17. DIAGENESIS OF ORGANIC MATTER, ISOTOPIC COMPOSITION OF CALCITE VEINS IN BASEMENT BASALT AND PORE WATER IN SEDIMENT—BARBADOS RIDGE COMPLEX, DEEP SEA DRILLING PROJECT LEG 78A[1]

George E. Claypool, U.S. Geological Survey, Denver, Colorado[2]

ABSTRACT

Sediments of the Barbados Ridge complex, cored on DSDP Leg 78A, contain low concentrations of acid-insoluble carbon (0.05–0.25%) and nitrogen (C/N 1.5–5) and dispersed C_1–C_6 hydrocarbons (100–800 ppb). The concentrations of organic carbon and ^{13}C in organic carbon decrease with depth, whereas the concentration of dispersed hydrocarbons increases slightly with depth. These trends may reflect the slow oxidation of organic matter, with selective removal of ^{13}C and slow conversion of the residual organic matter to hydrocarbons. Very minor indications of nitrogen gas were observed at about 250 meters sub-bottom at two of the drilling sites. Basement basalts have calcite veins with $\delta^{13}C$ values in the range of 2.0 to 3.2‰ and $\delta^{18}O_{SMOW}$ values ranging from 28.5 to +30.6‰. Interstitial waters have $\delta^{18}O_{SMOW}$ of 0.2 to −3.5‰ and δD_{SMOW} of −2 to −15‰. The oxygen isotopic composition of the calcite veins in the basement basalts gives estimated equilibrium fractionation temperatures in the range of 11 to 24°C, assuming precipitation from water with $\delta^{18}O_{SMOW}$ in the range of +0.1 to −1.0‰. This suggests that basalt alteration and precipitation of vein calcite occurred in contact either with warmer Campanian seawater or, later, with pore water, after burial to depths of 200–300 meters. Pore waters from all three sites are depleted in deuterium and ^{18}O, and dissolved sulfate is enriched in ^{34}S at Sites 541 and 542, but not at Site 543.

INTRODUCTION

Oil and gas fields are present on or near the islands of Barbados, Tobago, and Trinidad to the south of the Leg 78A drilling area. Sediments exhibiting sulfate reduction were cored at DSDP Hole 27 on the Barracuda Rise, about 150 km to the east. In view of these facts, a complete hydrocarbon monitoring program was planned for Leg 78A drilling in the sediments at the deformation front of the Barbados Ridge complex (Fig. 1). The sediments cored proved to be nearly barren of organic matter. Despite low absolute contents of hydrocarbons and organic carbon, there are suggestions of regular changes with depth that may be related to the age or temperature of the sediments, or both.

ANALYTICAL PROCEDURES AND RESULTS

Gas Analysis

With two exceptions, gas pockets were not present in Leg 78A cores. To monitor levels of gaseous hydrocarbons, it was necessary to extract gas from the sediment. This was done by disaggregating and heating core samples in a blender. Whole core sections 3 to 5 cm in length (100–170 cm^3) were extruded from the core liner and placed in the blender as soon as possible after the core was on board. The blender was filled with distilled, deionized water, except for a 200-cm^3 airspace.

The sediment in the blender was blended at low speed for 1 min., heated in a 75°C water bath for 30 min., blended again for another minute, and returned to the water bath for another 5 to 10 min. An empty 10-ml syringe with a 1.5-inch needle was inserted to beneath the water level through an off-center septa port on the blender top, and the contents of the blender were allowed to adjust to atmospheric pressure. A second heated 10-ml syringe was inserted through the center port on the blender top, and about 6 ml of blender airspace was withdrawn, adjusted to 5 ml, and injected into the cold trap of the Hewlett-Packard 5711A gas chromatograph (Whelan, 1979) on board the *Glomar Challenger.* The cold trap is an alumina-packed 3 × 20 cm pre-column chilled to −70°C. The $C_{2\text{-plus}}$ hydrocarbons are retained on the column while air and C_1 are vented. After 1.5 min., the cold trap is closed and heated in a 90–100°C water bath for 1 min. The carrier gas effluent from the cold trap is valved to the gas chromatograph, which is programmed to heat the column oven from 60 to 200°C at 8° per min. for analysis of C_2–C_6 hydrocarbons. Retention times for compound identification, response factors for quantitative analysis, and recovery factors relating gas in the headspace to gas in the mud, were obtained by internal standards and analysis of known amounts of pure compounds and analyzed reference-gas mixtures.

Extremely low levels of hydrocarbon gases (parts per billion) were present in cores drilled to depths of about 460 meters beneath the seafloor on Leg 78A. The quantities of C_2–C_6 hydrocarbons released from fresh sediment are shown in Table 1.

Visible separations or gaps in the sediment from Holes 541 and 543 were sampled through the clear plastic core liner by withdrawing gas into a vacutainer. Vacutainer samples were analyzed for air, CH_4, CO_2, and C_2H_6 by thermal conductivity gas chromatography, and for C_2 to C_6 hydrocarbons by flame ionization gas chromatography, on the *Glomar Challenger.* Vacutainer samples from Hole 541 were also submitted to Global Geochemistry, Inc. of Canoga Park, California, for complete mass-spectrometric gas analysis and for $^{15}N/^{14}N$ measurement of the N_2. Results of the shipboard hydrocarbon analyses are given in Table 2. Shore-based mass-spectrometric analyses of gas-pocket samples from Hole 541 and a sample of *Challenger* lab air are given in Table 3.

