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# PETROLOGIC AND GEOCHEMICAL CHARACTERISTICS OF THE VOLCANIC ROCKS IN THE BUČIM DISTRICT

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A b s t r a c t: The paper presents the latest data obtained during petrologic, mineralogical and geochemical studies carried out on the Tertiary volcanic rocks in the Bučim district. The latest petrologic studies have determined trachyandesites-latites and alkali trachyte-trachytes. Examinations on the chemical composition of individual mineralogical phases indicated that the plagioclases in the volcanic rocks are andesites and oligoclases; biotites are of the phlogopite-andesite series. Amphiboles are present as calcic amphiboles, pyroxenes are of the diopside-augite group, and calcic feldspars are present as sanidine. Geochemical studies indicated that the rocks are of the high calcic series, which is consistent with the calc-alkali characteristic of the volcanism. Examinations of the microelements indicated a pronounced positive Th and Y anomalies and light negative anomalies for Nb and TiO<sub>2</sub>, which is a characteristic of subduction magmas.

Key words: Bučim ore district; volcanism; volcanic rocks; petrologic features; mineralogy; geochemistry

## INTRODUCTION

The Bučim district is one of the smallest ore districts in the Republic of Macedonia occupying an area of 150 km<sup>2</sup>. Its geotectonics classifies it into two geotectonic units: the Vardar zone and the Serbo-Macedonian mass. The district has been defined as a separate metallogenic unit based on the regional and local factors of metallogenic control (Serfamovski et al., 1996). It is characterized by Tertiary calc-alkali volcanism present as subvollatite, canic-volcanic andesite, quartzlatites, trachytes, and trachyrhyolite facies. Numerous copper, iron, gold, lead-zinc mineralizations have been related to this volcanism.

The Bučim–Damjan–Borov Dol or the Bučim ore district has been explored many times (Ivanov, 1982; Petković, 1968; Janković et al., 1980; Serafimovski, 1982, 1990, 1993; Serafimovski et al., 1995, 1996; Čifliganec, 1987, 1993; Tudžarov, 1993; Čifliganec et al., 1994; Karamata et al., 1992; Stojanov et al., 1990. The investigations carried out by the present authors aimed at better understanding the petrologic characteristics with detailed examinations of individual mineralogical phases. The investigations aimed at determination of the geochemical characteristics through examination of microelements.

#### GEOLOGICAL FEATURES OF THE DISTRICT

The geotectonics of the Bučim district is part of the Serbo-Macedonian mass and the Vardar zone. The metallogeny is in close relationship with the evolution of the Tertiary magmatism to which numerous mineralization styles are related. Mineralization is related to the Young Alpine metallogenic epoch. The volcanic activity commenced at the end of the Oligocene and occurred during the Miocene. During that period significant porphyry copper, gold mineralization, hydrothermal-vein leadzinc and barium were formed (Serafimovski et al., 1996).

The geology is composed of several lithostratigraphic units: Precambrian, Palaeozoic, Mesozoic and Ceinozoic (Fig. 1).



Fig. 1. Geologic map of Bučim-Damjan-Borov Dol (Serafimovski et al., 1996).

1 - Palaeocene and Neogene sediments; 2 - pyroclasts; 3 - andesites and latites; 4 - carbonatites; 5 - granites; 6 - serpentinites;
 7 - amphibolites; 8 - gneisses; 9 - Pb-Zn vein type mineralization; 10 - Fe skarn; 11 - porphyry mineralization;
 12 - borders of ore field; 13 - borders of ore district; A - Bučim ore field; B - Damjan ore field; C - Borov Dol ore field

The Precambrian metamorphic complex is the oldest lithological member and comprises the bedrock of the terrain. The complex consists of various gneiss types (biotite, muscovite, two mica, augen, banded etc.), amphibolites, micaschists etc. The Palaeozoic rocks of the Bučim–Damjan– Borov Dol district are present as chloriteamphibole schists, schistose carbonate series, metagabros and diabases.

The Mesozoic is present as Jurassic ultrabasics, Jurassic granitoid and Cretaceous sediments. Ultrabasics are present as peridotites and pyroxenites that are more or less affected by serpentinitization. Granitoid rocks are present as granites, granodiorites, quartzmonzonites. Basal conglomerates that facially grade to marls, sandstones and slates form the so-called flysch series and represent the Cretaceous sediments in the region.

