

Dysfunctionalism in the Williston Basin: the Bakken/mid-Madison petroleum system

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ABSTRACT

Analyses of fifteen oils produced from fractured shales of the Upper Devonian and Lower Mississippian Bakken Formation in the Williston Basin were compared to the same analyses for eighteen Williston Basin oils produced from conventional reservoirs in the middle of the Lower and Upper Mississippian Madison Group. All oils came from the U.S.A. portion of the Williston Basin. These comparisons demonstrate that, contrary to previous studies and the models developed from those studies, the Bakken and mid-Madison oils are different oil families from different source rocks. Our findings thus agree with recent work on the Canadian side of the Williston Basin (Osadetz *et al.*, 1992).

Within the saturated hydrocarbons (HCs) the Bakken oils are more naphthenic, less paraffinic (especially less waxy), have different n-paraffin and isoprenoid-HC profiles, and have different compound ratios for "generic" saturated HCs, as compared to the Madison oils. Within the aromatic HCs the mid-Madison oils have an unusual trimethylnaphthalene distribution, high concentrations of dibenzothiophenes and alkylated variants thereof, and different aromatic-HC peak distributions in general (and thus different aromatic-HC compound ratio plots), as compared to the Bakken oils. Because of wide maturity ranges in both oil sets, biomarkers were of limited utility as source-facies indices and thus as correlation tools.

We have not yet found any oil generated by the Bakken shales or any mixing of Bakken and Madison oils in a Madison reservoir. We believe the range of variation in our correlation indices to be too large among the Madison oils for these oils to have a single source rock. For this and other reasons, we hypothesize that the Madison oils are from separate source rocks interbedded with the different mid-Madison reservoirs in the basin, rocks which appear to have the same, or very similar, depositional environments. Thus, the original Bakken/mid-Madison petroleum system appears dysfunctional.

The results of this study have significant implications for: 1) models of both oil expulsion and deep-basin fluid flow; and 2) the possible existence of very large oil-resource bases in mature, organic-rich, fractured, fine-grained rocks in petroleum basins worldwide.

RÉSUMÉ

Des analyses de quinze pétroles, produits de shales fissurés de la Formation Bakken du Dévonien supérieur et Mississippien inférieur du Bassin Williston, sont comparées aux mêmes analyses effectuées pour les dix-huit pétroles du bassin Williston produits de réservoirs traditionnels au mi-point du Mississippien inférieur et supérieur du Groupe Madison. Tous les pétroles proviennent de la partie américaine du bassin Williston. Ces comparaisons démontrent, que contrairement aux études déjà effectuées, et des modèles tirés de ces études, les pétroles du Bakken et du Madison moyen sont des familles différentes provenant de différentes roches mères. Ainsi, nos trouvailles concordent avec les travaux récents sur le bassin Williston du côté canadien (Osadetz *et al.*, 1992).

En ce qui à trait les hydrocarbures saturés (HC), si on compare les pétroles Madison aux pétroles Bakken ces derniers sont plus naphthéniques, moins paraffiniques (surtout moins cireux), ils possèdent différents profils de n-paraffine et d'hydrocarbure isoprenoïde et différents rapports composés "génériques" d'hydrocarbures saturés. En ce qui à trait les hydrocarbures aromatiques, si on compare ces pétroles à ceux du Madison moyen ces derniers possèdent une distribution inhabituelle de trimethylnaphtalène, des concentrations élevées de dibenzothiophènes et des variantes d'alkylation et en général différentes distributions maximum d'hydrocarbures aromatiques (et par conséquent, différentes restitutions de rapports composés d'hydrocarbures aromatiques). En résultat des vastes écarts de maturité pour les deux séries de pétroles, les dépistages biologiques ont eu une utilité limitée comme indice pour l'origine d'un faciès et comme outils de corrélation.

Aucun pétrole généré par les shales de Bakken et aucun mélange de pétroles Bakken et Madison n'a été trouvé dans les réservoirs Madison. Nous croyons que l'écart des variations avec nos indices de corrélations est trop important

pour les pétroles Madison pour que ceux-ci possèdent une seule roche mère. Pour cette raison et bien d'autres, l'hypothèse est que les pétroles Madison proviennent de roches mères distinctes interstratifiées avec les différents réservoirs du Madison moyen du bassin, les roches qui semblent être de même ou presque de même environnement de dépôts. Ainsi, le système de pétrole Bakken/Madison moyen semble être dysfonctionnel.

Les résultats de cette étude ont des conséquences importantes pour: 1) les modèles d'expulsion de pétrole et d'écoulement de fluide en bassin profond; et 2) l'existence de ressources de pétrole très importantes dans les bassins, à l'échelle internationale; matures, organiquement riches, fracturés, de roches à grains fins.

Traduit par Marie Louise Tomas

INTRODUCTION

In a pioneering petroleum-geochemical study, Williams (1974) concluded that the shales of the Upper Devonian and Lower Mississippian Bakken Formation were the source of the oils produced from the limestones in the middle of the Lower and Upper Mississippian Madison Group in the Williston Basin. Based on Williams' (1974) conclusions, Dow (1974) and Meissner (1978) postulated oil expulsion from the Bakken shales, vertical migration via fractures, and accumulation in the mid-Madison reservoirs. This early work is a foundation for current models of oil expulsion and accumulation. Many subsequent investigators have referenced and employed Williams' (1974) Bakken/mid-Madison oil-source correlation (and the subsequent oil expulsion and accumulation models) to research in other petroleum basins. Indeed, Dow's (1974) early synthesis was a foundation for the present-day "petroleum-system" (Magoon and Dow, 1991).

Osadetz *et al.* (1992), Osadetz and Snowdon (*in review*) and Osadetz *et al.* (*in review*) extensively studied many rocks and oils from the Canadian portion of the Williston Basin and concluded that the mid-Madison oils there had not been sourced by the Bakken shales (Osadetz *et al.*, 1992). (Canadian oil deposits make up 75-80% of the discovered, recoverable oil in the Williston Basin.) Price and LeFever (1992) reported that two large studies by U.S. major oil companies also concluded that the Bakken shales had not sourced the Williston Basin mid-Madison oils. Price and LeFever (1992) also analyzed three mid-Madison oils and three Bakken oils and demonstrated that the two oil sets apparently were different oil families. Price *et al.* (1984) attempted to correlate 28 Madison Williston Basin oils to 40 Bakken shale extracts and to bitumens generated by aqueous-pyrolysis of Bakken shale at nine different reaction temperatures. However, they could not correlate any of these Bakken shale bitumens to Madison oils using isoprenoid hydrocarbon (HC) profiles as a correlation tool. Price *et al.* (1984, p. 111) erroneously dismissed this lack of correlation as, "...due to the fact that isoprenoid hydrocarbon analysis is of no, or only limited, utility in oil-source rock correlations in some instances."

In this study, we interrelate with the work of Osadetz and coworkers and expand on the limited sample base and limited analyses of Bakken and Madison oils presented in Price and LeFever (1992). Our study hinges on a unique set of oils produced directly from a source rock. These oils allow a direct comparison of conventionally reservoir oils with oils generated by, but not yet expelled from, the hypothesized source rock of the conventionally reservoir oils. Price and Clayton

(1992) noted that unambiguous oil-source rock correlations are not always achieved using source rock bitumen. However, unambiguous oil-oil correlations, with discrimination of different oil families, are routinely realized.

Whether or not the Bakken shales sourced the Madison oils is more than academic. The answer to this question has fundamental implications for models of oil expulsion, secondary migration and accumulation.

RESULTS

OIL LOCATIONS AND GROSS CHARACTERISTICS

Geographic locations, well and field names, and gravities of the oils of this study are given in Figure 1 and in Tables 1 and 2. The eighteen Madison oils were picked for wide geographic coverage of the Williston Basin from twenty-eight Madison oils previously supplied by Jack Williams, Amoco Research Center, Tulsa, Oklahoma. Fourteen of the Bakken oils were supplied by operators on the U.S.A. side of the Williston Basin. Jack Williams also supplied one Bakken oil (N8-85, Hofflund Field). In this paper we use the original Amoco identification numbers (N8 for North Dakota, or M8 for Montana, followed by a one to three digit number) and the original North Dakota Geological Survey (NDGS) well identification numbers (a four or five digit number, possibly followed by an "A"). The "A" designates Bakken oils east of, or along, the Nesson Anticline. The other Bakken oils, without an "A", are from the so-called horizontal drilling "fairway area" of southern McKenzie and northern Billings Counties, North Dakota.

Figure 2 is a triangular plot of C_{15+} compound composition (experimental conditions are in the Appendix) for the Bakken and Madison oils we analyzed. The Bakken oils (crosses and dashed line) form a tight field and have low amounts (15% or less) of resins plus asphaltenes. The Madison oils (dots and solid line) form a larger field which significantly overlaps the Bakken envelope. As discussed directly below, the higher content of resins plus asphaltenes in some of the Madison oils is largely due to low maturity and has no bearing to correlation of oil families.

OIL MATURITIES

Wenger and Price (1991) and Price and Wenger (1992) based on aqueous-pyrolysis experiments on six different rocks of various organic matter types, including the Bakken shale, found that ratios of isoprenoid HCs to their adjacent n-paraffins (i-C/n-C ratios) were excellent maturity indices to track increases in experimental temperatures (maturity). Price has

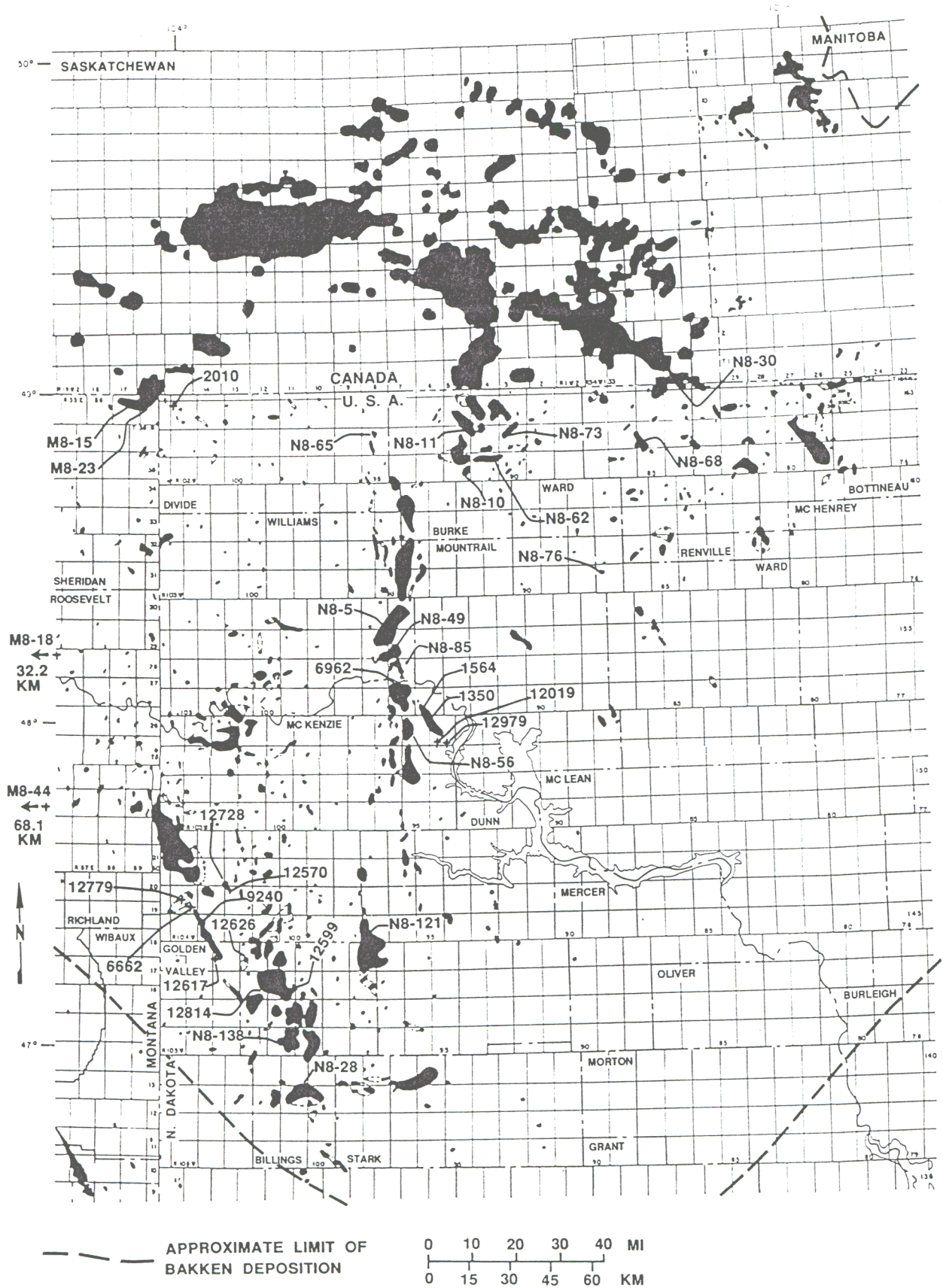


Fig. 1. Map of the principal oil-producing areas of the Williston Basin (U.S.A. and Canada) excluding the Poplar Field and Cedar Creek Anticline (Montana, U.S.A.). All N8-, M8- and four and five digit numbers are oil locations except (NDGS)-2010 (Divide County, North Dakota) which is discussed in the text. Richey (M8-44) and East Poplar (M8-18) are off the map due west of the locations shown in Figure 1. Oil field locations are given in Tables 1 and 2. Dashed lines show approximate limit of deposition of the Bakken shale.

Table 1. Vita on the mid-Madison oils of this study. S-T-R is section, township and range. Producing depths are given in feet and not metres so that a specific identifier will not be lost in numerical conversion. Oil gravity is given in API units (and not specific) to retain a specific identifier. The second API gravity is the number originally reported to NDGS for that well. The first numbers are measurements made for the Price *et al.* (1984) study. "I.D." is identification. Gp. is Group.

Field	Well	Corner S-T-R	County State	Producing: Unit and Depth (in Feet)	API Gravity	AMOCO I.D. Number
Beaver Lodge	#1 Aurthur Iverson	NESE 2 155N 96W	Williams, N.D.	Madison Gp. Rival beds 8,350-8,390	41.0°/43.4°	N8-5
Foothills	#1 Gilt Edge Realty Co.	NWSW 25 161N 92W	Burke, N.D.	Madison Gp. Rival beds 7,180-7,212	39.0°/36.2°	N8-10
Rival	#1 Village of Lignite	NENW 12 162N 92W	Burke, N.D.	Madison Gp. Rival beds 6,248-6,259	38.6°/39.6°	N8-11
Scoria	#1 Scoria Unit	NENE 10 139N 101W	Billings, N.D.	Madison Gp. Fryburg beds 9,213-9,258	41.7°/40.0°	N8-28
Elmore	#2 Aubrey Harkness	SWSE 27 164N 84W	Renville, N.D.	Madison Gp. Sherwood beds 3,957-3,978	33.5°	N8-30
Capa	Unknown	4 154N 96W	Williams, N.D.	Madison Group.	40.4°	N8-49
Hawkeye	Unknown	152N 95W	Williams, N.D.	Madison Group.	38.6°	N8-56
N.E. Foothills	#1 Mabel L. Doe	SWSW 11 161N 91W	Burke, N.D.	Madison Gp. Midale beds 6,420-6,427	35.8°/36.0°	N8-62
Baukol Wildcat	#1 Baukol-Noonan Inc.	10 162N 95W	Divide, N.D.	Madison Group.	39.0°	N8-65
Mouse River Park	#1-A Clarence Lund	SWNW 33 162N 85W	Renville, N.D.	Madison Gp. Sherwood beds 4,890-4,896	28.6°/30.0°	N8-68
Woburn	#1 Gehrke Heirs	SESW 162N 90W	Burke, N.D.	Madison Gp. Midale beds 5,828-5,851	35.2°/37.0°	N8-73
S.W. Aurelia	#1 Leo E. Johnson	NESW 7 157N 87W	Bottineau, N.D.	Madison Gp. Bluell beds 6,776-7,100	28.9°/27.0°	N8-76
Little knife	#1-19-2A Klatt	19 145N 97W	Dunn, N.D.	Madison Gp. Upper Fryburg beds 9,786-9,814	43.4°/43.0°	N8-121
T.R.	#1-23 State	NWNE 23 141N 101W	Billings, N.D.	Madison Gp. Fryburg beds 9,278-9,352	41.7°/40.0°	N8-138
Flat Lake	#1-A. McKinnon	NESE 9 37N 57E	Sheridan, MT	Madison Gp. Ratcliffe beds 6,555-6,585	31.9°	M8-15
East Poplar	#11 Unit	NENW 10 28N 51E	Roosevelt, MT	Madison Gp. Charles Fm. 5,721-5,796	40.4°	M8-18
Flat Lake	Unknown	18 37N 58E	Sheridan, MT	Madison Gp. Ratcliffe beds Range: 6,442-6,541	28.6°	M8-23
Richey	Unknown	24 23N 49E	McCone, MT	Mission Canyon Limestone	41.3°	M8-44

also found that where wide maturity ranges exist in rocks with uniform organic matter type, *i-C/n-C* ratios strongly decrease with increasing maturity. However, we stress that *i-C/n-C* ratios are valid maturity indices only for a single source rock, a single organic-matter type, or single oil family (in the absence of biodegradation), because these ratios also depend highly on facies. The phytane to *n-C*₁₈ ratio is plotted in Figure 3 for Bakken oils, versus the Rock-Eval Hydrogen Index (Table 3) for Bakken shales from the same well as the oil, or from a well no more than one section (1.6 km) from the producing well. In our opinion, the kerogen elemental hydrogen to carbon (H/C) atomic ratio most accurately indicates maturity for rocks with a single organic matter type. However, many of the Bakken oils of this study originated from the "fairway area" where the Bakken shales are thin (0.5-2 m) and not enough sample is available from the cuttings of these wells for kerogen maceration. Thus we used Rock-Eval analysis, and analyses on Bakken shales from over 250 wells (many with multiple analyses) have demonstrated that for Bakken shales the Hydrogen Index is the best Rock-Eval maturity index. In addition, Tissot and Welte (1984, p. 511; original data from Espitalié *et al.*, 1977) show a close correlation of increasing kerogen elemental H/C ratios with increasing Rock-Eval Hydrogen Indices for five rocks of variable organic matter types. Thus, the Rock-Eval Hydrogen Index is a good proxy for the kerogen elemental H/C ratio.

In Figure 3, phytane/*n-C*₁₈ ratios of Bakken oils regularly decrease with decreasing Rock-Eval Hydrogen Index for Bakken shales associated with the oils. In Figure 4, we plot ratios of *i-C*₁₃ to *i-C*₂₀ isoprenoids to their adjacent *n*-paraffins, versus oil gravity and versus resins plus asphaltenes, for our Madison oils. In spite of the apparent rudimentary nature of oil gravity and resin-plus-asphaltene content, these two parameters, in our opinion, remain among the best ways to rank maturities within a single family of undegraded oils. Again in Figure 4, *i-C/n-C* ratios regularly decrease with increase in oil maturity, as defined by decreasing resins plus asphaltenes and decreasing oil density. Thus, we used the *i-C/n-C* ratios of Figure 4 to initially rank the maturities of Madison oils (Table 4). However, we qualify this ranking. Two oils (N8-76 and N8-68) clearly fall outside the main trends of Figure 4. As stated, *i-C/n-C* ratios are valid maturity indices only for oils of a single family or for bitumen from a single rock. As discussed below, all the Madison oils do not appear to have the same source rock. Furthermore, other data (for example biomarker analysis of N8-76, discussed below) suggest that the N8-76 and N8-68 oils are less mature than their *i-C/n-C* ratios indicate.

SATURATED HCS

Gross Characteristics

In the oil comparisons which follow, source facies indices largely independent of maturity are used. However, where we

Table 2. Vita on the Bakken oils of this study. S-T-R is section, township and range. Producing depths are given in feet and not metres so that a specific identifier will not be lost in numerical conversion. Horizontal wells are shown by "HOR." with producing depths given by the NDGS convention of depth of production (and start of horizontal segment) by the first number and the end of the horizontal segment given by the second number. Oil gravity is given in API units to retain a specific identifier. I.D. is Amoco (N8-) or NDGS identification number. Fm. is Formation.

