29. ORGANIC GEOCHEMISTRY OF SOME CRETACEOUS BLACK SHALES FROM SITES 367 AND 368; LEG 41, EASTERN NORTH ATLANTIC

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ABSTRACT

The black shale encountered in Cretaceous cores of the Cape Verde area during the DSDP Leg 41 are of marine origin and correspond to excellent potential oil source rocks. They have a low content of humic compounds.

Pyrolysis assays, chloroformic extracts, and kerogen data attest to a relatively low stage of evolution for samples at Site 367 (Cape Verde Basin). The samples from Site 368 (Cape Verde Rise) are more evolved, and the deeper ones would be located at the beginning of the principal zone of oil formation.

INTRODUCTION

The aim of this paper is to define, from a geochemical point of view, the black shale recovered in Cretaceous cores of the Cape Verde area, during DSDP Leg 41.

A pyrolysis assay for the detection of hydrocarbons was run on raw samples and chloroformic extractions were performed. These are useful to characterize the type of organic matter in sediments. Also, a study was made of the insoluble fraction including the humic compounds and the kerogen fraction. The elemental composition of kerogen and the proportion of humic compounds in organic matter yield valuable indications about the marine autochthonous versus continental organic material. Furthermore, humic compounds are more abundant in immature than in mature sediments, whereas the kerogen fraction is present in both immature and mature sediments.

SAMPLING

Seven samples of 50 g each were studied from Sites 367 and 368 (Figure 1). Five samples are black shale of Late Cretaceous to Albian age and two are shale of Late and Early Cretaceous age. Their stratigraphy and lithological description are given in Figure 2. The two analyzed samples from Site 368 are from either side of a basalt sill.

ANALYTICAL METHODS

The samples were first freeze-dried. Then they were ground in an AUREC pulverizer (size grain $\cong$ 90 μm). The succession of analytical processes is shown on Figure 3. Organic carbon was analyzed with a LECO apparatus. A pyrolysis assay was made on raw samples for rapid source rock and maturation characterization. The method is deduced from kerogen experimental studies (Durand and Espitalie, 1973; Espitalie et al., 1973; Tissot et al., 1974). Equivalent parts of the
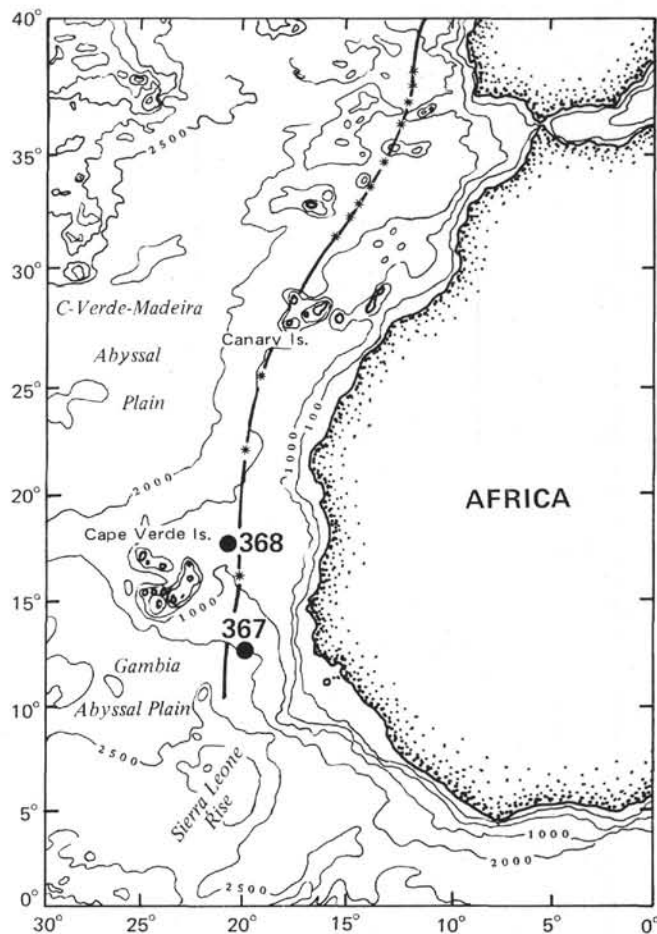

Figure 1. *Location of DSDP Sites 367 and 368.*

ground samples were then extracted with chloroform and the extracts fractionated according to a method described in Huc et al. (1976). The total humic compounds were extracted from the insoluble part of
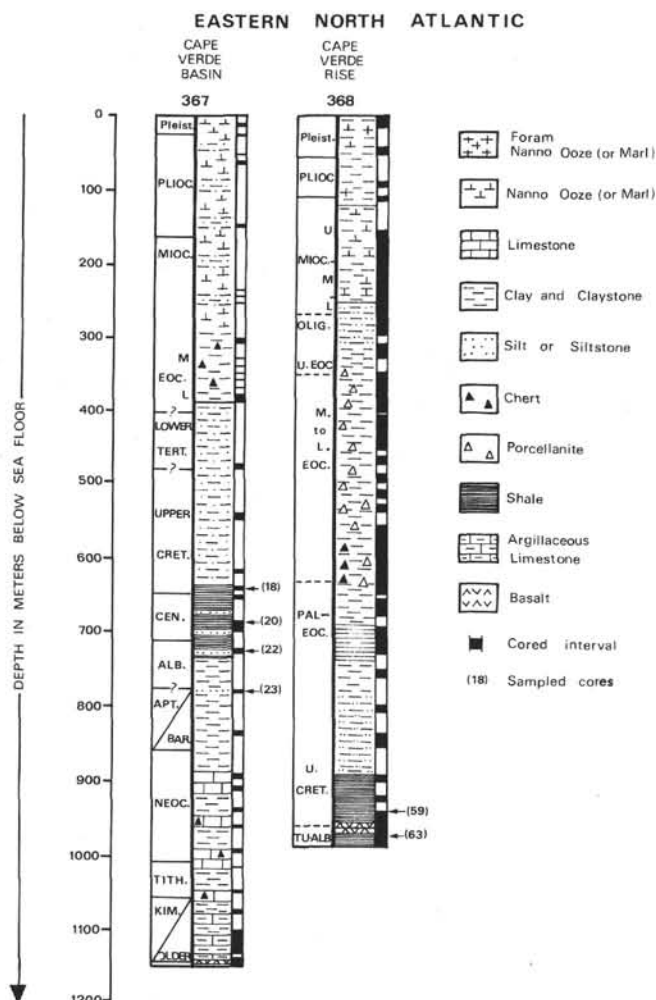
Figure 2. *Stratigraphic location of samples.*

