# Simulation of atmospheric methane distribution after releasing methane caused by plausible destabilization of methane hydrates\*

A.I. Krylova, V.N. Krupchatnikoff

Methane possesses the radiative efficiency higher than that of carbon dioxide. To estimate the potential impact of the change in the global distribution of methane concentration – due to CH<sub>4</sub> emission from marine sediments of the continental shelf – on climate, scenario calculations were carried out.

### 1. Introduction

It is well known [1], when pressures are reasonably high, cooling water molecules will begin to form solid structures at temperatures above the normal freezing point. Unlike ice, these structures are characterized by regular networks of large, open cavities and are therefore unstable. As cooling continues, a normally compact and stable ice structure will ultimately form, unless some outside molecule of an appropriate size enters the structure and fills the cavity. In nature, the most abundant molecule is methane (CH<sub>4</sub>). The resulting stable, solid compound is commonly called "methane hydrate". Naturally occurring gas hydrates are more appropriately formed within a special class of compounds called clathrates One of the most common host molecules is water, and the water-based clathrates are commonly referred to as "hydrates". Gas hydrates have guest molecules that exist in the gas phase at standard temperature and pressure. The most common is methane (methane hydrate), but many gases, including carbon dioxide, hydrogen sulfide, and larger hydrocarbons such as ethane and propane, can stabilize water lattices and form a "hydrate". When only very small molecules are present (hydrogen or helium, for example), no hydrate will form because the available guests are not large enough to support, or be trapped in, the cavities. Clathrates are compounds that consist of an inherently unstable network of host molecules characterized by regular open cavities. Guest molecules of appropriate size fill the cavities without bonding - they are

<sup>\*</sup>Supported by the Russian Foundation for Basic Research under Grants 00-05-65449, 01-05-65420 and Integration Project № 76 SB RAS.

held in place by Van der Waals forces. When a sufficient number of cavities are occupied, a stable solid structure is formed. Our current understanding of natural methane hydrate indicates that the principal control over the hydrate formation and stability is presented as follows: (1) adequate supplies of water and methane, (2) suitable temperatures and pressures, and (3) geochemical conditions.

## 2. Background and review of previous studies

Natural methane sources on the Earth's surface are known and well studied. However, these sources are not likely to release a great amount of methane into the atmosphere within a short period of time so that they might considerably affect the climate. Some recent studies suggest that these sources could be methane hydrates. Deposits of methane hydrates kept a great amount of methane nearby the Earth's surface. Methane is more potent greenhouse gas than CO2, although shorter-lived. Gas hydrates may contain three orders of magnitude more methane than there exists in today's atmosphere. Since the hydrate breakdown, causing release to the atmosphere, can respond to a global temperature increase, gas hydrates may play a significant role in the global climate change. Methane is formed in two ways. First, biogenic methane is a common by-product of bacterial ingestion of organic matter. The same process that produces methane in swamps, landfills, rice paddies, and the digestive tracts of mammals occurs continually within buried sediments in geologic media all around the globe. Biogenic processes are capable of producing vast amounts of methane, and are considered to be the primary source of the methane trapped in hydrate layers within the shallow sea floor sediments. Second, thermogenic methane is produced by the combined action of heat, pressure and time on a buried organic material. Over time and with a deep burial, these organic-rich sources are formed under pressure with the output being the production of large quantities of oil and natural gas. Along with oil, methane slowly migrates upwards due to its buoyancy relative to water. If sufficient quantities reach a hydrate stability zone, the gas will combine with local water to form hydrate. Given appropriate pressure and temperature conditions, hydrates will only form given adequate supplies of water and sufficient methane such that a necessary minimal percentage (70% or more) of the structural cavities within the hydrate lattice are filled. The presence of water is generally not a concern, as water saturates the vast majority of the sediments on the earth's surface. However, the supply of methane (including volumes and rates of methane production and migration) is not ensured. Given adequate supplies of water and methane, Figure 1 shows the combination of temperatures and pressures (the phase boundary) that marks the transition from a system of co-existing free methane gas and water/ice solid methane hydrate.