Field	Well	Corner S-T-R	County State	Producing: Unit and Depth (in Feet)	API Gravity	I.D. Number.D.
Hofflund	B.E. Hove-1	2 154N 95W	Williams, N.D.	Bakken Fm. 9,833-9,925	43.8°	N8-85
Antelope	Brenna-Lacey-1	N/2 E/2 1 152N 95W	McKenzie, N.D.	Sanish sand 10,330-10,435	45.4°	NDGS-1350
Antelope	F.E. Weedeman TR-1	NWNE 32 153N 94N	McKenzie, N.D.	Sanish sand 10,282-10,445, HOR.	45.7°	NDGS-1564
Antelope	Rose-1	SENE 33 152N 94W	McKenzie, N.D.	Sanish sand 10,606-10,615	45.0°	NDGS-12019
Antelope	Gudbranson-1	NWSE 34 152N 94W	McKenzie, N.D.	Sanish sand 10,650-10,660	46.0°	NDGS-12979
Bicentennial	Fed. 11-26H	NWNW 26 146N 104W	McKenzie, N.D.	Bakken Fm. 11,094-13,145, HOR.	39.6°	NDGS-6662
Bicentennial	MOI 41-19H	NENE 19 144N 103W	Golden Valley, N.D.	Bakken Fm. 10,868-12,385, HOR.	40.0°	NSGS-12617
Bicentennial	MOI 33-19	NWSE 19 145N 103W	McKenzie, N.D.	Bakken Fm. 11,200-12,712, HOR.	40.1°	NDGS-9240
Elkhorn Ranch	Short Com.-3	SWSW 26 143N 102W	Billings, N.D.	Bakken Fm. 10,386-12,696, HOR.	42.8°	NSGS-12814
Elkhorn Ranch	MOI 44-25H	SESE 25 143N 102W	Billings, N.D.	Bakken Fm. 10,660-13,150, HOR.	40.0°	NDGS-12599
Pierre Creek	MOI 44-7H	SESE 7 146N 102W	McKenzie, N.D.	Bakken Fm. 11,226-14,330, HOR.	41.0°	NDGS-12570
Pierre Creek	MOI 13-1H	NWSW 1 146N 103W	McKenzie, N.D.	Bakken Fm. 10,977-12,494, HOR.	41.0°	NDGS-12728
Charlson	T.G. Dorough "C" (NCT-1)	SESE 3 153N 95W	McKenzie, N.D.	Bakken-Three Forks Fms. 10,092-10,164	45.6°	NDGS-6962
Buckhorn	MOI 41-17H	NENE 17 144N 102W	Billings, N.D.	Bakken Fm. 10,400-12,802, HOR.	40.0°	NDGS-12617
Squaw Gap	MOI 34-21H	SWSE 21 146N 104W	McKenzie, N.D.	Bakken Fm. 10,839-13,221, HOR.	39.7°	NDGS-12779

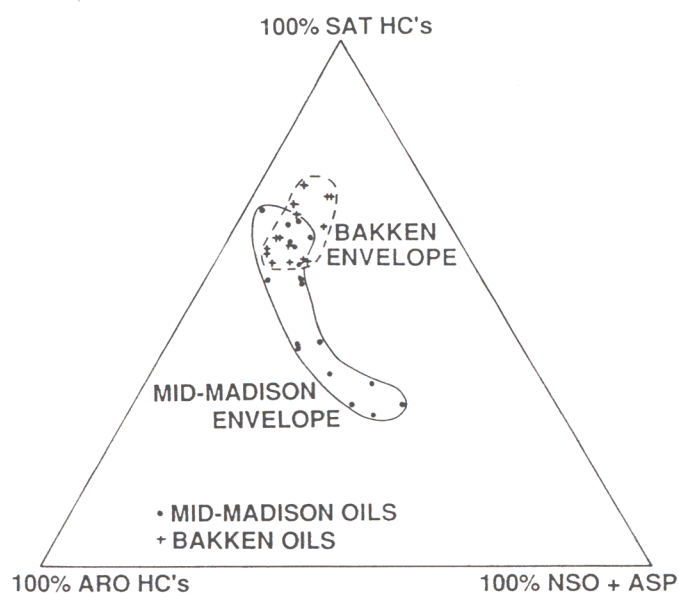


Fig. 2. Triangular C_{15+} compositional plot of Bakken (crosses and dashed line) and mid-Madison (dots and solid line) oils. SAT HCs are saturated HCs; ARO HCs are aromatic HCs; NSO+ASP are resins plus asphaltenes. Data from Tables 3 and 4.

use parameters with a maturity dependence, we compare only the more mature Madison oils to the Bakken oils. These mature Madison oils are, in descending maturity: M8-44,

N8-138, N8-5, N8-49, N8-28, N8-121, N8-56, N8-11, N8-65 and M8-18.

C_8+ gas chromatograms of saturated HCs of representative Madison (N8-138) and Bakken (NDGS-1350) oils are given in Figure 5. The enhanced naphthenic envelopes ("humps") of both these chromatograms are analytical artifacts from a high temperature-programming rate (ramp) for the gas chromatograph over the 12-18 carbon number (nC_{12} - nC_{18}) range. Superficially, the two chromatograms are similar; however, closer examination shows differences. In the Bakken sample (NDGS-1350): 1) the pristane to phytane ratio is much larger; 2) the naphthenic envelope is larger, which is much more apparent in C_{15+} HC gas chromatograms; 3) the C_{11} to C_{21} isoprenoid HC (i-11 to i-21) profile is different; 4) there are much lower concentrations of C_{20+} n-paraffins. These characteristics were largely present in all our Bakken and Madison oils.

Some of these characteristics discussed in Figure 5 are plotted (Fig. 6) for all our oils. Both oil sets are plotted with maturity increasing from top to bottom, although some oils are slightly out of order. The Bakken oils are generally plotted with Rock-Eval Hydrogen Index decreasing downward and the Madison oils are plotted with the isoprenoid HC to n-paraffin ratios of Figure 4 decreasing downward. The first four Bakken oils (Fig. 6) are significantly less mature (by Rock-Eval Hydrogen Indices) than the other Bakken oils, and we consider the first seven (M8-23 to N8-68) Madison oils, (and the N8-76 oil) less

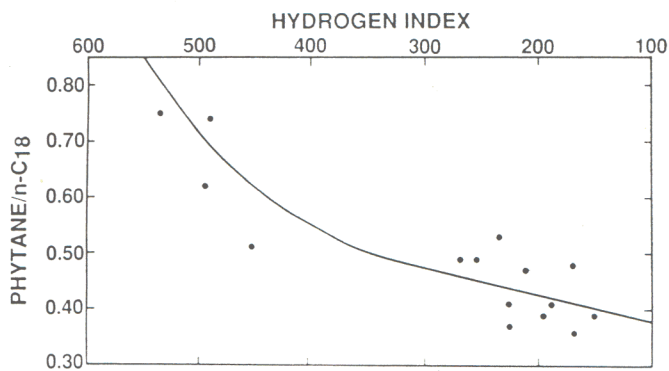


Fig. 3. The ratio of phytane to the C₁₈ n-paraffin (n-C₁₈) from Bakken oils versus the Rock-Eval Hydrogen Index from Bakken shales from the same, or a directly adjacent, well from which the oil was produced. Data from Table 3.

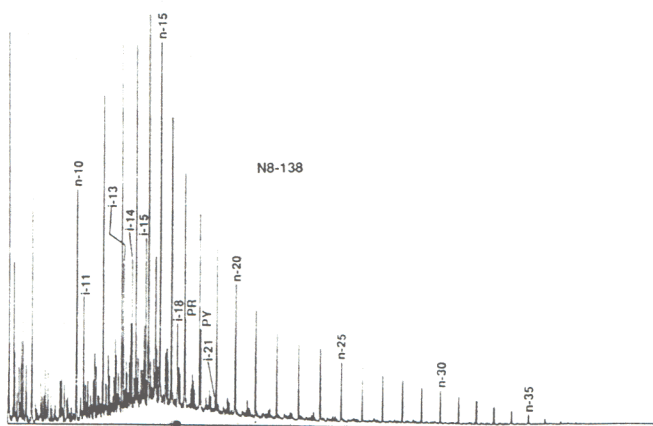
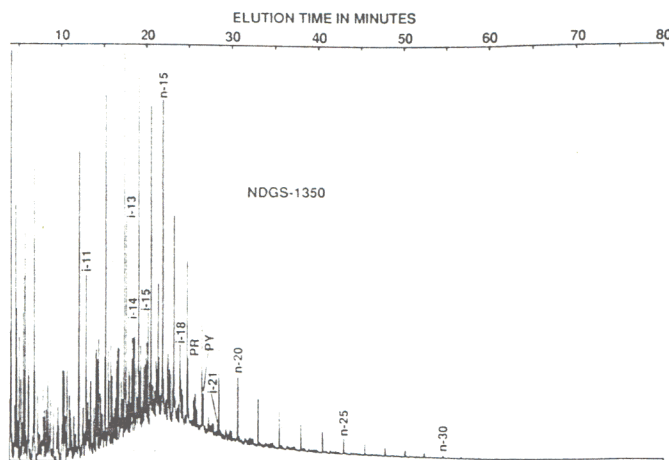


Fig. 5. C₈+ gas chromatograms from representative Bakken (NDGS-1350) and Madison (N8-138) oils. Every fifth n-paraffin is labeled by n- and its respective carbon number. Isoprenoid HCs are labeled by i- and their respective carbon number. PR is pristane, PY is phytane.

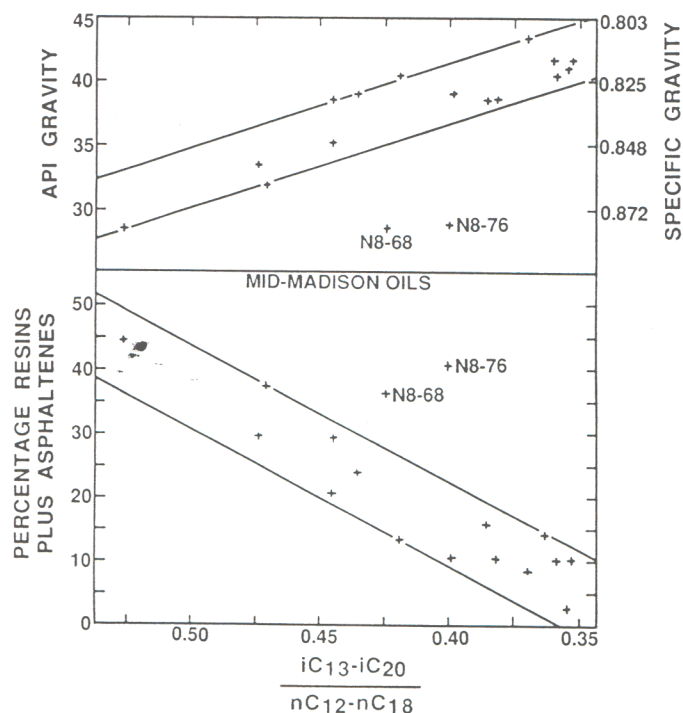


Fig. 4. Ratio of the sum C₁₃ to C₂₀ isoprenoid HCs to the sum of their adjacent n-paraffins ($iC_{13}-iC_{20}/nC_{12}-nC_{18}$) versus: 1) percentage of resins plus asphaltenes in the C₁₅+ fraction (bottom box), and 2) specific (and API) gravity (top box) for the Madison oils. Data from Tables 1 and 4.

mature than the other Madison oils (Fig. 6). The pristane to phytane ratio noticeably differs between the two oil sets: 0.76-1.46 for the Madison oils and 1.65-2.08 for the Bakken oils. Furthermore, the range of variation for the pristane to phytane ratio in the Madison oils (0.70) is noticeably greater than for the Bakken oils (0.43). This observation also is true for the other two parameters plotted in Figure 6 and for all the parameters examined in this study. The significance of this observation is discussed in the Discussion section below.

Hunt's (1974) carbon preference index for the nC₂₄-nC₃₂ range n-paraffins is plotted in Figure 6. This parameter is both source and maturity dependent; thus only the more mature

Madison oils (M8-18 to N8-138) should be compared to the Bakken oils. The Madison oils have even carbon preference indices (with two exceptions) with a dependence on maturity, with scatter. The Bakken oils all have values above 1.0 for this parameter (odd preferences) and are invariant with respect to maturity. Osadetz *et al.* (1992) noted that Canadian Madison oils had even n-paraffin carbon preferences which distinguished them from Canadian Bakken oils which had odd carbon preferences. This difference between the oils thus persists into the United States portion of the basin but is moderated by higher thermal maturities in both our oil sets.

The percentage of the n-paraffins in the total C₈+ saturated HCs is plotted in Figure 6 and the Madison oils are all noticeably more paraffinic than the Bakken oils. One of the Madison oils (M8-44) has a noticeably higher content of n-paraffins (33.0%) than the other oils and also has a very low isoprenoid HC to n-paraffin ($iC_{13}-iC_{20}/nC_{12}-nC_{18}$) ratio (0.184, not plotted in Fig. 4). These and other characteristics of this oil are identical to those in oils and source-rock bitumens which have been subjected to extreme thermal stress (as is discussed in Price and Wenger, 1992, and Price, 1993a). The M8-44 oil is from the Richey Field in central eastern Montana on the western

Table 3. Analytical data for the Bakken oils. Sample number is NDGS (or Amoco, N8-85) identification numbers from Tables 1 and 2. "A" on the end of the sample number is an oil from the Nesson Anticline. All other oils are from the "fairway" area of southern McKenzie and northern Billings counties. $C_{15}+$ FRACTION/% SATS, % AROS, % NSO are the percentages of the saturated (SATS) and aromatic (AROS) HCs and Billings counties. $C_{15}+$ FRACTION/% SATS, % AROS, % NSO are the percentages of the saturated (SATS) and aromatic (AROS) HCs and northern Billings counties. $C_{15}+$ FRACTION/% SATS, % AROS, % NSO are the percentages of the saturated (SATS) and aromatic (AROS) HCs and northern Billings counties. Although visible amounts of asphaltene were recovered from these oils, the recovered amounts were too small (< 0.1 mg) to obtain reliable weights. SAT/AROM is the ratio of $C_{15}+$ saturated to aromatic HCs. % n-Cs/TOTAL is the percentage of the n-paraffins in the total (C_{8+}) saturated HCs (by peak area). PRIS/PHY is the pristane to phytane ratio (by peak area). CPI Hunt (1974) is the n- C_{24} to n- C_{32} carbon preference index calculated by the formula of Hunt (1974). PRIS/n- C_{17} is the ratio of pristane to n- C_{17} (by peak area). PHY/n- C_{18} is the ratio of phytane to n- C_{18} (by peak area). $\Sigma iC_{13}-C_{20}/\Sigma nC_{12-18}$ is the ratio of the i- C_{13} to i- C_{20} isoprenoid HCs to the sum of their adjacent n-paraffins (n- C_{12} to n- C_{18}). SATURATED HCs/% C_{15}^- and $C_{15}^-/C_{25}+$ are the percentages of the C_{15}^- saturated HCs in the total (C_{8+}) saturated HCs (% C_{15}^-) and the ratio of the C_{15}^- to the $C_{25}+$ saturated HCs ($C_{15}^-/C_{25}+$). ARO HCs % C_{15}^- is the percentage of C_{15}^- aromatic HCs within the total aromatic HCs. Rock-Eval HI is the Rock-Eval Hydrogen Index of the Bakken shales from the well from which the oil sample was produced, or from a well no more than 1.6 km (one section) removed. MAT. RANK. is the maturity ranking (based on Rock-Eval Hydrogen Indices) with 1 being the least mature and 15 being the most mature.

SAMPLE NUMBER	$C_{15}+$ FRACTION/			SAT/AROM	% n-C's TOTAL	PRIS/PHY	CPI Hunt (1974)	PRIS/n-C ₁₇	PHY/n-C ₁₈	$\Sigma iC_{13-20}/\Sigma nC_{12-18}$	SATURATED HC's/		ARO	ROCK	MAT. RANK.
	% SATS	% AROS	% NSO								% C ₁₅ ⁻	C ₁₅ ⁻ /C ₂₅ ⁺	% C ₁₅ ⁻	HI	
NDGS-6662	57.7	29.9	12.4	1.93	14.98	1.74	1.04	0.88	0.74	0.609	46.13	3.33	50.00	491	3
NDGS-9240	60.8	28.5	10.7	2.14	16.87	1.92	1.06	0.81	0.62	0.531	47.94	3.78	39.09	495	2
NDGS-12779	57.5	32.8	9.7	1.75	14.48	1.84	1.06	0.96	0.75	0.646	43.84	3.07	47.90	535	1
NDGS-12617	70.2	21.8	8.0	3.22	17.55	2.08	1.05	0.71	0.51	0.642	47.89	4.66	49.45	453	4
NDGS-12728	58.5	27.3	14.3	2.15	12.78	1.88	1.02	0.65	0.49	0.460	43.78	2.34	39.51	268	5
NDGS-12570	58.2	26.8	15.0	2.17	13.32	1.93	1.05	0.66	0.48	0.378	45.95	2.70	50.40	170	13
NDGS-12979A	59.8	32.4	7.8	1.85	13.02	1.90	1.05	0.55	0.37	0.464	57.86	9.63	43.44	225	9
NDGS-12019A	60.1	32.6	7.2	1.84	12.45	1.79	1.01	0.58	0.41	0.452	51.47	5.94	44.64	226	8
NDGS-85A	64.5	20.7	14.8	3.12	12.60	1.97	1.07	0.59	0.39	0.529	49.48	3.66	55.88	156	15
NDGS-12626	66.8	24.1	9.2	2.78	16.30	1.77	1.02	0.74	0.53	0.471	46.75	3.92	53.69	234	7
NDGS-12814	70.1	22.2	7.7	3.15	17.46	1.90	1.08	0.68	0.49	0.493	48.42	4.53	44.75	254	6
NDGS-12599	72.1	20.1	7.8	3.59	17.60	1.86	1.05	0.66	0.47	0.473	47.90	4.41	56.30	212	10
NDGS-6962A	62.1	30.0	7.9	2.07	11.98	1.88	1.08	0.58	0.39	0.497	58.89	7.08	45.81	196	11
NDGS-1564A	62.3	29.1	8.6	2.14	12.39	1.65	1.08	0.52	0.41	0.478	49.35	4.20	46.58	188	12
NDGS-1350A	68.8	24.8	6.4	2.77	11.99	1.96	1.04	0.54	0.36	0.481	53.02	6.12	49.76	169	14

Table 4. Analytical data for the Madison oils. Sample number is Amoco identification from Table 1. $C_{15}+$ FRACTION/% SATS, % AROS, % NSO, % ASP are the percentages of the saturated (SATS) and aromatic (AROS) HCs, resins (NSO) and asphaltene (ASP). Samples with "0" asphaltene values had visible amounts of recovered asphaltene too small (< 0.1 mg) to obtain reliable weights. SAT/ARO is the ratio of the $C_{15}+$ saturated to aromatic HCs. % n-Cs/TOTAL is the percentage of the n-paraffins in the total (C_{8+}) saturated HCs by peak area. PRIS/PHY is the pristane to phytane ratio (by peak area). CPI HUNT (1974) is the n- C_{24} to n- C_{32} carbon preference index calculated by the formula of Hunt (1974). PRIS/n- C_{17} is the ratio of pristane to n- C_{17} (by peak area). PHY/n- C_{18} is the ratio of phytane to n- C_{18} (by peak area). $\Sigma iC_{13}-C_{20}/\Sigma nC_{12-18}$ is the ratio of the sum of the i- C_{13} to i- C_{20} isoprenoid HCs to the sum of their adjacent n-paraffins (n- C_{12} to n- C_{18}). SATURATED HCs/% C_{15}^- and $C_{15}^-/C_{25}+$ are the percentages of the C_{15}^- saturated HCs within the total (C_{8+}) saturated HCs (% C_{15}^-) and the ratio of the C_{15}^- to the $C_{25}+$ saturated HCs ($C_{15}^-/C_{25}+$). ARO HCs % C_{15}^- is the percentage of C_{15}^- aromatic HCs within the total aromatic HCs. MAT.RANK. is the maturity ranking based on the $\Sigma iC_{13-20}/\Sigma nC_{12-18}$ ratio and, in the case of the N8-68 and N8-76 samples, other parameters.

SAMPLE NUMBER	$C_{15}+$ FRACTION				SAT/ARO	% n-C's/TOTAL	PRIS/PHY	CPI HUNT (1974)	PRIS/n-C ₁₇	PHY/n-C ₁₈	$\Sigma iC_{13-20}/\Sigma nC_{12-18}$	SATURATED HC's		ARO	MAT. RANK.
	% SATS	% AROS	% NSO	% ASP								% C ₁₅ ⁻	C ₁₅ ⁻ /C ₂₅ ⁺	% C ₁₅ ⁻	
M8-23	30.7	24.8	23.7	20.8	1.24	20.7	0.95	0.96	0.45	0.65	0.527	42.76	2.91	30.81	1
N8-30	36.4	33.9	22.1	7.6	1.07	23.2	0.85	0.94	0.27	0.52	0.474	46.86	3.73	34.48	2
M8-15	34.6	27.9	20.1	17.4	1.24	23.8	1.27	0.94	0.44	0.45	0.471	42.81	2.55	35.75	3
N8-73	41.7	31.8	22.9	3.6	1.31	19.8	1.25	0.99	0.49	0.49	0.446	45.82	3.63	55.14	4
N8-62	42.0	36.3	21.7	0	1.16	20.4	1.18	0.95	0.51	0.54	0.446	48.25	3.99	50.10	4
N8-10	43.5	32.4	18.5	5.6	1.34	21.1	1.06	0.97	0.35	0.49	0.436	46.86	3.75	42.98	5
N8-68	30.4	33.1	17.3	19.1	0.92	23.7	0.80	0.94	0.27	0.57	0.424	44.82	3.36	40.83	6
M8-18	62.7	24.0	12.2	1.2	2.62	22.6	1.46	1.01	0.46	0.44	0.419	46.71	4.08	53.59	7
N8-76	28.6	30.6	19.3	21.5	0.93	25.4	0.76	0.95	0.24	0.57	0.404	46.17	3.36	45.29	8
N8-65	54.5	35.0	10.5	0	1.56	21.3	0.85	0.97	0.27	0.51	0.392	46.78	3.81	49.36	9
N8-11	54.8	29.5	15.7	0	1.86	20.3	1.21	1.05	0.30	0.41	0.386	51.70	5.51	56.58	10
N8-56	61.7	27.8	10.5	0	2.21	22.7	1.25	0.99	0.35	0.37	0.382	47.81	4.29	42.11	11
N8-121	65.0	26.4	8.6	0	2.46	20.8	1.44	0.99	0.43	0.35	0.370	50.62	4.92	59.69	12
N8-28	57.3	28.6	11.2	2.9	2.00	25.5	1.08	0.99	0.28	0.45	0.363	46.28	3.74	46.98	13
N8-49	65.6	24.3	10.2	0	2.70	19.7	1.34	1.00	0.38	0.37	0.359	47.20	4.12	58.36	14
N8-5	67.8	29.6	2.6	0	2.29	18.2	1.31	1.06	0.38	0.36	0.355	49.20	4.68	44.17	15
N8-138	61.6	28.0	10.4	0	2.20	23.0	1.05	0.96	0.27	0.41	0.353	48.68	4.15	44.97	16
M8-44	53.8	29.6	16.5	0	1.82	33.0	1.00	ND	0.10	0.39	0.184	49.58	4.77	43.60	17

shelf of the Williston Basin and together with several oil fields around it is largely isolated from the principal producing trends of the Williston basin. The apparent high maturity of the M8-44 oil may be due to an anonymously high (paleo?) heat flow in this area of the basin, possibly from a plutonic intrusion. However, a more likely and preferred explanation is that this oil has had multiple sources. Besides the low values for the iC/nC ratios (Table 4), this oil also has a pronounced odd n-paraffin preference over nC_{15} to nC_{20} (Fig. 7) and low

concentrations of higher numbered n-paraffins which prevented calculation of the CPI for this oil (Table 4). Osadetz *et al.* (1992) demonstrated that these are all characteristics of Ordovician-sourced oils (their family "A" oils). Thus, mixing of an Ordovician-sourced oil with Madison oil appears likely in this field. Hicks (1985) shows the Richey Field to be bounded by two faults which would have served as avenues for vertical oil migration for the Ordovician-sourced oil. These faults have been repeatedly active (J. Blume, *written comm.*, June, 1993).

