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# Mineralogy of the Plio-Pleistocene potassic and ultrapotassic volcanic rocks from the Republic of Macedonia

*Yotzo Yanev, Blazo Boev, Piero Manetti, Rositsa Ivanova, Massimo D'Orazio, Fabrizio Innocenti*

**Abstract**. Ultra- to high potassic volcanic rocks of Plio-Pleistocene age (3.24-1.47 Ma) crop out in the Vardar zone. On the basis of chemical composition, they are classified as phonotephrites to ultrapotassic shoshonites and latites, including also high-Mg latites. They contain pheno- and microphenocrysts of olivine, clinopyroxene, phlogopite, ± leucite. The groundmass consists of poikilitic Ba-Na sanidine and Ba-Ti phlogopite, ± Sr-rich oligoclase (up to 3 wt.% SrO), anorthoclase and Mg-bearing calcite, all enclosing microlites of clinopyroxene, phlogopite, Ti-magnetite, ± leucite. The olivine phenocrysts are zoned, forsterite-rich (up to Fo 93), and display a positive correlation between Fo component and NiO and negative one between the same component and MnO. The clinopyroxenes are diopside-augites, and some of them are rich in Al (up to 5.4 wt.% $Al_2O_3$), which correlates positively with Ti. On the other hand, Ti correlates negatively with $Mg^{\#}$ and Si. The micas are essentially phlogopites rich in Ti (up to 12 wt.% $TiO_2$). In some localities they are also highly enriched in Ba (up to 8.3 wt.% BaO) approaching to the Ti-kinoshitalite composition. Ba in micas correlates positively with Ti and Al, but negatively with K, $Mg^{\#}$ as well as with Si. A positive correlation between Ba and Sr and negative one between Ba and Si/Al ratio is observed in both sanidine and plagioclase. The leucite microphenocrysts are sometimes replaced by Na-sanidine, zeolites (laumontite, phillipsite, etc.) and clays or by nepheline and amorphous nephelinic masses. The obtained mineralogical features of the Macedonian ultrapotassic rocks assign them to the Roman Province Type rocks.

*Key words:* Macedonia, ultrapotassic rocks, clinopyroxene, Ba-Ti phlogopite, Ba-Sr feldspars

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**Йоцо Янев, Блажо Боев, Пиеро Манетти, Росица Иванова, Масимо Д'Орацио, Фабрицио Инночепти. Минералогия на плио-плейстоценските високо- и ултракалиеви вулканити в Република Македония**

**Резюме.** Плио-плейстоценските (3,24-1,47 Ma) високо- и ултракалиеви вулканити се разкриват във Вардарската зона. Според химическия си състав те са фонотефрити до ултракалиеви шошонити и латити, включвайки също така и високо-Mg латити. Вулканитите съдържат фено- и микрофенокристали от оливин, клинопироксен, флогопит, ± левцит. Матриксът е съставен от пойкилитен Ba-Na санидин и Ba-Ti флогопит, ± Sr-съдържащ олигоклаз (SrO до 3 wt.%), анортоклаз и Mg-съдържащ

калцит. Всичките те включват микролити от клинопироксен, флогопит, Ti-магнетит, ± левцит. Оливините са зонални, богати на форстеритова молекула (до Fo 93) и показват положителна корелация между Fo компонент и NiO и отрицателна – с MnO съдържание. Клинопироксените са диопсид-авгити, някои богати на Al (до 5,4 wt.% $Al_2O_3$), който корелира положително с Ti. От друга страна Ti корелира отрицателно с $Mg^{\#}$ и Si. Слюдите са почти изключително с флогопитов състав, богати на Ti (до 12 wt.% $TiO_2$). В някои находища те имат и високи Ba съдържания (до 8,3 wt.% BaO), приближавайки се до състава на Ti-киношиталит. Ba в слюдите корелира положително с Ti и Al, а отрицателно с K, $Mg^{\#}$ и Si. В санидините и плагиоклазите е установена положителна корелация между Ba и Sr и отрицателна между Ba и Si/Al отношение. Левцитовите микрофенокристали на места са заместени от Na-санидин, зеолити (ломонтит, филипсит и др.) и глини или от нефелин и аморфна нефелинова маса. Получените минераложки характеристики на македонските ултракалиеви вулканити ги отнасят към типа ултракалиеви скали от Романската провинция.

## Introduction

The widespread occurrence of Cenozoic ultrapotassic (UK) volcanism in the Mediterranean part of the Alpine system had given a reason to Niggli (1920) to distinguish a Mediterranean potassium magmatic suite. This volcanic activity takes place in distinct areas of the Alpine folded belt e.g. in Spain, Corsica, Western Alps, Central Italy, Central and Southern Serbia, Macedonia, Southern Bulgaria and Western Turkey (Fig. 1 and references therein). Na-alkaline volcanism also

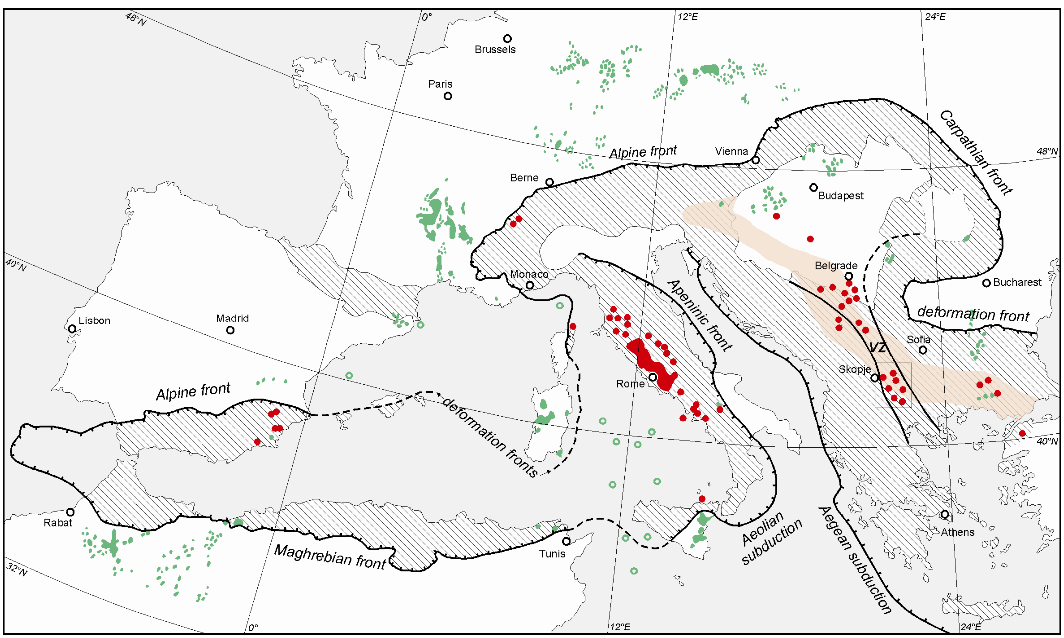



Fig. 1. Distribution of the Cenozoic ultrapotassic volcanic rocks (red) and Na-alkaline ones (green) with related rocks in the Alpine system (hachured, according to the European Tectonic Map 1984), its foreland and the rifting sea zones (green circles – Na-alkaline volcanic rocks from deep drilling). The tectonic fronts are after Cavazza et al. (2004). The location of the ultrapotassic rocks is according to Savelli (2002 and references therein), Serri et al. (1993 and references therein), Prelević et al. (2007 and references therein), Harangi (2001a) and authors' data (for the Eastern Rhodopes). Na-alkaline rocks are reported according to Kononova et al. (1985 and references therein), Savelli (2002 and references therein) and Harangi (2001b). In beige – the Paleogene to Miocene calc alkaline and shoshonitic volcanic belt. The area of the studied rocks in Macedonia is marked by a black square; (VZ) Vardar zone

occurs, but it is spatially clearly separated from the K-alkaline one. Na-alkaline volcanism is found in the Alpine foreland only and in some extensional areas located in the central parts of the Alpine system as the Pannonian, Tyrrhenian, Liguro-Provencal and Valencia Basins (see Savelli 2002 and references therein). Only in separate places as in Eastern Rhodopes (Marchev et al. 1998), Western Anatolia (Agostini et al. 2005) and others Na-alkaline and ultrapotassic volcanism overlap spatially, though they were active in different times.

This paper describes the mineralogical data obtained on ultra- and high potassic rocks erupted since the Pliocene to Pleistocene in the area located from the Scutari-Peć fault zone down to Macedonia. The area where K-alkaline volcanism took place belongs to a Cenosoic NNW-SSE volcanic belt (Fig. 1), developed in the central part of the Balkan Peninsula mainly on the Vardar Zone. It can be assumed that this belt continues to the north in South Hungary where two localities of ultrapotassic volcanic rocks are known – Balatonmária (in borehole) and Bár (Harangi 2001a). The Vardar volcanic belt cuts obliquely a NW-SE trending belt of orogenic Paleogene to Miocene calc alkaline and shoshonitic volcanism extending from SE Austria to NW Turkey longer than 1300 km (Yanev 2003).

The following Cenozoic ultra- and high potassic magmatic occurrences, listed from north to south, are included in Vardar volcanic belt (Fig. 2):

- Central Serbia, around the Zvornik tectonic line: the ultrapotassic rocks of Avala, Aranjelovac, Rudnik, Borač, Zabrdica, Mionica, Boljkovac, and Veliki Majdan – Early Oligocene to Early Miocene in age (from 33.5 to 22.7 Ma – Prelević et al. 2001; Cvetković et al. 2004);
- Southern Serbia: ultrapotassic rocks of Golija, Klinovac, Koritnik, and high potassic rocks of Nova Varoš, Trijebine, Krkina Cuka, Ugljarski Krš, Vrelo, and Novi Pazar – Oligocene to Late Miocene in age (from 32.7 to 9.1 Ma – Prelević et al. 2001; Cvetković et al. 2004);
- Southernmost Serbia (Cvetković et al. 2004), Macedonia (Yanev et al., in press) and northernmost Greece manifested south of Scutari-Peć transverse fault zone (Kissel et al. 1995):

1) Miocene to Pliocene:
– Devaje (21.8 Ma) and Slavujevci (6.57 Ma) in southernmost Serbia,
– Kožuf/Voras Massif (6.5–1.8 Ma) in southernmost Macedonia and northernmost Greece (Kolios et al. 1980; Boev et al. 1997; Boev & Yanev 2003);

2) Pliocene:
– Cer in southernmost Serbia (3.86 Ma),
– Mlado Nagorichane (near Kumanovo town, 1.81±0.07 Ma),
– Djurishte (near Sveti Nikole town, 3.19±0.12 Ma),
– Ejevo Brdo (near Shtip town, 3.24±0.11 Ma),
– Kureshnichka Krasta (near Demir Kapia town, 2.04±0.10 Ma);

3) Pleistocene:
– Gradishte (near Sveti Nikole town, 1.70±0.08 Ma),
– Kishino (near Veles town, 1.47±0.09 Ma).

These radiometric data (Z. Pecskay in: Yanev et al., in press) demonstrate that the Macedonian ultra- to high potassic volcanism took place about 20 Ma after the end of the orogenic calc alkaline to shoshonitic volcanism (Boev & Yanev 2003 with references therein).

The recentmost volcanic centers form an N-S alignment extending from M. Nagorichane (1.81 Ma) to the north to Kishino (1.47 Ma) and Kožuf/Voras Massif (up to 1.8 Ma) to the south, parallel to the axis of a minimum in the Moho discontinuity (Fig. 2).

The Macedonian Plio-Pleistocene ultra- to high potassic volcanic rocks listed above (except Nikushtak, Ostrovitsa, both situated near Skopje and Kumanovo, and Malino situated near Djurishte) are the object of this study. Their petrologic features are studied by Kononova et al. (1989) and the mineralogy of

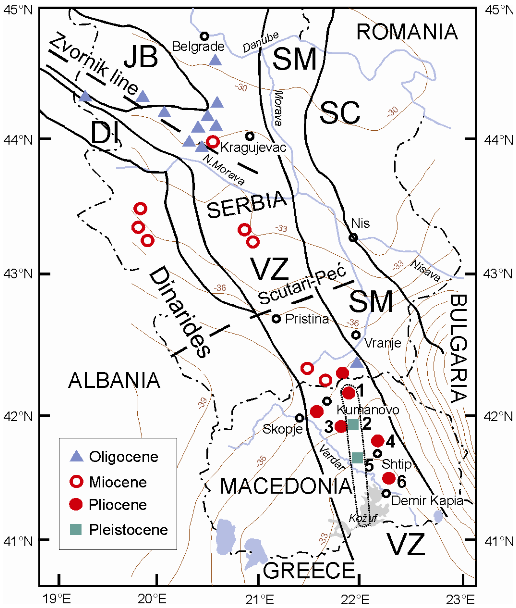



Fig. 2. Map of the localities and age distribution (Altherr et al. 2004; Cvetković et al. 2004 and Yanev et al., in press) of the Vardar ultra- to high potassic zone: (1) Mlado Nagorichane (1.81±0.07 Ma), (2) Gradishte (1.70±0.08 Ma), (3) Djurishte (3.19±0.12 Ma), (4) Ejevo Brdo (3.24±0.11 Ma), (5) Kishino (1.47±0.09 Ma), and (6) Kureshnichka Krasta (2.04±0.10 Ma). The recentmost volcanic centers are contoured by a dotted line. Kožuf/Voras volcano (6.5–1.8 Ma) with shoshonitic to trachy-rhyolitic composition is shown for comparison. Thin brown lines represent the depth of Moho discontinuity in km from the sea-level (Boykova 1999). Tectonic units: (JB) Jadar block; (DI) Drina-Ivanjica unit; (VZ) Vardar zone; (SM) Serbo-Macedonian massif; (SC) South Carpathian belt

the ultrapotassic rocks of M. Nagorichane, E. Brdo and K. Krasta only – by Sveshnikova et al. (1986). All these features are summarized in the review paper of Boev & Yanev (2001 and references therein). Yanev et al. (2003, 2006) presented new preliminary petrological, mineralogical and geochemical data. These papers evidenced the relatively primitive character of the rocks characterized with high $Mg^{\#}$ (>70) and high Ni and Cr contents (100–250 ppm and 170–420 ppm respectively). Altherr et al. (2004) also presented new mineralogical (regarding the phlogopite only), geochemical and isotope data, proposing an origin from earlier metasomatized mantle by subduction-collision processes. Božović et al. (2005) reported some preliminary data on the mineralogical composition of one locality (E. Brdo). Both petrochemical (including isotopes) and age characteristic of these rocks, together with a genetic and geodynamic model, have been recently presented in a companion paper (Yanev et al., in press).

The aim of this paper is to complete the mineralogical characteristics of the ultra- to high potassic volcanic rocks of Macedonia as well as to report some geothermobarometric data.

## Methods

The electron microprobe analyses have been performed at Istituto di Geoscienze e Georisorse (IGG-CNR) section of Florence using a Jeol 870 JXA-8600 instrument equipped with four wavelength-dispersion spectrometers and integrated with an energy-dispersion spectrometry system, with 15kV accelerating voltage and 10nA beam current. Variable counting times have been used in order to avoid alkali loss during the analytical routine and to improve the statistics for minor and trace elements. The data were corrected using the Bence & Albee (1968) and Albee & Ray (1970) methods. Accuracy and precision were evaluated using international reference samples as unknowns; the bias was smaller than 5% for major and minor elements.

A minor set of analyses has been performed at Geological Institute, Sofia (analyst Tz. Ilyev) using the Jeol 733 Superprobe equipped with EDS (with ZAF corrections): 15 kV accelerating voltage, 1 nA beam current and a beam 5 μm (standards: synthetic crystals of albite, K-feldspar, apatite, MgO, $Al_2O_3$, $SiO_2$, $TiO_2$, $BaF_2$, $Fe_2O_3$ and Cr pure metal).

In total a set of 210 microprobe analyses is used in this study.

## Petrochemical characteristics

The major variations in chemical composition of the studied rocks pertain to $SiO_2$ values, whereas the alkali contents are almost constant (Fig. 3). According to these parameters, two types of rocks are presented in both age groups (Yanev et al., in press; Table 1):

- Saturated (shoshonitic) – a differentiated series from shoshonite (some samples of Djurishte and K. Krasta), latite (Gradishte and Djurishte) to trachyte (Nikushtak, Ostrovitsa – Altherr at al. 2004);
- Undersaturated (alkaline) – phonotephrite (E. Brdo, Kishino, M. Nagorichane, Malino, and some samples of K. Krasta).

The major part of the studied volcanic rocks (all phonotephrites, some shoshonites and latites) has ultrapotassic character according to the criteria of Foley et al. (1984): $K_2O$>3 wt.%, $K_2O/Na_2O$>2 wt.%, and MgO>3 wt.% (Table 1). However, the alteration of the potassium-bearing minerals (especially leucite) in the rocks of some localities lowers the primary alkali ratio a bit below 2.

The non-ultrapotassic latite of Djurishte is also object of this paper because similarly to the UK-latite of Gradishte it has unusually high Mg content > 5 wt.% (Yanev et al., in press), due to the presence of very rich in Mg minerals as forsterite and phlogopite.

Foley et al. (1987) divided the ultrapotassic rocks according to their Al, Si, and Ca contents or K/Na ratio into 4 groups: lamproites, kamafugites, Roman Province type rocks, and one transitional group. On some of the discrimination diagrams proposed by these authors (Fig. 4), the Macedonian ultrapotassic rocks fall in the field of Roman Province Type, but on others they plot between the fields of lamproites and the rocks of Roman Province Type. Nevertheless Altherr at al. (2004), Božović et al. (2005), and Prelević et al. (2007) considered the Macedonian ultrapotassic rocks as lamproites. In this case, following the recommendation of the IUGS Subcommission on the Systematics of Igneous Rocks (Le Maitre 1989), only the mineralogical composition can provide the necessary information to reveal their real nature and to precise their name.

