

4. GAS CONTENT AND COMPOSITION OF GAS HYDRATE FROM SEDIMENTS OF THE SOUTHEASTERN NORTH AMERICAN CONTINENTAL MARGIN¹

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ABSTRACT

Gas hydrate samples were recovered from four sites (Sites 994, 995, 996, and 997) along the crest of the Blake Ridge during Ocean Drilling Program (ODP) Leg 164. At Site 996, an area of active gas venting, pockmarks, and chemosynthetic communities, vein-like gas hydrate was recovered from less than 1 meter below seafloor (mbsf) and intermittently through the maximum cored depth of 63 mbsf. In contrast, massive gas hydrate, probably fault filling and/or stratigraphically controlled, was recovered from depths of 260 mbsf at Site 994, and from 331 mbsf at Site 997. Downhole-logging data, along with geochemical and core temperature profiles, indicate that gas hydrate at Sites 994, 995, and 997 occurs from about 180 to 450 mbsf and is dispersed in sediment as 5- to 30-m-thick zones of up to about 15% bulk volume gas hydrate.

Selected gas hydrate samples were placed in a sealed chamber and allowed to dissociate. Evolved gas to water volumetric ratios measured on seven samples from Site 996 ranged from 20 to 143 mL gas/mL water to 154 mL gas/mL water in one sample from Site 994, and to 139 mL gas/mL water in one sample from Site 997, which can be compared to the theoretical maximum gas to water ratio of 216. These ratios are minimum gas/water ratios for gas hydrate because of partial dissociation during core recovery and potential contamination with pore waters. Nonetheless, the maximum measured volumetric ratio indicates that at least 71% of the cages in this gas hydrate were filled with gas molecules. When corrections for pore-water contamination are made, these volumetric ratios range from 29 to 204, suggesting that cages in some natural gas hydrate are nearly filled.

Methane comprises the bulk of the evolved gas from all sites (98.4%–99.9% methane and 0%–1.5% CO₂). Site 996 hydrate contained little CO₂ (0%–0.56%). Ethane concentrations differed significantly from Site 996, where they ranged from 720 to 1010 parts per million by volume (ppmv), to Sites 994 and 997, which contained much less ethane (up to 86 ppmv). Up to 19 ppmv propane and other higher homologues were noted; however, these gases are likely contaminants derived from sediment in some hydrate samples. CO₂ concentrations are less in gas hydrate than in the surrounding sediment, likely an artifact of core depressurization, which released CO₂ derived from dissolved organic carbon (DIC) into sediment.

The isotopic composition of methane from gas hydrate ranges from $\delta^{13}\text{C}$ of -62.5‰ to -70.7‰ and δD of -175‰ to -200‰ and is identical to the isotopic composition of methane from surrounding sediment. Methane of this isotopic composition is mainly microbial in origin and likely produced by bacterial reduction of bicarbonate. The hydrocarbon gases here are likely the products of early microbial diagenesis. The isotopic composition of CO₂ from gas hydrate ranges from $\delta^{13}\text{C}$ of -5.7 to -6.9 , about 15‰ lighter than CO₂ derived from nearby sediment.

INTRODUCTION

Gas hydrates have been recovered in gravity cores within 10 m of the seafloor in sediment of the Gulf of Mexico (Brooks et al., 1984, Brooks et al., 1989, MacDonald et al., 1994, Sassen and MacDonald, 1994, Sassen and MacDonald, 1997), the offshore portion of the Eel River Basin of California (Brooks et al., 1991), the Black Sea (Yefremova and Zhizhchenko, 1974), the Caspian Sea (Ginsburg et al., 1992), the Sea of Okhotsk (Ginsburg et al., 1993), offshore Norway in the Barents Sea (Ginsburg et al., 1997), and the eastern Mediterranean Sea (Woodside et al., 1996). Also, gas hydrates have been recovered at greater sub-bottom depths along the southeastern coast of the United States on the Blake Outer Ridge (Kvenvolden and Barnard, 1983, Shipboard Scientific Party, 1983), in the Gulf of Mexico (Bouma, Coleman, Meyer, et al., 1986), in the Cascadia Basin near Oregon (Shipboard Scientific Party, 1994), the Middle America Trench (Kvenvolden and McDonald, 1985; Shipley and Didyk, 1982), offshore Peru (Kvenvolden and Kastner, 1990), and on both the eastern and western margins of Japan (Shipboard Scientific Party, 1990, 1991).

Even though gas hydrates are known to occur in numerous arctic and marine sedimentary basins, little is known about the geologic parameters controlling their distribution or natural gas content. One of the major objectives of ODP Leg 164 was to establish the gas content of the Blake Ridge and an important part of that assessment is the gas content of the recovered gas hydrate.

In this paper we describe the gas content, composition, and carbon isotopic composition in recovered gas hydrate from three sites on Leg 164 (Fig. 1) and compare the results with those obtained 15 yr earlier at nearby Site 533 from Deep Sea Drilling Project (DSDP) Leg 76 (Kvenvolden and Barnard, 1983); from the Gulf of Mexico (Brooks et al., 1984, Brooks et al., 1989, and Davidson et al., 1986); from the Middle America Trench Leg 84 (Kvenvolden and McDonald, 1985); from Leg 112 offshore Peru (Kvenvolden and Kastner, 1990); and from Leg 146 offshore Oregon (Kastner et al., 1998).

Geologic Setting

The Atlantic continental margin of the United States is a classic "passive" margin and is generally used as an example of a geologic feature developed during continental rifting (Bally, 1981). A major geologic feature of the eastern margin of the United States is the Blake Ridge, a sediment drift deposit that was built upon transitional continental to oceanic crust by the accretion Tertiary to Quaternary hemipelagic muds and silty clays. The thickness of the methane-hydrate stability zone in this region ranges from zero along the north-western edge of the continental shelf to a maximum thickness of about 700 m along the eastern edge Blake Outer Ridge.

