საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 15, №4, 2021
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 15, no. 4, 2021

Geology

Geochemistry of Metamorphic Rocks of Dizi Series of the Southern Slope Zone of the Greater Caucasus

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(Presented by Academy Member David Shengelia)

The Dizi Series is exposed within the Southern Slope zone of the Greater Caucasus, in the core of the Svaneti anticlinorium. It is mainly composed of metaterrigenous phyllite-like and volcanogenic rocks, which are faunistically dated from the Devonian to the Triassic inclusive. During Variscan orogeny these rocks (sandstones, gravelstones, argillites, greywackes, carbonaceous-clayey shales, silicites, tuff sandstones, volcanics and limestones) underwent regional metamorphism of low-temperature subfacies of green schist facies. Later, due to the contact impact of the Middle Jurassic intrusions, they were transformed into graphitized phyllites, phyllitic schists, marbles, and various hornfelses. The aim of the presented study was the geochemical research of metamorphic rocks (except of silicites and limestones) of the Dizi Series. For this purpose the geochemical study of 20 key rock samples were performed including determination of major components, RE and REE; an XRD investigation of material was carried out; a number of diagrams were used for determination of primary rocks of the metamorphites and for restoration of conditions of their formation. The lithochemical types, lithological features and composition of the original rocks of the Dizi Series metamorphic rocks were studied. *© 2021 Bull. Georg. Natl. Acad. Sci.*

Greater Caucasus, Dizi Series, geochemistry, metamorphic rocks

The Dizi Series crops out within the Southern Slope zone of the Greater Caucasus in the core of the Svaneti anticlinorium, in the Enguri and Tskhenistskali river basins [1]. It is traced along the overall Caucasian direction for ca.70 km, with a thickness of 2000–2200 m. The Series is mainly composed of strongly dislocated, crenulated, finely folded and weakly metamorphosed terrigenous sediments, the age of which corresponds to the period from Lower-Middle Devonian to the uppermost Triassic [1–5]. Present knowledge on stratigraphy of the Dizi Series is mainly based on the palaeontological data (corals, foraminifers, crinoids) described or reported by various authors. During the Variscan orogeny these rocks (sandstones, gravelstones, argillites, carbonaceous-clayey shales, silicites, tuff sandstones, volcanics and limestones) underwent regional metamorphism of chlorite-sericite subfacies of green schist facies. Later, due to the contact impact of the Middle Jurassic Kirar-Abakuri intrusive complex, these

rocks transformed to phyllites, phyllitic schists, marbles, and various hornfelses.

It should be mentioned that despite the stratigraphy and tectonics of the Dizi Series were more or less well-studied, geochemistry of metamorphic rocks have not been previously studied at all.

Materials and Methods

Typical mineral associations of regional metamorphosed rocks of the Dizi Series are: Chl+Ser+Ab±Tur+Qz and Chl+Ser+Cal+Ab+Qz (mineral symbols are presented according to the Whitney and Evans classification [6]). Fine intercalation of graphite-sericite-quartz phyllites with Act+Phr+Ab±Qz greywacke is also observed. Contact metamorphosed rocks are represented by the following mineral associations:
Bt+Ms+Pl+Qz, MgHbl+Bt+Cal+Pl+Qz,
Bt+Ms+And+Gr+Ab±Qz±Chl,
Cal+Act+Czo, Cal+Cpx+Wo+Gr+Qz,
And+Bt+Crd+Chl+Ms+Pl+Mag+(Crn±Qz),
Bt+Ms+Crn, Bt+Ms±Qz, Act+Pl+Qz,
Qz+Cal, Bt+Ms+Crn+Chl±Qz,
Cpx+Hbl+Act+Czo+Pl+Bt±Qz,
Act+MgHbl+Pl±Qz, Bt+Ms±Qz, Act+Pl+Qz,
Qz+Cal, Cpx+MgHbl+Bt+Act+Scp+Cal,
And+Bt+Crd+Ms+Qz,
And(→Fi)+Bt+Crd+Ms+Qz,
MgHb+Aug+Bt+Czo+Scp+Grt+Pl,
And+Bt+Crd+Ms+Qz+Ilm.

