

## Organic geochemistry as an aid in the interpretation of the history of oil migration into different reservoirs at the Hibernia K-18 and Ben Nevis I-45 wells, Jeanne d'Arc Basin, offshore eastern Canada\*

MARTIN G. FOWLER and PAUL W. BROOKS

Institute of Sedimentary and Petroleum Geology, Geological Survey of Canada, 3303-33rd St. N.W.,  
Calgary, Alberta, Canada T2L 2A7

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**Abstract**—The Jeanne d'Arc Basin is situated in the northeastern part of the Grand Banks, off the east coast of Newfoundland. Several large oil and gas fields have been discovered in this basin, the largest of which is the giant Hibernia field.

The principal source rock of most of the oils in the Jeanne d'Arc Basin is the Kimmeridgian-aged Egret Member of the Rankin Formation. A characteristic feature of the biomarker distributions of both the oils and the Egret Member extracts is the very high abundance of 4-methyl steranes. The high concentration of these compounds prevents the accurate measurement of maturity and other parameters based on 4-desmethyl steranes using GC-MS-SIM. The use of Collision Activated Decomposition (CAD) GC-MS-MS is demonstrated as a method of overcoming the problem of chromatographically co-eluting compounds to obtain reliable biomarker data.

Biomarker and other geochemical data are then used to help elucidate the history of oil migration into stacked reservoirs in two wells in the Jeanne d'Arc Basin. All the Hibernia K-18 oils are sourced from the Egret Member. We interpret our data to indicate that all the reservoirs over a 1570 m depth interval were originally filled by a single pulse of oil that migrated vertically via faults. In the lowermost Hibernia reservoirs this event is being overprinted by more mature hydrocarbons leaking from the underlying overpressured zone. With increasing depth at Ben Nevis I-45, oils show an increase in maturity and in the proportion of hydrocarbons that are derived from a source rock other than the Egret Member. This second source is dominated by terrestrially-derived organic matter. Oils are found in other wells in the Jean d'Arc Basin with similar characteristics. All these wells are located in one small area of the basin and are in close proximity to the Trinity Fault.

**Key words**—Canada, Jeanne d'Arc Basin, biomarkers, GC-MS analysis, 4-methylsteranes, migration, gasoline-range hydrocarbons

### INTRODUCTION

The Jeanne d'Arc Basin is situated in the northeastern Grand Banks area, off the east coast of Newfoundland, eastern Canada (Fig. 1). Drilling in the Jeanne d'Arc Basin began in 1971, but it was not until 1979 with the discovery of the Hibernia field that large volumes of hydrocarbons were shown to be present in the basin. The Hibernia field (Fig. 1) has been estimated to contain recoverable reserves of between 94 and 137 million m<sup>3</sup> (591–862 million barrels) oil (Canada–Newfoundland Offshore Petroleum Board, 1986) and is the largest oil discovery on the eastern continental margin of North America (Brown *et al.*, 1989). Several more oil discoveries have subsequently been made in the Jeanne d'Arc Basin including major fields at Terra Nova and Whiterose (Fig. 1). Ben Nevis I-45 (Fig. 1) is a relatively minor oil discovery that was made in 1980.

Details on the geology of the Jeanne d'Arc Basin and the Hibernia field can be found elsewhere (e.g.

Grant *et al.*, 1986; Tankard and Welsink, 1987; Brown *et al.*, 1989; McAlpine, 1989). The Hibernia field was described by Brown *et al.* (1989) as a large roll-over anticline that is located in the hinge zone at the west end of an east-southeast trending transbasin fault zone. It is cut by a large number of smaller faults. At Hibernia, oil is trapped in a 2500 m thick sequence of alternating sandstone reservoirs and intervening shale and mudstone units that are Kimmeridgian to Albian in age (Fig. 2). The most important reservoir unit is the Hibernia Formation of Tithonian to Berriasian age. Oil is found in several individual sand members that are separated from each other by shales. The other important reservoirs from the viewpoint of future production are Avalon and Ben Nevis sandstones of late Barremian to late Albian age. Although not considered to be economic (Canada–Newfoundland Offshore Petroleum Board, 1986), oil was also tested in the Catalina and Jeanne d'Arc formations.

The source rock of Kimmeridgian age first reported by Swift and Williams (1980) and now defined as the Egret Member of the Rankin Formation

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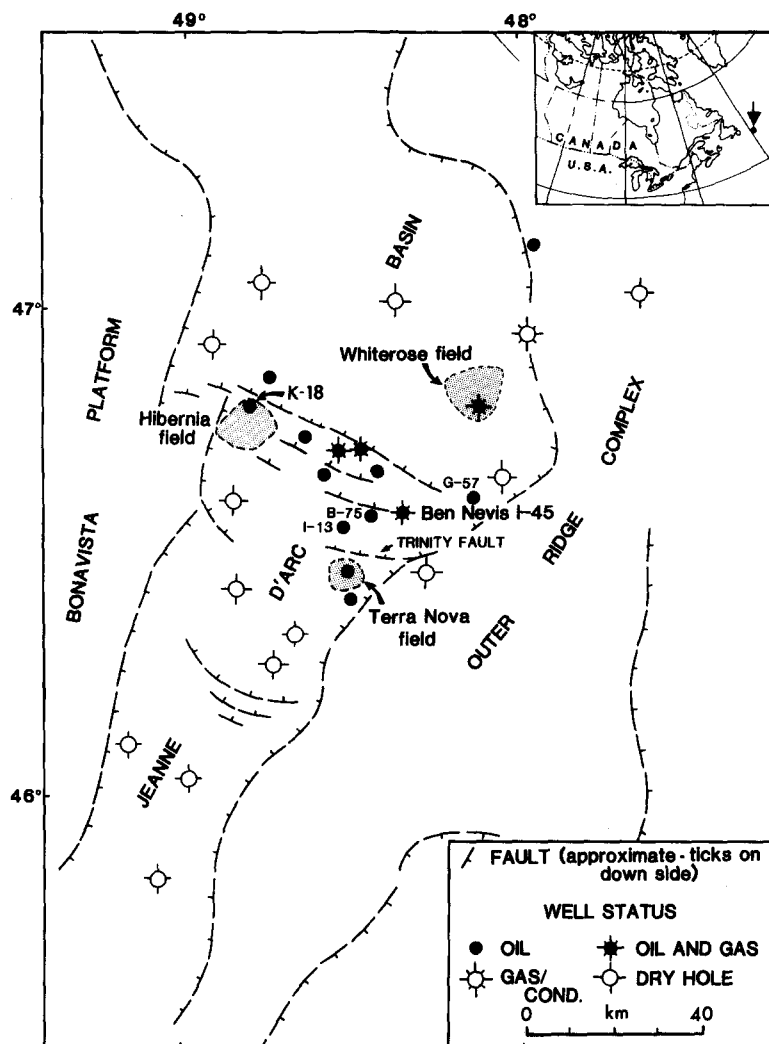


Fig. 1. Map of the Jeanne d'Arc Basin showing wells and other structural features mentioned in the paper. It should be noted that the map location of the faults is their intersection with the Mid-Cretaceous unconformity. At the stratigraphic level of the reservoir horizons, the Trinity fault would be located further north near the wells discussed in the text.

(McAlpine, 1989), has been shown to be the major source for the oils in the Jeanne d'Arc Basin (e.g. Powell, 1985; McAlpine *et al.*, 1986; Creaney and Allinson, 1987; von der Dick *et al.*, 1989, 1990). Some authors (Snowdon and Krouse, 1986; Fowler *et al.*, 1988, 1989; von der Dick *et al.*, 1989) have suggested a contribution from a second source to some oils, particularly those in the Ben Nevis area (Fig. 1).

At present, in the Hibernia field there is an over-pressured zone capped by the Fortune Bay shales which includes the Egret member source rock (Brown *et al.*, 1989). The reservoirs except the Jeanne d'Arc sands are all in the normal hydrostatically pressured regime. The principal mechanism for oil migration has been assumed to have been along faults and fractures that opened sporadically in response to the build-up of abnormally high pressures (Grant *et al.*, 1986). von der Dick *et al.* (1989) reported that the oils in the Hibernia field were of identical composition and maturity, which they took as evidence of "direct

fault-migration from a single expulsion event that coincided with peak maturation of the Jurassic source". Creaney and Allison (1987) thought that six oils obtained over a vertical distance of 1700 m from the Hibernia P-15 well were identical and had been generated from the source rock at similar maturity levels and subsequently migrated up faults into their respective reservoirs.

The intention of this paper is first to briefly demonstrate some advantages of GC-MS-MS over GC-MS in the analysis of oils, such as those from the Jeanne d'Arc Basin for which chromatographic co-elution is a problem. Biomarker and other data are then used to interpret the history of oil accumulation in two wells, Hibernia K-18 and Ben Nevis I-45.

