

Modeling the distribution of the World Ocean methane hydrates and the methane flow into the atmosphere

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Based on a 3-D quasi-geostrophic model of the World Ocean climate, supplemented with the model of the dissolved methane transport by ocean streams, a model describing consequences of possible destabilization of sub-floor methane hydrates in the World Ocean has been developed. The presences of methane and certain thermodynamic conditions, the so-called p,T -conditions, are necessary for the formation of methane hydrates. It is supposed that methane hydrates exist throughout in the sediment layer, where thermobaric conditions are favorable for their existence. To estimate the scale of their destabilization, the model parameter, namely, the depth of methane hydrates occurrence in the World Ocean deposits is important. The sub-floor depth is determined with the account of the thickness of the methane hydrate stability zone, geothermal gradient, sediment layer porosity, and percentage of sediments, the porous space of which contains the gas hydrates.

Gas hydrates are solid crystal compounds of a gas and water ice formed under certain thermobaric conditions, under which gas molecules (usually methane) occupy places in the water ice crystal structure taking the form of snow. The volume occupied by methane in a gas hydrate decreases by nearly 200 times. When gas hydrate degrades because of pressure decrease or temperature rise, large amount of gas is being released. Study of methane hydrates is closely connected with the environmental problems because of active role the methane plays in the greenhouse effect in the Earth atmosphere.

According to geophysical and other data, for example, data on core samples, more than 60 regions of gas hydrate deposits in sub-floor sediments have been revealed in the ocean waters (Fig. 1). A great

bulk of data on the distribution of solid-state methane hydrate accumulations has been compiled.¹⁻³

As *in-situ* investigations show, gas hydrates in sea can occur virtually in any rocks. They fill the pore spaces and fractures, moving rock layers apart when accumulating. Gas hydrates can be formed in the Earth crust under certain hydrodynamic conditions. The term "gas hydrate stability zone" (GHSZ) is commonly understood as the part of Earth lithosphere and hydrosphere, thermobaric and geochemical regimes of which correspond to conditions of stable living of gas hydrates of certain composition. Study of temperature conditions of seawater has shown that the cap of the methane GHSZ is located at the depth of 250–300 m in polar

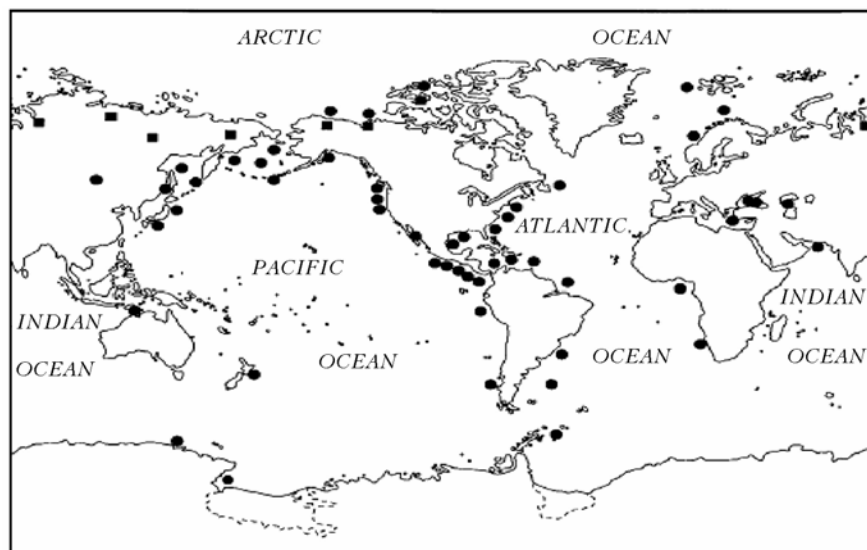


Fig. 1. Known regions of gas-hydrate occurrence on Earth.¹

seas and 500–650 m in the tropical ones. The depth of GHSZ base depends on the gas composition, water column height above bottom, geothermal gradient (heat flow) in sub-floor sediments, and mineralization of the interstitial waters. Currently, most researchers reason sediments of continental platform-slope coupling zones, as well as zones of slopes and foets of continental edges to be most promising as hydrate-bearing ones. These are characterized by the greatest thickness of sediments, comparatively high concentration of organic matters and methane in it, as well as by the absence of strong near-bottom flows.³

Methane hydrates (MH) are formed and exist near the boundary of their thermodynamic stability. Even slight changes in thermobaric conditions can result in decay of the compounds and release of large amounts of methane, the specific contribution of which to the greenhouse effect is known to be 20 times greater than that from the carbon dioxide.^{4,5}

