

15. HYDROCARBON GASES IN SEDIMENT OF THE VØRING PLATEAU, NORWEGIAN SEA¹

Keith A. Kvenvolden,² Margaret Golan-Bac,² Thomas J. McDonald,³
Ronald C. Pflaum,³ and James M. Brooks³

ABSTRACT

Geochemical studies at three ODP Leg 104 sites on the Vøring Plateau help define the distribution of hydrocarbon gases in sediment of this prominent feature of the Norwegian continental margin. Low levels of hydrocarbon gas were encountered in sediment of the outer part of the plateau, but sediment of the inner part of the plateau is very gassy. The molecular composition of inner plateau gases ($> 99.9\%$ methane) and the carbon isotopic composition of the methane (avg. = -76% relative to the PDB standard) clearly show that the gas is biogenic. Heavier hydrocarbon gases accompany this methane, and their presence is probably a result of both chemical and microbial low-temperature diagenesis. Although these heavier hydrocarbons were not detected in sediment of the outer part of the plateau during shipboard analyses, subsequent shore-based analyses showed that these compounds are present at very low concentrations. Methane in the gassy sediment of the inner part of the plateau may be present as gas hydrates, judging from sedimentological and inorganic geochemical considerations, but no discernible gas hydrates were recovered during drilling.

INTRODUCTION

Our study of hydrocarbon gases in sediments of the Vøring Plateau represents an extension of previous Deep Sea Drilling Project (DSDP) work initiated on Leg 18 in 1971 (McIver, 1973). In that early work, sediment samples were sealed in cans, and the composition of gas released into the cans was determined. This basic idea has been carried forward, and systematic studies using similar procedures have been conducted on Leg 76 (Kvenvolden and Barnard, 1983), Leg 84 (Kvenvolden and McDonald, 1985), and now on the Ocean Drilling Program (ODP) Leg 104 (Kvenvolden and McDonald, this volume).

From the DSDP studies (indexed through Leg 44 by Kvenvolden, 1981) and from other investigations of near-surface ocean sediment (for example, Bernard et al., 1978; Kvenvolden and Redden, 1980; Whelan, Hunt, and Berman, 1980; and Whelan and Hunt, 1983), it was expected that most, if not all, oceanic sediment would contain some measurable quantities of methane (C_1), ethane (C_2), possibly propane (C_3), and perhaps higher molecular weight gases such as normal butane and isobutane ($n-C_4$ and $i-C_4$). Also, near-surface sediments would be expected to contain low amounts of alkenes such as ethene ($C_{2:1}$) and propene ($C_{3:1}$) (Whelan, 1984). Therefore, detection of only C_1 at two sites (642 and 643) on ODP Leg 104 was unexpected, and a reanalysis of the samples was done in shore-based laboratories. In addition, sediment samples from Site 644 were reexamined, even though most of these samples contained some of the higher molecular weight hydrocarbons, as well as significant amounts of C_1 . Because C_1 was so abundant at that site, carbon isotopic compositions of this gas were determined. In this paper we present the results of the shore-based studies and compare these results with those obtained aboard ship.

SETTING

The three drilling sites of Leg 104 provide an opportunity to assess the regional distribution of gas in sediment of the Vøring

Plateau, a dominant geologic feature of the Norwegian continental margin. Site 643, located on the lower slope near the foot of the outer plateau, yielded Eocene-to-Holocene sediment overlying oceanic basement. Site 642 is on top of the outer part of the plateau where Eocene-to-Holocene sediment overlies a thick sequence of volcanic rocks. Site 644, located on the inner part of the plateau, yielded Pliocene to Holocene sediment of the Vøring Basin.

Previous work on DSDP Leg 38 in 1974 showed that high concentrations of C_1 -rich hydrocarbon gas were found in sediment of the inner Vøring Plateau (landward of the Vøring Plateau Escarpment) but not elsewhere on the plateau (Morris, 1976; Talwani, Udintsev, et al., 1976). This observation was confirmed when high concentrations of hydrocarbon gases were found at Site 644 but not at the other two sites (Kvenvolden and McDonald, this volume).

PROCEDURES

The shipboard procedures for gas analyses have been described in detail by Kvenvolden and McDonald (this volume). Briefly, sediment samples (approximately 170 cm^3) were canned in such a way that gas could be partitioned into a 100-cm^3 headspace. Part of this headspace gas mixture was examined on a Hewlett-Packard (HP) 820 Natural Gas Analyzer, which makes use of a HP 5890 Gas Chromatograph with a flame ionization detector. A second gas chromatograph (HP 5890A) with a Poropak Q column and a thermal conductivity detector was used to measure C_1 in gassy canned samples and in Vacutainer samples from Site 644 (note that any use of trade names or trademarks is for descriptive purposes only and does not constitute an endorsement). After the headspace gas was analyzed, the canned sediment samples were frozen and later transported to the shore-based laboratories. All of the samples were reanalyzed at a U.S. Geological Survey laboratory in Palo Alto, CA, identified here as USGS. Confirmation of some gas analyses and all carbon isotopic determinations were made at laboratories of the Department of Oceanography, Texas A&M University, in College Station, TX, identified here as TAMU.

