

NEW DATA ON PETROGEOCHEMICAL RESEARCH OF PRE-ALPINE QUARTZ DIORITES AND GRANITOIDS OF THE LOKI CRYSTALLINE MASSIF (LESSER CAUCASUS)

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Abstract. The issues of geochemistry and genesis of the Upper Devonian quartz diorites and Late Variscan granitoids of the pre-Alpine basement of the Loki crystalline massif are discussed. According to I, S and A types of the geochemical classification of granites, quartz diorites belong to S and partly M type granites, and granitoids belong to S and I types. The chemical composition of granitoids corresponds to normal, mostly normal alkaline-acid rocks. The granitoids and quartz diorites of the massif are characterized by the signs of magmatic rocks of volcanogenic-arc origin, which indicates mainly the subduction conditions of their formation.

Key words: petrogeochemistry; pre-Alpine granitoids; the Lesser Caucasus.

საკვანძო სიტყვები: პეტროგეოქიმია; ალპურამდეელი გრანიტოიდები; მცირე კავკასიონი.

გაფართოებული რეზიუმე

ახალი მონაცემები ლოქის კრისტალური მასივის (მცირე კავკასიონი) ალპურამდეელი კვარცდიორიტებისა და გრანიტოიდების პეტროგეოქიმიური კვლევის შესახებ.

თ. წუწუნავა, გ. ბერიძე, ი. ჯავახიშვილი, რ. ვეკუა. ლოქის კრისტალური მასივი მდებარეობს სამხრეთ საქართველოში, მცირე კავკასიონის ფარგლებში, რომელიც კავკასიის მთათა სისტემის შემადგენელი ნაწილია. კავკასია შედგება კავკასიონის, მცირე კავკასიონისა და ამიერკავკასიის მთათაშუა არისგან და წარმოადგენს ხმელთაშუა ზღვის (ალპურ-ჰიმალაური) კოლიზიური ოროგენული სარტყლის ნაწილს.

ლოქის მასივი წარმოადგენს სომხით-ყარაბაღის ტექტონიკური ზონის კრისტალური ფუნდამენტის შვერილს და მიეკუთვნება ბეიბურთ-სევანის ტერიენს. მასივი არის დიდი ანტიკლინიკური სტრუქტურა, რომლის გულში შიშვლდება ალპურამდეელი კრისტალური ქანები და რომელიც გარშემორტყმულია მეზოზოურ-კაინოზოური დანალექი საფარით.

ლოქის კრისტალური მასივი გავრცელებულია 400 კმ²-ზე და შედგება ავტოქონური დევიონური გნეისებრივი კვარც-დიორიტების, ქვედაპალეოზოური ალოქთონური მეტამორფული კომპლექსის, ზედაპალეოზოური გრანიტებისა და იურული, ცარცული და მესამეული ასაკის ინტრუზივებისგან. დევიონური კვარც-დიორიტები შიშვლდება მხოლოდ ღრმა ხეობებში. მეტამორფული კომპლექსი წარმოადგენილია ტექტონიკური ფირფიტებით, რომლებიც სხვადასხვა შედგენლობისა და ასაკის ქანებითაა აგებული. ყველა ზემოთ აღნიშნული ქანი იკვეთება გვიანვარისკული და ბათური გრანიტოიდებითა და ზედაცარცული და ეოცენური კვარცდიანი დიორიტ-პორფირიტებით.

მიუხედავად იმისა, რომ ლოქის კრისტალური მასივის ამგები ქანების პეტროლოგია საკმაოდ კარგად არის შესწავლილი, გრანიტოიდების გეოქიმია დღემდე თითქმის შეუსწავლელია. აღნიშნული ხარვეზის შესავსებად, ნაშრომის ავტორების მიერ განხორციელდა ალპურამდელი გრანიტოიდების პეტროგეოქიმიური კვლევა. კვლევის მეთოდოლოგია გულისხმობდა როგორც საველე, ასევე ანალიტიკურ ეტაპებს. დეტალური საველე სამუშაოები განხორციელდა GPS ტექნოლოგიების გამოყენებით; ქვიური მასალა შეგროვდა როგორც კვარც-დიორიტებიდან, ასევე ზედაპალეოზოური გრანიტოიდებიდან; ჩატარდა მასალის მიკროსკოპული შესწავლა. ალექსანდრე ჯანელიძის სახ. გეოლოგიის ინსტიტუტის გეოლოგიური კვლევის კომპლექსურ ლაბორატორიაში, XRF სპექტრომეტრის (SPECTRO XEP04) გამოყენებით, შესრულდა 28 ნიმუშის ქიმიური ანალიზი. მიღებული მონაცემები დატანილ იქნა სხვადასხვა თანამედროვე საკლასიფიკაციო და დისკრიმინაციულ-ტექტონიკურ დიაგრამაზე.

კვლევის შედეგად დადგინდა, რომ პეტროქიმიური მონაცემების მიხედვით, გნეისებრივი კვარციანი დიორიტები წარმოადგენს კირ-ტუტე სერიის ნორმულ-ტუტე ქანებს. შედგენილობით ისინი კალიუმ-ნატრიუმ-ნატრიუმ-სერიის გრანიტოიდებს შეესაბამება. გრანიტების გეოქიმიური კლასიფიკაციის I, S და A ტიპების მიხედვით, ეს ქანები უპასუხებს S და ნაწილობრივ M ტიპის გრანიტების შედგენილობას. ამაზე მიუთითებს კვარციან დიორიტებში თიხამიწის მომატებული შემცველობაც. S ტიპის გრანიტებთან აღნიშნული ქანების შესაბამისობა იმაზე მიუთითებს, რომ კვარციან-დიორიტული მაგმის წარმოშობის პირობებს სუბდუქციური გარემო წაროადგენდა. I ტიპის გრანიტების ველში რამდენიმე წერტილის მოხვედრა კი, შეიძლება შეესაბამებოდეს მოსაზრებას, რომ მათი ფორმირებისას გარკვეული როლი კვარციანი დიორიტების გავრცელების ზონაში, ქერქის ქვედა ნაწილში არსებულ გაბროიდული შედგენილობის მაგმასაც ქონდა (Gamkrelidze, Shengelia, 2005).

ავტორების მონაცემებით, გრანიტოიდები ქიმიური შედგენილობით გრანიტების ნორმული რიგის მჯავე ქანებს შეესაბამება. ტუტეების ფარდობით, ისინი ძირითადად, მიეკუთვნება ნორმულ, ზოგჯერ კი სუბტუტე რიგის კალიუმ-ნატრიუმ-ნატრიუმ-სერიას. გრანიტების S, I და A გეოქიმიური ტიპების მიხედვით, ეს გრანიტოიდები ძირითადად, მიეკუთვნება გრანიტების S ტიპს, პლაგიოკლასკიტები – I ტიპს, ხოლო გრანოდიორიტები კი ორივე – I და S ტიპებს. სავარაუდოდ, გვიანვარისკული გრანიტების დიდი ნაწილი წარმოიშვა სუბდუქციის პირობებში, კონტინენტური ქერქის გადადნობის გზით, ხოლო მცირე ნაწილი კი - ზედადევიანური გნეისებრივი კვარციანი დიორიტების პალინგენეზის შედეგად. გეოქიმიური კვლევის შედეგები მიუთითებს, რომ როგორც გრანიტოიდები, ასევე კვარციანი დიორიტები ვულკანოგენურ-რკალური წარმოშობის მაგმური ქანების ნიშნებით ხასიათდება, რაც ძირითადად მათი ფორმირების სუბდუქციურ პირობებზე მიუთითებს.

INTRODUCTION

The Loki crystalline massif is exposed in South Georgia within the Lesser Caucasus, which is a component of the Caucasian mountain system. The Caucasus is composed of the

Greater and Lesser Caucasus, adjacent foredeeps and intermountain troughs. It is a part of the Mediterranean (Alpine-Himalayan) collisional orogenic belt.

The Loki massif represents cropped out part of crystalline basement of the Loki-Karabakh tectonic zone and belongs to the Baiburt-Sevanian terrane (Gamkrelidze, Shengelia, 2005). The massif is a large anticlinal structure with pre-Alpine crystalline rocks exposed in the core and is surrounded by a Mesozoic-Cenozoic sedimentary cover.

The Loki crystalline massif is spread over 400 km² and is composed of autochthonous Devonian gneissose quartz-diorites, allochthonous Lower Paleozoic metamorphic complex, Upper Paleozoic granites and Jurassic, Cretaceous and Tertiary intrusives of various composition. Devonian quartz-diorites are exposed only in deep gorges. The metamorphic complex is represented by three tectonic plates, including the rocks of different composition and age. All these rocks are cut by Late Variscan and Bathonian granitoids, Upper Cretaceous and Eocene quartz-bearing diorite-porphyrites.

