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CLASSIFICATION OF THE VOLCANIC ROCKS OF KOZUF MOUNTAIN

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Abstract. 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 pyroclastiic 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.

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.

Key words: Classifications, volcanic rocks, Kozuf Mountain.

КЛАСИФИКАЦИЈА НА ВУЛКАНСКИТЕ КАРПИ ОД КОЖУФ ПЛАНИНА

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Апстракт. Вулканските карпи кои се формирани за време на плеоценот се сместени на попречните тектонски структури на протегањето на Вардарскиот правец и тие се присутни на планината Кожуф и Козјак во јужните маргинални делови на Тиквешко-Мариовскиот терциерен басен.

Вулканската активност се манифестира со појавата на бројни вулкански купи кои во основа го претставуваат замрзнатиот канал за снабдување, и големи маси на пирокластичен материјал. Обично, вулканските купи се распоредени во источно-североисточната зона на протегање, најчесто на тектонски структури, на места каде се вкрстуваат со постари структури од северозапад (Вардарски правец). Попречните неотектонски структури се од неотектонската доба, формирани за време на плиоценот и лежат паралелно со северните маргини на Егејската Долина помеѓу Солун и Кавала.

Вулканската активност на планините Кожув и Козјак е претставена со различни видови на вулкански карпи и вулканокласти (вулкански бречи, конгломерати и туфови). Вулканокластите се појавуваат како седиментни слоеви во јужните делови на Тиквешко-Мариовскиот терциерен басен, каде што ги сочинуваат најгорните слоеви на седиментот. На некои места вулканокластитите се со дебелина од 200 до 300 метри.

Вулканските карпи се присутни како алкален базалт (мали тела), кварцлатити (делинити), андезит-латити (трахиандезити), преоден латит-кварцлатит и кварцлатит-латит (делинит-латит), како и латити, трахити, трахириолити и риолити.

Вулканските карпи од планините Кожуф и Козјак покажуваат најмногу сличност со серијата вулкански карпи од рудната околина на Бучим - Боров Дол, во нивниот минерален и хемиски состав, со единствената разлика во периодот на нивното формирање. Имено, карпите од Кожув Планина и Козјак се формирани за време на плиоценот, додека оние од Бучим - Боров Дол се формирани за време на горен олигоцен. Првите се екструзивни (и експлозивни), а вторите се субвулкански и субвулкански до хипоабисални фации, што значи дека нивните индивидуални горни делови се подлабоко еродирани.

Клучни зборови: Класификација, вулкански карпи, Кожуф Планина.

1. Petrology

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 porphyrytic 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 $Si0_2$ ranging from 50.12 up to 51.20 % , containing fairly large amount of Mg0 - 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_2O_3	16.70	15.86	17.80
Fe_2O_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_2O	3.05	3.12	3.25
K_2O	3.51	3.45	3.65
P_2O_5	0.33	0.25	0.45
H_2O	6.37	6.50	5.72

Table1-1. CIPW norms for basalts

Normative Minerals	Weight % Norm	Volume % Norm
Quartz		
Plagioclase	45,58	51,47
Orthoclase	20,74	24,51
Nepheline		
Leucite		
Kalsilite		
Corundum	0,64	0,48
Diopside		
Hypersthene	6,40	5,96
Wollastonite		
Olivine	15,93	14,67
Larnite		
Acmite		
K2SiO3		
Na2SiO3		
Rutile		
Ilmenite	1,23	0,79
Magnetite	2,41	1,40
Hematite		
Apatite	0,76	0,72
Zircon		
Perovskite		
Chromite		
Sphene		
Pyrite		
Halite		
Fluorite		
Anhydrite		
Na2SO4		
Calcite		
Na2CO3		

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_2O_3	16.30	16.25	16.80
Fe_2O_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_2O	2.11	2.70	3.10
K_2O	0.83	0.85	0.92
P_2O_5	0.45	0.46	0.45
H_2O	3.60	6.35	5.75

Chemical composition (Table 2) shows that they are intermediary rocks with 59.20 to 59.94 % $Si0_2$ and that they have fairly large amount of Na_20 relative to K_20, whereas the Al_20_3 content ranges from 16.25 to 16.80 %.

Table2-2. CIPW norms for andesites

Normative Minerals	Weight % Norm	Volume % Norm
Quartz	27,26	30,27
Plagioclase	50,41	54,75
Orthoclase	4,90	5,64
Nepheline		
Leucite		
Kalsilite		
Corundum		
Diopside	0,68	0,62
Hypersthene	4,67	4,28
Wollastonite		
Olivine		
Larnite		
Acmite		
K2SiO3		
Na2SiO3		
Rutile		
Ilmenite	1,03	0,64
Magnetite	3,50	1,98
Hematite	1,56	0,87
Apatite	1,04	0,96
Zircon		
Perovskite		
Chromite		
Sphene		
Pyrite		
Halite		
Fluorite		
Anhydrite		
Na2SO4		
Calcite		
Na2CO3		

