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35. IDENTIFICATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SEDIMENTS FROM THE AMAZON FAN: OCCURRENCE AND DIAGENETIC EVOLUTION[1]

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ABSTRACT

The aromatic fractions of sediments from Hole 940A, Ocean Drilling Program, Leg 155, have been analyzed. A strong terrestrial contribution of organic matter was found, and some autochthonous inputs were recorded. The distributions of aromatic compounds were dominated by derivatives from amyrins. Diagenetic processes involved in aromatizations and isomerizations have been characterized.

INTRODUCTION

The objective of Leg 155 was to study the evolution of the deep-sea fan of the Amazon River for a better understanding of climatic changes and to evaluate circulation patterns in the western equatorial Atlantic. In that respect it was planned to characterize and understand the nature, origin, and diagenesis of organic carbon in this particular environment.

Aromatic compounds are ubiquitous. They are found in all ancient or recent sedimentary environments (Blumer, 1976). These compounds share two different origins: a biogenic origin, as degradation products of triterpenoids or steroids in the sedimentary environment, and an anthropogenic origin, as generated by high-temperature processes. They have proven to be useful indicators of the origin and of the thermal maturation stage of organic matter (Youngblood and Blumer, 1975; Wakeham et al., 1980a, 1980b; Garrigues et al., 1987b; Lipiatou and Saliot, 1991; Domine et al., 1994). Alkylated aromatic hydrocarbons of the phenanthrene or dibenzothiophene series are especially useful as markers of thermal maturity (Radke, 1987, 1988; Garrigues et al., 1988; Budzinski et al., 1993a, 1993b). They can also be used for origin assessments. Various studies have shown that the distributions of these compounds (i.e., alkylated phenanthrenes and dibenzothiophenes) in petroleums can be influenced by the origin of organic matter, and, therefore, may reflect its type (Hughes, 1984; Budzinski et al., 1995). The relative distribution of methyl-dibenzothiophenes can be related to paleoenvironments of source rocks and petroleums (Hughes, 1984; Connan et al., 1986; Schou and Myhr, 1988). The distribution of alkylated phenanthrenes is also influenced by the type of organic matter as evidenced by Cassini et al. (1988). A more recent study (Budzinski et al., 1995) has tentatively related the 1-methylphenanthrene to terrestrial origin and 9-methylphenanthrene to marine origin.

The goal of this study was to use aromatic hydrocarbons as molecular tools to elucidate the origin and fate of organic matter. Compounds ranging from tri- to penta-aromatics have been identified, and their distributions have been interpreted in terms of source assessment and diagenesis.

EXPERIMENTAL

Materials

Sediments from Site 940 were investigated. This site was chosen to study the processes associated with the development of the levee of the Amazon Fan system. Site 940 is located on the levee of the most recently active fan channel. The turbidite channel located near this site has fed several downstream channel and levee deposits, including the Aqua and Brown systems, during the Stage 2 glacial lowstand (Shipboard Scientific Party, 1995). The channel became inactive following the post-glacial sea-level rise. The sediments are silty clays and range from Holocene (uppermost sample) to late Pleistocene (isotope Stage 2) in age. The entire hole is younger than 40 ka (Shipboard Scientific Party, 1995). The geothermal gradient could be estimated at ~29°C/km. The analyzed samples are presented in Table 1. The correspondence between Ocean Drilling Program (ODP) sample numbers and the sample codes used in this study is also given in Table 1.

Sample Preparation

The samples were freeze-dried and then extracted with an ultrasonic bath (Hinrichs and Rullkötter, this volume) with a mixture of dichloromethane and methanol (99/1). The extracts were concentrated. After desulfurization on activated copper, they were fractionated by medium pressure liquid chromatography (Radke et al., 1980) to alkanes, aromatics, and polar compounds. The aromatic fraction was then analyzed by gas chromatography coupled with mass spectrometry.

Compounds

The compounds that were quantified are given in the Appendix. Aromatic compounds were identified according to their mass spectra, bibliographic data previously published, and co-injection with standards. Aromatic biogeochemical markers have been kindly supplied by Dr. Albrecht (University Louis Pasteur, Strasbourg, France). The compounds were quantified according to deuterated aromatic standards purchased from MSD isotopes (Canada). The concentrations are given with an accuracy of ±10. They are expressed in nanograms per gram of dry sediment (ng/g dry sed) and in nanograms per gram of total organic carbon (ng/g TOC).

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Table 1. Studied samples from Hole 940A.

Core, section, interval (cm)	Sample number used in the study	Depth (mbsf)	TOC* (%)
155-940A-			
1H-2, 20–25	923	1.69	0.83
2H-4, 41–47	924	7.55	0.93
5H-5, 50–56	926	36.34	0.95
6H-4, 102–108	927	45.84	0.89
7H-4, 54–61	928	54.33	1.01
8H-6, 50–57	929	67.71	0.88
10X-4, 48–55	930	81.94	1.05
15X-3, 40–45	932	126.71	0.66
19X-3, 33–39	936	165.26	0.85
23X-4, 83–90	938	205.40	0.76

Notes: TOC = total organic carbon. * = data from Hinrichs and Rullkötter (this volume).

Gas Chromatography/Mass Spectrometry

The aromatic fractions were analyzed by gas chromatography/mass spectrometry (GC/MS) using an HP5890 series II gas chromatograph coupled with an HP 5972 MSD mass spectrometer. The gas chromatograph was equipped with a splitless injector (purge delay 30 s and purge flow 60 mL/min; T_{inj} = 270°C). The column used was a PTE5 (Supelco, France), 60 m × 0.2 mm ID × 0.1 µm film thickness. Helium was used as carrier gas at 1 mL/min. The column was kept at 50°C for 2 min, then programmed to 290°C at 5°C/min, and kept at 290°C for 10 min. The interface was at 290°C. The mass spectrometer was operated from 50 to 500 dalton (SCAN mode) (electron impact at 70 eV, 2000 V, 1 scan/s).

Some compounds can be coeluted with structural isomers on the GC column that was used (nonpolar stationary phase). To check the validity of the measurements, another column was used. This column contained a liquid crystalline stationary phase. It was a SB-Smectic column (Dionex, Lee Scientific Division, Salt Lake City, Utah, U.S.A.), 50 m × 0.22 mm × 0.1 µm, which has been demonstrated to be very selective in the analysis of isomeric aromatic compounds (Budzinski et al., 1992a, 1992b; Wise et al., 1995). An example of the good chromatographic resolution obtained for methylated triaromatic compounds is shown in Figure 1. All the isomers are separated; more precisely, 9-methylphenanthrene is separated from 4-methylphenanthrene and 1-methylanthracene, which coelute with it on GC columns such as PTE5.

RESULTS AND DISCUSSION

The quantitative results for the aromatic compounds are given in Table 2.

Total Aromatic Hydrocarbons

The concentrations of aromatic compounds in the studied sediments are quite uniform (Table 2). No specific trend (increase or decrease) can be observed within depth. This suggests that in situ diagenetic processes are not the only ones to take into account for the formation of aromatic hydrocarbons. Most of these compounds are more likely formed on land and are transported to the marine environment by erosion and water runoff. This is corroborated by other studies that have observed that even in surface samples (Mahakam Delta, Indonesia), aromatic derivatives of triterpenes are present in quite important amounts (Tissier, 1981). The influence of in situ diagenetic processes on distributions and concentrations could be very limited.