For the reanalysis of gases, the frozen, canned samples were thawed and allowed to reach room temperature. Each can was shaken for 10 min on a paint-can shaker, and a portion of the headspace gas was removed for gas chromatography. In Table 1

¹ Eldholm, O., Thiede, J., Taylor, E., et al., 1989. *Proc. ODP, Sci. Results*, 104: College Station, TX (Ocean Drilling Program).

² U.S. Geological Survey, Menlo Park, CA 94025.

³ Department of Oceanography, Texas A&M University, College Station, TX 77843.

Table 1. Comparison of analytical conditions aboard ship, at USGS, and at TAMU.

Type	Shipboard		USGS	TAMU
Gas Chromatograph	Natural Gas Analyzer (HP 5890A + Option 820)	HP 5890A	Carle 311	HP 5790
Sample Loop	0.25 ml	None	1 ml	1 ml
Columns	1/8" × 6' 35% DC200 (80/100 mesh) 1/8" × 6' Poropak Q (80/100 mesh) 1/8" × 10' Molecular sieve (45/60 mesh)	1/8" × 12' Poropak QA (80/100 mesh)	1/8" × 17' <i>n</i> -octane on Porasil C (100/120 mesh) 1/8" × 7' 50% Poropak N + 50% Poropak Q (60/80 mesh)	1/8" × 10' alumina (80/100 mesh)
Oven Temp.	70°C isothermal	100°C isothermal	70°C isothermal	90°C, 2.5 min 12°C/min to 120°C 120°C, 15 min
Detectors	Flame ionization Thermal conductivity (not used)	Thermal conductivity Flame ionization (not used)	Flame ionization Thermal conductivity	Flame ionization
Separation	C ₁ , C ₂ , C ₃ , <i>i</i> -C ₄ , <i>n</i> -C ₄ , <i>n</i> -C ₅ , <i>n</i> -C ₆	C ₁ , C ₂	C ₁ , C ₂ , C _{2:1} , C ₃ , C _{3:1} , <i>i</i> -C ₄ , <i>n</i> -C ₄ , C ₅ +	C ₁ , C ₂ , C _{2:1} , C ₃ , C _{3:1} , <i>i</i> -C ₄ , <i>n</i> -C ₄

we compare the analytical conditions aboard ship with those at the USGS and TAMU laboratories. Quantification of chromatographic results from all laboratories (shipboard, USGS, and TAMU) was obtained by means of HP Model 3390A Reporting Integrators, except that at the USGS, methane at high concentrations was determined by peak height from a thermal conductivity detector. Results were originally calculated as volumes of each hydrocarbon gas per unit volume of total gas. To relate these results to the amount of sediment extracted, the data are represented here as volumes of each hydrocarbon gas per liter (L) of wet sediment. Volumes of a given hydrocarbon gas are reported in nanoliters (nL), microliters (μ L), or milliliters (mL). C_1 concentrations for gas collected in Vacutainers are reported as percentages of the gas mixture.

Samples of C_1 for the determination of carbon isotopic compositions were obtained after this gas was separated from other components by distillation at liquid-nitrogen temperatures and burned to CO_2 in a method similar to that of Sackett et al. (1970). The $\delta^{13}C$ of the resultant CO_2 was measured on a Finnigan-MAT 251 isotope-ratio mass spectrometer at TAMU. Results are reported relative to the Pee Dee Belemnite Standard (PDB) with a precision better than ± 0.2 ‰.

RESULTS

Sites 642 and 643

Shipboard analyses of hydrocarbon gases extracted from sediment samples at Sites 642 and 643 showed only C_1 at concentrations less than 25 ppm, equivalent to about 15 μ L/L, in all samples. In only one Section (104-643A-46X-5) was ethane detected, its concentration being 2.1 ppm or 1.2 μ L/L (Kvenvolden and McDonald, this volume). No other hydrocarbon gases were detected aboard ship at these sites.

Reanalysis of these samples (USGS) demonstrated that all hydrocarbon gases from C_1 to C_4 were present including the unsaturated gases ethene ($C_{2:1}$) and propene ($C_{3:1}$). In Table 2 we list the results. At Site 642 four holes were drilled, and samples are arranged in Table 2 in order of increasing depth in meters below sea floor (mbsf). C_1 is the dominant hydrocarbon gas; maximum concentration measured was about 18 μ L/L. C_2 to C_4 hydrocarbons are present at concentrations of less than 300 nL/L (maximum concentration 280 nL/L). C_1/C_2 ratios are generally low (710 and less), and the highest ratios were found in samples from intermediate depths between 53 and 182 mbsf. A very low ratio of 7 was observed at the bottom of the sediment section, which overlies a thick sequence of volcanic rocks.

A single hole was drilled at Site 643. C_1 is most abundant at this site, reaching maximum concentrations of about 19 μ L/L (Table 2), similar to concentrations at Site 642. The other hydrocarbon gases were also detected, and their concentrations, with two exceptions, were all less than 420 nL/L (Table 2). Sections 104-643A-46X-5 and -643A-49X-4 contained C_2 at concentrations of 1100 and 750 nL/L, respectively. C_1/C_2 ratios are remarkably consistent throughout the hole, averaging 37 ± 21 , although the deepest sample (534 mbsf) has an exceptionally high ratio of 140 (Table 2).