Carbon and Nitrogen Analysis

Shipboard organic carbon analysis was done with a Hewlett-Packard 185-B CHN analyzer. Samples selected from each core for carbonate-bomb measurements were reacted with HCl to remove carbonate, washed with deionized water, and dried at 110°C. A Cahn Electrobalance was used to weigh 20 mg of each sample of sediment for CHN analysis. Samples were burned at 1050°C in the presence of an oxidizing catalyst, and the volumes of N_2, CO_2, and H_2O were determined as measures of the C, H, and N contents of sediment organic matter, using a CSI mini-lab integrator. Samples with known carbon and nitrogen contents (AVB-2 and 66-488) were used to calibrate instrument response.

[1] Biju-Duval, B., Moore, J. C., et al., *Init. Repts. DSDP,* 78A: Washington (U.S. Govt. Printing Office).

[2] Address: U.S. Geological Survey, Denver Federal Center, Box 25046, Denver, Colorado 80225.

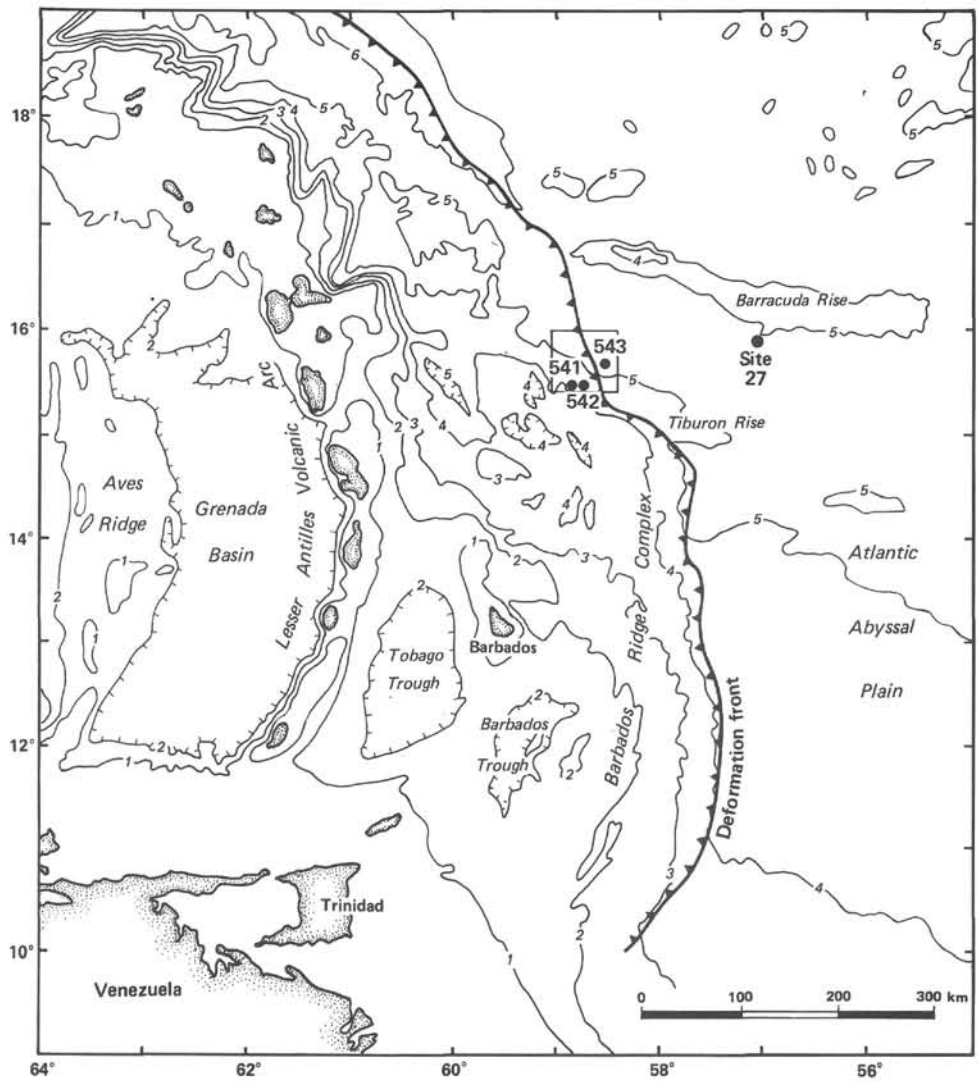

Figure 1. Locations of Sites 541, 542, and 543, drilled on and near the Barbados Ridge.

Table 1. C_2–C_6 hydrocarbon gas content of core samples, Leg 78A.

Core-section	Sub-bottom depth (m)	10^{-9} vol. gas per vol. sediment (nl/L or ppb by vol.) C_2	C_3	*i*-C_4	*n*-C_4	i-C_5	*n*-C_5	*n*-C_6	Total	C_1/C_2[a]
Hole 541										
3-2	30	4	n.d.	n.d.	1	n.d.	7	n.d.	12	n.a.
10-3	100	2	2	n.d.	n.d.	7	16	n.d.	27	n.a.
27-6	270	75	20	16	11	3	18	31	174	n.a.
39-5	360	89	27	84	2	2	n.d.	65	270	n.a.
42-3, 4	387	287	80	29	23	n.d.	14	48	480	22
48-4, 5	444	490	140	22	19	12	7	n.d.	690	17
Hole 542										
H2-4	150	88	21	42	7	16	1.2	n.d.	176	30
1-5	210	47	32	36	5	4	n.d.	27	151	17
Hole 542B										
4-3	263	32	5	6	n.d.	n.d.	n.d.	n.d.	43	n.a.
10-2	318	82	22	14	6	n.d.	n.d.	17	140	10
Hole 543										
5-2	41	168	84	26	45	11	13	38	385	18
26-2	241	42	37	22	6	1	n.d.	n.d.	110	n

Note: n.d. = not detected. n.a. = not analyzed.
[a] Estimate of methane : ethane ratio from separate analysis.

