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Organic facies and maturation of Jurassic/Cretaceous rocks, and possible oil-source rock correlation based on pyrolysis of asphaltenes, Scotian Basin, Canada

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Abstract - This paper establishes source rock characterization and oil-oil and oil-source rock correlations of selected organic-rich shale source rocks and selected light oils and condensates from Jurassic and Cretaceous formations of the Scotian Basin. Multiple source rocks of Kerogen Types IIA (oil-prone), IIA-IIB (oil- and condensate-prone), IIB (condensate and gas prone), III (gas-prone), and IV (nonsource) are identified in various stratigraphic horizons. Vitrinite reflectance and T_{max} data indicate variable maturation histories, in different parts of the basin, which are related to differences in lithology-related heat conductivity and the presence of older sediments closer to areas of rifting. Multiple linear regression and cluster analyses of aromatic hydrocarbon ratios reveal two oil families. Some Kerogen Type IIB rock extracts match many of the light oil and condensates in terms of the aromatic hydrocarbon distributions. A second family of oils could not be correlated with any of the analyzed source rock extracts. Pyrolysis-gas chromatography of asphaltenes from the Cohasset A-52 and Sable Island 3H-58 wells are significantly different in *n*-alkane, aromatics and phenol content. The asphaltene pyrolyzates of samples from Venture B-52 and S. Desbarres 0-76 have a high aromatic content, low content of *n*-alkanes, and high phenol values (S. Desbarres), which is typical of a terrestrial source. They correlate well with one another and also with Sable Island light oil. The N. Triumph G-43 whole rock and extract asphaltene pyrolyzates are dominated by normal hydrocarbons, with aromatic, phenolic and thiophenic compounds in low concentrations suggesting an algal source. Algal type organic matter may have made a contribution to the Cohasset petroleum, as its asphaltene pyrolyzate is also dominated by normal hydrocarbons.

Key words - organic facies, kerogen type, Rock-Eval pyrolysis, maturation, aromatic biomarkers, asphaltene pyrolyzate, Scotian Basin, Canada, condensate

INTRODUCTION

During the past 25 years, there have been 22 significant discoveries of natural gas, condensate, and light oil in Jurassic-Cretaceous reservoirs in the Sable Island area of the Scotian Basin south of Nova Scotia, Canada (Fig. 1). Since 1976, there have been a number of publications concerned with the petroleum geochemistry of the region, including studies on the source rock potential and maturation, oil quality, possible migration avenues, and possible oil-oil and oil-source rock correlation (Bujak et al., 1977; Cassou et al., 1977; Rashid and McAlary, 1977; Powell and Snowdon, 1979; Purcell et al., 1979; Barss et al., 1980; Nantais, 1983; Powell, 1982, 1985). However, the origin of the hydrocarbons still remains controversial.

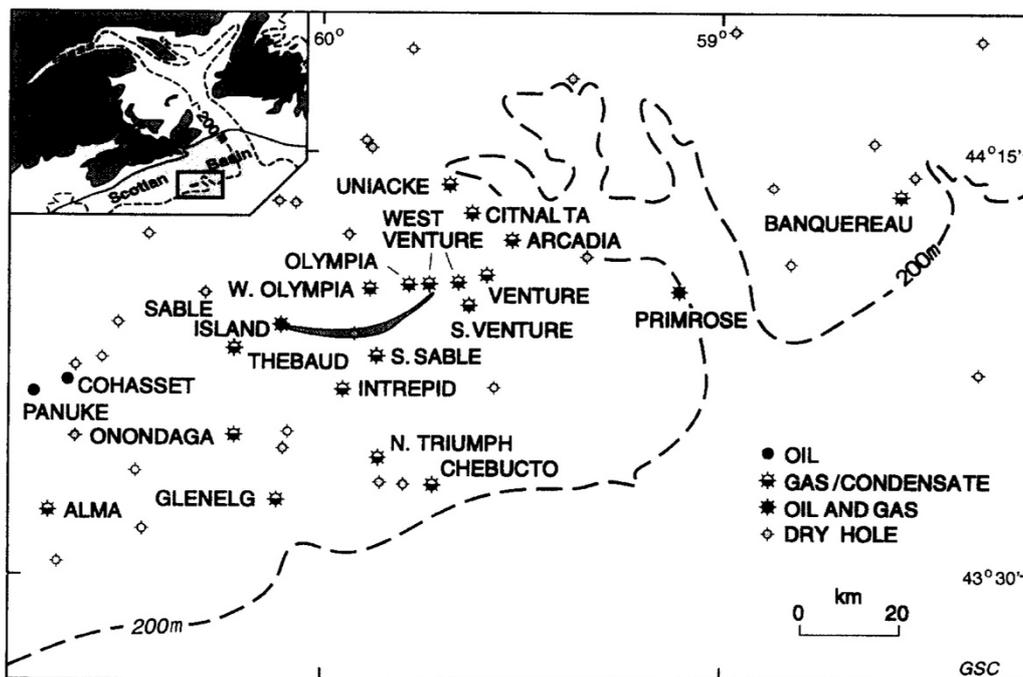


Fig. 1. Location of 22 significant hydrocarbon discoveries, Sable Island area of the Scotian Basin (modified after Wade and MacLean, 1990).

The major unresolved issues on hydrocarbon generation, migration, and entrapment, include: (a) the distribution of source rocks in various stratigraphic intervals; (b) variations in maturity for both source rocks and crude oils and condensates; (c) the relation between hydrocarbon generation and overpressuring; and (d) possible oil-oil and oil-condensate-source rock correlation.

Accordingly, in recent years, systematic studies were initiated which characterized some of the potential source rocks in various stratigraphic intervals, the geochemical properties of selected oils and condensates, and possible oil-oil and oil-source rock correlations (Fig. 2) (Mukhopadhyay and Birk, 1989; Mukhopadhyay, 1989a, b, 1990a, b, 1991; Mukhopadhyay and Wade, 1990; Kruge, 1990, 1991, 1992). This was done through extensive organic petrography, Rock-Eval analyses and from the study of aromatic biomarkers and isotope analyses which established the proportion of oil-, condensate-, and gas-prone source rocks in various formations as well as the possible correlation of oil-oil and oil-source rock pairs. In this paper, some of those unpublished data are summarized and combined with new data on pyrolysis-gas chromatography of selected organic-rich rocks and their asphaltene fractions and with the asphaltene fraction of two selected oils. Of particular interest is the source of the light oil in the Cohasset and Sable Island discoveries and similarities or differences with the condensates in other wells. Studies to delineate the source rocks for these discovered hydrocarbons have concentrated on the general Sable Island area of the Scotian Shelf (Fig. 2).

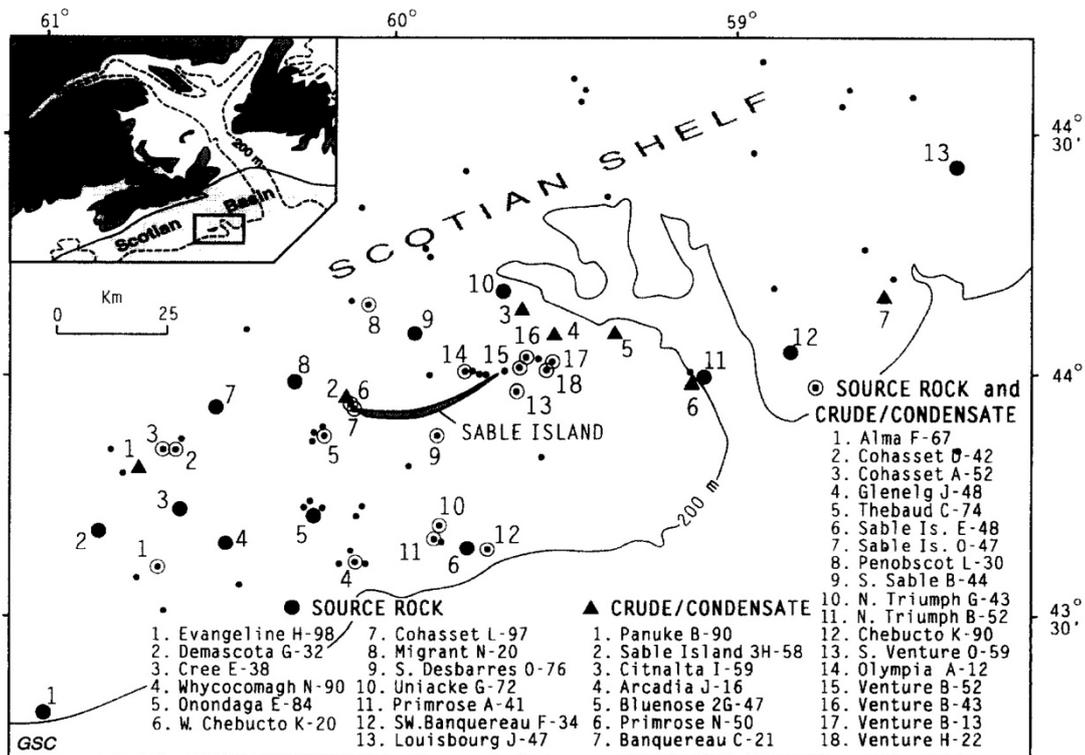


Fig. 2. Index map of Scotian Shelf wells with source rock and/or crude oil/condensate analyses. Small black dots are locations of other wells.

GEOLOGICAL SETTING AND RESERVOIR FORMATION

Geological setting

The Scotian Basin (inset map on Fig. 1), which lies on the continental margin south of Nova Scotia and Newfoundland, consists of a number of interconnected depocentres (subbasins) and a series of flanking, more positive elements. Separating the two is a basement hinge zone (Wade and MacLean, 1990). Twenty-two wells have discovered significant quantities of hydrocarbons in the Scotian Basin. Of these two are light oil, two are oil and gas, and 18 are gas and condensate. All of the discoveries are within 100 km of Sable Island (Fig. 1). Hydrocarbons occur in all formations from the Upper Cretaceous Wyandot to the Upper Jurassic Mic Mac (Fig. 3).

The Scotian Basin developed as a result of the breakup of Pangaea and the separation of North America and Africa during the Early Jurassic. Initial (synrift) fluvial, lacustrine and aeolian sediments comprise the Eurydice Formation (Late Triassic and Early Jurassic, Fig. 3). In the deeper grabens, the Eurydice Formation contains an evaporite facies and is overlain by large thicknesses of Argo Formation salt.

The first post-rift units are the clastic Mohican Formation and a local dolostone facies – the Iroquois Formation. The Mohican is overlain by a variety of continental to marine facies of Middle to Upper Jurassic age. These include the Mohawk (sandstone and shale); the Mic Mac (sandstone, shale and limestone); the Abenaki (carbonate bank); and the Verrill Canyon (basinal shale) formations. Generalized relationships are illustrated in Fig. 3.

