Chemical and Mineralogical Composition of Water-Bearing Materials of the Kuldur Geothermal Reservoir (Jewish Autonomous Region)

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Abstract. This article provides results of mineralogical and geochemical studies of granodiorites of the Kuldur low-mineralized thermal water reservoir. The site of geological and groundwater studies belongs to the Pionerskii massif located within the Lesser Khingan block of the Bureya composite terrain. Granitoids of the Tyrma-Bureya assemblage in the Pionerskii massif are considered to have formed in the early Mesozoic era, not in the late Paleozoic era, as deemed before. Granitoids of the assemblage under study were likely formed in the geodynamic backdrop of the collision of the North Asian and Sino-Korean cratons.

1. Introduction
This study is dedicated to granitoids of the Tyrma-Bureya assemblage in the Pionerskii massif located in the central part of the Bureya composite terrain. According to results of geochronological studies, the age of materials in this assemblage is similar to the age of granitoids in the Nizhnestoibinskii, Talakan, and Ust-Dikanskii massifs.

Even state-of-the-art geological studies leave a range of controversial issues regarding the age of plutons in the Lesser Khingan block and the geodynamic circumstances of their formation. According to the studies of Tyrma-Bureya assemblage's granitoids in the northern part of the Bureya massif, A.A. Sorokin et al. determined that the massif age (U-Pb dating applied to zircon) is 218-185 ± 1 m ny years [3, 9, 12], i.e. the massifs formed in the Mesozoic era, not in the Paleozoic era, as deemed before.

This article is dedicated to a study of chemical and mineralogical composition of water-bearing materials, as they directly affect composition of the Kuldur reservoir's thermal waters, and groundwater conditions of circulation and thermal spring formation.

To fulfill this goal, we had to and collected a rather large amount of factual evidence about the studied region, analyzed and processed the collected data.

2. Geologic composition of the region
The geological composition of this territory is rather complex due to the fact that the Jewish Autonomous Region is located at the juncture of the Bureya massif's Lesser Khingan block and the Sikhote-Alin fold belt. Intensively positioned and unevenly metamorphically altered terrigenous-
carbonate Proterozoic and Cambrian sequences, facies-changing Cretaceous volcanites, and intrusive formations of different age are widespread. The Kuldur nitric geothermal reservoir is located in the Bureya composite massif adjacent to the 400 km$^2$ Pionerskii granite massif. The Pionerskii massif belongs to phase II of the Tyrma-Bureya assemblage ($\gamma_2\delta_5C_2^3-t$) (Fig. 1), and is represented by quartz diorites, granodiorites, and granites. Phase 3 leucogranite stocks ($l_4\gamma_4C_2^3-t$) were discovered in the head of the Kuldur river; also, there are leucogranite dikes, pegmatite and aplite veins breaking intrusive bodies of the Tyrma-Bureya assemblage. Granodiorites prevail in the thermal water discharge area. These are light-gray or almost white (when enriched by biotite) medium-grained (less frequently - coarse-grained) and in most cases porphyritic minerals mottled with dark-colored minerals.

![Granodiorite massif outcrop with dikes 10 km up the Kuldur river.](image)

**Figure 1.** Granodiorite massif outcrop with dikes 10 km up the Kuldur river.

Stratified formations in the area are represented by Upper Archean Amur metamorphic rocks, Upper Riphean-Lower Cambrian Khingan terrigenous and carbonaceous formations, Cretaceous terrigenous and volcanic formations, Oligocene-Miocene and Pliocene-Quaternary loose deposits, and Miocene basaltoids.

In this area, the best manifested are north-east trending faults, the predominant one being the Khingan-Olono Fault. This fault is parallel to the deep-earth Khingan Fault. In the southern part of the area under consideration, there is large latitudinal Olono Fault that crosses the area from West to East. This fault is observed in the Olono River valley.

The Kuldur geothermal reservoir is adjacent to the Meridional Fault area where it coincides with the North-East-trending feathering fault steeply dipping (70-85$^\circ$) on the eastern side.

The surrounding formations within the tectonic fault in the Kuldur reservoir are hydrothermally altered and often feature caverns, as well as fractures filled with secondary minerals. Cavern and fracture walls are covered with deposits of secondary minerals of different generations (calcite, quartz, hydrous micas, etc.). The formations surrounding the orifice appear a practical aquifuge in comparison with permeability of the formations immediately inside the discharge orifice.

There are few North-West-trending faults, and they do not affect the area's structural geometry significantly.

The surrounding formations located within the discontinuous fault are hydrothermally altered, feature caverns and fractures filled with secondary minerals, such as calcite, quartz, or hydrous micas.
3. Study methods
The phase II formations of the Tyrma-Bureya assemblage were for the first time subjected to a whole range of mineralogical and chemical studies. Solid rocks were sampled during the field works at the Kuldur reservoir in 2018.

We used an Agilent 7500 spectrometer (Agilent Techn., USA) to analyze chemical composition of formation samples using the ICP-MS method (Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Pb, Th, U) at the analytical chemistry laboratory of the Far East Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences (Vladivostok, analyst - E.V. Elovskii). We used an iCAP 7600 Duo spectrometer to determine the primary elements of solid rock material samples using the atomic emission spectroscopy (Vladivostok, analysts - G.A. Gorbach, E.A. Tkalina, N.V. Khurkalo).

We also studied mineral and chemical composition of formations at the X-ray laboratory (guided by A.A. Karabtsov) using a JXA-8100 electron probe microanalyzer for wavelength/energy-dispersive spectroscopy (Japan) and a Rigaku MiniFlex II X-ray diffractometer (Rigaku, Japan).

