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The First Finds of Glendonites in the Upper Jurassic–Lower Cretaceous Bazhenovo Formation (West Siberia, Frolovskaya Megadepression) and Their Paleogeographic Significance

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Abstract—This article describes the first findings of glendonites (pseudomorph after calcium carbonate hexahydrate ikaite, which crystallize at near-freezing temperatures) from the Bazhenovo Formation (West Siberia, Upper Jurassic–Lower Cretaceous). Glendonites originate from the depressed structures of the central part of the Frolovskaya Megadepression and the deepest areas of the West Siberian paleobasin. Glendonite findings have received a reliable stratigraphic reference and originate from the interval of the Ryazanian Regional Stage. Based on the stable isotopic composition, we propose ikaite crystallized and transformed during organoclastic sulfate-reduction in the bottom sediments. Ikaite crystallization might be caused by the penetration of bottom cold currents from the Paleoarctic basin due to sea level fluctuations during the Ryazanian Stage.

Keywords: Bazhenovo Formation, Ryazanian Stage, West Siberia, paleogeography, glendonites, stable isotopes, diagenesis

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INTRODUCTION

Glendonites, pseudomorphs of the metastable mineral ikaite ($CaCO_3 \cdot 6H_2O$), have attracted the attention of sedimentologists and paleogeographers for many decades (Frank et al., 2008; Vickers et al., 2018; Counts et al., 2024). This is explained by the fact that ikaite is found in natural conditions at low bottom temperatures (below 7°C); with increasing temperature, this mineral dehydrates and can be preserved in a fossil state only if it is rapidly replaced by calcite (thereby forming a pseudomorph, glendonite). After the transformation of ikaite into calcite, glendonite can undergo a number of mineral replacements, mainly silicification and dolomitization (Mikhailova et al., 2019; Vasileva et al., 2021). Glendonite finds have been recorded at different stratigraphic levels and in a wide range of sedimentation environments (Rogov et al., 2023); In modern settings, ikaite is found only at low temperatures of bottom waters, which makes it possible to use glendonites as indicators of cold-water bottom environments of the past (Kaplan, 1980; Vickers et al., 2019; Schultz et al., 2023). Therefore, the study of the distribution of glendonites in sedimentary strata is an important task in interpreting paleogeographic and paleoclimatic sedimentation conditions.

In Jurassic and Cretaceous deposits, glendonites are common in sections of the Northern Hemisphere; however, their geographic and stratigraphic distribution is uneven (Rogov et al., 2023). They are least common in the Volgian and Ryazanian intervals, which is consistent with warming at the very end of the Jurassic according to the study of the oxygen isotope composition of mollusk shells at high latitudes of the Northern Hemisphere (Price and Mutterlose, 2004; Price and Rogov, 2009; Dzyuba et al., 2018; Rogov et al., 2019; Vickers et al., 2022).

Glendonites from the Ryazanian deposits[1] are sporadically found in the Yanovstan Formation in western Taimyr, where they originate from the Novoyakimovskaya-1 parametric well (Olenova et al., 2023; Rogov et al., 2024b), in the northeast of the Siberian Platform (Rogov et al., 2017), and in Arctic Canada (Rogov et al., 2023). It is noteworthy that glendonites from the Volgian and Ryazanian intervals have not been known in Western Siberia until now. This paper presents data on the stratigraphy, mineral composition, and isotopes of the first glendonite finds in black shales of the Bazhenovo Formation within the central part of the Frolovskaya Megadepression (central Western Siberia).

