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Sukhorukov V. P. et al. Composition and mineralogy of granitoids of the Ob-Zaisan folded region.

## **GEOLOGY OF MINERAL DEPOSITS**

Research paper

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# Composition and mineralogy of granitoids of the Ob-Zaisan folded region in the context of the prediction of groundwater radioactivity

V.P. Sukhorukov<sup>1,3</sup> Sc, A.F. Sukhorukova<sup>2,3</sup> Sc Z, D.A. Novikov<sup>2,3</sup> Sc, A.S. Derkachev<sup>2,3</sup>

<sup>1</sup> V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation

<sup>2</sup> A.A. Trofimuk Institute of Oil and Gas Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation

<sup>3</sup> Novosibirsk State University, Novosibirsk, Russian Federation

SukhorukovaAF@ipgg.sbras.ru

#### Abstract

The presented research is carried out in continuation of the works connected with studying the nature of radioactivity of drainage waters of quarries of Novosibirsk region, performed by the Laboratory of Hydrogeology of Sedimentary Basins of Siberia, INGG SB RAS, which showed that the waters of granite quarries are characterized by significantly higher radioactivity, than waters of other host rocks. The results of detailed mineralogical and geochemical studies of granitoids of the Ob-Zaisan region within the Kolyvan-Tom folded system are presented for the first time. The relevance of the present study is determined by the previously obtained data on high concentrations of uranium, thorium, and radon in drainage water of quarries developed in this territory. The granitoids of the Priobsky (Obsky and Novosibirsk massifs) and Barlak complexes were studied. It was established that the rocks of the complexes differ significantly in the spectrum of accessory minerals, which acted as the concentrators of natural radioactive and rare-earth elements: in the Barlak, in addition to apatite, sphene, and zircon, typical for all phases of the intrusion, fluorite, topaz, rutile, and minerals enriched with rare-earth elements are found: monazite, xenotime, bastnesite, parisite, less often uraninite. It was shown that a wide range of mineral-concentrators of radioactive and rare-earth elements determines higher concentrations of radionuclides in groundwater of the Barlak granitoid complex. Maximum uranium concentrations are one order of magnitude and those of thorium are two orders of magnitude higher in the groundwater of the Barlak granitoid complex compared to those of the Priobsky granitoid complex. The following peak concentrations,  $mg/dm^3$ , were established in the groundwater of the studied granitoid complexes:  $^{238}$ U up to 1.40 and  $^{232}$ Th up to 2.16  $\cdot$  10<sup>-3</sup>. One can predict a high background of radionuclides in the groundwater of the Barlak and Priobsky granitoid complexes, within the ranges, mg/dm<sup>3</sup>:  $^{238}$ U from  $0.1 \cdot 10^{-3}$ to 1.40 and  $^{232}$ Th from  $1 \cdot 10^{-6}$  to  $2.16 \cdot 10^{-3}$ . Radon  $^{222}$ Rn activity in the groundwater ranges 1-50 Bq/dm<sup>3</sup> in the contact zones of granitoids with different-aged sedimentary rocks to 600–5,000 Bq/dm<sup>3</sup> in the areas of granitoids occurrence.

#### Keywords

granitoids, mineral-concentrators of radioactive and rare-earth elements, groundwater, radionuclides, <sup>238</sup>U, <sup>232</sup>Th, <sup>222</sup>Rn, Novosibirsk region, Western Siberia

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### ГЕОЛОГИЯ МЕСТОРОЖДЕНИЙ ПОЛЕЗНЫХ ИСКОПАЕМЫХ

Научная статья

# Состав и минералогия гранитоидов Обь-Зайсанской складчатой области в связи с прогнозом радиоактивности подземных вод

В.П. Сухоруков<sup>1,3</sup> С. А.Ф. Сухорукова<sup>2,3</sup> С. Д.А. Новиков<sup>2,3</sup> С. А.С. Деркачев<sup>2,3</sup> С.

<sup>1</sup>Институт геологии и минералогии им. В.С. Соболева СО РАН, г. Новосибирск, Российская Федерация <sup>2</sup>Институт нефтегазовой геологии и геофизики им. А.А. Трофимука СО РАН, г. Новосибирск, Российская Федерация <sup>3</sup>Новосибирский государственный университет, г. Новосибирск, Российская Федерация

