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MINERALOGICAL-PETROGRPAHIC AND CHEMICAL COMPOSITION OF THE GRANITOID ROCKS FROM THE LOCALITY KALEN, WESTERN MACEDONIA

Sašo Stojkov, Orce Spasovski, Daniel Spasovski

Faculty of Natural and Technical Sciences, Institute of Geology, "Goce Delčev" University in Štip, Blvd. Goce Delčev, 89, Štip, Republic of Macedonia
orce.spasovski@ugd.edu.mk

A b s t r a c t: In this paper are shown the results of the mineralogical-petrographic and chemical study of granitoide rocks from the Kalen locality. The mineralogical-petrographic characteristics of samples that were taken, has been determined by use of the polarized light microscope Leitz Vetzlar, Germany. The mineralogical composition was determined by the X-ray diffraction method of the dust samples (XRD) and using scanning electron microscope. Based on the geological investigations performed on the field and laboratory study of the particular samples taken from the granitoid rocks from Kalen locality, were determined the following types of rocks: coarse grained granodiorite and porhpyroidal granodiorite.

Key words: granodiorite; Kalen; mineralogical-petrographic composition; chemical composition; X-ray diffraction; scanning; electron microscope

INTRODUCTION

The granodiorite of Kalen is located about 13.0 km southeastern from the Prilep city, in the series of gneisses which has been broken through with granite and granodiorite as part of the metamorphic complex of the Pelagonian (Fig. 1).

Fig. 1. Map of the R. Macedonia with position of the locality "Kalen"

This area is geographically close to the Selečka Mountain. In the past, search for good quality granite enclosed many other regions, on many occasions, in the area of Mariovo, but so far no significant results have been achieved.

The first brief data from the exploration area and its surroundings were represented in the works of Ami Boue (1891), Cvijić (1906, 1911). After that, Nikolov (1924), Kosmat (1924), Tucan (1926), Barić (1940), Marić (1936, 1940) studied granodiorites and provided additional data regarding their mineralogical, petrographical and genetic features. Stojanov (1958, 1960, 1968 and 1974) studied these terrains and distinguished many varieties of gneisses, micaschists, amphibolite and granitoide rocks. Some of these scientists came up with conclusions regarding the entire Pelagonian, which suggests that at the beginning of the Algonquian orogenic movements a progressive metamorphosis occurred in the lower Precambrian complex and towards the end of the orogenic movements, granodiorite-adamelite masses were initiated. In the period of preparation of the Basic Geological map of the SFRJ the authors of the Vitolište sheet (Dumurdžanov, Hristov, 1976a, 1976b) and Prilep (Rakičević, Stojanov, Arsovski, 1965a, 1965b) processed the map sheet content of the rocks where the granodiorite Lozjanska Reka river belongs.

Dumurdžanov (1985) explored granitoids in details and concluded that they are mainly represented with granodiorite (70%) and quartzdiorite (20%), and less with quartz monzonites and granites.

The Kosovska River grandiorites has been studied in details by Spasovski (2010a, 2010b), when for the first time were determined their mineralogical-petrographic composition. Later, granitoide rocks near this area were investigated by Stojkov and Spasovski (2014), as well as by Spasovski and Spasovski (2011, 2015).

METHODOLOGY

The location Kalen is explored using field and laboratory techniques. Field study provided an insight into the terrain, familiarization with its geological and structural-tectonic features as well as the collection of representative samples from the grandiorite and definition of their chemical-mineralogical composition and structural-textural features.

The mineralogical-petrographic study was performed at the Faculty of Natural and Technical Sciences in Štip, while the chemical composition of granodiorite was determined in the chemical laboratories at the Faculty of Natural and Technical Sciences with the inductive coupled plasma-atomic emission spetrometer (ICP-AES). Mineralogical composition of rocks was determined by XRD, while the chemical compositions of main mineral phases were determined by scanning electron microscope.

GEOLOGIC FEATURES

In the geologic structure of the area that is enclosed in our study and research there are three types of rocks: muscovite gneisses, amphibolite and granodiorite (Fig. 2). The muscovite gneisses are outspread in the northern and northeastern part of the area. They are characterized with grey color with glittering radiance from the muscovite flakes, which clearly can be noticed. They are characterized with slightly striking parallel schistosity texture. The structure of the gneisses is grano-lepidoblastic with distinguished striped texture. The main minerals in the rock are: quartz, feldspar and mica. Participation of salic and femic minerals is approximately equal in quantity, i.e. the salic are slightly more present. Quartz is found in xenomorphic crystals as well as in feldspars. The feldspar is K-feldspar – orthoclase, plagioclase. The orthoclase is fairly clayed while the plagioclase is more strongly clayed. The plagioclase is albite to intermediate plagioclase. It is rare to find some larger xenomorphic crystals of orthoclase, as porphyroblasts. Mica is represented with muscovite and biotite. As secondary minerals occur epidote, rarely granite and ore mineral in irregular shapes. The epidote is quite common in long crystals and is regularly associated with mica lines. Apatite and the zircon are accessory minerals.

Amphibolite appear as relatively sharply distinguished concordant stripes or irregular bodies. These rocks vary from light to dark green, miniscule to coarse grained, mostly schistose, rarely massive. The main minerals present within them are amphibol, oligoclase, andensine, less present are albite and epidote, while the granate, coesite, biotite, diopside, titanite, quartz and rutile vary with their presence. They are often present in minor quantities although locally they are present as major minerals.

