23. PETROLEUM-GENERATING POTENTIAL OF SEDIMENTS FROM LEG 47, DEEP SEA DRILLING PROJECT

J. W. Kendrick, A. Hood, and J. R. Castaño, Shell Development Company, Houston, Texas

ABSTRACT

The abundance, type, and thermal maturity of organic matter were used to characterize the petroleum-generating potential of sediments from Deep Sea Drilling Project Leg 47. Our results indicate that lower Miocene sediments off northwestern Africa contain sufficient amounts of thermally reactive organic matter to be considered potential, or future, source rocks of petroleum. Although Cretaceous sediments near the continental margin of Portugal contain one to two per cent organic carbon, not enough of that carbon is thermally convertible to petroleum for the sediments to generate significant amounts of petroleum. The differences in petroleum-generating potential are related to differences in the composition, as well as the amount, of preserved organic matter. Vitrinite reflectance data indicate that none of the sediments has attained sub-surface temperatures high enough for significant petroleum generation.

INTRODUCTION

RESULTS AND DISCUSSION

On Leg 47, the Deep Sea Drilling Project (DSDP) drilled at Site 397 on the continental rise of northwestern Africa ($26 \circ 50.7 'N$, $15 \circ 10.8 'W$), and at Site 398 near the Iberian continental margin ($40 \circ 57.6 'N$, $10 \circ 43.1 'W$). We obtained several sediment samples from these two drill sites for the purpose of evaluating their petroleum-generating potential. Our objectives were to determine whether the sediments contain enough thermally reactive organic matter for significant petroleum generation and whether the sediments have experienced sub-surface temperatures sufficiently high for the thermal conversion of kerogen to petroleum.

The sediment samples used in this study came from a collection of cores which were frozen and set aside for organic geochemical studies. On the basis of preliminary analyses by DSDP, we selected those cores which appeared to contain above-average amounts of organic carbon. With the exception of one Cretaceous sample, the sediments analyzed from Site 397 are Miocene and Quaternary in age. At Site 398, our attention was focused on Cretaceous sediments.

The analytical methods which we employed in this study have been described by Hood et al. (1976). Briefly summarized, we used analyses of organic carbon, effective carbon, and pyrolysis fluorescence to estimate the amounts of both total and thermally reactive organic matter in the sediments. To determine the thermal maturity of the organic matter in the sediments, we measured the reflectance (in oil) of vitrinite, a coal maceral which is disseminated in many sediments. During the analysis of vitrinite reflectance, we also estimated the relative abundance of the macerals which constitute the organic matter. We consider 1.0 to 1.5 per cent organic carbon (C_{org}) to be the minimum amount necessary for a sediment to be considered a potential, or future, source rock of petroleum. This criterion is based on work by Schraver and Zarella (1963) and Bonov (1958), who

Content of Organic Matter

Schrayer and Zarella (1963) and Ronov (1958), who measured the organic carbon contents of sediments in both petroliferous and non-petroliferous sedimentary basins. We regard laboratory pyrolysis techniques as better indicators of petroleum-generating potential, however, because they measure directly the amount of petroleum-like material generated by heating. Effective carbon (the pyrolyzable carbon measured by a flameionization detector) and pyrolysis fluorescence are two such measures of thermally reactive organic matter (Hood et al., 1976). It is our opinion that a sediment must have an effective carbon (C_{eff}) content of 0.26 per cent (0.3 per cent hydrocarbon) or a pyrolysis fluorescence value of 10 units before it can possibly be considered a potential petroleum source rock.

The sediments analyzed from Sites 397 and 398 contain between 0.36 and 2.34 per cent organic carbon (Table 1). Ten of the 18 samples contain more than 1.0 per cent $C_{org.}$, indicating that they may be potential source rocks. Pyrolysis measurements, however, indicate that only four sediment samples contain sufficient quantities of thermally reactive organic matter to merit consideration as potential source rocks. Some samples (such as 398D-95-3, 50-55cm) contain as much as 2.0 per cent organic carbon, but yield negligible hydrocarbons during laboratory pyrolysis and, consequently, are not considered to be potential source rocks of petroleum.

