

## 45. SEDIMENT C<sub>1</sub>-C<sub>7</sub> HYDROCARBONS FROM IPOD LEG 48—BAY OF BISCAY<sup>1</sup>

Jean K. Whelan and John M. Hunt, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

### ABSTRACT

Six core samples from about equal depths but different geologic ages (300-400 m) were examined for C<sub>1</sub>-C<sub>7</sub> hydrocarbons. Two of the three Cretaceous samples from Hole 402A showed high organic carbon content (2.3-2.4%) but low yields of C<sub>4</sub>-C<sub>7</sub>/Co. The deepest sample from this site showed lower organic carbon but higher C<sub>4</sub>-C<sub>7</sub>/Co. Three younger samples (Eocene) from Sites 403 and 404 showed low amounts of organic carbon (0.1 to 0.2%) but generally higher yields of C<sub>4</sub>-C<sub>7</sub>/Co.

### INTRODUCTION

Leg 48 provided some old (Cretaceous-Aptian) samples from Site 402 which were buried to about the same depth as some younger (Eocene) samples from Sites 403 and 404. Shipboard pyrolysis studies, lithology, and the measured downhole temperatures (less than 30°C) all suggested a low temperature history for both sites. In spite of the small number of samples obtained, the effect of time on two contrasting sample suites could be demonstrated from the sediment organic matter diagenesis.

### RESULTS AND DISCUSSION

Levels of C<sub>1</sub>-C<sub>7</sub> sediment hydrocarbons for Leg 48 are shown in Table 1. Three Cretaceous samples from Site 402 were examined—402A-15-1, 402A-24-1, and 402A-33-1—from depths of 270 to 441 meters (see Whelan, in press, for experimental details). Shipboard analysis of sediments from this site (Montadert and Roberts et al., this volume) indicates that the sediments are calcareous mudstones or marly limestones: which were probably deposited in shallow water and never deeply buried: because the maximum possible geothermal gradient indicates a current maximum possible bottom hole temperature of 30°C, these sediments probably had been exposed to a low temperature history. This idea is supported by shipboard pyrolysis data (Harrison, this volume) which indicated the sediments had been exposed to a very low temperature history and that bits of highly carbonized material found in these cores was probably detrital.

Our data are consistent with this picture (Table 1). All three of the samples have a moderate organic carbon content (1-2.4%) and yet generally show low yields of C<sub>4</sub>+C<sub>5</sub>/Co (where Co is organic carbon). The amounts of C<sub>4</sub>-C<sub>7</sub> increase with depth, both in absolute amount and with respect to Co. This is a trend found at other DSDP sites (Hunt, 1975) and is consistent with *in-situ* generation of these compounds which increases with temperature (depth). However, the hydro-

carbon distribution is more typical of much younger sediments we have examined from similar depths at other DSDP/IPOD sites, for example, the shallower samples at Sites 397 and 348 (Whelan, in press; Whelan and Hunt, 1978, in press). Here, the three samples show a fairly limited spectrum of hydrocarbons in spite of moderate to high organic carbon content. Thus, only four compounds including the gem-dimethyl-alkanes (2,2-dimethylbutane; 2,2-dimethylpentane; and 3,3-dimethylpentane) and toluene are major contributors to total C<sub>6</sub>-C<sub>7</sub> content in one or more of the samples. It was suggested previously (Whelan, in press; Whelan and Hunt, 1978, in press) that these compounds may be typical degradation products of terpene-derived organic material which is preserved without carbon skeleton alteration in immature sediments.

Sections 403-41-5, 404-17-5, and 404-22-6 are all younger (lower Eocene) and contain less organic carbon (0.1-0.2%) than the 402 samples. Their thermal history also appears to have been mild (current bottom hole temperatures 26° or less). Shipboard pyrolysis showed immature sediments with no indigenous hydrocarbons and low source rock potential. In spite of this, two of the three samples show C<sub>6</sub>+C<sub>7</sub> yields (4.1-4.6 ng/g) comparable to that of the much older sediment from Section 402A-15-1. Even more striking are the generally higher (C<sub>4</sub>+C<sub>5</sub>)/Co and (C<sub>6</sub>+C<sub>7</sub>)/Co yields for these sites than for Site 402. The amounts of gem-dimethylalkanes and toluene are not as large in these sediments. However, 2,2-dimethylbutane and toluene are still proportionately major contributors to the samples.

These results combined with other DSDP/IPOD sediments we have examined (Hunt 1975; Whelan, in press; Whelan and Hunt, 1978) suggest that:

1) *In-situ* generation of C<sub>1</sub>-C<sub>7</sub> hydrocarbons in organic lean sediments can be relatively fast when viewed in terms of the (C<sub>4</sub>-C<sub>7</sub>)/Co ratio. This result may reflect the influence of mineral catalysis in the process since sediments with low organic carbon would have a higher proportion of mineral catalyst surface/total organic carbon.

2) Temperature (depth) is more important in C<sub>1</sub>-C<sub>7</sub> sediment hydrocarbon generation than time. A similar conclusion has been reached by others in petroleum maturation studies as summarized by Hunt (1976).

<sup>1</sup>Woods Hole Oceanographic Institution Contribution No. 4183.

