# 22. PETROLEUM-GENERATING POTENTIAL OF SEDIMENTS FROM LEG 44, DEEP SEA DRILLING PROJECT

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#### ABSTRACT

The abundance, type, and thermal history of organic matter in sediments collected on Leg 44 of the Deep Sea Drilling Project were determined to evaluate the petroleum-generating potential of sediments in the Blake Plateau region. While several sediment samples contain more than 1 per cent organic carbon, the amount of organic matter which is thermally convertible to petroleum is too small for most samples to be considered potential source rocks of petroleum. The small proportions of thermally reactive organic matter are related to the hydrogen-lean nature of the material which constitutes the kerogen. Measurements of vitrinite reflectance further suggest that any potential source rocks would have to be buried more deeply before they could attain the subsurface temperatures necessary for significant petroleum generation.

# INTRODUCTION

To evaluate the petroleum-generating potential of sediments on the Blake Plateau and in the adjacent Blake-Bahama Basin, we acquired several sediment samples from Leg 44 of the Deep Sea Drilling Project (DSDP). Our objectives were to determine whether the sediments contain sufficient amounts of thermally reactive organic matter for significant petroleum generation and whether they have been exposed to subsurface temperatures high enough for the thermal conversion of kerogen to petroleum. In addition, we used visual kerogen observations to study the effect of organic composition on petroleum-generating potential.

To measure the abundance of organic matter in the sediments, we determined both the organic carbon  $(C_{\rm org})$  and effective carbon  $(C_{\rm eff})$  contents of the sediment samples. Organic carbon, or acid-insoluble carbon, reflects the total amount of organic matter in the sediment. It is determined by measuring the carbon dioxide evolved during combustion of an acid-treated sample. Effective carbon, on the other hand, represents the fraction of organic carbon which is thermally convertible to petroleum. As estimates of effective carbon, we used two laboratory pyrolysis procedures. One method, pyrolysis fluorescence (PF), is a rapid means of evaluating a sediment's petroleum-generating potential by measuring (in arbitrary PF units) the amount of fluorescing bitumen generated on heating. PF values in rocks may range from zero to several thousand units. The second method, pyrolysis FID (P-FID), provides a measure of the hydrocarbons and hydrocarbon-like compounds produced by heating the sample from 25° to 750°C. The effective carbon content is computed as 85 per cent of the hydrocarbons generated in the temperature range of 300° to 650°C; it does not include any pre-existing hydrocarbons which are distilled from the sample at lower temperatures.

The conversion of kerogen to petroleum is a temperature-dependent reaction, and the effects of organic metamorphism can be observed as changes in the chemical and physical properties of the kerogen. The reflectance (in oil) of vitrinite, a coal maceral which is disseminated in many sediments, is a commonly used method for measuring the level of organic metamorphism (LOM; Hood et al., 1975). Vitrinite reflectance  $R_o$  is applicable over the wide range of coal rank and LOM in which oil and gas are formed.

The analytical techniques have been described in greater detail by Hood et al. (1976).

## **RESULTS AND DISCUSSION**

The samples used in this study come from DSDP Sites 391 and 392 (Figure 1). As the respective site summary chapters in this volume indicate, the sediments from these two sites represent contrasting sedimentary histories. Site 391, located in the Blake-Bahama Basin, contains Mesozoic and upper Cenozoic deep-water sediments; the stratigraphy of the Mesozoic sediments is similar to that of other DSDP holes in the northwestern Atlantic (Lancelot et al., 1972). Site 392, on the other hand, received shallow water carbonate sediments until the outer portion of the Blake Plateau subsided to bathyal water depths in Barremian (Early Cretaceous) time.

Using available organic carbon data (Appendix I, this volume), we sampled those stratigraphic intervals in which potential source rocks seemed likely to occur. We were particularly interested in the dark colored, Cretaceous clays at Site 391, which shipboard scientists had described as carbonaceous. We also wished to determine whether age-equivalent sediments at Site 392 were carbonaceous.



Figure 1. Location map of DSDP Sites 391 and 392. Depth Contours in meters.

