

METHANE HYDRATES AND GLOBAL CLIMATE

Keith A. Kvenvolden

U. S. Geological Survey,
Menlo Park, California

Abstract. Methane hydrates are globally widespread in permafrost regions and beneath the sea in sediment of outer continental margins. The amount of methane sequestered in gas hydrates is probably enormous, but estimates of the amounts are speculative and range over three orders of magnitude (about 10^3 to 10^6 GT (gigatons = 10^{15} g)). A question of current interest concerns the possible consequences of an addition of methane to the atmosphere from destabilized methane hydrates due to global warming. Models of greenhouse warming predict that climatic change will be greatest in the Arctic. Thus, if methane from destabilized gas hydrates contributes to greenhouse warming, this destabilization will most likely take place first in the Arctic, particularly in the shallow nearshore regions of the Arctic Ocean where offshore permafrost is found. The process of permafrost warming and release of methane from gas hydrates may already be in progress, but the amount being released now and to be released in the 21st century is probably small. The positive feedback of this atmospheric methane on global climates will likely be minimal.

INTRODUCTION

Large amounts of natural gas, composed mainly of methane, can occur in sediment in the form of gas hydrates. These substances are solids, composed of rigid cages of water molecules that trap molecules of gas. Sediment containing gas hydrates is found within certain pressure-temperature conditions that occur in permafrost

This paper is not subject to U.S. copyright. Published in 1988 by the American Geophysical Union.

Paper number 8J0200.

regions and beneath the sea in continental margins. Because gas hydrates are so widespread and because methane is essentially concentrated within the gas hydrate structure, the potential amount of methane present on the Earth as methane hydrates is enormous. This report re-examines the possible consequences of the addition of this methane to the atmosphere due to global warming.

FORMATION OF GAS HYDRATES

In gas hydrates, water crystallizes in the cubic crystallographic system, forming structure I or II geometries, depending on gas compositions; the crystallography of gas hydrates was reviewed by Davidson [1973]. Of the two geometries, structure I is the more important; only structure I gas hydrates are expected in nature, unless the gas is rich in propane and isobutane relative to methane [Davidson et al., 1978]. Because this report is concerned with methane and methane hydrates, only structure I is considered. At standard conditions (STP), one volume of structure I methane hydrate may contain as much as about 164 volumes of methane gas [Davidson et al., 1978]. Methane is essentially concentrated within the solid framework of water molecules in gas hydrates.

The pressure-temperature conditions under which gas hydrates form were established by Katz et al. [1959]. These conditions for the formation of structure I methane hydrate in a pure water system are illustrated in Figure 1, which shows that higher pressures enable gas hydrates to form at correspondingly higher temperatures, and impurities in the methane and water affect the pressure and temperature at which the gas hydrates form. Nevertheless, the pure methane and pure water system provides a reasonable approximation for establishing the depth-temperature relation of naturally occurring gas hydrates [Claypool and Kaplan, 1974].

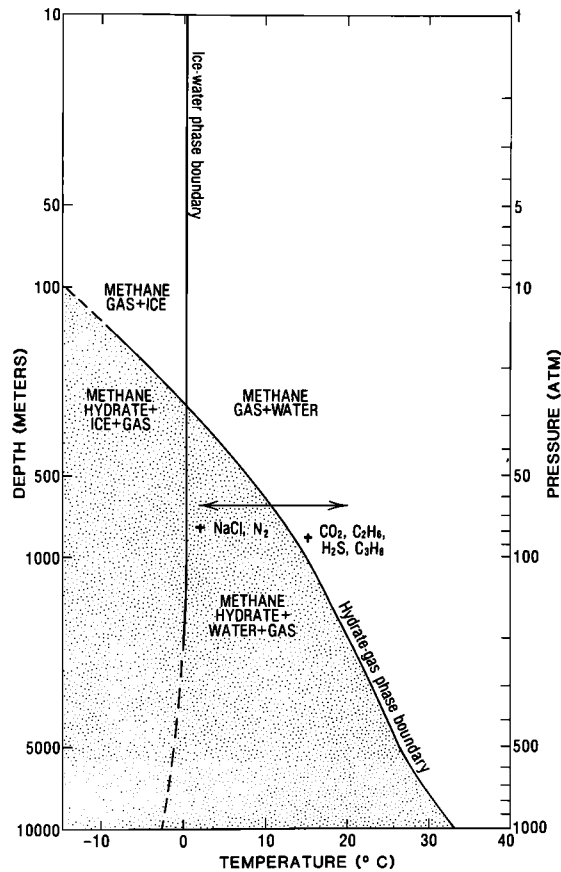


Fig. 1. Phase diagram showing boundary between free methane gas (no stippling) and methane hydrate (stippling) for a pure water and pure methane system. Addition of NaCl to water shifts the hydrate-gas phase boundary to the left. Adding CO_2 , H_2S , ethane, and propane to methane shifts that boundary to the right, increasing the region of the gas hydrate stability field. For natural gas composed mainly of methane, the effects approximately cancel each other [Claypool and Kaplan, 1974]. Depth scale assumes lithostatic and hydrostatic gradients of 0.1 atmospheres per meter. Redrawn after Katz et al. [1959] and modified from Kvenvolden and McMenamin [1980].

If geothermal gradients are superimposed on the methane hydrate equilibrium phase diagram (Figure 1), the depth limits of gas hydrates can be estimated. The following arbitrary examples illustrate the limits of gas hydrates in permafrost and offshore regions. Figure 2a shows the depth limits of methane hydrate where permafrost is 600 m thick. The geothermal gradient of $18^\circ\text{C}/\text{km}$ within the permafrost increases at the base of the permafrost to $27^\circ\text{C}/\text{km}$, owing to the higher thermal conductivities of frozen in comparison to unfrozen sediment. The diagram shows that methane hydrates may occur within the permafrost between depths of 200 and 600 m and below the permafrost between depths of 600 and 1,000 m. Figure 2b shows the depth limits for gas hydrates in an offshore

region where the water depth is 1,200 m, the geothermal gradient is $50^\circ\text{C}/\text{km}$, and bottom water temperature is 1°C . In this situation, methane hydrate may occur at sub-bottom depths between 0 and 250 m.