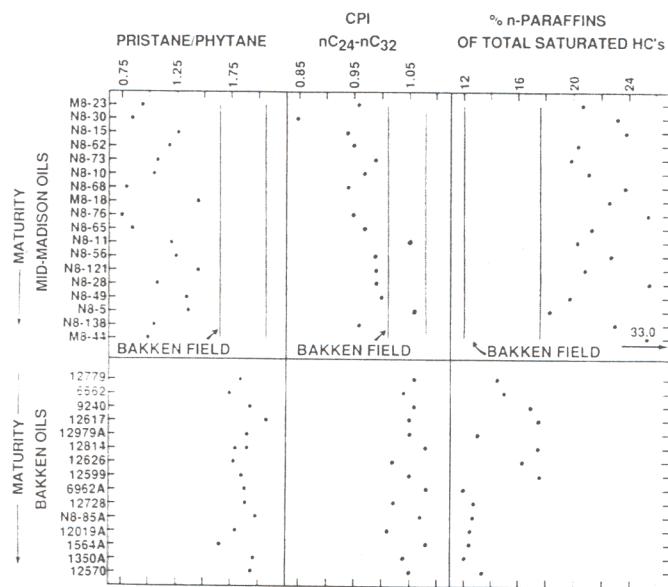


Fig. 6. Pristane to phytane ratio; the $n\text{-C}_{24}$ to $n\text{-C}_{32}$ n-paraffin carbon preference index (CPI $n\text{-C}_{24}/n\text{-C}_{32}$) after Hunt (1974); and the percentage (%) of the n-paraffins of the total saturated HCs for all the Bakken and Madison oils of this study. Maturity generally increases downward. The distribution for the Bakken oils is shown in the Madison plots by the stippled patterns. Data from Tables 3 and 4.

In Figure 6, the seven most mature Bakken oils have reduced n-paraffin concentrations, roughly 12-13% of the total saturated HCs. One might attribute this observation to increasing maturity among the oils; however, this is not the cause of the observation for two reasons. First, as discussed by Price (1993a) and as previously noted by Sassen and Moore (1988), the n-paraffins are the most thermally stable of the common saturated HCs. Second, the lower n-paraffin contents of some Bakken oils in Figure 6 are entirely facies controlled. Near the depositional edge of the Bakken shales, Price *et al.* (1984) documented a facies variation which resulted in changes in both the rock mineral matrix and in the organic matter type. Regarding organic matter changes near the depositional edge: 1) total organic carbon contents decrease; 2) in immature samples, Rock-Eval Hydrogen Indices strongly decrease and Oxygen Indices increase; 3) amounts of n-paraffins in the saturated HCs noticeably increase and the n-paraffins have a stronger odd carbon preference. Other changes also occur. Price *et al.* (1984) attributed these changes to a variation in depositional conditions in the Bakken shales, with a greater influx of terrestrial type III organic matter into the shales and more oxidizing conditions near the depositional edge.

Re-examining the n-paraffin percentage plot in Figure 6, we see that the samples with the lowest n-paraffin contents are from sites removed from the depositional edge of the Bakken shales, e.g., along the Nesson Anticline, with two exceptions, NDGS-12570 and -12728 (Fig. 1). However, from Figure 1, the 12570 and 12728 oils are most northeast and slightly separated from the other fairway oils and from the Bakken depositional edge. As such, the organic matter in the rocks which sourced the NDGS-12570 and -12728 oils appears to have a lesser terrestrial influence than fairway oils closer to the depositional

edge. Over half of our Bakken oils originate from the fairway area. However, this distribution is a sampling artifact, because this is the area of greatest Bakken horizontal drilling in the basin. Therefore, the largest number of samples are available from here. Data from Price *et al.* (1984), and much of our subsequent work, show, with a few qualifications, that away from the Bakken depositional edge, the organic matter, and therefore the Bakken depositional conditions, appear to be quite uniform in the North Dakota portion of the basin. We stress that oils removed from the depositional edge would be most representative of a Bakken oil family, because depositional-edge shales areally and volumetrically are only a small percentage of all Bakken shales. However, we choose to treat all the Bakken oils as one family, even though we believe that it would be more valid to compare only Bakken oils from the Nesson Anticline to the Madison oils.

N-paraffin Profiles

Williams (1974) used n-paraffin profiles to correlate Bakken shale bitumen to the Williston Basin Madison oils. Figure 7 shows $C_{10}+$ n-paraffin profiles for all our Madison oils. Except for M8-44, the profiles are all similar, especially in the $C_{15}\text{-}C_{38}$ range. This observation suggests that the Madison oils are one oil family from one source rock. Furthermore, a weak to moderately strong $n\text{-C}_{26}+$ even carbon preference in these oils would suggest that the source rock for these oils has a carbonate-facies influence (Palacas, 1992). N-paraffin profiles for all our Bakken oils are in Figure 8, where the distribution of n-paraffin plots for all the Madison oils (except for M8-44) is shown as a stippled pattern. M8-44 was deleted because (as discussed above) it is inferred to have a partial Ordovician source and thus is not a typical Madison oil. The upper box of Figure 8 contains only Bakken oils from the Nesson Anticline. One "anticline oil" is plotted in the second box which otherwise contains only fairway oils, as does the third (bottom) box. Two Bakken subfamilies are again apparent from differences between the n-paraffin profiles of Figure 8: 1) "anticline oils", and 2) "fairway oils". Anticline oils have lower total concentrations of n-paraffins (Fig. 6) and are characterized by relatively elevated concentrations of $C_{10}\text{-}C_{15}$ n-paraffins and reduced concentrations of $C_{20}+$ n-paraffins (waxes). Note that in the bottom box of Figure 8, NDGS-12728 and -12570 again are intermediate between the two subfamilies.

None of the Bakken oils falls in the Madison oil envelope. Furthermore, the n-paraffin profiles for the Bakken Anticline oils would be the most representative of expelled Bakken oil and are decidedly unlike those of Madison oils. Also, most Bakken oils have a pronounced maxima in their n-paraffin profiles at $n\text{-C}_{15}$ (Fig. 8). Except for M8-23, no Madison oil has a maximum at $n\text{-C}_{15}$ (Fig. 7); however, some Madison oils have a much weaker maximum at $n\text{-C}_{14}$. The reason for a $n\text{-C}_{15}$ maximum in the M8-23 oil is discussed below. Contrary to Williams (1974), we find Bakken n-paraffin profiles to be distinctly different than and simply not matching n-paraffin profiles of Madison oils.

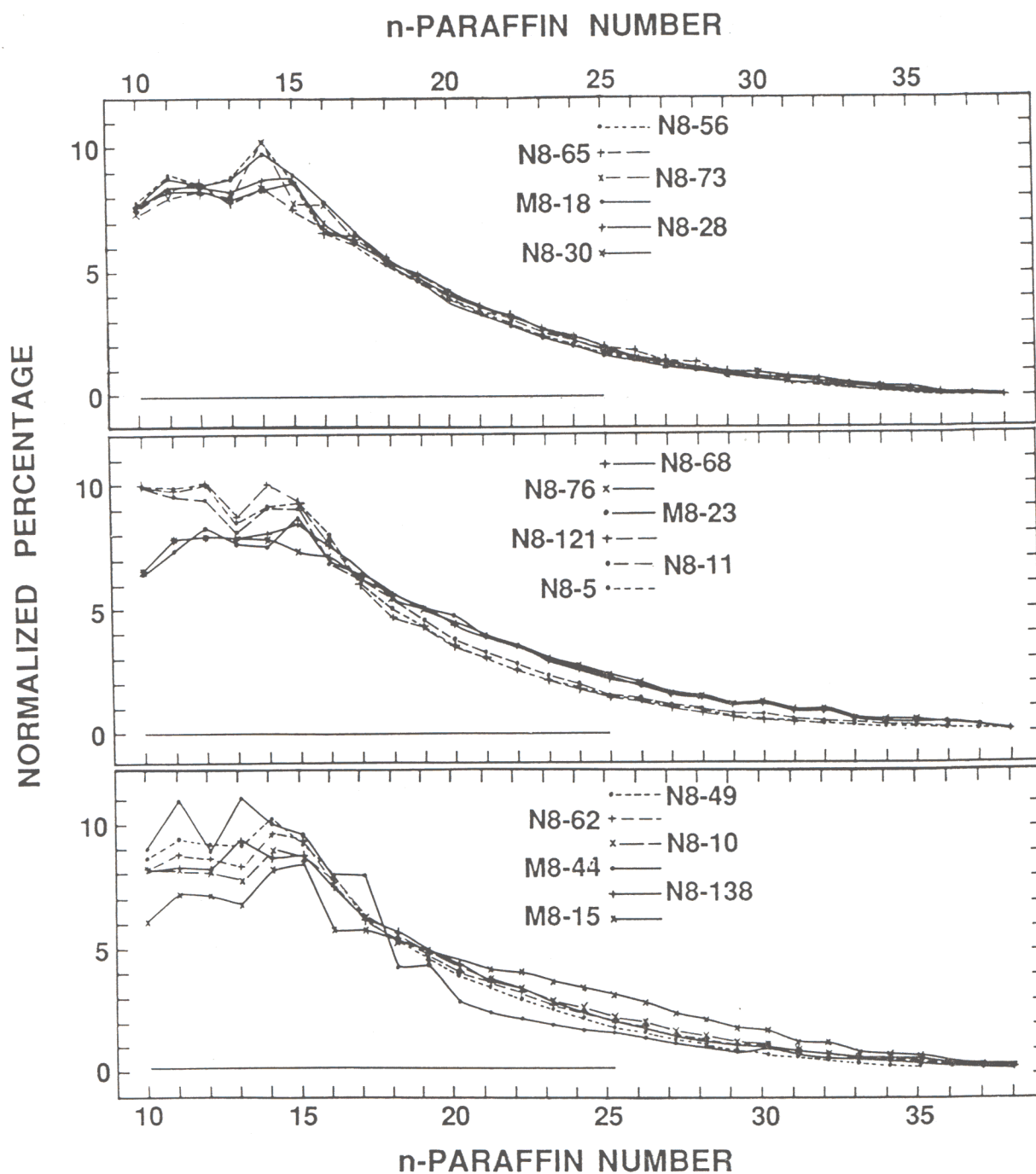


Fig. 7. Normalized percentage C_{10} to C_{38} n-paraffin plots for the Madison oils of this study.

Another difference between the Bakken and Madison oils is a significantly greater percentage of $n-C_{25}+$ n-paraffins in the Madison oils. Figure 9 shows $n-C_{22}+$ saturated HC gas chromatograms for a Bakken oil (NDGS-1350) and for a Madison oil (N8-138). The reduced concentration of $n-C_{25}+$ n-paraffins in the Bakken oil is obvious. In Figure 10, the envelopes for n-paraffin-normalized percentages are plotted for C_{20} to C_{38} n-paraffins for the two oil sets. The envelopes distinctly differ for the two oil sets. These differences are even more apparent when normalized n-paraffin percentages are calculated from

all the n-paraffins ($n-C_{10}$ to $n-C_{38}$) for only the $n-C_{25}+$ n-paraffins for the two oil sets (Fig. 11), as opposed to $n-C_{20}$ to $n-C_{38}$ normalized percentages (Fig. 10). In both Figures 10 and 11, the even n-paraffin preference in most Madison oils (Fig. 6) and the odd preference in all Bakken oils (Fig. 6) also would dictate that the two oil sets originated from different source rocks.

Isoprenoid HCs

Acyclic isoprenoid HCs are biomarkers and have been used to group oils into genetic families. For example, Clayton and

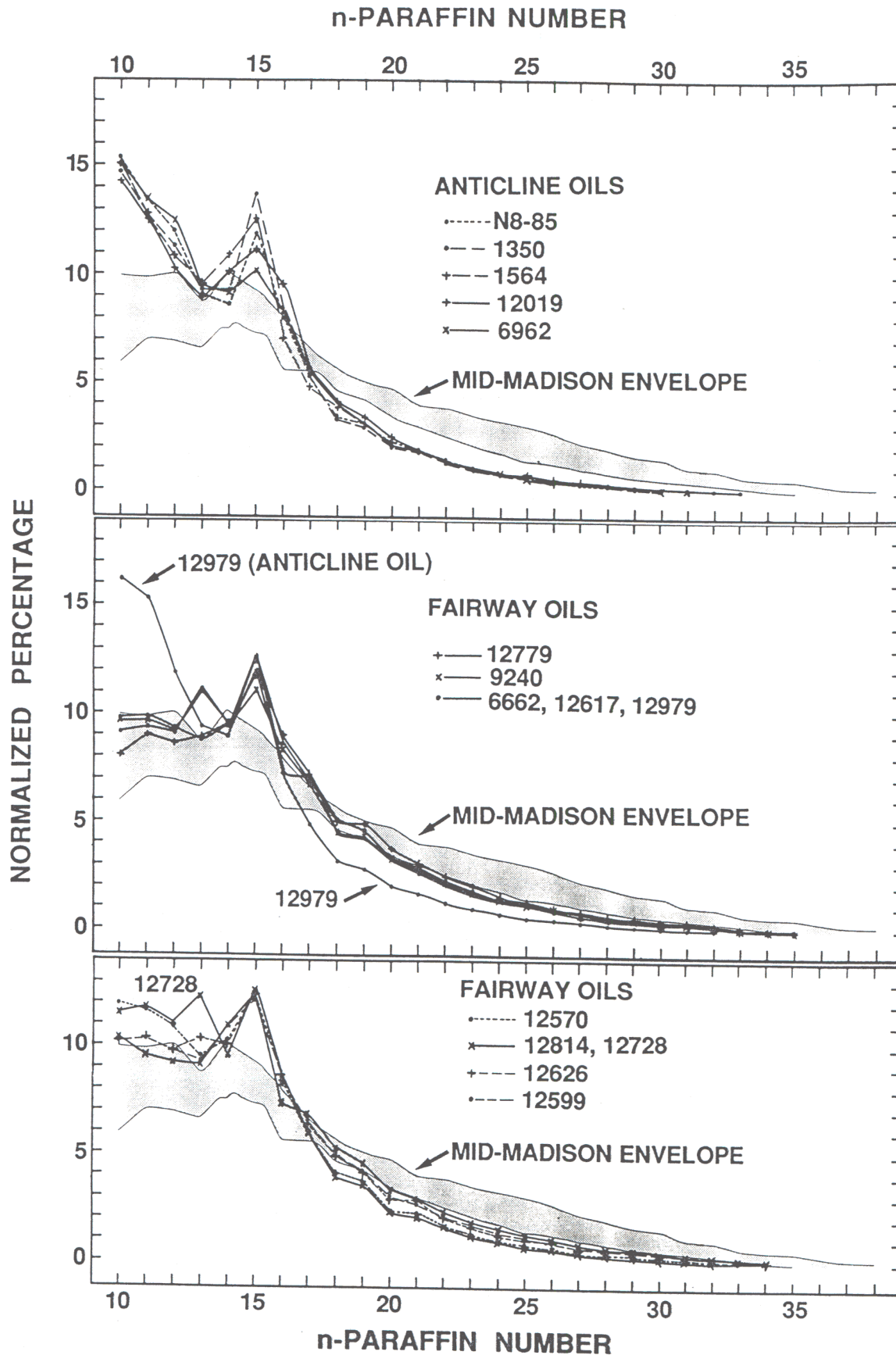


Fig. 8. Normalized percentage C_{10} to C_{38} n-paraffin plots for the Bakken oils of this study. The top box contains plots for only oils on or adjacent to the Nesson Anticline. N-paraffin profiles of oils only from the fairway area of northern Billings and southern McKenzie counties are plotted in the middle and bottom boxes except for one anticline oil in the middle box. Note that the plots for NDGS-12570 and -12728 (bottom box) are intermediate between the anticline and fairway oils. The distribution of the Madison oils (Fig. 7) is shown by the stippled pattern in Figure 8; the n-paraffin profile from M8-44 has been excluded because it is probably not a Madison oil (discussed in text).

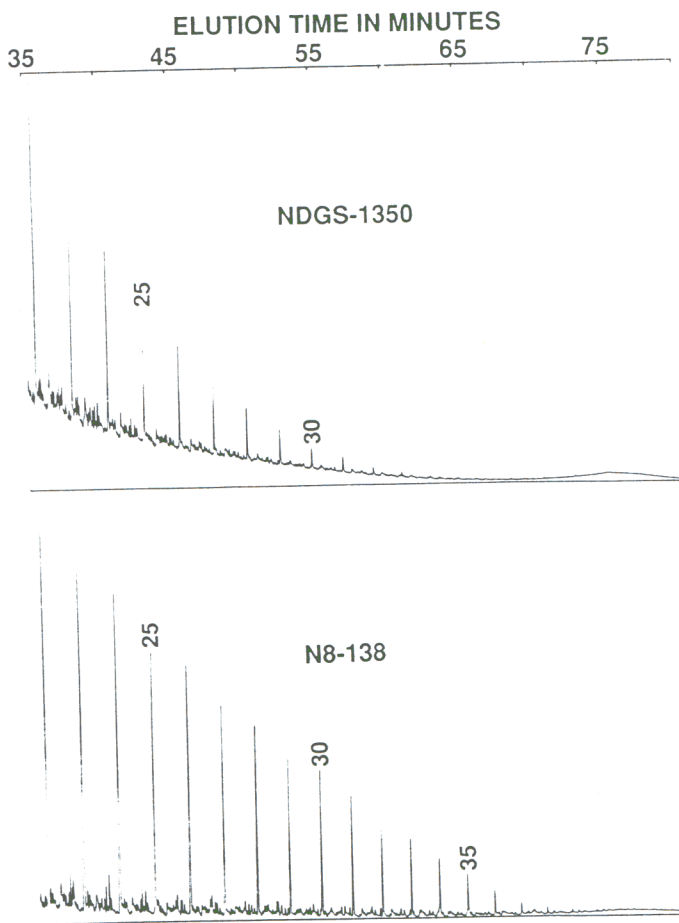


Fig. 9. C₂₂+ saturated-HC gas chromatograms for representative Bakken (NDGS-1350) and Madison (N8-138) oils.

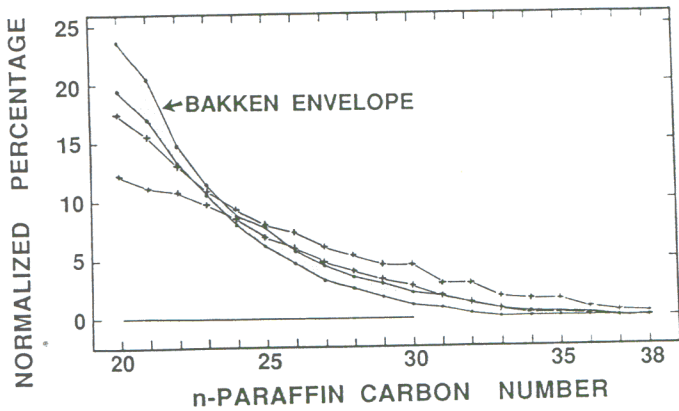


Fig. 10. Distributions of C₂₀ to C₃₈ n-paraffin normalized percentages (calculated from the n-C₂₀ to n-C₃₈ n-paraffins) for Bakken oils (dots and stippled pattern) and for Madison oils (crosses).

Swetland (1980) used i-C₁₅ to i-C₂₀ isoprenoids to classify Denver basin oils into different families. Price (1990) used isoprenoid HC distributions (and normalized percentages of "generic" HCs, discussed below) to demonstrate that a sequence of vertically stacked oils in sands over a 3524-m depth range in the Caillou Island oil field, Louisiana, belong to a single oil family. In our opinion, isoprenoid HC profiles are

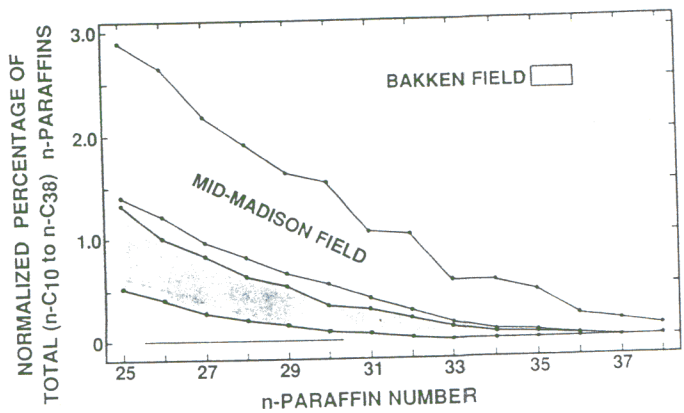


Fig. 11. Distributions of C₂₅ to C₃₈ n-paraffin percentages calculated from the sum of the C₁₀-C₃₈ n-paraffins for the Bakken oils (stippled area) and Madison oils.

an excellent oil-oil correlation tool because: 1) isoprenoids make up significant percentages of the whole oil; 2) isoprenoid HC profiles from single oil families plot tightly (Price, 1990); 3) unlike other geochemical measurements, isoprenoid HC measurements from different laboratories are easily comparable; and 4) isoprenoids are much more thermally stable than the n-C₂₄ to n-C₃₅ biomarkers. Isoprenoid-HC (i-C₁₆ to i-C₂₁) profiles (normalized percentages) for Bakken Anticline oils are plotted in Figure 12. The tight distribution (Fig. 12) is expected because the oils are from the same source rock. The same isoprenoid-HC distributions for the fairway oils are plotted in Figure 13, with the isoprenoid-HC distributions for the anticline oils (Fig. 12) shown by the stippled pattern. The two dashed lines in Figure 13 are for the two "fairway" oils (NDGS-12728 and -12570) most geographically removed from the Bakken depositional edge. Two conclusions are apparent from Figures 12 and 13: 1) the fairway and anticline oils have slightly different distributions; and 2) the NDGS-12728 and -12570 oils are intermediate between the anticline and fairway oils. Thus the data of Figures 12 and 13 support conclusions based on the C₁₀ to C₃₈ n-paraffin distributions of the Bakken oils (Fig. 8): 1) detectable organic matter facies shifts exist in Bakken oils as the Bakken-shale depositional edge is approached; 2) the Bakken oils can be divided into two subfamilies; and 3) the transition from one subfamily to the other is evident in the NDGS-12728 and -12570 oils which are only slightly removed from the Bakken-depositional edge.