Although the petrology of the crystalline massif rocks are quite well-studied, the geochemistry of granitoids is almost unstudied. Among the above-mentioned igneous rocks, the authors interest was the geochemical study of pre-Alpine granitoids. They conducted petrogeochemical investigation of the granitoids and summarized obtained results in the presented paper.

Methodology applied in presented study implied both field and analytical stages. GPS system-based mapping was carried out; sample material was collected from both quartz-diorites and Upper Paleozoic granites; microscopic study of thin sections was conducted. Chemical analysis of 28 samples was performed using the XRF spectrometer (SPECTRO XEP04) in the Complex Laboratory of Geological Research of Alexandre Janelidze Institute of Geology. The obtained data were plotted on various classification and discriminative-tectonic diagrams.

It was established that according to petrochemical data, gneissose quartz diorites represent normal-alkaline rocks of the calc-alkaline series. Their composition corresponds to granitoids of the potassium-sodium series. According to I, S and A types of the geochemical classification of granites, these rocks belong to the S and partially M type granites. This is also indicated by the increased content of alumina in the rocks. The attribution of the mentioned rocks to the S type shows that the origin conditions of the quartz-diorite magma were a subduction environment, although the occurrence of several points in the I granites field may correspond to the opinion (Gamkrelidze, Shengelia, 2005) that some role in their formation was also played by magma of gabroid composition presented in the lower part of the crust under the quartz diorites distribution area.

According to the authors' data, the chemical composition of granitoids corresponds to acid rocks of the normal series of granites. In terms of alkaline relation, they mainly belong to the potassium-sodium series of the normal and sometimes subalkaline rocks. According to the geochemical types of S, I, and A, these granitoids mainly belong to the S type granites, the plagioclaskites – to I type, and the granodiorites to both – I and S types. Presumably, a large part of the Late Variscan granites was formed by melting of the continental crust under subduction conditions, and a small part – as a result of palingenesis of Upper Devonian

gneissose quartz diorites. The results of geochemical research indicate that both granitoids and quartz diorites are characterized by signs of magmatic rocks of volcanogenic-arc origin, which indicates mainly the subduction conditions of their formation.

GEOLOGICAL BACKGROUND

A detailed study of the Loki crystalline massif began since the 30s of the last century. During this period, many scientists (Kazakhashvili, 1941; P. Gamkrelidze, 1949; Zaridze, Tatrishvili, 1953, 1958; Javakishvili, 1958; P. Gamkrelidze et al., 1958; Ivanitsky & Mgeliashvili, 1971; Kekelia, Chkhetia, 1977; Khutsishvili, 1978; Shengelia et al., 1989; S.Kekelia et al., 1990; Bartnitsky et al., 1992; Vashakidze, 1999; Gamkrelidze et al., 1991; Gamkrelidze, Shengelia, 2005; Gamkrelidze et al., 2019; Tsutsunava et al., 2024) were investigating the Loki crystalline massif. For today it is established that the massif is composed of autochthonous Devonian gneissose quartz-diorites, allochthonous Lower Paleozoic metamorphic complex and the leucocratic plagiogranites spatially connected to them, Upper Paleozoic granites and Jurassic, Cretaceous and Tertiary intrusives of various composition (Fig. 1). Devonian quartz-diorites are exposed only in deep gorges. The metamorphic complex is represented by the tectonic plates, including the rocks of different composition and age. The allochthonous-imbriate structure of the metamorphic complex of the massif are confirmed by the investigations of a number of scientists (Khutsishvili, 1978; Gamkrelidze et al., 1999; Gamkrelidze et al., 2002; Gamkrelidze, Shengelia 2005; Gamkrelidze et al., 2017; Gamkrelidze et al., 2018₁, 2018₂, Gamkrelidze et al., 2019). The complex is composed of three tectonic plates: metapelite (stratified), ophiolite and melange.

All these rocks are cut by mainly Late Paleozoic granitoids and by Jurassic and Cretaceous intrusions in subordinate quantities. All the intrusive rocks occupy two-thirds of the exposed part of the massif. Late Variscan (Sudetic) postmetamorphic granitoids have apparently a laccolith-like shape and are represented by two mica, alaskite and muscovitized granites and, to a lesser extent, granodiorites, aplites and pegmatites. The pre-Alpine metabasites to different extent are spread in all tectonic plates of the massif. The Middle Jurassic intrusive complex is represented by quartz diorites, granodiorites and granites, and in a very subordinate amount by amphibolic gabbro. The intrusives are small in size. Late Cretaceous intrusions are thin and are represented by quartz diorite-porphyrites and thin aplite veins (Dudaury, Togonidze, 2016).

The U-Pb age of gneissose quartz-diorites of the Loki massif is 370 ± 59 - 35 Ma (Bartnitsky et al., 1992; Vashakidze et al., 1999, 2000), but the age of granites, according to K-Ar method of dating corresponds to 327 ± 6 Ma (Dudaury et al., 1999; Vashakidze, 2000). This undoubtedly proves that the quartz-diorites are pre-Late Variscan (Upper Devonian) formations, but the granites are of Late Variscan age. The pre-Jurassic age of crystalline rocks is also determined by the transgressive bedding of Liassic terrigenous deposits on them and numerous geochronological determinations. As for the Mesozoic granitoids, their Bathonian age is also geologically confirmed. Upper Cretaceous small intrusives in the west of the massif are covered by Paleogene sediments, and their K-Ar age – 80 ± 3 Ma corresponds to Late Cretaceous time

(Vashakidze, 1999). In the Loki crystalline massif besides the rocks mentioned above, there are found leucocratic plagiogranites, which are spatially connected to the metabasite allochthonous plate (Gamkrelidze, Shengelia et al., 1999).

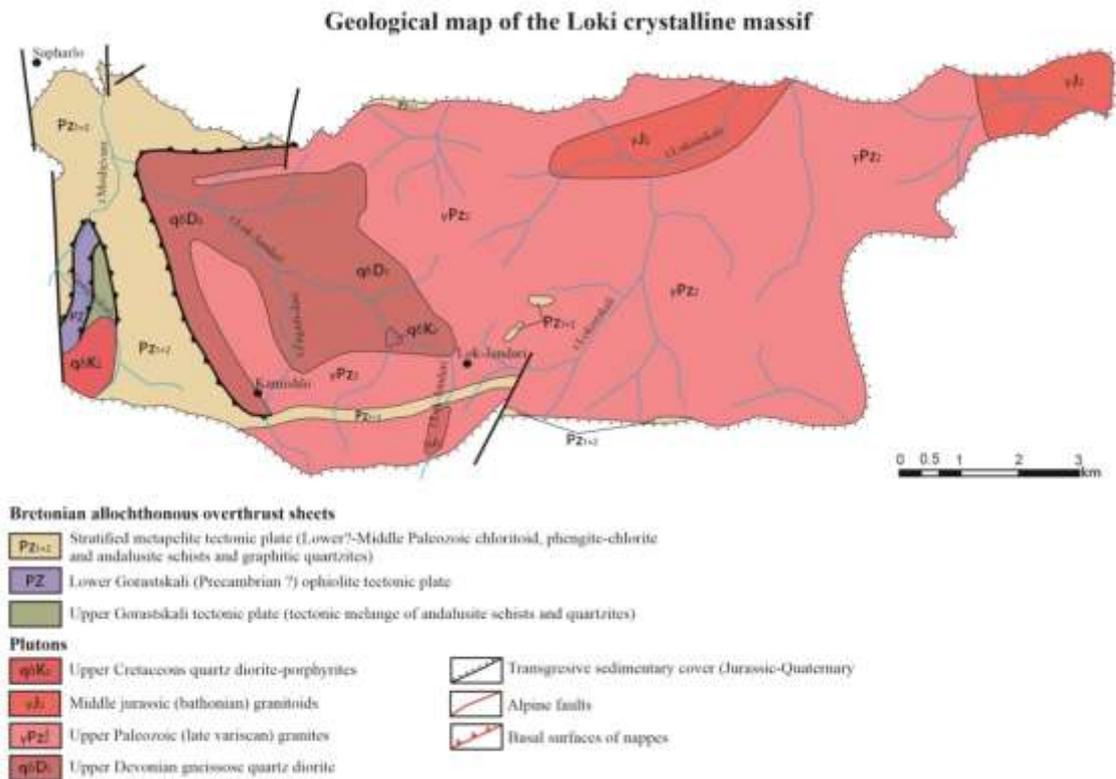


Fig.1 Geological map of the Loki crystalline massif (based on the 1:50 000 scale map, P. Gamkrelidze and I. Nazarov, 1959).

CHARACTERIZATION OF PRE-ALPINE QUARTZ DIORITES AND GRANITOIDS OF THE LOKI CRYSTALLINE MASSIF

Within the Loki crystalline massif Precambrian leucocratic plagiogranites, Upper Devonian gneissose quartz diorites and Upper Paleozoic granitoids are exposed.

