# Modeling of subbotom methane hydrates decomposition under climatic change at a time scale of a few thousands of years

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Received February 2, 2008

The global presence of methane gas hydrates in subbotom layers of the World Ocean, as well as results of investigation of air bubbles from ice cores in Greenland and Antarctica have led researchers to the hypothesis on prevailing influence of decomposition of methane gas hydrates on the change in the Earth climate and completion of the last ice age. The three-dimensional mathematical model of the dissolved gas transport by the ocean currents was used for quantitative evaluation of possible consequences of methane hydrate destabilization. A possibility of the subbottom methane hydrate destabilization under impact of the surface temperature variation for several thousands of years has been studied. A few scenario experiments with different scales of the surface ocean temperature changes were carried out, which have shown that changes in the concentration of methane, resulted from decomposition of the subbottom methane hydrates, can be the consequence of temperature changes. Thus, long period of warming can result in destabilization of hydrates in a sedimentary layer of the ocean. The calculated methane flux into the atmosphere turned to be equal to 18 Tg/year.

#### Introduction

Gas hydrates are solid crystalline compounds of gas and water formed in certain thermal and baric conditions, under which gas molecules (usually, methane) are located inside water molecules. Natural gas hydrates are such component of the geosphere, which can significantly influence the climate and the ecological situation due to uncontrollable emissions and leecages of methane into the atmosphere. According to different estimates, possible methane escape into the atmosphere from gas hydrate deposits accounting for their thermodynamic equilibrium, makes 5-200 mln t/year.

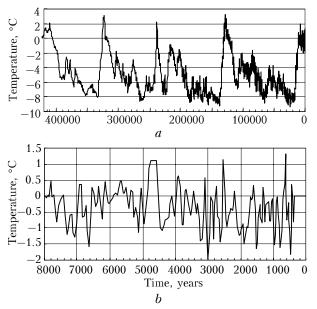
Studies of methane hydrates are closely connected with environmental problems due to the methane ability to cause the greenhouse effect in the atmosphere. The increase of methane concentration in the atmosphere became of justifiable concern. Its concentration has increased two times during the last two centuries, while the concentration of carbon dioxide increased only by a quarter. Today the mean methane content in the atmosphere is estimated as 1.8 ppm.<sup>2</sup>

As a result of core research and on the base of geophysical and other data we defined more than a hundred regions of gas hydrates distribution in subbottom depositions of seas and oceans. In seas and oceans gas hydrates are usually located at depths from 200-400 to 3000 m. They saturate the layer of bottom deposits and are contained in pores in the form of interlayers, lens, in sparse state, making 10-20\% of the deposit volume. Global presence of

methane gas hydrates in subbottom areas of World Ocean and in permafrost,<sup>3</sup> as well as the results of the analysis of air bubbles from ice core of Greenland and Antarctica<sup>4</sup> prompted some researchers to a hypothesis of methane gas hydrates decomposition dominating influence on the Earth climate change and, in particular, on the completion of the last ice age.5

The analysis of ice cores evidences that the increase of the temperature and the methane and carbon dioxide concentration in the atmosphere occurred simultaneously in that epoch. This is the first direct proof of correlation between the content of greenhouse gases in the atmosphere and the climate change throughout the climate cycle.<sup>4</sup> During the time available for the research via polar ice cores, significant variations in methane concentration were abrupt noticed. Thus, changes methane concentration happened during two interglacial periods: 150-135 and 18-9 thousands of years ago (Fig. 1). In those periods the methane concentration abruptly increased (from 0.35 ppm in the highest point of glaciation to 0.6-0.7 ppm in interglacial periods).4

correlation between variations temperature and greenhouse gases content indicates that there is a cause-effect relation. Unfortunately, the accuracy of estimations is not sufficient for determining the sequence of events: the temperature increase, which caused the decomposition of gas hydrates, was first or vice versa. Many specialists<sup>5</sup> think that the cause lies in the change of methane and carbon dioxide concentrations.



**Fig. 1.** Temperature variations for the past 420 thousand years (a) and 8 thousand years (b) according to the data on air bubbles analysis in the Antarctica ice.<sup>4</sup>