TABLE 1 Content of Organic Matter

Sample (Interval in cm)	Depth (m)	Age	%Corg.	PFa	%Ceff.	$\frac{C_{eff.}}{C_{org.}}$
Site 397						
6-3, 120-130	51	Pleistocene	0.72	0	0.14	0.19
10-6, 0-10	93	Pleistocene	0.43	8	0.06	0.14
12A-2, 0-45	1032	Miocene	1.74	150	0.42	0.24
16A-4, 25-30	1073	Miocene	1.84	20	0.47	0.26
23A-4, 25-36	1159	Miocene	1.24	10	0.28	0.23
51A-4, 140-150	1444	Hauterivian	0.73	8	0.05	0.07
Site 398						
57D-4, 145-150	961	Cenomanian	0.58	0	0.02	0.03
65D-4, 100-110	1037	Albian	0.36	0	0.01	0.03
69D-2, 100-103	1072	Albian	0.76	0	0.02	0.03
73D-4, 145-150	1123	Albian	1.14	0	0.03	0.03
77D-4, 108-113	1170	Albian	0.92	0	0.02	0.02
86D-4, 56-60	1255	Albian	1.56	0	0.04	0.03
90D-5, 30-40	1294	Albian	1.15	0	0.02	0.02
95D-3, 50-55	1331	Albian	2.01	0	0.08	0.04
97D-3, 0-7	1348	Albian	1.37	0	0.03	0.02
101D-3, 70-80	1386	Albian	0.63	0	0.01	0.02
122D-5, 118-120	1589	Aptian	2.34	0	0.35	0.15
130D-5, 134-137	1665	Barremian	1.38	0	0.01	0.01

^aArbitrary units.

Exhibiting effective carbon contents of 0.28 to 0.47 per cent, the lower Miocene sediments at Site 397 appear to have the greatest petroleum-generating potential of the formations we tested. These sediments were interpreted by shipboard scientists (see Site Report, this volume, Part 1) as representing a complex amalgamation of slump deposits, debris flows, and turbidites. The concentrations of organic matter in these sediments are higher than those of the overlying Quaternary hemipelagic sediments, even though the siliceous character of the younger sediments indicates conditions of high biological productivity. The low organic carbon contents of the Quaternary sediments suggest they were deposited below the oxygen-minimum zone which frequently develops at intermediate water depths in regions of high organic productivity (Hart and Currie, 1960). During the early Miocene, however, either the oxygen minimum extended to greater depths or substantial amounts of organic matter were redeposited from the oxygen-minimum zone into deeper water quickly enough to escape biochemical destruction.

The Cretaceous sediments, which are rich in organic matter elsewhere in the Atlantic (Lancelot et al., 1972; Kendrick et al., 1979; Berger and von Rad, 1972), contain comparatively little organic matter at Sites 397 and 398. It is difficult to explain why the petroleumgenerating potential of these sediments should be so low. The hydrogen-poor character of the organic matter indicates, however, that little of the biochemically and thermally reactive organic matter has been preserved. The preservation of the more stable organic components may indicate that the environment of deposition was only weakly reducing (Kendrick, 1979).

Maturity of Organic Matter

The thermal conversion of kerogen to petroleum is manifested by numerous changes in the chemical and physical properties of kerogen. The reflectance of vitrinite is commonly used to measure the thermal maturity of the kerogen. Because drilling at both Sites 397 and 398 penetrated more than 1.5 km of sediment, our chances of observing significant changes in vitrinite reflectance were better than usual.

The results of the vitrinite reflectance (R_0) measurements for Sites 397 and 398 are summarized in Table 2 and are displayed graphically as a function of depth in Figure 1.