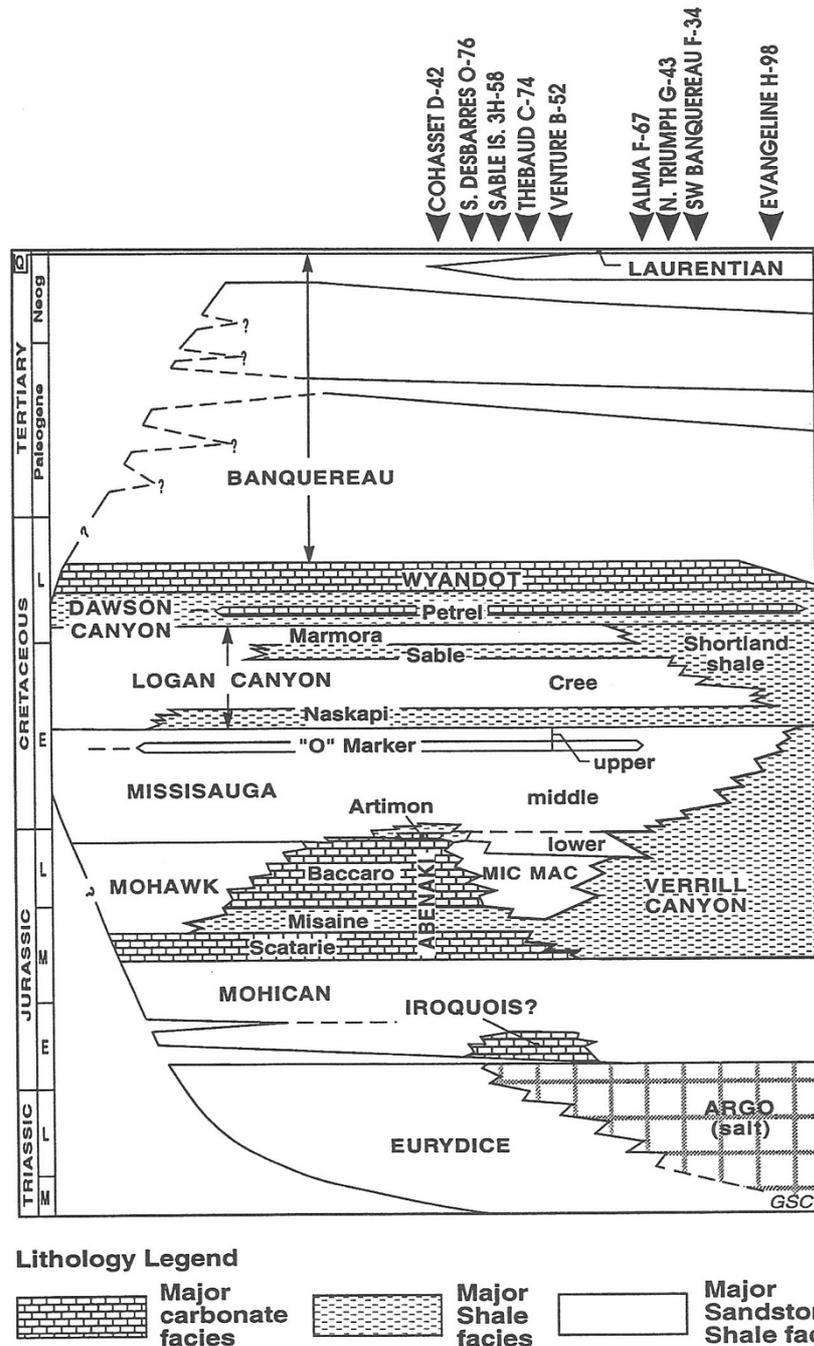


Fig. 3. Stratigraphic column, for the Mesozoic/Cenozoic of the central Scotian Shelf, showing major lithologies and the basin position of selected wells. Names in capitals are formations, other names are formal and informal members.

Lower Cretaceous strata include a generally regressive, (progradational) sandstone and shale sequence, the Mississauga Formation and the transgressive and regressive Logan Canyon Formation. The Verrill Canyon Formation and the Shortland Shale are the time equivalent basinal shales. The Late Cretaceous global rise in sea level resulted in two formations which were deposited in deeper water, the Dawson Canyon shale and the Wyandot chalk. The sands and shales of Tertiary age are included in the Banquereau Formation which completes the stratigraphic succession. Growth faults, common along the

outer shelf result from the accumulation of very thick clastic facies with unstable salt at depth (Fig. 3).

Reservoir formations

The Cohasset and Panuke light oil reservoirs are located approx. 50 km southwest of Sable Island along the edge of the Abenaki carbonate bank. The oil is reservoired in the Logan Canyon and Mississauga formations. The Venture field lies immediately east of Sable Island and South Venture is 5 km to the southeast (Fig. !). The Venture area gas and condensate reservoirs are in a 1500 m thick sequence of deltaic clastics in the upper part of the Mic Mac Formation and the lower member of the overlying Mississauga Formation (Fig. 3).

SAMPLES AND ANALYTICAL METHODS

Samples

A total of about 200 cuttings and core samples from various boreholes were selected for study. The cuttings and core samples from Alma F-67, N. Triumph G-43, and South Desbarres O-76 were thoroughly washed with Sunlight detergent and water because these wells were drilled with an oil-base drilling mud (Mukhopadhyay, 1990c).

Analytical methods

For the determination of kerogen type by organic petrography, three types of sample preparation were used: kerogen smear slide, whole rock polished pellet, and kerogen polished pellet. We used incident and transmitted white light and ultraviolet light excitation. The terminologies used for maceral composition and kerogen type determination are from Stach et al. (1982), Mukhopadhyay et al. (1985), Senftle et al. (1986), Teichmuller (1986), Hutton (1987), and Mukhopadhyay (1989a). Details on source-rock characterization using organic facies are given in Mukhopadhyay and Wade (1990).

Vitrinite reflectance was measured using both whole rock and kerogen pellets and a Zeiss Axioskop microscope with MPM 21 Controller for MPM 03 Photomultiplier. *Rock-Eval pyrolysis* was conducted on selected washed cuttings, hand-picked cuttings, or conventional cores using Rock-Eval II equipment. For details of Rock-Eval instrumentation and evaluation of various parameters, see Espitalié et al. (1985).

Bitumen extraction was performed using Soxhlet apparatus for 24 h with dichloromethane, *Liquid chromatography* was done using a 1:1 silica:alumina column and pentane. pentane + dichloromethane. and methanol as solvents for saturate, aromatics, and heterocompounds respectively.

Pyrolysis-gas chromatography was performed on two Scotian Shelf oils and three well-defined source rock samples selected for this study (Table 1). Raw rock samples and the asphaltenes previously separated from the solvent extracts of the rocks. were analyzed without further preparation. Due to the large amount of bitumen in N. Triumph G-43 source rock, a small aliquot was rinsed with dichloromethane and reanalyzed. The data reported for this sample is that collected after the solvent treatment. No excessive bitumen was detected in Venture B-52 or S. Desbarres O-76 source rocks so these were not rinsed. Cohasset A-52 and Sable Island 3H-58 asphaltenes were received as crude oils and required deasphalting.

An aliquot of each oil was taken up in high purity ("HPLC grade") *n*-pentane and chilled. Each mixture was transferred to a filter flask fitted with a glass microfibre filter disk (Whatman GF/A pre-rinsed with high purity dichloromethane). The residues in the filter were rinsed repeatedly with fresh *n*-pentane. After drying, the residues were dissolved in dichloromethane, collected in vials. dried under a nitrogen stream and weighed.

Table A. Oil deasphalting

<i>Sample</i>	<i>Oil (g)</i>	<i>Pentane (mL)</i>	<i>Precipitate (mg)</i>	<i>% Asphaltene</i>
Cohasset A-52	78	400	6.6	0.008
Sable Island 3H-58	51	700	61	0.12

Table 1. List of source rock and oil/condensate samples (with their depth and stratigraphic position) used by py-GC analysis.

<i>Type</i>	<i>Well</i>	<i>DST/depth</i>	<i>Litho-strat</i>
Oil asphaltene	Cohasset A-52	5 (2149 m*)	Logan Canyon
Oil asphaltene	Sable Island 3H-58	5 (2226 m*)	Logan Canyon
Rock extr. asph.	Venture B-52	5121 m	Mississauga
Raw rock	Venture B-52	5121 m	Mississauga
Rock extr. asph.	S. Desbarres O-76	3801 m	Mississauga
Raw rock	S. Desbarres O-76	3801 m	Mississauga
Rock extr. asph.	N. Triumph G-43	3695 m	Mississauga
Extracted rock	N. Triumph G-43	3695 m	Mississauga

*Starting depth.

Milligram quantities of asphaltene and powdered rock samples were analyzed by pyrolysis-gas chromatography, using a CDS 120 Pyroprobe directly coupled to the injector of a Hewlett Packard 5890 gas chromatograph, equipped with a flame ionization detector. Pyrolysis was at 610°C for 20 s, monitored by a thermocouple in the sample holder. The GC oven was held at -20°C for 1 min, then raised to 300°C at 5°C min, where it was held for 15 min. A 25 m (0.25 mm i.d., 0.33 µm film thickness) HP-1 column was employed. Data were collected by a Macintosh SE computer equipped with an A/D converter. Peaks were identified by comparison with standards (*n*-alkanes and *n*-alkenes), with results from py-GC-MS of other samples previously analyzed in this laboratory, and with published py-GC and py-GC-MS data. Peak areas were quantitated by summation of detector response after subtraction of the chromatographic baseline.

RESULTS AND DISCUSSION

Total organic carbon (TOC)

Drilling mud additives (lignite, asphalt, etc.), pipe dopes, oil-base drilling fluid, and cavings from younger horizons created problems when analyzing samples for TOC content and kerogen typing. This problem was partially resolved by hand-picking the cuttings samples and using the fluorescence characteristics of the contaminants.

The TOC content of samples varies between 0.07-18.5% (wt%). However, with a few exceptions, all samples with more than 5% TOC are contaminated by drilling mud additives (lignite, etc.) and/or cavings. Some of the contaminants remained in the samples even after hand-picking. None of the core samples contain more than 4% TOC.

There is no correlation between the stratigraphy of the samples and their TOC content. However, most of the samples from the Naskapi Member of Logan Canyon Formation, some samples from Mississauga Formation, and the Misaine Member of Abenaki Formation have TOC contents > 1 %.

Rock-Eval pyrolysis

Plots of Hydrogen Index (HI) vs Oxygen Index (OI) and HI vs T_{max} (Tissot and Welte, 1984; Espitalié *et al.*, 1985) showing the maturation path of Kerogen Types I, II, III, and IV (Fig. 4) and Kerogen Types I, II, and III (Fig. 5), illustrate the position of selected samples from twenty-seven wells. In Fig. 4, samples from the Mississauga Formation in W. Chebucto K-20; Naskapi Member and Mississauga Fm in N. Triumph G-43; Verrill Canyon Fm in Alma F-67 and S. W. Banquereau F-34; lie either close to Type II or within the Type II-III maturation paths indicating the presence of some oil-prone source rocks. A vast majority of samples from the Shortland Shale, Mississauga, Mic Mac, and Abenaki Formations from the Cohasset, Sable Island, Evangeline and Venture wells, are classified as Kerogen Type III, gas-prone, source rocks. The low oxygen index of some of the samples from the Mississauga, Abenaki, and Verrill Canyon Formations suggest possible advanced maturation. Most of those samples have HI values < 100 mg HC/g TOC. Figure 5 also shows the vast majority of the analyzed samples lie in the Kerogen Type III maturation path with a few samples falling within the Kerogen Type II or II-III maturation pathways. The maturity determined by T_{max} , suggests that most of the samples lie within the mature zone of hydrocarbon generation (430-465°C; Espitalié *et al.*, 1985). Comparing Figs 4 and 5, it is obvious that there are only a few oil-prone source rocks in the Logan Canyon (Naskapi and Cree members); Mississauga; distal Verrill Canyon; and Abenaki Formations (Misaine Member) within our selected data set. A majority of the samples are within or close to Kerogen Type III (Tissot and Welte, 1984). These data do not explain the abundance of condensate in the basin as gas-prone Kerogen Type III does not generate enough condensate (Mukhopadhyay and Wade, 1990).