SukhorukovaAF@ipgg.sbras.ru

#### Аннотация

Представленное исследование выполнено в продолжение работ, связанных с изучением природы радиоактивности дренажных вод карьеров Новосибирской области, выполненных лабораторией гидрогеологии осадочных бассейнов Сибири ИНГГ СО РАН, где показано, что воды гранитных карьеров характеризуются существенно более высокими значениями радиоактивности, чем воды других вмещающих пород. Впервые представлены результаты детальных минералогических и геохимических исследований гранитоидов Обь-Зайсанской области в пределах Колывань-Томской складчатой системы. Актуальность настоящего исследования определяется полученными ранее данными о высоких концентрациях урана, тория и радона в дренажных водах разрабатываемых карьеров этой территории. Изучены гранитоиды приобского (Обской и Новосибирский массивы) и барлакского комплексов. Установлено, что породы комплексов существенно различаются спектром акцессорных минералов, которые выступают концентраторами природных радиоактивных и редкоземельных элементов: в барлакском, помимо апатита, сфена и циркона, характерных для всех фаз внедрения, фиксируются флюорит, топаз, рутил и обогащенные редкоземельными элементами минералы: монацит, ксенотим, бастнезит, паризит, реже уранинит. Показано, что широкий спектр минералов-концентраторов радиоактивных и редкоземельных элементов определяет более высокие концентрации радионуклидов в подземных водах барлакского гранитоидного комплекса. Максимальные концентрации урана на порядок, а тория на два порядка выше в подземных водах барлакского гранитоидного комплекса, по сравнению с приобским. В подземных водах изученных гранитоидных комплексов установлены максимальные концентрации, мг/дм<sup>3</sup>: <sup>238</sup>U до 1,40 и <sup>232</sup>Th до 2,16 · 10<sup>-3</sup>. Можно прогнозировать высокий фон радионуклидов в подземных водах барлакского и приобского гранитоидных комплексов в пределах, мг/дм<sup>3</sup>: <sup>238</sup>U от 0,1 · 10<sup>-3</sup> до 1,40 и <sup>232</sup>Th от 1 · 10<sup>-6</sup> до 2,16 · 10<sup>-3</sup>. Активность радона <sup>222</sup>Rn в подземных водах при этом будет составлять от 1–50 Бк/дм<sup>3</sup> в зонах контактов гранитоидов с разновозрастными осадочными породами до 600-5000 Бк/дм<sup>3</sup> в областях развития гранитоидов.

#### Ключевые слова

гранитоиды, минералы-концентраторы радиоактивных и редкоземельных элементов, подземные воды, радионуклиды, <sup>238</sup>U, <sup>232</sup>Th, <sup>222</sup>Rn, Новосибирская область, Западная Сибирь

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#### Introduction

One of the most urgent problems of modern hydrogeochemistry is the study of the phenomenon of radioactivity of natural waters and identification of factors controlling it. It was shown previously that waters of granite quarries are characterized by significantly higher radioactivity in comparison with waters of other host rocks on the example of drainage waters of quarries of the Novosibirsk region [1] and natural groundwater outlets [2] within the Ob-Zaisan folded zone.

In many countries of the world, including China, India, Turkey, USA, Mexico, Norway, Great Britain, Hungary, Egypt, Asian countries, and others, the proMINING SCIENCE AND TECHNOLOGY (RUSSIA)



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cesses of radionuclide migration in groundwater are actively studied and simulated. The studies in southeastern Mexico by J.I. Morales-Arredondo et al. have shown that the concentrations of uranium and thorium isotopes in groundwater are low enough not to be dangerous for the population, but it is necessary to control the concentration of radon, which can be high [3]. According to Chinese scientists C. Yu, Z. Song and many others, the weathering processes of granite massifs enhances the dissemination and transfer of uranium and thorium into the aquatic environment. The scientists note the important role of changes in geochemical conditions [4]. P. Baják, K. Csondor, D. Pedretti et al. developed conceptual models of radionuclide mobility in rocks and groundwater that take into account the changing redox conditions in aquifers for the territory of Hungary [5]. S.M. Pérez-Moreno, J.L. Guerrero, F. Mosqueda et al. analyzed the hydrochemical behavior of long-lived natural radionuclides of uranium, thorium and radon in groundwaters of Spain in different geological conditions and performed dose estimates for the ingestion of these radionuclides with water. It was shown that their high concentrations are connected with the granitic base and reductive conditions [6].

Radon activity in water is universally assessed as a potential environmental risk for the population and is determined by radioactive decay of elements of the uranium-radium series. At the same time, there is no direct correlation between uranium concentration in host rocks and radon concentration in groundwater [3].

The results of studies of groundwater radioactivity in different regions show that the maximum concentrations of radionuclides such as uranium and thorium are usually associated with felsic intrusive rocks, in which the average concentrations (according to N.A. Grigoriev) of uranium and thorium are 3.2 and 14.0 g/t, respectively<sup>1</sup>. In waters of felsic igneous rocks of the zone of intensive water exchange, uranium concentration ranges  $2,0 \cdot 10^{-3}$  to  $3 \cdot 10^{-2}$  mg/dm<sup>3</sup>. The previously obtained data on uranium concentration in water samples allow to classify the groundwater of granitoids of the Ob-Zaisan region according to the classification A.N. Tokarev as uranium waters and, at higher concentrations, even to uranium deposit waters.

For the territory of Novosibirsk and its environs since 2018, the team of the Laboratory of Hydrogeology of Sedimentary Basins of Siberia, INGG SB RAS, has been carrying out work to study the chemical and radionuclide composition, radon levels in groundwater of various aquifers [7]. The waters both in the zone of granitoids occurrence and beyond its limits, in argillaceous shales and marmorized limestones of Upper Devonian-Lower Carboniferous age, were studied. The occurrences of radon waters Tulinskoye [8] and Kamenskoye [9], and drainage waters of Borok quarry [10] were studied in detail. Data on uranium and thorium concentrations in the groundwater were obtained. At the same time sampling of rocks of water-bearing horizons was carried out for it's detailed mineralogical and petrographic investigation.

Consequently, the main purpose of the study is to reveal the relationships between the composition, mineralogy, and spectrum of accessory minerals of the Priobsky and Barlak complexes of granitoids of the Ob-Zaisan folded region and the level of radioactivity of groundwater occurring within them.

#### **Research techniques and subject**

The study is based on the collection of geological rock samples and water samples collected by the authors of the paper during field work in 2022–2023 within the Ob-Zaisan folded region from the areas of occurrence of granitoids of the Priobsky and Barlak complexes. The rocks were sampled at 10 sites from Borok, Skala, Novobibeevsky, Gorsky, Tulinsky, Mochishche quarries, outcrops confined to groundwater outlets, and hole cores (Fig. 1).

