

25. ORGANIC-GEOCHEMICAL CHARACTER AND HYDROCARBON-SOURCE POTENTIAL OF SITE 635¹

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ABSTRACT

The organic matter contained within a series of Albian to Cenomanian, dark gray to black marls was characterized using pyrolysis techniques and analysis (elemental and carbon isotopes) of isolated kerogens. It was concluded that this material had a marine affinity. Variations in geochemical characteristics reflect differences in the extent of preservation, rather than changes in organic provenance. These changes appear to reflect differences in water depth and the position of the depositional site relative to the oxygen-minimum zone. Sediments displaying the most elevated levels of organic-carbon and hydrogen enrichment probably reflect sedimentation within the oxygen-minimum zone. Waters within the oxygen-minimum zone were probably dysaerobic, rather than anoxic. The presence of at least trace quantities of oxygen at the depositional site explains the poor degree of organic preservation and the material's largely gas-prone characteristics.

INTRODUCTION

Leg 101 of the Ocean Drilling Program (ODP) was the first drilling activity conducted on the Bahamian Platform in more than a decade. Site 635, one of 11 sites, was located in the thalweg of Northeast Providence Channel (Fig. 1). Hole 635B penetrated 117.7 m of sediment that terminated in nannoplankton marls of late Albian age (Austin, Schlager, et al., 1986). Drilling was through a series of dark gray to black indurated limestones and light gray chalky limestones. Although not the primary objective of the leg, these dark limestones offered another opportunity to examine the carbon cycle during the Cretaceous. In addition, Site 635 provided an opportunity to address the hydrocarbon-source potential of a limited part of the Bahamian Platform. This is a region where hydrocarbon exploration has not yet been successful. Site 635 also permitted a comparison of organic-matter type and degree of organic preservation with other, slightly older, organic-rich carbonates recovered in the southeastern Gulf of Mexico, such as those at DSDP Site 535. Consequently, an analytical program was designed to provide general information about organic richness, organic character, and potential sources of hydrocarbons.

ANALYTICAL METHODOLOGY

Following an examination of the cores at the East Coast Repository, 22 samples were selected for analysis and characterization. Their stratigraphic distribution is summarized in Figure 2. Upon receipt, each sample was oven-dried at 60°C and ground to approximately 325 mesh (44 µm). Organic-carbon contents (C_{org}) and total sulfur were determined for each sample using a LECO analyzer after decarbonation. The remainder of the analytical program included whole-rock pyrolytic assay using the Rock-Eval system described by Espitalié et al. (1977) and elemental (C, H, O, and N) and stable carbon-isotopic analysis of isolated kerogens. Total clay content of each sample was determined using a Philips APD 3600 X-ray diffractometer. Several samples also were subjected to whole-rock pyrolysis-gas chromatography (PGC) using a flame ionization detector (FID), as described by Colling et al. (1986), to assist with organic characterization.

ANALYTICAL RESULTS

Organic Carbon and Total Sulfur

Organic-carbon contents ranged from 0.51 to 4.06 wt%. These data are detailed in Table 1 and Figure 2. All samples con-

tain above-average quantities of organic carbon (>0.3 wt%) relative to deep-sea sediments (McIver, 1975), and 13 samples contain above-average quantities (>1.0 wt%) relative to all fine-grained sedimentary rocks (Bissada, 1982). The richest samples (from Cores 101-635B-10R and 101-635B-11R) are of late Albian to early Cenomanian age (Austin, Schlager, et al., 1986).

Total-sulfur contents also are included in Table 1. Total-sulfur contents range from 0.25 to 1.79 wt%. A general increase in sulfur content occurs with increasing carbon content (Fig. 3). The observed carbon/sulfur ratios are typical of normal (non-euxinic) marine sediments (Berner and Raiswell, 1983) and are consistent with either aerobic or dysaerobic conditions at the sediment/water interface, with sulfate reduction occurring in the subsurface.

The two samples (101-635B-8R-1, 115-118 cm, and 101-635B-12R-2, 30-32 cm) that exhibit higher sulfur contents than the general trend contain slightly more total clays (greater than 20% compared with the typical 5% to 13% of most samples studied) and, therefore, probably contain more iron (Table 1). Iron commonly is a limiting factor for pyrite formation in carbonate systems.

Rock-Eval Pyrolysis

Pyrolytic assay provides information about generation potential, organic character, and the extent of thermal diagenesis. Pyrolysis results are summarized in Table 1 and Figure 2.

Total pyrolytic yields [$S_1 + S_2 =$ free distillable hydrocarbons (HC) + generative hydrocarbons] range from 0.10 to 16.79 mg HC/g rock. Good potential and/or effective hydrocarbon source rocks yield >6 mg HC/g rock (Tissot and Welte, 1984). Within the present sample suite, sediments of this quality are confined to an interval represented in Cores 101-635B-10R and 101-635B-11R, of late Albian to early Cenomanian age. Shipboard data indicated that within this stratigraphic interval additional discrete intervals of good source potential may exist (Shipboard Scientific Party, 1986).

Rock-Eval data also provide a limited amount of information about the nature of the organic matter and type of hydrocarbon products that may be expected upon thermal maturation. This type of interpretation is accomplished using the hydrogen (mg S_2 HC/g C_{org}) and oxygen (mg CO_2 /g C_{org}) indices and a modified van Krevelen diagram (Espitalié et al., 1977), in a manner similar to elemental hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios. However, unlike elemental data, which are obtained for isolated kerogen, organic-matter characteriza-

¹ Austin, J. A., Jr., Schlager, W., et al., 1988. *Proc. ODP, Sci. Results*, 101.