The source of methane for gas hydrate formation may be either biogenic or thermogenic. Biogenic methane results from the microbial breakdown of organic matter in shallow sediment and thermogenic methane from the thermal alteration of organic matter in sediment at depth. Because gas hydrates occur in shallow sediment, biogenic sources are commonly implied, especially for gas hydrates in outer continental margins [Kvenvolden and Barnard, 1983]. Where gas migration pathways are available from deep within the sedimentary section, thermogenic gas may also form hydrates, as in the Gulf of Mexico [Brooks et al., 1984].

IDENTIFICATION AND DISTRIBUTION OF GAS HYDRATES

Natural gas hydrates have been identified by direct observation, by pressure core barrel measurements, by interpretation of well logs, and by seismic reflection methods, particularly for gas hydrates in oceanic sediment. Figure 3 shows the locations of known or inferred gas hydrates around the world. On land, the suspected or confirmed gas hydrates are associated within or beneath permafrost, whereas most of the gas hydrates offshore are inferred on the basis of marine seismic surveys; however, in sediment offshore from Mexico, Guatemala, Peru, and the southern and southeastern United States, and in sediment of the Black Sea, gas hydrates have actually been recovered in cores.

Permafrost Regions

During the 1940s, the pressure and temperature conditions beneath permafrost regions were recognized as appropriate for gas hydrate occurrence [Katz, 1971]. By 1970, well logging and formation tests in the Messoyakha gas field of western Siberia conclusively showed the presence of gas hydrates [Makogon et al., 1972]; in fact, this was the first gas hydrate field to be produced commercially. Besides the western Siberian platform, where the Messoyakha gas field is located, other permafrost areas of the northern U.S.S.R., including the Timan-Pechora province, the eastern Siberia craton, and the northeastern U.S.S.R. and Kamchatka areas, are believed to have gas hydrate deposits [Cherskiy et al., 1985]. The occurrences of permafrost-associated gas hydrates in the North American Arctic have been reviewed by K. A. Kvenvolden and A. Grantz (Decade of North American geology, unpublished data, 1987). Well log responses, consistent with the presence of gas hydrates, were obtained in the Mackenzie Delta [Bily and Dick, 1974; Judge, 1982], Sverdrup Basin, Arctic Platform and Arctic Islands [Davidson et al., 1978; Judge, 1982], and North Slope of Alaska [Collett, 1983].

The combined information from studies of gas hydrates in the northern U.S.S.R. and North American Arctic shows that where permafrost is present, gas hydrates may exist at depths as shallow as 130 m and as deep as 2,000 m. Antarc-

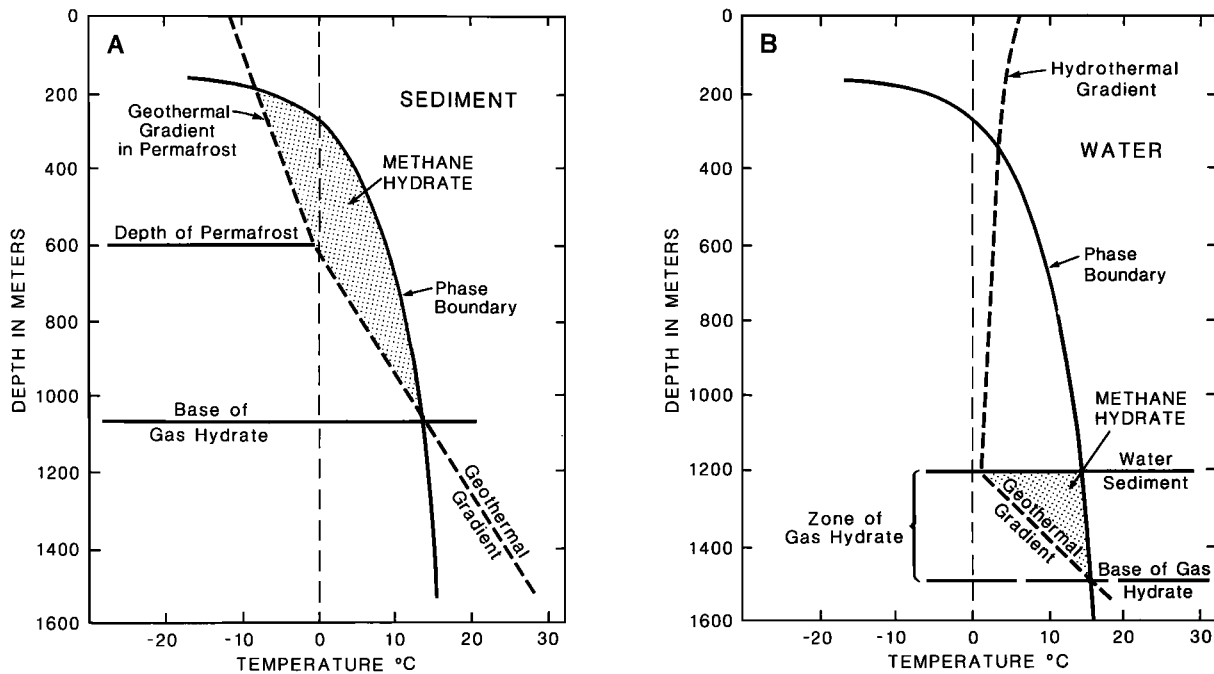


Fig. 2. Examples of different depth-temperature zones for gas hydrate occurrence: (a.) in a permafrost region. (b.) in an outer continental margin setting. (Graphs are from K. A. Kvenvolden and A. Grantz, Decade of North American geology, unpublished data, 1987).

tica may also have gas hydrate deposits, although few data on Antarctic permafrost areas are available [Hitchon, 1974; MacDonald, 1983]; land temperature profiles indicate that gas hydrates could exist at depths similar to those in the Arctic.

