GAS HYDRATES—GEOLOGICAL PERSPECTIVE AND GLOBAL CHANGE

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Abstract. Natural gas hydrates occur worldwide in polar regions, normally associated with onshore and offshore permafrost, and in sediment of outer continental and insular margins. The total amount of methane in gas hydrates likely exceeds \( 10^{19} \) g of methane carbon. Three aspects of gas hydrates are important: their fossil fuel resource potential, their role as a submarine geohazard, and their effects on global climate change. Because gas hydrates represent a large amount of methane within 2000 m of the Earth’s surface, they are considered to be an unconventional, unproven source of fossil fuel. Because gas hydrates are metastable, changes of pressure and temperature affect their stability. Destabilized gas hydrates beneath the seafloor lead to geologic hazards such as submarine slumps and slides, examples of which are found worldwide. Destabilized gas hydrates may also affect climate through the release of methane, a “greenhouse” gas, which may enhance global warming and be a factor in global climate change.

INTRODUCTION

Increasing interest in gas hydrates has spawned a wealth of ideas regarding their significance in the natural world. For example, Leggett [1990] points out that gas hydrates may produce a potentially enormous “greenhouse” feedback effect on future global climate. This positive feedback will result because of the large amount of methane (a “greenhouse” gas) that could be released from destabilized gas hydrates. MacDonald [1990a] emphasizes the importance of gas hydrates as a potential natural fuel resource of methane as well as of hydrogen, which can be abstracted from the hydrate methane. Just what are these substances that have captured the attention of environmental groups and appear to be so important to aspects of future global economics?

Definition

Gas hydrates, also called gas clathrates, are naturally occurring solids comprised of water molecules forming a rigid lattice of cages with most of the cages, each containing a molecule of natural gas, mainly methane. Gas hydrates are essentially water clathrates of natural gas in which water crystallizes in the isometric crystallographic system rather than the hexagonal system of normal ice. Two structures, I and II, of the isometric (cubic) lattice are recognized in nature with structure I (Figure 1) being most common. In structure I the cages are arranged in body-centered packing and are large enough to include methane, ethane, and other gas molecules of similar molecular diameters such as carbon dioxide and hydrogen sulfide. In structure II, diamond packing is present resulting in some cages being large enough to include not only methane and ethane but also gas molecules as large as propane and isobutane [Sloan, 1990].

The maximum amount of methane that can occur in a methane hydrate is fixed by the clathrate geometry. In a fully saturated structure I methane hydrate, one molecule of methane is present for every \( \frac{5}{17} \) molecules of water; in theory then, when appropriate hydrate expansion factors are considered, \( 1 \) m\(^3\) of methane hydrate can contain up to \( 164 \) m\(^3\) of methane gas at standard conditions (Figure 2). Thus gas hydrates in shallow reservoirs less than about \( 1.5 \) km beneath the surface can have more methane per unit volume than can be contained as free gas in the same space [Hunt, 1979]. This fact explains some of the serious interest in gas hydrates as a potential (1) future energy resource, (2) submarine geohazard, and (3) factor in global climate change. Each of these potential aspects of gas hydrates will be addressed in this paper.

Controls

The occurrence of gas hydrates in nature is controlled by an interrelation among the factors of temperature, pressure, and composition as illustrated by means of a phase diagram (Figure 3). In the pressure-temperature domain of methane hydrates the position of the phase boundary is determined not only by the composition of the gas mixture, that is, the presence of gases other than methane, but also by the ionic impurities in the water. Because the exact composition of
gas and water in sediment pore spaces is normally not known, a pure methane—pure water system is commonly assumed to predict the depth and temperature regime where naturally occurring gas hydrates are stable [Claypool and Kaplan, 1974].

The phase boundary information (Figure 3) suggests that the upper depth limit for methane hydrates is about 150 m in continental polar regions, where surface temperatures are below 0°C. In oceanic sediment, gas hydrates occur where the bottom water temperatures approach 0°C, and water depths exceed about 300 m. The lower limit of methane hydrate occurrence is determined by the geothermal gradient; the maximum lower limit is about 2000 m below the solid surface, although the lower limit is typically much less depending on local conditions. Thus the occurrence of gas hydrates is restricted to the shallow geosphere.

One feature of gas hydrate occurrence that is not apparent from the phase diagram (Figure 3) is the amount of gas (methane) that is necessary for gas

Figure 1. Gas hydrate structure. In this structure I methane hydrate the rigid cages are composed of hydrogen-bonded water molecules, and each cage, both exposed and covered in this figure, contains a methane molecule. Modified from Hitchon [1974].

hydrate formation. Gas hydrates will form with about 90% of the cages of the clathrate filled, that is with about 150 volumes of methane at standard conditions per volume of water [Sloan, 1990]. However, methane solubility in seawater is very low, about 0.045 volumes of methane at standard conditions per volume of water [Yamamoto et al., 1976]. Thus the amount of methane required for gas hydrates greatly exceeds the solubility of methane in water. This requirement for a source of enormous amounts of methane for gas hydrate formation limits the regions on Earth where gas hydrates can be expected and are found.

**Locations**

Gas hydrates occur worldwide, but, because of the pressure-temperature and gas volume requirements,

Figure 2. One cubic meter of gas hydrate yields 164 m³ of gas and 0.8 m³ of water at standard temperature and pressure.