### **Content of Organic Matter**

On the basis of published studies of organic carbon content in petroliferous and non-petroliferous sedimentary basins, we have considered 1.0 per cent to 1.5 per cent organic carbon to be a minimum requirement for a potential source rock of petroleum (Hood et al., 1976). We regard pyrolysis techniques as better indicators of petroleum-generating potential, however, since they measure directly the petroleum-like material generated by heating. We believe a sediment should have a minimum PF value of 10 units or a pyrolysis-FID yield greater than 0.3 per cent pyrolysis hydrocarbons (0.26%  $C_{eff}$ ) before it can be considered a potential source rock.

The sediments collected from Leg 44 have organic carbon contents ranging from 0.26 per cent to 1.85 per cent organic carbon (Table 1). Of the 15 samples which we analyzed, 10 contain more than 1.0 per cent organic carbon. The pyrolysis measurements indicate, however, that only a small proportion of the organic matter in each sample is thermally convertible to petroleum. Most of the analyzed samples contain less than 0.1 per cent effective carbon and have PF values less than 8 units. Only three samples (two Miocene and one Cretaceous from Site 391) exhibit high enough pyrolysis yields to be considered possible source rocks. Even these samples barely exceed our minimum requirements. Our failure to find sediments with larger concentrations of thermally reactive organic matter leads us to believe that the petroleum-generating potential of the sediments at Sites 391 and 392 is very limited.

Despite the different water depths in which the Cretaceous sediments at Sites 391 and 392 were deposited, the similar concentrations of organic matter in these sediments suggest that conditions of organic production and preservation were similar at both sites. Their organic contents appear, however, to be lower than those of similar age sediments elsewhere in the western North Atlantic (Kendrick, in press; Kendrick et al., in press). The smaller amounts of organic matter in Leg 44 sediments may reflect less favorable

 TABLE 1

 Content of Organic Matter – Sites 391 and 392

Sample (Interval in cm)	Depth (m)	Age	% C <sub>org</sub>	PF	% C <sub>eff</sub>	C <sub>eff</sub> /C <sub>org</sub>
Site 391						
4A-3, 0-10	206	Miocene	0.26	8	0.03	0.12
7A-1, 57-59	326	Miocene	1.85	11	0.32	0.17
13A-0, 0-3	526	Miocene	1.60	12	0.32	0.20
6C-3, 96-100	691	U. Cretaceous	1.09	2	0.02	0.02
7C-2, 110-112	728	Cretaceous	1.28	0	0.03	0.02
9C-3, 37-40	833	Albian/ Aptian	1.07	0	0.02	0.02
10C-3, 110-113	900	Albian/ Aptian	1.34	0	0.03	0.02
12C-4, 78-80	958	Aptian	1.46	0	0.08	0.05
16C-1, 130-132	1021	Neocomian	1.03	3	0.04	0.04
26C-3, 130	1147	Neocomian	0.48	2	0.02	0.04
27C-2, 8-9	1154	Neocomian	1.56	16	0.22	0.14
49C-2, 124-126	1364	Tithonian (U. Jur.)	0.37	3	< 0.01	
Site 392						
2A-1, 78-80	67	Albian	0.58	5	< 0.01	-
2A-1, 108-110	67	Albian	1.29	3	0.03	0.02
3A-1, 23-25	79	Aptian	0.95	4	0.02	0.02

conditions for the accumulation of organic matter in the Blake Plateau region. Alternatively, the analyzed samples may come from stratigraphic intervals which are poor in organic matter elsewhere too. Kendrick (in press) and McCave (in press) noted variations in the amounts of organic material in Cretaceous black clays which appear to be time related. Upper Cenomanian sediments, which were very rich in organic matter at DSDP Sites 386 and 387, were not recognized at Sites 391 or 392 either because they are undated or because they are missing altogether. Consequently, a period during which accumulation of organic matter in the North Atlantic was greatest may not be preserved in the sedimentary records of Sites 391 and 392.

Of the samples from Leg 44 which were analyzed, the Miocene sediments at Site 391 show the greatest source rock potential. The Miocene sediments consist largely of mudstone and intraclastic chalk, which have been interpreted as gravity-flow deposits (see Site 391 Report, this volume). The greater abundance of siliceous microfossils in the Miocene sediments suggests that organic productivity may have been higher during the Miocene than the Cretaceous. The interpretation of the variations in content of organic matter is complicated, however, by the allochthonous nature of the sediments. It is not clear, for instance, whether conditions in the Blake-Bahama Basin were favorable for preservation of organic matter or whether organic matter was preserved because it was rapidly buried following its transport by gravity flows from shallower water. Unfortunately, no Miocene sediments were recovered at Site 392, which would have provided a useful comparison.