GEOLOGY OF THE REGION AND LITHOLOGICAL CHARACTERISTICS OF THE STUDIED SECTION

The high-carbon carbonate–clay–silicite Bazhenovo Formation of Western Siberia and its stratigraphic analogs have been studied in detail based on drilling and seismic profiling data and described in numerous publications (Filina et al., 1984; Braduchan et al., 1986; Zakharov, 2006; Panchenko et al., 2016; Gilaev et al., 2018). These deposits accumulated over a long period (from the Kimmeridgian to the Early Valanginian) and covered most of the West Siberian Plate. At the same time, they have a relatively small thickness (20–60 m, on average about 30 m). In the studied area of the Frolovskaya Megadepression, they include the Bazhenovo and Kulomzin horizons (Lower Volgian Substage–Ryazanian Stage). Despite the lateral heterogeneity of the Bazhenovo Formation (Braduchan et al., 1986), it has a typical sequence of members (Panchenko et al., 2016): lower members 1, 2a, 2b, and 3 are composed of silicites and radiolarites with low clay (2–20 vol %) carbonaceous content (C_{org} 1–20 wt %), different textures, and inclusions. In particular, lenticular phosphorite interbeds are contained in members 1 and 2a, bivalve accumulations are characteristic of Member 2a, and lenticular pyrite is typical of members 1, 2a, and 3. Member 2b is the most siliceous interval of the Bazhenovo Formation, which is rich in radiolarian skeletons, and Member 3 contains lenticular radiolarites in the highly carbonaceous clay–silicite mass. Overlying members 4a and 4b are composed of homogeneous and very thinly layered, highly carbonaceous (C_{org} 10–30 wt %) clayey silicites (10–25 vol %); at the same time, their main finely dispersed mass is almost completely free of carbonate. Member 4a is characterized by a homogeneous composition and a minimum number of inclusions, while 4b is always rich in inoceramid shells (bivalves). Overlying members 5a and 5b contain a variable but noticeable amount of nanoplankton (coccolithophores), which performs a rock-forming function here. The lower strata of Member 5a mark fairly abundant finds of shells of the bivalve *Buchia* in low-carbonate deposits; higher up the section, the carbonate content increases nonlinearly, up to the appearance of limestones. Member 5b is formed from essentially clayey coccolithophore silicites. In thin layers of members 5a and 5b, the predominance of one of the following components regularly changes: clays, calcite, and siliceous material; this complicates the systematics of these rocks. Upper members 6a and 6b are the most clayey interval of the Bazhenovo section with transitional properties in relation to the overlying deposits. They are characterized by an almost complete absence of carbonate material and a highly significant and often predominant role of clays (40–50 vol %) with high concentrations of organic matter (C_{org} 10–30 wt %).

Members 1 to 4a belong to the Volgian Stage of the Upper Jurassic; inoceramid Member 4b occupies the Upper Volgian–Lower Ryazanian boundary position; overlying coccolithophore members 5a and 5b correspond to the Ryazanian Stage of the Lower Cretaceous, while Member 5b is dated to the lowermost strata of the Valanginian in some sites (*Resheniya*..., 2004; Panchenko et al., 2016, 2022). Members 6a and 6b are of Early Valanginian age.

MATERIALS AND METHODS

The material for the study included 14 samples of rock material from the core of a borehole drilled within the Priobskoye oil field (the central part of the Frolovskaya Megadepression). According to the lithological and stratigraphic reference, the studied core characterizes the upper part of Member 4b (high-carbon silicites with inoceramids) and Member 5a (coccolithophore silicites with buchias) of the Bazhenovo Formation (Fig. 1). At the same time, it is worth noting the atypically high saturation of Member 5a with carbonate material in the studied well. A relatively accurate biostratigraphic reference of the studied interval was determined based on the remains of macrofauna. The macrofauna is represented mainly by fragments of bivalves and ammonite moulds.

Glendonites were found in three samples (F9, F10, and F15 in Fig. 1). Petrographic and cathodoluminescent descriptions of the glendonites were made on an

[1] In this paper, the Volgian and Ryazanian stages are used for the Jurassic–Cretaceous boundary interval (Rogov et al., 2024a).