Figure 3. Phase diagram showing boundary between free methane gas (no pattern) and methane hydrate (pattern) for a pure water and pure methane system. The addition of NaCl to water shifts the curve to the left. Adding CO₂, H₂S, C₂H₆, C₄H₁₀ to methane shifts the boundary to the right and thus increases the area of the hydrate stability field. Depth scale assumes lithostatic and hydrostatic pressure gradients of 10.1 kPa m⁻¹. Redrawn after Katz et al. [1959].
they are restricted to two regions: polar and deep oceanic. In polar regions, gas hydrates are normally associated with permafrost both onshore in continental sediment and offshore in sediment of the continental shelves. In deep oceanic regions, gas hydrates are found in outer continental margins in sediment of slopes and rises where cold bottom water is present. The worldwide occurrence of known and inferred gas hydrates is shown on Figure 4. Samples of gas hydrates have been recovered on land in the West Prudhoe Bay oil field in Alaska (reviewed by Kvenvolden and McMenamin [1980]) and at 14 oceanic locations, providing irrefutable evidence of natural gas hydrate occurrence [Kvenvolden et al., 1993]. Deep ocean drilling has recovered gas hydrates at nine locations (offshore Peru, Costa Rica, Guatemala, Mexico, southeastern United States, western United States, two locations offshore from Japan, and in the Gulf of Mexico). Shallow sediment coring (piston and gravity cores) has also recovered gas hydrates at six locations (Black Sea, Caspian Sea, offshore from northern California, northern Gulf of Mexico, and two locations in the Okhotsk Sea). Examples of gas hydrate samples recovered from offshore from Guatemala are shown in Figure 5.

Geophysics

Most other oceanic occurrences of gas hydrates are inferred, based mainly on the appearance on marine seismic reflection profiles of an anomalous bottom simulating reflection (BSR). This reflection coincides with the depth predicted from the phase diagram (Figure 3) as the base of the gas hydrate stability zone (Figure 6). BSRs mark the interface between higher sonic velocity, hydrate-cemented sediment above and lower sonic velocity, uncemented sediment below. The seismic reflection from the base of the gas hydrate zone is generally characterized by reflection polarity reversals (reflections opposite to those from the seafloor) and large vertical reflection coefficients, for example $-0.12 \pm 0.04$ for BSRs of the Blake Outer Ridge offshore from the southeastern United States [Shipley et al., 1979]. Such negative reflection coefficients are indicative of a reflective interface between higher-velocity strata overlying lower-velocity strata.

Geothermal gradients. The depths to gas hydrate BSRs and bottom water temperatures have been used in conjunction with gas hydrate phase boundary information (Figure 3) to estimate geothermal gradients and heat flow in oceanic sediment [Shipley et al., 1979; Yamano et al., 1982]. This method has been applied to seismic data from the Blake Outer Ridge, around Central America, and in the Nankai Trough offshore from Japan. The estimated geothermal gradients and heat flow values are consistent with results obtained by conventional means using downhole temperature and surface heat flow measurements. An example of the use of the method comes from offshore Peru where geothermal gradients of $43^\circ$ and $49.5^\circ$C/km were estimated in two areas from BSRs [Kvenvolden and Kastner, 1990], and these results are similar to those obtained by direct measurements [Yamano and Uyeda, 1990].

Quantitative assessments. Multichannel seismic reflection data have been used to analyze several aspects of the zone of gas hydrate stability. For example, quantitative analyses of BSRs have been undertaken with reprocessed seismic records and synthetic seismograms to estimate the amount of gas hydrate at the BSR and the thickness of the underlying free-gas zone for a site offshore from Peru [Miller et al., 1991]. The results indicate that the BSR is laterally discontinuous. A free-gas zone 5.5 to 17 m thick beneath a zone where gas hydrate fills 10% of the porosity is estimated from
BSRs of high amplitude. Where the BSR amplitude is low, the free-gas zone is much thinner than 5.5 m or is absent. In a seismic study of gas hydrate BSRs, Hyndman and Spence [1992] studied BSRs from offshore Vancouver Island of Canada using amplitude-versus-offset and high-resolution velocity analyses as well as modeling of vertical incidence data. The results suggest that above the BSR is a 10- to 30-m-thick high-velocity layer with about 30% of its pore space filled with gas hydrate. Beneath the BSR there is no seismically detectable free gas.

Nature of BSRs. The presence or absence of free gas beneath BSRs is a controversial and as yet unresolved issue. Two models have been proposed to account for gas hydrate formation and the development of BSRs. In the first, methane is assumed to be generated microbially from organic matter within the zone of gas hydrate stability [Claypool and Kaplan, 1974]. Gas hydrate formation takes place concurrent with sedimentation. As the zone of methane hydrate thickens and deepens, its base eventually subsides into a temperature region where the gas hydrate is unstable. In this region free gas can occur, but this gas can migrate back into the overlying zone of gas hydrate stability if suitable migration pathways are available [Kvenvolden and Barnard, 1983a]. A consequence of this model is
that gas hydrates should occur throughout the zone of gas hydrate stability and free gas may or may not be present beneath the BSR.

In the second model, gas hydrates are formed through the removal of methane from rising pore fluids as they pass from below into the gas hydrate stability zone [Hyndman and Davis, 1992]. In this model, most of the methane is generated microbiolally at depths below the stability zone but not at depths sufficient for the formation of thermogenic methane. A consequence of this model is that gas hydrates should be concentrated at the base of the stability zone, i.e., at the BSR, and free gas is not to be expected beneath the BSR.

