

24. ORGANIC DIAGENESIS OF MIOCENE SEDIMENTS FROM SITE 341, VØRING PLATEAU, NORWAY

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INTRODUCTION

As was reported by the author in the Site 341 Report Chapter (this volume), light hydrocarbons were detected in the Tertiary section penetrated at this site located on the Vøring Plateau. Gas pockets formed in nearly every core recovered below a depth of 50 meters and shipboard analysis indicated all the gas containing methane and ethane was detected in Miocene age sediments. The middle Miocene cores taken below 400 meters had a pronounced petroliferous odor after they were split, and routine fluoroscopic examination revealed the 33-cc sample recovered from a depth of 446.5-447.0 meters had a bright yellow pinpoint fluorescence. It appeared likely that interstitial soluble hydrocarbons were present in these Miocene pelagic siliceous sediments, and thus drilling was terminated at a depth of 456 meters and the hole was cemented and plugged.

Because the Miocene contained some quantity of soluble hydrocarbons that appeared to increase with depth, a study was undertaken to characterize this material and determine the extent of organic diagenesis of the deep marine Tertiary section in this portion of the Vøring Plateau.

ANALYTICAL METHODS

The shipboard procedure followed for collecting and analyzing the gas samples is described in the section on Organic Geochemical Measurements in Chapter 1 (this volume). Gas samples were collected in specially designed 100-cc evacuated cans, and all gas pockets that formed in the core were sampled so a shipboard analysis could be made and additional analysis made at a later date in our laboratory, their composition was determined by a more sensitive gas chromatograph having a hydrogen flame ionization detector. The isotopic composition was then determined.

A Perkin-Elmer 900 gas chromatograph was utilized in carrying out the laboratory analysis. The valve on the can was connected to an evacuated Perkin-Elmer gas sampling valve fitted with a 1-cc loop. The sample was injected into a 12 foot \times 1/8 inch 80-100 mesh Chromasorb 102 column and programmed from -70°C to 100°C at a flow rate of 40 ml/min of helium. The effluent was monitored with a hot wire and hydrogen flame ionization detector arranged in series. Nitrogen, oxygen, argon, methane, and carbon dioxide were detected with the hot wire detector. The higher hydrocarbons were detected with the more sensitive flame ionization detector. Although butenes and pentenes were not detected in the samples, this technique permits their detection.

Carbon isotopic compositions were obtained on a Nier-type 35-cm radius, 90° sector isotope ratio mass

spectrometer. Isotope measurements are made on the $m/e = 45$ and $m/e = 44$ ions using carbon dioxide as the working gas. Values are reported using the conventional per mil deviations (δ) from the C^{13}/C^{12} ratio of the Cretaceous belemnite, *Belemnitella americana*, from the Peedee Formation (PDB). Instrument precision is ± 0.05 per mil.

Organic carbon samples were combusted to carbon dioxide for mass spectrometry in a vacuum system similar to that described by Craig (1953). Oxidation was carried out at 925°C over a copper catalyst in an oxygen atmosphere. Sulfur oxides were removed by a hot manganese dioxide catalyst. Carbon dioxide was purified of water by differential freezing at -123°C. Gas components were separated by gas chromatography prior to conversion to carbon dioxide.

The 20-cc sediment samples were collected according to standard shipboard sampling procedures, and care was exercised to minimize contamination and obtain samples representative of the section penetrated. The procedure followed for the geochemical characterization of these samples is shown in Figure 1. The solvents were distilled in glass prior to use.

