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REVIEW PAPER

A review of the geochemistry of methane in natural gas hydrate

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Abstract—The largest accumulations on Earth of natural gas are in the form of gas hydrate, found mainly offshore in outer continental margin sediment and, to a lesser extent, in polar regions commonly associated with permafrost. Measurements of hydrocarbon gas compositions and of carbon-isotopic compositions of methane from natural gas hydrate samples, collected in subaquatic settings from around the world, suggest that methane guest molecules in the water clathrate structures are mainly derived by the microbial reduction of CO_2 from sedimentary organic matter. Typically, these hydrocarbon gases are composed of >99% methane, with carbon-isotopic compositions ($\delta^{13}C_{PDB}$) ranging from − 57 to − 73‰. In only two regions, the Gulf of Mexico and the Caspian Sea, has mainly thermogenic methane been found in gas hydrate. There, hydrocarbon gases have methane contents ranging from 21 to 97%, with $\delta^{13}C$ values ranging from − 29 to − 57‰. At a few locations, where the gas hydrate contains a mixture of microbial and thermal methane, microbial methane is always dominant. Continental gas hydrate, identified in Alaska and Russia, also has hydrocarbon gases composed of > 99% methane, with carbon-isotopic compositions ranging from − 41 to − 49‰. These gas hydrate deposits also contain a mixture of microbial and thermal methane, with thermal methane likely to be dominant. Published by Elsevier Science Ltd

Key words—gas hydrate, methane, hydrocarbon gases, carbon-isotopic composition, microbial, thermal

INTRODUCTION

Large amounts of methane, the principal component of natural gas, occur in the form of solid gas hydrate in sediment and sedimentary rock within ~2000 m of the Earth's surface in polar and deep-water regions. In gas hydrate, water crystallizes in the cubic crystallographic system where the lattice contains cages (a clathrate structure) that are each large enough to accommodate a molecule of gas. The lattices are stabilized mainly by hydrogen bonding with energies similar to normal hexagonal ice. Two clathrate structures, I and II, have been recognized in the laboratory since about 1952 (summarized in Davidson, 1973), and a third structure, H, has been discovered later in the laboratory (Ripmeester *et al.*, 1987) and observed to occur naturally in the Gulf of Mexico (Sassen and MacDonald, 1994). In structure I, the cages are arranged in body-centered packing and are just large enough to include small hydrocarbons, methane (C_1) and ethane (C_2), and non-hydrocarbons such as N_2, CO_2, and H_2S. In structure II, diamond packing is present; not only can C_1 and C_2 be included in the cages, but larger cages in this structure can also be occupied by hydrocarbons such as propane (C_3) and isobutane (iC_4). Structure H has even larger cages and can accommodate molecules with molecular diameters exceeding that of iC_4. Structure II and structure H hydrate are more stable than structure I hydrate.

Naturally occurring gas hydrate is commonly expected to be structure I unless the methane in the natural gas is relatively enriched in higher molecular weight hydrocarbon gases. The stability conditions of structure I hydrate do not depend greatly on the composition of the natural gas, which is mainly methane, unless the gas is rich in H_2S, whereas structure II hydrate is more dependent on gas composition. Because of these reasons, as outlined by Davidson *et al.* (1978), discussion of the stability conditions for natural gas hydrate have generally referred to structure I, which is essentially a methane hydrate. The maximum amount of methane that can occur in a structure I methane hydrate is fixed by the clathrate geometry at $CH_4 \bullet 5.75H_2O$. It follows then that one volume of methane hydrate can contain as much as 164 volumes of methane under standard conditions (Davidson *et al.*, 1978). Because all cages are usually not occupied, the volume of methane in naturally occurring gas hydrate is expected to be less.

The stability of gas hydrate in nature is controlled by an interrelation among the factors of temperature, pressure, and gas–water composition that restricts the occurrence of gas hydrate to the shallow lithosphere (depths below the surface not exceeding ~2000 m). The interrelation among these factors, in turn, further restricts the occurrence of gas hydrate to continental and continental shelf sediment of polar regions, where surface temperatures are slightly higher to less than ~0°C, and to oceanic (aquatic) sediment worldwide, where bottom water temperatures are ~2°C (~0°C in bottom water of polar oceans) and water depths exceed ~300 m. The worldwide occurrence of known and inferred gas hydrate is shown in Fig. 1 (Kvenvolden, 1993).

Samples of gas hydrate were recovered on land in 1972 from the west end of the Prudhoe Bay oil field in Alaska (reviewed by Kvenvolden and McMenamin, 1980; discussed in detail by Collett, 1993a) and at 14 subaquatic locations (Kvenvolden *et al.*, 1993), providing irrefutable evidence that gas hydrate occurs as a natural substance in a variety of geologic settings. Most of these subaquatic samples come from sediment in active (convergent) margins, although passive (divergent) margins are also appropriate settings for gas hydrate occurrence (Kvenvolden, 1985). Of particular interest to the present paper are those recoveries of gas hydrate where the geochemistry of the methane and related hydrate has been studied. The main focus is on (1) the amount of C_1 in the hydrocarbon gas mixtures, composed of C_1, C_2, and C_3 and often described by the volumetric ratio $C_1/(C_2 + C_3)$, which for simplicity is defined here as "R", and (2) the carbon-isotopic composition of C_1 (given in δ notation relative to the PeeDee Belemnite standard in ‰). These data are the most commonly reported and serve as a basis for comparison of gas hydrate samples. This paper compiles and reviews this geochemical information in order to assess the possible sources of methane and the processes involved in gas hydrate formation.

