# Volcanic Zeolites from the Yagodninskoe Deposit, Kamchatka

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**Abstract**—This work is concerned with classification and study of the composition and properties of hydrothermal zeolites from the Yagodninskoe deposit, (Kamchatka) which were formed in volcanic rocks. The study involved X-ray phase analysis and X-ray fluorescence, optical and scanning electron microscopy. We determined specific syrface AREA the pore size distribution, as well as cation exchange capacity in zeolites. The study resulted in the identification of four main rock types at the deposit: the original unaltered perlites, zeolites rock, zeolitized tuffs, as well as poorly zeolitized tuff breccias. The Content of zeolite group minerals reaches 70%. The minerals mostly include clinoptilolite and, to a lesser degree, mordenite, stilbite, and heulandite. The zeolites are of the alkaline type, with the cation exchange capacity equal to 205.9 mg-equi/100 g. It has been found that these zeolites were mostly formed from perlites and tuff breccias. It is pointed out that the Yagodninskoe zeolites are high quality minerals, and make a promising object of further exploration.

Keywords: Kamchatka, volcanic rocks, Yagodninskoe deposit, zeolite, perlite, clinoptilolite, natural sorbents, hydrothermal genesis

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# INTRODUCTION

Zeolites are a valuable mineral raw material: apart from sorbents, zeolites are used in oil chemistry, in construction, agriculture, livestock farming, food production, and medicine. Zeolites make a mineral group; the group includes minerals such as clinoptilolite, mordenite, heulandite, shabazite, and several others. Due to isomorphous alteration and a specific structure, zeolites possess a high cation exchange capacity, which makes them effective as a sorbent in the sorption of heavy metals and some organic compounds.

The area of Russia has been found to contain about 120 zeolite deposits and occurrences, but the state register of reserves only includes 18 zeolite deposits with reserves of category  $A + B + C_1$  being 594 million tons and those of category  $C_2$  799 million tons (*Gosudarstvennyi balans*, 2019). Of these, only 3 deposits are being developed: the Khotynetskoe in Orel Region, Khonguruu in the Republic of Sakha, and the Kholinskoe deposit in Transbaikalia. An approximate total of 944 thousand tons zeolite is extracted annually worldwide. Russia holds the 10th place with an annual extraction on the order of 60–80 thousand tons. As well, a few thousand tons of raw zeolite are being imported by Russia from countries of the former Soviet Union. In Russia, zeolites are mostly used as a filler in concrete, in the production of glass foam, as a food additive for humans and animals, as a condenser of moisture and as soil for plants, as well as hygienic bedding for animals. The use of volcanic zeolites to purify household water and industrial waters is rather limited. The main requirements to be imposed on raw zeolite include cation exchange capacity, the concentration of zeolite minerals, the strength of the rock, as well as the absence of harmful admixtures, heavy metals, and radionuclides.

This insignificant degree of exploration for raw zeolite rock in Russia is due to the fact that high quality volcanic zeolites are mostly confined to the Russian Far East, hence are subject to complex logistics.

Consideration of the conditions favorable to the generation of zeolites yields their main genetic types: volcanogenic-sedimentary, volcanogenic-hydrothermal, and sedimentary (Distanov, 2000). All these three types have been discovered in Russia.

1. Characteristic for the **sedimentary type** of zeolite deposit is their generation in marine, platform basins with a quiet hydrodynamic environment in the conditions of humid or semi-arid climate. The materials from which they are generated include alumosilicate gels, clay minerals, and amorphous biogenic silica (diatom algae and tripoli). This material comes with river runoff into marine and lake basins. The type is typically found in deposits of the so-called zeolitecontaining tripoli, diatomite, and gaize, in which the concentration of zeolites does not exceed 30-35%(Belousov, 2023). Deposits of this type are widely abundant in central Russia and in Siberia.

