

SOURCE ROCK STUDIES OF NATURAL SEEP OILS NEAR
PARSONS POND ON THE WEST COAST OF
NEWFOUNDLAND

CENTRE FOR NEWFOUNDLAND STUDIES

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FAYE J. WEAVER



SOURCE ROCK STUDIES OF NATURAL SEEP OILS
NEAR PARSONS POND
ON THE WEST COAST OF NEWFOUNDLAND

BY

© FAYE J. WEAVER B.Sc. (Hons.)

A thesis submitted to the School of Graduate
Studies in partial fulfillment of the
requirements of the degree of
Master of Science

Department of Earth Sciences
Memorial University of Newfoundland

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Abstract

The seep oils occurring on the west coast of Newfoundland in the Parsons Pond region have presented numerous questions to the scientific community since the oils were first discovered in 1812. The area has been studied in detail for geological and depositional features. The purpose of this thesis was to ascertain the source, maturation and potential for recoverable hydrocarbons using geochemistry.

The Parsons Pond Region represents the destroyed margin of the eastern coast of ancient North America in Cambro-Ordovician time, now superimposed in northeast-southwest trending thrust sheets. Sediments include carbonate breccias/conglomerates, limestones and clastics with interbedded black shales. Organic content in these shales is moderate (TOC from 0.2 to 4.3%). The presence of trisnorhopane, gammacerane, abundant hopanes and rearranged steranes suggest admixed Type I/II kerogen, derived from prokaryotic organisms preserved under stratified marine anoxic conditions. Abundant C_{29} hopanes, odd dominance from nC_{17} to nC_{21} n-alkanes and the occurrence of C_{28} steranes suggest Ordovician type organic matter. The occurrence of pristane and phytane indicate the Cow Head Group shales are different in character from global G. Prisca facies common in Ordovician deposits.

The potential for hydrocarbon generation is good (70 l/t), although many of the samples in outcrop are immature and reservoirs may be limited. Samples are above to within the upper limits of the oil generation window and increase in

maturity across the Humber Arm Allochthon from the coast toward the Long Range Mountains. The source of the oils is within the Broom Point Member of the Green Point Formation.

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Chapter 1

Introduction

1.1. The Problem

The existence of oil in western Newfoundland was first reported in 1812 as a hydrocarbon seep near Parsons Pond. Exploration began in the 1860's when the first well was drilled, and has been carried out intermittently ever since.

Geochemical studies of the area are limited to recent work done by British Petroleum (BP) in 1983 and the Newfoundland Department of Mines and Energy. A number of potential sources for the oil have been proposed by previous researchers and include shales from the Shallow Bay and Green Point formations within the Cow Head Group. Other potential sources include the Table Head Group, Rocky Harbour melange and syndepositional sediments of the more southern Curling Group.

This thesis undertook an analysis and comparison of these potential sources for the seep oils, using detailed organic geochemistry.

1.2. Objectives

This thesis will assess the geochemical data accumulated, in conjunction with the knowledge of the depositional environments, burial history and structure of the Humber Arm Allochthon to elucidate the following objectives:

- Determine the source rock in terms of:
 - a specific stratigraphic member
 - a specific rock unit equivalent to the Cow Head Group numbered intervals (James and Stevens, 1986)
 - a specific chronostratigraphic interval.
- Evaluate trends in maturation (as noted by previous authors) and compare these with variations in stable isotope, aromatic and specific ion distributions.
- Assess variations in the preservation of organic matter content in relation to different lithologies (carbonate vs clastic), and different environments (marine vs nonmarine, anoxic vs oxic).
- Evaluate detailed organic geochemical methods that have been contrasted and compared to ascertain their potential as source rock indicators for natural seeps, outcrop samples and Lower Paleozoic strata.
- Evaluate the potential for hydrocarbon generation of the Cow Head Group shales based on maturation, organic matter type, quality and genetic potential.

Chemical methods include fraction analysis by column chromatography, total organic carbon (TOC), bitumen extraction, nitrogen and carbon stable isotope composition on crude oils, extracts and their fractions, saturate and aromatic chemistry using gas chromatography - mass spectrometry (GC-MS), biomarker analysis using select ion monitoring (SIM) and Rock Eval pyrolysis. Previous comparative studies stress the importance of a combination of

geochemical techniques (Peters et al., 1985). Interlaboratory comparisons of a single organic geochemical method has shown that the materials are complex and are easily contaminated. Procedures for analysis vary between laboratories eliminating successful interlaboratory comparisons (Dembicki, 1984). Reproducibility is based on relative values, not absolute values. A combination of different methods, and replicate sample analysis will reduce error, giving more reliable results that are internally consistent.

1.3. Location

A range of samples encompassing local chronostratigraphic and lithostratigraphic units was necessary for a detailed study. Samples were collected from within the Humber Arm Allochthon, and autochthonous platform from rock sequences that represent continental slope deposition in Cambro-Ordovician time. The study locality extends from Bonne Bay in the south to Table Point in the north (Figure 1-1, inset).

Three basic criteria were used in sample collection. The first incorporated a range of lithologies and depositional sequences, varying from near the original shoreline to the finer pelagic sediments of the deep continental rise. The second criteria related the tectonic/structural setting, to maturation and oil generation relative to the remobilization of the Long Range Igneous Inlier and the tectonic forces causing the original emplacement of the Allochthon as thrust slices, and the third related to location in reference to the seep oils. These slices are exposed in sediments from east to west, across the coastal platform. Samples chosen for the study were black shales or dark grey limestones, with a high percentage of organic

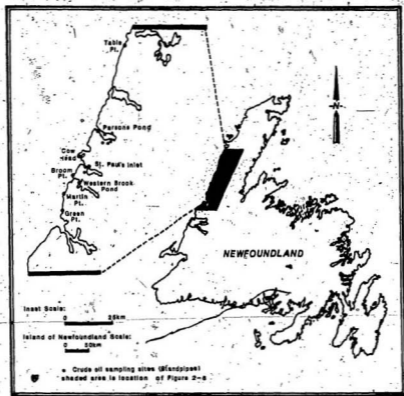


Figure 1-1: Location map of the study area with samples localities indicated.

detrital material. Specific sample localities include Lobster Cove, Green Point (type locality), Martin Point (south), Broom Point, Western Brook Pond (south), St. Paul's Inlet, Parsons Pond and Table Point. Detailed location and stratigraphic logs are described in section 2.4 (General Geology).

1.4. Previous Work

1.4.1. Source Rock Studies

The fact that crude oil is derived from nonreservoir rocks has been well established (Tissot and Welte, 1978). Sediment and rocks that have, can, or might generate oil are called source rocks (Hunt, 1979). The primary characteristic necessary for this classification is the amount of available organic matter in source rocks in the form of kerogen (insoluble organic matter; Tver and Berry, 1980). This, in turn, can be a useful tool in the exploration and reservoir estimation of future and current oil reserves.

Geochemical correlations between expelled oil and source beds involve a contrast and comparison of their specific chemical compositions, based on the fact that the hydrocarbon structure of oil, reflects the composition of organic matter from source rocks (Baker, 1962; Maximov et al., 1973; Connan et al., 1986). Successful source rock studies have become more common in recent years with the use of a variety of geochemical, geophysical and geological parameters which rely on the fact that every source rock has generated a specific type of oil (Maximov et al., 1973).

Source rock studies have been assessed using conventional geochemical methods. These include the determination of organic carbon and hydrocarbon contents and relative ratios of the various fractions (Baker, 1962). Petroleum can be divided into three main compounds (Tissot and Welte, 1978; Neumann et al., 1981). These are defined as:

- Saturated hydrocarbons: comprising alkanes (paraffins) and cycloalkanes (naphthenes).
- Aromatic hydrocarbons: comprising pure aromatics and complex hydrocarbons (naphthenoaromatics).
- Non-hydrocarbons made of high molecular weight colloid-dispersed particles.
 - Resins which contain for the most part basic oxygen, sulphur and nitrogen compounds, are soluble in n-pentane and are very polar.
 - Asphaltenes which are insoluble in n-pentane and contain very large high molecular weight compounds.

Recent studies have shown that bulk chemical compositions between bitumen in a source rock and the reservoir petroleum product, may be altered during migration (Pelet et al., 1986). Ratios of chemical fractions may be altered when less asphalt and aromatics are retained, relative to saturated hydrocarbons, which tend to migrate more readily (Deroo, 1976).

Recent studies have stressed the importance of knowing the composition of the original organic material (Ji-Yang et al., 1982; Longman and Palmer, 1987). Distinctive chemical patterns from unique biological forms strongly influence the character of specific organic materials (Reed et al.; 1986; Hoffmann et al., 1987). Gas chromatography (GC), and gas chromatography - mass spectrometry (GC-MS) give the characterization of both distributions of specific compounds and individual geochemical biomarkers (Tissot and Welte, 1978). GC fingerprint traces of saturates (C_{11+}) and aromatics can be used to recognize similar materials (Deroo, 1976; Dembicki et al., 1983) and to delineate the maturation of a

7

source shale (Radke et al., 1982). Detailed comparisons of the relative abundance of specific isomers such as pristane and phytane and specific ions for steranes, terpanes and hopanes give a good indication of source comparisons and maturation (McKirdy et al., 1983; Connan et al., 1986; Peters et al., 1985; Longman and Palmer, 1987; Zumbege, 1987).

Any petroleum source study should apply a multivariate approach to include more than one aspect of geochemistry (Peters et al., 1985) to define more clearly a specific source. Most recent studies combine bulk chemistry, biomarkers, GC distributions and stable carbon isotopes (Reed and Kaplan, 1977; McKirdy et al., 1983) with a limited reference to nitrogen isotopes (Reed and Kaplan, 1977; Stahl, 1977; Anderson et al., 1983). The use of carbon isotopes have become common in the evaluation of source rocks, depositional environments and organic matter type (Fuex, 1977; Grizzle et al., 1979; Sofer, 1984; Galimov and Frik, 1986). Correlations using values of source rock kerogen and extracts, compared to oils is most common (Stahl et al., 1976; Fuex, 1977). Isotope curves of $^{13}\text{C}/^{12}\text{C}$ ratios from one fraction to another, plotted relative to increasing polarity can indicate similarities in oils and source rocks, where their patterns correspond (Stahl, 1978; Galimov and Frik, 1986).

Rock Eval pyrolysis has become widely accepted in its use as an indicator of maturation, organic matter type and hydrocarbon potential. The type of organic matter limits the potential of a source rock and can help delineate the original environment (Snowden, 1984). The separation of kerogen into various types is common and necessary, for most geochemical studies (Hunt, 1967; Williams, 1974;

Waples, 1983; Tissot and Welte, 1984). The types (I, II, III) are separated on the basis of hydrogen and oxygen ratios relative to the total amount of preserved carbon. Type I organic matter is generally lipid rich with a high content of aliphatic chains and is generally lacustrine or reworked oil rich shales. Type II organic matter is most common in petroleum source rocks and is generally marine, deposited in a reducing environment. Type III organic matter originates from terrestrial higher plant waxes and vegetable fats and is gas prone, not favorable for oil generation (Tissot and Welte, 1978). It must be stressed here that Type III organic matter will not occur in Ordovician organic material as it predates the development of land plants.

Chapter-2

General Geology

2.1. Structure and Geological History

Natural oil seeps occur along the western margin of the province of Newfoundland and are found within the geological region known as the Humber Arm Allochthon (Williams, 1975; Figure 2-1). The region contains Cambro-Ordovician sediments of the Cow Head Group and is structurally underlain by syndepositional sediments of the Table Head Group (Stevens, 1970). This study is based on samples collected from within the Cow Head and Table Head groups. The two groups underly an area of more than 1200 square kilometers, which has an estimated total volume of more than 4800 km^3 (Williams, 1974), and forms the coastal lowlands of west-central Newfoundland. Both the Cow Head and Table Head groups occur within the Humber Zone (Williams, 1978), which represent the formation, evolution and destruction of the eastern margin of the Precambrian to early Paleozoic, North American continent in a manner similar to that of the modern Atlantic margin (Figure 2-2).

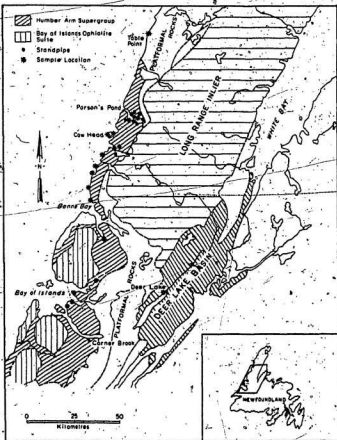


Figure 2-1: Regional Geology of Western Newfoundland,
(after Williams et al., 1985).

2.1.1. The Humber Zone

The Humber zone is a compilation of three sequential rock groups (Schenk, 1978): basement, autochthon and allochthonous cover. The basement rocks are Grenvillian in age (1130-840 Ma) and are, for the most part, metamorphic and igneous, and occur adjacent to the study area as the Long-Range Inlier. The autochthonous cover represents a miogeoclinal deposit on top of the basement, and is comprised of a basal conglomerate/sandstone overlain by igneous units, a middle carbonate bank with archaeocyathid reefs, shales, limestones and dolomites of Cambro-Ordovician age (Table Head Group) and topped by flysch sediments derived from the east (Mainland Sandstone). The allochthon (or transported rock) is composed of basal conglomerate and interbedded shale sequences (Cow Head Group), a middle unit of clastic flysch (Lower Head group) and an upper ophiolitic cap thrust from east to west on top of the preceding units.