Rock material was collected from all outcrops of the Dizi Series, including both contact and regionally metamorphosed rocks. For geochemical study the most typical 20 samples were chosen from several hundred samples. Analysis of petrogenic components, RE and REE was performed at the Complex Laboratory of Geological Research of Al. Janelidze Institute of Geology of Iv.Javakhishvili Tbilisi State University. Sample chips were finely powdered using RETSCH RS200 vibrating mill. Major and trace element were determined by X-Ray fluorescence spectrometry (XRF) using SPECTROSCOUT X-Ray spectrometer with Cu-Rh X-Ray tube. An XRD study was also conducted at the same laboratory using an X-ray diffractometer DRON 2.

Results and Discussion

An XRD analysis of three most characteristic samples from the Dizi Series revealed the following quantitative ratio of minerals in the rocks: in metapelites – Qz (75-85%); Ilt (10-12%); Fsp (3-5%); Px (3-5%) and in metabasites – Qz (60-65%); Ilt (5%); Chl (5%); Fsp (5%); Px (10%).

Several diagrams were applied for determining primary rocks of the Dizi Series metamorphites and for reconstruction of their depositional conditions. The obtained data of XRF analysis of metasedimentary rocks of the Series (Table) are plotted on a logarithmic-scaled module diagram for systematization of argillaceous rocks [7] (Fig.1). Distribution of figurative points shows that its main lithochemical types corresponds to the field V that represents the standard ternary mixture chlorite + montmorillonite + hydromica (±mixed-layered minerals of the montmorillonite–hydromica and rarely chlorite–hydromica). Fewer points are located within the field II, where montmorillonite is the predominant clay mineral, kaolinite is rare, and hydromicas are insignificant; a considerable number of points are also located in the area of overlapping each other fields V and II. Two points fell into overlapping area of fields IV and V, corresponding to the standard ternary mixture chlorite+montmorillonite+hydromica and standard binary mixture of chlorite+hydromica acid. Only one point is in the field I, where kaolinite is the predominant clay mineral. These data do not contradict, and in some cases completely meet the petrographic descriptions of rocks, as well as the XRD analysis data.

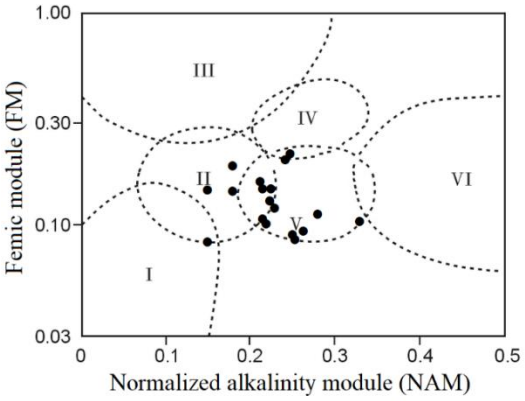

Fig. 1. Logarithmic-scaled module diagram for systematization of argillaceous rocks [7]. FM, femic module: $(Fe_2O_3+FeO+MgO)/SiO_2$ [8]; NAM, normalized alkalinity module: $(Na_2O+K_2O)/Al_2O_3$ [9]. Major lithochemical types of argillaceous rocks: I, kaolinite is a predominant clay mineral; II, montmorillonite is a predominant clay mineral, kaolinite is scarcer, and hydromica is minor; III, chlorite is a predominant clay mineral, and Fe-hydromicas are subordinate; IV, standard binary mixture chlorite+hydromica; V, standard ternary mixture chlorite + montmorillonite + hydromica (±mixed-layered minerals of the montmorillonite–hydromica series and rarer chlorite–hydromica series); VI, argillaceous hydromica-containing rocks with a high admixture of dispersed feldspar particles.

