21. ORGANIC GEOCHEMISTRY OF SOME ORGANIC-RICH SHALES FROM DSDP SITE 397, LEG 47A, EASTERN NORTH ATLANTIC

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ABSTRACT

Organic carbon-rich shales were encountered in the Tarfaya Basin on DSDP Leg 47A, both above and below a major Neogene unconformity. The overlying samples of early Miocene age contain organic matter mainly of marine origin, deposited in a reducing environment. They are similar to some Cretaceous black shales of the Cape Verde Basin (Leg 41, Site 367). The Hauterivian sediments beneath the unconformity contain continental organic matter which is partly of detrital origin. The maturation stage is low for all types of organic material examined.

INTRODUCTION

The aim of this paper is to characterize the organic matter of some shales encountered during DSDP Leg 47A. Organic-rich shales were penetrated both above the major Neogene unconformity (in allochthonous Miocene strata) and below (Lower Cretaceous sediments).

A pyrolysis assay on untreated samples and a chloroform extraction were performed to characterize the type of organic matter. Then, analysis of the elemental composition of kerogen after humic extraction was conducted to check these data and results.

SAMPLING

Middle Cretaceous black shales were not encountered during Leg 47A drilling (Figure 1), but some organic-rich shales were penetrated. They represent medium to fine-grained lower Miocene shales, and laminated and more massive Hauterivian shales and mudstones.

Nine samples of 40 to 70 grams each were studied from cores on both sides of the major erosional surface at a 1300-meter sub-bottom depth. Their stratigraphy and lithological description are summarized in Figure 2.

ANALYTICAL METHODS

The samples were freeze-dried, then ground in an AUREC pulverizer (size grain $\cong 90 \ \mu$ m). The succession of processes are schematized in Figure 3. Organic carbon was analyzed with a LECO apparatus. A pyrolysis assay was applied on raw samples as a method of rapid source rock and maturation characterization (Espitalié et al., 1977). Equivalent parts of ground samples were then extracted with chloroform followed by a thin-layer chromatography fractionation (Huc et al., 1976). The residual insoluble organic part of the

rock after humic compounds were extracted (Huc et al., 1978) corresponds to humin, its non-hydrolyzable fraction corresponds to kerogen. Organic carbon contents of the total humic compounds and of the fulvic fraction were determined with a CARMHOGRAPH WOSTHOFF apparatus. Elemental analyses of C, H, O, N, S, and Fe plus ash content were measured on kerogen and the values recalculated on a mineral-free basis.

DETAILED RESULTS

Mineral Carbon

The content of mineral carbon is low (0.76 to 2.16%) for the Cretaceous samples and higher (1.88 to



Figure 1. Location of DSDP Site 397 in the Tarfaya Basin.

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Figure 2. Stratigraphic position of sampled cores.

4.08%) for the overlying Miocene samples (see Table 1).

Organic Carbon

Cretaceous samples differ greatly in their organic content from the Miocene samples. Organic content is 2.14 to 4.78 per cent for Miocene sediments and 0.53 to 0.92 per cent for Cretaceous samples (see Table 1).

Pyrolysis Assay and Organic Matter Characterization

This method of pyrolysis performed on total rock provides three parameters, two of them being an approximate elemental analysis of the organic matter. They are the hydrogen index and the oxygen index (Espitalié et al., 1977), which are strongly correlated with the H/C and O/C ratios as measured by a true elemental analysis of the kerogen fraction.

By using a Van Krevelen diagram (H/C versus O/C ratios) for kerogen or, alternatively, the equivalent hydrogen index versus oxygen index for total rock, it is possible to define three main types of kerogen (Tissot et al., 1974). All studied samples of early Miocene age are close to the evolution path of kerogen Type II (Figure 4). They are characterized by a high hydrogen index and a low oxygen index (Table 2). This type of organic matter is mostly derived from planktonic and other algae, and marine zooplankton. The varved and massive Hauterivian mudstones show a low to very low hydrogen index and a high oxygen index (Table 2). They are related to kerogen Type III (Figure 4) which is derived mostly from continental material, i.e., either contemporaneous higher plants and humic compounds and/or reworked, more or less oxidized, organic matter.

The temperature of the maximum of the pyrolysis peak reached during pyrolysis assays corresponds to the immature oil zone in the 400° to 440°C range, to the main oil zone or mature zone from 440° to 460°C, and to the cracking or gas zone beyond 460°C. All the Neogene samples (Table 2) with a 414° to 425°C range belong to the immature zone. The Lower Cretaceous samples (Table 2) are also immature as shown by their 421° to 432°C temperatures.

