3. METHANE AND OTHER HYDROCARBON GASES IN SEDIMENT FROM THE SOUTHEASTERN NORTH AMERICAN CONTINENTAL MARGIN[1]

Keith A. Kvenvolden[2] and Thomas D. Lorenson[2]

ABSTRACT

Residual concentrations and distributions of hydrocarbon gases from methane to *n*-heptane were measured in sediments at seven sites on Ocean Drilling Program (ODP) Leg 164. Three sites were drilled at the Cape Fear Diapir of the Carolina Rise, and one site was drilled on the Blake Ridge Diapir. Methane concentrations at these sites result from microbial generation which is influenced by the amount of pore-water sulfate and possible methane oxidation. Methane hydrate was found at the Blake Ridge Diapir site. The other hydrocarbon gases at these sites are likely the product of early microbial processes.

Three sites were drilled on a transect of holes across the crest of the Blake Ridge. The base of the zone of gas-hydrate occurrence was penetrated at all three sites. Trends in hydrocarbon gas distributions suggest that methane is microbial in origin and that the hydrocarbon gas mixture is affected by diagenesis, outgassing, and, near the surface, by microbial oxidation. Methane hydrate was recovered at two of these three sites, although gas hydrate is likely present at all three sites.

The method used here for determining amounts of residual hydrocarbon gases has its limitations and provides poor assessment of gas distributions, particularly in the stratigraphic interval below about ~100 mbsf. One advantage of the method, however, is that it yields sufficient quantities of gas for other studies such as isotopic determinations.

INTRODUCTION

Hydrocarbon gases, particularly methane, are ubiquitous in oceanic sediment worldwide, and our study of the southeastern North American continental margin represents a continuation of our research on gaseous hydrocarbons in sediment drilled by the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP). The precedent for this work was established in 1971 during DSDP Leg 18 (McIver, 1973). In that early study, oceanic sediment samples from offshore Oregon were sealed in cans, and the composition of the gas, released into the headspace of the cans by shaking, was determined by gas chromatography. This basic procedure has been modified and used in systematic studies of hydrocarbon gases in sediment samples from DSDP Leg 76 (Blake Outer Ridge, Atlantic Ocean; Kvenvolden and Barnard, 1983) and Leg 84 (inner slope, Middle America Trench, Pacific Ocean; Kvenvolden and McDonald, 1985), and during ODP Leg 104 (Vøring Plateau, Norwegian Sea; Kvenvolden et al., 1989), Leg 112 (shelf and slope deposits, Peru-Chile Trench, Pacific Ocean; Kvenvolden and Kastner, 1990), Leg 141 (inner slope, Chile Trench; Froelich et al., 1995), and now Leg 164 (Carolina Rise and Blake Ridge, Atlantic Ocean).

At some drilling locations, methane is so abundant that it takes the form of methane hydrate, a solid, icelike clathrate structure in which a crystalline lattice of water molecules encases molecules of gas, mainly methane. For example, during the investigation of hydrocarbon gases in sediment, methane hydrate was observed on Leg 76 (Kvenvolden and Barnard, 1983), Leg 84 (Kvenvolden and McDonald, 1985), Leg 112 (Kvenvolden and Kastner, 1990), and Leg 164 (Paull, Matsumoto, Wallace, et al., 1996).

In this paper we describe the hydrocarbon gas distribution in sediment cored at seven sites on Leg 164 (Fig. 1) and compare the results with those obtained fifteen years earlier at nearby Site 533 (Fig. 1) from Leg 76 (Kvenvolden and Barnard, 1983). Methane is shown to be the most abundant hydrocarbon gas in these sediments, and the
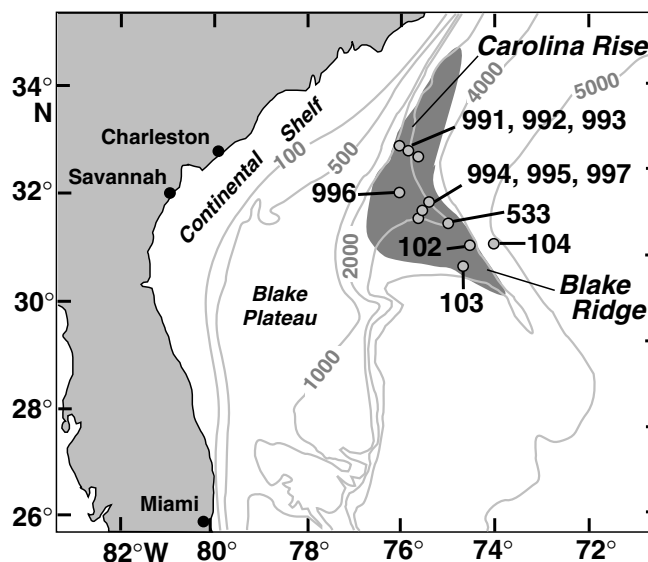

Figure 1. Location of drill sites for DSDP Legs 11 (102, 103, and 104) and 76 (533) and ODP Leg 164 (991–997) on the Carolina Rise and Blake Ridge, offshore from southeastern United States. Bathymetry in meters.

concentration of methane and its distribution with depth are similar at ODP Site 997 (Leg 164) and DSDP Site 533 (Leg 76).

GEOLOGIC SETTING

Seven sites (Sites 991–997) offshore southeastern North America were drilled during Leg 164 (Fig. 1) to provide information on the occurrence and history of gas hydrate in sediment of this region. 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. Site 996 was drilled in upper Pleistocene to lower Pleistocene nannofossil-bearing and nannofossil-rich

clays on the crest of the Blake Ridge Diapir, whereas 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 short distance of 9.6 km. Table 1 lists the average depth of water and the maximum penetration of the drill at the seven sites.