The microscopic description of 29 petrographic thin sections of granitoids was carried out by the classical method. The determination of petrogenic element concentrations was performed by X-ray fluorescence analysis using a SRM-25 unit at the Center for collective use of scientific equipment for multi-element and isotopic studies of the Siberian Branch of the Russian Academy of Sciences (TsKP MII SB RAS, Novosibirsk). The determination of the concentrations of rare and rare-earth elements in granites was carried out by ICP-MS method using a high-resolution mass spectrometer ELEMENT of Finnigan (Germany) in the TsKP MII SB RAS (Novosibirsk) according to the standard technique.

The accessory mineral paragenesis in the rocks of the Novosibirsk granitoid massif was studied in polished sections by scanning electron microscopy at a MIRA 3 LMU electron scanning microscope (TESCAN ORSAY Holding).

Groundwater collection amounted to 78 samples; pH, Eh, temperature, dissolved  $O_2$  concentration were determined directly at the sites using measuring facilities (Hanna HI9125, oxygen meter AKPM-1-02L) and a field hydrogeochemical laboratory. The measurements of radon concentration in natural waters were carried out using a complex

<sup>&</sup>lt;sup>1</sup> Geological Dictionary: in 3 vol. Ed. O.V. Petrov; Ed.comp.: S.I. Andreev et al. Ed. 3<sup>rd</sup>, reprint and add. St. Petersburg: VSEGEI Publ. House; 2010–2012. (In Russ.)



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"Alpharad Plus" in the Laboratory of Hydrogeology of Sedimentary Basins of Siberia, INGG SB RAS. Laboratory study of water chemistry was carried out by titrimetry, ion chromatography, and inductively coupled plasma mass spectrometry in the Topical Research Laboratory of Hydrogeochemistry at the Engineering School of Natural Resources of Tomsk Polytechnic University (TRL of Hydrogeochemistry IShPR TPU).

### **Geological Setting**

Carbonate-volcanogenic-terrigenous deposits of the Middle Devonian-Early Carboniferous age overlain by Quaternary alluvial and subaerial sediments are widespread within the Ob-Zaisan folded region. In the Permian-Triassic time, a granite intrusion intruded them, and granitoids of the Novosibirsk massif were formed. Within the territory of interest, the Priobsky and Barlak granitoid complexes are distinguished.

The Priobsky complex is represented by the petrotypical Obsky and Novosibirsk massifs in the Novosibirsk folded zone (Kolyvan-Tom folded system) and is characterized by a three-phase structure. The first phase is composed of monzonites and quartz monzonites ( $\mu P_3 - T_1 p_1$ ), with diorites occur-

ring less frequently. The second, main phase is represented by monzogranites  $(\epsilon \gamma P_3 - T_1 p_2)$ , granosienites, while granites and granodiorites are less common. The third phase includes small bosses and dikes of monzogranites  $(\epsilon \gamma P_3 - T_1 p_3)$ , monzoleucogranites, and their porphyritic analogs [11].

Two intrusion phases are distinguished within the Barlak complex. The first, main phase is predominantly composed of medium-grained monzoleucogranites ( $\epsilon l\gamma T_{1-2}b_1$ ), while leucogranites and monzogranites ( $\epsilon \gamma T_{1-2}b_1$ ) are observed less frequently. The second phase is represented by small bodies and dikes of fine-grained monzoleucogranites ( $\epsilon l\gamma T_{1-2}b_2$ ).

In the studied area, granitoids are represented by the second phase of the Priobsky complex  $(P_3 - T_1)$  and the first phase of the Barlak complex  $(T_{1-2})$ .

The multiphase **Priobsky complex** has a relatively simple petrographic composition. Diorites, quartz diorites, and their moderately alkaline analogues constitute the first phase and have limited occurrence. The second phase of the Priobsky complex composes the large Novosibirsk massif, located within the city limits, and is exposed in the Gorsky, Tulinsky, Bugrinsky, Trolleyny, and Borok quarry areas, as well as the Obsky massif in the Dubrovinsky



Fig. 1. Location of the study area and rock sampling sites:

1 – Priobsky complex, 2<sup>nd</sup> phase of intrusion; 2 – Priobsky complex, 1<sup>st</sup> phase of intrusion;
3 – Barlak complex, 1<sup>st</sup> phase of intrusion; 4 – Barlak complex, 2nd phase of intrusion; 5 – Late Permian-Middle Triassic granites;
6 – study areas (designations in Table 1); 7 – border of Novosibirsk city



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and Novobibeevsky areas (Fig. 2, a-d). The sampled rocks of the second phase are represented by biotite and biotite-amphibole granites, monzogranites, and less frequently leucogranites. The biotite-amphibole granites contain about 25% of quartz, 20–35% of K-feldspar and plagioclase, while the content of biotite and hornblende is insignificant, about 2–5 vol.%. Sphene, apatite, and zircon are present as accessory minerals. The structure of the rocks is predominant-

ly equigranular, hypidiomorphic with grain size of 2–3 mm, less often porphyritic with grain size up to 15 mm. At the Novobibeevsky area, the rocks show signs of deformation.