When conditions move to the left across the boundary, hydrate formation will occur. Moving to the right across the boundary results in the dissociation (related to melting) of the hydrate structure and the release of free water and methane. In general, a combination of low temperature and high pressure is needed to support methane hydrate formation. In addition to temperature and pressure, the composition of both water and gas are critically important when fine-tuning predictions of the stability of gas hydrates in specific settings. Experimental data collected thus far have included both fresh water and seawater. However, natural subsurface structures exhibit significant variations in the formation water chemistry, and these changes shift the pressure/temperature phase

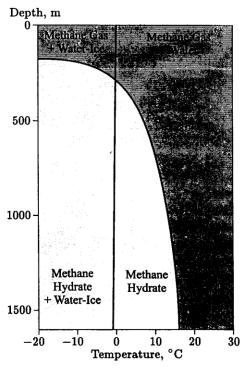


Figure 1. Methane hydrate phases

boundary (higher salinity restricts hydrate formation causing the phase boundary to shift to the left). Similarly, the presence of small amounts of other natural gases, such as carbon dioxide (CO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S) and larger hydrocarbons such as ethane (C2H6), will increase the stability of the hydrate, shifting the curve to the right. Commonly, methane hydrate phase diagrams are presented with pressure being converted to depth to place the diagram in the geologic dynamics. In addition, the natural geothermal gradient is shown to indicate the range of temperatures expected to exist as depth (i.e., pressure) increases. The range of depths in which the temperature gradient curve is to the left of the phase boundary indicates to the Gas Hydrate Stability Zone (GHSZ). This zone only delineates where hydrates will be stable if they form. Local conditions, in particular, availability and rate of supply of methane, will determine where hydrates will actually occur within the GHSZ. The phase diagram in Figure 2 illustrates typical conditions in a region of arctic permafrost (with depth of permafrost assumed to be 600 meters). The overlap of the phase boundary and temperature gradient indicates that the GHSZ should extend from a depth of approximately 200 meters to slightly more than 1,000 meters. (Note that both the permafrost thickness and pressure/temperature gradients in the chart are examples and can vary with locality, so specially-tailored diagrams should be made before site-specific predictions of hydrate stability can be attempted.)

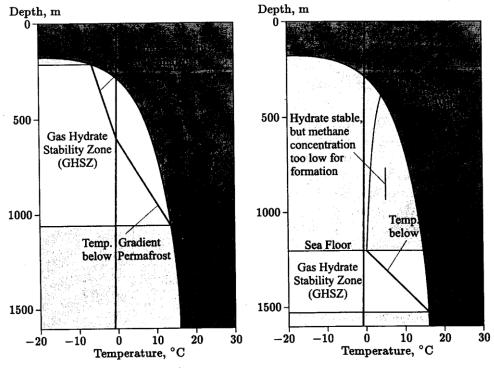


Figure 2. Hydrate stability for the Arctic permafrost

Figure 3. Gas Hydrate Stability Zone on deep water continental margins

The phase diagram in Figure 3 shows a typical situation on deep continental shelves. A seafloor depth of 1,200 meters is assumed. Temperature steadily decreases with water depth, reaching a minimum value near 0°C at the ocean bottom. Below the sea floor, temperatures steadily increase. In this setting, the top of the GHSZ occurs at roughly 400 meters - the base of the GHSZ is at 1,500 meters. Note, however, that hydrates will only accumulate in the sediments, which restrict them from floating up (they are less dense than water) and out of the stability zone. From the phase diagram in Figure 3 for oceanic settings, it would appear that hydrates should accumulate anywhere in the ocean-bottom sediments where water depth exceeds ≈ 400 meters. However, very deep (abyssal) sediments are generally not thought to house hydrates in large quantities. The reason is that deep oceans lack both the high biologic productivity (necessary to produce the organic matter that is converted to methane) and rapid sedimentation rates (necessary to bury the organic matter) that support hydrate formation on the continental shelves. Hydrates are not found in interior basins at subpolar latitudes. At every depth (pressure), subsurface temperatures are too high for methane hydrate to be stable. Methane hydrate can form in rocks or sediments of any type given suitable pressures, temperatures, and supplies of water and methane. In general, there are two primary geologic/geographic environments for hydrate accumulation: 1) areas with deep water in close proximity to land, and 2) continents in polar regions. Deep-water settings can be further classified as: 1) inland deep-water seas and lakes, 2) stable passive continental margins, 3) unstable passive continental margins, and 4) active tectonic boundaries.