Data on the distribution of oceanic methane hydrates illustrate their usual occurrence in sediment layers at sub-floor depths of hundreds of meters. Therefore, penetration of heat down to the ocean floor and deeper in a sediment layer is a necessary condition for the methane hydrates decay. The model of methane transfer from decaying gas hydrates in the sediment layer at a depth of 100–300 m under the ocean floor was considered in Refs. 6 and 7. A 3-D quasigeostrophic model of the World Ocean dynamics was supplemented with the model of heat transfer inside the bottom sediment layer in order to study the process of heat signal propagation into the ocean depth and its sediment layer. A series of scenario experiments has shown the model parameter H_{hyd} (depth of the hydrate deposit) to be important in estimating the methane hydrate destabilization scale. Any simulation of possible methane flows into the atmosphere resulting from the sub-floor gas hydrates decomposition needs for more accurate information on their spatial distribution. In this paper, we determine the distribution and the occurrence depth taking into account the geothermal gradient and porosity of the bottom sediment layer.

The ocean climatic state was determined using a 3-D model of the World Ocean dynamics involving seasonal variability and actual floor topography.⁸ The model is based on solving 3-D equations of heat and salt transfer over uniform 5-degree latitude-longitude grid and nonuniform vertical grid densening to the surface. Along the horizontal coordinate, a conservative nine-point procedure of the second approximation order, based on Richardson extrapolation, was applied while along the vertical one we used a procedure with counter-flow differences, having the first order of approximation. The problem has been solved for a polygonal region of the World Ocean between 72.5°S and 87.5°N with 24 vertical levels until a quasistationary state is achieved in about several thousand years.⁹

A climatic field of heat in a sediment layer of 1000 m thickness was calculated for each point of the latitude-longitude grid in a 20-m vertical step, using the heat conduction equations. As boundary conditions at the top of sediments coinciding with the ocean floor, the near-bottom water temperature $T_{s,b}$ was taken (obtained from the ocean dynamics model). At the bottom of the sediment layer we set the geothermal heat flow Q_t

$$\frac{\partial T_s}{\partial t} = \frac{\partial}{\partial z} k_s \frac{\partial T_s}{\partial z}, \quad (1)$$

$$z = H : T_s = T_{s,b}, \quad (2)$$

$$z = H + d : k_s \frac{\partial T_s}{\partial z} = Q_t, \quad (3)$$

$$t = 0 : T_s = T_{s,cl}(z), \quad (4)$$

where $k_s = 10^{-2} \text{ cm}^2/\text{s}$ is the sediment thermal conductivity; $T_s(z)$ is the sediment layer temperature; $T_{s,cl}(z)$ is the solution of stationary equation (1).

The climatic distribution of the dissolved methane was obtained from solution of a 3-D advection-diffusion equation of methane transfer with preset values of the surface methane concentration and zero methane flows through the bottom and the side surface:

$$\frac{\partial C}{\partial t} + \frac{u}{a \sin \theta} \frac{\partial C}{\partial \lambda} + \frac{v}{a} \frac{\partial C}{\partial \theta} + w \frac{\partial C}{\partial z} = \frac{\partial}{\partial z} \kappa \frac{\partial C}{\partial z} + \frac{\mu}{a^2} \Delta C \quad (5)$$

with the following boundary conditions:

$$z = 0 : C = C^*(\lambda, \theta, 0),$$

$$z = H : \kappa \frac{\partial C}{\partial z} = 0; \quad (6)$$

$$\text{on } \Gamma : \mu \frac{\partial C}{\partial n} = 0.$$

Here C is the dissolved methane concentration, $C^*(\lambda, \theta, 0)$ are the preset values of methane concentration on the ocean surface changing from zone to zone from 50 ppb in the low south latitudes to 100 ppb in the high latitudes, 1 ppb = 10^{-6} ml/l; u , v , w are the components of the velocity vector with coordinates λ , θ , and z (λ is the longitude; θ is the latitude completion to 90°; z is directed vertically downward); t is time; κ and μ are the coefficients of vertical and horizontal turbulent diffusion of the dissolved methane; a is the mean Earth radius; $H(\lambda, \theta)$ is the bottom relief; Γ is the side surface of the region.

