

STUDY OF ORGANIC MATTER ON SOME CENOZOIC SAMPLES FROM THE DSDP WALWIS RIDGE LEG 75 HOLES, WITH EMPHASIS ON ITS ORIGIN AND ITS PETROLEUM POTENTIAL

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ABSTRACT

The authors have studied the organic matter content of 11 Cenozoic core samples from four Walwis Ridge Leg 75 Holes by means of organogeochemical and palynological techniques. The kerogen concentrates of the Paleogene to Early Miocene samples contain planktonic and land-derived particles. These samples are scarce in organic matter ($C_{org} < 0.4\%$) due to the low sedimentation rate and/or the low surface biological productivity. The Upper Miocene to Pleistocene samples, rich in organic matter (C_{org} mostly $> 1\%$) also contain planktonic and land-derived organic particles. The proportion of the planktonic organic matter and C_{org} content increase from the Upper Miocene up to the Pleistocene. These observations can be explained by an upward increase in surface productivity and/or sedimentation rate. The upper, organic-rich part of the Cenozoic sequence accumulated in oxygen-depleted environment caused by the high plankton production due to the Benguela upwelling evolved in Late Miocene time. This part of the sequence may be regarded as a good potential oil source rock but the generation of a substantial amount of hydrocarbons in it has not started yet.

INTRODUCTION

The objectives of this study are to characterize the amount and composition of organic matter preserved in Walwis Ridge Cenozoic sediments and to evaluate of some conditions of their deposition and their petroleum potential.

We have received 11 frozen core samples from four holes — 530 A, 530 B, 532 A, 532 B — of the Leg 75 (Fig. 1). Their geological ages range from Pleistocene to Paleocene. The samples are diatomaceous and/or nanno-ooze and marl. They were studied for C_{org} , extractible organic matter and kerogen. For the chemical characterization of the kerogen a special pyrolysis device was used.

METHODS

The analyses of the samples started after their thawing. They were checked in UV-light and the stainings visible with eyes or by fluorescence were eliminated. Each samples were cut in two and one part was grinded in a Fritsch ball mill.

The extraction of rock powder was carried out with $CHCl_3$ (200 ml). The IR spectra of the extracts were recorded on Zeiss-Jena Spekdor IR 75 spectrophotometer using KBr disc technique, and evaluated by baseline method.

Asphaltenes were precipitated from the chloroform extracts with a large excess of petroleum ether (40—70 °C). Asphaltene-free extracts were separated on silica gel

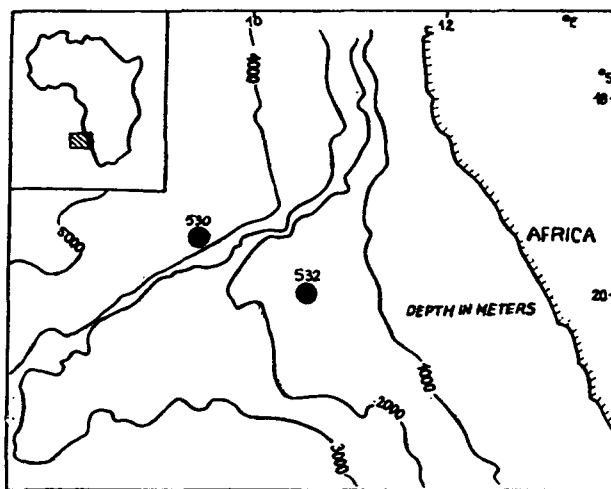


Fig. 1. Location of the Holes

column by elution technique. Eluents were: petroleum ether (40–70 °C) for the saturated HC fraction; benzene for the aromatic HC fraction; benzene-methanol (1 : 1) mixture for the resin fraction.

The saturated HC fraction was analysed on a CHROM ROM 41 type gas chromatograph using a 20 m × 0.25 mm capillary column coated with OV-1 stationary phase. The chromatograph was programmed from 100 to 250 °C at 6 °C per min. H₂ was the carrier gas. The n-alkane peaks were identified by addition of n-alkane standards, and response factors were applied.

The extracted rock powder was treated by hydrochloric acid to eliminate the carbonates. The C_{org} content of the carbonate-free samples was measured in a special equipment using CO₂-free dry air as a carrier gas and a catalytic postburner. The samples were heated up 700–800 °C at 6 °C per min. heating rate. The volatile C_{org} was measured in the same way but using purified N₂ gas as a carrier gas.

