The distribution and quantitation of organonitrogen compounds in crude oils and rock pyrolysates

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Abstract—Organonitrogen compounds are present in varying concentrations in aromatic fractions of various organic-rich geologic samples. Quinolines, benzoquinolines and carbazoles are the most important families of organonitrogen compounds in the aromatic fractions of crude oils and Phosphoria Formation pyrolysates. Aromatic fractions of oils generated from phosphatic shales contain higher concentrations of organonitrogen compounds than those from carbonate source rocks. Artificial maturation experiments on Phosphoria rocks at about 300°C yield high concentrations of quinolines relative to benzoquinolines and carbazoles, while higher temperature experiments yield high concentrations of benzoquinolines and carbazoles relative to quinolines. Organonitrogen compounds are potentially useful as indicators of the depositional environment of source rocks and maturity of crude oils.

Key words—organonitrogen compounds, nitrogen compounds, oils, Phosphoria Formation, thermionic specific detector

INTRODUCTION

The majority of published geochemical studies of organonitrogen compounds in crude oils have been concerned with the structural determination of these compounds (for example, Schmitter and Arpino, 1985). Organonitrogen compounds are of particular interest to the petroleum refining industry due to their effect on catalyst activity and product stability (Albert, 1978). Another incentive for the study of organonitrogen compounds in petroleum products has been their role as potential environmental pollutants (Schmitter and Arpino, 1985). The present study describes variations in a broad range of organonitrogen compounds in aromatic fractions of crude oils and source rock pyrolysates. Some of the geochemical factors important in determining the distribution of organonitrogen compounds in aromatic fractions of crude oils are also discussed. The results of this study suggest that organonitrogen compounds in crude oils are useful as indicators of depositional environments and maturity.

Organonitrogen compounds in crude oils

Organonitrogen compounds, first described in crude oils in the early 1800s (Lochte and Littmann, 1955 and references therein), played an important role in developing the hypothesis of a biogenic origin of crude oil. Treibs (1934) reported the occurrence of porphyrins in crude oils which, based on structural evidence, were thought to be derived from chlorophyll. In the 1930s and 40s a group at the University of Texas described organonitrogen compounds in distillates of a nitrogen-rich Los Angeles Basin (Wilmington) oil (Perrin and Bailey, 1933; Schenck

and Bailey, 1941a, b; Shive *et al.*, 1942). The University of Texas group identified several substituted pyridines (**I**, see Appendix for structures) and quinolines (**II**) in the Wilmington oil on the basis of physical and chemical properties of various derivatives.

In the early 1980's a great deal of work was done at the Laboratoire de Chimie Analytique Physique of École Polytechnique in France, on the identification of organonitrogen compounds in petroleum products. In a study of diaromatic nitrogen bases in crude oils, several alkyl-substituted quinolines were reported by Schmitter *et al.* (1983). In a review of the distributions of quinolines and benzoquinolines (**III–VII**) in crude oils, Schmitter and Arpino (1983) stated that similarities in the distributions of these compounds in oils suggested a common precursor. The nitrogen-rich Boscan crude oil was examined by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) and was found to contain C_{5-10} alkylpyridines and C_{1-9} alkylquinolines in the basic fraction, along with carbazole (**VIII**), C_{1-4} alkylcarbazoles, benzocarbazoles (**IX–XI**) and C_{1-4} alkylbenzocarbazoles in the neutral fraction (Ignatiadis *et al.*, 1985). Alkylated benzo[h]quinolines (**V**) (Schmitter *et al.*, 1982), along with carbazole and methylcarbazoles (Dorbon *et al.*, 1984a) were reported in coker gas oil and crude oils (Dorbon *et al.*, 1984b). Two benzocarbazoles, benzo[c]- and benzo[a]carbazole (**X** and **XI** respectively), were identified in Saudi Arabian crude oils (Dorbon *et al.*, 1982), and alkylated benzocarbazoles were found in both coker gas oils (Dorbon *et al.*, 1984b), and crude oils (Dorbon *et al.*, 1984a). Dibenzo[a,i]-, dibenzo[c,g]- and dibenzo[a,g]carbazole (**XII**, **XIII** and **XIV**

Table 1. Basic data for oils studied

Sample #	Origin	Reservoir	Field	Depth (ft)	API grav.[a]	%S[a]	%N[a]	$\frac{S}{S+R}C_{31}$h[b]	$\frac{S}{S+R}C_{29}$[c]	$\frac{\beta\beta}{\beta\beta+\alpha\alpha}C_{29}$[d]	MP1 1[e]	Pr/nC_{17}	Ph/nC_{18}	CPI
Shale Sourced Oils														
12	Oklahoma, USA	Deese	Sho-Vel Tum	3468	27.0	1.34	0.24	0.58	0.46	0.38	NA	0.49	0.47	0.96
9	Alaska, USA	Kup River	North Slope	6599-619	NA	NA	NA	0.49	0.61	0.28	0.88	0.62	0.42	1.04
39	California, USA	Monterey	Pt.Pedernales	4430-88	NA	NA	NA	0.71	0.60	0.44	0.84	1.76	2.49	1.01
16	California, USA	Puente, Ford	Wilmington	4735	26.1	0.97	0.54	0.57	0.54	0.29	1.06	1.45	0.09	1.10
Carbonate Sourced Oils														
31	UAE	NA	Bu Hasa 2	NA	37.8	0.77	0.03	0.44	0.37	0.49	0.61	0.15	0.22	0.83
2	Qatar	NA	Idd-el-Shargi	NA	32.8	1.99	0.07	0.60	0.48	0.50	0.52	0.18	0.27	0.96
37	Kuwait	Burgan	Sabiriyah	8000	32.1	1.82	0.10	0.62	0.41	0.45	0.71	0.29	0.42	1.00
Terrigenous Sourced Oils														
15	Sumatra	NA	Bekasap	NA	30.8	0.17	0.12	0.60	0.45	0.33	0.76	0.36	0.16	1.06
23	Sumatra	NA	Minas	NA	32.5	0.13	0.10	0.56	NA	NA	0.98	0.40	0.18	1.04
30	Sumatra	NA	Pematang	NA	30.2	0.10	0.16	0.54	0.43	0.41	0.83	0.34	0.15	1.07
29	Sumatra	NA	Musi	1890	NA	NA	NA	0.48	0.68	0.48	0.81	0.61	0.19	1.07

[a] Data obtained from the Bartlesville Project Office Crude Oil Data Bank.

[b] $\frac{22S}{22S+22R}$ $17\alpha(H),21\beta(H)$ C_{31} hopanes measured as peak heights on m/z = 191 chromatograms.

[c] $\frac{20S}{20S+20R}$ $\alpha\alpha\alpha C_{29}$ steranes measured as peak heights on m/z = 217 chromatograms.

[d] $\frac{\alpha\beta\beta}{\alpha\beta\beta+\alpha\alpha\alpha}$ (20R+20S) C_{29} steranes measured as peak heights on m/z = 217 chromatograms.

[e] As defined by Radke et al., 1982.

respectively), along with their methyl and dimethyl derivatives were identified in crude oils (Dorbon et al., 1984a). The studies mentioned above involved fractionation of the petroleum into basic, neutral and acidic fractions. Results reported in the present study are obtained directly from aromatic fractions of crude oils and Phosphoria pyrolysates isolated by column or high performance liquid chromatography.