The sum of all the quantified aromatic compounds ranges from ~200 ng/g of dry sediment (i.e., ~20 µg/g of TOC) to ~900 ng/g of dry sediment (i.e., ~100 µg/g of TOC). This sum does not correlate with the TOC content (correlation coefficient = 0.17), which could reflect the fact that the aromatic compounds represent a small part of the bulk organic carbon (the sum of all aromatic compounds <0.01% of bulk organic carbon). Also, these compounds are, in most of the cases, the ultimate products of molecular rearrangements.

The distributions of the aromatic compounds in the Amazon Fan samples are diverse with various molecular structures. The patterns are quite complicated with significant amounts of alkylated compounds present. For example, the ratio of the sum of the concentrations of the methylphenanthrenes vs. the concentration of the phenanthrene (ΣMP/P) exhibits, for all the samples except one (sample 923, 1.69 meters below seafloor [mbsf]), values >1 and near to 2, which demonstrates the predominance of alkylated phenanthrenes over phenanthrene.

When omitting perylene (see below), the polycyclic aromatic hydrocarbon (PAH) distribution is dominated by compounds derived from triterpenes. Some of these belong to the di-aromatic series such as alkylated octahydro-chrysenes and alkylated tetrahydro-phenanthrenes, others to the tri-aromatic series such as alkylated tetrahydrochrysenes and octahydro-picenes, and finally others to the tetra-aromatic series such as alkylated tetrahydro-picenes (see the Appendix for nomenclature and structures). Such distributions have already been observed in other environments such as the Cariaco Trench (Venezuela; Tissier and Dastillung, 1978), the Kayar Canyon (Senegal River; Corbet et al., 1979), lake sediments (Wakeham et al., 1980b), and the Mahakam Delta (Indonesia; Garrigues et al., 1987a). These compounds have been commonly related to strong terrestrial inputs. Most of them are mainly derived from higher plant triterpenoids such as α-amyrin or β-amyrin, and they can be used as biomarkers of a terrestrial origin. Typical marine environments, such as sediments from Cape Blanc (Senegal; Corbet et al., 1979) or deep-sea sediments from the North Atlantic Ocean (Atlantic coast of France; Parlenti, 1990), have proven to be very poor in these compounds. These different features (predominance of alkylated compounds, important amounts of derivatives of triterpenoids) demonstrate the prevailing biogenic origin of the organic matter of these sediments.

Some PAHs (with five rings) were detected at trace levels but not quantified. These include benzofluoranthenes, benzo(e)pyrene, and benzo(g,h,i)perylene (see Appendix for structures). These compounds are typical products of pyrolysis (Laflamme and Hites, 1979; McElroy et al., 1989) and could reflect minor inputs from natural pyrolytic processes like forest fires (Youngblood and Blumer, 1975).

When considering tetra-aromatic PAHs, fluoranthene, pyrene, benz(a)anthracene, and chrysene, it can be noted that one structural form dominates over the other, that is, pyrene over fluoranthene, and chrysene over benz(a)anthracene. The dominant isomers (i.e., pyrene and chrysene) are thermodynamically more stable. In the case of main pyrolytic origin for these compounds, the reverse trend is generally observed. Fluoranthene dominates over pyrene and benz(a)anthracene dominates over chrysene (Soclo, 1986). In the case of the sediments of Site 940, even if the existence of a slight pyrolytic source for pyrene and chrysene cannot be discarded, the main source for these two compounds must be biogenic due to their marked predominance over their structural isomers in the sediments. Chrysene coelutes with triphenylene on the PTE5 column that was used. On the liquid crystalline phase this coelution is resolved (Wise et al., 1995). The contribution of triphenylene was calculated and substracted by the use of the liquid crystal stationary phase.

Perylene

Perylene is the most abundant aromatic compound. It represents from 30% to 70% of all aromatic compounds that have been quantified. Large continental inputs, in conjunction with a reducing medium, could explain these high perylene abundances because of good preservation of possible precursors (Venkatesan, 1988). The average perylene concentration is higher in the upper part of the hole (an average of 413 ng/g of dry sediment or 47 µg/g of TOC for sample 923 (1.69 mbsf) to sample 928 (54.33 mbsf) than in the lower part (an av-

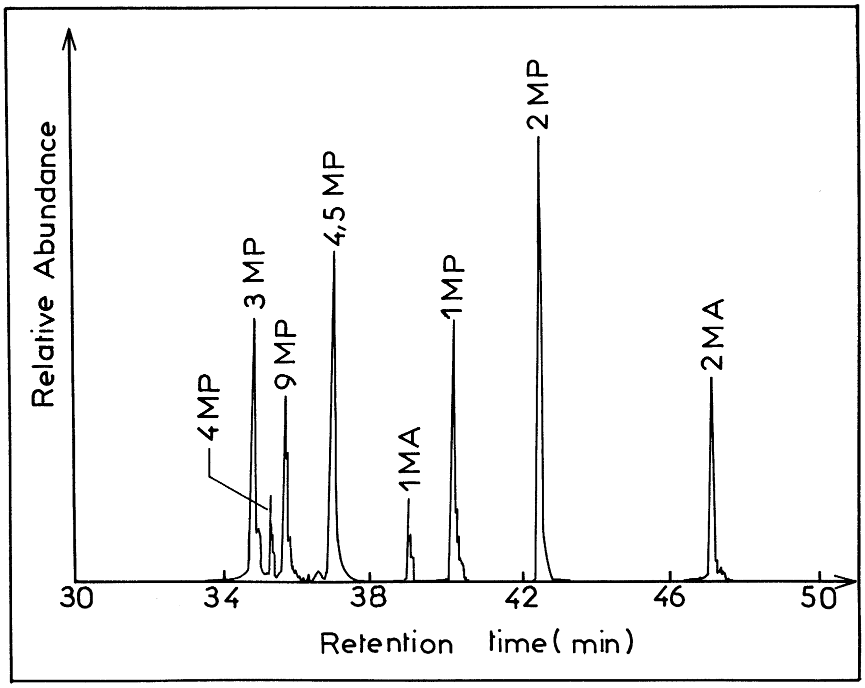


Figure 1. Total ion current trace of a standard mixture of methylated tri-aromatics obtained with the liquid crystalline stationary phase (SB-Smectic, Dionex). Note the perfect separation of all the isomers. MP = methylphenanthrene and MA = methylanthracene.

erage of 253 ng/g of dry sediment or 32 µg/g of TOC for sample 929 (67.71 mbsf) to sample 938 (205.40 mbsf)). This could be related to an increase in detrital inputs rich in plant material that could carry large amounts of precursors.

Phenanthrene Compounds

The distributions obtained for the methylphenanthrenes (MPs) are presented in Figure 2. It can be noted that for all samples, except for the first level (sample 923), 9-MP slightly dominates the methylphenanthrene distribution (it accounts for ~30% of all four MPs). The lack of 4-MP was checked with the liquid crystalline phase in GC in order to ensure the concentrations of 9-MP.

For sample 923 (1.69 mbsf), 1-MP dominates the methylphenanthrene distribution (it represents 44% of the four methylphenanthrenes). Phenanthrene dominates over methylphenanthrenes for the first sample (ΣMP/P = 0.32; Table 3). On the contrary, the methylphenanthrenes are more abundant than phenanthrene for the other samples (ΣMP/P > 1; Table 3). This could reflect diagenetic evolution. Indeed, alkylation processes of phenanthrene can occur during diagenesis (Radke et al., 1982), and position 9 is the most reactive. So the predominance of 9-MP may be associated with alkylation processes and correlated with high abundances of methylphenanthrenes relative to phenanthrene. However, where alkylation processes are not important, especially at the beginning of diagenetic evolution, phenanthrene can dominate over methylphenanthrenes, and the fingerprint of methylphenanthrene isomers could reflect the natural input of precursors. In this case, the high abundance of 1-MP in the upper sample (sample 923) could be related to large inputs of terrestrial organic matter (Alexander et al., 1987) and the case of MP distribution in sample 923 (relative to the nine other samples) could also reflect temporal change in input.