rock and humic acids were separated from fulvic acids (Huc, 1973). The new insoluble part corresponds to humic and the nonhydrolysable fraction to kerogen (Durand et al., 1972; Robin et al., 1976). Analysis of organic content from total humic compounds and from the fulvic fraction was performed with a Carmograph Wosthoff apparatus. Elemental analyses of C, H, O, N, S, and Fe plus ash content were measured on kerogen and calculations were made on a mineral-free basis.

DETAILED RESULTS

Carbonate Carbon (Table 1)

All samples show a low content of carbonates (1% to 23%) and the richest was an Albian black shale from Section 367-22-6.

Organic Carbon (Table 1)

The organic carbon content varied from 36% to 6% for the black shales, 4% for the Lower Cretaceous shale of Site 367, and 3% for the Upper Cretaceous sandy shale of Site 368.

Pyrolysis Assay and Organic Matter Characterization (Table 2, Figure 4)

The pyrolysis assay method (Espitalié et al., in press) gives a rough estimate of the elemental analysis method

on kerogen (Tissot et al., 1974). The combined oxygen and hydrogen indexes related to organic carbon are used for pyrolysis assays. H/C and O/C atomic ratios were used for kerogen. They allow three types of organic matter to be defined; types 1, 2, and 3 (Figure 4). 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. The temperature of the maximum hydrocarbon production during pyrolysis assays corresponds to the immature zone for the 400°-400°C range, to the main oil zone or mature zone from 440°-460°C, and up to 460°C to gas issued from cracking, i.e., the metamorphosed zone.

The maximum of hydrocarbon production during pyrolysis was reached within a low range of temperatures, between 396° and 436°C. Even for the oldest samples from Sites 367 and 368, the temperatures did not reach the main zone of oil formation.

The six black shale samples (Table 1) belong to high potential source rocks of petroleum (Table 2); the three Upper Cretaceous samples (367-18-2, and 368-63-3) are close to type 1 and the two others of Cenomanian and Albian ages (367-20-3 and 367-22-6) are close to type 2. They can be compared to immature material of type 1 where the hydrogen index value is around 600 or more and to type 2 with values of 450-500 (Table 2). Oxygen indexes for the two types are lower than 50.

Sections 368-59-1 and 367-23-2 have intermediate values between reference types 2 and 3. However, Section 368-59-1 is close to the type 2 and Section 367-23-2 is similar to type 3.

Type 3 kerogens correspond mainly to higher plant detritus and humic continental matter. Their potential for oil is usually lower than for types 1 and 2 even if their gas yield is of the same importance. Type 2 kerogens are common in marine sediments with autochthonous organic matter and type 1 corresponds to algal material. Both of them are rich in saturated C-H groups and their potential for oil is good to excellent.

Study of Chloroformic Extracts (Table 3, Figures 5, 6, 7, and 8)

All the studied samples (Table 3) provided large contents of extract (100 to 1700 mg). Their fractionation was performed with the thin layer chromatography (TLC) method. The extract/organic carbon ratio of Site 367 samples was medium (0.04 to 0.09) with a large fraction (Figure 5) of NSO compounds (78%-88%). The extract/organic carbon ratio was higher (0.11 and 0.24) for the two samples from Site 368 and the NSO compounds content was lower (63% and 68%). The gas chromatography analysis of the saturated fraction for the two groups of extracts revealed a C15 to C30 normal alkanes distribution plus the related isoprenoids, commonly present in the saturated fraction of ancient sediments (Figure 6). The normal alkanes distribution is characterized by a high odd-to-even carbon number predominance between C15 and C29 for Site 367 samples with an increasing distribution from C15 to C29. The n-alkanes distribution from Site 368 samples is relatively flat except for the predominance of odd-to-even carbon number n-alkanes in the C25-C29 range.
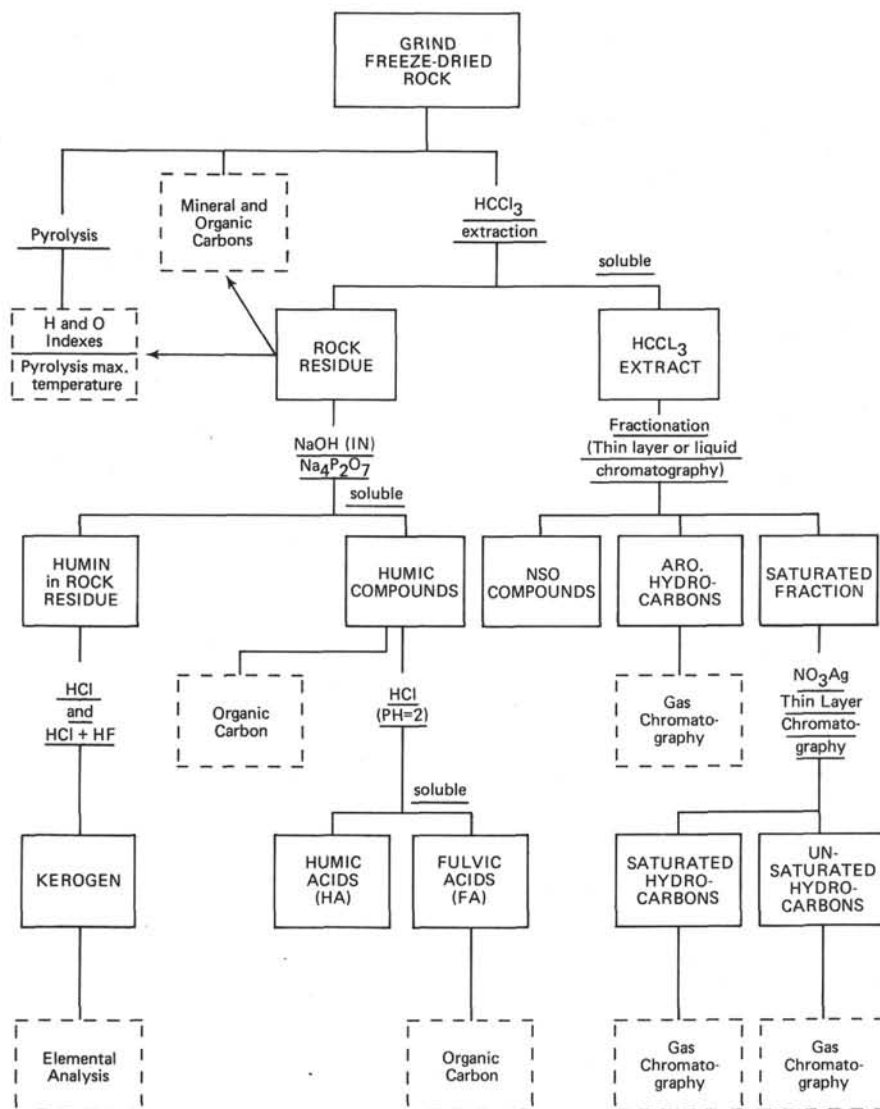
Figure 3. *Schematic analytical processes.*

