

The First Discovery of Authigenic Carbonates on the Laptev Sea Flank of Gakkel Ridge (Arctic Ocean)

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Abstract—This paper describes the first finding of authigenic carbonates on the southern flank of Gakkel Ridge in its junction with the continental margin of the Laptev Sea of the Russian Federation. The samples are represented by compact magnesian calcites and aragonites, including rounded and angular fragments of terrigenous material, as well as microphytoplankton and spores and pollen of terrestrial and aquatic plants of various ages. The elemental and organochemical characteristics are indicative of the predominant oxidation conditions or those intermediate between oxidation and reduction conditions of carbonate crystallization likely due to the fact that carbonates were formed near the bottom surface. The O, C, and Sr isotopic compositions make it possible to conclude that diagenetic carbonates of Gakkel Ridge were deposited mainly in isotopic equilibrium with bottom water at a temperature of about 0°C, corresponding to measurements from the research vessel. A wide range of $\delta^{13}\text{C}$ (from -23.5 to -37.3) is indicative of the fact that methane was an important, but not the sole source of carbon in carbonates. Based on wide variations in $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70906–0.70933) correlated with $\delta^{13}\text{C}$ values, the carbonate-forming fluid was not only modern seawater, but also diagenetic solutions coming from the sedimentary cover together with methane and methane and organic matter oxidation products. The active discharge of heterogeneous methane-bearing fluids can be related to the high modern tectonic activity of the study region.

Keywords: Gakkel Ridge, authigenic carbonates, Arctic Ocean, aragonite, magnesian calcite, methane, isotope geochemistry

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The bottom sediments of the Arctic Ocean (AO) are characterized by the almost complete absence of carbonates due to low temperatures and undersaturation of pore water relative to carbonate phases. Findings of authigenic carbonates represented mainly by magnesian calcites and ikaites [2–4, 9, 12, 13], as well as siderites and rhodochrosites [11], are rare. Authigenic aragonites were found in host peridotites in the northern part of Gakkel Ridge, where their crystallization was explained by the hydrothermal processes [6].

The first discovery of authigenic carbonates on the southern flank of the Gakkel Ridge in its junction with the Laptev Sea continental margin of Russia was made

during the Arctic-2022 special marine geological expedition of the Federal Agency for Subsoil Usage and the Chief Directorate for Deep Sea Research of the Ministry of Defense of the Russian Federation. The detailed bathymetric survey results are indicative of an extended structurally asymmetric rift valley, to the western side of which there is an extended main fault complicated in some areas by fault steps (Fig. 1). The bottom is characterized by distinct isostatic uplifts of fault ledges and tectonic terraces, characteristic for a lying wall and formed by disconnected sliding blocks of the hanging wall. The eastern side of the rift valley has a simpler structure. It is dominated by bending deformations typical for the areas where the roof of the hanging wall of the asymmetric semigraben comes out onto the daylight surface. These regularities are well-defined in the seismic profiles.

The active supply of clastic material from the Laptev Sea shelf leads to the development of a thick alluvial fan at the continental foot, which makes it difficult to trace the Gakkel Ridge structure towards the continental margin. Alongside with that, the existence

