

## REVIEW ARTICLE

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# Bentonite clays of Russia and neighboring countries

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Bentonite clay is an important natural material, widely used in many industries. The purpose of this article is to analyze the mineral resource base of bentonite clays in Russia. The data on reserves of deposits, the degree of their development and production volumes are given. The composition and uses of the main developed deposits of bentonite clay in Russia are characterized. A comparative analysis of the reserves and production growth of bentonite over the past decade is carried out. A brief description of the world situation is given, and the mineral resource base of the CIS countries is considered. Since the quality of raw materials, its properties and reserves directly depend on the conditions of origin, a characteristic of the geological and tectonic position and genesis of the bentonite clay deposits of Russia is given. Bentonite-bearing provinces with favorable conditions for the formation of bentonite deposits with volcanogenic-sedimentary genesis are considered. The most promising regions are proposed for the purposes of expanding the mineral resource base of bentonite materials. This work is the result of the authors' own geological works at various deposits of bentonite clays in Russia, the near and far abroad, as well as the study and interpretation of published materials on this subject over the past decades.

**Keywords:** bentonite, montmorillonite, clays, bentonite provinces, genesis of bentonite, industrial minerals, the 10th Khutor deposit, the Tikhmenevskoe deposit, coal basins, Far East

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## Introduction

The main rock-forming component of bentonite clays is montmorillonite (> 60-70 %), which is part of the smectite group. Quartz, feldspars, calcite, rarely pyrite, and organic matter, as well as other clay minerals (kaolinite, illite, mixed-layer clay minerals, and less often chlorite and vermiculite) are found as impurities. Smectites are hydrated aluminosilicates consisting of two tetrahedral and one octahedral network located between them, forming a 2:1 layer. Due to isomorphous substitutions in the composition of octahedral and tetrahedral networks, a negative charge of the layer takes form, which is compensated for by interlayer cations and accounts for the high sorption properties of bentonite clays (Drits, Kossovskaya, 1990). Montmorillonite is characterized by predominant charge localization in the composition of octahedral networks, which leads to high sorption of cations and organic components.

According to the nature of the exchange cations in the interlayer complex of montmorillonite, bentonite clays are subdivided into alkaline (sodium) and alkaline-earth (calcium, magnesium) types. Alkaline bentonites

have higher technological properties compared with alkaline-earth ones, due to the fact that alkali metal ions, primarily sodium, have a higher potential for hydration (Osipov, Sokolov, 2013). As a result, the swelling of Na-montmorillonites is much higher than that of Ca-montmorillonites. The properties of bentonites are also affected by charge localization. High sorption indices and high swelling are associated with the absence of charges in the tetrahedral network. On the contrary, the appearance of a small change in the tetrahedral charge leads to a decrease in sorption capacity and swelling. The sorption indicator is affected to the same degree by the mean quantity of the layer charge – a decrease in the sorption capacity results from an increase, or an excessive decrease in the value of the layer charge.

Such features of the montmorillonite structure determine its specific properties, especially its binding properties, high thermal resistance, and high sorption capacity. This makes bentonite clay a very important and widely used industrial material. In terms of consumption, the most important industrial applications of bentonite clay in Russia, as well as in other countries, are the following:

- **Disposal of radioactive waste**, as a sorbent and waterproofing material for engineering safety barriers;
- **In metallurgy**, as a binder for iron ore concentrates pelletization;

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- In **drilling mud production**: oil and gas drilling, horizontal directional drilling, and tunneling; and civil engineering. Bentonite is used in drilling fluids to lubricate and cool the boring tools, and to remove cuttings;

- In **metal casting**, as a binder agent in sand-clay molds in iron and steel foundries; and

- In **civil engineering**, in “slurry wall” technology, and as additives to cement mortars.

In total, there are more than 200 applications for bentonite clays and materials based on them, including in agriculture, in the rubber, polymer, and paper industries, in medicine, etc. A relatively new and very promising direction, for Russia, is the use of bentonites for the disposal of radioactive waste as a waterproofing and sorption material (Krupskaya et al., 2018).

## 2. Reserves and production

### 2.1. General information

Estimates of world reserves of bentonite exceed 10 Gt, approximately 45 % of which is located in China, 15 % in the United States and 7 % in Turkey (Industrial Minerals, 2012). In the list of countries with the largest reserves of bentonite, it is also necessary to include Greece, Russia, India, and the CIS countries. It should be

noted that most deposits worldwide are of the alkaline-earth type. The largest deposits of alkaline bentonite are located in the United States (Wyoming), Turkey (Resadiye), and Azerbaijan (Dash-Salahlinskoe) (British Geological Survey, 2015; United States Geological Survey, 2017).

Over the past 10 years, the annual production of bentonite clay has been on the rise. According to the U.S. Geological Service (United States Geological Survey, 2017), from 2008 to 2017, bentonite clay production increased from 12 to 19 Mt. About 30 % of the total production happens in the United States. This is followed by China in second place (23 %).

### 2.2. Russia

Measured and indicated reserves of bentonite clay (Russian A+B+C<sub>1</sub> categories) amount to 189 Mt while inferred resources (Russian C<sub>2</sub> category) are 146 Mt. In this article only measured and indicated reserves (Russian A+B+C<sub>1</sub> categories) will be considered, unless otherwise specified. Total production for 2017 amounted to more than 700 thousand tons. According to the classification of state balance of mineral reserves for 2018, bentonite clay deposits are included in the “Bentonite Clays” group, as well as