#### EXPERIMENTAL

Oil samples were derived from drill stem tests (DSTs). Gasoline range hydrocarbons were analysed

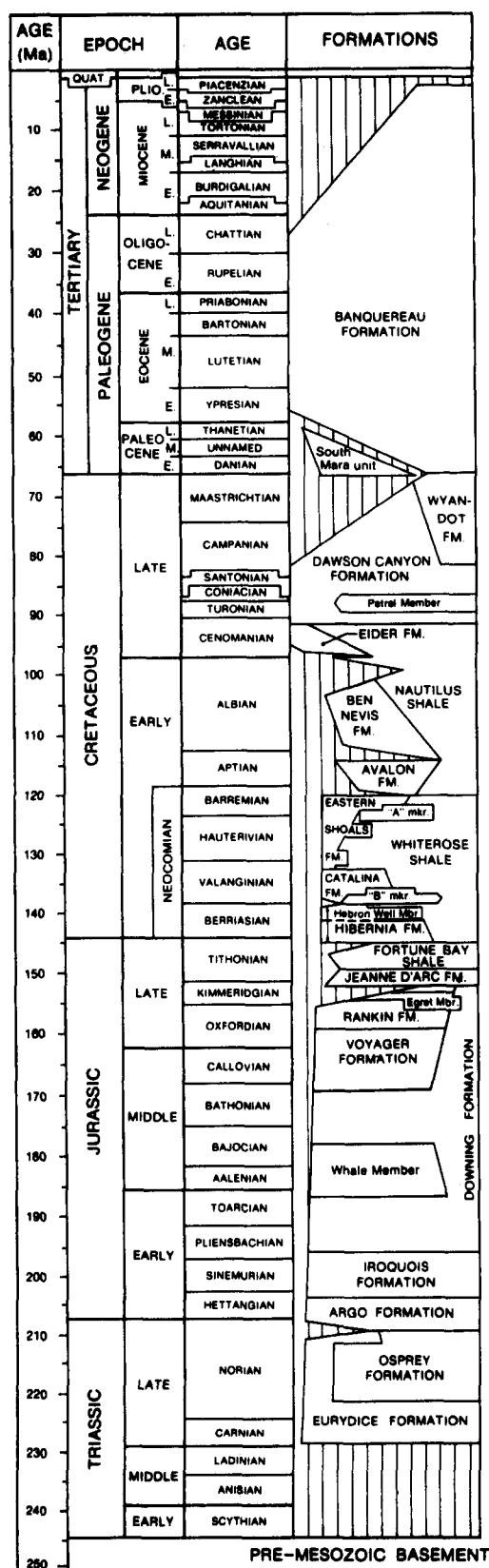


Fig. 2. Generalised stratigraphy of the Jeanne d'Arc Basin (after McAlpine, 1989).

using the method of Snowden and Osadetz (1988). Additional gasoline-range data were supplied to the ISPG by Shell and were derived from the gas chromatographic analysis of the fraction boiling below 114°C. Sulphur contents of oils were obtained using a LECO SC32 Sulphur Determinator.

A sample of each oil was distilled to remove material boiling below 210°C. This fraction was treated with  $\approx 40$  volumes of *n*-pentane to precipitate the asphaltenes. The deasphalted oil was then fractionated and analysed by gas chromatography as described by Snowden *et al.* (1987).

Gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS) data were obtained using a VG70 SQ hybrid MS-MS controlled by a VG11-250J+ data system. Gas chromatographic separation was carried out using a 25 m DB-5 (J&W Scientific) fused silica column programmed from 60 to 310°C at 4°C min<sup>-1</sup> and then held isothermal. The column effluent was fed directly into the source of the mass spectrometer which was operated at 70 eV electron energy, 100  $\mu$ A filament emission current and a temperature of 250°C. The hopane and sterane data were obtained using a method called Collision Activated Decomposition MS-MS. This was carried out using 10 Parent-Daughter ion relationships by focusing each parent ion into the collision cell (1st Quadrupole) using electrostatic switching of the first analyser and then monitoring the appropriate daughter ion intensity by switching the quadrupole analyser R.F. and D.C. Dwell time for each transition was 80 ms with a 20 ms reset time. Collision gas (N<sub>2</sub>) was added to the collision chamber and the collision activation energy was 18 eV.

Distributions of triaromatic and monomethyl nuclear substituted triaromatic steroid hydrocarbons were determined by high resolution GC-MS, monitoring ions *m/z* 231.1170 and 245.1330 respectively of the combined saturated and aromatic fractions of the oils.

#### ADVANTAGES OF USING GC-MS-MS TO MONITOR STERANE DISTRIBUTIONS IN JEANNE D'ARC BASIN OILS

The most commonly used method for the detection of steranes in geological samples is GC-MS monitoring of the *m/z* 217 ion (the major common fragment for steranes) with either a low resolution quadrupole analyser or a high resolution double focusing sector mass spectrometer. However, in samples such as the oils from the Jeanne d'Arc Basin, the above analytical methods are not sufficiently specific owing to the presence of abundant chromatographically co-eluting 4-methylsteranes (Fowler *et al.*, 1988, 1989; von der Dick *et al.*, 1989) which also have a minor *m/z* 217 fragment ion in their mass spectra (e.g. Summons *et al.*, 1987). These compounds are co-detected with the 4-desmethylsteranes making accurate quantitation of the compounds of interest impossible. Summons *et al.*

(1987) used multiple metastable peak monitoring to give simpler chromatograms. Here we compare the data obtained from GC-MS and GC-MS-MS methods including Collision Activated Decomposition (CAD) GC-MS-MS.

The problems associated with the co-elution of the 4-methylsteranes and the regular steranes are demonstrated in Fig. 3, which shows the results obtained from the analysis of an oil from Hibernia P-15. The data in Figs 3(a) and 3(b) were collected using low resolution magnetic MID (multiple ion detection) and are analogous to the data that could be obtained using a quadrupole MS. Figure 3(a) is the  $m/z$  217 fragmentogram showing the  $C_{27-30}$  sterane distribution and Fig. 3(b) is a  $m/z$  400 fragmentogram showing the distribution of  $C_{29}H_{52}$  compounds, in-

cluding the  $C_{29}$  steranes, over the same chromatographic range. Maturation parameters based on the distributions of regular steranes are normally obtained by measurement of the 24-ethylcholestane peaks (Mackenzie, 1984). Because of the high abundance of the 4-methylsteranes, both of these fragmentograms are extremely complex and quantitation of  $C_{29}$  desmethylsterane peaks is difficult. For this sample, the ratio of  $C_{29}$   $5\alpha(H), 14\alpha(H), 17\alpha(H)20S$  and  $20R$  isomers ( $\alpha\alpha\alpha S/\alpha\alpha\alpha R$ ) is 0.49 (Table 1), suggesting that the oil is very immature as the equilibrium value for this ratio is around 1 (Mackenzie, 1984).

Figure 3(c) shows an analysis of the same sample acquired at 3000 resolution (high resolution) using voltage switching, over the same chromatographic region as Figs 3(a) and 3(b). A comparison of the

