GC-C-IRMS: A NEW TECHNIQUE TO CHARACTERIZE AND CORRELATE OILS AND SOURCE ROCKS

by

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ABSTRACT

In this study, individual gasoline range hydrocarbons in Canadian crude oils are analyzed by a new isotope technique called gas chromatography-combustion-isotope ratio mass spectrometry using an alumina substrate, a helium purge, and a liquid nitrogen trapping mechanism for volatile sample application. The oils chosen for this analysis originate from a variety of source materials and are differentially affected by alteration processes. The choice of sample set enables testing of the new isotope technique to determine whether or not compound-specific, gasoline isotope ratios can be used as an independent parameter to characterize and correlate oils and source rocks. In addition, the effects of alteration on the isotopic composition of individual compounds are investigated.

The main conclusions of this study are as follows:

(1) The isotope ratios of C_5 to C_{10} hydrocarbons can be used to characterize and correlate related oils. The isotope variation between different oils is about 10 ‰ while the experimental error only ranges from ± 0.3 ‰ to 0.5 ‰.

(2) The Saskatchewan, Arctic, and East Coast oils separate into the three different groups consistent with previously known sources for the oils. The Alberta oils, from a variety of source environments, correlate with other, similar-sourced oils from other areas.

(3) Thermal maturation does not appear to result in a significant isotope effect since the high maturity Turner Valley oil correlates with low maturity Arctic oils and no significant isotopic differences were observed between Arctic condensates (higher maturity) and oils (lower maturity).

(4) The isotope ratios of the volatile hydrocarbons are resistant to secondary alteration processes such as biodegradation. The change in the isotope ratios (or isotope effect) due to alteration processes is generally less than 1 ‰ and often within the analytical uncertainty.

Previous molecular and isotopic geochemical techniques for correlating oils and sources can not be used independent of each other. The molecular compositions of oils change due to processes such as maturation, biodegradation, and water-washing. This makes the recognition of chemical similarities between related oils difficult. Traditional bulk oil and major oil fraction isotope analyses often yield non-specific information (averaged ratios of many compounds) which hinders the achievement of reliable correlations. The success of the individual gasoline range isotope ratios in correlating Canadian oils (which are differentially biodegraded) establishes this new isotope technique as a promising geochemical tool for correlation problems.

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LIST OF ABBREVIATIONS

$\propto$	fractionation factor
°API	degrees API (American Petroleum Institute)
B	magnetic field strength
ben	benzene
CAM	Crassulacean Acid Metabolism
CO_2	carbon dioxide
const.	a constant
CYC_5	cyclopentane
CYC_6	cyclohexane
C_x	carbon$_{number}$
C_3 pathway	Calvin-Benson
C_4 pathway	Hatch-Slack
δ	delta notation
DST#	drill stem test #
e	charge
EA	Elemental Analyzer
EIE	equilibrium isotope effect
$\in$	epsilon
FID	flame ionization detector
GC	gas chromatograph
GC-C-IRMS	gas chromatograph - combustion - isotope ratio mass spectrometer
HMW	high molecular weight
HV	Heptane Value
iC_x	iso-C_{number} (branched compound)
ISPG	Institute of Sedimentary and Petroleum Geology
k	equilibrium constant
KIE	kinetic isotope effect
LMW	low molecular weight
m	mass
$MCYC_5$	methylcyclopentane
$MCYC_6$	methylcyclohexane
MS	mass spectrometer
n-	normal
nC_5	normal pentane
nC_6	normal hexane
nC_7	normal heptane
nC_8	normal octane
NSO	nitrogen, sulfur, and oxygen containing compounds

LIST OF ABBREVIATIONS, continued

PDB	Peedee Belemnite
PEP	phosphoenolpyruvate
‰	per mil or parts per thousand
Ph	phytane
PI1	Paraffin Index 1
PI2	Paraffin Index 2
ppb	parts per billion
Pr	pristane
r	radius of curvature
R	isotope abundance ratio
% Ro	percent vitrinite reflectance
RT	retention time
RuBP	ribulose 1,5-biphosphate
SC	Similarity Coefficient
SEOS	School of Earth and Ocean Sciences
T_{max}	maximum temperature (in Rock-Eval pyrolysis)
TOC	total organic carbon
tol	toluene

v	velocity
22DMC$_4$	2,2-dimethylbutane
23DMC$_4$	2,3-dimethylbutane
2MC$_5$	2-methylpentane
3MC$_5$	3-methylpentane
2MC$_6$	2-methylhexane
11DMCYC$_5$	1,1-dimethylcyclopentane
23DMC$_5$	2,3-dimethylpentane
3MC$_6$	3-methylhexane
1c3DMCYC$_5$	1cis,3-dimethylcyclopentane
1t3DMCYC$_5$	1trans,3-dimethylcyclopentane
1t2DMCYC$_5$	1trans,2-dimethylcyclopentane
1c2DMCYC$_5$	1cis,2-dimethylcyclopentane
25DMC$_6$	2,5-dimethylhexane
24DMC$_6$	2,4-dimethylhexane
223TMC$_5$	2,2,3-trimethylpentane
3MC$_7$	3-methylheptane
1c4DMCYC$_6$	1cis,4-dimethylcyclohexane

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This thesis is dedicated to all my family in Newfoundland and to Dave here with me in British Columbia. I can not thank them enough for their unwavering love and support throughout the years.

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CHAPTER 1. SUMMARY

The correlation of oils to source rocks or other oils is based on the recognition of chemical similarities in the oils and source rocks or individual oils. There must be significant and diagnostic differences between oils for classification into groups or families. In addition, these differences must be conservative (i.e., they do not change) with respect to secondary alteration processes such as biodegradation and water-washing and to time.

In this study, individual gasoline range hydrocarbons of differentially biodegraded Canadian oils (with known sources) are isotopically measured to test whether these compound-specific isotope ratios can be used as an independent parameter to characterize and correlate oils. The molecular compound distributions and parameters associated with high and low molecular weight compounds are used to identify sources and levels of alteration such as biodegradation, water-washing, and maturation associated with petroleum samples. Then, the effects of alteration on the individual stable carbon isotopes of the gasoline range hydrocarbons are investigated.

A variety of molecular and isotope geochemical techniques have been used to obtain data for the comparison of oils (and source rocks). Traditionally, bulk oil and major oil fractions are measured, but the resulting isotope ratios or molecular parameters are averages of many compounds and often of limited diagnostic value. The trends in subsequent research moved towards more specific analyses yielding information such as compound distribution of the straight-chain alkanes, pristane/phytane ratios, and individual compound isotope ratios.

Although many studies have been performed on the C_{15+} hydrocarbons, the gasoline range hydrocarbons were largely ignored due to analytical difficulties associated with their volatility. However, these gasoline hydrocarbons constitute a significant portion of crude oils and may contain useful information for correlations. A new method of volatile application, using a helium purge and a liquid nitrogen trapping system, was developed by Lloyd Snowdon in the late 1970's which enabled gasoline range hydrocarbons to be molecularly analyzed by gas chromatography.

Isotope analysis of bulk oil and major oil fractions are commonly performed, but the isotopic analysis of individual compounds has only been possible in the last 5 years with the development of a new instrument known as a gas chromatograph - combustion - isotope ratio mass spectrometer. The combination of a gas chromatograph, an on-line combustion unit, and an isotope ratio mass spectrometer allows the separation and combustion of individual hydrocarbons (from an oil mixture) into carbon dioxide which can be isotopically measured by the mass spectrometer.

Oil correlations have been successfully performed in the past using combined geochemical techniques. However, if an oil is affected by maturation or secondary alteration processes such as biodegradation (most dominant) and water-washing, correlation is more difficult since the molecular composition of the oil changes. For example, microbes preferentially attack straight-chain alkanes over the branched alkanes or cycloalkanes (e.g., Deroo et al., 1974; Bailey et al., 1973). These changes can be observed in gas chromatograms or molecular parameters calculated from the gas chromatograms and have been documented by many researchers.

The effects of alteration processes on isotope ratios have not been well documented. Some investigators have suggested that the effect on bulk oils or major oil fractions is probably small (about 2 ‰; e.g., Stahl, 1978; Sofer, 1984). There have been virtually no isotopic studies performed on the gasoline range hydrocarbons. Since the procedure for isotopically measuring the volatile hydrocarbons was not established, the methodology had to be developed in this study. The helium purge and liquid nitrogen trapping system is used for volatile application to the gas chromatograph - combustion - isotope ratio mass spectrometer. The analytical system had to be tested including such things as purging times, temperature programs, and sample size.

From the isotope ratios obtained for pure standards and the individual hydrocarbons in an oil standard (Chester), the error associated with the compound-specific, gasoline, isotope measurement generally ranges from ± 0.3 to ± 0.5 ‰. The range in isotopic composition of the individual hydrocarbons is 10 ‰. This large variation can not be due to analytical error so it is likely due to precursor source material or other environmental conditions.

From the analysis of all the oil samples, the isotopic variation is carried throughout the compound classes (e.g., straight-chain alkanes, branched alkanes, cycloalkanes, and aromatics). For this reason, the measurement of all hydrocarbons may not be necessary for oil correlation (e.g., cycloalkane isotope ratios may be sufficient). The cycloalkanes and the branched alkanes seem to yield the most reliable isotope data while the straight-chain alkanes (especially nC_5 and nC_8) and the aromatics yield more variable isotope ratios (up to 1 ‰ in some cases).

Correlation between individual oils and regions for Canadian oils can be made through comparisons of the isotopic trends for each gasoline hydrocarbon in oils, cross-plots of isotope ratios, and statistical cluster analyses. Figures 1.1 and 1.2 are examples of the relationships between isotopes that can be used to correlate oils. Oils from Saskatchewan, the Arctic, and the East Coast were classified into three distinct groups, which were consistent with the known sources for these oils. Since the Alberta oils are derived from a variety of sources, these oils grouped with oils derived from similar precursor sources.

The hydrocarbons in the marine-derived Saskatchewan oils are the most depleted in ^{13}C (lightest), especially the Family C oils which have a carbonate, marine, anoxic source. The Family A oil from southeast Saskatchewan (Lake Alma), derived from a carbonate mudstone, correlates with Family C oils. Family F and E, both of Paleozoic marine clastic sources, often group together and separate from Family C oils.

The gasoline hydrocarbons in East Coast oils are the most enriched in ^{13}C (heaviest), reflecting a typical marine source. The hydrocarbons in terrestrially-derived Arctic oils have isotope ratios that are intermediate between the Saskatchewan and East

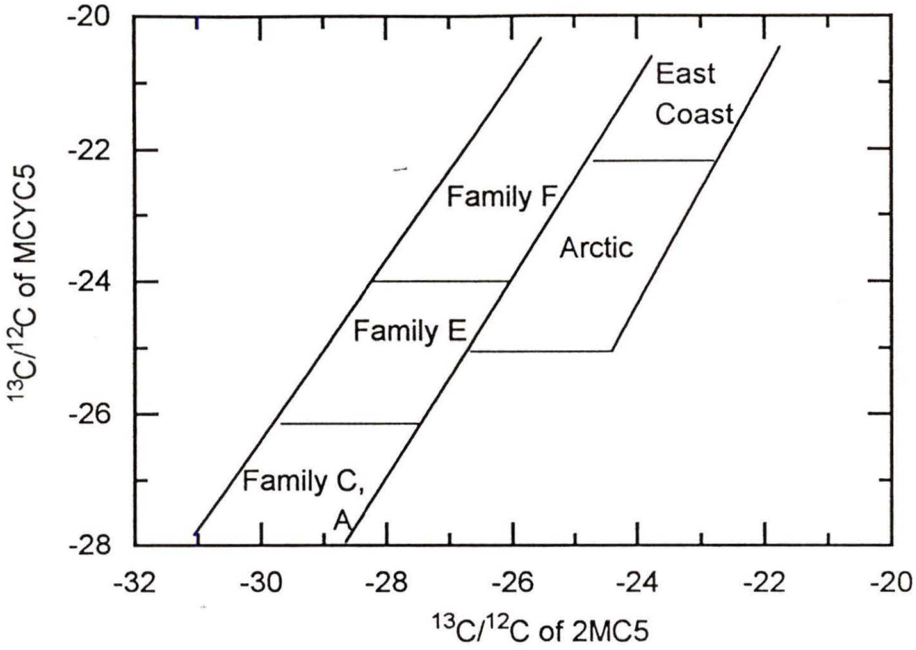


Figure 1.1 Overview diagram comparing the isotope ratios of MCYC5 and 2MC5 for Canadian oils.

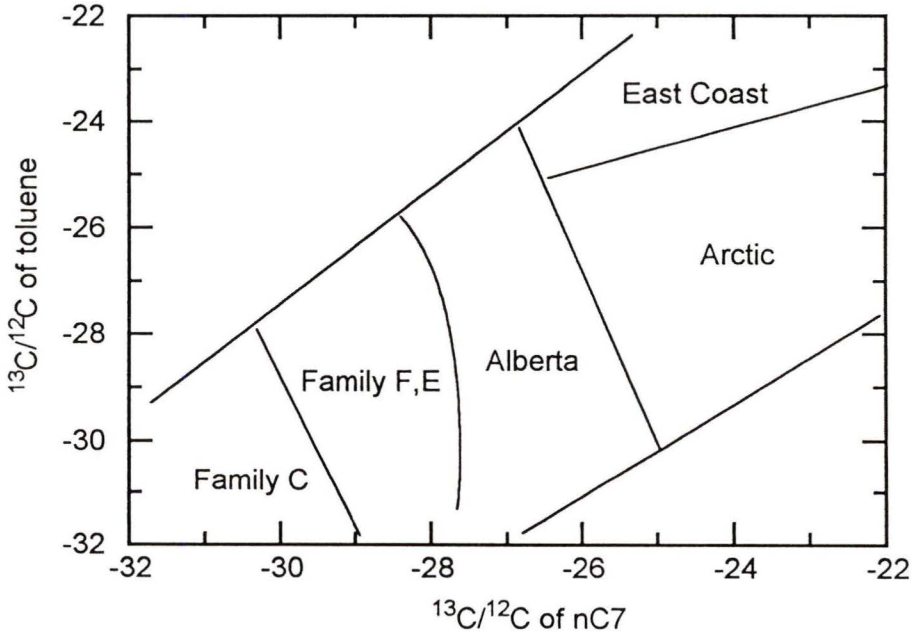


Figure 1.2 Overview diagram comparing carbon isotope ratios of toluene and nC7 for Canadian oils.

Coast oils, but more similar to the East Coast oils. This could be due to the possible terrestrial source noted in the literature for some East Coast oils (e.g., Hebron I-13).

The Rainbow and Shekilie oils from Alberta, both derived from organic matter in sediment deposited under anoxic, hypersaline conditions, correlate with each other and are isotopically similar to Saskatchewan oils. The Willesden Green oil, derived from marine shales, does not clearly correlate with one group of oils, but its isotopes are similar to the Family F, Family E, or the East Coast oils. The Chester oil correlates with Family F oils, and, therefore, probably has a marine clastic source similar to the source for the Family F oils. The high maturity Turner Valley oil correlates with the low maturity Arctic oils, and, therefore, it may have a terrestrial contribution to its precursor source material. In addition, since the isotope ratios of individual hydrocarbons in high and low maturity oils correlate and no significant differences are observed between condensates (higher maturity) and oils, thermal maturation does not appear to result in a significant change in the isotopic composition of hydrocarbons.

Although the similar Canadian oils were correlated using the gas-chromatograph-combustion-isotope ratio mass spectrometry technique, there are some uncertainties associated with the use of gasoline range isotopes for correlations. Most of the oils in this study are partially biodegraded so it is possible that an isotope effect associated with the biodegradation may result in a shift to greater ^{13}C enrichment in the hydrocarbons.

The changes in the molecular compositions of oils due to biodegradation are illustrated in Figure 1.3 where the n-alkanes are preferentially removed followed by the

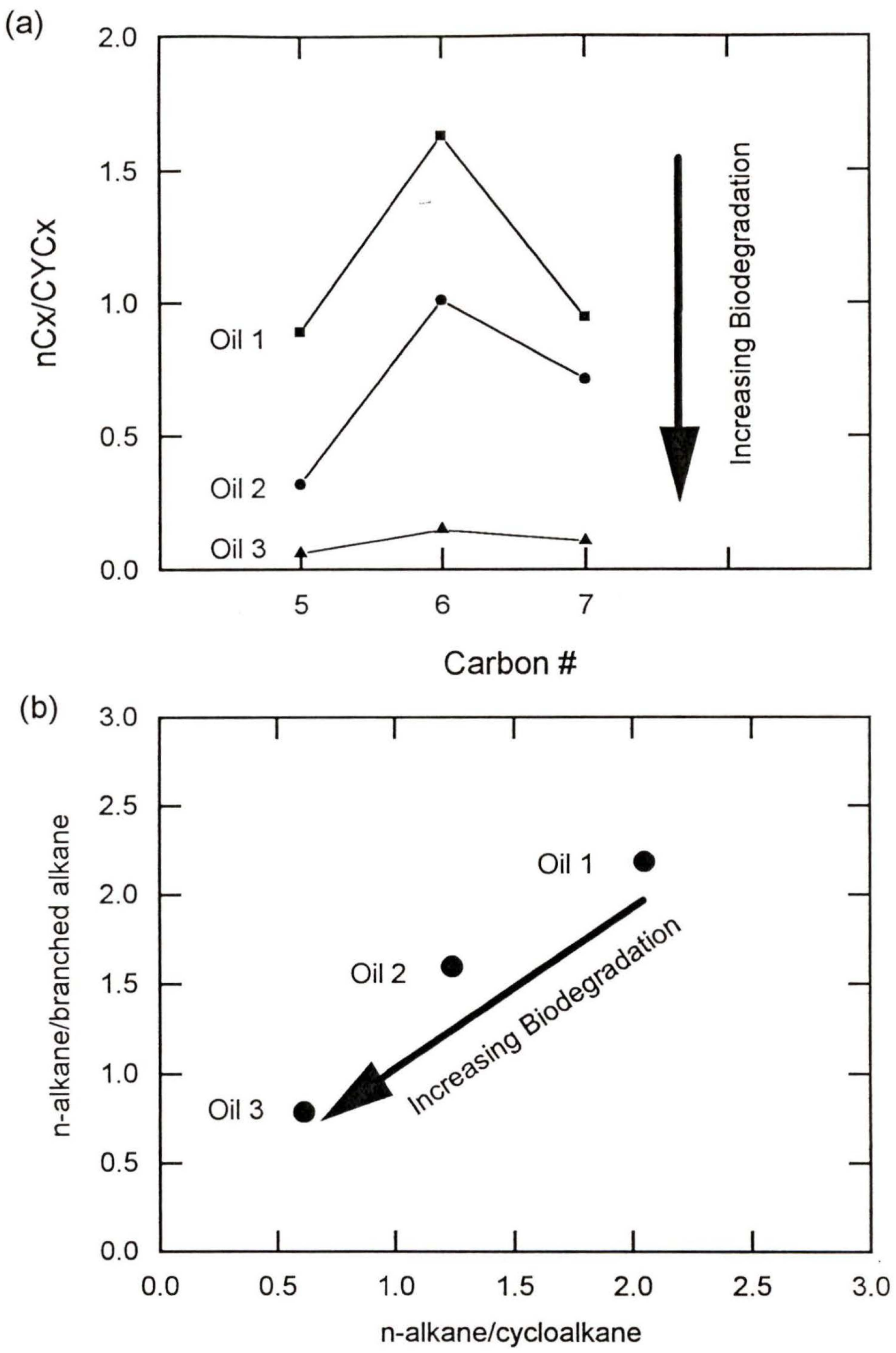


Figure 1.3 Change in molecular composition of oils due to biodegradation using (a) the n-alkane/cycloalkane ratio compared to carbon number and (b) the total n-alkane/branched alkane ratio compared to the total n-alkane/cycloalkane ratio. Oil 1 is the least degraded while Oil 3 is the most degraded.

more resistant branched alkanes and cycloalkanes. Molecular gasoline parameters such as the Similarity Coefficient developed by Philippi (1974, 1977) can be used to correlate non-biodegraded oils, but it does not reliably correlate biodegraded oils whose molecular compositions have been altered.

The isotope ratios of individual compounds are more resistant to biodegradation. The probability (based on the natural abundance of ^{13}C) of an isotope effect occurring due to biodegradation is low. The isotope ratios obtained from the individual hydrocarbons in Canadian oils generally do not change significantly with biodegradation. This is illustrated by an example in Figure 1.4 where the isotope ratios of a series of low to high degraded oils only exhibit a maximum change of 0.5 ‰. A natural isotope variation of 1 to 2 ‰ in non-biodegraded Hibernia oils was observed. The 0.5 ‰ variation that might be due to biodegradation is not significant.

The changes in the molecular and isotopic compositions of oils are illustrated schematically in Figure 1.5. The molecular parameter, Paraffin Index 2 (PI2), can change drastically in oils and approach 0 in highly biodegraded oils such as those from the Arctic. The isotope ratios of the hydrocarbons in these oils, however, are more resistant. If the natural isotopic variation between similar oils is ignored (e.g., 1 ‰ to 2 ‰), even extreme biodegradation does not result in a significant isotope effect.

Thus, gasoline range hydrocarbons can be characterized by individual isotope ratios within an error of ± 0.3 to ± 0.5 ‰. The isotope variation among the hydrocarbons in oils from different regions is approximately 10 ‰, much greater than

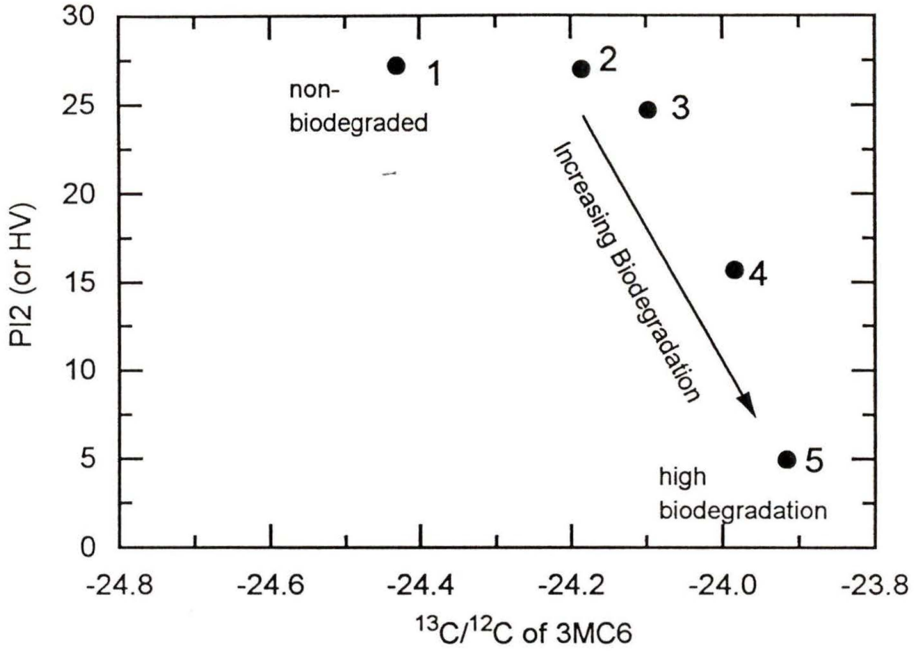


Figure 1.4 Overview diagram illustrating the change in molecular composition and isotope ratio due to biodegradation. Note: Oil 1 = least degraded, oil 5 = most biodegraded

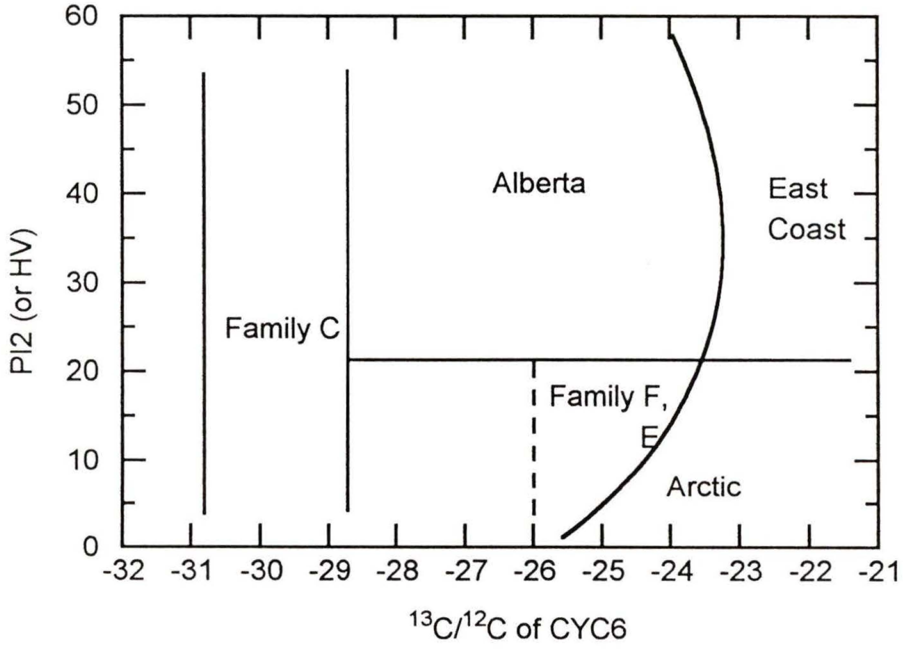


Figure 1.5 Overview diagram illustrating the molecular and isotope composition of Canadian oils.

the experimental error. These ratios are resistant to secondary alteration. The Canadian oils in this study can be correlated to other similar oils using the isotope ratios of individual gasoline range hydrocarbons.

CHAPTER 2. RESEARCH OBJECTIVES

There must be significant and diagnostic differences between oils for classification into groups or families. In addition, these differences must be resistant to secondary alteration processes. Oils are characterized through a variety of molecular and isotope techniques. Since the molecular compositions of oils are known to change as a result of secondary alteration, oil correlations can be difficult.

Although the effects of secondary alteration on stable carbon isotopes (especially with regard to volatile hydrocarbons) are not well documented, processes such as biodegradation or other secondary alteration processes are not expected apriori to have a significant effect on the C_5 to C_{10} isotopes. If they do have a significant effect, it may be predictable and reproducible. This offers the use of stable carbon isotopes as an independent parameter to characterize and correlate oils and source rocks even in cases of secondary alteration that eliminates molecular methods.

This research project tests the use of stable carbon isotopes of individual gasoline range hydrocarbons for the correlation of biodegraded oils from the Jeanne d'Arc Basin (offshore Newfoundland), the Canadian portion of the Western Canada Sedimentary Basin including the Williston Basin (southwest Saskatchewan) and the Alberta Basin, and the Beaufort-Mackenzie Basin (Northwest Territories).

The objectives can be summarized as follows:

- to develop a method for analyzing the stable carbon isotope ratios of the individual gasoline range hydrocarbons;

- to identify any systematic and diagnostic variations in the C_5 to C_{10} compounds dissolved in oils by molecular (or stereochemical) compound distribution and stable carbon isotopes;
- to characterize the effect of secondary alteration processes such as biodegradation and water-washing or maturation on individual gasoline range hydrocarbons;
- to search for reliable and independent geochemical parameters for oil to oil and oil to source rock correlation; and
- to apply the new GC-C-IRMS technique to Canadian oils.

Many studies have been performed on the C_1 to C_5 and the C_{15+} hydrocarbons. However, the gasoline range hydrocarbons (C_5 to C_{10}) have largely been neglected due to several analytical difficulties, even though they constitute a significant portion of crude oil. Figure 2.1 is a chromatogram for a whole Hibernia oil which shows the large quantity of hydrocarbons in the gasoline range (e.g., up to 30 % or 40 % in a 'typical' oil). These compounds may contain some useful information that was previously overlooked.

Technological advancements, such as high resolution capillary columns for gas chromatographs and an alumina dilution method (developed by Dr. Lloyd Snowdon, Organic Geochemistry Division, Institute of Sedimentology and Petroleum Geology (ISPG), Calgary) for volatile compounds have made possible the molecular analysis of the C_5 to C_{10} compounds by gas chromatography. The development of an instrument combining a gas chromatograph, a micro-combustion oven, and an isotope ratio mass

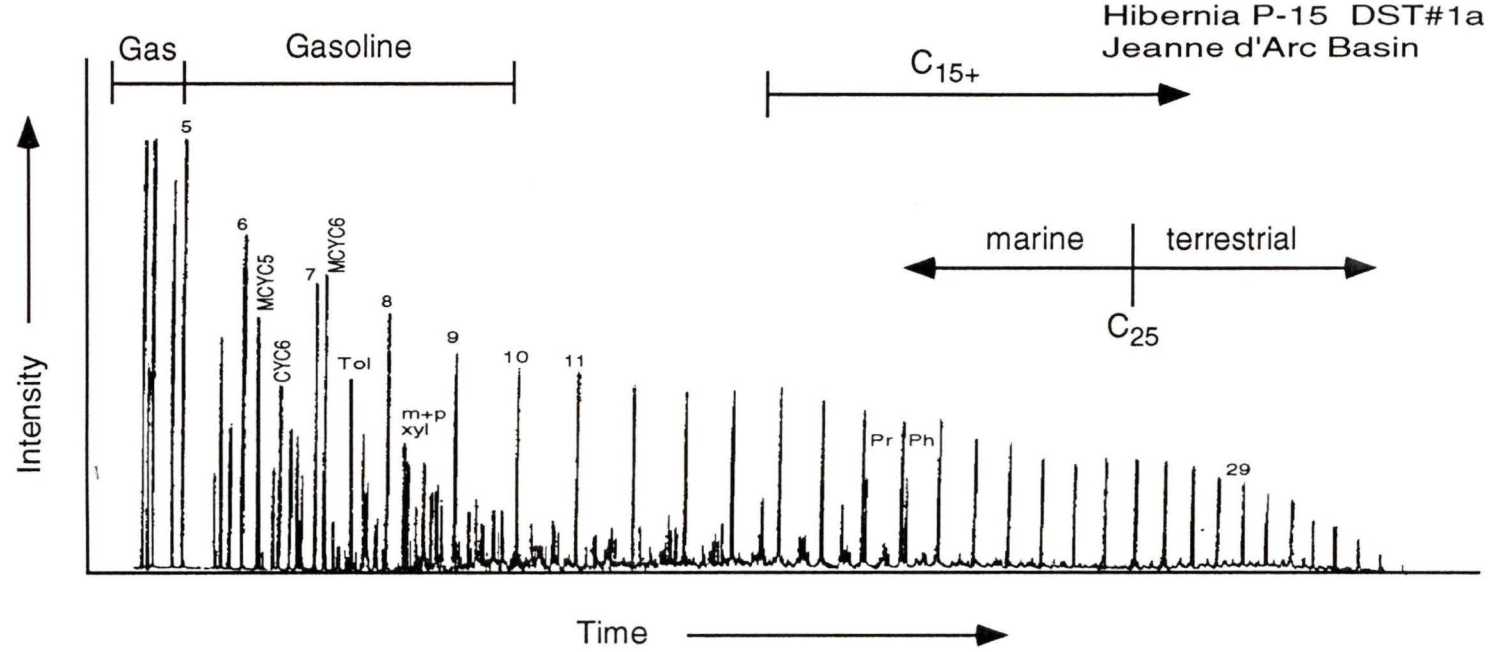


Figure 2.1 Chromatogram of whole oil, reflecting the high concentration of gasoline range hydrocarbons. C_{15+}, gas, and the traditional separation point for marine versus terrestrial input are also indicated on the chromatogram. Numbers indicate the number of carbons (e.g., 5 = C_5).

spectrometer (GC-C-IRMS) has provided the means to measure stable carbon isotopes on small amounts of individual hydrocarbons in the gasoline range.

This study is important for a variety of reasons. Oil is a very valuable natural resource in that it is used as an energy source in many industries (e.g., automotive). Biodegradation increases the density and sulfur content of oils which is not desirable in commercial accumulations. These oils are more difficult and costly to produce and refine. Approximately 10 % of the world's oil is biodegraded (Seifert and Moldowan, 1979) and, thus, areas containing these types of oils should be avoided during drilling. This biodegradation may only occur in the reservoir so source identification may lead to the discovery of other related but unaltered oil in different locations.

Today, the geochemical research of the oil industry is mainly focused on correlating between reservoirs. It is beneficial for exploration geologists and especially reservoir engineers to know the relationship between oils in neighboring areas (e.g., do they share a common migration path or source?). If the oil from fields is related through migration, the wells in each area must be simultaneously drilled to obtain maximum production from each. The production of oil from a field depends on drive (e.g., gas or water). If only one well is drilled, the drive can be reduced for a second related well, resulting in reduced total oil or gas production.

In addition, if biodegradation does not have a significant effect on the stable carbon isotopes of individual C_5 to C_{10} hydrocarbons and this technique can be used to identify the source of biodegraded oil, the environmental sector may benefit from this study. For example, if an oil spill from a tanker occurs, often the oil can be quickly degraded resulting in the removal of susceptible hydrocarbons (e.g., n-alkanes). Molecular information is not sufficient to correlate the oil since it is known to be affected by alteration processes. The isotopic technique employed in this study may enable the oil, despite the biodegradation, to be linked back to the tanker's oil.

This is one of the first studies to rigorously examine the stable carbon isotopes of individual compounds in the gasoline range and their application to biodegraded oils and correlation problems.

CHAPTER 3. BACKGROUND INFORMATION

3.1 PETROLEUM COMPOSITION AND FORMATION

Petroleum is a complex mixture of organic compounds, consisting of natural gas, condensate, and crude oil. Natural gas refers to very low molecular weight (LMW) compounds in the C_1 to C_4 range. Condensates are gaseous in the ground at higher temperature, but when brought to the surface at lower temperatures, they condense to form a liquid. Crude oil is the liquid portion of petroleum.

There are three main compound classes of petroleum (Tissot and Welte, 1978). One is the aliphatics (saturates or paraffins) which is composed of straight chain or normal-alkanes (n-paraffins), branched alkanes (iso-alkanes), or cycloalkanes (naphthenes). Concentrations of these saturated hydrocarbons generally peak around C_6 to C_8 and decrease above C_{10} (Figure 2.1). The cycloalkanes are composed of 5 to 6 carbon rings and are usually the most dominant group of compounds in oils (20 to 35 % of average crude). The n-alkanes are second in abundance (15 to 20 %). Branched alkanes have mainly been identified in the gasoline range and are generally in lower percentages (approximately 10 %). In the high molecular weight (HMW) range, there are too many possible isomers (different compounds with the same molecular formula) and the concentrations are too low for good identification.

The other two major petroleum classes are found in lower percentages than the saturates. The aromatics are unsaturated cyclic compounds which concentrate in the heavier fractions. These are usually found as less then 15 % of the total crude. Finally, NSO compounds (or asphaltenes; non-hydrocarbon compounds containing nitrogen, sulfur, and/or oxygen) are found in relatively small amounts in crude oil (e.g., a couple of %), but in higher percentages in crude oil residues. Unsaturated compounds are uncommon in crude because they can readily saturate into alkanes by hydrogen or thiols by hydrogen sulfide (Hunt, 1979; Tissot and Welte, 1985).

All petroleum is derived from precursor organic material, but some types are more conducive to hydrocarbon production (Tissot and Welte, 1978). Type I (algal) and Type II (mixed marine/terrestrial) materials with high hydrogen/carbon ratios are more conducive to oil generation than the terrestrial Type III material (Figure 3.1).

When organisms or plants die and begin to decay, diagenesis begins. The traditional hydrocarbon generation model is shown in Figure 3.2. Complex molecules such as proteins are broken down into smaller and simpler molecules. There are three main successive microbial systems to which organic matter is subjected (e.g., Claypool and Kaplan, 1974). These systems called the aerobic zone, the anaerobic sulfate-reducing zone, and the anaerobic carbonate-reducing (or methanogenesis) zone occur with increasing depth in the water column and the sediment. Degradation and natural oxidation reactions produce CO_2 (g) (one of several other products, e.g., methane) which is recycled back into the atmosphere (Tissot and Welte, 1978). Approximately 0.01 to 0.1% of the organic matter is isolated in environments where oxidation is not occurring. This material makes its way to the sedimentary reservoir.

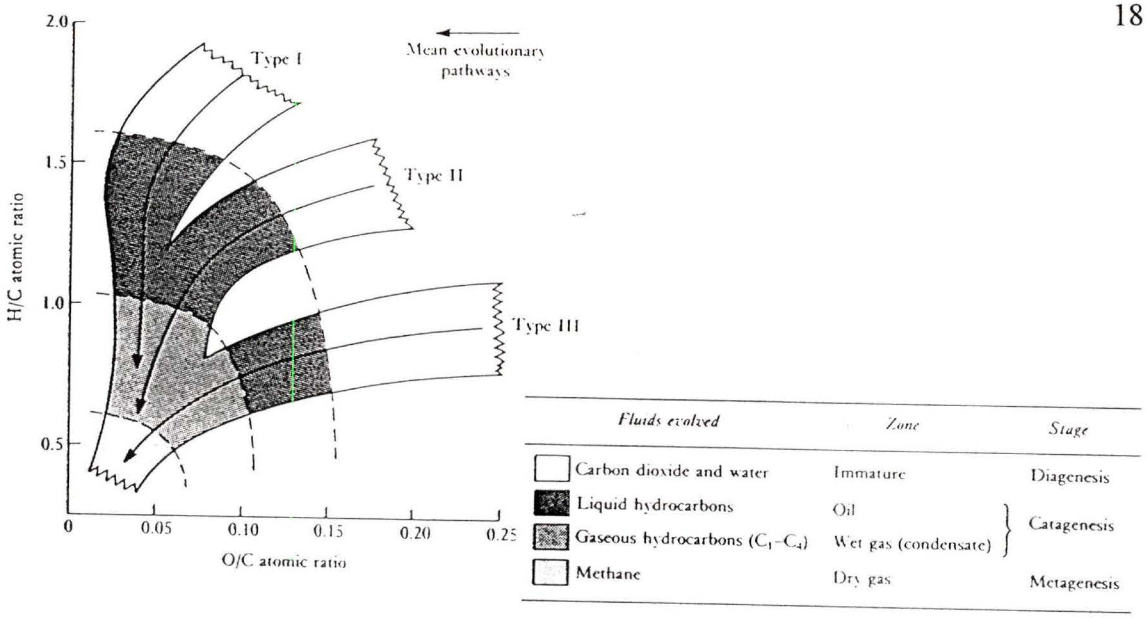


Figure 3.1 Kerogen types and associated H/C and O/C ratios (after Tissot and Welte, 1978).

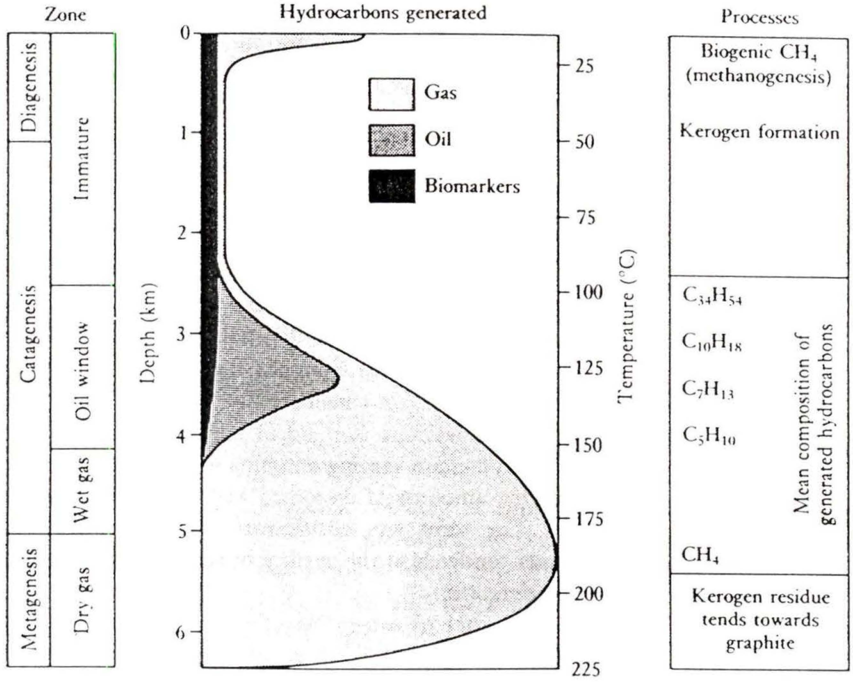


Figure 3.2 Traditional hydrocarbon generation model (after Tissot and Welte, 1978; Killops and Killops, 1993).

Organic matter resistant to bacterial decay (e.g., lignin or phenols) undergoes many reactions as burial and temperature increase. By the end of diagenesis, the organic matter has been condensed (loss of functional groups) to form insoluble kerogen. Oxygen is eliminated and CO_2 and H_2O are formed, generating mostly high molecular weight (HMW) nitrogen, oxygen, and sulfur-containing (NSO) compounds. As temperature increases and catagenesis proceeds, more bonds are broken (e.g., C to C bonds and ester linkages) and hydrocarbons in the C_{15} to C_{30} range form along with some gas.

With even greater increases in temperature, the kerogen (with only short side-chains remaining) and the generated hydrocarbons are cracked, producing lighter hydrocarbons such as wet gas (consisting of methane, ethane, and 50 % or more of propane and butane) or condensates. There is a certain temperature above which liquids can not exist. When temperatures within the earth exceed 150 °C and pressures are high, any liquid hydrocarbons are converted to the gas phase. When these temperatures and pressures are reduced, as is the case for surface conditions, these condensates or gaseous hydrocarbons condense to a liquid state. At high temperatures such as 200 ^{0}C during metagenesis, dry gas (composed of predominantly methane and ethane) is formed.

3.2 MOLECULAR CHARACTERIZATION OF HYDROCARBONS

3.2.1 Hydrocarbon Gases

The gas concentration, molecular composition, and several related molecular parameters (e.g., gas wetness, $\sum C_{2+}$, and the Bernard Parameter) are used to classify natural gas type (Claypool and Kaplan, 1974; Bernard et al., 1978: Hunt, 1979; Whiticar and Faber, 1986; Berner and Faber, 1988; and Whiticar, 1990 and 1993). This molecular information is useful for distinguishing between natural (thermogenic) and biogenic gases. However, more detailed classification information is obtained from stable carbon isotopes and combinations of molecular and isotope data (as will be shown later).

The concentration of gas can provide some general information regarding the source of gases (Whiticar, 1993). For example, in areas where there is no petroleum or bacterial action, there are only trace amounts of gas (e.g., 20 to 50 ppb of methane (CH_4) in surface sediment) while soil or sediment with bacteria present may have gas concentrations up to 10^5 ppb. Gas seepages of dominantly CH_4 with high flow rates (e.g., m^3/min) are usually representative of a source rock in the area.

Since natural gas refers mainly to methane (C_1 gas), ethane (C_2), propane (C_3), iso-butane (iC_4), and n-butane (nC_4), any molecular parameters only include combinations of these five gases. The 'wetness' of a gas refers to the amount of higher gases present (e.g. C_3 and C_4 gases). Two molecular ratios which describe 'wetness' are given below:

$$\text{gas wetness} = (C_2 + C_3 + iC_4 + nC_4) / (C_1 + C_2 + C_3 + iC_4 + nC_4) \times 100 \qquad (3.1)$$

(vol %)

ΣC_{2+} (vol % hydrocarbons) = $(C_2 + C_3 + iC_4 + nC_4)$ (3.2)

The Bernard Parameter can be used to describe compositional variations in gases from various areas (e.g., seeps or shallow sediment) (Bernard, 1978; Whiticar 1990, 1993). It also provides some information regarding maturity. The equation is given below:

Bernard Parameter (vol %) = $C_1 / (C_2 + C_3)$ (3.3)

As maturity increases, more methane is produced and less of the higher gases (e.g., C_2 or C_3), resulting in an increase in the Bernard Parameter (from 5 to 50 for overmature gas).

Although there are often varying amounts of ethane, propane, iso-butane, and n-butane, methane is the dominant hydrocarbon gas at all stages of hydrocarbon gas generation. Molecular parameters provide general classification information about thermogenic and biogenic gasses.

3.2.2 Bulk Information

A variety of techniques have been used to molecularly characterize oil and to aid in oil to source rock correlations. Research started with measurements on bulk samples, but as technology advanced it continually moved in the direction of more specific parameters. Most of the information associated with oil composition, formation, and alteration have been determined using molecular techniques. Some of the simple bulk measurements traditionally obtained are as follows:

- density or specific gravity of oils (in terms of °API gravity)
- sulfur content estimations

- vitrinite reflectance (% Ro)
- total organic carbon (TOC) of potential source rock
- proportion of major compound classes

These simple measurements were performed routinely by many researchers in the past and are still performed today (Bailey et al., 1974; Tissot and Welte, 1978; Hunt, 1979; Snowdon, 1980; Waples, 1985; Osadetz et al., 1993). Since these bulk parameters are not very specific and only yield limited information, more specific measurements were developed.

3.2.3 C_{15+} Information

Most of the early oil characterization and correlation work was performed on the C_{15+} hydrocarbons. This analysis is more specific and the compounds are relatively easy to measure (i.e., there are no significant analytical difficulties). Some examples of these parameters are as follows:

- gas chromatography (GC) of isolated oil fractions
- isoprenoid distribution (e.g., pristane/phytane (Pr/Ph) and C_{15}/C_{20})
- isoprenoid/n-alkane distribution (e.g., Pr/nC_{17} vs. Ph/nC_{18})
- odd/even predominance
- average chain length
- biomarkers (e.g., diterpanes, triterpanes, steranes, and hopanes)

The sources for many of the oils used in the current study are already known through reports undertaken by other researchers who use many of the above listed techniques in conjunction with additional analyses. For this reason, some of the techniques listed above are described to illustrate the way in which source information is obtained from the compounds in the C_{15+} range. The information regarding identification of secondary alteration is more important to the current study. This will be shown in a later section dealing with secondary effects. If a more complete review is desired, readers are directed to the original literature (Bray and Evans, 1961; Scalan and Smith, 1970; Powell and McKirdy, 1973; Didyk et al., 1978; Hunt, 1979; Volkman, 1986; Snowdon and Fowler, 1991; Brassell, 1992).

The type of precursor material for oils may be determined by observation of the average chain length of hydrocarbons in the C_{15+} saturate fraction. For example, terrestrial oils often have a dominance of n-alkanes in the C_{25} to C_{35} range (corresponding to long-chain compounds synthesized to prevent desiccation and provide structural support) while marine oils often have a dominance of n-alkanes in the less than C_{25} range (no desiccation or support problems) (e.g., Figure 3.3).

Pristane (C_{19}) to phytane (C_{20}) ratios are often useful in determining whether or not the original sedimentary organic material has been subjected to reducing or oxidizing conditions (Powell and McKirdy, 1973). Both compounds are derived from the phytol branch of chlorophyll. Pristane is the oxidized form while phytane is the reduced form. Thus, a value of greater than 3 usually indicates oxic conditions as are often found in terrestrial environments (e.g., Arctic oils, Table 3.1). Values between 1 and 3 are usually associated with more reducing or marine environments (e.g., Family F oils southwest Saskatchewan, Table 3.1). Extremely low values such as 0.1 to 1 are often found under

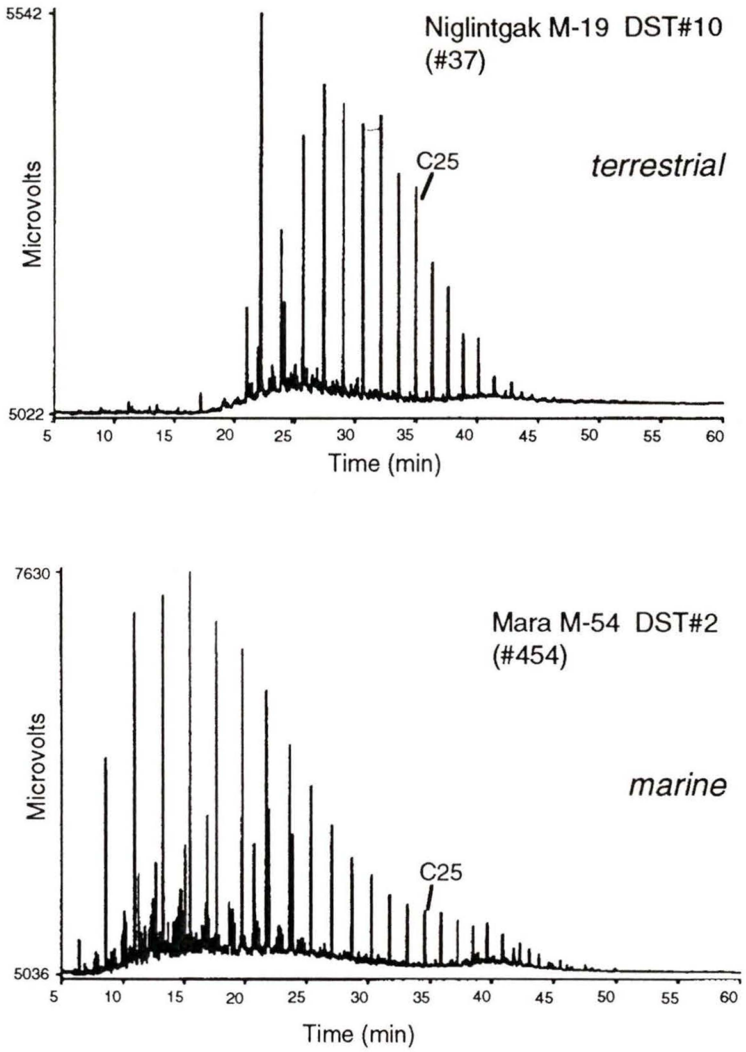


Figure 3.3 HMW compound distribution in marine and non-marine oils. The compounds of marine oils generally have carbon numbers less than C25. The compounds of terrestrial oils concentrate in the C25 to C35 range.

Table 3.1. Additional C_{15+} data collected from ISPG database for southwest Saskatchewan, Arctic, and East Coast samples.

Sample	Pr/Ph
SW Saskatchewan	
Family C Oils	
SW/CBattrum/675	0.57
SW/CButte/677	0.64
SW/CBatCrk/726	0.39
SW/CBatCrk/727	0.65
SW/CCantuar/733	0.55
Family E Oils	
SW/ENHoos/817	0.94
SW/ECourt/822	1.06
SW/ECactus/829	0.46
SW/EHearts/833	1.34
SW/EBuffalo/836	0.57
Family F Oils	
SW/FPlato/812	1.92
SW/FSmiley/816	ND
SW/FSEurek/818	2.23
SW/FKerrob/821	1.93
SW/FForgan/826	1.9
Arctic	
Niglintgak M-19	
A/NiglintM/73/11	9
A/NiglintM/37/10	5.3
A/NiglintM/74/9	6
East Coast	
Hibernia K-18	
E/HiberniaK/266/11	0.94
E/HiberniaK/263/8	0.93
E/HiberniaK/251/1	0.91
Hibernia C-96	
E/HiberniaC/DST#1	1.14
Mara M-54	
E/MaraM/455/3	0.82
E/MaraM/454/2	1.08
E/MaraM/453/1	0.57
Hebron I-13	
E/HebronI/248/10	1.45
E/HebronI/249/9	1.1
E/HebronI/250/7	1.02
E/HebronI/246/5	0.86
E/HebronI/245/1	1.12

Notes: Pr = pristane, Ph = phytane, ND = not detected
Region/Well/ISPG# (/DST#)

very reducing conditions near euxinic bottom water (e.g., Family C oils, southwest Saskatchewan, Table 3.1).

The interpretation of these pristane/phytane ratios must be performed with some caution because they are affected by maturity (i.e., maturity must be high enough to ensure relatively high pristane and phytane since immature sediments often have very little of both). Also, pristane and phytane are known to have other sources in addition to chlorophyll.

Although all of the data resulting from the analyses listed at the beginning of this section aid in source and sometimes secondary alteration identification, biomarkers often yield the most reliable information (Moldowan and Seifert, 1984; Volkman, 1986; Brassell, 1992). Biomarkers are organic compounds in sediments, sedimentary rocks or petroleum which are derived from biological precursors and retain recognizable, original structure. Since these compounds are resistant to degradation, the presence of these in sedimentary rocks or oils can lead to source identification.

For example, certain tri- and tetra-cyclic diterpanes are found in coals, lignins, and resins. If these biomarkers are found in a rock or oil, it would suggest a precursor plant material (Brassell, 1992). In contrast, the presence of C_{25} isoprenoid alkanes can be indicative of methanogenic bacteria. C_{30} steranes are often indicative of a marine origin (Volkman, 1986). Although these biomarkers are resistant to degradation, they can be altered under extreme conditions.

3.2.4 Gasoline (C_5 to C_{10}) Information

The C_5 to C_{10} compounds were largely ignored until the mid to late seventies because of analytical difficulties associated with their vapor pressures and with sample handling (e.g., evaporation problem). Once these were overcome, studies were performed by a variety of researchers such as Thompson, Philippi, Hunt, Mango, and Snowdon. Several parameters have been proposed for oil to source rock correlations and identification of secondary alteration (see section dealing with secondary effects).

Much of the gasoline work has been concentrated on the origin of the light hydrocarbons. In general, these gasoline range hydrocarbons are formed through the thermal breakdown of kerogenous material. However, there has been disagreement over the exact mechanisms involved in the generation process (Hunt, 1980; Schaefer, 1987; Philippi, 1975; Thompson, 1979, 1983, 1987, and 1988; Mango, 1987, 1990, 1991, and 1994).

Hunt et al. (1980), who believed that most petroleum is derived from the thermal alteration of organic matter in fine-grained sedimentary rocks, examined C_6 to C_7 hydrocarbons in shale samples from a Gulf of Mexico well to determine the time and temperature conditions of petroleum formation. They observed that different types of compounds are preferentially generated at different time and temperature conditions. For example, hydrocarbons with tertiary carbons (e.g., 2,3-dimethylbutane and 2,3-dimethylpentane) form earlier than those with quaternary carbons (e.g., 2,2-

dimethylbutane and 2,2-dimethylpentane). This observation was linked to two types of cracking (free radical and carbonium-ion) that occur at different depths.

In free radical cracking, the electron pair splits with each carbon retaining an electron. In carbonium-ion cracking, both of the electrons are transferred from one carbon to another. The portion of the molecule that loses the electrons becomes the carbonium ion. Primary or secondary structures will rearrange to form a more stable tertiary structure. Hunt et al. (1980) suggested that, at depths around 10 000 feet (approximately 115 ^{0}C), increased tertiary structures are present due to increased carbonium-ion cracking and associated rearrangements. At depths of approximately 13 000 feet (approximately 150 ^{0}C), increased free radical cracking occurs. The amount of quaternary compounds increases since saturated free radicals do not rearrange.

Schaefer and Littke (1987) studied compositional changes in the light hydrocarbons of sedimentary rocks and petroleum from northern Germany. They found that the ratios of C_7 paraffins/naphthenes, (2-methylhexane + 3-methylhexane)/(1c3-dimethylcyclopentane + 1t3-dimethylcyclopentane + 1t2-dimethylcyclopentane), and 1t2-dimethylcyclopentane/1c2-dimethylcyclopentane increase with increasing maturity (or % vitrinite reflectance).

Philippi (1975, 1977), who believed that the light hydrocarbons may be a direct product of the thermal breakdown of ancient biological molecules, examined C_1 to C_7 compounds derived from recent sediments in two California basins to determine how gasoline range hydrocarbons are generated (e.g., temperature conditions). He only found small amounts of gas and no gasoline range saturated hydrocarbons in shallow sediment. As the depth increased, the concentration of gasoline range hydrocarbons varied depending on temperature. He noted a large increase in heavy and light gas at depths greater than 8000 feet (in accordance with an exponential increase associated with the temperature of the petroleum-forming reactions, e.g., a combination of thermal cracking and hydrogen transfer). From this information, he suggested that light hydrocarbons are produced at greater depth with temperature as the controlling factor.

In this study, he also developed a parameter called a 'Similarity Coefficient' which increased with increasing maturity (i.e., with increasing temperature and depth). He showed that this parameter could be used for oil to source rock correlations of 'normal' (not of high maturity or biodegradation) oils (Philippi, 1981). The equations and parameters used for calculation of the Similarity Coefficient and the normal oils are given below:

(3.4 i) parameters used in the calculation of the Similarity Coefficient:

nC_6 hydrocarbons

n-hexane
2-methylpentane
3-methylpentane
2,3-dimethylbutane
methylcyclohexane plus cyclohexane

as a percentage of the total C_6 paraffins and naphthenes (excluding the aromatics)

nC_7 hydrocarbons

n-heptane
2-methylhexane

as a percentage of the C_7 paraffins

3-methylhexane	and naphthenes (excluding the aromatics)
2,3-dimethylpentane	
total C_7 naphthenes	

(3.4ii) parameters used to determine 'normal' oils:

n-heptane / total C_7 paraffins ≥ 0.34
n-heptane / (2,3-dimethylpentane + 2,4-dimethylpentane) ≥ 2
(total dimethylpentanes + trimethylbutanes) / total C_7 paraffins ≤ 0.18

For the Similarity Coefficient, each C_6 (or C_7) hydrocarbon is calculated as a percent of the total C_6 (or C_7) paraffins and naphthenes (excluding aromatics) for each oil or source rock. A comparison can be made between each ratio for two oils or an oil and a source rock. If a value is greater than 1, the reciprocal is used. If the value is less than one, the ratio is not altered. The ratios of these parameters for each oil or source rock are averaged. Theoretically, the ratios in related oils and source rocks should be identical (with a ratio of 1).

Philippi (1981) tested this Similarity Coefficient on shales from C_6 to C_7 hydrocarbons in 10 different formations in the western states and made good correlations for all, corresponding to a ratio of greater than 0.8. However, all of the oils he tested were carefully selected as 'normal'. This parameter is calculated (based on area counts) for biodegraded oils in the current study to test whether or not this Similarity Coefficient can be used to correlate biodegraded oils (see Discussion).

Thompson and Mango strongly disagree over the origin of gasoline range hydrocarbons. **Thompson** (1979, 1983, and 1987) believes that cycloalkanes are produced from the thermal decomposition of heavier polycycloalkanes such as steranes.

Mango (1987, 1990, 1991, and 1994) does not dispute the importance of temperature in the origin of the light hydrocarbons, but he does not agree that they are formed directly from polycycloalkanes. Instead, he suggests a kerogen-specific, steady-state catalytic process for the origin of the gasoline range hydrocarbons.

Thompson (1979) examined C_2 to C_7 hydrocarbons in sediments and observed that the concentration of cycloalkanes reaches a maximum at a temperature of approximately 77 °C (not kerogen-specific). From the concentrations of gasoline range hydrocarbons, Thompson developed four stages of diagenesis for light hydrocarbons which he called the aromatic stage (trace levels of gasoline up to 65 °C), naphthenic stage (light hydrocarbons are continually generated and accumulate with the naphthenes increasing between 66 and 77 °C), paraffinic stage (paraffins become dominant at higher temperatures around 100 °C), and the destructive stage (at high temperatures the concentration of light hydrocarbons decreases).

Thompson (1979) also proposed two temperature dependent indices called the Paraffin Index 1 (PI1; see equation 3.5 below and Table 3.2 for a list of the compound abbreviations) and the heptane value (HV; see equation 3.6 below) or a Paraffin Index 2 (PI2). He observed an exponential increase in the PI1 value from 0.1 to 8 during catagenesis and a linear increase in the HV with increasing temperature.

$$\mathrm{PI1} = (2\mathrm{MC}_6 + 3\mathrm{MC}_6) / (1\mathrm{c}3\mathrm{DMCYC}_5 + 1\mathrm{t}3\mathrm{DMCYC}_5 + 1\mathrm{t}2\mathrm{DMCYC}_5) \qquad (3.5)$$

$$\begin{aligned}\mathrm{HV} = \{\text{heptane x } 100\} / \{&\mathrm{CYC}_6 + 2\mathrm{MC}_6 + 11\mathrm{DMCYC}_5 + 23\mathrm{DMC}_5 + \\ &3\mathrm{MC}_6 + 1\mathrm{c}3\mathrm{DMCYC}_5 + 1\mathrm{t}3\mathrm{DMCYC}_5 + \\ &1\mathrm{t}2\mathrm{DMCYC}_5 + \mathrm{nC}_7 + \mathrm{MCYC}_6 + 223\mathrm{TMC}_5 + \\ &25\mathrm{DMC}_6\}\end{aligned} \qquad (3.6)$$

Table 3.2. Compound names and corresponding abbreviations for gasoline range hydrocarbons dissolved in crude oils.

Compound Name	Abbreviation
isopentane	iC5
normal pentane	nC5
2,2-dimethylbutane	22DMC4
cyclopentane	CYC5
2,3-dimethylbutane	23DMC4
2-methylpentane	2MC5
3-methylpentane	3MC5
normal hexane	nC6
methylcyclopentane	MCYC5
benzene	ben
cyclohexane	CYC6
2-methylhexane	2MC6
1,1-dimethylcyclopentane	11DMCYC5
2,3-dimethylpentane	23DMC5
3-methylhexane	3MC6
1cis, 3-dimethylcyclopentane	1c3DMCYC5
1trans, 3-dimethylcyclopentane	1t3DMCYC5
1trans, 2-dimethylcyclopentane	1t2DMCYC5
normal heptane	nC7
methylcyclohexane	MCYC6
1cis, 2-dimethylcyclopentane	1c2DMCYC5
2,5-dimethylhexane	25DMC6
2,4-dimethylhexane	24DMC6
2,2,3-trimethylpentane	223TMC5
toluene	tol
3-methylheptane	3MC7
1cis, 4-dimethylcyclohexane	1c4DMCYC6
normal octane	nC8

In Thompson's study (1979), he proposed a thermal cracking mechanism for the early dominance of the cycloalkanes followed by a change to a dominance of straight chain alkanes during catagenesis. Steranes and triterpanes (polycycloalkanes) are a large source of reactive tertiary compounds in kerogen. He suggested that at lower temperatures free radical cracking occurs (which is faster for tertiary compounds than secondary or primary compounds) to break open ring structures in the polycycloalkanes yielding cyclopentane (CYC_5) and cyclohexane (CYC_6) hydrocarbons. Free radical cracking is slower for secondary structures as found in long, straight chain alkanes. Thus, generation of the gasoline range, straight chain alkanes is slower.

In 1983, Thompson used several indices such as the PI1 and the HV to identify normal, mature, supermature, and biodegraded oils. This is described in the section dealing with secondary effects. The PI1 and the HV indices are calculated for the oils in the current study to determine whether or not similar oil classification can be made from Thompson's parameters (see discussion).

In subsequent studies, Thompson (1987, 1988) noted that some of the samples were of higher maturity than indicated by his paraffinicity parameters (e.g., heptane/ methylcyclohexane ($nC_7/MCYC_6$). In addition, these samples had higher toluene/nC_7 (aromaticity) ratios than expected. He explained these anomalies by a process called 'evaporative fractionation' where light hydrocarbons would undergo fractionation due to multiple gas extractions. After one fractionation event, the residual material would be enriched in the less volatile hydrocarbons while the evaporated material would be enriched in the volatile compounds. Repeated gas extractions would yield the reverse composition. Eventually, the aromatic content of the remaining oil could become very high. He suggested that this process altered Gulf of Mexico oils (up to 75 %).

Mango (1987) noted an invariance in the ratio of 2-methylhexane ($2MC_6$) plus 2,3-dimethylpentane ($23DMC_5$) to 3-methylhexane ($3MC_6$) plus 2,4-dimethylpentane ($24DMC_5$) in approximately 2000 oils (some degraded) which could not be explained by thermal cracking of polycycloalkanes (e.g., sterane). To find supporting evidence for this, he examined the chemical events occurring before thermal cracking. His arguments against thermal cracking of polycycloalkanes for the generation of light hydrocarbons are summarized below.

If polycycloalkanes are the precursors for the gasoline range hydrocarbons, these compounds would have to contain a C_7 terminal, structural unit so that cleavage would produce the appropriate gasoline structures. There has been no single family of natural products identified with this characteristic. Since the composition of petroleum reflects that of its precursor material, there should be some organic matter (biological compounds) in nature with a similar invariant ratio of isoheptanes, but, again, none have been found. In thermal cracking reactions, product formation is controlled by the concentration of reactants and their activation energies. Since the products would be affected by the precursor compound, the ratio of isoheptanes would not be constant over time (as observed by Mango) from a thermal cracking of polycycloalkanes (as suggested by Thompson).

Mango (1987, 1990, 1991, and 1994) offers a steady state chemical process, where the relative rates of product formation are constant, as an alternate explanation for the generation of cycloalkanes. Pairwise products (e.g., $2MC_6$ and $3MC_6$) are formed sequentially which act as reactants to produce another pair of compounds (e.g., $23DMC_5$ and $24DMC_5$). These two sets of products are formed by thermal cracking, but the reactants are continually regenerated and the products continually formed which acts as the catalytic process at steady-state.

In subsequent studies, Mango (1990, 1991, and 1994) showed that, at the thermal conditions necessary to cleave carbon bonds in paraffins, polycycloalkanes are stable (i.e., they will not undergo ring opening). He also showed that the variance in the toluene/nC_7 and $nC_7/MCYC_6$ ratios was not related to boiling point differences in the compounds. This acts as evidence against Thompson's 'evaporative fractionation'.

Although the correct theory for gasoline range hydrocarbon generation is still uncertain, Mango provides more supporting evidence for his theory than the other investigators. Mango's isoheptane ratio (see equation 3.7 below) is calculated for the oils in the current study to determine whether or not it remains constant for the Canadian oils (see Discussion).

$$\text{Isoheptane Ratio} = (2MC_6 + 23DMC_5) / (3MC_6 + 24DMC_5) \qquad (3.7)$$

The Shell and Mobile Oil companies have calculated a variety of gasoline range parameters on over 7000 oils, but unfortunately the results are confidential and not published. This information could provide insight into the processes of gasoline range hydrocarbon formation.

Other researchers have used the gasoline range data to support other geochemical data in oil correlation studies. **Snowdon and Powell** (1979) examined crude oil from the Beaufort-Mackenzie Basin in the Canadian Arctic. They used gasoline range data to show that Tertiary condensates from Taglu, Niglintgak, and Kumak wells are related and similar to Lower Cretaceous Parsons/Siku condensates. Since no relationships were obvious from the gasoline data, cluster and factor statistical analyses were performed on the data. From these statistical analyses, five oil groupings were obtained.

Osadetz et al. (1994) described three oil families in southwest Saskatchewan (Canadian Williston Basin) using biomarker and other HMW data as well as gasoline range data. The gasoline range parameters (e.g., Thompson's PI1, PI2) were mainly used to aid in the identification of secondary alteration.

3.3 STABLE CARBON ISOTOPIC CHARACTERISTICS OF OILS

3.3.1 Isotope Definition, Effects, and Fractionation

Isotopes are atoms of the same element with the same number of protons and electrons (chemically identical), but with a different number of neutrons (different mass). Carbon has 2 stable isotopes, namely ^{12}C (with 6 protons and 6 neutrons; abundance of 98.89 %, see Table 3.3) and ^{13}C (with 6 protons and 7 neutrons; abundance of 1.11 %).

Table 3.3 Relative natural abundances of selected carbon, hydrogen, and oxygen isotope species (after Faure, 1986).

Element	Isotope Species	Relative Abundance (%)
hydrogen	^{1}H	99.984
	D, ^{2}H	0.016
carbon	^{12}C	98.89
	^{13}C	1.11
	^{14}C	10^{-10}
oxygen	^{16}O	99.763
	^{17}O	0.0375
	^{18}O	0.1905

The isotopic composition of carbon can be expressed in several ways. An isotope abundance ratio can be calculated as shown in equation 3.8.

$$R = \frac{\text{abundance of heavy isotope (e.g., } ^{13}\text{C)}}{\text{abundance of light isotope (e.g., } ^{12}\text{C)}} \qquad (3.8)$$

The isotope ratios in this study will be reported in terms of delta notation as shown in equation 3.9. Since the change in the absolute ratios of two isotopes is very small, it is difficult to accurately measure this absolute difference. Instead, the isotope ratio of an organic species is compared to a standard and this ratio expressed in units of per mil or parts per thousand (‰).

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{standard}}{(^{13}C/^{12}C)_{standard}} \right] \times 1000 \qquad (3.9)$$

where: $\delta^{13}C$ = deviation in parts per thousand (‰) of a sample as compared to a standard

$^{13}C/^{12}C$ = isotope ratio of ^{13}C to ^{12}C in the sample or standard.

A standard is required for calibration of the mass spectrometer (instrument used to measure isotopic composition) so that isotope ratios of unknown samples can be calculated (see Methods). If the standard material (e.g., CO_2 for carbon analysis) with a known isotope abundance ratio is injected at the beginning and end of each analytical run, the calibration of the instrument can be checked to ensure that no fluctuation has occurred and that the isotope ratios are obtained in a consistent manner.

Although several carbon standards have been used, the most common is the carbonate shell of a belemnite cephalopod from the Peedee Formation of South Carolina (abbreviated as PDB). A positive $\delta^{13}C$ value is indicative of an enrichment in ^{13}C (heavy) as compared to the standard while a negative value is indicative of an enrichment in ^{12}C (light).

The original PDB standard with an isotope ratio of 0 ‰ is no longer available so many laboratories use primary gas standards that have been calibrated to the PDB scale. Since the availability of primary isotope standards (from US agencies) is limited and these primary isotope standards can be contaminated or fractionated with regular use, a secondary gas standard is used as a working standard for the lab.

For reference gas calibration to PDB, both the lab and primary CO_2 gas standards are injected into the MS through a normal duel inlet system. The primary gas standard is set in the MS at its isotope ratio relative to PDB. The normal inlet system allows the lab and primary reference gases to be alternately measured while the gas not being measured is expelled as waste. The peaks corresponding to masses 44, 45, and 46 for each gas are integrated and compared, and an isotope ratio relative to PDB (calibrated against the primary standard) is obtained for the lab standard.

Craig (1957) developed an equation (3.10) to calculate (or relate) the isotope ratios of a sample relative to PDB that had originally been measured against another standard. In this way, ratios could still be reported relative to PDB which would allow interlab comparisons.

$$\delta_{(X\text{-}PDB)} = \delta_{(X\text{-}B)} + \delta_{(B\text{-}PDB)} + 10^{-3}\,\delta_{(X\text{-}B)}\,\delta_{(B\text{-}PDB)} \tag{3.10}$$

where x = sample
B = a lab gas standard

Different compounds can have varying amounts of the light (^{12}C) or heavy isotope (^{13}C). An isotope effect is a chemical or physical process that concentrates heavy or light isotopes in particular compounds (Hayes, 1982). An isotope effect can lead to isotope fractionation which is an observable effect described as an enrichment or depletion of the heavy isotope.

Chemical behavior of an atom depends on the electron structure of an atom and on the number of protons. One would expect isotopes to react almost identically, but slight differences in mass can lead to significant differences in the behavior of isotopes during natural processes (Anderson and Arthur, 1983). Several of the thermodynamic properties of molecules are dependent upon the masses of the atoms composing the molecules. Some of the studies detailing this work have been performed by a variety of authors (Bigeleisen and Mayer, 1947; Urey, 1947; Broecker and Oversby, 1971; Bottinga and Javoy, 1973). These mass differences have two important consequences that lead to fractionation as given below.

The first consequence is that heavier isotopic molecules have lower mobility. The kinetic energy ($1/2mv^2$) of a molecule is constant regardless of the isotopic composition (Mook, 1983). Thus, if the mass (m) is larger, then the average molecular velocity (v) must be lower. Heavier isotopic species have lower diffusion velocities and reduced collision frequencies due to lowered mobility. This collision frequency with other molecules is important because it is fundamental to chemical reactions. This contributes to the faster reaction times for lighter molecules.

The second consequence is that heavier molecules have higher binding energies (see Figure 3.4). Any two particles will experience both attractive and repulsive forces. The repulsive force rapidly increases with decreasing interatomic distance while the attractive force decreases less rapidly. The difference in these forces causes the particles to be placed at a interatomic distance. If the two particles are to separate, one of them must have enough kinetic energy to overcome the attractive force (referred to as binding energy).

Interactions among electrons, translational, vibrational, and rotational motions all contribute to the difference in energy between the light (mass of m_1) and heavy isotopes (mass of m_2), especially the vibrational component since it is mass and bond strength dependent (e.g., Faure, 1986). Vibrational frequency is inversely proportional to the square root of the reduced mass (m_1m_2/m_1+m_2) so that isotopic substitutions cause a change in vibrational frequencies. Light isotopes have higher vibrational frequencies so bonds formed with light isotopes are more easily broken when a primary isotope effect

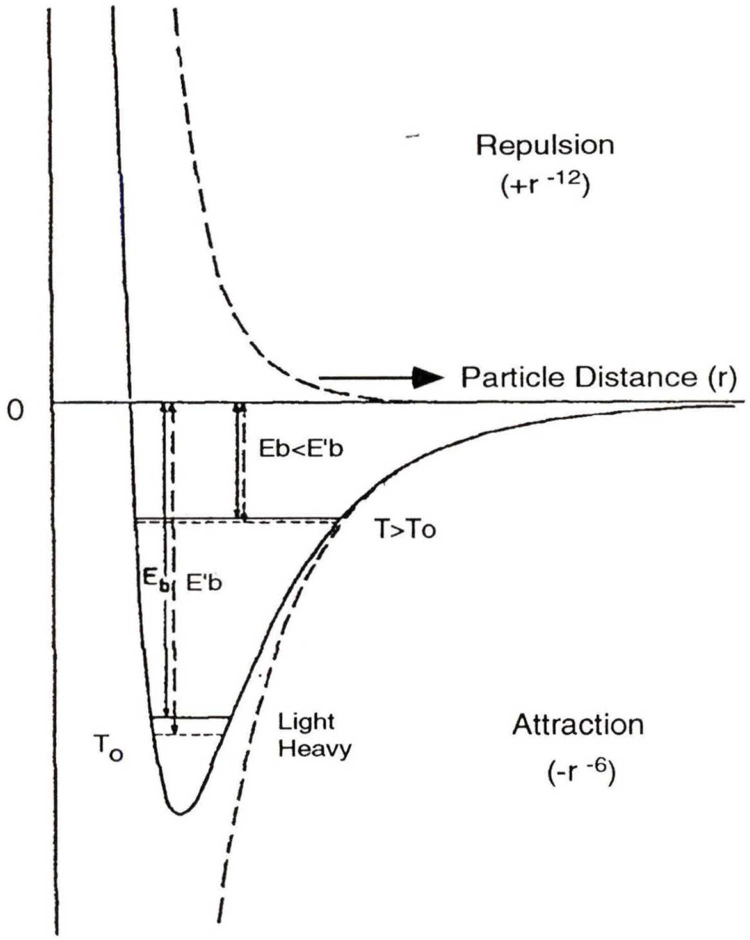


Figure 3.4 Differences in binding energies between light and heavy isotopes. Eb refers to the energy of the light compound, E'b refers to the energy of the heavy compound, and To refers to temperature (after Mook, 1983).

(isotopic substitution occurs at the location where chemical bonding changes) is present. Thus, the lighter isotopic species reacts faster chemically (Mook, 1983).

The two basic types of isotope effects are kinetic (KIE) and equilibrium (EIE). KIE deal with irreversible physical or chemical processes such as evaporation with complete removal of the vapor from further contact with the liquid. Kinetic isotope effects occur when the rate of a reaction is sensitive to mass at a certain location in one of the reactants (e.g., Hayes, 1982). If a normal isotope effect occurs, the first-formed product will be enriched in the light isotope while the residual material will be enriched in the heavy isotope. If a reverse vapor pressure isotope effect occurs, the first-formed product will be enriched in the heavy isotope while the residual is enriched in the light isotope (e.g., rain; binding energy for the heavy species would be smaller than that of the light species).

EIE deal with reversible reactions where isotopes rearrange themselves to obtain a state of minimum energy. Isotope effects can be determined by laboratory experimentation and can occur as long as there is some sort of isotope exchange mechanism (see 3.11 below). The heavy isotope will preferentially go to the compound in which the element is most strongly bonded (Bigeleisen, 1965).

$$A^* + B \overset{k}{\Leftrightarrow} A + B^* \qquad \text{where * indicates the heavy isotope} \qquad (3.11)$$

The magnitude of an equilibrium isotope effect can be represented by the equilibrium constant of the exchange reaction or a fractionation factor can be calculated (Hayes, 1982).

Fractionation factors (α) compare the isotope ratios of one compound or phase to another. The equilibrium constant for an isotope exchange reaction as in 3.11 is equal to the ratio of the isotope ratios for the exchanged species as in 3.12. The absolute ratios (R) of the compounds can be converted to delta notation by a rearrangement of equation 3.9 (e.g., 3.13 below).

$$k = \frac{[A]\,[B^*]}{[A^*]\,[B]} = \frac{[B^*]\,/\,[B]}{[A^*]\,/\,[A]} = \frac{R_B}{R_A} = \alpha_A(B) \qquad (3.12)$$

where R_A = $^{13}C/^{12}C$ of compound A
R_B = $^{13}C/^{12}C$ of compound B
$[A]$ = concentration of A
$*$ = heavy isotope species

$$R_{sample} = {}^{13}C/{}^{12}C = (\delta^{13}C/1000 + 1) \times R_{PDB} \qquad (3.13)$$

where $\delta^{13}C$ = isotope ratio of sample in ‰
R_{PDB} = 0.0112372 (Craig, 1957)

An α value greater than one is indicative of enrichment in the heavy isotope of B relative to A while a value less than one is indicative of a depletion in the heavy isotope of B relative to A (Mook, 1983). Commonly, fractionation factors are very small and are cited in epsilon notation ($\in$) (see equation 3.14 below).

$$\in = (\alpha - 1) \times 10^3 ‰ \qquad (3.14)$$

3.3.2 Range in Isotope Ratios of Precursor Organic Matter and Petroleum

3.3.2.1 Organic Matter

Precursor organic matter for petroleum generation is composed of plant material or necromass (organism remains) derived from marine or non-marine environments. The isotopic composition of the precursor depends on a variety of factors such as the isotopic content of the carbon source, isotope effects associated with the assimilation of carbon (during photosynthesis), isotope effects associated with metabolism and biosynthesis, and the availability of carbon (Hayes, 1993).

Craig (1953) was one of the first investigators to publish a summary of the $^{13}C/^{12}C$ variations in nature. He showed that marine plants and carbonates were enriched in ^{13}C (-18 to -8 ‰) relative to nonmarine plants (-29 to -21 ‰). Silverman and Epstein (1958) noted a similar finding. Marine organisms were enriched in ^{13}C by about 10 ‰ as compared to those in nonmarine environments. Figure 3.5 gives a summary of the isotopic ranges for important precursor organic material (Stahl, 1979; Whiticar, 1992).

In general, aquatic plants ($\delta^{13}C_{org}$ from -13 ‰ to -27 ‰) are isotopically heavier than terrestrial plants ($\delta^{13}C_{org}$ from -22 ‰ to -33 ‰). This difference between marine and land plants is related to the isotopic composition of the carbon source. Land plants take up atmospheric CO_2 which has a $^{13}C/^{12}C$ ratio of -7 ‰ to -8 ‰. In contrast, marine plants take up surface dissolved CO_2 or bicarbonate. Dissolved CO_2 is lower in $\delta^{13}C$ by 1 to 1.2 ‰ relative to gaseous CO_2 (e.g., -8 to -9 ‰; Schidlowski and Aharon, 1992). The difference in the isotope ratios of dissolved CO_2 and bicarbonate ranges from 7.4 to 10.8

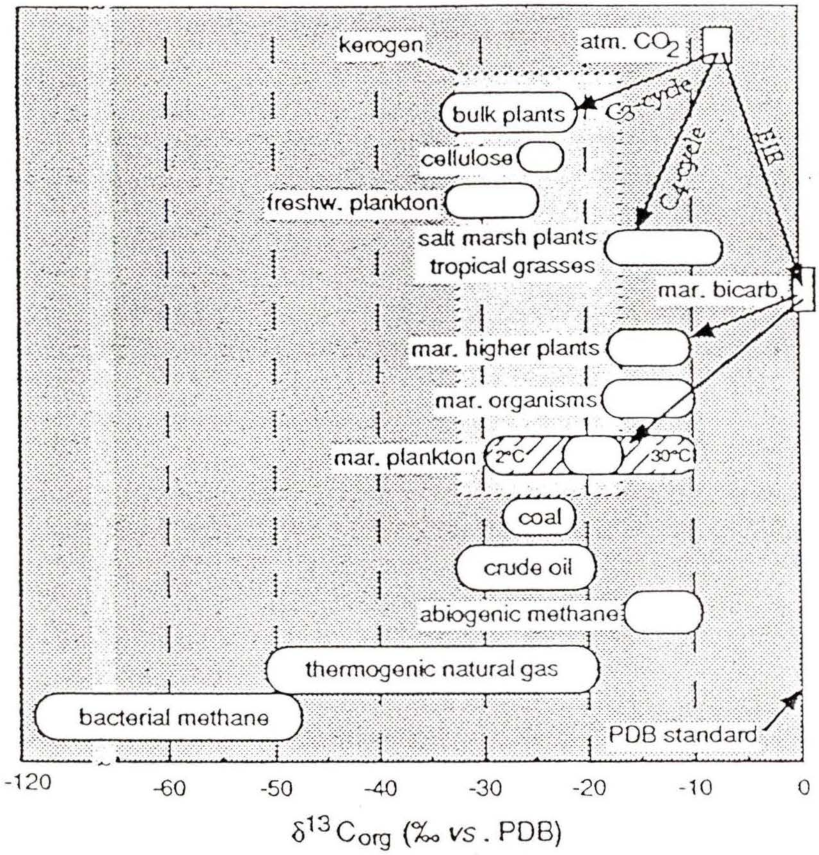


Figure 3.5 Carbon isotope ratios of organic matter and petroleum (after Whiticar, 1992).

‰ between temperatures of 0 and 30 °C, resulting in a bicarbonate ratio close to 0 (e.g., -1 ‰ to -2.5 ‰; Mook et al., 1974). Thus, differences in precursor carbon pools account for approximately 8 ‰ of the difference in the $^{13}C/^{12}C$ ratio of terrestrial and aquatic plants.

Photosynthesis is the major source of primary production. Any carbon fixed through this process will have isotopic distributions governed by isotope effects which fractionate carbon (Deines, 1980; Park and Epstein, 1960; Smith and Epstein, 1971; Schidlowski and Aharon, 1992; Hayes, 1993; Collister et al., 1994). There are 2 main steps where isotope effects can occur during photosynthesis. The magnitude of the isotope effect depends upon the pathway utilized.

The first one is the preferential incorporation of atmospheric, isotopically light carbon dioxide ($^{12}CO_2$) across cell walls and its dissolution into the cytoplasm. The velocity of $^{12}CO_2$ is greater than that of $^{13}CO_2$ since gas velocity is inversely proportional to mass. The lighter molecule will collide more frequently with the plant and therefore will be utilized more frequently (Whiticar, 1992). The isotope effect associated with diffusion is small (e.g., -1.6 to -3.2 ‰; Vogel, 1980).

The second step where fractionation occurs is during enzymatic fixation of the CO_2 (in cytoplasm) to phosphoglyceric acid. An enrichment in ^{13}C in dissolved CO_2 results. The isotope effect associated with this step varies depending on pathway and enzymes utilized. The isotope effect, which results from the action of the RuBP carboxylase enzyme (as for C_3 plants), is between -20 and -40 ‰ (depending on temperature, pH). The isotope effect associated with the PEP carboxylase enzyme (as in C_4 plants) is between -2 and -3 ‰ (Schidlowski and Aharon, 1992).

Thus, different types of plants have different isotopic ranges. For example, Smith and Epstein (1971) determined that Calvin-Benson (C_3) plants are more efficient at using ^{12}C (range -22 to -33 ‰) than Hatch-Slack (C_4) plants (range -8 to -18 ‰). Crassulacean Acid Metabolism (CAM) plants use both the C_3 and C_4 pathways, and thus their isotopic range spans that of the C_3 and C_4 plants. Marine phytoplankton show a rather large range in isotopic composition from -10 to -30 ‰ which could be due to temperature (Sackett et al., 1965) or CO_2 concentrations (Abelson and Hoering, 1961).

There is also some evidence put forth by authors (e.g., Deines, 1980; Hayes et al., 1990; Hayes, 1993) to show that the different compounds within a plant have different isotope ratios (e.g., lipids are depleted in ^{13}C relative to the total biomass), that is, there is isotope partitioning in the biosynthesis which occurs in a plant. Isotope effects associated with biosynthesis can be complex since the magnitude of the effect will depend on the isotope effects associated with carbon assimilation, carbon excretion, and the pathways linking the metabolic intermediates to the biosynthetic product (Hayes et al., 1990; Hayes, 1992). The isotopic characteristics of all these processes are not well established, but the isotope effects associated with biosynthesis may be significant (Hayes, 1992).

Plants or organisms die and undergo varying amounts of remineralizations before they are incorporated into sediment (Deines, 1980). Biopolymers (e.g., proteins and nucleic acids) are broken down into smaller, soluble compounds (e.g., short chain carbon fragments and amino acids with the release of compounds such as CO_2 and H_2O) by microbes. There may be isotope effects associated with the bacterial degradation of organic matter at this time since it is energetically more favorable for bacteria to consume ^{12}C rather than ^{13}C. This has been demonstrated by Whiticar and Faber (1986) with regard to the anaerobic oxidation of methane in sediments.

Some of the product CO_2 or H_2O is used by living organisms or they condense to base soluble humic substances (which eventually are incorporated into kerogen). As temperature in the subsurface increases, some compound groups are more susceptible to alteration processes (e.g., oxidation) such as carbohydrates and proteins (enriched in ^{13}C). Other compounds are more resistant to alteration such as lipids, lignin, and cellulose (depleted in ^{13}C). The preferential retention of isotopically light, resistant compounds may influence the isotope composition of the remaining material which is eventually incorporated into kerogen.

Conditions present during accumulation of organic matter may also affect the isotopic ratios of the material that is incorporated into kerogen and eventually oil. For example, under strict marine conditions, algae would be the only source of the organic carbon while under strict terrestrial (non-lacustrine) conditions higher plants would be the only source material. The isotopic ranges for these algae or terrestrial plants can be seen in Figure 3.5. There may be additional organic material with a particular isotopic composition transported into the area in this sediment. This 'exogenous' organic matter could combine with the 'endogenous' material, and the isotopic composition of the organic matter in the samples would change as a function of the mixing of two isotopically different materials.

3.3.2.2 Hydrocarbon Gas

Individual gas compounds have been characterized by both molecular and isotope information in correlation studies by a variety of investigators (Colombo et al., 1965; Silverman, 1971; Schoell, 1980; Faber and Stahl, 1984; Whiticar et al., 1984; Whiticar, 1993; Baylis et al., 1994). There are several characteristics of gases which make them useful for correlations. These compounds have low carbon numbers (C_1 to C_5) with reduced chemical diversity. Their isotope range is large and predictable.

The two main types of gases are called primary and secondary. Primary gases are generated from a single source while secondary gases have been mixed or altered (e.g., from bacterial oxidation). These gases have different carbon isotope ranges. The main type of gas is methane followed by ethane, propane, and butane.

Some of the various types of methane gases and the corresponding isotope ratios are as follows: bacterial gas (-55 to -110 ‰), thermogenic gases (-15 to -50 ‰), geothermal, hydrothermal, and crystalline gases (-15 to -45 ‰), abiogenic gas (0 to -15 ‰), and artificial gas (-4 to -30 ‰) (Schoell, 1980; Whiticar, 1990 and 1993). The characterization of gas is often aided by combinations of molecular and isotope information as well as hydrogen isotope ratios (see Whiticar, 1990 and 1993). New compound-specific isotope analysis has enabled the measurement of gases previously too small to measure such as seep and headspace gas (Baylis et al., 1994)

Silverman (1971) showed the $\delta^{13}C$ values of petroleum distillation fractions (Figure 3.6a). The ratios increased rapidly from -200 to 45 °C. There was very little change in the isotope ratios above 45 °C. The gasoline range hydrocarbons correspond to a distillation temperature range of 27 to 126 °C (Stahl, 1978). From this graph, it appears as if there is no variation in the gasoline range isotopes. Erdman et al. (1969) measured the isotope ratios of methane, ethane, propane, iso-butane, and butane in a gas sample and found that the largest isotopic variation occurred between methane, ethane, and propane. There was little change in the isotope ratios of the branched and normal butanes (Figure 3.6b).

Gases are isotopically studied since their ranges are so large. In molecular and isotope studies, initially only the C_{15+} fraction was examined. The isotopic ratios for gasoline range n-alkanes were thought to be relatively constant and therefore of little interest. The lighter fraction below C_{15} was removed through distillation to ensure that a stable C_{15+} fraction resulted. The gasoline range isoalkanes and cycloalkanes were not measured so the early investigators missed much of the data structure.

3.3.2.3 Bulk Oil

Initially, isotopes were measured on bulk oil since the bulk oil required little sample preparation before analysis and the sample injection methods for mass

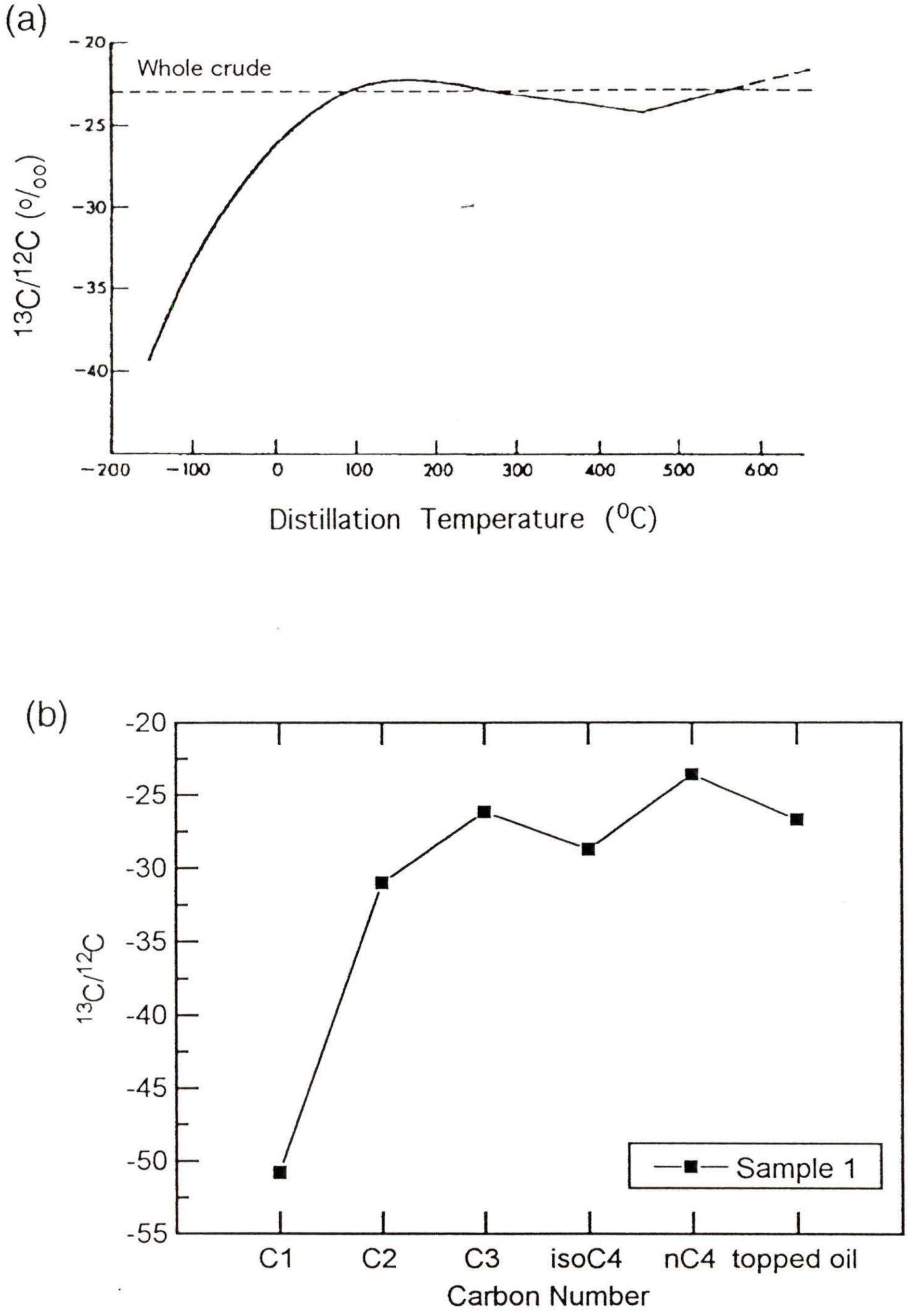


Figure 3.6 Carbon isotope ratios of light hydrocarbons: (a) petroleum distillation fractions (after Silverman, 1971) and (b) C_1 to C_4 (after Erdman, 1969).

spectrometers were not sophisticated enough to allow specific isotope measurements. From this work, a crude link between petroleum and precursor organic material was established (Silverman, 1964; Degens, 1969). These bulk isotope ratios have been widely used as indicators of depositional environment and as tools in correlation studies.

Wickman (1956) measured 10 petroleum samples from widely separated geographical areas and found a 6 ‰ range in $^{13}C/^{12}C$. Silverman and Epstein (1958) observed higher (less negative) ^{13}C in petroleums of a marine origin than those of a non-marine origin, corresponding to the isotopic composition of the respective marine and non-marine organisms (typically in the range of 10 ‰). They also found that crude oils have lower $^{13}C/^{12}C$ (about 10 ‰) than their biological sources. Lipids were proposed as the main portion of plants contributing to petroleum formation since they are lighter (i.e., enriched in ^{12}C up to 8 ‰) than whole plants or most other biogenic compounds (Silverman, 1964). The origin of petroleum is still debated today (e.g., Deines, 1980; Eglinton, 1994)

Degens (1969) performed isotope analyses on 600 whole crude oils, showing the average of these ratios was the same as the average isotopic composition of the lipid fraction of modern marine plankton. He also showed a variation in isotopic composition with average age, but there was a lot of variation in the isotope ratios for each oil group (of different age).

In a review study of the use of stable carbon isotopes in hydrocarbon exploration, Fuex (1977) determined that the isotopic composition of most crude oils fell between -21 and -32 ‰. Yeh and Epstein (1981) proposed that the $\delta^{13}C$ ratios of crude oils appear to be largely due to the isotopic compositions of organic precursors, and the terrestrial input to many marine crudes is probably significant.

Some researchers have used bulk isotopes for correlation purposes. For example, Kvenvolden and Squires (1967) measured the isotope ratios of 103 whole oils from the Permian Basin in Texas. A large range in isotopic composition from -27.2 to -34.6 ‰ was attributed to source differences so they interpreted 5 different families for lower Ordovician oils. However, in their study, only other bulk molecular data was provided.

The problem with earlier studies is that bulk isotopes are only averaged ratios. Oils are composed of various fractions (e.g., saturates, aromatics, NSO compounds) each of which has an isotope ratio. Whole oil isotope ratios are only weighted averages of the isotopic composition of these fractions, and therefore they are of restricted diagnostic value. Although these bulk ratios are used in more recent studies (Leenheer, 1984; Bustin, 1988; von der Dick et al., 1989), they are only a small component of the total geochemical data utilized.

3.3.2.4 Major Oil Fractions

The major oil fractions (e.g., saturate, aromatics, and NSO compounds) were isolated chemically and their isotopic ratios determined. In most samples, the lighter compounds were distilled off to give a stable suite of C_{15+} compounds. There was concern that the volatility of the LMW compounds would be detrimental to comparisons between samples. These isotope ratios are more specific, providing greater detail than bulk ratios previously measured.

The methodology to separate aromatic and paraffinic-naphthenic fractions existed in the 1950's. Silverman and Epstein (1958) observed that the $^{13}C/^{12}C$ ratio of the aromatic fraction (maximum of 0.7 ‰ heavier than whole oil) did not differ by more than 1 ‰ from the ratio of the paraffinic-naphthenic fraction (approximately 0.3 ‰ lighter than whole oil). This lead them to believe that the chemical composition of an oil was not independently responsible for the 10 ‰ isotopic range present in whole crude oil. The chemical processes occurring during transformation of source material to petroleum must have been different from those responsible for the chemical composition of an oil. Isotopic fractionation probably occurred as organic matter was converted to petroleum or from the accumulation of certain fractions enriched in ^{12}C (Silverman, 1978).

Galimov (1973) used 'isotope type curves' to show the $\delta^{13}C$ of different structural groups in crude oil of upper Carboniferous age in the Permskaya Oblast, Ural area. The oil fractions became heavier in the following order: light n-paraffins, branched paraffins, naphthenes, and aromatics (Figure 3.7a). His study did not provide support for the use of isotopes in distinguishing marine from non-marine environments.

