

## 15. ORGANIC GEOCHEMICAL CHARACTER OF SOME DEEP SEA DRILLING PROJECT CORES FROM LEGS 76 AND 44<sup>1</sup>

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### ABSTRACT

Pyrolysis assay, bitumen analysis, and elemental analysis of kerogen were used to characterize the organic matter of selected core samples from Hole 534A (Leg 76) and Hole 391C (Leg 44) on the Blake-Bahama Plateau. The organic matter throughout the stratigraphic section appears to be principally of a terrestrial origin. The data from several isolated horizons in the Hatteras and Blake-Bahama Formations imply the presence of significant quantities of autochthonous marine organic matter. However, these horizons appear so limited that they cannot be considered potential liquid hydrocarbon source rocks. All the analyzed samples are immature and have not evolved sufficiently to enter into the main stage of hydrocarbon generation.

The temporal and spatial restrictions of strata rich in marine organic matter suggest that they do not represent major expansions and contractions of anoxic bottom-water masses, but represent limited occurrences of anoxic conditions.

### INTRODUCTION

The type, quantity, and distribution of organic matter in sediments offer insight into paleoceanographic conditions and hydrocarbon potential of a region. This chapter is aimed at determining the level of organic enrichment and the character of organic matter present within the stratigraphic columns of two closely spaced DSDP sites, Sites 391 and 534 (Fig. 1). It is hoped that this information can suggest a mechanism that will explain the variations in the carbonaceous sediments of the North Atlantic noted earlier by Tissot et al. (1980).

Organic matter can be characterized through several different procedures. This chapter relies principally on pyrolysis assay and the analysis of both soluble (bitumen) and insoluble (kerogen) organic components. Three types of organic matter are identified in this study: two are primary and the third is secondary or recycled.

One of the primary types has a marine origin. This material is derived from marine plankton. It is characterized by high atomic H/C ratios, moderate atomic O/C ratios, and high yields of total extractables and pyrolytic hydrocarbons relative to organic carbon content. This marine material has good potential for the generation of oil upon thermal maturation. It would be termed type II organic matter in the scheme of Tissot et al. (1974).

The second primary type is derived from higher continental plant detritus. This material is characterized by low to moderate atomic H/C ratios, moderate to high atomic O/C ratios, and low yields of total extractables and pyrolytic hydrocarbons relative to organic carbon content. It will normally generate gas upon thermal maturation and would be classified as type III organic matter (Tissot et al., 1974).

The third type of organic matter is derived from previously sedimented deposits and/or has undergone either

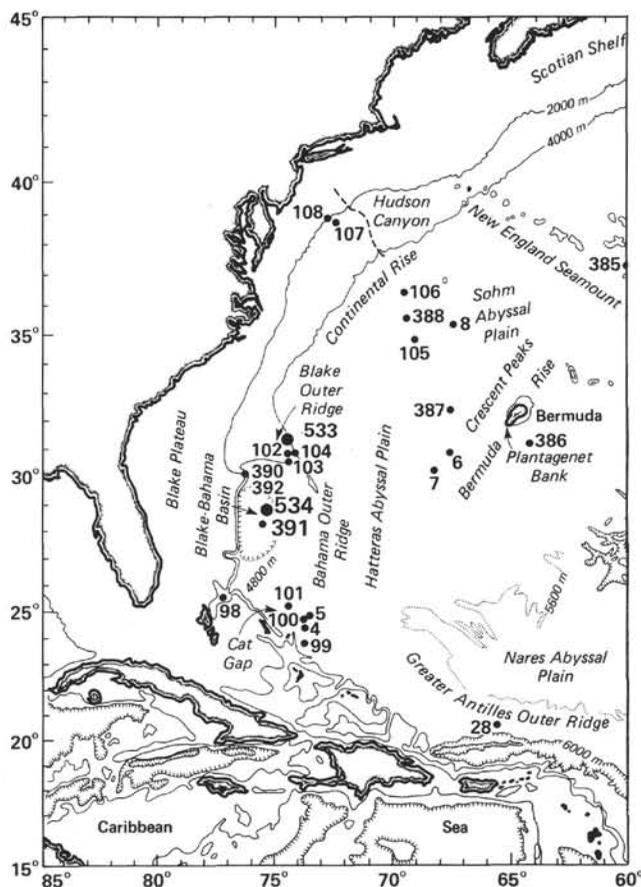


Figure 1. Location map for DSDP Sites 391 and 534.

severe thermal stress or oxidation. The material has very low atomic H/C ratios and characteristically highly variable O/C ratios. This material has very low yields of total extractables and pyrolytic hydrocarbons relative to organic carbon content. It is no longer capable of generating either gaseous or liquid hydrocarbons. This type

<sup>1</sup> Sheridan, R. E., Gradstein, F. M., et al., *Init. Repts. DSDP, 76*: Washington (U.S. Govt. Printing Office).

of organic matter is commonly termed either R.O.M. (recycled organic matter) or type IV (Tissot et al., 1980).