Table 2. Hydrocarbon composition of gas removed from core-liner gas pockets.

Section	Sub-bottom depth (m)	Volumes of component per 10^6 volumes of gas (ppm) C_1	C_2	C_3	*i*-C_4	*n*-C_4	*i*-C_5	*n*-C_5	C_1/C_2
541-28-2	249	36	2.2	0.70	0.24	0.24	0.16	0.22	16.4
541-28-6	257	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
543-26-2	241	51.5	1.2	0.5	n.d.	n.d.	n.d.	n.d.	43
543-26-3	242	66.3	2.2	0.4	n.d.	n.d.	n.d.	n.d.	30

Note: n.d. = not detected.

One hundred five samples from Leg 78A were analyzed for organic carbon and nitrogen by combustion of the HCl-insoluble residue. The results are given in Table 4. Carbon is reported on both a calculated whole-rock and a measured carbonate-free basis. The relationship between whole-rock and carbonate-free carbon content is

$$\%C_{(\text{whole rock})} = \%C_{(\text{HCl-insol})} \times 1 - \frac{\%CaCO_3}{100}$$

where $\%CaCO_3$ (and the HCl-insoluble residue) are obtained from the shipboard carbonate-bomb determination. Nitrogen content is reported as the C/N atomic ratio. Hydrogen values are not reported, because of presumed interference from mineral-bound water.

Table 3. Gas composition (%) and $\delta^{15}N$ of gas removed from core-liner gas pockets.

Sample (hole-core-section, cm level)	N_2	O_2	Ar	CO_2	H_2O	$\delta^{15}N$ (air)
541-26-2, 120 cm	85.93	12.26	Trace	0.43	1.38	+0.87
541-26-3	84.73	12.87	Trace	0.42	1.74	+1.52
541-28-2	82.90	5.69	0.68	0.77	9.98	+1.34
541-28-5	70.04	19.08	—	0.57	10.32	+0.46
541-28-6	78.58	19.04	Trace	0.10	2.29	+3.21
Challenger lab air	75.74	21.65	Trace	0.18	2.43	+1.03

Note: — = not reported.

Pyrolysis Assay and $^{13}C/^{12}C$ of Organic Matter

Selected samples were later subjected to Rock-Eval pyrolysis (Espitalie et al., 1977) at the U.S. Geological Survey, Lakewood, Colorado. Samples were heated in helium at 250°C for 5 min. and then from 250°C to 550°C at a rate of 25°C per minute. Detector response was calibrated with n-C_{20} alkane and with the IFP standard rock 27251, a lower Toarcian shale from the Paris basin. Organic carbon in HCl-insoluble rock residues was converted to CO_2 by combustion, and the $^{13}C/^{12}C$ ratio of the purified CO_2 was determined at the U.S. Geological Survey, Lakewood, Colorado. The results were expressed as $\delta^{13}C$, where (‰) = $[R_{sample}/R_{standard}) - 1] \times 10^3$, $R = {}^{13}C/{}^{12}C$ or $^{18}O/^{16}O$, and the standard is PDB marine carbonate. The results of pyrolysis assay and $\delta^{13}C$ of organic carbon for 12 samples from Hole 541 are given in Table 5.

Isotopic Composition of Calcite Veins in Basalt

Calcite samples were analyzed for $\delta^{13}C$ and $\delta^{18}O$ by Global Geochemistry, Inc. Standard preparation techniques (reaction with 100% H_3PO_4 at 25°C; McCrea, 1950) were employed, and the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios were measured on a triple-collecting MAT 250 mass spectrometer. The isotopic compositions of 16 samples of calcite veins from the basement basalts penetrated in Hole 543A are give in Table 6.

Isotopic Composition of Pore-Water Constituents

Interstitial water samples were analyzed by Global Geochemistry, Inc. Total dissolved CO_2 was recovered by acidification and $\delta^{13}C$ was measured. Dissolved sulfate was precipitated as $BaSO_4$, converted to SO_2, and $\delta^{34}S$ was determined. The δD and $\delta^{18}O$ of the water itself were measured by standard techniques (Esptein and Mayeda, 1953; Friedman and Hardcastle, 1970). The results are presented in Table 7.

DISCUSSION

Organic carbon contents (carbonate-free basis) of analyzed Leg 78A sediments (Fig. 2) are low (<0.3%) in all samples, and carbon content is low relative to nitrogen, as indicated by the smaller than normal (1.5–5) C/N ratios (Table 4). In addition, a trend of decreasing carbon content with increasing depth beneath the seafloor is apparent at each drilling site (Fig. 2). Whole-rock organic carbon contents show effects of dilution with $CaCO_3$ during periods of deposition above the carbonate compensation depth. If the rate of deposition of noncalcareous sediment is approximately constant, then the carbon-free organic carbon content at any given depth reflects the balance between organic matter deposited and organic matter oxidized. The trends in Figure 2 could be caused by (1) regular increase with time in the rate of deposition of organic matter, and preservation of organic matter; (2) a constant rate of deposition of organic matter and slow decomposition (oxidation) with advancing time or increasing depth; and (3) a constant rate of deposition of organic matter, with increasing dilution by noncalcareous clastic sediment at greater depths.