Stahl (1977, 1978) was one of the first researchers to apply 'isotope type curves' to the correlation of oils and source rocks. The isotope ratios for the various oil fractions are measured and plotted in a 'type curve'. Asphaltic oil fractions should have isotopic values similar to the kerogen from which it was derived. If the crude oil and kerogen are

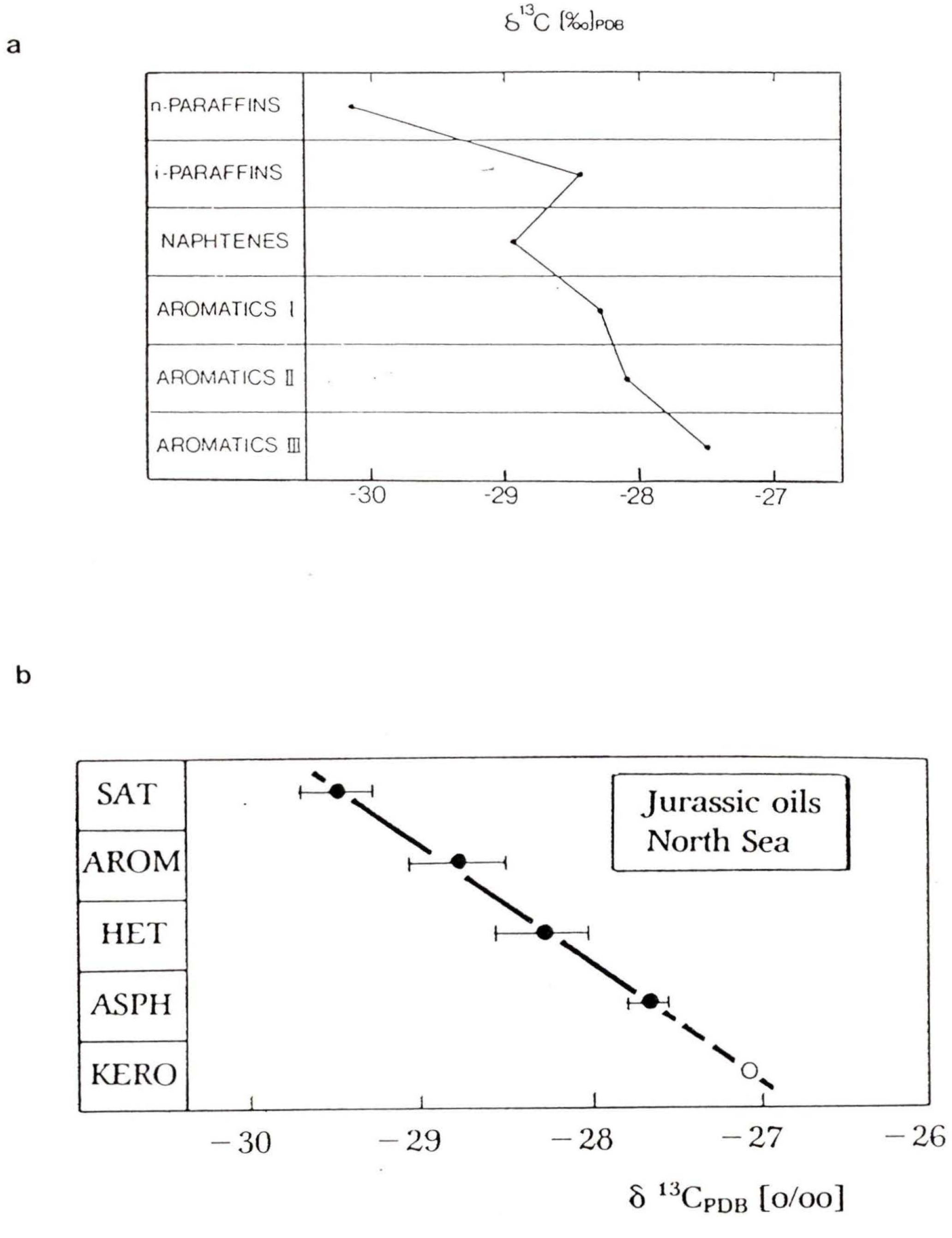


Figure 3.7 Isotope type curves: (a) initial work by Gamilov, 1973 and (b) application of the isotope type curve to oil correlation by Stahl, 1978.

related, the type curve can be extrapolated to give an approximation of the isotope value for the kerogen (Figure 3.7b). This method was an important advancement in the use of carbon isotopes for oil to source correlation. One of the weaknesses in the use of isotope type curves by Galimov and Stahl is that they did not perform mass balances to determine the effect (if any) on bulk oil from the removal of the various oil fractions.

The difference between the isotope ratios of the aromatic and saturate fractions is low, rarely exceeding 2 ‰ for the same oil (Fuex, 1977). Thus, these HMW compounds are relatively free of primary and secondary fractionation effects (as will be seen in section dealing with secondary effects). Fuex suggested maturity may be the causative factor of the 2 ‰ range, while Stahl (1977) suggested source control as a possible factor. This minimal change in isotopic composition of the HMW compounds makes them useful as correlation tools in that the oils can be linked back to a source by comparison of isotope ratios despite any alteration processes (e.g., maturity or biodegradation).

Sofer (1984) used the relationship between the isotope ratios of aromatic and saturate hydrocarbons for distinguishing between marine and terrestrial oils. He statistically evaluated the difference through a parameter called a 'canonical variable' which correctly classified approximately 90 % of marine and non-marine oils (Figure 3.8).

The isotope information from the major oil fractions is often used in routine oil correlation studies. Many advancements were made, but there were still a few areas that

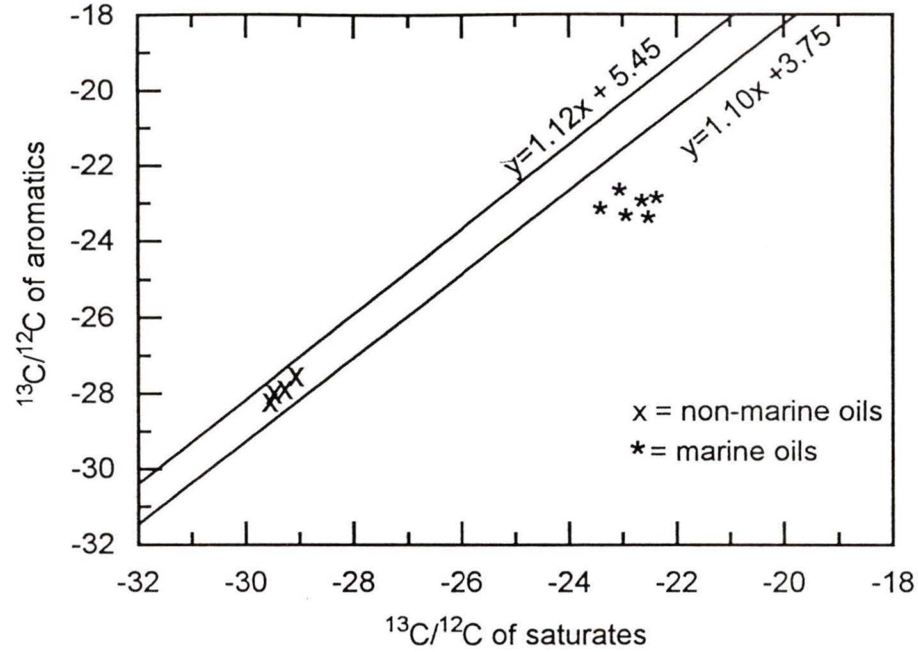


Figure 3.8 Sofer's classification of marine and non-marine oils (after Sofer, 1984).

required further work. The technology was not available for individual compound studies, but this specific information might provide even more insight into oil characterization and correlation. Also, the gasoline range hydrocarbons, even though they constitute a significant portion of crude oils (e.g., approximately 30 %), were largely ignored because of analytical difficulties associated with their volatility,

3.3.2.5 Individual Hydrocarbons

The sample introduction techniques for MS were not developed to measure individual compounds until about five years ago. The traditional mode for sample preparation is to purify a single compound off-line and then use a probe or inlet system to load the sample into a MS. Recent technological advancements have lead to the connection of a gas chromatograph (GC) with a MS and on-line combustion capabilities.

The group headed by Dr. John Hayes, Indiana University, pioneered the development of an analytical instrument system known as a GC-C-IRMS to address the question of isotopes on individual compounds in complex mixtures (Matthews and Hayes, 1978; Ricci et al., 1994). This system combines a gas chromatograph (separation of individual compounds), a micro-combustion oven (on-line combustion), and an isotope ratio mass spectrometer (see details in methods section). Since the use of this technique has only been possible in the last five years, there has only been a limited amount of studies performed.

Most of this type of work has been concentrated on the C_{10+} fraction (e.g., Gilmour et al., 1984; Mycke and Leplat, 1991; Rieley et al., 1991; Ishiwatari et al., 1994; Boreham et al., 1994; Schoell, et al., 1994; Hayes et al., 1994). The only investigators examining hydrocarbons in the gasoline range of oils are Schoell and Bjorøy (see below).

Rieley et al. (1991) used the individual isotope ratios of n-alkanes from leaves of lakeside trees and from lake sediments to discriminate between the sources of sedimentary carbon. The leaves had isotope ratios between -30.1 and -38.7 ‰ while the lake sediments had isotope ratios ranging from -30.1 to -35.9 ‰. Since these two sets of isotope ratios were similar, they concluded that the tree leaves were one of the precursor carbon sources for the sedimentary carbon. Lipids from the sediment with lower carbon number had isotope ratios between -20 and -22 ‰ which the investigators attributed to a possible algal source.

Ishiwatari et al. (1994) measured the isotope ratios of individual long chain n-alkanes in recent sediment from Tokyo Bay. The $\delta^{13}C$ values for shallow, C_{27} to C_{33} n-alkanes range from -31.5 to -28.2 ‰. The isotope ratios of even carbon number alkanes were found to be isotopically heavier than the corresponding odd n-alkanes. In deeper locations, the $\delta^{13}C$ values of n-alkanes range from -29.6 to -32.9 ‰ with no difference between the odd and even numbered compounds. The isotope pattern observed in the shallow n-alkanes was attributed to the mixing of higher plant wax n-alkanes and n-alkanes from oil pollution.

Hayes et al. (1994) measured the isotope ratios of individual geoporphyrins and geolipids in shale samples. The isotope ratios of the porphyrins were related to a common source that had been structurally altered. Differences in the isotope ratios of the porphyrins and the lipids were also related to a common source. These differences were equal to differences seen in modern biosynthetic products. From observations made in this study, the investigators proposed that the isotopic compositions of individual compounds can be interpreted in terms of ancient biogeochemical processes.

Schoell et al. (1994) measured the individual isotope ratios in C_{28} and C_{29} steranes ($\delta^{13}C$ = -25 to -32 ‰), pristane and phytane ($\delta^{13}C$ = -33 to -34‰), carotane ($\delta^{13}C$ = -33.2 ‰), C_{29}, C_{31}, and C_{32} hopanes and moretanes ($\delta^{13}C$ = -40.9 to -44.3 ‰), and C_{30} hopanes and moretane ($\delta^{13}C$ = -51.9 to -60.5 ‰) in gilsonites (asphaltic bitumens) in the Uinta Basin and shale extracts from the Green River Formation. From these ratios, it was suggested that the organisms producing these compounds probably grew near a lake surface. The source beds for the gilsonites were interpreted as being derived from a paleolake. The isotope ratios of the gilsonites were similar to the isotope ratios in the shale extracts, indicating that they both have similar sources.

Gilmour et al. (1984) measured the isotopic ratios of individual n-alkanes in the C_{16} to C_{24} range in 3 oils. They found that the variations in the isotope ratios of the individual compounds were significant (i.e., outside the analytical error margin). Two of the oils were grouped together on the basis of isotopic similarity while the third oil was separated due to dissimilarity.

Sofer et al. (1991) performed isotopic analysis on the n-alkanes in the C_{13} to C_{31} range from oils in the Congo Basin and the North Viking Graben. The short chain n-alkanes in the Congo Basin had an isotopic range of -26 to -28 ‰ while the long chain n-alkanes had a range of -32 to -34 ‰. The Congo oils have a lacustrine source so it was suggested that this kind of dual composition might be characteristic of lacustrine derived oils (but testing of additional samples was required). All of the isotope ratios for the marine-sourced North Viking oils fell between -30 to -32 ‰ irrespective of carbon number.

Bjorøy et al. (1991) examined the individual stable carbon isotopes of n-alkanes and isoprenoids in the C_6 to C_{32} range in Congo and North Viking oils. The n-alkanes in oil derived from a terrestrial source had the heaviest isotopic compositions while the lacustrine-derived oils had the lightest compositions. The isotopic composition of marine oils fell in between these two. In the terrestrial oils, as carbon number increased, the isotopic ratios became lighter while the lacustrine and marine oils did not show very much variation. There was also isotopic variation between the isoprenoids and the n-alkanes for each oil group. From the results, the authors believed that individual carbon isotopes may be useful in oil classification and correlation.

Bjorøy et al. (1994), in a follow-up study, further examined the C_4 to C_{20} individual hydrocarbons of oils and condensates in the Central Graben and the Viking Graben. They showed that related oils and condensates do not show significant differences in $\delta^{13}C$ of individual hydrocarbons. Compound-specific, stable carbon isotopes were used to identify multiple sources for oils and condensates in the Central Graben and to divide the Viking Graben oils and condensates into three groups (Figure 3.9).

Gas (C_1-C_5) and HMW (C_{15+}) compounds have been studied both molecularly and isotopically. Although there have been some recent, compound-specific, stable carbon isotope studies, few investigators have examined gasoline range hydrocarbons. Thus, more research is required in this area.

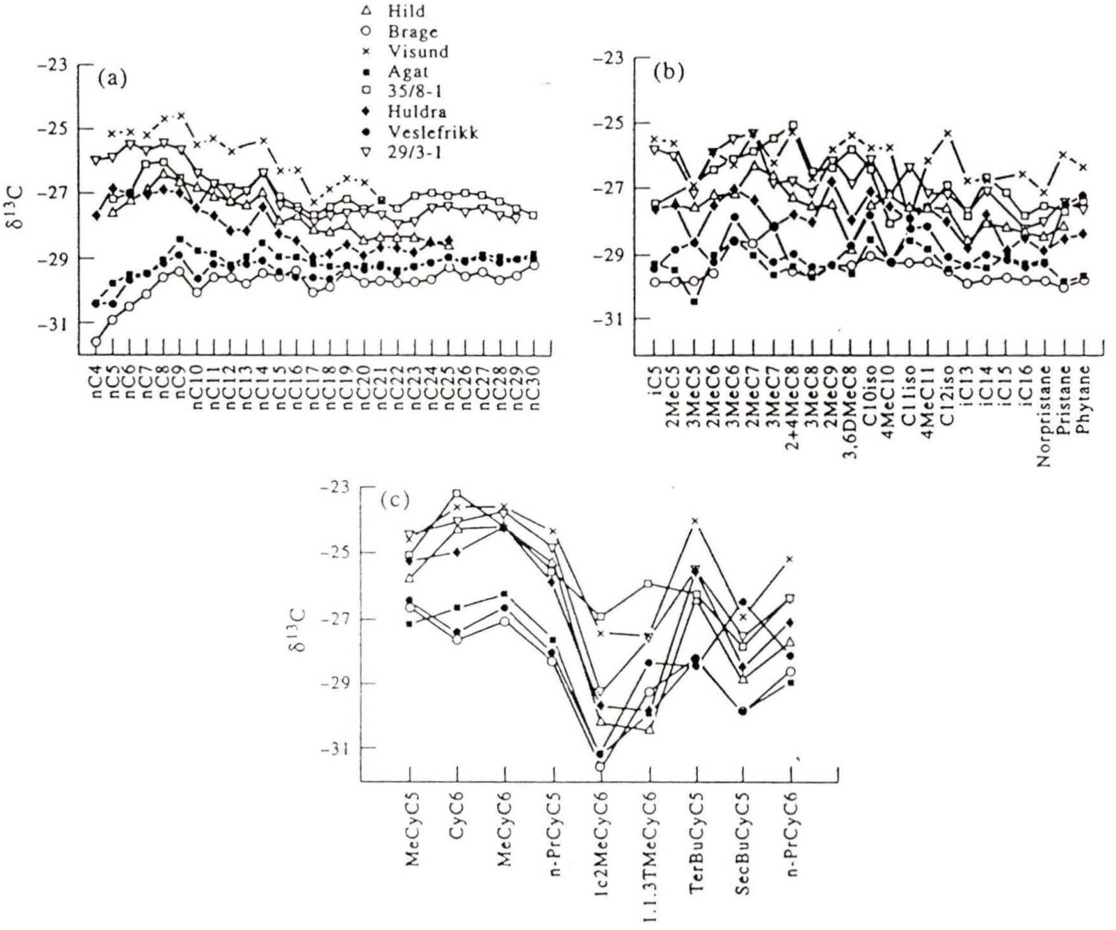


Figure 3.9 Results of a compound-specific study of Bjorøy (1994). The isotopes of the n-alkanes, branched alkanes, and cycloalkanes are given for 8 oil samples from the Central Graben and the Viking Graben. From this and other data, two main groups of oils based on source were classified: 35/8-1, 29/3-1, and Hild and Brage, Visund, and Veslefrikk.

3.4 THERMAL ALTERATION

3.4.1 Molecular Effects

Thermal alteration occurs as a result of heat in the subsurface and increases with increasing burial depth, temperature, and time (Tissot and Welte, 1978). Oils can be subjected to thermal alteration as they migrate or after they accumulate in a reservoir. As the depth and therefore temperature increase, crude oil tends to become lighter. Initially, condensation reactions occur where two reactive molecules link to form a higher molecular weight than either reactant. During this reaction, LMW compounds such as methane and water are released. As the temperature and depth of burial increase, the HMW compounds are cracked into the LMW compounds (Tissot and Welte, 1978). When extreme temperatures are reached (e.g., 200 ^{0}C), only methane is produced.

Thermal maturity is identified using several molecular parameters. For source rocks, vitrinite reflectance, spore coloration, and the maximum temperature of hydrocarbon generation (T_{max}) in Rock-Eval pyrolysis are measured (Tissot et al., 1987; Morrow and Issler, 1993). For oils, concentrations of biomarkers and several gasoline range parameters developed by Thompson (1983, 1987) and Mango (1987, 1990) aid in the recognition of maturity. Several of these maturity parameters are described here.

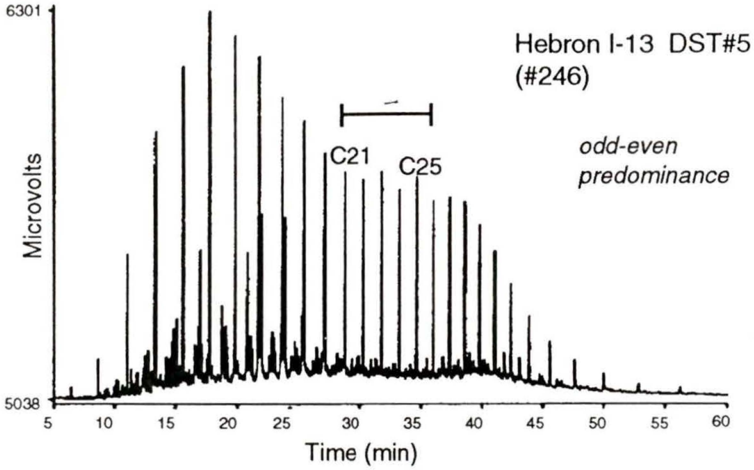
Vitrinite is derived from higher plant material (Tissot and Welte, 1978). The reflectance on a polished surface of vitrinite (measured as % reflectance) in a source rock increases with maturation because of a change in the molecular structure of the vitrinite. Vitrinite is composed of stacked clusters of condensed aromatic rings with side chains.

As maturity increases, the clusters fuse into larger, condensed aromatic rings, eventually forming ordered sheets of condensed structures. The increased reflectivity is a result of the size and orientation of the sheets.

A Rock-Eval instrument subjects potential source rocks to increasing temperatures, and the generated hydrocarbons are collected and analyzed (Snowdon and Fowler, 1991). T_{max} is the temperature of the highest point on the peak (in the results of the analysis) corresponding to the amount of material volatilized between 300 and 600 °C. As maturity increases, the T_{max} values also increase.

Pyrolysis experiments are often used to determine the maturity of kerogen or oils and to investigate the generation of hydrocarbons (Tissot et al., 1987; Lewan et al., 1986; Ayache and Oberlin, 1990). For example, Behar et al. (1990) performed cracking experiments on two oils of different composition. From examination of similarities in the pyrolysis products, they developed a unified model of hydrocarbon generation.

Some maturity information can be determined from the compound distribution in the C_{15+} gas chromatograms. The average chain length of n-alkanes in the C_{15} to C_{35} range decrease as temperature increases since longer chain hydrocarbons are cracked into shorter (lower carbon number) fragments. A predominance of odd carbon compounds can be found in oils as a result of the biosynthetic process. This odd/even predominance can be masked as maturity increases (Figure 3.10). The cracking reactions, which occur at higher temperatures, break the higher molecular weight compounds and there is no discrimination between odd and even carbon compounds.



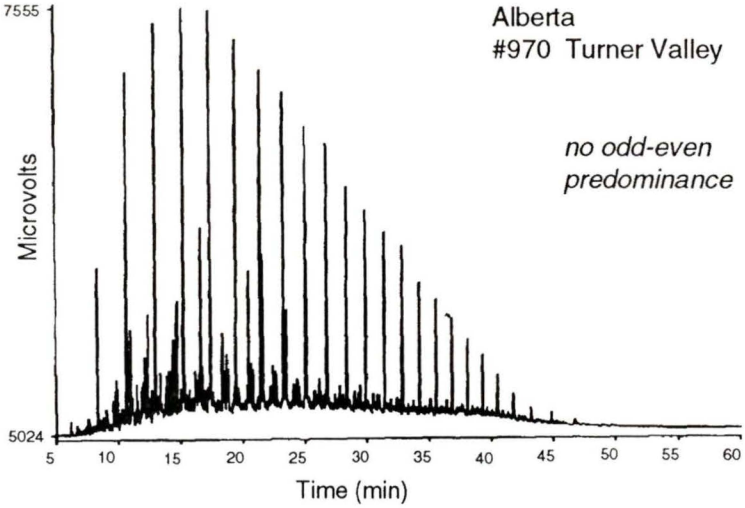


Figure 3.10 Odd-even predominance in HMW hydrocarbons. In high maturity oils such as Turner Valley, the odd-even predominance is masked.

Gasoline range parameters can also be used to obtain maturity information. For example, according to Thompson, his paraffin indices (PI1, PI2, and $nC_7/MCYC_6$) should increase with increasing maturity (see section on gasoline information). Thompson (1983) also used iC_5/nC_5 and $3MC_5/nC_6$ ratios to identify maturity. These values decrease with increasing maturity since cracking reactions occur which increase the amount of shorter chain n-alkanes. Mango's isoheptane index (see section on gasoline information) showed a strong invariance, but the $2MC_6/3MC_6$ and the $24DMC_5/23DMC_5$ ratios increased with increasing maturity. The gasoline range parameters are calculated for the oils in the current study (see Discussion).

3.4.2 Isotope Effects

The isotope effects associated with thermal alteration result from binding energy differences (see section on why isotopes fractionate) in the affected hydrocarbons (Stahl, 1977). Cracking reactions proceed either thermally or catalytically (Sackett, 1978). In general, the binding energy associated with a ^{12}C-^{12}C bond is less that associated with a ^{13}C-^{12}C bond. Thus, the ^{12}C-^{12}C bonds are easier to break than the ^{13}C-^{12}C. As thermal alteration increases and the isotopically light carbons are cracked more frequently, the residual oil can become heavier. Several researchers performed studies which show that the isotope effect associated with thermal alteration is small.

For example, Sackett et al. (1970) conducted experiments on thermal cracking and found that the fractionation between the methane produced and the source hydrocarbons increases with increasing chain length to a maximum of 2 ‰ (residual material became enriched in ^{13}C).

Sofer (1984) examined 339 oils from marine and nonmarine environments. He found that the isotopic changes due to maturity were less than 2 ‰ and that the larger isotopic variations associated with source could mask the effect of maturation. Sofer et al. (1985) examined 15 oils from the Cretaceous Vivian and Chonta Formations in the Peruvian Oriente Basin and again found the isotope effect associated with thermal maturation to be low (1 to 2 ‰). A study by Fuex (1977) reaffirmed this 1 to 2 ‰ shift.

Bjorøy et al. (1992) performed an artificial hydrous-pyrolysis experiment on C_{10+} hydrocarbons and found that the isotopic composition of the n-alkanes did not shift more than 3 ‰ as a function of increasing maturity. A preliminary compound-specific isotope study performed by Sofer et al. (1991) on the North Viking Graben and Congo Basin oils grouped a condensate sample from the North Viking Graben with all of the other North Viking oils. This study suggests that maturity does not have a significant effect on the isotopes of individual compounds and that GC-C-IRMS may be useful in obtaining analytical data for the correlation of high maturity oils and condensates (with no biomarkers) to related less mature oils. In a recent study, Clayton and Bjorøy (1994) performed a compound-specific isotope analysis of North Sea oils and found that isotope ratios become 2 to 3 ‰ heavier with increasing maturity.

Mycke et al. (1994) performed a compound-specific isotope study where the products of the pyrolysis of asphaltenes were isotopically compared with the individual compounds in oils from various marine and deltaic environments. Their main objective was to develop a quantitative pyrolysis method which would yield easily identifiable products. The isotope results between the n-alkane pyrolysis products and the compounds in oils showed a good agreement. They also analyzed sediment and coal samples, but they did not find any maturity relationships. From the isotopic composition of the pyrolized CO_2, the investigators were able to establish the depositional environment of the source rocks.

A similar pyrolysis study was performed by Wilhelms et al. (1994). For marine oils, they found that the individual n-alkanes of asphaltene pyrolysates were enriched in ^{13}C by 4 ‰ as compared to the isotopic composition of the corresponding oil. For deltaic land plant oils, the opposite was found which may be indicative of different sources for the n-alkanes in oils and the n-alkanes derived from the corresponding asphaltenes.

Clayton and Bjorøy (1994) measured the individual stable carbon isotopes of hydrocarbons in North Sea oils with variable thermal maturity. From the results of the analysis, they found that maturity accounts for up to 3 ‰ (50 to 90 %) of the variation in the samples with all values becoming heavier with increasing maturity. Despite this maturity effect, the investigators could still identify source differences.

3.5 MOLECULAR EFFECTS OF SECONDARY ALTERATION OF PETROLEUM

Petroleum can be altered by processes such as biodegradation, water-washing, and addition of new compounds to the reservoir from further migration. The changes in molecular composition due to secondary alteration have been documented and will be summarized in the following section. This change in composition reduces the ability of molecular analysis to correlate oils to other oils or source rocks. It must be noted that some of the variations of crude oil compositions arise from differences in the types of sources (Tissot and Welte, 1978) and not only from alteration processes. For example, coaly material with low hydrogen/carbon ratios produces more gaseous compounds while algal material with high hydrogen/carbon ratios can produce higher quantities of oil (Figure 3.1).

3.5.1 Biodegradation

Changes in compound distribution due to biodegradation are the most significant of all the secondary alteration processes. It has been estimated that approximately 10 % of the world's crude oil reserves have been altered by microbes (Seifert and Moldowan, 1979). Biodegradation occurs together with water-washing, but the effects of each are different. Biodegraded oils or condensates are usually found in areas that contain reservoirs close to the surface (as a result of change in level of burial through subsidence or erosion) where the oil can be affected by the action of meteoric waters.

The meteoric water carries nutrients such as dissolved oxygen, nitrate, and sulfate and microbes into a reservoir. These microbes can either be aerobic (e.g., pseudomonas or bacillus) or anaerobic (e.g., sulfur-reducing desulfo or desulfovibrio) strains (e.g., Cassani and Eglinton, 1991; Bosecker et al., 1991). The biodegradation will proceed as long as a compound (e.g., oxygen) is present which can act as a terminal electron acceptor for the reaction and the temperatures are not too high (e.g., not > 80 °C). For example, aerobic microbes use molecular oxygen directly whereas the anaerobic microbes must use dissolved sulfate ions as a terminal electron acceptor.

Some microbes (e.g., Acinetobacter) are thought to encapsulate hydrocarbon chains in membrane microvesicles and actively move them into the cell (Watkinson and Morgan, 1990; Smith, 1990). They use their enzymes to oxidize and thus break the carbon to carbon bonds. From this reaction, the microbes obtain a 2-carbon compound which can enter their central metabolic pathways (e.g., Bailey et al., 1973; Deroo et al., 1974; Connan, 1984; Blair et al., 1985; Rowland et al., 1986; Watkinson and Morgan, 1990; Smith, 1990). The product of complete oxidation or degradation is CO_2 while incomplete degradation can yield oxygenated by-products such as alcohols and acids.

The straight chain n-alkanes are preferred over cyclic hydrocarbons because the oxidation of the straight chain n-alkanes can be completed in one step whereas the cyclic hydrocarbons require multiple reactions to break open the rings before any energy yielding processes can occur. Many cyclic compounds can not be fully oxidized and end up in the non-hydrocarbon portion of oil (asphaltenes).

Figure 3.11 is a classic example of the effect of biodegradation on oils in the Western Canada Sedimentary Basin (Deroo et al., 1974). The removal pattern of hydrocarbons generally occurs in the following order: first the light n-alkanes, followed by the branched alkanes, aromatics, and low-ring cycloalkanes, and finally the heavier alkanes. The effects of this type of secondary alteration have been noted by a variety of authors (Bailey et al., 1973; Bailey et al., 1974; Evans et al., 1971; Deroo et al., 1977; Jobson et al., 1979; Connan, 1984; Rowland, 1986; Kvenvolden et al., 1993).

Biological marker compounds such as steranes, triterpanes, and hopanes are very resistant to biodegradation because they are complex cyclic structures in the HMW range. It is difficult for the bacteria to attack these compounds and cleave the carbon to carbon bonds. This resistancy of the biomarkers makes them useful for correlation of oils (Seifert et al., 1984; Chosson, et al., 1991; Cassani and Eglinton, 1991) that have undergone secondary alteration. However, if petroleum is highly degraded, even some biological marker compounds can be removed.

3.5.2 Water-washing

Water-washing often occurs near the surface. Formation waters, that are undersaturated with hydrocarbons and move along the oil to water interface, selectively extract hydrocarbons changing the composition of the remaining oil (Bailey et al., 1973; Evans et al., 1974; Price, 1976; Deroo et al., 1977; Dickey et al., 1987; Lafargue and Barker, 1988).

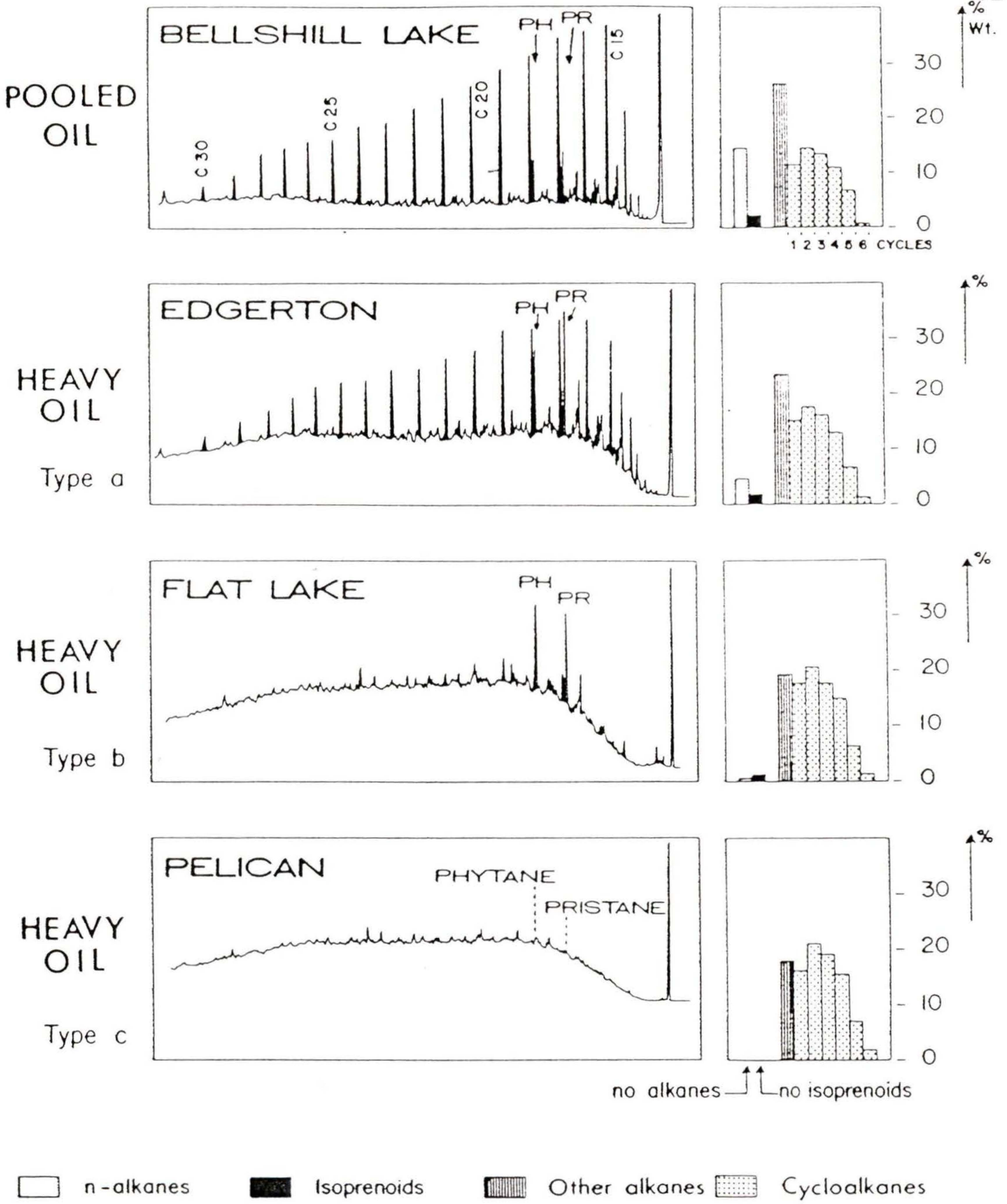


Figure 3.11 Compositional changes due to biodegradation in the Western Canada Sedimentary Basin oils (Deroo et al., 1974).

The susceptibility of hydrocarbons depends on their solubilities in water (or in oil) (see Figure 3.12 and Table 3.4). In general, light hydrocarbons are more affected than heavier hydrocarbons (Price, 1976). The light aromatics, such as toluene and benzene, are more susceptible than straight chain, branched, or cyclic alkanes. The heavy n-alkanes are the most resistant to water-washing. The solubilities of hydrocarbons increase with increasing temperature (Table 3.4). The solubilities of the more insoluble compounds increase at a greater rate as a function of temperature than the more soluble compounds.

Lafargue and Barker (1988) water-washed crude oils from Venezuela, Oklahoma, and New Mexico in the laboratory. They found that the C_{15-} fraction was particularly susceptible to water-washing and that compounds were removed in the following order: aromatics, n-alkanes, and naphthenes. They also found that if temperature (e.g., > 80 °C) was sufficiently high to inhibit microbial activity but not to promote thermal cracking and dissolved oxygen was low, water-washing could become dominant.

3.5.3 De-asphalting

A process called de-asphalting can also alter petroleum (Bailey et al., 1974; Tissot and Welte, 1978). When large amounts of gas either from thermal alteration of oil or external gas injection from secondary migration dissolve in heavy to medium oils, the asphaltenes precipitate resulting in a lighter oil. Bailey et al. (1974) observed de-

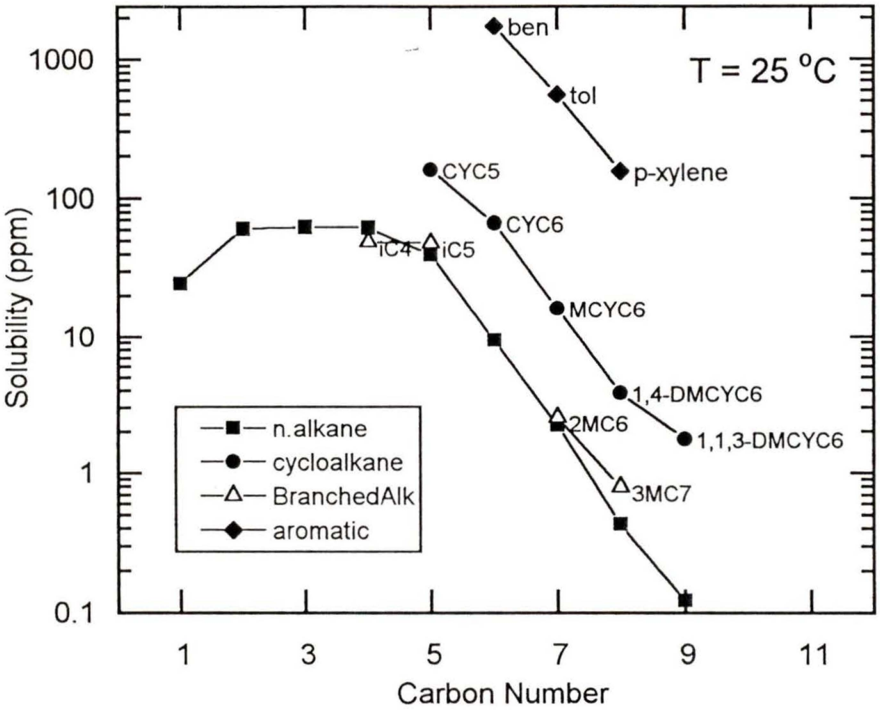


Figure 3.12 Solubilities of individual hydrocarbons in water at 25 °C. The solubilities are given in parts per million (ppm) on a weight basis.

Table 3.4. Aqueous solubilites of selected petroleum compounds at 25 and 100 °C in parts per million (ppm) (or weight/weight) taken from Price (1973 and 1976) and Yaws et al. (1993).

Compound	**Aqueous Solubilities (ppm)** **(25 °C)**	**(100 °C)**
methane	24.4 ± 1	
ethane	60.4 ± 1.3	
propane	62.4 ± 2.1	
n-butane	61.4 ± 2.1	
n-pentane	39.5 ± 0.6	79.12
n-hexane	9.47 ± 0.2	24.12
n-heptane	2.24 ± 0.04	7.178
n-octane	0.431 ± 0.012	2.156
isobutane	48.9 ± 2.1	
isopentane	48 ± 1.0	98.87
2-methylhexane	2.54 ± 0.2	9.588
3-methylheptane	0.792 ± 0.028	3.12
cyclopentane	160 ± 2.0	611
cyclohexane	66.5 ± 0.8	
methylcyclohexane	16 ± 0.2	
1,trans-4-dimethyl-cyclohexane	3.84 ± 0.17	
1,1,3-trimethyl-cyclohexane	1.77 ± 0.05	
benzene	1740 ± 17.0	
toluene	554 ± 15.0	
p-xylene	157 ± 1.0	

asphalting in reef areas of Alberta. Since thermal maturation and de-asphalting are often synchronous, it is difficult to differentiate their effects.

3.5.4 Identification of Secondary Alteration

3.5.4.1 Bulk Sample

Although bulk measurements are not very specific, they do provide some useful information regarding oil quality. From a variety of alteration studies, it has been shown that sulfur content and density increase as an oil becomes more degraded or water-washed (Bailey et al., 1973; Cassani and Eglinton, 1991). These two processes cause the removal of lighter compounds (e.g., n-alkanes), leaving the heavier ones (e.g., aromatics or NSO compounds) behind. For example, the heavily biodegraded oils of the Athabasca Tar Sands in Alberta have very low °API values (e.g., < 10), a high sulphur content (e.g., > 5 %), and a high percentage of resins and asphaltenes (45 to 50 %) (Erdman, 1962; Cassani and Eglinton, 1991).

3.5.4.2 C_{15+} Fraction

The general compound distribution in the saturate fraction gas chromatograms can provide a rough estimate of biodegradation in oil samples. However, often biomarker information is more specific and reliable.

A prominent feature of the C_{15+} chromatograms of many biodegraded Canadian oils is a hump of unresolved compounds (also called 'naphthene envelope') in low, subequal concentrations. This unresolved complex mixture (UCM) may be due to biodegradation or maturity. If the oil is biodegraded, the n-alkanes are preferentially removed and the complex mixture of unresolved compounds at the baseline undergo a relative amplification effect to produce the UCM.

However, low maturity in oils may result in several humps of UCM (e.g., sesquiterpanes eluting near nC_{17}, diterpanes near nC_{21}, and steranes and triterpanes near nC_{28}) (Snowdon and Fowler, Course Notes, 1991). When maturity increases, the UCM breaks down and eventually disappears as the compounds are cracked into smaller fragments.

The peaks in the gas chromatograms that are distinct despite the biodegradation are the more resistant biomarkers such as hopane, pristane (Pr), or phytane (Ph). The ratios of nC_{18}/Ph and nC_{17}/Pr have also been used to indicate biodegradation (Osadetz et al., 1992). For example, samples with ratios of nC_{18}/Ph less than 1.1 and nC_{17}/Pr less than 1.4 have been classified as biodegraded in Saskatchewan oils. However, it should be noted that low maturity can also yield low alkane/isoprenoid ratios. For samples with high biodegradation, the ratio of Pr/hopane can be used to identify the amount of biodegradation and to correlate the oil (Brooks et al., 1988). Since the triaromatic steranes are the most resistant biomarkers, they are the best compounds to use for the correlation of extremely biodegraded oils (e.g., Seifert and Moldowan, 1984; Chossen et al., 1991; Cassani and Eglinton, 1991).

In this study, the compound distributions in the C_{15+} saturate fraction gas chromatograms as well as biomarker data from other studies (e.g., Snowdon and Powell, 1979; Snowdon and Osadetz, 1988; Osadetz et al., 1994) are used to aid in the estimation of the amount of biodegradation Canadian oils (e.g., ranking of the samples from least to most degraded; Table 3.5).

3.5.4.3 Gasoline (C_5 to C_{10}) Fraction

Degradation processes are often first detected in the gasoline range hydrocarbons because their relatively simple structures (as compared to the HMW compounds) are easier for the microbes to attack. (see section on Molecular effects of secondary alteration). Simple observation of the molecular distribution, as determined from chromatograms, provides important information. Non-biodegraded oils will show an n-alkane predominance. Biodegradation generally results in a decrease of the n-alkanes with the more resistant branched and cyclic alkanes becoming more dominant (Bailey et al., 1973; Deroo et al., 1977; Rowland, et al., 1986; Osadetz et al., 1994). In oils that are water-washed, aromatic compounds such as benzene and toluene are expected to be reduced or absent. It should be noted that other factors such as maturity and source type may affect the observed molecular distribution.

Several authors have calculated parameters from gasoline hydrocarbon concentrations to yield information about secondary alteration effects (see section 3.2.4 for calculations). The two paraffin indices (PI1 and PI2) developed by Thompson (1979,

Table 3.5. Levels of biodegradation in Canadian oil samples. The symbol '-' represents no biodegradation while '+++' represents extreme biodegradation. Note: o = oil, c = condensate, s = source

Sample #	**Well Name**	**Notes**	**Depth (m)**
East Coast Oils		**Biodegradation Ranking/Notes**	
455	Mara M-54 DST#3	++	1851.5-1857
454	Mara M-54 DST#2	+	2403-2408.5
453	Mara M-54 DST#1	+	2704-2708.5
248	Hebron I-13 DST#10	++	1866-1876
249	Hebron I-13 DST#9	++	1905-1915
250	Hebron I-13 DST#7	+	2923-2940
247	Hebron I-13 DST#6	+	2974.8-2986
246	Hebron I-13 DST#5	+	3842-3857
245	Hebron I-13 DST#1	-	4368-4381
431	Hibernia C-96 DST#5	-	3784-3787
429	Hibernia C-96 DST#3	-	3869-3875
428	Hibernia C-96 DST#2	-	3940-3946
266	Hibernia K-18 DST#11	-	2313-2330
263	Hibernia K-18 DST#8	-/mature	3120-3135
251	Hibernia K-18 DST#1	-/mature	3850-3859
Alberta Oils			
970	Turner Valley	high matur.	2203-2353
914	Willesden Green		
703	Shekilie	euxinic s.	
205	Rainbow	euxinic s.	
1439	Chester	lab oil std.	2540-2574

Table 3.5. Levels of biodegradation in Canadian oil samples, continued.

Sample #	Well Name	Biodegradation Ranking	Depth (m)
Arctic Oils and Condensates			
309	Nerlerk M-98 DST#9	+	3055-3070
311	Nerlerk M-98 DST#8	+	3135-3172
312	Nerlerk M-98 DST#7	++	3265-3297
1626	Nerlerk M-98 DST#6	++	3435.2-3490.6
1625	Nerlerk M-98 DST#5	+++	3470-3490
310	Nerlerk M-98 DST#4A	+++	
Niglintgak	**M-19**		
33	DST#22	o+++	1324.4-1330.5
69	DST#20	o++	1385.9-1392
70	DST#19	c++	1721.2-1727.3
34	DST#16	o++	1746.5-1752.6
71	DST#14	c++	1845.6-1851.7
72	DST#13	c+	1862.31868.4
37	DST#10	o+	2106.2-2116.8
74	DST#9	o+	2174.8-2180.8
75	Niglintgak B-19 DST#14	o++	1595.3
1263	Amauligak O-86 DST#3	biodeg/terr.	2845-2853
Saskatchewan Oils			
FAMILY C:			
675	Battrum U1	++	888.6-892.6
733	Cantuar Main	+	961.3-969.3
677	Butte	+	1340-1352
726	Battle Creek	++	1385-1386.8
FAMILY E:			
833	Hearts Hill	++	758.3-763.5
836	Buffalo Coulee B	+++	799.5-801.3
829	Cactus Lake	+++	813-825
817	North Hoosier	++	831.8-836.3
822	Court	+	860-866
FAMILY F:			
812	Plato	++	645.9-647.7
821	Kerrobert	-	693-698
818	South Eureka	-	709.2
826	Forgan	+	732-740
816	Smiley	++	747.4-755
FAMILY A			
550	Lake Alma	-	3061.5

1983) have been used to assess both maturity and biodegradation. Thompson found that PI1 and PI2 increase during catagenesis (with increasing maturity). He identified class boundaries for oils as follows: biodegraded (HV = 0-18, PI1 = 0-0.8), normal (HV = 18-22, PI1 = 0.8-1.2), mature (HV = 22-30, PI1 = 1.2-2), and overmature (HV = 30-60, PI1 = 2-4). Thompson (1983) also used iC_5/nC_5 and $3MC_5/nC_6$ ratios to identify maturity or biodegradation. These ratios decrease with increasing maturity since cracking reactions occur which increase the amount of shorter chain n-alkanes. The values increase with increasing biodegradation since bacteria preferentially remove the n-alkanes, leaving behind the more resistant branched and cyclic alkanes. Oils with values greater than one for both ratios are thought to be biodegraded.

A set of parameters to show water-washing in samples is $3MC_5$/benzene and CYC_6/benzene (Thompson, 1983). The aromatic compounds are removed from or present in very low amounts in water-washed samples, and therefore high values for these ratios are expected. Thompson (1988) believed that oils are often vaporized in reservoirs. For this reason, he used the ratios toluene/nC_7 (aromaticity) and $nC_7/MCYC_6$ (paraffinicity) to identify evaporative fractionation in oils. The paraffinicity index decreases and the aromaticity index increases with increasing vaporization. Osadetz et al. (1994) have used gasoline range parameters to identify water-washing in oil samples from Saskatchewan..

All of the gasoline range parameters described in this section are calculated for the Canadian oils in this study (see Discussion). The combination of C_{15+} and gasoline range molecular analyses can provide information regarding secondary alteration. Since the molecular composition of an oil changes with increasing alteration, molecular techniques are not effective in identifying sources of altered oils (unless the alteration is very weak).

3.6 ISOTOPE EFFECTS OF SECONDARY ALTERATION OF OILS

The secondary processes such as biodegradation and water-washing which affect the molecular composition of oil also may have an effect on stable carbon isotopes. There are several reasons why one would not expect a large change (e.g., > 2 ‰) in isotopic composition (or isotope effect) with increasing alteration in the gasoline range hydrocarbons. These will be illustrated in the discussion section. The information in the following section summarizes the alteration processes as applied to isotope analysis and some of the work completed by others which supports the idea of a limited effect on the carbon isotopes of petroleum due to secondary alteration. There has only been limited research dealing with the isotope effects of alteration on individual hydrocarbons, especially those in the gasoline range. This is one area where more work was required.

3.6.1 Biodegradation

Microbes, as previously noted, preferentially attack the n-alkanes, causing a relative increase in the asphalts and NSO compounds. Any isotope effects associated with this process are due to differences in binding energies (as shown earlier) of the hydrocarbons being subjected to the bacterial oxidation (Stahl, 1977), resulting in the preferential breakage of a ^{12}C-^{12}C bond as compared to a ^{13}C-^{12}C bond (e.g., residual enriched in ^{13}C). Several researchers have suggested that the isotope effect associated with biodegradation is small (Galimov, 1973; Hunt, 1979; Stahl, 1980; Sofer, 1984).

For example, Stahl (1980) conducted a laboratory experiment where hydrocarbons were degraded in a closed system. The initial CO_2 in the degradation chamber had a typical isotope ratio of CO_2 derived from marine bicarbonate. As the experiment proceeded, the isotope ratio of the CO_2 became more enriched in ^{12}C. The isotope ratio of the residual saturate fraction shifted about 0.8 ‰ while the aromatic fraction did not show any shift in isotopic composition.

Sofer et al. (1986) examined 15 oils from the Cretaceous Vivian and Chonta formations in the Northern Peruvian Oriente Basin and found that the isotope effect associated with biodegradation for whole oils was less than 1 ‰. Schoell (1984) suggested that only heavily biodegraded oils may show any isotope variations. Sofer et al. (1991) performed a compound-specific isotope study of C_{12} to C_{32} n-alkanes of oils from the Congo Basin and the North Viking Graben. The North Viking oils all had similar individual carbon isotope ratios and were grouped together even though one of the oils was biodegraded. This suggests that biodegradation does not have a significant impact on individual isotopes. Since the effect of biodegradation on isotopes seemed to be low, many authors believed that stable carbon isotopes would be useful in the correlation of oils affected by biodegradation.

Since biomarkers are resistant to biodegradation and are derived from precursor biological compounds, they are often isotopically measured for correlation purposes. The isotope ratios do not change due to secondary alteration so the oils can be correlated to their sources (Wehner et al., 1985; Peters and Moldowan, 1991; Schoell, et al., 1992).

3.6.2 Water-washing

Water-washing causes the removal of the more soluble hydrocarbons (e.g., benzene and toluene) from an oil (and can transport them to a reservoir). An isotope effect may occur as the hydrocarbons dissolve in water since isotopically light compounds dissolve faster than the isotopically heavy compounds (e.g., enriched in ^{13}C). Any change in the isotopic composition of oils affected by this process may also result from the preferential removal of more soluble compounds that are enriched in ^{13}C. The removal of these isotopically heavy compounds may leave the residual oil more enriched in the light isotope. Palmer (1984) observed that water-washing depleted the ^{13}C in alkanes by up to 2 ‰. She found no isotopic change in the aromatic fraction despite its preferential removal because of its relatively high solubility in water.

3.6.3 De-asphalting

Any change in the isotopic composition of an oil from de-asphalting results from the removal of the asphaltenes which are enriched in ^{13}C. The residual petroleum can become enriched in the light isotope (^{12}C). It is possible that there is an isotope effect associated with the condensing of the asphaltene molecule as it is precipitated. However, de-asphalting is not as dominant as biodegradation or water-washing, and the effects of this process have not been well documented.

CHAPTER 4. GEOLOGICAL AND GEOCHEMICAL SETTING

The four regions selected for this study were the Jeanne d'Arc Basin (offshore Newfoundland), Beaufort-Mackenzie Basin (Canadian Arctic), and the Canadian portion of the Western Canada Sedimentary Basin including the Williston Basin (southwest/ southeast Saskatchewan) and the Alberta Basin (Figure 4.1, Table 4.1, Appendix A). They were chosen for two main reasons. Firstly, these areas undergo much exploration, the oils from these areas have been extensively analyzed, and many of the producing formations and sources have already been documented. Secondly, these oils have different sources, ages (Ordovician to Tertiary), and compositions and have been differentially affected by processes such as biodegradation (nil to extensive) and maturation (low to high). The following summaries highlight some of the research completed in the sample areas used in this study and some of the variations that can be can be expected in the oils.

4.1 JEANNE D'ARC BASIN, OFFSHORE NEWFOUNDLAND, EAST COAST OF CANADA

Samples from this area are located in the Jeanne d'Arc Basin in the northeastern portion of the Grand Banks, offshore Newfoundland (Figure 4.2). The basin is bound to the west by the listric Murre Fault, to the east by the Central Ridge, and to the north and

Figure 4.1 Map of Canada indicating the four regional sample locations. '**X**' represents the provinces from which samples were collected.

Table 4.1. Location, depths, biodegradation indices, and other notes for the oil and condensate samples. Note: o = oil, c = condensate, s = source.

Sample #	Well Name	Notes	Depth (m)	Reservoir Location
East Coast Oils		**Biodegradation Ranking/Notes**		
455	Mara M-54 DST#3	++	1851.5-1857	Banquereau Fm.
454	Mara M-54 DST#2	+	2403-2408.5	Dawson Canyon Fm.
453	Mara M-54 DST#1	+	2704-2708.5	
248	Hebron I-13 DST#10	++	1866-1876	Avalon/Ben Nevis Fm.
249	Hebron I-13 DST#9	++	1905-1915	
250	Hebron I-13 DST#7	+	2923-2940	Hibernia Formation
247	Hebron I-13 DST#6	+	2974.8-2986	
246	Hebron I-13 DST#5	+	3842-3857	Jeanne d'Arc Formation
245	Hebron I-13 DST#1	-	4368-4381	
431	Hibernia C-96 DST#5	-	3784-3787	
429	Hibernia C-96 DST#3	-	3869-3875	
428	Hibernia C-96 DST#2	-	3940-3946	
266	Hibernia K-18 DST#11	-	2313-2330	Avalon Fm.
263	Hibernia K-18 DST#8	-/mature	3120-3135	Catalina Fm.
251	Hibernia K-18 DST#1	-/mature	3850-3859	Hibernia Fm.
Alberta Oils				
970	Turner Valley	high matur.	2203-2353	Foothills, Rundle Gp.
914	Willesden Green			Cardium Fm.
703	Shekilie	euxinic s.		Upper Keg River Fm.
205	Rainbow	euxinic s.		Keg River Fm.
1439	Chester	lab oil std.	2540-2574	Okotoks,Wabamun B Gp.

Table 4.1. Location, depths, indices, and other notes, continued.

Sample #	Well Name	Biodegrad Ranking	Depth (m)	Reservoir Location
Arctic Oils and Condensates				
309	Nerlerk M-98 DST#9	+	3055-3070	Akpak Formation
311	Nerlerk M-98 DST#8	+	3135-3172	Kugmallit Formation
312	Nerlerk M-98 DST#7	++	3265-3297	
1626	Nerlerk M-98 DST#6	++	3435.2-3490.6	
1625	Nerlerk M-98 DST#5	+++	3470-3490	Kugmallit Formation
310	Nerlerk M-98 DST#4A	+++		
Niglintgak	**M-19**			
33	DST#22	o+++	1324.4-1330.5	Taglu Seq of Reindeer Fm
69	DST#20	o++	1385.9-1392	"
70	DST#19	c++	1721.2-1727.3	"
34	DST#16	o++	1746.5-1752.6	"
71	DST#14	c++	1845.6-1851.7	"
72	DST#13	c+	1862.31868.4	"
37	DST#10	o+	2106.2-2116.8	"
74	DST#9	o+	2174.8-2180.8	"
75	Niglintgak B-19 DST#14	o++	1595.3	"
1263	Amauligak O-86 DST#3	biodeg/terr.	2845-2853	Kugmallit Sequence
Saskatchewan Oils				
FAMILY C:				
675	Battrum U1	++	888.6-892.6	Rosery
733	Cantuar Main	+	961.3-969.3	Cantuar
677	Butte	+	1340-1352	Upper Shaunavon
726	Battle Creek	++	1385-1386.8	Madison
FAMILY E:				
833	Hearts Hill	++	758.3-763.5	Bakken
836	Buffalo Coulee B	+++	799.5-801.3	Bakken
829	Cactus Lake	+++	813-825	Bakken
817	North Hoosier	++	831.8-836.3	Bakken
822	Court	+	860-866	Bakken
FAMILY F:				
812	Plato	++	645.9-647.7	Viking
821	Kerrobert	-	693-698	Viking
818	South Eureka	-	709.2	Viking
826	Forgan	+	732-740	Viking
816	Smiley	++	747.4-755	Viking
FAMILY A				
550	Lake Alma	-	3061.5	Bighorn Gp., Herald Fm.

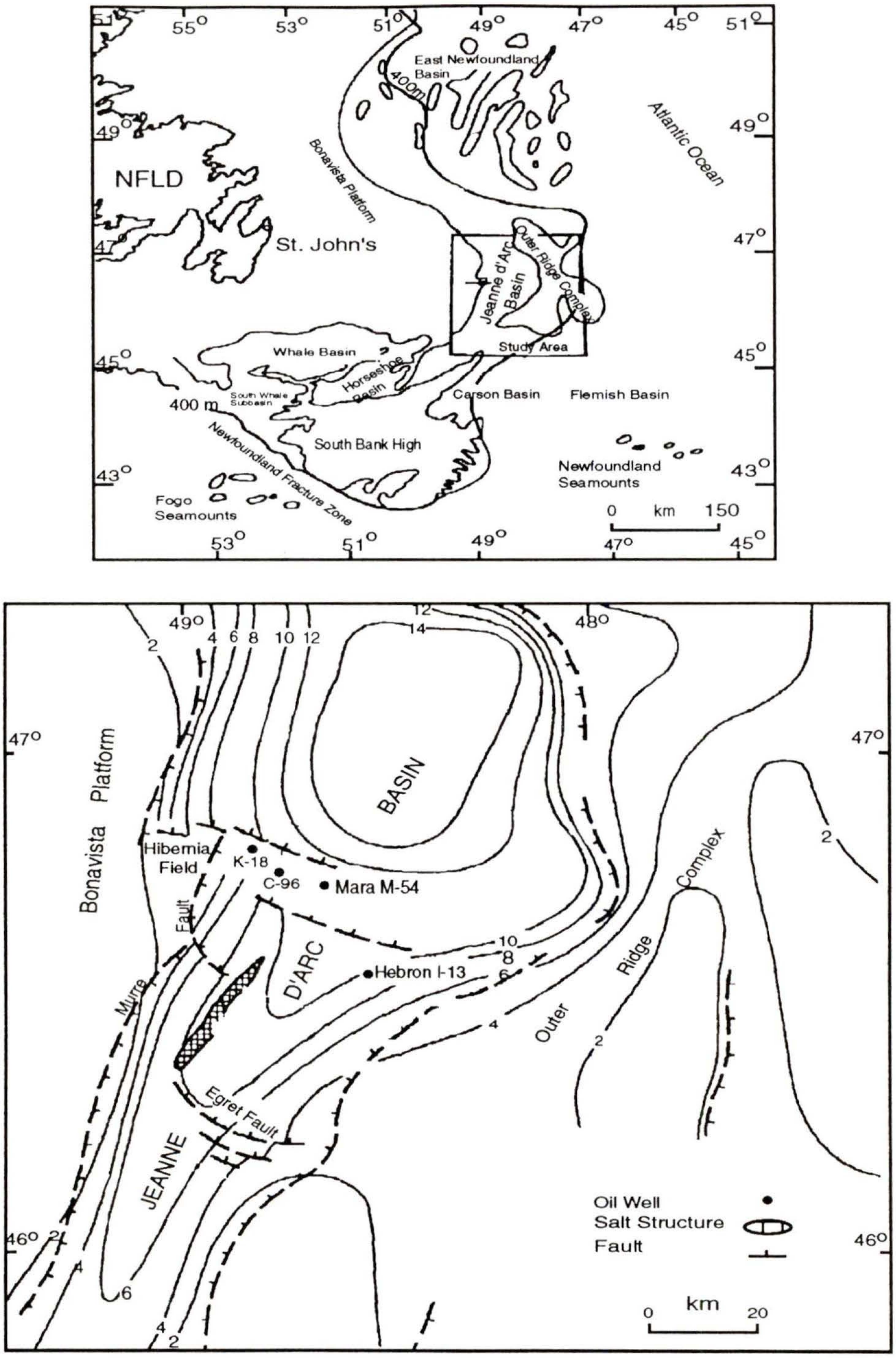


Figure 4.2 Location of oil samples from the Jeanne d'Arc Basin, East Coast of Canada.

south by structural highs. The Jeanne d'Arc Basin is the most northern basin in a series of elongate, narrow, NE trending basins (Sinclair et al., 1992).

Two periods of rifting were very important in sediment deposition (Figure 4.3). The first occurred during the Late Triassic to Early Jurassic and resulted in evaporite deposition. The second occurred during Late Jurassic and Neocomian, resulting in the deposition of coarse clastics. These two rift periods were separated by a tectonically quiet period in the Middle Jurassic when fine clastics and limestones were laid down. It was during this time that the source rocks, for much of the oil in the Jeanne d'Arc Basin, were deposited (McAlpine, 1990). The oil source rocks are believed to be organic rich shale of Kimmeridgian age from the Egret Formation, with its kerogen source composed mainly of dinoflagellate debris (Type II kerogen, Figure 3.1; see Tissot and Welte, 1978) (Swift and Williams, 1980; Creaney and Allinson, 1987; McAlpine, 1990; von der Dick et al., 1989). The shale unit has an average TOC content of 3 % and an initial H-index value between 500 to 800 mg/g TOC which are favorable for oil generation (von der Dick et al., 1989).

There are many faults associated with the Jeanne d'Arc Basin which define its shape and create the traps to hold hydrocarbons. After the continental breakup of shales deposited at the end of the tectonically quiet period, oil was generated. This is now trapped in stacked sandstone reservoirs that were deposited during the second rifting period.

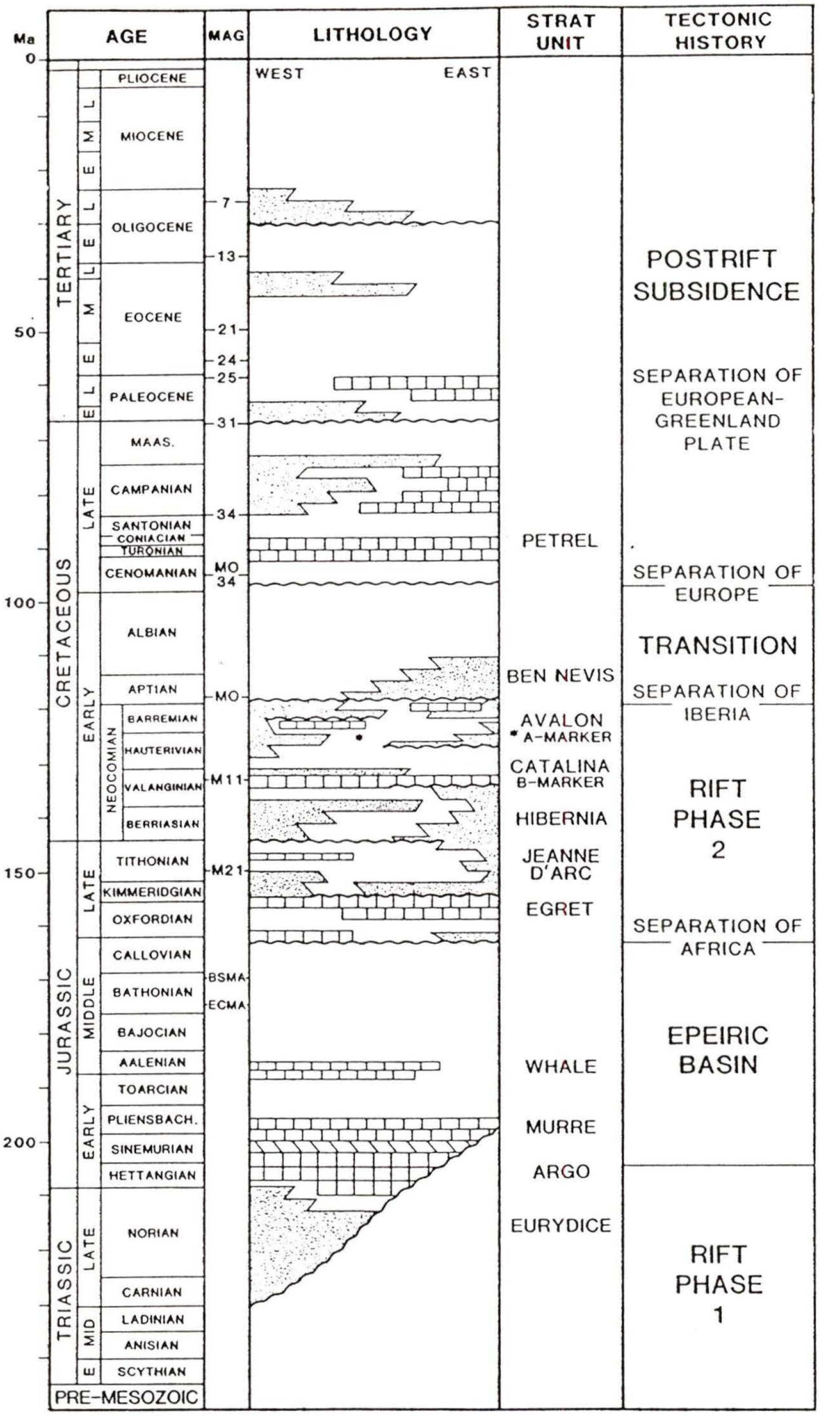


Figure 4.3 Stratigraphic column for the Jeanne d'Arc Basin, offshore Newfoundland (after Tankard and Welsink, 1987).

Potential oil in the Jeanne d'Arc Basin is estimated at 41 billion barrels (McAlpine, 1990). With a recovery factor of about 30 %, approximately 12.3 billion barrels could be recovered. The best estimate of discovered recoverable oil is approximately 1.2 billion barrels. Thus, as little as 10 % of the recoverable reserves have been discovered (McAlpine, 1990).

There have been 98 deep exploration wells drilled on the Grand Banks which includes 56 in the Jeanne d'Arc Basin by mid 1987. The wells chosen for this study are: (1) Hibernia K-18, (2) Hibernia C-96, (3) Hebron I-13, and (4) Mara M-54.

- **Hibernia** was the first huge field discovered by Chevron in 1979. It is located 300 kilometers east of St. John's and is suspected to contain up to one billion barrels of recoverable resources. Much of the oil from the Hibernia field in Cretaceous reservoirs has been capped by Tertiary shale which protects the oil from biodegradation. Since Hibernia oil is not degraded, its composition reflects the average composition of a typical marine-sourced oil, that is, it is a 'conventional' oil. There have been conflicting reports of the maturity of the basin. von der Dick et al. (1989) described the Hibernia oils as having mostly the same composition and maturity which could be interpreted as evidence of oil migration alongs fault from a single pulse of oil or at least the same source conditions. Fowler and Brooks (1990) examined maturity in the Hibernia K-18 well and found that all the reservoirs located at depths greater than 1570 meters could be explained by such oil migration along faults from a single expulsion event. However, in the lowest reservoirs, more mature hydrocarbons leak in from the underlying overpressured zone. These mature hydrocarbons do not reach the shallower reservoirs due to some fault closures in these areas.

- **Mara M-54** is located 7 kilometers southeast of Hibernia. Oil from this well is tarry and of low API gravity. The Mara M-54 DST#1 oil (2704 to 2708.8 m) has a low concentration of nC_{26} to nC_{38} hydrocarbons and a low gravity of 11 °API (von der Dick et al., 1989). Its chromatogram is similar to a Hibernia chromatogram, but n-alkanes above C_{25} of the Mara oil are reduced and the phytane peak is larger than the nC_{18} peak (typical of a biodegraded oil). von der Dick et al. (1989) have explained this as a two phase oil generation event. The first oil was probably a highly biodegraded Hibernia-type oil. The second oil, generated at a later time from the same source interval, was more mature, leading to a shortening of the n-alkanes to approximately nC_{25}. At shallower depths (e.g., 1852 m), the oils (DST#2 and #3) are undergoing continuous biodegradation with the removal of low and some medium molecular weight compounds (von der Dick et al., 1989).

- **Hebron I-13** is located 28 kilometers southeast of Hibernia. The Hebron structure is a horst and graben along the Trans-Basin Fault trend. These samples show moderate to intense biodegradation in shallow reservoirs where the shale cap rock has been faulted by later Tertiary tectonics. Snowdon and Krouse (1986) performed an isotope study of the distillation fractions of two Arctic oils and a Hebron oil. Although the Hebron oil was thought to be a marine-derived oil, the isotope ratios of the low boiling fractions indicated that there may be terrestrial source input (e.g., condensate of LMW with lighter isotope ratios than the HMW compounds in the sample) to the oil.

4.2 BEAUFORT-MACKENZIE BASIN, NORTHWEST TERRITORIES, CANADIAN ARCTIC

Samples from this area are located in the Beaufort-Mackenzie Basin (Figure 4.4) which underlies the Northern Yukon Territory, the present day Mackenzie Delta, and the Tuktoyaktuk Peninsula of the Northwest Territory as well as some offshore shelf regions of the Beaufort Sea (Snowdon, 1981). The area is geologically rather complex with structures capable of trapping hydrocarbons. For example, a major phase of folding created the 'Beaufort Fold Belt'. There is also an area of listric faults consisting of two major zones known as the Tarsiut-Amauligak and Taglu Fault Zones. Most of the faults have had several phases of episodic growth. The rollover anticlines and tilted fault blocks, which are associated with most of the faults, can act as traps for hydrocarbons.

Subsidence and sediment loading in the Beaufort-Mackenzie Basin occurred simultaneously with the opening of the Canadian Basin in the north and subsequent thermal subsidence (Enachascu, 1990). Upper Cretaceous to Tertiary sediments were deposited as three major deltaic pulses with one underlying and two intervening mudstone-shale sections representing transgressive marine tongues (Lerand, 1973).

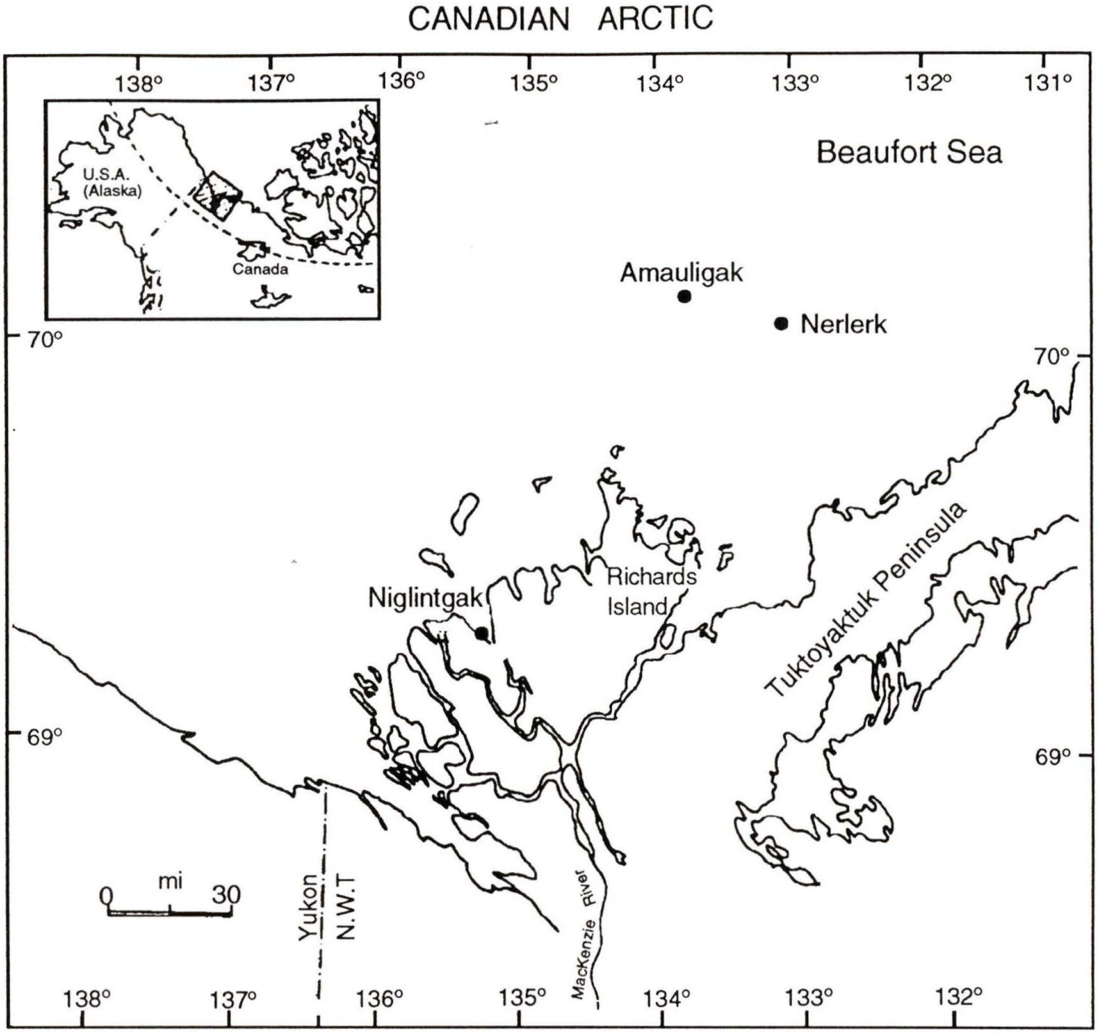


Figure 4.4 Location of oil samples from the Beaufort-Mackenzie Basin in the Canadian Arctic.

Snowdon (1978) published one of the first major reports describing the organic geochemistry of sediments from the upper Cretaceous/Tertiary delta complexes. He showed that these sediments are dominated by terrestrial organic matter (Type III kerogen; see Tissot and Welte, 1978) with low thermal maturity (e.g., between 0.5 to 0.7 % vitrinite reflectance (Ro); see Tissot and Welte, 1978) which is usually too low or only marginal sufficient for extensive oil production.

However, observation of other parameters reveals a good petroleum potential for the source rocks in the area (greater than 50 mg/g TOC). Some 'early stage' oils and condensates are produced from this Type III material (Snowdon, 1980 and 1991; Snowdon and Powell, 1982; Powell and Snowdon, 1983). Type III organic material, at levels of thermal maturity within the oil window (0.7 to 1.2 % Ro), usually contains less than the critical 30 to 50 mg/g TOC.

Due to the presence of diterpenoid compounds in the oils and condensates and resinite in kerogen smear slides, this 'good' petroleum potential was attributed to the presence of tree resins in the terrestrially derived organic matter (Snowdon, 1978 and 1991). A local mass balance calculation shows that substituting 10 % of Type I or II organic matter (e.g., resinite) is sufficient to raise the hydrocarbon yield from below 25 to 50 mg/g to 60 mg/g (Snowdon, 1991).

The Beaufort-Mackenzie Basin in the Canadian Arctic has been drilled with success despite the difficulties associated with such an endeavor (e.g., politics and weather conditions-ice, expense). More than 170 wells have been drilled and 42 oil and gas fields discovered thus far (Enachescu, 1990). The resources for this region are estimated at 9 billion barrels of oil and 112 trillion cubic feet of gas (Norris, 1985). The recoverable portion of this is estimated at 1.5 billion barrels of oil and 11 trillion cubic feet of gas (Trigueiro, 1989). Most of the oil, gas, and condensate discoveries have occurred in Lower Cretaceous and Tertiary reservoirs.

The four oil wells from the Arctic to be examined in this study are: (1) Niglintgak M-19, (2) Niglintgak B-19, (3) Nerlerk M-98, and (4) Amauligak O-86. These fields represent series of stacked reservoirs which provided samples of varying degrees of biodegradation.

- **Niglintgak** oils and condensates are found in the Taglu Sequence of the Reindeer Supersequence (Figure 4.5) which is Upper Paleocene to Middle Eocene in age (Snowdon and Powell, 1979). They are southerly located in the Richards Island area (Figure 4.3). The Taglu Sequence (lower to middle Eocene) consists mainly of interbedded sandstone and shale successions. Significant amounts of oil and gas have been found in coarsening upwards cycles of lower prodelta shales grading upward into sandstone-dominant delta front and lower delta-plain beds.

The Niglintgak field contains biodegraded oils less than 1 km below the Kugmallit unconformity (a prominent Tertiary erosional event). The biodegradation may be associated with this erosional event. In this case, hydrocarbon generation and migration must have occurred before the Kugmallit sequence was deposited.

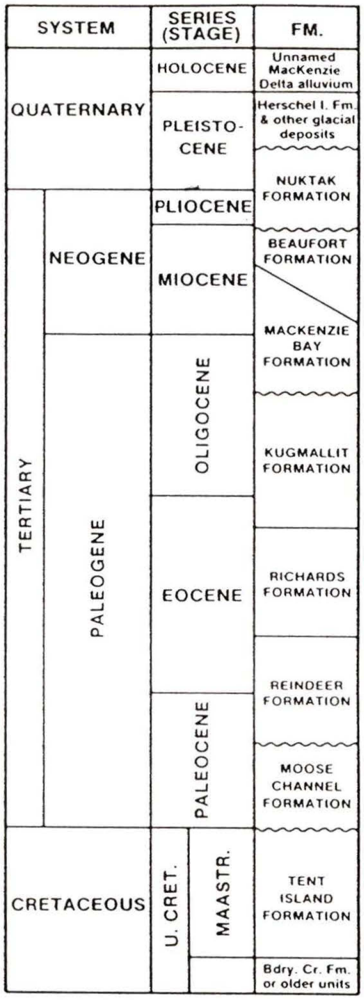


Figure 4.5 Stratigraphic column for the Beaufort-Mackenzie Basin, Canadian Arctic (after Curiale, 1991).

- **Nerlerk M-98** oil and gas are found in the north in the Kugmallit Sequence (Oligocene; Figure 4.5). This sequence consists mainly of shale, but there are some significant sandstone-rich intervals within the submarine-fan deposit which contain hydrocarbons. North of the Tarsiut-Amauligak fault zone, Kugmallit deep water sandstones are found in the long, broad anticlines of the Beaufort Fold Belt which act as stratigraphic traps. Reservoir facies here are usually isolated sandstone bodies encased in shale (Dixon et al., 1992).

Much of the offshore Nerlerk oil was found in rocks younger than the Kugmallit unconformity. These oils must have been emplaced after the Richards Island reserves. Some of the shallowest oils are not biodegraded while some of the deepest oils have been partially or highly biodegraded. The two deeper reservoirs could have been filled and biodegraded at an earlier time. The younger and shallower reservoirs could have been filled with oil at a later time. Thus, this basin may have undergone several episodes of hydrocarbon migration (Snowdon, 1988).

- The **Amauligak** field is a fault-bounded structure in the Kugmallit Trough (Enachescu, 1990). It contains oil and gas in multiple sandstone reservoirs of the Oligocene Kugmallit sequence. The upper sandstones are cut by an unconformity and capped by overlying shale. The Amauligak O-86 sample examined in this study is a Tertiary, partially biodegraded condensate with a terrestrial source.

4.3 WILLISTON BASIN, SASKATCHEWAN, WESTERN CANADA

The Williston Basin (Figures 4.6, 4.7, and 4.8) extends through Montana, North Dakota, and Saskatchewan and is an integral part of the larger Western Canada Sedimentary Basin (Stasiuk et al., 1993). It is a Phanerozoic basin situated near the center of the North American craton. Complex stratigraphic and diagenetic traps for hydrocarbons, unconformity bound stratigraphic plays, and intrabasinal structures are found throughout the basin which are important in reservoir formation (Osadetz et al., 1990).

Five unconformity bound sequences make up the stratigraphic succession (Figure 4.7). The oldest material is a part of the marginal clastic belt of the Lower Paleozoic miogeocline of Western Canada (Deadwood Formation). This was followed by onlap of shallow marine clastics of the Winnipeg Formation and carbonates of marginal clastics and carbonate belts of Middle Ordovician to Silurian epeiric platform of eastern North America in the Bighorn and Interlake Groups. After the Taghanic onlap, a very conformable succession of middle Devonian to Carboniferous age was laid down. Deposition ended in the Carboniferous and a large erosion event occurred. In the Jurassic, sedimentation resumed and a succession of evaporites, carbonates, and clastics were deposited. This was overlain by Cretaceous and Cenozoic clastics deposited in the Cretaceous interior seaway and as molasse from the Western Cordillera (Brooks et al., 1987; Osadetz et al., 1990).

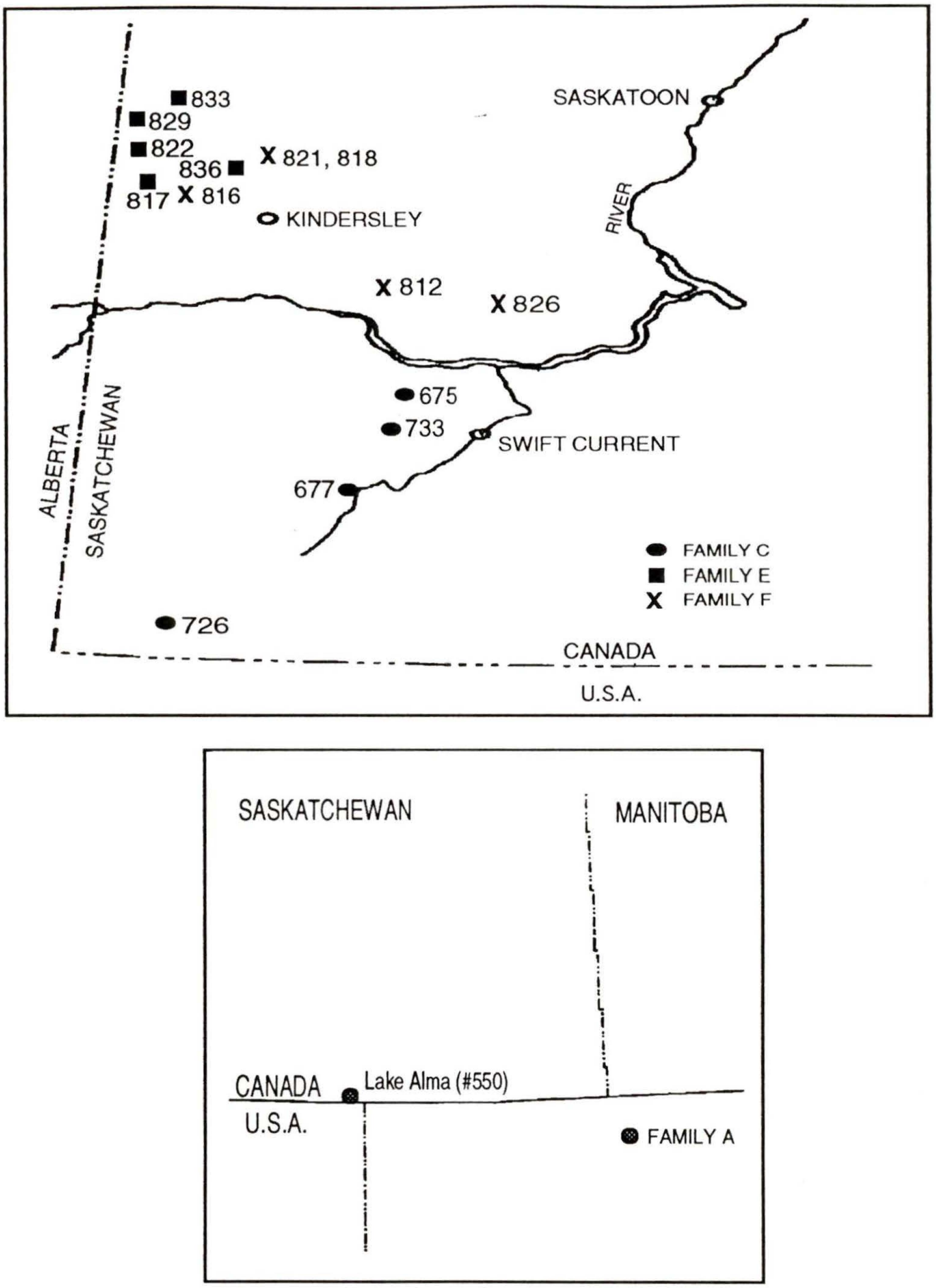


Figure 4.6 Location of Saskatchewan oil samples from the Williston Basin.

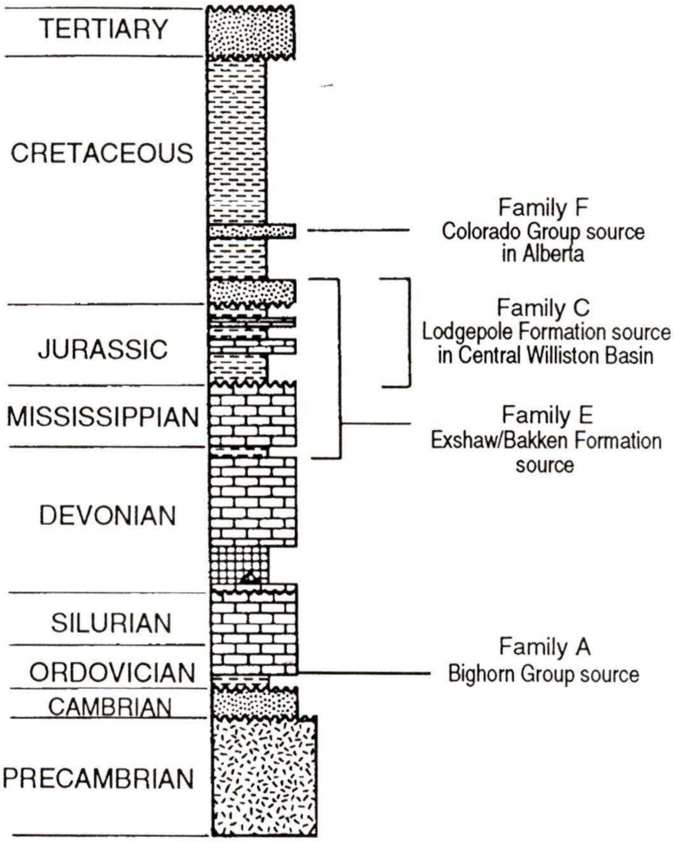


Figure 4.7 Stratigraphic column for the Williston Basin, Saskatchewan (Osadetz et al., 1994).

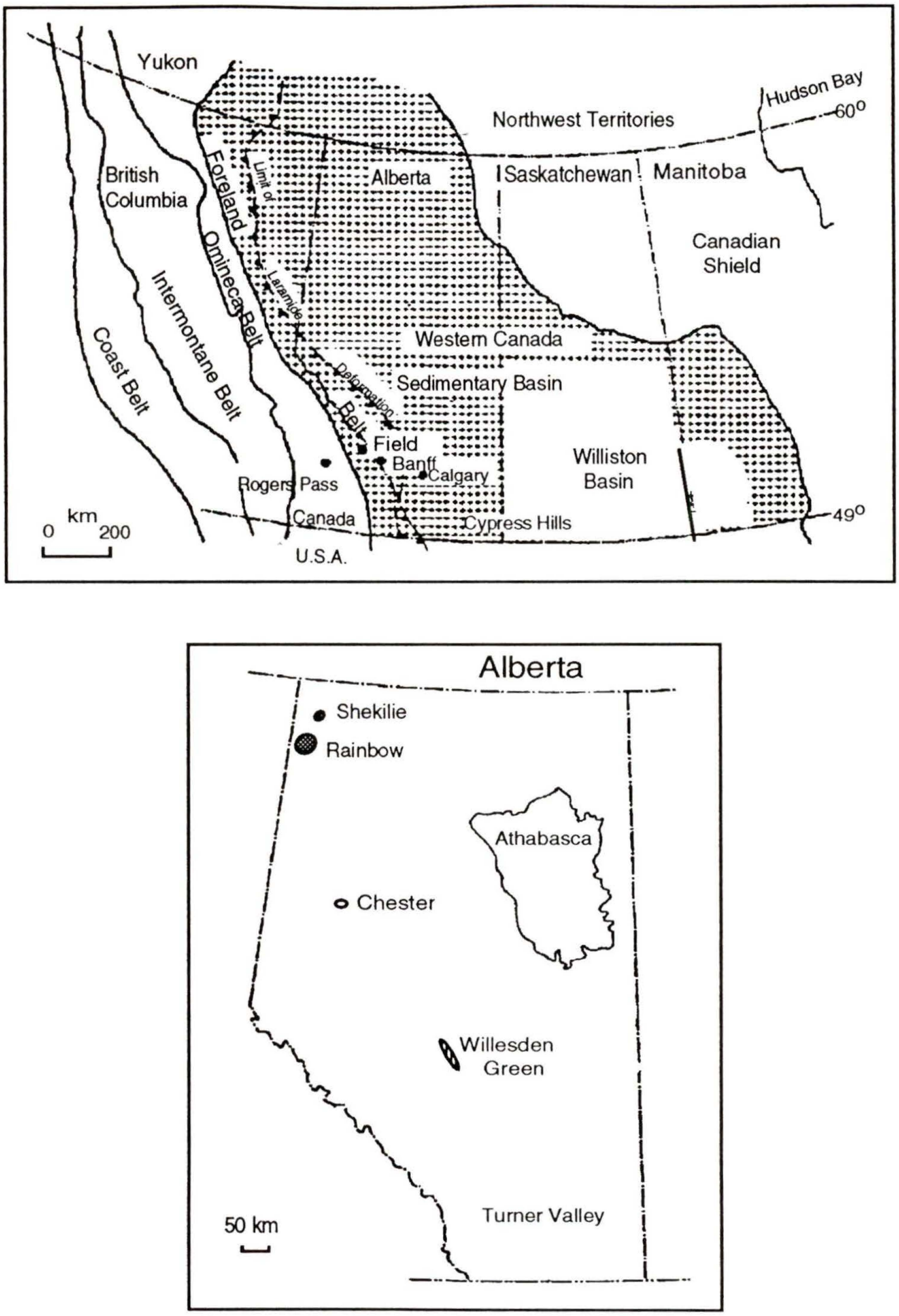


Figure 4.8 Location of the Western Canada Sedimentary Basin and the contained Williston Basin. The location of the Alberta oils are specified in the lower diagram.

In the Canadian portion of the Williston Basin, the first oil was discovered in 1951 at Daly, Manitoba (McCabe, 1963). Exploration then spread to Saskatchewan. Initial recoverable reserves were estimated at approximately 1.4 billion barrels.

The southeastern portion of Saskatchewan has been more extensively drilled than the southwestern. Different oil pools have been assigned to different sources. Bakken pools were thought to originate in Manville shales (Reasoner and Hunt, 1954). Other authors thought that Bakken oils had a Bakken shale source and that Viking oils had a Colorado Group source (White, 1969). Most of the oil produced in the Williston Basin is thought to be from carbonate reservoirs ranging from Cambrian to Pennsylvanian in age (Leenheer and Zumberge, 1987). In southeast Saskatchewan and southwest Manitoba, four regionally significant Paleozoic source rocks were used to identify 4 oil families, including the Family A oil (Lake Alma) included in this study (Osadetz et al., 1992).

Evans et al. (1971), Jobson et al. (1972), and Bailey et al. (1973) noted oil quality variations in the Williston Basin that they attributed to biodegradation and water washing. Thode (1981) observed isotopic shifts accompanying density variations that were consistent with biodegradation. Allan and Creaney (1991) studied some Saskatchewan Manville and Viking pools. Osadetz et al. (1991, 1992) used newer oil to source rock correlation parameters and biodegradation resistant maturity parameters. They showed that the compositional variations noted in the oils of the Williston Basin were due to source and maturity.

Oils have been classified into slightly different families and groups by several authors (Williams, 1974; Leenheer and Zumberge, 1987; Zumberge, 1983; Brooks et al., 1987). Any classification of oils into families referred to in this study will be based on recent work by Osadetz et al. (1994) with the exception of the one southeast Saskatchewan sample (Lake Alma) (Osadetz, 1992).

Five oil samples from each of the Families C, E, and F are chosen for analysis as well as one sample from Family A in southeastern Saskatchewan (Table 4.1). Families C, E, and F (Figure 4.7) are all derived from Type II (mixed) organic matter sources whose initial oil quality depends on maturity (Osadetz et al., 1994) while the Family A oil has a Type I (algal) source (Osadetz, et al., 1992) .

- **Family F** oils are the highest maturity oils in western Saskatchewan and are found in Viking reservoirs. They are derived from Colorado Group sources more than 400 km to the west. These oils are differentially biodegraded and water washed, but the initial high maturity counteracts the effects.

- **Family E** oils are found in Bakken and Manville reservoirs. The source of these oils lies in either Bakken or Lodgepole formations in either northeast or central Montana. Initially, the oils were of medium gravity and expelled from low to moderate maturity sources. These are biodegraded and water-washed.

- **Family C** oils are found in oil pools of Mississippian, Jurassic, and Lower Cretaceous age. They are very similar to the low maturity Lodgepole-sourced oils in the northeastern portion of the Williston Basin and come from the central Williston Basin or the same region as Family E oils. These oils were expelled early and migrated in a northwest direction up the western side of the basin. Cross strata migration may have occurred in the Shaunavon Syncline before late Cretaceous and early Tertiary salt dissolution. The oils are water-washed and some are biodegraded. However, the medium gravity of these oils is most likely due to low to moderate maturity (Osadetz et al., 1994).

- **Family A** oils occur in Ordovician to middle Devonian strata (Osadetz et al., 1992; Jacobson et al., 1988; Kohm and Louden, 1982; Kendall, 1976) in *southeastern* Saskatchewan. Lake Alma, the oil chosen from this locality, is 'conventional' or non-degraded, medium to light crude. Its source is a marine Type I rock (a kukersite; kerogenous carbonate mudstone containing organic matter) from middle and upper Ordovician formations of the Bighorn Group.

4.4 WESTERN CANADA SEDIMENTARY BASIN, ALBERTA, WESTERN CANADA

The Western Canada Sedimentary Basin (Figures 4.8, 4.9) extends from eastern British Columbia and Alberta into Saskatchewan, southern Manitoba, and some of the

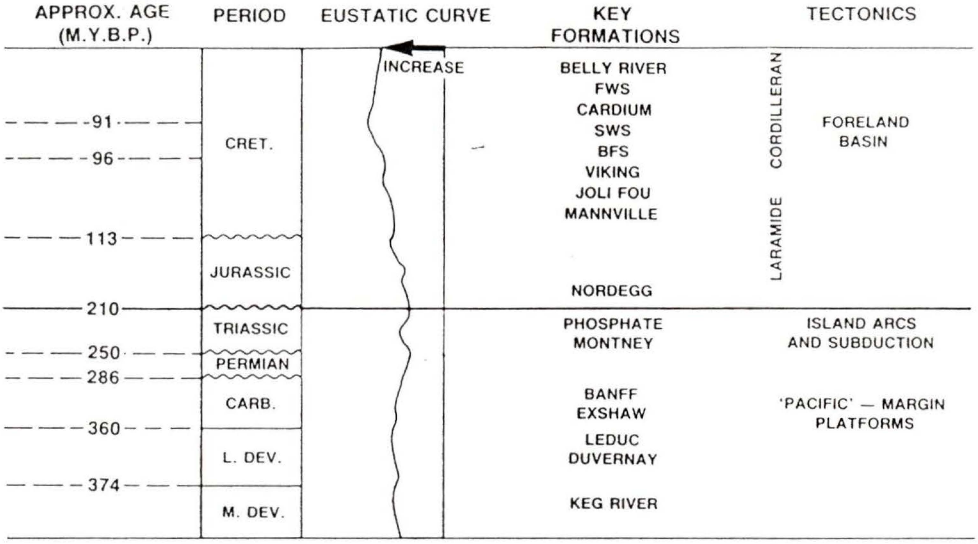


Figure 4.9 General stratigraphic column for the Western Canada Sedimentary Basin (after Creaney and Allan, 1990).

northern central states. It is an asymmetrical, synclinal basin bounded to the west by the Rocky Mountains and to the east by the Precambrian Shield (Porter et al., 1982). The preserved sediments are mixed carbonates and clastics which accumulated from the Tertiary through the Paleocene. The total sediment thickness today is approximately 6 kilometers.

This basin has undergone extensive exploration in the past 80 years (Allan and Creaney, 1991). It contains about 1.75 trillion barrels of crude oil in place. Only 2.5 % of the oil from this basin (approximately 41 billion barrels) is considered conventional. The remaining oil is very heavy, making up deposits such as the Athabasca Tar Sands.

The oils chosen from this basin are as follows: (1) Rainbow, (2) Shekilie, (3) Willesden Green, (4) Chester, and (5) Turner Valley (Table 4.1).

- The source for **Rainbow and Shekilie** oils is located in basinal areas of the Lower Keg River and Muskeg Formations of the Elk Point Group (Creaney and Allan, 1990). The sediment was deposited under anoxic, hypersaline conditions. Since there was a low siliciclastic influx, greater amounts of sulfur were incorporated into the kerogen. This source rock is immature through most of the basin, but, in Rainbow and Shekilie, it is fully mature.

  Although these two oils are similar chemically, there are subtle differences. The source rocks are restricted since they are located between pinnacle reefs and capped by shale or evaporites. This allows for local sourcing, leading to a progression of oil properties from low gravity and maturity oils at eastern locations (at the end of the Zama subbasin) to high gravity and maturity oils in the west.

- **Willesden Green** is found in Belly River sands and is sourced from late Cretaceous Colorado Shales. Oils derived from these shales have undergone secondary migration from the source area updip to stratigraphic traps (e.g., pinch-outs). Willesden Green is one of the least migrated oils (about 100 km). The system here is closed since it contains the source rock and no oils can be found that have migrated out of the section. The oils are high quality with low sulfur. All late Cretaceous oils can be identified by sterane assemblages. However, the hopane biomarkers of the Willesden Green oil have no unique characteristics and instead look like those of late Devonian oils (Creaney and Allan, 1991).

