29. ISOTOPIC ANALYSIS OF CORE GASES AT SITES 565-570, DEEP SEA DRILLING PROJECT LEG 84[1]

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ABSTRACT

Methane carbon-isotopic compositions ($\delta^{13}C$ values relative to the PDB standard) at Sites 565, 566, 567, and 569 were lighter (enriched in ^{12}C) than -60‰, indicating a biogenic origin. In the deeper sections at Sites 568 and 570, $\delta^{13}C$ values were heavier, approaching -40‰, and therefore suggest a thermogenic source. A significant thermogenic source was discounted, however, because the carbon dioxide $\delta^{13}C$ values in these sections were also anomalously heavy, suggesting that the methane may have formed biogenically by reduction of the heavy carbon dioxide. $\delta^{13}C$ values of ethane and higher hydrocarbons were measured in several sections from Sites 566 and 570 that contained sufficient C_2-C_4 hydrocarbon concentrations. Ethane values in six sections (245-395 m sub-bottom) from Site 570 were fairly uniform, ranging from -24 to -26‰. These values are among the heaviest ethane values reported for natural gases. The isobutane/n-butane and isopentane/n-pentane ratios of the core gases suggested that the C_2-C_5 hydrocarbons are thermally produced by low-temperature chemical diagenesis of indigenous organic matter. This process apparently generates isotopically heavy C_2-C_5 hydrocarbons. High gas concentrations in the serpentinite basement rocks at Sites 566 and 570 appear to have resulted from migrated biogenic methane gas containing small amounts of immature C_2-C_5 hydrocarbons.

INTRODUCTION

Carbon dioxide (CO_2) and methane (C_1) are the predominant carbon-containing gases in marine sediments. Both are present in overlying seawater, although CO_2 in the form of dissolved bicarbonate has concentrations several orders of magnitude higher than C_1. Both gases are incorporated into pore waters of marine sediments from the overlying seawater, but important production and consumption reactions also occur within the sediment.

In near-surface sediments, the most important mechanisms affecting CO_2 and C_1 concentrations are biological. In the oxygenated zone, CO_2 is produced from sediment organic matter during aerobic bacterial respiration. Below the aerobic zone, organic matter continues to be oxidized to CO_2 during anaerobic bacterial respiration utilizing dissolved sulfate as the major electron acceptor (ZoBell and Rittenberg, 1948). Below the zone of sulfate reduction, bacteria consume bicarbonate-derived CO_2 and produce C_1. This reduction of CO_2 to C_1 may extend to considerable depths in the sediment column, and is evident in the generally parallel trends in carbon-isotope ratios of the two species below the zone of sulfate reduction (Claypool and Kaplan, 1974; Claypool and Threlkeld, 1983). A more detailed discussion of biologically mediated reductions in the upper sediment column is given by Rice and Claypool (1981).

Chemical reactions involving CO_2 and C_1 do not appear to be important in shallow sediments, except for the chemical equilibrium between dissolved bicarbonate and solid carbonates, controlled predominantly by pore-water pH. With increasing depth and temperature in the sediment column, chemical diagenetic reactions become increasingly important. Chemical decarboxylation of organic acids generates CO_2, and C_1 is produced by carbon-bond cleavage in the thermogenic reduction of organic matter. Small amounts of higher hydrocarbons are produced during initial cracking of organic matter (Rice and Claypool, 1981). As sediment temperatures increase above $\sim 50°C$, thermogenic decomposition of organic matter generates increased amounts of methane and higher hydrocarbons which, if present in sufficient quantities, may form commercially exploitable liquid and gaseous hydrocarbon accumulations.

Much of the information on gases from thermally immature sediments comes from analysis of cores taken in the Deep Sea Drilling Project. Carbon isotopic ratios ($\delta^{13}C$ values[3]) of C_1 in these cores, from a wide variety of DSDP sites, have been compiled by Claypool and Kvenvolden (1983). In most of the cores, $\delta^{13}C$—C_1 values are lighter (enriched in ^{12}C) than -55‰, indicating a biologically produced gas (Bernard et al., 1977). Methane heavier than -55‰, which indicates a thermogenic origin (Fuex, 1977), was isolated from cores in areas of high geothermal gradients, such as the Gulf of California (Galimov and Simoneit, 1982). The higher temperatures at the bottom of these cores promoted thermogenic decomposition of the indigenous organic matter, generat-

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[3] $\delta^{13}C$, ‰ vs. PDB = $\left[\dfrac{^{13}C/^{12}C_{sample}}{^{13}C/^{12}C_{std}} - 1 \right] \times 1000$.

ing isotopically heavy methane. Methane heavier than −55‰ was also present in cores drilled above salt diapirs in the Gulf of Mexico (Claypool et al., 1973). In this case, the methane appeared to have migrated vertically with the diapir from more thermally mature sediments. These thermogenic occurrences are rather unusual in the DSDP cores, since most DSDP core gases come from low-temperature ($<50°C$) sediments in which biologically produced methane predominates over the much smaller amount of thermogenic methane. The only evidence of nonbiological gaseous hydrocarbons at these sites is the small concentrations of ethane and higher hydrocarbons, since these are not direct products of the microbiological decomposition of organic matter (Claypool and Kvenvolden, 1983).