The second part of the sample was crushed, then it was treated with hydrochloric and hydrofluoric acid and centrifugated in ZnCl₂-solution. The concentrate was mounted on a glass slide and examined microscopically.

The path of the sample preparation and the analysis are shown on a flow chart (Fig. 2).

RESULTS

The organogeochemical and palynological data are shown in the Tables 1–3 and Figs 3–6.

A separation of the samples in two groups is clearly visible from these data.

The Paleogene to Early Miocene samples are characterized by a low C_{org} content (0.04–0.36%) and a relatively high extract to C_{org} ratio (78–1100 mg/g) (Table 1, Fig. 3).

The absence of the 960 cm⁻¹ absorption band, the predominance of the esthers as carbonyl bearing molecules and the presence of absorption bands in the 600–

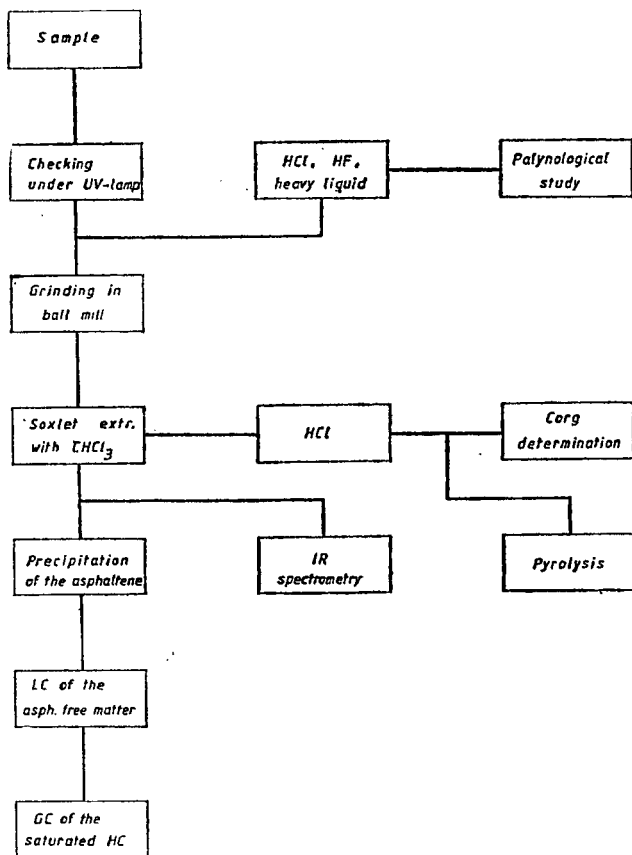


Fig. 2. Flow chart of the analytical procedures

400 cm^{-1} range (organic sulphur compounds) in IR spectra are characteristic for the extracts (Table 2, Fig. 4 b).

The palynological concentrate does not contain woody particles, the sporomorphs are very scarce. (Fig. 5). The palynomorphs proved to be well preserved and light.

The Upper Miocene to Pleistocene samples are characterized by a high C_{org} content (0.39—3.66%) and a relatively low extract to C_{org} ratio (23—39 mg/g) (Table 1, Fig. 3), the 29.2 sample from the Hole 532 A has a petroliferous odor. The presence of a 960 cm^{-1} absorption band (saturated cyclic hydrocarbons) and the predominance of the acids and ketones as carbonyl-bearing molecules in IR spectra are characteristic for the extracts (Table 2, Fig. 4. a).

The quantity of extract obtained from these samples was sufficient for the determination of the bulk composition and for GC-study of the alkanes (Table 3, Fig. 6). The extracts are characterized by a high resin content (55—75%). In the n-alkane spectra the $C_{23}+$ molecules are dominating and a strong odd predominance was found. The pristane to phytane, pristane to n- C_{17} and phytane to n- C_{18} ratios are varying between 0.75—1, 0.5—0.8 and 0.8—1.2, respectively.

