# 31. MIGRATION OF C<sub>1</sub> TO C<sub>8</sub> VOLATILE ORGANIC COMPOUNDS IN SEDIMENTS FROM THE DEEP SEA DRILLING PROJECT, LEG 75, HOLE 530A<sup>1</sup>

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#### ABSTRACT

The distribution of  $C_1$  to  $C_8$  hydrocarbons in sediment samples from DSDP Leg 75, Hole 530A, indicates that significant amounts of methane and ethane have migrated from organic-rich to organic-lean shales in close proximity. Most compounds larger than ethane are not migrating out of black shales, where they occur in high concentrations. These results lead to a general model for assessing migration. In addition, three shale types are identified on the basis of organic carbon and pyrolysis products and patterns.

# INTRODUCTION

Sediments of Cretaceous age were recovered from the Southeastern Atlantic, Hole 530A. The generally green and gray shales contained thin layers (generally of millimeter thicknesses) of black shale. The organic matter in these shales was analyzed to determine (1) whether depositional conditions for the black shale layers were similar; (2) whether migration of  $C_1$ - $C_8$  hydrocarbons could be observed between the alternating green and black shales; and (3) whether volatile  $C_1-C_8$  hydrocarbons occurred as found in many other DSDP sediments (see, for example Hunt, 1975; Whelan and Hunt, 1982 and references cited therein). The close sampling of interbedded shales and large differences in organic carbon over short intervals presented the possibility of determining whether migration is occurring between these geothermally immature (<40°C) shales. Previous analyses from this laboratory have suggested that the sorbed light hydrocarbons in Deep Sea Drilling Project (DSDP) sediments correlate well with lithology (see, for example, Hunt and Whelan, 1978; Whelan, 1979); however, in many cases, it has been difficult to define the influence of migrational changes on these compositions.

#### **EXPERIMENTAL METHOD**

Sediment samples collected on DSDP Leg 75, Hole 530A, were analyzed for (1)  $C_1$  to  $C_8$  hydrocarbons by a headspace technique, (2) pyrolyzable hydrocarbons by a thermal distillation-pyrolysis technique, and (3) total carbon (mass percent relative to dry weight of sediment) and organic carbon by a combustion technique.

The headspace technique employed here was described previously (Whelan, 1982) with a minor modification: Sample sizes were 2 to 6 g wet weight of sediment. Some of the methane and ethane is lost during coring so that all levels reported here are *minimum* values and represent primarily gases sorbed on the sediment (see discussion section). The headspace technique involves placing the frozen sediment in a stainless steel vessel equipped with a septum, a screw cap, and two metal ball bearings. Distilled water (100 ml) and a helium gas headspace are sealed into the vessel along with the sediment. The vessel is shaken on a commercial paint shaker (the stainless steel balls break up the sediment during this process) and heated in a 95°C water bath for

30 minutes. The headspace gases are then analyzed by gas chromatography.

The thermal distillation-pyrolysis technique is that of Whelan, Hunt, and Huc (1980), with the following modification to the heating program. The samples were heated from room temperature to  $250^{\circ}$ C at  $140^{\circ}$ C/min. and remained at  $250^{\circ}$ C for 20 minutes to drive off volatile ( $P_1$ ) hydrocarbons. They were then heated at  $40^{\circ}$ C/min. to  $550^{\circ}$ C, pyrolyzing the organic matter and releasing pyrolysis ( $P_2$ ) hydrocarbons. The samples remained at the final temperature for 10 minutes before cooling.

Carbon content was determined by combustion, using a Leco Apparatus. Total carbon was determined on ground, dried samples and organic carbon was determined on ground, dried, and decarbonated (by HCl vapor) samples.

## **RESULTS AND DISCUSSION**

The results of headspace analysis for  $C_1$  to  $C_8$  hydrocarbons are presented in Table 1. Analyses of the solid phases are presented in Table 2. Calculation of production indices (*PI*) from the relationship  $PI = P_1/(P_1 + P_2)$  gives low values (0.0004 to 0.1), indicating that the sediments are immature with respect to petroleum generation (Barker, 1974; Espitalie, et al., 1977; Huc and Hunt, 1980).