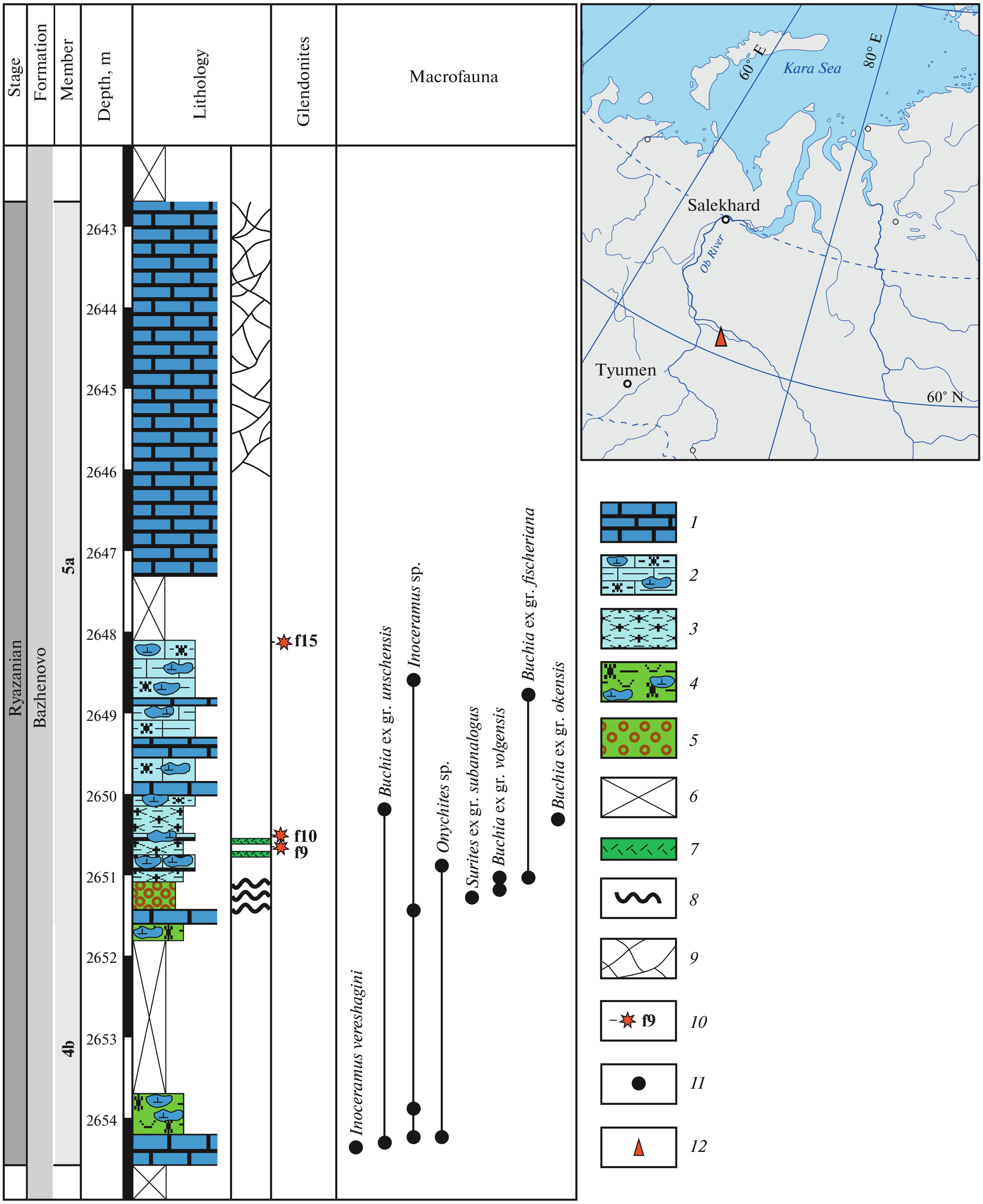

Fig. 1. Litho- and biostratigraphic reference of the studied interval and position of the studied glendonites. (*1*) Limestones of various genesis; (*2*), (*3*) thin alternation of coccolithophore carbonaceous silicites with clayey–siliceous carbonaceous limestones (*2*) with numerous and variable carbonate nodules, (*3*) almost without nodules); (*4*) highly carbonaceous clayey silicites with inoceramids and calcareous nodules; (*5*) interval of silicite development with allochthonous accumulations of ichthyodetritus; (*6*) core drilling gap; (*7*) thin (mm) interbeds of altered ash tuffs (Panchenko et al., 2022); (*8*) erosional boundaries and layers with rewashed material; (*9*) multidirectional cracks; (*10*) position of samples with the studied glendonites in the section; (*11*) locations of macrofauna finds (cephalopods and bivalves); (*12*) location of the studied well.

