21. ORGANIC GEOCHEMISTRY OF SOME CRETACEOUS CLAYSTONES FROM SITE 391, LEG 44, WESTERN NORTH ATLANTIC

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ABSTRACT

The dark Cretaceous claystones recovered from Site 391 in the Blake-Bahama Basin during DSDP Leg 44 are definitely not sapropelitic sediments. Most of their organic matter is thermally immature and derived from a continental source.

INTRODUCTION

We have studied the organic geochemistry of the Cretaceous claystones cored during DSDP Leg 44 in the post-Barremian sediments of the Blake-Bahama Basin to define the type of organic sediments present and to determine whether or not they are sapropelitic shales.

First, we performed a pyrolysis assay to detect hydrocarbons in raw samples and chloroformic extractions which allowed us to characterize the type of organic matter in the sediments. We then studied the remaining insoluble fraction, i.e., the humic compounds and the kerogen fraction in the organic matter to determine whether the organic material is of marine or continental origin. Humic compounds are more common in immature than in mature sediments, whereas the kerogen fraction forms a significant part of both the immature and mature sediments.

SAMPLING

The eight samples, of 150-200 g each, from Site 391 (Figure 1) were recovered from the Blake-Bahama Basin halfway between Sites 104 (Blake Outer Ridge) and 101 (Bahama Outer Ridge). Four of them are Upper Cretaceous silty claystones; the others are lower Albian and/or Aptian calcareous claystones (Table 1).

ANALYTICAL METHODS

The eight samples were freeze-dried and ground in an AUREC pulverizer (grain size ≅ 90μm). The succession of analytical processes is shown on Figure 2. The organic carbon content was determined with a LECO analyzer. A pyrolysis assay was applied to the raw samples (Espitalie et al., 1977) to rapidly determine source rock and maturation characteristics. (The methods are taken from kerogen experimental studies by Durand and Espitalie, 1973; Espitalie et al., 1973; and Tissot et al., 1974.) Equivalent fractions of ground samples were then extracted with chloroform and fractionated by thin-layer chromatography (Huc et al., 1976). The total humic fraction was extracted from the insoluble part of rock and humic acids were separated from fulvic acids (Huc et al., 1978). The related insoluble fraction corresponds to kerogen (Durand et al., 1972; Robin et al, in press). Organic content analysis from total humic compound and from fulvic fraction were performed on a Carmhograph Wosthoff apparatus. Elemental analyses of carbon, hydrogen, oxygen, nitrogen, sulfur, and iron, and the ash content were measured on kerogen and calculated on a mineral-free basis.

