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Содржина/Contents

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PETROLOGY OF VOLCANIC ROCKS OF AREA DOBRO POLE-GRADESNICA NORTH MACEDONIA

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Abstract. This paper presents the results of the petrological, chemical and geochemical characteristics of the volcanic rocks in the area Kravica-Dobro Pole-Gradesnica in samples collected in the summer of 2019. These rocks belong to the group of trachytes to trachyandesites. The spider diagrams of the normalized values indicate volcanic rocks that are silica-poor volcanics and are associated with subductional related processes.

Key words: volcanic rocks, trahyandesites.

ПЕТРОЛОГИЈА НА ВУЛКАНСКИТЕ КАРПИ ОД ОБЛАСТА ДОБРО ПОЛЕ ГРАДЕШНИЦА РЕПУБЛИКА СЕВЕРНА МАКЕДОНИЈА

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Апстракт. Направените петролошки испитувања на вулканските карпи од областа Добро Поле-Градешница покажуваат дека тука се работи за вулкански карпи од типот на трахити до трахи-андезити. Хемискиот и геохемискиот состав на овие карпи зборува и за нивната генетска и геотектонска поврзаност со процесите кои се случувале во горната обвивка на овие простори за време на субдукциските процеси и појавата на субдукцискиот магматизам во плиоцен. Големата концентрација на К и асоцираните елементи како што се Sr и Pb укажуваат на фактот дека основната магма од која се генерирани вулканските карпи потекнува од топењето на осиромашена обвивка.

Клучни зборови: вулкански карпи, трахиандезити.

1. Introduction

The area of Dobro Pole – Gradesnica area is part of a wider area Kozuf-Kajmakcalan (Boev, 1988, 1991) within the borders of the Republic of North Macedonia and at the same time it represents the northern part of the Almopia area in Greece that covers the Voras mountain range (Fytikas et al., 1984). This volcanism that occurred in this part of the Aegean region is mainly related to the subduction of the African plate below the southern margins of the Eurasian plate (Boccaletti et al., 1974). Several isotope studies have been performed on this volcanism that define its age as Tertiary to Quaternary (Boev, 1988., Kolios et al, 1980., Fytikas et al, 1984; Eleftheriadis, 1989, 1991; Eleftheriadis et al, 2003). This volcanism is of intermediary chemical nature and is enriched with potassium and LILE elements (Boev, 1988; Soldatos, 1955; Mercier, 1968; Clapsopoulos, 1991). Petrological and mineralogical data indicate a high-K calc-alkaline to shoshonitic nature of these volcanic rocks (Boev 1988; Kolios et al., 1980; Eleftheriadis, 1988). In the series of crystalline schists from which mountain range from Mala Rupa to Kajmakcalan is built, there are numerous volcanic clusters formed of volcanic rocks of Neogene age that are remnants of the great volcanic activity of this region that occurred in the Tertiary. The volcanic cones are made of trachyte, trachyandesite to andesite, and the most remarkable parts of this massif are the cones from Gradesnica to Kravicki Kamen. In the summer of 2019, a number of samples of these rocks were collected for their more detailed mineralogical, petrographic and petrological-geochemical determination.

2. Geology

Geology in the Dobro Pole – Gradesnica area is part of a wider area Kozuf-Kajmakcalan, mainly represented with the following lithological complexes (Fig.1).

The complex of Precambrian metamorphic rocks (Gmb) in the vicinity of the the west (Dobro Pole-Gradesnica) the complex is built of gneisses and micaschists located in the Elen Supe tectonic block, Arsovski (1962) determined a Precambrian age, but Mersier et all,(1965) reported Mesozoic or Triassic age for the rocks.

Gneisses and marbles have been found in the tectonically emersion block at Mala Rupa, west of the village of Konsko. Mersier (1973) reported Mesozoic or Triassic age for the rocks.

Gneisses are developed in the lower, but marbles in the upper parts of the complex. The gneisses of the lowermost part are albites with pronounced porphyroblastic texture, whereas those of the upper parts have amphibolite-biotitic composition with lenses of micaschists and cipolines. Besides albite, they contain potassium feldspar-microcline. They also contain colored minerals such as amphibole, biotite, chlorite and mica.

Marbles are medium to large-grained rocks built of calcite. They overlie gneisses and grade into cipolines and calc-schists and along with gneisses comprise one metamorphic complex. The marble horizon is estimated at 600 m, while the horizon of gneisses at approximately 1000 to 1500 m thick.

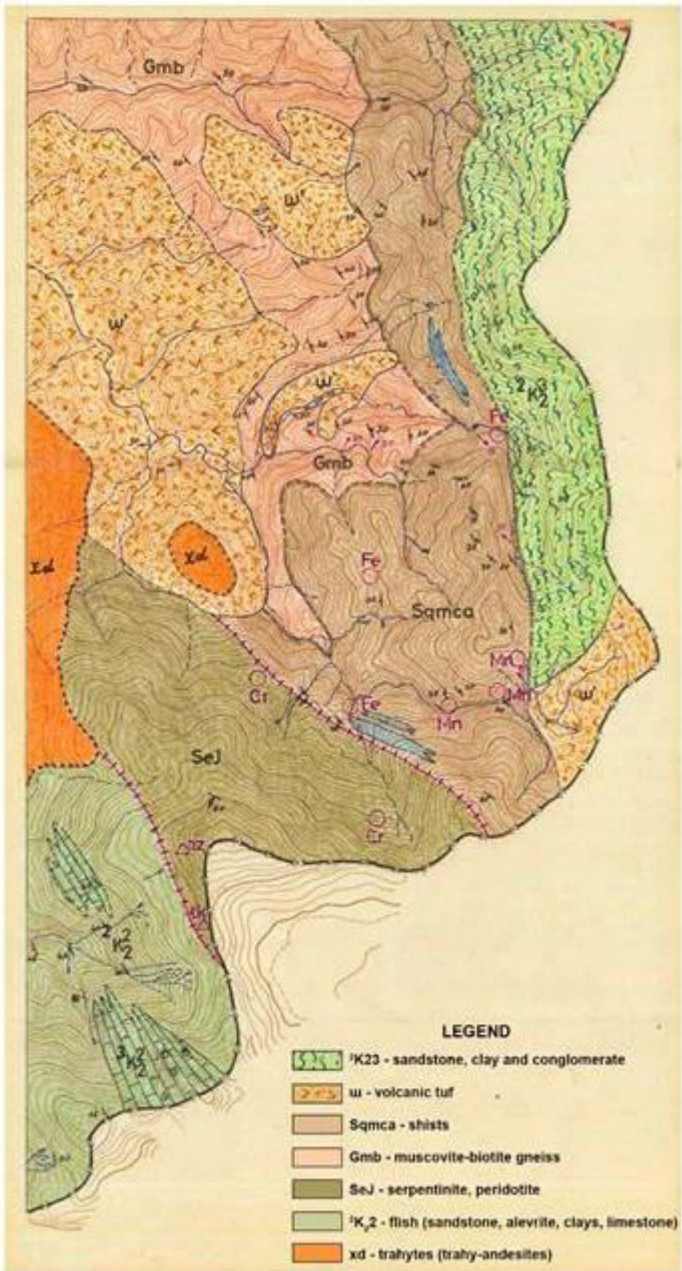


Fig.1. Geological map of the area Dobro Pole-Gradesnica (1:25 000)