To isolate a water area with thermobaric conditions sufficient for hydrate formation and to estimate the GHSZ thickness, the following parameters should be known: the pressure, the temperature of the near-bottom water layer, and geothermal gradient within first hundreds of meters of sediment. The rock thickness, in which the pressure and temperature correspond to

thermodynamic conditions of gas hydrate occurrence stability, is the zone of hydrate formation. It can be determined mathematically through simultaneous solution of the equation of the thermal gradient variation in a rock profile and the equation of equilibrium stable occurrence of hydrate in a given porous medium. It is supposed that methane hydrates occur in sediment wherever the thermobaric conditions for their existence hold, which are calculated as¹⁰

$$\frac{1}{T_{\text{stab}}} = 3.79 \cdot 10^{-3} - 2.83 \cdot 10^{-4} \log p_{\text{stab}}, \quad (7)$$

where T_{stab} is the gas hydrate stability temperature, K; p_{stab} is the pressure, MPa. Determine the stability diagram for the system “methane–seawater–sediment” based on measurement data.¹¹

The curve of the hydrate formation thermobaric conditions (7) is superposed on the line of hydrothermal and geothermal gradients; points of the two lines intersection allow us finding the GHSZ top and bottom, the top, therewith, is limited by the ocean floor. The phase diagram is obtained for all model points of the ocean. Figure 2 presents the methane hydrate stability diagram for the depth of 1700 m. The geothermal gradient in sediment is equal to 30°C/km, bottom temperature is 1.9°C. The thickness, Δz , of zone of the gas hydrate possible stability under these conditions is 144 m. In such a way we set Δz at all points of the model oceanic region.

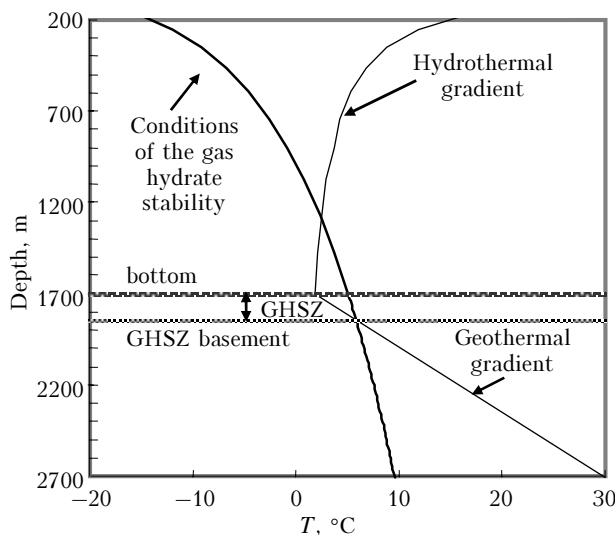


Fig. 2. Phase diagram of the methane hydrate stability.

The GHSZ top is always in the water depth, while the bottom one inside the rock. Having in mind thermal pattern of the deep oceanic regions and that sediments and organic matter are mostly accumulated in the peripheral oceanic regions, like shelves, continental slopes, and deep continental troughs, deep-water shelf sediments and sediments of the continental platform slopes should be considered the zones most promising for gas hydrate

accumulation. As to the abyssal zones of the huge ocean floor, the sediment there is characterized by the organic matter deficiency and high geothermal gradient; therefore, there is a little chance for the hydrate to exist there. The condition for gas accumulation in sediment is a significant content of organic matter at a high sedimentation rate. So, oceanic regions with insufficient, for hydrate formation, amount of gas and regions, where the depth exceeds 3000 m, do not refer to hydrate-bearing ones.¹²

The temperature in the ocean sediment layer and the thickness of the gas hydrate zone strongly depend on the vertical temperature gradient in deposits Q_t . Information on the geothermal gradient in different regions of the World Ocean is quite scanty. In earlier calculations⁶ the geothermal flow was taken constant and equal to 30°C/km. In this work the heat flow $Q_t(\theta, \lambda)$ is taken different for 22 regions based on data from Ref. 13 and varies from 30°C/km in the southern part of the Pacific Ocean to 87°C/km in its northern part.

The gas hydrates do not form a solid blanket in the thermodynamic zone of the hydrate formation, as the proper temperature and pressure conditions are not yet sufficient for hydrate formation. High content of organic matter (between 0.5 to 4% and higher), as well as active generation and migration of hydrocarbons to the hydrate formation zone are required as well. Investigations of the core samples show that hydrates do not occupy the overall stability zone, rather they exist as layers near its bedding.¹¹ The sediment porosity $P(z)$ can change linearly or nonlinearly depending on the sediment composition. We take a simple exponential decrease of porosity with the increasing sub-floor depth, obtained from empirical data^{11,13}:

$$P = P_0 \exp[-(\Delta z)]/L, \quad (8)$$

where $P_0 = 0.7$ is the porosity of the ocean floor sediment; $L = 1500$ m is the thickness of the sediment layer¹¹; Δz is the GHSZ thickness.

