Минно-геоложки университет "Св. Иван Рилски"
Годишник, том 47, свитък I, Геология и геофизика, София, 2004, стр. 27-32

ALKALINE BASALTS FROM THE VILLAGE DOBRINOVO AREA, KARNOBAT DISTRICT (Southeastern Bulgaria)

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ABSTRACT. Alkaline basalts are determined in the explosive facies products of the Draganovo Formation in the village Dobrinovo area to the south of Karnobat. They are composed from clinopyroxene, olivine, pseudoleucite, K-feldspar, analcime, plagioclase, biotite, apatite, magnetite and titanomagnetite. Alkaline basalts are undersaturated in SiO_2, olivine and nepheline normative. They are with increased potassium alkalinity and refer to the shoshonitic series. The geochemical features determine them as within-plate ocean-island basalts. The petrochemical indexes and parameters are close to these of the primary weakly differentiated magmas. The establishment of these alkaline basalts around Dobrinovo village enlarges the area of distribution of such rocks outside the area of the St. Spas and Tamarino Bakadjik leucite-bearing rocks to which they display close affinity.

АЛКАЛНИ БАЗАЛТИ ОТ РАЙОНА НА СЕЛО ДОБРИНОВО, КАРНОБАТСКО (Югоизточна България)

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РЕЗЮМЕ. Алкалните базалти са установени в продуктите на експлозивния фациес на Драгановската свита, в района на село Добриново, южно от Карнобат. Те са изградени от клинопироксен, оливин, псевдолевцит, К-фелдшпат, аналцим, плагиоклаз, биотит, апатит, магнетит и титаномагнетит. Алкалните базалти са ненаситени на SiO_2, оливин и нефелин нормативни. Те са с повишена калиева алкалност и шошонитова сериалност. Геохимичните особености ги определят като вътрешноплочови океанско-островни базалти. Петрохимичните индекси и параметри са близки до тези на първичните, слабо диференцирани магми. С установяването на алкални базалти около село Добриново се разширява ареала на разпространение на тези скали, извън района на описаните в Св. Спаски и Тамарински Бакаджик левцитсъдържащи скали, с които показват близко петрохимично сродство.

Introduction

In spite of the alkaline rocks insignificant spread, their specific composition, unusual mineral combinations and formation conditions have always risen interest among the research workers. One of the most important reasons of the described alkaline basalts from the Eastern Srednogorie is the presence of pseudoleucite aggregates, which composition and genesis are not well clarified yet.

In the Eastern Srednogorie central parts the leucite-bearing rocks are described in the St. Spas Bakadjik area (Stoinov, 1955, Banushev, 2003) and Tamarino Bakajik (Stanisheva, 1969). Short information about similar rocks in other Eastern Srednogorie areas has been published by Rashkov (1973) and Marinov and Bairaktarov (1981) (Fig. 1). Essentially, the rocks described at the researches are pseudoleucites because there is no intact leucite but only its typical crystal forms and altered products could be determined. The pseudoleucite rocks determination around Dobrinovo village expands the area of these volcanics spread in the Eastern Srednogorie. The paper presents the results from petrology researches of the alkaline basalts containing pseudoleucite aggregates, which are undescribed to the moment for the region. A connection between the rocks geochemical features and the tectonic settings is made. Some aspects of the so called pseudoleucite problem are discussed.

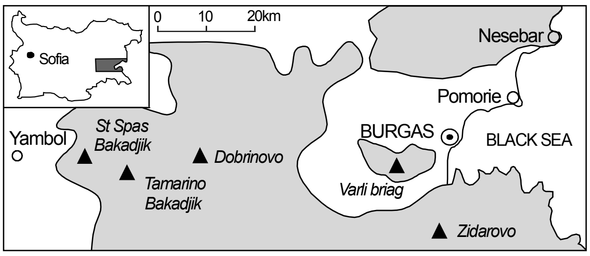

Fig. 1. Simplified sketch of leucite-bearing rocks spread in the Eastern Srednogorie

Geological setting

The researched region is built from the volcanogenic materials of Draganovo, Tankovo and Medovo Formations. The alkaline basalts are determined in the explosive facies of the Draganovo formation products at about 2 km to the northeast of Dobrinovo village, Karnobat region in the Goliamata river valley. They are as lithoclasts in the pyroclastites, widely disclosing in the area. The Tankovo and Medovo Formations disclose to the north of the Dobrinovo village. They are submitted with agglomerates (containing varied volcanics fragments), ash tuffs and lava rivers. The Upper Cretaceous volcanics and pyroclastites in the region are assigned to different lithostratigraphic units – Novopancharevo Formation (Popov and Antimova, 1982), Burgas group (Petrova and Simeonov 1989), Bakadjik Formation (Popov et al., 1993) and Draganovo Formation (Savov and Filipov, 1995).