# Level of Organic Metamorphism (LOM)

Most samples from Sites 391 and 392 show a broad range in vitrinite reflectance values which suggests that some of the vitrinite grains with high reflectance values either have been oxidized or have been reworked from sedimentary units with a prior thermal history (Hood and Castaño, 1974). Because of the difficulty in distinguishing primary vitrinite from reworked or oxidized vitrinite, we cannot accurately estimate the level of organic metamorphism for many of the Leg 44 sediment samples. Samples containing substantial amounts of reworked vitrinite will yield LOM estimates which are too high if made on the basis of the entire population of reflectance values.

The results of the vitrinite reflectance measurements are summarized in Table 2. For each sample, an "X" value is listed, which denotes the range and mean of all vitrinite reflectance measurements made on the sample. For some samples an "A" value is also given which indicates those measurements interpreted as primary vitrinite.

Because drilling at Site 391 penetrated more than 1400 meters of sediment, it presented a good opportunity to examine the changes in R<sub>o</sub> over a considerable depth range. The reflectance measurements for Site 391 are summarized graphically in Figure 2. Unfortunately, it becomes very difficult to infer the reflectance of primary vitrinite from deeper than 600 meters. The histograms of vitrinite reflectance below this depth do not exhibit modes which are consistent from sample to sample and which might represent primary vitrinite. What primary vitrinite is present probably constitutes the lower range of reflectance values for each histogram. Consequently, we interpret R<sub>o</sub> of primary vitrinite at 1364 meters to be about 0.43 per cent, corresponding to an LOM of about 7. Although the uncertainty in estimating the reflectance of primary vitrinite is apparent from Figure 2, the available data suggest that the Jurassic and younger sediments at Site 391 have not been buried deeply enough to reach the LOM (about 8; Hood et al., 1975) at which level significant oil generation begins.

The measurements of vitrinite reflectance at Site 392 appear to be affected by the presence of reworked vitrinite as were the Mesozoic sediments at Site 391. Because of the shallow depth of burial and the numerous values of R, less than 0.43 per cent, however, these sediments probably have not reached LOM's greater than 7.

## **Types of Organic Matter**

During the measurements of vitrinite reflectance, semiquantitative visual estimates of organic matter were made, according to the classification scheme in Table 3. Liptinite and amorphous kerogen represent lipid-rich material which is either structured (spores, algae, etc.) or unstructured, respectively. Vitrinite represents hydrogen-lean organic matter, typically derived from land plants. Inertinite includes thermally inert macerals such as fusinite, semifusinite, and micrinite. In contrast with previous reports (Hood et al., 1976), we no longer include reworked vitrinite in the category of inertinite because of the difficulty in distinguishing between primary and reworked vitrinite.

	TABLE 2			
Vitrinite Reflectance and	Level of Organic Metamorphism,	Sites 391	and	392

Sample (Interval in cm)		Vitrinite Reflectance (in oil)					
	Depth (m)	Reflectance Measurements <sup>a</sup>	No. of Observations	Range of % R.	Mean % R <sup>b</sup>	LOM <sup>C</sup>	
Site 391							
4A-3, 1-10	206	A X	26 29	0.20-0.45	$0.20 \pm 0.03$ $0.32 \pm 0.04$	<7 N.D. <sup>d</sup>	
7A-1, 57-59	326	A X	48	0.11-0.46	$1.24 \pm 0.02$ $0.26 \pm 0.03$	<7 N.D.	
13A-0, 0-3	526	X	24	0.22-0.54	$0.35 \pm 0.04$	N.D.	
7C-2, 110-112	728	X	69	0.28-1.00	$0.63 \pm 0.04$ $0.66 \pm 0.03$	N.D. N.D.	
9C-3, 37-40 10C-3, 110-113	833 900	X X	82 101	0.22-0.98 0.20-0.92	$0.61 \pm 0.04$ $0.53 \pm 0.03$	N.D. N.D.	
12C-4, 78-80	958	X	84	0.21-0.81	$0.49 \pm 0.03$	N.D.	
26C-3, 130	1147	x	85	0.25-0.88	$0.49 \pm 0.03$ $0.55 \pm 0.03$	N.D.	
27C-2, 8-9 49C-2, 124-126	1154 1364	X X	50 52	0.17-0.85 0.39-1.23	$0.43 \pm 0.05$ $0.86 \pm 0.04$	N.D. N.D.	
Site 392							
2-1, 78-80	67	x	60	0.26-1.00	0.69 ±0.04	N.D.	
2-1, 108-110 3-1, 23-25	67 79	X X	57 50	0.19-0.86 0.21-0.80	$0.47 \pm 0.04$ $0.49 \pm 0.04$	N.D. N.D.	

