

## 2023;24(1):86-94

NORMAL RESERVED

ISSN 2312-8143 (Print); ISSN 2312-8151 (Online) journals.rudn.ru/engineering-researches

DOI: 10.22363/2312-8143-2023-24-1-86-94 EDN: EEDRTQ UDC 550.8+550.4+550.3

Research article / Научная статья

# Geochemical features of granitic rocks using x-ray spectral fluorescence in the Miass region, Southern Ural

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## Article history

Received: December 14, 2022 Revised: February 25, 2023 Accepted: February 28, 2023

## **Keywords:**

geochemistry, magma process, high-K calc-alkaline, metaluminous

**Abstract.** The goals of the research are the geochemistry and identification of granite rocks. The granitic rocks are part of the Syrostan massive, which is located in Southern Ural. Understanding the magma process and probable mineralization deposition can be gained by classifying granite and determining geochemical characteristics. X-ray spectral fluorescence analysis was used to collect samples from outcrops for geochemical analysis. The results indicate that the rocks belong to the high-K calc-alkaline to calc-alkaline series. The granites are metaluminous to slightly peraluminous and are classified as I-type granites, with A/CNK values ranging from 0.73 to 1.01. The majority of the rock samples are trondhjemite to slightly tonalite in composition. The most observable samples in the normative Na<sub>2</sub>O-k<sub>2</sub>O-CaO scheme have defined a continuous range, varying from tonalite/trondhjemite to granodiorite. The findings provide valuable information about the petrogenesis of the rocks and their composition.

## Acknowledgements

This paper has been supported by the RUDN University Strategic Academic Leadership Program.

## **Conflicts of interest**

The authors declare that they have no know competing financial interests or personal relationships that could have appeared to influence the study presented in the paper.

## For citation

Ibrahim MAE, Kuleshov VN, Kotelnikov AE, Georgievskiy AF, Ibrahim SA. Geochemical features of granitic rocks using x-ray spectral fluorescence in the Miass region, Southern Ural. *RUDN Journal of Engineering Research*. 2023;24(1):86–94. http://doi.org/10.22363/2312-8143-2023-24-1-86-94

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## Геохимическая характеристика и классификация гранитов с использованием рентгеновской спектральной флуоресценции Миасского района Южного Урала

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#### История статьи

Поступила в редакцию: 14 декабря 2022 г. Доработана: 25 февраля 2023 г. Принята к публикации: 28 февраля 2023 г.

#### Ключевые слова:

геохимия, рентгеноспектральная флуоресценция, магматический процесс, высококалиевый, известково-щелочной, металлургический Аннотация. Основные задачи исследования – геохимия и идентификация гранитных пород. Гранитные породы входят в состав Сыростанского массива, расположенного на Южном Урале. Понимание магматического процесса и вероятного отложения минерализации можно получить путем классификации гранита и определения геохимических характеристик. Рентгеноспектральный флуоресцентный анализ использован для отбора проб из обнажений для геохимического анализа. Результаты показали, что породы относятся к известково-щелочной серии. Граниты – от металлуминозных до слабоглиноземистых – относятся к I типу со значениями A/CNK от 0,73 до 1,01. Большинство образцов пород имеют состав от трондьемита до слабого тоналита. Наиболее наблюдаемые образцы в нормативной схеме Na<sub>2</sub>O-k<sub>2</sub>O-CaO определяют непрерывный диапазон от тоналита/трондьемита до гранодиорита. Находки дают ценную информацию о петрогенезе горных пород и их составе.

#### Благодарности

Работа выполнена при поддержке Программы стратегического академического лидерства РУДН.

#### Заявление о конфликте интересов

Авторы заявляют, что им неизвестны конкурирующие финансовые интересы или личные отношения, которые могли бы повлиять на представленное в статье исследование.

#### Для цитирования

*Ibrahim M.A.E., Kuleshov V.N., Kotelnikov A.E., Georgievskiy A.F., Ibrahim S.A.* Geochemical features of granitic rocks using x-ray spectral fluorescence in the Miass region, Southern Ural // Вестник Российского университета дружбы народов. Серия: Инженерные исследования. 2023. Т. 24. № 1. С. 86–94. http://doi.org/10.22363/2312-8143-2023-24-1-86-94

## Introduction

Different deposits and mineralization were discovered associated with granite intrusions, such as gold deposits, tin, tungsten and several deposits of rare earth elements [1; 2]. Type, origin, and petrogenesis of granite is significant key in formation of specific deposits. Some studies revealed that, various of rare earth elements deposits related to highly fractionated granite intrusions. Also, the Syrostan massive in the southern Ural linked with many deposits such as gold, rare earth elements, and skarn deposits. Therefore, determine the type of granite, identification the magma evolution process, and the geochemistry of granite could lead to a potential ore deposit. Although, several research were conducted in the Syrostan massive and intrusions in southern Ural looking for potential mineralization [2–6]; however, the massive area was not covered with the investigation of the petrogenesis and the geochemistry and conducted them to the mineralization. The aim of this study is to identify geochemical characteristic and type of the granite in order to connect them with type of mineralization and use the result for future researches.