Some typical depth profiles of  $C_1$  through  $C_7$  compounds at Hole 530A are shown in Figures 1 through 3. Black shales (typically with  $C_{org}$ , >3%) are indicated by solid horizontal lines and less organic-rich gray shales  $(1.5\% < C_{org} < 3\%)$  are indicated by broken horizontal lines on the scale at the far right. All other samples are green shales (with  $C_{org} < 1.5\%$ ), and they are indicated by dotted horizontal lines. Figures 1 through 3 show that almost all compounds (except methane and ethane) are concentrated mainly in black shales and are relatively depleted in the gray and green shales. It appears that the lightest hydrocarbons (e.g., methane and ethane) are migrating from organic-rich to organic-lean shales, whereas heavier hydrocarbons are remaining in the black shale laminae where they were generated.

On an organic carbon normalized basis, the nonblack shales (that is, the green shales and gray shales, hereafter referred to as "green shales") have disproportionately high concentrations of methane and ethane. In order to demonstrate this fact, we define a parameter called the "enrichment factor" (*EF*), extending ideas original-

<sup>&</sup>lt;sup>1</sup> Hay, W. W., Sibuet, J.-C., et al., *Init. Repts. DSDP*, 75: Washington (U.S. Govt. Printing Office).

Table 1. C1 to C8 hydrocarbons and total amounts of volatile compounds, DSDP Leg 75, Walvis Ridge (headspace analysis).

Sub-bottom depth (m)		62-3, 106-108	87-4, 103-105	87-4, 125-127	88-3, 31-33	93-2, 36-39	93-3, 44-46	93-6, 89-92	94-2, 38-40	96-2, 18-20
Shale type	169 Gray	708 Green	945 Black	945.7 Green	952.3 Black	992 Green	993.5 Green	998 Gray	1001 Black	1019 Black
Agea	e. Plio.	Creta. (Camp.)	Creta. (Coniac.)	Creta. (Coniac.)	Creta. (Coniac.)	Creta. (Coniac.)	Creta. (Coniac.)	Creta. (Coniac.)	Creta. (Coniac.)	Creta. (Turon.)
Compound					(ng compound	/g dry sediment wt	.)			
Methane	140	293	172	293	247	220	154	98	204	111
Ethane	0	15	20	16	25	14	7.4	8	17	32
Propane	0	0	5.5	4.6	47	0	0	0	71	85
<i>i</i> -Butane	0	0	1.4	0	113	0	0	0	168	181
n-Butane	0	0	3	6.6	199	0	0	0	233	139
i-Pentane	0	0	4.1	0	173	0	0	0	220	118
n-Pentane	0	0	9.2	0	356	0	0	0	322	112
2,2 Dimethylbutane	0	0	4.0	0	0			0	0	0
Cyclopentane	0	0	0	0	14	0	0	0	9	0
2,3 Dimethylbutane	0	0	1.7	0	16.8	0	0	1.7	13	15
2-Methylpentane	0	0	20	0	16.6	0	0	18.6	120	86
3-Methylpentane	0.1	0	3.3	0	21	0	0	1.9	16	13
n-Hexane	0	0	24	0	208	0	0	10.4	117	49
Methylcyclopropane + 2,2 Dimethylpentane	0	0	3.7	0	24	0	0	2.4	68	44
2,4 Dimethylpentane	0	0	4	0	7	0	0	0	25	4.7
Benzene	0	0	5	0	100	0	0	0	102	31
2,2,3 Trimethylbutane	0	0	0	0	0	0	0	0	0	0
Cyclohexane	0	0	4.6	0	14	0	0	0	27	5
3,3 Dimethylpentane	0	0	1	0	0	0	Ō	0	0	0
2 Methylhexane + 2,3 Dimethylpentane	0	0	4.5	0	67.6	0	0	2	58	12
3 Methylhexane	0	0	2	0	14	0	0	0.5	7	5.4
1-t-3 Dimethylcyclopentane	0	0	0	0	7	0	0	0	8	0
1-t-2 Dimethylcyclopentane	0	0	0	0	7	0	0	0	14	15
3 Ethylpentane + 2,2,4 Trimethylpentane	0	0	2	0	0	0	0	0	0	40
1-c-3 Dimethylcyclopentane	0	0	0	0	0	0	0	0	11	17.5
n-Heptane	0	0	25.6	0	126	0	0	5.5	74	16
1-c-2 Dimethylcyclopentane	0	0	0	0	0	0	0	0	0	0
Methylcyclohexane +	0	0	4	0	34.5	0	0	0	71.5	16
1,1 Dimethylcyclopentane										
2,2 Dimethylhexane	0	0	0	0	0	0	0	0	0	2.3
Ethylcyclopentane	0	0	0	0	0	0	0	0	0	0
Toluene	0	0	15	0	290	0	0	0	140	0
2,3,4, Trimethylpentane	0	0	4	0	0	0	0	0	0	0
1-t-4 Dimethylcyclohexane	0	0	0	0	0	0	0	0	0	0
n-Octane	0	0	7	0	100	0	0	0	0	0
Totals										
Alkenes	5	15	46	0	42	5.6	1.2	20	4.8	81
$C_{2} + C_{3}$	ō	15	25.5	20.6	72	14	7.4	8	88	117
$C_A - C_7$	0.1	0	140.1	6.6	1822.3	0	0	43	1823.5	879.6
Ce	0	0	11	0	100	0	0	0	0	2 3
Aromatics	õ	õ	20	0	390	0	0	0	242	31