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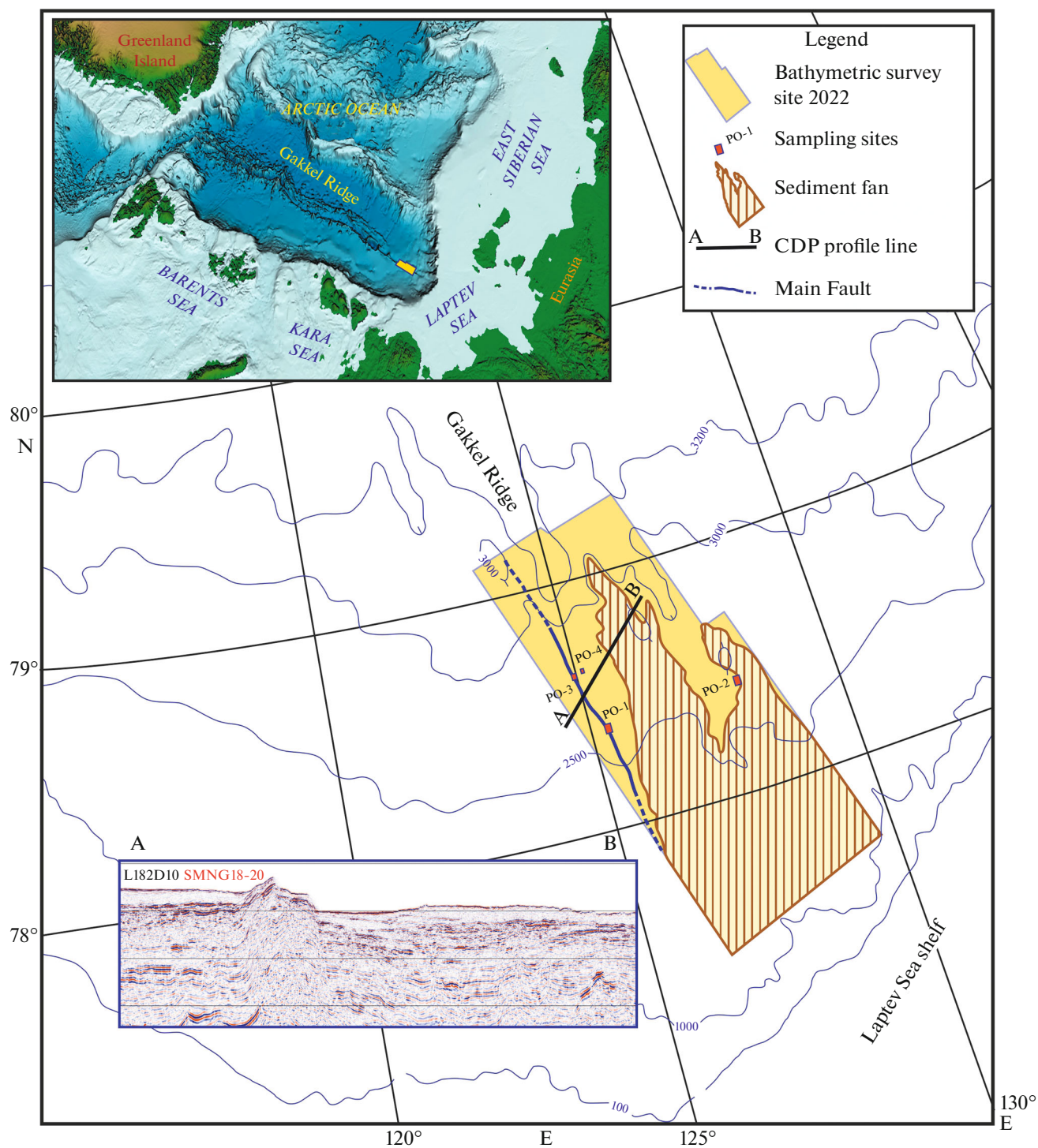


Fig. 1. Work area of the Arktika-2022 expedition. Inset: position of Gakkel Ridge in the structure of the bottom of the Arctic Ocean.

and growth of the cone testifies to the constantly growing accommodation space and, accordingly, the progressive subsidence of the ridge's southern flank.

The use of special technical equipment on the oceanographic R/V *Yantar* made it possible to study

the bottom visually. The bottom mineral samples were collected using manipulators of underwater vehicles from the surface of bottom sediments in the wall of the Gakkel Rift Valley. The material collected within four geological stations at three research sites (PO-1, PO-3, and PO-4) (Fig. 1) included nine authigenic carbon-



Fig. 2. Authigenic carbonate rocks in Gakkel Ridge: (a) sample A22-1t-1, magnesian calcite; (b) sample A22-8R-2, aragonite.

ate samples. The maximum size was $50 \times 20 \times 10$ cm (sample A22-10R1 from PO-4). The authigenic carbonate rocks are confined to the western side of the rift valley in the depth interval from 2600 to 3000 m both on the slopes and in the isometric depression (pock-mark (?)) at its base.

