

Faculty of Natural and Technical Sciences, University “Goce Delčev”-Štip, R. Macedonia with a grant from the CEI-ES Know How Programme organize



**1st INTERNATIONAL WORKSHOP
ON THE PROJECT**

**Environmental Impact assessment of the Kozuf
metalogenic district in southern Macedonia in
relation to groundwater resources, surface
waters, soils and socio-economic
consequences (ENIGMA)**

PROCEEDINGS

**Edited by:
T. Serafimovski & B. Boev
Kavadarci, 10th October 2013**

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Language: English for presentations and papers

PETROLOGY AND GEOCHEMISTRY OF THE KOZUF VOLCANIC AREA, REPUBLIC OF MACEDONIA

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Abstract

The magmatic complex of the Kozuf district is a segment of the widespread magmatic activity in the petrographic province formed in the Vardar zone and the Serbo-Macedonian Mass. Magmatic activity are presented by calco-alkaline volcanic rocks :latite, quartz-latite, andesite, trahite, riolite and transitional rocks between them. On the base of the geochemical data this volcanic rocks are derivate from the materials from upper part of the mantle.

Key words: volcanic, rocks, geochemistry, Kozuf

Introduction

During the Tertiary, from the Eocene to the Pliocene, granodioritic magmas in this terrain intruded and extruded to the surface in individual tectonic zones. The evolution of this magmatism was first reported by Ilic (1962), and later shown in detail by Karamata (1962), and Karamata and Djordjevic (1980). The principal geochemical features of this magmatism were given by Karamata (1984) and Antonovic and Filipovic (1987), and individual areas were investigated in detail by Boev (1988) and Serafimovski (1990).

The Tertiary magmatism in the the Vardar zone and the Serbo-Macedonian Mass took place after closure of the Mesozoic oceanic basin (Karamata, 1983). This closure is due to the approach of the Dinaride slab and the Carpatho-Balkan block to the Serbo-Macedonian mass and the successive collision of the continental segments (Dimitrievic, 1974, Karamata, 1975, 1981). The process related to subduction during Dogger and Upper Jurassic was accompanied by calc-alkaline magmatism during the Middle and Upper Cretaceous in the Carpatho-Balkanides.

Following-up continental collision resulted in thickening of the continental crust and its intrusion into the upper envelop and isostatic upliftings. Discontinuous compression caused temporary melting of the basal parts of the continental crust and mixing with larger or smaller amounts of material from the envelop (Knezevic et al., 1989). These pulsations and tactionomagmatic activities took place in the Oligocene, Miocene and Pliocene for several times (Thompson et al., 1982).

Magmas were distributed in individual areas, most commonly, in the middle parts of arch-dome structures and formed volcano-plutonic belts. Rocks formed from granodiorite, quartzdiorite to quartzmonzonite magmas and built intrusive bodies of various sizes and very large and small volcanic complexes. Rocks occur at and / or near the surface due to upliftings of individual tectonic blocks and the intensity of erosion. However, these complexes can be interpreted as volcano-plutonic complexes in which deep intrusive parts are sometimes revealed by deep erosion processes.

Generally viewed, these rocks occur in two belts that join in their middle parts (the area of Kopaonik) and separate to the north and northwest and southeast and south-southeast. These belts are not connected to one geologic unit, and are located on both sides of the ophiolite belt and intersect the geotectonic units of the Balkan Peninsula - the Dinarides, the Vardar zone and the Serbo-Macedonian mass under a slight angle.

Petrology and geochemistry

The volcanic rocks formed during the Pliocene along transverse tectonic structures of Vardar strike are revealed on Kozuf and Kozjak Mts. in the southern marginal parts of the Tikves - Mariovo Tertiary basin. Volcanic activity is manifested by the occurrence of numerous volcanic heaps which basically represent frozen supply channel, and large masses of pyroclastic materials. Generally, the volcanic domes are distributed in a zone of east-northeast extension, most commonly on tectonic structures, in the places where they intersect older structures of northwest orientation (the Vardar strike). The transverse tectonic structures are of neotectonic age, formed in the Pliocene and lie parallel to the north margin of the Aegean valley between Thessaloniki and Kavala (Fig.1)

