

32. C₁-C₈ HYDROCARBONS IN IPOD LEG 63 SEDIMENTS FROM OUTER CALIFORNIA AND BAJA CALIFORNIA BORDERLANDS¹

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ABSTRACT

Low-temperature diagenetic reactions (less than 50°C) are held responsible for the generation of small amounts of C₁-C₈ hydrocarbons (less than 100 ng hydrocarbon/g dry weight of sediment) at outer continental shelf Deep Sea Drilling Project Sites 468 and 469 (sub-bottom depths 415 m and 454 m, respectively). In contrast, Site 471 shows an exponential rise in hydrocarbon yields at depths greater than 500 meters. The high yields of C₄-C₈ hydrocarbons (up to 30 ng hydrocarbon/g dry weight of sediment) in this area of high geothermal and volcanic activity suggest the penetration of an active petroleum-generating zone. Similar arguments apply to Site 467, where relatively high levels (up to 3 μg hydrocarbon/g dry weight sediment) occurred in very shallow (250-600 m) sediments.

INTRODUCTION

We have investigated occurrences of traces of C₁-C₇ volatile organic compounds at a number of DSDP sites (see Whelan and Hunt, 1980a). In most cases investigated to date, the amounts and distributions of these compounds have been most consistent with low-temperature (less than 50°C), in situ chemical and/or biological generation processes. In contrast, Sites 467 and 471 showed exponential increases and a wide distribution of saturated and aromatic C₁-C₈ hydrocarbons commencing at shallow depths (230 m at Site 467 and 500 m at Site 471). Because of high geothermal gradients and episodic volcanic activity in this area, we interpret these increases as resulting from catagenic petroleum formation. Catagenesis, or the main phase of petroleum formation, begins at a temperature of about 50°C, if the proper type and content of organic matter is present in the sediment (for reviews, see Hunt, 1979, and Tissot and Welte, 1978).

None of the four sites—including 468 and 469, which contained much lower levels of hydrocarbons—showed volatile compounds other than saturated and aromatic hydrocarbons. The only exceptions were traces of alkenes detected in a few sections of Site 467. These functionalized compounds are the dominant compounds in surface gravity cores having an oxic sediment/water interface (Hunt and Whelan, 1979; Whelan et al., in press). In contrast, the sediments analyzed in the present work make up a particularly good suite—especially those from Sites 467 and 471—for studying hydrocarbon changes produced predominantly by thermal processes.

EXPERIMENTAL TECHNIQUES

Sediments were analyzed by methods described previously (Whelan, 1979). Briefly, the method involves sealing a frozen sample and water in a container equipped with a septum and a helium headspace. The volatile compounds are driven out of the sediment by vigorous shaking and heating of the container to 100°C. The head-

space gas is then analyzed by gas chromatography (GC). The only difference in this work from that described previously was that GC conditions were modified so that C₈ compounds could also be analyzed. This was accomplished either by maintaining the hexadecane/hexadecene capillary column at 35°C (rather than 30°C) or by using columns for which retention times had shortened because of bleeding of the liquid phase.

Compounds were identified by subjecting one or more samples from each site to gas chromatography-mass spectrometry (GC-MS) and comparing spectra either with those of standards run under the same conditions or with standard reference spectra (Cornu and Masot, 1975). Organic carbon and total carbon were run on a LECO carbon analyzer.

RESULTS AND DISCUSSION

Site 467

C₁-C₈ hydrocarbon data, sampled depths, lithology, and geologic age are presented in Table 1. Site 467 contained very high (2-8%) amounts of organic carbon levels, as shown in Figure 1. Also shown are high levels of C₁-C₈ alkanes. In general, maxima in C₄-C₈ profiles correlate well with organic carbon profiles—a trend we have not generally found at other DSDP sites except for the deepest and hottest (such as the Moroccan Basin, Leg 50, Whelan and Hunt, 1980b). Figure 2 shows that total levels of C₁-C₈ hydrocarbons increase exponentially at very shallow depths (200-300 m). Such a rise is typical of a potential petroleum source sediment undergoing catagenesis at temperatures in excess of 50°C.

It does not seem likely that these substances are migrated hydrocarbons in these young (Pliocene/Miocene), fine-grained sediments at shallow burial depths. The correlation of organic carbon with C₂-C₈ hydrocarbon levels shown in Figure 1 is also consistent with in situ generation rather than migration.

The ratio of C₁ to higher alkanes (C₂-C₄) has been used to differentiate thermally and biologically generated methane (Claypool, 1976; Bernard, 1978). The C₁/C₂ ratios for absorbed hydrocarbons in these sediments are very low—in the range of 5 to 10—consistent with catagenically generated hydrocarbons. This measurement is a qualitative one only, because unknown

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Table 1. C₁-C₈ volatile compounds in sediments from IPOD Leg 63 (amounts reported as ng compound/g dry weight of sediment).