The complex of Paleozoic metamorphic rocks, (Sqmca) unlike the Precambrian gneisses and marbles, is of lower metamorphic degree. It conformably overlies the marbles of Precambrian age.

Paleozoic metamorphic rocks are most common in Adzibarica, between Keci Kaj and Gladnica, Jelovarnik and Porta as a phyllite horizon, a horizon of phyllitic schists and cipolines, quartzporphyry, phyllites, argilloschists and metasandstones with marble interlations and finally a horizon of quartzites, quartz schists and metadiabases in the area of Dobro Pole-Gradesnica.

The phyllite horizon also contains sericitic and epidotic schists, cipolines and marbles and metamorphosed quartz-porphyry intruded by quartz veins (Adzibarica, between Keci Kaj and Gladnica).

Graphitic schists have also been noticed in the series of sericitic schists. The horizon is approximately 750 m thick. It was also revealed in Adzibarica, Jelovarnik and Porta as well as in the vicinity of the Dusnica River source.

Cipolines and marbles alternate phyllitic schists in the horizon of cipolines and phyllitic schists west of Flora, Alcak, Ursa and Jelovranik along the River Dosnica course. They are overlain by schistose quartz porphyry distinguished as a separate horizon. They possess micro porphyroblastic texture, built of sericitized and kaolinized feldspars of albitic composition. They also contain potassium feldspar, quartz, epidote and chlorite.

A horizon of quartzites and metasandstones was determined in Boulska Reka near Dina, Kalugjerica and Usevica. It also contains metadiabases with sporadic sulphide mineralization.

Mersier (1973) determined the age of this series and that of Porta as Jurassic based on the degree of metamorphism and because it concordantly overlies the Mala Rupa - Tsena series which he determined as Triassic.

The complex of serpentinized ultramafic rocks* (SeJ*) is situated in the Studena Voda - Rzanovo - Kumanicevo zone and zone Kozjak-Alsar and west part of Kozuf Mts, in the area of Crna Tumba-Dobro Pole-Gradesnica. It represents a tectonic structure on which serpentinites along with Jurassic and Upper Cretaceous metasediments cover Paleozoic and Triassic metamorphic rocks.

Lateritic deposits of nickeliferous iron ore developed over the Rzanovo - Studena Voda, Crna Tumba-Dobro Pole-Gradesnica zone and along with sediments of the top parts were dynamo metamorphosed in conditions of prehnite pumpelite up to greenschist facies (Jankovic et all, 1977).

The complex of Upper Cretaceous rocks ($^2K_2^3$, $^2K_2^2$) is present as a series of limestones and conglomerates that corresponds to the Barremian and Albian, as well as a series of limestones of Turonian age.

The series of limestones is present in the Cardak, Dudica and Gladnica localities and in the Rzanovo and Studena Voda where these sediments comprise the top part of the nickeliferous-iron ores. The stratified limestones in the lower parts consist of marls with residues of *Nerinea olisoponensis cf. optuca, O. Turonica* fauna considers them to be of Turonian age (Boev, 1988).

Large portion of the Kozuf district is occupied by massive limestones, particularly in the Cardak, Dudica and Gladnica areas where they transgressively overlie Paleozoic rocks. Limestones are rather broken and karstified and 400 to 600 m thick. This is the largest thickness determined for the Senonian limestones found in the Republic of Macedonia. Poorly preserved rudists are discovered in them and based on that data the age of these limestones was determined as Senonian. Because of the large fissure density and karstification they represent water collectors for the rich sources of the Rivers Stara and Zarnica. The limestones of the Dudica district are intensively hydrothermally altered and intruded by young subvolcanic rocks.

The complex of volcanic rocks (xα), 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.

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 complex of Pliocene sediments and pyroclasts (ɯ) is widespread in the Kozuf district. Essentially lacustrine sediments are built of coarse-clastic sediments that overlie the basement of various geologic formations. They overlie Upper Eocenic sediments between Barovo and Krnjevo. They are present as large-grained conglomerates and clayey sandstone sediments (between the villages of Dolna Bosava and Krnjevo).

Gravel sediments have been determined in the basement of the tuffs near the village of Gorna Bosava in the valley of the River Nistaica above the village of Cemersko. There are sands and clayey sands with intercalations of sand-clays or clayey sediments over the series of conglomerates near Krnjevo which itself is overlain by clayey carbonate rocks.

Marls overlain by clayey sand and clayey carbonate sediments with large amounts of fossil residues, bones and fauna (of mammals) occur near the village of Barovo. The last skeletons of this fauna were found in the topmost level of these clastic lacustrine sediments in diatomaceous earth beneath volcanic sediments - tuffs near Stukovi Orai in the vicinity of the village of Barovo (Jankovic et al, 1977). The age of the sediments was determined as lower part of the Upper Pliocene.

The Pliocene clastic sediments in the southern parts of the basin end with a travertine and lie immediately beneath the pyroclastic sediments (above the village of Boula).

Pyroclastic sedimentary rocks cover Pliocene lacustrine sediments in the south parts of the basin near Vitacevo and Gatenovo. In the southernmost part they overlie the rocks of the northern slopes of Mount Kozuf and extend along the Macedonian - Greek border, south of the village of Mrezicko. In the north they extend close to the town of Kavardci and Dolni Disan (south of Negotino). The final tuffs and conglomerates can be seen in the vicinity of the village of Radnja. The volcanic sediments are from several meters up to several hundred meters thick.