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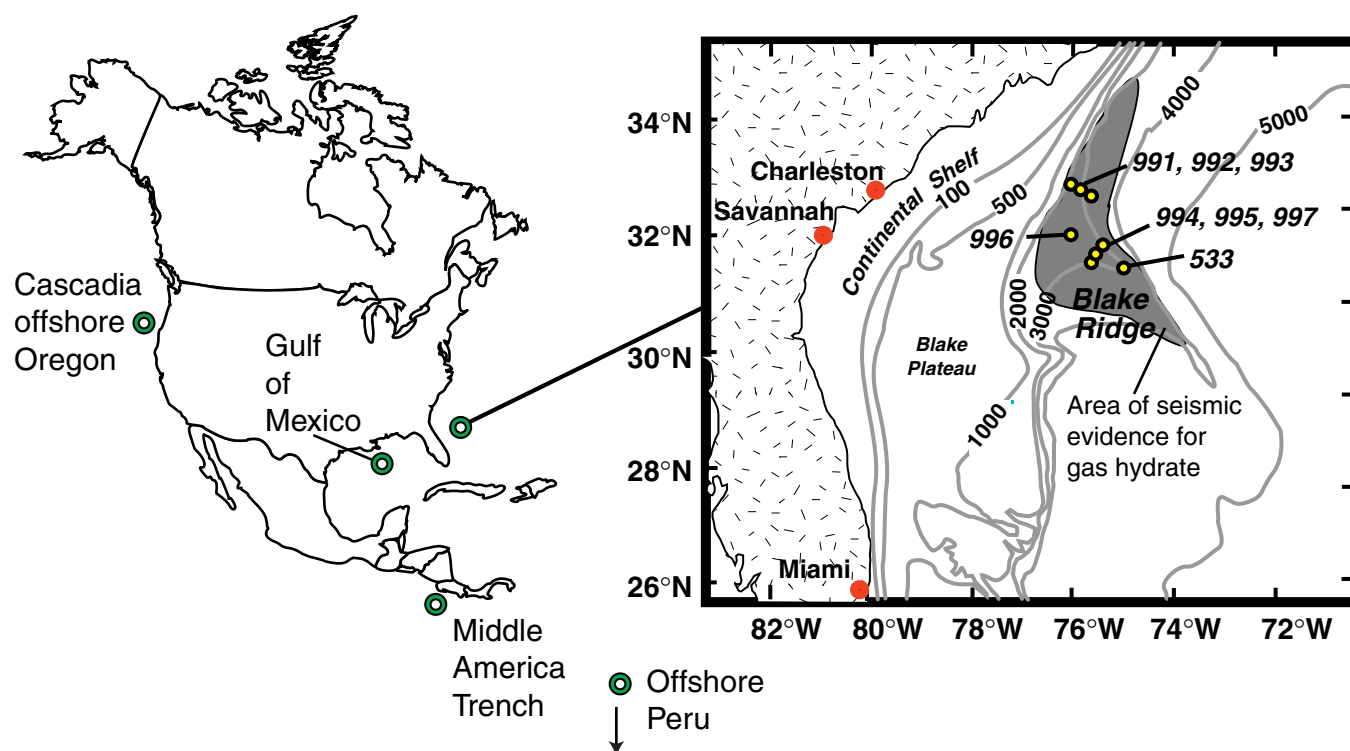


Figure 1. DSDP Leg 76 (Site 533) and ODP Leg 164 (Sites 991–997) on the Carolina Rise and Blake Ridge, offshore from southeastern United States. Other drilling locations referred to in the text are also shown.

Seven sites (Sites 991–997) were drilled during Leg 164 (Fig. 1). Sites 991 through 993 were drilled in upper Pleistocene to upper Miocene nannofossil clays and silty clays on the crest and flanks of the Cape Fear Diapir of the Carolina Rise. No gas hydrate was recovered, nor were there any proxy indicators of gas hydrate occurrences here. Site 996 was drilled in upper Pleistocene to lower Pleistocene nannofossil-bearing and nannofossil-rich clays on the crest of the Blake Ridge Diapir. Gas hydrate was recovered in abundance here. At Sites 994, 995, and 997, Holocene to upper Miocene nannofossil-rich clay and nannofossil clay were drilled over the crest of the Blake Ridge on a transect of holes that penetrated below the base of gas hydrate stability over a distance of 9.6 km. Gas hydrate was recovered from each site along the transect, although the majority was recovered at Sites 994 and 997.

PROCEDURES

Gas Hydrate Dissociation Pressure-Measuring System

Our system for measuring the gas and water content of dissociating gas hydrate consisted of a sample holder, a gauge block, a pressure gauge, and a manifold (Fig. 2). The manifold had a interchangeable gas-sampling port with septum or a quick connection to vacuum, a steel cylinder for collection of gas, and a pressure gauge. The device was first used on DSDP Leg 76 and a more complete description of it can be found in Kvenvolden et al., 1984. For each experiment, gas hydrate that was temporarily stored in liquid nitrogen was placed on aluminum foil and broken up. Pieces with as little sediment as possible were placed into the sample device previously cooled by liquid nitrogen. The system was sealed and then the lower portion of the device was placed into a water bath. As the gas hydrate dissociated, pressure inside the device increased, then stabilized. After about 10 min. of stable pressure, the pressure and the temperature of the water

bath were recorded. Dissociated gas was allowed to expand into the sample manifold and the pre-evacuated cylinder. Gas was sampled from the manifold and analyzed by both gas chromatographs on board, as detailed in the Explanatory Notes of the Leg 164 *Initial Reports* (Shipboard Scientific Party, 1996a). After gas sampling, the residual water and any sediment was weighed and their respective volumes calculated and subtracted from the volume of the reaction chamber. Gas volumes were calculated according to the ideal gas law at standard temperature and pressure (STP). Residual water was decanted after centrifugation, then sealed and refrigerated pending chlorinity measurements and shore-based isotopic analyses of the water. Sediment was dried and selected samples were analyzed for mineral content by X-ray diffraction.

Unpublished gas to water volumetric ratios of a synthetic gas hydrate made from granular ice (Stern et al., 1996) give an evaluation of the accuracy of this device. For five samples of a fully gas-filled hydrate (gas to water ratio of 216) our average measured ratio was 210.6 with a standard deviation of ± 16.2 .

Gas Sampling, Composition, and Isotopic Composition Determination

Gas composition was determined shipboard by gas chromatography. Isotopic composition of methane carbon, hydrogen, and carbon from carbon dioxide are given in Paull et al., Chapter 7, this volume. Hydrogen isotopic composition of gas hydrate water were determined by Egeberg (Chap. 22, this volume) and Bouma, Coleman, Meyer, et al. (1986).

Sediment gas was collected by three different methods: the standard ODP headspace technique; exsolved gases from sealed, whole 1.5-m-long cores; and from free gas that had expanded into the core liner during recovery (Shipboard Scientific Party, 1996a). Free-gas sample analyses are primarily used in this study. Free gas primarily