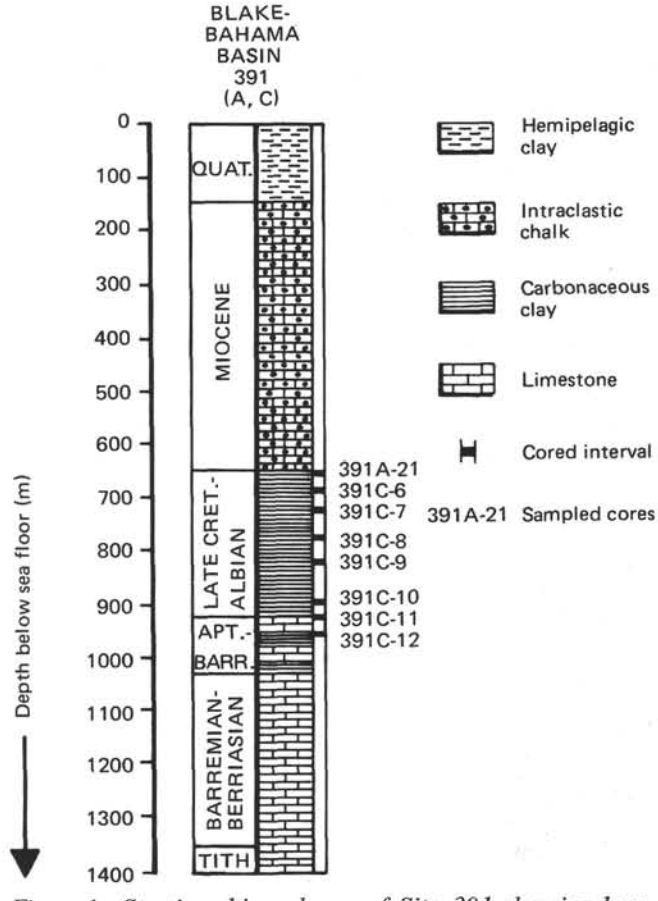

Figure 1. *Stratigraphic column of Site 391 showing location of samples.*

TABLE 1
Sub-Bottom Depths, Lithology, Age, and Carbon Data for Samples Studied From Site 391

Sample (Interval in cm)	Depth Below Sea Floor (m)	Lithology and Age	% CO_3Ca	Organic Carbon (%)	
				Before $HCC\ell_3$ Extraction	After $HCC\ell_3$ Extraction
Hole 391A					
21-4, 125-130	655	Claystone (Upper Cretaceous)	2	0.29	0.28
Hole 391C					
6-3, 145-150	690	Claystone with silt stringers (Upper Cretaceous)	8	0.72	0.71
7-2, 136-142	730	Claystone and silty claystone (Upper Cretaceous)	2	1.27	1.26
8-2, 145-150	785	Claystone and siltstone (Upper Cretaceous)	2	1.12	1.11
9-3, 145-150	842	Claystone and marly limestone (Upper Aptian Lower Albian)	7	1.50	1.48
10-3, 145-150	905	Silty claystone with limestone (Upper Aptian Lower Albian	32	2.72	2.69
11-2, 145-150	925	Silty calcareous claystone (? Upper Aptian)	68	0.92	0.90
12-4, 120-125	959	Calcareous claystone with limestone (Aptian)	10	2.07	1.80

DETAILED RESULTS

Mineral Carbon (Table 1)

Two samples, 391C-10-3, 145-150 cm (upper Aptian-lower Albian) and 391C-11-2, 145-150 cm (supposed upper Aptian) had a high carbonate content (32% and 68%). All others, either from Upper Cretaceous and upper Aptian-lower Albian or Aptian sediments, had low carbonate contents (less than 10%).

Organic Carbon (Table 1)

The two samples, 391A-21-4, 125-130 cm and 391A-6-3, 145-150 cm, from the upper part of the interval had a low content of organic carbon (less than 0.8%). The others ranged from 0.92 per cent to 2.72 per cent.

Pyrolysis Assay and Organic Matter Characterization (Table 2)

The pyrolysis assay method is a rough simulation of the elemental analysis method used upon kerogen (Tissot et al., 1974). The combined oxygen and hydrogen indexes related to organic carbon of rock are used for pyrolysis assays in the same manner as the hydrogen/carbon and oxygen/carbon atomic ratios were used for kerogen. They allow us to characterize the same three types of organic matter defined as types 1, 2 and 3 (Figure 3). The hydrogen index is expressed in milligrams of hydrocarbon compounds related to a gram of organic carbon, and the oxygen index in milligrams of carbon dioxide related to a gram of organic carbon. There is a correlation between the temperature of the maximum hydrocarbon production during pyrolysis (peak temperature) and the evolution stages of the kerogen. The 400°-440°C range of peak temperatures corresponds to immature kerogen, the 440°-460°C range corresponds to the main zone of oil genesis and to the main gas zone (or cracking zone) up to 460°C.

The maximum hydrocarbon production during pyrolysis was reached for all the samples at low temperatures between 430°C and 434°C — the latter in the most deeply buried sample. The samples are thus immature with regard to oil genesis.

In all the studied samples, the hydrogen index is very low (less than 80) and the oxygen index ranges between 80 to 200 (Table 2). The oxygen-hydrogen diagram (Figure 3) shows that all the samples fall in the type 3 category, which indicates relatively higher contents of plant detritus and humic matter from a continental source. That type of organic matter, if matured, would yield preferentially gaseous hydrocarbons. The very low hydrogen index can be caused by a low content of pyrolysable organic matter diluted by large amounts of detrital material devoid of any pyrolysis potential.

