IECMS 2020

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Conference Proceedings Paper

Carboniferous bentonites of 10th Khutor deposit (Russia): geology, mineralogy, genesis and properties.

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Received: date; Accepted: date; Published: date

Abstract: 10th Khutor deposit is located in the Republic of Khakassia and confined to the coal-bearing formation of Carboniferous age within the development of continental tuff-sandy-argillaceous sediments. In terms of mineral composition, bentonites are mainly composed of Al-rich montmorillonite. The content of montmorillonite reaches a maximum of 70-75%, with an average content of 55 to 70%. It is one of the main sources of bentonite for the metallurgical and foundry industries in Russia. One of the distinctive features of bentonites from the 10th Khutor deposit is that despite the age of the deposit, about 350 million years, and the presence of an initial phase of metamorphism, as evidenced by the formation of hard coal, these bentonites retained the ability to swell and have high thermal stability. The formation of bentonites is associated with the decomposition of volcanic ash of rhyodacite and dacite composition in zones of shallow seawater - bays and lagoons. The properties of bentonite were influenced by the initial stage of metamorphism.

The main purpose of this work was to establish the conditions for the formation of this deposit, as well as to study the features of the mineral composition and physicochemical properties of these raw materials. In addition to fundamental issues, the aim of the work was applied research on the properties and quality of bentonites.

Keywords: bentonite, montmorillonite, genesis, volcano-sedimentary rocks, diagenetic alteration, volcanic glass.

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1. Introduction

The 10th Khutor deposit is located in Siberia, 8 km southwest of the city of Chernogorsk (Republic of Khakassia, Russia) and is the main source of bentonite in Russia, with an annual production of about 300 thousand tons of bentonite products. One of the distinctive features of bentonites from the 10th Khutor deposit is its high thermal stability, due to the structure of montmorillonite. It should also be noted that despite the age of the deposit, about 350 million years, and the presence of an initial phase of metamorphism, as evidenced by the formation of hard coal, these bentonites retained the ability to swell.

Despite the detailed exploration of the 10th Khutor deposit in previous periods, studies of the genesis and structural features of bentonites have not yet been carried out. The main purpose of this work was to establish the conditions for the formation of this deposit, as well as to study the features of the mineral composition and physicochemical properties of these raw materials. In addition to fundamental issues, the aim of the work was applied research on the properties and quality of bentonites.

2. Materials and Methods

The work is based on field works at the 10th Khutor deposit in 2014 and 2019, during which the authors took the samples from productive layers of bentonite. For comparison and detailed study of montmorillonite structure, an industrial sample from the 6th productive layer (IB-6) with a relatively high content of montmorillonite (72%) was added to the studied collection. Also, to study the structural features of montmorillonite, a fine fraction <1 μm was separated from a 3% aqueous suspension using an OS-6MTs laboratory centrifuge (Dastan, Kyrgyzstan). The centrifugation conditions: 9.5 min at 1200 rpm.

X-ray diffraction patterns were obtained with an Ultima-IV X-ray diffractometer (Rigaku, Tokyo, Japan). The mineral composition was analyzed according to the method of Moore & Reynolds [1], the quantitative composition was estimated with the Rietveld method [2] using the Profex software (Version 3.14.3), [3].

Chemical analysis was determined with X-ray fluorescence spectrometry (XRF) using an Axios mAX XRF spectrometer (PANalytical, Almelo, The Netherlands) at IGEM RAS (Moscow). Samples were dried at 110 °C and prepared by fusion with lithium borate at 1200 °C. The iron content was determined only as the total Fe2O3, regardless of the actual valence state of the Fe.

The microstructure of the sorbents was studied with scanning electron microscopy (SEM) using a LEO1450VP SEM (Carl Zeiss, Oberkochen, Germany). Samples for SEM were prepared in the form of individual particles and aggregates.

The specific surface area was determined with a Quadrasorb SI/Kr analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). Adsorption was performed at liquid nitrogen temperature (77.35 K). Microporosity was determined by the T-Method.

Determination of CEC was carried out by two methods [4] - by adsorption of methylene blue (MB) [5] and of Cu (trien) [6,7].

Technological properties were determined on industrial samples of bentonite powder.