Gas hydrate dissociation chamber and gas sampling system

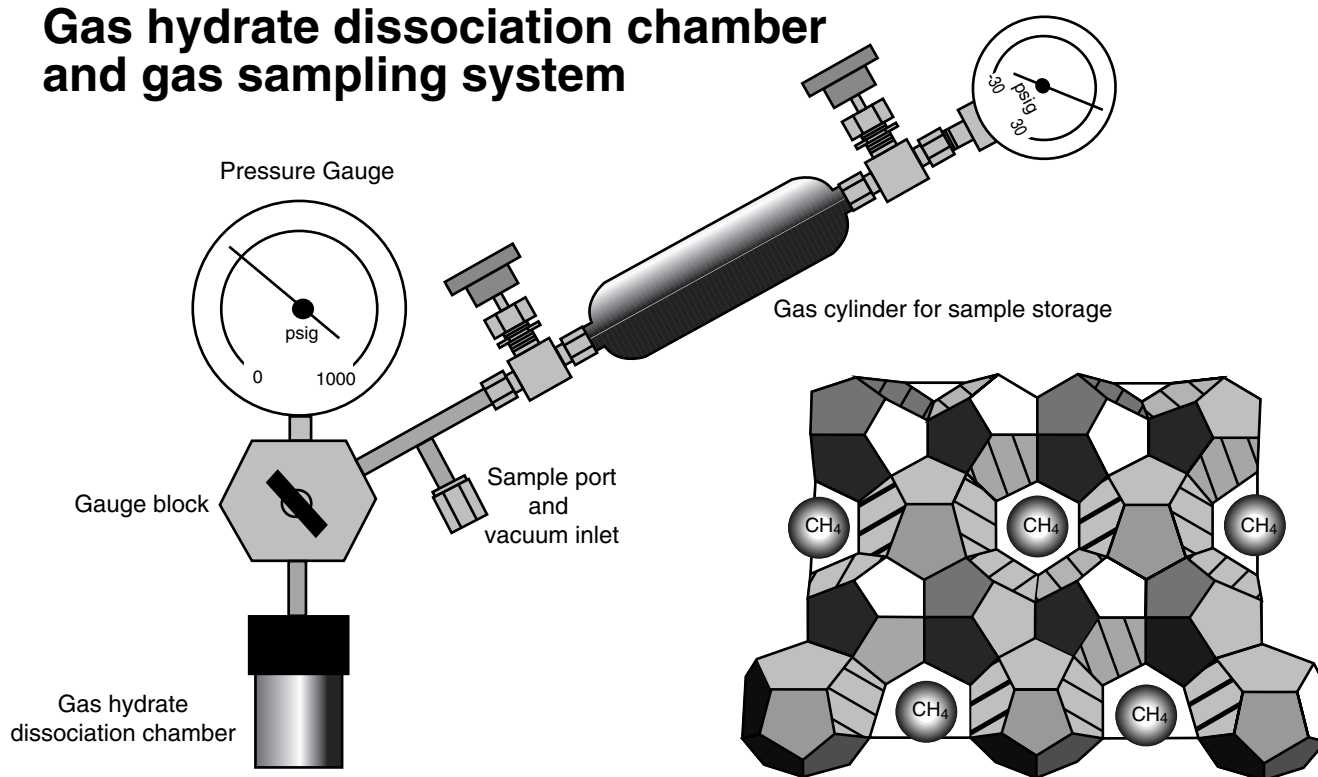


Figure 2. Diagram of the gas hydrate dissociation device used onboard the *JOIDES Resolution* during Leg 164 and the crystal structure of gas hydrate Structure I.

represents exsolved gases once dissolved in pore water, and/or present in situ as gas bubbles or possibly dissociated gas hydrate. Free gas and analyses were preferred since sediment gas is trapped inside the core liner and contact with the atmosphere is minimal. This technique works well for insoluble gases such as the hydrocarbons; however, all gas sampling methods employed lack finesse for soluble gases such as CO_2 and H_2S .

RESULTS

Occurrence of Gas Hydrate on the Blake Ridge

A total of eleven gas hydrate samples were recovered and measured from Sites 994, 996, and 997 (Table 1). Water depths at the sites ranged from 2170 m at Site 996 to 2798 m at Site 994. Nine gas hydrate samples were analyzed from Site 996, two of these in duplicate, from depths ranging from 0.2 to 58.6 meters below seafloor (mbsf). Two gas hydrate samples were analyzed, one each from Sites 994 and 997, from depths of 259.9 to 331.0 mbsf, respectively. A 1-cm-diameter wafer of gas hydrate was recovered from Section 164-995A-11X-3 (414 mbsf) but proved too small and decomposed on which to perform any reliable analyses.

Site 996 was drilled directly over the Blake Ridge Diapir where fault conduits intersect the seafloor, resulting in an area of active gas venting, pockmarks, and chemosynthetic communities (Paull et al., 1995). Nodular (Fig. 3) and vertical veins of gas hydrate were recovered from less than 1 mbsf and intermittently through the maximum cored depth of 62 mbsf.

Sites 994, 995, and 997 on a transect across the Blake Ridge (Fig. 1) were selected because geophysical indicators of gas hydrate occurrence were particularly distinct. This information includes (1) a well-developed bottom-simulating reflector (BSR) that marks the base of gas hydrate stability on marine seismic records and is present at Sites 995 and 996 but not at Site 994, and (2) the occurrence of seismic blanking, a region of low impedance contrast on marine seismic records above the BSR and a possible indicator of gas hydrate (Lee et al., 1994). Holes were drilled to maximum depths of 750 mbsf, exceeding that of the BSR at ~450 mbsf.

Downhole logging data, in concert with geochemical and core temperature profiles, indicate that gas hydrate at Sites 994, 995, and 997 occurs from about 180 to 450 mbsf and is disseminated in sediment as 5- to 30-m-thick zones that contain up to 15% bulk volume gas hydrate (Collett and Ladd, Chap. 19, this volume). Massive gas hydrate samples were recovered from depths of 260 mbsf at Site 994, and one 30-cm-long piece was recovered from 331 mbsf at Site 997. Occurrences of massive gas hydrate were rare and are probably fault filling and/or stratigraphically controlled.

Decomposed Gas Hydrate Gas to Water Volume Measurements

Shipboard measurements of dissociated gas hydrate are reported as the volumetric ratio of gas volume to water at STP. Blake Ridge gas hydrate gas to water volumetric ratios have a wide range of values from 29 to 154 (Tables 1, 2). The same is true of previous measurements, which range from 4 to 177 listed in Table 2. Calculations of

Table 1. Important gas hydrate measurements and comparisons to nearby sediment gas composition.

Sample type	Hole, core, section	Depth (mbsf)	Volume gas/ volume water	Volume gas/ volume water (chlorinity correction)	Chlorinity (mM)	C ₁ (%)	C ₂ (ppmv)	C ₃ (ppmv)	<i>i</i> -C ₄ (ppmv)	<i>n</i> -C ₄ (ppmv)	CO ₂ (%)	C ₁ /C ₂ +C ₃	δ ¹³ C C ₁ (‰ PDB)	δD C ₁ (‰ SMOW)	δ ¹³ C CO ₂ (‰ PDB)	δD H ₂ O (‰ SMOW)
Gas tube	994A-30X-5	246.8				83.6	64	32.2	13.8	4.6	16.4	8670	-68.1			-5.3
Gas tube	994A-31X-5	257.3				93.9	86	2.0			2.8	10670				
Free gas	994C-31X-3	255.1				92.0	125	0.0	14.3	3.3	8.0	7330				
Hydrate gas	994C-31X-7	260.0	154	173	57	98.8	86	2.0	0.0	0.0	1.2	11230	-67.0			-5.7
Hydrate gas	996A-1H-1	0.1				99.3	1010	12.0	1.2	0.7	0.4	970				
Free gas	996A-8H-3	50.3				99.3	629	28.2	11.1	2.5	0.8	1510				
Hydrate gas	996A-8H-4	52.5				99.8	772	0.5	0.0	0.0	0.1	1290	-69.3			-23.2
Free gas	996A-8H-5	52.8				99.8	697	19.5	4.5	1.0	0.2	1390				
Hydrate gas	996A-9H-CC	63.8				99.9	754	6.8	1.7	0.7	0.0	1310	-67.4			-19.9
Hydrate gas	996B-1H-1	2.1	43	58	169	99.3	969	11.9	2.5	0.6	0.6	1010		-199.7		13.8
Hydrate gas	996B-1H-1	2.1	18	29	248	99.4	753	8.9	1.7	0.4	0.5	1310				10.4
Hydrate gas	996C-1H-1	2.3	45	78	294	99.3	719	7.3	1.6	0.5	0.4	1370				9.2
Hydrate gas	996C-1H-1	2.3	58	90	245											10.3
Hydrate gas	996-C-2H-CC	2.4	24	48	352	99.8	857	15.8	4.3	0.9	0.0	1140	-65.9			-26.9
Free gas	996D-4H-5	26.9				98.5	720	6.5	1.8	0.6	1.5	1360				
Hydrate gas	996D-5X-CC	32.1	59	107	317	99.7	747	18.3	3.2	0.8	0.3	1300				12.9
Free gas	996D-6H-4	45.0				98.9	776	22.3	5.6	1.9	1.0	1240				
Hydrate gas	996D-6H-5	45.9				99.6	744	10.9	2.4	0.6	0.3	1320	-66.6	-175.0		-22.3
Free gas	996E-7X-5	48.5				98.1	637	20.4	6.2	1.6	1.9	1490				
Hydrate gas	996E-7H-CC	58.6	142	145	21	99.7	719	6.9	1.6	0.4	0.2	1370	-70.7	-193.1		-21.9
Free gas	997A-41X-3	321.8				76.4	138	15.8	18.4	6.4	23.5	4980	-65.0	-195.8		-4.4
Free gas	997A-42X-2	329.0				95.8	142	0.0	1.7	0.4	4.2	6730	-68.2			-11.7
Hydrate gas	997A-42X-3	331.0	139	204	167	98.4	196	3.8			1.6	4940	-65.8	-196.1		-21.2
Free gas	997A-43X-1	337.1				73.9	143	20.0	23.4	6.2	26.1	4520	-65.0			-6.5