Shipboard and shore-based determinations of C_1 concentrations are compared in Table 3. It is apparent that the amount of C_1 as measured in the shore-based laboratories is usually greater, in some cases by as much as a factor of five, than that in the shipboard results. There are several explanations, besides calibration errors, for the observed variability in the measured methane values, but they will be appropriately considered in the discussion section. USGS results are in general confirmed by a spot check of six samples from Site 642 analyzed at TAMU (Table 2).

Site 644

Results obtained at Site 644 contrast with those obtained at Sites 642 and 643 in that high concentrations of C_1 are accompanied by measurable quantities of hydrocarbon gases to C_5 (Kvenvolden and McDonald, this volume). In Table 4 we compare the shipboard results for C_1 at this site with C_1 determinations made at USGS and TAMU. In the shallowest section (104-644A-1H-4) there is good agreement between all laboratories on the concentration of C_1 (between 17 and 22 μ L/L). Although C_2 was not detected aboard ship, the shore-based laboratories did detect it, and their results agree for this sample and the one below (Table 5). There is a rapid increase in the amount of C_1 with depth, reaching a maximum concentration at 77.6 mbsf of 300 mL/L. Reanalysis of these samples showed that below about 40 mbsf the amount of C_1 measured in the shore-based laboratories was generally less than that measured aboard ship, and the results from the two shore-based laboratories agree rather well (Table 4).

Concentrations of C_2 as measured aboard ship and by the USGS are in reasonable agreement (Table 5). $C_{2:1}$ and $C_{3:1}$, which are present at very low levels, were not detected onboard. C_3 and $n-C_4$ were observed onboard starting at depths of 125 and 184 mbsf, respectively, whereas these compounds were detected in all samples in shore-based analyses; however, shore-based values are generally lower by as much as a factor of three relative to shipboard results. This discrepancy may be due to integration problems in that the peak for C_3 comes on the tail of the enormous C_1 peak in the USGS chromatographic analysis of these gas-rich samples. Isobutane ($i-C_4$) was detected in all USGS analyses, whereas $n-C_5$ was found only in the shipboard analyses below depths of about 209 mbsf.

The C_1/C_2 ratios measured on shipboard are varied, ranging from 1,900 to 43,000. Because the concentrations of C_1 measured in the shore-based laboratories were lower than those measured aboard ship, the C_1/C_2 ratios calculated for shore-based data are consequently also lower, ranging from 3,000 to 11,000 (Table 5). The shallowest sample has a C_1/C_2 ratio of 28 which is comparable to many of the values of this ratio found at Site 643 (Table 2).

DISCUSSION

Sites 642 and 643

Our finding more C_1 in the shore-based analyses of samples from Sites 642 and 643 than in shipboard analyses probably resulted from a number of factors, including effects of additional shaking, continued desorption of gas with time, *in-situ* generation of hydrocarbons during storage, and the effects of freezing. It has not been possible to define the exact cause, but the freezing process apparently frees some C_1 not initially extracted. In previous work elsewhere, particularly on sediment with low amounts of C_1 from the Bering Sea off Alaska, samples frozen and then thawed, consistently released more C_1 than did samples that were not frozen (K. A. Kvenvolden, unpublished results). The higher molecular weight hydrocarbon gases, however, usually yield about the same amounts whether or not the sediment sample has been frozen. It is impossible to demonstrate this latter result with samples from Sites 642 and 643 because C_2 was detected only in one sample aboard ship. However, in the USGS reanalysis of Section 104-643A-46-5, the C_2 concentration was 1,100 nL/L, which is close to the shipboard value of 1,200 nL/L. Comparison of results by USGS and TAMU shows very general agreement to one significant figure between concentrations for C_2 and C_3 (Table 2); the detection limit at the USGS laboratories appears to be slightly lower.

Table 2. Concentrations of hydrocarbon gases ($\mu\text{L/L}$ of wet sediment) at Sites 642 and 643; reanalysis by USGS.