Regarding the methylphenanthrenes, different concentration ratios have evolved and are used in petroleum geochemistry as thermal maturity indices (Radke, 1987, 1988). For example, the MPI_3 ratio, calculated as (2-MP + 3-MP) / (9-MP + 1-MP + 4-MP), can increase with greater thermal maturity (Garrigues et al., 1988). Indeed, previous studies have reported a relative increase in the abundance of 2-MP and 3-MP relative to 9-MP and 1-MP when maturity increases (Radke et al., 1982). The values obtained for this ratio in the case of the present study are given in Table 3. It increases regularly with a depth up to 120 mbsf (Fig. 3). This behavior could indicate diagenetic evolution. When considering this trend, it appears that more rapid diagenetic evolution seems to take place between the two upper samples (923 and 924), between 1.69 and 7.55 mbsf. The drop of the values of this ratio for the two deeper samples could reflect a change in input.

Biogeochemical Markers

Aromatic compounds derived from amyrin and lupeol were identified in the different samples. Some derivatives from hopanoids were also detected. A typical partial total ion current trace encountered in this study is presented in Figure 4. The chemical structures and the names of the aromatic biomarkers that were identified are given in the Appendix.

To simplify the discussion, the designations were adapted from Garrigues et al. (1987a) for the compounds derived from the triterpenoids. When the aromatic part of the molecule is a naphthalene structure, the letter *N* is used; when the skeleton shows a phenanthrene structure, the letter *P* is used; and for a chrysene structure, the letter *C* is used. When a methyl group is present on ring A (see Appendix), the letter *M* is added; α is added for the derivatives of α-amyrin, and β for the derivatives of β-amyrin. Finally, if the compounds have been generated by microbial degradation (cleavage of one ring), the letter *d* is added.

Derivatives from β-amyrin are predominant over derivatives from α-amyrin. The two classes of compounds show similar behavior vs. depth (Fig. 5). This suggests that they share identical pathways of formation. This observation corroborates those of Garrigues et al. (1987a) in the case of the sediments from the Mahakam Delta (Indonesia) and those of Tissier and Dastillung (1978) in the case of the sediments from the Cariaco Trench. The predominance of derivatives from β-amyrin could be explained by the fact that this alcohol could be degraded more preferentially than α-amyrin (Dastillung, 1976; Corbet, 1980). Indeed, the double bond in β-amyrin is less hindered than in α-amyrin. So functionalization and the subsequent evolution of derivatives of β-amyrin would be easier than those of α-amyrin. This explanation could be corroborated by the fact that only derivatives of β-amyrin are encountered in crude oils of the Mahakam Delta

Table 2. Concentrations of identified aromatic compounds.

	Concentrations (ng/g of dry sediment)										Concentrations (µg/g of TOC)									
Sample number:	923	924	926	927	928	929	930	932	936	938	923	924	926	927	928	929	930	932	936	938
Compounds																				
P	5.42	1.76	1.81	1.76	2.07	1.62	2.14	2.07	1.11	1.19	0.65	0.21	0.22	0.21	0.20	0.18	0.20	0.31	0.13	0.16
3MP	0.31	0.90	0.72	0.73	0.85	0.70	0.66	0.63	0.38	0.47	0.04	0.11	0.09	0.09	0.08	0.08	0.06	0.10	0.04	0.06
2MP	0.41	1.18	0.97	0.90	1.07	0.92	0.86	0.90	0.50	0.60	0.05	0.14	0.12	0.11	0.11	0.10	0.08	0.14	0.06	0.08
9MP	0.45	1.34	1.01	1.00	1.18	0.97	0.85	0.88	0.53	0.69	0.05	0.16	0.12	0.12	0.12	0.11	0.08	0.13	0.06	0.09
1MP	0.57	1.14	0.81	0.89	0.87	0.74	0.64	0.62	0.44	0.54	0.07	0.14	0.10	0.11	0.09	0.08	0.06	0.09	0.05	0.07
2EtP+9EtP+3,6DMP	0.08	0.19	0.17	0.13	0.14	0.14	0.11	0.11	0.07	0.09	0.01	0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.01	0.01
1EtP	0.17	0.31	0.19	0.20	0.25	0.21	0.16	0.19	0.14	0.16	0.02	0.04	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02
3,5DMP	0.26	0.58	0.37	0.41	0.44	0.35	0.32	0.31	0.21	0.28	0.03	0.07	0.04	0.05	0.04	0.04	0.03	0.05	0.02	0.04
2,6+2,7DMP	0.21	0.42	0.28	0.33	0.32	0.28	0.21	0.25	0.16	0.19	0.03	0.05	0.03	0.04	0.03	0.03	0.02	0.04	0.02	0.03
1,3+2,10+3,9+3,10DMP	0.85	1.93	1.28	1.43	1.48	1.29	1.04	1.11	0.74	1.01	0.10	0.23	0.15	0.17	0.15	0.15	0.10	0.17	0.09	0.13
1,6+2,9DMP	0.53	1.15	0.75	0.82	0.85	0.77	0.57	0.59	0.41	0.55	0.06	0.14	0.09	0.10	0.08	0.09	0.05	0.09	0.05	0.07
1,7DMP	0.49	1.05	0.64	0.80	0.72	0.64	0.51	0.57	0.37	0.47	0.06	0.13	0.08	0.10	0.07	0.07	0.05	0.09	0.04	0.06
2,3DMP	0.71	0.98	0.70	0.81	0.65	0.57	0.34	0.34	0.44	0.45	0.09	0.12	0.08	0.10	0.06	0.06	0.03	0.05	0.05	0.06
1,9DMP	0.19	0.39	0.24	0.31	0.31	0.26	0.13	0.32	0.15	0.23	0.02	0.05	0.03	0.04	0.03	0.03	0.01	0.05	0.02	0.03
1,8DMP	0.11	0.20	0.12	0.12	0.12	0.13	0.08	0.06	0.10	0.08	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
1,2,8TMP	0.26	0.40	0.26	0.33	0.26	0.25	0.17	0.20	0.15	0.21	0.03	0.05	0.03	0.04	0.03	0.03	0.02	0.03	0.02	0.03
Retene	0.13	0.46	0.32	0.33	0.38	0.27	0.15	0.42	0.27	0.25	0.02	0.06	0.04	0.04	0.04	0.03	0.01	0.06	0.03	0.03
Pyrene	0.91	1.30	0.86	1.05	0.94	0.87	0.90	0.85	0.68	0.85	0.11	0.16	0.10	0.13	0.09	0.10	0.09	0.13	0.08	0.11
Fluoranthene	0.64	0.92	0.53	0.72	0.70	0.66	0.73	0.78	0.44	0.63	0.08	0.11	0.06	0.09	0.07	0.08	0.07	0.12	0.05	0.08
Benz(a)anthracene	0.36	0.48	0.20	0.25	0.27	0.18	0.24	0.31	0.15	0.19	0.04	0.06	0.02	0.03	0.03	0.02	0.02	0.05	0.02	0.03
Chrysene	1.90	3.01	1.94	2.52	2.28	1.91	2.07	1.65	1.27	1.59	0.23	0.36	0.23	0.30	0.23	0.22	0.20	0.25	0.15	0.21
Perylene	134	446	189	613	685	173	172	358	136	423	16.14	53.73	22.77	73.86	67.82	19.66	16.38	54.24	16.00	55.66
MPαd	2.82	13.70	44.42	11.51	10.05	7.90	11.89	6.47	6.48	9.52	0.34	1.65	5.35	1.39	1.00	0.90	1.13	0.98	0.76	1.25
MNαd	3.39	20.76	14.29	36.10	29.82	19.02	27.95	19.78	19.97	22.36	0.41	2.50	1.72	4.35	2.95	2.16	2.66	3.00	2.35	2.94
MPα	2.42	5.41	5.24	7.54	6.88	4.36	5.75	5.85	4.68	4.96	0.29	0.65	0.63	0.91	0.68	0.50	0.55	0.89	0.55	0.65
MCα	0.53	1.18	0.85	1.57	1.50	0.95	0.78	1.03	0.79	1.02	0.06	0.14	0.10	0.19	0.15	0.11	0.07	0.16	0.09	0.13
Cα	0.17	0.44	0.38	0.58	0.53	0.44	0.52	0.44	0.33	0.39	0.02	0.05	0.05	0.07	0.05	0.05	0.05	0.07	0.04	0.05
MPβd	7.87	67.08	235	70.96	72.59	32.23	33.41	51.86	64.01	71.28	0.95	8.08	28.31	8.55	7.19	3.66	3.18	7.86	7.53	9.38
MNβd	8.03	46.56	30.43	36.34	31.27	19.10	27.29	20.61	21.38	22.16	0.97	5.61	3.67	4.38	3.10	2.17	2.60	3.12	2.52	2.92
MCβ	0.71	1.42	0.96	1.62	1.51	1.24	1.03	1.16	0.86	0.18	0.09	0.17	0.12	0.20	0.15	0.14	0.10	0.18	0.10	0.02
MPβ	4.39	9.85	7.89	11.86	10.24	6.27	9.35	9.42	7.90	8.92	0.53	1.19	0.95	1.43	1.01	0.71	0.89	1.43	0.93	1.17
Cβ	5.36	14.70	11.43	19.48	16.97	12.63	14.40	17.11	14.61	17.56	0.65	1.77	1.38	2.35	1.68	1.44	1.37	2.59	1.72	2.31
MPx	5.50	13.61	12.57	17.63	16.50	10.31	14.42	14.01	11.87	12.14	0.66	1.64	1.51	2.12	1.63	1.17	1.37	2.12	1.40	1.60
MCx	1.16	3.06	2.91	4.29	4.11	2.82	3.00	3.11	2.47	2.97	0.14	0.37	0.35	0.52	0.41	0.32	0.29	0.47	0.29	0.39
MPh	0.88	1.62	1.64	2.26	1.94	1.61	1.24	1.31	0.93	1.32	0.11	0.20	0.20	0.27	0.19	0.18	0.12	0.20	0.11	0.17
MCh	5.83	7.23	6.36	12.99	11.90	9.28	5.51	6.83	5.29	7.29	0.70	0.87	0.77	1.57	1.18	1.05	0.52	1.03	0.62	0.96
Pl	0.39	1.02	0.83	1.06	1.03	0.72	1.11	0.62	0.57	0.67	0.05	0.12	0.10	0.13	0.10	0.08	0.11	0.09	0.07	0.09
Nl	2.35	9.49	5.21	13.86	10.80	7.56	11.96	8.38	7.33	8.74	0.28	1.14	0.63	1.67	1.07	0.86	1.14	1.27	0.86	1.15