TABLE 1

C_{org}, extract and HCl-insoluble residue data of the Leg 75 samples

Site	Core	Section	Sub-bottom depth m	C _{org} %	mg extract / g rock	mg extract / g C _{org}	HCl-insoluble residue %
530 A	5	5	162	1.65			90
	13	5	249	0.39	0.15	39	62
	24	6	343	0.21			71
	37	3*	467	0.04—0.05	0.13—0.55	380—1100	50—47
	43	1	523	0.08	0.15	190	48
530 B	1	1	0	0.36	0.28	78	22
	33	1	126	0.95	0.35	36	49
532 A	7	3	25	3.39	0.93	27	37
	29	2	121	3.66	0.98	27	52
	49	2	199	1.96	0.43	22	44
532 B	63	1	256	0.63	0.19	29	29

* The sample was separated to two parts before grinding

TABLE 2

Significant bands and the position of maximum of broad overlapped bands in IR spectra of extracts of the Leg 75 samples

Site	Core	Section	Sub-bottom depth m	Position of absorption bands. Wave number (cm ⁻¹)									
				3500—3200	2960—2850	1740—1670 maximum 1740 1710	1650—1600	1460	1370	960	900—690 maximum 870 790	720	600—400
530/A	13	5	249	+	+	+	+	+	+	+	+	+	+
	37	3/A	467	+	+	+	+	+	+	+	+	+	+
	37	3/B	467	+	+	+	+	+	+	+	+	+	+
	43	1	523	+	+	+	+	+	+	+	+	+	+
530/B	1	1	0	+	+	+	+	+	+	+	+	+	+
	33	1	126	+	+	+	+	+	+	+	+	+	+
532/A	7	3	25	+	+	+	+	+	+	+	+	+	+
	29	2	121	+	+	+	+	+	+	+	+	+	+
	49	2	199	+	+	+	+	+	+	+	+	+	+
532/B	63	1	256	+	+	+	+	+	+	+	+	+	