By petrochemical composition the rocks belong to moderately alkaline granites. The silica content varies from 66 to 71 wt.%, rarely up to 75% in leucogranites. The content of Na<sub>2</sub>O + K<sub>2</sub>O lies in the range of 8.1–9.5 wt.% (Fig. 3, *a*).





the Priobsky complex: *a* – biotite-amphibole granite (Borok area); *b* – biotite-amphibole granite (Bugrinsky area); *c* – monzogranite (Gorsky area); *d* – biotite-amphibole granite (Tulinsky area); *e* – pyroxene-amphibole-biotite granodiorite (Dubrovinsky area); *f* – biotite-porphyritic granite (Novobibeevsky area); Barlak complex: *g* – biotite monzogranite (Skala area); *h* – porphyritic leucogranite (Mochishche area)



**Fig. 3.** The composition of granitoids of the Priobsky and Barlak complexes on diagrams:  $a - K_2O/Na_2O-SiO_2$  diagrams; b – discriminant diagrams. 1 – Priobsky complex; 2 – Barlak complex; 3 – the granitoid complexes occurrence fields (according to A. G. Babin et al. [11])

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The **Barlak complex** is characterized by a monotonous composition. It is represented by biotite monzogranites, less frequently by porphyritic leucogranites with yellowish-reddish tints appearing in their coloring within undulose zones due to weathering. Dotted sulfide impregnation and cassiterite are found in quartz veins, while beryl and topaz are found in pegmatites. Ultra-acid granites belong to moderately alkaline potassium granites (rocks of this complex were sampled in the Mochishche quarry, where the massif of granitoids of the Barlak complex intrudes the granites of the second phase of the Priobsky complex, and at the Skala and Bibikha areas (Fig. 2, *h*, *g*).

The rocks are represented by biotite monzogranites and less frequently by leucogranites. The rocks contain quartz, 30-35%, K-feldspar and plagioclase, 30-40%, and biotite of 2 to 10%. The structure of the rocks is granitic, hypidiomorphic, can vary from finegrained (0.5-1 mm) to medium-grained (2-4 mm). Zircon and apatite are found as accessory minerals in granites; in some samples, orthite and monazite occur.

By petrochemical composition, the rocks belong to the moderately alkaline series that is consistent with their high content of K-feldspar, and less frequently to the normal- and low-alkaline series. The content of the sum of  $K_2O + Na_2O$  is mainly in the range of 6.5–8.6 wt.%, rarely decreasing to 3–4.3 wt/%. SiO<sub>2</sub> content (69–82 wt.%) of the granites of the Barlak complex distinguishes them from the granites of the Priobsky complex, in which it is mainly at the level of 66–71 wt.% (see Fig. 3, *a*).

Table 1

| Main 1 | rock types | of granito | oids of the | <b>Ob-Zaisan</b> | region |
|--------|------------|------------|-------------|------------------|--------|
|--------|------------|------------|-------------|------------------|--------|

| No.              | Area           | Rock type                   |  |  |  |
|------------------|----------------|-----------------------------|--|--|--|
| Priobsky complex |                |                             |  |  |  |
|                  | Nov            | vosibirsk massif            |  |  |  |
| 1                | Borok          | Biotite-amphibole granite   |  |  |  |
|                  |                | Monzogranite                |  |  |  |
| 2                | Bugrinsky      | Biotite-amphibole granite   |  |  |  |
| 3                | Gorsky         | Monzogranite                |  |  |  |
|                  |                | Leucogranite                |  |  |  |
| 4                | Tulinsky       | Biotite-amphibole granite   |  |  |  |
| 5                | Trolleyny      | Biotite-amphibole granite   |  |  |  |
| Obsky massif     |                |                             |  |  |  |
| 6                | Dubrovinsky    | Pyroxene-amphibole-biotite  |  |  |  |
|                  |                | granodiorite                |  |  |  |
|                  |                | Biotite granite             |  |  |  |
|                  |                | Melanocratic diorite        |  |  |  |
|                  |                | Leucogranite                |  |  |  |
| 7                | Novobibeyevsky | Biotite porphyritic granite |  |  |  |
| Barlak complex   |                |                             |  |  |  |
| 8                | Skala          | Biotite monzogranite        |  |  |  |
| 9                | Bibikha        | Biotite monzogranite        |  |  |  |
| 10               | Mochishche     | Porphyritic leucogranite    |  |  |  |

On the discriminant diagrams (Fig. 3, *b*), the granitoids of the Priobsky complex according to the results of ICP assays of the collected rock samples are located in the field of syncollisional and post-collisional granites, and the granitoids of the Barlak complex, in the field of island arc granites that corresponds to the data of A.G. Babin et al. [11].

# Mineralogical and petrographic characterization of rocks

The most widely sampled rocks were the rocks of the Priobsky complex, where a collection of 15 samples was taken from 7 areas, and six rock types were identified. The Barlak complex was studied at three areas in 14 rock samples, and two rock types were identified. Table 1 shows the main rock types that were collected for mineralogical and petrographic study; the general view is shown in the photo table in Fig. 2, and the description is given below.

#### Priobsky complex rocks

Biotite-amphibole granite (Fig. 4, *a*). These rocks were sampled within the Novosibirsk massif (Tulinsky, Trolleyny, Bugrinsky, Gorsky areas) and Priobsky massif (Dubrovinsky area).