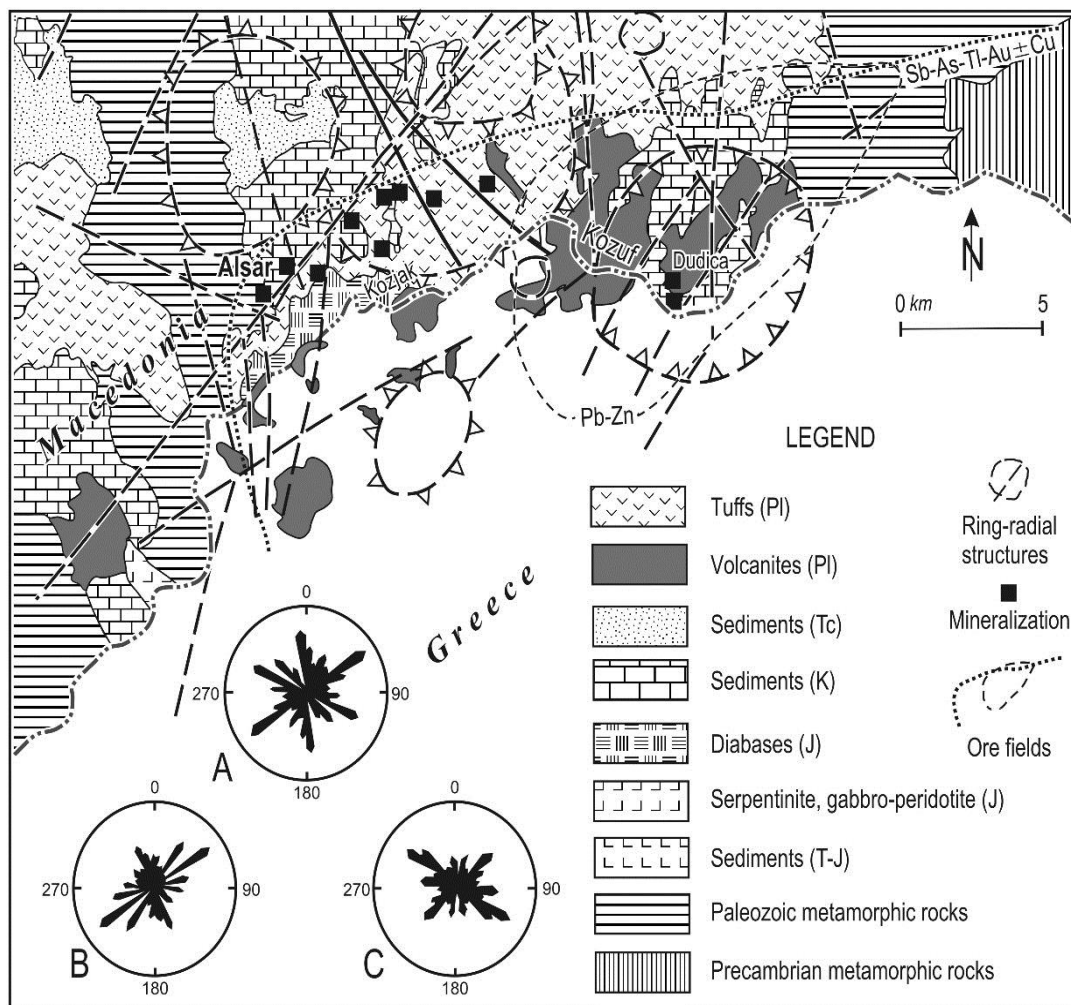


Fig.1. Schematic morphostructural map of the Kozuf district (BOEV, 1988)

Volcanic activity in Mts. Kozuf and Kozjak is represented as various types of volcanic rocks and volcanoclasts (volcanic breccias, conglomerates and tuffs). Volcanoclasts occur as sedimentary layers in the southern parts of the Tikves- Mariovo Tertiary basin where they comprise the topmost parts of the sediments. In some places the volcanoclasts are 200 to 300 meters thick.

Volcanic rocks are present as alkali basalt (small bodies), quartzlatites (delenites), andesite-latites (trachyandesites), transitional latite-quartzlatite and quartzlatite-latite (delenite-latite), as well as latite, trachyte, trachyrhyolites and rhyolites.

The volcanic rocks of Kozuf and Kozjak Mts display greatest similarity to the series of volcanic rocks of the Buchim-Borov Dol ore district, both in their mineralogy and chemical compositions the only difference being in the time period of their formation. Namely, the rocks of Kozuf and Kozjak Mts. formed in the Pliocene, whereas those from Buchim- Borov Dol formed in the Upper Oligocene. The former are extrusive (and explosive), the latter are subvolcanic and subvolcanic to hypoabyssal facies which means that their individual upper parts are eroded deeper.

Alkali basalts (trachybasalts) are the least abundant rocks in Kozuf district. They are established in the Bara locality near the source of the River Nisava. Similar rocks are found in the wider Tikves basin such as the marginal parts of the valley near the village of Koresnica, near Demir Kapija, Karaudzule on the Negotino-Stip road, near the villages of Debriste, Mrzen, Oraovec and Gaber north of Bojanciste (Tajder, 1940, Boev, 1988).