**ANALYTICAL METHODOLOGY**

Fifty-three samples of approximately 50 g each were analyzed. Stratigraphic positions of the samples are summarized in Figures 2 and 3. Each sample was oven-dried at 60°C and ground to approximately 44 microns. Organic carbon content was determined using a LECO combustion system after decarbonating. Those samples with ≥0.5 wt.% organic carbon were analyzed further by pyrolysis in a Rock-Eval unit as described by Espitalié et al. (1977). Kerogen isolation and subsequent elemental analysis (C, H, O, and N) were performed on samples containing ≥ 1.0 wt.% organic carbon. A portion of each sample was extracted using an azeotropic mixture of chloroform, acetone, and methanol, followed by the precipitating of asphaltenes with pentane and separation by liquid chromatography.

**ANALYTICAL RESULTS**

**Organic Carbon**

At both sites, total organic carbon (TOC) contents are highly variable, ranging from less than 0.1 wt.% to greater than 4.6 wt.% (Table 1). The vertical variability of organic richness is presented in Figures 2 and 3. The

two richest sections (534A-48-5 and 534A-53-2), with organic carbon contents of greater than 4.0 wt.%, are Barremian/Hauterivian. Other samples with organic carbon values in excess of 1.0 wt.% are common to the Albian and Aptian of both holes and are present within the Valanginian, Berriasian, and Kimmeridgian strata of Hole 534A. In general, samples with less than 0.3 wt.% TOC, the mean for DSDP material (McIver, 1975), are restricted to the pre- and post-Cretaceous samples of Hole 534A.

**Pyrolysis Assay (Rock-Eval)**

The total hydrocarbon yields, S<sub>1</sub> (free, distillable hydrocarbons) + S<sub>2</sub> (generatable hydrocarbons), range from less than 1 mg hydrocarbons/g rock to greater than 18 mg hydrocarbons/g rock (Table 1; Figs. 2 and 3). Potential or effective hydrocarbon source rocks display hydrocarbon yields of greater than 6 mg hydrocarbons/g rock (Tissot and Welte, 1978). In the present study, source rocks of this quality are limited to Sections 534A-48-5 and 534A-53-2, which have yields of 14.32 and 18.19 mg hydrocarbons/g rock, respectively.