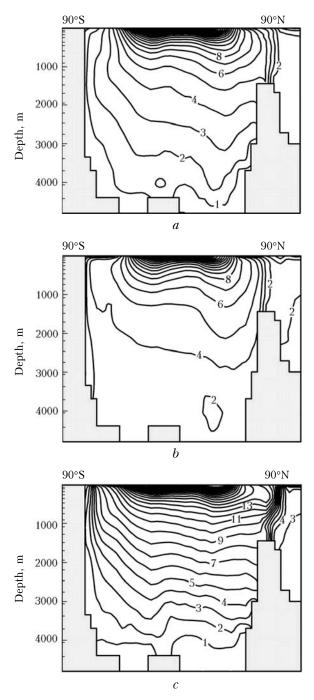
The observed past and present-day concentration variations of greenhouse gases can be not the cause but a direct consequence of temperature variations.<sup>6</sup> For example, even a slight increase of the mean temperature of the ocean surface layer can lead to emission of a huge amount of the carbon dioxide due to variation of its solubility in sea water. At the same time, a large emission of methane into the atmosphere is possible due to thermal decomposition of unstable gas hydrates both on the land and the sea shelf. A strong feedback, realized through the mechanism of greenhouse effect, can multiply increase even slight temperature variations caused by any possible reason. The estimations of possible methane emission in the atmosphere in the periods of glacial-interglacial cycle are different. Thus, according to modeling results, 1500-2700 Gt. of methane could be emitted in the atmosphere 120 thousands of years ago and about 800 Gt. 55.5 thousands of years ago as a result of gas hydrate decomposition.

In this article we consider the modeling of methane flux into the atmosphere at the ocean surface temperature variation at a scale of several millenniums.

## Model description

The ocean climatic state has been obtained by a 3D model of World Ocean, including seasonal variation with accounting for the actual bottom topography. The model is based on the solution of 3D equations of heat and salt transfer at a uniform 5-degree longitude-latitude grid and at irregular vertical grid condensing to the surface. On the horizontal coordinate, we used a conservative 9-point difference scheme of second order of approximation,

based on the Richardson extrapolation. On the vertical coordinate we used the second scheme with upstream differences of first order of approximation. The task was solved at a polygonal area of World Ocean at a 5-degree grid from 72.5°S to 87.5°N with 24 vertical levels till the reaching of the quasistationary state over the period of several thousands of years (Fig. 2a).



**Fig. 2.** Zone-average fields of temperature and salinity in the World Ocean: the numerical experiment with thermohaline circulation model after integration over 5000 years (a); the "Cooling" experiment after 5000 years (b); the "Warming" experiment after 10000 years (c).

Further, we calculated the heat climatic field in the bottom sedimentary layer of a 1000 m thickness for every point of the longitude-latitude grid, using the heat conductivity equation. 9 As the boundary conditions at the top boundary of the sedimentary layer, coinciding with the ocean bottom, the temperature of bottom water was taken, obtained from the ocean dynamics model. Geothermal heat flux was set for the low boundary of the sedimentary

Climatic distribution of the dissolved methane was obtained from the 3D model of the World Ocean dynamics supplemented with the advection-diffusion equation of the methane transfer<sup>9</sup>:

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

with boundary conditions:

at the ocean surface z = 0:  $C = C^*(\theta)$ ,

at the side surface  $\Gamma$ :  $\frac{\partial C}{\partial n} = 0$ ,

at the ocean bottom  $z = H(\lambda, \theta)$ :

$$\begin{cases} \kappa \frac{\partial C}{\partial z} = 0, & \text{without source,} \\ C = 5000 \text{ ppb, source.} \end{cases}$$

Here  $C(z, \lambda, \theta)$  is the concentration of the dissolved methane;  $C^*(\theta)$  is a given value of the methane concentration at the ocean surface, which changes zonally from 50 ppb in southern high-latitude regions of the ocean to 100 ppb in the northern ones; u, v, ware components of the velocity vector by the coordinates:  $\lambda$ ,  $\theta$ , z, where  $\lambda$  is the longitude,  $\theta$  is the latitude addition to 90°; z is directed vertically downwards;  $\kappa$ ,  $\mu$  are the coefficients of vertical and horizontal turbulent diffusion; a is the Earth mean radius; t is time;  $H(\lambda, \theta)$  is the bottom relief;  $\Gamma$  is the side surface of the region; n is the normal to the surface.

At the next stage, the distribution of gas hydrates and the depth of their deposition have been determined. 10 The zone of the hydrate formation is the rock mass, in which the temperature and the pressure correspond to thermodynamic conditions of the gas hydrate stable existence. The zone of hydrate formation can be determined mathematically by means of joint solution of the equation of thermal gradient variation in the rock section and the equation of stable equilibrium hydrate existence in the given porous medium. 11 It is supposed that methane hydrates are universally present in the sedimentary layer, where thermobaric conditions for their existence are fulfilled. These conditions are calculated by the formula<sup>12</sup>

$$\frac{1}{T_{\rm stab}} = 3.79 \cdot 10^{-3} - 2.83 \cdot 10^{-4} \log P_{\rm stab},$$

where  $T_{\rm stab}$  is the temperature of the gas hydrate stability, K;  $P_{\rm stab}$  is the pressure, MPa.

