

## II. HYDROCARBON STUDIES

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### ABSTRACT

Eighteen core samples from Holes 259, 263, 265, 280A, 281, and 282 were analyzed for organic carbon and detailed C<sub>4</sub> to C<sub>7</sub> hydrocarbons. A total of 27 alkanes were identified in this range, the total yields ranging from 12 to 3585 parts per billion. In addition, the C<sub>15</sub>+ hydrocarbons and nonhydrocarbons were determined for nine of these samples. Total C<sub>15</sub>+ hydrocarbon yields ranged from 18 to 205 parts per million. The naphthene content of the saturate fraction in all samples ranged between 80% and 90%. The organic matter in the samples is largely amorphous-sapropellic with traces of woody material. All evidence to date indicates that the C<sub>4</sub> to C<sub>7</sub> hydrocarbons are forming in situ from the decomposition of the organic matter.

### RESULTS AND DISCUSSION

The cores in this study were obtained from holes drilled west and south of Australia during DSDP Legs 27 and 29. Nine cores were analyzed in detail for both light and heavy hydrocarbons. An additional nine were analyzed only for C<sub>4</sub> to C<sub>7</sub> hydrocarbons. The methods of analysis were previously reported in the Initial Reports Volume, Leg 22. Analytical data on cores from holes south and west of Tasmania are shown in Table 1. These samples ranged in depth from 28 to 511 meters, and range in age from upper Miocene to lower Eocene.

Saturate and aromatic hydrocarbon yields in the C<sub>15</sub>+ range varied from 18 to 205 ppm. The yield of nitrogen, sulphur, oxygen compounds plus asphaltenes ranged from 153 to 801 ppm. This large excess of non-hydrocarbons to hydrocarbons is typical of organic

matter which has undergone very little alteration. Despite the age of these samples, they were not buried to sufficient depths to cause appreciable thermal-catalytic cracking of the organic matter to form hydrocarbons. The hydrocarbon mix appears to be largely the compounds deposited with the sediments with minor diagenetic changes. The ratio of hydrocarbons to non-hydrocarbons is definitely not indicative of a seep. If this were true, there would be a much higher C<sub>15</sub>+ hydrocarbon content.

Small aliquots of all the samples listed in Table 1 were treated with acids to dissolve the mineral matter, and the organic material was examined microscopically. Most of the organic matter was of the amorphous-sapropellic type indicating marine plankton as a dominant source. However, several samples had a high spore pollen content indicating some contribution of terrestrial organic

TABLE 1  
Analytical Data on Leg 29 Cores

Sediment Data	S. of Tasmania (48°57.44'S, 147°14.08'E)						W. of Tasmania (42°14.76'S, 143°29.18'E)		
	280A-6-2	280A-10-4	280A-19-0	280A-21-1	281-12-0	281-14-0	281-16-0	282-4-0	282-17, CC core catcher
Core No.	280A-6-2	280A-10-4	280A-19-0	280A-21-1	281-12-0	281-14-0	281-16-0	282-4-0	282-17, CC core catcher
Core Interval (cm)	125-150	130-150	0-50	130-150	35-50	0-50	25-40	33-55	
Depth (m)	109	203	443	511	102	121	140	28	265
Age	Upper Oligocene	Lower Eocene	M. to L. Eocene	M. to L. Eocene	Upper Miocene	Lower Eocene	Lower Eocene	Upper Miocene	Lower Eocene
Organic Carbon (wt. %)	0.36	0.12	0.83	0.61	0.10	0.36	0.57	0.21	3.51
<b>Extractable Bitumen in PPM</b>									
C <sub>15</sub> + Saturates	20	16	15	10	22	18	169	27	22
C <sub>15</sub> + Aromatics	2	2	33	24	1	5	36	2	26
N, S, O Compounds	48	26	61	67	22	36	102	30	308
Asphaltenes	389	127	301	251	237	239	288	127	493
Total	459	171	410	352	282	298	595	186	849
<b>Saturate Hydrocarbon Analysis</b>									
Paraffins	14	18	10	10	9	17	9	9	17
Isoprenoid	2	1	2	2	1	2	1	1	1
Naphthenes	84	81	88	88	90	81	90	90	82
CPI (C <sub>24</sub> -C <sub>32</sub> )	1.7	1.9	1.4	1.3	1.4	1.8	1.5	1.6	0.8
Pristane/Phytane ratio	0.9	0.7	1.7	1.6	0.8	0.8	0.8	0.8	1.0

TABLE 2  
C<sub>4</sub>-C<sub>7</sub> Alkane Yields From Legs 27, 28, 29, PPB (by wt.)