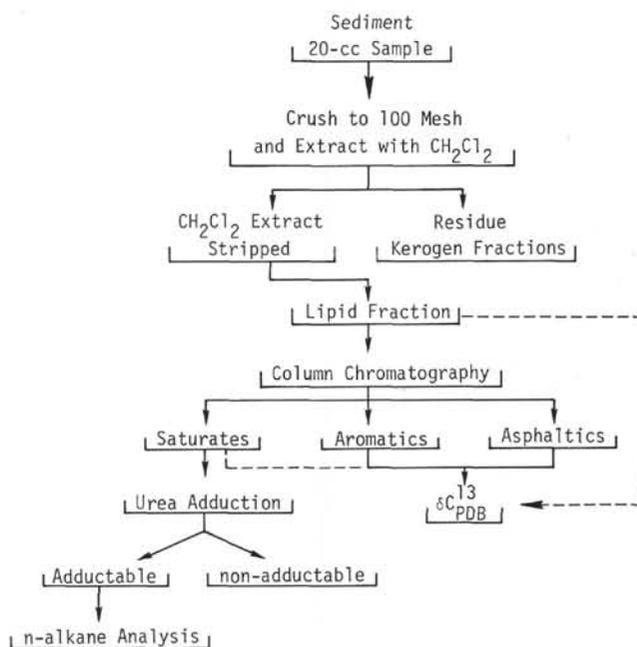


Figure 1. General laboratory procedure followed in characterizing the organic matter in sediment samples. In the case of these samples there was insufficient material to obtain an isotopic value for the lipid and saturates fractions.

DISCUSSION

Data resulting from this study are provided in Tables 1 through 4 and Figures 2 and 3. Carbonate content, organic carbon values, quantity of lipid material, and OEP values are provided in Table 1, along with sampling depth and stratigraphic age. Carbon isotopic values for the aromatic and asphaltic fractions of the sediment samples are provided in Table 2. Compositional analysis and $\delta C_{\text{POB}}^{13}$ values for the methane component of the canned gas samples are provided in Table 3, along with sampling depth and sedimentary age. Table 4 constitutes a tabulation of weight percents of *n*-alkane by carbon number over the range that could be analyzed for the individual samples. Plots showing the normalized distribution of *n*-alkanes by carbon number for the Pliocene-Pleistocene and middle Miocene samples are provided, respectively, in Figures 2 and 3.

The average Odd-Even Predominance (OEP), which was developed in this laboratory by Scalan and Smith (1970), is a mathematically correct expression of the predominance of odd and even carbon numbers as a function of carbon number for the *n*-alkane series. This value is computed according to the following equation

$$\text{OEP} = \left[\frac{C_i + 6C_{i+2} + C_{i+4}}{4C_{i+1} + 4C_{i+3}} \right] (-1)^{i+1}$$

As is the case with the Carbon Preference Index (CPI), which was developed by Bray and Evans (1961), an OEP value of unity indicates no predominance, whereas a value greater than unity indicates an odd-number predominance. An OEP or CPI value less than unity indicates an even-numbered predominance. With increasing depth of burial, organic diagenesis generally

increases and OEP and CPI values approach unity. Crude oils commonly have an OEP value close to unity. Erdman (1975a, b) discusses some of the factors affecting organic diagenesis and indicates how OEP can be used as an index for the genesis of petroleum.

The Tertiary section penetrated at Site 341 generally is high in organic matter; the Pliocene-Pleistocene section averages 0.58 weight percent, and the middle Miocene sediments average 1.83%, with organic content generally increasing with depth. All the samples contain some quantity of petroleum-like compounds and many contain sufficient amounts to be classified as source rocks of petroleum according to the criteria of Philippi (1956). However, the OEP values listed in the last column of Table 1 indicate the lipid (oil) fraction has a marked odd-number carbon predominance. This is also evident from the *n*-alkane plots shown in Figures 2 and 3. The observation that OEP values increase slightly rather than decrease with increasing depth is evidence that organic diagenesis has not proceeded very far in the section. Samples having the lowest OEP values (1.51-1.82) are from the Pliocene-Pleistocene section, and the organic matter in these "glacial" sediments may not be indigenous to this location.

Over the 219.9 through 420.8 meter depth interval, the value of the ratio of lipid (oil) to total organic matter of kerogen averages 31%, whereas that of the underlying section averages only 1.1%. The lipid content of the 200.9-meter-thick interval averages 0.26%, and is comprised by 42% saturates, whereas the lipid content of the underlying interval averages only 0.02% and contains only about 24% saturates. These data suggest that migration has occurred and that some quantity of the lipid material in the section is not indigenous to the interval. Probably migration of material into the interval originated from the surround-