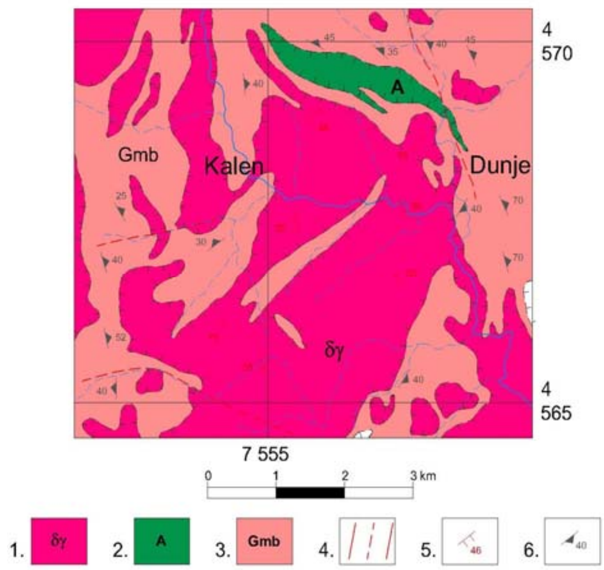


Fig. 2. Geological map of the "Kalen" locality:
1 – granodiorite, 2 – amphibolite, 3 – muscovite gneisses,
4 – fault (fixed, assumed), 5 – fissure elements,
6 – foliation elements

Based on the structural-textural characteristics and mineralogical composition, there are two basic varieties within the granodiorites including porphyroidical granodiorites and massive medium to coarse grained granodiorites. Microscopic observation has shown significant variation in granodiorite mineralogical, especially within the massive type. Porphyroidical grandiorites are grey, coarse grained rocks with porphyric structure and massive texture. They are composed of oligoclase, K-feldspar, quartz and biotite as major minerals, and titanite, granate, apatite and zircon as a minor minerals. As a result of secondary changes chlorite, epidote, coesite, sericite, kaoline and limonite are present. The massive granodiorites are not completely homogenous in their composition and there are significant variations regarding the presence of certain minerals. In distinguished part K-feldspar is more common and the rocks represent quartz monzonite or granite and on some occasions when they are present with less than 5% they transition to quartz-diorite. Massive granodiorite is grey to dark-grey, medium to largely granular. They are composed of plagioclase, K-feldspar, quartz and biotite as major minerals, and apatite, titanite, amphibole, zircon, granate and magnetite as minor or less frequent minerals. Secondary there are epidote, coesite, sericite, albite, chlorite, kaoline and limonite.

MINERALOGICAL AND PETROGRAPHIC FEATURES

There were some representative samples from the locality Kalen selected for the mineralogical - petrographic study. Petrographic samples were observed under the polarized microscope with transmitted light (type Leitz, Wetzlar, Germany). The mineralogical-petrographic examinations were performed at the Faculty of Natural and Technical Sciences, Institute for Geology, by the author of the paper.

At the locality Kalen were found two types of granitoid rocks: coarse grained granodiorites and porfiroidical granodiorites. Largery granular granodiorite is mainly gray through which can be found dark gray patches of colored mineral. It consists of coarse grained minerals, with grain diameter 5 – 6 mm, which is massive and hard texture.

It has hypidiomorphic granular structure and consists mainly of: plagioclase, orthoclase, quartz and biotite, but, however, plagioclase clearly prevails in the rock.

Plagioclase appears as hypidiomorph crystals, it is significantly altered, so that, very rarely can be seen polysynthetic lamellae in certain plagioclases. The size of the crystals is in range from 0.3 – 6 mm, and the most of them are nearly 2 mm in length. Often, can be seen thin edge of fresh albite along the marginal parts of the crystals, mainly at the contact parts with plagioclase (Figures 3a, b, c). The products of the alteration are: coesite, epidote and sericite. Crystals of the coesite are long up 0.3 mm (300 microns), and the remaining products are minor constituents. The products of alterations have chaotic distribution of their crystals. Plagioclase has an intermediary character, type oligoclase – andensine. Often, the major plagioclase are found as double-twinned crystals.

Orthoclase is rarely found in xenomorphic crystals in size up to 5 mm. Often fits minor hypidiomorphic and allotriomorphic grains of plagioclase. There are rare the crystals of orthoclase in which can be seen some transformation in microwedge, actually they are slightly micro-wedged.

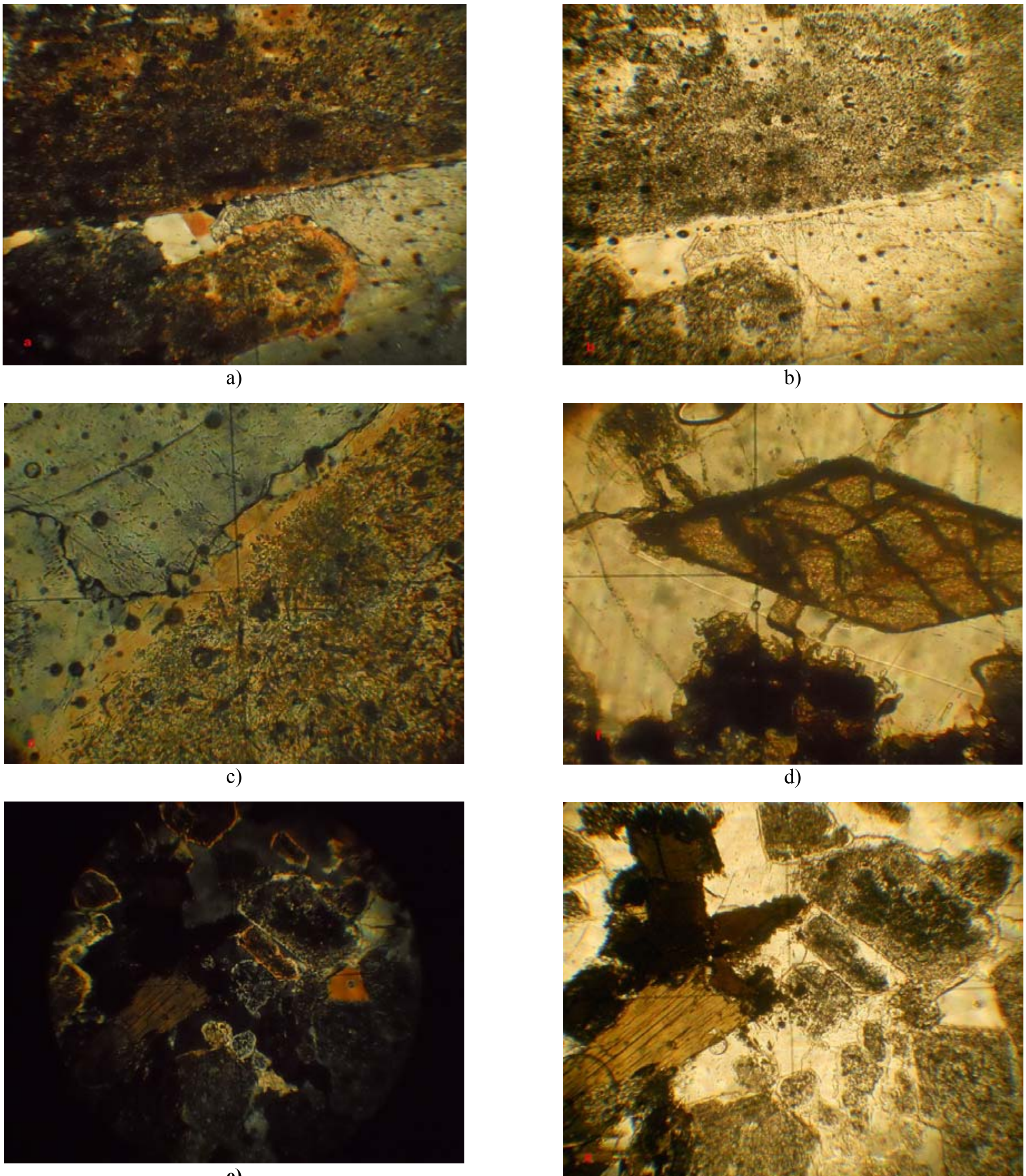
The quartz is xenomorphic and it fills the interspace between the crystals, it is cracked and slightly crushed.

