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# Diatom characteristic of the Far East siliceous organogenic deposits

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**Abstract**

Three Far East diatomites, Puzanov (Kunashir Island, Kuril Islands), Sergeevskii, and Terekhovka (Southern Primorye) are characterized in detail. Rock-forming taxa are identified (Puzanov—*Aulacoseira subarctica* (O. Müll.) Hawort, and *Stephanodiscus niagarae* var. *Pusanovae* Genkal et Cherepanova; Sergeevskii—*Staurosira construens* var. *Venter* (Ehr.) Grun., *Aulacoseira italica* (Ehr.) Sim., and representatives of the genus *Cymbella* with large valves (up to 175 μm in length); Terekhovka—*Aulacoseira praegranulat a* var. *praeislandica* f. *praeislandica* (Sim.) Moiss.). Morphometric analysis of valves of the dominant taxa showed a low variability of valve parameters for the Puzanov diatomite and a high one for the Sergeevskii and Terekhovka diatomites. The lake environments of the diatoms forming the diatomites were reconstructed based on the elemental composition of diatom shells and the ecological structure of diatom paleocommunities. The high oxygen concentration and low silicon concentration in valves of the Puzanov diatomite most likely indicate that that the diatoms were part of plankton communities formed in a large deep freshwater lake. Significant concentrations of silicon in valves of the Terekhovka diatomite, in contrast, suggest that the diatoms occurred in benthic ecotopes in a shallow lake. The age of the deposits was refined by detailed studies of *Aulacoseira* valves using optical and scanning electron microscopes. For example, the presence of *Aulacoseira* taxa of the prae group in the Terekhovka diatomite confirms its Pliocene age, and the presence of valves of the present species *A. italica* in the Sergeevskii diatomite points to its Late Pliocene age. The identified features of the diatomites permit their use in practice.

*Keywords:* diatomite; freshwater deposits; diatoms; Quaternary system

## Introduction

Diatomite is a rock containing more than 50% valves of microscopic diatoms which once lived in ancient waters (Losev, 2002; Proshkin-Lavrenko, 1974). These algae build their shells with genetically programmed complex patterns of nanostructures using silicic acid (Crawford et al., 2001; Pickett-Heaps et al., 1990; Round et al., 1990). They are able to reproduce at an unusually high rate. Elevated concentrations of dissolved silicic acid in water, sufficient supply of nutrients, especially phosphates and nitrates, a minor addition of the mineral and organic impurities worsening the conditions of active development of diatoms, and the absence of strong currents and waves lead to the deposition of diatomaceous sediments (Distanov, 1998). Another important condition for the preservation of diatom valves in sediments is the low degree of their dissolution in both the water column and sediments (Barker et al., 1994; Dove, 1995; Levin et al., 2001; Ryves et al., 2001).

Diatomites have different rock-forming diatom compositions and mineral and organic impurities and, consequently, different chemical and physicomechanical properties and fields of application, depending on sedimentation conditions and age (Demidov and Shelekhova, 2006).

Diatomites are non-metal fossil minerals characterized by chemical inertness, low density, high porosity, etc. They are used as catalysts, filters and sorbents with specified pore sizes, reinforcing composite fillers, diffraction gratings of optical sensors, additives to certain types of cement, raw materials in the production of waterglass, glazes, paper, antibiotics, dyes, and even as microcapsules for drugs (Cummins, 1973; Flynn, 2003; Fustinoni et al., 2005; Obanijesu et al., 2004). Due to the need for more efficient use of natural resources, even in small quantities, the range of uses for diatomites is constantly expanding. Thus, nanotechnologists hope to use diatom shells as reaction vessels for producing nanometer-size crystals. The design of structures similar to the three-dimensional silica skeleton of diatoms but having a different chemical composi-

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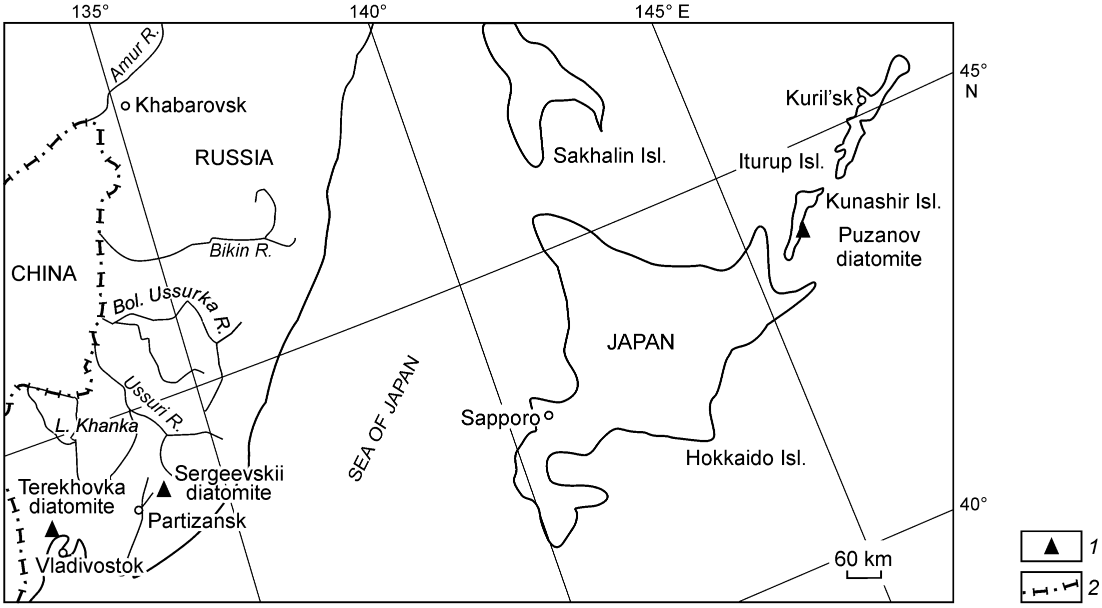


Fig. 1. Schematic of the study area. *1*, location of diatomites; *2,* state border.

tion offers even wider opportunities (Haluska et al., 2005; Sandhage et al., 2002; Unocic et al., 2004). Chemical transformations of diatomites are used to produce new materials, for example, the mineral wollastonite (Yarusova et al., 2012), which has unique technological properties (Tyulnin et al., 2003).

To determine the scope of application of a particular diatomite, it is necessary to perform a comprehensive study of the characteristics of the rock, in particular, to analyze the taxonomic composition of diatoms and identify rock-forming species and the main morphometric parameters of their valves.

A comprehensive study of the Far East diatomites to determine their quality has not yet been carried out. The taxonomic composition of the diatom flora of some deposits of the region has been investigated to determine the age and origin of the sediments. Thus, diatoms from the biogenic siliceous sediments of the Kuril Islands have been studied on the Iturup Island in the Miocene and Pliocene marine diatomites (José, 1962; Kozyrenko and Sheshukova-Poretskaya, 1967; Vekshina, 1968) and the Puzanov diatomite of Pleistocene age (Cherepanova and Grebennikova, 2001). The latter is best studied using diatom analysis methods. In these sediments, the taxonomic composition of the diatom flora was determined, the rock-forming taxa were identified, and the morphometric characteristics of their shells were evaluated. SEM examination of the valves of one of the dominant taxa made it possible to describe the new species *Stephanodiscus niagarae* var. *Pusanovae* Genkal et Cherepanova (Genkal and Cherepanova, 2009). The taxonomic composition of the diatom flora isolated from the Eocene, Miocene, and Pliocene diatomites has been studied in Primorye (Likhacheva et al., 2009; Moiseeva, 1971, 1995; Pavlyutkin et al., 1993, 2004).