A horizon of agglomerative tuffs overlain by a horizon of fine-grained volcanic ashes and glass occurs in close proximity to the Mokliski Monastery in the valley of the River Luda Mara over the clastic lacustrine sediments present as carbonate clayey material. The latest horizon of volcanic sediments consists of brecciated well banded volcanic tuffs - pyroclasts. The largest blocks of volcanic rocks were found in the north slopes of Mount Kozuf, beneath the volcanic craters and domes (above the village of Radnja and Bara, in the vicinity of Gladnica, Ametkova Glava and Konopiste).

3. Methodology and results

The applied methodology included: preparation of petrographic preparations from substituted volcanic rock samples; microscopic processing of the preparations made using the method of optical microscopy with polarized light; making microscopic photographs of the samples; preparation of chemical analyses and analyses of micro elements and rare earths using the ICP-MS method; computer data processing.

3.1 Petrography

At the very border between the Republic of North Macedonia and Greece, at an altitude of 1680 meters is the volcanic cone Kravitza (Fig. 2) and there are several more volcanic cones near the site Dobro Pole placed in a series of metamorphic schists.

Fig. 2. Volcanic cone Kravitza

These volcanic cones are extremely characteristic morphological shapes that can be seen from a distance. The volcanic cones have very steep sides made of volcanic rocks that are of dark gray color, compact texture and a visible holocrystalline porphyry structure. Visible plagioclases and glassy alkaline feldspars make the macroscopic structure.

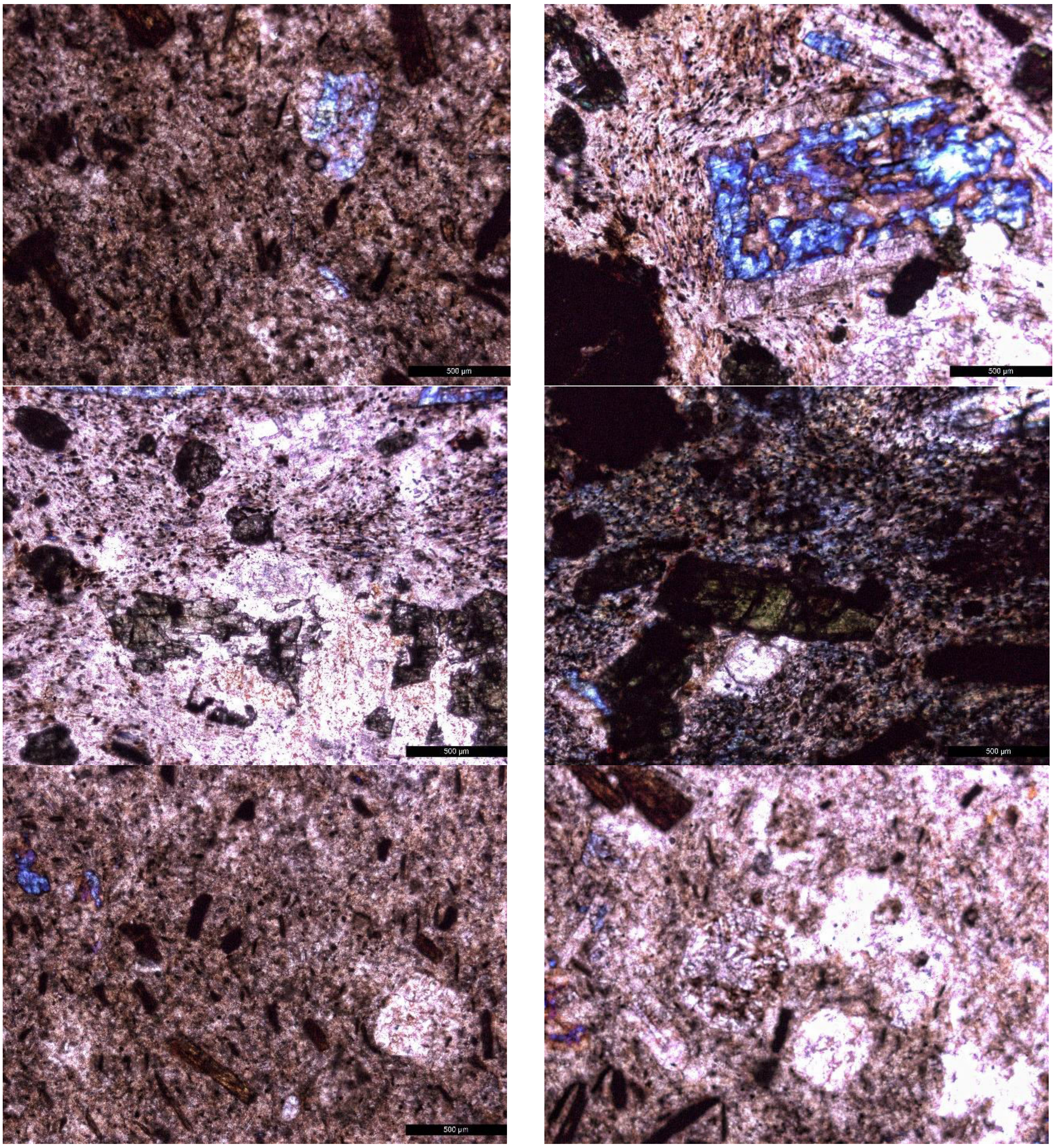
Under the microscope the rocks from the locality Kravitza-Dobro Pole-Gradesnica have a typical holocrystalline porphyry structure (Fig. 3). In a fairly dense aphanitic basic mass, phenocrystals of sanidine and plagioclases (andesine) occur in some places with a fluid texture, followed by pyroxenes having diopside-augitic composition. The rocks also contain biotite, magnetite, and zircon.

Plagioclases are the most present phenocrysts, appearing in plate forms that rarely have idiomorphic shapes. They are about 1 mm in size, and have no pronounced zonal structure so they are not suitable for optical tests.

The anorthoclase occurs between phenocrystals in separate individual forms and in larger crystals. The augite appears both as phenocryst and as a microlith in the ground mass. It has idiomorphic shapes and octagonal sections and characteristic pyroxene cleavage along the prism directions can be seen.

Of the accessory minerals there is biotite that is magmatically resorbed and almost always filled with fine grains of magnetite (opacite). Magnetite occurs in small grains that appear scattered in the ground mass. Apatite occurs in idiomorphic short columnar crystals up to 0.4 mm in size.

The ground mass consists of non-oriented tiny individuals of potassium feldspar (sanidine-anorthoclase) that sometimes appear in the form of tiny fluidly oriented that are building a typical trachyte structure. In the basal mass there are also tiny plagioclases and very small pyroxene grains having sharp idiomorphic contours. Based on microscopic studies, it can be concluded that these are volcanic rocks of the trachyte to trachy-andesite type.