Gneissose quartz diorites are widespread rocks in the Loki crystalline massif (Fig. 1). They are mainly exposed in the western part of the massif in the valley of the river Lok-Jandari and gorges of its tributaries and small outcrops are noted in the valleys of the rivers Loki, Dambludi, Ikhtibulati and gorges of their tributaries as well. These rocks are recorded also as xenoliths in Late Variscan granites. The gneissose quartz diorites have a tectonic contact with the rocks of the metapelite tectonic plate of the allochthonous metamorphic complex; here cataclasis and mylonitization processes are developed. Late Variscan granitoids have an intrusive contact with quartz diorites; in the latter the processes of granitization are fixed: K-feldspar, acid plagioclase and quartz appear as secondary minerals. According to G.Vashakidze (1999) xenoliths of gabbro-diorites have been established in gneissose quartz diorites. Presumably, they are rocks of different ages and belong to different phases of magmatic paroxysm (Gamkrelidze, Shengelia, 2005). It should be noted that the authors of the article did

not find any gabbro-diorite xenoliths.

In the Loki massif gneissose quartz diorites and diorites are distinguished (Gamkrelidze, Shengelia, 2005). The mineralogical composition of these rocks is: quartz, andesine plagioclase, hornblende, biotite and secondary minerals - chlorite, epidote group minerals and carbonate (Fig. 2). In the granitized types of quartz diorites formed as a result of the impact of Late Variscan granitoids on them the appearance of K-field spar is noted. Among the accessories, zircon is mentioning.

Late Variscan granitoids are very widely spread in the Loki crystalline massif and are represented by two mica granites, muscovite-bearing varieties and alaskites, but granodiorites, aplites and pegmatites are rarely found (Ivanitsky, Mgliashvili, 1971).

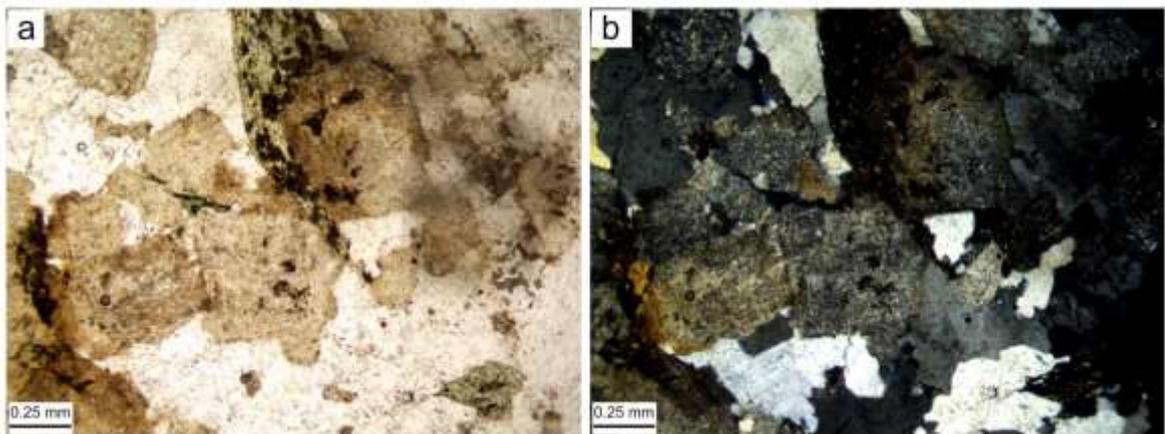


Fig. 2. Microscope image of gneissose quartz diorite: a) PPL; b) XPL.

Late Variscan granites are yellowish, pink or light gray coarse- or medium-grained rocks (Fig. 3). Rock-forming minerals are represented by quartz, plagioclase, K-feldspar, muscovite and biotite, and secondary minerals are chlorite and sericite (Fig. 8, 9). Among the accessory minerals, zircon and apatite, as well as an ore mineral, should be noted.

Muscovite-bearing granites are widespread in the Loki crystalline massif. They are spread in the form of veins, the thickness of which varies from centimeters to several meters. The main minerals of the rocks are: K- feldspar, plagioclase, quartz and muscovite.

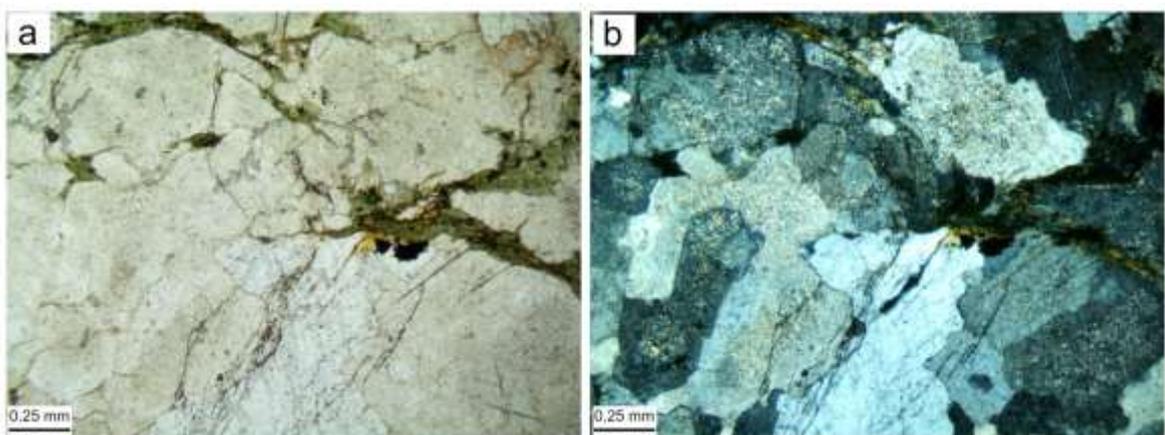


Fig. 3. Microscope image of granite: a) PPL; b) XPL.

Alaskite is pinkish, reddish or grayish coarse-crystalline rock, which is characterized by granitic and sometimes porphyry texture (Fig. 4). Its main rock-forming minerals are: quartz, highly pelitized K-feldspar and a very small amount of muscovite. Plagioclase occurs as a secondary mineral.

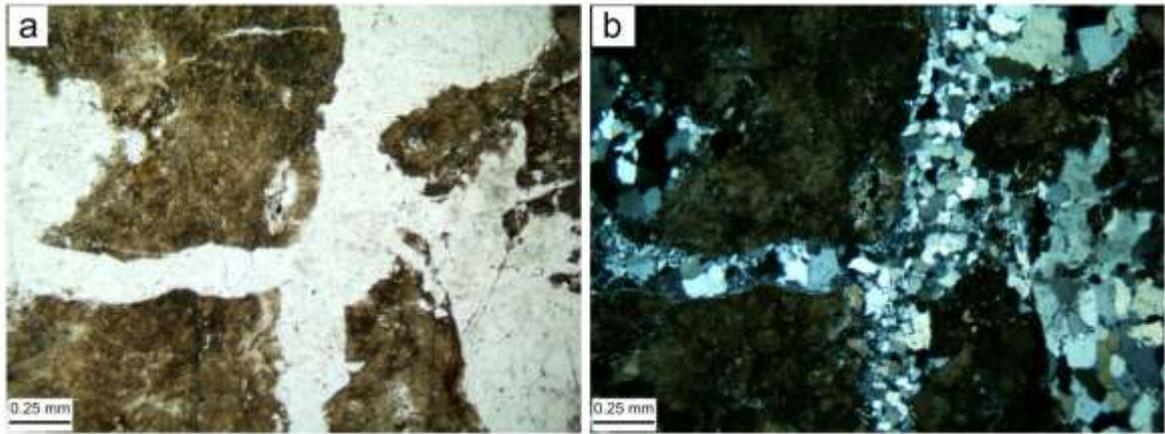


Fig. 4. Microscope image of alaskite: a) PPL; b) XPL.

Late Variscan granodiorite is a coarse-crystalline gray rock with a hypidiomorphic-granular texture. Rock-forming minerals are represented by quartz and intermediate plagioclase and K-feldspar; Melanocratic minerals are muscovitized and chloritized biotite and amphibole. Secondary minerals are represented by chlorite and epidote; pelitization process is also observed (Fig. 5).

Aplites are pink or pale pink fine-crystalline rocks. They are mainly represented by veins with the thickness from several centimeters to even one meter. The main minerals are: quartz, plagioclase and K- feldspar. From the accessory minerals garnets and ore minerals are observed (Vashakidze, 1999).

Pegmatites are rare. They are coarse-crystalline pink rocks, the main rock-forming minerals of which are quartz, albite, microcline-perthite and muscovite.