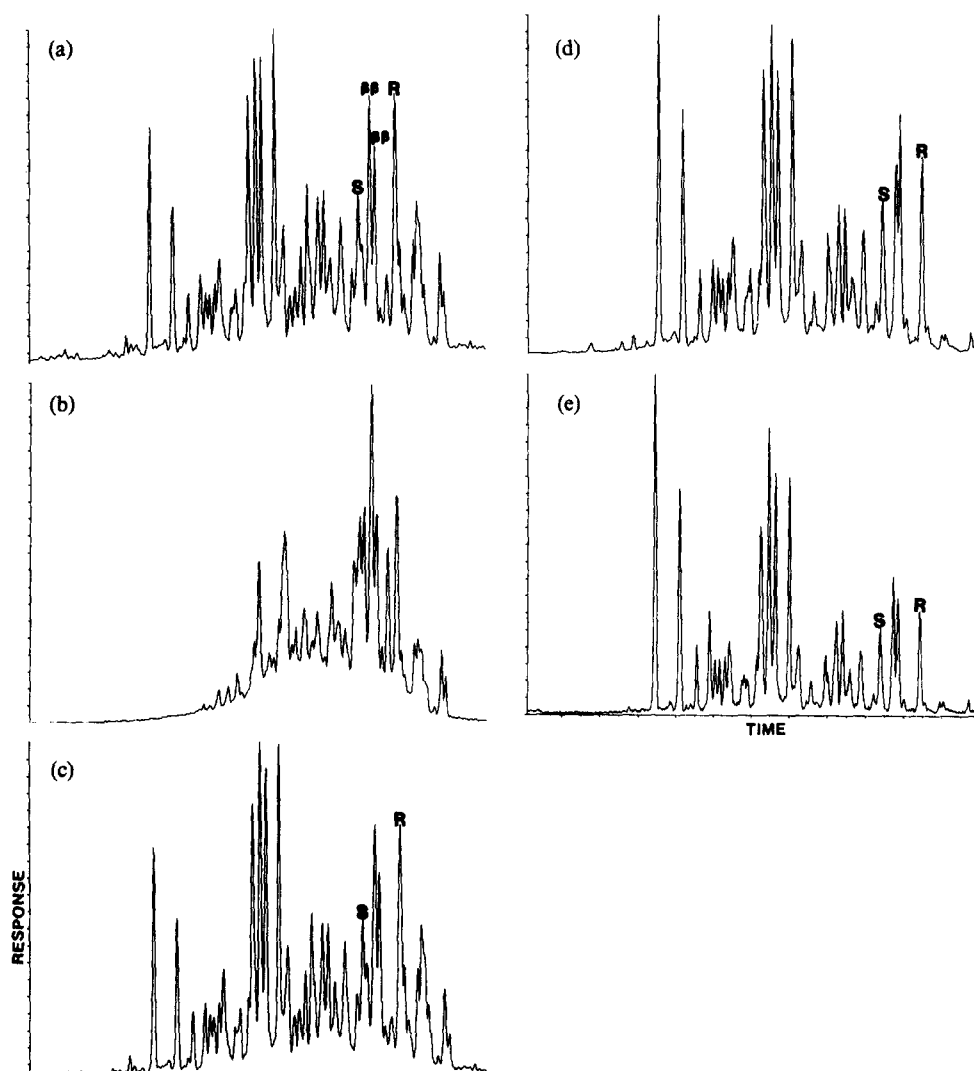


Fig. 3. Monitoring steranes using different GC-MS techniques: (a) low resolution MID monitoring of  $m/z$  217 fragment ion; (b) low resolution monitoring of  $m/z$  400 molecular ion; (c) high resolution MID monitoring of  $m/z$  217.1950 fragment ion; (d) sum of  $m/z$  372,  $m/z$  386,  $m/z$  400 and  $m/z$  414  $\rightarrow$   $m/z$  217 transitions in the 1st Field Free Region of mass spectrometer (metastable MID); (e) sum of  $m/z$  372,  $m/z$  386,  $m/z$  400 and  $m/z$  414  $\rightarrow$   $m/z$  217 transitions in the 3rd Field Free Region of hybrid MS-MS. The sample is an oil from Hibernia P-15 DST 11. R and S are  $C_{29}$   $5\alpha(H), 14\alpha(H), 17\alpha(H) 20R$  and  $20S$  steranes respectively, and  $\beta\beta$  are the  $C_{29}$   $5\alpha(H), 14\beta(H), 17\beta(H)$  steranes.

Table 1. Comparison of the values obtained measuring the ratio of  $5\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H})$  20S- to  $5\alpha(\text{H}), 14\alpha(\text{H}), 17\alpha(\text{H})$  20R-ethylcholestanes using different forms of GC-MS analysis. See text for more details

Analysis Mode	$\text{C}_{29}$ $\text{aaaS/aaaR}$	$\text{C}_{29}$ $\text{aaaS/aaaS+R}$
Magnetic M.I.D.	0.49	0.33
High resolution M.I.D.	0.50	0.34
Metastable M.I.D.	0.72	0.42
CAD MS-MS M.I.D.	0.82	0.45

high resolution and low resolution  $m/z$  217 fragmentograms shows them to be almost identical. As expected, increasing the mass spectrometer resolution does not remove the interference to the regular sterane peaks caused by the presence of 4-methylsteranes because the fragment ions of both groups of steranes have the same atomic composition. The ratio of the  $\text{C}_{29}$   $\alpha\alpha\alpha$  S and R steranes using high resolution MID is almost the same as that using low resolution MID (Table 1).

Figure 3(d) shows the summation trace obtained by monitoring the transitions of the  $\text{C}_{27}$ ,  $\text{C}_{28}$ ,  $\text{C}_{29}$  and  $\text{C}_{30}$  molecular ions to give the  $m/z$  217 daughter fragment ions in the 1st field free region (1FFR) of the mass spectrometer. This form of analysis is often referred to as metastable MID and has been used to overcome the problem of sterane co-elution by several workers (e.g. Warburton & Zumbege, 1982; Steen, 1986; Summons *et al.*, 1987). Individual transitions (e.g.  $m/z$  372  $\rightarrow$   $m/z$  217) may be plotted, but for comparison with the magnetic and voltage switching results [Figs 3(a) and 3(c)] the summed trace is shown. Clearly, in the chromatographic region of interest the pattern of peaks is less complicated. This is expected because the transitions monitored are not important for the 4-methylsteranes whose equivalent strong transition is  $\text{M}^+ \rightarrow 231$ . Measurement of the ratio of the  $\text{C}_{29}$   $\alpha\alpha\alpha$  20S and 20R isomers from these data gives a value for 20S/20R of 0.72. This is a considerably higher value than that obtained from magnetic MID and voltage MID (Table 1) and is considered to be a more realistic value for this oil.

Figure 3(e) shows the same transitions that were monitored for Fig. 3(d) but brought about by Collision Activated Decomposition in the 3rd FFR of the hybrid MS-MS and analysed using a quadrupole. Further improvement over the metastable MID is observed due to the greater resolution of both parent and daughter ions achieved using CAD GC-MS-MS. Metastable MID has extremely limited resolution (c. 200) resulting in low specificity of parent ion selection ( $M \approx 1$  amu) and daughter ion detection. Using CAD MID the parent ion is selected at 1000 resolving power, ensuring no overlap of fragment ions from higher homologues with molecular ions of interest and the daughter ion is detected at unit mass resolution avoiding overlap of ions such as  $m/z$  217 and  $m/z$  218 [a prominent daughter ion of  $5\alpha(\text{H}), 14\beta(\text{H}), 17\beta(\text{H})$  steranes]. The value of the ratio of  $\text{C}_{29}$   $\alpha\alpha\alpha$  S

to  $\alpha\alpha\alpha$  R steranes is 0.82 which is believed to reflect the true maturity of the crude oil. There are some differences in values obtained for other ratios between metastable MID and CAD GC-MS-MS that cannot be easily explained simply by the greater specificity of the latter method such as the relative abundance of  $\text{C}_{27}$ - $\text{C}_{29}$  steranes and of diasteranes to regular steranes. Steen (1986) has previously pointed out that biomarker parameters are significantly affected by the method employed for GC-MS analysis and that only one method should be used in a particular study. All sterane and hopane data in this present study were obtained using CAD GC-MS-MS.

Previous workers (e.g. von der Dick *et al.*, 1989a,b) who have examined oils in the Jeanne d'Arc Basin did not have access to data from either metastable or GC-MS-MS techniques. In the following sections we hope to show how the superior data obtained from GC-MS-MS can assist in providing a greater understanding of the petroleum geology of the Jeanne d'Arc Basin.

#### HIBERNIA K-18

##### Results

Data from the analysis of oil samples from Hibernia K-18 are presented in Table 2. The oil samples from Hibernia K-18 cover a depth range of 1577 m. DSTs 1-6 were recovered from sands of the Hibernia Formation that are separated from each other by shale units. DST 8 is from the Catalina Formation and DSTs 11 and 13 are from the Avalon Formation (Fig. 2).

Generally, the oils from the K-18 well are similar to each other in their gross chemistries. There is no evidence that any of them has been affected by biodegradation or water-washing. API gravities are slightly lower for the Avalon and Catalina oils than for the Hibernia oils (Table 2). Parameters that are considered to be source-related such as the relative distribution of  $\text{C}_{27-29}$  regular steranes,  $\text{C}_{26-28}$  triaromatic steranes and the pristane to phytane ratio (pr/ph) indicate that all the Hibernia K-18 oils are sourced from the Egret member as stated by other workers (Powell, 1984; Creaney and Allison, 1987; von der Dick *et al.*, 1989, 1990).

Closer observation of the data suggests that some parameters do show a trend with depth (Figs 4 and 5). For example, oils from the Hibernia Formation with the exception of DST 6 (the highest test in this formation) contain significantly less sulphur than those from the upper formations (Table 2, Fig. 4). Two parameters derived from analysis of the gasoline-range hydrocarbons are also shown in Fig. 4, the isoheptane index (2- and 3-methylhexane/1c3-, 1t3-, and 1t2-dimethylcyclopentanes) and toluene/n-heptane ratio (Thompson, 1983, 1987). These also show little variation between the top Hibernia oil (DST 6) and the Avalon and Catalina oils but higher values

Table 2. Geochemical data from the analysis of oil samples from Hibernia K-18. Table headings explained in footnotes