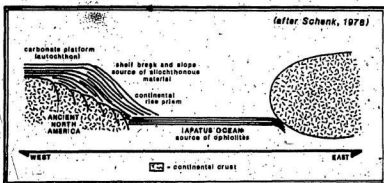


Figure 2-2: Schematic cross section of the ancient margin of the Cambro-Ordovician continental shelf.

2.1.2. Structural Evolution

The Humber Zone evolved from initial rifting of the basement with related volcanic and intrusive sequences, followed by thick accumulations of clastic sequences during the late Precambrian (Williams, 1978). A thinner, carbonate sequence formed on the continental shelf between Early Cambrian and Early Ordovician, thickened eastwards, off the shelf into a rise prism, and is preserved in vertical section, as a transition from immature clastics to limestone and then dolomites (Figure 2-2). Coarse limestone breccias derived from the west and interbedded with turbidites and shales were deposited on the shelf break and on the slope. These are now represented in the allochthonous sequence, structurally transported above the carbonate platform and capped by up to 10 km of ophiolitic suites, representing overthrust oceanic crust and mantle (Stevens, 1970). The formation and evolution represents a cycle of oceanic growth, shelf sedimentation and eventual closing of Iapetus (James and Stevens, 1986).

2.1.3. Margin Destruction

The destruction of this ancient margin began toward the end of the Early Ordovician epoch and records the greatest plate activity in the Appalachians (Schenk, 1978). Instability was first noted by the development of karst across the carbonate shelf associated with Mississippi Valley type zinc deposits (Williams, 1975). There is no evidence for subduction and the shelf was stable until it was destroyed by a later margin collapse. This is noted by deposition of deep water carbonate shelf and flysch sediments in the Early Ordovician towards the east, and Middle Ordovician on the west of the Humber Zone in Newfoundland. These

are structurally overlain by the Allochthon, emplaced during the Taconic Orogeny (Ordovician), as tectonic slices driven from the southeast in a stack of gravity slices (Stevens, 1970). Rocks on each successive higher slice are stratigraphically older and more easterly than below (Williams, 1975). Deeper water sequences were transported westward across shallow water sequences. The structural slices are bounded by thin zones of shale melange and exotic blocks, which are a result of sliding and tectonic mixing during imbrication (Williams, 1979). General metamorphism is recorded in eastern exposures which probably accompanied ophiolite obduction, as the edge of North America moved under ocean crust (James and Stevens, 1986). The basement (Long Range Inlier) usually has an unconformable relationship to overlying sediments, but structural contacts have been observed in several places (Cawood and Williams, 1986). Thrusts and faults separate the Long Range and Paleozoic carbonate sequences in several areas, and are noted by limestone banding, repetition of stratigraphic sequences, recrystallization and overturned sequences. This implies remobilization of the igneous complex westward (Williams et al., 1985), during the more pervasive deformational period of Appalachian shortening in the Devonian (Acadian Orogeny). The youngest deformational period was in the Carboniferous (Alleghanian Orogeny) and seems to represent a regional extension with northeast-southwest strike slip movement (Bosworth, 1985). The orogenic phases had a profound effect on the level of thermal alteration of preserved organic matter. The levels of maturation are of great importance in determining potential source rocks. Samples must be in or have passed through the oil window at some stage in their evolution to be considered a source.

2.2. The Depositional Model

The Cow Head Group is a deep water sedimentary sequence characteristic of an accumulation between a carbonate platform and the basin floor (Figure 2-3). The Table Head Group, in contrast represents a collapsed carbonate platform that subsequently attained a deep basin topography, and detrital sedimentation consisting predominantly of shale. Samples important to this study are those rocks which have potential as sources for local natural oil seeps, chosen based on the quantity of preserved organic matter that could eventually be transformed from original biological detritus with diagenesis to kerogen and bitumen.

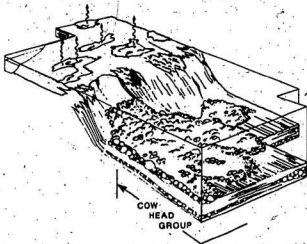


Figure 2-3: Depositional environment of study area during the Middle Ordovician, representing a continental slope deposit (after James et al.; 1987).

2.2.1. The Anoxic Environment

Sediments are richer in organic matter when they are derived from anoxic (oxygen-poor) environments due to limited benthic scavenging, reduced decay and preservation. The term anoxia is defined as an environment where oxygen concentrations are <0.2 ml/l based on the introduction of a transition zone known as disaerobia (0.2 to 0.5 ml/l, Fischer and Arthur, 1977). Oxidic sediments are those that have oxygen levels >0.5 ml/l, and usually show bioturbation. Demaison and Moore (1980) have established 5 limiting factors for the existence of an anoxic environment. These are as follows:

- Primary biological productivity ... limited by nutrient supply
- Biochemical degradation by scavengers to the most stable lipid rich state
- Mode of transport ... pelagic sedimentation
- Particle size ... the finer grained the sediment, the more restrained is oxygen diffusion
- Stability and stratification of the water column

Wyrki (1962) stated, "Biochemical processes are responsible for the existence of an oxygen minima but circulation is responsible for the position." The anoxic environment proposed by Demaison and Moore (1980) must comply with the original depositional framework proposed by the preserved sediment and considering paleoceanographic conditions necessary to lay that sediment down in the original form.

2.2.2. Paleozoic Anoxic Events

The paleoenvironment, as expressed by sedimentary sequences of both the Cow Head and Table Head groups, represents an open ocean anoxic event. Demaison and Moore (1980) describe this as an intermediate layer associated with the lee of cold water sources, commonly found on eastern margins as a result of restricted global circulation patterns and the Coriolis effect. Graptolites found both above and below the selected groups have been described as genera which occur in oxic environments. Genera within the two groups express a tolerance to a minimum amount of dissolved oxygen found in the disaerobic environment (Williams and Stevens, 1987).

Intermittent oversteeping and slumping of the carbonate shelf break created breccia lobes that pinch out laterally along the slope indicating possible multiple sources for the lobes (James and Stevens, 1986). These lobes are thin and tapered within the Green Point Formation and pinch out with depth. Shales within the Cow Head Group are grey to green and contain little bioturbation. There is some evidence of biological activity, which cannot represent a totally anoxic environment with the minimum allowable percent of dissolved oxygen (Demaison and Moore, 1980). Therefore the environment for the Cow Head Group is considered to be oxygen depleted or disaerobic, instead of completely anoxic.

Wilson (1966) hypothesized the existence of a Proto-Atlantic Ocean at the time of deposition of the Cow Head and Table Head groups in the Cambro-Ordovician, which had continental margins intersecting central Newfoundland, Maine and New Brunswick, and extended across the Atlantic to divide England.

This hypothesis is supported by the faunal and structural similarities found within these locations.

The depositional environment of the Cow Head Group was located along the northwest coast of the Proto-Atlantic, along an extensional continental margin, the deposition occurred during a period of relative subsidence of the shelf and slope areas, in response to isostatic pressure due to sediment accumulation along the margin (Stevens, 1970). The Proto-Atlantic model suggested by various authors (Wilson, 1966; Fortey et al., 1982; James and Stevens, 1982) represents either a margin or several marginal basins, (perhaps even developing into an ocean), with an assumed intermediate oxygen minimum zone. This is characteristic of present day oceanic conditions, as opposed to the typical enclosed basin model which has an anoxic bottom layer (Demaison and Moore, 1980). This suggests that there was definite interaction between the deep ocean floor and surficial oxic layers. Depositional patterns preserved in sediments are related to characteristic anoxic and oxic sediments, and circulation patterns associated with the Proto-Atlantic are defined.

The worldwide distribution of Ordovician black shales must be considered to complete the overall picture that relates the early Paleozoic Proto-Atlantic and present day environments of anoxia. In the early Paleozoic, a geographical widespread black shale facies sequence and a later reduction in the extent of shale distributions in the early Paleozoic suggest a variation in worldwide dissolved oxygen content in the open ocean (Berry and Wilde, 1978). The oxygen distribution model proposed by Cloud (1978) suggests that the oceans became

progressively more oxygenated as a result of increased biological activity. Ventilation was relatively shallow, and was a result of mixing, limited by a demand, created by decaying organic matter originally produced at the surface. Deep ocean circulation is partly a result of sea ice formed at high latitudes which attributes to convection circulation (Leggett, 1978). In the Late Precambrian and early Paleozoic, ventilated waters in deep ocean environments expanded and contracted the extent of the anoxic event (Berry and Wilde, 1978; Leggett, 1978). During the early Paleozoic, extensive areas across continental margins were flanked by oxygen minima layers extending to great depths with large amounts of marine black shales being deposited (Cloud, 1976), similar to those seen at Cow Head. The general mechanism behind plate tectonics in this era was perhaps different than today, and the oceans themselves were not as deep with the extent of anoxic events limited to less than the 3 kilometer depths found in Cretaceous sediments (Cloud, 1976), resulting in comparably thinner shale sequences. The concentration of atmospheric carbon dioxide may have been much greater and the hydrosphere contained much less dissolved oxygen causing the oceans to be more prone to anoxic events (Berry and Wilde, 1978), and more suitable for preservation of organic matter.

In summary the extent and distribution of shales indicate that the study area was located along the margin of a basin or ocean system. Fauna give an approximate indication of the conditions necessary for their existence. In the Cow Head and Table Head groups, preserved marine sediments vary from anoxic to oxic. The worldwide occurrence of abundant marine "oil prone" black shales in

the Cambro-Ordovician record indicate a general global anoxic event, possibly due to restricted ocean circulation. High primary productivity, intermediate anoxic zones and low dissolved oxygen content influence the original depositional environment.

2.3. Burial History

In any assessment of the hydrocarbon potential of a basin, or in determining source rocks, it is necessary to first determine whether the sequences in question have undergone the levels of maturation necessary for the creation of oil and/or gas. In areas where natural seeps occur, the source must have passed through the oil window, defined in conventional terms as 60-120°C. Maturation of the units within the Cow Head and Table Head groups can be assessed on the basis of fluorescence, conodont alteration index (CAI), and Rock Eval pyrolysis. These methods give an indication of the extent of burial and thermal maturation the sediments have undergone.

2.3.1. Fluorescence

Fluorescence studies indicate that sediment from both the Cow Head and Table Head groups show differential thermal maturation (Hogan, 1986). Levels of diagenesis are based on the color and intensity of the kerogen in fluorescent light. Studies indicate that, based on maturation levels, potential for hydrocarbon generation is limited to the Cow Head Group, with a thermal alteration index (TAI) of 2.5-3.0, equivalent to the oil window (Staplin, 1969). The Table Head Group shows higher thermal maturation levels (TAI >3.5) corresponding to the base of the oil window; however, those samples contain relatively poor quality and

quantity of kerogen. Levels of maturity were also noted to increase proximal to the Long Range Mountains but Hogan (1986) omitted documentation of sample collection adjacent to decollement surfaces and fault zones, and the results can only be used for a broad assessment.

The type of kerogen assessed in fluorescence studies indicate that organic matter levels are inadequate for an interpretation of the Table Head (Macauley et al., 1987). Type II kerogen is found within the two groups (Hogan, 1986; Macauley et al., 1987), and indicate that marginal and low maturation levels could generate only low grade bitumens.

2.3.2. Conodont Alteration Index

Detailed assessment of maturation of the Cow Head and Table Head Groups was done based on CAI levels. The variation in color of preserved conodonts equals specific levels of maturity, and CAI values of 1 to 2 corresponding to the oil window (Nowlan and Barnes, 1987a). Thermal maturation of Paleozoic strata from west-central Newfoundland have been assessed using a representative sample suite of conodonts (>10 specimens of well defined age). The Cow Head Group have CAI levels of 1.5 corresponding to an oil window temperature of 50 - 90°C; and the only exception is the Lobster Cove locality (CAI > 4.5, equaling a supermature dry gas temperature of 190-300°C.), considered to represent a floundered melange block (James and Stevens, 1986). The CAI values from the Table Head Group average 2.5 and increase towards the north, which is interpreted as an increase in burial depth (Nowlan and Barnes, 1987b). Oil generation commences with a CAI of 2.5, and thus a good potential source, based on this relationship would be the Cow Head Group.

2.3.3. Rock Eval Pyrolysis

Another assessment of the level of maturation attained, has been done using the Rock Eval technique (Macauley et al., 1985, 1987). Maturation is based on the ratio of the amount of hydrocarbons present and potentially generated, the bound water, carbonate and the temperature of the experiment (Tissot and Welte, 1984). A continuous increase of this ratio as a function of depth of burial make it an excellent index of maturation. The general assumption of low maturity within the Table Head Group and marginal maturity for the Cow Head Group (not yet in the oil window) was calculated by Macauley et al. (1987). Their study was difficult to compare to this thesis as stratigraphic terms and sample locations were not defined clearly.

2.4. Description of Rock Units

Sample collection was based on 3 factors: 1) the sample availability and relative location in relation to the observed oil seeps, 2) the organic matter content preserved in local stratigraphic units. The most organic rich units are grey to black. Selection was mostly of black shales with exceptions being those shales with secondary nodular limestone features assumed to concentrate organic matter (Coniglio, 1985). 3) Finally, The average grain size is relative to the amount of organic matter preserved. The finer the size, the more the potential for preservation (Demaison and Moore, 1980).