It is unlikely that the observed regular decrease in carbon content with increasing burial depth results from a change in rates of deposition of organic matter, and total sediment accumulation rates do not support the idea

Table 4. Organic (acid-insoluble) carbon and carbon/nitrogen ratios, Leg 78A.

Section or sample (interval in cm)	Sub-bottom depth (m)	Organic carbon (wt.%) Whole rock	$CaCO_3$-free	C/N
Hole 541				
1-1	1.5	0.24	0.27	4.2
2-5	7.5	0.20	0.22	3.5
2-6	9.2	0.18	0.23	4.3
3-1	11.4	0.21	0.22	3.8
4-1	20.7	0.16	0.26	3.5
4-4	25.5	0.20, 0.23	0.21, 0.23	3.1, 3.3
5-2	31.1	0.15	0.24	4.2
6-1	39.7	0.14	0.15	2.8
7-2	51.0	0.17	0.19	3.3
8-1	58.7	0.16	0.23	3.3
8-5	64.5	0.15	0.20	3.2
8-7	67.5	0.18, 0.17	0.24, 0.22	4.2, 4.2
9-6	75.9	0.14	0.23	3.2
10-2	79.3	0.14	0.26	3.7
11-4	91.3	0.13	0.20	3.5
13-1	106	0.11	0.19	3.5
13-7	115	0.14	0.24	3.9
14-5	122	0.13, 0.13	0.20, 0.20	3.5, 3.6
15-5	131	0.13	0.19	3.5
16-3	138	0.14	0.19	1.9
17-5	150	0.10	0.18	3.9
18-1	154	0.11	0.18	3.4
19-1	163	0.11	0.14	2.5
20-1	173	0.10, 0.094	0.17, 0.15	3.6, 4.1
21-1	182	0.11, 0.12	0.15, 0.15	2.9, 3.0
22-6	199	0.11	0.14	3.0
23-1	201	0.098	0.13	2.9
24-1	211	0.16	0.16	3.8
25-1	221	0.19	0.19	3.3
26-2	231	0.15, 0.16	0.15, 0.16	3.3, 3.9
27-5	245	0.13	0.13	2.7
29-2	259	0.14	0.14	5.2
30-2	269	0.12	0.14	3.4
31-6	285	0.089	0.15	3.1
32-5	292	0.096	0.16	2.8
33-7	305	0.093	0.17	2.6
34-6	314	0.091	0.13	2.4
35-6	322	0.074	0.12	2.2
36-2	326	0.085	0.11	2.8
37-1	335	0.12	0.12	2.2
38-1	344	0.12	0.13	2.8
39-5	359	0.080	0.080	2.4
41-4	376	0.077	0.10	2.0
42-4	386	0.065	0.078	3.8
43-5	398	0.069	0.080	3.6
45-1	411	0.064	0.064	2.9
47-1	429	0.058	0.058	3.1
48-1	439	0.043	0.043	2.6
48-6	447	0.074	0.074	3.2
49-4	452	0.057	0.058	2.6
Hole 542				
H1-2, 46–49 cm	80	0.13	0.21	3.5
H2-4, 80–83 cm	150	0.11	0.16	2.5
H3-3, 37–41 cm	196	0.10	0.14	2.5
1-4, 71–75 cm	207	0.064	0.098	2.2
2-6, 62–66 cm	220	0.076	0.086	1.5
4-5, 81–86 cm	237	0.072	0.081	1.8
Hole 542A				
1-4, 133–136 cm	179	0.084	0.11	2.8
2-7, 43–47 cm	249	0.079	0.080	2.4

Table 4. (Continued).

Section or sample (interval in cm)	Sub-bottom depth (m)	Organic carbon (wt.%) Whole rock	$CaCO_3$-free	C/N
Hole 542A (Cont.)				
3-5, 106-109 cm	257	0.10	0.10	2.9
5-3, 108-112 cm	273	0.061	0.081	2.4
6-6, 58-62 cm	286	0.087	0.088	2.9
7-2, 12-15 cm	289	0.086	0.086	3.3
9-3, 29-32 cm	310	0.086	0.094	2.5
Hole 543				
1-2, 56-59 cm	2	0.0	0.19	4.1
1-4, 111-118 cm	5	0.0	0.22	3.9
2-3, 44-47 cm	14	0.0	0.14	2.9
2-5, 44-47 cm	17	0.18	0.18	3.3
3-5, 40-43 cm	26	0.0	0.18	3.8
4-4, 60-63 cm	35	0.0	0.25	4.0
5-3, 13-16 cm	42	0.19	0.23	4.3
6-4, 70-72 cm	54	0.0	0.19	3.6
7-4, 41-44 cm	63	0.0	0.14	3.1
8-4, 50-54 cm	73	0.14	0.14	2.8
9-1, 104-107 cm	78	0.12	0.12	2.9
9-4, 65-68 cm	82	0.0	0.15	3.2
10-4, 81-84 cm	92	0.15	0.15	3.1
11-3, 59-63 cm	100	0.18	0.18	4.7
12-4, 70-72 cm	111	0.092	0.092	2.8
13-6, 70-74 cm	123	0.14	0.14	4.0
14-5, 110-113 cm	132	0.14	0.14	4.0
16-4, 23-27 cm	148	0.089	0.089	3.0
18-6, 99-102 cm	171	0.15	0.15	5.5
19-6, 13-16 cm	180	0.11	0.11	3.0
20-3, 88-92 cm	186	0.087	0.087	1.7
23-1, 138-142 cm	211	0.10	0.10	2.3
24-4, 103-106 cm	222	0.13	0.13	2.7
25-2, 55-59 cm	231	0.076	0.076	2.1
26-5, 55-58 cm	245	0.13	0.13	3.7
28-3, 59-62 cm	261	0.096	0.096	3.6
29-3, 61-65 cm	271	0.0	0.057	5.4
30-6, 82-88 cm	285	0.051	0.051	5.7
31-2, 8-11 cm	288	0.057	0.057	4.0
33-3, 22-26 cm	308	0.046	0.046	3.5
34-2, 94-97 cm	317	0.046	0.046	4.2
Hole 543A				
2-2, 52-55 cm	334	0.071	0.071	3.0
3-2, 101-104 cm	344	0.082	0.082	1.8
4-3, 36-39 cm	354	0.067, 0.059	0.067, 0.059	1.3
5-2, 58-61 cm	363	0.059	0.059	1.4
6-1, 49-52 cm	370	0.062	0.062	1.8
7-3, 100-104 cm	384	0.039	0.051	1.4
8-1, 87-91 cm	390	0.071	0.075	2.7
9-1, 50-54 cm	399	0.074	0.10	4.3
10-1, 28-32 cm	408	0.044, 0.044	0.094, 0.094	3.6, 4.4
10-1, 120-124 cm	409	0.052, 0.051	0.063, 0.059	n.d.
11-2, 30-34 cm	419	0.063, 0.055	0.064, 0.056	6.8, 8.8