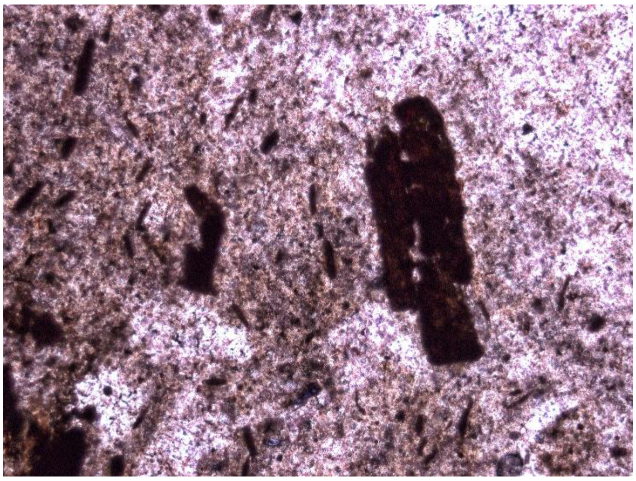


Fig. 3. Microscopic photographs of trachytes and trachyandesites in the area Kravitza-Dobro Pole-Gradesnica (P ob 25 x, crossed N)

3.2 Analytical results

The results of the specific chemical composition of the major elements as well as the trace elements and the elements of the group of rare earths are shown in Table 1. Chemical analysis shows that these are intermediary volcanic rocks with a SiO_2 content of 55.52 to 61.32% and a high amount of alkali (K_2O + Na_2O) of 10.5%, of which K_2O accounts for 5.01 to 5,87%, so these rocks have a pronounced alkaline character. These results of the chemical analysis indicate that these rocks could be classified as trachyte but the large amount of CaO (5.21%) in relation to the amount of MgO (2.11%) slightly changes the image of these rocks relative to of the classical family of rocks from the group of trachytes (Fig. 4). The normative composition of C.I.P.W shows the presence of normative olivine in the rocks of the Kravitza area, while in the areas of Dobro Pole and Gradesnica there is no normative olivine in the rocks (Table 2).

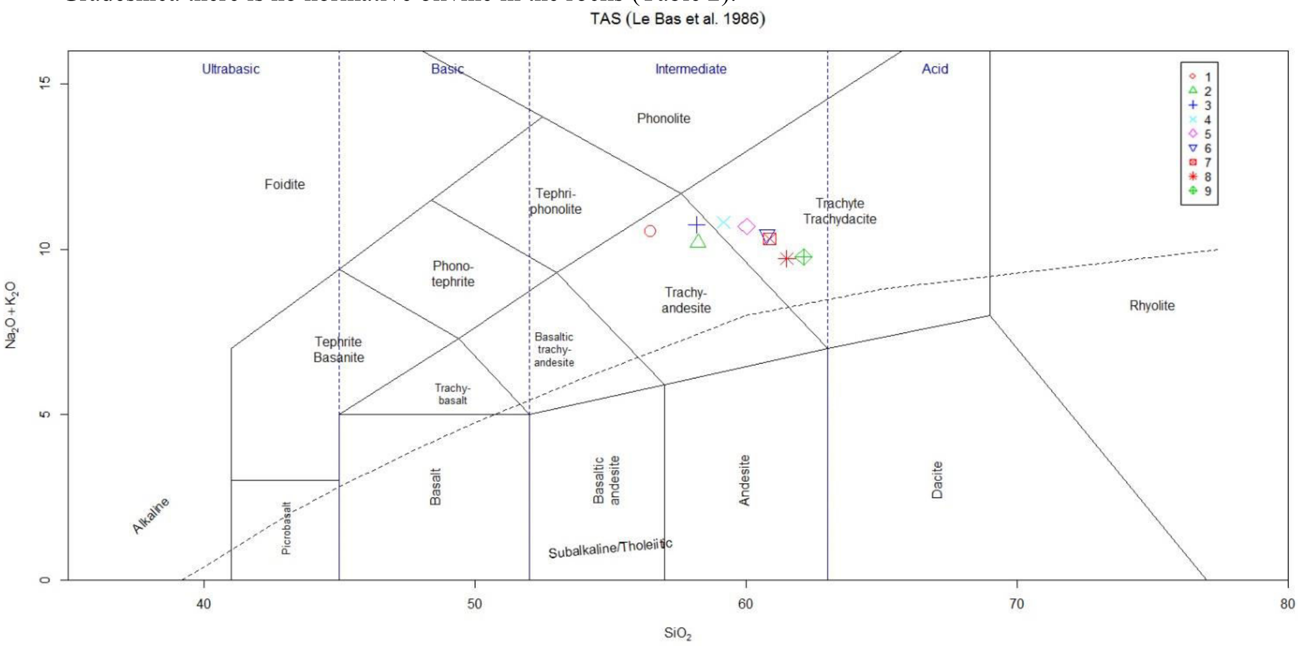


Fig.4. TAS diagram of volcanic rock of Kravitza-Dobro Pole-Gradesnica area (Le Maitre, R.W. (1989)

Table 1: Chemical and geochemical composition of the volcanic rocks from the area of Dobro Pole-Gradesnica-Kravitza (ICP-MS method)

