New Data on Stratigraphy and Distributions of Glendonites from the Carolinefjellet Formation (Middle Aptian–Lower Albian, Cretaceous), Western Spitsbergen

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Abstract—The Aptian deposits on Spitsbergen Island are poorly studied. Moreover, there were no published data on fossil distribution in the Aptian and Albian in the vicinity of the town of Longyearbyen. This article provides new data on ammonite-based biostratigraphy of the Carolinefjellet Formation, indicating the presence of Beds with Tropaeum arcticum (middle Aptian) and Beds with Grantziceras (lower Albian). The age of the formation was verified and the presence of lower Albian strata was justified. The results of microscopic and isotope studies of five samples of glendonites collected from the middle Aptian of the Carolinefjellet Formation are composed of three calcite phases: ikaite-derived calcite and two successive types of cement, which fill cavities and develop partially after the first-phase calcite. The O and C isotope compositions of glendonites were measured in five bulk samples from the middle Aptian interval of the section. The δ^{18} O isotope composition of glendonites is significantly different from that of seawater, indicating the input of diagenetic fluids; the δ^{13} C values are characteristic of sedimentary organic matter and methanotrophy. For the first time, findings of ammonites allowed us to clarify the stratigraphic intervals of glendonite occurrence and associated cold-climate episodes and prove the early Albian age of glendonites from the top of the Carolinefjellet Formation.

Keywords: ammonite, glendonite, Spitsbergen, stratigraphy, stable isotopes, Lower Cretaceous **DOI:** 10.1134/S0869593821010056

INTRODUCTION

Compared to other stages of the Lower Cretaceous, the biostratigraphy of Aptian deposits of Spitsbergen Island is poorly studied. There are only scarce data on the distribution of bivalve mollusks, ammonites, and dinocvsts in this stratigraphic interval. The ammonitebased subdivision of the Spitsbergen Aptian is mainly based on studying the Cape Festningen section over 80 years ago (Hoel and Orvin, 1937). Later, no data on the distribution of ammonites in any section were published. At present, the only Tropaeum arcticum "Zone," which is included in the Boreal Zonal Standard, is distinguished in the middle Aptian sediments of Spitsbergen (Baraboshkin, 2004; Baraboshkin and Guzhikov, 2018). Given that this zone is underlain and overlain by thick strata, which are not characterized by findings of ammonites, it would be correct to call this stratigraphic unit "Beds with T. arcticum" (Ershova, 1983). The stratigraphic distribution of an index species of these beds and other taxa is still not clear.

The Albian in Spitsbergen is studied much better compared to the Aptian. On the basis of numerous findings of ammonites, rather detailed zonal scales of Albian of this region were developed (Ershova, 1983; Nagy, 1970). At this time, the Albian Stage is recognized reliably only in southern areas of Spitsbergen. The only evidence of the possible occurrence of the Albian deposits near Longyearbyen is the findings of ammonites (Spath, 1921) on Mt. Breinosa, located about 15 km southeast of the studied section. Unfortunately, the author did not provide images of these findings.

Glendonites are calcite pseudomorphs, often used as an indicator of low near-bottom temperatures (Kaplan, 1979; Kemper and Schmitz, 1981). It was proved that they were developed after ikaite, a metastable calcium carbonate hexahydrate (CaCO₃ \cdot 6H₂O) (Kaplan, 1979; Suess et al., 1982). Unlike other carbonates, the stability of ikaite increases with decrease in the temperature. The most stable ikaite is formed at 0–4°C (Bischoff et al., 1993). The carbon necessary for the development of ikaite crystals comes from three sources: inorganic dissolved carbon, decomposing organic matter, and anaerobic methane (Whiticar and Suess, 1998). The elevated concentrations of Mg ions, orthophosphates, sulfates, and amino acids in porous or near-bottom waters can also contribute to crystallization of ikaite (Whiticar and Suess, 1998) since such conditions inhibit precipitation of unhydrated forms of calcium carbonate—calcite and aragonite. Experimental data indicate a wide variety of formation conditions of ikaite. Hu et al. (2014) established that an increase in seawater salinity accelerates growth of ikaite crystals, and the experimental maximum growth temperatures can reach 12°C (Purgstaller et al., 2017).