EXPERIMENTAL

Sample preparation

A number of oils (Table 1) were obtained from various sources and individual fractions were isolated in the following manner. The asphaltenes were removed from the crude oil by precipitation from n-pentane. The deasphaltened oils were fractionated by silica/alumina column chromatography into saturate, monoaromatic, di- and tri-aromatic and polar (NSO) fractions by elution with pentane, cyclohexane, toluene and methanol, respectively.

Artificial maturation of Phosphoria Formation rock

Artificial maturation experiments were carried out at the United States Geological Survey on a number of source rocks, including the Phosphoria Formation. Powdered rock was heated isothermally in a steel bomb at twelve temperatures ranging from 150 to 425°C for 30 days. A small amount of water, amounting to 10% of the weight of the rock, was added prior to heating. It should be noted that water was not present in quantities sufficient to cover the rock powder with liquid water during the experiment. The residues were removed from the bombs after the 30 day heating period and extracted with a mixture of chloroform/methanol (1:1). The extracts were deasphaltened as described for the oils and fractionated into saturate, aromatic and polar fractions using high performance liquid chromatography.

Gas chromatography–thermionic specific detector (GC–TSD)

The gas chromatograph used in this study was a Varian 3300 GC equipped with a TSD and a flame ionization detector (FID). Splitless injection was used and the He flow rate was 1.8 ml/min. The fused silica capillary column (30 m × 0.32 mm i.d.) was coated with a 0.25 μm film of DB-WAX (J & W Scientific). An effluent splitter was attached to the column to permit simultaneous acquisition of data from both detectors.

The TSD is a selective detector for nitrogen compounds and has a high response for nitrogen-containing compounds compared to hydrocarbons. The Varian TSD used in this study was flameless and employed an electrically heated bead coated with an alkali metal salt (Rb_2SO_4) operating in a hydrogen-air atmosphere. The effluent stream from the chromatographic column is decomposed in a layer of radicals surrounding the heated bead by a surface

Table 2. Response factors for the organonitrogen compounds in the test mixture in units of thousands of area counts per nanogram of compounds

Compound	Response Factor
Pyridine	71.0
Quinoline	46.0
8-Methylquinoline	42.5
2,6-Dimethylquinoline	34.6
2,4-Dimethylquinoline	35.8
Benzoquinoline	31.8
Carbazole	29.4

ionization mechanism. Nitrogen compounds decompose in this environment to form the highly electronegative products (CN^- and NO_2) which are detected (Dressler, 1986). Hydrocarbons do not produce electronegative products upon decomposition and therefore, are not detected.

Calibration of the TSD for the quantitative determination of organonitrogen compounds

A mixture of seven organonitrogen compounds (see Table 2) was prepared in concentrations ranging from 0.008 to 450 ng/ml and analyzed using the gas chromatograph equipped with the TSD. Calibration curves were drawn for each compound in the mixture and all were found to be linear with response factors (slope of the calibration curve) between 29,400 and 71,000 area counts per nanogram solute (Table 2).

Quantitation of the organonitrogen compounds in the samples (aromatic fractions from crude oils and artificially matured Phosphoria Formation rocks) was accomplished by an internal standard method which required addition of quinoline to the Phosphoria samples and pyridine to the natural oils. Under the chromatographic conditions used quinoline was eluted as a very narrow peak, whereas the pyridine peak exhibited slight tailing. Therefore, measuring areas of quinoline peaks was more accurate than measuring areas for pyridine peaks, making quinoline a more desirable internal standard. Quinoline was not detected in the aromatic fractions of the Phosphoria pyrolysates and was therefore an appropriate internal standard. Pyridine was used as an internal standard in the analysis of the crude oil aromatic fractions because quinoline was present in detectable concentrations in some of these samples. Absolute concentrations of individual organonitrogen compounds in the aromatic fractions of the oils and extracts (Tables 3 and 4) were determined using the GC–TSD data along with data derived from the calibration curves of standard organonitrogen compounds by the following equation:

$$m_{sol} = (R_{std}/R_{sol}) \times (m_{std}/A_{std}) \times A_{sol}$$

m_{sol} = nanograms of solute;
R_{std} = response factor of internal standard (Table 2);
R_{sol} = response factor of solute (Table 2);

Table 3. Concentrations of various organonitrogen compounds in crude oil

Sample #	Origin	Depth (ft)	Reservoir	Field	Quin[a,b]	8MQ	2,6DMQ	2,4DMQ	BnzQ	Carb
Shale Sourced Oils										
12	Oklahoma, USA	3468	Deese	Sho-Vel Tum	0.0	37.1	0.0	0.0	15.8	191.9
9	Alaska, USA	6599-619	Kup River	North Slope	0.0	13.2	0.0	24.1	0.0	55.3
39	California, USA	4430-88	Monterey	Pt.Pedernales	35.0	80.1	0.0	0.0	54.1	1261.0
16	California, USA	4735	Puente, Ford	Wilmington	24.2	34.7	49.2	79.1	125.1	937.9
Carbonate Sourced Oils										
31	UAE	NA	NA	Bu Hasa 2	0.0	0.0	0.0	14.9	0.0	0.0
2	Qatar	NA	NA	Idd-el-Shargi	0.0	36.3	4.3	0.0	5.6	0.0
37	Kuwait	8000	Burgan	Sabiriyah	0.0	1.6	4.5	4.3	1.6	0.0
Terrigenous Sourced Oils										
15	Sumatra	NA	NA	Bekasap	0.0	112.2	0.0	11.9	40.2	159.2
23	Sumatra	NA	NA	Minas	0.0	23.5	0.0	0.0	0.0	21.3
30	Sumatra	NA	NA	Pematang	17.9	216.2	0.0	0.0	41.2	1019.2
29	Sumatra	1890	NA	Musi	4.8	12.0	6.3	139.4	53.4	20.1

[a] Concentrations in parts per million.

[b] Abbreviations are as follow: Quin = Quinoline, 8MQ = 8-Methylquinoline, 2,6DMQ = 2,6-dimethylquinoline, 2,4DMQ = 2,4-dimethylquinoline, BnzQ = Benzoquinoline, and Carb = carbazole.

m_{std} = nanograms of internal standard (known);

A_{std} = area counts under the peak representing the internal standard (from GC–TSD data);

A_{sol} = area counts under the peak representing the solute (from GC–TSD data).

Note: "solute" is the compound of known identity and unknown concentration.

Gas chromatography–mass spectrometry (GC–MS)

GC–MS was performed using a Finnigan MAT TSQ70 with a capillary column identical to that used in the Varian 3300 GC. The mass spectrometer was operated in multiple ion detection (MID) and full scan modes with an electron energy of -70 eV and a transfer line temperature of 300°C.

RESULTS

GC–MS was performed in both the full scan and MID modes on aromatic fractions of two pyrolysates to identify the organonitrogen compounds present. Samples were chosen which, on the basis of their GC–TSD analyses, contained high concentrations of organonitrogen compounds. Ionization of organonitrogen compounds yields large percentages of molecular ions (Schmitter, 1983) permitting their examination in the MID mode by monitoring the ions corresponding to their molecular weight. The full scan mode was used to obtain mass spectra of unknown organonitrogen compounds which, whenever possible, were compared to mass spectra of standard compounds.