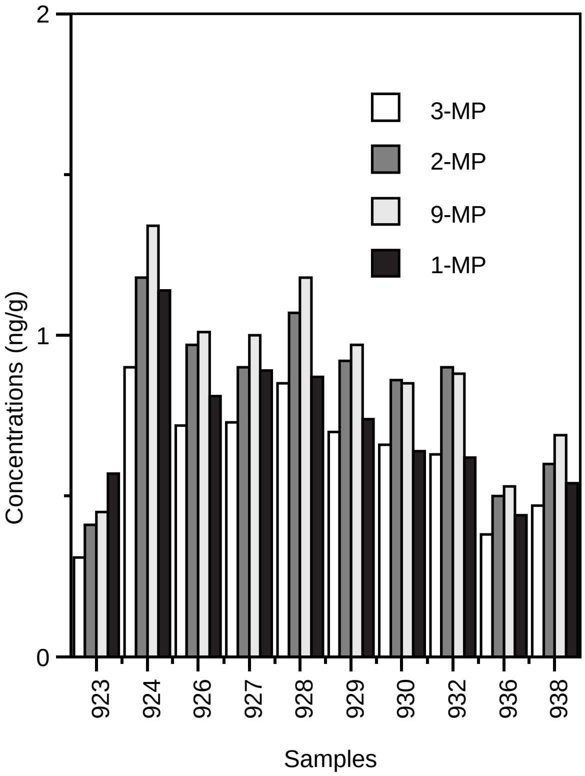


Figure 2. Distributions of methylphenanthrenes.

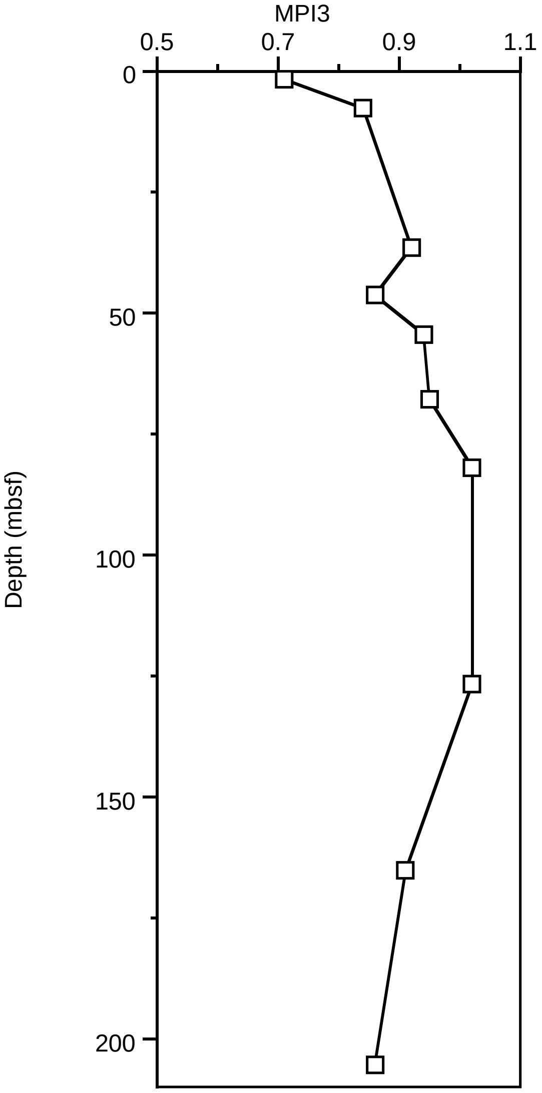
Table 3. Concentration ratios for various aromatic compounds in samples from Hole 940A.

Samples:	923	924	926	927	928	929	930	932	936	938
Ratios										
ΣMP/P	0.32	2.59	1.94	2.01	1.93	2.05	1.41	1.47	1.66	1.93
MPI_3	0.71	0.84	0.93	0.86	0.94	1.24	1.02	1.02	0.91	0.87
MPβd:MPβ	1.79	6.81	29.77	5.98	7.09	5.14	3.57	5.50	8.10	7.99
MPαd:MPα	1.17	2.53	8.48	1.53	1.46	1.81	2.07	1.10	1.39	1.92
MCβ:MPβ	0.16	0.14	0.12	0.14	0.15	0.20	0.11	0.12	0.11	0.13
MCα:MPα	0.22	0.22	0.16	0.21	0.22	0.22	0.13	0.18	0.17	0.20
Mpβd:MNβd	0.98	1.44	7.71	1.95	2.32	1.69	1.22	2.52	2.99	3.22

(Garrigues, 1985). Another explanation could be a higher abundance of β-amyrin in higher plants in comparison to α-amyrin (De Mayo, 1959).