Sample (interval in cm)	467-3-3, 100-105	467-25-6, 131-142	467-36-2, 125-134	467-41-4, 121-149	467-54-2, 118-128	467-63-2, 100-108	467-74-1, 100-104	467-85-4, 100-105	467-104-1, 107-113	468-2-3, 129-134	468-18-3, 128-133	468B-6-3, 115-210	
Sub-bottom Depth (m)	19.5	233	332	382	503	588	691	800	967	7.8	160	68	
Lithology	Diatom silty clay	Nanno clay	Nanno silty clay	Nanno clay- stone	Silty clay- stone	Calc. clay- stone	Calc. clay- stone	Nanno clay- stone	Calc. silty clay- stone	Diatom nanno ooze	Diatom nanno silty clay- stone	Nanno ooze diatom ooze	
Chronostratigraphy	Quaternary	Pliocene	Pliocene	Pliocene	upper Miocene	upper Miocene	upper Miocene	middle Miocene	middle Miocene	Pliocene	middle Miocene	middle Miocene	
Compound													
Methane	29	2157	1896	1138	2824	2026	91	20	45	14	11	18	
Ethane	3.1	75	193	59	332	443	15	5	99	2.0	2.6	2.1	
Propane	1.9	56	494	349	1682	911	34	8	275	2.9	3.6	2.1	
i-Butane	0	27	497	336	1070	619	3.5	0	157	0	0.01	0	
n-Butane	0.5	8.5	183	112	436	204	4.0	1.7	172	0.9	1.0	0	
Neopentane	0	0	0	0	4.0	1.7	1.7	0	1.0	0	0	0	
i-Pentane	0	11.9	467	157	347	559	0.9	1.2	244	0	1.8	0	
n-Pentane	0	3.5	60	56	130	115	0	2.8	131	0.01	2.0	0	
Cyclopentane	0	0.5	56	16	56	33	0	0	60	0	0	0	
2,2-Dimethylbutane	0	0.8	1.0	0	4.2	11.4	0.1	0.4	0.5	0	0	0	
2,3-Dimethylbutane	0.5	3.2	9.4	1.5	7.6	39	0	0.4	13	0.7	0.6	0.5	
2-Methylpentane	0.5	3.1	24	17.6	29	173	0.1	1.6	65	1.4	0.7	0.5	
3-Methylpentane	0.2	4.4	19.	2.8	8.4	70	0.2	0.6	55	1.3	0.8	0.4	
n-Hexane	0.7	2.1	18	10.8	20	45	0.2	1.7	40	1.5	1.4	0.4	
Methylcyclopentane	0.1	2.5	108	14.9	35	508	0.1	1.1	151	0.3	0.2	0.4	
2,2-Dimethylpentane	0.4	0.6	0.0	0.1	0.01	0.9	0	0.1	0.2	0.2	0.2	0	
Benzene	2.4	3.6	4.2	4.4	62	13	0.2	0.7	10	1.0	0.3	0	
2,4-Dimethylpentane	0	0	0	0	0	0	0	0	0	0	0	0	
2,2,3-Trimethylbutane	0	2.0	2.4	0.5	0.1	3.0	1.2	0.2	0.9	0.01	0	0	
Cyclohexane	0	10.2	30.0	3.1	9.5	49	0.1	0.3	15	0.2	0.1	0.2	
3,3-Dimethylpentane	0	0.3	0	0	0.01	1.5	0.03	0	0.4	0	0	0	
1,1-Dimethylcyclopentane	0	0.8	2.1	0.2	0.01	0	0	0.1	1.3	0	0	0	
2-Methylhexane	0	0	0.1	0.7	2.1	16	0	0.3	9.7	0.4	0.4	0.2	
2,3-Dimethylpentane	0	6.5	1.6	1.8	7.3	54	0.2	0.7	23	0.6	0.2	0.2	
1C3-Dimethylcyclopentane	}	0	9.9	33	4.4	9.0	173	0.1	2.7	160	0.66	0.57	0.25
3-Methylhexane													
1T3-Dimethylcyclopentane	0	13	32	4.1	7.0	168	0	1.8	127	0.01	0.1	0.05	
1T2-Dimethylcyclopentane	0	3.9	28	3.3	27	162	0.1	2.0	156	0.44	0.24	0.2	
3-Ethylpentane	0	0.01	0	0.1	0.01	7.2	0.05	0.2	11	0.44	0.56	0.27	
n-Heptane	0.4	4.4	17	7.4	11	17	0.12	1.6	24	1.9	1.5	1.1	
1C2-Dimethylcyclopentane	0	1.8	6.8	1.6	9.0	99	0	2.8	132	0.01	0	0	
Methylcyclohexane	0	9.8	30	3.7	13	96	0.2	0.9	87	1.1	0.34	0.47	
2,2-Dimethylhexane	0	0.2	0	0	0.01	0	0	0	0	0	0	0	
Ethylcyclopentane	0	2.6	10.4	0.9	2.6	63	0	0.8	44	0	0	0	
2,5-Dimethylhexane	0	0.2	0	0.1	0.01	1.9	0	0.05	2.5	0	0	0	
2,4-Dimethylhexane	0	0.8	5.8	0.2	0.01	6.1	0	0.1	5.9	0	0	0	
Toluene	1.2	7.8	13	16	441	192	14	8.3	400	19	0	0	
1,1,3-Trimethylpentane	0	5.7	20	11	0.01	83	0	1.8	27	0	0	0	
2,3,4-Trimethylpentane	0	2.7	3.8	1.0	2.6	7.6	0.02	1.0	5.0	1.0	4.0	0.1	
1,1,2-Trimethylpentane	0	1.7	20	0.8	2.7	7.3	0	1.0	7.8	0	0	0	
1C2T4-Trimethylcyclopentane	0	0.4	17	0.4	1.3	13	0.07	0.4	9.0	1.1	0	0	
1C2T3-Trimethylcyclopentane	0	3.8	3.3	0.6	4.6	72	0	1.9	65	0	0	0	
3-Methylheptane	0	1.8	5.3	0.5	0.01	13	0.02	0.5	2.5	0.7	0	0	
1,1-Dimethylcyclohexane	0	0.7	2.9	0.2	20	6.7	0	0.2	2.0	0	0	0	
1T4-Dimethylcyclohexane	0	7.8	10	2.3	20	79	0.1	0.8	15	1.6	0	0	
1T2-Dimethylcyclohexane	0	6.2	3.1	0.1	7.9	29	0	4.0	95	38	0	0	
1C4-Dimethylcyclohexane	0	1.0	30	1.4	3.7	19	0	0	1.2	0	0	0	
n-Octane	0	3.3	6.7	1.5	4.2	28	0.2	1.5	2.0	3.9	0	1.0	
1C2-Dimethylcyclohexane	2.4	1.9	0	0	2.1	31	0	0	0	0	0	0	
C ₈ -Cycloalkane or Ethylbenzene	0.5	5	8	0.5	25	10	1.2	10	120	80	0	0	
Other Compounds													
Cyclohexene	0.3	0	0	0	0	0	0	0	0	0	0	0	
1,3-Dimethylcyclopentene	0	0	0	0	0	0	0	0.2	0	0	0	0	
1T2C4-Trimethylcyclopentane ^b													
Totals													
Organic carbon (%)	2.4	2.2	5.7	2.5	4.3	8.6	4.8	2.8	2.7	3.1	1.9	3.3	
Total carbon (%)	3.2	8.5	8.9	8.7	10.7	13.0	10.9	6.4	7.2	8.2	3.9	10.9	
C ₁	29	2157	1896	1138	2824	2026	91	20	45	14	11	18	
C ₂ + C ₃	5.0	130	686	408	2014	1354	49	13	374	5	6	4	
ΣC ₄ -C ₇	6.9	145	1656	775	2748	3435	27	39	2291	33	13.3	5.2	
ΣC ₈	2.9	43	136	21	94	407	1.6	24	360	126	4.0	1.2	

^a Toluene small as determined by GCMS.^b 1T2C4-TMCP coelutes with toluene and was identified by GCMS.^c nd means not determined.

Table 1. (Continued).