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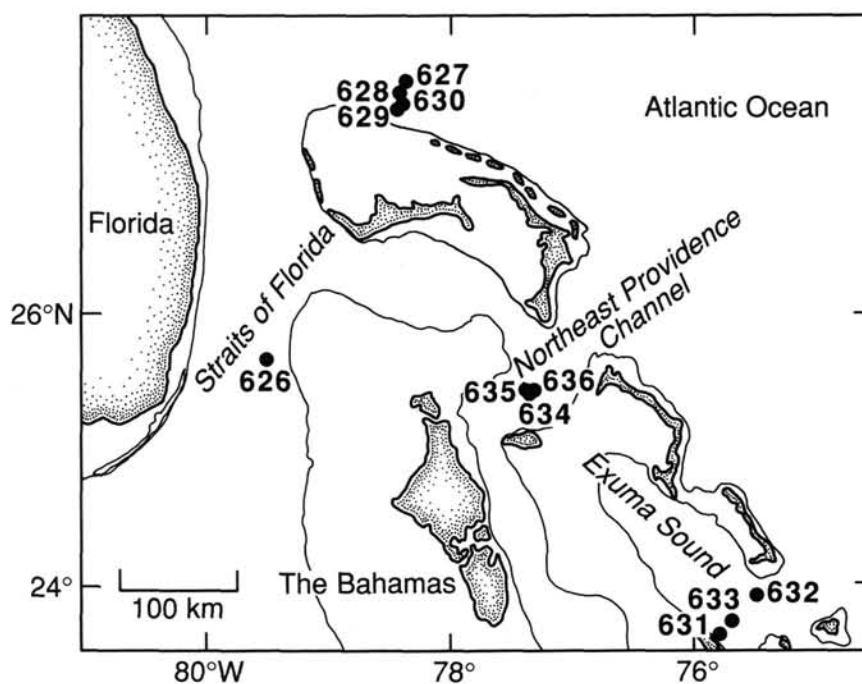


Figure 1. Location map for Leg 101 sites.

Table 1. Summary of LECO, Rock-Eval, and clay-content data for Hole 635B.

Core/section-interval (cm)	Depth (mbsf)	Organic carbon (wt%)	Total sulfur (wt%)	S_1 S_2		HI ^a	OI ^b	T_{max} (°C)	Total clays
				(mg HC/g rock)					
8R-1, 53-57	61.53	1.59	0.31	0.11	4.10	258	123	434	5
8R-1, 115-118	62.15	1.03	1.53	0.05	0.81	79	205	— ^c	26
8R-CC, 3-6	70.53	0.99	0.25	0.05	1.88	192	185	431	6
9R-1, 40-43	71.00	0.83	0.26	0.04	1.48	178	164	431	4
9R-1, 87-90	71.47	1.36	0.26	0.11	3.82	280	114	434	5
10R-1, 15-18	80.35	0.55	0.63	0.04	0.32	58	274	—	13
10R-2, 56-60	82.26	0.84	0.26	0.05	1.38	165	191	431	4
10R-2, 73-77	82.43	3.03	0.63	0.31	12.96	428	89	427	8
10R-3, 67-70	83.87	2.82	0.70	0.27	10.08	358	102	428	10
10R-3, 83-86	84.03	1.36	0.34	0.11	3.24	238	166	434	8
10R-CC, 0-5	89.40	1.23	0.37	0.09	2.98	242	176	433	7
11R-1, 61-64	90.21	2.54	0.51	0.25	9.30	366	106	426	6
11R-1, 88-92	90.48	3.20	0.60	0.33	14.52	454	79	427	8
11R-2, 26-30	91.36	4.06	0.99	0.34	16.45	405	73	425	10
11R-3, 5-9	92.65	2.05	0.63	0.13	5.63	275	122	431	0
12R-1, 60-62	99.70	0.60	0.31	0.02	0.57	95	218	—	7
12R-2, 30-32	100.90	1.60	1.79	0.12	2.55	159	202	427	23
12R-3, 12-15	102.22	0.68	0.36	0.03	0.65	96	212	—	8
13R-1, 11-13	108.41	1.11	0.56	0.04	1.21	109	154	431	13
13R-2, 7-10	109.87	0.87	0.45	0.03	0.63	72	166	—	13
13R-2, 105-109	110.85	0.85	0.41	0.03	0.67	79	189	—	11
14R-3, 145-149	116.87	0.51	0.70	0.01	0.09	18	372	—	11

^a Hydrogen index; mg S_2 HC/g C_{org} .^b Oxygen index; mg S_3 CO_2 /g C_{org} .^c No reliable determination.

Note: R = rotary drill.

tion by whole-rock pyrolysis is affected by both the mineral matrix and the level of organic enrichment (Katz, 1983).

Both hydrogen and oxygen indices exhibit wide variability (Fig. 4). The organically richer samples fall between the type II and type III reference curves. Type II material typically is well-preserved marine organic matter. The remaining samples appear more closely aligned with the type III reference curve. Type III material represents either oxidized marine or terrestrially derived organic matter. The highest oxygen indices are associated with the organically leanest samples. This represents the poorest degree of preservation (i.e., highest degree of oxidation), a

crease in the signal/noise ratio (caused by an increase in the relative proportion of inorganically derived CO_2 from the limestone matrix; Palacas et al., 1981; Katz, 1983), or both.

Pyrolysis also provides two measures of thermal maturity: the transformation ratio [$TR = S_1/(S_1 + S_2)$] and T_{max} , the temperature at which maximum or peak pyrolytic hydrocarbon generation occurs. The T_{max} values, which are less than 435°C (Table 1), and the TR values, which are below 0.10, indicate that these samples are thermally immature and have not yet entered into the main phase of hydrocarbon generation and expulsion (see Shipboard Scientific Party, 1986).