The two alcohols, α- and β-amyrin, can undergo two different mechanisms of degradation (Fig. 6; adapted from Laflamme and Hites, 1979). In both cases, the degradation starts from ring A, and aromatization progresses from ring A to ring D. Concerning the first mechanism (I), the cleavage of the ring A leads to tetracyclic structures and is associated with microbial processes (Trendel et al., 1989).

Compounds generated from bacterial degradation (I), MPβd and MPαd, are predominant in the case of the triaromatic derivatives. The ratios MPβd:MPβ and Mpαd:MPα are always >1 (Table 3). The weak abundance of MPβ and MPα could be explained by a rapid aromatization (mechanism II) of the pentacyclics to generate tetra-aromatics (MCβ and MCα). But in this case, the ratios MCβ:MPβ and MCα:MPα would have shown high values, which is not the case. Their values (Table 3) are low (~0.14 and 0.19, respectively). The microbial process (I) seems to be the major mechanism in the degradation of the two alcohols.



Colonne 7

Figure 3. MPI_3 index vs. depth.

In the case of microbial degradation (pathway I), the diaromatics are generally less abundant than the triaromatics. The ratio MPβd:MNβd is greater than 1 for all the samples, except for the first depth (Table 3). This indicates that the transformation of triterpenoid alcohols like amyrins (defunctionalization, cleavage of ring A, aromatization) is nearly complete within the first 2 m. Nevertheless, for the first sample (sample 923, 1.69 mbsf), the microbial transformation of β-amyrin has not reached the end product (formation of triaromatics) because, for this sample, diaromatics are slightly more abundant than triaromatics (MPβd:MNβd = 0.98; Table 3).

When considering the derivatives from both degradation pathway I and pathway II, a different behavior vs. depth can be noted (Fig. 7). If the sum of all the compounds from pathway I (microbial degradation) is considered, there is a strong increase of absolute concentration corresponding to sample 926 (36.34 mbsf). This trend is not not-

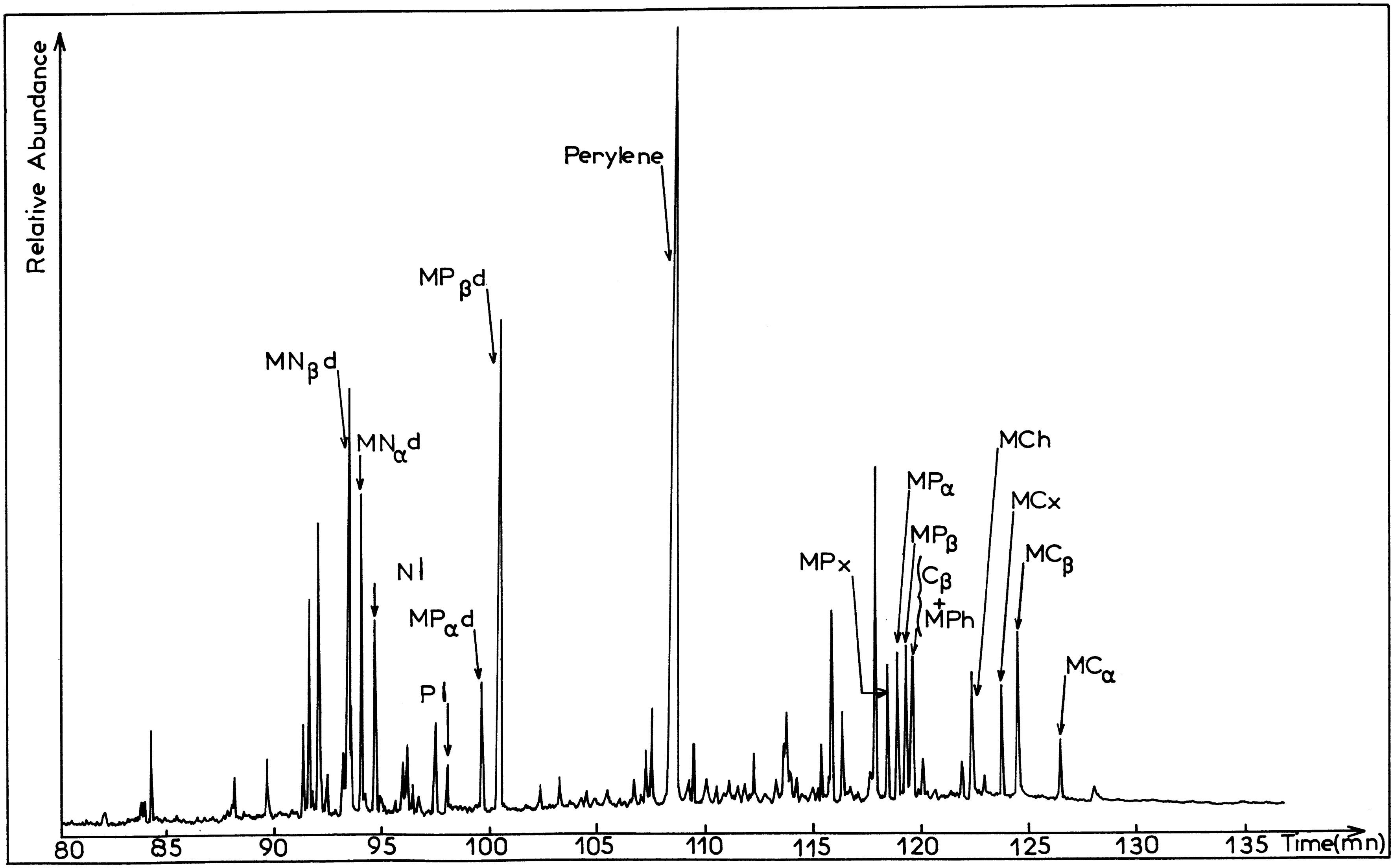


Figure 4. Partial total ion current trace for a typical aromatic fraction. The identification of aromatic biomarkers is given in the Appendix.

