25. C_2 TO C_7 HYDROCARBONS FROM IPOD HOLE 398D[1]

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ABSTRACT

Levels of organic carbon and C_1 to C_7 hydrocarbons in Hole 398D were generally low, and the levels of specific compounds were erratic. The number of detectable different hydrocarbon isomers and the total amount of C_2 to C_7 were larger in deeper clay-claystone Cretaceous sediments below 1050 meters than in younger marly nannofossil ooze-siliceous nannofossil ooze sediments above 800 meters, possibly due to the larger organic matter content of the former.

INTRODUCTION

Two sites were drilled on Leg 47: Site 397 between the Canary Islands and former Spanish Sahara, and Site 398 near the Vigo Seamount off the coast of Spain. On the basis of shipboard core gas analysis, the two sites were completely different. Cores from Holes 397 and 397A showed gas pockets containing mostly methane from 200 meters to the bottom of the hole. In contrast, cores from Hole 398D showed virtually no gas in pockets except traces of methane at about 1200 meters. The reasons for these differences were not apparent onboard ship, since the nannofossil ooze section above 500 meters seemed to be quite similar at both sites. Organic carbon and light hydrocarbon (C_1 to C_7) analyses were carried out on frozen samples to determine whether these parameters showed corresponding differences between the two sites, in addition to the observations made concerning gas pockets.

EXPERIMENTAL

Methods were the same as described for Hole 397/397A (Whelan, Volume 47, Part 1). The Hole 398D frozen sediment samples also were stored for several weeks at 4°C during transit; thus, the total hydrocarbon levels reported here may be low.

RESULTS AND DISCUSSION

The distribtuion of individual C_1 to C_7 hydrocarbons and organic carbon was determined for 28 samples including 7 from the top marly-siliceous nannofossil ooze section (323 to 838 m), and 9 from the deeper clay-claystone sediments (1122 to 1330 m). Representative analytical data are summarized in Table 1. In general, levels of organic carbon in the top nannofossil ooze section are low (0.1% or less) compared to values of 1 to 2 per cent for the similar 0 to 500 meter section of Holes 397 and 397A. The levels of $C_4 + C_5$ and $C_6 + C_7$ per gram dry weight of sediment are also generally lower in Hole 398D than in Holes 397 and 397A. The limited distribution of C_6 and C_7 isomers is the one striking similarity between the upper sections of the two sites. In contrast with earlier studies (Hunt, 1975), only a few compounds make up most of the total C_6-C_7 yield, with toluene being a sporadic major contributor. Such a limited distribution may result from low-temperature (less than 50°) *in-situ* generation of these compounds from an organic matrix that contains relatively unaltered biogenic remains or from the diagenesis of an organic lean sediment. It was argued for Site 397 that terpenes are known to be associated with sulfate-reducing bacteria as well as with diatomaceous material, and that toluene and benzene can arise when these substances undergo decomposition. A similar process may occur here with the remains of these bacteria contributing part of the compounds observed. Sites 397 and 398 both showed traces of pyrite and other iron sulfides throughout. These are probably derived from sulfide produced by sulfate-reducing bacteria. Section 398D-62-4 is a good example of the possible relationship between bacterial suflate reduction and light hydrocarbon distribution. Described as a calcareous mudstone containing pyrite, it contains a much higher level of toluene than the sediments above (9.4 ng/g sediment in contrast to 0.3 to 0.7 ng/g in shallower sections). In addition, the toluene accounts for about 75 per cent of the total C_6-C_7 hydrocarbon content of this particular sample. In shallower sections, even though total C_6-C_7 levels are lower, toluene often contributes 30 to 109 per cent of the total C_6 and C_7 compounds observed.

In deeper sections, the organic carbon content is again lower than at Site 397, generally, 1 per cent or less in Hole 398D as opposed to 1 to 3 per cent in deeper Miocene sections of Holes 397 and 397A. Correspondingly, the maximum C_6+C_7 yields of Hole 398D (14 and 37 ng/g dry sediment) are lower than those observed in Holes 397 and 397A (73 ng/g dry weight). However, the deeper clay-claystone sediments of Hole 398D show the wide distribution of C_6 and C_7 compounds similar to that observed in deeper sections of Holes 397 and 397A and in other DSDP sediments (Hunt, 1975). The total yields of C_4 to C_7 hydrocar-

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TABLE 1
C_1 to C_7 Sediment Hydrocarbons in Hole 398D (ng/g dry weight sediment)