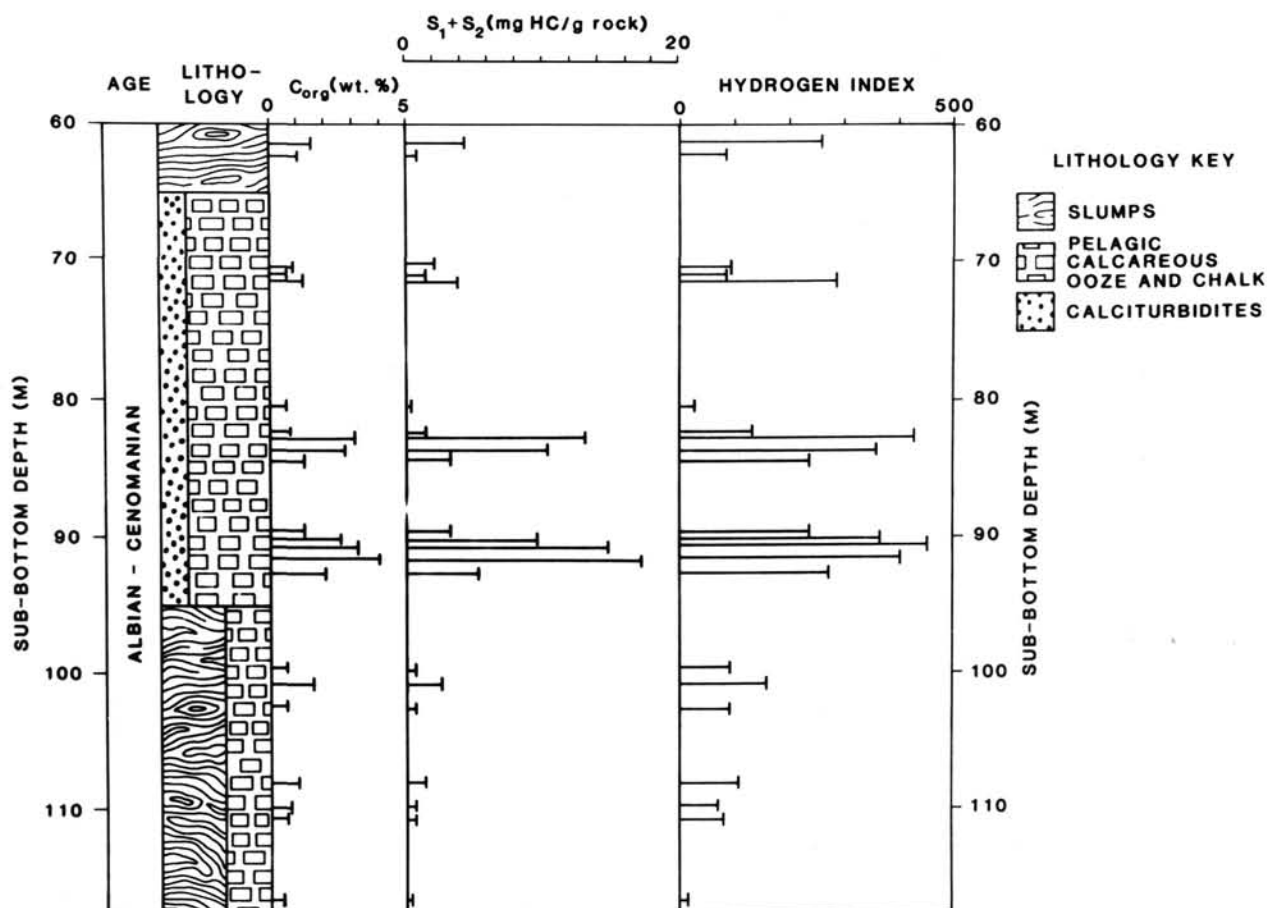


Figure 2. Stratigraphic and geochemical summary of Hole 635B.

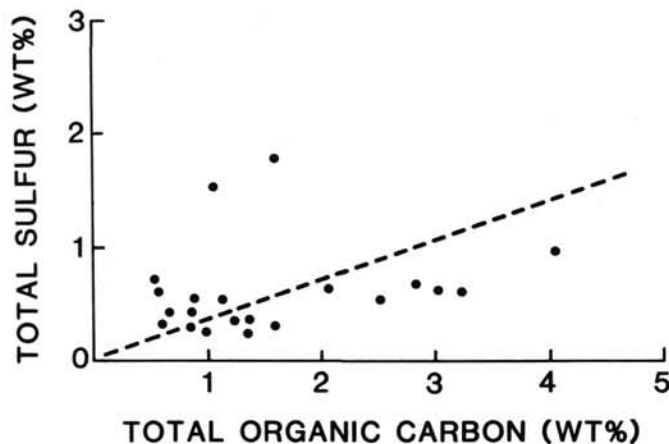


Figure 3. Relationship between total organic carbon and total sulfur. The dashed line represents the observed relationship for normal, modern marine sediments (Bernier and Raiswell, 1983).

Elemental Analysis

Elemental compositions of isolated kerogens are presented in Table 2 and Figure 5. The atomic H/C and O/C ratios confirm the general characterization of the organic matter obtained by pyrolysis. In general, the material is intermediate between the type II and type III reference curves, which suggests either an intermediate kerogen resulting from a mixture of sources or moderate and variable oxidation of marine-derived organic matter.

The most significant difference between these data and the Rock-Eval data occurs in apparent oxygen content. The elemental data (O/C ratio) do not exhibit the same elevated values or variability as those of the Rock-Eval (oxygen index) data. This confirms, at least in part, that the elevated pyrolysis oxygen indices resulted from matrix contributions and/or analytical complications, but not from severe oxidation such as was observed at DSDP Site 402 (Bay of Biscay), where the atomic O/C ratios were commonly greater than 0.25 (Deroo et al., 1979).

Stable Carbon-Isotopic Analysis

Carbon-isotope data obtained for kerogen isolates also are presented in Table 2. These data exhibit variation of about 1.5 ppt, with $\delta^{13}\text{C}$ values ranging from -27.07 to -25.56% , relative to PDB. These values are typical of those reported elsewhere for marine-derived Cretaceous material (Dean et al., 1986) and exhibit a similar relationship with respect to their hydrogen index values (Fig. 6) as samples of the Niobrara Limestone (Arthur et al., 1985). The slightly heavier nature of the organically leaner units, compared with the more enriched units, has been noted elsewhere (Pratt and Threlkeld, 1984) and was attributed to early diagenetic changes during transport and deposition (Pratt et al., 1986).