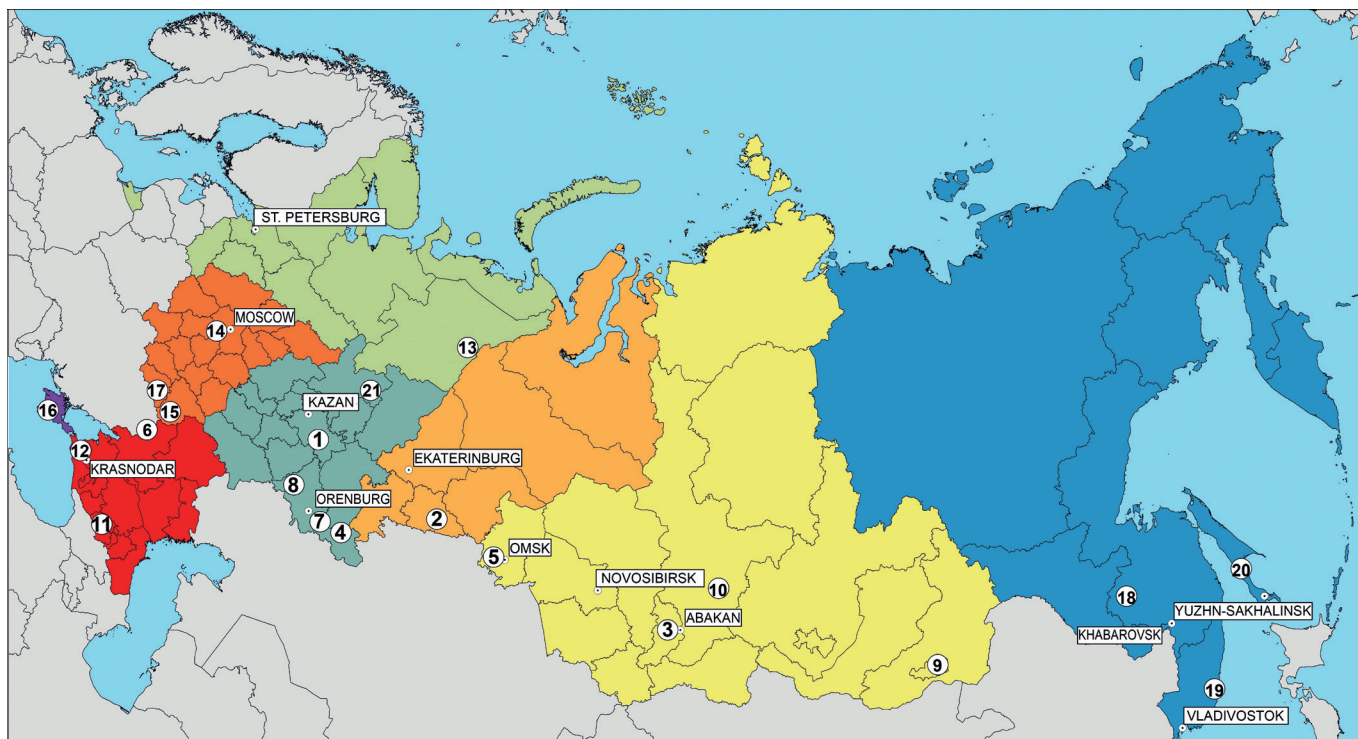


Fig. 1. Overview map of bentonite clay deposits in Russia. 1 – Biklyanskoe, Berezovskoe, Verhne-Nurlatskoe, Tarn-Variskoe (Republic of Tatarstan); 2 – Zyryanskoe (Kurgan Region); 3 – 10<sup>th</sup> Khutor (Republic of Khakassia); 4 – Izherdinskoe, Saraybashskoe, Sarinskoe, Uchastok V'yuzhny-2 (Orenburg Region); 5 – Lyublinskoe (Omsk Region); 6 – Tarasovskoe, Yuzhno-Tarasovskoe (Rostov Region); 7 – Aktivnoe, Zheltoe (Orenburg Region); 8 – Sobolevskoe (Orenburg Region); 9 – Haranorskoe (Trans-Baikal Territory); 10 – Kamalinskoe (Krasnoyarsk Region); 11 – Nalchinskoe, Kheu, Gerpegezskoe (Republic of Kabardino-Balkaria); 12 – Chernomorskoe (Krasnodar Territory); 13 – Bad'inskoe (Republic of Komi); 14 – Kalinovo-Dashkovskoe (Moscow Region); 15 – Nikolskoe, Maydan-Bentonitovoe (Voronezh Region); 16 – Kudrinskoe, Kurcovskoe (Republic of Crimea); 17 – Uchastok Samarinsky (Belgorod Region); 18 – Urgalskoe (Khabarovsk Territory); 19 – Zerkalnoe (Primorsky Territory); 20 – Tikhmenevskoe (Sakhalin Region); 21 – Vasil'evskoe, Chernoholunickoe (Kirov Region).

partially in “Clays for Drilling Fluids” and “Molding Materials” groups.

A significant part of Russian deposits (Fig. 1) belongs to the “Bentonite Clays” group, which includes 22 deposits, with estimated reserves of 101 Mt (Table 1, State balance of mineral reserves of the Russian Federation: Bentonite Clays, 2018).

The main reserves are located in the regions of Tatarstan (43.8 %), Omsk (20 %) and Kurgan (13.8 %). At the beginning of 2018, production was ongoing only in four deposits: the 10th Khutor (Republic of Khakassia), with estimated resources of 3 Mt; Biklyanskoe and Berezovskoe (Republic of Tatarstan), with 37.9 Mt; and Zyryanskoe (Kurgan Region), with 14 Mt. It is also

worth noting the Yuzhno-Tarasovskoe deposit (Rostov Region); with estimated reserves of 3.1 Mt and Uchastok V'yuzhny-2 (Orenburg Region), with 6.4 Mt, which are not currently exploited but belong to the list of important Russian deposits.

In the distributed reserves of mineral resources, the Kheu deposit (Republic of Kabardino-Balkaria), as well as the deposits of Solnechnoe and Karatigeyskoe (Republic of Khakassia) with total reserves of 4.7 Mt, are ready for development and exploitation. The remaining reserves are spread amongst 14 deposits which make up 59.4 Mt. Prospection is under way at the Tikhmenevskoe deposit (Sakhalin Region), with inferred reserves of 702,000 tons.

Deposits	Geographical position	Type, Genesis	Age	Measured and indicated reserves, mln tons	Geotectonic position
Currently exploited					
Biklyanskoe, Berezovskoe	Republic of Tatarstan	Alkaline-earth, sedimentary	N <sub>2</sub>	37.9	Volga-Ural anteclise
Zyryanskoe	Kurgan Region	Alkaline-earth, sedimentary	N <sub>1</sub>	14	Trans-Ural upland
10 <sup>th</sup> Khutor	Republic of Khakassia	Alkaline-earth, volcanogenic-sedimentary	C <sub>1-2sr</sub>	3	Altay and Sayans orogenic belt
Unexploited					
Lyublinskoe	Omsk Region	Alkaline-earth, sedimentary	N <sub>1</sub>	20.3	Ishimo-Irtyshskaya monoclise
Verhne-Nurlatskoe, Tarn-Variskoe	Republic of Tatarstan	Alkaline-earth, sedimentary	N <sub>2</sub>	6.7	Volga-Ural anteclise
Nalchinskoe, Kheu	Republic of Kabardino-Balkaria	Alkaline, alkaline-earth, volcanogenic-sedimentary	P <sub>1</sub>	6.6	Pre-Caucasian foredeep
Uchastok V'yuzhny-2	Orenburg Region	Alkaline-earth, sedimentary	K <sub>2</sub>	6.4	Pre-Uralian foredeep
Yuzhno-Tarasovskoe	Rostov Region	Alkaline-earth, sedimentary	P <sub>2</sub>	3.1	Voronezh anteclise
Karatigeyskoe, Solnechnoe	Republic of Khakassia	Alkaline-earth, volcanogenic-sedimentary	C <sub>1-2sr</sub>	3	Altay and Sayans orogenic belt
Kudrinskoe, Kurcovskoe	Republic of Crimea	Alkaline, alkaline-earth, volcanogenic-sedimentary	K <sub>2</sub>	0.4	Gorno-Crimean fold-and-thrust belt *
Urgalskoe	Khabarovsk Territory	Alkaline-earth, volcanogenic-sedimentary	K <sub>1</sub>	0.3	Sikhote-Alin orogenic belt
Zerkalnoe	Primorsky Territory	Alkaline-earth, volcanogenic-sedimentary	P <sub>2</sub>	0.1	Sikhote-Alin orogenic belt
Vasil'evskoe, Chernoholunickoe	Kirov Region	Alkaline-earth, sedimentary	J <sub>2</sub>	- C <sub>2</sub> – 4.8	Volga-Ural anteclise
Uchastok Samarinsky	Belgorod Region	Alkaline-earth, sedimentary	P <sub>2</sub>	- C <sub>2</sub> - 4	Voronezh anteclise
Tikhmenevskoe	Sakhalin Region	Alkaline, volcanogenic-sedimentary	N <sub>1</sub>	- C <sub>2</sub> – 0.7	Central Sakhalin depression

Table 1. Estimated reserves of the bentonite deposits in the “Bentonite Clay” category. \* (Sabitov, Belyaev, 2018).