Production Index ($PI = S1 / (S1 + S2)$) is an indicator of the amount of volatile "free" hydrocarbons relative to the presence of migrated oil or the amount of redistributed liquid hydrocarbons (generated by the cracking of kerogens) by primary migration. The vast majority of the samples that have more than 1.0% TOC show anomalously high PI values (0.10-0.72) suggesting the presence of redistributed hydrocarbons, or migrated oil, in most of the non-contaminated samples. Anomalously high PI (> 0.2) in non-contaminated, immature samples at shallow depths indicate the presence of allochthonous (migrated) hydrocarbons. For example, the PI increases gradually from 0.10 at 3938 m through 0.39 at 4990 m to 0.45 at 5220 m in South Sable B-44 which suggests the generation of crude oil-like bitumen by progressive cracking of kerogens with increasing maturity (Mukhopadhyay, 1991).

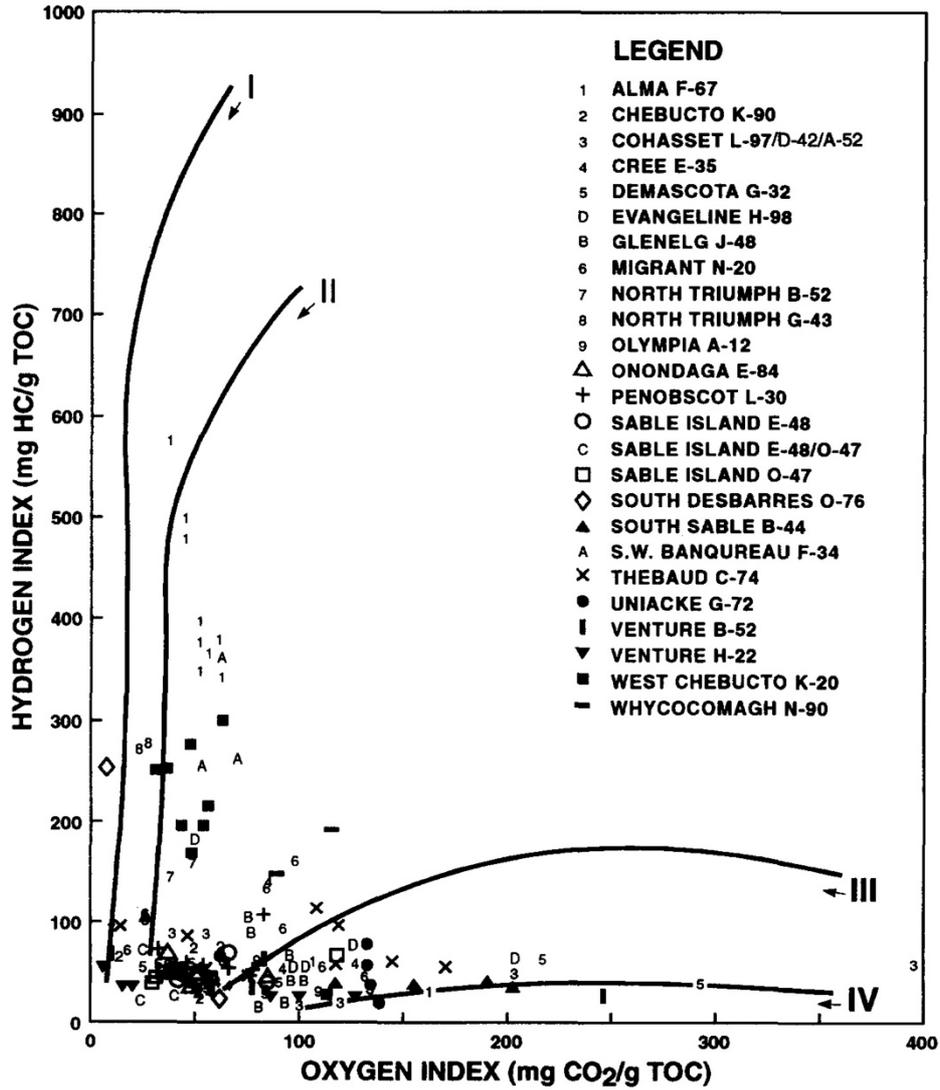


Fig. 4. A plot of HI vs OI from Rock-Eval pyrolysis showing position of various samples from 27 analyzed wells (revised after Mukhopadhyay *et al.*, 1992).

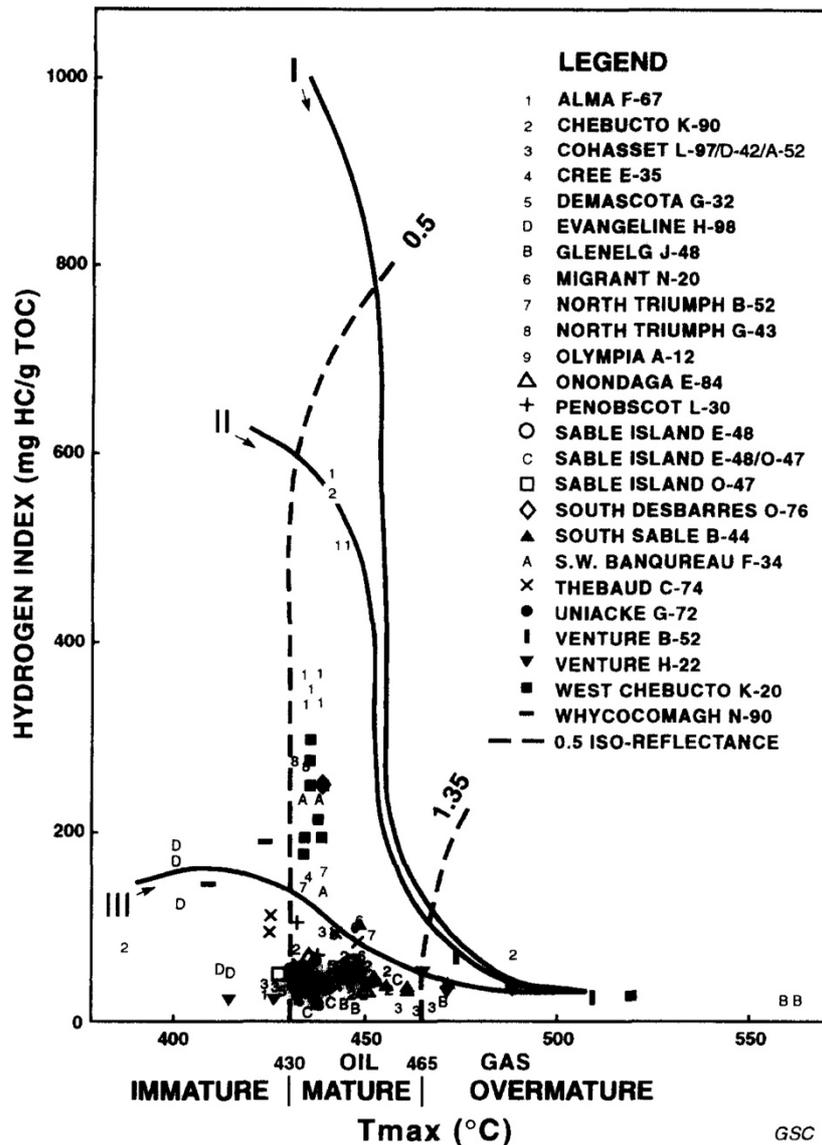


Fig. 5. A plot of HI vs T_{max} from Rock-Eval pyrolysis showing position of various samples from 27 wells.

Macerals, organic facies, and kerogen typing

As discussed above, many of the analyzed samples lie just above the Kerogen Type III maturation path or between Kerogen Types II and III. This raises the question as to which source rock can generate normal gravity oil, light oil or condensate. The question cannot be resolved solely with Rock-Eval pyrolysis data. Our earlier studies on organic facies based maceral analysis, using fluorescence characteristics and oxidation features, and combined with Rock-Eval pyrolysis, showed how less mature condensate and light oils were generated in a basin with low concentrations of resinite (Snowdon and Powell, 1982; Mukhopadhyay, 1989a; Mukhopadhyay and Wade, 1990).

As discussed by Mukhopadhyay and Wade (1990), kerogen which plots between Types II and III of Tissot and Welte (1984) can be subdivided into Kerogen Type IIA-IIB and IIB. Kerogen Type IIA-IIB is derived from a mixture of amorphous organic matter (AOM 2), desmocollinite (vitrinite), and exinite (cutinite or suberinite) with minor tel- and lamalginite [Fig. 6(A, B)]. Kerogen Type IIB is derived from a mixture of vitrinite (desmo-

and telocollinite), terrestrial exinite and minor AOM 2 [Fig. 6(C,D)]. Based on previous research, using a combination of pyrolysis-gas chromatography (py-GC), kinetics, and organic facies, it was shown that Kerogen Type IIA-IIB generates crude oil and condensate within 0.8% R_o , whereas Kerogen Type IIB generates condensate and gas within 1.1 % R_o (Gormly and Mukhopadhyay, 1981; Larter and Senftle, 1985; Mukhopadhyay *et al.*, 1985; Jones, 1987; Senftle *et al.*, 1987; Horsfield, 1989; Mukhopadhyay, 1989a; Mukhopadhyay and Wade, 1990, Mukhopadhyay *et al.*, 1994). The results of our analyses and interpretation are combined in two ternary diagrams, to illustrate a maceral-based kerogen classification which uses Rock-Eval pyrolysis and py-GC data [Fig. 7(a, b)]. Although this kerogen classification scheme was developed from marine and deltaic facies in the Scotian Basin, it may have much broader applications.

