

50. HYDROCARBON GEOCHEMISTRY AND BIOLOGICAL MARKERS IN ORCA AND PIGMY BASIN SEDIMENTS (SITES 618 AND 619)¹

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ABSTRACT

The C₁₅₊ hydrocarbon geochemistry of sediments from Sites 618 and 619 (Orca and Pigmy basins) has been examined as part of a biogeochemical study of microbial activity and biological markers in Leg 96 sediments. Total hydrocarbon concentrations (13–78 µg/g dry weight) are elevated in comparison to those reported for Recent sediments from the Gulf of Mexico continental shelf, but there is little evidence that these sediments contain petroleum hydrocarbons originating from seepage. The presence of weathered fossil hydrocarbons is suggested, however, by the unresolved envelope feature observed in gas chromatograms of most sediments and also by the distribution of C₂₇–C₂₉ steranes and triterpanes. Normal alkane distributions are consistent with a predominant input or preservation of terrestrial organic matter in these offshore basins. At Site 619 an enhanced terrestrial contribution below 113 m sub-bottom is indicated by an increase in the ratio of odd to even *n*-alkanes over the range C₂₆ to C₃₀. Pristane/phytane ratios at both sites range between 0.97 and 1.74 which, in conjunction with the occurrence of significant concentrations of perylene (10–500 ng/g dry weight), suggest the prevalence of reducing depositional conditions over the time period covered by the cores. A hydrocarbon tentatively identified as a C₂₅ multibranched compound similar to those found in Recent sediments was detected in most samples.

INTRODUCTION

Microorganisms play a major role in the decomposition of organic matter in the deep sea (reviewed by Jannasch, 1979; Morita, 1980; Karl, 1982). Until recently, it had generally been accepted that viable microorganisms were limited to the upper 1 m of the sediment column, where a succession of different metabolic types are found depending on the prevailing redox conditions and the availability of organic and inorganic substrates (Fenchel and Jorgensen, 1977). However, recent geochemical evidence indicates that microbiological activity may extend to considerably greater depth. For example, Oremland and Culbertson (1982) have pointed out the strong resemblance of sulfate and methane profiles in deep-sea sediments to those of nearshore sediments, the only difference being that the depletion of sulfate and the appearance of methane occurs over hundreds of meters (in the former case) instead of over centimeters (in the latter case). Rice and Claypool (1981) summarized the case for microbiological methane production extending to considerable depth in Deep Sea Drilling Project (DSDP) sediments. Methanogenic microbiological activity was detected to at least 12 m sub-bottom in DSDP cores from the Guaymas Basin in the Gulf of California (Oremland and Culbertson, 1982). It is unknown how much deeper this activity might have extended because deeper sam-

ples were not tested. However, there is a recent report that microbial activity extends to 90–110 m sub-bottom in Caspian Sea sediments (Belyaev et al., 1980).

The existence of microbiological activity at these great depths implies active synthesis of bacterial biomass, which in turn raises the possibility that specific organic compounds are being produced that might serve as biological markers of microbial activity and community structure. Sediments collected at Sites 618 and 619 (Orca and Pigmy basins, respectively) were selected for an extensive biogeochemical characterization aimed at establishing the distribution of viable microbial communities with depth and determining whether any biological markers of these communities exist. In the present study, the C₁₅₊ hydrocarbon geochemistry of sediments at these two sites has been examined in detail. Our investigations have focused on hydrocarbon distributions as related to depositional history and source inputs, as well as the occurrence of specific biological marker hydrocarbons. With regards to the latter category, samples have been examined for the occurrence of a series of C₂₅ and C₃₀ alkenes, which are ubiquitous in Recent surface sediments and whose origin is thought to be associated with organic matter decomposition (Requejo and Quinn, 1983; Requejo et al., 1984), and for the polycyclic aromatic hydrocarbon perylene. Perylene, although strictly not a biological marker of anaerobic microbial activity, is gaining increasing acceptance as a paleoenvironment marker for early sedimentary anoxia (Louda and Baker, 1984 and references therein). In addition, we have examined the distribution of triterpanes and steranes, biological markers that have received extensive application in petroleum geochemistry, and their relationship to inferred hydrocarbon origins.

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METHODS

Samples for organic geochemical analysis were collected on board the *Glomar Challenger* from Holes 618, 618A, and 619 (Table 1). Site 618 is located in the Orca Basin at a water depth of approximately 2420 m. The bottom 200 m of the overlying water column consists of a hypersaline, anoxic brine (salinity 260‰ and density of 1.185 g/ml; Shokes et al., 1977). The sediments between 16 and 41 m sub-bottom were found to contain several zones of black anoxic clay; above and below this interval sediments consisted of gray clays that were likely deposited in a more oxic environment (Site 618 chapter, this volume). Site 619 is located in the nearby Pigmy Basin at a water depth of 2273 m. This narrow, elongate basin is characterized by steep walls that rise to about 700 m above the basin floor. Sediments at this site consisted primarily of clays and muds showing some lamination (Site 619 chapter, this volume). All sediment samples were frozen immediately after collection and kept frozen until analyzed.

Lipid extractions were conducted using the ambient temperature extraction technique of Brown et al. (1980). A known amount of wet sediment (generally 5–10 g dry weight) was sealed in a Teflon jar and extracted by shaking sequentially with methanol (three times, 30 min. each) and a 1:9 methanol:methylene chloride mixture (three times 8 hr. each, 2:1 solvent volume: wet weight). An internal standard (androstande) was added prior to extraction with the methanol:methylene chloride mixture. Following each extraction, the solvent was isolated by centrifugation and decanting. The combined methanol/methylene chloride extracts were diluted with an equal volume of organic-free water acidified to pH 2 with 6 N HCl, and partitioned three times versus methylene chloride. These methylene chloride extracts were dried over Na_2SO_4 and concentrated to near dryness on a rotary evaporator, at which time the methylene chloride was displaced with hexane. The solution volume was adjusted to exactly 1 ml and an aliquot weighed on a Cahn 25 electrobalance to determine total extractable material (TEM) content. The remaining extract was chromatographed on a column of alumina/silica gel and saturate and aromatic hydrocarbons isolated as described in Boehm (1983). For the purposes of this study, eluates containing saturated and aromatic hydrocarbons were combined to yield a total hydrocarbon fraction, which was concentrated by rotary and N_2 evaporation in preparation for gas chromatographic analysis.