Humic Compounds

Preparation of humic compounds was performed on five selected samples. The content of humic compounds, i.e., fulvic plus humic acids, is expressed in Table 3 by the percentage of total organic carbon contained in these compounds. It is low for all the samples: 0.24 to 0.55 per cent of humic carbon relative to the weight of rock. However the ratios of humic carbon to total organic carbon fall into two distinct groups for the Neogene and the Cretaceous samples; a low ratio (8 and 9%) is seen for Neogene samples while a higher ratio (40 to 80%) was obtained for the Cretaceous. Huc and Durand (1977) showed that the humic fraction composes a larger part of the total organic carbon (>15%) in immature material of Type III than for Types II and I. Consequently, a continental origin is deduced for the kerogen fraction of the analyzed Cretaceous samples.

Kerogen Fraction

Seven samples were selected for detailed analysis. Their acidic treatment with HC1 and HF under nitrogen atmosphere was followed by the elemental analysis of kerogen. The data (Table 4) are presented on a Van Krevelen diagram (Figure 5) where the three main evolution paths (I, II, and III) are shown for reference.

The results are in agreement with those obtained from the pyrolysis assay method. The three Neogene samples are close together and somewhat below the evolution path of kerogen Type II which corresponds to marine planktonic material. Moreover, these sam-

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Figure 3. Schematic analytical processes.

TABLE 1 Location of Samples From Hole 397A, With Lithology, Age, and Carbon Data

					Organic Carbon (wt. %)		
Sample (Interval in cm)	Depth Below Sea Floor (m)	Lithology	Age	Mineral Carbon (wt. %)	Before CHCl ₃ extrac.	After CHCl ₃ extrac.	
15-6, 6-10	1066.06	Medium fine- grained shale	Early Miocene	3.88	4.56	4.47	
16-5, 81-90	1074.81		-	2.00	3.59	3.69	
17-1, 144-150	1078.94	-		3.08	4.78	4.84	
24-4, 60-66	1177.60	-	-	1.88	2.92	3.06	
28-2, 112-117	1241.62	-		4.08	2.14	2.17	
35-3, 98-108	1309.48	Laminated shale	Hauterivian	1.76	0.56	0.54	
46-3, 127-137	1395.27	Laminated mudstone	-	2.16	0.53	0.51	
48-1, 92-105	1410.92	Slighter more massive mudstone	-	1.00	0.66	0.69	
52-1, 104-117	1449.04	More mussive mudstone	7	0.76	0.92	0.92	

ples are located near the origin of the evolution path which confirms a low degree of maturity. For two of the four Cretaceous samples, elemental analysis was not significant: the sample from Section 397-46-3, because of an excessive pyrite content (>70% of total kerogen); and the sample from Section 397-48-1, with more than 50 per cent unexplained ashes in the kerogen. The other two samples (from Cores 397-35-3 and 397-52-1) are above or close to the evolution path of kerogen Type III, as expected, and correspond to a material of continental origin.

Chloroform Extracts

All the samples provided low extract content, i.e., between 78 and 4 milligrams (Table 5). The extract to



Figure 4. Pyrolysis assays with hydrogen and oxygen indexes (data related to organic carbon).

TABLE 2 Pyrolysis Assay Data of Hole 397A Samples

Sample (Interval in cm)	Depth Below Sea Floor (m)	Organic Carbon (wt. %)	Hydrogen Index (mg hydroc, compounds related to g org. carb.)	Oxygen Index (mg CO ₂ related to g org. carb.)	Pyrolysis Temperature (°C)
15-6, 6-10	1066.06	4.56	470	32	414
16-5, 81-90	1074.81	3.59	439	51	418
17-1, 144-150	1078.94	4.78	458	55	415
24-4, 60-66	1177.60	2.92	366	73	425
28-2, 112-117	1241.62	2.14	419	76	423
35-3, 98-108	1309.48	0.56	68	288	432
46-3, 127-137	1395.27	0.53	48	260	421
48-1, 92-105	1410.92	0.66	72	395	421
52-1, 104-117	1449.04	0.92	95	162	430

organic carbon ratio was low (0.022 to 0.031) for the Neogene extracts as well as for the two Lower Cretaceous extracts (0.015 and 0.019). The latter were too lean (8 and 4 mg) to be fractionated.

The thin-layer chromatography method analysis of the three Neogene samples reveals a large fraction of NSO compounds (83 to 87%). The gas chromatography of their saturated + unsaturated hydrocarbons (Figure 6) shows a C_{15+} normal alkanes distribution characterized by a high odd to even carbon number predominance in the C_{21} to C_{33} range, which increases

TABLE 3 Humic Compounds and Organic Carbon Content in Hole 397A Samples

			Humic Compounds			
Sample (Interval in cm)	Depth Below Sea Floor (m)	Total Organic Carbon ^a (wt. %)	Humic Carbon (% relative to rock wt.)	Humic Carbon Total Org. C (%)		
16-5, 81-90	1074.81	3.69	0.33	9		
24-4, 60-66	1177.60	3.06	0.24	8		
46-3, 127-137	1395.27	0.51	0.33	65		
48-1, 92-105	1410.92	0.69	0.55	80		
52-1, 104-117	1449.04	0.92	0.37	40		

^aAfter CHCl₃ extraction.