- **Chester** is a conventional, non-biodegraded oil from Alberta located in the Wabamun B group. It is the oil used as a laboratory standard in this study.

- **Turner Valley** is an oil found in the Permian Turner Valley Formation in southwest Alberta. It is unique from the other oils in that it has a very high maturity. Since it has such high maturity, even biomarker data can not be obtained. It may have a Devonian source (personal communication with Lloyd Snowdon).

CHAPTER 5. ANALYTICAL METHODOLOGY

5.1 SAMPLE COLLECTION

All of the oil samples are obtained from the library of oils stored at ISPG. Aliquots (approximately 10 ml) of the oil samples are transferred to small vials using Pasteur pipettes, sealed with an aluminum-foil covered cap, and shipped to the School of Earth and Ocean Sciences (SEOS) in Victoria for refrigerated storage. The wells and the corresponding oil or condensate samples chosen from the four study regions are included in Figure 4.1 and Table 4.1.

Usually, frontier basin oil samples (e.g., in Jeanne d'Arc Basin or the Beaufort-Mackenzie Basin) are collected using a drill stem test (DST) or a wireline. The DST technique replaces the drill bit with a testing tool. This apparatus is lowered into a well and oil samples collected at particular depths. A wire line tool is similar, but it is lowered into the well on a cable. The Alberta and Saskatchewan oils (more developed basin samples) are usually collected from wells that are in production. In this case, a container is carried to the well head via a pipe string where the valve is opened and closed to allow collection of oil samples.

The oils had already been collected and placed in storage at ISPG. Government regulations specify that companies drilling wells on federally controlled lands must send a sample of the oil (and drill cuttings or gas) to ISPG for cataloging. The advantage

Analytical Methodology

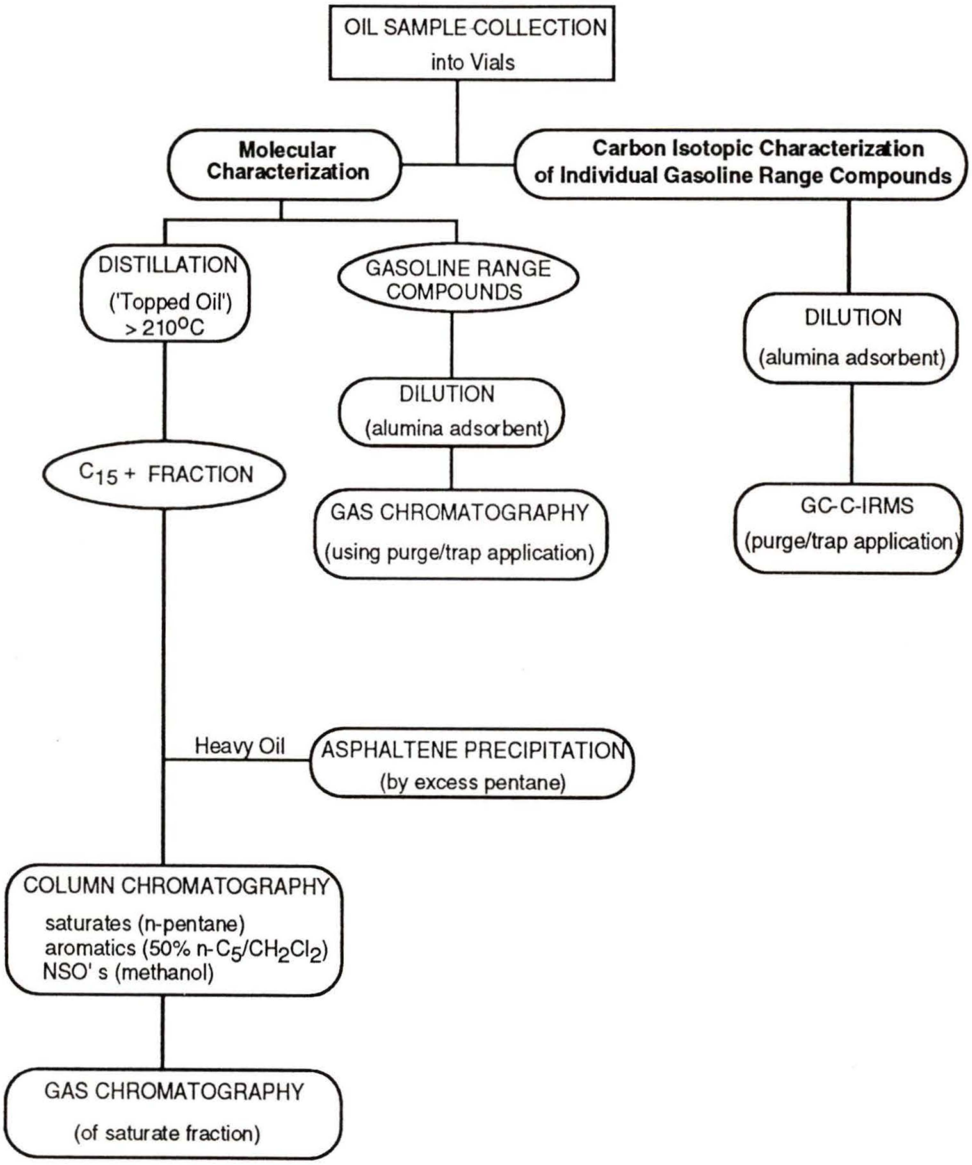


Figure 5.1 Flowchart for analytical methodology.

Table 5.1. Boiling and melting points for the selected hydrocarbons (CRC Handbook of Chemistry and Physics, 1992).

Compound Name	Abbreviation	Melting Point (^{0}C)	Boiling Point (^{0}C)	Phase at 25 ^{0}C
ethane	C2	-172	-89	***GAS***
propane	C3	-187.0	-42.0	
butane	C4	-135	-0.5	
isopentane	iC5	-159.9	27.8	***Liquid***
normal pentane	nC5	-130.0	36.1	
2,2-dimethylbutane	22DMC4	-99.9	49.7	
cyclopentane	CYC5	-93.9	49.2	
2,3-dimethylbutane	23DMC4	-128.5	58.0	
2-methylpentane	2MC5	-153.7	60.3	
3-methylpentane	3MC5		63.3	
normal hexane	nC6	-95.0	69.0	
methylcyclopentane	MCYC5	-142.4	71.8	
benzene	ben	5.5	80.1	
cyclohexane	CYC6	6.5	80.7	
2-methylhexane	2MC6	-118.3	90.0	
1,1-dimethylcyclopentane	11DMCYC5		87.5	
2,3-dimethylpentane	23DMC5		89.8	
3-methylhexane	3MC6	-119.0	92.0	
1cis, 3-dimethylcyclopentane	1c3DMCYC5			
1trans, 3-dimethylcyclopentane	1t3DMCYC5			
1trans, 2-dimethylcyclopentane	1t2DMCYC5	-120.0	91.8	
normal heptane	nC7	-90.6	98.4	
methylcyclohexane	MCYC6	-126.6	100.9	
1cis, 2-dimethylcyclopentane	1c2DMCYC5			
2,5-dimethylhexane	25DMC6	-91.2	109.0	
2,4-dimethylhexane	24DMC6		111.0	
2,2,3-trimethylpentane	223TMC5	-112.3	110.0	
toluene	tol	-95.0	110.6	
3-methylheptane	3MC7		115.8	
1cis, 4-dimethylcyclohexane	1c4DMCYC6	-87.4	124.3	
normal octane	nC8	-56.8	125.7	
heptadecane	C17H6	22.0	303.0	***Solid***
octadecane	C18H38	28.0	303.0	
nonadecane	C19H40	32.0	330.0	

associated with using these ISPG oils is that there is a large choice of over 1500 oils from varying regions, wells, and depths. Therefore, the desired oil suites can be chosen from previously known compositional, source, and depth information.

Some information is logged at the well head such as geographic location, total depth drilled, the number of drill stem tests (DST), the depths of the DST where the oils originated, formations drilled, and bottom hole temperature or pressures. Most of the oils are received by ISPG in 1 or 4 liter cans or plastic bottles (1 liter). However, there is no control over the handling of the samples from the time they reach the surface to refrigeration at ISPG. It is desirable to standardize the collection procedure, taking into account the volatile nature of the compounds to be analyzed (e.g., quick collection in air tight containers with immediate transport to refrigeration), but this is not possible. Some of the lightest gasoline range compounds (in particular C_5) may be reduced or lost.

5.2 MOLECULAR CHARACTERIZATION OF THE C_{10+} SATURATE FRACTION

All the C_{10+} saturate analysis was performed at ISPG (most of it in the course of other activities completed there). The procedure shown below (also see Figures 5.1 and 5.2) for the C_{10+} saturate analysis is derived from the standard procedures used in the organic geochemistry laboratory of ISPG.

5.2.1 Distillation (or Topping)

Approximately 100 ml of crude oil is weighed out and the fraction boiling below 210 °C is distilled into a clean, dry, weighed round bottom flask. This is then weighed and stored separately. The residual oil is allowed to cool. Approximately 4 to 5 g of this fraction (boiling above 210 °C) is weighed to the nearest 0.1 mg for further analysis. (If the oil sample contains any water, the sample is refluxed for 3 to 4 hours and then the oil layer decanted before distillation.)

5.2.2 Asphaltene Precipitation

For heavy oils, the asphaltenes (NSO compounds) must be precipitated since they are not hydrocarbon compounds (of little interest here) and they make subsequent elution of hydrocarbons in column chromatography more difficult. They can block the column. De-asphalting is accomplished by adding a minimal amount of distilled chloroform to dissolve the oil fraction and an excess of pentane to precipitate the asphaltenes from it. Using glass fiber filter paper, the oil mixture is vacuum filtered. The flask is washed with 2 to 3 more volumes of pentane, filtering each time. The precipitate is washed 2 to 3 times with pentane to ensure that all the pentane insoluble material (asphaltenes) is removed.

5.2.3 Column Chromatography

Approximately 50 to 100 mg of the de-asphalted oil is weighed out for column chromatography which separates out oil into saturate, aromatic, and NSO fractions. The support material used for the column is composed of one third Silica Gel and two thirds alumina kept overnight at 400 °C. This is cooled and stored in a desiccator.

The length and diameter of the column depends upon the amount of sample being run through it. In general, if the sample is between 30 and 100 mg, a 25 ml burette is used with a diameter of 1.5 cm. It is prepared by placing a glass wool plug on the bottom, a 1 cm layer of sand above this, and filling with distilled pentane (see Figure 5.2, not to scale). The support is slowly added (volume depending on the amount of de-asphalted extract; e.g., 1 gram support per 10 milligrams extract or 100 adsorbent/1 sample by weight) with slight tapping and shaking of the column so that all air bubbles are removed. The column is then drained, by opening the small valve at the bottom of the column, so that the pentane rests just above the surface of the support.

The elution series is as follows:

❶ a minimum amount of *n-pentane* (e.g., 3.5 ml per gram of support) is added to the column, which is also rinsed several times with pentane, to remove the **saturate fraction** for gas chromatographic analysis;

❷ a *50:50* $nC5/CH_2Cl_2$ solvent (4 ml/g) is run through the column (at slow flow rate) to isolate the **aromatic** fraction;

❸ *methanol* (4 ml/g) is used to allow collection of the **NSO** compounds; and

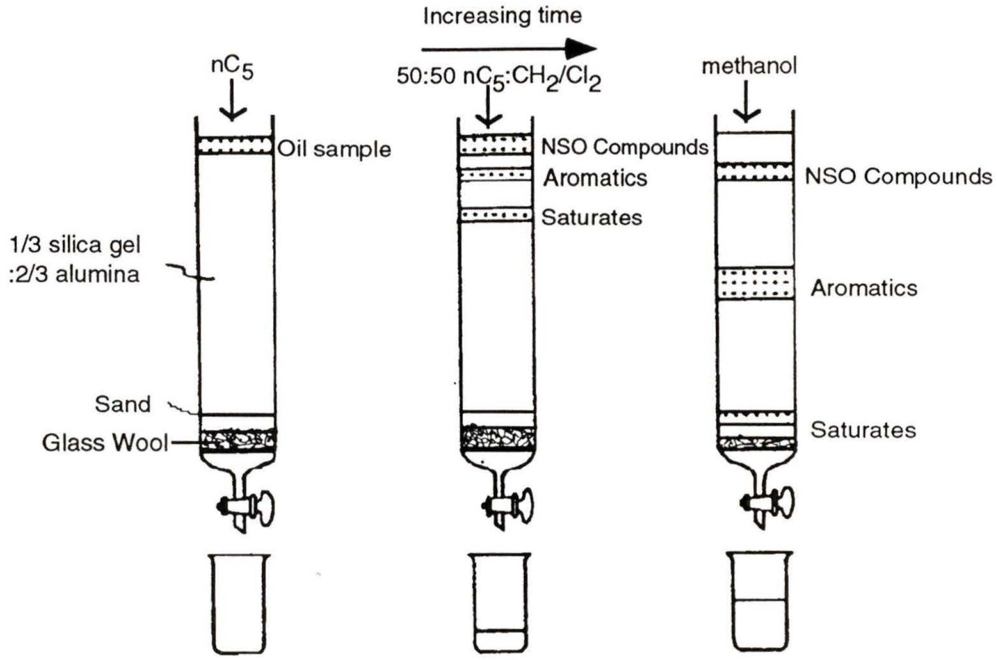


Figure 5.2 Elution of C_{10+} hydrocarbons by column chromatography. The columns shown above are not drawn to scale.

➍ *chloroform*, the last solvent to be run through the column, is used to collect any residual **asphaltenes**.

These various fractions are evaporated to dryness and stored in a freezer (Sneh Achal, personal communication).

5.2.4 Gas Chromatography

The saturate fraction of the de-asphalted oil (fraction boiling above 210 °C) is redissolved in a minimum amount of pentane (10 μl/mg) for injection into the GC. The final analysis was carried out at ISPG on a Varian 3700 using a DB-1, 30 meter, fused silica column coated with 0.25 μm of a polymethyl siloxane gum. The temperature conditions are as follows:

- Initial column temperature : 60 °C
- Column hold time : 0 min
- Temperature increase : 6 °C/min
- Final temperature : 300 °C
- Final hold time : 30 min
- Endtime : 70 min.

5.3 MOLECULAR CHARACTERIZATION OF THE C_5 - C_{10} (GASOLINE RANGE) COMPOUNDS

The GC work is performed prior to GC-C-IRMS analysis to obtain molecular information about the oils and condensates (molecular parameters are calculated for oils and discussed later), to test the method for volatile application onto the chromatographic column which is used in both the isotope and molecular analyses, and to determine the appropriate concentration of hydrocarbons for GC-C-IRMS (e.g., number of grains). The gasoline range data for Saskatchewan oils had already been obtained at ISPG in the course of other activities performed there. The East Coast, Arctic, and Alberta oils were analyzed there to acquire a complete set of ISPG data. All of the samples were also analyzed at SEOS to allow comparison and cross-correlation between the results from the methodologies.

5.3.1 Choice of Column Type and Chromatographic Conditions

5.3.1.1 Column Specifications

The gasoline range hydrocarbons were analyzed with a Varian 3400 GC equipped with a high resolution, fused silica capillary column that separates compounds according to boiling point. The column specifications are given below:

- Liquid stationary phase : DB-1 (non-polar)
- Film thickness : 1 µm
- Column diameter : 0.322 µm (wide bore)
- Column length : 60 m.

Although there are complex relationships among the 4 parameters listed above which contribute to column efficiency and compound resolution, they will not be described here (see Sandra at al., 1987 and Sandra, 1989 for details). This fused silica column is routinely used in oil analysis for several reasons as will be shown briefly here. Fused silica is highly inert, thermally stable, mechanically strong, and easy to install. It will not react with the hydrocarbons passing through the column, and it can withstand the high temperatures necessary for the compound elution. Since fused silica is strong, it can be handled without fear of breakage.

The efficiency, selectivity, and resolution of a column are important in GC analysis and should be maximized for optimal results. The efficiency of a column describes the ability of a column to separate components sharply as a function of sample residence time (Bruno, 1991). It is affected by theoretical plate number. A theoretical plate is an imaginary zone or volume element where rapid equilibration of the solute between the mobile and stationary phase occurs. In general, the larger the number of plates, the higher the efficiency. The number of theoretical plates in a column increases as the column length increases.

A long column (e.g., 60 m) is required for oil analysis since oil is composed of a mixture of many compounds, each of which needs to be separated (better efficiency and resolution with longer column). In the gasoline range alone, there could be up to 40 compounds. One disadvantage to using a longer column is the unavoidable increased analytical time. The column diameter of 0.322 µm, which is relatively wide, has a larger sample capacity. This is important for gasoline range analysis since they are in such high concentrations in oils.

The selectivity of a column refers to the ability of a column to isolate 2 or more solutes (hydrocarbons) into distinct peaks (Bruno, 1991; Sandra, 1989). This depends on the relative magnitudes of intermolecular forces between the solute and the stationary and mobile phases. Thus, the choice of stationary phase is important. The stationary phase (phase which determines the interaction between the individual components in the mixture and the chromatographic system and the retention times of compounds) is coated on the interior capillary column wall (1 µm thick in this column) which is superior to other methods of coating and is the most common type used in oil analysis (Sandra et al, 1987). This stationary phase is composed of a nonpolar polymethyl siloxane gum. Nonpolar phases are efficient and more resistant to oxidation than polar phases.

Resolution is a measure of the isolation between components (or hydrocarbons). In GC analysis, well separated, sharp peaks are desirable with short run time. The resolution of a column can be increases by improving the column efficiency or selectivity.

5.3.1.2 Chromatographic Conditions

The operation of a GC relies on consistent gas flow through the system (e.g., column and flame ionization detector; FID) so that compounds can elute at constant, identifiable times (retention times; RT). Optimal gas flows for the analysis are listed below:

- Make-up He gas to FID : ~ 55 ml/min
- Make-up He through column : ~ 2 ml/min
- Air : 300 ± 15 ml/min
- Carrier H gas : 30 ± 1 ml/min
- Split flow : 40 ml/min
- Purge He : 3 ml/min
- Purge time (for trapping) : 8 min .

These flows are checked at least daily and periodically through the day if there is any abnormality observed in the chromatograms (e.g., alteration of RT or peak shape).

A column temperature program is utilized which contains two ramps as shown below in point form. The first ramp increases the temperature very slowly, by only 2 °C/min, from 35 °C to 90 °C. This slow increase allows the large number of compounds in the C_5 to C_8 range to separate according to their respective boiling points (Table 5.1) and form well resolved peaks. Once these compounds are separated, the temperature is increased more rapidly to help shorten the run time. Compounds with greater than 8 carbons are not being analyzed in this particular study. Therefore, poor resolution (resulting from similar boiling points and a fast temperature program) in these heavier compounds is not of any concern.

- Initial column temperature : 35 °C
- Column hold time : 1 min
- Temperature increase : 2 °C/min
- Final column temperature : 90 °C
- Hold time : 2 min
- Temperature increase : 20 °C/min
- Final temperature : 300 °C
- Hold time : 5 min
- Endtime : 46 min

5.3.2 Oil Dilution and Volatile Application to GC

The gasoline range compounds have certain analytical difficulties associated with their measurement. Although they are all liquids at room temperature (25 °C), they occupy a very volatile region of phase stability. The compounds, especially those in the lower range, have very high vapor pressures and low boiling points so they approach a gas at room temperature (i.e., C_5 is a gas at 36 °C; see Table 5.1). The compounds at the higher end of the range (C_{10}) are not as troublesome (volatile) since they have lower vapor pressures and higher boiling points. The HMW compounds (C_{17-20}) are solids at room temperature, but their melting points are low so they are easily converted to a liquid (e.g., C_{17} is converted to a liquid at 22 °C). Thus, evaporation or melting may occur during handling of the oil samples.

The preparation techniques for GC analysis of the C_{10+} hydrocarbons lead to the removal of the volatile compounds so the oil samples cannot be diluted in this manner. In addition, traditional solvents such as hexane can not be used for dilution since they fall within the range of the compounds being analyzed.

However, if the gasoline range hydrocarbons are to be analyzed, the oil samples must be diluted and the C_5 to C_{10} compounds isolated. Lloyd Snowdon has developed an elegant method for achieving dilution which was used in this study. Deactivated alumina (80-200 mesh) is used as a substrate onto which oil droplets are coated. Approximately 1 ml of the alumina is placed in a vial. A drop of oil is transferred to the alumina by a clean wire. The alumina/oil mixture is stirred and then mixed to ensure an even oil distribution on the substrate. Several grains are transferred to a smaller vial for application to the gas chromatograph (Figure 5.3).

The smaller vial containing grains is connected to a 6 port valve. The vial is sealed with a cap lined with a Teflon septa. Purge helium flows into the small vial through a needle. From the vial, the helium plus the hydrocarbons flow though a needle (and tubing) to the valve and into the trap. The sample is purged with helium for 8 minutes while liquid nitrogen is used to trap the volatiles. The liquid nitrogen is removed as the 6 port valve is switched to the on column position, and the sample flows into the GC for analysis.

All vials, wires (for oil transfer), or other glassware to be used for the analysis are combusted at 450 ^{o}C for 4 hours to ensure the removal of contaminants. The alumina

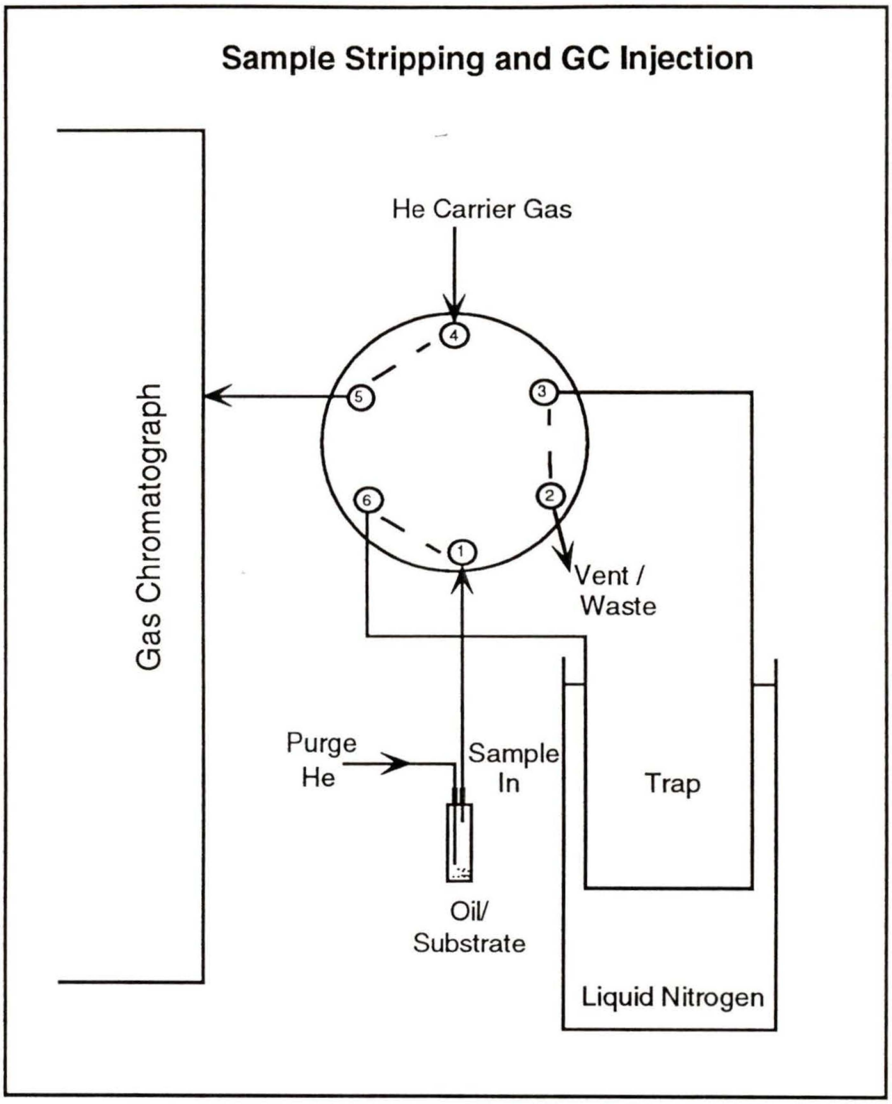


Figure 5.3 Schematic diagram illustrating the stripping of volatiles for GC injection.

adsorbent is deactivated by exposing it to air for 24 hours. A drop of water is added to about 100 grams of adsorbent to ensure that it is deactivated.

5.3.3 Optimization of Method

The optimization of this gasoline sample application method is very important since it is also used to inject the volatiles onto the column in GC-C-IRMS analysis. The GC data from ISPG has been acquired for comparison with SEOS results to aid in the optimization process. There is no isotope data available for comparison purposes so all of the development of the gasoline trapping and application system must be completed during the independent GC analysis.

5.3.3.1 Blank

A vial containing only alumina was run (in duplicate) as a blank at the beginning of the analysis and after the oven was regenerated to ensure that there were no contaminants in the gasoline trapping system. The resulting chromatogram (Figure 5.4) showed a flat baseline (i.e., no peaks were detected). Thus, there are no contaminants in the analytical system.

5.3.3.2 Pure Standards

Next, a pure standard was made up with a mixture of n-pentane, n-hexane, cyclohexane, and toluene. The purpose of the standard was to test the response of the flame ionization detector (FID) to hydrocarbons throughout the column (e.g., test

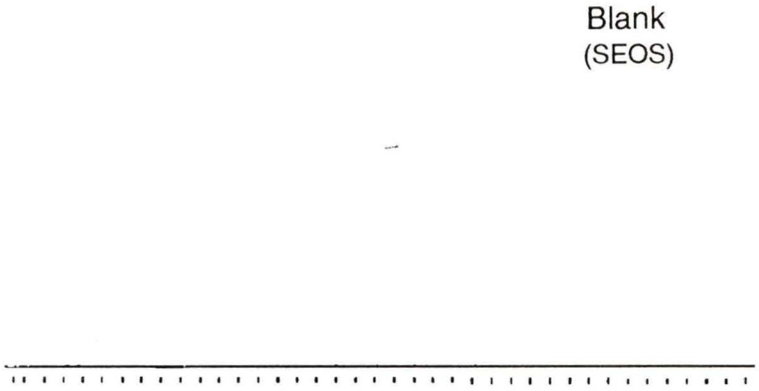


Figure 5.4 Baseline in GC analysis. The absence of any peaks indicates no contamination in the system.

consistency of RT). Both the injector and the gasoline trapping methods for sample input to the GC were tested. The retention times for both methods were consistent (i.e., only differing by a few seconds in multiple runs), easily identifying the pure compounds. All of the compounds were well resolved (baseline separation). The chromatographic peak corresponding to pentane seemed to be lower in all of the purge/trap applications as compared to the direct injections. Thus, there may be slight evaporation occurring during the purge/trap sample application.

These standards were run only in a semi-quantitative manner. The amount of hydrocarbons in the standards, representing the optimal concentrations for the IRMS (e.g., 1 to 10 nmoles CO_2), were calculated. The area counts resulting from the standard calculations were approximately 100 000. This is useful information in determining the appropriate number of alumina/oil grains required to give the best GC-C-IRMS results. The goal is to apply the right amount of grains (hydrocarbon concentration) to give an area count of 100 000.

5.3.3.3 Chromatographic Separation of Hydrocarbons in Oils

Chester was the first oil sample analyzed. It was chosen as an internal lab oil standard since it was not degraded and its composition reflected the average composition found in a typical oil. Twenty-seven gasoline range hydrocarbons were identified (Table 5.2) in total. One thing to note is that the ISPG data shows 2,3-dimethylbutane (23DMC$_4$) and cyclopentane (CYC$_5$) as separate peaks while the results from SEOS show only one peak in that area (referred to as 23DMC$_4$).

The desirable compound separation is at the baseline where one compound elutes independently to create a 'sharp' peak in the GC trace. Sometimes, however, this is not possible. In oil analysis, there are so many isomeric compounds (different compounds with the same molecular formula and similar boiling points and polarities) and so many different compounds contained within one sample that there is continual tailing of one peak into the other (e.g., not baseline separated) and some co-elution of compounds (Figure 5.5).

Many of the hydrocarbons are well resolved and occur in significant amounts such as 3-methlypentane (3MC$_5$), normal hexane (nC$_6$), benzene (ben), cyclohexane

Table 5.2. Compound name, abbreviation, and retention time (RT) for gasoline range hydrocarbons (taken from #266, Hibernia K-18 DST#11).

Compound Name	**Abbreviation**	**RT (sec.) (GC-C-IRMS)**	**RT (min.)**	**RT (min.) (from GC)**
isopentane	iC5	285.69	4.762	4.849
normal pentane	nC5	313.38	5.223	5.326
2,2-dimethylbutane	22DMC4	363.44	6.057	6.194
cyclopentane	CYC5	413.88	6.898	7.07
2,3-dimethylbutane	23DMC4	413.88	6.898	7.07
2-methylpentane	2MC5	424.99	7.083	7.228
3-methylpentane	3MC5	453.37	7.556	7.75
normal hexane	nC6	492.78	8.213	8.429
methylcyclopentane	MCYC5	568.49	9.475	9.693
benzene	ben	637.27	10.62	10.905
cyclohexane	CYC6	670.18	11.169	11.457
2-methylhexane	2MC6	695.52	11.592	11.894
1,1-dimethylcyclopentane	11DMCYC5	707.61	11.794	12.023
2,3-dimethylpentane	23DMC5	718.4	11.973	12.229
3-methylhexane	3MC6	728.96	12.149	12.428
1cis, 3-dimethylcyclopentane	1c3DMCYC5	754.2	12.57	12.871
1trans, 3-dimethylcyclopentane	1t3DMCYC5	767.03	12.784	13.054
1trans, 2-dimethylcyclopentane	1t2DMCYC5	778.07	12.968	13.224
normal heptane	nC7	814.16	13.569	14.003
methylcyclohexane	MCYC6	903.01	15.05	15.498
1cis, 2-dimethylcyclopentane	1c2DMCYC5	922.66	15.378	15.66
2,5-dimethylhexane	25DMC6	954.86	15.914	16.277
2,4-dimethylhexane	24DMC6	968.48	16.14	16.42
2,2,3-trimethylpentane	223TMC5	992.55	16.543	16.909
toluene	tol	1058.09	17.635	18
3-methylheptane	3MC7	1163.43	19.391	19.691?
1cis, 4-dimethylcyclohexane	1c4DMCYC6	1260.59	21.01	21.402
normal octane	nC8	1279.99	21.333	21.728

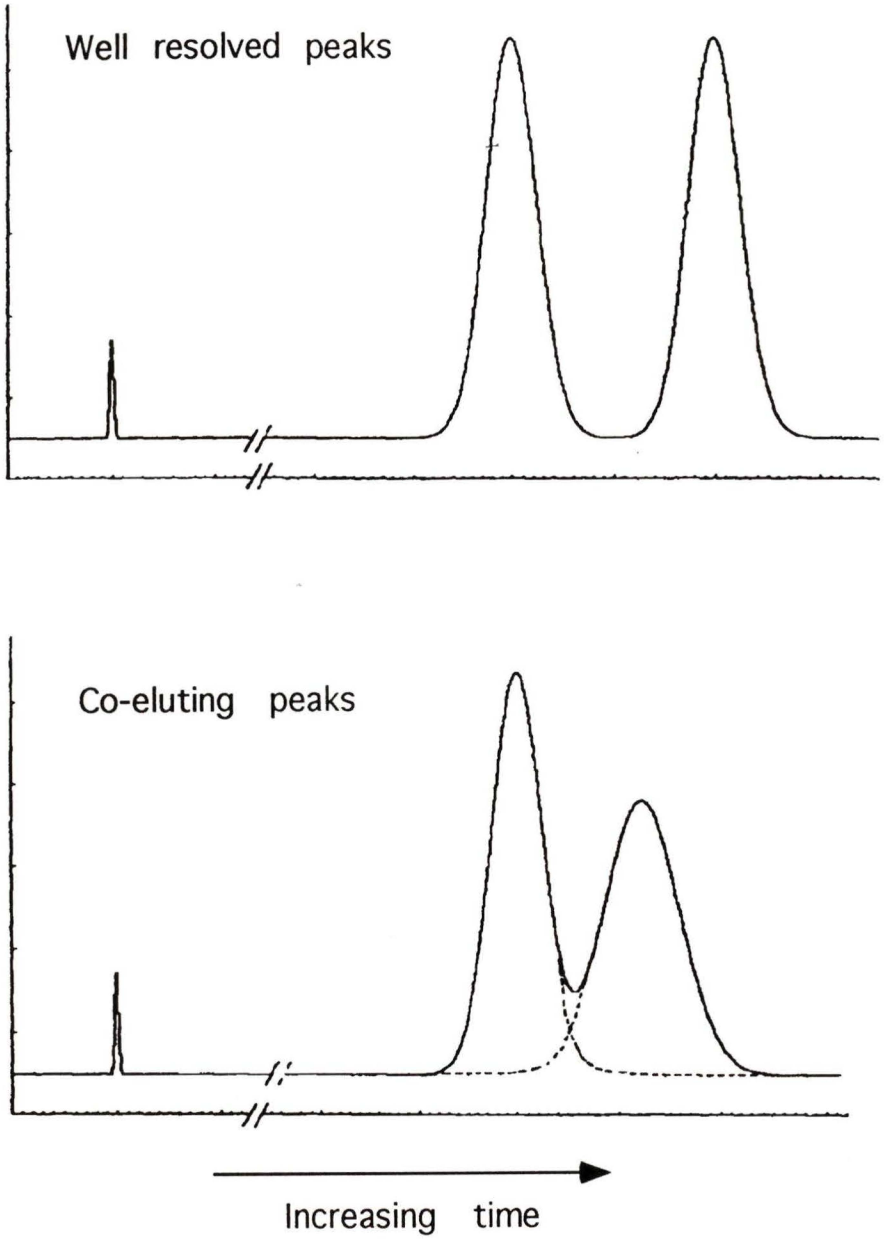


Figure 5.5 Comparison of well resolved and co-eluting peaks.

(CYC_6), normal heptane (nC_7), 2,2,3-trimethylpentane ($223TMC_5$), and toluene (tol). Some compounds are consistently low in concentration (e.g., 2,2-dimethylbutane; $22DMC_4$). Others appear as doublets or triplets where baseline separation is not quite reached such as $23DMC_4$ and 2-methylpentane ($2MC_5$), the methylcyclopentane ($MCYC_5$) group (3 peaks together; $MCYC_5$ plus two smaller, unidentified peaks), 2-methylhexane ($2MC_6$) and 1,1-dimethylcyclopentane ($11DMCYC_5$), 1cis3-dimethylcyclopentane ($1c3DMCYC_5$), 1trans3-dimethylcyclopentane ($1t3DMCYC_5$), and 1trans2-dimethylcyclopentane ($1t2DMCYC_5$), methylcyclohexane ($MCYC_6$) and 1cis2-dimethylcyclopentane ($1c2DMCYC_5$), and 2,5-dimethylhexane ($25DMC_6$) and 2,4-dimethylhexane ($24DMC_6$). However, most of the groups have one member in much higher concentration than the other.

Although some tailing occurs throughout the sample run, the resolution of the gasoline mixture seems to worsen as the end of each run is reached. This is probably due to the greater number of possible C_7 and C_8 species as compared to the number of possible species in a compound with lower carbon number. The numerous C_7 and C_8 species can have similar structures (e.g., differing only in the placement of a branch) and therefore similar boiling points. These similarities would cause the different isomers to sometimes elute at the same RT, leading to co-elution.

After the retention time for toluene is reached (18 min), many peaks are visible (some in low concentrations) but none exhibit baseline separation (i.e., many overlapping peaks are present). The last 2 compounds identified are 1cis4-dimethylcyclohexane

(1c4DMCYC$_6$) and normal octane (nC$_8$). These are rarely well resolved and it is sometimes difficult to distinguish between them. In general, if nC$_7$ or other n-alkanes are present and dominant, the larger peak at the end of the run around the retention time of 21.8 minutes will be nC$_8$.

Better resolution can often be obtained by using a more efficient column. The efficiency of a column can be increased by increasing the column length (e.g., resolution is proportional to the square root of the plate number so increasing the plate number by a factor of 4 would double the resolution), utilizing a slower temperature program, or increasing the thickness of the column films. However, the column used for the analysis is long (60 m), the temperature program is very slow (2 °C per minute), and the stationary phase is of average thickness (1 μm). Improvements to the compound resolution are not possible in this analysis (or for GC-C-IRMS analysis) without significantly increasing the analytical time. There may be new capillary columns developed in the future which can give better resolution than those available today. These columns would have to cover a wide range of boiling points and must have the capacity to elute the right sample mass into the combustion oven and MS.

5.3.3.4 Modifications to Method

The peak shapes and sizes in the Chester chromatogram obtained at SEOS are similar to those obtained from ISPG except for the occurrence of a large hexane peak in the SEOS chromatogram (Figure 5.6). Another set of blanks were run, and the resulting

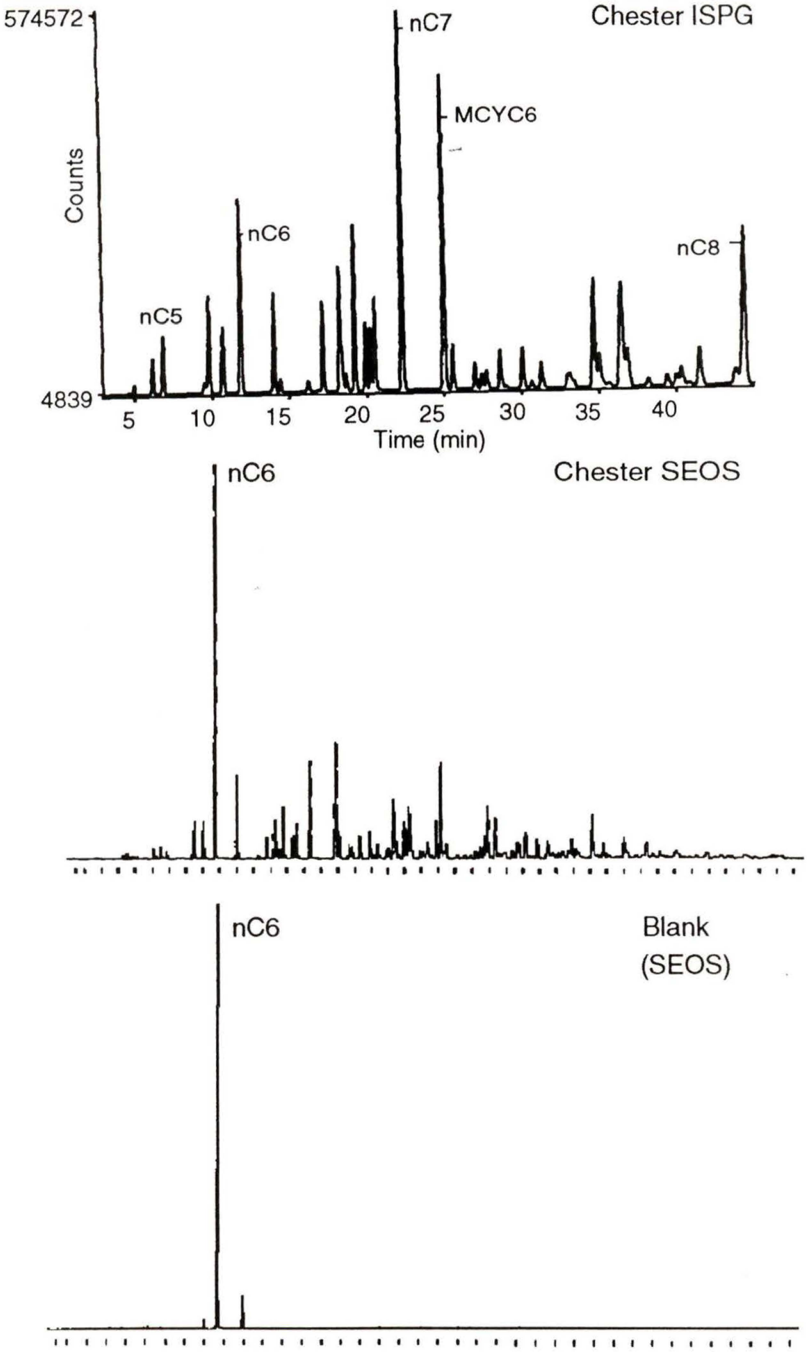


Figure 5.6 Comparison of gas chromatograms of Chester obtained from ISPG and SEOS to illustrate the difference in the concentration of hexane (nC_6). The lower chromatogram of a SEOS blank contains a large hexane peak.

chromatograms contained a hexane peak (Figure 5.6). A problem in the purge/trap system was suspected so a variety of tests were performed.

A heat gun was applied to the sample to try to determine whether or not more volatiles could be released in this way, but it did not result in any change (i.e., there was no increase in the amount of volatiles due to heating). Purging times were manipulated, but the hexane peak still remained large. After several other tests, it was later found that the copper tubing in the purge/trap apparatus held a certain degree of 'memory'. Some of the material, which had passed through it, was lingering in the system. This copper tubing was replaced by tubing composed of Teflon. A blank run after the replacement resulted in a flat baseline with no peaks.

Some of the aromatic compounds were high (e.g., toluene and benzene) as compared to the ISPG analysis, especially in more viscous oils. The results may be dependent on the amount of substrate used. Varying amounts of alumina were tested with varying purge times. The best combination seemed to be a long purge time (8 minutes) and a minimal amount of alumina. When this is used, slightly more compounds such as toluene are released.

The temperature program used in the preliminary stages of this study was 69 minutes long. Variations of this program were tested. The only modifications made to produce the temperature program given earlier were a shortening of the first hold time, an increase in the second temperature ramp, and a decrease in the final hold time. None of these changes seemed to have any appreciable effect on the column efficiency or the compound separation since the majority of the compounds of interest are separated by 90 °C.

5.3.3.5 Sample Size

Several oils were run multiple times (5 each) to test sample size requirements. The viscous oils do not distribute as evenly as the non-viscous oils (and often contain less volatiles). Therefore, a greater amount of alumina/oil is required for the viscous oils as compared to the non-viscous oils or condensates.

In general, if a viscous oil is being analyzed, a wire with a loop on the end is used to transfer the oil to the vial containing the alumina. Then, the oil and alumina are mixed quickly with the wire. The vial is capped and then shaken again to give an evenly distributed mixture. Non-viscous oils or condensates can be transferred by a Pasteur pipette to the alumina-filled vial, dropped at the alumina surface, and immediately capped. An even mixture is easily obtained with a little shaking.

If the alumina/oil particles are fine, an amount of grains equivalent to a volume of approximately 5 mm x 3 mm x 3 mm is placed in the small vial attached to the 6 port valve. If the alumina/oil particles are coarser, about 10 grains are used. If the run shows that the amount is too low (i.e., compounds are in very low concentrations or absent) or high the sample size is adjusted accordingly. From the work with the pure standards, the area count (approximately 100 000 in this case) corresponding roughly to an optimal amount of material for GC-C-IRMS analysis acts as a guide for determining the appropriate number of grains. The choice of the number of grains is made easier if some sample information is available before the analysis (e.g., amount of biodegradation since highly degraded oils have lower concentrations of gasoline range hydrocarbons).

Since the amount of sample applied to the GC (or GC-C-IRMS) could not be quantified, the flame ionization detector (FID) could not be calibrated. Any molecular parameters calculated later will therefore be based on area counts. The relative response of the FID should be similar for each of the gasoline range hydrocarbons so any parameters calculated using area counts in this study should be comparable to parameters calculated in other studies using concentrations.

5.3.4 Reproducibility of the Technique

All of the samples analyzed at SEOS were run in triplicate to test the internal reproducibility of the sample application technique and GC analysis. The resolution and compound distribution are similar for each run. Since it is difficult to apply the same amount of sample for each run, the average area counts (from 2 runs) normalized to cyclohexane for selected hydrocarbons in 3 oils analyzed at SEOS are compared in Table 5.3. The standard deviations for each oil are low, usually less than ± 0.1 or 0.2. All of the standard deviations calculated for the data in this study are obtained using formula 5.1.

$$\text{standard deviation} = [(\sum_{i=1}^{n}(x_i-\overline{x})^2)/n-1]^{1/2} \qquad (5.1)$$

where x_i = individual data value

$\overline{x}$ = mean

n = number of data values

Table 5.3 Comparison of the area counts normalized to CYC6 for SEOS and ISPG oils. The averages and standard deviations are obtained from two runs.

Sample	iC5	nC5	2MC5	nC6	MCYC5	CYC6	3MC6	nC7	MCYC6	tol
SEOS										
#263	0.310	0.617	0.793	1.885	1.000	1.000	0.943	2.923	2.732	2.119
#263	0.353	0.716	0.966	2.212	1.063	1.000	1.024	3.111	2.760	1.952
average	0.332	0.667	0.880	2.048	1.031	1.000	0.983	3.017	2.746	2.035
stdev	0.030	0.070	0.123	0.231	0.044	0.000	0.058	0.132	0.020	0.118
#822	0.507	0.520	1.253	1.869	0.910	1.000	1.611	2.760	3.285	0.193
#822	0.379	0.395	1.144	1.734	0.865	1.000	1.673	2.981	3.665	0.260
average	0.443	0.458	1.199	1.801	0.887	1.000	1.642	2.871	3.475	0.227
stdev	0.090	0.089	0.077	0.095	0.031	0.000	0.044	0.156	0.269	0.048
#733	0.568	0.626	1.428	2.304	1.355	1.000	2.029	3.804	2.855	0.307
#733	0.408	0.594	1.563	2.787	1.366	1.000	2.449	4.903	3.355	0.444
average	0.488	0.610	1.495	2.546	1.361	1.000	2.239	4.354	3.105	0.376
stdev	0.112	0.023	0.096	0.341	0.008	0.000	0.297	0.777	0.353	0.097
#263 (SEOS)	0.332	0.667	0.880	2.048	1.031	1.000	0.983	3.017	2.746	2.035
#263 (ISPG)	0.371	0.956	1.118	2.808	1.267	1.000	1.009	2.926	2.356	0.442
average	0.351	0.811	0.999	2.428	1.149	1.000	0.996	2.972	2.551	1.239
stdev	0.028	0.204	0.168	0.537	0.167	0.000	0.018	0.064	0.275	1.126

Results for the oils and condensates obtained at SEOS were compared with those obtained at ISPG using a similar gasoline stripping method and GC conditions. Figure 5.7 shows the similarity between the chromatograms (in terms of compound distribution and peak shape and resolution) obtained for a Hebron oil from the 2 laboratories. In Table 5.3, a comparison is also made between the CYC_6-normalized area counts of Hibernia K-18 DST#8 (#263) obtained at SEOS and ISPG. The standard deviations between the two sets of results are low (e.g., generally less than ± 0.2). It should be noted that both laboratories have found slight variations in the levels of certain compounds between runs.

Molecular parameters (e.g., PI1 and PI2) calculated on the SEOS data (Table 5.4) are similar to those calculated from the ISPG results (as found in the ISPG database). Although there are some spurious values, the two sets of results are in agreement with low standard deviations (e.g., usually less than ± 0.2). If a larger difference in the results occurred, it would have been difficult to identify the causative factors since similar operating conditions are used for both analyses.

This consistency and reliability are important for the isotope analysis in the current study because the same method of volatile application is used for the isotope analysis. The chromatographic separation of compounds in GC-C-IRMS should be the same as the independent GC analysis. If a problem with the GC-C-IRMS occurs (e.g., change in gas flows, overloading of sample), it may be detected from comparing the RT and peak shapes of the two analyses.

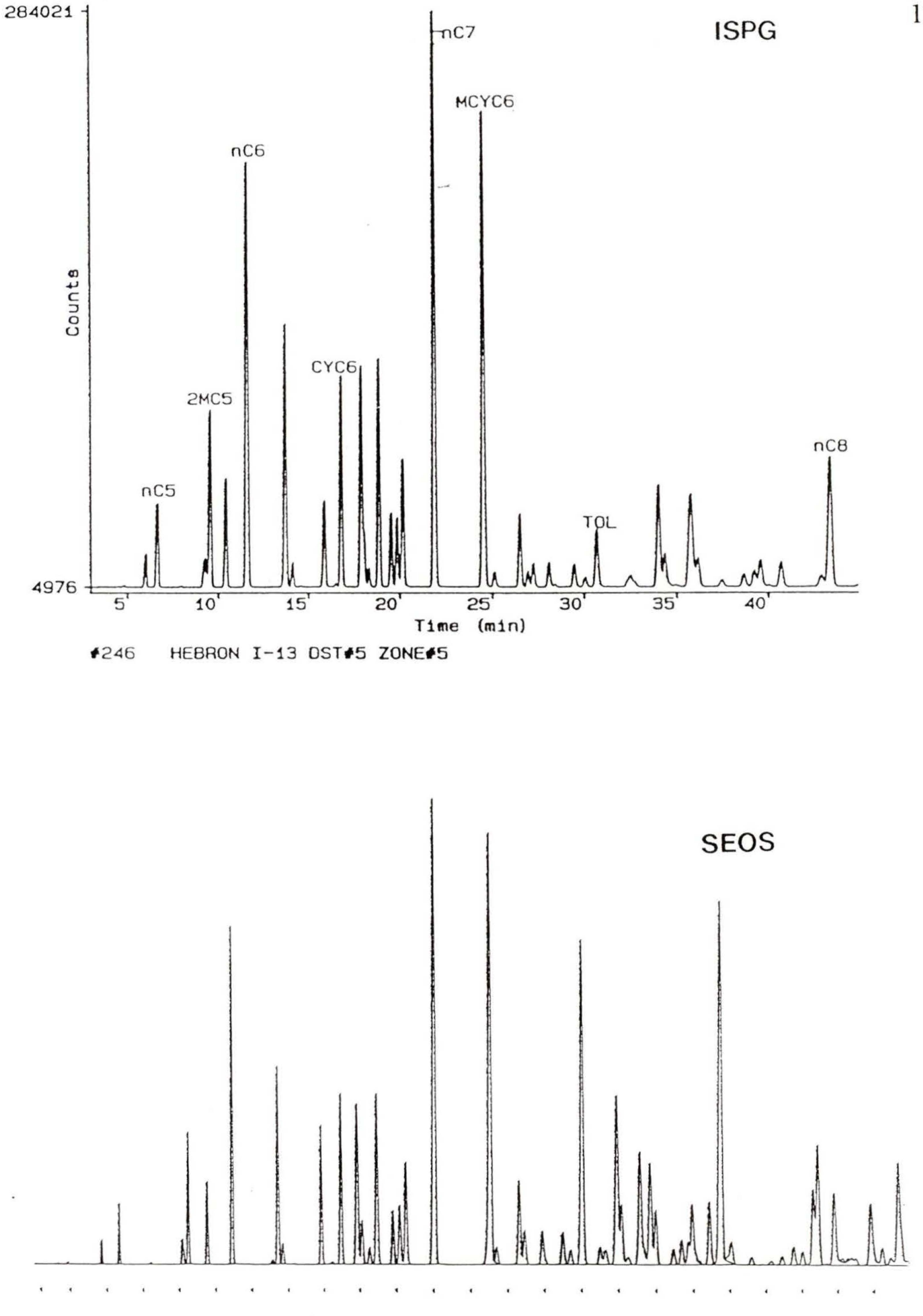


Figure 5.7 Gasoline chromatogram of a Hebron I-13 oil obtained from SEOS and ISPG.

Table 5.4. Comparison of Paraffin Index I (PI1) and Paraffin Index 2 (PI2) for selected oils analyzed both at SEOS and ISPG to check reproducibility.

Sample	PI1		Average	Stdev	PI2		Average	Stdev
	(SEOS)	(ISPG)			**(SEOS)**	(ISPG)		
E/HibC/429/3	1.72	1.82	1.77	0.07	27.63	34.30	30.97	4.72
E/HibC/428/2	1.56	2.08	1.82	0.37	26.18	30.20	28.19	2.84
E/HibC/431/5	1.70	2.12	1.91	0.30	27.97	31.70	29.84	2.64
E/HibK/251/1	1.77	2.12	1.94	0.25	27.05	25.60	26.33	1.03
E/HibK/263/8	1.67	2.04	1.86	0.26	27.83	30.20	29.01	1.68
E/HibK/266/11	1.61	1.92	1.77	0.22	27.87	29.00	28.43	0.80
E/Mara/453/1	2.06	2.94	2.50	0.62	26.44	33.90	30.17	5.27
E/Mara/454/2	1.85	2.28	2.07	0.30	23.92	27.70	25.81	2.67
E/Mara/455/3	0.54	0.59	0.57	0.03	4.75	3.30	4.03	1.03
E/Hebron/245/1	2.07	2.47	2.27	0.28	28.51	31.00	29.76	1.76
E/Hebron/246/5	1.49	1.82	1.66	0.23	26.83	28.20	27.51	0.97
E/Hebron/247/6	1.75	2.27	2.01	0.37	26.41	31.80	29.10	3.81
E/Hebron/248/10	0.66	0.81	0.74	0.11	3.29	5.60	4.45	1.63
E/Hebron/249/9	1.13	1.50	1.31	0.26	18.36	23.40	20.88	3.56
E/Hebron/250/7	1.68	2.33	2.01	0.46	26.22	35.40	30.81	6.49
A/NiglintM/33/22	0.60	0.69	0.65	0.06	3.47	4.60	4.03	0.80
A/NiglintM/74/9	0.61	0.69	0.65	0.06	5.99	6.20	6.10	0.15
A/NiglintM/70/19	0.03	0.19	0.11	0.12	0.03	0.10	0.07	0.05
A/NiglintB/75/14	0.06	0.39	0.22	0.23	0.33	0.80	0.57	0.33
A/NiglintM/34/16	0.06	0.17	0.11	0.08	0.02	0.10	0.06	0.05
A/NiglintM/72/13	0.32	0.39	0.35	0.05	0.08	0.10	0.09	0.01
A/NiglintM/37/10	0.63	0.74	0.69	0.08	0.30	0.30	0.30	0.00
A/NiglintM/71/14	0.22	0.28	0.25	0.04	0.11	0.20	0.16	0.06
A/NiglintM/69/20	0.69	0.77	0.73	0.06	0.77	1.90	1.34	0.80
SW/CBattrum/675	0.66	0.60	0.63	0.04	4.76	4.80	4.78	0.03
SW/CButte/677	1.52	1.34	1.43	0.13	29.51	28.30	28.91	0.86
SW/CBatCrk/726	0.59	0.92	0.75	0.23	0.06	0.00	0.03	0.04
SW/CCantuar/733	1.41	1.48	1.45	0.05	24.88	26.50	25.69	1.15
SW/FKerrob/821	1.12	1.05	1.08	0.05	20.04	19.20	19.62	0.59
SW/FSEurek/818	1.10	1.03	1.06	0.05	19.61	20.50	20.06	0.63
SW/FSmiley/816	1.02	0.95	0.98	0.05	4.36	5.10	4.73	0.52
SW/FForgan/826	0.99	0.93	0.96	0.04	12.62	12.60	12.61	0.01
SW/FPlato/812	0.81	1.05	0.93	0.17	7.42	18.00	12.71	7.48
SW/ECourt/822	1.14	1.15	1.15	0.00	17.81	18.60	18.20	0.56
SW/EHearts/833	1.23	1.30	1.27	0.05	10.92	11.90	11.41	0.69
SW/ECactus/829	1.35	1.60	1.47	0.18	8.84	10.40	9.62	1.10
SW/EBuffalo/836	0.90	0.85	0.87	0.03	11.58	12.20	11.89	0.44

Note: Region/Well/ISPG# (/DST#)

5.4 CARBON ISOTOPIC CHARACTERIZATION

The gasoline range compounds of the various oil or condensate samples are analyzed by GC-C-IRMS at the Biogeochemistry Lab in SEOS.

5.4.1 Analytical Instrumentation

To measure the isotopic ratios of single compounds in a complex mixture such as an oil sample, GC-C-IRMS can be used (Matthews and Hayes, 1978; Santrock et al., 1995; Boutton, 1991; Habfast, 1991; Merritt et al., 1994; Ricci et al., 1994). The instrument at SEOS combines a Varian 3400 GC and a micro-combustion oven with a Finnigan Mat 252 MS (Figure 5.8a). A reference CO_2 gas (with known proportions of mass/atomic number 44/45/46) is injected into the MS before and after the sample runs for calibration of the MS.

The GC separates the compounds of a complex mixture according to the boiling points of the compounds. The subsequent on-line micro-combustion oven is operated at 800 °C. It is made of a ceramic capillary containing a wire composed of copper and platinum (copper oxide oxygen source, platinum combustion catalyst). Since the oxygen will stream slowly and continuously from the oven if it is kept at 800 °C, the oven is turned down to 400 °C when not in use. If too much oxygen is removed from the combustion capillary, there may not be enough oxygen remaining to completely combust the hydrocarbons which could lead to isotope fractionation. Therefore, it is necessary to

(a)

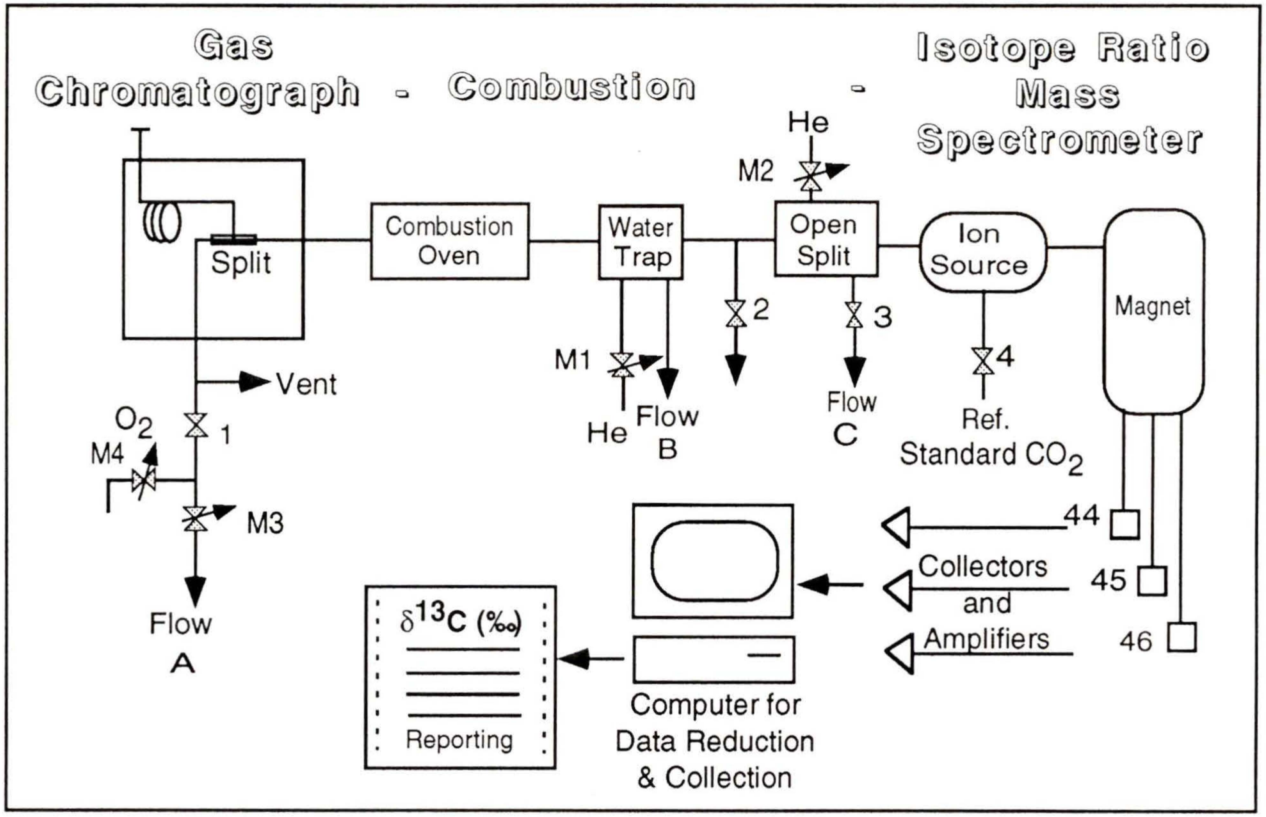


Figure 5.8 Schematic diagram of the GC-C-IRMS analytical system illustrating: (a) the instrumentation and (b) an example of the hydrocarbon species which are converted to CO2 (g). The numbers in brackets following the CO2 (g) species in (b) refer to mass.

periodically regenerate the oven by flowing oxygen through it. The sample is combusted to CO_2 and H_2O in the oven.

Water should not enter the ion source because it can react with CO_2 to form HCO_2^+ simulating the presence of $^{13}CO_2$. There is a separator to remove the water (e.g., a capillary made of a water-permeable material called Nafion). A flow-determining capillary couples the combustion oven to the MS. All the sample is introduced into the ion source at once, measured, and only pumped away after the measurement is completed. This helps to prevent isotope effects during sample introduction, improves the output signal, and increases precision. There are two modes of operation for this GC-C-IRMS: foreflush and backflush. For backflush mode, the reversal of the pressure gradient and flow and the use of a splitter can stop the GC output from entering the combustion oven (e.g., material is diverted away by the splitter). This can be used to prevent the solvent from entering the oven and using up the oxygen or to prevent tailing.

As noted previously, the hydrocarbons entering the combustion oven are converted to CO_2 (Figure 5.8b). The ion source contains a tungsten filament which produces electrons upon heating. CO_2 flows into the source and is converted to CO_2^+. The ionized gas is accelerated into the analyzer where it is focused. This focused ionized gas then moves to the curved sector of a magnetic field where it is deflected in circular patterns according to mass (e.g., $m/e = \text{const.x } (B^2r^2/v)$, where m = mass, e = charge, r = radius of curvature, B = magnetic field strength, v = accelerating voltage; Anderson and Arthur, 1983). The ion beam splits into separate masses (e.g., 44, 45, and 46), and these

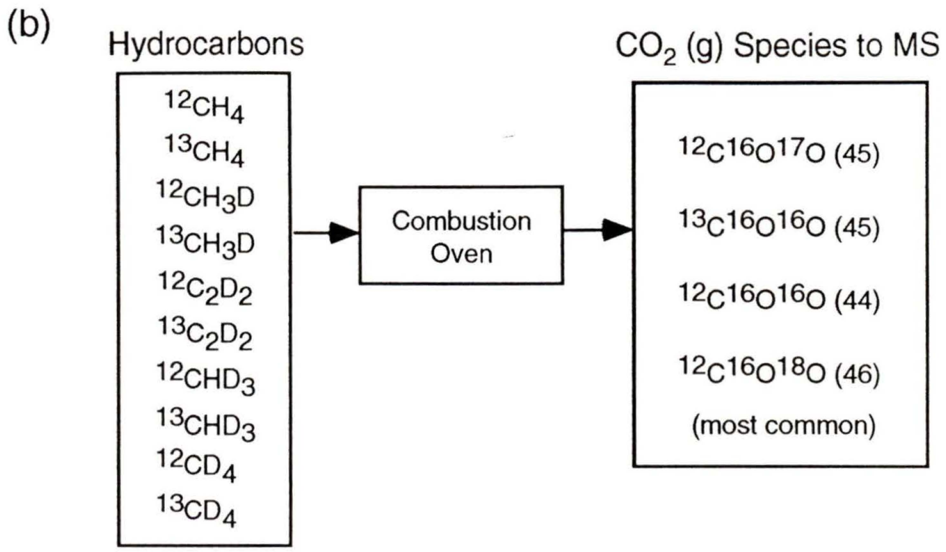


Figure 5.8 Schematic diagram of the GC-C-IRMS analytical system, continued.

species with particular masses are collected in separate Faraday cups. The most dominant isotope species collected are shown in Figure 5.8b. Some of the species are in very low concentrations (negligible) since the natural abundances are low. The Faraday cups are connected to feedback electrometers. The ion currents corresponding to masses 44, 45, and 46 are converted to voltage by the feedback resistors (Ricci et al., 1994). These are amplified and the sent to a computer for data collection and calculation.

The output is a plot of the gas chromatogram in the form of CO_2 (mass 44) ion voltage (similar to FID trace in a regular GC chromatogram) and a plot of the isotope ratio of the combusted sample as compared to the standard gas (unitless) (Figure 5.9a).

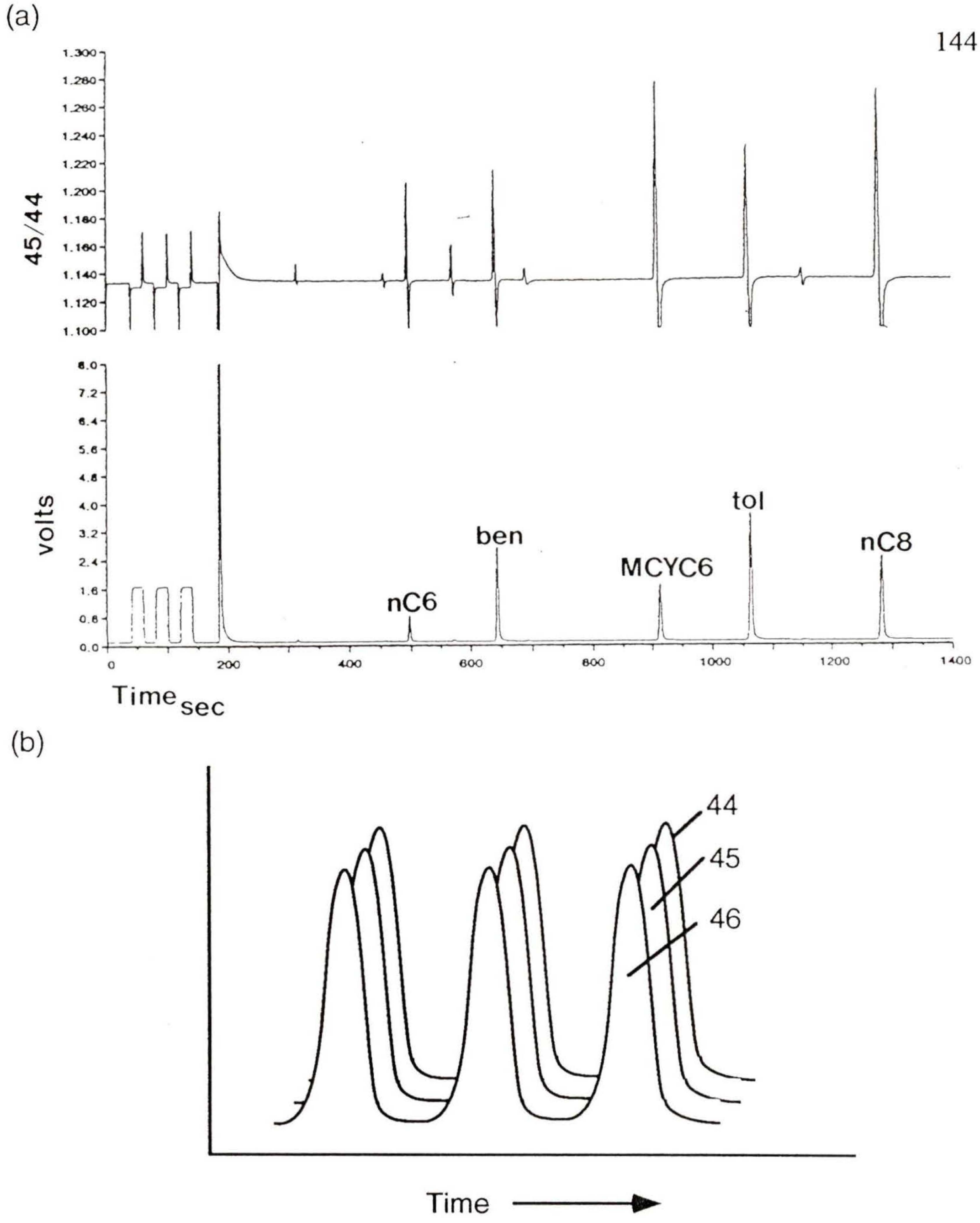


Figure 5.9 GC-C-IRMS resolution and calculation of isotope ratios: (a) pure standard illustrating good compound separation and (b) mass 44, 45, and 46 traces for the integration process which yields the isotope ratios.

The isotope results are presented in typical delta notation (relative to PDB) (see equation 3.9, section 3.3.1).

The 45/44 ion-current ratio observed at any particular time is an average of all of the ion-current ratios for all contributing species (Matthews and Hayes, 1978). Since the isotope ratios can not be obtained directly from the MS output plots, extensive data processing is required (usually performed by the computer software) to extract accurate isotope data.

There is a partition of heavy and light isotopes across each peak which is evident from the isotope signal in Figure 5.9a. CO_2 enriched in ^{13}C (m/z = 45) elutes from the column just before the ^{12}C enriched CO_2 (m/z = 44; i.e., the ^{13}C has a shorter RT than ^{12}C). Since this partition of isotopes across each peak exists, a 3D integration of the areas under the peaks corresponding to masses 44, 45, and 46 for each hydrocarbon must be performed. An isotope ratio is obtained by calibrating this 3D-integrated value to the PDB isotope standard used for the analysis (Figure 5.9b).

A background correction and an ^{17}O correction must also be performed to give more accurate $^{13}C/^{12}C$ ratios (Matthews and Hayes, 1978; Ricci et al., 1994). The computer uses the data just before or after a peak (or an average of the two) to correct for any background ion current resulting from electronic offset, residual gases in the ion source, and non-sample gas (e.g., combusted column bleed). For each ion beam, the background collector current is subtracted from the total collector current to form a ratio of integrated corrected currents.

Since the ratio of $^{13}C/^{12}C$ (mass 45/44) is actually derived from the ratio of $^{13}C^{16}O^{16}O$ and $^{12}C^{16}O^{17}O$ to $^{12}C^{16}O^{16}O$ (other species are negligible due to low natural abundances), a correction factor must be applied to account for the abundance of ^{17}O in the mass 45 species (Craig, 1957; Matthews and Hayes, 1978; Santrock et al., 1985; Ricci et al., 1994). The mass 46 species (e.g., $^{12}C^{16}O^{18}O$) is measured since it gives information about the abundance of ^{18}O in the sample. The relationship between ^{16}O and ^{18}O is known (from oxygen-isotope abundances in standards and similar combustion systems). From this information, the contribution of ^{17}O to the mass 45 can be calculated, and it must be subtracted from the number of ions of mass 45. Carbon isotope ratios are then calculated from the integrated and corrected (background and ^{17}O) mass 45 and 44 signals.

5.4.2 Sample Preparation

The independent GC analysis was a precursor to the GC-C-IRMS work. Any oil sample preparation, dilution, and application for isotopic analysis is done in the same manner as for the GC work. One exception to this is that all samples analyzed by GC-C-IRMS have to be a certain size for detection (equivalent to 1 to 10 nmoles of CO_2). If the amount of sample is too low, it may not be detected. If the amount of sample is too high, there may be insufficient oxygen in the combustion oven for complete oxidation of all the material. This could lead to fractionation. Also, if the amount of sample is high, the response of the amplifier may be non-linear. In this case, the isotopic composition of a sample may vary with the rate of sample input (or pressure in the ion source). The amount of grains corresponding to the optimal range for the GC-C-IRMS was determined from GC runs of pure standards and several oils.

5.4.3 Blank

Several blanks, with only alumina in the vial attached to the 6 port valve, were run at the beginning of the isotope analysis and after the oven was regenerated. Reference CO_2 gas (calibrated to a Washington State University CO_2 gas standard with a known isotope ratio relative to PDB) was injected sequentially to allow the detection of and correction for drifts in instrumental performance. The ion current ratios of the first standard can be used to calculate the ion current ratios expected for the second standard (or any additional standards) and the results compared. If a drift is observed, a change has occurred in the performance of the instrument. The standard gas in this study has an isotope ratio of -36.11 ‰ (relative to PDB) and was stable during all of the blank runs.

When actual samples are run, the instrument still checks the calibration of the system (with respect to the standard), but CO_2 standards are only injected before and after each run. Although there are no standards throughout the run to continually check the calibration, the instrument is very stable and little change is expected. The isotope ratios of the standard gas injections in actual sample runs do not vary. If they varied significantly, the isotope ratios measured for the samples would not be reliable.

5.4.4 Pure Standards

Three pure isotope standards are run through the GC-C-IRMS in the beginning of the analysis as a check of the procedure and to determine whether or not the results are reproducible. The first standard contains equal amounts of nC_5, nC_6, $MCYC_6$, ben, tol, and nC_8. The second is composed of varying hydrocarbon concentrations (in *rough* proportions expected naturally in crude oil; e.g., 1:2:6:1:1:2) to determine whether different concentrations will have an effect on the resulting isotopes. These two standards were run 5 times each. A third pure $MCYC_6$ standard was run in duplicate as a check on the mixed standards.

The averages and standard deviations (using calculation 5.1) for the corresponding isotopes were calculated (Table 5.5). The isotope ratio for nC_5 was not reported because it was in a very low concentration and not detected in many of the runs. The isotope ratios in all the standard runs varied within ± 0.3 ‰ with a maximum of ± 0.5 ‰. The standard deviations for the averages of the individual compounds in the 2 mixed standards were generally less than ± 0.2 ‰ with a maximum of ± 0.3 ‰ (e.g., nC_6). Thus, there were no significant differences between the isotopes of the two mixed standards. Varying concentrations of compounds do not appear to have an effect on the isotope ratios. The isotope ratio of the $MCYC_6$ standard was -26.99 ‰ which is also the average $MCYC_6$ ratio for the 9 standard runs.

Since there are no gasoline range standards available with known isotope ratios, these individual standards (10 aliquots of each standard) were also isotopically measured

Table 5.5 Isotope ratios of pure standards and corresponding standard deviations from both GC-C-IRMS and EA analyses.

Run #	nC6	Ben	MCYC6	Tol	nC8
GC-C-IRMS					
Std.1 D	-26.42	-22.76	-27.01	-26.11	-30.05
Std.1 E	-27.05	-23.21	-27.3	-26.33	-30.46
Std.1 F	-26.15	-22.69	-26.9	-26.11	-30.18
Std.1 G	-27.11	-22.9	-27.05	-26.13	-30.12
Std.1 H	-26.88	-22.76	-27.13	-26.19	-30.25
Std.2 A	-26.81	-23.14		-26.37	
Std.2 B	-26.67	-23.13	-27.04	-26.21	-30.43
Std.2 C	-25.33	-22.17	-26.55	-25.76	-29.91
Std.2 D	-26.41	-22.8	-26.98	-25.68	-30.09
Total Average	-26.54	-22.84	-26.99	-26.1	-30.19
Std. dev	0.551	0.317	0.215	0.235	0.188
Std.1					
Average	-26.72	-22.86	-27.08	-26.17	-30.21
Std. Dev	0.419	0.208	0.149	0.093	0.158
Std. 2					
Average	-26.3	-22.81	-26.85	-26	-30.14
Std. Dev	0.668	0.456	0.266	0.337	0.263
Average 1,2	-26.51	-22.835	-26.965	-26.085	-30.175
Std. Dev 1,2	0.297	0.035	0.163	0.120	0.049
MCYC6 Std.			-26.99		
EA					
Average of 10	-28.57	-23.4	-27.42	-27.15	-31.25
Std. Dev	0.54	1.29	0.56	0.29	0.23
Std. Dev EA and GC-C-IRMS	1.435	0.396	0.304	0.742	0.750

at SEOS by a variable split elemental analyzer (EA) connected on line to the IRMS (Figure 5.10, after Jensen, 1991; Barrie and Lemley, 1989) as an independent check on the $\delta^{13}C$ of the standards.

Samples are enclosed within tin capsules and placed in an autosampler. These capsules are dropped from the autosampler to a combustion tube where the samples are completely combusted with the aid of chromium trioxide and silver coated cobalt oxide catalysts. The combustion products then pass through a reduction tube containing metallic copper which removes any excess oxygen from the combustion products. An absorbent filter traps any water before the combusted sample flows in the IRMS.

The isotopic results from the EA are compared to those from the GC-C-IRMS analysis in Table 5.5. The lighter compounds such as nC_5 and nC_6 could not be analyzed since they evaporated too quickly. The decrease in weight due to evaporation could even be detected when the lighter compounds were being weighed. In addition, it is very likely that as the tin capsules (containing sample) are released from the auto-sampler to drop to the combustion tube, the heat between the two may cause vaporization of some of the volatiles before they can reach the combustion tube and be available for later detection. Thus, the nC_5 isotope ratio could not be reported (i.e., no nC_5 reached the combustion tube due to evaporation). The standard deviations of the average isotope ratios for the other compounds in the 2 analyses ranged from 0.30 to 1.44 (relatively high as compared to the standard deviations for the nine standard runs through the GC-C-

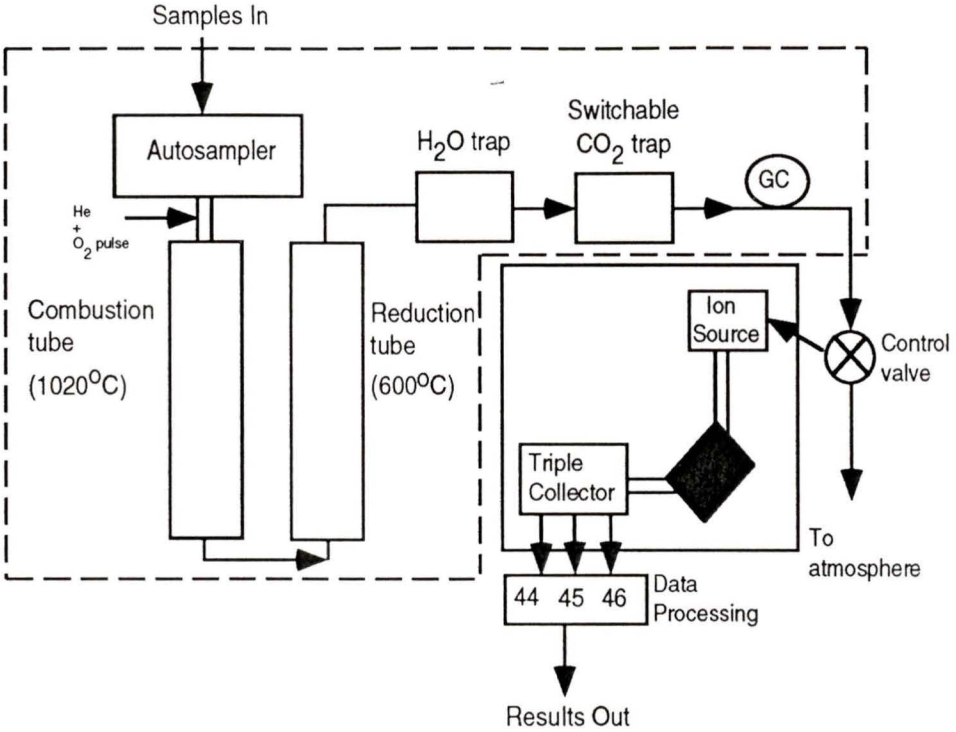


Figure 5.10 Schematic diagram of the Elemental Analyzer apparatus (after Barrie and Lemley, 1989).

IRMS). Thus, EA analysis is not really suitable for volatile analysis and cross-calibration (to GC-C-IRMS).

A better method to obtain more reliable external standard isotope ratios is to combust each individual standard in sealed, evacuated quartz tubes containing excess copper oxide (CuO) as an oxygen source (Buchanan and Corcoran, 1957; Boutton, 1991). Since each standard is placed in its own combustion tube, there is no chance for memory effects. The procedure also minimizes fractionation. Although this method of standard isotope measurement was not performed in this study, pure standards were analyzed by GC-C-IRMS and a standard Chester oil was run at the beginning and end of each day. The isotope results obtained for Chester were consistent (see next section on reproducibility) throughout the period of analysis. In addition, the isotope ratios of the triplicate runs for each sample were consistent.

Collaborative research in various laboratories is currently being designed to develop a set of standards with known isotope ratios for gasoline range hydrocarbons. It is possible that these standard isotope ratios will be offset from the ones measured in this study, but the offset should be consistent for all compounds in the same direction (e.g., more negative or positive).

5.4.5 Resolution and Reintegration

5.4.5.1 Effect of Resolution on Isotope Ratios

Good separation is very important to isotope analysis. If compounds are well resolved, the GC peaks and the corresponding signals composing the isotope trace of the GC-C-IRMS output will be well separated as shown in Figure 5.9 for pure standards. Sometimes, however, this is not possible (see Figures 5.5 and 5.11).

As compounds elute from a GC column into an IRMS, those enriched in the heavier isotope (^{13}C) come off first (shorter RT) followed by those enriched in the lighter isotope (^{12}C) (Figure 5.12 a,b). This isotope partitioning is due to the nonpolarity of the GC column which separates compounds according to boiling point. ^{13}C, which has a slightly higher boiling point than ^{12}C, elutes just before ^{12}C. Since the isotope signal is derived from the ion current associated with masses 45/44, this difference in elution time is detected (Figure 5.12b). Thus, across each peak, there is a temporal (or spatial) gradation of the heavy and light isotopes. For this reason, tailing and co-elution have a greater adverse effect on the resulting isotopes of compounds than on the molecular data (Figure 5.12c).

For example, if a compound is separated from other compounds but still tails, the choice of the end point may cause the exclusion of a portion of the peak. The resulting isotope could undergo a loss of light carbon (Figure 5.13). Also if two or more peaks overlap (or tail into each other), the small overlapping portions of peaks can undergo co-addition of isotope ratios. This is illustrated below by a mass balance calculation:

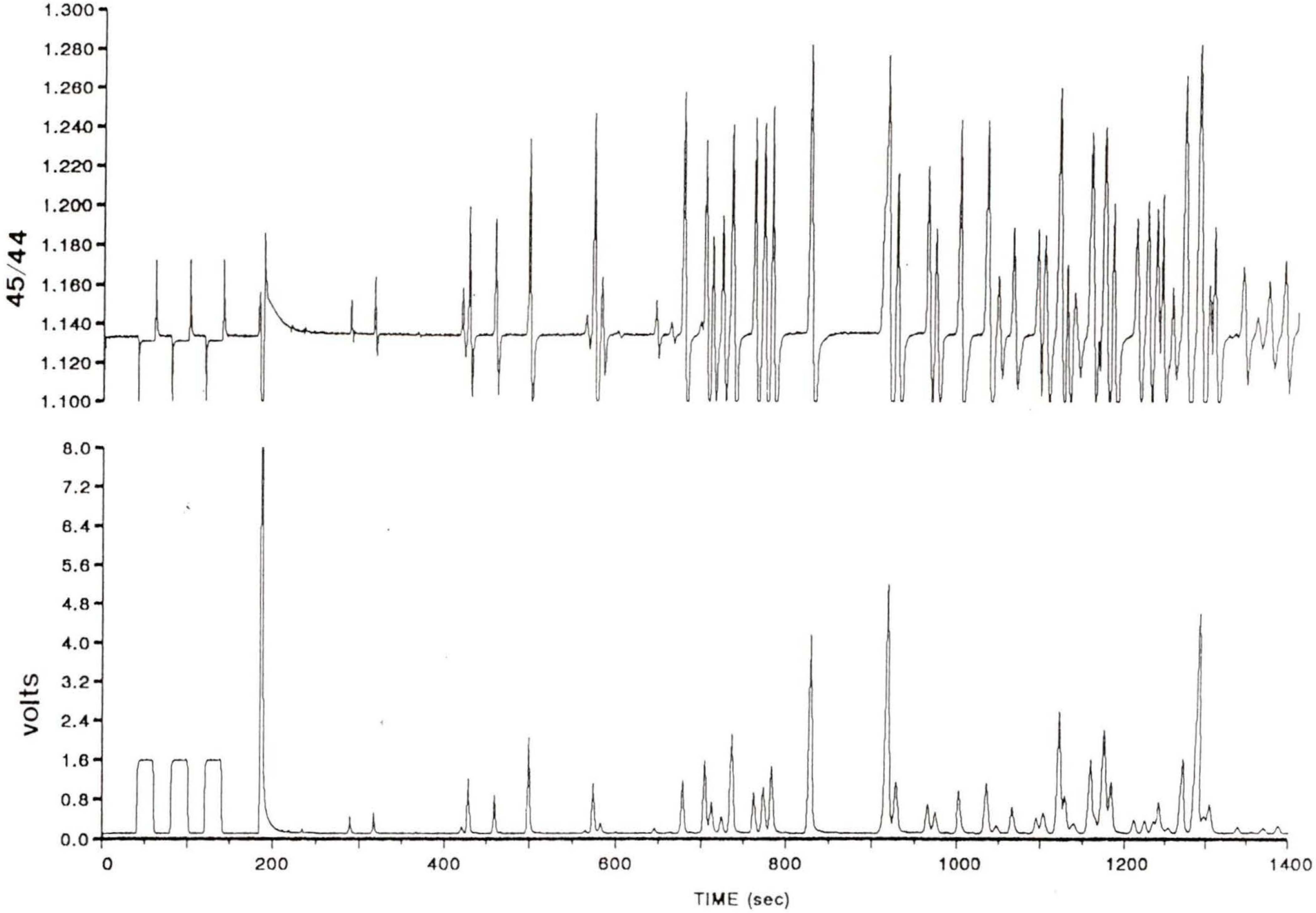


Figure 5.11 GC-C-IRMS output for Chester oil.

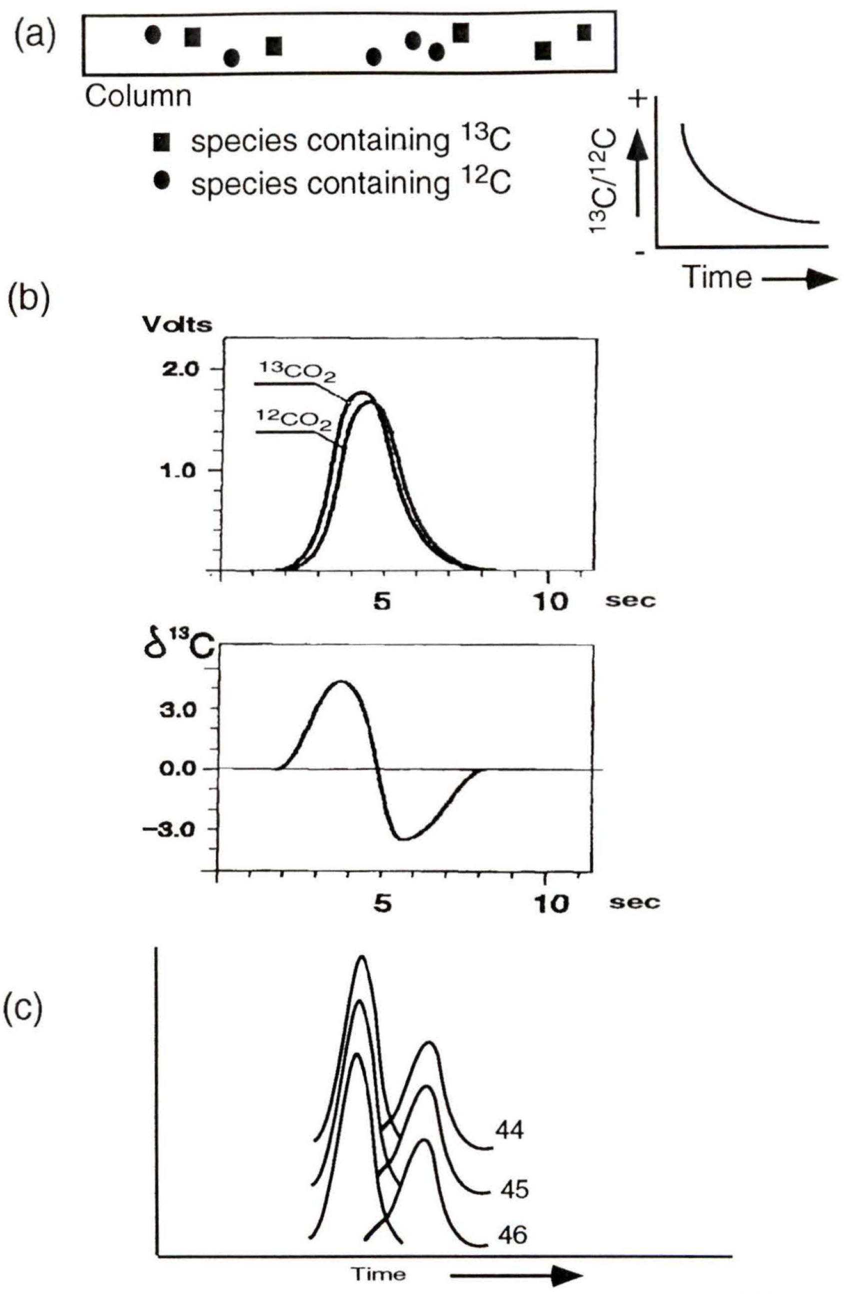
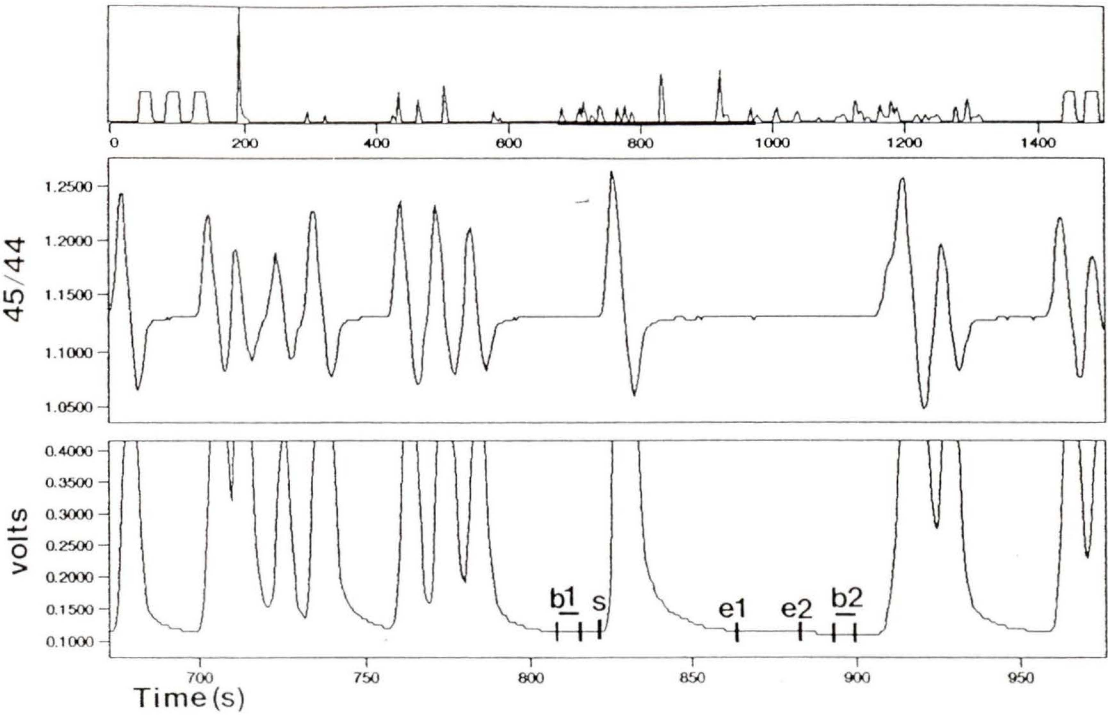


Figure 5.12 Schematic diagrams to illustrate the elution of $^{13}CO_2$ before $^{12}CO_2$. (a) Column illustrating the faster elution of the heavy rather than the light isotope, (b) isotope output illustrating the ^{13}C peak slightly offset and before the ^{12}C peak (after Habfast, 1991), and (c) overlapping mass 44, 45, and 46 traces occurring during co-elution of 2 peaks.



where:

s = start
e1 = end point
e2 = choice of different end point
b1 and b2 = 2 examples of background levels

Ex.

s, e1, b1 = -26.1 $^{o}/_{oo}$ for individual hydrocarbon
s, e2, b1 = -26.4 $^{o}/_{oo}$ for individual hydrocarbon
s, e1, b2 = -26.14 $^{o}/_{oo}$ for individual hydrocarbon

Figure 5.13 Oil example to illustrate the change in an isotope ratio due to a change in the peak start or end and the peak background level.

$$m_T\delta_T = m_1\delta_1 + m_2\delta_2$$

$$1 \times \delta_T = (0.90 \times -23 ‰) + (0.10 \times -150 ‰)$$

$$\delta_T = -35.7 ‰$$

where m_T = total amount of peak or compound = 1
m_1 = amount of most dominant compound 1 = 0.90
m_2 = amount of compound 2 affecting compound 1 = 0.10
δ_T = total isotope ratio
δ_1 = isotope ratio of compound 1 = -23 ‰
δ_2 = isotope ratio of compound 2 = -150 ‰

From the addition of 10 % of compound 2 to compound 1, the isotope ratio of compound 1 changes from -23 ‰ to -37.5 ‰.

5.4.5.2 Compound Resolution in GC-C-IRMS Analysis

The twenty-seven compounds detected in the regular GC analysis were also detected in the GC portion of the GC-C-IRMS analysis (Table 5.2). Thus, for each run, twenty-seven isotope measurements can be obtained (one for each peak corresponding to each compound). Resolution or separation of these compounds is similar to that of the independent GC analysis (Figure 5.14).

Although some compounds do not quite reach baseline separation and exist as slightly co-eluting groups, usually the members of the group are distinctive with one of the compounds in higher concentration than the others. In this way, any adverse effect of co-elution is reduced since the amount of the smaller peak affecting the larger peak will be reduced (i.e., it will have a lower percentage; refer to mass balance calculation given

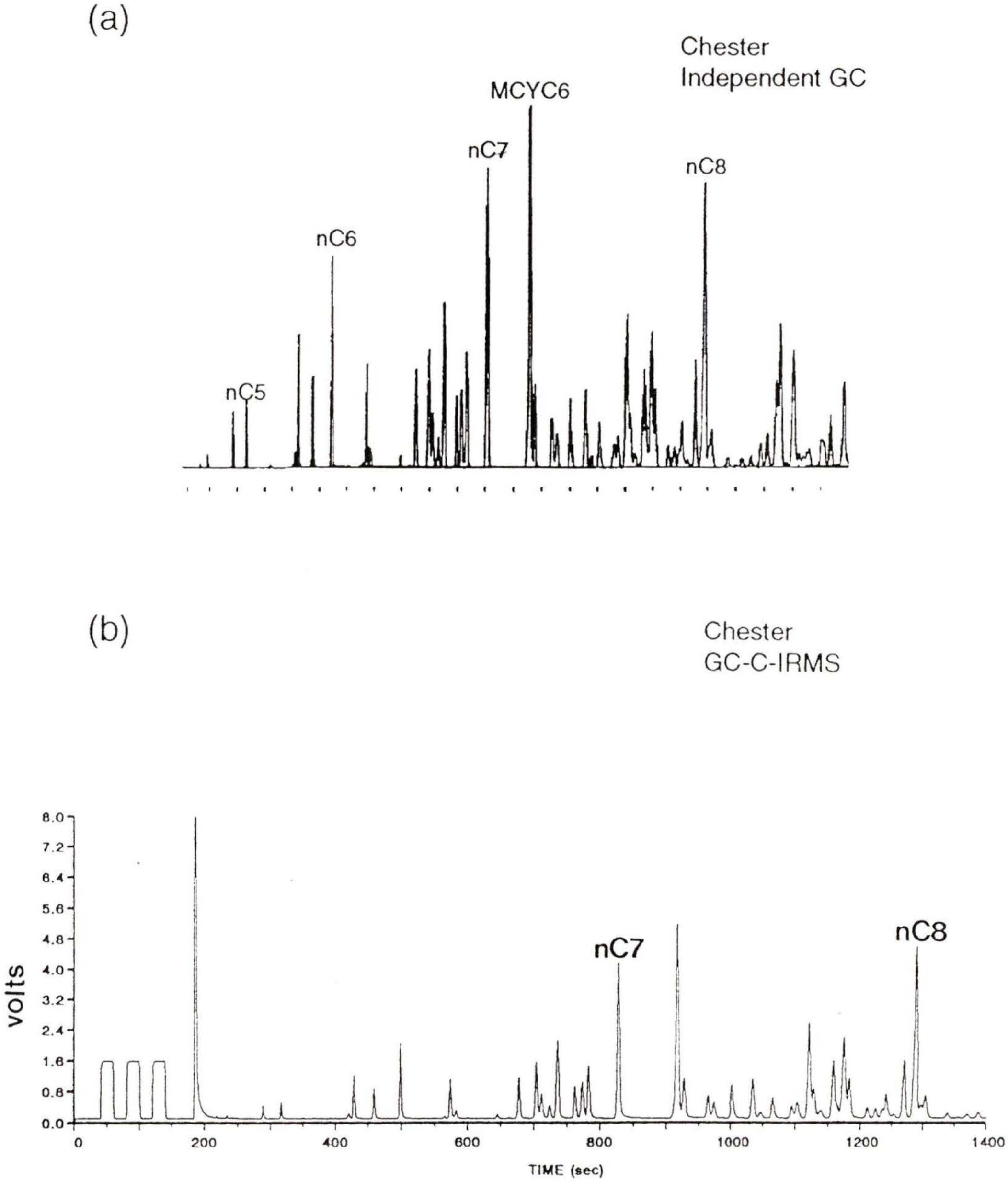


Figure 5.14 Comparison of compound resolution for Chester oil in (a) the independent GC analysis and (b) the GC-C-IRMS analysis.

earlier). Several pairs of these co-eluting compounds are as follows: 23DMC_4 (or CYC_5) with the larger 2MC_5 peak, the larger MCYC_5 peak with 2 other unidentified isomers, 23DMC_5 with the larger 3MC_6, and a very large MCYC_6 with 1c2DMCYC_5.