This paper presents a detailed study of three Far East diatomites using methods of comprehensive diatom analysis.

## Material and methods

The material for this study was collected from three small deposits of diatomites (Fig. 1) located in various parts of the Far East: (1) at Cape Puzanov (Kunashir Island, Kuril Islands); (2) on the south of Primorsky Krai, in the headwaters of the Sergeevskii stream; (3) near the Terekhovka Village (Nadezhdinskii District, Primorsky Krai).

The thickness of the **Puzanov diatomite** deposit is about 10 m. It is exposed at a 70-meter coastal cliff about 50 m above sea level near Cape Puzanov. The apparent length of the diatomite lens is 50 m. The diatomaceous sediments overlie bluish-gray thin-flaky Early Pleistocene silts of marine origin (Pushkar' and Cherepanova, 2001). The diatomaceous deposits are overlain by an 8-m-thick tephra with aeolian sandy loam and soil. The age of the diatomite is supposedly Middle Pleistocene (Cherepanova and Grebennikova, 2001). The rock is light, weakly cemented, white with a slightly yellowish tinge, and makes the hands dirty like chalk. Eight samples from the diatomite section were studied.

Three samples of the **Sergeevskii diatomite** were collected from interlayers of siliceous biogenic sediments at the base of the Upper Miocene Pliocene basalt stratum (Kovalenko, 1989) at a depth of 89.5–82.5 m penetrated by boreholes 27 and 28 drilled by Primorgeologiya company in 1988. The total thickness and extent of the diatomite deposit were not determined. The diatomite is light, weakly cemented, and colored white to yellow.

Five samples of the **Terekhovka diatomite** were collected from site 4131 near Terekhovka Village, where the Shufan horizon sediments composing the alluvial terrace of the Paleorazdol'naya River are penetrated (Pavlyutkin and Petrenko, 2010). The diatomite layer is about 4 m thick. The diatomite is weakly cemented, white, with a slightly yellowish tinge. The age of the diatomite is Pliocene (Likhacheva et al., 2009; Pavlyutkin, 2008; Pavlyutkin and Petrenko, 2010).

For each of the diatomites, we determined: the number of diatom valves per 1 g of dry rock, taxonomic composition, rock-forming taxa, and the dimension and chemical composition of their valves.

The samples were treated by a standard procedure using hydrogen peroxide (Proshkin-Lavrenko, 1974).

Taxonomic analysis, counting of diatom valves, and measurements of the diameter, length, and width of the valves were performed on an Amplival Carl-Zeiss and an Axioskop 40 Carl Zeiss light microscopes (LM) using a 18 × 18 mm glass at a magnification of ×2000 with an immersion liquid at the Center for Collective Use of Institute of Biology and Soil Science, Far East Branch, Russian Academy of Sciences. 250–300 diatom valves were counted to determine the percentage of individual species in diatom taphocenoses. Morphological features of valves were also examined with a Carl Zeiss EVO 40 scanning electron microscope (SEM) at a magnification of up to 15,000. The sediment remaining after the preparation of the specimen for LM studies was dried. The resulting powder was applied on special tables with glued bilateral carbon tape. The samples were sputter coated with gold in a vacuum chamber (JEOL JFC-1600 auto fine coater).

The diatom valve concentration in 1 g of sediment ($N$) was determined by the formula $N = (d \cdot nr \cdot ns / g \cdot v \cdot nrs) \cdot 3$, where $d$ is the dilution (100 ml), $nr$ is the number of rows in the specimen at a ×2000 magnification (225), $ns$ is the number counted valves, $g$ is the sample weight, $v$ is the volume of the drop (0.04–0.06 ml), $nrs$ is the number of scanned rows (Minyuk et al., 2003).

The chemical composition of the rock-forming valves diatom taxa was studied in the Laboratory of Micro- and Nanoresearch of Far East Geological Institute of Far Eastern Branch of Russian Academy of Sciences (FEGI FEB RAS) using a JSM 6490 LV analytical SEM with an INCA Energy energy-dispersive spectrometer (EDS).

## Characteristics of diatomites

The diatomite flora of Cape Puzanov includes 155 species and intraspecific varieties of diatoms, but planktonic centric diatoms play the most important role in the formation of the Puzanov diatomite (Fig. 2*a*). SEM study of diatom valves made it possible to refine the species identification made in a previous study (Cherepanova, Grebennikova, 2001). It has been found that the rock-forming taxa for this diatomite are *Aulacoseira subarctica* (O. Müll.) Hawort (see Fig. 2*b, c*) with an estimated abundance of 46.0% of the total number of valves counted in the specimen and *Stephanodiscus niagarae* var. *pusanovae* Genkal et Cherepanova (see Fig. 2*d, e, f*), whose