TABLE 1
Organic Geochemical Data for Tertiary Sediments, Site 341

Stratigraphic Age	Depth Below Mud Line (m)	Sample (Interval in cm)	Weight Percent									Total Lipids ^c	Odd-Even Predominance OEP
			Carbonate ^a		Organic Carbon ^a			Lipid Fractions ^b					
			Carbon	CaCO ₃	Total	Lipid	Kerogen	Saturates	Aromatics	Asphaltics			
Pleistocene With Oligocene (Mixed)	38.0	4, CC	0.25	2.08	0.97	0.012	0.96	59.7	31.8	8.5	1.3	2.75	
	47.5	5, CC	0.26	2.17	0.68	0.022	0.66	69.0	15.6	15.4	3.2	1.82	
Pliocene or Pleistocene	100.1	11-3, 60-65	1.23	10.25	0.43	0.021	0.41	28.4	46.0	25.6	4.8	1.59	
	105.2	12-6, 70-75	1.21	10.08	0.41	0.017	0.39	35.7	42.1	22.2	4.1	2.46	
	161.1	16-1, 60-65	1.57	13.08	0.55	0.026	0.54	12.6	59.7	27.7	4.6	3.30	
	200.3	18-1, 75-80	1.10	9.17	0.49	0.012	0.48	16.3	18.1	65.6	2.5	1.51	
	219.9	19-1, 140-145	1.32	11.00	0.45	0.195	0.43	46.1	13.9	40.0	43.4	2.03	
	259.9	21-2, 40-45	1.83	15.25	0.32	0.153	0.17	43.8	25.0	31.2	47.8	2.39	
	317.4	24-2, 99-104	0.03	0.25	0.96	0.253	0.71	49.1	20.2	30.7	26.3	2.82	
	407.7	29-6, 120-124	1.02	8.50	1.55	0.293	1.26	22.1	29.9	48.0	18.9	2.04	
	413.5	30-4, 50-55	0.14	1.17	1.40	0.246	1.15	54.2	15.5	30.3	17.5	2.13	
	420.8	31-2, 130-135	0.04	0.33	1.33	0.434	0.90	37.0	25.3	37.7	32.7	2.43	
Middle Miocene	435.5	32-5, 105-110	0.24	2.00	2.00	0.018	1.98	18.2	30.2	51.6	0.9	2.26	
	436.9	32-6, 5-10	0.05	0.43	1.73	0.014	1.72	18.5	27.6	53.9	0.8	3.24	
	438.5	33-1, 135-140	0.03	0.25	1.89	0.022	1.87	33.7	28.1	38.2	1.1	3.05	
	439.2	33-2, 70-75	0.03	0.25	2.02	0.026	1.99	40.8	21.7	37.5	1.3	2.98	
	446.7	34-1, 20-25	0.10	0.83	2.52	0.034	2.49	10.3	28.3	61.4	1.3	3.28	
	449.7	34-3, 20-25	0.06	0.50	2.04	0.022	2.02	25.3	30.3	44.4	1.1	3.27	

^aWeight percent with respect to total core sample.

^bWeight percent with respect to total lipid fraction.

^cWeight percent with respect to total organic carbon.

TABLE 2
Carbon Isotopic Compositions of Lipid Fractions Extracted from Tertiary Sediments, Site 341

Stratigraphic Age	Depth (m) Below Mud Line	Sample (Interval in cm)	$\delta^{13}\text{C}_{\text{PDB}}$			
			Total	Saturates	Aromatics	Asphaltics
Pleistocene with Oligocene (mixed)	38.0	4, CC	— ^a	— ^a	-25.4	-24.5
	47.5	5, CC	—	—	—	-24.9
Pliocene or Pleistocene	100.1	11-3, 60-65	—	—	—	-26.4
	105.2	12-6, 70-75	—	—	-27.2	-26.9
	161.1	16-1, 60-65	—	—	-26.0	-26.9
	200.3	18-1, 75-80	—	—	-26.1	-25.3
	219.9	19-1, 140-145	—	—	—	-25.8
	259.9	21-2, 40-45	—	—	-26.4	-25.1
	317.4	24-2, 99-104	—	—	-27.1	-27.0
	407.7	29-6, 120-124	—	—	-24.6	-26.3
	413.5	30-4, 50-55	—	—	-26.2	—
	420.8	31-2, 130-135	—	—	-26.1	-26.6
Middle Miocene	435.5	32-5, 105-110	—	—	-26.2	—
	436.0	32-6, 5-10	—	—	-25.8	-24.4
	438.5	33-1, 135-140	—	—	-25.8	-26.0
	439.2	33-2, 70-75	—	—	-25.7	-26.8
	446.7	34-1, 20-25	—	—	—	-25.3
	449.7	34-3, 20-25	—	—	-26.0	-26.1

^aInsufficient sample to obtain an isotopic value.