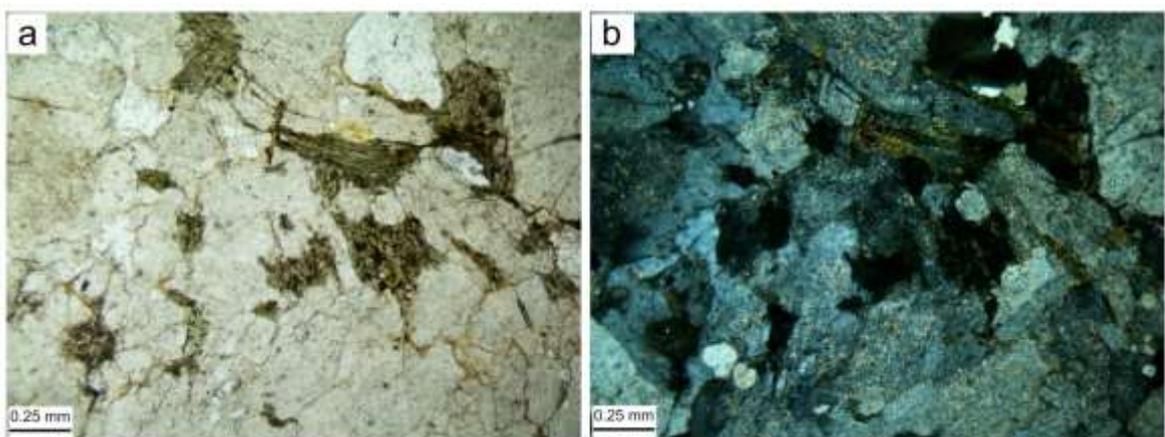


Fig. 5. Microscope image of granodiorite: a) PPL; b) XPL.

PETROGEOCHEMICAL DATA AND DISCUSSION

28 samples of pre-Alpine granitoids from the Loki crystalline massif – Upper Devonian quartz diorites and Upper Paleozoic granitoids, granodiorites and plagioclaskites were analyzed for determining major, RE and REE. The results of the analysis are presented in the table below (Table 1). The obtained data were plotted on different classification diagrams.

Traditionally, the AFM diagram (Kuno, 1968) has been used. Most of points indicating quartz diorites and granitoids are located in the field of the calc-alkaline series rocks (Fig. 6.).

Table 1

Composition of major, RE and REE in the pre-Alpine granitoids of the Loki crystalline massif (wt %)

Component	R-3	R-5	R-7	R-23	R-25	R-30	R-43	R-45	R-46	R-58
SiO ₂	65.02	71.39	68.91	69.87	73.49	68.28	65.23	71.39	69.11	68.98
Al ₂ O ₃	16.55	14.10	14.01	13.20	12.12	14.03	16.70	13.87	14.34	12.97
CaO	0.28	0.35	0.45	0.82	0.26	1.55	0.28	0.35	0.46	0.78
Fe ₂ O ₃	3.14	1.04	2.23	2.29	1.03	2.77	3.15	1.02	2.31	2.19
K ₂ O	4.34	4.06	4.41	3.39	5.51	3.78	4.45	4.05	4.38	3.45
Na ₂ O	2.09	2.51	2.13	2.30	2.62	2.90	2.20	2.46	2.08	2.31
TiO ₂	0.25	0.25	0.30	0.26	0.09	0.25	0.29	0.26	0.28	0.27
MgO	0.15	0.08	1.03	1.62	0.23	0.93	0.13	0.08	1.02	1.68
SO ₃	0.02	0.02	0.02	0.12	0.04	0.02	0.03	0.03	0.03	0.13
P ₂ O ₅	0.10	0.10	0.14	0.14	0.03	0.15	0.12	0.01	0.15	0.14
MnO	0.04	0.01	0.05	0.07	0.02	0.05	0.05	0.01	0.06	0.08
Cl	524.70	443.50	454.40	401.80	401.80	484.00	521.40	438.00	451.00	397.00
Cu	184.10	208.90	260.00	179.10	172.80	121.40	187.60	201.30	264.00	175.00
Ba	249.80	304.90	464.20	356.10	289.30	469.70	251.20	307.50	462.30	361.00
Zr	107.60	102.80	108.10	65.25	63.31	74.54	107.80	106.60	109.30	68.00
Rb	104.50	99.25	126.00	66.97	103.30	82.45	103.70	98.78	121.00	66.00
Zn	75.10	61.39	226.60	48.89	32.02	32.08	76.30	60.75	223.10	49.12
Sr	69.65	90.02	150.90	152.30	68.33	201.00	70.10	91.34	147.00	151.79
Ce	30.00	64.67	30.33	10.37	19.74	36.76	29.80	63.11	31.30	10.79
Nd	5.70	46.08	66.14	25.59	21.65	37.24	5.72	44.73	65.78	24.89
V	31.38	26.36	53.30	31.79	12.26	25.92	31.12	26.98	53.92	32.56
La	8.86	34.67	27.07	8.30	20.81	8.83	8.91	32.36	26.89	8.72
Cr	12.69	13.45	12.84	6.84	8.79	10.02	11.98	12.98	12.71	6.93
Y	14.16	16.28	15.55	15.50	19.46	24.23	13.93	15.78	16.89	14.98
Cs	4.86	4.63	4.54	4.45	4.68	4.98	4.89	4.56	4.79	4.71
Ga	9.98	7.95	7.71	4.04	5.20	6.69	9.91	7.84	7.81	4.34
Pb	21.82	7.95	72.93	35.63	49.66	26.47	22.11	7.21	73.98	34.97
Ta	5.56	5.52	6.55	5.44	5.14	4.75	5.46	5.67	6.71	5.83
Th	14.94	7.95	17.00	4.57	17.62	8.25	15.43	7.76	15.00	4.69
Co	5.61	3.35	4.65	4.78	3.37	5.37	5.61	3.39	5.30	4.87
Nb	5.70	5.64	6.10	3.23	4.48	7.09	5.73	5.72	6.78	3.48
As	2.50	1.35	2.98	4.72	0.71	1.30	2.54	1.44	3.23	5.00
Hg	1.75	1.65	1.73	3.23	1.67	1.77	1.75	1.68	1.52	3.68
Sn	1.48	1.38	1.39	1.34	1.40	1.52	1.44	1.35	1.45	1.26
Sb	1.35	1.27	1.25	1.23	1.26	1.37	1.39	1.32	1.12	1.20
W	1.21	1.12	1.21	1.18	1.13	1.22	1.32	1.23	1.30	1.21

Hf	1.00	0.91	0.99	0.96	0.92	1.00	1.00	0.87	1.10	1.10
U	1.12	1.12	2.02	0.96	1.67	1.54	1.23	1.19	2.40	0.87
Ni	1.20	0.81	4.80	3.91	0.82	1.83	1.24	0.86	5.43	4.02
Bi	0.67	0.64	0.66	0.68	0.67	0.68	0.68	0.60	0.72	0.69
Ge	0.64	0.61	0.64	0.62	0.61	0.66	0.64	0.63	0.61	0.65
Tl	0.60	0.59	0.53	0.58	0.55	0.61	0.63	0.59	0.48	0.61
Mo	0.52	0.49	0.52	172.00	0.49	0.52	0.51	0.51	0.50	168.00
Se	0.43	0.41	0.43	0.41	0.42	0.43	0.45	0.40	0.51	0.40
Br	0.25	0.69	0.42	0.22	0.59	0.57	0.25	0.72	0.38	0.24
Total	92.13	94.06	93.90	94.20	95.60	94.88	92.62	93.53	94.22	92.98