2. Zeolites of the volcanogenic-sedimentary type are formed under the conditions of marine and lake basins in arid or humid climate. The necessary requirement for their generation consists in high pH of the sedimentation environment (>7.5), the closed type of sedimentation basin or the presence of stagnant water, low water/volcanic ash ratios, an excess of free silica, and a sufficient amount of magnesium in the solution. Zeolite generation is related to devitrification of volcanic ash and tuffs in alkaline solutions. The final formation of a zeolitized deposit occurs during the diagenetic phase. As regards the tectonic setting, this type of deposit is confined to areas of Mesozoic-Cenozoic folding and activation, to marginal continental and rift-related structures: zones of marginal platforms, of intermontane troughs, and to areas of active tectonic activity. Zeolites of this genetic type, as well as bentonite clays (Belousov and Rumvantseva, 2023), are formed in spatial conjunction with coal basins, but are situated along their periphery, unlike bentonites. Zeolites are represented by clinoptilolite, more rarely by mordenite, analcime or phillipsite.

3. The Yagodninskoe deposit belongs to the **hydro**thermal type whose generation is similar to the volcanogenic-sedimentary type, i.e., metasomatic replacement of tuffs and acid volcanic rocks as a result of low temperature leaching. This type of deposit is confined to volcanic belts where deposits are formed on slopes of paleo volcanoes, or occasionally near zones of deep-seated faults. Zeolites of the hydrothermal genesis frequently lie in the same geological structure where perlite and bentonite deposits are situated, while occasionally being within the same complex deposit. This type of deposit yields high-quality raw materials.

The main studies of geological structure and mineral composition for the rocks of the Yagodninskoe deposit were carried out in the 1980–1990s, and are reported in the publications of V.V. Nasedkin (Nasedkin, 1985) and in reports<sup>1</sup> of L.P. Zhdanov and A.V. Makhanko. More recent research was concerned with the petrophysical properties of zeolites (Demina, 2015) and with changes in the physical and mechanical properties of perlites (Frolova, 2017). The main goal of the present paper is to develop a classification of hydrothermal zeolites at the Yagodninskoe deposit based on detailed mineralogical surveys, on the identification of structural and textural features of the rocks, as well as on a study of their properties.

## THE GEOLOGY OF THE YAGODNINSKOE DEPOSIT

The Yagodninskoe deposit lies in southern Kamchatka, in Elizovo District, 60 km west of Petropavlovsk-Kamchatsky and 5 km north of the Bolshe-Bannye Springs; it is situated near the eponymous perlite deposit. The area is a mountainous volcanic region with absolute heights of 900–1200 m.

Geologically, the area is confined to the Verkhne-Karymshina volcano-tectonic structure that is part of the South Kamchatka anticlinorium. The Verkhne-Karymshina structure shows a complex tectonic pattern; it is subdivided by a set of nearly east—west, northeast, and ring faults (Fig. 1). Thermal waters of the Bolshe-Bannye hydrothermal system are discharged along one of these major nearly east—west striking faults (Nasedkin, 1985).

With regard to age, and the character of displacements in the structural plan, the features of this area are classified as belonging to the same structural stage with three substages: the lower structural substage is composed of rocks of the Paratunka and Berezovsky Formations; the intermediate substage is composed of volcanogenic rocks of the Alnean series and of Lower Quaternary volcanics; and the upper structural substage is composed of unconsolidated Quaternary deposits and volcanics.

The central part of the area contains an Upper Miocene to Pliocene acid volcanic massif which is in immediate relation to the deposit of zeolites and perlite. The volcano is a complex system of lava flows, pyroclastic deposits, and extrusive bodies (Fig. 2). The crater pit is filled with tuffs and tuffites that have been cut through by isometric basalt bodies. The tufogene rocks are coarse-grained (Nasedkin, 1985).

The geological structure of the deposit involves acid volcanics of the Upper Miocene to Pliocene age overlain by present-day eluvial-deluvial-proluvial deposits. The area mostly contains different-sized zeolitized acid tuffs, as well as perlites.

The rocks that underlie the tuffs are Alnean dacites. They have brecciated, porous, subparallel texture, and are little altered by secondary processes. The dacites are overlain by a sequence of different-sized, intensely zeolitized tuffs of acidic composition. This rock sequence mimics the dacite paleo relief, dipping northnorthwest at angles below 30°. The tuff sequence has a thickness varying between 5 m and 100 m.