There are several sets of 'problem' compounds where the peaks overlap so much that the individual isotope ratio for each would not be reliable. A triplet of similar-sized compounds, namely 1c3DMCYC_5, 1t3DMCYC_5, and 1t2DMCYC_5, occurred together in all of the samples analyzed. These did not reach baseline separation and were obviously tailing into one another. Also, 2MC_6 and 11DMCYC_5 and 25DMC_6 and 24DMC_6 always occurred as co-eluting doublets of similar size. These had to be either left out of the analysis or dealt with in some other manner. It should be noted that depending on the sample (i.e., whether or not it is extensively biodegraded) being examined, the separation, co-elution, shape, or size of the peaks may vary.

5.4.5.3 Re-Integration

The isotopic measurement of individual gasoline range hydrocarbons is a new area of research and, therefore, few reference materials have been published regarding the technique. In this study, several different tests were performed to investigate the reliability of the analysis and the isotope results (e.g. re-integration).

To increase the reliability of the isotope ratios of poorly resolved compounds, a trial set of approximately 25 isotope runs were re-integrated. The software program called *Isodat* (developed by Finnigan) that controls the GC-C-IRMS allows one to review and change certain parameters used by the computer to integrate the peak areas. Peak start and ends and background levels (choice of baseline) can be manipulated and the results re-calculated (affecting the corresponding isotope ratios).

Initially, six runs of the standard mixtures were re-examined. Since these runs only included four or five pure compounds, it was easier to use them in the development of a criteria for re-integration. After focusing in on the lower portion of a particular peak, one can examine where the computer has chosen the start and end points in greater detail. If it looks as if the computer has chosen these points in an inappropriate location (too far away from or close to the peak base), the start and ends can be manually manipulated (Figure 5.13). This type of alteration was attempted, but it did not significantly change the isotope ratios (maximum change of ± 0.3 ‰, but often less).

Background levels can be changed in a similar manner (Figure 5.13). The computer may have chosen the start and end points of the background in an area where the 44 and 45 signals were not superimposable. The choice of background can be altered by choosing a quiet area (where the signals for masses 45 and 44 are in synch) in the GC and isotope outputs and re-calculating the results. This kind of change has a greater effect (up to a maximum of ± 3 ‰) than manipulating the peak start and ends, but it is not significant for the larger peaks. Smaller peaks with amplitudes less than 0.3 to 0.5 volts are greatly affected, almost to the extent that one can generate any isotope ratio desired.

After the standards were re-integrated, four Chester runs were re-examined followed by 15 runs from the oil samples. Again, changing the peak start or ends did not lead to any major changes in the re-calculated isotope ratios. Several background changes were attempted, but the resultant isotopes were too random and subjective to be useful. After trying many different combinations, it was decided that any re-integration of the computer's initial results would not be beneficial. The computer could choose the baseline and peak start and ends more consistently than a manual attempt. This consistency is important to ensure that each isotope ratio is being calculated the same way which will reduce randomness in the isotope ratios and allow meaningful comparisons to be made between samples.

The problematic compounds, whose individual isotopes were not reliable due to strong co-elution, were grouped together to determine whether or not the bulk isotopes of the groupings could be meaningful. $2MC_6$ and $11DMCYC_5$, $1c3DMCYC_5$, $1t3DMCYC_5$, and $1t2DMCYC_5$, and $25DMC_6$ and $24DMC_6$ composed three different groups. This was accomplished by changing the peak start and ends of the compounds, collapsing the individual peaks into one larger peak, and re-calculating the isotope ratios. Any results from these groups must be interpreted with caution since the groups are 'artificial' and their construction may mask some of the natural variation in the individual compounds.

5.4.6 Reproducibility

Chester, the 'conventional' oil used as a lab standard to check the operating condition or calibration of the GC-C-IRMS, was run (new sample mixed for each run) at the beginning and end of each day during the period of analysis. In the middle of the analysis, the combustion oven was regenerated by turning off the oven and slowly flowing oxygen through it overnight (to ensure that there is sufficient oxygen in the oven for complete sample combustion, reducing the chance of fractionation). In Table 5.6, the individual isotopes for Chester are given and the standard deviations (calculated using equation 5.1) for the whole period of analysis (2 runs/day for 21 days) are calculated. Some of the lightest and most volatile compounds, such as iC_5 and nC_5, do show variation (up to a maximum of ± 1 ‰). The other compounds being analyzed do not show very much variation (about ± 0.5 ‰) (Figure 5.15). New research on individual isotope ratios has resulted in similar reproducibility (e.g., Bakel et al., 1994; Ishiwatari et al., 1994; Ricci et al., 1994; Bjorøy et al., 1994).

The stability of the isotopes (from newly mixed samples for each run) with increasing time is shown graphically in Figure 5.16 for the n-alkanes, the cycloalkanes, the branched alkanes, and the aromatics. In general, the isotopes do not change in any systematic way over time, but there are a few exceptions. During the first day of analysis, the isotope ratios of the n-alkanes, cycloalkanes, and aromatics seem to be lighter (more negative). The branched alkanes and nC_5 appear more variable throughout the period of analysis which may be due to low compound concentration (resulting in an

Table 5.6 Carbon isotope ratios (‰) of individual gasoline range hydrocarbons in Chester oil from Alberta that was used as a lab standard. The 'a' refers to the Chester oil run at the beginning of the day while 'b' refers to Chester oil run at the end of the day.

Runs	iC5	nC5	23DMC	2MC5	3MC5	nC6	MCYC5	Ben	CYC6	2MC6g
Day1a	-25.0	-27.6		-29.2	-27.4	-29.1	-24.1		-27.0	-26.5
Day1b	-27.5	-28.2	-27.5	-27.1	-26.4	-28.9	-23.4	-29.6	-26.2	-27.3
Day2a	-27.4	-26.2		-26.6	-25.7	-28.8	-23.2		-25.2	
Day2b	-26.4	-27.1	-27.2	-26.6	-25.2	-28.2	-22.5	-29.1	-25.5	-27.1
Day3	-28.4	-28.9	-26.6	-26.4	-25.5	-28.2	-22.6		-25.2	-27.0
Day4a	-26.3	-28.7	-26.8	-26.7	-26.0	-28.8	-23.3		-26.2	-27.2
Day4b	-27.4	-28.7	-26.2	-26.3	-24.9	-27.8	-22.5	-29.6	-25.4	-26.6
Day5a	-30.3	-29.7	-27.3	-26.9	-26.1	-28.4	-22.8		-26.0	-27.5
Day5b	-27.0	-30.1	-28.2	-27.2	-25.9	-28.5	-23.0		-25.8	-27.4
Day6	-27.0	-29.9	-27.0	-27.0	-25.8	-28.4	-23.2	-29.5	-25.9	-27.3
Day7	-26.6	-28.8		-27.4	-26.2	-29.1	-23.4	-28.9	-26.3	
Day8a	-25.6	-28.0		-27.4	-26.6	-29.3	-23.5		-26.6	
Day8b	-27.5	-28.7	-26.9	-27.4	-26.9	-29.1	-23.9		-26.9	-27.5
Day9a	-26.6	-28.0	-27.6	-27.3	-26.0	-28.9	-23.4	-29.8	-26.2	-27.5
Day9b	-26.2	-28.7		-27.2	-25.4	-28.6	-23.0	-29.7	-25.9	
Day10a	-25.9	-27.6		-27.1	-25.8	-28.8	-23.3	-29.1	-26.3	
Day10b	-26.0	-29.1		-27.5	-26.3	-28.9	-23.2	-29.3	-26.6	
Day11a	-25.6	-28.3		-27.4	-26.1	-28.9	-23.2	-29.9	-26.1	
Day11b		-28.5		-27.2	-25.6	-28.7	-23.1		-26.0	
Day12	-26.1	-27.9	-26.9	-26.9	-26.1	-28.6	-23.0	-29.8	-26.1	-27.3
Day13	-26.5	-28.0	-27.3	-27.5	-26.6	-29.1	-23.6		-27.0	
Day14a	-26.7	-29.0	-27.3	-27.2	-26.6	-29.0	-23.7		-26.5	-27.2
Day14b	-25.7	-28.6	-27.3	-27.6	-26.2	-28.7	-23.1		-26.2	
Day15	-26.1	-28.3	-26.8	-27.5	-26.2	-29.2	-23.3	-29.0	-26.4	
Day16a	-25.7	-29.9	-28.9	-27.7	-25.5	-28.7	-24.1		-26.7	-27.2
Day16b	-26.5	-29.1	-26.8	-27.4	-26.2	-29.2	-23.3	-28.9	-26.4	
Day17a	-26.5	-28.8	-27.4	-27.7	-26.5	-29.3	-23.6	-29.5	-26.5	
Day17b	-26.2	-28.8		-26.8	-26.5	-28.6				
Day18		-27.9	-25.9	-27.3	-26.1	-28.8	-22.5	-29.4	-26.3	-27.2
Day19a	-26.6	-28.8		-27.4	-26.2	-29.1	-22.5	-29.6	-26.5	
Day19b	-25.0	-28.3		-26.9	-26.5	-28.6		-28.8	-26.0	
Day20a	-26.9	-28.5		-26.9	-26.1	-28.5			-26.0	
Day20b	-25.8	-28.4		-27.3	-26.2	-29.0	-22.3	-28.9	-26.2	
Day21	-26.8	-27.8	-25.6	-27.7	-26.2	-29.0	-22.5	-29.4	-26.6	-27.0
Average	-26.6	-28.5	-27.1	-27.2	-26.1	-28.8	-23.2	-29.4	-26.2	-27.2
Std dev	1.01	0.79	0.73	0.51	0.49	0.34	0.47	0.34	0.46	0.29

Table 5.6 Carbon isotope ratios (‰) of individual gasoline range hydrocarbons in Chester oil from Alberta, continued.

Runs	3MC6	1c3DMg	nC7	MCYC6	25DMC6	223TMC5	Tol	1c4DMC	nC8
Day1a	-27.3		-27.3	-25.2		-26.1	-27.4		-29.0
Day1b	-27.1	-22.1	-29.5	-23.6	-25.8	-24.5	-27.9	-24.6	-28.3
Day2a	-26.9		-29.0	-24.3		-23.8	-27.0	-24.0	-27.9
Day2b	-25.9	-21.9	-28.4	-23.6	-25.5	-23.0	-27.1	-23.7	-27.5
Day3	-25.9	-21.4	-28.3	-23.5	-25.0	-23.2	-26.6	-23.2	-26.9
Day4a	-27.4	-22.3	-29.1	-24.3	-26.3	-24.0	-27.2	-23.9	-27.7
Day4b	-25.6	-22.0	-28.4	-23.5	-25.5	-23.3	-26.4	-23.3	-27.0
Day5a	-26.7	-22.5	-29.0	-24.2	-26.1	-24.0	-27.4	-23.9	-27.6
Day5b	-28.0	-22.4	-28.7	-23.9	-25.4	-23.9	-26.5	-23.9	-27.5
Day6	-26.4	-22.8	-29.1	-24.3	-26.2	-24.1	-27.4	-24.1	-27.7
Day7	-25.0		-29.2			-23.9	-27.4	-23.8	-27.4
Day8a	-27.1		-29.6			-24.5	-27.9	-24.2	-27.8
Day8b	-26.5	-22.6	-29.3	-24.4	-26.0	-24.3	-27.7	-23.5	-27.1
Day9a	-26.5	-22.6	-29.3	-24.3	-25.9	-24.3	-27.7	-23.9	-27.6
Day9b	-26.2		-29.0	-24.2		-23.8	-26.9	-23.3	-27.0
Day10a	-25.8		-29.3	-24.5		-24.1	-27.5	-23.9	-27.7
Day10b	-26.2		-29.1	-24.3		-24.1	-27.3	-24.1	-27.5
Day11a	-26.5		-29.1			-24.0	-27.8	-23.8	-27.3
Day11b	-26.3		-29.2	-24.2		-23.8	-26.9	-23.9	-27.5
Day12	-26.8	-22.5	-29.2	-24.1	-26.1	-24.0	-27.9	-23.7	-27.6
Day13	-26.7		-29.4	-23.6		-23.9	-28.1	-24.0	-27.4
Day14a	-30.2	-22.7	-29.5	-24.4	-25.9	-24.5	-28.1	-24.4	-27.9
Day14b	-26.6		-29.0	-24.1		-23.7	-27.3	-23.9	-27.4
Day15	-26.4		-29.3			-23.7	-27.5	-23.6	-27.3
Day16a	-25.8	-22.5	-29.2	-24.5	-25.8	-24.1	-27.9	-24.4	-27.6
Day16b	-26.6		-29.2			-23.8	-27.8	-23.7	-27.4
Day17a	-26.7		-29.4			-24.2		-24.0	-27.4
Day17b	-26.3		-28.7	-23.7		-23.9	-26.7	-23.6	-27.2
Day18	-26.4	-22.6	-29.2	-23.5	-26.2	-23.9	-27.9	-23.7	-27.2
Day19a	-27.3		-29.7	-23.8		-24.4	-27.8	-24.1	-27.6
Day19b	-26.6		-29.5	-23.7		-24.2	-28.2	-23.8	-27.5
Day20a	-26.5		-28.9	-22.8		-23.8	-27.5	-23.5	-27.0
Day20b	-26.5		-29.3	-23.4		-24.1	-27.7	-23.6	-27.2
Day21	-26.7	-22.7	-29.3	-23.5	-26.3	-24.2	-28.8	-24.1	-27.3
Average	-26.6	-22.4	-29.1	-24.0	-25.9	-24.0	-27.5	-23.9	-27.5
Std dev	0.85	0.38	0.45	0.48	0.39	0.50	0.53	0.31	0.40

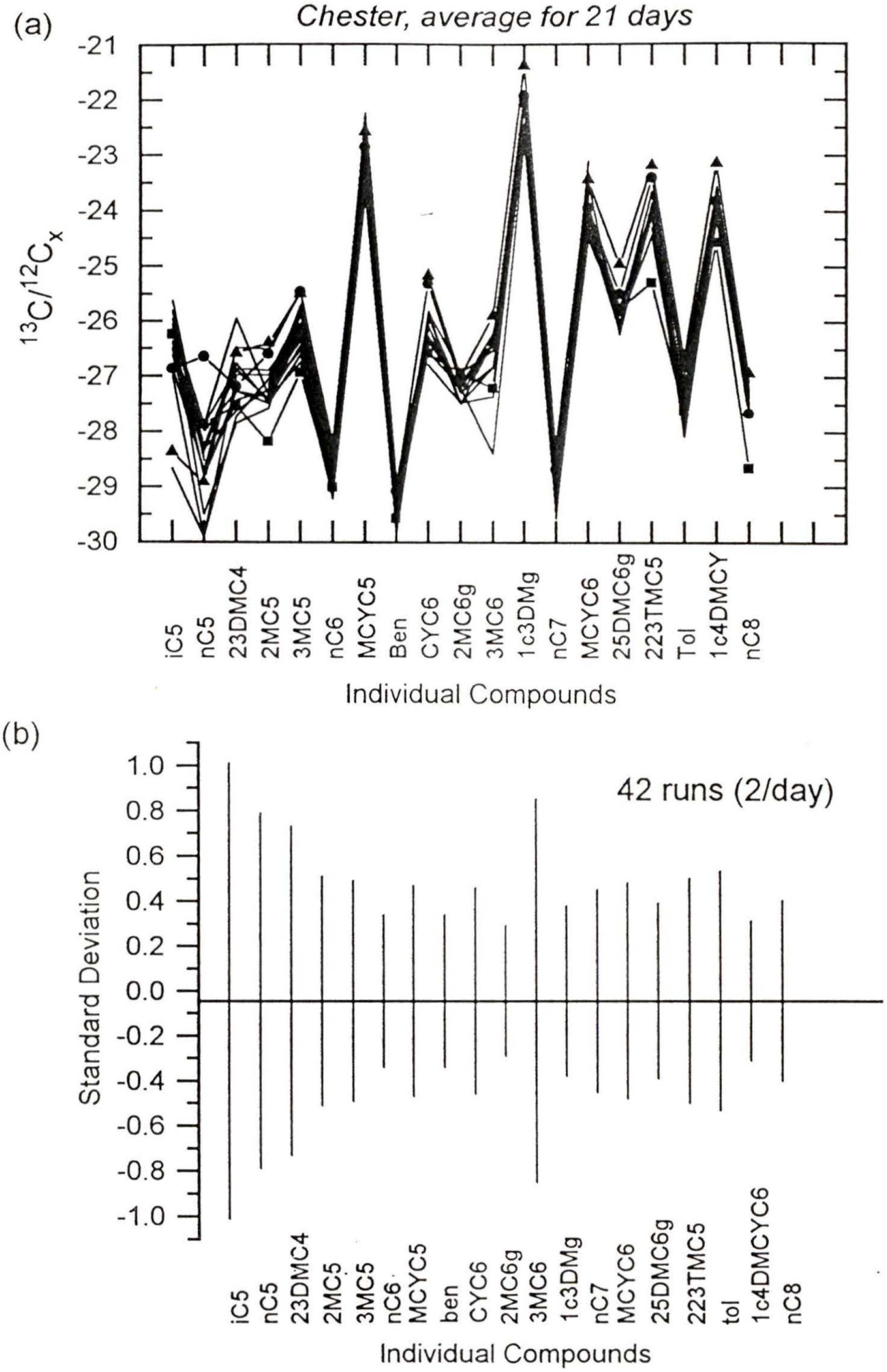


Figure 5.15 Stability of Chester oil from Alberta: (a) isotope ratios of each run (new sample mixed for each run) and (b) expanded scale to emphasize the standard deviation of the average isotope ratio for each compound.

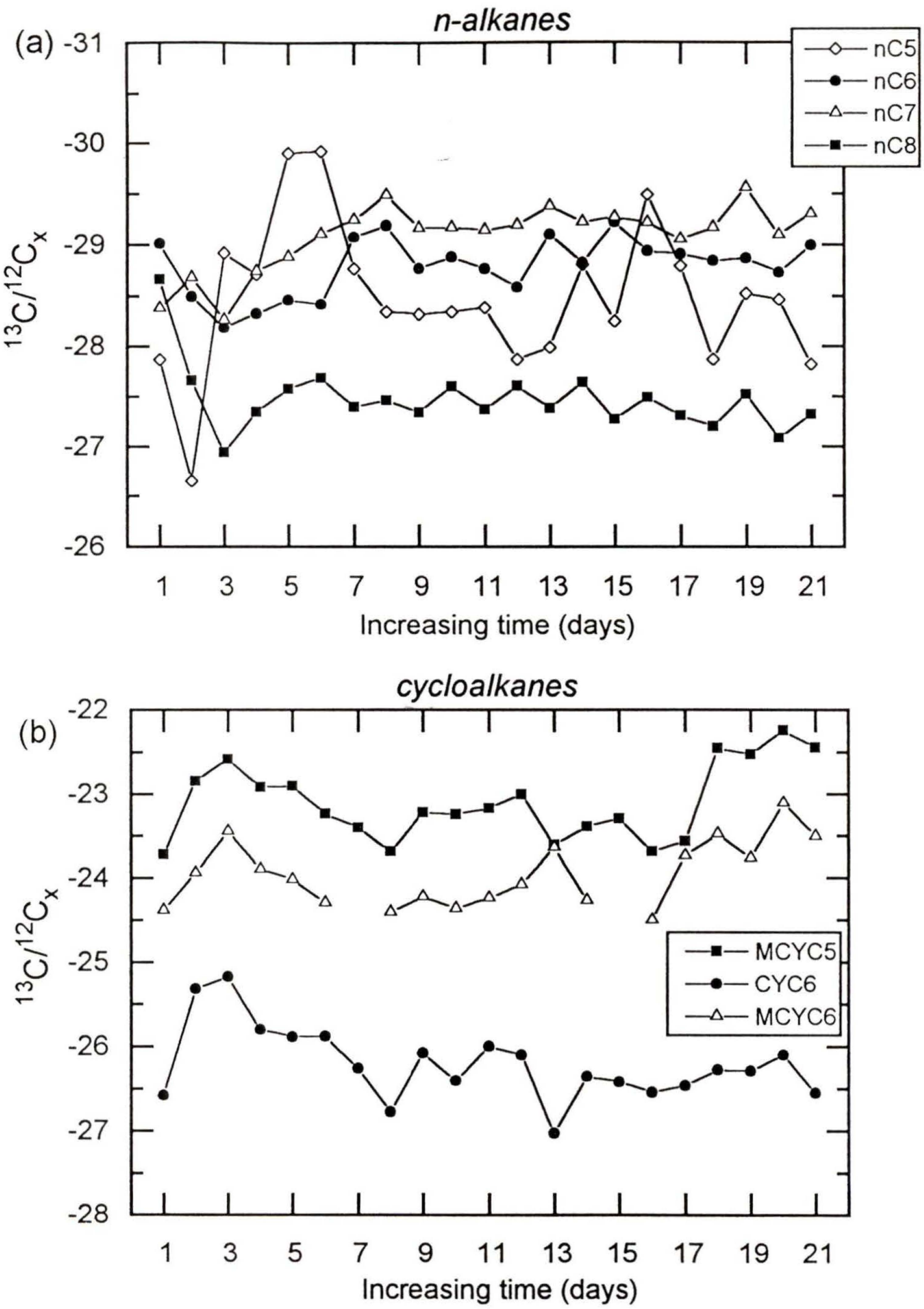
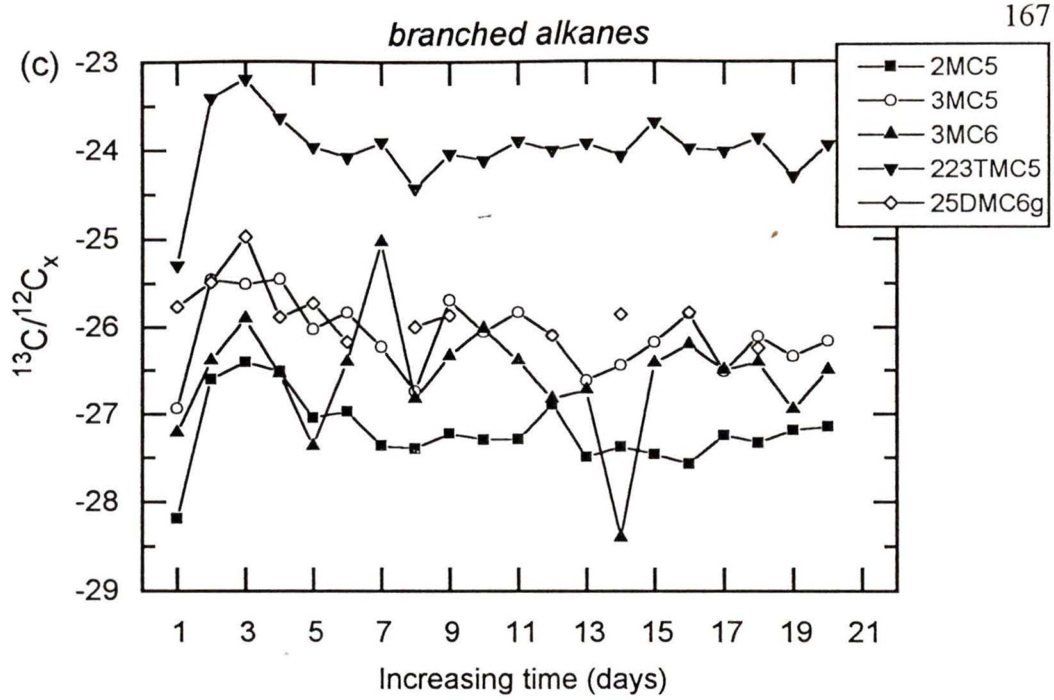


Figure 5.16 Stability of individual compounds in the Chester standard oil from Alberta over the 21 days of analysis for (a) n-alkanes, (b) cycloalkanes, (c) branched alkanes, and (d) aromatics.



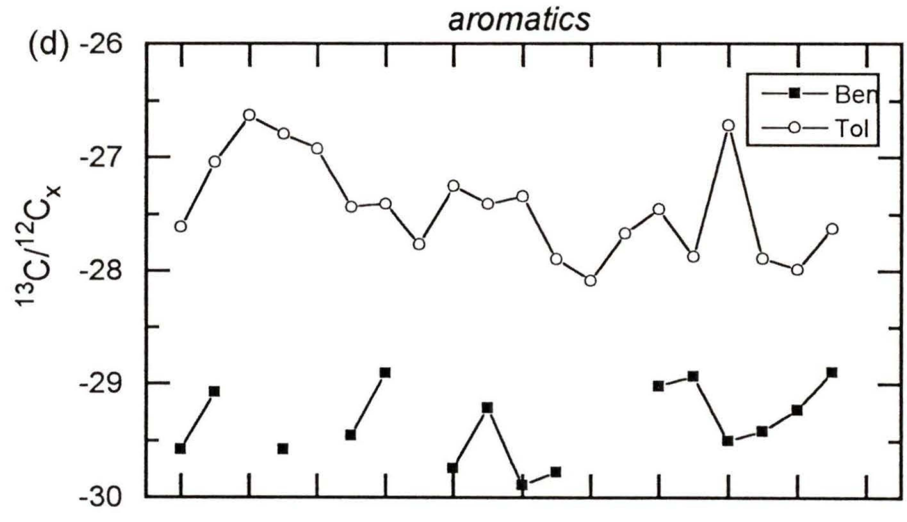


Figure 5.16 Stability of individual compounds in the Chester standard, continued.

unreliable isotope measurement). Bjorøy et al. (1994) also found greater variability in the branched and aromatic hydrocarbons which he attributed to low concentration.

All of the oil samples are run in triplicate to check reproducibility. In Figures 5.17, 5.18, and 5.19, the individual carbon isotope ratios for 3 oils are given. The Hibernia oil shows little variation between runs except for the lightest compounds such as nC_5. Most of the isotopes are within ± 0.3 ‰ with a maximum of about 0.6 ‰. The Niglintgak oil again shows good reproducibility, but there is larger variation at nC_8 (up to a maximum of ± 0.6 ‰) where the compounds are often not baseline-separated. The reproducibility of the individual isotopes for the South Eureka oil is good (± 0.3 ‰) except with regard to the very light compounds (e.g., iC_5 and nC_5). Thus, for most of the compounds being analyzed, the standard deviations range between ± 0.3 ‰ and ± 0.5 ‰.

Overall, there is no significant change in instrument calibration during the period of analysis and any differences observed in isotopes must be due to the variation found in the natural environment and not experimental error (between ± 0.3 and 0.5 ‰). As long as peaks are fairly well separated, any resulting isotope measurements should be reliable.

5.4.7 Sources of Error

The main source of error in this analysis deals with the amount of sample applied to the instrument. From several of the tests performed, the required amount of sample can be estimated (i.e., amount within the optimal range for the GC-C-IRMS; 1 to 10 nmoles). However, it is easy to misjudge the amount of grains and overload the system.

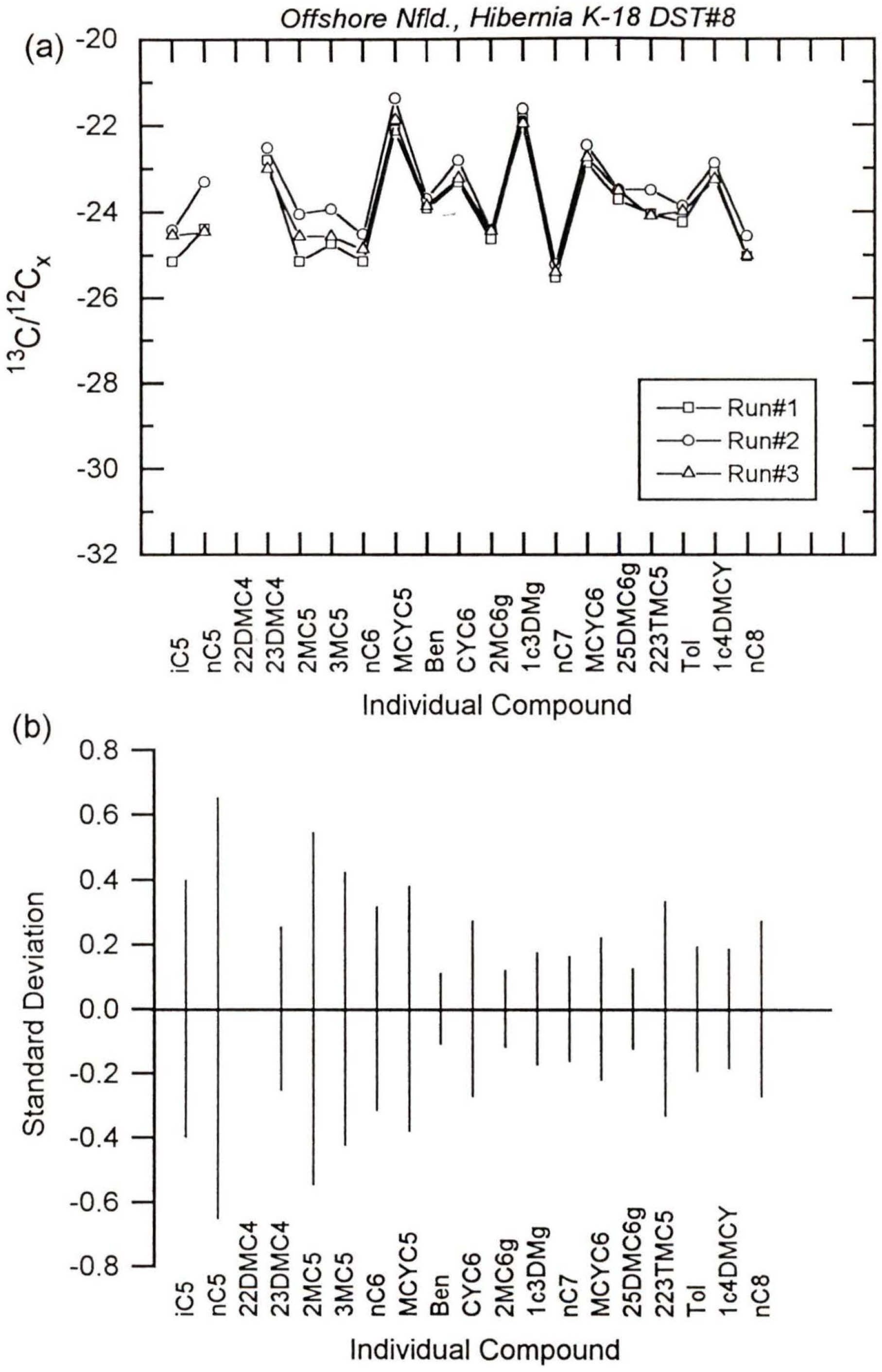


Figure 5.17 Reproducibility of Hibernia K-18 DST#8 from Offshore Nfld.:
(a) isotope ratios of each run (new sample mixed for each) and
(b) expanded scale to emphasize the standard deviation of the average isotope ratio for each compound.

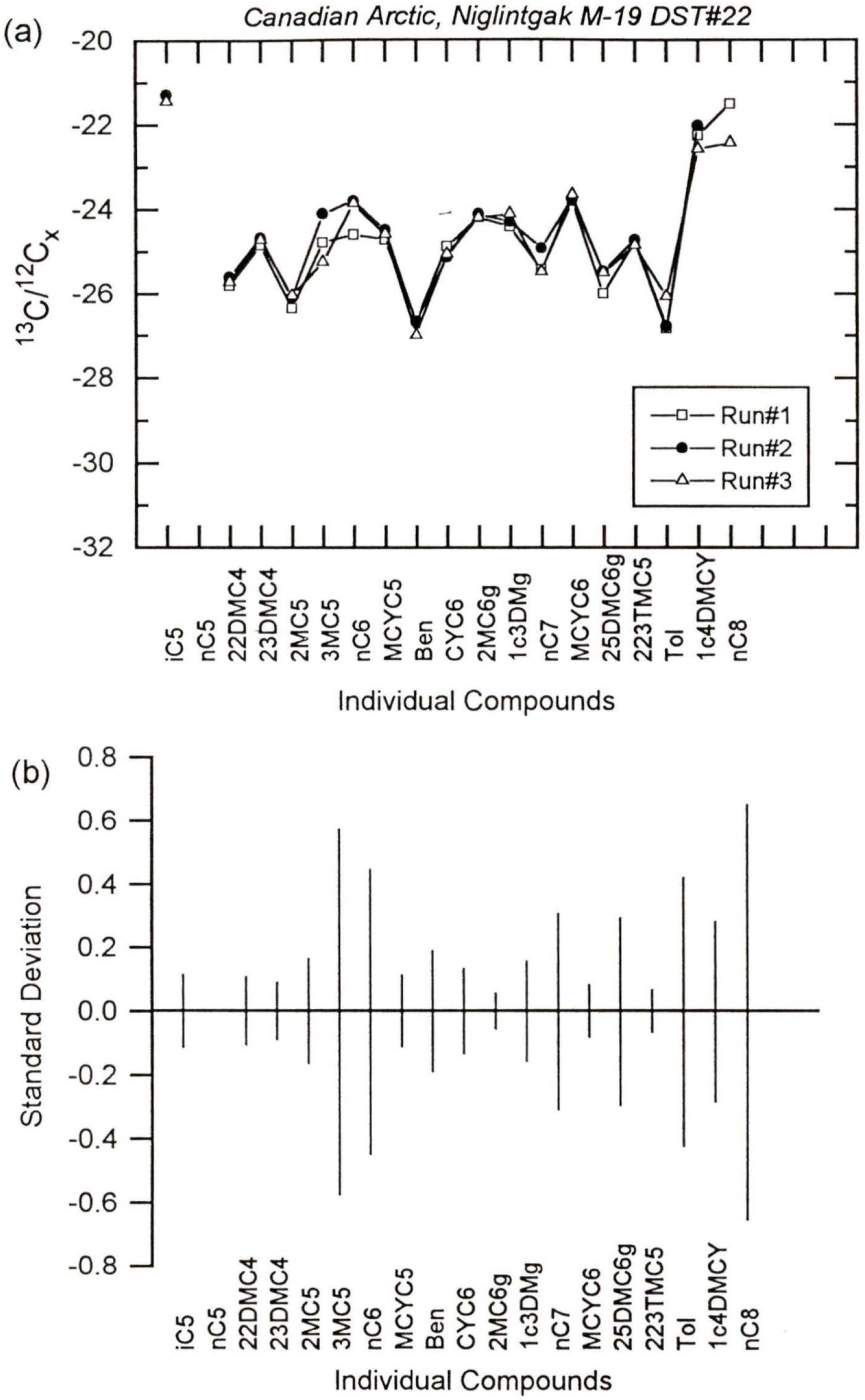


Figure 5.18 Reproducibility of Niglintgak M-19 DST#22 from the Canadian Arctic: (a) isotope ratios of each run (new sample mixed for each run) and (b) expanded scale to emphasize the standard deviation of the average isotope ratio for each compound.

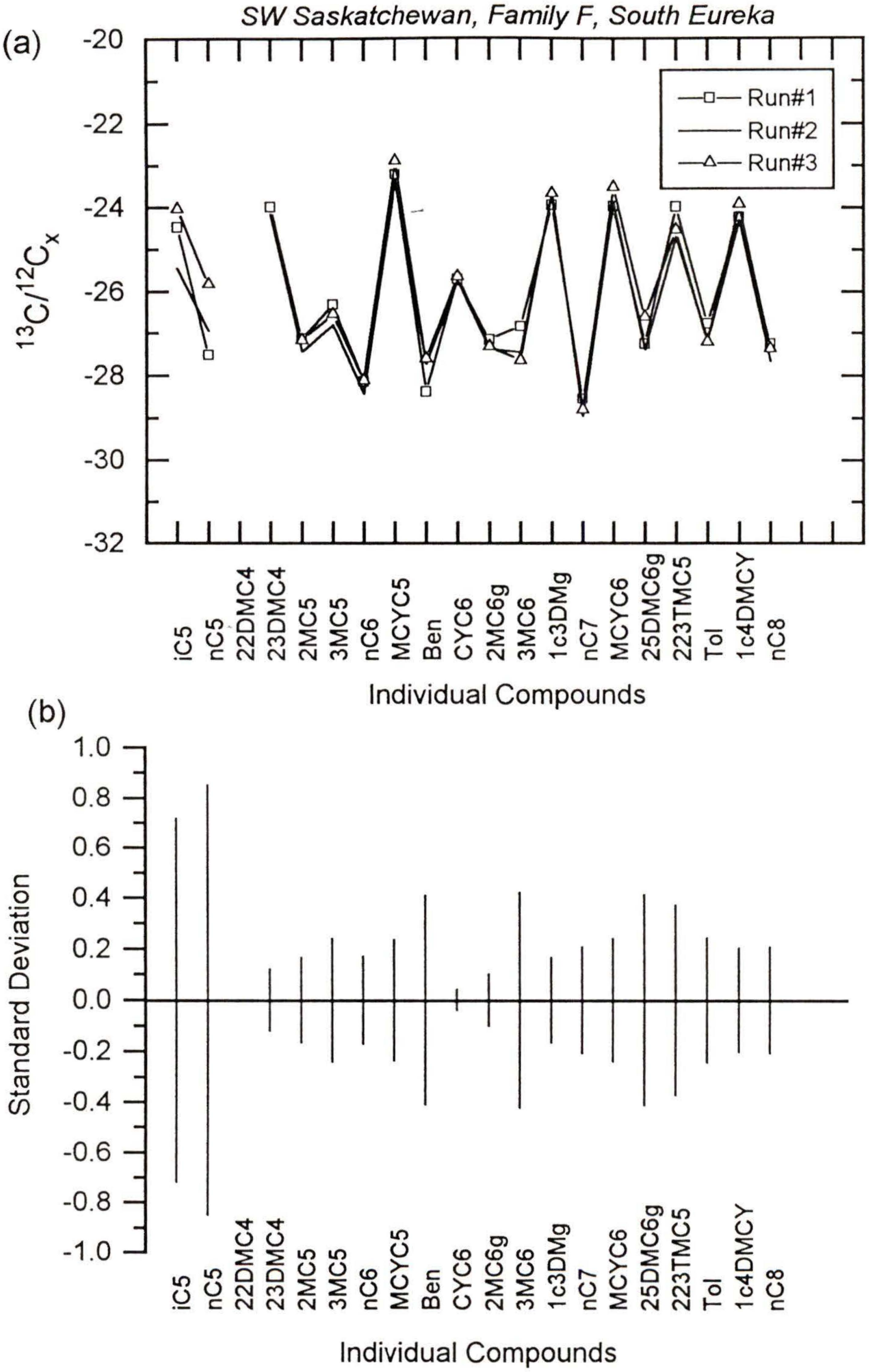


Figure 5.19 Reproducibility of South Eureka, Family F, SW Saskatchewan. (a) isotope ratios of each run when a new sample is mixed for each run and (b) expanded scale to emphasize the standard deviation of the average isotope ratio for each compound.

Also, the individual hydrocarbons are in varying concentrations in oils (e.g., $MCYC_6$ is always very large as compared to nC_5 which is usually very small.), making it virtually impossible to obtain good isotope ratios on every compound in every run.

Usually, only a couple of compounds in each run will be outside the working range for the IRMS. Since duplicates or triplicates are run for each oil, an isotope ratio can be acquired for all compounds (even though it may take additional time). If too much (or too little) sample is initially applied, the subsequent runs can be performed with a lower (or higher) amount of sample.

Although it was not tested in the current study, there may be errors associated with 'storage' of such volatile samples. If the same mixture of oil/alumina is used for duplicate runs, there may be some evaporation of the sample (during storage) in the mixing vial while the first run is proceeding. In the current study, a new sample is mixed for each run to minimize evaporation effects.

The co-elution of peaks can have a detrimental effect on isotope ratios as already described, but there is little that can be done about this. Also, the bleeding of oxygen from the combustion oven can leave the oven depleted in oxygen. Any sample passing through such an oxygen-depleted oven may not be completely oxidized leading to fractionation. This problem can be overcome by regenerating the oven as previously described. Any change in gas flows can alter the retention times of peaks leading to incorrect peak identification. This was avoided by checking the flows at the beginning and end of each day.

CHAPTER 6. RESULTS

6.1 MOLECULAR OIL ANALYSIS

Molecular data, as previously described in the Background section, can yield important information regarding source and secondary alteration. For this reason, the HMW (C_{15+}) and LMW (C_5 to C_{10}) hydrocarbons dissolved in 51 Canadian oils are molecularly analyzed. The information obtained from these analyses are used as a basis for comparison with the isotope results.

6.1.1 C_{10+} Saturate Fraction

Retention times of hydrocarbons found within the C_{10+} saturate fraction of oils are provided in Table 6.1. A reference gas chromatogram is given in Figure 6.1 to aid in identification of HMW hydrocarbons in the oils. Much of this HMW analysis has been performed by authors such as Snowdon (1987 and 1991), Fowler and Brooks (1990), Osadetz et al. (1994), and Brooks et al. (1987, 1992).

In this study, the saturate fraction gas chromatograms are referenced in Appendix B for examination of the C_{10+} compound distribution and the shape of the hump of UCM. Some of the biomarker data for the oils in this study has been obtained by other investigators such as Snowdon (1991) and Osadetz et al. (1994). Examples of the Pr/Ph ratios are included in Table 3.1. The information obtained from the C_{10+} analysis (a

Table 6.1. Compounds and corresponding retention times for the C_{10+} hydrocarbons.

Compound	Abbreviations	Retention Time (min.)
decane	C10	6.72
undecane	C11	8.97
dodecane	C12	11.29
tridecane	C13	13.54
tetradecane	C14	15.80
iso-hexadecane	iC16	17.22
pentadecane	C15	17.98
hexadecane	C16	20.05
iso-octadecane	iC18	21.09
heptadecane	C17	22.03
pristane	Pr	22.22
octadecane	C18	23.91
phytane	Ph	24.15
nonadecane	C19	25.70
isosane	C20	27.41
henicosane	C21	29.05
docosane	C22	30.62
tricosane	C23	32.13
tetracosane	C24	33.58
pentacosane	C25	34.97
hexacosane	C26	36.32
heptacosane	C27	37.62
octacosane	C28	38.88
nonacosane	C29	40.11
triacontane	C30	41.40
hentriacontane	C31	42.81
tritriacontane	C33	46.83
	C34	48.91
	C35	51.46
	C36	54.49
	C37	58.38
	C38	62.95

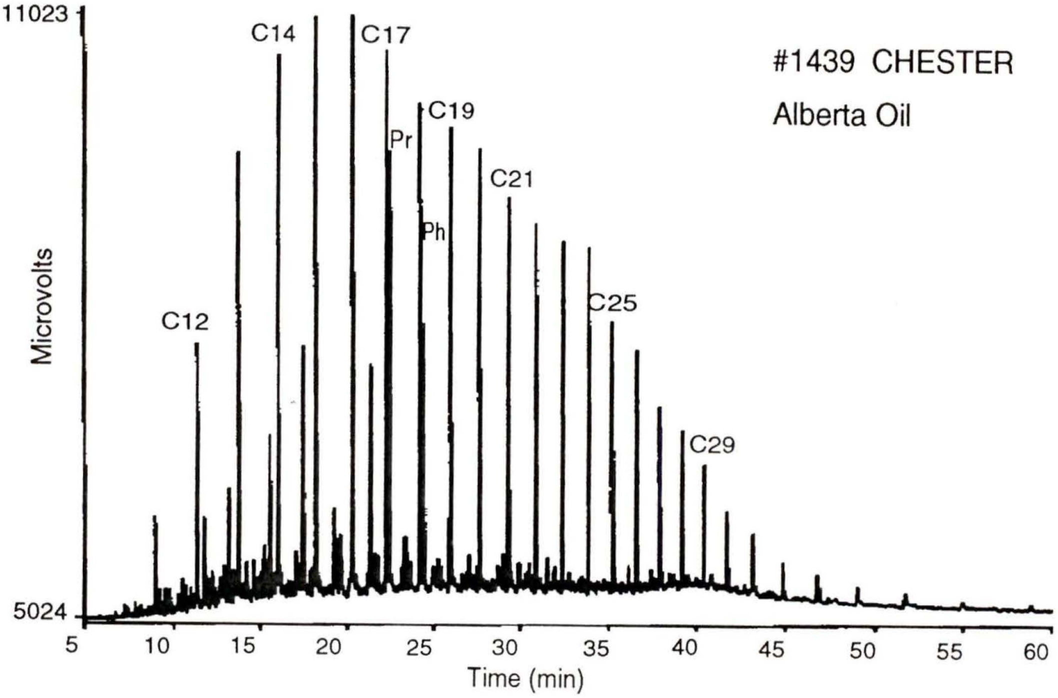


Figure 6.1 High molecular weight chromatogram for the Chester oil standard. This chromatogram can be used as a reference for the other oils.

standard geochemical technique) is used for comparison with the results of the newer gasoline range analysis.

To demonstrate the difference between a saturate fraction gas chromatogram of a non-biodegraded and a biodegraded, two representative chromatograms are provided in Figure 6.2. Chester, a non-biodegraded, conventional oil, has a dominance of n-alkane peaks with a smooth baseline (absence of UCM). In contrast, Family C #726 Battle Creek oil has a large reduction in the n-alkanes as well as increased UCM.

6.1.1.1 East Coast Oils

All of the Hibernia oils (Figure B1) have a prominent n-alkane distribution and a smooth naphthenic envelope (unresolved branched and cyclic compounds; low UCM), indicating that the samples are not biodegraded and that they are relatively mature. Fowler and Brooks (1990), using biomarker data, observed that the original maturity of the lowermost oil (e.g., Hibernia K-18 DST#1) is being subtly changed from the upward migration of more mature oil while the shallower oils are not affected (due to fault closure more mature oils can not reach shallower depths). This maturity trend is not clear from simple observation of the C_{10+} chromatograms.

Mara M-54 oil (Figure B2) from DST#2 (#454) is probably not degraded (or has very low biodegradation) since it has the most prominent n-alkane distribution and the smoothest naphthenic envelope of the three oils from this well. Oils from DST# 1 (#453) and 3 (#455) have more visible UCM, and the n-alkanes are more reduced. It is difficult

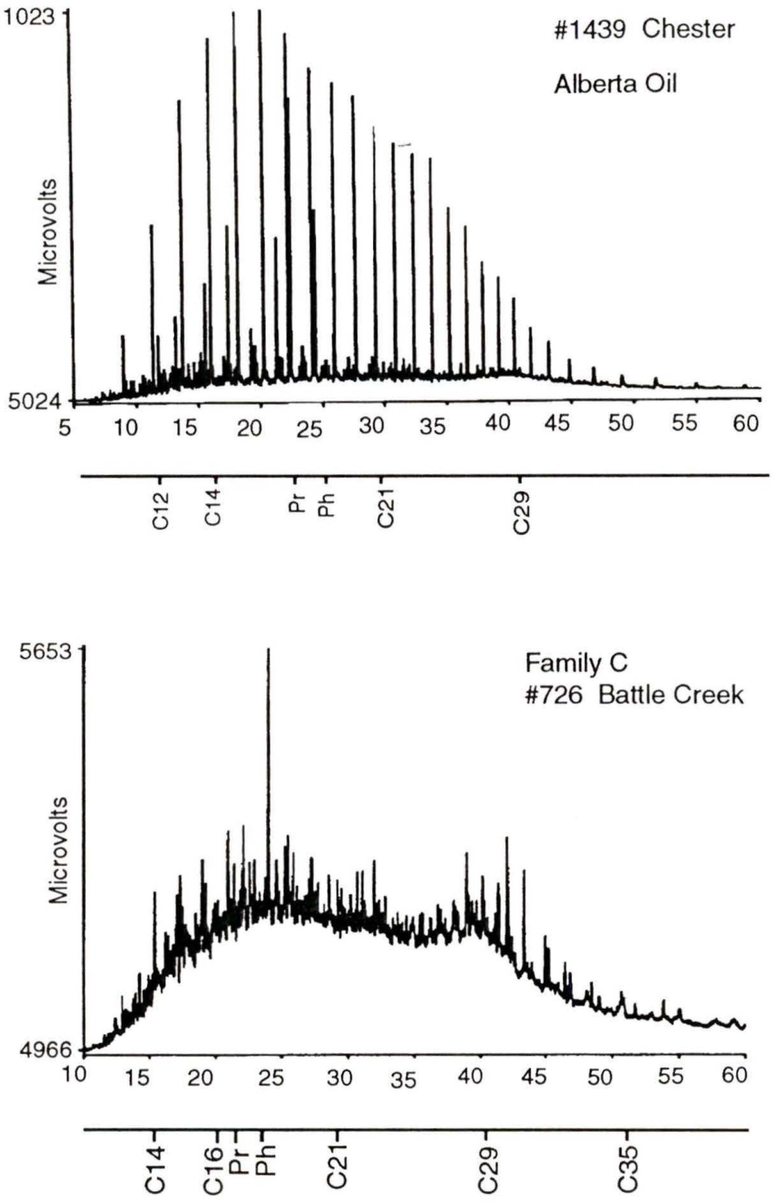


Figure 6.2 HMW gas chromatogram comparison of a non-biodegraded (Chester) and biodegraded (#726 Battle Creek) oil.

to determine which of these two oils is more degraded. The DST#1 (#453) oil appears to have slightly more n-alkanes, and it is located at a greater depth. The DST#3 (#455) oil, located at the shallowest depth, appears to have lower n-alkane concentrations and is probably the most biodegraded oil of the samples studied from this well. Von der Dick et al. (1989) has suggested that the Mara M-54 DST#1 oil (2704 to 2708.8 m) is derived from a mixed, biodegraded Hibernia-type oil with a later generated, more mature oil from the same source interval. At depths of 1852 m, the oils (DST#2 and #3) undergo continuous biodegradation (see section 4.1).

The biodegradation trends in the oils from Hebron I-13 (Figure B3) are not very clear since all have dominant n-alkanes. The biodegradation in this well is probably not very strong. Oil from DST#1 is not biodegraded since it is located at the greatest depth in the well and contains dominant n-alkanes with a smooth naphthenic envelope. Oil from DST#5 and DST#7 are slightly more biodegraded. The compound distribution in oil from DST#6 (#247) is different from the other oils in this well in that the heavier and lighter compounds are greatly reduced with the mid-range compounds very prominent and the naphthene envelope is beginning to rise. DST#9 (#249) and DST#10 (#248) are the most biodegraded samples in this well since the n-alkanes are reduced and the corresponding naphthene envelopes are not very smooth. It is difficult to determine which of these 2 oils has undergone the greatest degradation. DST#9 (#249) seems to have the greatest reduction in n-alkanes and the baseline is not really smooth so it may be the most degraded oil from this well.

All of the n-alkanes in the East Coast oils are mainly concentrated in the less than C_{25} range which is indicative of a relatively mature, marine source (Snowdon and Fowler, Course Notes, 1991). This source has been described as an organic rich shale of the Egret Formation with kerogen composed of dinoflagellate material (Swift and Williams, 1980; McAlpine, 1989). Pr/Ph ratios for the East Coast oils range between 0.8 and 1.2 (Table 3.1) which is indicative of a marine or reducing environment.

6.1.1.2 Arctic Oils and Condensates

The Arctic suite of samples is composed of both oils and condensates (Snowdon, 1978). All of the Arctic samples are biodegraded to some extent since the chromatograms indicate a reduction in the concentration of n-alkanes. In addition, the Arctic samples all have low maturity (Snowdon and Powell, 1982; Snowdon, 1991).

In the Niglintgak M-98 well (Figure B4), the DST#9 (#74) oil is the least degraded followed by DST#10 (#37). Oils from DST #16 (#34), 20 (#69), and 22 (#33) all exhibit greater biodegradation since the n-alkanes are reduced with increased UCM. DST#22, located at the shallowest depth, is the most degraded of the 3 oils. Niglintgak B-19 (#75) is similar to these 3 biodegraded oils.

Samples from DST#13 (#72), DST#14 (#71), and DST#19 (#70) are all condensates (Snowdon, 1978). They do not have any compounds present above nC_{19}. These condensates (Figure B5) all appear to be biodegraded since the n-alkanes are present in low concentrations and each chromatogram has prominent UCM. As depth decreases, the reduction in n-alkanes of the corresponding condensates (e.g., DST#13, 14, and 19) becomes more pronounced. DST#13 is the least biodegraded condensate while DST#19 is the most degraded.

The use of C_{10+} data for providing genetic or alteration information about the Niglintgak condensates is limited. The data may represent only a small portion of the compounds in the samples. Condensates contain mostly light hydrocarbons with chain lengths less than C_{19}. The techniques used to isolate the C_{10+} compounds (e.g., distillation) may exclude the majority of hydrocarbons which compose the condensates.

The sequence of biodegradation in the Nerlerk M-98 oils (Figure B6) is opposite to the expected trend. There is an increase in biodegradation with depth. As depth increases, the reduction in n-alkanes and the presence of the two humps of UCM in the corresponding oils (DST#9, 8, 7, 6, 5, and 4A respectively) generally become more pronounced. Therefore, DST#9 is the least biodegraded while DST#4a is the most biodegraded oil.

In general, most of the Arctic oils and condensates have Pr/Ph ratios greater than 3 (Table 3.1) which is indicative of terrestrial organic matter that has been partially oxidized at some time (Snowdon and Powell, 1979). The chromatograms for Arctic samples show individual humps of UCM, probably due to terpenoid derivatives, which indicate relative immaturity (e.g., approximately 0.5 to 0.7 % vitrinite reflectance (Ro); Tissot and Welte, 1978).

6.1.1.3 Saskatchewan Oils

'Family F' chromatograms resemble those of 'Family C' to a great extent. Family C oils (Figure B7) Butte (#677) and Cantuar Main (#733) have an n-alkane dominance and a smooth naphthene envelope which indicate no biodegradation (or little). Battle Creek (#727) has intermediate biodegradation. Battle Creek (#726) and Battrum U1 (#675) have greatly reduced n-alkane compositions as well as more pronounced UCM which indicate these two oils are the most degraded samples of the 5 chosen from this family.

'Family F' oils (Figure B9) Kerrobert (#821) and South Eureka (#818) are not biodegraded. Forgan (#826) exhibits intermediate biodegradation. Plato (#812) has been affected by intermediate or high biodegradation. Smiley (#816), with more reduced n-alkanes and increased UCM, is probably the most biodegraded oil of the five samples studied from this family.

The compound distributions in 'Family E' oil chromatograms (Figure B8) are different than those for Family C and F oils. All Family E oils may have been subjected to a greater degree of biodegradation as indicated by their lower n-alkane concentrations and prominent UCM as compared to Family F and C oils. Also, there appears to be a bimodal distribution of n-alkanes in this family (n-alkanes concentrated in the less than C_{25} range with some additional alkanes in the greater than C_{25} range) whereas Families C and F have a smooth distribution of n-alkanes up to approximately nC_{30}.

Although all Family E oils are biodegraded, Court (#822), with the most prominent n-alkane distribution and the smoothest naphthene envelope of the oils from this family, is the least biodegraded. North Hoosier (#817) and Hearts Hill (#833) exhibit intermediate biodegradation. Cactus Lake (#829) and Buffalo Coulee B (#836), with the lowest concentrations of n-alkanes and the most prominent UCM, are the most degraded oils. There is no clear trend here for biodegradation with depth.

The saturate fraction gas chromatogram of Lake Alma oil from Family A (Figure B9) has a smooth baseline with an n-alkane dominance. The compound distribution indicates that this oil is not biodegraded.

The Pr/Ph ratios for the southwest Saskatchewan oils are less than 3 (Table 3.1). Most of these values fall below 2, indicating a more marine or reducing environment for the source organic matter (e.g., Family F). Family E oils have 2 members with Pr/Ph values less than one while Family C has all values less than 1. These low values are indicative of a very reducing or anoxic bottom water environment.

6.1.1.4 Alberta Oils

All of the Alberta oils (Figure B10) in this study from the Western Canada Sedimentary Basin are not biodegraded. The naphthenic envelopes (baselines) of the oils are smooth and the n-alkanes are present in high concentrations. The compound distribution of Willesden Green (#914), Turner Valley (#970), and Chester (#1439) are

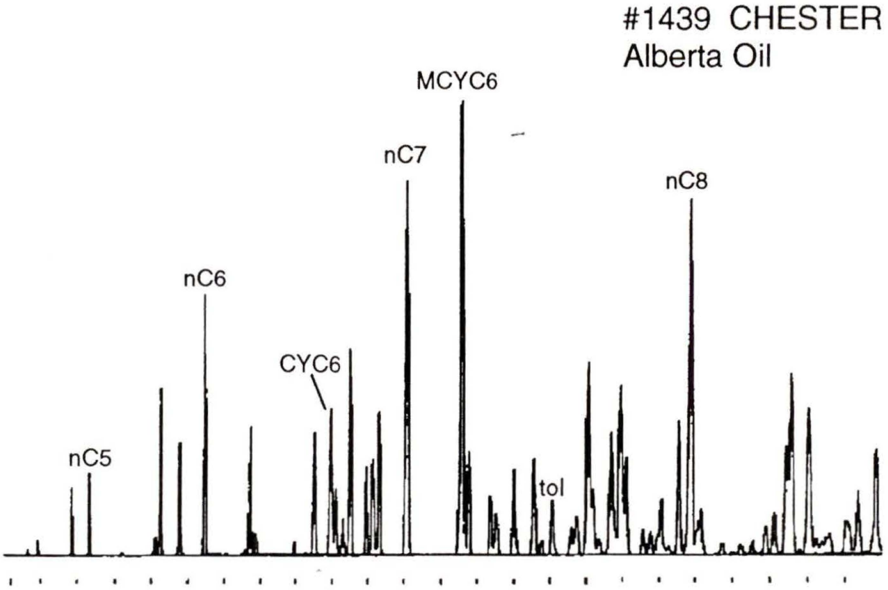


Figure 6.3 Gasoline range chromatogram for the Chester oil standard. This chromatogram can be used as a reference for the other oils.

similar and slightly different from the compound distribution of Rainbow (#205) and Shekilie (#703).

6.1.2 C_5-C_{10} Gasoline Range Fraction

The retention times of the gasoline range hydrocarbons are included in Table 5.2. A reference chromatogram of the non-biodegraded Chester oil is given in Figure 6.3 to aid in the identification of the individual hydrocarbons. All other chromatograms are included in Appendix C. The distribution of gasoline range hydrocarbons in the oils are reported here.

To demonstrate the difference in compound distribution between the gasoline range gas chromatograms for a biodegraded and a non-biodegraded oil, two chromatograms are given in Figure 6.4. The non-biodegraded Chester oil has an n-alkane dominance, but several other compounds are also present in significant concentrations such as $MCYC_6$. The biodegraded Mara M-54 DST#3 has reduced n-alkanes with more dominant cycloalkanes.

6.1.2.1 East Coast Oils

All of the non-biodegraded Hibernia oils (Figure C1) have similar gasoline range compound distributions with high concentrations of most hydrocarbons, especially the n-alkanes. Benzene and toluene are also present in high concentrations (no water-washing effect). Since the differences in compound distribution among the oils here are subtle, they may be better represented through plots of particular molecular parameters such as Thompson's PI1 and PI2 or Mango's isoheptane index (see Discussion).

In the Mara M-54 well (Figure C2), the gasoline range compound distributions in oils from DST#2 (#454) and DST#1 (#453) both exhibit high concentrations of n-alkanes as well as benzene and toluene (typical of non-biodegraded oils lacking water-washing). Several other branched and cyclic compounds are present in significant quantities especially $MCYC_6$. Some of the hydrocarbons in lower concentrations in these samples are $22DMC_4$, $23DMC_4$, $223TMC_5$, $1c3DMCYC_5$, $1t3DMCYC_5$, $1t2DMCYC_5$, and $223TMC_5$. Although these two oils have similar compound distributions, they are clearly

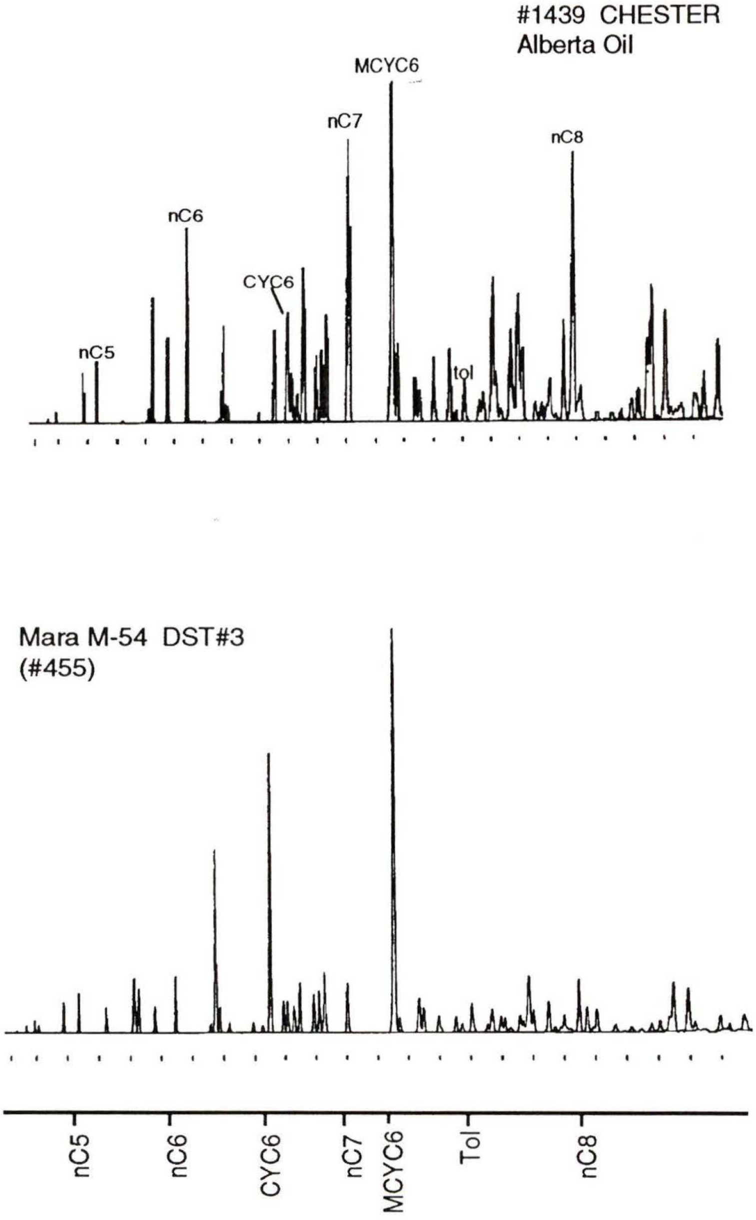


Figure 6.4 Gasoline range chromatogram comparison of a non-biodegraded (Chester) and a biodegraded (Mara DST#3) oil.

different from the compound distribution in the most biodegraded DST#3 (#455) oil which has reduced hydrocarbon concentrations (especially the n-alkanes). The dominant hydrocarbons remaining in this biodegraded oil are cyclic and branched compounds such as $MCYC_5$, CYC_6, $MCYC_6$, and $23DMC_4$.

Hebron I-13 oils (Figure C3), in general, show a trend with depth in that the n-alkanes become more dominant with increasing depth (DST#10, 9, 7, 6, 5, and 1 respectively). The chromatograms from DST#7, 6, 5, and 1 oils are similar with high concentrations of most compounds (especially the n-alkanes) which indicates no (or low) biodegradation. DST#10 and 9 oils are more degraded since they have a greater reduction in n-alkanes. The most degraded oil, located at the shallowest depth, is DST#10. Benzene and toluene have not been reduced very much in this suite of oils except in DST#10, indicating that only limited water-washing has occurred except in the case of extreme biodegradation.

6.1.2.2 Arctic Oils and Condensates

Gasoline range compound distributions in chromatograms from the Arctic oils (Niglintgak M-19 DST#9, 10, 16, 20, and 22; Niglintgak B-19 DST#14) and condensates (Niglintgak M-19 DST#19, 14, and 13) are different from those of the East Coast oils. In general, the hydrocarbon concentrations in all Arctic oils are reduced, indicating greater biodegradation for Arctic oils as compared to the East Coast oils.

All of the Arctic oils are biodegraded to some extent. The least biodegraded oil (Figure C4) of the Niglintgak M-19 well (DST#9) has relatively high concentrations of $MCYC_5$, CYC_6, $MCYC_6$, toluene, benzene, and the n-alkanes. The concentrations of these compounds in oils decrease with decreasing depth. The most biodegraded oil (DST#22) has low concentrations of n-alkanes, branched alkanes, and some of the cycloalkanes such as $MCYC_5$, $1c3DMCYC_5$, $1c3DMCYC_5$, and $1t2DMCYC_5$. The other intermediate oil samples have similar compound distributions and concentrations to each other and to the endmember oils of this well.

The Niglintgak B-19 (#75) oil sample has a different compound distribution than all of the Niglintgak M-19 oils and condensates. $23DMC_4$, $1c3DMCYC_5$, $1t3DMCYC_5$, $1t2DMCYC_5$, and $3MC_7$ are present in the highest concentrations, followed by $MCYC_5$, CYC_6, $11DMCYC_5$, $MCYC_6$, $1c2DMCYC_5$, $223TMC_5$, and $1c4DMCYC_6$. The n-alkanes and some of the branched hydrocarbons are reduced, but the cycloalkanes are present in the highest concentrations. This sample may be only mildly affected by biodegradation and water-washing. It could have been subjected to slightly different geochemical conditions than the oils from the other well.

Niglintgak M-19 DST#13, the least biodegraded condensate (Figure C5), has high concentrations of many cyclic compounds such as $MCYC_5$, CYC_6, $MCYC_6$, $3MC_7$, $1c3DMCYC_5$, $1t3DMCYC_5$, and $1t2DMCYC_5$. Toluene and $223TMC_5$ are also present in significant quantities. Many of the branched compounds are reduced as well as the n-alkanes and benzene. Niglintgak M-19 DST#19, the most biodegraded condensate, has a compound distribution similar to oil from DST#13, but the compounds in the DST#19 oil are more reduced.

Nerlerk M-98 DST#9 (#309, Figure C6), which is classified as the least biodegraded oil in this well from the C_{10+} saturate fraction chromatograms (and previous studies), has almost all of the compounds eluting before $MCYC_6$ absent. Toluene, $MCYC_6$, and $223TMC_5$ are more dominant, but even these are present in low concentrations. It is possible that the gasoline range hydrocarbons were lost (e.g., gas/oil separation) during collection at the well.

The gasoline hydrocarbons are present in higher concentrations in the DST#8 (#311) oil than in the DST#9 oil. Some of the cycloalkanes such as $MCYC_5$, CYC_6, and $MCYC_6$ are present in the highest concentrations followed by the n-alkanes and aromatics (e.g., benzene and toluene). Compounds in lower concentrations include $22DMC_4$, $1c3DMCYC_5$, $1t3DMCYC_5$, $1t2DMCYC_5$, and $2MC_6$, and $3MC_6$. As depth and biodegradation increase (DST#7, 6, 5, 4A respectively), several changes in compound distribution take place. Hydrocarbons eluting before $MCYC_5$ are reduced to almost absent while the n-alkanes, branched alkanes, and cycloalkanes are reduced to a smaller degree. $MCYC_6$, toluene, and $223TMC_5$ are the only hydrocarbons remaining in significant amounts.

6.1.2.3 Saskatchewan Oils

Consistent with the results of the C_{10+} saturate fraction, the gasoline range compound distribution of Saskatchewan oils is not dependent on depth. The non-biodegraded Family C oil (Figure C7), Cantuar Main (#733), has an n-alkane dominance with some branched compounds and MCYC6 in high concentrations. Benzene and toluene are low, indicating a possible water-washing effect. These compounds are gradually reduced as biodegradation increases through the series of samples Butte (#677), Battrum U1 (#675), and Battle Creek (#726). The cyclic compounds such as $MCYC_5$, $MCYC_6$, and CYC_6 as well as some branched such as $2MC_5$ and $3MC_5$ become more dominant.

In Family F (Figure C8), similar trends from no (or low) biodegradation to high biodegradation occur through the series Kerrobert (#821), South Eureka (#818), Forgan (#826), Plato (#812), and Smiley (#816). In Family E (Figure C9), similar trends occur through the series Court (#822), North Hoosier (#817), Hearts Hill (#812), Buffalo Coulee B (#836), and Cactus Lake (#829). North Hoosier, unexpectedly, is lacking in almost all of its gasoline range compounds. These gasoline range hydrocarbons may have been lost during collection of the sample. Lake Alma from Family A, which is not biodegraded, has compounds nC_6, nC_7, and nC_8 in high concentrations. All other compounds are present in significantly lower concentrations than these n-alkanes.

Another observation to note is an inconsistency between the C_{10+} and the gasoline range data of some of the southwest Saskatchewan oils (e.g., especially within Family E).

In Figure 6.5, Cactus Lake is composed of few n-alkanes in the C_{10+} range, but a significant portion of n-alkanes in the gasoline range. This unexpected observation could be due to the addition of light hydrocarbons (C_5 to C_{10}) to pre-existing, possibly biodegraded oil.

6.1.2.4 Alberta Oils

All of the Alberta oils (Figure C10) examined in this study from the Western Canada Sedimentary Basin have dominant n-alkane concentrations as well as relatively high aromatic concentrations. They have not been subjected to secondary alteration processes such as biodegradation or water-washing. The composition of Turner Valley (#970) is different from the other Alberta oils in that all of the hydrocarbons eluting before nC_7 are reduced.

Oil and condensate information such as location, depth, and presence or absence of secondary alteration are noted in Table 4.1 for reference.

6.2 STABLE CARBON ISOTOPE ANALYSIS OF GASOLINE RANGE HYDROCARBONS

The molecular composition of an oil changes as a result of secondary alteration processes which can lead to difficulties in oil correlations. The isotope ratios of hydrocarbons in oils may be more resistant to degradation than molecular composition, allowing correlation of altered oils. The stable carbon isotopes of individual gasoline

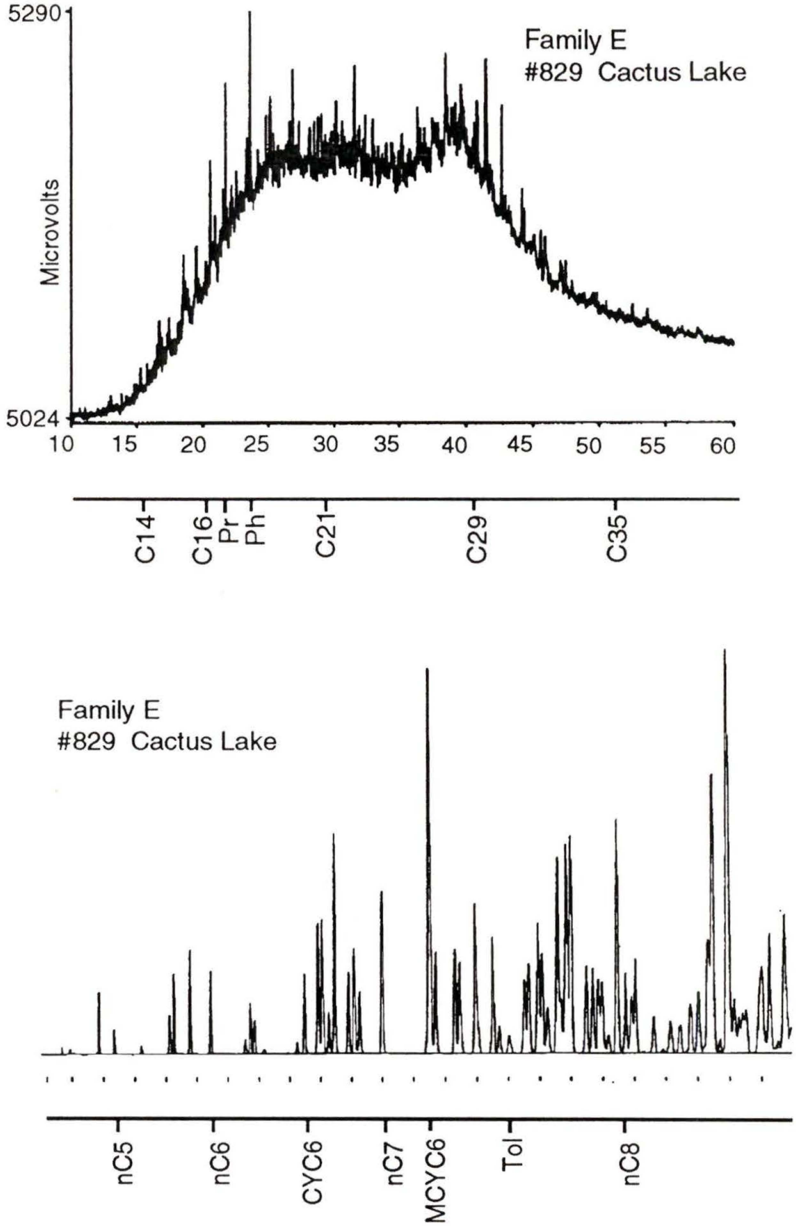


Figure 6.5 HMW and LMW chromatogram comparison of Cactus Lake of Family E in Saskatchewan.

range hydrocarbons in the 51 Canadian oils are measured by GC-C-IRMS analysis. These isotope ratios are listed in Table D1 (Appendix D).

Several compounds were omitted from this isotope data for a variety of reasons. In general, all of the isotopes corresponding to compounds eluting between toluene and 1c4DMCYC$_6$ were not reported since the separation was poor (leading to unreliable isotopes as shown in Methods). For particular oils, different compounds may be excluded if their concentrations are not within the working range for the IRMS (e.g., too low such as nC$_5$, 23DMC$_5$, or 1c2DMCYC$_5$ or too high such as occasionally MCYC$_6$).

It is important to remember that several of the isotope ratios are artificial (e.g., the 1c3DMCYC$_5$, 1t3DMCYC$_5$, 1t2DMCYC$_5$ group and several others as given in Methods). It is possible that by grouping these compounds together and thus creating a 'bulk' isotope ratio for them, some of the natural variation in the oils may be reduced.

6.2.1 General Isotope Variation in Oil or Condensate Samples

The lightest isotope measured in this study was -32 ‰ (for benzene in #675 Battrum U1 of Family C) while the heaviest isotope measured was -20 ‰ (CYC$_6$ of #75 Niglintgak B-19). The variation in the individual isotope ratios of gasoline range hydrocarbons in 12 oil samples representative of the four study areas (one from each of the wells) is approximately 10 to 12 ‰ (Figure 6.6). The isotopic variation within any one oil is between 4 and 6 ‰. The Hibernia oil shown in Figure 6.7 has an isotopic

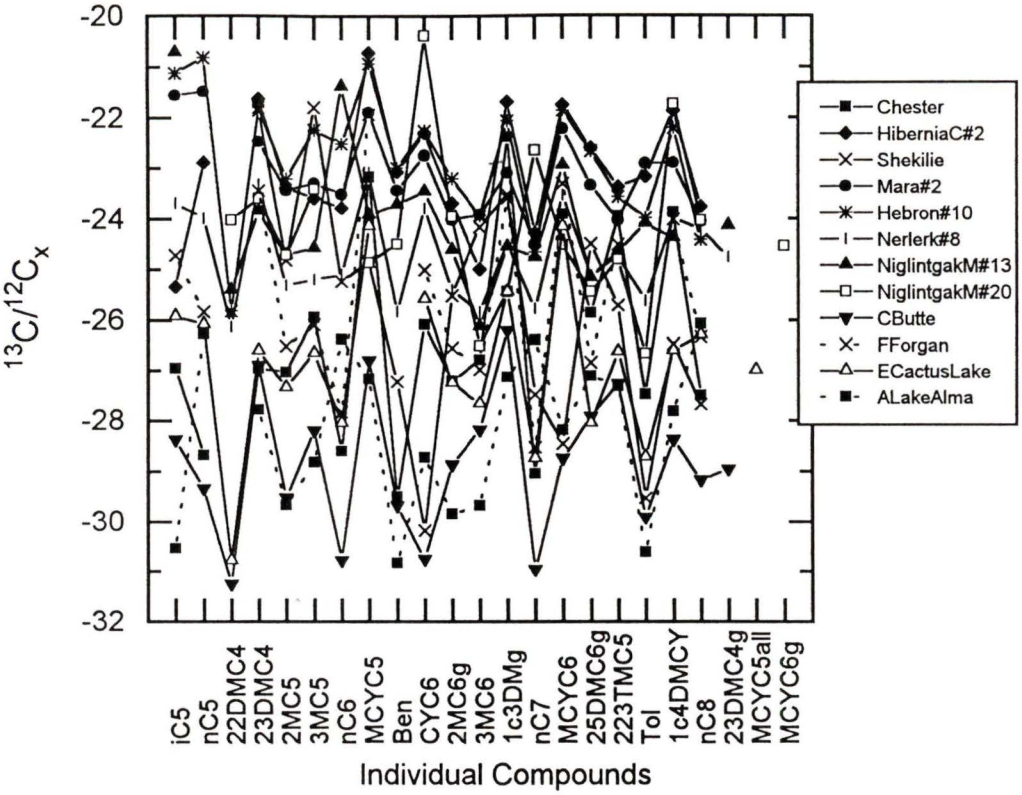


Figure 6.6 Large isotope variation in 12 oils from the four study regions.

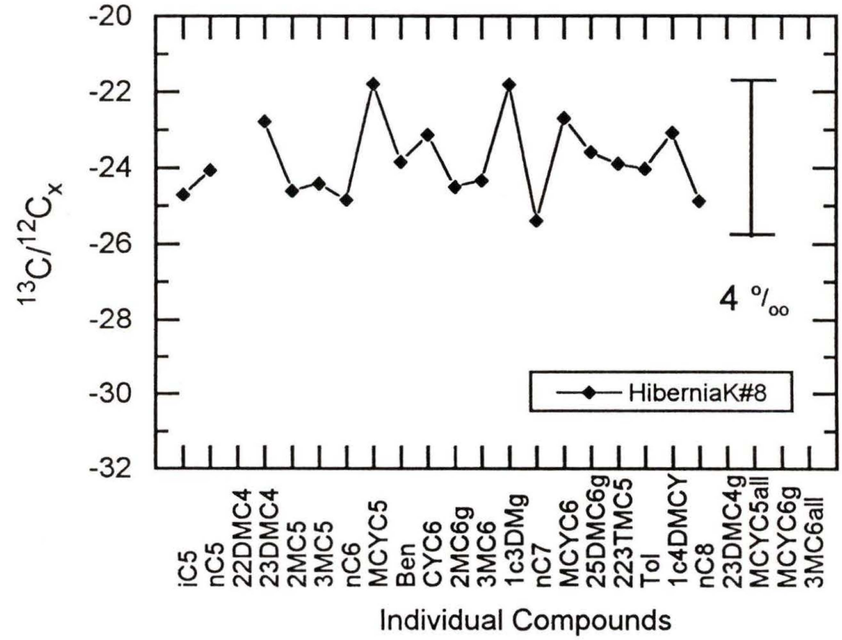


Figure 6.7 Carbon isotope variation for gasoline hydrocarbons in an individual oil. Depending on the sample, the variation ranges from 4 to 6 ‰ .

range of 4 ‰, but this can vary up to 6 ‰ depending on the oil and its location (or source).

The range in carbon isotopic composition of major oil classes (e.g., n-alkanes, cycloalkanes, branched alkanes, and aromatics) is approximately 10 ‰ (Figure 6.8). The variation in carbon isotopic composition of particular hydrocarbons (e.g., nC_6, $MCYC_6$, $2MC_5$, and ben) for all the oil samples as well as the standard deviations (from 3 runs) for each oil measurement are given in Figure 6.9. This variation is again about 10 ‰. The standard deviations for the isotope measurements are usually low (e.g., ± 0.3 ‰ or less, but up to a maximum of 1‰ in some cases). The isotope ratios of benzene, the aromatic hydrocarbon (Figure 6.9d), show a high variance (about 2 to 4 ‰) in 4 oil samples which may be attributed to low benzene concentrations. Thus, the isotopic variation is carried throughout the individual hydrocarbons.

The 10 to 12 ‰ carbon isotope variation associated with the oil samples in this study is much larger than the average experimental error (as seen in the Methods section and from the standard deviations shown in Figure 6.9 for individual hydrocarbons) of ± 0.3 to 0.5 ‰.

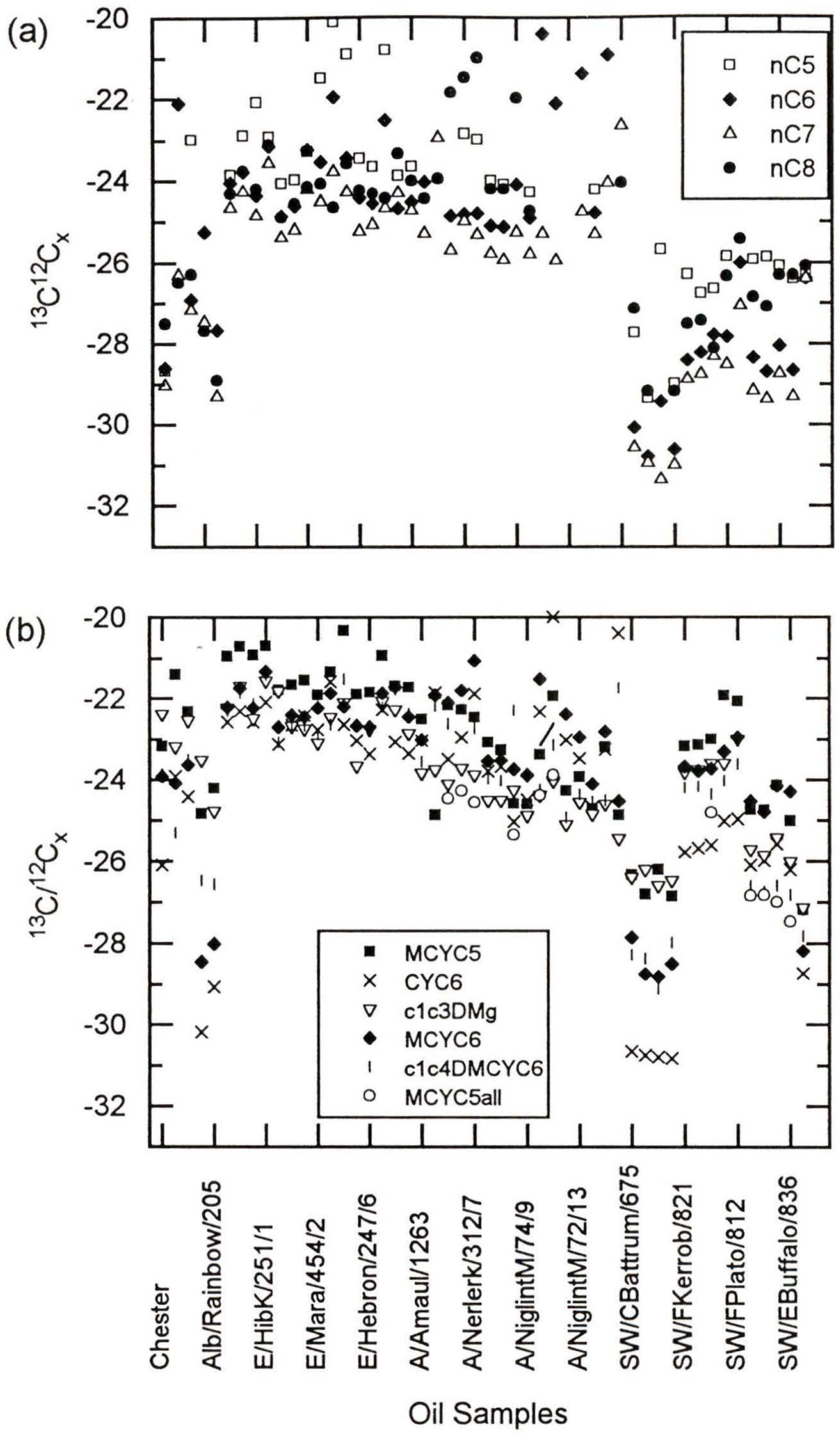


Figure 6.8 Carbon isotope variation in major oil classes such as (a) n-alkanes, (b) cycloalkanes, (c) branched alkanes, and (d) aromatics. The majority of the compounds in each class show a 6 $^{o}/_{oo}$ variation, but since there are some oils in each class with extremely different isotope ratios, the overall variation for each class is about 10 $^{o}/_{oo}$.

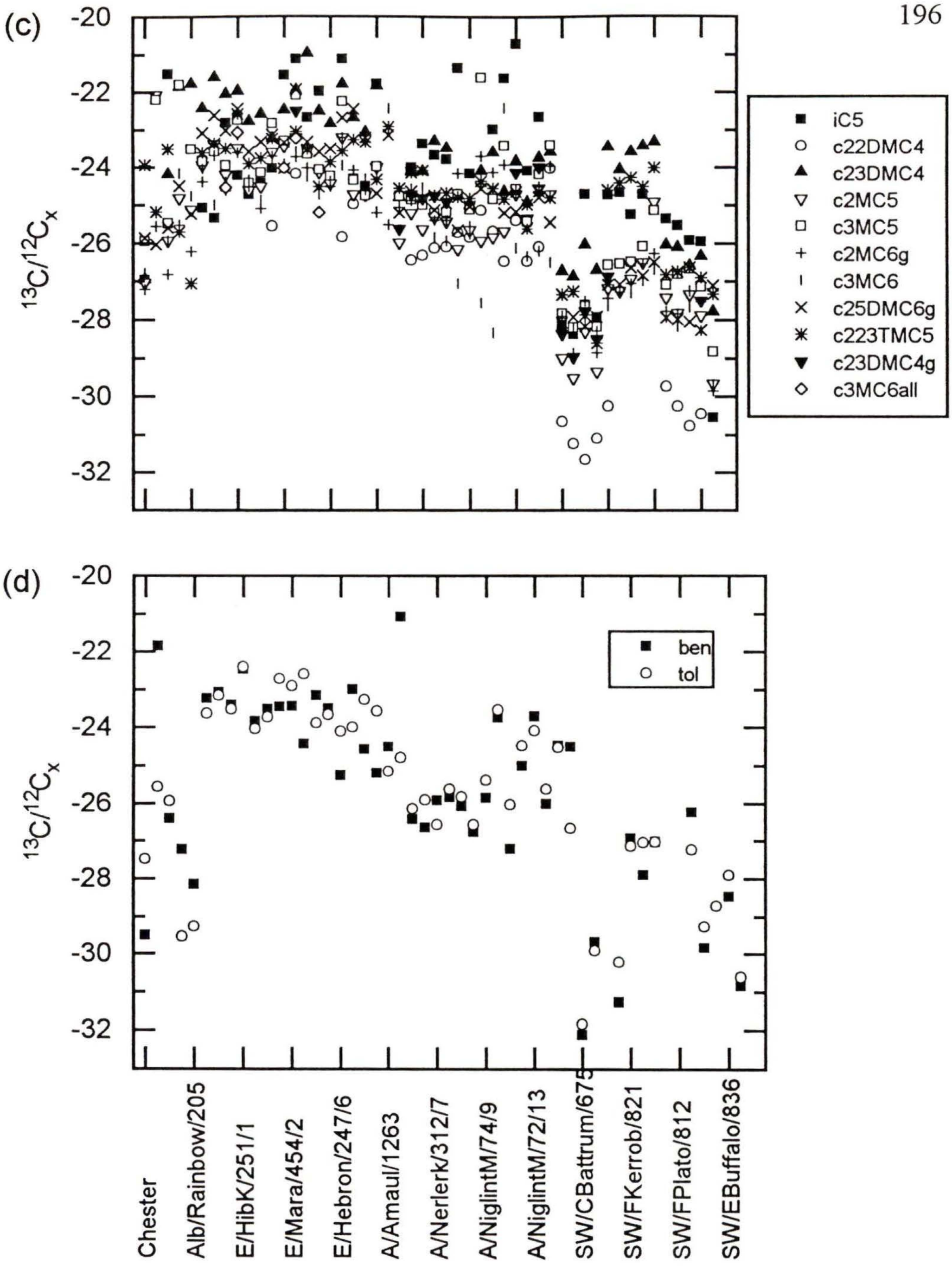


Figure 6.8 Carbon isotope variation in major oil classes, continued.

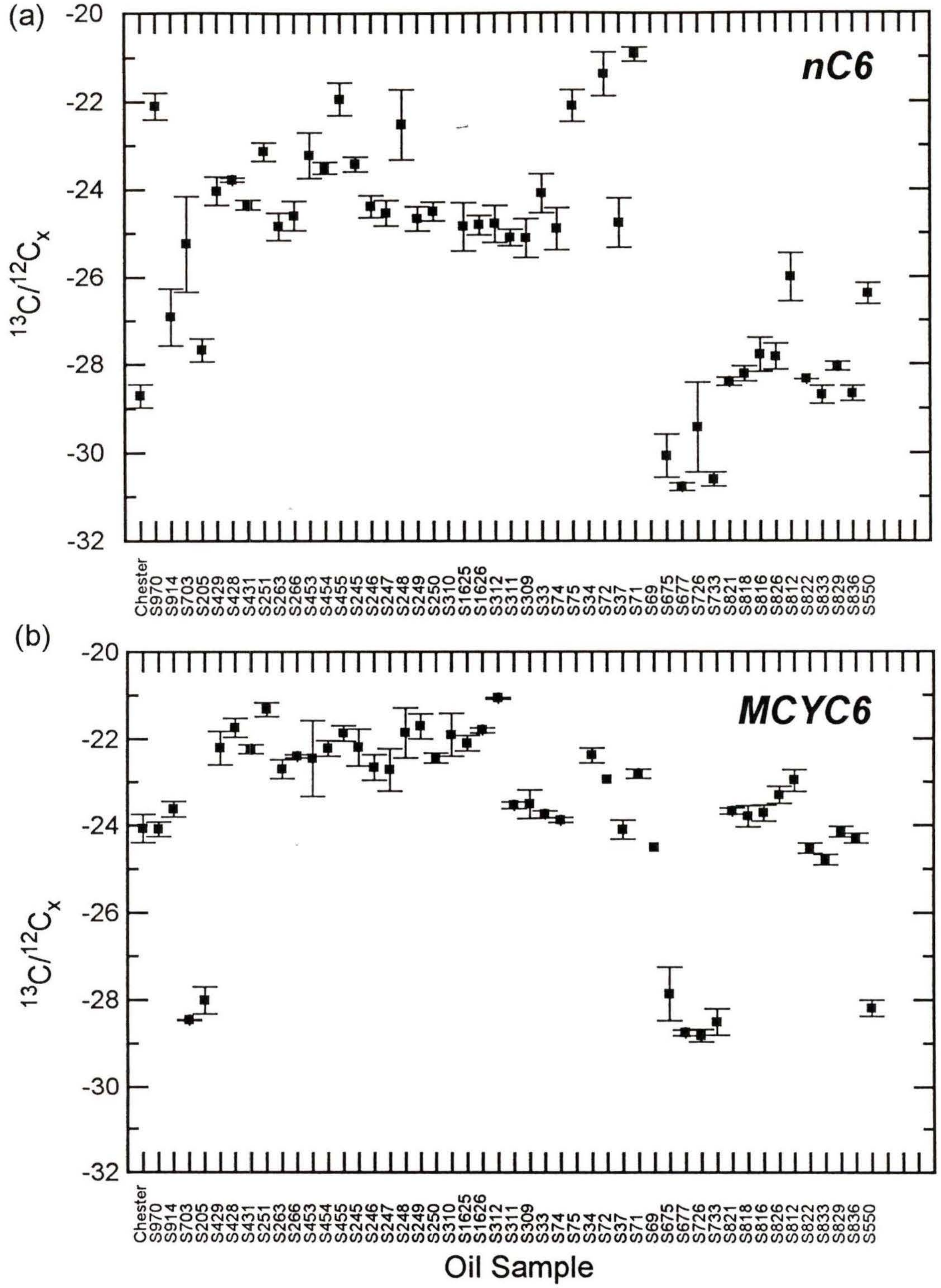


Figure 6.9 Carbon isotope variation in an individual hydrocarbon. Examples are given of the (a) n-alkanes, (b) cycloalkanes, (c) branched alkanes, and (d) aromatic hydrocarbons.

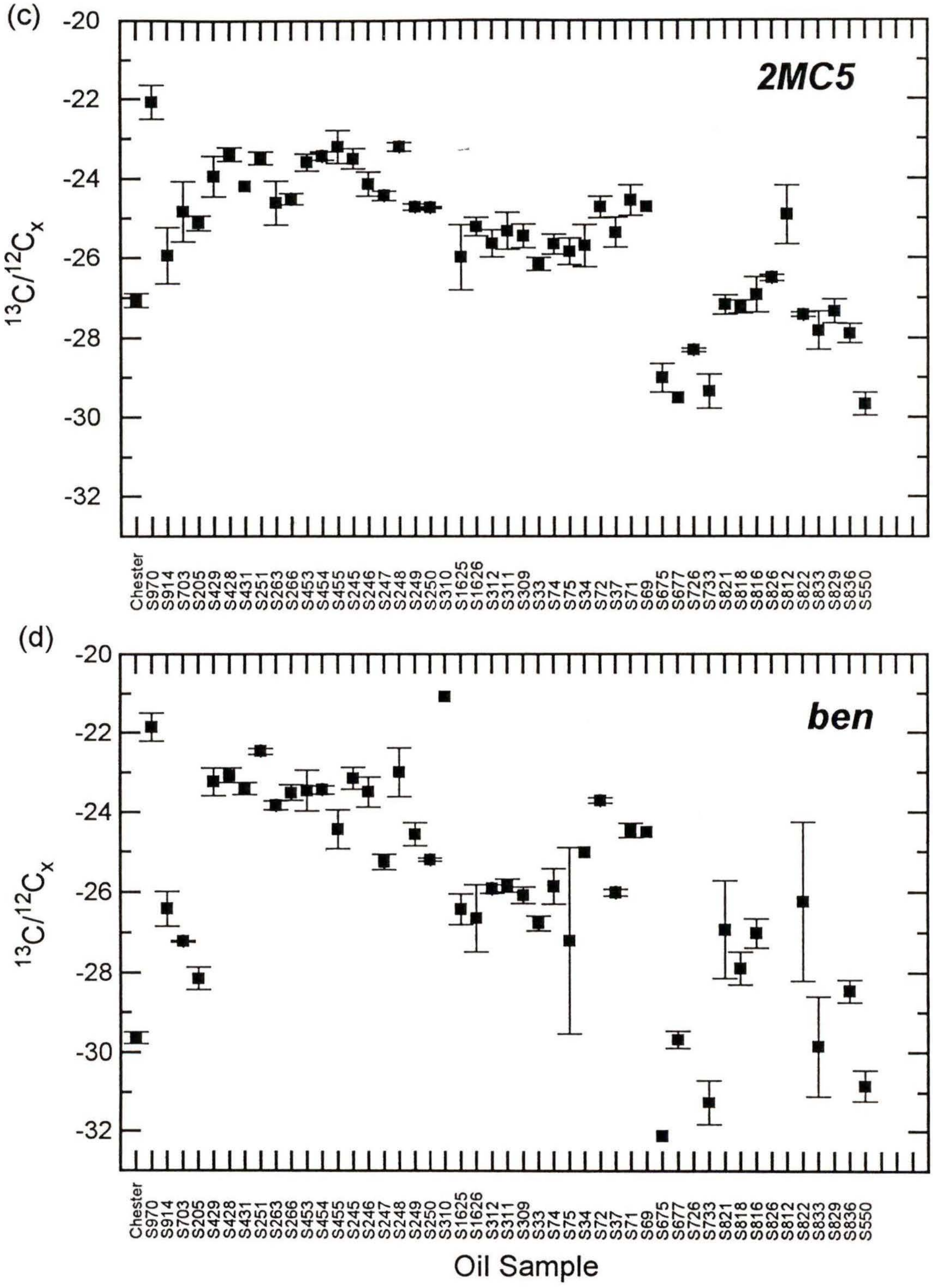


Figure 6.9 Carbon isotope variation in an individual hydrocarbon, continued.

6.2.2 Isotope Characterization of Oils and Condensates from the Four Study Regions

The isotope ratios of hydrocarbons in the oils from the **Jeanne d'Arc Basin** range between -20 and -26 ‰ (Figure 6.10a). The isotope ratios associated with each of the Hibernia, Mara, and Hebron wells are plotted separately in Figure 6.10 b, c, and d. The general trends for the isotope ratios of oils in a particular well are similar. There is, sometimes, a larger spread in the isotopes around iC_5 and nC_5 (approximately ± 2 ‰).

Individual isotope ratios of hydrocarbons in the oils from the **Beaufort-Mackenzie Basin** range between -20 and -28 ‰ (Figure 6.11a). The isotope trends for the Nerlerk, Amauligak, and Niglintgak wells are plotted separately in Figure 6.11 b and c. The trends for these oils are not as similar as the trends for the East Coast oils. There is again a larger spread in the isotopes around iC_5 and nC_5 (± 2 ‰) especially for the Niglintgak oils.

The hydrocarbons of the **Williston Basin** oils have isotope ratios ranging between -22 and -32 ‰ (Figure 6.12a) which are, on average, heavier than the oils from the East Coast or the Arctic. Families C and A, E, and F are plotted separately in Figure 6.12 b, c, and d. The hydrocarbons of Family C and A oils are isotopically light with isotope ratios between -26 and -33 ‰. Family E hydrocarbons have isotope ratios ranging from -24 to -30 ‰. Most of the isotope ratios of hydrocarbons from Family F oils range from -23 to -29 ‰.