The morphology of authigenic carbonates varies greatly (Fig. 2). They are compact rocks that stand out among the framing of the unlithified bottom sediments and consist of a solid matrix with rounded and angular fragments of local (edaphogenic) material. The latter is represented by deposits of underwater fans, often deformed by landslide processes. The primary sedimentary relics of alluvial fan deposits (gravitation sorting of a clastic material, stratification fragments, and elongated fragments of terrigenous rocks oriented along the bedding) are indicative of the authigenic formation of carbonates, in particular, crystallization *in situ* in the host sediment as cement deposited directly from the solution. There are both single formations on the flat areas of the bottom and ridge-like carbonate deposits. A landslide separation line was observed along one of these ridges. Some carbonate samples resembling flattened tubes (for example, sample A22-10R1 from PO-4) could be formed in a cramped interlayer or interfault space under the influence of a focused fluid discharge. This suggestion is also confirmed by internal channels in the samples.

According to the results of X-ray phase analysis, in terms of the mineral composition, authigenic carbonates are represented by magnesian calcite (samples A22-1t1, A22-1t4, and A22-1t5 from PO-1; A22-10R1 from PO-4) and aragonite (A22-8R1 and A22-8R2 from PO-3). All studied authigenic carbonates contain an impurity of terrigenous material that was “captured” during their crystallization: quartz, clay minerals, feldspars, and, more rarely, mica and amphiboles.

Based on the palynological and micropaleontological analysis of the major fossil groups, nine authigenic carbonate samples contain spores and pollen of terrestrial and aquatic plants, as well as microphytoplankton of various ages (from Jurassic to Quaternary) mixed in different proportions (Fig. 3). Obviously, a wide age range of fossils relates to terrigenous material, while the proper authigenic (diagenetic) carbonate cement was likely deposited in the Quaternary.

The distribution of rare-earth elements (REEs) demonstrates the absence of any fundamental changes relative to the post-Archaean Middle Australian Shale (PAAS). Some enrichment in heavy REEs (HREEs) is recorded for sample A22-8R-1. Y/Ho is less than 32 for all studied samples due to enrichment in a terrigenous (or volcanic) impurity. The Ce anomaly (Ce/Ce^*) typical for the oxidation conditions (0.64–0.95) is noted for samples A-22-8R2, A22-8R1, and A22-10R1. Intermediate values between the oxidation and reduction conditions were measured in samples A22-1t5, A-22-1t1, and A-22-1t4.

The distribution of n-alkanes and isoprenoids was studied in two samples (aragonite A22-8R1 and Mg-calcite A22-10R1). The C_{org} concentrations in these samples are 0.12 and 0.52%, respectively. A difference in C_{org} by more than four times can be indicative of different formation conditions of carbonate structures and the different involvement of organic matter (OM) in their crystallization. The distribution pattern of n-alkanes shows an obvious similarity in the short chain region (C15–C18). OM is depleted in n-alkanes with an increasing number of carbon atoms in the sample A22-8R1. The opposite trend is noted in A22-10R1: an increase in C21–C33 contents with a clear dominance of odd homologues (C25, C27, C29, and C31) marking the contribution of terrigenous OM supplied to marine sediments by river runoff. The C16 and C18 peaks are local maxima of the “short-chain” range