TABLE 1
Location of Samples, Lithology and Age, and Carbon Data

Sample (Interval in cm)	Depth Below Sea Floor (m)	Lithology	Age	% CaCO₃	Organic Carbon Before HCCl₃ Extraction	After HCCl₃ Extraction
Site 367						
18-2, 80-85	638.30	Black shale	Upper Cretaceous	6	36.09	33.40
18-2, 104-109	638.54	Black shale	Upper Cretaceous	1	36.09	33.40
20-3, 38-48	687.88	Black shale	Cenomanian	13	9.93	9.49
22-6, 0-10	728.00	Black shale	Albian	23	6.10	5.83
23-2, 0-10	777.50	Interbedded shale and clay	Lower Cretaceous	13	4.08	3.96
Site 368						
59-1, 97-107	939.47	Sandy black shale	Upper Cretaceous	4	3.30	3.00
63-3, 17-27	978.17	Black shale	Turonian-Albian	10	7.60	6.12

Phytane and pristane isoprenoids are also present in abundance and phytane is the most important (17.35%-26.86% of total C14-C30 n-alkanes) isoprenoid (Figure 6). A large hump in the C29-C33 range of n-alkanes (Figures 7a, b) is present, except for the older section (368-63-3) (Figure 7c). It corresponds to unsaturated

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TABLE 2
Data of Pyrolysis Essays

Sample (Interval in cm)	Depth Below Sea Floor (m)	Organic Carbon (wt %)	Hydrogen Index (mg Hydroc. Compounds/ g. Org. Carb.)	Oxygen Index (mg CO_2/ g. Org. Carb.)	Pyrolysis Temperature (°C)
Site 367					
18-1, 80-85	638.30	30.86	655	23	403
18-2, 104-109	638.54	34.19	604	20	396
20-3, 38-48	687.88	9.71	477	44	411
22-6, 0-10	728.00	6.13	453	58	419
23-2, 0-10	777.50	4.15	181	86	431
Site 368					
59-1, 97-107	939.47	3.14	313	24	423
63-3, 17-27	978.17	6.92	496	12	436

TABLE 3
Chloroformic Extracts

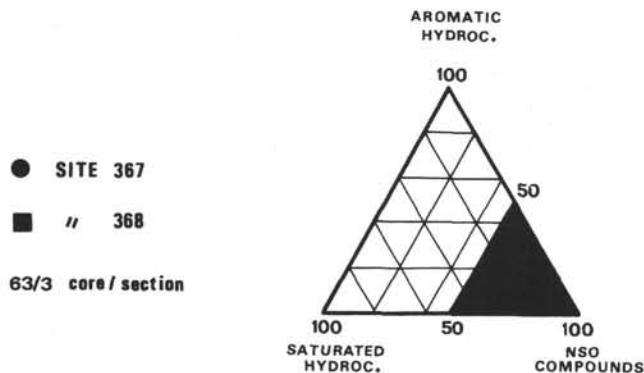| Sample (Interval in cm)	Depth Below Sea Floor (m)	$HCCl_3$ Extract (wt mg)	Extract Rock (wt %)	Extract Org. Carb. (wt)	NSO Compounds (%)	Thin-Layer Chromatography Hydrocarb. Fractions Aro. (%)	Sat. (%)
Site 367							
18-2, 80-109	638.30	1680.9	3.36	0.093	88	7	5
20-3, 38-48	687.88	290.3	0.54	0.055	78	12	10
22-6, 0-10	728.00	265.4	0.33	0.043	81	11	8
23-2, 0-10	777.50	101.7	0.15	0.037	88	7	5
Site 368							
59-1, 97-107	939.47	244.8	0.37	0.114	68	18	14
63-8, 17-27	978.17	1424.3	1.85	0.243	63	18	19
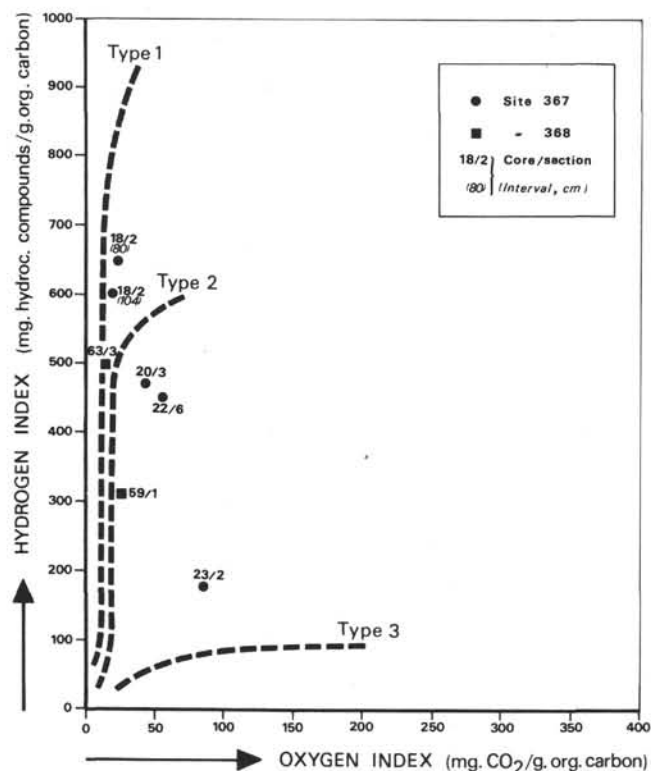
Figure 4. *Pyrolysis essays. Hydrogen and oxygen index (data related to organic carbon).*