The Palaeocene sediments consist of several facies: a facies of conglomerates, flysch tuffaceous sediments and limestones. These sediments are sporadically intruded by Neogene volcanics. The Neogene sediments are present as clastic sediments: conglomerates, gavels, sands, sandstones, loams etc. The Quaternary is present as proluvialdeluvial and alluvial layers present mainly as slatysandy material.

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#### PETROLOGIC AND GEOCHEMICAL CHARACTERISTICS OF THE VOLCANIC ROCKS

Magmatism is present as subvolcanicvolcanic facies (the Bučim block) of trachytes and trachyrhyolites as dikes and necks intruded into the crystalline complex along fault zones. In the Damjan block there are developments of calderas present as latite-quartzlatites in the form of heaps, necks, dikes and lava extrusions (Serafimovski, 1990; Stojanov et al., 1990). Volcanic rocks are present as various shapes such as volcanic necks and elongated volcanic bodies that often end on the surface as cones distributed along fault structures. Morphostructural investigations carried out indicated the possibility of the presence of a large body intruded by the end or after termination of volcanic activity (Tudžarov, 1993).

Volcanic rocks belong to an intermediary to acid magma with fairly high alkali contents present as andesites, latites, trachytes and rhyolites as well as transition rock types.

Chemical examinations carried out (Stefanova, 2005; Stefanova et al., 2005) on samples of the region yielded the results given in Table 1.

Data made it possible to classify the volcanic rocks according to the TAS diagram (Fig. 2) which shows that the results obtained fall in the field of trachyandesites-latites and alkali trachy-trachytes.

Table 1

	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub>	59.92	59.73	59.32	60.68	66.14	57.99	60.18	60.24	58.56
TiO <sub>2</sub>	0.51	0.66	0.60	0.58	0.41	0.71	0.74	0.52	0.63
Al <sub>2</sub> O <sub>3</sub>	16.42	17.24	16.68	17.29	15.69	17.36	16.45	15.96	16.38
Fe <sub>2</sub> O <sub>3</sub>	2.54	3.43	2.93	2.29	1.15	2.85	2.52	2.63	3.37
FeO	2.33	1.76	2.18	1.09	0.61	1.99	1.79	3.09	2.53
MnO	0.17	0.14	0.13	0.13	0.01	0.15	0.11	0.1	0.10
MgO	2.39	2.14	2.43	2.52	0.36	2.38	2.20	2.73	1.78
CaO	5.54	4.73	4.23	4.04	0.65	5.81	4.99	5.8	5.15
Na <sub>2</sub> O	4.15	4.78	5.46	5.70	1.75	4.24	5.34	4.65	4.97
K <sub>2</sub> O	2.98	3.21	4.63	3.83	11.84	3.19	2.72	2.69	3.87
P <sub>2</sub> O <sub>5</sub>	0.50	0.51	0.43	0.59	0.31	0.52	0.57	0.35	0.43
H <sub>2</sub> O <sup>-</sup>	0.21	0.27	0.23	0.26	0.12	0.55	0.38	0.39	0.51
$H_2O^+$	1.99	1.29	1.37	0.83	0.78	1.77	1.26	0.67	1.62
Σ	99.65	99.89	100.62	99.83	100.12	99.51	99.24	99.82	99.90
Cr	65	38	29	29	64	26	50	56	36
Ni	10	7	70	15	11	22	71	5	14
Со	14	7	13	10	5	13	8	10	5
Li	18	9	12	4	4	3	9	7	5
Rb	54	46	57	61	271	46	42	37	62
Sr	1028	1027	1061	1048	400	1035	1061	47	2584
Zn	170	298	95	84	31	313	57	75	116
Cu	38	40	66	323	10	29	44	13	133
Pb	29	67	89	30	45	17	28	2451	13

Chemical composition of the rocks of Bučim-Damjan-Borov Dol

Note: 1, 2 - latites south of Pamukluk; 3 - trachyte south of Pamukluk; 4 - latite of Damjan; 5 - trachyte of Crkvište;

6 - latite of Borov Dol; 7, 8 - latite of Damjan; 9 - latite of Borov Dol



Fig. 2. Classification of the volcanic rocks of Bučim–Damjan–Borov Dol based on TAS diagram (Le Bas et al., 1986).