Total hydrocarbon fractions were analyzed by fused silica capillary gas chromatography using flame ionization detection (GC/FID). GC/FID analyses were carried out on a Hewlett-Packard 5840A gas chro-

matograph using He as carrier gas. Analytical conditions were as follows: splitless injection on a 30 m \times 0.25 mm DB-5 bonded phase fused silica capillary column that was temperature programmed from 40 to 290°C at 4°C/min. after an initial 0.5 min. isothermal period. The column was outfitted with a precolumn consisting of a 1 m \times 0.25 mm length of deactivated fused silica. Specific saturated (*n*-alkanes, pristane, phytane) and aromatic (perylene) compounds were identified by GC/FID retention time comparison versus authentic standards; their concentrations were calculated by integrated peak area comparison versus the androstande internal standard. Response factors relative to the internal standard were calculated from analysis of standard mixtures and applied to the final quantitative results. Concentrations of total resolved hydrocarbons were calculated by comparison of total resolved area in gas chromatograms to that of the internal standard. Unresolved hydrocarbon concentrations were calculated by determining the area beneath the unresolved envelope feature in chromatograms using planimetry, converting this area to integrated area units and applying the same internal standard technique. Total hydrocarbon concentrations (THC) were calculated by summing the concentrations of resolved and unresolved components.

Selected samples were also analyzed by capillary gas chromatography/mass spectrometry (GC/MS) to identify unknown peaks and to determine triterpane and sterane distributions. A Finnigan 4530 quadrupole GC/MS equipped with an INCOS 2300 data system was used for these analyses. The identical chromatographic conditions employed in the GC/FID analyses were also used in the GC/MS analyses. MS conditions were: ionizing voltage 70 eV; *m/e* scan range 50–450; scan rate 1 scan/s. Plots of *m/e* 191 and 217 were used to generate mass chromatograms corresponding to triterpanes and steranes, respectively. Mass chromatograms of additional diagnostic fragments (e.g., 218, in addition to molecular ions) served to elucidate and confirm the identity of specific compounds.

Organic carbon was determined by high temperature combustion as described in Whelan et al. (this volume).

RESULTS AND DISCUSSION

Organic Carbon

Organic carbon concentrations in Hole 619 are relatively invariant with depth and range between 0.66 and

Table 1. Summary of C_{15+} hydrocarbon geochemical data, Holes 618, 618A, and 619.

Core-Section (interval in cm)	Sub-bottom depth (m)	Organic carbon (%)	Total extractable material ($\mu\text{g/g}$ dry wt.)	Total hydrocarbons ($\mu\text{g/g}$ dry wt.)	Resolved (%)	Unresolved (%)	OEPI ^a	<i>n</i> -C ₁₇ / <i>n</i> -C ₂₉	Pris/Phy	R ₁ ^b 2081 (ng/g dry wt.)	Perylene (ng/g dry wt.)
Hole 618											
10-2 (30–60)	77	ND	990	30	27	73	3.21	0.31	1.13	500	300
Hole 618A											
1-4 (122–130)	15	ND	510	46	37	63	4.21	0.29	1.38	<10	430
1-5 (115–120)	16	ND	510	24	23	77	3.72	0.24	1.39	<10	260
2-5 (70–75)	34	0.93	480	33	29	71	3.68	0.32	1.03	34	450
3-2 (33–39)	40	0.71	220	33	28	72	4.37	0.19	1.30	10	450
Hole 619											
1-2 (130–150)	4	ND	310	56	15	85	3.08	0.21	1.05	ND	ND
4-5 (130–150)	28	0.78	330	38	33	67	2.64	0.39	1.61	61	96
6-5 (130–150)	47	1.02	470	54	17	83	2.88	0.43	1.52	170	160
8-4 (130–150)	65	0.82	490	78	25	75	2.69	0.82	1.42	180	140
10-4 (124–144)	79	0.74	360	38	23	77	3.05	0.23	1.19	50	100
11-3 (130–150)	92	0.78	760	26	30	70	2.80	1.21	1.27	58	10
12-3 (105–120)	102	0.09	250	25	23	77	2.92	0.37	1.02	46	80
13-4 (130–150)	113	0.81	370	65	20	80	1.81	0.11	0.97	57	500
14-2 (44–64)	119	0.69	380	36	16	84	2.87	0.37	1.09	13	280
16-4 (83–103)	141	0.66	230	22	32	68	3.86	0.12	1.48	<10	130
17-3 (130–150)	150	0.79	220	16	22	78	3.92	0.17	1.49	<10	210
19-2 (120–140)	167	0.74	310	13	64	36	5.54	0.05	1.74	<10	30

Note: ND = not determined.

^a Odd-even preference index (OEPI), defined as $2(n\text{-C}_{27} + n\text{-C}_{29})/n\text{-C}_{26} + 2(n\text{-C}_{28}) + n\text{-C}_{30}$ (Farrington and Tripp, 1977).

^b Hydrocarbon with retention index (RI) 2081, suspected to be a C_{25} -branched compound.

1.02% (Table 1), with the exception of Sample 619-12-3, 105–120 cm, where the concentration decreases to 0.09%. Two samples from Hole 618A (Samples 618A-2-5, 70–75 cm and 618A-3-2, 33–39 cm) that were analyzed for organic carbon content also fell within this same concentration range (Table 1). The range of organic carbon concentrations found at both sites is slightly lower than that reported by Northam et al. (1981) for the upper 10 m of the sediment column at two sites within the Orca Basin (representing approximately 20,000 yr.).