Tests of these models were possible on Ocean Drilling Program (ODP) legs 141 (offshore from Chile) and 146 (offshore from Vancouver Island) where seismic reflectors indicated by BSRs were purposely cored. Previously the coring of these kinds of reflectors during deep ocean drilling had been avoided because of presumed safety hazards [Ocean Drilling Program, 1986]. Unfortunately, results from leg 141 are equivocal [Behrmann et al., 1992], and appropriate information from leg 146 is not yet available.

**Wire line logs.** In addition to seismic data, geophysical information from wire line well logs, used in combination with each other, can be valuable in the detection and evaluation of gas hydrate intervals [Kvenvolden and Grantz, 1990]. Well logs for gas hydrate studies include caliper, gamma ray, spontaneous potential, resistivity, sonic velocity, and neutron porosity [Goodman, 1980]. Figure 7 illustrates the wire line log responses, including a mud gas log, in one gas hydrate-bearing interval drilled at the NW Eileen State 2 well on the North Slope of Alaska. The resistivity and sonic velocity responses have proved most useful in a comprehensive study of well log data from 445 wells on the North Slope where six gas hydrate-bearing intervals have been identified and mapped in 50 of these wells [Collett et al., 1988]. A comparison between logs from the NW Eileen State well and logs from Deep Sea Drilling Project (DSDP) hole 570 located offshore from Guatemala showed similar characteristics and clearly defined the gas hydrate zones [Mathews, 1986]. Well logs provide a basis for estimation of gas quantity, and, in conjunction with seismic data, hold the key to future worldwide gas hydrate assessment.

**Geochemistry**

**Sources of methane.** In both models for gas hydrate formation discussed previously, the methane is considered to be mainly microbial in origin. This conclusion is based on geochemical investigations of recovered gas hydrates and of hydrocarbon gases from sediment sections known to contain gas hydrates, such as occur offshore from the southeastern United States, northern California, and Peru, and in the Black Sea and at some sites in the Gulf of Mexico (Table 1). These investigations have shown that the molecular compositions of the hydrocarbon gases and the isotopic compositions of methane are consistent with results expected from microbial gas generation processes. Methane in all cases constitutes more than 99% of the hydrocarbon gas mixtures, and the isotopic composition of methane ($\delta^{13}C$) is normally lighter than $-60\%$ relative to the Pee Dee Belemnite (PDB) standard. The molecular and isotopic ranges are diagnostic of gas of microbial origin [Bernard et al., 1976].

In a sedimentary section where methane is being microbiolally generated, there is a carbon isotopic consistency between methane, the product, and carbon dioxide, the immediate precursor, as illustrated in Figure 8. In this example from the Blake Outer Ridge [Galimov and Kvenvolden, 1983], carbon isotopic
### Table 1. Carbon Isotopic Compositions and Concentrations of Methane in Natural Gas Hydrates and Hydrate-Containing Sediment

<table>
<thead>
<tr>
<th>Regions</th>
<th>Type of Sample</th>
<th>CH₄, %</th>
<th>δ¹³C, ‰</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Offshore SE United States,</td>
<td>sediment</td>
<td>&gt;99</td>
<td>−88 to −70</td>
<td>Claypool et al. [1973]</td>
</tr>
<tr>
<td>Blake Outer Ridge</td>
<td>gas hydrate</td>
<td>&gt;99</td>
<td>−68.0</td>
<td>Kvenvolden and Barnard [1983b]; Galimov and Kvenvolden [1983]</td>
</tr>
<tr>
<td>DSDP leg 11</td>
<td></td>
<td></td>
<td></td>
<td>Brooks et al. [1983]</td>
</tr>
<tr>
<td>DSDP leg 76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Offshore Peru, Peru-Chile Trench</td>
<td>sediment</td>
<td>&gt;99</td>
<td>−59 to −55</td>
<td>Kvenvolden and Kastner [1990]</td>
</tr>
<tr>
<td>ODP leg 112</td>
<td>gas hydrate</td>
<td>&gt;99</td>
<td>−65.0, −59.6</td>
<td>Kvenvolden and Kastner [1990]</td>
</tr>
<tr>
<td>Offshore northern California</td>
<td>gas hydrate</td>
<td>&gt;99</td>
<td>−69.1 to −57.6</td>
<td>Brooks et al. [1991]</td>
</tr>
<tr>
<td>Eel River Basin</td>
<td></td>
<td></td>
<td>−63.3, −61.8</td>
<td>Ginsburg et al. [1990]</td>
</tr>
<tr>
<td>Black Sea</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Gulf of Mexico</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DSDP leg 96</td>
<td>sediment</td>
<td>&gt;99</td>
<td>−73.7 to −70.1</td>
<td>Pflaum et al. [1986]</td>
</tr>
<tr>
<td>DSDP leg 96</td>
<td>gas hydrate</td>
<td>&gt;99</td>
<td>−71.3</td>
<td>Pflaum et al. [1986]</td>
</tr>
<tr>
<td>Garden Banks</td>
<td>gas hydrate</td>
<td>&gt;99</td>
<td>−70.4</td>
<td>Brooks et al. [1986]</td>
</tr>
<tr>
<td>Green Canyon</td>
<td>gas hydrate</td>
<td>&gt;99</td>
<td>−69.2, −66.5</td>
<td>Brooks et al. [1986]</td>
</tr>
<tr>
<td>Green Canyon</td>
<td>gas hydrate</td>
<td>62, 74, 78</td>
<td>−44.6, −56.5, −43.2</td>
<td>Brooks et al. [1986]</td>
</tr>
<tr>
<td>Mississippi</td>
<td>gas hydrate</td>
<td>97</td>
<td>−48.2</td>
<td>Brooks et al. [1986]</td>
</tr>
<tr>
<td>Caspian Sea</td>
<td>gas hydrate</td>
<td>59 to 96</td>
<td>−44.8 to −55.7</td>
<td>Ginsburg et al. [1992]</td>
</tr>
<tr>
<td>Offshore Guatemala,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle America Trench</td>
<td></td>
<td></td>
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<tr>
<td>DSDP leg 84</td>
<td>sediment</td>
<td>&gt;99</td>
<td>−71.4 to −39.5</td>
<td>Kvenvolden and McDonald [1985]; Jeffrey et al. [1985]</td>
</tr>
<tr>
<td>DSDP leg 84</td>
<td>gas hydrate</td>
<td>&gt;99</td>
<td>−43.6 to −36.1</td>
<td>Kvenvolden et al. [1984]</td>
</tr>
<tr>
<td>DSDP leg 84</td>
<td>gas hydrate</td>
<td>&gt;99</td>
<td>−46.2 to −40.7</td>
<td>Brooks et al. [1985]</td>
</tr>
</tbody>
</table>