PROCEDURES

Core sections destined for gas analysis were treated using a procedure modified from Kvenvolden and Redden (1980). A 6.6-cm-diameter, 5-cm-long section of whole-round core was cut from the recovered core as it lay on the catwalk core cradle within 5 to 10 min of core retrieval. The section was extruded into a 500-mL metal can equipped with two septa. The can containing the sample was filled with degassed water to the rim, and then 100 mL of water was removed. About 2 to 3 g of sodium azide was added as a bactericide. The sample with water was sealed in the can, leaving a 100-mL headspace. The headspace was purged with helium at a rate greater than 500 mL/min for a period of about 5 min; some cans were purged for longer periods of up to 10 min. The samples were frozen in the upside-down position and shipped to our shore-based laboratory for hydrocarbon gas analyses.

In the laboratory, the frozen samples were allowed to thaw until they reached ~20°C. They were then placed into a high-speed shaker and shaken for 5 min. The hydrocarbon gases were partitioned into the headspace and analyzed. With a syringe, about 10 mL of gas was removed from the headspace for analysis. A similar volume of helium was injected to replace the volume of gas removed.

A Shimadzu GC-14A gas chromatograph equipped with a Chemipack C-18, 6 ft × 1/8 in 80/100 mesh stainless steel column was used to measure hydrocarbon gases from C_1 to C_7. The GC-14A is configured with a 1-mL, valve-actuated, sample loop for injection and a flame ionization detector (FID) for gas detection. Samples were introduced by syringe at atmospheric pressure, and a minimum of 10 mL of gas was used to flush the injection loop. Run conditions were 35°C for 1.5 min, increasing at a rate of 20°/min to 150°C and held at this temperature. Helium was used as the carrier gas at a constant flow rate of 3 kg/cm². FID temperature was held at 150°C. The gas chromatograph was calibrated using hydrocarbon gas standards of known concentrations.

Results are reported relative to the volume of wet sediment from which the gases were extracted (i.e., microliters of gas per liter of wet sediment [μL/L]). These units are unconventional, but they are convenient for expressing gas concentrations that result from this procedure and for comparison with previously reported results, for example, Kvenvolden et al. (1990).

GAS GEOCHEMISTRY

Hydrocarbon gas concentrations (μL/L of wet sediment) obtained from extraction of samples collected on Leg 164 are listed in Tables 2 and 3. The following hydrocarbon gases are reported: methane (C_1), ethane (C_2), ethene ($C_{2=}$), propane (C_3), propene ($C_{3=}$), isobutane (iC_4), n-butane (n-C_4), neopentane ($neoC_5$), isopentane (iC_5), n-pentane (n-C_5), cyclopentane ($cycloC_5$), neohexane ($neoC_6$), isohexane (iC_6), n-hexane (n-C_6), isoheptane (iC_7), and methylcyclohexane + n-heptane (methylcycloC_6 + n-C_7). In addition, the ratio $C_1/(C_2 + C_3)$ is given in Tables 2 and 3. The concentrations of gases obtained by the procedures used here are method and time dependent. That is, the concentrations represent the residual gas present after the samples have been recovered from the cores and stored. The samples have undoubtedly outgassed during core recovery. Length of time taken in sampling will affect the amount of gas that is eventually measured.

Table 1. Water depths and maximum penetration at Leg 164 sites.

Site	Water depth (m)	Maximum penetration (mbsf)
991	2568	56.6
992	2587	50.3
993	2642	51.9
994	2798	703.5
995	2778	704.6
996	2171	63.0
997	2770	750.7

Notes: Data from Paull, Matsumoto, Wallace, et al., 1996. Water depth measured from drill pipe.

Consequently, the reported concentrations are referred to as "residual." In situ concentrations of gases can only be obtained through the use of pressure-core samplers (Dickens et al., 1997).

SITES ASSOCIATED WITH DIAPIRS
(Sites 991, 992, 993, and 996)

Results obtained from samples collected from coring diapirs are listed in Table 2. Samples from Sites 991, 992, and 993, on the crest and flank of the Cape Fear Diapir, contain residual hydrocarbon gases, with methane dominant. In general, methane concentrations increase with depth (Fig. 2; see Table 2 for details); methane concentrations at Site 993 are more complex. Maximum depth sampled was 51.5 meters below seafloor (mbsf). At all sites, the residual methane distribution is controlled by the availability of sulfate (for sulfate distributions, see Paull, Matsumoto, Wallace, et al., 1996) and follow the classical model of Claypool and Kaplan (1974). At Sites 991 and 993, the rapid increase in methane concentrations near 40 m and 25 m, respectively, corresponds to the intervals where sulfate values, rapidly depleting with depth, approach 0 mM. In contrast, at Site 992 the methane concentrations are relatively low, and sulfate concentrations in the same stratigraphic interval range from ~30 mM near the surface to ~5 mM at a depth of ~50 mbsf. The presence of sulfate apparently limits the generation of methane in sediment at Site 992. Higher molecular weight hydrocarbon gases are also present at these sites, with $C_1/(C_2 + C_3)$ ratios <100 in many cases (Table 2).

Samples from Site 996, located on the crest of the Blake Ridge Diapir, also contain residual hydrocarbon gases (Table 2), but in this case concentrations of methane are very high (between 10,000 and 40,000 μL/L) within the sampled interval of 3.6 to 63.0 mbsf. Sulfate concentrations in this same stratigraphic interval are depleted to 0 mM, and massive and vein-filling gas hydrate was recovered to a depth of ~60 mbsf (Paull, Matsumoto, Wallace, et al., 1996). Absolute concentrations of residual higher molecular weight hydrocarbons are larger in samples from Site 996 than at the three sites on the Cape Fear Diapir (Table 2), but the concentrations relative to methane are lower as reflected in $C_1/(C_2 + C_3)$ ratios ranging from 1100 to 1600.