Offshore Regions

Gas hydrates in continental margin sediment have been inferred mainly from the widespread occurrence on marine geophysical records of an anomalous seismic reflector that coincides with the predicted transition boundary at the base of the gas hydrate zone. This reflector is commonly referred to as a bottom-simulating reflector (BSR) because it nearly parallels the topography of the seafloor. BSRs lie anywhere from about 100 to 1,100 m below the bottom at water depths greater than about 300 m (reviewed by Kvenvolden and McMenamin [1980]). The upper limit of the gas hydrate zone in oceanic sediment is ordinarily the seafloor; gas hydrates have been recovered within 6.5 m of the seafloor in sediment of the Black Sea [Yefremova and Zhizhchenko, 1975] and the Gulf of Mexico [Brooks et al., 1986].

Kvenvolden and Barnard [1983] described 23 offshore localities around the world where gas hydrates are known or inferred to occur in oceanic sediment. Additional offshore localities where gas hydrates are expected include the Canadian Beaufort Sea [Neave et al., 1978], Beaufort Sea shelf [Judge, 1984], Sverdrup Basin [Judge, 1982], off North Island, New Zealand [Katz, 1981], off Norway [Bugge, 1983; K. A. Kvenvolden et al., leg 104, Ocean

Drilling Program, unpublished data, 1987], and off Peru (Shipboard Party, leg 112, Ocean Drilling Program, unpublished data, 1987). Offshore Peru, not only is seismic evidence abundant for gas hydrates, but gas hydrates were also recovered during drilling.

ESTIMATES OF THE AMOUNT OF METHANE IN GAS HYDRATES

Although gas hydrates are now known to be widespread in permafrost regions and in outer continental margin sediment, resource estimates for methane in gas hydrates are highly speculative owing to incomplete knowledge of gas hydrate occurrences and poor methods of estimating reserves in known occurrences. The Potential Gas Committee [1981] summarized such estimates, and much of what follows is from their work. Regional and world estimates of gas hydrate resources have been made by scientists in both the U.S.S.R. and the United States (Table 1). Trofimuk et al. [1977] attempted to incorporate many complex factors into their calculations, including regional and world coefficients of present and past temperatures, sediment thicknesses, percentage of organic material, and percentage of methane production and conservation. The estimates by Dobrynin et al. [1981] were based on permafrost coverage and physical zones of gas hydrate stability in the world's oceans without apparent regard for the distribution of sedimentary basins or the availability of natural gas. None of these estimates apparently takes into account reservoir porosity and permeability. McIver [1981] and Meyer [1981] have made their gas hydrate re-

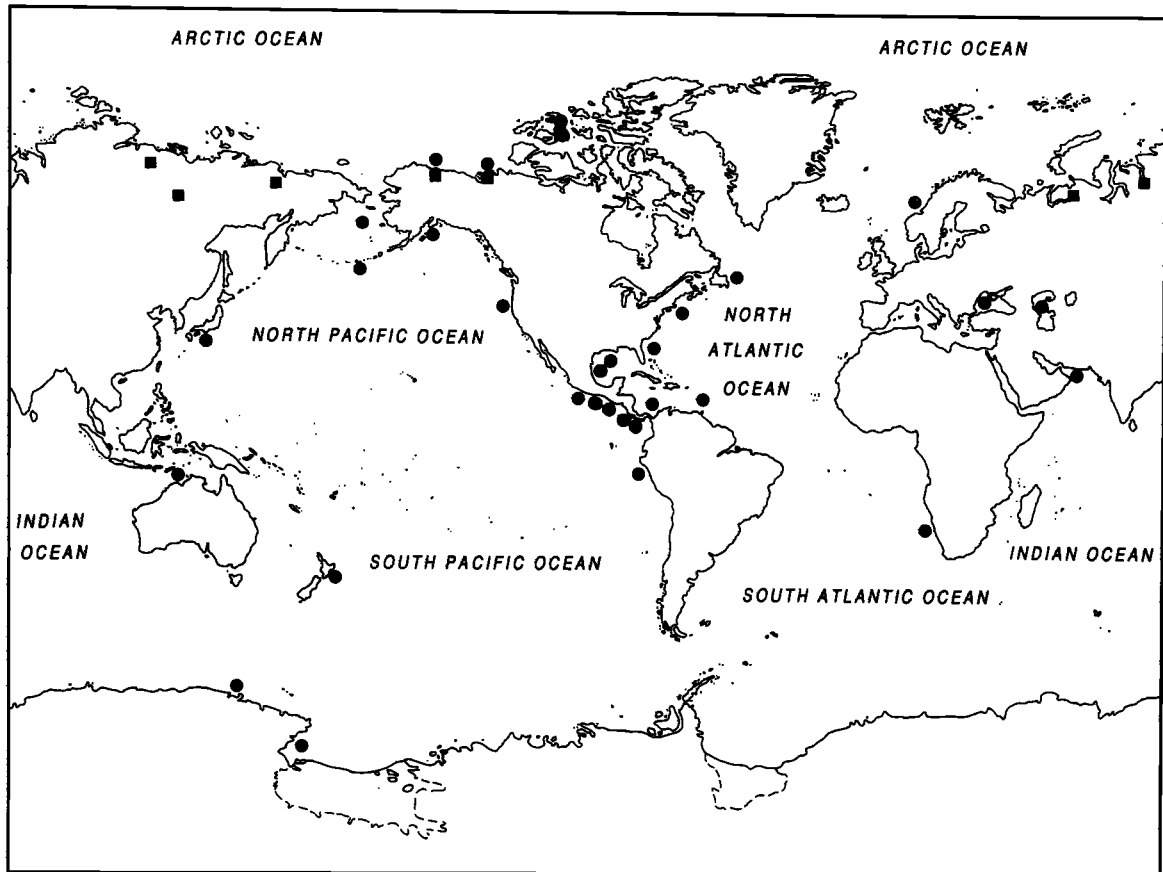


Fig. 3. Locations of known or inferred gas hydrates.

source estimates on the basis of interpretations of calculations made mainly by U.S.S.R. scientists [Cherskiy and Makogon, 1970; Trofimuk et al., 1977].