468B-21-2, 113-119	468B-37-1, 120-126	469-2-2, 109-116	469-7-4, 132-139	469-12-5, 120-126	469-20-3, 134-140	469-30-1, 94-99	469-37-1, 145-150	469-43-1, 106-110	471-3-2, 146-150	471-13-7, 136-141	471-44-1, 100-105	471-63-3, 135-139	471-69-3, 111-115	471-74-3, 100-105
257	407	10	69	110	183	274	341	388	22	124	410	593	650	698
Calc. silty clay- stone	Calc. silty clay- stone (+ sand)	Clay	Foram/ nanno ooze; pyrite	Nanno ooze/ diatom ooze + pyrite	Nanno ooze/ diatom ooze + pyrite	Silty clay- stone (burrows + tuffs)	Calc. silty clay- stone + tuff	Clayey nanno chalk- nanno claystone	Silty clay/ nanno clay	clayey diatom ooze	Silty clay- stone	Silty claystone	Silty claystone	Silty claystone
middle Miocene	lower Miocene	Quaternary	Pliocene	upper Miocene	middle Miocene	middle Miocene	lower Miocene	lower Miocene	Pliocene	upper Miocene	middle Miocene	middle Miocene	middle Miocene	middle Miocene
15	5	10	15	10	8	14	5	4	16	29	367	16	28	48
2.2	1.0	0.6	1.2	0.4	0	2	0.2	0.2	1	3	25	16	30	4
2.4	0.8	0	0.1	0	0	1.7	0	0	0	3.5	6.8	28	172	34
0	0	0	0	0	0	0	0	0	0	0	2.0	91	471	118
0.01	0	0	0.01	0	0	0	0	0	0	0	3.8	57	576	153
0	0	0	0	0	0	0	0	0	0	0	4.8	1.7	0	1.9
0	0	0	0	0	0	0	0	0	0	0	2.7	380	1779	674
0	0	0	0	0	0	0	0	0	0	0	2.0	99	844	286
0	0	0	0	0	0	0	0	0	0	0	0	34	327	106
0	0	0	0	0	0	0	0	0	43	0	4.3	8.8	0	2.1
0	0.9	0	0	0.2	0.35	0.6	0.4	0.2	0.4	0	1.1	62	108	154
0.2	0.56	0.05	0.5	0	0	0.5	0.3	0.05	0	0	1.4	224	605	26
0.2	0.54	0.56	0.2	0.4	0.8	0.8	0.8	0.85	0.8	0	1.5	319	738	180
0.3	0.3	0.2	0.8	0.05	0.3	0.6	0.5	0.2	0.5	0	2.2	114	412	81
0	0.6	0.5	0.1	0.4	0.8	0.5	0.5	0.9	0.5	5.4	2.7	927	3833	278
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.7
0.6	0	0	2.6	0	0	0	0	0	0	0	0.6	8.3	4	3
0	0	0	0	0	0	0	0	0	0	0	0.6	22	40	20
0	0	0	0	0	0	0.2	0	0	0.2	0	0	8.2	0	1.7
0	0.3	0.2	0	0.1	0.2	0	0.4	0.1	3.1	0	5.4	147	475	91
0	0	0	0	0	0	0.8	0	0	0.6	0	2.6	4.0	0	0.5
0	0	0	0	0	0	0.8	0	0	0.9	0	0	21	42	0
0	0.3	0.02	0.2	0.08	0.5	0	0.2	0.01	0	0	0	66	108	13
0	0	0.65	0.2	0	0	0	0.3	0.1	0	0	0	130	196	0
0	0.5	0.36	0.2	0.2	0	0	0.4	0.4	0	0	2.1	1670	2346	88
0	0.2	0	0	0	0	0	0.05	0.1	0.05	0	0	1128	1950	439
0	0.2	0	0	0	0	0	0.03	0.1	0	0	2.0	1667	3561	767
0	0.2	0	0	0.24	0	0	0	0	0	0	0	0	0	0
0.2	0.7	0.8	1.0	0.4	0.75	1.4	0.5	0.7	0.8	3.3	4.9	73	220	59
0	0	0.08	0	0	0	0	0	0	0	0	0	1001	1454	220
0.2	0.7	0.5	1.0	0.35	0.56	1.01	0.6	0.6	0	12	1.0	1391	2661	588
0	0	0	0	0	0	0	0	0	0	0	0	114	152	0
0	0	0	0	0	0	0	0	0	0	0	0	490	820	152
0	0	0	0	0	0	0	0	0	0	0	0	9.5	0	3.3
0	0	0	0	0	0	0	0	0	3.5	0	0	16	0	7.6
0	0	0	2.0	0	0	0	0	0	0.1	small ^a	small ^a	small ^a	small ^a	small ^a
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	94	63	35
0	0.05	0.2	0	0.2	0	0	0	0	0.6	0	1.8	393	0	18
0	0	0	0	0	0	0	0	0	0.7	0	2.3	2614	2264	291
0	0.05	0	0.5	0.05	0	0	0	0	0	0	0	52	0	0
0	0	0	0	0	0	0	0	0	0	0	0	53	44	17
0	0.2	0.4	4.5	0.1	0	26	0	0.1	0.8	0	11.0	0	0	498
0	0	0	0	0	0	0	0	0	0	0	0	812	0	471
0	0	0	0	0.1	0	0	0	0	0	0	0	220	0	113
0	0.6	0.4	0	0.6	0	1.0	0.3	0.01	1.0	0.5	0.5	49	71	14
0	0	0	0	0	0	0	0	0	0	0	0	284	2314	158
0	20	1.6	0	0	5.5	25	5	9	12	0	0	nd ^c	nd ^c	nd ^c
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	34	7.6	3437	5074	1720
2.0	0.41	0.74	1.1	0.83	0.69	1.0	0.48	0.44	0.85	0.93	1.04	1.0	0.78	0.65
2.6	1.5	1.3	4.2	2.2	4.2	2.1	1.1	2.2	1.4	0.92	1.39	1.1	0.81	0.84
15	5	10	15	10	8	14	5	4	16	29	367	16	28	48
5	2	0.6	1.3	0.4	0	3.7	0.2	0.2	1	6.5	31.8	44	202	38
1.7	6.0	4.0	8.8	2.4	4.3	7.2	5.0	4.3	50	21	48	10,144	23,570	4503
0	21	2.6	5	1.0	5.5	52	5.3	9.1	19	34.5	23.2	8148	9982	3346