2.4.1. Stratigraphy

Detailed stratigraphic and sedimentological studies of the west-central coast of Newfoundland with formation, group and member divisions has been summarized in James and Stevens (1986) and James et al. (1987). Samples have been selected from specific formations and a summary of these units is included, based on the proposed intervals of James and Stevens (1986) (Figure 2-4).

The Cow Head Group consists of two contemporaneous facies, a collection of predominantly coarse-grained proximal lithology (Shallow Bay Formation) and a finer grained distal lithology (Green Point Formation). The section is capped by the Lower Head Sandstone Formation composed of interbedded sandstones, greywackes and some shales. A summary of formations and individual members follows:

- **Shallow Bay Formation:** a sequence of limestone conglomerates interbedded with limestones and shales and subdivided into four members.
 - **Downes Point Member:** the basal unit of the Shallow Bay Formation composed predominantly of conglomerates with minor interbedded limestones.
 - **Tuckers Cove Member:** interbedded calcareous sandstones and conglomerates with minor shales, silts and limestones.
 - **Steering Island Member:** composed of megaconglomerates with minor interbeds of limestone, sandstone and shale.
 - **Factory Cove Member:** thick sequences of limestone and minor shales punctuated by megaconglomerates
- **Green Point Formation:** of predominantly red, grey and black shales with minor conglomerates and limestone; this can be divided further into three members.
 - **Martin Point Member:** mostly green and black shales with minor sandstone, siltstone, parted limestone and few conglomerates.

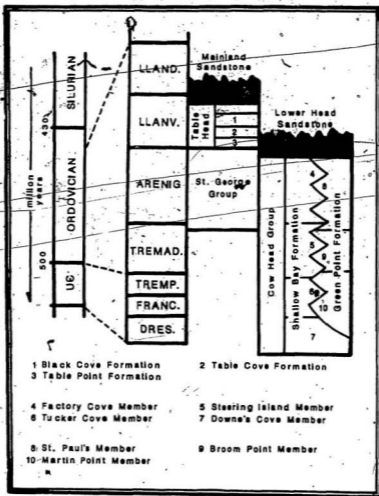


Figure 2-4: Stylized stratigraphic column of the Cow Head and Table Head Groups, (after James and Stevens, 1986).

- o Broom Point Member: composed of parted limestone with minor siltstone, sandstone and conglomerates.
- o St. Paul's Member: the upper member with thick sequences of distinctive red, green and black shales with minor variable

limestones, thin conglomerates, siltstones and dolomites that are generally extensively weathered.

The Table Head Group, is composed of four formations detailed below and is a sequence of bioturbated grey limestones interbedded with black shales, megabreccias and sandstones (Kappla et al., 1980).

- Table Point Formation: massive limestones interbedded with minor dolomites
- Table Cove Formation: crinoidal and shaley limestones with shale and slump features increasing in content upwards
- Black Cove Formation: solely black shales and mudstones
- Cape Cormorant Formation: grey to black shales, green siltstones with interbedded turbidites and conglomerates.

2.4.2. Sample Logs

The location of samples with relation to outcrop lithology and geographic position is presented in Figure 2-6. The logs were simplified from Williams and Stevens (1987) and James and Stevens (1986), and are based on the field assessment of the outcrops by the author. 32 Samples were selected from the members and formations, indicated in Figure 2-5 and itemized in Table 2-1. Comparative biostratigraphic and chronostratigraphic logs for the Table Head Group, Lobster Cove and Parsons Pond outcrop localities were not available for detailed stratigraphic log profiles and samples have been given only formation names and approximate member names where identified (Cawood and Williams, 1986).

Sample #	Bed #	Formation	Member
PP1	-	Green Point	-
PP3	-	Green Point	St. Paul's Inlet
PP4	-	Green Point	-
PP5	-	Green Point	Broom Point
PP6	-	Green Point	St. Paul's Inlet
PP7	-	Shallow Bay	-
CH8	8	Shallow Bay	Steering Island
CH9	9	Shallow Bay	Factory Cove
CH10	10	Shallow Bay	Factory Cove
CH11	13	Shallow Bay	Factory Cove
SP12/13	11	Green Point	St. Paul's Inlet
SP14	11	Green Point	St. Paul's Inlet
SP15	13	Green Point	St. Paul's Inlet
SP16	13	Green Point	St. Paul's Inlet
BP17	8	Green Point	Broom Point
BP18	8	Green Point	Broom Point
WB19	13	Green Point	St. Paul's Inlet
WB20	11	Green Point	St. Paul's Inlet
MP21	9	Green Point	St. Paul's Inlet
MP22	11	Green Point	St. Paul's Inlet
MP23	-	Lower Head	-
GP24	6	Green Point	Martin Point
GP25	8	Green Point	Broom Point
GP26	8	Green Point	Broom Point
GP27	8	Green Point	Broom Point
GP28	6	Green Point	Martin Point
LC29	11	Green Point	St. Paul's Inlet
LC30	11	Green Point	St. Paul's Inlet
LC31	15	Lower Head	-
LC32	11	Green Point	St. Paul's Inlet
TH1	-	Black Cove	-
TH37	-	Black Cove	-

Table 2-1: Identification of samples in relation to formations and members.

2.5. Exploration History

Oil seeps in western Newfoundland have been recorded since 1812, when M. Parsons collected seep oils and used the crude for the treatment of rheumatism. The exploration for oil was not actively pursued until 1867, when the first well drilled produced an oil show. Nine more wells were drilled between 1892 and 1906 by the Newfoundland Oil Company, six of which encountered oil and/or

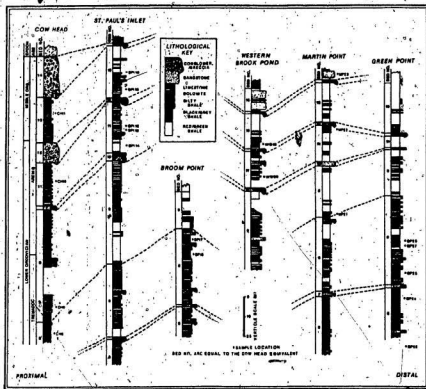


Figure 2-5: Individual sample outcrop logs with relative positions of sample locations.

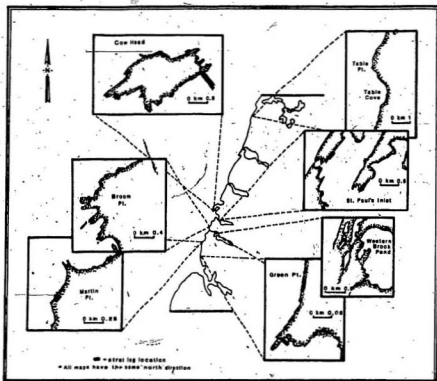


Figure 2-6: Location maps for the individual sample logs.

gas. The deepest well was drilled to 2050 feet (Flemming, 1970). By 1908, approximately 700 to 800 barrels of oil had been shipped from the Parsons Pond area. From 1906 to 1920, no new wells were drilled but three wells were drilled between 1920 and 1925 (Brown, 1938). A further lull in drilling occurred between 1925 and 1952, but wells prior to 1925 were reinvestigated (Brown, 1938), and the oils analysed were described as amber in color, paraffin-intermediate type and with a specific gravity of 0.8008 at 60 °F. In 1952 a company owned by J. Fox

drilled at Parsons Pond but the drill logs of these efforts were not recorded. The most recent drilling was in 1965, by the Newfoundland and Labrador Corporation (NALCO), which drilled one well to a depth of 4271 feet before caving prevented further drilling (Flemming, 1970). The Petroleum Directorate of Newfoundland reopened the area to exploration in 1983 (Kunkle, 1986). The number of known wells is 28 (Figure 2-7); and a more detailed account is recorded in Fleming (1970). Oil continues to stand in abandoned open drill stems and along the water table, in shallow water wells both at St. Paul's Inlet and Parsons Pond.

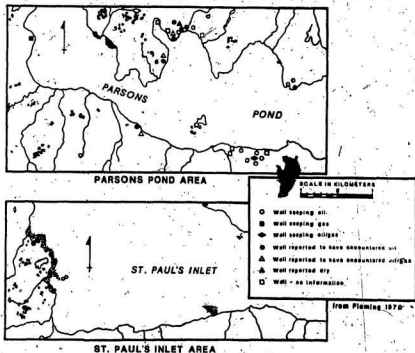


Figure 2-7: Well location in Parsons Pond and St. Paul's Inlet.

2.5.1. Petroleum Potential

Western Newfoundland is the only onshore area within the province with a potential for petroleum production. Most of the earliest work was purely speculative and wildcat in nature, based on tidbits of information, passed by word of mouth and assumptions with some reference to petroliferous and bitumenous rocks in the Cambro-Ordovician sequences on the west coast (Flemming 1970). An assessment of petroleum possibilities in and around the Gulf of St. Lawrence, determined that commercial oil and gas pools might exist, but would probably be difficult to find, as a result of complex geological structures (Williams, 1974). A total gross of 30 million barrels and 0.3 trillion cubic feet of gas were estimated to be present; however, most wells were drilled in clusters proximal to seeps and few have been considered as significant, due to the influence of local seeps from a reservoir on the well flow. It is obvious that the area does possess some value as a potential petroleum field and it is hoped that this study will resolve some of the unanswered questions. unanswered.

Chapter 3

Analytical Methods

3.1. Sampling Procedure

All rock samples were obtained at approximately 15 cm depth along bedding planes from exposed outcrops, wrapped in precleaned tinfoil and stored in plastic sample bags. Oil samples were collected from relic standpipes by skimming the surface of the water table and storing the oils in solvent cleaned glass vials which were sealed with teflon caps.

3.1.1. Crushing and Grinding

Outcrop samples were trimmed to remove obviously weathered surfaces and rinsed with distilled water to clear residual soil. Samples were crushed to fragments of approximately 0.5 cm by hand using a maul and plate which had been cleaned with methanol. Samples were then powdered for 5 minutes in an agate disk mill to the optimum grain size of 70 μm necessary for the most efficient extraction of hydrocarbons (Ferguson, 1962; Powell, 1978). Overgrinding was avoided to prevent oxidation and premature pyrolysis (Peters, 1986). Samples were stored in precleaned glass jars until analysis.

3.2. Solvent extraction

Samples were solvent extracted to isolate and quantify the amount of bitumen (soluble organics) retained in the shales. A variety of methods were initially compared to determine the most useful procedure for this study. All solvents used during analyses were redistilled for purification with the exception of reagent grade diethyl ether used in the liquid chromatography.

3.2.1. Extraction Techniques

Many methods have been developed for the solvent extraction of oil rich shales. Rohrback (1979) compared five techniques which included variations in both physical and chemical processes. Four of the five techniques were further compared in this study, to assess their suitability for the sample suite. These are:

- 1) shaker table
- 2) sonicator
- 3) reflux
- 4) soxhlet

Two methods, the shaker table and sonication, were compared based on physical agitation of samples in solvents. The reflux and soxhlet were compared on the basis of utilizing distillation procedures. Reproducibility was determined from replicate analysis. Sample size for the procedures varied from 15 to 30 gm, dependent on the volumes of the containers and apparatus used. The powdered shale used in the comparative study was from the Albert Formation oil shales in New Brunswick, chosen because of its high organic content and availability (L.A. Ferguson, pers. com.).

3.2.2. Shaker Table

Shaker table efficiency was calculated from five samples run in two different solvent mixtures in multiples of five hour periods for 25 hours in a water bath of 25°C. Samples of 15 gm were slurried in 30 ml of solvent. At each five hour interval samples and solvent were centrifuged and the extract removed by pipette; fresh solvent was then added. The extracts were combined and filtered on preashed solvent rinsed filters, evaporated at 40°C and quantified. This procedure was performed using chloroform/methanol and toluene/methanol solvent mixtures. The results indicate that even after 5 extractions the amount of bitumen was still increasing (Figure 3-1). A comparison of the solvent mixtures shows similar yield between the toluene/methanol and chloroform/methanol (Table 3-1).

Disadvantages with the shaker table include the amount of time and handling necessary for complete sample analysis; at least 25 hours for the shaker table, plus an additional 25 minutes for centrifuging is required. Further, it is necessary to add clean solvent every 5 hours to maximize the solvent extraction; and when combined with periodic pipetting this would increase the chance of contamination.

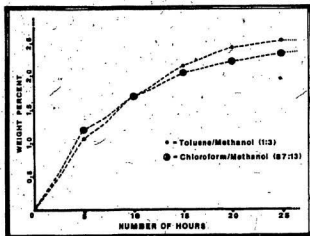


Figure 3-1: Relationship of time to the amount of bitumen extracted from shales using two different solvent mixtures and the shaker table.

