Numerical modeling of methane hydrates dissociation in the submarine permafrost

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Abstract. In this study, we evaluate the sensitivity of gas hydrate reservoirs associated with submarine permafrost conditions to changes in global climate. We apply numerical simulations to assess the timings of methane hydrate dissociation on the East Siberian Arctic Shelf after flooding the shelf with the seawater. The modeling combines a model of submarine permafrost evolution with a model of methane hydrate dissociation that accounts for the consumption of latent heat during hydrate dissociation. Based on the analysis of the performed experiments, we found that the endothermic reaction is a significant mechanism for slowing hydrate dissociation in frozen sediments. As a result, it additionally increases the lag of the subsea permafrost and hydrates stability zone response to glacial cycles.

1. Introduction
Permafrost is widespread in the Arctic region, both in the continental region and in the vast areas of the shallow shelf of the Arctic seas [1-3]. A large amount of methane can be found in permafrost in a hydrated form [4]. Gas hydrates are crystalline ice-like compounds that form from gas molecules caged in a lattice of water molecules [5]. Methane hydrates are prevalent in the bottom sediments of seas and oceans and exist under stability conditions, which include: the presence of a sufficient amount of methane and water, as well as the required range of temperatures and pressures (thermobaric conditions) [6, 7]. Hydrates are formed at low temperatures and generally high pressures which are typical of relatively shallow depths in oceanic sediments or deeper frozen sediments in the Arctic [8-11]. Temperature increase [12-17] or pressure drop (sea-level drop, glacier collapse) [18-20] is effective enough to dissociate hydrate deposits, as a result, methane is released from the hydrate structure and may enter the atmosphere.

In the sediments of the shallow-water Arctic shelves, in the presence of submarine permafrost, there are thermobaric conditions for the hydrate formation in the methane hydrate stability zone (MHSZ) [4, 21, 22]. It is commonly believed that they formed during the Pleistocene glaciations when sea level was below the current value by up to 130 m. This exposed the shelf to very cold temperatures [1, 23]. Cycles of hydrate formation and dissociation could take place during geological time. For example, such movements of the hydrate-bearing zone are reported in the MacKenzie delta region [24, 25], in Mount Elbert [26]. Insufficient research has been done on the stability and formation of...
hydrates associated with relic submarine permafrost. Measurements in bores on the Alaska North Slope indicate that the conversion of common free gas accumulations to gas hydrate during climate cooling is the most likely mechanism for the formation of hydrate deposits in this region [9, 10].

To date, in the sediments of the shallow East Siberian Arctic Shelf, the MHSZ begins at depths of 200 - 250 m from the bottom according to the modeling results [1, 23]. With additional freezing of the sediment which occurred during ice ages, the conditions for the methane hydrates formation were met at depths of the order of several tens of meters [1, 23]. In the future, part of the gas hydrates could be retained due to the manifestation of the self-preservation effect at negative temperatures of the ground. The presence of methane hydrates in the upper layers of permafrost under non-equilibrium conditions is considered one of the possible reasons for constant gas manifestations during the operation of wells in gas fields. The thawing subsea permafrost and the destabilization of methane hydrates on the Arctic shelf could lead to emitting large quantities of methane. Significant point emissions have been detected along the East Siberian Arctic Shelf [27, 28].

In [21] it is shown that in the shallow shelf areas (lower 50 m water depth) after flooding (10-5 kyr ago), the hydrate presence conditions in the upper 100 - meter layer of the MHSZ are violated. This suggests that the methane coming from this reservoir is concentrated in the bottom sediments of the shelf. However, in [21] phase transitions of methane hydrates are not considered in the model. This approach neglects the endothermic reaction of hydrate dissociation, which is an important dynamic process that decreases the rate of dissociation [29]. The latent heat of fusion for methane hydrates is 28% larger than for pure water [30]. Based on analysis [29], the endothermic reaction is the dominant mechanism-slowing dissociation in sediments.

We study the permafrost and methane hydrate stability zone evolution in the Laptev Sea region using a numerical model to illustrate how changes in the environment affected hydrate stability. The purpose of the study is to analyze the state of a gas hydrate reservoir formed in shallow permafrost sediment and subsequently found to be in non-equilibrium conditions. We use an approach in which the conditions of stability of methane hydrate are determined, and, in the event of their violation, the degradation of the gas hydrate reservoir is modeled taking into account heat consumption.

2. Model Setup

To study the formation processes of the submarine permafrost and associated methane hydrates, we use a model of the dynamics of permafrost for the last 400 thousand years [23]. The model solves the one-dimensional equation for heat and salt diffusion in the sediment column taking into account phase changes [31]. The distribution of thermal conductivity and heat capacity of the frozen and thawed rocks with depth remains constant during the simulation of the permafrost evolution. Thermal conductivity and heat capacity correspond to the values in the region sedimentary basin [19].