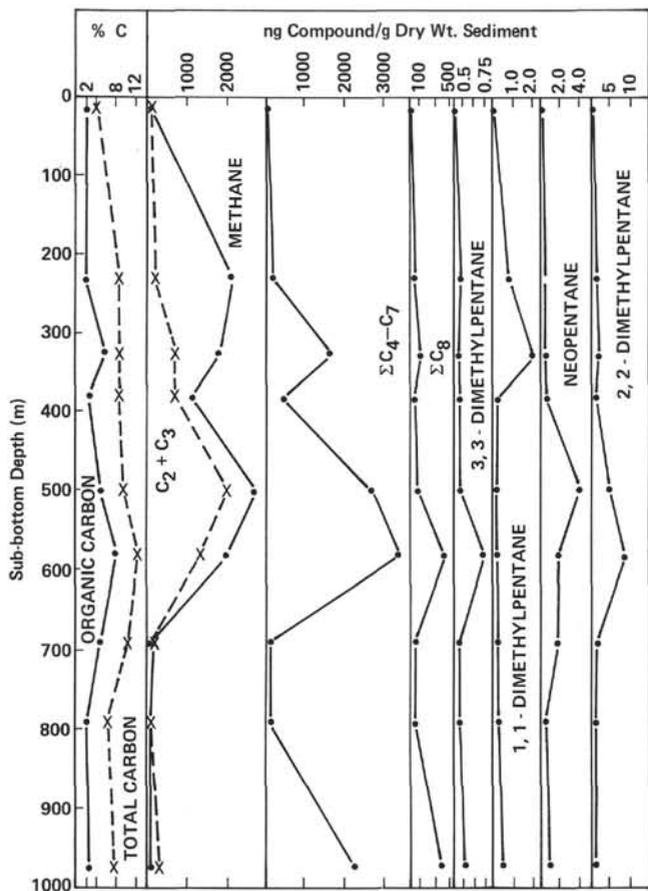


Figure 1. C₁-C₈ hydrocarbons and organic carbon in Site 467 sediments.

amounts of methane are lost during handling of the sediments. However, for comparison, sediments we have previously analyzed that contain methane produced predominantly by bacteria have shown C₁/C₂ ratios of 300 to 100 (the Black Sea, Leg 42, Whelan and Hunt, 1978), 30 to 50 (the Canary Islands, Leg 47, Whelan, 1979) and 100 to 1000 (Japan Trench, Legs 56 and 57, Whelan and Hunt, 1980a). These measurements, representing absorbed hydrocarbons remaining in frozen cores, are lower than those of free core gas obtained on board ship. The differences probably result from loss of the lightest component, methane, during core storage.

The depth profiles of many of the individual hydrocarbons detected are very similar, as can be seen from a few examples plotted in Figure 3. A rough way of quantifying this similarity is by calculation of the correlation coefficients for each of the compounds with the next compound below it, as shown in Table 2. The most interesting result of this calculation is that aromatic and gem-dimethyl hydrocarbons generally do not correlate with the other compounds. These aromatic and gem-dimethyl compounds include neopentane, benzene, 3,3-dimethylpentane, 1,1-dimethylcyclopentane, toluene, and 1,1-dimethylcyclohexane. The analysis suggests that some of the gem-dimethyl and aromatic compounds may have sources different from other molecules listed in Tables 1 and 2. Some other specific C₈ compounds also do not correlate well, such as 1,4-dimethylcyclohexane (both isomers) and 1,2-dimethylcyclohexane. The concentrations of the noncorrelatable compounds are generally not as high as the concentrations of the others shown in Table 1. The rather specific occurrences

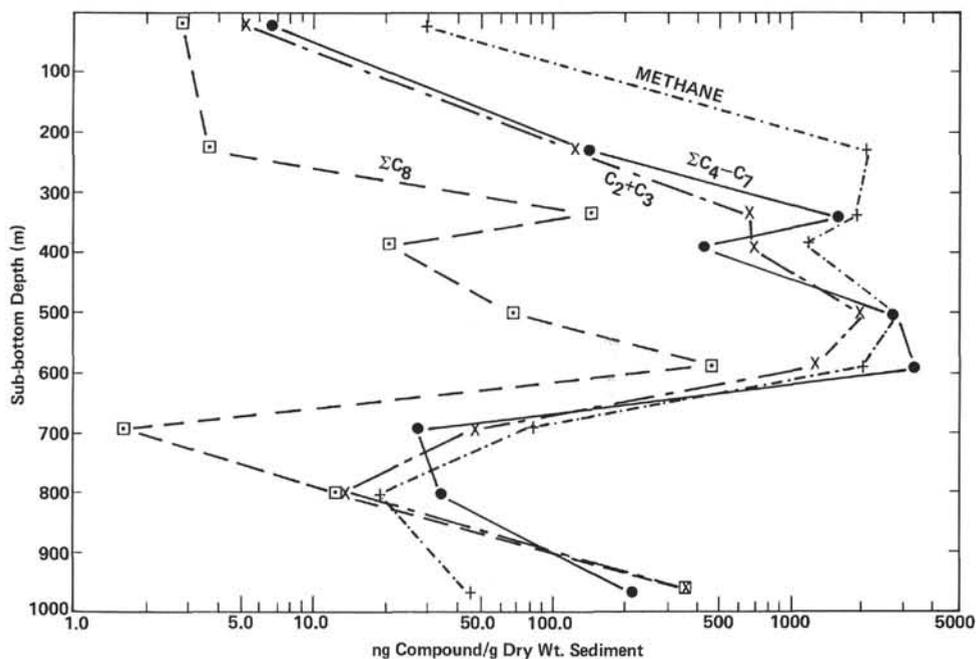


Figure 2. Levels of total C₁, C₂ and C₃, ΣC₄-C₇ and ΣC₈ compounds at Site 467.

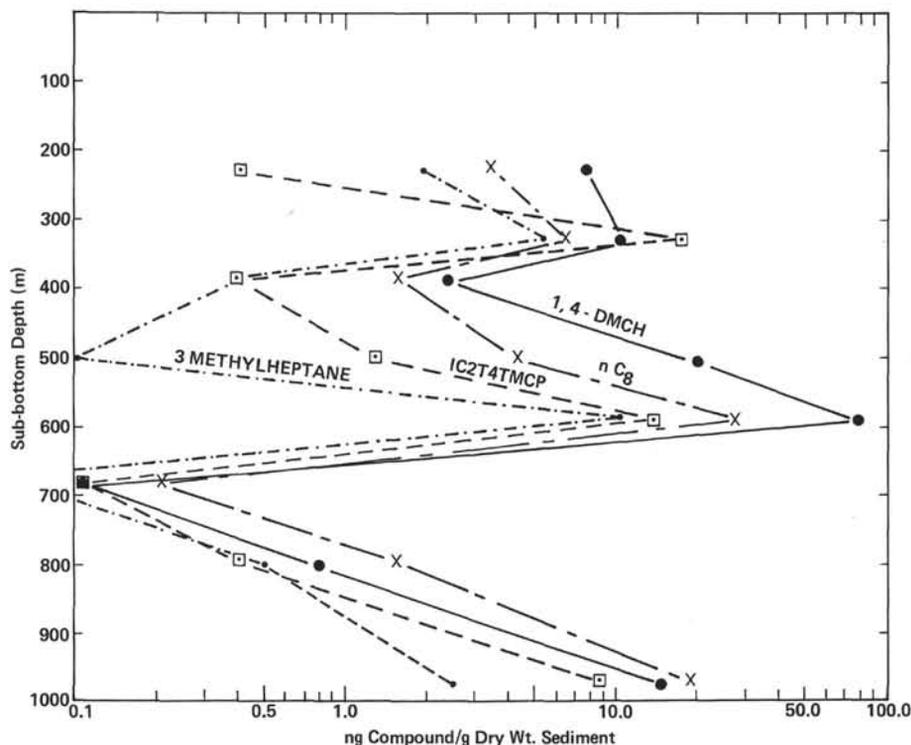


Figure 3. Levels of selected compounds at Site 467.

of some of these noncorrelatable molecules are consistent with our previous suggestion that some or all of these molecules may have specific biological and/or low-temperature chemical formation pathways (Whelan et al., in press).