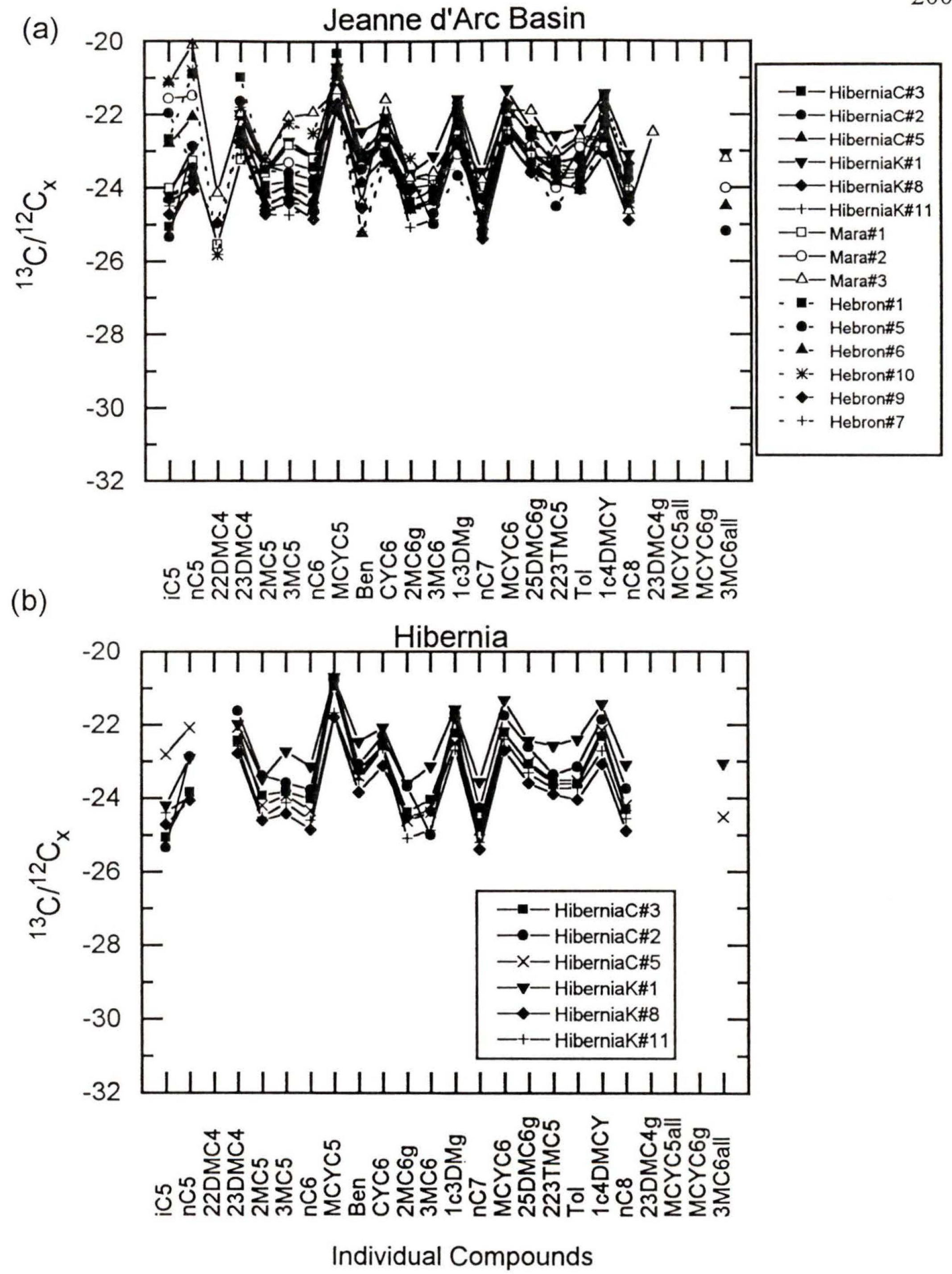


Figure 6.10 Isotope ratios of individual gasoline range hydrocarbons in (a) the Jeanne d'Arc Basin and (b) isolated Hibernia oils. The value following the '#' symbol refers to the DST#.

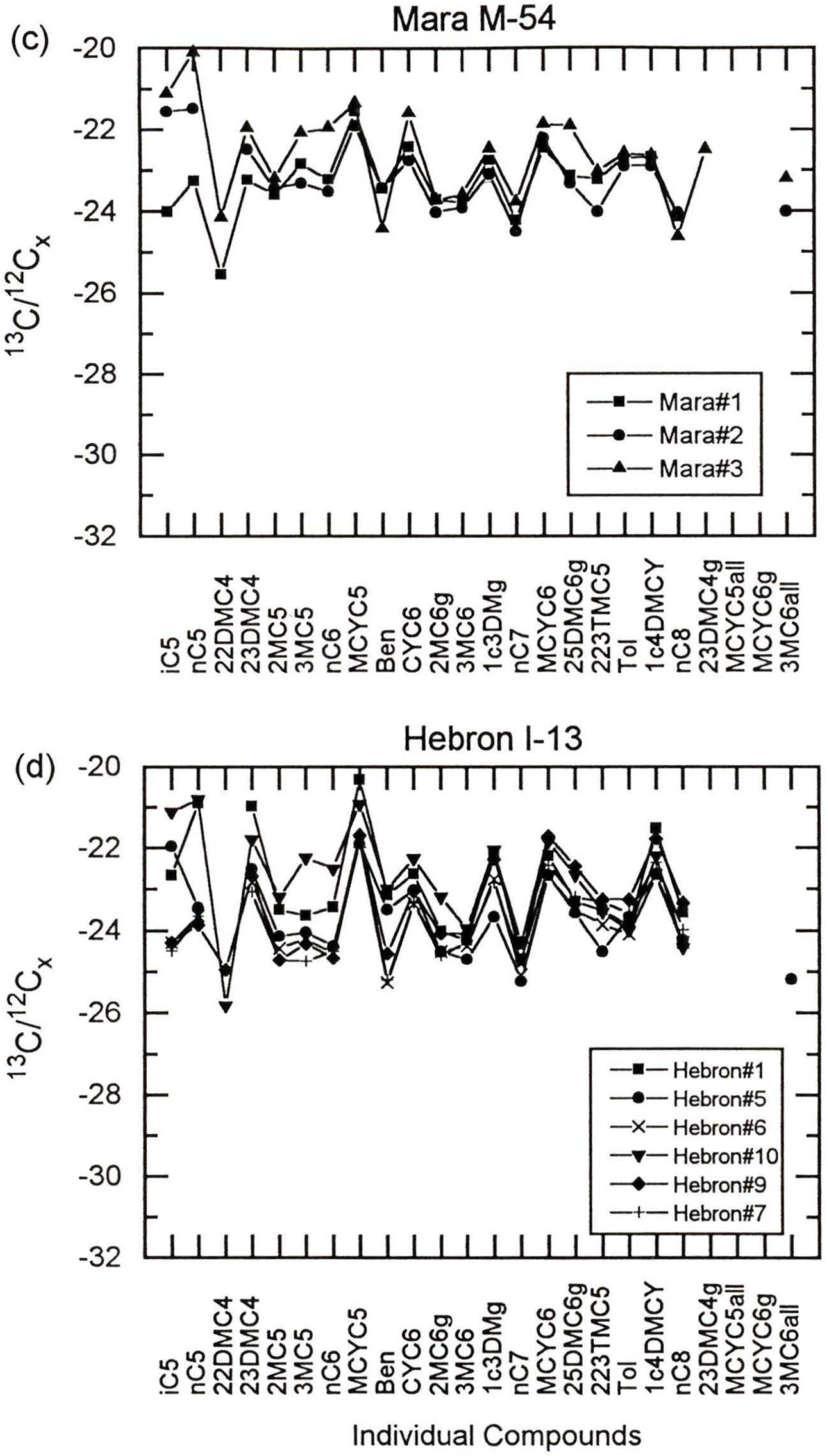


Figure 6.10 Isotope ratios for individual gasoline range hydrocarbons, continued, for isolated (c) Mara M-54 oils and (d) Hebron I-13 oils.

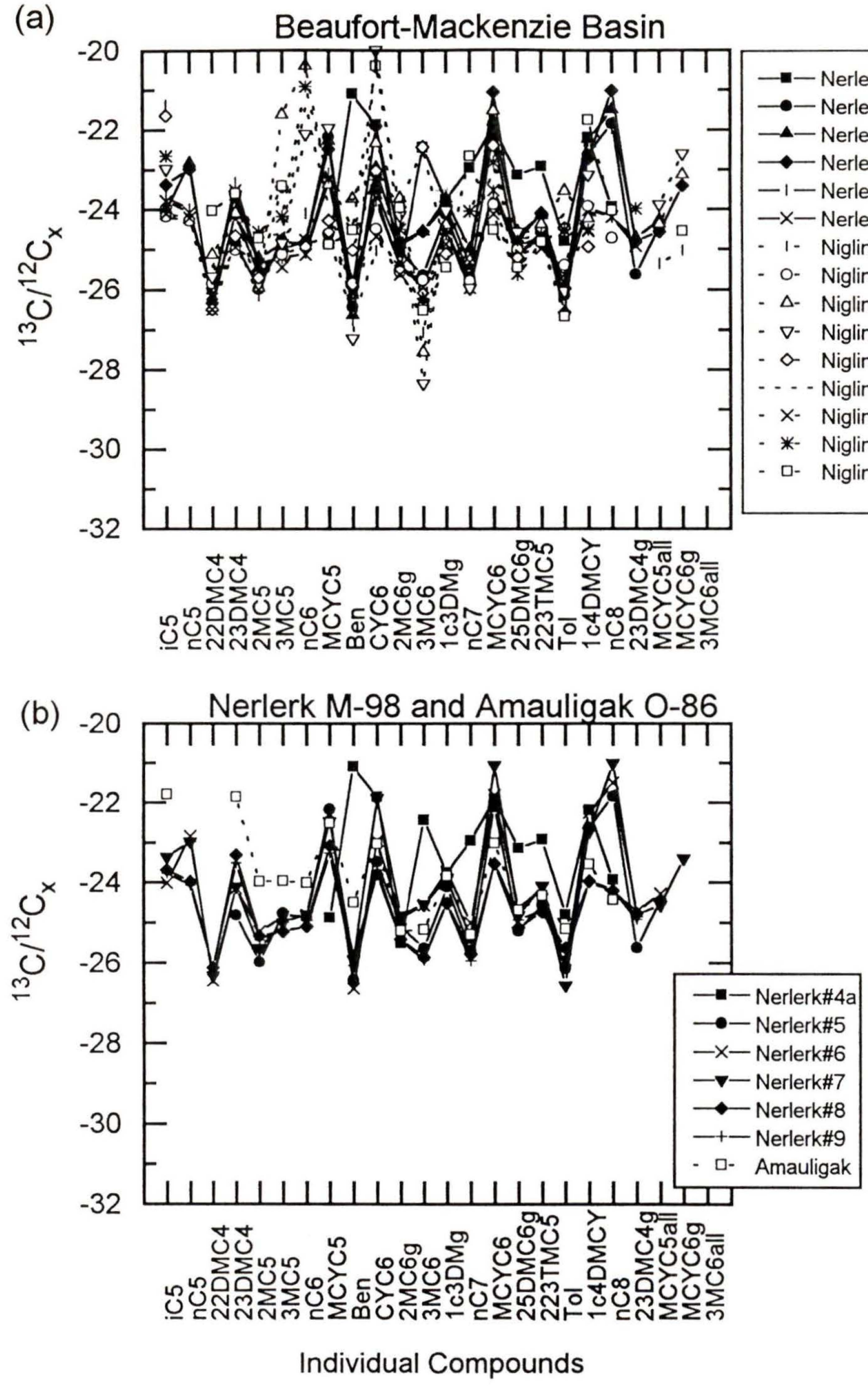


Figure 6.11 Isotope ratios of individual gasoline range hydrocarbons in (a) all of the Beaufort-Mackenzie Basin oils, (b) the isolated Nerlerk M-98 and Amauligak O-86 oils, and (c) the Niglintgak M-19 and B-19. The value following the '#' symbol represents the DST#.

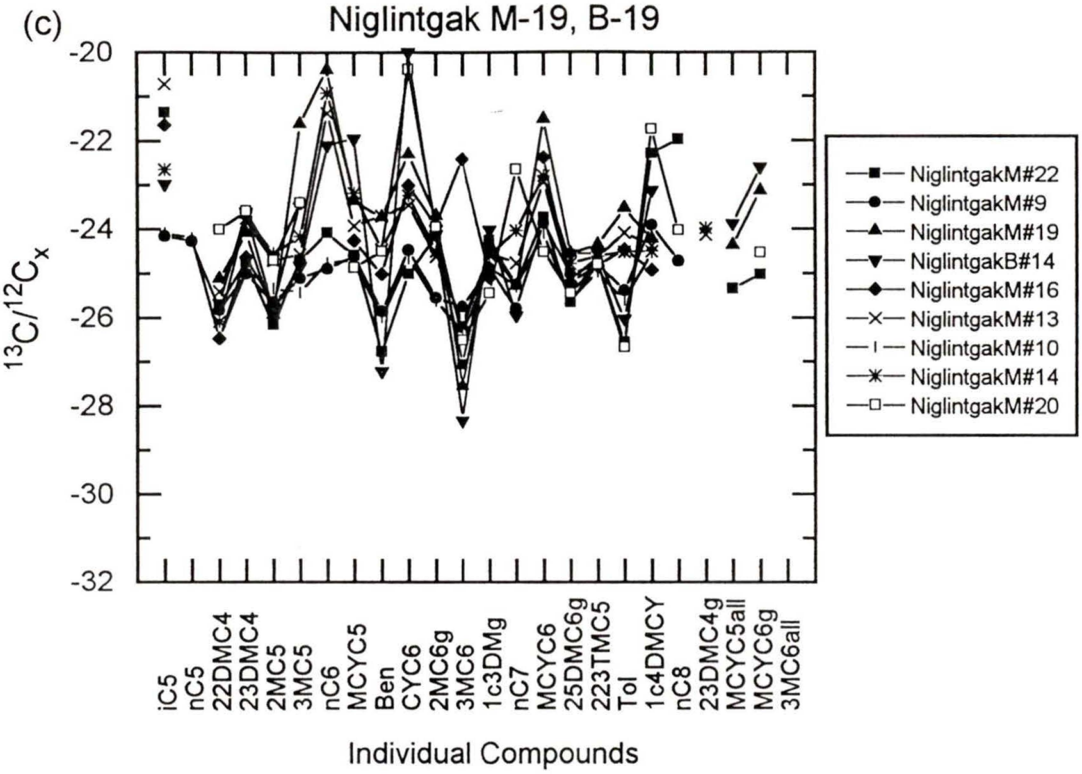


Figure 6.11 (c) Isotope ratios of individual gasoline range hydrocarbons, continued.

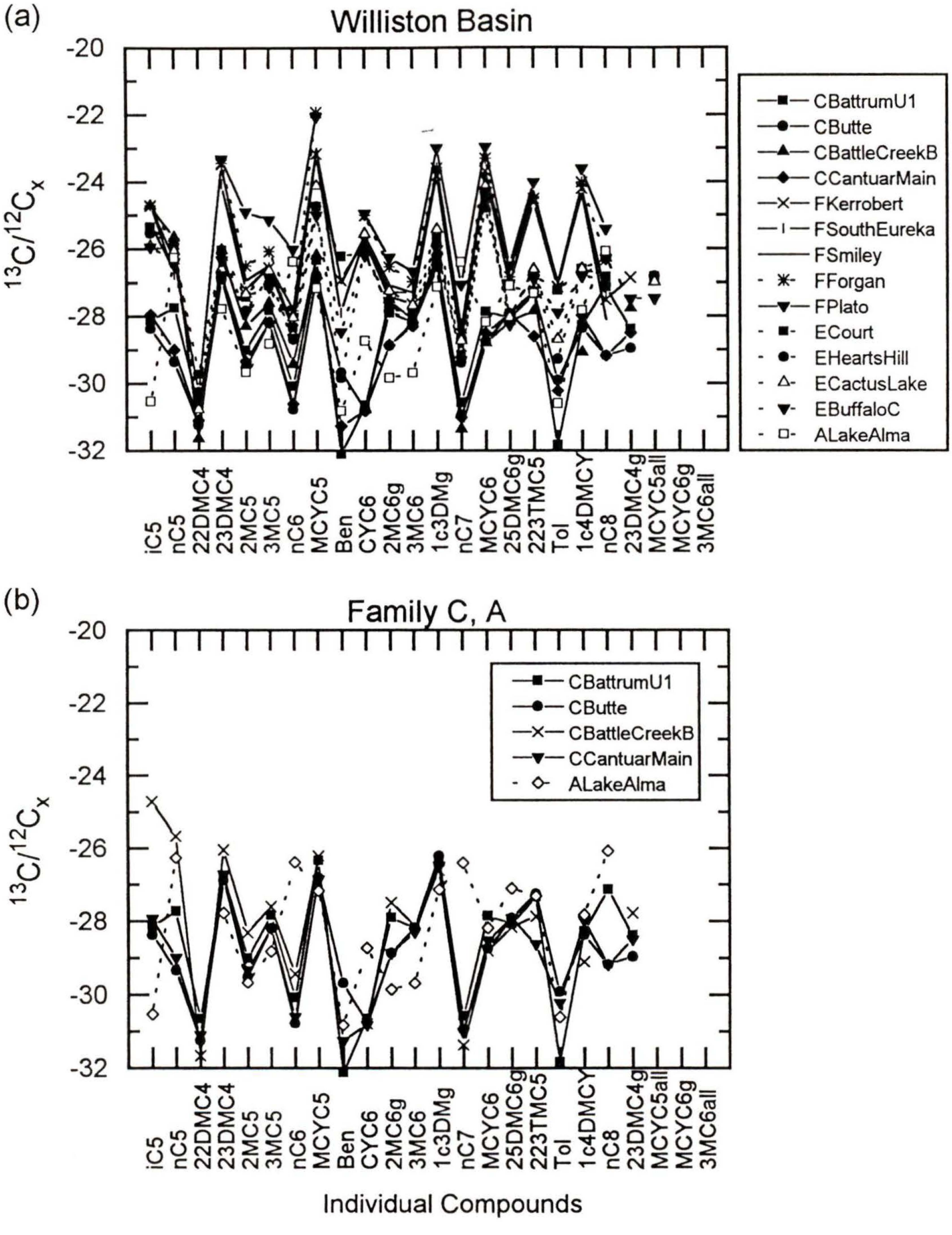


Figure 6.12 Isotope ratio for individual gasoline range hydrocarbons in (a) all the Williston Basin oils, (b) the isolated Family C and A oils, (c) Family E oils, and (d) Family F oils.

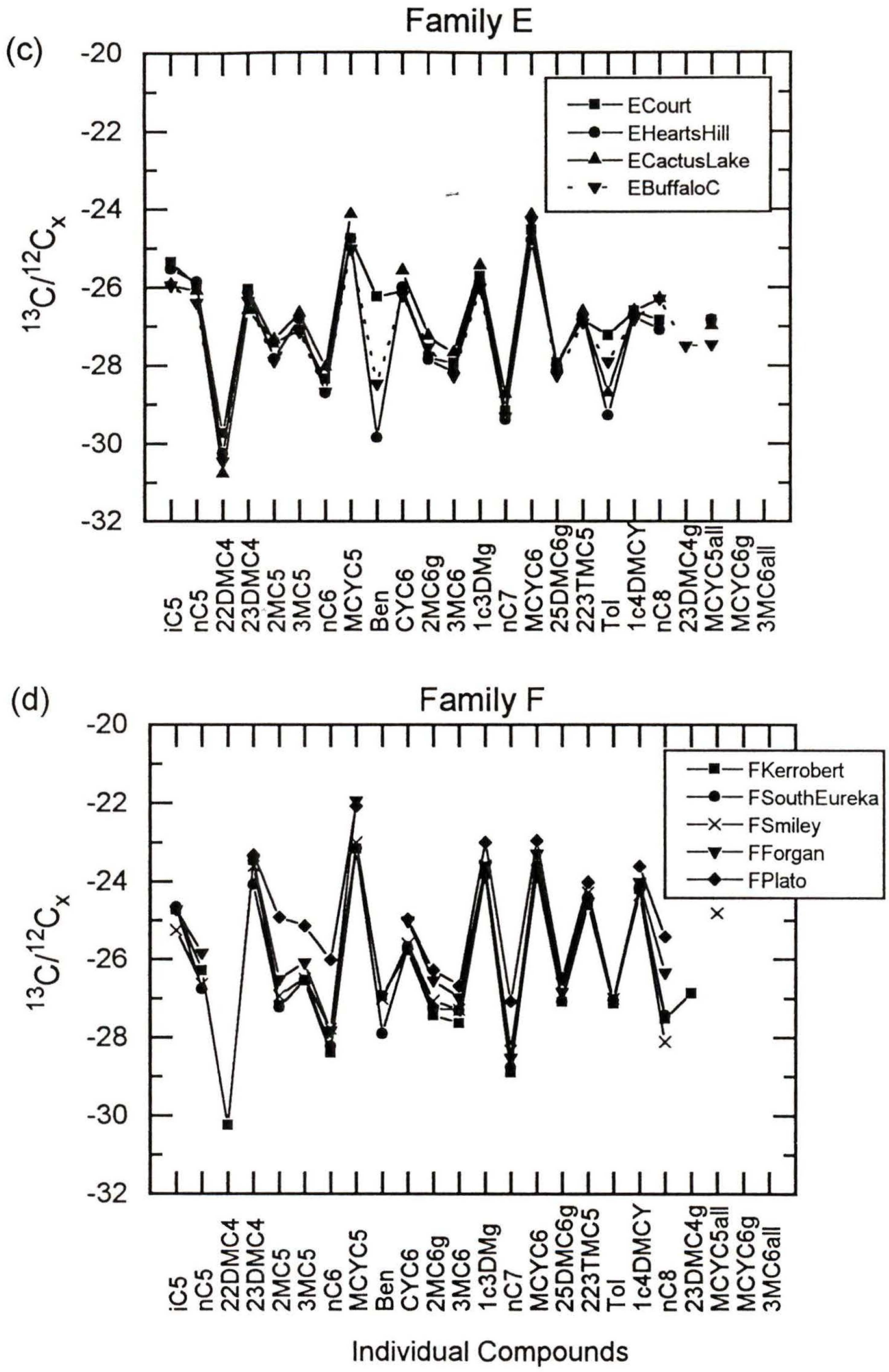


Figure 6.12 Isotope ratios of individual gasoline range hydrocarbons, continued, in (c) Family E oils and (d) Family F oils.

The isotope ratios of the oils from the **Western Canada Sedimentary Basin** range from -21 to -30 ‰ (Figure 6.13). There is no clear trend here in the isotope ratios for the 5 oils chosen from this region which is not unexpected since the oils originated from different types of environments (see Background).

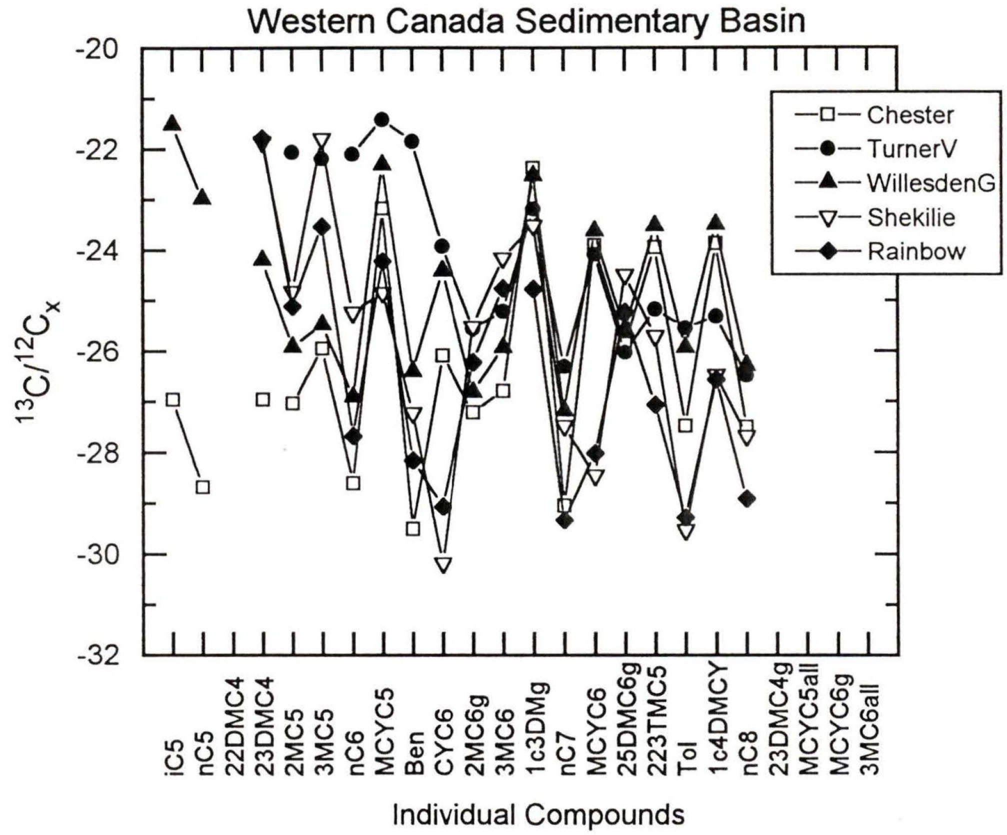


Figure 6.13 Isotope ratios for individual gasoline range hydrocarbons for all the oils studied from the Western Canada Sedimentary Basin.

CHAPTER 7. DISCUSSION

7.1 USE OF INDIVIDUAL ISOTOPE RATIOS TO CHARACTERIZE C_5 TO C_{10} HYDROCARBONS

GC-C-IRMS is a new technique to measure stable carbon isotopes on individual compounds. Although several investigators have recently performed compound-specific isotope studies (e.g., Ishiwatari et al., 1994; Bjorøy et al., 1994; Freeman, et al., 1994; Ricci et al., 1994), individual gasoline range hydrocarbons have not been previously measured or examined in any detail due to analytical difficulties. In the current study, gasoline range hydrocarbons in 51 Canadian oils (including several condensates) have been characterized isotopically by GC-C-IRMS. Most of the discussion regarding the use of individual isotope ratios to characterize C_5 to C_{10} hydrocarbons is located in the methods section. However, several of the important points from the methods section are summarized here.

To obtain reliable isotope measurements, good resolution (e.g., baseline separation) of the individual compounds is required (see Methods). Most of the compounds (present in high concentrations) measured in this study are sufficiently resolved to give reliable isotope measurements. However, several compounds such as $11DMCYC_5$, $23DMC_5$, and $3MC_7$ are not well resolved. In these cases, a 'bulk' isotope ratio of artificial groups composed of two or three unresolved compounds have been reported (Table D1, Appendix D) to try to retain some of the information associated with these compounds. Many compounds in the C_7 and C_8 range (e.g., eluting between toluene and C_8) are poorly resolved due to the increased amount of possible species (with similar boiling points) associated with the longer carbon chains. If a compound is present in too low or too high a concentration, its isotope ratio also may not be reliable.

Thus, approximately 16 out of the 30 identified compounds in the gasoline range are present in sufficient concentrations and have sufficient resolution to yield reliable isotope ratios. The isotope ratios of three artificial groups, namely 2MC6g, 1c3DMCYC5g, and 25DMC6g, are reported for all the samples. The isotopic compositions of several other groups, namely 23DMC4g, MCYC5all, MCYC6g, and 3MC6all, are reported only for those samples where resolution for those particular compounds is not adequate.

The typical experimental error of $\delta^{13}C_x$ with the GC-C-IRMS technique for gasoline range hydrocarbons ranges between ± 0.3 and 0.5 ‰ as determined from the pure and Chester standards (Table 5.5 and 5.6, Figure 5.16). The reproducibilities of the gasoline range isotopes for 3 oil samples are given in Figures 5.17, 5.18, and, 5.19. In general, most of the compounds only vary by ± 0.5 ‰ which is significantly less than the range in isotopic composition within an oil (Figure 7.1). However, the shorter-chained hydrocarbons such as iC_5 and nC_5 and the longer-chained hydrocarbons such as nC_8 often have larger standard deviations. The light compounds may have undergone evaporation (low concentration) while the heavier compounds may not be resolved well (increased isomers with larger carbon number).

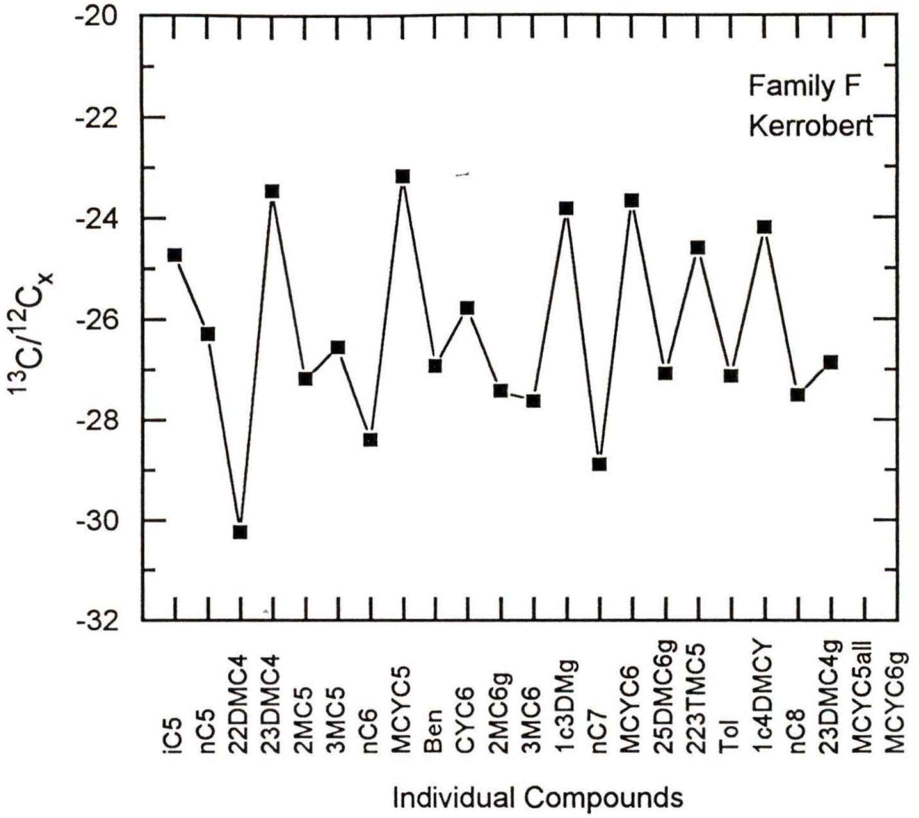


Figure 7.1 Isotope ratios of C5 to C10 hydrocarbons in Kerrobert, a Family F oil from southwest Saskatchewan. The isotopic variation is greater than the ± 0.3 to 0.5 $^{o}/_{oo}$ experimental error.

In Figure 7.2, single isotope ratios (representative of n-alkanes, branched alkanes, cycloalkanes, and aromatics in oil samples) and their corresponding standard deviations are presented for each oil sample. These plots indicate that the isotopic variation in oil samples is carried throughout the different compound classes. The n-alkanes, branched alkanes, and aromatics seem to exhibit larger isotopic variation than the cycloalkanes. The standard deviation or error (obtained from triplicate runs of each sample) associated with the isotope measurement is smallest for the cyclic and branched compounds, such as $MCYC_6$ and $2MC_5$ respectively. The n-alkanes and the aromatic hydrocarbons exhibit the greatest deviations (up to several ‰).

The aromatic compounds are often present in low concentrations in oil samples as compared to some of the other cycloalkanes and n-alkanes (e.g., $MCYC_6$ and nC_7) which may lead to unreliable isotope measurements. Most of the oil samples in this study are biodegraded to some extent except for those from Hibernia, offshore Newfoundland and several isolated Saskatchewan or Hebron oils. The n-alkanes are more susceptible to microbial attack since the bonds in such simple, straight-chain structures are easier to break than the bonds in cyclic or aromatic structures. The variability of the n-alkanes may be related to a small isotope effect associated with biodegradation (discussed later). Combinations of cyclic and branched isotopes may be more useful for correlation when the oils have been affected by secondary alteration processes.

Despite the large standard deviations (e.g., 2 to 4 ‰) for specific compounds in several oil samples, the standard deviation or error is generally significantly less than the

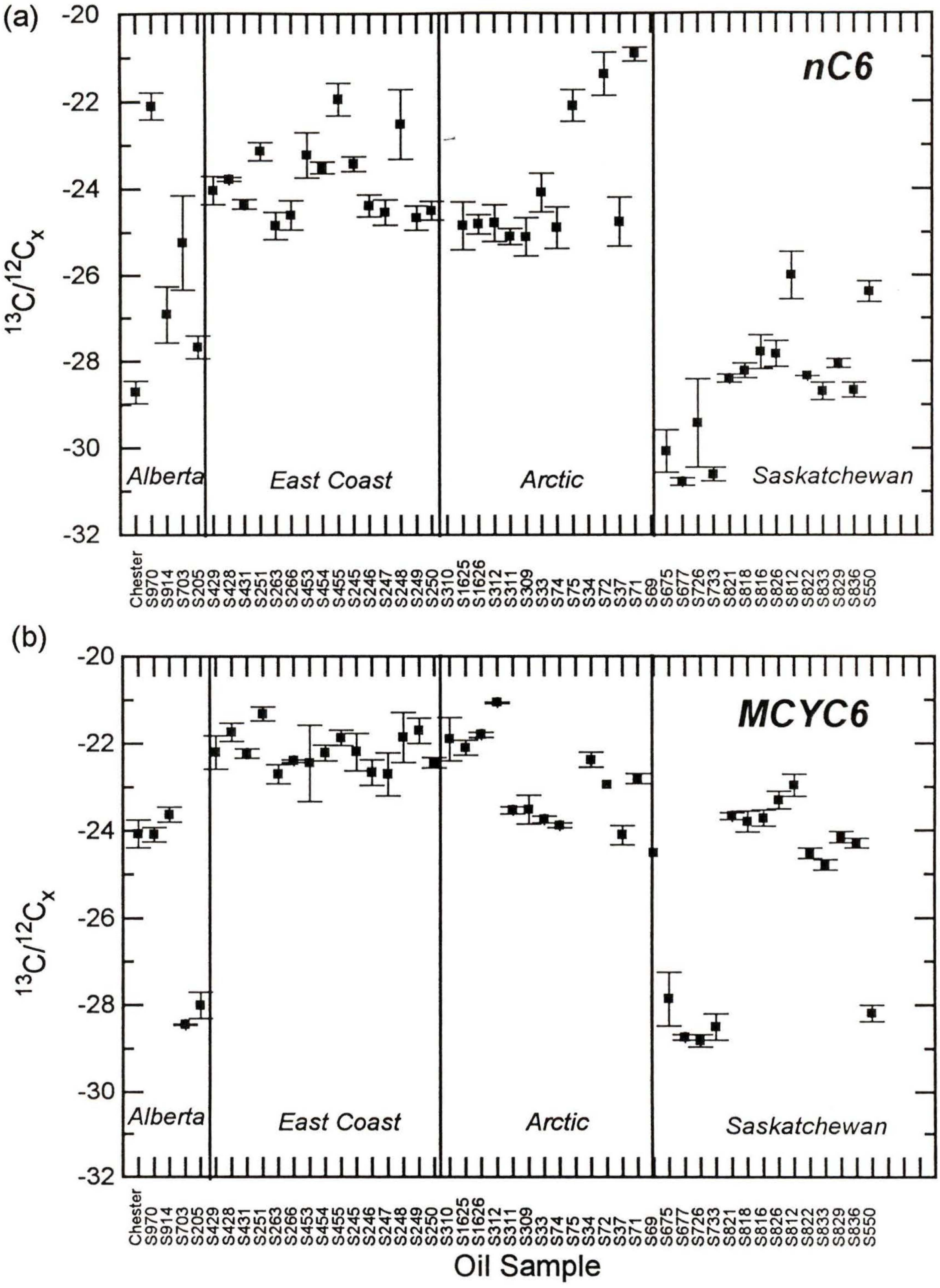


Figure 7.2 Carbon isotope variation in an individual hydrocarbon and regional differences in oils. Examples are given of the (a) n-alkanes, (b) cycloalkanes, (c) branched alkanes, and (d) aromatic hydrocarbons.

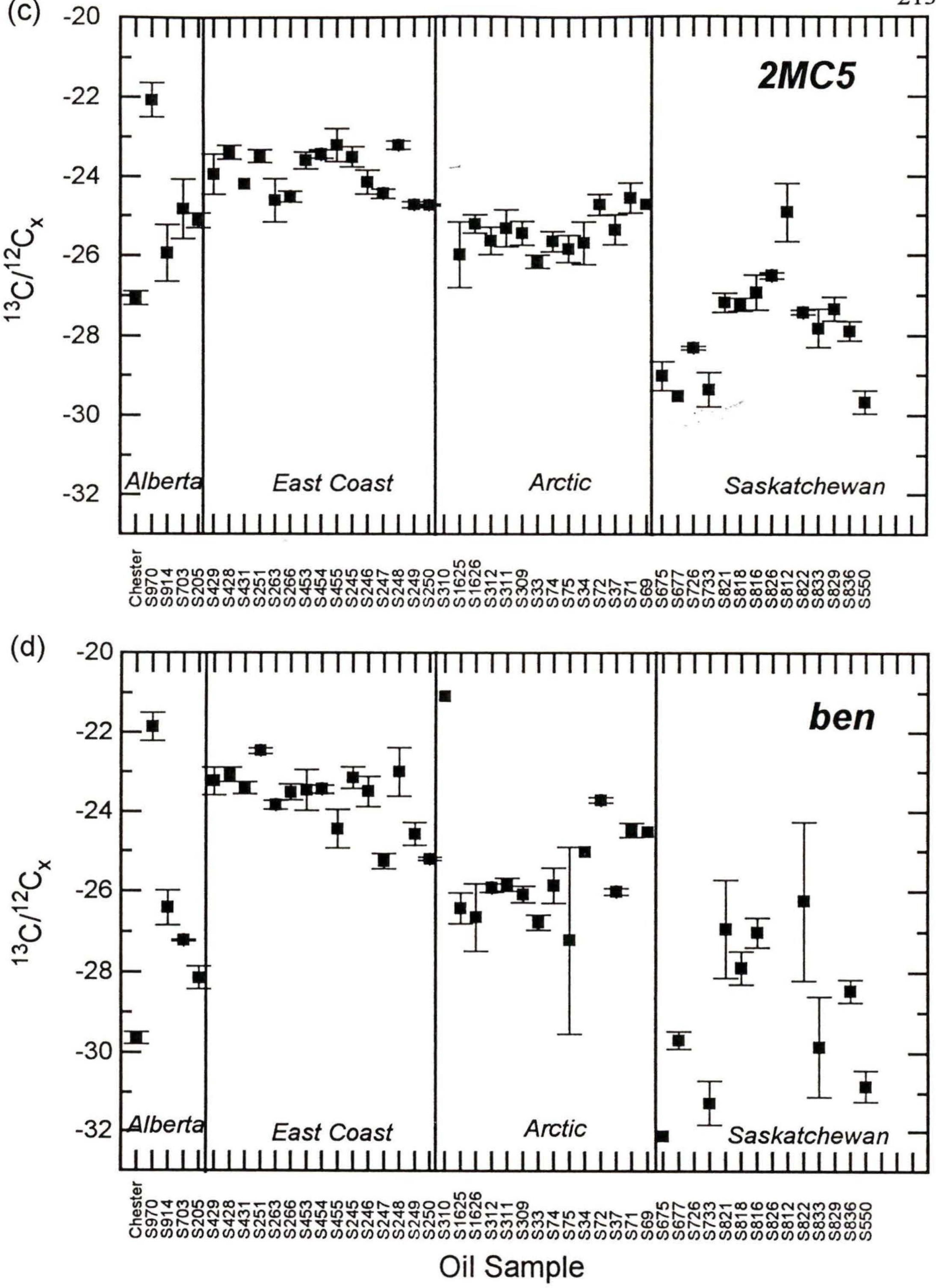


Figure 7.2 Carbon isotope variation in an individual hydrocarbons and regional differences in oils, continued.

variation in the oil samples. The isotope ratios of individual hydrocarbons in any one oil can vary up to 6 ‰ (Figure 7.1, 7.2), but the isotope ratios of the C_5 to C_{10} hydrocarbons in all of the Canadian oils vary by up to 10 ‰ (Figure 6.6, 7.2). This isotope variation must be due to factors other than the experimental error such as source or secondary alteration.

Summary Points:

- Compound resolution is sufficient to yield reliable isotope ratios in gasoline hydrocarbons.
- Isotopic variation in gasoline hydrocarbons is carried throughout the compound classes.
- Isotope variation of 10 ‰ in C_5 to C_{10} hydrocarbons is significantly less than the typical experimental error of ± 0.5 ‰.

7.2 USE OF INDIVIDUAL ISOTOPE RATIOS FOR OIL CORRELATION

The correlation of oils is based on the recognition of chemical similarities or differences between oils. The isotope pattern associated with the hydrocarbons in any individual oil may be unique (i.e., the isotope pattern is a fingerprint). If two oils are derived from the same source conditions or belong to the same family (based on other compositional characteristics), the isotope fingerprints in the related oils will be similar. Oils from different sources or families will have different isotope fingerprints.

If isotopes are used for oil correlation, they must be conservative or resistant to alteration from thermal maturation and secondary alteration processes such as water-washing or biodegradation. The use of specific gasoline range isotopes for the correlation of individual oils and major regional groups of oils will be discussed here. The effects of thermal maturation and secondary alteration on the molecular composition of an oil are already known (see Background). The effect of thermal maturation, biodegradation and water-washing, if any, on stable carbon isotope ratios will be discussed later.

7.2.1 Correlation between Oils

7.2.1.1 Uni-dimensional Approach

The sources for most of the Canadian oils are already known (Background) so these are good test oils to determine whether or not isotope ratios can be used to correlate between oils. The isotope ratios of all of the individual hydrocarbons in oils vary, some ranging up to 10 ‰ (see Results; Figure 6.6). In Figure 7.2, the oils have been separated according to region. Related oils from one region do have similar isotope ratios that are different from oils of another region (general regional trends discussed in more detail in next section).

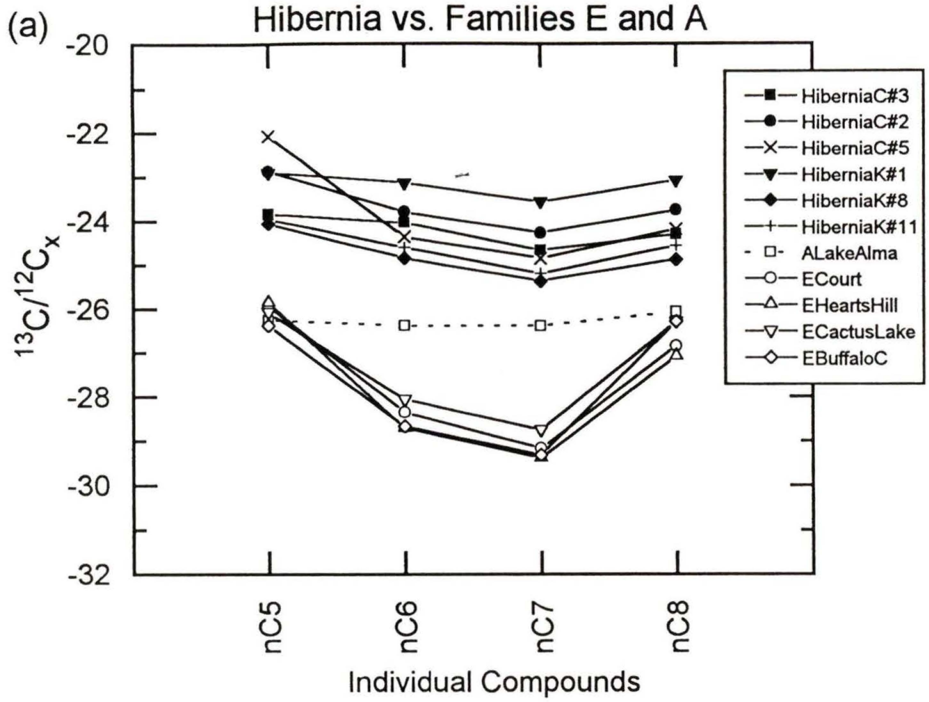
In the Results section, the isotope ratios of all the gasoline hydrocarbons are given for each oil, grouped either by well or major geographic region (Figures 6.10, 6.11, 6.12, and 6.13). From observation of these plots, it is evident that oils can be grouped together on the basis of isotopic similarity of specific gasoline hydrocarbons. For example, oils from the East Coast ($\delta^{13}C_x$ = -20 to -26 ‰, Figure 6.10) and the Arctic

($\delta^{13}C_x$ = -20 to -28 ‰, Figure 6.11) are more enriched in ^{13}C (isotopically heavy) as compared to the Saskatchewan oils ($\delta^{13}C_x$ = -23 to -32 ‰, Figure 6.12).

From the isotope results, it was determined that the isotope variation is carried throughout the compound classes. Isotopic measurement of all gasoline range hydrocarbons may not be necessary for oil correlation. The inclusion of all the compounds may even complicate the situation if some compounds co-vary, co-elute, or are present in low concentrations.

To emphasize some of the isotopic similarities or differences in these oils which are important for correlation, the individual hydrocarbons of the various oil classes (e.g., n-alkanes, branched alkanes, and cycloalkanes) for selected oils are presented in Figures 7.3, 7.4, and 7.5. The hydrocarbons in the East Coast and Arctic oils are isotopically heavier than those in the Saskatchewan oils. The Alberta oils vary in isotopic composition (Figure 6.13), depending on the precursor source material. Although it is easy to differentiate the East Coast and Arctic oils from the Saskatchewan oils, it is more difficult to isotopically differentiate similar oils such as Mara and Hibernia oils.

In any one well, the gasoline range hydrocarbons can vary up to 2 ‰ (Figure 7.3a) as is the case for Hibernia oils. However, the isotopic differences in the oils are large (10 ‰). The isotope ratios for the n-alkanes of Hibernia and Families E and A oils are given in Figure 7.3a. Each of these groups of oils has distinct isotope ratios. All Hibernia oils are enriched in ^{13}C ($\delta^{13}C_x$ = -22 to -25 ‰) as compared to the other 2 oil groups. Lake Alma, the only oil from Family A, has a relatively constant isotope ratio for



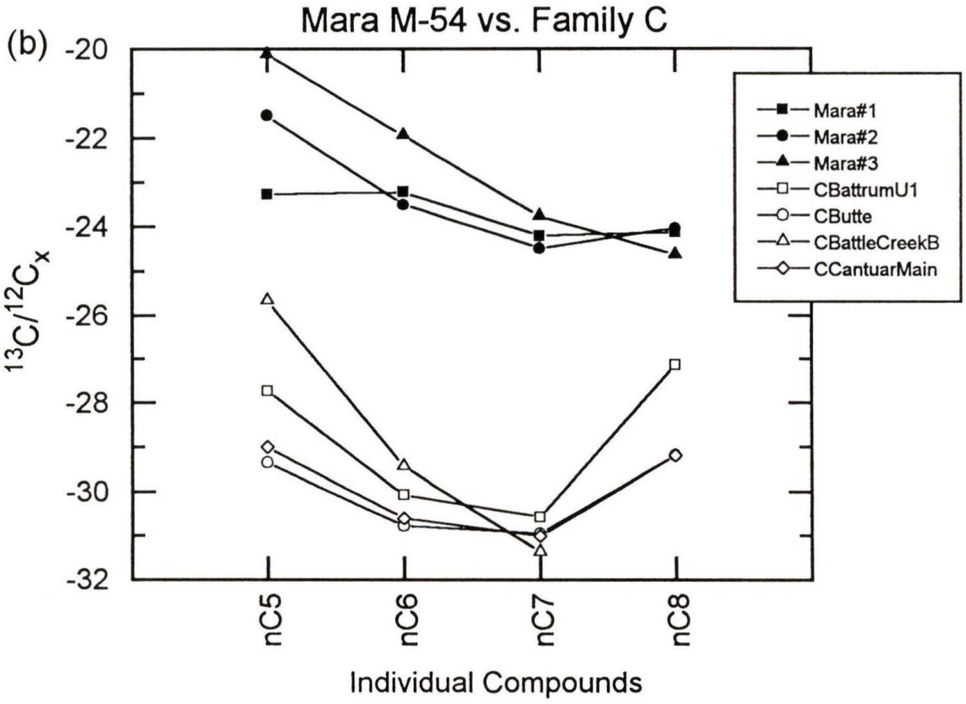


Figure 7.3 Correlation of similar oils based on the isotope ratios of the n-alkanes: (a) Hibernia oils compared to Families E and A oils and (b) Mara M-54 oils compared to Family C oils.

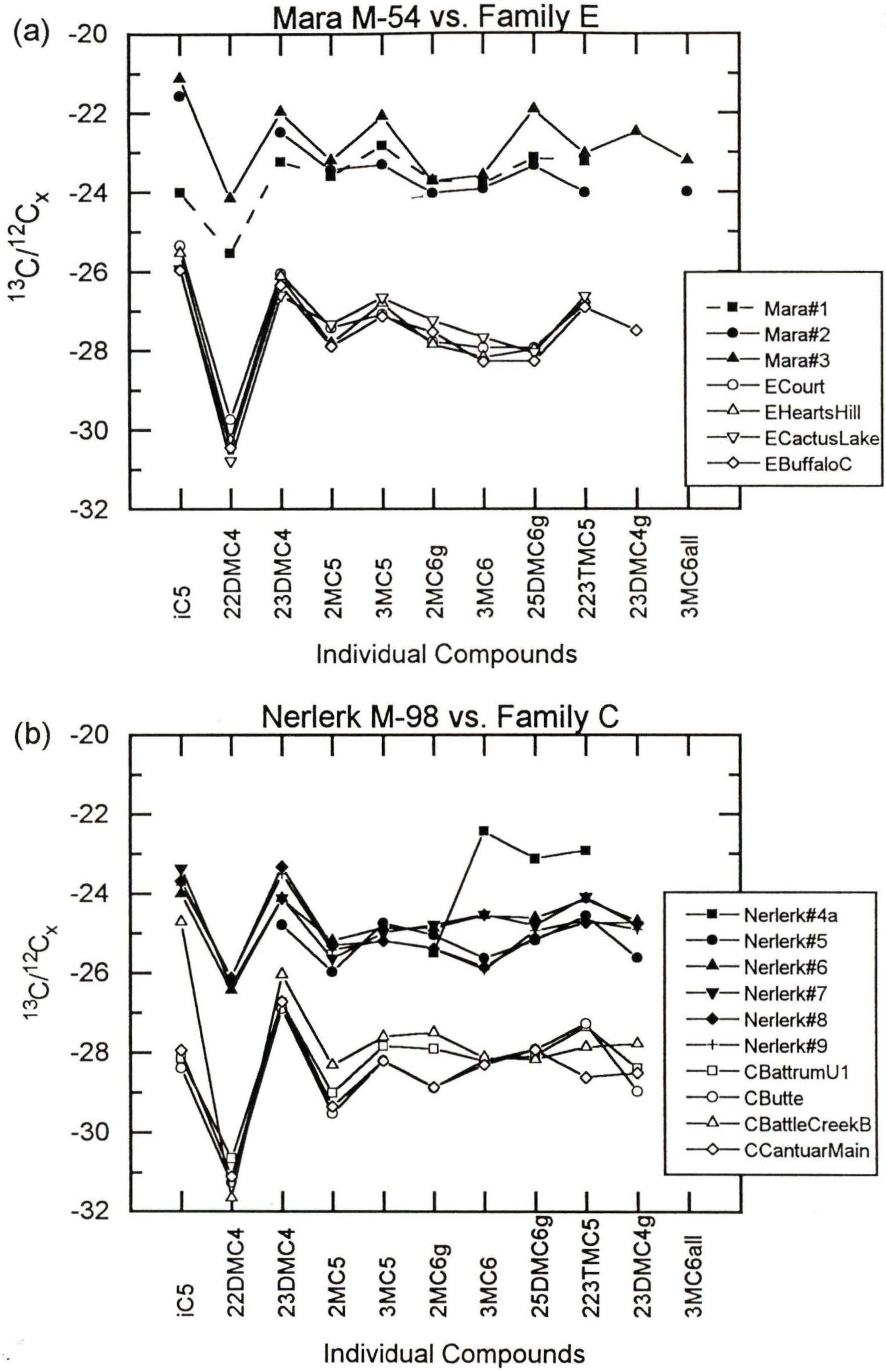


Figure 7.4 Correlation of similar oils based on the isotope ratios of branched hydrocarbons: (a) comparison between Mara M-54 and Family E oils and (b) comparison between Nerlerk M-98 and Family C oils.

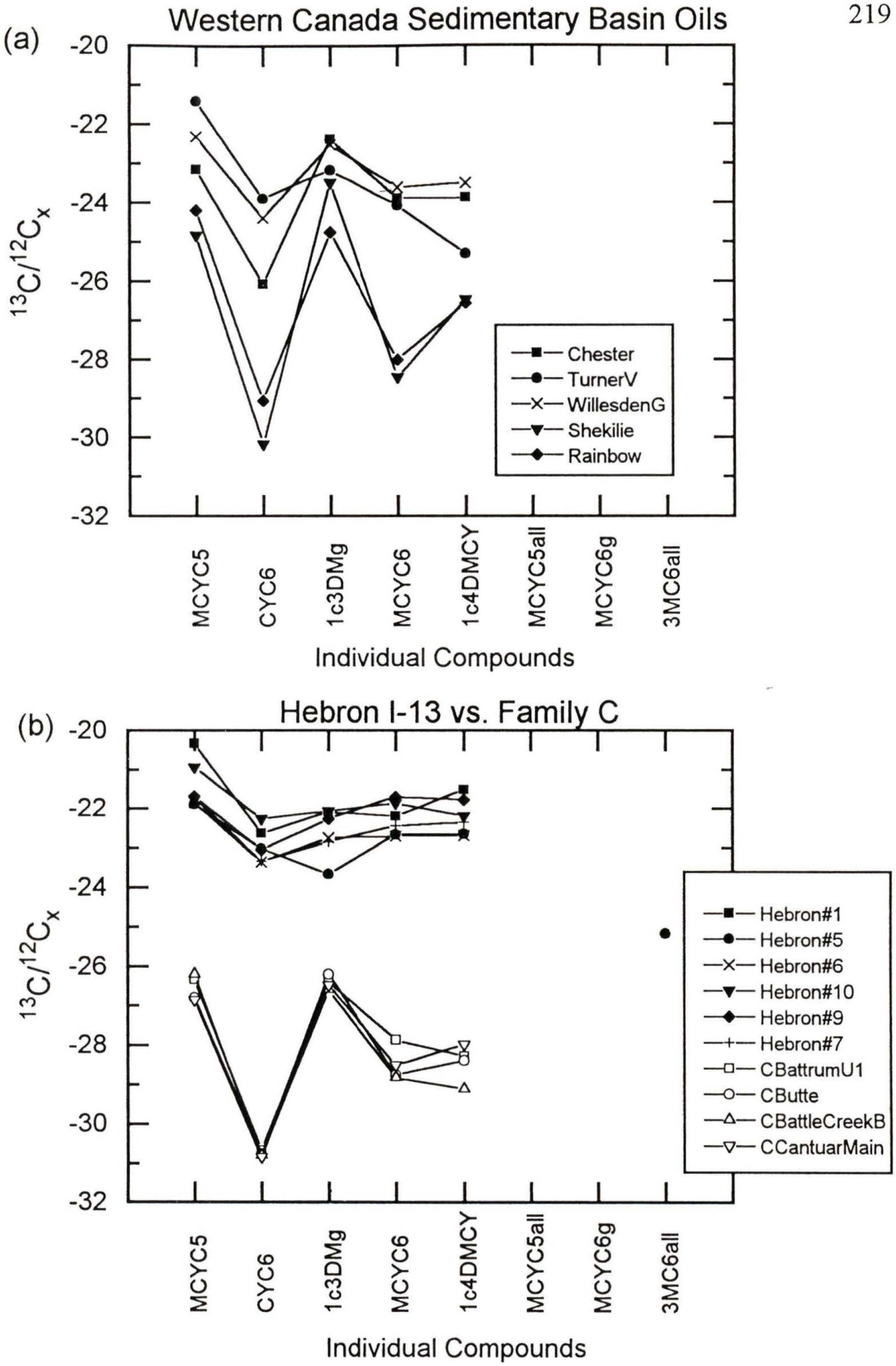


Figure 7.5 Correlation of similar oils based on the isotope ratios of the cycloalkanes for: (a) Western Canada Sedimentary Basin oils and (b) Hebron I-13 and Family C oils.

all the n-alkanes ($\delta^{13}C_x$ = -26 ‰). Family E oils are depleted in ^{13}C ($\delta^{13}C_x$ = -26 to -29 ‰). In Figure 7.3b, the n-alkane isotope ratios of Mara M-54 are compared to Family C oils, and again the isotope ratios of related oils are similar to each other and different from unrelated oils from a different source.

In Figure 7.4, the isotope data of branched compounds for some East Coast and Saskatchewan oils are presented. All Mara M-54 oils have similar isotope ratios (e.g., $\delta^{13}C_x$ = -21 to -24 ‰) that are consistently enriched in ^{13}C as compared to the Family E hydrocarbons ($\delta^{13}C_x$ = -26 to -32 ‰) (Figure 7.4a). The Nerlerk oils ($\delta^{13}C_x$ = -23 to -26 ‰) in Figure 7.4b are more enriched in ^{13}C (heavier) as compared to the Family C oils ($\delta^{13}C_x$ = -26 to -32 ‰; lighter). The cycloalkanes of Hebron I-13 oils are also distinctly heavier than those of Family C oils (Figure 7.5a). The cycloalkanes in oils from the Western Canada Sedimentary Basin show a wide range in isotopic composition from -21 to -30 ‰ (Figure 7.5b).

The large range in isotopic composition of the Western Canada Sedimentary Basin oils is expected since the oils chosen from this basin originate from a variety of environments. Rainbow and Shekilie, two oils derived from a euxinic environment, are more similar to each other than the other three oils. Chester is derived from a typical marine environment. Willesden Green is sourced from marine shales. This oil has undergone secondary migration (100 km). Turner Valley has been subjected to such high temperatures that biomarker data can not be obtained. The source for the Turner Valley oil is unknown (Lloyd Snowdon, personal communication).

Most of the oils discussed above are all sufficiently different so that correlations can be made with relative ease. The oils from Saskatchewan are similar (e.g., only subtle differences), but, from other molecular data, they have been separated out into three separate families derived from three different sources. The isotope ratios of n-alkanes and branched alkanes for Family C and F oils are presented in Figure 7.6. The isotope ratios of Family C hydrocarbons are lighter for both types of compounds. When the cycloalkanes are plotted for the two families, the differentiation into family groupings is very distinct (Figure 7.7a). In Figure 7.7 b, the isotope ratios of all the compounds in the oils are plotted. Although the difference between Family C and F oils is still evident, the cycloalkanes provide the same oil correlation with fewer required measurements.

The hydrocarbons of Family F and E oils are isotopically very similar. The isotope ratios of the n-alkanes do not provide any differentiation information (Figure 7.8a). The oils all appear to be group together from this data. The isotope ratios of the branched compounds are more useful in distinguishing between the two families (i.e., in detecting more subtle differences). The branched compounds of Family F oils are isotopically heavier than those in the Family E oils (Figure 7.8b). The cycloalkane isotope data leads to two distinct groupings corresponding to Family F and E (Figure 7.9a). When all of the compounds are included (Figure 7.9b), the differentiation of oils into families is not quite as clear.

The East Coast samples are composed of oils from four different wells with the same marine source (Egret Formation). These oils have similar isotope ratios and no

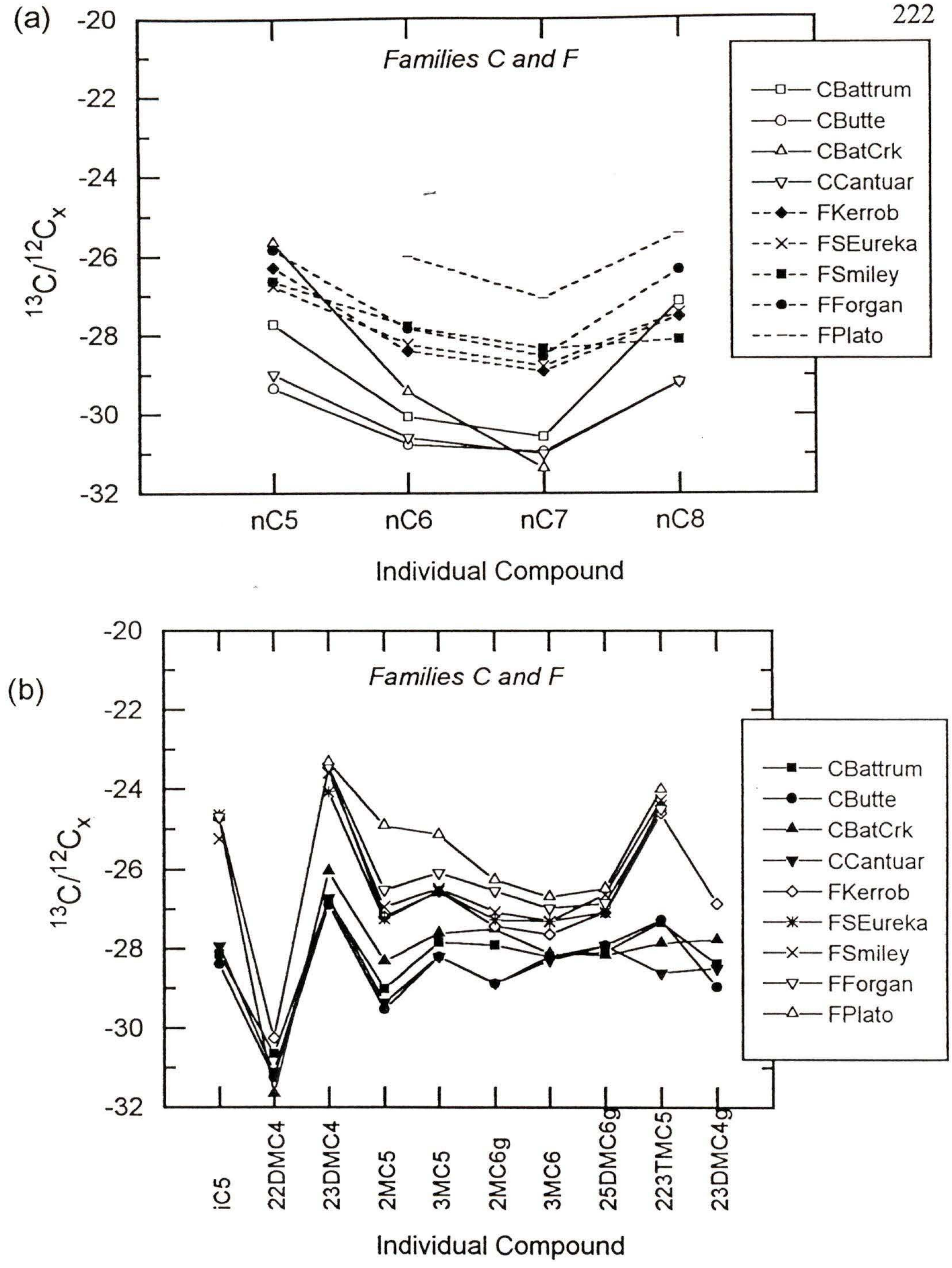


Figure 7.6 Differentiation between oils from Families C and F in Saskatchewan using isotope ratios of the (a) n-alkanes and (b) branched alkanes.

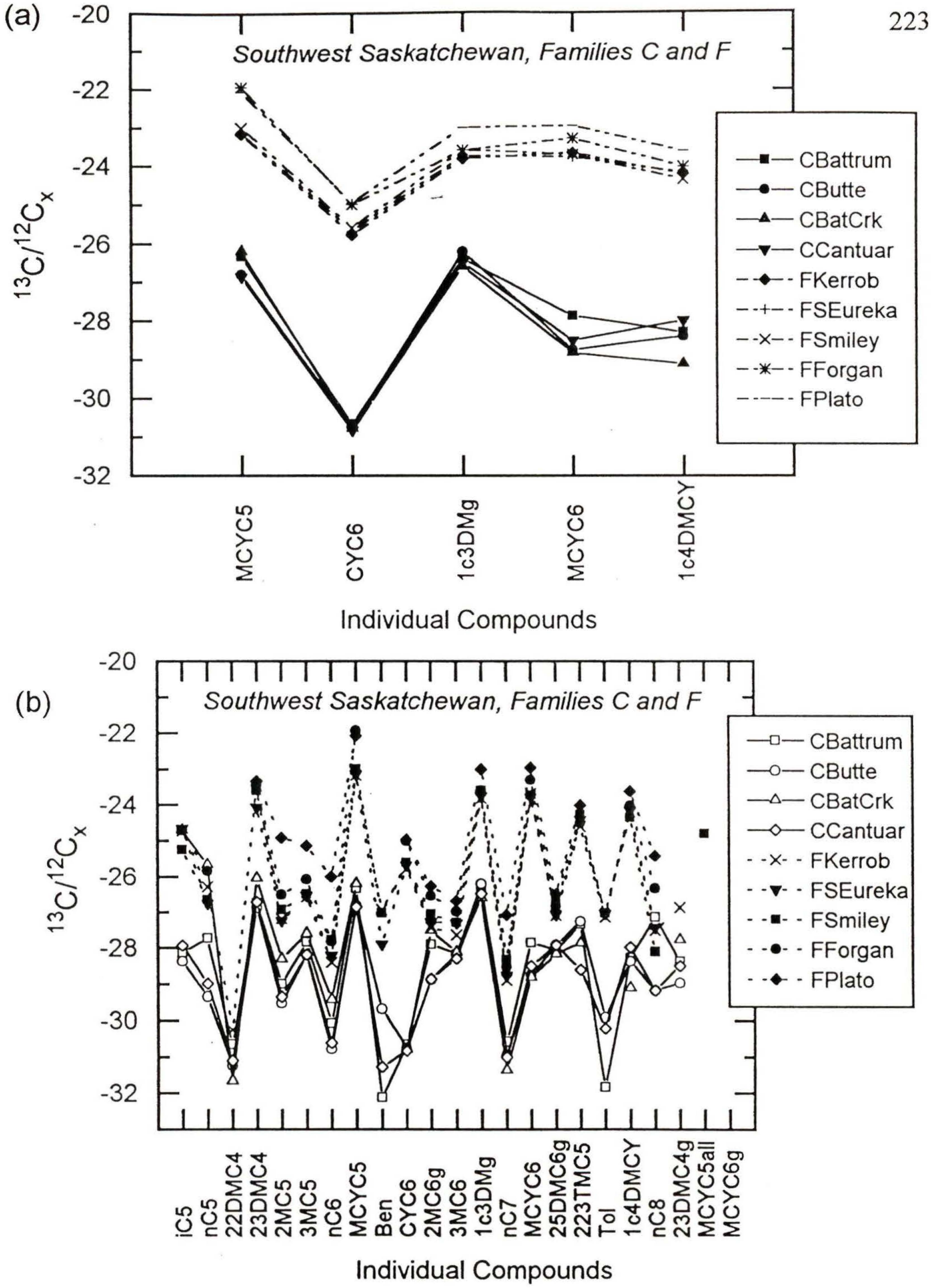


Figure 7.7 Differentiation between Family C and F oils: (a) using the isotope ratios of cycloalkanes and (b) using the isotope ratios of all hydrocarbons.

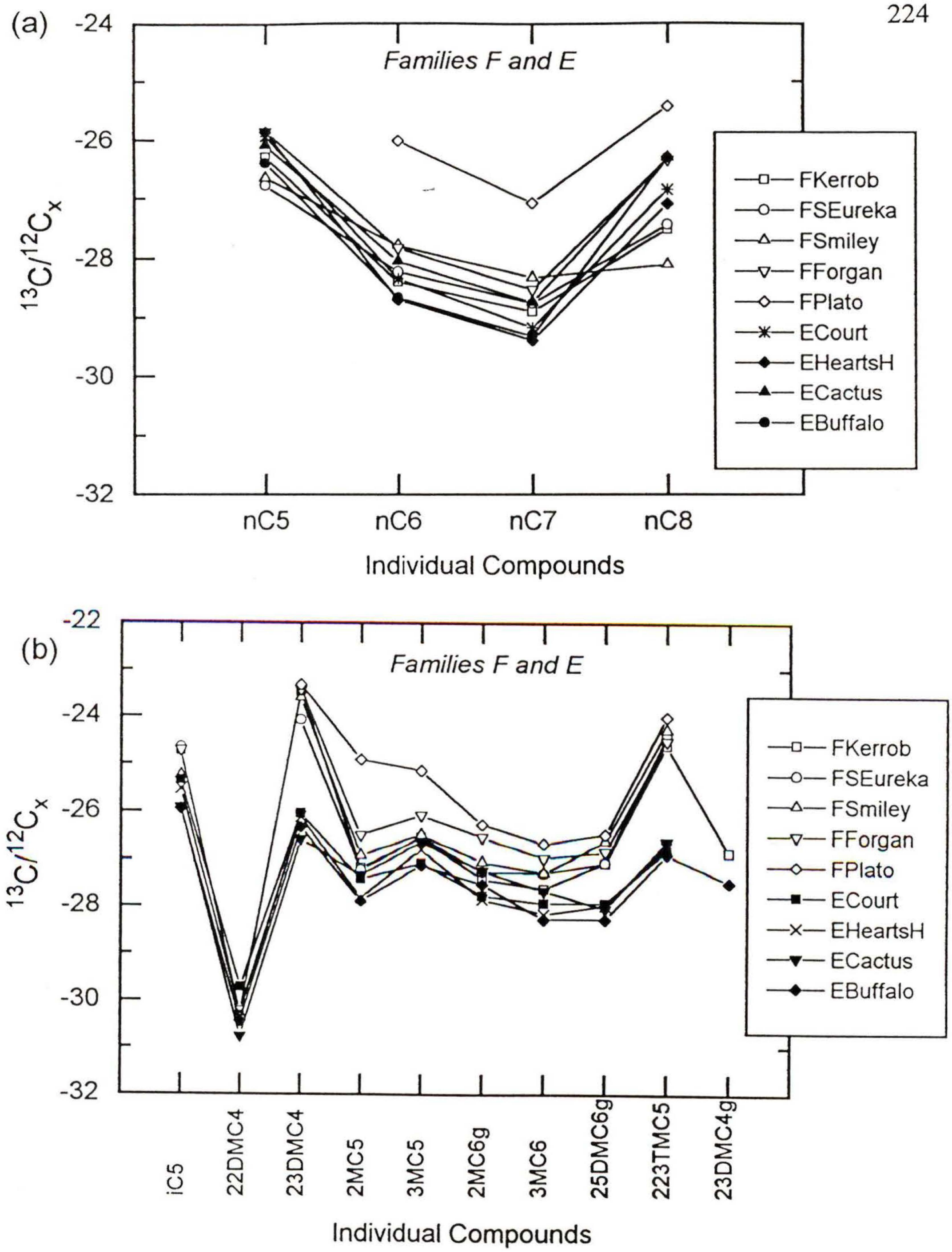


Figure 7.8. Comparison of similar Family F and E oils from Saskatchewan using the isotope ratios of the (a) n-alkanes and (b) branched alkanes.

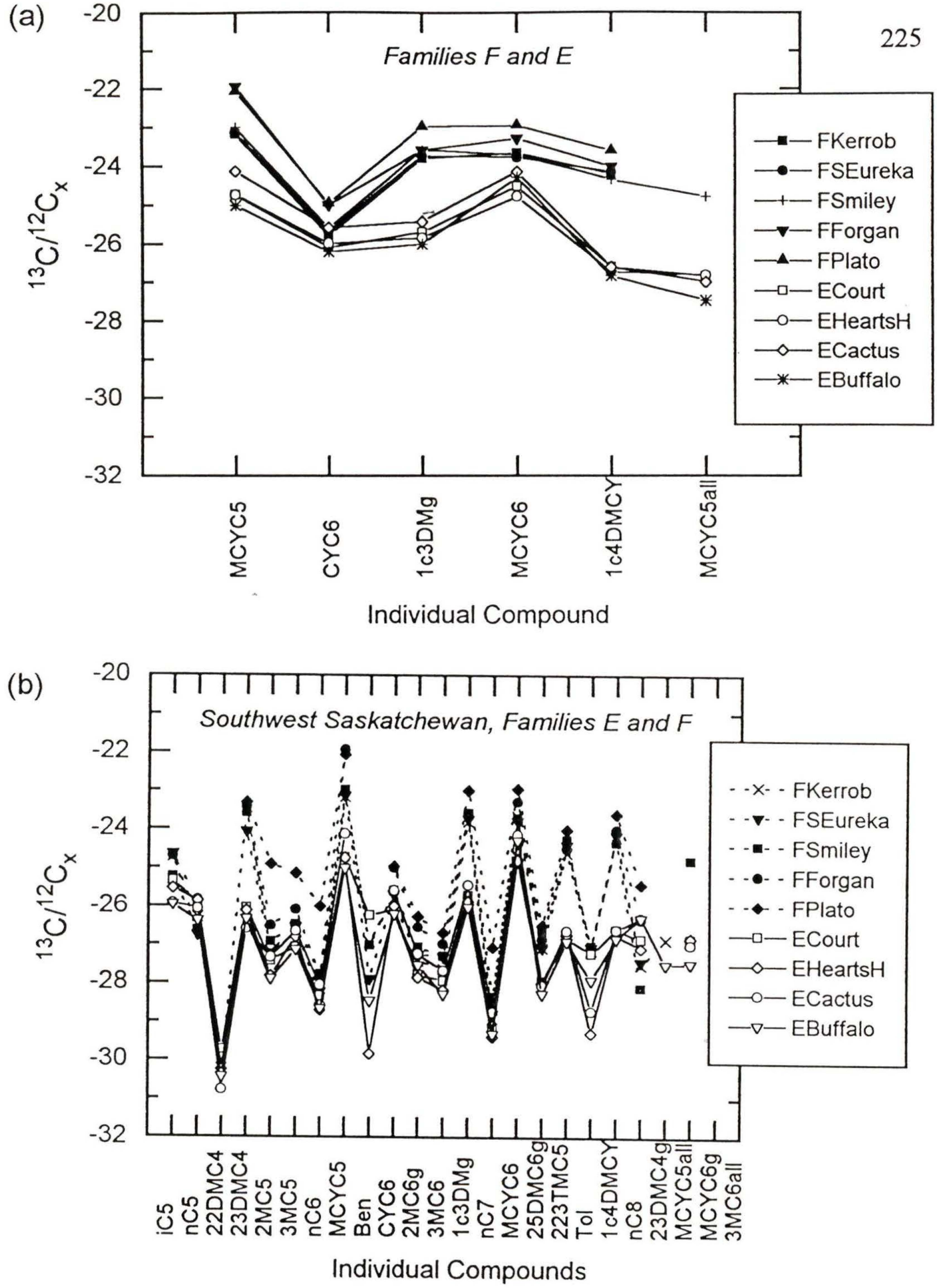


Figure 7.9. Comparison of Family E and F oils from Saskatchewan using the isotopes ratios of (a) the cycloalkanes and (b) all compounds.

systematic differences were detected. The Hebron, Hibernia, and Mara oils correlate with each other (see Figure 7.10). The cycloalkane data is not sufficient to differentiate between the East Coast oils (Figure 7.10b). The Niglintgak, Nerlerk, and Amauligak oil samples also correlate with each other. The differences among these oils are not sufficient to group the oils according to wells since they are all derived from the same source.

The Saskatchewan oils separated out into families because each family of oils is derived from a slightly different source. Family C oils were generated from a fully mature, Paleozoic, anoxic, marine, carbonate source rock. Family E oils were generated from a fully mature, Paleozoic, marine, clastic source rock. Family F oils were generated from an Upper Cretaceous, algal, marine, clastic source rock. Also, the three families of oils have been differentially affected by maturation and secondary alteration processes. Family F oils have been subjected to the highest thermal conditions while Families C and E have been subjected to lower thermal conditions. Levels of biodegradation for each of these oils are included in Table 4.1.

Summary Points:

- Similarities or differences in the individual gasoline range isotopes are sufficient to correlate oils.

- Cycloalkanes appear to be more useful for oil correlation as compared to the n-alkanes, branched alkanes, or aromatics when a uni-dimensional approach is utilized.

- Saskatchewan oils correlate with each other, but they can be divided into three families due to source or other environmental differences. The isotopes of East Coast and Arctic oils do not yield sub-groups because there is only one dominant source material for all the oils.

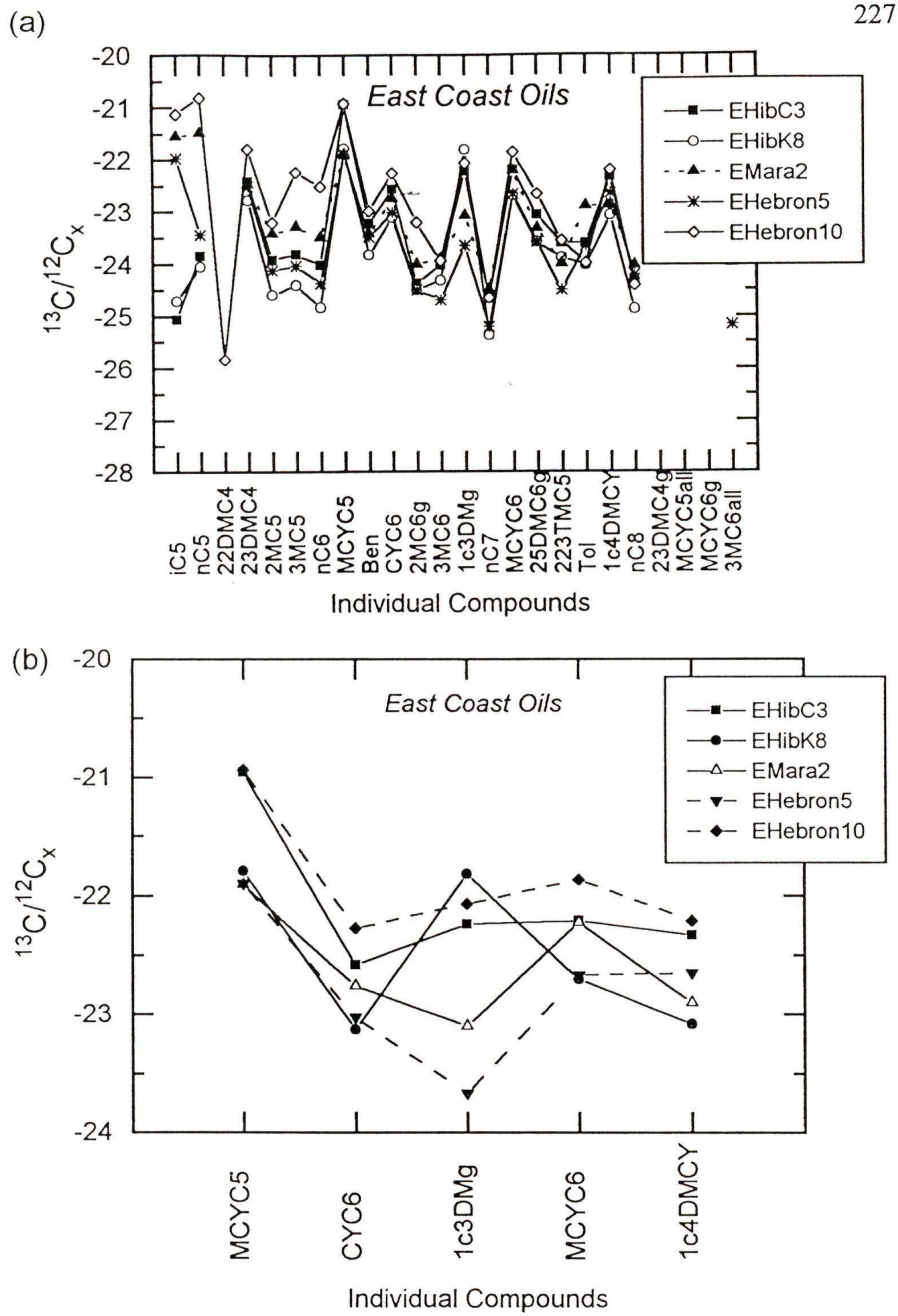


Figure 7.10 Comparison of oils from three East Coast wells: (a) using the isotope ratios of all gasoline hydrocarbons and (b) using the isotope ratios of the cycloalkanes.

7.2.1.2 Bi-dimensional Approach

From the discussion in the preceding section, it has been established that isotope ratios of gasoline range hydrocarbons contain information useful for oil correlation and that all the compounds are not essential to the correlations. Sometimes, the comparison between two isotopes is sufficient to group together similar oils. The isotopes chosen for comparison have similar carbon lengths.

In Figure 7.11, the isotope ratios of $MCYC_5$ and $2MC_5$ are compared. These two compounds were chosen since they have low standard deviations or error associated with their measurement and previous plots indicate that the cycloalkanes may be more useful for correlation. Similar oils belonging to Families C, E, and F fall into distinct groups. The Lake Alma oil from Family A of the Bighorn Group (southeast Saskatchewan) appears to be more related to the Family C oils than any of the other oils while Chester, an Alberta oil, appears to be isotopically similar to Family F oils. Oils from the Arctic plot in a field different from the East Coast and the Saskatchewan oils. The boundary between the Family F and Arctic oils is uncertain. Plato (Family F) and Willesden Green (Alberta) are located in this area. Family F oils are of high maturity while the Arctic oils are of low maturity. This observation may indicate that maturity has little effect on the isotope ratios of $MCYC_5$ and $2MC_5$ (perhaps all of the gasoline range cyclic and branched alkanes). Rainbow and Shekilie plot within the region for the Arctic oils and Turner Valley is separate from the other oils.

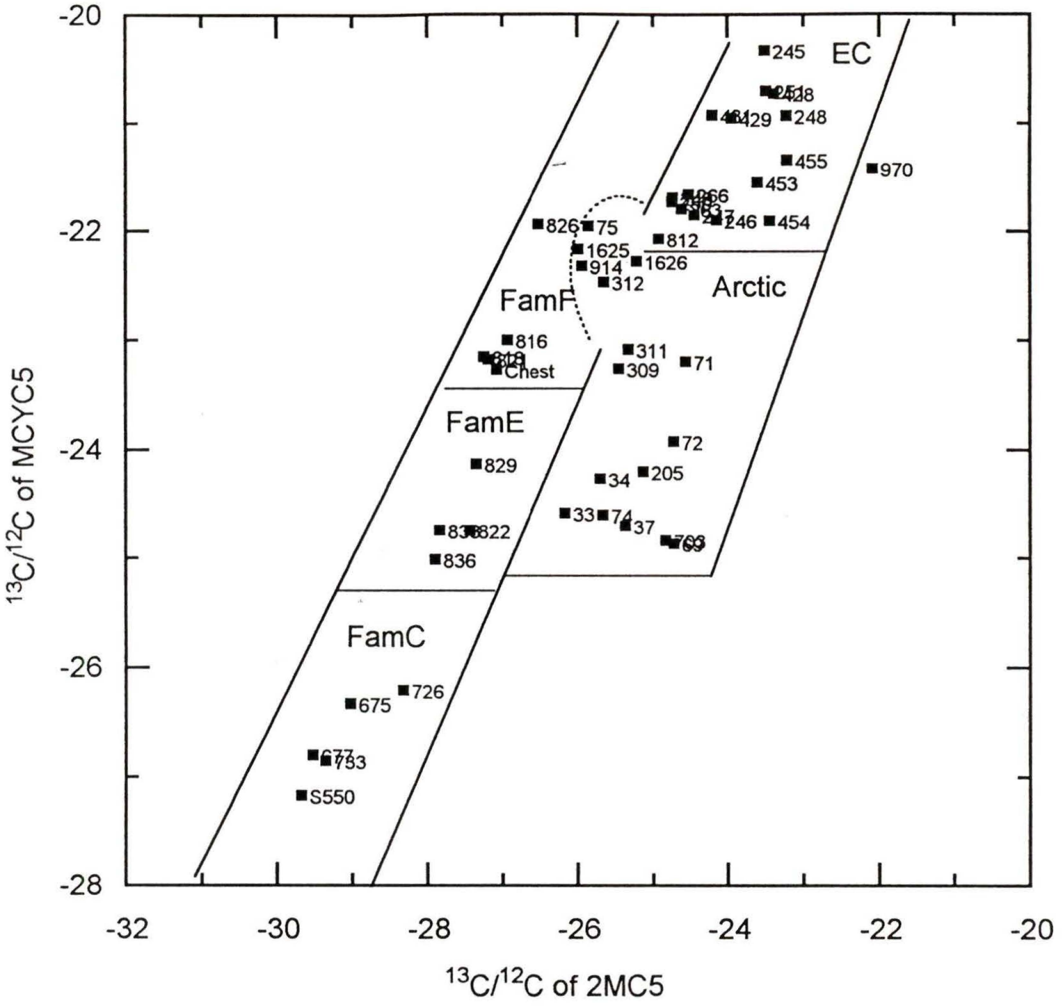


Figure 7.11 Relationship between the isotope ratios of MCYC5 and 2MC5 for all Canadian oils to demonstrate the use of stable carbon isotopes for correlation between oils. Note: EC = East Coast, Fam = family

Another example of a cross-plot which provides correlation information is given in Figure 7.12. Comparison of the isotope ratios of $MCYC_6$ and toluene results in the same correlations as determined from the previous cross-plot of isotope ratios. The Arctic and East Coast oils have greater isotopic similarity with each other than with the Saskatchewan oils. The gasoline range hydrocarbons of the East Coast oils are, on average, isotopically the heaviest (enriched in ^{13}C), followed by the Arctic oils. The oils of the East Coast and the Arctic do not separate into sub-groups.

Similar oils from Saskatchewan group according to family. From the gasoline isotope ratios, Family C oils are different from the Family E and F oils which share greater similarities. In contrast, through molecular data Osadetz et al. (1994) observed Family F as distinct from all other Williston Basin families. Figure 7.12 also indicates that Lake Alma of Family A is similar to Family C oils. Although the oils from both families are derived from Paleozoic marine source rocks, it is unclear why Family A oil would correlate with oils from Family C and not Family F or E. Family C is derived from a marine *carbonate* source while Family F and E are derived from clastic marine sources. The Family A oil is derived from a *carbonate* mudstone. Therefore, Family C and A oils may be derived from similar precursor material in similar environments.

The correlation of Rainbow and Shekilie oils is uncertain. These two oils appear to be similar to Family C oils here whereas they were more similar to the Arctic oils in the previous plot. The high maturity Turner Valley oil plots near Arctic oils which have low maturity. Also, the individual gasoline isotope ratios of the Arctic condensates

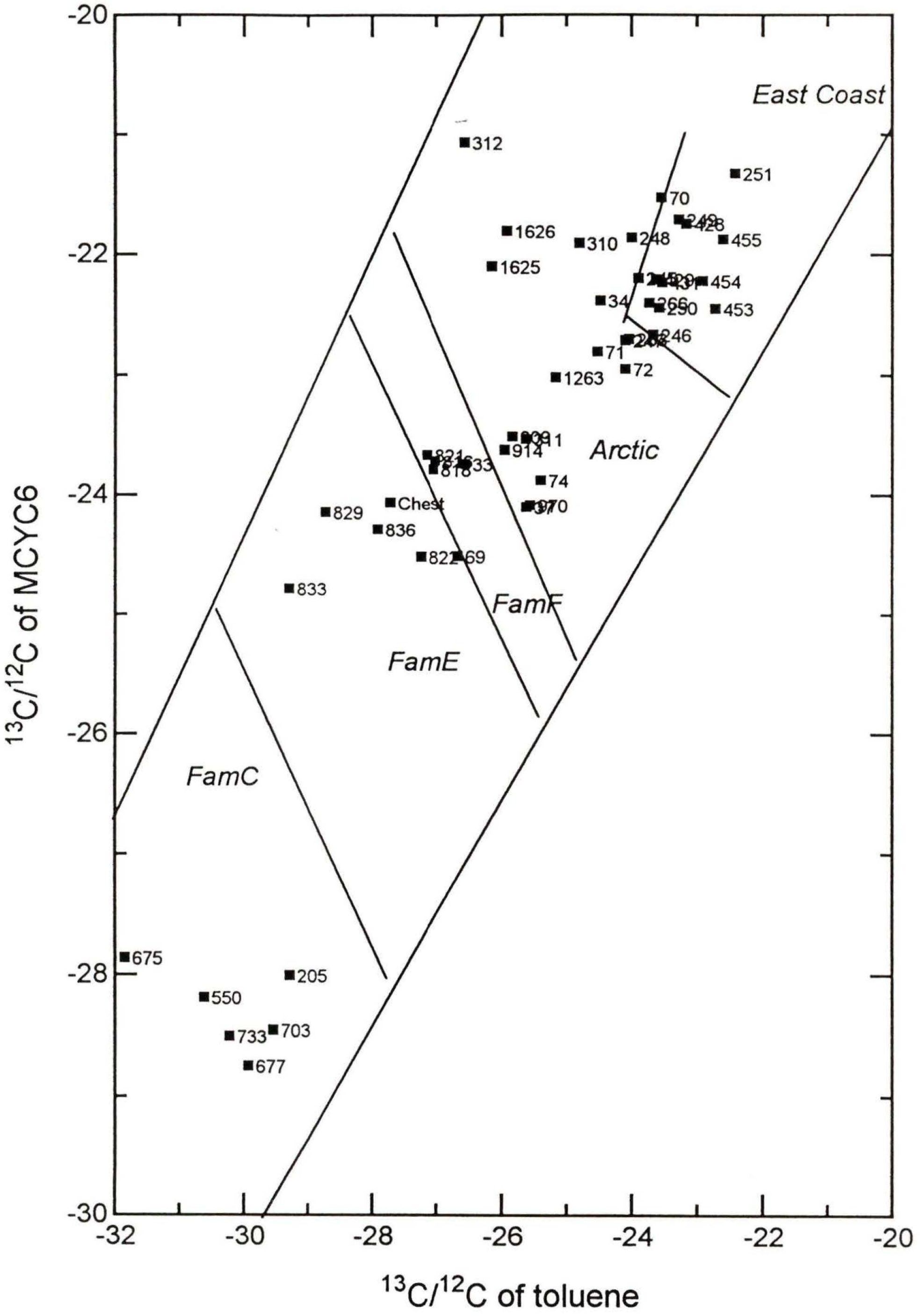


Figure 7.12 Oil correlation using the isotope ratios of methylcyclohexane and toluene.

(which form at higher temperatures and therefore maturities than oils) are not significantly different from the isotope ratios of the Arctic oils. This indicates that maturity may not have a significant effect on isotopes and that precursor source material has a greater effect on isotope ratios than alteration processes.

In general, the information obtained from comparison of two isotopes is sufficient to group Canadian oils according to similarities or differences. Although there is some uncertainty associated with two or three oils, the majority of the oils do separate into groups which are consistent with the source information already known about the oils (see Background).

This correlation between oils is important, especially for reservoir engineers. When two wells are located near each other, studies must be performed on oil from these wells to determine whether or not the oils are related through migration paths. The drive in the subsurface for oil production depends on gas or water. If the two oils (and therefore wells) are related, the wells must be drilled simultaneously to obtain maximum oil recovery from both wells. If only one of the oil wells is drilled, the drive for the other well will be reduced, leading to lowered overall production for the two wells.

Summary Points:

- Canadian oils can be effectively correlated by cross-plotting two isotope ratios.
- Lake Alma of Family A shares isotopic similarities with and is correlated to Family C oils.
- High maturity Turner Valley oil shares isotopic similarities with low maturity Arctic oils and the isotope ratios of Arctic oils and condensates are not significantly different, indicating that thermal maturity does not result in a

significant isotope effect.

7.2.2 Differentiation between Regional Areas

The correlation of oils based on regional area is relatively easy since the differences between the four different areas are generally larger than the differences within any one area. Variability can exist in the exact correlation of certain oils, but the larger groupings prevail. Although plots of isotope ratios relative to sample do reveal regional differences, a bi-dimensional approach is a more concise and effective way of presenting the information.

7.2.2.1 Bi-dimensional

From Figure 7.11 and 7.12 presented in an earlier section, the oils from the Jeanne d'Arc Basin (offshore Newfoundland) and the Beaufort-Mackenzie Basin (Canadian Arctic) are similar and different from the Williston Basin (Saskatchewan) group of oils. The Alberta oils do not correlate closely together since they all have different sources. Instead, they share similarities with oils from the other regions. These general trends are consistently detected in all bi-dimensional and multi-dimensional isotope relationships, but some difficulty exists in differentiating the East Coast and Arctic.

The relationships between toluene and nC_7 and benzene and nC_6 are used in Figures 7.13 and 7.14, respectively, to differentiate the major regional areas of oils.

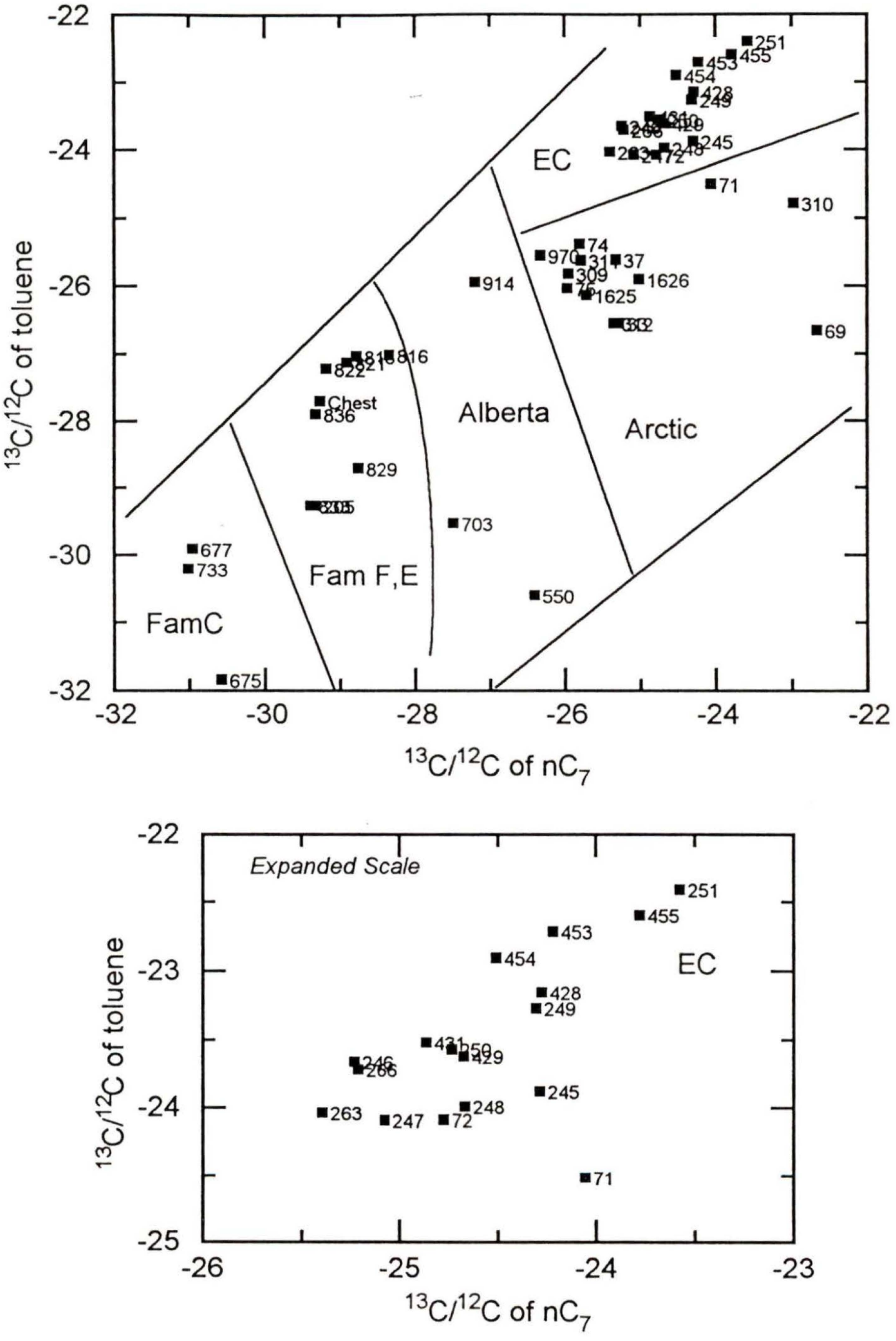


Figure 7.13 Comparison of carbon isotope ratios of toluene and and nC7 for Canadian oils. Note: fam = family, EC= East Coast

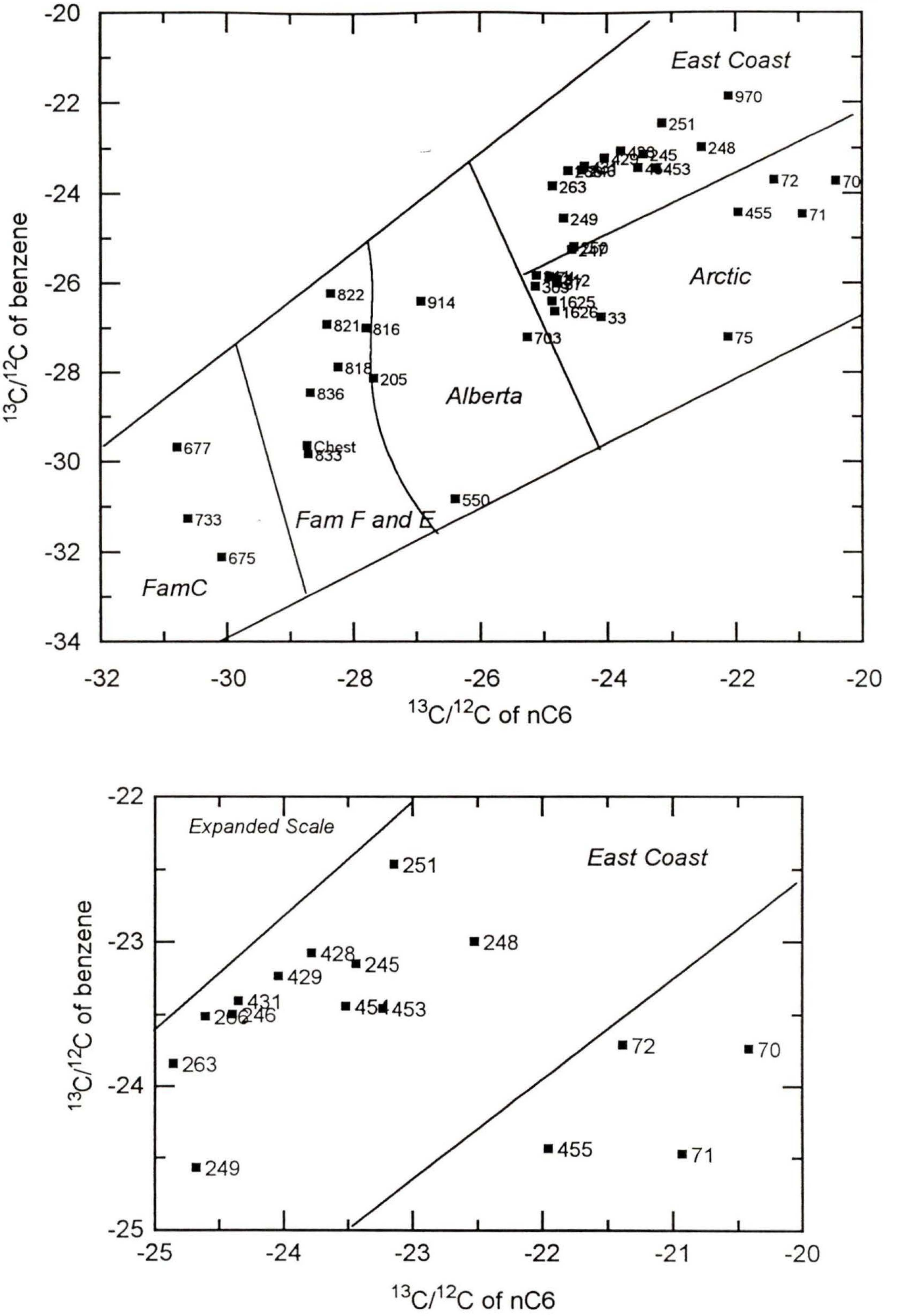


Figure 7.14 Oil correlation using the isotope ratios of benzene and nC6.