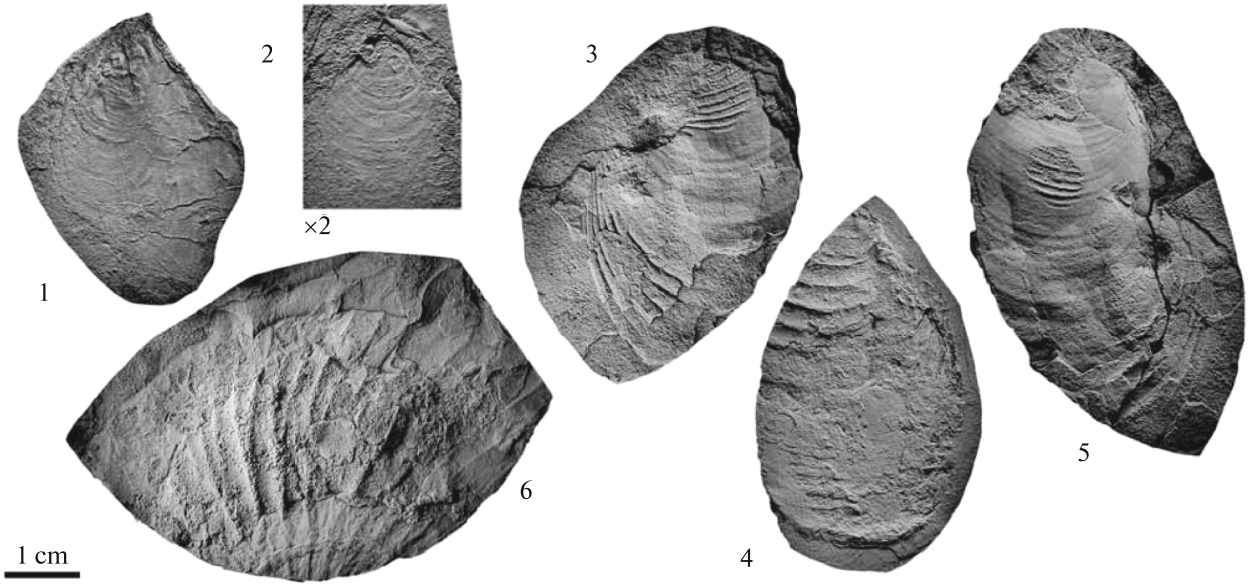

Fig. 2. Remains of mollusks from the studied well. Specimens are coated with ammonium chloride. The collection is deposited at the Aprelevka Branch of the All-Russia Research Geological Institute. (1) *Inoceramus vereshagini* Pokhialaynen, specimen MAR7/1, depth of 2654.34 m; (2) *Buchia* ex gr. *unschensis* (Pavlow), specimen MAR7/2, depth of 2654.28 m; (3), (5) *Buchia* ex gr. *volgensis* (Lahusen); (3) *Buchia* ex gr. *volgensis* (Lahusen), specimen MAR7/7, depth of 2651.19 m, (4) *Buchia* ex gr. *okensis* (Pavlow), specimen MAR7/10, depth of 2650.28; (5) *Buchia* ex gr. *volgensis* (Lahusen), specimen MAR7/8, depth of 2651.04 m; (6) *Surites* ex gr. *subanalogus* Schulgina, specimen MAR7/6, depth of 2651.30 m.

Olympus BX53 microscope with a CITL5 Cambridge Technology cold cathodoluminescence attachment (at the Department of Regional Geology, St. Petersburg State University); isotopic studies were also carried out for samples from the glendonite-hosting rock (bulk sample), bivalve shells (indeterminate due to poor preservation), and bulk samples of glendonites from samples F9, F10, and F15 (Laboratory of Isotope and Elemental Analysis, Kazan Federal University, Delta V Plus Thermo Fisher Scientific mass spectrometer, Germany, with a GasBench II attachment for carbonate analysis by acid treatment, analytical measurement accuracy ±0.2‰); samples were normalized to the Vienna PeeDee Belemnite standard (‰ V-PDB).

RESULTS

Substantiation of the Age of the Studied Section

We studied the remains of mollusks encountered together with glendonites in the lower half of the interval characterized by the core (depth of 2848.4–2654.3 m, Fig. 1). The most widespread mollusks are bivalves characteristic of the Bazhenovo Formation: *Buchia* and *Inoceramus* (Fig. 2). The degree of preservation makes it possible to identify these specimens only in open nomenclature; nevertheless, this makes it possible to determine the age of the interval. Inoceramids can only be identified to the genus level except a single specimen. In Western Siberia, representatives of *Inoceramus* are common mainly in the interval from the Upper Volgian Substage to the lower strata of the Upper Ryazanian Substage and found in large numbers in the Lower Ryazanian Substage (Panchenko et al., 2016; 2022). In particular, their largest accumulations in the Bazhenovo Formation are confined to "inoceramoid" Member 4b of the Late Volgian–Early Ryazanian age (Panchenko et al., 2022). *Buchia* are represented by species that occur mainly in the Lower Ryazanian Substage: *Buchia* ex gr. *volgensis* (Lahusen), *B.* ex gr. *fischeriana* (d'Orb.), *B.* ex gr. *okensis* (Pavlow), and *B.* ex gr. *unschensis* (Pavlow). A related assemblage, represented by *B. volgensis*, *B. okensis* and *B. fischeriana*, has been recently described from the upper part of the Lower Ryazanian Substage in the Novoyakimovskaya-1 borehole (Rogov et al., 2024b). The distribution of *B. okensis* and *B. volgensis* is limited by the boundary interval of the lower and upper Ryazanian substages (Zakharov, 1987; Zakharov, 1990); the species *B. unschensis* is present in the upper strata of the Volgian Stage–lower strata of the Ryazanian Stage, where it is encountered up to the Buchia top of the Okensis Zone (Zakharov, 1990). In the Bazhenovo Formation, the most frequent occurrence of *Buchia* shells is observed everywhere in the lower part of Member 5a (Panchenko et al., 2015). Onychites, coleoid arm hooks with no stratigraphic significance were found at two stratigraphic levels (Fig. 1). Of greatest interest for substantiating the age is the find of an ammonite fragment (depth of 2651.30 m). Based on the combination of predominantly biplicate ribs inclined towards the aperture and a wide umbilicus,