AMOUNT OF METHANE AND ITS RESOURCE POTENTIAL

One reason for the increasing interest in natural gas hydrate is that large amounts of economically producible methane may exist in hydrate form within the shallow geosphere (Kvenvolden, 1993; Collett, 1993a). Estimates of the amount of methane in gas hydrate are highly speculative and vary widely (Kvenvolden, 1988). Although it is generally known that gas hydrate occurs worldwide (Fig. 1), such knowledge is very incomplete, resulting in a wide range of estimates from a minimum of 1.4×10^{13} m^3 of methane at standard conditions in gas hydrate of permafrost regions to a maximum of 7.6×10^{18} m^3 of methane in gas hydrate of oceanic regions (Potential Gas Committee, 1981). Factors making estimates of methane in gas hydrate difficult include the non-applicability of conventional reservoir evaluation methods, lack of accurate mapping methods, paucity of samples, and a general ignorance of gas hydrate occurrence on both regional and worldwide scales. Current estimates of the total amount of methane in natural gas hydrate are in rough accord at ~2.0×10^{16} m^3 (Kvenvolden, 1988; MacDonald, 1990). If these estimates are correct, then the amount of methane carbon in gas hydrate may be twice as large as the carbon present in all

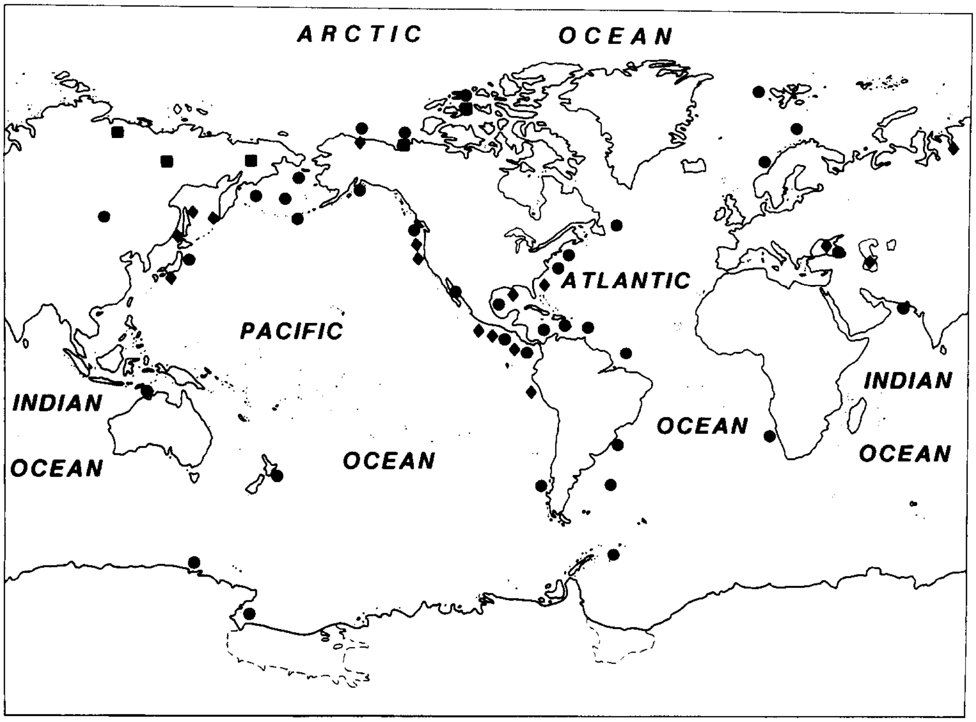

Fig. 1. Worldwide locations of known and inferred gas hydrate in oceanic (aquatic) sediment (circles) and in continental (permafrost) regions (squares), and locations where gas hydrates have been observed (diamonds). Modified from Kvenvolden (1993).

known fossil fuel (coal, crude oil, and natural gas) deposits (Kvenvolden, 1988).

These estimates of the amount of methane in gas hydrate need to be improved in order to evaluate better its energy resource potential. Two factors make gas hydrate particularly attractive from the energy point of view (Kvenvolden, 1993). First, the apparently large amount of methane in gas hydrate is present at shallow depths within 2000 m of the surface. Second, the gas hydrate has a worldwide distribution. However, most gas hydrate occurs in oceanic sediment in water deeper than 300 m which complicates any methane recovery schemes, and reservoir properties of oceanic occurrences of gas hydrate are generally unknown. Continental gas hydrate provides a better opportunity for resource evaluation. In fact, gas hydrate on the North Slope of Alaska offers a particularly good target for resource evaluation (Collett, 1993a). For gas hydrate to meet the expectations suggested by the estimated methane content, however, oceanic gas hydrate will eventually have to be proven to be a producible source of methane. Sloan (1990) suggested that wide-scale recovery of methane from gas hydrate will probably not occur until sometime in the next century.

CONTINENTAL GAS HYDRATE

Naturally occurring gas hydrate was first recognized in the 1960s in polar continental settings in Russia (reviewed by Makogon, 1981); however, in the Messoyakha field of western Siberia its recognition was based on engineering and geophysical measurements, not on direct sampling of gas hydrate. Nevertheless, gas composition from drill-stem tests at the Messoyakha field within the inferred gas hydrate interval was determined to be: C_1, 98.6%; C_2, 0.1%; C_3, 0.1%; CO_2, 0.5%; and N_2, 0.7% (summarized in Sloan, 1990). The hydrocarbon gas ratio of $C_1/(C_2 + C_3)$, that is the *R* value, is about 490, and C_1 composes 99.8% of the hydrocarbon gas mixture. On the basis of work by Collett (1993b) the carbon-isotopic composition of this methane is likely to fall within the range of − 41.0 to − 48‰. The Messoyakha field is the only known example where gas hydrate has been a producible source of methane; however, production of gas from gas hydrate at this field is currently shut in (Collett, 1992). Because the Messoyakha field is often cited as an example of successful gas hydrate production of methane (Makogon *et al.*, 1971; Makogon, 1981; Collett, 1992, 1993b), it is important to understand the occurrence well in order to evaluate realistically the potential of natural gas hydrate as an energy resource elsewhere.

The first confirmation that gas hydrate occurs in polar continental sediment was obtained from two pressure cores (577–580 m and 664–667 m deep) at the Arco-Exxon N.W. Eileen State No. 2 wildcat well on the North Slope of Alaska at the west end of Prudhoe Bay oil field (Collett, 1993a). When the cores were recovered, it was uncertain whether or not they contained gas hydrate or only sediment with pressurized natural gas. Results of pressure-core tests, similar to those described by Hunt (1979), confirmed, however, that gas hydrate was present. The sampled gas contained 87.0–99.2% C_1, and the rest of the gas was mostly N_2, with only trace amounts of C_2 and C_3 (Collett, 1993b); a drill-stem test within the gas hydrate interval (663–671 m) showed 92.8% C_1, 0.01–0.02% C_2, and 7.2% N_2, with a hydrocarbon gas ratio (*R* value) of ~4600.