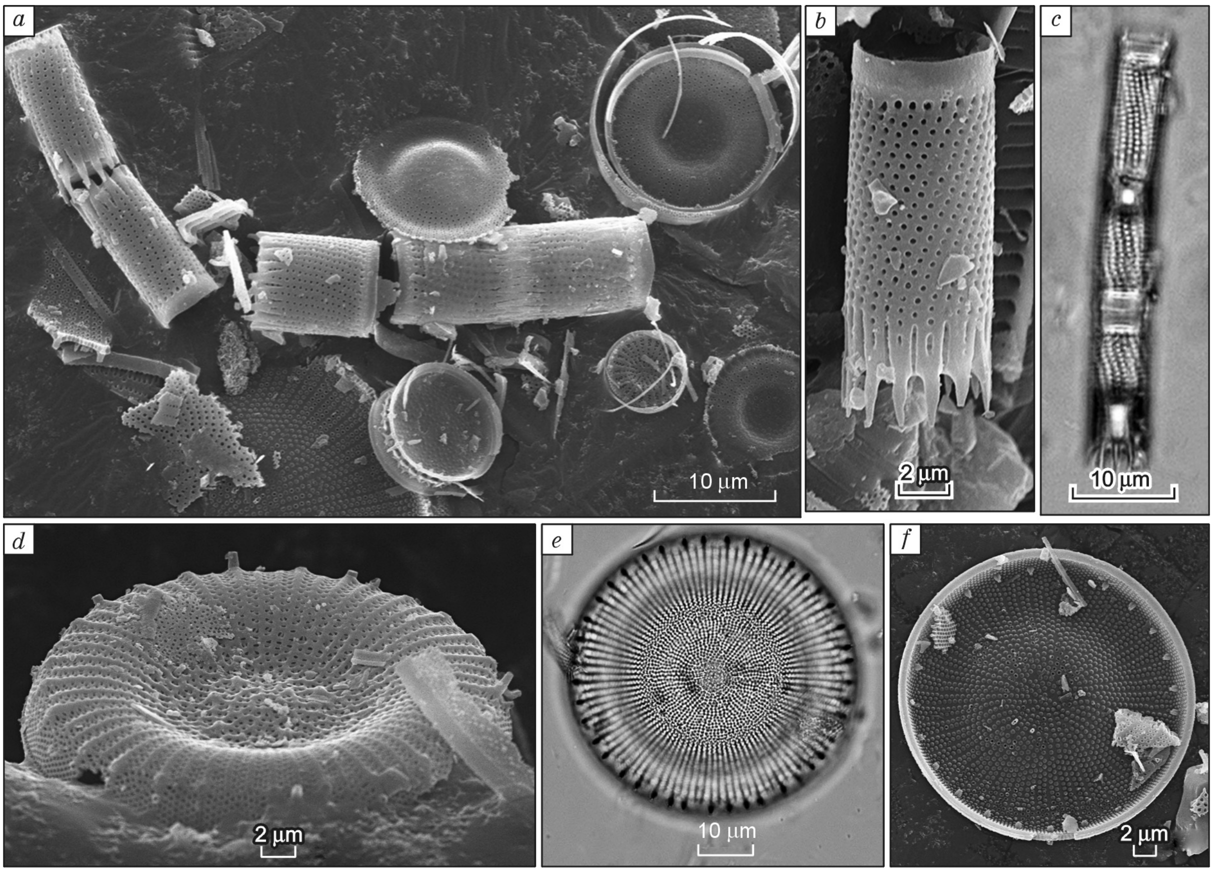


Fig. 2. Rock-forming taxa of the Puzanov diatomite: *a*, general view of the diatomite SEM; *b*, *c*, *Aulacoseira subarctica* (O. Müller) Hawort (*b*, SEM; *c*, LM); *d*, *e*, *f*, Stephanodiscus niagarae var. *pusanovae* Genkal et Cherepanova, SEM (*d*, *f*, SEM; *e*, LM).

Table 1. Valve sizes of the rock-forming taxa of the Puzanov diatomite

| Species | Number of valves | Size, µm | | | σ | $C_v$ |
|---|---|---|---|---|---|---|
| | | minimum | maximum | mean | | |
| Stephanodiscus niagarae var. pusanovae Genkal et Cherepanova | 240 | 19.67 | 61.88 | 32.41 ± 0.38 | 5.84 | 18.02 |
| Aulacoseira subarctica (O. Müller) Hawort (valve height) | 216 | 6.78 | 17.42 | 12.45 ± 0.09 | 1.45 | 11.68 |
| Aulacoseira subarctica (O. Müller) Hawort ( valve diameter) | 248 | 1.88 | 8.16 | 3.73 ± 0.06 | 1.00 | 26.75 |

Note. $C_v$ is the coefficient of variation; σ is the standard deviation; ± the standard error of the mean.

Table 2. Concentration (%) of chemical elements in valves of the rock-forming taxa of the Puzanov diatomite

*Aulacoseira subarctica* (O. Müll.) Hawort

| Element | AS-1-1-1* | AS-2-1-1 | AS-3-1-1 | AS-4-1-1 | AS-5-1-1 | AS-6-1-1 | AS-7-1-1 | AS-8-1-1 | AS-9-1-1 | AS-10-1-1 |
|---|---|---|---|---|---|---|---|---|---|---|
| Si | 30.22 | 15.42 | 10.71 | 9.18 | 15.01 | 22.02 | 12.61 | 21.04 | 18.82 | 15.57 |
| O | 66.38 | 84.35 | 89.29 | 90.82 | 84.35 | 75.63 | 87.39 | 78.69 | 80.32 | 84.43 |
| Al | 0.49 | – | – | – | 0.26 | 1.12 | – | 0.27 | 0.43 | – |
| Ca | 0.29 | – | – | – | – | – | – | – | – | – |
| Fe | 0.51 | 0.23 | – | – | 0.38 | 1.23 | – | – | 0.43 | – |
| W | 2.11 | – | – | – | – | – | – | – | – | – |

*Stephanodiscus niagarae* var. *pusanovae* Genkal et Cherepanova

| Element | SN-1-1-1 | SN-2-1-1 | SN-3-1-1 | SN-4-1-1 | SN-5-1-1 | SN-6-1-1 | SN-7-1-1 | SN-8-1-1 | SN-9-1-1 | SN-10-1-1 | SN-11-1-1 | SN-12-1-1 | SN-13-1-1 | SN-14-1-1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Si | 23.86 | 20.32 | 32.32 | 33.92 | 12.44 | 24.90 | 21.31 | 21.56 | 34.56 | 23.82 | 10.63 | 25.13 | 17.73 | 23.07 |
| O | 73.27 | 78.67 | 67.68 | 62.82 | 86.82 | 73.81 | 78.69 | 78.12 | 64.50 | 75.09 | 83.44 | 71.55 | 80.81 | 74.68 |
| Al | 0.56 | 0.44 | – | 0.99 | 0.25 | 0.61 | – | – | – | 0.40 | – | 0.51 | 0.41 | – |
| Ca | 0.20 | – | – | 0.32 | – | – | – | – | – | – | 5.93 | 0.17 | – | – |
| Fe | 0.37 | 0.57 | – | 1.97 | – | 0.69 | – | 0.31 | – | 0.70 | – | 0.53 | 1.05 | – |
| W | 1.74 | – | – | – | – | – | – | – | – | – | – | 2.12 | – | 2.25 |
| Cu | – | – | – | – | 0.48 | – | – | – | – | – | – | – | – | – |
| Br | – | – | – | – | – | – | – | – | 0.94 | – | – | – | – | – |

*Here and below—the spectrum number: letters are the abbreviated name of a taxon; figures: the first figure is the object (valve) number, the second figure is the measurement number; the third figure is the point number on the object at which the concentration of chemical elements was determined.

percentage in the fossil diatom communities reaches 26.0%. The diatom shells are well preserved. The valve concentration in 1 g of sediment is $9.6 \times 10^8$.

Valve sizes of the rock-forming taxa are presented in Table 1. The valve diameter of *S. niagarae* var. p*usanovae* varies from 19.67 to 61.88 µm, the variability of this parameter is relatively low, and the coefficient of variation ($C_V$) is 18.02. In *A. subarctica*, the valve diameter and height were measured. The minimum diameter was 1.88 µm, the maximum diameter 8.16 µm, and the valve height was 6.78 and 17.42 µm, respectively. The valve height is more constant in this species, $C_V = 11.68$. The valve height-to-diameter ratio is in the range of 1.55–7.10, with a mean of 3.58, although for a larger number of valves, this ratio is limited to within 3.0–3.96.

The concentration of chemical elements was determined in shells of rock-forming taxa (Table 2). The oxygen concentration in valves varied from 66.38 to 90.82% in *A. subarctica* and from 62.82 to 86.82% in *S. niagarae* var. *pusanovae*, and the silicon concentration in valves varied from 9.18 to 30.22% in *A. subarctica* and from 10.63 to 34.56% in *S. niagarae* var. *pusanovae* . The most abundant impurities were iron (0.23–1.23% in valves of *A. subarctica,* and 0.31–1.97% in valves of *S. niagarae* var. *pusanovae)* and aluminum (0.72–1.12% in valves of *A. subarctica,* and 0.25–0.09% in valves of *S. niagarae* var. *pusanovae).* Relatively high concentration of tungsten (up to 2.25%) was found in large valves of *S. niagarae* var. p*usanovae.*

The diatom flora of the **Sergeevskii diatomite**, composed of 25 species and intraspecific varieties, is dominated by benthic pennate small-valved forms, and planktonic diatoms have lower abundance estimates (Fig. 3*a*). The sediments are characterized by monodominant diatom paleocommunities with *Staurosira construens* var. *venter* (Ehr.) Grun. (see Fig. 3*b*) (a frequency index of 84.8%). *Aulacoseira* italica (Ehr.) Sim. has relatively high abundance estimates (see Fig. 3*c, g*) with a percentage of up to 15.6%. It is necessary