Traces of alkenes also appear in a few samples: cyclohexene in Sections 467-3-3 (19.5 m) and 467-85-4 (800 m); methylpentene in Section 467-41-4 (382 m); and 1,3-dimethylcyclopentene in Section 467-85-4 (800 m). As mentioned previously, we currently believe these functionalized molecules are relics of past biological activity in the sediment (e.g., see Whelan and Hunt, 1980a, and Whelan et al., in press). However, we also conclude that most of the more abundant saturated hydrocarbons found in the deeper cores at this site were generated thermally.

GC-MS mass chromatograms (not shown here) also revealed the presence of small amounts (about 0.1-1 ng/g) of several sulfur-containing compounds including carbon disulfide, thiophene, 2-methylthiophene, and 3-methylthiophene in Section 467-54-2 (503 m). In addition, another sulfur-containing compound, which has not been previously detected in our work, eluted in the C₈ region. This compound was tentatively identified by comparison to standard reference spectra (Cornu and Massot, 1975) as 2-methylthiacyclohexane (via strong peaks at *m/e* [mass to charge ratio] of 101 and 116). We have not previously detected this compound in sediments, but cyclic sulfur compounds that have been isolated from marine algae (Moore, 1978) may be the source of this compound. We have identified all of the other sulfur compounds listed above both in surface

gravity cores (Whelan et al., in press) and in DSDP cores (see Whelan and Hunt, 1980a). We have postulated that these compounds are relics of the community of anoxic sulfate-reducing microorganisms that existed at the sediment/water interface at the time of burial (Whelan et al., in press).

Site 468

Site 468 sediments contain about 1000 times less C₁-C₈ hydrocarbon levels than Site 467 sediments (see Table 1 and Fig. 4). Levels of C₁-C₃ are all low, with C₂ levels approximately equal to those of C₃, a situation that may reflect an oxic sediment/water interface at the time of deposition with little subsequent hydrocarbon generation (Whelan et al., in press). The levels of many of the C₆-C₈ alkanes are higher at the surface than in deeper samples, a result similar to that for surface gravity cores taken from the Persian Gulf and Arabian Sea (Hunt and Whelan, 1979). This may be partly because the quantity and type of organic matter present in the diatomaceous ooze (at a sub-bottom depth of 7.8-68 m) changes in the more clastic sediments (sub-bottom depth of 257-407 m) (see Table 1). This phenomenon may also be related to variations in microbial degradation at the time that each sample was near the surface. Variations in source material plus biological and/or low-temperature chemical reactions that determine hydrocarbon composition may account for the specific occurrences in the surface of a few compounds (such as toluene, ethylbenzene, and 1T2-dimethylcyclohexane).

Figure 4 also shows depth profiles of several compounds that appear to correlate with each other:

Table 2. Correlation coefficients C₁-C₈ hydrocarbons with nearest neighbors from Table 1.

Compound	Site					
	467	468	469	471 ^b		
				Top 3 Samples	Bottom 4 Samples	
Methane	+0.80	+0.70	+0.84	+0.46	+0.76	+0.31
Ethane	+0.84	+0.93	nd	+0.66	+0.90	+0.86 ^a
Propane	+0.98	nd	nd	nd	nd	+0.99
i-Butane	+0.95	nd	nd	nd	nd	+0.99
n-Butane	+0.75	nd	nd	nd	nd	-0.81
Neopentane	+0.38	nd	nd	nd	nd	-0.87
i-Pentane	+0.76	nd	nd	nd	nd	+0.99
n-Pentane	+0.84	nd	nd	nd	nd	+1.00
Cyclopentane	+0.30	nd	nd	nd	nd	-0.75
2,2-Dimethylbutane	+0.91	nd	nd	-0.41	nd	-0.49
2,3-Dimethylbutane	+0.96	+0.59	+0.26	+0.46	nd	+0.25
2-Methylpentane	+0.97	+0.97	-0.07	+0.98	nd	+0.98
3-Methylpentane	+0.95	+0.90	-0.21	+0.92	nd	+0.98
n-Hexane	+0.84	-0.11	-0.55	+0.99	nd	+0.99
Methylcyclopentane	+0.77	nd	nd	nd	nd	nd
2,2-Dimethylpentane	-0.10	nd	nd	nd	nd	nd
Benz-2,4-Dimethylpentane	-0.15	nd	nd	nd	nd	-0.01
2,2,3-Trimethylbutane	+0.82	nd	nd	nd	nd	+0.92
Cyclohexane	+0.71	nd	nd	nd	nd	-0.69
3,3-Dimethylpentane	-0.12	nd	nd	nd	nd	-0.25
1,1-Dimethylcyclopentane	-0.04	nd	nd	nd	nd	+0.99
2-Methylhexane	+0.93	+0.63	-0.26	nd	nd	nd
2,3-Dimethylpentane	+0.89	+0.83	nd	nd	nd	+0.67 ^a
3-Methylhexane	+0.99	+0.38	nd	nd	nd	+0.97
1T3-Dimethylcyclopentane	+0.98	+0.01	nd	nd	nd	+0.99
1T2-Dimethylcyclopentane	0.95	+0.77	nd	nd	nd	nd
3-Ethylpentane	+0.77	+0.91	+0.98	nd	nd	+0.98
n-Heptane	+0.80	nd	nd	nd	nd	+0.90
1C2-Dimethylcyclopentane	+0.95	+0.65	+0.88	nd	nd	+0.98
Methylcyclohexane	+0.98	nd	nd	nd	nd	+0.99
Ethylcyclopentane	+0.83	nd	nd	nd	nd	+0.04
2,4-Dimethylhexane	+0.74	nd	nd	nd	nd	+0.99
2,5-Dimethylhexane	+0.57	nd	nd	nd	nd	+0.19
Toluene	+0.24	nd	nd	nd	nd	nd
1,1,3-Trimethylpentane	+0.98	nd	nd	nd	nd	+0.24
2,3,4-Trimethylpentane	+0.57	nd	nd	nd	nd	+0.76
1,1,2-Trimethylpentane	+0.93	nd	nd	nd	nd	+0.76
1C2T4-Trimethylcyclopentane	+0.57	nd	nd	nd	nd	+0.64
1C2T3-Trimethylcyclopentane	+0.72	nd	nd	nd	nd	nd
3-Methylheptane	+0.10	nd	nd	nd	nd	+0.98
1,1-Dimethylcyclohexane	+0.39	nd	nd	nd	nd	nd
1T4-Dimethylcyclohexane	+0.27	nd	nd	nd	nd	nd
1T2-Dimethylcyclohexane	-0.05	nd	nd	nd	nd	+0.90
1C4-Dimethylcyclohexane	+0.44	nd	nd	nd	nd	nd
n-Octane	+0.76	nd	nd	nd	nd	nd
1C2-Dimethylcyclohexane	0.06	nd	nd	nd	nd	nd
Ethylbenzene						
Totals						
Organic Carbon	+0.41	+0.89	+1.00	+0.45	+0.92	+0.49
C ₁	+0.77	+0.57	+0.72	-0.12	+0.99	+0.36
C ₂ + C ₃	+0.82	+0.35	+0.38	+0.92	+0.99	+0.90
ΣC ₄ -C ₇	+0.82	+0.93	+0.17	+0.92	+0.19	+0.88
ΣC ₈						