<sup>a</sup> Ages correspond to those of Steinmetz et al., this volume.



Figure 1. Variation of *n*-alkane concentration with depth and lithology, Hole 530A.

Table 1. (Continued).

96-4, 14-16 1021.6 Green Creta. (Turon.)	96-4, 29-31 1021.8 Gray Creta. (Turon.)	98-3, 37-39 1038 Black Creta. (Turon.)	99-3, 105-107 1048 Green Creta. (Turon.)	99-5, 130-132 1051 Black Creta. (Cenoman.)	100-1, 97-99 1053 Gray Creta. (Cenoman.)	100-3, 38-40 1056 Green Creta. (Cenoman.)	101-1, 108-110 1063.1 Green Creta. (Cenoman.)	102-3, 84-86 1077.8 Green Creta. (Cenoman.)	104-5, 142-144 1092 Green Creta. (Alb.)	105-4, 135-138 1100 Green Creta. (Alb.)
				(ng	compound/g dry sed	iment wt.)				
112	139	140	48	67	181	86	88	311	104	110
6.8	8.1	60	2.5	9.4	27	4.8	6.6	11	5.8	7.8
0.96	0	181	0.66	41.1	29	0.82	0	3.9	0	1.4
0	3.3	245	0	101	119	0	0	2.1	0	0
0	4.7	264	0.57	102	135	0	0	2.9	0	0
0	12.3	205	0	97.4	281	0	0	12.6	0	0
0	11.6	253	0	97	296	0	0	22	0	0
0	0	0	0	0	2	0	0	0	0	0
6.9	0	3.2	0	2	38	0	0	6.9	0	0
0	4	10.2	0	8.6	11	0	0	0	0	0
0	40.2	10.5	0	42	61	0	0	0	4.7	0
0	4.2	11.4	0	7.2	9	0	0	12	0	0
0	17.6	13	0	33	76	0	0	10	3.3	0
0	9.1	14.6	0	22.5	26	0	0	0	0	0
0	100	10.6	0	4.1	2.4	0	0	0	0	0
0	1.6	48.6	0	23.6	7.8	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	15.3	0	5.9	4	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0
0	14	31.2	0	14.6	13.3	0	0	0	0	0
0	2.0	8.2	0	4.1	4.9	0	0	0	0	0
0	0	27.4	0	11	0	0	0	0	0	0
0	5.3	40.3	0	16.2	10	0	0	0	0	0
0	10.5	0	0	0	21	0	0	0	0	0
0	7	223	0	8.5	10.3	0	0	0	0	0
0	6.7	58.7	0	19	22	0	0	18	0	0
0	0	28.8	0	12.4	0	0	0	0	0	0
0	10	267	0	18.3	11	0	0	10	0	0
0	0	0	0	0	0	0	0	0	0	0
0	0	14.6	0	0	4.8	0	0	0	0	0
0	0	30.8	0	41.2	15	0	0	0	0	0
0	0	0	0	0	8.3	0	0	0	0	0
0	0	0	0	0	9	0	0	0	0	0
0	0	0	0	o	9	0	0	0	0	0
9	280	1000	a.				22	10	8	
0	56	8.6	0	7.9	0	4	0	0	3	1
7.76	8.1	241	3.16	50.5	56	5.62	6.6	14.9	5.8	9.2
6.9	253.6	1834.4	J.57	691.6	1159.5	0	0	96.5	8	0
0	0	0	0	0	26.3	0	0	0	0	0
0	1.6	79.4	0	64.8	22.8	0	0	0	0	0

Table 2. Pyrolysis and carbon data.