Its mineralogical composition, rock-forming minerals, %: quartz 25–30, plagioclase 30–45, microcline 23–35, amphibole 2–5, biotite 3–7; accessory minerals: sphene, apatite, zircon (see Fig. 2, *a*). The rock is formed by idiomorphic crystals of plagioclase and melanic (mafic) minerals and xenomorphic grains of K-feldspar and quartz located between them. Plagioclase forms prismatic and elongated idiomorphic crystals, often with pronounced faceting, polysynthetic twins, and zonal structure. The grain size is predominantly 1.5–2 mm. Microcline forms xenomorphic grains 2-4 mm in size, located between idiomorphic plagioclase laths. The microcline is characterized by perthitic structures. Quartz forms xenomorphic grains 1-2 mm, the grain shape is isometric or weakly elongated, with irregular boundaries, often with blocky extinction. Hornblende forms idiomorphic crystals of 1-1.5 mm, elongated up to prismatic, occasionally with pronounced faceting. The coloration is dark green to black. Biotite is of tabular habitus 1–2 mm in size, the color is dark brown; the mineral is partially replaced by chlorite. Sphene forms well-faceted rhomboid crystals about 0.5 mm in size or larger grains up to 1 mm without pronounced faceting. Apatite forms long prismatic colorless crystals up to 0.2–0.5 mm in size.

Monzogranite porphyritic (Borok area, Fig. 4, *b*). The mineral composition, %: quartz about 30, plagioclase 15–20, microcline 45–50, biotite 3–5. Accessory minerals: zircon, apatite, sphene. The structure of the rock is porphyritic, the structure of the rock ma-

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trix is hypidiomorphic. The phenocrysts are formed by crystals of K-feldspar and plagioclase with the sizes ranging from 4 to 8–10 mm. The grain size in the rock matrix is about 1-2 mm. Plagioclase forms elongated crystals, some of which with good faceting, while others have curved, jagged facets. Microcline forms isometric grains with irregular edges. Its phenocrysts demonstrate zones of growing, characterized by abundant quartz inclusions. The microcline is typically perthitic. Biotite is brown, forms individual grains and lenticular clusters. The accessory minerals occur as single grains. Zircon occurs as isometric grains of about 0.1 mm in size; sphene – idiomorphic rhomboid grains in intergrowths with an ore mineral. The secondary alteration is presented by minor sericitization of plagioclase and pelitization of microcline.

Leucogranite – Gorsky and Dubrovinsky areas (Fig. 4, c). Its mineral composition, %: quartz 30–35, plagioclase 35–50, orthoclase 15–30, biotite not more than 2. The accessory minerals are rare and represented mainly by sphene and apatite. At the Dubrovinsky

area, garnet occurs as an accessory mineral of leucogranites. The structure is uniform, granitic. The grain size ranges from 0.5 to 1-2 mm. Plagioclase forms more idiomorphic grains with irregular edges, while orthoclase and quartz form isometric, xenomorphic grains. Biotite is dark brown, wide-tabular, partially replaced by chlorite. Sphene forms rhomboid shape crystals up to 0.5 mm long. Garnet forms isometric crystals, colorless, up to 0.2-0.3 mm in size, evenly distributed in the rock, composes up to 1 vol.% of the rock. The garnet crystals are often with pronounced faceting and rhythmic and zonal structure.

Pyroxene-amphibole-biotite granodiorite – Dubrovinsky area (Fig. 4, d). The rocks are similar in composition and structure to biotite-amphibole granites, but are characterized by a lower quartz content and the presence of an insignificant amount of clinopyroxene. Its mineral composition, %: quartz – 20, plagioclase – 30, microcline – 30, biotite – 10, pyroxene – 3, amphibole – 7. The accessory minerals are represented by significant amounts of apatite (up to 1 vol.% of



**Fig. 4.** Microphotographs of granitoids from the sampled massifs (see Table 1): The Priobsky complex: *a* – biotite-amphibole granite; *b* – monzogranite; *c* – leucogranite; *d* – pyroxene-biotite-amphibole granodiorite; *e* – melanocratic diorite; *f* – biotite granite; The Barlak complex: *g* – biotite monzogranite; *h* – leucogranite. The photos are given on the left with one polar and on the right with crossed polars. All photos are taken at the same scale. The mineral designations: Bt - biotite; Hbl - hornblende; Kfs – K-feldspar; Pl – plagioclase; Qz – quartz, Sph – sphene

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the rock), as well as sphene and zircon. The structure of the rock is hypidiomorphic, with the grain size of 1–2 mm. Plagioclase forms partially faceted grains with polysynthetic twins, while microcline and quartz form isometric xenomorphic grains without faceting. Mafic minerals form clusters and spots. Clinopyroxene is colorless, often replaced by a rim of light green amphibole. Biotite is brown to light brown. Apatite forms prismatic crystals up to 0.3–0.5 mm with abundant inclusions of a needle ore mineral. Sphene forms isometric, non-faceted grains up to 0.1 mm in size, while zircon forms faceted grains up to 0.1 mm.

Melanocratic diorite – Dubrovinsky area (Fig. 4, e). Its mineral composition, %: plagioclase - 30, hornblende - 40, clinopyroxene - 20, biotite - 10; accessory minerals: apatite and zircon. The rock structure is hypidiomorphic, the texture is inequigranular. The rock consists mainly of plagioclase and amphibole (the grain size of about 2-3 mm), clinopyroxene (0.3–0.5 mm), and biotite (0.3 mm). Plagioclase forms xenomorphic grains located between amphibole grains and is partially sericitized. Light green colored hornblende forms idiomorphic grains, often faceted. Clinopyroxene forms smaller grains of isometric habitus, located as inclusions in plagioclase; sometimes clusters of such grains surround amphibole. Biotite of light brown color forms growths in the grains of amphibole. Apatite is frequent, forming elongated crystals up to 1 mm in size with abundant inclusions of an ore mineral. Zircon forms faceted crystals up to 0.15 mm in size.