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_2O_3	18.20	17.81	17.65	17.38	17.53	17.61
Fe_2O_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_2O	4.35	4.05	4.44	4.35	3.83	3.87
K_2O	4.75	4.71	4.99	4.76	4.94	4.18
P_2O_5	0.56	0.68	0.73	0.73	0.56	0.16
H_2O	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
Sc	10	15	11	12	10	11
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
W	4	3	4	4	4	3
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 idiomoprhous phenocrysts of andesine (40 - 47 % An), sanidine, amphibole, biotite and pyroxene. The groundmass is microcrystalline composed of microliths and plagioclases, sandinie, 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 $Si0_2$ content ranges from 58.67 to 60.86 %, and that of Al_20_3 from 17.38 to 18.20 %. It should be mentioned that they have relatively uniform amounts of major oxides such as Ca0, Na_20, and K_20 that classifies these rocks as monzonites. The Mg0 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. 1. 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 digrams 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.

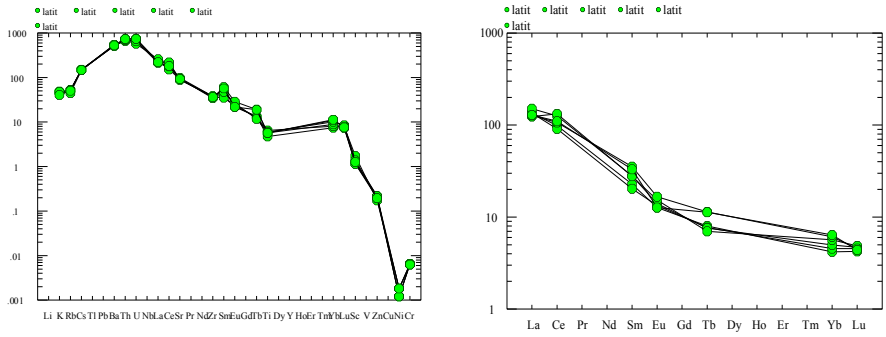

Fig. 1.: Distributinot pattern of trace elements and rare earth elements in the latie and andesite-latite of the Kozuf district (Boev, 1988)

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 femic 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 silicium 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_2O_3	17.86	16.72	17.04	16.62	17.84	18.54
Fe_2O_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_2O	4.21	4.56	4.34	3.92	4.09	4.74
K_2O	4.38	4.12	3.84	4.26	4.77	4.44
P_2O_5	0.19	0.39	0.54	0.50	0.54	0.19
H_2O	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.2). 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.

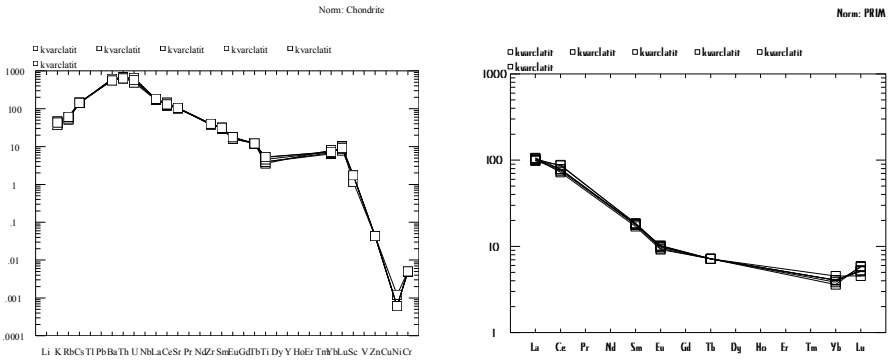

Fig. 2.: Distributinot pattern of trace elements and rare earth elements in the quqrtzlatites of the Kozuf district (Boev, 1988)

Trachytes and trachyrhyolites are located in the westernmost parts of Kravica near the Sokol watch-house. The Kravica trachyte, 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_2O_3	18.41	18.06	18.88	19.17	17.76	17.84
Fe_2O_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_2O	4.80	3.53	4.39	5.31	4.38	3.86
K_2O	5.74	6.50	6.37	6.10	6.26	5.05
P_2O_5	0.75	0.73	0.57	0.50	0.71	0.36
H_2O	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_2O_3	11.22	12.85	10.20	9.46	9.78	13.30
Fe_2O_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_2O	2.87	3.21	2.15	2.32	2.46	3.24
K_2O	4.83	4.85	3.95	3.84	4.31	4.79
P_2O_5	0.06	0.60	0.08	0.03	0.07	0.03
H_2O	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 porphyrytic. 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).

Classification of the volcanic rocks of Kozuf

Classification of the volcanic rocks of Kozuf and Kozjak Mts is based on TAS diagram (Fig. 3).

The diagram (Fig. 3) shows that only a small number of volcanic rocks analyzed belong to the field of andesites of subalkali nature. Most of the data related to the chemistry of the rocks plot in the field of latites and quartz latites (calc-alkaline rocks) with transition to trachytes (alkali rocks). The most acidic volcanic rocks plot in the field of rhyolites.

Fig. 4 shows classification of the volcanic rocks of Kozuf based on $Si0_2$ and K_20 contents. It shows that they contain high potassium contents. Only andesites plot in the field of rocks of low potassium.