Sample	Pyrolysis h $\left(\frac{\mu g}{g  dry}\right)$	$\frac{\text{HC}}{\text{sed. wt.}}$	Production	Mass percent carbon relative to dry sediment		
(interval in cm)	P1	P2	$[P_1/(P_1 + P_2)]$	Ctotal	Corg	
Hole 530A						
5-5, 32-33	95	5200	0.018	4.48	2.03	
62-3, 106-108	22	227	0.088	1.72	1.12	
87-4, 103-105	95	10,000	0.0095	4.83	4.83	
87-4, 125-127	0	0	n.d.	0.605	0.56	
88-3, 31-33	480	89,000	0.0054	9.2	9.2	
93-2, 36-39A	25.4	321	0.0073	0.66	0.67	
93-2, 36-39B	8.4	193	0.042	0.66	0.67	
93-3, 44-46	14	821	0.017	0.76	0.62	
93-6, 89-92	40	4080	0.0097	3.15	2.51	
94-2, 38-40	101	41,000	0.0025	7.71	7.71	
96-2, 18-20	708	96,000	0.0073	17.1	17.1	
96-4, 14-16	0	475	0.0	0.60	0.60	
96-4, 29-31	69	4420	0.015	2.1	2.1	
98-3, 37-39	120	73,000	0.0016	12.5	12.5	
99-3, 105-107	—	_	—	2.08	0.693	
99-5, 130-132	48	16,000	0.0030	4.9	4.9	
100-1, 97-99	51	9,540	0.0053	2.2	2.2	
100-3, 39-40	16	313	0.049	2.76	0.74	
101-1, 108-110A	1.2	261	0.0046	0.80	0.78	
101-1, 108-110B	23	513	0.043	0.8	0.78	
102-3, 84-86	58	472	0.11	1.12	0.94	
104-5, 142-144A	54	540	0.091	1.2	1.2	
104-5, 142-144B	23	538	0.041	1.2	1.2	
105-4, 135-138	19	290	0.061	0.80	0.80	
Hole 532						
8-2, 24-26	14	33,000	0.00042	11.1	5.01	
12-2, 31-34A	250	20,000	0.012	7.10	4.61	
12-2, 31-34B	610	21,000	0.028	7.10	4.61	
19-2, 42-44	140	17,000	0.0082	5.81	3.30	
42-1, 146-148	110	9,900	0.011	7.77	3.58	

Note: n.d. = not defined. "A" and "B" designate replicate samples.

ly proposed by Schaefer et al., 1982. The enrichment factor is the ratio of a hydrocarbon, X, normalized to mass percent of organic carbon in a green shale to the same hydrocarbon, X, normalized to organic carbon in the black shale, that is:

$$EF = \frac{(\text{mass of hydrocarbon } X/\text{mass } C_{\text{org}}, G) "_{\text{Green}}}{(\text{mass of hydrocarbon } X/\text{mass } C_{\text{org}}, B)}_{\text{Black}}$$

A migration model can be derived using the enrichment factor. Two assumptions are made:

1) Mass transfer of hydrocarbon X can occur between "green shale," black shale, and the surrounding system (migration).

2) The mass of hydrocarbon X as analyzed by headspace analysis is proportional to the mass of organic carbon in a given sediment sample (see, for example, Karickhoff, et al., 1979) unless hydrocarbon migration has occurred (proportionality). The assumption of proportionality is made because pyrolysis results indicate that potential hydrocarbon production is proportional to mass organic carbon in sediments (see Figs. 4, 5, and 6).

If these assumptions are valid, the enrichment factor can be used to detect migration. For example, an enrichment factor of 1 would indicate that both shales released the expected amounts of hydrocarbon gases upon head-



Figure 2. Variation of *n*-alkane and aromatic hydrocarbon concentration with depth and lithology, Hole 530A.



Figure 3. Variation of total alkene and n-heptane concentrations and percentage organic carbon with depth and lithology, Hole 530A.



Figure 4. Graph and regression of percentage organic carbon versus total pyrolysis-produced  $(P_2)$  hydrocarbons for all samples in Table 2, Holes 530A and 532.



Figure 5. Graph and regression of percentage organic carbon versus pyrolysis-produced  $(P_2)$  methane for all samples in Table 2, Holes 530A and 532.