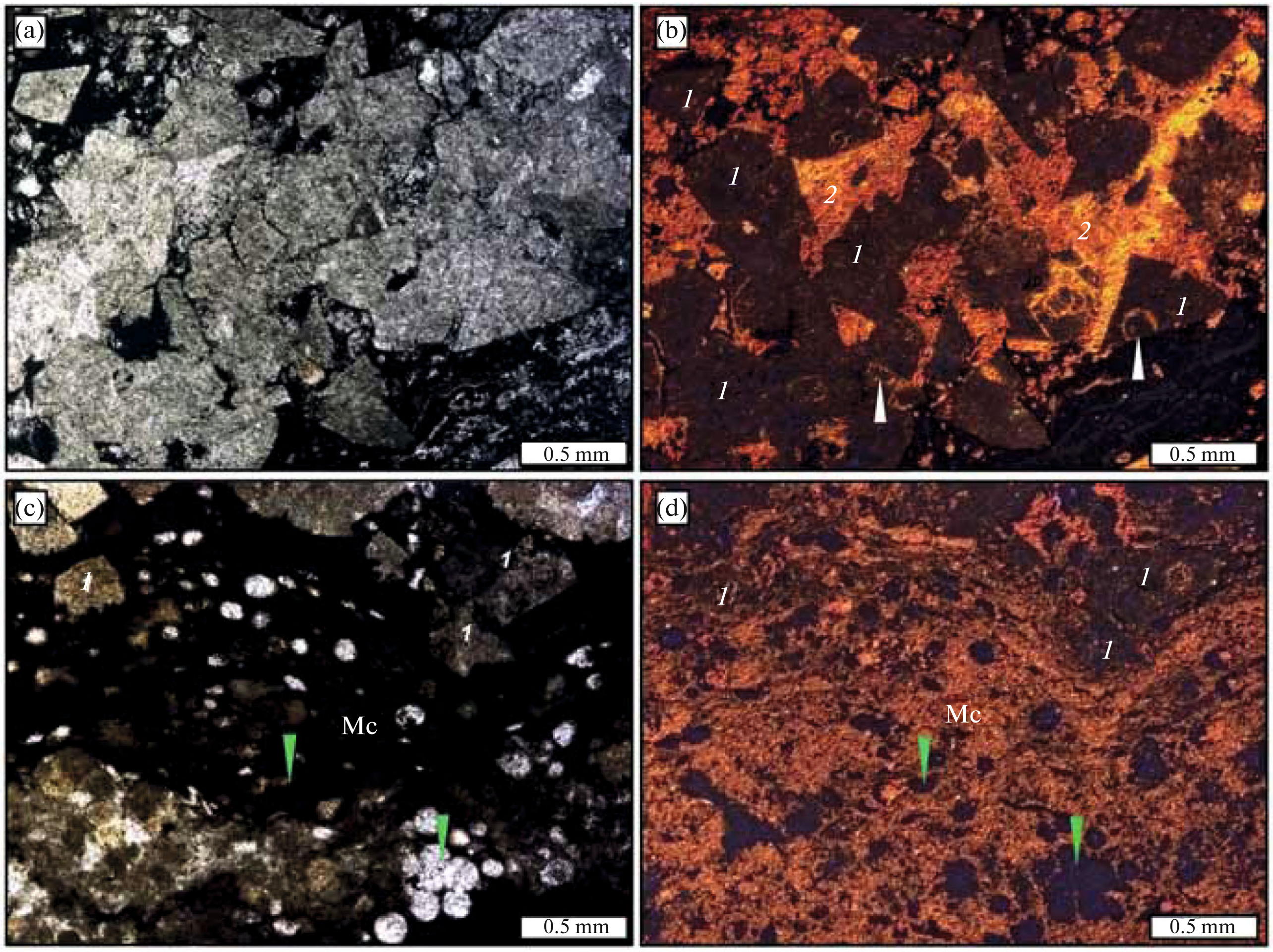

Fig. 3. Photographs of fragments of a thin section of sample F9: (a) glendonite, in transmitted light without an analyzer; (b) the same, with CL illuminescence; (c) host rock, in transmitted light with an analyzer; (d) the same, with CL illuminescence. (*1*), (*2*) types of calcite, Mc, micrite; white arrows show relics of radiolarian shells inside calcite crystals and green arrows show radiolarian shells composed of chalcedony.

this specimen is assigned to the genus *Surites*. It resembles the species *S. subanalogus* Schulgina, which is widespread from the upper part of the Kochi zone to the top of the Subanalogus zone (Igol'nikov, 2006). However, the degree of preservation of the specimen, which makes it impossible to establish the cross-sectional shape of the whorls, does not exclude the possibility of assigning this find to *S. praeanalogus* Alekseev, which is widespread only in the Kochi Zone. Therefore, the mollusk assemblage encountered in the core of the studied well makes it possible to determine the age of the interval characterized by the mollusks as most likely belonging to the upper part of the Lower Ryazanian Substage (Hectoroceras kochi Zone) and, possibly, to the lower part of the Upper Ryazanian Substage (Surites subanalogus Zone).