# 3. Simulation spatial distribution of methane and estimates of methane-hydrate stores

Estimates of the total volume of methane in natural gas hydrate have ranged widely, from roughly 3,000 trillion cubic meters (Tcm) to as much as 8,000,000 Tcm. In recent years, as more information is gained and real data slowly replace the best guesses, estimates have tended to fall in a narrower range – from 3,000 to 30,000 Tcm. All current estimates of methane content in hydrates are primarily based on data indicating to the location and potential thickness of the Gas Hydrate Stability Zone (GHSZ). Critical data, such as concentrations within the GHSZ, should be extrapolated from detailed analyses that have thus far only been accomplished at a few localities. As more sites are studied in detail, the new data may bring about further significant refinement of these numbers. Methane is rather stable in the aggregative state [1]. However, if for some reasons this amount of methane emits into the atmosphere and is held there for dozens of years, then in this case a pronounced climatic change may be expected.

As noted before, methane as greenhouse gas has a radiative efficiency higher than that of carbon dioxide. To estimate the potential impact of the change in the global distribution of methane concentration - due to CH<sub>4</sub> emission from marine sediments of the continental shelf - on climate, scenario calculations were carried out. In the experiment, methane hydrates, which are widely spread in marine sediments of the World's ocean offshore zone and in permafrost regions, have been considered (Figure 4). The data on the gas hydrate locations were obtained from numerical data of the distribution of the organic carbon concentration in the ocean [2]. As methane flux estimation the following value has been taken. According to the estimates derived from [3, 4] the amount of methane in gas hydrates of an oceanic margin setting is approximately  $11 \times 10^{12}$  kg, and the area of the corresponding gas hydrates according to our estimates was  $25.6 \times 10^{12}$  m<sup>2</sup>. Then, the methane flux is calculated as  $W \approx 1.5 \times 10^{-2}$  g/(m<sup>2</sup>s). If one considers methane hydrates as sources of power W, acting within one year period, then the experiments have shown that this would lead to an increase of the atmospheric CH<sub>4</sub> concentration by the factor of 10<sup>6</sup>. To perform a more realistic experiment on the CH<sub>4</sub> emission from gas hydrates, the estimates obtained

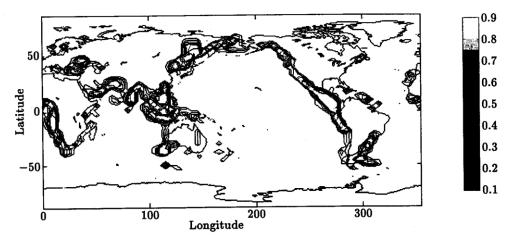


Figure 4. Distribution of known methane hydrate in marine sediments of the World's ocean offshore zone and in permafrost regions (in fractions of one)

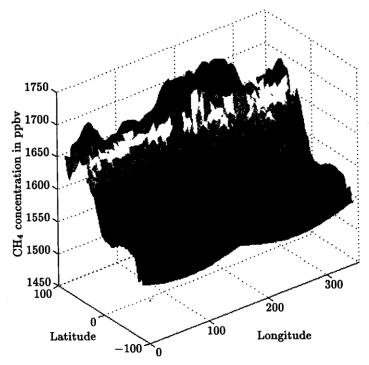


Figure 5. The simulated background atmospheric CH<sub>4</sub> concentration at the level of 1,000 mb (a reference experiment)

in [2] have been used, and there has been introduced the so-called availability coefficient for methane hydrates decomposition at  $1-2^{\circ}$ C increase of the mean annual temperature, which reflects realistic climatic changes over 100 years.