Biotite granite – Dubrovinsky, Novobibeevsky areas (see Fig. 2, f). The mineral composition, %: quartz – 20, biotite – 10, microcline – 15, plagioclase – 55; the accessory minerals: apatite and zircon (Fig. 4, *f*). The structure of the rock is hypidiomorphic, cataclastic. Porphyritic varieties are common at the Novobibeevsky area. Plagioclase in the rock forms isometric and weakly elongated grains 2-3 mm in size, partly with faceting, while microcline and quartz occur as xenomorphic non-faceted grains. Biotite forms reddish-brown elongated scales 0.5-1 mm, which are often located along the boundaries of quartz and feldspar grains, deformed in places. In porphyritic varieties, phenocrysts are composed of orthoclase, their size is about 10 mm. Apatite forms slightly elongated crystals up to 0.3 mm, the central part of which is gravish due to dust-like impurities. Zircon forms isometric grains up to 0.1 mm in size.

#### **Rocks of the Barlak complex**

The Barlak and Kolyvansky massifs are composed of similar composition rocks. They were sampled in the area of Bibikha and Skala settlements respectively. The rocks are represented mainly by equigranular medium-grained biotite monzogranites. The rocks are biotitic; hornblende is subordinately abundant in leucogranites of the Mochishche boss and in rare cases in monzoleucogranites of the Barlak Massif. In all these rocks, K-feldspar predominates over plagioclase.

Biotite monzogranites – Skala and Bibikha areas (Fig. 4, g). Mineral composition of the rocks, %: quartz – 35, microcline – 30, plagioclase – 25, biotite – 10. The rock structure is granitic. Plagioclase forms idiomorphic crystals of prismatic habitus 0.5-2 mm in size, microcline forms prismatic crystals with irregular edges and poikilitic growths of plagioclase. Quartz forms xenomorphic isometric grains. Biotite is dark brown to black, forms wide tabular scales, often associated with accessory minerals.

Porphyritic leucogranite – Mochishche area (Fig. 4, *h*). The Mochishche boss located in the edge of the Novosibirsk massif was sampled in the Mochishche quarry. The rocks are represented by porphyritic leucogranite. Its mineral composition, %: quartz -30, orthoclase - 30, plagioclase - 38, biotite - 2. Accessory minerals: zircon, orthite, apatite. The rock structure is porphyritic, granitic. The phenocrysts are represented by orthoclase 3-4 mm in size. It forms isometric grains with irregular edges, often zoned. In the rock matrix, the grain size is 0.5–1 mm. Plagioclase is idiomorphic and forms prismatic faceted grains, while quartz and orthoclase are xenomorphic. Biotite forms tabular and elongated scales of dark brown to black color, partially or completely replaced by secondary chlorite. Orthite (Fig. 4, g) forms sharply zoned prismatic grains 0.8 mm long. The central part of the grain is light brown, the marginal parts are almost colorless. Zircon is zonal, forms faceted crystals about 0.15 mm in size.

#### **Accessory minerals**

Paragenesis of accessory minerals in the studied rocks is represented by a wide range of minerals, most of which can serve as mineral-concentrators of uranium, thorium, and other rare-earth elements, which determines the radioactivity of the rocks themselves and that of fracture-vein groundwater.

The rocks of the Barlak complex are characterized by a wider range of accessory minerals compared to the rocks of the Priobsky complex. The main accessory minerals encountered in the rocks of the Priobsky complex are apatite, sphene, and zircon; they were identified in the Borok, Bugrinsky, Gorsky, Tulinsky, Dubrovinsky, and Novobibeevsky areas and are described in the rock characterization.

In the Kolyvansky massif of the Barlak complex (Skala, Bibikha areas), apatite, sphene, and zircon, widespread in all granitoids of the Ob-Zaisan region, ukhorukov V. P. et al. Composition and mineralogy of granitoids of the Ob-Zaisan folded region..



were also identified as accessory minerals. In addition, fluorite, topaz, and rare earth element-enriched minerals such as monazite and xenotime are characteristic minerals; uraninite is less common. Superimposed greisen mineralization with cassiterite, associated with sericite veins, was also found.

Fluorite forms mainly xenomorphic grains, usually colorless or spotted purple. Topaz occurs in monzogranites, but predominantly is contained in quartz veins and pegmatoidal clusters, in which it forms faceted prismatic crystals up to 1 cm in size. Monazite and xenotime form grains without a clear faceting, zoning is not visible in them, and they often associate with dark brown biotite. Rutile is rare, also occurs in association with biotite, forms small (0.03 mm) oval grains of dark brown color. Uraninite is rare, found in association with monazite in the form of isometric grains in biotite monzogranite in the Skala quarry.

In the Barlak complex within Mochishche area, the following minerals were identified as accessory: fluorite, calcite, rutile, zircon, orthite, and REErich minerals: mainly fluorocarbonates bastnesite ((Ce, La, Y) CO<sub>3</sub>F) and parisite (CaLa<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>F<sub>2</sub>), pwhile monazite (CePO<sub>4</sub>) and xenotime (YPO<sub>4</sub>) are less common. Bastnesite forms irregularly shaped grains, mostly without faceting, 30–50 microns in size; parisite occurs as split crystals or clusters of needle-like crystals 20–30 microns in size, sometimes forming intergrowths with bastnesite. Monazite and xenotime form mainly isometric grains 20–30 microns in size, sometimes also forming intergrowths with parisite , which is consistent with the data of V. I. Sotnikov et al. [12].