Compositions of methane increase (become heavier) with depth from approximately −94‰ in the uppermost sediment to approximately −66‰ in the deepest sediment, reflecting a systematic but nonlinear depletion of ¹³C with depth. The carbon isotopic compositions of carbon dioxide also increase with depth of sediment from approximately −25‰ to approximately −4‰, showing a depletion of ¹³C that closely parallels the trend of isotopic compositions of methane. The magnitude and parallel distribution of carbon isotopic values for both methane and carbon dioxide are consistent with the concept that the formation of methane resulted from the microbial reduction of carbon dioxide derived from organic matter. The results strongly suggest that the methane in gas hydrates at this site is microbial in origin. Other localities with similar depth trends in carbon isotopic compositions of methane and/or carbon dioxide are offshore from Guatemala [Jeffrey et al., 1985] and offshore from Peru [Kvenvolden and Kastner, 1990] where gas hydrates have also been recovered in DSDP and ODP drilling, respectively.

**Microbial versus thermogenic methane.** Methane in gas hydrates of the Gulf of Mexico [Pflaum et al., 1986; Brooks et al., 1986] is microbial at some sites and thermogenic at others (Table 1). Samples of hydrate hydrocarbon gas from Garden Banks and Green Canyon contain more than 99% methane with carbon isotopic compositions lighter than −60‰. In a different sample from Green Canyon and one from Mississippi Canyon the hydrate hydrocarbon gas is 62 to 78% methane, and this methane has carbon isotopic com-

![Figure 8. Distribution with depth of carbon isotopic compositions of methane and carbon dioxide from site 533, DSDP leg 76, Blake Outer Ridge. Modified from Galimov and Kvenvolden [1983].](image)
positions ranging from −43.2 to 56.5‰. Gas hydrates associated with mud volcanos in the Caspian Sea contain hydrocarbon gases with 59 to 96% methane having carbon isotopic compositions of −44.8 to −57.3‰. These samples fall within the molecular and isotopic compositional field diagnostic of thermogenic methane [Bernard et al., 1976].

Molecular and isotopic compositions of gases associated with gas hydrates found on DSDP leg 84 offshore from Guatemala support either a microbial or thermal source for the methane [Kvenvolden et al., 1984]. Hydrocarbon gases from cores of the deepest sediment samples and from dissociated gas hydrates all contain <99% methane [Kvenvolden and McDonald, 1985]. This observation suggests that the methane is microbial in origin. Although many methane samples had carbon isotopic compositions lighter than −60‰, suggesting a microbial source, at two sites, methane in sediments at depths below 210 m increased in carbon isotopic value to as heavy as about −40‰; methane from a massive gas hydrate sample had a carbon isotopic composition of −44‰ [Jeffrey et al., 1985]. A detailed study of the dissociation of this massive gas hydrate under controlled laboratory conditions showed carbon isotopic compositions of methane ranging from −36.1 to −43.6‰ [Kvenvolden et al., 1984]. These heavy carbon isotopic values are normally considered to reflect thermogenic gas. However, this isotopically heavy methane was accompanied by isotopically very heavy carbon dioxide, +16.3‰ for gaseous carbon dioxide [Jeffrey et al., 1985] and +37‰ for total dissolved carbon dioxide [Claypool et al., 1985].

The isotopically heavy methane could have been derived from the isotopically heavy carbon dioxide by microbial processes similar to those described previously for the Blake Outer Ridge. Alternatively, the isotopically heavy methane could have migrated up from deeper sediments where it was thermally derived from deeply buried organic matter. The association of isotopically heavy methane with isotopically heavy carbon dioxide could be coincidental or controlled by some unknown isotopic interaction between methane and carbon dioxide. The microbial explanation is preferred, but a thermal origin of the methane cannot be ruled out [Kvenvolden et al., 1984].

Implicit in the preceding discussion is that the ultimate source of hydrate methane is buried organic matter which can be altered microbiologically producing carbon dioxide as an intermediate product in the process of methane formation. Deeply buried organic matter, experiencing temperatures from approximately 80° to 150°C, can be altered thermally to produce methane directly [Claypool and Kvenvolden, 1983]. The amount and quality of organic matter present is critical to the methane generation process. Because gas hydrate formation requires amounts of methane that greatly exceed the water solubility of methane, the amount of organic matter needed for gas hydrate formation is very large. Observations on the present organic matter content of gas hydrate containing sediments offshore from Guatemala suggest that 2.0 to 3.5% organic carbon is sufficient if only in situ and not migrated methane is involved [Hesse and Harrison, 1981]; on the Blake Outer Ridge the present organic matter content of sediment associated with gas hydrate occurrence averages about 1% organic carbon [Kvenvolden and Barnard, 1983b]. At the time of gas hydrate formation the organic carbon content in the gas hydrate zone was undoubtedly higher, perhaps double the present amounts.