a"X" represents the range of all vitrinite reflectance measurements; "A" represents the range of reflectance measurements interpreted as primary vitrinite.

 $^{6}$  R<sub>o</sub> ±95% confidence limit.  $^{6}$  R<sub>o</sub> values less than 0.43% are assigned LOM <7 because of the difficulty of resolving the LOM 0-7 CAll R<sub>o</sub> values less than 0.43% are assigned LOM <7 because of the difficulty of resolving the LOM 0-7 because of the difficulty of resolving th range by means of vitrinite reflectance.  $R_0$  values > 0.43% are converted to LOM on the basis of Castano's  $R_0$ -LOM relationship (Hood and Castano, 1974). LOM's are indicated only for samples of primary vitrinite.

dNot determined.





 TABLE 3

 Relative Abundance of Types of Organic Matter

 By Visual Kerogen Analysis, Sites 391 and 392

Sample (Interval in cm)	Amorphous Kerogen	Liptinite	Vitrinite	Inertinite
Site 391				
4A-3, 0-10	7	2	2	3
7A-1, 57-59	7	2	4	2
13A-0, 0-3	7	2	3	2
6C-3, 96-100	1	2	7	4
7C-2, 110-112	1	2	7	4
9C-3, 37-40	1	2	7	4
10C-3, 110-113	1	2	7	4
12C-4, 78-80	1	2	6	4
16C-1, 130-132	1	2	7	4
26C-3, 130	1	1	7	4
27C-2, 8-9	2	2	7	4
49C-2, 124-126	1	1	7	1
Site 392				
2A-1, 78-80	1	1	7	1
2A-1, 108-110	1	2	7	4
3A-1, 23-25	1	1	7	3

<sup>a</sup>Numerical abundance scale and percentages (by area): 1=0-1%; 2=2-5%; 3=6-10%; 4=11-25%; 5=26-50%; 6=51-75%; 7=76-100%.

The visual kerogen analyses (Table 3) indicate that the Miocene and Mesozoic sediments differ in their maceral composition. Vitrinite is the dominant maceral in the kerogen of the Cretaceous and Jurassic sediments. The previously presented measurements of vitrinite reflectance suggest that a substantial portion of the vitrinite has been reworked from sediments with a prior thermal history. The organic matter in the Miocene sediments, on the other hand, is composed predominantly of amorphous kerogen, which may indicate a more pronounced contribution of marinederived organic matter.

A kerogen's maceral composition can influence its thermal reactivity. This effect can be seen by comparing the visual kerogen observations (Table 3) with the values of  $C_{eff}/C_{org}$  (Table 1). The  $C_{eff}/C_{org}$  values of the Mesozoic sediments at Sites 391 and 392 are mostly less than 0.05. Such low values of  $C_{eff}/C_{org}$  reflect the hydrogen-poor nature of the organic matter and, to some extent, the effects of a prior thermal history. While  $C_{eff}/C_{org}$  values of 0.12 to 0.20 are not very high, they nonetheless indicate that a greater fraction of the organic matter in the Miocene sediments is thermally reactive. The differences in organic composition between the Miocene and Mesozoic sediments may explain, in part, why the petroleum-generating potential of the Miocene sediments is greater though their organic carbon contents are not substantially higher.

### SUMMARY

The results of this study indicate that the petroleumgenerating potential of sediments recovered on DSDP Leg 44 is generally poor. Only a few sediment samples recovered at Sites 391 contain enough thermally reactive organic matter to be considered possible petroleum-source rocks. Visual kerogen observations reveal that most Mesozoic sediments contain large amounts of hydrogen-poor, land-plant material which explains why so little of the organic carbon is thermally convertible to petroleum. The petroleum-generating potential of these sediments is further limited because they have not been buried deeply enough to reach the temperatures at which significant petroleum generation occurs.

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