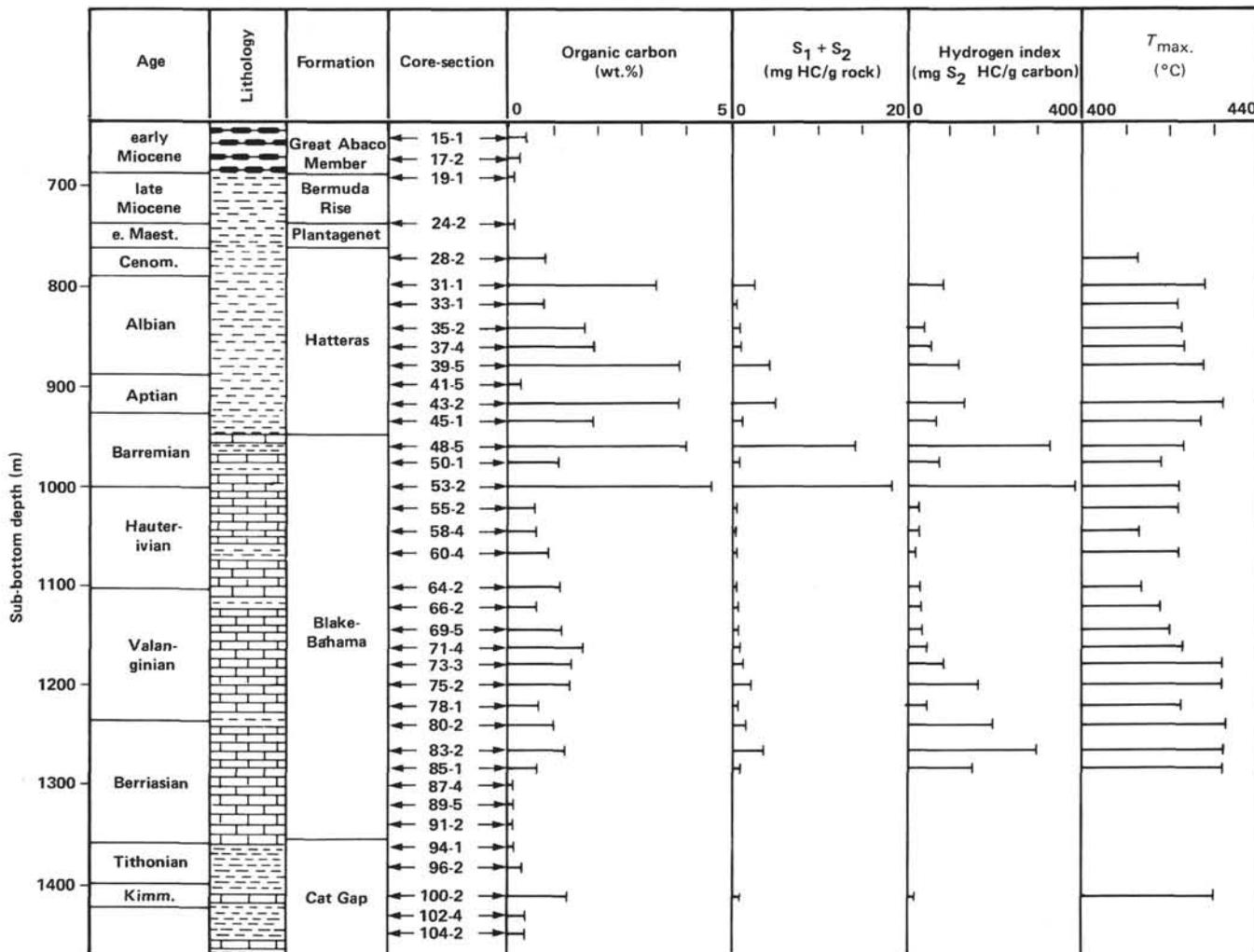


Figure 2. Stratigraphic summary of organic carbon and pyrolysis data from Hole 534A.

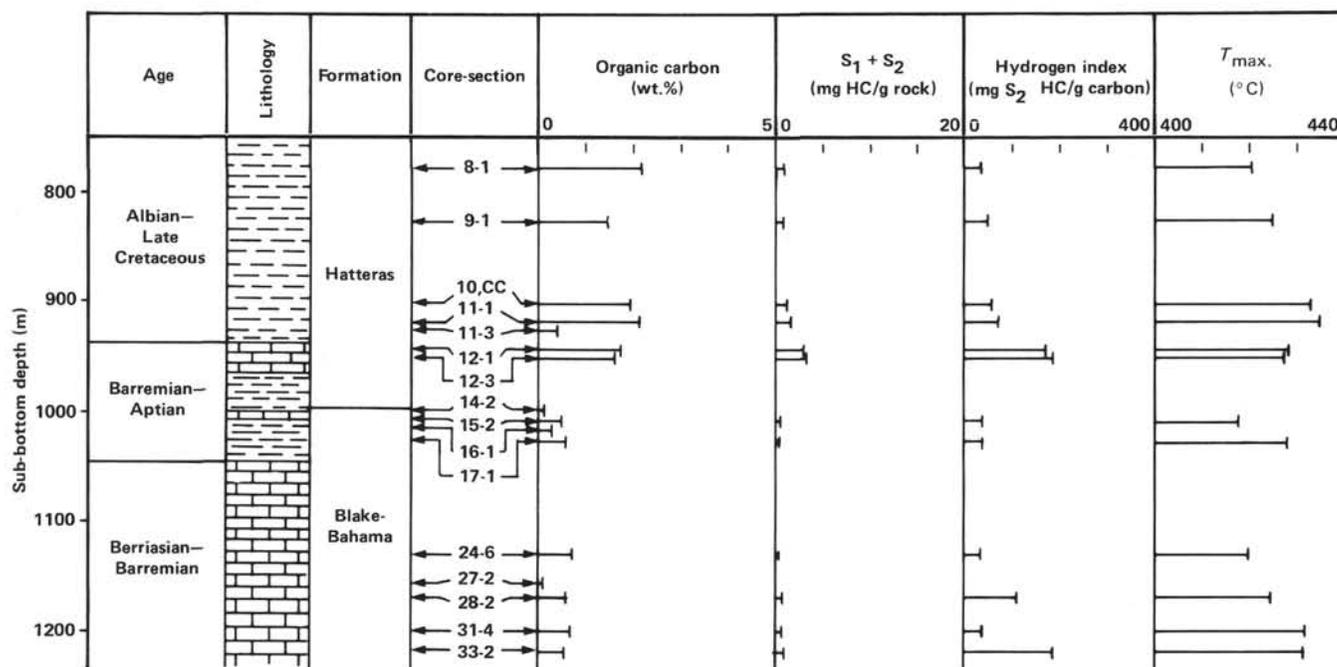


Figure 3. Stratigraphic summary of organic carbon and pyrolysis data from Hole 391C.