4. Study results
Water-bearing materials are represented by variously altered granitoids (Fig. 2) characterized by massive and partly gneissose structures [8].

Figure 2. Granodiorite sample from the Kuldur reservoir. A - a gneissose-structured granitoid, sample K-1; B - a massive-structured granitoid, sample K-2.

The main rock-forming leucocratic minerals of the granodiorites under consideration are quartz (Q), potassium feldspar (PFS) and plagioclase (Pl). Biotite is a primary melanocratic rock-forming mineral. The secondary minerals formed as a result of hydrothermal processes include calcite, chlorite, epidote, and muscovite.

As mass fractions of SiO₂ and Na₂O + K₂O are 61-63% and 5.5-6%, respectively (table 1), the Pionerskii massif’s formations are classified as granodiorites according to the TAS diagram [1]. Petrochemical peculiarities of formations include slightly increased concentrations of Al₂O₃ and Fe₂O₃_tot.
Table 1. Mass fractions of the primary elements in samples of the Kuldur geothermal reservoir’s water-bearing materials.

| Sample No. | SiO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | MnO | MgO | CaO | Na₂O | K₂O | P₂O₅ | H₂O loss on ignition | Σ   |
|------------|------|------|-------|-------|-----|-----|-----|------|-----|------|---------------------|-----|
| K-1        | 61.16| 0.72 | 17.64 | 5.68  | 0.09| 2.10| 4.49| 3.68 | 2.10| 0.18 | 0.30                | 1.39| 99.52 |
| K-2        | 63.28| 0.63 | 17.21 | 5.06  | 0.07| 1.80| 4.23| 3.50 | 2.51| 0.16 | 0.30                | 0.85| 99.60 |

Biotite is poorly chloritized (although the replacement covered more than 1%). Sometimes they are characterized by granophyric structure, which is why we may assume that granitoids crystallized in hypabyssal conditions.

Myrmekites are observed at the rims of plagioclase and potassium feldspar aggregates (Fig. 3).

One of the granitoid phases is characterized by development of a pyroxene-corniferous association (Fig. 4), which indicates pyroxene amphibolitization in the event of autometamorphism. All the formations under consideration were intensively altered at about the same time as tectonic deformations as identified in granites by distinct dislocations and corrugation of plagioclase crystals.

Figure 3. Myrmekites. K-1 sample.

Figure 4. A - pyroxene-corniferous association in granites; B - tectonic deformations in granites.

Амфибол Amphibole
Пироксен Pyroxene
Плагиоклаз Plagioclase
Кварц Quartz
Биотит Biotite
Dark-colored minerals are replaced with chlorite and epidote. The replacement degree varies from 0 to 95%. At the same time, leucocratic granite components are intensively replaced with sericite; potassium and sodium feldspar is perthitic and pelitized. Biotite and apatite relics survive the replacement process; it ought to be mentioned that sometimes ore mineral rims visually similar to opacitization form metasomatically around apatite.

Epidote is one of the minerals that accompany chlorite in the process of hydrothermal alteration of earth materials; it forms in various amount in microcline-like minerals and other granitoids.

Replacement of dark-colored minerals in granite is accompanied by loss of bivalent metals and formation of calcite-chlorite microruns.

The share of accessory minerals in samples may reach 5-10%. In the formations under study, the most widespread accessory minerals are apatite and zircon. Titanite, titanium oxides, and pyrite are found less frequently (Fig. 5).

**Figure 5.** Concentration of accessory minerals in K-1 and K-2 samples.

The concentration of rare-earth metals (REM) in granodiorites of the Pionerskii massif varies from 0.43 ppm to 44.56 ppm. We performed C1 chondrite normalization of formations [17]. The REM distribution graph is rather steep (Fig. 6) [2] explained by lightweight REM enrichment; the La<sub>nr</sub>/Yb<sub>n</sub> ratio is 11.8 and 14.2, respectively.

REM lighting is explained by the presence of plagioclase and titanite. For this type of formations, there are no clear manifestations of Ce and Eu anomalies. The Eu/Eu* (europium) increment is 0.58.

As long as La<sub>nr</sub>/Yb<sub>n</sub> > 1, and there is no europium anomaly, we may assume presence of a REM- and Y-concentrating mineral [15]. For instance, this is the reason why the La<sub>nr</sub>/Yb<sub>n</sub> ratio is high for tonalite-trondhjemite-granodiorite assemblage formations resulting from metabasite melting at P ≥ 10-15 kbar in equilibrium with garnetiferous restite [10].

The La/Nb (2.44) and Ce/Y (2.86) ratios demonstrate that the Pionerskii massif's formations are closer to the trend of mixing with crust substrates, which is why we may talk about mantle-crust interaction here [15].

**Figure 6.** Graph: REM distribution in the Pionerskii massif's granodiorites.
According to the Sr/Y ratio and Y, the formations under study belong to the field covering formations of typical volcanic arcs (andesites, rhyolites, dacites).

According to the diagram compiled by J. Pearce [16], we may imagine the geodynamical circumstances of formation of granitoids of the massif under study. Such elements as Rb, Y, and Nb were selected for identification. The studied samples ended up in the lower part of the VAG field; this corresponds to oceanic-island-arc granitoids [14]. According to paleoreconstructions of the Late Paleozoic and Early Mesozoic eras, the Solonkerskii Ocean [5, 6, 7] was consumed, and the North Asian and Sino-Korean cratons collided in the Early Triassic period. This may have promoted numerous granitoids intrusions in the Early Mesozoic era [10, 13, 18].

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