Hole- Core Section	Depth (mbsf)	Vol. Sed. (cm ³)	Gas concentrations (μL/L)							
			C ₁	C ₂	C _{2:1}	C ₃	C _{3:1}	i-C ₄	n-C ₄	C ₁ /C ₂
Site 642										
B-1-2	3	170	3,000 (2,900)	81 (94)	26	78 (n.d.)	46	16	18	37
A-1-3	6	170	5,300 (4,900)	210 (210)	160	130 (n.d.)	64	44	37	26
B-2-5	12	170	6,500	99	35	82	52	12	18	66
B-4-4	27	170	8,800	190	130	140	89	18	48	47
B-5-4	35	170	9,900	190	47	110	58	26	29	52
B-7-4	53	170	15,400 (18,400)	110 (140)	41	72 (53)	n.d.	11	10	140
B-8-4	63	170	10,400	42	26	63	n.d.	n.d.	12	250
B-10-4	82	170	15,400	21	28	45	n.d.	3	7	710
B-11-4	91	170	6,400	42	81	75	35	6	16	150
B-13-4	110	170	11,300 (10,500)	18 (n.d.)	24	49 (n.d.)	n.d.	n.d.	7	630
B-16-6	137	170	15,600	59	51	66	n.d.	4	14	270
B-19-4	164	170	12,400	101	56	86	43	8	15	120
C-22-3	182	170	13,200	110	46	95	n.d.	8	26	120
B-22-4	193	170	17,600 (15,900)	180 (190)	52	160 (120)	n.d.	36	26	96
D-4-5	217	170	13,400 (11,400)	190 (94)	140	130 (82)	n.d.	11	25	72
B-25-4	219	170	9,500	170	76	130	n.d.	15	25	55
D-7-5	246	170	17,880	170	28	160	n.d.	13	24	110
D-10-5	275	170	7,600	120	67	120	61	13	26	61
D-13-2	299	170	1,400	84	66	110	82	5	11	17
D-18-2	326	170	1,900	280	160	190	160	28	65	7
Site 643										
A-1-2	3	204	1,900	61	210	75	95	10	22	31
A-4-4	30	177	5,300	220	97	160	51	15	14	24
A-7-5	60	184	3,000	77	120	110	56	8	29	39
A-10-5	89	180	3,200	180	100	160	61	24	33	17
A-13-5	117	187	1,800	72	130	93	93	9	20	28
A-16-5	146	170	1,800	42	77	92	58	9	19	42
A-19-5	174	170	2,200	96	100	110	78	9	28	23
A-22-4	201	153	2,100	89	67	150	80	12	30	23
A-25-5	232	170	5,500	170	180	180	160	16	32	32
A-28-5	262	163	8,400	110	63	110	59	10	24	79
A-31-5	291	180	4,200	54	81	78	74	4	11	77
A-34-5	316	194	3,100	85	220	88	110	10	20	36
A-37-5	347	170	7,000	310	330	190	290	37	45	23
A-44-5	418	180	10,700	310	160	120	130	12	34	35
A-46-5	437	173	17,600	1,100	70	420	87	25	110	16
A-49-4	464	146	16,800	750	120	260	130	14	57	23
A-52-5	495	177	18,600	240	47	110	40	14	27	79
A-56-5	534	170	15,800	110	85	81	100	9	25	140

n.d. = not detected; () = concentrations determined at TAMU; mbsf = meters below seafloor.

These results indicate that C_1 to C_4 hydrocarbon gases are present in sediment at Sites 642 and 643, but the detection limit of the shipboard instrumentation is not sufficient to permit identification and quantification at concentrations less than about 500 nL/L. One problem is that a 0.25-ml sample loop was used aboard ship (Table 1). Replacing this loop with a 1.0-ml sample loop would improve the detection limit by as much as a factor of four. Further refinements probably will be needed to reach the capabilities of shore-based laboratories, however.

The hydrocarbon gases at these sites represent the general background of gases seen in near-surface oceanic sediment worldwide (summarized by Claypool and Kvenvolden, 1983). These compounds probably result from both chemical and biological processes. The alkenes $C_{2:1}$ and $C_{3:1}$ are believed to be from biological sources. C_1 formation by methanogenesis involving CO_2 reduction following sulfate depletion is probably not an important process at Sites 642 and 643 because sulfate is still present in the sediment. It ranges from about 8 to 27 mmol/L (see Site chapters in Eldholm, Thiede, Taylor, et al. (1987)). The small amounts of C_1 may be produced biologically by alternate pathways, and the other hydrocarbon gases may result from either chemical or biological processes. The generally low C_1/C_2 ratios (Table 2) are typical of near-surface oceanic sediments (for example, see Kvenvolden and Redden, 1980, and Whelan and Hunt,

1983). The sediment gases have probably formed in place. Migration of these gases from below is unlikely because Site 643 sediment overlies oceanic basement, and Site 642 sediment covers a thick sequence of volcanic rocks.

Site 644

The large differences between the high C_1 concentrations at Site 644 as measured aboard ship and in the shore-based laboratories (Table 4) have not been fully explained. On the ship, the high concentrations of C_1 were determined on a separate gas chromatograph with a thermal-conductivity detector because the natural-gas analyzer with its flame ionization detector could not handle C_1 at high concentrations and still determine the other hydrocarbon gases, which occur in much lower amounts than C_1 . The gas chromatograph used for C_1 was not equipped with a sample loop; thus the amount of gas analyzed (0.25 ml) was measured in an open syringe where precise quantification is difficult. Another possibility to explain the differences in results is that the cans leaked C_1 during storage; however, we have never observed such a significant preferential loss of C_1 from cans used in previous studies.

Although there is a discrepancy between shipboard and shore-based results, particularly for C_1 , the trends with depth shown by both data sets are similar. Figure 1 compares C_1 and C_2 con-

Table 3. Comparison of methane concentrations (C_1) in $\mu\text{L/L}$ of wet sediment at Sites 642 and 643, measured onboard ship (ODP) and by USGS and TAMU.