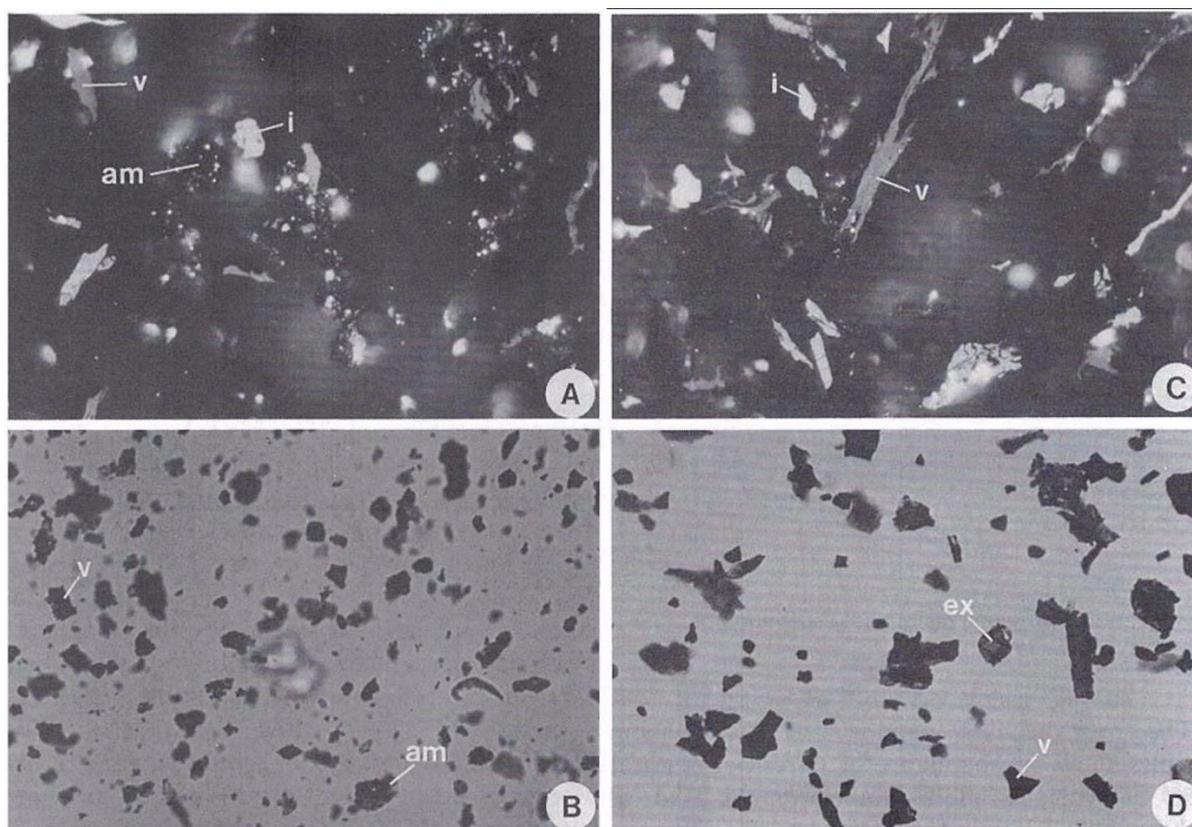


Fig. 6. Photomicrographs in white light. x250. (A) Kerogen type IIA-IIB: AOM 2 (am), vitrinite (v), inertinite; reflected light; N. Triumph G-43, 3695 m. (B) Same as (A) in transmitted light. AOM 2 (am) and vitrinite (v). (C) Kerogen Type IIB: vitrinite (v), inertinite (i), reflected light, S. Desbarres O-76, 3801 m. (D) Same as (C) in transmitted light; exinite (e), vitrinite (v).

The overwhelming majority of the analyzed samples show an abundance of terrestrial macerals such as vitrinite (both autochthonous and allochthonous), inertinite (inertodetrinite, fusinite, macrinite etc.), sporinite, cutinite, and AOM 3. Some samples contain more than 80-90% terrestrial organic matter. As a result, most of the black shales form either Kerogen Type IIB or III and are major condensate- and gas-prone source rocks.

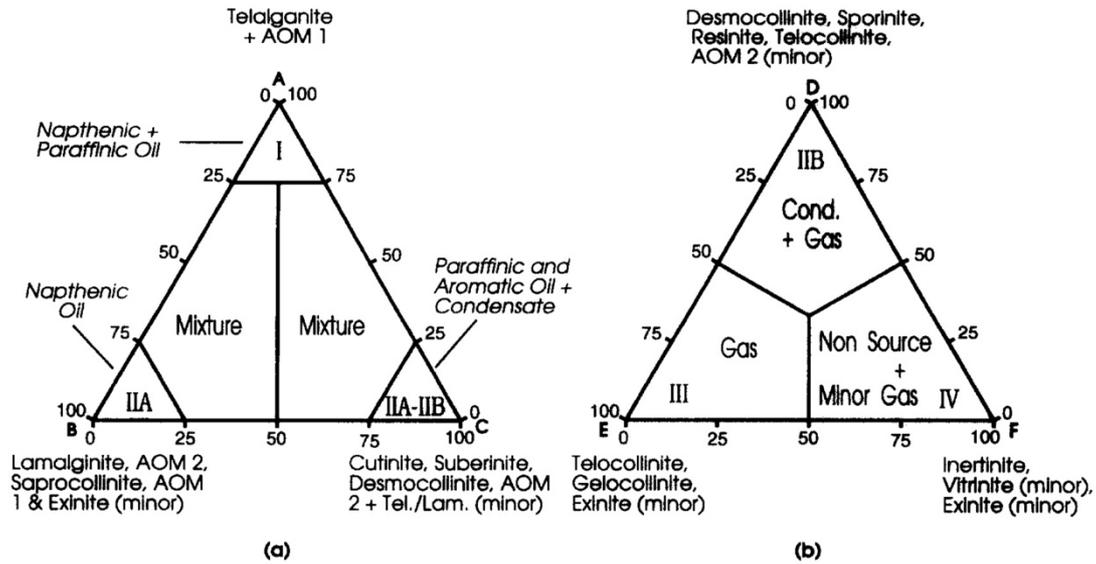
Kerogen Type IIA-IIB samples also contain some amounts of terrestrial organic matter. Usually, Kerogen Type IIA-IIB samples contain more than 50-70% AOM 2. A few

samples contain non-oxidized marine phytoplankton (lamalginite) such as dinoflagellates and acritarchs. Some samples from the Cree and Naskapi Members of the Logan Canyon Formation contain partially oxidized *Botryococcus* algae (telalginite), whereas others contain mainly marine alginite of unknown affinity.

The terrestrial exinites in Kerogen Type IIA-IIB show higher fluorescence intensity compared to Kerogen Type IIB. The lower fluorescence suggests partial oxidation during transport to the marine environment. The presence of some non-biodegraded terrestrial exinite, partially oxidized vitrinite, and partially oxidized framboidal pyrite suggest that none of the analyzed samples from the Scotian Basin were deposited in an anoxic environment as were some of the Kimmeridgian source rocks in the Jeanne d'Arc Basin on the Grand Banks of Newfoundland and the North Sea Basin.

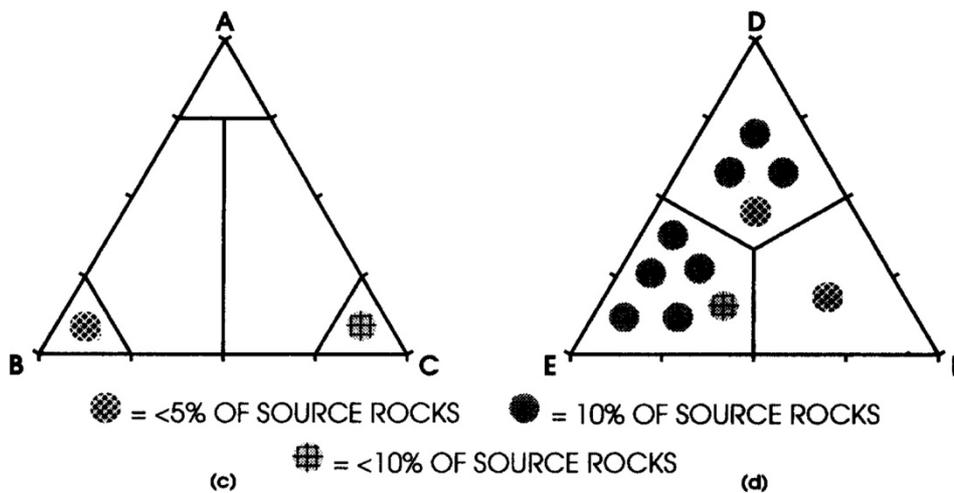
Kerogen typing by microscopic methods is complicated by the formation of secondary macerals due to advanced maturation (Mukhopadhyay et al., 1985; Mukhopadhyay and Wade, 1990). These macerals, such as rank-inertinite, solid bitumen, clustered micrinite, and micrinite, are formed at the expense of oil-generating liptinites, AOM 2, alginite, cutinite, etc. Secondary liptinites, solid bitumen and oil droplets, are common to rare in various organic carbon-rich rocks from the Scotian Basin. The most striking examples of large solid bitumen were observed in the samples from Cree E-35 (10,300 ft) and Chebucto K-20 (5220 m). The most striking example of liquid hydrocarbon generation was noted in a sample at 5210 m from W. Chebucto K-20 where oil droplets with orange fluorescence were derived from AOM 2.

Hydrocarbon Type Determination By Organic Facies



Scotian Shelf

Dark Shales and Limestones



GSC

Fig. 7. Ternary diagrams showing hydrocarbon type determination by organic facies and distribution of kerogen types (after Mukhopadhyay *et al.*, 1993).

Maturation by vitrinite reflectance and T_{max}

The onset of the so-called oil window (0.4-0.5% R_o) in various wells is between 2600 and 3100 m. Peak hydrocarbon generation (0.7-0.8% R_o) is between 4000 and 4500 m and the end of the so-called oil window (1.3-1.4% R_o) is around 5500-5800 m. Most noncontaminated samples show good correlation between vitrinite reflectance and T_{max} values (according to Espitalié *et al.*, 1985; Mukhopadhyay, 1991). For example, in Cree E-35, at 12,980 ft, the R_o is 0.70 and T_{max} is 445°C. However, in some cases, the reflectance value does not correlate with the T_{max} value; e.g. the sample at 14,660 ft from Migrant N-20 where R_o is 0.79% and T_{max} is 431°C. In this case, the lower maturity than R_o is possibly caused by the presence of abundant allochthonous bitumen which also suppresses the T_{max} values (Mukhopadhyay, 1991). The highest vitrinite reflectance observed was 1.7% R_o in

S. Desbarres O-76 at 5957.2 m (core sample) which has a corresponding T_{\max} value of 559°C. The lowest vitrinite reflectance (0.33% R_o) was observed in Sable Island O-47 at 6229.5 ft which has a T_{\max} value of 427°C. Contaminated samples have very low T_{\max} values (generally <400°C).

Figure 8 illustrates the maturation trends and their corresponding oil and gas zones within a structural cross-section between Cohasset D-42 and Venture B-52 wells via Thebaud C-74 which is derived from the Basin/1.fod program (Mukhopadhyay, 1993). Figure 9 illustrate a comparison of the maturation profiles for the Cohasset D-42 and Venture B-52 wells. It shows that Cohasset D-42 has a higher reflectance gradient compared to Venture R-52. Figures 8 and 9 suggest that Cohasset D-42, with its mixed lithologic package of carbonate, sandstone and shale, has a higher heat flow than Venture B-52 with its mainly sand and shale facies. Thebaud C-74 has the lowest maturity although it has a similar lithologic package to Venture B-52. These two figures illustrate that there are different maturity trends in various sections of the Scotian Basin.

Source-rock potential

Comparing maceral composition and organic facies; hydrogen and oxygen indices from Rock-Eval pyrolysis; and maturation parameters; the source rock potential of about 200 selected shale samples from the Scotian Basin can be evaluated as follows: According to petrographic criteria and Rock-Eval pyrolysis, only one or two samples of the 200 analyzed shale samples were formed in a typical anoxic environment (Demaison and Moore, 1980). Most sediments were deposited in a partially sheltered or open basin as indicated by the Jack of samples with > 75% AOM 1 or 2, alginite (tel- or lam-), and the presence of partially oxidized framboidal pyrite and coarser clastics (such as quartz grains > 10 μm in size).