In a second well on the North Slope of Alaska (Kuparuk River Unit 2D-15) a 30 m thick interval (1230–1328 m) was inferred to contain gas hydrate on the basis of well-log interpretations (Collett *et al.*, 1990), but no gas hydrate was recovered or collected. Nevertheless, geochemical measurements of gas collected from the inferred gas hydrate interval showed an average *R* value of 5900 and an average methane $\delta^{13}C$ value of − 49.5‰.

SUBAQUATIC GAS HYDRATE FROM DEEP OCEANIC DRILLING

Much of our knowledge of the geochemistry of methane in natural gas hydrate results from the opportunities afforded by the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP). Through these major international programs oceanic gas hydrate has been discovered and sampled in the sediment of outer continental margins around the world. Gas hydrate samples were recovered on DSDP Legs 66, 67, 76, 84, and 96, and on ODP Legs 112, 127, 131 and 146. A description of each of these discoveries follows, and the results are listed in Table 1.

DSDP Leg 66—Pacific continental margin, offshore southern Mexico, Middle America Trench

The first quantitative evidence for naturally occurring, deep sea gas hydrate was found at three sites (490, 491, 492) on Leg 66 (Shipley and Didyk, 1982). The gas hydrate occurred as ice-like inclusions or, more commonly, as hydrate-cemented volcanic ash and fine sand interlayered with mud. Gas samples were obtained directly and analyzed from decomposing gas hydrate samples from Sites 490 and 492 (Table 1). Although gas hydrate was recovered at Site 491, gas analyses were not made directly on the samples, but instead, on gas recovered from the core liner in which the samples were later found. The analysis of this core liner gas did not differ significantly from the direct analyses of gas hydrate; however, the results are omitted from Table 1, which is restricted to the results obtained from directly analyzed gas hydrate samples. Methane was the dominant hydrocarbon gas in these samples, with *R* values ranging from 540 to 1200. One ice-like

Table 1. Composition of gases from natural gas hydrate recovered by DSDP and ODP

Leg	Site	WD[1] (m)	SD[2] (mbsf)	C_1[3] % of gas	C_2[3] % of gas	C_3[3] % of gas	C_1[4] % of HC	*R*[5]	$\delta^{13}C$ (‰)	CO_2 (%)	Comment	References
66	490	1761	140	76.8	na	na	99+?	na	na	23	Icelike inclusion	Shipley and Didyk, 1982
	492	1935	141	99.6	0.18	0.0050	99.8	540	na	0.2	Hydrate-cemented volcanic ash	
	492	1935	170	99.7	0.08	0.0037	99.9	1200	na	0.2	Hydrate-cemented volcanic ash	
67	497	2347	368	90.4	0.0501	nd	99.9	1800	na	0.1	Icelike solid	Harrison and Curiale, 1982
	498	5478	310	83.0	0.1990	0.00042	99.8	420	na	0.2	Hydrate-cemented vitric sand	
76	533	3191	238	36	0.0123	0.0002	99.9	2900	−68.0	0.5	Matlike white crystals in sediment	Kvenvolden and Barnard, 1983; Brooks *et al.*, 1983
84	565	3099	319	89	0.0440	0.0005	99.9	2000	na	0.03	Icelike frothing solid in stiff mud	Kvenvolden and McDonald, 1985
	568	2010	404	64	0.2200	0.00003	99.8	530	na	0.1	Icelike solid in tuffaceous mudstone	
	570	1698	192	44	0.0390	0.00009	99.9	1100	na	0.3	Hydrate-laminated ash	
	570	1698	249	58	0.2600	0.0079	99.5	220	na	0.3	Icelike solid in dolomite fracture	
	570	1698	~263	75	0.0890	0.0011	99.9	840	na	0.2	Icelike solid in mudstone fracture	
	570	1698	249	93.9	0.2300	na	99.7	410	−41.4	0.3	Massive gas hydrate	Kvenvolden *et al.*, 1984
	570	1698	249	61.3	0.1400	0.0040	99.8	430	−42.9	0.3	Massive gas hydrate	Brooks *et al.*, 1985
96	618	2412	27	39.5	0.13	0.11	99.4	159	−71.3	0.09	Scattered white crystals associated with sand	Pflaum *et al.*, 1986
112	685	5070	166	95	0.0039	0.0028	99.9	14200	−65.0	nd	Icelike solids with mud	Kvenvolden and Kastner, 1990
	688	3820	141	91.5	0.0022	nd	99.9	42000	−59.6	nd	Hydrate-cemented mud	
127	796	2571	90	~33	0.0115	na	99.9	2900	na	nd	Icelike solid and hydrate-cemented sand	Shipboard Scientific Party, 1990, p. 259
131	808	4684	90–140	na	na	na	na	na	na	nd	Hydrate-cemented sand	Shipboard Scientific Party, 1991, p. 143
146	892	670	2~20	42.5	0.02	na	99.9	2100	−64.5	0.06	Platy crystals and thin layers, ~10% H_2S *in gas*	Kastner *et al.*, 1993; Kastner, *pers. commun.* (1993).

[1]Water Depth; [2]Subbottom Depth; [3]As reported; [4]% of hydrocarbon gases; [5]Ratio of $C_1/(C_2 + C_3)$; na, not analyzed; nd, not detected

inclusion had a surprisingly high CO_2 content of 23%, whereas two samples of hydrate-cemented volcanic ash contained only 0.2% CO_2, consistent with the values reported from most other samples obtained elsewhere (Table 1). The occurrence of CO_2 in natural gas hydrate needs to be better understood. The gas hydrate recovered during Leg 66 came from the upper part of the accretionary zone in the Middle America Trench within unconsolidated sediment, generally associated with porous zones of volcanic ash or sand layers interbedded with layers of mud or mudstone (Shipley and Didyk, 1982).