Quinolines

Quinolines were present in the aromatic fraction isolated from the extract of a Phosphoria Formation rock heated at 333°C for 30 days. These compounds were examined by MID, full scan GC–MS and coinjection with authentic standards. In the MID mode, a series of ions corresponding to the molecular ions of alkyl-substituted quinolines (up to C_{10}) were monitored (Fig. 1). The pattern of peaks suggests a series of alkyl-substituted quinolines. The peaks labeled A–F in Fig. 1 coelute with quinoline, 8-methylquinoline, 2-methylquinoline, 6-methylquinoline, 2,6-dimethylquinoline and 2,4-dimethylquinoline, respectively.

Full scan mass spectra supported the identification inferred by MID and coinjection studies. The mass spectrum labeled "standard quinoline" in Fig. 2 has a base peak at $m/z = 129$, which is the molecular weight of quinoline, and a major fragment at $m/z = 102$, corresponding to the loss of CHN fragment ($m/z = 27$) from the molecular ion. The spectrum of the component which coelutes with quinoline (labeled "PEAK A" in Fig. 2) in an aromatic fraction of a Phosphoria pyrolysate contains ions at $m/z = 129$, and 102. Due to the low concentration of this component, several fragment ions with masses above $m/z = 129$ are present in the spectrum. The

results of coinjection of standard compounds and examination of mass spectra suggest that in addition to quinoline, the sample contains a series of alkyl-substituted quinolines.

Benzoquinolines

The mass chromatograms obtained by monitoring the molecular ions of benzoquinoline and a series of alkyl-substituted benzoquinolines (C_1–C_2) in the aromatic fraction of an artificial maturation experiment on Phosphoria Formation rock heated at 375°C are shown in Fig. 3. This sample was chosen due to its high concentration of benzoquinolines, as indicated by GC–TSD analysis. The spectrum of standard benzoquinoline (Fig. 4) contains a base peak at $m/z = 179$, which is the molecular ion and a fragment ($m/z = 151$) which represents a loss of H + CHN ($m/z = 28$). The spectrum of a component ("A" in Figs 3 and 4) which coelutes with standard benzoquinoline is similar to the spectrum of the authentic standard, apart from the absence of the M-28 fragment. The spectrum of the component producing peak "B" (Fig. 4) has a base peak corresponding to the molecular ion of methylbenzoquinoline ($m/z = 193$) and an important fragment ($m/z = 165$) representing a loss of $m/z = 28$ and is similar to published spectra for methylbenzoquinoline (Schmitter, 1983). Mass spectrometry and coinjection studies show that this fraction contains benzoquinoline and by extrapolation it can be proposed that higher alkyl-substituted benzoquinolines are also present.

Carbazoles

Mass chromatograms obtained by monitoring the molecular ions for alkyl-substituted carbazoles show a series of these compounds (Fig. 5). The peak labeled "A" in Fig. 5 coelutes with, and yields a mass spectrum similar to that of carbazole (Fig. 6). Several of the peaks thought to represent alkyl-substituted carbazoles elute near, or prior to the carbazole peak. This observation can be explained by examination of boiling points of pyrroles. Carbazole is dibenzo-substituted pyrrole, and is thus expected to behave in a similar manner to pyrrole with respect to boiling points of its methyl derivatives. A methyl group attached to the nitrogen atom of the pyrrole ring lowers the boiling point relative to the parent compound, and other methyl-substituted pyrroles (Katritzky, 1985). The hydrogen attached to the nitrogen in the unsubstituted pyrrole ring is capable of hydrogen bonding while the N-methyl derivative cannot hydrogen bond and therefore has a lower boiling point. On the basis of boiling points, the component producing peak "B" is thus tentatively identified as N-methylcarbazole. A spectrum of this component (peak "B" in Fig. 6), contains the expected $m/z = 181$ base peak along with a fragment ($m/z = 152$) which may represent a loss of $m/z = 29$ (H + H + CHN). These data further support the suggestion that peak
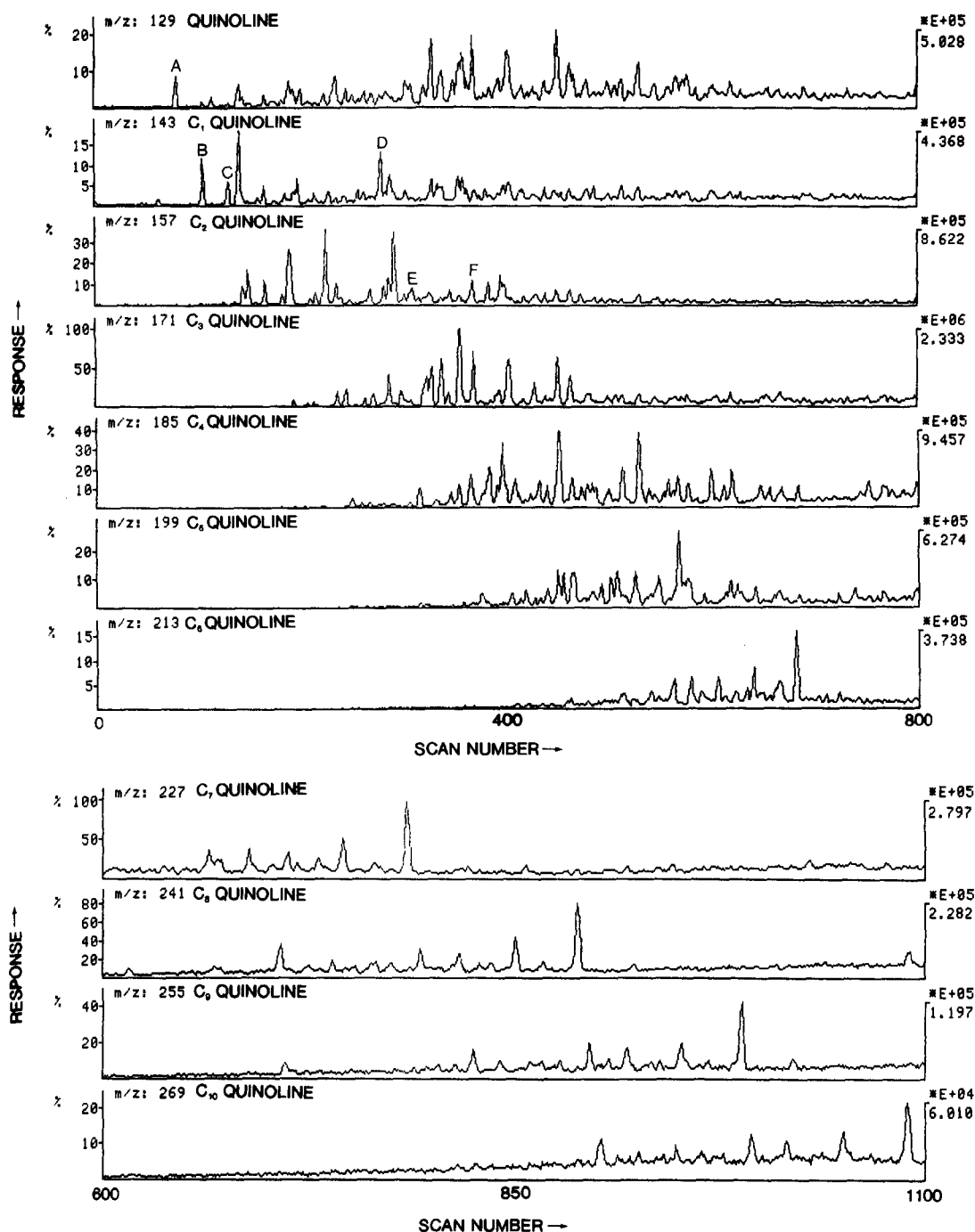
Fig. 1. Mass chromatograms obtained by monitoring the molecular ions for quinolines and various alkylated quinolines. Coinjections support the following peak identifications: A = quinoline; B = 8-methylquinoline; C = 2-methylquinoline; D = 6-methylquinoline; E = 2,6-dimethlyquinoline; F = 2,4-dimethylquinoline. Note that the bottom chromatograms have a different scale than those on top.

