ISSN 1028-334X, Doklady Earth Sciences, 2024, Vol. 517, Part 1, pp. 1234–1239. © Pleiades Publishing, Ltd., 2024.
ISSN 1028-334X, Doklady Earth Sciences, 2024. © Pleiades Publishing, Ltd., 2024.

OCEANOLOGY

Spatial Variability of the Methane Hydrate Stability Zone's Upper Boundary Parameters in the Water Column of the Sea of Okhotsk

R. B. Shakirov[a], V. A. Luchin[a], and E. A. Petrova[a,*]

Presented by Academician S.A. Dobrolyubov February 24, 2024

Received February 24, 2024; revised March 11, 2024; accepted March 18, 2024

Abstract—Based on all the available oceanological information (131 286 stations carried out from 1929 to 2020), for the first time for the Sea of Okhotsk, the spatial patterns of the upper boundary distribution parameters of the methane hydrate stability zone (water temperature, salinity, depth of the upper boundary in the water column) are presented and discussed. A model of the methane hydrate stability zone is considered. We revealed that the minimum water temperature and the minimum depth of the upper boundary of the gas hydrate stability zone (less than 1°C and 300–320 m, respectively) in the Sea of Okhotsk are located near the eastern slope of Sakhalin Island. The maximum water temperature and maximum depth of the upper boundary (1.5–1.7°C and 340–350 m, respectively) are characteristic of the area adjacent to the central and northern straits of the Kuril Islands Arc, as well as above the slope of the Kamchatka Peninsula. The salinity at the upper boundary of the methane hydrate stability zone in the Sea of Okhotsk varies within a narrow range from 33.4 to 33.6 psu, which is quite close to the conditions assume for the stability of methane hydrate in seawater. An area where the thermobaric conditions in the water column not favorable for the formation of methane hydrates has been identified.

Keywords: gas hydrates, methane, upper boundary of the stability zone, water temperature, salinity, Sea of Okhotsk

DOI: 10.1134/S1028334X24601901

Gas hydrates (GHs) are crystalline compounds of low molecular weight formed under certain thermobaric conditions from water and gas. Gas molecules within GHs are enclosed in crystalline cells consisting of water molecules held together by hydrogen bonding. When the pressure is lowered or the temperature is raised, the hydrogen bond is easily broken. Apart from temperature and pressure, the lithological setting, namely, the presence of porous and permeable sedimentary rocks, is also a crucial factor in hydrate formation [1, 2].

The gas hydrate stability zone (GHSZ) is a part of the Earth's lithosphere and hydrosphere, where thermobaric and lithological–geochemical conditions ensure the stability of GHs of a certain composition. The upper boundary of the GHSZ in water areas always lies in the water column, while the lower boundary occurs within the sedimentary strata [1, 3].

[a] *V.I. Il'ichev Pacific Oceanological Institute, Far East Branch, Russian Academy of Sciences, Vladivostok, 690041 Russia*
**e-mail: petrova@poi.dvo.ru*

GHs are extremely sensitive to the environmental parameters. Their dissociation may be caused even by small changes in temperature or pressure and accompanied by the release of a huge amount of free gas: 1 m^3 of gas hydrate corresponds to about 160 m^3 of methane [1, 4]. According to various estimates, up to 98% of all GH resources are concentrated in the world ocean, while the remaining 2% occur on land. The GHSZ in the World Ocean is confined to depths from 200 m in the circumpolar regions and from 500–700 m in the equatorial regions [5].

Known GH deposits and manifestations are usually represented by methane with minor admixtures of other gases (ethane, propane, butane, carbon dioxide, etc.). For example, the composition of hydrates recovered from the Sea of Okhotsk included 97.80% methane, 0.04% ethane, and 0.09% carbon dioxide [6]. Even the presence of a small percentage of gaseous methane homologues shifts the phase boundary to higher temperatures, and the presence of propane has the maximum effect on the equilibrium temperature compared to other gases [7].

Natural GH occurrences should be regarded as a potential hydrocarbon resource, as well as within the framework of the environmental and climatic agenda. An increasing temperature of near-bottom water may cause shrinkage of the GHSZ and, therefore, partial GH dissociation and methane liberation [2, 8]. The gas released by hydrate decomposition enters the bottom water and migrates into the atmosphere by currents, diffusion, and bubble transport, enhancing the greenhouse effect [9]. Since methane is a powerful greenhouse gas (the absorbing effect of CH_4 on radiation exceeds that of CO_2 by 28–34 times [4]), such a release can have a serious climatic impact [2, 5].