In this study gases in cores from Sites 565–570 were analyzed for molecular and isotopic compositions. The core gases were predominantly C_1, with generally less than one percent CO_2, except at Site 570, where CO_2 concentrations were generally a few percent, with values up to 6.3%. The C_1/C_2 ratios were >1000, except in several deeper sections, where up to 1.0% C_2–C_5 hydrocarbons were present. Gases at the bottoms of the cored sections from Holes 566C and 570 were unique, as they were recovered from the basement rocks at these sites and so could not have been generated *in situ* from indigenous carbon. The gases presumably migrated into the basement rocks from an as yet unknown source.

METHODS

Gas pockets visible in the cores through clear plastic core-liners were tapped with a hollow punch, and samples were withdrawn into 20-ml evacuated sample tubes (vacutainers). C_1 was separated from the other gaseous components by fractional distillation at liquid-nitrogen temperature, and combusted to CO_2 in a system similar to that described by Sackett et al. (1970). CO_2, ethane (C_2), and higher hydrocarbons were separated using a Carle Model 8000 gas chromatograph equipped with a silica-gel column, and individual components were isolated in traps packed with Poropak Q adsorbant at liquid-nitrogen temperature. In samples with sufficient higher-hydrocarbon concentrations, ethane, propane (C_3), and a combined fraction consisting of butanes and pentanes (designated the C_{4+} fraction) were isolated. The higher hydrocarbons were combusted to CO_2 in the same system that was used for methane. Isotopic analysis of CO_2 was performed on a Nuclide RMS 60 ratio mass spectrometer, and the results were reported relative to the PDB standard. Precision on replicate samples was better than ±0.2‰.

RESULTS AND DISCUSSION

Methane isotopic values were obtained on vacutainer gases from Sites 565 through 570 (Tables 1 through 6). Methane isotopic profiles with depth for each site are presented in Figures 1 and 2. Carbon dioxide was present in sufficient quantities for isotopic analysis in vacutainer samples from Sites 568, 570, and one section from Site 565 (Tables 1, 4, and 6). Carbon dioxide isotopic profiles for Sites 568 and 570 are compared with methane isotopic profiles in Figure 3. Ethane and higher hydrocarbons were present in sufficient concentrations for isotopic analysis in only a few vacutainer samples from Sites 566 and 570 (Tables 2 and 6).

Methane

Methane isotopic values at Sites 565, 567, and 569 ranged from as light as −88.2‰ at 59 m sub-bottom at

Table 1. Isotopic compositions and hydrocarbon isomer ratios of core gases, Hole 565.

Core-Section, Interval (cm)	Sub-bottom depth (m)	Isobutane[a] / n-butane	Isopentane[a] / n-pentane	$\delta^{13}C$ (‰)	
				C_1	CO_2[b]
6-6	58	6.3	6.0	−70.3	
19-4, 48	177	6.8	24.6	−65.9	
21-3, 126	195	6.4	—	−62.6	−7.3
22-6, 86	209	4.7	72.3	−62.0	
23-5, 85	217	6.0	36.2	−61.5	
24-3, 61	223	4.5	—	−63.7	
25-6, 6	238	5.3	33.3	−61.4	
26-4, 14	243	7.9	—	−61.5	
27-2, 123	251	7.0	41.7	−63.2	
29-2, 149	270	6.9	10.5	−60.4	
31-5, 104	293	7.7	25.0	−62.6	
34-1, 96	320	6.7	9.3	−63.6	

[a] A dash indicates that one or both components were not detected in the sample.
[b] Isotopic analysis was not performed where insufficient CO_2 was present for measurement.

Table 2. Isotopic compositions and hydrocarbon isomer ratios of core gases, Hole 566C.

Core-Section, Interval (cm)	Sub-bottom depth (m)	Isobutane / n-butane	Isopentane / n-pentane	$\delta^{13}C$ (‰)			
				C_1	C_2	C_3	C_{4+}
6-1, 121	120	18.6	1.4	−60.5	−30.6	−33.3	−33.0
7-1, 90	129	13.6	0.08	−60.2	−27.4	−28.4	−31.8

Table 3. Isotopic compositions and hydrocarbon isomer ratios of core gases at Site 567.