A common problem in the interpretation of reflectance data is the presence of vitrinite which we think may have been either oxidized or reworked from older sediments with a prior thermal history (Hood and Castaño, 1974). Such particles will have reflectance values higher than those of primary vitrinite. The frequent overlap in reflectance values between reworked and primary vitrinite, however, makes it difficult to distinguish which values will be too high if the samples contain a large proportion of reworked vitrinite. Therefore, for several of the samples in Table 2, we have listed two values of vitrinite reflectance. The "X" value represents the mean and range for all reflectance observations which were made on the sample. For some samples, we have also designated an "A" value, which comprises those reflectance measurements that we interpret as primary vitrinite. We use the latter value as our estimate of the sediment's true level of maturity.

At Site 397, the samples shallower than 100 meters contain too little vitrinite to yield a reliable estimate of maturity (Figure 1). The Miocene and Cretaceous sedi-

TABLE 2 Vitrinite Reflectance

Sample (Interval in cm)	Depth (m)	R _o Popu- lation ^a	No. of Obser- vations	Range of %R ₀	Mean % Ro ^b
Site 397					
6-3, 120-130	51	X	8	0.15 - 0.41	0.32 ± 0.07
10-6, 0-10	93	X	14	0.18 - 0.64	0.42 ± 0.08
12A-2, 0-45	1032	A	45	0.23 - 0.50	0.35 ± 0.02
1972 (S.) 47 S. (1977)		X	45	0.23 - 0.50	0.35 ± 0.02
16A-4, 25-30	1073	A	60	0.23 - 0.46	0.34 ± 0.02
		X	67	0.23 - 0.59	0.35 ± 0.02
23A-4, 25-36	1159	A	51	0.26 - 0.46	0.35 ± 0.02
		X	51	0.26 - 0.46	0.37 ± 0.02
51A-4, 140-150	1444	A	120	0.30 - 0.58	0.42 ± 0.01
		х	120	0.30 - 0.58	0.42 ± 0.01
Site 398					
57D-4, 145-150	961	A	20	0.18 - 0.42	0.34 ± 0.04
		x	36	0.18 - 0.64	0.43 ± 0.04
65D-4, 100-110	1037	X	19	0.20 - 0.62	0.44 ± 0.06
69D-2, 100-103	1072	X	27	0.14 - 0.67	0.34 ± 0.06
73D-4, 145-150	1123	A	29	0.19 - 0.45	0.36 ± 0.03
		x	47	0.19 - 0.75	0.45 ± 0.04
77D-4, 108-113	1170	A	20	0.20 - 0.43	0.33 ± 0.03
		X	32	0.20 - 0.63	0.41 ± 0.04
86D-4, 56-60	1255	A	29	0.22 - 0.39	0.32 ± 0.02
		X	48	0.22 - 0.68	0.40 ± 0.03
90D-5, 30-40	1294	A	41	0.17 - 0.48	0.38 ± 0.03
		x	49	0.17 - 0.66	0.42 ± 0.03
95D-3, 50-55	1331	A	47	0.21 - 0.44	0.34 ± 0.02
		x	63	0.16 - 0.72	0.38 ± 0.03
97D-3, 0-7	1348	X	63	0.23 - 0.71	0.49 ± 0.03
101D-3, 70-80	1386	x	52	0.28 - 0.77	0.58 ± 0.03
122D-5, 118-120	1589	A	35	0.19 - 0.43	0.31 ± 0.03
		Х	44	0.19 - 0.57	0.36 ± 0.04
130D-5, 134-137	1665	A	31	0.19 - 0.40	0.27 ± 0.02
1		X	62	0.19 - 0.84	0.43 ± 0.05

^a"X" represents the range of all vitrinite reflectance measurements; "A" represents the range of reflectance measurements interpreted to be primary vitrinite. $b_{\rm e}^{\rm SR}R_{\rm O} \pm 95\%$ confidence limits.