Hole- Core- Section	Depth (mbsf)	C ₁ (μL/L)	
		ODP	USGS
Site 642			
B-1-2	2.9	1.6	3.0
A-1-3	5.7	6.5	5.3
B-2-5	12.2	1.4	6.5
B-4-4	26.6	1.0	8.8
B-5-4	35.3	1.9	9.9
B-7-4	53.3	2.6	15.4
B-8-4	62.8	2.9	10.4
B-10-4	81.8	5.4	15.0
B-11-4	91.3	5.0	6.4
B-13-4	110.1	3.6	11.3
B-16-6	137.0	7.0	15.6
B-19-4	163.6	9.0	12.4
C-22-3	181.9	8.5	13.2
B-22-4	192.6	13.5	17.6
D-4-5	216.6	12.8	13.4
B-25-4	219.0	7.6	9.5
D-7-5	245.6	6.4	17.8
D-10-5	274.5	3.4	7.6
D-13-2	299.1	0.8	1.4
D-18-2	326.4	n.d.	1.9
Site 643			
A-1-2	3.0	0.4	1.9
A-4-4	30.3	2.9	5.3
A-7-5	60.3	0.7	3.0
A-10-5	88.7	1.7	3.2
A-13-5	117.3	0.5	1.8
A-16-5	145.8	0.8	1.8
A-19-5	174.3	1.7	2.2
A-22-4	201.2	2.4	2.1
A-25-5	232.2	2.4	5.5
A-28-5	261.6	5.7	8.4
A-31-5	291.0	1.0	4.2
A-34-5	315.8	0.6	3.1
A-37-3	346.7	2.9	7.0
A-44-5	417.5	3.1	10.7
A-46-5	436.9	5.2	17.6
A-49-4	464.4	3.4	16.8
A-52-5	494.8	7.2	18.6
A-56-5	533.5	5.7	15.8

n.d. = not detected; mbsf = meters below seafloor.

centrations as a function of depth and demonstrates this similarity. In addition, this figure shows the values for $\delta^{13}\text{C}$, organic carbon, sulfate, chlorinity, salinity, and alkalinity plotted against depth. Data for the last five parameters are taken from the Site 644 chapter of Eldholm, Thiede, Taylor, et al. (1987). The profile of C_1 concentrations with depth (Fig. 1) shows maxima at 78 and 235 mbsf. The highest concentrations of gas measured (USGS) are large and correspond with amounts observed during previous DSDP drilling at gassy sites on Legs 76 and 84 (Kvenvolden, 1984). The largest amounts of gas measured aboard ship (ODP) are a factor of three higher than observed previously. In earlier work (Kvenvolden, 1984), only a single C_1 maximum has been observed in a given hole, and that occurs within the upper 100 m of sediment. At Site 644, the second, deeper C_1 maximum is unusual; it occurs near a lithologic boundary and sharp seismic marker (Eldholm, Thiede, Taylor, et al., 1987).

The concentrations of C_2 at various depths measured aboard ship (ODP) and onshore (USGS) are comparable and range from about 0.2 to 12 $\mu\text{L/L}$. They generally follow the C_1 concentrations but increase slightly with depth (Fig. 1). This in-

crease in amount of C_2 with depth is common in oceanic sediment and probably results from the increasing effects of diagenesis (reviewed by Claypool and Kvenvolden, 1983). The other saturated hydrocarbons, C_3 , $i\text{-C}_4$, $n\text{-C}_4$, and $n\text{-C}_5$ (Table 5) also tend to increase in concentration with depth. $C_{2:1}$ and $C_{3:1}$ are present in sediment at this site, and these alkenes probably are products of microbial processes (Davis and Squires, 1954).

Large C_1/C_2 ratios at Site 644 suggest that C_1 is mainly from biogenic sources (Bernard et al., 1976). The very low ratio of 28, found in the uppermost sample, is typical of values commonly found in near-surface marine sediment. This low C_1/C_2 ratio in the top sample probably results from biological activity in the zone of sulfate reduction, where C_1 generation is inhibited and C_1 consumption is possible. These processes have been discussed by Claypool and Kaplan (1974), Bernard (1979), and many others. The processes apply particularly to shallow samples where low concentrations of gas occur.

The biogenic origin of C_1 at Site 644 is confirmed by the carbon isotopic measurements. Table 4 shows the carbon isotopic composition of C_1 from headspace analyses and from Vacutainer gas collected at this site. Headspace carbon isotopic values range downhole from -90.3‰ at 40 mbsf to -68.8‰ at 252 mbsf, with the heaviest value of -62.3‰ occurring at 209 mbsf. Vacutainer gas samples recovered from both holes drilled at this site cover an interval from 80 to 150 mbsf. Apart from the $\delta^{13}\text{C}_1$ value of -80.4‰ for the sample at 80 mbsf, the remaining nine values fall in a range from -77 to -75‰ . All carbon isotopic values from headspace analyses and Vacutainers fall in a range that is consistent with a biogenic source (Fuex, 1977) for the C_1 at this site.

Above 210 mbsf the $\delta^{13}\text{C}_1$ profile (Fig. 1) follows the generalized path common in anoxic marine sediment (Whelan, 1979; Rice and Claypool, 1981; Galimov and Kvenvolden, 1983; and Claypool and Kvenvolden, 1983); light isotopic compositions of C_1 in the shallow sediments give way to heavier isotopic compositions with depth. At this site, $\delta^{13}\text{C}_1$ in the upper zone of C_1 generation has a minimum value of -90.3‰ , and the values become heavier in a regular manner with depth, reaching -62.3‰ at 209 mbsf. Below this depth, a second possible zone of C_1 production is indicated by the increase in C_1 concentrations and the lighter methane carbon isotopic compositions (-72.3 and -68.8‰).