Core-Section, Interval (cm)	Sub-bottom depth (m)	Isobutane[a] / n-butane	Isopentane[a] / n-pentane	$\delta^{13}C$ (‰)[b] C_1
Hole 567				
H1-7, 2	1–176	17.1	—	−70.5
Hole 567A				
H1-3, 142	1	17.3	—	−70.0
1-6, 20	203	4.8	68.0	−70.5
2-5, 56	212	5.8	19.7	−70.7
3-3, 73	219	5.5	55.0	−70.9
4-1, 128	232	5.1	17.0	−72.9
5-3, 25	237	4.7	12.2	−72.6
6-5, 22	250	41.0	21.6	−72.4
7-2, 50	255	3.8	10.3	−72.8
8-4, 114	268	3.7	78.0	−73.1
9-5, 26	278	3.7	—	−71.8
10-1, 30	281	4.0	—	−72.7
11-2, 32	291	4.2	4.2	−73.2
12-2, 114	301	3.1	11.4	−71.5
13-4, 144	313	3.0	—	—
14-2, 131	319	3.5	17.3	−72.3
16-2, 48	336	3.2	9.6	−70.8
17-2, 132	346	3.5	10.8	−72.0
18-1, 64	352	1.4	0.6	−72.0
19-1, 79	360	—	—	—
20-1, 31	377	0.7	0.8	−70.6
23-1, 1	412	2.5	0.7	−66.9
24-1, 52	421	2.3	2.1	−71.4
25-1	430	—	—	−57.9
26-1	439	2.6	—	−61.0
27-1, 64	446	1.5	2.6	−73.8
29-2, 29	486	3.0	—	—

[a] A dash indicates that one or both of the components were not detected.
[b] A dash here indicates that leakage reduced the concentration of methane below the level required for isotopic analysis.

Table 4. Isotopic compositions and hydrocarbon isomer ratios of core gases, Hole 568.

Core-Section, Interval (cm)	Sub-bottom depth (m)	Isobutane[a] / n-butane	Isopentane[a] / n-pentane	$\delta^{13}C$ (‰)[b] C_1	CO_2
3-5, 30	19	3.1	0.5	−71.4	−2.6
4-4, 43	28	3.3	4.1	−69.0	+0.6
5-5, 89	39	8.2	4.7	−67.3	+4.7
6-4, 30	47	6.1	14.2	−66.7	+3.2
7-3, 142	56	5.8	10.2	−64.6	+4.2
8-5, 95	68	4.1	12.5	−64.6	+5.4
9-4, 128	76	5.1	15.5	−63.0	+3.3
10-4, 82	85	5.0	14.6	−64.4	+5.4
12-4, 101	104	4.7	26.8	−65.0	+4.9
13-4, 128	114	4.6	82.0	−62.7	+7.1
14-6, 32	126	5.6	17.2	−61.7	+8.8
15-6, 54	135	8.1	7.1	−64.3	—
16-4, 131	143	4.7	11.1	−61.4	+5.5
17-4, 125	152	6.1	7.6	−56.2	—
18-3, 43	160	6.1	11.6	−56.7	+4.7
19-7, 46	176	5.3	6.2	—	—
20-6, 58	184	6.1	6.3	−54.0	—
22-5, 105	202	15.8	0.9	−50.7	—
23-2, 89	208	10.8	0.2	−49.4	—
24-4, 20	220	28.3	6.5	−49.0	—
25-6, 2	232	12.5	0.46	−48.2	—
27-3, 52	247	15.8	1.2	−46.8	—
28-4, 98	259	14.7	4.1	−46.5	—
29-5, 93	270	—	0.5	−46.2	—
30-6, 127	281	19.2	3.8	−45.2	—
32-6, 85	300	4.7	0.3	−46.0	—
33-6, 101	310	9.6	0.6	−45.6	—
34-6, 39	319	12.6	0.8	−45.1	—
35-4, 107	327	15.0	1.9	−45.5	—
36-6, 93	339	16.4	2.5	−39.5	—
37-4, 30	346	15.6	11.5	−42.8	—
38-6, 69	358	23.0	16.0	−44.3	—
39-3, 34	363	15.6	2.0	−45.8	—
40-3, 86	374	17.3	2.6	−44.2	—
41-5, 117	387	8.5	8.0	−43.4	—
42-6, 117	398	—	1.4	−43.1	—
43-4, 40	404	33.0	—	−44.0	—
44-4, 97	414	—	0.42	−42.5	—

[a] A dash indicates that one or both of the components were not detected.
[b] A dash here indicates that concentrations were insufficient for isotopic analysis.

Table 5. Isotopic compositions and hydrocarbon isomer ratios of core gases at Site 569.

Core-Section, Interval (cm)	Sub-bottom depth (m)	Isobutane[a] / n-butane	Isopentane[a] / n-pentane	$\delta^{13}C$ (‰)[b] C_1
Hole 569				
5-4, 85	36	3.5	0.8	—
6-6, 122	49	—	2.4	—
7-7, 45	59	3.6	—	−88.2
8-3, 100	63	10.3	0.05	—
9-1, 45	66	2.0	0.4	−85.4
10-1, 67	79	11.5	0.3	−83.5
11-2, 66	90	10.7	3.0	−82.2
12-6, 20	105	33.5	—	−79.1
13-3, 45	110	32.7	—	−79.9
14-1, 129	117	17.0	0.22	−76.7
15-3, 83	129	16.8	—	−78.0
16-1, 90	136	—	—	−77.6
17-6, 41	153	—	—	—
18-2, 23	156	11.3	0.5	−77.2
20-1, 134	175	—	—	−71.7
21-2, 75	186	26.0	1.0	—
22-2, 55	195	4.2	—	−72.5
23-3, 97	207	33.0	—	−71.6
24-5, 75	219	35.3	—	−70.3
25-2, 73	224	—	—	−68.9
26-5, 20	238	30.0	—	−68.5
27-3, 26	244	28.3	—	−67.5
Hole 569A				
1-2, 55	248	25.5	1.2	−79.9
1-2, 77	258	9.0	—	−76.6
4-1, 65	275	18.5	—	−74.4
6-1, 24	294	5.7	0.5	−69.2
7-1, 76	304	11.4	—	−67.9
9-1, 88	333	8.0	1.0	−65.2

[a] A dash indicates that one or both components were not detected.
[b] A dash here indicates that concentrations were insufficient for isotopic analysis.