If these data were interpreted in relation to Neogene material, they should indicate an abundance of terrestrial material, which typically exhibits a $\delta^{13}\text{C}$ range between -33 and -23% , relative to PDB (Sackett, 1964). Dean et al. (1986) suggest, however, that $\delta^{13}\text{C}$ fractionation by marine organisms was greater during the Cretaceous. Consequently, marine material should be isotopically lighter (i.e., more negative) than Neogene plank-

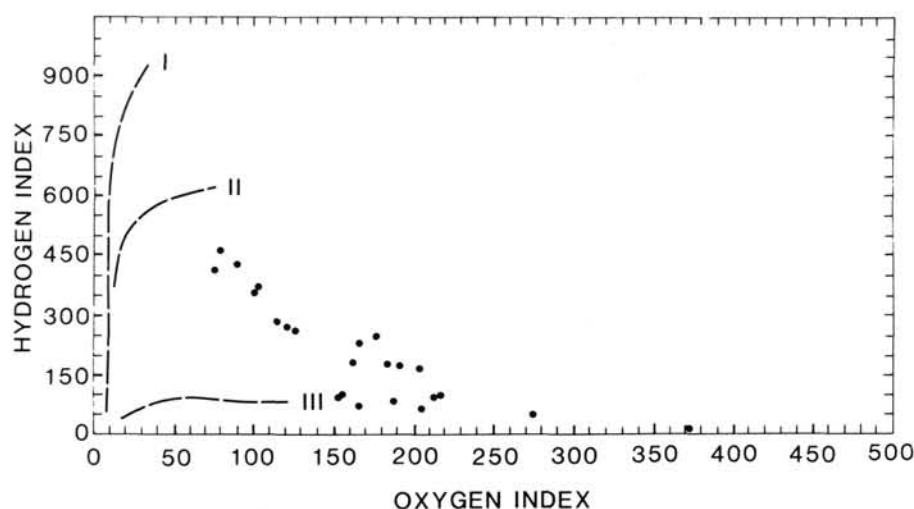


Figure 4. Modified van Krevelen diagram using the pyrolysis-derived hydrogen and oxygen indices.

Table 2. Elemental and isotopic analyses of isolated kerogens for Hole 635B.

Core/section-interval (cm)	Depth (mbsf)	H	C	O	N	Ash	H/C	O/C	$\delta^{13}\text{C}$ (% PDB)
		(wt%)					Atomic ratios		
8R-1, 53-57	61.53	5.29	59.62	14.51	2.31	8.73	1.06	0.183	-26.79
8R-1, 115-118	62.15	^a —	—	—	—	59.63	—	—	-27.07
8R-CC, 3-6	70.53	4.18	48.44	4.25	1.82	10.31	1.03	0.066	-26.69
9R-1, 40-43	71.00	5.19	57.62	10.68	1.99	14.51	1.07	0.139	-26.63
9R-1, 87-90	71.47	5.70	63.79	12.02	2.66	6.22	1.07	0.141	-26.40
10R-1, 15-18	80.35	—	—	—	—	38.39	—	—	-26.29
10R-2, 56-60	82.26	5.47	63.85	12.37	2.19	6.83	1.02	0.146	-25.89
10R-2, 73-77	82.43	5.27	59.78	9.52	2.30	6.33	1.05	0.120	-26.41
10R-3, 67-70	83.87	5.22	58.83	13.33	2.49	6.84	1.06	0.170	-26.64
10R-3, 83-86	84.03	5.13	58.34	12.08	2.16	0.36	1.05	0.155	-26.21
10R-CC, 0-5	89.40	4.20	51.16	11.41	1.85	21.63	0.98	0.167	-26.56
11R-1, 61-64	90.21	5.01	60.01	10.36	3.10	3.22	1.00	0.130	-26.64
11R-1, 88-92	90.48	5.12	59.52	9.77	3.21	5.64	1.02	0.123	-26.38
11R-2, 26-30	91.36	3.75	45.03	10.34	2.10	2.69	0.99	0.172	-26.51
11R-3, 5-9	92.65	4.66	58.16	10.07	5.50	22.04	0.95	0.130	-26.49
12R-1, 60-62	99.70	5.23	56.70	4.75	0.66	14.66	1.10	0.063	-26.46
12R-2, 30-32	100.90	3.04	35.00	6.06	0	5.05	1.04	0.130	-26.41
12R-3, 12-15	102.22	3.88	44.34	7.31	0	20.43	1.05	0.124	-25.62
13R-1, 11-13	108.41	—	—	—	—	38.71	—	—	-25.56
13R-2, 7-10	109.87	2.91	41.16	9.22	0	13.78	0.84	0.168	-25.59
13R-2, 105-109	110.85	4.39	57.50	12.19	0.27	29.20	0.91	0.159	-25.60
14R-3, 145-149	116.87	3.27	50.80	10.83	0	21.77	0.77	0.160	-25.67

^a Ash content too high for reliable determination.
Note: R = rotary drill.

ton and lighter by several parts per thousand than Cretaceous terrestrial vegetation. Interpretation of these data, therefore, is not clear cut, but the data do suggest marine-derived material. The relationship exhibited between $\delta^{13}\text{C}$ and the hydrogen index values (Fig. 6) suggests that the organic matter is of a single type that exhibits varying degrees of preservation, rather than varying input sources.

Pyrolysis-Gas Chromatography

Pyrolysis-gas chromatography (PGC) is thought to be more sensitive for establishing differences in kerogen compositions than Rock-Eval pyrolysis or the elemental analysis of isolated kerogens (Larter and Douglas, 1980). PGC provides a means of qualitatively and/or quantitatively characterizing the principal generation products of a sample using the chromatographic "fingerprint" of the pyrolysate (Dembicki et al., 1983).

The chromatograms obtained can be divided into two groups. One group, represented by Sample 101-635B-11R-1, 88-92 cm (Fig. 7A), is associated with the organically richer samples. These

samples, based on Rock-Eval and elemental data, display the greatest type II affinity. The associated chromatograms exhibit a well-defined series of alkane-alkene doublets and a naphthenic envelope. These alkane-alkene doublets exhibit a harmonic decrease in abundance with increasing carbon number. Such patterns are typical of those obtained for samples containing well-preserved marine organic matter (i.e., type II, Fig. 7B).