The upper boundary condition is the temporally varying sediment surface temperature. The model of thermophysical processes in bottom sediments is supplemented by the scenario of a climate change on the East Siberian Arctic Shelf for the last 400 thousand years [23]. We used the output of the simulation with an Earth system model of intermediate complexity model CLIMBER-2 forced by time-varying orbital parameters and atmospheric CO₂ content [32]. Sea level is directly simulated by this model. The data for a grid cell, which corresponding to the Laptev Sea shelf is selected. When a shelf is exposed to the atmosphere, this temperature is calculated as a sum of the present-day annual mean surface ground temperature at the nearshore and is a time-varying anomaly by CLIMBER-2. It is assumed that after the flooding of the shelf by the sea, the seawater temperature does not significantly differ from that of today, corresponds to the average annual values for the shelf seas. We assume a seafloor temperature ~1.2 °C after the flooding of the shelf [2]. The changes in average monthly surface temperature for the last 400 thousand years were assumed as the upper boundary conditions, figure 1A.

The lower boundary condition is a constant heat flow 60mWm⁻² which is estimated as typical at the Eurasian shelf out of the rift zones [33]. It is believed that the vertical component of the model domain
is large enough so that submarine permafrost does not form here throughout the entire estimated time and it extends to 1500 m.

Figure 1. (A) Temperature at the upper boundary of the sea sediments, which are used to force our model for the contemporary shelf depth 10 m. (B) Submarine permafrost evolution (shaded area based) and gas hydrates stability zone (marked in blue) variations in the last 400 ka according to the sediment surface temperature history.

We have combined two numerical models: a model of permafrost dynamics based on the paleoclimatic scenario of changes in temperature and ocean level, and a model of the methane hydrates stability zone. The MHSZ thickness was calculated simultaneously with the sediment temperature as a function of time. The dissociation pressure and temperature of hydrates at depth are obtained from the hydrate model [34].

\[
\ln(P_H) = \sum_{n=0}^{s} a_n (T + T_D)^n
\]

where \(P_H\) is the phase equilibrium pressure (MPa), \(T\) is the sediment temperature (K), \(T_D\) is the salt-induced temperature depression (K) and \(a_n\) are empirical constants for the unfrozen and frozen layers. This shift in the equilibrium temperature can be solved as follows [35]: \(T_D = 0.6825T_F\). This temperature depression depends on the freezing pore water temperature \(T_F\) in °C and is incorporated into the pressure-temperature equilibrium relationship for the methane–hydrate system (1). Methane is assumed to be the only gas component in the system so that all values apply to pure methane hydrate.

The works [20, 21, 29] assume that the subsurface pressure regime is hydrostatic at any time. This condition is not evident in permafrost when sediment freeze during ice ages. Most pores are filled with ice, likely generating pore pressures above the hydrostatic [36]. The configuration of MHSZ strongly depends on the ground temperature and pressure. In this case, the depth of the base of the MHSZ would be deeper and the depth of the top would be less than in the hydrostatic case [21]. Based on these considerations, we assumed the phase curves of methane hydrate under the corresponding
lithostatic ground pressure [22]. The ground pressure was calculated as hydrostatic for the thawed layer and as geostatic for the frozen. Variations because of sea-level changes are supposed to propagate instantaneously throughout the sediment column.

Gas hydrate reservoirs of the Arctic shelves are believed originally to be natural gas accumulations converted to hydrate after being placed in the gas hydrate stability zone in response to ancient climate cooling [37]. In numerical experiments, we assume that a gas column accumulates and subsequently is converted to hydrate in sub-permafrost formations in the upper part of the MHSZ.

One of the most important parameters in modeling the dissociation of gas hydrates is the heat of hydrate formation (or enthalpy of dissociation) [6]. It is equal to the amount of heat that is needed to decompose the hydrate into water and gas. The experimentally obtained values for the heat of phase transition of hydrates are in the range of 430–540 kJ/kg [38]. During hydrate formation, heat is released and the enthalpy is positive; during hydrate decomposition, it is negative. This process is considered in the model using the approach [20].