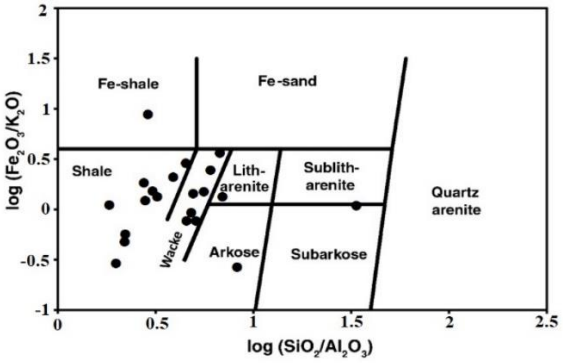

Fig. 2. Diagram $\log(Fe_2O_3/K_2O)/\log(SiO_2/Al_2O_3)$ [10].

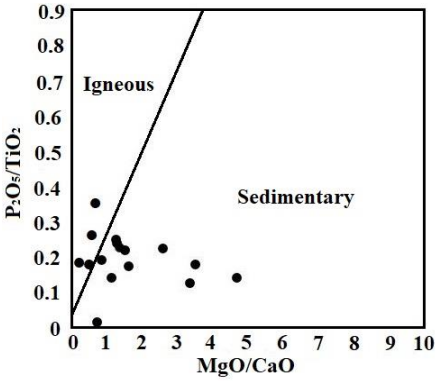

Fig. 3. Diagram $P_2O_5/TiO_2/MgO/CaO$ [11].

To characterize the lithological features of the primary rocks, obtained geochemical data (Table) are plotted on the $\log(Fe_2O_3/K_2O)$ vs. $\log(SiO_2/Al_2O_3)$ diagram [10] (Fig. 2). Distribution of points shows that the primary rocks of metamorphites of the Series are represented mainly by shales and, to a lesser extent, by wackes. Only one point at a time disposed in different fields corresponding to the high-ferruginous varieties of schists, litharenites and arkoses. Since the source material for these rocks could be of both sedimentary and volcanic origin, the diagram P_2O_5/TiO_2 vs. MgO/CaO is used for specification of composition of primary rocks [11]. Most of points on the diagram are disposed in the field of reworked sedimentary origin (Fig. 3). However, some of the samples fell into the field of magmatic origin.

Geochemical studies have shown that the petrogenic components of metamorphic rocks of the Dizi Series have the following compositional variations: SiO_2 –51.06-67.68 wt.%, Al_2O_3–9.99-26.45 wt.%, MgO–0.94-6.32 wt.%, FeO_{total}–1.88-8.57 wt.%, K_2O–1.36-6.99 wt.%, TiO_2–0.31-1.03 wt.%, CaO–0.25-14.16 wt.%, Na_2O–0.14-2.42 wt.% and P_2O_5–0.01-0.35 wt.%. Due to the presence of microcline and biotite in the metapelites, they are characterized by a high content of K_2O+Na_2O (mean 3.76 wt.%); On the TAS classification diagram of K_2O+Na_2O/SiO_2 (wt.%) [12], figurative points of metamorphic rocks fall into the fields of andesites and dacites, and basaltic andesites as well; only a small amount are located in the field of basalts (Fig. 4). The amount of alkaline components is mainly less than 7% that is also typical for andesite [13]. TiO_2 content is low, which is typical for volcanic rocks of the subduction zone [14].