Findings of glendonites in Lower Cretaceous deposits of Spitsbergen are known from the 1960s (Nagy, 1970; Pchelina, 1965a, 1965b, 1967, 1983). In this case, their occurrence has been often considered as a characteristic feature of some units and formations. Recently, Lower Cretaceous glendonites of Spitsbergen have attracted much attention of researchers (Price and Nunn, 2010; Vickers et al., 2016, 2018, 2019). Our predecessors studied samples of glendonites from the upper Hauterivian interval of the Festningen section (Price and Nunn, 2010), and the C and O isotope compositions of bulk samples of calcite pseudomorphs after glendonites were determined. Vickers et al. (2016, 2018, 2019) established that Aptian-Albian glendonites from the Festningen and Airport Road sections in Western Spitsbergen Island were formed in the shallow-water shelf zone, at a depth up to 100 m, above the zone of storm wave action. This article presents new data on Aptian and Albian glendonites and the stratigraphy of the Carolinefjellet Formation obtained during the study of the Airport Road section (Vickers et al., 2018), located in the environs of the town of Longyearbyen. Glendonites from this outcrop are described in (Vickers, 2017; Vickers et al., 2018, 2019). The authors proposed the division of this section into members, which is accepted in our work. Some paleontological and sedimentological data on this section (Mt. Sverdruphamaren in (Birkenmajer, 1966); the western part of the Advent Bay (Frebold, 1930; Stolley, 1912)) were published earlier. However, information on the stratigraphic levels of glendonites and ammonites has not yet been provided.

GEOLOGICAL STRUCTURE OF THE STUDY AREA

The outcrops of Aptian–Albian deposits, unconformably overlapped by Paleogene strata, are widespread in the vicinity of Longyearbyen (Major and Nagy, 1972). Pre-Aptian deposits in this area are exposed only in core sections.

In the late Barremian and beginning of early Aptian, continental sedimentation settings prevailed within the territory of the present-day Western Spitsbergen Island (Dallmann, 2015). The subsequent marine transgression at the end of the early Aptian-Albian led to the distribution of shallow-water shelf zones in this area and accumulation of the terrigenous Carolinefjellet Formation (Vickers et al., 2018). This formation is subdivided into two members: the lower Dalkjegla Member, composed mostly of sandstones, and the overlying Innkjegla Member, composed predominantly of mudstones and siltstones, with rare sandstone interbeds. Both units include abundant authigenic carbonate nodules of different morphology: large bun-shaped nodules, small cannon ball nodules, vertically oriented nodules, and calcite pseudomorphs (glendonites) (Vickers et al., 2018). Sedimentation occurred predominantly in the open sea shelf zone (Vickers, 2017). Remains of ammonites and bivalve mollusks are regularly found in the Carolinefjellet deposits near Longyearbyen. However, only specimens from this area without a stratigraphic tie to the section were depicted (Frebold, 1930; Lindström, 1865; Lundgren, 1883; Stolley, 1912). Some fossils from this stratigraphic interval were attributed to the original publications to the Aptian species. At the same time, other forms were assigned erroneously to the Valanginian, Hauterivian, or Jurassic species. No information on the distribution of macrofossil remains through the section has yet been published.

This article presents the preliminary data on the distribution of ammonites, which are important in both the dating of stratigraphic levels of glendonite occurrence and the verification of the Aptian and lower Albian stratigraphy of Western Spitsbergen Island.

MATERIALS AND METHODS

We studied five samples of Lower Cretaceous (Aptian) glendonites and the ammonite collection (20 specimens of the most satisfactory preservation) collected by M.A. Rogov and K.Yu. Mikhailova (2018–2019) in the Carolinefjellet Formation in the environs of Longyearbyen (Spitsbergen Archipelago, Western Spitsbergen Island). Several sections on the northern slope of Mount Sverdruphamaren were studied. Considering the facies variability of separate beds, the boundary between Dalkjegla and Innkjegla members served as the most reliable benchmark to which all findings were tied. In contrast, the comparison of specific beds in adjacent sections was practically impossible.

We performed a petrographic description of five thin sections using an Olympus BX-53 optical microscope equipped with a Mk5-2 cathodoluminescence attachment (Department of Regional Geology of St. Petersburg State University). Operating parameters: vacuum 0.003 mbar, voltage 324 kV, current $6-13 \mu A$.

To verify the formation conditions of glendonites, the C and O isotope compositions (δ^{13} C and δ^{18} O) of calcite of pseudomorphs were studied. The measurements were performed using a Delta V Advanced mass spectrometer with a Thermoelectron elemental ana-



Fig. 1. Geological map of the Longyearbyen area with localities of the studied sections: (a) geographical position of the Spitsbergen archipelago; (b) geological map with indication of the Airport Road section; (c) localities of the studied sections on Mt. Sverd-ruphamaren.

lyzer and a Gas-Bench-II system. To analyze the carbon and oxygen isotope compositions, no pretreatment of the samples was performed. The δ^{13} C are δ^{18} O values are given in per mille (‰) relative to the V-PDB standard. The analytical accuracy and reproducibility of δ^{13} C and δ^{18} O were within ±0.2‰ (Zaitsev and Pokrovskii, 2014).

The studied collection of ammonites is stored in the Earth Science Museum at Moscow State University.

THE GEOLOGICAL STRUCTURE OF THE "AIRPORT ROAD" SECTION

Although Aptian and Albian deposits are widespread in the environs of Longyearbyen, they are poorly exposed in general. The only exception is a set of sections along the road from the airport to Longyearbyen, called Airport Road (Vickers et al., 2018,

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2019). Here, sandstones, mudstones, and siltstones of the Carolinefjellet Formation with a total thickness of about 170 m are exposed for several kilometers in the cliffs lining the road and in the valleys of streams flowing down from Mount Sverdruphamaren to the sea (Vickers et al., 2018) (Fig. 1).