	1 Kravitza	2 Kravitza	3 Kravitza	4 Dobro Pole	5 Dobro Pole	6 Dobro Pole	7 Gradesnica	8 Gradesnica	9 Gradesnica
%									
SiO_2	55.52	56.81	56.98	58.23	59.54	60.21	60.54	60.87	61.32
TiO_2	0.87	0.74	0.65	0.55	0.87	0.98	0.96	0.78	0.84
Al_2O_3	18.21	17.68	17.87	18.01	17.54	17.11	17.54	17.77	17.32
Fe_2O_3	5.15	5.45	4.78	4.87	4.54	4.65	4.32	4.21	4.11
MnO	0.15	0.11	0.12	0.13	0.15	0.18	0.20	0.17	0.14
MgO	2.11	1.85	1.98	1.74	2.01	1.88	1.92	1.86	1.93
CaO	5.21	4.32	4.51	3.78	3.54	3.32	3.42	3.29	3.01
Na_2O	4.50	4.31	4.87	4.87	5.02	5.35	5.25	4.47	4.33
K_2O	5.87	5.64	5.65	5.78	5.65	5.01	5.02	5.15	5.31
P_2O_5	0.71	0.65	0.54	0.45	0.61	0.38	0.30	0.40	0.41
H_2O	1.01	1.56	1.50	1.11	0.50	0.70	0.50	1.01	1.11
ppm									
Rb	170	190	200	220	230	190	180	250	240
Cs	14	16	20	21	25	20	17	18	20
Be	4	4	5	6	8	10	10	9	9
Sr	1100	1000	1200	1500	1900	1400	1700	1600	2000
Ba	1400	1500	1800	2100	2300	2000	2300	2200	2400
Ga	14	15	18	16	20	20	17	18	20
Y	22	25	21	26	30	30	28	28	25
Zr	280	320	310	380	350	410	420	400	390
Hf	5	4	5	6	8	10	12	11	8
U	15	14	18	20	21	14	15	15	12
Th	51	55	42	60	60	42	45	45	42
Nb	2	3	3	3	4	2	3	3	4
Ta	1.1	1.5	2.1	1.8	1.5	1.4	1.7	1.6	2.0
Ni	12	15	17	21	25	16	14	20	24
Co	15	18	20	22	19	17	21	16	14
Cr	32	34	35	38	40	41	45	38	32
Pb	75	65	70	55	82	62	87	68	60
Zn	55	58	60	62	60	57	63	61	60
Cu	25	28	31	30	32	25	26	24	28
V	70	75	80	81	84	94	90	87	80
As	11	12	10	10	14	12	11	10	10
Sb	1	2	1	2	3	2	1	2	2
La	85	80	88	90	90	95	98	100	100
Ce	170	180	160	180	160	160	170	180	170
Pr	15	16	18	18	16	16	20	22	20
Nd	70	80	70	80	60	60	60	70	70
Sm	10	11	10	12	12	10	11	11	12
Eu	2.1	2.3	2.5	2.4	2.6	2.3	2.1	2.2	2.2
Gd	5	4	6	5	4	6	6	7	6
Tb	1	1	1	1	1	1	1	1	1
Dy	3.8	4.1	4.2	3.9	4.0	4.2	4.1	4.2	3.9
Ho	1.9	2.0	2.1	2.2	2.0	1.9	2.3	2.1	2.0
Er	2.0	2.0	1.9	1.8	1.8	1.9	2.1	2.2	2.0
Tm	0.25	0.26	0.27	0.25	0.28	0.30	0.30	0.28	0.28
Yb	1.8	1.8	1.9	2.0	1.9	1.8	1.8	1.7	1.8
Lu	0.28	0.28	0.29	0.30	0.31	0.30	0.29	0.29	0.30

Table 2: Normative (C.I.P.W) composition of the volcanic rocks from the area of Kravitz- Dobro Pole- Gradesnica-

	1 Kravitza	2 Kravitza	3 Kravitza	4 Dobro Pole	5 Dobro Pole	6 Dobro Pole	7 Gradesnica	8 Gradesnica	9 Gradesnica
Quartz		1.11			0.95	2.49	2.73	6.87	7.96
Plagioclase	48.05	51.62	51.72	53.78	53.02	55.48	55.86	52.80	50.57
Orthoclase	37.85	36.62	36.39	36.94	35.75	31.87	31.76	32.65	33.72
Nepheline	2.69		1.38						
Corundum									
Diopside	4.47	1.91	4.61	2.81	1.65	2.27	1.98		
Hypersthene		3.15		1.19	3.51	2.96	3.16	3.96	4.12
Olivine	1.47		1.50	0.87					
Rutile								0.29	0.43
Ilmenite	0.19	0.14	0.15	0.16	0.19	0.22	0.25	0.21	0.17
Hematite	2.74	2.92	2.54	2.57	2.37	2.44	2.25	2.20	2.15
Apatite	1.44	1.32	1.09	0.90	1.21	0.76	0.60	0.80	0.82
Perovskite	0.83		0.61						
Sphene		1.21		0.78	1.35	1.50	1.41	0.27	0.06

CIPW Norm	1	2	3	4	5	6	7	8	9
Quartz						0.16	0.58	4.47	5.69
Orthoclase	34.68	33.32	33.38	34.15	33.38	29.60	29.66	30.43	31.37
Albite	28.98	36.46	34.87	38.90	42.47	45.26	44.42	37.82	36.63
Anorthite	12.15	12.23	10.20	10.20	8.63	7.87	9.46	13.20	12.13
Corundum									
Nepheline	4.92		3.43	1.24					
Leucite									
Kaliophilite									
Na_2SiO_3									
Calcite									
Apatite	1.77	1.62	1.35	1.12	1.53	0.95	0.75	1.00	1.03
Pyrite									
Ilmenite	1.65	1.40	1.23	1.04	1.65	1.86	1.82	1.48	1.59
Magnetite	0.97	1.03	0.90	0.92	0.85	0.89	0.82	0.80	0.77
Rutile									
Titanite									
Perovskite									
Diopside	7.51	4.13	7.17	4.68	4.08	5.06	4.57	0.41	0.09
Hypersthene		1.84			2.96	7.06	7.04	9.05	9.09
Olivine	5.32	5.13	5.07	5.78	3.61				
Wollastonite									
Larnite									
Acmite									
Norm En	50	43.7	49.3	44.0	52.2	51.3	53.7	51.2	53.6
Norm An	24.6	25.1	20.1	19.9	16.9	14.8	17.6	25.9	24.9
Norm Color	15.5	13.6	14.4	12.4	13.2	14.9	14.3	11.7	11.6
Indices									
Mg/(Mg+Fe)	0.44	0.40	0.45	0.41	0.46	0.44	0.46	0.46	0.48
Mg/Mg+Fe^{2}+1/MgO	0.48	0.43	0.48	0.44	0.50	0.48	0.50	0.50	0.51
Mod.larson	0.46	0.52	0.49	0.56	0.49	0.52	0.51	0.53	0.51
Thort.Tutt.	16.11	17.70	17.19	18.73	18.65	18.57	18.45	19.11	19.69
	68.59	69.79	71.69	74.30	75.86	75.04	74.67	72.72	73.71
Ratios									
(Na+K)/Al	0.75	0.74	0.79	0.79	0.82	0.83	0.80	0.72	0.74
Na+K+2Ca/Al	1.27	1.19	1.25	1.17	1.18	1.18	1.15	1.06	1.05
K/(K+Na)	0.46	0.46	0.43	0.43	0.42	0.38	0.38	0.43	0.44
Mg/Fe	0.93	0.77	0.94	0.81	1.00	0.92	1.01	1.00	1.07