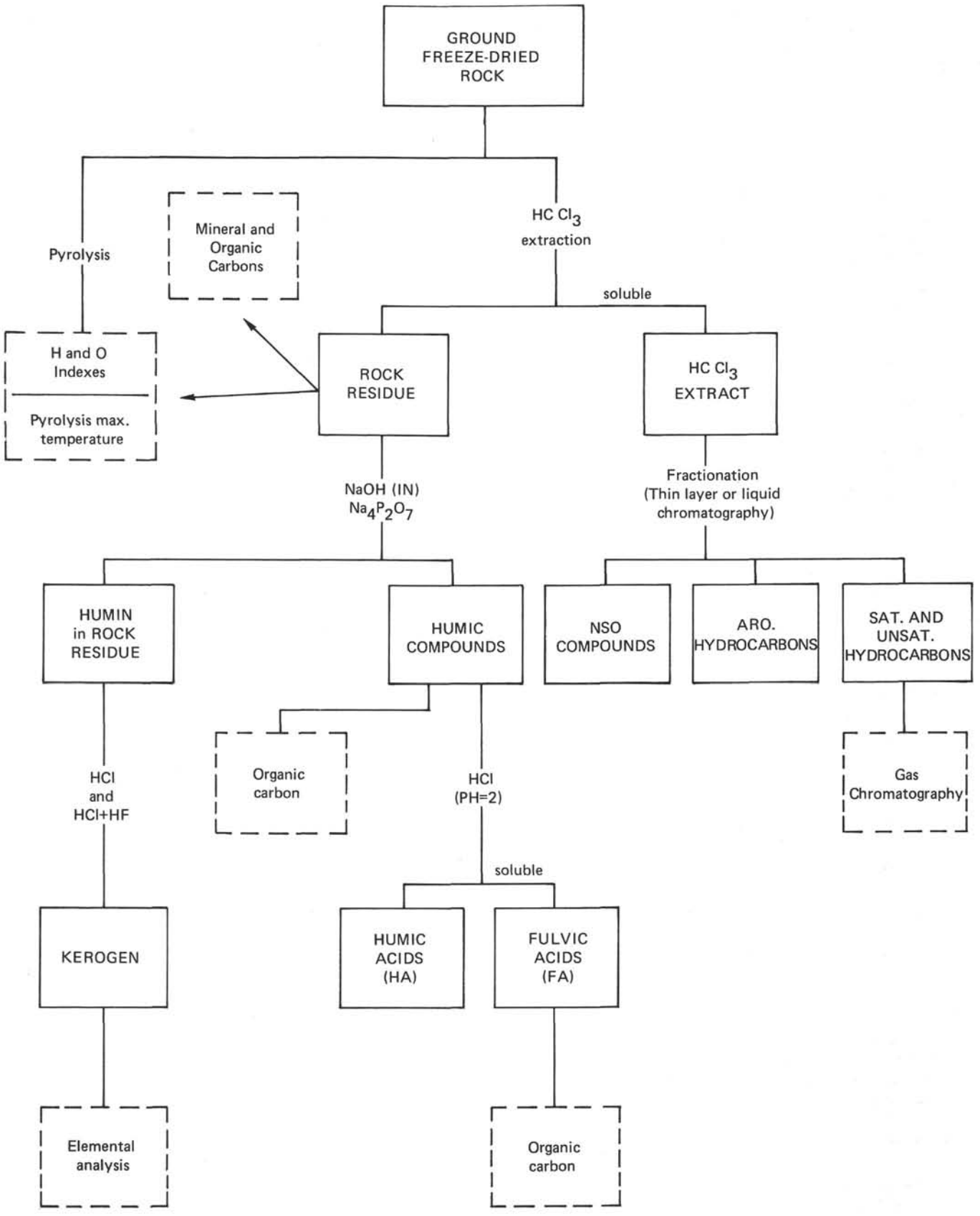

Figure 2. *Schematic presentation of analytical processes.*

TABLE 2
Pyrolysis Assays for Samples From Site 391

Sample Interval in cm	Below Sea Floor (m)	Organic Carbon (% weight)	Hydrogen Index (mg. hydroc. compounds/ g. org. carb.)	Oxygen Index (mg. CO_2/ g. org. carb.)	Pyrolysis Temperature (°C)
Hole 391A					
21-4, 125-130	655	0.37	31	151	
Hole 391C					
6-3, 145-150	690	0.70	34	80	430
7-2, 136-142	730	1.33	19	84	430
8-2, 145-150	785	1.13	15	93	430
9-3, 145-150	842	1.57	39	85	430
10-3, 145-150	905	2.72	79	122	430
11-2, 145-150	925	0.89	52	198	430
12-4, 120-125	959	1.77	48	98	434