If the conditions for the stability of the hydrate are violated, the calculated temperature of the sediment at the point at which methane hydrate dissociation occurs is corrected by taking into account the latent heat of dissociation of gas hydrate. At the depth where hydrate exists (hydrate saturation \( S_H > 0 \)), the temperature is corrected to \( T_{DIS} \) (temperature of the onset of dissociation). At depth where the phase transition occurs, the amount of heat \( dQ \) per time step equal to:

\[
dQ = C \cdot dT
\]

\( dQ \) is then added to the heat that has accumulated \( (Q_A) \) over previous time steps since the start of the phase transition. The equation applies to a unit mass of hydrate, \( C \) - denoting the isobaric heat capacity of this phase. The hydrate dissociates completely if the accumulated heat exceeds the latent heat of the gas hydrate \( L_H \). The response of the hydrate saturation to the accumulation of heat upon melting is approximated as follows:

\[
S_H(t) = S_H(t-1) \cdot \frac{L_H - Q_A}{L_H}
\]

where \( S_H(t) \) represents the hydrate saturation at time \( t \), the latent heat of melting gas hydrate \( L_H \) is 430 kJ/kg [20]. The hydrate saturation decrease as heat accumulates and eventually turns zero once the accumulated heat equals \( L_H \).

3. Results

Numerical experiments were performed for the Laptev Sea shelf with a water depth of 10 m. The following numerical experiments were carried out:

- SH0 - The methane hydrate stability simulation was performed without hydrates in the sediment [21], \( S_H = 0\% \).
- SH20 – We assume that the formation of a gas hydrate reservoir in the upper part of the MHSZ occurs during the period of maximum freezing of sediments in the last glacial (20 kyrs ago). Initially, \( S_H = 20\% \). The decomposition of the hydrate occurs with the consumption of heat.
- SH40 - Similar to SH20, but initially period \( S_H = 40\% \).

3.1 HS0

The model results illustrate the evolution of the permafrost and MHSZ over the past 400 thousand years (kyrs), figure 1. For the shallow shelf, the periods of ocean flooding are relatively short and the permafrost does not disappear in the interglacial period. During oceanic regressions, the depth of the lower permafrost boundary, depending on the glacial cycle, ranges from 540 to 680 m, figure 1B. Methane hydrate can occur within sediment columns across a depth interval of the hydrate stability zone. The subsurface temperature and pressure regime control the stability of the MHSZ. Modeling of MHSZ response to the changing seafloor temperature and the increasing sea level on the Laptev Sea shelf is shown in figure 1B. When the permafrost thickness reaches about 250 m, the formation of the
MHSZ begins. Like the permafrost, the MHSZ does not disappear during the periods of marine transgressions, and its thickness changes insignificantly.

The key obtained result is the depth of the upper boundary of the gas hydrate as it varies with time. Figure 2 shows the stability curve of the equilibrium phase methane hydrate as a function of water depth and its intersection with model temperature profiles obtained for different times. The modeling MHSZ top in the last glacial, 20 kyr ago, is 103 m below seafloor (figure 2, point 1). The model predicts that the methane hydrates in the upper 60 m of MHSZ dissociated completely within ten millennia after the last glacial (figure 2, point 2). The Holocene sea level rise is modeled with a 10-meter sharp rise that occurred 5 kyr ago (figure 2, point 2). In the initial period of the transgression (with a corresponding increase in pressure on the bottom), the MHSZ increases over several centuries (figure 2, figure 3A). Subsequently, an increase in temperature in bottom sediments led to a reduction in the zone of stability of gas hydrates and shifted the MHSZ top boundary. The effects of seabed warming are more important and lasting for the shallow shelf than the pressure effects accompanying sea level rise. The current model MHSZ top for water depth 10 m is at 229 m below seafloor (figure 2, point 4).

![Figure 2. Sediment temperature profiles obtained in numerical experiment HS0 corresponding periods: 20 kyr ago (dark blue line TS_20kyr), 10 kyr ago (TS_10kyr), 5 kyr ago (TS_5kyr), and industrial period (TS_0kyr). Methane hydrate P-T stability (Tstab) in subaerial conditions. P-T stability of methane hydrate (Tstab10m) assuming a water depth equal to 10 m after the flooding of the shelf. The depth migration of the top of the MHSZ responding to temperature variations is marked by points 1, 2, 3, 4.](image)

3.2 HS20

In SH20, the dissociation of gas hydrate begins when the temperature and pressure conditions are violated and occurs with heat absorption (figure 3). Within the hydrate stability zone, the hydrate saturation in matrix porosity was inferred to be 20%. A change in the hydrate saturation (2) over the calculation period of 20 thousand years is shown in figure 3A. Dissociation takes place at the upper boundary of the deposit, which gradually deepens. Hydrate dissociation slows down under the conditions of permafrost transition to subsea conditions (5ka ago). A methane-hydrate reservoir with a saturation of 20% in a 1 m-thick layer decomposes in about 100 years, figure 3B. Dissociation rates for the HS20 model run are significantly slower than the HS0 approach. Comparing the HS0 and HS20 simulations, the time for complete dissociation is increased by an average of 20% (figure 3A).
Figure 3. Time variation of the hydrate saturation of bottom sediments during the decomposition of hydrate deposits obtained in HS20. (A) Results for a period of 20 thousand years. The blue line is the depth of the upper boundary of the MHSZ, corresponding to the HS0 experiment. (B) Results for the last 500 years.