The basalt of Bara is a dark to black rock of porphyritic texture. It is composed of andesine (with 42% An), amphibole, biotite and augite as phenocrysts and cryptocrystalline groundmass. Chemical analyses (Table 1) show that it is a basic rocks that contains SiO₂ ranging from 50.12 up to 51.20 % , containing fairly large amount of MgO - the largest magnesium content among the volcanic rocks of Kozuf. It also contains some alkalis which classifies it as alkali basalt.

Table 1. Chemical composition of alkali basalts of the Kozuf area (%)

	1	2	3
SiO ₂	50.12	50.75	51.20
TiO ₂	0.65	0.58	0.60
Al ₂ O ₃	16.70	15.86	17.80
Fe ₂ O ₃	1.66	1.58	2.01
FeO	2.39	2.12	2.42
MnO	0.07	0.07	0.06
MgO	10.80	10.50	11.20
CaO	4.42	4.70	4.60
Na ₂ O	3.05	3.12	3.25
K ₂ O	3.51	3.45	3.65
P ₂ O ₅	0.33	0.25	0.45
H ₂ O	6.37	6.50	5.72

Andesite porphyry volcanic rocks are established near Studena Voda, Tresten Kamen and Sreden Rid (Boev, 1988). They have pronounced porphyritic texture in which phenocrysts are represented by plagioclase that is consistent with basic andesine to acid labrador (about 50 % An), amphibole, biotite and augite. The groundmass of the rock is microcrystalline, with vitrophyre base.

Table 2: Chemical composition of andesites of Kozuf (%)

	1	2	3
SiO ₂	59.94	59.75	59.20
TiO ₂	0.54	0.56	0.60
Al ₂ O ₃	16.30	16.25	16.80
Fe ₂ O ₃	3.97	3.88	3.71
FeO	1.52	1.48	1.50
MnO	0.05	0.06	0.06
MgO	2.00	1.95	2.12
CaO	7.33	5.52	5.60
Na ₂ O	2.11	2.70	3.10
K ₂ O	0.83	0.85	0.92
P ₂ O ₅	0.45	0.46	0.45
H ₂ O	3.60	6.35	5.75

Chemical composition (Table 2) shows that they are intermediary rocks with 59.20 to 59.94 % SiO₂ and that they have fairly large amount of Na₂O relative to K₂O, whereas the Al₂O₃ content ranges from 16.25 to 16.80 %.

Table 3: Chemical composition (in %) and microelements (in ppm) of the latite and andesite-latite

	1	2	3	4	5	6
SiO ₂	60.86	58.67	59.97	59.68	60.37	60.04
TiO ₂	0.52	0.71	0.62	0.65	0.62	0.62
Al ₂ O ₃	18.20	17.81	17.65	17.38	17.53	17.61
Fe ₂ O ₃	4.64	5.51	4.87	4.97	4.88	4.24
MnO	0.11	0.11	0.09	0.12	0.10	0.07
MgO	1.11	1.50	1.25	2.07	1.18	2.43
CaO	4.10	5.48	4.45	4.58	4.71	5.32
Na ₂ O	4.35	4.05	4.44	4.35	3.83	3.87
K ₂ O	4.75	4.71	4.99	4.76	4.94	4.18
P ₂ O ₅	0.56	0.68	0.73	0.73	0.56	0.16
H ₂ O	0.80	0.78	0.92	0.72	1.28	1.17
Zn	100	80	100	100	90	90
Mo	1	2	1	2	1	1
Ni	20	30	30	20	20	30
Co	20	20	20	20	20	20
Cd	1	1	1	1	1	1
As	13	12	11	10	10	11
Sb	0.9	0.8	0.8	0.9	1	0.9
Se	0.2	0.2	0.1	0.3	0.2	0.1
Hf	5	6	5	5	5	5
Ta	0.8	0.8	0.7	0.6	0.8	0.9
Th	31	28	29	30	31	31
U	9	8	7	8	9	9
Rb	180	174	154	181	180	174
Zr	210	200	210	210	190	200
Sr	1170	1100	1110	1050	1120	1100
Ba	1760	1800	1850	1750	1850	1800
Cr	25	26	25	26	26	25
Cs	41	42	41	42	42	41
La	85	85	95	78	80	81
Ce	157	145	200	210	170	175
Sm	9.1	8.13	11.2	11.1	14.1	13.2
Eu	1.9	2.0	2.1	2.3	2.5	1.9
Tb	0.78	0.75	0.74	0.68	1.11	1.10
Yb	1.85	2.01	2.20	2.50	2.70	2.82
Lu	0.28	0.30	0.31	0.32	0.30	0.29

1. Latite of Dobro Pole; 2. Latite of Crna Tumba; 3. Latite of Dobro Pole; 4. Latite of Kozjak;
5. Latite of Kozjak; 6. Andesite-latite of Bela Voda