The highly speculative resource estimates for gas hydrates vary widely (Table 1). For example, estimates of the

amount of carbon in methane in gas hydrates of oceanic sediment range from 1,700 to 4,100,000 GT (gigatons or 10^{15} g). In Arctic permafrost regions, the amount of carbon in methane from gas hydrates is estimated to range from 7.5 to 18,000 GT. K. A. Kvenvolden and A. Grants

TABLE 1. Estimates of Methane Hydrate Resources

m^3	Tcf	GTC	Reference
<i>Oceanic</i>			
3.1×10^{15}	1.1×10^5	1.7×10^3	McIver [1981]
$5-25 \times 10^{15}$	$1.8-8.8 \times 10^5$	8.0×10^3	Trofimuk et al. [1977]
7.6×10^{18}	2.7×10^8	4.1×10^6	Dobrynin et al. [1981]
<i>Continental</i>			
1.4×10^{13}	5.0×10^2	7.5	Meyer [1981]
3.1×10^{13}	1.1×10^3	1.7×10^1	McIver [1981]
5.7×10^{13}	2.0×10^3	3.1×10^1	Trofimuk et al. [1977]
3.4×10^{16}	1.2×10^6	1.8×10^4	Dobrynin et al. [1981]

Abbreviations used are as follows: m^3 , cubic meters; Tcf, trillions of cubic feet; and GTC, gigatons (10^{15} g) of methane carbon. Adapted from Potential Gas Committee [1981].

(Decade of North American geology, unpublished data, 1987) have attempted to estimate the extent of gas hydrates in the Arctic Basin by extrapolating information from the seismically inferred gas hydrate offshore from northern Alaska. By taking into account areal extent, sediment thickness, sediment porosity, and the yield of methane from gas hydrate, they calculated a total amount of 10^{15} m³ of methane, or 540 GT of carbon, in sediment of the offshore Arctic Basin.

ATMOSPHERIC METHANE, CARBON DIOXIDE, AND GLOBAL CLIMATIC CHANGE

The principal carbon-containing component of the atmosphere is carbon dioxide, the concentration of which is presently increasing at the rate of about 0.35%, or 2.6 to 3.8 GT of carbon, per year [MacDonald, 1982; Chamberlain et al., 1983]. In the next 40–50 years, the concentration of atmospheric carbon dioxide is expected to increase [Rasmussen and Khalil, 1981] to about 1140 GT of carbon. In contrast, methane is one of the important trace components of the atmosphere. Its concentration is also increasing, but at a faster rate of about 1 to 2% per year or about 0.07 GT of methane (0.05 GT of carbon) per year [Revelle, 1983]. At this rate, the amount of methane in the atmosphere is expected to double in the next 40–50 years [Rasmussen and Khalil, 1981] to an equivalent of about 7.2 GT of carbon. The atmospheric fate of methane is complex, however, depending mainly on the concentration of the hydroxyl radical (HO) which, in turn, depends on the concentration of several trace constituents including CO, NO_x, O₃, etc. Future levels of methane, therefore, are difficult to predict [Chamberlain et al., 1983].

The effect of increasing atmospheric carbon dioxide concentrations on global climate has received much attention [MacDonald, 1982; National Research Council, 1982, 1983]. Generally, an increase in the amount of atmospheric carbon dioxide is thought to result in an increasing retention of radiant heat by the atmosphere (greenhouse effect) and a higher equilibrium temperature for the whole Earth. In the next 40–50 years, an increase of carbon dioxide is expected to result in a global warming up to 4 K with an increase of approximately 5 to 10 K predicted for the polar regions [Moore and Bolin, 1987]. Methane also has greenhouse gas properties (summarized by Rasmussen and Khalil [1981]): A doubling of atmospheric methane concentrations in the next 40–50 years is predicted to result in a global warming of about 0.3 to 0.4 K. Thus, whatever the ultimate course of global warming, methane concentration is undoubtedly going to contribute, second perhaps only to carbon dioxide.

EFFECT OF METHANE HYDRATE ON GLOBAL CLIMATE

The possible additions to the atmosphere of gas-hydrate-derived methane and the potential effects of these additions have been addressed previously [MacDonald, 1982; Bell, 1983; Chamberlain et al., 1983; Revelle, 1983]. In their considerations, each of these workers started with a speculative and highly variable estimate of the amount of methane present in gas hydrates. Revelle [1983] com-

mented that estimates of the total amount of methane in methane hydrates differ by a factor of 500, from 1,000 GT to 500,000 GT. These estimates are about two orders of magnitude larger than the conservative estimates by McIver [1981], Meyer [1981], and Trofimuk et al. [1977], and about one order of magnitude less than those by Dobyrynin et al. [1981] as listed in Table 1.