3. Results and Discussion

3.1. Regional geology and geology of the 10th Khutor bentonite deposit

The deposits in the Republic of Khakassia are localized within 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. 1) [8]. In addition to the 10th Khutor deposit, the Karatigeyskoe, Solnechnoe, Karasukskoe and Solnechnoe bentonite deposits are confined to the same age range within the basin. The geological structure of the the Minusinskiy basin consists of volcanic, volcano-sedimentary, terrigenous and carboniferous sediments of Devonian and Carboniferous age. The coal-bearing strata of the Middle and Upper Carboniferous age contain large deposits of hard coal. A special geological and genetic type of bentonites, associated with coal-bearing formations, is distinguished [9,10].

The 10th Khutor deposit is located in the northwestern part of the Chernogorsky basin. The bentonite-bearing strata is confined to the lower part of the coal formation. The formation is composed of conglomerates, sandstones, siltstones, mudstones, limestones, carbonaceous rocks with seams and interlayers of hard coals and bentonites.

In the structure of the tuffaceous-sandy-clayey bentonite-bearing formation of the Carboniferous age, 5 benches containing layers of bentonite are distinguished [11]. The second bench is of industrial importance, confined to Sarskaya suite (C1-2sr) of the Early-Middle Carboniferous strata, with a thickness of 35 m. This bench consists of 6 bentonite layers, interbedded with coal seams and tuff-terrigenous material. Bentonite layers have monoclinal bedding with a northeastern course and dip to the southeast at an angle of 6–8 °, with a mean thickness from 1.5 to 4 m. The layers are separated by terrigenous and carbonaceous rocks.