In addition to the screening of potential source facies, it has been suggested that the hydrogen index ( $S_2/TOC$ ) and oxygen index ( $S_3$  or organic  $CO_2/TOC$ ) are comparable to the H/C and O/C ratios, respectively (Espitalié et al., 1977). These indices (Fig. 4) suggest that the organic matter contained within the examined samples is principally of a terrestrial origin, largely vitrinitic or recycled, with a small mixed population plotting between type II (marine) and type III (vitrinitic) kerogens. This interpretation is tentative and must be confirmed by elemental analysis. The characterization of organic matter using pyrolysis data alone is subject to error because of the effects of both mineral matrix and level of organic enrichment (Katz, 1981).

Pyrolysis also offers an indication of organic maturity through both  $T_{max}$ , the temperature at which there is maximum hydrocarbon generation, and the transformation ratio ( $S_1/S_1 + S_2$ ). All  $T_{max}$  values from the two sites are  $435^\circ C$  or less (Table 1; Figs. 2 and 3), indicating that the organic matter is thermally immature and has not entered into the stage of peak hydrocarbon generation. The transformation ratios obtained on those samples with sufficient hydrocarbon yields for the ratio to be meaningful are below 0.1 (Table 1), confirming the thermal immaturity of the organic matter.

#### BITUMEN CHARACTERIZATION

Bitumen yields ranged from as low as 59 ppm, essentially background, to as high as 2838 ppm total extract (TOE, Table 2). Extract fractionation identified the material to be largely resins (NSOs) and asphaltenes with low hydrocarbon contents. The relative lack of hydrocarbons appears to reflect the immaturity of the sediment and the largely continental character of its organic matter.

Some samples have total extract yields inconsistent with both the low level of thermal maturity and the total organic carbon content. These anomalies are represented by extract to organic carbon ratios greater than 0.2 (TOE/TOC; Table 2). These elevated bitumen values may be due to either contamination or migration of mature "petroleumlike" material and subsequent alteration due to bacterial attack and/or gas deasphalting. The low level of hydrocarbons contained within these extracts favors the latter interpretation.

The elevated extractable yields do not appear to indicate favorable hydrocarbon generation potential within the section. Although according to some interpretational schemes (GeoChem Laboratories, Inc., 1980), total extractable yields in excess of 1000 ppm indicate very good source potential, most such samples analyzed in the present study have pyrolytic hydrocarbon yields consistent with either poor or fair source rocks (Tissot and Welte, 1978). These low pyrolysis yields confirm that the bitumens are hydrogen depleted and are incapable of yielding hydrocarbons upon thermal cracking.

#### ELEMENTAL ANALYSIS OF KEROGEN

The elemental data, summarized in Table 3 and Figure 5, confirm that the organic matter is largely derived from higher plants of terrestrial origin. The H/C and O/C ratios, plotted on a conventional van Krevelen-type diagram, indicate that most of the analyzed material is rather closely aligned with the type III reference curve. A very small population, having H/C and O/C ratios that plot below the type III reference curve, was derived either from recycled material or from primary organic matter that had been strongly oxidized prior to its incorporation into the sedimentary column.