Latites and andesite-latites of Kozuf and Kozjak Mts. are porphyry volcanic rocks (calc-alkaline) composed of idiomorphic phenocrysts of andesine (40 - 47 % An), sanidine, amphibole, biotite and pyroxene. The groundmass is microcrystalline composed of microliths and plagioclases, sanidine, biotite and pyroxene. Apatite, ilmenite, rutile, pyrite and magnetite occur as accessory minerals. Chemical and geochemical analyses show that latites are intermediary rocks in which the SiO₂ content ranges from 58.67 to 60.86 %, and that of Al₂O₃ from 17.38 to 18.20 %. It should be mentioned that they have relatively uniform amounts of major oxides such as CaO, Na₂O, and K₂O that classifies these rocks as monzonites. The MgO content ranges from 1.11 to 2.43 % which is a characteristic of calc-alkaline rocks (Table 3).

The distribution of microelements and rare earth elements is given in Fig. 2. The diagrams and data about the content of microelements and rare earths (Table 3) display that latites possess increased concentrations of incompatible LIL elements such as Rb, Ba, and Sr. The diagrams also indicate a pronounced minimum of europium that gives information about fractionation processes of primary magmas or the character of partial meltings. It is obvious that the rocks are fairly rich in light rare earths with respect to heavy rare earths, with amount of rare earths of 280 ppm.

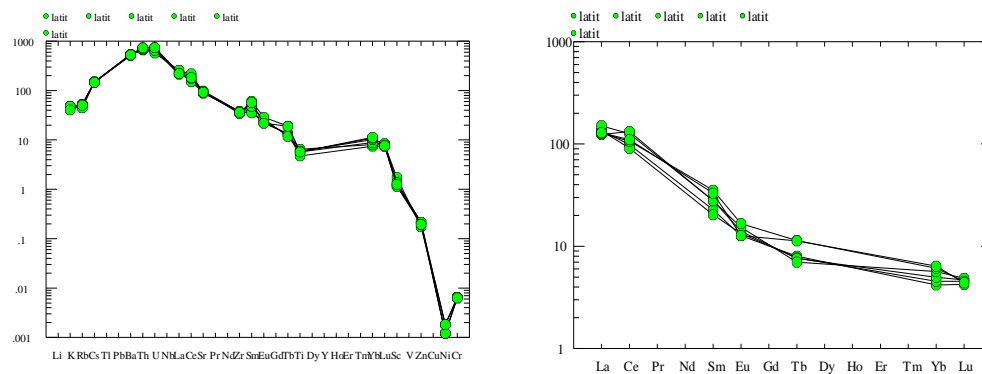


Fig.2. Distribution pattern of trace elements and rare earth elements in the latite and andesite-latite of the Kozuf district (Boev, 1988)

Quartzlatites (delenites) are transition varieties to latites. They are the most widespread volcanic rocks in Kozuf. They have been discovered in Blatec, Golubec, Miajlovo, in the vicinity of Dudica (Cardak, Sarena a.a.), Porta, Bela Voda, up to typical quartzlatites (delenites) near Momina Cuka. This group of volcanic rocks contains all transition varieties from latites to quartzlatites and has leucocratic nature. Quartzlatites are rocks with porphyritic structure composed mainly of andesine phenocrysts (38 to 45 % An) and sanidine. They also contain low amounts of ferrous minerals such as amphibole, biotite and augite. Individual types of quartzlatites such as those at Bela Voda, Cardak, Golubec etc. contain large-grained idiomorphic amphibole as well as more glass in the groundmass that gives the rocks dark-grey to black colour. Quartzlatites contain higher silicon dioxide content, almost equal content of alkali oxides and lower potassium oxide content than that in latites which gives the volcanic rocks (quartzlatite of Momina Cuka) more acidic nature (Table 4).

Table 4: Chemical composition (in %) of quartzlatites and content of microelements (in ppm)