There are multiple mature potential source rocks in Jurassic and Cretaceous formations in the general Sable Island area of the Scotian Shelf. Quantitatively, 1% of the sampled intervals are typical oil-source (Kerogen Type IIA), 6% are oil and condensate source rocks (Kerogen Type IIA-IIB), 32% are condensate and gas source rocks (Kerogen Type IIB), 58% are gas source (Kerogen Type III), and 3% are nonsource (Kerogen Type IV) rocks [Fig. 7(c,d)]. Comparing the percentages of nonsource; condensate/gas-bearing source rock; and gas-bearing source rock with the maturity trends for the basin; more deep gas or gas/condensate-bearing reservoirs are to be expected in currently unexplored areas of the Scotian Basin.

Thin and local oil prone, mature, Kerogen Type IIA-IIB shales in the Logan Canyon, Mississauga and Abenaki Formations, could be the source of Cohasset and Sable Island light oils.

There are different maturity profiles in various parts of the basin: e.g. 1.2% R_o in Cohasset D-42 is at 4386 m (Middle Jurassic) compared to 5122 m at Venture B-52 (Upper Jurassic). This is possibly due to (a) major differences in lithology (carbonate-shale vs sandstone-shale) and hence differences in thermal conductivity and heat capacity, or (b) the presence of older rocks at a shallower depth in Cohasset D-42. Older rocks have experienced higher heat flow due to nearness to rifting (Mukhopadhyay et al., 1994).

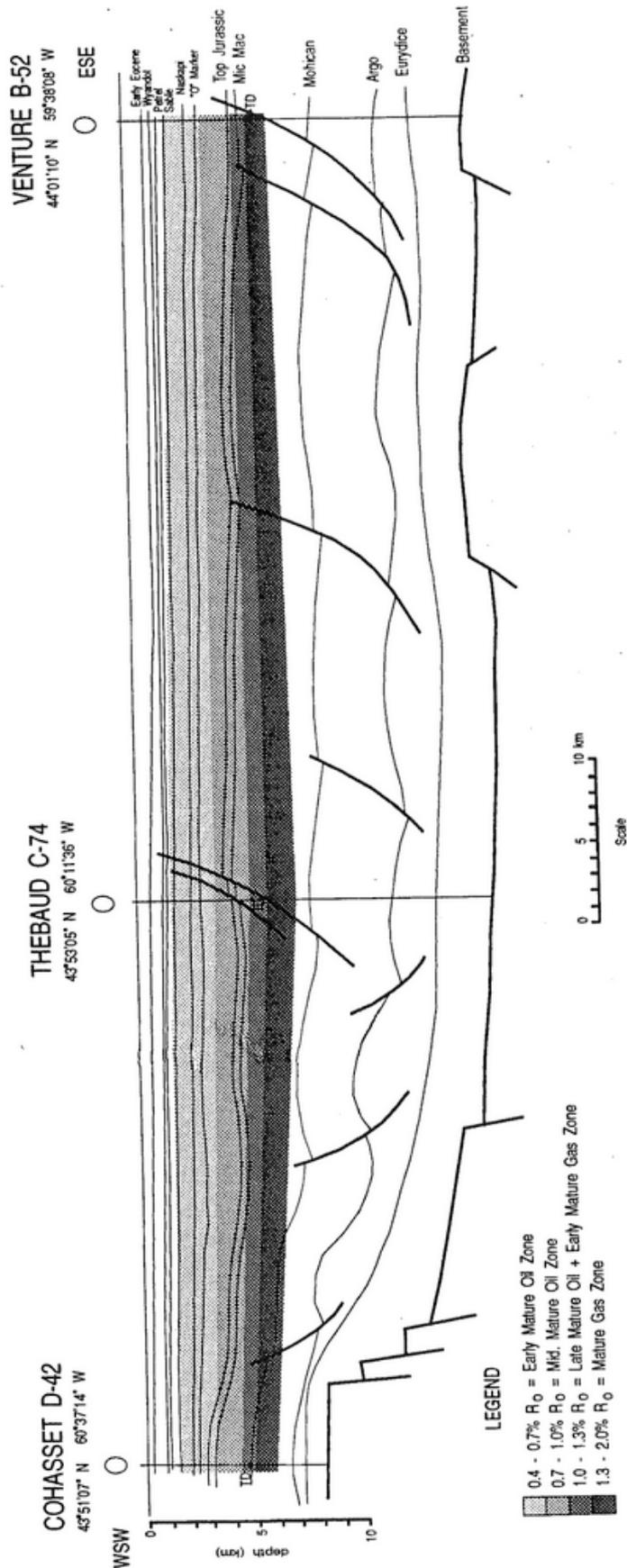


Fig. 8. Structural cross-section showing the maturation profile for three Scotian Shelf wells (after Mukhopadhyay *et al.*, 1994). For location of wells see Fig. 1.

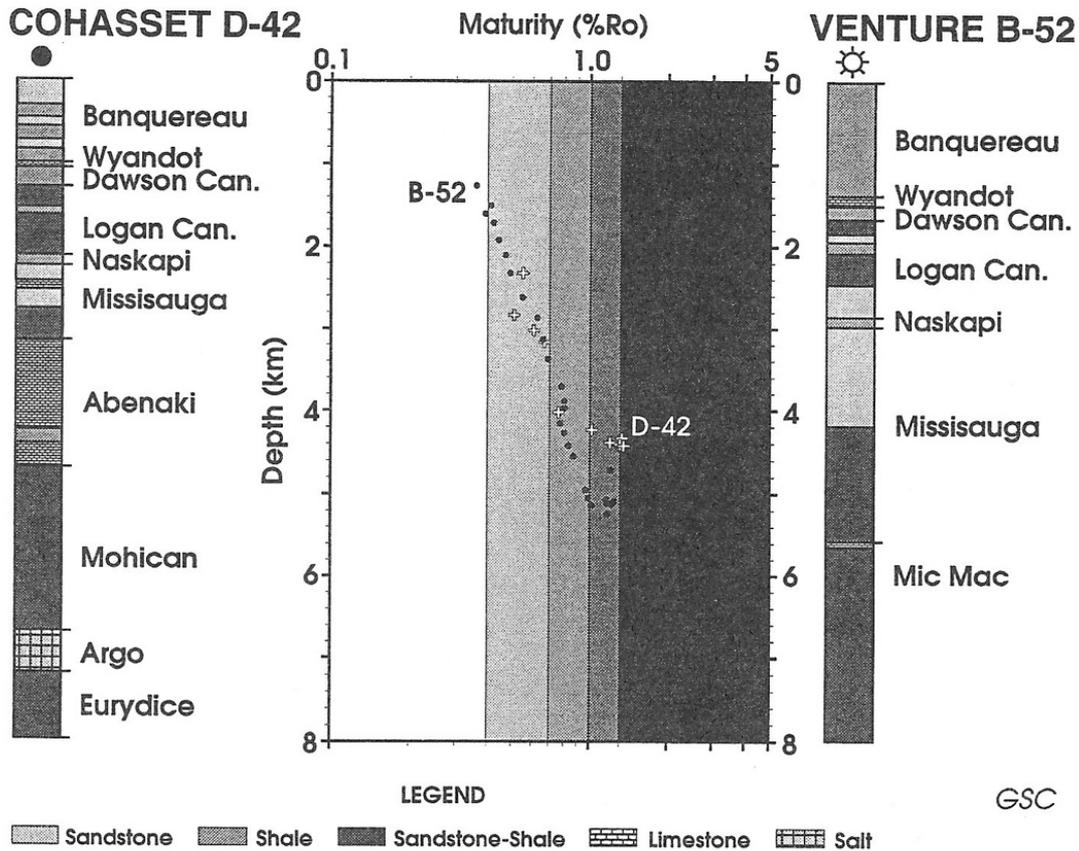


Fig. 9. A comparison of maturity vs depth plots for Cohasset D-42 (+) and Venture B-52 (●) (after Mukhopadhyay *et al.*, 1994).

Oil-oil and oil-source rock correlation

Correlation of Scotian Shelf oils to their source rocks has proven difficult, due to low concentrations of the commonly used biological marker compounds. An attempt at correlation and maturation determination was made using the more abundant polycyclic aromatic hydrocarbons (Kruger, 1991).

The great majority of light oil/condensates and rock extracts in this study are at advanced levels of thermal maturity (middle to late oil window), as indicated by values of the methylphenanthrene, dimethylphenanthrene, chrysene, C₃-alkylnaphthalene and C₄-alkylnaphthalene indices (White and Lee, 1980; Alexander *et al.*, 1983, 1986; Radke and Welte, 1983; Rowland *et al.*, 1984; Radke, 1987, 1988; Garrigues *et al.*, 1988; Kruger *et al.*, 1989, 1990a, b; Budzinski *et al.*, 1991). Those data corroborate the data of the other maturity parameters such as R_o and T_{max} for the source rock extracts.

Multiple linear regression and cluster analysis of aromatic GC-MS parameters reveals a closely related family of oils including those from the wells Chebucto K-90, N. Triumph B-52, Olympia A-12, S. Venture O-59 (two samples), Glenelg J-48, Bluenose 2G-47, Arcadia J-16, Venture H-22 and Thebaud C-74 (Fig. 10). Three rock extracts, from the Venture B-52 (5121 m), Thebaud C-74 (3911 m) and S. Desbarres O-76 (3861 m), correlate well with the light oil/condensates mentioned above, according to the cluster analysis. Hence, those rocks should be evaluated as a potential source for the liquid hydrocarbons. A second oil family, whose members are less closely related than the first, includes light oil from Cohasset D-42 and A-52, Panuke B-90 and Sable Island 3H-58 (Fig. 10). None of the analyzed source rocks match with these oils for oil-source correlation.

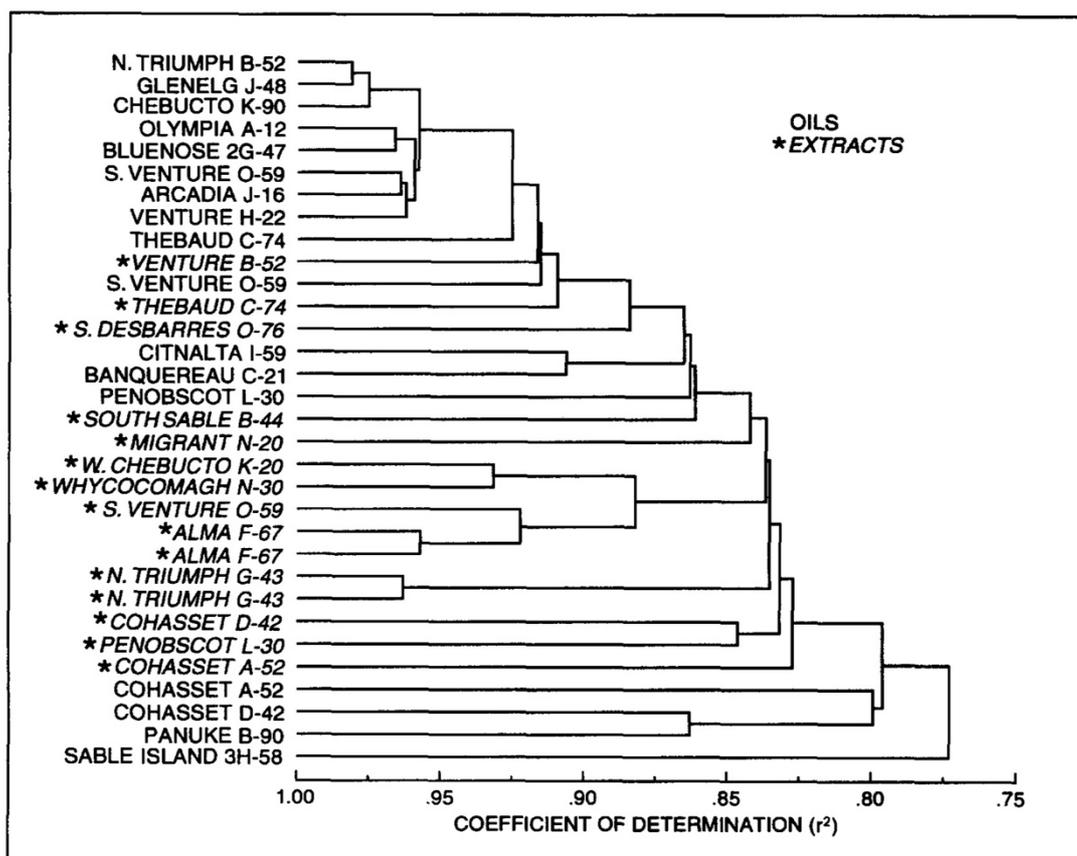


Fig. 10. Dendrogram of Scotian Shelf oils and selected source rock extracts formed by the single linkage method (Massart and Kaufman, 1983) using coefficients of determination from the multiple linear regression of 29 maturation insensitive polyaromatic compounds (modified after Kruge, 1991). Well names in *italics* are source rocks; others are oils or condensates.