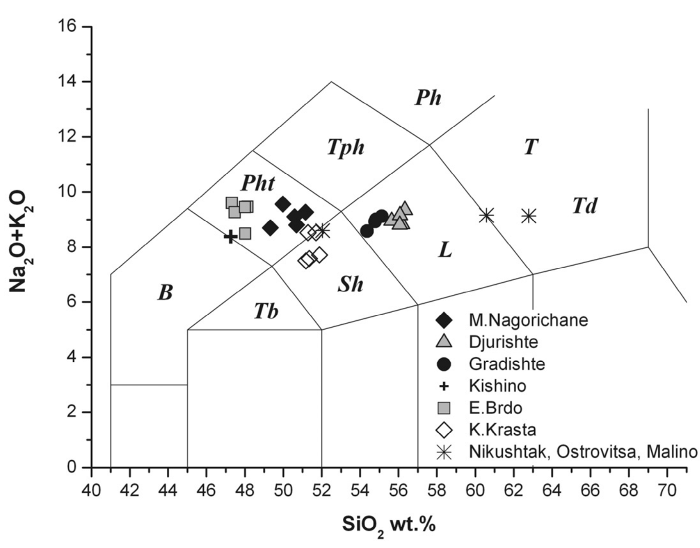



Fig. 3. TAS diagram (Le Maitre 1989) for the Plio-Pleistocene ultra- to high potassic volcanic rocks from Macedonia (authors' data from Table 1 and Altherr et al. 2004):
(*Tb*) trachybasalt;
(*Sh)* shoshonite;
(*L)* latite;
(*T)* trachyte;
(*Td)* trachydacite;
(*B)* basanite;
(*Pht)* phonotephrite;
(*Tph)* tephrophonolite
and (*Ph)* phonolite

Table 1. *Chemical composition and CIPW norms of the Macedonian ultrapotassic and high-Mg potassic rocks*

| Locality | Mlado Nagorichane | | Djurishte | | | | | Gradishte | | | Kishino | Ejevo Brdo | | | | Kureshnichka Krasta | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample number | MN13* | MN14 | GU 3 | GU 4 | GU 5* | MN10 | MN11* | GR 2 | GR 3* | MN12 | MN 9* | EB 2 | MN5 | MN6* | MN7 | K 01* | K 06 | MN2 | MN1 |
| Rock type | phonotephrite | | high-Mg latite | | | | | UK-latite | | | phono-tephrite | phonotephrite | | | | UK-shoshonite | | | phono-tephrite |
| $SiO_2$ | 49.62 | 50.70 | 54.93 | 54.55 | 55.27 | 54.27 | 55.83 | 53.93 | 53.79 | 54.13 | 46.69 | 46.36 | 46.13 | 46.36 | 46.99 | 50.87 | 49.23 | 50.07 | 50.15 |
| $TiO_2$ | 1.16 | 1.13 | 0.90 | 0.91 | 0.94 | 0.88 | 0.92 | 1.19 | 1.15 | 1.18 | 1.23 | 2.19 | 2.22 | 2.24 | 2.39 | 1.47 | 1.34 | 1.42 | 1.45 |
| $Al_2O_3$ | 12.25 | 12.63 | 14.56 | 14.25 | 14.70 | 14.46 | 15.19 | 13.11 | 12.81 | 13.28 | 13.05 | 14.14 | 14.27 | 14.17 | 13.87 | 11.39 | 10.79 | 11.41 | 11.37 |
| $Fe_2O_3$** | t7.24 | t7.17 | 3.69 | 3.95 | 2.49 | t5.47 | t5.72 | 5.30 | 2.25 | t6.58 | t8.71 | 4.40 | t7.60 | t7.53 | t7.34 | 2.58 | 3.97 | t7.17 | t7.09 |
| FeO | n.d. | n.d. | 1.75 | 1.42 | 2.87 | n.d. | n.d. | 1.09 | 3.70 | n.d. | n.d. | 2.90 | n.d. | n.d. | n.d. | 4.13 | 2.65 | n.d. | n.d. |
| MnO | 0.12 | 0.12 | 0.10 | 0.10 | 0.11 | 0.11 | 0.11 | 0.12 | 0.12 | 0.12 | 0.15 | 0.12 | 0.12 | 0.12 | 0.11 | 0.11 | 0.11 | 0.12 | 0.11 |
| MgO | 9.95 | 9.14 | 5.43 | 5.78 | 6.40 | 5.30 | 5.51 | 6.91 | 8.22 | 7.41 | 9.04 | 7.92 | 7.4 | 7.76 | 7.83 | 9.71 | 9.34 | 9.88 | 9.47 |
| CaO | 7.80 | 7.55 | 6.00 | 6.61 | 6.18 | 7.28 | 6.08 | 6.28 | 6.26 | 6.28 | 10.00 | 8.82 | 8.71 | 8.75 | 8.13 | 8.91 | 10.28 | 8.66 | 8.43 |
| $Na_2O$ | 2.35 | 2.43 | 3.76 | 3.41 | 3.57 | 3.53 | 3.71 | 3.00 | 2.86 | 2.88 | 2.78 | 2.08 | 2.98 | 2.72 | 2.59 | 1.49 | 1.11 | 1.34 | 1.88 |
| $K_2O$ | 7.14 | 6.76 | 5.35 | 5.16 | 5.29 | 5.20 | 5.41 | 5.92 | 5.98 | 5.93 | 5.50 | 6.11 | 6.38 | 6.32 | 6.64 | 6.07 | 6.11 | 6.05 | 6.46 |
| $P_2O_5$ | 1.65 | 1.48 | 1.05 | 0.96 | 0.99 | 1.03 | 1.09 | 0.97 | 0.97 | 1.02 | 1.62 | 1.50 | 1.67 | 1.69 | 1.73 | 1.33 | 1.28 | 1.40 | 1.42 |
| L.O.I. | 0.55 | 0.60 | 0.84 | 2.42 | 0.57 | 2.90 | 0.68 | 1.29 | 0.83 | 0.63 | 1.03 | 2.37 | 1.21 | 1.25 | 1.31 | 2.88 | 4.68 | 2.60 | 2.33 |
| Total | 99.83 | 99.71 | 98.36 | 99.52 | 99.38 | 100.43 | 100.25 | 99.11 | 98.94 | 99.44 | 99.80 | 98.91 | 98.69 | 98.91 | 98.93 | 100.94 | 100.89 | 100.12 | 100.16 |
| $K_2O/Na_2O$ | 3.0 | 2. 8 | 1.4 | 1.5 | 1.5 | 1.5 | 1.5 | 2.0 | 2.1 | 2.1 | 2.0 | 2.9 | 2.1 | 2.3 | 2. 6 | 4.1 | 5.5 | 4.5 | 3.4 |
| or | 40.91 | 39.95 | 31.61 | 30.49 | 31.26 | 30.73 | 31.97 | 34.98 | 35.34 | 35.04 | 25.20 | 35.02 | 29.27 | 31.61 | 37.77 | 35.87 | 36.11 | 35.75 | 38.17 |
| ab | 0.00 | 5.59 | 30.45 | 28.85 | 29.68 | 26.63 | 31.39 | 23.27 | 21.13 | 23.28 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 8.92 | 2.22 | 8.66 | 5.65 |
| an | 1.79 | 3.59 | 7.05 | 8.34 | 8.46 | 8.25 | 8.82 | 4.82 | 4.45 | 5.79 | 6.89 | 11.20 | 6.72 | 7.79 | 6.61 | 6.46 | 6.41 | 7.25 | 3.51 |
| ne | 10.77 | 8.11 | 0.74 | 0.00 | 0.29 | 1.75 | 0.00 | 1.14 | 1.67 | 0.59 | 12.74 | 9.53 | 13.66 | 12.47 | 11.87 | 2.00 | 3.88 | 1.45 | 5.56 |
| lc | 1.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 5.72 | 0.85 | 6.61 | 4.49 | 1.15 | 0.00 | 0.00 | 0.00 | 0.00 |
| di | 20.80 | 19.30 | 12.70 | 14.53 | 12.55 | 16.92 | 11.39 | 15.96 | 16.12 | 14.91 | 25.76 | 18.11 | 20.38 | 19.56 | 17.81 | 23.09 | 28.81 | 21.12 | 23.09 |
| hy | 0.00 | 0.00 | 0.00 | 0.75 | 0.00 | 0.00 | 0.08 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| ol | 14.91 | 13.97 | 8.44 | 7.81 | 10.22 | 6.68 | 9.03 | 10.27 | 12.48 | 11.58 | 12.68 | 11.28 | 9.53 | 10.38 | 10.76 | 13.27 | 10.63 | 14.31 | 12.81 |
| mt | 2.51 | 2.49 | 2.16 | 2.12 | 2.18 | 2.10 | 2.19 | 2.50 | 2.44 | 2.52 | 3.02 | 2.65 | 2.64 | 2.61 | 2.55 | 2.49 | 2.40 | 2.49 | 2.46 |
| il | 2.20 | 2.15 | 1.71 | 1.73 | 1.78 | 1.67 | 1.75 | 2.26 | 2.18 | 2.24 | 2.34 | 4.16 | 4.22 | 4.25 | 4.54 | 2.79 | 2.54 | 2.70 | 2.75 |
| ap | 3.82 | 3.43 | 2.43 | 2.22 | 2.29 | 2.39 | 2.53 | 2.25 | 2.25 | 2.36 | 3.75 | 3.48 | 3.87 | 3.92 | 4.01 | 3.08 | 2.97 | 3.24 | 3.29 |

*According to Yanev et al. (in press); **letter “t” indicates total Fe presented as $Fe_2O_3$

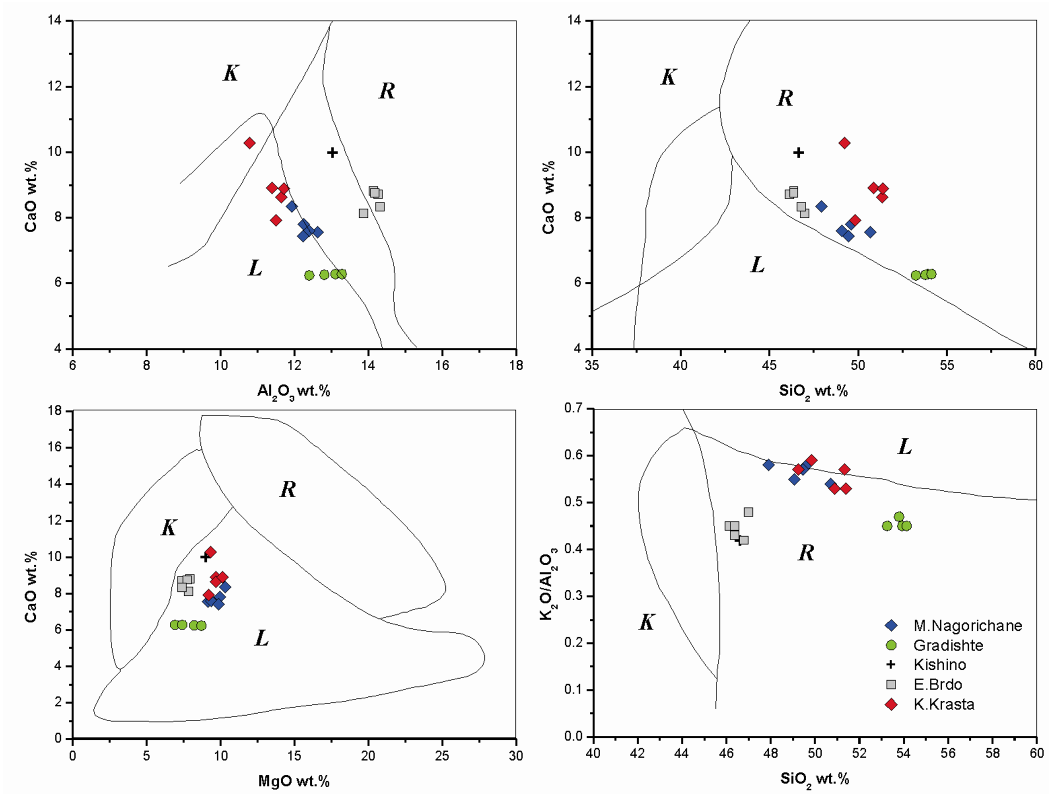



Fig. 4. Discrimination diagrams for ultrapotassic rocks (Foley et al. 1984) showing the data points of the Macedonian ultrapotassic rocks (authors' data from Table 1 and Altherr et al. 2004): *(L)* lamproites; *(K)* kamafugites and *(R)* Roman Province Type rocks

## Mineralogy

The studied volcanic rocks consist of phenocrysts, microphenocrysts and microlites in a crystallized groundmass. The summarized data on the mineralogy of the individual localities is presented in Table 2, and selected microprobe analyses – in the appendix tables.

The *phenocrysts* are of olivine, clinopyroxene (excepting in Kishino), phlogopite, and leucite (found in M. Nagorichane only). In some samples the phenocrysts form glomeroporphyritic aggregates. Altherr et al. (2004) indicated the presence of alkali amphibole in Malino and orthopyroxene in Nikushtak (these localities are not studied in our paper). The microphenocrysts are represented by the same mineral assemblage + Ti-magnetite (as well as ilmenite in Djurishte), ± anorthoclase and/or leucite.

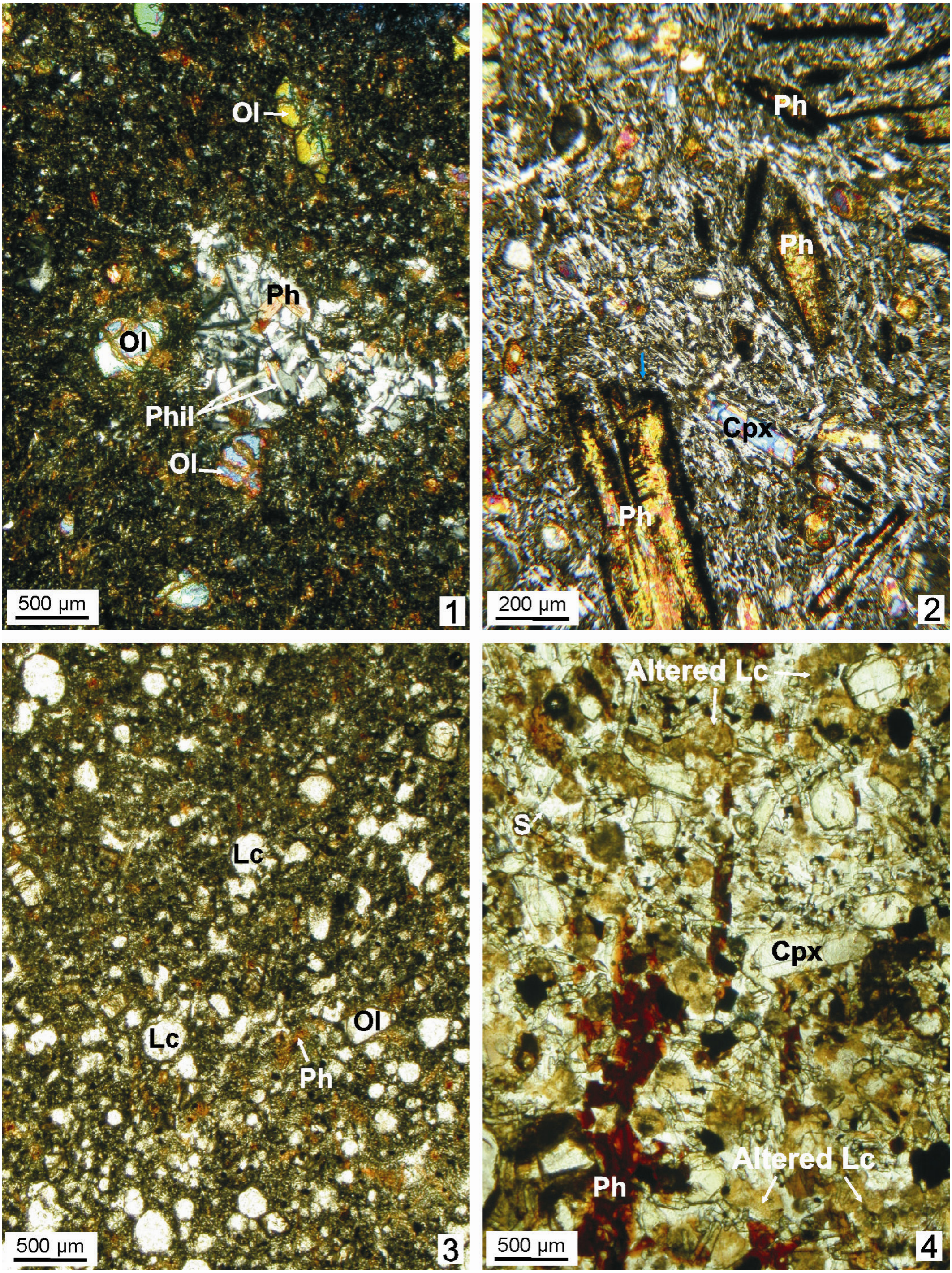
Up to 1 cm large phlogopite flakes are observed by Altherr et al. (2004) in all localities. These phlogopites are described as mantle xenocrysts based on their chemistry (Cr rich, Ti and Ba poor).