Biotite is found as tabular and elongated flake-like forms, with length of the up to 2 mm. There is clear pleochroism in brown-slightly green nuance. It appears in thin jets, suppressed in the interspace of the salic minerals. Biotite is very slightly *chloritized*. The biotite jets are very often associated with fine-grained epidote-ortite and rare granate crystals, which represent secondary minerals. Approximately, it is found that the modal composition of the rock, based on the microscopic investigations consists of: plagioclase 40%; orthoclase 15%; quartz 25%; biotite 13%; secondary minerals 7%.

Porphyroidal granodiorite represents rock with gray color, intersected with white feldspar and dark-grey green-like colored minerals. The structure is coarse grained with size of the feldspar up to 5 – 6 mm, where can be seen rare major crystals up to 1.3 cm. (most probably K-feldspar). It is hard an massive texture.

Based on the microscopic observation, it could be seen that there is hypidiomorphic grainy structure. It consists of plagioclase, orthoclase, quartz and biotite, as main minerals, despite of the secondary minerals epidote – ortite and rare sphene (Fig. 3d).

The *plagioclase* clearly prevails in the rock. It was found as hypidiomorphic crystals with length of the crystals up to 0.3 – 3-4 mm. It is significantly altered, and the products are: epidote, coesite and sericite, which are found as grained and needle-like microcrystals that chaotically fill the plagioclase. Often in plagioclase crystals integrated by the orthoclase, can be seen thin edge of fresh albite along with the edges of the crystals (Figures 3e and f). The plagioclase was of intermediary character type (oligoclase – andensine – labradorite).



a) b) c) d) e) f)

Fig. 3. Microphotos of the granodiorites of the locality Kalen:
a) coarse-grained hypidiomorphic plagioclase and minor with thin edge of albite and contact with orthoclase N+, 3×;
b) coarse-grained hypidiomorphic plagioclase and minor with thin edge of albite and contact with orthoclase N–, 3×;
c) contact of the plagioclase with orthoclase with clear albite edge, N+, 10×; d) hypidiomorphic plagioclase, thin leaves of biotite fitted in orthoclase, N+, 10×; e) hypidiomorphic plagioclase, thin leaves of biotite fitted in the orthoclase, N–, 3×;
f) idiomorphic sphene , quartz, biotite flakes, N– , 10×

The orthoclase is rarer than the plagioclase and can be seen in crystals, larger and as last product of crystallization, which integrates many crystals of plagioclase and rare thin biotite flakes. The size of these orthoclase crystals is up to 0,8 cm. There are rare crystals of orthoclase also in xenomorphic crystals.

The quartz is also less comon, slightly cataclazed with size of the crystals up to 1 mm. It fills the interspace between the plagioclase in single grains as well as small lenses.

The biotite appears in large table-like and elongated thin flakes with size from 0,5 – 2 mm. The biotite is fresh with pleochroism in light-brown greenish nuance. The biotite contains rare microcrystals of epidote and needles of coesite. Together with it or separated are found irregular shards shapes built of minor crystals and fine grained epidote thick grouped, as minor thin leaves of biotite, fresh, as newly formed biotite. Usually, thin leaves of biotite are around these shards shapes, which could be some colored mineral that is fully metamorphosed in secondary products. Very slightly could be seen some elongated orthogonal shape.

The biotite and the jets are suppressed in the interspace of the crystals, so that close to them could be found thin veinlets with limonitization. In particular biotite grains along the margins was determined iron component in thin irregular forms as well as fine grained epidotization.

Approximately, based on the microscopic review, is found the modal composition of the rock as following: plagioclase 50%; orthoclase 13%; quartz 17% ; biotite and secondary minerals 20%.

In addition to the microscopic observations there were made X-ray diffractograms of rocks. In this manner were defined very fine mineral grains. For this study was selected one sample. The mineralogical composition determined with XRD is shown on the diagrams presented on Fig. 4.