compounds probably of polycyclic structures as by gas chromatography of the unsaturated fraction (Figures 7a, c, bottom).

The unsaturated compounds were obtained from TLC fractionation upon layers coated with $AgNO_3$.

The odd predominance shown by n-alkanes, a large content of isoprenoids (compared to n-alkanes), and the occurrence of unsaturated cyclic hydrocarbons are indicative of an early stage of evolution sometime before the beginning of oil genesis and expulsion. A somewhat higher evolution is shown by the samples of Site 368, especially for the oldest sample (Section 368-63-31). This sample shows a more flattened or slightly decreasing distribution of the C14-C30 n-alkanes and a much lower content of unsaturated hydrocarbons (Figure 7), compared to a larger content of extract and hydrocarbons in the samples from Site 367. The important contribution of supposed polycyclics in the total saturated fraction is characteristic of the marine type of organic matter usually found associated with immature samples of the type 2 kerogen. The polycyclics correspond to possible precursors of sterane and triterpane groups of compounds.

The chromatograms obtained with the flame ionization detector (FID) were generally low, especially in the C30 + range because the yield of aromatic fraction was poor for all the samples. However, a C15-C20 mode was detected. That mode, located at the beginning of the chromatogram, corresponds to mono- and

Figure 5. *Gross composition of the chloroformic extracts.*

diaromatic molecules with a probable monoaromatic predominance. The chromatogram from the flame photometric detector (FPD) show in the older samples, such as 368-63-3 (Figure 8), benzothiophenes in the C15-C20 range (Castex et al., 1974).

Study of Humic Compounds (Table 4)

Five samples were analyzed for humic compounds (Table 4). The contents of humic material in cores from Site 367 are generally low compared with their low stage of evolution (< 14% of total organic carbon). The lowest content is for the black shale with the highest organic carbon content, Core 18, Section 2. Such a low proportion of humic material is related to a relatively low stage of the catagenesis and is indicative of a marine origin for the organic matter.

The only black shale sample from Site 368 (Core 63, Section 3) yielded a very poor content of humic material (1.08% of total organic carbon) composed only of fulvic acids. This indicates marine organic matter.

Study of Kerogen (Table 5, Figure 9)

Six samples were analyzed for kerogen content. The elemental composition of the kerogen fraction (Table 5) is interpreted using the H/C and O/C atomic ratios on a Van Krevelen diagram (Figure 9) in order to define the types of organic matter (Tissot et al., 1974). Pyrite represents a large proportion of the ashes (41%) in the

Upper Cretaceous Section 368-59-1. The black shale of Core 18, Section 2, which has the highest content of organic carbon, is located between path I and path II but close to the beginning of path II. All the other samples from Site 367 are located close to the beginning of path II, except Core 23, Section 2, which is in an intermediate position between types II and III. This sample corresponds to "shale and clay" material. All the samples show a very low evolution stage on the diagram.

Samples from Site 368 are also close to path II, but they are farther from the beginning of path II than the other samples. That location indicates a somewhat more advanced stage of evolution, and the older Core 63, Section 3 is even farther from path II.

All the black shale can be compared with aliphatic and alicyclic-rich kerogens of type II which are commonly found in organic matter from marine origin deposited in a reducing environment. The Lower Cretaceous sample of Section 367-23-2 is attributed to a mixture of continental and marine organic matter. All
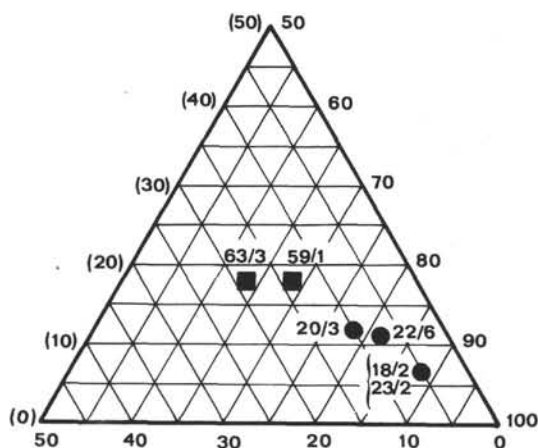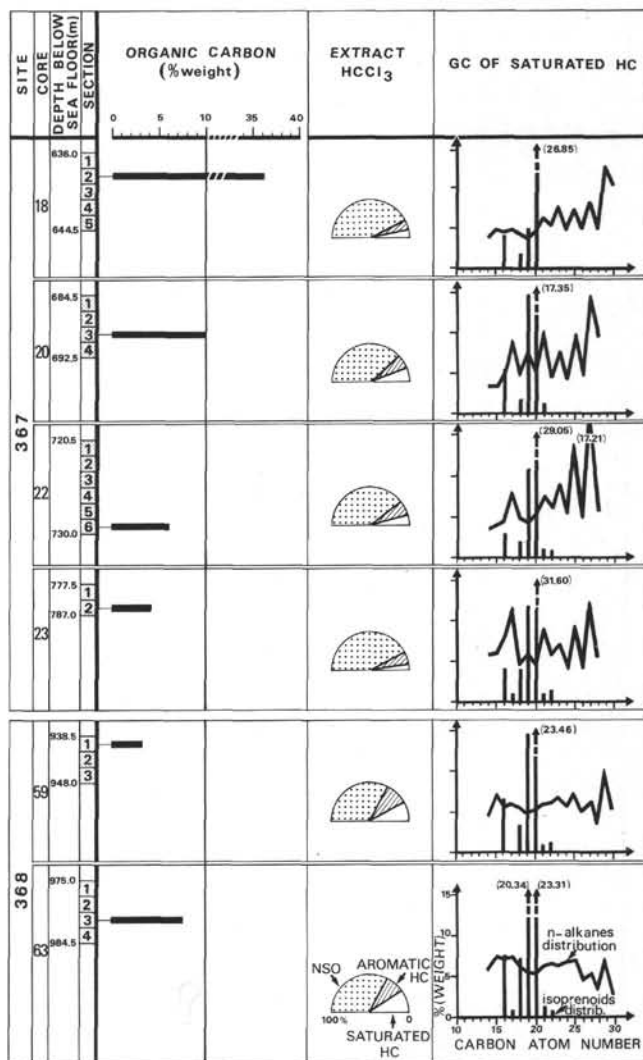