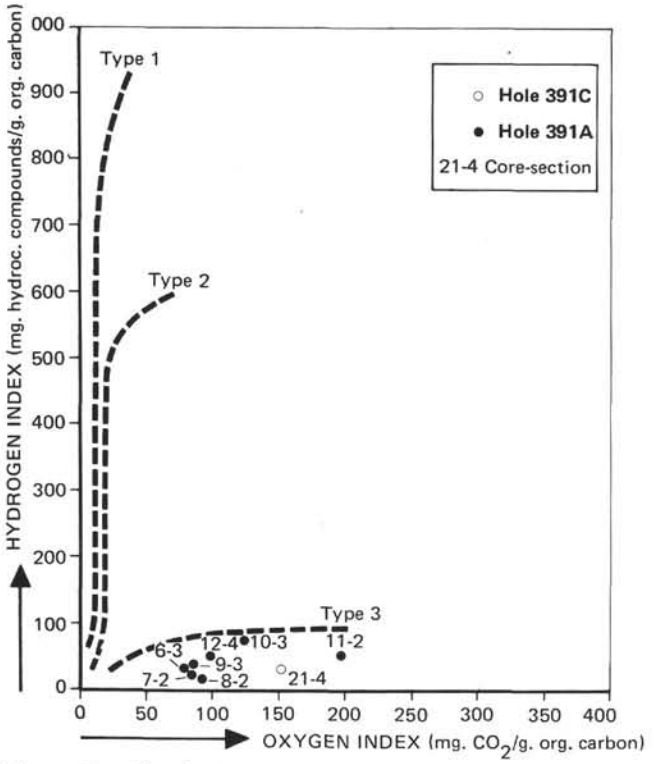

Figure 3. *Pyrolysis assays. Hydrogen and oxygen indexes (data versus organic carbon content).*

Study of Chloroformic Extracts (Table 3, Figure 4)

All samples (Table 3) had low contents of chloroformic extract (11 to 90 mg), except for Sample 391C-12-4, 120-125 cm. This sample yielded more chloroformic extract, but it was unfractionable by the usual thin-layer chromatography method. The extract to organic carbon ratio is generally low (0.01 to 0.02 and 0.04) and the non-soluble organic (NSO) compounds (Figure 4) comprise most of the samples (71%, 84% to 92%).

The low content of extracts, related to predominantly heteroatomic compounds, generally indicates an immature material. There is a saturated fraction in the hydrocarbons larger than the aromatics. The gas chromatography analysis of the saturated fraction

TABLE 3
Chloroformic Extracts (after Site 391 Report, this volume) for Samples From Site 391

Sample Interval in cm	Depth Below Sea Floor (m)	HCCℓ3 Extract (weight mg)	Extract/ Rock (weight %)	Extract/ Org. Carbon (weight)	Thin Layer Chromatography: NSO Compounds (%)	Thin Layer Chromatography: Hydroc. Fractions Aro. (%)	Thin Layer Chromatography: Hydroc. Fractions Sat. (%)
Hole 391A							
21-4, 125-130	655	11.4	0.008	0.028	71	10	19
Hole 391C							
6-3, 145-150	690	28.4	0.013	0.018	87	5	8
7-2, 136-142	730	25.2	0.015	0.012	89	4	7
8-2, 145-150	785	21.1	0.014	0.012	88	3	9
9-3, 145-150	842	34.2	0.020	0.013	84	4	12
10-3, 145-150	905	90.5	0.043	0.015	90	5	5
11-2, 145-150	925	56.1	0.024	0.026	92	4	4
12-4, 120-125	959	447.6	0.332	0.160	no fraction		