# Geochemical peculiarities of fracture-vein waters of granitoids

Fracture-vein waters of Upper Paleozoic granites are predominantly neutral and slightly alkaline with pH 6.9–7.8, properly fresh with total salinity of 330 to 690 mg/dm<sup>3</sup>, characterized mainly by HCO<sub>3</sub> Mg-Ca and SO<sub>4</sub>-HCO<sub>3</sub> Na-Mg-Ca composition, have high silicon concentration, from 10 to 23 mg/dm<sup>3</sup>, averaging at 15 mg/dm<sup>3</sup>. The medium geochemical parameters range from reducing to oxidizing conditions with Eh ranging from -81.2 to +509.6 mV; O<sub>2</sub>*dissolv* ranges from 1.62 to 9.91 mg/dm<sup>3</sup>. The average values of geochemical coefficients for this group are: Ca/Si - 11.49; Mg/Si - 2.48; Na/Si - 1.25; Si/Na - 0.87; Ca/Na - 10.02; Ca/Mg -4.76; rNa/rCl – 8.79  $\mu$  SO<sub>4</sub>/Cl – 4.35, indicating the accumulation of calcium, magnesium, and proceeding sulfide oxidation processes in the waters. In terms of microcomponent composition, rather high for waters concentrations of Fe, Mn, Zn were identified, averaging, mg/dm<sup>3</sup>, 1.18; 0.16; 0.02, respectively. At the same time, it should be noted that the microcomponents distribution spectrum in the waters in general has an inherited character when compared with the host granites [7].

Table 2

| Water compline location                                      | U · 10⁻²                      | Th • 10⁻⁵                    | Th/U ⋅ 10-4                  | Rn                         |  |  |  |
|--|-------------------------------|------------------------------|------------------------------|----------------------------|--|--|--|
| water sampling location                                      |                               | Bq/dm <sup>3</sup>           |                              |                            |  |  |  |
| Priobsky complex   |                               |                              |                              |                            |  |  |  |
| Borok quarry   | <u>0.9–21.3 *</u><br>8.3 (9)  | <u>0.1–9.6</u><br>4.2 (9)    | <u>0.97–14.9</u><br>3.1 (9)  | <u>18–89</u><br>53 (9)     |  |  |  |
| Tulinsky quarry  | 1.2 (2)                       | 0.3-0.7 (2)                  | 2.4-5.7 (2)                  | 2 (1)                      |  |  |  |
| Gorsky quarry  | 1.0-1.2 (2)                   | 0.1-0.15(2)                  | 9.3-10.4 (2)                 | 0 (2)                      |  |  |  |
| Bridge-4 (well)  | <u>0.7–1.8</u><br>1.4 (4)     | <u>0.1–1.7</u><br>0.6 (4)    | <u>0.1–2.5</u><br>0.7 (4)    | <u>285–597</u><br>561 (7)  |  |  |  |
| Hospital-34 (borehole)                                       | <u>1.5–1.7</u><br>1.6 (11)    | <u>0.05–1.1</u><br>0.1 (11)  | <u>1.6–9.2</u><br>4.1 (11)   | <u>98–276</u><br>183 (11)  |  |  |  |
| Novobibeevsky quarry   | <u>1.0–1.2</u><br>1.1 (5)     | $\frac{0.3-3.1}{2.0(5)}$     | <u>2.4–26.6</u><br>15.6 (11) | <u>6-39</u><br>21 (5)      |  |  |  |
| Novobibeevo settlement (borehole)                            | 11.4                          | 4.2                          | 36.5                         | 429                        |  |  |  |
| Chkalovskie Prostory DNG, boreholes                          | $\frac{1.1-4.4}{3.1}$ (6)     | <u>0.3–1.0</u><br>0.5 (6)    | <u>0.3–0.9</u><br>0.7 (6)    | <u>45–141</u><br>98 (6)    |  |  |  |
| Barlak complex   |                               |                              |                              |                            |  |  |  |
| Skala quarry   | <u>94–140</u><br>118 (4)      | <u>3.9–216.3</u><br>72.2 (4) | <u>3.3–17.8</u><br>5.9 (4)   | <u>154–474</u><br>334 (4)  |  |  |  |
| Aeroflot horticultural non-commercial partnership (borehole) | <u>30.9–34.8</u><br>32.3 (11) | <u>0.1–1.4</u><br>0.1 (11)   | <u>0.1–0.4</u><br>0.1(11)    | <u>196–352</u><br>272 (13) |  |  |  |
| Mochishche quarry**  | 8-29                          | n/a                          | n/a                          | 103-630                    |  |  |  |
| Yuzhno-Kolyvansky occurrence**                               | 110-250                       | n/a                          | n/a                          | 4150-4960                  |  |  |  |

Radionuclide composition of groundwater of Ob-Zaisan region granitoids

*Note:* \* in the denominator, minimum and maximum values; in the numerator, average values; in parentheses, number of determinations; \*\* – archive data, n/a – no data available

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#### Groundwater radionuclide composition