Note: n.d. = not determined, because of undetectable nitrogen in basalt.

Table 5. Pyrolysis assay and $\delta^{13}C$ of organic matter, Hole 541.

Core-section	Sub-bottom depth (m)	Hydrocarbon yield (mg/g)	$\delta^{13}C_{org}$ (‰ vs. PDB)
1-1	1.5	0.42	−25.5
4-1	20.7	0.34	−25.9
5-2	31.1	0.18	−26.1
8-1	58.7	0.28	−25.9
10-2	79.3	0.31	−25.5
13-7	115	0.20	−25.6
21-1	182	0.24	−26.6
26-2	245	0.50	−26.7
32-5	292	0.12	−26.4
41-4	376	0.38	−26.3
43-5	398	0.15	−26.7
49-9	452	0.32	n.a.

Note: n.a. = not analyzed.

Table 6. Isotopic composition of calcite veins in basalt, Hole 543A.

Sample (hole-core-section, cm level)	$\delta^{13}C$ (‰ vs. PDB)	$\delta^{18}O$ (‰ vs. SMOW)	°C[a]
543A-10-1	2.01	30.26	16.2
543A-10-2	2.55	30.57	14.9
543A-11-1, 2 cm	2.95	29.77	18.3
543A-11-1, 68 cm	2.70	28.48	24.1
543A-12-1	3.07	29.36	20.1
543A-12-1	2.77	29.19	20.9
543A-12-4	3.14	29.87	17.9
543A-13-1	3.05	29.60	19.0
543A-13-2	2.83	28.59	23.6
543A-13-5	3.22	29.87	23.6
543A-14-1	2.63	29.13	21.1
543A-15-3	3.14	29.86	17.9
543A-15-3	2.94	29.47	19.6
543A-16-3	2.19	28.97	21.8
543A-16-5	3.11	30.25	16.3
543A-16-7	3.25	29.87	18.1

[a] Equilibrium temperature with water of $\delta^{18}O = 0.00$.

of decreasing dilution by noncalcareous clastic material. More probably, reaction within the sediment leads to a decrease in organic carbon content with advancing time or increasing depth of burial.

The regular decrease of organic carbon content with depth in marine sediments has been studied in both shallow (0–5 m) cores (Heath et al., 1977; Mueller and Mangini, 1980) and in DSDP (0–500 m) cores (Waples and Sloan, 1980). In a variety of environments, each with relatively uniform sediment accumulation rates, the decrease in organic carbon with time is consistent with first-order decay at half-lives that range from 15,000 to 866,000 years. The different rates of organic carbon decay have been interpreted as reflecting different reactivities of organic matter.

The slight offset at the depth of the reverse fault in the organic-carbon-vs.-depth curve for Hole 541 (Fig. 2) suggests that the systematic carbon decrease might be used to infer the timing of the fault movement, as Waples (1980) used organic carbon profiles to estimate the age of implacement of a basalt intrusion at Hole 444 (Leg 58). To examine this question and the more general question of what is controlling the organic carbon decrease, the Leg 78A organic carbon contents are plotted against age in Figure 3, and apparent rates of decay of organic carbon are estimated and summarized in Table 8. The apparent half-lives for decrease in organic carbon in Leg 78A sediments are much longer than have been observed elsewhere, and range from 4 to 38 Ma. Shorter apparent half-lives are associated with more rapid sediment accumulation rates (Table 8). This association of slower carbon decrease with slower sediment accumula-

Table 7. Isotopic composition of interstitial water and major anions.

Core-section	Sub-bottom depth (m)	Interstitial water δD (‰ vs. SMOW)	Interstitial water $\delta^{18}O$ (‰ vs. SMOW)	Dissolved sulfate $\delta^{34}S$ (‰ vs. CDM)[a]	Dissolved total CO_2 Alkalinity[b] (meq L^{-1})	Dissolved total CO_2 $\delta^{13}C$ (‰ vs. PDB)
Hole 541						
2-5	8.5	−12	−0.79	25.7	2.91	n.d.
5-1	31	−12	−0.80	31.7	1.57	−7.2
8-4	64	−7	−0.72	33.3	1.60	+2.6
13-4	113	−9	n.d.	31.4	0.73	+0.6
18-4	159	−7	−1.12	30.6	0.53	−6.1
33-4	301	−11	−1.44	31.9	0.31	−8.8
38-5	350	−15	−1.51	28.3	1.05	n.d.
Hole 542						
H1-6	0–88	−9	−2.66	25.5	0.99	+7.5
H2-3	88–154	−12	−1.66	28.7	0.79	−2.0
H3-2	154–202	−15	−3.49	27.9	0.38	−5.1
Hole 543						
2-4	16.5	−8	−0.90	20.6	2.69	−4.0
5-3	43.5	−6	−0.48	21.5	1.94	−7.5
9-5	84.5	−2	+0.20	21.5	1.79	n.d.
29-4	273	−9	−0.66	21.2	0.85	n.d.