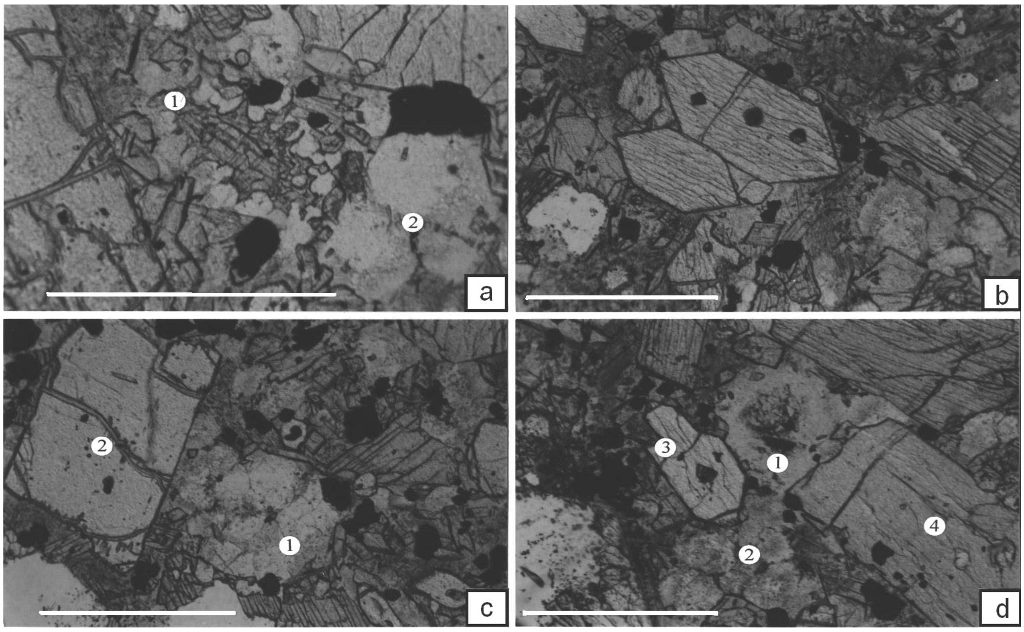

Fig. 2. Photomicrographs of alkaline basalts from the Dobrinovo village area: a- magmatically corroded clinopiroxene (1) with pseudoleucite in the periphery and pseudoleucite aggregates built from analcime in the central and K-feldshpar in peripheral parts (2); b - fresh olivine with regular crystallographic shapes and magnetite inclusions; c - pseudoleucite crystal with well intact primary morphology (1) and olivine (2); d - pseudoleucite crystal with inclusions in the central parts (1), a group of pseudoleucite aggregates (2), olivine (3) and clinopyroxene (4). Figures a-d II N. Scale bars – 0.5 mm

Analytical techniques

The microprobe researches of the alkaline basalts from the Dobrinovo villege area are made by microscopes Amplival and Leitz Orthoplan. The microprobe analyses are made by Eurotest-Control LTD, Sofia by JEOL JCM 35 CF electron microprobe (Tracor Northern TN - 2000 microanalyser) using an energy-dispersive system with counting times of 100 s at 20 kV with sample current of 2.10^{-9} A. The rocks chemical composition is determined in the University of Mining and Geology “St. Ivan Rilski” – Sofia by an atomic-emission spectral analysis with inductively connected plasma (ICP-AES). The trace elements are determined by ICP in Amman, Jordan by Phillips 3410 equipment, design A.