In the shallow sediment at this site, sulfate is rapidly depleted with depth, whereas alkalinity increases. A rapid increase in C_1 concentrations occurs as sulfate is depleted (Fig. 1), following the classic model of Claypool and Kaplan (1974). The deeper C_1 concentration maximum at 235 mbsf is preceded by a slight increase, then decrease in sulfate; these relations support the suggestion of a second, deeper zone of C_1 generation.

The organic carbon content of these sediment samples is quite uniform (Fig. 1); it ranges from 0.37 to 0.96% and averages $0.70 \pm 0.16\%$. The organic matter serves as the ultimate source for the hydrocarbon gases. At the sediment depths where sulfate is depleted (< 40 mbsf) much of the observed C_1 probably was derived by methanogenesis through the reduction of CO_2 from organic matter (Claypool and Kaplan, 1974).

The sediments of the inner Vøring Plateau are characteristically gassy. This generalization is based on the results of previous DSDP drilling on Leg 38, on our work on ODP Leg 104, and on experience by industry. Drilling at Site 341 on Leg 38 encountered hydrocarbon gas in the upper 250 m of sediment beginning at about 50 mbsf. The gas was dominantly C_1 (99.9+%) accompanied by traces of ethane (Morris, 1976). This site is about 110 km northeast of ODP Site 644, where we also found significant amounts of hydrocarbon gas deeper than about 22 mbsf. Gas composition at Site 644 was similar to that at Site 341, except that more detail is now known about the gas

Table 4. Comparison of concentrations and carbon isotopic compositions of C_1 extracted from sediment (mL/L of wet sediment) and that recovered by Vacutainers (% of gas mixture) at Site 644. $\delta^{13}C$ values are in ‰ relative to PDB standard.

Hole- Core- Section 104-644	Depth (mbsf)	Vol. Sed. (cm ³)	Gas extracted from sediment C ₁ (mL/L)			δ ¹³ C ₁ (‰)	Gas recovered by Vacutainer		
							C ₁ (%)		δ ¹³ C ₁ (‰)
			ODP	USGS	TAMU		ODP	TAMU	
A-1-4	5.9	139	0.017	0.021	0.022				
A-3-4	22.1	173	0.470	0.980	1.000				
A-5-3	39.6	167	20.0	60.0	62.0	-90.3			
A-7-2	57.1	177	230.0	58.0	63.0	-83.8			
A-9-3	77.6	170	300.0	99.0	100.0	-78.9			
A-9-5	80.2						81.3	63.5	-80.4
A-10-1	83.0						56.3	24.7	-76.9
B-11-3	93.5							12.4	-77.0
A-11-4	96.8						84.1	1.7	
A-11-5	99.6	170	97.0	25.0	24.0				
B-13-3	110.0							61.6	-76.9
A-12-7	111.0						84.5	76.5	-75.0
B-14-1	111.7							90.5	-76.3
B-14-3	115.7							88.9	-76.5
A-14-2	122.4						89.9	81.1	-75.6
A-14-3	125.1	170	230.0	62.0	33.0				
A-15-4	136.1	170	140.0	35.0	34.0	-68.2			
A-15-5	136.2						45.0	14.3	-75.3
A-16-2	141.4						89.4	89.1	-76.3
A-17-1	150.3						47.7	6.2	
A-17-2	152.1	187	71.0	21.0	19.0				
A-20-4	183.6	197	37.0	29.0	27.0				
A-22-4	192.7	170	14.0	18.0	17.0				
A-23-4	200.0	170	6.0	15.0	2.0				
A-25-2	208.9	163	140.0	36.0	36.0	-62.3			
A-28-2	219.0	204	160.0	36.0	35.0				
A-29-2	224.0	187	77.0	20.0	19.0				
A-31-2	235.0	170	240.0	62.0	68.0	-72.3			
A-34-4	251.9	204	130.0		36.0	-68.8			

mbsf = meters below seafloor.

Table 5. Concentrations of ethane (C_2), ethene ($C_{2:1}$), propane (C_3), propene ($C_{3:1}$), isobutane ($i-C_4$), normal butane ($n-C_4$), and normal pentane ($n-C_5$) at Site 644.