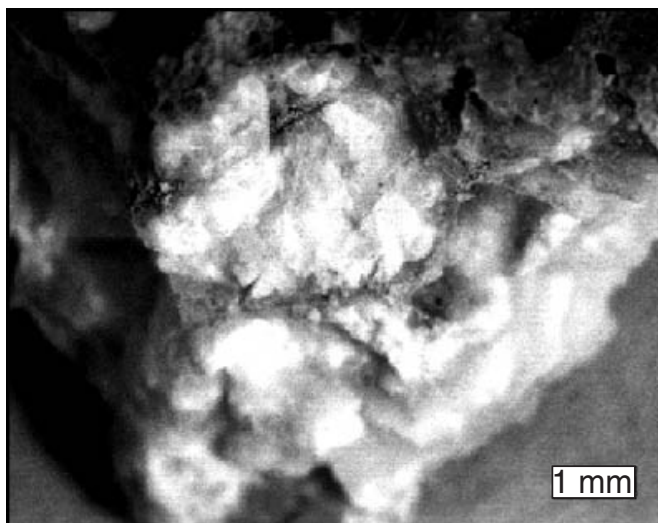


Figure 3. Photograph of a massive gas hydrate recovered from Site 996. Note the exposed cubic faces.

maximum expected ratios in theory and in nature are tabulated in Table 3.

Comparisons of Blake Ridge gas hydrate gas to water volumetric ratios were made to all known measurements worldwide (Fig. 1; Tables 1, 2). The measurement is rare, mainly because gas hydrate samples are rare, and because specialized equipment and procedures needed to be in place when gas hydrates were recovered.

Gas Geochemistry

The following hydrocarbon gases in gas hydrate and surrounding sediment are reported in Table 1: methane (C_1), ethane (C_2), and the sum C_3^+ composed of propane (C_3), isobutane ($i-C_4$), and n -butane ($n-C_4$). In addition, carbon dioxide concentrations and the ratio $C_1/(C_2+C_3)$ are given. Other hydrocarbon gases are present in Blake Ridge sediments including: neopentane (neo C_5), isopentane ($i-C_5$), n -pentane ($n-C_5$), cyclopentane (cyclo C_5), neohexane (neo C_6), isohexane ($i-C_6$), n -hexane ($n-C_6$), isoheptane ($i-C_7$), and methylcyclohexane + n -heptane (methylcyclo C_6+n-C_7). They are discussed in more detail in Kvenvolden and Lorenson (Chap. 3, this volume).

Gas hydrate median composition was 99.5% C_1 , ranging from 98.4% to 99.9%; 0.4% CO_2 , ranging from 0.0% to 1.6%; 750 ppmv C_2 , ranging from 86 to 1010 ppmv; and 10.4 ppmv C_3^+ , ranging from 0.5 to 23.8 ppmv. C_3^+ compounds in dissociated Structure I gas hydrate gas are likely contaminants. Adjacent sediment gas (within 11 m of gas hydrate occurrences) median composition was 98.1% C_1 , ranging from 73.9% to 99.8%; 1.9% CO_2 , ranging from 0.2% to 26.1%; 629 ppmv C_2 , ranging from 125 to 776 ppmv; and 27.6 ppmv C_3^+ , ranging from 2.1 to 52.1 ppmv (Fig. 4).

Hydrogen sulfide (H_2S) has been found previously in near-surface gas hydrate (Kastner et al., 1998). H_2S was also detected and measured in sediments and gas hydrate at Site 996. Because H_2S is very soluble in water and the gas hydrate dissociation measurements are always contaminated with some sediment and pore water, we are doubtful the H_2S was within the gas hydrate structure.

Isotopic Composition of Gas Hydrate and Adjacent Sediment Gas

Gas hydrate methane carbon isotopic values range from -70.7‰ to -65.8‰ with a median of -67.0‰ , whereas hydrogen values range

Table 2. Compilation of previous gas hydrate dissociation gas to water measurements.

Volume gas/ volume water	Volume gas/ volume hydrate	n (mol H_2O /mol gas)	Cages occupied (%)	Hydrate density (kg/m^3)
Pressure conditions on Blake Ridge: Average = 28 MPa; range = 22-32 MPa				
216.4	173.0	5.75	100.0	924.0
210.9	168.6	5.9	97.5	920.9
207.4	165.8	6.0	95.8	919.0
204.0	163.1	6.1	94.3	917.1
200.7	160.5	6.2	92.7	915.3
197.5	157.9	6.3	91.3	913.5
195.4	156.2	6.4	90.3	912.3
194.4	155.5	6.4	89.8	911.8
191.5	153.1	6.5	88.5	910.2
188.6	150.8	6.6	87.1	908.5
185.7	148.5	6.7	85.8	907.0
183.0	146.4	6.8	84.6	905.5
151.8	121.5	8.2	70.1	888.1
Pressure conditions of 1 MPa				
216.4	168.5	5.75	100.0	900.0
210.9	164.2	5.9	97.5	896.9
207.4	161.5	6.0	95.8	895.0
204.0	158.9	6.1	94.3	893.1
200.7	156.3	6.2	92.7	891.3
197.5	153.8	6.3	91.3	889.5
195.4	152.1	6.4	90.3	888.3
194.4	151.4	6.4	89.8	887.8
191.5	149.1	6.5	88.5	886.2
188.6	146.8	6.6	87.1	884.5
185.7	144.6	6.7	85.8	883.0
183.0	142.5	6.8	84.6	881.5
151.8	118.2	8.2	70.1	864.1

Notes: The range is given from the maximum theoretical limit to the lower limit expected in nature. The molar ratio of water to gas (n), percentage of cage occupancy, and corresponding gas hydrate density is also listed.

from -199.7‰ to -175.0‰ with a median value of -194.6‰ . Gas hydrate CO_2 carbon isotopic values range from -26.9‰ to -5.7‰ with a median of -21.9‰ . Adjacent sediment gas methane carbon isotopic values range from -68.2‰ to -65.0‰ with a median of -65.0‰ , whereas just one hydrogen value of -195.0‰ was measured. Sediment gas CO_2 carbon isotopic values range from 11.7‰ to -4.4‰ with a median of -6.5‰ .