Niggli Endmembers									
Olivine									
FO	2.9	2.49	2.72	2.78	2.04				
FA	2.38	2.56	2.31	2.83	1.51				
Dipside									
DI	4	1.99	3.76	2.23	2.25	2.71	2.56	0.22	0.05
HD	3.3	2.04	3.19	2.27	1.67	2.16	1.84	0.17	0.03
Hypersthene									
EN		0.88			1.65	3.82	3.98	5.04	5.34
FS		0.91			1.22	3.04	2.87	3.82	3.66
CIPW Endmembers									
Olivine									
FO	2.42	2.06	2.27	2.33	1.73				
FA	2.89	3.07	2.79	3.44	1.86				
Diopside									
DI	3.86	1.90	3.63	2.16	2.20	2.65	2.50	0.22	0.05
HD	3.64	2.23	3.53	2.52	1.87	2.41	2.07	0.19	0.04
Hypersthene									
EN		0.78			1.50	3.45	3.62	4.53	4.78
FS		1.06			1.46	3.61	3.42	4.52	4.31

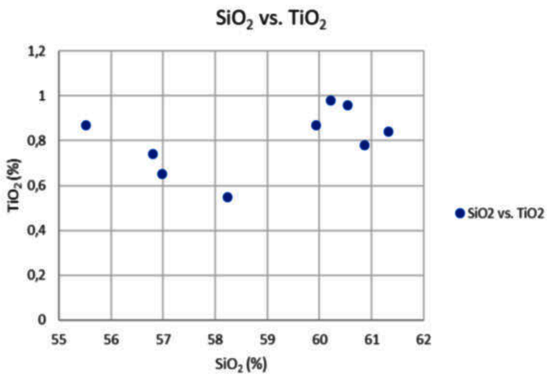
The discrimination diagrams (Fig. 5) show a clearly expressed negative correlation between the content of SiO_2 vs CaO, SiO_2 vs Al_2O_3, going from the rocks at the site Kravitza to the rocks at the site Gradesnica. This can be explained by the decrease of the amount of basic plagioclases in the differentiation of the magmatic melt.

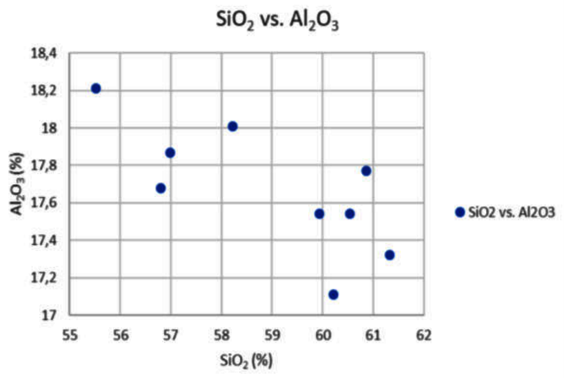
A pronounced positive correlation is seen in the discrimination diagrams of SiO_2 vs Rb, SiO_2 vs Ba, SiO_2 vs Sr as well as SiO_2 vs Zr, which clearly speaks of the fact that we have a pronounced fractional crystallization and assimilation in the primary magmatic melt.

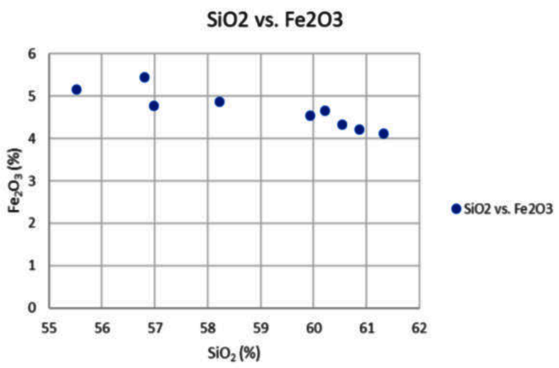
In Fig. 4, on the discrimination diagram of SiO_2 vs Ni a weak positive correlation can be noticed that clearly indicates the assimilation processes occurring in the eastern part of the area (Dobro Pole-Gradesnica) that is much closer to the ultrabasic rock complex in the segment of the Elen Supe metamorphic block located within the Vardar Zone.

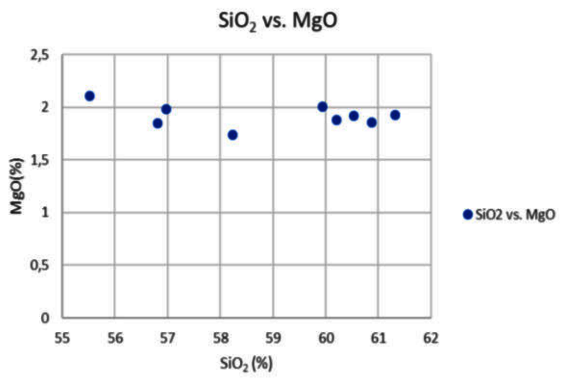
Fig.6a is a diagram of normalized REE values in the volcanic rocks form the Kravitza-Dobro Pole-Gradesnica area with respect to Hondritic values (Boynton, 1984) characterized by significant enrichment values of LREE and MREE, relatively low HREE concentration, and a small negative Eu anomaly. It can be concluded that the amount of REE decreases with the increasing amount of SiO_2.

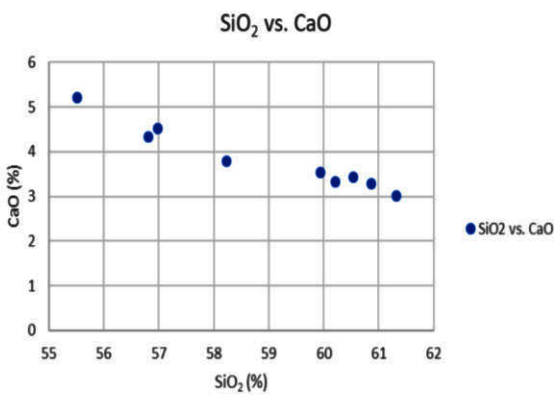
Fig. 6b shows a diagram of the normalized REE values in the volcanic rocks of the Kravitza-Dobro Pole-Gradesnica area with respect to the values of the primitive mantle (Sun and McDonough, 1989). It can be seen from the diagram that in all the samples studied there is a significant negative anomaly of Nb, P and Ti and a pronounced positive anomaly of Pb.