TABLE 1  
C<sub>1</sub> - C<sub>7</sub> Sediment Hydrocarbons From Leg 48

Section	402A-15-1	402A-24-1	402A-33-1	403-41-5	404-17-5	404-22-6
Lithology	Calcareous mudstone (bioturbated)	Carbonaceous marly limestone (pyrite filled burrows)	Calcareous mudstone siderite filled burrows	Olive-black mudstone with volcanics	Dark glauconite/mudstone with volcanics	Dark mudstone with pyrite and bioturbation
Depth (m)	270	355.5	441	381.3	298.5	351
Age	Cretaceous Aptian	Cretaceous Aptian	Cretaceous Aptian	Lower Eocene	Lower Eocene	Lower Eocene
Hydrocarbon	ng/g Dry Weight Sediment					
Methane	11.5	8.08	2.03	3.81	1.2	0.13
Ethane	2.30	1.58	1.37	0.38	2.1	0.07
Propane	1.69	1.02	1.21	0.18	2.29	0.05
<i>i</i> -Butane	0.38	0.11	0.89	0	0	0
<i>n</i> -Butane	1.14	1.28	1.84	0.53	0	1.90
neoPentane	0	0	0	0	0	0
<i>i</i> -Pentane	0.50	0	2.99	0	0	0
<i>n</i> -Pentane	0.21	0.45	1.09	0	0	0
Cyclopentane	0	0	0	0	0	0
2, 2-Dimethylbutane	1.22	5.40	3.27	1.28	0.37	1.79
2, 3-Dimethylbutane	0.04	0	0.13	0.03	0	0.02
2-Methylpentane	0.02	0.08	0.48	0.05	0	0.03
3-Methylpentane	0	0.03	0.16	0.05	0	0.04
<i>n</i> -Hexane	0.09	0.02	0.46	0	0	0.07
Methylcyclopentane	0	0.08	0.26	0	0	0.01
2, 2-Dimethylpentane	0	0.17	1.05	0.23	0.04	0.04
Benzene	0	0	0.38	0.06	0	1.0
2, 4-Dimethylpentane	0	0	0	0	0	0
2, 2, 3-Trimethylbutane	0	0.02	0.03	0	0	0
Cyclohexane	0	0	0.15	0	0.15	0.015
3, 3-Dimethylpentane	0	2.75	0.006	0	0	0
1, 1-Dimethylcyclopentane	0	0.02	0.01	0	0	0
2-Methylhexane	0.02	0.004	0.11	0.02	0.06	0
2, 3-Dimethylpentane	0.05	0.02	0.16	0.03	0.05	0.01
3-Methylhexane	0.04	0.009	0.19	0.02	0	0
1- <i>t</i> -3-Dimethylcyclopentane	0	0	0.11	0	0	0
1- <i>t</i> -2-Dimethylcyclopentane	0	0	0.13	0	0	0
3-Ethylpentane	0.02	0	0.03	0.009	0.22	0
<i>n</i> -Heptane	0	0	0.34	0	0.10	0.03
1- <i>c</i> -2-Dimethylcyclopentane	0	0	0.03	0	0	0
Methylcyclohexane	0	0.01	0.41	0.02	0	0.015
Ethylcyclopentane	0	0	0.06	0	0	0
Toluene	4.36	2.81	6.33	2.79	0	1.06
C <sub>2</sub> + C <sub>3</sub>	3.99	2.60	2.58	0.56	4.4	0.12
C <sub>4</sub> + C <sub>5</sub>	2.23	1.84	6.81	0.53	0	1.90
C <sub>6</sub> + C <sub>7</sub>	5.86	11.4	14.3	4.6	0.99	4.13
Organic Carbon (Co) (%)	2.31	2.42	0.98	0.12	0.11	0.19
[ng(C <sub>4</sub> + C <sub>5</sub> )/ng Co] × 10 <sup>7</sup>	0.97	0.76	7.0	4.4	0	10.0
[ng(C <sub>6</sub> + C <sub>7</sub> )/ng Co] × 10 <sup>7</sup>	2.54	4.71	14.6	38.2	9.0	21.7

3) Sediments subjected to a low thermal history tend to have a narrower distribution of C<sub>4</sub>-C<sub>7</sub> compounds than those exposed to higher temperatures. The influence of the type of organic source material (terrigenous versus planktonic, etc.) on this effect must await further investigation.

#### ACKNOWLEDGMENTS

We wish to thank Fred Connors and Jenny Jasinska for analyses and Susan Palmer and Robert Gagosian for reviewing this manuscript. This work was supported by National Science Foundation Grant OCE73-06575.

#### REFERENCES

- Hunt, J. M., 1975. Origin of gasoline range alkanes in the deep sea, *Nature*, v. 254, p. 411-413.
- , 1976. Light hydrocarbons in deep sea sediments, presented at the 89th Annual Meeting of Geol. Soc. Am., Denver, Colorado, November 8-11, 1976.
- Hunt, J.M. and Whelan, J. K., 1978. Light hydrocarbons at Sites 367-370, Leg 41. In Lancelot, Y., Seibold, E., *Initial Reports of the Deep Sea Drilling Project*, v. 41: Washington (U.S. Government Printing Office), p. 859-860.

Whelan, J. K., in press. C<sub>1</sub> to C<sub>7</sub> hydrocarbons from IPOD Holes 397/397A. In Ryan, W.B.F., von Rad, U., et al., *Initial Reports of the Deep Sea Drilling Project*, v. 47, Part 1: Washington (U.S. Government Printing Office).

Whelan, J.K. and Hunt, J.M., 1978. C<sub>1</sub> to C<sub>7</sub> hydrocarbons in Holes 379A, 380/380A and 381. In Ross, D., Neprochnov, Y.,

et al., *Initial Reports of the Deep Sea Drilling Project*, v. 42, Part 2: Washington (U. S. Government Printing Office).

\_\_\_\_\_, in press. C<sub>2</sub>-C<sub>7</sub> hydrocarbons from IPOD Hole 398D. In Ryan, W.B.F., von Rad, U., et al., *Initial Reports of the Deep Sea Drilling Project*, v. 47, Part 2: Washington (U.S. Government Printing Office).