DISCUSSION

Theoretical Consideration of Gas Hydrate Gas Content

Under appropriate conditions of temperature and pressure, gas hydrates usually form one of two basic crystal structures known as Structure I and Structure II (Fig. 1; Structure II not shown). Each unit cell of Structure I gas hydrate consists of 46 water molecules that form two small dodecahedral cages and six large tetradecehedral cages, leading to the ideal formula of eight gas molecules to 46 water molecules. Structure I gas hydrates can only hold small gas molecules such as methane and ethane, with molecular diameters not exceeding 5.2 Å. The unit cell of Structure II gas hydrate consists of 16 small dodecahedral and eight large hexakaidecahedral cages formed by 136 water molecules with an ideal formula of 24 gas molecules to 136 water molecules. Structure II gas hydrates can contain gases with molecular dimensions in the range of 5.9 to 6.9 Å, such as propane and isobutane.

Structure I gas hydrates appear to be the most common hydrate structure occurring in nature (reviewed by Kvenvolden, 1993, Booth et al., 1996, Sloan, 1997, and Makogon, 1997). The ideal water/gas molar ratio (n , also called the hydrate number) of Structure I gas hydrate is 46/8, or $n = 5.75$, whereas the ideal water/gas molar ratio of Structure II gas hydrate is 136/24, or $n = 5.67$. These ideal water/gas molar ratios confirm the observation that gas hydrates contain a substantial volume of gas. For example, if all the cages of Structure I gas

Table 3. Calculated gas to water volumetric ratios and gas to gas hydrate volumetric ratios expected from dissociated Structure I gas hydrate containing only methane at conditions expected at the Blake Ridge (22–32 MPa), as compared to gas hydrate equilibrium pressures at 1 MPa.

Location	Site/Hole	Depth (msf)	Gas to water volume ratio	Gas to water volume ratio (chlorinity correction)	Chlorinity (mM)	Reference
Blake Ridge	533A	238	20		NA	Kvenvolden and Barnard, 1983
Middle America Trench	565	319	133	137	15	Kvenvolden et al., 1984
Offshore Costa Rica	568	404	30	36	92	
	568	404	7	8	89	
	570	192	4?		NA	
	570	192	29	30	19	
	570	192	29	30	19	
	570	259–268	24–42		NA	
	570	273	12		NA	
Gulf of Mexico*	Green Canyon*	<5	152		NA	Davidson et al., 1986
	Green Canyon*	1–1.5	70	94	138	Brooks et al., 1984
	Green Canyon*		70	102	169	
	Green Canyon-184*		70		NA	Brooks et al., 1989
	Green Canyon-204*	85		NA	NA	
	Green Canyon-234*		177		NA	
	Garden Banks-388		68		NA	
	Green Canyon-257		35		NA	
	Green Canyon-320		66		NA	
Offshore Peru	685A	165.6	100	111	51.4	Kvenvolden and Kastner, 1990
	688A	141	13	16	90.6	
	688A	141	20	35	232.3	
Cascadia, offshore	892D	18	70	81**	NA	Lorenson and Kastner,
Oregon	892D	18	53	62**	NA	unpublished data

Notes: NA = not analyzed. * = structure II gas hydrate is likely though not confirmed; maximum gas to water ratio is 220, ** = calculated pore-water dilution of 14% from oxygen isotopic shift between gas hydrate water and pore water. Maximum values in nature are expected to be about 195–204. Values less than these reflect partial decomposition during core recovery. Values range from 4 to 177. A chlorinity correction made to some ratios using the nearest sediment pore-water concentration results in a revised range of 8–137.

hydrate are occupied, each volume of gas hydrate at Blake Ridge in situ equilibrium pressures (between about 22 and 32 MPa) will contain about 173 volumes of gas when converted to STP.

Most researchers believe that a completely filled clathrate is not likely to be found in nature (reviewed by Sloan, 1997). However, gas hydrates are not stable if the clathrate cages are less than 70% occupied by gas (Holder and Hand, 1982). For the purpose of this study, we have assumed a minimum threshold hydrate gas yield of 139 m³ gas/m³ gas hydrate (70% cage occupation, 1 MPa) and a maximum hydrate gas yield of 159 m³ gas/m³ gas hydrate (94% cage occupation, 1 MPa). This range represents the likely minimum and maximum values that occur in nature.

Our direct measurements of gas hydrate are made of the volume of gas released to the volume of water from dissociated gas hydrate, a measurement that is independent of considerations of gas hydrate formation equilibrium pressure and density. The theoretical upper limit of this ratio is 216 at STP as calculated from the ideal formula for Structure I methane hydrate of C₁ · n H₂O where n = 5.75 for gas hydrate with 100% cage occupancy. There is reason to believe that the molar ratio in nature is greater than the ideal 5.75. Holder and Hand (1982) calculated the likely molar ratio of 6.37 (90% cage occupancy) based on considerations of enthalpy for methane in Structure I hydrate in oceanic sediments. Furthermore, a molar ratio of 5.75 is predicated on pressures exceeding the equivalent water depths of 7000 m. If one takes n = 6.37 to be the likely molar ratio for natural gas hydrate, then the upper limit of the gas to water volumetric ratio from dissociated gas hydrate likely in nature is 195. Makogan (1997) states that the likely molar ratio for natural gas hydrate should range from 5.8 to 6.0, and thus gas to water volumetric ratios of 215 and 207, respectively. If one considers the variation of n with pressure (Saito et al., 1964) at in situ pressures of the Blake Ridge study area (from about 22 to 32 MPa), then n = 6.1 with a resultant gas to water volumetric ratio of 204, or 94% cage occupancy.

At the lower limit of gas hydrate cage occupation, 70% of the gas hydrate cages must be occupied for a stable gas hydrate structure to exist. This corresponds to n = 8.2 or a gas to water volumetric ratio of 152. Thus the likely range for natural gas hydrate lie between n = 6.1 to 6.8 and gas to water ratios of 204 to 152, respectively.

Table 3 lists a range of expected values for the volumetric ratio of gas to water, gas to gas hydrate, n, cages occupied, and gas hydrate

density at pressure conditions expected at the Blake Ridge (28 Mpa, ave.), then compared gas hydrate pressure conditions at sea level (about 1 Mpa).