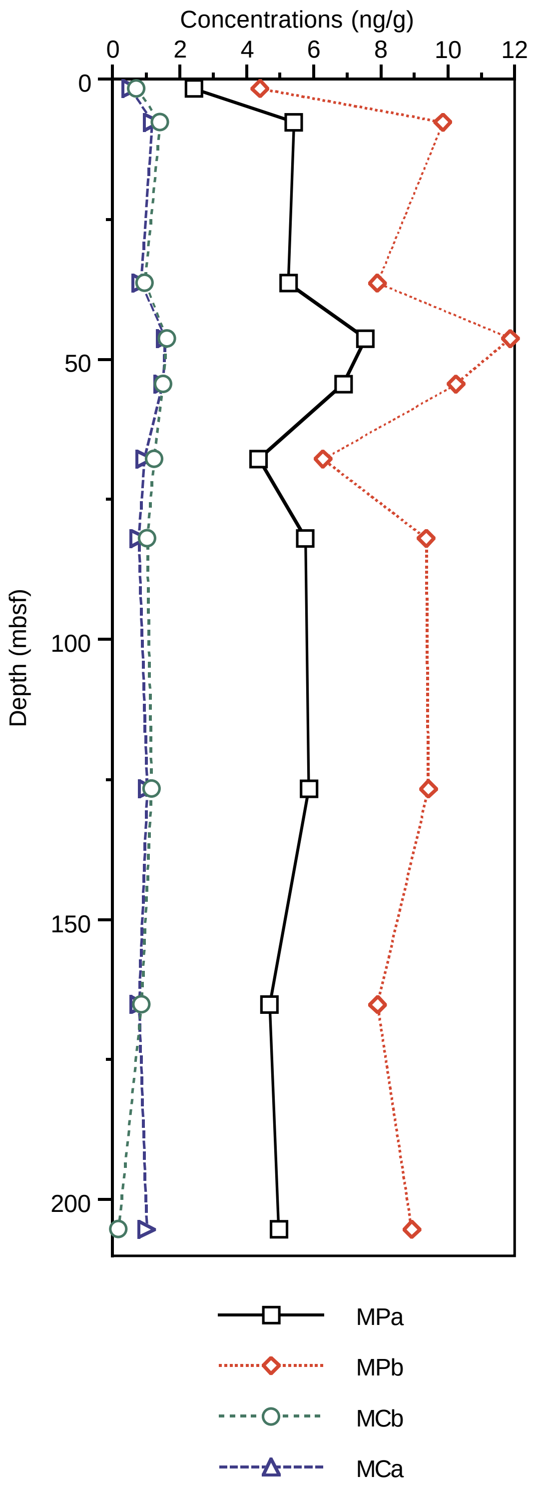


Figure 5. Concentrations of some aromatic derivatives from amyrins vs. depth (a = α and b = β-amyrin precursor).

ed for the compounds generated from pathway II. This feature can tentatively be related to high microbial activity during the deposition of this sample. The cleavage of ring A would have been favored yielding the diaromatics and triaromatics in high amounts. This could be linked to the depth of sulfate penetration that was found to be about 30 m (Shipboard Scientific Party, 1995), and which might be consistent with intense microbial action at this depth.

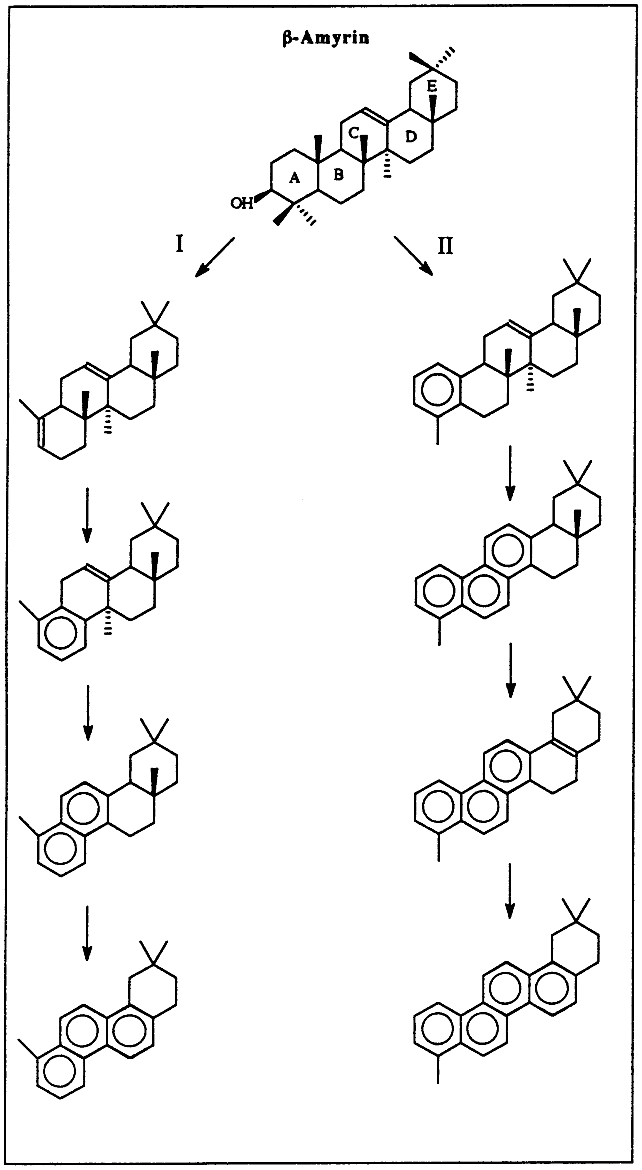


Figure 6. Degradation pathways of amyrins (β-amyrin shown, adapted from Simoneit, 1977; Laflamme and Hites, 1979).

Another difference can be observed between pathway I and II. When considering derivatives generated from amyrins solely by defunctionalization and aromatization (pathway II), triaromatics (MPβ and MPα) are more abundant than the tetra-aromatics (MCβ, MCα). The ratios MCβ:MPβ and MCα:MPα have low values (between 0.10 and 0.20; Table 3). The compounds generated during the last step of aromatization in pathway II (tetra-aromatics) are minor in comparison to triaromatics. This is the opposite trend as to what was observed for pathway I. It can be stated that microbial degradation (pathway I) is not only a predominant transformation process but is also faster than the transformation involved in pathway II.

Nl and Pl have been identified as derivatives of lupeol. In the case of lupeol, two degradation pathways can also be considered. The cleavage of ring A, followed by aromatization, gives Nl and Pl. On the other hand, aromatization without cleavage of ring A gives Cl (Laflamme and Hites, 1979). Cl is totally absent in the samples that have been studied. As for the derivatives from amyrins, it appears that microbial degradation of lupeol (with cleavage of ring A) is favored.

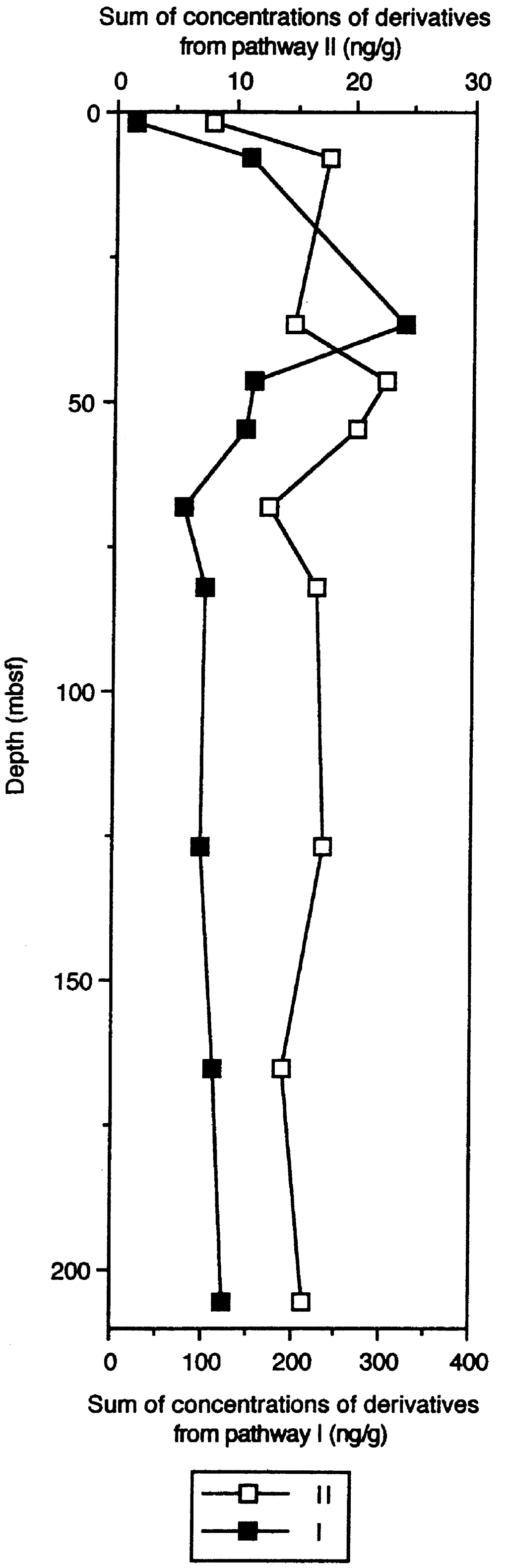


Figure 7. Sum of concentrations of derivatives of amyrins (α and β) depending on the degradation pathway (I and II) vs. depth.