Total production in the “Bentonite Clays” group in 2017 amounted to 574,000 tons of bentonite clay. Most of that was mined in the Khakassia Republic at the 10th Khutor deposit (82 %), in the Tatarstan Republic at the Biklyanskoe and Berezovskoe deposits (14.2 %), as well as in the Kurgan region at the Zyryanskoe deposit (3.8 %).

The group referred to as “Clays for Drilling Fluids” (State balance of mineral reserves of the Russian Federation: Clays for drilling fluids, 2018) includes 10 clay deposits of montmorillonite composition, which also belongs to the bentonite and bentonite-like clays group. Estimated reserves at these deposits are in the range of 61.9 Mt (Table 2). These include: Izhberdinskoe, Saraybashskoe, Aktivnoe, Zheltoe, Sarinskoe and Sobolevskoe (Orenburg Region), with reserves of 40.1 Mt; Haranorskoe (Trans-Baikal Territory), with reserves of 8.4 Mt; Bad’inskoe (Republic of Komi), with reserves of 2.4 Mt; Tarasovskoe (Rostov Region), with reserves of 5.1 Mt;

and also Chernomorskoe (Krasnodar Territory), with reserves of 5.9 Mt. Mining operations are carried out only at the Izhberdinskoe and Saraybashskoe deposits. In total, of the group “Clays for Drilling Fluids” 125,000 tons of raw materials was mined in 2017.

The group “Molding Materials” includes 6 clay deposits of predominantly montmorillonite composition suitable for the manufacture of sand-clay molds, with total estimated reserves of 26.2 Mt (State balance of mineral reserves of the Russian Federation: Molding materials, 2018). These include: Kalinovo-Dashkovskoe (Moscow Region), with 1.9 Mt; Nikolskoe and Maydan-Bentonitovoe (Voronezh Region), with 1 Mt; Gerpegezhskoe (Republic of Kabardino-Balkaria), with 8.1 Mt; and Kamalinskoe (Krasnoyarsk Region), with 15.2 Mt (Table 3). Despite the fact that the Gerpegezhskoe and Kalinovo-Dashkovskoe deposits are considered to be developed, as of 2017, real exploration was conducted only at the deposits in the Voronezh region (36 kt).

Deposits	Geographical position	Type, Genesis	Age	Measured and indicated reserves, mln tons	Geotectonic position
Currently exploited					
Izhberdinskoe, Saraybashskoe	Orenburg Region	Alkaline-earth, sedimentary	K <sub>2</sub>	7	Pre-Uralian foredeep
Unexploited					
Aktivnoe, Zheltoe, Sarinskoe, Sobolevskoe	Orenburg Region	Alkaline-earth, sedimentary	N <sub>2</sub>	33.1	Pre-Uralian foredeep
Haranorskoe	Trans-Baikal Territory	Alkaline-earth, volcanogenic-sedimentary	K	8.4	Mongolo-Okhotsk orogenic belt
Chernomorskoe	Krasnodar Territory	No information	N <sub>2</sub>	5.9	Pre-Caucasian foredeep
Tarasovskoe	Rostov Region	Alkaline-earth, sedimentary	P <sub>2</sub>	5.1	Voronezh anteclise
Bad’inskoe	Republic of Komi	Alkaline-earth, sedimentary	C <sub>1</sub>	2.4	Pre-Uralian foredeep

Table 2. Estimated reserves of the bentonite deposits in the “Clays for Drilling Fluids” category

Deposits	Geographical position	Type, Genesis	Age	Measured and indicated reserves, mln tons	Geotectonic position
Currently exploited					
Nikolskoe, Maydan-Bentonitovoe	Voronezh Reg	Alkaline-earth, sedimentary	P <sub>1</sub>	1	Voronezh anteclise
Unexploited					
Kamalinskoe	Krasnoyarsk Region	Alkaline-earth, volcanogenic-sedimentary	C <sub>1</sub>	15.2	Altay and Sayans orogenic belt
Gerpegezhskoe	Republic of Kabardino-Balkaria	Alkaline, Alkaline-earth	P <sub>1</sub>	8.1	Pre-Caucasian foredeep
Kalinovo-Dashkovskoe	Moscow Region	Alkaline-earth, sedimentary	C <sub>1</sub>	1.9	Moscow syncline

Table 3. Estimated reserves of the bentonite deposits in the “Molding Materials” category

Over a nine-year period (Sabitov et al., 2010), the increase in estimated reserves amounted to 45 Mt. Due to an increase in production at the 10th Khutor and the Maydan-Bentonitovoe deposit, and the commissioning of the Berezovskoe and Saraybashskoe deposits, production was increased by 150,000 tons. Meanwhile mining activities at the Kalinovo-Dashkovskoe and Nikolskoe deposits have been interrupted.

Based on their mineral composition, the deposits currently being developed consist of alkaline-earth montmorillonite up to 60-75 %. The exception to this is the deposits in the Orenburg (Izhberdinskoe, Saraybashskoe) and Voronezh (Nikolskoe) regions, with an average content of montmorillonite of about 50-60 % and 42-65 % (Table 4), respectively.

To improve the quality of the raw material, bentonite and bentonite-like clays from most of the deposits exploited in Russia are activated by soda ash. Due to its high heat resistance capacity and strength characteristics, the main material source for mining and processing plant and foundries is bentonite from the 10th Khutor deposit. Bentonites from the Zyryanskoe, Biklyanskoe, and Berezovskoe deposits are used for the same purpose; however, their use is, for the most part, associated with vertical and horizontal directional drilling, as well as civil engineering. Bentonites from the Izhberdinskoe and Saraybashskoe deposits can also be used for the preparation of drilling fluids for various purposes. The products from the Nikolskoe and Maydan-Bentonitovoe deposits are mainly used for the manufacture of low-grade drilling fluids, in agriculture, and in small quantities in foundries.

It is worth noting that at present the two most common methods for analyzing the cation exchange capacity are: by adsorption of methylene blue (MG), which is part of GOST 21283-93 (Bentonite clay for fine and building ceramics), and by adsorption of the Cu (trien) complex, which at the moment is an accepted technique in the scientific community as the most appropriate for studying the properties of bentonites and, especially, alkaline earth differences (Lorenz, 1999). In view of the higher adsorption capacity of the copper complex, it easily displaces calcium and magnesium cations from

the surface of the clay particles, which makes it possible to glean accurate information on the value of CEC. In turn, the cation exchange capacity is determined not only by the smectite content, but also by the features of its structure, as indicated above.