**Inorganic geochemistry.** During gas hydrate formation, water molecules crystallize into a cubic lattice structure, and, as in the formation of normal hexagonal ice, the hydrate crystals exclude salt ions from the crystal structure. Measurements of chlorinity of samples of gas hydrate water recovered offshore from Guatemala ranged from 0.51 to 3.2‰ [Kvenvolden and McDonald, 1985] and from 1.8 to 8.2‰ for samples from offshore Peru [Kvenvolden and Kastner, 1990]. These samples, all of which were likely contaminated to varying degrees with seawater, had chlorinity values much less than average seawater chlorinity of 19.8‰. During DSDP leg 67 drilling offshore from Guatemala, Hesse and Harrison [1981] first noticed that the chlorinities of pore water samples in the gas hydrate-bearing zones decreased significantly with depth from about 19 to 9‰. Concurrently the oxygen isotopic composition (δ18O relative to Standard Mean Ocean Water (SMOW)) of pore water increased with depth from near zero close to the sediment surface to values as large as +2.6‰ at depth. Oxygen isotopic fractionation of pore water apparently takes place during gas hydrate formation, leading to 18O enrichment with depth of pore fluids recovered after gas hydrate dissociation. This same trend of oxygen isotopic compositions was observed in pore waters of gas hydrate-bearing sediments recovered on ODP leg 112 offshore from Peru [Kvenvolden and Kastner, 1990].

The decreasing chlorinity trends with depth in gas hydrate-bearing sediments as noticed on DSDP leg 67 have been observed in the Blake Outer Ridge (DSDP leg 76) [Kvenvolden and Barnard, 1983b; Jenden and Gieskes, 1983], offshore from Guatemala (DSDP leg 84) [Kvenvolden and McDonald, 1985; Hesse et al., 1985], and offshore from Peru (ODP leg 112) [Kvenvolden and Kastner, 1990]. These chlorinity trends are derived to a large extent from the dissociation of gas hydrates during core recovery. The chloride concentrations are measured on mixtures composed of in situ pore water and dissociated gas hydrate water. Thus a progressive dilution artifact is produced in the pore water that can be squeezed from the sediment with increasing depths. Pore water freshening is a useful signal for the presence of gas hydrates, although it is not a unique signal. Freshwater migration in sediments
neat continents and clay mineral dewatering are also processes that can cause pore waters to have decreased chlorinities. However, where pore water freshening is observed in sediments having large amounts of methane within the depth range of the gas hydrate stability zone, gas hydrates are likely to be present.

Estimates of Methane

Estimates of the amount of methane in gas hydrates are highly speculative and highly varied [Kvenvolden, 1988a]. Although it is generally known that gas hydrates occur worldwide (Figure 4), knowledge of their occurrence is very incomplete, resulting in a wide range of estimates of the amount of methane that is present in them. The Potential Gas Committee [1981] summarized such estimates that show ranges of methane carbon values from a low of 7.5 × 10^15 g in Arctic permafrost regions to a high of 4.1 × 10^21 g in oceanic sediment. Current estimates of the amount of methane carbon in gas hydrates are in rough accord at 10 × 10^18 g [Kvenvolden, 1988a] and 11.4 × 10^18 g [MacDonald, 1990b]. The volume of methane at standard conditions represented by 10^18 g of methane carbon is equal to about a 40-m-thick blanket of methane covering the entire surface of the Earth. The relative magnitude of gas hydrates as a reservoir of organic carbon on the Earth is illustrated in Figure 9. If these estimates of reservoir sizes are correct, then the amount of methane carbon in gas hydrates is a factor of 2 larger than the carbon present in all known fossil fuel deposits (coal, oil, and natural gas).

ASPECTS OF GAS HYDRATES

Chemists have known about gas hydrates since the early part of the 19th century (reviewed by Sloan [1990]). The petroleum industry became aware of these substances in the 1930s when gas hydrate formation was discovered to be the cause of pipeline blockage during transmission of natural gas [Hammerschmidt, 1934]. In the 1960s naturally occurring gas hydrates were found in the Siberian Messoyakha gas field (reviewed by Makogon [1981]), and in the 1970s it was recognized that gas hydrates occur naturally not only in polar continental regions but also in shallow, deepwater sediment of oceanic regions at outer continental margins [Claypool and Kaplan, 1974]. Kvenvolden and McMenamin [1980] reviewed the geological occurrences of natural gas hydrates. Since the time of this review it has become increasingly evident that naturally occurring gas hydrates are significant components of the shallow geosphere and are of societal concern in at least three major ways: resource, hazard, and climate.

Potential Energy Resource

Two factors make gas hydrates attractive as a potential energy resource. First is the enormous amount of methane that is apparently sequestered within clathrate structures at shallow sediment depths within 2000 m of the Earth’s surface. Second is the wide geographical distribution of the gas hydrates (Figure 4). The energy density (volume of methane at standard conditions per volume of rock) of methane hydrates is 10 times greater than the energy density of other unconventional sources of gas, such as coal beds, tight sands, black shales, and deep aquifers, and 2 to 5 times greater than the energy density of conventional natural gas [MacDonald, 1990a].