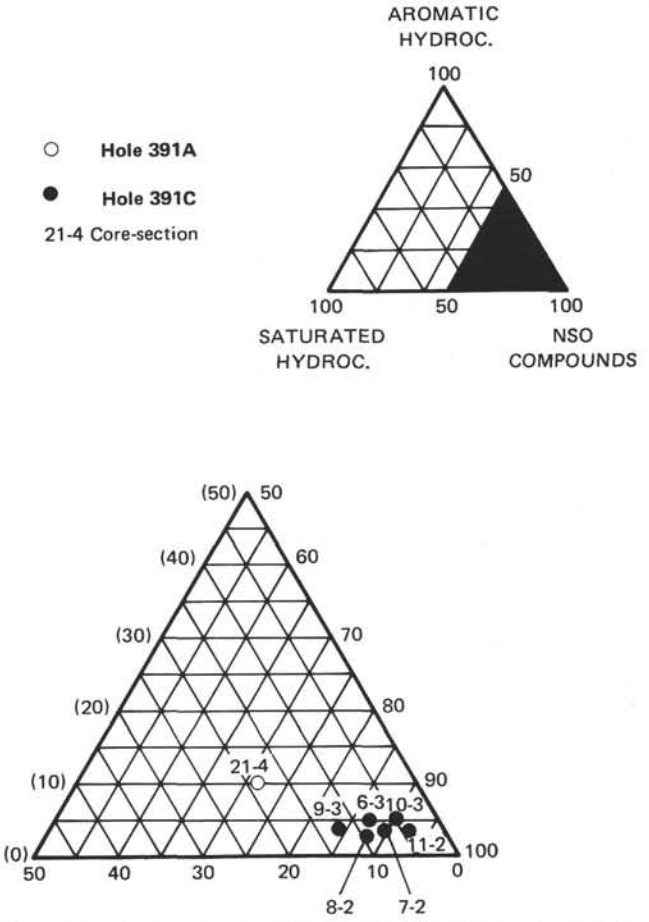

Figure 4. *Gross composition of the chloroformic extracts.*

reveals a normal alkanes distribution with an odd carbon number predominance in the C_{25}-C_{29} range (Figure 5). The large proportion of C_{25+} odd normal alkanes suggests an important contribution of higher plants waxes.

[1]That study was performed by P. Albrecht and M. Dastillung, Institut de Chimie, Strasbourg (France).

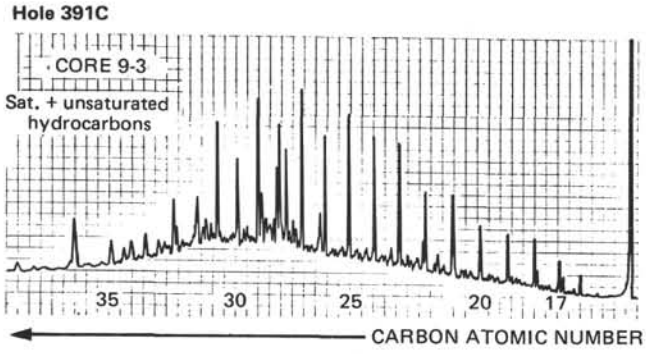

Figure 5. *Extracts. Gas chromatography of saturated fraction.*

Some polycyclic saturated hydrocarbons were investigated by computerized GC-MS[1] in a composite sample comprising the saturates from the Upper Cretaceous Samples 391A-21-4, 125-130 cm to 391A-8-2, 145-150 cm. The mass chromatograms registered from masses 191, 217, and 231 are shown on Figure 6. They correspond, respectively, to the hopane, steranes, and methylsteranes series.

Steranes and methylsteranes were sparse to be analyzed, but triterpanes of the hopane type could be identified (Figure 6); the compounds belong to hopane series ([17βH, 21βH] hopane and [17αH, 21βH] hopane). The more stable (17αH, 21βH) hopane series occurred in large quantities which indicates that the sediments are in a relatively advanced stage in early diagenesis.