At present there is no information on spatial displacements of the upper boundary of the GH stability zone in the water column of the Sea of Okhotsk. Paper [10] presents cartographic schemes (including the Sea of Okhotsk) of GH distribution, bottom water temperatures, and forecast of the possible distribution (yes/no by thermobaric conditions) of methane hydrates (MHs) in the Arctic and the northern part of the World Ocean (from 45° to 90° N). Baseline data for the calculations included: bottom water temperature; water mineralization in shallow sediments (34.5 and 0 psu), and hydrate gas composition (100% methane).

The data on the depth of the upper boundary of the GHSZ is crucial for the following issues:

—modeling the dynamics of dissolution of ascending gas bubbles in the water column [11, 12];

—modeling the scenarios of GH response to changes in water temperature and assessing the possibility of methane release into the ecosystem (the necessary conditions are the position of the upper and lower boundaries and the thickness of the GHSZ) [2, 13, 14];

—assessing the GH sensitivity to changes in external environmental factors (their dissociation and formation depend on the distance from the upper boundary to the bottom) [15];

—planning of prospecting works on detection and research into GHs in marine areas [16];

—classification of plumes into shallow-water and deep-water ones [12].

The authors aim to identify patterns of the spatial distribution of the methane hydrate stability zone upper boundary parameters distribution (water temperature and salinity, depth of the upper boundary in the water column) based on all available oceanological information in the Sea of Okhotsk.

This study considers only the upper boundary of the GHSZ in the water column. The data from deep oceanological observations in the Sea of Okhotsk, such as bathymetric observations (OSD), CTD observations and data from Argo drifting buoys, Mechanical Bathythermograph Data (MBT), and Expendable Bathythermograph Data (XBT) were used for calculations. Additionally, the depth of each oceanological station site was obtained from the GEBCO website (The General Bathymetric Chart of the Oceans: https://www.gebco.net/).

Unreliable and duplicated data being excluded, the resulting oceanological data set still contains 131 286 stations made from 1929 to 2020. The entire area of the Sea of Okhotsk is generally quite well covered by observations. However, there are very few oceanological stations carried out during the cold period of the year in the sea area. This is especially true for the extensive shelf, covered with ice during the winter period. Therefore, observations of the northern and western parts of the sea are practically absent from January to April.

The upper boundary of the GHSZ was determined by the intersection of the equilibrium curve of GH dissociation (which depends, in addition to thermobaric conditions, on the gas composition and salinity) with the curve of temperature distribution in the water column. Based on the materials of expeditionary studies of the Far East Branch, Russian Academy of Sciences, in the Sea of Okhotsk, as well as publications [6, 16], in the present work we assume that the main component of the GH is pure methane. The stability conditions for the MHs were taken from [8] for the "pure methane–seawater" system (100% CH_4; S = 33.5 psu). As follows from [5], salinity varying from 0 to 36 psu may shift the MH equilibrium stability curve by dozens of meters. In this regard, it can be noted that the conditions we have adopted in terms of salinity are most suitable for the Sea of Okhotsk.

Although the depth of the GHSZ upper boundary was calculated for all 131 286 stations, it was not identified in the predominant part of the stations (99 105) in the shallow waters of the Sea of Okhotsk. The vertical temperature distribution and bottom pressure at these stations indicate that these shallow parts of the sea do not provide the appropriate conditions for GH formation and stable occurrence. The necessary thermobaric conditions were identified only at 32 181 stations. The outer boundary of the distribution of the methane hydrate stability zone in the Sea of Okhotsk was determined from the geographical position of the peripheral stations of this data set (32 181 stations).

Calculations of the mean annual parameters for the GHSZ upper boundary were performed within the 0.35° × 0.55° trapezoids along the meridian and the parallel, respectively. Median averaging of the initial data was applied to each trapezoid. Note the following operation performed when calculating the mean multi-year statistical characteristics in all trapezoids (to normalize the contribution of daily, multi-serial stations and possible duplicated values). First, all data available for a particular day in each trapezoid were averaged. The resulting daily averages were treated as a single value in further calculations of the climatic variables.