Geology of the study area. The Syrostan massive locates in the southwest of the Miass city, southern Ural in the zone of the main Ural deep fault. The massive is among metabasites, shales of several composition and fragment of metamorphosed oceanic crust and the crust of passive margin of the Ural paleocean. The massive is formed in the lower carbonian and has three phases: the first is granodiorite and quartz diorite, the second is double feldspar and plagiogranite, and the third is vein complex [6–8].

The location of the study area almost 15 km northwest of the Miass city (Figure 1). The area of

the massive consists of metamorphic complex and marble body lies in the form of lenses crossed by several granite veins and the marble mainly in contact with diorite. The magmatic complex includes quartz diorite, granodiorite, biotite granite, and leucogranite [6; 9; 10]. After intensive of petrographic investigation, nine samples have been selected for major oxides analysis.



Figure 1. The Syrostan granite massive's modified geological map, which includes the Dark Kingdom of Marble Deposit:
1 – gneiss; 2 – mica quartz schist; 3 – marble limestone; 4 – quartzite; 5 – shale; 6 – marble; 7 – carbonaceous shale;
8 – quaternary sediments; 9 – granodiorite, quartz diorite, diorite; 10 – porphyric biotite granites; 11 – pink porphyric biotite granites;
12 – veined granite and plagiogranite; 13 – pegmatites; 14 – serpentinites; 15 – tectonic faults; 16 – occurrence of niobium

## 1. Analytical methods

Determination of the concentration of major oxides in the samples was executed by x-ray spectral fluorescence analysis (XRF) on a sequential vacuum spectrometer (with wavelength dispersion), model Axios mAX manufactured by PAN alytical (Netherlands). The analysis was performed at the Center for Collective Use of the IGEM RAS (Moscow, Russia).

## 2. Results and discussion

## 2.1. Petrography and mineral compositions

Microgranite is composed primarily of quartz (15–25%), microcline (20–50%), plagioclase (20–40%), and biotite (5–10%) and has a medium to coarse grained texture (Figure 2, a). Recrystallized quartz has two generations. This indicates that there



has been deformation. Sericite and muscovite are discovered after plagioclase. Plagioclase exhibits sericitization and epidotization as a result of hydro-thermal activity [11; 12]. Plagioclase zoning shows epidote and sericite from core to rim (Figure 2, b). Furthermore, chlorite, epidote, and calcite are secondary minerals. Accessory minerals include opaque minerals such as zircon and apatite.



**Figure 2.** A microscopic examination of granitic and diorite rocks: *a* – granitic rocks with quartz, plagioclase, and biotite (analyzer out); *b* – plagioclase grain partially mixed with a sericite aggregate (analyzer in)

# **2.2. Geochemical properties and granitic rocks types**

Table 1 shows the major oxides and geochemical compositions of granitoids rocks. Classification of granitoids rocks using TAS diagram [13] shows that most rocks are granite and one sample is syenodiorite (Figure 3, a), similarly the classification based on Middlemost diagram [14], total alkali vs. silica demonstrate the rocks as granite, monzodiorite, and monzonite (Figure 3, b). The investigated granite samples have a high SiO<sub>2</sub> contents ranging from 76.15 to 59.55 wt.%.

Diorite shows and silica content about (52.9 wt.%). Granite samples have high total alkalis  $K_2O + Na_2O$  ranging between (7–10 wt.%), moderate  $K_2O/Na_2O$  ratios ranging from 0.35 to 0.85, and low to intermediate CaO (0.5 to 6 wt.%), that followed by low content of  $P_2O_5$  (0.01 to 0.5%). The LOI (loss on ignition) values ranging from 0.6 to 2 wt.% which is reflect low value. On the  $K_2O$  with SiO<sub>2</sub> diagram [15], the investigated samples fall into the

high-K calc-alkaline series to slightly calc alkaline series (Figure 3, c).