DSDP Leg 67—Pacific continental margin, offshore Guatemala, Middle America Trench

With the discovery of gas hydrate during Leg 67 (Harrison and Curiale, 1982), it became evident that continental slope sediment of the Middle America Trench is rich in gas hydrate deposits. As on Leg 66, the gas hydrate of Leg 67 occurred as ice-like solids and as hydrate-cemented volcanic sand. Analyses were reported on cores that had been forcibly ejected from core liners and from gas pockets. Two samples of gas hydrate from Sites 497 and 498 were directly measured; hydrocarbon gas compositions were similar to the results obtained on Leg 66 (Table 1). The dominant hydrocarbon gas was methane, with R values ranging from 410 to 1800 and CO_2 contents ranging from 0.1 to 0.2%. The gas hydrate recovered during Leg 67 was invariably associated with high porosity sediment of the middle and lower continental slope adjacent to the Middle America Trench.

DSDP Leg 76—Atlantic continental margin, Blake Outer Ridge, offshore southeastern United States

Although no gas hydrate samples were recovered during drilling at three sites (102, 103, 104) on the Blake Outer Ridge on Leg 11 (Ewing and Hollister, 1972), the occurrence of gas hydrate in sediment at these sites had been previously suggested by Stoll *et al.* (1971) and discussed later by Ewing and Hollister (1972) and Lancelot and Ewing (1972), on the basis of a concurrence of geophysical and geochemical evidence. These ideas proved correct when a sample of gas hydrate was recovered on Leg 76 at Site 533 in 1980. This sample consisted of a few centimeter-thick layer of frothy sediment containing mat-like white crystals that quickly disappeared (Kvenvolden and Barnard, 1983). Analyses of the sample showed that methane was the dominant hydrocarbon gas with an R value of 2900 (Table 1). The total gas mixture contained about 0.5% CO_2. The finding of gas hydrate on Leg 76 confirmed that gas hydrate can occur in a passive margin setting, as well as in an active margin setting where most samples have thus far been found.

DSDP Leg 84—Pacific continental margin, offshore Central America, Middle America Trench.

Coring on Leg 84 at Sites 568 and 570 confirmed what was already known about gas hydrate occurrence offshore Guatemala from Leg 67, but also extended knowledge of gas hydrate to include its presence offshore Costa Rica at Site 565. Recovered gas hydrate appeared as solid pieces of white, ice-like material occupying fractures in mudstone, or as cement in coarse-grained sediment that exhibited rapid outgassing (Kvenvolden and McDonald, 1985). Possibly most surprising was the unexpected recovery of a 1.05 m long core of massive gas hydrate at Site 570, leading to a detailed shore-based study of gas geochemistry (Kvenvolden *et al.*, 1984). Shipboard analyses of samples (Table 1) again showed, as on Legs 66 and 67, that the dominant hydrocarbon gas was methane, with R values ranging from 220 to 2000, and CO_2 contents ranging from 0.03 to 0.3%. The results obtained from Legs 66, 67, and 84 show that gas hydrate is common in landward slope sediment of the active margin of the Middle America Trench from Mexico to Costa Rica, at water depths ranging from ~1700 to 5500 m.

DSDP Leg 96—Gulf Coast continental margin, Orca Basin, Gulf of Mexico

Gas hydrate was observed and sampled in the Orca Basin at Site 618 between 20 and 40 m subbottom (Pflaum *et al.*, 1986). The samples consisted of scattered white crystals, a few millimeters to a centimeter in diameter. Some of the gas hydrate appeared to be associated with sandy sediment layers. Analysis of one sample (Table 1) showed that the gas hydrate contained primarily methane with small amounts of C_2 (0.13%) and C_3 (0.11%) and CO_2 (0.09%). The hydrocarbon gas ratio R value of 160 is the lowest yet reported for gas hydrate recovered during DSDP and ODP. This gas hydrate discovery provided evidence, in addition to that from Leg 76, for the presence of gas hydrate in a passive margin setting.

ODP Leg 112—Pacific continental margin, offshore Peru, Peru–Chile Trench

Gas hydrate was recovered within 200 m of the sea floor during coring at Sites 685 and 688 on the Peruvian outer continental margin (Kvenvolden and Kastner, 1990). Pieces of dark-grey gas hydrate and gas hydrated cemented mud were analyzed revealing a methane-rich composition (R = 14,200 and 42,000) (Table 1). This discovery amplified previous observations and showed that gas hydrate is present in many of the mid-latitude active margins of the eastern Pacific Ocean.

ODP Leg 127—Eastern margin of the Japan Sea, offshore western Hokkaido, eastern flank of Okushiri Ridge

Two samples of gas hydrate from a backarc basin of an active continental margin were recovered in sandy sediment from Site 796 at ~90 m subbottom. One sample was a hydrate-cemented sand, and the other a white crystalline solid (Shipboard Scientific Party, 1990, p. 289). Methane dominated the hydrocarbon gas mixture (R = 2900), with only ethane present in minor amounts (Table 1).

ODP Leg 131—Pacific continental margin, offshore Japan, Nankai Trough

Although gas hydrate was anticipated at Site 808 in sediment at the toe of the Nankai accretionary prism, only a single sample of hydrate-cemented sand was recovered in a wash core between 90 and 140 m subbottom (Shipboard Scientific Party, 1991, p. 143). No gas analyses were carried out. This gas hydrate occurrence shows that gas hydrate is also present in an active margin of the western Pacific Ocean. Thus, it appears that much of the Pacific Basin is rimmed with sediment that can contain gas hydrate.

ODP Leg 146—Pacific continental margin, offshore Western United States (Oregon), Cascadia Margin

Gas hydrate was recovered unexpectedly at Site 892 at shallow subbottom depths of 2–20 m. The gas hydrate occurred as platy crystals and crystal aggregates, irregularly disseminated in patchy zones and in thin layers or veinlets, parallel or oblique to bedding (Kastner *et al.*, 1993). The gas hydrate contained mainly methane, with *R* values of ~2100 and CO_2 (0.06%) (Table 1). Of important significance was the presence of 1–10% H_2S which should enhance the stablility of the gas hydrate at this locality.

Summary of DSDP and ODP Results

The most consistent observation is that hydrocarbon gases in gas hydrate samples recovered from deep ocean sediment always contain > 99% methane. Thus these gas hydrate examples are really methane hydrate and are likely to be structure I. The only exception may be the gas hydrate obtained from Leg 96 in the Gulf of Mexico. Its low *R* value of 160 suggests the possibility of structure II. Deep ocean drilling has shown that gas hydrate is present in both passive and active margin settings, but most samples have come thus far from active margin sites.