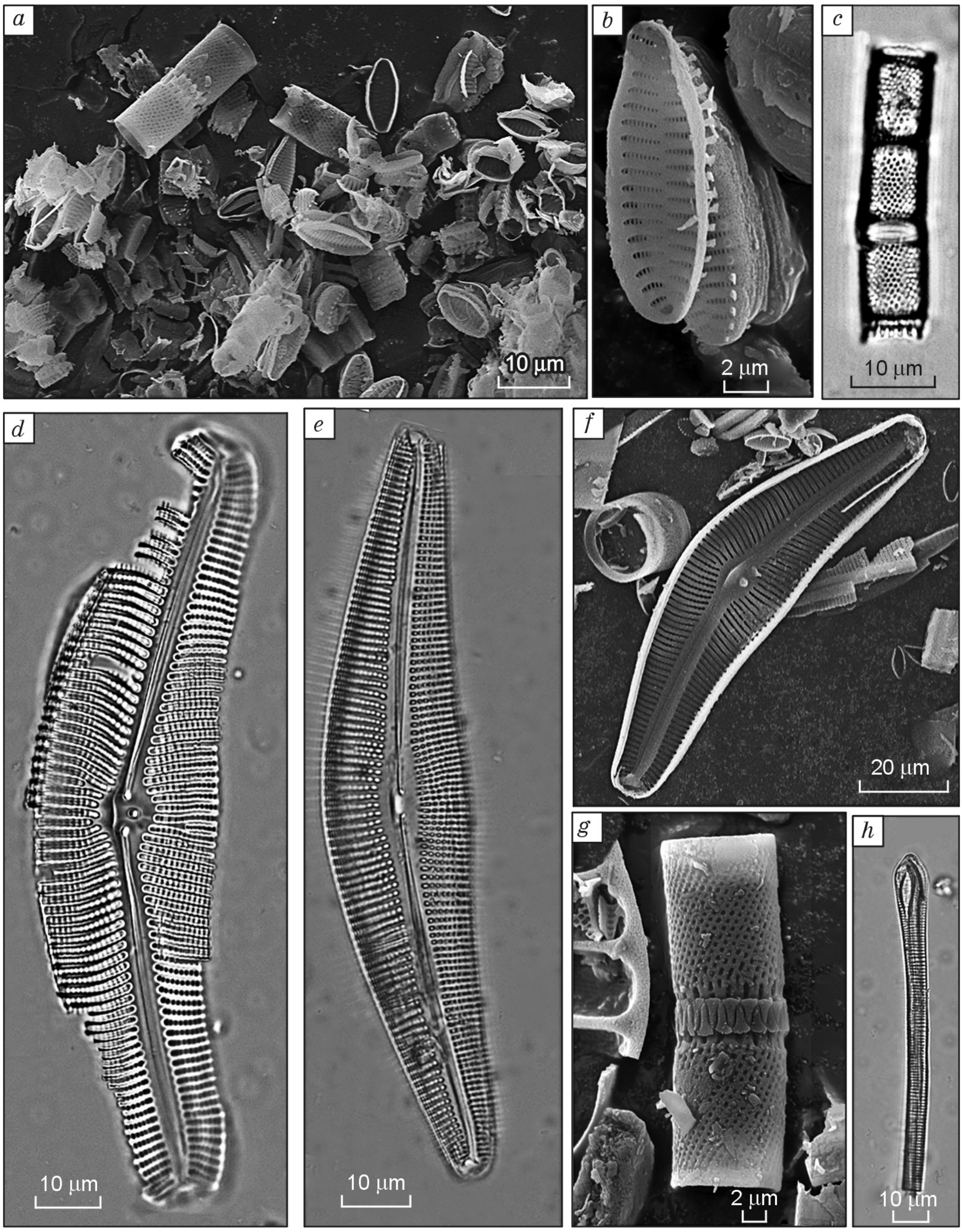


Fig. 3. Rock-forming taxa of the Sergeevskii diatomite: *a*, general view of the diatomite, SEM; *b*, *Staurosira construens* var. *Venter* (Ehr.) Grun., SEM; *c*, *g*, *Aulacoseira italica* (Ehr.) Sim. (*c*, LM; g, SEM); *d*, *f*, *C.* aff. *australica* A. S. (*d*, LM; *f*, SEM), *e*, *Cymbella aspera* (Ehr.) Cl., SM; *h*, *Actinella brasiliensis* Grun., LM.

to note the presence of the large-valved species of the genus *Cymbella: C. aspera* (Ehr.) Cl. (see Fig. 3*e*) and *C.* aff. australica AS (see Fig. 3*g, e).* Although their concentration in the sediment is low (about 2%) and their contribution to the formation of fossil diatom communities is small against the pronounced dominance of small-valved *S. construens*, the large valve size of these taxa (up to 175 μm in length) allow them to be provisionally considered rock-forming. The diatom shells encountered in the sediments are well preserved. The valve concentrations per 1 g of sediment is $6.1 \times 10^8$.

The valve length of the dominant *S. construens* var. *venter* varies from 3.79 to 23.22 μm (Table 3), the valve width varies from 2.96 to 5.65 μm, and $C_v$ for the latter parameter = 10.94. The valve diameter of the accompanying species *A. italica* varies from 3.2 to 19.14 μm, and the valve height from 6.53 to 20.47 μm. The latter parameter is less variable ($C_v$ = 17.49) than the valve diameter, for which $C_v$ = 33.27 (see Table 3). The valve height-to-diameter ratio is in the range of 0.97–3.62, and in a substantial portion of the valves, it is within 1.20–1.89 with a mean of 2.02. The valve length of *C.* aff. *australica* varies from 94.94 to 175.04 μm, and the valve width from 25.05 to 33.43 μm.

The chemical composition of valves of the rock-forming taxa of the Sergeevskii diatomite is presented in Table 4. The concentration of the main elements varies as follows: the oxygen concentration varies from 68.63 to 89.77% in *S. construens* var. *venter* valves, from 59.89 to 83.11% in *A. italic* valves, and from 43.56 to 83.26% in *C.* aff. *australica* valves;

Table 3. Valve sizes of the rock-forming taxa of the Sergeevskii diatomite

| Species | Number of valves | Size, µm | | | σ | $C_v$ |
|---|---|---|---|---|---|---|
| | | minimum | maximum | mean | | |
| *Staurosira construens* var. *venter* (Ehr.) Grun. (valve length) | 240 | 3.79 | 23.22 | 10.64 ± 0.26 | 4.06 | 38.2 |
| *Staurosira construens* var. *venter* (Ehr.) Grun. (valve width) | 255 | 2.96 | 5.65 | 4.19 ± 0.03 | 0. 45 | 10.94 |
| *Aulacoseira italica* (Ehr.) Sim. ( valve diameter) | 252 | 3.2 | 19.14 | 7.81 ± 0.16 | 2.59 | 33.27 |
| *Aulacoseira italica* (Ehr.) Sim. ( valve height) | 244 | 6.53 | 20.47 | 11.87 ± 0.13 | 2.07 | 17.49 |

Table 4. Concentration (%) of chemical elements in valves of the rock-forming taxa of the Sergeevskii diatomite

*Aulacoseira italica* (Ehr.) Sim.