Extractable Content and Bulk Hydrocarbon Composition

The TEM content of sediments from both Sites 618 and 619 is relatively high (Table 1), significantly exceeding that reported by Gearing et al. (1976) for Recent sediments from the northeastern Gulf of Mexico continental shelf and of a comparable magnitude to those found in some fine-grained Recent sediments receiving anthropogenic inputs (Farrington and Tripp, 1977). No clear-cut relationship between organic carbon and TEM content is evident at either site. The variation in TEM content with depth in Hole 619 is shown in Figure 1. The principal feature of this profile is a sharp increase in concentration at a sub-bottom depth of 92 m (Sample 619-11-3, 130–150 cm). Extractable content in Hole 618A was found to be relatively constant down to 34 m sub-bottom (Table 1), but exhibits a decrease at 40 m. The highest TEM concentration at either Site 618 or 619 was found in a sample from Hole 618, corresponding to a sub-bottom depth of 81 m (990 $\mu\text{g/g}$ dry weight in Sample 618-10-2, 60–80 cm). This sample also exhibited some unique hydrocarbon compositional features, which are further discussed below. Calculated sedimentation rates for Sites 618 and 619 (Site 618 and 619 chapters, this volume; Wetzel and Kohl, this volume) indicate that the maximum TEM content observed at each site does not result from coincident deposition of lipid-enriched organic material. Instead, the presence of a black iron sulfide layer in Core 618-10 would suggest that the maximum in Hole 618 is associated with enhanced preservation of organic matter deposited during periods of bottom water anoxia.

Total hydrocarbon concentrations at both sites (Table 1) are also slightly elevated in comparison to similar values reported for Recent sediments along the Gulf of Mexico continental shelf and slope (Stevens et al., 1956; Aizenshtat et al., 1973; Gearing et al., 1976; Boehm and Feist, 1980). However, no direct correlation was found between sediment TEM content and hydrocarbon concentrations. In fact, the maximum in TEM content in Hole 619 is associated with a minimum in hydrocarbon concentration (see Fig. 1). In general, total hydrocarbon concentration throughout Holes 618A and 619 represents $\leq 20\%$ of the TEM content (Table 1). These values are significantly less than the 60–70% reported by Anderson et al. (1983) and Brooks et al. (1984) for oil-stained near-surface (0 to 4 m) sediments in the northwestern Gulf of Mexico and indicate that the sediments at Sites 618 and 619 do not contain petroleum originating from seepage. The hydrocarbons at both sites appear, how-

ever, to originate at least in small part from a fossil source, as evidenced by the relative proportion of resolved versus unresolved components. With but one exception (Sample 619-19-2, 120–140 cm) hydrocarbons in all samples are dominated by unresolved components (63–85% of the total; Table 1), a distribution characteristic of fossil hydrocarbons that have undergone some degree of weathering (Tissot and Welte, 1978). The most likely source of these fossil hydrocarbons would be offshore transport of particles originating from erosion of organic-rich continental rocks or resuspension of petroleum-containing shelf and slope sediments, with subsequent deposition and burial in these sedimentary basins over the geologic period represented by the cores. Representative gas chromatograms of the sedimentary hydrocarbons isolated from Holes 619 and 618 illustrating the prevalence of the unresolved envelope feature are shown in Figures 2 and 3, respectively.

n-Alkanes and Isoprenoids

Normal alkanes ranging in carbon number from C_{14} to C_{33} are present in all samples, although these resolved components account for a small fraction of the total hydrocarbons (15–37% of the total with the exception of Sample 619-19-2, 120–140 cm, which contains 64% resolved components). Two parametric ratios were calculated to characterize sources and quantify the variations in *n*-alkane distributions versus depth. The odd-even preference index (OEPI), as defined in Farrington and Tripp (1977) and Boehm (1984), is a measure of the relative contribution of hydrocarbons from higher land plants and increases as inputs from this source become more significant. Petroleum hydrocarbons would generally exhibit an OEPI around 1.0. Similarly, the weight ratio of *n*-heptadecane to *n*-nonacosane ($n\text{-C}_{17}/n\text{-C}_{29}$) has been employed as an indicator of relative hydrocarbon contributions from algal versus higher land plant sources (Giger et al., 1980).

Values for both parameters in the sediments analyzed are listed in Table 1. In Holes 618 and 618A the OEPI ranges between 3.21 and 4.37 and the ratio $n\text{-C}_{17}/n\text{-C}_{29}$ ranges between 0.19 and 0.32. Both sets of values are typical of marine sediments receiving significant hydrocarbon inputs from land plant sources (Farrington and Tripp, 1977; Boehm, 1984). There is no apparent trend versus depth in either parametric ratio at Site 618. The OEPI for Site 619 sediments is also relative invariant with depth to 102 m sub-bottom, ranging between 2.64 and 3.08, then exhibits a sharp decrease at 113 m, followed by a continuous increase to the bottom of the hole (Table 1, Fig. 1). The value corresponding to the deepest sediment analyzed at this site (5.54 for Sample 619-19-2, 120–140 cm) was the highest found throughout the hole. This increase in the OEPI below 113 m suggests a significant increase in the contribution of land plant hydrocarbons. The ratio of $n\text{-C}_{17}/n\text{-C}_{29}$ also reflects this trend, decreasing below 113 m sub-bottom to a minimum value of 0.05 in Sample 619-19-2, 120–140 cm (Table 1). In general, the sub-bottom profile of $n\text{-C}_{17}/n\text{-C}_{29}$ in Hole 619 was found to parallel that of TEM, also exhibiting a maximum at 92 m sub-bottom depth (Sample 619-11-3,