Production methods. Although naturally occurring gas hydrates were recognized in the 1960s, the gas industry has been slow to develop methodologies to recover methane from these substances. Three principal methods are being considered: thermal stimulation, depressurization, and inhibitor injection [Holder et al., 1984]. In thermal stimulation, thermal energy is released into the gas hydrate-bearing strata in order to increase the local temperature enough to cause gas hydrates to dissociate. In depressurization, the pressure in the gas hydrate deposit is lowered sufficiently to cause gas hydrate dissociation; heat energy for the process comes from the Earth’s interior (geothermal heat flow). Injection of inhibitors such as methanol shifts the pressure-temperature equilibrium so that the gas hydrates are no longer stable at in situ pressure-temperature conditions. Of these three production methodologies, depressurization combined with hot-water injection appears to be the most practical where free gas is trapped beneath the gas hydrate [Holder et al., 1984]. That free gas is trapped beneath the gas
hydrate has yet to be established with certainty as discussed previously. Gas hydrates will become a potential energy resource when it can be shown that the energy required to release methane from the hydrate is significantly less than the thermal energy of the methane that can be recovered from the dissociated gas hydrate deposits. Circulation of warm surface water into gas hydrate deposits and horizontal drilling techniques provide possible future approaches to the exploitation of hydrated methane.

**Recovery of methane.** The production of methane from gas hydrates requires that the deposit occur in geologic contexts wherein the elements of a conventional gas deposit are present; that is, in association with a reservoir of adequate porosity and permeability, with a methane source, and with a seal to form a trap. Dissociated gas hydrate can serve as one source of methane; migrated methane from deep below the gas-hydrate zone is another possible source. The ability of the gas hydrate to act as a seal, however, has not been well established. *Miller et al.* [1991] present geophysical evidence from the Blake Outer Ridge that suggests gas hydrates are trapping gas beneath the BSR (Figure 6). Examples of possible traps caused by gas hydrates are shown in Figure 10. These examples assume that the gas hydrate-containing interval is impermeable and that free gas can be trapped. The free gas below the gas hydrate has migrated up from depth and is likely thermogenic. As methane is removed by production, however, the gas hydrate seal will begin to decompose, providing more producible methane. Thus the seal becomes a source. Two of the trapping situations in Figure 10 are in effect structural, caused by the domal or anticlinal shapes of the gas hydrate layer. The other trap is stratigraphic where gas-bearing strata are sealed at their updip ends by the presence of gas hydrates [*Dillon et al.*, 1980].

Development of the Messoyakha gas field in western Siberia during the past 25 years has proven that methane can be recovered from naturally occurring gas hydrates [*Makogon*, 1981], but the methanol injection methods used for production proved to be prohibitively expensive. Recovery of gas hydrates in pressurized core barrels at the Arco-Exxon NW Eileen State 2 wildcat well on the North Slope of Alaska confirmed the presence of gas hydrates in the region of the Prudhoe Bay and Kuparuk River oil fields [*Kvenvolden and McMenamin*, 1980]. It has been estimated that approximately $1.1 \times 10^{12}$ m$^3$ of methane ($440 \times 10^{12}$ g methane carbon) are present in gas hydrates of this region [*Collett*, 1992]. This amount of methane is approximately 1.4 times the conventionally reser-voired methane of the same region but is only 13% of the conventional U.S. gas reserves (Figure 11). If methane from gas hydrates is ever to be recovered commercially in the United States, larger accumulations will have to be identified and exploited. Initial production, however, is likely to come from the North Slope of Alaska where the industrial infrastructure for gas handling is already in place. Methane first produced from gas hydrates on the North Slope will likely be used for repressurization of waning oil fields rather than as a source of fuel. Although methane from gas hydrates should be considered a potential energy resource, wide-scale recovery of methane from gas hydrates will probably not be accomplished until the 21st century [*Sloan*, 1990].

**Geologic Hazard**

Before gas hydrates form in normal geologic settings, vast quantities of methane and water are free to migrate within the interstitial pore spaces of consolidating sediment. During gas hydrate formation, methane and water become immobilized as a solid, restricting pore space and retarding the migration of fluids. Solid water rather than liquid water occupies the pore spaces, and the sedimentological processes of consolidation and mineral cementation are greatly inhibited, although gas hydrates themselves can act as metasta-

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**Figure 10.** Schematic diagrams of geological situations in which gas hydrates serve as seals forming traps for methane. Developed from *Dillon et al.* [1980].

**Figure 11.** Comparison of the amount of methane estimated to be present in the region of the Prudhoe Bay and Kuparuk River oil fields with the amount of conventionally reser-voired methane of the same region and amount of methane in U.S. conventional gas reserves.
ble cementation (bonding) agents. The permeability of the sediment to gases and liquids decreases as more gas hydrate forms. Eventually, gas hydrates may occupy much of the sedimentary section within the zone of gas hydrate stability. Continued sedimentation leads to deeper burial of the gas hydrate. Finally, the gas hydrate will be buried so deeply that temperatures at the base of the stability zone will be reached at which the gas hydrates are no longer stable. The solid gas-water mixture (i.e., the gas hydrate) will become a liquid gas-water mixture. Thus the basal zone of the gas hydrate becomes underconsolidated, possibly overpressured due to the newly released gas, leading to a zone of weakness (low shear strength) where failure could be triggered by gravitational loading or seismic disturbances, and submarine landslides result [McIver, 1982].