### CIS countries

The reserves at the main deposits of bentonite clay in the CIS countries (excluding the Russian Federation) amount to 740 Mt. Slightly more than a third of these (270 Mt) occurs in the Republic of *Azerbaijan* – the most important source of high-quality industrial material with the Dash-Salahlinskoe, Aploidskoe, and Khizin group of alkaline hydrothermal bentonite deposits (Nasedkin et al., 2001; Nasedkin, Shirinzade, 2008; Belousov, 2013).

The next important CIS country is the Republic of *Armenia*, with the Sarigyuhscoe deposit with total reserves of 57 Mt. Only 24 of those have been put on the state balance of mineral reserves. It lies within the same geological structure as the Dash-Salahlinskoe deposit and is located near the border with Azerbaijan (British Geological Survey, 2015; United States Geological Survey, 2014; Nasedkin et al., 2001).

The deposits of the Republic of *Kazakhstan* have become a relatively new source of high-quality bentonite imported into Russia. They are the Taganskoe, Dinozavrovoe, Kelesskoe, and Andreevskoe deposits. The bentonites are of the alkaline and alkaline-earth type with red and pink colors, sometimes with a gel-like structure. Their origin at the moment is rather unclear: the occurrence of several bentonite formation processes with dominance of the hydrothermal process is assumed (Sapargaliev, Kravchenko, 2007). Total reserves are estimated at about 55 Mt. But as a result of constant geological exploration work in the Republic of Kazakhstan, reserves increase every year (Nasedkin et al., 2001; British Geological Survey, 2015; United States Geological Survey, 2017).

*Georgian* bentonite, well known as “Askan-gel,” named after the Askanskoe deposit and because of its gel-like structure, is not currently supplied to Russia in significant quantities. Total reserves in Georgia, together with the Gumbrijskoe, Askanskoe, and Kumistavskoe

Deposit	Smectite content, %	CEC, mg-eq/100 gr	
		MB adsorption	Cu (trien) adsorption
Biklyanskoe, Berezovskoe (Republic of Tatarstan)*	60-70	36-38	-
Zyryanskoe (Kurgan Region)**	60-75	27	78
10th Khutor (Republic of Khakassia)**	60-75	37	80
Izhberdinskoe, Saraybashskoe (Orenburg Region)**	45-60	35-45	-
Nikolskoe (Voronezh Region) ***	42-65	55	-

Table 4. Averaged mineral composition and cation exchange capacity (CEC) of developed Russian deposits. \* Sabitov et al., 2008; \*\* analysis results of the IGEM RAS laboratory; \*\*\* Goryushkin, 2006

deposits, amount to 12 Mt (Nasedkin et al., 2001; British Geological Survey, 2015; United States Geological Survey, 2017).

**Ukraine** is a former member of the CIS, and it was an important supplier of bentonite clay to Russia during the second half of the 20th and the beginning of the 21<sup>st</sup> century. The raw material base in Ukraine consists of deposits of bentonite clays of various qualities. For example, the Dashukovskoe (Cherkasskoe) deposit belongs to the category of high-quality alkaline-earth bentonite clays previously supplied to mining and processing plants in Russia. There are five main deposits of bentonite clay in Ukraine, some of which are not currently exploited, with total reserves of about 50 Mt: Dashukovskoe (Cherkasskoe), Gorbskoe, Grigorievskoe, Berezhanskoe, and Pyzhevskoe (Nasedkin et al., 2001; British Geological Survey, 2015; United States Geological Survey, 2017).

To round up the list of the CIS countries with industrial reserves of bentonite clay, it is worth noting **Turkmenistan** with reserves of 14 Mt (Oglaglinskoe dep.), **Uzbekistan** with reserves of 10 Mt (Azkamar and Novbahor dep.), and **Kyrgyzstan** with reserves of 0.6 Mt (Beshkent dep.) (Nasedkin et al., 2001; British Geological Survey, 2015; United States Geological Survey, 2017).

It should be noted that the deposits described above are related to the major sources of industrial bentonites. The total reserves in the CIS countries are much larger.

### 3 Geological position

#### 3.1 Genesis

The classification of bentonite clays by origin is a debatable issue. For example, M. Wilson (2013) divides bentonites into the following groups: weathered rocks, pedogenesis, sedimentary, diagenesis, and hydrothermal transformation of parent rocks. D. Christidis and W. Huf (Christidis, Huf, 2009) classify bentonites into diagenetic, hydrothermal, and sedimentary types. In these contexts, a sedimentary type assumes the formation of smectite-rich sediments in salt lakes and sabkha environments without the processes of volcanic ash alteration.

Russia has its own classification of bentonites based on their origin (Kirsanov, 1972; Nasedkin et al., 2001). Deposits of bentonite clay are divided into the following groups:

- sedimentary (redeposited clay);
- hydrothermal (hydrothermal transformation of volcanic and sedimentary rocks);
- eluvial (weathering crust);
- volcanogenic-sedimentary (devitrification of volcanic ash in slightly alkaline waters);

In this case, we consider the sedimentary type mostly as redeposited clays with the presence of clay of diagenetic genesis.

The main bentonite types present in Russia are sedimentary and volcanogenic-sedimentary in type. The eluvial type is represented by a series of medium-quality alkaline-earth deposits that are not currently developed.

#### 3.1.1 Sedimentary type

This type encompasses most of the Russian bentonite clay deposits. The formation of redeposited, sedimentary bentonite clays is of complex origin. The main process involved here is redeposition and washing away of the original detrital and colloidal-dispersion material from eroded continental areas to basins of sedimentation. Since the compositions of the parent rocks are diverse, the resulting deposits of bentonite clay inherit this diversity of component compositions and the structural features of the minerals they contained. Moreover, in addition to the mechanical processes of redeposition and rewashing, the formation of sedimentary deposits can be accompanied by diagenetic and chemogenic processes. Also, the composition and quality of bentonite is affected by the hydrochemical environment of the sedimentation reservoir (Kirsanov, 1972).

Sedimentary deposits are usually characterized by a simple geological structure, a high thickness of the layers, and large reserves. Sedimentary deposits are distinctly subdivided into three subtypes: marine, lagoon, and continental. The quality of a bentonite clay depends both on the amount of impurities (quartz, feldspars, illite, etc.) and the conditions of its formation. Deposits of the marine subtype are of higher quality compared to continental ones.

The main issue is the reasons for the deterioration of the quality of the clay after its redeposition, as well as the lack of alkaline (sodium) varieties. It is assumed that during the transportation of the clay minerals by water, the structure of montmorillonite and the composition of the absorbed complex is transformed to a degree (Kirsanov, 1972).

Sedimentary bentonites are commonly of dark colors – gray-green, brown, dark-gray and almost black. On the mineralogical side, these bentonites mostly consist of alkaline-earth (Ca-Mg) montmorillonite. Chemically, they are characterized by a high content of  $Al_2O_3$  (20 %) and  $Fe_2O_3$  (4,5 % or more), and often silicon oxide (up to 60-70 %), due to their high content of quartz.