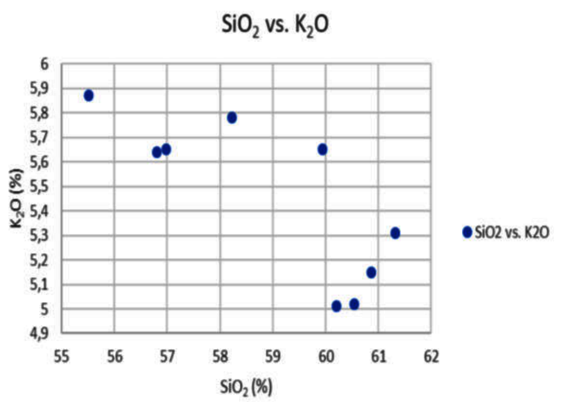

SiO2 vs. TiO2
TiO2 (%)
SiO2 (%)
SiO2 vs. TiO2

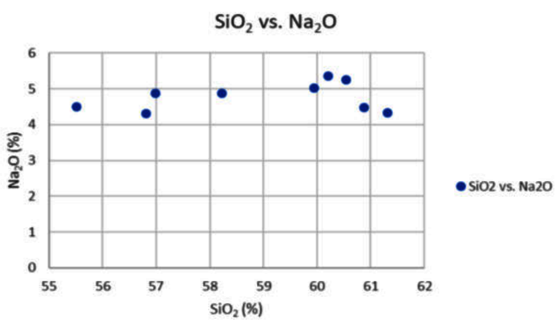

SiO2 vs. Al2O3
Al2O3 (%)
SiO2 (%)
SiO2 vs. Al2O3

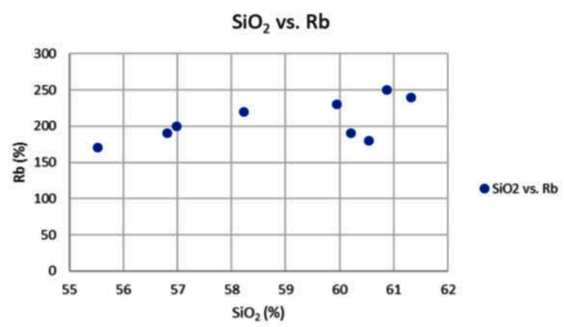

SiO2 vs. Fe2O3
Fe2O3 (%)
SiO2 (%)
SiO2 vs. Fe2O3


SiO2 vs. MgO
MgO(%)
SiO2 (%)
SiO2 vs. MgO


SiO2 vs. CaO
CaO (%)
SiO2 (%)
SiO2 vs. CaO


SiO2 vs. K2O
K2O (%)
SiO2 (%)
SiO2 vs. K2O


SiO2 vs. Na2O
Na2O (%)
SiO2 (%)
SiO2 vs. Na2O


SiO2 vs. Rb
Rb (%)
SiO2 (%)
SiO2 vs. Rb

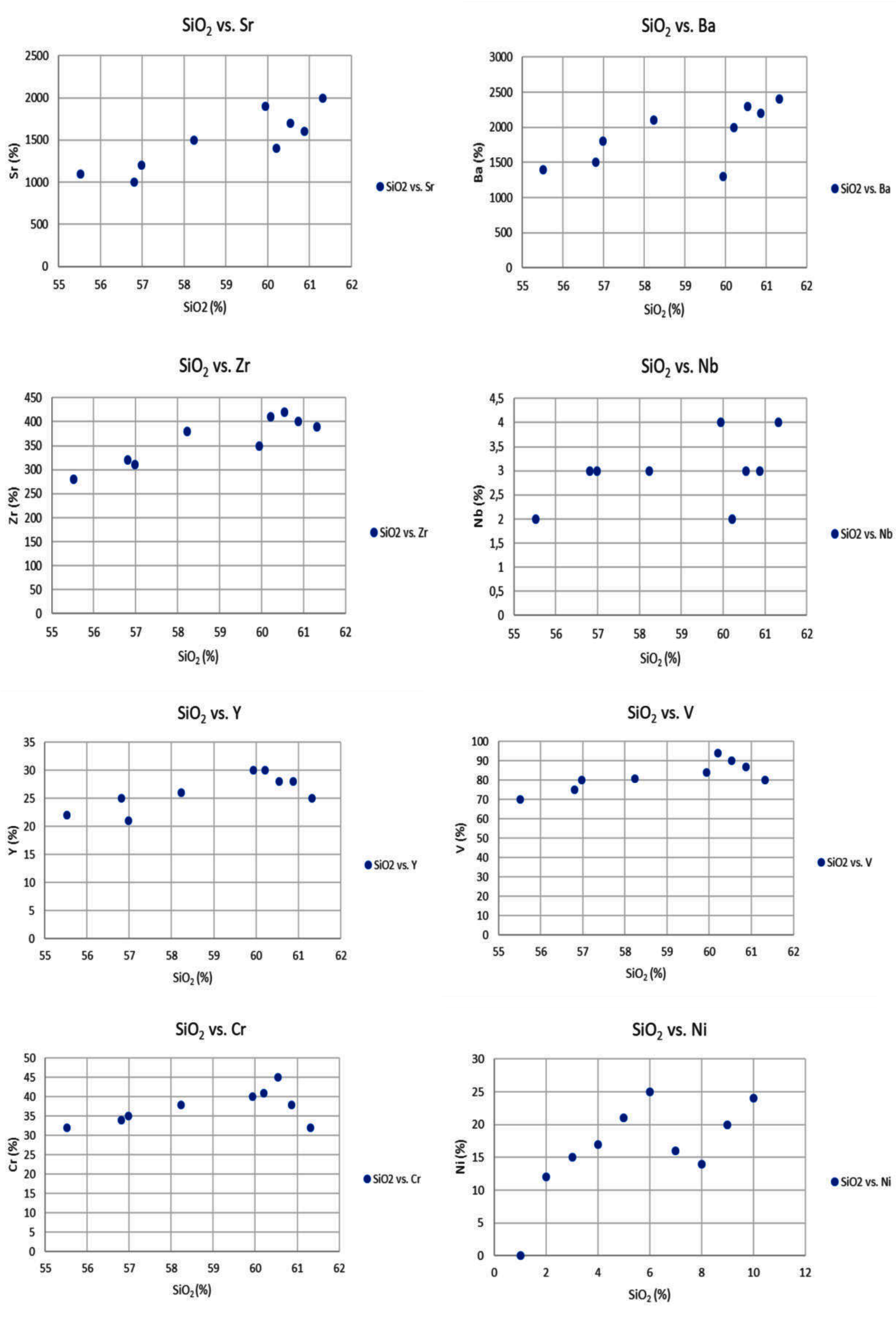


Fig. 5. Major (wt.%) and selected trace element (ppm) vs. silica diagrams for the Kravitza-Dobro Pole-Gradesnica volcanic rocks (Wedepohl, KH 1974)