The *groundmass* of phonothephrites differs from that of high-Mg latites. The former (except Kishino phonotephrites) consists of poikilitic feldspar crystals (Fig. 5-5), phlogopite (Fig. 5-4) and sporadically calcite rich in Mg up to 5–7 wt.% $MgCO_3$ (in E. Brdo – Fig. 5-6, M. Nagorichane and Kishino). All groundmass minerals contain clinopyroxene, phlogopite to Mg-rich biotite, Ti-magnetite and

Table 2. *Mineralogical composition and petrochemical characteristics of the Macedonian ultrapotassic to high-Mg potassic rocks*

| Locality | Rock type | Texture | Phenocrysts | Groundmass (Gm) and microlites |
|---|---|---|---|---|
| Mlado Nagorichane | phonotephrite (Roman Type affinity) $Mg^{\#}$ 76.9-78.2; Ni 235 ppm $SiO_2$ 49.6-50.7 %; norm. Neph 8-11+Lc1.0 | porphyric; Gm – poikilitic | Ol ($Fo_{84-86.3}$); Cpx ($Wo_{45-47.7}En_{44.5-48.7}$); Lc (with cpx microlites) | Gm: Na-San ($Or_{51.6-66}Ab_{32-45.7}Cn_{0-9.6}$), Ba-Ti Phl ($Mg^{\#}$79-81; $TiO_2$ 9.6-10.2, BaO 3-5 wt.%). Microlites: Cpx ($Wo_{46.}En_{47}$), Ti-mg, Ap, Lc altered into zeolite or Na-San ($Or_{45-66}Ab_{32-50.4}$) |
| Djurishte | high-Mg latite $Mg^{\#}$ 72.2-75.2; Ni 132-134 ppm $SiO_2$ 54.3-55.8 wt.%; norm. Neph 0.3-1.8 or hy 0.8 | porphyric; Gm – poikilitic | Ol ($Fo_{80-88.6}$; NiO 0.1-0.2wt.%); Cpx ($Wo_{42.2-457}En_{39.6-50.6}$); Ti-Phl ($Mg^{\#}$82-85; $TiO_2$ 6.7-8, BaO 0.4-0.5 wt.%) | Microlites: Cpx ($Wo_{41-45}En_{45.8-49}$), Ti-Phl ($Mg^{\#}$83; $TiO_2$ 7.1-7.8 wt.%); Na-San ($Or_{43.4-49}Ab_{43-49.5}Cn_{0.7-1}$) to Anorth ($Or_{35.4-38}Ab_{54.4-55.4}Cn_1$), Ti-mg; Ilm; Ap |
| Gradishte | UK-latite to UK-shoshonite (Roman Type affinity) $Mg^{\#}$ 74.1-77.7; Ni 243 ppm $SiO_2$ 53.8-54.1 wt.%; norm. Neph 0.6-1.7 | porphyric; Gm – trachytic | Ol ($Fo_{78.8-93.4}$; NiO 0.2-0.6wt.%); Cpx ($Wo_{41-45}En_{41.2-49}$); Phl ($Mg^{\#}$92; $TiO_2$ 1.6-1.9, BaO 0.3 wt.%) | Microlites: Cpx ($Wo_{41.4}En_{49}$), Na-San ($Or_{47-51.3}Ab_{39-46.2}Cn_{1.1-4.5}$), Phl, Ti-mg, Ap |
| Kishino | phonotephrite (Roman Type affinity) $Mg^{\#}$ 73; Ni 98 ppm $SiO_2$ 46.7 wt.%; norm. Lc 5.7 | porphyric; Gm - microlitic | Ol ($Fo_{88-89.3}$); Lc microphenocrysts, partially altered into Neph ($Ab_{91.5}Or_8$) + zeolite | Microlites: Cpx ($Wo_{47}En_{42-45}$), Ol ($Fo_{87-89}$), Na-San ($Or_{56}Ab_{41}Cn_{0.7}$), Anorth ($Or_{39.8}Ab_{53.7}Cn_{4.1}$), Ti-Phl ($Mg^{\#}$85-86, $TiO_2$ 7.8-8.2, BaO~1.2 wt.%), Ti-mg, Ap, Carbonate in the Gm |
| Ejevo Brdo | phonotephrite (Roman Type affinity) $Mg^{\#}$ 71.7-73.5; Ni 146 ppm $SiO_2$ 46.1-47 wt.%; norm. Lc 0.9-6.6 | micro-porphyric; Gm – poikilitic | Ol ($Fo_{74.1-82.5}$; NiO 0.1-0.16 wt.%); Cpx ($Wo_{45.5-49.3}En_{39-46}$); microphenocrysts – Ba-Ti Phl ($Mg^{\#}$67-72; $TiO_2$~11, BaO~8.2 wt.%) | Gm: Sr-Ba Anorth ($Or_{19.7-29}Ab_{56-65.7}Cn_{0.2-6}$, Sr 0.25-3wt.%), Sr-Ba Pl ($An_{18.4-26}Or_{7.6-15.4}Cn_{0.7-3.7}$, Sr<2.7 wt.%), Ba-Ti Phl ($Mg^{\#}$67-76; $TiO_2$ ~6-12, BaO 0.15-7 wt.%), Na-San ($Or_{53.8}Ab_{43.7}Cn_{0.3}$), Mg-bearing carbonate. Microlites: Cpx ($Wo_{46-46.5}En_{41.5-45}$), Ba-Ti Phl ($Mg^{\#}$67-75; $TiO_2$ ~11-12, BaO 3.9-6.5 wt.%), Lc (with Cpx inclusion), Ti-mg, Ap |
| Kureshnichka Krasta | phonotephrite to UK-shoshonite (Roman Type affinity) $Mg^{\#}$ ~78; Ni 131 ppm $SiO_2$ 49.2-50.9 wt.%; norm. Neph 1.5-5.5 | porphyric; Gm – poikilitic | Ol ($Fo_{78.4-90.1}$; NiO 0.08-0.28 wt.%) Ba-Ti Phl ($Mg^{\#}$58-78; $TiO_2$ 6-9.7, BaO 0-4 wt.%), Cpx ($Wo_{45.5-45.8}En_{46.2-50}$) | Gm: San ($Or_{54-74}Ab_{25-44}Cn_{0.1-0.3}$), Ba-Ti Phl ($Mg^{\#}$74-78, $TiO_2$ 8.4-9.2, BaO 3.3-3.5%). Microlites: Cpx ($Wo_{44.2-47}En_{48.4-50}$), Ol ($Fo_{80}$), Lc (altered into zeolites+clays), Ti-mg, Ap |

Notes: $Mg^{\#}$ calculated with $Fe^{2+}/Fe^{3+}$ atomic ratio according to Bergman
Abbreviations: (Ol) olivine; (Cpx) clinopyroxene; (Phl) phlogopite; (San) sanidine; (Anorth) anorthoclase; (Lc) leucite; (Neph) nepheline; (Ti-mg) Ti-magnetite; (Ilm) ilmenite; (Ap) apatite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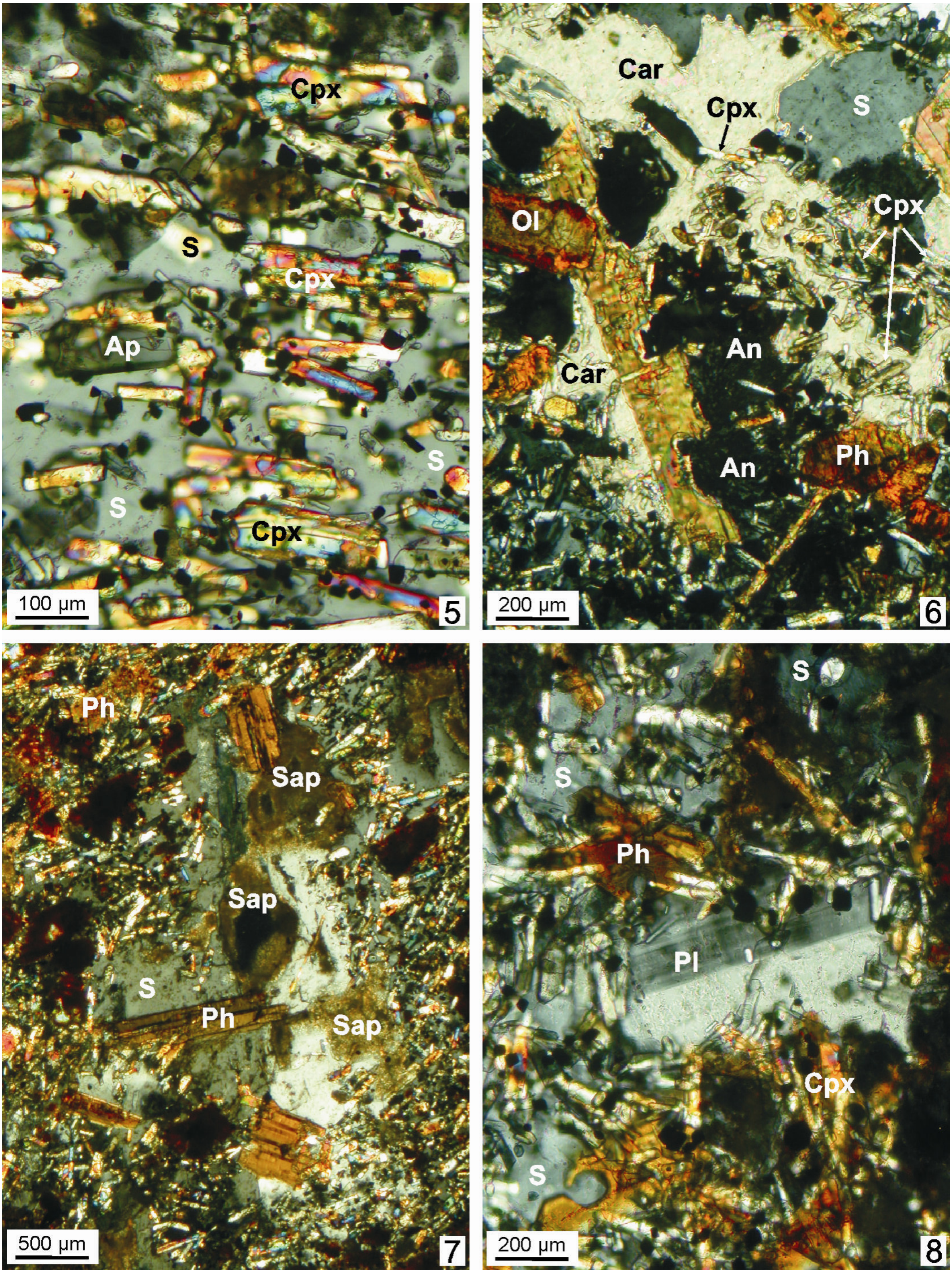
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Fig. 5. Selected photomicrographs of Macedonian ultra- and high potassic volcanic rocks: (1) miarolitic cavity filled with phlogopite (Ph), and phillipsite (Phil): (Ol) olivine microphenocrysts, *Kishino phonotephrite*; (2) trachytic texture in the groundmass of the *Gradishte UK-latite* with Ba-sanidine microlites: (Cpx) clinopyroxene microphenocryst and (Ph) opacitized phlogopite phenocrysts; (3) leucite (Lc) microphenocrysts in fine grained feldspars groundmass, *Kishino phonotephrite:* (Ol) olivine microphenocrysts; (4) poikilitic phlogopite (Ph), clinopyroxene (Cpx) and altered leucite (Lc) microphenocrysts in groundmass of Na-sanidine (S), *K. Krasta phonotephrite*; (5) poikilitic Na-sanidine (S) including oriented clinopyroxene (Cpx) and apatite (Ap) microlites, groundmass of *M. Nagorichane phonotephrite*; (6) Mg-calcite (Car) and phlogopite (Ph) including clinopyroxene (Cpx) microlites, groundmass of the *E. Brdo phonotephrite:* (S) Na-sanidine, (An) anorthoclase; (7) vacuoles filled with phlogopite (Ph) and Ba-sanidine (S), covered by saponite (Sap), *M. Nagorichane phonotephrite*; (8) poikilitic oligoclase (Pl), phlogopite (Ph) and Na-sanidine (S) including clinopyroxene (Cpx) microlites, groundmass of *E. Brdo phonotephrite*. Photographs 3 and 4: plane-polarized light; the rest: cross-polarized light

apatite microlites. Often they have lower $Mg^{\#}$ than corresponding phenocrysts. The microlites, and in places the phenocrysts, are strongly oriented. The groundmass of the phonotephrites, especially those of Kishino contains different amounts of leucite microphenocrysts and microlites (Fig. 5-3).

The groundmass of Djurishte and Gradishte latites (Fig. 5-2) has trachytic texture and consists of microcrystalline feldspar mass with oriented Na-sanidine microlites and smaller amount of microphenocrysts and microlites of olivine, clinopyroxene, Ti-magnetite, anorthoclase (in Djurishte only), phlogopite and apatite.

Some volcanic rocks contain miarolitic cavities (Kishino, Fig. 5-1) with Ba-bearing anorthoclase, nepheline and K-Ca phillipsite, or vacuoles (M. Nagorichane) filled with phlogopite and Ba-sanidine, covered by saponite (Fig 5-7). In the rocks of K. Krasta mm-sized "pegmatitic" veins are found. They consist of Na-sanidine with magnetite dendrites, large Ti-Ba-phlogopite crystals and zeolites.

### *Mineral description*

The *olivine* phenocrysts, up to 1-2 mm in size, are slightly rounded by the melt corrosion and often zoned with Fe rich rim (in Gradishte, E. Brdo and K. Krasta). A negative correlation is found between Fo molecule and their MnO content, and a positive one – between the same molecule and NiO content. Therefore, the cores of olivine phenocrysts are enriched in Ni (Fig. 6). Cr contents are very low and display no correlation with other elements. No Cr-spinel inclusions are found in olivine phenocrysts

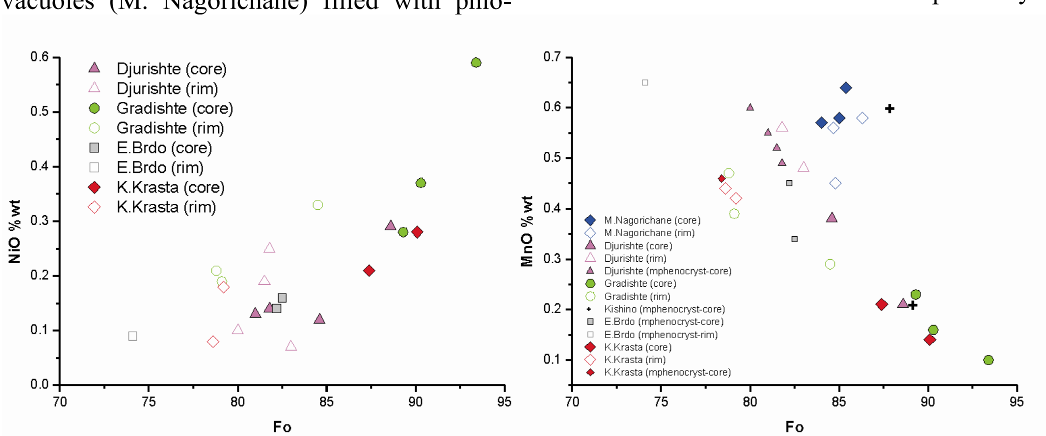


Fig. 6. Plot of NiO and MnO contents *vs.* Fo in olivines of Macedonian ultra- and high potassic rocks. Filled and open symbols represent cores and rims of the phenocrysts, respectively

although they were described in other ultrapotassic rocks (e.g. in Serbia – Prelević et al. 2005, 2007).

A rim of clinopyroxene + phlogopite coats the olivines in the K. Krasta rocks resulting from the reaction between olivine and surrounding melt. An alteration to serpentine minerals occurs in the rim of olivines and along the crystals cracks.

The *clinopyroxene* phenocrysts**,** up to 1 mm in size, are idiomorphic, slightly zoned (e.g. in Gradishte and K. Krasta), sometimes with altered or corroded rims. Their composition (Fig. 7) varies in very narrow limits. They are diopsides (M. Nagorichane and E. Brdo) to diopside-augites (K. Krasta) in the phonotephrites and essentially augites, but plotting very close to the diopside field in the latites and shoshonites (Gradishte and Djurishte). Usually the rims of clinopyroxene phenocrysts are slightly enriched in Fs molecule. $Al_2O_3$ contents vary between 0.26 and 6.4 wt.%. They are higher in the pyroxenes from E. Brdo phonotephrites, but Al quantities are not sufficient to occupy all of the tetrahedral sites that is characteristic for many ultrapotassic magmas (e.g. Carmichael 1967; Conticelli et al. 1992 etc.). The $Fe^{3+}$ enters pyroxene structure in order to compensate the tetrahedral deficit. The lack of $^{VI}Al$ in these clinopyroxenes is suggestive of a low-pressure origin. Similar high Al contents are observed mainly in basic alkaline rocks, especially in ultrapotassic varieties – e.g. Al contents in Vesuvius leucite phonotephrite reach 7.6 wt.% (Rahman 1975). Octahedral Al is present only in pyroxenes from latites and shoshonites in Djurishte and Gradishte, (up to 0.15 and 0.11 *apfu*, respectively). It is indicative of an origin at greater depths (see below).