Figure 6. *Organic carbon content; gross composition of chloroformic extracts; distribution of normal alkanes and isoprenoids in the C14-C30 range.*
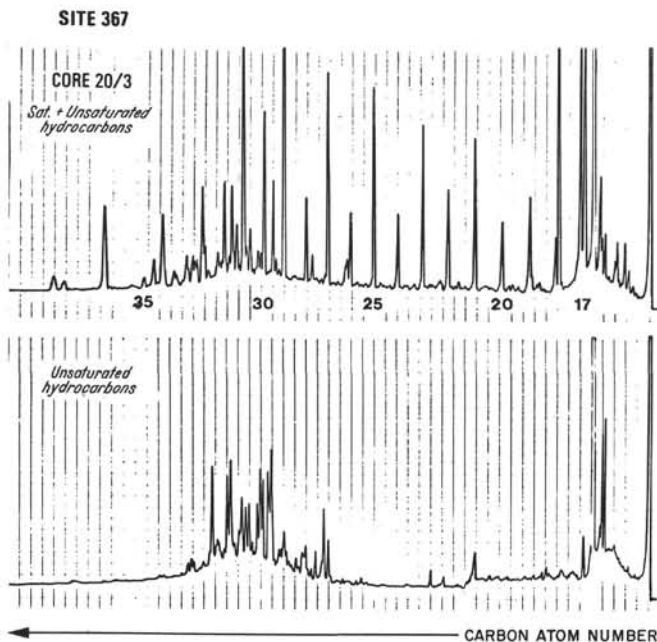
SITE 367

Figure 7a. *Extracts. Gas chromatography of saturated (top chromatogram) and unsaturated (bottom chromatogram) hydrocarbons. Site 367, Core 20, Section 3. Black shale, Cenomanian.*
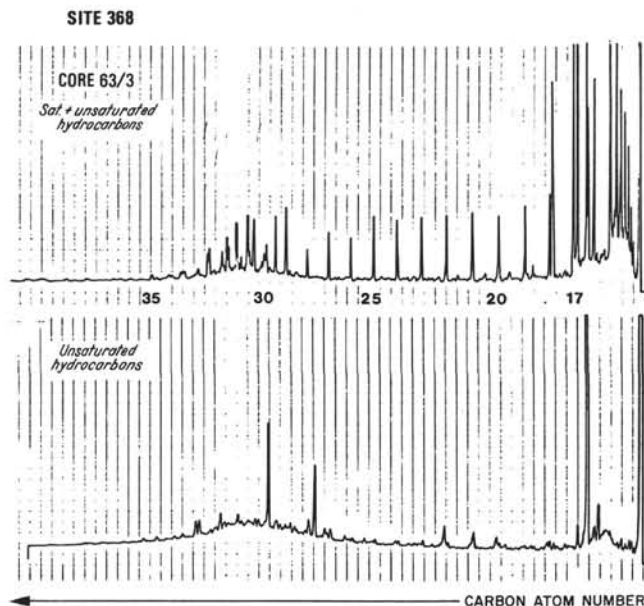
SITE 368

Figure 7b. *Extracts. Gas chromatography of saturated (top chromatogram) and unsaturated (bottom chromatogram) hydrocarbons. Site 368, Core 59, Section 1, Sandy black shale, Upper Cretaceous.*

these characteristics were largely comparable with the previous conclusions deduced from the pyrolysis assays.

DISCUSSION AND CONCLUSIONS

The organic matter of black shale of Cretaceous age from Leg 41 sediments is of marine origin, and the shales correspond to excellent potential oil source rocks. Their low content of humic compounds suggest a