In Figures 14 to 16, isoprenoid-HC (i-C₁₆ to i-C₂₁) plots are given for all our Madison oils. The distribution of all the Bakken oils is shown by stippled patterns. Several conclusions are obvious from Figures 14 to 16. First, none of the isoprenoid-HC plots for the Madison oils falls cleanly within the Bakken envelope, although several are close. However, as discussed above, if Bakken shales sourced the Madison oils, the oils would have originated from shales in the centre of the Williston Basin, away from the Bakken-depositional edge. None of the Madison isoprenoid-HC distributions of Figures 14 to 16 is close to the isoprenoid-HC envelope for only the Bakken Anticline oils (Fig. 13). The second point to consider

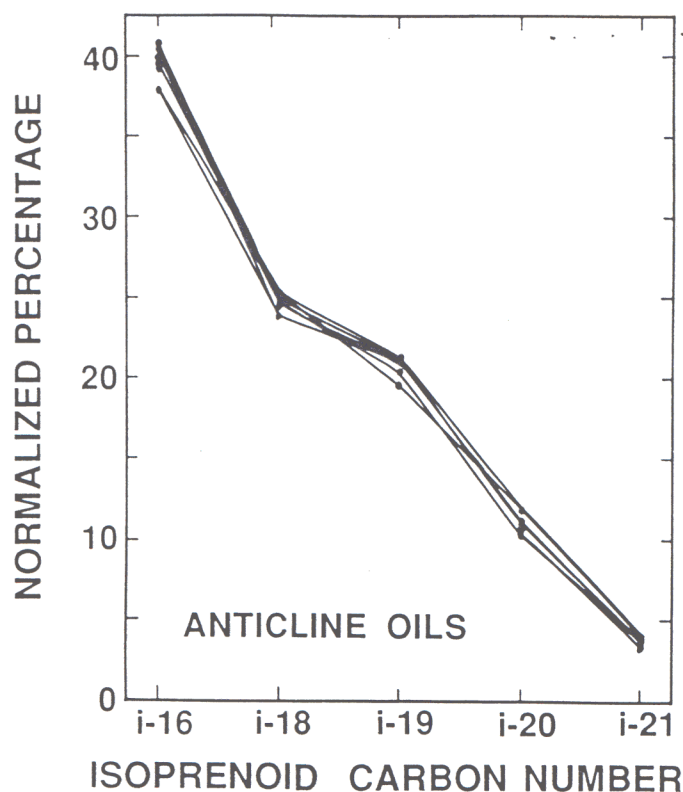


Fig. 12. Normalized percentages of the C_{16} to C_{21} isoprenoid HCs (i-16 to i-21) for Bakken oils on or adjacent to the Nesson Anticline.

is the wide distribution of the Madison oil isoprenoid-HC plots and the lack of parallelism in Figures 14-16 which, with the plots of Figure 6: 1) contrasts with the tight distributions for the Bakken oils in equivalent plots (Figs. 6, 12-13); and 2) suggests that the Madison oils may not all have the same source rock.

Some of the Madison oils along or just off the Nesson Anticline do have similar isoprenoid-HC profiles (one subfamily includes N8-56, N8-49, N8-15, N8-121 and N8-5, Figure 14; a second subfamily includes N8-11, N8-73, N8-62 and N8-10, Figure 15). However, the isoprenoid-HC profiles of none of the other Madison oils matches the profiles of the oils listed above, although two other subfamilies are suggested by isoprenoid-HC profiles. One subfamily includes N8-28 and N8-138 (T.R. and Scoria fields) which are near each other and M8-44 which is 183 km (114 mi) west of those two oil fields. The second oil family includes N8-76, N8-68 and N8-30, all in Renville county, and N8-65, significantly west of the Renville county. We feel that if more Madison oils were analyzed, especially oils away from the principal producing trends, even more subfamilies would emerge. For example, two other oils we analyzed, M8-18 and M8-23, have isoprenoid-HC profiles different from one another and different from those of all the other oils we analyzed. Furthermore, M8-23 is one of two oils (M8-15 being the other, Fig. 1) which are from different areas of the same field (Flat Lake Field, Sheridan Co., Montana) and which produce from the same reservoir. Yet these two oils have quite different isoprenoid-HC

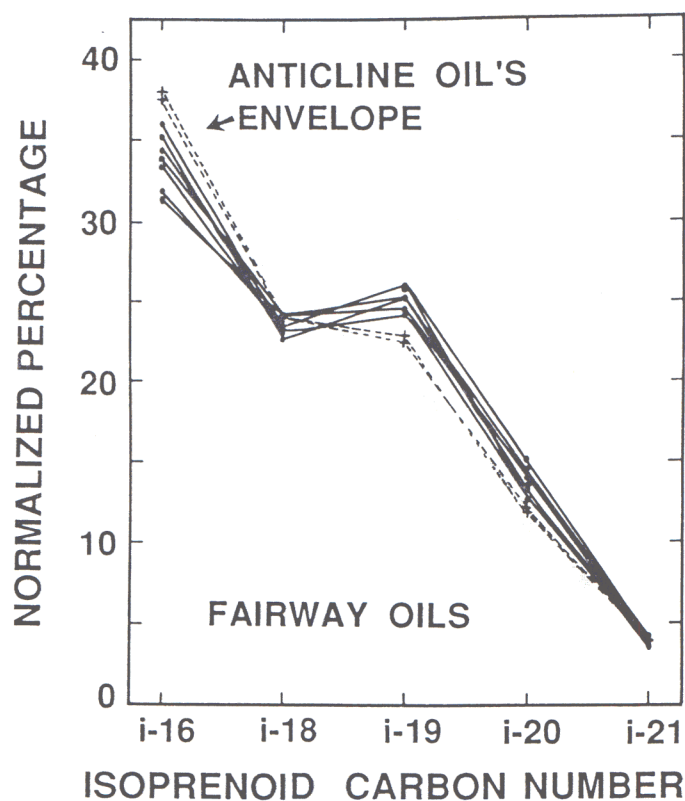


Fig. 13. Normalized percentages of the C_{16} to C_{21} isoprenoid HCs (i-16 to i-21) for Bakken oils from the fairway area of northern Billings and southern McKenzie counties. The stippled pattern is the distribution for the C_{16} to C_{21} isoprenoid-HC plots of the anticline oils from Figure 12. The crosses and dashed lines are plots for the NDGS-12570 and -12728 oils, which are the fairway oils geographically closest to the Nesson Anticline.

profiles (Fig. 14). These differences can be explained by work of Osadetz *et al.* (1992) who assigned Mississippian Ratcliffe interval production in the Flat Lake Field to a source rock in the Middle Devonian Winnipegosis Formation (their family "D1"). Vertical oil migration was made possible by salt dissolution of the Middle Devonian Prairie Formation of the Elk Point Group. Thus, some mixing of Winnipegosis-sourced oil with Madison production seems apparent here. Considering the evidence for vertical oil migration at the Richey field (discussed above), vertical oil migration has apparently occurred in the Williston Basin when avenues of transport are available.

Generic HC Plots

An arguably superior method of oil-oil correlation was presented by Kaufman *et al.* (1990) and Price (1990), by coincidence at the same conference. By this technique, ratios or percentages are calculated and plotted for the common generic HCs found between the n-paraffin peaks in either saturated HC or whole-oil gas chromatograms or for any of the peaks in gas chromatograms of the aromatic HCs. These peaks: 1) are found over all boiling ranges of oils; 2) are in much higher concentrations than C_{19} to C_{36} biomarkers; and 3) are thus much more representative of the oil than biomarkers. Both Kaufman *et al.* (1990) and Price (1990) found this oil-oil

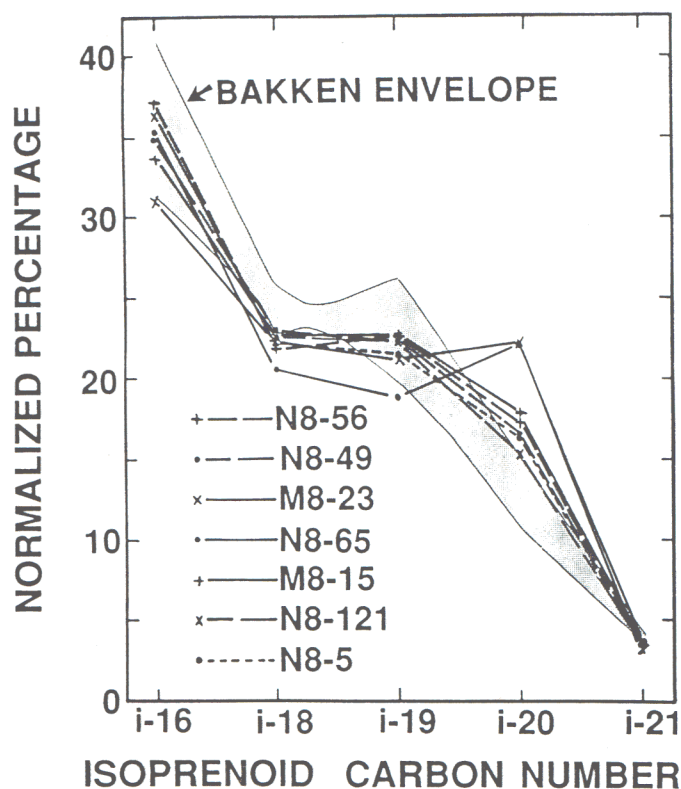


Fig. 14. Normalized percentages of the C_{16} to C_{21} isoprenoid HCs (i-16 to i-21) for seven Madison oils. The distribution for the C_{16} to C_{21} isoprenoid-HC plots for all the Bakken oils (Figs. 12, 13) is shown by the stippled pattern.

correlation technique to be very powerful. Kaufman *et al.* (1990) were even able to discriminate between very similar oils from the same source rock but in different parts of the same oil field not hydraulically-connected. In contrast, single-family oils in different parts of the same hydraulically-connected oil field gave exact matches.

We applied this oil-correlation technique to a large number of saturated and aromatic HCs for all our oils. For brevity, only a portion of these results will be shown here. Some of the saturated HCs we used (none of which have been identified) are labelled by the numbers 5A through 66 in Figure 17 for both a Madison (N8-138) and Bakken (NDGS-1564) oil. Figure 18 presents compound ratios for some of the numbered peaks of Figure 17 for seven Bakken oils. In this and following plots, only seven or eight oils are plotted because more than seven or eight lines in one plot is confusing. In all generic-HC plots for the Bakken oils, we could not distinguish the oils from one another either on the basis of geographic location (anticline versus fairway oils) or maturity. Bakken oils geographically adjacent to one another (*e.g.*, 12570 and 12728, or 12599 and 12814, or 1350 and 1564) had identical, or nearly identical, profiles. The compound ratio plots herein corroborate Price (1990) who noted that maturity differences within oils of the same family apparently do not affect this oil-oil correlation technique when percentages or ratios are calculated from peaks not separated by more than four carbon numbers.

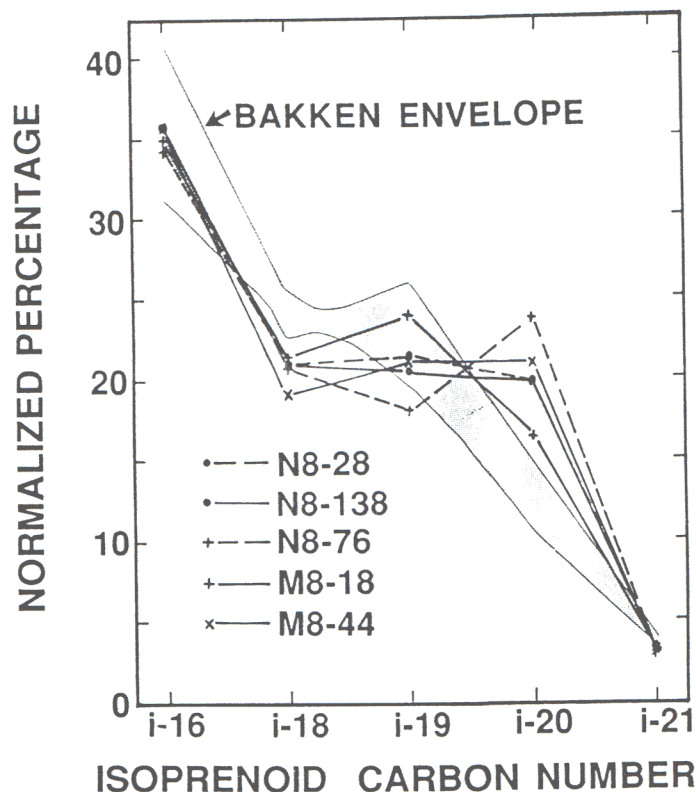


Fig. 15. Normalized percentages of the C_{16} to C_{21} isoprenoid HCs (i-16 to i-21) for six Madison oils. The distribution for the C_{16} to C_{21} isoprenoid-HC plots for all the Bakken oils (Figs. 12, 13) is shown by the stippled pattern.

In Figure 19, the same compound ratios plotted in Figure 18 for the Bakken oils are plotted for the Madison oils, with the distribution for the Bakken oils shown by the stippled pattern. Three observations are obvious from Figure 19. 1) None of the plots for the Madison oils is close to a match with the Bakken envelope, which again suggests that these two sets of oils do not have the same source. 2) The plots for the Madison oils (Fig. 19) have a significantly greater range of values and less parallelism than do the plots for the Bakken oils in Figure 18. Price (1990), using this oil correlation technique, found that both a lack of parallelism and a wide range of values characterized oils from different sources. 3) Five of the Madison oils in Figure 19 (N8-121, N8-73, N8-56, N8-5; and and N8-11) exhibit less scatter and more parallelism than the eight Madison oils as a whole. These five oils were part of the Madison subfamily proposed above from isoprenoid-HC profiles (Figs. 14, 15).

Other compound ratio plots, using other saturated HCs labelled in Figure 17, are given in Figure 20 for the Madison oils of Figure 19. In Figure 20, the distribution for the Bakken oils in Figure 18 is shown by the stippled pattern. The Madison and Bakken oils clearly have different distributions (Fig. 20), which again supports the conclusion that these two oil sets have different sources. However, note that in Figure 20 the distributions of both oil sets are roughly the same size. Furthermore, the parallelism within the Madison oils is significantly greater than that in the plots of Figure 19. Unlike some previous data for the Madison oils (Figs. 6, 14-16, 19), the

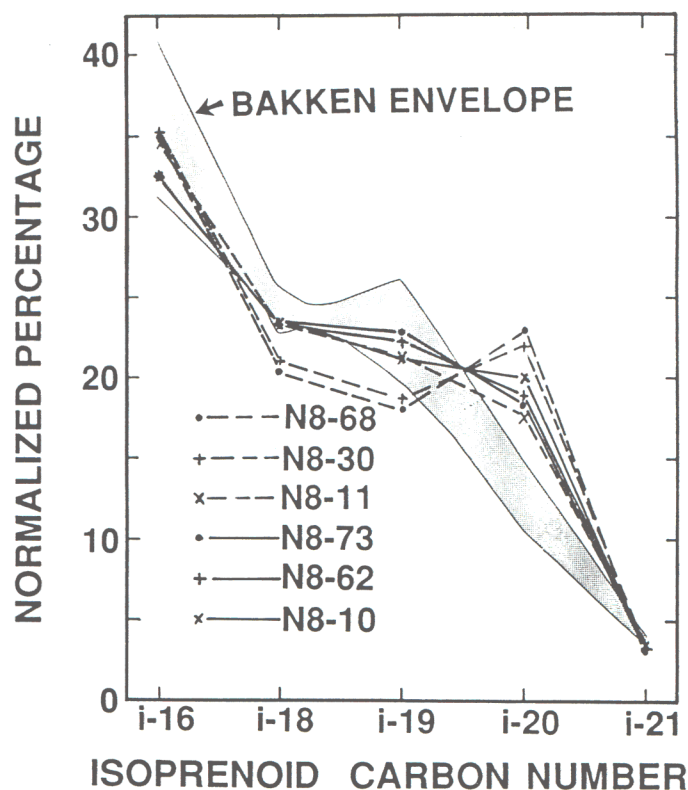


Fig. 16. Normalized percentages of the C_{16} to C_{21} isoprenoid HCs (i-16 to i-21) for five Madison oils. The distribution for the C_{16} to C_{21} isoprenoid-HC plots for all the Bakken oils (Figs. 12, 13) is shown by the stippled pattern.

data of Figure 20 suggest that the Madison oils have a single source rock (whatever it may be). The apparent large distributions for the two oil sets in Figure 20 are a drafting artifact because the vertical scale was expanded to better illustrate the contrasting distributions between the two oil sets.

AROMATIC HCS

Gas chromatograms for aromatic HCs from representative Bakken and Madison oils are shown in Figure 21 for compounds eluting from the dimethylnaphthalenes to the pentamethylphenanthrenes, with many of the numbered peaks identified in Table 5. The aromatic HCs from the oils in this study were analyzed by flame-ionization detection gas chromatography. One Bakken oil and several Madison oils were also analyzed by flame-photometric detection (FPD, sulfur-sensitive) and one Bakken and one Madison oil were also analyzed by full-scan mass spectrometry. We identified peaks by standards, FPD gas-chromatography, full-scan mass spectrometry, and published analyses (Radke *et al.*, 1982a, b, 1986; Radke and Welte, 1983; Alexander *et al.*, 1986; Rowland *et al.*, 1986; Kvalheim, *et al.*, 1987; Püttman and Vilar, 1987; Wise *et al.*, 1988; Price and Clayton, 1990).

In Figure 21, the chromatograms have noticeable differences which are present in all the oils. The dimethylnaphthalene distribution (peaks 98-106) is similar for the two oil sets; however, the trimethylnaphthalenes (peaks 123-129) are quite different. All the mid-Madison oils have a characteristic

dominance of 1,3,6-trimethylnaphthalene (peak 124). This is unusual, because commonly peaks 123, 124, 127 and 128 have roughly the same height, with peak 129 being smaller. The Bakken chromatogram displays this typical trimethylnaphthalene distribution. The unusual trimethylnaphthalene distribution in all the Madison oils suggests that the Madison oils are a single oil family from the same source rocks. The two oil sets also have different tetramethylnaphthalene distributions (peaks 137, 142, 144, 146, 147, 152, 156, 158 and 161). For example, peak 156 is always the dominant tetramethylnaphthalene in the Bakken oils but not in the Madison oils.

The Madison oils have distinctly greater concentrations of sulfur-bearing aromatic HCs than the Bakken oils, with large peaks of dibenzothiophene (peak 173), the methyl-dibenzothiophenes (peaks 191, 195 and, partially, 196), ethyl and dimethyl-dibenzothiophenes (peaks 204, 206-209, 215, 216, 216A) and trimethyl-dibenzothiophenes (peaks 227, 230-234). However, in the Bakken oils, these peaks are small or not detectable. Close examination of distribution of other peaks not discussed above in the two chromatograms of Figure 21, from peak 123 to the end of the chromatogram, reveals other differences between the two chromatograms. These differences were present in all our oils.

Compound-ratio plots are presented in Figure 22 for some of the aromatic-HC peaks of Figure 21 for seven Bakken oils. NDGS-6962 was in the saturated-HC generic plots of Figures 18-20 and was repeated to demonstrate that continuity of family persists between the oils in Figures 18-20 and those in Figures 22 and 23. All but one peak (201) in Figures 22 and 23 are positively, or tentatively, identified in Table 5. Compound ratios for the same aromatic HCs plotted in Figure 22 for the Bakken oils are plotted in Figure 23 for the Madison oils. None of the Madison oils in Figure 23 is in the saturated-HC compound-ratio plots of Figures 19 and 20. The same conclusions previously drawn in the other cross comparisons of the two oil sets apply here: 1) the plots for the Bakken oils have a tight distribution and pronounced parallelism, both characteristics of a single oil family; 2) the distributions of all the Madison oils distinctly differ from that of the Bakken oils and none of the Madison oils are therefore in the same oil family nor from the same source rock as the Bakken oils; and 3) the Madison oil plots have a wide distribution and some are distinctly nonparallel, which suggests that all the Madison oils of Figure 23 are not from the same source.