The curve of equilibrium conditions of methane hydrate formation is imposed on the line of natural distribution of temperatures and pressures in the analyzed area. The top and bottom boundaries of hydrate stability zone (HSZ) are determined by the cross points of these two lines.

The data on the distribution of the ocean methane hydrates evidence that their release to the surface of ocean bottom exists, but is quite rare. The direct drilling shows that, as a rule, methane hydrates occur in sedimentary layer at subbottom depths of about several hundreds of meters. Therefore, very important model parameter for estimation of the scale of the methane hydrate destabilization is the depth of hydrate occurrence in World Ocean deposits. The subbottom depth is determined taking into account the HSZ depth, geothermal gradient, depositary layer porosity, and the percentage of the sedimentary rocks, in the porous space of which gas hydrates occur. <sup>13</sup> In this article, the geothermal gradient is defined different for 22 regions<sup>10</sup>: from 30°C/km in the southern part of the Pacific Ocean to 87°C/km in its northern part. We take a simple exponential decrease of the porosity with the subbottom depth. Hydrate saturation of the deposits, i.e., the percentage of the porous space occupied by gas hydrates is taken as 50% of the porous space located right near the foot of the stability zone, which smoothly decreases to zero in the sea bottom direction.<sup>14</sup>

As a result, the methane hydrate deposition depth distribution from 20 to 400 m in the depositary layer beneath the ocean bottom was obtained.

## Numerical experiments

Based on the data on climate changes for the last 420 thousands of years<sup>4</sup> received from the analysis of ice cores from Antarctic and Greenland, four long-term climatic cycles were determined from the mean atmospheric temperatures. These cycles consist of warming and cooling periods alternating with intervals of 90-120 thousands of years. Fast warming, i.e., rather quick and almost monotonous increase of the mean atmospheric temperature for 10 thousands of years approximately by 10° and then non-monotonous decrease by the same magnitude during quite a long period (~70-100 thousands of years) (see Fig. 1) is typical for all four cycles. This refers to the periods 322-332, 233-348, 124-134 and 18-8 thousands of years to the present time, which in this work is taken as 1950. Each period was preceded by a long non-monotonous cooling, which was alternated by a shorter periods of warming by several degrees.

The temperature curve shows that the mean temperature during the whole period equal to 420 thousands of years was lower by 4-5° as compared to the present-day temperature.

Starting from an established climatic state of the World Ocean (see Fig. 2a), three scenario experiments were conducted.

"Cooling." The ocean surface temperature, seasonally changing in each point of the longitude-latitude grid, excluding areas covered with ice, decreases linearly during 5000 years with a rate of 1° per 1000 years. The negative temperature values are restricted to  $-2^{\circ}$ .

"Warming" starts after the previous "Cooling" experiment. In the same way the surface water temperature increases linearly during 10000 years with the same rate of  $1^{\circ}$  per 1000 years.

"Paleodata" is the ocean surface temperature, seasonally changing in each point of the longitude-latitude grid, excluding the areas covered with ice. The data on climate change, obtained from studies of ice cores for the last 8000 years (see Fig. 1), are evidences of the temperature variations.

The presence of ice is implicitly taken into account in the areas higher than 80°N and lower than 70°S at the cost of zero stresses of wind friction and permanent negative temperature of surface waters. It is assumed that in experiments with warming, the surface water temperature does not increase in the areas covered with ice, i.e., the ice does not melt.

In each experiment, the time till the beginning of methane hydrates destabilization is found; then it is determined, which part of the bottom contains methane hydrate sources; and the methane diffusion flux into the atmosphere is found.

Thermal signal is transported from the ocean surface deep into near-bottom layers by convective mixing and currents. Further, the increase of the sedimentary layer temperature in comparison with the initial climatic values<sup>9</sup> is modeled using the one-dimensional thermal conductivity equation. As soon as this increase exceeds some permitted  $\Delta T_H$  value,<sup>9</sup> at some subboottom depth, where methane hydrates reside, their decomposition is supposed to commence.

This decomposition maintains the dissolved methane near-bottom concentration, which is equal to 5000 ppb. It is assumed that the methane, released during the process of decomposition, is fully dissolved in the sea water. This value is further taken as a boundary condition (instead of the boundary condition with zero methane flux used in obtaining climatic data) in this point of the bottom in order to solve the methane transfer equation. Thus, the methane source participates in the model. Provided the further heat increment in the sedimentary layer becomes lower than the given  $\Delta T_H$ , it is assumed that the destabilization has stopped and the source is "turned off." In this case, the boundary condition for the methane transfer equation from a given value of 5000 ppb again changes to the zero methane flux.