The productive rock sequence consists of several tuff varieties: different-sized vitroclastic, lithovitro-

<sup>&</sup>lt;sup>1</sup> Zhdanov, L.P., Kozovaya, T.V., Murakhtova, E.M., et al., Report on the Results of Search for Zeolite raw materials in Promising Areas around the Yagodninskoe Deposit of Active Additives and in the Basins of the Bannaya, Levaya Bystraya, Karymshina, and Plotnikova Rivers in 1987–1989. Kamchatka Region, Petropavlovsk-Kamchatsky: Kamchatgeologiya, 1989. 110 pp. *Makhanko, A.V. and Kozovaya, T.V.*, Report on the Results of Preliminary Exploration at the Yagodninskoe Deposit of Zeolite Raw Materials and Active Mineral Additives. Petropavlovsk-Kamchatsky: oAO Kamchattsement, 1998. 110 pp.



**Fig. 1.** A tectonic map of the study area after (Slyadnev et al., 2006) with modifications and supplements (the star in the inset marks the deposit location). (1, 2) Middle Miocene to Quaternary structural stage: (1) coastal marine and volcanic rocks of the Pliocene–Quaternary substage, (2) sedimentary deposits and volcanic rocks of the Middle Miocene to Pliocene substage; (3) sedimentary deposits and volcanic rocks of the Middle Eocene to Lower Miocene structural stage; (4) metamorphosed terrige-nous deposits, terrigenous–volcanogenic and volcanic rocks of the Lower Cretaceous to Lower Eocene structural stage; (5) metamorphic rocks of the pre-Mesozoic structural stage; (6) Tertiary–Quaternary unstratified terrigenous–siliceous–volcanogenic rocks (within the water body); (7) Eocene–Pliocene intrusive features of varying composition; (8) superimposed volcanic belts and zones ((*a*) East Kamchatka belt; (*b*) South Kamchatka belt; (*c*) Tolbachik–Klyuchevskoi riftogenic volcanic zone); (9) volcano-tectonic structures (KR Karymshina, Akh Akhomten, As Asacha); (10) faults ((*a*) main structure-forming faults emerging at the ground surface; (*b*) faults that are buried under overlying rocks; (*c*) deep-seated faults identified from geophysical data: BB Bolshe-Banny, WK West Kamchatka, CK Central Kamchatka, PP Petropavlovsk, Khd Khodutka)); (11) boundaries ((*a*) of stages, substages, superimposed volcanic belts and zones, intrusive bodies; (*b*) of grabens and horsts); (12) boundary of continental slope; (13) Yagodninskoe deposit.

clastic, pumice-clastic, and ash tuffs. They have no persistent strike, the contacts between them are not distinct, and there is considerable hydrothermal alteration of the rocks with formation of secondary minerals. This tuff sequence is found to contain four horizons: The lower horizon of the tuff sequence consists of interbedded lithovitroclastic different-sized zeolitized tuffs of acidic—intermediate and acidic composition. The acidic—intermediate tuffs are usually confined to the bottom of the horizon whose maximum thickness



**Fig. 2.** A geological map of the Yagodninskoe deposit after (Nasedkin, 1985) with modifications and supplements. (1) proluvial deposits of Quaternary rocks (blocks, rock debris, gruss, sandy loam); (2) Miocene–Pliocene dacites, zeolitized acid tuffs; (3) Pliocene liparite extrusions; (4) Lower Quaternary stock-like basaltic bodies and dikes; (5) Pliocene andesite dikes; (6) dacites; (7) acid (liparite) and acid-intermediate tuffs; (8) thin-sliced and spherulite-containing liparites and their lava breccias; (9) volcanic glasses (perlites); (10) basalts; (11) geological boundaries: *a* certain, *b* same-age lithologic units; (12) tectonic faults; (13) productive sequences of zeolitized tuffs at the Yagodninskoe deposit; (14) sampling site.



Fig. 3. Opened sequence of zeolite rock at the Yagodninskoe deposit.

reaches 6 m. The rocks have been intensely altered by hydrothermal solutions; the concentration of zeolites varies in the range 27-80%, with the mean concentration being 50%.