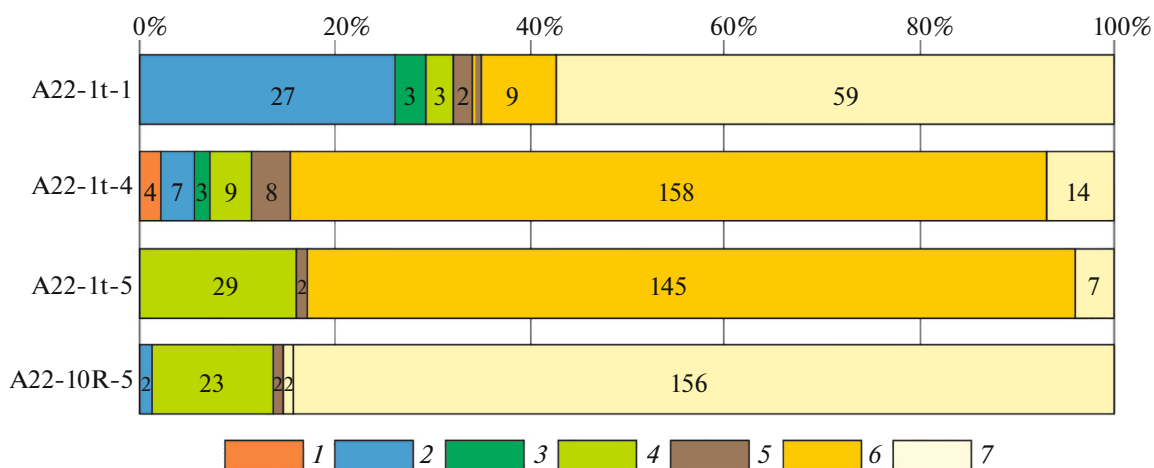


Fig. 3. Distribution of palynomorphs of various ages in the samples studied. Digits inside the diagrams show the number of samples taken into account for statistics. (1) Permian–Jurassic (pollen); (2) Early Jurassic (dinocysts); (3) Lower Cretaceous (dinocysts, spores); (4) Late Cretaceous (dinocysts, pollen); (5) Paleogene (dinocysts); (6) Cenozoic (pollen); and (7) Neogene/Quaternary (pollen).

(C15–C18) in both samples. In general, the predominance of even homologues over odd ones can be related to the microbiota activity in the course of early diagenesis [8, 10]. The predominance of phytane over pristane, especially pronounced in sample A22-8R1 (Pr/Ph = 0.4), is due mostly to the reduction conditions of OM sedimentation. This conclusion contradicts the REE study results (cerium anomaly value) and requires additional analysis. The predominance of C17 and C18 n-alkanes over isoprenoids (pristane and phytane, respectively), recorded by a Kiso index of no more 1, is due to the diagenetic OM maturity. Sample A22-8R1 demonstrates a greater diagenetic transformation of OM (Kiso = 0.87) compared to sample A22-10R1 (Kiso = 0.45). The chromatograms of the complete extract (before separation into fractions) of both samples show the characteristic peak of an unresolved complex mixture (UCM) with a maximum in the C16–C18 region. The UCM may be due to active processing of biolabile OM by heterotrophic microbiota.

The O isotope composition in 24 authigenic carbonate samples (including individual crust zones) is in the range of $\delta^{18}\text{O} = 2.0\text{--}5.9\text{‰}$ VPDB ($\delta^{18}\text{O} = 4.3 \pm 0.9\text{‰}$ ($n = 24$), on average). This scatter can be due to a few reasons: variations in $\delta^{18}\text{O}$ in water, temperature fluctuations, mechanical impurity of carbonates formed under other conditions, and the mineral composition of carbonates (aragonite and magnesian calcite, under the same conditions, are somewhat enriched in ^{18}O compared to standard calcite). It is not possible to determine the ratio of these factors. Taking $\delta^{18}\text{O} = 0.3\text{‰}$ (average according to [1]) for the bottom water of the Laptev Sea and using the equilibrium temperature formula according to [7], the average sedimentation temperature of the analyzed carbonates can be estimated at $1.5 \pm 2.9^\circ\text{C}$ which, within the error, does not differ from the temperatures measured from the research vessel (from -0.74 to -0.75°C).

Contrary to expectations, the Sr isotopic composition in carbonates demonstrates a significant scatter in $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70906–0.70933). Obviously, their formation, along with modern seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70921$ [5]), involved solutions taking Sr from the sedimentary cover. Some of them ($^{87}\text{Sr}/^{86}\text{Sr} > 0.70921$) are undoubtedly related to the terrigenous component of sediments, while others ($^{87}\text{Sr}/^{86}\text{Sr} < 0.70921$) are related to either ancient carbonates or Miocene/Early Pleistocene seawater buried in sediments.