 2 – latites south of Pamukluk; 3 – trachyte south of Pamukluk; 4 – tracyte of Damjan; 5 – alkali trachyte of Crkvište; 6 – latite of Borov Dol; 7, 8 – latites of Damjan; 9 – latite of Borov Dol

#### CHEMISTRY OF PETROGENIC MINERALS

**Plagioclases** in latites and trachytes are present as two generations. The first is present as large phenocrysts (0.7 to 1.5 cm) with obscured composition. In most cases the zonal composition contains increased Ab component towards the periphery. In some case chemical zoning does not occur. Reverse zoning has been found with small variations in latite composition (core  $An_{29.32}$ , periphery  $An_{38.39}$ ).

The second generation of plagioclases is present as smaller phenocrysts and groundmass minerals. They are of the order of andesite to oligoclases ( $An_{31-14}$ ) with no zonal structure. Their composition is similar to that in the outer zone consisting of phenocrysts of normal zonal composition.

Table 2 shows that Or component in plagioclases is constant and with very small variations (Or<sub>1-5</sub>). Cn component was not determined in the plagioclases in latites (no Ba in the composition). The large phenocrysts often include small biotites and amphiboles (Fig. 3).

Based on the chemical composition of plagioclases and the calculated crystallochemical relationships, classification was carried out on plagioclases (Fig. 4) from which it can be seen that data fall into the andesite and oligoclase field.



Fig. 3. Microphotograph of the plagioclases of Borov Dol, Porphyry of zonal plagioclases, XN; magnification 6.3



Fig. 4. Classification of the volcanic rocks of Bučim-Damjan-Borov Dol based on TAS diagram (Deer et al., 1972). Note: 4 - sample no. 1; ▶ - sample no. 2; ◊ - sample no. 3;
□ - sample no. 4; ◊ - sample no. 6; □ - sample no. 8

# Table 2

Chemical composition of part of plagioclases studied of the Bučim–Damjan–Borov Dol (calculated on 8 0).

Sample	1	2	3	4	6	8
Mineral	Pl / Hb	Pl (c)	Pl (r)	P 1/ Hb	Pl/Hb	Pl / Hb
SiO <sub>2</sub>	60.35	59.54	64.93	64.20	61.45	64.13
TiO <sub>2</sub>	0.00	0.00	0.00	0.00	0.00	0.06
Al <sub>2</sub> O <sub>3</sub>	25.37	26.41	17.71	21.86	23.21	21.36
FeO	0.00	0.00	0.11	0.54	0.63	0.39
MnO	0.14	0.00	0.00	0.00	0.00	0.00
MgO	0.00	0.00	0.00	0.00	0.00	0.00
CaO	7.18	7.46	8.22	2.98	6.42	5.74
Na <sub>2</sub> O	6.59	5.97	8.25	9.83	7.50	7.56
K <sub>2</sub> O	0.54	0.43	0.73	0.58	0.59	0.61
Total	100.18	99.83	99.97	100.00	99.83	99.88
Si	2.68	2.65	2.91	2.84	2.75	2.85
Ti	0.00	0.00	0.00	0.00	0.00	0.00
Al	1.33	1.38	0.94	1.14	1.22	1.12
Fe	0.00	0.00	0.00	0.02	0.02	0.01
Mn	0.01	0.00	0.00	0.00	0.00	0.00
Mg	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.34	0.36	0.39	0.14	0.31	0.27
Na	0.57	0.51	0.72	0.84	0.65	0.65
K	0.03	0.02	0.04	0.03	0.03	0.03
Ba	0.00	0.00	0.00	0.00	0.00	0.00
An	36.00	40.00	34.00	14.00	31.00	28.00
Ab	61.00	57.00	63.00	83.00	66.00	68.00
Or	3.00	3.00	3.00	3.00	3.00	3.00
Cn	0.00	0.00	0.00	0.00	0.00	0.00

Note: 1, 2 – latites south of Pamukluk; 3 – trachyte south of Pamukluk; 4 – latite of Damjan; 6 – latite of Borov Dol; 7, 8 – latites of Damjan; Pl – plagioclase; Hb – hornblende; c – centre; r – rim

**Biotites** are idiomorphic to hypidiomorphic (Fig. 5) of up to 1.4 mm in size. They show clear pleochroism and Mg# 0.53 - 0.7. Based on the chemical composition of biotites and on the calculated crystallochemical relations, classification was carried out on biotites (Fig. 6). Biotites fall in the field of phlogopite-anite with small pronounced phlogopite component.