Structure I Gas Hydrate in Blake Ridge Sediments

Blake Ridge gas hydrate samples preserved in liquid nitrogen and analyzed by X-ray powder diffraction in the laboratories of the National Research Council of Canada revealed that gas hydrate from the Blake Ridge is solely Structure I (J. Ripmeester, pers. comm., 1996). A total of five gas hydrate samples were analyzed from Sites 994, 995, and 997 at depths spanning the range of all gas hydrate recoveries. The confirmation of Structure I gas hydrate eliminates the need to consider Structure II gas hydrate at the Blake Ridge.

Comparison of Gas to Water Ratios Measured Elsewhere

A limited number of gas to water volumetric ratios have been made of gas hydrate from the continental margin of North and South America (Fig. 1; Table 2). The gas to water volumetric ratios, ranging from 4 to 177, are similar to the range presently observed on the Blake Ridge (29–154). There is no apparent geographic pattern to the ratios; rather we believe that all of these ratios are minimum values resulting from partial gas hydrate dissociation during recovery. The amount of dissociation during recovery is strongly dependent on the magnitude and time the sample encounters conditions outside of the gas hydrate pressure-temperature (P-T) stability field. These parameters are in turn affected by the water temperature through which the core is recovered and the core recovery transit time. Other factors include time and temperature on deck and so on—thus the amount of sample dissociation can be quite variable and location dependent (e.g., hot climate vs. cold climate).

Chlorinity Corrections to the Gas to Water Volumetric Ratio

Gas hydrate excludes all ions upon formation, thus the chlorinity of gas hydrate water reflects the amount of pore water that accompanies gas hydrate in our measurements. Therefore, pore-water contamination can be estimated by the observed chlorinity concentration in

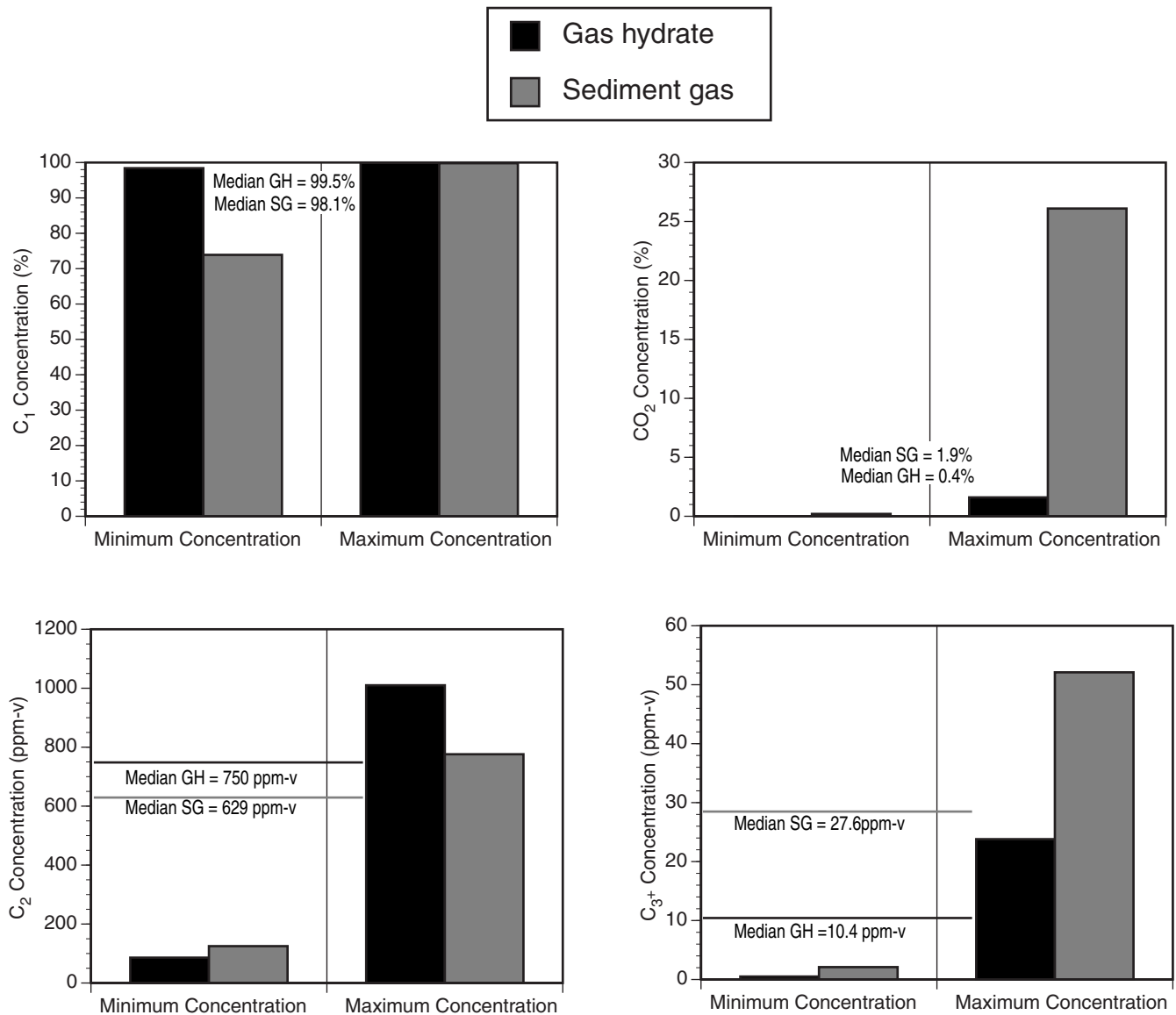


Figure 4. Gas hydrate and nearby sediment gas concentrations for C_1 , CO_2 , C_2 and C_3^+ . Sediment gas samples were located from 0.3 to 11 m of gas hydrate samples.

dissociated gas hydrate residual water. Chlorinity concentrations observed from dissociated gas hydrate water vary from 352 to 167 mM. When compared to nearby Cl^- concentrations from sediment pore water (ranging from 520 to 997 mM; Shipboard Scientific Party, 1996b, 1996d, 1996e), the amount of pore-water contamination can be calculated by the percentage excess chlorinity in gas hydrate water. In cases of slight dilution of pore waters by dissociated gas hydrate, a value was chosen that corresponded to a chlorinity trend given by undiluted pore-water samples. The results show that the contamination ranges from 2% to 50%. If these results are applied to the gas to water volumetric ratios released by dissociated gas hydrate seen in Table 3, the chlorinity-corrected gas to water volumetric ratios vary from 29 to 204. Thus gas hydrate samples from Leg 164 may be fully saturated with gas. It should also be noted that there is a correlation of the chlorinity-corrected gas to water volumetric ratios with depth; that is, the deeper samples are more saturated with gas than the shallow gas hydrate samples. Only the deepest gas hydrate sample (Section 164-997A-42X-3, 331 mbsf) is fully saturated with

methane. Whether this is a drilling and core-recovery artifact or a geological curing process is unclear.