There is general agreement, however, that with global warming due mainly to an increasing concentration of CO₂, there will be a positive feedback that will release methane from methane hydrates; all workers caution, however, on the uncertainties in their calculations. One approach has been to assume that some fraction of the total amount of gas hydrate in sediment will decompose. For example, Revelle [1983] reasoned that in the average depth interval of 100 m on continental slopes worldwide, gas hydrates would become unstable owing to the temperature increase caused by a doubling of carbon dioxide in the atmosphere. He calculated that 0.64 GT of methane (0.48 GT of carbon) would be released per year from unstable gas hydrates. This additional atmospheric methane may contribute an extra 1 to 2 K of global warming. Chamberlain et al. [1983] estimated that a 1° increase in temperature would lead to a worldwide release of 90 GT of methane (70 GT of carbon) over several decades.

The approach taken by Revelle [1983] and Chamberlain et al. [1983] assumes that gas hydrates worldwide will decompose. However, most gas hydrates occur in outer continental margin sediment at water depths greater than 300 to 500 m. At these depths, bottom water temperatures should be insulated from rapid temperature change, and the buried gas hydrate deposits will be affected only very slowly by heat conducted downward from the seafloor. Thus, the estimates of the amount of methane released from gas hydrates as calculated by Chamberlain et al. [1983] and Revelle [1983] are believed to be too large.

A second approach to estimating the amount of methane to be released from gas hydrates is to examine critically those areas of gas hydrate occurrence that are most likely to be affected by global warming. This approach was taken by Bell [1983], who pointed out that most gas hydrate occurrences worldwide are in such a stable thermal environment that they will generally be insulated from the effects of global warming resulting from a doubling of atmospheric carbon dioxide. Bell [1983] believes, however, that there is a small area of the Arctic Ocean where gas hydrate could be affected adversely by global warming, which is expected to be accentuated in the Arctic [National Research Council, 1982]. This area would include a gas-hydrate-containing layer 250 m thick, of which a 40-m-thick layer will decompose over an area corresponding to water depths of 300±45 m and extending halfway around the Arctic Ocean in the Canada Basin, where bottom water temperatures are anticipated to rise from -0.5 to 3°C. The mass of methane that would be released from this area was calculated to be about 8 GT of carbon per year which would cause a significant positive feedback on carbon-dioxide-induced warming. However, Revelle [1983] pointed out that the value of 8 GT per year should be reduced to 0.12 GT per year if the erroneous areal extent of assumed gas hydrates, used in the original calculations,

is corrected. This amount of carbon translates to 0.16 GT of methane added per year to the current estimate of total methane emissions of 0.55 GT per year [Khalil and Rasmussen, 1983]. Such a new source of methane could become the single most important source of methane addition to the atmosphere. A release of 0.12 GT per year of carbon as methane, therefore, would probably have some effect on global warming.

But there are questions concerning Bell's [1983] analysis. First, it is unlikely that a continuous layer, 250 m thick, of gas hydrate exists in sediment, because wherever gas hydrate occurrences have been studied in detail, they are present in discrete layers and occupy only a small part of the potential field of gas hydrate stability. For example, in the eastern part of the Kuparuk River oil field and the western part of the Prudhoe Bay oil field, where most gas hydrates of the North Slope of Alaska are believed to occur, these substances are present in about four to six laterally continuous, but restricted, units ranging in thickness from 2 to 28 m [Collett and Kvenvolden, 1987]. The gas hydrates are present in a series of sands and gravels which are interbedded with multiple thick silt units. Well logs on Figure 4 illustrate the point that gas hydrates tend to occur in layers. Further evidence for the layered, but restricted, nature of gas hydrate occurrence is found in well log analysis at Deep Sea Drilling Project site 570 off-shore of Guatemala [Mathews and von Huene, 1985]. The occurrence of gas hydrates appears to be controlled by lithology, with coarse-grained porous units favored. Thus a continuous exposure of 40 m of gas hydrate at a specific depth of about 300 m in the Arctic Ocean is unlikely. Second, circulation of Arctic Ocean water into the Canada Basin is restricted [Aagaard et al., 1985], and this isolation of Canada Basin waters may provide an insulation against thermal changes, such as those resulting from global warming. Thus, the temperature increase envisioned by Bell [1983] may be greatly inhibited.

One region of the Arctic, however, that may be critical to the problem of gas hydrates and global warming is the region of offshore permafrost. Although onshore permafrost may also be important to the problem, its role is secondary to that of offshore permafrost because gas hydrates present within and under offshore permafrost should be the first to be destabilized by global climatic warming. This destabilization results because of their shallow occurrence and the effects of the transition from ice to water. Because the extent of offshore permafrost and the distribution of gas hydrates associated with this material are both poorly known, no reliable estimate regarding possible release of methane from these gas hydrates can be made. The amount of methane involved, however, is likely to be less than the minimum of previous estimates, i.e., less than 0.12 GT per year.

Offshore permafrost in the Arctic is known to occur on the Beaufort Sea shelf of Canada [Neave et al., 1978; Weaver and Stewart, 1982]. Also, offshore permafrost occupies a part of the vast continental shelf of Siberia as shown by Bell [1983, Figure 1]. Studies by Rogers and Morack [1980] on subsea permafrost and sea level history lead to the inference that offshore permafrost may persist beneath any part of the Arctic shelf inshore from about the