Note: Compounds that show predominantly zero levels for one of the compounds are indicated by "nd" (not determined). Double headed arrows indicate other pairs of compounds for which correlation coefficients were calculated.

^a Determined for bottom three samples only.

^b Correlation was attempted in three ways: (1) all 6 samples, (2) the top 3 samples (471-3-2, 471-13-7, and 471-44-1), and (3) the bottom four samples (471-44-1, 471-63-3, 471-69-3, and 471-74-3). The grouping was tried in this way because Sample 471-44-1 showed hydrocarbon concentrations between those of shallower and deeper samples. Thus we did not know, a priori, how to group the samples.

namely, n-hexane, 2-methylhexane, 3-ethylpentane, and, to some extent, n-heptane. The correlation suggests that the compounds have related sources. In contrast, many other compounds do not correlate with each other, as indicated in Table 2. The limited number of compounds present further suggests fairly specific biological and/or low-temperature chemical diagenetic (less than 50°C) formation pathways, in comparison to the catagenic thermal route that is postulated for Sites 467 and 471.

Site 469

Site 469 sediments (Fig. 5) are similar to those at Site 468 in showing low levels of C₁-C₈ hydrocarbons. Levels of C₁-C₃ are lower than for 468, and no C₄-C₅ were detected; n-heptane and methylcyclohexane are present in higher levels than other C₆-C₇ compounds. Site 469 differs from Site 468 in that most of the C₆-C₇ hydrocarbons show an increase rather than a decrease with depth. The presence of only a few specific hydrocarbons and lack of correlation between them (Table 2) is further support for *in situ* biological and/or low-temperature chemical generation processes.

C₈ compounds were also detected sporadically. For example, 1,2-dimethylcyclohexane (only one isomer) appears in Section 469-30-1 at 274 meters along with the gem dimethyl alkanes: 3,3-dimethylpentane and 1,1-dimethylcyclopentane. The core descriptions suggest that this sample has more worm burrows than the rest of the section. Thus all of these compounds may be left as debris from activities of aerobic microorganisms and burrowing organisms that oxidized straight chains more readily than branched chains, as argued previously (Whelan and Hunt, 1980a).

Figure 5 shows three different apparent hydrocarbon correlations: one for organic carbon, C₁, C₂-C₃, 2-methylpentane, n-hexane, n-heptane, and methylcyclohexane; and a second for 3-methylpentane and methylcyclopentane. It is interesting that the isomers 2-methylpentane and 3-methylpentane, though chemically similar, do not show the same change with depth (see Fig. 5 and Table 2). The specificity of the different correla-

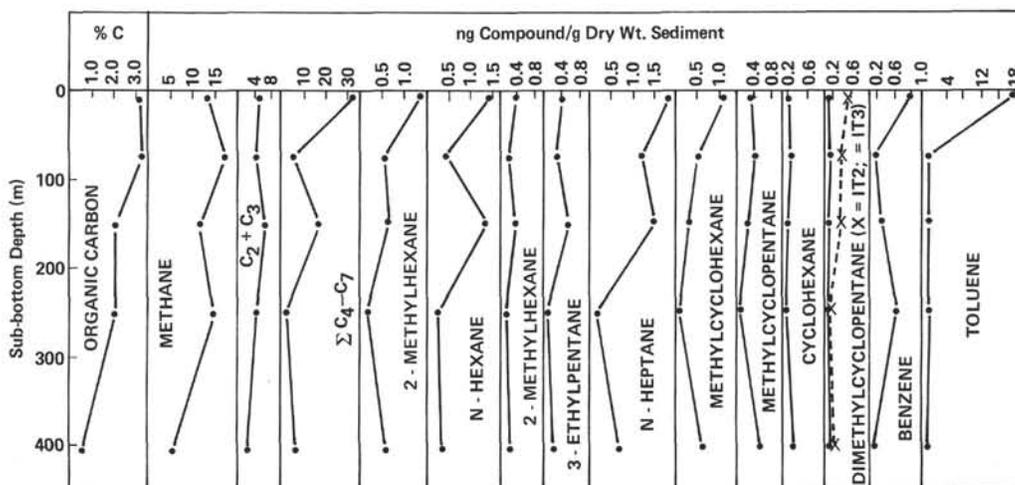


Figure 4. Levels of C₁-C₇ hydrocarbons and organic carbon in Site 468 sediments.

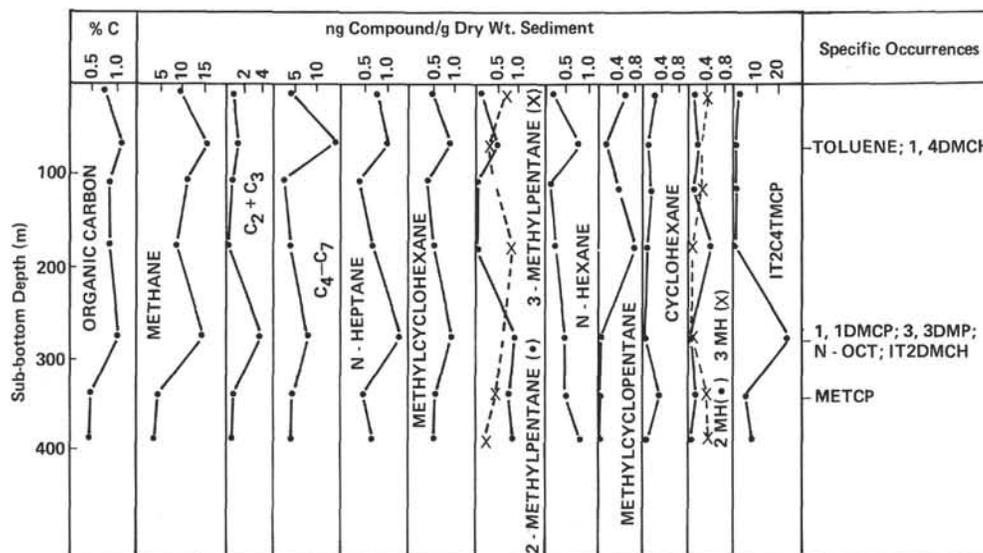


Figure 5. Levels of C₁-C₇ hydrocarbons and organic carbon in Site 469 sediments.