Ti also varies significantly (from 0.22 to 3.51 wt.% $TiO_2$) and its maximum contents are observed in clinopyroxenes in the phonotephrites from E. Brdo, so they can be described as titaniferous diopside to titandiopside. An increase of Ti contents (Fig. 8) towards the rims of the phenocrysts as well as in the lately crystallized microlites is observed. Ti

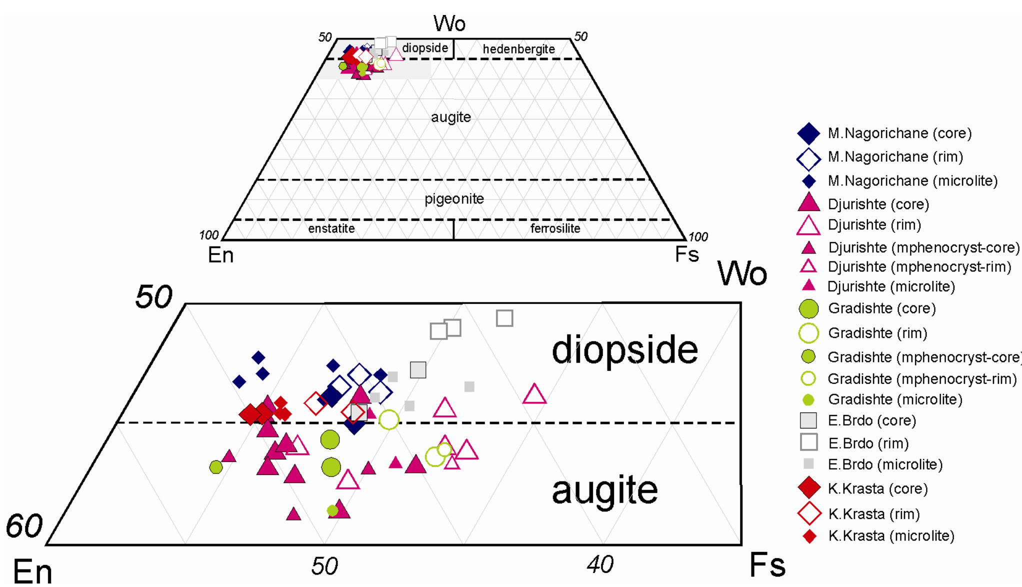


Fig. 7. Systematics of the clinopyroxene from Macedonian ultra- and high potassic rocks. Below: detailed part of the diagram

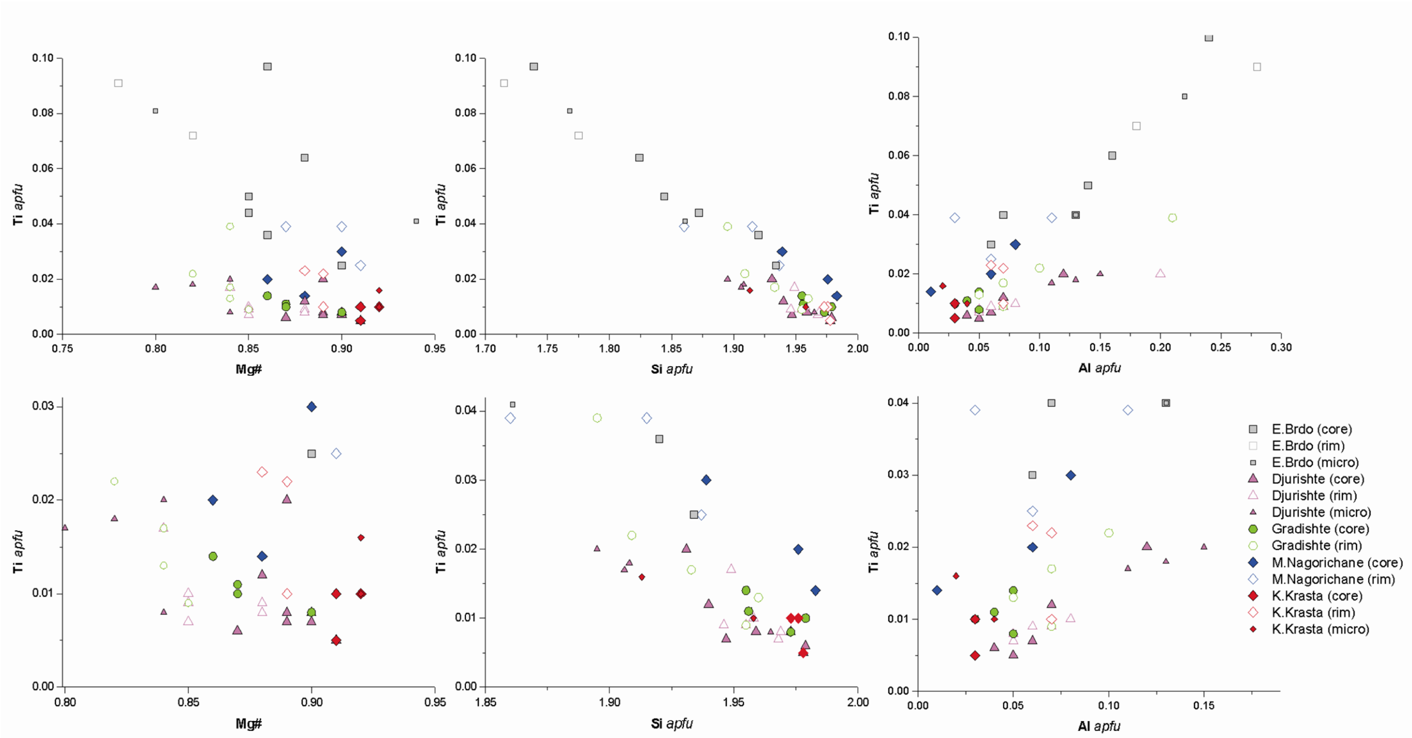


Fig. 8. Ti contents in the clinopyroxenes *vs.* $Mg^{\#}$, Si and Al contents. Below: detailed part of the diagrams

correlates positively with Al contents in the majority of the studied volcanic rocks. It is the most important non-quadrilateral substitution in the pyroxene structure because Al and Ti form TAL component – $CaTiAl_2O_6$ (Papike et al. 1974). On the other hand Ti contents correlate negatively with Si that is observed in many basic alkaline volcanic rocks as a result of $TiAl_2 \leftrightarrow MgSi_2$ exchange reactions (Sack & Carmichael 1984). In E. Brdo and Gradishte clinopyroxenes only the Ti content decreases progressively, following the Mg–$Fe^{2+}$ substitution (i.e. the $Mg^{\#}$ ratio, Fig. 8). This correlation is experimentally proved at QMF buffer by Sack & Carmichael (1984) and explained by the intervalence $Fe^{2+} \leftrightarrow Ti^{4+}$ substitution. It is strongly depending on the oxidation-reduction environment in melts and probably cannot take place under more oxidizing conditions. In our case the oxygen fugacity is evaluated as being close to Ni–NiO buffer (see below) only for Djurishte latites where no correlation between Ti and $Mg^{\#}$ is observed.

The clinopyroxenes of M. Nagorichane (Sveshnikova et al. 1986) and K. Krasta contain also Cr (up to 0.35 and 0.5 wt.%, respectively) and can be classified as chromdiopsides.

The *mica* phenocrysts form long spiny (Fig. 5-2) or platy crystals, slightly rounded, often having opacitized (magnetite + pyroxene) rims and/or intermediate zones. In some cases (e.g. in K. Krasta) they are strongly zoned with rims depleted in Ba (see the appendix table).

The compositions of the micas vary from almost pure *phlogopite* (up to $Mg^{\#}$ 92 in Gradishte) to *Mg-rich biotite* (up to $Mg^{\#}$ 67, rarely detected in some microphenocrysts and microlites in E. Brdo) – Fig. 9. Three groups of micas can be distinguished on the basis of their Ba and Ti contents (Fig. 10): high Ti and Ba phlogopites in M. Nagorichane and E. Brdo rocks similar to these in the leucitites, i.e. the Roman Province Type rocks; high Ti and low

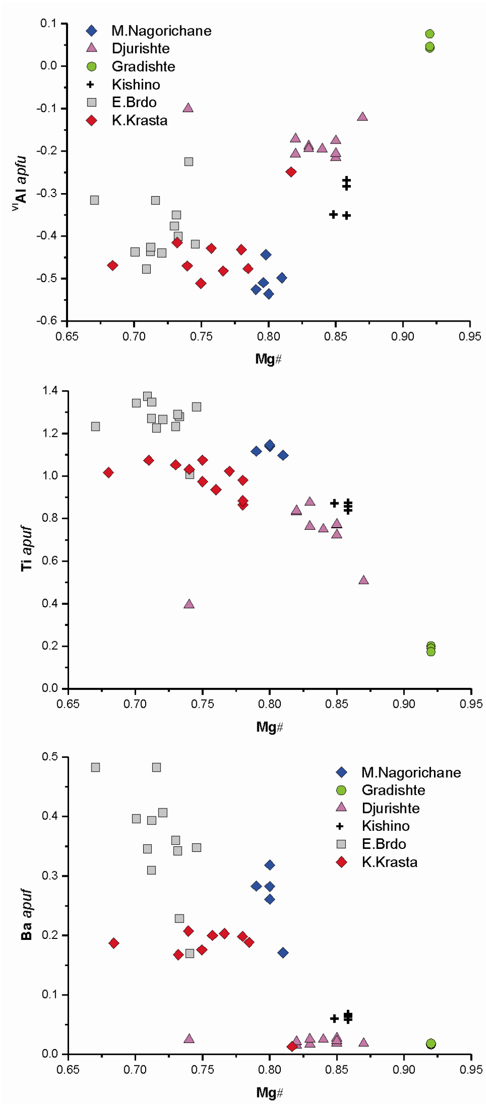


Fig. 9. Plots of $^{VI}$Al, Ti and Ba *vs.* $Mg^{\#}$ for the studied micas (according to our data and Altherr et al. 2004). Al tetrahedral deficiency is presented as -$^{VI}$Al

Ba phlogopites in Djurishte latite and Kishino phonotephrite similar to these in the lamproites; and finally, low Ti and Ba phlogopites in Gradishte UK-latites resembling

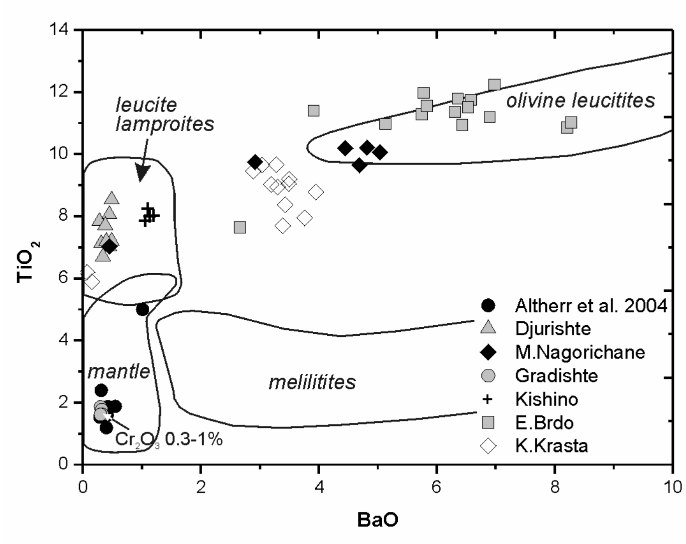


Fig. 10. Plot of $TiO_2$ *vs.* BaO (wt.%) for the studied micas (the $Cr_2O_3$ content of the Gradishte phlogopites is also shown). The fields of phlogopites of various rock types from Dunworth & Wilson (1998) and the mantle phlogopite xenocrysts of Macedonian ultrapotassic rocks (Altherr et al. 2004) are outlined too

the mantle xenocrysts of Macedonian ultrapotassic rocks (Altherr et al. 2004). The phlogopite of the last locality is also characterized by its high Cr content (0.35 – 1 wt.%) as in some lamproites, ultramafic mantle xenoliths in the Latium area in Italy (Cruciani & Zanazzi 1994) and other ultrapotassic rocks (Feldstein et al. 1996) displaying a negative correlation between Cr and Ti (not shown here).

Regarding the first group of micas, the microlites of E. Brdo are particularly rich in Ba (up to 8.2 wt.% BaO), so they can be classified between the Ti-Ba phlogopite and Ti-kinoshitalite end members (Fig. 11). The high amounts of Ba and Ti cause a deficiency of tetrahedral Al (Fig. 9), typical for ultrapotassic magma (Wagner & Velde 1986) and "filled" by tetra-$Fe^{2+}$ ion as in the tetra-ferriphlogopite (Cruciani at al. 1995).

Some correlations are observed in the micas of Macedonian ultrapotassic rocks. Here we present a negative correlation between Ti and $Mg^{\#}$ as well as this between Ba and $Mg^{\#}$, as the last one is better displayed in micas from E. Brdo rocks (Fig. 9).

Where is the place of Ba and Ti in mica structure? In the micas of alkali rocks in general, and in Macedonian rocks in particular (Fig. 12) Ba shows a negative correlation with Si and K, but a positive one with Ti and Al. Mansker at al. (1979) and Velde (1979) proposed a coupled substitution for Ba and Ti with participation of all mica cations including high amount of Si and Al following the next equation:

$$^{XII}Ba+2^{VI}Ti+3^{IV}Al = {}^{XII}(K+Na+Ca)+3^{VI}(Mg+Fe+Mn)+3^{IV}Si \text{ (Fig. 13)}$$

or similar to the substitution proposed by Guo & Green (1990) for mantle phlogopite:

$$Ba+3Ti+4Al = 2K+4(Mg, Fe)+4Si.$$

The *leucite microphenocrysts* are abundant in the phonotephrites and display slightly higher Fe contents (up to 1 wt.% in M. Nagorichane). Often their crystals are automorphous (Fig. 5-3), with concentric inclusions of clinopyroxene and/or apatite spines. In the older lavas the leucite microphenocrysts are partially (M. Nagorichane) or completely transformed (K. Krasta) into Na-sanidine, zeolites (laumontite, phillipsite and other not determined species) and clays (Fig. 5-4). The leucite microphenocrysts in Kishino

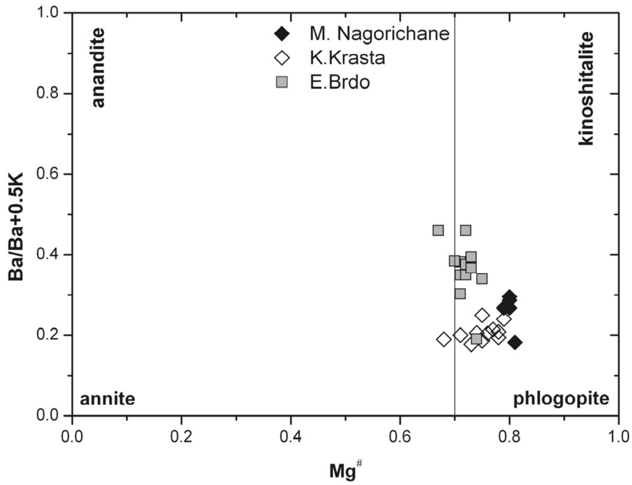


Fig. 11. The systematics of Ba-rich micas of Macedonian ultrapotassic rocks (according to our data and Altherr et al. 2004)

are partially transformed into nepheline ($Ab_{91.5}Or_8$) and amorphous nephelinic mass ($Ab_{87.7}$ $Or_{11.2}$) with 4.5-7 wt.% $H_2O$.

Sveshnikova et al. (1986) reported in M. Nagorichane the presence of another type of leucite micro- and phenocrysts, rich in Ba (up to 3.12 wt.%) and Sr (up to 0.9 wt.%).

The *feldspars* from the groundmass in most of the rocks are essentially Na-sanidines (Fig. 14). In Kishino they are essentially anorthoclases, some of them rich in Ba (up to 2.23 wt. %). In E. Brdo only the feldspars have a composition covering a continuous range between Na-sanidine and oligoclase.

The Na-sanidine forms large xenomorphic crystals, some of them with BaO up to 5.2 wt.% (M. Nagorichane). Sveshnikova et al. (1986) found in the groundmass of K. Krasta Na-sanidine very rich in Sr and Ba ($Or_{44.2}Ab_{31.1}An_{6.3}Sr_{10}Cn_{8.4}$). The Sr-rich sanidine is found also in some ultrapotassic rocks of the Roman Province (Della Ventura et al. 1993) and in the olivine leucitite of Mexico Volcanic Belt (Wallace & Carmichael 1989).

The groundmass of E. Brdo phonotephrites contains also twinned and zoned plagioclases (Fig. 5-8) some of them with core of oligoclase or anorthoclase, both rich in Sr (up to 2.7 and 3.4 wt.% SrO, respectively) and Ba (up to 2.11 and 3.9 wt.% BaO, respectively); the rim is also of oligoclase, but poor in these elements. Andesine crystals, also rich in Ba and Sr (up to $Or_{9.1}Ab_{47.1}An_{41.5}Sr_{12.3}Cn_{4.1}$), were found by Sveshnikova et al. (1986).

A positive correlation between Ba and Sr is observed in E. Brdo feldspars. On the other hand Ba correlates negatively with Si/Al ratio in plagioclases and sanidines from all localities (Fig. 15). This is indicative of ($Ba^{2+}$, $Al^{3+}$) → ($K^+$, $Si^{4+}$) isomorphic substitution (Afonina et al. 1978). This correlation is not presented in the anorthoclases.

Since the alteration affects leucite microphenocrysts and microlites only in places and does not affect the sanidine in the groundmass the $K_2O/Na_2O$ ratio do not change drastically and maintains the ultrapotassic character of the rocks. Inversely, the Serbian ultrapotassic rocks are often affected by analcimization that modify their ultrapotassic signature (Prelević et al. 2005).