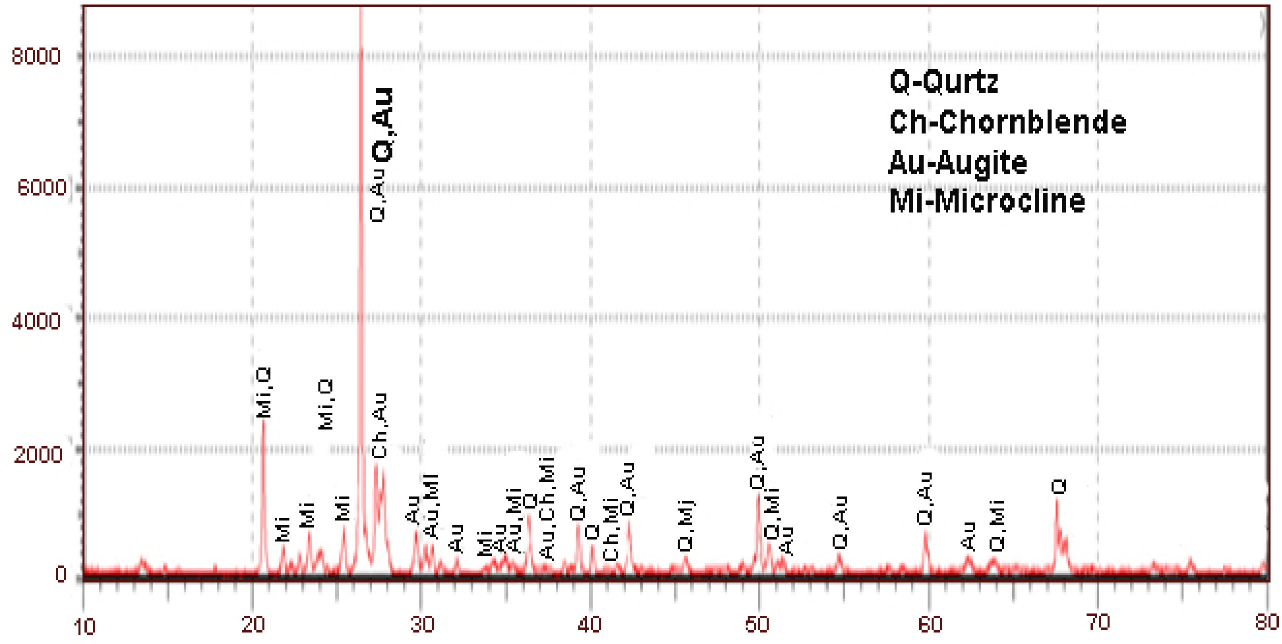


Fig. 4. X-ray diagram of granodiorite

Based on the position of the peaks, considering the angle 2Θ, identification of minerals was performed, and based on intensity of their peaks conclusion about their relative quantity in the sample was made.

The quartz is the most common in the studied sample, which suggests that quartz is represented in great percentage in the matrix of the rock. On the second place comes feldspar. Feldspars in the granitoide rocks from this particular locality are represented with microwedge.

In the sample taken from granitoide rocks of the Kalen locality, hornblende and augite were found, too.

CHEMICAL COMPOSITION OF MINERALS

For determination of chemical composition of minerals with scanning electron microscopy (SEM) there were separated representative and fresh granodiorites.

Of the pyroxene with XRD is found augite whose chemical composition is determinated with Scanning electron microscopy (SEM). With the microscopic investigations and the investigations preformed with the Scanning electron microscopy (SEM) pyroxene is determined as augite (Table 1). SEM images of augite are given in Figures 5 and 6, while Figures 7 and 8 show EDX spectrum of augite.

Of feldspars is confirmed presence of microcline which chemical composition is presented in Table 2, and SEM images of microcline are given in Figure 9, and EDX spectrum of microcline is shown on Figure 10. Of plagioclases, with Scanning electron microscopy is determined albite with chemical composition presented in Table 2, SEM images of albite are given in Figure 11, and EDX spectrum of albite is shown on Figure 12..

Scanning electron microscopy study determined mica (muscovite), which chemical composition is presented in Table 3, and respective SEM images of muscovite are given in Figure 13, and respective EDX spectrum shown on Figure 14.

Quartz, as the most common mineral in the granitoide rocks, was confirmed and its chemical composition is given in Table 3, while an SEM images of quartz are given in Figure 15, while an EDX spectrum of quartz is presented on Figure 16