Comparison of Hydrate Gas and Sediment Gas

It appears that disseminated gas hydrate cannot be recovered with conventional coring techniques, and therefore measurements have been made only on massive or vein-like gas hydrate. The geochemistry of disseminated or massive gas hydrates are likely similar in gas composition and concentration, because we observed no change in sediment gas composition in areas where disseminated gas hydrate occurs (Shipboard Scientific Party, 1996b, 1996c, 1996d, 1996e). Dissociated gas from disseminated gas hydrate would likely result in perceptible shifts in sediment gas geochemistry because C_3^+ gases in sediment should be diluted by methane from dissociated gas hydrate.

The distribution of hydrocarbon gases released from dissociated gas hydrates is compared to the distribution of hydrocarbon gases expelled from sediment into voids in the core liner (free gas). We make

Table 4. Average, median, minimum, and maximum values for gas composition and isotopic compositions of sediment gas from within 0.3 to 11 m of recovered gas hydrate and gas from dissociated gas hydrate listed in Table 3.

Sample type	Function	C ₁ (%)	C ₂ (ppmv)	C ₃ (ppmv)	i-C ₄ (ppmv)	n-C ₄ (ppmv)	CO ₂ (%)	C ₁ /C ₂ +C ₃	δ ¹³ C C ₁ (‰ SMOW)	δD C ₁ (‰ PDB)	δ ¹³ C CO ₂ (‰ PDB)	δD H ₂ O (‰ SMOW)
Free gas	Average	92.5	445	14.7	9.7	2.7	7.5	3390	-66.1		-7.6	
Free gas	Median	98.1	629	19.5	6.2	1.9	1.9	1510	-65.0	-195.8	-6.5	
Free gas	Min. value	73.9	125	0.0	1.7	0.4	0.2	1240	-68.2	-195.8	-11.7	
Free gas	Max. value	99.8	776	22.3	23.4	6.4	26.1	7330	-65.0	-195.8	-4.4	
Hydrate gas	Average	99.4	694	8.8	1.8	0.5	0.5	2380	-67.5	-191.0	-20.2	11.7
Hydrate gas	Median	99.5	750	8.1	1.7	0.6	0.4	1310	-67.0	-194.6	-21.9	10.4
Hydrate gas	Min. value	98.4	86	0.5	0.0	0.0	0.0	970	-70.7	-199.7	-26.9	8.1
Hydrate gas	Max. value	99.9	1010	18.3	4.3	0.9	1.6	11200	-65.8	-175.0	-5.7	17.1

the assumption that gas incorporated into gas hydrate is derived from nearby sediments, unless there is evidence of active gas seepage from depth such as at Site 996. The concentration of gases can be normalized to 100% of C₁, CO₂, and total gaseous hydrocarbons (Table 1). Oxygen and nitrogen were eliminated from the calculation because they are considered contaminants from the atmosphere. In Table 1, the gas from gas hydrates is compared with sediment gas obtained close to where the gas hydrates were found. The minimum and maximum distance between sediment gas sample points and those where gas hydrate was recovered was 0.3 and 11 m, respectively. At Site 994 sediment gas released over a period of hours from whole 1.5-m core sections is used for isotopic composition of methane comparison only.

Higher C₂ concentrations in gas hydrates than in core gas possibly results from the preferential inclusion of C₂ in Structure I gas hydrate, where C₂ acts to stabilize the forming crystal by filling the larger cages first (Sloan, 1997). In addition, higher molecular weight hydrocarbon gases (C₃ to C_n, where $n > 3$) are excluded from Structure I hydrate. Thus C₂ is expected to be more concentrated in Structure I hydrate, whereas C₃⁺ (C₃, i-C₄, and n-C₄) is excluded. Following this line of reasoning, higher concentrations of C₂ should be found in gas hydrate relative to C₂ concentrations in nearby sediment (Hand et al., 1974). In addition, C₃⁺ should be more concentrated in surrounding sediment relative to C₃⁺ concentrations in gas hydrate. This relationship has been observed in the Middle America (Kvenvolden et al., 1984,) and in the Gulf of Mexico (Brooks et al., 1989).

The gas analyses shown in Table 1 are less conclusive, yet favor the above supposition. In five of eight cases, gas hydrate compositions show some, although minor, enrichment of C₂, whereas in two cases C₂ concentrations are nearly equal, and one case the opposite is observed. In contrast, the exclusion of C₃⁺ from gas hydrate is evident. In every case, the sum of C₃⁺ gases from dissociated gas hydrate is less than nearby sediment gases. The presence of C₃⁺ gases in Structure I gas hydrate is enigmatic because they are larger than the size of any cage and is attributed to contamination by minor volumes of sediment and dissolved pore-water gases that cannot be removed from gas hydrate used for analyses.

Comparison of sediment gas collected in closest proximity to gas hydrate occurrences (0.3 and 0.9 m in Sections 164-996A-8H-4 and 164-996D-6H-5, respectively) illustrate these relationships. For example, gas hydrate gas from Hole 996A is enriched in ethane by 9.8% whereas nearby sediment gas is enriched in C₃⁺ by 63% relative to gas hydrate gas. These relationships can become less distinct or even contrary when comparing samples from greater distances apart. Nonetheless, when a group of comparative samples are analyzed with the simple statistical parameters as done in Table 4 and Figure 4, these observations are validated. For example, the average and median C₂ concentration for gas hydrate gases are 694 and 750, respectively, whereas those of sediment gases are 445 and 629, or a median enrichment of C₂ in gas hydrate gas of 16%. The same comparison made for C₃⁺ gases yields a median enrichment of C₃⁺ gases in sediment of 62%. Because of the small number of samples used for comparison, we have chosen to use the median rather than the average,

however the conclusions are the same. Comparisons of C₁ and CO₂ median values in Table 4 and Figure 4 reveal that gas hydrate gas appears to be enriched in C₁ and depleted in CO₂ relative to sediment gas. This result is somewhat surprising because CO₂ fits snugly into the larger Structure I hydrate cage and therefore is not expected to be selectively excluded. We suggest that CO₂ gas concentration in sediment gas is artificially enriched in gaseous CO₂ during core recovery. Most or all of CO₂ at in situ pressure and temperature is in the form of dissolved bicarbonate ion (Paull et al., Chap. 7, this volume). Exsolution of CO₂ resulting from the depressurization of the core during recovery also artificially dilutes methane concentration in sediment gas samples, and for this reason, a meaningful comparison is difficult.

Comparison of Isotopic Composition Between Sediment Gas and Gas Hydrate

Comparison of median isotopic compositions of methane carbon and hydrogen are listed in Table 4. Median methane isotopic carbon and hydrogen of sediment gas is -65.0‰ and -195.8‰, respectively (one sample for methane hydrogen isotopic composition), and that of gas hydrate is -67.0‰ and -194.6‰, respectively. The differences between the median methane carbon and hydrogen isotopic compositions of sediment gas and gas hydrate are small and the very limited number of samples demands prudence; thus we observe no obvious fractionation.

In contrast, the CO₂ carbon isotopic median composition is depleted in gas hydrate gas (-21.9‰) relative to sediment gas CO₂ (-6.5‰) likely derived from nearby DIC (+6.6‰; Paull et al., Chap. 7, this volume). Thus there are significant differences between DIC, sediment gas CO₂, and CO₂ gas incorporated into gas hydrate.