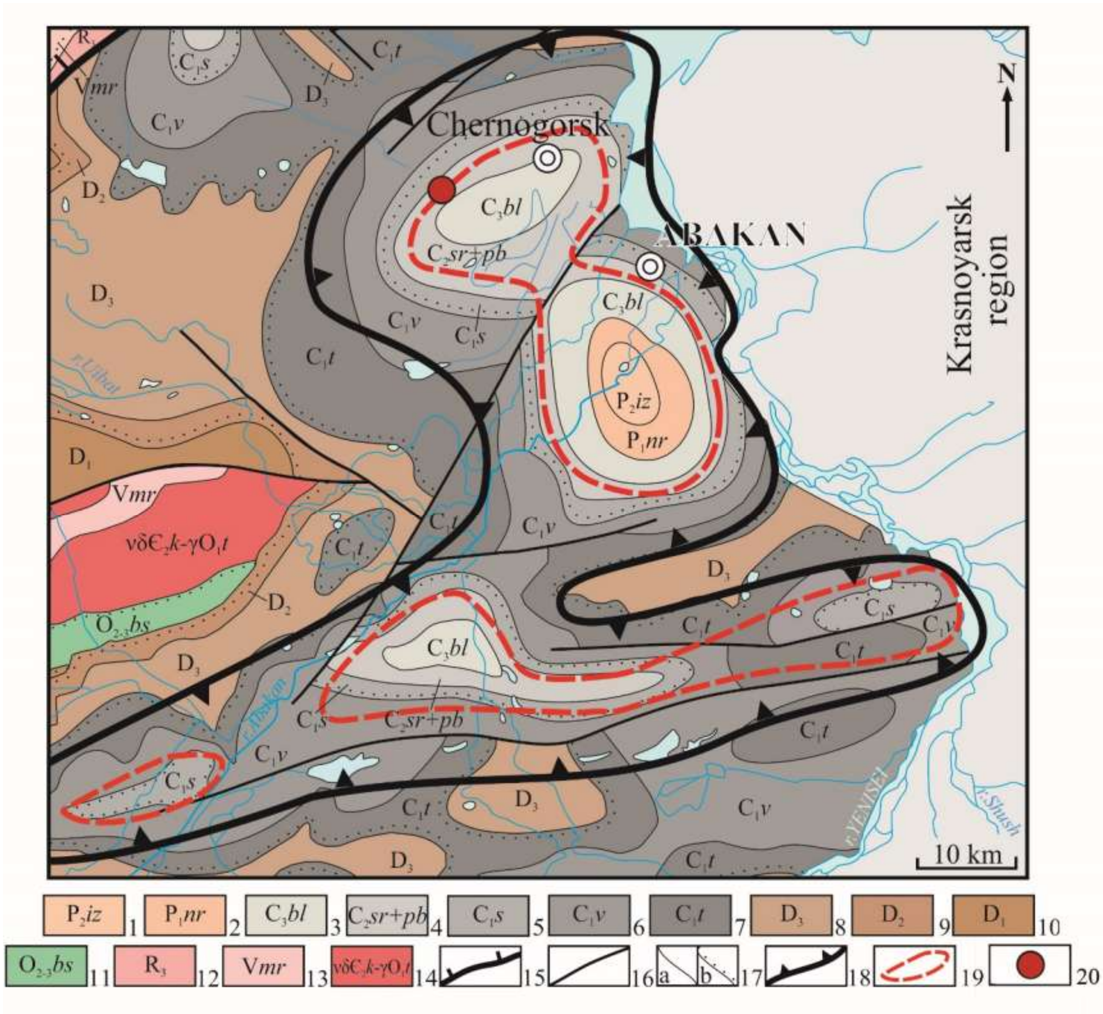

Figure 1. Geological map of the Chernogorsky basin (Strunin, Glukhov, 2002, with edition). Legend: 1-3 - Paleiogene system, Paleocene-Eocene, siltstones, mudstones, sandstones, coal: 1 - Iikh suite; 2 - Narylk Formation; 4-7 - Carboniferous system, lower-upper sections (3 - Beloyarskaya suite, sandstones, siltstones, mudstones, coal, 4 - Sarsky, Montenegrin, coastal retinues, siltstones, sandstones, mudstones, limestone, bentonite clay, coal, 5 - the Serpukhov layer, sandstones, conglomerates, siltstones, coal, 6 - the Visean layer, sandstones, conglomerates, siltstones, coal, 7 - the Tournaisian layer, 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, 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 - thrusts; 16 - faults; 17 - geological boundaries (a - reliable; b - facies different); 18 -

borders of the Yuzhno-Minusinsk coal basin; 19 - bentonitiferous and potentially promising areas; 20 - 10th Khutor deposit.

3.2. *Analytical research*

3.2.1. *Structure and texture*

Bentonites are mostly gray, dark gray, less often greenish or bluish gray with a massive texture (fig. 2a) with interlayers of coal or coalified rocks of 0.1-1 m thick (fig. 2b). The main part of the bentonite mass has a pelitic or silty-pelitic structure with inclusions of individual detrital grains and authigenic minerals up to 0.7 mm and sometimes with lenses and interlayers of carbonized organic matter. Montmorillonite is represented by flat and wavy smectite flakes ranging in size from 0.5 to 2-3 microns. The clay mass contains meso- and macropores with a diameter of 4 to 7 μm. Studies of the crystalline fraction, washed from the clay, made it possible to find isomorphic fragments of volcanic glass (fig.2c,d). Transformed feldspar grains, as well as relics of volcanic glass with a porous structure, are observed in the electron microscope images.