The second group of chromatograms, represented by Sample 101-635B-9R-1, 87-90 cm (Fig. 7C) is associated with the organically leaner samples. This group, based on Rock-Eval and elemental data, exhibits more of a type III affinity. The chromatograms display poorly defined peaks. This pattern clearly is different from that of terrestrially dominated samples (Fig. 7D). Samples containing predominantly terrestrial organic matter exhibit abundant aromatic compounds as well as alkane-alkene doublets. Unlike marine-dominated systems, however, the alkane-alkene doublets do not exhibit a harmonic decrease in abundance with increasing carbon number. The poorly defined peaks, as observed in Sample 101-635B-9R-1, 87-90 cm (Fig. 7C), are

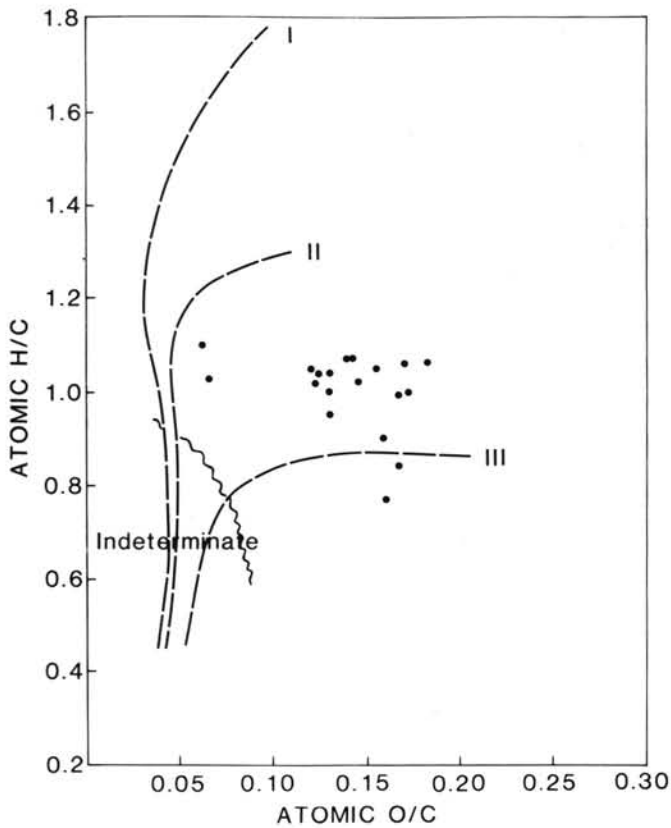


Figure 5. Conventional van Krevelen diagram using the atomic H/C and O/C ratios derived from isolated kerogens.

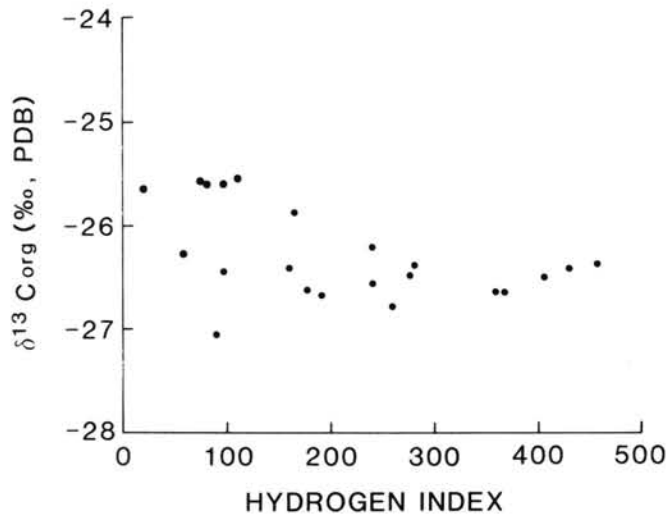


Figure 6. Relationship between the $\delta^{13}\text{C}$ content obtained using kerogen isolates and whole-rock hydrogen indices.

more typical of poorly preserved, oxidized organic matter independent of organic provenance.

Discussion

Bulk geochemical data have been used commonly to characterize both hydrocarbon products and sources of organic matter. Tissot and Welte (1984) suggest that the "kerogen type" is principally the result of the organic source, i.e., marine plankton, terrestrial plant debris, algal remains, and the like. Jones and Demaison (1982), however, state that bulk geochemical char-