The beds are subhorizontal, but they are slightly dislocated in some places; in the section, one can observe both faults with vertical displacement of layers by several meters and small folds. In the section uncovered along the Airport Road, over a section about 4 km long, the layers are mainly SW dipping, becoming almost horizontal closer to the airport. Members in the sections are distinguished with confidence, but most of the interbeds of sandstones and conglomerates (this is especially characteristic of the Dalkjegla Member) are lenticular. In addition, concretion carbonate interbeds are also lenticular. Find-

ings of glendonites within beds are also distributed sporadically, being confined, as a rule, to unextended sites within the separate beds. The upper part of the Innkjegla Member, where sandstone interbeds occur rarely, contains large lenticular carbonate nodules. Considering that some intervals of the section are inaccessible for direct observation, difficulties arise in tracing layers in different outcrops. In general, beds can be correlated with confidence on the basis of their position relative to the boundary between members (Fig. 2).

Mollusks in the section are sporadically distributed. They are rare in the lower Dalkjegla Member, being abundant in the overlying Innkjegla Member. Single mollusks occur in sandstones, siltstones, and carbonate nodules; accumulations of mollusks are confined, as a rule, to lenses of gravelites and conglomerates, lying at the base of thick sandstone interbeds. Fossil-rich lenses are well recognized in the section owing to the occurrence of numerous dissolved tubicolous serpulid shells. These fossils are so typical of the Carolinefjellet Formation that this stratigraphic interval was previously called "Ditrupen Schichten" after the serpulid genus Ditrupa (Stolley, 1912). According to A.P. Ippolitov (oral communication), these serpulids should be attributed to the genus *Tetraserpula*. Along with pebbles, redeposited carbonate nodules (including those with redeposited glendonites at some levels), and serpulids, there are small bivalve mollusks and fragments of ammonites. Complete ammonites are rare; they usually come from finer grained rock varieties (sandstones, siltstones, and upper parts of conglomerate interbeds).

The first information on findings of mollusks in the Carolinefjellet deposits in environs of Longyearbyen appeared at the beginning of the second half of the 19th century when Lindström (1865) studied fossil remains collected on the western coast of the Adventfjorden during expeditions of Nordenskjold (1858) and Blomstrand (1861). These were mainly the remains of bivalve mollusks and serpulids, on the basis of which Lindström concluded the Jurassic age of the deposits. He also mentioned the finding of ammonite from the Ammonites falciferum group (Lindström, 1865, p. 10). Later, this specimen was described and depicted by Frebold (1930, p. 31; Plate VI, Fig. 2), who assigned this ammonite to the Early Jurassic genus Grammoceras, considering that it was a redeposited specimen from the conglomerates. Despite the fact that conglomerate lenses are abundant in the Carolinefjellet Formation, none of the researchers mentioned such findings. In our opinion, this ammonite is very close to aconeceratids from the Aptian of Spitsbergen, assigned by Ershova (1983, Plate LII, figs. 1–2) to Sanmartinoceras sp. ind., and was not redeposited. At the same time, these findings cannot be attributed to any known species of aconeceratids.

Later, Lundgren (1883) described and depicted some more bivalve mollusks from the Carolinefjellet deposits in the studied area. He also attributed them to the Jurassic.

The Early Cretaceous age of deposits, which are now attributed to the Carolinefjellet Formation, was determined only in the early 20th century, when Stolley (1912) depicted and described ammonites, bivalves, and serpulides collected on the western coast of the Adventfjorden. Also, he described a new species Crioceras arcticum (assigned now to the genus Tropaeum), which made it possible to determine the Aptian age of deposits. At the same time, Stolley believed that there had to be also more ancient ("Middle Neocomian," i.e., Valanginian-Hauterivian) deposits, as evidenced, in his opinion, by the findings of ammonites close to Garnieria (=Delphinites) and Polyptychites or Simbirskites. Since the even lower part of the Carolinefjellet Formation is not exposed on the western coast of the Adventfjorden (Major and Nagy, 1972), one can assume that Stolley referred the Aptian aconeceratids for "Garnieria," and the ammonite identified by him as Polyptychites or Simbirskites (Stolley, 1912; Plate 2, Fig. 4) may belong to the early Albian genus Colvillia.

RESEARCH RESULTS

New Biostratigraphic Data

Until now, the studied sections of the Carolinefjellet Formation have not been dated by biostratigraphic methods. On the basis of the study of C isotope composition of organic matter ($\delta^{13}C_{org}$) and taking into account the thicknesses of beds and units, Vickers et al. (2018, 2019) proposed a scheme for comparing the main (AR1) section with the section on Cape Festningen, assigning the entire studied interval to the Aptian Stage (Vickers et al., 2019).