The same conditions that cause gas hydrate dissociation during continued sedimentation can also be brought about by the lowering of sea level or by an increase in bottom water temperatures. These processes change the in situ pressure or temperature regime. In adjusting to the new pressure-temperature conditions, the gas hydrates dissociate producing an enhanced fluidized layer at the base of the gas hydrate zone. Submarine slope failure can follow giving rise to debris flows, slumps, and slides, accompanied by the release of methane gas into the water column. A situation illustrating submarine slope failure is shown in Figure 12.

Examples. The possible connection between gas hydrate boundaries and submarine slide and slump surfaces was first recognized by McIver [1977], and several possible examples have been described later. These examples include surficial slides and slumps on the continental slope and rise of South West Africa [Summerhayes et al., 1979], slumps on the U.S. Atlantic continental slope [Carpenter, 1981], large submarine slides on the Norwegian continental margin [Jansen et al., 1987; Bugge et al., 1987], sediment blocks on the seafloor in British Columbia fjords [Bornhold and Prior, 1989], and massive bedding-plane slides and rotational slumps on the Alaskan Beaufort Sea continental margin [Kayen and Lee, 1991]. In the Caspian Sea [Ginsburg et al., 1992] and offshore from north Panama [Reed et al., 1990], submarine mud volcanoes, another kind of geohazard, have also been attributed to the release of gas from gas hydrates.

Periodic Pleistocene eustatic sea level transgressions and regressions provide a mechanism to account for the waxing and waning of submarine gas hydrates. During the last Pleistocene regression, sea level lowered approximately 100 m between approximately 28 and 17 ka, resulting in a reduction of total stress acting on the seafloor of about 1000 kPa [Kayen and Lee, 1991]. The reduction in the total pressure initiates dissociation at the base of the gas hydrates, releasing excess methane and water. Failure follows on moderate slopes unless the increased fluid pressures can be adequately vented. On the Beaufort Sea continental slope is a zone of massive slides and slumps that coincides with a region of sediment inferred from seismic reflection studies to contain gas hydrates (Figure 13). Fluctuations in global climate, reflected in Pleistocene sea level lowering, likely caused these submarine landslides and perhaps caused other slides on other continental margins where gas hydrates are present [Kayen and Lee, 1991].

Local geohazards. Besides the global scale geologic hazards created by destabilized gas hydrates, local scale hazards also result when the pressure-temperature conditions of gas hydrates are perturbed anthropogenically, for example, during drilling and production operations. These operations can result in hazardous situations such as uncontrolled gas releases, casing failures, and well site subsidence, if appropriate precautions are not taken to minimize the disturbance to the gas hydrate deposit [Yakushev and Collett, 1992].

Global Climate Change

Methane is an important trace components of the atmosphere, having a current concentration of about 4.9 \times 10^{15} \text{g} (3.7 \times 10^{15} \text{g methane carbon}), approximately one half of the minimum amount of methane estimated by the Potential Gas Committee [1981] to occur in gas hydrates of Arctic permafrost regions. The concentration of atmospheric methane is increasing at a rate of almost 1.0\% \text{yr}^{-1} [Watson et al., 1990]. Because methane is radiatively active, it is a "greenhouse" gas that has a global warming potential 20 times larger than an equivalent weight of carbon diox-
Figure 13. Map of the continental margin of the Beaufort Sea offshore from Alaska showing the coincident regions of large landslides and gas hydrates. Adapted from Kayen and Lee [1991].

ide when integrated over a 100-yr span of time [Shine et al., 1990]. The Earth’s atmosphere has a wide variety of sources and sinks for methane [Cicerone and Oremland, 1988], including gas hydrates, which exist in metastable equilibrium with their environment and are affected by changes in pressure and temperature. The amount of methane that is trapped in gas hydrates onshore and offshore is perhaps 3000 times the amount in the atmosphere; a large release of methane from this source could have a significant impact on atmospheric composition and thus on the radiative properties of the atmosphere that affect global climate [MacDonald, 1990b].

Warming and cooling. Pleistocene global climate changes likely caused methane release from gas hydrate deposits as suggested previously in Figure 12. However, the opposite may also be true. Methane released from gas hydrates may in turn have caused changes in global climate. The arguments go as follows: During global warming, glaciers and ice caps melt, contributing water to the oceans; oceans also thermally expand, and these factors cause a rise in sea level. This sea level rise causes an increase in subsurface hydrostatic pressure that stabilizes submarine gas hydrate deposits on outer continental margins and on polar continental shelves. Meanwhile, onshore the increasing air temperatures eventually destabilize continental gas hydrates at time scales of hundreds to thousands of years, releasing methane that may reach the atmosphere. Water temperatures also increase during global warming, although deepwater temperatures on the outer continental margins probably do not change significantly because of the heat capacity of the large mass of water involved. Thus for deepwater gas hydrates on outer continental margins (water depths greater than 300 to 500 m), the effects on hydrate stability caused by increasing sea level outweigh the destabilizing effects of any possible increase in bottom water temperature.

The same results are not true for the gas hydrate deposits underlying polar continental shelves. Increasing air temperatures increase shallow shelfal water temperatures. More important is the increase in submarine bottom surface temperatures caused by the transgression of the polar ocean over the exposed, colder continental shelf surface as sea level rises. Flooding of the shelf by relatively warm water offsets the effects of increasing pressure due to the sea level rise. Gas hydrates of the polar continental shelves are thus destabilized, releasing methane. Therefore, during global warming, deep-sea gas hydrates become more stable, but gas hydrates of polar continents and continental shelves are destabilized, leading to methane release over long time scales [Kvenvolden, 1988b]. Methane reaching the atmosphere from these sources contributes to the global warming trend.