Component	R-65	R-70	R-16	R-19	R-27	R-51	R-54	R-67	R-24
SiO ₂	73.70	68.94	75.08	76.22	70.04	74.81	75.14	71.23	67.42
Al ₂ O ₃	11.78	14.45	11.67	12.80	14.78	11.80	13.30	14.30	13.91
CaO	0.22	1.52	0.27	0.38	0.72	0.26	0.41	0.78	1.10
Fe ₂ O ₃	1.14	2.83	1.11	0.44	2.11	1.20	0.52	2.43	3.05
K ₂ O	5.57	3.98	2.72	1.86	1.50	2.81	1.94	1.53	2.31
Na ₂ O	2.78	2.69	3.51	3.64	4.22	3.48	3.73	4.36	2.64
TiO ₂	0.07	0.24	0.21	0.33	0.26	0.20	0.34	0.27	0.36
MgO	0.26	1.00	0.08	0.08	1.56	0.08	0.08	1.63	2.05
SO ₃	0.05	0.03	0.31	0.03	0.02	0.35	0.05	0.03	0.02
P ₂ O ₅	0.05	0.16	0.00	0.00	0.14	0.00	0.01	0.14	0.17
MnO	0.04	0.06	0.01	0.01	0.05	0.00	0.01	0.06	0.09
Cl	404.00	485.00	398.70	403.50	426.90	401.00	400.00	423.00	374.80
Cu	173.00	123.00	209.50	243.40	168.20	211.00	245.00	167.00	229.60
Ba	287.00	468.00	637.00	155.20	244.90	642.00	153.00	247.00	396.00
Zr	63.87	75.64	85.94	116.40	62.84	87.00	118.00	62.00	192.30
Rb	107.00	81.60	45.11	36.37	38.22	44.20	37.30	39.00	63.14
Zn	36.00	33.23	39.89	50.36	41.08	42.23	55.00	44.90	60.56
Sr	69.00	205.00	132.60	167.20	286.20	133.10	169.00	287.00	192.30
Ce	19.34	36.74	23.01	32.78	40.47	22.45	31.50	41.00	70.68
Nd	22.76	37.46	15.29	24.67	40.00	14.98	25.35	43.00	63.60
V	12.98	23.95	17.00	28.78	35.00	14.00	29.87	37.00	48.15
La	21.86	8.94	12.24	20.75	8.69	11.75	18.78	8.85	42.13
Cr	8.87	10.00	9.51	13.63	7.82	10.14	14.00	7.40	12.48
Y	18.94	24.80	3.37	8.14	11.19	3.51	7.70	11.24	15.28
Cs	4.57	4.77	4.57	4.24	4.58	4.67	5.30	4.97	4.87
Ga	5.57	6.85	4.72	5.24	6.69	4.81	5.80	6.83	8.44
Pb	48.23	27.98	10.63	7.98	4.97	10.41	8.40	4.45	12.67
Ta	5.85	4.98	5.50	5.71	5.21	5.61	6.1	5.46	6.19
Th	18.34	8.85	9.40	8.74	7.41	9.40	9.34	7.85	11.92
Co	3.47	5.85	3.39	2.27	4.55	3.45	2.56	4.56	5.42
Nb	4.52	7.23	4.00	6.87	4.06	5.00	7.40	4.25	5.04
As	0.85	1.48	0.37	0.37	0.52	0.39	0.46	0.68	6.61
Hg	1.73	1.68	1.65	1.57	1.67	1.71	1.63	1.74	1.73
Sn	1.52	1.56	1.35	1.25	1.37	1.28	1.45	1.29	1.49
Sb	1356.00	1.46	1.26	1.15	1.28	1.32	1.40	1.36	1.34
W	1.23	1.25	1.10	1.07	1.15	1.21	1.40	1.25	1.21
Hf	0.95	1.03	0.90	0.87	0.94	0.89	0.98	0.89	0.99
U	1.72	1.68	0.90	2.00	0.81	0.79	3.00	0.79	1.26

Ni	0.93	1.35	0.80	0.78	0.83	0.79	0.77	0.85	2.16
Bi	0.76	0.69	0.62	0.59	0.62	0.72	0.55	0.65	0.67
Ge	0.66	0.67	0.60	0.56	0.60	0.52	0.53	0.66	0.63
Tl	0.53	0.63	0.60	0.58	0.61	0.55	0.57	0.70	0.62
Mo	0.48	0.58	5.57	0.47	0.49	5.71	0.59	0.42	0.52
Se	0.49	0.48	0.40	0.38	0.40	0.41	0.41	0.36	0.43
Br	0.52	0.60	0.50	0.40	0.24	0.61	0.47	0.30	0.25
Total	95.65	95.89	95.06	95.90	95.54	95.06	95.52	96.76	93.30

Component	R-33	R-62	R-73	R-36	R-40	R-42	R-76	R-80	R-82
SiO ₂	64.84	68.20	65.74	56.12	49.82	60.73	55.74	51.98	60.54
Al ₂ O ₃	15.63	14.27	14.87	16.29	14.05	15.01	15.98	14.32	15.35
CaO	1.26	1.07	1.34	2.72	4.52	1.41	2.87	4.60	1.35
Fe ₂ O ₃	3.29	3.02	3.34	7.40	10.00	4.89	7.67	10.36	4.98
K ₂ O	2.71	2.50	2.83	1.48	0.15	1.48	1.64	0.16	1.64
Na ₂ O	3.39	2.70	3.65	1.75	1.28	2.52	1.73	1.28	2.76
TiO ₂	0.29	0.36	0.27	0.81	0.81	0.52	0.85	0.84	0.55
MgO	1.60	2.12	1.50	4.50	6.82	3.81	4.47	6.77	3.76
SO ₃	0.02	0.03	0.02	0.07	0.02	0.08	0.09	0.03	0.08
P ₂ O ₅	0.14	0.19	0.18	0.24	0.17	0.19	0.25	0.18	0.18
MnO	0.09	0.10	0.09	0.18	0.26	0.19	0.17	0.27	0.19
Cl	443.10	371.00	445.00	633.90	487.10	544.60	635.40	489.50	546.00
Cu	124.80	232.00	127.00	152.10	105.80	117.10	155.60	105.70	118.90
Ba	520.90	398.00	523.00	231.90	21.24	212.70	233.30	21.76	214.80
Zr	74.09	195.00	73.00	67.56	46.03	80.23	68.50	46.07	80.45
Rb	60.41	62.00	62.00	47.36	2.89	51.16	46.78	2.85	53.50
Zn	41.90	60.90	43.00	70.54	170.80	131.90	71.50	171.30	135.90
Sr	202.50	191.00	201.00	324.30	197.80	279.90	322.60	196.90	278.30
Ce	21.94	68.80	23.00	26.89	11.62	11.30	27.90	11.65	12.80
Nd	48.72	62.00	47.80	48.42	28.83	11.00	49.00	28.94	12.00
V	37.90	49.00	36.98	176.70	181.80	68.54	175.00	181.50	66.90
La	20.17	46.40	21.98	12.14	12.45	9.09	12.43	11.42	9.20
Cr	7.86	11.78	7.74	11.42	13.82	41.68	11.65	13.65	41.45
Y	13.50	14.98	13.98	17.74	15.17	10.37	17.76	15.93	10.54
Cs	4.86	4.77	4.64	5.52	8.39	5.06	5.76	8.66	5.13
Ga	7.55	8.54	7.86	13.25	11.03	7.82	13.65	11.83	7.88
Pb	10.54	12.75	11.84	8.85	5.48	19.99	8.99	5.48	20.32
Ta	2.10	6.58	2.75	2.55	2.85	2.26	2.45	2.46	2.54
Th	6.91	11.45	6.66	4.82	0.48	4.08	4.46	0.46	4.24
Co	5.74	5.47	5.46	19.91	31.50	13.03	19.65	32.60	13.54
Nb	4.95	5.46	4.86	3.98	1.84	6.30	3.98	1.76	6.53
As	0.40	7.98	0.42	3.97	2.19	0.42	3.95	2.27	0.42
Hg	1.76	1.68	1.56	1.98	2.04	1.82	1.88	2.87	1.85
Sn	1.46	1.37	1.96	1.70	1.80	1.54	1.98	1.94	1.56
Sb	1.34	1.39	1.77	1.57	1.66	1.42	1.68	1.74	1.74
W	1.23	1.86	1.86	1.48	1.67	1.32	1.32	1.76	1.42
Hf	1.00	0.97	1.03	1.22	1.65	1.08	1.43	1.93	1.35
U	0.94	1.22	1.00	0.94	0.59	3.46	0.98	0.53	3.75
Ni	2.70	2.24	2.76	8.86	13.44	11.32	8.67	13.52	12.53
Bi	0.67	0.65	0.70	0.76	0.79	0.71	0.75	0.74	0.74

Ge	0.65	0.66	0.62	0.73	0.79	0.66	0.79	0.74	0.65
Tl	0.63	0.67	0.68	0.69	0.71	0.63	0.68	0.71	0.64
Mo	0.52	0.52	0.45	0.60	0.63	0.55	0.59	0.67	0.55
Se	0.42	0.45	0.49	0.48	0.49	0.44	0.46	0.50	0.44
Br	0.48	0.22	0.44	0.28	0.29	0.30	0.29	0.30	0.33
Total	93.40	94.55	93.83	91.75	88.03	91.00	91.45	88.77	91.36

Note: 3, 5, 7, 23, 25, 30, 43, 45, 46, 48, 65, 70 - granite; 16, 19, 27, 51, 54, 67 - plagioliaskite; 24, 33, 62, 73 - granodiorite; 36, 40, 42, 76, 80, 82 - gneissose quartz diorite.

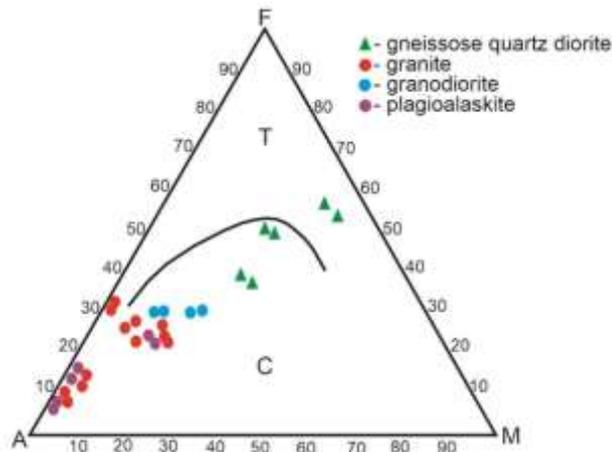


Fig. 6. AFM diagram (Kuno, 1968).