	Sample (Interval in cm)																		
	27-259-9-5, 130-150	27-263-6-5, 130-150	28-265-2-3, 120-140	29-280A-6-2, 125-150	29-280A-10-4, 130-150	29-280A-17-6, 100-110	29-280A-19-0, 0-50	29-280A-21-1, 130-150	29-280A-23-3, 114-121	29-281-12-0, 35-50	29-281-14-0, 0-50	29-281-15-2, 125-135	29-281-16-0, 25-40	29-282-4-0, 33-55	29-282-11-1, 120-130	29-282-16-1, 70-80	29-282-17, CC	29-282-18-1, 90-100	
Isobutane	0.06	0.21	0	0.34	0.09	22	28.6	138	4.3	0.37	0.40	7.4	1.09	0.29	9.3	11.6	9.3	8.7	
<i>n</i> -Butane	0.26	0.55	0.19	1.63	0.05	65	63.0	219	5.6	1.57	1.22	18.0	1.99	1.49	20.5	21.0	4.3	25.6	
Isopentane	0.38	0.09	0.28	0.54	9.60	144	151	401	3.3	1.35	2.00	12.6	1.27	0.68	16.7	18.5	73.6	32.5	
<i>n</i> -Pentane	5.95	1.30	15.0	4.64	0.05	132	98.9	297	34.8	2.89	4.13	64.9	5.13	4.41	58.9	40.5	21.3	93.6	
2,2-Dimethylbutane	0.48	0.25	0	0.65	0.06	53	41.2	110	9.5	0.35	0.19	6.4	0.65	0.60	2.8	3.5	10.8	12.4	
Cyclopentane	0.10	0.07	0.24	0.30	0.03	17	11.7	50	38.2	0.30	0.19	220	0.42	0.45	6.2	2.6	1.8	185	
2,3-Dimethylbutane	0.10	0.26	0	0.23	0.11	57	38.8	151	0.7	0.36	0.30	0	0.47	0.41	2.5	7.9	11.0	30.0	
2-Methylpentane	0.54	0.37	1.51	0.59	0.11	149	116	430	4.9	1.02	1.13	19.4	1.64	1.19	4.5	10.0	26.9	43.3	
3-Methylpentane	0.38	0.52	1.00	3.17	0.20	55	43.6	230	9.3	1.27	0.72	17.4	1.41	0.98	9.0	11.9	16.8	21.2	
<i>n</i> -Hexane	0.44	0.40	0.90	0.68	0.42	104	62.5	249	4.9	1.06	1.29	17.6	1.37	1.24	3.2	10.7	28.8	36.5	
Methylcyclopentane	0.34	0.55	0.81	0.38	0.16	133	137	733	10.2	2.62	1.66	24.5	2.71	2.36	8.3	12.4	10.9	18.1	
2,2-Dimethylpentane	0.37	0.33	0.23	0	0.02	11	4.8	16	0.9	3.13	1.98	1.5	0	0	1.5	2.4	2.4	28.4	
2,4-Dimethylpentane	0	0	0	0	0	20	11.4	34	0	0	0	0	0	0	0	5.4	10.7	14.1	
2,2,3-Trimethylbutane	0	0	0	0	0	20	0	0	0	0	0	0	0	0	0	0	0	0	
Cyclohexane	0.55	2.20	0.64	0.03	0.18	98	34.7	184	3.1	0.87	0.60	7.2	1.01	1.18	10.1	10.6	10.1	35.3	
3,3-Dimethylpentane	0.44	1.14	0.30	0	0.06	23	3.5	7	1.2	0.13	0.07	1.4	0.18	0.56	3.7	4.0	3.5	9.3	
1,1-Dimethylcyclopentane	0.34	2.59	0.52	0	0.03	83	2.2	12	2.0	0.13	0.07	4.8	0.15	0.42	12.5	10.8	3.0	35.3	
2-Methylhexane	1.03	6.66	1.95	0.65	0.23	873	32.4	197	21.1	1.84	0.99	0	1.19	1.39	15.4	33.2	30.2	618	
2,3-Dimethylpentane	0	0	0	0	0	0	0	0	0	0	0	72.5	1.55	1.22	8.7	13.6	53.3	0	
1,cis-3-Dimethylcyclopentane	0.26	0	0	0	0	102	0	0	1.6	0	0	4.7	0	0	4.3	9.9	0	62.4	
3-Methylhexane	1.0	9.30	2.29	0.86	0.40	87	53.5	557	2.5	2.84	1.65	8.2	2.09	2.01	5.7	10.6	47.7	35.7	
1,trans-3-Dimethylcyclopentane	0.88	8.55	1.23	0	0	103	30.0	1,177	1.7	0	0	5.2	2.62	2.80	4.9	10.7	56.7	63.0	
1,trans-2-Dimethylcyclopentane	0.54	1.88	0.45	0	0	295	95.7	0	5.2	0	1.78	13.9	0	0	24.9	28.4	0	118	
3-Ethylpentane	0	0	0	0	0	34	0	0	0.8	0	0	3.1	0	0	3.0	4.4	0	12.1	
<i>n</i> -Heptane	1.73	3.21	3.84	1.40	0.17	54	55.5	260	5.0	1.95	1.94	13.0	2.61	2.53	3.9	13.4	46.5	58.8	
1,cis-2-Dimethylcyclopentane	0.35	1.97	0.49	0	0	103	37.3	398	2.4	1.74	1.02	5.8	1.50	1.56	9.5	9.1	8.7	34.5	
Methylcyclohexane	3.55	22.6	5.94	1.61	0.42	748	131	536	16.9	4.50	3.13	50.4	4.81	4.63	74.1	89.0	47.2	332	
Total	20.1	65.0	37.8	17.7	12.4	3,585	1,284	6,386	190	30.3	26.5	600	35.9	32.4	324	406	536	1,964	
Organic Carbon (wt. %)	0.06	0.56	0.27	0.36	0.12	1.92	0.83	0.61	0.07	0.10	0.36	0.69	0.57	0.21	0.91	4.1	3.51	4.8	