The calculated depths of the upper boundary of the GHSZ were compared with the position of the lower boundary of the active layer in the Sea of Okhotsk, where the seasonal variations in water temperature are not statistically significant [17]. The upper boundary of the GHSZ was found to be significantly deeper than the lower boundary of the active layer in the predominant part of the Sea of Okhotsk. The only exceptions were the area near the Kuril Ridge and a small area above the TINRO Basin.

Figure 1 shows the spatial distribution of the GHSZ upper boundary parameters. The temperature pattern obtained exposed that the water area studied can be divided into two subareas, the boundary between which is the 1.4°C isotherm (Fig. 1a). The maximum temperature of water (1.5–1.7°C) in the comparatively warm eastern sector of the sea was distinguished in the straits of the Kuril Ridge (and the adjacent area of the Sea of Okhotsk) and in the near-slope regions of western Kamchatka. The thermal regime of these regions is determined by advection of Pacific waters, as well as by intensive tidal mixing in the straits, which results in heat transfer to the depths of the upper boundary of the GHSZ from both over- and underlying horizons. The spatial distribution of the water temperature at the upper boundary of the GHSZ is also in well agreement with the cyclonic system of currents in the sea presented in [18–20].

The lowest temperature (less than 1°C) at the upper boundary of the GHSZ in the colder sector of the sea was determined in the extreme western part of the sea. This water area is bounded from the north by a canyon located to the south of Iona Island and Kashevarov Bank, and from the south, by the slope of Terpeniya Bay. This area is shaped by two main factors. First, autumn–winter convection and ice formation on the northern sea shelf play a role. This dense and supercooled shelf water with the lowest water temperature in the Sea of Okhotsk [21, 22] is formed in winter in the coastal areas of the northwestern part of the sea and then is transported by the current system to the area of the continental slope. An additional effect of the low water temperature area formation in the extreme western part of the study region is the intensification of tidal and nonperiodic currents over the continental slope of the sea, as well as in shallow waters near Iona Island and Kashevarov Bank. The shape of the 1°C isotherm shows the movement of supercooled water southward (to the parallel of Cape Aniva) and then eastward (in accordance with the cyclonic system of water movement in the sea).

As follows from Fig. 1b, the salinity at the upper boundary of the GHSZ in the Sea of Okhotsk varies within a fairly narrow range from 33.4 to 33.6 psu, which is close enough to the conditions of methane hydrate stability in seawater that we have adopted according to [8]. The minimum salinity values are highlighted in the peripheral areas of the Sea of Okhotsk (Fig. 1b). The exceptions are small areas of the main inflow of Pacific waters into the sea (near the central and northern straits of the Kuril Ridge). The area with increased salinity near the Shiretoko Peninsula on Hokkaido Island is associated with the advection of saline water from the Sea of Japan by the Soya Current. Here, elevated salinity values are formed due to the interaction and vertical mixing of the Soya Current waters and the waters of the Sea of Okhotsk [21, 22], which leads to an increase in both temperature and salinity (Figs. 1a, 1b).

The most extensive area with reduced salinity (and low water temperature) is observed near the slope of Sakhalin Island and in the western part of the Kuril Basin of the Sea of Okhotsk. Here, as is known [21, 22], the formation of water salinity is dominated by the bottom shelf waters of the northwestern part of the sea (with low temperature and salinity), which are formed as a result of autumn–winter convection. The salinity of the water in this stationary region east of Sakhalin also depends on advection of relatively fresh waters, the regime of which is strongly dependent on the flow of the Amur River. The shape of the region with salinity below 33.5 psu (Fig. 1b) implies that, as this desalinized water reaches the southern part of the sea, it enters the Pacific Ocean, which contributes to the formation of an intermediate water mass with reduced salinity in its northwestern part [21, 22]. Moreover, according to the existing schemes of sea currents [18–20], these desalinized waters move eastward at the southern periphery of the cyclonic circulation of sea water, reaching the meridian of the central straits of the Kuril Ridge.

The depth of the GHSZ boundary in the Sea of Okhotsk (Fig. 1c) is in full accordance with the oceanological conditions discussed above and the main factors of their formation (autumn–winter convection, lateral and vertical mixing at the current boundaries and in the Kuril Ridge straits, advection of waters of the Pacific and Sea of Japan, and intensification of tidal and non-periodic currents in areas of sharp depth differences) and varies from 300 to 350 m. It is maximal (up to 340–350 m) near the central and northern straits of the Kuril Ridge. According to the contours of the 330 and 340 m isolines, the topography of the GHSZ upper boundary limits, respectively, the western and eastern margins of the cyclonic water cycle of the Sea of Okhotsk (Fig. 1c).