DST	Formation	Interval (m)	API	%S	I <sup>1</sup>	H <sup>2</sup>	ToI/ nC <sub>3</sub> <sup>3</sup>	pr/ ph <sup>4</sup>	pr/ nC <sub>17</sub> <sup>5</sup>	C <sub>29</sub> <sup>6</sup> S/R	C <sub>29</sub> <sup>7</sup> β/αα + ββ	C <sub>27</sub> <sup>8</sup> D/αααR	c <sub>2</sub> C <sub>27</sub> <sup>9</sup>	% C <sub>28</sub> <sup>9</sup>	% C <sub>29</sub> <sup>9</sup>	Ts/ Tm <sup>10</sup>	29/ X <sup>11</sup>	29s/ Hop <sup>12</sup>	Triarom cracking <sup>13</sup>
13	Avalon	2282-2293	28.7	0.85	-	-	-	0.91	0.53	0.70	0.53	0.56	45	23	34	1.11	2.73	0.22	0.09
11	Avalon	2313-2330	30.0	0.72	1.58	27.7	0.75	0.94	0.52	0.67	0.58	0.57	44	22	34	1.22	2.55	0.16	0.10
8	Catalina	3120-3135	32.0	0.76	1.59	27.6	0.73	0.93	0.54	0.67	0.52	0.56	47	20	33	1.37	2.67	0.17	0.09
6	Hibernia	3735-3740	33.8	0.79	1.61	27.6	0.76	0.85	0.48	0.73	0.57	0.66	45	21	34	1.20	2.59	0.13	0.10
5	Hibernia	3783-3788	34.2	0.44	1.79	26.6	0.93	0.95	0.41	0.73	0.58	0.73	43	21	36	1.52	2.40	0.14	0.12
4	Hibernia	3804-3812	34.4	0.40	1.79	27.0	1.02	0.96	0.43	0.71	0.61	0.92	45	22	33	1.93	1.88	0.12	0.12
3	Hibernia	3831-3843	32.5	0.46	1.78	28.4	1.01	0.86	0.41	0.75	0.61	1.02	44	22	34	2.12	1.81	0.14	0.16
.	Hibernia	3850-3859	32.2	0.47	1.83	26.9	1.00	0.91	0.40	0.73	0.61	1.02	42	21	37	2.00	1.76	0.14	0.17

1 Isoheptane value; 2- + 3 - methylhexanes/1c3-. 1t2- and 1t2-dimethylcyclopentanes.

2 Heptane value; 100 X n-heptane / (Σcyclohexane through methylcyclohexane excluding 1c-2-dimethylcyclopentane).

3 toluene/n-heptane

4 pristane/phytane

5 pristane/n-heptadecane

6 5α(H),14α(H)17α(H) 20S / 5α(H)14α(H)17α(H) 20R-C29 steranes

7 5α(H)14β(H)17β(H)5α(H)14α(H)17α(H) + 5α(H)14β(H)17β(H)-C29 steranes

8 13β(H)17α(H) 20S dicholestanes/5α(H)14α(H)17α(H) 20R-cholestone

9 normalised proportion of C<sub>27</sub>:C<sub>28</sub>:C<sub>29</sub>:4-desmethylsteranes

10 18α(H)-trisnorhopane/17α(H)-trisnorhopane

11 17α(H)21β(H)-norhopane / X: unknown C<sub>29</sub> terpene

12 5α(H)14α(H)17α(H) 20R-ethylcholestone / 17α(H)21β(H)-hopane

13 Triaromatic sterane cracking ratio; C<sub>20</sub> + C<sub>21</sub>/C<sub>26</sub>-C<sub>28</sub>

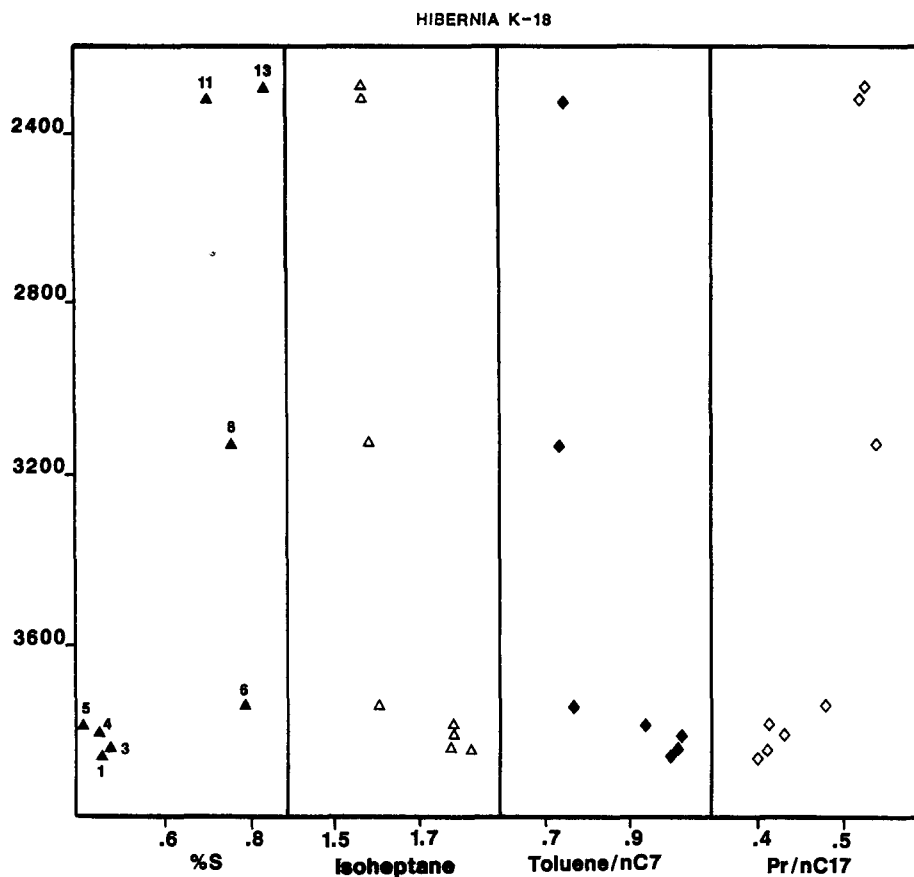


Fig. 4. Data from geochemical analyses of Hibernia K-18 oils plotted vs reservoir depth. Parameters are % sulphur (whole oil), Isoheptane value (2-methyl- and 3-methylhexane/1c3- 1t3- and 1t2-dimethylcyclopentanes), toluene/*n*-heptadecane and pristane/*n*-heptadecane. Numbers refer to the DSTs.

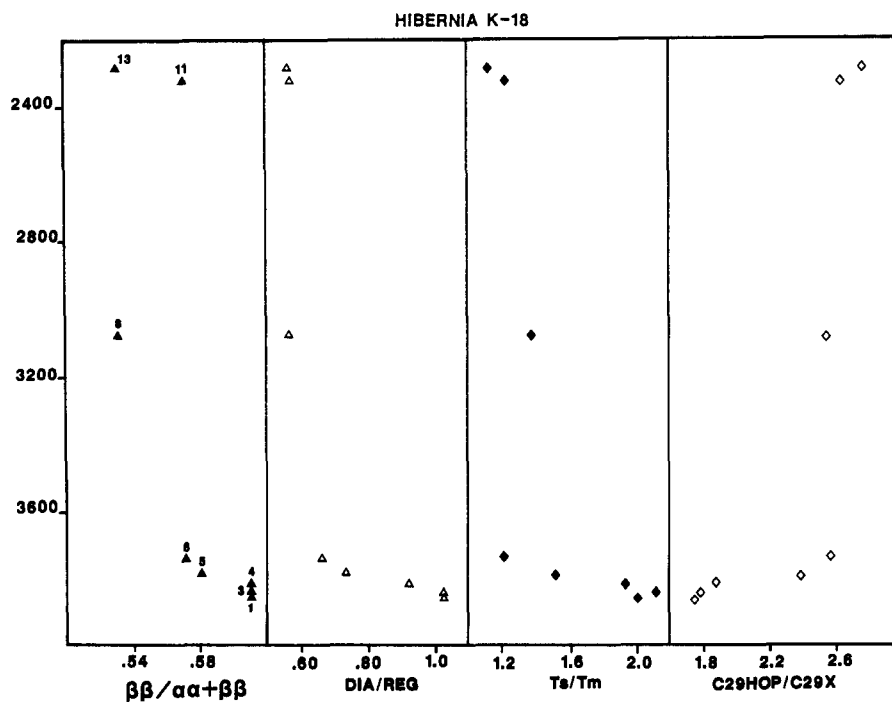


Fig. 5. Biomarker parameters from CAD GC-MS-MS analyses of Hibernia K-18 oils plotted versus reservoir depth.  $\beta\beta/\alpha\alpha+\beta\beta$  is  $5\alpha(\text{H})14\beta(\text{H})17\beta(\text{H})/5\alpha(\text{H})14\alpha(\text{H})17\alpha(\text{H})+5\alpha(\text{H})14\beta(\text{H})17\beta(\text{H})$  24-ethylcholestanes, DIA/REG is  $13\beta(\text{H})17\alpha(\text{H})$  20S diacholestane/ $5\alpha(\text{H})14\alpha(\text{H})17\alpha(\text{H})$  20R-cholestane, Ts/Tm is  $18\alpha(\text{H})$ -trisinorhopane/ $17\alpha(\text{H})$ -trisinorhopane and C29 HOP/C29X is  $17\alpha(\text{H})21\beta(\text{H})$ -norhopane/'X' an unknown C<sub>29</sub> pentacyclic terpane.

in the three oils from the lower Hibernia Formation. Other ratios of gasoline range hydrocarbons (not plotted) that show a similar trend with depth include  $nC_7$ /methylcyclohexane and 3-methylcyclopentane/benzene. The heptane index (Thompson, 1983) shows no significant variation with depth (Table 2). The final parameter plotted on Fig. 4 is  $pr/nC_{17}$ , measured from the saturate fraction gas chromatograms. This ratio decreases with depth in the Hibernia Formation. The  $ph/nC_{18}$  ratio displays a similar trend.