SUBAQUATIC GAS HYDRATE FROM SHALLOW SAMPLING

In addition to discoveries through deep ocean drilling by DSDP and ODP, piston and gravity coring at shallow subbottom depths in subaquatic sediment has revealed that gas hydrate near the sediment–water interface is also a common mode of occurrence. Gas compositions from the gas hydrate in shallow subbottom sediment (non-deep ocean drilling) are listed in Table 2.

Brooks *et al.* (1984, 1986) discovered near-surface gas hydrate in three different areas of the Gulf of Mexico at water depths ranging from 530 to 1300 m (Table 2). The hydrocarbon gas chemistry of these samples was particularly interesting. In contrast to all gas hydrate samples recovered by deep ocean drilling, where methane composed > 99% of the hydrocarbon gas mixture (Table 1), four of seven samples had hydrocarbon gas mixtures containing significantly less than 99% methane (62.1–97.4%), with *R* values ranging from 1.9 to 37.4. Three of these samples were oil stained and had a petroleum-like odor. The hydrocarbon gas chemistry of these samples suggests they are structure II (Brooks *et al.*, 1984), and analyses by nuclear magnetic resonance (NMR) confirmed this structural configuration (Davidson *et al.*, 1986). Three of the seven samples contained white layers of probable structure I gas hydrate in which methane composed > 99% of the hydrocarbon gases. At nearby Bush Hill, Sassen and MacDonald (1994) found surficial structure H gas hydrate having 21.2% methane (*R* value of 1.3 and a $\delta^{13}C$ value of − 29.3‰); the hydrocarbon gases in this unusual gas hydrate contain 41.1% isopentane (iC_5) as the most abundant component. Thus in the Green Canyon area structures I, II, and H are present. The gas hydrate occurrences are associated with faults and active venting of fluids at the seafloor.

Offshore northern California, six samples of gas hydrate were found near the sediment surface (Table 2) in which methane composed > 99% of the hydrocarbon gas mixture, and H_2S was also present (Brooks *et al.*, 1991). These results are similar to the observations made earlier in the Gulf of Mexico, particularly at Green Canyon 320 (Table 2).

Although gas hydrate was first discovered in shallow subbottom sediment of the Black Sea (Yefremova and Zhizhchenko, 1974), detailed geochemical results were unavailable until later (Ginsburg *et al.*, 1990). Samples recovered from 2050 m water depth (Table 2) contained hydrocarbon gas mixtures rich in methane (99.9%). In striking contrast, gas hydrate samples recovered from the floor of the Caspian Sea (Table 2) contained hydrocarbon gas mixtures with significant amounts of higher molecular weight hydrocarbons (Ginsburg *et al.*, 1992). Methane composed 59.1–96.2% of the hydrocarbon gas mixtures, with *R* values ranging from 1.7 to 45. This gas hydrate is likely to be structure II. The gas hydrate of the Caspian Sea is associated with fluid venting from Buzdag and Elm mud volcanos. Finally, fluid venting in the Sea of Okhotsk has resulted in gas hydrate (Ginsburg *et al.*, 1993), and hydrocarbon gas compositions (Table 2) contain mainly methane (99.9%), suggesting the presence of structure I hydrate rather than structure II as in the Caspian Sea.

CARBON-ISOTOPIC COMPOSITION OF METHANE IN GAS HYDRATE

An important element of the geochemistry of methane in natural gas hydrate is the carbon-isotopic composition of the methane. This information is contained in Tables 1 and 2 and in Fig. 2 for gas hydrate recovered from around the world. In those gas hydrate samples where methane composes

Table 2. Composition of gases from natural gas hydrate recovered by piston and gravity coring in shallow subbottom sediment

Area	WD[1] (m)	SD[2] (mbsf)	C_1[3] % of gas	C_2[3] % of gas	C_3[3] % of gas	C_1[4]% of HC	R[5]	CO_2 (%)	$\delta^{13}C_1$ (‰)	Comment
Gulf of Mexico (Brooks *et al.*, 1986):										
Green Canyon 184	530	nr	70.9	4.7	15.6	73.9	3.5	4.1	− 44.6	Chips, chunks, oil stained yellow brown
Green Canyon 204	850	1.4–4.2	61.9	9.2	22.8	62.1	1.9	0.2	− 56.5	Chips, chunks, oil stained yellow brown
Green Canyon 234	590	< 2.8	74.3	4.0	13.0	77.9	4.4	4.6	− 43.2	Solid plug, whitish-yellow color
Mississippi Canyon	1300	3.8	93.4	1.2	1.3	97.4	37.4	4.0	− 48.2	Small pieces, no oil stain
Garben Banks 388	850	2.5–3.8	99.5	0.12	nd	99.9	830	0.26	− 70.4	Thin to thick white masses
Green Canyon 257	880	4.2–4.5	99.7	nd	nd	99.7	> 10,000	0.26	− 69.2	Flat white masses
Green Canyon 320	800	3.2–3.6	99.7	0.08	nd	99.9	1300	0.12	− 66.5	White layers, H_2S odor
Offshore Northern California (Brooks *et al.*, 1991):										
ER-82	512	0–0.3	66.3	0.03	nd	99.9	2200	nd	− 59.6	Crystals in mudstone, H_2S odor
ER-83	518	< 1.5	92.9	0.02	nd	99.9	5200	nd	na	Hydrate-cemented sand and silt, H_2S odor
ER-105	*567*	*0–0.2*	*93.2*	*0.01*	*0.01*	99.9	*11,000*	nd	− 57.6	*Layered bands in mud, H_2S odor*
ER-139	623	1.5–2.0	93.4	0.12	nd	99.9	800	nd	− 61.1	Nodules of gas hydrate, H_2S odor
ER-148	642	0–1.8	90.5	0.02	nd	99.9	5300	nd	− 59.7	Layered gas hydrate, H_2S odor
ER-202	559	2.2–2.8	86.6	0.05	nd	99.9	1600	nd	− 69.1	Layered gas hydrates, H_2S odor
Black Sea (Ginsburg *et al.*, 1990):										
Sta. 18	2050	nr	97.3	0.022	0.0002	99.9	4400	0.85	na	Veinlet of gas hydrate
Sta. 53	2050	0.4–2.2	97.3	0.021	nd	99.9	4600	0.85	− 63.3	Veinlet of gas hydrate
Sta. 57	2050	0.7	99.2	0.045	0.0004	99.9	2200	0.90	− 61.8	Massive gas hydrate
Caspian Sea (Ginsburg *et al.*, 1992):										
Buzdag mud volcano 7c	475	nr	nr	nr	nr	nr	nr	nr	− 44.8	Hydrate-cemented breccia
Buzdag mud volcano 7s	475	0.5–0.6	77.1	18.2	2.4	77.5	3.7	0.45	na	"
	"	"	74.7	17.4	2.4	77.6	3.8	3.6	na	"
	"	"	80.8	13.6	4.2	81.4	4.5	0.65	na	"
	"	"	87.0	10.4	1.3	87.7	7.4	0.70	na	"
Buzdag mud volcano 7p	475	0–1.2	74.2	17.0	6.0	75.0	3.2	1.10	na	"
	"	"	58.7	19.4	15.8	59.1	1.7	0.85	na	"
Buzdag mud volcano 1B + 1C	475	0–0.6	76.0	19.3	2.4	77.0	3.5	1.18	na	Hydrate aggregates
Elm mud volcano 17	600	0–0.5	95.3	0.60	1.5	96.2	45	0.90	− 56.5	Hydrate-cemented breccia
Elm mud volcano 18A	"	0–0.4	81.4	15.3	1.6	82.1	4.8	0.81	na	Hydrate aggregates
Okhotsk Sea (Ginsburg *et al.*, 1993):										
Vent Field 1	710	0.3–1.2	97.1	0.0026	0.0018	99.9	22,000	0.6	− 64.3	Layers and lenses of white gas hydrate