Taking into account the sequence of rocks and the paleontological characteristics of the core, the studied interval is attributed to the upper strata of members 4b and 5a of the Bazhenovo Formation (Panchenko et al., 2015, 2022).

Description of Glendonites

Glendonites appear in the studied section in clayey limestones and clayey silicites. They are small (less than 1 cm in samples F15 and F10) and elongated. In sample F9, the glendonite is elongated, up to 3 cm long. The glendonites are dark brown in the samples.

Petrographic and cathodoluminescent analysis shows that the glendonite is composed of several types of calcite. Euhedral calcite crystals (Type 1) with a triangular or rhombic cross-section (scalenohedra) have a crystal size of up to 1 mm and have almost no luminescence; radiolarian relicts can be seen inside such crystals on cathodoluminescent (hereinafter, CL) photographs. The remaining space inside the glendonite is filled with calcite with a brighter non-zonal cathodoluminescent glow of yellow, orange, and red colors (Type 2, Figs. 3a, 3b).

Previous studies of glendonites and processes of ikaite-to-glendonite transformation showed that ikaite dehydration resulted in the formation of zonal

Table 1. Isotopic composition of glendonites and bivalve shells from samples of the studied well

No.	Sample number	$\delta^{13}C$, ‰ V-PDB	$\delta^{18}O$, ‰ V-PDB
1	F9, fragment of a bivalve shell	1.5	−2.2
2	F9, fragment of a bivalve shell	−12.1	−4.7
3	F9, fragment of a bivalve shell	−9.7	−6.4
4	F9, glendonite, bulk sample	−4.9	−6.5
5	F9, glendonite, bulk sample	−5.2	−4.7
6	F10, glendonite, bulk sample	−0.9	−4.3
7	F15, fragment of a bivalve shell	0.5	−5.6
8	F15, glendonite, bulk sample	−1.0	−2.7
9	Host limestone, bulk sample	−16.1	−5.5

calcite crystals with a darker core and a light rim (Huggett et al., 2005; Morales et al., 2017; Vickers et al., 2019); the darker core usually has dark luminescence or has no luminescence at all, while the lighter rim of late calcite cements is characterized by luminescence in bright red-yellow colors (Frank et al, 2008; Vasileva et al., 2021). In terms of the microscopic appearance (absence of zoning within calcite crystals), the studied glendonites from the Bazhenovo Formation resemble anthraconitic concretions from high-carbon Lower Ordovician shales in the northwest of the East European Plate, described in (Mikhailova et al., 2019; Popov et al., 2019). The absence of zoning in the calcite crystals that make up the glendonite is most likely a consequence of the processes of ikaite–glendonite transformation and catagenesis alterations of glendonites is a topic for futher research based on more extensive material.

The host rock in sample F9 is represented by heterogeneous siliceous limestone (Fig. 3); the main components are radiolarians, which can be partially replaced by calcite, calcite peloids, and fragments of carbonate and phosphate shells oriented parallel to the bedding surface; at the contact with glendonite, the layers of the host rock are inclined parallel to the edges of the pseudomorphosis. Crystals of type 1 calcite are scattered in small quantities in the host rock. The space between the remains of fauna and calcite crystals is filled with micrite with a bright orange–yellow CL glow.

Isotopic Composition of Glendonites, Host Limestone, and Bivalve Shells

The results of studies of stable oxygen and carbon isotopes in the samples from the studied borehole are shown in Table 1 and Fig. 4. The $\delta^{13}C$ values in glendonites vary from −5.2 to −1.0‰ V-PDB and $\delta^{18}O$ from −6.5 to −2.7‰ V-PDB; therefore, organic matter decomposing during diagenesis and inorganic carbon dissolved in seawater were the source of carbon; seawater and, possibly, basin fluids were the source of oxygen (the reference values are given in (Campbell, 2006)). The oxygen (−6.4 to −2.2‰ V-PDB) and carbon (−12.1 to +1.5) isotope ratios in the mollusk shells, albeit different from those determined for the