	1	2	3	4	5	6
SiO ₂	64.06	65.81	65.08	63.16	62.72	61.97
TiO ₂	0.39	0.43	0.43	0.57	0.50	0.58
Al ₂ O ₃	17.86	16.72	17.04	16.62	17.84	18.54
Fe ₂ O ₃	3.02	2.90	3.39	4.44	4.12	3.82
MnO	0.03	0.05	0.08	0.09	0.08	0.07
MgO	1.44	0.61	0.47	1.32	0.79	0.52
CaO	3.69	3.12	5.04	4.20	3.64	2.40
Na ₂ O	4.21	4.56	4.34	3.92	4.09	4.74
K ₂ O	4.38	4.12	3.84	4.26	4.77	4.44
P ₂ O ₅	0.19	0.39	0.54	0.50	0.54	0.19
H ₂ O	0.98	1.47	0.47	0.92	0.90	1.28
Zn	20	20	20	20	20	20
Mo	1	1	1	1	1	1
Ni	10	10	20	10	10	10
Co	10	10	10	10	10	10
Cd	1	1	1	1	1	1
As	10	10	10	10	10	10
Sb	0.8	0.7	0.8	0.7	0.8	0.8
Se	0.1	0.2	0.1	0.2	0.1	0.1
Sc	15	15	10	15	15	15
Hf	5	5	4	5	5	4
Ta	0.8	0.9	0.6	0.7	0.7	0.7
Th	27	28	28	29	28	27
U	7	8	8	7	6	7
Rb	190	210	200	180	190	210
Zr	220	210	220	220	210	220
Sr	1200	1250	1250	1200	1250	1250
Ba	1950	2000	2100	2100	1950	1900
Cr	20	20	20	20	20	20
W	3	4	4	3	4	5
Cs	40	41	39	39	40	40
La	62	65	66	63	63	67
Ce	140	138	115	120	125	125
Sm	7.3	7.4	6.8	7.1	7.2	7.2
Eu	1.52	1.50	1.38	1.47	1.42	1.54
Tb	0.7	0.7	0.7	0.7	0.7	0.7
Yb	2.0	1.6	1.7	1.8	1.8	1.8
Lu	0.30	0.39	0.38	0.34	0.34	0.35

The composition determined for quartzlatites classifies them in the alkali calcium group of rocks. Because of the large calcium and silica contents they are transitions between intermediary to acidic type of rocks. Their chemical composition is in agreement with their mineralogical composition since they are basically composed of plagioclases, potassium feldspars, amphibole and accessory minerals. It should be mentioned that taking in consideration the chemical composition of the rocks alone, would classify them as trachy- andesites or latites. However, from the aspect of their chemical composition, the presence of 14 % of normative quartz in particular, the plagioclase and potassium feldspar ratio of 60 : 40, it is clear that they are quartzlatites.

Data related to the presence of microelements and REE indicates that the quartzlatites are enriched in LIL elements or the incompatible elements (Fig.3). They possess high contents of light elements, while total rare earths amount to 240 ppm. The rocks also contain fairly high arsenic and antimony amounts along with nickel and cobalt concentrations which is an indication of character of the deep fundament in the area.

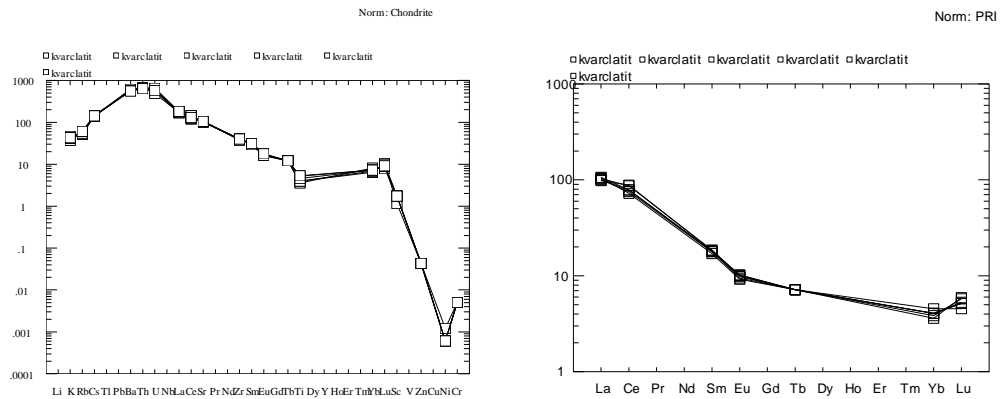


Fig. 3. Distributinot pattern of trace elements and rare earth elements in the quqrtzlatites of the Kozuf district (Boev, 1988)

Trachytes and trachyrhyolites are located in the westernmost parts of Kravica near the Sokol watch-house. The Kravica trachyte (an arsoite according to Tajder, 1940), occurs as a neck close to the Macedonian-Greek border in the territory of Greece. It is a well crystallized porphyry rock different in mineral composition from the rocks already described. It is composed of andesine, alkali feldspars such as sanidine and orthoclase and augite as femic mineral. The trachytes of the wider vicinity of Kravica are calc-alkaline in composition with large amounts of alkali oxides and higher potassium than sodium amounts that gives them pronounced potassic nature (Table 5). Chemical analyses indicate the presence of transition varieties called trachyrhyolites.