Table 1. Organic carbon and pyrolysis assay.<sup>a</sup>

Sample (interval in cm)	Sub-bottom depth (m)	Total organic carbon (wt. %)	S <sub>1</sub> <sup>b</sup>	S <sub>2</sub> <sup>b</sup>	S <sub>3</sub> <sup>c</sup>	HI <sup>d</sup>	OI <sup>e</sup>	T <sub>max.</sub> (°C)	S <sub>1</sub> /(S <sub>1</sub> + S <sub>2</sub> ) <sup>f</sup>
Hole 534A									
15-1, 63-70	660.67	0.29							
17-2, 109-116	681.13	0.21							
19-1, 85-92	697.39	0.07							
24-2, 36-41	743.39	0.02							
28-2, 107-114	776.60	0.84	0.15	0.04	0.82	5	98	413	— <sup>g</sup>
31-1, 83-90	803.37	3.30	0.08	2.98	1.38	88	42	428	0.03
33-1, 138-145	822.92	0.77	0.13	0.08	0.77	10	101	422	—
35-2, 85-94	842.90	1.63	0.06	0.69	0.76	43	47	423	—
37-4, 128-135	865.32	1.93	0.10	1.07	0.86	56	45	423	—
39-5, 0-7	884.03	3.79	0.12	4.52	1.02	125	28	428	0.03
41-5, 105-112	903.09	0.23							
43-2, 94-101	916.48	3.88	0.07	5.16	1.47	133	38	432	0.01
45-1, 42-49	932.46	1.88	0.05	1.33	2.06	71	110	427	—
48-5, 0-7	965.03	4.00	0.28	14.04	3.21	329	75	423	0.02
50-1, 26-33	972.80	1.11	0.05	0.86	1.91	77	172	418	—
53-2, 45-52	1001.49	4.62	0.08	18.11	2.26	392	49	422	0.00
55-2, 44-51	1019.48	0.64	0.02	0.20	1.34	32	210	422	—
58-4, 62-69	1049.66	0.60	0.02	0.13	1.01	22	168	413	—
60-4, 126-133	1068.30	0.83	0.04	0.19	1.18	23	148	422	—
64-2, 40-47	1100.44	1.10	0.06	0.32	0.95	29	87	413	—
66-2, 17-24	1118.21	0.59	0.05	0.19	1.00	33	169	418	—
69-5, 16-23	1145.20	1.19	0.03	0.43	1.12	36	95	420	—
71-4, 83-90	1162.37	1.63	0.04	0.73	1.03	45	63	423	—
73-3, 117-124	1179.21	1.39	0.02	1.16	1.12	84	80	432	0.02
75-2, 143-150	1195.97	1.36	0.06	2.24	0.96	166	71	432	0.03
78-1, 37-45	1215.91	0.65	0.05	0.34	0.77	52	120	432	—
80-2, 120-125	1236.23	1.00	0.05	1.92	0.97	192	97	433	0.03
83-2, 33-40	1262.37	1.20	0.04	3.55	1.16	296	97	432	0.01
85-1, 33-40	1277.37	0.65	0.05	0.95	1.06	147	163	432	0.05
87-4, 78-85	1300.32	0.09							
89-5, 113-120	1320.17	0.10							
91-2, 62-68	1333.15	0.08							
94-1, 42-49	1353.96	0.09							
96-2, 16-23	1373.20	0.26							
100-2, 68-75	1403.22	1.28	0.07	0.16	0.54	12	46	430	—
102-4, 84-91	1424.38	0.30							
104-2, 132-140	1439.86	0.28							
Hole 391C									
8-1, 126-133	783.56	2.15	0.07	0.77	1.35	36	63	420	—
9-1, 133-140	831.13	1.41	0.06	0.62	1.06	44	76	425	—
10, CC (0-7)	901.30	1.93	0.07	1.00	1.16	52	60	433	0.07
11-1, 130-137	926.10	2.12	0.07	1.61	2.76	80	130	435	0.04
11-3, 90-97	928.70	0.41							
12-1, 53-60	953.83	1.78	0.05	3.00	2.04	169	114	428	0.02
12-3, 37-45	956.67	1.65	0.09	2.98	2.33	181	141	427	0.03
14-2, 53-60	1004.33	0.12							
15-2, 40-47	1012.20	0.51	0.04	0.20	1.85	40	369	418	—
16-1, 90-97	1020.70	0.29							
17-7, 100-107	1030.30	0.55	0.03	0.22	1.81	40	330	428	7
24-6, 37-44	1132.17	0.68	0.03	0.22	1.54	33	230	420	—
27-2, 52-60	1154.80	0.08							
28-2, 20-27	1164.00	0.66	0.05	0.77	1.63	118	251	425	—
31-4, 23-30	1195.03	0.70	0.04	0.89	1.47	129	212	432	—
33-2, 83-90	1212.13	0.56	0.06	1.08	1.33	192	238	432	0.05

Note: Blank spaces represent no analysis.

<sup>a</sup> Pyrolysis was limited to samples with greater than 0.5 wt. % organic carbon.

<sup>b</sup> Hydrocarbons.

<sup>c</sup> CO<sub>2</sub>.

<sup>d</sup> Hydrogen index (mg S<sub>2</sub> hydrocarbons/g organic carbon).

<sup>e</sup> Oxygen index (mg S<sub>3</sub> CO<sub>2</sub>/g organic carbon).