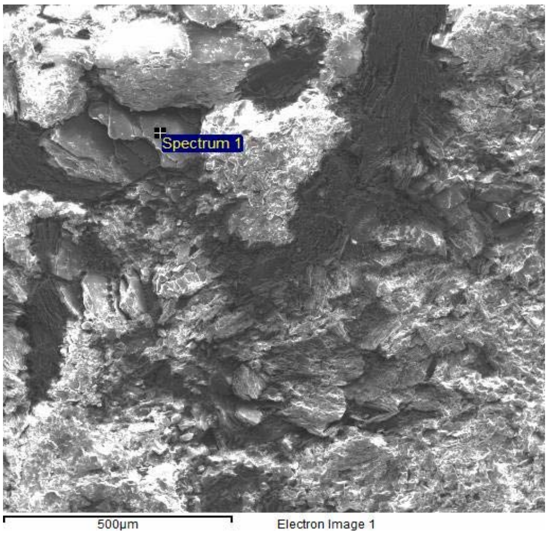


Fig. 5. SEM image of augite

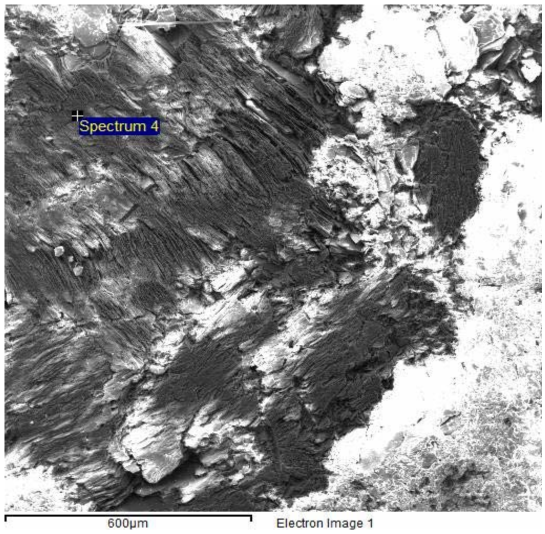


Fig. 6. SEM image of augite

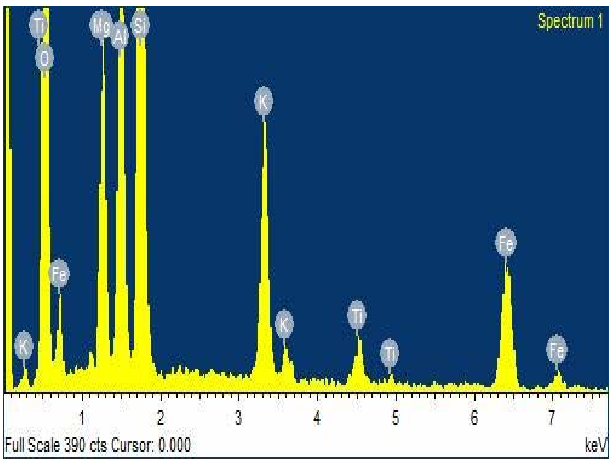


Fig. 7. EDX spectrum of augite, samle 1

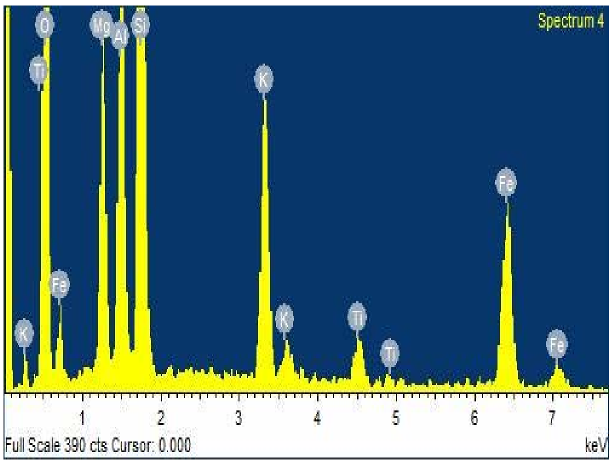
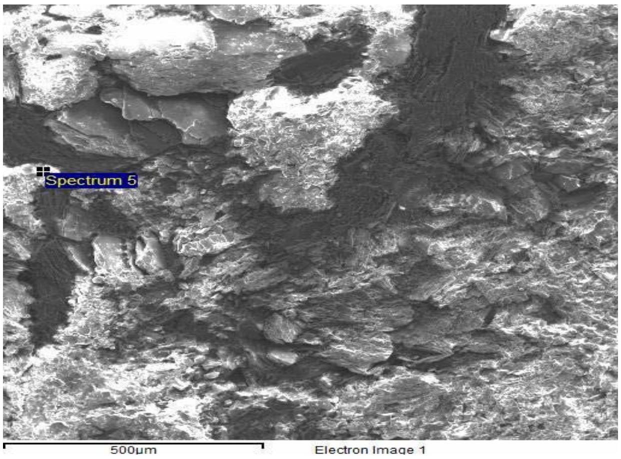


Fig. 8. EDX spectrum of augite, sample 2

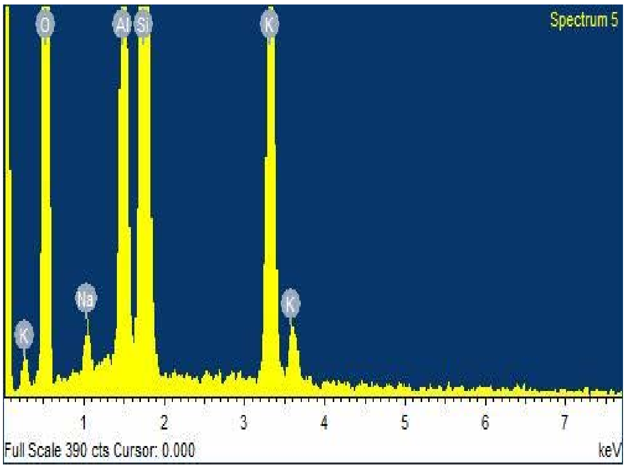
T a b l e 1

Chemical composition of augite from the "Kalen" locality (%)

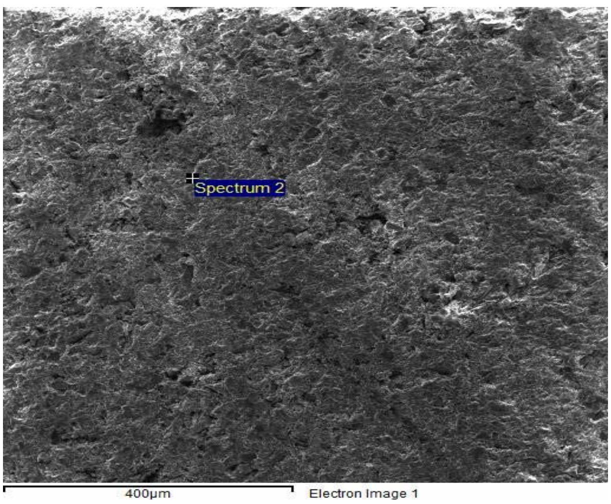
Element (K)	Sample 1		Element (K)	Sample 2	
	Weight	Atomiцс		Weight	Atomic
O	54.72	70.50	O	49.90	67.07
Mg	6.17	5.24	Mg	6.62	5.85
Al	7.52	5.74	Al	7.40	5.89
Si	16.16	11.86	Si	16.09	12.32
K	5.60	2.95	K	6.50	3.57
Ti	1.33	0.57	Ti	1.55	0.70
Fe	8.49	3.13	Fe	11.95	4.60
Total	100.00		Total	100.00	