The largest Russian deposits of bentonite clay belong to this type and are located in the Republic of Tatarstan, the Kurgan region, Omsk region, and Orenburg region (Table 1). The deposits of alkaline-earth bentonite of sedimentary origin, the raw materials of which are successfully used in various industries, include the Zyryanskoe, Izhberdinskoe, and Saraybashskoe deposits.

### 3.1.2 Hydrothermal type

Hydrothermal deposits are associated with faults and fissured volcanogenic and magmatic rocks. Bentonite bodies shear from host rock with rod-shaped, or have dike-like or plastiform shapes and usually of a greater thickness. These bentonites are formed due to hydrothermal transformation in particular basalt porphyres and tuffs, as well as ashes. Hot thermal waters from the depths penetrate into the porous material of a bedrock (ash, tuff, etc.), which leads to the destruction of these tuffs and ashes, with the formation of smectite clays.

The quality of the resulting bentonites and their content of mineral impurities also depend on the composition of the mother rock, thermal water, its temperature and alkalinity. A favorable temperature of hydrothermal water for the conversion of tuffs into montmorillonite ranges from 50-200 °C, with a high alkalinity (pH 9-10).

A distinctive feature of bentonites of hydrothermal genesis is the presence of gradual transitions: bentonite ↔ montmorillonitized rock ↔ parent rock (Nasedkin, Shirinzade, 2008; Wilson, 2013). Also, a diagnostic sign is the presence of nearby magmatic rocks (basalts, andesites, etc.), as well as the presence of minerals such as agate, chalcedony, cristobalite, pyrite, chalcopyrite, galena, sphalerite, magnesite, pyrolusite, and zeolite. Sometimes they contain relicts of parent rocks. The content of montmorillonite, usually of the alkaline type, ranges from 60 to 80 %. The increased content of trace elements (F, Sc, Cr, Mn, Cu, Zn, Ga, Rb, Cs, Pb, Th, etc.) adsorbed by clay minerals from hot waters or preserved as relicts from the parent rocks is another characteristic. Often, bentonites of this genesis display upridging of beds and extend along tectonic cracks (Kirsanov, 1972).

Bentonites of the hydrothermal variety form deposits of large and extra-large reserves with a gray-greenish, bluish, yellowish, or cream color and become lighter when dried.

There are no hydrothermal bentonite deposits in Russia. The main reserves are located in the CIS countries, the USA, Europe, India, and Iran. Examples of such deposits are: Dash-Salahlinskoe (Azerbaijan), Sarigyuhscoe (Armenia), Askanskoe (Georgia), Milos Island (Greece), Ponzo Island (Italy), Hattari (Japan), Hector (USA).

### 3.1.3 Eluvial type (residual)

The process of formation of eluvial-type bentonites is rather complicated, since it is associated with weathering crusts and depends mainly on three factors: the composition of the original parent rocks, the climate, and tectonics. The tectonics of the region determines the relief, the depth of the weathering profile, and the possibility of formation of weathering crusts. For the formation

and sustainable preservation of montmorillonite, a humid-temperate and warm-humid climate is favorable. Time also plays a significant role – the duration of the weathering process (Kirsanov, 1972).

This type includes deposits of bentonites formed by deep weathering of the bedrock (igneous, metamorphic, pyroclastic, or sedimentary), with physicochemical changes. Based on the composition of the parent rocks that serve as the starting material for their formation, eluvial bentonites are subdivided into three subtypes: intrusive rocks (ultrabasic, rich in iron and magnesium compounds), effusive rocks (acidic, rarely basic rocks), and sedimentary rocks (marls, calcareous clays). Deposits formed on sedimentary rocks have little industrial value due to their small size and high lithological variability.

The shape of these bentonite bodies varies – lenticular, plastiform, and pocket-like. The thickness of the strata is usually measured by the first meters; the area of propagation can reach tens of square kilometers. Impurities are presented with kaolinite, illite, mixed-layer minerals, chlorite, and palygorskite. Eluvial deposits often appear together with deposits of mineral paints, zeolites, nickel, iron and manganese ores. The eluvial type is represented by a series of medium-quality alkaline-earth deposits of bentonite, which currently are of no particular industrial use in Russia (Kirsanov, Sabitov, 1980).

Examples of deposits are: Ust'-Maninskoe (Khanty-Mansiysk Autonomous Okrug), Vorontsovskoe (Sverdlovsk Region), Razgonskoe (Irkutsk Region), Aspidnoe (Georgia), Verkhne-Ubaganskoe (Northern Kazakhstan), Kostyukovichskoe (Republic of Belarus), and deposits in India, Iran and Vietnam.

### 3.1.4 Volcanogenic-sedimentary type

The volcanogenic-sedimentary type is of high quality and has a complicated geological structure. The montmorillonite content ranges from 50 to 80 % (both alkaline and alkaline-earth types).

They form through the underwater transformation of volcanic ash. The quality and purity of the resulting bentonites are determined by the composition of the initial material (ashes) and the character of the water basin in which the deposition and transformation of the material occurred (Belousov, Nasedkin, 2015).

After volcanic eruptions, volcanic ash is deposited in water basins and the process of destruction of their crystal lattice begins, with the formation of silicon and aluminum hydroxides, a gel-like mass, and its subsequent crystallization into montmorillonite. Volcanic centers (sources of ash) can be located hundreds of kilometers away from the future bentonite deposit (Wilson, 2013; Belousov, 2013; Belousov, Nasedkin, 2015).

The type of water reservoir where the ashes were deposited influences the cation-exchange composition

of the clay. Alkaline-earth-type bentonites form in fresh waters (with a predominance of Ca and Mg in the structure), while alkaline bentonites with a predominance of sodium cations in the interlayer space form in seawater enriched with sodium salts.

Volcanogenic-sedimentary bentonites often have a light color. One of the obvious diagnostic features is the presence of relicts of porous volcanic glass (Fig. 2) which failed to decompose into montmorillonite and the opal-cristobalite phase. The chemical composition of volcanogenic-sedimentary bentonites is characterized by an increased  $\text{SiO}_2$  content (on average 65 %), with an  $\text{Al}_2\text{O}_3$  content of 12-17 % and an elevated content of trace elements (Cr, V, Rb, Sr, Zr, Ba, etc.). Often, bentonites of this genesis interlay with sandstones, tuff-sandstone, limestone, as well as with hard or brown coals. The layers are uniform, aged, lenticular, or sheet-like, with a thickness of up to 10 m.