<sup>f</sup> Transformation ratio (rounded to nearest hundredth).

<sup>g</sup> — indicates insufficient hydrocarbon yield.

The data for a third population plot between reference curves II and III. The organic matter in these samples is a mixture of terrestrial- and marine-derived material. The relative amount of marine material varies from Section 534A-53-2, which plots very close to the type II reference curve, to Section 534A-48-5, which plots midway between the type II and type III reference curves. These discrete strata enriched in marine organic matter are Barremian/Hauterivian and Valanginian/Berriasian at Site 534 and Aptian at Site 391.

## DISCUSSION

The preservation in the sedimentary column of primarily terrestrially derived organic matter does not re-

quire strongly anoxic conditions (Demaison and Moore, 1980). Terrestrial material is partially oxidized and degraded during transport so that only the more stable components reach the final depositor. As a result, terrestrial material may be preserved under oxic conditions. Therefore, although most of the Cretaceous and some of the Jurassic sediments examined contain above-average quantities of organic carbon, they need not have been deposited under anoxic conditions. Their organic richness may reflect high continental organic productivities reflecting the warm and humid climatic conditions of the Cretaceous and Jurassic (Barron, 1980). Such conditions could have provided the large quantities of terrestrial material observed in the sediments

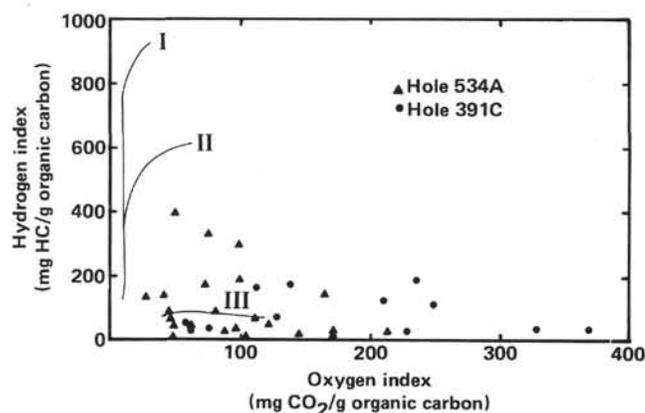


Figure 4. Modified van Krevelen diagram providing preliminary characterization of organic matter utilizing "Rock-Eval" pyrolysis.

without regard to the oxidative state of the depositional environment. An oxic depositional environment is also consistent with the general paleocirculation patterns described by Sclater et al. (1977). For the Cretaceous and Jurassic, Sclater et al. (1977) suggest that deep water entered the North Atlantic through a gap between the Bahama Platform and the Guinea Nose. This would have resulted in oxygen renewal and maintenance of an oxic depositional environment.

Preservation of marine-derived organic matter, however, requires an anoxic environment. Such a condition implies isolation of a water mass, and a supply of consumable organic matter in excess of the available oxygen. Because of the poorly developed stratigraphic and spatial distribution of those strata found by this study to be enriched in type II kerogen, it is unlikely that they reflect the development of long-lived large anoxic water

Table 2. Bitumen characterization.

