, suggests that fractional crystallization is not responsible for the observed variations. Two main hypotheses can be suggested: i) contamination with crustal material, ii) mixing between magma of UK-SLP trend with latite having relatively low MgO content (double arrow in Fig. 3*A*). The second hypothesis is preferred because the latite with lowest MgO content is characterized also by the lowest $^{87}Sr/^{86}Sr$ and highest $^{143}Nd/^{144}Nd$ ratios, which is exactly the contrary of what we would expect in case of a crustal contamination process (Djurishte, sample n°5: MgO=6.40%, $^{87}Sr/^{86}Sr$=0.708179, $^{143}Nd/^{144}Nd$=0.512394; Gradishte sample n°3: MgO=8.22% ; $^{87}Sr/^{86}Sr$=0.710404, $^{143}Nd/^{144}Nd$ =0.512149).

The overall distribution of trace element is depicted in Fig. 3B. All analysed samples show similar profiles, characterized by significant enrichment of LILE relative to HFSE; furthermore, they exhibit a marked negative anomaly in Ta, Nb and Ti and a relative enrichment in Pb and, to a lesser extent, in Zr and Hf. These features are generally considered as an orogenic signature, and interpreted as an effect of subduction component metasomatizing a mantle source.

As far as Sr and Nd isotopic compositions are concerned, we note that the obtained values are generally high and low respectively, falling in the field commonly associated

Table 1

Summary of petrographic and mineralogical features of Late Miocene-Pliocene K-alkaline volcanic rocks in Macedonia

Locality	Rock type	Texture	Phenocrysts	Microlites & Groundmass (Gm)
Demir Kapia area: Koreshnichka Krsta	UK-shoshonite (Roman Type affinity) $Mg^{\#}$ ~78; Ni 131 ppm SiO_2 49.2-50.9%; norm. ne 1.5-5.5	porphyric; Gm-poikilitic	Ol (Fo 78-90) Cpx (Wo45-46En46-50) Phl ($Mg^{\#}$ 74-78; BaO~4%) Lc (micropheno. with many inclus.)	Phl Cpx (Wo44En49) Ti-mg, Ap Gm: San (Or59-74Ab25-39)
Shtip area: Ejovo Brdo	phonotephrite (Roman Type affinity) $Mg^{\#}$ 71.7-73.5; Ni 146 ppm SiO_2 46.1-47%; norm. lc 0.9-6.6	microporphyric Gm-poikilitic	Ol (Fo 68-83) diopside (~Wo48En40) Mg-rich biotite ($Mg^{\#}$ 72-76; BaO~2.7-8.2%) Lc (micropheno.)	Cpx (Wo46-47En42-45) Bi ($Mg^{\#}$ 67; BaO~8.2%; TiO_2~11.4%) Ti-mg, Ap, Lc Gm: San (Or~98), Anorth (Or8-29Ab56-70)
Sveti Nikole area: Djurishte	latite $Mg^{\#}$ 72.2-75.2; Ni 132-134 ppm SiO_2 54.3-55.8%; norm. ne 0.3-1.8 or hy 0.8	porphyritic; Gm-trachytic	Ol (Fo 80-88) Cpx (Wo42-46En40-50) Phl ($Mg^{\#}$ 82-85)	Cpx (Wo41-45En45-49) Phl ($Mg^{\#}$ 82-83) Ap, Ti-mg, Ilm Na-San (Or35-51Ab43-55)
Gradishte	latite & UK-latite (Roman Type affinity) $Mg^{\#}$ 74.1-77.7; Ni 243 ppm SiO_2 53.8-54.1; norm. ne 0.6-1.7	porphyritic; Gm-trachytic	Ol (Fo 79-93) Cpx (Wo41-44En44-49) Phl ($Mg^{\#}$ 92)	Cpx (Wo41En49) Phl, Ti-mg Na-San (Or48-50Ab39-45)
Kishino	phonotephrite $Mg^{\#}$ 73; Ni 98 ppm SiO_2 46.7; norm. lc 5.7	porphyric; Gm-poikilitic	Ol (Fo 61-77) diopside (~Wo48En41) Phl, Lc (micropheno.)	San, Cpx, Lc (analcimized) Ap, Ti-mg Gm: Na-San (?)
Kumanovo area: Malo Nagorichane	phonotephrite (Roman Type affinity) $Mg^{\#}$ 76.9-78.2; Ni 235 ppm SiO_2 49.6-50.7; norm. ne 8-11; lc1.0	porphyric; Gm-poikilitic	Ol (Fo 81-84.5) Cr-diopside (~Wo47En48, Cr_2O_3 ~0.5%) Phl ($Mg^{\#}$ 78)	Lc, Cpx, Ti-mg Gm: Na-San (?)