The second horizon consists of vitroclastic zeolitized tuffs whose mean thickness is 14 m. The rocks are compact, have high strength, are monolithic, and are light-green and whitish in color. The concentration of zeolites in this tuff horizon varies in the range 34–98%, with the mean being 72%.

The third horizon consists of tuffs dominated by litho-vitroclastic different-sized varieties. It can be followed through the entire deposit. The thickness of the horizon is rather constant, varying in the range 31–47.6 m. The distribution of clastic material in the tuffs is nonuniform, the color range is diverse: greenish, greyish, brownish, and pinkish. The lithovitroclastic tuffs have psephitic and psammitic texture. The secondary alterations in the tuffs are seen as intense zeolitization. The concentration of zeolites over the horizon varies between 20 and 100%, with the mean being 65%.

The upper horizon mostly consists of vitroclastic tuffs. Its mean thickness is 17 m. These tuffs are dense, high-strength rocks with greenish, occasionally pinkish, colors. They typically show large-block jointing. The tuffs are intensely zeolitized and argillized. The concentration of zeolites in the tuffs varies in the range 30-92%, with the mean being 73%. It is this horizon that was the target of field surveys and sampling.

It should be noted that the zeolitization of acid tuffs is areal in character at the deposit. The acid tuff sequence within the area of exploration is penetrated by small extrusive bodies that are confined to tectonic faults striking northwest and northeast. The sequence consists of perlites and fluidal rhyolites. The deposit was found to contain a series of faults striking west, northwest, and northeast, and a zone of intensive rock cracking.

The formation of zeolites is related to the action of hydrothermal solutions on the primary acid tuffs and perlites, producing zeolites in volcanic glass.

In the 1990s the deposit was developed, and produced an insignificant amount of zeolites from a prepared industrial area (Fig. 3). At present the deposit is registered, but is not being developed. The reserves of raw zeolite material are 7.2 million tons of category  $A + B + C_1$  and 12.4 million tons of category  $C_2$ .

In addition to zeolite raw material, the area of study contains the eponymous deposits of perlites and active nutrient additives, but no extraction is presently done.

## MATERIALS AND METHODS OF STUDY

The dataset for this study consisted of over 30 kg of samples consisting of zeolites, perlites, and volcanic rocks of varying degrees of zeolitization. The rocks were sampled by the team of IGEM RAS at the Yagodninskoe deposit in 2022.

Mineral compositions were determined using X-ray diffraction and an ULTIMA-IV diffractometer manufactured by Rigaku, Japan; the operating mode parameters are 40 kV, 40 mA, copper radiation, a nickel filter, the range of measurement was  $3^{\circ}-65^{\circ}2\theta$  at a step of 0.02°2 $\theta$ ; a semiconductor detector of the

Sample	Zeolite	Smectite	Illite	Quartz	Opal- cristobalite	Microcline	Albite
Perlite	—	—	_	5	90	5	_
Zeolite rock	69.3	—	14.1	—	7.8	8.8	_
Zeolitized tuff	40.7	14.8	4.0	2.9	4.2	18.1	15.3
Smectite nest	23.4	34.2	_	1	5.1	26.4	9.8

**Table 1.** The mineral composition of Yagodninskoe rocks, wt %

new generation (DTex/Ultra), the scanning rate was  $5^{\circ}2\theta$ /min. The results were analyzed in accordance with the recommendations described in (Drits and Kossovskaya, 1990; Moore and Reynolds, 1997).

Quantitative mineralogical analysis was performed by the Rietveld method using the PROFEX GUI program package for BGMN.

The concentrations of rock-forming chemical elements were determined in samples by the method of X-ray fluorescence analysis (XRF) using an Axios Advanced PANalytical sequential spectrometer (Netherlands). The spectrometer is equipped with a 4 kW X-ray tube with an Rh anode. The maximum voltage at the tube is 60 kV; the maximum anode current is 160 mA. The loss on ignition was determined at 1000°C, in atmospheric air until the sample achieved a constant mass.