tions might be useful in deciphering past sediment history, if each set could be correlated with specific types of biological precursors and depositional environments. We are presently attempting to do this using surface gravity cores at locations where more is known about recent depositional conditions. Some of these include anaerobic areas such as Walvis Bay (Whelan et al., in press) and the Peru Basin (Whelan and Hunt, unpublished results) as well as aerobic, carbon-rich areas such as the Persian Gulf and the Arabian Sea (Hunt and Whelan, 1979) and carbon-depleted areas such as the Gulf of Maine (Whelan and Hunt, unpublished results).

Site 471

At other DSDP sites, we have found high concentrations of C₄-C₇ hydrocarbons and a large number of different compounds that correlate well with areas of high (>50°C) geothermal gradient (Hunt, 1975). Site 471 shows the highest levels of C₄-C₇ hydrocarbons that we have seen in any sediment examined to date—13,600 and 28,600 ng hydrocarbon per gram dry weight of sediment in Sections 471-63-3 (593 m) and 471-69-3 (650 m), respectively (see Figs. 6 and 7). The only comparable sediment we have examined to date was from offshore Tasmania; it contained 1000 to 6000 ng/g (Hunt, 1975)—values closer to those found at Site 467 than at 471. In the case of the Tasmanian samples, it was postulated that hydrocarbons migrated from deeper sediments heated by an igneous intrusion. A similar explanation is reasonable for the Site 471 samples, because evidence of a high-temperature magmatic intrusion is present in the form of a diabase sill at 823 m.

An alternate source for the high levels of C₁-C₈ hydrocarbons found at this site could be *in situ* thermal generation in a region of high geothermal gradient (7-15.4°C/100 m), rapid deposition rate (20 cm/1000 yr for the 400-700 m section), and moderate organic carbon content (0.6-1.2%). The minimum temperature required for catagenesis or the principal phase of petro-

leum generation is generally believed to be 50°C (see, for example, Hunt, 1979 and references cited therein), a temperature that could occur at 400 meters sub-bottom depth at this site. However, the fact that very high levels of hydrocarbons are present (in comparison to all other DSDP sites we have examined) is more consistent with the occurrence of a more dramatic thermal event—such as volcanism. The sediments throughout the 400-700-meter section are described as silty claystone and might be permeable enough to allow early hydrocarbon migration.

In order to distinguish the two alternatives—*in situ* generation versus migration—total values and compositions of C₁-C₈ n-alkanes can be compared, as shown at the bottom of Table 1. No clear pattern emerges, if it is assumed that diffusion migration should favor the lighter, faster traveling n-alkanes, as observed by Leythaeuser et al. (1979). The bottom four lines of the table do show the significant change in composition that occurs in the bottom three samples. The methane values are undoubtedly low because of loss during collection and storage, as mentioned earlier. However, the trend of a significant decrease in methane in deeper sections is clear. The large increases in C₄-C₈, also distinguish the bottom three samples from the top three.

The cycloalkanes C₆-C₈ predominate over other types of hydrocarbons such as n-alkanes and branched alkanes in the bottom three samples from this site. A few other compounds occur in lower levels throughout the hole and do not appear to correlate with other profiles, as shown in Figure 8 and Table 2. These include the gem-dimethylalkanes, including neopentane; 2,2-dimethylbutane; 2,2,3-trimethylbutane; 3,3-dimethylpentane; 1,1-dimethylcyclopentane; and 1,1-dimethylcyclohexane. The levels of gem-dimethyl compounds are comparable to those observed for the Site 467 samples and are lower than for most of the other C₄-C₈ components at this site, particularly in the bottom three samples.

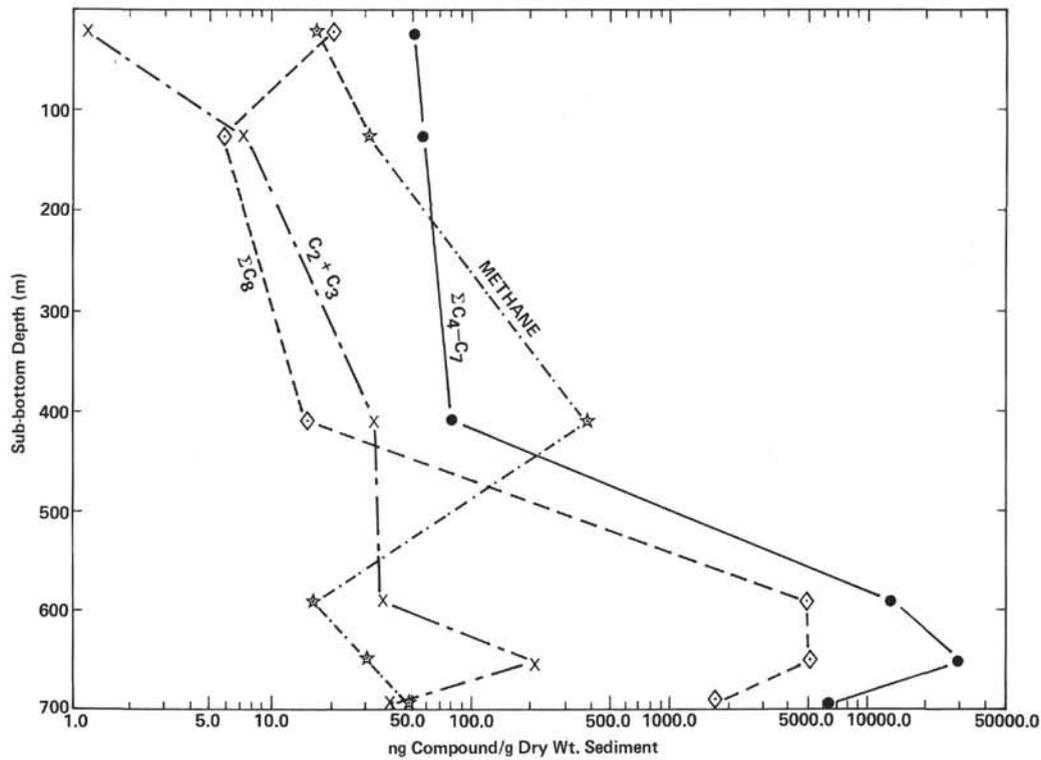


Figure 6. Levels of C_1 , $C_2 + C_3$, ΣC_4-C_7 and ΣC_8 in Site 471 sediments.