On the $\text{Na}_2\text{O}+\text{K}_2\text{O}$ vs SiO_2 diagram (Andreeva et al., 1978) the points of both quartz diorites and granitoids fall within the field of normal-alkaline granitoids, although they are grouped separately from each other. It is also worth noting that the points indicating granitoids are located closer to the sub-alkaline field (Fig. 7).

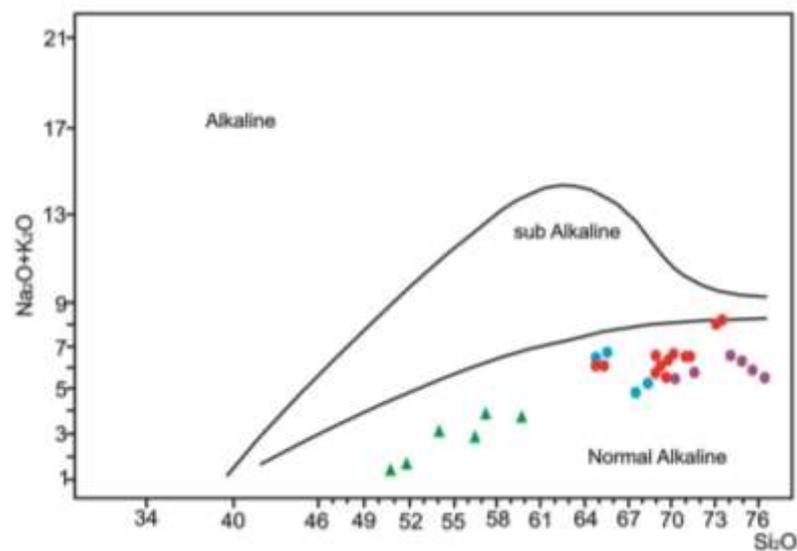


Fig. 7. $\text{Na}_2\text{O}+\text{K}_2\text{O}$ vs SiO_2 discriminative diagram (Andreeva et al., 1978). Symbols see on the Fig. 6.

According to A. Ewart's (1982) K_2O vs SiO_2 classification diagram, in the Variscan granitoids there is also a tendency towards increasing alkalinity (Fig. 8).

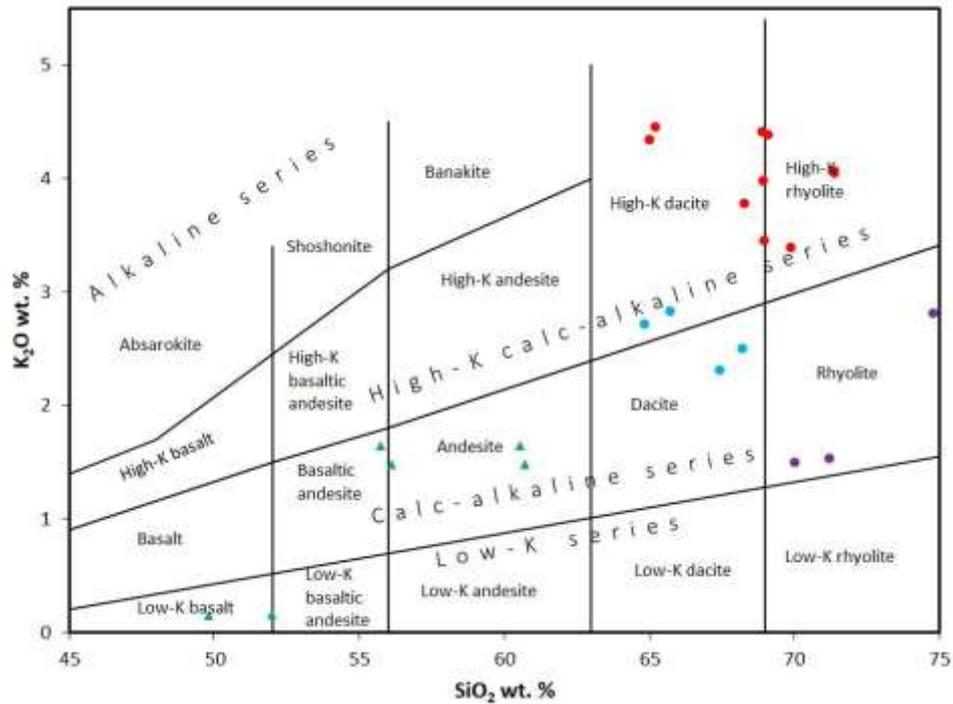


Fig. 8. K_2O vs SiO_2 classification diagram (Ewart, 1982). Symbols see on the Fig. 6.

According to Le Bas et al. (1986), the points of the Late Variscan granitoids are, as expected, sharply separated from the Late Devonian quartz diorites. Most of the points corresponding to granitoids positioned in the fields of dacites and rhyolites, and those of quartz diorites - in basalt – andesite fields (Fig. 9).

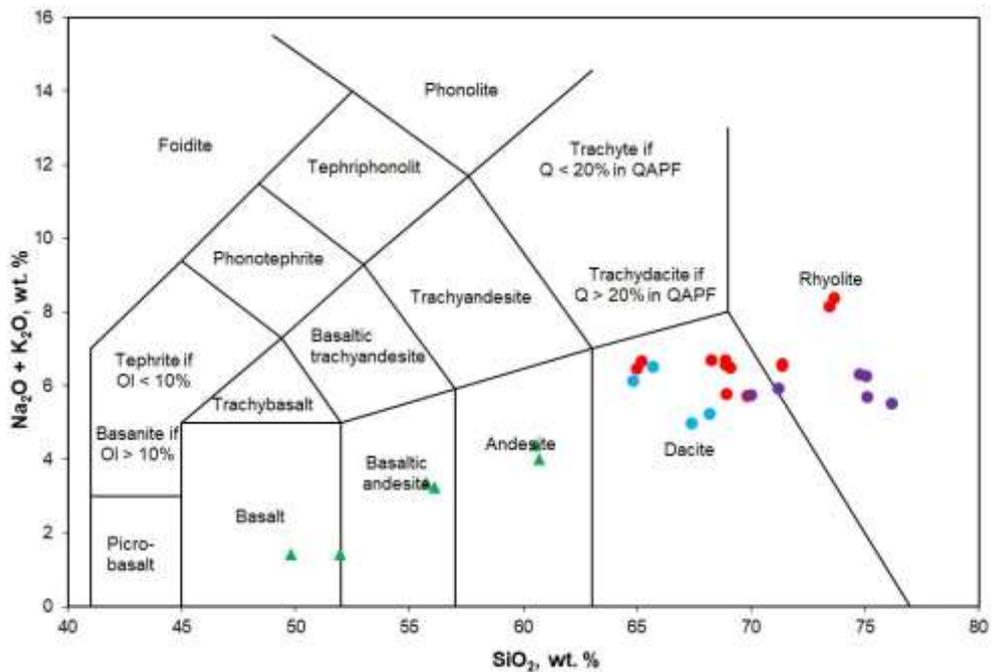


Fig. 9. $\text{Na}_2\text{O}+\text{K}_2\text{O}$ vs SiO_2 discriminative diagram (Le Bas et al., 1986).

Symbols see on the Fig. 6.

On the $\text{Na}_2\text{O}+\text{K}_2\text{O}-\text{CaO}$ vs SiO_2 discriminative diagram, the points indicating quartz diorites are located mainly in the alkaline-calc field, and some – in the calc-alkaline field. Points of Variscan granitoids, most of them are almost equally distributed in the calc-alkaline and alkali-calc fields, only a part of the points indicating plagioclaskites are into the calc-alkaline field (Fig. 10).

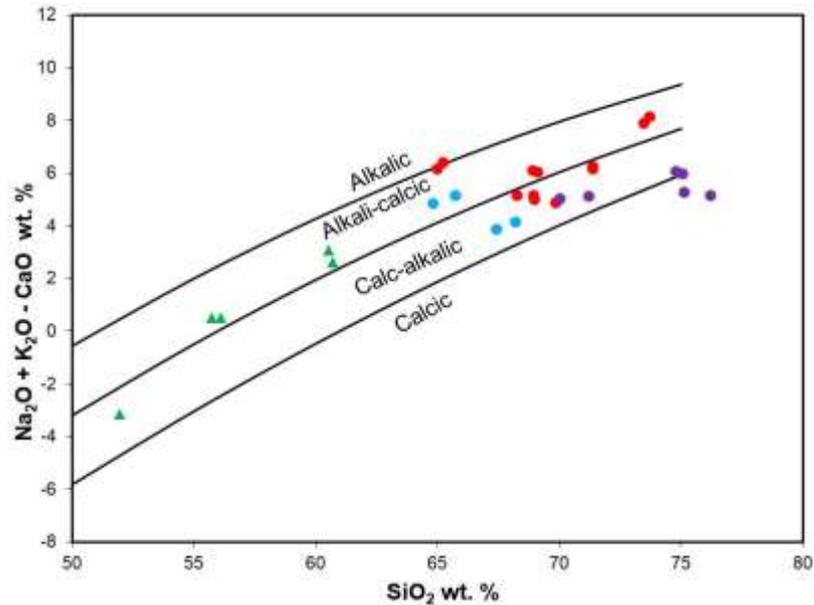


Fig. 10. $\text{Na}_2\text{O}+\text{K}_2\text{O}-\text{CaO}$ vs SiO_2 discriminative diagram (Frost et al., 2001).