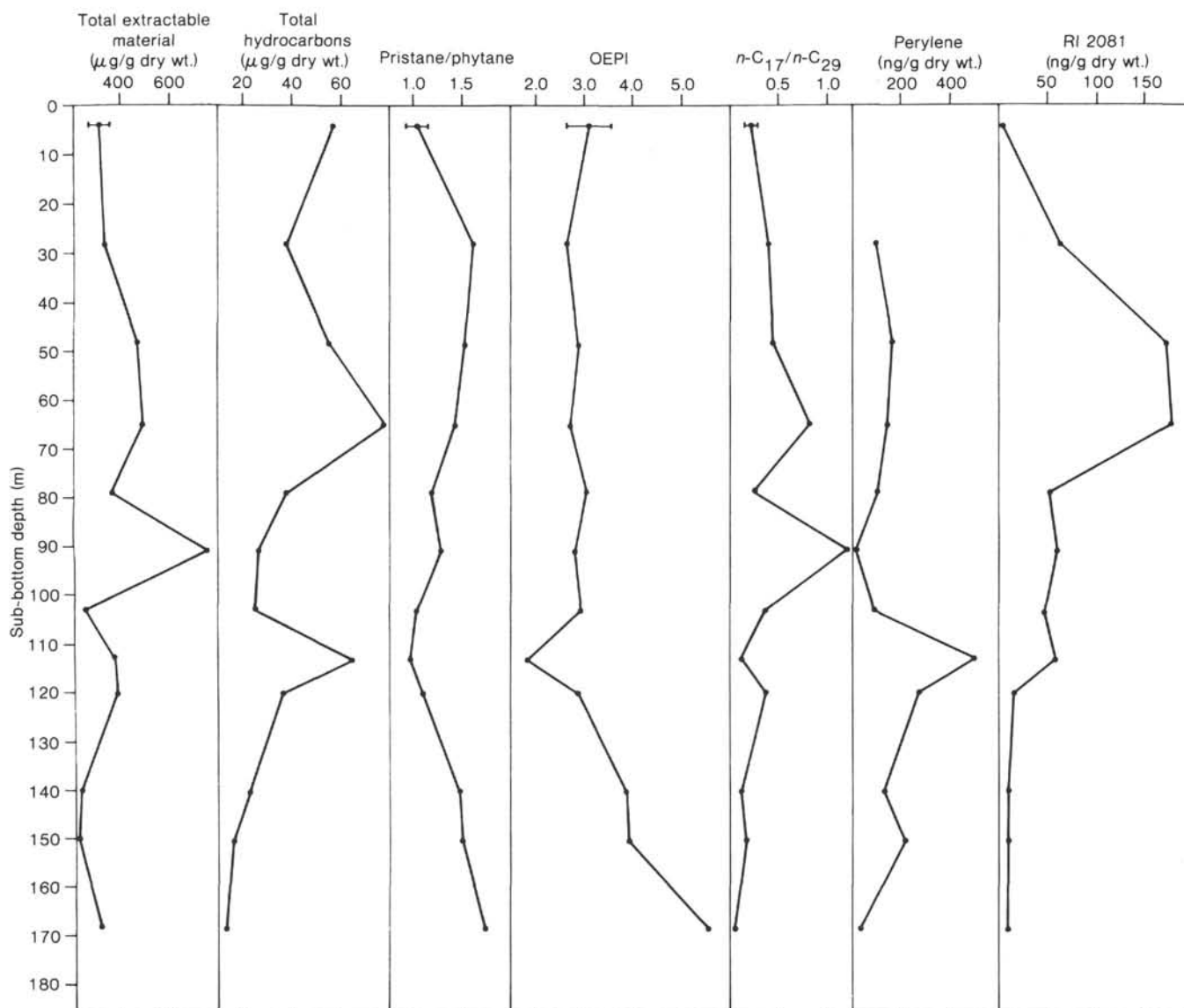


Figure 1. Variations in selected hydrocarbon geochemical parameters with depth at Site 619 (Pigmy Basin). Data given in Table 1.

130–150 cm). We interpret these similarities as being indicative of variations in the deposition and preservation of organic matter from planktonic and other marine sources, which would be enriched in both extractable (lipid) material and $n\text{-C}_{17}$ (Blumer et al., 1971).

Weight ratios of the isoprenoid hydrocarbons pristane and phytane (pristane/phytane) have been used both as paleoindicators of depositional environments and also as indicators of the relative contribution from terrestrial and marine organic sources (Tissot and Welte, 1978; Rashid, 1979). Sediments from Sites 618 and 619 exhibit pristane/phytane ratios between 0.97 and 1.74 (Table 1). Values <1.0 are generally characteristic of marine organic contributions and/or reducing depositional environments (Didyk et al., 1978; Hunt, 1979). It is difficult to interpret the values reported here as resulting exclusively from a predominantly marine input or from reducing depositional conditions. Further, we are unable to evaluate accurately the extent to which the observed

ratios have been affected by inputs of fossil hydrocarbons possessing a characteristic ratio. Given the anoxic nature of bottom waters overlying the sediments of these offshore basins and the prevalence of terrestrial contributions implied by OEPI and $n\text{-C}_{17}/n\text{-C}_{29}$ ratios in these sediments, it would appear that the pristane/phytane ratios have been more influenced by the existence of reducing sedimentary conditions. However, some evidence for the influence of organic source variations is evident in the sediments from Site 619. Figure 1 shows that pristane/phytane ratios in these samples steadily decrease from a value of 1.61 at 28 m sub-bottom (Sample 619-4-5, 130–150 cm) to a minimum of 0.97 at 113 m sub-bottom (Sample 619-13-4, 130–150 cm). Below this depth values increase to a maximum of 1.74 at 167 m sub-bottom (Sample 619-19-2, 120–140 cm). This increase parallels that of OEPI over the same interval and is consistent with an increase in organic contributions from terrestrial sources, which would result in increased pris-

tane/phytane ratios (Hunt 1979; Rashid, 1979). Hole 618 sediments show little variation in pristane/phytane ratios versus depth.