TABLE 3
Compositional and Isotopic Analysis of Canned Gas Samples^a
From Site 341 (Laboratory-Generated Data)

Stratigraphic Age	Depth Below Mud Line (m)	Sample (Interval in cm)	Composition Normalized Air Free Basis (Mol%)						Isotopic Composition of Methane $\delta^{13}\text{C}_{\text{PDB}}$
			Carbon Dioxide	Methane	Ethane	Propane	<i>i</i> -butane	<i>n</i> -butane	
Pleistocene with Oligocene (mixed)	50.5	6-2, 0	2.17	97.82	0.01	<0.001	nd	nd	-87.3
	74.0	8-4, 150	nd	99.94	0.06	nd	nd	nd	-86.6
Pliocene or Pleistocene	74.5	8-5, 150	nd	nd ^b	nd(4)	nd	nd	nd	—
	80.5	9-2, 150	nd	99.91	0.09	nd	nd	nd	-79.4
	83.0	9-4, 150	nd	99.99	0.01	<0.001	nd	nd	-80.7
	110.5	12-3, 150	12.65	87.31	0.04	<0.001	nd	nd	-78.1
	163.9	16-1, 90	nd	nd ^b	nd	nd	nd	nd	—
	246.5	20-6, 150	0.57	99.37	0.05	0.01	nd	nd	-78.7
	256.6	21-0, 10	nd	nd ^c	nd	nd	nd	nd	-78.1
	277.0	22-1, 0	1.49	98.37	0.13	0.01	nd	nd	-77.9
	278.5	25-2, 10	12.29	87.81	nd	nd	nd	nd	—
	342.9	25-6, 140	5.32	94.59	0.07	0.02	nd	nd	-78.4
Middle Miocene	370.5	27-0, 0	4.09	95.28	0.51	0.12	nd	nd	-76.7
	398.5	28-6, 0	7.32	91.85	0.69	0.14	nd	nd	-74.3
	403.5	29-3, 0	1.92	97.88	0.16	0.04	nd	nd	-75.2
	455.5	34-6, 0	19.81	80.05	0.11	0.03	<0.001	<0.001	-71.2

Note: nd indicates component was not detected in laboratory analysis.

^aGas samples collected according to procedure described under Geochemical Measurements for Site 337. None of the samples contained sufficient quantity to obtain the isotopic composition of the higher hydrocarbons, nor for the CO₂.

^bSample container leaked in transit.

^cInsufficient sample for compositional analysis after isotopic composition determined.

ing sediments. Compaction of the sediments and expulsion of interstitial water probably lead to the migration. McIver (1971, 1973) also has cited evidence for the occurrence of hydrocarbon migration in similar age sediments from previous DSDP cores. Apparently such migration can occur rather early in the stage of petroleum migration and may be more common in geochemically immature sediments than expected.

Laboratory analysis of the canned gas samples indicates that in addition to methane, which was present in nearly all samples, ethane also was present and increases in quantity with depth. Below a depth of 342.9 meters in the Miocene, propane is present and also increases in quantity with depth. At a depth of 455.5 meters near the bottom of the hole, *i*-butane and *n*-butane were detected. This suggests that some thermal

TABLE 4
n-Alkane Distribution by Carbon Number for Lipids Extracted from Tertiary Sediments, Site 341^a