Symbols see on the Fig. 6.

According to the $\text{K}_2\text{O}/\text{Na}_2\text{O}$ diagram, the fields of points corresponding to quartz diorites and different types of Variscan granitoids are distinctly separated (Fig. 11).

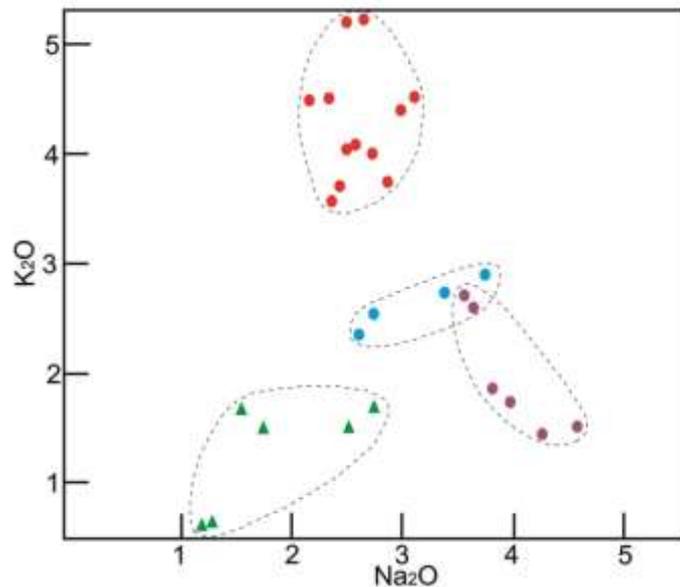


Fig. 11. K₂O vs Na₂O discriminative diagram (Middlemost, 1985). Symbols see on the Fig. 6.

On the FeO_{total}/(MgO+FeO_{total}) vs SiO₂ discriminative diagram (Frost and Frost, 2008) points are distributed as follows: points corresponding to quartz diorites are completely located in the field of magnesian rocks, points of granitoids are almost equally distributed in fields of ferroan and magnesian rocks, except for granodiorites, which are completely disposed in the field of magnesian rich rocks (Fig. 12).

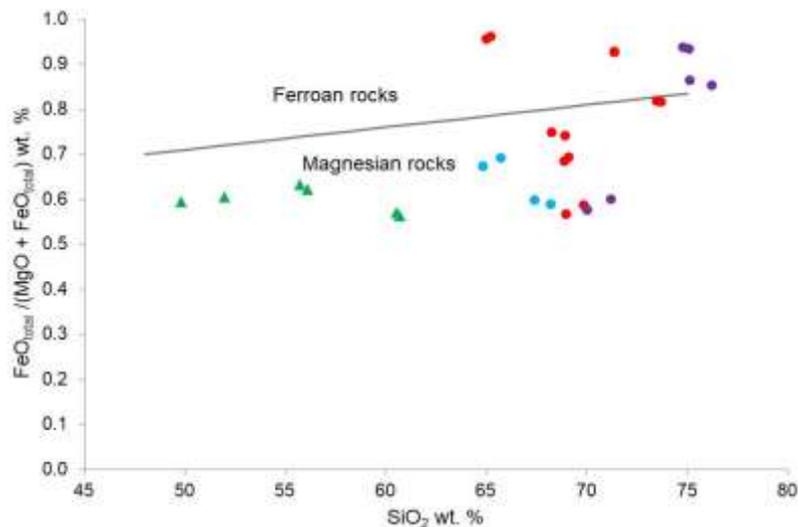


Fig. 12. FeO_{total}/(MgO+FeO_{total}) vs SiO₂ discriminative diagram (Frost and Frost, 2008)

Symbols see on the Fig. 6.

As mentioned above, a number of geochemical diagrams were used, A.R. Hastie et al. (2007) Th vs Co discriminative diagram among them. As a result of plotting the obtained data on the diagram, it turned out that the points indicating quartz diorites mainly fell into the basaltic-andesite – andesite field of the calc-alkaline composition, while the points corresponding to all types of granitoids are distributed in the calc-alkaline and high-K and shoshonitic fields of dacite-rhyolite-latitude-trachyte (Fig. 13), as in the Na₂O+K₂O vs SiO₂ discriminative diagram (see Fig. 10).

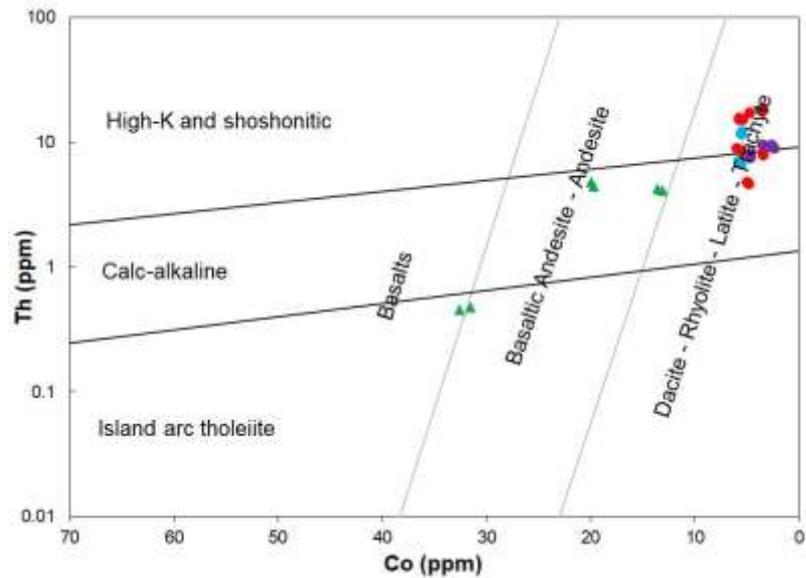


Fig. 13. Th vs Co discriminative diagram (Hastie, 2007). Symbols see on the Fig. 6.

Analytical data were also plotted on Nb vs Y and Rb vs Nb+Y tectonic-interpretative diagrams (Pearce et al, 1984). On the Nb vs Y diagram, all points representing the Loki massif granitoids are located within the field of volcanic arcs and syncollision granites. On the Rb vs Nb+Y diagram, all points are disposed in the field of volcanic arcs, although the majority of normal granites were distributed close to the field of syncollision granites (Fig. 14).

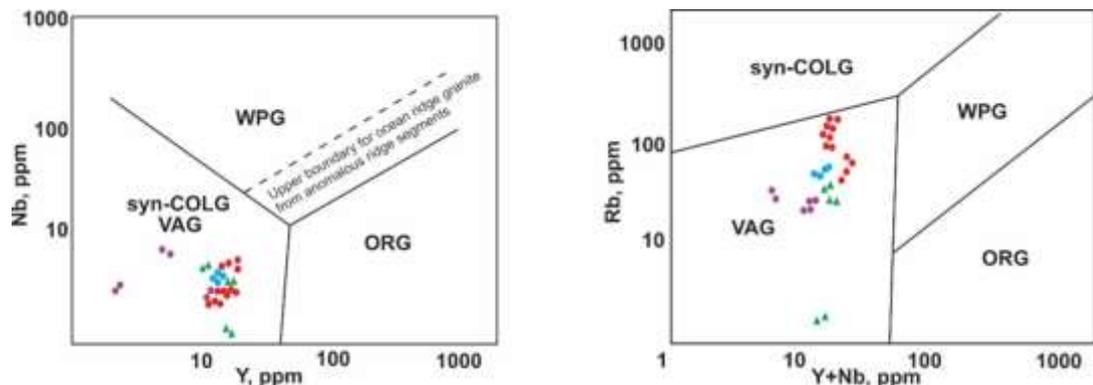


Fig. 14. Tectonic-interpretative diagrams: Nb vs Y; Rb vs Nb+Y (Pearce et al., 1984).

Symbols see on the Fig. 6.

For the geochemical classification of the Loki crystalline massif granitoids, the determination diagram of I, S and A granite types was used (Hassan, McAllister, 1992). On the diagram symbols are arranged as follows: most of the quartz diorite points are arranged in the field of S-type granites, and less – on the boundary of I and S fields. The symbols of granites are arranged in the field of S-type granites, the plagioclaskites – in the field of I – type granites, and the granodiorites – equally distributed in the fields of I- and S-type granites (Fig. 15).