Specific surface area was determined using a Quadrasorb SI/Kr installation. Adsorption was carried out at the temperature of liquid nitrogen (77.35 K). The adsorbent was nitrogen with purity 99.999%, the volume of measuring cells was calibrated using 6.0 (99.9999%). The surface was calculated using the BET method based on several points of the isotherm in the range of P/Ps between 0.05 and 0.30. The samples were first dried in a vacuum installation at 100°C during a definite time (5–24 h), depending on the properties of the original samples.

The cation exchange capacity (CEC) was determined by the method of multiple replacement of exchange cations with ammonium chloride. The composition of exchange cations in the solution was determined by the ICP-MS method.

Scanning electron microscopy (SEM) was conducted on a sample coated with carbon (15 nm) using a TESCAN VEGA 3 SBU microscope equipped with an OXFORD X-Max 50 X-ray fluorescence energy dispersive detector with an Si/Li crystal detector. The accelerating voltage was 20 kV with a current in the range 3.5–12.2 nA.

# THE RESULTS

The main types of zeolites have been identified at the Yagodninskoe deposit by field surveys and analytical work.

The first type includes unaltered perlites (Fig. 4a). These rocks are dark brown to black in color, they are characterized by a well-pronounced perlite texture, the surface is covered with a series of concentric and radial cracks produced by hydration of volcanic glass (Fig. 5a). With regard to mineral composition, these rocks largely consist of an opal—cristobalite phase with an admixture of feldspar and quartz (Table 1, Fig. 6).

Zeolites rock and highly zeolitized tuffs whose concentrations of zeolite minerals is 60-70% include homogeneous greenish and grey-greenish bedrock with massive structure and lithoclastic relicts up to 5– 10 cm in length (see Fig. 4). They have a high mechanical strength. The minerals are dominated by clinoptilolite and, to a lesser degree, by mordenite and stilbite (see Table 1, Fig. 6). The admixtures include illite, cristobalite, and microcline, making a typical association for zeolites of hydrothermal genesis. Also, these rocks typically show perlitic micro texture, but their groundmass is a cryptocrystalline substance that seems to consist of clinoptilolite (see Fig. 4).

Zeolites and perlites have an abundance of spherulites (radially structured concretions) and segregations having the form of crusts. These features have sizes varying in a wide range, between 200  $\mu$ m and 1–2 cm (see Figs. 5b, 5c). However, while the original perlites can contain large inclusions, the zeolite rock mostly has micro inclusions. Macroscopically, the spherulites are dark brown, and have a fibrous, radial structure (see Fig. 5c). The origin of such spherulites was examined by Frolova et al. (2017). These authors showed that such concretions are composed of aggregates of potassium or potassium-sodium feldspar and microcrystalline quartz with inclusions of ilmenite and hematite; their origin is due to crystallization of acidic, potassium-containing hydrated volcanic glass during the postmagmatic period.

The third group of rocks includes zeolitized tuffs where the concentration of zeolite minerals is 30-60%. They look like the zeolite rock, since they are pale greenish, contain numerous inclusions of lithoclasts and angular variously colored fragments up to 2-3 cm across. In some cases rocks of this type have brecciated structure where the cementing groundmass is zeolite. The latter is mostly a mixture of clinoptilolite and heulandite with less abundant mordenite. The admixtures include smectite, feldspars, as well as illite, opal-cristobalite, and quartz.



Fig. 4. Macro photographs of samples taken at the Yagodninskoe deposit. (a) unaltered perlite; (b) zeolite rock; (c) zeolitized tuffs; (d) poorly zeolitized tuffs with brecciated texture.

Poorly zeolitized tuff breccias are mostly composed of rudaceous material consisting of classical tuffs where zeolitization occurred at a lower rate, resulting in the concentration of tuffs being below 20-30% (see Fig. 4d). The rocks have frequently inherited brecciated structure, while the zeolitization of the original material has been selective. Micrographs (see Fig. 5d) clearly show that some fragments of parent substance

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Fig. 5. Micrographs of transparent polished sections of Yagodninskoe samples. (a) unaltered perlite; (b) zeolite rock; (c) zeolite rock (in crossed nicols); (d) a rock fragment replaced with clinoptilolite crystals in zeolitized breccia.

have been frequently replaced with well-crystallized zeolite crystals reaching 80 µm in length.