Study of Humic Compounds

The eight samples were analyzed to determine per cent and ratios of the humic compounds (Table 4). The four samples of Upper Cretaceous sediments (391A-21-4, 125-130 cm; 391C-6-3, 145-150 cm; 391C-7-2, 136-142 cm; 391C-8-2, 145-150 cm) had a relatively high humic material content ($\geq$30% of total organic carbon) as found in continental material at an immature stage of evolution. The relative content decreased in the upper Aptian-lower Albian (391C-9-3, 145-150 cm and 391C-10-3, 145-150 cm samples (11% and 15%). It reached 33 per cent in the Aptian Sample 391C-11-2, 145-150 cm and 13 per cent in the deepest sample, 391C-12-4, 120-125 cm, of supposed Aptian age. The abundance of humic compounds in sediments buried to 600-1000 meters below the sea floor indicates that they contain a significant contribution of land-derived organic matter (Huc and Durand, 1977).

Study of Kerogen

The elemental composition of the kerogen fraction[2] of the eight samples studied (Table 5) allows us to define the organic matter (Tissot et al., 1974) by plotting the hydrogen/carbon and oxygen/carbon atomic ratios on a Van Krevelen diagram (Figure 7).

The three Upper Cretaceous samples (391C-6-3, -7-2, -8-2) have the lowest hydrogen/carbon ration. They fall just below the other kerogen samples, 391C-9-3, -10-3, -11-2, -12-4, which lie close to reference path III. That location suggests that the kerogen was derived from a continental source higher plants as previously deduced from pyrolysis assays on whole samples. The position of the four deepest samples (391C-9-3 to 12-4) on path III suggests that their stage of diagenesis is close to that of the main period of oil formation.

CONCLUSIONS

Despite a relatively high content of organic carbon, the Cretaceous clays cored at Site 391 are not-geochemically speaking sapropelic black shale.

From pyrolysis assays the major fraction of their organic matter is probably detrital and derived from continental higher plants. The study of kerogen and humic compounds confirms that the organic matter is of continental origin and has not yet reached the main phase of oil genesis.

[2]The proportion of unexplained ashes was so large (43%) in Sample 391-C-12-4, 120-125 cm, that its elemental analysis was insignificant.