Hole- Core- Section 104-644	Depth (mbsf)	Vol. Sed. (cm ³)	C_2 (μ L/L)		$C_{2:1}$ (μ L/L)	C_3 (μ L/L)		$C_{3:1}$ (μ L/L)	$i-C_4$ (μ L/L)	$n-C_4$ (μ L/L)		$n-C_5$ (μ L/L)	C_1/C_2^3 ratio	
			ODP	USGS		ODP	USGS			ODP	USGS		ODP	USGS
A-1-4	5.9	139	n.d.	0.76 ¹	0.290	n.d.	0.34	0.19	0.11	n.d.	0.096	n.d.		28
A-3-4	22.1	173	n.d.	0.16 ¹	0.041	n.d.	0.03	n.d.	0.007	n.d.	0.013	n.d.		6,100
A-5-3	39.6	167	4.7	5.90	0.025	n.d.	1.5	n.d.	0.024	n.d.	0.026	n.d.	4,300	10,000
A-7-2	57.1	177	5.3	6.00	0.016	n.d.	2.0	n.d.	0.087	n.d.	0.041	n.d.	43,000	9,700
A-9-3	77.6	170	8.2	9.10	0.024	n.d.	2.9	0.028	0.12	n.d.	0.081	n.d.	37,000	11,000
A-11-5	99.6	170	3.5 ²	4.00	0.029	n.d.	1.0	0.018	0.061	n.d.	0.072	n.d.	28,000	6,300
A-14-3	125.1	170	9.1	9.80	0.060	6.8	2.8	n.d.	0.25	1.47	0.230	n.d.	25,000	6,300
A-15-4	136.1	170	7.4	5.10	0.070	3.8	1.3	0.036	0.12	n.d.	0.120	n.d.	19,000	6,900
A-17-2	152.1	187	4.4	4.70	0.073	4.1	1.5	0.046	0.22	1.37	0.210	n.d.	16,000	4,500
A-20-4	183.6	197	6.2	6.80	0.073	3.9	2.0	0.041	0.26	0.31	0.220	n.d.	6,000	4,300
A-22-4	192.7	170	4.9	4.90	0.069	3.1	1.7	0.044	0.29	0.31	0.240	n.d.	2,900	3,700
A-23-4	200.0	170	3.2	5.00	0.130	1.6	1.9	0.065	0.38	0.35	0.290	1.07	1,900	3,000
A-25-2	208.9	163	7.1	7.50	0.091	5.1	2.4	0.078	0.43	0.49	0.310	0.43	20,000	4,800
A-28-2	219.0	204	5.8	9.60	0.100	2.9	3.5	0.088	0.51	0.27	0.350	0.46	28,000	3,800
A-29-2	224.0	187	5.1	5.20	0.034	3.3	1.9	0.028	0.41	0.37	0.270	0.44	15,000	3,900
A-31-2	235.0	170	12.0	12.20	0.065	6.4	3.6	n.d.	0.65	0.54	0.350	0.39	20,000	5,100
A-34-4	251.9	204	8.2	n.a.	n.a.	4.9	n.a.	n.a.	n.a.	0.63	n.a.	0.43	16,000	n.a.

¹ Identical values obtained at TAMU.² Estimated value from peak height.³ C_1 value from Table 4.

n.d. = not detected; n.a. = not analyzed; ? = uncertain value; mbsf = meters below seafloor.

chemistry at Site 644. Finally, industrial drilling in October 1985 at Haltenbanken on the continental shelf part of the inner Vøring Plateau about 800 km southeast of Site 644 found sufficient biogenic hydrocarbon gas near 500 mbsf to cause the loss of the drilling platform by explosion and fire. In contrast to the high gas content in sediment of the inner Vøring Plateau, sediment of the outer Vøring Plateau, as tested at Sites 643 and 642,

has almost no hydrocarbon gas. The causes of this extreme variation in content of sediment gas in this region are not known, but several sedimentologic factors probably contribute to the described differences. Sedimentation rates at Site 644 are more than four times those of the outer sites. Compositionally, the proximity of Site 644 to terrigenous sources relative to Sites 642 and 643 is apparent in clay mineralogic studies (Froget et al.,