C₂₅ and C₃₀ Alkenes

Unsaturated hydrocarbons in ancient sediments are rare because of their labile nature in comparison to saturated compounds. Sediments from Sites 618 and 619 were examined for the occurrence of a series of C₂₅ and C₃₀ structurally-related unsaturates reported in Recent sediments, which are thought to be formed during early diagenesis as a result of microbial activity (Requejo and Quinn, 1983; Requejo et al., 1984). C₃₀ constituents of this hydrocarbons series could not be detected in any of these samples, based on the absence of characteristic mass spectral fragments in the region of GC/MS chromatograms where these compounds would be expected to elute (other C₃₀ unsaturates were detected, however, and are described below). However, one component possessing a gas chromatographic retention index (RI) of 2081 (characteristic of the C₂₅ alkenes) was detected in most samples. GC/MS characterization of this compound (its mass spectrum is shown in Fig. 3) revealed several fragments common to the C₂₅ constituents of this series (*m/e* 207, 221, 318; Requejo and Quinn, 1983). This compound may be one of the C₂₅-multibranched hydrocarbons found in Recent sediments, although further characterization (i.e., structural features such as the number of double bonds and/or rings) could not be attempted because of an inability to detect a molecular ion in its mass spectrum. Molecular ions for these compounds can be difficult to detect by electron impact MS because of ease of fragmentation resulting from their high degree of branching (Requejo and Quinn, 1983).

Variations in the sub-bottom concentration of this compound in Hole 619 are shown in Figure 1. Its concentration is seen to increase to a maximum at 65 m sub-bottom (Sample 619-8-4, 130–150 cm) below which it generally decreases to low, constant values. This profile does not parallel those of any of the other hydrocarbon parameters calculated, although it does bear some similarity to that of total hydrocarbon concentrations (Fig. 1). Comparison of the sub-bottom profiles of acetate and percentage CH₄ in core gas (Whelan, this volume) to that of RI 2081 similarly reveals little correlation. An inverse relationship, however, is evident between the sub-bottom profile for the sulfate content of pore water (Whelan et al., this volume) and this compound. The significance of this correlation (and lack thereof for the other parameters) in relation to inferred and measured anaerobic microbiological activity is discussed in the Summary Geochemistry chapter by Whelan et al. (this volume).

Concentrations of RI 2081 in Hole 618A sediments are generally low (Table 1). Sample 618-10-2, 30–60 cm, however, was found to contain the highest concentration of this compound among all the sediments analyzed. In this sediment, RI 2081 represents the single major resolved component and is present in a greater relative abundance than all *n*-alkanes (Fig. 3).

Perylene

Perylene concentrations in the sediments from Holes 618 and 618A (260–450 ng/g dry weight) are generally higher than those from Hole 619 (10–500 ng/g dry weight). Both concentration ranges are comparable to those reported for near-surface sediments from several freshwater lakes (Wakeham et al., 1980) and the Namibian Shelf region (Wakeham et al., 1979) and of a lower magnitude than those reported by Louda and Baker (1984) for several Leg 64 DSDP sediments in the Guaymas Basin, Gulf of California. Perylene is thought to be formed *in situ* from as yet unidentified precursor(s) during early diagenesis and has been variously proposed as an indicator of both terrestrial and marine organic contributions to sediments. Generally, high concentrations of perylene are associated with sediments deposited under strongly reducing conditions, whereas sediments deposited in oxic environments contain negligible concentrations (Wakeham et al., 1979; Louda and Baker, 1984), and this compound has therefore been suggested as a marker of sedimentary anoxic conditions. The higher concentrations found in Holes 618 and 618A thus likely reflect the persistence of bottom-water anoxia in Orca Basin, where intrusions of oxygenated water would be inhibited by the extreme vertical stratification resulting from the presence of a hypersaline brine. Sub-bottom profiles of perylene in Hole 619 (Table 1, Fig. 1) were found to exhibit a maximum at 113 m sub-bottom (Sample 619-13-4, 130–150 cm). This is the same depth at which the pristane/phytane ratio exhibited a minimum and below which the other hydrocarbon parameters indicate an increase in terrestrial organic contributions, which suggests that an anoxic event may have been associated with deposition of this strata. Perylene concentrations below 120 m in Hole 619 were also found to exhibit an inverse correlation with the percentage CH₄ core gas (Whelan et al., this volume).

Triterpanes and Steranes

These polycyclic hydrocarbons have received widespread application in the field of petroleum exploration geochemistry (reviewed by Seifert and Moldowan, 1978 and Philp, 1982). Mass chromatograms corresponding to the distribution of triterpanes (*m/e* 191) and C₂₇–C₂₉ steranes (*m/e* 217) in Samples 619-6-5, 130–150 cm and 618-10-2, 30–60 cm are shown in Figures 2 and 3, respectively. The biomarker distribution in each sample is nearly identical, suggesting a common source for these compounds at each site. An "immature" fossil source for these compounds is indicated based on (a) the significant abundance of unsaturated biological precursor compounds such as diploptene (peak no. 6 in triterpane mass chromatograms; Simoneit and Kaplan, 1980; Simoneit, 1982), (b) a distribution of C-22*S* to C-22*R* isomers in the C₃₁ hopanes (doublet labeled no. 7 in triterpane mass chromatograms) less than the 60:40 22*S*/22*R* distribution expected at higher maturity (Seifert and Moldowan, 1978; Rowland and Maxwell, 1984), and (c) the higher