| Element | AI-1-1-1 | AI-1-1-2 | AI-2-1-1 | AI-2-1-2 | AI-3-1-1 | AI-3-1-2 | 4I-4-1-1 | AI-4-1-2 | AI-5-1-1 | AI-6-1-1 | AI-6-1-2 | AI-8-1-1 | AI-8-1-2 | AI-9-1-1 | AI-9-1-2 | AI-10-1-1 | AI-10-1-2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Si | 32.97 | 36.79 | 32.30 | 40.11 | 21.48 | 32.99 | 24.41 | 16.89 | 18.81 | 21.47 | 25.65 | 17.21 | 19.31 | 21.76 | 21.40 | 20.66 | 22.89 |
| O | 66.73 | 63.21 | 67.70 | 59.89 | 77.89 | 67.01 | 75.59 | 83.11 | 80.94 | 78.53 | 74.35 | 81.01 | 80.69 | 76.01 | 78.33 | 79.34 | 77.11 |
| Al | 0.30 | – | – | – | – | – | – | – | 0.25 | – | – | 0.24 | – | 0.30 | – | – | – |
| Br | – | – | – | – | 0.63 | – | – | – | – | – | – | – | – | – | – | – | – |
| Fe | – | – | – | – | – | – | – | – | – | – | – | – | – | 0.35 | 0.27 | – | – |
| W | – | – | – | – | – | – | – | – | – | – | – | 1.54 | – | 1.58 | – | – | – |

*Staurosira construens* var. *venter* (Ehr.) Grun.

| Element | SC-1-1-1 | SC-1-1-2 | SC-2-1-1 | SC-2-1-2 | SC-3-1-1 | SC-4-1-1 | SC-4-1-2 | SC-4-1-3 | SC-5-1-1 | SC-6-1-1 | SC-7-1-1 | SC-8-1-1 | SC-9-1-1 | SC-10-1-1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Si | 23.36 | 23.13 | 26.10 | 24.0 | 31.37 | 20.34 | 12.17 | 16.44 | 23.68 | 18.80 | 15.30 | 10.90 | 12.75 | 10.23 |
| O | 76.64 | 76.60 | 73.90 | 76.00 | 68.63 | 79.39 | 87.63 | 83.32 | 75.85 | 81.20 | 84.70 | 89.10 | 87.25 | 89.77 |
| Al | – | 0.27 | – | – | – | 0.27 | 0.20 | 0.24 | 0.27 | – | – | – | – | – |
| Ca | – | – | – | – | – | – | – | – | 0.20 | – | – | – | – | – |

*Cymbella* aff. *australica* A.S.

| Element | Ñ-2-1-1 | C-2-1-2 | C-3-1-1 | C-3-1-2 | C-4-1-1 | C-4-1-2- | C-4-1-3 | C-4-1-4 | C-5-1-1 | C-5-1-2 | C-6-1-1 | C-6-1-2 | C-7-1-1 | C-7-1-2 | C-8-1-1 | C-8-1-2 | C-9-1-1 | C-9-1-2 | C-10-1-1 | C-10-1-2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Si | 42.77 | 36.52 | 36.01 | 27.46 | 31.02 | 33.62 | 17.97 | 21.84 | 28.61 | 20.02 | 33.26 | 24.79 | 33.08 | 16.75 | 32.07 | 56.44 | 33.01 | 24.45 | 41.37 | 28.83 |
| O | 57.23 | 63.49 | 63.99 | 72.53 | 68.98 | 66.38 | 81.63 | 77.67 | 71.39 | 79.47 | 65.00 | 75.21 | 64.78 | 83.26 | 65.49 | 43.56 | 64.71 | 75.55 | 56.34 | 70.95 |
| Al | – | – | – | – | – | – | 0.26 | 0.49 | – | – | – | – | – | – | – | – | – | – | – | 0.21 |
| K | – | – | – | – | – | – | 0.15 | – | – | – | – | – | – | – | – | – | – | – | – | – |
| Cu | – | – | – | – | – | – | – | – | – | 0.51 | – | – | – | – | – | – | – | – | – | – |
| W | – | – | – | – | – | – | – | – | – | – | 1.74 | | 2.13 | – | 2.44 | – | 2.28 | – | 2.29 | – |

the silicon concentration varies from 10.23 to 31.37% in *S. construens* var. *venter* valves, from 16.89 to 40.11% in *A. italica* valves, and from 16.75 to 56.44% in *C.* aff. *australica* valves. Among impurities, the highest concentrations (up to 2.44% in *C.* aff. *australica* valves) are typical of tungsten. The iron and aluminum concentrations are not high, and these elements are not permanent components of valves of this diatomite. We can provisionally speak of the presence of aluminum (up to 0.27%) in valves of *S. construens* var. *venter.*

The **Terekhovka diatomite** flora consists of 36 species and intraspecific taxa. Planktonic centric diatoms play an important role in the formation of the deposits. The rock- forming taxa are representatives of the genus *Aulaco* seira Thw. The dominant taxon is *Aulacoseira praegranulata* var. *praeislandica* f. *praeislandica* (Sim.) Moiss. (Fig. 4*a, b*); its percentage in diatom paleocommunities reaches 93.2%. Analysis of the characteristics of valves of this species from the Terekhovka diatomite revealed two separate assemblages. The first is formed by valves of *A. Praegranulata* var. *praeislandica* f. *praeislandica,* whose content in paleocommunities reaches 72.4%. They have a high mantle and a small diameter and, consequently, a higher valve height-to-diameter ratio. The second assemblage contains valves with a low mantle (see Fig. 4*d, e, f*), a large diameter, and a low valve height-to-diameter ratio. Their concentration in paleocommunities reaches (20.1%). Forms with these characteristics were found by A.P. Jousé (1952) in the Miocene sediments of Lake