Apart from the four types of rock listed above, there are zeolite varieties with large relicts of lithoclasts up to 10-15 cm in length, mostly brown (see Fig. 7a), as well as rocks containing pink nests up to 10 cm across (see Fig. 7b). The results of X-ray phase analysis showed that the composition of these nests is consistent with smectite with an admixture of zeolites, feldspar, and quartz.

The groundmass of a zeolite rock consists of dense aggregates with cryptocrystalline texture. However,

pores and voids are observed to contain well-crystallized zeolites of different morphologies. These structural and textural features are characteristic of all rock types described above. One encounters both prismatic and tabular crystals up to 20  $\mu$ m across (Figs. 8a, 8b), as well as spherical aggregates up to 20–30  $\mu$ m in diameter, which in turn consist of thin-sliced crystals of a few microns or below one micron in size (see Figs. 8c, 8d).

All four rock types have high concentrations of silica (67-72%) and low concentrations of alumina (12-14%). The titanium module TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> for all sam-



Fig. 6. X-ray diffractogram of zeolite samples. (1) perlite; (2) zeolite rock; (3) zeolitized tuff; (4) smectite nest.



Fig. 7. Macro photographs of zeolite samples. (a) zeolite with an inclusion of a large lithoclast; (b) a smectite nest in zeolite rock.

ples was below 0.02, thus identifying the samples as acid rocks (Table 2). The maximum concentration of silica was found in the original perlites. As well, the latter typically show high concentrations of potassium (~5.1%), its concentration in zeolites is 4.5% (see Table 2).

The ratio between rock-forming elements and trace elements as shown by the Winchester–Floyd diagram

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Fig. 8. Micrographs of a zeolite rock sample. (a) a pore filled with zeolite crystals; (b) tabular zeolite crystals; (c) spherical zeolite aggregates; (d) thin-sliced crystals below one micron across which make a spherical aggregate.

(Winchester and Floyd, 1977; Spears and Kanaris-Sotiriou, 1979) has classified the original parent rocks as acid rhyodacites and dacites, which is not inconsistent with geological evidence (Table 3).

A study of properties showed that the cation exchange capacity for the zeolite rock is 205.9 mgequi/100 g, with cations of alkaline metals (potassium and sodium) being the exchange cations (Table 4). Comparison of the Yagodninskoe zeolites with the other Russian deposits under development enables one to state that this raw material has high capacity properties, and belongs to the most valuable type (alkaline), unlike the others.

The specific surface area for the Yagodninskoe zeolites is 25.3 m<sup>2</sup>/g (Table 5). It should be noted that the method that was employed to measure specific surface based on nitrogen adsorption can only characterize the outer surface of particles and the pore space between them, while the inner channels remain inaccessible for nitrogen molecules. The bulk of the surface is occupied by mesopores (>50 nm) and macropores (50–2 nm), with their total volume being 84% of the entire porosity. The micropores (<2 nm) occupy a

 $K_2O$ 

5.10

4.54

4.51

CaO

0.62

2.27

1.78

TiO<sub>2</sub>

0.14

0.14

0.28

MnO

0.075

0.052

0.064

Fe<sub>2</sub>O<sub>3</sub>

0.80

0.91

1.48

 $P_2O_5$ 

0.01

0.01

0.01

SiO<sub>2</sub>

72.38

71.81

67.47

Smectite nest	3	.15	1.4	2	1.11	15	.09	70.9	4	5.16	1.	04	0.28	3 0	.141	1.	56	0.02		
Table 3. The ch	Table 3. The chemical composition of trace elements, $g/t$																			
Sample	Cr	V	Co	Ni	Cu	Zn	Rb	Sr	Zr	Ba	U	Th	Y	Nb	Pb	As	Cl	Mo	La	W
Perlite	193	18	53	3	6	34	115	48	165	695	9	8	14	8	14	<10	757	<5	_	<5