Depth Below Mud Line (m)	Normalized Weight Percent																	
	38.0	47.5	100.1	105.2	161.1	200.3	219.9	259.9	317.4	407.7	413.5	420.8	435.5	436.0	438.5	439.2	446.7	449.7
13	b	—	—	—	—	—	—	—	—	—	0.16	—	—	—	—	—	—	—
14	—	—	—	—	—	—	—	—	—	—	0.00	—	—	—	—	—	—	—
15	—	—	—	—	—	—	0.62	—	—	—	0.27	—	—	—	—	—	—	—
16	—	—	—	—	—	0.00	—	—	—	—	0.14	—	—	0.28	—	—	—	—
17	—	—	—	—	0.44	—	0.00	—	—	—	0.00	0.77	—	0.19	—	0.39	0.21	0.21
18	—	0.35	0.38	1.62	0.00	—	0.00	0.83	0.29	1.91	0.43	2.85	—	0.21	—	1.13	0.57	0.34
19	0.93	0.31	0.44	1.62	0.00	0.32	0.00	2.12	1.08	3.27	1.33	3.99	—	0.10	—	1.29	1.12	0.99
20	2.35	2.77	1.91	2.69	3.31	1.25	3.66	4.41	3.05	6.35	4.34	5.76	0.97	1.65	—	5.66	2.39	1.75
21	1.30	0.89	1.89	0.00	2.45	1.21	5.45	4.93	4.10	6.18	4.92	5.71	1.59	2.25	—	14.01	3.35	2.58
22	0.00	1.57	3.34	0.00	3.67	1.05	7.60	5.50	5.12	6.83	6.30	5.77	4.11	3.65	3.26	4.46	2.79	2.60
23	2.94	3.92	6.82	7.87	6.16	0.88	9.28	7.43	7.78	6.30	5.00	5.83	3.49	3.05	6.67	6.21	4.42	4.57
24	2.48	5.27	8.19	4.74	4.55	7.22	8.21	6.56	6.49	5.93	5.74	5.17	6.02	3.76	3.76	4.33	3.19	3.51
25	5.62	10.69	11.75	10.88	10.22	10.13	10.70	8.73	9.78	7.67	7.76	7.00	10.82	7.78	8.97	6.47	7.45	8.15
26	2.98	3.31	10.69	5.60	5.61	10.42	7.01	6.20	6.23	6.08	6.61	5.05	10.68	5.59	5.22	4.88	4.60	6.46
27	12.80	15.46	13.74	14.89	14.24	14.64	12.30	9.98	11.68	8.45	9.46	9.10	14.09	13.52	11.95	8.93	7.80	11.00
28	8.89	12.38	9.04	4.52	4.86	10.13	5.96	5.32	4.88	5.34	6.12	5.17	7.80	5.62	5.75	4.04	5.44	5.33
29	18.36	14.37	10.86	14.00	14.03	14.33	10.42	10.81	11.11	10.39	12.68	11.64	13.69	18.26	15.76	11.00	15.56	14.03
30	5.96	8.79	5.38	8.30	2.77	6.62	3.67	4.07	3.55	4.28	5.25	4.23	4.67	4.61	4.70	2.78	4.29	3.78
31	20.01	10.06	7.30	12.93	14.13	9.49	9.17	11.64	12.98	10.42	12.24	11.76	12.44	16.29	18.56	13.27	20.32	18.74
32	3.87	3.30	2.21	2.26	2.64	3.36	2.82	2.58	2.61	2.73	2.91	2.35	2.46	2.89	2.76	2.52	2.58	2.41
33	6.87	3.34	2.68	5.82	5.62	3.49	3.13	5.69	6.86	4.29	5.07	4.17	4.16	6.86	7.27	5.24	7.05	7.12
34	1.29	1.01	0.74	2.26	1.92	2.31	—	1.02	0.97	1.13	0.83	0.70	0.63	0.25	2.44	0.97	1.31	1.68
35	1.99	0.35	0.56	—	2.42	0.52	—	1.11	0.80	1.83	1.79	1.74	1.31	1.73	2.93	2.33	2.89	2.58
36	1.36	1.85	1.28	—	0.00	2.65	—	0.68	0.49	0.42	0.53	0.41	0.81	0.72	—	—	1.07	0.34
37	—	—	0.54	—	0.96	—	—	0.27	0.13	0.10	—	0.58	0.16	0.64	—	—	0.51	0.41
38	—	—	0.26	—	—	—	—	0.11	—	—	—	0.15	—	—	—	—	1.09	1.37

^aDSDP core identification provided in Table 1.

^bIndicates value not determined because of sample limitations.