Site 569 (the shallowest sample analyzed at this site) to −57.9‰ at 430 m at Site 567. These values are within the isotopic range of biogenic methane (Fuex, 1977; Bernard et al., 1977). The large predominance of methane over ethane at these sites, with C_1/C_2 ratios averaging several thousand, also indicates biogenically produced gas (Bernard et al., 1976).

At Sites 568 and 570, methane isotopic values indicative of biogenic gas were present in the upper 143 and 205 m of the cored sections, respectively. Below these depths, methane isotopic values became rapidly heavier, reaching fairly constant values of −40 to −45‰ at the bases of the cored sections. Considered alone, these values indicate a gas of thermogenic origin, but the C_1/C_2 ratios do not substantiate this conclusion. For example, from 150 to 390 m at Site 568, C_1/C_2 ratios averaged about 6400, except for two samples from around 250 m, in which methane was lost during sampling, accounting for the low C_1/C_2 ratios. At Site 570 between 205 and 395 m, C_1/C_2 ratios were lower, averaging about 970.

$\delta^{13}C$—CO_2 profiles at Sites 568 and 570 provide a possible explanation for the heavy methane values. As shown in Figure 3, the isotopic profile of CO_2 appears to parallel approximately that of C_1, especially at Site 570, for which more data are available. Carbon dioxide concentrations in vacutainers from sections below 284 m were too low for isotopic analysis, but isotopic analysis of bicarbonate from pore waters in these deeper sections (Claypool et al., this volume) has established that the CO_2 isotopic trend does indeed follow that for C_1 to the bottom of the cored section. This relationship indicates that the methane may not be thermogenic in origin, but may have been produced, as in shallower sections, by bacterial reduction of CO_2.

A fractionation effect of approximately −70‰ is involved in the bacterial production of C_1 (Rosenfeld and Silverman, 1959). When CO_2 has an isotopic value within its normal range of −15 to +5‰, biogenic methane of −85 to −65‰ is produced. Where CO_2 is constantly being removed from a sediment system by reduction to C_1, and addition of fresh, isotopically light CO_2 from fermentation of organic matter is limited, CO_2 would be expected to become progressively heavier. This trend would be reflected in the methane profile because the fractionation effect should remain constant. This process apparently is taking place in these cores, because Claypool et al. (this volume) have determined an isotopic value of about +30 to +37‰ for bicarbonate at the bottom of

Table 6. Isotopic compositions and hydrocarbon isomer ratios of core gases, Hole 570.

Core-Section, Interval (cm)	Sub-bottom depth (m)	Isobutane[a] n-butane	Isopentane[a] n-pentane	δ13C (‰)				
				C1[b]	CO2[c]	C2[c]	C3[c]	C4+[c]
1-4, 15	5	5.0	—	—	—			
2-5, 59	11	3.0	—	−80.7	—			
3-6, 132	22	3.9	—	−78.9	−8.3			
4-2, 117	30	5.8	—	−77.0	−4.4			
5-3, 147	41	0.4	0.5	−75.6	−4.1			
6-5, 55	53	4.5	—	−72.5	−2.3			
7-4, 10	61	6.1	14.0	−71.1	−1.5			
8-3, 55	69	3.8	16.3	−69.9	—			
9-2, 89	78	4.3	12.5	−69.3	−2.7			
10-2, 143	88	4.1	13.2	−69.1	−0.2			
11-1, 148	96	3.7	17.1	−68.3	−1.1			
14-5, 27	130	2.7	2.7	−68.1	0.0			
15-2, 114	136	13.0	5.2	−67.8	−0.1			
16-6, 8	151	2.7	3.3	−67.1	+0.5			
17-3, 120	157	2.1	11.2	−65.8	—			
18-1, 138	164	2.6	23.0	−66.5	0.0			
19-3, 51	176	2.2	18.7	−65.1	—			
20-1, 106	183	1.6	1.6	−64.8	+1.9			
21-2, 17	193	3.2	6.0	−63.0	+4.3			
22-3, 84	205	3.9	18.0	−61.3	+3.9			
23-2, 73	213	3.9	7.7	−56.6	—			
24-3, 54	224	3.6	4.6	−57.7	—			
25-4, 25	234	1.8	1.1	−55.5	+4.8			
26-4, 148	246	1.3	1.4	−53.5	+0.3	−25.7	−29.0	
28-6, 84	267	1.3	3.9	−40.8	+10.7	—		
29-4, 118	274	1.1	4.8	−42.8	+9.9	−25.6		
30-4, 140	284	4.4	7.4	−42.3	+16.3	−24.2		
31-3, 122	289	1.3	3.4	−42.2				
32-4, 63	302	2.1	2.3	−42.1				
34-1, 115	318	—	—	−41.4				
35-2, 114	329	—	—	−41.8				
36-1, 88	337	10.0	2.4	−41.2	—	−24.9		
37-1, 82	346	6.8	2.6	−41.3	—	−24.3		
41-2, 148	387	8.2	0.8	−41.2	—	—	−21.4	−22.6
42-1, 145	395	6.6	2.7	−40.2	—	−24.3	−21.6	−26.0