The latites in the Pamukluk biotites indicate chemical zoning (Table 4) with more magnesian central parts (Mg# = 0.7) than their periphery (Mg# = 0.55). Trachytes with small phenocrysts of Damjan are characterized by relatively high and constant Mg# = 0.64 value in biotites. Biotites in trachytes of Pamukluk possess low amounts of Al<sub>2</sub>O<sub>3</sub>.

Chemical composition of biotites (calculated	on
22 O) of the volcanics of Bučim-Damjan-Borov	Dol
(in %).	

Sample	1	2	3	4	6	9
Mineral	Bi / Hb	Bi	Bi	Bi	Bi	Bi / Hb
SiO <sub>2</sub>	38.19	37.79	40.46	38.27	38.24	44.11
TiO <sub>2</sub>	3.31	2.99	2.80	3.39	3.35	2.60
Al <sub>2</sub> O <sub>3</sub>	15.37	15.73	11.42	13.30	16.33	14.48
FeO	18.03	16.84	15.74	15.49	16.11	9.15
MnO	0.33	0.31	0.39	0.26	0.00	0.00
MgO	11.98	13.18	14.49	15.09	13.09	17.40
CaO	0.00	0.00	0.00	0.00	0.00	0.00
Na <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	9.48	9.56	10.97	10.19	8.90	8.75
Total	96.72	96.44	96.30	96.02	96.04	96.51
Si	5.68	5.60	6.04	5.72	5.64	6.18
Al IV	2.32	2.40	1.96	2.28	2.36	1.82
AI VI	0.38	0.35	0.05	0.06	0.48	0.57
Ti	0.37	0.36	0.31	0.38	0.37	0.27
Fe	2.24	2.09	1.96	1.93	1.99	1.07
Mn	0.04	0.04	0.05	0.03	0.00	0.00
Mg	2.66	2.91	3.22	3.36	2.88.	3.64
Ca	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00
K	1.8	1.81	2.09	1.94	1.68	1.57
Mg#	0.54	0.59	0.62	0.64	0.59	0.77

Note: 1, 2 – latites south of Pamukluk; 3 – trachyte south of Pamukluk; 4, 8 – latites of Damjan; 6, 9 – latites of Borov Dol; Bi – biotite; Hb – hornblende



Fig. 5. Microphotograph of biotite (1) in porphyry of plagioclase (2) in the Bučim district; II N; magnification 6.3





Amphiboles are idiomorphic, greenish with clear pleochroism. They are up to 2 mm in size and seldom include plagioclases or biotites. Zoning can not be noticed and Mg# varies within 0.77 and 0.31. They are the least magnesian femic minerals in latites.

The amphiboles of the northern part of the volcanic district (near Pamukluk) show the highest amplitude in Mg# variation and the highest total Al content. The amphiboles in the latite possess higher  $Al_2O_3$  and MgO contents than those in trachytes (Table 4).

Three types of amphiboles can be distinguished according to the crystallization processes: 1) rare small amphiboles with relatively high Mg# (0.62) and relatively high Al<sub>2</sub>O<sub>3</sub> contents (edenite, pargasite) enclosed in the phenocrysts of the plagioclase; 2) relatively large phenocrysts of plagioclase, potassium feldspar, and biotite of moderate Al<sub>2</sub>O<sub>3</sub> contents and relatively low Mg# (0.35 – 0.45) and in the classification diagram (Fig. 7) plots in the field of edenite, ferroedenite, pargasite and ferropargasite; 3) small euhedral phenocrysts in the groundmass with relatively low contents of Al<sub>2</sub>O<sub>3</sub> and low Mg# (ferroedenite).

In the classification scheme for amphiboles (Leake et al., 1997) they have been determined as calcic amphiboles.

Microphotograph of zonal plagioclase that includes amphiboles is shown on Fig. 8.