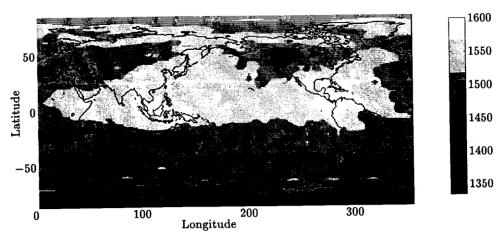


Figure 6. The simulated background atmospheric CH<sub>4</sub> concentration at the level of 500 mb (a reference experiment)

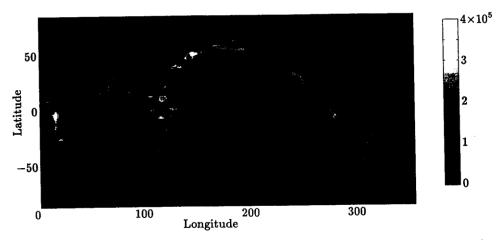


Figure 7. The difference between the CH<sub>4</sub> concentration obtained with destabilization of gas hydrates and the concentration obtained in the reference experiment (at the level of 1,000 mb)

In Figures 5 and 6, there are presented the results of the simulation of the background atmospheric CH<sub>4</sub> concentration at levels of 1000 and 500 mb. In this experiment, the contribution to methane fluxes from the gas hydrate decomposition is no more than 1% per year (according to the present-day estimates [5]) of the annual CH<sub>4</sub> emission into the atmosphere from all methane sources (a reference experiment).

In Figures 7 and 8, there are shown the difference between the CH<sub>4</sub> concentration obtained with the destabilization of gas hydrates with the power release of  $500 \times 10^{12}$  g/yr at levels of 1000 and 500 mb and the concentration obtained in the reference experiment.

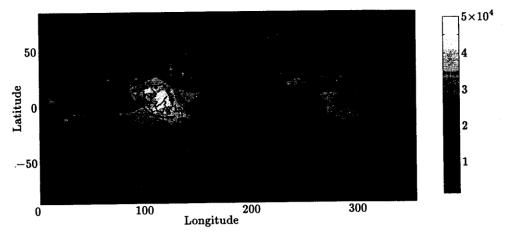


Figure 8. The difference between the CH<sub>4</sub> concentration obtained with destabilization of gas hydrates and the concentration obtained in the reference experiment (at the level of 500 mb)

## 4. Conclusion

All current estimates of the methane emission from hydrates are primarily based on the data indicating to the location and potential thickness of the Gas Hydrate Stability Zone (GHSZ). Critical data, such as concentrations within the GHSZ, should be extracted from detailed analyses that have thus far only been accomplished at a few localities.

### References

- A Strategy for Methane Hydrates Research and Development. U.S. Department of Energy Office of Fossil Energy Washington, DC, August, 1998.
- [2] Gornitz V., Fung I., Potential distribution of methane hydrates in the world's oceans // J. Geophys. Res. - 1994. - Vol. 99. - P. 335-347.
- [3] Trofimuk A.A., Chersky N.V., Tsaryov V.P. The role of continental glaciation and hydrate formation on petroleum occurrence // The Future Supply of Nature-Made Petroleum and Gas / Edited by R.F. Meyer. New York: Pergamon, 1977. P. 916–926,
- [4] Kvenvolden K.A., Methane hydrates and global climate // Global Biogeochem.
  Cycles. 1988. Vol. 2. P. 221-229.
- [5] Fung I., John J., Lerner J., Matthews E., Pratner M., Steele L.P., Fraser P.J. 3-dimensional model synthesis of the global methane cycle // J. Geophys. Res. – 1991. – Vol. 96, № D7. – P. 13033–13065.