[1]Water depth; [2]Subbottom depth; [3]As reported; [4]% of hydrocarbon gases; [5]Ratio of $C_1/(C_2 + C_3)$; na, not analyzed: nd, not detected; nr, not reported.

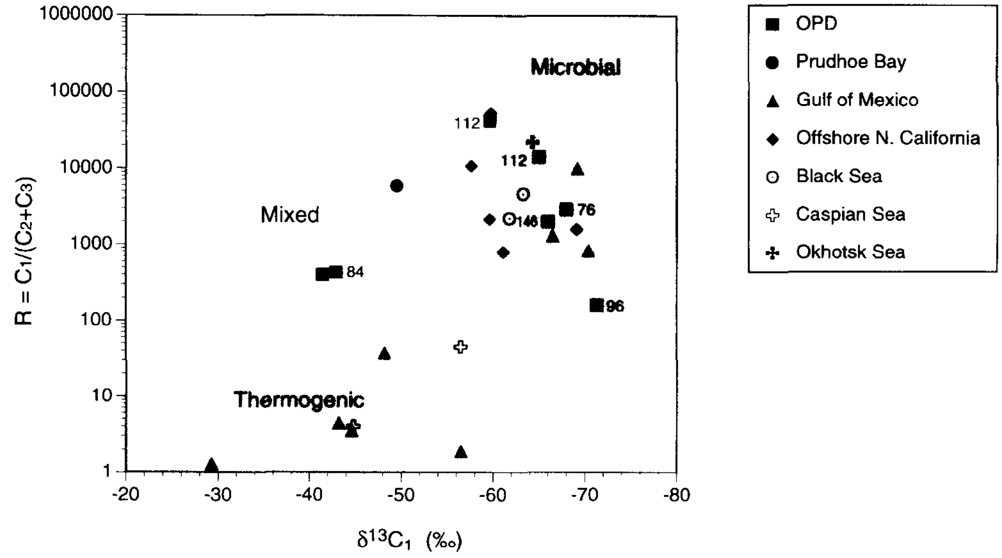

Fig. 2. Volumetric hydrocarbon gas ratio (R) of $C_1/(C_2 + C_3)$ versus δ^{13}C of C_1 in samples of gas hydrate (Tables 1 and 2). Compositional fields for microbial and thermal sources of methane are shown. Modified from Bernard *et al.* (1976).

> 99% of the hydrocarbon gas mixture, the δ^{13}C values of methane are always lighter than −60‰, with a few exceptions that are discussed below. Thus, in most gas hydrate, methane has molecular and isotopic characteristics that are diagnostic of a microbial origin, according to the criteria of Bernard *et al.* (1976), who used hydrocarbon gas compositions (R values) and the isotopic composition of methane to establish the origin of the methane: microbial, thermal, and mixed. Use of these criteria provides a guideline for interpretation, but exceptions do occur such as results from DSDP Leg 84, discussed below.

Microbial

Where methane is being microbially generated within a sedimentary section (the zone of methanogenesis), there is a carbon-isotopic relationship between the methane and CO_2 (Fig. 3). This

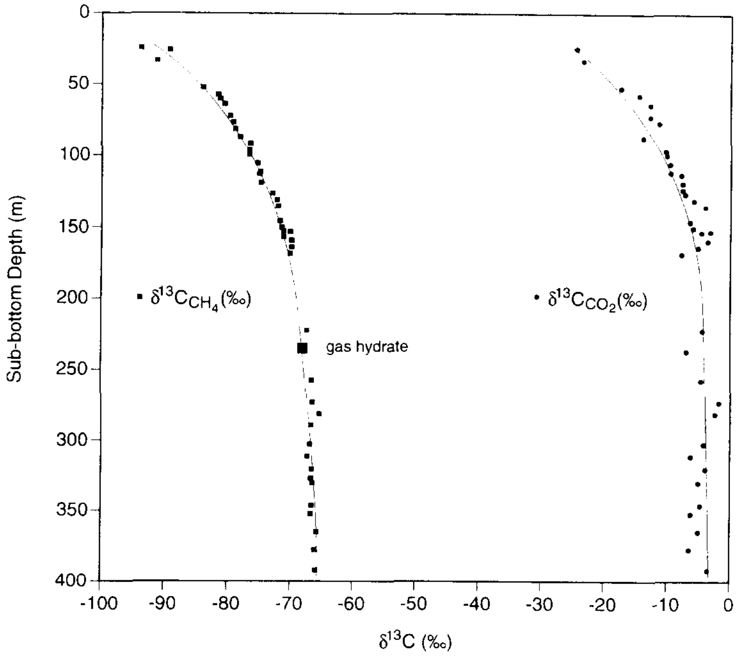

Fig. 3. Distribution with depth of carbon-isotopic compositions of methane and carbon dioxide from DSDP Leg 76, Site 533, Blake Outer Ridge, offshore from southeastern United States. Modified from Galimov and Kvenvolden (1983).