The *oxide accessories* are represented by Ti-magnetite (and ilmenite in Djurishte latites). Both minerals are characterized by high Mg contents indicating presence of magnesioferritic molecule. Ti-magnetite of E. Brdo is enriched in Si, Al, alkali-earth and alkali elements, probably due to the presence of micro impurities of silicate minerals.

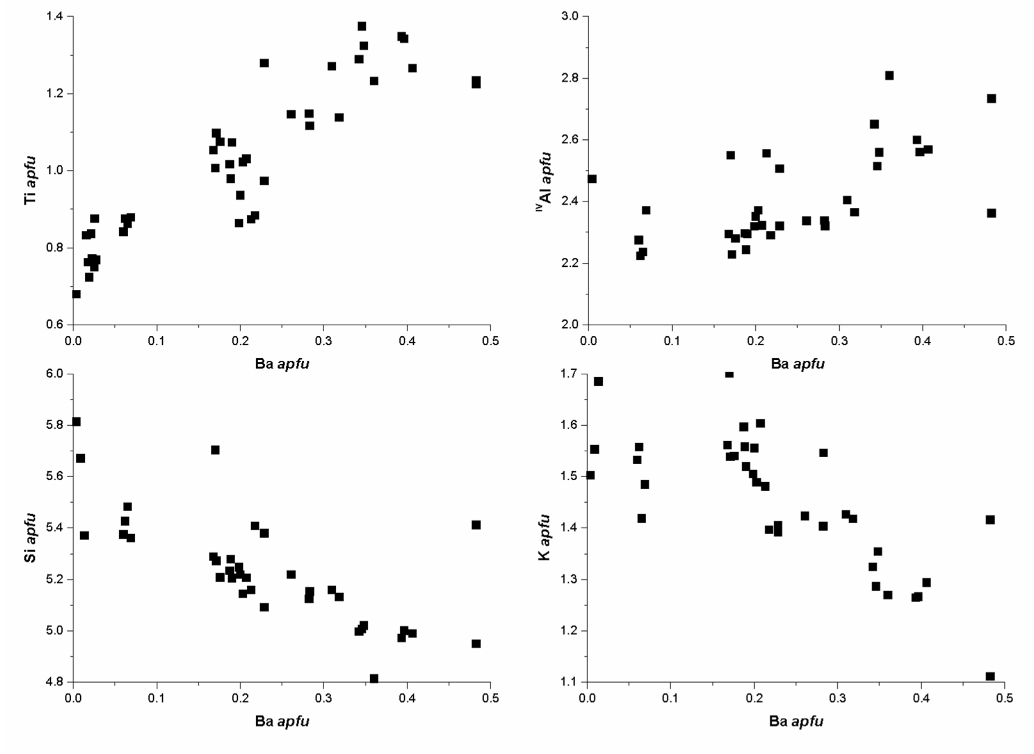


Fig. 12. Correlations between Ba and Ti, $^{IV}Al$, Si and K in the micas (according to our data and Altherr et al. 2004)

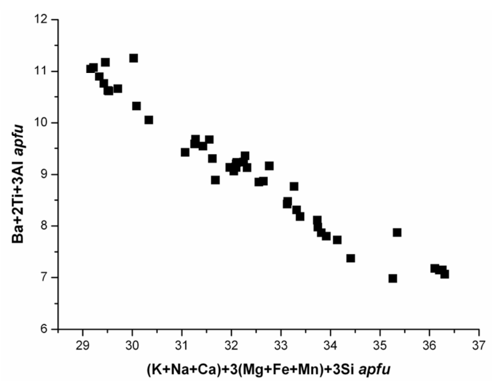


Fig. 13. The substitution mechanism of Mansker et al. (1979) and Velde (1979) in the Ba-Ti phlogopites with the points of the micas of the studied volcanic rocks (according to our data and Altherr et al. 2004)

### *Ti, Cr and Ba partition between the phenocrysts*

When comparing the partition of Ti and Cr between phlogopite and clinopyroxene it is clearly visible that both elements are concentrated mainly in phlogopite or the partition pattern is $(phl>>cpx)_{Ti,Cr}$.

The behavior of Ba regarding phlogopite and feldspars is much more complex, although in all of the rocks phlogopite crystallizes earlier. In phonotephrites (except Kishino) partition pattern is $(phl>>feld)_{Ba}$; in the other volcanic rocks where these minerals have low Ba contents the partition pattern is $(feld \geq phl)_{Ba}$. A clear negative correlation is detected

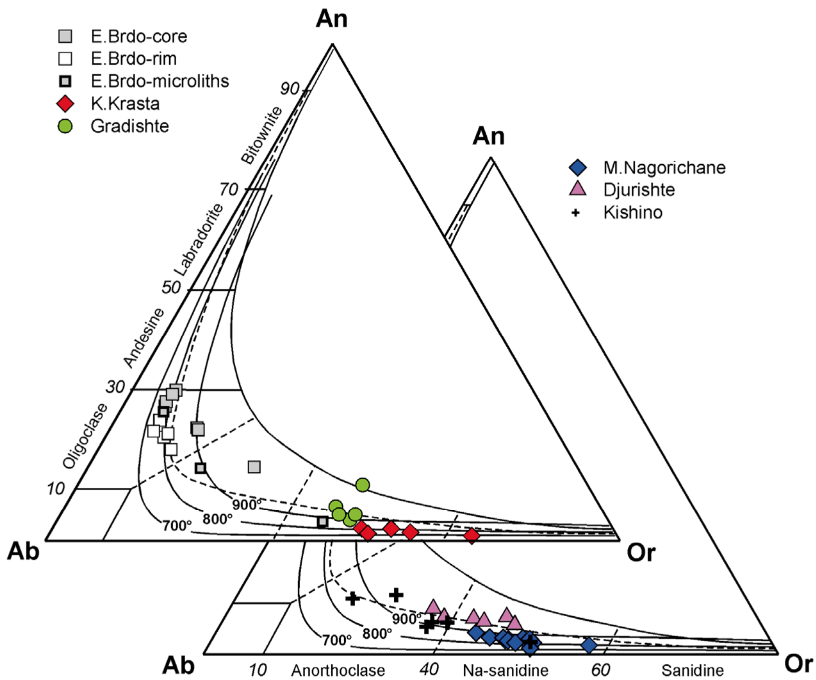


Fig. 14. Systematics of the disordered feldspars (Smith 1974) from Macedonian ultra- and high potassic rocks. Temperature curves are after Elkins & Grove (1990)

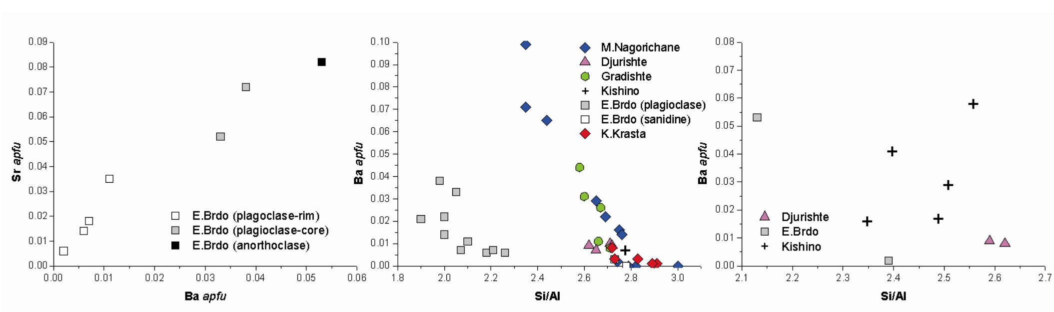


Fig. 15. Correlation between Ba and Sr in the plagioclase and anorthoclase of E. Brdo phonotephrites *(left)*; correlation between Ba and Si/Al in the plagioclases of E. Brdo phonotephrites and the sanidines of all studied rocks *(center)*; in the anorthoclases only (*right*)

between partition coefficient of Ba and $Mg^{\#}$ of phlogopite i.e. the purer the phlogopite, the more Ba in lately crystallized feldspars (Fig. 16).

## Temperature/pressure parameters

According to the olivine/liquid geothermometer of Putirka et al. (2007) and Beattie

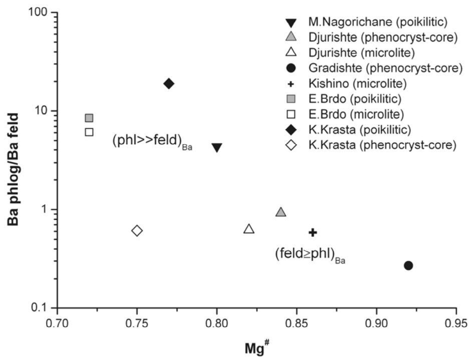


Fig. 16. Distribution of Ba between phlogopite and sanidine *vs.* $Mg^{\#}$ of the phlogopite in different Macedonian ultra- and high potassic rocks

(1993) the olivine crystallization temperature varies between 1190 and 1310°C; those of clinopyroxene, according to the clinopyroxene/liquid geothermobarometer (Putirka et al. 2003), are 1150–1305°C (Table 3). In almost all of the studied rocks the temperatures calculated for the crystal rims are a little bit higher than for the cores.

The calculated pressure according to the geothermobarometer of Putirka et al. (2003) is variable. For the majority of the studied samples the calculated values are between 6 and 8 kbar (corresponding to the depth of 17–23 km). This suggests crystallization in the crustal level since the dept of Moho discontinuity in this part of the Vardar zone is between 33 and 36 km (Boykova 1999) – Fig. 2. The increase in CaO contents in olivine from some phonotephrites (up to 0.56 wt.% in the rims of E. Brdo olivine) probably indicates a significant ascent rate of the magma (Sveshnikova et al. 1986).

Higher values of the pressure (14-17 kbar, corresponding to a mantle depth of 40–48 km) are obtained for Gradishte UK-latites. The features of the phenocrysts observed in Gradishte rocks are indicative of their deep origin. The most significant are the following: the olivine phenocrysts have highest contents of Ni (Fig. 6) and Cr (see appendix table); the clinopyroxenes show also high octahedral Al (see the appendix table). Only in these volcanic rocks the phlogopites have mantle characteristics (Fig. 10) – strongly depleted in Ti, but enriched in Cr reflecting the influence of pressure on the behavior of these elements: together with increasing pressure Ti contents in phlogopite decrease and Cr contents increase (Trönnes et al. 1985; Fleet 2003).

Table 3. *Temperature and pressure of the olivine and clinopyroxene crystallization*

| Locality | Mineral | Temperature | | | Pressure |
|---|---|---|---|---|---|
| | | olivine/melt | | cpx/melt | cpx/melt |
| | | Putirka et al. (2007) | Beattie (1993) | Putirka et al. (2003) | |
| Mlado Nagorichane | pheno - core | 1298°C | 1312°C | 1305°C | 6.1 |
| | rim | 1297°C | 1312°C | | |
| Djurishte | pheno - core | 1177°C | 1210°C | 1203°C | 8.3 |
| | rim | 1189°C | 1210°C | 1198°C | 8.2 |
| Gradishte | pheno - core | 1222°C | 1267°C | 1255°C | 14.5 |
| | rim | 1259°C | 1267°C | 1298°C | 17.2 |
| Kishino | micropheno | 1259°C | 1284°C | n.d.* | n.d.* |
| Ejevo Brdo | pheno - core | 1247°C | 1262°C | – | – |
| | rim | 1287°C | 1262°C | 1144°C** | 6.6** |
| Kureshnichka Krasta | pheno - core | 1266°C | 1290°C | 1178°C | 8.2 |
| | rim | 1310°C | 1290°C | 1278°C | 11.7 |

* no cpx phenocrysts; ** microphenocrysts

The presence of magnetite and ilmenite as accessory phases in Djurishte rocks permits to determine (according to the method of Buddington & Lindsley 1964) the temperature of oxide crystallization (988–994°C) and the oxygen fugacity lg $f_{O2}$ – from -9.46 to -9.58, i.e. a little above Ni–NiO buffer.

Ternary-feldspar geothermometer of Fuhrman & Lindsley (1988) applied to E. Brdo rocks only indicates the temperature of groundmass crystallization as 868–882°C for the cores and 818–856°C for the rims of the feldspar crystals (Fig. 14). These are typical magmatic temperatures above the glass transition temperature *Tg* of this type of melt (e.g. *Tg* of dry diopside is 730-750°C, of dry albite – 705-710°C and melt of $An_{15}Ab_{32}Di_{53}$ composition – 725-732°C, Webb & Knoche 1996). Therefore, we cannot agree with Sveshnikova et al. (1986) who described these feldspars as post-magmatic glass-replacing products. The crystallization temperature of the other feldspars can be estimated using the isotherms of Elkins & Grove (1990) plotted in the Fig. 14. The crystallization temperature of the feldspars in the phonotephrites (except Kishino) is close to these of E. Brdo rocks. Temperatures higher than 900°C are obtained for the sanidines of Gradishte and Djurishte latites.

## Conclusions

The Macedonian ultrapotassic (phonotephrite, UK-shoshonite and UK-latite) to high potassic (high-Mg latite) rocks consist of forsteritic olivine, diopside-augite, phlogopite (some of them very rich in Ti and in Ba), ± leucite phenocrysts. The groundmass of the ultra-potassic rocks is formed by poikilitic feldspars (Na-sanidine and Sr-plagioclase), phlogopite and sporadically Mg-rich calcite (up to 5–7 wt.% $MgCO_3$) all containing microlites of the mentioned above minerals, Ti-magnetite, ± Mg-rich biotite, leucite, anortoclase. The groundmass of the latites consists of microcrystalline feldspar mass with oriented Na-sanidine microlites and smaller amounts of microphenocrysts and microlites of olivine, clinopyroxene, Ti-magnetite, and phlogopite, ± anorthoclase.

The composition of mineral assemblages in the studied rocks provides a possibility to better classify these ultrapotassic rocks. Many authors (e.g. Altherr et al. 2004; Božović et al. 2005; Prelevic et al. 2007) consider them as lamproites. Indeed, they contain Ti rich phlogopite phenocrysts, forsteritic olivine and poikilitic titanian (up to 12 wt.% $TiO_2$) phlogopite in the groundmass, all that being characteristic of lamproites. But according to the IUGS Subcommission on the Systematics of Igneous Rocks (Le Maitre 1989) "*the presence of the following minerals precludes a rock from being classified as a lamproite: primary plagioclase* (here presented in E. Brdo), *Na-rich alkali feldspars* (presented in the groundmass of all phonotephrites as Na-sanidine and also anorthoclase in E. Brdo and Kishino) *and Al-rich pyroxene*" (here up to 5 wt.% $Al_2O_3$). In addition the sanidine and leucite are Fe-poor (<1 wt.% FeO). Thus, these volcanic rocks are not lamproites according to the mineralogical criteria; they are Roman Province Type rocks – leucitic phonotephrites.

The olivine crystallization temperature varies between 1190 and 1310°C and those of clinopyroxene is 1150–1305°C according to the geothermometer of Putirka et al. (2007) and Beattie (1993). As most realistic pressure values according to the geothermobarometer of Putirka et al. (2003) we assume these between 6 and 8 kbar, corresponding to a depth of 17-23 km except for Gradishte ultrapotassic latites where the estimated pressure is 14–17 kbar, corresponding to a depth of 40–48 km. The olivine of these latites has highest Ni and Cr contents, their clinopyroxenes – highest $^{VI}Al$ values and the phlogopites have mantle characteristics (low Ti, Ba and high Cr contents). The temperature of groundmass crystallization for one of the bodies (E. Brdo), calculated by the ternary-feldspar geothermometer is 818–882°C, above the glass transition temperature *Tg*.