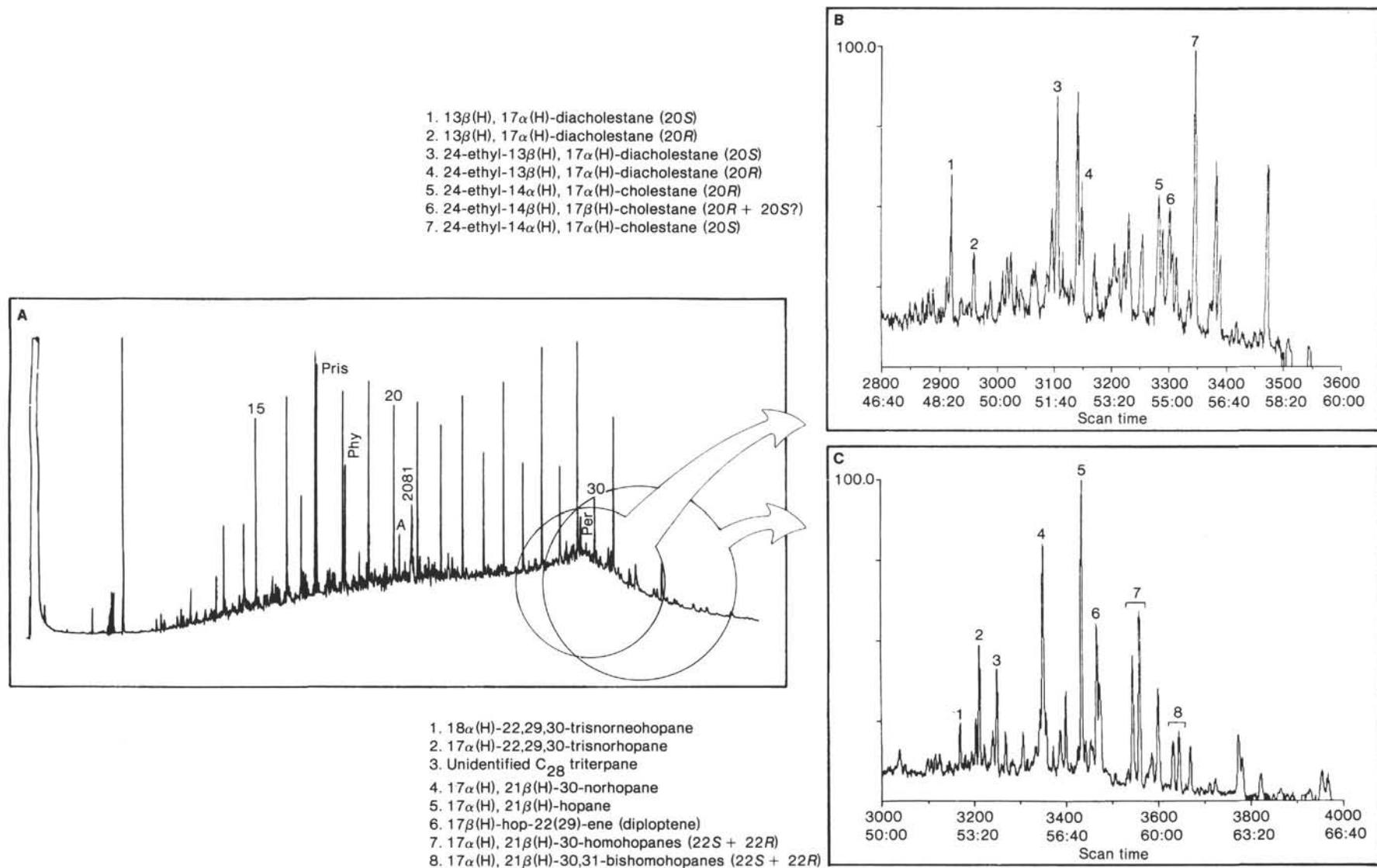


Figure 2. A. Capillary gas chromatogram of the total hydrocarbon fraction isolated from Sample 619-6-5, 130–150 cm (47 m sub-bottom). Numbers over peaks denote n -alkane carbon numbers; other abbreviations include: Pris = pristane, Phy = phytane, A = androstane internal standard, 2081 = hydrocarbon having a retention index 2081, suspected to be a C_{25} -multibranched compound, Per = perylene. Inset to the right are (B) GC/MS mass chromatograms of C_{27} – C_{29} steranes (m/e 217) and (C) triterpanes (m/e 191). Individual constituents are designated by the number over the peaks and identified to the left of each mass chromatogram. Analytical conditions are stated in the text.