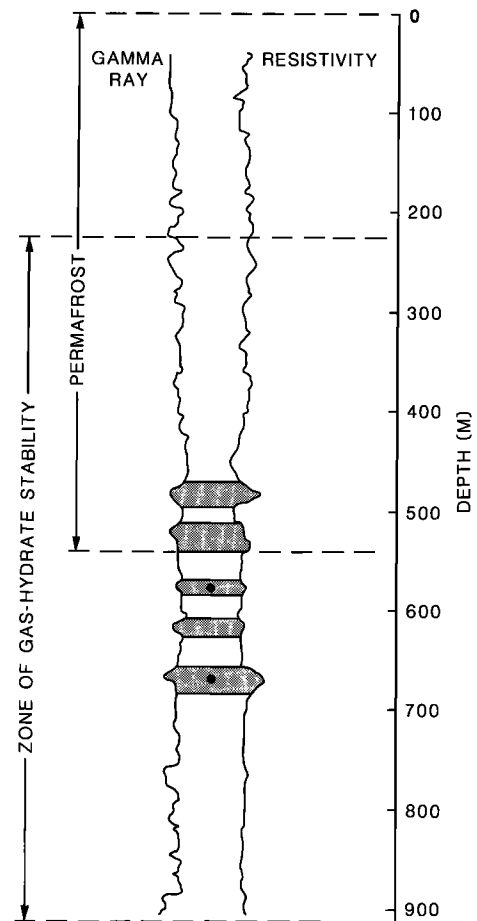


Fig. 4. Well log responses (gamma ray and resistivity) at the N.W. Eileen 2 well on the North Slope of Alaska. Shaded areas show gas hydrate occurrences; filled circles indicate locations of cores that tested positive for gas hydrates by pressure core barrel measurements (reviewed by Kvenvolden and McMenamin [1980]).

90-m isobath. The distribution of gas hydrates associated with offshore permafrost in this region is probably similar to that of gas hydrates associated with permafrost onshore. The distribution of gas hydrates onshore is apparently restricted, patchy, and confined to porous sedimentary units. Thus the amount of gas hydrate actually present in permafrost regions is much smaller than previously estimated because gas hydrates occupy only a small part of the potential region of gas hydrate stability. Most previous calculations have assumed that much of the gas hydrate stability field is occupied by gas hydrate [e.g., Bell, 1983; Chamberlain et al., 1983; Revelle, 1983]. If less gas hydrate is actually present than previously thought, then the potential for the release of methane due to global warming is greatly reduced.

Evidence already exists that warming of the onshore permafrost is currently taking place. Lachenbruch and

TABLE 2. Isotopic Composition of Methane Hydrates

Region	^{13}C , per mil	Reference
Gulf of Mexico	-43.2 to -56.5	Brooks et al. [1986]
Gulf of Mexico	-66.5 to -71.3	Brooks et al. [1986]
Offshore Guatemala	-36.1 to -43.6	Kvenvolden et al. [1984]
Offshore Guatemala	-40.7 to -46.2	Brooks et al. [1985]
Offshore SE USA	-68.0	Brooks et al. [1983]
Offshore Peru	-59.6 and -65.0	G. E. Claypool, unpublished data (1987)

Marshall [1986] showed anomalous temperature profiles in the upper 100 m of permafrost in northern Alaska. They believe that these profiles indicate a varying but widespread secular warming of 2 to 4°C of the permafrost surface during the 20th century. The offshore permafrost could also be undergoing similar thermal changes. These thermal changes will eventually penetrate deep enough to destabilize gas hydrates within and below the permafrost. The time scale, however, for this thermal penetration is probably thousands of years (A. H. Lachenbruch, personal communication, 1987). Nevertheless, there is speculation that the gas hydrates associated with offshore permafrost are currently decomposing; Clarke et al. [1986] suggested that the cold plumes emanating from Bennett Island on the Soviet Arctic shelf result from methane, released by the breakup of permafrost and accompanying gas hydrates.

A test of the idea that methane is currently being released from methane hydrates could possibly be made if the isotopic compositions (i.e., $\delta^{13}\text{C}$, δD , or ^{14}C) of that methane were known. The isotopic signature might be used to follow the release of methane from permafrost. Unfortunately, these values have not been reported for methane hydrates associated with permafrost; however, ancillary information is available. For example, $\delta^{13}\text{C}$ values for methane from drill cuttings recovered from an inferred gas hydrate interval in a well on the North Slope of Alaska are -49.6 and -48.9 per mil (relative to the Pee Dee Belemnite [PDB] Standard) (T. S. Collett, personal communication, 1986). A second example comes from the Messoyakha field where methane from a depth of 830 m has a $\delta^{13}\text{C}$ value of -48.0 per mil [Grace and Hart, 1986]. This depth is within the interval in which gas hydrates are stable, and the Messoyakha field is known to have gas hydrates [Makogon et al., 1972]. These values serve as the best estimates of the carbon isotopic composition of methane hydrates in permafrost regions until direct isotopic measurements can be made on methane hydrate samples. Of interest is the fact that these best estimates are only slightly depleted in ^{13}C relative to carbon isotopic composition of atmospheric methane of -47.0 per mil as measured by Stevens and Rust [1982]. No measurements of δD or ^{14}C have been reported for methane hydrates although a limited number of $\delta^{13}\text{C}$ values have been determined on methane from gas hydrates recovered from oceanic sediment of nonpolar regions. These data (Table 2) show that the carbon isotopic signature of methane hy-

drates is not unique but is quite variable, depending on the region and the processes involved in gas generation.

With present knowledge, it is impossible to predict with certainty the amount of methane that is currently being released and that will be released as a result of the degradation of offshore permafrost and the consequent destabilization of associated gas hydrate. What does seem certain, however, is that the gas hydrates that may be associated with offshore permafrost are currently the most vulnerable to thermal change due to global warming. Gas hydrates in sediment of outer continental margins and in and under continental permafrost are better insulated from the effects of global warming for at least the next few hundred years.

SUMMARY

Present evidence suggests that global warming is under way, with its effects already noticeable in the Arctic. This warming likely results, in part, from the greenhouse effect, due to the ever increasing amounts of atmospheric carbon dioxide. The amount of atmospheric methane is increasing more rapidly than that of carbon dioxide, but the current greenhouse effect of methane is almost an order of magnitude less than that of carbon dioxide. Global warming will eventually penetrate the surface of the Earth and in the process destabilize gas hydrates. This destabilization will likely occur first and most intensely in the very shallow, nearshore regions of the Arctic Ocean where offshore permafrost exists. The processes of offshore permafrost warming and methane release may already be in progress, but the amount of methane presently being released and to be released during global warming in the 21st century is probably not particularly large and will contribute minimal positive feedback to the global-warming phenomenon.