Note: n.d. = no determination.
[a] Canon Diablo Meteorite.
[b] Shipboard alkalinity.

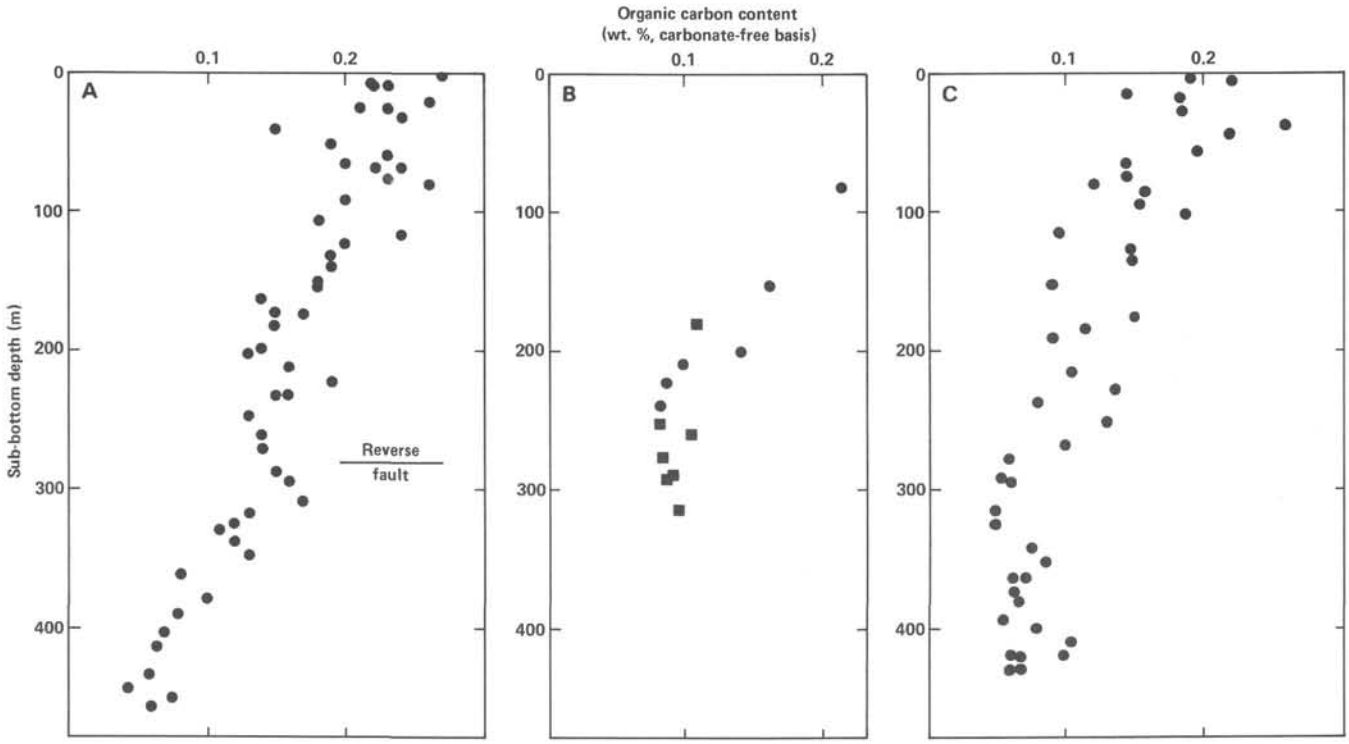

Figure 2. Plot of organic carbon ($CaCO_3$-free) vs. burial depth in (A) Hole 541, (B) Holes 542 (●) and 542B (■), and (C) Hole 543.

tion and the unreactive organic matter indicates that the organic carbon decay is more depth-dependent than time-dependent, and that the limiting factor is probably diffusion of oxygen from overlying seawater rather than reactivity of organic matter. Since organic carbon decay cannot be systematically associated with burial time, it is not obvious how these data can be used to estimate time of faulting.

The C_2–C_6 gas contents of Leg 78A sediments generally increase exponentially with linear increase in depth of burial (Figure 4). Thermogenic hydrocarbons are produced by nonbiological decomposition of sedimentary organic matter at temperature-dependent rates. If the hydrocarbons were diffusing from a deeper source, the concentration gradient with depth should be linear rather than exponential. In addition, if the gases indicated migrating hydrocarbons in the sedimentary section, much higher concentrations should have been detected, especially in more porous zones or adjacent to migration pathways. Therefore, the Hole 541 data support a