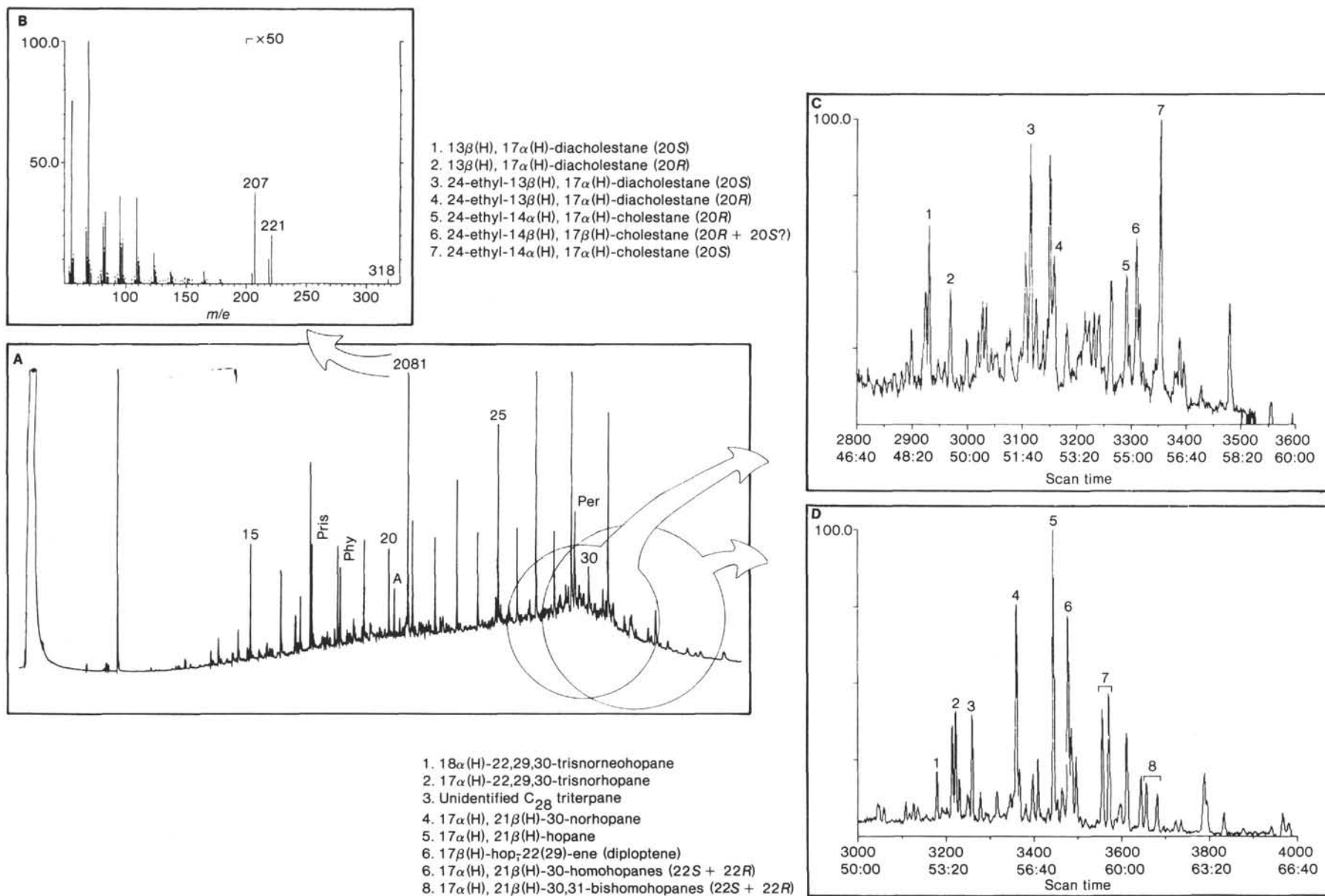


Figure 3. A. Capillary gas chromatogram of the total hydrocarbon fraction isolated from Sample 618-10-2, 30–60 cm (77 m sub-bottom). Numbers and symbols over peaks designate individual components as described in Figure 2 caption. B. The mass spectrum of the component identified as 2081 is shown above the gas chromatogram. GC/MS mass chromatograms of (C) steranes and (D) triterpanes in this sample are inset to the right. Individual constituents in mass chromatograms are labeled and identified as in Figure 2. Analytical conditions are stated in the text.

proportion of C_{29} steranes possessing the $5\alpha(H)$, $14\alpha(H)$, $17\alpha(H)$ configuration (peaks 5 and 7 in the sterane mass chromatogram) relative to those possessing the $5\alpha(H)$, $14\beta(H)$, $17\beta(H)$ configuration, which are known to increase in abundance with increasing maturity (Mackenzie et al., 1980). We cannot ascertain whether the observed biomarker distributions are the result of early sedimentary diagenetic processes (i.e., a distribution generated primarily *in situ*) or are due to an input of fossil hydrocarbons of immature diagenetic history, such as immature shales, via particulate matter transport and deposition (i.e., a "preformed" distribution). However, the latter possibility would be consistent with the presence of the unresolved envelope feature in most samples, which is characteristic of contributions from a weathered fossil source.

SUMMARY

Characterization of the C_{15+} hydrocarbon geochemistry of sediments from Sites 618 and 619 has revealed the following:

1. Total hydrocarbon concentrations are elevated in comparison to those reported for Recent sediments along the Gulf of Mexico continental shelf. There is, however, little evidence for the contamination of these sediments by petroleum originating from seepage, as reported recently for nearby slope and rise sediments (i.e., Anderson et al., 1983; Brooks et al., 1984).

2. Calculated odd-even preference index and $n-C_{17}/n-C_{29}$ ratios suggest deposition and preservation of terrestrial organic matter in these offshore basins. At Site 619, there is evidence for an enhanced terrestrial contribution in sediments below 113 m, based on these parametric ratios.

3. Pristane/phytane ratios at both sites are consistent with a prevailing reducing depositional environment, although some variation due to source input is also evident. Perylene concentrations are also indicative of a reducing environment, which has persisted to a greater extent in Orca Basin (Site 618) than in Pigmy Basin (Site 619).

4. One compound tentatively identified as a constituent of the C_{25} -multibranched hydrocarbon series found in Recent sediments was present in most samples analyzed.

5. Triterpane and sterane distributions are consistent with an immature fossil source, the exact nature of which is uncertain.