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# Appendix

*Selected microprobe analyses of* ***olivines*** *and calculated formulae (based on 4 oxigens)*

| Locality | Mlado Nagorichane | | | | Djurishte | | | | Gradishte | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | phenocryst | | | | phenocryst | | microphenocryst | | phenocryst | | | |
| | core | rim | core | rim | core | rim | | | core | rim | core | rim |
| $SiO_2$ | 39.93 | 39.67 | 39.98 | 39.33 | 40.46 | 39.27 | 39.65 | 39.19 | 40.51 | 39.41 | 41.43 | 40.64 |
| FeO | 13.90 | 14.46 | 14.18 | 14.34 | 11.16 | 16.25 | 17.96 | 17.33 | 9.49 | 14.75 | 6.60 | 18.63 |
| MnO | 0.64 | 0.56 | 0.58 | 0.45 | 0.21 | 0.48 | 0.55 | 0.49 | 0.16 | 0.29 | 0.10 | 0.47 |
| MgO | 45.69 | 44.79 | 45.15 | 44.74 | 48.65 | 44.43 | 42.89 | 43.72 | 49.62 | 45.26 | 52.20 | 38.90 |
| CaO | 0.24 | 0.16 | 0.14 | 0.26 | 0.22 | 0.19 | 0.11 | 0.10 | 0.31 | 0.14 | 0.14 | 0.35 |
| NiO | n.d. | n.d. | n.d. | n.d. | 0.29 | 0.07 | 0.13 | 0.25 | 0.37 | 0.33 | 0.59 | 0.21 |
| $Cr_2O_3$ | n.d. | n.d. | n.d. | n.d. | 0.02 | 0.00 | 0.02 | 0.07 | 0.03 | 0.03 | 0.08 | 0.03 |
| Total | 100.40 | 99.64 | 100.03 | 99.12 | 101.01 | 100.69 | 101.31 | 101.15 | 100.49 | 100.21 | 101.14 | 99.23 |
| Si | 0.996 | 0.999 | 1.001 | 0.996 | 0.990 | 0.988 | 0.998 | 0.987 | 0.990 | 0.989 | 0.992 | 1.043 |
| Fe | 0.290 | 0.305 | 0.297 | 0.304 | 0.228 | 0.342 | 0.378 | 0.365 | 0.194 | 0.310 | 0.132 | 0.400 |
| Mn | 0.014 | 0.012 | 0.012 | 0.010 | 0.004 | 0.010 | 0.012 | 0.010 | 0.003 | 0.006 | 0.002 | 0.010 |
| Mg | 1.699 | 1.681 | 1.685 | 1.688 | 1.775 | 1.666 | 1.609 | 1.641 | 1.807 | 1.694 | 1.864 | 1.488 |
| Ca | 0.006 | 0.004 | 0.004 | 0.007 | 0.006 | 0.005 | 0.003 | 0.003 | 0.008 | 0.004 | 0.004 | 0.010 |
| Ni | - | - | - | - | 0.006 | 0.001 | 0.003 | 0.005 | 0.008 | 0.007 | 0.012 | 0.005 |
| Cr | - | - | - | - | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.001 | 0.002 | 0.001 |
| Total M1 | 2.009 | 2.002 | 1.998 | 2.009 | 2.019 | 2.024 | 2.005 | 2.025 | 2.021 | 2.022 | 2.016 | 1.914 |
| Fo% | 85.4 | 84. 7 | 85.0 | 84.8 | 88.6 | 83.0 | 81.0 | 81.8 | 90.3 | 84.5 | 93.4 | 78.8 |

| Locality | Kishino | | Ejevo Brdo | | | | Kureshnichka Krasta | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | microphenocryst core | | microphenocryst | | | | phenocryst | | | | micro-phenocryst |
| | | | core | rim | core | core | core | rim | core | rim | |
| $SiO_2$ | 40.39 | 40.13 | 39.38 | 37.63 | 39.74 | 38.81 | 40.32 | 38.63 | 40.65 | 39.21 | 39.01 |
| FeO | 10.42 | 11.45 | 17.04 | 22.36 | 16.77 | 19.02 | 12.23 | 19.77 | 9.75 | 19.48 | 20.43 |
| MnO | 0.21 | 0.60 | 0.45 | 0.65 | 0.34 | 0.06 | 0.21 | 0.44 | 0.14 | 0.42 | 0.46 |
| MgO | 48.53 | 47.02 | 44.28 | 35.81 | 44.39 | 40.86 | 47.69 | 40.64 | 49.77 | 41.53 | 41.63 |
| CaO | 0.18 | 0.21 | 0.33 | 0.56 | 0.26 | 0.40 | 0.15 | 0.25 | 0.20 | 0.31 | 0.27 |
| NiO | n.d. | n.d. | 0.14 | 0.09 | 0.16 | n.d. | 0.21 | 0.08 | 0.28 | 0.18 | 0.10 |
| $Cr_2O_3$ | n.d. | n.d. | 0.01 | 0.02 | 0.03 | n.d. | n.d. | n.d. | 0.01 | n.d. | n.d. |
| Total | 99.73 | 99.41 | 101.63 | 97.12 | 101.69 | 99.15 | 100.81 | 99.81 | 100.80 | 101.13 | 101.90 |
| Si | 0.996 | 0.999 | 0.985 | 1.013 | 0.991 | 1.000 | 0.993 | 0.996 | 0.990 | 0.996 | 0.988 |
| Fe | 0.215 | 0.238 | 0.357 | 0.503 | 0.350 | 0.410 | 0.252 | 0.426 | 0.199 | 0.414 | 0.433 |
| Mn | 0.004 | 0.013 | 0.010 | 0.015 | 0.007 | 0.001 | 0.004 | 0.01 | 0.003 | 0.009 | 0.010 |
| Mg | 1.784 | 1.745 | 1.651 | 1.437 | 1.650 | 1.570 | 1.750 | 1.563 | 1.807 | 1.573 | 1.572 |
| Ca | 0.005 | 0.006 | 0.009 | 0.016 | 0.007 | 0.011 | 0.004 | 0.007 | 0.005 | 0.008 | 0.007 |
| Ni | - | - | 0.003 | 0.002 | 0.003 | - | 0.004 | 0.002 | 0.006 | 0.004 | 0.002 |
| Cr | - | - | 0.000 | 0.000 | 0.001 | - | - | - | - | - | - |
| Total M1 | 2.008 | 2.002 | 2.030 | 1.973 | 2.018 | 1.992 | 2.014 | 2.008 | 2.020 | 2.008 | 2.024 |
| Fo% | 89.3 | 40.13 | 82.2 | 74.1 | 82.5 | 79.3 | 87.4 | 78.6 | 90.1 | 79.2 | 78.4 |

*Selected microprobe analyses of* ***clinopyroxenes*** *and calculated formulae (based on 6 oxygens)*

| Locality | Mlado Nagorichane | | | | | | Djurishte | | | | | | | Gradishte | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | phenocryst* | | | | | micro-pheno. | phenocryst | | | | | | micro-pheno. | phenocryst | | | | micro-lite |
| | core | rim | core | core | rim | | core | rim | core | rim | core | rim | | core | rim | core | rim | |
| $SiO_2$ | 54.48 | 51.97 | 53.35 | 54.20 | 50.77 | 52.85 | 53.53 | 52.64 | 54.31 | 52.64 | 53.60 | 52.34 | 53.02 | 53.60 | 52.34 | 52.93 | 52.00 | 52.33 |
| $TiO_2$ | 0.50 | 1.39 | 1.11 | 0.73 | 1.40 | 0.92 | 0.27 | 0.34 | 0.22 | 0.34 | 0.28 | 0.32 | 0.28 | 0.28 | 0.32 | 0.41 | 0.62 | 0.46 |
| $Al_2O_3$ | 0.26 | 1.73 | 1.33 | 0.79 | 2.55 | 1.27 | 1.43 | 1.70 | 1.09 | 1.82 | 1.11 | 1.62 | 1.17 | 1.11 | 1.62 | 0.92 | 1.62 | 1.20 |
| FeO | 4.67 | 5.90 | 5.60 | 4.58 | 5.97 | 4.59 | 4.11 | 4.40 | 3.31 | 7.85 | 3.33 | 7.37 | 6.10 | 3.33 | 7.37 | 5.08 | 6.04 | 5.78 |
| MnO | 0.21 | 0.10 | 0.22 | 0.08 | 0.14 | 0.23 | 0.14 | 0.18 | 0.12 | 0.36 | 0.09 | 0.31 | 0.29 | 0.09 | 0.31 | 0.17 | 0.23 | 0.20 |
| MgO | 16.75 | 15.52 | 16.24 | 16.46 | 15.85 | 16.67 | 18.18 | 17.30 | 17.68 | 14.86 | 17.58 | 15.08 | 17.36 | 17.58 | 15.08 | 16.99 | 16.33 | 17.12 |
| CaO | 22.97 | 22.27 | 21.92 | 23.09 | 22.89 | 22.69 | 21.37 | 21.34 | 22.49 | 20.83 | 22.21 | 20.95 | 20.14 | 22.21 | 20.95 | 22.01 | 21.34 | 20.15 |
| $Na_2O$ | 0.49 | 0.70 | 1.00 | 0.33 | 0.61 | 0.49 | 0.45 | 0.41 | 0.28 | 0.57 | 0.28 | 0.62 | 0.25 | 0.28 | 0.62 | 0.28 | 0.37 | 0.29 |
| $K_2O$ | 0.13 | 0.20 | 0.07 | 0.16 | 0.11 | 0.03 | 0.04 | 0.00 | 0.00 | 0.02 | 0.02 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.02 | 0.02 |
| $Cr_2O_3$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.02 | 0.00 | 0.18 | 0.03 | 0.09 | 0.00 | 0.00 | 0.09 | 0.00 | 0.04 | 0.00 | n.d. |
| NiO | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.05 | 0.00 | 0.05 | 0.00 | 0.03 | 0.02 | 0.02 | 0.03 | 0.02 | 0.05 | 0.03 | n.d. |
| Total | 100.46 | 99.78 | 100.84 | 100.42 | 100.29 | 99.74 | 99.59 | 98.31 | 99.73 | 99.32 | 98.62 | 98.63 | 98.63 | 98.62 | 98.63 | 98.88 | 98.60 | 97.55 |
| $Si^{4+}$ | 1.983 | 1.915 | 1.939 | 1.976 | 1.860 | 1.937 | 1.947 | 1.946 | 1.978 | 1.958 | 1.973 | 1.955 | 1.965 | 1.973 | 1.955 | 1.956 | 1.933 | 1.960 |
| $Al^{3+}$ | 0.011 | 0.075 | 0.057 | 0.024 | 0.110 | 0.055 | 0.053 | 0.054 | 0.022 | 0.042 | 0.027 | 0.045 | 0.035 | 0.027 | 0.045 | 0.040 | 0.067 | 0.040 |
| $Fe^{3+}$ | 0.006 | 0.010 | 0.004 | 0.000 | 0.030 | 0.008 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.004 | 0.000 | 0.000 |
| $Al^{3+}$ | 0.000 | 0.000 | 0.000 | 0.010 | 0.000 | 0.000 | 0.009 | 0.020 | 0.025 | 0.038 | 0.021 | 0.027 | 0.016 | 0.021 | 0.027 | 0.000 | 0.004 | 0.013 |
| $Fe^{3+}$ | 0.013 | 0.038 | 0.063 | 0.000 | 0.046 | 0.025 | 0.062 | 0.044 | 0.000 | 0.026 | 0.008 | 0.045 | 0.021 | 0.008 | 0.045 | 0.040 | 0.056 | 0.024 |
| $Ti^{4+}$ | 0.014 | 0.039 | 0.030 | 0.020 | 0.039 | 0.025 | 0.007 | 0.009 | 0.005 | 0.010 | 0.008 | 0.009 | 0.008 | 0.008 | 0.009 | 0.011 | 0.017 | 0.013 |
| $Cr^{3+}$ | - | - | - | - | - | - | 0.001 | 0.000 | 0.005 | 0.001 | 0.003 | 0.000 | 0.000 | 0.003 | 0.000 | 0.001 | 0.000 | - |
| $Ni^{2+}$ | - | - | - | - | - | - | 0.001 | 0.000 | 0.001 | 0.000 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | - |
| $Mg^{2+}$ | 0.909 | 0.853 | 0.880 | 0.895 | 0.866 | 0.912 | 0.920 | 0.927 | 0.962 | 0.824 | 0.959 | 0.839 | 0.954 | 0.959 | 0.840 | 0.936 | 0.905 | 0.950 |
| $Fe^{2+}$ | 0.064 | 0.070 | 0.027 | 0.075 | 0.049 | 0.038 | 0.000 | 0.000 | 0.002 | 0.101 | 0.000 | 0.079 | 0.000 | 0.000 | 0.079 | 0.010 | 0.017 | 0.000 |
| $Mg^{2+}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.066 | 0.027 | 0.000 | 0.000 | 0.006 | 0.000 | 0.005 | 0.006 | 0.000 | 0.000 | 0.000 | 0.007 |
| $Fe^{2+}$ | 0.057 | 0.058 | 0.066 | 0.065 | 0.049 | 0.066 | 0.063 | 0.092 | 0.099 | 0.116 | 0.095 | 0.107 | 0.168 | 0.095 | 0.107 | 0.103 | 0.115 | 0.157 |
| $Mn^{2+}$ | 0.006 | 0.003 | 0.007 | 0.002 | 0.004 | 0.007 | 0.004 | 0.006 | 0.004 | 0.011 | 0.003 | 0.010 | 0.009 | 0.003 | 0.010 | 0.005 | 0.007 | 0.006 |
| $Ca^{2+}$ | 0.896 | 0.880 | 0.854 | 0.903 | 0.899 | 0.891 | 0.833 | 0.846 | 0.877 | 0.831 | 0.875 | 0.838 | 0.800 | 0.875 | 0.839 | 0.872 | 0.850 | 0.809 |
| $Na^{+}$ | 0.035 | 0.050 | 0.070 | 0.023 | 0.043 | 0.035 | 0.032 | 0.029 | 0.020 | 0.041 | 0.020 | 0.045 | 0.018 | 0.020 | 0.045 | 0.020 | 0.027 | 0.021 |
| $K^{+}$ | 0.006 | 0.009 | 0.003 | 0.007 | 0.005 | 0.001 | 0.002 | 0.000 | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.001 | 0.001 |
| Wo | 46.1 | 46.3 | 45.0 | 46.5 | 47.0 | 46.0 | 42.8 | 43.6 | 45.2 | 43.5 | 45.0 | 43.7 | 40.9 | 45.0 | 43.7 | 44.3 | 43.6 | 41.4 |
| En | 46.7 | 44.8 | 46.4 | 46.2 | 45.2 | 47.0 | 50.6 | 49.1 | 49.4 | 43.1 | 49.6 | 43.8 | 49.0 | 49.6 | 43.8 | 47.6 | 46.4 | 49.0 |
| Fs | 7.2 | 8.9 | 8.6 | 7.3 | 7.8 | 7.0 | 6.6 | 7.3 | 5.4 | 13.4 | 5.4 | 12.5 | 10.1 | 5.4 | 12.5 | 8.1 | 10.0 | 9.6 |
| $Mg^{\#}$ | 0.88 | 0.87 | 0.90 | 0.86 | 0.90 | 0.90 | 0.89 | 0.88 | 0.91 | 0.85 | 0.90 | 0.85 | 0.84 | 0.90 | 0.85 | 0.87 | 0.84 | 0.84 |

* They contain $Cr_2O_3$ 0.22-0.35 wt.% according to Sveshnikova et al. (1986)

| Locality | Ejevo Brdo | | | | | | | Kureshnichka Krasta | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | phenocryst | | | | | microlite | | phenocryst | | | | micro-lite |
| | core | core | core | rim | rim | | | core | rim | core | rim | |
| $SiO_2$ | 52.25 | 47.08 | 49.41 | 47.9 | 46.26 | 47.07 | 51.13 | 54.43 | 52.65 | 54.47 | 52.50 | 52.3 |
| $TiO_2$ | 1.29 | 3.51 | 2.30 | 2.59 | 3.25 | 2.86 | 1.48 | 0.36 | 0.78 | 0.38 | 0.83 | 0.59 |
| $Al_2O_3$ | 1.68 | 5.42 | 3.60 | 4.18 | 6.41 | 4.95 | 2.98 | 0.62 | 1.55 | 0.58 | 1.48 | 0.43 |
| FeO | 5.44 | 6.90 | 6.20 | 7.07 | 6.91 | 7.39 | 5.85 | 3.15 | 4.19 | 2.99 | 5.07 | 4.94 |
| MnO | 0.17 | 0.01 | 0.38 | 0.21 | 0.25 | 0.13 | 0.09 | 0.11 | 0.09 | 0.11 | 0.15 | 0.27 |
| MgO | 16.32 | 13.72 | 14.67 | 14.27 | 13.02 | 13.82 | 15.93 | 18.01 | 16.74 | 18.22 | 16.30 | 17.54 |
| CaO | 22.46 | 22.83 | 22.37 | 23.34 | 22.94 | 21.53 | 22.63 | 22.98 | 22.52 | 23.02 | 22.33 | 23.68 |
| $Na_2O$ | 0.26 | 0.73 | 0.78 | 0.38 | 0.74 | 0.62 | 0.55 | 0.21 | 0.29 | 0.17 | 0.39 | 0.11 |
| $K_2O$ | 0.05 | 0.08 | 0.10 | 0.06 | 0.17 | 0.15 | 0.04 | 0.00 | 0.00 | 0.00 | 0.03 | 0.00 |
| $Cr_2O_3$ | n.d. | n.d. | n.d. | 0.0 | 0.0 | 0.06 | 0.07 | 0.16 | 0.51 | 0.26 | 0.25 | n.d. |
| NiO | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Total | 99.92 | 100.28 | 99.81 | 100 | 99.95 | 98.58 | 100.75 | 100.03 | 99.32 | 100.20 | 99.33 | 99.86 |
| $Si^{4+}$ | 1.920 | 1.738 | 1.823 | 1.775 | 1.715 | 1.768 | 1.861 | 1.976 | 1.938 | 1.973 | 1.936 | 1.913 |
| $Al^{3+}$ | 0.073 | 0.236 | 0.157 | 0.183 | 0.280 | 0.219 | 0.128 | 0.024 | 0.062 | 0.025 | 0.064 | 0.019 |
| $Fe^{3+}$ | 0.007 | 0.026 | 0.020 | 0.042 | 0.005 | 0.013 | 0.011 | 0.000 | 0.000 | 0.002 | 0.000 | 0.068 |
| $Al^{3+}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.003 | 0.005 | 0.000 | 0.000 | 0.000 |
| $Fe^{3+}$ | 0.013 | 0.068 | 0.065 | 0.000 | 0.000 | 0.121 | 0.097 | 0.011 | 0.020 | 0.011 | 0.040 | 0.000 |
| $Ti^{4+}$ | 0.036 | 0.097 | 0.064 | 0.072 | 0.091 | 0.081 | 0.041 | 0.010 | 0.022 | 0.010 | 0.023 | 0.016 |
| $Cr^{3+}$ | - | - | - | 0.000 | 0.000 | 0.002 | 0.002 | 0.005 | 0.015 | 0.008 | 0.007 | - |
| $Ni^{2+}$ | - | - | - | - | - | - | - | - | - | - | - | - |
| $Mg^{2+}$ | 0.893 | 0.756 | 0.807 | 0.788 | 0.720 | 0.773 | 0.860 | 0.971 | 0.918 | 0.970 | 0.896 | 0.957 |
| $Fe^{2+}$ | 0.058 | 0.079 | 0.064 | 0.140 | 0.189 | 0.023 | 0.000 | 0.000 | 0.020 | 0.001 | 0.034 | 0.027 |
| $Mg^{2+}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.005 | 0.004 | 0.000 | 0.014 | 0.000 | 0.000 |
| $Fe^{2+}$ | 0.090 | 0.040 | 0.043 | 0.036 | 0.020 | 0.077 | 0.069 | 0.084 | 0.089 | 0.078 | 0.084 | 0.056 |
| $Mn^{2+}$ | 0.005 | 0.000 | 0.012 | 0.007 | 0.008 | 0.004 | 0.003 | 0.003 | 0.003 | 0.003 | 0.005 | 0.008 |
| $Ca^{2+}$ | 0.884 | 0.904 | 0.884 | 0.927 | 0.911 | 0.867 | 0.882 | 0.894 | 0.887 | 0.893 | 0.882 | 0.928 |
| $Na^{+}$ | 0.019 | 0.052 | 0.056 | 0.027 | 0.053 | 0.045 | 0.039 | 0.015 | 0.021 | 0.012 | 0.028 | 0.008 |
| $K^{+}$ | 0.002 | 0.004 | 0.005 | 0.003 | 0.008 | 0.007 | 0.002 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 |
| Wo | 45.5 | 48.9 | 47.2 | 48.8 | 49.3 | 46.5 | 46.1 | 45.5 | 45.8 | 45.4 | 45.5 | 47.0 |
| En | 46.0 | 40.9 | 43.0 | 41.5 | 38.9 | 41.5 | 45.1 | 49.5 | 47.4 | 50.0 | 46.2 | 48.4 |
| Fs | 8.5 | 10.2 | 9.8 | 9.7 | 11.8 | 12.0 | 8.8 | 5.0 | 6.8 | 4.6 | 8.3 | 4.6 |
| $Mg^{\#}$ | 0.86 | 0.86 | 0.88 | 0.82 | 0.78 | 0.80 | 0.94 | 0.91 | 0.89 | 0.92 | 0.88 | 0.92 |