3.2.3. Sonicator

Sonication was undertaken in an ultra-sound container with samples retained at a constant temperature of 25°C. The water heated rapidly and had to be changed frequently. The experiment was run in a similar manner to the shaker table method except that the extraction time was reduced to 20 minutes. A total of 5 runs, each with 30 ml solvent aliquots were run for both solvent mixtures and centrifuging. The results indicate less extractable material was obtained (Table

Solvent	Sample Weight	Extract Weight	Weight %	Runtime (hours)
Chloroform/methanol	14.98g	0.17g	1.17	5
	14.83	0.25	1.67	10
	15.07	0.31	2.03	15
	14.92	0.33	2.21	20
	15.01	0.36	2.37	25
Toluene/methanol	15.13	0.16	1.07	5
	15.01	0.25	1.67	10
	14.86	0.32	2.17	15
	14.93	0.37	2.45	20
	15.02	0.39	2.62	25

Table 3-1: Weight percent of extractable material from powdered shales as a result of varying time intervals.

3-2, Figure 3-2). As with the shaker table method, similar disadvantages were found, including excessive handling, but total time was reduced to 1 hour and 40 minutes, with 25 minutes for centrifuging. A further problem of molecular alteration of organic compounds was not assessed.

3.2.4. Reflux

The last two methods utilized solvent reflux and were performed in completely enclosed pre-cleaned glass apparatus. Simple reflux entailed boiling 30 gm of powdered shales in a 500 ml round bottom flask connected to a condensation column and filled with 100 ml of solvent (Figure 3-3). The reflux was continuously run for 48 hours, with solvent changed after the first 24 hours. The extracted material was combined after each reflux run. It was necessary at this point to filter the sediment remaining in the round bottom flask, as well as the collected extract to remove fine clays. All filters were preashed and rinsed with solvents prior to filtration.

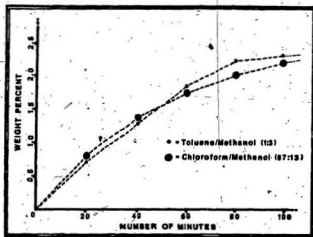


Figure 3-2: Relationship of time to the amount of bitumen extracted from powdered shales using two different solvent mixtures and the sonicator.

The reflux method proved to be more efficient than either of the two previous methods, in that a slightly greater amount of extract was obtained per unit (Table 3-3), and the use of larger samples yielded more extract for analysis. There is no significant difference in solvent mixture extract volumes. Problems encountered involved difficulty in filtration, as well as the handling required for the samples. Run time was 48 hours with at least 2 hours for a pre-run to clean the glassware.

Solvent	Sample Weight	Extract Weight	% Weight	Runtime
Chloroform/Methanol	15.00g	0.12g	0.80	20min
	15.02	0.20	1.36	40
	14.89	0.26	1.75	60
	14.92	0.31	2.04	80
	15.03	0.33	2.22	100
Toluene/methanol	15.06	0.11	0.70	20
	15.01	0.20	1.31	40
	14.99	0.28	1.83	60
	15.06	0.32	2.14	80
	14.97	0.36	2.42	100

Table 3-2: Weight percent of extractable material from powdered shales as a result of varying time intervals.

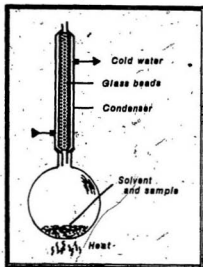


Figure 3-3: Representation of the apparatus used in the reflux extraction procedure.

Solvent	Sample Weight	Extract Weight	Weight %	Runtime (hours)
Chloroform/methanol	30.03g	0.78g	2.60	24
	29.98	0.87	2.91	48
Toluene/methanol	29.97	0.78	2.61	24
	30.04	0.90	3.01	48

Table 3-3: Weight percent of reflux extracted material from powdered shales as a result of varying time intervals and solvents.

3.2.5. Soxhlet

The final method compared was soxhlet extraction; which uses a completely enclosed system that incorporates the use of condensation, evaporation and extraction to supply continuous fresh solvent to the powdered sample (Figure 3-4). This method differs from the reflux procedure in that the solvent and powder are separated and the extracted bitumen collects in the round bottom reservoir requiring little or no filtration. Sample sizes were 30 gm and the volume of solvent used was 200 ml. The extraction ran for 48 hours with a fresh solvent flask added after 24 hours. Final weight percent was determined by combining the two flask contents, evaporating the solvent and weighing the material.

This procedure required 48 hours to run, plus initial thimble extraction for 24 hours. Filtration was performed only where the thimble had overflowed and fine clay escaped down into the flask. Minor handling was necessary and this reduced the chance of contamination. Extract results were comparable to the reflux procedure (Table 3-4) with differences in results likely due to less sample loss during transfer.

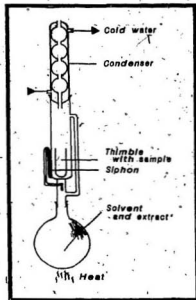


Figure 3-4: Representation of the apparatus used in the soxhlet extraction technique.

Solvent	Sample Weight	Extract Weight	Weight %
Chloroform/methanol	30.05g	0.85g	2.84
Toluene/methanol	30.08	0.98	3.26

Table 3-4: Weight percent of soxhlet extracted material from powdered shales as a result of varying solvents.

On assessing the results for all the extraction techniques, the most

acceptable for use with the samples analysed was the soxhlet method (Table 3-5), based on the amount of handling required for each procedure and quantity of the final extract. This agrees with previous studies which have preferred the soxhlet method as well, (Leythahuser, 1973; Koots and Speight, 1975; Clayton and Bostick, 1985). The extract size from all methods was extremely small and it was necessary to choose a method with the least possibility of human error, while eliminating the possibility of contamination of the extract results. Both the shaker table and sonicator table are good methods for large numbers of samples, but require a great deal of handling, increasing the potential for error. Reflux is useful for large quantities of samples but requires filtration not necessary for soxhlet extracts.

Technique	Total Runtime	Amount of Handling*	Sample Size	Amount Solvent
Shaker Table	25.5hr	high	15g	150ml
Sonicator	2.5	high	15	150
Reflux	50.0	moderate	30	400
Soxhlet	72.0	low	30	400

*high = more than 1.5 hr/sample
 moderate = more than 0.5 to 1 hr/sample
 low = less than 0.5 hr/sample

Table 3-5: Comparison of various extraction methods based on individual samples.

3.2.6. Solvent Selection

Each procedure was run with two solvent mixtures, toluene:methanol (1:3) and chloroform:methanol (87:13). These were chosen based on a literature survey (Durand et al., 1970; Radke, 1978; Dembicki, 1984; Snowden, 1984; Crisp and Ellis, 1986) as well as azeotropic properties. Azeotropic compositions were chosen based on standards in Weast and Astle (1982) and presented in Table 3-6.

Solvent Mixture	Ratio	Boiling Point
Chloroform/methanol	87.3:12.6	53.4°C
Toluene/methanol	27.5:62.5	63.5°C

Table 3-6: Azeotropic solvent mixtures and their boiling points, (Weast and Astle, 1982).

Extraction techniques were also useful in assessing azeotropic mixtures to determine the most suitable combination of solvents for this specific sample suite. Although both solvent mixtures gave similar results, toluene/methanol worked better (See Figures 3-1 and 3-2). The bitumen obtained in the sonicator and shaker table methods extracted by chloroform/methanol was initially larger than the toluene/methanol results. However, this changed about 2/5 of the way into the extraction, and the final amounts with the toluene/methanol were slightly larger than with chloroform/methanol. Extraction with the reflux and soxhlet proved superior with the toluene/methanol mixture extracting up to 12% more than the chloroform/methanol. This was verified with replicate samples and toluene/methanol was chosen for the extraction of bitumens.

3.3. Oil and Extract Fractionation

Bitumens collected using the soxhlet extraction procedure, as well as stored oils collected from the abandoned standpipes were evaporated (25°C and 10 mm Hg), and quantified prior to column chromatography. The dried oils were extremely black-brown and tarry in comparison to the extracts which ranged in color from clear amber to deep brown.

Analysis of oils, extracts and other complex mixtures requires separation into individual classes or families and then eventual characterization of the class into individual compounds. Methods of separation have been developed based on various structural types of compounds and molecular distributions and how these are accommodated in solvent solutions (Durand et al., 1970; Oudin, 1970). Separations were accomplished according to the scheme shown in Figure 3-5.

3.3.1. Asphalt Precipitation

Prior to charging extracts and oils on to a liquid chromatographic column, asphaltene were removed. Various solvents have been used for the precipitation of asphaltene. A few examples include n-hexane (Tissot and Welte, 1978), n-heptane (Oudin, 1970), petroleum naphtha (Tver and Berry, 1980; McKirdy et al., 1981) and n-pentane (Hirsch et al., 1972; Powell et al., 1984, Longman and Palmer, 1987). For this study n-pentane was chosen as it is the most commonly used method (Powell et al., 1984), and complimented future techniques.

Solvent to sample ratios for pentane precipitation vary from 10/1 (Hirsch et al., 1972; ASTM D2007, 1984), to 20/1 (Sawatzky et al., 1976) to as high as 100/1

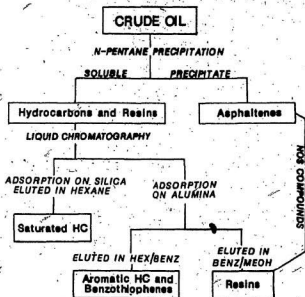


Figure 3-5: Flow chart schematic of petroleum separation by liquid column chromatography.

(ASTM D4055, 1984). Tests carried out by Quick (in preparation) assessed n-pentane to sample ratios, and determined that a 60:1 ratio of bitumen to solvent was needed for complete precipitation. Samples in this study did not exceed 0.33 ml and thus a maximum of 20 ml was necessary for precipitation at a 60:1 ratio.

Oils and extracts were redissolved in 0.5 ml of toluene/methanol (1:3) and then diluted with 20 ml of n-pentane. The samples were agitated for 5 minutes, and stored for 24 hours at 25°C. Asphaltenes were filtered on pre-weighed, fired glass fiber filters and rinsed with n-pentane. The filters with asphaltenes were dried at 45°C, and weighed. Following this procedure, asphalts were redissolved in toluene/methanol (1:3) and stored for later analysis. The pentane filtrate was dried, redissolved in hexane and separated by liquid chromatography.

3.3.2. Column Chromatography

A variety of methods have been used for petroleum separation, aside from the conventional liquid column method (Baker, 1962; Ferguson, 1962; Leythaeuser, 1973; Drushel, 1966; Palmer, 1984); many studies have incorporated high performance (HPLC) (Longman and Palmer, 1987; Zumburgh, 1987) and thin-layer chromatography (TLC) (Monin et al., 1981; Simoneit et al., 1981; Comet et al., 1986).

The conventional method of adsorption chromatography is a physical process of separation based on a two phase system, one mobile and one other stationary (Yost et al., 1980). The process is a result of repeated adsorption-desorption dependant upon the distribution coefficients of each compound. This study used normal phase chromatography with a strongly polar stationary bed (silica:alumina) and nonpolar mobile phase (organic solvent). Polar samples are retained on the column longer than nonpolar. In general polarity increases from saturates to aromatics to resins (Neumann et al., 1981). Removal of these can be done with the use of more polar solvents. Various solvent combinations and stationary beds have been used (Oudin, 1970; Hirsch et al., 1972; Sawatzky et al., 1976; ASTM D2007, 1984). The procedure chosen was based on a combination of several methods. Flow rates range from 200 ml/hr (Sawatzky et al., 1976) to 50 ml/hr (McRae, 1986). McRae (1986) indicated that speed of elution is critical in fractionation and that with rapid rates almost no sample diffusion occurs (Yost et al., 1980). An elution flow rate of 50 ml/hr was selected.

Burets used were 6 mm ID after Durand et al. (1970), fitted with 30 ml

eluant reservoirs. A teflon stopcock at the bottom was used to regulate flow. The bottom part of the column was packed with a hexane slurry of silica gel at a ratio of 40 gm/50 mg of hydrocarbon feed (Oudin, 1970). This was covered with a slurry of alumina at a ratio of 30 gm/gm column feed. Both silica and alumina were fully activated for the separation of nonpolar compounds. Activation was carried out by low temperature heat over a period of time to remove bonded water molecules. In this study, absorbants were activated at 200 °C for 8 hours in small batches every two days during the chromatography experiments (Durand et al., 1970; Sawatzky et al., 1976).

The procedure used by Durand et al. (1970) is designed for 233 mg of feed and was scaled down for this study as the maximum sample size from extraction was 70 mg. A total of 2.1 gm (2.5 ml) of alumina and 3.3 gm (4.9 ml) of silica were employed for a total volume of 7.3 ml. Columns were packed with stopcocks open to allow tighter column pore spacing. Elution volumes were calculated according to Quick (in preparation) and Durand et al. (1970). Initial saturate collection was based on 2.5x column pore volume of approximately 4.4 ml. Chromatographic procedures from various authors are presented in Table 3-7.