Sample (interval in cm)	Sub-bottom depth (m)	Total extract (ppm)	Asphaltenes (%)	Saturates <sup>a</sup> (%)	Aromatics (%)	NSOs (%)	TOE/TOC <sup>b</sup>
Hole 534A							
15-1, 63-70	660.67	138	20.0	7.5	12.5	60.0	0.05
17-2, 109-116	681.13	106	16.1	24.9	24.9	34.2	0.05
19-1, 85-92	697.39	97	0.0	45.2	41.9	12.9	0.14
24-2, 36-41	743.39	155	45.5	13.6	22.7	18.2	0.78
28-2, 107-114	776.60	312	45.6	15.2	13.1	26.1	0.04
31-1, 83-90	803.37	735	41.7	6.4	6.0	45.9	0.02
33-1, 138-145	822.92	211	54.2	11.1	12.6	22.1	0.03
35-2, 85-94	842.90	281	18.8	8.8	11.3	61.3	0.02
37-4, 128-135	865.32	436	37.5	9.4	8.6	48.5	0.02
39-5, 0-7	884.03	685	37.6	6.9	5.9	59.5	0.02
41-5, 105-112	903.09	59	0.0	34.8	32.6	32.6	0.03
43-2, 94-101	916.48	811	33.7	9.1	11.1	46.0	0.02
45-1, 42-49	932.46	1016	63.9	8.0	4.0	24.2	0.05
48-5, 0-7	965.03	2090	51.2	4.3	11.2	33.2	0.05
50-1, 26-33	972.80	1143	71.3	5.3	8.8	14.6	0.10
53-2, 45-52	1001.49	1971	53.7	5.2	11.6	28.6	0.04
55-2, 44-51	1019.48	1985	90.2	2.3	3.1	4.3	0.30
58-4, 62-69	1049.66	831	81.3	5.4	5.4	7.8	0.14
60-4, 126-133	1068.30	2344	90.6	2.0	1.2	6.2	0.28
64-2, 40-47	1100.44	1073	79.3	6.6	6.9	7.2	0.10
66-2, 17-24	1118.21	1652	89.2	2.0	5.0	3.8	0.28
69-5, 16-23	1145.20	1795	87.0	1.6	3.9	7.6	0.15
71-4, 83-90	1162.37	1150	77.8	6.1	7.8	8.4	0.07
73-3, 117-124	1179.21	1224	75.3	6.0	8.5	10.1	0.09
75-2, 143-150	1195.97	2838	86.4	3.7	2.8	7.2	0.21
78-1, 37-45	1215.91	2119	87.4	4.1	4.2	4.4	0.33
80-2, 120-125	1236.23	609	62.4	7.2	9.9	20.5	0.06
83-2, 33-40	1262.37	1345	68.2	4.5	5.5	21.8	0.11
85-1, 33-40	1277.37	854	73.1	7.4	6.6	12.9	0.13
87-4, 78-85	1300.32	484	75.8	5.4	6.7	12.0	0.54
89-5, 113-120	1320.17	821	82.8	5.7	4.9	6.6	0.82
91-2, 62-68	1333.15	399	62.8	11.6	13.2	12.4	0.50
96-2, 16-23	1373.20	457	59.9	13.4	11.3	15.5	0.18
100-2, 68-75	1403.22	1591	90.2	1.8	2.2	5.9	0.12
102-4, 84-91	1424.38	1833	91.4	1.6	2.2	4.7	0.61
104-2, 132-140	1439.86	120	23.7	16.2	25.4	34.7	0.04
Hole 391C							
8-1, 126-133	783.56	1371	55.1	25.8	6.3	12.8	0.06
9-1, 133-140	831.13	522	37.1	9.9	11.7	41.3	0.04
10, CC (0-7)	901.30	549	37.5	9.4	24.4	28.8	0.03
11-1, 130-137	926.10	658	34.2	9.2	8.7	48.0	0.03
11-3, 90-97	928.70	238	8.5	17.8	24.6	49.2	0.06
12-1, 53-60	953.83	966	46.0	6.7	20.3	27.0	0.06
12-3, 37-45	956.67	873	45.2	9.6	9.6	34.5	0.05
14-2, 53-60	1004.33	124	0.0	30.6	27.8	41.7	0.10
15-2, 40-47	1012.20	232	16.9	17.2	27.2	38.7	0.05
16-1, 90-97	1020.70	124	11.1	25.0	22.2	41.7	0.04
17-1, 100-107	1030.30	229	38.8	14.9	14.9	31.3	0.04
24-6, 37-44	1132.17	263	35.1	13.0	14.3	37.7	0.04
27-2, 52-60	1154.80	112	3.0	24.2	24.2	48.5	0.14
28-2, 20-27	1164.00	373	35.1	16.8	29.2	18.9	0.06
31-4, 23-30	1195.03	388	35.0	18.0	12.8	34.2	0.06
33-2, 83-90	1212.13	285	31.8	13.9	21.2	34.1	0.05

<sup>a</sup> Paraffins and naphthenes.

<sup>b</sup> Total organic extract/total organic carbon.

Table 3. Elemental composition (ash-free basis).