Some biomarker ratios obtained from CAD GC-MS-MS analyses are plotted versus depth in Fig. 5. These are the ratio of  $\alpha\beta\beta$  to  $\alpha\alpha\alpha$   $C_{29}$  steranes, the ratio of diasteranes to regular steranes, the ratio of the  $C_{27}$  trisnorhopanes Ts and Tm, and the ratio of

$17\alpha(H)$ -norhopane to a  $C_{29}$  compound "X" of unknown structure that elutes just after it (Fig. 6). These ratios also reveal little difference between oils in the Avalon, Catalina and uppermost Hibernia reservoirs. The three lower Hibernia samples (DSTs 1, 3 and 4) have similar values whereas in contrast to Fig. 4, DST 5 shows intermediate values for the parameters in Fig. 5. The ratio of  $\alpha\beta\beta$  to  $\alpha\alpha\alpha$   $C_{29}$  steranes shows the above trend less convincingly than the other parameters. Other biomarker ratios that display a similar trend include  $C_{29}$   $\alpha\alpha\alpha S/\alpha\alpha\alpha R$  steranes,  $C_{29}$   $\alpha\alpha\alpha$  20R sterane/hopane and the cracking of triaromatic steranes (Table 2). Some ratios that do not show any trend with depth, besides those source-related parameters mentioned previously, are  $17\alpha(H)$ -

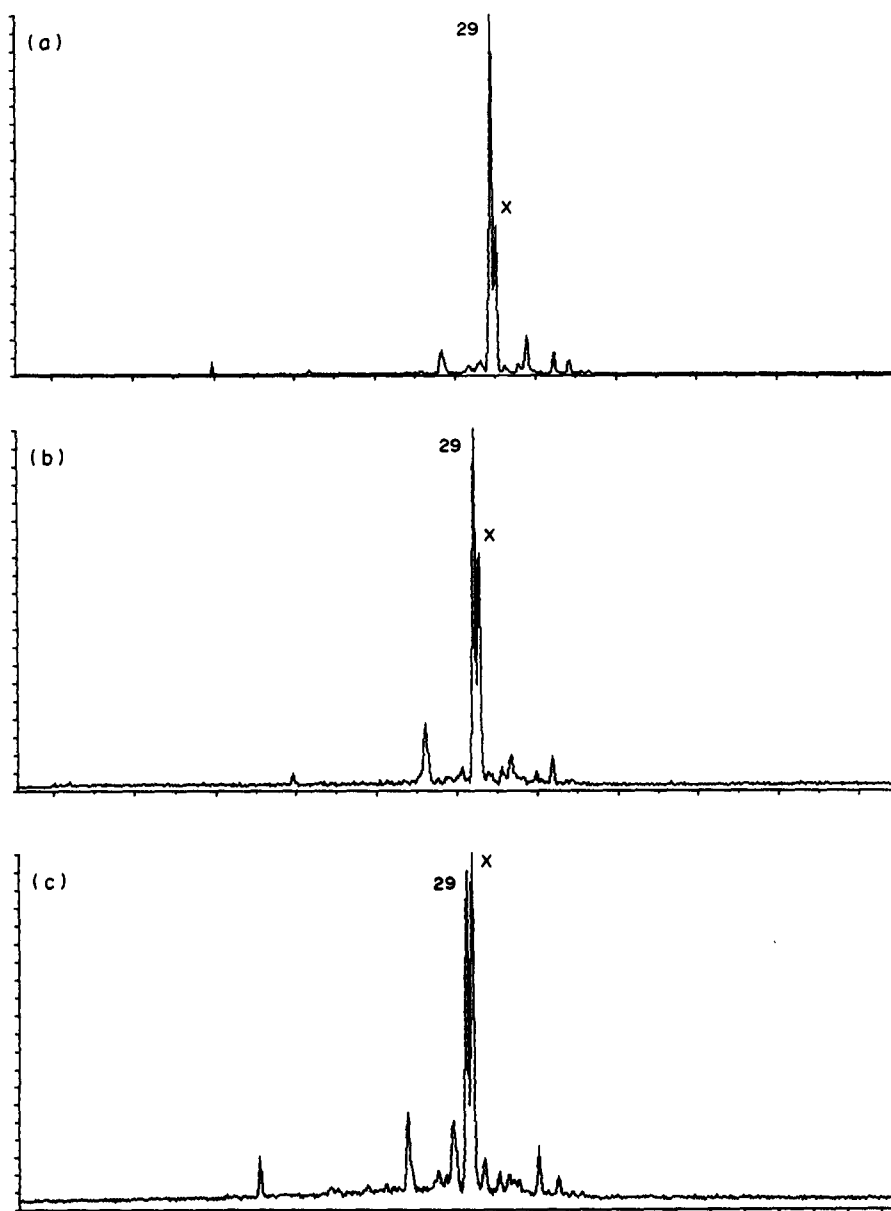


Fig. 6.  $m/z$  398  $\rightarrow$   $m/z$  191 transitions monitored by CAD GC-MS-MS analysis of Ben Nevis I-45 oils: (a) DST 10; (b) DST 9; (c) DST 1. 29 is  $17\alpha(H)21\beta(H)$ -hopane and X is unknown  $C_{29}$  pentacyclic terpane.



norhopane/17 $\alpha$ (H)-hopane, C<sub>23</sub> tricyclic terpane/17 $\alpha$ (H)-hopane (measured using SIM GC-MS), and the abundance of 4-methylsteranes relative to 4-desmethylsteranes. These parameters and others suggest a single source for the oils found in Hibernia K-18, the Egret member.

Many of the parameters plotted in Figs 4 and 5 or given in Table 2 are known to be influenced by maturity. These include the sulphur content (Tissot and Welte, 1984; Hughes *et al.*, 1985), the pr/nC<sub>17</sub> ratio (Tissot and Welte, 1984), and the ratios of  $\alpha\beta\beta$  to  $\alpha\alpha\alpha$  steranes (Mackenzie, 1984), of diasteranes to regular steranes and Ts to Tm although these latter two can also be affected by the lithology of the source rock (Seifert and Moldowan, 1978). The C<sub>29</sub> pentacyclic terpane, X, that elutes immediately after the 17 $\alpha$ (H)-norhopane is often annotated on published *m/z* 191 mass fragmentograms and its relative abundance has occasionally been used as a maturation parameter (Hughes *et al.*, 1985; Sofer *et al.*, 1986; Cornford *et al.*, 1988). In common with the results of these authors, we have observed in oils and source rock extracts from the Jeanne d'Arc Basin and elsewhere that compound X increases relative to 17 $\alpha$ (H)-norhopane with increasing maturity. However, like the ratio of diasteranes to regular steranes and Ts to Tm (Seifert and Moldowan, 1978; Hughes *et al.*, 1985), the value of this ratio is also influenced by some combination of source or lithology as the range of values varies between different families of oils.

Gasoline range data (Table 2) require more explanation. Both of Thompson's (1987) aromaticity parameters (benzene/*n*-hexane and toluene/*n*-heptane, Fig. 4) show an increase with depth for the Hibernia Formation reservoirs. The paraffinicity indices display contradictory trends. With depth, the isoheptane value increases (Fig. 4), F (*n*C<sub>7</sub>/methylcyclohexane) and C (*n*C<sub>6</sub> + *n*C<sub>7</sub>/cyclohexane + methylcyclohexane) slightly decrease and the heptane value does not show any trend (Table 2).

On the summary figure of aromaticity (B) vs paraffinicity (F) of Thompson (1987; Fig. 12) the Hibernia samples plot in the direction indicative of evaporative fractionation, rather than that of increasing maturation. However, the range of values displayed by these Hibernia oils is much less than in those groups of oils claimed by Thompson (1987, 1988) to have undergone evaporative fractionation. Although an increase in paraffinicity is the general trend with increasing maturity (Thompson, 1983), a slight increase in aromaticity does occur in mature oils, which are defined by Thompson (1987) as those with F values of between 0.8 and 1.5. The Hibernia K-18 oils fall within this range and hence the increase in aromaticity can be attributed to increasing maturation. The ambiguity of the gasoline range hydrocarbon parameters may be because there is only a small difference in maturity between the samples or because some of these ratios are more affected by source than the results of Thompson (1983, 1987) indicate.