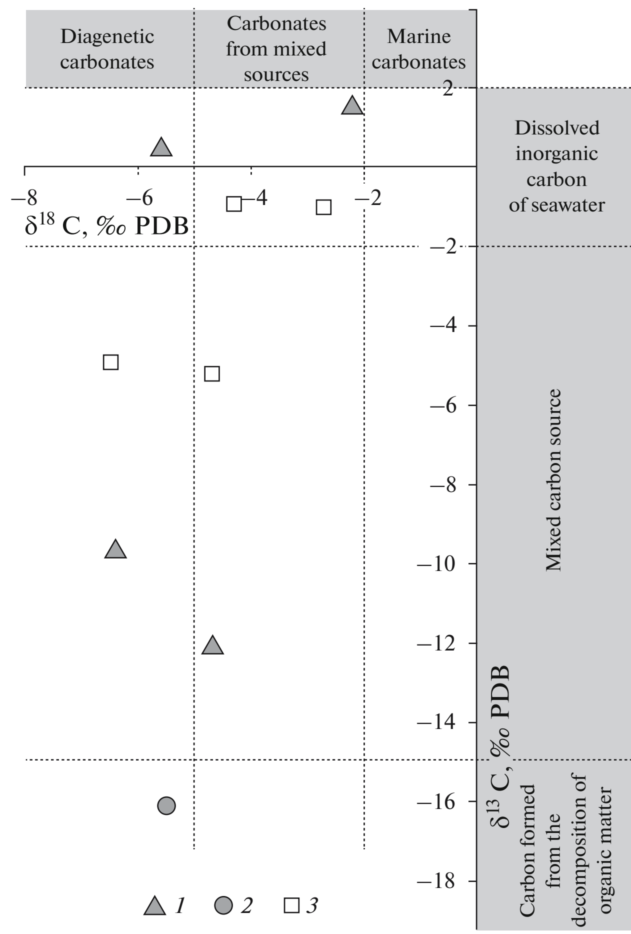

Fig. 4. Ratios of stable oxygen isotopes ($\delta^{18}O$, ‰ V-PDB) and carbon ($\delta^{13}C$, ‰ V-PDB) in the studied samples of glendonites and bivalve shells. (*1*) samples from bivalve shells, (*2*) sample from host limestones, (*3*) samples from glendonites.

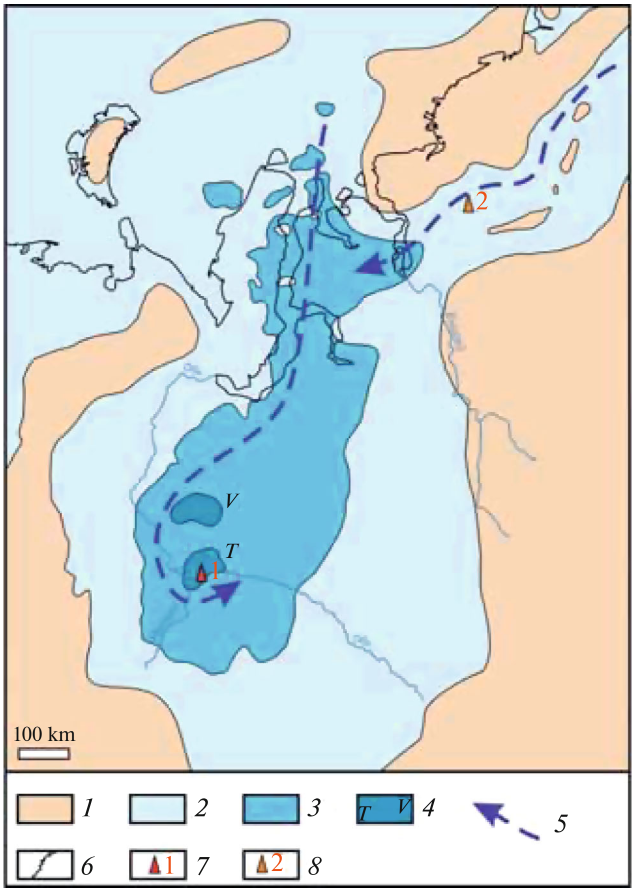

Fig. 5. Paleogeographic scheme of the West Siberian Basin in the Ryazanian (Kontorovich et al., 2014, with simplifications) and with the supposed direction of the bottom cold currents (Zakharov, 2006). (*1*) land and transitional settings; (*2*) shallow-marine settings (up to 200 m); (*3*) deep-water settings (200–400 m); (*4*) contours of the deepest depressions (basins) (according to (*Atlas*…, 2004)), V, Vynglor depression, T, Tundra depression; (*5*) supposed distribution of cold-water bottom currents; (*6*) modern coastline; (*7*) position of the studied well; (*8*) position of the Novoyakimovskaya-1 well.

glendonites, indicate that the oxygen and carbon sources were the same as those used during the crystallization and transformation of ikaite. The lowest $\delta^{13}C$ value (–16.1‰ V-PDB) was recorded for the host limestone; the $\delta^{18}O$ value in this sample was –5.5‰ V-PDB.