Note that the division of the water area of the Sea of Okhotsk into segments fit/unfit for GH formation and occurrence shown on all maps in Fig. 1 agrees well with the published data [10, 23]. At the same time, the partition of the water area presented in Fig. 1 is more detailed, and the differences with [10, 23] are mainly due to the more accomplished database of the initial oceanological data, consideration of the actual thermal structure of the Sea of Okhotsk waters in the calculations, and a more realistic assumption of the GH

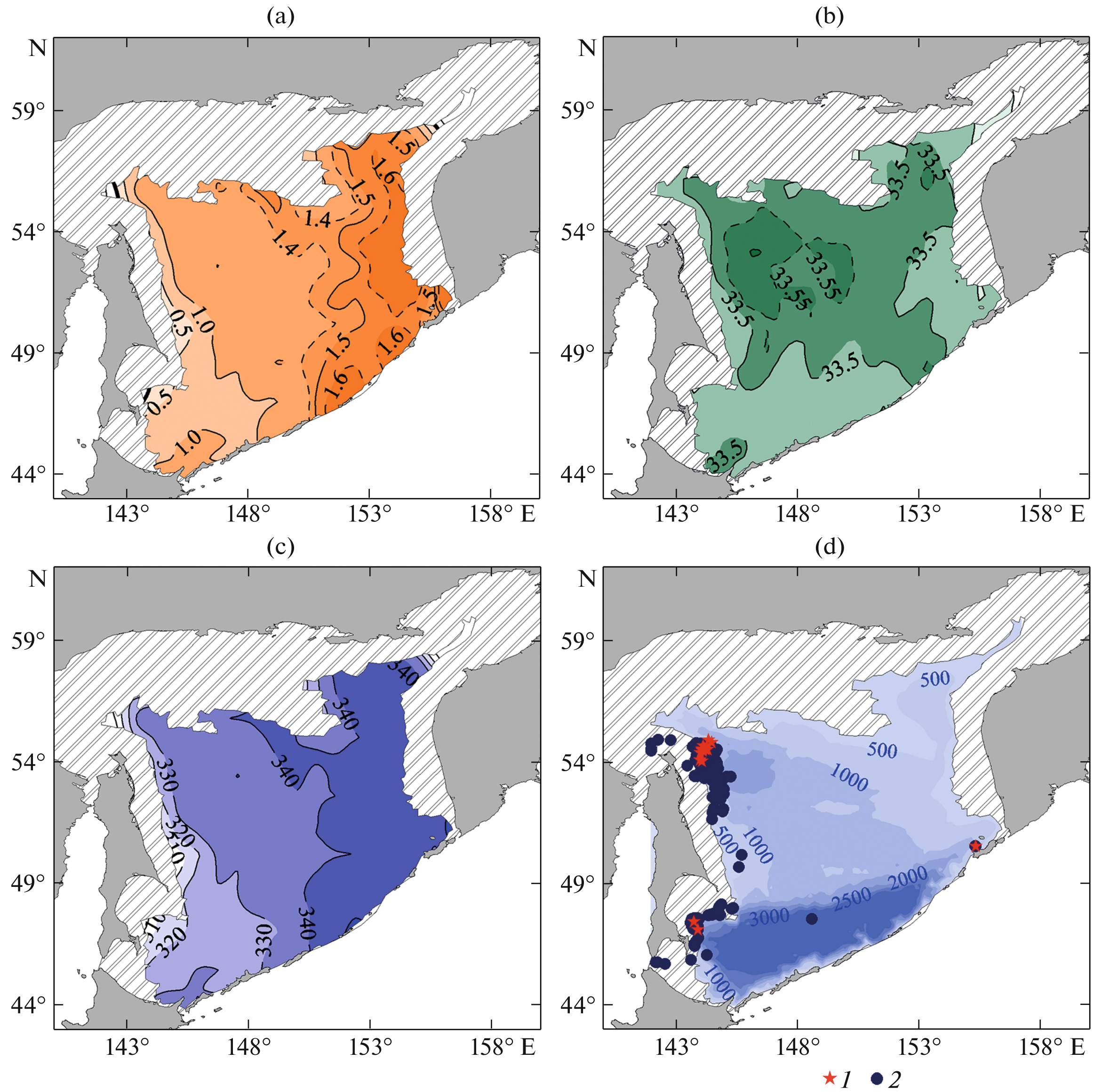

Fig. 1. Spatial distribution of the mean annual values of the parameters of the upper boundary of the GHSZ: (a) water temperature (°C); (b) salinity (psu); (c) depth of the upper boundary (m). (d) (*1*) known GH accumulations confirmed by direct methods and (*2*) methane plumes (figures give depths in meters). The shaded area is the water area where thermobaric conditions within the water column do not allow for the occurrence of GHs.

stability condition for the "pure methane–seawater" system (S = 33.5 psu).