FeO_{total}/MgO vs $Zr+Nb+Ce+Y$ discriminative diagram was also used to determine the genetic types of granites (Whalen et al., 1987). The symbols of granitoids are arranged in the "other granites" field. Points indicating quartz diorites are grouped, but points corresponding to

granitoids are scattered throughout the field (Fig. 16). Unlike the previous diagram, not only I and S type granites, but also M type granites are united in the mentioned field.

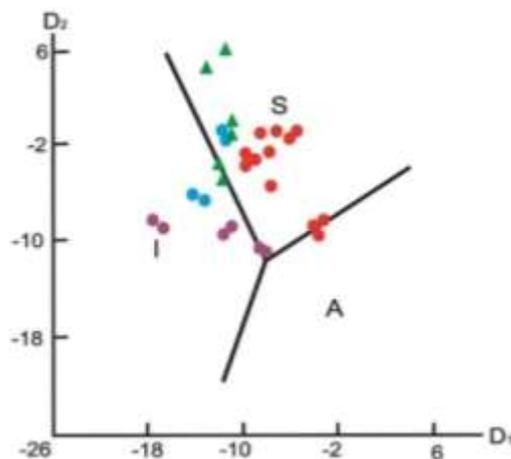


Fig. 15. Discriminative diagram for I, S and A types of granites (Hassan, McAllister, 1992). Symbols see on the Fig. 6.

A discussion of the study results is provided below. It is known that S-type granites are formed by selective melting of sedimentary material, and I-type granites are formed on the basis of igneous rocks. The assignment of the studied Late Variscan granitoids to S-type granites confirms that a large part of the granites formed under subduction conditions, through melting of the continental crust. The presence of some of granitoids – namely granodiorites in I field, can be considered as a result of palingenesis of Upper Devonian gneissose quartz diorites (Gamkrelidze, Shengelia, 2005). As for the disposition of plagioclase symbols in the field I, it makes us think that they are leucocratic plagiogranites spatially related to the metabasic tectonic plate of the Loki crystalline massif (Gamkrelidze, Shengelia, et al., 1999).

It should be noted that the results received by the authors of the article on the determination of the genetic types of Variscan granitoids differ from the results of previous researchers; they attribute these granitoids, except for aplite-alaskites, to type I. According to Whalen et al, (1987) it is known that, in general, S type granitoids, in contrast to I type granitoids, have low CaO, Na₂O and Sr contents. In addition, the ASI of S-type granitoids, which describes the relationship $Al_2O_3/(Na_2O+K_2O+CaO)$ (Zen, 1986), varies from 1.01 to 1.99. Above parameters are in full agreement with our data (see Table 1).

As for quartz diorites, according to the types of geochemical classification of granites, they belong to S and partially M type granites. Part of the quartz diorites were formed in the subduction conditions by melting of the continental crust. This is also proved by the increased content of alumina in them. Previous scientists (Gamkrelidze, Shengelia, 2005) explained the presence of these rocks in the field of I type granites by their formation at the expense of gabbroid magma presented in the lower part of the crust under the spreading area of quartz diorites. On the discriminative diagram used by the authors of the presented work M type granites are indicated as well (Fig. 16). M (mantle) type of granites, which is formed in the subduction zone due to melting of the oceanic crust, was later distinguished by B. Chappel and A. White (1979).

According to Whalen et al, (1987) this type of granitoids is known to be represented by quartz diorites and tonalites. They, unlike other types, are depleted in SiO_2 and K_2O and Rb and Nb, and are enriched in MgO and CaO; they are also characterized by $\text{K}_2\text{O}/\text{Na}_2\text{O} < 1$. It is also determined that M type granitoids unlike S, I and A types, contain maximum quantity of ferroan-magnesian minerals. The quartz diorites under studying meet all the above criteria for M-type granites (see Table 1), except for Rb and Nb contents. This inconsistency is quite possibly caused by the influence of Late Variscan granites on the studied quartz diorites, which in some cases caused intense granitization process resulting granodiorites formation. The results of determination of the genetic type of the quartz diorites obtained by the authors of the article also differ from the results of previous researchers.

According to previous researchers (Vashakidze 1999; Gamkrelidze, Shengelia 2005; Gamkrelidze et al. 2019), the Late Devonian quartz diorites of the Loki crystalline massif belong to sub-alkaline rocks of the calc-alkaline series, but the Late Paleozoic granitoids – to sub-alkaline and normal-alkaline rocks of the calc-alkaline series. It is known that with relatively low silica content (up to 74% SiO_2), to the normal series rocks with the sum of alkali ($\text{K}_2\text{O} + \text{Na}_2\text{O}$, wt %) less than 7.5, and to the subalkaline series – from 7.5 to 8.1 are attributed. According to the authors of the presented article, the granitoids and gneissose quartz diorites of the massif belong to normal-alkaline rocks of the calc-alkaline series; although they are close to a subalkaline composition (see Table 1).

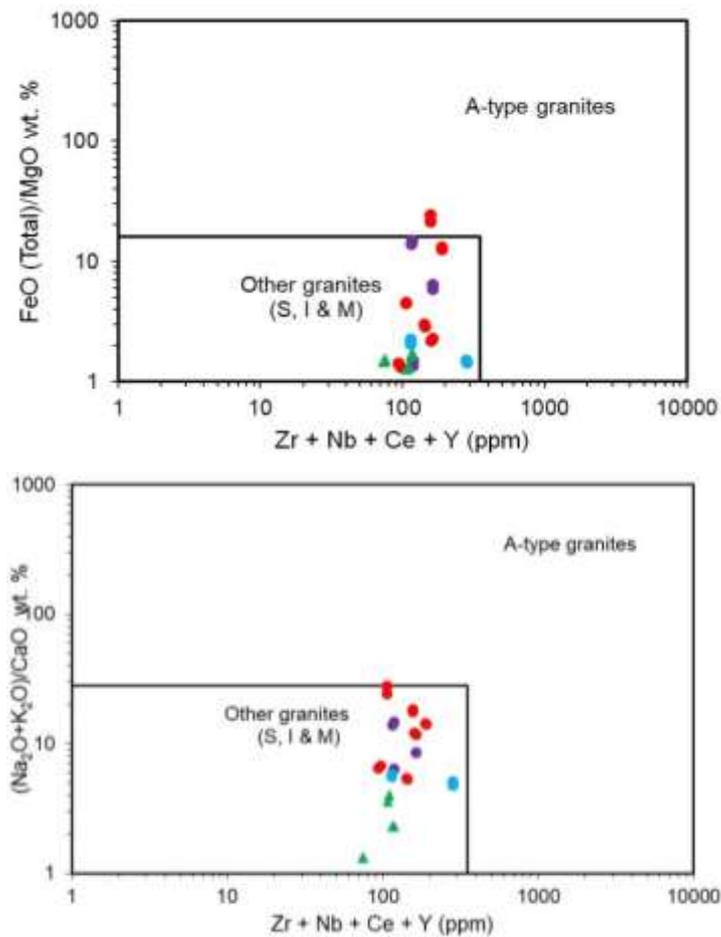


Fig16. $\text{FeO}_{\text{total}}/\text{MgO}$ vs $\text{Zr}+\text{Nb}+\text{Ce}+\text{Y}$ and $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{CaO}$ vs $\text{Zr}+\text{Nb}+\text{Ce}+\text{Y}$ discriminative diagram (Whalen et al, 1987). Symbols see on the Fig. 6.

CONCLUSION

Granitoids of the pre-Alpine basement of the Loki crystalline massif are represented by autochthonous Upper Devonian gneissose quartz diorites and cutting those Upper Paleozoic granitic intrusions.

According to petrochemical data, gneissose quartz diorites are normal-alkaline rocks of the calc-alkaline series. Their composition corresponds to granitoids of the potassium-sodium series. According to I, S and A types of the geochemical classification of granitoids, these rocks belong to S and partially M type granites. This is also proved by the increased content of alumina in quartz diorites. The attribution of the mentioned rocks to the S type shows that formation of their magma took place in a subduction conditions; although the disposition of several points in the field of I type granites may correspond to the opinion (Gamkrelidze, Shengelia, 2005) that some role in formation of quartz diorites was played by gabroid magma existed in the lower part of the crust, under the area of quartz diorites distribution.

According to the authors' data, the chemical composition of granitoids corresponds to acid rocks of the normal series of granites. In terms of alkaline relation, they mainly belong to the potassium-sodium series of the normal and sometimes subalkaline series. According to the geochemical types of S, I, and A, these granitoids mainly belong to the S type granites, the plagioclaskites – to I type, and the granodiorites – to both I and S types. Probably, a large part of the Late Variscan granites was formed by melting of the continental crust under subduction conditions, and a small part – as a result of palingenesis of Upper Devonian gneissose quartz diorites. The results of geochemical research indicate that both granitoids and quartz diorites are characterized by signs of magmatic rocks of volcanogenic-arc origin, which indicates mainly the subduction conditions of their formation.

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