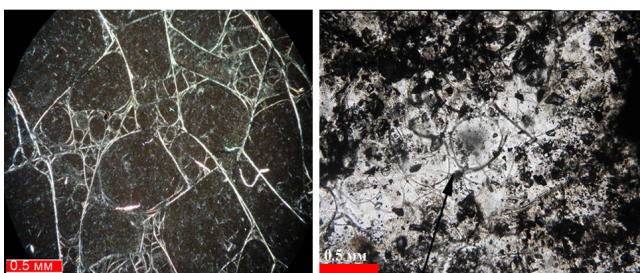


Fig. 2. Devitrification of acidic volcanic glass (Tikhmenevskoe deposit, Sakhalin Region)

In Russia, this genetic type is represented by a group of deposits in the Republic of Khakassia (10th Khutor, Karakukskoe, Izykhscoe, etc.) and the Sakhalin Island (Tikhmenevskoe, Vakhrushevskoe, Makarovskoe). According to the geotectonic position and composition of the rocks, it can be assumed that the Gerpegezhskoe and Nalchinskoe (Republic of Kabardino-Balkaria) deposits (Machabeli, 1980), as well as the Urgalskoe (Khabarovsk Territory) and Kamalinskoe (Krasnoyarsk Territory) deposits, also belong to this category. Wyoming (USA), one of the most famous bentonite deposits, also belongs to this category.

### 3.2. Tectonic and stratigraphic position

Structurally, Russian deposits of bentonite clays can be divided into three groups:

1. Deposits associated with plates and platforms: West Siberian plate, East European platform;
2. Deposits associated with orogenic belts: Altai and Sayans, Sikhote-Alin, Mongolo-Okhotsk, Central Sakhalin depression and Gorno-Crimean fold-and-thrust belt;
3. Deposits associated with foredeeps: Pre-Uralian and Pre-Caucasian foredeep.

Considering their stratigraphic confinement, it is

worth noting that all Russian bentonite deposits mainly belong to the Lower Carboniferous, Paleogene, or Neogene systems (Table 1) and to a lesser degree to the Cretaceous.

**Sedimentary deposits** are associated with ancient plates, platforms, as well as foredeeps in the era of stabilization of tectonic movements. **Volcanogenic-sedimentary deposits** are associated with orogenic belts and foredeeps (marginal-continental orogens and adjacent marginal parts of platforms on the sea shelf and lakes of volcanic regions) during active volcanism. Usually, deposits of the volcanogenic-sedimentary type are of Neogene-Paleogene age, and less often of the Cretaceous and Carboniferous. **Eluvial deposits** form in conditions of platform development in the marginal parts of cratons and marginal-continental orogens, in a period of stabilization of tectonic movements (Distanov et al., 2000) and have a small distribution in Russia. **Hydrothermal deposits** are confined to marginal-continental orogens with zones of deep faults, on the edges of continental blocks in the era of activation of hydrothermal processes in zones of active volcanism.

## 4. Formation of volcanogenic-sedimentary bentonite-bearing provinces

As we have mentioned above, only two genetic types of bentonites are found in Russia: volcanogenic-sedimentary and sedimentary. A.A. Sabitov (Sabitov et al., 2010) identified 8 bentonite provinces including both genetic types. This article considers the structural features and formation of only volcanogenic-sedimentary bentonite provinces, as most promising sources of high-quality raw material.

Volcanogenic-sedimentary bentonite-bearing provinces are a series of bentonite deposits close in age and genesis, occurring in the same geological structure and, as a rule, associated with the zones of development of coal basins (Machabeli, 1980; Belousov, 2016; Belousov et al., 2017). The relationship between bentonite clays and coal deposits is rooted in the fact that coal sedimentation conditions are favorable to the formation of bentonites from volcanic material: coastal shallow basins, bays, lakes or swamps with standing fresh or saltwater.

The largest and most well-studied volcanogenic-sedimentary bentonite-bearing provinces of Russia are located in the Republic of Khakassia and in the Sakhalin region.

The deposits in the **Republic of Khakassia** are localized, with the occurrence of the continental tuff-sand-clay argillaceous coal-bearing formation of the Carboniferous age and are located within the Chernogorskiy and Izykhskiy coal areas of the Minusinskiy basin, confined to the Altai-Sayanfolded zone (Fig. 3). This bentonite-bearing province includes the