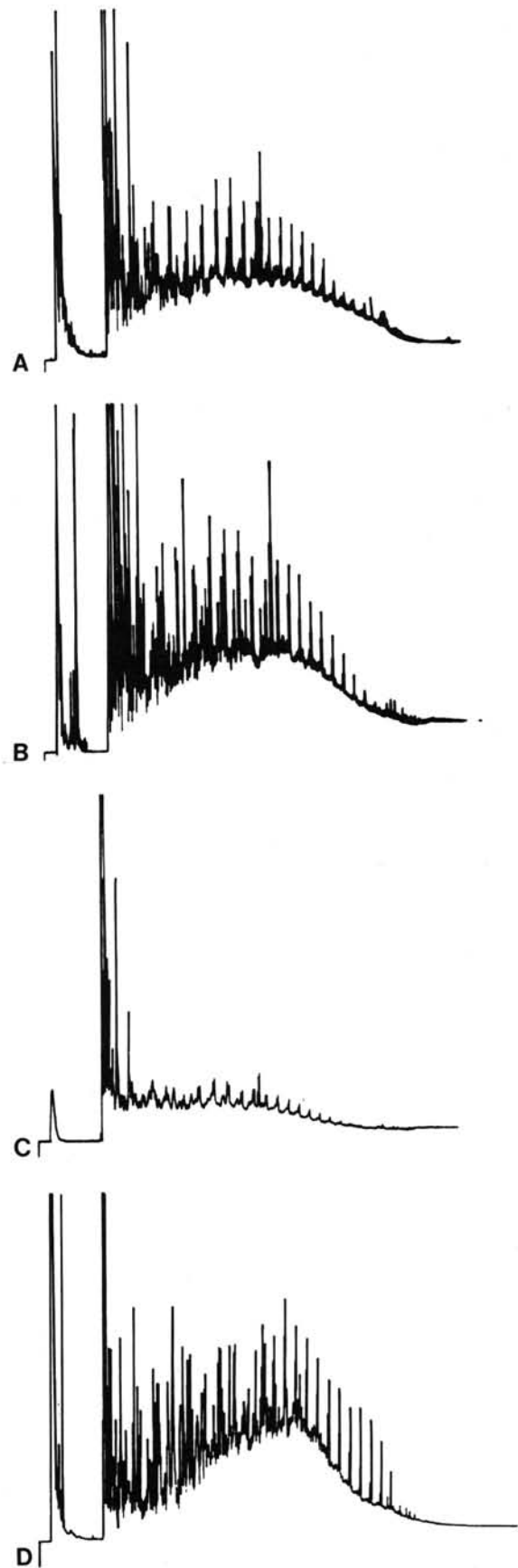


Figure 7. Representative pyrolysis-gas chromatograms; A. Sample 101-635B-11R-1, 88-92 cm. B. Immature Antelope Shale (San Joaquin Basin). C. Sample 101-635B-9R-1, 87-90 cm. D. Immature Brazil Block Coal (Parke Co., Indiana). See text for details.

acteristics reflect not only original organic-matter character, but also the conditions associated with its deposition and preservation. Specifically, the levels of both organic-carbon and hydrogen enrichment largely reflect the concentration of oxygen throughout the water column and exposure time (settling time and sedimentation rate). In other words, higher oxygen content and/or longer exposure time will generally result in smaller quantities of more degraded kerogens in the rock record.

Typically, carbonate rocks are of local intrabasinal origin (Ham and Pray, 1962). Such a sedimentary provenance affects not only the inorganic rock matrix but also the associated organic matter. Consequently, in most carbonate depositional systems it is unlikely that there is a large influx of allochthonous land-plant debris (Hunt, 1967). Therefore, this should be taken into consideration when the data are interpreted.

A lack of significant higher plant input implies that although the bulk organic-geochemical data suggest an intermediate composition between types II and III, such data should not, in this instance, simply be attributed to a mixture of two organic sources. The data more likely reflect the depositional system as a whole and its inability to preserve the more labile hydrogen-enriched organic compounds. Waples (1983) suggested that marine kerogens, because of their amorphous and "spongy" nature, which provides a high surface-area/volume ratio, are prone to degradation (i.e., oxidation). This degradation need not be complete. Koyama et al. (1973) showed that the relative rates of decrease in elemental concentration during degradation are organic H > organic N > organic C. Therefore, situations may exist where organic hydrogen is reduced, while elevated levels of organic carbon may still be preserved.

Both carbon-isotope and PGC data suggest that differences in bulk geochemical parameters are caused by variations in the extent of preservation, rather than organic provenance. The carbon-isotope data are nearly uniform and suggest a principally marine affinity, using a Cretaceous interpretive scale (Dean et al., 1986). The PGC data display a reduction in peak magnitude and definition with increasing type III affinity and do not display an increase in aromaticity. In general, one may conclude that the organic matter present in all of the examined samples represents degraded type II (marine-derived) kerogens with only marginal oil-generation potential and that the sediments, upon thermal maturation, will generate principally gas. The reduction in hydrogen is greatest for the organically leanest samples; i.e., the amount of residual or inert carbon is inversely proportional to the organic-carbon content (Fig. 8). The observed variations

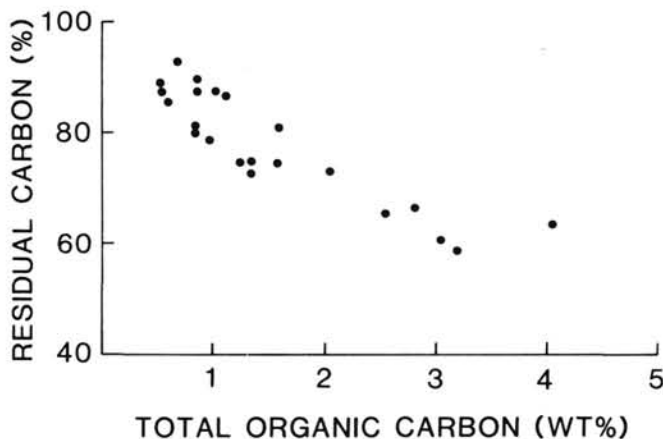


Figure 8. Relationship between residual (nonpyrolyzable) carbon and total-organic-carbon content. Residual carbon is the percentage of the original C_{org} present after pyrolysis.

in both C_{org} and organic-hydrogen content clearly indicate variability in the degree of preservation through time. Similar conclusions were drawn by Pratt (1984) for the Greenhorn Formation, where relative hydrogen enrichment increases with C_{org} and the degree of preservation.

The observed variability in the organic-geochemical character may reflect the oxygen content of the bottom waters, the exposure time to oxygenated waters, or both. While numerous authors have suggested that bottom waters in the North Atlantic had intermittently become anoxic during the Cretaceous (Arthur and Schlanger, 1979; Jenkyns, 1980; Summerhayes and Marsaran, 1983), no evidence for truly anoxic waters was present at Site 635. Even the most organically enriched samples in Hole 635B, which display the greatest type II affinity and highest degree of organic preservation, do not exhibit bulk characteristics typical of well-preserved marine organic matter, as observed, for example, in the Monterey Formation (Katz and Elrod, 1983), the lower Toarcian shales of the Paris Basin (Tissot and Welte, 1984), or at DSDP Site 367 (Deroo et al., 1978).

Furthermore, both the dark and light limestones generally are heavily bioturbated (Shipboard Scientific Party, 1986). The presence of macroscopic benthic burrowers and scavengers indicates at least some oxygen in the bottom waters (Theede et al., 1969) during deposition of both the light (organically lean) and dark (organically rich) layers. Therefore, both the sedimentologic and organic-geochemical data indicate that the maximum degree of organic preservation occurred during periods when the bottom waters were dysaerobic and that more oxygenated conditions were present during periods of poorer preservation.