"B" is produced by the presence of N-methylcarbazole.

GC–TSD of crude oils

Several of the oils (#12, 9, 39 and 16) examined in this study are from geologic provinces known to have generated nitrogen-rich oils from phosphatic shales (Powell et al., 1975). Aromatic fractions of the four oils from phosphate-rich source rocks contain high concentration of organonitrogens compounds (Fig. 7 and Table 3).

The aromatic fractions of three oils (#31, 2 and 37) from the Persian Gulf area were examined for organonitrogen compounds. Most of the crude oils in
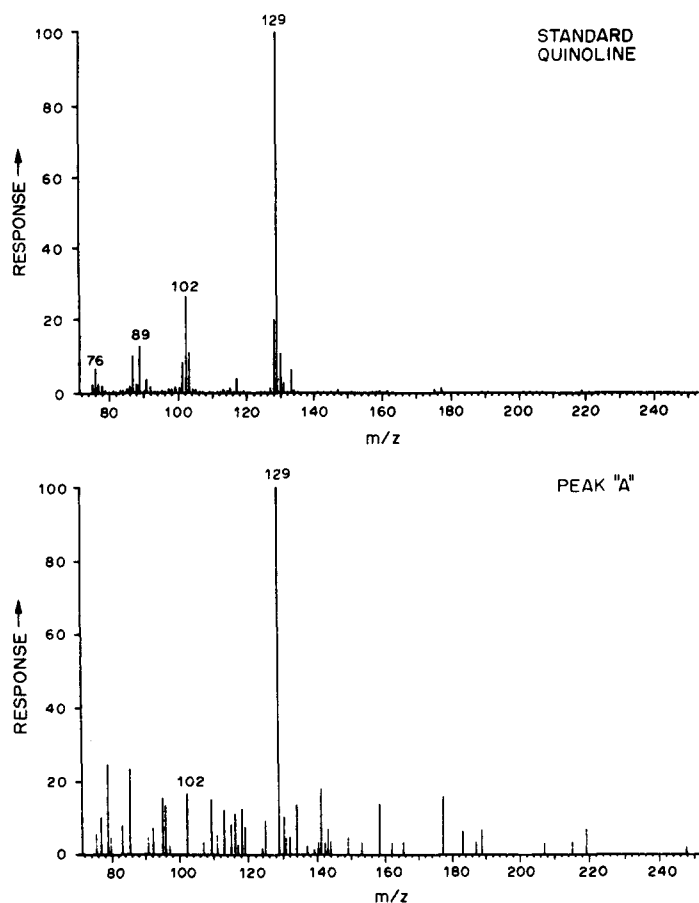
Fig. 2. Full scan mass spectra of standard quinoline and of peak "A" (Fig. 1), which coelutes with quinoline.
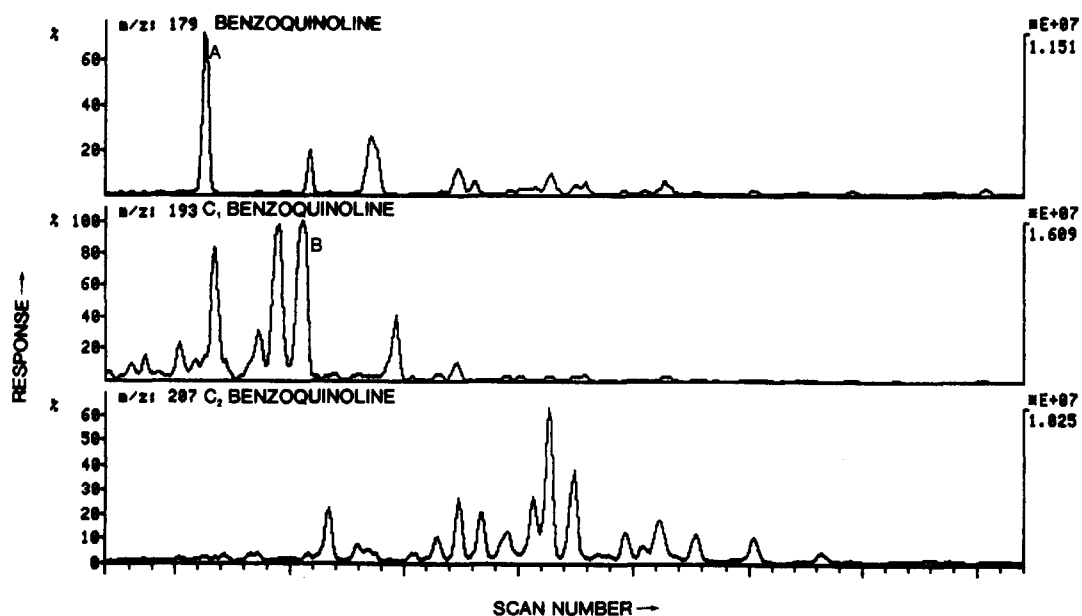