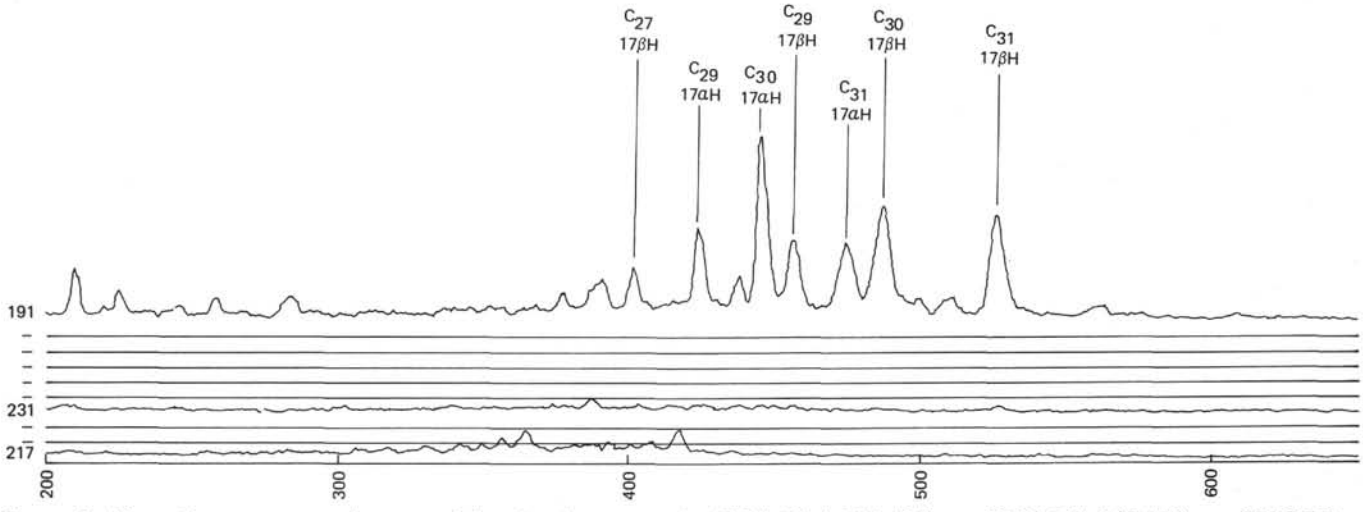

Figure 6. *Mass chromatogram of saturated fraction for composite 291A-21-4, 125-130 cm; 391C-6-3, 145-150 cm; 391C-7-2, 136-142 cm; 391C-8-2, 145-150 cm; samples corresponding to peaks 191, 217, and 231.*

TABLE 4
Total Organic and Per Cent Humic Compounds of Samples From Site 391

Sample (Interval in cm)	Depth Below Sea Floor (m)	Total org. Carbon (weight %)	Carbon content (% of total org. carbon)			FA/HA
			Humic Compounds (FA + HA)	Fulvic Acids (FA)	Humic Acids (HA)	
Hole 391A						
21-4, 125-130	655	0.37	30.0	22.7	7.3	3.11
Hole 391C						
6-3, 145-150	690	0.70	67.1	5.7	61.4	0.09
7-2, 136-142	730	1.33	31.6	2.5	29.1	0.08
8-2, 145-150	785	1.13	38.0	3.6	34.4	0.10
9-3, 145-150	842	1.57	10.8	3.4	7.4	0.45
10-3, 145-150	905	2.72	14.8	2.7	12.7	0.16
11-2, 145-150	925	0.89	33.7	3.9	29.8	0.13
12-4, 120-125	959	1.77	13.6	3.2	10.4	0.30

TABLE 5
Elemental Composition and Ash Content of Kerogens From Site 391 Samples

(Interval in cm)	Depth Below Sea Floor (m)	Weight %, on Ash-Free Basis					Atomic		Ash (weight %)
		C	H	O	S	N	H/C	O/C $\times 10^2$	
Hole 391A									
21-4, 125-130	655	48.75	3.64	28.12	16.26	3.24	0.89	43.25	52.22
Hole 391C									
6-3, 145-150	690	65.58	3.97	22.14	5.41	2.90	0.73	25.33	46.84
7-2, 136-142	730	63.08	3.75	21.76	9.43	1.98	0.71	25.88	35.73
8-2, 145-150	785	73.72	3.37	18.89	1.84	2.17	0.55	19.22	22.63
9-3, 145-150	842	66.64	4.29	21.12	5.56	2.39	0.77	23.77	31.56
10-3, 145-150	905	69.83	4.87	20.78	1.74	2.78	0.84	22.32	30.78
11-2, 145-150	925	73.09	4.66	15.52	4.37	2.35	0.77	15.93	33.22
12-4, 120-125	959	68.98	4.47	20.25	3.57	2.72	0.78	22.02	32.60

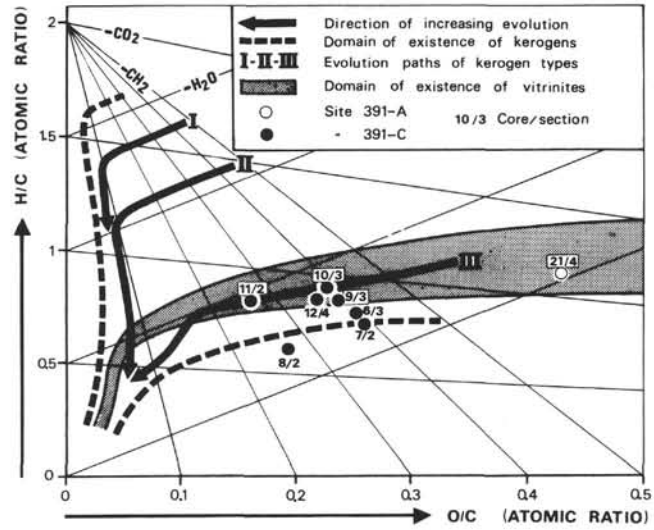

Figure 7. *Kerogens. H/C and O/C diagram.*

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