Figure 6. Graph and regression of percentage organic carbon versus pyrolysis-produced  $(P_2)$  ethane for all samples in Table 2, Holes 530A and 532.

space analysis (i.e., in proportion to their respective amounts of organic carbon) and migration did not occur. An enrichment factor greater than 1 would indicate a mass transfer from black shale to the "green" shale because "green" shale would have a disproportionately high amount of hydrocarbon X relative to the black shale. (This result could also be obtained by lateral migration of hydrocarbons from other sections into the green shales section). An enrichment factor less than 1 would indicate that the "green" shale released a disproportionately low amount of hydrocarbon X relative to the black shale or that more hydrocarbons migrated out of the green shales than out of the black shales. We believe that all measurable hydrocarbons in green shales have migrated there because: (1)  $C_{3+}$  hydrocarbons were generally not detected in green shales in amounts greater than the headspace detection limit (20 pg hydrocarbon/g dry weight of sediment) and (2) no  $C_1$ - $C_{28}$  hydrocarbons could be generated by pyrolysis in the green shale sections (detection limits:  $10 \,\mu g/g$  for methane and  $1 \mu g/g$  for other hydrocarbons). The pyrolysis gives a theoretical "upper limit" on the amount of hydrocarbon a sediment could generate under optimum petroleum generation conditions.

This model can be applied to shale pairs using data from Tables 1 and 2. Five "green" shale-black shale pairs were selected for this analysis on the bases that their percentage of organic carbon differed by at least a factor of three (denoted  $C_B/C_G$  in Table 3) and that they were relatively closely spaced (from 20 cm to 7.5 m in a 155-m section containing the black shales). For all five shale pairs examined, the enrichment factors (*EF*) are significantly greater than one for methane and ethane. The model would predict that the hydrocarbons had mi-

Table 3A. Enrichment factors for black shale-"green" shale pairs.<sup>a</sup>

Sample	Depth (m)	Corg (%)	Compound (ng HCX/g Corg)					
(interval in cm)			Methane	Ethane	Propane	n-Butane		
Black-green pairs 87-4, 125-127 87-4, 103-105 Enrichment factor $\Delta$ Depth = 0.7 m $C_B/C_G = 8.6^{b}$	945.7 945	0.56 4.83	52,100 3,560 14.6	2,850 410 6.9	820 110 7.2	0 62 0		
99-3, 105-107 99-5, 130-132 Enrichment factor $\Delta$ Depth = 3 m $C_B/C_G$ = 7.0	1,048 1,051	0.693 4.85	6,930 1,400 5.0	360 190 1.9	95 847 0.11	82 2,100 0.039		
96-4, 14-16 96-2, 18-20 Enrichment factor $\Delta$ Depth = 2.6 m C <sub>B</sub> /C <sub>G</sub> = 28.5	1,021.6 1,019	0.60 17.1	18,700 649 28.8	1,100 187 6.1	160 813 0.32	0 1,060 0.0		
93-3, 44-46 94-2, 38-40 Enrichment factor $\Delta$ Depth = 7.5 m C <sub>B</sub> /C <sub>G</sub> = 28.5	993.5 1,001	0.620 7.71	24,800 2,650 9.39	1,190 220 5.41	0 921 0	0 2,180 0		
Black-gray pair 93-6, 89-92 94-2, 38-40 Enrichment factor $\Delta$ Depth = 3 m C <sub>B</sub> /C <sub>G</sub> = 3.07	998 1,001	2.51 7.71	3,820 2,650 1.45	320 220 1.45	0 920 0	0 3,020 0		

a "Green" shale = nonblack shale = green shale or gray shale.

<sup>b</sup> CB/CG = %Corg black/% Corg 'green.'

Table 3B. Enrichment factors for "gray" shale-"green" shale pairs.<sup>a</sup>

Sample	Depth	Corg (%)	Compound (ng HCX/g Corg)				
(interval in cm)	(m)		Methane	Ethane	Propane	n-Butane	
Gray-green shale pairs							
93-3, 44-46	993.5	0.620	24,800	1,190	0	0	
93-6, 89-92	998	2.51	3,800	320	920	3,020	
Enrichment factor			6.5	3.7	0	0	
$\Delta$ Depth = 4.5 m							
$C_{A}/C_{E} = 4.05^{a}$							
96-4, 14-16	1,021.6	0.60	18,700	1,100	160	0.1	
96-4, 29-31	1,021.8	2.10	6,560	380	0	220	
Enrichment factor			2.85	3.0	n.d.	0	
$\Delta$ Depth = 0.2 m							
$C_{A}/C_{E} = 3.5$							
100-3, 38-40	1.056	0.74	11,600	650	110	0.1	
100-1, 97-99	1,053	7.2	8,200	1,200	1,300	6,100	
Enrichment factor			1.4	0.53	0.084	0	
$\Delta$ Depth = 2.4 m							
$C_{A}/C_{E} = 3.01$							