DISCUSSION

According to the existing knowledge, most of the territory of Western Siberia was covered with the vast epicontinental sea throughout the Bazhenovo; at the same time, the deepest part of the basin (Central Basin) is recorded in the western part of the basin with depths from 100 m or less (Stupakova et al., 2016) to 200–400 m or more (Kontorovich et al., 2014). Climate conditions (subtropical semiarid and semihumid climate (Zakharov, 2006)) contributed to good heating of the waters, and the bottom waters outside the Central Basin warmed up to temperatures of 8–10°C (*Paleobiofatsii*…, 1978). However, Filina et al. (1984) note that the deepening of the basin might led to repeated penetrations of cold waters from the northern seas into the West Siberian sedimentary basin, with cold currents primarily penetrating into the most submerged areas of the paleorelief (the central depression).

Glendonites from the Bazhenovo Formation were unknown before this study. Therefore, some authors emphasize that the absence of such finds makes it impossible to confidently state low bottom temperatures of the Bazhenovo basin (Braduchan et al., 1986; Grishkevich, 2022). The formations that we studied are confidently diagnosed as glendonites close to the glendonites described from the Lower Ordovician of Estonia and Leningrad Region.

The isotopic characteristics of the host rock, glendonites, and the studied bivalve shells show that the isotope ratios in all samples are shifted relative to the ratios typical of marine carbonates (from –2 to +2‰ V-PDB (Campbell, 2006)) towards negative values, which is a characteristic feature of the carbonate interbeds of the Bazhenovo Formation (Yurchenko et al., 2016) and most likely associated with postsedimentary transformations of these deposits. The shift in the isotopic composition as a result of postsedimentary changes is a characteristic feature of glendonites of different ages (Rogov et al., 2023); however, the absence of low negative (below –30‰ V-PDB) $\delta^{13}C$ values characteristic of methane seeps of chemosymbiotic fauna species suggests that the influence of methane seeps was insignificant during the crystallization and transformation of ikaite.

Summarizing the above data, we can say that the bottom temperature in the West Siberian Basin, within local areas, could drop to near-zero temperatures at least in the Ryazanian; otherwise, the crystallization of ikaite would have been impossible. Such temperatures might result from the significant depth and, possibly, the influence of cold bottom currents that could penetrate into the West Siberian Basin through the Taimyr and Khatanga straits (Baraboshkin et al., 2007) (Fig. 5). Glendonites were also described from the age analogs of the Bazhenovo Formation, the Yanovstan Formation within the Yenisei–Khatanga Trough (Novoyakimovskaya-1 well) (Olenova et al., 2023) (Fig. 5); however, an additional role was played here by the proximity of this area to the paleoarctic basin, in which colder waters circulated. In the Novoyakimovskaya-1 well, glendonites are present not only in the Ryazanian, but also in the Lower and Middle Volgian deposits (Rogov et al., 2024b). The isotope ratios for glendonites and bivalve shells from the studied well show that carbon in the Bazhenovo Formation was extracted during the decomposition of organic matter and sulfate reduction, while there was apparently no significant influence of methane seeps;

after the transformation of ikaite into glendonite and the subsidence of the sedimentary basin, the glendonites underwent late transformations, which determined lower oxygen isotope ratios than normal sedimentary ones.

CONCLUSIONS

Glendonites were found and studied in the Bazhenovo Formation for the first time. They are confined to Member 5a, in the interval of development of carbonaceous clay–carbonate silicites and clay–siliceous limestones. The bivalve mollusks, *Buchia* and *Inoceramus*, and the ammonite *Surites* ex gr. *subanalogus* Schulgina, associated with glendonites make it possible to determine the age of the studied part of the section as the boundary interval between the Lower and Upper Ryazanian substages of the Lower Cretaceous. The discovered glendonites are intergrowths of scalenohedral crystals. These findings indicate that near-zero temperatures were established in the bottom layers in the deepest parts of the West Siberian paleobasin.

Based on the optical properties, glendonites are composed of two types of calcite: an earlier one without cathodoluminescence and a later one with bright orange cathodoluminescence. Based on the paleogeographic reconstructions, the locality of the studied glendonites coincides with the area of the greatest depths of the West Siberian sedimentation basin in the Ryazanian and the low bottom temperatures may be associated with great depths (up to 400 m according to (Kontorovich et al., 2014)) and penetration of cold water masses together with bottom cold currents. The ratios of stable oxygen and carbon isotopes in the glendonites show that oxygen was extracted from seawater and basin fluids during crystallization and transformation of ikaite and carbon was extracted during the decomposition of organic matter and from inorganic dissolved carbon. The crystallization of calcite and its dehydration during the immersion and interaction with the basin fluids of the strata involved processes that led to change in the isotopic marks $\delta^{18}O$ of the glendonites.

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CONFLICT OF INTEREST

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

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