In the AR1 section, our predecessors discovered a single stratigraphic horizon with ammonites. This horizon (a conglomerate interbed 34.5 m above the base of the Innkjegla Member) was not indicated in the lithological column (Vickers et al., 2019). By courtesy of M. Vickers, who provided us with the field data, we identified this horizon in the section (see also Vickers, 2017). Indeed, this is the most ammonite-rich level, in which we collected 19 fragments of heteromorph ammonites *Tropaeum* (*T*.) *arcticum* and *T*. (*T*.) cf. *arcticum* (Plate I, figs. 6, 9, 10).

Ammonites of good preservation found at several levels in two of three studied sections allow one to

Fig. 2. Lithological columns with levels of the occurrence of ammonites and glendonites. (1) Conglomerate; (2) siltstone; (3) sandstone; (4) findings of glendonites; (5) leached glendonites; (6) carbonate nodules ("cannonballs"); (7) studied glendonites; (8) findings of ammonites.

Systemt Series	Stage	Member	Beds	stolleyi		
Cretaceous Lower	Albian Albian	Innkjegla	Beds with Grantziceras	AR-22, RM2019/36 AR-23 AR-21 AR-20 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25 AR-25		
	Aptian	Dalkjegla Catolii	Beds with Tropaeum arcticum	AR-19 RM2019/32 AR-18 RM2019/31, 33.35 mututone f/g m/g c/guc/g congl. sandstone Sect. 5(2)	m 1 0	
				nubeon ^e f/g m/g c/g uc/g congl. sandstone Sect. AR1		nucleone Sect. 4
	• • •	•	1	$2 \boxed{3} \cancel{4} \cancel{5} \boxed{6}$	7	8 🛞

determine the age of these deposits. In most cases, these are heteromorph ammonites, similar to ammonites found in other sections of Spitsbergen (Ershova, 1983; Frebold, 1930; Nagy, 1970; Sokolov and Bodylevsky, 1931; Stolley, 1912). Here, monomorphic ammonites were found in smaller quantities. It should be noted that we follow the threefold subdivision of the Aptian adopted in Russia. According to this, the middle and upper Aptian correspond to the upper Aptian of the West European schemes.

Monomorphic ammonites have relatively coarse bipartite sigmoidal ribs characteristic of the genus *Sanmartinoceras*. Unfortunately, all specimens are poorly preserved: the keel and often the keel area are not preserved anywhere; therefore, all definitions are given according to the open nomenclature. The taxonomy of the genus *Sanmartinoceras* is controversial, and we accept it in accordance with the work (Kennedy and Klinger, 1979).

Ribs in most specimens (Plate I, figs. 1b, 3a, 4, 5) appear at the early stages of development, which is typical of both *Sanmartinoceras* (*Theganeceras*) and Sanmartinoceras (Sinzovia). It is of interest that the ribs are rather coarse and relatively rare at early whorls (Plate I, figs. 1b, 4). At the early stage of development, all known Sanmartinoceras (Theganeceras) are characterized by numerous thin ribs (Kennedy and Klinger, 1979). Here, there is the species S. (S.) stolleyi Casey among Sanmartinoceras (Sinzovia) representatives, which is characterized by similar coarse ribbing. Therefore, we have identified these ammonites as Sanmartinoceras (Sinzovia) cf. stolleyi Casey. It should be noted that S. (S.) stolleyi in middle Aptian sections (Parahoplites nutfieldiensis Zone) of Northern Germany (Gaida et al., 1978) occurs together with Tropaeum (T.) arcticum (Stolley), exactly as in Spitsbergen sections. The subgenus Sanmartinoceras (Thegan*eceras*) is widespread at the base of lower Aptian in the German sections, Deshayesites weissi Zone (Koenen, 1902). Sanmartinoceras (Sinzovia) is noted in Spitsbergen sections for the first time. Representatives of the genus *Sanmartinoceras* depicted earlier from this region are different from our findings in less developed sculpture and more evolute coiling (Ershova, 1983, Plate XLII, fig. 2), but it is not easy to ascribe them to any species or subgenus.

Heteromorph ammonites can be ascribed to Tropaeum (T.) arcticum (Stolley) (Plate I, figs. 8–9) and Tropaeum (T.) cf. arcticum (Stolley) owing to their fragmentary preservation (Plate I, figs. 3b, 5a, 6–7, 10-11). The complete specimens of T. (T.) arcticum that we have found are close to specimens from the type series of this species from Spitsbergen (Stolley, 1912, p. 16) and to those from Northern Germany (Gaida et al., 1978; Kemper, 1982, 1995). They are characterized by a weak uncoiling of a spiral and frequent single ribs (30-35 per a half-whorl), oblique and curving slightly anteriorly. Tropaeum n. sp. aff. arcticum, also known from the upper Aptian in northern Canada, are different from typical T. (T.) arcticum in a sharp uncoiling of a spiral and more frequent ribs (Jeletzky, 1964) and probably belong to another species. The representatives of Sanmartinoceras are unknown in the sections of Canada.