Sample (interval in cm)	Sub-bottom depth (m)	H	C	O (wt.%)	N	Atomic ratios	
						H/C	O/C
<b>Hole 534A</b>							
31-1, 83-90	803.87	5.7	69.5	15.3	2.8	0.99	0.165
35-2, 85-94	842.90	5.4	73.4	14.6	2.4	0.89	0.149
37-4, 128-135	865.32	5.7	73.5	14.8	2.6	0.93	0.151
39-5, 0-7	884.84	5.5	72.3	14.7	2.4	0.92	0.153
43-2, 94-101	916.48	5.7	73.1	14.7	2.8	0.94	0.151
45-1, 42-49	932.46	5.3	72.4	14.7	2.5	0.87	0.152
48-5, 0-7	965.03	6.5	71.8	11.8	2.8	1.08	0.123
53-2, 45-52	1001.49	7.2	69.0	11.5	2.1	1.25	0.125
64-2, 40-47	1100.44	4.5	72.9	16.5	1.9	0.73	0.170
69-5, 16-23	1145.20	4.0	65.0	13.4	1.6	0.73	0.155
71-4, 83-90	1163.37	4.9	67.3	14.4	2.1	0.87	0.161
73-3, 117-124	1179.21	5.8	73.6	13.4	2.4	0.95	0.136
75-2, 143-150	1195.97	6.9	71.8	12.4	2.6	1.16	0.130
80-2, 120-125	1236.23	7.0	72.0	13.4	2.4	1.17	0.139
83-2, 33-40	1262.37	7.4	73.1	12.7	2.5	1.22	0.130
<b>Hole 391C</b>							
9-1, 133-140	831.13	4.6	71.2	15.1	2.1	0.78	0.159
10, CC (0-7)	901.30	5.2	71.7	14.4	2.2	0.87	0.150
11-1, 130-137	926.10	5.4	70.5	14.5	2.5	0.92	0.154
12-1, 53-60	953.83	6.7	68.7	12.8	2.6	1.17	0.140
12-3, 37-45	956.67	5.8	72.1	12.1	2.0	0.96	0.126
31-4, 23-30	1195.08	5.2	70.4	15.2	2.3	0.88	0.162

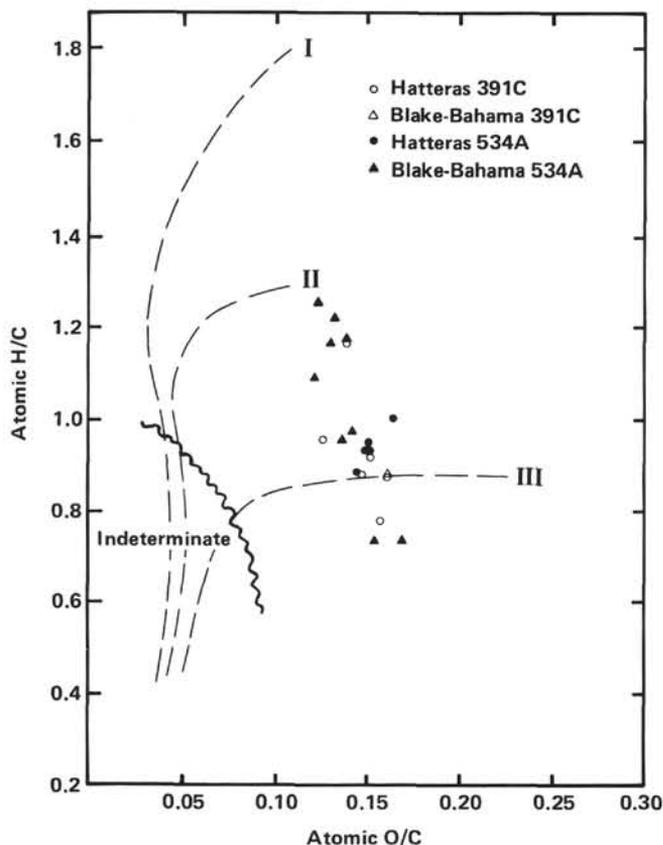


Figure 5. Van Krevelen diagram providing final characterization of organic matter.

masses. It is possible that they represent brief periods of stagnation and high productivity, which may or may not be synchronous basin-wide. These stagnant conditions

may have resulted from changes in general bottom-water circulation, whereby oxygenated bottom water was briefly cut off from the Pacific by tectonic activity of the "Panama barrier" (Saunders et al., 1973) or by transient changes in deep-water eddy patterns capable of isolating bottom-water pockets.

As a consequence of the limited stratigraphic distribution of these marine organic facies, it does not appear probable that they represent potential oil source facies. These data also imply that broad generalizations and predictions of hydrocarbon source qualities based solely on limited well control data should be viewed cautiously.

## SUMMARY

1. The preserved organic matter is principally continental in origin and therefore has only limited potential to generate liquid hydrocarbons.

2. Discrete Aptian, Barremian/Hauterivian, and Valanginian/Berriasian strata contain significant contributions of marine organic matter, suggesting anoxic depositional conditions.

3. Only strata within the Barremian/Hauterivian sections of Hole 534A have hydrocarbon yields indicative of good potential source facies.

4. The spatial and temporal distribution of marine horizons at these two sites on the western Atlantic continental margin suggests that they are not related to development of long-lived anoxic water masses, but rather may reflect brief changes in bottom-water circulation.

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