In the Gakkel Ridge samples, $\delta^{13}\text{C}$ varies from -23.5 to -37.3 VPDB ($\delta^{13}\text{C} = -32.2 \pm 4.3\text{‰}$ /24/, on average) due to the fact that most of them were formed ($\delta^{13}\text{C} < -25\text{‰}$) with the involvement of methane oxidation products. However, purely “methane” carbonates ($\delta^{13}\text{C} \sim -70\text{‰}$), such as, for example, in the Chukchi Sea [2], were not found in the Laptev Sea part of Gakkel Ridge. The wide range of $\delta^{13}\text{C}$ values in carbonates may be related to the fact that they were formed, along with low-temperature microbial methane ($\delta^{13}\text{C} \sim -70\text{‰}$), with the involvement of high-temperature thermogenic methane ($\delta^{13}\text{C} \sim -40\text{--}50\text{‰}$), organic matter oxidation products ($\delta^{13}\text{C} \sim -25\text{‰}$), or bicarbonate ion dissolved in seawater ($\delta^{13}\text{C} \sim 0\text{‰}$) or in diagenetic fluids dissolved ancient carbonates.

The negative correlation between $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 4) confirms the involvement of at least two sources of diagenetic fluids in the formation of authigenic carbonates in Gakkel Ridge.

CONCLUSIONS

(1) The Laptev Sea flank of Gakkel Ridge is characterized by a high activity of landslide processes and by widespread deposits of underwater fans.

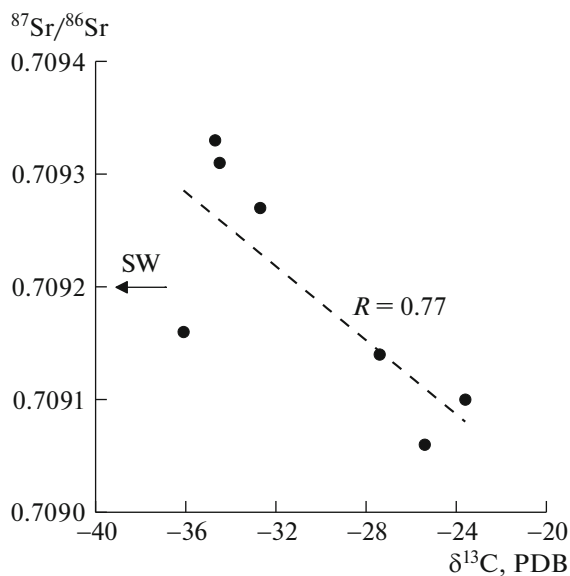


Fig. 4. Correlation between the C and Sr isotopic compositions in authigenic carbonates of Gakkel Ridge. SW is $^{87}\text{Sr}/^{86}\text{Sr}$ in modern seawater [5].

(2) Numerous authigenic carbonate rocks composed of magnesian calcite and aragonite with an impurity of terrigenous clay material were discovered for the first time in this region. The rocks contain spores and pollen of terrestrial and aquatic plants, as well as a microphytoplankton of various ages (from Jurassic to Quaternary) mixed in various proportions. Most likely, the authigenic (diagenetic) carbonate cement proper was formed in the Quaternary. The REE study results are indicative of the predominant oxidation conditions or those intermediate between oxidation and reduction conditions of carbonate crystallization likely due to the fact that carbonates were formed near the bottom surface.

(3) The high $\delta^{18}\text{O}$ values ($4.3 \pm 0.9\%$, on average) make it possible to conclude that diagenetic carbonates of Gakkel Ridge were deposited mainly in isotopic equilibrium with the bottom water at a temperature of about 0°C corresponding to the measurements from the research vessel. $\delta^{13}\text{C}$ varies from -23.5 to -37.3 VPDB in carbonates due to the fact that they were formed, along with methane oxidation products, with the involvement of organic matter oxidation products and, possibly, bicarbonate dissolved in seawater. As follows from wide variations in $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70906 – 0.70933), the carbonate-forming fluid was not only modern seawater, but also diagenetic solutions coming from the sedimentary cover together with methane and methane and organic matter oxidation products. The negative correlation of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ suggests at least two principal sources of carbonate-forming solutions.

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