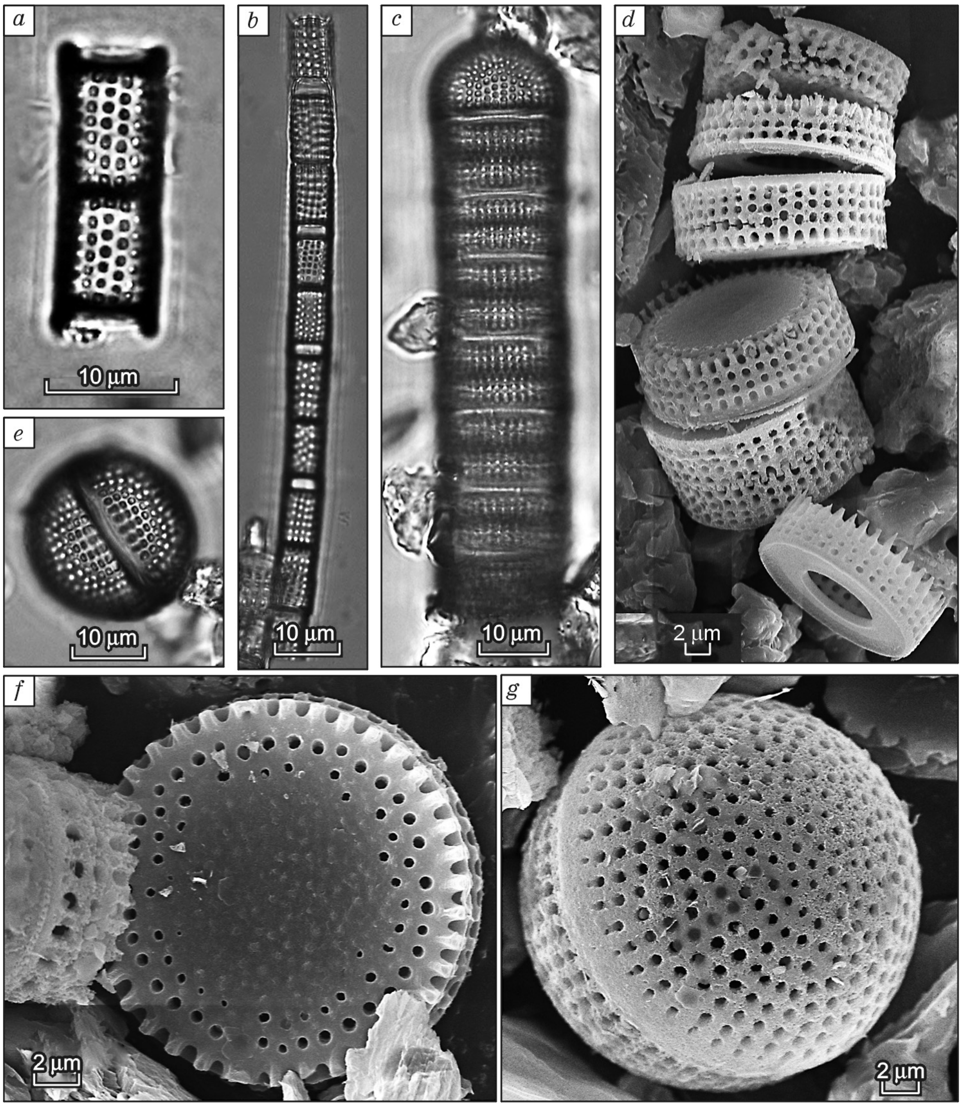


Fig. 4. Rock-forming taxa of the Terekhovka diatomite: *a*, *c*, *Aulacoseira praegranulata* var. *praeislandica* F. *praeislandica* (Sim.) Moiss., LM; *b*, g, *Aulacoseira auxospore* shells (*b,* LM; *g*, SEM); *d*, *e*, *f*, *A. praedistans* morphological group (*g,* LM; *d*, *e,* SEM).

Khanka and assigned to *Melosira praedistans* Jousé. Later this species was included in the synonymy *Aulacoseira praegranulata* var. *praeislandica* f.*praeis landica* (Sim.) Moiss. (Diatoms ..., 1992). The identified morphological assemblages of valves were called for convenience *praeislandica* and *praedistans,* respectively. The abundance estimates of other taxa are low, less than 1%; the only exception is *Melosira undulata* (Ehr.) Kütz., whose frequency index is 2.7%. Diatom shells in the rock are well preserved. The valve concentrations in 1 g of sediment is $5 \times 10^{9}$.

The valve sizes of the rock-forming taxa are presented in Table 5. Because of the large morphological variability of the valves of the dominant taxon, the size characteristics of the first (*praeislandica*) assemblage and the second (*praedistans*) assemblage are considered separately. In the *praeislandica* group, the minimum valve diameter is 4.45 μm, the maximum valve diameter is 10.21 μm, and the height is 7.84 and 12.34 μm, respectively. It should be noted that the valve height is more constant in this taxon, $C_V = 10.84$. In the *praedistans* group, the minimum valve diameter is 11.77 μm, the maximum valve diameter is 22.80 μm, and the valve height is 3.25 and 8.75 μm, respectively. The valve height-to-diameter ratio in both representatives of the genus *Aulacoseira* varies insignificantly. In *praeislandica*, it varies from 0.56 to 2.16, with a mean of 1.13, and for most of the valves, this parameter varies from 0.60 to 0.69; in *praedistans*, it varies from 0.24 to 0.63, with a mean of 0.36, and for most of the valves, this parameter is limited to within 0.24–0.28 and 0.40–0.47. The variability of the valve height is high, $C_V = 19.46$, and the valve diameter is more constant, $C_V = 15.\ 22$.

The chemical composition of valves of the rock-forming taxa of the Terekhovka diatomite is presented in Table 6. The concentration of the main elements varies as follows: the oxygen concentration varies from 50.47 to 52.86% in valves of the *praedistans* group*,* from 49.54 to 52.59% in valves of the *praeislandica* group; the silicon concentration varies from 35.49 to 43.73% in valves of *praedistans* and from 29.33 to 44.13% in valves of *praeislandica*. Among impurities, the

Table 5. Valve sizes of the rock-forming taxa of the Sergeevskii diatomite

| Species | Number of valves | Size, µm | | | σ | $C_v$ |
|---|---|---|---|---|---|---|
| | | minimum | maximum | mean | | |
| *Aulacoseira praegranulata* var. *praeislandica* f. *praeislandica* (Sim.) Moiss. (valve height) | 53 | 7.84 | 12.34 | 9.95 ± 0.15 | 1.15 | 10.84 |
| *Aulacoseira praegranulata* var. *praeislandica* f. *praeislandica* (Sim.) Moiss. (valve diameter) | 52 | 4.45 | 10.21 | 6.66 ± 0.15 | 1.05 | 15.83 |
| Morphological group *Aulacoseira praedistans* (valve height) | 65 | 3.25 | 8.75 | 5.00 ± 0.10 | 0.99 | 19.64 |
| Morphological group *Aulacoseira praedistans* (valve diameter) | 98 | 11.8 | 22.8 | 16.35 ± 0.25 | 2.48 | 15.22 |

Table 6. Concentration (%) of chemical elements in valves of the rock-forming taxa of the Terekhovka diatomite

*Aulacoseira praegranulata* var. *praeislandica* f. *praeislandica* (Sim.) Moiss.

| Element | API-1-1-1 | API-1-1-2 | API-2-1-1 | API-16-1-1 | API-16-1-2 | API-23-1-1 | API-23-1-2 | API-23-1-3 | API-23-1-4 | API-23-1-5 | API-23-1-6 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Si | 41.71 | 39.37 | 38.5 | 44.13 | 44.07 | 34.74 | 33.82 | 41.34 | 41.19 | 42.51 | 29.33 |
| O | 52.59 | 52.11 | | 52.62 | 52.60 | 49.99 | 49.98 | 52.06 | 51.90 | 52.30 | 49.54 |
| Al | 5.7 | 7.65 | 8.18 | 2.33 | 2.39 | 9.26 | 10.53 | 4.78 | 3.93 | 3.99 | 16.69 |
| Ca | – | – | – | – | 0.23 | – | – | – | – | – | – |
| Cu | – | – | 0.57 | – | – | – | – | – | – | – | – |
| Fe | – | 0.33 | 0.51 | 0.41 | 0.40 | 2.39 | 2.41 | 0.55 | 0.94 | 0.88 | 4.19 |
| W | – | – | | – | – | – | – | – | – | – | – |
| Mg | – | 0.27 | 0.31 | – | – | 1.03 | 0.72 | 0.27 | – | – | – |
| Ti | – | 0.28 | – | – | – | 0.27 | 0.50 | 0.22 | 1.69 | – | – |
| K | – | – | 0.26 | 0.21 | 0.31 | 1.19 | 0.92 | 0.31 | 0.35 | 0.32 | – |
| Na | – | – | – | 0.30 | – | 1.12 | 1.12 | 0.46 | – | – | 0.24 |

Morphological group *Aulacoseira praedistans*

| Element | APD-8-1-1 | APD-8-1-2 | APD-8-1-3 | APD-8-1-4 | APD-8-1-5 | APD-13-1-1 | APD-13-1-2 | APD-13-1-3 |
|---|---|---|---|---|---|---|---|---|
| Si | 42.43 | 43.73 | 41.59 | 42.76 | 40.79 | 38.45 | 37.60 | 35.49 |
| O | 52.60 | 52.86 | 52.39 | 52.48 | 52.17 | 50.47 | 51.17 | 50.75 |
| Al | 4.69 | 3.41 | 5.48 | 3.89 | 6.14 | 6.27 | 8.41 | 10.41 |
| Ca | – | – | – | – | – | – | – | – |
| Fe | 0.28 | – | – | – | 0.30 | 0.33 | 0.68 | 0.74 |
| W | – | – | – | – | – | – | – | – |
| Cu | – | – | 0.54 | 0.60 | 0.60 | – | 0.51 | 1.15 |
| Br | – | – | – | – | – | – | – | – |
| K | – | – | – | 0.16 | – | 3.97 | 0.88 | 0.52 |
| Na | – | – | – | – | – | 0.51 | 0.46 | 0.56 |
| Mg | – | – | – | – | – | – | 0.30 | 0.37 |

highest concentrations (up to 2.39% in valves of the *praeislandica* group) are characteristic of iron. Copper, potassium, sodium, and magnesium impurities are constant for valves of both representatives. In valves of the praeislandica group, titanium was found.