Petrography

The area around Dobrinovo village is predominantly built from the Draganovo Formation agglomerates, which are the prevalent rock species. The lappili, ash (crystal and vitric) tuffs and epiclastites are subordinate quantities. Trachybasalts dykes with thickness of about 1 m and lava flow with alkaline-basaltoid composition are determined among the agglomerates. Often, the upper and lower river parts are brecciated and in some parts they turn into typical lava breccia. The agglomerates are massive, built from various volcanics fragments, which quantity exceed to 50-60% of the rock volume, and sizes - predominantly about 10-20 cm. The cement is pyroclastic, consisting of crystal, vitric and fine lithic fragments. The volcanic clasts are presented by olivine basalts, olivine melabasalts (ankaramites), feldspar free basaltoids with transitions to picrites, K-trachybasalts, shoshonites and rarely – to pseudoleucite basanites and latites.

The alkaline basalts are dark green to black with massive structure. They are built from clinopyroxene, olivine, pseudoleucite, K-feldspar, analcime, plagioclase, biotite, apatite, magnetite and titanomagnetite. The phenocrysts are from 25 to 60% from the rock volume. In quantitative ratio, the clinopyroxenes poorly prevail over the olivine. Rarely, the ratio clinopyroxene/olivine is almost equal. The clinopyroxenes (15-35%) are light green, fresh, short-prismatic (1.5-6mm x 0.5-2mm), with zonal-sector structure type “sand-watch”. They contain rare inclusions of volcanic glass, olivine subphenocrysts, and magnetite. In some places in their peripheral parts a magmatic corrosion – result from their reactionary interaction with the liquid (Fig. 2a) is observed. The olivine (10-25%) is in typical crystallographic forms in sizes 0.5-1.5 mm (Fig. 2b). It is fresh, rarely - with insignificant peripheral serpentinization, contains rare magnetite inclusions (Fig. 2b). The subphenocrysts generation is presented by pseudoleucite, clinopyroxene and olivine. The pseudoleucite aggregates (5-15%) are equant, rounded, with average sizes 0.09-0.18mm and rarely to 0.4mm (Fig. 2c, d). They are unequally spread as single crystals or in groups and have well intact primary morphology (Fig. 2c). Some of them contain clinopyroxene inclusions, which most often are located in parallel with the crystal walls. They consist of analcime in the central parts and K-feldspar - in peripheral and often they are totally of columnar fabric aggregate from K-feldspar and form pseudomorphosis on leucite without intact relics. The groundmass is holocrystalline, built from a large quantity of thin-prismatic clinopyroxenic microlites olivine grains, pseudoleucite, K-feldspar, fine biotite flakes and very rare poorly individualized plagioclase microlites without clear end contours. The accessory minerals are presented by magnetite, rare skeletal-nuclear crystals of titanomagnetite and strongly lengthened acicular apatite. The texture is porphyritic, seriate-porphyritic, with tendency to glomeroporphyritic in places. The minerals crystallization order, determined by the crystals morphology and mineral interactions is: magnetite - olivine-clinopyroxene - pseudoleucite.

Table 1.
Representative microprobe analyses of the clinopyroxenes, olivines, K-feldspars and analcimes from the alkaline basalts from the Dobrinovo village: c – core; r – rim; s - subphenocrysts

Mineral	clinopyroxenes			olivines			K-feldspars			analcimes	
Sample	424c	424r	377s	424c	424r	377s	424	377	377/1	424	377
SiO_2	50.33	50.96	49.15	40.18	41.73	39.42	61.62	64.14	63.98	55.10	53.67
TiO_2	0.36	0.58	0.43	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00
Al_2O_3	4.24	3.18	2.94	0.00	0.11	0.26	20.65	20.05	18.85	22.93	23.63
$FeO^{(t)}$	6.72	8.27	8.48	9.29	10.01	18.59	1.03	0.93	0.44	0.94	0.77
MnO	0.04	0.06	0.27	0.35	0.20	0.15	0.00	0.00	0.00	0.00	0.00
MgO	14.83	14.98	17.74	49.15	47.39	41.16	0.00	0.00	0.00	0.00	0.00
CaO	23.10	21.44	20.31	0.49	0.51	0.31	2.32	1.18	0.94	1.00	0.87
Na_2O	0.03	0.14	0.22	0.00	0.00	0.00	0.76	0.97	1.09	11.74	12.17
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	13.29	12.48	14.17	0.26	0.21
H_2O*	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	8.03	8.68
Total	99.65	99.61	99.54	99.46	99.95	99.89	99.67	99.75	99.53	100.00	100.00
Wo	47.13	43.95	39.19								
En	42.10	42.72	47.63								
Fs	10.77	13.33	13.18								
$Mg^{\#}$	79.7	76.3	78.8								
Fo				90.40	89.41	79.79					
Fa				9.60	10.59	20.21					
Or							81.06	83.49	85.30		
Ab							7.05	9.87	9.96		
An							11.89	6.64	4.74		