The method chosen was verified to check parameters altered from accepted methods. This was done by charging 2 pure standard compounds at a concentration of 1 mg/ml on the columns. These included a large chain alkane ($n-C_{40}$) to determine the saturate elution endpoint, and a highly condensed polyaromatic (coronene) to determine the aromatic endpoint. Every one ml of solvent that passed through the column was individually collected and analysed

Authors	Volumes and Solvents		
	Saturates	Aromatics	Resins
Sawałski et al. 1976	n-pentane 25ml	benzene (50) n-pentane (50) 60ml	
Durand et al. 1970	heptane 35ml	heptane (66) benzene (33) 150ml	methanol (50) benzene (50) 30ml ether 30ml
Hirsch et al. 1972	n-pentane 2500ml	n-pentane (85) benzene (15) 6000ml	methanol (60) benzene (20) ether (20) 1000ml
Quick (in preparation)	hexane 50ml	hexane (66) benzene (33) 205ml	benzene (50) methanol (50) 40ml ether 40ml
Peters et al. 1986	hexane 20ml	hexane (60) benzene (40) 20ml	
Galimov and Frik 1986	hexane (50) benzene (50)	benzene	methanol (50) benzene (50)
This Study	Hexane 11ml	Hexane (66) benzene (33) 45ml	benzene (50) methanol (50) 9ml ether 9ml

Table 3-7: Comparison of chromatography methods used by various authors.

for the standard compounds. Observations of n-C₄₀ after 7 ml resulted in a decision to retain the total 11 ml volume from the scaled down original method which gave <1% mono-aromatics in the saturates (Oudin, 1970). Coronene appeared in the hexane/benzene elution at about 32 ml, and thus 45 ml calculated from the scaled original method was chosen to ensure complete collection of aromatics. Elution with pure benzene resulted in some of the resins being desorbed. This was evident in the comparable colors of the columns and eluants. Similar hydrocarbon charges to the column were compared in a series of trials using a bulk Hibernia (I-46) crude oil.

Separation involved dissolution of evaporated asphalt free bitumens and oils in hexane. Charging of the columns was done with three 1 ml aliquots of sample and hexane followed by pure hexane, allowing the solution to become level with the alumina. This allowed the sample to move through the column as a unit with no residual hydrocarbons left on the buret walls. The procedure was repeated for solvent changes. Individual fractions were collected in cleaned vials and allowed to dry overnight at 25°C and 10 mm Hg, and were then transferred to cleaned, preweighted 2 ml vials, redried and quantified. Saturate and aromatic fractions were redissolved in 0.5 ml hexane and resins were dissolved in 0.5 ml benzene. The saturate fraction was a clear mixture, the aromatics were yellow to amber with a subtle green fluorescence, and the resins were brown to amber retaining the color of the initial column feed material. Elution of resins returned the columns to their original color. Each sample required 2 hours, but five samples could be run simultaneously in 4 hours, including initial packing, separation and cleanup.

3.3.3. Sample Loss

Standard deviations based on an external sample (Hibernia I-46 crude) were for saturates: 1.73%, aromatics: 0.95% and resins: 0.52%. Weighing of bitumens at various stages allowed evaluation of sample loss. Asphalt precipitation gave an average loss of 9.2% with standard deviation of 0.87% during transfer. Bitumen amounts used in the study were thus based on asphaltene free weights.

Liquid chromatography gave an average loss on the column of 5.2% due to either evaporation, retention on the stationary phase (silica/alumina) or transfer. Drying between procedures produced negligible weight differences and resulted in loss of light HC ($<nC_{13}$).

3.4. Total Organic Content

All rock samples were analysed for total organic carbon content (TOC). A variety of methods have been used to determine TOC, including: LECO analysis (Leythausen, 1973; Snowden, 1984; Vlierboom et al., 1986), titration (Gaudette et al., 1974) and CO_2 calibration on a manometer (Macko and Quick, 1986). A comparison of both the titration and manometer methods was undertaken for this study.

It is necessary prior to any TOC calculation, to remove carbonate carbon completely as the distinction between carbonate and organic carbon cannot be made by any procedure. Removal of carbonate was done by first drying a preweighed powdered sample at 45°C for 24 hours, and then reweighing to determine water content. The calculations for TOC are based on dry weight. The powdered samples were acidified for 24 hours at 45°C with 3.0N HCl, and filtered on ashed and dried preweighed glass fiber filters rinsing with distilled water. The filters and acidified samples were dried for 24 hours at 45°C , reweighed and loss calculated. Samples were then used for TOC analysis.

3.4.1. Titration

The titration method was based on studies by Gaudette et al. (1974). The original study found that the analytical procedure worked fairly well for recent sediments with little carbonate, that have not as yet undergone lithification. The titration method was not originally performed with carbonate free samples; however, it was found that the samples used in this study contained up to 80% carbonate as compared to those used in the original study that contained 5%

carbonate (Gaudette et al., 1974). Ancient sediments rich in CaCO_3 , using titration gave a 15% error in TOC results from a replicate suite of four samples.

For samples containing a large percent of total organic material, titration posed some difficulties. The procedure required scaling of the relative volumes used or retitration to accommodate the large quantity of organic carbon present. These larger volumes reduced the accuracy when small samples were analysed and thus it was necessary to assess relative concentrations of carbon within selected samples prior to titration. These necessary assumptions were at times, difficult, and resulted in repeated titrations and sample wasting. Results from titrations indicate that for recent sediments the method works well but does not offer any improvements over other methods for ancient sediments.

3.4.2. Gas Calibration

In comparison to the previous method, the manometer gas calibration proved effective, not only for TOC calculation but also in collection of CO_2 and N_2 gases for eventual use in isotope analysis. Weighed samples (and filters) with carbonate removed were loaded into a pre-fired (450°C , 1 hour) 10 mm quartz tubes with a volume of ground CuO BDH wire, (pre-fired at 900°C for 1 hour), at least twice the sample size and a volume of granular Cu metal (Alpha Resources) at least equal to the sample size (Macko, 1981). Tubes were then sealed under vacuum and heated to 850°C for 1 hour. They were then slowly cooled to 300°C to allow a gradual temperature decrease for complete combustion of the samples.

After combustion the tubes were opened under vacuum into a glass manifold

(Figure 3-6) and the CO_2 was cryogenically purified. Initially, water and CO_2 were frozen out with liquid nitrogen. The N_2 gas was collected on a molecular sieve in a liquid N_2 bath. This was sealed and saved for isotope analysis. The CO_2 as a vapor and water were kept frozen by replacing the liquid N_2 bath with dry ice-methanol. The quantity of CO_2 was measured on a calibrated manometer. The manometer was previously calibrated using weighed portions of $n\text{-C}_{24}$ combusted in the same method (Quick, in preparation). Calculation of TOC was based on dry rock weight. Finally, the CO_2 was collected in a pyrex tube by freezing with liquid N_2 , sealed and retained for later isotope analysis.

3.5. Carbon Isotope Analysis

Carbon isotope values were determined for all whole oils, bitumen and oil fractions, and whole rock samples. All isotope analyses were done using CO_2 that had been purified and isolated on the vacuum line. Analysis was accomplished on a V.G. Micromass 903E mass spectrometer using a laboratory standard calibrated to PDB (Peedee Belemnite) for carbon. Values are reported in standard delta notation (δ) as the difference between the isotope ratios of the sample and a standard:

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

The method chosen in this study was based on a modified Dumas technique involving the oxidation of organic material by copper oxide (Macko 1981). Procedures generally used incorporate combustion (Hoefs, 1980), these include; 1) combustion in a stream of oxygen (Stahl, 1978) and 2) by an oxidizing agent such

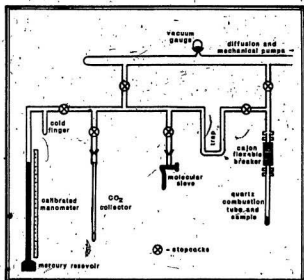


Figure 3-6f: Sketch of the manifold used for the separation of gases used in TOC and isotope analysis.

as copper oxide (Silverman, 1963; Grizzle et al., 1979; Macko, 1981). Temperatures range from 590°C (Sofer, 1984) to 1000°C (Stahl, 1978), and time of combustion from 1 hour (Macko, 1981) to 2 hours (Grizzle et al., 1979). Samples from this study were combusted at 850°C for one hour with a slow cooling program.

Analysis of the liquid chromatography fractions proved difficult as samples were occasionally extremely small. Based on concentration values, a volume of the fraction solvent mixture was pipetted from each fraction vial to yield 5 mg of sample. This was dropped slowly over 4 gm of copper oxide at 40°C to allow evaporation. The coated oxide was loaded into 6 mm ID quartz tubes with 2 gm of copper metal. The samples were then evacuated, sealed, combusted and gases collected.

Reproducibility and errors were calculated using duplicate trial samples and blanks. Blank samples indicated no noticeable contamination from copper oxide, copper metal or clean filters processed in the same manner as the samples. A suit of duplicate samples of fractionated I-46 bulk crude oil and whole rock powder from the Albert Formation in New Brunswick indicate an average error of $\pm 3.5\%$.

3.6. Nitrogen Isotope Analysis

Limited publications are available on the application of nitrogen isotopes to source rock evaluation studies (Hoering and Moore, 1958; Grizzle et al., 1979; Hoefs, 1980; Macko and Quick, 1986). Nitrogen isotope ratios are measured in the form of gaseous N_2 relative to atmospheric nitrogen (Hoefs, 1980). Only the nitrogen rich fractions (resins and asphaltenes) and whole rock powders were analysed for ^{15}N content. Measurements were done on a 90° sector V.G. Micromass 903E mass spectrometer (Macko, 1981). Collection of N_2 gas was done during CO_2 separation. Compositions are expressed as the difference in the $^{15}N/^{14}N$ ratio between the sample and standard atmospheric nitrogen (Hoering and Moore, 1958).

$$\delta^{15}\text{N} = \left[\frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}} - (^{15}\text{N}/^{14}\text{N})_{\text{std}}}{(^{15}\text{N}/^{14}\text{N})_{\text{std}}} \right] \times 1000$$

3.7. Gas Chromatography - Mass Spectrometry

Saturate and aromatic fractions isolated by liquid chromatography were analysed by capillary gas chromatography - mass spectrometry (GC-MS). Analysis of n-alkanes, acyclic isoprenoids and selected biomarkers was conducted using a Hewlett Packard 5792GC coupled to a Hewlett Packard 5970A mass selective detector. Columns normally used are at least 25 m (Bjoroy et al, 1981, Tannenbaum et al., 1986). Injection temperatures range from 30°C (Lewan and Williams, 1987) to 100°C (Palmer, 1984; Zumbege, 1987). Programmed rates are most commonly recorded around 4°/min. (McKirdy et al., 1983; Huizinga et al., 1987), with a high of 8°/min. (Palmer, 1984) and a low of 2.5°/min. (Zumbege, 1983). The final temperature never exceeded 330°C (Lewan and Williams, 1987) with the average being 280°C.

Separations were performed for this study on a methyl silicone (Ultra 1) fused silica capillary column (10m x 0.2mm) injected in the split mode using helium as the carrier gas and mass spectrometric detection. Operating conditions include: injection port, 280°C; column oven held at initial temperature of 70°C for 8min., programmed 4°C/min. from 70°C to 270°C, and held 20min. at the final temperature of 270°C. Evaporated fractions were diluted in 50µl of hexane and 2 µl were injected for each analysis. Syringes were rinsed at least 3 times between samples with clean hexane, and injection port septums were changed after 10 injections.

Resolution of specific ions and biomarkers was improved by the application of Select Ion Monitoring (SIM) mode on the GC-MS. This procedure allows for the repeated scanning of a specific ion within an allotted period of time selected by the user. The improved resolution in this mode allows more detailed studies of the relative abundances and distributions of selected biomarkers. Biomarkers were programmed for 10 min. hold at 100°C, 4°C/min. to 210°C, 1.5°C/min. to 325°C, 10 min. hold at 325°C, with injector temperature at 275°C. SIM dwell time was 100 msec/ion. Aromatic and saturated chromatograms were run in the SCAN mode of the GC-MS which allows collection of all ions.

Chapter 4

Results and Discussion

4.1. Bulk Chemical Compositions

4.1.1. TOC and Bitumen Composition

The observed range for TOC values was 0.1 to 4.3 % (Table 4-1) with the richest samples occurring in Green Point, Western Brook Pond and Broom Point. Gehman (1962) suggested that carbonate-rich rocks may be a more effective oil source at lower TOC contents than shales, siltstones and mudstones. A minimum of 0.3 wt % TOC for carbonates, and 0.5 wt % for shales has been suggested (Hunt, 1967; Tissot and Welte, 1984), with an average >1.5% TOC for good quality source rocks. All samples with the exception of three from St. Paul's Inlet are above 0.5 wt % (Table 4-1). The St. Paul's samples below 0.5 wt % TOC contain an extremely high percent of carbonate (>85%).

TOC are observed to decrease with age and location of the sample in relation to the original depositional environment. Samples that are Tremadocian in age have a larger percent of extractable material and higher TOC than the younger Arenig samples. This could be interpreted as a response to the initiation of the Taconic Orogeny and eventual closing of the ancient Iapetus Ocean. The subsequent destruction of the continental margin would create an enclosed basin

setting that would enhance preservation of organic matter through limited ocean circulation. Geographically, the samples show an increase in hydrocarbon yield from the nearshore to offshore. This indicates greater preservation of organic matter in deeper continental margin sediments, and is perhaps a result of increased organic preservation in fine sediment (Demaison and Moore, 1980).