This paper does not consider the possibility of the existence of cryogenic GHs (although negative temperature values exist on the predominant part of the Sea of Okhotsk shelf). This problem, firstly, is beyond the scope of this study (sea water column), and secondly, the possibility for the existence of cryogenic GHs and their presumed location within the Sea of Okhotsk were discussed in sufficient detail in [10].

The reliability of the results obtained was verified by the location of the identified accumulations of GHs and methane plumes. These data were obtained within the framework of long-term observations of the V.I. Il'ichev Pacific Oceanological Institute, Far East Branch, Russian Academy of Sciences, for the period 1988–2021 and partially published in the reports and paper [16]. As follows from Fig. 1d, the GH accumulations detected by contact methods gravitate to the water area where the upper boundary of the GHSZ is in the water column.

The distribution of the identified methane plumes in the Sea of Okhotsk is more complicated, but explainable (Fig. 1d). Those are distributed not only in the zone where the water column lacks thermobaric conditions for GHs, but also in the deep-water parts of the sea. First, the presence of methane plumes in shallow parts of the studied water area is associated, on the one hand, with the presence of oil and gas deposits and active faults and, on the other, with the absence of GH, which, cementing the bottom sediments, could have played the role of a fluid-impermeable sea. Secondly, the GHSZ upper boundary can be located in these areas of the sea both on the sea bottom and in the upper part of the sedimentary layer. Therefore, the thermal conditions favoring GH dissociation are possible there. This can be confirmed by the known facts of both seasonal and interannual water temperature fluctuations in the Sea of Okhotsk [17, 22, 24, 25].

The presence of methane plumes in the deep sea, where the thermobaric conditions of the water column allow for GH occurrences, can be explained by the following. First, the seismo-tectonic processes there may cause disturbances in the structure of the host sediment column, especially in fault zones, which may trigger gas emissions. As is known, episodes of seismic and volcano-magmatic activity were observed in the Sea of Okhotsk. Secondly, there may be additional sources, e.g., hydrocarbon accumulations, foci of postmagmatic activity, etc. The latter issue, however, is to be considered elsewhere.

This study revealed the spatial distribution of parameters (water temperature, salinity, depth) of the upper boundary of the GHSZ in the Sea of Okhotsk using average annual data for the period 1929–2020. The minimum water temperature and depth of the upper boundary of the GHSZ were found near the eastern slope of Sakhalin Island, while the maximum values were characteristic of the area adjacent to the central and northern straits of the Kuril Ridge. The reliability of the obtained results was assessed using the actual data of expedition observations (presence of GHs and methane "plumes").

The results obtained would be useful for GH prospecting in the Sea of Okhotsk, as well as for studying the impact of GHs and the consequences of their dissociation on the distribution of benthic fauna. In addition, the position of the upper boundary of the GHSZ and the extent of it in the water column are necessary conditions for modeling scenarios of GH response to changes in the seafloor temperature and assessing the possibility of methane release into the ecosystem. The patterns revealed in the presented work may be used in modeling the dynamics of dissolution of rising gas bubbles in the water column.

ACKNOWLEDGMENTS

The authors thank the reviewers for their constructive comments. This work contributed to the objectives of the GEOMIR project under the National Plan of Action of the UN Decade of Ocean Sciences for Sustainable Development (2021–2030) and the WESTPAC Working Group on Gas Hydrates and Methane Fluxes in the Indo-Pacific (CoSGAS).

FUNDING

This study was carried out within the framework of a state assignment for the V.I. Il'ichev Pacific Oceanological Institute, Far East Branch, Russian Academy of Sciences, for 2024–2026 "Study of the Structure and Dynamics of the World Ocean Waters under the Conditions of Modern Climate Change," project nos. 124022100079-4 and 124002210076-3.