matter. Sample 280A-10-4 had the highest content of coaly organic matter, and this is reflected in its low hydrocarbon yield.

The high naphthene content of the saturate hydrocarbon fraction is typical of what was reported for Legs 22 and 24. Naphthenes have been predominant in all  $C_{15}+$  saturate hydrocarbon fractions of DSDP cores to date. Since they have not been identified as a major constituent of plankton, they must be a result of either microbial alteration or terrestrial-derived sources. The low value of the correlation preference index (CPI) is more typical of marine organic matter which is around 1, than of terrestrial organic matter which ranges from 5 to 10.

Data on the  $C_4$  to  $C_7$  alkanes and cycloalkanes (naphthenes) for 18 samples from Legs 27-29 are shown in Table 2. Twenty-seven hydrocarbons were identified in this range in some, but not all samples. Yields varied from 12.4 to 6386 ppb. In addition to the paraffins and naphthenes shown in Table 2, benzene, toluene, and some unidentified olefins were found. Quantities of the aromatics are not listed because the analytical procedure is so sensitive that we are having problems in eliminating all traces of benzene in repeated blank runs. Benzene is a universal solvent occurring in so many materials that it is very difficult to completely eliminate it from an environment. Small amounts of olefins would be expected in immature sediments, but their exact identification must await mass spectrometer analysis.

As mentioned in previous DSDP Leg Reports, the hydrocarbons shown in Table 2 are not found in living organisms and have never been identified as microbiological products. Consequently, at present they can only be explained by in situ thermal-catalytic cracking of the organic matter, or by seepage from deeper horizons. In

previous discussions, Samples 280A-17-6, 280A-19-0, and 280A-21-1 had been explained as seeps since their yield of  $C_4$  to  $C_7$  hydrocarbons was much higher than the other samples with comparable organic carbon contents. However, the  $C_{15}+$  hydrocarbon data on these same samples indicate that no seepage has occurred in this higher hydrocarbon range. This means that if these samples are from seepage or diffusion, it must be limited to the light hydrocarbon range. However, one would expect that diffusion from the deeper source would show some gradation up the hole, but this is not evident from either Hole 280A or Hole 281.

The distribution of isomeric hexanes, heptanes, and cyclopentanes in petroleum generally follows a certain order. Thus, petroleum generally contains more *n*-heptane than either of the methylhexanes, which in turn are more predominant than the dimethylpentanes. The composition of the alkane fractions shown in Table 2 only follows this order part of the time. This suggests that we are observing an immature hydrocarbon mix which results from the hydrocarbon compounds that are most readily broken off from the particular organic matrix. It does appear that these hydrocarbons are not resulting from pure thermal cracking since the relative quantities would be predictable from thermodynamic data. Probably a variety of catalytic reactions are going on with some hydrocarbons being more predominant in the product, because their structures existed in the original matrix.

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