Table. Results of XRF analysis of metamorphic rocks of the Dizi Series

Component	81-13	62-12	45-12	41-12	15-13	17-13	19-13	23-13	8-13	3-13
SiO_2	53.73	51.11	66.03	67.68	54.93	57.87	62.67	55.82	53.08	64.04
TiO_2	0.96	1.03	0.49	0.43	0.67	0.59	0.87	1.00	0.82	0.52
Al_2O_3	23.96	15.59	10.97	10.4	9.99	15.35	14.72	16.88	17.51	13.20
Fe_2O_3	3.90	8.57	3.10	4.97	4.96	7.60	5.48	8.21	7.85	3.92
MnO	0.06	0.14	0.06	0.10	0.29	0.15	0.07	0.12	0.06	0.04
MgO	1.40	5.95	3.03	2.80	2.55	3.43	3.08	6.32	4.74	2.75
CaO	0.40	8.72	6.00	4.46	9.93	2.56	1.95	2.46	3.17	2.44
Na_2O	0.14	2.42	1.53	0.14	0.14	0.14	1.14	0.72	0.14	0.64
K_2O	6.37	1.36	2.28	2.14	2.12	2.30	3.03	3.43	3.08	2.38
P_2O_5	0.17	0.35	0.09	0.12	0.13	0.13	0.15	0.22	0.18	0.13
SO_3	0.03	0.05	0.13	0.60	0.64	0.52	0.14	0.01	0.02	0.02
Total	**91.27**	**95.50**	**93.91**	**93.92**	**86.45**	**90.71**	**93.50**	**95.43**	**90.71**	**90.24**
Cr	219	229.9	446.2	430	434	321.1	229.5	341.1	201.6	218
Co	7.0	33	7.63	9.5	15.3	15.1	10.2	27.6	30.2	6.2
Ni	31	99.3	50.5	28.6	73.6	65.9	34.1	126	93.6	38
Rb	227.5	52.4	87.3	110.6	95.2	139.1	96.8	101.5	106.1	71.4
Sr	55.9	268.8	238.1	164.3	284	136.2	98.1	121.3	127.5	116.5
Y	51.7	32	19.7	22.5	23.6	28.2	25.7	28.7	24.6	19.4
Zr	222.2	140	145.3	120.9	202	169.4	195.8	149.1	136.1	141.3
Ba	919	210.3	227.6	246	260.9	238.4	412.5	472.1	402.5	296.6
Th	31.9	3.8	9.7	8.7	11.1	20.5	13.1	11.8	10.8	8.0
U	7.5	1.0	2.5	1.7	1.2	4.4	2.1	1.3	1.5	1.0
Zn	41.9	120.9	42.5	88.2	123.5	85.2	61.6	103.5	110.1	54.8
Component	**4-13**	**75-13**	**10-13**	**21-13**	**18-13**	**25-13**	**6-13**	**13-13**	**26-13**	**58-19T**
SiO_2	62.37	66.29	51.06	66.68	53.25	60.65	59.04	72.19	58.4	80.95
TiO_2	0.78	0.63	0.93	0.75	1.01	0.90	0.69	0.31	0.61	0.33
Al_2O_3	14.86	11.42	26.45	10.54	19.35	16.14	13.98	14.35	14.63	9.00
Fe_2O_3	5.90	4.05	2.65	5.60	6.50	7.17	5.28	2.38	6.63	0.78
MnO	0.04	0.07	0.03	0.09	0.27	0.10	0.07	0.02	0.09	0.01
MgO	3.63	2.87	0.93	4.76	3.65	2.45	3.62	0.94	5.41	0.50
CaO	0.25	7.36	0.28	3.84	3.32	0.53	2.89	1.13	2.39	0.04
Na_2O	0.14	1.89	0.23	0.14	0.33	0.15	0.14	0.65	2.96	0.14
K_2O	2.66	1.39	6.98	2.19	3.85	3.54	2.82	3.06	2.21	2.35
P_2O_5	0.16	0.14	0.12	0.19	0.14	0.13	0.16	0.06	0.18	0.08
SO_3	0.00	0.05	0.09	0.15	0.03	0.19	0.09	0.49	0.02	0.49
Total	**90.80**	**96.38**	**90.03**	**95.00**	**91.97**	**91.94**	**88.84**	**95.78**	**93.70**	**94.71**
V	90.7	57.1	122.7	103.6	173.4	102.8	87.4	44.1	145.4	155.9
Cr	272.4	324	150.9	442.1	228.3	231.4	369.3	449.5	130.3	593.2
Co	22.5	14.9	5.34	18.7	18.6	26.7	8.4	5.0	9.9	2.9
Ni	116.6	50.5	13.8	85.3	83.9	49.7	86.3	19.7	14.3	10.5
Rb	87	48.8	252.2	69.8	115	123	81.6	96.1	43.3	62.9
Sr	46	255.5	73.5	120	120.6	64.7	99.9	65.9	93.6	5.8
Y	22.6	23.2	47.1	21.9	30.1	18.8	22.3	18.3	22.5	17.9
Zr	153.6	170.4	216.7	154.5	155	147.2	173.1	144.8	124.9	37.6
Ba	336.2	244.2	809	224.1	533	369.3	311.9	310.2	465.9	263.7
Th	8.2	7.6	29.4	5.8	12	8.6	8.0	14.1	9.9	4.4
U	1.8	1.2	4.6	1.0	1.8	1.2	1.1	2.5	2.0	1.3
Zn	74.2	59.7	39.8	77.3	82.6	80.3	79.1	50.3	49.9	6.0