***H_2O is calculated by difference to 100%**

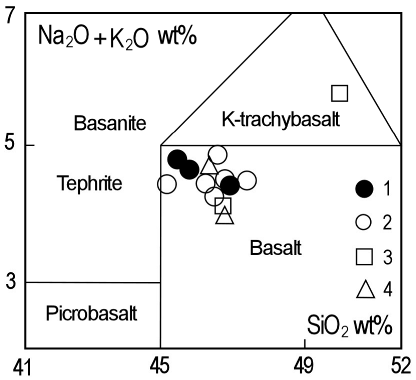

Fig. 3. Total alkali vs. silica classification diagram (after Le Maitre et al., 1989) with the point of volcanics from the Eastern Srednogorie:
1 – Dobrinovo village; 2 - St. Spas Bakadjik (Banushev, 2003);
3 – Pobeda village (Stoinov, 1955); 4 - Tamarino Bakadjik (Stanisheva, 1969)

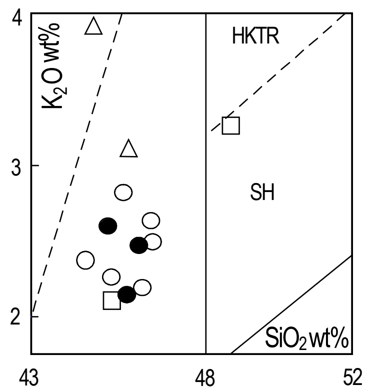

Fig. 4. SiO_2 vs. K_2O (Peccerillo and Taylor, 1976) diagram with the point of volcanics from the Eastern Srednogorie. Series: SH – shoshonitic; HKTR – high K transitional. Symbols as in Fig. 3

Mineral chemistry

The clinopyroxenes are Mg-rich ($Mg^{\#}$ - 76.3-79.7). In accordance with the Morimoto classification (1988) they are augites and diopsides. The clinopyroxenes have zonal structure. The content in their central parts is $Wo_{47}En_{42}$ and in peripheral $Wo_{43}En_{42}$. An increase of the FeO, Na_2O and SiO_2 is observed to the crystals peripheral parts (Table 1). The subphenocrysts content is $Wo_{39}En_{47}$. The olivines are high-Mg – $Fo_{90}Fa_9$ in the central and $Fo_{89}Fa_{10}$ in the peripheral parts. There is an increase in SiO_2 and FeO and decrease in MgO contents from the central to the peripheral parts of the crystals (Table 1). The analcime from the pseudoleucite aggregates has a comparatively constant content without considerable alterations of the major oxides. The most typical feature of the researched K-feldspars, from the pseudoleucite aggregates, chemistry is the Or-molecule ($Or_{81-85}Ab_{7-10}$) high content corresponding to K-sanidine.

Chemical composition

Major elements

The described alkaline basalts are high-K (according to the Le Maitre et al., 1989 nomenclature), high-Mg and low-Al. The ratio K_2O/Na_2O is from 0.92 to 1.47. The peralkaline index (P.I.) is between 0.63 and 0.66 and a little lower (0.56-0.59) in the St. Spas Bakadjik volcanics (Table 2). The solidification index (S.I. – 39-47) and the differentiation one (D.I. 13-20) are close to those of the primary poorly differentiated magmas.

Table 2.