SITES TO EXAMINE GAS HYDRATE OCCURRENCE
(Sites 994, 995, and 997)

Sites 994, 995, and 997, on a northeast-bearing transect across the Blake Ridge, were selected because geophysical information pertinent to gas-hydrate occurrence are particularly distinct. This information includes (1) a well-developed bottom-simulating reflector (BSR), which marks on marine seismic records, the base of gas-hydrate stability, and present at Sites 995 and 996, and (2) the occurrence at all three sites 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 depths

Table 2. Residual hydrocarbon gas concentrations (µL/L) at Sites 991, 992, 993, and 996.

Core, section	Depth (mbsf)	C_1	$C_{2=}$	C_2	C_3	$C_{3=}$	iC_4	$n\text{-}C_4$	$neoC_5$	iC_5	$n\text{-}C_5$	$cycloC_5$	$neoC_6$	iC_6	$n\text{-}C6$	iC_7	methylcyclo C_6 and $n\text{-}C_7$	$C_1/(C_2+C_3)$
								µL/L wet sediment										
164-991A-																		
1H-5	7.4	25	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	78
2H-2	12.1	110	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	64
3H-2	21.5	240	0.0	6.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	36
4H-2	31.1	420	0.0	13.8	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	29
5H-2	40.5	19,100	0.0	32.7	3.0	0.0	1.9	0.4	0.0	0.8	0.0	0.0	0.0	0.4	0.4	0.0	0.0	540
6H-3	51.5	26,900	0.0	38.7	4.7	0.3	3.2	0.4	0.1	0.9	0.0	0.0	0.0	0.6	0.4	0.0	0.0	620
164-992A-																		
1H-2	2.5	18	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	140
2H-2	5.7	3	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	16
3H-2	15.2	10	0.0	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	36
4H-2	24.7	27	0.0	0.4	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	54
5H-4	37.3	140	0.1	2.8	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	46
6H-3	45.3	220	0.0	7.4	0.3	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	28
164-993A-																		
1H-1	0.9	11	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	54
2X-2	4.8	4	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	14
3X-2	16.7	260	0.0	7.0	1.4	0.3	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	31
4X-2	25.9	20,100	0.0	45.8	2.8	0.0	2.5	0.3	0.5	0.4	0.0	0.0	0.0	0.5	0.3	0.4	0.0	410
5X-2	35.1	16,000	0.0	67.8	2.7	0.0	2.4	0.2	0.5	0.3	0.0	0.0	0.2	0.4	0.2	0.3	0.0	230
6X-2	45.1	14,300	0.0	74.9	2.7	0.0	2.8	0.2	0.6	0.3	0.0	0.0	0.2	0.4	0.0	0.0	0.0	190
164-996A-																		
1H-6	3.6	13,900	0.0	8.5	1.9	0.0	0.9	0.3	0.0	1.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1,330
3X-2	10.2	19,900	0.0	18.0	1.5	0.0	0.2	0.0	0.2	0.1	0.0	0.0	0.2	0.5	0.2	0.9	0.0	1,020
9H-3	70.4	38,400	0.0	28.7	6.8	0.0	7.4	3.3	0.3	18.5	1.4	0.3	0.5	4.2	4.0	1.5	0.3	1,080

Note: 0.0 = concentrations are below the detection limits of the method.

Table 3. Residual hydrocarbon gas concentrations (µL/L) at Sites 994, 995, and 997