Note: n.d. = not defined. <sup>a</sup>  $C_A/C_E = \% C_{org} \text{ gray}/\% C_{org} \text{ green.}$ 

grated into the "green" shale. For almost all other compounds examined in the headspace analysis, the enrichment factors approach the EF detection limit of about  $3 \times 10^{-4}$  for these samples.

If the model is correct, then all shale samples containing any organic carbon (above the detection limit of 0.02% Corg) should release some hydrocarbon (above the detection limit of 20 pg HC/g dry sediment), yielding an EF greater than  $3 \times 10^{-4}$ . (The EF detection limit of  $3 \times 10^{-4}$  for this set of samples is determined by assuming organic carbon levels of about 0.6% and 3% as commonly found for green and black shales, respectively, and levels of about 360 ng hydrocarbon/g for the black shale [a maximum observed] and 0.02 ng/g for the green shale [the minimum detectable]). Therefore, when the enrichment factor is less than 1 and approaches  $3 \times$  $10^{-4}$ , either no hydrocarbon X (>20 pg/g sediment) has been produced in the green shales or all hydrocarbon X (>20 pg/g sediment) has migrated out of the green shale. The former alternative (i.e., no measurable production) is more likely considering three observations:

1) All the shales in this sedimentary column are immature with respect to petroleum generation.

2) Regression analyses (Figs. 4, 5, 6) of hydrocarbons released by pyrolysis show that there is a critical concentration of organic carbon (about 1% Corg) below which detectable levels of hydrocarbons are not produced.

3) Since both black shales and green shales are finegrained they probably have very similar permeabilities (Fancher and Lewis, 1933; Barrer, 1941). Thus, a preferential migration of hydrocarbons out of the green shale section seems unlikely.

For green shale-black shale pairs, the enrichment factors approach zero (i.e.,  $\leq 3 \times 10^{-4}$ ) in most cases other than methane and ethane because no measurable hydrocarbons are released by the green shales, as indicated by headspace analysis. In these cases, the mass of hydrocarbon gas X as analyzed from the headspace is clearly not proportional to the mass of organic carbon in the green shale sample. In the green shales, only two compounds are found consistently (methane and ethane) and five compounds intermittently, whereas in black shales an average of 26 compounds (including methane and ethane) are found. In all cases for methane and ethane, the enrichment factor is greater than one; that is, the concentrations of methane and ethane are always disproportionately large in the green shales. Thus, even if it were shown that significant hydrocarbon production were occurring in these green shales, their methane and ethane concentrations would still be disproportionately high relative to organic carbon.

If it could be demonstrated that no measurable hydrocarbons (i.e,  $\leq 20 \text{ ng/g}$ ) are produced in the green shale, an enrichment factor greater than  $3 \times 10^{-4}$ ) (i.e., any detectable free hydrocarbon at all in the headspace analysis of the green shale) would indicate hydrocarbon migration.

Employing an analysis similar to that of Whelan and Hunt (1982), it was found that plotting the total  $(P_2)$  pyrolysis hydrocarbons against percentage of organic carbon, the organic carbon intercept is 1.19% (Fig. 4). This result suggests that this value is a threshold level of organic carbon (1.19%) in this set of samples below which detectable hydrocarbons are not produced, providing that the linear (rather than a curvilinear) relationship is valid. All the samples that are called green shales based on pyrolysis fall below 1.19%; their average is about 0.6% organic carbon. This result indicates that no detectable hydrocarbons are produced in the green shale, so that all hydrocarbons (predominantly methane and ethane) in green shales have migrated there.