Pyrolysis-gas chromatography of asphaltenes and whole rocks

An attempt was made, using py-GC to correlate selected oil asphaltenes with extract asphaltenes from several candidate source rocks. Py-GC has been used extensively for the characterization of solid sedimentary organic matter. Kerogen and petroleum source rock evaluation is one of the most common uses of the technique (e.g. Dembicki *et al.*, 1983; Douglas *et al.*, 1983; Horsfield, 1989; Mukhopadhyay, 1989a). Due to the macromolecular nature of asphaltenes, pyrolytic degradation is also a useful tool for their characterization. Several oil-oil correlation studies have employed confined pyrolysis of asphaltenes (Cassani and Eglinton, 1986; Fowler and Brooks, 1987; Jones and Douglas, 1987). Flash ("open") pyrolysis has shown asphaltenes to be structurally similar to their parent kerogens (Behar *et al.*, 1984) and has been employed in the correlation of bio-degraded oils to source rocks (Michael *et al.*, 1989). Sinninghe Damste *et al.* (1989) used flash pyrolysis to study the organosulfur chemistry of asphaltenes, comparing them to their parent kerogens and coals.

Two light oils (Cohasset A-52, API gravity = 49.7; Sable Island 3H-56, API = 30.0) were selected because (a) they have enough asphaltenes to be extracted, and (b) they do not correlate to any of the source rock extracts using aromatic hydrocarbons. The detailed information on these two oils and three source samples are given in Table 1. Table 2 lists data from Rock-Eval pyrolysis and kerogen type based on microscopy. Table 3 shows a comparison of liquid chromatographic data of both source rock extracts and light oils. Note

that both oils and the source rock extract from N. Triumph G-43 have quite high saturate components and saturate/aromatics ratios.

The yields of asphaltenes from the crude oil samples were extremely low, particularly in the case of Cohasset A-52. While this caused some inconvenience, necessitating repetition of the deasphalting process (see Table A), the results of the py-GC analyses nevertheless appear satisfactory (Fig. 11). There is no large increase in normal hydrocarbons or in unresolved compounds beyond C₁₅, indicating successful deasphalting of these oils.

The py-GC trace of Cohasset A-52 asphaltene is dominated by *n*-alkanes and alkenes, shows minor amounts of the alkylbenzene series and very low quantities of naphthalenes, phenols and thiophenes (Fig. 11). Tbc Sable Island 3H-58 asphaltene pyrogram shows some differences with higher amounts of aromatic hydrocarbons, particularly the alkylbenzenes. The naphthalenes and phenols are readily detectable. but thiophenes are not. These features may be summarized by quantifying the key peaks and presenting them in a normalized plot. Figure 12 shows an example of such a plot for Cohasset A-52 and Sable Island 3H-58. Normal hydrocarbons above C₁₁ were not quantified, as there are many large, interfering, unknown peaks in this retention time region in the source rock asphaltenes, which may arise from contamination. Samples may be readily compared to one another. as in Fig. 12, where the relative depletion of alkenes and alkanes in Sable Island 3H-58 is clearly apparent. The presence of abundant phenols is characteristic of the pyrolyzates of Kerogen Type III having terrestrial organic matter (Senftle *et al.*, 1986; Nip *et al.*, 1988).

The quantities of C₁-C₃ gases from the asphaltenes overloaded the detection capabilities of the gas chromatograph, even though only 1-2 mg of sample were employed. The values given in Fig. 12 for these gases are thus the minimum. The C₄ hydrocarbons were successfully recorded and their enrichment in Sable Island 3H-58 relative to Cohasset A-52 is noteworthy. The distributions of C₅-C₁₃ normal hydrocarbons in these two samples show little similarity (Fig. 12). The apparently high concentration of *n*-tridecene in Sable Island 3H-58 oil is due to the coelution of 1-methylnaphthalene.

Table 2. Rock-Eval pyrolysis data and kerogen type

<i>Well No.</i>	<i>Depth</i>	<i>TOC</i>	<i>HI</i>	<i>T_{max}</i>	<i>Kerogen type*</i>
	<i>(m)</i>	<i>(wt %)</i>	<i>(mg HC/g T0C)</i>	<i>(°C)</i>	
N. Triumph G-43	3695	4.67	270	433	IIA-IIB
S. Desbarres O-76	3801	3.56	251	438	IIB
Venture B-52	5121	2.01	69	473	IIB (overmature)

• = Kerogen type is based on organic facies.

Table 3. Liquid chromatographic data of source rocks and oil/condensate samples

<i>Well No</i>	<i>Depth/DST</i>	<i>%Sat.</i>	<i>%Arom.</i>	<i>%NSO+Asph.</i>	<i>Sat/Arom.</i>
Cohasset A-52	5	76.5	19.5	3.6	3.8
Sable Island (3H-58)	5	72.9	23.7	3.2	3.1
N. Triumph G-43	3695	41.2	3.2	51.4	12.9
S. Desbarres O-76	3801	4.8	10.5	80.1	0.46
Venture B-52	5121	10.1	7.5	77.1	1.4

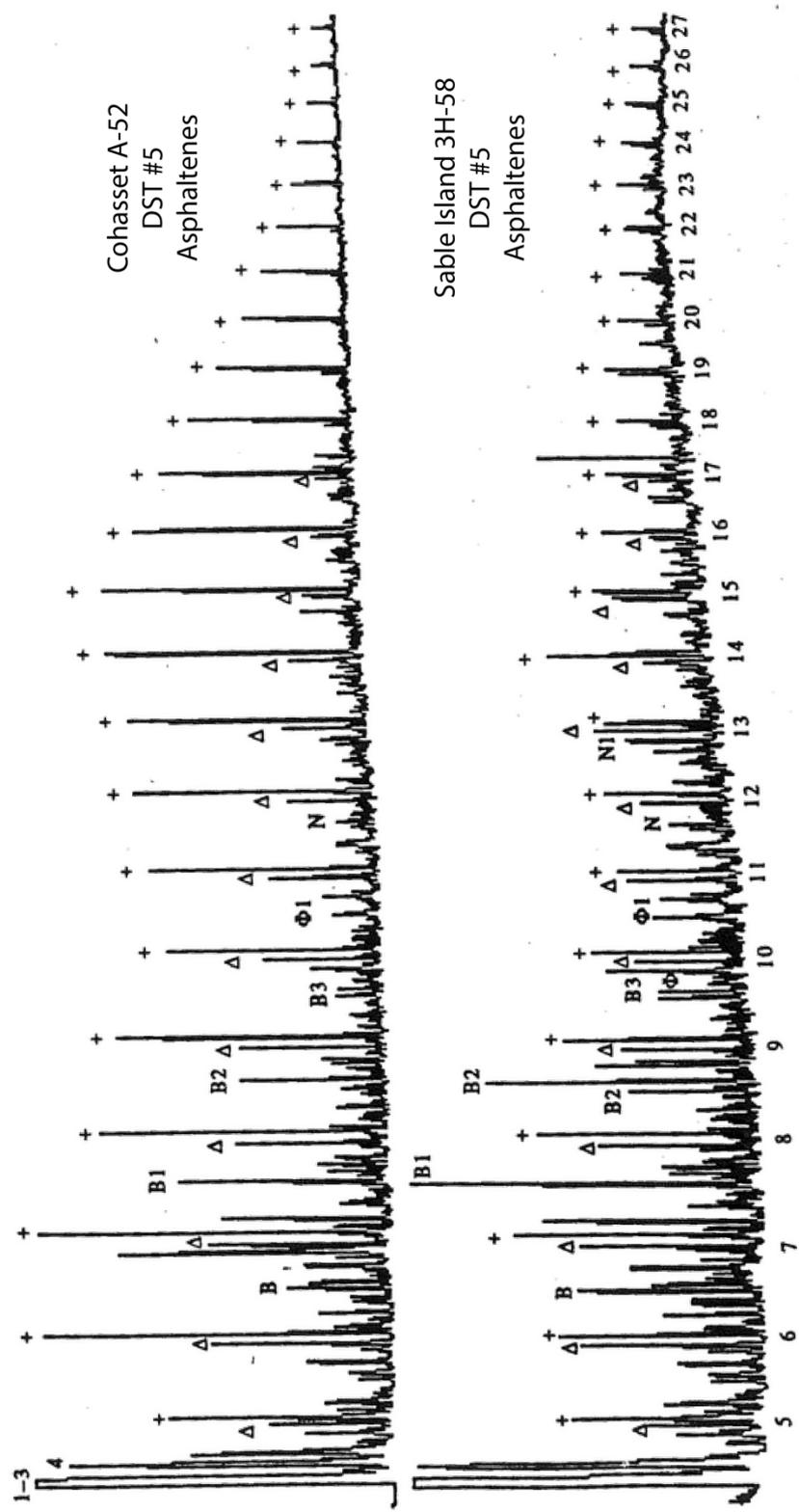


Fig. 11. Py-GC traces of asphaltenes separated from two oil samples (Cohasset A-52 and Sable Island 3H-58); for peak identification see Table 4 (after Kruege, 1992).

Table 4. Py-GC peak identifications. Symbols are those used in Figs 11, 13, and 14.