Fig. 3. Mass chromatograms obtained by monitoring the molecular ions for benzoquinoline and various alkylated benzoquinolines. Coinjections support the following peak identifications: A = benzoquinoline; B = methylbenzoquinoline.
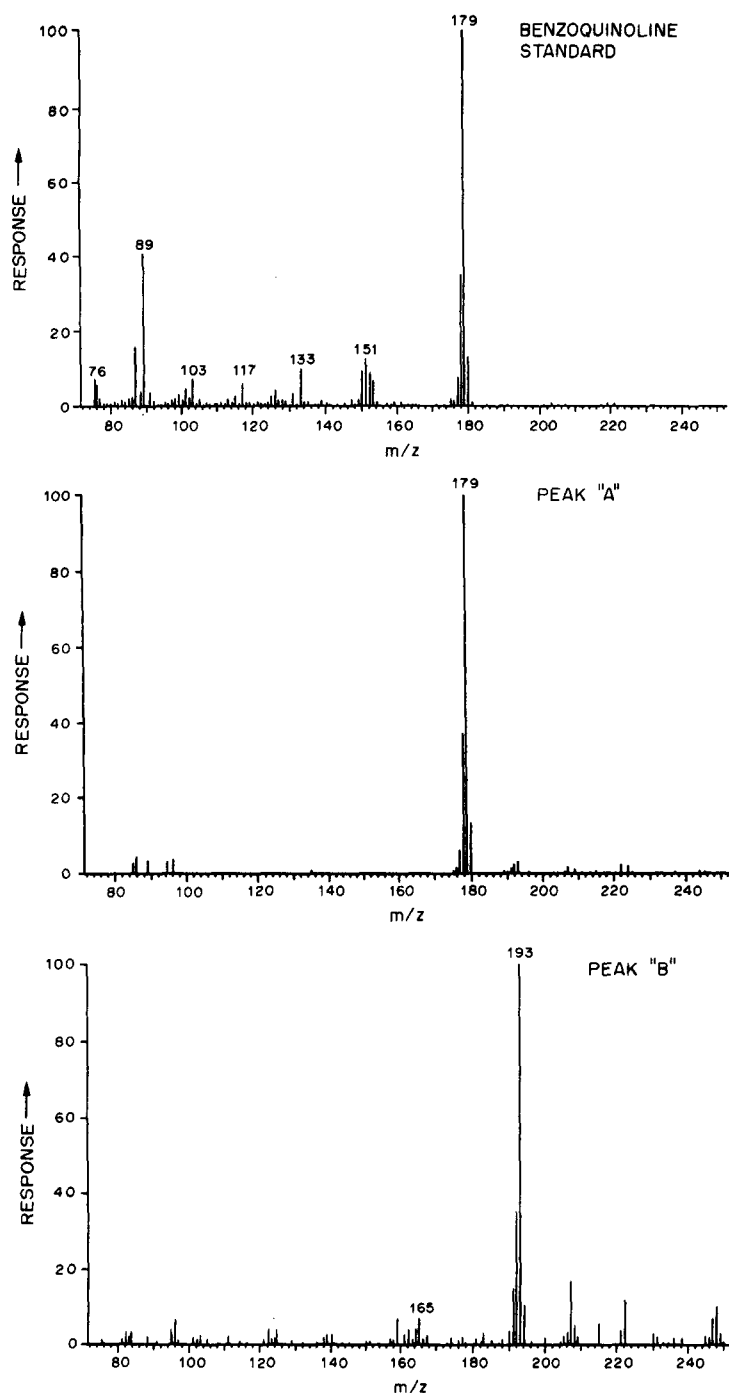
Fig. 4. Full scan mass spectra of standard benzoquinoline and of peak "A" (Fig. 3), which coelutes with
benzoquinoline and peak "B" which is thought to represent methylbenzoquinoline.

the Persian Gulf area are thought to have been
generated from carbonate source rocks deposited
during the lower Jurassic transgression (North,
1985). The GC–TSD traces of the three Persian Gulf
oils reveal that they contain small concentrations
of alkylquinolines and no detectable carbazole or
alkylcarbazoles (Fig. 8). Carbonate-sourced oils
tend to have low concentrations of organonitrogen
compounds as illustrated by Persian Gulf oils
(Table 3).

Oils from Central Sumatra are thought to be
generated from nonmarine source rocks which con-
tain type III organic matter (Moldowan et al., 1985).
Several oils from central Sumatra (#15, 23, 30 and
29) were found to contain varying amounts of
organonitrogen compounds (Fig. 9 and Table 3). This
variation within the oils, all of which are generated
from type III material, indicates that the distribution
of organonitrogen compounds is affected by factors
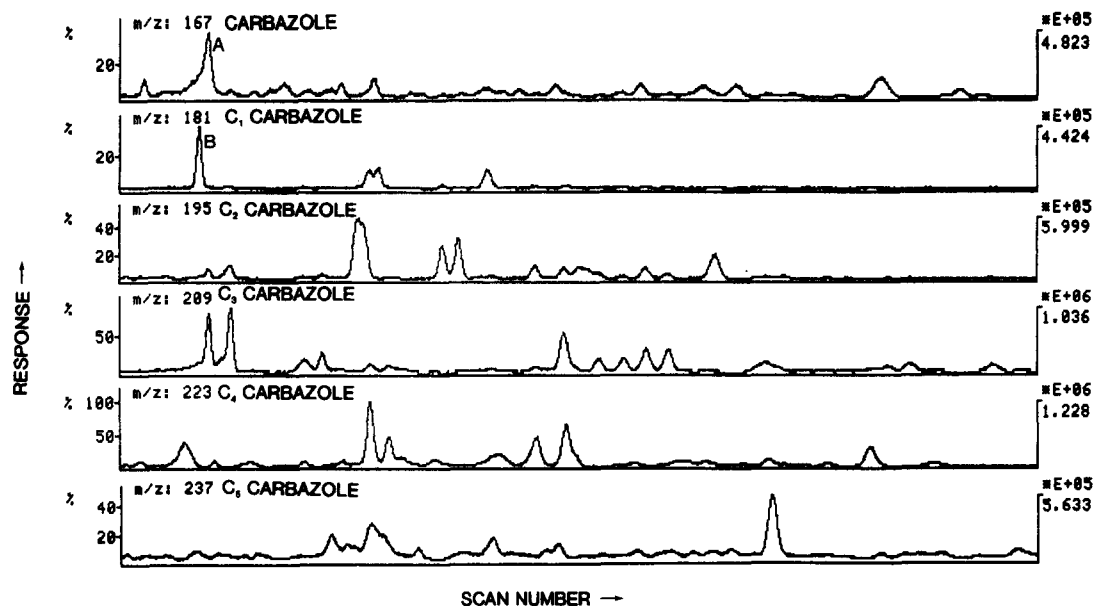other than source materials.

Fig. 5. Mass chromatograms obtained by monitoring the molecular ion for carbazole and various alkylated carbazoles. Coinjections show that A = carbazole, boiling point data indicate that B = N-methylcarbazole.

Examination of Figs 7–9 shows that oils generated from lithologically different source rocks have different distributions of organonitrogen compounds in their aromatic fractions. Aromatic fractions of oils sourced from phosphatic shales contain high concentrations of organonitrogen compounds relative to ,22 aromatic fractions of oils generated from limestones (Table 3).

Artificial maturation of Phosphoria retort shale

Rock-Eval and molecular data, to be published elsewhere, show that pyrolysis experiments performed at the United States Geological Survey serve as a reasonable model for natural maturation of the Phosphoria Formation (L. Price and L. Wenger personal communication). The extractable products produced by these experiments were examined to describe the changes in the distribution of organonitrogen compounds during maturation.

Table 4. Concentration of organonitrogen compounds in Phosphoria pyrolysates

Heating Temp. (°C)	2,4DMQ[a]	BnzQ	Carb
275	0.69	0.72	1.16
300	3.08	2.28	3.40
316	2.84	2.75	3.70
333	2.18	3.00	4.73
350	3.16	7.11	13.25
375	0.92	35.14	231.25
400	0.73	12.58	215.13

[a]Abbreviations are as follow: 2,4DMQ - 2,4-dimethylquinoline, BnzQ - Benzoquinoline and Carb - Carbazole.

Quantitative analysis using GC–TSD of the aromatic fractions from extractable artificial maturation products of Phosphoria rock at various temperatures (Fig. 10) shows that benzoquinoline (peak #3) and carbazole (peak #4) are predominant at higher temperatures while quinoline (peak #1) and 2-methylquinoline (peak #2) are present in higher concentrations at lower temperatures. Specifically, in the aromatic fraction, absolute concentrations of carbazole and benzoquinoline increase as maturation temperature increases, while the concentration of 2,4-dimethylquinoline decreases with increasing temperature (Table 4).

DISCUSSION

Origins of organonitrogen compounds in crude oils

Three possible sources for the pyridine ring in crude oils have been proposed by Schmitter and Arpino (1983): degradation of natural products already containing the pyridine ring (alkaloids); modification of other ring systems such as pyrrole; and cyclization and incorporation of nitrogen into acyclic compounds by reaction of ammonia with 1,5 dioxo groups (XV). A number of plant alkaloids (for example XVI) contain the bicyclic quinoline structure and yield alkylquinolines upon degradation (Brody and Ruby, 1960). Alkaloids are present only in higher plants (Pelletier, 1970) and therefore, can only be invoked as precursors of organonitrogen compounds in oils generated from higher plant material.