Figure 1. Histograms of vitrinite reflectance (R_0) plotted as a function of depth for Sites 397 and 398. The dashed lines represent the inferred traces of R_0 for primary vitrinite. The histogram of the deepest sample at Site 397 is displayed at half-scale because of the large number of observations.

ments, on the other hand, appear to provide very good estimates of primary vitrinite reflectance. The mean reflectance of the Miocene sediments is about 0.35 per cent R_o while that of the Cretaceous sediment is 0.42 per cent.

The vitrinite reflectance values of the samples from Site 398 appear to be more broadly distributed than those from Site 397, implying that some of the vitrinite may have been oxidized or reworked. Recognition of primary vitrinite is complicated by the fact that the reflectance histograms in Figure 1 exhibit more than one mode which could be interpreted as primary vitrinite. The samples at 1589 and 1665 meters display a prominent mode at about 0.26 per cent R_o, whereas several other samples (at 961, 1123, 1331, and 1589 m) exhibit a mode at about 0.35 to 0.40 per cent R_o. While the significance of these different modes is unclear, we have included all reflectance values less than about 0.45 per cent R_o in our estimate of primary vitrinite reflectance. The resulting values of mean reflectance are in the range of 0.27 to 0.38 per cent.

The measured values of vitrinite reflectance are less than the value (about 0.5 per cent) at which significant oil generation begins (Vassoyevich et al., 1970; as modified by Teichmuller, 1971), indicating that the sediments recovered from Sites 397 and 398 are only thermally immature.

Types of Organic Matter

During the measurements of vitrinite reflectance, visual estimates of the types of organic matter were made, according to the classification shown in Table 3. Hydrogen-rich organic matter is classified as liptinite or amorphous kerogen, depending on whether it is structured (spores, algae, etc.) or unstructured. Vitrinite represents hydrogen-lean organic matter, typically derived from woody land plants. Inertinite includes thermally inert macerals such as fusinite, semi-fusinite, and micrinite.

The visual kerogen analyses (Table 3) indicate that vitrinite is the dominant maceral in most of the samples, implying that land-derived organic matter has strongly influenced the composition of the organic matter in the sediments. The common occurrence of liptinite (primarily spores, pollen, resins) and inertinite further attest to the terrestrial origins of the organic matter. Only the Miocene sediment samples from Site 397 contain large amounts of amorphous kerogen, possibly indicating an important component of marine-derived organic matter.

The differences in maceral composition observed visually correspond roughly to differences in the chemical composition of the organic matter. The ratio of effective carbon to organic carbon can be used as an index of a kerogen's hydrogen content (Kendrick, 1979). Those samples with the highest $C_{eff.}/C_{org.}$ values (Table 1) are those which contain predominantly amorphous kerogen (Table 3). Most of the remaining samples, which contain predominantly land-plant material, have $C_{eff.}/C_{org.}$ ratios less than 0.10. The liptinite in the Cre-

 TABLE 3

 Relative Abundance of Types of Organic Matter^a

Sample (Interval in cm)	Amorphous Kerogen	Lipti- nite	Vitri- nite	Interti- nite
Site 397				
6-3, 120-130	1	1	7	1
10-6, 0-10	1	1	7	3
12A-2, 0-45	7	1	2	1
16A-4, 25-30	7	1	1	1
23A-4, 25-36	7	1	2	1
51A-4, 140-150	1	2	7	1
Site 398				
57D-4, 145-150	1	2	7	3
65D-4, 100-110	1	1	7	3
69D-2, 100-103	1	1	7	4
73D-4, 145-150	1	1	7	3
77D-4, 108-113	1	1	7	3
86D-4, 56-60	1	4	6	4
90D-5, 30-40	1	3	6	4
95D-3, 50-55	1	4	6	4
97D-3, 0-7	1	2	7	4
101D-3, 70-80	1	1	7	4
122D-5, 118-120	3	3	6	3
130D-5, 134-137	2	3	6	4

^aNumerical abundance scale and percentage (by area): 1 = 0 to 1%; 2 = 2 to 5%; 3 = 6 to 10%; 4 = 11 to 15%; 5 = 26 to 50%; 6 = 51 to 75%; 7 = 76 to 100%.

taceous sediments at Site 398 appears to have no effect on the C_{eff}/C_{org} ratio of the kerogen.