relationship is evident in sediment of the Blake Outer Ridge (Galimov and Kvenvolden, 1983) where gas hydrate was identified at DSDP Site 533 (Kvenvolden and Barnard, 1983). In this sediment, $\delta^{13}C$ values of methane become heavier with depth, from ~ − 94‰ in the uppermost sediment to approximately − 66‰ in the deepest sediment, reflecting a systematic but non-linear depletion of ^{12}C with depth. The $\delta^{13}C$ values of CO_2 also increase with depth of sediment, from ~ − 25‰ to ~ − 4‰, showing a depletion of ^{12}C that closely parallels the trend of isotopic composition of methane. The ~60‰ difference between the isotopic composition of methane and CO_2 at the same depth is believed to result from a kinetic effect of microbial methanogenesis (Rosenfeld and Silverman, 1959). The magnitude and parallel distributions of carbon-isotopic values for both methane and CO_2 are consistent with the formation of methane by the microbial reduction of CO_2 derived from organic matter. At Site 533 the carbon-isotopic composition of methane in the gas hydrate sample is similar to that in the sediment at the depth at which the gas hydrate sample was found (Fig. 3). Taken together these results suggest that the methane in gas hydrate at this site is microbial in origin and that the gas hydrate formed in place from the surrounding methane. Other localities with similar depth trends in carbon-isotopic compositions of methane, methane hydrate, and/or CO_2 are offshore from Guatemala (Claypool *et al.*, 1985; Jeffrey *et al.*, 1985) and offshore from Peru (Kvenvolden and Kastner, 1990). These results strongly support the conclusions of Whiticar *et al.* (1986), who clearly demonstrated that in the marine environment, after sulfate has been reduced, methane is generated by the microbial reduction of CO_2.

Microbial vs. thermal methane

Molecular and isotopic compositions of gases associated with gas hydrate 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 hydrate all contain > 99% methane (Kvenvolden and McDonald, 1985; Jeffrey *et al.*, 1985), suggesting that the methane is microbial in origin. Although many methane samples had $\delta^{13}C$ values lighter than − 60‰, suggesting a microbial source, at Sites 568 and 570, methane in sediment at depths below 210 m increased in $\delta^{13}C$ value to as heavy as ~ − 40‰. Methane from a massive gas hydrate recovered at Site 570 had a carbon-isotopic composition of − 41.4‰ and an *R* value of 410 (Kvenvolden *et al.*, 1984); similar results showing an average $\delta^{13}C$ value of − 42.9‰ and an *R* value of 410 were obtained by Brooks *et al.* (1985). These results (Table 1) are shown on Fig. 2. A detailed study of the dissociation of this massive gas hydrate under controlled laboratory conditions showed $\delta^{13}C$ values of methane ranging from − 36.1 to − 43.6‰ (Kvenvolden *et al.*, 1984). The observed heavy carbon-isotopic compositions are normally considered to indicate thermogenic gas; however, this isotopically heavy methane was accompanied by isotopically very heavy CO_2, with compositions of + 16.3‰ for gaseous CO_2 (Jeffrey *et al.*, 1985) and + 37‰ for total dissolved CO_2 (Claypool *et al.*, 1985).

The isotopically heavy methane could have been derived from the isotopically very heavy CO_2 by microbial processes similar to those described previously for the Blake Outer Ridge. Alternatively, the isotopically heavy methane could have migrated upward from deeper sediment where it was thermally derived from deeply buried organic matter. If so, however, one would expect much lower *R* values, (< 100), whereas the *R* values actually measured ~400. The association of isotopically heavy methane with isotopically very heavy CO_2 could be coincidental or controlled by some unknown isotopic interaction between methane and CO_2. Although a microbial explanation for these Leg 84 results is preferred, a thermal origin cannot be completely ruled out.

Results from ODP Leg 112 suggest that some thermal methane is present in the sediment. At Sites 685 and 688 gas hydrate samples were recovered at 166 and 141 m subbottom, respectively (Table 1). Although the carbon-isotopic results from Site 685 are consistent with the trends observed at Site 533 (Fig. 3), the results from Site 688 are not. At Site 688 the $\delta^{13}C$ value of methane is heavier than − 60‰ at subbottom depths exceeding about 150 m, where there is no longer a consistent relation between methane and CO_2 (Kvenvolden and Kastner, 1990). These results may reflect a situation in which thermogenic methane begins to dilute microbial methane at deeper depths. However, in the gas hydrate sample from Site 688, methane composed > 99.9% of the hydrocarbon gases (Table 1) and had a $\delta^{13}C$ value of − 59.6‰ (Table 1; Fig. 2). These results suggest that the methane in this gas hydrate is mainly microbial with only a minimal contribution of thermal methane.

Methane composes > 99.9% of hydrocarbon gases in five samples of gas hydrate recovered offshore from northern California (Table 2), suggesting a microbial origin. Although the carbon-isotopic compositions, ranging from − 57.6 to − 69.1‰ (Table 2), includes three values heavier than − 60‰ (Fig. 2), the methane in all five of these samples was considered to be of microbial origin (Brooks *et al.*, 1991). Ethane contents ranging from 0.01–0.12% were considered insufficient to indicate thermogenic hydrocarbon gas and structure II hydrate.

Methane in continental gas hydrate at the west end of the Prudhoe Bay oil field constitutes > 99.9% of the hydrocarbon gas mixture (*R* = 5900), with a $\delta^{13}C$ value of − 49.5‰ (Fig. 2), as discussed previously. Collett (1993a) has suggested that from 50 to 70% of the methane in this gas hydrate is thermogenic and has migrated upward from the Prudhoe Bay gas cap to mix with microbial gas. This idea requires that ethane and propane are stripped from the thermal gas during the migration process to produce such a pure methane gas in the gas hydrate (> 99.9%). Stripping of heavy hydrocarbons during migration has been discussed by Schoell (1983) and Jenden and Kaplan (1986). The same explanation may apply to the methane in gas hydrate of the Messoyakha field in Russia.