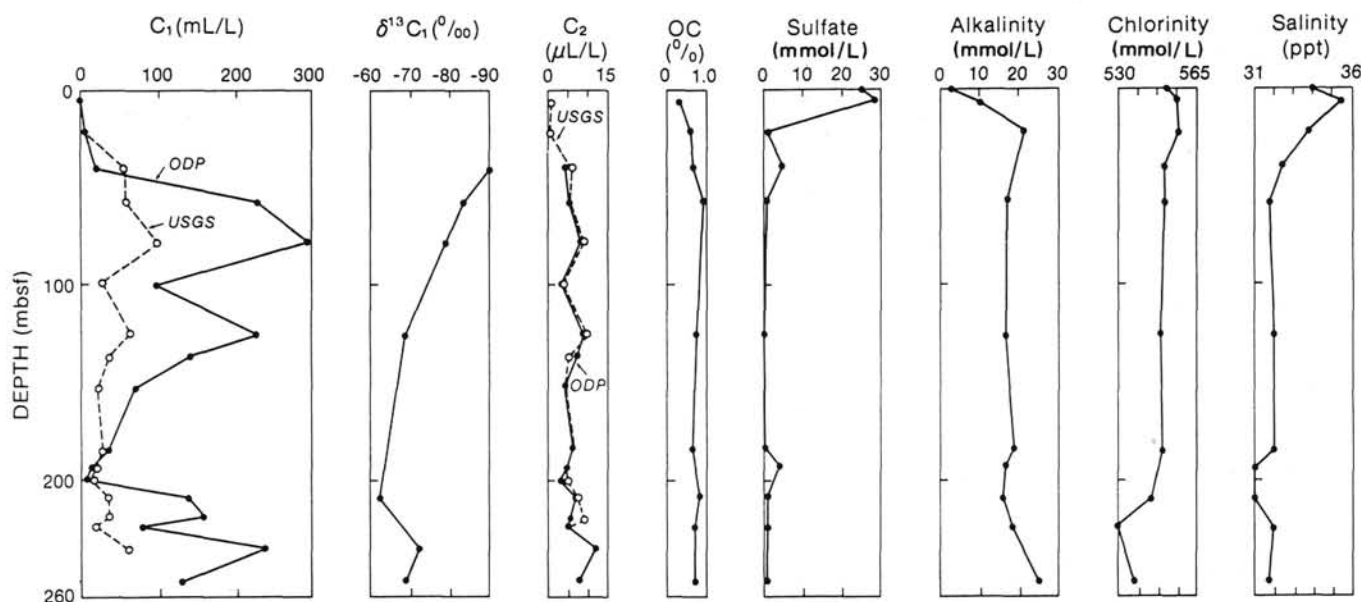


Figure 1. Profiles with depth at Site 644 of C_1 (mL/L), $\delta^{13}C_1$ (‰), C_2 (μ L/L), organic carbon or OC (%), sulfate (mmol/L), chlorinity (mmol/L), salinity (ppt), and alkalinity (mmol/L). C_1 and C_2 concentrations were measured onboard ship (ODP) and onshore (USGS). Depth is given in meters below seafloor (mbsf).

this volume). These factors, plus differences in sediment oxidation states and ability of the sediment organic matter to serve as a source for the generation of C_1 , are likely reasons for the different gas concentrations across the Vøring Plateau.

Gas Hydrates

Gassy sediment was anticipated at Site 644 on the basis of previous results from Site 341 on Leg 38 (Morris, 1976). The mode of occurrence of the gas was not known, but presence of gas hydrate could provide a means of accommodating large amounts of C_1 in this sediment. The pressure and temperature conditions within the sediment are well within the stability field for the gas hydrates (Kvenvolden and McMenamin, 1980). No visual evidence for gas hydrates was found, however, although it was vigorously sought. The drilling program on the *JOIDES Resolution* is not optimized for the search for gas hydrates in that there can be a long time interval between core recovery and inspection. During this time gas hydrates can completely decompose and disappear. Gas pockets, indicating gas expansion, did form in the interval between 80 to 150 mbsf and were possibly the result of gas hydrate decomposition. In the recovery of one core (104-644B-11H) at about 90 mbsf, the delay time was minimized, and a search for solid gas hydrates was made in one section (described in the core-log as "disturbed by crazed chemist"); no gas hydrates were found. Nevertheless, ancillary evidence at this site suggests that gas hydrates are present.

In comparing gas hydrates in various continental margin settings, Kvenvolden (1984) listed geochemical characteristics that appear to define some minimum requirements for the occurrence of biogenic gas hydrates. These characteristics include (a) rates of sedimentation greater than 30 m/m.y.; (b) organic carbon content exceeding 0.5%; (c) C_1 content greater than 10 mL/L; and (d) decreasing pore-water salinity (chlorinity) with depth, because salts are excluded from the water that forms gas hydrates. These characteristics are all satisfied at Site 644: (a) rate of sedimentation was estimated to be about 100 m/m.y. (Eldholm, Thiede, Taylor, *et al.*, 1987); (b) the organic carbon content averages 0.7%; (c) C_1 concentration reaches at least 100 mL/L in sedi-

ment deeper than 40 mbsf; and (d) salinity and chlorinity decrease about 4 ppt and about 30 mmol/L, respectively, with increasing depth (Fig. 1).

Although our geochemical evidence suggests that gas hydrates are present at Site 644, no supporting geophysical evidence, such as bottom-simulating reflectors (BSRs) on marine seismic reflection profiles, is known. To the south of the Vøring Plateau, however, on the Norwegian continental margin, BSRs have been noted on marine seismic records and attributed to gas hydrates (Bugge, 1983). Thus, gas hydrates may be disseminated in sediment at Site 644, and the visual evidence has likely been lost through the delays inherent in the core-recovery procedure.

SUMMARY

Significant concentrations of hydrocarbon gases can be expected in sediment of the inner Vøring Plateau from the Norwegian continental shelf out to the Vøring Plateau Escarpment. Analyses at ODP Site 644 demonstrated that the gas there is composed mainly of methane (> 99.9%) that is isotopically light (avg. $\delta^{13}C_1 = -76.6$ ‰). The molecular composition of the hydrocarbon gases, the carbon isotopic composition of methane, and the pore-water chemistry suggest that the gases are a product mainly of microbial diagenesis. In some sediment at this site these gases may be present in the form of gas hydrates; this inference is based on considerations of pressure-temperature conditions for gas hydrate stability, rates of sedimentation, organic carbon contents, residual methane concentrations, and chlorinity or salinity profiles with depth. However, no gas hydrates were visually observed. In contrast, the sediment of the outer Vøring Plateau, as tested at ODP Sites 642 and 643, has only minimal amounts (ppm) of hydrocarbon gases. Our hydrocarbon results are based on comparisons of data obtained aboard ship and at onshore laboratories. Limits of detection of the onshore laboratories exceeded those of the shipboard laboratories. Measured amounts of hydrocarbon gases, other than C_1 are comparable for all laboratories. C_1 at low concentrations is affected by the processes taking place during sample storage; the discrepancy in the measurements of C_1 at high concentra-

tions most likely resulted from questionable quantification of total gas volumes used for gas chromatography.

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