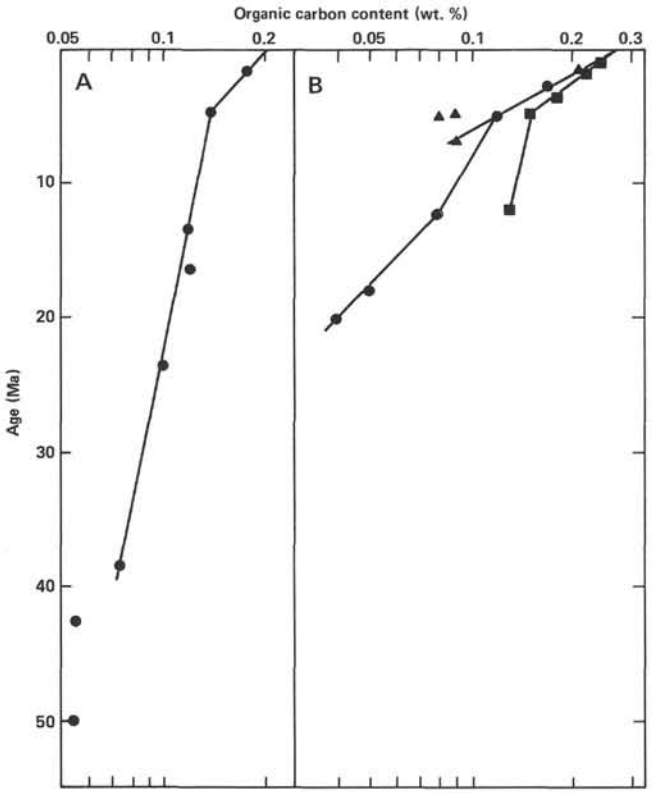

Figure 3. Organic carbon content ($CaCO_3$-free) versus age, in (A) Hole 543; (B) Holes 541 (■, ●) and 542 (▲). (Different symbols for Hole 541 represent analyses of sediment samples of comparable age above [■] and below [●] the reverse fault.)

Table 8. Apparent decay constants and half-lives for organic carbon decomposition, DSDP Leg 78A.

Hole (depth interval in m)	k (Ma)	$t_{1/2}$ (Ma)	Sediment accumulation rate (m/MA)
541 (0–85)	0.12	5.7	40
541 (85–275)	0.02	35	6
541 (275–350)	0.18	3.9	45
541 (350–400)	0.05	12.8	?
541 (400–450)	0.09	7.5	?
543 (0–80)	0.03	25.6	16
543 (80–220)	0.02	38.5	7

conclusion of *in situ* generation of hydrocarbons rather than migration from depth. The regular increase of C_2–C_6 hydrocarbons with depth was not noted in Holes 542 and 543 (Table 1). The sampling was infrequent, however, and gas contents were very low in any case. Diesel fuel was added to the mud in Hole 542B, in an attempt to free stuck drill pipe, but no effects were noted in the cores.

In both Hole 541 and Hole 543, at about the same depth of burial (260 m), minor indications of non-hydrocarbon gas were noted. The cores obviously were releasing minor amounts of gas, which caused small (~2-cm) separations in the core; this gas as sampled by puncturing the core liner and allowing gas to expand into evacuated glass tubes closed by a ruber septum (vacutainer).

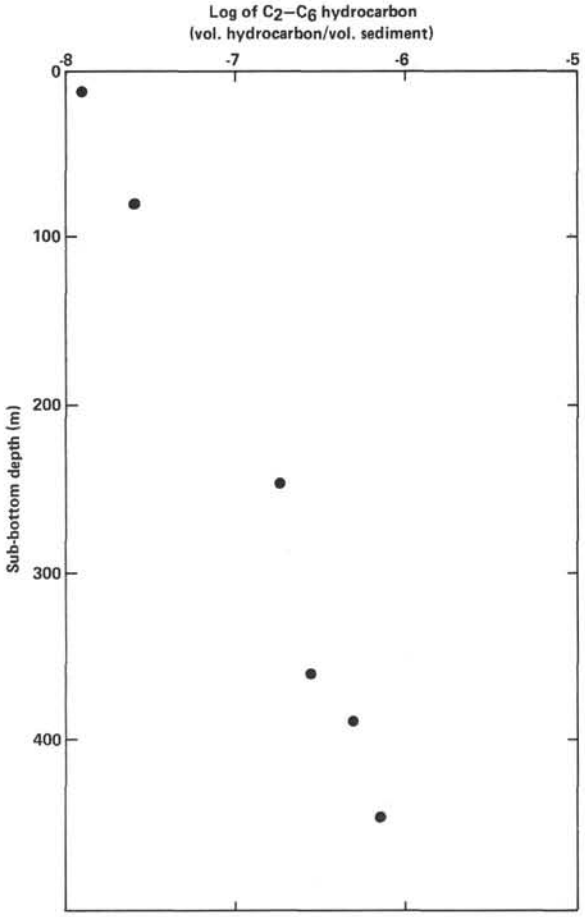

Figure 4. Plot of log of C_2–C_6 hydrocarbon content vs. burial depth for core samples, Hole 541.

The gas contains only traces of hydrocarbons (Table 2; parts per million relative to total gas volume). The balance of the gas is either nitrogen or atmospheric air (Table 3). A possible explanation is that the gas is dissolved nitrogen, produced by denitrification in the sediments according to the overall reaction

$$5CH_2O + 4HNO_3 \rightarrow 2N_2 + 5CO_2 + 7H_2O$$

This process is consistent with the apparent increasing consumption of organic matter with depth. These pelagic sediments may be characterized by extended "suboxic diagenesis" (Froelich et al., 1979), in which aerobic respiration is followed first by denitrification and then by reduction of MnO_2 and FeOOH. The $\delta^{15}N$ of the N_2 does not support this hypothesis, because only one sample is significantly different from ambient air.