In the studied sections, the only lower 35 m of the Innkjegla Member and the upper part of the Dalkjegla Member, in the talus of which *Tropaeum* remains were found, can be attributed to the beds with Tropaeum arcticum (Plate I, fig. 12).

Grantziceras cf. *affine* (Whiteaves) was found above the occurrence of Aptian ammonites (Plate I, fig. 2). Despite the poor preservation, this ammonite has the main signs of species: involute coiling, relatively frequent narrow constrictions, and slightly thin ribbing. Similar forms were already described from the Innkjegla Member, where they occur together with typical early Albian *Leymeriella* (L.) *germanica* and *Freboldiceras singulare* (Nagy, 1970). Thus, the recorded ammonites allow us to establish two stratigraphic intervals: Beds with Tropaeum (T.) arcticum in the middle Aptian and Beds with Grantziceras in the lower Albian.

New Data on Glendonites

Glendonites from the Carolinefjellet Formation are morphologically very diverse. Stellate glendonites with a diameter varying from 0.3 to 5-7 cm are the most common (Figs. 3b, 3c, 3e, 3g, 3i). Such glendonites occur in carbonate interbeds, in siltstone and sandy sequences, and probably in conglomerates as redeposited material. As a rule, glendonites are well recognizable on the weathered surface of beds. The

Plate I. Ammonites from the Innkjelga Member (environs of the town of Longyearbyen). (1b, 3a, 4, 5b) *Sanmartinoceras (Sinzo-via)* cf. *stolleyi* Casey, section 5 (2), 11.4 m above the section base, middle Aptian, Beds with Tropaeum arcticum: (1b) spec. MZ MGU 141/1, (3a) spec. MZ MGU 141/3, (4) spec. MZ MGU 141/4, (5b) spec. MZ MGU 141/5; (2) *Grantziceras* cf. *affine* (Whiteaves), early Albian, section 1, ~80 m above the base of the Innkjegla Member, Beds with Grantziceras, spec. MZ MGU 141/2; (1a, 3b, 5a, 6, 7, 10, 11) *Tropaeum (T.)* cf. *arcticum* (Stolley), middle Aptian, Beds with *Tropaeum arcticum*: (1a, 5a) section 5 (2), 11.4 m above the section base; (6) section 1, 34.7 m above the base of the Innkjegla Member, spec. MZ MGU 141/6; (7) section 1, 2–2.5 m above the base of the Innkjegla Member, spec. MZ MGU 141/6; (7) section 1, 2–2.5 m above the base of the Innkjegla unit, spec. MZ MGU 141/1; (3b) section 5 (2), 11.4 m above the section base; (10) section 1, 12 m above the base of the Innkjegla unit, spec. MZ MGU 141/1; (3b) section 1, 25–27 m above the base of the Innkjegla Member, spec. MZ MGU 141/1; (8) *Propaeum (T.) arcticum* (Stolley), middle Aptian, Beds with Tropaeum arcticum: (8) section 1, 10 m above the base of the Innkjegla Member, spec. MZ MGU 141/8; (9) section 1, 34.7 m above the base of the Innkjegla Member, spec. MZ MGU 141/1; (8) section 1, 10 m above the base of the Innkjegla Member, spec. MZ MGU 141/10; (11) section 1, 25–27 m above the base of the Innkjegla Member, spec. MZ MGU 141/10; (11) section 1, 4.7 m above the base of the Innkjegla Member, spec. MZ MGU 141/2; (20) mould of *Tropaeum (T.)* sp. indet., middle Aptian, Beds with Tropaeum arcticum: (8) section 1, talus of the Dalkjegla Member, spec. MZ MGU 141/2; (12b) imprint of *Tropaeum (T.)* sp. indet., middle Aptian, Beds with Tropaeum arcticum, Section 1, talus of the Dalkjegla Member, spec. MZ MGU 141/12; (12b) imprint of *Tropaeum (T.)* sp. indet., middle Aptian, Beds with Tropaeum arcticum, Section 1, talus of the D





Fig. 3. Morphological types of glendonites from the Carolinefjellet Formation. (a, d) Imprints of dissolved/leached glendonite nodules; (b, c, e, g, i) stellate concretions; (f, h) single elongated crystals.



Fig. 4. Cathodoluminescent (a, c) and transmitted light (b, d) images of thin sections of glendonites with indication of predominant phases (Sample AR-2). Cal1—the first calcite phase, Cal2—the second calcite phase, Cal3—the third calcite phase.

carbonate material is often dissolved, and, and as a result, one can observe only imprints of glendonites (Figs. 3a, 3d). Nevertheless, such imprints are well identified owing to their specific morphology. Glendonites in the form of single crystal "blades" are found much less frequently and only at some stratigraphic levels (including those glendonites of which we have studied in detail) (Figs. 3f, 3h).