Derivatives, MPh, and MCh, have been identified in the hopane series. They reflect microbial activity and can be related to an autochthonous origin. The tetraaromatic compound (MCh) is more abundant than the triaromatic (MPh). This is the opposite trend to what was observed for the compounds derived from amyrins. Garrigues et al. (1987a) showed similar results in the case of samples from the Mahakam Delta (Indonesia), and Chaffee and Johns (1983) have observed the lack of MPh in an Australian coal. The derivatives from hopanes are expected to aromatize more rapidly than those from amyrins (Garrigues et al., 1986, 1987a).

CONCLUSIONS

Phenanthrene and chrysene compounds, derived from triterpenoids, are the most predominant aromatic compounds in the samples studied from Site 940, and they reflect high terrestrial inputs. This strong terrestrial origin is also corroborated by the large amounts of perylene that have been detected. A slight trace of autochthonous inputs (based on aromatic hopane derivatives) was also recorded.

In situ diagenetic processes cannot explain the formation of aromatic compounds in the studied environment. Most of the aromatic compounds observed in the samples appear to be land-derived and transported by erosion; the influence of diagenetic transformations is therefore limited.

Derivatives of α- and β-amyrin were found to be the most abundant aromatic derivatives. When considering the evolution of the concentrations of these biomarkers with depth, it appears that some diagenetic processes could take place between the two upper samples, that is, between 1.69 and 7.55 mbsf. This was also recorded by the evolution of the methylphenanthrenes with depth. These isomers, which are useful markers of thermal evolution, follow the terpenoid isomerization or rearrangement reactions vs. depth in this study.

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REFERENCES

Alexander, R., Kagi, R.I., and Noble, R.A., 1987. Fossil resin biomarkers and their application in oil to source-rock correlation, Gippsland Basin, Australia. *APEA J.,* 27:63–72.

Blumer, M., 1976. Polycyclic aromatic compounds in nature. *Sci. Am.,* 234:35–45.

Budzinski, H., Garrigues, P., and Bellocq, J., 1992a. Gas chromatographic retention behavior of alkylated phenanthrenes on a smectic liquid crystalline phase. *J. Chromatogr.,* 627:227–239.

Budzinski, H., Garrigues, P., and Bellocq, J., 1992b. Gas chromatographic retention behavior of dibenzothiophene derivatives on a smectic liquid crystalline phase. *J. Chromatogr.,* 590:297–303.

Budzinski, H., Garrigues, P., Connan, J., Devillers, J., Domine, D., Radke, M., and Oudin, J.L., 1995. Alkylated phenanthrene distributions as maturity and origin indicators in crude oils and rock extracts. *Geochim. Cosmochim. Acta.,* 59:2043–2056.

Budzinski, H., Radke, M., and Garrigues, P., 1993a. Thermodynamic calculations on alkylated phenanthrenes: Geochemical applications to maturity and origin studies. *Org. Geochem.,* 20:917–926.

Budzinski, H., Radke, M., Garrigues, P., Rayez, M.T., and Rayez, J.C., 1993b. Use of molecular modelling as a tool to evaluate thermodynamic stability of alkylated polycyclic aromatic hydrocarbons. *Energy and Fuels,* 7:505–511.

Cassini, F., Gallango, O., Talukdar, S., Vallejos, C., and Ehrmann, U., 1988. Methylphenanthrene maturity index of marine source rock extracts and crude oils from the Maracaibo Basin. *Org. Geochem.,* 13:73–80.

Chaffee, A.L., and Johns, R.B., 1983. Polycyclic aromatic hydrocarbons in Australian coals I—Angularly fused pentacyclic tri- and tetraaromatic components of Victoria brown coal. *Geochim. Cosmochim. Acta,* 47:2141–2155.

Connan, J., Bouroullec, J., Dessort, D., and Albrecht, P., 1986. The microbial input in carbonate-anhydrite facies of a sabkha paleoenvironment from Guatemala: a molecular approach. *In* Leythauser, D., and Rullkötter, J (Eds.), *Advances in Organic Geochemistry 1985*: Oxford (Pergamon), 29–50.

Corbet, B., Albrecht, P., and Tissier, M.J., 1979. Hydrocarbures et acides des sédiments. mer-sédiment. *In* Arnould, M., and Pelet, R., (Eds.), *Géochimie organique des sédiments marins profonds (Orgon III)—Mauritanie-Sénégal-Iles du Cap-Vertt:* Paris (CNRS), 353–374.

Corbet, B., 1980. Origine et transformation de triterpènes dans des sédiments récents [Ph. D. dissert.]. Louis Pasteur Univ., Strasbourg, France.

Dastillung, M., 1976. Lipides de sédiments récents [Ph.D. dissert.]. Louis Pasteur Univ., Strasbourg, France.

De Mayo, P., 1959. *The Higher Terpenoids*: New York (Intersciences).

Domine, D., Devillers, J., Garrigues, P., Budzinski, H., Chastrette, M., and Karcher, W., 1994. Chemometrical evaluation of the PAH contamination in the sediments of the Gulf of Lion (France). *Sci. Total Environ.,* 155:9–24.

Garrigues, P., 1985. Origine et évolution de séries de composés aromatiques dans l'environnement sédimentaire [Ph.D. dissert.]. Louis Pasteur Univ., Strasbourg, France.

Garrigues, P., Bellocq, J., Albrecht, P., Saliot, A., and Ewald, M., 1987a. Etude des marqueurs biogéochimiques tri-, tétra- et pentaaromatiques dans les sédiments quaternaires et pliocène supérieur du delta de la Mahakam (Indonésie). In *Géochimie organique des sédiments plio-quaternaires du delta de la Mahakam (Indonésie). Le sondage MISEDOR.* Edition Technip, Paris, 317–342.

Garrigues, P., de Sury, R., Angelin, M.L., Bellocq, J., Oudin, J.L., and Ewald, M., 1988. Relation of the methylated aromatic hydrocarbon distribution pattern to the maturity of organic matter in ancient sediments from the Mahakam delta. *Geochim. Cosmochim. Acta,* 52:375–384.

Garrigues, P., Saptorahardjo, A., Gonzalez, C., Wehrung, P., Albrecht, P., Saliot, A., and Ewald, M., 1986. Biogeochemical aromatic markers in the sediments from Mahakam Delta (Indonesia). *Org. Geochem.,* 10:959–964.

Garrigues, P., Soclo, H., Marniesse, M.P., and Ewald, M., 1987b. Origin of Polycyclic Aromatic Hydrocarbons (PAH) in recent sediments from the continental shelf of the "Golfe de Gascogne" (Atlantic Ocean) and in the Gironde estuary. *Int. J. Env. Anal. Chem.,* 28:121–131.

Hughes, W.B., 1984. Use of thiophenic organosulfur compounds in characterizing crude oils derived from carbonate versus siliciclastic sources. *In* Palacas, J.G. (Ed.), *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks*: Tulsa (AAPG Studies in Geology), 18:181–196.

Laflamme, R.E, and Hites, R.A., 1979. Tetra- and pentacyclic, naturally-occurring aromatic hydrocarbons in recent sediments. *Geochim. Cosmochim. Acta,* 43:1687–1691.