Core, section	Depth (mbsf)	C_1	$C_{2=}$	C_2	C_3	$C_{3=}$	iC_4	$n\text{-}C_4$	$neoC_5$	iC_5	$n\text{-}C_5$	$cycloC_5$	$neoC_6$	iC_6	$n\text{-}C_6$	iC_7	methylcyclo C_6 and $n\text{-}C_7$	$C_1/(C_2+C_3)$
								µL/L wet sediment										
164-994C-																		
2H-3	8.9	80	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	250
5H-4	38.9	33,700	0.0	2.3	6.3	0.0	0.6	0.0	0.0	0.3	0.0	0.0	0.0	0.1	0.1	0.0	0.0	3,900
7H-6	60.9	31,400	0.0	1.8	1.1	0.0	0.6	0.0	0.0	0.2	0.0	0.0	0.0	0.1	1.0	0.0	0.0	11,000
8H-2	64.4	14,300	0.0	1.4	1.4	0.0	0.6	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.3	0.0	0.0	5,000
11H-2	84.3	18,900	0.0	1.6	1.9	0.0	1.1	0.3	0.0	0.8	0.0	0.0	0.0	0.3	0.3	0.0	0.0	5,400
14H-5	117.3	13,500	0.0	1.2	0.9	0.0	1.0	0.2	0.0	1.0	0.0	0.0	0.0	0.1	0.8	0.0	0.0	6,500
17H-2	141.4	4,150	0.0	0.7	1.2	0.0	1.6	0.4	0.0	3.9	0.0	0.1	0.0	0.4	0.4	0.2	0.3	2,200
21X-2	167.8	24,600	0.0	3.1	4.4	0.0	6.2	1.5	0.0	17.6	0.4	0.2	0.0	1.0	0.5	0.2	0.3	3,300
21X-1	195.1	33,100	0.0	3.6	5.6	0.0	10.2	2.8	0.0	36.4	0.9	0.4	0.0	4.5	1.9	0.7	0.8	3,600
30X-2	243.7	7,020	0.0	2.3	2.1	0.0	2.2	1.2	0.0	8.0	0.6	0.2	0.0	0.9	1.0	0.2	0.2	1,600
31X-6	259.4	18,100	0.0	6.3	4.9	0.0	5.1	2.9	0.0	12.2	0.9	0.3	0.1	1.5	1.7	0.3	0.4	1,600
33X-2	273.2	6,610	0.0	1.7	2.6	0.0	3.0	1.9	0.0	11.4	0.9	0.2	0.1	2.0	2.4	0.6	0.5	1,500
39X-1	319.5	7,130	0.0	5.4	4.7	0.0	5.2	2.8	0.0	8.5	0.8	0.2	0.0	0.7	1.5	0.5	0.5	710
39X-1	319.5	10,100	0.0	3.9	4.1	0.0	4.0	2.4	0.0	5.6	0.7	0.2	0.0	0.8	1.8	0.5	0.5	1,300
42X-3	352.0	5,260	0.0	4.9	1.5	0.0	1.6	1.0	0.0	9.1	0.6	0.1	0.0	0.9	1.4	0.2	0.3	820
46X-2	379.3	4,210	0.0	4.3	0.6	0.0	1.4	0.9	0.0	9.4	0.6	0.2	0.0	1.0	1.5	0.4	0.4	860
50X-1	406.7	18,300	0.0	17.0	8.1	0.0	6.5	3.4	0.0	18.5	0.9	0.2	0.1	1.9	2.3	0.5	0.3	730
54X-4	440.0	12,500	0.0	14.9	3.9	0.0	3.0	2.0	0.0	10.6	0.8	0.2	0.1	1.2	2.2	0.6	0.3	660
57X-1	464.6	6,020	0.0	7.7	3.3	0.0	2.2	1.7	0.0	6.3	0.6	0.1	0.1	1.0	2.3	0.9	0.5	550
61X-2	495.7	12,600	0.0	20.7	4.2	0.1	3.0	1.9	0.1	6.4	0.8	0.2	0.2	1.6	3.9	1.5	1.2	510
64X-3	525.1	9,060	0.2	18.7	4.9	0.2	1.5	1.6	0.1	2.5	0.3	0.1	0.1	0.6	1.3	0.5	0.0	390
68X-3	553.3	15,000	0.0	21.2	4.1	0.0	1.2	1.5	0.0	2.8	0.4	0.0	0.1	0.6	2.4	0.9	0.4	590
72X-2	581.2	13,900	0.0	30.9	4.6	0.0	2.1	1.6	0.0	2.6	1.3	0.1	0.1	0.8	9.3	0.4	0.0	390
75X-4	613.0	4,680	0.3	21.2	8.6	0.2	3.8	5.5	0.1	6.0	1.2	0.3	0.4	2.2	6.1	1.9	1.9	160
78X-2	639.0	10,900	0.0	36.0	8.0	0.0	2.7	3.4	0.1	3.3	0.6	0.2	0.2	1.2	3.2	1.9	2.6	250
81X-3	668.3	9,120	0.0	29.0	5.7	0.0	2.7	2.3	0.2	4.3	0.9	0.2	0.3	1.3	4.5	1.8	0.9	260
84X-2	696.5	14,600	0.5	71.3	16.3	0.2	3.9	4.1	0.1	4.5	0.6	0.2	0.2	1.4	3.5	1.8	1.3	170
164-995A-																		
2H-2	4.7	10	0.2	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	40
5H-1	31.6	24,400	0.0	1.4	0.9	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	10,400
8H-2	61.6	3,450	0.0	0.4	0.6	0.0	0.4	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3,500
12H-5	94.6	2,460	0.0	0.6	0.9	0.0	1.0	0.1	0.0	1.0	0.0	0.0	0.0	0.1	0.3	0.0	0.0	1,700
15H-3	121.2	26,100	0.0	2.3	2.3	0.0	2.3	0.3	0.0	2.9	0.0	0.0	0.0	0.2	0.3	0.0	0.1	5,600
17H-4	141.4	12,100	0.0	1.7	2.7	0.0	5.2	0.7	0.0	9.7	0.0	0.1	0.0	0.4	0.4	0.1	0.1	2,700
19H-5	152.7	2,340	0.0	0.6	1.0	0.0	1.9	0.4	0.0	9.5	0.0	0.1	0.0	0.8	0.5	0.0	0.0	1,500
22X-2	177.6	9,530	0.0	1.4	2.1	0.0	4.5	0.9	0.0	8.5	0.4	0.2	0.0	1.9	0.4	0.2	0.3	2,700
25X-3	208.0	12,300	0.0	3.1	1.9	0.0	2.9	0.7	0.0	16.4	0.4	0.1	0.0	2.2	1.0	0.3	0.3	2,500
30X-2	246.8	13,700	0.0	5.8	1.4	0.0	0.9	0.6	0.0	3.6	0.3	0.1	0.0	0.6	0.9	0.0	0.0	1,900
30X-3	248.5	21,500	0.0	5.0	5.8	0.0	5.3	2.5	0.0	9.3	0.5	0.3	0.0	0.8	1.2	0.2	0.2	2,000
33X-2	274.5	12,000	0.0	5.2	2.4	0.0	2.6	1.1	0.0	5.9	0.6	0.2	0.0	1.0	1.5	0.2	0.0	1,600
40X-2	331.6	6,610	0.0	2.7	2.9	0.0	2.2	1.6	0.0	2.7	0.4	0.2	0.0	0.7	1.3	0.2	0.0	1,200
43X-3	362.7	18,700	0.0	14.0	0.9	0.0	3.4	2.1	0.0	3.4	0.5	0.2	0.1	0.8	1.3	0.3	0.0	1,300
47X-2	389.8	10,800	0.0	14.0	4.0	0.0	2.5	1.5	0.0	4.8	0.5	0.1	0.0	0.6	1.0	0.0	0.0	600
51X-2	418.7	16,000	0.0	31.2	5.6	0.0	3.0	1.7	0.0	5.4	0.5	0.1	0.0	0.6	1.3	0.3	0.0	430
54X-3	439.7	13,700	0.0	29.6	4.5	0.0	2.4	1.4	0.0	5.8	0.6	0.2	0.2	1.1	2.6	0.7	0.4	400
57X-2	467.2	3,740	0.0	5.8	5.4	0.0	2.7	1.6	0.0	4.3	0.3	0.1	0.1	0.3	1.7	0.7	0.2	330
62X-3	506.5	3,740	0.0	6.8	1.7	0.0	0.6	0.4	0.0	0.9	0.0	0.0	0.0	0.2	0.2	0.3	0.0	440
65X-3	536.5	8,650	0.0	14.3	3.2	0.0	1.0	0.8	0.0	1.3	0.0	0.0	0.0	0.2	0.7	0.3	0.0	490
68X-2	563.4	8,190	0.0	16.3	3.1	0.0	0.9	0.8	0.0	1.4	0.2	0.0	0.0	0.3	1.0	0.5	0.0	420
73X-4	613.0	7,190	0.0	33.7	10.9	0.0	3.0	2.9	0.2	4.4	0.5	0.1	0.2	0.9	2.5	0.9	0.5	160
77X-3	640.2	8,190	0.2	27.3	6.8	0.2	1.8	2.2	0.1	2.5	0.4	0.1	0.2	0.6	2.2	0.9	0.5	240
80X-4	671.4	8,950	0.0	26.8	6.8	0.0	1.8	1.6	0.0	1.8	0.2	0.0	0.0	0.0	0.7	0.4	0.0	270
83X-4	700.8	6,670	0.0	25.0	6.0	0.0	1.6	1.5	0.0	2.2	0.2	0.0	0.1	0.2	1.0	0.5	0.0	210
164-997A-																		
3H-4	18.3	370	0.2	2.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	130
6H-1	42.4	12,200	0.0	1.2	1.2	0.0	0.7	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4,900
9H-6	70.4	62,000	0.0	3.0	4.5	0.0	1.7	0.2	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	8,300
12H-2	92.8	11,900	0.0	1.6	2.4	0.0	3.5	0.5	0.0	3.1	0.0	0.0	0.0	0.3	0.2	0.0	0.0	3,000
15H-6	127.3	4,040	0.2	0.9	1.3	0.2	1.5	0.3	0.0	4.3	0.0	0.0	0.0	0.2	0.0	0.1	0.2	1,900
18P-1	147.0	10,100	0.0	3.6	2.9	0.0	6.7	1.3	0.0	18.8	0.1	0.2	0.0	1.2	0.3	0.0	0.0	1,600