## Discussion of results

The conditions of formation of the diatom paleocommunities identified in the diatomites were determined by studying their taxonomic composition and ecological structure. The pronounced dominance and high concentration of valves of plankton centric diatoms in the Puzanov diatomite indicate that it formed in a large deep freshwater lake. It is this diatom flora composition that is typical of present large lakes (Davydova, 1985; Gibson et al., 2003). The high diversity of fouling and benthic forms is due to the presence of a well-developed littoral zone with aquatic vegetation in the lake. During the period of formation of the diatomite, the depths of the lake were relatively great (> 10 m). The water was transparent with good aeration, high oxygen concentration, low acidity, low salt concentration, and high eutrophy. The disappearance of the lake, as well as its appearance, is due to tectonic shifts or the resumption of volcanic activity—the diatomite layer is blocked and underlain by interbedded pyroclastic material (Cherepanova and Grebennikova, 2001).

The rock-forming taxa for the Puzanov diatomite are *A. subarctica* and *S. niagarae* var. *pusanovae*. A similar composition of the dominant diatom assemblage was identified in the diatom flora of the Early Pliocene–Late Quaternary Salli diatomite deposit in Armenia (Golovenkina, 1981) and the Lower Pleistocene lacustrine sediments of the Uryuzaka (Tanaka, 2000) and Onikobe (Tanaka and Nagumo, 2006) formations in Japan.

The diatom flora of the Sergeevskii diatomite is dominated by benthic pennate small-valved forms and the percentage of planktonic diatoms is insignificant. Accumulation of the valves forming the Sergeevskii diatomite occurred in a shallow eutrophic lake with swampy banks (representatives of the genera *Eunotia, Cymbella,* and *Neidium* are present), perhaps in an oxbow lake located in the floodplain of a small river (small-valved *Staurosira, Pseudostaurosira, Staurosirella*). Similar taxonomic composition and ecological community structure are typical of small lakes in forest areas (Cherepanova et al., 2013; Laing and Pienitz, 1999; Pienitz and Smoll, 1993). An interesting finding in the sediments is *Actinella brasiliensis* Grun. (see Fig. 3*h*), which suggests the relatively warm climatic conditions of the development of the diatom flora. The taxonomic composition and ecological structure of the Sergeevskii diatomite flora are similar to those of the diatom zone Aulacoseira praegranulata var. praeislandica F. praeislandica corresponding to the Late Pliocene (Likhachev et al., 2009). However, the absence of valves of the index species of the zone *A. praegranulata* var. *praeislandica* F. *praeislandica* and the participation of present *A. italica* in paleocommunities are likely to indicate that the sediments formed at the end of the Late Pliocene.

The rock-forming taxa of the Sergeevskii diatomite are *S. constuens* var. *venter*, and *A. italica* and *Cymbella* aff. *australica*. Holocene diatomites similar in the composition of the rock-forming group and assigned by I.N. Demidov and T.S. Shelekhova (2006) to the type II identified by them have been reported in Karelia, on Kunashir island (Cherepanova and Grebennikova, 2001), and in Armenia (Golovenkina, 1981).

An important role in the formation of the Terekhovka diatomite was played by planktonic centric diatoms of the genus *Aulacoseira*. Valve accumulation occurred in a small low-mineralized lake, most likely, swampy in places (representatives of the genus *Eunotia* are present), which periodically dried up and was filled with water during floods. This is evidenced by the clays present in the sedimentary column and inclusions of sand. It should be noted that during the accumulation of the diatomite layer, the Razdol'naya River in its present state did not yet exist (Pavlyutkin and Borovskii, 1988).

The rock-forming taxa are representatives of the genus *Aulacoseira*. Diatomites of similar composition were found by I.N. Demidov and T.S. Shelekhova (2006) in Karelia and assigned to the type I identified by these authors.

The diatom shells in all diatomites are well-preserved as there were certain favorable conditions for preservation of the valves of dead diatoms: near neutral acid-base balance (pH) of both bottom and entrapped waters and the presence of areas of calm water, in which sedimentation of diatom shells occurred.

In all diatomites we have studied, the valve concentration in 1 g of rock is quite high. The valve concentration is the highest (1.5 billion valves/1 g of dry sediment) in the Terekhovka diatomite, somewhat lower (960 million valves/1 g of dry sediment) in the Puzanov diatomite, and the lowest concentration in the Sergeevskii diatomite (610 million valves/1 g of dry sediment). These valve concentrations in sediments may indicate that the lakes contain high concentrations of the chemical elements stimulate the growth and reproduction rate of diatoms (Militenko and Labutin, 2000). They could enter lakes with volcanic products containing silicon, aluminum, iron, titanium, phosphorus, etc., needed to build diatom valves. Evidence of volcanic activity is intercalations of volcanic ash and basalt, opened by the sections studied. The valve concentration in the sediments may suggest different types of volcanic eruptions. Explosive volcanic eruptions of the Kuril Islands with associated emissions of pyroclastic material (Belousov, 2006) provided deposition of ash material over a large territory, including the surface of the lake in which the Puzanov diatomite formed. Similar sedimentation conditions of the Terekhovka diatomite are evidenced by the results of particle-size analysis of sediments from borehole 415 (Pavlyutkin and Petrenko, 2010). Small volcanic particles entering the lake more actively provide it with the material necessary for valve construction, as compared, for example, with the interbedded basalt lining the bottom, as is noted for the lake in which the Sergeevskii diatomite formed. During the formation of siliceous deposits, the Sergeevskii River basin was the marginal part of a graben-like structure situated in the tectonic magmatic activity area of the East Sikhote-Alin (Kovalenko, 1989).

At the same time, we should bear in mind another possible cause of the high productivity of diatoms. This is the long growing season due to the paleoclimatic characteristics of the region. In the present waters of temperate latitudes, the production of diatoms is maximal in the spring-autumn period, and often, they have a subordinate position in the algal flora in comparison with the other divisions of algae, so that their concentration in sediments is insignificant. During global cooling periods, accompanied by an increase in illuvial horizons, the growing season of diatoms becomes much longer, resulting in diatoms becoming leading in the algological composition. Assessing the climatic conditions of the diatomite accumulation period, it should be noted that the Puzanov diatomite formed in a wet and relatively cool climate (Cherepanova and Grebennikova, 2001); palynological data obtained for the Pliocene deposits of Primorye indicate that the climate here was also cool (Pavlyutkin and Petrenko, 2010).