Similarly, the AFM diagram ( $A = K_2O + Na_2O$ , F = FeOt, and M = MgO) [16], demonstrates the evolution of magma form tholeiite into calc alkaline series (Figure 3, *d*).

Al saturation index A/CNK molar  $(Al_2O_3/CaO + Na_2O + K_2O)$  vs. A/NK molar  $(Al_2O_3/Na_2O + K_2O)$  diagram is plotted and shows the samples plot within the metaluminous field to slightly peraluminous (Figure 3, *e*) based on the SiO<sub>2</sub> vs. FeOt/(FeOt + MgO) diagram (Figure 3, *f*), determine the samples are magnesian. Both diagrams indicate the type of granite as I-type granite which is related to igneous origin and absence of involving of sedimentary materials.

The result of CIPW norm present in Table 2, norm of granite shows quartz ranging from 5 to 30 wt.%, that indicates the granite standard. The investigated samples have a high albite with values ranging from 37.5 to 50.5 wt.%, and mode-

rate orthoclase content, with values ranging between, 14.5 to 21.5 wt.%. The norm of corundum in most sample shows 0 value and the rest of samples shows values less than 1 in the average of 0.5 wt.%. These result implying, I-type granite [17; 18]. Using the normative result with more than 10% of Quartz, Ab-An-Or diagram has been plotted (Figure 4, a). the diagram shows the trondhjemite as dominant plutonic rock type, granite and tonalite represent the rest of the samples.

Table 1

Major oxides, wt.%	Samples									
	MG1	MG2	MG3	LG1	LG2	LG3	BG1	BG3	D1	
SiO <sub>2</sub>	70.64	70.45	69.85	73.43	76.17	74.62	69.52	59.54	52.89	
Al <sub>2</sub> O <sub>3</sub>	14.62	15.17	14.82	12.71	12.89	13.84	15.38	17.3	17.95	
Na₂O	5.29	4.89	4.94	5.98	5.84	5.63	4.42	5.33	5.34	
MgO	0.53	0.46	0.75	0.19	0.1	0.08	0.82	1.65	3.95	
K2O	3.47	3.43	3.45	2.44	2.47	3.61	3.67	3.5	2	
CaO	2.06	1.81	1.99	2.77	0.95	0.53	2.23	4.81	6.37	
TiO <sub>2</sub>	0.23	0.22	0.21	0.02	0.03	0.02	0.39	0.66	1.18	
MnO	0.043	0.037	0.038	0.015	0.022	0.007	0.033	0.093	0.096	
Fe <sub>2</sub> O <sub>3</sub>	1.93	1.82	1.98	0.28	0.52	0.36	2.51	5.02	7.61	
P <sub>2</sub> O <sub>5</sub>	0.09	0.07	0.07	0.01	0.02	0.02	0.14	0.28	0.53	
LOI	0.81	1.19	1.58	2.13	0.83	1.13	0.64	1.34	1.08	
SUM	99.71	99.55	99.68	99.98	99.84	99.85	99.75	99.52	98.99	
A/NK	1.17	1.29	1.25	1.02	1.05	1.05	1.37	1.38	1.64	
A/CNK	0.902	1.01	0.957	0.725	0.92	0.979	1.005	0.812	0.796	
K <sub>2</sub> O/Na <sub>2</sub> O	0.655	0.701	0.698	0.408	0.422	0.641	0.83	0.656	0.374	
Na <sub>2</sub> O/K <sub>2</sub> O	1.52	1.43	1.42	2.45	2.36	1.56	1.2	1.52	2.67	