Table 3 (continued).

Core, section	Depth (mbsf)	C_1	$C_{2=}$	C_2	C_3	$C_{3=}$	iC_4	$n\text{-}C_4$	$neoC_5$	iC_5	$n\text{-}C_5$	$cycloC_5$	$neoC_6$	iC_6	$n\text{-}C_6$	iC_7	methylcyclo C_6 and $n\text{-}C_7$	$C_1/(C_2+C_3)$
									μL/L wet sediment									
19H-5	154.6	1,890	0.2	0.9	1.3	0.1	2.5	0.5	0.0	10.1	0.2	0.1	0.0	0.8	0.3	0.0	0.0	870
22X-5	179.5	10,100	0.0	1.4	2.1	0.0	4.5	1.0	0.0	19.2	0.4	0.2	0.0	2.7	0.7	0.3	0.1	2,900
25P-1	203.1	32,100	0.0	0.6	1.8	0.2	1.8	0.6	0.0	8.1	0.6	0.1	0.0	1.5	4.1	0.5	0.3	13,000
26X-3	207.8	11,800	0.0	1.8	2.2	0.1	3.5	0.7	0.0	9.9	0.3	0.1	0.0	1.0	0.5	0.1	0.0	3,000
30X-3	236.3	4,150	0.0	1.2	1.9	0.0	4.6	1.7	0.0	7.6	0.2	0.2	0.0	0.7	0.9	0.1	0.0	1,400
34X-4	266.7	14,300	0.0	2.1	3.3	0.2	4.4	2.0	0.0	11.6	0.6	0.4	0.0	0.9	1.2	0.0	0.0	2,700
37X-4	294.8	21,300	0.4	4.3	6.7	0.5	10.4	4.3	0.0	40.1	2.7	0.9	0.1	4.6	6.1	1.1	0.7	1,900
41X-1	320.2	10,700	1.1	4.9	5.4	0.3	10.7	3.9	0.1	30.5	2.1	0.8	0.0	2.8	6.4	0.9	0.6	1,000
44X-4	352.7	13,900	0.4	4.3	6.3	0.0	11.3	4.0	0.0	22.3	1.3	0.7	0.1	1.2	3.1	0.5	0.4	1,300
47X-3	379.7	5,090	0.0	3.7	1.7	0.0	5.8	1.8	0.0	20.1	0.8	0.1	0.0	1.3	2.3	0.2	0.1	930
49P-1	395.4	2,130	0.5	4.1	0.4	0.2	1.2	0.6	0.1	13.2	0.4	0.1	0.0	2.6	4.1	0.7	0.6	470
52X-4	411.2	4,390	0.4	7.8	2.1	0.1	6.4	2.0	0.1	31.0	1.3	0.1	0.0	4.1	7.0	1.2	1.0	450
55P-1	433.6	10,800	0.6	14.2	1.3	0.3	0.6	0.5	0.3	5.2	0.9	0.2	0.0	1.4	3.4	1.4	0.8	690
164-997B-																		
3X-3	341.6	14,500	0.0	8.3	2.2	0.0	6.4	2.4	0.0	15.1	1.0	0.4	0.0	1.2	3.0	0.3	0.0	1,400
8X-4	448.8	20,100	1.5	50.8	2.1	0.5	2.1	1.3	0.4	5.5	0.4	0.0	0.0	0.7	1.9	1.2	0.2	380
10P-1	462.2	12,900	0.0	19.0	5.4	0.3	7.8	7.3	0.5	43.3	4.7	0.7	1.3	8.8	18.0	3.7	2.1	530
12X-3	475.5	12,600	0.0	19.3	4.8	0.1	3.8	2.2	0.1	8.4	0.8	0.1	0.3	1.2	2.8	0.7	0.0	530
15P-1	500.9	25,400	1.0	27.7	6.6	0.3	4.6	3.7	0.3	12.1	1.4	0.2	0.4	1.9	5.0	1.8	1.0	740
16X-3	506.2	12,500	0.0	34.9	8.9	0.0	7.4	5.4	0.3	16.8	2.4	0.3	0.6	2.9	8.7	2.1	1.2	290
19X-1	531.5	17,600	0.0	34.0	8.7	0.1	5.1	4.2	0.2	7.8	1.7	0.4	0.5	0.9	9.1	1.0	0.2	410
23X-6	567.3	17,100	2.0	55.7	14.3	0.4	8.5	6.9	0.4	12.4	1.9	0.3	0.6	2.5	6.5	1.9	1.0	240
27X-5	594.7	17,400	0.0	41.0	12.3	0.0	5.2	3.2	0.0	7.1	0.9	0.3	0.3	1.0	3.4	1.6	1.1	330
30X-1	617.6	17,800	0.0	41.3	17.3	0.0	10.9	5.8	0.3	15.7	1.4	0.5	0.7	3.0	5.6	1.5	0.5	300
34X-1	646.4	18,100	0.0	53.8	21.3	0.0	11.7	6.4	0.4	16.7	2.0	0.4	0.6	3.2	5.7	36.7	0.9	240
37X-1	666.5	24,300	0.0	74.3	24.6	0.2	11.3	7.5	0.5	17.6	2.3	0.5	0.8	3.5	7.5	2.6	1.8	250
42X-3	706.0	10,500	0.0	50.4	17.8	0.0	7.0	5.5	0.3	13.5	1.5	0.3	0.5	2.8	4.6	1.5	0.7	150
46X-6	739.2	13,900	0.0	55.4	15.1	0.0	4.4	4.3	0.3	8.0	2.0	0.3	0.4	2.0	4.0	1.5	0.7	200
47X-5	748.5	15,300	0.0	79.5	23.4	0.0	5.8	5.3	0.3	7.2	1.1	0.2	0.4	1.7	3.2	1.0	0.1	150