Our predecessors distinguished two glendonite horizons in the studied section: the first one is near the visible base of the Dalkjegla Member, while the second one is about 80 m above the base of the Innkjegla Member. During the study of sections of the Carolinefjellet Formation in 2018 and 2019, we distinguished a few previously unknown levels with glendonites (Fig. 2). This article presents the results of studying glendonites from a horizon located 15–16 m above the Innkjegla Member base (Fig. 2). The studied calcite pseudomorphs are represented by single crystals and stellate intergrowths without signs of abrasion and/or rounding. Because of this, we suggest that they were not redeposited. The length of single crystals is 0.6–10 cm; the crystal habit is bipyramidal. Stellate aggregates are 2.5–5 cm in diameter.

Petrographic description of glendonites. Glendonites are nonporous structures; their inner space is filled with calcite. The internal structure of pseudomorphs is rather homogenous in transmitted light; at the same time, a successive change of calcite phases is clearly distinguished in cathodoluminescent light images, reflecting individual stages of the formation and transformation of the glendonite substance.

The cathodoluminescence study of carbonate minerals is based on the ability of an electron ability to excite a weak cathodoluminescent light in minerals. Depending on the chemical composition, structure, or its defects and impurities, different phases of carbonates have different cathodoluminescent light (hereinafter, CL light) (Boggs and Krinsley, 2006). The stage analysis of glendonites is based on the idea that late phases overgrew the earliest calcite phase. In contrast, the early calcite could have been corroded partially by later phases. At the replacement of the initial ikaite crystals with calcite of different phases, their habit and size could have been preserved, and the difference between the phases in transmitted light is not evident.

We have distinguished three calcite phases on the basis of the variations in the intensity of CL light. According to the spatial relationships of crystal boundaries of calcite crystals of three different phases, we have established the succession of their formation (Fig. 4).

Sample no.	δ ¹³ C, ‰ (PDB)	δ ¹⁸ O, ‰ (PDB)	δ ¹⁸ O, ‰ (SMOW)
AR-1	-28	-3.94	26.8
AR-2	-26.6	-5.4	25.3
AR-3	-27.1	-5.1	25.6
AR-4	-25.9	-5.59	25.1
AR-5	-26.6	-5	25.7

Table 1. C and O isotope compositions in calcite from glendonites

The first calcite phase (Cal1), characterized by dark brown, almost black CL light, occupies about 30% of the glendonite volume and is represented by crystals up to 0.2 mm in size. We have recognized elongated isometric crystals of irregular habit. The crystal boundaries are usually intensely corroded. In some places, the first calcite phase is almost entirely replaced by the later second calcite phase. The first calcite phase of glendonites was formed during the ikaite transformation (De Lurio and Frakes, 1999), since initial ikaite crystals consist of water and calcium carbonate molecules, accounting for 69 and 31% of the crystal structure of the mineral, respectively. During ikaite-calcite transformation, ikaite loses 2/3 of its volume accounted for by water; the remaining water "forms" the first calcite phase. Secondly, the laboratory study of ikaite revealed that the change in the physicochemical conditions leads to its decomposition into calcite and water (Ito, 1998; Krylov et al., 2015; Tang et al., 2009). Sometimes, an admixture of vaterite (a polymorph of calcium carbonate) was noted. Later, when studying the mineral composition of glendonites, vaterite was not recognized (Vickers et al., 2018).

The second calcite phase (Cal2) occupies about 70% of the volume of pseudomorphs and has a bright orange CL light. Calcite of the second phase was formed owing to the decomposition of organic matter with the participation of pore water (Vickers et al., 2018). This is correlated with the bright orange CL light, which is caused by Mn^{2+} ions, a luminescence activator, while Fe²⁺ ions interact with organic matter (Boggs and Krinsley, 2006).

The third calcite phase (Cal3) fills the remaining cavities and is characterized by a brown CL light. This is the least common calcite phase; it accounts for about 5% of the internal structure of pseudomorphs.

C and O isotope compositions in calcite of glendonites. We have studied the C and O isotope compositions in bulk samples of glendonites. The δ^{18} O values in glendonites are presented in Table 1 and Fig. 4. The δ^{18} O values change from -3.94 to -5% (VPDB), while the δ^{13} C values change from -25.9 to -28% (PDB).

DISCUSSION

The vertical distribution of ammonites was first established in the Carolinefjellet Formation of environs

of the town of Longyearbyen. The data obtained made it possible to distinguish Beds with Tropaeum (T.) arcticum in the middle Aptian interval and, for the first time in this area, to prove the early Albian age of the upper part of the Innkjegla Member, attributed to the Beds with Grantziceras. This makes it possible to specify the age of the studied glendonites.