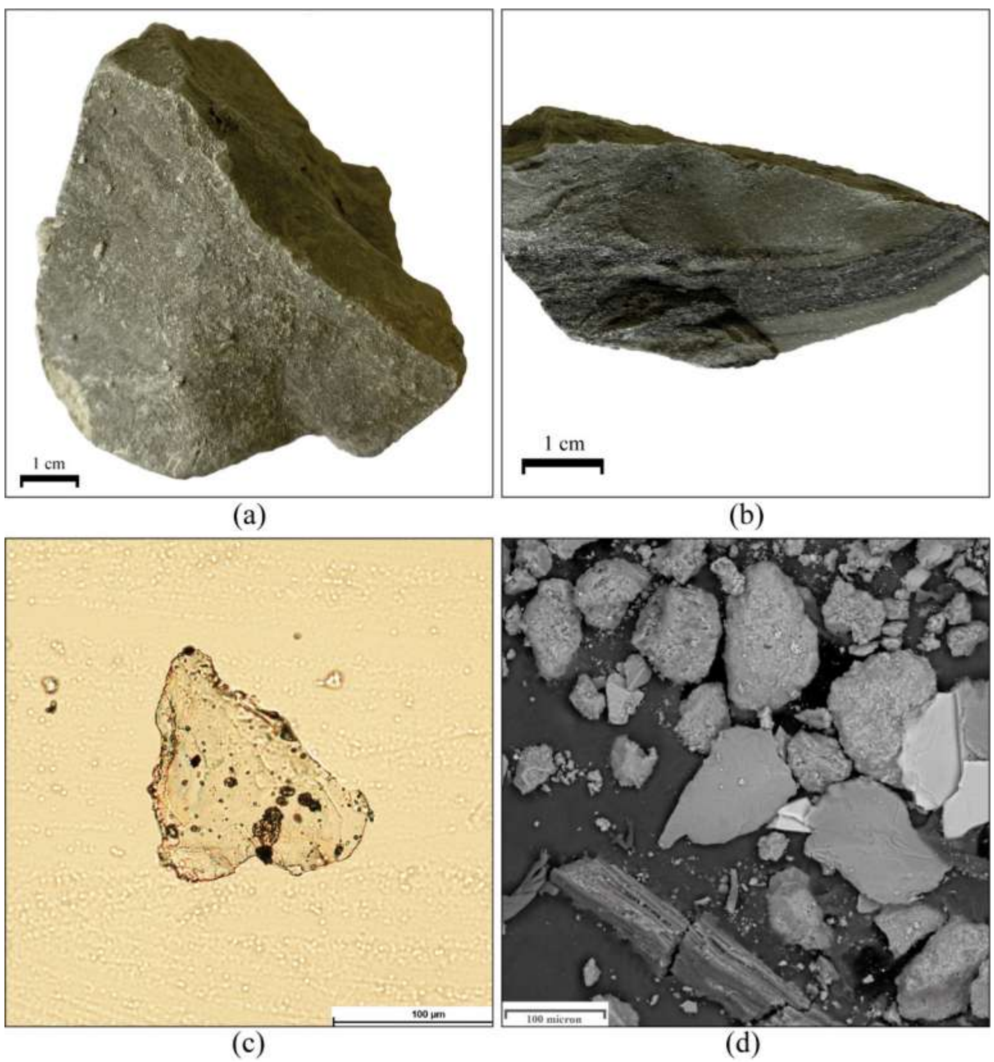

Figure 2. Macro- and microphotographs of bentonite samples and crystalline fraction*: a, b – bentonite samples; c, d* - relics of volcanic glass.

3.2.2. *Mineral* composition

Bentonites of the 10th Khutor deposit are rocks of predominantly montmorillonite composition with admixture of kaolinite, chlorite, illite, quartz, field spars, calcite and gupsum (table 1). The maximum content of montmorillonite is typical for the IV, V and VI layers and reaches a maximum of 70-75% with an average content of 63%. In addition to montmorillonite, all beds contain kaolinite (0.7-6.8%), illite (2-5%) and chlorite (0.1-6.2%). Quartz, potassium feldspar and plagioclase are the most widespread among non-clay minerals. Small amounts of gypsum (0-3.1%), calcite (0-4.6%), ankerite (0-1.4%) and hematite (average of 0-0.6%, with single samples of up to 3%) are present in all layers. At the same time, gypsum crystals in bentonite samples reach rather large sizes - up to 0.5 cm diameter. Siderite (up to 10-11%) is present only in the top of the V and the bottom of the VI layer. Also, there are single grains of jarosite (up to 3%) and rutile (up to 0.5%).

The purified sample of bentonite (fraction <1 μm) predominantly consisted of 92.4% Na-montmorillonite [12]. The bulk sample is of alkaline-earth type. Thus, the natural bentonite contains two phases of montmorillonite with different cationic compositions, which possibly traces different stages of bentonite formation or transformation of pore water composition.

Table 1. Mineral composition of the examined samples, %.

Layer	Smectite	Kaolinite	Illite	Chlorite	Quartz	Microcline	Albite	Gypsum	Calcite	Siderite	Ankerite	Goethite	Anataz	Hematite
II	65,5	2,9	3,7	1,4	9,8	5,5	5,7	0,4	4,6	0	0,4	0	0	0,1
IV	72	1	4,5	0,5	10,1	5,3	5,3	0	1,3	0	0	0	0	0
V	63,4	3,3	3,6	0,3	13,6	6,3	7	0,3	1,3	0	0,8	0	0	0,1
VI	70,2	1,6	2,4	1,2	12,6	5,6	4,7	0,5	1,1	0	0	0	0	0,1
IB-6	72,3	0,5	3,7	0,7	12,1	4,1	4,4	0	0,7	0,7	0,8	0	0,7	0
<1 μm	92,4	0,5	3,7	0,7	2,0	0	0	0	0	0	0	0	0,7	0

3.3. Genesis and conditions of formation

The bentonite occurrence of this area is confined to the Minusinsk coal basin. As is known, the conditions of sedimentation of fossil coals are favorable for the formation of bentonites from pyroclastic material, and at the same time, the composition of trace elements of the studied bentonites is characteristic of igneous rocks [13]. For this reason, a diagenetic model of bentonite formation has been proposed. The original tuff material has not been preserved along the deposit. The ratios of trace elements were used to establish some characteristics of the source rocks [14,15]. The results obtained indicate the rhyodacite and dacite composition of the initial ashes.