Note: 0.0 = concentrations are below the detection limits of the method.
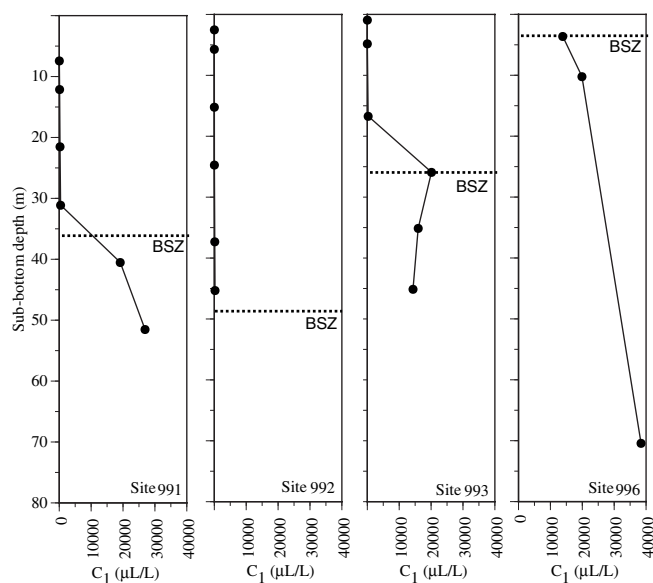
Figure 2. Comparison of residual C_1 concentrations with depth for sediment samples from Sites 991, 992, and 993 on the Cape Fear Diapir and Site 996 on the Blake Ridge Diapir. BSZ = base of sulfate reduction zone.

Figure 3. Profiles of residual C_1 concentrations with depth for sediment samples from Sites 994, 995, and 997 on the Blake Ridge. These profiles are compared with that from Site 533. GH = gas-hydrate sample recovered; BSZ = base of sulfate reduction zone; BSR = bottom-simulating reflector, which is near the base of the gas-hydrate stability zone.

exceeding that of the BSR at ~450 mbsf (Table 1). Results obtained from samples collected at these three sites are listed in Table 3. As in the case of samples recovered from the diapirs, all samples from this transect of three sites contained hydrocarbon gases, with methane the most abundant. Distributions of methane with depth are shown in Figure 3 and are discussed below.

Site 994 is considered the reference site on the three-hole transect; no BSR is observed at this site, but the BSR is well-developed at the other two sites. Methane concentrations at Site 994 increase rapidly from 80 to 34,000 µL/L between 8.9 and 38.9 mbsf, whereas sulfate is depleted to 0 mM in the same interval and remains near this value to the bottom of the hole. Higher molecular weight hydrocarbon gases are also present, but the amounts relative to methane are always small as reflected in the $C_1/(C_2 + C_3)$ ratios, which decrease with depth and are always larger than 200.

Although no BSR is present at Site 994, gas hydrate was recovered at 259 and 261 mbsf. The residual methane concentrations do not show anomalously high values in this stratigraphic interval. Thus, residual methane measurements do not appear to be useful in identifying intervals of gas-hydrate occurrence. Inorganic geochemical and logging data from this site suggest, however, that disseminated gas hydrate occurs intermittently throughout the stratigraphic interval extending between ~195 and ~450 mbsf (Paull, Matsumoto, Wallace, et al., 1996). Even in the transition interval at the projected depth of the BSR at ~450 mbsf, there is no marked change in the trend in concentrations of methane (Fig. 3).