[a] A dash indicates that one or both components were not detected.
[b] A dash here indicates that concentrations were insufficient for isotopic analysis.
[c] A blank space indicates that the component was not detected.

the cored sections from Sites 568 and 570. Bacterial reduction of this heavy CO_2, with a fractionation effect of about −70‰, would produce methane with an isotopic value of about −40‰, as is in fact observed.

C_2–C_5 Hydrocarbons

Ethane and higher hydrocarbons, which generally increase in concentration with depth in these and other DSDP cores (Rice and Claypool, 1981), are thought to result from both diagenesis of the indigenous organic matter in the sediments (Claypool and Kvenvolden, 1983) and/or upward migration from deeper, more mature strata (Summerhayes and Gilbert, 1981). There is strong evidence for migration of hydrocarbons into the rocks sampled at 120 and 129 m in Hole 566C, and at 387 and 395 m in Hole 570. These sections contain basement rocks, serpentinite, in which the hydrocarbons would not have been generated, but had appreciable concentrations of C_2–C_5 hydrocarbons (up to 1.0%), with C_1/C_2 ratios ranging from 85 to 420. Although the isotopic ratios from these sections indicate that the methane is predominantly biogenic, the C_2–C_5 hydrocarbon trends seem to indicate a significant thermogenic gas component. For example, in Hole 570, ethane and higher hydrocarbons increase with depth to 274 m, decrease rapidly between 274 and 328 m, and then increase to the bottom of this hole. This concentration profile is evident in the C_1/C_2 ratios, which
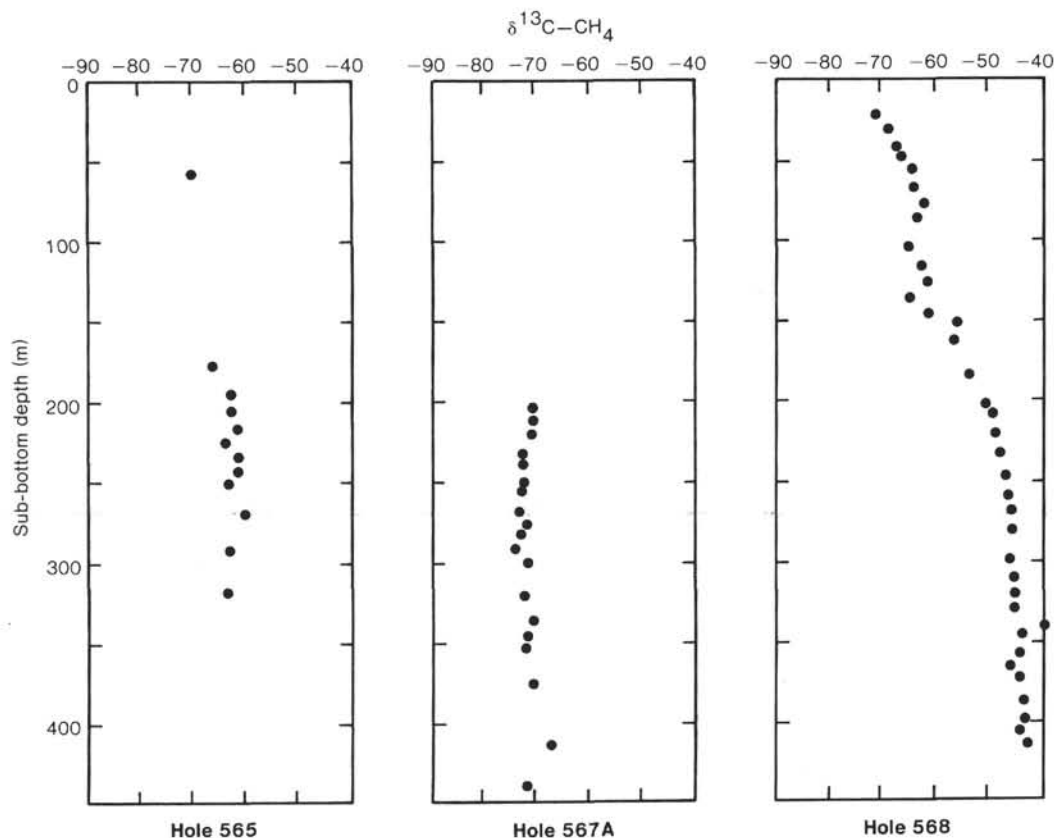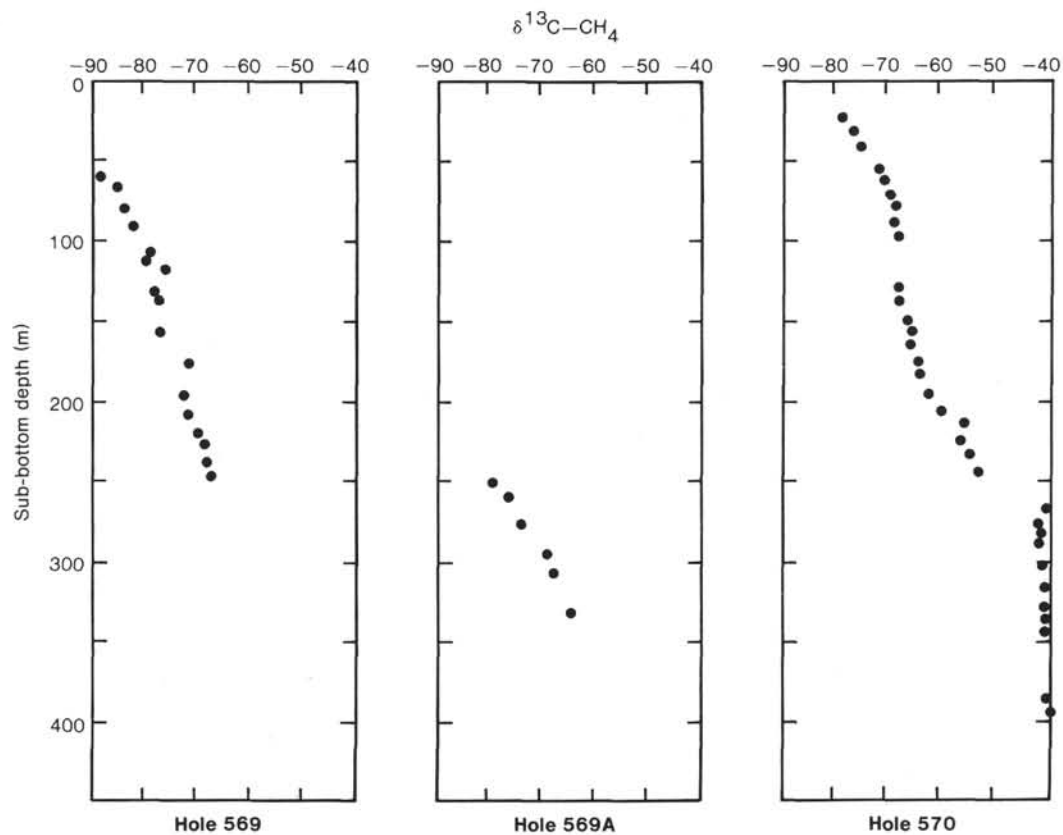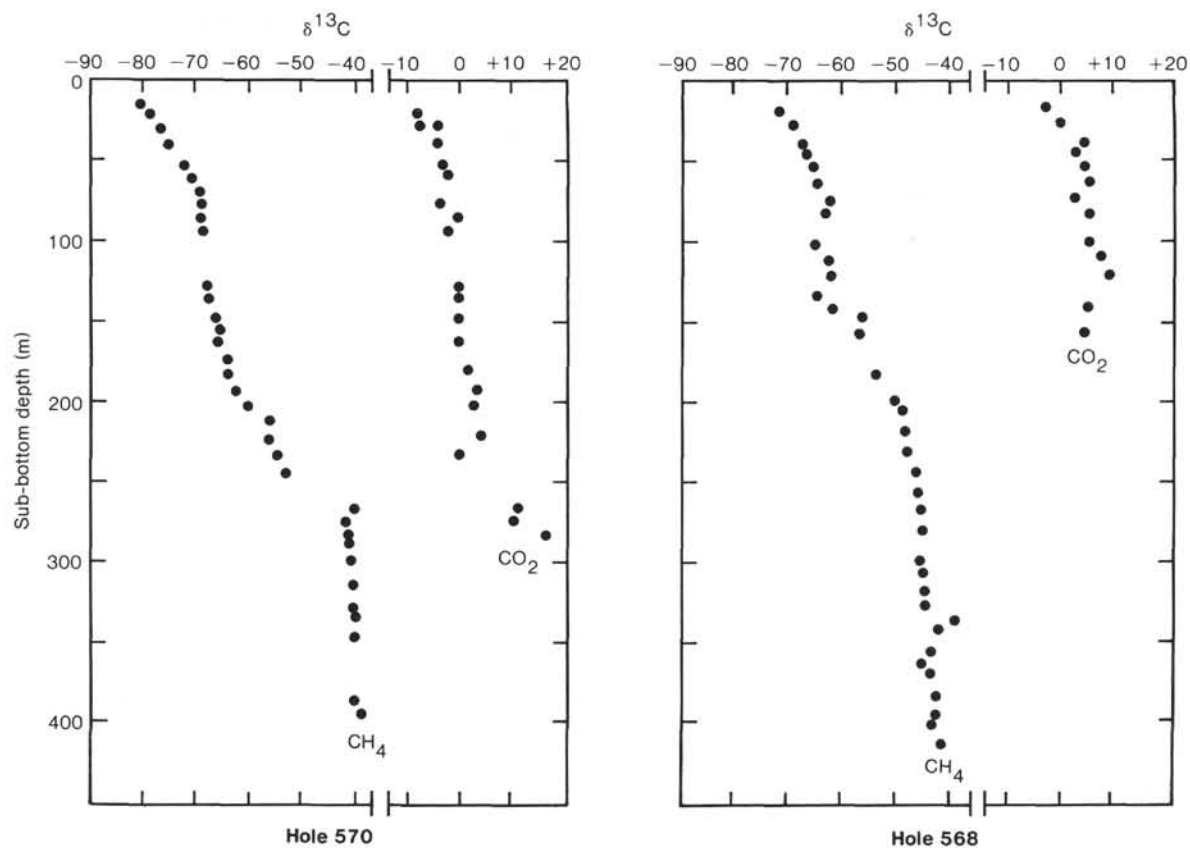