From this analysis, a sediment can be defined as either a green shale or black shale on the bases of the pyrolysis  $(P_2)$  capillary chromatograms and percent organic carbon in addition to the sediment color. Black shales have a complex and characteristic pattern of organic compounds generated by pyrolysis, consisting primarily of alkenes and alkanes from  $C_7$  to  $C_{27}$  (the range of our analysis) as shown in capillary gas chromatograms of  $P_2$ hydrocarbons of two black shales (Fig. 7). The two samples illustrated in Figure 7 were selected because they were representative of all the black shales examined in this study, and they were widely spaced in the sedimentary column. Their pyrolysis (P2) chromatograms are similar, indicating that black shale organic matter composition is remarkably similar over the 27 m.y. range sampled. In contrast, green shale pyrolysis  $(P_2)$  chromatograms are virtually blank. The green shale pyrolysis patterns never exceed blank levels and are clearly different from the black shale patterns, thus enabling pyrolysis-gas chromatography to be used to differentiate green and black shales. Capillary gas chromatograms of pyrolysis  $(P_2)$  hydrocarbons allow definition of a third shale, the gray shale. The gray shale GC pattern is significantly greater than the blank levels, but not as complex as that seen in the black shales. The percentage of organic carbon in the grey shale is in the range of 1.5-3%-between those of the green and black shales.

There are a few compounds (typically  $C_3$ , n- $C_4$ , and i-C<sub>4</sub>) whose EF's are greater than  $3 \times 10^{-4}$ , but often less than 1. Since it has been shown that detectable hy-



Figure 7. Capillary gas chromatograms of pyrolyzable  $(P_2)$  hydrocarbons in black shales, Hole 530A.

drocarbon production does not occur in the green shales, these *EF*'s indicate migration of a small amount of hydrocarbon. These compounds are slightly heavier than methane and ethane, which migrate into the green shales, but are smaller than the heavier  $C_{5^+}$  compounds which do not.

The application of this migration model is not limited to "green" shale-black shale pairs. In principle, it can be applied to any lithology, up to the limitations imposed by the error in the required measurements and sample variability. In such cases, the enrichment factor is defined such that the mass of hydrocarbon X and the percentage of organic carbon in the sample containing less organic carbon is in the numerator and those of the sample containing more organic carbon are in the denominator.

Applying this methodology to green shale-gray shale pairs, it can be seen that in all cases examined (Table 3, Part B), migration of methane and ethane from the gray shale to the green shales could be occurring.

Whelan (1982) has noted that the measurement of methane in the headspace analysis is qualitative because of losses during and after sample collection. Kartsev et al. (1959) indicated that sorption of light hydrocarbons by "soil" and "rock" samples is proportional to the amount of organic matter contained in them. Karickhoff et al. (1979) observed the same proportionality in unconsolidated lacustrine and fluvial sediments. This proportionality would favor organic-*rich* sediments in retaining volatile hydrocarbons. In spite of both these facts, methane and ethane were retained in disproportionately high amounts relative to the percentage of organic carbon in the organic-*lean* sediment samples, and migration was still demonstrable on the basis of the enrichment factor.

No less significant than the demonstration of migration of methane and ethane is the fact that an average of 21 hydrocarbons in the  $C_3$  to  $C_8$  range have not migrated from the black and/or gray shales to the green shales in these sediments that are an average 95 m.y. old. Significant concentrations of these compounds are found in black shales which are within centimeters to meters of green shales where no detectable amounts of the same hydrocarbons are found (see Table 1).

# CONCLUSIONS

1. Most of the 36  $C_1$  to  $C_8$  hydrocarbons from sediment samples analyzed by headspace analysis are found in black shales.

2. The localized distribution of most hydrocarbons larger than methane and ethane in black shales and enrichment factors less than or equal to about  $3 \times 10^{-4}$  for "green" shale-black shale pairs indicate that these compounds have not migrated from the black to the "green" shale.

3. Methane and ethane are distributed through all lithologies.

4. The distribution of methane and ethane can be attributed to migration on the basis of the enrichment factor.

5. Migration of methane and ethane from gray shales to green shales is indicated by the enrichment factor.

6. The organic matter in all the black-shale layers is similar, as indicated by pyrolysis products. This result implies similarity in depositional conditions for the various layers.

7. A general model is proposed for migration based on the enrichment factor.

#### ACKNOWLEDGMENTS

We would like to thank Christine Burton and Martha Tarafa for providing invaluable technical assistance. This work was supported by the National Science Foundation Grant OCE 8019508 and the Basic Energy Science Division of the U.S. Department of Energy, Contract No. EG-77-S-02-4392. John Jasper is supported by the MIT/WHOI Joint Program in Oceanography. This is WHOI Contribution No. 5199.

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Date of Initial Receipt: September 28, 1982