The Sanmartinoceras-Tropaeum (T.) arcticum assemblage, typical of Beds with Tropaeum (T.) arcticum, is known from sections of Northern Germany (Gaida et al., 1978; Kemper, 1982; 1995), Spitsbergen (Frebold, 1930; Ershova, 1983; Ershova and Korchinskaya, 1980), and East Greenland, where it is situated above the early Aptian Deshayesites (Bøgvad and Rosenkrantz, 1934; Frebold, 1935). Ershova (Ershova and Korchinskaya, 1980) proposed to divide this complex (bottom-up) in Spitsbergen into Beds with Sanmartinoceras sp. and Beds with Tropaeum arcticum, corresponding to the middle and upper Aptian, respectively. Later, Ershova (1983) backed away from this division, leaving only Beds with Tropaeum arcticum in the Aptian. Our findings also do not support the possibility of identifying "Beds with Sanmartinoceras" since these ammonites occur together with Tropaeum arcticum. On the basis of the correlation with the sections of Northern Germany, the beds with Tropaeum arcticum can be dated to the second half of the middle Aptian, comparing them with the Parahoplites nutfieldiensis Zone, where Sanmartinoceras (Sinzovia) stolleyi occur together with Tropaeum (T.) arcticum (Gaida et al., 1978; Kemper, 1982, 1995).

The finding of ammonite *Grantziceras* above Beds with Tropaeum (T.) arcticum allows one to establish the lower Albian interval, correlated with the Freboldiceras praesingulare Zone of the Boreal Zonal Standard (Baraboshkin and Guzhikov, 2018). Nagy (1970) noted this genus in the "*Freboldiceras* fauna"; Ershova (1983) included this assemblage in Leymeriella tardefurcata Zone. Similar assemblages with *Grantziceras affine* are known from the lower Albian of Arctic Canada (Jeletzky, 1964), South Alaska (Jones, 1967), and other areas.

At present, Aptian–Albian glendonites are known from the Spitsbergen Archipelago (Maher et al., 2004; Vickers et al., 2016, 2018, 2019), on Mackenzie King Island and Axel Heiberg Island of the Canadian Arctic Archipelago (Grasby et al., 2017), in the Eromanga



Fig. 5. The O and C isotope compositions in Aptian (Early Cretaceous) glendonites of the Arctic Region. (1) The Airport Road section, this work; (2) the Airport Road section (Vickers et al., 2018); (3) Festningen section (after Vickers et al., 2018); (4) sections of the Sverdrup Basin, Canadian Arctic Archipelago (after Grasby et al., 2017). Outlines (dashed lines) of fields with δ^{13} C values of oxidized methane and sedimentation organic matter and fields with δ^{18} O values in seawater, meteoric waters, and late diagenetic solutions are given after (Campbell, 2006; Vickers et al., 2018), with amendments.

Basin of Australia (De Lurio and Frakes, 1999), and in Greenland (Hovikoski et al., 2018), as well as in Northeast Russia, in the Oloi Trough and the north of Kamchatka (Alabuschev, 1995; Efimova et al., 1970). It is assumed that glendonites are indicators of coldwater bottom environments. If they are found in shallow-water sediments, they can also serve as indicators of a relatively cold climate, or at least seasonal low temperatures (Tollefsen et al., 2018). A number of authors distinguished several cooling stages for the Cretaceous environment, which was considered to be predominantly warm ("greenhouse"): late Berriasian (Rogov et al., 2017), Valanginian (Kemper and Shmitz, 1975; Price and Nunn, 2010), Hauterivian (Frakes and Francis, 1988), late Aptian–Albian (Frakes and Francis, 1988), late Valanginian-the first half of the Hauterivian, mid-Aptian-early Albian (Baraboshkin, 2007). The presence of intervals with cold water environments favorable for the formation of ikaite in the middle Aptian-early Albian is confirmed by the following data:

(i) The finding of dropstones and glendonites at the same stratigraphic levels (Dalland, 1976; Frakes et al., 1995; Rodríguez-López et al., 2016);

(ii) low average annual temperatures calculated from the oxygen isotopic composition in the bivalve mollusk shells from the shelf deposits of the upper Aptian–Albian of the Carolinefjellet Formation of Spitsbergen (8.3°C; Harland and Kelly, 1997) and in the rostra of Albian belemnites in Australia (mean annual temperature 5°C; De Lurio and Frakes, 1999) and late Aptian belemnites of the Vocont Basin (4°C; Bodin et al., 2015); (iii) significant seasonal temperature fluctuations at high latitudes (Zakharov et al., 2011);

(iv) the widespread distribution of conifers in the Canadian Arctic in the Aptian–Albian, indicating that the average annual temperature in the Arctic Region was $3-10^{\circ}$ C (Harland et al., 2007);

(v) the minimum content of *Classopollis* pollen in the Aptian–Albian interval (Baraboshkin, 2007; Vakhrameyev, 1980, 1982);

(vi) a decrease in surface water temperature by about 5° C, determined by the TEX86 method (McAnena et al., 2013);

(vii) a decrease in the diversity of calcareous nannoplankton (Herrle and Mutterlose, 2003) and the flora of the polar regions (Francis and Poole, 2002; Harland et al., 2007);

(viii) the results of paleobiogeographic analysis supplemented by mathematical modeling (Baraboshkin, 2007).