Peak	Compound name
Δ	<i>n</i> -Alk-1-ene *
+	<i>n</i> -Alkanes*
	(*Carbon numbers indicated below chromatogram)
B	Benzene
B1	Methylbenzene (toluene)
B2	C ₂ -Alkylbenzenes (B2a: ethylbenzene. B2b: <i>m</i> - and <i>p</i> -xylenes. B2c: <i>o</i> -xylene)
B3	C ₃ -Alkylbenzenes
Φ	Phenol
Φ 1	Methylphenols (Φ 1a: <i>o</i> -cresol, Φ 1b: <i>m</i> - and <i>p</i> -cresols)
Φ 2	Dimethylphenols
N	Naphthalene
N1	2-Methylnaphthalene

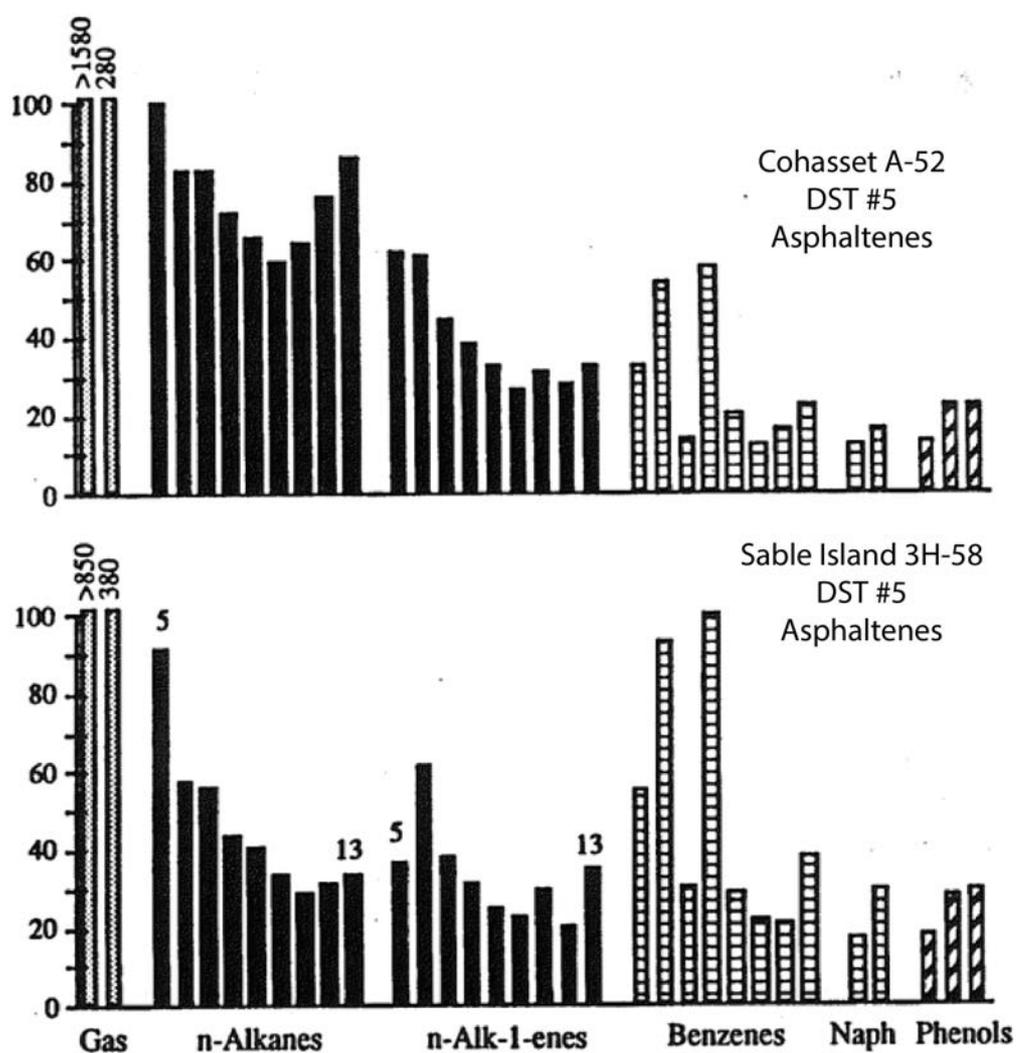


Fig. 12. Quantitation results from py-GC for asphaltenes from Cohasset A-52 and Sable Island 3H-58 (after Kruge, 1992).

The py-GC results for the whole rock sample from S. Desbarres O-76. show high concentrations of aromatic hydrocarbons. including both the benzene and naphthalene series. and exceptionally large amounts of phenols (Figs. 13 and 14). The aliphatics and olefins are correspondingly weak. This is due, in part, to the catalytic effect of the clay minerals in the whole rock sample during pyrolysis (Dembicki *et al.*, 1983; Mukhopadhyay, 1989a). The high phenol content clearly indicates a high proportion of terrestrial kerogen. The Venture B-52 rock sample is very similar to S. Desbarres O-76 in its aromatic and normal hydrocarbon contents, but is distinguished by its lower phenol concentrations. Vitrinite reflectance, T_{max} , and polyaromatic hydrocarbon distributions indicate that, due to present depth, Venture B-52 has an upper oil window maturity level. whereas S. Desbarres O-76 is in the lower to middle oil window (Kruge, 1991; Mukhopadhyay, 1991). The higher maturity of the Venture B-52 sample can account for its lower concentration of phenols. as this effect has been previously noted in Type III organic matter (Senftle *et al.*, 1986). It also had only about half the total pyrolyzate yield of S. Desbarres O-76, which, in this case, may be attributed to the maturity difference. It is reasonable to assume that the Venture and S. Desbarres samples could have originally contained the same kerogen type. They are also shown to possess significant similarities. in their distribution of polyaromatic compounds, to each other and to several of the condensate samples (Kruge, 1991).

In contrast, the N. Triumph G-43 rock pyrolyzate is dominated by aliphatics. While benzene and toluene are also prominent, larger aromatics and phenols are relatively weak (Fig. 13). The total pyrolyzate yield is the largest of the 3 rock samples, nearly double that of S. Desbarres O-76 rock and the proportion of gases is the least (Fig. 15). It should be noted that the C_1 - C_3 gas peaks were recorded on scale for the rock samples. due to their overall lower response. The greater aliphatic content and the lack of phenols is indicative of an algal-dominated kerogen. Again, due to the presence of clay minerals, the apparent aromaticity of the sample has been increased as an artifact of the pyrolysis. Even so, the greater aliphatic content of N. Triumph G-43 is clear. This sample shows little similarity with the other two rocks. The polyaromatic compound distributions also indicated that this rock bears little resemblance to the others (Kruge, 1991).

The source rock extract asphaltene samples presented a severe problem of broad, interfering peaks in the $C_{15} +$ range (Fig. 14). In the case of N. Triumph G-43 asphaltene, they are mostly *n*-alkanes and are likely from residual bitumen remaining after asphaltene separation. The series of unknown peaks in Venture B-52 and S. Desbarres O-76 asphaltenes are apparently the same and might be contaminants, possibly phthalates from any plastic equipment used in the course of extraction or deasphalting. For the three source rock asphaltenes, the data eluting prior to *n*- C_{14} appears satisfactory and are discussed below. The rock asphaltene pyrolyzates all appear less aromatic than their whole rock counterparts (Figs 13-15), due to their pyrolysis in the absence of catalytic clay minerals. Nevertheless, many of the same features seen in the whole rock pyrolysis results are also apparent with the asphaltenes. S. Desbarres O-76 and Venture B-52 asphaltenes have similar aromatic hydrocarbon contents which are much higher than N. Triumph G-43 (Figs 14 and 15). Phenols are strong in both the S. Desbarres rock and asphaltene. They are much weaker for Venture B-52 rock, yet are still clearly discernible. In contrast, phenols are barely detectable in N. Triumph G-43 asphaltene as are aromatic hydrocarbons larger than toluene. Venture and S. Desbarres asphaltenes and whole rock samples are all characterized by a prominence of *m*- and *p*-xylenes (peak B2b, Figs 13 and 14) over *o*-xylene (peak B2c), a feature not seen in N. Triumph samples. In summary, the conclusions from the useful portions of the source rock asphaltene data are the same as those from the whole rock. Venture B-52 and S. Desbarres source rocks are very similar, both containing large proportions of terrestrially-derived organic matter, with their differences largely attributable to the high thermal maturity

level at Venture. N. Triumph G-43 has the signature of an algal-derived material, classified as Kerogen Type IIA-IIB from the organic facies diagram (Fig. 4).

It was noted previously (Kruge, 1991), that the Venture B-52 sample, in particular, correlated well with many of the Scotian Shelf condensates, based on polyaromatic compound distributions. Some similarities are apparent between the petroleum asphaltene Sable Island 3H-58 and the two rock asphaltenes Venture B-52 and S. Desbarres O-76. In particular, the aromaticity and phenol content of the Sable Island 3H-58 asphaltene from pyrolyzate suggest that it may have received a contribution from source rocks containing terrestrial kerogen. similar to Venture and S. Desbarres O-76 source rock asphaltenes. Cohasset A-52 oil asphaltene is clearly more aliphatic and shows much less of a terrestrially-derived component. N. Triumph G-43 source rock asphaltene does not correlate well with either oil but a source rock of similar type may have made a contribution to the Cohasset A-52 petroleum.

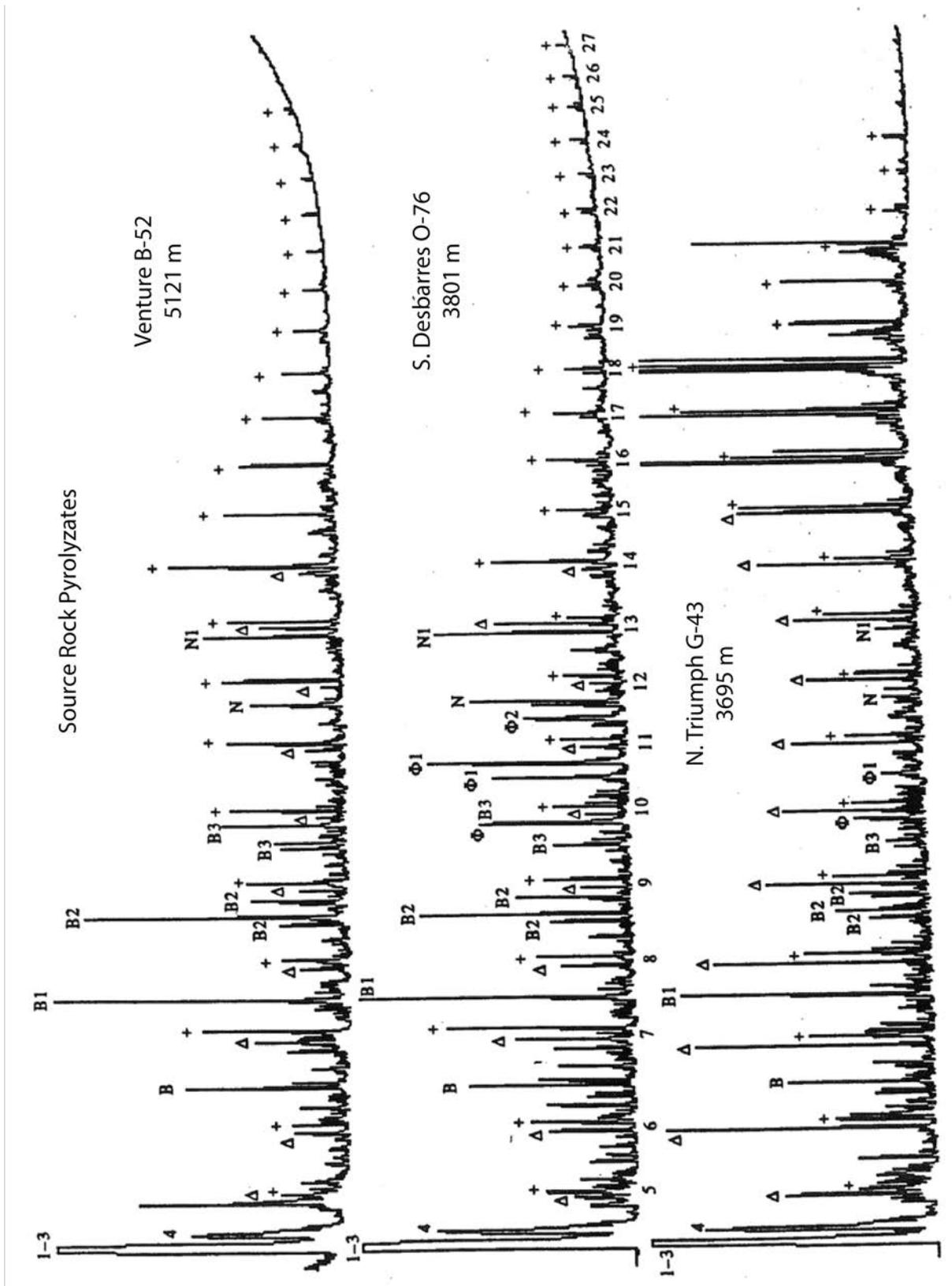


Fig. 13. Py-GC traces of three selected source rocks; for peak identification see Table 4 (after Kruger, 1992).