Table 5 : Chemical composition of trachytes (in %)

	1	2	3	4	5	6
SiO ₂	55.82	55.81	55.52	58.39	56.16	60.12
TiO ₂	0.95	0.86	0.92	0.93	0.93	0.55
Al ₂ O ₃	18.41	18.06	18.88	19.17	17.76	17.84
Fe ₂ O ₃	5.11	5.26	5.14	3.95	5.06	3.86
MnO	0.15	0.13	0.16	0.12	0.19	0.09
MgO	1.81	1.61	2.01	0.88	1.70	1.51
CaO	5.81	4.76	4.76	4.37	5.07	4.62
Na ₂ O	4.80	3.53	4.39	5.31	4.38	3.86
K ₂ O	5.74	6.50	6.37	6.10	6.26	5.05
P ₂ O ₅	0.75	0.73	0.57	0.50	0.71	0.36
H ₂ O	1.09	2.26	2.22	1.15	1.38	1.27

1. Trachyte of Kravica
2. Trachyte of Ano Paternik (Soldatos, 1955)
3. Trachyte of Ano Paternik (Soldatos, 1955)
4. Trachyte of Greka (Soldatos, 1955)
5. Trachyte of Kravica (Soldatos, 1955)
6. Trachyte of Kapina (Soldatos, 1955)

The Gradesnica Rhyolites are represented by lava extrusions of perlitic composition. Chemical analyses (Table 6) show that they are the most acid rocks occurring in the vicinity of Gradesnica west of Kozjak Mt.

Table 6 : Chemical composition of rhyolites of Kozuf (%)

	1	2	3	4	5	6
SiO ₂	72.49	71.32	71.89	73.39	72.89	71.09
TiO ₂	0.30	0.30	0.26	0.25	0.28	0.32
Al ₂ O ₃	11.22	12.85	10.20	9.46	9.78	13.30
Fe ₂ O ₃	6.19	4.95	6.61	8.04	8.04	4.13
MnO	0.12	0.12	0.12	0.11	0.15	0.26
MgO	0.14	0.22	0.93	0.37	0.25	0.18
CaO	0.78	0.75	0.55	0.40	0.60	0.71
Na ₂ O	2.87	3.21	2.15	2.32	2.46	3.24
K ₂ O	4.83	4.85	3.95	3.84	4.31	4.79
P ₂ O ₅	0.06	0.60	0.08	0.03	0.07	0.03
H ₂ O	1.08	0.60	3.23	2.18	1.52	1.95

1, 2, 3, 4, 5, 6 - Rhyolites of Gradesnica

They are the last volcanic rocks formed in Kozuf and Kozjak Mts. They are of the Pleistocene (the Lower Quaternary) age and possess rhyolitic or vitrophyre composition. They are composed of glass with microliths of feldspars as small needles that have lava flow orientation. Large sanidine and plagioclase phenocrysts in their composition in some places make them typically porphyritic. The rocks are fairly rich in silicium dioxide that gives them acidic nature. They are rich in alkalis, particularly potassium, but poor in calcium and magnesium oxides (Table 6).

ISOTOPIC AGE OF IGNEOUS ROCKS

Determination of isotopic age of Tertiary magmatism in the Republic of Macedonia was carried out by K/Ar method. Data obtained along with ⁸⁷Sr/⁸⁶Sr ratio are shown in Table 7. Data indicate that the isotopic age in Tertiary volcanic and intrusive rocks ranges from 1.8 up to 29.0 m.y. depending on the locality. The youngest magmatic activity was determined for the Kozuf district (the south of Macedonia) where magmatic activity began in the period between the Miocene and Pliocene and terminated in the Quaternary. The highest isotopic value was determined for the rocks of Buchim-Borov Dol where the magmatic activity took place in the Oligocene. The isotopic values for ⁸⁷Sr/⁸⁶Sr ratio indicate that they range from 0.706318 up to 0.710641.

Table 7: Isotopic age of Tertiary magmatic rock from territory of the Republic of Macedonia (Boev et al., 1991)

Locality	Type of rock	Age in Ma	⁸⁷ Sr / ⁸⁶ Sr
Kozuf	Latite	1.8 ± 0.1	
Kozuf	Latite	5.0 ± 0.2	0.708546
Kozuf	Quartzlatite	6.5 ± 0.2	0.709019
Kozuf	Andesite	4.8 ± 0.2	
Bucim	Latite	24.6 ± 2.0	0.706928
Borov Dol	Andesite	29.0 ± 3.0	0.706897
Damjan	Andesite	28.6 ± 0.6	0.706633
Zletovo	Quartzlatite	26.5 ± 2.0	0.706318
Zletovo	Latite	24.7 ± 0.4	
Zletovo	Monconite	21.9 ± 0.4	0.707770
Sasa	Andesite-latite	14.0 ± 3.0	0.710641
Sasa	Quartzlatite	24.0 ± 3.0	0.710244

The first data related to the age of volcanic rocks from Kozuf were reported by Cvijic (1906). He discovered round pebbles of extrusive rocks in Neogene lacustrine sediments. He came to the conclusion that andesite in the area of Kozuf intruded Cretaceous limestones and that they are post Cretaceous in age, even older than the Tikves Neogene.