Fig. 7. Nomenclature of amphiboles in the volcanic rocks of Bučim-Damjan-Borov Dol (Leake et al., 1997)

#### Table 4

Chemical composition of part of the amphiboles analyzed in the volcanics of Bučim–Damjan–Borov Dol (23 O – 13 CKN)

Sample	1	2	3	4	6	8	9
Mineral	Hb/ Pl	Hb(c)	Hb(r)	Hb/Pl	Hb	Hb/Pl	Hb/Pl
SiO <sub>2</sub>	44.42	42.78	41.87	42.90	42.84	45.40	50.07
TiO <sub>2</sub>	0.73	1.00	1.12	0.98	1.19	1.22	0.95
Al <sub>2</sub> O <sub>3</sub>	12.29	13.43	12.87	10.52	11.43	10.31	11.06
FeO	16.08	17.62	20.65	19.24	20.23	18.17	13.66
MnO	0.33	0.26	0.49	0.50	0.28	0.56	0.20
MgO	10.30	7.91	5.95	8.59	6.49	8.29	9.54
CaO	11.91	11.75	12.04	12.03	11.46	12.14	10.71
Na <sub>2</sub> O	1.37	1.65	1.16	2.33	2.20	1.01	1.09
K <sub>2</sub> O	1.21	1.48	1.35	1.21	1.61	1.22	1.39
Total	98.88	97.93	97.56	98.34	97.76	98.37	98.72
Si	6.523	6.460	6.447	6.535	6.628	6.824	7.263
Al	1.477	1.540	1.553	1.465	1.372	1.176	0.737
Т	8.000	8.000	8.000	8.000	8.000	8.000	8.000
AI	0.649	0.848	0.781	0.422	0.710	0.649	1.152
Fe(III)	0.302	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.081	0.114	0.130	0.112	0.138	0.138	0.104
Mg	2.255	1.781	1.366	1.951	1.497	1.858	2.063
Fe(II)	1.672	2.225	2.659	2.591	2.617	2.284	1.657
Mn	0.041	0.033	0.064	0.065	0.037	0.071	0.025
С	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	1.874	1.901	1.986	1.963	1.900	1.955	1.664
Na	0.126	0.099	0.014	0.037	0.100	0.045	0.307
В	2.000	2.000	2.000	2.000	2.000	2.000	1.971
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.264	0.384	0.333	0.651	0.560	0.249	0.000
К	0.227	0.285	0.265	0.235	0.318	0.234	0.257
Α	0.491	0.669	0.598	0.887	0.877	0.483	0.257
oxy	23.000	23.052	23.036	23.015	23.196	23.094	23.257
Mg#	0.53	0.44	0.34	0.43	0.36	0.49	0.55

Note: 1, 2 – latites south of Pamukluk; 3 – trachyte south of Pamukluk; 4 – latite of Damjan; 6 – latite of Borov Dol; 8 – latite of Damjan; 9 – latite of Borov Dol; Pl – plagioclase; Hb – homblende; c – centre; r – rim



Fig. 8. Microphotograph of zonal plagioclase (1) that includes amphiboles (2) I N magnification 6.3

*Pyroxenes* have been analyzed and determined in one trachyte sample only of the Damjan skam-iron deposit (Table 5).

They are monoclinic of 0.5 mm in size and high Mg# of 0.72 - 0.90. Clinopyroxenes are the most magnesian coloured minerals in latites and most probably crystallized the first. Only augite phenocrysts (pijonite) have been preserved during the melting process of parent rocks.

Based on this chemical composition and the crystallochemical calculations, classification on pyroxenes was done (Fig. 9). The results obtained indicate that pyroxenes belong to the diopside augite, the largest part being from the diopside.



Fig. 9. Classification of the clinopyroxenes in the volcanic rocks of Bučim–Damjan–Borov Dol (Morimoto et al., 1993). Note: • - sample no.4

Ľ	a	bl	e	5

Chemical	composition of clinopyroxenes
of the volcar	nics of Bučim-Damjan-Borov Dol
	(calculated on 6 0).