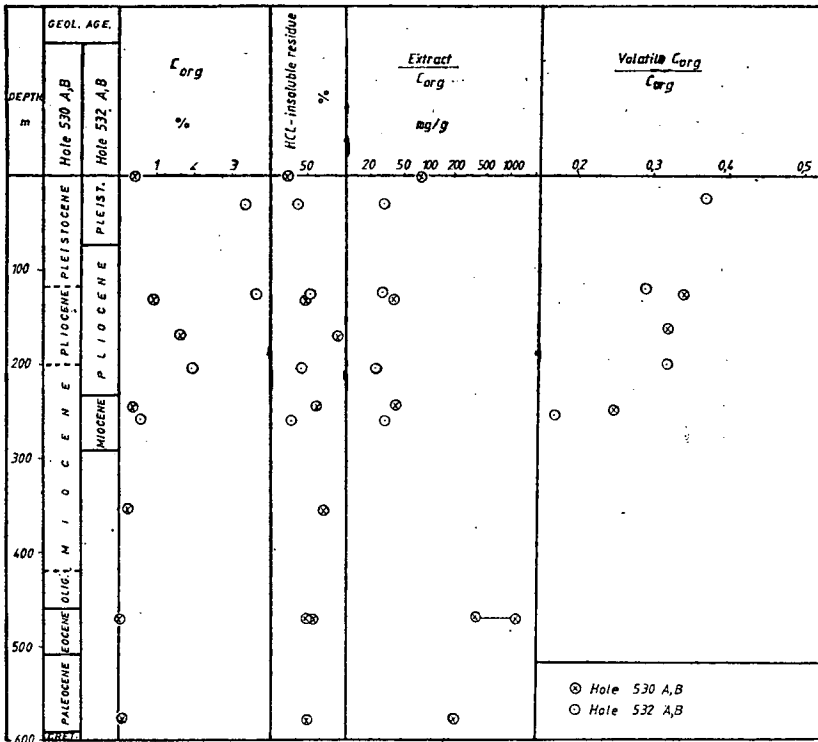


Fig. 3. Basic organochemical parameters vs depth in the Leg 75 samples

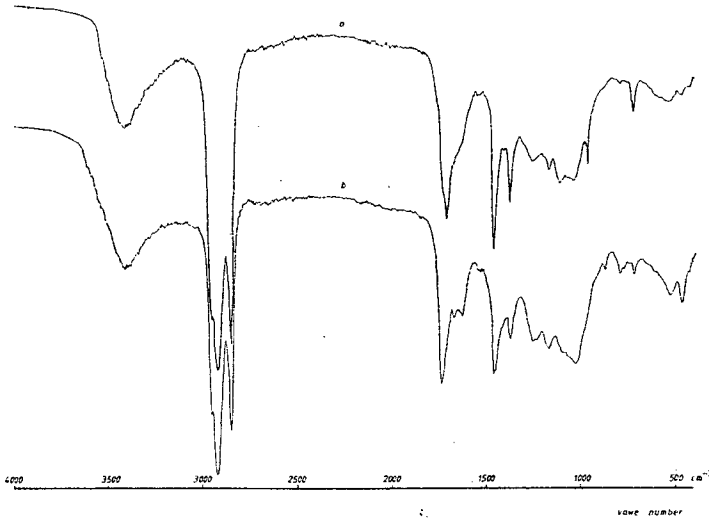


Fig. 4. Typical IR spectra of the Leg 75 samples
 a) Hole 532 A, 29-2 sample
 b) Hole 530 A, 37-3

OCC. AGE	O R G A N I C										M A T T E R				Preservation of woody particles	Size of woody particles	
	A B U N D A N C E					C O M P O S I T I O N					Woody particles		Diameter	Shape			
	Very scarce	Scarce	Medium	Abundant	Very abundant	Woody particle	Sporomorphs	Plankton	Other particles	Calciferous	Preserved	Altered					
1	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
2	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
3	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
4	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
5	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○

Fig. 5. Characters of the particulate organic matter vs depth in the Leg 75 samples. 1) very scarce, 2) scarce, 3) medium, 4) abundant, 5) very abundant (For other explanations, see Fig. 2)

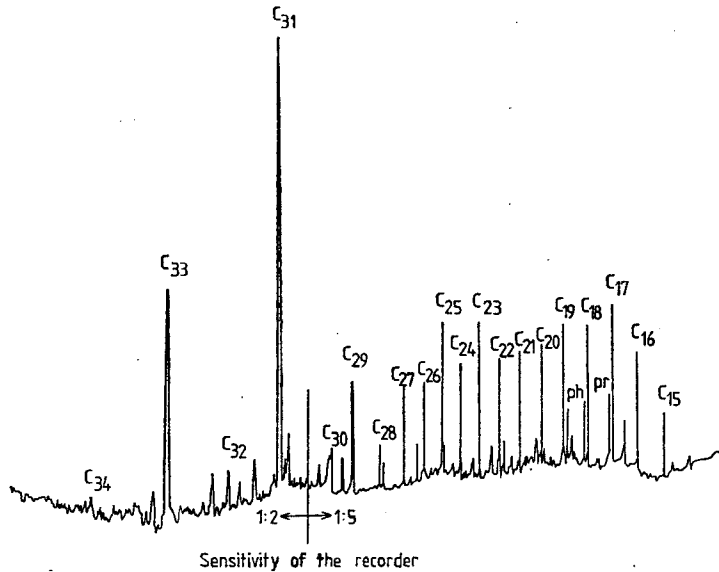


Fig. 6. GC spectra of the saturate fraction of the extract from the Hole 532A, 49-2 sample

In the palynological concentrate mainly woody particles, sporomorphs and plankton remains can be observed (Fig. 5.) The 7—3 and 29—2 samples of the Hole 532 A contain a lot of microscopic resinite grains. The palynomorphs proved to be well preserved and light.

The volatile C_{org} to C_{org} ratio decreases with increasing depth (Table 3).

The 1—1 sample of the Hole 530 B and the 13—5 sample of the Hole 530 A show intermediate character between the two sample groups.

TABLE 3

Extract bulk composition, alkane distribution parameters and kerogen pyrolysis data of the Leg 75 samples

Site	Core	Section	Sub bot- tom depth m	Saturated	Aromatic	Resins	Asphalt	$\frac{n-C_{22}^-}{n-C_{23}^+}$	CPI ($n-C_{24}$ — $n-C_{34}$)	$\frac{pr}{ph}$	$\frac{pr}{n-C_{17}}$	$\frac{ph}{n-C_{18}}$	Volatile C_{ORG}
				HC	HC								% in extract
530 A	5	5	162										0.32
	13	5	249										0.25
530 B	33	1	126	16.7	8.1	57.4	11.7	0.77	2.08	0.83	0.81	1.05	0.34
532 A	7	3	25	8.7	4.9	64.0	21.4	0.39	3.05	0.85	0.75	1.17	0.37
	29	2	121	7.7	5.3	68.6	16.9	0.43	3.51	0.79	0.76	1.17	0.29
	49	2	199	6.1	6.1	73.2	12.6	0.26	3.53	0.91	0.58	0.82	0.32
532 B	63	1	256	17.7	6.2		76.0	0.42	2.21	0.91	0.68	0.94	0.17