Metapelites of the Dizi Series are enriched in incompatible elements such as Rb (av. 109 ppm), Sr (av. 140 ppm), Ba (av. 387 ppm), Y (av. 25.77 ppm), Zr (av. 163 ppm), Th (av. 12.6 ppm) and U (av. 2.2 ppm). The average contents of compatible elements are as follows: Cr – 305.5, Ni – 61.6, Co

– 15 ppm. An increase of U, Rb, Ba, and K is observed that is also characteristic of andesites [13]. The Zn/Ti diagram [15] (Fig. 5), also confirms the andesitic and, to a lesser extent, basaltic origin of the primary metamorphic rocks.

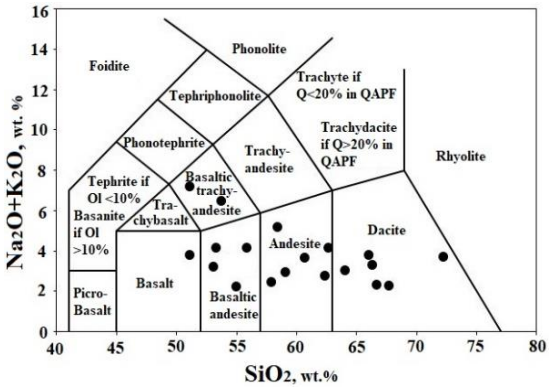

Fig. 4. Classification diagram TAS (Total Alkali Silica) [12].

For tectonic interpretation of the data, a tectonic discrimination diagram for sandstones and argillites K_2O/Na_2O vs. SiO_2 [16] (Fig. 6) was used. Plotted geochemical data show that their absolute majority falls into the field of the Passive continental margin, confirming the issue about the formation of metasedimentary rocks of the Dizi Series under the conditions of a Passive continental margin [17].

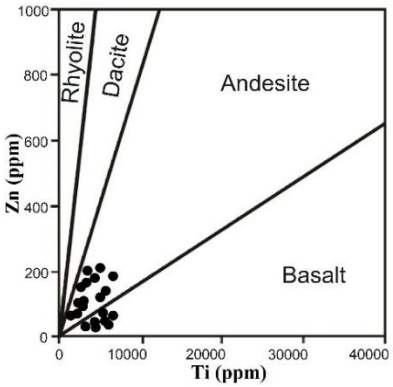

Fig. 5. Zn/Ti diagram [15].