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REFERENCES

- Aizenshtat, Z., Baedeker, M. J., and Kaplan, I. R., 1973. Distribution and diagenesis of organic compounds in JOIDES sediment from Gulf of Mexico and western Atlantic. *Geochim. Cosmochim. Acta*, 37:1881-1898.
- Anderson, R. K., Scalan, R. S., Parker, P. L., and Behrens, E. W., 1983. Seep oil and gas in Gulf of Mexico slope sediment. *Science*, 224:619-621.
- Belyaev, S. S., Lem, A. Y., and Ivanov, M. V., 1980. Role of methane-producing and sulfate-reducing bacteria in destruction of organic matter. In Trudinger, P. A., and Walter, M. A. (Eds.), *Biogeochemistry of Ancient and Modern Environments*: Canberra (Australian Academy of Sciences).
- Blumer, M. R., Guillard, R. L., and Chase, T., 1971. Hydrocarbons of marine phytoplankton. *Mar. Biol.*, 8:183-189.
- Boehm, P. D., 1983. Estuarine-continental shelf and benthic-water column coupling of organic pollutants in the New York Bight region. *Can. J. Fish. Aquat. Sci.*, 40(Suppl. 2):262-276.
- , 1984. Aspects of the saturated hydrocarbon geochemistry of recent sediments in the Georges Bank region. *Org. Geochem.*, 7:11-24.
- Boehm, P. D., and Feist, D. L., 1980. Aspects of the transport of petroleum hydrocarbons to the offshore benthos during the IXTOC I blowout. In *Proceedings of a Symposium on the Preliminary Results from the September 1979 Researcher/Pierce IXTOC I Cruise*: Boulder (NOAA/Office of Marine Pollution Assessment), pp. 207-238.
- Brooks, J. M., Kennicutt, M. C., Fay, R. R., McDonald, T. J., and Sassen, R., 1984. Thermogenic gas hydrates in the Gulf of Mexico. *Science*, 225:409-411.
- Brown, D. W., Ramos, L. S., Friedman, M. Y., and MacLeod, W. D., 1980. Ambient temperature extraction of hydrocarbons from marine sediment—comparison with boiling solvent extractions. In Petrakis, L., and Weiss, F. T. (Eds.), *Petroleum in the Marine Environment. Advances in Chemistry Series No. 185*: Washington (American Chemical Society), pp. 313-326.
- Didyk, B. M., Simoneit, B. R. T., Brassell, S. C., and Eglinton, G., 1978. Geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature*, 272:216-222.
- Farrington, J. W., and Tripp, B. W., 1977. Hydrocarbons in western North Atlantic surface sediments. *Geochim. Cosmochim. Acta*, 41:1627-1641.
- Fenchel, T. M., and Jorgensen, B. B., 1977. Detritus food chains of aquatic ecosystems: the role of bacteria. In Alexander, M. (Ed.), *Advances in Microbial Ecology*: New York (Plenum Press), pp. 1-58.
- Gearing, J. N., Gearing, P., Lytle, T. F., and Lytle, J. S., 1976. Hydrocarbons in 60 northeast Gulf of Mexico shelf sediments: a preliminary survey. *Geochim. Cosmochim. Acta*, 40:1005-1017.
- Giger, W., Schaffner, C., and Wakeham, S. G., 1980. Aliphatic and olefinic hydrocarbons in recent sediments of Greifensee, Switzerland. *Geochim. Cosmochim. Acta*, 44:119-129.
- Hunt, J. M., 1979. *Petroleum Geochemistry and Geology*: San Francisco (W. H. Freeman).
- Jannasch, H. W., 1979. Microbial turnover of organic matter in the deep sea. *Bioscience*, 29:228-230.
- Karl, D. M., 1982. Microbial transformations of organic matter at oceanic interfaces: a review and prospectus. *Trans. Am. Geophys. Union*, 63:138-140.
- Louda, J. W., and Baker, E. W., 1984. Perylene occurrence, alkylation and possible sources in deep ocean sediments. *Geochim. Cosmochim. Acta*, 48:1043-1058.
- Mackenzie, A. S., Patience, R. L., Maxwell, J. R., Vandenbroucke, M., and Durand, B., 1980. Molecular parameters of maturation in the Toarcian shales, Paris Basin, France—I. Changes in the configuration of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim. Cosmochim. Acta*, 44:1709-1721.
- Morita, R. Y., 1980. Microbial life in the deep sea. *Can. J. Microbiol.*, 26:1375-1385.
- Northam, M. A., Curry, D. J., Scalan, R. S., and Parker, P. L., 1981. Stable carbon isotope ratio variations of organic matter in Orca Basin sediments. *Geochim. Cosmochim. Acta*, 45:257-260.
- Oremland, R. S., and Culbertson, C., 1982. Methanogenic activity in sediment from Leg 64, Gulf of California. In Curran, J. R., Moore, D. G., et al., *Init. Repts. DSDP*, 64: Washington (U.S. Govt. Printing Office), 759-762.
- Philp, R. P., 1982. Application of computerized gas chromatography/mass spectrometry to fossil fuel research. *Spectra*, 8:6-31.
- Rashid, M. A., 1979. Pristane-phytane ratios in relation to source and diagenesis of ancient sediments from the Labrador Shelf. *Chem. Geol.*, 25:109-122.

- Requejo, A. G., and Quinn, J. G., 1983. Geochemistry of C_{25} and C_{30} biogenic alkenes in sediments of the Narragansett Bay estuary. *Geochim. Cosmochim. Acta*, 47:1075-1090.
- Requejo, A. G., Quinn, J. G., Gearing, J. N., and Gearing, P. J., 1984. C_{25} and C_{30} biogenic alkenes in a sediment core from the upper anoxic basin of the Pettaquamscutt River (Rhode Island, U.S.A.). *Org. Geochem.*, 7:1-10.
- Rice, D. D., and Claypool, G. E., 1981. Generation, accumulation, and resource potential of biogenic gas. *Bull. Am. Assoc. Pet. Geol.*, 65:5-25.
- Rowland, S. J., and Maxwell, J. R., 1984. Reworked triterpenoid and steroid hydrocarbons in a recent sediment. *Geochim. Cosmochim. Acta*, 48:617-624.
- Seifert, W. K., and Moldowan, J. W., 1978. Application of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochim. Cosmochim. Acta*, 42:77-95.
- Shokes, R. F., Trabant, P. K., Presley, B. J., and Reid, D. R., 1977. Anoxic, hypersaline basin in the northern Gulf of Mexico. *Science* 196:1443-1446.
- Simoneit, B. R. T., 1982. Hydrothermal effects on recent diatomaceous sediments in Guaymas Basin, Gulf of California: genesis of petroleum and evolution of protokerogen. *Spectra*, 8:52-57.
- Simoneit, B. R. T., and Kaplan, I. R., 1980. Triterpenoids as molecular indicators of paleoseepage in recent sediments of the Southern California Bight. *Mar. Environ. Res.*, 3:113-128.
- Stevens, N. P., Bray, E. E., and Evans, E. D., 1956. Hydrocarbons in sediments of Gulf of Mexico. *Bull. Am. Assoc. Pet. Geol.*, 40: 975-983.
- Tissot, B. P., and Welte, D. H., 1978. *Petroleum Formation and Occurrence. A New Approach to Oil and Gas Exploration*: Berlin (Springer-Verlag).
- Wakeham, S. G., Schaffner, C., and Giger, W., 1980. Polycyclic aromatic hydrocarbons in Recent lake sediments—II. Compounds derived from biogenic precursors during early diagenesis. *Geochim. Cosmochim. Acta*, 44:415-429.
- Wakeham, S. G., Schaffner, C., Giger, W., Boon, J. J., and DeLeeuw, J. W. 1979. Perylene in sediments from the Namibian shelf. *Geochim. Cosmochim. Acta*, 43:1141-1144.

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