Table 2. The chemical composition of rock-forming elements, wt %

MgO

0.10

0.33

0.47

 $Al_2O_3$ 

12.30

11.85

14.03

Na<sub>2</sub>O

3.63

1.66

2.42

LOI

4.77

6.29

7.47

Sample

Zeolitized tuff

Perlite

Zeolite

			-																	
Sample	Cr	V	Co	Ni	Cu	Zn	Rb	Sr	Zr	Ba	U	Th	Y	Nb	Pb	As	Cl	Mo	La	W
Perlite	193	18	53	3	6	34	115	48	165	695	9	8	14	8	14	<10	757	<5	_	<5
Zeolite	9	37	7	6	13	39	63	86	149	821	<5	8	24	7	11	<10	85	<5	_	<5
Zeolitized tuff	27	31	<5	10	9	43	104	91	152	719	<5	9	17	8	14	<5	20	<5	24	<5
Smectite test	15	37	<5	6	18	43	63	96	134	946	<5	<5	24	7	16	<5	47	<5	58	<5

Table 4. Cation exchange capacity for some zeolite deposits in Russia, mg-equi/100 g

Deposit	$\mathrm{EKO}_{\mathrm{NH}_4\mathrm{Cl}}$									
Doposit	Total	Na <sup>+</sup>	$K^+$	Ca <sup>2+</sup>	Mg <sup>2+</sup>					
Khotynetskoe, Orel Region	78.1	12.2	18.7	40.1	7.1					
Yagodninskoe, Kamchatka	205.9	43.5	71.3	81.0	10.1					
Khonguruu, Republic of Sakha	203.4	74.3	7.4	90.4	31.3					

Table 5. Specific surface and the pore distribution over pore size for some zeolite deposits in Russia

	/g	n	m	icro /g	Pore distribution over pore size, %					
Sample	Specific surface, m <sup>2</sup>	Pore volume, m	Mean diameter, n	Volume of m pores, cm <sup>3</sup>	Micro pores	Meso pores and macro pores				
Khotynetskoe, Orel Region	26.8	0.089	3.77	<0.001	14	86				
Yagodninskoe, Kamchatka	25.3	0.068	8.14	0.002	16	84				
Khonguruu, Republic of Sakha	13.3	0.042	8.46	<0.001	<1	100				

mere 16% of total volume. The mean pore diameter is 8.14 nm. These properties of the surface are comparable with those for the other zeolite deposits in Russia under development (see Table 5).

# CONCLUSIONS

It has been found that the Yagodninskoe zeolites were largely formed from perlites and tuff breccias. We identified four main rock types: (1) unaltered perlites with a characteristic perlite texture; (2) zeolite rocks, which are greenish and grey–greenish and have massive structure, and where the concentration of zeolite minerals is on the order of 60-70%; (3) pale green zeolitized tuffs with massive structure and where the concentration of zeolite minerals is 30-60%; (4) poorly zeolitized tuff breccias that consist of rudaceous material and where the concentration of zeolites is 20-30%.

The rocks studied here typically have inclusions of dark brown spherulites with fibrous and radial structure between 200  $\mu$ m and 2–3 cm across, relicts of well-reserved brown lithoclasts up to 10–15 cm in length, as well as pink nests up to 10 cm diameter;

SO<sub>3</sub>

< 0.01

< 0.01

these mostly have a smectite composition with admixtures of zeolites, feldspar, and quartz.

The zeolites are mostly clinoptilolite and, to lesser degrees, heulandite, mordenite, and stilbite. The zeolitic groundmass is composed of dense aggregates with cryptocrystalline texture. The pores and voids contain well-crystallized zeolites of prismatic and tabular shapes with size ranging between below one micro and 20  $\mu$ m (see Figs. 1a, 1b). These occasionally make spherical aggregates reaching 20–30  $\mu$ m in diameter. The cation exchange capacity of zeolite rocks is 205.9 mg-equi/100 g. The exchange complex mostly contains cations of alkaline metals, which classifies the zeolites studied here as the most valuable alkaline type. The specific surface of the zeolite rock is 25.3 m<sup>2</sup>/g. The bulk of the surface consists of mesopores and macropores. The mean diameter of the pores is 8.14 nm.

These results tell us that the Yagodninskoe zeolites are a high quality raw material whose development will not only make up for the existing deficiencies in this kind of raw material in Russia, but will help promote the development of new high-tech branches of industry.