SITE 368

Figure 7c. *Extracts. Gas chromatography of saturated (top chromatogram) and unsaturated (bottom chromatogram) hydrocarbons. Site 368, Core 63, Section 3, Black shale, Turonian to Albian.*
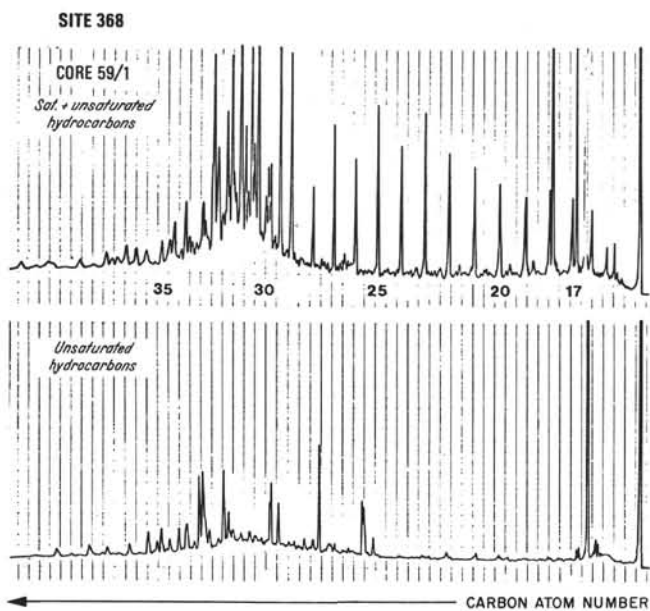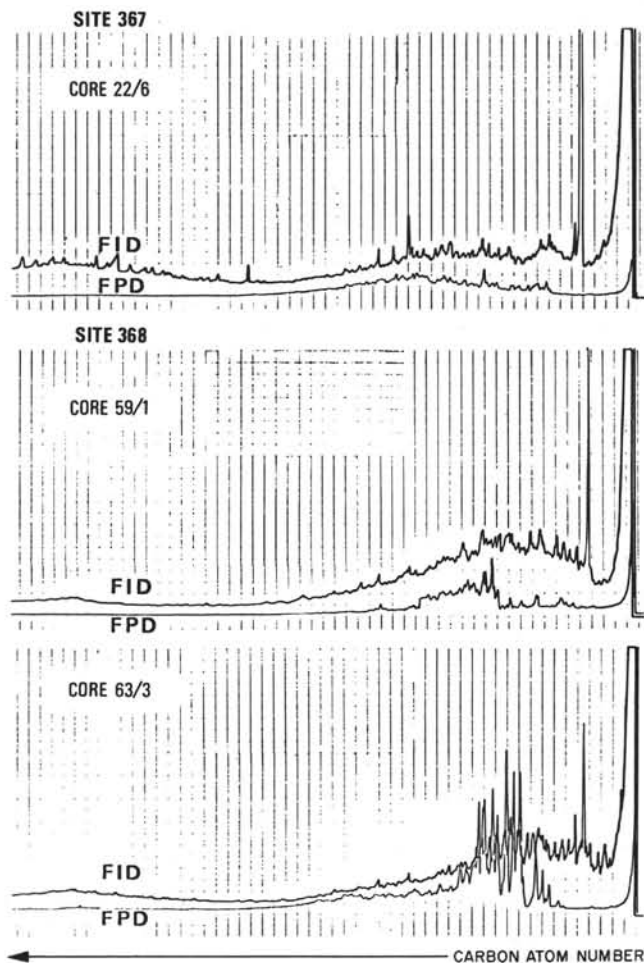

Figure 8. *Extracts. Gas chromatography of aromatic fraction (FID) and thiophenic compounds (FPD).*

TABLE 4
Humic Compounds – Carbon Organic Content

Sample (Interval in cm)	Depth Below Sea Floor (m)	Total Organic Carbon (wt %)	Carbon Content (Percent Total Org. Carbon)			FA	
			Humic Compounds (FA + HA)	Fulvic Acids (FA)	Humic Acids (HA)		HA
Site 367							
18-2, 80-109	638.30	32.52	0.52	0.43	0.09	(4.89)	
20-3, 38-38	687.88	9.71	10.00	1.65	8.35	0.20	
22-6, 0-10	728.00	6.13	11.58	1.63	9.95	0.16	
23-2, 0-10	777.50	4.15	14.22	1.44	12.78	0.11	
Site 368							
63-3, 17-27	978.17	6.92	1.08	1.08	0.00	indet.	

TABLE 5
Kerogens – Elemental Composition and Ash Content

| Sample (Interval in cm)	Depth Below Sea Floor (m)	Weight Percent, on Ash-Free Basis					H/C	O/C ×10²	Ashes (wt %)
		C	H	O	S	N			
Site 367									
18-2, 80-109	638.30	67.12	7.90	11.33	11.44	2.21	1.41	12.66	7.94
20-3, 38-48	687.88	67.81	7.02	14.97	7.36	2.84	1.24	16.55	17.00
22-6, 0-10	728.00	65.78	7.25	13.75	10.85	2.37	1.32	15.67	19.88
23-2, 0-10	777.50	69.10	6.37	16.80	4.60	3.13	1.11	18.24	31.22
Site 368									
59-1, 97-107	939.49	77.61	7.53	9.61	2.79	2.47	1.16	9.28	43.04
63-3, 17-27	978.17	78.47	7.65	5.75	5.27	2.86	1.17	6.49	22.46
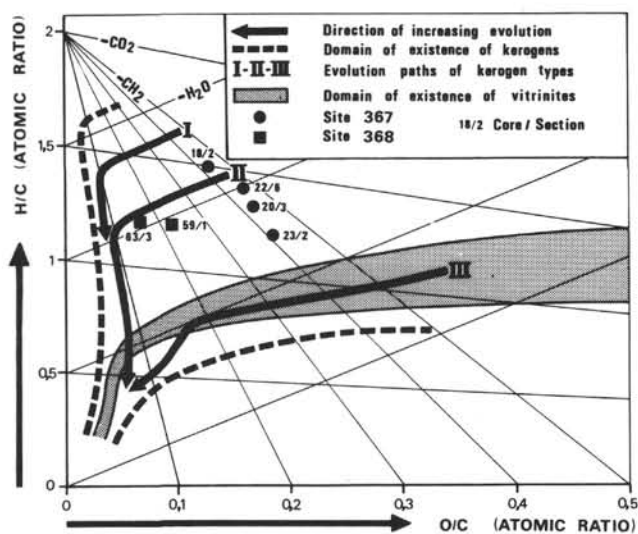
Figure 9. *Kerogens. H/C and O/C diagram.*

low original content of continental organic matter as confirmed with pyrolysis assays. However, some continental input is present in the Lower Cretaceous shale of Section 367-23-2. The relatively low stage of evolution of sediments from Site 367 is shown from pyrolysis indices, chloroformic extracts, and kerogen data. A somewhat higher evolution is apparent for the samples from Site 368, especially for the oldest sample, from beneath a volcanic sill. This latter sample

corresponds to the beginning of the principal zone of oil formation.