Core-Section	3-3	8-2	15-4	37-3	48-3	62-4	69-2	75-2
Lithology	Marly Nannofossil Chalk-Traces Pyrite	Marly Nannofossil Chalk-Siliceous Nannofossil ooze	Nannofossil Chalk Siliceous Nannofossil ooze	Nannofossil Chalk/ Mudstone	Claystone Mudstone (burrowed)	Calcareous Mudstone; Traces Pyrite (burrowed)	Marly Chalk Mudstone	Clay-Claystone
Depth (m)	322.7	454.2	552.2	759.5	864.3	1008.1	1071.6	1138.1
Age	Miocene	Miocene	Oligocene	Paleogene	Late Cretaceous	Late Albian	Late Albian	Middle Albian
Hydrocarbon								
Ethane	1.3	0.39	0.29	0.27	0.75	1.49	1.48	5.87
Propane	0.65	0.005	0.15	0.06	0.73	2.72	1.16	4.74
i-Butane	0	0	0	0.01	0	0.11	0	1.22
n-Butane	2.9	0	0	0.08	5.60	0.97	0	2.06
Neopentane	0	0	0	0	0	0.12	0	1.24
i-Pentane	0	0	0	0	0.03	0.67	0	3.92
n-Pentane	1.1	0	0.44	0	0.44	1.08	0	0.46
Cyclopentane	0	0	0	0	0	0	0	0
2-2-Dimethylbutane	0.19	0.12	0.16	0	0	0	1.0	0.49
2,3-Dimethylbutane	0.02	0.04	0.02	0	0.08	0	0	0.17
2-Methylpentane	0.03	0.03	0.02	0	0.05	0.30	1.32	0.42
3-Methylpentane	0.05	0.07	0	0	0.02	0.14	0.10	0.10
n-Hexane	0	0.06	0	0	0.09	0.53	0.14	0.16
Methylcyclopentane	0	0.08	0	0	0	0.06	0.02	0.28
2,2-Dimethylpentane	0.23	0.10	0	0	0.013	0.12	0.14	0
Benzene	0	0.12	0	0	0	0.25	0.26	0.11
2,4-Dimethylpentane	0	0	0	0	0	0	0	0
2,2,3-Trimethylbutane	0	0.24	0	0	0	0.03	0.02	0.03
Cyclohexane	0	0.05	0	0	0	0.06	0.10	0.22
3,3-Dimethylpentane	0	1.10	0	0	0	0.02	0.02	0.01
1,1-Dimethylcyclopentane	0	0.04	0.79	0	0	0	0.05	0.01
2-Methylhexane	0	0.01	0	0	0.006	0.18	0.07	0.04
2,3-Dimethylpentane	0	0.05	0	0	0.025	0.37	0.19	0.17
3-Methylhexane	0	0.05	0	0	0	0.19	0.11	0.08
1-*t*-3-Dimethylcyclopentane	0	0.02	0	0	0	0.03	0.03	0.04
1-*t*-2-Dimethylcyclopentane	0	0	0	0	0	0.06	0.04	0.07
3-Ethylpentane	0	0.02	0	0	0.02	0.08	0.03	0.02
n-Heptane	0.05	0.07	0	0	0.26	0.36	0.05	0.05
1-*c*-2-Dimethylcyclopentane	0	0	0	0	0	0	0.05	0.02
Methylcyclohexane	0	0	0	0	0	0.21	0.24	0.32
Ethylcyclopentane	0	0	0	0	0	0	0	0
Toluene	1.65	0.34	0.30	0.18	0.69	9.44	3.14	3.12
$C_2 + C_3$	1.95	0.39	0.44	0.33	1.48	4.2	2.64	10.6
$C_4 + C_5$	4.0	0	0.44	0.09	6.07	3.0	0	8.9
$C_6 + C_7$	2.2	2.61	1.29	0.18	1.25	12.4	7.07	5.9
Organic Carbon (C_o)	0.19	0.10	0.09	0.11	0.06	0.75	0.68	2.83
$[ng(C_4+C_5)/ng\ C_o] \times 10^7$	21.0	0	4.9	3.0	101.2	3.9	0	3.1
$[ng(C_6+C_7)/ng\ C_o] \times 10^7$	11.6	26.1	14.3	1.64	20.8	16.5	10.4	2.0

bons found at this site are generally in the low range (1 to 20 ng/g dry weight [ppb] of sediment) when compared to other DSDP sites containing immature sediments. The values at other sites vary by five orders of magnitude: from 6386 ppb sample from Section 29-280A-21-1 from the site south of Tasmania to 0.46 ppb from Section 26-250A-10-6 from the Indian Ocean (Hunt, 1975).