Aromatic-HC gas chromatograms, from the xylenes to just after the methylnaphthalenes, are given for the same two oils of Figure 21 in Figure 24. The vertical scale for the Madison oil (N8-138) was increased 174% to make the two chromatograms comparable, with a maximum at peak 9 (1,2,4-plus, 1,3,4-trimethylbenzene). Thus, para- and metaxylene peak (peak 2) is off scale for N8-138. On superficial examination, the two chromatograms of Figure 24 appear similar. However, closer examination reveals differences between the two chromatograms. These differences are in part demonstrated by the compound-ratio plots of Figure 25. [Because of their high numeric values, the last three ratios of higher molecular

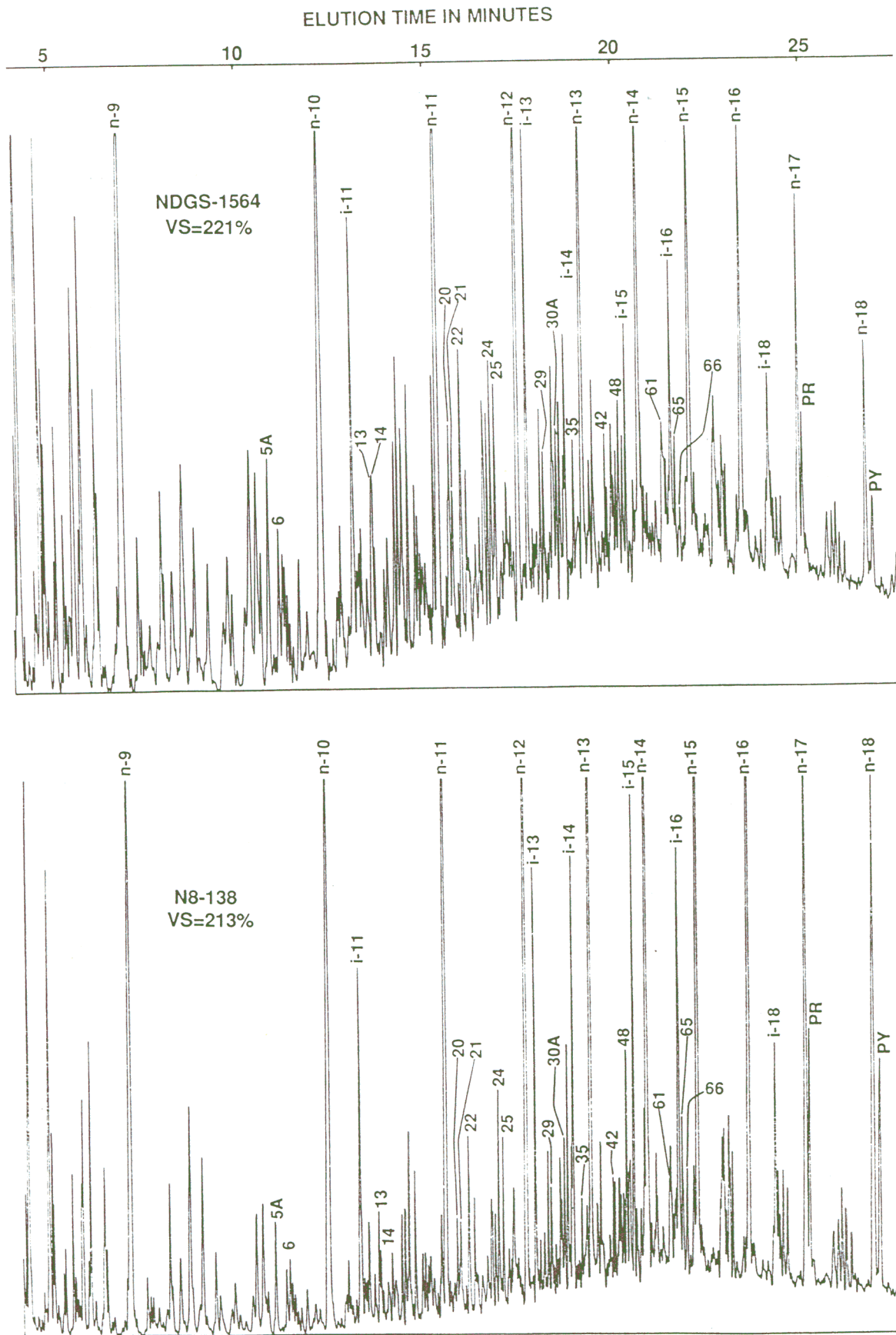


Fig. 17. C₈ to C₁₈ saturated-HC gas chromatograms from a representative Bakken oil (NDGS-1564, vertical scale increased 221%) and from a representative Madison oil (N8-138, vertical scale increased 213%). N-paraffins are labelled by n- and their respective carbon number; isoprenoid HCs are labelled by i- and their respective carbon number; PR is pristane; PY is phytane. Unidentified compounds used in the saturated-HC compound-ratio plots of this paper (Figs. 18-20) are labelled 5A to 66. Vertical scales (VS) were increased to better illustrate these labelled compounds. As is typical, note the greater naphthenic envelope of the Bakken oil compared to the mid-Madison oil.

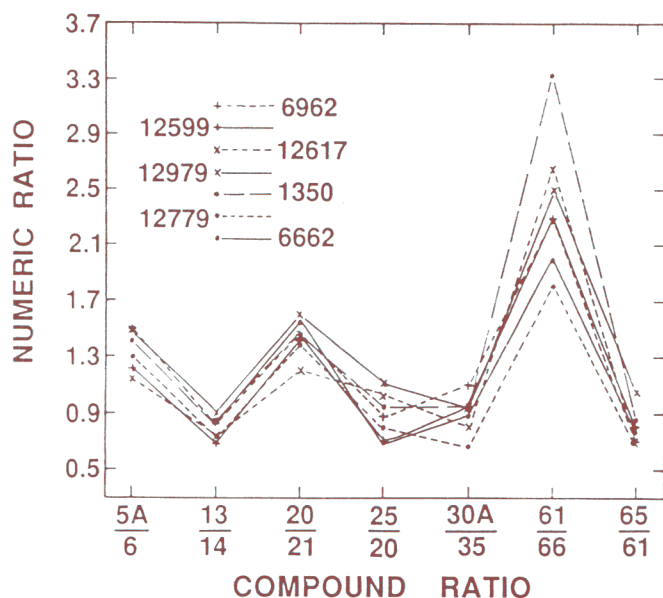


Fig. 18. Compound-ratio plots for seven Bakken oils for some of the compounds labelled in Figure 17. The oils were picked to represent a full range of maturity and geographic distribution.

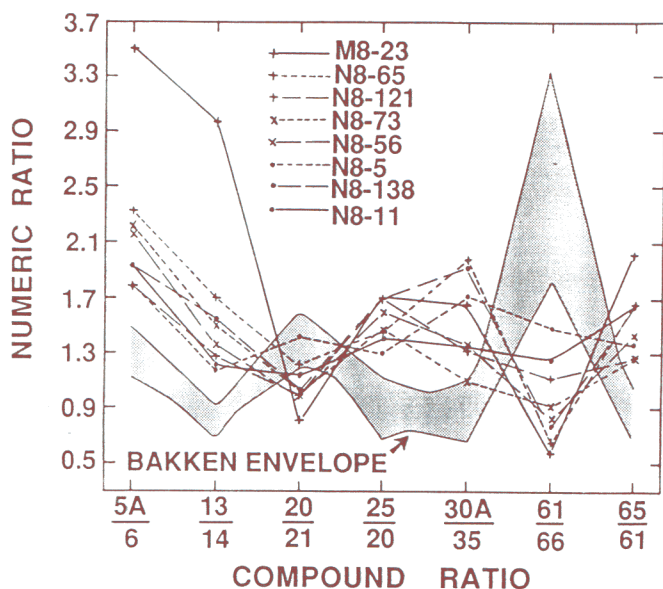


Fig. 19. Compound-ratio plots for eight (randomly selected) mid-Madison oils for the same compounds used in Figure 18. The distribution for the same plots of the Bakken oils in Figure 18 is shown by the stippled pattern.

weight compounds (peaks 156, 173, 179, 191 and 205) were put on Figure 25 and not on Figure 23]. The plots for the Bakken oils exhibited a high degree of parallelism (not shown) and were tightly distributed, shown by the stippled pattern (Fig. 25). The plots for the Madison oils are all outside of the distribution for the Bakken oils, again demonstrating that the Madison oils are not of the same oil family as the Bakken oils. Furthermore, the wide distribution of the Madison oils suggests all the oils do not have the same source rock.

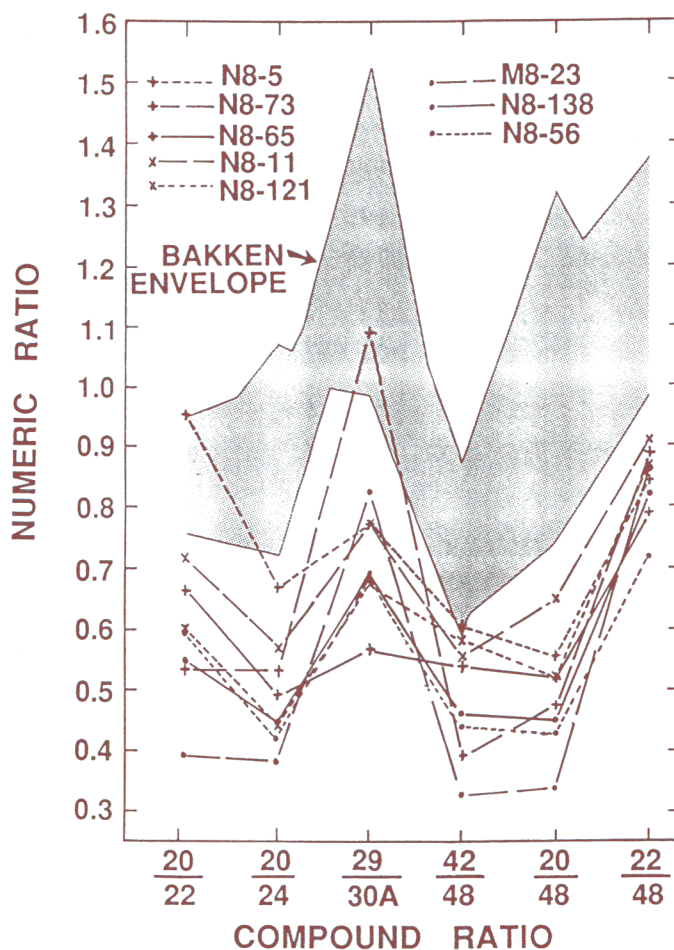


Fig. 20. Compound-ratio plots for the eight mid-Madison oils of Figure 19 for other compounds from Figure 17. The distribution for the same plots of the Bakken oils in Figure 18 is shown by the stippled pattern.

BIOMARKERS

Biomarker analyses were run on six Bakken oils and on six Madison oils. The Bakken oils were chosen to provide the widest possible maturity and geographic ranges. The Madison oils were chosen based on their proximity to the Nesson Anticline (either on or adjacent to it).

Steranes

A fragmentogram for the steranes for a Madison oil (N8-10) is shown in Figure 26 with many of the numbered peaks identified in Table 6. Fragmentograms from three other Madison oils and three Bakken oils are given in Figure 27. The fragmentograms from the two least mature Bakken oils analyzed (NDGS-12779 and -9240) were exact overlays and a third sample (NDGS-12814) was very close, (NDGS-9240 and -12814 not shown in Fig. 27). The peak distributions in the other three (very mature) Bakken oils (NDGS-12979, -12570 and -1350) were vaguely similar to the first three, the differences no doubt being due to the much different maturities. Thus peaks 6, 9, 14, 20 and 24 (all diasteranes) increasingly become the five dominant peaks in the fragmentograms of the most mature Bakken samples, reflecting the enhanced thermal

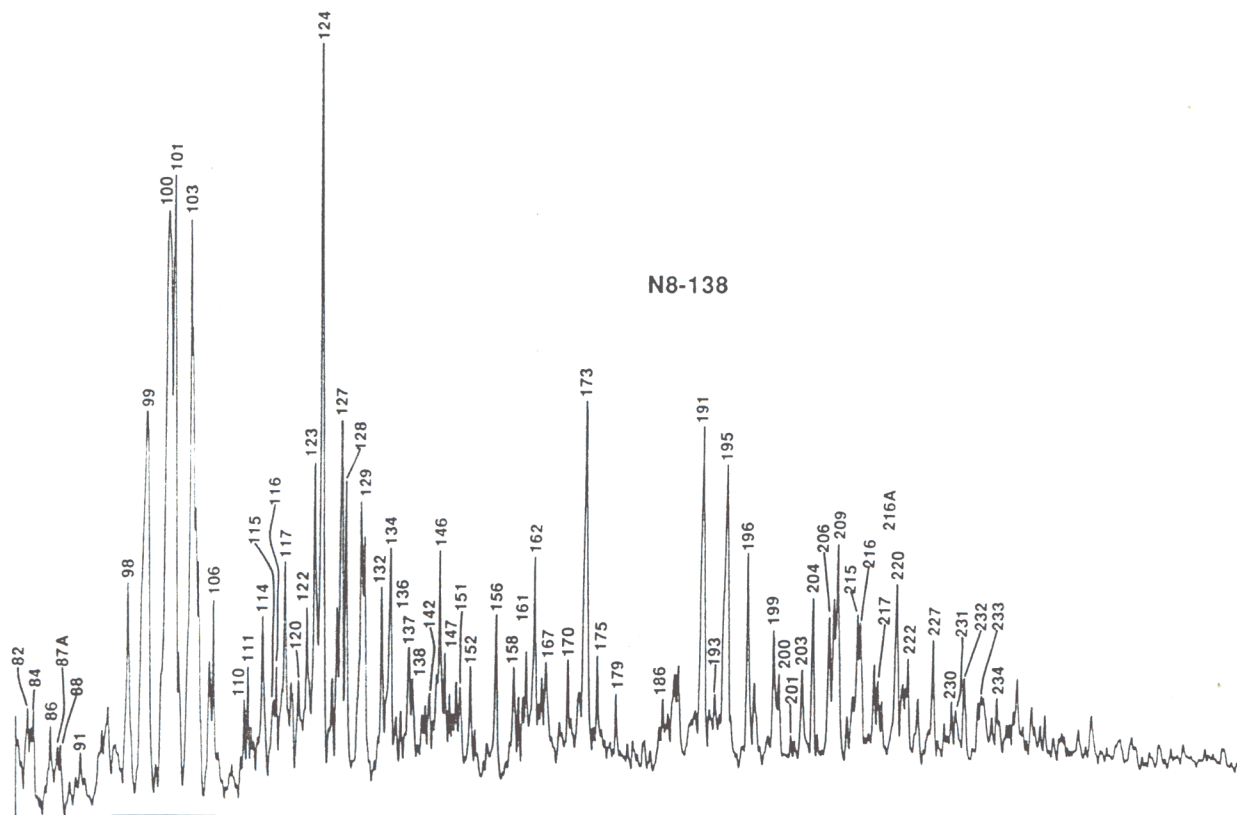
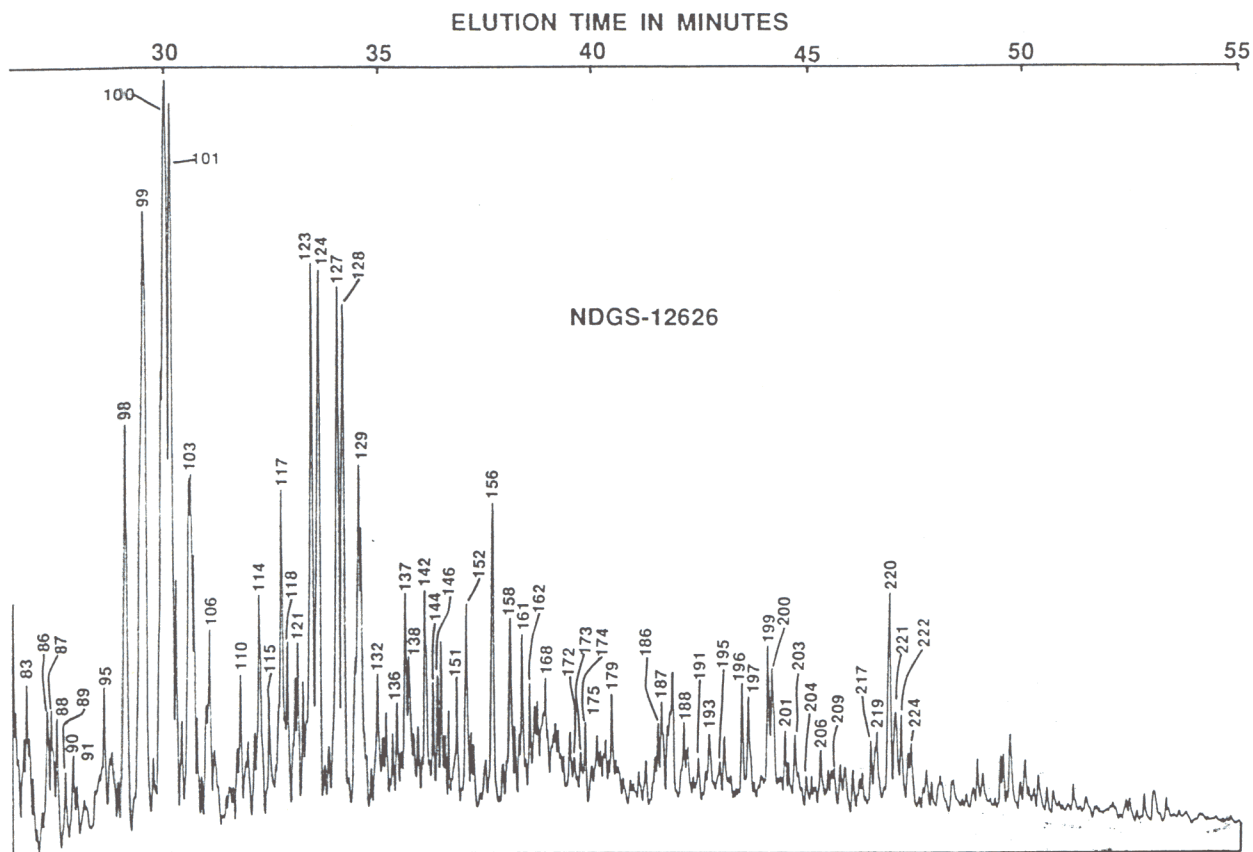


Fig. 21. C₁₈ to C₃₀ aromatic-HC gas chromatograms for a representative Bakken oil (NDGS-12626) and a representative mid-Madison oil (N8-138). Many of the labelled peaks are identified in Table 5 and are used in the aromatic-HC compound-ratio plots of Figures 22, 23 and 25.

Table 5. List of aromatic HCs identified in Figures 21 and 24. MW is molecular weight.

Peak Number	Compound
1	Ethylbenzene
2	Pra- and methylxenes
3	Orthoxylene
4	Isopropylbenzene
5	N-propylbenzene
6	Pra- and meta-ethylolene
7	Unknown (MW-120)
8	Orthoethylolene
9	1,2,4- + 1,3,4-trimethylxenes
10	Isobutylbenzene
11	Sec-butylbenzene
12	1,2,3-trimethylbenzene
13	Unknown (MW-120, Trimethylbenzene?)
14	Unknown (MW-120, Trimethylbenzene?)
15	Methylstyrene
16	Tetramethylinaphthalene
17	Tetramethylinaphthalene
18	Tetramethylinaphthalene
19	Phenanthrene
20	Radialstyrene - Tert-butylbenzene
21	Orthodistyrene
22	1,3-dimethyl-4-ethylbenzene
23	Unknown (MW-134)
24	Unknown (MW-148)
25	Unknown (MW-148)
26	Unknown (MW-148)
27	Unknown (MW-148)
28	Unknown (MW-148)
29	1,4,5-tetramethylbenzene
30	1,3,5-tetramethylbenzene
31	1,2,3,5-tetramethylbenzene
32	Unknown (MW-148)
33	Unknown (MW-148)
34	Unknown (MW-148)
35	Unknown (MW-148)
36	1,2,3,4-tetramethylbenzene
37	Naphthalene
38	1-methylinaphthalene
39	2-methylinaphthalene
40	1-ethylinaphthalene
41	2,6,7,2-dimethylinaphthalene
42	1,3,7-dimethylinaphthalene
43	1,3,7-trimethylinaphthalene
44	1,3,6-trimethylinaphthalene
45	Unknown (MW-170ethylstyrene?)
46	Unknown (MW-168methylbiphenyl?)
47	Unknown (MW-168methylbiphenyl?)
48	1,5,7+1,2-dimethylinaphthalene
49	1,6-dimethylinaphthalene
50	1,3,7+1,4-dimethylinaphthalene
51	1,6-dimethylinaphthalene
52	1,3,5+2,6-dimethylinaphthalene
53	1,3,5+2,6-dimethylinaphthalene
54	2,2-dimethylphenanthrene
55	1,3,5+3,9+2,10+3,10-dimethylphenanthrene
56	1,6,7+2,9+2,5-dimethylphenanthrene
57	1,9,7+4,9+4,10-dimethylphenanthrene
58	1,9,7+4,9+4,10-dimethylphenanthrene
59	Trimethylidibenzothio-phenanthrene
60	230-234 Trimethylidibenzothio-phenanthrene + ?
61	3-methylphenanthrene + 1-methylidibenzothio-phenanthrene in all mid-Madison samples

Of the six Madison oils analyzed, the stearane fragmentograms from N8-5, -56, -121 and -28 (N8-28 and -121 shown in Fig. 27) were somewhat similar but also had some significant differences. The stearane fragmentograms from N8-10 and N8-76 (Figs. 26 and 27) distinctly differ from one another and from those of the other four Madison oils. In fact, the fragmentograms from the three least mature Bakken oils analyzed (NDGS-12779, -9240 and -12814) resembled the four Madison (N8-5, -56, -121 and -28) fragmentograms as closely as the four Madison fragmentograms resembled each other. For example, in Figure 27 note the similarity of NDGS-12779 to N8-28 and N8-121. However, minor differences are present: peaks 27, and 38-40, usually distinct in Madison oils, are absent or very small in the Bakken oils. Nonetheless, the similarity of the stearane distributions in the least mature Bakken oils with those from four of the Madison oils suggests that all the oils could belong to a single family. However, this is not our conclusion, because of the profound differences we detailed above between the two oil sets. Instead we conclude that: 1) stearane peak distributions can be quite similar for moderately mature to mature oils from different and distinct source

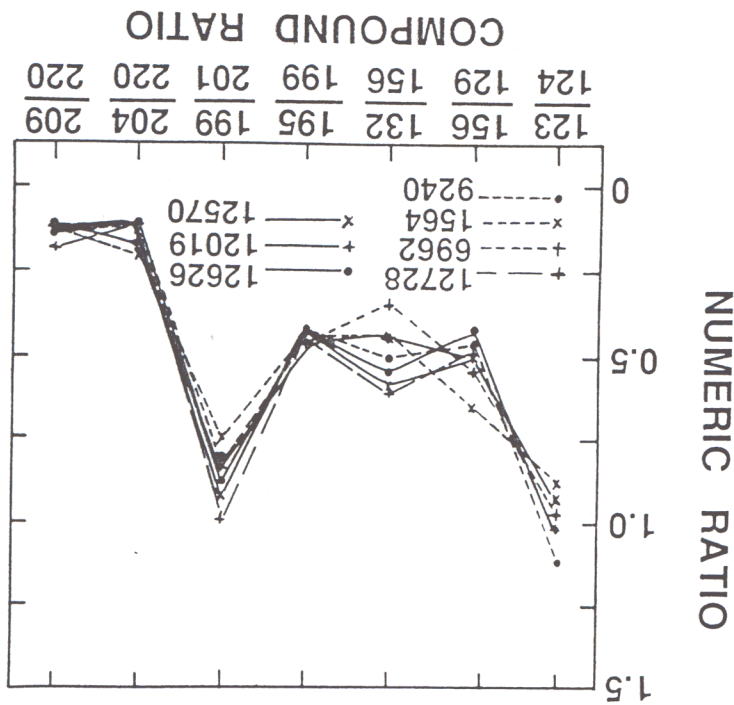


Fig. 22. Aromatic-HC compound-ratio plots for seven Bakken oils (full range of maturity and geographic distribution) for some of the compounds labelled in Figure 21.