Organic matter in Hole 541 at selected depths was characterized by pyrolysis assay and $^{13}C/^{12}C$ measurements (Table 5). The hydrocarbon yield occurred mainly at low heating temperature (250°C), and ranged from 0.12 to 0.50 mg/g. Total pyrolytic hydrocarbon yield normalized by whole-rock organic carbon increased with increasing depth of burial, partly because of a slight increase in total hydrocarbon yield, but mainly because of the decrease in organic carbon. The $\delta^{13}C$ of the organic carbon decreases (becomes more negative) with increas-

ing depth of burial, apparently reflecting preferential ^{13}C removal in the process causing the organic carbon decrease.

Sixteen samples of calcite veins in Hole 543A basalt have uniform isotopic composition, with $\delta^{13}C_{PDB}$ of 2.6 ± 0.6‰ and $\delta^{18}O_{SMOW}$ of 30.5 ± 1‰. The oxygen isotopic composition of this calcite can be used to calculate a temperature of vein formation, assuming equilibrium fractionation and a $\delta^{18}O$ value for the water in which the calcite precipitated. The temperatures—calculated using the equation of O'Neil et al. (1969), the observed $\delta^{18}O$ of the calcite vein, and an assumed $\delta^{18}O$ of 0.00 for the water—are reported in Table 6, and range from 14.9 to 24.1°C. Using $\delta^{18}O = -1.00$‰ for the water would lower the calculated temperatures by about 4°C. The calculated temperatures are higher than present-day Atlantic Bottom Water (~4°C), but comparable to the temperatures estimated from the $\delta^{18}O$ values of Upper Cretaceous benthic calcareous microfossils (Savin, 1977). The Hole 543A basalt is overlain by Maestrichtian–Campanian sediment, so the basalt may have undergone alteration and calcite vein formation by contact with warm Campanian seawater. Alternatively, alteration of the basalt could have occurred later, after burial to depths of about 200 to 300 meters sub-bottom, by contact with pore waters heated to the 11 to 24°C temperature range.

Pore waters from all three sites on Leg 78A are slightly depleted in both dueterium and ^{18}O, compared with seawater, but consistent trends are not apparent (Table 7).

Dissolved sulfate is enriched in ^{34}S in the pore water from Holes 541 and 542, indicating possible effects of sulfate reduction. Pore water from Hole 543 sediments has essentially the same $\delta^{34}S$ as seawater sulfate. The degree of ^{34}S-enrichment in dissolved sulfate from the three sites is roughly proportional to the respective levels of organic carbon content in the sediments from the sites. The amount and $\delta^{13}C$ of total dissolved CO_2 in Leg 78A pore waters do not show any consistent evidence for oxidation of organic matter in the sediments. The alkalinities systematically decrease with increasing depth, and $\delta^{13}C$ shows both positive and negative values compared with seawater.

CONCLUSION

Organic matter is present in very low concentrations in the sediments cored on Leg 78A, but differences between the drill sites and trends of decreasing organic carbon content with depth indicate that diagenetic processes involving organic matter are occurring.

ACKNOWLEDGMENTS

I thank T. Daws for pyrolysis assays, C. Threlkeld for organic carbon $\delta^{13}C$ measurements, B. Law, W. Dean, and K. Kvenvolden for helpful reviews, and D. Malone for manuscript preparation.

REFERENCES

Epstein, S., and Mayeda, T. K., 1953. Variations of the $^{18}O/^{16}O$ ratio in natural waters. *Geochim. Cosmochim. Acta,* 4:213–224.

Espitalié, J., Laporte, J. L., Madec, M., Marguis, F., Leplat, P., Paulet, J., Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pet.,* 32:23–42.

Friedman, I., and Hardcastle, K., 1970. A new technique for pumping hydrogen gas. *Geochim. Cosmochim. Acta.,* 34:125–126.

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta,* 43:1075–1090.

Heath, G. R., Moore, T. C., and Danphin, J. P., 1977. Organic carbon in deep-sea sediments. *In* Andersen, N. R., and Malahoff, A., (Eds.), *Fate of Fossil Fuel CO_2 in the Oceans:* New York (Plenum), pp. 605–625.

McCrea, J. M., 1950. On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.,* 18:849–857.

Mueller, P. J., and Mangini, A., 1980. Organic carbon decomposition rates in sediments of the Pacific Manganese Nodule Belt dated by ^{230}Th and ^{231}Pa. *Earth Planet. Sci. Lett.,* 51:94–114.

O'Neil, J. R., Clayton, R. N., and Mayeda, T. K., 1969. Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Physics,* 51:5547–5558.

Savin, S. M., 1977. The history of the Earth's surface temperature during the past 100 million years. *Ann. Rev. Earth Planet. Sci.,* 5: 319–355.

Waples, D. W., 1980. Age of a basalt intrusion estimated by organic geochemistry. *In* Klein, G. deV., Kobayashi, K., et al., *Init. Repts. DSDP,* 58: Washington (U.S. Govt. Printing Office), 741–743.

Waples, D. W., and Sloan, J. R., 1980. Carbon and nitrogen profiles in deep-sea sediments: new evidence for bacterial diagenesis at great depths of burial. *In* Klein, G. deV., Kobayashi, K., et al., *Init. Repts. DSDP,* 58: Washington (U.S. Govt. Printing Office), 745–754.

Whelan, J. K., 1979. C_1 to C_7 hydrocarbons from IPOD Holes 397 and 397A. *In* von Rad, U., Ryan, W. B. F., et al., *Init. Repts. DSDP,* 47, Pt. 1: Washington (U.S. Govt. Printing Office), 419–432.

Date of Initial Receipt: January 31, 1983
Date of Acceptance: August 19, 1983