*Selected microprobe analyses of **micas** and calculated formulae (based on 22 oxygens)*

| Locality | Mlado Nagorichane | | | | | Djurishte | | | | | Gradishte | | | | Kishino | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | poikilitic in the groundmass | | | | | microphenocryst | | | | micro-lite | phenocryst | | | | microphenocrys | | | |
| | | | | | | core | rim | core | rim | | core | core | core | rim | | | | |
| $SiO_2$ | 35.21 | 34.86 | 33.44 | 34.26 | 34.06 | 39.87 | 39.88 | 39.19 | 38.98 | 39.49 | 40.17 | 40.69 | 40.69 | 40.27 | 37.60 | 36.70 | 38.14 | 38.30 |
| $TiO_2$ | 9.75 | 10.19 | 9.64 | 10.21 | 10.06 | 6.70 | 7.19 | 8.06 | 7.71 | 7.13 | 1.86 | 1.77 | 1.62 | 1.61 | 7.84 | 8.00 | 7.99 | 8.22 |
| $Al_2O_3$ | 12.63 | 13.25 | 12.78 | 13.27 | 13.32 | 12.39 | 12.39 | 12.57 | 12.73 | 13.10 | 13.23 | 13.15 | 13.35 | 13.30 | 13.51 | 13.78 | 13.2 | 13.32 |
| FeO | 7.27 | 7.43 | 7.69 | 7.57 | 7.63 | 6.55 | 6.34 | 6.93 | 7.36 | 7.34 | 3.99 | 3.91 | 3.75 | 3.76 | 5.99 | 5.59 | 5.64 | 6.38 |
| MnO | 0.06 | 0.24 | 0.21 | 0.21 | 0.01 | 0.10 | 0.09 | 0.08 | 0.08 | 0.14 | 0.00 | 0.05 | 0.02 | 0.05 | 0.02 | 0.05 | 0.14 | 0.24 |
| MgO | 17.37 | 16.48 | 16.30 | 17.01 | 16.72 | 20.09 | 19.94 | 18.38 | 18.64 | 19.63 | 24.27 | 24.42 | 24.49 | 24.53 | 20.54 | 18.88 | 19.78 | 20.06 |
| CaO | 0.37 | 0.27 | 0.27 | 0.23 | 0.15 | 0.07 | 0.04 | 0.10 | 0.13 | 0.08 | 0.07 | 0.02 | 0.05 | 0.06 | 0.22 | 1.11 | 0.16 | 0.24 |
| $Na_2O$ | 0.84 | 0.76 | 0.79 | 1.11 | 1.11 | 0.77 | 0.87 | 0.80 | 0.71 | 0.71 | 0.46 | 0.55 | 0.29 | 0.32 | 1.44 | 1.25 | 1.60 | 1.16 |
| $K_2O$ | 8.06 | 7.46 | 7.87 | 7.36 | 7.38 | 7.82 | 8.09 | 8.05 | 8.41 | 8.39 | 8.66 | 8.75 | 8.97 | 8.72 | 8.41 | 7.97 | 7.74 | 8.62 |
| $Cr_2O_3$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.03 | n.d. | 0.03 | 0.35 | 0.66 | 0.71 | 1.01 | n.d. | n.d. | n.d. | n.d. |
| BaO | 2.92 | 4.45 | 4.69 | 4.82 | 5.04 | 0.34 | 0.40 | 0.45 | 0.38 | 0.31 | 0.30 | 0.32 | 0.33 | 0.30 | 1.07 | 1.21 | 1.15 | 1.11 |
| Total | 94.48 | 95.39 | 93.68 | 96.05 | 95.48 | 94.70 | 95.23 | 94.64 | 95.13 | 96.35 | 93.45 | 94.29 | 94.30 | 93.93 | 96.64 | 94.54 | 95.54 | 97.65 |
| Si | 5.273 | 5.219 | 5.153 | 5.125 | 5.133 | 5.727 | 5.706 | 5.665 | 5.628 | 5.617 | 5.794 | 5.828 | 5.825 | 5.824 | 5.375 | 5.362 | 5.483 | 5.428 |
| $^{IV}Al$ | 2.229 | 2.338 | 2.321 | 2.339 | 2.365 | 2.097 | 2.089 | 2.141 | 2.166 | 2.196 | 2.206 | 2.172 | 2.175 | 2.176 | 2.276 | 2.372 | 2.236 | 2.225 |
| $^{IV}Fe^{2+}$ | 0.498 | 0.443 | 0.526 | 0.536 | 0.502 | 0.176 | 0.205 | 0.194 | 0.206 | 0.187 | 0.000 | 0.000 | 0.000 | 0.000 | 0.349 | 0.266 | 0.281 | 0.347 |
| $^{VI}Al$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.043 | 0.047 | 0.076 | 0.090 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ti | 1.098 | 1.147 | 1.117 | 1.148 | 1.140 | 0.723 | 0.773 | 0.876 | 0.837 | 0.762 | 0.202 | 0.191 | 0.174 | 0.175 | 0.842 | 0.879 | 0.863 | 0.876 |
| $^{VI}Fe^{2+}$ | 0.412 | 0.487 | 0.465 | 0.411 | 0.459 | 0.611 | 0.554 | 0.643 | 0.682 | 0.686 | 0.481 | 0.468 | 0.449 | 0.455 | 0.367 | 0.417 | 0.397 | 0.409 |
| Mn | 0.008 | 0.030 | 0.027 | 0.027 | 0.001 | 0.012 | 0.011 | 0.010 | 0.010 | 0.017 | 0.000 | 0.006 | 0.002 | 0.006 | 0.002 | 0.006 | 0.017 | 0.029 |
| Mg | 3.875 | 3.675 | 3.742 | 3.790 | 3.753 | 4.299 | 4.250 | 3.958 | 4.009 | 4.159 | 5.214 | 5.210 | 5.222 | 5.284 | 4.374 | 4.109 | 4.238 | 4.235 |
| Ca | 0.059 | 0.043 | 0.045 | 0.037 | 0.024 | 0.011 | 0.006 | 0.015 | 0.020 | 0.012 | 0.011 | 0.003 | 0.008 | 0.009 | 0.034 | 0.174 | 0.025 | 0.036 |
| Na | 0.244 | 0.221 | 0.236 | 0.322 | 0.324 | 0.214 | 0.241 | 0.224 | 0.199 | 0.196 | 0.129 | 0.153 | 0.080 | 0.090 | 0.399 | 0.354 | 0.446 | 0.319 |
| K | 1.539 | 1.424 | 1.547 | 1.404 | 1.418 | 1.432 | 1.476 | 1.484 | 1.548 | 1.522 | 1.593 | 1.598 | 1.637 | 1.608 | 1.533 | 1.485 | 1.419 | 1.558 |
| Ba | 0.171 | 0.261 | 0.283 | 0.282 | 0.297 | 0.019 | 0.022 | 0.025 | 0.021 | 0.017 | 0.017 | 0.018 | 0.020 | 0.017 | 0.060 | 0.069 | 0.065 | 0.062 |
| $Mg^{\#}$ | 0.81 | 0.80 | 0.79 | 0.80 | 0.80 | 0.85 | 0.85 | 0.83 | 0.82 | 0.83 | 0.92 | 0.92 | 0.92 | 0.92 | 0.86 | 0.86 | 0.86 | 0.85 |

| Locality | Ejevo Brdo | | | | | | | | | | Kureshnichka Krasta | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | micropheno-crysts | | microlite | | | | | poicilitic in the groundmass* | | | poicilitic in the grounmass | | | | | phenocryst | | | |
| | | | | | | | | rim | rim | rim | | | | | | core | rim | core | rim |
| $SiO_2$ | 33.41 | 32.98 | 32.80 | 32.20 | 32.95 | 33.47 | 32.75 | 32.47 | 36.42 | 38.45 | 34.76 | 34.31 | 36.21 | 35.12 | 35.04 | 36.57 | 39.77 | 36.42 | 38.45 |
| $TiO_2$ | 11.03 | 10.86 | 11.98 | 10.94 | 11.56 | 10.97 | 11.79 | 12.24 | 8.77 | 5.89 | 9.19 | 9.04 | 8.94 | 7.69 | 8.36 | 7.95 | 6.19 | 8.77 | 5.89 |
| $Al_2O_3$ | 15.47 | 15.46 | 13.98 | 14.38 | 14.25 | 13.24 | 14.20 | 14.88 | 13.33 | 11.63 | 13.6 | 12.99 | 13.06 | 13.17 | 13.4 | 13.14 | 14.36 | 13.33 | 11.63 |
| FeO | 11.38 | 9.84 | 9.74 | 10.11 | 8.51 | 9.84 | 9.73 | 9.10 | 9.76 | 9.56 | 9.51 | 9.97 | 8.76 | 9.16 | 9.79 | 8.84 | 9.09 | 9.76 | 9.56 |
| MnO | 0.08 | 0.14 | 0.45 | 0.00 | 0.26 | 0.06 | 0.19 | 0.00 | 0.11 | 0.13 | 0.00 | 0.00 | 0.05 | 0.21 | 0.00 | 0.09 | 0.13 | 0.11 | 0.13 |
| MgO | 12.99 | 13.91 | 13.32 | 14.09 | 13.99 | 13.65 | 13.71 | 13.73 | 16.25 | 17.92 | 17.5 | 15.88 | 17.91 | 18.2 | 17.14 | 17.35 | 14.44 | 16.25 | 17.92 |
| CaO | 0.21 | 0.07 | 0.55 | 0.14 | 0.34 | 0.04 | 0.26 | 0.19 | 0.03 | 1.77 | 0.14 | 0.09 | 0.18 | 0.14 | 0.19 | 0.02 | 0.96 | 0.03 | 1.77 |
| $Na_2O$ | 0.56 | 0.59 | 0.36 | 1.00 | 0.64 | 0.62 | 0.87 | 0.78 | 0.58 | 0.51 | 0.69 | 1.09 | 1.10 | 0.68 | 0.91 | 0.60 | 0.85 | 0.58 | 0.51 |
| $K_2O$ | 5.96 | 5.81 | 6.61 | 6.38 | 6.97 | 7.26 | 6.49 | 6.58 | 7.39 | 8.26 | 7.89 | 8.29 | 8.38 | 7.90 | 8.19 | 7.41 | 8.06 | 7.39 | 8.26 |
| $Cr_2O_3$ | 0.20 | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.02 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.05 | 0.04 | n.d. | 0.02 |
| BaO | 8.22 | 8.21 | 5.78 | 6.43 | 5.83 | 5.13 | 6.36 | 6.98 | 3.95 | 0.15 | 3.50 | 3.49 | 3.30 | 3.39 | 3.43 | 3.76 | 0.07 | 3.95 | 0.15 |
| Total | 99.51 | 97.91 | 95.57 | 95.67 | 95.30 | 94.28 | 96.35 | 96.95 | 96.59 | 94.29 | 96.78 | 95.15 | 97.89 | 95.66 | 96.45 | 95.78 | 93.96 | 96.59 | 94.29 |
| Si | 4.972 | 4.950 | 5.008 | 4.940 | 5.022 | 5.159 | 4.976 | 4.907 | 5.381 | 5.672 | 5.146 | 5.207 | 5.280 | 5.249 | 5.219 | 5.409 | 5.814 | 5.381 | 5.672 |
| $^{IV}Al$ | 2.713 | 2.734 | 2.515 | 2.599 | 2.559 | 2.405 | 2.542 | 2.650 | 2.320 | 2.021 | 2.372 | 2.323 | 2.244 | 2.319 | 2.352 | 2.290 | 2.186 | 2.320 | 2.021 |
| $^{IV}Fe^{2+}$ | 0.315 | 0.316 | 0.477 | 0.461 | 0.419 | 0.436 | 0.482 | 0.443 | 0.299 | 0.307 | 0.482 | 0.470 | 0.476 | 0.432 | 0.429 | 0.301 | 0.000 | 0.299 | 0.307 |
| $^{VI}Al$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.974 | 0.653 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.288 | 0.000 | 0.000 |
| Ti | 1.234 | 1.225 | 1.375 | 1.262 | 1.324 | 1.271 | 1.347 | 1.390 | 0.906 | 0.872 | 1.023 | 1.031 | 0.980 | 0.864 | 0.936 | 0.884 | 0.680 | 0.974 | 0.653 |
| $^{VI}Fe^{2+}$ | 1.100 | 0.919 | 0.766 | 0.836 | 0.665 | 0.832 | 0.753 | 0.707 | 0.014 | 0.016 | 0.695 | 0.795 | 0.591 | 0.713 | 0.790 | 0.792 | 1.111 | 0.906 | 0.872 |
| Mn | 0.010 | 0.018 | 0.058 | 0.000 | 0.034 | 0.008 | 0.024 | 0.000 | 3.576 | 3.937 | 0.000 | 0.000 | 0.006 | 0.027 | 0.000 | 0.011 | 0.016 | 0.014 | 0.016 |
| Mg | 2.880 | 3.110 | 3.029 | 3.220 | 3.176 | 3.134 | 3.103 | 3.091 | 0.005 | 0.280 | 3.859 | 3.590 | 3.890 | 4.052 | 3.803 | 3.822 | 3.145 | 3.576 | 3.937 |
| Ca | 0.033 | 0.011 | 0.090 | 0.023 | 0.055 | 0.007 | 0.042 | 0.031 | 0.166 | 0.146 | 0.022 | 0.015 | 0.028 | 0.022 | 0.030 | 0.003 | 0.150 | 0.005 | 0.280 |
| Na | 0.162 | 0.172 | 0.107 | 0.297 | 0.189 | 0.185 | 0.256 | 0.228 | 1.392 | 1.554 | 0.198 | 0.321 | 0.311 | 0.197 | 0.263 | 0.172 | 0.241 | 0.166 | 0.146 |
| K | 1.131 | 1.112 | 1.287 | 1.248 | 1.355 | 1.427 | 1.257 | 1.268 | 0.229 | 0.009 | 1.489 | 1.604 | 1.558 | 1.506 | 1.556 | 1.397 | 1.503 | 1.392 | 1.554 |
| Ba | 0.483 | 0.483 | 0.346 | 0.386 | 0.348 | 0.310 | 0.378 | 0.413 | 0.750 | 0.770 | 0.203 | 0.207 | 0.188 | 0.198 | 0.200 | 0.218 | 0.004 | 0.229 | 0.009 |
| $Mg^{\#}$ | 0.67 | 0.72 | 0.71 | 0.71 | 0.75 | 0.71 | 0.72 | 0.73 | 0.70 | 0.73 | 0.77 | 0.74 | 0.78 | 0.78 | 0.76 | 0.78 | 0.74 | 0.75 | 0.77 |