Figure 1. $\delta^{13}C_{PDB}$ of methane in vacutainer gas from Sites 565, 567, and 568.

$\delta^{13}C-CH_4$

Figure 2. $\delta^{13}C_{PDB}$ of methane in vacutainer gas from Sites 569 and 570.

$\delta^{13}C$

$\delta^{13}C$

Figure 3. $\delta^{13}C_{PDB}$ of methane and of CO_2 in vacutainer gas from Sites 568 and 570.

decrease from about 90,000 near the surface to 440 at 274 m, and then increase to 1900 at 317 m. At the bottom of the hole there is a dramatic increase in ethane and higher hydrocarbon concentrations and a corresponding decrease in C_1/C_2 ratios to 190 and 85 in the serpentinite basement rocks at 387 and 395 m, respectively. This contrasts with the steady increase with depth in concentrations of higher hydrocarbons at Site 568, more indicative of *in situ* production by diagenesis of sedimentary organic matter.

The hydrocarbon gases appear to be extremely immature at all the sites, judging by the isobutane/n-butane and isopentane/n-pentane ratios. Throughout each core, iso/n butane and pentane ratios are consistently greater than 1, and in many cases greater than 10 (Tables 1 through 6). Hunt, Huc, et al. (1980) have shown that iso/n pentane ratios are typically less than 1 in surface sediments, owing to biogenic contribution of the normal isomer. With increasing depth, diagenetic reactions preferentially generate iso-pentane, and iso/n pentane ratios up to 5 are found. With increasing burial, thermogenic reactions produce normal isomers, and the iso/n alkane ratio decreases with increasing maturity of the hydrocarbon gas, so that mature natural gases and petroleum-associated gases have ratios typically less than 1 (Maksimov et al., 1959; Reznikov, 1969; Astaf'ev et al., 1973).

It is possible that the ratios of butane and pentane isomers analyzed in the Sites 565–570 sediments may be altered by migration or gas-hydrate formation. Leythaeuser et al. (1980) have shown that branched isomers are lost to the atmosphere at a faster rate than the normal isomers in short surface cores because of the apparently higher diffusion rate of the branched isomers through sediments. Since the relatively high hydrocarbon accumulations found in serpentinite at Sites 566 and 570 may be due to migration, the high iso/n butane and pentane ratios may be attributable to the more rapid migration of the branched isomers. The isomer ratios are not significantly different, however, in areas of presumed migration, compared with areas where the hydrocarbons appear to have been generated *in situ*. At Site 566, for example, the iso/n butane ratios at 120–130 m average 16 in a gas that has undoubtedly migrated into the basement rock at this depth. This value is similar to average ratios observed in cores from other sites (565, 568, and 570) that show no evidence of hydrocarbon migration.

Isomeric ratios of butanes may be changed by gas hydrate formations if a structure II type of hydrate is present, because this structure can accommodate isobutane but not n-butane (Hand et al., 1974), owing to the different molecular sizes of the isomers. Gas hydrates were observed at Site 565, 568, and 570; there were several gas hydrate occurrences at Site 570, including a 3-m section at 249 m sub-bottom (Kvenvolden and McDonald, this volume). Kvenvolden and McDonald (this volume) have suggested, however, that the gas hydrates here are structure I, which would have no effect on the ratios of the isomers of either butane or pentane. In addition, there appears to be no significant difference between butane and pentane isomer ratios in sections with extensive hydrate formation and in those sections where hydrates appeared

to be absent. Thus, the presence of hydrates does not appear to affect the isomer ratios.