REFERENCES

- Aagaard, K., J. H. Swift, and E. C. Carmack, Thermohaline circulation in the Arctic Mediterranean Sea, *J. Geophys. Res.*, 90, 4833-4846, 1985.
- Bell, P. R., Methane hydrate and the carbon dioxide question, in *Carbon Dioxide Review, 1982*, edited by W. C. Clark, pp. 401-406, Oxford University Press, New York, 1983.
- Bily, C., and J. W. L. Dick, Naturally occurring gas

- hydrates in the Mackenzie Delta, N.W.T., *Bull. Can. Pet. Geol.*, *32*, 340–352, 1974.
- Brooks, J. M., L. A. Barnard, D. A. Wiesenburg, M. C. Kennicutt, and K. A. Kvenvolden, Molecular and isotopic compositions of hydrocarbons at site 533, Deep Sea Drilling Project leg 76, in *Initial Reports of the Deep Sea Drilling Project*, vol. 76, edited by R. E. Sheridan et al., pp. 377–389, U.S. Government Printing Office, Washington, D.C., 1983.
- Brooks, J. M., M. C. Kennicutt, R. R. Fay, T. J. McDonald, and R. Sasson, Thermogenic gas hydrates in the Gulf of Mexico, *Science*, *225*, 409–411, 1984.
- Brooks, J. M., A. W. A. Jeffrey, T. J. McDonald, R. C. Pflaum, and K. A. Kvenvolden, Geochemistry of hydrate gas and water from site 570, Deep Sea Drilling Project leg 84, in *Initial Reports of the Deep Sea Drilling Project*, vol. 84, edited by R. von Huene et al., pp. 699–703, U.S. Government Printing Office, Washington, D.C., 1985.
- Brooks, J. M., H. B. Cox, W. R. Bryant, M. C. Kennicutt, R. G. Mann, and T. J. McDonald, Association of gas hydrates and oil seepage in the Gulf of Mexico, *Org. Geochem.*, *10*, 221–234, 1986.
- Bugge, T., Submarine slides on the Norwegian continental margin with special emphasis on the Storegga area, Continental Shelf Norway (IKU, Trondheim, Norway), *Pub. 10*, Section 5.7.3, 1983.
- Chamberlain, J. W., H. M. Foley, G. J. MacDonald, and M. A. Ruderman, Climate effects of minor atmospheric constituents, in *Carbon Dioxide Review, 1982*, edited by W. C. Clark, pp. 255–277, Oxford University Press, New York, 1983.
- Cherskiy, N. V., and Yu. F. Makogon, Solid Gas—World reserves are enormous, *Oil Gas Int.*, *10* (8), 82, 1970.
- Cherskiy, N. V., V. P. Tsarev, and S. P. Nikitin, Investigation and prediction of conditions of accumulation of gas resources in gas-hydrate pools, *Pet. Geol.*, *21*, 65–89, 1985.
- Clarke, J. W., P. St. Amand, and M. Matson, Possible cause of plumes from Bennett Island, Soviet Far Arctic, *Am. Assoc. Pet. Geol. Bull.*, *70*, 574, 1986.
- Claypool, G. E., and I. R. Kaplan, The origin and distribution of methane in marine sediments, in *Natural Gases in Marine Sediments*, edited by I. R. Kaplan, pp. 99–139, Plenum, New York, 1974.
- Collett, T. S., Detection and evaluation of natural gas hydrates from well logs, Prudhoe Bay, Alaska, M.S. thesis, 78 pp., Univ. of Alaska, Fairbanks, 1983.
- Collett, T. S., and K. A. Kvenvolden, Evidence of naturally occurring gas hydrates on the North Slope of Alaska, *U.S. Geol. Surv. Open File Rep.*, *87-255*, 8 pp., 1987.
- Davidson, D. W., Clathrate hydrates, in *Water: A comprehensive treatise*, vol. 2, edited by F. Franks, pp. 115–234, Plenum, New York, 1973.
- Davidson, D. W., M. K. El-Defrawy, M. O. Fuglem, and A. S. Judge, Natural gas hydrates in northern Canada, in *Proceedings, Third International Conference on Permafrost, 1978*, vol. 1, pp. 938–943, National Research Council of Canada, Ottawa, Ont., 1978.
- Dobrynin, V. M., Yu. P. Korotajev, and D. V. Plyushev, Gas hydrates: A possible energy resource, in *Long-Term Energy Resources*, vol. 1, edited by R. F. Meyer and J. C. Olson, pp. 727–729, Pitman, Boston, Mass., 1981.
- Grace, J. D., and G. E. Hart, Giant gas fields of northern West Siberia, *Am. Assoc. Pet. Geol. Bull.*, *70*, 830–852, 1986.
- Hitchon, B., Occurrence of natural gas hydrates in sedimentary basins, in *Natural Gases in Marine Sediments*, edited by I. R. Kaplan, pp. 195–225, Plenum, New York, 1974.
- Judge, A., Natural gas hydrates in Canada, in *Proceedings of the Fourth Canadian Permafrost Conference, 1981*, *Roger J. E. Brown Mem. Vol.*, edited by M. H. French, pp. 320–328, National Research Council of Canada, Ottawa, Ont., 1982.
- Judge, A., Natural gas hydrates in the Mackenzie Delta-Beaufort Sea areas northern Canada, paper presented at 1984 Winter National Meeting, Am. Inst. of Chem. Eng., Atlanta, Ga., 1984.
- Katz, D. L., Depths to which frozen gas fields (gas hydrates) may be expected, *J. Pet. Technol.*, *23*, 419–423, 1971.
- Katz, D. L., D. Cornell, R. Kobayashi, F. H. Poettmann, J. A. Vary, J. R. Elenbass, and C. F. Weinaug, *Handbook of Natural Gas Engineering*, 802 pp., McGraw-Hill, New York, 1959.
- Katz, H. R., Probable gas hydrate in continental slope east of the North Island, New Zealand, *J. Pet. Geol.*, *3*, 314–324, 1981.
- Khalil, M. A. K., and R. A. Rasmussen, Sources, sinks, and seasonal cycles of atmospheric methane, *J. Geophys. Res.*, *88* (C9), 5131–5144, 1983.
- Kvenvolden, K. A., and L. A. Barnard, Hydrates of natural gas in continental margins, in *Studies in Continental Margin Geology, Mem. 34*, edited by J. S. Watkins and C. L. Drake, pp. 631–640, American Association of Petroleum Geologists, Tulsa, Okla., 1983.
- Kvenvolden, K. A., and M. A. McMenamin, Hydrates of natural gas: A review of their geological occurrences, *U.S. Geol. Surv. Circ.*, *825*, 11 pp., 1980.
- Kvenvolden, K. A., G. E. Claypool, C. N. Threlkeld, and E. D. Sloan, Geochemistry of a naturally occurring massive marine gas hydrate, *Org. Geochem.*, *6*, 703–713, 1984.
- Lachenbruch, A. H., and B. V. Marshall, Changing climate: Geothermal evidence from permafrost in the Alaskan Arctic, *Science*, *234*, 689–696, 1986.
- MacDonald, G. J. (Ed.) *The Long-Term Impacts of Increasing Atmospheric Carbon Dioxide Levels*, 253 pp., Ballinger, Cambridge, Mass., 1982.
- MacDonald, G. J., The many origins of natural gas, *J. Pet. Geol.*, *5*, 341–362, 1983.
- Makogon, Yu. F., F. A. Trebin, A. A. Trofimuk, V. P. Tsarev, and N. V. Cherskiy, Detection of a pool of natural gas in a solid (hydrated gas) state, *Dokl. Acad. Sci. USSR, Earth Sci. Section*, Engl. Transl., *196*, 197–200, 1972.
- Mathews, M. A., and R. von Huene, Site 570 methane hydrate zone, in *Initial Reports of the Deep Sea Drilling Project*, vol. 84, edited by R. von Huene et al., pp.