*the cores are opacitised

*Selected microprobe analyses of **feldspars** and calculated formulae (based on 8 oxygens)*

| Locality | Mlado Nagorichane | | | | | | | | | Djurishte | | | | Gradishte | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | Na-sanidine | | | | Ba-Na sanidine | | | Na-sanidine | | Na-sanidine | | anorthoclase | | Na- to Ba-Na sanidine | | | |
| | groundmass | | miarolic | | | | | after leucite | | microlites | | | | microlites | | | |
| $SiO_2$ | 60.90 | 64.78 | 63.98 | 63.53 | 60.85 | 59.99 | 59.35 | 64.55 | 64.70 | 63.66 | 63.19 | 63.77 | 63.12 | 63.01 | 61.75 | 62.26 | 62.74 |
| $Al_2O_3$ | 20.33 | 18.33 | 19.77 | 20.31 | 21.17 | 21.69 | 21.45 | 20.01 | 19.46 | 20.60 | 20.23 | 20.65 | 20.68 | 20.53 | 19.64 | 19.88 | 20.61 |
| FeO | 0.57 | 0.78 | 0.50 | 0.32 | 0.62 | 0.85 | 0.50 | 0.48 | 0.30 | 0.53 | 0.54 | 0.40 | 0.56 | 0.64 | 0.84 | 0.50 | 0.41 |
| CaO | 0.41 | 0.36 | 0.55 | 0.68 | 0.60 | 0.56 | 0.62 | 0.91 | 0.65 | 1.38 | 1.23 | 1.39 | 1.72 | 1.30 | 2.10 | 0.76 | 1.01 |
| $Na_2O$ | 4.40 | 3.58 | 5.15 | 5.35 | 4.39 | 4.65 | 4.76 | 5.88 | 4.86 | 5.21 | 4.91 | 5.62 | 5.76 | 4.81 | 4.01 | 4.57 | 4.92 |
| $K_2O$ | 7.97 | 11.23 | 8.68 | 8.07 | 8.42 | 8.01 | 7.92 | 8.05 | 9.76 | 6.95 | 7.10 | 6.00 | 5.59 | 7.48 | 7.71 | 7.87 | 7.85 |
| SrO | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.16 | 0.19 | 0.41 | 0.18 | 0.00 | 0.48 | 0.16 | n.d |
| BaO | 5.19 | 0.00 | 0.89 | 1.63 | 3.53 | 3.87 | 5.37 | 0.10 | 0.00 | 0.48 | 0.37 | 0.47 | 0.50 | 1.73 | 1.43 | 0.58 | 2.47 |
| Total | 99.77 | 99.06 | 99.52 | 99.89 | 99.58 | 99.62 | 99.97 | 99.98 | 99.73 | 98.97 | 97.76 | 98.71 | 98.11 | 99.50 | 97.96 | 96.58 | 100.01 |
| Si | 2.862 | 2.981 | 2.922 | 2.904 | 2.839 | 2.806 | 2.801 | 2.920 | 2.940 | 2.900 | 2.912 | 2.904 | 2.890 | 2.888 | 2.888 | 2.916 | 2.881 |
| Al | 1.126 | 0.994 | 1.064 | 1.094 | 1.164 | 1.196 | 1.193 | 1.067 | 1.042 | 1.106 | 1.099 | 1.108 | 1.116 | 1.109 | 1.083 | 1.097 | 1.116 |
| $Fe^{2+}$ | 0.020 | 0.027 | 0.019 | 0.011 | 0.022 | 0.030 | 0.020 | 0.016 | 0.011 | 0.018 | 0.019 | 0.014 | 0.019 | 0.022 | 0.030 | 0.018 | 0.014 |
| Ca | 0.021 | 0.018 | 0.027 | 0.033 | 0.030 | 0.028 | 0.031 | 0.044 | 0.032 | 0.067 | 0.061 | 0.068 | 0.084 | 0.064 | 0.105 | 0.038 | 0.050 |
| Na | 0.401 | 0.319 | 0.456 | 0.474 | 0.397 | 0.422 | 0.436 | 0.516 | 0.428 | 0.460 | 0.439 | 0.496 | 0.511 | 0.427 | 0.364 | 0.415 | 0.438 |
| K | 0.478 | 0.659 | 0.506 | 0.471 | 0.501 | 0.478 | 0.477 | 0.465 | 0.566 | 0.404 | 0.417 | 0.349 | 0.327 | 0.437 | 0.460 | 0.470 | 0.460 |
| Sr | - | - | - | - | - | - | - | - | - | 0.004 | 0.005 | 0.011 | 0.005 | - | 0.013 | 0.004 | - |
| Ba | 0.096 | 0.00 | 0.016 | 0.029 | 0.065 | 0.071 | 0.099 | 0.002 | 0.000 | 0.009 | 0.007 | 0.008 | 0.009 | 0.031 | 0.026 | 0.011 | 0.044 |
| An | 2.3 | 1.8 | 2.8 | 3.4 | 3.2 | 3.0 | 3.3 | 4.3 | 3.1 | 7.2 | 6.6 | 7.4 | 9.2 | 6.9 | 11.3 | 4.2 | 5.3 |
| Ab | 44.6 | 32.1 | 46.1 | 48.5 | 42.8 | 45.5 | 46.2 | 50.4 | 41.7 | 49.4 | 47.9 | 54.4 | 55.4 | 46.0 | 39.1 | 44.9 | 46.2 |
| Or | 53.1 | 66.1 | 51.1 | 48.1 | 54.0 | 51.5 | 50.5 | 45.3 | 55.2 | 43.4 | 45.5 | 38.2 | 35.4 | 47.1 | 49.5 | 50.9 | 48.5 |
| Cn | 9.6 | 0.0 | 1.6 | 2.9 | 6.5 | 7.1 | 9.5 | 0.2 | 0.0 | 0.9 | 0.7 | 0.9 | 1.0 | 3.2 | 2.7 | 1.1 | 4.5 |

| Locality | Kishino | | | | Ejevo Brdo | | | | | | | | | Kureshnichka Krasta | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | Na-sanidine | anorthoclase | | | Ba-Sr-plagioclase | | | | | Ba-Sr feldspars | | Na-sani-dine | anorth oclase | Na-sanidine | | sanidine | |
| | microlite | | miarolic | | micro | core | rim | core | rim | core* | rim* | | | microlites | | | radial |
| $SiO_2$ | 63.56 | 61.06 | 63.20 | 61.27 | 59.58 | 59.06 | 60.09 | 57.93 | 62.27 | 58.76 | 60.29 | 64.58 | 63.79 | 65.09 | 64.58 | 65.12 | 64.46 |
| $Al_2O_3$ | 19.4 | 21.55 | 21.52 | 22.11 | 24.47 | 24.43 | 24.27 | 24.86 | 23.42 | 23.46 | 23.2 | 20.09 | 22.63 | 18.99 | 20.09 | 19.14 | 19.30 |
| FeO | 0.52 | 0.40 | 0.31 | 0.45 | 0.33 | 0.53 | 0.49 | 0.53 | 0.49 | 0.53 | 0.54 | 0.72 | 0.42 | 0.61 | 0.65 | 0.56 | 0.68 |
| CaO | 0.54 | 1.24 | 1.34 | 2.36 | 5.21 | 4.02 | 4.68 | 4.00 | 3.69 | 2.51 | 4.22 | 0.50 | 2.91 | 0.46 | 0.50 | 0.19 | 0.34 |
| $Na_2O$ | 4.72 | 5.63 | 6.30 | 7.80 | 7.34 | 6.06 | 7.22 | 6.14 | 7.64 | 5.25 | 7.40 | 4.92 | 7.24 | 4.06 | 4.92 | 2.69 | 4.05 |
| $K_2O$ | 9.80 | 6.35 | 6.32 | 3.66 | 1.28 | 2.23 | 1.25 | 2.31 | 2.14 | 4.11 | 1.25 | 9.20 | 3.29 | 9.42 | 9.20 | 11.91 | 10.85 |
| SrO | n.d | n.d. | n.d. | n.d. | n.d. | 1.97 | 1.35 | 2.72 | 0.54 | 3.04 | 0.68 | n.d. | 0.25 | n.d. | n.d. | 0.21 | n.d |
| BaO | 0.39 | 2.23 | 0.94 | 0.87 | 0.42 | 1.84 | 0.64 | 2.11 | 0.37 | 2.94 | 0.39 | 0.18 | 0.11 | 0.06 | 0.18 | 0.03 | 0.18 |
| Total | 98.93 | 98.46 | 99.93 | 98.52 | 98.63 | 100.14 | 99.99 | 100.60 | 100.56 | 100.6 | 97.97 | 100.19 | 100.64 | 98.69 | 100.12 | 99.85 | 99.86 |
| Si | 2.930 | 2.834 | 2.861 | 2.802 | 2.701 | 2.694 | 2.708 | 2.655 | 2.772 | 2.719 | 2.752 | 2.923 | 2.827 | 2.977 | 2.925 | 2.973 | 2.944 |
| Al | 1.054 | 1.179 | 1.148 | 1.192 | 1.307 | 1.314 | 1.289 | 1.343 | 1.229 | 1.279 | 1.248 | 1.072 | 1.182 | 1.024 | 1.072 | 1.030 | 1.039 |
| $Fe^{2+}$ | 0.018 | 0.014 | 0.011 | 0.015 | 0.011 | 0.018 | 0.017 | 0.018 | 0.016 | 0.018 | 0.019 | 0.025 | 0.014 | 0.021 | 0.022 | 0.019 | 0.023 |
| Ca | 0.027 | 0.062 | 0.065 | 0.116 | 0.253 | 0.196 | 0.226 | 0.196 | 0.176 | 0.124 | 0.206 | 0.024 | 0.138 | 0.023 | 0.024 | 0.009 | 0.017 |
| Na | 0.422 | 0.507 | 0.553 | 0.692 | 0.645 | 0.536 | 0.631 | 0.546 | 0.660 | 0.471 | 0.655 | 0.432 | 0.622 | 0.360 | 0.432 | 0.238 | 0.359 |
| K | 0.576 | 0.376 | 0.365 | 0.214 | 0.074 | 0.130 | 0.072 | 0.135 | 0.122 | 0.243 | 0.073 | 0.531 | 0.186 | 0.550 | 0.532 | 0.694 | 0.632 |
| Sr | - | - | - | - | - | 0.052 | 0.035 | 0.072 | 0.014 | 0.082 | 0.018 | - | 0.006 | - | - | 0.006 | - |
| Ba | 0.007 | 0.041 | 0.017 | 0.016 | 0.007 | 0.033 | 0.011 | 0.038 | 0.006 | 0.053 | 0.007 | 0.003 | 0.002 | 0.001 | 0.003 | 0.001 | 0.003 |
| An | 2.6 | 6.5 | 6.6 | 11.3 | 26.0 | 22.8 | 24.3 | 22.4 | 18.4 | 14.9 | 22.1 | 2.5 | 14.6 | 2.4 | 2.5 | 1.0 | 1.7 |
| Ab | 41.2 | 53.7 | 56.3 | 67.8 | 66.4 | 62.2 | 67.9 | 62.2 | 68.9 | 56.2 | 70.1 | 43.7 | 65.7 | 38.6 | 43.7 | 25.3 | 35.6 |
| Or | 56.2 | 39.8 | 37.1 | 20.9 | 7.6 | 15.0 | 7.8 | 15.4 | 12.7 | 28.9 | 7.8 | 53.8 | 19.7 | 59.0 | 53.8 | 73.7 | 62.7 |
| Cn | 0.7 | 4.1 | 1.7 | 1.5 | 0.8 | 3.67 | 1.2 | 4.1 | 0.7 | 6.0 | 0.7 | 0.3 | 0.2 | 0.1 | 0.3 | 0.1 | 0.3 |

*core – Ba-Sr anorthoclase, rim – plagioclase

*Selected microprobe analyses of **foides** and calculated formulae (based of 6 oxigens for leucite, and 8 for nepheline)*

| Locality | Mlado Nagorichane | | Kishino | | | | | | Ejevo Brdo | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | leucite | | leucite | | | | nepheline | | leucite | | |
| | phenocryst | | microphenocryst | | | | after leucite | miarolic | microphenocryst | | |
| $SiO_2$ | 55.87 | 55.90 | 54.54 | 55.39 | 55.35 | 54.54 | 48.63 | 49.19 | 54.78 | 55.37 | 54.51 |
| $TiO_2$ | n.d. | 0.04 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.27 | n.d. | 0.28 |
| $Al_2O_3$ | 22.21 | 22.11 | 23.72 | 23.50 | 23.34 | 23.72 | 29.77 | 30.73 | 22.56 | 22.48 | 21.90 |
| $Fe_2O_3$ | 0.98 | 0.49 | 0.63 | 0.51 | 0.56 | 0.63 | 0.99 | 0.84 | 0.82 | 0.40 | 0.63 |
| MgO | n.d. | n.d. | 0.56 | 0.14 | 0.19 | 0.56 | n.d. | n.d. | n.d. | n.d. | n.d. |
| CaO | 0.49 | 0.71 | 0.27 | 0.17 | 0.31 | 0.27 | 0.16 | 0.16 | 0.49 | 0.43 | 0.37 |
| $Na_2O$ | 0.14 | 0.06 | 0.37 | 0.47 | 0.35 | 0.37 | 17.41 | 16.40 | 0.49 | 0.20 | 0.06 |
| $K_2O$ | 20.04 | 20.54 | 18.85 | 19.71 | 19.47 | 18.85 | 2.34 | 2.52 | 20.67 | 20.94 | 21.59 |
| BaO | 0.27 | 0.14 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Total | 100.00 | 99.99 | 98.94 | 99.89 | 99.57 | 98.94 | 99.30 | 99.84 | 100.08 | 99.82 | 99.34 |
| Si | 2.027 | 2.029 | 1.981 | 2.000 | 2.002 | 1.981 | 2.294 | 2.297 | 1.992 | 2.014 | 2.005 |
| Ti | - | 0.001 | - | - | - | - | - | - | 0.007 | - | 0.008 |
| Al | 0.950 | 0.946 | 1.016 | 1.000 | 0.995 | 1.016 | 1.656 | 1.691 | 0.967 | 0.964 | 0.950 |
| $Fe^{3+}$ | 0.030 | 0.015 | 0.019 | 0.015 | 0.017 | 0.019 | 0.035 | 0.030 | 0.220 | 0.011 | 0.170 |
| Mg | - | - | 0.030 | 0.008 | 0.010 | 0.030 | - | - | - | - | - |
| Ca | 0.019 | 0.028 | 0.011 | 0.007 | 0.012 | 0.011 | 0.008 | 0.008 | 0.019 | 0.017 | 0.015 |
| Na | 0.010 | 0.004 | 0.026 | 0.033 | 0.025 | 0.026 | 1.593 | 1.485 | 0.035 | 0.014 | 0.004 |
| K | 0.928 | 0.951 | 0.874 | 0.908 | 0.898 | 0.874 | 0.141 | 0.150 | 0.959 | 0.972 | 1.003 |
| Ba | 0.004 | 0.002 | -- | -- | - | - | - | - | - | - | - |

*Selected microprobe analyses of* ***Fe-Ti oxides***

| Locality | Djurishte | | | | | Gradishte | Ejevo Brdo | | | Kureshnichka Krasta | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mineral | ilmenite | | Ti-magnetite | | | Ti-magnetite | Ti-magnetite | | | Ti-magnetite | | | |
| $SiO_2$ | 0.97 | 1.35 | 0.04 | 0.02 | 0.36 | 0.00 | 5.59 | 19.11 | 19.55 | 0.07 | 0.09 | 0.06 | 0.12 |
| $TiO_2$ | 43.10 | 40.72 | 9.46 | 14.92 | 14.54 | 16.11 | 13.26 | 13.16 | 11.63 | 15.79 | 16.11 | 15.24 | 12.66 |
| $Al_2O_3$ | 0.43 | 0.56 | 2.86 | 2.67 | 2.80 | 0.72 | 4.22 | 6.98 | 9.16 | 0.96 | 1.56 | 0.59 | 0.63 |
| $Cr_2O_3$ | 0.19 | 0.00 | 0.03 | 0.06 | 0.07 | 0.13 | 0.14 | 0.05 | 0.13 | 0.00 | 0.00 | 0.03 | 0.00 |
| FeO | 41.70 | 45.85 | 77.17 | 71.31 | 70.08 | 75.22 | 64.63 | 52.60 | 49.22 | 75.84 | 74.87 | 77.05 | 79.00 |
| MnO | 0.84 | 0.49 | 0.65 | 0.78 | 0.84 | 0.78 | 0.80 | 0.53 | 0.59 | 0.82 | 0.66 | 0.68 | 0.86 |
| MgO | 4.31 | 3.08 | 3.51 | 5.12 | 5.06 | 1.76 | 3.09 | 1.72 | 3.03 | 2.42 | 3.16 | 1.88 | 1.78 |
| CaO | 0.07 | 0.07 | 0.08 | 0.05 | 0.16 | 0.20 | 1.08 | 0.39 | 1.81 | 0.00 | 0.07 | 0.08 | 0.01 |
| $Na_2O$ | 0.00 | 0.14 | 0.11 | 0.07 | 0.00 | 0.00 | 0.18 | 1.15 | 0.34 | 0.24 | 0.05 | 0.19 | 0.00 |
| $K_2O$ | 0.19 | 0.15 | 0.04 | 0.06 | 0.13 | 0.11 | 0.16 | 0.46 | 0.87 | 0.01 | 0.00 | 0.05 | 0.01 |
| NiO | 0.08 | 0.04 | 0.12 | 0.11 | 0.12 | 0.16 | 0.00 | 0.04 | 0.03 | 0.06 | 0.12 | 0.05 | 0.03 |
| BaO | 0.28 | 0.27 | 0.05 | 0.10 | 0.12 | 0.15 | 0.07 | 0.11 | 0.55 | 0.12 | 0.13 | 0.17 | 0.04 |
| Total | 92.16 | 92.72 | 94.12 | 95.27 | 94.28 | 95.34 | 93.22 | 96.30 | 96.91 | 96.33 | 96.82 | 96.07 | 95.14 |