Thus, our new data on the wide distribution of glendonites in the middle Aptian–lower Albian of Western Spitsbergen Island (Carolinefjellet Formation) agree with the previously obtained data on climate cooling in the middle Aptian–early Albian. The obtained C and O isotope compositions of calcite in the glendonites are close to that established earlier in the glendonites of the same series of sections, as well as other sections of the Carolinefjellet Formation of the Spitsbergen Archipelago (Fig. 5). The δ^{18} O values in the studied samples vary from -3.94 to -5% PDB. They are quite comparable with the values previously published for glendonites of the Carolinefjellet For-

mation (δ^{18} O from -12.3 to -1.0% PDB, 7.0% PDB on average; Vickers et al., 2018).

The Arctic basin, where the studied strata accumulated, represented a partially isolated basin at the beginning of the Cretaceous (Price and Nunn, 2010; Smith et al., 1994; Stein, 2019). Apparently, its waters were characterized by a lighter oxygen isotopic composition compared to that in the seawater of open basins. Moreover, fluctuations in salinity could also have affected the isotopic composition of seawater. Price and Nunn (2010) suggested that the seawater isotope composition could have been lower than $\delta^{18}O = -1\%$ SMOW (Zhou et al., 2008) accepted for open sea basins, but did not drop below -5.1% SMOW (Price and Nunn, 2010).

At the same time, the recent data indicate that the isotope composition in the Arctic seawater in the Early Cretaceous was close to the mid-oceanic one and reached 1.5% SMOW (Price et al., 2020). Some researchers have shown that, during the ikaite-calcite transformation, the oxygen isotope composition changes slightly (within 1‰; Greinert and Derkachev, 2004; Krylov et al., 2015). Owing this, it is possible to reconstruct the temperature of formation of ikaite according to the δ^{18} O values of glendonite and the initial composition of seawater in which ikaite was formed. The paleotemperatures of the Arctic Basin calculated for the studied samples according to the equation $T(^{\circ}C) = 15.7 - 4.36(\delta^{18}O_{Cal} - \delta^{18}O_{water}) + 0.12(\delta^{18}O_{Cal} - \delta^{18}O_{water})^2$ (De Lurio and Frakes, 1999) turn out to be relatively high for the crystallization of ikaite. At $\delta^{18}O = -1\%$ SMOW, the crystallization temperatures of the initial ikaite range from 29 to 38°C; if $\delta^{18}O = -1.5$, then the temperature varies from 27 to 32°C; if $\delta^{18}O = -2$, then, it varies from 24° to 32°C. The calculated high temperatures are apparently due to the opening of isotope systems during the ikaite-calcite transformation and the displacement of the initial geochemical marks during the interaction of ikaite (or calcite) with pore solutions with a lighter oxygen isotope composition. This assumption is in good agreement with the mineralogical features of the studied glendonites. Calcite formed during the ikaite transformation (Vickers et al., 2018) occupies only about 30% of the pseudomorph, while the greater part (about 70%) is composed of later diagenetic calcite. The analysis of the first calcite phase, possibly, preserving the isotopic composition of the original ikaite, is complicated because of the impossibility of obtaining a sufficient amount of pure substance of the above phase for the isotopic analysis. The published data show that later calcite phases have a lighter oxygen isotope composition than earlier calcite phases that replaced ikaite (below –10% PDB; Frank et al., 2008; Vasileva et al., 2019). In addition, a similar oxygen isotope composition (δ^{18} O from -3.1 to -16.6% PDB) was obtained for carbonate cannonballs of diagenetic origin (Krajewski and Luks, 2003).

The C isotope composition makes it possible to assess how different components affect the isotopic composition of authigenic carbonate minerals (Campbell, 2006): methane undergoing anaerobic oxidation ($\delta^{13}C < -40\%$ PDB), decomposing organic matter ($\delta^{13}C$ from -40 to -15\% PDB), inorganic carbon dissolved in seawater ($\delta^{13}C$ from -2 to +2‰ PDB), or residual carbon during methanogenesis ($\delta^{13}C$ from +5 to +24‰ PDB). New data obtained for the Aptian glendonites of Western Spitsbergen lie in the range of values from -25.9 to -28‰ PDB. This means that carbon was extracted from a mixed source—decomposing organic matter and oxidizing methane—during the formation of the initial ikaite and the transformation of ikaite to glendonite.

CONCLUSIONS

(1) The vertical distribution of ammonites in the Carolinefjellet Formation (Dalkjegla and Innkjegla members) was established in the vicinity of the town of Longyearbyen for the first time. Identifying the middle Aptian Beds with Tropaeum arcticum and early Albian Beds with Grantziceras has been substantiated.

(2) Findings of glendonites in the entire studied interval suggest that the climate during the middle Aptian–early Albian of Spitsbergen was rather cold.

(3) The oxygen isotope composition of glendonite calcite indicates that the initial isotope–geochemical characteristics (presumably, of ikaite) were not preserved because of subsequent diagenetic transformations. During the formation of ikaite and pseudomorphic development of calcite, carbon was extracted from decomposing organic matter and oxidizing methane.

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