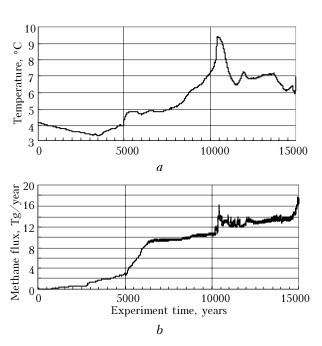
The methane flux through the ocean surface is calculated by the following formula:

$$F = a^2 q \iint_{\Omega} \left[ \kappa \frac{\partial C}{\partial z} \right]_{z=0} d\Omega,$$

where  $q = 0.7169 \cdot 10^{-3}$  is methane specific weight. The methane flux is  $10^{12}$  Tg. It is assumed that methane is completely dissolved in the sea water and methane bubbles do not reach the atmosphere.

## Results of numerical modeling

In the "Cooling" experiment, the mean ocean temperature changes monotonously during first 2900 years (Fig. 3) and then it changes non-monotonously during 2100 years; after 3670 years it even begins to increase.



**Fig. 3.** Ocean mean temperature change (a) and methane flux into the atmosphere from decomposed methane hydrates (b), obtained in "Cooling"+"Warming" experiments.

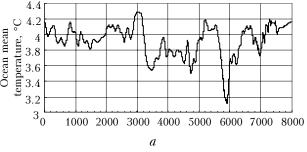
This can be explained by the involving of convective mixing of subtropical surface waters into the process. The temperature of these waters decreases by  $3-5^{\circ}$ . These warmer surface waters fill the deep-ocean part of the World Ocean due to deep convection, thus increasing the mean temperature. That is, the water temperature decreases only in the main thermocline as the result of cooling surface waters, while the temperature of intermediate levels and deep ocean increases (see Fig. 2b).

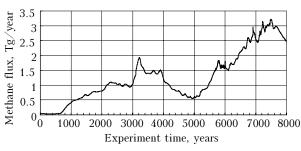
This process, in its turn, leads to subbottom destabilization of the methane hydrates. As is seen in Fig. 3, after the cooling period of approximately 2500 years, the methane flux into the atmosphere makes up 1 Tg/year and increases up to 4 Tg/year closer to the end of the experiment in 5000 years. The mean concentration of dissolved methane in the ocean increases about 14-fold and makes up 700 ppb.

The "Warming" experiment has found a significant warming of the whole ocean mass,

especially in high latitudes, where gas hydrate methane sources are concentrated. The temperature and the depth of the main thermocline increase. The temperature of the deep ocean changes negligibly (see Fig. 2c). As a result of this process the area of the ocean bottom, under which methane hydrates are destabilized, increase by 28%. This, in its turn, causes the increase of methane flux into the atmosphere up to 18 Tg/year (see Fig. 3b). The mean concentration of the dissolved methane increases up to 2050 ppb. During this process, methane sources at all depths are activated, thus increasing the methane concentration in all oceans.

Paloeclimate evidence show that climatic changes have a periodical character. Warmings alternate coolings and the periods of these oscillations vary from tens to thousands of years (see Fig. 1). Let us consider the reaction of the World Ocean climate model to oscillations of the ocean surface temperature at the secular scale. In the "Paleodata" experiment, ocean surface temperature variations were specified based on the climate change data, obtained from the analysis of ice cores for the last 8000 years (see Fig. 1). A significant difference of this experiment is in the rate of the warming and cooling of surface waters. As is seen in Fig. 4, the temperature variability of surface waters at the secular scale does not lead to serious methane hydrate destabilization. The methane flux changes negligibly making up 1-3 Tg/year.





**Fig. 4.** Ocean mean temperature variation (a) and methane flux from decomposed methane hydrates into the atmosphere (b), obtained in "Paleodata" experiment.

### Conclusion

The experiments conducted have shown that methane concentration change resulted from the destruction of a part of methane deposits can be both the cause and the effect of temperature variations.

Since the deep ocean temperature increases by more than  $1-2^{\circ}$  during the period of long-term cooling in 5000 years, this can lead to a significant heating of bottom layers and to mass destabilization of subbottom methane hydrates and, consequently, to methane emission in the atmosphere. Besides, due to decrease of the carbon dioxide solubility in warmer waters, the emission of the dissolved carbon dioxide, into the atmosphere can occur. The atmosphere warming, caused by such emission of the greenhouse gases can be one of the mechanisms, which blocks the ice age and returns the climatic state to the initial one. Long-term warming can lead to a more significant destabilization of methane hvdrates residing in the sedimentary layer of the World Ocean. The maximal obtained methane flux into the atmosphere is equal to 18 Tg/year.

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