Chemical composition (wt %) of the alkaline basalts from the Dobrinovo village region

	377	377/1	424	376/1	376	361
SiO_2	45.18	45.82	46.06	45.58	46.55	46.30
TiO_2	0.60	0.54	0.50	0.56	0.62	0.65
Al_2O_3	9.99	9.80	8.76	10.23	9.97	10.57
Fe_2O_3	10.37	9.50	8.94	8.92	9.36	7.44
FeO	3.30	4.66	3.59	3.78	4.10	4.75
MnO	0.23	0.20	0.18	0.14	0.19	0.18
MgO	13.79	12.10	15.41	12.41	11.15	11.03
CaO	10.35	10.08	9.75	11.89	12.31	12.09
Na_2O	2.05	2.32	1.89	2.17	1.89	1.82
K_2O	2.66	2.14	2.46	2.27	2.52	2.69
P_2O_5	0.50	0.87	0.68	0.44	0.43	0.47
LOI	1.19	1.71	1.63	1.58	1.15	2.21
Total	100.21	99.74	99.85	99.97	100.24	100.20
K/Na	1.30	0.92	1.30	1.04	1.33	1.47
P.I.	0.63	0.63	0.66	0.59	0.59	0.56
K_f	49.8	53.9	44.8	50.5	54.0	52.4
CIPW norms						
Or	15.89	12.91	14.81	13.65	15.04	16.24
Ab	8.60	18.70	13.71	8.59	10.35	8.52
An	10.27	10.18	8.27	11.63	11.35	12.96
Ne	4.82	0.71	1.38	5.45	3.13	3.89
Di	30.03	27.73	28.70	35.54	37.11	35.74
Hy	0.00	0.00	0.00	0.00	0.00	0.00
Ol	14.64	12.75	18.15	10.56	7.66	9.40
Mt	9.74	14.05	10.90	11.19	12.14	11.01
Hm	3.76	0.00	1.58	1.35	1.07	0.00
Il	1.15	1.05	0.97	1.08	1.19	1.26
Ap	1.10	1.94	1.51	0.98	0.95	0.98

K/Na = K_2O/Na_2O; P.I. = $(Na_2O + K_2O)/Al_2O_3$ (mol); K_f = 100. $(Fe_2O_3 + FeO)/(Fe_2O_3 + FeO + MgO)$; 361, 376 и 376/1 (Banushev, 2003)

In the total alkali-silica classification diagram the researched volcanics are in the basalts field. Some of the earlier described alkaline basaltoids are on the border with basanites (Banushev, 2003) and others are in the K-trachybasalts field (Stoinov, 1955), (Fig. 3). According to the diagram of SiO_2 saturation, the basalts from the TAS diagram field B could be divided to alkali (with normative nepheline) and subalkali (without normative nepheline), (Le Maitre et al., 1989), which provides reason to assign the researched rocks to the alkaline basalts. On the normative tetrahedron of Yoder and Tilley (1965) these volcanics are located to the left of the critical plane of undersaturation – in the field of alkaline basalts with normative olivine and nepheline. The olivine presence in the phenocrysts and groundmass is an indication of magma undersaturation with SiO_2, which is confirmed by pseudoleucite aggregates. The K-sanidine and biotite microlites presence is an additional indication for increased alkalinity. On the ground of petrochemical features and minerall composition, which according to the IUGS principles are of great importance at the classification, of the described rocks around Dobrinovo village (Karnobat region), should be determined as alkaline olivine basalts and some varieties - as olivine melabasalts (ankaramites) and pseudoleucite basanites.

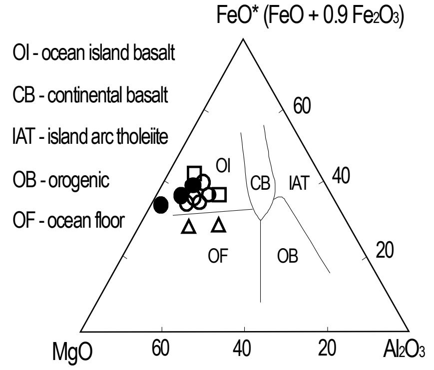

Fig. 5. MgO-Al_2O_3-FeO* discrimination diagrams (after Pearce et al.,1977) with the point of volcanics from the Eastern Srednogorie. Symbols as in Fig. 3

Table 3.