One of the main characteristics of diatomites is their particle-size distribution. For this, we analyzed the morphometric characteristics of valves of the rock-forming taxa. Indicators of the granulometric homogeneity of the rocks may be the coefficient of variation of some morphometric parameters of valves and the valve height-to-diameter ratio in centric taxa, which is also used as a criterion for their taxonomic diagnosis (Genkal, 1999; Krammer and Lange-Bertalot, 1991; Usol'tseva, 2005). According to these indicators, the Terekhovka diatomite is the most homogeneous (the total $C_v$ for the valves of the diatomite is 48.6). This is primarily due to the fact that the rock is composed of valves of taxa belonging to one genus of centric diatoms. The coefficients of variation of the mantle height and valve diameter of the rock-forming *A. praegranulata* var. *praeislandica* F. *praeislandica* are relatively low and equal to 10.8 and 15.8, respectively. The valves included in the *praedistans* assemblage are more variable ($C_v$ of 19.6 for mantle height and 15.2 for valve diameter). The high values of the valve height-to-diameter ratio, three times those in the first assemblage of valves, served as the basis for the identification of two morphological groups. The presence of these assemblages may be indicative of the pronounced seasonality typical of the time of formation of the diatomite. A similar situation is noted for mesotrophic Lake Krasnoe, located in the central part of the Karelian Isthmus (Trifonov, 2008). Long-term studies of the population dynamics of the structure-forming algae species in the lake have showed the dominance of different species of *Aulacoseira* in the algological communities in different seasons. For example, *A. granulata* (Ehr.) Sim. dominates in summer and autumn, with maximum abundance in July-August, and *A. islandica* (O. Müll) Haworth dominate in spring and autumn with a sharp increase in the population number in the middle or end of May.

The Puzanov diatomite is less homogeneous. The total coefficient of variation of the morphometric characteristics of valves of its rock-forming taxa is 78.45. The sedimentary communities are dominated by representatives of two centric genera with large differences in valve diameter, from the minimum diameter of 1.9 μm in *Aulacoseira subarctica* to the maximum of 61.9 μm in *S. niagarae* var. *pusanovae*. It is necessity to note that for valves of each taxon, the variability of morphometric parameters is low ($C_v$ of 11.68 for valve height and 26.75 for diameter in *A. subarctica*, and $C_v$ of 18.02 for diameter in *S. niagarae* var. *pusanovae* ). The wide range of the valve height-to-diameter ratio in *A. subarctica* (1.55–7.10), most likely indicates a long growing season and favorable habitat conditions for this species in the lake.

The Sergeevskii diatomite is the most inhomogeneous in granulometric characteristics: the total $C_v$ of valves =169.3. The group of dominant taxa includes both small-valved *S. construens* var. *Venter* and *A. italica* (minimum size of 2.96, and maximum size of 23.22 μm), and large-valved representatives of the genus *Cymbella*, up to 175 μm in length. Considerable variability of valves was also determined for each individual taxon, in particular, the coefficient of variation is 38.2 for length and 10.9 for width in *S. construens* var. *venter*, 33.3 for diameter and 17.5 for mantle height in *A. italica*, and 14.9 for length in representatives of *Cymbella.* The high species richness of the dominant group is evidence of the relatively shallowness of the lake and instability of its hydrological regime.

A new and promising, but not yet completely developed direction of diatom analysis is the study of the elemental composition of diatom shells by SEM with X-ray spectrometers of different types (Loseva and Filippov, 2012). This method can be used to determine both the sedimentation conditions and sediment age.

It is known that diatom shells consists of silicon oxide hydrate similar to opal ($SiO_2 + xH_2O$, density 2.07) with metal impurities (aluminum, iron, magnesium) and an organic component (Vasser, 1989). In fossil diatoms, protein is lost and silicon increasingly crystallizes with time (Proshkin-Lavrenko, 1974). The most persistent components of diatom shells are Al and K; Fe and Ca are also common. A notable component may be Mg. Other elements (Ti, S, Cl, Na) are much less common. It is possible that the presence of certain elements is associated with subsequent contamination of diatom valves (Losev and Filippova, 2012), although foreign scientists (Hamilton et al., 1997) who studied purified shells believe that elements such as Fe, Cu, and Al are important chemical components in the siliceous structure of the valves.

In valves of the rock-forming taxa of all three diatomites studied, the main elements are silicon and oxygen, but their concentration varies in different species. At the same time, the ratio of the concentrations of these elements makes it possible to draw some conclusions about the environmental habitats of the diatoms forming siliceous rocks. For example, high oxygen concentrations and relatively low silicon concentration in valves of the Puzanov diatomite are likely to indicate that the rock-forming taxa evolved in deep-water plankton communities. Slight silicification of the valves allows the diatoms to float in the water column. The fairly high silicon concentration in valves of the Terekhovka diatomite, in contrast, may indicate that the main habitat of the diatoms were benthic ecotopes in a shallow lake. The existence of shallow lakes in the Razdol'naya River valley, where this diatomite was mined, is also confirmed by other data (Pavlyutkin and Petrenko, 2010).

We have identified a wide range of impurities in the investigated diatomites. The largest number of them in relatively high concentrations in the valves was found in valves of the Terekhovka diatomite (Al, K, Fe, Ca, Ti, Na, W, Cu, Br, and Mg). Of these, Al, Fe, Ca, W, Cu, and Br are persistent impurities in valves of all investigated diatomites. Such a variety of impurity elements is most likely due to volcanic activity near the lakes in which the diatomites formed. At the same time, there is the point of view that the presence of impurities may be due to the ability of silica gel to adsorb cations (Gilian and Caade, 2000).

## Conclusions

The studies performed allowed a comprehensive characterization of diatomites from three localities of the Far East, formed in freshwater lakes of different types. The lacustrine origin of the sediments is supported by the presence (even dominance in two diatomites) of the genus *Aulacoseira.* The participation percentage of diatoms of this genus has also made it possible to refine the age of the sediments. The oldest Terekhovka diatomite of Pliocene age is characterized by an almost monodominant paleocommunity composed of *Aulacoseira* taxa of the prae morphological group (93.2%). This time period is generally characterized by the wide occurrence of diatoms of this morphotype: in Lake Baikal (Kuz'min et al., 2009) and the lakes of Primorsky Krai (Likhachev et al., 2009). This is likely due to a certain evolutionary step in the history of this genus. It has been established that in the Pliocene there is a gradually extinction of the ancient *Aulacoseira* taxa of the prae group, and from the Middle Pleistocene, species have emerged that exist to the present day (Kuz'min et al., 2009).

Geologists date the Sergeevskii diatomite as Upper Miocene–Pliocene, but the presence of valves of the present species *A. italica* in it suggests that the sediments formed in the Late Pliocene (according to the new Quaternary scale, the Early Pleistocene).

Based on a detailed diatom analysis of siliceous sediments, we have identified the following main characteristics of the investigated diatomites.

The Terekhovka diatomite, formed in a small low-mineralized lake, is distinguished by a very high concentration of valves per 1 g of rock and a uniform taxonomic composition, which determines the most uniform particle-size characteristics of the sediments. Valves of a single species constitute over 90% of the rock, although a detailed study has identified two morphological assemblages, one with a low mantle and a large diameter and the other with high mantle and a small diameter, within which the variability of valves is low. Valves of the diatomite have a high silicon concentration and a large amount of impurity elements.

The Puzanov diatomite, formed in a deep freshwater lake, is characterized by a high concentration of valves and the most diverse taxonomic composition. It is less uniform in particle-size characteristics than the Terekhovka diatomite. The range of variability of the diameters of the two dominant taxa belonging to different genera is rather wide, but the fact that the fact that they belong to the same class (centric diatoms) allow these rocks to be considered high quality with a wide range of possible applications. The valves are slightly silicified, and the number of impurity elements is common to all diatoms.

In the Sergeevskii diatomite, formed in a shallow eutrophic lake, the valve concentration is the lowest and the variability in the valve sizes is the highest. This fact and the small thickness of the deposit limits the possibility of using this diatomite.

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