Site 995 was the first site on Leg 164 at which drilling penetrated through a strong BSR. The site is located 3.0 km northeast of Site 994, and the drill cored the same stratigraphic interval as at Site 994. As at the previous site, residual methane concentrations increase rapidly and immediately with depth reaching maximum concentrations at 32 and 121 mbsf of 24,000 and 26,000 µL/L, respectively. In general, methane concentrations are lower at this site than at Site 994; sulfate concentrations below ~20 m are depleted (~0 nM). Higher molecular weight hydrocarbon gases are present in amounts comparable to those at Site 994, and $C_1/(C_2 + C_3)$ ratios show the same trends.
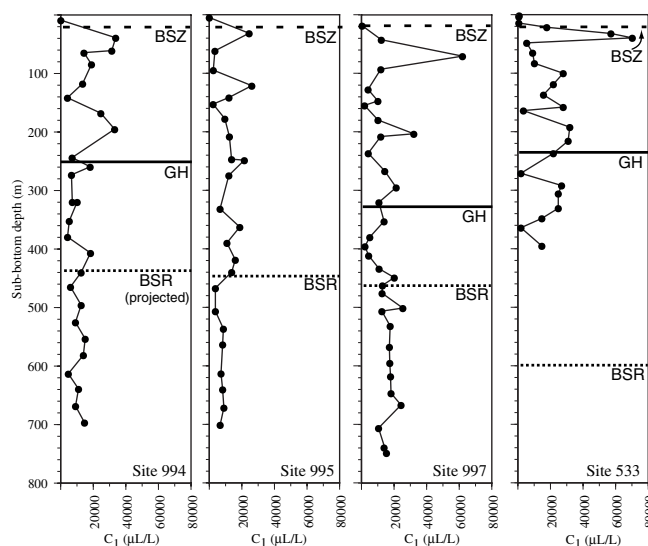
In spite of the fact that a strong BSR was penetrated at Site 995, no samples of gas hydrate were recovered in any core from this site; however, chemical and thermal data indicate that gas hydrate is likely present in a disseminated form in the section of the cored sequence between about 190 and 460 mbsf (Paull, Matsumoto, Wallace, et al., 1996). In this stratigraphic interval, methane concentrations are generally in the range from 10,000 to 20,000 µL/L. Below the BSR, the concentrations are less than 10,000 µL/L in the zone where free gas exists beneath the gas hydrate (Fig. 3). Thus the presence of a free-gas zone is not obvious from the residual gas results.

Site 997 is located on the topographic crest of the Blake Ridge, and there is a very well-developed BSR that was penetrated during drilling. The site is about 6.6 km northeast of Site 995, and the stratigraphic interval of the two sites is similar. As at Site 995, concentrations of residual methane increase rapidly at the top of the hole, reaching a maximum of 62,000 µL/L at 70 mbsf. With depth, the concentrations are variable and usually larger then 10,000 µL/L and generally greater than the amounts observed at Site 995; sulfate concentrations at Site 997 are depleted (~0 mM) below 23 mbsf (Paull, Matsumoto, Wallace, et al., 1996). Higher molecular weight hydrocarbon gases are present in amounts usually exceeding those observed at Site 995, but the $C_1/(C_2 + C_3)$ ratios are similar and show a decreasing trend with depth.

In contrast to Site 995, at Site 997 one large gas-hydrate sample was recovered from 331 mbsf; however, the presence of dispersed gas hydrate was inferred, based on inorganic chemical, thermal, and logging data, to be present over a zone extending from 180 to 450 mbsf (Paull, Matsumoto, Wallace, et al., 1996). At Site 997, beneath the BSR, there was a slight increase in methane concentration in the free-gas region (Fig. 3), but this increase may not be significant as the free-gas region was not reflected in the residual gas results from Sites 994 and 995 (Fig. 3).

The concentrations and distributions of residual hydrocarbon gases as determined by the procedures described here are similar to results obtained shipboard using a headspace procedure in which ~5 cm³ of sediment was heated in a sealed glass vial (Paull, Matsumoto, Wallace, et al., 1996). In contrast, our procedure used ~170 cm³ of

sediment. The main advantage of the larger sample size is that more gas can be extracted, and this gas can be analyzed for other components and for isotopic compositions.

COMPARISON WITH DSDP LEG 76, SITE 533

About 150 km southeast of the Sites 994, 995, 997 transect is a transect of three other sites (102, 103, and 104) from DSDP Leg 11 (Fig. 1). These three sites were drilled in 1970 (Ewing and Hollister, 1972) to investigate the causes of BSRs seen on seismic profiles along the Blake Outer Ridge. Although the effects of high concentrations of gas were observed, no obvious gas hydrate was recovered. Nevertheless, the occurrence of gas hydrate in sediments at these sites was postulated on the basis of the concurrence of geophysical and geochemical evidence (Stoll et al., 1971; Ewing and Hollister, 1972; and Lancelot and Ewing, 1972).

The postulation for gas-hydrate occurrence in sediment of the Blake Outer Ridge led to the drilling in 1980 of Site 533 during DSDP Leg 76, about 70 km northwest of Sites 102, 103, and 104 (Fig. 1); thus, Site 533 is located about 80 km from the newly occupied Sites 994, 995, and 997. Site 533 was intentionally placed on the periphery of a major gas-hydrate accumulation (mapped distribution of BSRs), and drilling to 399 m did not pass through sediment showing significant seismic blanking and did not penetrate the calculated base of the gas-hydrate stability zone at ~600 mbsf (Kvenvolden and Barnard, 1983). The distribution of methane concentrations with depth is shown in Figure 3, based on data summarized in Kvenvolden et al. (1990). A gas-hydrate sample was recovered at 238 mbsf at Site 533. These methane concentrations and depth distributions compare favorably with those reported for Site 997.

SOURCES OF METHANE AND OTHER HYDROCARBON GASES

The sources of methane and other hydrocarbon gases in residual gas in sediments can be inferred from molecular ratios and from isotopic compositions. At the three Cape Fear Diapir sites (Sites 991, 992, and 993), the residual methane apparently is controlled by the availability of sulfate, as discussed earlier. The implication is that methane is microbial in origin, resulting from CO_2 reduction following the microbial depletion of sulfate (Claypool and Kaplan, 1974). However, the $C_1/(C_2 + C_3)$ ratios are <100 in many cases (Table 2), suggesting the presence of thermogenically formed hydrocarbons, according to criteria of Bernard et al. (1976). Methane carbon isotopic compositions ($\delta^{13}C$) of one sample from each of Sites 991 and 993 measured –72.4 and –77.7‰$_{PDB}$, respectively (Paull et al., Chap. 7, this volume). These isotopically light values suggest that the methane is microbial in origin (Bernard et al., 1976).