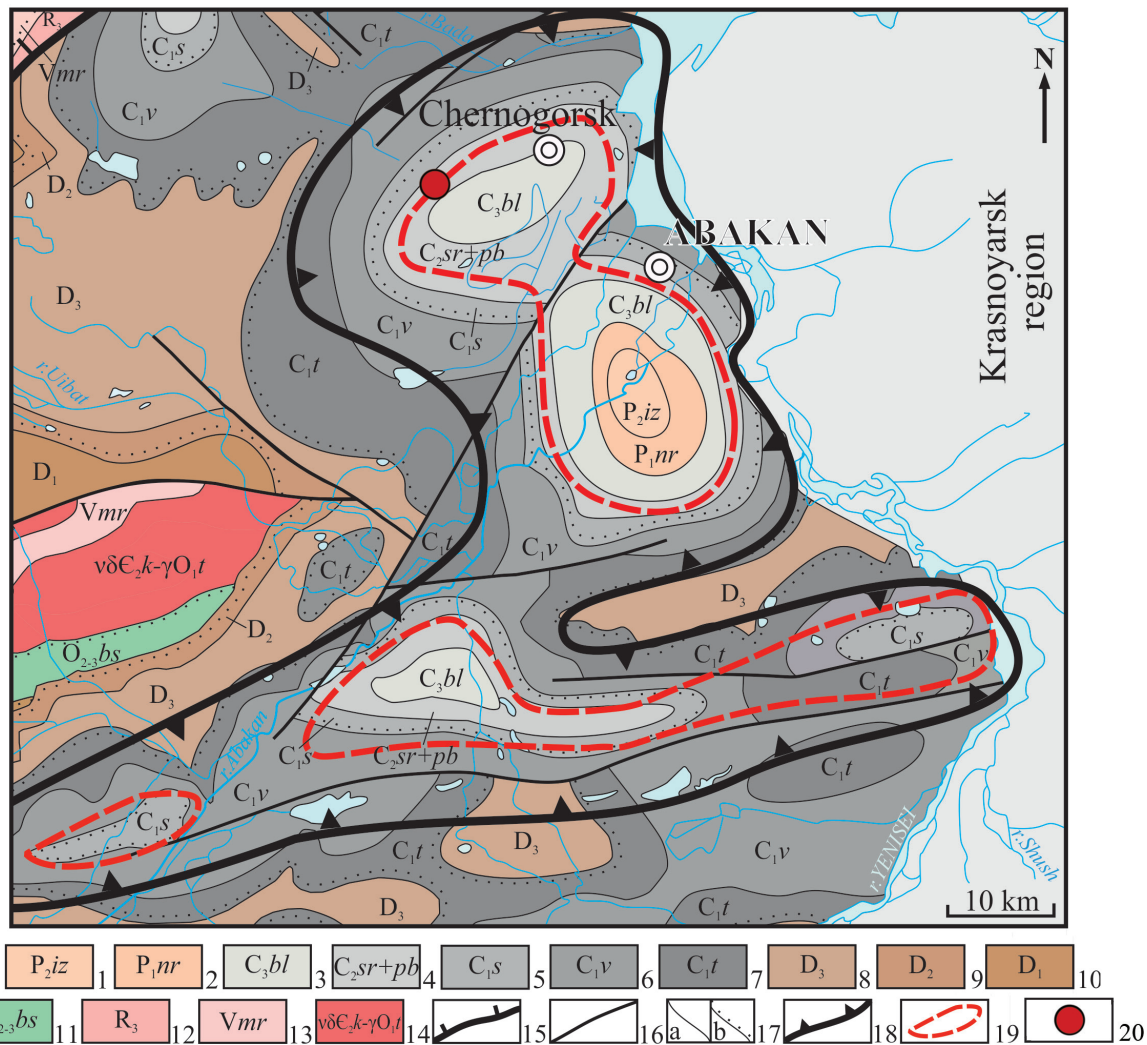


Fig. 3. Geological map of the Chernogorsky basin (Strunin, Glukhov, 2002, with edition). 1-3 – Paleogene system, Paleocene-Eocene, siltstones, mudstones, sandstones, coal: 1 – Izykhskiy suite; 2 – Narilkovskaya suite; 4-7 – Carboniferous system, Lower-Upper sections (3 – Beloyarskaya suite, sandstones, siltstones, mudstones, coal, 4 – Sarskaya, Chernogorskaya, Poberezhnaya suite, siltstones, sandstones, mudstones, limestone, bentonite clay, coal, 5 – Serpukhov stage, sandstones, conglomerates, siltstones, coal, 6 – Viséan stage, sandstones, conglomerates, siltstones, coal, 7 – Tournaisian stage, tuff sandstones, limestone, conglomerates); 8-10 – Devonian system (8 – Upper section, mudstones, sandstones, marls, 9 – Middle section, sandstones, limestone, siltstones, marls, 10 – Lower section, sandstones, siltstones, gravelites, basalts); 11 – Ordovician system, Middle-Upper sections (Bolshesyrskaya suite, tuffs, trachyandesites, trachybasalts); 12 – Riphean, Upper section (limestone, dolomites, silicites); 13 – Vendian (Martyukhinskaya suite, limestone, dolomites, silicites); 14 – Middle Cambrian-Late Ordovician intrusions (granites, granodiorites, syenites, gabbrodiorites, gabbro, monocytes); 15 – overthrusts; 16 – faults; 17 – geological boundaries (a – reliable; b – of different facies); 18 – borders of the Yuzhno-Minusinsk coal basin; 19 – bentonite-bearing and potentially promising areas; 20 – 10th Khutor deposit.

following deposits and sites: 10th Khutor, Karatigeyskoe, Solnechnoe, Karasukskoe, Izykhskoe, and Podsinenskoe. At the moment, active work is underway in the region to expand the raw material base, which is likely to lead to the development of new deposits in the coming years. The volcanogenic-sedimentary formation is composed of tuffs, tuffites, conglomerates, sandstones, siltstones, mudstones, limestones, carbonaceous rocks with layers, and interbeds of coal and bentonites.

The highest quality and most studied deposit of bentonite is the 10th Khutor, located 8 km southwest of the city of Chernogorsk, Ust-Abakan region. Most of the deposit has been abandoned. The remaining reserves

amount to 3 Mt (State balance of mineral reserves of the Russian Federation: Bentonite Clays, 2018). Five layers can be distinguished by their lithological composition of sediments: underlying, lower productive, interproductive, upper productive, and overlapping. The bedding of the rocks within the deposit is monoclinic with a north-east strike and fall to the southeast at an angle of 6-8 degrees. Based on the fall, the layers were traced at 100-125 m and a depth of up to 25 m. No tectonic disturbances were found within the field. Quaternary sediments have insignificant (up to 1 m) thickness and are represented by loam, sandy loam, and sand. According to their mineral composition, the

bentonites of the 10th Khutor deposit consist of 60-75 % alkaline earth montmorillonite and are characterized by high sorption and heat-resistant properties. Impurities are represented by quartz, microcline, albite, calcite, and fragments of coal. Gypsum and pyrite may be present in an insignificant amount (less than 1 %), depending on the formation (Krupskaya et al., 2016; Belousov et al., 2017; Krupskaya et al., 2018).

It is worth noting that the entire Yuzhno-Minusinsk Depression is a promising region for bentonite exploration. The coal-bearing formation is bentonite-bearing and includes a series of smaller deposits and occurrences of bentonite clays (Belousov et al., 2017).

Another important region is the **Sakhalin region**, within which bentonites are genetically and spatially associated with the Miocene tuff-sedimentary coal-bearing strata of the Upper Danube and Lower Danube Formations present in the southern part of the island. On the east coast they are found in the area of Makarov town, Tikhmenevo, Vakhrushevo, and Vzmorie villages; on the west coast – in the Ulegorsk, Gornozavodsk towns, and on the Tonin-Anivsky peninsula. The region's total prognostic resources amount to 37 Mt (Merenkov, 2002). Tikhmenevskoe, Vakhrushevskoe, and Makarovskoe are the most interesting deposits. They are located in the Poronaysky district along the east coast of the island. Estimated resources amount to 4.6 Mt (Sabitov et al., 2007). The geological structure and mineral composition will be considered on the example of the Tikhmenevskoe deposit, as the most studied in the region.

The Tikhmenevskoe deposit of bentonite clays is located 1.5 km west of the village Tikhmenevo in the Poronaysky district. The West coal mine is located in its northern part. In the area among the tufa-sedimentary coal-bearing sediments of the Upper Danube formation (Fig. 4), six sub-meridional bentonite layers with an eastward dip at angles of 30 to 80° have been identified. The layers are confined both to the roof and to the bottom of the coal seams. The thickness of the layers varies from 0.5 to 10 m. The length of the layers can reach 1.5 km (Sabitov et al., 2007; Belousov, Nasedkin, 2015).

According to their mineral composition, clays consist of 60-95 % of Na- and Ca-Mg-montmorillonite. Quartz, cristobalite, feldspars, amorphous silica, fragments of coal, and volcanic glass are present as impurities. The inferred resources of bentonites in the area of the village Tikhmenevo amount to 862,000 tons; and estimated resources – to 3.4 Mt (Sabitov et al., 2007)

## Conclusion

Having studied the mineral resource base of bentonite clay deposits in Russia and the CIS countries, their geological and tectonic position, and their formation features, the following conclusion can be drawn.

The estimated reserves of bentonite clays in Russia

amount to 335 Mt. The most important, currently exploited deposits are (measured and indicated resources): 10th Khutor in the Republic of Khakassia, with reserves of 3 Mt; Biklyanskoe and Berezovskoe in the Republic of Tatarstan, with total reserves of 37.8 Mt; Zyryanskoe in the Kurgan region, with reserves of 14 Mt; Izhberdinskoe and Saraybashskoe in the Orenburg region, with total reserves of 7 Mt; and Nikolskoe and Maydan-Bentonitovoe in the Voronezh region, with total reserves of 1 Mt. The Kheu deposit (Republic of Kabardino-Balkaria), as well as the Solnechnoe and Karatigeyskoe (Republic of Khakassia), with estimated reserves of 5.4 Mt, are ready for development.

Production volumes in Russia in 2017 amounted to more than 735,000 tons of bentonite products, a 150,000-ton increase compared to 2008. In the coming years, the production of bentonite clay might increase with the commissioning of deposits in the Republics of Kabardino-Balkaria (Kheu) and Khakassia (Solnechnoe and Karatigeyskoe).