Alternatively, the degree of preservation may have been controlled by exposure time, as reflected by sedimentation and burial rates. Such variability is consistent with the episodic nature of slumping and turbidity flows observed at the drilling site (Shipboard Scientific Party, 1986). Crevello et al. (1984) noted that turbidity flows were a major factor controlling the extent of organic preservation in Pliocene to Holocene sediments in the Tongue of the Ocean. Better organic preservation was observed in the rapidly deposited turbidites, compared with the slowly deposited periplatform oozes. At Site 635 the poor degree of organic preservation within a rapidly deposited debris flow (Sections 101-635B-12R-2 through 101-635B-13R-2) suggests that oxygen content, rather than sedimentation rate, played the dominant role.

If these sediments are compared with the slightly older, organic-rich carbonate sediments recovered at DSDP Site 535 in the southeastern Gulf of Mexico, several significant differences can be noted. Principally, the organic matter contained in the Lower Cretaceous section of Site 635 is better preserved. This is manifested by higher levels of hydrogen enrichment. H/C ratios at Site 635 typically are greater than 1.2 (Katz, 1984), compared with a maximum of 1.1 at Site 535.

At DSDP Site 535 the sediment appears to have originated at much shallower depths than the final bathyal depositional environment. This interpretation is based on benthic foraminifers, which include several shallow-water platform species (Sliter and Premoli-Silva, 1984). The initial depositional site was probably within a region where a strong, well-defined oxygen-minimum zone impinged upon the continental shelf and upper slope. Anoxic or near-anoxic conditions probably existed within the oxygen-minimum zone. As a result of downslope transporting processes, the organic matter was brought rapidly to its final depositional site. Both the initial deposition within an oxygen-minimum zone and the rapid final burial permitted relatively efficient preservation.

At Site 635 the degree of organic preservation was controlled principally by the depositional site's position relative to the oxygen-minimum zone. At Site 635 paleontologic evidence (calcare-

ous nannofossils and planktonic foraminifers) exist to show a progressive increase in water depth with time (Shipboard Scientific Party, 1986). Initially at this site, deposition appears to have occurred above the oxygen-minimum zone. As time progressed and the water depth increased, deposition probably took place within the oxygen-minimum zone. This depositional period is best represented by Sections 101-635B-10R-2 through 101-635B-11R-3. Available organic-geochemical data suggest that conditions within the oxygen-minimum zone were less intense than those associated with DSDP Site 535 (i.e., dysaerobic compared to anoxic). The cyclic alternations observed within the limestone sequence probably reflect changes in both the intensity and width of the oxygen-minimum zone. With continued deepening, deposition may have occurred near the base of or below the oxygen-minimum zone.

SUMMARY

1. All examined samples contained elevated levels of organic carbon relative to deep-sea sediments, with the richest samples recovered from Cores 101-635B-10R and 101-635B-11R (late Albian to early Cenomanian age).

2. Pyrolytic yields indicated that good hydrocarbon source potential was limited to Cores 101-635B-10R and 101-635B-11R. The bulk geochemical characteristics of this material suggested that if these sediments had matured thermally, their principal product should be gas and that only minor quantities of oil could be expected to be generated and expelled.

3. Other geochemical data suggested that the gas-proneness of the sampled interval resulted from oxidation of originally oil-prone, hydrogen-enriched organic matter before final burial.

4. The sedimentologic and geochemical data suggested that the degree of organic preservation was controlled by the depositional site's position relative to the oxygen-minimum zone. The best preserved organic matter was deposited within the oxygen-minimum zone.