$Mg^{\#}$ calculated with Fe^{2+}/Fe^{3+} atomic ratio according to [14] with crustal rocks (UK-SLP: $^{87}Sr/^{86}Sr$=0.708693-0.710404, $^{143}Nd/^{144}Nd$=0.512149-0.512359; LG: $^{87}Sr/^{86}Sr$=0.708179, $^{143}Nd/^{144}Nd$=0.512394). However, the relatively high content of Sr and Nd in MgO-rich rocks (Sr 1050-1300 ppm; Nd 45-70 ppm for MgO>9%) indicates that crustal contamination process, if any, had a minor role in the geochemical characterization of the most primitive magmas. Thus, we conclude that the peculiar isotopic composition of KMR supports the geochemical signature of a mantle metasomatized by subduction-collision processes.

Geodynamic significance. Widespread extension developed in the Dinarides-Hellenides-Taurides orogen was possibly related to the faster advancement toward southwest of the European plate over Africa with respect to the velocity of the Anatolian plate. This extension determined the lower topography of the orogen with respect to adjacent belts such as the Alps and the Zagros, or the Himalayas. In the Balkans, in the Rhodopes, and in the Serbo-Macedonian massifs, structural and stratigraphic data indicate interplay of the compressional and extensional tectonics [16]. The climax of the magmatism here reported corresponds to the Miocene stage of the subduction process, and the so-called later anomalous "backarc" extension: this tectonic evolution from compression to extension in the hangingwall plate is possibly responsible for the transition from calc-alkaline to alkaline magmatic signatures.

REFERENCES

[1] Prelević D., S. Foley, V. Cvetković, M. Jovanović, S. Melzer. Acta Vulcanol., **13**, 2001, No 1-2, 101–115. [2] Pamić J., D. Balen. Ibid., **13**, 2001, No 1-2, 9–24. [3] Le Maitre R. W. (ed.) A Classification of Igneous Rocks and Glossary of Terms. Oxford, Blackwell Sci. Public., 1989, 193 pp. [4] Boev B., Y. Yanev. Acta Vulcanol., **13**, 2001, No 1-2, 57–72. [5] Kolios N., F. Innocenti, P. Manetti, A. Peccerillo, O. Giuliani. Bull. Volcanol., **1** , 1980, 3–43. [6] Sveshnikova E. V., M. Terzić, I. P. Laputina. In: Peculiarities of the Rock Forming Minerals of the Magmatic Rocks. Moscow, Nauka, 1986, 165–192 (in Russian). [7] Terzić M., E. V. Sveshnikova. In: Sbornik Serb. Acad. Nauki, Belgrade, **3**, 1986, 283–288 (in Serbo-Croatian with English abstract). [8] Kononova V. A., M. Terzić, E. V. Sveshnikova. Macedon. Acad. Sci. and Arts, Skopje, 1989, 29–44 (in Russian). [9] Foley S. F., G. Venturelli, D. H. Green, L. Toscani. Earth Sci. Rev., **24**, 1987, 81–134. [10] Harangi Sz., M. Wilson, S. Tonarini. Acta Vulcanol., **7**, 1995, No 2, 125–134. [11] Edgar A. D. Eur. J. Mineral., **4**, 1992, 321–330. [12] Mitchell R. H. Kimberlites, Orangeites and Related rocks. New York, Plenum, 1995, 410 p. [13] O'Brien H. F., M. Tyni. Proceed. 7th Intern. Kimberlite Conf., 1999, 625–636. [14] Bergman S. C. In: Alkaline Igneous Rocks, Geol. Soc. Spec. Publ., 1987, 103–190. [15] McDonough W. F., S.-S. Sun. Chem. Geol., **120**, 1995, 223–253. [16] Doglioni C., S. Agostini, M. Crespi, F. Innocenti, P. Manetti, F., Riguzzi, Y. Savascin. J. Virtual Explorer, **7**, 2002, 117–131.

Geological Institute
Bulgarian Academy of Sciences
1113 Sofia , Bulgaria
e-mail: yotzo@geology.bas.bg

**St. Ciril and Metodii University*
Faculty of Mining and Geology
Shtip, Republic of Macedonia
e-mail: bboev@rgf.ukim.edu.mk

***Dipartimento di Scienze della Terra*
00185 Roma, Italy
e-mail: carlo.doglioni@uniroma1.it

****Dipartimento di Scienze della Terra & IGG, CNR*
50126 Pisa, Italy
e-mail: innocen@dst.unipi.it

*****Istituto di Geoscienze e Georisorse*
56124 Pisa, Italy
e-mail: manetti@cesit1.unifi.it