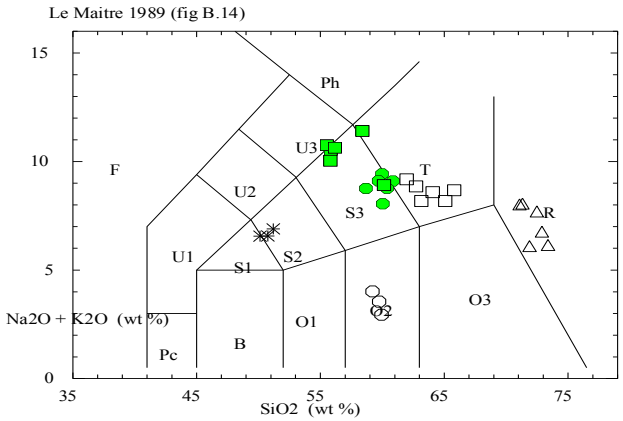

Fig. 3.: Clasification of the Kozuf volcanic rocks based on the Le Maitre (1989) diagram (from Boev, 1988)

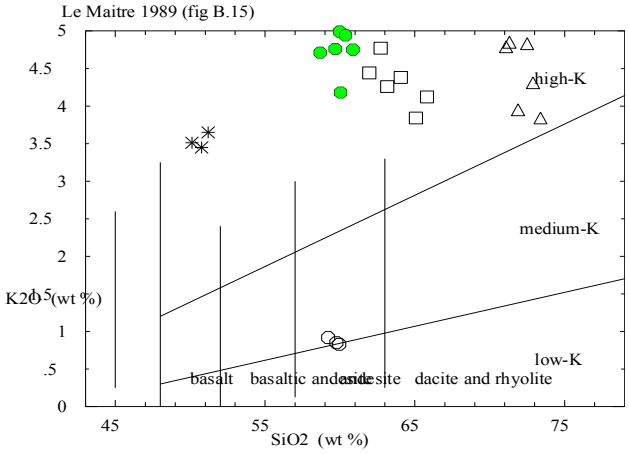

Fig. 4.: Clasification of the Kozuf volcanic rocks based on SiO_2 / K_2O contents (Le Maitre, 1989) (from Boev, 1988)

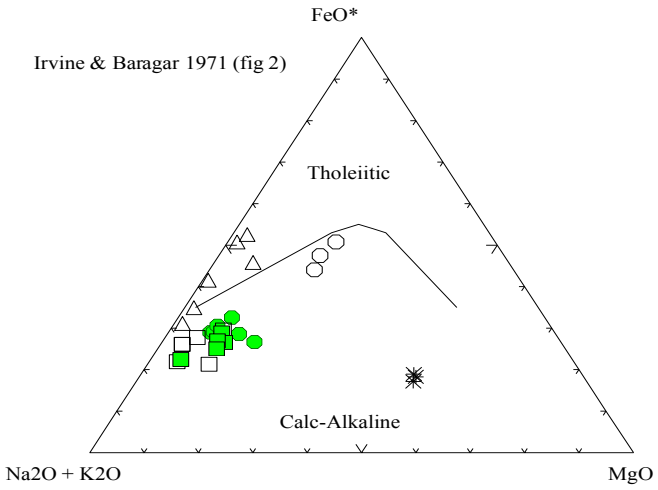

Fig. 5.: Chemical composition of the Kozuf volcanic rocks (Irvine and Baragar, 1971) (from Boev, 1988)

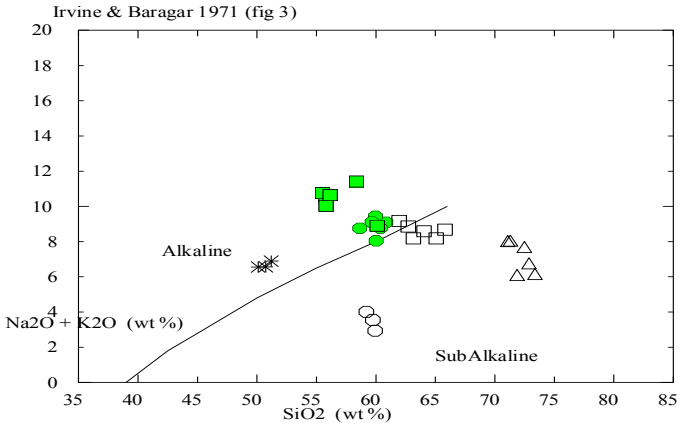

Fig. 6.: Chemical composition of the Kozuf volcanic rocks (Irvine and Baragar, 1971) (from Boev, 1988)

The diagrams in Figs 5 and 6 show that the volcanic rocks of Kozuf belong to the calc-alkaline series and that they are transitions between subalkali and alkali rocks.

2. Conclusion

The common feature of the volcanic rocks of Kozuf is the fairly high feldspar and almost equal amounts of plagioclases and potassium feldspar present as high potassium, calcium and sodium oxide in their mineral composition. Sporadically potassium content is higher than that of sodium oxides.

The disequilibrium in plagioclase and potassium contents results in the occurrence of transitional rocks types - from alkali to calc-alkaline series.

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