From investigations carried out on volcanic rocks of Kozuf, Radovanovic (1930) concluded that the products of the volcanic activity are lacustrine and coeval with the Neogene sediments.

Based on investigations carried out in the terrains of Greece, Kosmat (1924) reports of possible Pliocene age for the volcanic rocks of Kozuf.

Based on superposition relationships between the volcanic agglomerative tuffs and the Neogene lacustrine sediments in which pikermi fauna was discovered in the top parts Ivanov (1960) infers that, most probably, the rocks are of the Pontian age.

Based on investigations carried out on pollens Mersier and Sauvage (1965) infer that these rocks are of Pliocene age.

Measurements of the isotopic composition of the volcanic rocks on Voras Mt. (Kozuf) in Greece gave the following data (Table 8).

Table 8: Isotopic age of volcanic rocks in Kozuf in the territory of Greece (Kolios et al, 1980)

Rock	K %	Ar 40 / gr K $\times 10^{-5}$	Ar 40 % r	m.y
Latite	5.87	1.98	41	5.0 ± 0.2
Quartzlatite	3.12	1.84	68	4.6 ± 0.2
Quartzlatite	9.04	1.81	49	4.5 ± 0.2
Quartzlatite	8.91	1.79	55	4.5 ± 0.2
Quartzlatite	7.00	1.76	45	4.4 ± 0.2
Latite	6.44	1.72	21	4.3 ± 0.2
Latite	8.01	1.60	42	4.0 ± 0.2
Latite	4.65	7.50	10	1.9 ± 0.1
Latite	7.35	2.96	20	1.8 ± 0.1

Boev (1988) carried out measurements on the isotopic composition of volcanic rocks of Kozuf in the Republic of Macedonia. Results obtained are shown in Table 9.

Table 9: Isotopic age of volcanic rocks of the Kozuf district (Boev, 1988)

Rock type and locality	K%	K^{40} g/g $\times 10^{-6}$	Ar %	Ar^{40} cm ³ $\times 10^{-6}$	Ar^{40} g/g $\times 10^{-9}$	Ar^{40}/K^{40} g/g $\times 10^{-3}$	m.y.
Latite of Baltova Cuka	4.36	5.08	3.0	0.84	1.50	0.29	5.0
			3.0	0.76	1.36	0.27	4.7
Latite-Quartzlatite of Vasov Grad	2.55	3.04	2.0	0.64	1.14	0.38	6.5
			3.0	0.64	1.16	0.38	6.5

Lipolt and Fuhrman (1986) measured some volcanic materials as products of the hydrothermal zone of Alsar and obtained results as follow (Table 10):

Table 10: Age of volcanics of the hydrothermal zone of Alshar (Lippolt and Fuhrman, 1986)

Rock	mineral	K%	^{40}Ar (ccm/g) $\times 10^{-6}$	^{40}Ar atm %	m.y.
Tuff	biotite	5.19	0.83	80.4	4.1±0.7
	feldspar	1.55	0.28	63.0	4.6±0.4
Tuff	biotite	7.04	1.21	52.2	4.4±0.4
	feldspar	5.90	1.01	51.7	4.4±0.5
Andesite	biotite	4.07	0.80	78.5	5.1±1.9
	feldspar	1.18	0.22	78.7	4.8±1.9
	ground mass	5.62	0.86	25.2	3.9±0.2

The following conclusions can be drawn based on data of isotopic investigations: the age of the rocks is in the span of 6.5 to 1.8 m.y. that determines a Pliocenic age. Individual differentiates are of Lower Pliocene age. Troesch, Frantz and Lepitkova (1995) report of data about the subvolcanic phase in Alshar that is in accord with the Miocene (12.1 m.y.).

Conclusion and genesis of the volcanic rocks of the Kozuf district

Boev (1988) reports of some conclusions related to the origin of magmas that formed the volcanic rocks of the Kozuf district. He considered that magma sources were located in the marginal parts between the continental crust and the envelope. He gives data about isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio that supports this assumption. Further investigations carried out by Lepitkova (1991) confirmed the earlier assumptions about origin of the magma that gave the material for the formation of the volcanic rocks. Namely, values determined for the isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are within 0.708568 and are very close to those that Boev (1988) determined for the volcanic rocks of Kozuf.