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### CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

#### REFERENCES

- Belousov, P.E. and Rumyantseva, A.O., The mineral composition, properties, and conditions of generation for zeolites of varying genesis, in *Materialy Vserossiiskoi* nauchnoi konferentsii "Fundamentalnye problemy izucheniya vulkanogenno-osadochnykh, terrigennykh i karbonatnykh kompleksov (Litol 2023)" (Proc. All-Russian conference "Fundamental Problems in the Study of Volcanogenic-Sedimentary, Terrigenous, and Carbonate Complexes (Litol 2023)"), Moscow, 2023, pp. 16–19.
- Belousov, P.E., Karelina, N.D., Morozov, I.A., Rudmin, M.A., Milyutin, V.V., Nekrasova, N.A., Rumyantseva, A.O.,

and Krupskaya, V.V., The conditions of generation, mineral composition, and sorption properties of the zeolite-containing tripoli at the Khotynetskoe deposit, Orel Region, *Izv. Tomsk. Polit. Univers. Inzh. Geores.*, 2023, vol. 334, no. 5, pp. 70–84. https://doi.org/10.18799/24131830/2023/5/4001

- Demina, Y., Frolova, J., and Rychagov, S., Hydrothermal alterations and petrophysical properties: A case study of Yagodninskoe zeolite deposit, Kamchatka Peninsula, in *Proceedings World Geothermal Congress*, Melbourne, Australia, 2015.
- Distanov, U.G., Aksenov, E.M., Sabitov, A.A., et al., Fanerozoiskie osadochnye paleobaseiny Rossii: problemy evolyutsii i minerageniya nemetallov (The Phanerozoic Sedimentary Paleo Basins in Russia: Problems of Evolution and the Generation of Nonmetals), Moscow: Geoinformatika, 2000.
- Drits, V.A. and Kossovskaya, A.G., *Glinistye mineraly: smektity, smeshanosloinye mineraly* (Clay Minerals: Smectites and Mixed-Layer Minerals), Moscow: Nauka, 1990.
- Frolova, Yu.V., Spiridonov, E.M., Ladygin, V.M., Rychagov, S.N., and Bolshakov, I.E., Changes in the physical and mechanical properties of perlites by hydrothermal processes: Yagodninskoe deposit, southern Kamchatka, *Inzh. Geol.*, 2017, vol. XII, no. 5, pp. 26–38.
- Gosudarstvennyi balans zapasov poleznykh iskopaemykh Rossiiskoi Federatsii "Tseolity" (State Register of Mineral Resources of Russian Federation "Zeolites"), Moscow, 2019.
- Mineral Commodity Summaries, U.S. Geological Survey, USA, 2022. pubs.usgs.gov/publication/mcs2022
- Moore, D.M. and Reynolds, R.C., X-ray Diffraction and the *Identification and Analysis of Clay Minerals*, Oxford: Univ. Press, 1997.
- Nasedkin, V.V., Solovieva, T.N., Mager, A.V., et al., Kompleksnoe izuchenie syrievoi bazy i fiziko-mekhanicheskikh svoistv vulkanicheskikh porod (pemz, shlakov, tufov, perlitov) Dalnego Vostoka i Kamchatki (Multidisciplinary Study of the Raw Materials Sources and Physical and Mechanical Properties of Volcanic Rocks: Pumice, Cinder, Tuffs, Perlites) of the Russian Far East and Kamchatka), Moscow: Nauka, 1985.
- Slyadnev, V.I., Khasanov, Sh.G., and Krikun, N.F., Gosudarstvennaya geologicheskaya karta masshtaba 1 : 1000000 list N-57 (State Geological Map, Scale 1 : 1000000 Sheet N-57), St. Petersburg: FGUP VSEGEI, FGUGP Kamchatgeologiya, 2006.
- Spears, D.A. and Kanaris-Sotiriou, R., A geochemical and mineralogical investigation of some British and other European tonsteins, *Sedimentology*, 1979, vol. 26, pp. 407–425.
- Winchester, J.A. and Floyd, P.A., Geochemical discrimination of different magma series and their differentiation products using immobile elements, *Chem. Geol.*, 1977, vol. 20, pp. 325–343. https://doi.org/10.1016/0009-2541(77)90057-2

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