The percent TOC increases inversely in relation to the percent of carbonate (Figure 4-1a). Concentrations of <12 wt % carbonate corresponds to >2 wt % TOC; >27 wt % carbonate occurs where TOC is <2 wt %. This relationship is observed in hydrocarbon (HC) and extract yields (Jones, 1984). An increase in HC or extract/g organic carbon shows an inverse correlation to TOC (Jones, 1984) (Figures 4-1b and 4-1c). Those samples with TOC >1.5% and high HC yields are generally considered to be mature. Carbonate rich samples do not contain a higher percent of HC or extract as compared to those depleted in carbonate (Jones, 1984). Samples from St. Paul's Inlet which have an anomalously high HC and extract yields have light carbon isotope values (Figures 4-1b and 4-1c), as a result of staining.

A ratio of HC yield to total extract yield (Table 4-1) of approximately 50 indicates low to moderate maturity and values of 40 indicate immaturity (Snowden, 1984). Most samples are immature based on this ratio with the exception of PP4 and PP6 from Parsons Pond, CH8 and CH11 from Cow Head, SP12 from St. Paul's Inlet, BP18 from Broom Point and WB20 from Western Brook Pond. These samples are low to moderately mature and are found within the Green Point Formation. Several samples which had extremely low total

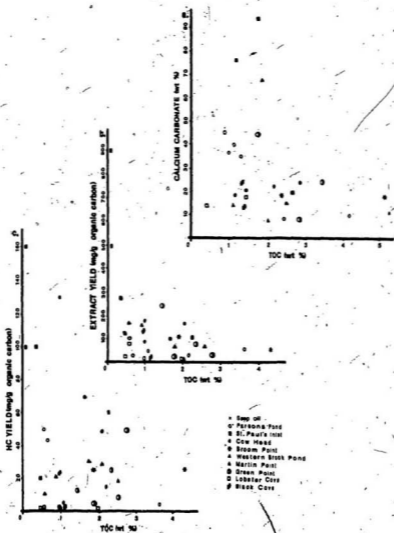


Figure 4-1: a: carbonate % versus TOC
 b: extract yield versus TOC
 c: HC yield versus TOC.

extracts and non-recordable levels of HC (Table 4-1) can be considered as overmature. These include three Lobster Cove samples (LC29,30 and 32), suggested to be part of a thermally altered floundering melange block (James and Stevens, 1986), and Parsons Pond 3 (PP3), Martin Point 22 (MP22) and Table Head (TH37), possibly associated with secondary tectonism (thrust faults).

CONTINENTAL LOCATION UNIT		CaCO ₃	TOC	EXTRACT YIELD mg/g c	HC YIELD mg/g c	TOTAL EXTRACT mg/g sed.	TOTAL HC mg/g sed.	HC EXT
PROXIMAL	PP2 GP	35.3	1.1	45	6	0.5	0.1	20
	PP3 SP	40.7	0.7	29	43	0.2	0.3	2
	PP4 GP	7.8	2.2	32	14	0.7	0.3	43
	PP5 BP	11.2	3.7	46	5	1.7	0.2	12
	PP6 SP	37.6	0.6	100	50	0.6	0.3	50
	PP7 SB	82.6	0.5	-	-	-	-	-
	CH8 SI	23.1	1.7	100	71	1.7	1.2	71
	CH9 FC	19.6	1.0	90	2	0.9	0.0	0
	CH10 FC	25.3	2.1	162	48	3.5	1.2	35
	CH11 FC	21.3	1.0	180	130	1.8	1.3	72
	SP12 SP	20.6	2.3	113	61	2.6	1.4	54
	SP13 SP	96.5	0.1	500	100	0.5	0.1	20
	SP14 SP	76.3	0.4	275	100	1.1	0.4	36
	SP15 SP	94.2	0.5	129	20	0.6	0.1	17
	SP16 SP	96.6	0.1	900	160	0.9	0.1	11
	BP17 BP	17.0	1.9	116	26	2.2	0.5	23
	BP18 BP	18.2	4.3	50	26	2.5	1.1	41
WB19 SP	21.1	2.6	62	19	1.6	0.5	31	
WB20 SP	8.6	1.8	61	33	1.1	0.6	55	
MP21 SP	14.9	0.9	156	22	1.4	0.2	14	
MP22 SP	16.4	2.1	1	29	0.2	0.5	23	
MP23 BP	67.3	0.6	433	10	2.6	0.1	38	
GP24 MP	45.2	1.5	253	13	3.8	0.2	5	
GP25 BP	25.5	2.6	38	8	1.0	0.2	20	
GP26 BP	8.5	2.4	88	25	2.1	0.6	29	
GP27 BP	9.1	2.8	50	0	0.4	-	-	
GP28 GP	33.0	1.9	21	5	0.4	0.1	25	
LC29 GP	19.8	1.0	0	2	0.0	0.0	0	
LC30 GP	19.3	0.5	20	2	0.1	0.0	0	
LC31 GP	44.5	0.6	83	3	0.5	0.0	0	
LC32 SB	16.4	2.0	0	2	0.0	0.0	0	
DISTAL	TH1 BC	15.2	0.9	144	22	1.4	0.2	14
	TH37 BP	12.7	1.1	9	2	0.1	0.0	0

Table 4-1: Absolute values of TOC, extract and hydrocarbon yields. "-" indicates below limit of detection.

HC yield range from 2 to approximately 160 with few samples having > 50 mg HC/g TOC necessary to constitute a good potential source between immaturity and low maturity (Powell, 1978). Four samples from St. Paul's Inlet (SP12, SP13, SP14 and SP16); two from Cow Head (CH8 and CH11) and one each from Parsons Pond (PP6) and Green Point (GP27) have a high yield (Table 4-1). Extremely low to no amounts of HC yield in the Lobster Cove samples (LC29 - LC32) and Table Head (TH37) were expected as a result of high levels of thermal alteration, observed in CAI and fluorescence (Hogan, 1986; Nowlan and Barnes, 1987b).

4.1.2. Petroleum Potential

Maturation and HC potential in source rocks has been evaluated based on relative correlations of bitumen compositions to TOC and sediment volume (Oudin, 1970; Hunt, 1976; Powell et al., 1984; Tissot and Welte, 1984). Limitations may exist for calculations based on bitumen and TOC content; for example shales with migrated hydrocarbons will plot as excellent source rocks. Isotopic and biomarker data indicate no migration has effected the Cow Head Group shales (see Sections 4.2 - 4.5).

Oudin (1976) evaluated a suite of oil shales using a relation of total extract (mg/g sediment) and TOC. Shales with an extract yield >200 mg/g TOC are considered contaminated; and those <50 mg/g TOC, detrital or Type III organic material. The fair to excellent range for potential source rocks is between 50 and 200 mg/g TOC (Oudin, 1976).

When applying this relationship to the present, the bulk of the samples lie within the fair to excellent region proposed by Oudin (1976), (Figure 4-2). Those below the accepted boundary of 50 mg/g TOC include metamorphosed samples from Lobster Cove (LC29 - LC32) and Black Cove (TH37). Samples classified as good to very good source rocks include Cow Head, Broom Point and Western Brook Pond shales and 4 Green Point (GP24, GP25, GP27 and GP28).

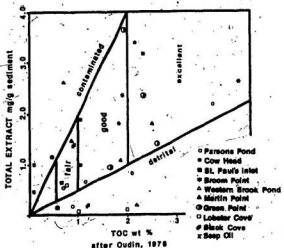


Figure 4-2: Evaluation of source rock potential using total organic and extract values.

A limitation of this type of analysis is no distinction for those samples that have a high HC content. These types of shales can be classified equally with nonhydrocarbons (NHC: asphaltenes and resins) enriched bitumens that will not be potentially as effective a source for expelled oil (Oudin, 1976).

Potential and maturation for source shales can be evaluated by a comparison of HC yield (mg/g TOC) to % HC in extractable bitumen (Powell, 1978). The polar axis represents the HC yield and the angle θ the percent of HC in bitumen (Figure 4-3). Using this relationship bitumens can be classified as follows:

- A: Immature
- B: Marginally Mature
 - B1: Dry Gas
 - B2: Gas/Heavy Oil
- C: Mature
 - C1: Gas
 - C2: Gas condensate, minor oil source
 - C3: Intermediate oils [50 - 80 HC yield]
 - C4: Prolific oil source [80 - 160 HC yield]
 - C5: Contaminated [>160 HC yield]
- D: Overmature
 - D1: Light oil and gas
 - D2: Gas condensate, minor oil source
 - D3: Gas condensate, wet gas
 - D4: Dry gas

Cow Head Group bitumens range from immature to overmature (Figure 4-3). Approximately half of the samples are immature, with most being marginally mature. Five mature samples are potentially oil producing, however most will produce gas. None of the samples exceed the contamination limit of >160 HC yield (Powell, 1978). Samples which are immature in outcrop, may be considered a source rock at a higher maturity with depth.

Limitations of Powell's relationship are a result of no correlation to TOC, and for the Cow Head shales, by the small samples size which increases the error in determination of % HC/g TOC. Samples from the Cow Head Group have already been interpreted as marginally mature to immature (Hogan, 1986;

Macauley et al., 1987; Nowlan and Barnes, 1987b), and according to Powell (1978) are limited to having poor petroleum source potential.



Figure 4-3: Maturation and petroleum potential utilizing a polar plot.

A final classification was attempted using a relationship proposed by Hunt (1979). Total HC and TOC are compared using a double logarithmic scale. An upper limit of 240 mg/g TOC for contamination is greater than the 160 proposed by Powell (1978), and the lower limit of 70 mg/g TOC (Hunt, 1979) is also higher than the limit determined by Powell (1978). The range from 70 and 240 is arbitrarily divided into three categories, including: fair, good and excellent, based on frequency contours (Leenheer, 1984).

Cow Head Group shales are fair to excellent source rocks and lie within the range of good potential source shales (Figure 4-4). Exceptions are the metamorphosed samples from Lobster Cove shales (LC29 - LC33), and one sample each from Parsons Pond (PP6), Cow Head (CH9) and Green Point (GP24), (assumed to be more immature). None of the samples exceed the upper boundary of 240 mg/g TOC. Using this scheme, samples with high concentration of NHC will be interpreted as poor source rocks. Major limitations, for this association, are in the arbitrary divisions proposed as limiting ranges for fair to excellent source rocks and no proposed lower boundary.

A summary of source assessment indicates low to early stage maturity for most of the Cow Head Group shales and the HC potential is fair to excellent. Major exceptions are those shales from Lobster Cove, which are of poor petroleum potential, and thermally altered or metamorphosed.

4.1.3. Fraction Analysis

In a fraction analysis it is common for extracts from the source to contain more of the less polar saturated HC (Tissot and Pelet, 1971). Migration from the source to the reservoir alters the composition of petroleum when compared to extractable bitumens, as a result of retention by adsorption and solubility of the heavier petroleum fractions (Pelet et al, 1988; Tissot and Welte, 1984). Extracted bitumens from western Newfoundland show an increase in NHC relative to HC when compared to the seep oils (Table 4-2). Cow Head extracts contain an average of 37% NHC in contrast to 8% from the seep oils; an increase of 29%. The amount of saturate from the oil to the source decreases from 74% to 49%,

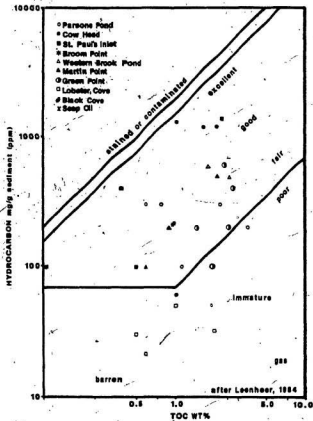


Figure 4-4: Petroleum potential based on double logarithmic scales.

similar to a study of average bitumen and oil compositions done by Tissot and Pelet (1971) (Figure 4-5). In general source rocks are enriched in NHC as compared to reservoir oils (Hunt, 1979), although this can vary with extraction solvent (Ferguson, 1982).

Relative proportions of the individual fractions can be an indicator of

UNIT	ASPHALT	RESINS	AROMATIC	SATURATE
FP2	16.5	36.8	8.0	41.5
FP3	20.6	37.6	19.2	26.2
FP4	17.0	36.3	12.3	36.8
FP5	19.0	40.8	14.1	29.2
FP6	14.1	33.0	27.0	26.9
FP7	15.2	20.2	7.7	57.2
CH8	5.9	21.7	27.4	45.0
CH9	4.3	63.1	6.9	25.7
CH10	9.1	19.5	23.1	48.2
CH11	8.6	19.3	20.6	51.6
SP12	8.8	19.3	10.6	61.3
SP13	19.1	17.2	3.1	60.4
SP14	19.5	27.8	4.1	48.5
SP15	14.6	21.1	7.0	57.4
SP16	6.4	45.4	18.9	29.2
BP17	7.2	22.5	7.8	62.6
BP18	13.3	35.7	9.7	41.3
WB19	13.3	27.7	11.9	43.1
WB20	10.0	31.0	8.3	50.9
MP21	12.3	39.7	12.6	36.8
MP22	29.6	25.5	11.7	33.1
MP23	8.4	32.6	8.3	54.7
GP24	2.3	39.9	15.5	42.2
GP25	17.2	41.1	7.9	33.8
GP26	5.0	22.3	15.8	58.1
GP27	15.4	37.5	9.0	38.1
GP28	19.5	14.9	24.9	43.8
LC29	38.1	30.1	10.5	21.9
LC30	10.4	30.8	22.2	37.6
LC31	11.2	61.4	12.5	15.9
LC32	27.7	39.4	11.2	22.1
TH37	50.4	22.0	8.5	19.1
SPo11	1.4	4.2	17.5	76.9
FPo11	1.8	10.8	22.2	65.1

Table 4-2: Relative portions of individual petroleum fractions calculated to 100%.

original composition, maturity and/or biodegradation. Saturated-HC are usually more abundant than NHC and aromatics (>60%), except that those petroleum products are biodegraded with <25% saturates (Tissot and Welte, 1984). NHC are usually <40% of normal oils, but can range from 25 to 60% in altered, oxidized or degraded hydrocarbons (Tissot and Welte, 1984). Aromatics are secondary in importance, usually from 20 to 45% of the total bitumen (Hunt,

COMPARISON OF GROSS CHEMICAL COMPOSITIONS
OF SHALE AND SAND BITUMENS TO CRUDE OILS

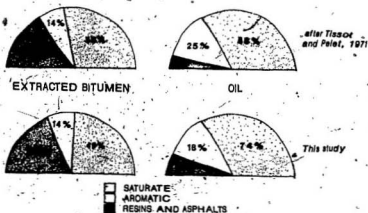


Figure 4-5: Pie diagrams showing fraction comparisons between bitumens and oils.