Table 2 shows the concentrations of uranium, thorium, and radon in the waters of the Priobsky and Barlak complexes. Peak concentrations of uranium and thorium were measured in waters within the formations of the Barlak complex (areas Skala, Aeroflot, Mochishche), where natural radionuclides are contained in waters within the following ranges, mg/dm<sup>3</sup>:  ${}^{238}$ U from 2.0  $\cdot$  10<sup>-2</sup> to 1.4 and  ${}^{232}$ Th from 1 to  $216.3 \cdot 10^{-5}$ . <sup>232</sup>Th/<sup>238</sup>U ratio in the waters ranges from 0 to  $1.78 \cdot 10^{-3}$ . <sup>222</sup>Rn activity ranges from 154 to  $630 \text{ Bg/dm}^3$ , which allows to classify the waters as weakly radon and moderately radon. The waters of the Priobsky complex are characterized by significantly lower radionuclide concentrations, mg/dm<sup>3</sup>:  $^{238}$ U from 0.7  $\cdot$  10<sup>-2</sup> to 21.3  $\cdot$  10<sup>-2</sup> and  $^{232}$ Th from 0.1 to  $9.6 \cdot 10^{-5}$ . The <sup>232</sup>Th/<sup>238</sup>U ratio in the waters varies between 0 and  $36.5 \cdot 10^{-4}$ . The <sup>222</sup>Rn activity in these waters varies in the range from 6 to 597  $Bq/dm^3$ , which allows assigning them to the classes of non-radon to moderately radon waters (according to the N.I. Tolstikhin classification).

According to the data obtained by the team of the Laboratory of Hydrogeology of Sedimentary Basins of Siberia in 2018-2023 [1, 2, 11], in fracture groundwater of argillaceous and calcareous-argillaceous shales the uranium and thorium concentrations are typically lower (in some cases by several orders of magnitude) than in the granitoids. For instance, in the Insky springs waters in clay shales, natural radionuclides are contained in the following ranges. mg/dm<sup>3</sup>:  ${}^{238}$ U from 2.83  $\cdot$  10<sup>-3</sup> to 4.13  $\cdot$  10<sup>-3</sup>;  ${}^{232}$ Th from  $2.39 \cdot 10^{-6}$  to  $1.16 \cdot 10^{-5}$ , the ratio  ${}^{232}$ Th/ ${}^{238}$ U in the waters varies from  $8.85 \cdot 10^{-4}$  to  $3.61 \cdot 10^{-3}$ , the activity of <sup>222</sup>Rn varies from 7 to 149 Bq/dm<sup>3</sup>. Groundwater in the vicinity of the Verkh-Tula settlement (spring, boreholes) are characterized by even lower radionuclide concentrations in the range, mg/dm<sup>3</sup>: <sup>238</sup>U from

3.8 · 10<sup>-6</sup> to 7.2 · 10–3; <sup>232</sup>Th from 0.1 to 8.0 · 10<sup>-5</sup>, radon activity up to 28 Bq/dm<sup>3</sup>. Such concentrations are characteristic of the water-bearing complex of widespread clay shales.

#### Conclusion

A detailed study of the composition and mineralogy of granitoids of the Ob-Zaisan folded zone was carried out, and for the first time a wide range of accessory minerals differing in the Priobsky and Barlak complexes was identified. In addition to apatite, sphene, and zircon, which were determined in both complexes, fluorite, topaz, monazite, xenotime, cassiterite, rutile, orthite, and less frequent uraninite and rich in rare-earth elements bastnesite and parisite were identified in the Barlak complex. Waters of the Barlak massif (areas Skala, Mochishche, Aeroflot) are characterized by the highest uranium and thorium concentrations.

It should be noted that on the whole the obtained data are well correlated with radionuclide concentrations in groundwater of the study area (historical data). The concentrations of uranium and thorium in the granitoids are several orders of magnitude higher than those in other water-bearing rocks of the Ob-Zaisan folded region - widespread argillaceous and calcacerous shales, as well as intrusions of intermediate composition, limestones, and coals. The obtained data will be further used for modeling of interaction processes in a water-rock system.

One can predict a high background of radionuclides in the groundwater of the Barlak and Priobsky granitoid complexes, within the ranges, mg/dm<sup>3</sup>: <sup>238</sup>U from 0.1 · 10<sup>-3</sup> to 1.40 and <sup>232</sup>Th from 1.0 · 10<sup>-6</sup> to 2.16 · 10<sup>-3</sup>. Radon <sup>222</sup>Rn activity in groundwater ranges 1–50 Bq/dm<sup>3</sup> in the contact zones of granitoids with different-aged sedimentary rocks to  $600-5,000 \text{ Bg/dm}^3$  in the areas of granitoids occurrence.

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#### Information about the authors

**Vasiliy P. Sukhorukov** – Cand. Sci. (Geol. and Mineral.), Head of Laboratory, V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation; Associate Professor, Novosibirsk State University, Novosibirsk, Russian Federation ORCID 0000-0002-6658-2360, Scopus ID 56268382200; e-mail svp@igm.nsc.ru

**Anna F. Sukhorukova** – Cand. Sci. (Geol. and Mineral.), Senior Researcher, A.A. Trofimuk Institute of Oil and Gas Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation; Associate Professor, Senior Researcher, Novosibirsk State University, Novosibirsk, Russian Federation; ORCID 0000-0003-4228-7946, Scopus ID 56524401600; e-mail SukhorukovaAF@ ipgg.sbras.ru

**Dmitry A. Novikov** – Cand. Sci. (Geol. and Mineral.), Head of Laboratory, A.A. Trofimuk Institute of Oil and Gas Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation; Associate Professor, Leading Researcher, Novosibirsk State University, Novosibirsk, Russian Federation; ORCID 0000-0001-9016-3281, Scopus ID 35318389700; e-mail NovikovDA@ipgg.sbras.ru

Anton S. Derkachev – Junior Researcher, A.A. Trofimuk Institute of Oil and Gas Geology and Geophysics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russian Federation; Engineer, Novosibirsk State University, Novosibirsk, Russian Federation; ORCID 0000-0001-6101-6573, Scopus ID 57223290521; e-mail Derkachyovas@ipgg.sbras.ru

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