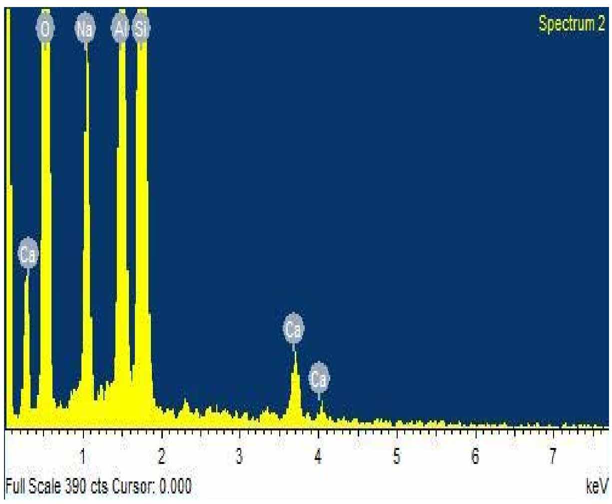
Fig, 9. SEM image of microcline



Fig, 10. EDX spectrum of microcline



Fig, 11. SEM image of albite



Fig, 12. EDX spectrum of albite

T a b l e 2

Chemical composition of microcline and albite from the "Kalen" locality (%)

Element (K)	Mиcrocline		Element (K)	Albite	
	Weight	Atomic		Weight	Atomic
O	56.84	70.83	O	61.15	72.61
Na	0.87	0.76	Na	7.66	6.33
Al	7.75	5.73	Al	8.81	6.20
Si	25.36	18.00	Si	20.99	14.20
K	9.18	4.68	Ca	1.39	0.66
Total	100.00		Total	100.00	

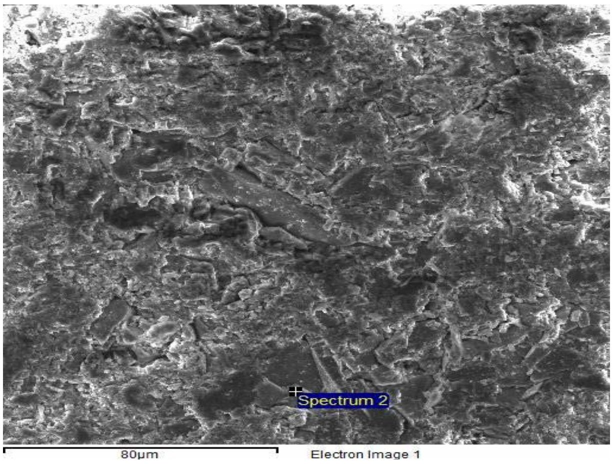


Fig. 13. SEM image of muscovite

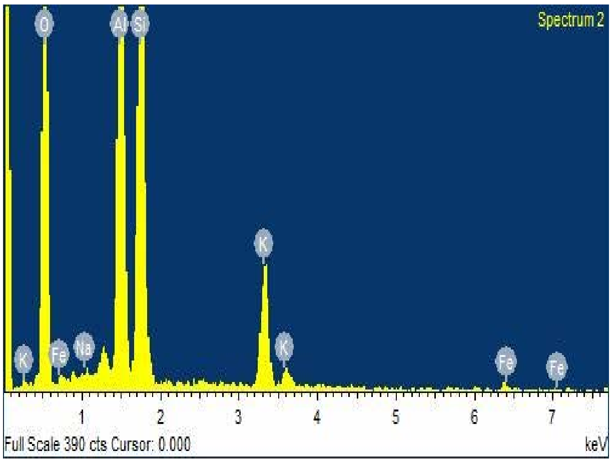


Fig. 14. EDX spectrum of muscovite

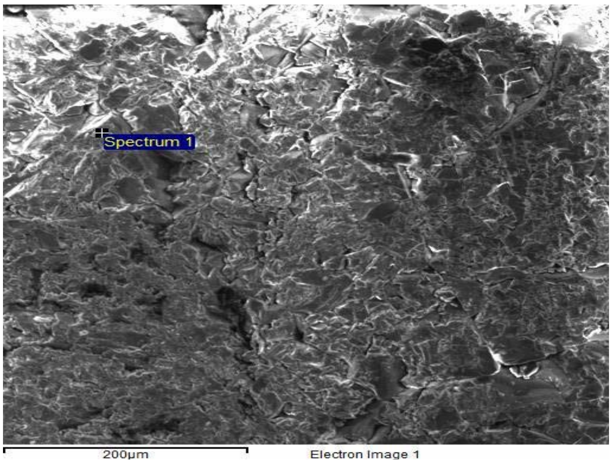


Fig. 15. SEM image of quartz

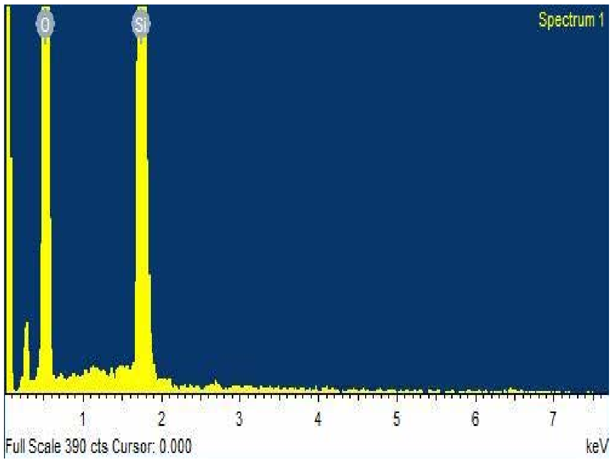


Fig. 16. EDX spectrum of quartz

T a b l e 3

Chemical composition of quartz and muscovite from the "Kalen" locality (%)

Element (K)	Quartz		Element (K)	Muscovite	
	Weight	Atomic		Weight	Atomic
O	71.85	81.75	O	62.26	74.87
Si	28.15	18.25	Na	0.36	0.30
Total	100.00		Al	14.43	10.29
			Si	17.36	11.89
			K	4.89	2.40
			Fe	0.70	0.24
			Total	100.00	

CHEMICAL ANALYSES

The chemical analyses of the granitoide rocks from Kalen locality, represent a contribution into the broadening of the knowledge for this massive on the territory of the Republic of Macedonia. This massif is evidently different from the surrounding rocks by its content, structural-tectonic features, color and the manner of its origin. Basically, granodiorite is characterized with homogeneous – solid to compact texture, which locally turns to porphyroide. With such arrangement and intergrowth of the mineral components, beige to greenish basic color spotted with biotite of black color is formed in the mineral aggregate. For more detailed presentation of the chemical composition of the granodiorites from the Kalen locality, four representative samples were taken from the granodiorites and one sample from a light grey rock with great compactness. The examinations of the taken samples were performed at the Faculty of Natural and Technical Sciences with the instrument AES-ICP. The chemical content of the analyzed samples are presented in Table 4.