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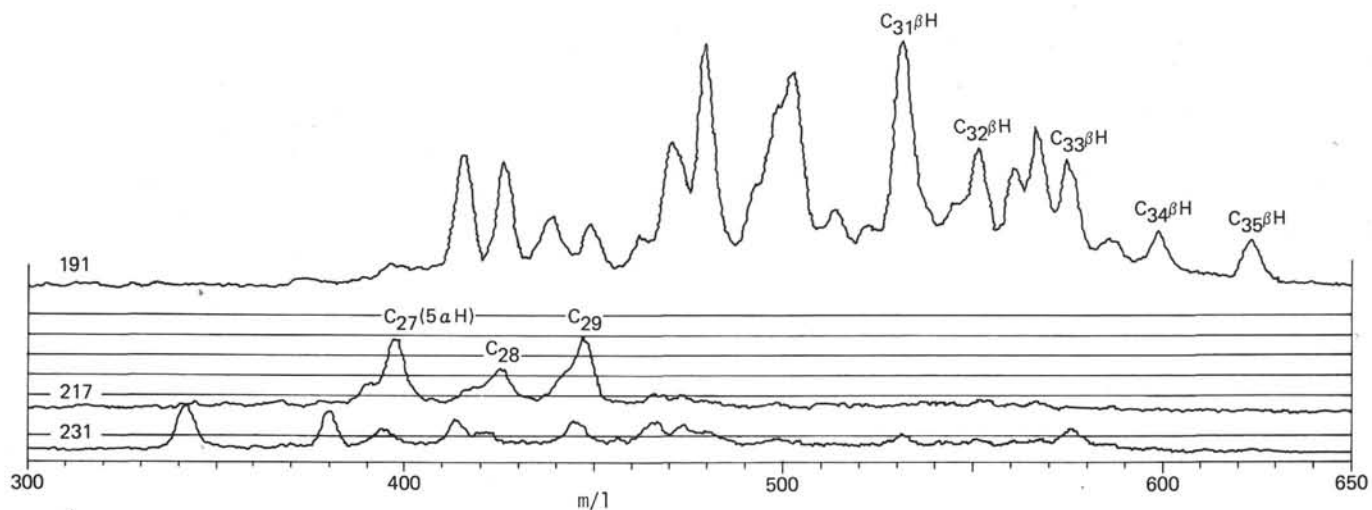
Figure 10. *Mass chromatogram of Sample 367-18-2, 80-109 cm, corresponding to peaks 191, 217, and 231.*
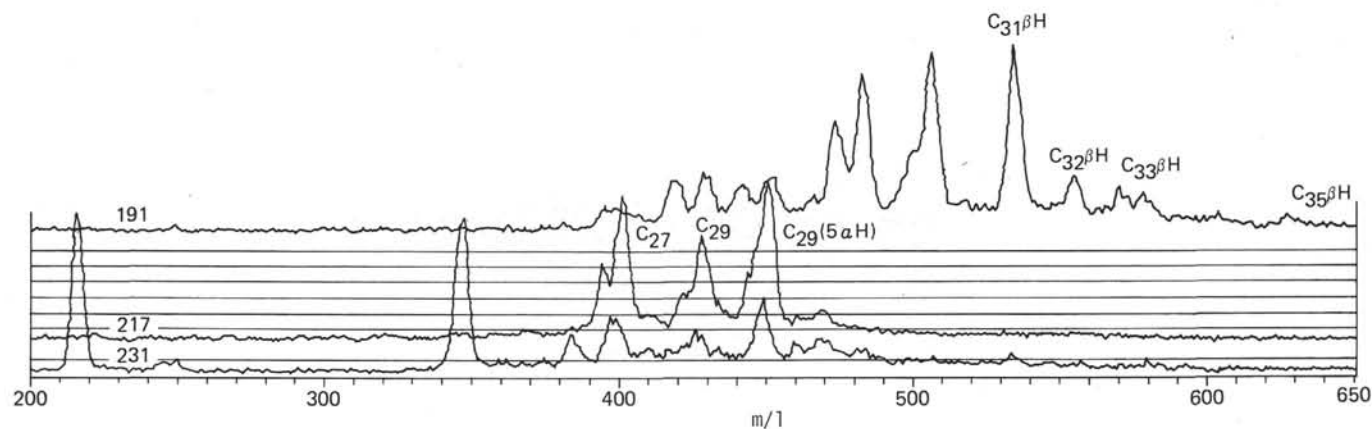

Figure 11. *Mass chromatogram of Sample 367-23-2, 6-10 cm corresponding to peaks 191, 217, and 231.*
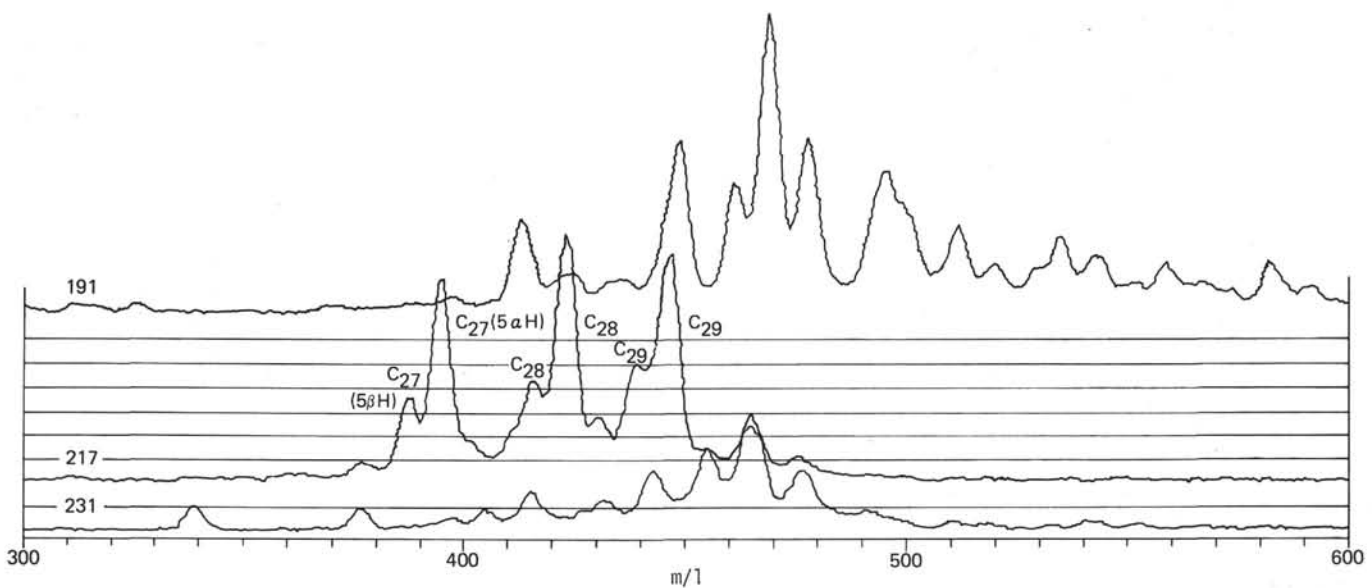