## Compositions of whole rock major oxides in granitoid rocks

Table 2

Mineral, wt.%	Samples									
	MG1	MG2	MG3	LG1	LG2	LG3	BG1	BG3	D1	
Quartz	22.45	24.5	23.05	25.95	31.25	27.01	24.15	5.15	0	
Corundum	0	0.23	0	0	0	0	0.5	0	0	
Orthoclase	20.5	20.3	20.5	14.5	14.5	21.5	21.5	20.6	11.8	
Albite	44.7	41.5	41.8	50.5	49.5	47.6	37.4	45.1	45.2	
Anorthite	5.8	8.5	8	0.63	1.66	1.83	10.15	12.94	19.10	
Diopside	2.4	0	0.59	1.02	0.53	0.43	0	5.57	3.85	
Wollastonite	0	0	0	4.89	0.92	0.03	0	0	0	
Hypersthene	0.2	1.14	1.594	0	0	0	2.04	1.53	1.67	
Olivine	0	0	0	0	0	0	0	0	4.47	
Ilmenite	0.09	0.07	0.08	0.03	0.04	0.02	0.071	0.3	0	
Hematite	1.9	1.82	1.98	0.28	0.52	0.36	2.51	5.02	7.6	
Sphene	0.5	0	0.41	0.008	0.02	0.03	0	1.4	2.89	
Rutile	0	0.17	0	0	0	0	0.35	0	0	
Apatite	0.2	0.16	0.16	0.02	0.05	0.05	0.33	0.66	1.25	
Pyrite	0	0	0	0	0	0	0	0	0.16	
Sum	98.9	98.4	98.11	97.85	99.02	98.73	99.13	98.20	98.02	

**CIWP** norm for investigated samples



Figure 3. Plots and classification of the Miass granitoid's major oxides:

a – total alkali silica of plutonic rocks [13]; b – TAS diagram for granitoid classification [14];

c - SiO<sub>2</sub> versus K<sub>2</sub>O diagram [15], showing the presence of granitoid rocks among the high-K calc-alkaline series;

d - AFM diagram with  $A = (k_0 + Na_2O)$ , F = FeOt, and M = MgO [16], showing rock samples from the calc-alkaline series with high  $k_0O + Na_2O$ ; e - AI saturation index A/CNK molar [Al<sub>2</sub>O<sub>3</sub>/(CaO+Na<sub>2</sub>O+K<sub>2</sub>O)] versus A/NK molar (Al<sub>2</sub>O<sub>3</sub>/(Na<sub>2</sub>O+K<sub>2</sub>O)] diagram, indicating metaluminous to peraluminous samples; f - as a result of the SiO<sub>2</sub> vs FeOt/(FeOt + MgO) diagram, all of the samples are magnesian



Figure 4. Classifying the igneous rocks using the norm and cations: a - normative Ab-An-Or ternary plot and classification of rocks in the study area using Barker's scheme (1979) [20]; $<math>b - Na_2O-K_2O-CaO$  ternary plot for Southern Ural studied rocks, Barker's (1979) [20], calc-alkaline (CA) and trondjhemitic (TR) differentiation trends are represented by dashed curves; c - the classification of plutonic rocks using the parameter R1 & R2 after [19] caculated from millication proportions, R1 = 4Si - 11(Na + K) - 2(Fe + Ti), R2 = (Al + 2Mg + 6Ca)

On Na<sub>2</sub>O-k<sub>2</sub>O-CaO diagram (Figure 4, b) define a continuous range from tonalite/trondhjemite to granodiorite as the most observable samples.

Using the categorization diagram (Figure 4, c) from [19], for plutonic igneous rocks based on their millications or cation proportions, that widely use and more accurate in classification of plutonic rocks. The plotting parameters RI and R2 are used

to plot the data on an x-y bivariate graph. R1 is defined as [4Si - 11(Na + K) - 2(Fe + Ti)] and is displayed on the *r*-axis. Fe stands for total iron. R2 is shown as a plot along the *y*-axis and has the formula R2 = (A1 + 2Mg + 6Ca). The samples define a continuous range from granite to alkali granite, granodiorite, and syenodiorite, with granite being the most common.

## Conclusion

Granite is silica-enriched with SiO<sub>2</sub> ranging between (~76.14–59.54 wt.%) however, diorite shows intermediate chemical composition of SiO<sub>2</sub> (~52.89 wt.%). The studied samples show high total alkalis K<sub>2</sub>O + Na<sub>2</sub>O = (7.34–9.24 wt.%), K<sub>2</sub>O/Na<sub>2</sub>O display moderate ratios ranging from (~0.83–0.37). Low CaO (0.53–6.37 wt.%), and P<sub>2</sub>O<sub>5</sub> (0.01–0.53 wt.%) contents. The rocks belong to the high-K calc-alkaline series to slightly calc alkaline series, and they are metaluminous.

The results show that the majority of the rock samples are classified as trondhjemite to slightly tonalite. The samples in the normative Na<sub>2</sub>O-k<sub>2</sub>O-CaO have defined a continuous range as the most observable samples, ranging from tonalite/trondhjemite to granodiorite.

The petrography investigation of this study revealed ore minerals and indications of hydrothermal solution suggesting mineralization process. The massive associated with many deposits and mineralization such as gold, skarn, and rare earth deposits.

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