Sample	4	4	4	4
Mineral	Срх	Срх	Срх	Срх
SiO <sub>2</sub>	51.58	54.94	53.35	53.54
TiO <sub>2</sub>	0.29	0.75	0.35	0.00
Al <sub>2</sub> O <sub>3</sub>	0.00	2.72	1.49	0.00
FeO	10.56	11.51	7.56	4.72
MnO	0.54	0.44	0.19	0.15
MgO	11.77	16.64	12.18	15.66
CaO	25.24	12.46	25.13	25.69
Na <sub>2</sub> O	0.00	0.00	0.00	0.00
K <sub>2</sub> O	0.00	0.37	0.00	0.00
Total	100.01	99.86	100.29	99.78
Si	1.952	2.047	1.996	1.974
AI	0.000	0.000	0.004	0.000
Fe	0.048	0.000	0.000	0.026
Т	2.000	2.047	2.000	2.000
Al	0.000	0.119	0.061	0.000
Ti	0.008	0.021	0.010	0.000
Fe(III)	0.031	0.000	0.000	0.026
Fe(II)	0.256	0.000	0.236	0.094
Mg	0.664	0.860	0.679	0.861
MI	0.959	1.000	0.986	0.981
Mg	0.000	0.065	0.000	0.000
Fe(II)	0.000	0.359	0.000	0.000
Mn	0.017	0.014	0.006	0.005
Ca	1.024	0.498	1.007	1.015
к	0.000	0.018	0.000	0.000
M2	1.041	0.954	1.013	1.020
cat	4.000	3.982	4.000	4.000
Wo	50.123	27.723	52.215	50.096
En	32.567	51.514	35.212	42.489
Fs	17.240	20.763	12.573	7.415
Mg#	0.72	0.72	0.74	0.90

Note: 4 - trachytes of Damjan; Cpx - clinopyroxene

**Potassium feldspars** have been analyzed in latites and trachyandesites of Damjan, Crkvište and Borov Dol. Sanidine phenocrysts are euhedral or corroded indicating zoning in chemical composition depending on the content of Ba that increased to the centre of the minerals. BaO content is relatively high attaining 3.21% in sanidines (Table 6). Based on the chemical composition and crystallochemical calculations potassium feldspars plot in the sanidine group (Fig. 10).



Fig. 10. Classification of the potassium feldspars in the volcanic rocks of Bučim–Damjan–Borov Dol (Deer et al., 1972). Note ≫ - sample no. 5; ♥ - sample no. 6; □ - sample no. 8; ◀ - sample no..9

Т	a	b	1	e	6

Chemical composition of part of the potassium feldspars in the volcanics of Bučim–Damjan– Borov Dol (calculated on 8 0)

Sample	5	6	8	9
Mineral	Kfs(m)	Kfs(r)	Kfs / Hb	Kfs
SiO <sub>2</sub>	64.55	65.15	66.96	65.33
TiO <sub>2</sub>	0	0.13	0.1	0.18
Al <sub>2</sub> O <sub>3</sub>	18.74	16.86	15.27	17.02
FeO	0	0.17	0.37	0
MnO	. 0	0	0.07	0.15
MgO	0	0	0	0
CaO	0.35	0.26	0.39	0.34
Na <sub>2</sub> O	3.99	3.34	1.78	4.59
K <sub>2</sub> O	11.51	11.95	14.66	9.65
BaO	0.79	1.42	0	2.42
Total	99.96	99.31	99.63	99.71
Si	2.97	3.03	3.1	3.02
Ti	0	0	0	0.01
Al	1.01	0.92	0.83	0.93
Fe	0	0.01	0.01	0
Mn	0	0	0	0.01
Mg	0	0	0	0
Ca	0.02	0.01	0.02	0.02
Na	0.36	0.3	0.16	0.41
К	0.67	0.71	0.87	0.57
Ba	0.01	0.03	0	0.04
An	2	1	2	2
Ab	34	28	15	39
Or	63	68	83	55
Cn	1	3	0	4

Note: 5 – trachyte of Crkvište; 6 – latite of Borov Dol; 8 – latite Damjan; 9 – latite of Borov Dol; Kfs – potassium feldsj Hb – hornblende; (m) – medium; (r) – rim

# GEOCHEMISTRY OF MAJOR AND RARE ELEMENTS IN VOLCANICS

Examinations carried out on major elements yielded data of calc-alkaline series formed owing to differentiation of magmatic melt. The differentiation is conditioned on the mutual relationship between components and their distribution in individual differentiates of magmatic melt. The diagram  $K_2O$ -SiO<sub>2</sub> shows that all rocks plot in the field of high potassium series that is consistent with the calc-alkaline nature of the volcanism (Fig. 11).

Besides the major elements, microelements of volcanic rocks of the Bučim district were also studied (ppm).