Figure 12. *Mass chromatogram of Sample 368-59-1, 97-107 cm, corresponding to peaks 191, 217, and 231.*
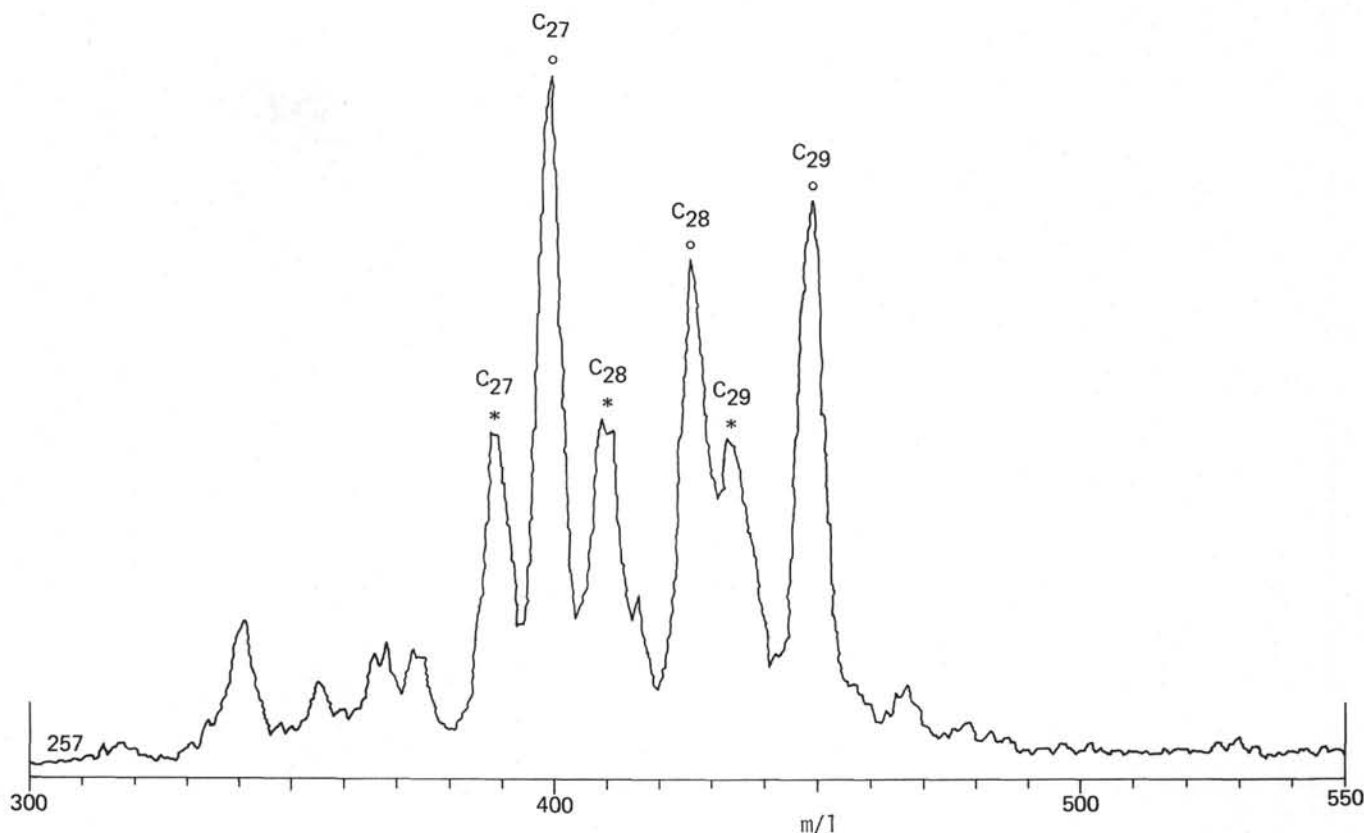
Figure 13. *Mass chromatogram of Sample 367-23-2, 10-10 cm, corresponding to peak 257 (sterenes).*

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APPENDIX
Analysis by Gas Chromatography-Mass Spectrometry of Polycyclic Hydrocarbons

The hopane, steranes, and methyl steranes have been investigated by computerized GC-MS on Samples 367-18-2, 80-109 cm; 367-23-2, 0-10 cm; and 368-59-1, 97-107 cm. The mass chromatograms corresponding to peaks 191, 217, and 231 are shown on Figures 10, 11, and 12. They correspond, respectively, to the hopane, steranes, and methylsteranes series.

Steroids are present in all samples, and are relatively abundant. They occur mostly as steranes in Sections 368-59-1, and mostly as unsaturated sterenes in Sections 367-18-2 and 367-23-2. The sterenes correspond to two different series, which could be the Δ^4 and Δ^5 sterenes (Figure 13).

Steranes of Section 368-59-1 also correspond to a different series: the 5 α H steranes (C_{27}, C_{28}, C_{29}) are the major series and the subordinate one is probably the 5 β H steranes (C_{27}, C_{28}, C_{29}). Methylsteranes show a low abundance in all sediments compared to steranes or sterenes.

Triterpanes of the hopane type are particularly abundant in Section 367-18-2. The naturally occurring and less stable 17 (βH) hopane series is predominant in Sections 367-18-2 and 367-23-2 (up to C_{35}, with a single diastereomer in position 22). However, the more stable 17 (αH) hopane series occurs in subordinate amounts. In Section 368-59-1, the 17 (αH) hopanes are predominant.

The occurrence of unsaturated compounds and of the 17 (βH) hopane series indicates a low stage of diagenesis. However, Section 368-59-1 may correspond to a more advanced stage of diagenesis.