Trace element (ppm) in alkaline basalts from the Dobrinovo village region

	377	377/1	424	376/1	376	361
Li	19	25	24	12	12	27
Be	2	3	3	3	3	3
Sr	910	951	992	1000	1033	888
Ba	270	255	308	292	273	318
Zr	281	272	262	165	161	200
V	202	221	191	194	190	183
Cr	487	692	564	455	455	423
Co	76	77	67	55	54	42
Ni	183	289	206	209	211	177
Cu	102	128	99	145	95	90
Zn	97	102	81	89	83	78
As	84	106	103	98	78	71
Mo	7	18	12	11	11	5
Ag	1	2	1	2	1	1
Pb	7	13	8	17	6	1
Bi	n.d.	19	n.d.	23	10	n.d.
La	31	29	30	28	26	26
Ce	68	65	71	60	52	49
Y	15	13	16	13	12	13
Nb	25	26	22	15	15	12

The alkaline basalts have shoshonitic series. The rest of St. Spas paleovolcano products have prevailing shoshonitic series as well (Banushev, 2001). In contrast to them, the pseudoleucite basanites from Tamarino Bakadjik are high-K transitional series (Fig. 4).

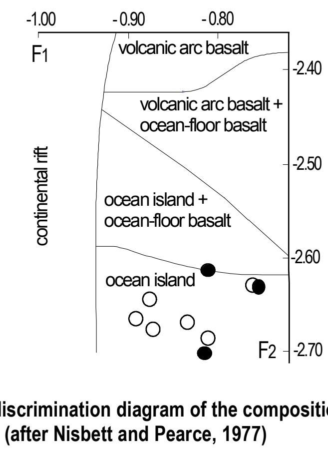

Fig. 6. F_1-F_2 discrimination diagram of the composition of the clinopyroxene phenocrysts (after Nisbett and Pearce, 1977)

The volcanics major oxides and the clinopyroxenes chemistry have been used for the tectonic settings discrimination. In the diagram MgO - Al_2O_3 - FeO^*, (Pearce et al., 1977), the alkaline basalts from Dobrinovo village have features of within-plate ocean-island basalts (Fig. 5). The alkaline basaltoids from St. Spas Bakadjik show the same features, which is confirmed by the clinopyroxene chemical composition (Fig. 6). The leucite basanites from Tamarino Bakadjik have the different substantial characteristic of ocean-floor basalts (Fig. 5).

Trace elements

The trace elements contents are presented in Table 3. In the discrimination diagram for potassic volcanic rocks, the researched alkaline basanites find place in the continental arcs field (Fig. 7). The researched volcanics spidergrams differ from the typical models of basalts in different geodynamic settings. The chondrite-normalized trace elements show enrichment in Nb and Zr, which makes them akin to the model of the alkaline basalts from the ocean islands (OIB). On the other hand, Ti and Y low concentrations are not typical of the basalts from these conditions (Fig. 8a). The MORB-normalized spidergram shows enrichment of the all elements from Sr to Zr regarding the contents in MORB, which is typical for the within-plate ocean-island basalts (Fig. 8b). The rocks geochemical features do not exclude the possibility of mixing the components from two different sources - volcanic-arc and alkaline (within-plate).

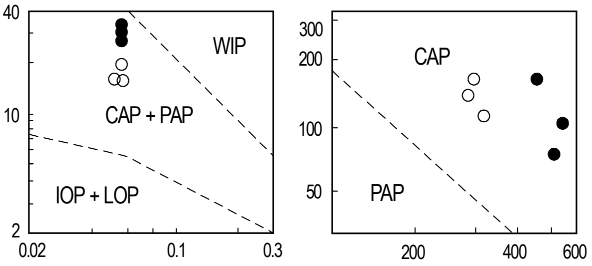

Fig. 7. Discrimination diagrams for potassic volcanic rocks (after Muller et al., 1992). WIP – Within-plate, CAP –Continental Arc, PAP – Postcollisional Arc, IOP – Initial Oceanic Arc, LOP – Late Oceanic Arc. Symbols as in Fig. 8