1967; Tissot and Welte, 1984). Samples in this study are depleted in aromatic HC, possibly as a result of limited input of aromatic compounds into Ordovician sediments (Connan et al., 1986; Hoffmann et al., 1987), or lower concentrations of sulphur compounds in the depositional environment (C. Walters, Pers. Com.). Oils with a high content of n-alkanes are viscous, have low specific gravities and are common in North American Paleozoic oils. (Tissot and Welte, 1984).

Parsons Pond oil falls within the range of normal crude oils, containing a very low percent of asphalt <8%, 74% saturates and approximately 18% aromatics. Total bitumen composition by relative concentrations is determined on a ternary diagram, by grouping resins and asphaltenes together as NHC. Tissot and Welte (1984) have delineated a zone of "normal crude oils" based on

isofrequency contours for nC_{15+} . Cow Head Group bitumens fall outside the range for normal crude oils (Figure 4-6). Most samples lie between the saturate and NHC endpoints and are depleted in aromatic HC (Figure 4-6). Cow Head samples with >60% asphalt and resins are overmature. These include three metamorphosed samples from Lobster Cove (LC29, LC31 and LC32), one from Black Cove (TH37) and a contaminated sample from Cow Head (CH9).

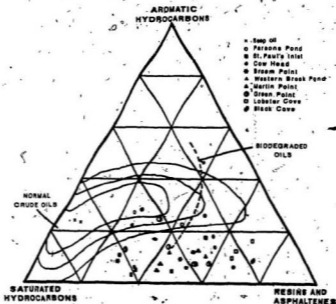


Figure 4-6: Ternary diagram showing normal crude oil proportions and superimposed sample values, (after Tissot and Welte, 1984).

4.2. Saturated HC

Saturated HC comprises normal and branched alkanes (paraffins) and cycloalkanes (naphthenes) and are the most important constituent in normal oils. Geochemical biomarkers found in saturates such as steranes and triterpanes are relatively inert molecules, and are little affected by chemical alteration, n-alkanes are very stable and unaffected during catagenesis (Tissot and Welte, 1984). It is this preservation of biomarkers or "fossils" that can aid in correlation and interpretation of original biogenic material.

4.2.1. Distribution of n-alkanes

The distribution and presence of specific n-alkanes reflects the chemical nature of the biogenic material preserved during deposition. N-alkanes from specific geological periods contain a variety of characteristic compositions (Reed et al., 1986). This study compares the Cow Head Group shales and associated oils with organic facies distinctive of the Ordovician and early Paleozoic.

All samples have similar distribution curves decreasing from nC_{15} , (loss of nC_{15} is from evaporation and weathering), to nC_{33} (Appendix A). Abundances were normalized to the total amount of n-alkanes. These normalized distribution patterns can be compared graphically (Figure 4-7). All samples have similar distribution curves, decreasing systematically from nC_{15} to nC_{33} , common for Paleozoic, marine sourced hydrocarbons (Tissot and Welte, 1984). Non-marine (waxy) oils are most abundant above nC_{20} . Marine (non-waxy) oils are more abundant below nC_{20} and decrease parabolically as molecular weight increases (Sofer, 1984). Slight decreases in the curve are noted at nC_{18} , nC_{20} , nC_{23} and

nC_{25} , with the bitumens containing a slightly greater percent of higher chained n-alkanes as compared to the oil. Characteristic maxima at nC_{17} and nC_{19} with a dip at nC_{18} are observed in all localities except one at Parsons Pond (PP5).

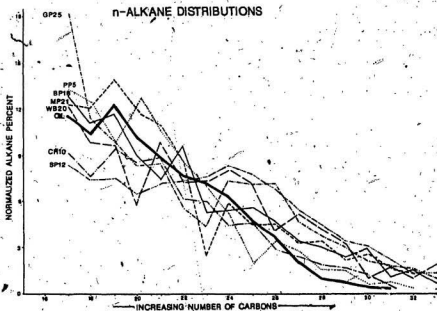


Figure 4-7: Normalized n-alkane distributions.

4.2.2. Chromatograms

Saturate gas chromatograms generally consist of a series of distinctive peaks, decreasing regularly in spacing from lower molecular weights to high number carbon chains, representing increasing n-alkanes. Unevenly spaced peaks between n-alkanes and an indistinguishable mass below are a combination of isoprenoids and various other minor saturate compounds of unresolved branched and cyclic compounds. This unresolved complex mixture generally appears as a single hump (Fowler and Douglas, 1984) with little noticeable division between high and low carbon numbers. This "hump" ranges from approximately C_{13} to C_{34} (Figure 4-8, Appendix A). Only 5 of the GC (PP7, BP18, GP25, GP26 and GP27) have a two hump profile which is common of abundant steranes and triterpanes and can be characteristic of Type III organic matter or low maturity bitumens (Tissot and Welte, 1984). A relative abundance of nC_{19+} alkanes is noted as a result of algal input (Hoffmann et al., 1987). This is in contrast to a normal, rapid decrease in n-alkanes after nC_{19} observed in other Ordovician oils (Reed et al., 1986; Longman and Palmer, 1987). Loss of nC_{26+} and removal of n-alkanes is generally interpreted as biodegradation (Ji-Yang et al., 1982; Palmer, 1984); however, abundant n-alkanes in Ordovician oil beyond nC_{19} may be a result of biodegradation (M. Fowler, pers. com.). Loss of lower carbon chains up to nC_{21} in LC30 is a result of volatilization in nature during low level diagenesis. Visual inspection of all chromatograms shows a fairly even baseline with the exception of PP7, CH8, CH11, SP15, BP17 and GP25 - GP27 (Appendix A). A reduction in n-alkanes after nC_{19} is not found in the study suite, with the exception of MP21, and strong peaks are maintained up to nC_{29} . Compositions of the saturate

fractions from Cow Head extracts are found to be close to those of the seep oils, and useful as a correlation parameter (Williams, 1974; Powell et al., 1984).

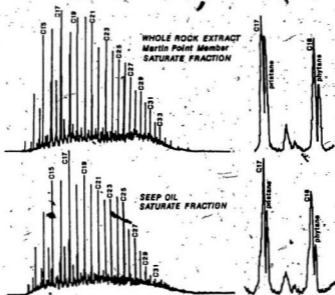


Figure 4-8: Gas chromatograms with enlargement of the isoprenoid peaks.

4.2.3. OEP/CPI

The relationship of odd n-alkanes to even alkanes (odd-even predominance: OEP) can be used to indicate maturation, source and environment (Scalan and Smith, 1969; Tissot and Welte, 1984). Values close to 1.0, such as those observed in the Parsons Pond seep oils, indicate peak oil generation for sediments of high original OEP at low maturity. Low original OEP does not indicate a specific

maturity (Sclan and Smith, 1989). A visual inspection of OEP curves from the bitumens and seep oils shows a variety of results (Figure 4-9). Curves from the various bitumen extracts exhibit a range around unity. Martin Point extracts have relatively high OEP and Broom Point extracts become low after nC_{25} . The curves most similar to the oils are from St. Paul's Inlet, Cow Head and Green Point (26, 27 and 28), with minima at nC_{21} and nC_{27} and maxima at nC_{19} , nC_{26} and nC_{28} (Figure 4-9). Maxima around nC_{17-18} are observed in all but one sample PP3, which was extremely low in n-alkane concentrations (Figure 4-9).

Characteristics common in Ordovician normal paraffinic distributions include strong odd dominance in nC_9 to nC_{19} molecular weight range, with significantly reduced n-alkanes above nC_{19} and no OEP at high molecular weights (Powell et al., 1984; Reed et al., 1986; Hoffmann et al., 1987; Macauley et al., 1987). This has been suggested as a function of original organic matter as opposed to maturity (Martin et al., 1983). The origin of a dominance between nC_{13} and nC_{19} is suggested to be linked to input from fossil algae referred to as *Gloeocapsomorpha prisca* Zalesky 1917 (Hoffmann et al., 1987). Odd dominance from nC_{15} to nC_{19} is common in early Paleozoic oils and attributed to organic matter with high input from phytoplankton and benthic algae rich in acyclic isoprenoids (Tissot and Welte, 1984). Odd-dominance at nC_{30} is commonly associated with input from terrestrial plants and is absent in these samples. Even predominance is common in strongly anoxic conditions with deposition of various lithologies (Connan et al., 1986). The Cow Head Samples exhibit some features associated with the *G. Prisca* facies but not all. This indicates the conditions associated with *G. Prisca* are not globally characteristic of all Ordovician oils.

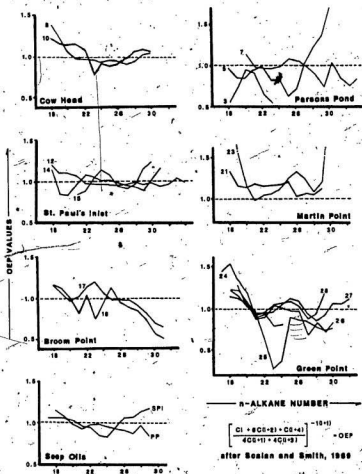


Figure 4-9: Odd-even predominance distribution curves.

Computation of carbon preference index (CPI) which is centered at $C_{20}H_{42}$ n-alkanes is based on weight percent of odd to even molecules. A visual comparison such as OEP curves is subjective and similarities from one part of a

curve can be difficult to compare. For this reason a report of the actual running ratio (OEP) may be more effective (Scalan and Smith, 1969). CPI < 1 indicate an even dominance with values < 0.8 being rare and indicating material from carbonate/evaporate deposits (Tissot and Welte, 1978). CPI \approx 1 are generally mature (Hoffmann et al., 1987). CPI > 1.2 (odd-dominance) indicates immaturity. CPI > 2.5, continental input (Tissot and Welte, 1984). Probable source rocks generally have a CPI < 1.2 (Hunt, 1979). Extracts and oils from western Newfoundland are close to one (Table 4-3). Those samples that have a greater percent of high chain n-alkanes (nC_{30+}) tend to have low CPI, whereas those that generally decrease around nC_{27} have high CPI. This indicates an odd carbon preference in lower n-alkanes and even dominance where higher molecular weight molecules are present. CPI were calculated based on the following two proposed equations for comparison of any variations in results. No significant differences were observed.

- Phillippi (1965)

$$\frac{2C_{29}}{C_{28}+C_{30}}$$

- Bray and Evans (1961)

$$\frac{1}{2} \left[\frac{C_{27}+C_{29}+C_{31}}{C_{26}+C_{28}+C_{30}} + \frac{C_{27}+C_{29}+C_{31}}{C_{26}+C_{30}+C_{32}} \right]$$

Carbon preference index can be correlated with average OEP (nC_{25-33}) (Figure 4-10) (Scalan and Smith, 1969). Samples below the line of equivalence on Figure 4-10 are immature on previous HC potential graphs (see Section 4.1.1) and include one sample each from Parsons Pond (PP8), Cow Head (CH11), Green Point (GP26) and Martin Point (MP22).

Unit Number	CPI Bray and Evans	CPI Phillippi
PP2	0.98	1.00
PP4	1.11	1.17
PP5	1.38	1.76
PP7	0.95	0.91
CH8	0.95	1.06
CH10	1.04	0.86
CH11	1.00	0.96
SP12	1.00	0.93
SP14	1.01	0.95
SP15	1.00	0.96
BP17	1.00	1.01
BP18	1.00	0.97
WB20	0.99	0.99
MP21	0.99	1.17
MP23	1.54	1.06
GP24	0.99	0.96
GP25	1.01	1.00
GP26	1.03	1.00
GP27	0.97	0.86
SPp11	1.08	1.00
PPp11	0.92	0.76

* = no values above nC₃₁

Table 4-3: Carbon Preference Index, (after Bray and Evans, 1961 and Phillippi, 1965).