These two sets of parameters yield the same major oil groupings. For example, the East Coast and Arctic oils have similar nC_6 ratios, but are separated into 2 individual groups by the heavier (enriched in ^{13}C) benzene ratios in East Coast oils. It has been suggested by several investigators (e.g., Snowdon and Krouse, 1986; von der Dick et al., 1989) that some of the oils in the center of the Jeanne d'Arc Basin (e.g., Hebron) have had contributions from a second terrestrial source (in addition to the dominant marine source). The isotope ratios of Arctic and East Coast samples may be similar due to the terrestrial source contributions in each area. The Saskatchewan oils from a variety of marine sources are depleted in ^{13}C (lighter) for both ratios. The Alberta have a relatively wide range in isotopic composition, reflecting the variety of source conditions.

In Figure 7.15, the CYC_6 and nC_6 isotope ratios are compared for all oil samples. The differentiation between East Coast and Arctic oils is not as clear from this plot. However, the Saskatchewan and Alberta oils are all isotopically lighter than the other oils and separate from the East Coast or Arctic oils.

Summary Points:

- The differentiation of oil groups according to major geographic regions can be accomplished through cross-plots of isotope ratios.

7.2.2.2 Artificial Groups

Artificial groups were constructed from the poorly resolved compounds to determine whether or not the 'bulk' isotope ratios obtained from them could provide information for oil correlation. The three cyclic compounds, 1c3-$DMCYC_5$, 1t3-

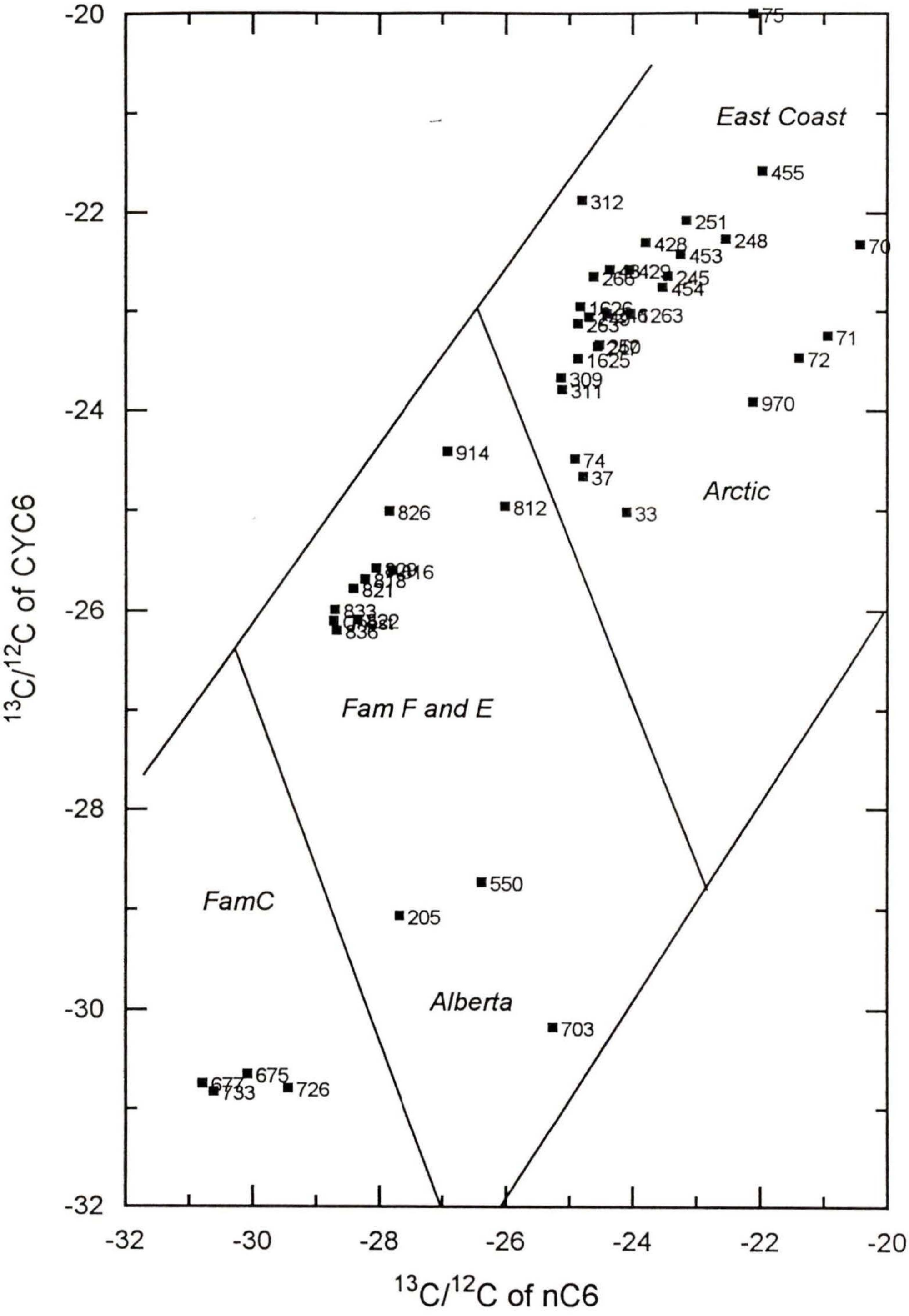


Figure 7.15 Oil correlation using the isotope ratios of CYC6 and nC6 in Canadian oils.

DMCYC$_5$, and 1t2-DMCYC$_5$, are prominent in almost all of the oils. An example of the relationship between the isotope ratios of this group and nC$_7$ are given in Figure 7.16. The comparison of these ratios result in the separation of oils into their respective groups based on source environments.

Although these 'artificial' groups may aid in the correlation of oils, the actual isotope ratios should be interpreted with caution (with regard to determining source conditions) since they are only an average of three individual isotope ratios. Artificial groups composed of hydrocarbons in low concentrations do not yield reliable correlations. Therefore, if an artificial group is to be used for correlation purposes, a group composed of hydrocarbons in high concentrations should be used.

Summary Points:

- Artificial groups composed of hydrocarbons in high concentrations may be useful in oil correlation studies, but the 'bulk' isotope ratios must be interpreted cautiously with regard to providing source information.

7.3 INTERPRETATION OF ISOTOPIC VARIATION IN OILS

The isotope ratios of the oil samples in the current study can provide some information regarding source conditions. Several investigators have determined that marine plants are sometimes more enriched in ^{13}C than non-marine plants. Therefore, it may be expected that isotopes in oils derived from marine environments are less negative than those from non-marine environments.

Sofer (1984) used the isotope ratios of the aromatic and saturate fractions to differentiate between marine and non-marine oils. In Figure 7.17, the lines (relationship

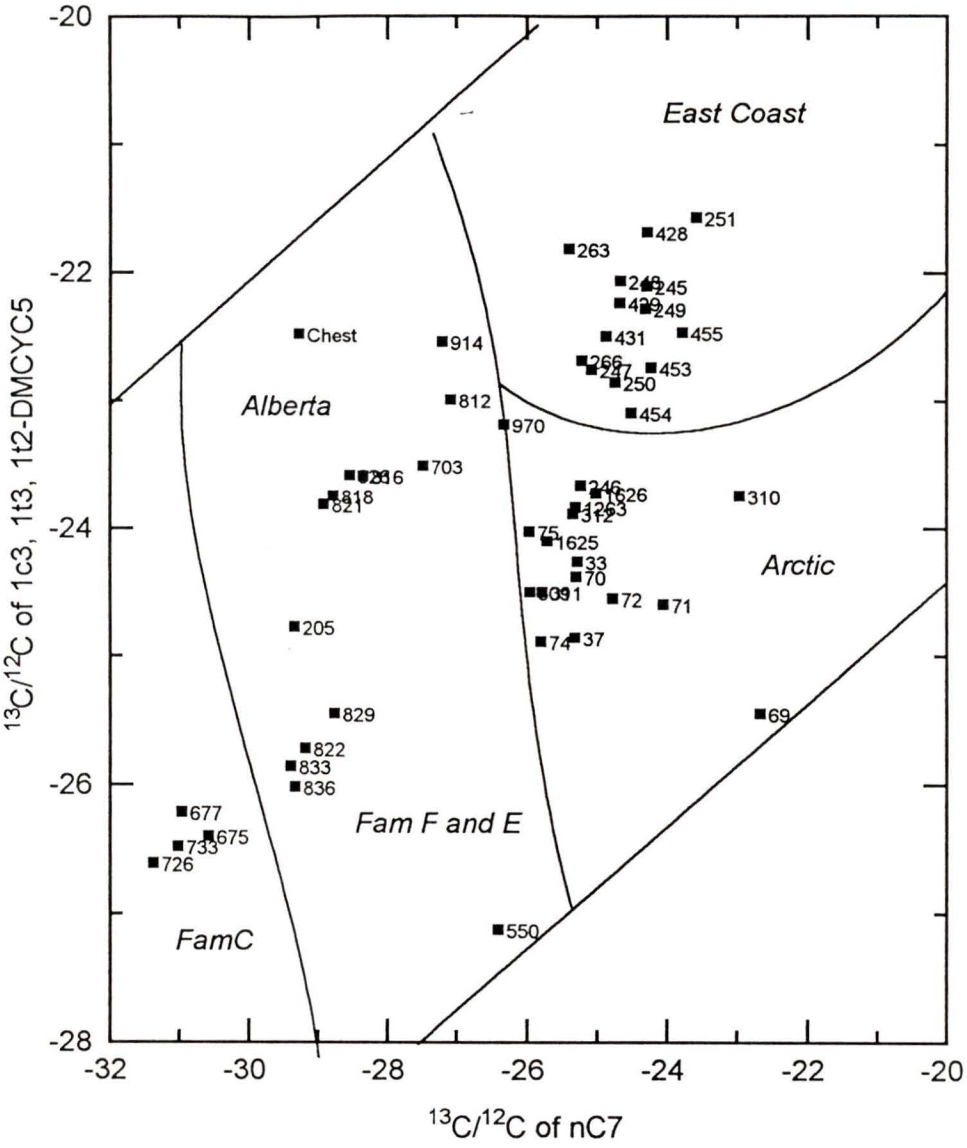


Figure 7.16 Oil correlation using an 'artificial' isotope group.

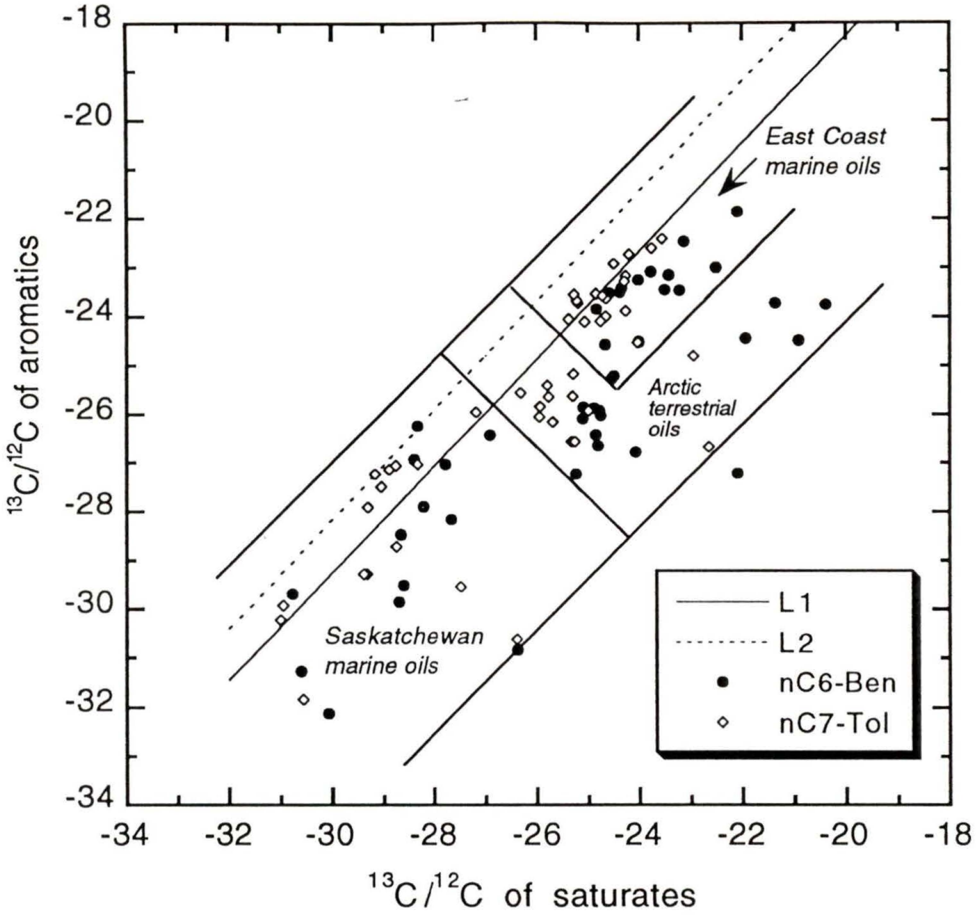


Figure 7.17 Use of isotope ratios of individual saturate and aromatic compounds for distinguishing between marine and non-marine oils (after Sofer's 1984 work). L1 and L2 are obtained from Sofer's work with the bulk aromatic and saturate fractions. Terrestrial oils should plot between L1 and L2 with more negative isotope ratios while marine oils should plot to the right of L1 with less negative isotope ratios (see Figure 3.8).

between the two oil fractions) Sofer used to differentiate between marine and non-marine oils are plotted along with the isotope data for the individual gasoline range hydrocarbons in Canadian oils. For comparison with Sofer's work, the nC_6 and nC_7 saturate hydrocarbons of Canadian oils are compared to the aromatic benzene and toluene compounds.

The individual saturate and aromatic compounds for Canadian oils do not result in the division or classification of non-marine and marine oils. Most of the Arctic oils, which are derived from a terrestrial source, plot in Sofer's marine field. Some of the marine-derived Saskatchewan and East Coast oils plot within the non-marine field. Sofer used *bulk* isotope ratios of the aromatic and saturate fractions for classification while the isotope data set in Figure 7.17 for the Canadian oils is composed of *individual* gasoline range saturate and aromatic hydrocarbons. The relationships between the aromatic and saturate ratios in these two types of data sets are not comparable.

Marine oils are not always enriched in ^{13}C, and terrestrial oils are not always depleted in ^{13}C. There are certain marine environments which may lead to light (depleted in ^{13}C) isotope ratios. For example, in anoxic areas, methanogens (which utilize methane) preferentially utilize ^{12}C and can incorporate this light isotope into their biomass (Deines, 1980; Whiticar, 1993). These bacteria, enriched in ^{12}C, can become incorporated into the kerogen and eventually produce light isotopes in oil. It is possible that the microbes altering the gasoline range hydrocarbons incorporate ^{12}C in a similar manner and eventually result in isotopically light oil.

From Figure 6.10 and 6.11 (Results), the carbon isotope ratios of the hydrocarbons in Jeanne d'Arc Basin oils range from -20 to -26 ‰ while those in the Arctic oils range from -21 to -28 ‰. The East Coast oils are all derived from a marine source while the Arctic oils are derived from a terrestrial source. The isotope ratios of most of the individual hydrocarbons in the East Coast oils are slightly less negative (enriched in ^{13}C) than any hydrocarbons in the Arctic oils. The Saskatchewan oils (Figure 6.12), which are also derived from a variety of marine sources, have more negative gasoline isotope ratios (-22 to -32 ‰) than the terrestrial oils. Thus, it does not always hold true that marine oils have less negative (enriched in ^{13}C) isotopes ratios than non-marine oils.

Family C oils separate into a group which is different from the other southwest Saskatchewan oils. The light isotope ratios of Family C oils are indicative of an anoxic, carbonate, marine source environment. The other southwest Saskatchewan families are derived from marine sources, but none are derived from carbonates in anoxic environments (Osadetz, 1994) like Family C. Although the southeast Family A oil (Lake Alma) also has light isotope ratios similar to those of Family C, the same source conditions have not been reported for Family A (e.g., Osadetz et al., 1992). However, Lake Alma is derived from a carbonate mudstone containing alginite (Osadetz et al., 1992). The isotopic similarity between Family A and C may be related to the similarity of source material or Lake Alma (Family A) may have been subjected to similar anoxic conditions as Family C that were not detected by other analyses.

Osadetz et al. (1994), from compositional data (e.g., biomarkers), identified Family F oils as a distinct group in the Williston Basin. In this study, the isotope ratios of gasoline range hydrocarbons indicate that Family C is the distinct Williston Basin group. The isotope ratios of Family F and E oils are similar because they are both derived from similar marine, clastic sources.

The Alberta oils have isotope ratios spanning 10 ‰ (Figure 6.13). Some of these Alberta oils may have similar sources (see Background) which are reflected in the isotope ratios. For example, Figure 7.18a gives the isotope ratios for Shekilie and Rainbow which are both sourced from sediment deposited under anoxic, hypersaline conditions (Creaney and Allan, 1990). The isotope trends for these two oils are similar. It is expected that these oils might correlate with the anoxic Family C oils. In Figure 7.11, Rainbow and Shekilie do plot within the Family C region, but this is not observed in all cross-plots (e.g., Figure 7.12).

The other Alberta oils have different (e.g., Willesden Green or Chester) or unknown sources (e.g., Turner Valley). The isotope ratios for these oils are given in Figure 7.18b. Although the isotope trends are similar, there is variability especially in the shorter-chained hydrocarbons between iC_5 and CYC_6. From cross-plots of isotope ratios, Chester appears to be most similar to Family F oils, and, therefore, it was probably derived from a marine clastic source. The correlation of Willesden Green is uncertain, but it often groups with or near the Saskatchewan Family F oils or East Coast oils (Figure 7.11, 7.13, 7.14).

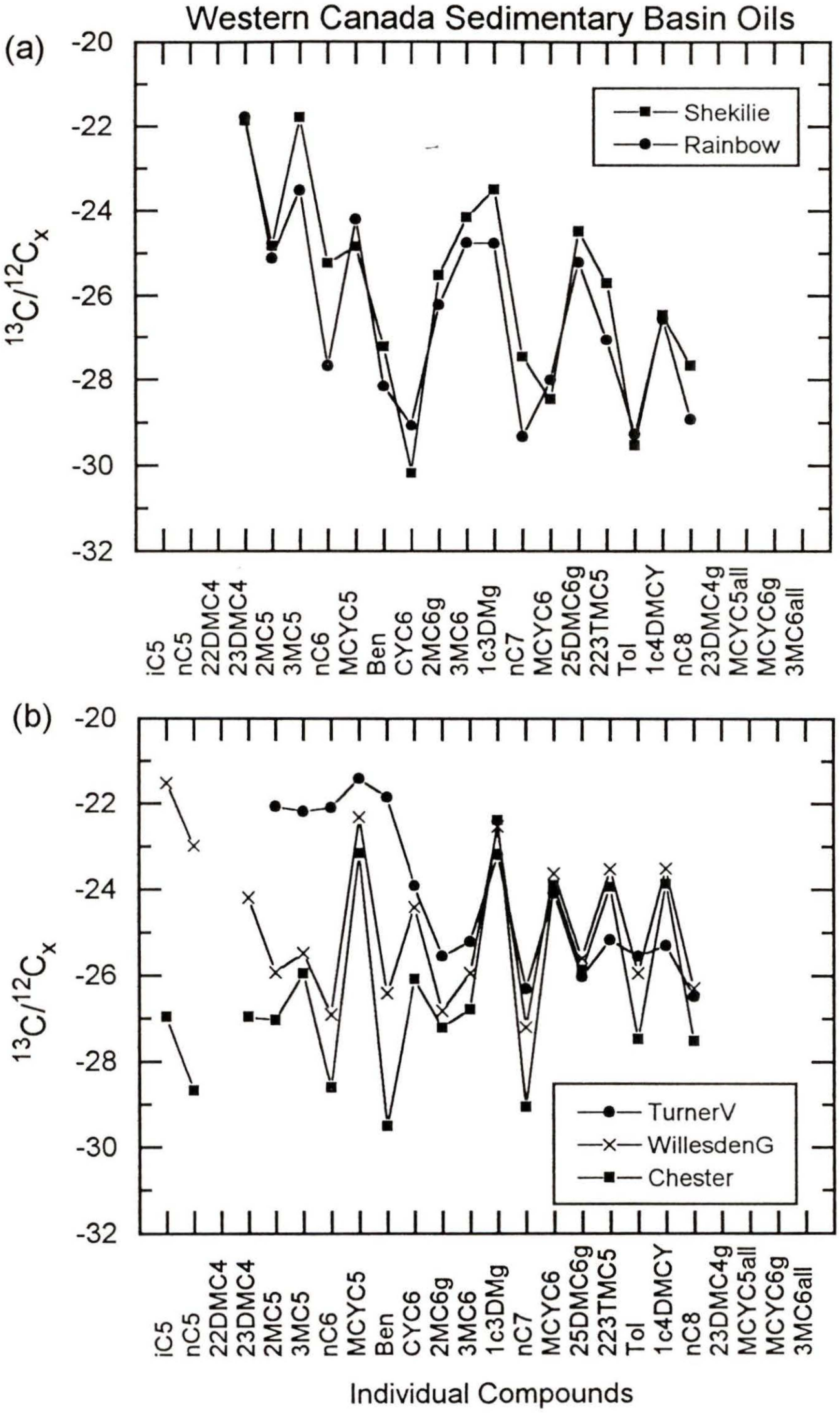


Figure 7.18 Isotope ratios of hydrocarbons in Western Canada Sedimentary Basin oils: (a) similarity of Rainbow and Shekilie oils and (b) comparison of Turner Valley, Willesden Green, and Chester oils.

The source of Turner Valley oil is unknown since its maturity is too high to obtain reliable biomarker data (Lloyd Snowdon, personal communication). Turner Valley is often correlated with Arctic oils (e.g., Figure 7.12, 7.13, 7.15) so its source may have a terrestrial contribution.

Summary Points:

- Individual isotopes of saturate and aromatic hydrocarbons do not result in the classification of marine and non-marine oils as in the work of Sofer on bulk isotope ratios of saturate and aromatic oil fractions.

- Isotope ratios associated with East Coast oils are usually the most enriched in ^{13}C corresponding to a typical marine source environment.

- The correlation of Family C and A oils may be related to similar precursor material or anoxic source conditions.

- Alberta oils correlate with other oils that are derived from similar source material.

7.4 ALTERATION OF MOLECULAR OIL COMPOSITION

Oils can be affected by thermal maturation or secondary alteration processes such as biodegradation and water-washing. These processes change the molecular composition of oils. These changes often make correlations difficult because many of the correlation techniques are based on the recognition of molecular similarities between oils or oils and source rocks.

For example, the sulfur content and density of bulk oils can increase as a result of biodegradation. More specific information can be obtained from major oil fractions or the individual compounds. The change in compound distribution related to biodegradation can be observed in the gas chromatograms of the C_{15+} saturate and the C_5 to C_{10} fractions (Figures 6.2 and 6.4). Other researchers have mainly used biomarker data such as Pr/Ph ratios to identify source or secondary alteration (e.g., Osadetz et al., 1994). Since the focus of this thesis centers on the use of gasoline range hydrocarbons, the molecular parameters in this range are calculated for the Canadian oils and discussed.

Several researchers such as Thompson (1983, 1987), Mango (1987, 1991, and 1994), Schaefer (1987), and Philippi et al. (1977, 1981) have developed specific gasoline range parameters to characterize oils and to aid in the recognition of thermal alteration or secondary alteration processes such as biodegradation or water-washing. This calculation of molecular parameters (e.g., PI1 and PI2; see equations 3.5 and 3.6 in section 3.2.4) allows automatic normalization so that samples varying in concentration between runs can be compared.

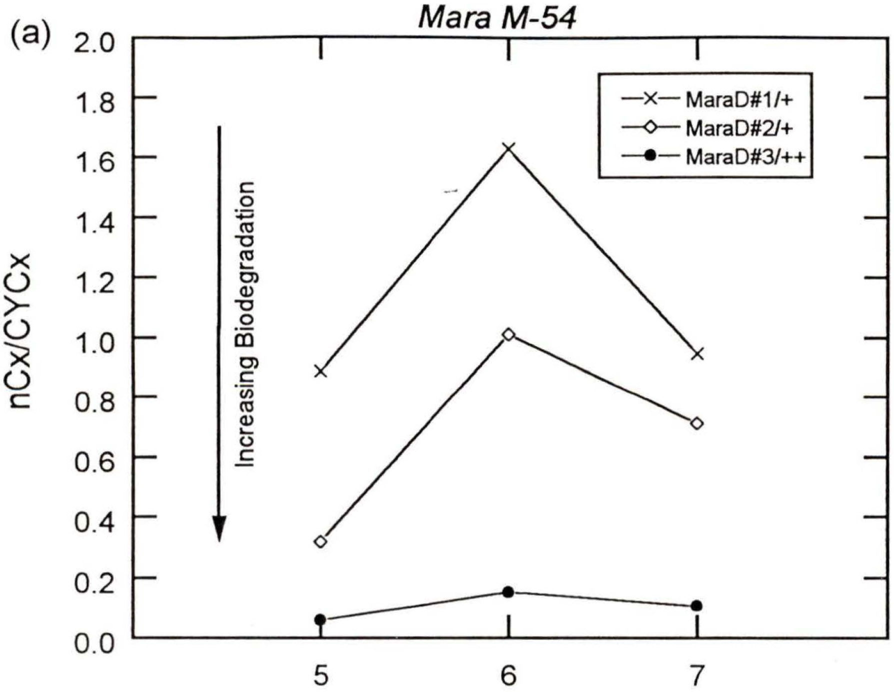
7.4.1 General Biodegradation Indices

To illustrate the effect of biodegradation on the molecular composition of gasoline range hydrocarbons, the ratios of individual n-alkanes and cycloalkanes for carbon numbers 5, 6, and 7 (e.g., $nC_5/MCYC_5$, nC_6/CYC_6, and $nC_7/MCYC_6$) in Mara M-54 and Saskatchewan Family C oils are compared (Figure 7.19). The oils with the lowest values for these ratios should be the most degraded, and this holds true for the Canadian oils.

In Figure 7.19, Mara oil DST#3 (455) has the lowest value for the ratios as compared to DST#2 (454) and DST#1 (453) which corresponds to the degree of biodegradation in the samples (determined from HMW data; see Results and Table 4.1) with DST#3 as the most degraded and DST#1 and DST#2 with low biodegradation. In Figure 7.19b, Battle Creek (#726) and Battrum Unit1 (#675) have low ratios. These 2 oils are the most degraded samples in Family C. Butte (#677) and Cantuar Main (#733) have the highest values for these ratios, indicating lower biodegradation in these samples. It is difficult to determine the exact levels of biodegradation in each oil, but it is easy to differentiate (in this plot and in the gas chromatograms in Figure B7 in Appendix B) between the 2 degraded and the 2 non-degraded oils.

The relationship between total n-alkanes/branched alkanes and total n-alkanes/cycloalkanes can also be used to demonstrate the effect of biodegradation on molecular composition of oils. Since the n-alkanes are preferentially removed over the branched alkanes and cycloalkanes, the ratios of n-alkanes to branched alkanes or cycloalkanes are expected to be lower for biodegraded oils as compared to non-biodegraded oils. These ratios are plotted for all oils in Figure 7.20. From the relationship between these two parameters, any oils with values less than approximately one for both ratios have high levels of biodegradation.

Hebron I-13, Mara M-54, Families F and E, and Nerlerk M-98 oils are plotted in Figures 7.21, 7.22, and 7.23 to give more detail. The level of biodegradation in samples is indicated by '+' or '-' symbols (levels derived from other analyses and noted in Table



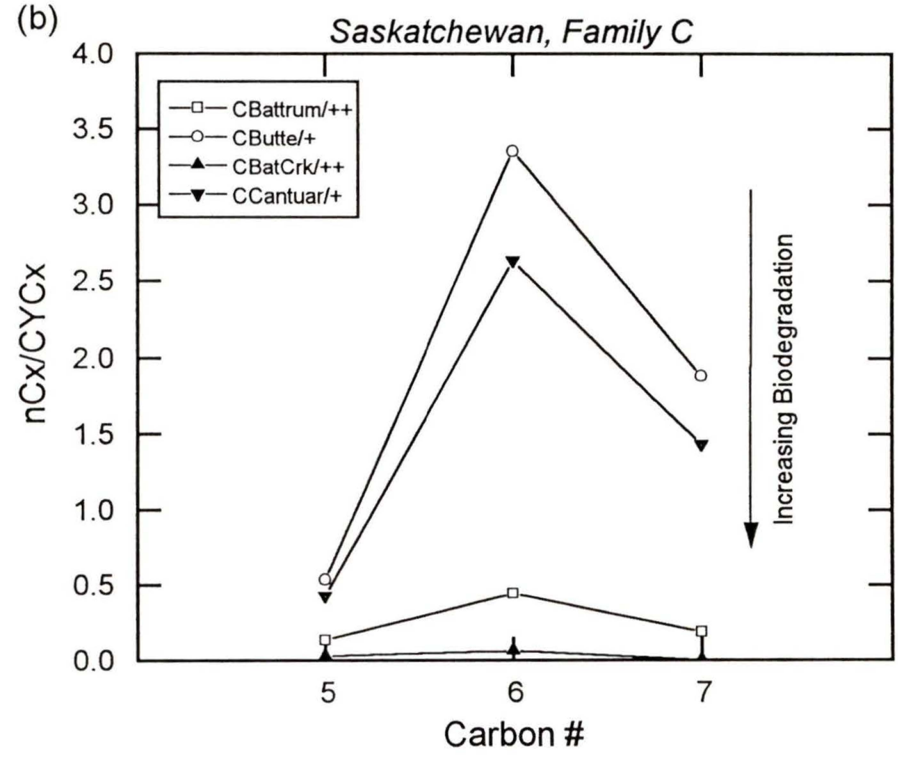


Figure 7.19 Comparison of nCx/CYCx (nC5/MCYC5, nC6/CYC6, nC7/MCYC6) to illustrate biodegradation: in (a) Mara M-54 oils and (b) Saskatchewan Family C oils. Note: '+' indicates level of biodegradation

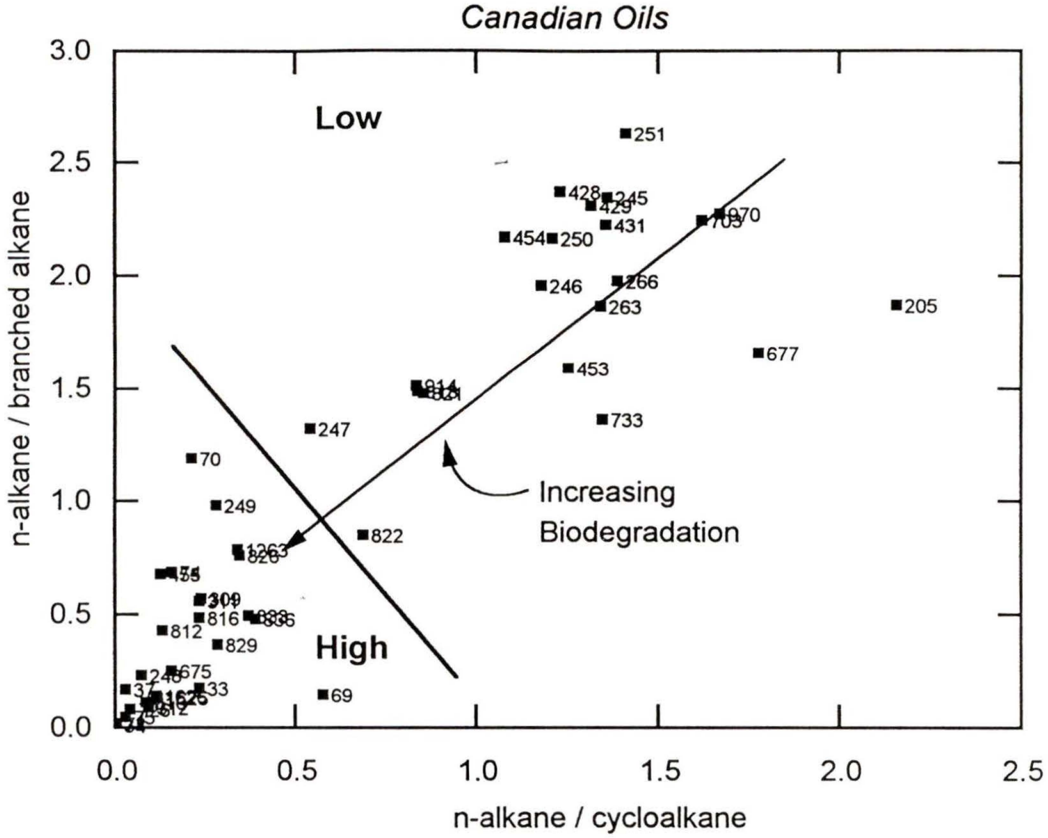


Figure 7.20 Comparison of total n-alkanes/branched alkanes and total n-alkanes/cycloalkanes for all Canadian oils examined in this study.

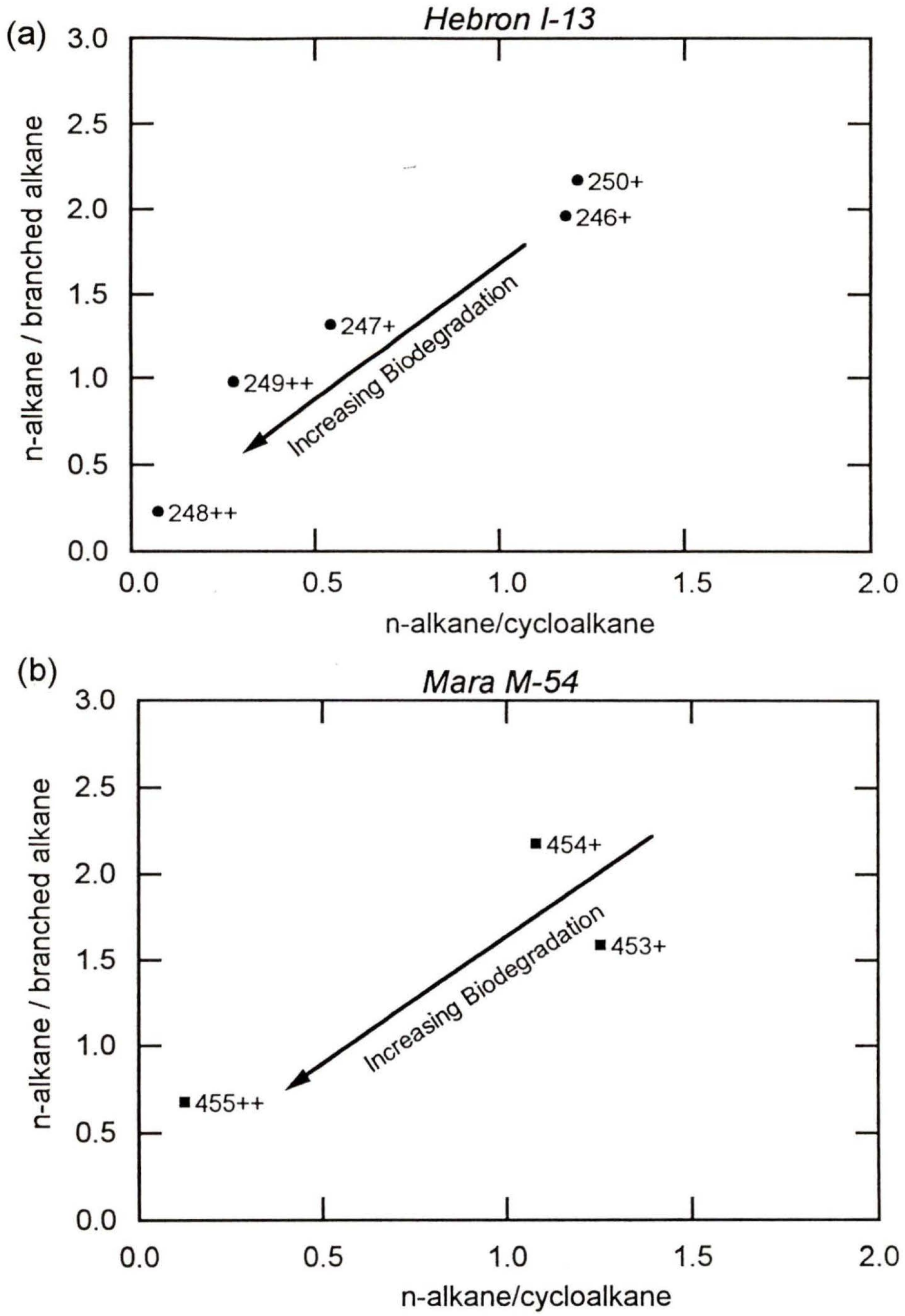


Figure 7.21 Relationship between total n-alkanes/branched alkanes and total n-alkanes/cycloalkanes for East Coast oils: (a) Hebron I-13 oils and (b) Mara M-54 oils to illustrate degradation pathways. The '+' and '-' symbols represent degree of biodegradation ranging from none (-) to high (+++).

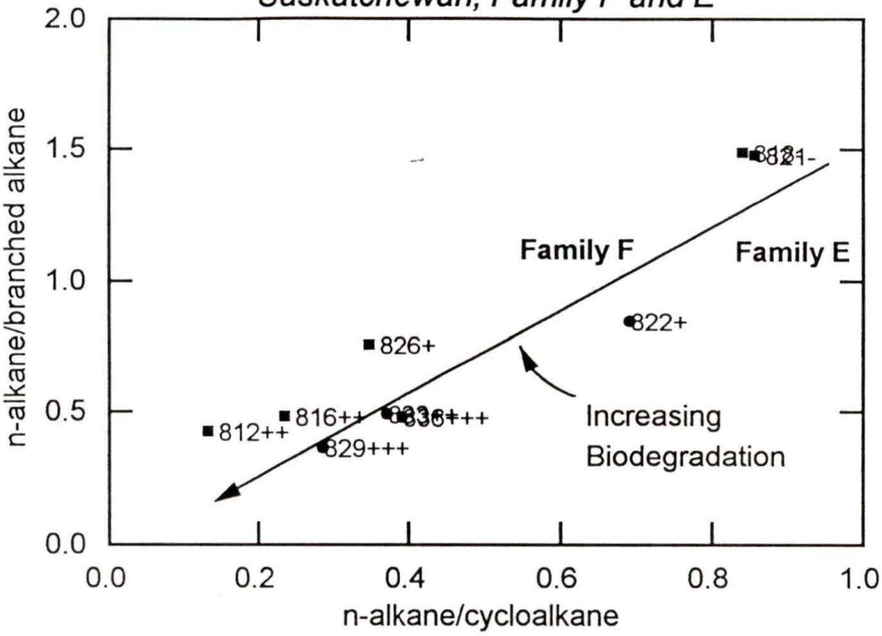

Saskatchewan, Family F and E

Figure 7.22 Comparison between total n-alkanes/branched alkanes and total n-alkanes/cycloalkanes ratios for Saskatchewan Family F and E oils.

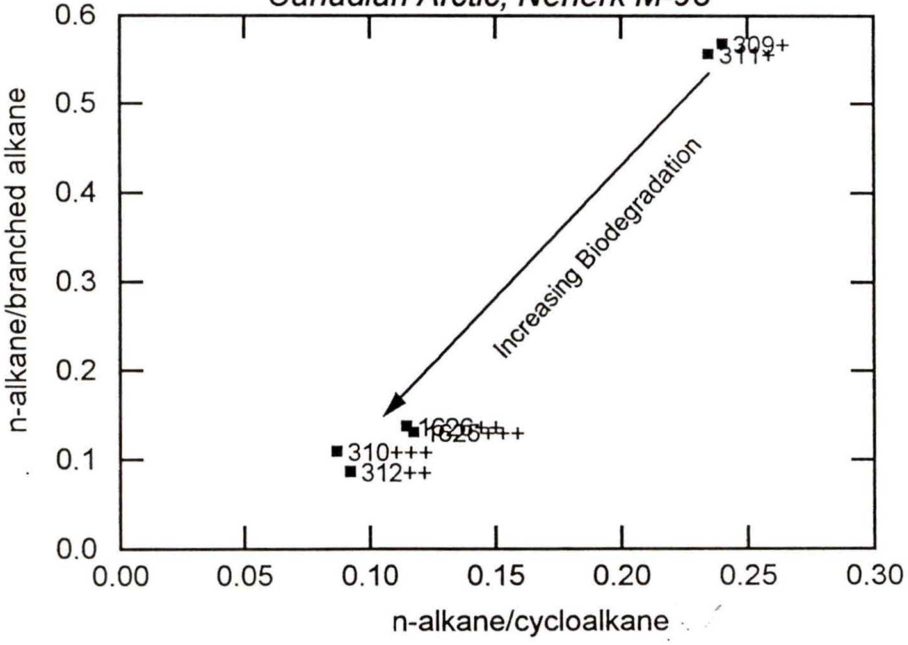

Canadian Arctic, Nerlerk M-98

Figure 7.23 Comparison between total n-alkanes/branched alkanes and total n-alkanes/cycloalkanes ratios for Nerlerk oils from the Canadian Arctic.

4.1). A '-' symbol indicates a non-biodegraded oil and one, two, or three '+' symbols indicate low to high biodegradation.

The Hebron I-13 oils are presented in Figure 7.21a. As biodegradation increases, the values for the two ratios decrease. The most biodegraded oil (determined from HMW data) in this suite of oils does have the lowest values for the ratios of total normal/branched and normal/cyclic alkanes. In Figure 7.21b, these ratios are compared for Mara M-54 oils. DST#3 (#455) is clearly the most degraded while DST#1 (#453) and DST#2 (#454) are less biodegraded. It is, however, difficult to determine whether DST#2 or DST#1 is the least degraded oil.

Figure 7.22 gives the relationship between total normal/branched and normal/cyclic alkanes for Saskatchewan Family F and E oils. Kerrobert (#821) and South Eureka (#818), the non-biodegraded oils from Family F, have the highest values for the two ratios. Forgan (#826), with intermediate biodegradation, has intermediate values for the two ratios. The two highly biodegraded, Plato (#812) and Smiley (#816), have the lowest values for these two ratios. In Family E, Court (#822) is the non-biodegraded (or least biodegraded) oil with high values for the ratios of normal/branched and normal/cyclic alkanes. Hearts Hill (#833) has intermediate biodegradation. Cactus Lake (#829) and Buffalo Coulee B (#836) are the most degraded oils with the lowest values for the ratios of n-alkanes to branched alkanes and cycloalkanes. Although the Family E oil with no or low biodegradation is distinct from the other oils of this family, it is difficult to differentiate between the intermediate and highly biodegraded oils. It is possible that most of the oils in this family have been subjected to similar levels of biodegradation and have undergone similar changes in molecular composition.

The Nerlerk and Niglintgak oils and condensates are the most biodegraded of all the samples examined in this study. The values of the ratios of normal/branched and normal/cyclic alkanes are the lowest of all the samples studied. For example, Nerlerk M-98 oils (Figure 7.23) have values less than 0.6. DST#9 (#309) and DST#8 (#311) are the clearly the least biodegraded while the other four samples from this well are more degraded.

In general, the degree of biodegradation in the oils determined from gasoline range data is in agreement with the degree of biodegradation determined from other HMW data. There may be some discrepancies in the intermediate and highly biodegraded oils since their compositional differences may be small.

Summary Points:

- Biodegradation results in the preferential removal of the n-alkanes over the cyclic alkanes and can be identified by the ratios of total normal/branched and normal/cyclic alkanes. Low values for both of these ratios (e.g., < 1) are indicative of the presence of biodegradation.

7.4.2 Thompson's Indices

Some of the gasoline range indices developed by Thompson, such as PI1, PI2, iC_5/nC_5 to $3MC_5/nC_6$, and $3MC_5$/ben to CYC_6/ben, are calculated for the Canadian oils to aid in the characterization and correlation of the oils.

Thompson (1979, 1983) found that the relationship between PI1 and PI2 (equations 3.5 and 3.6) results in the grouping of oils into biodegraded, normal, mature, and supermature classes. The PI1 and PI2 indices for all the oil samples in the current study are presented in Figure 7.24 and compared to Thompson's results (e.g., the boundaries Thompson determined for the different classes are drawn on the graph).

The highly degraded oils such as Nerlerk and Niglintgak do plot within Thompson's biodegraded class. In addition, highly degraded oils from Hebron I-13 (e.g., DST#10; #248) and Mara M-54 (e.g., DST#3; #455) also plot in this biodegraded category. None of the Saskatchewan oils plot within the biodegraded class of Thompson. The Saskatchewan oils may have a lower level of biodegradation than oils from the Arctic or the Hebron and Mara wells of the East Coast. Most of the Saskatchewan plot in the normal class even though some are biodegraded.

All of the Hibernia samples plot within the mature class as well as Turner Valley (#970), two Saskatchewan Family C oils (e.g., Butte (#677) and Cantuar Main (#733)), and most of the Hebron oils. Shekilie (#703) and Rainbow (#205) from the Western Canada Sedimentary Basin and Hebron I-13 DST#1 (#245) and Mara M-54 DST#1 (#453) for the Jeanne d'Arc Basin plot within Thompson's supermature class. From the background information related to these oils, it is expected that these oils would be mature.

Although the boundaries for the different classes of oils developed by Thompson hold true for most of the samples, there are some exceptions. The separation of oils into

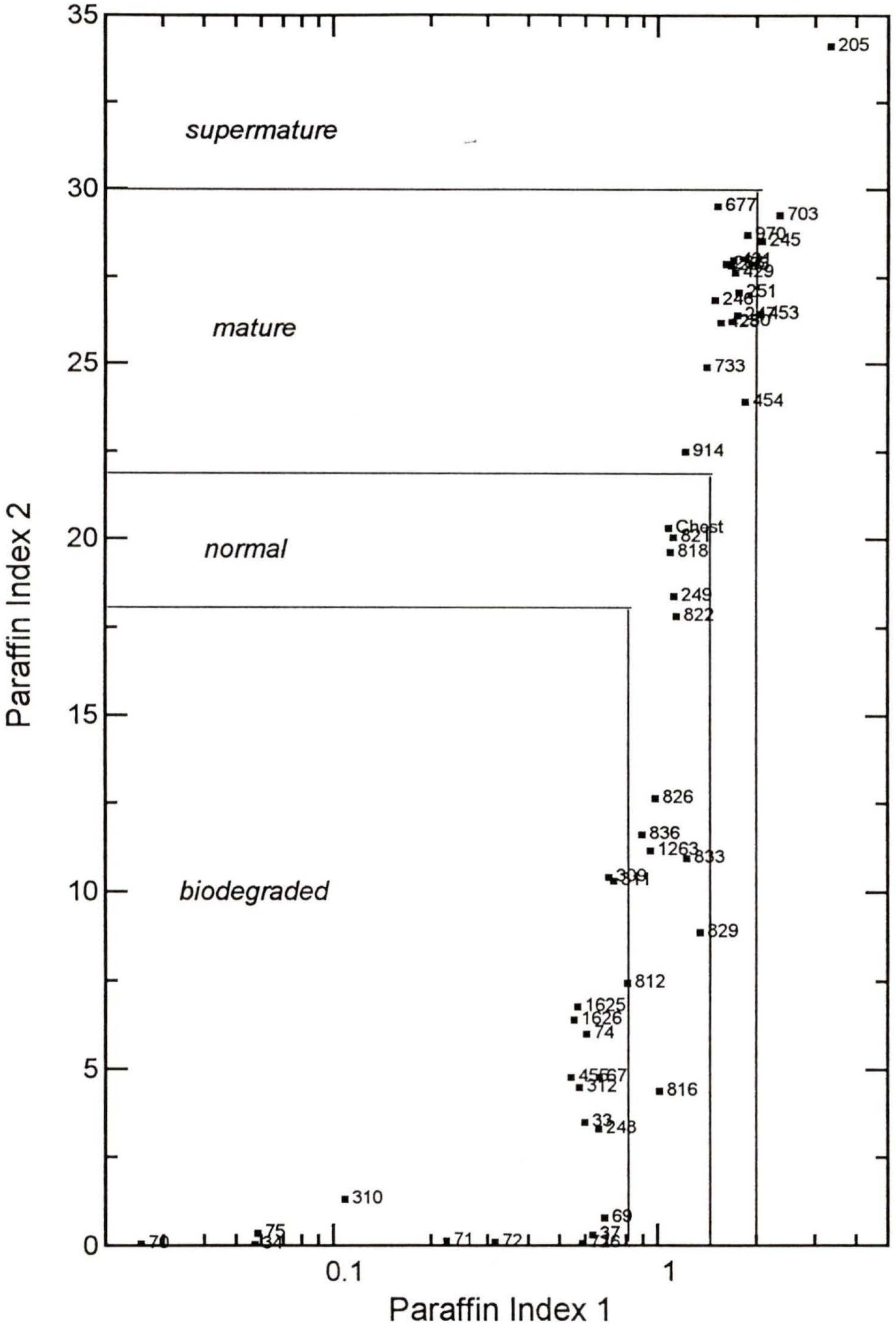


Figure 7.24 Thompson's paraffin indices calculated for the Canadian oils. The boundaries used by Thompson to differentiate between mature, supermature, normal, and biodegraded oils are drawn on the graph.

biodegraded, normal, or mature classes is not always clear (e.g., biodegradation in the Southwest Saskatchewan samples was not detected). Similar observations were made by Osadetz et al. (1993). It is possible that these parameters are only valid for classifying extremely biodegraded oils.

The ratio between iC_5/nC_5 and $3MC_5/nC_6$ can also lead to differentiation between maturity and biodegradation since oils with values for both ratios greater than one are classified as biodegraded (Thompson, 1983). These ratios decrease with increasing maturity since cracking reactions occur that increase the amount of the shorter chained n-alkanes. Biodegradation results in the preferential removal of the n-alkanes leaving behind the more resistant branched and cyclic compounds so the ratios of iC_5/nC_5 and $3MC_5/nC_6$ should increase with increasing degradation.

These ratios are compared for all the oils in Figure 7.25. The oils with values greater than one for both ratios, such as the Arctic oils, are all highly biodegraded and relatively immature. Family C has been documented as having the lowest maturity of the southwest Saskatchewan oils while Family F has been described as having the highest maturity (Osadetz et al., 1994). Most of the Family F oils have lower ratios than Family C oils. Family E oils, however, have higher ratios than Family C oils, indicating that the Family E oils are either less mature or more biodegraded than Family C oils. A maturity trend has been noted by some authors in the Hibernia K-18 well (e.g., DST#11 (#266) least mature, DST#1 (#251) most mature; Fowler and Brooks, 1989). Sample #251 does have the lowest value of the 3 oils studied in this well.

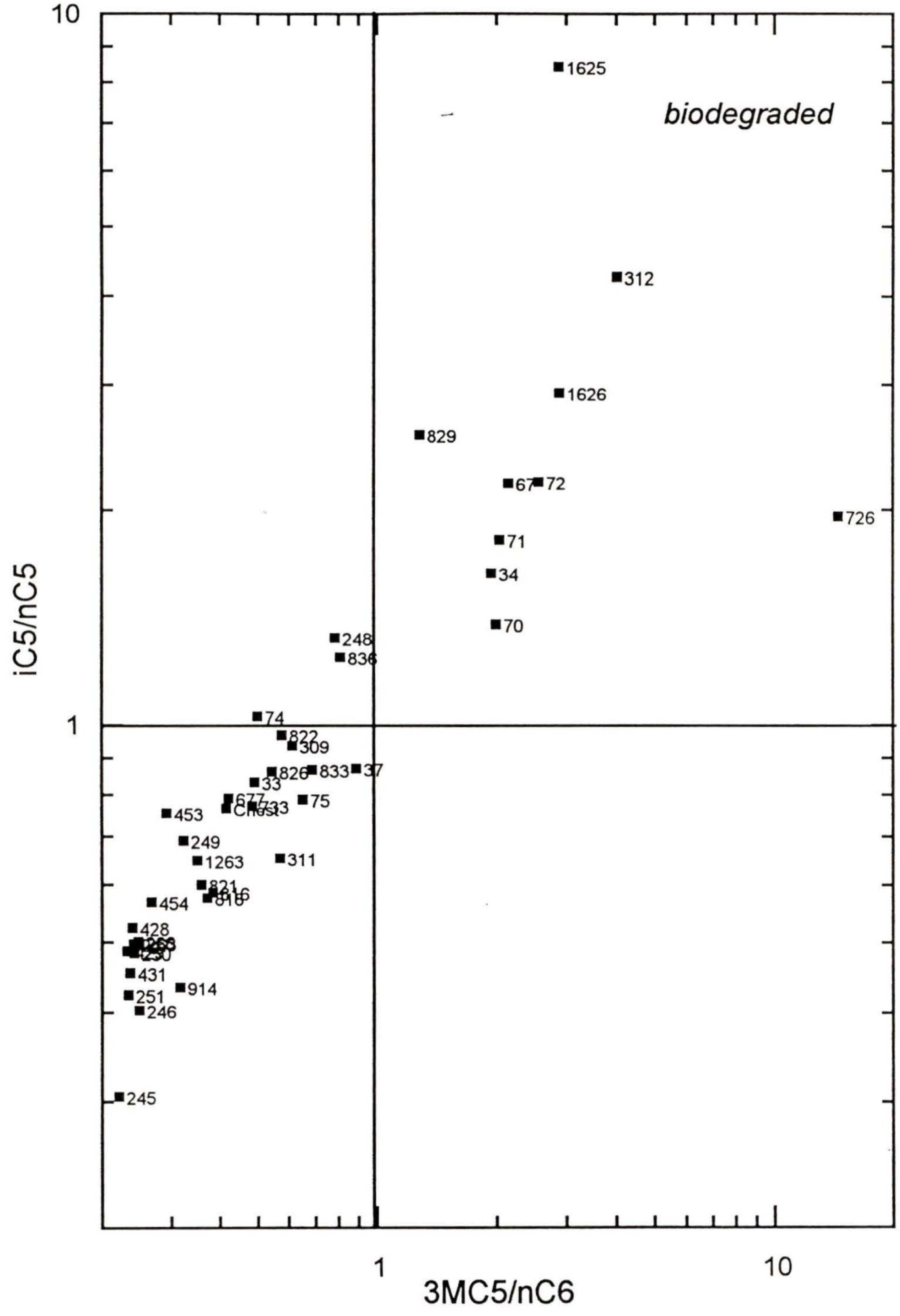


Figure 7.25 Thompson's iC5/nC5 and 3MC5/nC6 ratios calculated for the Canadian oils.

There is some ambiguity present when the ratios of iC_5/nC_5 and $3MC_5/nC_6$ are used to distinguish between biodegradation or maturity. The only oils in the current study classified (according to the scheme of Thompson) as biodegraded are samples which are highly biodegraded (as determined from previous work; see Chapter 4). There are many oils which are biodegraded, but classified as mature following Thompson's guidelines. This ambiguity may be related to the basic assumption made in using these parameters to show processes. It is possible that the parameters are not as source-independent as Thompson (1979) originally thought. Also, most of the samples in this study are biodegraded to some degree and maturity differences may be subtle. Thus, boundaries such as those of Thompson (included in the Figure 7.25) may be difficult to draw for this sample set.

A set of parameters sensitive to water-washing is the $3MC_5$/ben and CYC_6/ben ratios (Thompson, 1983). The aromatics are more water soluble (e.g., at 25 °C, benzene is approximately 10 times more soluble than CYC_5; Table 3.4) and therefore more easily removed during water-washing than the branched or cyclic alkanes. These ratios will be high for oils that are water-washed. This relationship between $3MC_5$/ben and CYC_6/ben is presented in Figure 7.26. The Hibernia samples, which are not biodegraded, have some of the lowest values. The samples with the highest values are biodegraded as well as water-washed, but some with only low levels. From Figure 7.26, some of the samples which exhibit the greatest water-washing effects are Court (#822) and Buffalo Coulee (#836) of Family E, Cantuar Main (#733) of Family C, and Kerrobert (#821) of Family F.

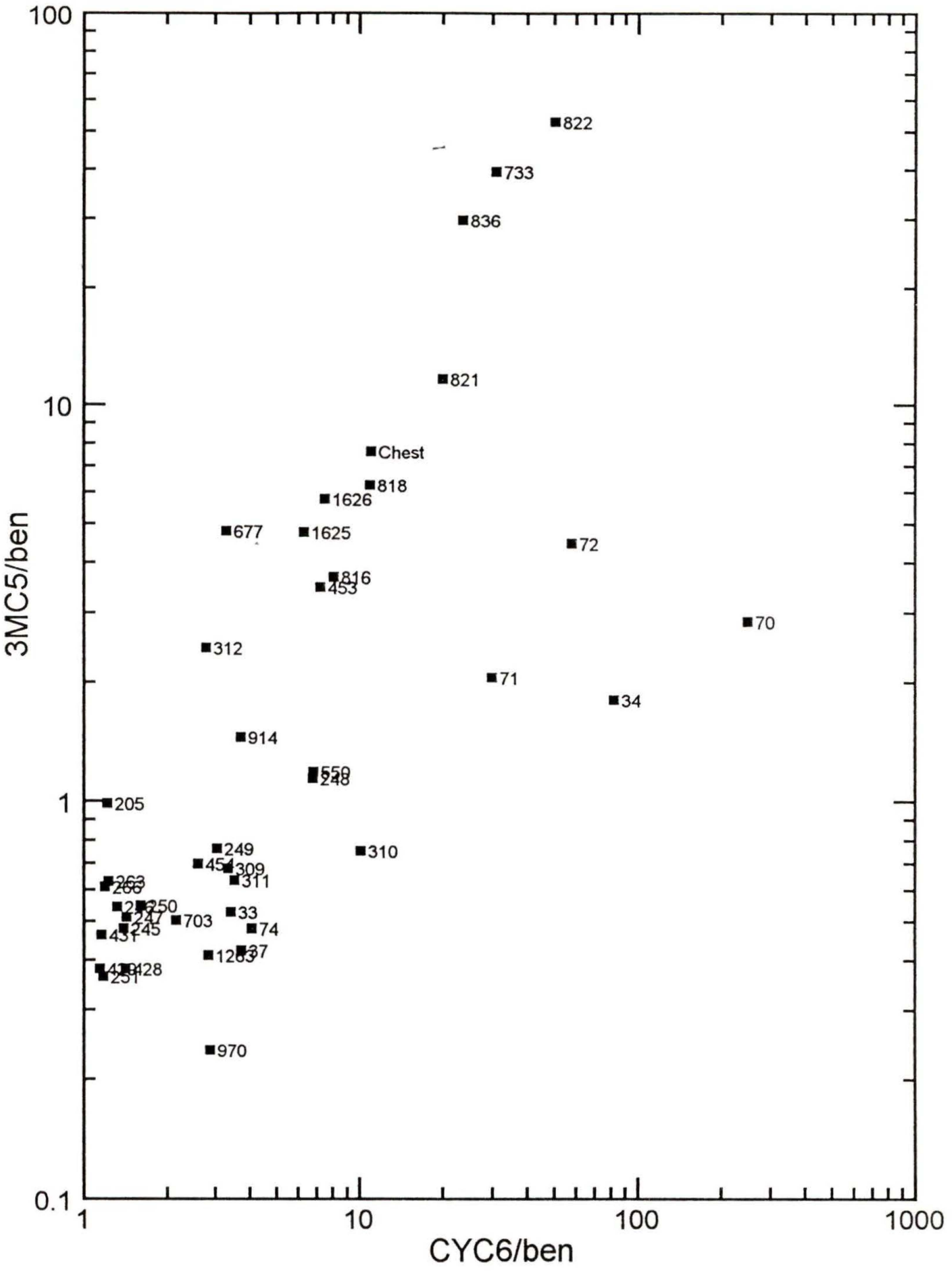


Figure 7.26 Thompson's 3mC5/ben and CYC6/ben ratios calculated for Canadian oils.

Summary Points:

- Although Thompson's parameters can be used as a rough guide for identifying alteration in oil samples, uncertainties exist which may be due to a greater dependence of the parameters on source conditions than originally assumed.

7.4.3 Mango's Indices

Mango used his isoheptane index (equation 3.7) as support of his theory for gasoline generation (see section 3.2.4). Although the ratio of $(2MC_6 + 23DMC_5)/(3MC_6 + 24DMC_5)$ is close to one for all the samples he analyzed, the ratios of $2MC_6/3MC_6$ and $23DMC_5/24DMC_5$ increase with increasing maturity. In Tables 7.1 and 7.2, the ratios calculated in this study for Canadian oils are listed.

The Canadian oils have isoheptane indices close to one, ranging from 0.821 to 1.214 (Table 7.2). The sums of $2MC_6$ and $23DMC_5$ and $3MC_6$ and $24DMC_5$ are plotted in Figure 7.27. This relationship between the sums of the C_7 isomers is another way to present Mango's isoheptane index. The relationship between these two sums for Canadian oils is linear and close to one.

Mango's calculations (1987) of the isoheptane index for 1880 oils resulted in a greater invariance than the results of the calculations for Canadian oils. The compounds used in the ratio are usually in low concentrations in the Canadian oils and not well resolved or separated in a GC column. For example, $23DMC_5$ is usually in low concentration and slightly co-eluting with $11DMCYC_5$. The $2MC_6$ and $3MC_6$

Table 7.1. Isoheptane values for Canadian oils after work of Mango (1987, 1990).

Sample	Isoheptane Index	2mC6/ 3mC6	23dmC5/ 24dmC5	2MC6+ 23DMC5	3MC6+ 24DMC5
Chester	0.807	0.712	1.854	220173.0	272725.0
Alb/TurnVal/970	0.825	0.776	1.720	1.921	8.331
S/LkAlma/550	1.040	1.048	0.344	2.877	2.582
Alb/WillGr/914	0.885	0.805	1.488	13.842	15.502
Alb/Shekil/703	0.631	0.604	1.243	4.553	7.118
Alb/Rainbow/205	0.868	0.901	0.370	5.752	7.097
E/HibC/429/3	0.958	0.938	1.135	87417.0	91170.5
E/HibC/428/2	0.949	0.908	1.359	40310.5	42494.5
E/HibC/431/5	0.948	0.933	1.079	77923.0	82272.5
E/HibK/251/1	0.965	0.947	1.120	95960.5	99318.5
E/HibK/263/8	0.947	0.953	0.900	244626.5	258475.5
E/HibK/266/11	0.933	0.937	0.899	106002.0	113604.0
E/Mara/453/1	0.966	1.006	0.719	365782.5	379471.0
E/Mara/454/2	0.964	0.965	0.959	121346.5	126124.0
E/Mara/455/3	0.695	0.600	0.615	2590.0	3499.0
E/Hebron/245/1	0.991	0.972	1.144	199665.5	201365.5
E/Hebron/246/5	0.935	0.936	0.926	231544.0	247074.5
E/Hebron/247/6	0.963	0.963	0.966	95256.5	98922.5
E/Hebron/248/10	0.858	0.457	2.517	29659.0	34390.5
E/Hebron/249/9	1.065	0.770	1.291	8937.0	8636.0
E/Hebron/250/7	0.954	0.943	1.051	37332.5	39055.0
A/Amaul/1263	0.000	0.000	0.000	0.0	9.837
A/Nerlerk/310/4a		0.558	0.000	0.035	0.032
A/Nerlerk/1625/5	0.625	0.589	0.710	4.188	6.758
A/Nerlerk/1626/6	0.642	0.610	0.711	3.797	5.916
A/Nerlerk/312/7	0.595	0.455	0.834	4.153	6.979
A/Nerlerk/311/8		0.721	1.674	11.109	12.387
A/Nerlerk/309/9	0.864	0.727	1.439	7.085	8.196
A/NiglintM/33/22	0.776	1.644	0.381	23809.5	30701.5
A/NiglintM/74/9	1.208	0.921	3.574	154336.0	127797.0
A/NiglintM/70/19		0.000	1.468	106048.5	52660.0
A/NiglintB/75/14	3.244	0.457	3.681	72906.0	25895.0
A/NiglintM/34/16	3.145	0.627	3.593	241553.5	71134.5
A/NiglintM/72/13	1.439	1.001	2.507	362601.0	251065.0
A/NiglintM/37/10	1.174	0.901	3.644	345608.5	288447.5
A/NiglintM/71/14	1.682	1.125	2.590	286998.0	170774.5
A/NiglintM/69/20	0.391	1.727	0.044	5191.5	12769.0
SW/CBattrum/675	0.669	0.608	1.094	67393.5	100673.5
SW/CButte/677	0.708	0.699	0.856	47452.0	67195.0
SW/CBatCrk/726	0.203	0.121	1.018	12689.7	63289.0
SW/CCantuar/733	0.695	0.677	1.000	120115.0	172907.7
SW/FKerrob/821	0.965	0.857	1.803	637559.5	650273.5
SW/FSEurek/818	0.943	0.832	1.796	318837.5	337092.5
SW/FSmiley/816	0.892	0.766	1.944	402365.5	447157.5
SW/FForgan/826	0.875	0.752	1.808	116153.0	132558.0
SW/FPlato/812	0.985	0.693	3.435	36648.0	37246.0
SW/ECourt/822	0.805	0.728	1.245	221600.5	274653.5
SW/EHearts/833	1.541	0.672	7.724	275558.5	191621.0
SW/ECactus/829	0.683	0.581	1.483	71668.0	105009.5
SW/EBuffalo/836	0.715	0.595	1.234	97699.5	136650.0

Table 7.2. Summary of Mango's parameters. Vitrinite reflectances (%R), indicating maturity, are approximate because good data is not available (Lloyd Snowdon, personal communication). The average vitrinite reflectance value for Alberta oils is not given since the oils have been subjected to a variety of conditions. Data for Turner Valley is included independently because this oil has the highest maturity of all the oil samples. Note: Stdev = standard deviation.

Location	mean Isoheptane	Stdev	%Ro (approximate)	2MC6/ 3MC6	Stdev	23DMC5/ 24DMC5	Stdev
Offshore Nfld.	0.939	0.079	0.8	0.882	0.155	1.112	0.435
Arctic	1.214	0.985	0.6	0.754	0.477	1.678	1.398
Saskatchewan	0.821	0.296	0.7	0.660	0.183	2.034	1.836
Alberta	0.843	0.132	variable	0.760	0.0988	1.335	0.525
Turner Valley	0.825		0.9	0.776		1.720	

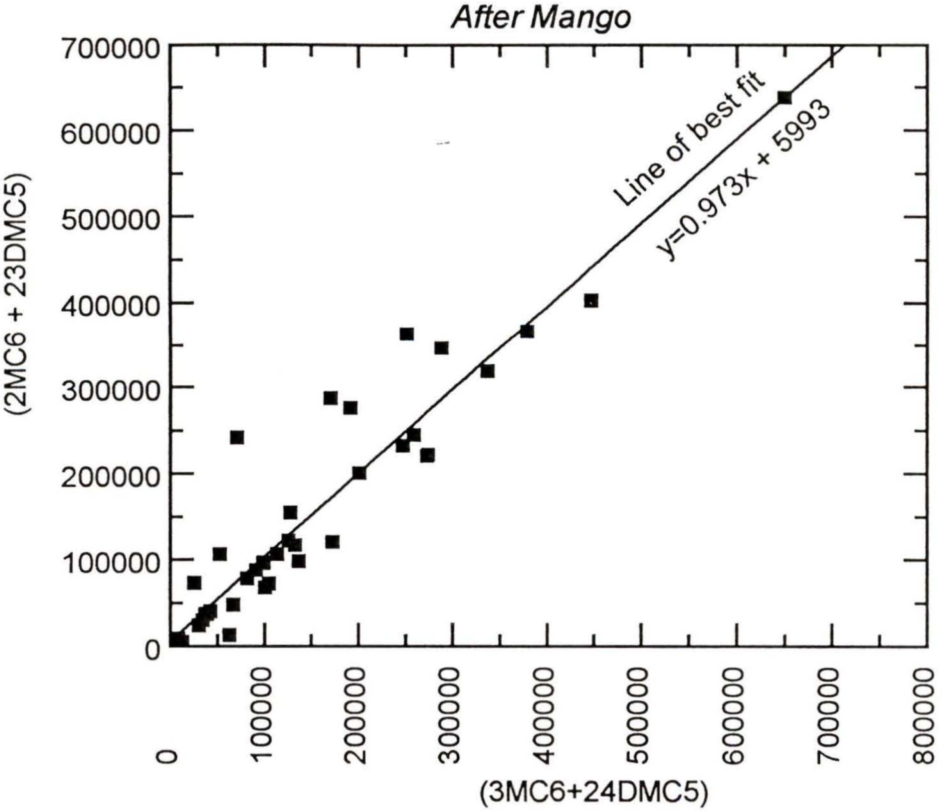


Figure 7.27 Relationship between (2MC6 + 23DMC5) and (3MC6 + 24DMC5) for all the Canadian oils in this study (after Mango, 1987).

hydrocarbons co-elute with smaller compounds eluting near them. The area counts obtained for each compound may not be accurate.

Many of the Canadian oils (except for Hibernia) included in this study are differentially biodegraded or water-washed. The highly degraded Niglintgak oils cause the scatter in Figure 7.27. If these are excluded, the relationship between the C_7 isomers in Canadian oils is very similar to Mango's results.

In Figure 7.28, the change in the average ratios of $2MC_6/3MC_6$ and $23DMC_5/24DMC_5$ with increasing maturity is presented. According to Mango, these ratios should increase with increasing maturity. However, these ratios in Canadian oils do not seem to change systematically with maturity (or increasing % Ro values). Mango's ratios for each Canadian oil are variable, even within particular groupings (e.g., standard deviations are high). The vitrinite reflectance values are only estimations because good measurements have been difficult to obtain (Lloyd Snowdon, personal communication). The ratios in Canadian oils can only be effectively examined if each oil has an accurate Ro value, and the oils are independently compared (averages are too variable and not representative of the group). However, the Ro values are not available for all of the kerogens associated with the oils.

Summary Points:

- The calculations of Mango's parameters for the Canadian oils in this study do provide support for Mango's theories.
- Uncertainties in the data required for calculation of Mango's parameters and the effects of secondary alteration on Canadian oils are the most likely causes of any variance in the isoheptane index for oils in this study.

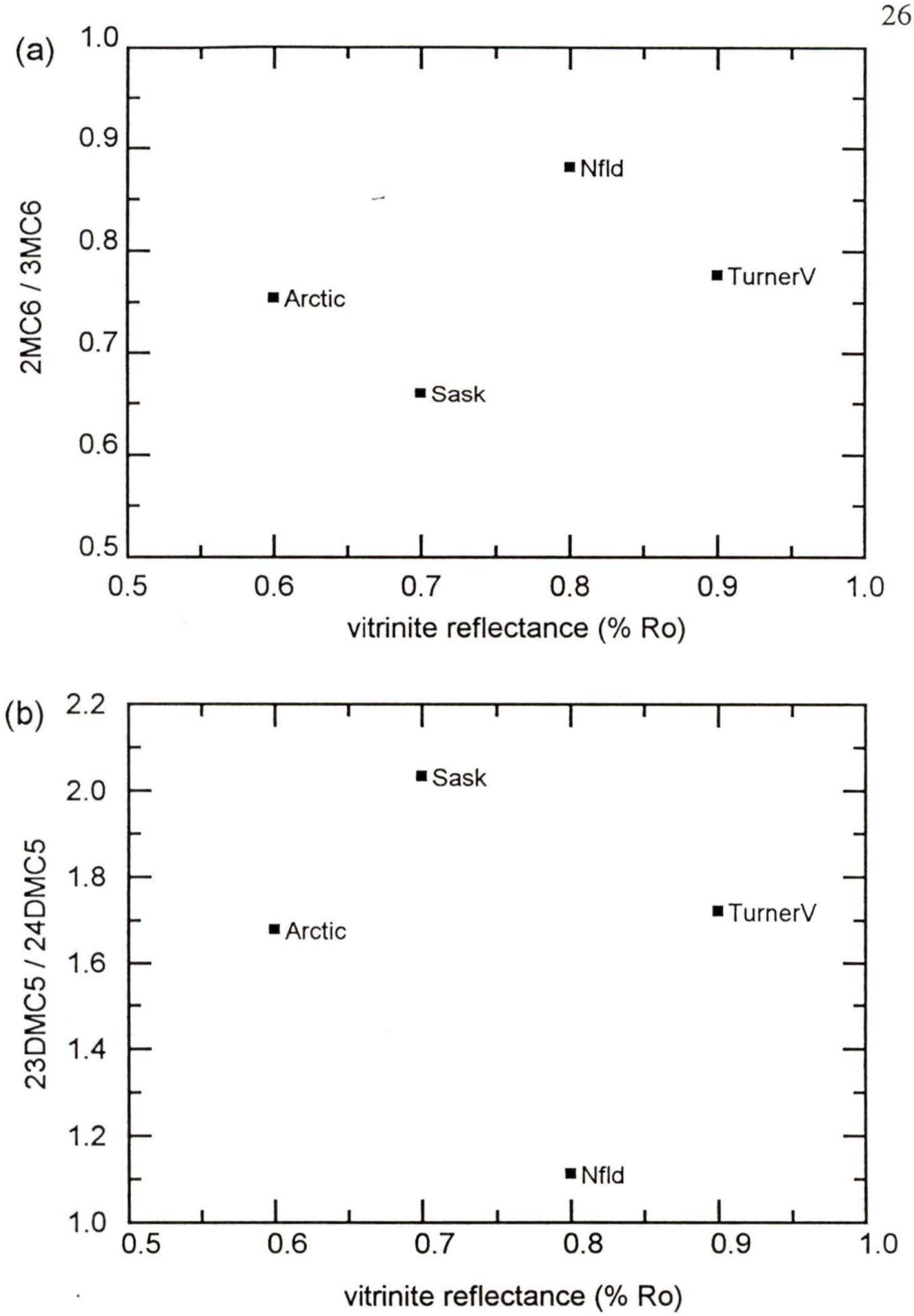


Figure 7.28 Change in ratios of C7 isomers with increasing maturity (or % Ro) for (a) 2MC6/3MC6 and (b) 23DMC5/24DMC5.

7.4.4 Schaefer's Indices

Schaefer (1987) examined maturity-related compositional changes in LMW hydrocarbons. He calculated average paraffin/naphthene, 1t2DMCYC$_5$/1c2DMCYC$_5$, and PI1 ratios for hydrocarbons in shales and found that these ratios increases with increasing maturity (or vitrinite reflectance values).

These ratios were calculated for the groups of related Canadian oils (Table 7.3) to determine if any maturity information could be obtained. These ratios vary for the oils included in the groupings, and thus the average ratios for each group have high standard deviations. Since the vitrinite reflectance data for Canadian oils is not reliable and these ratios are so variable, no systematic trends with maturity are observed.

Many of the Canadian oils included in this study have been differentially biodegraded and water-washed. These secondary alteration processes have probably affected the compounds composing the ratios used by Schaefer and resulted in a masking effect of maturity trends. The oils are also derived from a variety of precursor materials, which could also contribute to the variation in the ratios.

Summary Points:

- Secondary alteration or differential sources associated with Canadian oils have probably contributed to the variability of maturity-sensitive parameters used by Schaefer, resulting in masked maturity trends.

Table 7.3 Maturity-sensitive gasoline hydrocarbon parameters for Canadian oils. These ratios are calculated for comparison to Schaefer's work (1987). There is only one Saskatchewan Family A (SaskA) oil in this study so a standard deviation could not be calculated for this oil. Turner Valley is included independently because it has the highest maturity of all the oils studied. Note: a = $1t2DMCYC_5/1c2DMCYC_5$, b = paraffin/naphthene, c = Paraffin Index 1, and stdev = standard deviation.

Oil Groups	a	stdev	b	stdev	c	stdev
Nfld	4.399	1.482	1.542	0.639	1.551	0.446
Arctic	2.586	3.613	0.934	1.033	0.464	0.289
Sask	2.661	2.044	1.491	1.104	1.068	0.269
Alberta	1.550	0.470	2.201	0.770	1.974	0.922
SaskF	1.764	0.359	0.967	0.444	1.006	0.123
SaskE	0.815	0.265	1.229	0.196	1.156	0.191
SaskC	5.506	1.055	1.645	1.131	1.047	0.489
SaskA	3.155		4.549		1.120	
TurnerV	2.405		0.998		1.872	

7.4.5 Philippi's Indices

Philippi (1977) calculated a Similarity Coefficient from gasoline range hydrocarbons that could be used to correlate oils and/or source rocks (see section 3.2.4). The Similarity Coefficient was calculated for selected Canadian oils and groups of oils.

In Table 7.4, an example of the process of calculating the ratio is given for a Hibernia and a Hebron oil. The individual C_6 and C_7 compounds are first normalized to the C_6 or C_7 total paraffins plus naphthenes (excluding aromatics). Then, these 10 ratios are compared between two oils. If any ratio is greater than one, the reciprocal is used. The resulting ratios from the comparison between two oils are averaged to produce a

Table 7.4 Example of Similarity Coefficient calculation for Hibernia C-96 DST#3 and Hebron I-13 DST#1. The compounds on the left are ratios of the particular compound to C_6 or C_7 paraffins plus naphthenes (excluding aromatics). For the calculation, any individual ratio greater than one is converted to its reciprocal (after Philippi, 1977).

Parameter	Ratio bt Oils	Reciprocal	List parameters
nC6	0.917		0.917
2MC5	0.950		0.950
3MC5	0.963		0.963
23DMC4	1.591	0.629	0.629
MCYC5+CYC6	1.066	0.938	0.938
nC7	0.991		0.991
2MC6	0.920		0.920
3MC6	0.954		0.954
23DMC5	0.859		0.859
total C7 naphthenes	1.042	0.959	0.959
Similarity Coefficient	0.908		

Similarity Coefficient (SC). The values of the SC can indicate a good or bad correlation as follows:

SC	**Correlation**
0.8 - 1.0	good
0.73 - 0.79	fair
< 0.73	poor

The example of the two East Coast oils in Table 7.4 yields a SC of 0.908 which is indicative of a good correlation. The Hibernia and Hebron oils are derived from the same source and are located in the same basin. Therefore, this SC coefficient appears to be a good correlation tool. However, these two East Coast samples are conventional, non-biodegraded oils. Philippi (1977) specifically chose non-biodegraded oils to demonstrate the usefulness of his SC for correlation.

The ratios involved in the calculation of the SC are averaged for each well so that major groups of oils and not just individual oils can be compared (Table 7.5). Some of the average ratios have large standard deviations, especially those for the Arctic (Nerlerk and Niglintgak) wells. The ratios of related oils are not constant because the oils have been differentially biodegraded and water-washed. However, comparisons were still made to test the usefulness of the SC for correlating biodegraded oils (Table 7.6).

In Table 7.6, individual oils and groups of oils are compared. According to Philippi's criteria, the oil examples given in Table 7.6 would yield poor correlations (SC <0.73) even though the oils being compared are known to be related through other data. The two sets of Arctic oils tested yield SC of 0.657 and 0.43. The comparison of the

Table 7.5 Averages of the parameters of groups of oils required for calculation of the Similarity Coefficient. Standard deviations (stdev) are included to illustrate the variance around the mean ratios. The parameters listed are actually ratios of the individual compound to C_6 or C_7 paraffins plus naphthenes (excluding aromatics).

	nC6	2MC5	3MC5	23DMC4	MCYC5 +CYC6	nC7	2MC6	3MC6	23DMC5	total C7 naphthenes
Hibernia	0.339	0.135	0.081	0.037	0.407	0.316	0.092	0.098	0.012	0.470
Stdev	0.022	0.017	0.007	0.005	0.044	0.006	0.006	0.006	0.000	0.018
Mara	0.237	0.105	0.065	0.055	0.528	0.216	0.077	0.085	0.013	0.595
Stdev	0.141	0.072	0.043	0.032	0.224	0.133	0.037	0.023	0.002	0.192
Hebron	0.283	0.128	0.079	0.040	0.466	0.249	0.078	0.091	0.021	0.549
Stdev	0.105	0.008	0.005	0.014	0.101	0.110	0.025	0.011	0.015	0.127
Niglintgak	0.037	0.033	0.028	0.204	0.649	0.016	0.028	0.024	0.048	0.850
Stdev	0.036	0.035	0.021	0.215	0.248	0.026	0.019	0.013	0.058	0.076
Nerlerk	0.105	0.077	0.187	0.068	0.542	0.065	0.037	0.058	0.021	0.798
Stdev	0.035	0.011	0.094	0.037	0.100	0.041	0.014	0.024	0.012	0.088
SaskFamF	0.239	0.144	0.110	0.028	0.477	0.145	0.076	0.097	0.025	0.645
Stdev	0.088	0.027	0.012	0.016	0.136	0.079	0.013	0.013	0.004	0.083
SaskFamE	0.234	0.179	0.186	0.075	0.316	0.141	0.080	0.125	0.051	0.581
Stdev	0.046	0.015	0.025	0.015	0.030	0.044	0.006	0.010	0.046	0.043
SaskFamC	0.197	0.171	0.182	0.058	0.381	0.171	0.072	0.139	0.013	0.593
Stdev	0.170	0.023	0.034	0.019	0.130	0.166	0.039	0.017	0.005	0.198

Table 7.6 Similarity Coefficients (SC) for selected Canadian oils. The first five examples compare individual oils. The rest of the examples compare groups of oils (e.g., wells). Letters in brackets refer to families. 'D#' refers to DST#.

Oil Samples	SC
HiberniaCD#3 - HebronD#1	0.908
NerlerkD#8 - NiglintgakD#10	0.657
NerlerkD#5 - NiglintgakD#20	0.430
Battrum (C) - Plato (F)	0.720
Battrum (C) - Butte (C)	0.218
Mara - Hebron	0.843
Hibernia - Mara	0.781
Niglintgak - Nerlerk	0.490
Family F and E	0.749
Family C and E	0.822
Hibernia - Nerlerk	0.497
Niglintgak - Family C	0.302

two Saskatchewan Family C oils results in a SC of 0.218. The Family C (Battrum U#1) and Family F (Plato) oils result in a SC of 0.720.

When the average ratios of wells are compared, better results or correlations are obtained. Good correlations are made between Mara and Hebron wells (SC of 0.843), Hibernia and Mara wells (SC of 0.781), Families F and E (SC of 0.749) oils, and Families C and E (SC of 0.822). This is consistent with the known information about the oils in the wells. The Arctic wells, which contain the most biodegraded oils in this study, are poorly correlated (SC of 0.490). Hibernia and Nerlerk (SC of 0.497) and Niglintgak and Family C (SC of 0.302) are poorly correlated as expected since they are derived from different sources.

Philippi's SC is a good correlation tool for conventional or non-biodegraded Canadian oils, but it can not be used to correlate individual, biodegraded oils. It may be possible to use the SC for correlating larger related groups of biodegraded oils to each other, but this should be interpreted with caution. The severely biodegraded Arctic oils in this study could not be effectively correlated by the SC.

Summary Points:

- The SC of Philippi can be used to correlate non-biodegraded Canadian oils.
- Oils affected by secondary alteration processes, as are most of the oils in this study, cannot be correlated by the SC with confidence due to the change in their molecular compositions as a result of the degradation processes.

The gasoline range parameters are useful guides to aid in the description of oils. If an oil has not been affected by secondary alteration, the gasoline range parameters can be used to correlate related oils. However, if the oils have been affected by alteration processes such as biodegradation and water-washing, the resulting changes in molecular composition make correlation more difficult. It is, then, necessary to use other geochemical techniques which are more resistant to alteration, such as biomarker analysis, for correlations. If the level of degradation increases, even biomarkers can be removed from an oil. Molecular techniques can not adequately correlate oils affected by secondary alteration. In this study, compound specific isotope ratios of gasoline hydrocarbons are used to correlate degraded oils.

7.5 ISOTOPE SECONDARY EFFECTS

The specific isotope ratios of gasoline range hydrocarbons are more resistant to alteration than the molecular compositions of oils, and therefore they are useful for oil correlation, especially with regard to biodegraded oils. Many of the groupings of oils and isotope variation in the oils can be related to source conditions and not secondary alteration (see sections 7.1 and 7.2). However, the usage of isotopes for correlations is not perfect. There is some uncertainty associated with the correlation of particular oils such as Turner Valley. In addition, some of the Arctic oils correlate with the East Coast or Family F oils. Boundaries for the Arctic oils, in bi-dimensional plots, are often unclear. These uncertainties may be due to a small isotope effect associated with secondary alteration processes such as biodegradation.

The limitations of molecular techniques in correlating altered oils have been previously discussed. Some of the possible changes in isotope ratios as a result of alteration processes will be investigated here. Theoretical experiments and actual data from this study will be presented to suggest that secondary alteration has a low (< 1 ‰) isotope effect. Since biodegradation in oils is the most dominant secondary alteration process and the use of isotopes to correlate such biodegraded oil was one of the goals of this research, the focus of this portion of the discussion is centered on biodegradation.

7.5.1 Theoretical Change in Bulk Isotope Ratio from Degradation

A bulk oil is used as an example to demonstrate the type of effect that biodegradation can have on isotope ratios. The change in the isotope ratio of the bulk oil due to differential loss of its major constituent fractions (saturates, aromatics, and NSO compounds) is not as complicated to calculate as the change in isotopic composition due to removal of independent compounds. Four different sets of conditions or experiments are performed (Table 7.7, Figures 7.29, 7.30, 7.31, and 7.32). The initial conditions are identical for each experiment and are chosen to represent average values found in a typical oil as follows:

Fraction	**% of Bulk**	**Isotope Ratio (‰)**
Saturates	50	-28
Aromatics	35	-26
NSO's	15	-24
Bulk		-26.7

Table 7.7 Bulk isotope change due to removal of varying amounts of saturate and aromatic fractions. See text for description of experiment 1, 2, 3, and 4.

Composition Change		Isotope Ratio Change	
(1) saturates (%)		Bulk (‰)	
50		-26.70	
40		-26.56	
30		-26.38	
20		-26.14	
10		-25.83	
0		-25.40	
(2) Aromatics (%)		Bulk (‰)	
35		-26.70	
30		-26.74	
25		-26.78	
20		-26.82	
15		-26.88	
10		-26.93	
5		-27.00	
0		-27.08	
(3) Saturates (%)	Aromatics (%)	Bulk (‰)	
50	35	-26.70	
45	33	-26.65	
40	31	-26.58	
35	29	-26.51	
30	27	-26.42	
25	25	-26.31	
20	23	-26.17	
15	21	-26.00	
10	19	-25.77	
5	17	-25.46	
0	15	-25.00	
(4) Saturates (%)		Saturates (‰)	Bulk (‰)
50		-28	-26.7
40		-27.8	-26.47
30		-27.5	-26.19
20		-27.1	-25.88
10		-26.4	-25.57
5		-25.7	-25.43
2.5		-25.0	-25.38

The isotope ratio of the bulk oil, after a change in the amount of one of its fractions, is calculated by a mass balance calculation as follows:

$$m_T\delta_T = m_s\delta_s + m_a\delta_a + m_n\delta_n \quad \text{where } T = \text{total} \tag{7.1}$$

s = saturates
a = aromatics
n = NSO compounds
m = amount of fraction
δ = isotope ratio

In the first experiment, the aromatics and the NSO compounds are not degraded while the saturate compounds are degraded from the initial 50 % to 0 % (Figure 7.29). As the oil is degraded and the saturates removed, the aromatic and NSO compounds proportionally increase and the isotope ratio of the bulk oil becomes heavier (from -26.7 to -25.4 ‰). An example of the mass balance equation used to calculate this change in the bulk isotope ratio of the oil is given below:

e.g., saturates decrease from 50 % to 40 % of the oil

$$m_T\delta_T = m_s\delta_s + m_a\delta_a + m_n\delta_n$$

$$(0.9)\ \delta_T = (0.4 \text{ x } -28\ ‰) + (0.35 \text{ x } -26\ ‰) + (0.15 \text{ x } -24\ ‰)$$

$$\delta_T = -26.56\ ‰$$

The saturates are isotopically light compounds so the removal of this light material results in a heavier residual oil. The saturate compounds initially compose half of the bulk oil. A reduction in this material would cause one of the most significant changes in the bulk isotope ratio. For this case, with 60 % reduction in the saturates, the bulk isotope ratio has only changed by approximately 0.5 to 0.6 ‰.

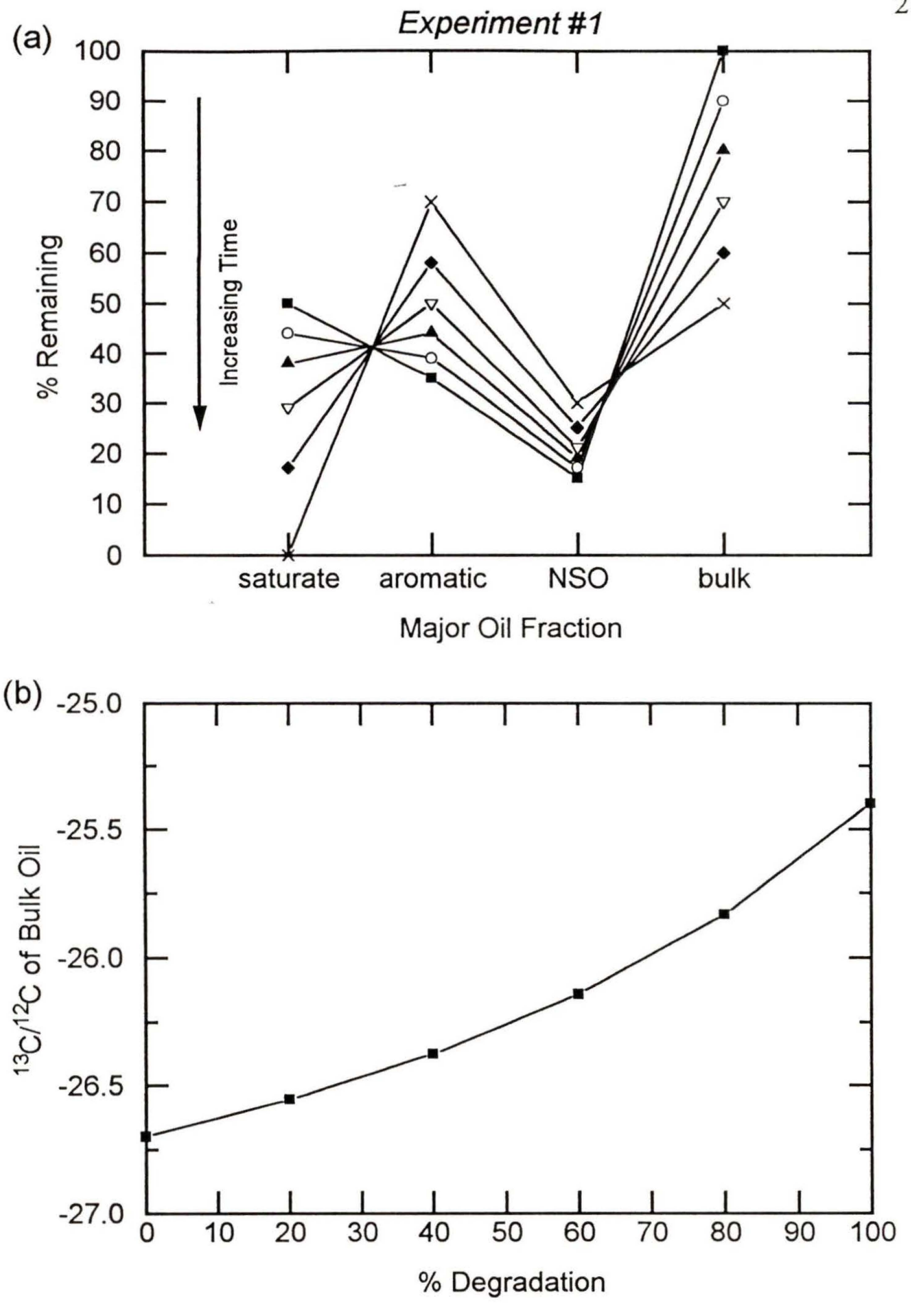


Figure 7.29 Theoretical experiment illustrating the change in bulk isotope ratio as a function of saturate reduction: (a) change in molecular composition and (b) resulting change in bulk isotope ratio.

In the second experiment, only the aromatic fraction is degraded while the saturates and the NSO compounds proportionally increase (Figure 7.30). The aromatic fraction is isotopically heavy (enriched in ^{13}C) as compared to the other fractions so the removal of it would deplete the residual oil in the heavy isotope. As degradation increases, the bulk oil changes from -26.7 ‰ to -27.08 ‰. This change in isotope ratio is small in this case because the aromatics initially compose only 35 % of the bulk oil.

In the third experiment, both the saturate and the aromatic fractions are being removed (Figure 7.31), but the saturates are reduced at a faster rate (as would be expected from naturally occurring biodegradation). Since the saturates initially compose 50 % of the oil and they are reduced to 0 %, both the aromatic and NSO compounds proportionally increase. The overall effect of degradation on the bulk isotope ratio of the oil in this case is larger than in the first two experiments because more material is degraded. The bulk oil shifts to heavier isotope ratios, reflecting the greater initial proportion of saturates. When the saturate fraction is 80 % degraded, the isotope ratio of the bulk has changed from -26.7 ‰ to -26 ‰ (0.7 ‰). For comparison, the smaller effect of removing only the saturate fraction (experiment #1) on the isotope ratio of the bulk oil is also given in Figure 7.31.