The saturation of sediment with hydrates, i.e., percentage of the pore space occupied by gas hydrates is accepted to be 50% immediately near the GHSZ bedding while smoothly decreasing to zero toward the ocean floor. This assumption is based on the known decrease of chloride ions in the pore water (which is a standard of the hydrate content) as the depth grows, which was observed at stations 496 and 497 (Deep Sea Drilling Project)² in the Central American trough. This approach is based on Hyndman and Davis hydrate formation model (Ref. 11), which was proposed in Ref. 13:

$$HP(z) = 100\% \cdot 0.5P(\Delta z)(z - z_0)/\Delta z, \quad (9)$$

where

$$z_0 < z < z_0 + \Delta z;$$

$HP(z)$ increases linearly from 0 at the ocean floor z_0 to $P/2$ at the stability zone bottom.

At $HP(z)$ no less than 10% (Ref. 14) $H_{\text{hyd}}(\lambda, \theta) = z$. Thus, the depth distribution for methane hydrate occurrence was estimated between 20 and 320 m in the deposit under the ocean floor. Figure 3 shows the methane hydrate distribution for 100 m depth, which is mainly seen in the north of Atlantic Ocean and in the continental shelf.

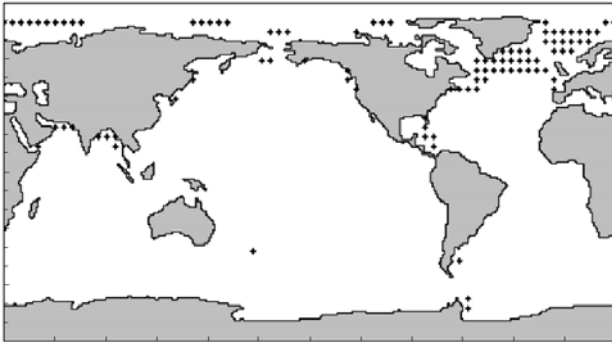


Fig. 3. Model distribution of the methane hydrates in sediment at the depths between 20 and 100 m below the ocean floor.

Figure 4 presents the methane hydrates distribution at a depth of 300 m below the ocean floor.

Two scenario experiments were conducted taking different zones of the methane hydrate occurrence and sediment depths. For comparison, in the first experiment HYDRATE-1 the deposit depth is supposed, as earlier, to be 100 m for the whole continental shelf and basins of Arctic and Antarctic; and 300 m for the rest of the ocean area, where the conditions for methane hydrate occurrence hold. In the second experiment HYDRATE-2, $H_{\text{hyd}}(\lambda, \theta)$ is determined between 20 and 320 m allowing for the GHSZ thickness, as described below.

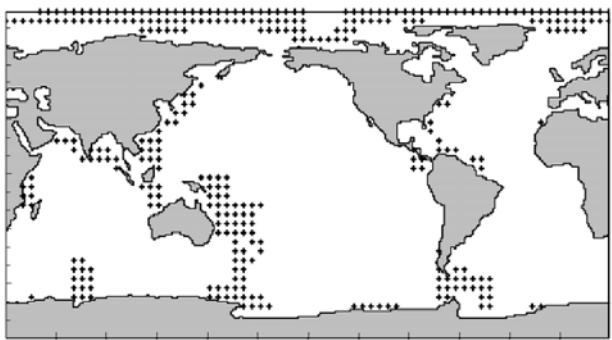


Fig. 4. Model distribution of methane hydrates in sediment at a depth of 300 m below the ocean floor.

Each experiment started using the same calculated climatic fields. In each experiment, the time preceding the methane hydrate destabilization has been found, as well as the part of the ocean floor containing the methane hydrate sources, and the intensity of the diffusion methane flow into the atmosphere. In the beginning, the seasonally varying

temperature of the ocean surface linearly increased by 1.5° for the first 50 years everywhere, except for polar regions covered with ice all the year round, and then linearly decreased to the initial values for the same period.

Further, it went on to vary in accordance with seasonal climatic data. The heat signal from the surface was transported into the ocean deep through convective mixing and streams. Using Eq. (1) and conditions (2)–(4), the sediment temperature increase relative to the initial climatic value has been modeled. It was supposed that the methane hydrate decay begins at the moment, when the increase exceeded some tolerance,¹⁵ $dT_h = 0.01^\circ$, which can occur at the under-floor depth $H_{\text{hyd}}(\lambda, \theta)$, where the methane hydrate occur.