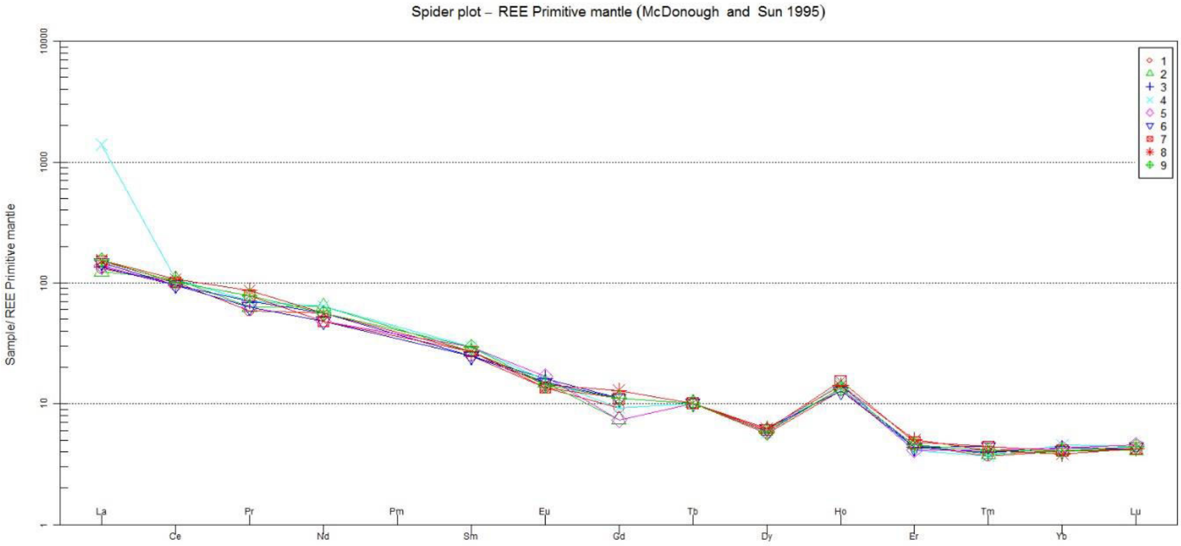


Fig. 6a Chondrite normalized REE patterns for the Kravitza-Dobro Pole-Gradesnica volcanic rocks Chondrite values after Boynton (1984).

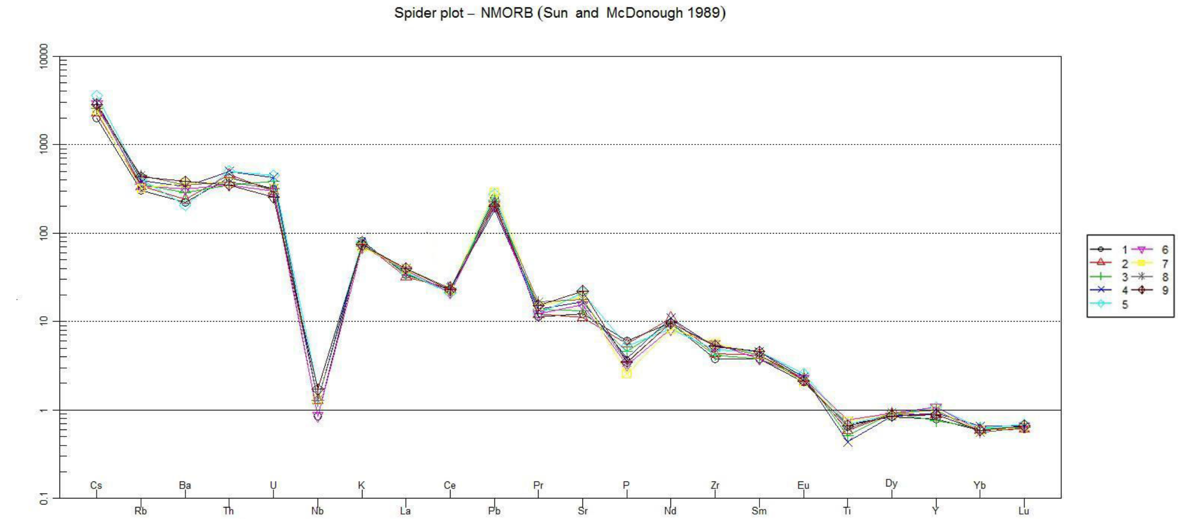


Fig. 6b Primitive mantle normalized trace element diagram for the Kravitza-Dobro Pole-Gradesnica volcanic rocks. Normalization factors after Sun and McDonough (1989).

3.3 Geodynamics

The chemical characteristics of the volcanic rocks of the site Kravitza (analyses 1, 2, 3 in Table 1) indicate that the composition of these rocks is very close to the composition of the rocks from a magmatic source. In the normative composition of these rocks the presence of olivine can be noticed. The chemical composition of these rocks shows a higher presence of MgO, CaO, Fe_2O_3 and, on the other hand, low concentrations of Ni, Co, Cr. This clearly indicates the conditions of crystallization of the primary magma in a system where spinel emerges as a solid phase and a pronounced crustal contamination shortly before volcanic eruption. The pronounced small anomaly of Eu most likely points to variations in oxygen fugacity in the magma that was greater during plagioclase fractionation, which is indicated by a relatively increased CaO concentration. Increased concentrations of K_2O coupled with the increased concentration of LILE elements clearly indicate that the primary source of magma should be located in the upper mantle, whereas increased concentrations of Pb, U, Th indicate a pronounced presence of crustal contamination processes (Wedepohl, 1974). From the data presented, it is evident that the source of the primary magma is the upper mantle that is extremely enriched with K_2O and LILE (including Sr), that is, primary molten MORB. The strong Nb depletion that can be seen in the spider diagram (Fig. 5b) indicates the association of this volcanism with the subduction processes. (Kolios et al, 1980, Boev, 1988).

4. Conclusion

Petrological investigations of volcanic rocks in the area Kravitza-Dobro Pole-Gradesnica show that these are volcanic rocks of the type trachyte to trachyandesite. The chemical and geochemical composition of these rocks also speaks of their genetic and geotectonic association with the processes occurring in the upper mantle of these areas during the subduction processes and the occurrence of subduction magmatism in the Pliocene. The high concentration of K and associated elements such as Sr and Pb indicate that the parental magma from which the volcanic rocks are generated originates from the melting of the depleted mantle.

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