## Discussion

It is evident from Figs 4 and 5 that there are subtle differences between the oils in the different reservoirs in Hibernia K-18. Unlike some other wells in the Jeanne d'Arc Basin (such as Ben Nevis I-45, discussed later), there is no evidence that strongly suggests a contribution from a source rock other than the Egret Member. The compositional variation between the upper and lower Hibernia K-18 oils is most easily explained by maturation changes. The relative maturities of the oils do not reflect the difference in their present day reservoir depths. There is little change in most parameters over the 1500m interval encompassing the Avalon, Catalina and the upper Hibernia reservoirs, followed by a relatively rapid increase over a 100 m interval in the lower part of the Hibernia Formation.

Generally, the Hibernia K-18 oils are similar and it is reasonable to assume, as suggested by previous workers (Creaney and Allison, 1987; Brown *et al.*, 1989; von der Dick *et al.*, 1990) that some time in the past all the reservoir units received the same pulse of oil via faults. This would be the most logical explanation for why DST 6 and the Catalina and Avalon oils are so similar. However, the results of this study suggest that a more recent process is starting to overprint this initial migration episode. Hydrocarbons more mature than those originally present appear to be migrating into the lower Hibernia reservoir sands. The source of these hydrocarbons is probably the Egret member which is about 1000m below the Hibernia Formation in this part of the basin. Biomarker and Rock-Eval data indicate that the source rock is of greater maturity than all the K-18 oils (von der Dick *et al.*, 1990; Fowler, unpublished results). The Egret member is presently part of an overpressured system with the generation of hydrocarbons from this interval a possible cause for the existence of the overpressuring (McAlpine, 1989).

The source rock is presently at its greatest depth of burial and maturity. It appears therefore that more recently generated hydrocarbons are leaking from the overpressured zone into the lower Hibernia Fm. reservoirs. Vertical movement of fluids must be uninhibited between the three lowermost reservoir formations (DSTs 1, 3, 4) as these are of very similar maturity (Figs 4 and 5). Figure 4 suggests that DST 5 is also closely connected to the lower oils but Fig. 5 indicates that its biomarker parameters are nearer to those of the upper oils. This could be an indication of the preferential movement of lighter hydrocarbons between DSTs 4 and 5. Vertical communication between the stacked fluvial channel sands of the Hibernia Formation has been considered possible because they are each thought to have been incised into pre-existing channels (Canada-Newfoundland Offshore Petroleum Board, 1986). On the other hand, DST 6 is located within thinner bedded and finer-grained sandstones of the upper part of the Hibernia

Formation that have been interpreted as the product of a shallow marine, upper delta-front environment (Brown *et al.*, 1989). Such sandstones are less likely to be in hydraulic communication with each other or with the thicker bedded fluvial sands beneath them. The more recently generated hydrocarbons have not migrated into DST 6 and the Catalina and Avalon reservoirs either because the faults that were previously conduits for the transport of hydrocarbons are now sealed or, less likely, because hydrocarbons are migrating only very slowly up into the upper reservoirs.

In conclusion, our results indicate that at present oil is migrating into the lower Hibernia Formation reservoirs from the overpressured zone, and that there is no direct conduit from these lower sands to the upper reservoir in the Hibernia Formation that contains DST 6 and to the Avalon and Catalina formations.

#### BEN NEVIS I-45

The Ben Nevis I-45 well was drilled in 1980 at the opposite end of the trans-basin fault trend, about 40 km south east of the Hibernia structure (Fig. 1). Oil was tested at several intervals in this well. The most important test (DST 1) produced 1596 barrels per day (bbl d<sup>-1</sup>) of 38.9 API oil from an overpressured zone at a depth of 4535–4550m in the Hebron Well Member of the Hibernia Formation. The only other significant test produced 261 bbl d<sup>-1</sup> of 48.1

API oil from 2891 to 2894m just below an unconformity at the top of the Eastern Shoals Formation (DST 9). Minor quantities of oil were also obtained from a second test in the overpressured Hebron Well Member (DST 3), and from two tests in the Ben Nevis Formation.

Data from the analyses of the Ben Nevis oil samples are shown in Table 3. The Ben Nevis oils exhibit two trends with increasing depth: increasing maturity and an increasing contribution from a second source rock. Figures 7 and 8 illustrate the maturity and source trends, respectively.

#### Maturity

The Ben Nevis I-45 oils were recovered over a considerable depth range (2130m). It is therefore not surprising that they show a wide range of maturities. This is indicated both by gross chemistry (e.g. API gravity, %S and sat/arom) and by molecular parameters.

The relative maturities of the oils as indicated by biomarker indices, are consistent with their present-day reservoir depths. All the parameters suggest that the DST 10 and 11 oils are of similar maturity but considerably less mature than those from DST 1 and 3. DST 9 has an intermediate maturity. However, parameters that are considered to be only affected by maturity such as the ratio of R to S  $\alpha\alpha$  steranes and the triaromatic cracking ratio show DST 9 to be closer to the maturity of the Ben Nevis Formation samples than the Hibernia Formation samples as

Table 3. Geochemical data from the analysis of oil samples from Ben Nevis I-45. Table headings not used in Table 2 are explained in footnotes

DST	Formation	Interval (m)	API	GOR <sup>a</sup> ft <sup>3</sup> /bbl	%S	Sat/Arom <sup>b</sup>	I	H	Tol/nC <sub>7</sub>	nC <sub>17</sub> /nC <sub>27</sub> <sup>c</sup>	pr/ph	C <sub>29</sub> S/R	C <sub>29</sub> ββ/αα+ββ
11	Ben Nevis	2420-2423	24.8		0.64	1.38	1.76	22.97	0.81	4.74	1.26	0.73	0.56
10	Ben Nevis	2428-2446	20.3		0.71	1.26				4.63	1.12	0.75	0.56
9	Eastern Shoals	2890.5-2894	48.1	39586	0.50	3.08	2.20	25.79	0.90	7.18	1.62	0.77	0.61
3	Hibernia	4426-4438			0.15	1.82	1.45	19.26	1.05	3.06	1.56	0.94	0.68
1	Hibernia	4535-4550	38.9	7520		2.54	2.14	26.22	0.63	3.54	2.11	1.28	0.66

DST	C <sub>27</sub> D/ααR	%C <sub>27</sub>	%C <sub>28</sub>	%C <sub>29</sub>	27/29 <sup>d</sup>	4-Me/St <sup>e</sup>	Ts/Tm	29/X	Triaromatic steranes				ppm steranes <sup>f</sup>	ppm hopanes <sup>g</sup>
									%26 <sup>f</sup>	%27 <sup>f</sup>	%28 <sup>f</sup>	cracking		
11	0.42	48	21	31	1.58	1.31	1.19	2.34	21	34	45	0.08	1043	2179
10	0.41	48	22	30	1.58	1.32	1.10	2.42	21	34	45	0.08		
9	0.64	35	23	42	0.83	1.02	1.87	1.54	27	29	44	0.20	243	391
3	0.79	29	23	48	0.82	0.83	2.15	1.10	17	35	48	0.63		
1	0.82	34	20	46	0.74	0.71	2.85	0.95	18	34	48	1.05	779	2222

<sup>a</sup> Gas to oil ratio in cubic feet gas per barrel of oil

<sup>b</sup> Ratio of C<sub>15</sub><sup>+</sup> saturate and aromatic fractions after column chromatography

<sup>c</sup> C<sub>17</sub>/C<sub>27</sub> n-alkanes

<sup>d</sup> Ratio of C<sub>27</sub> to C<sub>29</sub> 4-desmethylsteranes

<sup>e</sup> Ratio of 4-methylsteranes to 4-desmethylsteranes

<sup>f</sup> Normalised proportion of C<sub>26</sub>:C<sub>27</sub>:C<sub>28</sub> triaromatic steranes

<sup>g</sup> Concentration in ppm of whole oil. DSTs 9 and 11 measured on saturates distilling above 210°C and then calculating for whole oil. DST 1 measured on "total saturates fraction". Loss of light ends occurred during fractionation, therefore true figure probably lies between this and half this figure (based on comparison of distillation results of other oils of this API gravity).