Pyrrole structures are present in porphyrins and related biologic pigments. Chemical and biological degradation of porphyrins produces substituted pyrroles (Falk, 1964) and chains of linked pyrrole rings (Schmid and McDonagh, 1979). Pyrrole rings
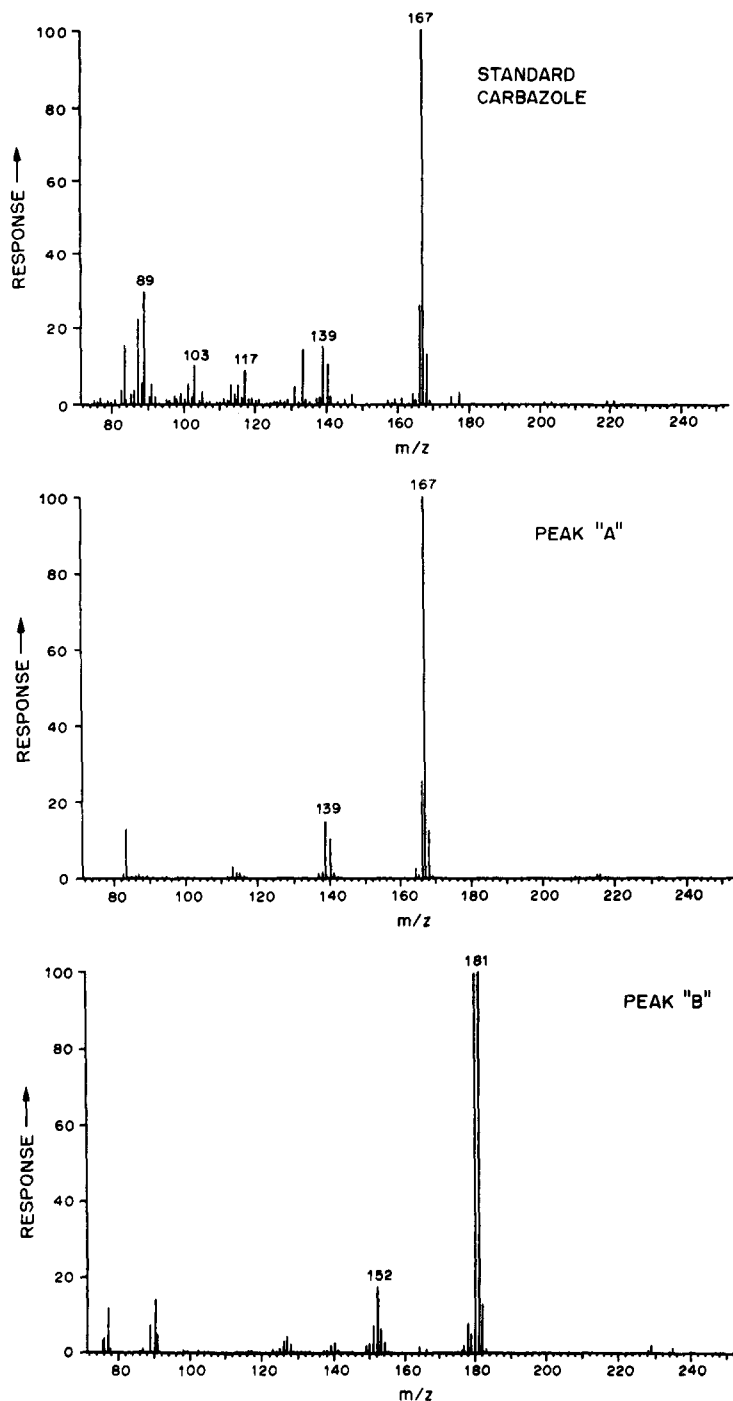
Fig. 6. Full scan mass spectra of standard carbazole and of peak "A" (Fig. 5) which coelutes with carbazole.

can be expanded to form six-member pyridine rings in synthetic and biosynthetic reactions (Brody and Ruby, 1960). Ring closure by addition of ammonia to 1,5-dioxo-acyclic compounds is another well-known synthetic reaction capable of producing pyridine rings (Brody and Ruby, 1960). Ring expansion and ring closure are both thought to be viable mechanisms for the formation of pyridine rings under geologic conditions (Schmitter and Arpino, 1983).

Most of the peptide groups in Recent sediments are degraded during early diagenesis (Tissot and Welte, 1984) and nitrogen in kerogen occurs primarily as heterocyclic structures (Behar and Vandenbroucke, 1987). A possible mechanism for preservation of nitrogen involves incorporation of the peptide nitrogen into the kerogen matrix. The nitrogen incorporated into the kerogen matrix would be released upon catagenesis as aromatic heterocyclic compounds.
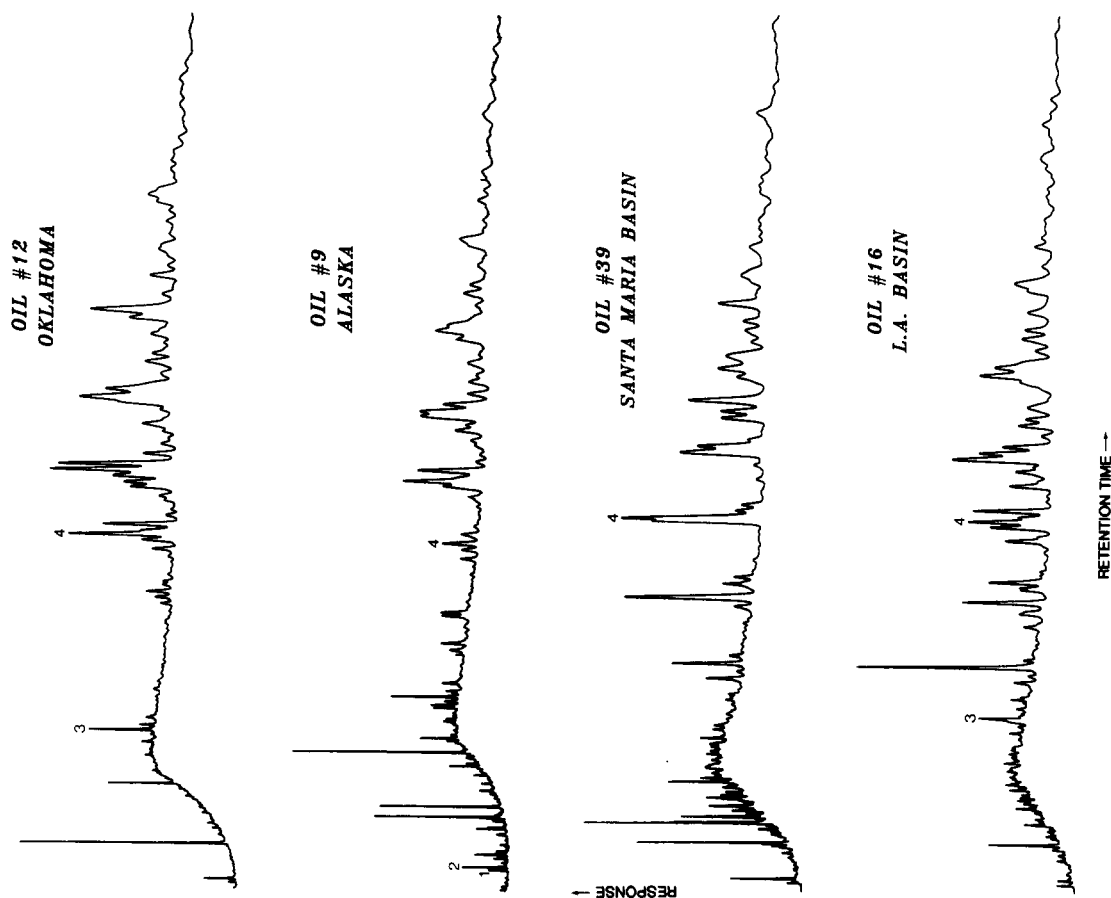
Fig. 7. TSD chromatograms of aromatic fractions of four oils generated from phosphatic shales. Peak identifications are as follows: 1 = quinoline; 2 = 8-methylquinoline; 3 = benzoquinoline; 4 = Carbazole.