C_2–C_5 Isotopic Composition

The heavy carbon-isotopic values at Sites 566 and 570 for ethane and higher hydrocarbons indicate apparently immature diagenetic gas. At Site 570, $\delta^{13}C$—C_2 values of core gases are fairly uniform, ranging from −24.2 to −25.7‰ in six sections. Ethane in the massive gas hydrate at 249 m sub-bottom depth has a $\delta^{13}C$ value of −26.7‰ (Brooks et al., this volume). In serpentinite basement rocks at Site 570, the $\delta^{13}C$—C_2 is −24.3‰, and $\delta^{13}C$—C_3 values are −21.4 and −21.6‰. Ethane and propane $\delta^{13}C$ values are somewhat lighter in the serpentinite of Hole 566C, and in both sections analyzed, the propane value was lighter than the ethane value. Our values agree well with a single measurement of −25.4‰ obtained by Claypool et al. (1973) for ethane in a sample from DSDP Site 102.

$\delta^{13}C$ values of ethane and higher hydrocarbons have been reported for a suite of 34 petroleum-associated gases (Galimov et al., 1970), a suite of mature to overmature natural gases (Stahl and Carey, 1975), and other natural gases and petroleum-associated gases (Fuex, 1977; Erdman and Morris, 1974). The isotopic values of ethane and propane in the cored sections from Sites 566 and 570, especially site 570, are among the heaviest reported, and do not appear to fit a maturity trend for natural gases from marine-derived organic matter established by Stahl and Carey (1975) and Stahl (1977). In this trend, methane, ethane, and propane are isotopically light in the least mature gases, and become progressively heavier with increasing maturity. Very immature gases such as those in this study appear to be much heavier than would be predicted.

In a study by Chung and Sackett (1979), involving pyrolysis of kerogens, coals, and petroleum samples, the earliest formed gas, in effect the least mature gas, was isotopically heavy compared with gas formed later. Chung and Sackett (1979) suggested that one explanation for this anomalously heavy gas could be isotopic heterogeneity in precursor molecules, with hydrocarbons formed earliest being generated from isotopically heavy regions of the precursor molecules. There is evidence from pyrolysis work, however, that catalytic decomposition of long-chain hydrocarbons in the presence of clay minerals, a process involving a carbonium-ion mechanism, generates initially isotopically heavy gaseous hydrocarbons (Sackett, 1978; Jeffrey, 1981). The higher concentrations of the branched-chain alkanes, isobutane and isopentane, in the immature sediments at Sites 565–570, may also be due to reactions involving the carbonium-ion mechanism (Hunt, Huc, et al., 1980; Hunt, Whelan, et al., 1980).

The methane isotopic profiles in the cores analyzed in this study are consistent with a biological origin for the methane. It seems likely, however, that the nonbiological reactions generating ethane and higher hydrocarbons in the deeper sediment sections also form methane. If the nonbiological methane concentration is assumed to be about 10 times the ethane concentrations (Claypool

and Kvenvolden, 1983), biological methane is still more than 95% of the total methane in the gas from 387 m sub-bottom at Site 570, which has the highest ethane concentration (0.36%). This predominance of biological methane makes it difficult to establish whether methane generated in the earliest stages of diagenesis is anomalously heavy, as ethane and propane appear to be. Comparison of methane, ethane, and propane isotopic values in natural gases (Stahl and Carey, 1975; Fuex, 1977), petroleum gases (Galimov et al., 1970; Erdman and Morris, 1974), and pyrolysis gases (Jeffrey, 1981) indicate, however, that reactions which form heavy ethane and propane also form heavy methane.

If a comparison between the methane, ethane, and propane isotopic values in the overmature gases studied by Stahl and Carey (1975) and the sediment gases at Site 570 is valid, a methane isotopic value heavier than $-40‰$ would be predicted for the nonbiological methane component. In sediment gases such as these, where methane is from a mixture of biological and nonbiological sources, the isotopic values of ethane and propane may be useful in arriving at an estimate of the isotopic value of the nonbiological methane component.

SUMMARY

$\delta^{13}C$—C_1 values at Sites 565, 566, 567, and 569 were lighter than $-60‰$, indicating a biogenic origin for these gases. $\delta^{13}C$—C_1 values in gases from Site 568 and 570 were lighter than $-60‰$ in the upper parts of the cored sections, but in the lower parts the values approached $-40‰$, much heavier than expected for biogenic gas. $\delta^{13}C$—CO_2 values, however, were also anomalously heavy at these sites, and the general parallel trends with depth of the C_1 and CO_2 isotopic values indicate that the isotopically heavy C_1 is formed biogenically by reduction of heavy CO_2.

High iso/n ratios of butane and pentane in these core gases indicate that the gases are thermally immature, consistent with low-temperature chemical diagenesis of indigenous organic matter as the source of ethane and higher hydrocarbons. $\delta^{13}C$ values of ethane and propane are very heavy, especially at Site 570, where $\delta^{13}C$ values are heavier than $-27‰$, and are among the heaviest values reported for these hydrocarbons. Consequently, the higher hydrocarbons in these gases do not fit established trends of $\delta^{13}C$ values and maturity for hydrocarbons in more mature natural gases, which would predict much lighter $\delta^{13}C$ values for the core-gas hydrocarbons. This indicates that the early stages of chemical diagenesis generate anomalously heavy ethane and propane, and by analogy, methane also, although this is difficult to prove, owing to the predominance of biogenic methane in the gases.

ACKNOWLEDGMENTS

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