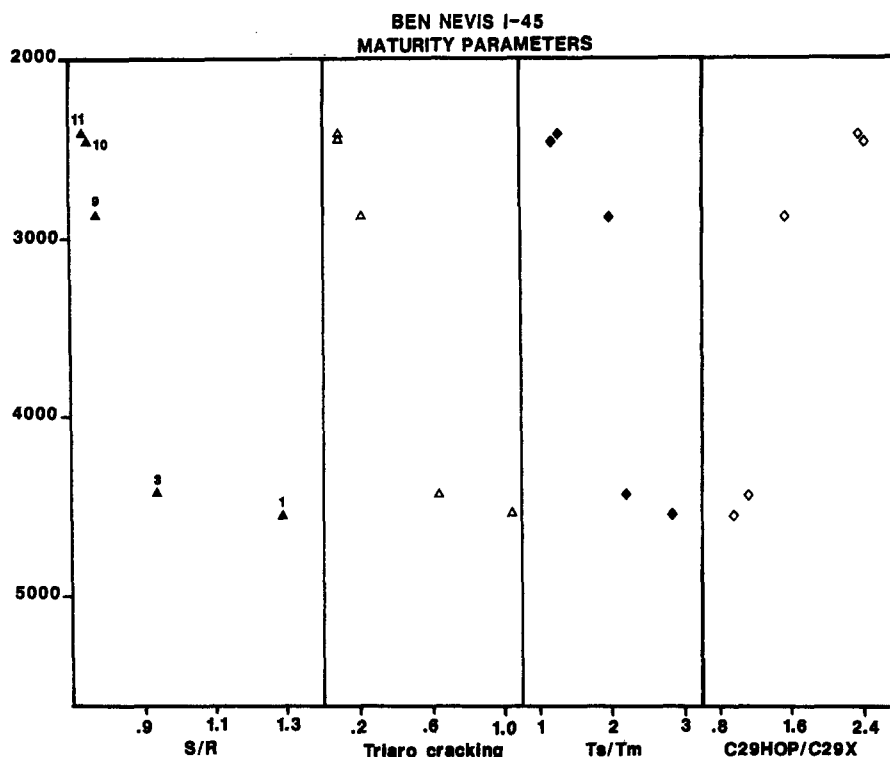


Fig. 7. Biomarker parameters from GC-MS analysis of Ben Nevis I-45 oils, chosen to indicate maturity, plotted vs reservoir depth. S/R is the ratio of  $5\alpha(\text{H})14\alpha(\text{H})17\alpha(\text{H})$  20S and 20R 24-ethylcholestanes. Triaro cracking is the triaromatic cracking ratio ( $\text{C}_{20} + \text{C}_{21}/\text{C}_{25-28}$ ), Ts/Tm is  $18\alpha(\text{H})$ -trisnorhopane/ $17\alpha(\text{H})$ ,  $21\beta(\text{H})$ -norhopane and C29 HOP/C29X is  $17\alpha(\text{H})21\beta(\text{H})$ -norhopane/'X' an unknown  $\text{C}_{29}$  pentacyclic terpene.

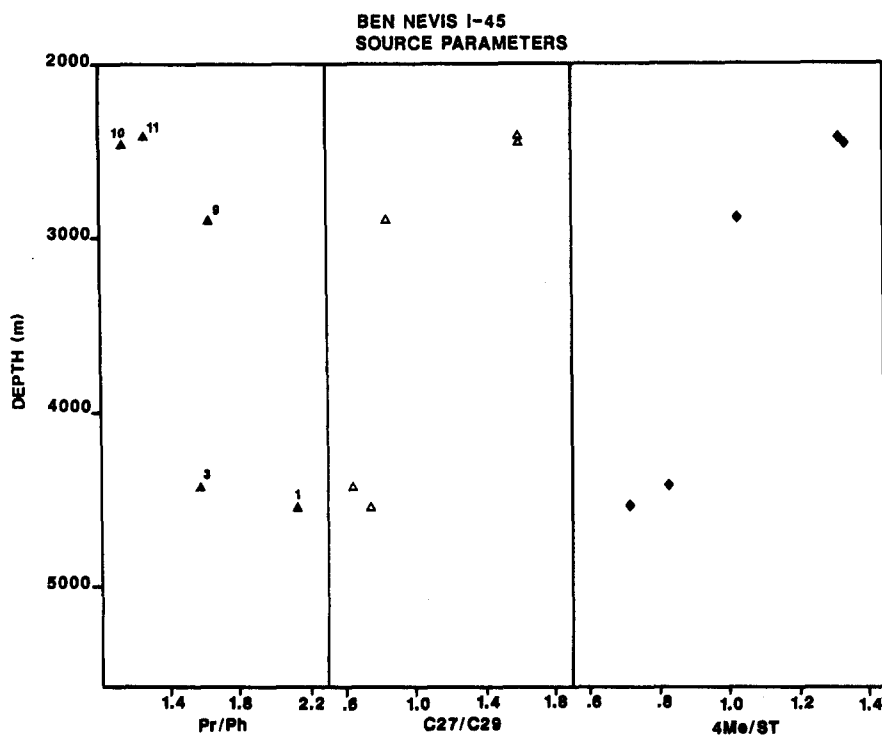


Fig. 8. Biomarker parameters chosen to indicate changes in source of Ben Nevis I-45 oils with depth. pr/ph is pristane/phytane,  $\text{C}_{27}/\text{C}_{29}$  4-desmethyl steranes and 4 Me/ST is the ratio of 4-methylsteranes/4-desmethylsteranes.

might be expected from their relative depths. Parameters such as the ratio of Ts to Tm and  $17\alpha(\text{H})$ -norhopane to  $X$  that are also affected by source rock character place DST 9 closer to the Hibernia Formation oils, possibly reflecting a different source. API gravity, GOR, sat/arom and many of the gasoline-range hydrocarbon indices suggest DST 9 is more mature than DST 1, contradicting the biomarker evidence (Table 3). An explanation for this apparent discrepancy is given below. The gasoline parameters generally show a poor correlation with the biomarker parameters for maturity, possibly because there are competing processes that may affect their occurrence or concentration in this well.

#### Source

The ratio of pristane to phytane (Fig. 8) increases with depth. Egret Member extracts and most Jeanne d'Arc Basin oils have pr/ph values of less than one to just over one. The value of 2.11 shown by DST 1 is far outside of this range. Pristane to phytane values are often higher in sediments deposited under relatively oxic conditions with a high terrestrial contribution (Powell and McKirdy, 1973; Didyk *et al.*, 1978).

DSTs 1 and 3 have much lower concentrations of  $C_{27}$  relative to  $C_{29}$  steranes than the other Ben Nevis I-45 samples (Fig. 8) and most other Jeanne d'Arc Basin oils. This difference in the regular sterane carbon number distributions for Ben Nevis oils was also observed using a ternary diagram of  $C_{27-29}$  regular sterane abundance by von der Dick *et al.* (1989). Although interpretation of the significance of the relative abundance of  $C_{27}$  and  $C_{29}$  steranes must be treated with caution (e.g. Volkman, 1986), the higher abundance of  $C_{29}$  steranes in the Hibernia Fm. reservoirs is thought to indicate that the second source rock had a greater terrestrial contribution (Huang and Meinschein, 1979). Interestingly, no change was observed in the relative abundance of  $C_{26-28}$  triaromatic steranes with depth.

The ratio of 4-methylsteranes to desmethyl steranes is much lower for DSTs 1 and 3 than for DSTs 10 and 11 (Fig. 8). This indicates that dinoflagellates were less important contributors to the organic matter of the second source rock. In addition the distribution of  $C_{30}$  4-methylsteranes shows a major change. The Ben Nevis Fm. oils, in common with most other Jeanne d'Arc Basin oils contain much higher amounts of the 4,23,24-trimethylcholestane (dinosterane) isomers than the 24-ethyl-4-methylsteranes (Fig. 9). In DST 1 the two types of  $C_{30}$  4-methylsteranes are in about equal abundance (Fig. 9). The 24-ethyl-4-methylcholistanes have been found to predominate in non-marine sediments and their derived oils whilst marine sediments and oils contain more 4,23,24-trimethyl-steranes (Summons *et al.*, 1987; Goodwin *et al.*, 1988). This again suggests that the source rock contributing to the Hibernia Fm. oils in Ben Nevis I-45 is dominated by terrestrial organic matter.

Additional evidence for a contribution from higher land plant material to the lower DST 1 and 3 oils is seen in their higher abundance of  $C_{20+}$   $n$ -alkanes compared to the other samples (Table 3;  $nC_{17}/nC_{27}$ ) despite their greater maturity.

The above data indicate that the Hibernia Fm. oils, and to a lesser degree the Eastern Shoals sample have received a contribution from a source rock other than the Egret Member. Although the parameters in Fig. 8 define a trend with depth which somewhat resembles that shown by the maturity parameters in Fig. 7 this is considered coincidental. Comparison with other wells in the Jeanne d'Arc Basin containing oils with a wide range of maturities indicates that the three ratios in Fig. 8 do not vary much with maturity, and for most wells show a relatively narrow range of values. The evidence therefore indicates that the major source of the oils in the Hibernia Formation at Ben Nevis I-45 contained predominately terrestrial organic matter and was deposited under more oxidising conditions than the Egret Member.

#### Discussion

The oils from the Ben Nevis Fm. (DSTs 10 and 11) are very similar to most other Jeanne d'Arc oils and are compatible with being solely sourced from the Egret member which was not penetrated in Ben Nevis I-45. Its depth of burial in this part of the basin should ensure it to be at least in the later stages of the oil window (McAlpine, 1989). The hydrocarbons in these reservoirs therefore either were generated early and migrated into these shallow reservoirs via faults shortly afterwards or, if they were generated more recently, they must have migrated laterally over some distance.