Fig. 8. TSD chromatograms of aromatic fractions of four oils from the Persian Gulf. For peak identifications see Fig. 7 caption.
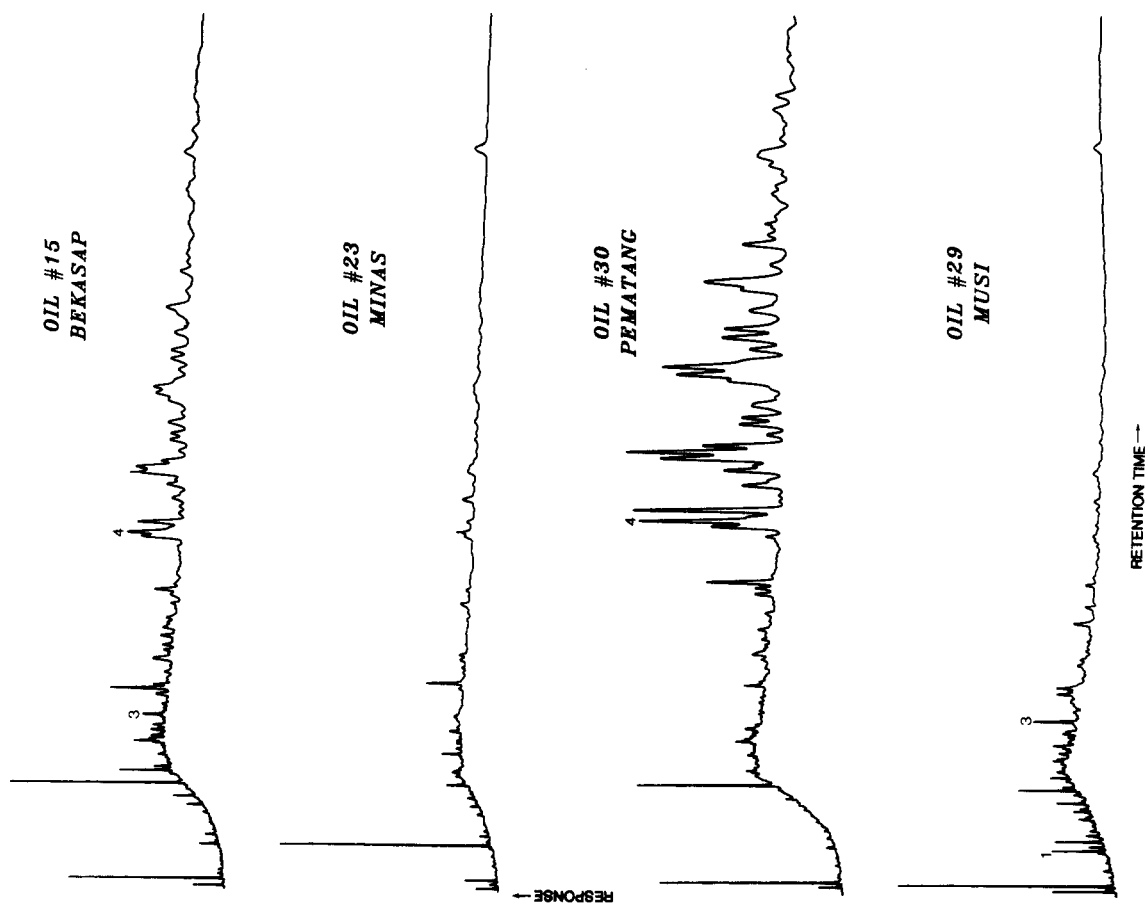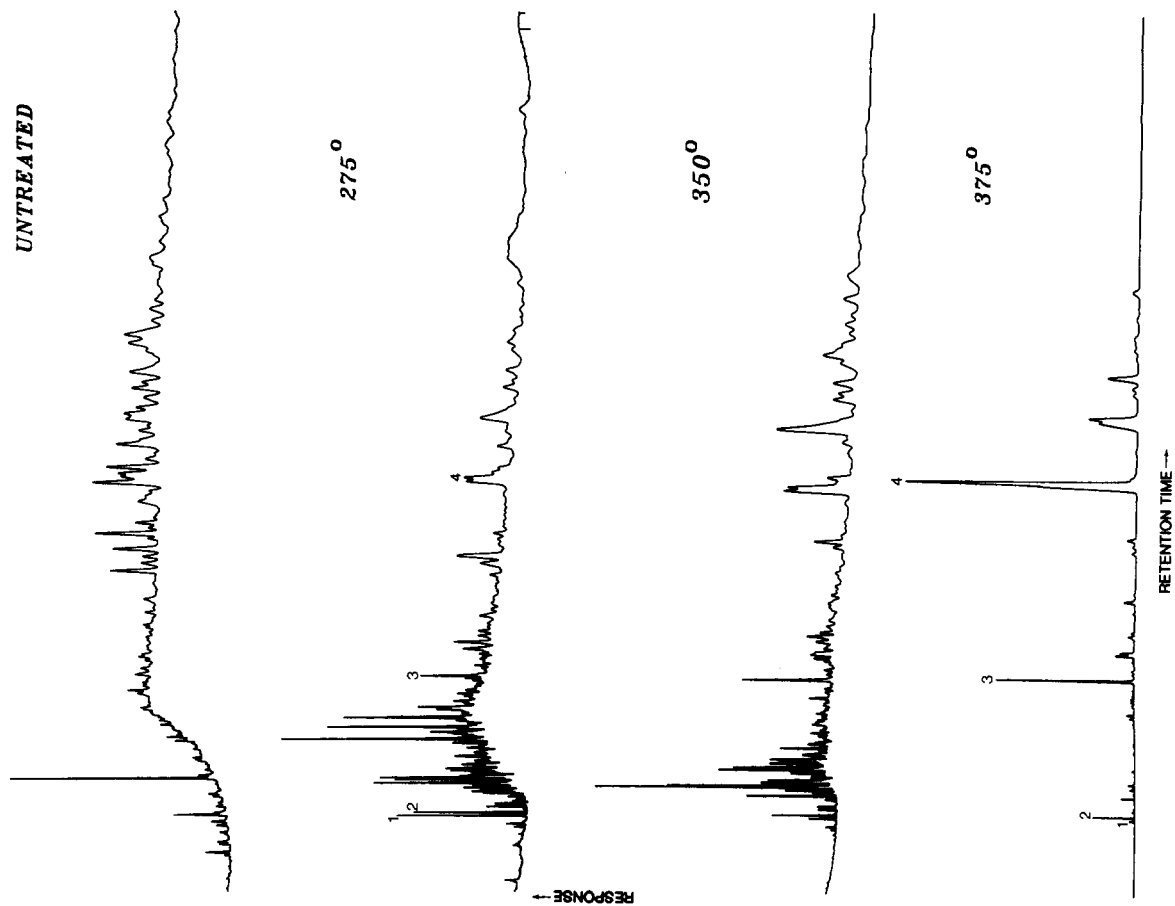
UNTREATED

275°

350°

375°

RETENTION TIME →

Fig. 10. TSD chromatograms of aromatic fractions isolated from Phosphoria Formation rocks heated at the indicated temperatures. For peak identifications see Fig. 7 caption.