It was postulated that the gas pocket C_2 to C_5 hydrocarbons found with biogenic methane in Holes 397 and 397A somehow arose from low-temperature chemical alteration of bacterial remains. The question then arises as to why Hole 398D which, in the top 500 meters is very similar to 397, showed no evidence of methane gas pockets. The answer probably lies in the low levels of organic carbon in the upper sections of Hole 398D. This lack of carbon availability may have limited bacterial sulfate reduction as reflected by the possible appearance of the unstable forms of iron sulfide-greigite and mackinawite (as reported in the shipboard report), rather than the more stable pyrite which forms when excess sulfur is available (Berner, 1974). In sediment anaerobic bacterial processes, sulfate reduction to sulfide generally occurs until sulfate is used up, assuming adequate organic carbon for microbial metabolism. When sulfate is gone, bacterial methane production from CO_2 begins with concurrent breakdown of more reduced forms of organic carbon. Thus, the evidence for incomplete sulfate reduction would seem to preclude the formation of the methane-producing bacterial community.

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TABLE 1 – *Continued*

Core-Section	84-4	90-5	97-3	99-4	103-4	112-3	130-5
Lithology	Claystone/ Marly Chalk	Claystone/ Dolomite Laminae	Claystone/ Dolomite + Limestone Layers	Claystone; 2-4% Pyrite; 1% Dolomite	Clay/Claystone 3% Pyrite	Sand/Mudstone Claystone	Marly Nannofossil Chalk Claystone
Depth (m)	1235	1294	1347.2	1368	1406	1489	1665
Age	Middle Albian	Middle Albian	Early Albian	Early Albian	Early Albian	Early Cretaceous (Aptian)	Early Cretaceous (Barremian)
Hydrocarbon							
Ethane	0.29	0.36	4.16	1.21	0.85	1.01	31.6
Propane	2.22	0.15	3.31	0.67	0.48	0.42	26.9
i-Butane	0.37	0.39	1.45	0	0.93	0	5.7
n-Butane	1.06	0.15	1.66	0.12	0.55	0.92	7.4
Neopentane	0	0	0	0	0	0	1.9
i-Pentane	0	0	6.13	0	0.90	0	0
n-Pentane	0	0	1.79	0	1.87	0.21	6.9
Cyclopentane	0	0	1.18	0	0	0	3.4
2,2-Dimethylbutane	0.47	0.18	0.42	1.50	0.30	0.43	0.27
2,3-Dimethylbutane	0.07	0.14	0.17	0.06	0	0.03	0.16
2-Methylpentane	0	1.22	0.63	0.15	0.08	0.12	0.44
3-Methylpentane	0.08	0.09	0.21	0.21	0.02	0.04	0.16
n-Hexane	0.06	0.09	0.28	0.25	0.05	0.13	0.22
Methylcyclopentane	0.01	0.20	0.62	0.11	0.02	0.02	0.35
2,2-Dimethylpentane	0.16	0	0	0	0	0	0.32
Benzene	0.14	0.14	0.38	0.17	0.06	0.06	0.38
2,4-Dimethylpentane	0	0	0	0	0	0	0
2,2,3-Trimethylbutane	0	0.03	0.04	0	0	0.006	0.32
Cyclohexane	0.03	0.12	0.53	0.05	0.03	0.06	0.24
3,3-Dimethylpentane	0	0	0.01	0	0	0.008	0.13
1,1-Dimethylcyclopentane	0	0.006	0.02	0	0	0	0.05
2-Methylhexane	0.01	0.07	0.06	0.11	0.02	0.03	0.20
2,3-Dimethylpentane	0.16	0.19	0.42	0.40	0.05	0.06	0
3-Methylhexane	0.03	0.19	0.23	0.06	0.01	0.02	0.04
1-*t*-3-Dimethylcyclopentane	0.04	0.08	0.24	0.05	0	0	0.25
1-*t*-2-Dimethylcyclopentane	0.13	0.14	0.30	0.04	0	0.14	0.03
3-Ethylpentane	0.006	0.009	0.05	0.04	0	0.02	0.01
n-Heptane	0.02	0.04	0.10	0.14	0.65	0.10	0.07
1-c-2-Dimethylcyclopentane	0	0.03	0.07	0	0	0	0.05
Methylcyclohexane	0.05	0.27	0.76	0.18	0.04	0.06	0.29
Ethylcyclopentane	0	0	0.08	0	0	0	0.03
Toluene	5.29	2.42	2.28	28.2	0.75	1.24	6.68
$C_2 + C_3$	2.51	0.51	7.47	1.88	1.33	1.43	58.5
$C_4 + C_5$	1.43	0.54	12.2	0.12	4.25	1.13	25.3
$C_6 + C_7$	6.76	5.66	7.90	31.7	2.08	2.57	10.7
Organic Carbon (C_o)	0.61	1.44	1.25	0.85	0.99	0.30	3.55
$[ng(C_4+C_5)/ng\ C_o] \times 10^7$	2.3	0.38	9.76	0.14	4.29	3.77	7.13
$[ng(C_6+C_7)/ng\ C_o] \times 10^7$	11.1	3.93	6.32	37.3	2.10	8.58	3.01