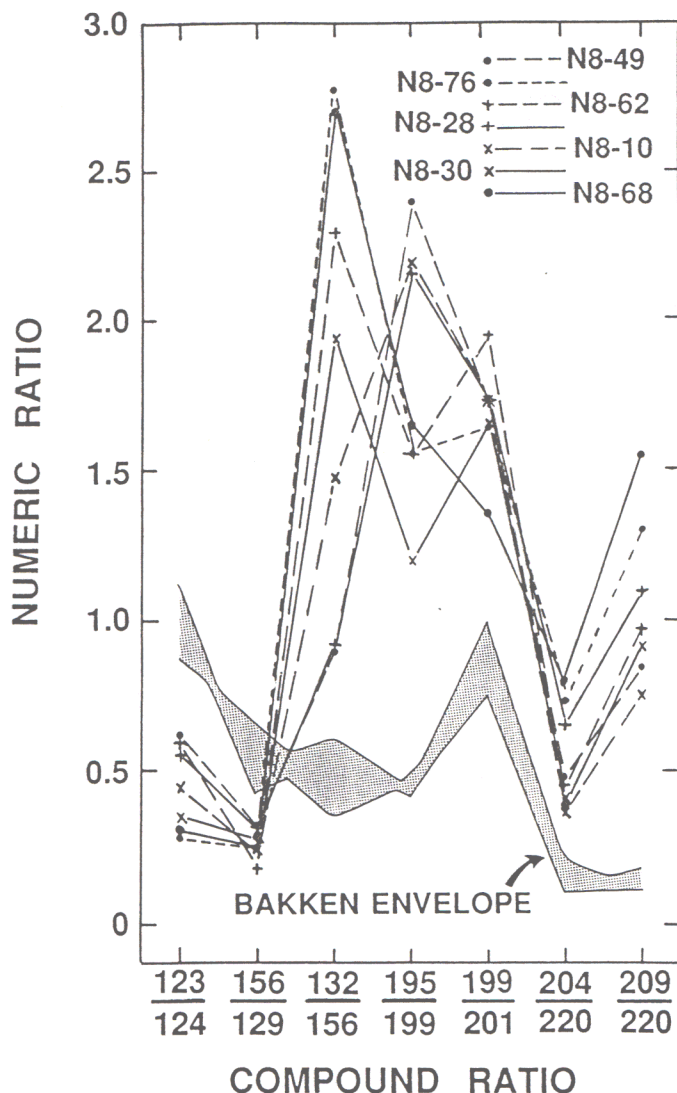


Fig. 23. Aromatic-HC compound-ratio plots for seven randomly selected mid-Madison oils for the same compounds used in Figure 22. The distribution for the same plots of the Bakken oils in Figure 22 is shown by the stippled pattern.

rocks and thus in some cases have only marginal utility as a source-facies index to group oil families; 2) within the same oil family with a wide maturity range, steranes cannot discriminate oils into a single oil family; and 3) ratios of certain diasteranes and steranes appear to be excellent maturity indices and thus sterane distributions may be better maturity indices than source-facies indices.

However, we qualify the above conclusions. None of the sterane distributions from the six Madison oils analyzed are close to exact matches. This fact supports our conclusion above that not all the Madison oils have the same source rock. On the other hand, the sterane distributions from the three least mature Bakken oils analyzed are exact overlays. Thus, it does appear that *for oils of roughly the same maturity*, exact matches of sterane distributions, and not just similar distributions, can discriminate source-facies.

Terpanes

Relevant terpane distributions (Fig. 28) were obtained from only two (NDGS-12779 and -9240) of the six Bakken oils we analyzed. The terpanes in the other four oils were so thermally stressed that source-facies comparisons are meaningless. The terpane distributions from the two Bakken oils in Figure 28 do not match each other. However, we believe that this is mainly due to maturity; with increasing maturity in the Bakken oils, hopane (peak 75, Fig. 28) decreased in size relative to all other peaks in the terpane fragmentograms. This maturity change would account for the differences in the terpane fragmentograms for the two Bakken oils of Figure 28. The least-stressed terpane distribution that we obtained from a Bakken oil (NDGS-12779) distinctly differs from those of all six Madison oils that we analyzed.

None of the C_{19} to C_{36} terpane distributions from the six analyzed Madison oils matched each other, although two (N8-56 and -5) were similar. This observation again supports our hypothesis that not all the Madison oils we analyzed have the same source rock.

The C_{19} - C_{29} tricyclic terpanes are numbered in Figure 29 and many of the numbered peaks are identified in Table 7. C_{19} - C_{29} tricyclic-terpane fragmentograms are shown in Figure 30 for three Bakken oils and three Madison oils. The C_{19} to C_{29} tricyclic terpanes have extended thermal stabilities (Seifert and Moldowan, 1978; Peters and Moldowan, 1993) and thus were more useful as source-facies indices than other biomarkers. A distinct distribution, different from that in the Madison oils, was present in four of the Bakken oils. Furthermore, although the C_{19} to C_{29} tricyclic terpanes were thermally stressed in the other two Bakken oils, remnants of that distribution were also evident.

Among the identified peaks (Fig. 29), the C_{19} tricyclic terpane (peak 1) and the C_{24} tetracyclic terpane (peak 38) are always larger in the Madison oils than in the Bakken oils, with peak 38 always much larger (Fig. 30). However, the most distinctive differences are in the unidentified peaks of Figure 30. Peaks 1-6 form a group of roughly the same size in the Bakken oils, whereas in the Madison oils peaks 2-6 are small or missing. In the Madison oils, peaks 7-10 decrease in intensity with increasing elution time, a distribution not present in the Bakken oils. Peak 33 was always large in the six Madison oils analyzed and was very small in the Bakken oils. Lastly, peak 34, in the mid-Madison oils, is absent in the Bakken oils. The characteristic differences in the unidentified peaks of the C_{19} to C_{29} tricyclic-terpane fragmentograms between the two oil sets suggest that: 1) the Bakken and Madison oils have different source rocks; 2) the six Madison oils we analyzed have the same source rock, contrary to the conclusion drawn from the total (C_{19} - C_{36}) terpane fragmentograms for the Madison oils; 3) the unidentified peaks in the C_{19} - C_{29} tricyclic-terpane fragmentograms (rather than the commonly employed tricyclic terpanes) may be much more useful than other biomarkers as source-facies indices. This is because these compounds are

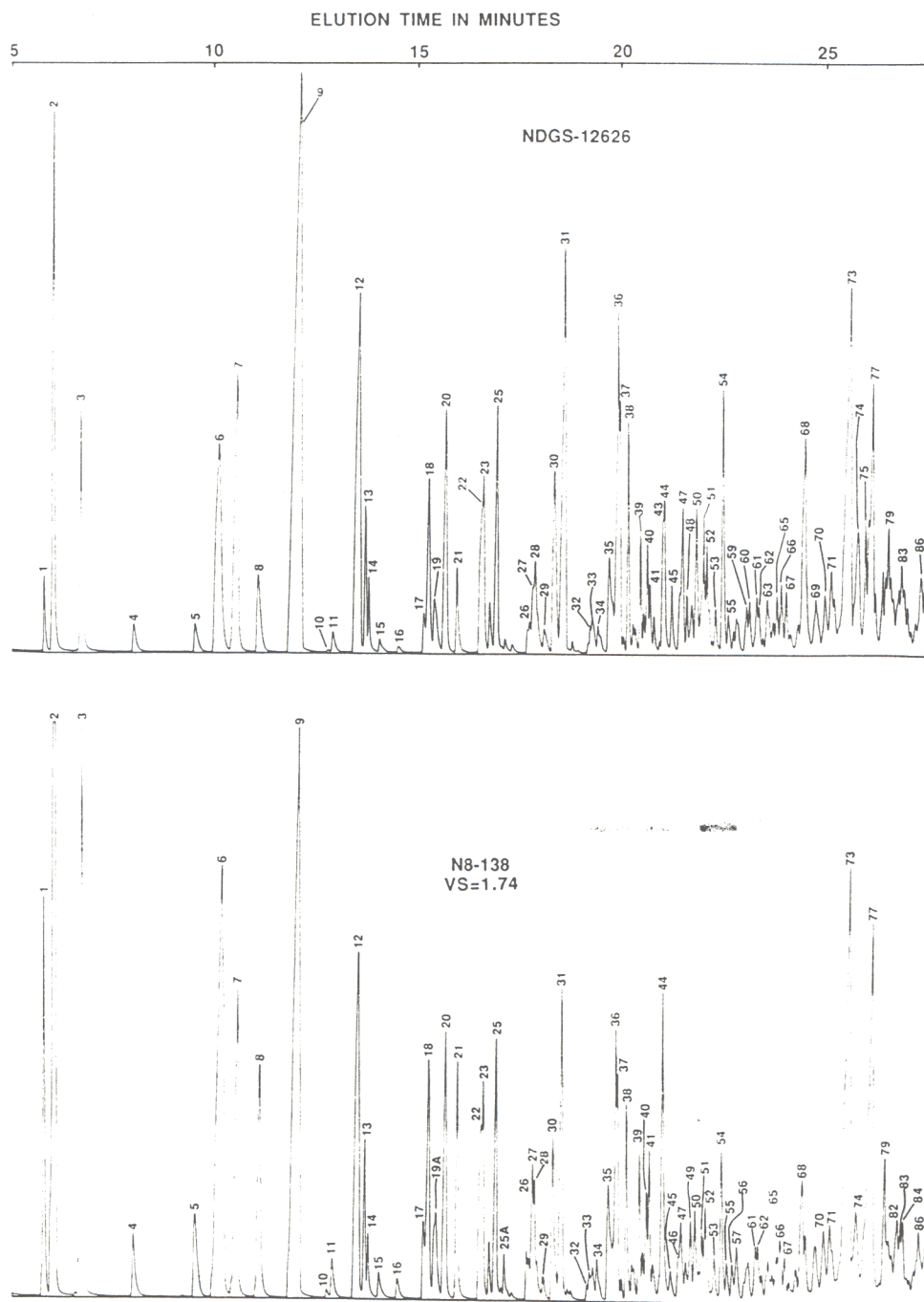


Fig. 24. C_8 to C_{18} aromatic-HC gas chromatograms for a representative Bakken oil (NDGS-12626) and a representative mid-Madison oil (N8-138). The vertical scale (VS) of the mid-Madison oil was increased 174% to make the two chromatograms more comparable. Some of the identified peaks are identified in Table 5 and are used in the aromatic-HC compound-ratio plots of Figure 25.

more thermally stable than other (none tricyclic-terpane) biomarkers and thus retain characteristic distributions inherited from the source rock over wider maturity ranges than do the other biomarkers. On the other hand, the commonly employed tricyclic terpanes (peaks 1, 7, 13, 22, 25, 30, 38, 50, 51, 55 and 56) appear to be much less useful as source-facies indices than the unidentified peaks because of the uniform distributions observed, at least in this case.

Aromatized Steranes

Of the oils examined, only the most immature Bakken oil (NDGS-12779) and two of the Madison oils (N8-76 and N8-10) had viable fragmentograms of either the mono- or diaromatic steroids. Thermal stress caused low signal-to-noise ratios in the fragmentograms of all other oils which precluded the possibility of any useful source-facies information from those fragmentograms.

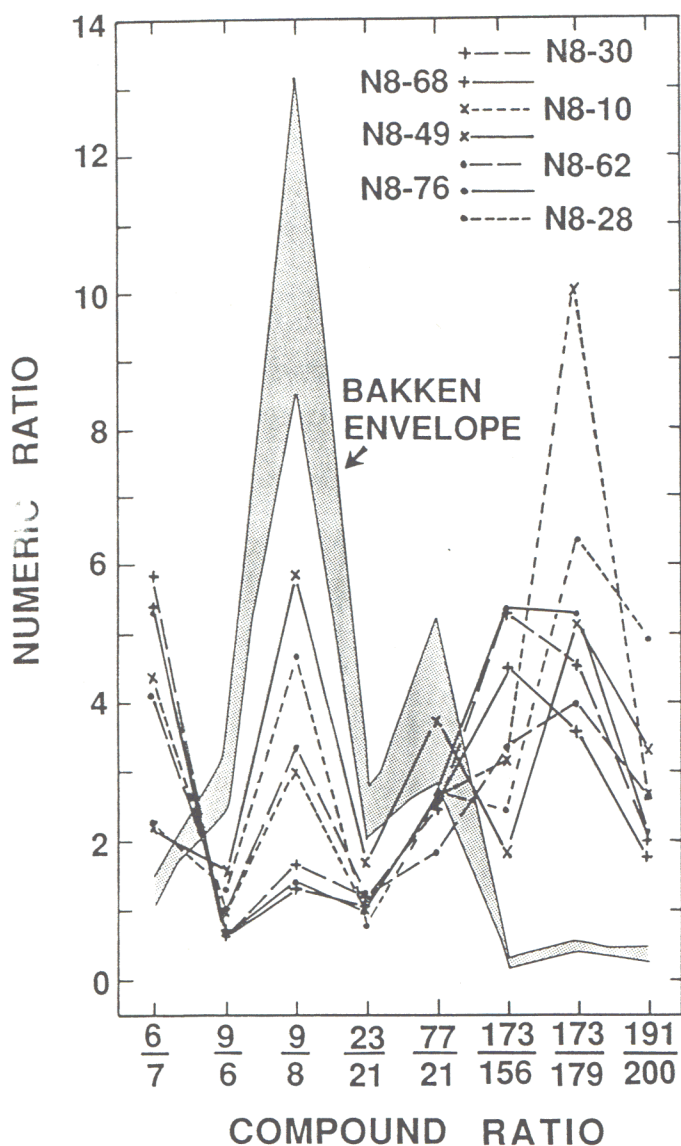


Fig. 25. Aromatic-HC compound-ratio plots for the seven Madison oils plotted in Figure 23 for some aromatic HCs labelled in Figure 24 and Figure 21. The distribution for the same plots for the Bakken oils used in Figure 22 is shown by the stippled pattern in Figure 25.

DISCUSSION

PREVIOUS WORK

Our data and conclusions disagree with those of Williams (1974) and, therefore, with the subsequent models developed by Dow (1974), Meissner (1978) and other investigators (including Price *et al.*, 1984). Our differences with Williams (1974) are due to the fact that we used different correlation tools than he to group Williston Basin oils and to attempt correlation of those oils to their source rocks. He used: 1) n-paraffin profiles over a limited (C_{15} to C_{30}) carbon number range; 2) nondiscriminatory gasoline-range HC ternary (n-paraffin iso-paraffin and cyclo-paraffin) compositional plots; 3) whole bitumen carbon isotopic ratios; and 4) plots of optical rotation versus carbon isotopic ratios. It should be noted that these

Table 6. List of sterane biomarkers identified in Figure 26.

Peak Number	Compound
6	$13\beta,17\alpha$ -(20S) diacholestane (C_{27})
9	$13\beta,17\alpha$ -(20R) diacholestane (C_{27})
11	$13\alpha,17\beta$ -(20S) diacholestane (C_{27})
12	$13\alpha,17\beta$ -(20R) diacholestane (C_{27})
13	$13\beta,17\alpha$ -(20S) 24-methyldiacholestane (C_{28} , I)
14	$13\beta,17\alpha$ -(20S) 24-methyldiacholestane (C_{28} , II)
16	24-methyldiacholestane (C_{28})
18	$13\beta,17\alpha$ -(20R) 24-methyldiacholestane (C_{28} , I)
19	24-ethyldiacholestane (C_{29})
20	$13\alpha,17\beta$ -(20S) 24-methyldiacholestane (C_{28})
21	$5\alpha,14\alpha,17\alpha$ -(20S) cholestane (C_{27})
22	$5\alpha,14\beta,17\beta$ -(20R) cholestane (C_{27}) + $5\alpha,14\beta,17\beta$ -(20S) cholestane (C_{27}) + unknown C_{29} diasterane
24	$5\alpha,14\alpha,17\alpha$ -(20R) cholestane (C_{27}) + $13\alpha,17\beta$ -(20R) 24-methyldiacholestane (C_{28})
25	$13\beta,17\alpha$ -(20R) 240-ethyldiacholestane (C_{29})
26	$5\alpha,14\alpha,17\alpha$ -(20S) 24-methylcholestane (C_{28}) + unknown C_{29} diasterane
30	$5\alpha,14\beta,17\beta$ -(20R) 24-methylcholestane (C_{28})
31	$5\alpha,14\alpha,17\alpha$ -(20R) methylcholestane (C_{28})
33	$5\alpha,14\alpha,17\alpha$ -(20S) 24-ethylcholestane (C_{29})
34	$5\alpha,14\beta,17\beta$ -(20R) 24-ethylcholestane (C_{29})
35	$5\alpha,14\beta,17\beta$ -(20S) 24-ethylcholestane (C_{29})
37	$5\alpha,14\alpha,17\alpha$ -(20R) 24-ethylcholestane (C_{29})

tools are in only limited use today: 1) C_8 to C_{38} n-paraffin profiles are useful discriminatory tools; however, more limited C_{15} to C_{30} profiles are much less utilitarian, except where n-paraffin distributions of two oil families are vastly different; 2) specific ratios of gasoline-range HCs are useful discriminatory tools but simple ternary compositional plots for the gasoline-range HCs are rarely used for this purpose; 3) optical rotation of oils is rarely used in present-day studies; and 4) carbon isotopic values are useful as discriminatory tools but Williams (1974) compared carbon isotopic values of whole rock bitumen to the oils. Thus resins and asphaltenes, which make up high percentages of source rock bitumen, are unduly weighted. Carbon isotopic values of whole rock bitumen are not compared to oils in present-day investigations. Instead carbon-isotopic values of saturated and aromatic HC fractions from oils and rock bitumens are compared to each other. However, carbon isotopic values of Leenheer (1984) do support Williams' (1974) data and conclusions (discussed below).

It should also be noted that the Bakken shale cuttings samples used for the Williams' (1974) study appear heavily contaminated by cavings from other units. The total organic carbon (TOC) contents of Williams' (1974) 26 Bakken shale samples ranged from 0.65 to 10.33% and averaged 3.84%. Published (Price *et al.*, 1984) and unpublished data from our analyses of over a thousand Bakken shale samples demonstrate that away from vertical or horizontal contacts Bakken shale TOCs range from 7.00% (for very mature samples) to 26.0% (for immature samples) and probably average around 10.0 to 13.0% (basin-wide). Thus, the bitumen from Williams' (1974) "Bakken shale" cuttings was not totally composed of Bakken shale bitumen but was contaminated by bitumen from caving of other stratigraphic units.

Williams' (1974) correlation tools were discriminatory enough to separate three distinct oil families. However, these

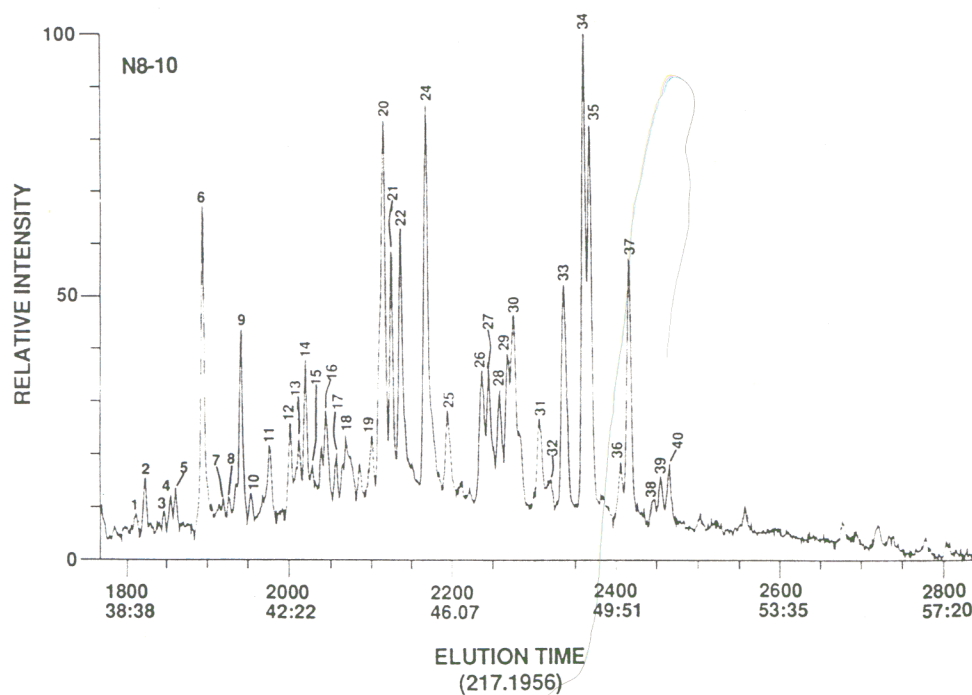


Fig. 26. Sterane (mass 217.1956) fragmentogram of a Madison oil (N8-10). Many of the numbered peaks are identified in Table 6.

tools could not discriminate grossly similar Madison oils from Bakken oils, even though these two oils have different sources. Nor can Williams' (1974) tools definitively correlate the Madison oils to a given source rock. It may appear that we are highly critical of Williams' (1974) study. This is not the case. Williams (1974) is one of the early pioneering studies in petroleum geochemistry, continues to strongly influence petroleum-geochemistry, and provides a foundation on which subsequent petroleum-geochemical studies of the Williston Basin (including this one) have been built. However, Williams' (1974) study was carried out 20 to 25 years ago with petroleum-geochemical analytical tools which are rudimentary by today's standards. Furthermore, petroleum-geochemical analytical philosophies, techniques and approaches also have significantly evolved from those of twenty-five years ago.

Some of Williams' (1974) data supports one of our findings, that the Madison oils appear to have more than one source, *e.g.*, are composed of more than one oil family. The distribution of Williams' (1974) *n*-paraffin profiles for the Madison oils is much larger than that of his other two oil families (Williams, 1974, his figure 6). Also, Williams' (1974) range of carbon-isotopic values of his Madison oils is much larger than that of his other two oil sets (Williams, 1974, his figures 12, 14 and 15). Both these observations suggest that multiple subfamilies of Madison oils may exist.

Our data and conclusions also differ from those of Leenheer (1984) who claimed to correlate bitumen extracted from Bakken shales from both the Williston and Western Canadian basins to Mississippian oils reservoirs in both basins. Leenheer (1984) found similar carbon isotopic values for saturated and aromatic HCs from six Williston Basin Madison oils and from bitumen from five mature (U.S.A.)

Bakken shales and from 25 Canadian Bakken shales. Her data thus support Williams (1974). However, this similarity of carbon isotopic values alone is insufficient to correlate Bakken shale bitumen to Madison oils. Instead, we believe that data presented by Leenheer (1984) support some of our conclusions.