The study of paleogeographic maps [16] made it possible to reconstruct the sedimentary environment in the studied region. It was a foredeep with the accumulation of sediments transported from the neighboring mountain structures. The beginning of the accumulation of sediments of the Sarskaya suite was accompanied by the activation of the Western Sayan volcanism. The Minusinsk basin at that time was a shallow water zone with an inland sea, bays and lagoons or a system of interconnected large lakes, forming a single water body of sea-lake type.

3.4. Properties

The geological conditions of the formation of bentonites of the 10th Khutor deposit had a strong influence on their properties. After the diagenetic stage, the already formed bentonites were affected by the initial stage of metamorphism, as evidenced by the seams of hard coal. Such conditions led to significant compaction of bentonites, mainly due to the degradation of microporosity, so that the specific surface area is determined only by the presence of meso- and macropores and equal to 13 m2/g while preserving the ability to swell.

The testing of technological samples indicates the high quality of sandy-clayey forms based on this bentonite. However, to achieve such quality characteristics, it is necessary to carry out mechanical activation and aging of the bentonite with the addition of soda ash. The swelling index of the original bentonite is 4 ml/2g, however, after activation with soda ash, it increases to 27 ml/2g.

The result of CEC determination by MB on natural sample ranges from 23–27 cmol.kg−1 for samples from layer II and 54-63 cmol.kg−1 for samples from layers IV, V and VI. The CEC values measured with the copper complex showed higher values, namely 31-35 cmol.kg−1 for layer II and 50-80 cmol.kg−1 for samples from layers IV, V and VI.

4. Conclusions

The 10th Khutor bentonite deposit, located in the Republic of Khakassia (Russia) within the development of continental tuff-sandy-argillaceous formation of the Chernogorsky basin which is confined to the Early-Middle Carboniferous sediments of the Sarskaya suite (C1-2sr). The bench consists of 6 layers of bentonite, interbedded with coal seams and tuff-terrigenous material. An average content of montmorillonite is 55-70%. It was found that sample of raw bentonite belongs to the alkaline-earth type, while purified sample with fraction <1 μm corresponds to sodium montmorillonite.

The trace element composition of bentonites, as well as the presence of relics of volcanic glass and feldspar with a porous and layered structure, indicate that these bentonites belong to the diagenetic type with rhyodacite and dacite composition of the initial ashes.

The study of paleogeographic maps, as well as the peculiarities of the mineral composition, suggest that the accumulation of tuff material took place in the zone of shallow sea water - bays and lagoons or in the system of interconnected lakes. The influence of metamorphism, as evidenced by seams and packs of hard coal, affected the textural and surface properties of bentonites resulting in the absence of microporosity, a low specific surface area and low moisture content in the raw materials.

Author Contributions: Petr Belousov: geological exploration, preparation of the material, and wrote the Paper; Nikita Chupalenkov, Victoria Krupskaya, Olga Dorzhieva: geological exploration, preparation of the material; George Christidis: analysis and preparation of the material, wrote the Paper, Sergey Zakusin, Ivan Morozov: carried out X-ray diffraction analysis; Mikhail Chernov: carried out SEM pictures.

Funding and Acknowledgments: This work was financially supported by the Russian Science Foundation (project No. 16-17-10270). The authors also express their gratitude to the "Bentonit Company" and "Bentonite of Khakassia" companies for the provided materials and the opportunity to conduct field work at the 10th Khutor deposit.

Conflicts of Interest: Declare conflicts of interest or state "The authors declare no conflict of interest." Authors must identify and declare any personal circumstances or interest that may be perceived as inappropriately influencing the representation or interpretation of reported research results. Any role of the funders in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript, or in the decision to publish the results must be declared in this section. If there is no role, please state "The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results".

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