with the increasing carbon number for samples from Cores 397-15-6 and 397-17-1. The only hydrocarbons synthesized by organisms beyond the C22 n-alkane are derived from higher plants and bacteria. Thus, the continental input usually determines the C22 to C30 distribution. The C_{16} to C_{18} mode is important in the sample from Core 397-28-2. It may have been derived from the lipids of algal material (Tissot et al., 1977). Furthermore, the predominance of even-numbered molecules suggests reduction processes. The C₁₆ to C₁₈ molecules are less important in samples from Cores 397-17-1 and 397-15-6. There, phytane predominates over pristane; this also suggests a reducing environment of deposition. A hump of the base line is present in the C₂₉ to C₃₃ n-alkanes range that indicates some polycyclic structures, saturated and unsaturated. The gas chromatogrphy of the unsaturated hydrocarbon fraction (Figure 7) of samples from Cores 397-15-6 and 397-17-1 shows sterenes and triterpenes in the C_{25} + range which would correspond to precursors of sterane and triterpane compounds. Large amounts of steranes are only observed in marine sediments where they probably originate from plankton, although a wide distribution of sterols is found in the plant and animal kingdoms. The chromatogram of the sample from Core 397-15-6, obtained from the saturates + unsaturates fraction in the C₂₉ to C₃₅ n-alkanes range, is similar to that found in Cenomanian black shales from DSDP Site 367 (Deroo et al., 1978).

CONCLUSIONS

The organic matter of lower Miocene sediments in the samples studied is considered to be mainly of marine origin and deposited in a reducing environment. This conclusion is based on data from pyrolysis, humic and kerogen analysis, and chloroform extracts. Its geochemical characteristics are comparable to those of some black shales samples previously examined (Deroo et al., 1978) in Cenomanian and Albian of the Cape Verde Basin (Leg 41, Site 367). By contrast, the underlying Lower Cretaceous samples of Hauterivian age, despite a presumed quiet water depositional environment, correspond to continental material which probably includes a reworked or oxidized fraction of detrital origin. The maturation stage was low for all types of organic material.

 TABLE 4

 Elemental Composition and Ash Content of Kerogen From Hole 397A Samples

Sample (Interval in cm)	Depth Below Sea Floor (m)	Weight, Per Cent, on Ash-Free Basis					Ashes	Atomic		
		С	Н	Ν	0	S	Fe	%)	H/C	O/C
15-6, 6-10	1066.06	46.5	4.9	2.3	11.8	19.0	10.8	20.3	1.25	0.19
17-1, 144-150	1078.94	47.1	5.0	2.5	11.8	18.5	11.6	19.8	1.27	0.19
28-2, 112-117	1241.62	54.9	5.7	2.5	12.6	13.3	7.0	24.0	1.25	0.17
35-3, 98-108	1309.48	44.7	3.6	1.1	14.2	8.6	3.6	23.9	0.96	0.24
46-3, 127-137	1395.27	15.5	1.6	0.9	5.4	40.7	34.2	39.1	1.22	0.26
48-1, 92-105	1410.92	31.7	3.0	1.1	13.5	11.4	2.8	30.4	1.15	0.32
52-1, 104-117	1449.04	46.2	3.4	1.9	18.3	10.7	3.8	10.8	0.89	0.30



Figure 5. Kerogens plotted in a H/C and O/C diagram.

TABLE 5 Gross Composition of Chloroformic Extracts From Hole 397A Samples

Sample (Interval in cm)		HCCl ₃ Extract (wt. mg)	Extract Related to Rock (wt. %)	Extract Related to Organic Carbon (wt.)	Thin-Layer Chromatography Fractionation			
	Depth Below Sea Floor (m)				NSO Compounds (%)	Hydrocar Aro. (%)	bon Fractions Sat. + Unsat. (%)	
15-6, 6-10	1066.06	46.7	0.11	0.024	83	10	7	
17-1, 144-150	1078.94	77.8	0.11	0.022	87	7	6	
28-2, 112-117	1241.62	38.8	0.07	0.031	84	8	8	
35-3, 98-108	1309.48	4.0	0.01	0.019	Non-fractionable			
52-1, 104-117	1449.04	8.0	0.01	0.015				

Middle Cretaceous black shales were not encountered at Site 397, so the question remains whether the lowermost Neogene series are or are not partly composed of reworked Cenomanian-Aptian material slumped off the edge of the continental shelf during Neogen time. If the organic matter is definitely not reworked, then it has to be considered as the first indication of Neogene organic-rich shales in the area.



Figure 6. Extracts: gas chromatography of saturated + unsaturated hydrocarbons. (A) Section 397A-15-6, fine-grained shale, early Miocene; (B) Section 397A-17-1, finegrained shale, early Miocene; (C) Section 397A-28-2, fine-grained shale, early Miocene.

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Figure 7. Extracts: gas chromatography of saturated (top chromatogram) and unsaturated (bottom chromatogram) hydrocarbons. Composite Sections 397A-15-6 and 397A-17-1.

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