Biomarker data indicate that the Eastern Shoals oil (DST 9), has a maturity intermediate between those of the Ben Nevis and Hibernia formations. However, it has a greater API gravity, saturate to aromatic ratio and gas to oil ratio than the deeper oil from DST 1. Gasoline range parameters also suggested it was more or about the same maturity as DST 1. DST 9 was taken from an interval immediately below an unconformity in the uppermost part of a 100 m sandstone unit at the top of the Eastern Shoals Fm. (K. D. McAlpine, personal communication). If the shales above the unconformity are acting as the seal, this test would have preferentially sampled the lighter hydrocarbons in Eastern Shoals reservoir. Hence, this oil could have a higher API gravity, a higher gas to oil ratio and a lower concentration of biomarkers (Table 3) than a much deeper oil but actually be of lower maturity. The possibility of "geological contamination" by the biomarkers of another formation cannot be ruled out because of their low concentration in this oil. However, the biomarkers present do give a maturity that is about what would be expected for an oil at this depth (i.e. between those of the Ben Nevis and Hibernia formation samples) suggesting that this has not occurred.

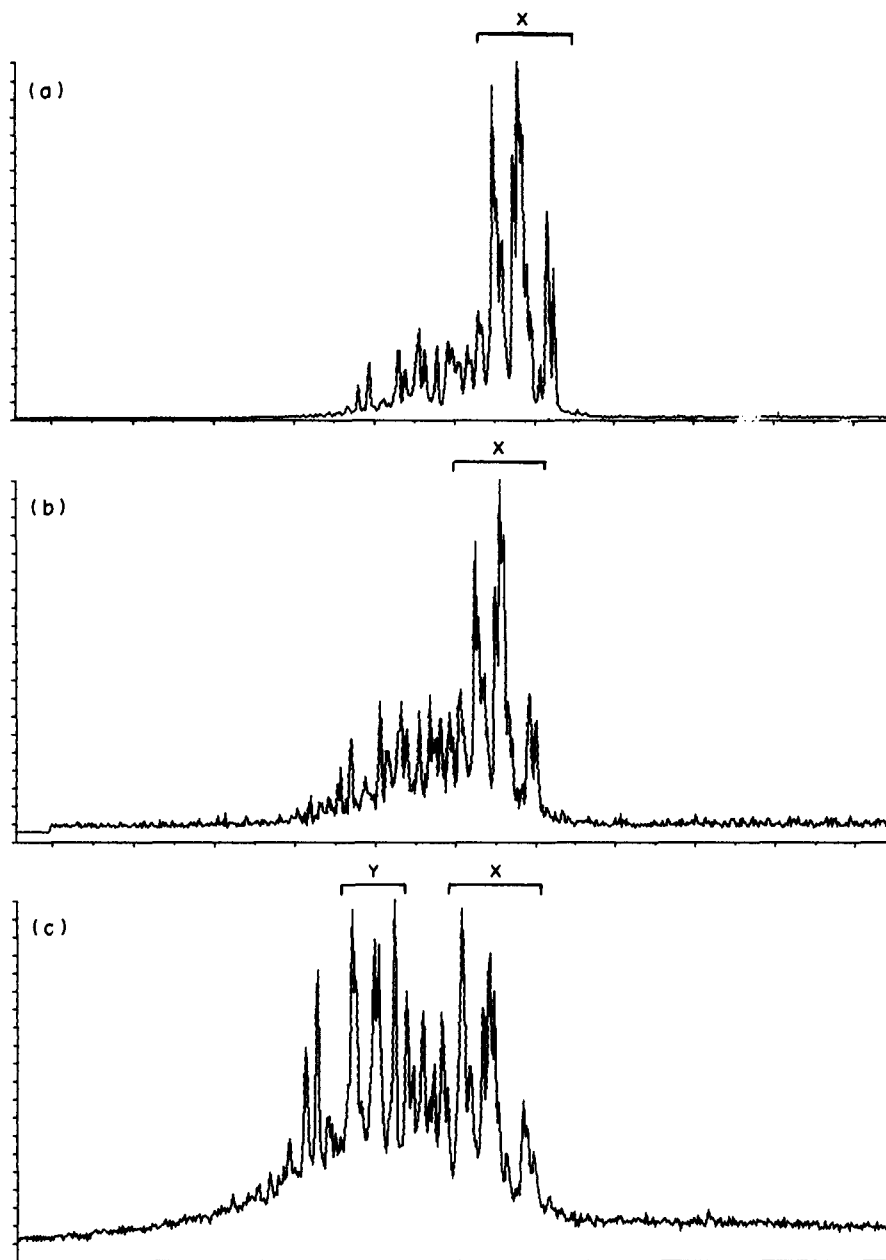


Fig. 9.  $m/z$  414  $\rightarrow$   $m/z$  231 transitions monitored by CAD GC-MS-MS analysis of the Ben Nevis I-45 oils: (a) DST 10; (b) DST 9; (c) DST 1.  $X$  are 4, 23, 24-trimethylcholestanes and  $Y$  are 24-ethyl-4-methylcholestanes. Note increased abundance of 24-ethyl-4-methylcholestanes relative to 4, 23, 24-trimethylcholestanes in DST 1.

As discussed above, the biomarker signatures of the Ben Nevis Hibernia Formation oils are very different from most other Jeanne d'Arc Basin oils suggesting that they are not sourced from the Egret Member. Further support for the existence of a second source rock in the Jeanne d'Arc Basin, besides the Egret Member, is that other oils have been found with some of the same geochemical characteristics. These include the oils from Fortune G-57 and West Ben Nevis B-75. There is evidence that indicates the lowermost oil in Hebron I-13 (DST 1) also has a contribution from a terrestrially dominated source

rock (Snowdon and Krouse, 1986). Ben Nevis I-45 DST 1 shows the highest terrestrial contribution of these oils. All these oil accumulations are located geographically in one small area of the Jeanne d'Arc Basin (Fig. 1). They are also all in close proximity to the Trinity Fault (A. Edwards, personal communication) which suggests this fault may be acting as migration pathway or control for these oils.

The identity of the second source rock has not yet been confirmed. Two candidates have been proposed. von der Dick *et al.* (1989) suggested that "Ben Nevis" type oils received a contribution from a shale

unit of Tithonian age in the Jeanne d'Arc Formation whilst Fowler *et al.* (1988) thought that an interval of Callovian–Oxfordian age in the Voyager Formation was the possible source. No other proven good potential source rocks have been identified in the Jeanne d'Arc Basin and even these, which are mostly dominated by Type III terrestrially derived organic matter, have nowhere near the hydrocarbon potential of the Egret Member, which contains marine-derived Type II–I organic matter.

The oils that show a terrestrial contribution are all in close proximity to the Trinity fault. The Trinity fault is unique in that it represents the southern termination of the trans-basin fault system which is the major play within the Jeanne d'Arc Basin. The Trinity fault is therefore thought to represent the most likely structural control on the migration of hydrocarbons from the second source rock, whatever it is.

### CONCLUSIONS

(1) Collision Activated Decomposition (CAD) GC–MS–MS provides more reliable biomarker data than do most other forms of GC–MS analysis, especially when there are chromatographically co-eluting compounds interfering with the compounds of interest.

(2) Biomarker and other geochemical data can provide important additional information on the history of hydrocarbon migration beyond that which can be obtained from geological considerations alone. This has been demonstrated with the analysis of oils from stacked reservoirs over large depth intervals from two wells drilled in the Jeanne d'Arc Basin, offshore Eastern Canada.

(3) All the oils at Hibernia K-18 are sourced from the Kimmeridgian-aged Egret Member. Our results are consistent with the suggestions of previous workers that at some time in the past all the reservoirs received the same pulse of hydrocarbons from this source rock. Vertical movement occurred via faults as the composition of the oils is very similar over a depth range of 1500m. In the lowermost Hibernia Fm. reservoirs (DSTs 1, 3, 4 and 5) the signature of this event is being geochemically overprinted by the migration of more recently generated and more mature hydrocarbons. These recently generated hydrocarbons have not yet migrated into the upper Hibernia Fm. sand (DST 6) and up into the Catalina and Avalon Formation reservoirs. This suggests that the faults previously operating for hydrocarbon movement into these reservoirs are now closed.

(4) With increasing depth of reservoir at Ben Nevis I-45, the oils show an increase in maturity and in the proportion of hydrocarbons derived from a source rock other than the Egret member which contains predominately terrestrial organic matter. Two minor oil shows in the Ben Nevis Formation appear to have been solely sourced from the Egret member. Their

maturity compared to that of the Egret member today in this area indicates that they migrated vertically approximately 3000m soon after generation or alternately that they have migrated laterally over a long distance. Biomarkers indicate that the Eastern Shoals Formation oil has a minor contribution from the second source rock and an intermediate maturity between those of the Ben Nevis and Hibernia Formation oils in accordance with its reservoir depth. The oils from the Hibernia Formation are sourced predominately from the second source rock. Oils with similar characteristics are found in other wells in this area of the basin. All of these wells are in close proximity to the Trinity Fault suggesting that this fault may control the migration of hydrocarbons from the second source rock.

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