The reserves of the main bentonite deposits located in the CIS countries (excluding Russia) amount to 740 Mt of raw materials. About a third of that is located in the Republic of Azerbaijan with the Dash-Salahinskoe and Aplidskoe deposits, as well as the Khizyn group of high-quality alkaline hydrothermal bentonite deposits. Important suppliers of bentonite clay to Russia are also the Republics of Armenia and Kazakhstan.

In terms of genetic classification, sedimentary and volcanogenic-sedimentary bentonites are the only types found in Russia, with a small amount of eluvial bentonites. The majority of bentonite deposits in the Russian Federation belongs to the sedimentary type (Biklyanskoe, Berezovskoe, Zyryanskoe, Izhberdinskoe, Saraybashskoe, Nikolskoe, Maydan-Bentonitovoe, etc.). Volcanogenic-sedimentary-type bentonites are characterized by the high quality of the raw materials and the complex geological structure of the deposits. These types include the 10th Khutor deposit in the Republic of Khakassia, a group of deposits on the island of Sakhalin (Table 1), and deposits in the Republic of Crimea.

Deposits of volcanogenic-sedimentary genesis are often spatially and genetically related to coal basins and form bentonite-bearing provinces. The connection between bentonite clays and coal deposits is explained by the fact that the conditions of sedimentation of fossil coals are favorable for the formation of bentonite deposits. The presence of acid volcanism in the region and the widespread development of coal basins are potentially favorable conditions for the formation of volcanogenic-sedimentary bentonite-bearing provinces. In Russia, examples of such provinces are the Republic of Khakassia and Sakhalin Island.

Based on their geological and tectonic position and the characteristics of their mineral composition, we

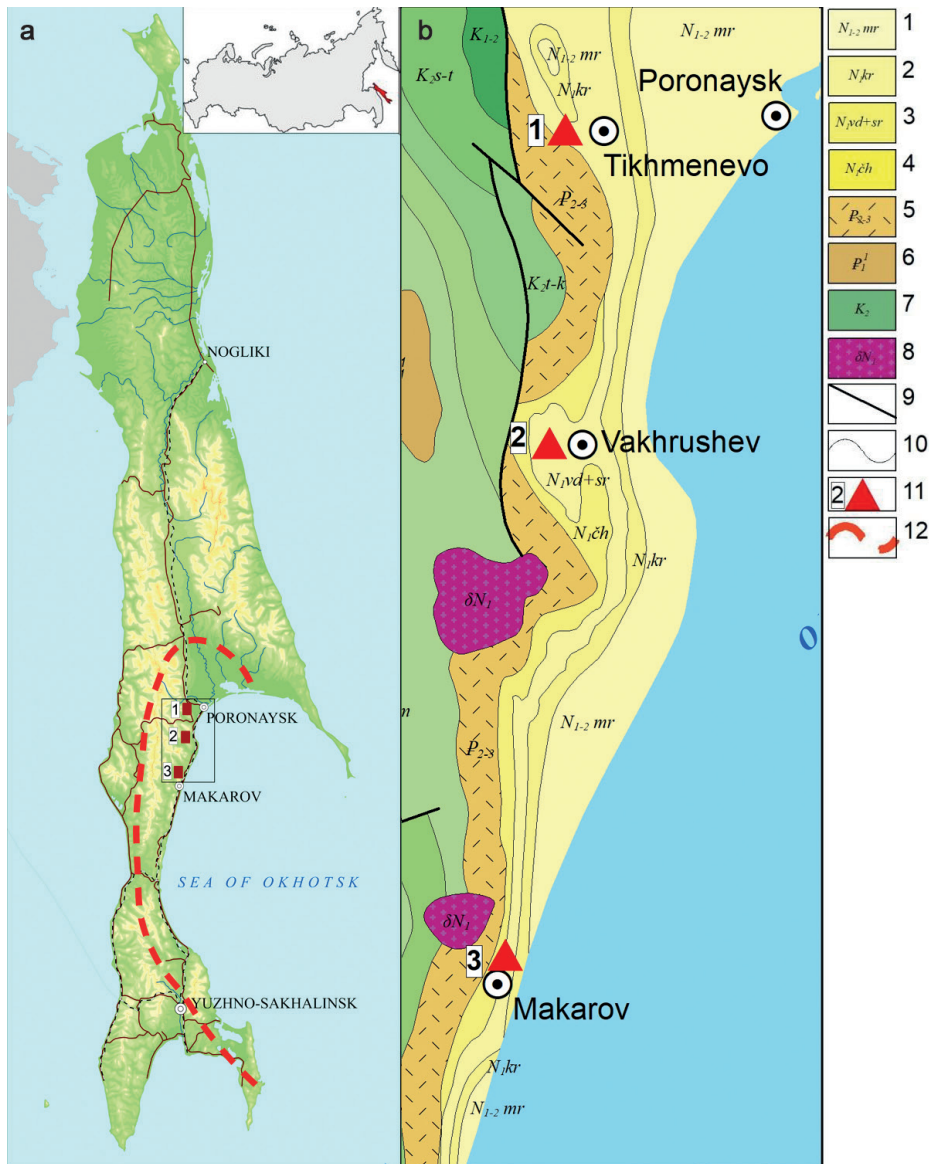


Fig. 4. Bentonites of the Sakhalin Island: a – location of promising sites (Sabitov et al., 2007); b – geological diagram of the structure of the southwestern part of the island (Strelnikov, 2016, with additions and revision). 1-4 – Middle-Lower Miocene (1 – Maruyamskaya suite, sands, sandstones, silts, loose clays, brown coals, 2 – Curassiyskaya suite, siliceous siltstones, diatomites, sandstones, tuffites, marl nodules, 3 – Verkhneduyskaya and Sertunayskaya suites, ore-bearing, sandy-clay coal-bearing formation, 4 – Chekhovskiy sedimentary-volcanogenic complex, tuff-aleurolites, tuffs, basaltic lava, andesibasalt); 5-6 – Paleogene system (5 – Kolchanskaya and Sizimanskaya suites, trachyriolites, trachytes, rhyodacites and andesites and their tuffs, andesibasalts, basalts, trachybasalts, 6 – Sinegorskaya suite, siltstones, mudstones, sandstones, carbonate nodules); 7 – Lower Cretaceous system (siltstones, mudstones, sandstones, tuffs); 8 – Early Neogene, Chekhovskiy complex (diorites, granodiorites, quartz diorites, diorite-porphyrines); 9 – faults; 10 – geological boundaries; 11 – prospective sites (1 – Tikhmenevskoe, 2 – Vakhrushevskoe, 3 – Makarovskoe); 12 – the areola of the development of bentonite deposits within the Sakhalin Island.

can assume that the bentonite deposits in the Republic of Kabardino-Balkaria, in Khabarovsk, and in the Primorsky and Krasnoyarsk Territories also belong to the volcanogenic-sedimentary bentonite-bearing provinces. These regions could be promising for deposits exploration and could serve as sources for expanding the mineral resources base of high-quality alkaline bentonites in Russia.

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