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REFERENCES

- Arthur, M. A., Dean, W. E., and Claypool, G. E., 1985. Anomalous ^{13}C enrichment in modern marine organic carbon. *Nature*, 315:216-218.
- Arthur, M. A., and Schlager, S. O., 1979. Cretaceous "oceanic anoxic events" as causal factors in development of reef-reservoired giant oil fields. *AAPG Bull.*, 63:870-885.
- Austin, J. A., Jr., Schlager, W., et al., 1986. *Proc. ODP, Init. Repts.*, 101: College Station, TX (Ocean Drilling Program).
- Berner, R. A., and Raiswell, R., 1983. Burial of organic carbon and pyrite sulfur in sediments over Phanerozoic time: a new theory. *Geochim. Cosmochim. Acta*, 47:855-862.
- Bissada, K. K., 1982. Geochemical constraints on petroleum generation and migration—a review. *Proc. 2nd ASCOPE Conf. Exhib.*, 69-87.
- Colling, E. L., Burda, B. H., and Kelley, P. A., 1986. Multi-dimensional pyrolysis-gas chromatography: applications in petroleum geochemistry. *J. Chromatogr. Sci.*, 24:7-12.
- Crevello, P. D., Patton, J. W., Oesleby, T. W., Schlager, W., and Droxler, A., 1984. Source rock potential of Bahamian trough carbonates. In Stow, D.A.V., and Piper, D.J.W. (Eds.), *Fine-Grained Sediments: Deep-Water Processes and Environments*: Oxford (Geol. Soc.), 469-480.
- Dean, W. E., Arthur, M. A., and Claypool, G. E., 1986. Depletion of ^{13}C in Cretaceous marine organic matter: source, diagenetic, or environmental signal? *Mar. Geol.*, 70:119-157.
- Demaison, G., Holck, A.J.J., Jones, R. W., and Moore, G. T., 1984. Predictive source bed stratigraphy: a guide to regional petroleum occurrence—North Sea basin and eastern North American continental margin. *Proc. 11th World Pet. Congr.*: New York (John Wiley), 2: 17-29.
- Dembicki, H., Jr., Horsfield, B., and Ho, T.T.Y., 1983. Source rock evaluation by pyrolysis-gas chromatography. *AAPG Bull.*, 67:1094-1103.
- Deroo, G., Herbin, J. P., Rouchache, J., Tissot, B., Albrecht, P., and Schaeffle, J., 1978. Organic geochemistry of some Cretaceous black shales from Sites 367 and 368, Leg 41, eastern North Atlantic. In Lancelot, Y., Seibold, E., et al., *Init. Repts. DSDP*, 41: Washington (U.S. Govt. Printing Office), 865-873.
- Deroo, G., Herbin, J. P., Rouchache, J., and Tissot, B., 1979. Organic geochemistry of Cretaceous mudstones and marly limestones from DSDP Sites 400 and 402, Leg 48, eastern North Atlantic. In Montadert, L., Roberts, D. G., et al., *Init. Repts. DSDP*, 48: Washington (U.S. Govt. Printing Office), 921-930.
- Espitalié, J., Madec, M., Tissot, B., Menning, J. J., and Leplat, P., 1977. Source rock characterization methods for petroleum exploration. *Proc. 1977 Offshore Technol. Conf.*, 3:439-443.
- Ham, W. E., and Pray, L. C., 1962. Modern concepts and classifications of carbonate rocks. In Ham, W. E. (Ed.), *Classification of Carbonate Rocks*: Tulsa (Am. Assoc. Petrol. Geol.), 2-19.
- Hunt, J. M., 1967. The origin of petroleum in carbonate rocks. In Chilingar, G. V., Bissell, H. J., and Fairbridge, R. W. (Eds.), *Carbonate Rocks*: New York (Elsevier), 225-251.
- Jenkyns, H. C., 1980. Cretaceous anoxic events: from continents to oceans. *J. Geol. Soc. London*, 137:171-188.
- Jones, R. W., and Demaison, G. J., 1982. Organic facies—stratigraphic concept and exploration tool. *Proc. 2nd ASCOPE Conf. Exhib.*, 51-68.
- Katz, B. J., 1983. Limitations of "Rock-Eval" pyrolysis for typing organic matter. *Org. Geochem.*, 4:195-199.
- , 1984. Source quality and richness of Deep Sea Drilling Project Site 535 sediments, southern Gulf of Mexico. In Buffler, R. T., Schlager, W., et al., *Init. Repts. DSDP*, 77: Washington (U.S. Govt. Printing Office), 445-450.
- Katz, B. J., and Elrod, L. W., 1983. Organic geochemistry of DSDP Site 467, offshore California, middle Miocene to lower Pliocene strata. *Geochim. Cosmochim. Acta*, 47:389-396.
- Koyama, T., Nikaido, M., Tomino, T., and Hayakawa, H., 1973. Decomposition of organic matter in lake sediments. *Proc. Int. IAGC Hydrogeochem. Biogeochem. Symp.*, 2:512-535.
- Larter, S. R., and Douglas, A. G., 1980. A pyrolysis-gas chromatographic method for kerogen typing. In Douglas, A., and Maxwell, J. R. (Eds.), *Advances in Organic Geochemistry, 1979*: New York (Pergamon Press), 584-597.
- McIver, R. D., 1975. Hydrocarbon occurrences from JOIDES Deep Sea Drilling Project cores. *Proc. 9th World Pet. Congr.*: London (Applied Science Publ.), 2:269-280.
- Palacas, J. G., Daws, T. A., and Applegate, A. V., 1981. Preliminary petroleum source-rock assessment of pre-Punta Gorda rocks (lowermost Cretaceous—Jurassic?) in south Florida. *Trans. Gulf Coast Assoc. Geol. Soc.*, 31:369-376.
- Pratt, L. M., 1984. Influence of paleoenvironmental factors on preservation of organic matter in the mid-Cretaceous Greenhorn Formation, Pueblo, Colorado. *AAPG Bull.*, 68: 1146-1159.
- Pratt, L. M., Claypool, G. E., and King, J. D., 1986. Geochemical imprint of depositional conditions on organic matter in laminated-bioturbated interbeds from fine grained marine sequences. *Mar. Geol.*, 70:67-84.
- Pratt, L. M., and Threlkeld, C. N., 1984. Stratigraphic significance of $^{13}\text{C}/^{12}\text{C}$ ratios in Mid-Cretaceous rocks of the western interior, U.S.A. In Stott, D. F., and Glass, D. J. (Eds.), *The Mesozoic of Middle North America*: Calgary (Can. Soc. Pet. Geol.), 305-312.
- Sackett, W. M., 1964. The depositional history and isotopic organic carbon compositions of marine sediments. *Mar. Geol.*, 2:173-185.
- Shipboard Scientific Party, 1986. Sites 635 and 636: Northeast Providence Channel. In Austin, J. A., Jr., Schlager, W., et al., *Proc. ODP, Init. Repts.*, 101: College Station, TX (Ocean Drilling Program), 526-556.
- Sliter, W. V., and Premoli Silva, I., 1984. Autochthonous and displaced (allochthonous) Cretaceous benthic foraminifers from Deep Sea Drill-

- ing Project Leg 77, Sites 535, 536, 537, 538, and 540, Gulf of Mexico. *In* Buffler, R. T., Schlager, W., et al., *Init. Repts. DSDP*, 77: Washington (U.S. Govt. Printing Office), 593-627.
- Summerhayes, C. P., and Masran, T. C., 1983. Organic facies of Cretaceous and Jurassic sediments from Deep Sea Drilling Project Site 534 in the Blake-Bahama Basin, western North Atlantic. *In* Sheridan, R. E., Gradstein, F. M., et al., *Init. Repts. DSDP*, 76: Washington (U.S. Govt. Printing Office), 469-480.
- Theede, H., Ponat, A., Hiroki, K., and Schlieper, C., 1969. Studies on the resistance of marine bottom invertebrates to oxygen-deficiency and hydrogen sulphide. *Mar. Biol.*, 2:325-337.
- Tissot, B. P., and Welte, D. H., 1984. *Petroleum Formation and Occurrence* (2nd ed.): New York (Springer-Verlag).
- Waples, D. W., 1983. Reappraisal of anoxia and organic richness, with emphasis of Cretaceous of North Atlantic. *AAPG Bull.*, 67:963-978.

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