These differences in kerogen composition strongly influence the petroleum-generating potential of the sediments. Those sediments which we judged to be potential source rocks have an average $C_{eff.}/C_{org.}$ ratio of 0.21, whereas the corresponding value for the nonsource rocks is 0.04. Therefore, while the average organic carbon content of the potential source rocks (1.8%) is less than twice that of the non-source rocks (1.0%), five times as much carbon in the source rock is convertible to hydrocarbon as in the non-source rock.

ACKNOWLEDGMENT

Difficulties in sample preparation led initially to anomalous vitrinite reflectance values for Site 397. The authors wish to thank W. G. Dow and D. B. Pearson, who lent us their vitrinite mounts for comparative study, and J. G. Erdman, who provided supplementary sample material. The manuscript was reviewed by J. M. Hunt and P. R. Mommessin.

REFERENCES

- Berger, W. H. and von Rad, U., 1972. Cretaceous and Cenozoic sediments from the Atlantic Ocean In Hayes, D. E., Pimm, A. C., et al., Initial Reports of the Deep Sea Drilling Project, v. 14; Washington (U. S. Government Printing Office) p. 787-954.
- Hart, T. J. and Currie, R. I., 1960. The Benguela Current, Discovery Reports, v. 31, p. 123-298.
- Hood, A. and Castaño, J. R., 1974. Organic Metamorphism: Its relationship to petroleum generation and application to studies of authigenic minerals, United Nations ES-CAP, CCOP Tech. Bull., v. 8, p. 85-118.
- Hood, A., Castaño, J. R., and Kendrick, J. W., 1976. Petroleum-generating potential and thermal history of DSDP Leg 39 sediments. *In* Talwani, M., Udintsev, G., et al.,

Initial Reports of the Deep Sea Drilling Project, v. 38: Washington, (U.S. Government Printing Office), p. 801-804.

- Kendrick, J. W., 1979. Geochemical studies of black clays from Leg 43, Deep Sea Drilling Project. In Tucholke, B., Vogt, P., et al., Initial Reports of the Deep Sea Drilling Project, v. 43: Washington (U.S. Government Printing Office), p. 633-642.
- Kendrick, J. W., Hood, A., and Castaño, J. R., 1979. Petroleum-generating potential of Cretaceous sediments from Leg 43, Deep Sea Drilling Project. In Tucholke, B., Vogt, P., et al., Initial Reports of the Deep Sea Drilling Project, v. 43: Washington (U.S. Government Printing Office), p. 663-668.
 - ncelot, Y., Hathaway, J. D., and Hollister, C. D., 1972. Lihology of sediments from the western North Atlantic, eg 11, Deep Sea Drilling Project. *In* Ewing, J. I., Hollis-

ter, C. D., et al., *Initial Reports of the Deep Sea Drilling Project*, v. 11: Washington (U. S. Government Printing Office), p. 901-949.

- Ronov, A. B. 1958. Organic carbon in sedimentary rocks (in relation to the presence of petroleum), *Geochemistry* (a translation of Geokhimiya), no. 5, p. 510-536.
- Schrayer, G. J. and Zarella, W. M., 1963. Organic geochemistry of shales — 1. Distribution of organic matter in siliceous Mowry Shale of Wyoming, *Geochim. Cosmochim. Acta*, v. 27, p. 1033-1046.
- Teichmüller, M., 1971. Anwendung Kohlenpetrographischer Methoden bei der Erdöl Und Erdgasprospection, Erdöl und Kohle, v. 24 p. 69-76.
- Vassoyevich, N. B., Korchagina, Yu. I., Lopatin N. V., and Chernyshev, V. V., 1970. Principal phase of oil formation, *Internatl. Geol. Rev.*, v. 12, p. 1276-1296.