During a global cooling cycle the whole system reverses. Glaciers and ice caps grow, removing water from the oceans, and oceans thermally contract. The result is a eustatic fall in sea level and regression of the oceans from continental shelves. During regression the pressure on gas hydrates decreases, and the gas hydrates become unstable. As polar continental and exposed continental shelves become colder, the cold temperatures eventually stabilize the buried gas hydrate deposits, offsetting the effects of decreasing pressures on the gas hydrates. In polar regions, continental gas hydrate deposits buried under an increas-
CLIMATE CHANGE

Figure 14. Diagrams illustrating how gas hydrate decomposition may affect glacial cycles: (a) continental gas hydrates (positive environmental feedback loop); (b) oceanic gas hydrates (negative environmental feedback loop).

...ing ice load of advancing glaciers experience increased pressure and further stabilization. As sea level falls, only the deepwater gas hydrates of continental slopes and rises become unstable, releasing methane that may reach the atmosphere. To get to the atmosphere, however, the methane must escape from the sediment and traverse a long water column without being dissolved and oxidized. Thus during global warming and cooling, that is, during interglacial and glacial climates, gas hydrate deposits should respond to surface pressure and temperature changes; however, the extent of influence that methane from gas hydrates has on global climate is still very uncertain.

Past climate change. Nevertheless, interesting ideas have been proposed to explain the role of gas hydrates in global climate change. For example, Nisbet [1990] suggests that methane from continental gas hydrates contributed to the rapid rise in atmospheric methane, carbon dioxide, and global temperature at the end of the last major glaciation about 13.5 ka ago. The basic elements of his idea are shown in Figure 14a, where polar continental gas hydrate deposits are destabilized by pressure reduction of melting ice sheets and temperature increases. The resulting warming provides a strong positive feedback that amplifies methane emissions and ultimately helps to end the ice age. Taken to extremes, however, this situation would lead to uncontrolled methane release from gas hydrates and consequent enhanced global warming, but evidence from the Vostok ice core shows that no uncontrolled release of methane to the atmosphere has taken place at least during the last 160 ka [Chappellaz et al., 1990].

A different situation has been proposed by Paull et al. [1991]. They suggest that outer continental margin gas hydrate deposits release methane during a falling sea level, that is, during global cooling. The resulting decrease in pressure causes these gas hydrates to dissociate. The released methane enhances global warming and triggers deglaciation (Figure 14b). Thus methane derived from outer continental margin gas hydrate deposits may be a important factor in limiting the extent of glaciation during a glacial cycle.

Present climate change. As rich as these ideas are, they are all speculative. How gas hydrates behave in the present climate regime is not known. Greater understanding of the present is needed to unravel the past and to predict the future. I have suggested that gas hydrate deposits of the polar continental shelves are presently most vulnerable to climate change [Kvenvolden, 1988b]. These areally extensive shelves, formerly exposed to very cold surface temperatures (−10°C to −20°C) have been and are being transgressed by a much warmer polar ocean (−0°C). The polar shelf surface therefore has experienced a +10°C or more change in temperature over at least the past 10,000 year. Although pressure on shelfal gas hydrates has increased owing to a rise in sea level of about 100 m, this pressure increase that tends to stabilize the gas hydrates is more than offset by the large temperature increase that destabilizes the gas hydrates. The amount of methane released by this process has been estimated to be about 3 × 1012 g yr−1 of methane carbon [Kvenvolden, 1991] or about 1% of all current sources of atmospheric methane (Figure 15). If this suggestion and estimate are correct, then escape of methane from gas hydrate deposits of polar continental shelves should be observable.

A test of this idea was conducted on the continental shelf north from Oliktok Point, Alaska (Figure 16) [Kvenvolden et al., 1992]. We discovered that methane

Figure 15. Distribution of annual methane release rates for identified sources. Adapted from Cicerone and Oremland [1988].
concentrations in the water under the ice (Figure 16) are 6 to 28 times greater than the atmospheric equilibrium concentration of about 4 nM. These preliminary data suggest that there is a submarine source of methane on the continental shelf and that methane apparently is trapped by the ice. Questions to be answered include whether the methane is actually coming from destabilized gas hydrate deposits and whether the observed methane contributes to the seasonal cycle of atmospheric methane.

CONCLUSIONS

From a geological perspective, gas hydrates are an important feature of the shallow geosphere. If current estimates are correct, gas hydrates contain more potential fossil fuel energy than is present in conventional oil, gas, and coal deposits. Uncertain, however, is the portion of this potential energy source that can actually be exploited. Because of unsolved technological problems in producing methane from gas hydrates, wide-scale recovery of methane from these substances probably will not take place until sometime in the 21st century.

Besides being an unconventional potential source of methane, gas hydrates are also geological agents that affect the properties of sediments. For example, gas hydrates alter (1) physical properties, such as shear strength, porosity, and permeability, (2) geophysical properties, such as acoustic velocity and resistivity, and (3) geochemical properties, such as fluid composition and movement. The change in physical properties and flow regimes caused by gas hydrates leads to geologic hazards in the form of sediment failures particularly on the seafloor. Many submarine slumps and slides are likely caused by gas hydrate decomposition.

Because methane is both sequestered and released from gas hydrates, depending on the pressure-temperature regime, the possibility exists that methane from gas hydrates can reach the atmosphere. Because methane is a strong "greenhouse" gas, the methane from gas hydrates may influence global climate, past, present, and future, but the extent of this influence has not yet been determined even for the present climatic cycle.

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