Leenheer (1984, p. 522) noted that comparison of saturated-HC gas chromatograms of immature Bakken shale bitumen (which represents the majority of her sample base) to that of Madison oils would be invalid. She also noted that the saturated-HCs from her immature Bakken shales were less paraffinic than saturated HCs from her Williston basin Madison oils. She assumed that with increasing maturity this characteristic would change, and Bakken shale bitumen would become more paraffinic. Based on the composition of the Bakken oils of this study and on the data of Price *et al.* (1984) this is an incorrect assumption. To support her assumption, Leenheer (1984, her figure 5) provided a mature Bakken shale saturated-HC gas chromatogram strikingly similar to that of both a Williston Basin Madison oil and to a Mississippian oil from the Alberta Basin. From this similarity, Leenheer (1984) concluded that the Bakken shales had sourced both the Madison and Mississippian oils in the Williston and Alberta Basins, respectively. However, Leenheer's (1984) "Bakken" shale in her figure 5 was from Alberta and had a TOC of only 1.85 percent.

We believe Leenheer's (1984) assumption to be erroneous that Mississippian shales [from the Exshaw (?) Formation] in Alberta, Canada, sourced the Madison oils in the U.S.A. portion of the Williston Basin. Furthermore, Leenheer's (1984) conclusion is incorrect that very similar characteristics are present within the saturated HCs from both Bakken shales and Madison Williston Basin oils. Leenheer (1984) had five mature Bakken shale samples from the U.S.A. side of the

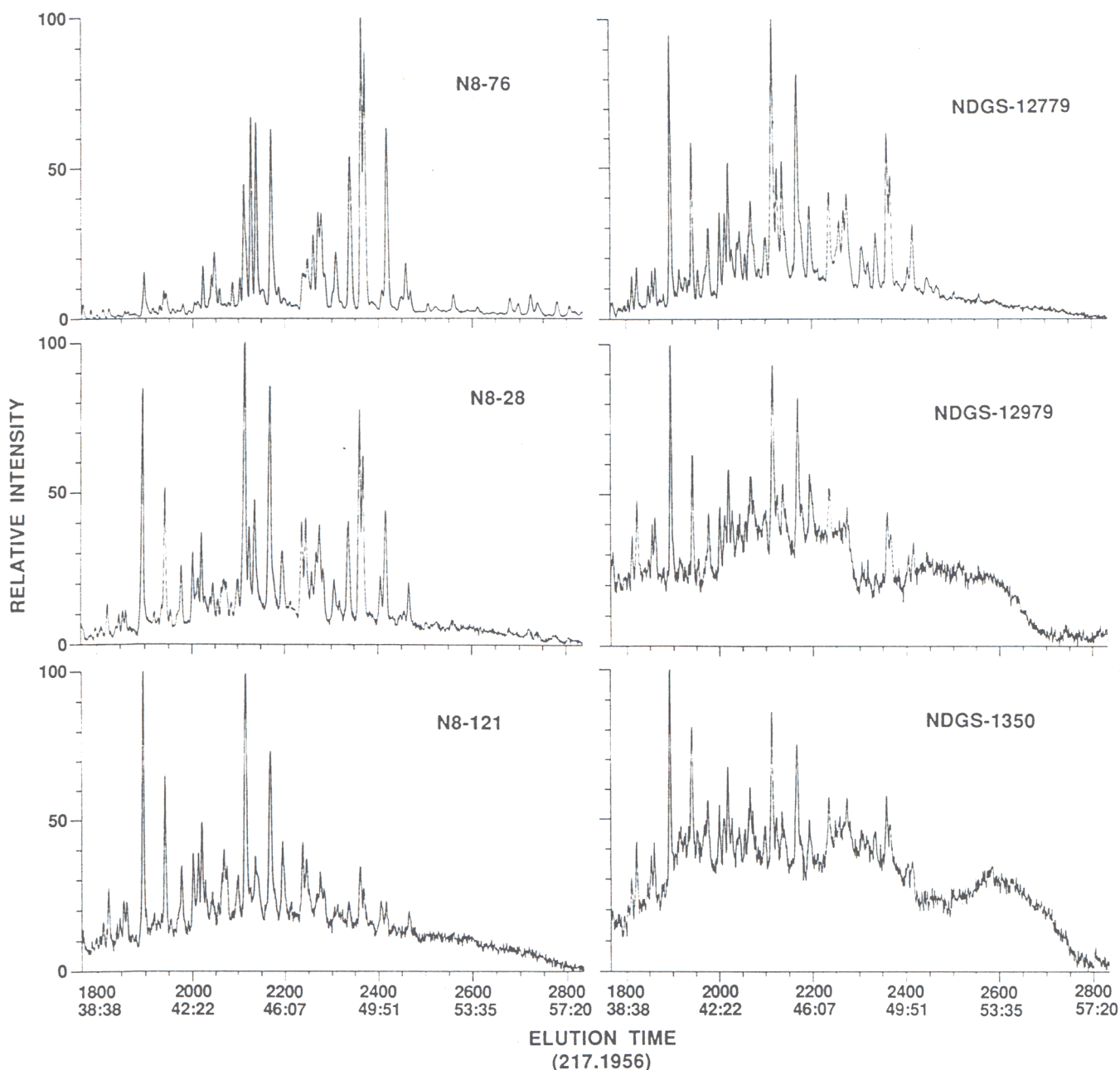


Fig. 27. Sterane (mass 217.1956) fragmentograms of three Bakken (NDGS-12779, -12979 and -1350) and three Madison (N8-76, -28 and -121) oils. Use Figure 26 and Table 6 for peak identification.

Williston Basin. However, she did not present $C_{15}+$ saturated-HC gas chromatograms from these samples for comparison to the Madison Williston Basin oils. From the well locations supplied by Leenheer (1984), four of her five Bakken cores came from two wells (NDGS-527 and -607). We have numerous Bakken shale extracts and gas chromatograms from these two wells, chromatograms which bear no resemblance to those from Madison Williston Basin oils. In fact, characteristic differences noted in this study between saturated HCs from the Bakken and Madison oils are also present in our Bakken shale extracts from NDGS-527 and -607 (see figure 20 of Price *et al.*, 1984). These characteristic differences are also present in

Leenheer's (1984) two examples from true Bakken shales she presented ("Upper Bakken 6324" and "Lower Bakken 6362", her figure 5). These differences are: 1) different Bakken shale bitumen pristane/phytane ratios which do not change as a function of increasing maturity (Fig. 6, this paper); and 2) a much greater naphthenic hump and less n-paraffins in the saturated HCs from Bakken shale bitumen and oils, compared to the Madison oils. Had Leenheer (1984) supplied a saturated-HC gas chromatogram from the Bakken shales of NDGS-527 or -607, her conclusion would have been untenable that Bakken shale saturated HCs matched those of Williston Basin Madison oils.

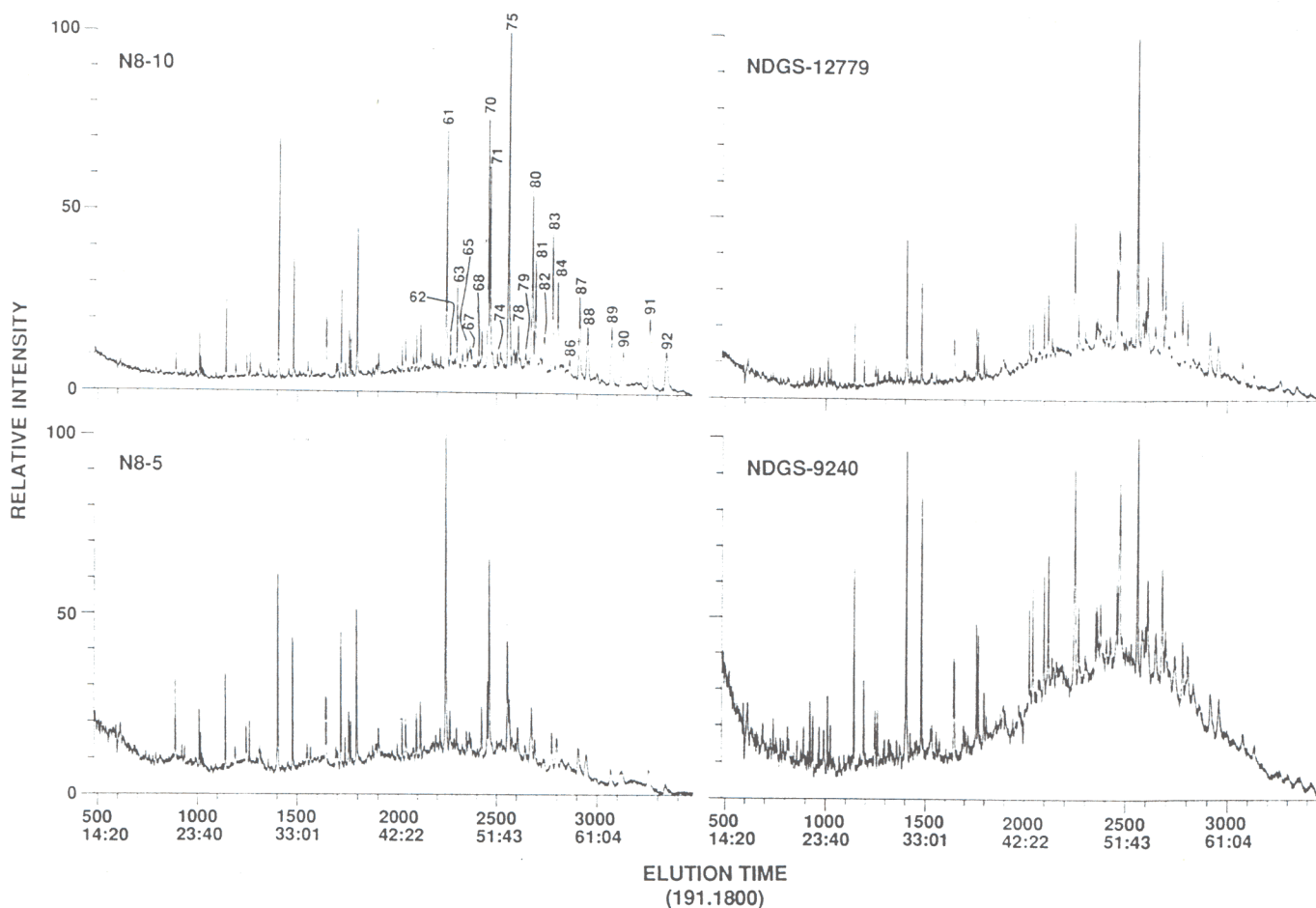


Fig. 28. C_{19} to C_{36} terpane (mass 191.1800) fragmentograms of two Bakken (NDGS-12779 and -9240) and two Madison (N8-5 and -10) oils. The numbered compounds in the N8-10 fragmentogram are identified in Table 7 and serve as an index for the other three fragmentograms of Figure 28.

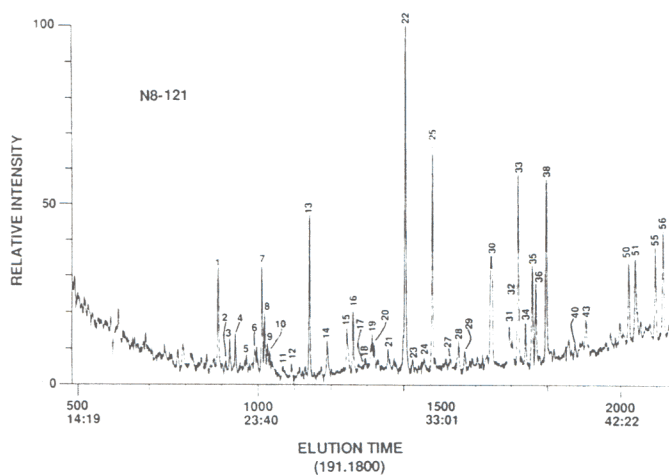


Fig. 29. C_{19} to C_{29} tricyclic-terpane (mass 191.1800) fragmentogram of a Madison oil (N8-121). Many of the numbered peaks are identified in Table 7.

Leenheer (1984) also employed biomarkers to compare Bakken bitumen to Madison oils. She noted that sterane distributions from different mature sources appear fairly uniform and thus are not always good correlation tools. We agree.

Furthermore, as we did, she found the tricyclic terpanes more useful for correlation, although she presented only C_{19} to C_{26} tricyclic distributions. Leenheer (1984) found two unknown peaks ("A" and "B", her figure 7) between the C_{25} and C_{26} tricyclic terpanes in the Madison oils. These peaks correspond to the unknown peaks 33 (her "A") and 34 (her "B") in our Madison oils, peaks which are not found in the Bakken oils. Leenheer (1984) found neither peak A nor B in the analyses of the two true Bakken shales which she presented, and found only peak B in her bitumen from an Alberta Exshaw shale (TOC = 0.56). Disregarding this, she concluded that the tricyclic terpanes from the Bakken shales were similar to those in the Madison oils and that the Bakken shales had therefore sourced these oils. We disagree. Leenheer's (1984) carbon isotopic values of the saturated and aromatic HCs do support a tie between Bakken shale bitumen and Madison oils. However, as stated above, these values alone (or values from any single correlation tool, alone) do not conclusively correlate oils to source rocks.

Leenheer and Zumberge (1987) used C_{15+} saturated and aromatic HC gas chromatograms and diterpane, triterpane and sterane distributions (presented in their figure 3) to correlate Williston Basin Madison oils to Bakken shale bitumen.

Table 7. List of terpanes and hopanes identified in Figures 28 and 29.

Peak Number	Compound
1	C ₁₉ tricyclic terpane
7	C ₂₀ tricyclic terpane
13	C ₂₁ tricyclic terpane
16	C ₂₂ tricyclic terpane
22	C ₂₃ tricyclic terpane
25	C ₂₄ tricyclic terpane
30	C ₂₅ tricyclic terpane
35	C ₂₆ (22S) tricyclic terpane
36	C ₂₆ (22R) tricyclic terpane
38	undetermined C ₂₄ tetracyclic terpane
50	C ₂₈ (22S) tricyclic terpane
51	C ₂₈ (22R) tricyclic terpane
55	C ₂₉ (22S) tricyclic terpane
56	C ₂₉ (22R) tricyclic terpane
61	18 α -trisorneohopane (C ₂₇ T _s)
62	C ₃₀ (22R) tricyclic terpane
63	17 α -trisorneohopane (C ₂₇ T _m)
65	C ₃₁ (22S) tricyclic terpane
67	C ₃₁ (22R) tricyclic terpane
68	bisnorhopane (C ₂₈)
70	norhopane (C ₂₉)
71	18 α -neonorhopane (C ₂₉)
74	hopane (C ₃₀ , I) + 17 β ,21 α normoretane (C ₂₉)
75	hopane (C ₃₀)
78	C ₃₃ (22R) tricyclic terpane + 17 β ,21 α -moretane (C ₃₀)
79	C ₃₄ (22S) tricyclic terpane
80	22S homohopane (C ₃₁)
81	C ₃₄ (22R) tricyclic terpane + 22R homohopane (C ₃₁)
82	gammacerane (C ₃₀)
83	22S bishomohopane (C ₃₂)
84	22R bishomohopane (C ₃₂) + C ₃₅ (22S) tricyclic terpane
87	22S trishomohopane (C ₃₃)
88	22R trishomohopane (C ₃₃) + C ₃₆ (22R) tricyclic terpane
89	22S tetrakishomohopane (C ₃₄) + 17 β ,21 β ,-(22R) bishomohopane (C ₃₂)
90	22R tetrakishomohopane (C ₃₄)
91	22S pentakishomohopane (C ₃₅)
92	22R pentakishomohopane (C ₃₅)

However, we find no similarity of their Bakken shale bitumen to their Madison oils in the parameters they discussed in their figure 3. For example, they observed the high concentrations of dibenzothiophenes in the Madison oil aromatic HCs, versus the low concentrations in Bakken shale aromatic HCs, both of which we observed in our study. In our opinion, the disparate nature of Leenheer and Zumberge's (1987) Madison oil and Bakken shale bitumen preclude any possible match between these two sample groups.

Thode (1981) used organic sulfur isotopes to correlate Bakken shale bitumen to Williston Basin Madison oils. Although he examined a number of Madison oils, he examined the bitumen from only an upper and lower Bakken shale from a single well. The sulfur value for the upper shale fell outside the range of the Madison oils. The single value from the lower Bakken shale fell within the range of the Madison oils. This led Thode (1981) to conclude that the lower Bakken shale sourced the Madison oils.

The conclusion that the Bakken shales have sourced the Williston Basin Madison oils is firmly embedded in both petroleum-geochemical literature and thought. However, after careful examination of the evidence for it we find that there is no foundation for this conclusion.

Osadetz *et al.* (1992), in a large study of Canadian rocks and oils of the Williston Basin found that Madison oils did not correlate to either bitumen from Bakken shales or to their three Bakken-sourced oils. These three oils (Rocanville, Roncott and Daly) are reservoirized in the middle Bakken member, which in Canada often is a permeable and porous sandstone compared to the dense siltstone on the U.S.A. side of the basin. Osadetz *et al.* (1992) used gasoline-range HC analyses, C₁₅+ saturated-HC gas chromatograms, and biomarkers to differentiate oil families and possible source rocks.

Both the rocks and oils that Osadetz *et al.* (1992) studied are less mature than the oils and rocks examined here and in the Price *et al.* (1984) study. The Madison oils that Osadetz *et al.* (1992) studied would be the first oils expelled from whatever the source rock(s) are for these oils because these oils have migrated furthest from the HC kitchen on the U.S.A. side of the Williston Basin. Being the first expelled oils, they would also be less mature than the Madison oils expelled later on the U.S.A. side of the basin. Three points result from the rock-oil maturity differences on the U.S.A. and Canadian sides of the basin. First, this study augments Osadetz *et al.* (1992) in that the full spectrum of Williston Basin Madison oils is now analyzed. Second, two different studies using different oil samples, approaches, analyses and source facies indices have now reached the same conclusion. Third, because of the immaturity of most of the rocks on the Canadian side of the basin, it would be difficult, or impossible, to establish the true source rock(s) for the Madison oils by examining only Canadian Williston Basin rocks. This would be especially true if facies changes occur in the source rocks for the Madison oils, from the HC kitchen on the U.S.A. side of the basin to age-equivalent rocks on the Canadian side of the basin.

THE LACK OF BAKKEN/MID-MADISON OIL MATCH

None of our Madison oils, nor those of Osadetz *et al.* (1992), are in the Bakken oil family. Fundamental differences, outlined above, exist between the two oil groups. We recognize only three explanations for these observations: 1) the two oil families have different source rocks, *e.g.*, the Bakken shales did not source the Madison oils; 2) the Bakken shales did source the Madison oils, and after expulsion the oils were modified such that they no longer resembled the original oils expelled from the Bakken shales; and 3) after expulsion of the Madison oils from the Bakken shales, the oil remaining in the shales was exposed to higher maturation ranks than the expelled oils such that the residual oil thermally cracked and no longer resembled the expelled oils.

We do not favour the latter two possibilities for a number of reasons. Assume that light, undegraded oils always become so modified after source-rock expulsion such that expelled oils no longer match oil (or bitumen) remaining in the source rock. Then oil/source-rock matches could never be achieved, which is clearly not the case. Furthermore, with the exception of mixing and gas remigration, we are not aware of a mechanism which could cause such a modification. Nor can maturation differences between the expelled oils and the oils remaining in

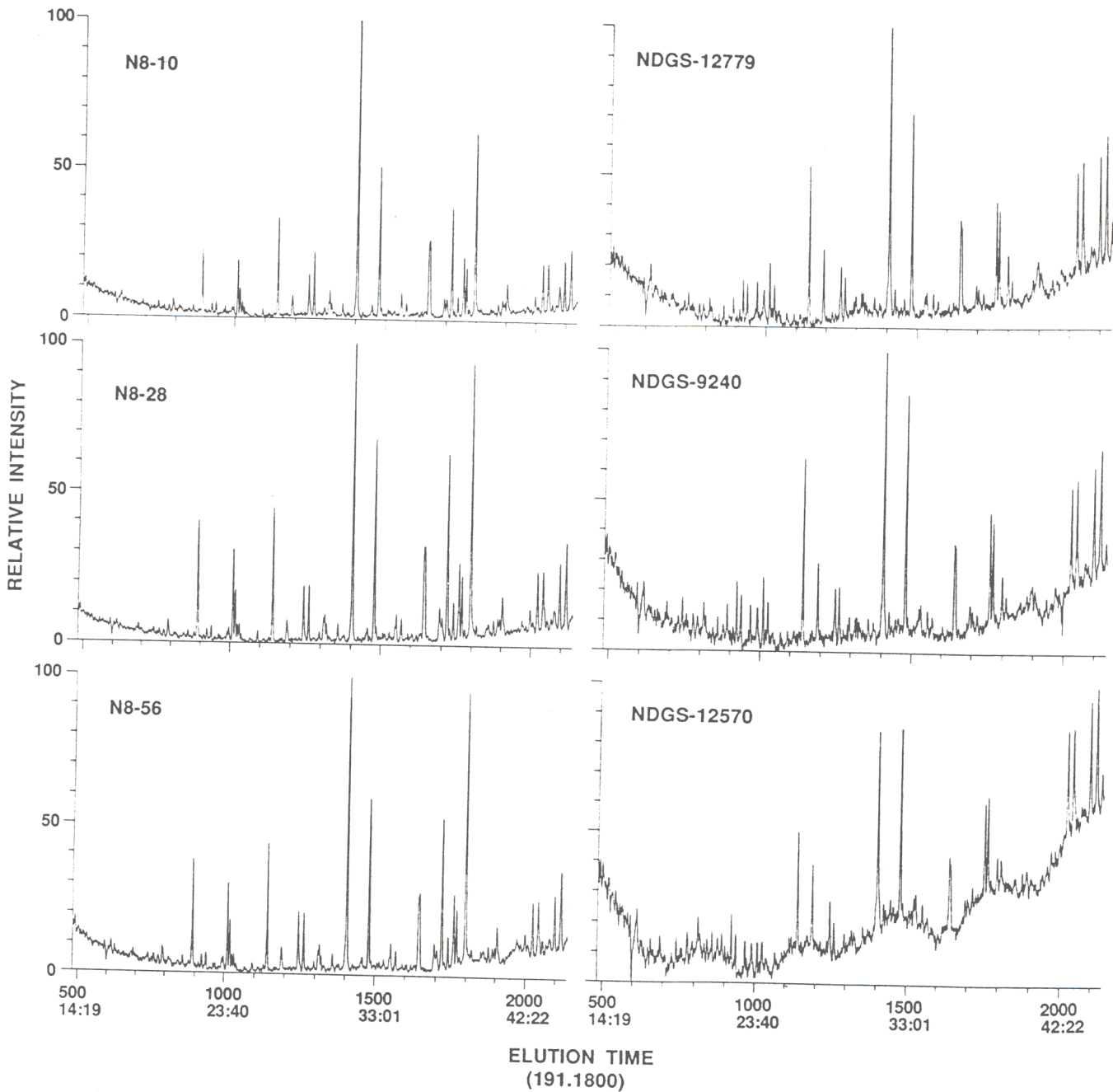


Fig. 30. C_{19} to C_{29} tricyclic-terpane (mass 191.1800) fragmentograms of three Madison (N8-10, -28 and -56) and three Bakken (NDGS-12779, -9240 and -12570) oils. Use Figure 29 and Table 7 for peak identification.

the source rocks be called upon. First, although most of the Bakken oils are more mature than most of the Madison oils, some oils from both sets do have a significant maturity overlap. This is partially demonstrated by the Rock-Eval Hydrogen Index data for the shales associated with the least mature Bakken oils of Table 3 (discussed above). Second, oil properties affected by maturity such as oil gravity, percentage of resins plus asphaltenes, percentage of C_{15+} saturated and/or aromatic HCs, biomarker distributions, *etc.*, all have significant overlap between the two oil sets. Third, source-facies compositional features in the Bakken oil saturated HCs contradict the hypothesis that the differences between the two oil

sets are due to postexpulsion maturity differences. For example, as discussed above, in Price and Wenger (1992), and in Price (1993a), during extreme thermal stress, the naphthenes are destroyed and the n-paraffins increasingly make up higher percentages of the saturated HCs. However, the Bakken oils, most of which are more mature than the Madison oils, are poor in n-paraffins and rich in naphthenes compared to the Madison oils. These are source-facies characteristics exactly opposite of the expected maturity trends. As another example, dibenzothiophene and the methyl- and dimethyldibenzothiophenes are among the most stable of all aromatic HCs (Price, 1993a). Yet the less mature Madison oils contain abundant dibenzothiophenes

compared to small amounts in the more mature Bakken oils (another source facies inheritance).