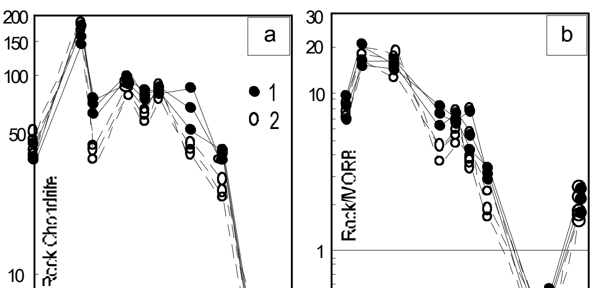

Fig. 8. Spidergrams of the volcanics from the Eastern Srednogorie: a – chondrite-normalized trace element; b – MORB-normalized trace element; 1 - Dobrinovo village region, 2 - St. Spas Bakadjik

Discussion and conclusions

The alkaline basalts from the Dobrinovo village area have analogous mineral composition, texture-structural, petrochemical and geochemical features to the basaltoids from the St. Spas Bakadjik area. Pseudoleucite aggregates present in the volcanics from both areas. Their composition, morphological features, sizes and quantitative ratios display close affinity.

The leucite conversion into nepheline-feldspar pseudomorphosis is researched on part of many research workers (Bowen and Ellestad, 1937; Fudali, 1963; Taylor and MacKenzie, 1975, etc.). Most often the pseudoleucite genesis has been connected with the following processes: reaction of the earlier-formed leucite with a sodium-rich liquid, the so called pseudoleucite reaction; sodium-rich leucite breakdown; pseudomorphosis on K-analcime; ion exchange between the leucite solid solution and sodium glass or with enriched with sodium water vapour.

In contrast to the nepheline-feldspar pseudomorphosis the processes of the substitution of analcime for leucite are not so thoroughly studied. According to Barrer and Hinds, (1953) and Deer et al. (1992) at ion exchange the analcime and leucite easily transform from one to the other: $NaAlSi_2O_6.H_2O + K^+_{(aq)} \leftrightarrow KAlSi_2O_6 + Na^+_{(aq)} + H_2O$. The experimental researches (made by Gupta and Fyfe, 1975) show that the leucite transformation to analcime under the impact of NaCl solution in temperature interval 150-300°C accomplishes too fast. At temperature 150°C in thirteen days the leucite transformation to analcime is 14%, and at temperature 325°C the leucite transformation to analcime up to 100% is accomplishes in four days only.

The microprobe researches of the pseudoleucite crystals from the alkaline basalts around Dobrinovo village display that there is no intact leucite. It is totally replaced with analcime and K-feldspar. The leucite transformation way is likely analogous to that described in pseudoleucite basanites from St. Spas Bakadjik (Banushev, 2003). The mineral paragenesis (olivine + clinopyroxene + pseudoleucite), the pseudoleucite crystals morphology, the zonally ordered inclusions in them and the rocks petrochemical features give reason to presume that initially the pseudoleucite has crystallized as leucite. Later, in the subsolidus area the latter is transformed to analcime as a result from ion exchange. The released potassium enters the composition of the newly formed K-feldspar, which localizes in the peripheral parts of the analcime crystals and in the interstitial space. There is a possibility that the process of pseudoleucite substitution for leucite to have occurred at low temperatures (about 25°C), under the see water (NaCl) impact, for about 10^5 – 10^7 years (Gupta and Fyfe, 1975), at that the leucite is replaced with analcime according to the diagram: $KAlSi_2O_6\ _{(solid)} + Na^+_{(aq)} + H_2O \rightarrow NaAlSi_2O_6.H_2O_{(solid)} + K^+_{(aq)}$. The analysis of petrographycal and geochemical features give a reason to be regarded as more likely that the leucite has been transformed to analcime in the first way by ion exchange.

The alkaline basalts from the Dobrinovo village area have been formed in conditions of low pressures and fast crystallization. Olivine, clinopyroxene and leucite have crystallized from the SiO_2 undersaturated liquid. It is considered that as a result from ion exchange, the leucite is transformed in analcime - K-feldspar pseudoleucite aggregates. The alkaline basalts from the researched region display close affinity to the alkaline basaltoids from St. Spas and Tamarino Bakadjik by mineral composition, texture-structural and geochemical features. Their substantial features show that they are the most likely products of primary, slightly differentiated, mantle olivine-basalt magma with increased K-alkalinity.

Aknowledgements

The author expresses gratitude to prof. B. Kamenov for the beneficial discussions.

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Препоръчана за публикуване от
катедра "Минералогия и петрография", ГПФ