The three previous experiments assume that there is no isotope effect associated with the removal of the particular hydrocarbon fractions. For example, as the saturates are being degraded, there is no change in the isotope ratio of the residual saturates. The

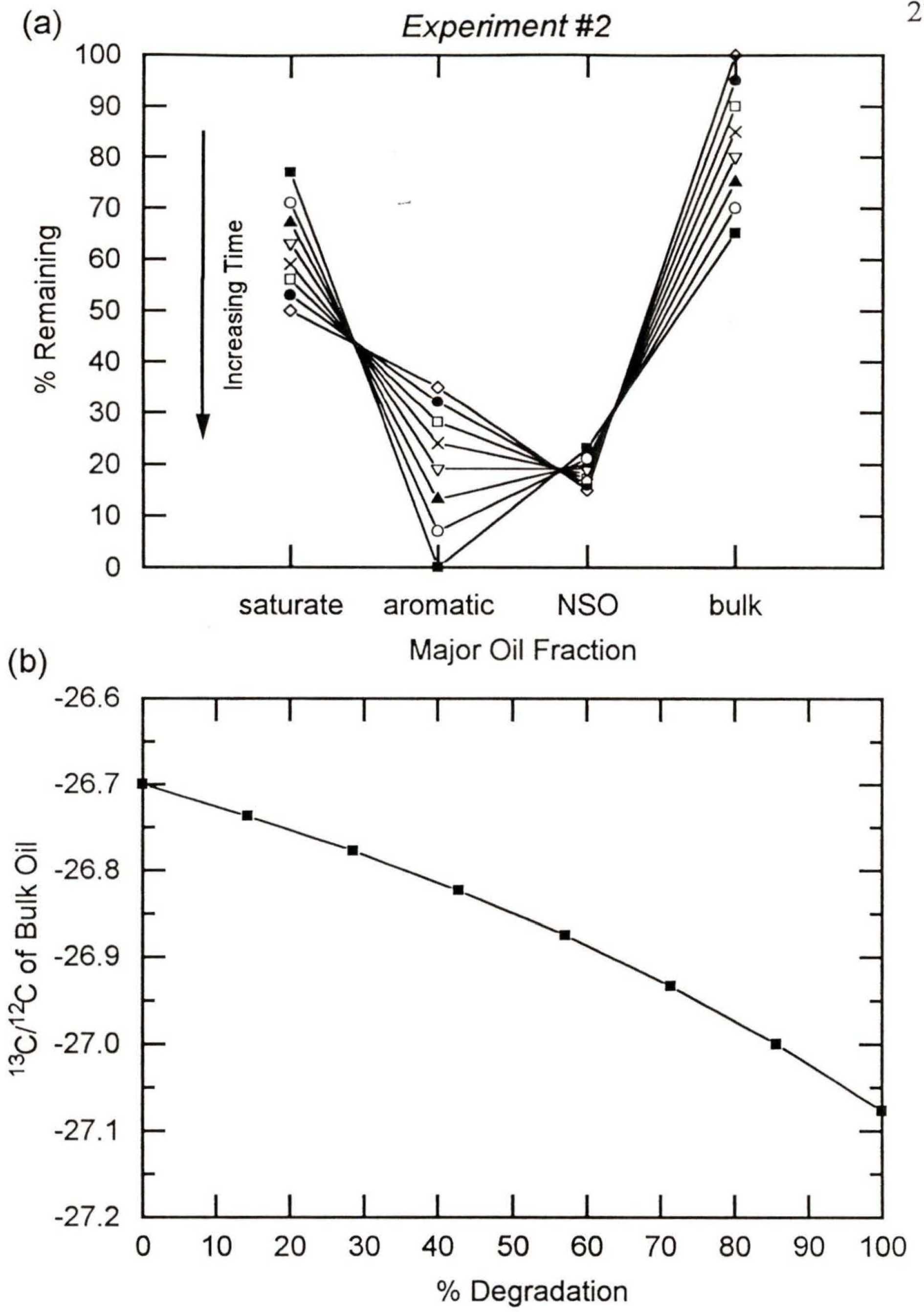


Figure 7.30 Theoretical experiment illustrating the change in bulk isotope ratio as a function of aromatic reduction: (a) Change in molecular composition and (b) resulting change in bulk isotope ratio.

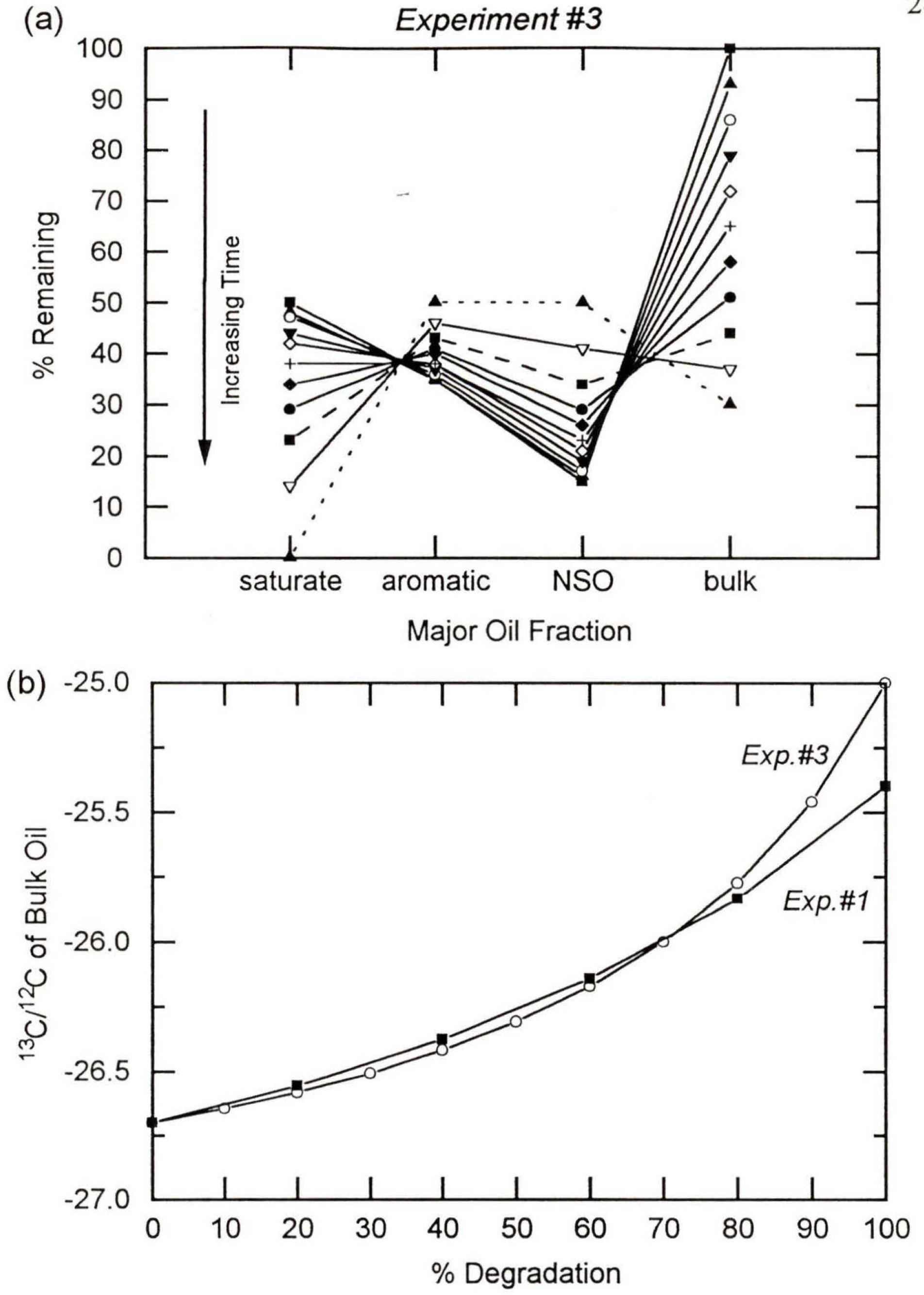


Figure 7.31 Theoretical experiment illustrating the change in bulk isotope ratio as a function of saturate and aromatic reduction: (a) change in molecular composition and (b) resulting change in bulk isotope ratio. The change in bulk isotope ratio illustrated in (b) is graphed as a function of percent saturate degradation. The change in the bulk isotope ratio due to the saturate removal in Experiment 1 is also provided for comparison.

fourth experiment mimics the first experiment except that a 1 ‰ isotope effect is assumed to accompany the degradation of the saturates (Figure 7.32).

The change in the isotope ratio of the saturates as a function of degradation must first be calculated before the isotope ratio of the bulk is calculated. The isotope ratio of the residual saturates can be approximated by the Rayleigh Distillation equation (Hayes, 1982; Whiticar and Faber, 1986) which assumes that the saturates are removed and isolated from the system.

$$\delta^{13}C_r = \delta^{13}C_0 + \{1000 \times (1/\alpha - 1) \times \ln(f)\} \qquad (7.2)$$

where f = fraction remaining (1 = 0 % degradation)
α = fractionation factor = 1.001 for saturates
$\delta^{13}C_r$ = isotope ratio of residual saturates in sigma notation
$\delta^{13}C_0$ = isotope ratio of the initial saturates in sigma notation.

In experiment #4, the isotope ratio of the bulk oil undergoes a change from -26.7 ‰ to -25.38 ‰ (at 95 % degradation, 1.32 ‰ isotope change). If all of the saturates are removed, the biodegradation would be strong. If 80 % of the saturates are removed, the change in the isotope ratio of the bulk oil would be 0.82 ‰, still less than 1 ‰ .

These theoretical experiments demonstrate that the change in isotope ratio of the bulk oil, as a function of biodegradation, depends on the composition of its major fractions and their corresponding isotope ratios. Strong biodegradation only results in a small change in the isotope ratio of the residual bulk oil of less than 1 ‰. Other investigators have observed large natural variation, approximately 10 ‰ (see Background), in the composition of bulk oil which is much greater than the effect of

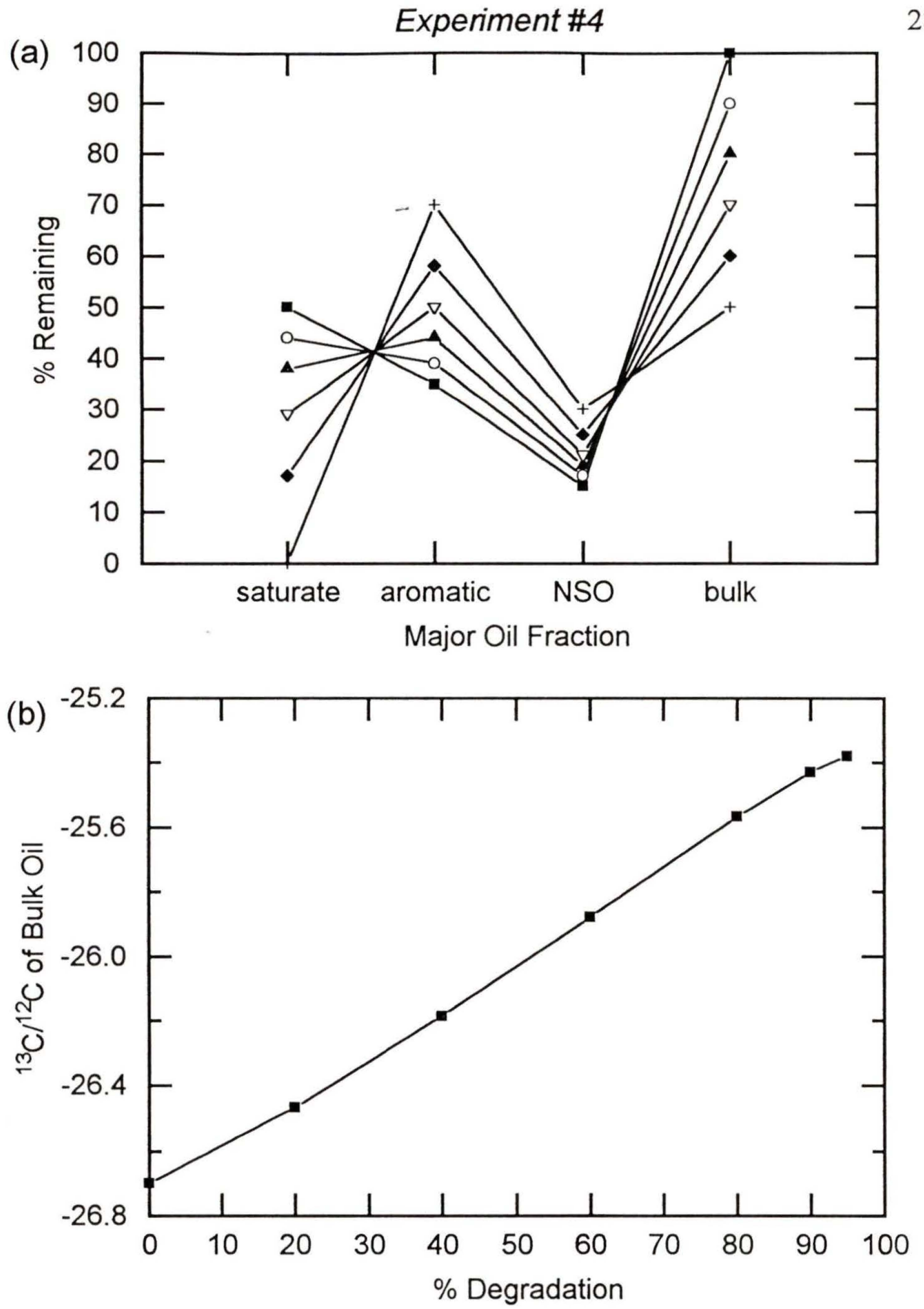


Figure 7.32 Theoretical experiment illustrating the change in bulk isotope ratio as a function of saturate reduction with a 1 $^{o}/_{oo}$ isotope effect: (a) change in molecular composition and (b) resulting change in bulk isotope ratio.

biodegradation. Bulk isotope ratios are useful for correlations, but they are non-specific and yield only limited information.

Summary Points:

- The isotope ratio of bulk oil can be altered by biodegradation, but the effect is probably less than 1 ‰.

7.5.2 Isotope Effect from Biodegradation of Individual LMW Hydrocarbons

Although some investigators have suggested an isotope effect of 1 to 2 ‰ associated with biodegradation of major oil fractions, few studies have been performed on individual gasoline range hydrocarbons. Bacteria must have some mechanism for differentiating between heavy and light isotopes and rejecting the molecule containing ^{13}C, if an isotope effect is to occur. Although biodegradation is an accepted process, little is known about the exact mechanism used by the bacteria to differentiate between ^{12}C and ^{13}C isotopes.

It is generally accepted that bacteria engulf whole molecules at once and not remove carbon atoms sequentially. This is reasonable because if the bacteria could sequentially remove carbons from a compound, the effect would be a change to lower average carbon number in the remaining hydrocarbons as biodegradation increases. This change in carbon number is not observed. When degradation increases, the total LMW n-alkanes are reduced first followed by the branched alkanes and cycloalkanes (e.g., Deroo et al., 1977). As bacteria metabolize the hydrocarbons, the main product from complete biodegradation is CO_2. Partial degradation can result in the production of oxygenated compounds such as alcohols or acids which are more difficult for bacteria to degrade (e.g., Litherathy et al., 1989).

Possible mechanisms used by the bacteria to distinguish between isotopes are theoretically discussed here. From this theoretical examination of biodegradation, the probability of alteration of individual compounds causing an isotope effect is low.

7.5.2.1 Recognition of Mass Difference

The first microbial mechanism discussed is the differentiation of isotopes based on mass differences in the hydrocarbons. It is possible that bacteria can reject a molecule based on the (reduced) mass difference of the individual hydrocarbon. If the bacteria can recognize a mass difference in hydrocarbons, then the probability of hydrocarbon rejection is the same as the probability of the presence of a ^{13}C atom.

The probability of a molecule containing a ^{13}C is based on the natural abundance of ^{13}C which is 1:100 (Figure 7.33). For example, CH_4 has a 1:100 chance of its carbon atom being ^{13}C. As the number of carbon atoms increase, the chances of a ^{13}C being present also increase. A $C_{10}H_{22}$ molecule has 10:100 chances of containing a ^{13}C (10 times 1:100 chances). Thus, there is a 10:100 or a 10 % chance that a $C_{10}H_{22}$ molecule will be rejected by bacteria based on mass.

However, the chance of bacteria being able to recognize mass differences, leading to the occurrence of an isotope effect, is small. In Table 7.8, the mass differences

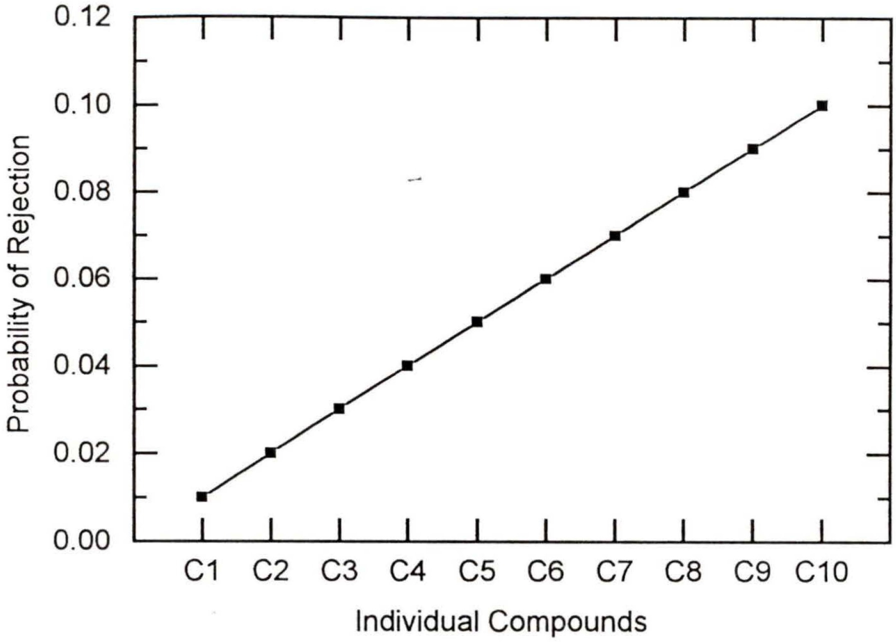


Figure 7.33 Probability of a bacteria rejecting a hydrocarbon based on mass differences.

accompanying the substitution of a ^{13}C atom for a ^{12}C atom in various hydrocarbons with lengths less than 10 carbons are given.

Table 7.8 Mass differences for selected hydrocarbons to show the diminishing effect of mass difference as carbon number increases.

Compound (alkanes)	Mass with ^{12}C (m_1)	Mass with ^{13}C Substitution (m_2)	Mass Difference (m_1x m_2) / (m_1 + m_2)
CH_4	16	17	1/8.2
C_2H_6	30	31	1/15.3
C_3H_8	44	45	1/22.3
C_5H_{12}	72	73	1/36.3
$C_{10}H_{22}$	142	143	1/71.3

A compound such as methane (CH_4) has a low MW, and, therefore, the effect of the mass difference between CH_4 with only ^{12}C and that with a ^{13}C atom can be significant (e.g., relatively large mass difference). This effect decreases rapidly as the chain length and MW increase. The compounds being analyzed in this study are in the C_5 to C_{10} range. The effect of substituting in a ^{13}C atom is not very significant even in C_5 compounds (e.g., low mass difference). It is unlikely that the microbes are sophisticated enough to recognize such small mass differences.

Summary Points:

- If microbes reject molecules based on mass differences, an isotope effect is unlikely because the microbes would have to be capable of recognizing very small changes in mass.

7.5.2.2 Recognition of Terminal ^{13}C

Another potential mechanism, for the rejection of ^{13}C-containing compounds causing an isotope effect, could be the recognition of a terminal ^{13}C atom in a molecule. It is likely that microbes attack (or approach) the terminal sites in a molecule instead of the more central locations. Since there has been no real proof put forth thus far, it is assumed that the distribution of ^{13}C is random and that a heavy isotope can occur anywhere in a molecule. The chance of the presence of a ^{13}C in a molecule is based its natural abundance and dependent on the number of carbon atoms in the molecule, each with a probability of 1:100 for containing a ^{13}C.

Microbes preferentially utilize ^{12}C over ^{13}C. If the microbe can recognize a ^{13}C in a molecule, it will ignore that molecule. The accumulation of isotopically heavy molecules results in isotope fractionation. If a microbe rejects molecules based on the recognition of a terminal ^{13}C, then a low probability of this terminal carbon being a ^{13}C would decrease the chance that an isotope effect occurs.

When a microbe approaches a hydrocarbon, it is assumed that the microbe can only reject the hydrocarbon based on the isotopic composition of the terminal carbon. In this case, irregardless of the number of carbons in the molecule, the probability of that terminal carbon being a ^{13}C is 1:100. Therefore, there is a 1 % chance of rejection. If the microbe can somehow consider the terminal carbons on both ends of the molecule, the probability of rejection would be 2 % (2 times 1:100 chance of the terminal carbon being ^{13}C). If the microbe can recognize a ^{12}C- ^{13}C bond structure at the terminal sites of the molecule, the probability of rejection would be 4 %.

Microbes may be able to recognize buried carbons (within molecule, not end carbons) if they have some sort of template to direct them to a certain central location in a molecule. In this case, the probability of ^{13}C recognition and rejection would be the same as the probability for the existence of ^{13}C (Figure 7.33). However, this recognition of buried ^{13}C isotopes implies a level of sophistication that the bacteria probably have not reached, and therefore this case is an unlikely one.

Thus, based on the recognition of a ^{13}C at a terminal site, the probability of an isotope effect occurring from biodegradation is likely to be low (maximum of 4 %) in all individual compounds. There are two main limitations to the scenarios discussed. The cases presented above are only applicable to straight chain alkanes. The degradation of cycloalkanes or aromatics compounds is probably more complex. Also, if an isotope effect occurs, no estimation of the magnitude of the effect is possible.

Summary Points:

- The probability of a microbe rejecting any individual hydrocarbon and causing an isotope effect, based on the recognition of ^{13}C at terminal sites, is low (e.g., up to a maximum of 4 %).

7.5.3 Isotope Effect of Water-washing

Water-washing can occur during hydrocarbon migration through water-saturated rock beds or after accumulation of oil in a reservoir. As compounds dissolve in water, the more soluble compounds enriched in the ^{12}C isotope will dissolve faster than the compounds with heavy carbons (see Background). The residual oil could become enriched in the heavy isotope as lighter molecules dissolve faster.

However, the LMW aromatics such as benzene and toluene are more susceptible to water-washing than any of the other compounds (e.g., benzene is 10 times more soluble than CYC_5 at 25 °C; see Figure 3.12, Table 3.4). Aromatic compounds are isotopically heavier than the alkanes. The preferential removal of isotopically heavy compounds would result in the residual oil being enriched in the light isotope. This light enrichment could counteract the effect of the faster removal of aromatic compounds with ^{12}C. Aromatic compounds are not in high concentrations in oils. The dominant class of hydrocarbons in crude oil is the alkanes. The removal of these more soluble aromatics, therefore, would not have a great effect on the hydrocarbons of the remaining oils.

Water-washing effects will increase as the length of the migration path increases (Lafargue and Barker, 1988). The oils in the current study have not undergone extensive migration. If water-washing occurs after the oil has accumulated, only the oil close to the oil-to-water interface will be affected. Benzene and toluene are rarely absent from crude oils, indicating that water-washing is usually not severe. Biodegradation is more dominant than water-washing (Lafargue and Barker, 1989). If there is an isotope effect due to secondary alteration, it will most likely be associated with the most dominant process (biodegradation).

7.5.4 Other Alteration Processes

De-asphalting and inorganic oxidation are other secondary alteration processes which can affect oils and potentially cause isotope effects. However, biodegradation and water-washing are the most dominant secondary alteration processes and their effects will dominate (e.g., Canadian oils).

Thermal maturity is a primary effect (although oils migrating between reservoirs can be subjected to differential temperatures). It is briefly mentioned here because it is not expected to cause a significant isotope effect for the same reasons as given for biodegradation.

7.5.5 Example of Hexane Evaporation

Figure 7.34 uses the evaporation of hexane as a hypothetical example to illustrate that the isotope ratio of a particular hydrocarbon does not change very much during alteration until almost all of the initial material is removed. The vapor pressures of a hexane molecule with all ^{12}C atoms and another with a substituted ^{13}C atom do not vary very much at a constant temperature (25 ^{0}C). Thus, there is no strong discrimination between these isotopically different hexane molecules during evaporation.

The fractionation factor, representing a change in the isotope ratio of the original material from evaporation of individual hydrocarbons in the gasoline range, is not known, but it is expected to be small (e.g., 1 ‰ change corresponds to a fractionation factor of 1.001). For this reason, a variety of fractionation factors ranging from 1.0005 to 1.005 are used to calculate the isotope ratio of the remaining hexane after some has evaporated.

An average initial isotope ratio of -28 ‰ for hexane is assumed. The isotope ratio of the remaining fraction can be calculated using the following Rayleigh Distillation equation (7.3) (Whiticar and Faber, 1986):

$$\delta^{13}C_r = \delta^{13}C_0 + \{1000 \text{ x } (1/\alpha - 1) \text{ x } \ln(f)\} \qquad (7.3)$$

where f = fraction remaining (1 = 0 % evaporation, 100% remaining)
α = fractionation factor
$\delta^{13}C_r$ = isotope ratio of residual compound in sigma notation
$\delta^{13}C_0$ = isotope ratio of the initial compound in sigma notation.

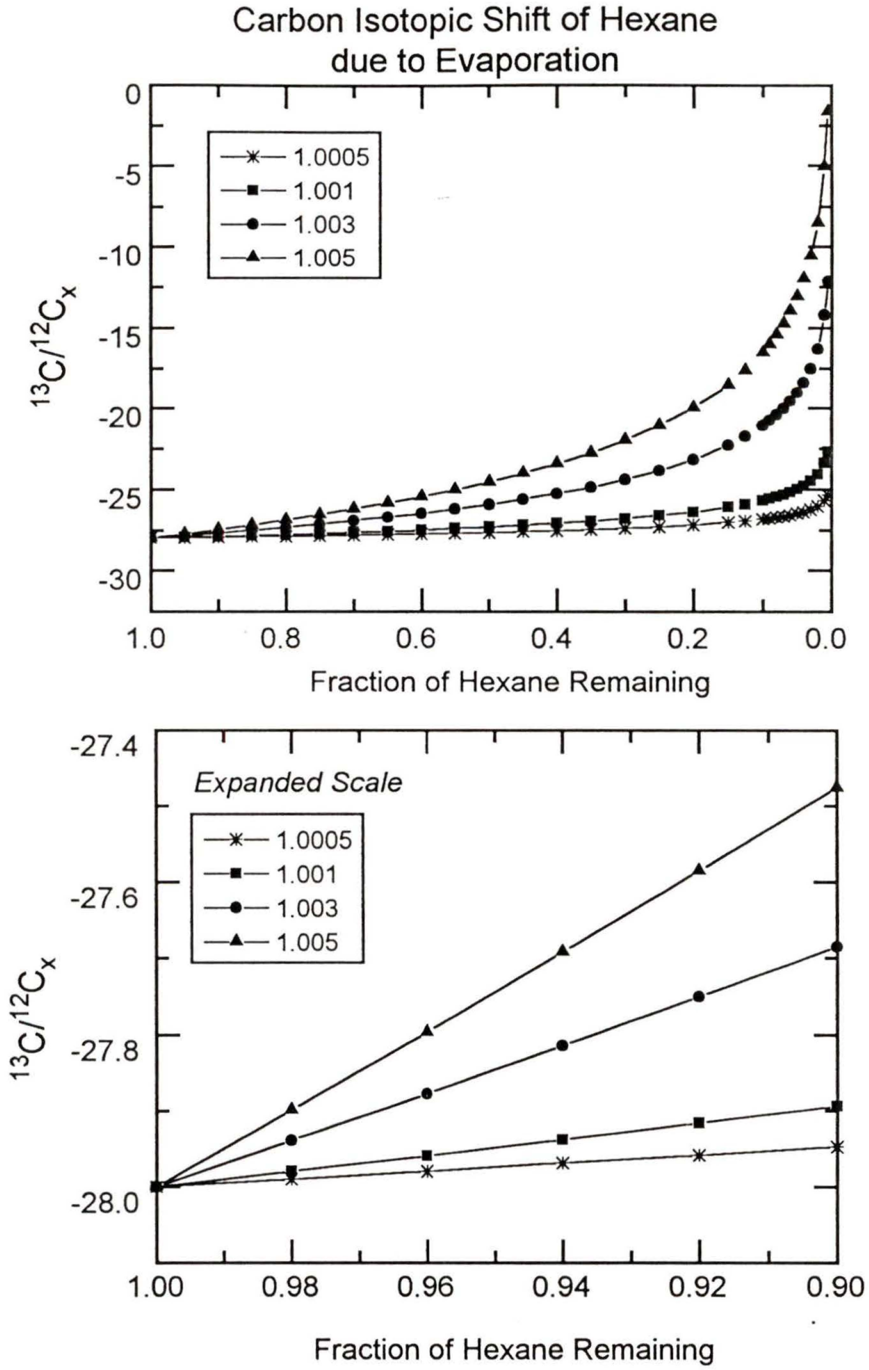


Figure 7.34 Theoretical shift in carbon isotope ratio of the remaining hexane as evaporation proceeds (where f=1.0=0% evaporation). The lower graph is an expanded version of the upper graph illustrating the change in isotopic composition with a maximum of 10 % evaporation.

The change in the original hexane isotope ratio as a function of the amount of hexane remaining is calculated, assuming several possible fractionation factors. When the fractionation factor is 1.0005, the isotope ratio of hexane remains relatively constant until about 85 % of the initial compound has been removed. After 85 % is removed, the isotope ratio begins to change more rapidly to heavier (less negative) values. If a larger fractionation factor was associated with evaporation (e.g., 1.001, 1.003 or 1.005), then the change in isotopic composition would be larger and occur earlier (Figure 7.34 b). If the fractionation factor is 1.005 (unlikely since it indicates a large shift of 5 ‰), even at 10 % evaporation there is only approximately a 0.5 ‰ shift in the isotope ratio of the remaining hexane. The fractionation factor is probably closer to 1.0005 or 1.001.

A recent study by Bjorøy et al. (1994) provides support for a low fractionation factor associated with evaporation. They tested the effect of evaporation on individual hydrocarbons ranging from C_4 to C_{30} over a 48 hour period. The results show that there is a maximum change of 0.5 ‰ (heavier) in the isotopic composition of hydrocarbons with evaporation up to 90 % of the original compound.

Summary Points:

- During hexane evaporation, the isotope ratio of the original hexane does not change significantly until about 80 % has been removed for an isotope effect of 1 to 2 ‰.
- If biodegradation results in a 1 ‰ isotope effect, the isotope ratios of the hydrocarbons probably will not change significantly until the oils have undergone extreme biodegradation.

From the theoretical discussion presented thus far, it appears reasonable to assume that secondary alteration will not have a significant effect on the isotope ratios of individual gasoline range hydrocarbons. Isotope and molecular data from the Canadian oils will be presented next which indicate that the effects of biodegradation on isotopes are much smaller than the effects on the molecular composition.

7.5.6 Relationship between Molecular and Isotope Ratios

The relationship between certain molecular and related isotope ratios (one of compounds composing the molecular ratio) provide evidence that the 10 ‰ variation in the oil samples is not due to secondary alteration processes. Although the molecular ratios change due to increasing degradation, the isotope ratios remain relatively constant.

In Figure 7.35, the relationship between the molecular PI2 ratio and the $3MC_6$ isotope ratio are given for Mara M-54 and Hebron I-13 oils to emphasize the greater resistance of individual isotopes as compared to molecular composition to biodegradation. In both wells, the molecular composition significantly decreases with increasing biodegradation. The effect of biodegradation on the individual isotope ratios is not clear.

In Figure 7.35a, the isotope ratios of individual gasoline hydrocarbons in Hebron oils may differ by 0.5 ‰ between oils that have undergone high and low biodegradation, but, from the data, a clear trend with increasing biodegradation is not visible. This 0.5 ‰

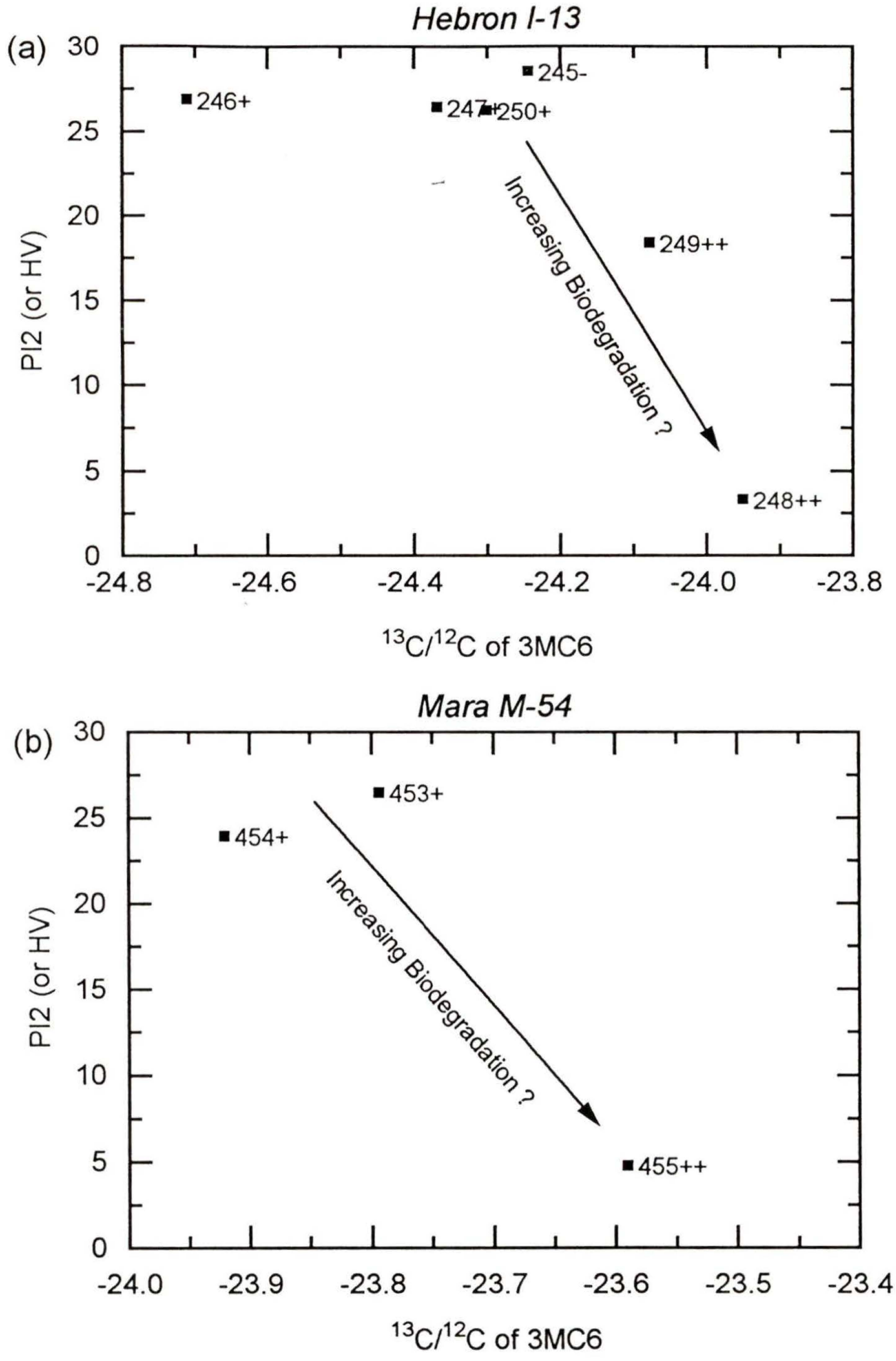


Figure 7.35 Change in molecular and isotope composition of East Coast oils due to biodegradation: (a) Hebron I-13 oils and (b) Mara M-54 oils.

difference is within the analytical error (± 0.3 ‰ to 0.5 ‰). For Mara M-54 oils (Figure 7.35b), the difference between the isotope ratios for the least and most degraded oils is about 0.3 ‰ (well within the analytical error). Since the total isotope variation present in the oils is approximately 10 ‰, the changes in the isotopes due to biodegradation do not appear to be significant.

In Figure 7.36a, the relationships between the molecular PI2 ratio and the $3MC_6$ isotope ratio for Nerlerk M-98 and Saskatchewan Family C oils are given. The isotope ratios of Family C oils only change about 0.2 ‰ as degradation increases (PI2 decreases).

For Nerlerk M-98 oils, one of the most degraded oils (#310) has an isotope ratio of about -22.5 ‰ for $3MC_6$ while the oils with low biodegradation have isotope ratios of about -26.5 ‰. The $3MC_6$ isotope ratio for #310 that is enriched in ^{13}C is probably due to analytical error (or some other factor) and not biodegradation. If this isotope ratio for #310 is ignored, the Nerlerk isotopes would only vary by 1.5 ‰. In Figure 7.36c, all the branched and cyclic compounds are given for the Arctic oils. The #310 oil (Nerlerk#4a) exhibits a different isotope trend than the other oils, especially for $3MC_6$. Also, from the Chester runs (oil standard), $3MC_6$ had one of the largest analytical errors (± 1.0 ‰) of all the compounds measured. When the isotope ratio of CYC_6 is plotted for the Nerlerk oils (Figure 7.36b), there is a change in the isotope ratios of about 2 ‰.

In Figure 7.37a, the $3MC_6$ isotope and the PI2 ratios of the Hibernia oils are plotted. Although the Hibernia oils are not biodegraded, there is a 2 ‰ isotope variation.

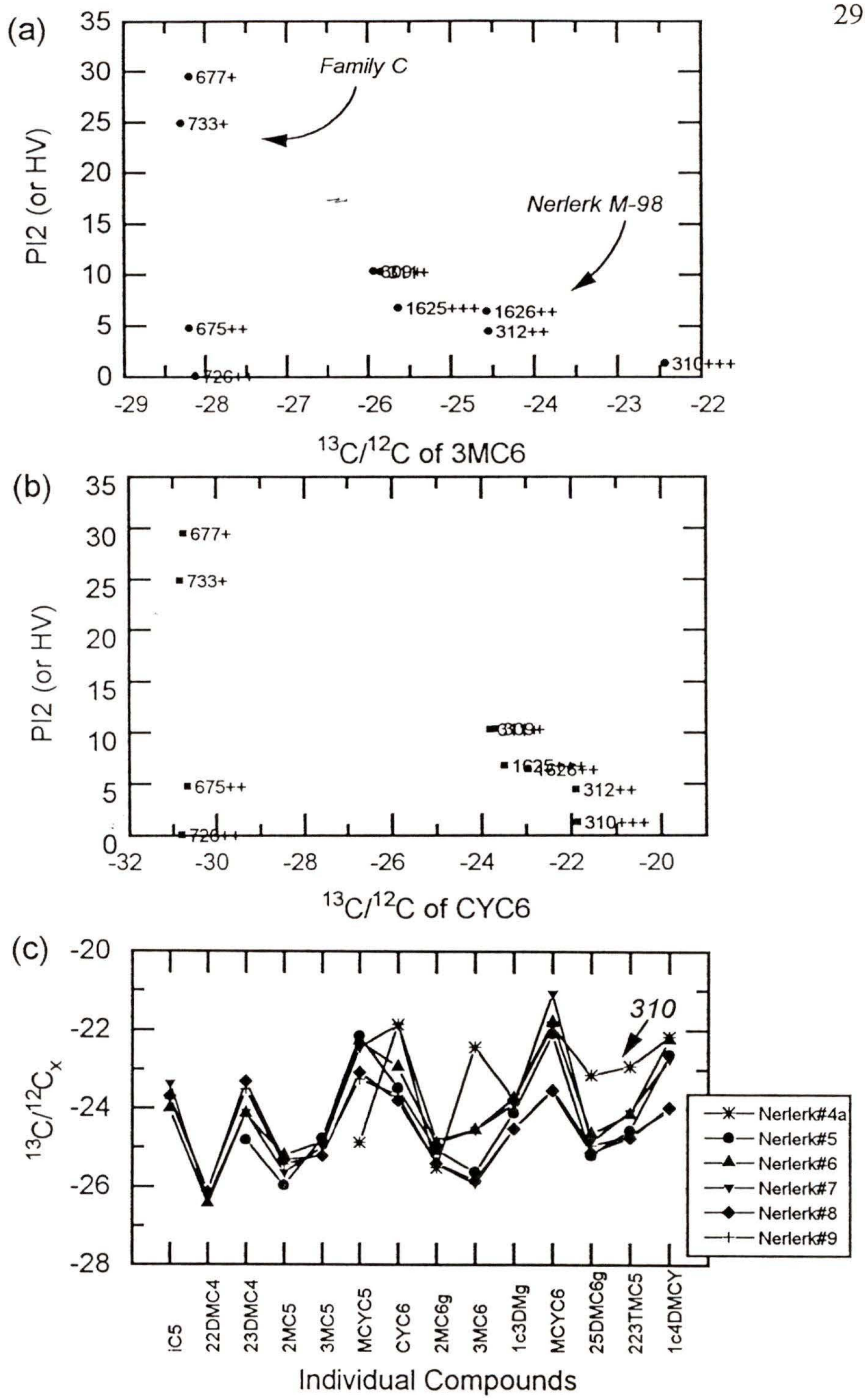
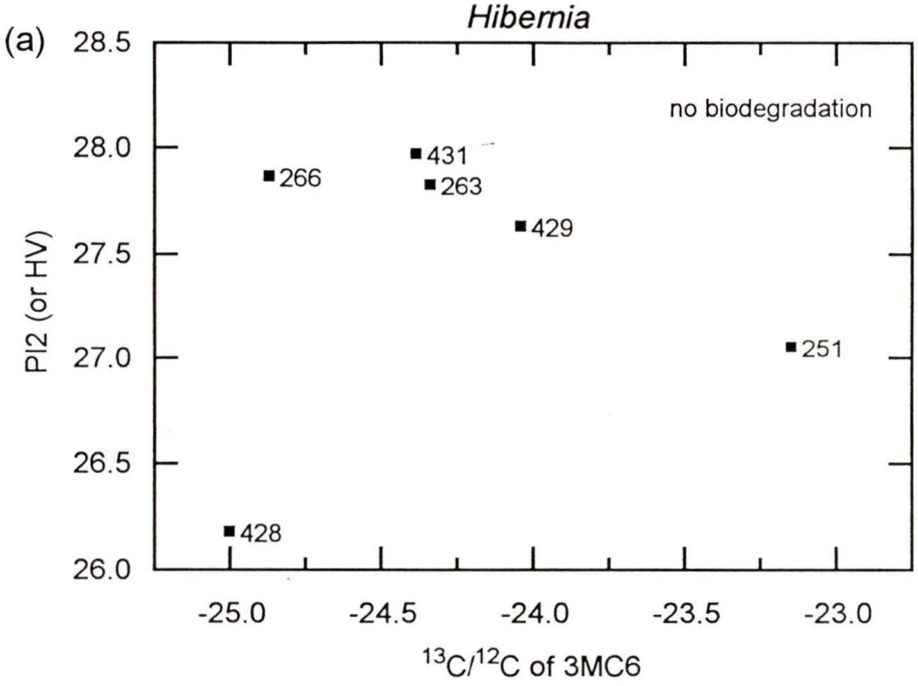


Figure 7.36 Change in the molecular and isotope compositions of Arctic (Nerlerk M-98) and Saskatchewan (Family C) oils: (a) using the individual 3MC6 ratio, (b) using the CYC6 ratio, and (c) isotope composition of branched and cyclic hydrocarbons in the Nerlerk oils.



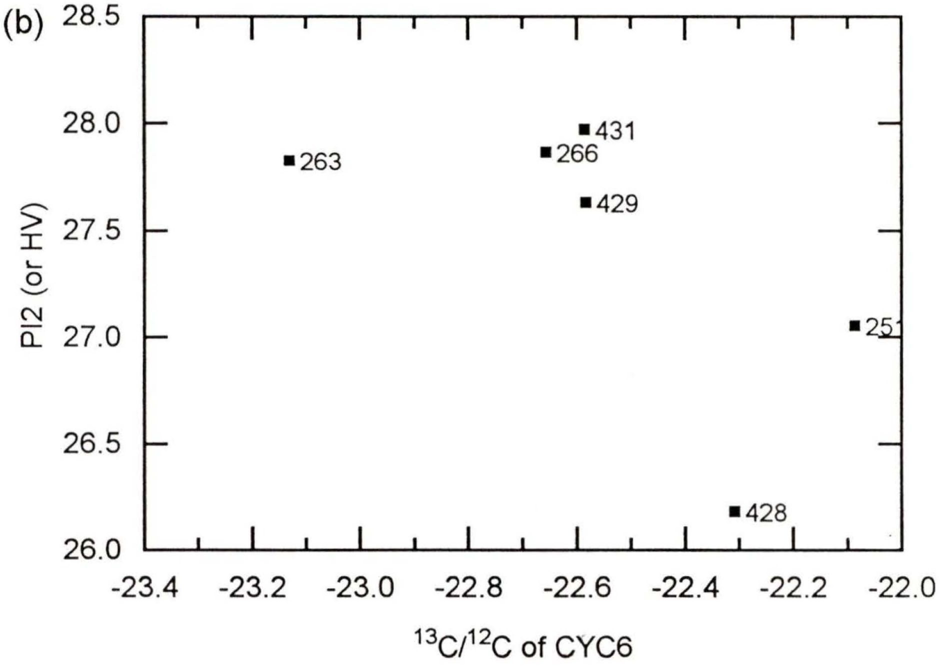


Figure 7.37 Variation in the molecular composition and isotope ratios of non-biodegraded Hibernia oils with: (a) the individual 3MC6 isotope and (b) the individual CYC6 isotope.

This suggests that there is a natural isotope variation within oils from any well. The 2 ‰ isotope variation is probably the worst case since $3MC_6$ has a large analytical error (± 1 ‰). In Figure 7.37b, the CYC_6 isotope ratio is plotted for Hibernia oils and the isotope variation is approximately 1 ‰.

The molecular ratios of Nerlerk oils (less than one) are low compared to those of Mara and Hebron oils (up to 30). The Arctic oil samples are the most biodegraded oils in the current study. The Nerlerk DST#4a (#310) oil has undergone severe biodegradation since its molecular ratio is close to 0. It is likely that an isotope effect is associated with biodegradation, but the data suggests it is small (less than 1 ‰). If the natural isotope variation of 1 to 2 ‰ is subtracted from the isotope variation in the Nerlerk oils, any isotope effect due to biodegradation will be less less than 1 ‰ and often within the analytical error (± 0.3 ‰ to 0.5 ‰).

Several other combinations of molecular parameters and associated isotope ratios are compared and similar results obtained. Two examples of these relationships are included in Figures 7.38. The relationships between the molecular PI2 ratio and the nC_7 and CYC_6 isotope ratios are given for all oil samples in Figure 7.38a and 7.38b. Both of these graphs reveal similar trends.

The resistance of the isotope ratios of oils to biodegradation is evident from these graphs. The isotope ratios of the Saskatchewan Family C, E, and F oils do not change by more than about 1 ‰ even though the molecular ratios decrease significantly with increasing alteration. Most of the East Coast oils cluster together in one main group with

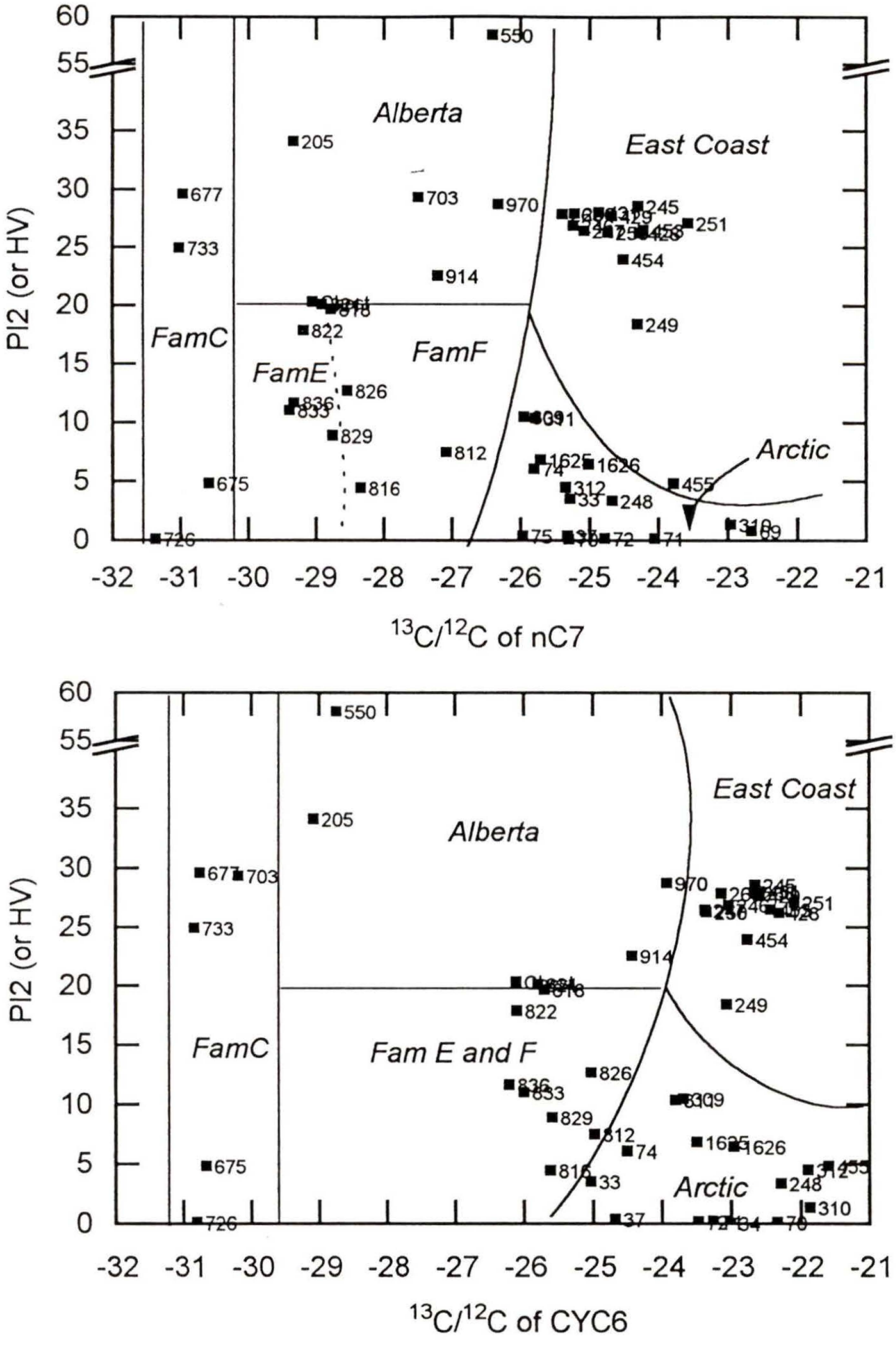


Figure 7.38 Change in molecular and isotope composition of hydrocarbons in all oils due to secondary alteration: (a) PI2 and nC7 isotope and (b) PI2 and CYC6 isotope.

a variation of approximately 2 ‰. The only oils which exhibit larger variation in isotope ratios are the highly degraded Arctic oils. However, if the natural variation within a well is subtracted from the variation, there is no significant isotope effect associated with biodegradation. The non-biodegraded Alberta oils exhibit even greater natural variation in isotopes (approximately 4 ‰) which is reasonable since these oils originate from a variety of environments and source conditions.

The relationships between molecular and isotope data provide evidence for a small isotope effect due to biodegradation. Plots of this type provide a lot of information about oils. The relative amounts of biodegradation in oil samples can be compared, and oils can be regionally correlated from the isotope ratios.

Summary Points:

- A small isotope effect (e.g., less than 1 ‰, often within the analytical error) accompanies biodegradation so altered oils can still be correlated by compound-specific isotope ratios of gasoline range hydrocarbons.

- Approximately 1 to 2 ‰ of the variation in related oil samples is natural and should not be confused with biodegradation effects.

CHAPTER 8. OUTLOOK

The effectiveness of traditional geochemical methods for correlating oils (and source rocks) is limited, especially with regard to those oils affected by alteration processes. The molecular composition of an oil changes as a result of biodegradation, water-washing, or maturation which makes it difficult to identify similarities between the oils. Isotope ratios of bulk and major oil fractions are averages of many hydrocarbons (with different isotope ratios) and therefore are often not diagnostic. Thus, none of the previous methods for oil correlation could be used independently to achieve reliable correlations.

In this study, the analysis of individual gasoline range hydrocarbons is effective in correlating Canadian oils into groups based on source. The experimental error is low (± 0.3 to 0.5 ‰) while the isotopic variation in the individual compounds is high (10 ‰). These isotope ratios are resistant to change. The effect of secondary alteration on the isotope ratios of gasoline range hydrocarbons is small (less than 1 ‰, often within the analytical error). Neither secondary alteration processes nor the experimental error associated with the isotope measurements can account for the large isotope variation in the oils. Instead, this variation must be due to source composition.

The results from this study of individual stable carbon isotopes in gasoline range hydrocarbons establishes this new isotope technique as a promising tool for correlating oils. It is particularly useful for oils that are affected by secondary alteration, where other correlation techniques fail.

Further advancements in the field of stable carbon isotopes regarding the identification of specific locations of ^{12}C or ^{13}C in hydrocarbon chains (intra-compound studies) may yield more insight into the mechanisms used by microbes for distinguishing between ^{12}C and ^{13}C in hydrocarbons and provide more specific information about the magnitude of the effect.

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APPENDIX A

Table A1 Locations of oil samples from Canada.

Sample #	Well Name	Well Location Township-Range	Latitude	Longitude
East Coast				
455	Mara M-54 DST#3		46/43/48.79-N	48/38/43.58-W
454	Mara M-54 DST#2		"	"
453	Mara M-54 DST#1		"	"
248	Hebron I-13 DST#10		46/32/33.94-N	48/31/45.48-W
249	Hebron I-13 DST#9		"	"
250	Hebron I-13 DST#7		"	"
247	Hebron I-13 DST#6		"	"
246	Hebron I-13 DST#5		"	"
245	Hebron I-13 DST#1		"	"
431	Hibernia C-96 DST#5		46/45/10.19-N	48/44/35.74-W
429	Hibernia C-96 DST#3		"	"
428	Hibernia C-96 DST#2		"	"
266	Hibernia K-18 DST#11		46/47/34.66-N	48/47/17.02-W
263	Hibernia K-18 DST#8		"	"
251	Hibernia K-18 DST#1		"	"
Arctic				
1263	Amauligak O-86 DST#3			
309	Nerlerk M-98 DST#9		70/27/47.62-N	133-29-44.37-W
311	Nerlerk M-98 DST#8		"	"
312	Nerlerk M-98 DST#7		"	"
1626	Nerlerk M-98 DST#6		"	"
1625	Nerlerk M-98 DST#5		"	"
310	Nerlerk M-98 DST#4A		"	"
33	Niglintgak M-19 DST#22		69/18/49.00-N	135/19/26.00-W
69	Niglintgak M-19 DST#20		"	"
70	Niglintgak M-19 DST#19		"	"
34	Niglintgak M-19 DST#16		"	"
71	Niglintgak M-19 DST#14		"	"
72	Niglintgak M-19 DST#13		"	"
73	Niglintgak M-19 DST#11		"	"
37	Niglintgak M-19 DST#10		"	"
74	Niglintgak M-19 DST#9		"	"
75	Niglintgak B-19 DST#14		69/18/11.00-N	135/18/19.00-W

Table A1 Locations of oil samples from Canada, continued.

Sample #	Well Name	Well Location Township-Range	Latitude	Longitude
Saskatchewan				
Family C:				
675	Battrum U1	15-15-18-17W3	50/31/32.46-N	108/15/34.93-W
733	Cantuar Main	8-11-16-17W3	50/19/44.68-N	108/13/52.05-W
727	Battle Creek	12-27-3-26W3	49/14/28.31-N	109/25/59.78-W
677	Butte	3-2-12-19W3	49/57/43.72-N	108/29/54.63-W
726	Battle Creek	15-22-3-26W3	49/13/48.26-N	109/25/16.96-W
Family E:				
833	Hearts Hill	2-29-36-26W3	52/06/58.05-N	109/40/36.43-W
836	Buffalo Coulee B	15-22-32-24W3	51/45/43.32-N	109/19/18.19-W
829	Cactus Lake	12-35-35-28W3	52/03/02.34-N	109/54/13.58-W
817	North Hoosier	9-33-31-27W3	51/42/05.66-N	109/45/52.24-W
822	Court	12-25-33-28W3	51/51/42.41-N	109/51/07.94-W
Family F:				
812	Plato	12-13-25-18W3	51/08/02.59-N	108/23/43.59-W
821	Kerrobert	1-2-33-23W3	51/47/47.89-N	109/08/51.49-W
818	South Eureka	14-18-31-22W3	51/39/40.91-N	109/06/48.90-W
826	Forgan	10-17-24-13W3	51/02/49.11-N	107/46/47.13-W
816	Smiley	15-36-30-26W3	51/37/07.44-N	109/31/40.16-W
Family A				
550	Lake Alma	7-23-1-17W2		
Alberta				
970	Turner Valley	6-27-20-3W5	50/43/22.66-N	114/20/14.61-W
914	Willesden Green	16-15-40-5W5		
703	Shekilie	5-17-119-7W6		
205	Rainbow	4-7-110-7W6		
1439	Chester	10-13-22-29W4	50/52/23.46-N	113/53/20.60-W

APPENDIX B
C_{10+} Gas Chromatograms

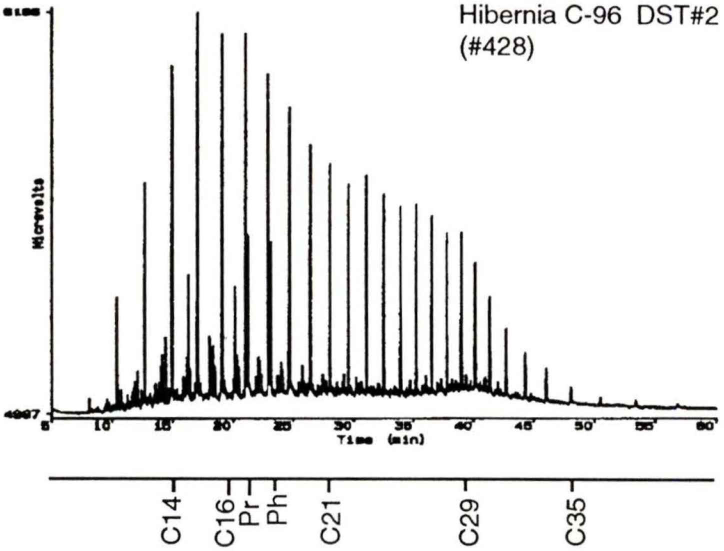


Figure B1 HMW gas chromatograms for Hibernia oils from the Jeanne d'Arc Basin, offshore Newfoundland.

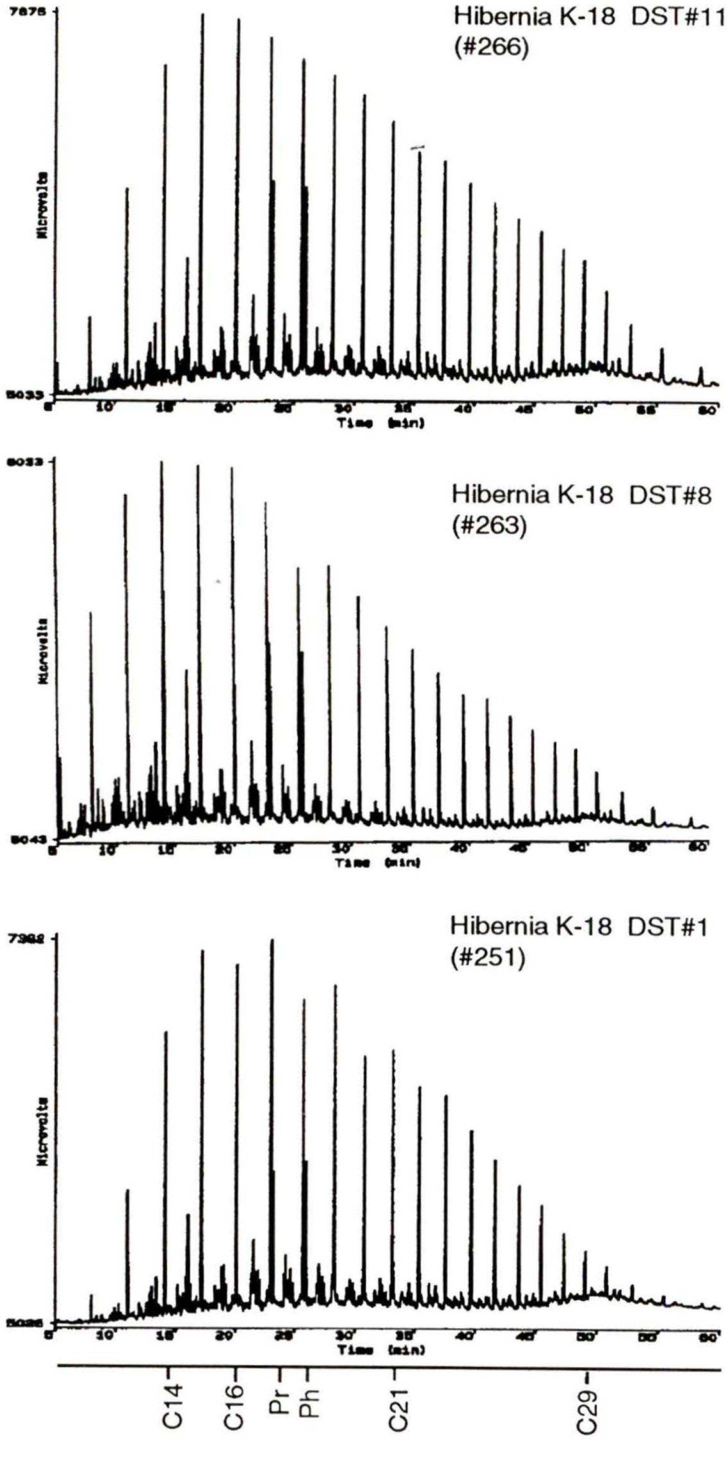


Figure B1 HMW gas chromatograms of Hibernia oils, continued.

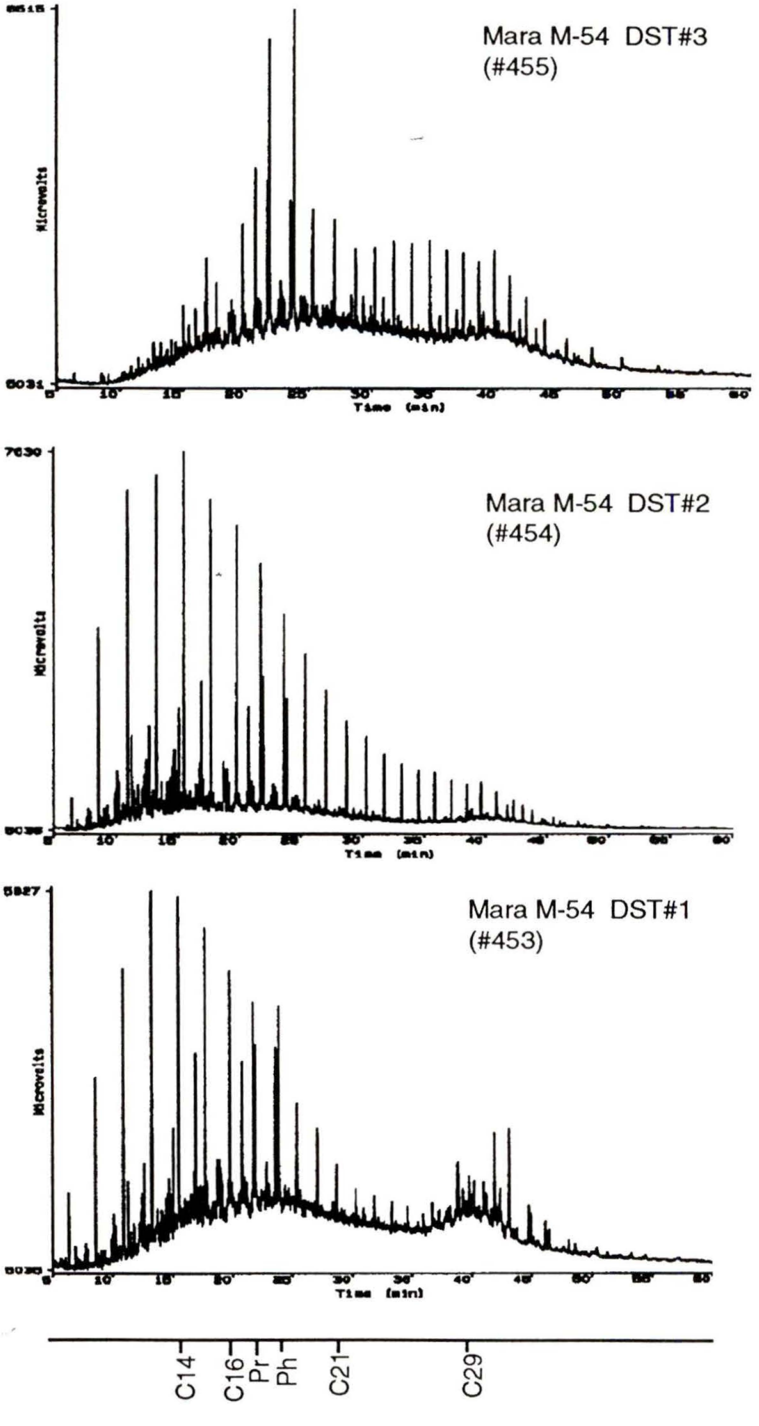


Figure B2 HMW chromatograms for Mara M-54 oils from the Jeanne d'Arc Basin, offshore Newfoundland.

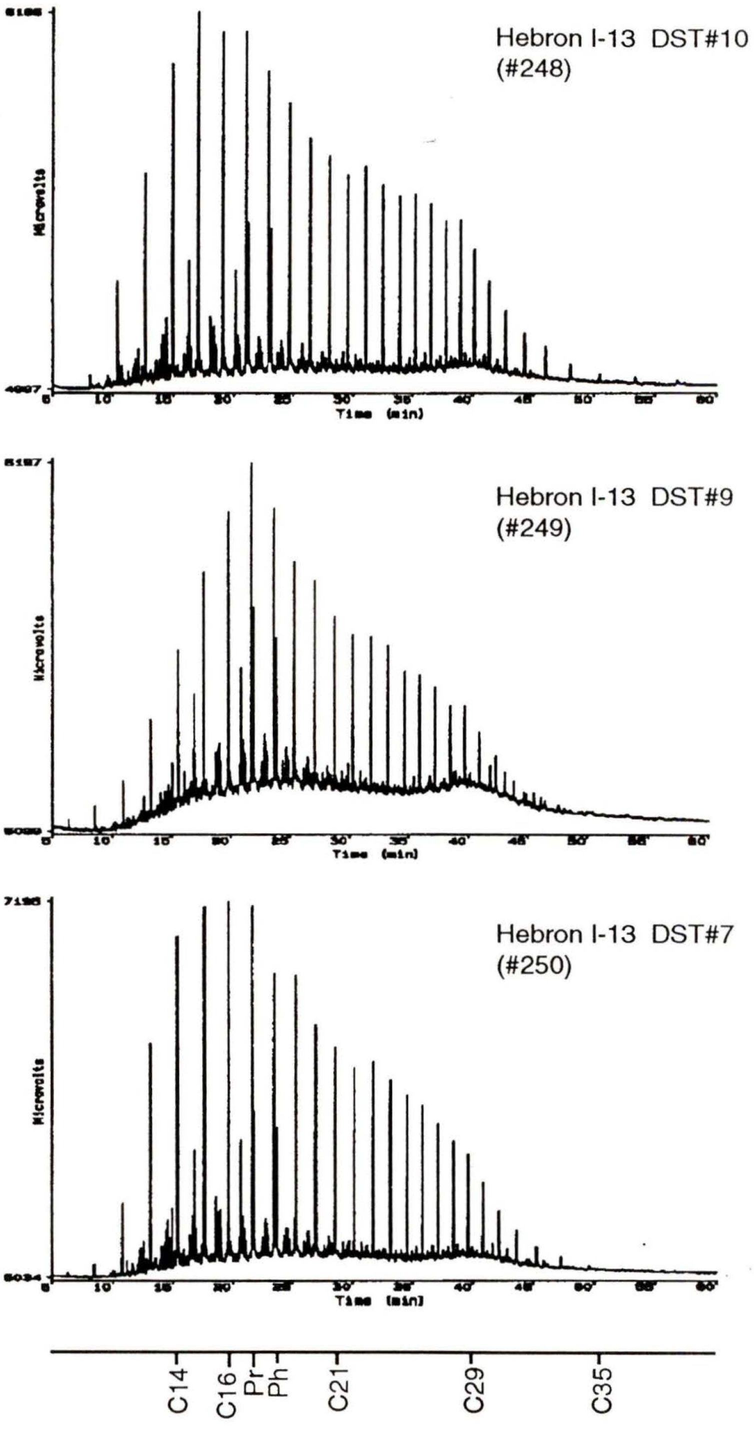


Figure B3 HMW chromatograms for Hebron I-13 oils from the Jeanne d'Arc Basin, offshore Newfoundland.

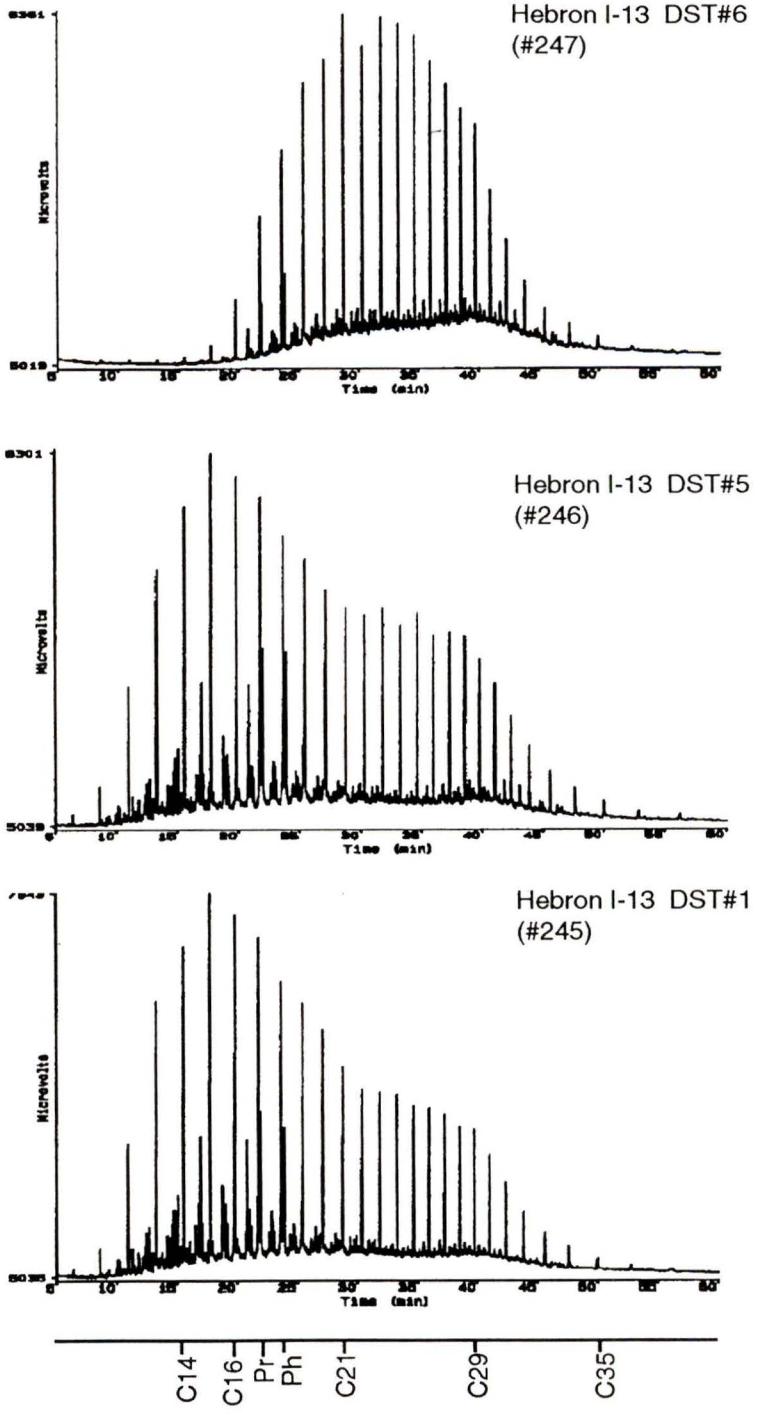


Figure B3 HMW chromatograms for Hebron I-13 oils, continued.

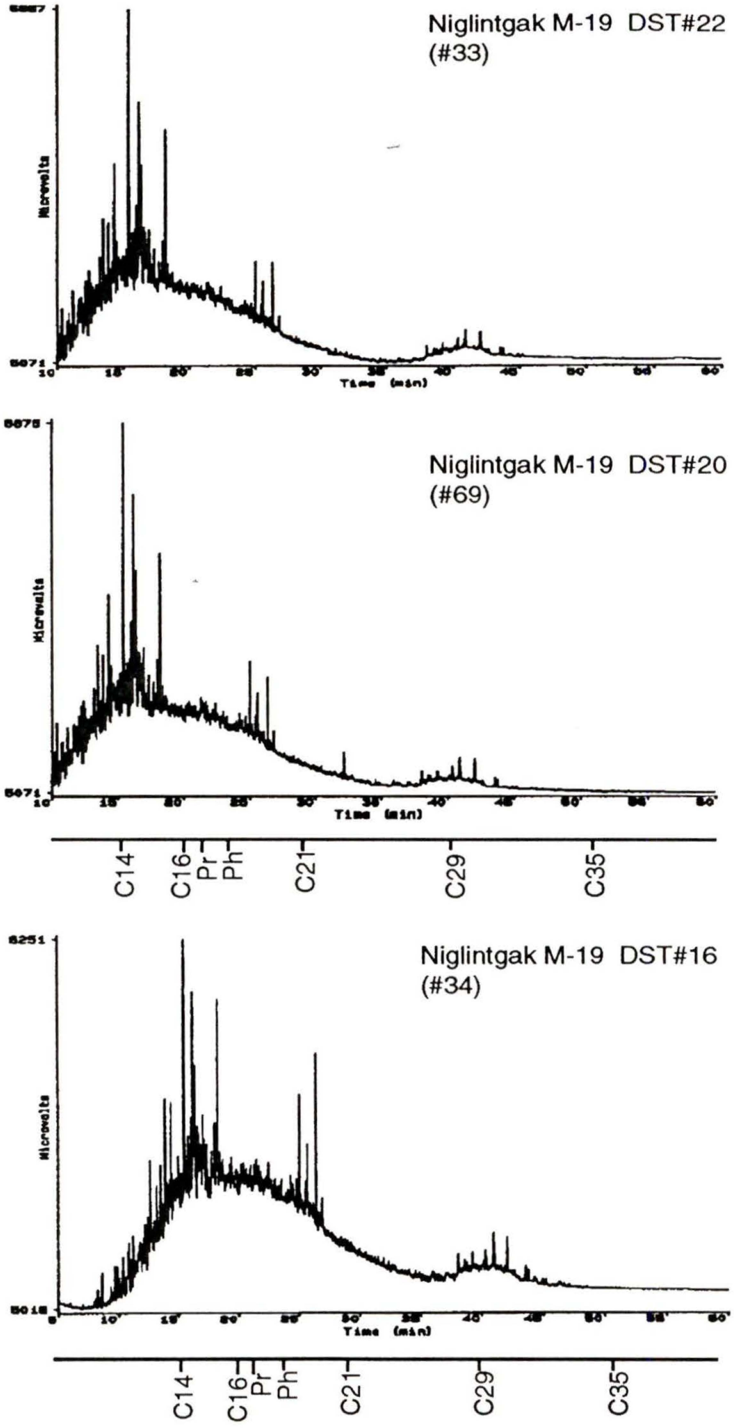


Figure B4 HMW chromatograms for Niglintgak oils from the Beaufort-Mackenzie Basin in the Canadian Arctic.

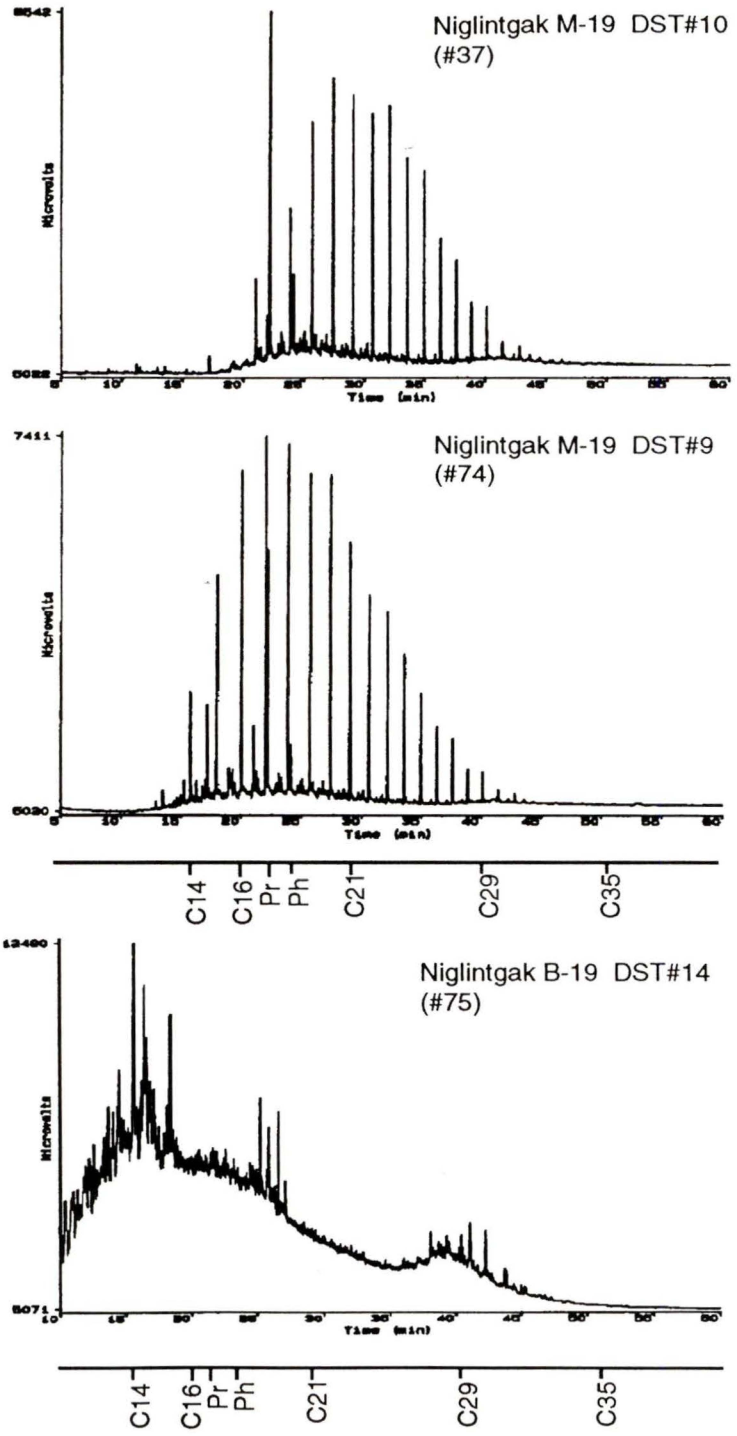


Figure B4 HMW chromatograms for Niglintgak oils, continued.

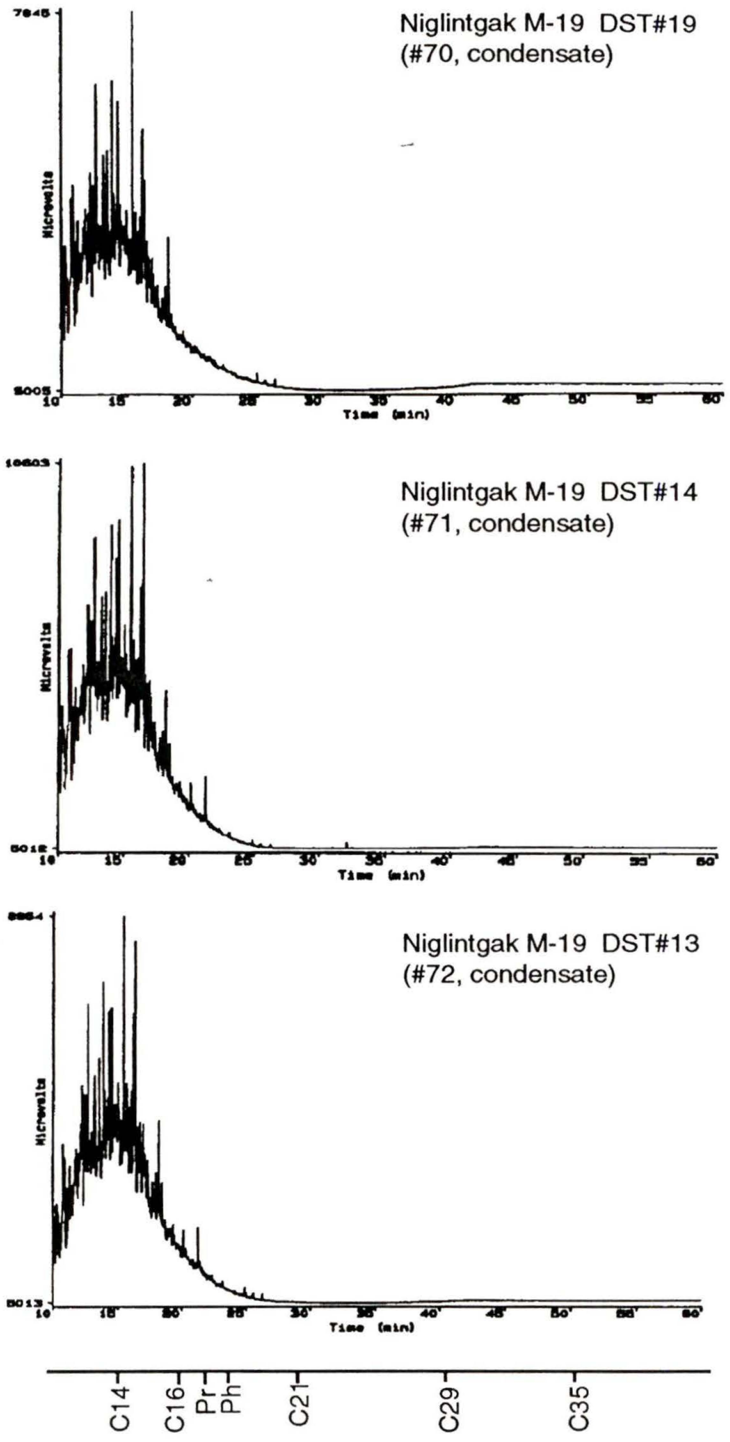


Figure B5 HMW chromatograms for Niglintgak condensates from the Beaufort-Mackenzie Basin, Canadian Arctic.

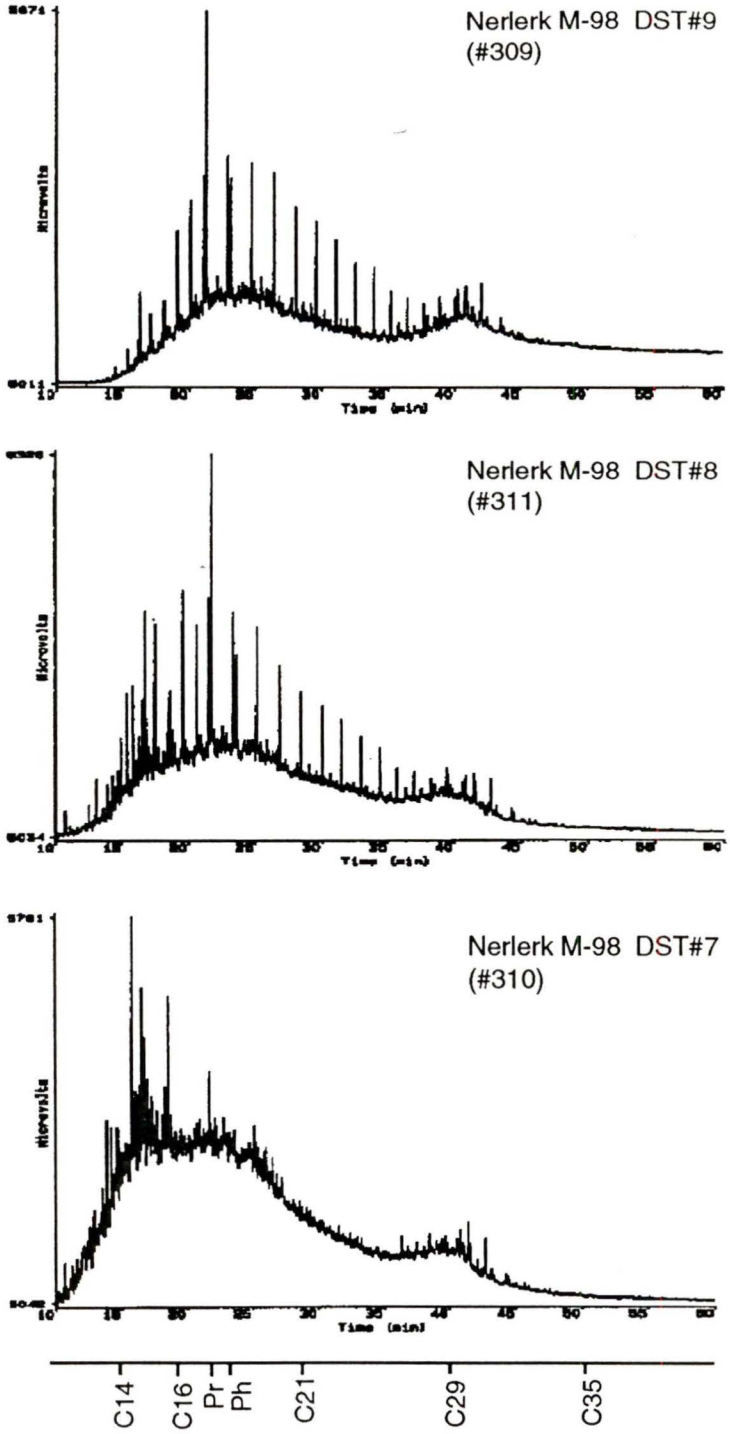


Figure B6 HMW chromatograms for Nerlerk M-98 oils from the Beaufort-Mackenzie Basin in the Canadian Arctic.

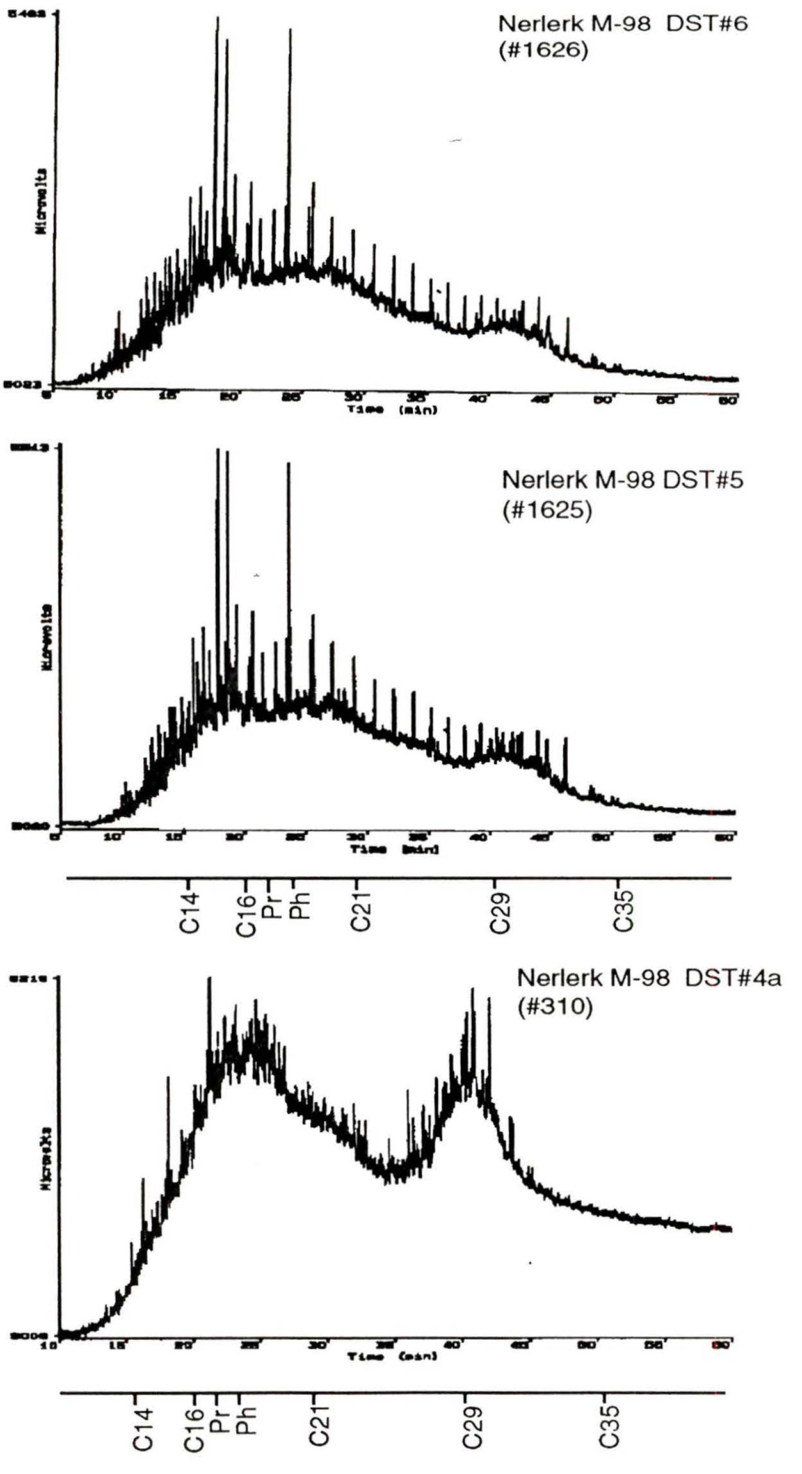


Figure B6 HMW chromatograms for Nerlerk M-98 oils, continued.

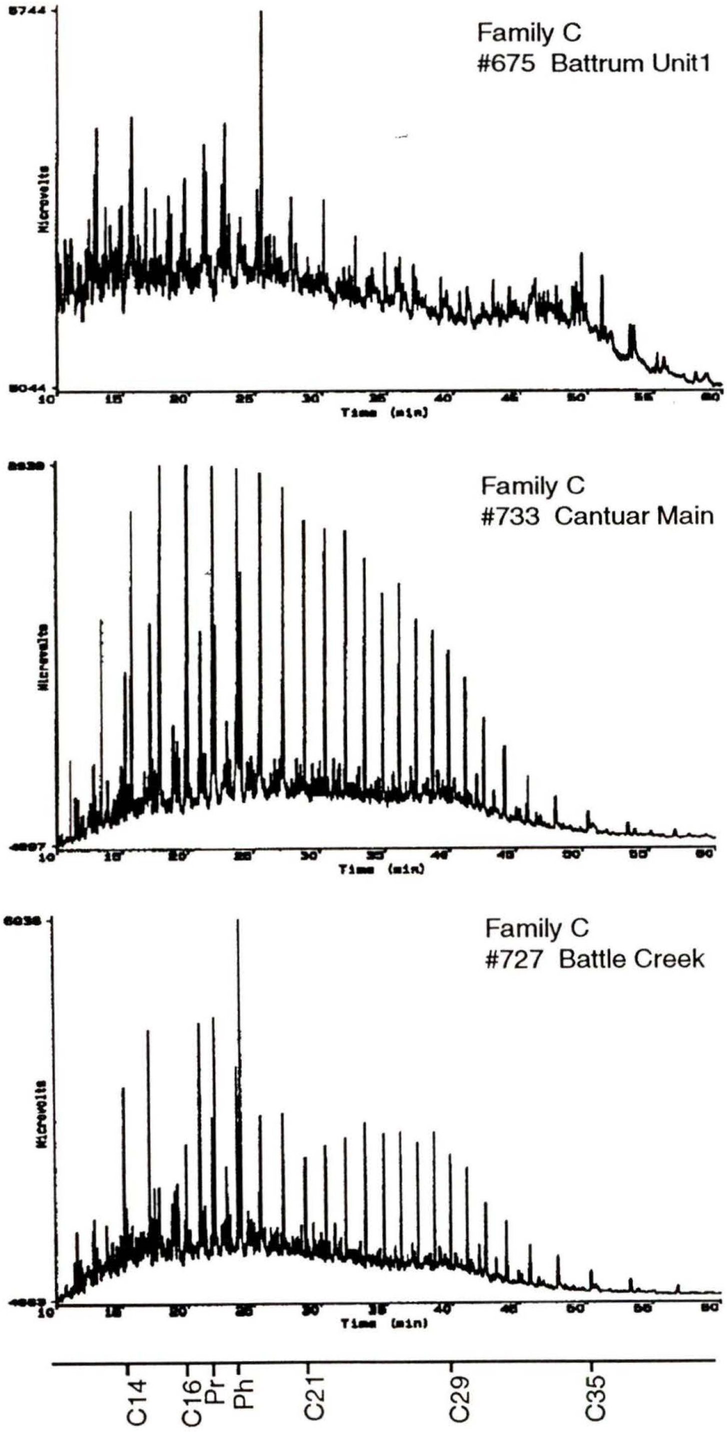


Figure B7 HMW chromatograms for Family C oils from the Williston Basin in southwest Saskatchewan.

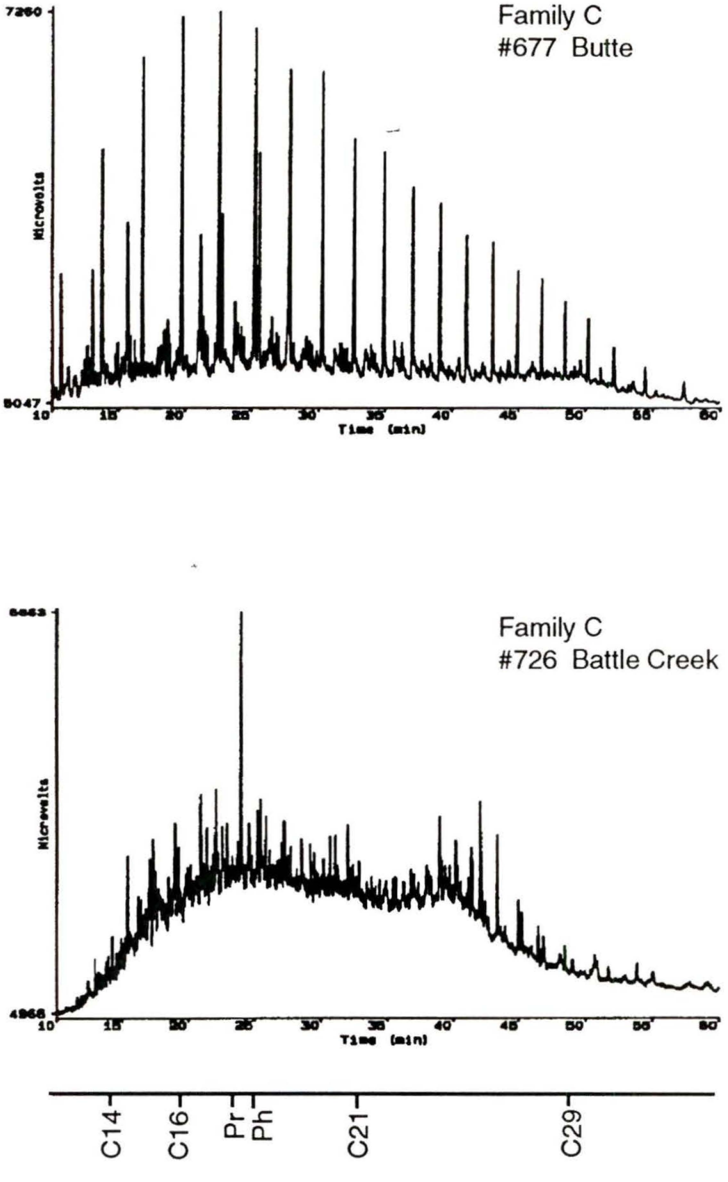


Figure B7 HMW chromatograms for Family C oils, continued.

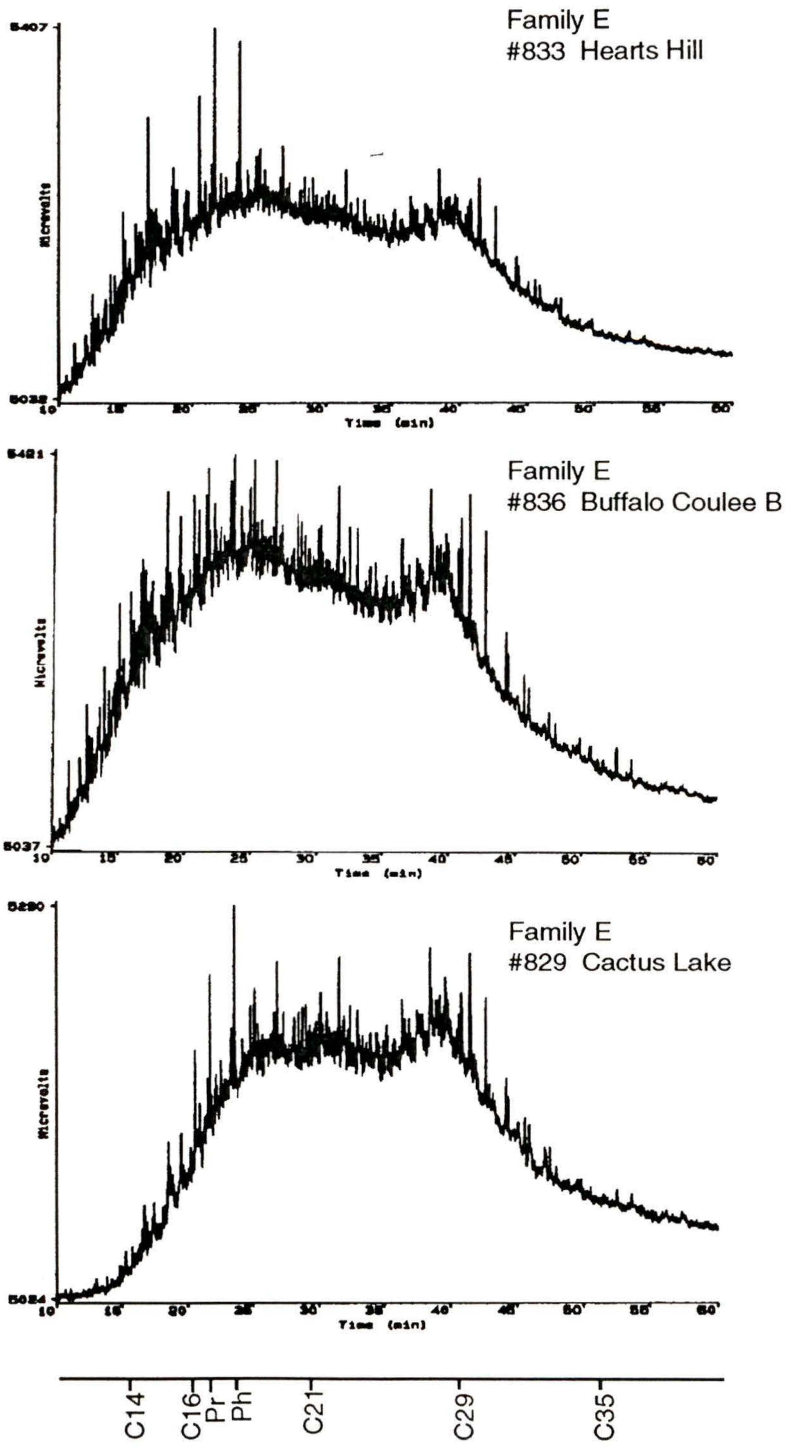


Figure B8 HMW chromatograms for Family E oils from the Williston Basin, southwest Saskatchewan.