Lipiatou, E., and Saliot, A., 1991. Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the western Mediterranean Sea. *Mar. Chem.,* 32:51–71.

McElroy, A.E., Farrington, J.W., and Teal, J.M., 1989. Bioavailability of PAH in the aquatic environment. *In* Varanasi, U. (Ed.*), Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*: Boca Raton, Florida (CRC press), 1:41–68.

Parlenti, E., 1990. Utilisation des hydrocarbures comme traceurs d'origine et d'évolution de la matière organique sédimentaire en milieu marin. Étude du golfe du Lion et du golfe de Gascogne [Ph.D. dissert]. Bordeaux I Univ., Talence, France.

Radke, M., 1987. Organic geochemistry of aromatic hydrocarbons. *In* Brooks, J, and Welte, D.H. (Eds.), *Advances in Petroleum Geochemistry*: London (Academic Press) 2:141–207.

————, 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Mar. Pet. Geo.,* 5:224–236.

Radke, M., Willsch, H., and Welte, D., 1980. Preparative hydrocarbon group type determination by automated medium pressure liquid chromatography. *Anal. Chem.,* 52:406–411.

————, 1982. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochim. Cosmochim. Acta,* 46:1–10.

Schou, L., and Myhr, M.B., 1988. Sulfur aromatic compounds as maturity parameters. *Org. Geochem.,* 13:61–66.

Shipboard Scientific Party, 1995. Site 940. *In* Flood, R.D., Piper, D.J.W., Klaus, A., et al., *Proc. ODP. Init. Repts.,* 155: College Station, TX (Ocean Drilling Program), 463–501.

Simoneit, B.R.T., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. *Geochim. Cosmochim. Acta,* 43:463–476.

Soclo, H., 1986. Étude de la distribution des hydrocarbures aromatiques polycycliques dans les sédiments marins récents, identification des sources [Ph. D. dissert.]. Bordeaux I Univ., Talence, France.

Tissier, M.J., 1981. Les hydrocarbures aromatiques polycycliques dans l'environnement marin. Distribution, origine et transfert [Ph. D. dissert.]. P. et M. Curie Univ., Paris, France.

Tissier, M.J., and Dastillung, M., 1978. Inventaire et dynamique des lipides à l'interface eau de mer-sédiment. *In* Combaz, A., and Pelet, R., (Eds.), *Géochimie organique des sédiments marins profonds (Orgon II)—Atlantique, Nord-Est Brésil:* Paris (Editions of CNRS), 275–283.

Trendel, J.M., Lohman, F., Kintzinger, J.P., and Albrecht, P., 1989. Identification of des-A-triterpenoid hydrocarbons occurring in surface sediments. *Tetrahedron*, 45:4457–4470.

Venkatesan, M.I., 1988. Occurrence and possible sources of perylene in marine sediments—a review. *Mar. Chem.,* 25:1–27.

Wakeham, S.G., Schaffner, C., and Giger, W., 1980a. Polycyclic aromatic hydrocarbons in recent lake sediments. I—Compounds having anthropogenic origin. *Geochim. Cosmochim. Acta,* 44:403–413.

Wakeham, S.G., Schaffner, C., and Giger, W., 1980b. Polycyclic aromatic hydrocarbons in recent lake sediments. II—Compounds derived from biogenic precursors during early diagenesis. *Geochim. Cosmochim. Acta,* 44:415–429.

Wise, S.A., Schantz, M.M., Benner, B.A., Hays, M.J., and Schiller, S.B., 1995. Certification of polycyclic aromatic hydrocarbons in a marine sediment standard reference material. *Anal. Chem.,* 67:1171–1178.

Youngblood, W.W., and Blumer, M., 1975. Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. *Geochim. Cosmochim. Acta,* 39:1303–1314.

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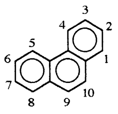
Date of acceptance: 11 July 1996
Ms 155SR-251

APPENDIX

Chemical Structures Cited in Text



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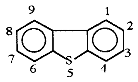
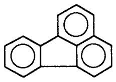


Dibenzothiophene (DBT)



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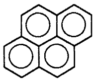

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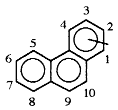

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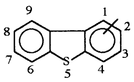
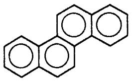


Methyldibenzothiophene (MDBT)



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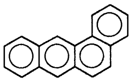
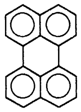
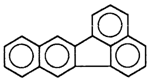


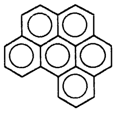
Benz(a)anthracene (BaA)



Perylene (Per)



Benzo(k)fluoranthene (BkF)



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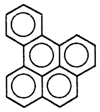
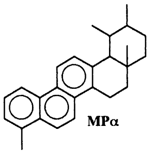


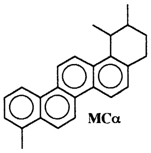
Benzo(e)pyrene (BeP)

DERIVATIVES OF THE α-AMYRIN



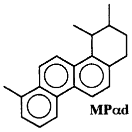
MPα

1,2,4a,9-Tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene



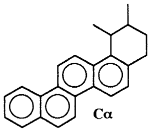
MCα

1,2,9-Trimethyl-1,2,3,4-tetrahydropicene



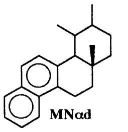
MPαd

3,4,7-Trimethyl-1,2,3,4-tetrahydrochrysene



Cα

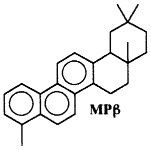
1,2-Dimethyl-1,2,3,4-tetrahydropicene



MNαd

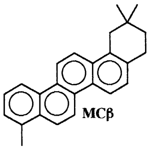
3,4,12a-Trimethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene

DERIVATIVES OF THE β-AMYRIN



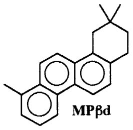
MPβ

2,2,4a,9-Tetramethyl-1,2,3,4,4a,5,6,14b-octahydropicene



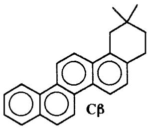
MCβ

2,2,9-Trimethyl-1,2,3,4-tetrahydropicene



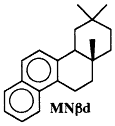
MPβd

2,2,9-Trimethyl-1,2,3,4-tetrahydropicene



Cβ

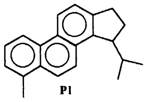
2,2-Dimethyl-1,2,3,4-tetrahydropicene



MNβd

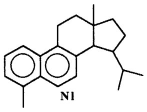
3,3,12a-Trimethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene

DERIVATIVES OF LUPEOL



Pl

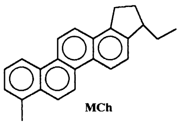
1-Methyl-10'-isopropyl-7,8-cyclopenteno-phenanthrene



Nl

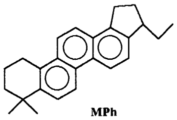
1-Methyl-10'-isopropyl-7,8-cyclopenteno-5,6,7,8-tetrahydrophenanthrene

DERIVATIVES OF HOPANES



MCh

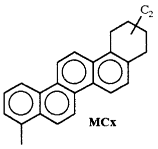
7-Methyl-3'-ethyl-1,2-cyclopenteno-chrysene



MPh

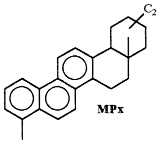
7,7-Dimethyl-3'-ethyl-1,2-cyclopenteno-7,8,9,10-tetrahydrochrysene

DERIVATIVES FROM AMYRINS



MCx

Tetrahydrochrysene



MPx

Octahydrochrysene

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