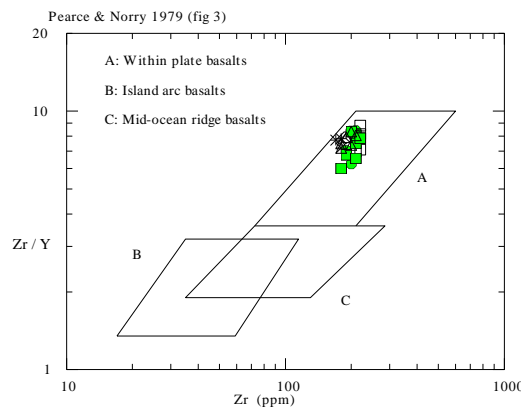


Fig.4. Relations between the volcanic rocks of Kozuf and individual tectonic zones (based on Pearce and Norry, 1979) (From Boev, 1988)

Fig. 4 shows the relationship between the volcanic rocks of Kozuf and individual geotectonic areas in which magmatic processes took place. The diagram indicates that data on the volcanic rocks of Kozuf plot in the field of continental slab- like basalts or the so called within plate basalts. This confirmation can be applied to explain the processes that contributed to the formation of the volcanic rocks in Kozuf.

It should be mentioned that CFB is related to the evolution of continental rift areas. The explanation about the genesis of magmas that gave the material for the formation of the

volcanic rocks during the consolidation processes should be searched in the development of these structures present in the continental areas.

Chemistry of magmas related to continental rift zones is conditioned by heterogeneity of mineral and chemical compositions of the source in the envelop, the degree of partial melting and depth of its occurrence, the amount of magma that comes out on the surface etc. There is poor geophysical data related to the presence of magmatic sources in the upper parts of the petrographic provinces. This is important for the fractionation crystallization along with the evolution of the chemistry in magmas.

The major problem in the study of continental magmatism is the estimation of the role of the envelop in the genesis of primary magmas. There is some geophysical data indicating to the existence of diapir in the envelop that moved upwards along the axis of the rift structure. Thinning of the lithosphere in a wider area could have caused a significant enlargement of the melt zone that underlies the axis of the rift structure but in the envelop. Thus, the greatest influence of the envelop on the processes of partial melting exerted in the rift zones with largest thinning of the crust and the largest uplifting of the envelop.

The genesis of the volcanic rocks of Kozuf can be explained best within the evolution of the Vardar zone as a rift zone, recurred several times during its evolution.

Based on available data related to the magmatic activity that took place in the Vardar zone from Oligocene to the Pleistocene it can be assumed that the processes of this geotectonic unit can be related to processes that took place in continental rift zones.

Primary magmas formed in this mode penetrated the surface along individual structures that formed as a result of the evolution of the area changing their composition by contamination and assimilation processes.

In addition, normalized values of distribution of rare earths (Fig. 5) are applied to explain the genesis of the volcanic rocks.

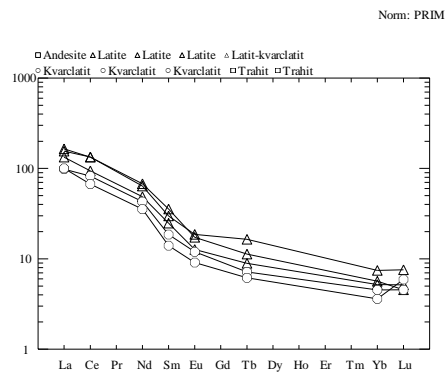


Fig. 5. The REE contents of the Kozuf volcanic rocks (From Boev, 1988)

Fig. 5 displays that there is no pronounced anomaly of Eu or predominance in fractionation processes of primary magma materials. The content of rare earth elements, enrichment in light rare earths as well as the high content of LIL elements indicate that primary melt consisted of crystallized garnet that was conformable with residual plagioclase melt. Pressure in such systems amounts to some 15 Kb or 45 to 50 km depth.

From geophysical data of continental crust beneath Kozuf it can be inferred that the crust is about 40 km thick.

Based on the aforementioned data a conclusion can be drawn that magma sources were located in the marginal parts of the upper envelope and the lower crust taking in consideration, of course, erosional processes of several million years.

The change in chemical composition of the extrusive magma yielding the series of volcanic rocks can be explained by assimilation processes that magma performed passing

through different lithologic environments assimilating them but altering its composition as well. According to their mode of occurrence and spatial distribution the volcanic rocks of Kozuf are riftogenic, formed by magmatic activation in the marginal parts of the earth's crust and the upper envelop. This can be inferred from isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio that amounts from 0.7088 to 0.7090 (Boev, 1988). Consolidation time, and the occurrence of volcanic rocks in the area were determined as 6 to 1.8 m.y. by K/Ar method (Boev, 1988) which is consistent with their stratigraphic age.

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