CONFLICT OF INTEREST

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

REFERENCES

1. Yu. F. Makogon, Geol. Polezn. Iskop. Mirovogo Okeana, No. 2, 5–21 (2010).
2. M. T. Reagan, G. J. Moridis, S. M. Elliott, and M. Maltrud, J. Geophys. Res. **116**, C09014 (2011).
3. A. A. Trofimuk, N. V. Cherskii, and V. P. Tsarev, Dokl. Akad. Nauk SSSR **212** (4), 931–934 (1973).
4. *Methane and Climate Changes: Scientific Problems and Technological Aspects,* Ed. by V. G. Bondur, I. I. Mokhov, and A. A. Makosko (Russ. Acad. Sci., Moscow, 2022) [in Russian].
5. V. I. Bogoyavlenskii, A. S. Yanchevskaya, I. V. Bogoyavlenskii, and A. V. Kishankov, Arktika: Ekol. Ekon., No. 3 (31), 42–55 (2018).
6. O. V. Veselov, V. V. Gordienko, and V. V. Kudel'kin, Geol. Polezn. Iskop. Mirovogo Okeana, No. 3 (5), 62–68 (2006).
7. Z. Chen, W. Bai, and W. Xu, Chin. J. Geophys. **48** (4), 936–945 (2005).
8. G. R. Dickens and M. S. Quinby-Hunt, Geophys. Rev. Lett. **21** (19), 2115–2118 (1994).
9. A. V. Eliseev, Fundam. Prikl. Klimatol. **1**, 52–70 (2018).
10. V. Bogoyavlensky, A. Kishankov, A. Yanchevskaya, and I. Bogoyavlensky, Geosciences **8** (12), 453 (2018). https://doi.org/10.3390/geosciences8120453
11. D. F. McGinnis, J. Greinert, Y. Artemov, S. E. Beaubien, and A. Wuest, J. Geophys. Res. **111**, C09007 (2006). https://doi.org/10.1029/2005JC003183
12. N. G. Granin, M. M. Makarov, K. M. Kucher, and R. Y. Gnatovsky, J. Geophys. Res. **30** (3-4), 399–409 (2010). https://doi.org/10.1007/s00367-010-0201-3
13. A. Biastoch, T. Treude, L. H. Rupke, U. Riebesell, C. Roth, E. B. Burwicz, W. Park, M. Latif, C. W. Boning, G. Madec, and K. Wallmann, Geophys. Rev. Lett. **38**, L08602 (2011). https://doi.org/10.1029/2011GL047222
14. M. Giustiniani, U. Tinivella, M. Jakobsson, and M. Rebesco, J. Geol. Res. **2013**, 783969 (2013). https://doi.org/10.1155/2013/783969
15. M. T. Reagan and G. J. Moridis, Geophys. Rev. Lett. **34**, L22709 (2007). https://doi.org/10.1029/2007GL031671

16. A. I. Obzhirov and R. B. Shakirov, in *Eurasian Continental Boundaries: Geology and Geoecology,* Spec. Iss. No. 4: *Eurasian Boundary Seas: Geology and Mineral Resources* (GEOS, Moscow, 2012), pp. 122–136 [in Russian].

17. V. A. Luchin, in *Russian Far Eastern Seas* (Nauka, Moscow, 2007), Vol. 1, pp. 232–252 [in Russian].

18. K. V. Moroshkin, Okeanologiya **4**, 641–643 (1964).

19. V. A. Luchin Tr. DVNII, No. 96, 69–76 (1982).

20. P. A. Fayman, S. V. Prants, M. V. Budyansky, and M. Y. Uleysky, Izv., Atmos. Oceanic Phys. **57** (3), 329–340 (2021).

21. L. D. Talley, Deep Sea Res. A, No. 38, Suppl. 1, 171–190 (1991).

22. S. Gladyshev, L. Talley, G. Kantakov, G. Khen, and M. Wakatsuchi, J. Geophys. Res. **108** (C6), 3186 (2003). https://doi.org/10.1029/2001JC000877

23. G. D. Ginsburg, I. S. Gramberg, and V. A. Solov'ev, Sov. Geol., No. 11, 12–19 (1990).

24. V. A. Luchin and V. I. Matveev, Izv. TINRO **187**, 205–216 (2016).

25. A. L. Figurkin, Izv. TINRO **166**, 255–274 (2011).

Translated by M. Hannibal