Combined δ¹³C C₁ and δ¹³C CO₂ profiles of gas and gas hydrate from Sites 994, 995, 996, and 997 are seen in Figure 5. Measurements from sediment gas, gas tubes, and gas from the pressure coring system are combined in Figure 4 and show little variation (Paull et al., Chap. 7, this volume). δ¹³C C₁ of gas hydrate gas closely resembles sediment gas at all sites and at all depths. However δ¹³C CO₂ of gas hydrate is depleted of ¹³C by about 15‰ from the corresponding sediment gas δ¹³C CO₂. This relationship is best illustrated by gas hydrate samples from Site 996 and a single gas hydrate sample from Site 997. At Site 994, gas hydrate δ¹³C CO₂ is nearly that of the sediment gas and does not appear depleted. Isotopic fractionation of CO₂ between gas hydrate and sediment gas has never been reported to our knowledge. However Finley and Krasen (1986), in their report on Site 570 from the Middle America Trench, plot the carbon isotopic composition of C₁, CO₂, and total CO₂ (DIC) from cores with depth. A shift of about 15‰–20‰ between the trend of CO₂ and DIC with depth occurs within the hydrate zone. Brooks et al. (1989) noted differences in δ¹³C CO₂ of gas hydrate and δ¹³C of associated authogenic carbonate extracted from sediment. In two cases the δ¹³C CO₂ of gas hydrate was heavier by 2.8‰–16.5‰ than that of nearby sedimentary carbonate. Unfortunately no analyses of sediment δ¹³C CO₂

was made for direct comparison to our results. To explore these observations we have attempted to constrain the fractionation processes for CO_2 in these sediments.

Paull et al. (Chap. 7, this volume) discuss the offset between $\delta^{13}\text{C}$ values of CO_2 gas and DIC. They note a significant isotopic offset ($\sim 12.5\%$) between the $\delta^{13}\text{C}$ values of CO_2 gas and DIC. A similar offset ($\sim 10\%$) was reported between these carbon pools at DSDP Site 533 (Claypool and Threlkeld, 1983). The offset is presumed to be an artifact of CO_2 outgassing during sediment recovery. Equilibrium fractionation of $8.38 \pm 0.12\%$ (at 20°C ; Emrich et al., 1970) occurs between DIC and gaseous CO_2 .

C_1 is supersaturated in sediments adjacent to gas hydrate, and the majority (likely $\sim 99\%$) of the original C_1 in the sediments below ~ 100 mbsf is lost during the core-recovery process (Dickens et al., 1997; Kvenvolden and Lorenson, Chap. 3, this volume). Paull et al. (Chap. 7, this volume) infer that part of the DIC pool is sparged by degassing C_1 , and thus much of the original in situ DIC pool vents as CO_2 . Thus, the measured pore-water DIC samples reflect the residual DIC that remains in the pore water after vigorous degassing and fractionation. $\delta^{13}\text{C}$ values of the DIC probably lie in between the measured CO_2 gas and DIC pools, but closer to the CO_2 gas values because these samples may reflect the majority of the original DIC input.

If $\delta^{13}\text{C}$ DIC values in sediment adjacent to gas hydrate are nearly that of sediment gas CO_2 , then the same fractionation process that occurs between DIC and sediment gas CO_2 could possibly account for most of the 15% isotopic shift between sediment gas CO_2 and gas hydrate CO_2 . In such a scenario, a phase change of the DIC from ion to gas before inclusion in the hydrate is required for fractionation to occur. Thus gas hydrate would appear to form most efficiently when sediment gas is present rather than from water saturated with a particular gas.

CONCLUSIONS

Gas hydrates were recovered from sediments at Sites 994, 995, 996, and 997. Disseminated gas hydrate was not recovered, although indirect observations such as Cl^- dilution in pore water implied its presence. Gas hydrates from Site 996 were associated with active gas venting and chemosynthetic communities and typically occurred as nodules or vertical veins. Gas hydrates from Sites 994, 995, and 997 were mainly disseminated in sediment pore space of marine silt and clay or, as at Site 997 (331 mbsf), occurred as a massive hydrate presumably filling fracture or fault. Gas and water released from gas hydrate decomposition yielded 18 to 154 volumes of gas per volume of water at STP. When correcting for excess Cl^- in gas hydrate water, the volumetric ratios were from 29 to 204, as compared to a likely maximum value in nature of about 195 to 204. Gas analyses showed that the hydrocarbon gas included in the gas hydrates was mainly C_1 with minor amounts of CO_2 and C_2 . C_3^+ hydrocarbons were present, but in lower concentrations than in samples of sediment gas from sediments near where gas hydrates were found. C_2 appears to be preferentially included in the gas hydrate. CO_2 carbon isotopic composition in gas hydrate is lighter by about 15% relative to CO_2 sources in the surrounding sediment. It is unclear if this fractionation occurs in situ or is an artifact of sample processing.

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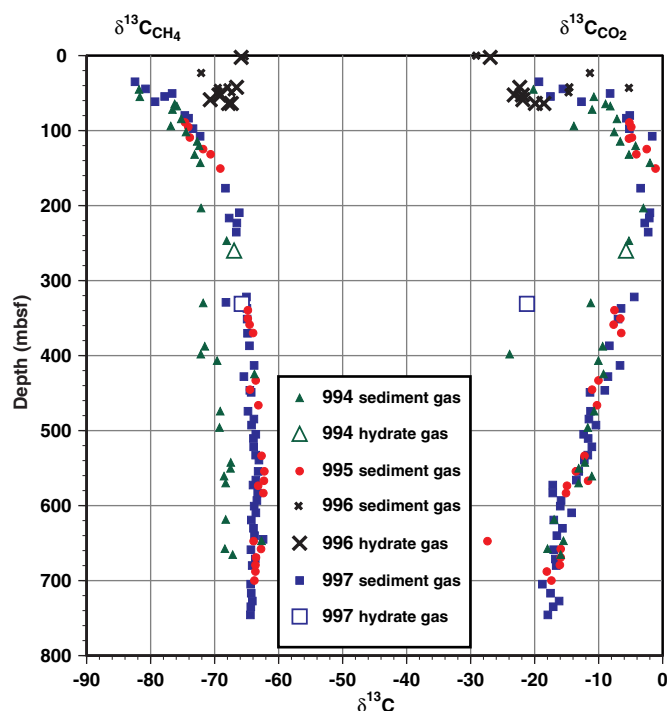


Figure 5. Combined $\delta^{13}\text{C}$ C_1 and $\delta^{13}\text{C}$ CO_2 profiles of gas and gas hydrate from Sites 994, 995, 996, and 997. Gases from sediment gas, gas tubes, and gas from the pressure coring system are in solid shapes, whereas those of gas hydrate are hollow shapes. $\delta^{13}\text{C}$ C_1 of gas hydrate gas closely resembles sediment gas. $\delta^{13}\text{C}$ CO_2 of gas hydrate is fractionated by about 15% from the corresponding sediment gas $\delta^{13}\text{C}$ CO_2 . This relationship is best illustrated by gases from Site 996 and the single measurement from Site 997. At Site 994, gas hydrate $\delta^{13}\text{C}$ CO_2 is nearly that of the sediment gas and does not appear fractionated.

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