The final argument against the differences between the two oil sets being due to postexpulsion maturity differences is the wide maturity ranges in both oil sets. The Bakken oils range from "post-mature" to just beginning intense HC generation (NDGS-12779, Rock-Eval Hydrogen Index equals 535, Table 3). Yet the least mature Bakken oils type with the most mature Bakken oils and have few familial characteristics with either the least (or most) mature Madison oils.

We conclude that the Bakken oils and the Madison oils are two distinct oil families with fundamental differences inherited from different source rocks.

We offer two other comments. First, our examination of both published and unpublished analyses has not yet revealed a Madison reservoir in the Williston Basin with Bakken-sourced oil. Second, we see no evidence of mixing of Bakken and Madison oils in the same reservoir. This is not to say that examples of either case do not exist. Indeed some mixing of Bakken and Madison oils would be expected because two examples of mixing of lower Paleozoic and Madison oils were evident in our study (M8-23 and M8-44, discussed above). The data of Osadetz *et al.* (1992), the data of this study, and unpublished analyses we have seen all probably account for over 95% of the known Madison production in the Williston Basin. We are amazed that so little (if any) of the oil generated by the Bakken shales has accumulated in the Madison reservoirs.

THE MID-MADISON OIL SOURCE ROCK

An acceptable understanding of petroleum geochemistry in the Williston Basin requires the identification of the source rocks for the Madison oils, the most important conventional oil deposits of the basin. We are proceeding with such a study with the hypothesis that the Madison oils are locally sourced by laterally discontinuous (or perhaps continuous) organic-rich marls deposited spatially close to, and in hydraulic connection with, the reservoir units. Several reasons lead us to this hypothesis. 1) Exploration geologists who are working, and have worked, in the Williston Basin have occasionally observed such rocks (Parker and Hess, 1980; and various personal communications). 2) The stratigraphy of the reservoir units and the geochemical characteristics of the Madison oils both constrain the source rock(s). 3) We follow Williams' (1974, p. 1248) criteria to identify possible source rocks for a given oil family: "In some basins, the search for specific source beds or source sequences usually can be narrowed down by the simple procedure of observing the stratigraphic distribution of each oil type. It would be expected that the frequency of any given oil type would be greatest in those reservoirs closest to the source". 4) By our working hypothesis, discussed below, in the absence of significant faulting (as in the Williston Basin), adequate drainage of generated HCs from source rocks only occurs where laterally continuous units (e.g., the mid-Madison reservoir units) can transmit fluids and are also directly adjacent to the source rock. That a generally

unrecognized and enigmatic source rock has yielded 9-10 billion barrels of in-place Madison oil in the Williston Basin absolutely requires adequate drainage (efficient oil expulsion) of generated HCs from the source rock(s).

Regarding the constraints on the source rocks for the Madison oils from stratigraphy of reservoir units (above), there are about fifteen separate significant mid-Madison reservoir units in the North Dakota portion of the Williston Basin, with several others in Montana, Saskatchewan (Peterson, 1985; Kent *et al.*, 1988; Lindsay, 1988) and Manitoba. Most of these reservoir units have excellent lateral continuity and good fluid transmissibility over large areas of the Williston Basin. Although some of these units occasionally interconnect vertically, generally they are hydraulically isolated in a vertical sense, except at unconformities in Canada. These observations suggest to us that multiple source rocks exist for the Williston Basin Madison oils.

As to the Madison oils, they are a chameleon-like group of oils which, depending on the correlation tool, can exhibit striking similarities, for example, peak distributions in the tricyclic terpanes and trimethylnaphthalenes. Such similarities strongly suggest that these oils are of one oil family. Concurrently, other source-facies indices have wide ranges, suggesting to us that the oils are of different families. Furthermore, these wide ranges in certain measurements are evident in the data of Williams (1974) and Osadetz *et al.* (1992). We envision only two possibilities for these observations. First, the oils originated from one source rock which has some lateral organic-facies variations but still retains some of its other source-facies characteristics. However, the predominantly vertically isolated hydraulic nature of the reservoir units seems to preclude this possibility. Second, different source rocks exist for some of the different Madison reservoirs, source rocks which were deposited in similar environments such that some petroleum-geochemical characteristics are common to all the rocks. We favour this second possibility as our current working hypothesis.

Characteristics exist within the Madison oils which are commonly attributed to a carbonate source: 1) the even preference in the n-alkanes (Figs. 5 to 11; Palacas, 1992); 2) low amounts of diasteranes (Fig. 27; Palacas, 1992; Peters and Moldowan, 1993); and 3) elevated amounts of organic sulfur in the form of benzothiophenes and/or dibenzothiophenes (Fig. 21; Palacas, 1992). These observations support the hypothesis that the source rocks for the Madison oils are organic-rich marls interbedded with the Madison limestones.

Several other source rocks have been suggested for the Madison oils. Williams (1974) suggested the lowermost shale of the Lower Mississippian Lodgepole Limestone. We have analyzed mature samples of this shale (marl) which is both generally laterally continuous throughout North Dakota and is found 2-6 m above the upper Bakken shale with Lodgepole Limestone between the two shales. TOC values for mature samples of this shale range from 5 to 8%. Thus, we expect that immature examples of this rock would have TOC values of 7 to 12%. Although thin (1-2 m), this shale would be an excellent source rock. Osadetz *et al.* (1992) suggested a shale (marl?) in

the middle of the Lodgepole Limestone which is laterally persistent on the Canadian side of the basin. Osadetz also pointed out the depths of this unit to us in a well (NDGS-2010, Fig. 1) in the most extreme northwest corner of Divide County and North Dakota (S.7, T.163 R.102). We visually examined these mid-Lodgepole shales from this well and they are obviously organic-rich and significantly thicker than the lowermost Lodgepole shale and would thus also be excellent source rocks. However, both these units are separated from the mid-Madison reservoirs by several hundred metres (or more) of dense impermeable limestone. We see no reason why oil generated by these two units could reach the Madison reservoirs when Bakken-generated oil could not. Thus, we do not favor either of these organic-rich units as source rocks for the Madison oils.

IMPLICATIONS

We suggest that the absence of Bakken-generated oil in the Williston Basin Madison reservoirs has important implications for both models of oil expulsion and accumulation and for the existence of very large in-place oil resource bases in self-sourced fractured shales. As discussed in Price and LeFever (1992) and Price (1993b), by conventional wisdom oil expulsion from organic-rich rocks is efficient. This is because the large decreases in Rock-Eval Hydrogen Indices which occur in such rocks with increasing maturity are not accompanied by equivalent increases in Soxhlet-extractable HCs. Also, the much greater volumes of HCs generated by these rocks, than found as conventional deposits in petroleum basins worldwide, have been attributed to loss from leakage at the earth's surface over geologic time and/or to dispersion during secondary migration. However, this disparity between the amounts of generated and conventionally reservoirized HCs is better explained by the known large losses of generated HCs to drilling fluids during the rock trip up the wellbore (Price and LeFever, 1992; Price, 1993b). By this reasoning, and using the Bakken shale as an example, Price and LeFever (1992) proposed that, in the absence of significant faulting and/or lacking an efficient carrier bed adjacent to a source rock, most generated HCs would remain in (or adjacent to) their source rocks. (They envisioned such generated HCs to be expelled into nonpermeable rocks sandwiching source rocks by vertically limited fracture networks created by overpressuring from organic-matter volume expansion in source rocks during HC generation.)

Given these hypotheses and observations, and the apparent lack of Bakken-generated oil in the Williston Basin Madison reservoirs, Price and LeFever (1992) proposed the existence of very large in-place oil-resource bases in self-sourced, organic-rich, fractured mature shales. The size of this resource base is suggested by mass-balance calculations of Schmoker and Hester (1983), Webster (1987) and Artindale (1990) who have estimated that the Bakken shales generated from 92 to 150 billion barrels (14.6 to 23.8 x 10⁹m³) of oil. We consider these to be conservative estimates because of low TOC and Rock-Eval Hydrogen Indices assumed in the above calculations. For example, a very large unpublished Rock-Eval data base which

we have compiled demonstrates that TOC contents are at least 15 to 17% for immature Bakken shales which surround the HC kitchen of the Williston Basin and which are removed from both vertical contacts with adjacent formations and from the Bakken depositional edge. These shales also have average original Rock-Eval Hydrogen Indices of at least 550-600. By contrast, we have documented that mature Bakken shales after generation have TOC values of 8 to 11% and Hydrogen Indices of 100 to 150. However, Schmoker and Hester (1983), who noted that their calculations were preliminary, averaged all the Bakken TOC values they measured to arrive at average immature values of 11.5% for the lower shale and 12.1% for the upper shale and assumed a Hydrogen Index loss for mature shales of only 167. Webster's (1987) values were similarly conservative. By using realistic higher initial TOC contents for immature shales (15 to 17% TOC) and higher Hydrogen Index losses (400 to 500 for mature shales) in the mass balance calculations of the above workers, we would arrive at significantly greater amounts of generated oil. Also, the above investigators did not consider: 1) the oil generated by the lowermost shale of the Lodgepole Limestone (discussed above); or 2) the decrease in original shale volume (estimated at about 15%) due to HC generation and expulsion from the Bakken shales to the adjacent units.

Whatever the volume of Bakken-generated oil, it is very large, in the range of hundreds of billions of barrels. Furthermore, the results of Osadetz *et al.* (1992) and our study suggest that very little, if any, of the oil generated by the Bakken shales has left the Bakken source system, because this oil could not have leaked out of the Williston Basin without charging the conventional Madison reservoirs. Results of Bakken horizontal drilling on the U.S.A. side of the Williston Basin demonstrate that part of this oil is mobile and recoverable. However, as Price and LeFever (1992) stressed, only a minute fraction of this oil-resource base appears recoverable by conventional drilling, completion, stimulation, maintenance and production techniques. For example, these authors suggested that the introduction of water into these oil-wet systems greatly damages or destroys their oil-productive capabilities. Furthermore, aqueous-pyrolysis experiments performed on the Bakken shales (Wenger and Price, 1991) demonstrate that the organic matter of these rocks has only a limited generation capacity for HC gases compared to type III organic matter. Thus the "reservoir drive" of these shales would be quickly lost during production, causing the producing cracks around the wellbore to close and severely limit oil recoveries. As Price and LeFever (1992) suggested, recovery of significant amounts of this oil-resource base may only be possible by a gas (preferably CO₂) injection program *at the start of production*.

The principal conclusion of, and purpose for, this study is to provide further evidence that huge, in-place oil-resource bases may exist in and adjacent to mature shales not cut by significant faulting nor bounded by laterally transmissive units, not only in the Williston Basin but in all petroleum

basins. We hope that underscoring this proposition and stressing the size of the resource base would result in meaningful research on nonconventional recovery techniques for it.

A second important implication of our study regards models of oil expulsion and accumulation of conventional oil deposits. That the Bakken shale, the richest and most areally extensive source rock in the well-explored Williston Basin, has yielded neither significant conventional commercial deposits of mature oil in any reservoir unit in the basin nor known deposits in the Madison rocks, the most important reservoir in the basin, is startling. Furthermore, Riediger *et al.* (1990) demonstrated a similar situation in the Alberta Basin where the Lower Jurassic "Nordegg Member" of the Fernie Formation, the richest source rock in the basin, has apparently sourced few of the conventional oil deposits and little or none of the tar sands. The currently accepted model of oil expulsion from organic-rich rocks centres on open-system fluid flow in the depocenters of sedimentary basins, highly efficient oil expulsion and trapping of only small percentages of expelled oil, with most expelled oil being lost to surface leakage over geologic time or lost to dispersion along secondary migration paths. This model, recently reiterated by Miller (1992), arguably has been heavily influenced by the pioneering work in the Williston Basin of Williams (1974), Dow (1974) and Meissner (1978). Dow's (1974) model appears to us as the foundation for the present-day concept of "petroleum-systems" (Magoon and Dow, 1991). However, this model of expulsion and accumulation is clearly dysfunctional in the Williston Basin, where the model first originated.

Two explanations are possible: 1) the model of deep-basin, open-system fluid flow with efficient oil expulsion and loss of large oil volumes over geologic time is incorrect and generally does not occur in basins worldwide; and 2) the model is correct and does generally occur except in the Williston Basin which is "abnormal". While anything seems possible in the inexact science of geology, we prefer the first explanation for several reasons. First, the Williston Basin has long been considered a model for other petroleum basins. It does not seem logical to us that the basin be unilaterally declared abnormal and dropped from consideration. Second, we prefer our alternate model of deep-basin fluid flow and oil expulsion which we suggest better fits existing data. Our model centres on the hypotheses that deep sedimentary basins are closed (or semi-closed) systems with regards to fluid flow and that HC expulsion, contrary to accepted paradigms, is highly inefficient. We believe that significant HC expulsion occurs only when source rocks are physically disrupted by faulting or are bounded by porous and permeable laterally continuous units which transmit fluids well. This alternative model, and evidence for the model, was detailed by Price and LeFever (1992) and Price (1992, 1993b). Briefly, four principal lines of evidence support our alternative model: 1) the petroleum-geochemistry of the Williston Basin; 2) the strong correlation of increasing basin richness (recoverable oil normalized to sediment area or volume) to increasing intensity of faulting in deep HC kitchens in basins worldwide (Price, 1993b); 3) the work of Powley

(1990) and other investigators (Tigert and Al-Shaieb, 1990; Al-Shaieb, 1991; Ghaith *et al.*, 1990) which demonstrates that rock volumes with significantly high (or low) fluid pressures exist adjacent to rock volumes with much different fluid pressures over geologic time – only possible in systems closed to fluid-flow; and 4) the existence of high concentrations of CO₂ and H₂S in gas deposits for tens to hundreds of millions of years – only possible in systems closed to fluid-flow, because of the high aqueous solubilities of these two gases (Price, 1992).

A third implication of our study involves the level of insight we may expect into the petroleum geochemistry of other petroleum basins. The Williston Basin is the, or among the, structurally simplest basins in the world with significant oil reserves (Price, 1993b). This basin has also had an atypically simple geologic history. We believe that until the petroleum geochemistry of the relatively simple Williston Basin is understood, it will be very difficult to achieve an acceptable understanding of the petroleum geochemistry of much more complex basins such as Los Angeles, the North Sea, the Persian Gulf, Alberta or the U.S. Gulf Coast. This is especially true considering the excellent sample base available for study from the Williston Basin and the large amount of published and unpublished research carried out there.

CONCLUSIONS

- 1) Oils from fractured Bakken shales fundamentally differ from oils in the mid-Madison carbonate reservoirs in the Williston Basin. Within the saturated HCs, Bakken oils are more naphthenic, much less waxy and less paraffinic as a whole, have different n-paraffin and isoprenoid-HC profiles, and have different "generic-HC" compound ratios than Madison oils. Within the aromatic HCs, the Madison oils have much higher concentrations of dibenzothiophenes, and methylated variants thereof, have a distinctive distribution within the trimethylnaphthalenes, and have different compound ratios than the Bakken oils.
- 2) The Bakken and Madison oils are thus different oil families from different source rocks.
- 3) Biomarkers were of little use as source-facies indices (correlation tools) in this study because of the wide range in maturity of both oil sets. If the results from our study are representative, the functionality of biomarkers as correlation tools over wide maturity ranges may have been overstated.
- 4) The Madison oils have wide ranges of variation in the correlation tools we and other investigators have utilized. This observation suggests to us that multiple oil families exist within the Madison oils. Thus, we hypothesize that the Madison oils have several source rocks interbedded, and in hydraulic connection, with the different mid-Madison reservoir rocks in the Williston Basin. Concurrently, other uniform characteristics among the Madison oils suggest that these different source rocks had the same, or very similar, depositional environments.

- 5) The results of this study, and the fact that we have not yet observed either mixing of Bakken and Madison oils or an example of a Bakken-generated oil in a Madison reservoir, all support a model of deep-basin fluid flow and oil expulsion alternate to current paradigms. Thus, we hypothesize that lacking significant faulting and/or laterally continuous carrier beds bounding source rocks in the deep basin:
- oil expulsion is highly inefficient and most generated HCs remain localized to their source rocks;
 - the deep basin is a closed, or semiclosed, system, regarding fluid flow.
- 6) We envision the existence of very large in-place oil-resource bases in or adjacent to mature, self-sourced, organic-rich, fractured, fine-grained rocks in the unstructured areas of deep petroleum basins, worldwide.

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APPENDIX: EXPERIMENTAL METHODS

150-200 mg aliquots of oil were deasphalted in 1 ml of hexane. The resulting precipitated asphaltenes were filtered from the solution, mobilized from the filter by CH_2Cl_2 into a tared 2 dram vial and weighed after solvent loss. Silica gel-alumina fraction-separation chromatography was carried out in 5 ml serological pipettes, 5.30 cm in length. 1.835 g of 923-grade activated silica gel was packed on a glass wool plug at the bottom of the column, 0.87 g of 62-grade activated silica gel was added, followed by 2.5 g of activated alumina. The columns were built in hexane. The asphaltene-free bitumen sample, dissolved in hexane, was passively evaporated to 0.5-1.0 ml and quantitatively transferred to the silica gel-alumina column. Saturated HCs were eluted with 10 ml of hexane, aromatic HCs with 10 ml (or more) of benzene and resins with 15 ml of 1:1 benzene-methanol. The saturated and aromatic HC fractions were both eluted into 10 ml volumetric flasks from which 3 ml were pipetted into tared 2 dram vials for $\text{C}_{15}+$ saturated and aromatic HC weight determinations. The remaining 7 ml of solvent, with dissolved C_8+ saturated and aromatic HCs were never taken to dryness and were saved for C_8+ HC gas chromatography. The weight of the eluted resins was determined after solvent evaporation.

Flame-ionization detection gas chromatography was performed on a DB-5 50 m x 0.2 mm inside diameter capillary column using hydrogen as the carrier gas. Column conditions for the saturated HCs were: initial oven temperature 40°C for 10 minutes (min), followed by a 10°C/min. heating rate to 100°C, followed by a 3.0°C/min. heating rate to 320°C, with a 30 min. final temperature (320°C) hold. Injector temperature was 340°C. Detector temperature was 350°C. Aromatic HCs were run under the same conditions except for oven heating parameters: initial oven temperature 40°C for 10 min., followed by a 4°C/min. heating rate to 320°C, with a 10 min. final temperature (320°C) hold. Data processing was carried out with a Nelson Analytical System.

Samples were prepared for mass spectrometry by deasphalting 30 mg of whole oil in 0.5 ml of iso-octane. The iso-octane and deasphalted oil were added to a disposable activated alumina (1 gram) column (Fisher Prep Sep P467R). Saturated and aromatic HCs were eluted with 5 ml of benzene leaving the resins on the column. The elutant was evaporated

to dryness, 1 ml of iso-octane was added, and enough 5 angstrom molecular sieve was added to completely cover the solution. The mixture stood in a tightly capped vial for 48 hours to completely remove the n-paraffins and the solution then was transferred to a tared vial by a transfer pipette, taken to dryness and weighed, such that another solution with an appropriate concentration (5-20 micrograms/microlitre) could be made up. 1.8 ul of this solution were injected onto a Hewett Packard 5890 gas chromatograph with a 60 m x 0.31 mm I.D. column with a 0.15 micron coating of DB-1701 coupled to a VG-7035 double focusing magnetic sector mass spectrometer. Gas chromatograph conditions were: 10 psi helium head pres-

sure; injection block temperature 300°C; initial column temperature 100°C, with a 2 min. hold; followed by a heating rate of 50°C/min. to 150°C, followed by a 3°C/min. heating rate to 300°C, with a 17 min. final temperature hold. Mass spectrometer conditions were: interface temperature 310°C; source temperature 225°C; source pressure 2×10^{-6} torr; source filament emission current 50 microamps; source electron energy 70 eV; analyzer pressure 1×10^{-7} torr; electron multiplier voltage 2000 V; and amplifier gain 1×10^8 . Selected ion monitoring was accomplished by accelerating voltage switching with a constant magnetic field controlled by a Kratos Mach 3 data system with which data processing was also carried out.