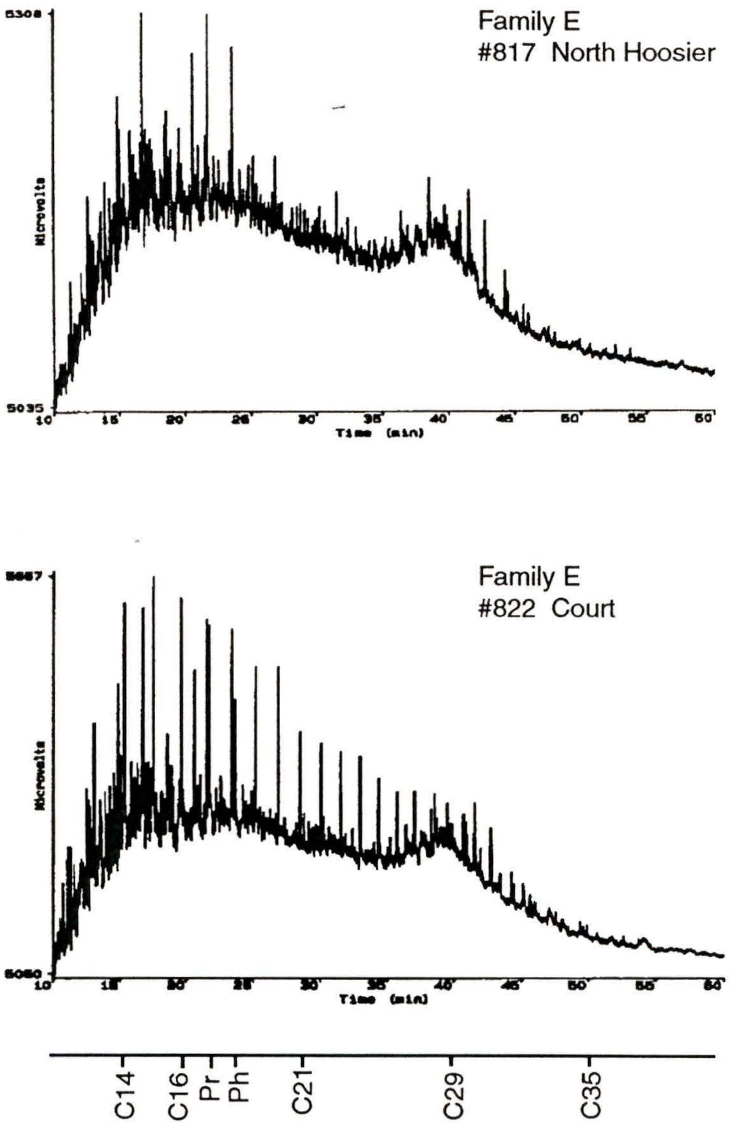


Figure B8 HMW chromatograms for Family E oils, continued.

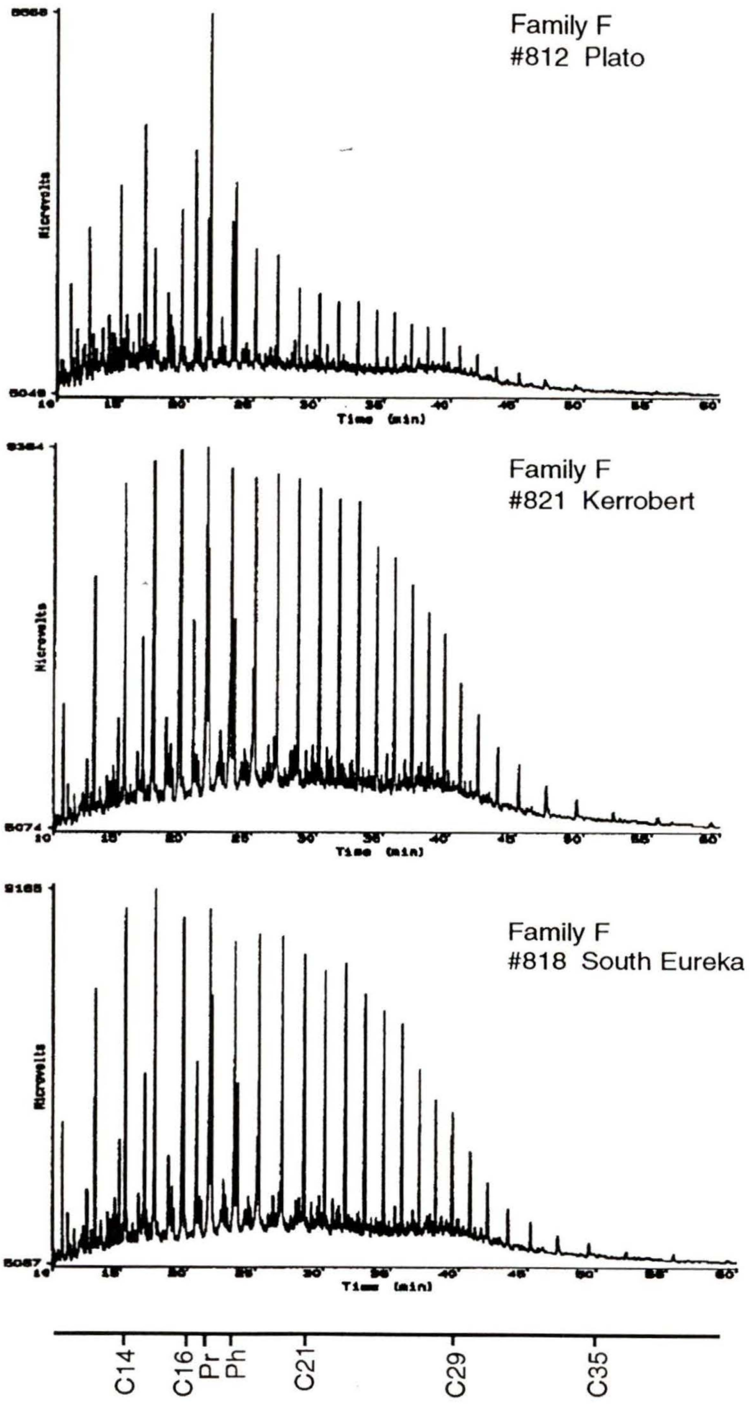


Figure B9 HMW chromatograms for Family F and A oils from the Williston Basin in southwest and southeast Saskatchewan.

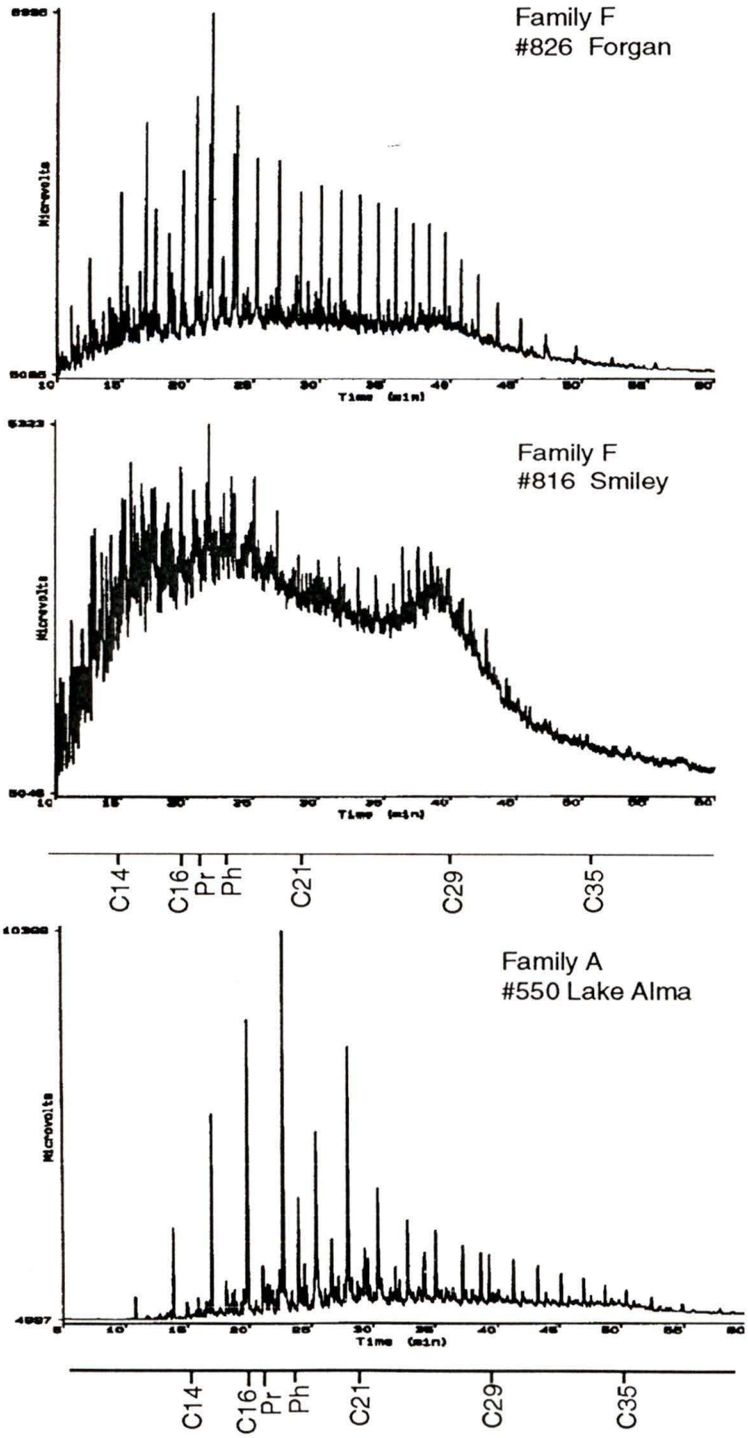


Figure B9 HMW chromatograms for Family F and A oils, continued.

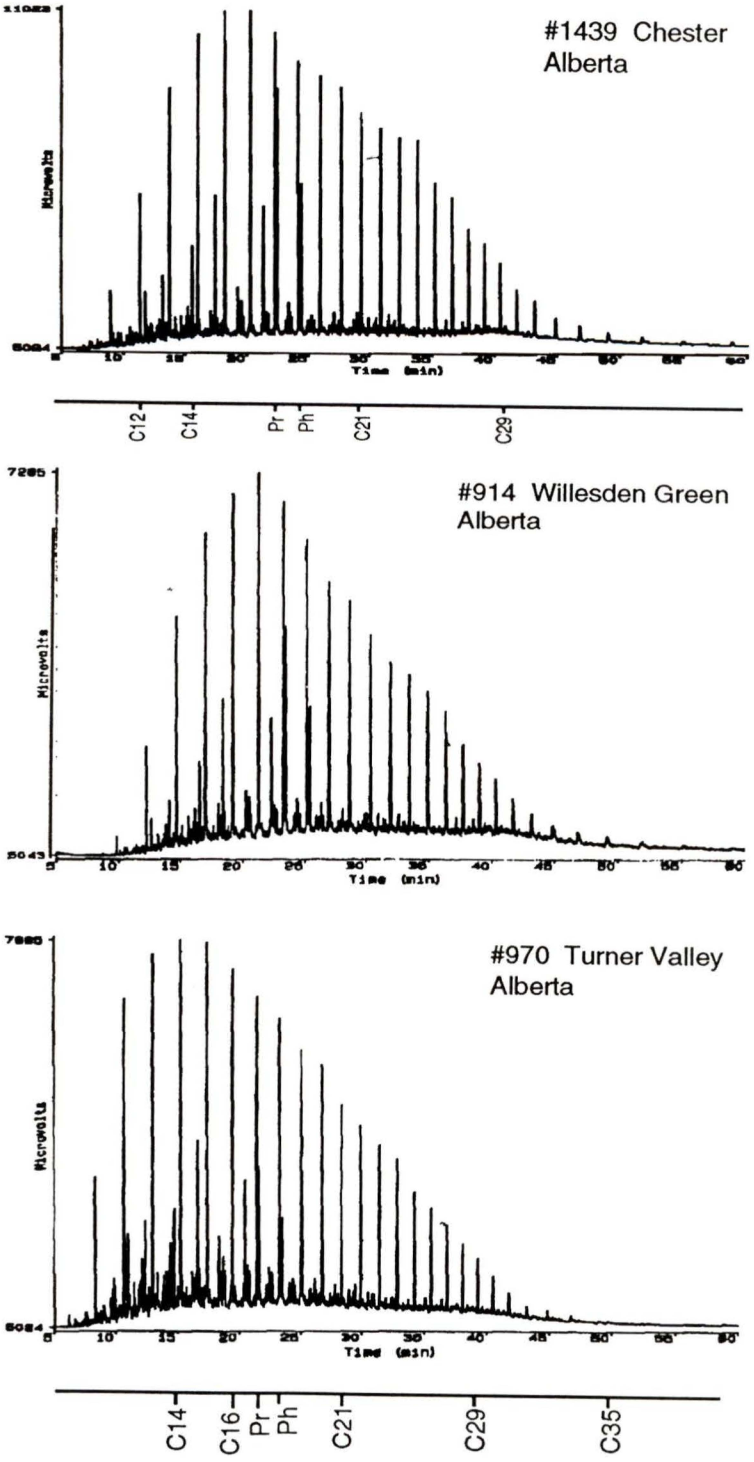


Figure B10 HMW chromatograms for Alberta oils from the Western Canada Sedimentary Basin.

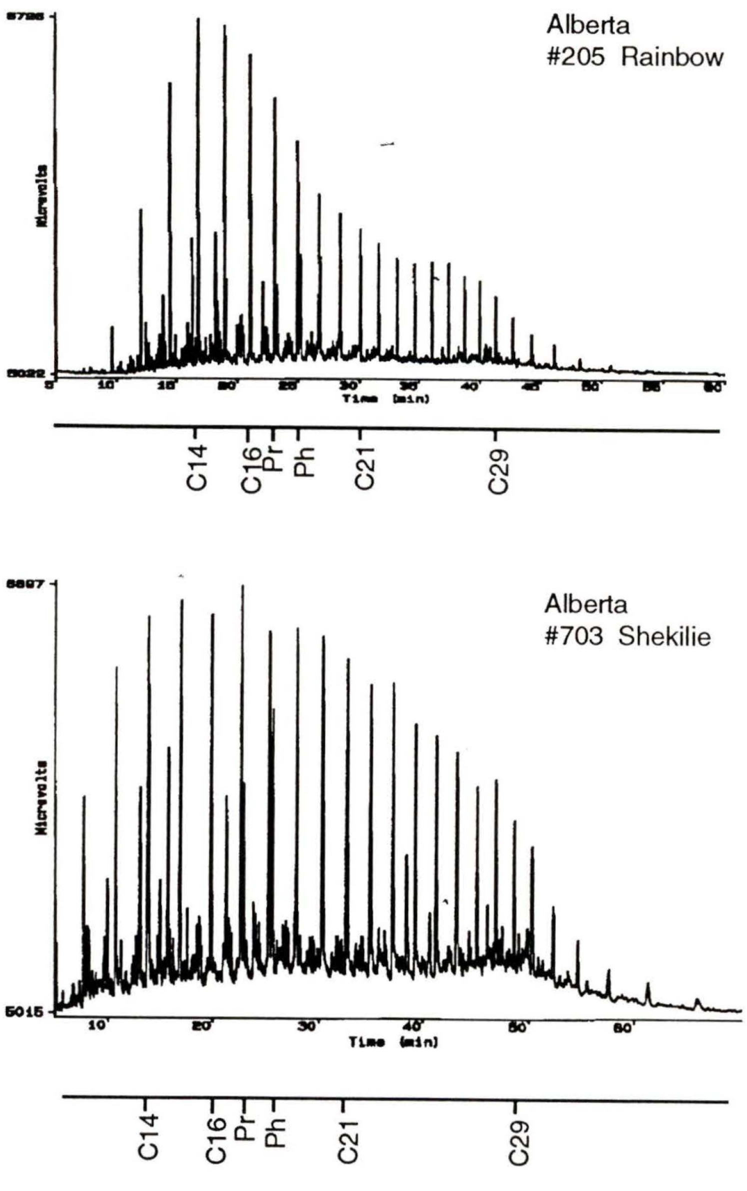


Figure B10 HMW chromatograms for Alberta oils, continued.

APPENDIX C

C_5 - C_{10} Gas Chromatograms

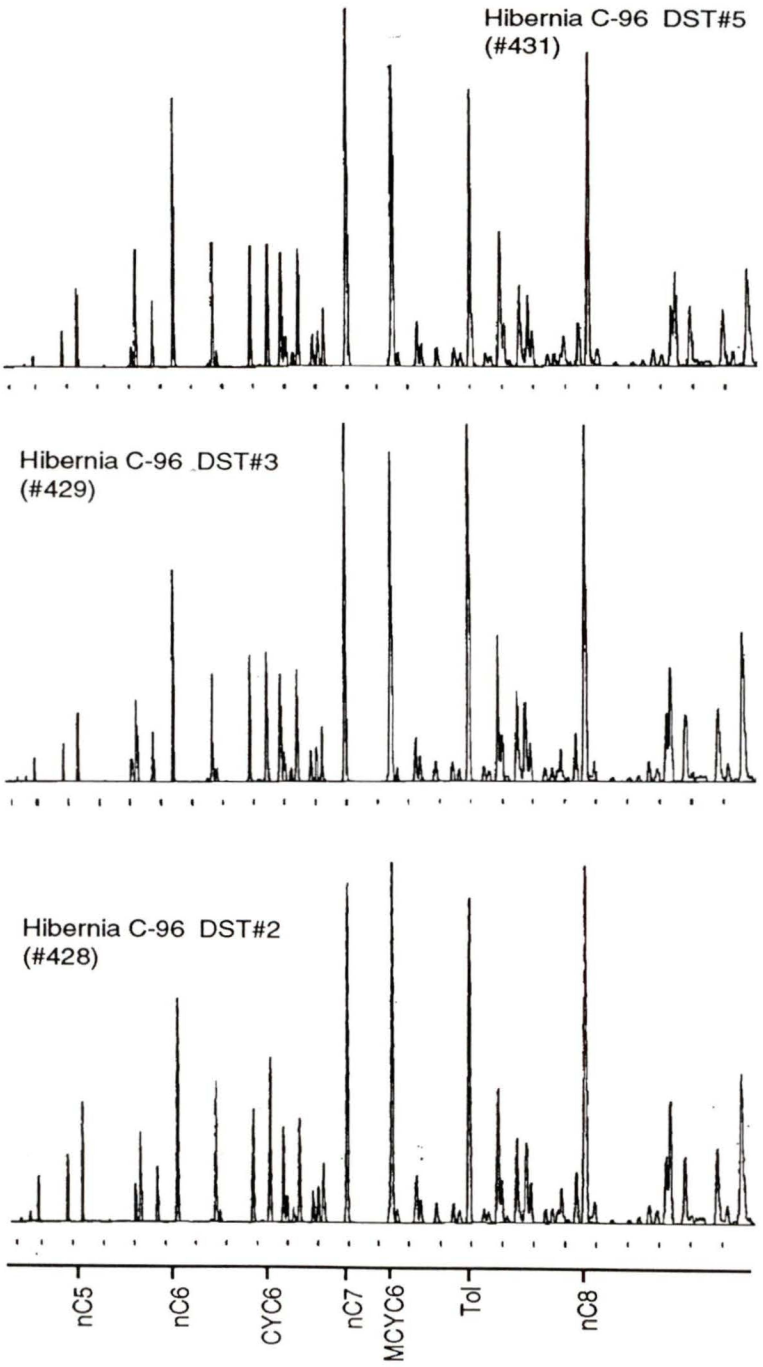


Figure C1 LMW chromatograms for Hibernia oils from the Jeanne d'Arc Basin, offshore Newfoundland.

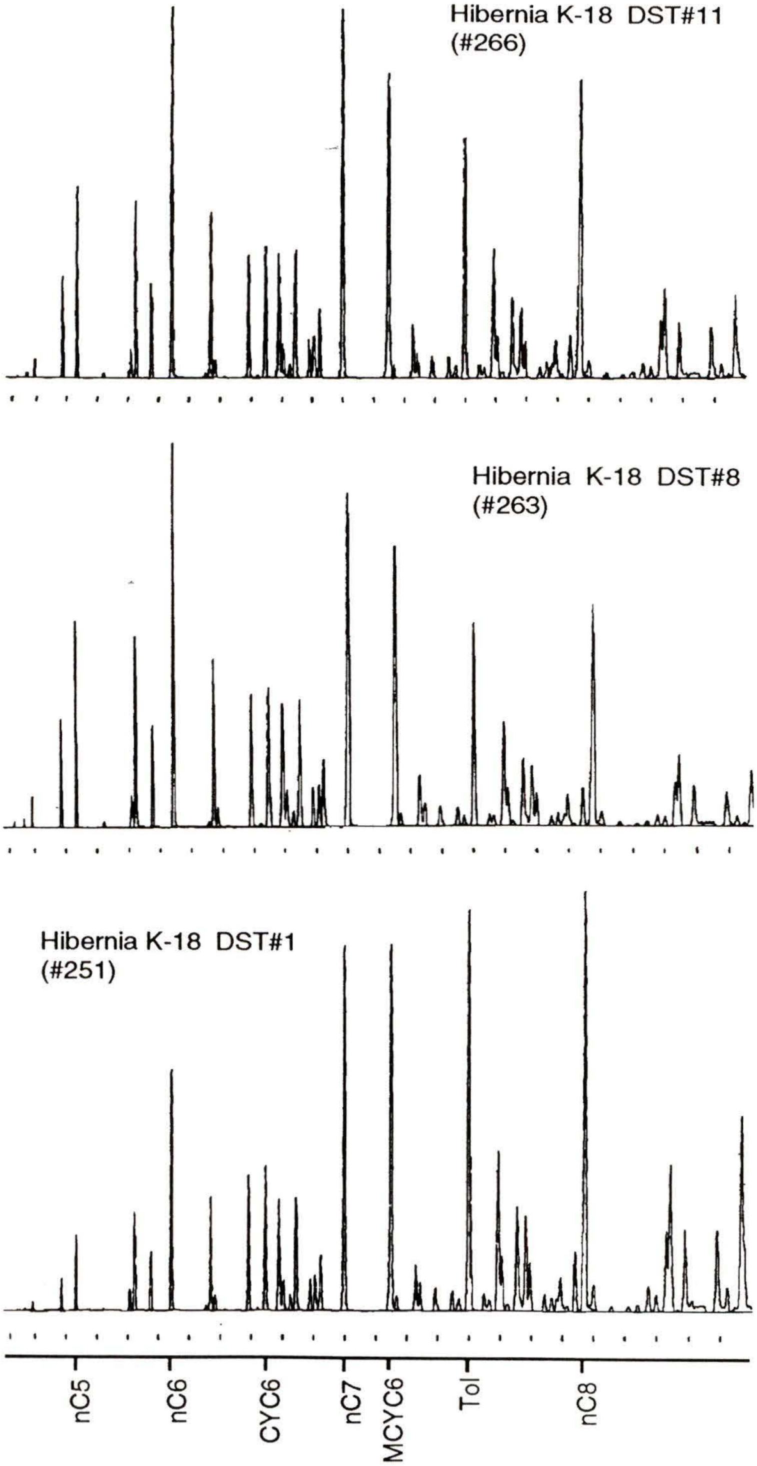


Figure C1 LMW chromatograms for the Hibernia oils, continued.

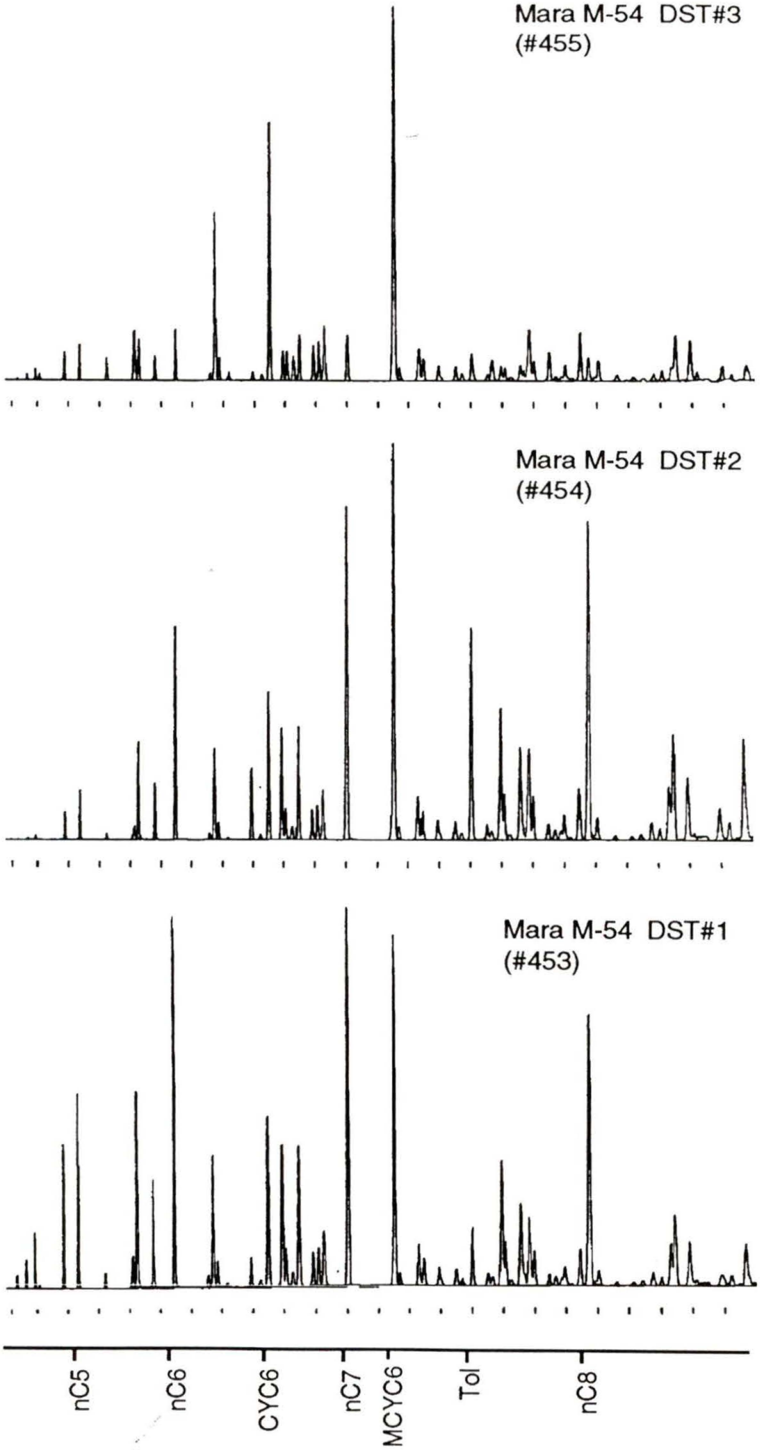


Figure C2 LMW chromatograms for Mara M-54 oils from the Jeanne d'Arc Basin, offshore Newfoundland.

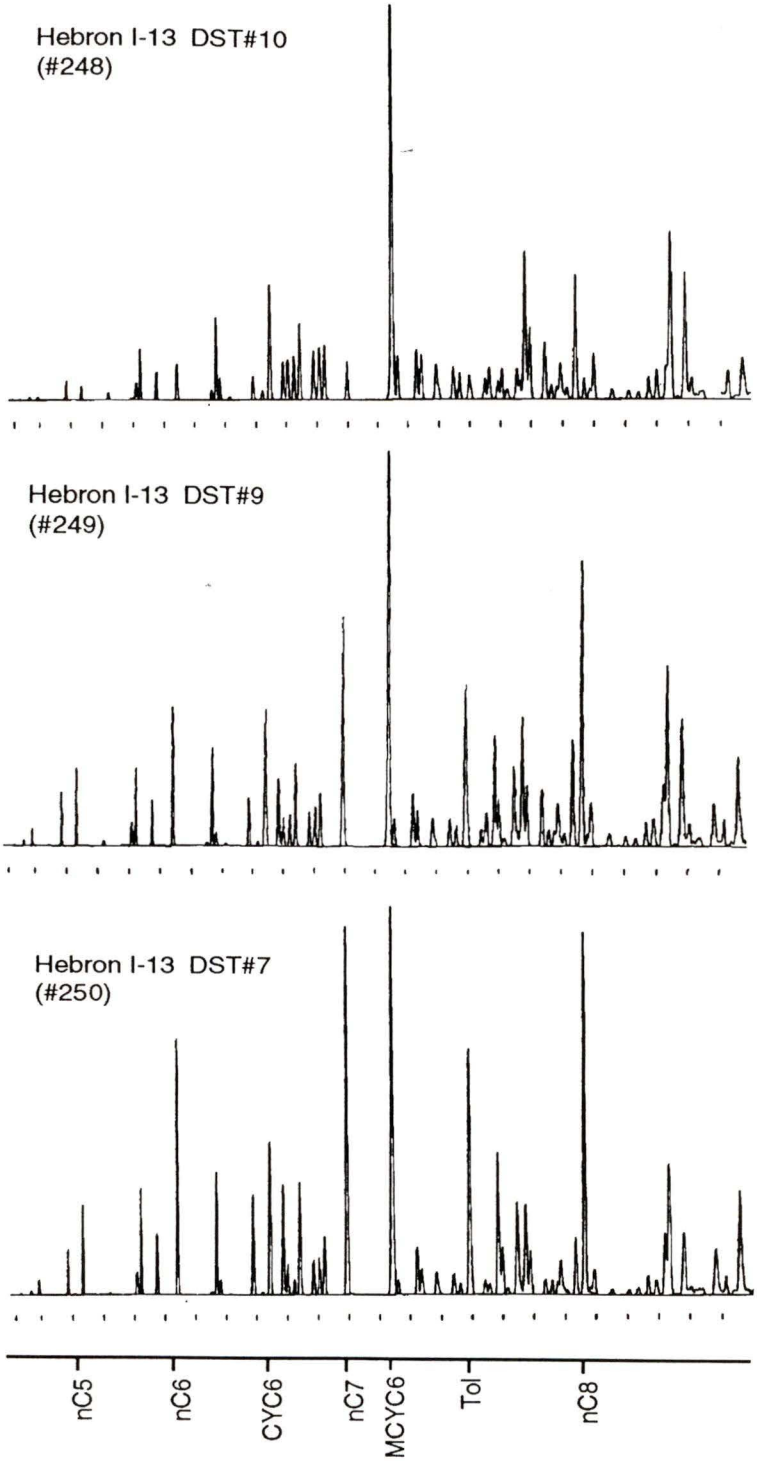


Figure C3 LMW chromatograms for Hebron I-13 oils from the Jeanne d'Arc Basin, offshore Newfoundland.

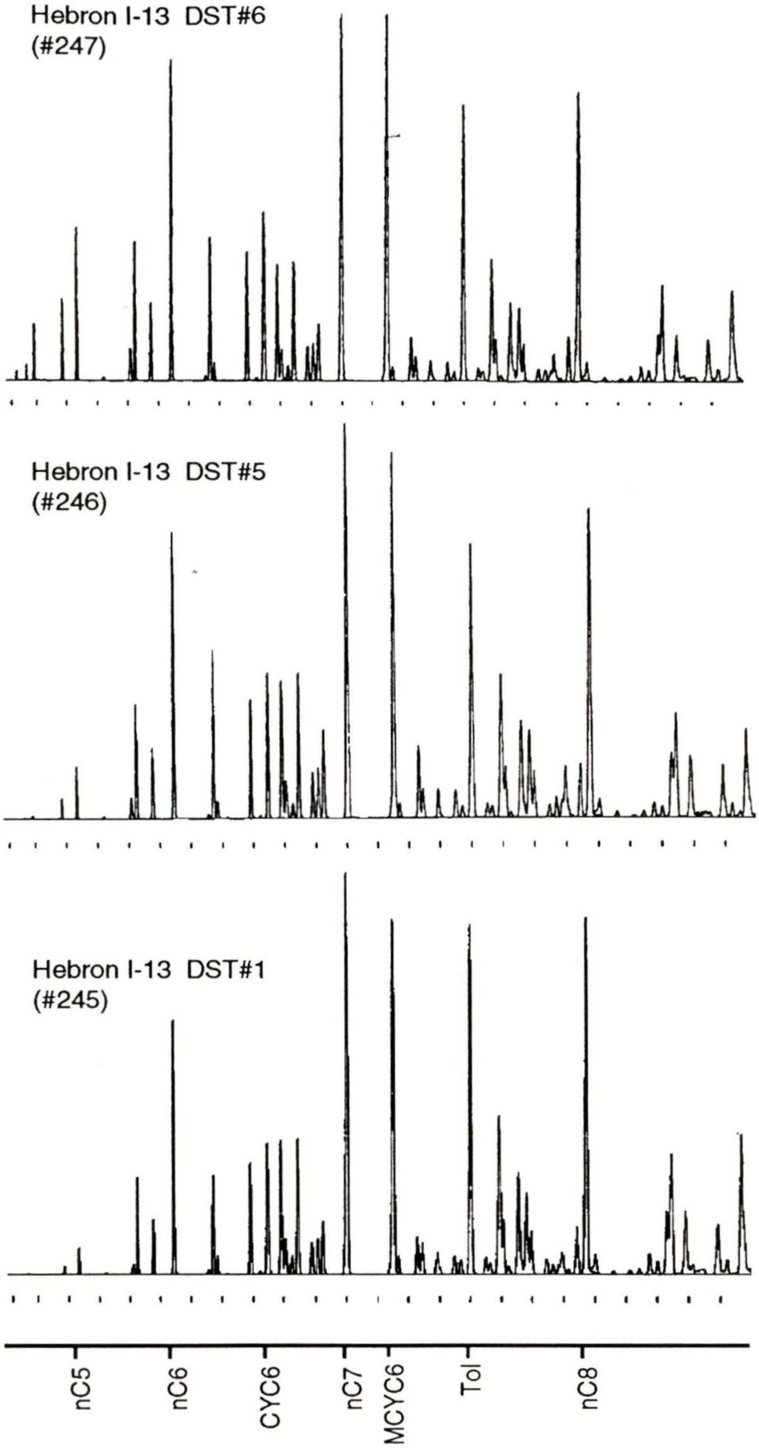


Figure C3 LMW chromatograms for Hebron I-13 oils, continued.

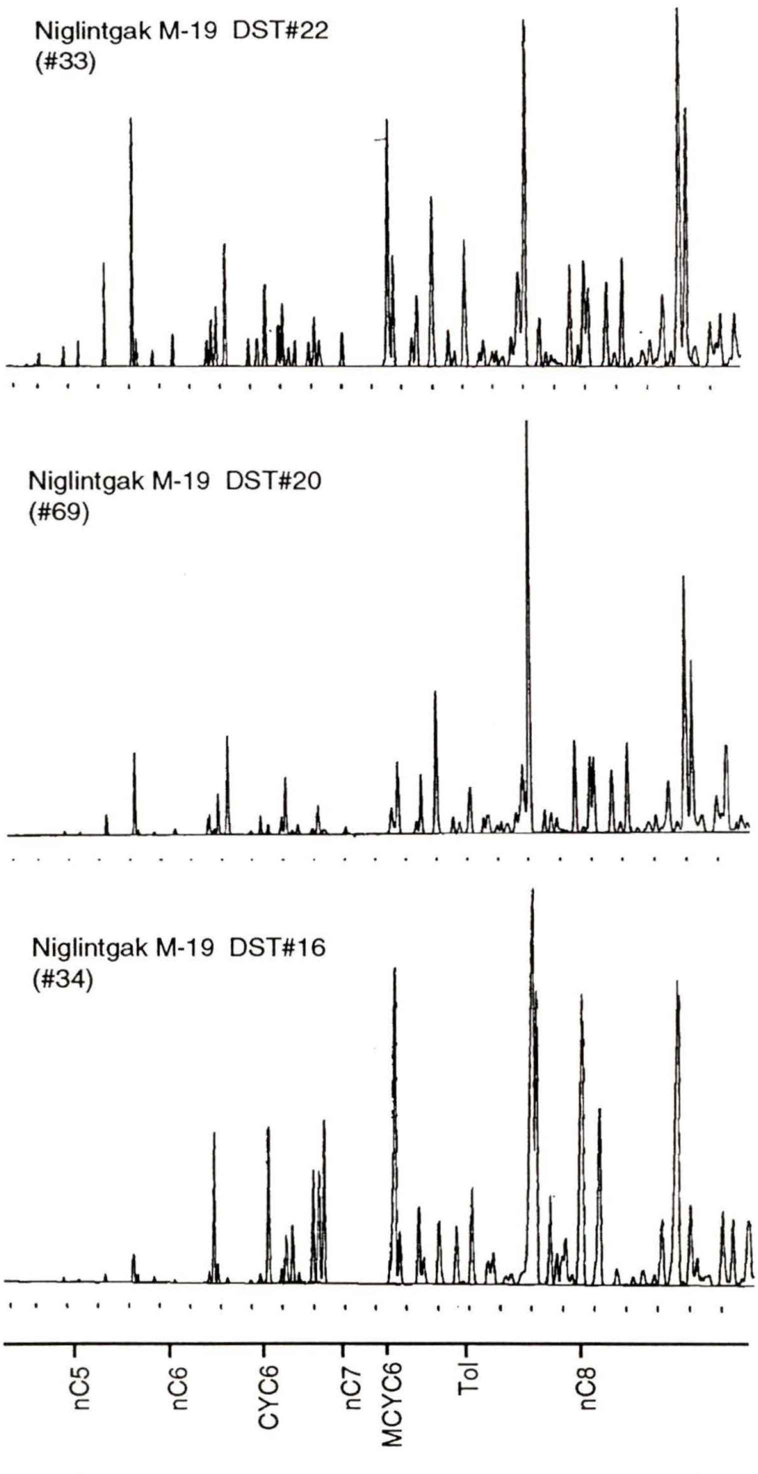


Figure C4 LMW chromatograms for Niglintgak oils from the Beaufort-Mackenzie Basin, Canadian Arctic.

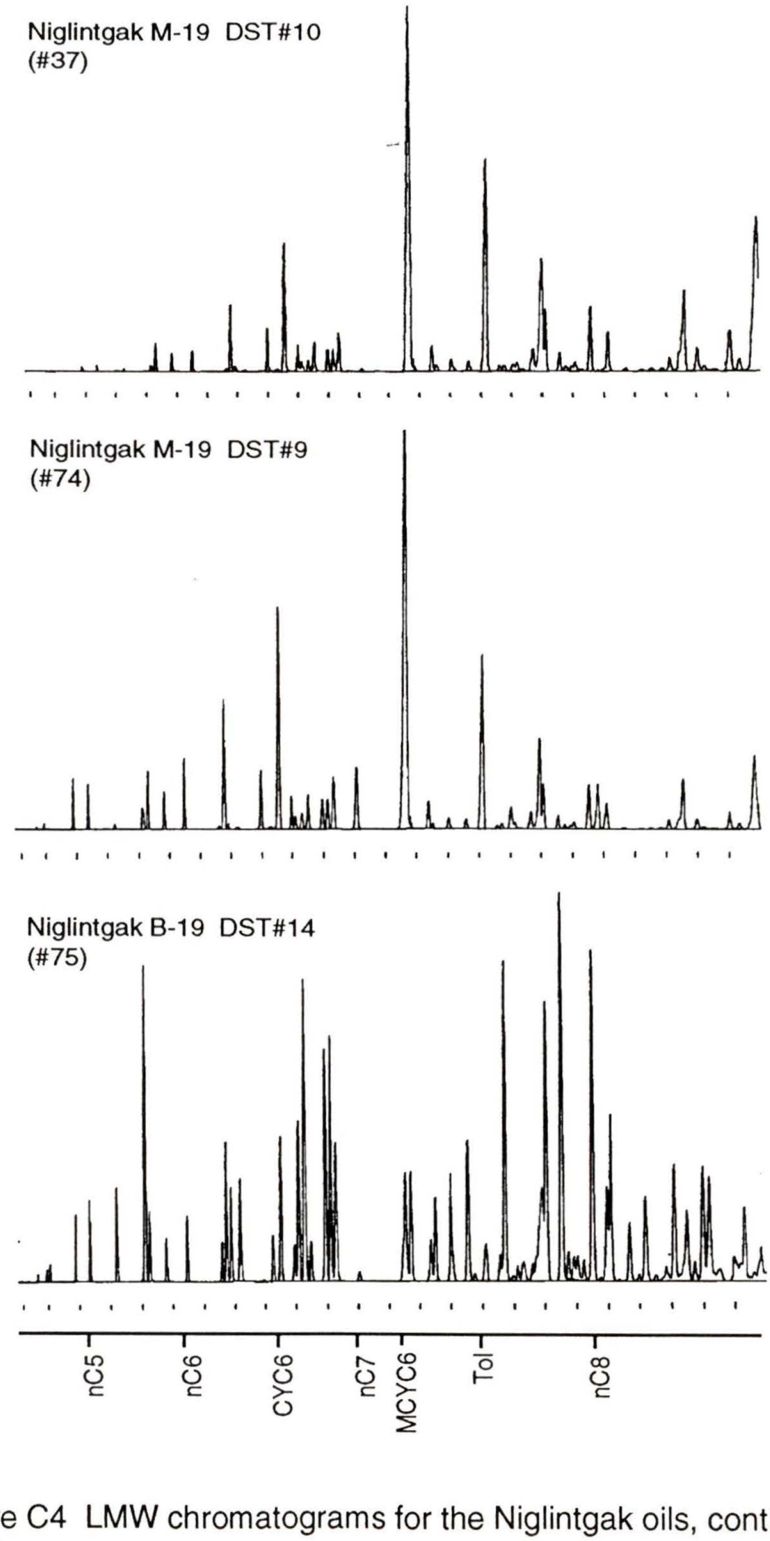
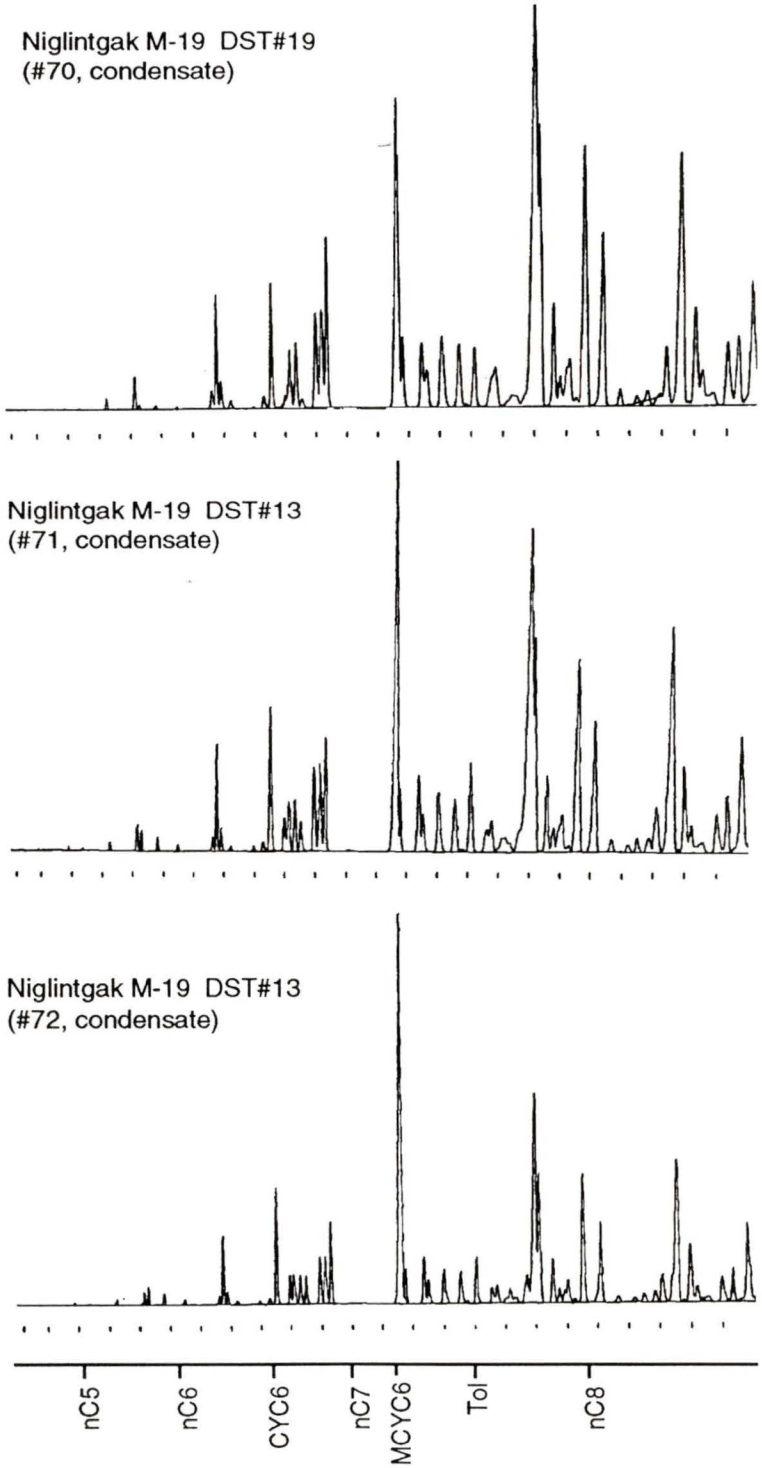


Figure C4 LMW chromatograms for the Niglintgak oils, continued.

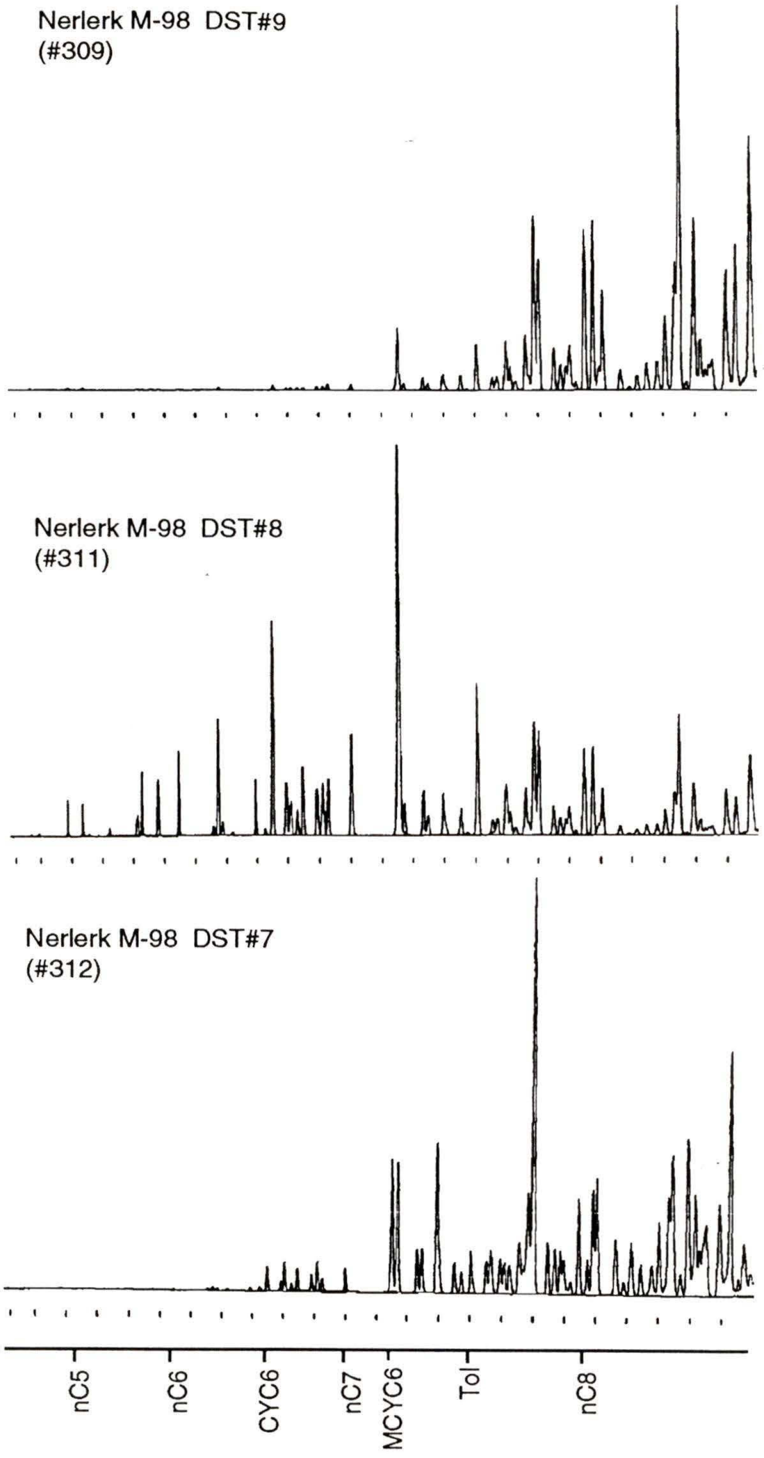


Niglintgak M-19 DST#19
(#70, condensate)

Niglintgak M-19 DST#13
(#71, condensate)

Niglintgak M-19 DST#13
(#72, condensate)

Figure C5 LMW chromatograms for Niglintgak condensates from the Beaufort-Mackenzie Basin, Canadian Arctic.



Nerlerk M-98 DST#9
(#309)

Nerlerk M-98 DST#8
(#311)

Nerlerk M-98 DST#7
(#312)

Figure C6 LMW chromatograms for Nerlerk M-98 oils from the Beaufort-Mackenzie Basin, Canadian Arctic.

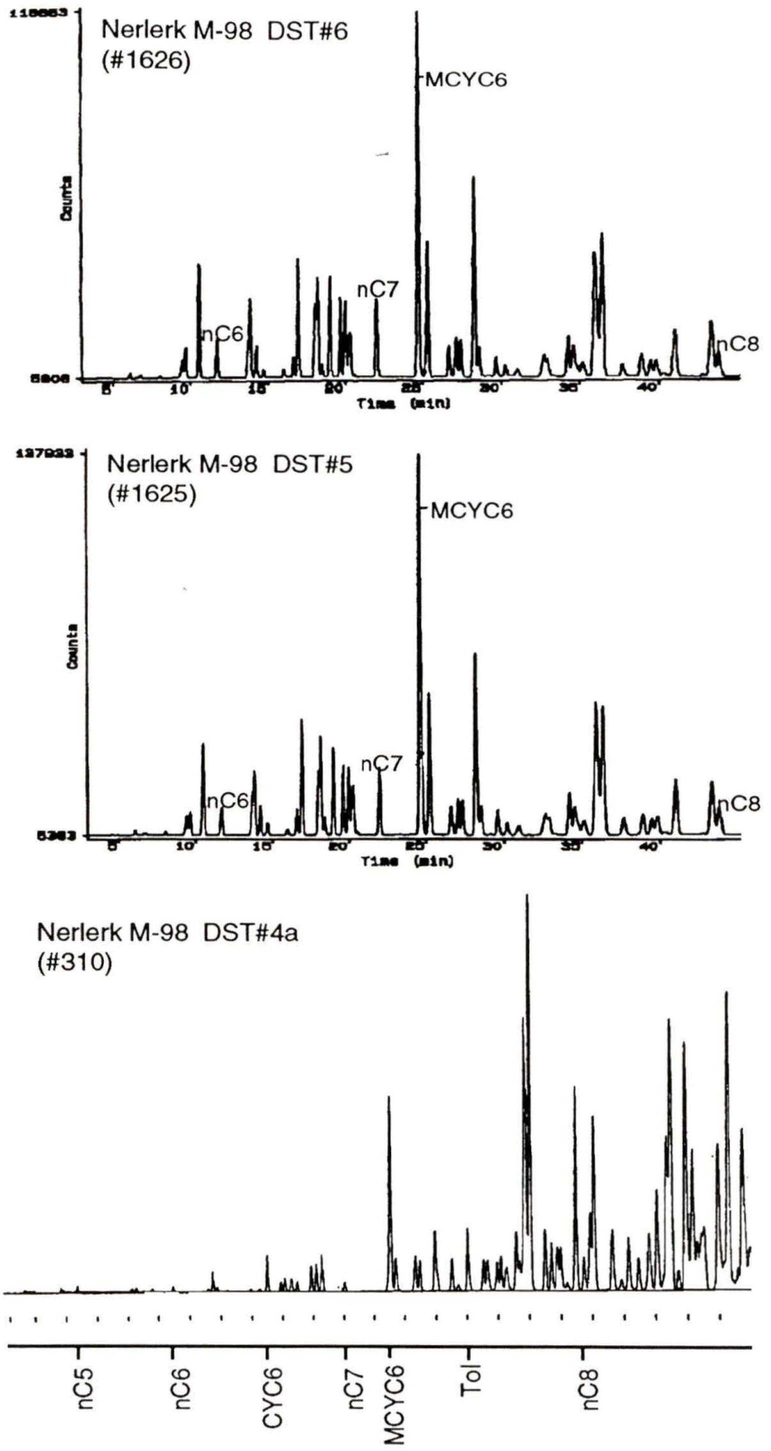
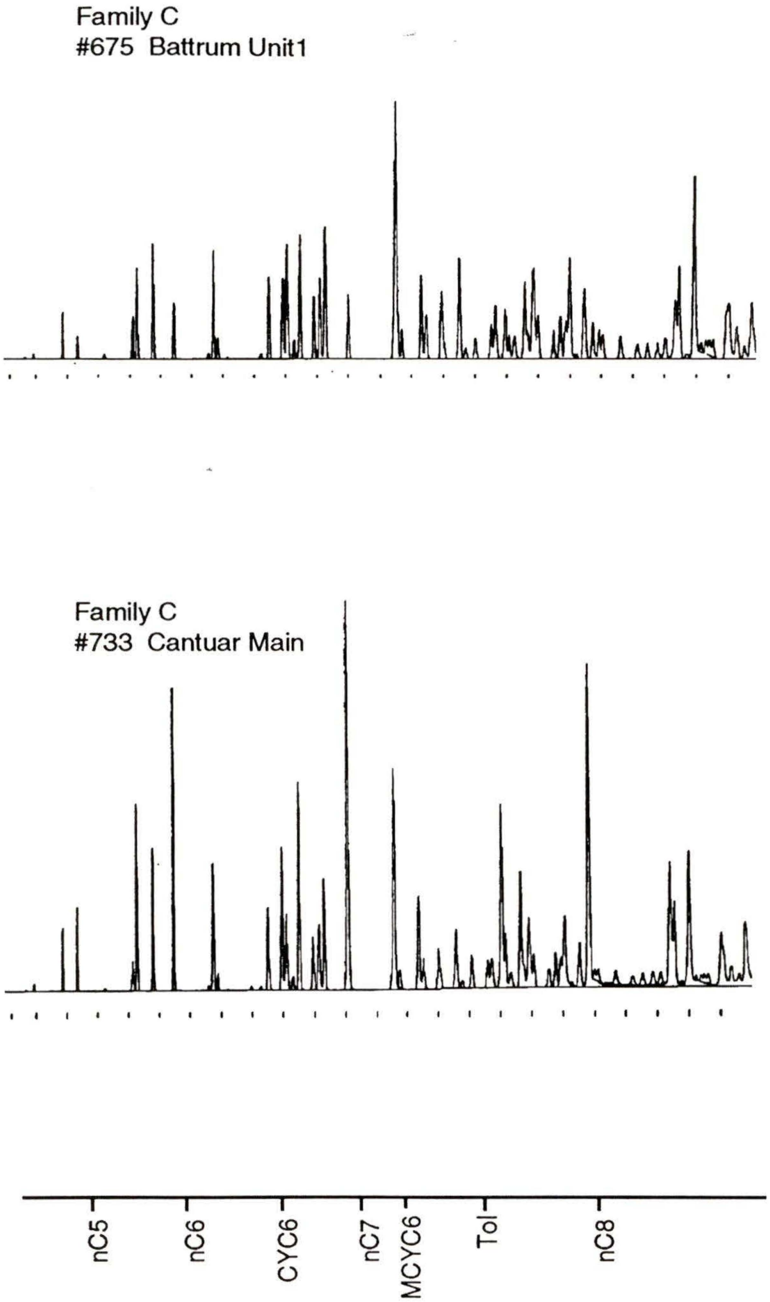


Figure C6 LMW chromatograms for Nerlerk M-98 oils, continued.

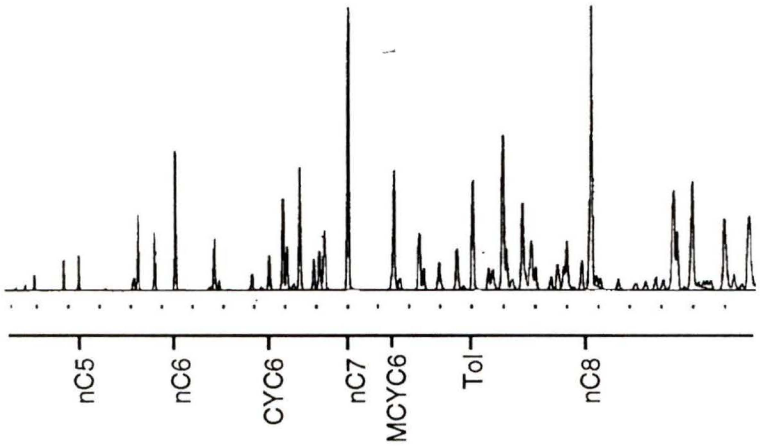


Family C
#675 Battrum Unit1

Family C
#733 Cantuar Main

Figure C7 LMW chromatograms for Family C oils from the Williston Basin, southwest Saskatchewan.

Family C
#677 Butte



Family C
#726 Battle Creek

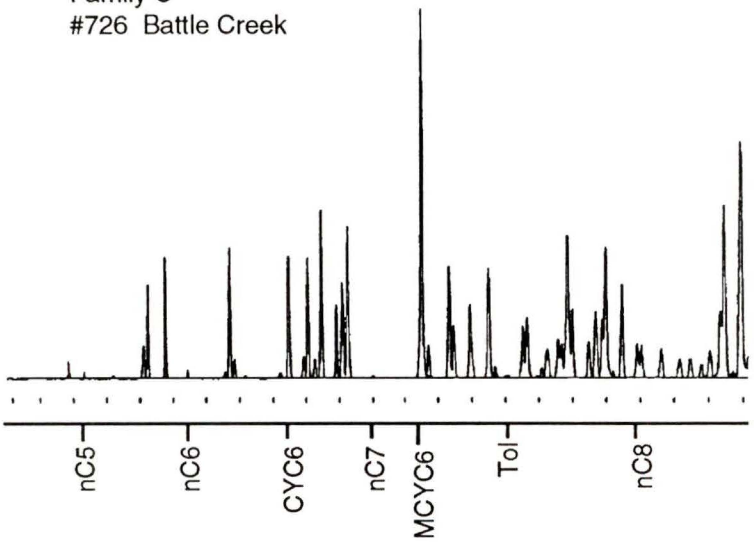


Figure C7 LMW chromatograms for Family C oils, continued.

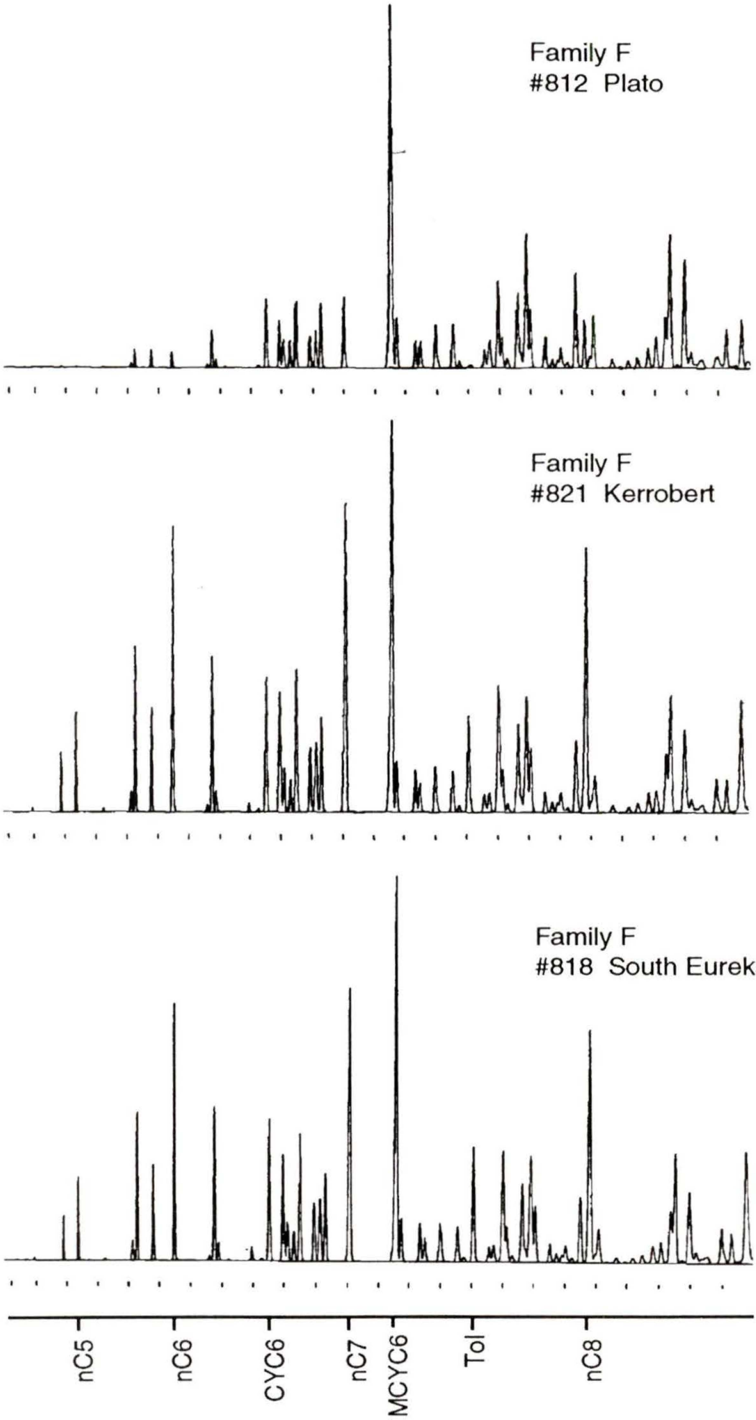


Figure C8 LMW chromatograms for Family F and A oils from the Williston Basin, southwest and southeast Saskatchewan.

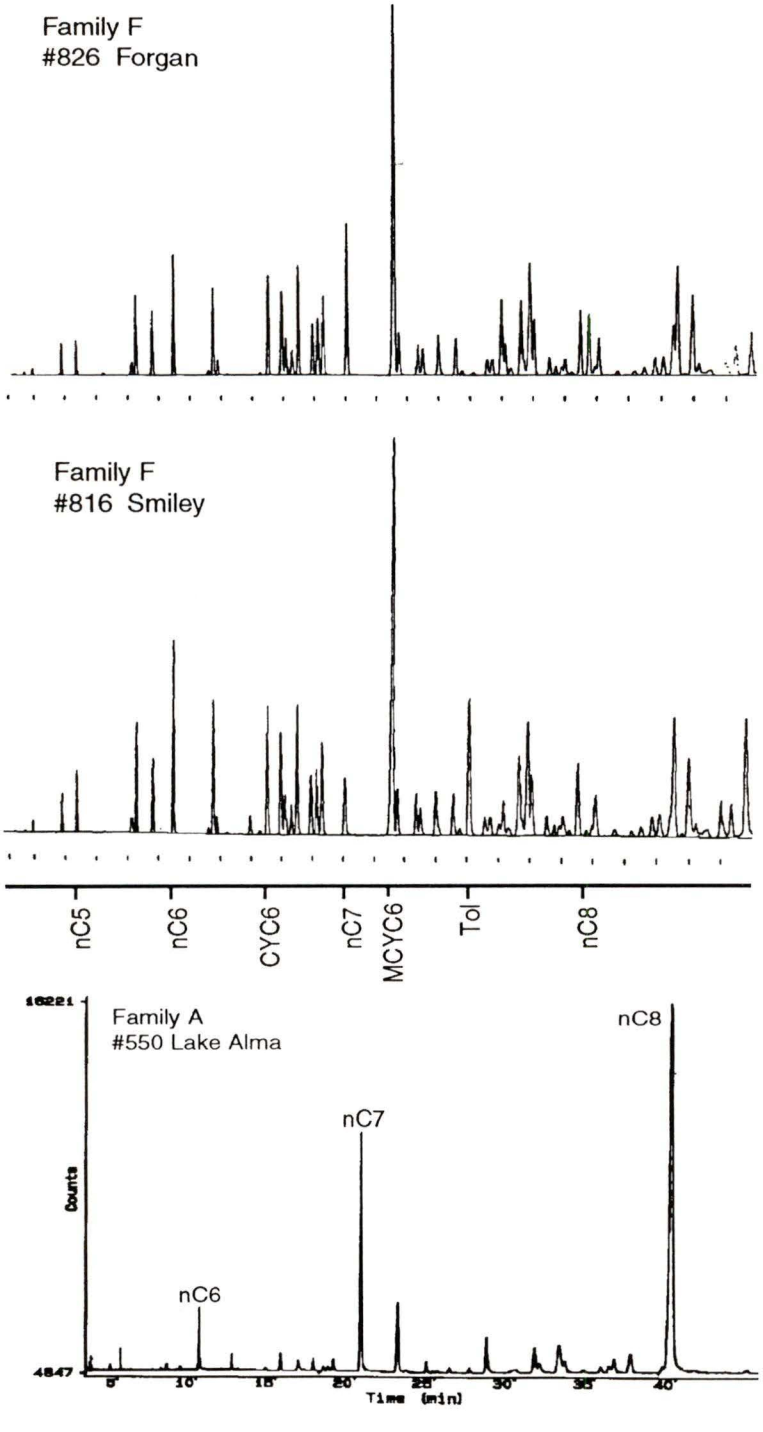
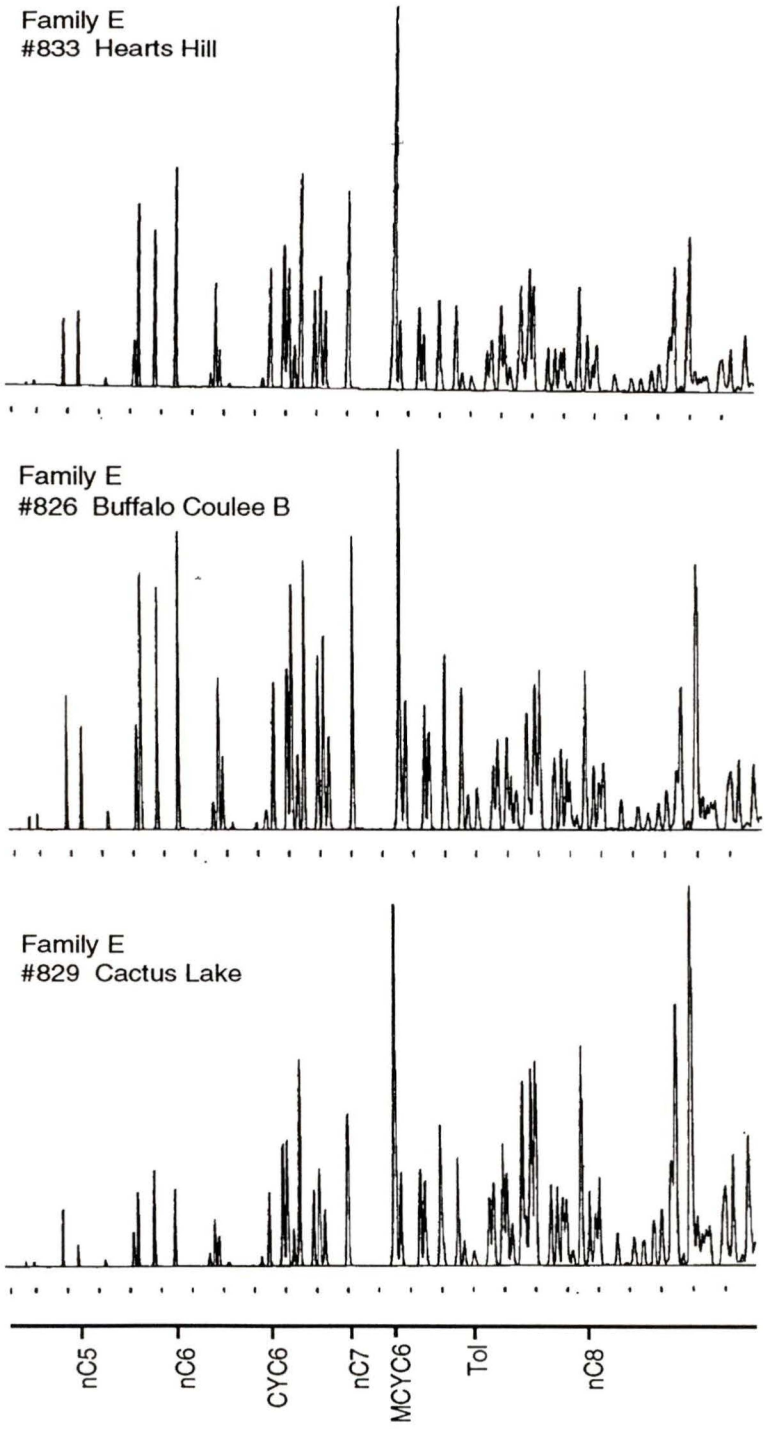


Figure C8 LMW chromatograms for Family F and A oils, continued.



Family E
#833 Hearts Hill

Family E
#826 Buffalo Coulee B

Family E
#829 Cactus Lake

Figure C9 LMW chromatograms for Family E oils from the Williston Basin, southwest Saskatchewan.

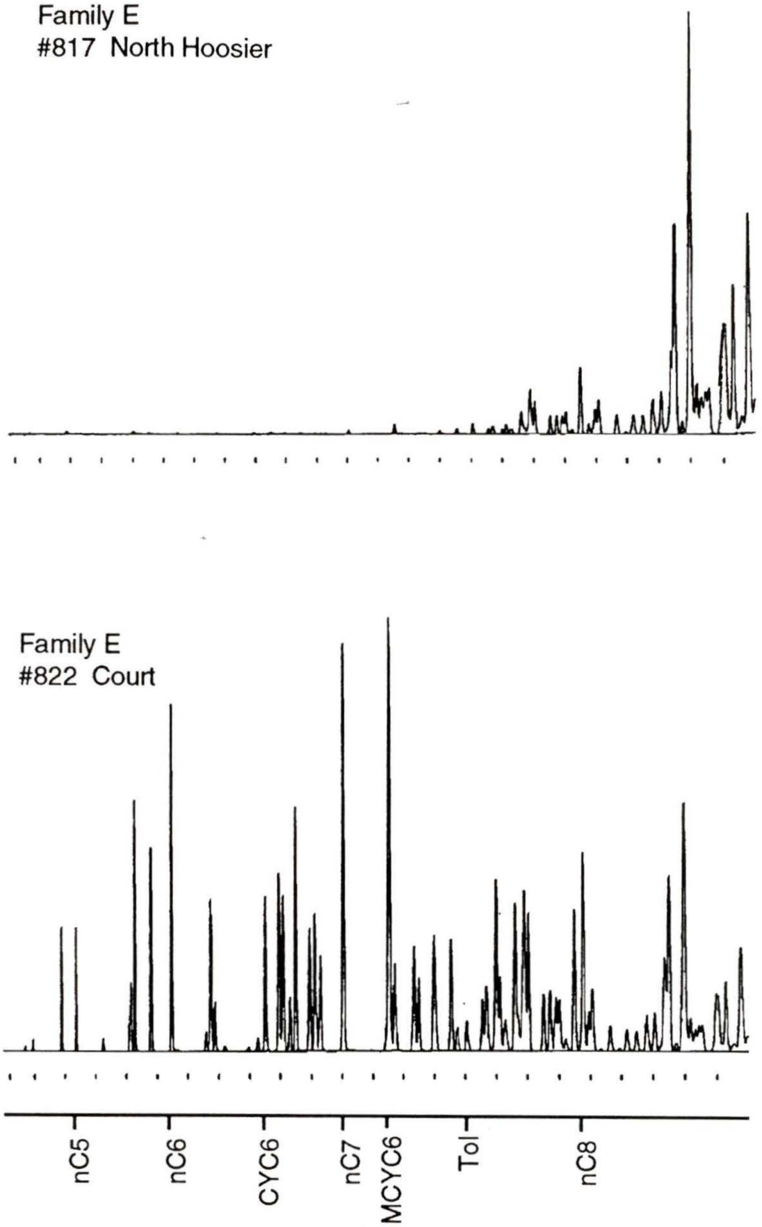


Figure C9 LMW chromatograms for Family E oils, continued.

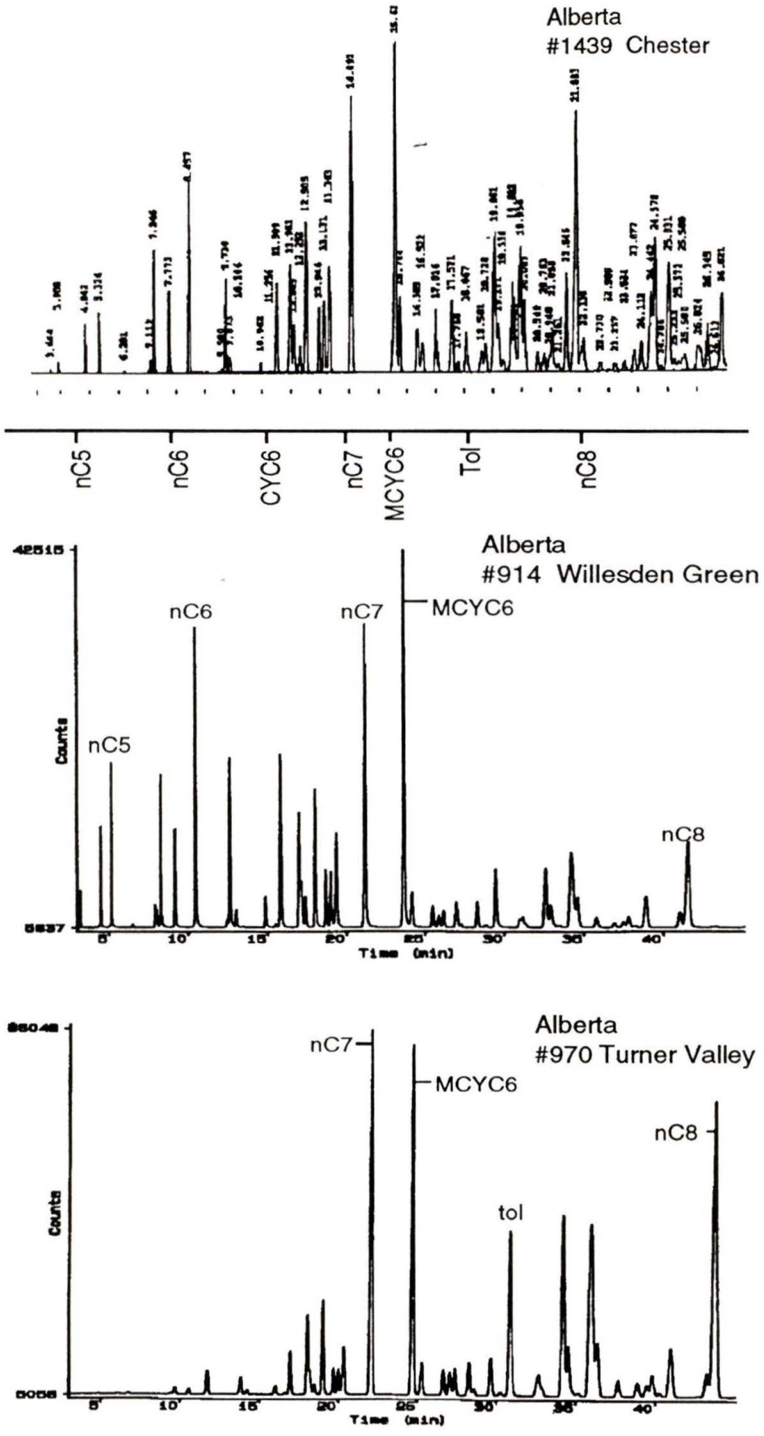


Figure C10 LMW chromatograms for Alberta oils from the Western Canada Sedimentary Basin.

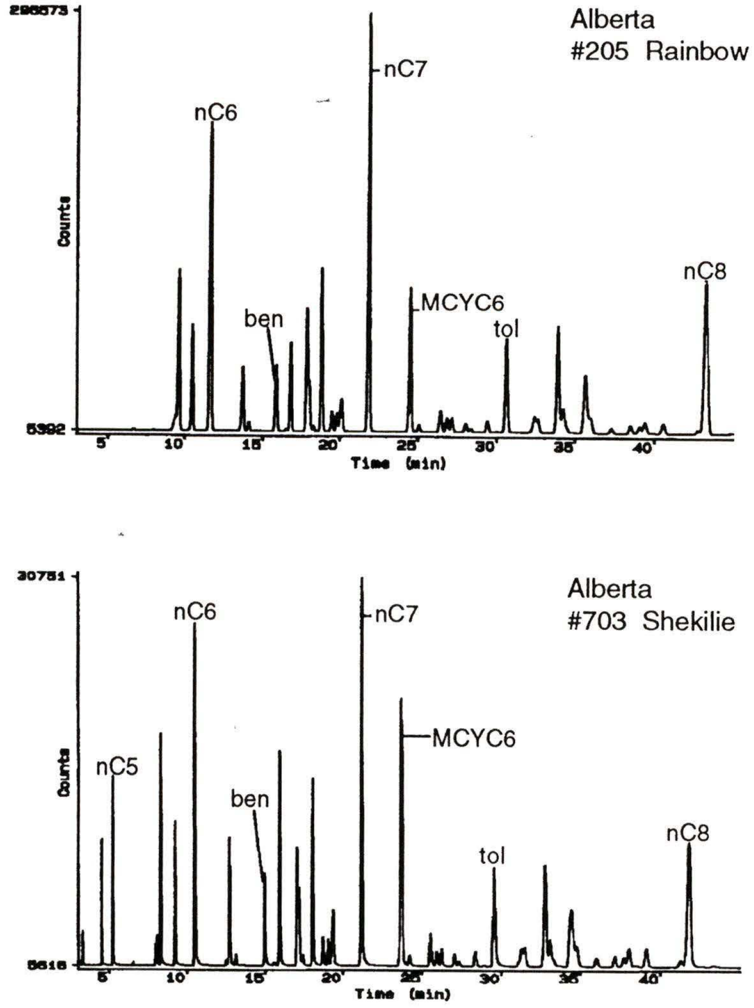


Figure C10 LMW chromatograms for Alberta oils, continued.

APPENDIX D

Table D1 Stable carbon isotopes of gasoline range hydrocarbons in Canadian oils.

Table D1. Stable carbon isotope ratios of gasoline range hydrocarbons in Canadian oils.

Sample	iC5	nC5	22DMC4	23DMC4	2MC5	3MC5	nC6	MCYC5	Ben
Chester	-27.0	-28.7		-27.0	-27.0	-26.0	-28.6	-23.2	-29.5
Alb/TurnVal/970					-22.1	-22.2	-22.1	-21.4	-21.9
Alb/WillGr/914	-21.5	-23.0		-24.2	-25.9	-25.5	-26.9	-22.3	-26.4
Alb/Shekil/703				-21.9	-24.8	-21.8	-25.2	-24.8	-27.2
Alb/Rainbow/205				-21.8	-25.1	-23.5	-27.7	-24.2	-28.2
E/HibC/429/3	-25.1	-23.8		-22.4	-23.9	-23.8	-24.0	-21.0	-23.2
E/HibC/428/2	-25.4	-22.9		-21.6	-23.4	-23.6	-23.8	-20.7	-23.1
E/HibC/431/5	-22.8	-22.1		-22.1	-24.2	-23.9	-24.4	-20.9	-23.4
E/HibK/251/1	-24.2	-22.9		-22.0	-23.5	-22.7	-23.1	-20.7	-22.5
E/HibK/263/8	-24.7	-24.1		-22.8	-24.6	-24.4	-24.9	-21.8	-23.8
E/HibK/266/11	-24.4	-24.0		-22.6	-24.5	-24.1	-24.6	-21.7	-23.5
E/Mara/453/1	-24.0	-23.3	-25.5	-23.2	-23.6	-22.8	-23.2	-21.6	-23.5
E/Mara/454/2	-21.6	-21.5		-22.5	-23.4	-23.3	-23.5	-21.9	-23.4
E/Mara/455/3	-21.1	-20.1	-24.2	-22.0	-23.2	-22.1	-22.0	-21.3	-24.4
E/Hebron/245/1	-22.7	-20.9		-21.0	-23.5	-23.6	-23.4	-20.3	-23.2
E/Hebron/246/5	-22.0	-23.5		-22.5	-24.1	-24.1	-24.4	-21.9	-23.5
E/Hebron/247/6	-24.3	-23.6		-22.8	-24.4	-24.2	-24.5	-21.9	-25.3
E/Hebron/248/10	-21.1	-20.8	-25.8	-21.8	-23.2	-22.2	-22.5	-20.9	-23.0
E/Hebron/249/9	-24.3	-23.9	-25.0	-22.7	-24.7	-24.3	-24.7	-21.7	-24.6
E/Hebron/250/7	-24.5	-23.7		-23.1	-24.7	-24.7	-24.5	-21.7	-25.2
A/Amaul/1263	-21.8			-21.9	-24.0	-24.0	-24.0	-22.5	-24.5
A/Nerlerk/310/4a								-24.9	-21.1
A/Nerlerk/1625/5				-24.8	-26.0	-24.8	-24.9	-22.2	-26.4
A/Nerlerk/1626/6	-24.0	-22.8	-26.4	-24.1	-25.2	-24.9	-24.8	-22.3	-26.6
A/Nerlerk/312/7	-23.4	-23.0	-26.3	-24.1	-25.6	-25.0	-24.8	-22.5	-25.9
A/Nerlerk/311/8	-23.7	-24.0	-26.1	-23.3	-25.3	-25.2	-25.1	-23.1	-25.8
A/Nerlerk/309/9	-23.8	-24.1	-26.1	-23.5	-25.4	-25.2	-25.1	-23.3	-26.1
A/NiglintM/33/22	-21.4		-25.7	-24.8	-26.2	-24.7	-24.1	-24.6	-26.8
A/NiglintM/74/9	-24.2	-24.3	-25.8	-25.0	-25.7	-25.1	-24.9	-24.6	-25.9
A/NiglintM/70/19			-25.1	-24.1	-25.9	-21.6	-20.4	-23.4	-23.7
A/NiglintB/75/14	-23.0		-25.7	-23.6	-25.8	-24.8	-22.1	-22.0	-27.2
A/NiglintM/34/16	-21.6		-26.5	-24.7	-25.7	-23.4		-24.3	-25.0
A/NiglintM/72/13	-20.7		-25.4	-23.9	-24.7	-24.6	-21.4	-23.9	-23.7
A/NiglintM/37/10	-24.1	-24.2	-26.5	-24.9	-25.4	-25.4	-24.8	-24.7	-26.0
A/NiglintM/71/14	-22.7		-26.1	-23.8	-24.6	-24.2	-20.9	-23.2	-24.5
A/NiglintM/69/20			-24.0	-23.6	-24.7	-23.4		-24.9	-24.5
SW/CBattrum/675	-28.1	-27.7	-30.7	-26.7	-29.0	-27.8	-30.1	-26.3	-32.1
SW/CButte/677	-28.4	-29.4	-31.2	-26.9	-29.5	-28.2	-30.8	-26.8	-29.7
SW/CBatCrk/726	-24.7	-25.7	-31.7	-26.1	-28.3	-27.6	-29.4	-26.2	
SW/CCantuar/733	-27.9	-29.0	-31.1	-26.7	-29.4	-28.2	-30.6	-26.9	-31.3
SW/FKerrob/821	-24.7	-26.3	-30.2	-23.5	-27.2	-26.6	-28.4	-23.2	-26.9
SW/FSEurek/818	-24.7	-26.8		-24.1	-27.2	-26.5	-28.2	-23.2	-27.9
SW/FSmiley/816	-25.3	-26.6		-23.6	-26.9	-26.5	-27.8	-23.0	-27.0
SW/FForgan/826	-24.7	-25.8		-23.4	-26.5	-26.1	-27.8	-21.9	
SW/FPlato/812				-23.3	-24.9	-25.1	-26.0	-22.1	
SW/ECourt/822	-25.4	-25.9	-29.7	-26.1	-27.4	-27.1	-28.3	-24.8	-26.2
SW/EHearts/833	-25.5	-25.9	-30.3	-26.1	-27.8	-26.8	-28.7	-24.7	-29.8
SW/ECactus/829	-25.9	-26.1	-30.8	-26.6	-27.3	-26.7	-28.1	-24.1	
SW/EBuffalo/836	-26.0	-26.4	-30.5	-26.3	-27.9	-27.1	-28.7	-25.0	-28.5
S/LkAlma/550	-30.5	-26.3		-27.8	-29.7	-28.8	-26.4	-27.2	-30.8

Table D1 continued

Sample	CYC6	2MC6g	3MC6	1c3DMg	nC7	MCYC6	25DMC6g	223TMC5
Chester	-26.1	-27.2	-26.8	-22.4	-29.1	-23.9	-25.9	-24.0
Alb/TurnVal/970	-23.9	-25.6	-25.2	-23.2	-26.3	-24.1	-26.0	-25.2
Alb/WillGr/914	-24.4	-26.8	-25.9	-22.5	-27.2	-23.6	-25.6	-23.5
Alb/Shekil/703	-30.2	-25.5	-24.2	-23.5	-27.5	-28.5	-24.5	-25.7
Alb/Rainbow/205	-29.1	-26.2	-24.8	-24.8	-29.3	-28.0	-25.2	-27.1
E/HibC/429/3	-22.6	-24.4	-24.0	-22.2	-24.7	-22.2	-23.1	-23.6
E/HibC/428/2	-22.3	-23.7	-25.0	-21.7	-24.3	-21.7	-22.6	-23.4
E/HibC/431/5	-22.6	-24.6	-24.4	-22.5	-24.9	-22.2	-23.0	-23.5
E/HibK/251/1	-22.1	-23.6	-23.1	-21.6	-23.6	-21.3	-22.4	-22.6
E/HibK/263/8	-23.1	-24.5	-24.3	-21.8	-25.4	-22.7	-23.6	-23.9
E/HibK/266/11	-22.7	-25.1	-24.9	-22.7	-25.2	-22.4	-23.3	-23.8
E/Mara/453/1	-22.4	-23.7	-23.8	-22.7	-24.2	-22.5	-23.1	-23.2
E/Mara/454/2	-22.8	-24.0	-23.9	-23.1	-24.5	-22.2	-23.3	-24.0
E/Mara/455/3	-21.6	-23.7	-23.6	-22.5	-23.8	-21.9	-21.9	-23.1
E/Hebron/245/1	-22.6	-24.0	-24.2	-22.1	-24.3	-22.2	-23.3	-23.5
E/Hebron/246/5	-23.0	-24.5	-24.7	-23.7	-25.2	-22.7	-23.6	-24.5
E/Hebron/247/6	-23.4	-24.5	-24.4	-22.8	-25.1	-22.7	-23.5	-23.9
E/Hebron/248/10	-22.3	-23.2	-24.0	-22.1	-24.7	-21.9	-22.7	-23.6
E/Hebron/249/9	-23.1	-24.1	-24.1	-22.3	-24.3	-21.7	-22.5	-23.3
E/Hebron/250/7	-23.3	-24.6	-24.3	-22.9	-24.7	-22.4	-23.2	-23.3
A/Amaul/1263	-23.0	-25.2	-25.2	-23.8	-25.3	-23.0	-24.7	-24.3
A/Nerlerk/310/4a	-21.9	-25.5	-22.4	-23.8	-23.0	-21.9	-23.1	-22.9
A/Nerlerk/1625/5	-23.5	-25.1	-25.6	-24.1	-25.7	-22.1	-25.2	-24.6
A/Nerlerk/1626/6	-23.0	-24.9	-24.6	-23.7	-25.0	-21.8	-24.6	-24.2
A/Nerlerk/312/7	-21.9	-24.8	-24.5	-23.9	-25.3	-21.1	-24.8	-24.1
A/Nerlerk/311/8	-23.8	-25.4	-25.9	-24.5	-25.8	-23.5	-25.1	-24.7
A/Nerlerk/309/9	-23.7	-25.4	-25.9	-24.5	-25.9	-23.5	-24.9	-24.7
A/NiglintM/33/22	-25.0	-24.2	-27.1	-24.3	-25.3	-23.7	-25.7	-24.8
A/NiglintM/74/9	-24.5	-25.6	-25.8	-24.9	-25.8	-23.9	-25.0	-24.8
A/NiglintM/70/19	-22.3	-23.7	-27.6	-24.4	-25.3	-21.5	-24.6	-24.4
A/NiglintB/75/14	-20.0	-24.1	-28.4	-24.0	-26.0		-24.6	-24.6
A/NiglintM/34/16	-23.0	-23.9	-22.4	-25.1		-22.4	-25.2	-24.8
A/NiglintM/72/13	-23.5	-24.6	-26.1	-24.6	-24.8	-23.0	-25.2	-24.7
A/NiglintM/37/10	-24.7	-25.6	-26.4	-24.9	-25.3	-24.1	-25.6	-25.0
A/NiglintM/71/14	-23.3	-24.5	-26.2	-24.6	-24.1	-22.8	-24.8	-24.6
A/NiglintM/69/20	-20.4	-24.0	-26.5	-25.5	-22.7	-24.5	-25.5	-24.8
SW/CBattrum/675	-30.7	-27.9	-28.2	-26.4	-30.6	-27.9	-28.1	-27.3
SW/CButte/677	-30.8	-28.9	-28.2	-26.2	-31.0	-28.8	-27.9	-27.3
SW/CBatCrk/726	-30.8	-27.5	-28.1	-26.6	-31.4	-28.8	-28.2	-27.9
SW/CCantuar/733	-30.8	-28.9	-28.3	-26.5	-31.0	-28.5	-27.9	-28.6
SW/FKerrob/821	-25.8	-27.4	-27.6	-23.8	-28.9	-23.7	-27.1	-24.6
SW/FSEurek/818	-25.7	-27.3	-27.3	-23.8	-28.8	-23.8	-27.1	-24.4
SW/FSmiley/816	-25.6	-27.1	-27.3	-23.6	-28.3	-23.7	-26.6	-24.3
SW/FForgan/826	-25.0	-26.5	-27.0	-23.6	-28.5	-23.3	-26.8	-24.5
SW/FPlato/812	-25.0	-26.3	-26.7	-23.0	-27.1	-23.0	-26.5	-24.0
SW/ECourt/822	-26.1	-27.8	-27.9	-25.7	-29.2	-24.5	-27.9	-26.8
SW/EHearts/833	-26.0	-27.8	-28.2	-25.9	-29.4	-24.8	-28.0	-26.7
SW/ECactus/829	-25.6	-27.2	-27.7	-25.4	-28.8	-24.2	-28.0	-26.6
SW/EBuffalo/836	-26.2	-27.5	-28.3	-26.0	-29.3	-24.3	-28.3	-26.9
S/LkAlma/550	-28.7	-29.9	-29.7	-27.1	-26.4	-28.2	-27.1	-27.3

Table D1 continued

Sample	Tol	1c4DMCY	nC8	23DMC4g	MCYC5all	MCYC6g	3MC6all
Chester	-27.5	-23.9	-27.5				
Alb/TurnVal/970	-25.6	-25.3	-26.5				
Alb/WillGr/914	-25.9	-23.5	-26.3				
Alb/Shekil/703	-29.5	-26.5	-27.7				
Alb/Rainbow/205	-29.3	-26.6	-28.9				
E/HibC/429/3	-23.6	-22.3	-24.3				
E/HibC/428/2	-23.2	-21.9	-23.8				
E/HibC/431/5	-23.5	-22.1	-24.2				-24.5
E/HibK/251/1	-22.4	-21.4	-23.1				-23.1
E/HibK/263/8	-24.0	-23.1	-24.9				
E/HibK/266/11	-23.7	-22.7	-24.6				
E/Mara/453/1	-22.7	-22.7	-24.1				
E/Mara/454/2	-22.9	-22.9	-24.1				-24.0
E/Mara/455/3	-22.6	-22.6	-24.6	-22.5			-23.2
E/Hebron/245/1	-23.9	-21.5	-23.6				
E/Hebron/246/5	-23.7	-22.7	-24.2				-25.2
E/Hebron/247/6	-24.1	-22.7	-24.3				
E/Hebron/248/10	-24.0	-22.2	-24.4				
E/Hebron/249/9	-23.3	-21.8	-23.3				
E/Hebron/250/7	-23.6	-22.4	-24.0				
A/Amaul/1263	-25.2	-23.6	-24.4				
A/Nerlerk/310/4a	-24.8	-22.2	-23.9				
A/Nerlerk/1625/5	-26.1	-22.6	-21.8	-25.6	-24.5		
A/Nerlerk/1626/6	-25.9	-22.3	-21.5	-24.7	-24.3		
A/Nerlerk/312/7	-26.6	-22.7	-21.0	-24.8	-24.6	-23.4	
A/Nerlerk/311/8	-25.6	-24.0	-24.2	-24.8			
A/Nerlerk/309/9	-25.8	-24.0	-24.2	-24.9			
A/NiglintM/33/22	-26.6	-22.3	-22.0		-25.4	-25.0	
A/NiglintM/74/9	-25.4	-23.9	-24.7				
A/NiglintM/70/19	-23.5	-24.2			-24.4	-23.1	
A/NiglintB/75/14	-26.0	-23.1			-23.9	-22.6	
A/NiglintM/34/16	-24.5	-24.9					
A/NiglintM/72/13	-24.1	-24.4		-24.1			
A/NiglintM/37/10	-25.6	-24.5					
A/NiglintM/71/14	-24.5	-24.5		-24.0			
A/NiglintM/69/20	-26.7	-21.7	-24.0			-24.5	
SW/CBattrum/675	-31.8	-28.3	-27.1	-28.4			
SW/CButte/677	-29.9	-28.4	-29.2	-29.0			
SW/CBatCrk/726		-29.1		-27.8			
SW/CCantuar/733	-30.2	-28.0	-29.2	-28.5			
SW/FKerrob/821	-27.1	-24.2	-27.5	-26.9			
SW/FSEurek/818	-27.1	-24.2	-27.4				
SW/FSmiley/816	-27.0	-24.4	-28.1		-24.8		
SW/FForgan/826		-24.0	-26.3				
SW/FPlato/812		-23.6	-25.4				
SW/ECourt/822	-27.2	-26.6	-26.8		-26.8		
SW/EHearts/833	-29.3	-26.7	-27.1		-26.8		
SW/ECactus/829	-28.7	-26.6	-26.3		-27.0		
SW/EBuffalo/836	-27.9	-26.8	-26.3	-27.5	-27.5		
S/LkAlma/550	-30.6	-27.8	-26.1				

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Dr. Maurice Saval Scholarship	1988-1989
Provincial Electoral District Scholarship	1987

Publications:

Murphy, D. E. and Abrajano, T. 1994. Carbon isotope compositions of fatty acids in mussels from Newfoundland estuaries. Estuarine, Coastal, and Shelf Science vol.39.

Abrajano, T., Murphy, D., Fang J., Comet P., and Brooks, J. 1994. ^{13}C/^{12}C ratios in individual fatty acids of marine mytilids with and without bacterial symbionts. Organic Geochemistry, vol.21, no. 6/7.

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Title of Thesis/Dissertation: GC-C-IRMS: A New Technique to Characterize and Correlate Oils and Source Rocks.

Author [redacted]
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(Name in Block Letters)

Nov. 1, 1994
(Date)