Thermal methane

Only in the Gulf of Mexico and the Caspian Sea has gas hydrate been found in which the methane is mainly thermogenic (Brooks *et al*., 1986; Ginsburg *et al*., 1992; Sassen and MacDonald, 1994). Methane in gas hydrate of the Gulf of Mexico is both thermal and microbial (Fig. 2). In three samples from Green Canyon and another from Mississippi Canyon, the hydrate hydrocarbon gas contains 62–78% methane, with $\delta^{13}C$ values ranging from − 43.2 to − 56.5‰ (Table 2); at Bush Hill the hydrate hydrocarbon gas contains 21.2% methane, having a $\delta^{13}C$ value of − 29.3‰. These samples fall within the molecular and isotopic compositional field (Fig. 2) diagnostic of thermal methane. In contrast, samples of hydrate hydrocarbon gas from Garden Banks and Green Canyon contain 99.5–99.7% methane with $\delta^{13}C$ values ranging from − 66.5 to − 70.4‰ (Table 2), indicating microbial methane. Gas hydrate associated with mud volcanos in the Caspian Sea consists of hydrocarbon gases containing 59–96% methane, with $\delta^{13}C$ values of − 44.8 to − 57.3‰ (Table 2). These results suggest a thermal methane source for the methane (Fig. 2).

GAS HYDRATE FORMATION AND OCCURRENCE

Subaquatic gas hydrate samples have been found in sediment ranging from the seafloor to depths of about 400 m (Tables 1 and 2). Where buried below about 20 m, gas hydrate appears to have been formed with microbial methane generated in place. This conclusion is based in part on considerations of the similarity of methane carbon-isotopic compositions between gas hydrate and the surrounding sediment gas (Galimov and Kvenvolden, 1983; Claypool *et al*., 1985; Jeffrey *et al*., 1985; Pflaum *et al*., 1986; Kvenvolden and Kastner, 1990). Shallow gas hydrate, found at and just below the seafloor, is composed of microbial methane that has migrated along faults, joints, and from diapirs. Examples include the gas hydrate found in the Gulf of Mexico (Brooks *et al*., 1986) offshore from northern California (Brooks *et al*., 1991), and on the Cascadia margin offshore from Oregon (Kastner *et al*., 1993). Microbial methane may be actively venting into the water at gas hydrate sites such as in the Sea of Okhotsk (Ginsburg *et al*., 1993).

The migration distance may have been short, perhaps limited by the base of the zone of gas hydrate stability and the processes taking place there (Paull *et al*., 1994). The carbon-isotopic composition of this methane is usually within the heavier range of values assigned to microbial methane, that is, − 60 to − 70‰ (Fig. 2). Isotopically lighter methane is not common in natural gas hydrate. In sediment where methane is being microbially generated, the isotopically lightest methane is near to the surface and becomes heavier with depth as illustrated in Fig. 3. The fact that isotopically light methane, lighter than 70‰, has not often been found in gas hydrate samples supports the idea that the microbial methane in shallow gas hydrate samples has migrated short distances.

On the other hand, the migration distance of methane may have been long, bringing thermogenic gas from deeply buried sediment into shallow sediment to form gas hydrate. Examples of thermogenic methane in surface or near-surface sediment are found in the Gulf of Mexico (Brooks *et al*., 1986; MacDonald *et al*., 1994; Sassen and MacDonald, 1994) and the Caspian Sea (Ginsburg *et al*., 1992).

In contrast to gas hydrate from subaquatic settings, the continental gas hydrate deposits of the Prudhoe Bay–Kuparuk River areas on the North Slope of Alaska and of the Messoyakha field in the West Siberian basin of Russia occur within stratigraphically discrete siltstone and sandstone reservoirs at depths less than 800 m (Collett, 1993a, b). The gas hydrate is assumed to contain a mixture of microbial and migrated thermal methane which has been stripped of heavy hydrocarbon gases.

SUMMARY

Sufficient information has been obtained in the study of the geochemistry of methane in natural gas hydrate to permit a few generalizations to be made. One striking observation is the very common occurrence worldwide of almost pure methane hydrate. That is, methane usually composes > 99% of the hydrocarbon gas mixtures. This compositional information leads to the conclusion that these gas hydrate samples are likely to have structure I crystallography. Only in the Gulf of Mexico and the Caspian Sea has gas hydrate been found in which methane is accompanied by significant amounts of ethane and propane such that structure II hydrate is present. In the Gulf of Mexico, structure H gas hydrate with iC_5 as the main hydrocarbon gas has also been observed.

Information on the molecular composition of hydrocarbon gases in gas hydrate samples coupled with measurements of carbon-isotopic compositions of methane provide a basis for interpreting the origin of the methane in gas hydrate. In most of the methane hydrate samples, methane has a carbon-isotopic composition lighter than − 60‰, suggesting that the methane is mainly microbial in origin. This microbial methane is believed to result from methanogenic processes, taking place in shallow sediment, in which CO_2 from organic matter is reduced to methane. In contrast, the gas hydrate samples with possible structure II and H crystallography from the Gulf of Mexico and structure II crystallography from the Caspian Sea contain methane with carbon-isotopic compositions heavier than − 60‰. This methane is considered to be thermal in origin, resulting from the thermal decomposition of organic matter at great depth. Methane from mixed sources possibly explains the continental gas hydrate of Alaska and Russia.

Subaquatic gas hydrate samples have been found in sediment ranging, thus far, from the seafloor to a depth of about 400 m. These gas hydrate occurrences are generally formed in place from methane that is either generated microbially nearby or has migrated. Microbial methane was likely to have migrated only short distances to form gas hydrate that occurs at or near the surface. Thermal methane, on the other hand, was likely to have migrated long distances from deeply buried sediment in order to form gas hydrate at or near the seafloor as in the Gulf of Mexico and the Caspian Sea.

The very large accumulations of natural gas, mainly methane, in the form of gas hydrate make this substance attractive as a potential energy resource for the future. Uncertainties about the mode of occurrence and the lack of applicable production techniques, however, augur that wide-scale exploitation, if proven feasible, could take place sometime in the 21st century when conventional natural gas deposits have been depleted.

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