From the Table 4 it can be stated that the analyzed samples are characterized with a constant chemical composition, which can be seen in the content of SiO_2 (range of 76.375–77.307% SiO_2).

In the granitoide rocks from Kalen the content of P_2O_5 is low and vary in close interval which is from 0.097 to 0.112. The content of the total iron (FeO*) systematically decreases with the increase of SiO_2 and is between 1.25 and 1.62%.

The content of MgO granitoides from Kalen ranges from 0.053 to 0.060%, content of CaO was from 1.25 to 1.50, while the content of MnO is within the limits from 0.509 to 0.650%. The content of Na_2O was from 2.93 to 3.06%, while the content of K_2O ranged from 3.55 to 3.95% and content of TiO_2 was from 0.279 to 0.335%.

Variation of the mass participation of the oxides of the main elements in function of the mass participation of SiO_2 are shown of the Harker's diagrams (Figure 17). Correlational trends in Harker's diagrams point on different magmatic processes that happen in the series of the connected magmas (Protić, 1998). The geochemical connection between the main elements is used to point on if there is one or more basic processes which will explain the connection between the main elements (Rollinson, 1993).

T a b l e 4

Chemical composition of the granodiorites from the "Kalen" locality (%)

Components	Ka/1	Ka/2	Ka/3
SiO_2	76.437	76.375	77.307
Al_2O_3	12	12.045	11.9
FeO	1.59	1.62	1.25
MgO	0.058	0.060	0.053
MnO	0.646	0.650	0.509
CaO	1.49	1.50	1.25
Na_2O	3.02	3.06	2.93
K_2O	3.61	3.55	3.95
TiO_2	0.333	0.335	0.279
P_2O_5	0.112	0.108	0.097
LOI	0.704	0.697	0.475
Total	100.00	100.00	100.00
Ti *(%)*	0.201	0.168	0.190
Sr (mg/kg)	151	141	150
Ba (mg/kg)	380	401	380
Zn (mg/kg)	40.1	15.6	39
Pb (mg/kg)	20.5	19.3	20
Co (mg/kg)	5.2	4.3	4.9
Ni (mg/kg)	11.8	4.6	11
Cd (mg/kg)	13.56	5.8	13.25
Cu (mg/kg)	9.5	9.2	9.4
Li (mg/kg)	34.5	31.4	33
B (μg/kg)	<10	11283	<10 000
V (μg/kg)	34976	29003	33875
Mo (μg/kg)	1396	2015	1400
Be (μg/kg)	2155	1925	2123
Ga (μg/kg)	13196	13544	13186
Sn (μg/kg)	2933	2507	2933
Pd (μg/kg)	1824	1641	1785

The variation of the main elements compared with the increasing of the content of SiO_2 points on, that crystal's functioning was very important process in the control of the chemism of the granitoid rocks. However, geochemical variations of the elements in shreds with the SiO_2, point on the conclusion that the rocks are incurred during combined processes. On the chemism of the rock, in different degree, affect the processes of alteration.