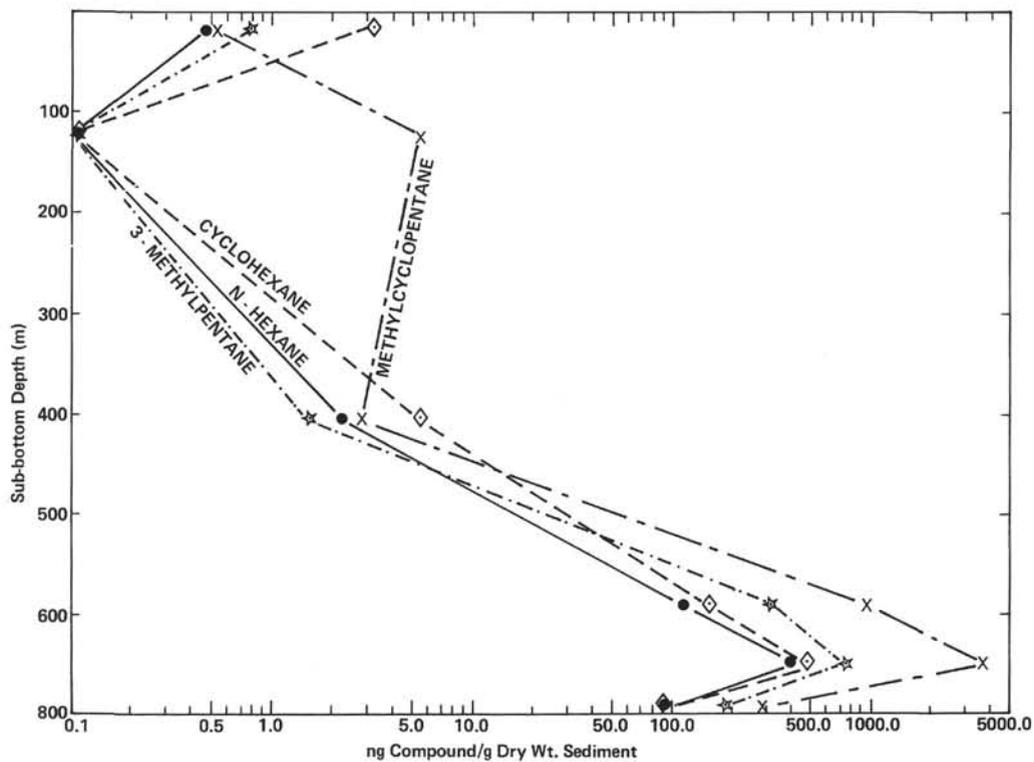


Figure 7. Levels of some representative C_6 and C_7 compounds in Site 471 sediments.

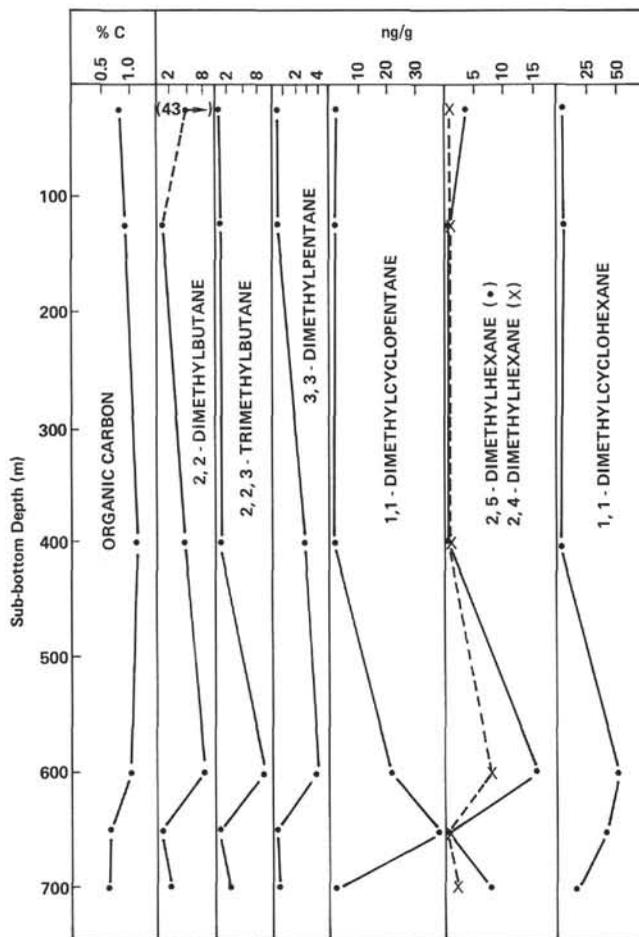


Figure 8. Levels of organic carbon and C₆-C₈ compounds (mostly gem-dimethyl) that do not show a logarithmic increase with depth at Site 471.

The lower levels and high negative correlation of gem-dimethyl compounds, such as neopentane, with other components (as shown in Fig. 8 and in Table 2 for the bottom four samples of Site 471) suggest that sources for gem-dimethyl compounds are different from those of most of the other C₄-C₇ components. The source variability may result from levels of exposure of the sediment to oxygen during initial stages of deposition. For example, it is known that burrowing organisms can expose the top few centimeters of sediment to oxygen and, therefore, to aerobic microbiological attack for significant periods of time (see, for a review, Demaison and Moore, 1979). The result, upon further burial, is the production of more oxidized organic matter in the sediment that does not have as good a petroleum potential as organic-rich sediment not exposed to such burrowing. The gem-dimethyl alkanes may come primarily from the more oxidized sedimentary organic matter, because, as mentioned earlier, aerobic microbial degradation is stopped by branch points in organic hydrocarbons. Thus aerobic microorganisms cannot completely degrade branched hydrocarbons.

Conclusions

1. Lack of significant levels of functionalized organic molecules suggests that most of the molecules detected in this study were generated by low-temperature reactions or during catagenesis rather than biologically.

2. The high levels and large variety of C₄-C₈ hydrocarbons found at Sites 467 and 471 are consistent with the possibility that organic-rich sediments were subjected to temperatures above 50°, typical of catagenic hydrocarbon generation.

3. Samples from the lower part of Hole 471 show the highest levels of C₄-C₈ hydrocarbons that we have ever observed in a DSDP core. These high levels at relatively shallow depths suggest hydrocarbon generation by a fairly spectacular thermal event such as heating of sediments by a magmatic intrusion; this type of intrusion is also found deeper in this hole.

4. The inverse correlation of gem-dimethyl compounds with most other C₄-C₇ components suggests that the gem-dimethyl compounds may have been produced primarily from more oxidized organic matter in the top few centimeters of burrowed sediments.

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