This decay favors preserving near-bottom concentration of the dissolved methane equal to 5000 ppb. It is assumed that the methane released due to decay totally dissolves in water. The above value is further used as a boundary condition for the given point of bottom in solving the transfer equation instead of the zero methane flow used earlier in obtaining climatic data. Thus, the methane source is involved into the model. As soon as the heat increase in the sediment at the depth of methane hydrate occurrence becomes less than dT_h , the decay is supposed to stop and the source is being switched off. This means, for the transfer equation, that the boundary condition is replaced back from 5000 ppb to the zero methane flow. In experiments, the time, for which the model integration, supplemented with transfer equation for the dissolved methane, was conducted, made 2000 years.

In the first experiment, the time preceding the methane hydrate destabilization made 68 years. Total methane flow into the atmosphere has reached its maximum (5 Tg/year) within 409 years after the experiment initial time. The sources were involved on the area no more than 11% of the ocean floor and provided maximum mean concentration of the dissolved methane of 957 ppb within 492 years after the initial time. In the numerical experiment HYDRATE-2, the decay began already within 10 years after the start of heating the surface oceanic water. The sources were involved on the area less than 6% of the ocean floor and provided the maximum mean concentration of the dissolved methane only 500 ppb within 1000 years. The maximum methane flow decreased 2.5 times and made 2.02 Tg/year within 500 years of the model time.

The distribution of the dissolved methane at the depth of 250 m within 100 years after the start of the HYDRATE-2 experiment is presented in Fig. 5. The start of methane hydrate destabilization within 100 years of climatic changes is seen in Arctic shelf, near Greenland shore, as well as in Far East seas adjacent to Russia and Japan. Within 400 years, the area of methane hydrate decomposition increases. Most methane-saturated regions turn out to be the Atlantic Ocean being the best ventilated by a system of streams and the Indian Ocean.

Overall, the experimental results show a good agreement with the available estimates¹⁶ for methane flows and start times of destabilization. The main

result is in the fact that the model gives quite realistic magnitudes of methane flows into the atmosphere from the destabilized methane hydrates.

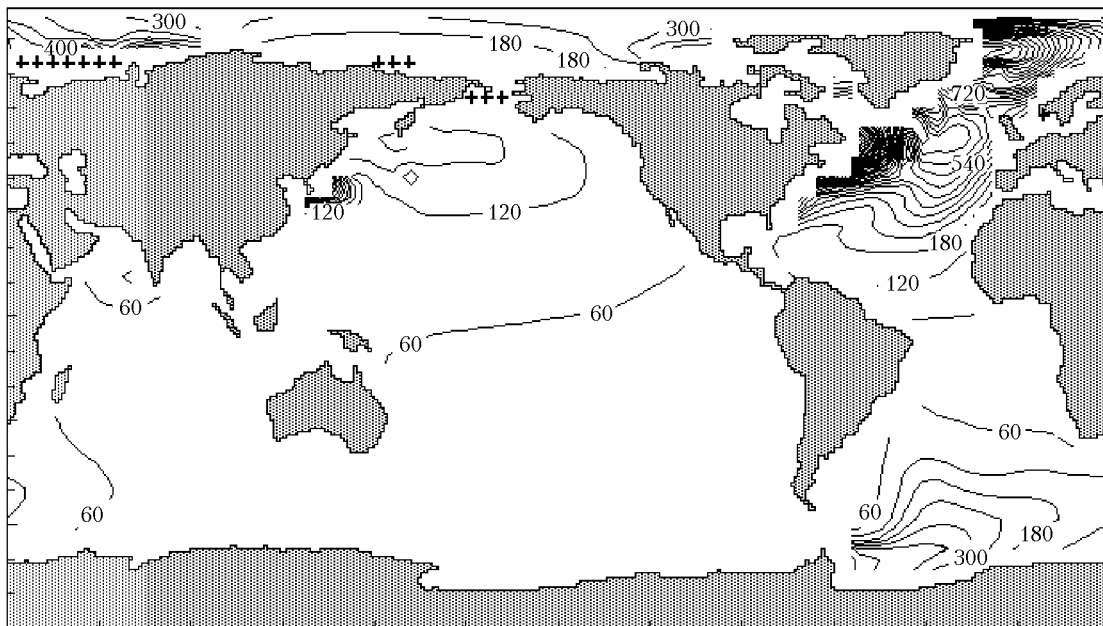


Fig. 5. Isolines of dissolved methane at the depth of 250 m within 100 years after start of climatic changes in the experiment HYDRATE-2 (ppb). Maximum methane concentration is 2400 ppb.

Acknowledgments

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