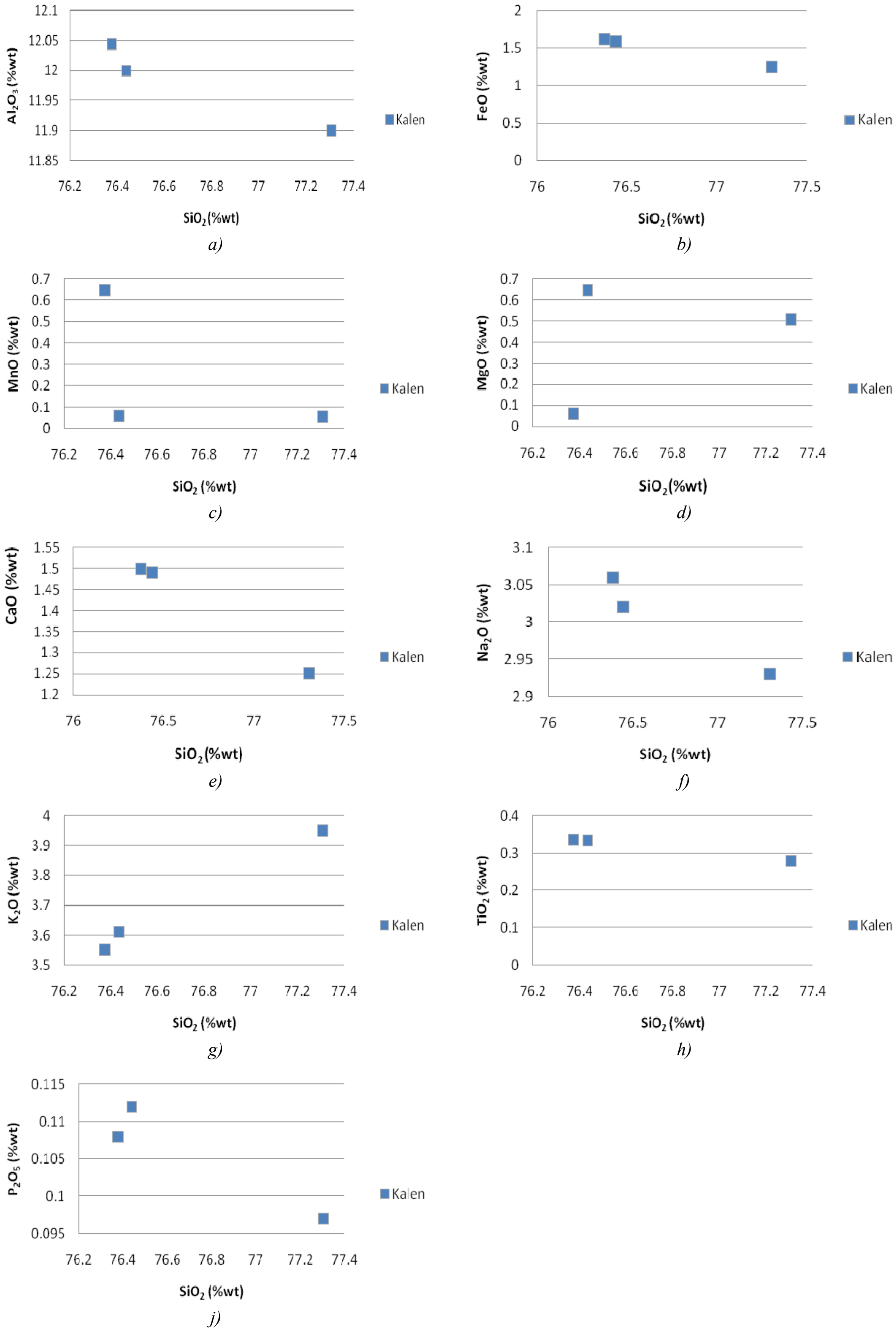


Fig. 17. Variation diagrams for the oxides of major elements compared with SiO_2

The correlation ratio between the main elements and SiO_2 in the investigated samples of the locality Kalen are shown on the variation diagrams on Fig. 17.

On the Figure 17 could be noticed very slight correlation between the SiO_2 and Al_2O_3. This is due to the fact that the studied samples were exposed to hydrothermal alterations. With the increase of SiO_2 content the Al_2O_3 decrased. Correlation ratio between SiO_2 and FeO, shown on the Figure 17b, proved that with increase of SiO_2, the content of the FeO decreases. Also, it can be seen that as the content of the SiO_2 increases, the content of MnO decreases. Correlation ratio between SiO_2 and MgO is shown as well, where an increase of the SiO_2 content was associated with an increase the MgO content, too. Correlation between SiO_2 and CaO, shown on the Fig. 17, confirms that with an increase of SiO_2 content of the CaO decreases. Correlation ratio between SiO_2 and Na_2O is shown on Figure 17, too. There an increase of the SiO_2 resulted in Na_2O decrease. Also, an increase of the SiO_2 resulted in decrease of K_2O that was repeated for SiO_2 and TiO_2 as well as for SiO_2 and P_2O_5 (Figure 17, respectively).

Trace elements are given in mg/kg and μg/kg concentrations. Based on distribution of single trace elements, approximately can be followed petrochemical characteristics of the studied rocks. Some differential series are characterized with enrichment or dilution of microelements due to character of the magma and it's consolidation at particular levels.

Ba is found as content component in K-feldspar and the biotite, while Sr is mainly present in the plagioclase. In the granitoid rocks from the Kalen locality the contents of the Ba is in the limits from 380 to 401 ppm, while the contents of Sr are within the limits from 141 to 150 ppm.

The Pb participate in silicate minerals, where isomorphically replaces the K. The contents of Pb were within the limits from 19.3 to 20.5. Ti is mainly connected with the sphene. The contents of the Ti are in range from 0.168 to 0.201.

V, Co and Ni are concentrated in Fe–Mg minerals. The vanadium could be found in the hornblende and the biotite. In the greatest part it is connected with the iron minerals. Co and Ni are with the similar radiuses as Mg, which results in presence of this elements in Mg-minerals.

CONCLUSION

Based on the structural-textural characteristics and mineralogical composition, there are two basic varieties within the granodiorites, including porphyritic granodiorites and massive to coarse granular granodiorites. Based on the microscopic observations, significant varieties within the mineralogical composition of the granodiorites are seen, especially within the massive type.

The chemical characteristics of the granitoide rocks from Kalen locality, represent a contribution to the broadening of the knowledge for this massives on the territory of the Republic of Macedonia. This massif is evidently different from the surrounding rocks by its content, structural - tectonic features, color and the manner of its origin. Basically, granodiorite is characterized with homogeneous – solid to compact texture, which locally turns to porphyroidic.

Analyzed samples are characterized with a constant chemical content which can be seen in the content of SiO_2 which is in range of 76.375 to 77.307%.

Approximately, based on the microscopic observations was found the modal composition of rock: plagioclase 50%; orthoclase 13%; quartz 17 % ; biotite and secondary minerals 20% .

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Р е з и м е

МИНЕРАЛОШКО-ПЕТРОГРАФСКИ И ХЕМИСКИ СОСТАВ НА ГРАНИТОИДНИТЕ КАРПИ ОД ЛОКАЛИТЕТОТ КАЛЕН, ЗАПАДНА МАКЕДОНИЈА

Сашо Стојков, Орце Спасовски, Даниел Спасовски

Факултет за природни и технички науки, Институт за геологија, Универзитет "Гоце Делчев", Бул. Гоце Делчев бр. 89, 2000 Штип, Република Македонија
orce.spasovski @ugd.edu.mk

Клучни зборови: гранодиорит; Кален; минералошко-петрографски состав; хемиски состав; рендгенска дифракиција; сканинг; електронски микроскоп

Во трудот се прикажани резултатите од минералошко-петрографските и хемиските испитувања на гранитоидните карпи од локалитетот Кален. Минералошко-петрографските карактеристики на земените примероци од карпите се одредувани со поларизационен оптички микроскоп Leitz Vetzlar, Germany. Минералошкиот состав е одредуван и со методот на рендгенска дифракција на примероци во прав (XRD) и со помош на сканинг електронски микроскоп. Врз основа на теренските и лабораториските испитувања на земените примероци од гранитоидните карпи од локалитетот Кален, утврдени се следните типови карпи: крупнозрнест гранодиорит и порфироиден гранодиорит.