- 773-790, U.S. Government Printing Office, Washington, D.C., 1985.
- McIver, R. D., Gas hydrates, in *Long-Term Energy Resources*, vol. 1, edited by R. F. Meyer and J. C. Olson, pp. 713-726, Pitman, Boston, Mass., 1981.
- Meyer, R. F., Speculations on oil and gas resources in small fields and unconventional deposits, in *Long-Term Energy Resources*, vol. 1, edited by R. F. Meyer and J. C. Olson, pp. 49-72, Pitman, Boston, Mass., 1981.
- Moore, B., and B. Bolin, The oceans, carbon dioxide, and global climate change, *Oceanus*, 29 (4), 9-15, 1987.
- National Research Council, *Carbon Dioxide and Climate: A Second Assessment*, 72 pp., National Academy Press, Washington, D.C., 1982.
- National Research Council, *Changing Climate*, 496 pp., National Academy Press, Washington, D.C., 1983.
- Neave, K. G., A. S. Judge, J. A. Hunter, and H. A. MacAulay, Offshore permafrost distribution in the Beaufort Sea as determined from temperature and seismic observations, in Current Research, part C, *Pap. 78-1C*, pp. 13-18, Geol. Surv. of Can., Ottawa, Ont., 1978.
- Potential Gas Committee, Potential supply of natural gas in the United States (as of December 31, 1980), report, 119 pp., Potential Gas Agency, Colo. Sch. of Mines, Golden, 1981.
- Rasmussen, R. A., and M. A. K. Khalil, Atmospheric methane (CH₄): Trends and seasonal cycles, *J. Geophys. Res.*, 86 (C10), 9826-9832, 1981.
- Revelle, R. R., Methane hydrates in continental slope sediments and increasing atmospheric carbon dioxide, in *Changing Climates*, pp. 252-261, National Academy Press, Washington, D.C., 1983.
- Rogers, J. C., and J. L. Morack, Geophysical evidence of shallow nearshore permafrost, Prudhoe Bay, Alaska, *J. Geophys. Res.*, 85 (B9), 4845-4853, 1980.
- Stevens, C. M., and F. E. Rust, The carbon isotopic composition of atmospheric methane, *J. Geophys. Res.*, 87 (C7), 4879-4882, 1982.
- Trofimuk, A. A., N. V. Cherskiy, and V. P. Tsarev, The role of continental glaciation and hydrate formation on petroleum occurrence, in *Future Supply of Nature-Made Petroleum and Gas*, pp. 919-926, Pergamon, New York, 1977.
- Weaver, J. S., and J. M. Stewart, In situ hydrates under the Beaufort Sea Shelf, in *Proceedings of Fourth Canadian Permafrost Conference 1981*, Roger J. E. Brown Mem. Vol., edited by M. H. French, pp. 312-319, National Research Council of Canada, Ottawa, Ont., 1982.
- Yefremova, A. G., and B. P. Zhizhchenko, Occurrence of crystal hydrates of gases in sediments of modern marine basins, *Dokl. Acad. Sci. USSR, Earth Sci. Section*, Engl. Transl., 214, 219-220, 1975.

Keith A. Kvenvolden, U.S. Geological Survey, Branch of Pacific Marine Geology, 345 Middlefield Road, Mail Stop 999, Menlo Park, CA 94025.

(Received November 6, 1987;
revised February 29, 1988;
accepted March 1, 1988.)