DISCUSSIONS AND CONCLUSIONS

Because of the low organic matter content of the Paleogene to Early Miocene samples these could not be analyzed for pyrolysis or gas chromatography, respectively. For this reason, only tentative conclusions can be drawn as to the sequence in question.

The palynological concentrate is composed of planktonic and land-derived particles (Fig. 5). but their ratios do not enable us to draw any quantitative conclusion concerning the composition of the kerogen (POWELL *et al.*, 1981). The predominance of bands corresponding to ester-type carbonyl groups in the IR spectra of the extracts (Table 2) suggests the organic matter of marine origin to play an important role (MAKSIMOV *et al.*, 1975).

The low C_{org} content may be due to both the low quantity of organic matter reaching the sea bottom or an intense bacterial oxidation owing to the low sedimentation rate (4.5 m/m. y.). The organic sulphur compounds found in the extracts also suggest an intense bacterial oxidation (NERUCHEV *et al.*, 1975).

The palynological concentrate of Upper Miocene to Pleistocene samples is richer in both sporomorphs and planktonic organisms than it is the case with the Paleogene to Earlier Miocene samples, the abundance of woody particles and resinite being conspicuous (Fig. 5). The predominance of the C_{23+} molecules in the n-alkan spectra (Table 3) proves the importance of the land-derived components, too. All these circumstances, however, do not allow us to conclude quantitatively as to the kerogen composition.

The definite increase of the volatile C_{org}/C_{org} ratio up in the vertical section (Fig. 3) cannot be ascribed to a depth-controlled maturation, as the extract/ C_{org} ratio in the interval in question is low (a maximum of 40 mg/g), the CPI values being higher than 2 and one of the maturation parameters does not show any correlation with depth (Table 3). Therefore it is considered doubtless that the upward growth of the volatile content of the kerogen is caused by a change in the character of the original organic matter, i. e. that the proportion of planktonic organic matter increases from the Upper Miocene up to the Pleistocene. Since the quantity of C_{org} increases in the same direction, an increase in biological production and/or the sedimentation rate must be suggested. Let us remark that in the uppermost 400 m (Upper Miocene-Pleistocene) of Hole 362 located at less than 2 nautic miles away from Hole 532 the kerogen was observed to become more and more enriched in C^{13} isotope (ERDMAN and SCHORNO, 1970). (Table 3) proceeding up the section which suggests an upward growth of the proportion of organic matter of marine origin.

According to our earlier experiences (BRUKNER and SZÚCS, 1982; BRUKNER, unpublished data) the absorption observed at 960 cm^{-1} in the IR spectra of the extracts suggests an very oxygen-depleted environments of sedimentation and a still immature organic matter.

The high C_{org} content, the marine character of the organic matter and the oxygen-depleted environment can be attributed to a very high plankton production due to upwelling. These results and conclusions are in good accordance with the opinion suggesting that the Benguela upwelling in the vicinity of Walvis Ridge evolved in Late Miocene time (HAY, SIBUET *et al.*, 1982).

HYDROCARBON POTENTIAL

The C_{org} content of the Paleogene to Early Miocene sequence is too low to consider it as a potential source rock. According to the colour of the palynomorphs and their preservation state, the kerogen is immature. The comparatively high extract (C_{org} ratio) does not contradict this, since this is generally the case at a low C_{org} content (the so-called VASSOEVICH—USPENSKI rule known from the Russian-language literature). The significant extract content observed in the sample 37/3 of Hole 530 A may be considered a migration trace, the IR spectrum providing no ground for suspecting a contamination.

The average C_{org} content of the Upper Miocene to Pleistocene sequence is over 1%, i. e. the sediments may be regarded as good source rocks. Its kerogen seems to oil-prone. Judging by the colour and preservation state of the palynomorphs and the immature character of the extracts, the oil generation has not started yet in the sequence.

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