There are differences between HS0 and HS20 in terms of both dissociation rate and sediment temperature. The difference arises from the endothermic dissociation reaction. Sediments near the hydrate degradation front are cooled. Estimates of present-day sediment temperature differ substantially between the HS0 approach and HS20 simulation (figure 4). With the transition of permafrost grounds to the submarine state, the sediment temperature rises and becomes higher than minus 2 °C. Under the influence of hydrate decomposition, this process slows down. And near the front of the hydrate decomposition lower temperatures of -3…-4 °C are preserved. The heat of decomposition of the hydrate in HS20 is assumed to be 430 kJ / kg, higher than the heat of melting of ice, which is 320 kJ / kg. The absorption of heat from the formation during the destruction of the hydrate reservoir reduces the heat flux from the lower layers. Such thermal effects can affect the thickness of the permafrost layer, as well as lead to the formation of new permafrost during the destabilization of gas hydrates. Similar areas of submarine permafrost were found on the outer shelf of the Kara Sea in sediment [39].

The evolution of permafrost and MHSZ under the impact of climate change and transgression–regression cycles on the shelf is characterized by a time lag [1, 23]. Malakhova and Eliseev (2020) estimated apparent response time scales via time lags between the temperature at the upper boundary of the sediments, and MHSZ thickness [23]. Apparent response time scales for MHSZ thickness are relatively small for the shallow shelf, from 4 to 5.4 kyr. However, these works used an approach similar to HS0, without implementation of phase transitions of methane hydrates in the model. For the last 5 kyr, the additional lag can be from 250 to 2100 years, depending on time interval.
Figure 4. Sediment temperature profiles obtained in numerical experiments HS0 (blue line), HS20 (red line), and HS40 (green line) for the modern climatic conditions.

3.3 HS40

The hydrate saturation used in the simulation is entirely conjectural, given the general lack of high-quality seismic lines and the absence of scientific boreholes. The maximum saturation found in part of the Mallik well section [24] is 60%. To illustrate how the modeling is sensitive to hydrate saturation, an alternative level, 40%, was considered. In SH40, within the hydrate stability zone, the hydrate saturation in matrix porosity was inferred to be 40%. MHSZ top boundary migrates downward faster when the saturation is lower (HS20) due to the smaller latent heat released during less saturated hydrate formation. The present-day modeled MHSZ top is at 216 m below seafloor, 6 m higher than in the model with lower saturation (HS20). Due to the assumed 40% hydrate saturation of the pore space during the hydrate decomposition, the sediment temperature decreases, and as it cools, permafrost may form (figure 4). For the last 5 kyr, the additional lag increases by 30-40% and can reach 2900 years.

4. Conclusion

We present an assessment of changes in the gas hydrates stability zone of the Arctic Ocean associated with subsea permafrost conditions. The calculations have been carried out for the interval ranging from 400 kyr ago up to the present. In this study, we evaluate the sensitivity of gas hydrate reservoirs associated with submarine permafrost conditions to changes in global climate during successive glacial-interglacial cycles. Based on the analysis of the performed experiments, we found that the endothermic reaction is a significant mechanism for slowing hydrate dissociation in frozen sediments. Hydrate decomposition is an endothermic process in which heat is absorbed and the nearby sedimentary layer is cooled. The degradation of hydrates in bottom sediments occurs due to the accumulated heat in the sediments since the heat flux from the surrounding rocks is insignificant. As a result, heat sink occurs, which slows down the propagation of the temperature impulse through the sedimentary column, and reduces the rate of melting of permafrost and methane hydrate deposits in the bottom sediments of the Arctic shelf. The process of degradation of gas hydrate deposits leads to heat absorption, thereby causing the development of frozen rocks.

We found that implementation of phase transitions of methane hydrates in the model delays the subsea permafrost thaw and the MHSZ disappearance during interglacials. As a result, it additionally...
increases the lag of the subsea permafrost and MHSZ response to glacial cycles. Methane hydrate dissociation occurs even more slowly because the reaction is not only endothermic, it also decreases pore water salinity, and increases the local pore pressure. These effects were not considered in our study. It supports the view that the current changes in the thermal state of the subsea permafrost may be related to the adjustments to the last glacial cycle termination rather than to the contemporary, century-scale climate warming. The process of methane hydrates degradation in the subsea permafrost of the shallow Arctic shelf, which began after the Last Glacial Maximum, is one of the possible reasons for increased methane fluxes in this region [27, 28].

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