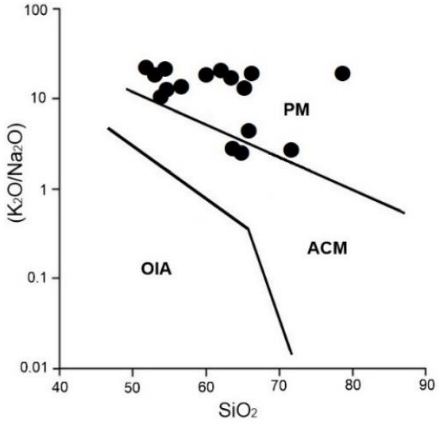

Fig. 6. Diagram of tectonic discrimination of sandstones and argillites [16]. PM – Passive continental margin, ACM – Active continental margin, OIA – Ocean island arc.

Conclusions

Geochemical studies were carried out on metamorphic rocks (except of silicites and limestones) of the Dizi Series, formed in the conditions of the continental slope and its foot on the southern Passive margin of the small oceanic basin of the southern slope of the Greater Caucasus. According to the applied diagrams, the composition of their initial rocks correspond to andesites and, to a lesser extent, to basalts of calc-alkaline composition. The lithochemical types of the primary rocks of the series are rocks with mixed-layered minerals of the montmorillonite–hydromica and chlorite–hydromica series, and, to a lesser extent, rocks with a predominance of montmorillonite. Most of rocks are reworked material of sedimentary origin, and only a few of them are of magmatic origin. In terms of lithological features, the initial rocks of the metamorphic rocks of the Series are represented mainly by schists and, to a lesser extent, by wackes.

This work was supported by Shota Rustaveli National Science Foundation of Georgia (SRNSF) [PHDF-19-159, Regional and Contact Metamorphism of the Dizi Series].

გეოლოგია

კავკასიონის სამხრეთი ფერდობის ზონის დიზის სერიის მეტამორფული ქანების გეოქიმია

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(წარმოდგენილია აკადემიის წევრის დ. შენგელიას მიერ)

დიზის სერია შიშვლდება კავკასიონის სამხრეთი ფერდობის ზონაში, სვანეთის ანტიკლინორიუმის გულში. იგი აგებულია ძირითადად ფილიტისებრი და ვულკანოგენური ტერიგენული ქანებით, რომლებიც ფაუნისტურადაა დათარიღებული დევონურიდან ტრიასულის ჩათვლით. ვარისკული ოროფაზისის დროს ამ ქანებმა (ქვიშაქვები, გრაველიტები, არგილიტები, გრაუვაკები, კირქვოვან-თიხოვანი ფიქლები, სილიციტები, ტუფოქვიშაქვები, ვულკანიტები და კირქვები) განიცადა მწვანე ფიქლების ფაციესის დაბალტემპერატურული რეგიონული მეტამორფიზმი. მოგვიანებით, აღნიშნულ ქანებზე შუაიურული ინტრუზივების ზემოქმედების შედეგად, ისინი გარდაიქმნა გაგრაფიტებულ ფილიტებად, ფილიტიზებულ ფიქლებად, მარმარილოებად და ნაირგვარ რქაულებად. წარმოდგენილი კვლევის მიზანს წარმოადგენდა დიზის სერიის მეტამორფული ქანების (გარდა სილიციტების და კირქვებისა) გეოქიმიური კვლევა. ჩატარდა 20 საკვანძო ნიმუშის გეოქიმიური ანალიზი, რომელიც მოიცავდა პეტროგენული, იშვიათი და იშვიათმიწა ელემენტების განსაზღვრას და მასალის XRD კვლევას. მეტამორფიტების დედაქანების დასადგენად და მათი ფორმირების პირობების რეკონსტრუქციისთვის, გამოყენებულ იქნა სხვადასხვა დიაგრამა. შესწავლილ იქნა დიზის სერიის მეტამორფიტების პირველადი ქანების ლითოქიმიური ტიპები, ლითოლოგიური თავისებურებები და ქიმიური შედგენილობა.

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Received September, 2021