OIL #15
BEKASAP

OIL #23
MINAS

OIL #30
PEMATANG

OIL #29
MUSI

RETENTION TIME →

Fig. 9. TSD chromatograms of aromatic fractions of three oils from the central Sumatra. For peak identifications see Fig. 7 caption.

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Factors affecting the distribution of organonitrogen compounds

It has been shown that most of the nitrogen preserved in Recent sediments is present in the clay fraction (Pillon *et al.*, 1986). Preferential preservation of nitrogen compounds in fine-grained sediments suggests that shale-sourced oils would have higher nitrogen contents than oils from clay-poor source rocks. The data presented in this study confirm that the lithology of the source rock has an effect on the organonitrogen compound distribution in the aromatic fractions of various oils. Oils generated from phosphatic shales have higher concentrations of organonitrogen compounds than oils generated from limestones (Table 1). An association between high nitrogen crude oils and phosphatic source rocks has been observed in several oil producing areas including the Los Angeles Basin and the Prudhoe Bay Field (Powell *et al.*, 1975). Recent phosphate-rich sediments are being deposited in upwelling zones which support high biological productivity (Maughan, 1984). Since nitrogen-rich oils are known to be generated from phosphatic shales they can also be correlated with upwelling zones. In areas of high biological productivity high concentrations of nitrogen compounds are delivered to the sediment in the form of peptides or other biologically produced nitrogen compounds. Clay-sized sediment aids in preservation of nitrogen compounds which can be incorporated into kerogen. Environments in which limestone is being deposited typically contain very low percentages of clay minerals. The nitrogen is not preserved, cannot be incorporated into the kerogen and the resultant nitrogen-poor kerogen generates nitrogen-poor oil.

According to the data shown in Table 1, secondary processes such as maturation and biodegradation cannot account for the differences observed in the distributions of organonitrogen compounds in the oils studies. The maturity parameters (S/S + R C_{31} hopane, S/S + R C_{29} sterane, $\beta\beta/\beta\beta + \alpha\alpha$ C_{29} sterane and MPI 1) do not indicate any significant maturity differences between the carbonate and shale sourced oils examined in the this study. In addition, the central Sumatran oils do not exhibit any broad variation in maturity (Table 1). Therefore the differences observed in the organonitrogen compound distributions of these groups of oils do not appear to be due to maturity variations. The dominance of normal alkanes over isoprenoids, as witnessed by the Pr/C_{17} and Ph/C_{18} ratios (Table 1) suggests that most of the oils examined have not undergone severe biodegradation. Two oils from California (#16 and #39) contain high concentrations of isoprenoids relative to normal alkanes (Table 1), however the organic nitrogen compound distributions for these two oils is similar to that for the other shale-sources oils (#12 and #9). Therefore, while it is difficult to compare oils from different geologic provinces, maturity differences or biodegradation cannot account for the differences observed in the distributions of organonitrogen compunds in the oils in this study.

Oils from central Sumatra contain widely varying concentrations of organonitrogen compounds. As has already been discussed, differences in the distributions of organonitrogen compounds in these oils cannot be due to variations in maturity. Migration through clay-rich rocks is thought to be capable of altering the nitrogen content of crude oils (Charlesworth, 1986). Hence, migration provides a possible explanation for varying concentrations of organonitrogen compounds in these oils. Examination of Recent Mahakam Delta sediments shows that nitrogen and clay contents are proportional (Pillon *et al.*, 1986). This suggests that different clay and therefore, nitrogen contents of source rocks may be partially responsible for the varying organonitrogen compound concentrations in central Sumatran crude oils.

The Phosphoria Formation as a model of a nitrogen rich source rock

The Permian Phosphoria Formation occurs in Montana, Idaho, Wyoming and Utah and is thought to be the source rock for most of the oil and gas in Paleozoic reservoirs of the Big Horn Basin (Claypool *et al.*, 1978). The Phosphoria Formation has been shown to generate a naphthenic, asphaltic extract at relatively low thermal maturity and the phosphate-rich members are thought to produce high-nitrogen oils (Claypool *et al.*, 1978). Early generation of hydrocarbons, along with high sulfur content suggests that the Phosphoria kerogen can be classified as a Type II-S kerogen (Orr, 1986). Other high-nitrogen oils generated from phosphatic shales (#12, #9, #39 and #16) are expected to have an organonitrogen compound distribution similar to the Phosphoria Formation pyrolysates. Comparison of Figures 7 and 10 indicates that the TSD chromatograms of aromatic fractions isolated from phosphatic shale-sourced oils are similar to TSD chromatograms of the aromatic fractions isolated from pyrolysates of the Phosphoria Formation, which were heated at temperatures between 275 and 350°C. Quantitative analysis of the organonitrogen compounds in the aromatic fractions of extracts of the Phosphoria Formation heated at different temperatures shows that quinolines are dominant at lower heating temperatures while at higher temperatures, benzoquinolines and carbazoles are dominant (Fig. 10 and Table 4). At low temperatures, quinolines are generated from the kerogen in higher quantities than benzoquinolines and carbazoles. Benzoquinolines and carbazoles are more stable at higher temperatures, leaving the benzoquinolines and carbazoles as the predominant organonitrogen compounds in the aromatic fraction.

CONCLUSIONS

—Three classes of organonitrogen compounds, quinolines, benzoquinolines and carbazoles are found in aromatic fractions of crude oils and Phosphoria pyrolysates.

—Oils sourced from phosphatic shales contain relatively higher concentrations of organonitrogen compounds in their aromatic fractions than oils sourced from limestones.

—The distribution of organonitrogen compounds in Phosphoria pyrolysates is affected by the pyrolysis temperature.

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APPENDIX

Structures of Organonitrogen Compounds

I PYRIDINE

II QUINOLINE

III BENZO[g]QUINOLINE

IV ACRIDINE

V BENZO[h]QUINOLINE

VI BENZO[f]QUINOLINE

VII BENZO[c]QUINOLINE

VIII CARBAZOLE

IX 5 H BENZO[b]CARBAZOLE

X 7 H BENZO[c]CARBAZOLE

XI 11H BENZO[a]CARBAZOLE

XII DIBENZO[a,i]CARBAZOLE

XIII DIBENZO[c,g]CARBAZOLE

XIV DIBENZO[a,g]CARBAZOLE

XV 1,5 DIOXO COMPOUND

XVI CINCHONINE