Fig. 11. Correlation diagram K<sub>2</sub>O-SiO<sub>2</sub>

## Table 7

Sample no	1	2	3	4	5	6	7	8
Cr*	65	38	29	29	64	26	60	50
Li•	18	9	12	4	4	3	9	9
Rb*	54	46	57	61	271	46	3	42
Nb	10	11	10	. 8	16	12	9	10
Y	26	26	23	25	33	28	26	27
Sr	1227	1501	1349	1491	926	1702	1327	1633
U	5	3	4	<2	9	6	6	<2
Th	21	30	25	31	37	37	27	23
РЬ	51	•67	60	65	72	43	26	71
Ga	19	19	18	19	20	18	17	19
Zn	•170	69	75	67	33	49	66	60
Cu	43	51	70	•323	8	32	11	52
Ni	9	7	8	6	6	9	6	6
Co	16	13	14	13	5	16	6	11
Nd	46	59	50	48	-	59	50	52
La	65	76	88	69	61	84	74	98
S	51	-	-	96	27	-	90	28
Hf	9	7	11	13	10	11	14	9
Sc	11	14	11	10	<2	12	16	14
40	9	1	6	-3	14	-3	8	3

Major elements and microelements of volcanic rocks of the Bučim district

The spidergram for MORB normalization (Fig. 12) clearly expresses the positive anomalies for Th and Y, and light negative anomalies for Nb and TiO<sub>2</sub> which is characteristic for magmas related to subduction processes. The trachytes of Crkvište (aphanite – sample no. 5) differ from other volcanics of the Damjan block with higher  $K_2O$ , Rb. and Nb values and pronounced Sc negative anomaly.

The paper presents the results of the petrologic and geochemical examinations carried out on rocks of the Bučim district. Examinations indicated that the volcanic rocks in the district are trachyandesite latites and trachytes. Examinations of individual mineral phases indicate that the plagioclases in the volcanic rocks are andesites and oligoclases, whereas biotites are of the phlogopie-andesite series. Amphiboles are present as calcic amphiboles, and pyroxenes are of the diopside-augite group. Calcic feldspars are present as sanidine.





Sr-Rb diagram (Fig. 13) points out the chemical evolution, which depends on biotite behaviour. The diagram shows that plagioclase and hornblende fractionation resulted in such changes in strontium and rubidium during the magmatic evolution.





The distribution of rare elements normalized according to MORB attest to the subduction volcanism that is in accordance with earlier investigations (Boev et al., 1992; Boev, Yanev, 2001) for the Tertiary magmatism in the Republic of Macedonia in which the volcanic activity in the Borov Dol district was related to the subduction process in active continental margins.

### CONCLUSION

The pronounced presence of hydroxile minerals (amphiboles and biotites) point out the fairly high water content in the magma. The early biotite crystallization and potassium feldspars included in large amphibole crystal point out the high K potential of the magma. Geochemical examinations indicate that the rocks in the district are of the high potassium series that is in accordance with the calc-alkaline affinity of the volcanism.

Analyses carried out on AA in Sofia. Other analyses were carried out by X-ray in Switzerland

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The study of microcomponents offered pronounced positive anomalies for Th and Y and light negative anomalies for Nb and  $TiO_2$ , which is characteristic of magmas related to subduction. The distribution of rare elements normalized in MORB and the discrimination diagram based on the chemical composition of biotite attest to the sinsubduction volcanism.

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#### Резиме

# ПЕТРОЛОШКИ И ГЕОХЕМИСКИ КАРАКТЕРИСТИКИ НА ВУЛКАНСКИТЕ КАРПИ ОД БУЧИМСКИОТ РУДЕН РЕОН

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Клучни зборови: бучимски руден реон; вулканизам; вулкански карпи; петролошки карактеристики; минералогија; reoxeмија

Во овој труд се презентирани најновите податоци од петролошките, минералошките и геохемиските испитувања на терцијарните вулкански карпи во бучимскиот руден реон. Со најновите петролошки испитувања се потврди присуството на трахиандезитителатити и алкалните трахити-трахити. Исто така се извршија и испитувања на хемискиот состав на одделни минералошки фази, кои покажаа дека плагиокласите во вулканските карпи се од групата на андезити и олигокласи, биотитите се од групата на флогопитанитската серија. Калцитските амфиболи се претставници на амфиболите, пироксените се од групата на диопсид-аугит а калцитските фелдспати се претставени со санидинот. Геохемиските испитувања покажаа дека карпите во овој руден реон се од групата на висока калцитска серија што е во согласност со калкоалкалниот карактер на овој вулканизам. Испитувањата на микроелементите дадоа изразита позитивна аномалија за Th и Y и лесна негативна аномалија за Nb и TiO<sub>2</sub>, што е карактеристично за магми врзани за субдукција.