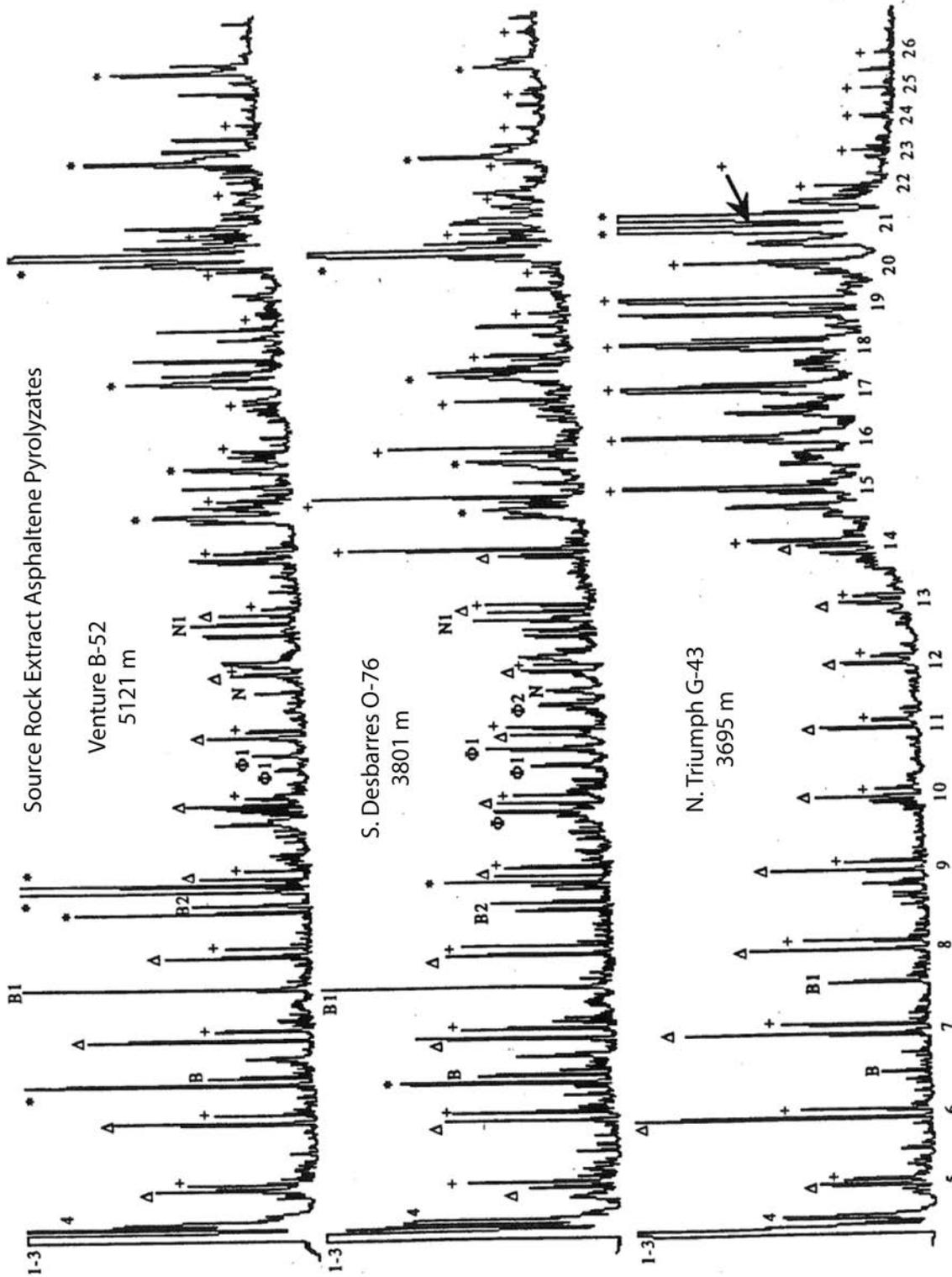


Fig. 14. Py-GC traces of asphaltenes from the same source rock extracts: for quantitation. see Table 4 (after Kruge, 1992).

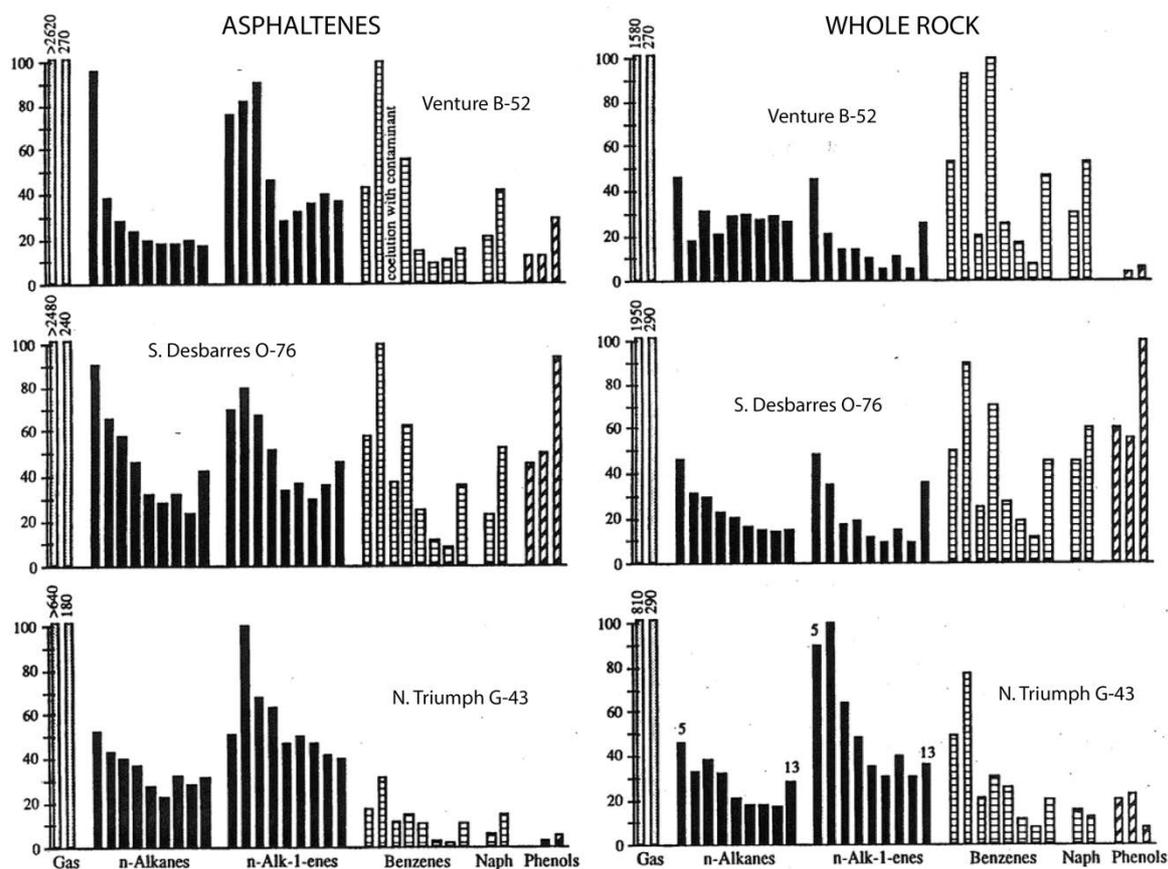


Fig. 15. Quantitation results comparing the py-GC for asphaltenes and whole rock from three samples (modified from Kruege, 1992).

CONCLUSIONS

Source rock characterization

Multiple mature to overmature source rocks of Kerogen Types IIA (II), IIA-IIB (II-III), IIB (Kerogen Types II-III of Tissot and Welte, 1984), and III occur below a depth of 2.5 km in the Sable Island area of the Scotian Basin. A modified concept of organic facies, and the hydrocarbon potential of those facies types determined by Rock-Eval pyrolysis and pyrolysis-gas chromatography can be related on a ternary diagram. Kerogen Type IIA-IIB generate and expel liquid hydrocarbons earlier in the maturation process than Kerogen Type IIB and III.

A majority (58%) of the analyzed Jurassic and Cretaceous source rocks (black shales) can generate only gas, whereas 32% will generate mainly condensate and gas; 6% equal amounts of crude oil and condensate; and 1% mainly crude oil. Only 3% of the sampled black shales are not source rocks. Thin and local oil-prone mature source rocks of Kerogen Type IIA-IIB are observed in the Naskapi Member of the Logan Canyon Fm; Mississauga Fm; Misaine Member of the Abenaki Fm; and distal Verrill Canyon Fm.

Based on vitrinite reflectance and T_{max} from Rock-Eval pyrolysis, a variable maturity profile occurs in different parts of the basin.

Oil-oil and oil--source rock correlation

Aromatic GC-MS biomarker and py-GC were useful in evaluating oil-oil and oil-source rock correlation because of the low concentrations of standard sterane and triterpane biomarker compounds.

Multiple linear regression and cluster analysis of aromatic GC-MS of selected light oil, condensate, and source rock extract reveal the presence of two families of light oil and condensate. One family includes light oil/condensate from Cohasset, Panuke B-90, and Sable Island 3H-58 and the other family includes light oil/condensate from several other discovery wells. Some of the Kerogen Type IIB source rocks from Venture B-52, S. Desbarres O-76 and Thebaud C-74 match with the second oil family.

Pyrolysis-gas chromatography of the asphaltene fractions from Cohasset A-52 and Sable Island 3H-58 show significant differences and indicate that these two oils do not correlate well with each other. The Sable Island asphaltene suggests a contribution from a source rock with terrestrially-derived kerogen, whereas the asphaltene pyrolyzate of Cohasset A-52 suggest a possible algal source.

The Venture B-52 and S. Desbarres O-76 Kerogen Type IIB source rock extract asphaltene pyrolyzates correlate well with the Sable Island light oil. The N. Triumph sample does not correlate well with either oil but a source rock of similar type may have made a contribution to the Cohasset petroleum.

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