The molecular and isotopic evidence are thus in conflict. One possible explanation is that the gas mixture is microbial but has incurred preferential loss of methane through methane oxidation, leading to diminished $C_1/(C_2 + C_3)$ ratios. For this idea to be correct, the $\delta^{13}C$ values of the pre-oxidized methane should have been lighter than about –72‰. Unfortunately, no $\delta^{13}C$ determinations were made on methane occurring immediately below the zone of sulfate reduction at these sites. However, at sites on the nearby Blake Ridge transect, the $\delta^{13}C$ values of methane in this zone are lighter, ranging from about –80 to –101‰ (Paull et al., Chap. 7, this volume). The pre-oxidized methane at the diapir sites may have had similar carbon isotopic compositions. If this interpretation is correct, then methane oxidation explains the molecular and isotopic compositions observed at these diapir sites.

Concentrations of methane relative to other hydrocarbon gases are higher at the Blake Ridge Diapir site (Site 996) as reflected in $C_1/$ $(C_2 + C_3)$ ratios ranging from 1100 to 1600 (Table 2), indicating a microbial origin for the gas mixture (Bernard et al., 1976). The $\delta^{13}C$ values of 13 samples of methane measured –68.0 ± 2.4‰, a range suggesting microbial diagenesis (Paull et al., Chap 7, this volume). Thus both molecular and isotopic compositions indicate that these hydrocarbon gases are likely the product of very early microbial diagenesis, and the methane is likely the product of intense microbial methanogenesis, leading to sufficient methane for gas-hydrate formation.

At the three sites (Sites 994, 995, and 997) on the Blake Ridge transect, methane dominates the hydrocarbon gas mixtures, and $C_1/$ $(C_2 + C_3)$ ratios are large, ~10,000 below ~30 mbsf, and decrease with depth to ~500 (Table 3). The diminishing $C_1/(C_2 + C_3)$ ratios with depth can be explained, in part, as the result of (1) diagenesis wherein amounts of C_2 and C_3 increase with depth, and/or (2) preferential loss of methane during outgassing. For example, during core recovery, methane saturates the pore fluid and is preferentially lost while the other hydrocarbon gases, which are present in much lower concentrations, do not reach saturation and thus are retained in the pore waters. Preferential methane outgassing affects methane concentrations and the $C_1/(C_2 + C_3)$ ratios, but not the methane carbon isotopic compositions, which are determined for the most part by the isotopic fractionation that occurs during microbial methane formation from CO_2 reduction as suggested by Galimov and Kvenvolden (1983).

The $\delta^{13}C$ values of methane fall in the range –68.4 ± 7.0‰ with values becoming uniform (–64.0 ± 0.9‰) below 300 mbsf (Paull et al., this volume). The molecular ratios $C_1/(C_2 + C_3) > 500$) and the isotopic results suggest that methane is the product of microbial methanogenesis, following the criteria of Bernard et al. (1976). Although C_2 concentrations tend to increase with depth, amounts never reach levels suggestive of a thermal origin, and the $\delta^{13}C$ values of ethane (–65.7 ± 2.1‰) in 12 samples from Site 997 (Paull et al., this volume) are consistent with the ethane also being microbial as proposed by Waseda and Didyk (1995) for Leg 141 results, and are supported by arguments given by Vogel et al. (1982) and Oremland et al. (1988).

The low $C_1/(C_2 + C_3)$ ratios in residual gas samples collected within the thin zone of sulfate reduction (most shallow sample at each site in Table 3) likely result from methane oxidation, leaving behind less methane and microbially produced C_2 and C_3. The $\delta^{13}C$ values of this residual methane should be isotopically heavy, but, unfortunately, samples of this methane were not measured for carbon isotopic compositions.

All of the hydrocarbon gas results from Sites 994, 995, and 997 extend and do not contradict results obtained earlier from Site 533 (Kvenvolden and Barnard, 1983; Galimov and Kvenvolden, 1983; Kvenvolden et al., 1990). The molecular and isotopic compositions of the residual hydrocarbon gases found in coring the Blake Ridge thus indicate that these gases are a product of microbial processes including microbial diagenesis. Sufficient methane was generated and recycled in sediment of the Blake Ridge to cause gas-hydrate formation. There is no evidence for a significant contribution of thermogenic methane, although thermogenesis may be responsible for some of the hydrocarbon gases larger than methane, for example, isopentane, which often occurs in anomalous concentrations (Table 3).

CONCLUSION

The distributions of residual hydrocarbon gases correlate well with the record of sulfate depletion in the upper ~60 m of sediment at each site reported here. In the lower stratigraphic intervals, especially in the intervals where gas hydrate was recovered and where chemical, thermal, and logging data indicated disseminated gas hydrate, the measured residual gas concentrations did not reflect anomalously high amounts of methane indicative of the presence of gas hydrate.

Also, the free-gas interval beneath the gas-hydrate zone was not clearly revealed. The residual-gas method employed here and the method used shipboard (Paull, Matsumoto, Wallace, et al., 1996) are not adequate to yield even qualitative, proxy information concerning the in situ hydrocarbon gas concentrations and distributions below the zone of sulfate reduction and early methane production. However, the molecular and isotopic compositions of residual gases collected by the methods described here permit interpretations of hydrocarbon gas sources and processes affecting these gases. To understand the true distribution and concentration of hydrocarbon gases in oceanic sediments will require the use of pressure-core–samplers (Dickens et al., 1997), but because of difficult deployment logistics, these kinds of samplers currently can only provide a spotty record. Improvements in pressure-core–sampling technology and strategy are required.

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