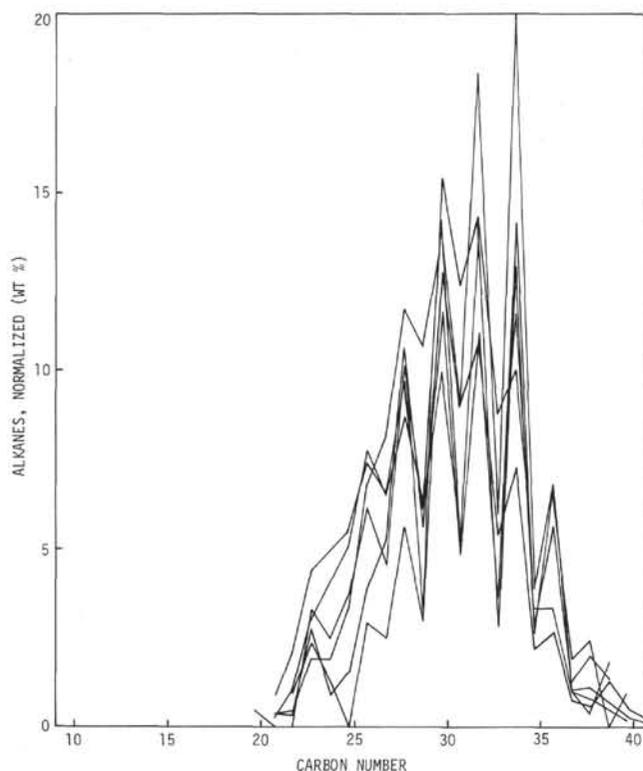


Figure 2. Normalized *n*-alkane plots for Pliocene-Pleistocene sediments from Site 341.

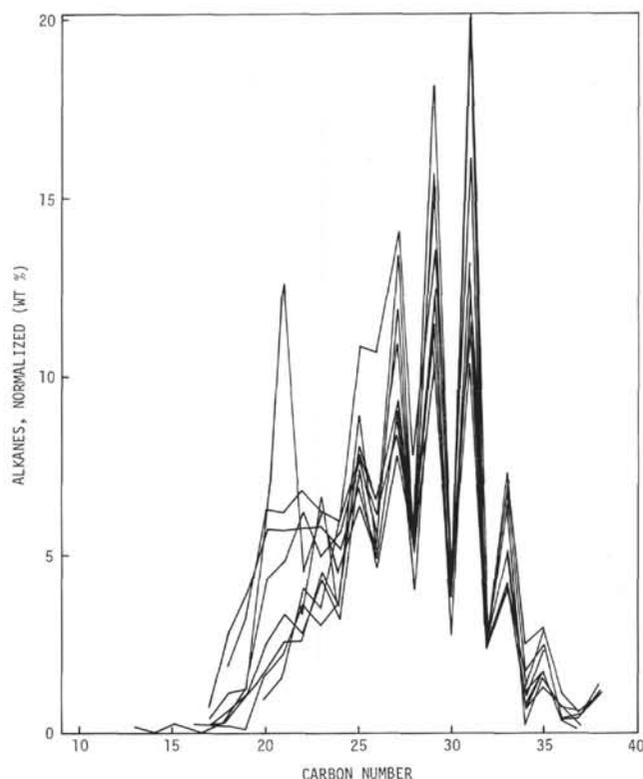


Figure 3. Normalized *n*-alkane plots for middle Miocene sediments from Site 341.

degradation of organic matter has taken place in these sediments, and is becoming more pronounced with depth.

As shown in Table 3, δC_{PDB}^{13} values for methane become progressively isotopically heavier with depth. At a depth of 50.5 meters in the Pleistocene, methane has a value of -87.5, whereas at a depth of 455.5 meters in the Miocene the methane has a value of -71.2. Although very light isotopic values for methane have been attributed to a bacterial origin (Rosenfeld and Silverman, 1959), this gas is believed to have originated primarily from abiogenic degradation of the organic matter and represents the early products of organic diagenesis. A theoretical study of the chemical kinetic effects on carbon isotopic compositions by Smith et al. (1971, p. 21-24) predicts a progressive change in isotopic compositions with depth toward heavier values as organic diagenesis becomes more pronounced. The measured isotopic values for methane in this Tertiary section are quite similar to values predicted from this kinetic model.

CONCLUSIONS

Although petroleum genesis is indicated to be in an early stage in the Miocene section, there is evidence that abiogenic diagenesis has begun and some light hydrocarbons have been generated. Evidence suggests the first product of this abiogenic diagenesis was an isotopically light methane. As organic diagenesis increased with depth, isotopically heavier methane and a greater quantity of ethane and higher homologs were

produced. Generation of liquid oil is not very far advanced in the Miocene, although clearly some lipid material has migrated. However, the quantity is small and certainly is not of economic importance. Probably this movement of lipids was caused by expulsion of pore fluid as the sediment was compacted.

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