4.2.4. Isoprenoids

An isoprenoid or i-alkane is a carbon-chain usually with every fourth carbon atom methyl branched (Neumann et al., 79). The most common and useful isoprenoids are pristane (PI19) and phytane (PI20), that appear on chromatograms in relation to nC₁₇ and nC₁₈ (Figure 4-8, Appendix A). The ratio of isoprenoid to either n-alkane or isoprenoid can be an indicator of maturity and/or depositional environment. Pristane/phytane can be used as an indicator for the degree of anoxity and salinity but different precursors will give different ratios, therefore they should be used with caution, (ten Haven et al., 1985). An isoprenoid/n-alkane ratio > 1 and low pristane/phytane (Pr/Ph) are typical of oils

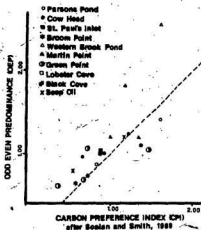


Figure 4-10: Relationship between Carbon Preference Index and Odd-Even Predominance.

generated from carbonate/evaporate sequences in the early to mid maturation stage under extremely reducing conditions (Tissot and Welte, 1984). Conventional HC generally have a Pr/Ph ratio of 1.3 to 1.5 and low isoprenoid/n-alkane ratios (Powell et al., 1984). Cow Head Group extracts have Ph/C₁₈ ratios of approximately 0.3 at moderate maturity, varying from 0.23 to 0.47. Pr/Ph ratios from Cow Head Group samples vary between 1.1 and 5.7 and are comparable to work carried out on Cow Head Group samples by Macauley et al., (1987; 1.5 to 2.9). Results >1.7 may indicate that the organic matter was oxidized to a great extent during transportation and deposition (Snowden, 1984), and values <0.75 may indicate extreme reducing conditions (Connan et al., 1986). Pr/Ph for the Cow Head Group samples are between these boundaries and indicate that

dysaerobic conditions may have existed, with the exception of PP6, WB19 and WB20, MP21 and GP24. These samples may be affected by maturity. The oil is also of high maturity and Pr/Ph averages 2.04. Pr/Ph ratios of the reservoir oil is similar to the mean of extracts from the Green Point Formation which averages 1.84. Pr/C₁₇ range from 0.22 to 0.86 and cover a narrower range when compared to a study by Macauley et al (1987; 0.33 to 1.9) (Table 4-4). High values of Pr/C₁₇ indicate biodegradation or evaporative loss (Palmer, 1984). Pr/C₁₇ for the oils average 0.46, most similar to the Green Point (0.41). Ph/C₁₈ of oils average a low of 0.23, nearly equal to the mean of 0.29 for Green Point and Martin Point extracts (Table 4-4). Assessment of the previous ratios on the basis of formation indicates that the Green Point Formation in the Cow Head Group has the nearest affinity to the seep oils.

The classification of bitumens can be illustrated by comparing Pr/Ph to nC₁₆. With a few exceptions (PP4, PP6, CH10 and CH11), the sample suite correlates with the Cambro-Ordovician window proposed by Powell et al., (1984) (Figure 4-11). Concentrations of pristane and phytane are relatively low in Ordovician oils associated with the *G. prisca* facies and may be a result of overwhelming n-alkanes that swamp the isoprenoid signature (Reed et al., 1986; Hoffmann et al., 1987; Longman and Palmer, 1987). Cow Head Group shales and oils have significant abundances of pristane and phytane (Figure 4-8, Appendix A), not dominated by the *G. prisca* organism.

Unit/formation	Pr/nC ₁₇	Pr/nC ₁₈	Pr/Ph
FP2/GPfa	0.42	0.43	1.47
FP3/SFubr	0.73	-	-
FP4/GPfa	0.32	0.50	1.42
FP5/SFubr	0.29	0.24	1.30
FP6/GPfa	0.66	0.63	4.00
FP7/SFubr	0.72	0.48	1.70
mean	0.62	0.44	2.23
CH10/FCabr	0.33	0.30	1.31
CH11/FCabr	0.43	0.43	1.41
mean	0.38	0.37	1.36
SP12/SFubr	0.25	0.24	1.16
SP14/SFubr	0.23	0.16	1.10
SP15/SFubr	0.35	0.36	1.09
mean	0.25	0.30	1.14
SP17/SFubr	0.37	0.30	1.32
SP18/SFubr	0.41	0.33	1.41
mean	0.39	0.33	1.37
WB19/SFubr	0.83	0.53	2.25
WB20/SFubr	0.68	0.41	2.58
mean	0.76	0.47	2.42
WP21/SFubr	0.86	0.27	5.67
WP23/SFubr	0.36	0.28	1.82
mean	0.61	0.28	3.74
GP24/WFubr	0.32	0.17	2.74
GP25/SFubr	0.45	0.27	1.59
GP26/SFubr	0.35	0.30	1.48
GP27/SFubr	0.38	0.24	1.58
GP28/SFubr	0.52	0.49	1.37
mean	0.41	0.29	1.84
FPoll	0.47	0.26	2.00
SPoll	0.45	0.20	2.08
mean	0.46	0.23	2.04

nbr = number fm = formation FP = Parsons Pond
 GP = Green Point MP = Marlin Point SF = Stearing Isl.
 FC = Factory Cove WB = Western Br. WF = Brown Point
 SF = St. Paul's Inlet CH = Cow Head

Table 4-4: Isoprenoid ratios.

4.2.5. Specific Ions

The distribution of specific biomarker compounds in petroleum source rocks and oils can give insights into depositional environments (McKirdy et al., 1983; Connan et al., 1986), source rock correlation (McKirdy et al., 1983; Fowler and Brooks, 1987), maturation (Ji-Yang et al., 1982; Connan et al., 1986), and original organic material (Reed et al., 1986; Hoffmann et al., 1987). Biomarkers, such as

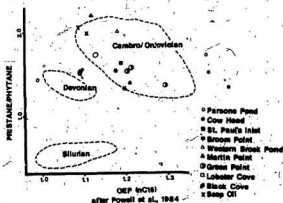


Figure 4-11: Pristane/phytane (Pr/Ph) versus the nC_{16} OEP value.

steranes and hopanes alter only slightly with transformation from source to associated oil and are therefore useful in these types of interpretations (Tissot and Welte, 1984).

Data for biomarker assessment were collected by selective ion monitoring (SIM) at m/z 191 (terpanes) and 217, 218 and 231 (steranes). Ratios were calculated from peak heights of the appropriate peak chosen based on relative retention times determined by previous authors (McKirdy et al., 1983; Connan et al., 1986; Longman and Palmer, 1987; C. Walters, Pers. Com.).

4.2.5.1. Hopanes

Terpanes are derived from lipids of algae and bacteria, and were selectively analysed for distributions of hopane and tricyclic terpane. Maturation and source parameters are calculated in Table 4-5, and based on peaks selected from chromatograms in Appendix B and Figure 4-12. Designation for peak labels are listed in Appendix B.

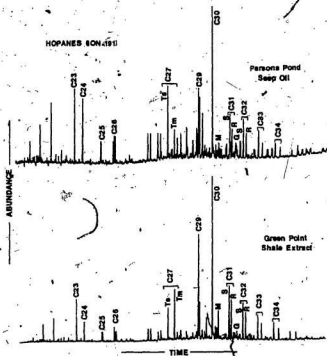


Figure 4-12: Distribution of hopanes, m/z 191. Peak designation in Appendix B.

Cow Head shale extracts and seep oils contain a relatively high abundance of terpanes indicating strong preservation with a maximum peak at C_{30} in a range from C_{23} to C_{35} ; C_{29} is secondary in dominance. This type of distribution is common to Ordovician type hydrocarbons (Hoffmann et al., 1987; Longman and Palmer, 1987). Distribution patterns indicate similarities between oils and extracts from the Green Point and Broom Point locations within the Green Point Formation (Appendix B, Figure 4-12). Occurrences of C_{35} , 18 α trisnorhopane (Ts) and gammacerane (G) are observed in the Cow Head shale extracts and seep oils

and are frequent in Ordovician hydrocarbons (Fowler and Brooks, 1987, Longman and Palmer, 1987). C_{35} concentrations are limited in the Cow Head Group extracts, but when abundant commonly indicate bacterial origin (Longman and Palmer, 1987). Tricyclics (C_{23} to C_{26}) are less abundant than pentacyclics (C_{27} to C_{35}).

Reliable source parameters can be calculated using C_{29} norhopane to C_{30} hopane (C_{29}/C_{30}) (McKirdy et al., 1983; Fowler and Brooks, 1987). Values of C_{29}/C_{30} within 0.1 of the oil ($PP_{oil} = 0.96$) include GP25, GP26 and SP15 from the Green Point Formation. T_m/T_s trisnorhopanes are useful as an indicator of maturity T_s is relatively rare or absent in some Cow Head samples (GP24, GP25, GP26, MP21, WB20) similar to other Ordovician shales (Fowler and Brooks, 1987). MP21 indicates oxidation or carbonate influence in the original depositional environment ($T_m/T_s = 6.03$, $Pr/Ph = 5.67$). Seifert and Moldowan (1978) and McKirdy et al. (1983) suggest that as the value of T_m/T_s decreases, maturity increases. Based on T_m/T_s ratios, extracts and oil from this study are mature with the exception of CH8, CH10 and CH11 which are low to immature.

The isomer $C_{30\beta\alpha}$ is less stable than $C_{30\alpha\beta}$ and decreases as maturity increases (Seifert and Moldowan, 1978; Ji-Yang, 1982). $C_{30\beta\alpha}/\alpha\beta$ ratios range between 0.07 and 0.22, the oil being more mature (Table 4-5). $C_{32}S/R$ indicates maturity as the left isomer (S) increases in relation to the right isomer, (R) (McKirdy et al., 1983). The ratios indicate that the oils (1.76) are slightly more mature than the extracts (Table 4-5). Relative values of R to S stereoisomers indicate maturity at the isomerization endpoint (0.55 to 0.80). Ratios of

UNIT	C_{10}^{ob}/C_{10}^{st}	C_{14}/C_{29}	C_{18}/C_{29}^{st}	C_{22}/C_{29}	C_{27}/C_{29}	C_{30}^{ob}/C_{30}^{st}
FP2	0.15	0.31	0.76	1.36	0.60	0.87
PP4	0.11	0.42	0.72	1.25	0.56	0.86
CH8	0.12	0.25	0.81	1.57	0.52	0.84
CH10	0.22	0.18	1.33	1.63	0.58	0.82
CH11	0.07	0.47	0.81	0.81	0.58	0.93
SP14	0.13	0.39	0.76	1.45	0.60	0.89
SP15	0.13	0.38	0.86	1.47	0.61	0.86
BP17	0.11	0.26	0.69	1.28	0.59	0.89
BP18	0.11	0.25	0.71	1.37	0.61	0.90
MB20	0.15	0.25	0.78	1.42	0.59	0.87
MP21	0.39	0.22	0.95	1.45	0.60	0.72
GP24	0.14	0.17	0.80	1.48	0.60	0.88
GP25	0.15	0.18	0.86	1.50	0.61	0.87
GP26	0.14	0.17	0.89	1.46	0.57	0.89
PPoll	0.10	0.19	0.96	1.76	0.60	0.91

after: Ji-Yang et al., 1982; McKirdy et al., 1983;
Fowler and Brooks, 1987 and Hoffmann et al., 1987.

a = alpha, b = beta

Table 4-5: Hopane parameters.

$C_{31}S/S+R$ and $C_{32}S/S+R$ are at equilibrium indicating location within the oil window, (Ji-Yang et al., 1982; Connan et al., 1986; Hoffmann et al., 1987). $C_{30}^{a\beta}/a\beta+\beta a$ indicates maturity (≈ 0.90) in all samples.

Indicators of source include C_{23}/C_{24} , C_{34}/C_{29} and $C_{30}^{a\beta}/a\beta+\beta a$. In this study, all samples including the oil have minimal concentrations of $C_{30}^{a\beta}$ (M: Figure 4-12). Large C_{23}/C_{24} values > 1.02 indicate prokaryotic input (Table 4-5) (Connan et al., 1986). Low C_{34}/C_{29} (< 0.10) indicate carbonate depositional environments (Connan et al., 1986). More positive C_{34}/C_{29} in the Cow Head Group shales (> 0.17) indicate shale origin (Table 4-5).

Terpane indices show shale sourced hydrocarbons deposited in reducing conditions, although the influence of carbonate is evident in some of the samples.

Prokaryotic organisms are suggested as the original biogenic source. Oils and extracts are at a maturity equivalent to the oil window. Source correlations based on distribution patterns and relative ratios indicate similarities between the Green Point Formation and the seep oils of Ordovician character (Appendix B, Figure 4-5).

4.2.5.2. Steranes

Steroids (eukaryotes) are widely distributed in living organisms and are derived partly from animals and partly from plants (Tissot and Welte, 1984). Relative abundances of steranes and terpanes may vary. Terpanes (hopanes) originate in part from plants, however the main sources are prokaryotic organisms (Tissot and Welte, 1984). Calculated ratios are based on ion m/z 191 selected isomers C_{27} to C_{35} hopanes and ion m/z 217 selected isomers C_{27} to C_{29} steranes. A large percent of sterane (hopane/sterane < 1) indicates "Type III" organic matter. Where hopanes are greater than steranes preservation is under anoxic conditions (Connan et al., 1986). Hopane concentrations dominate over sterane for the Cow Head Group shale extracts and seep oils. (hopane/sterane average = 2.39; Table 4-6). Typically, steranes are absent (Fowler, 1984), or in low concentrations in Ordovician type oils (Hoffmann et al., 1987; Longman and Palmer, 1987). This indicates prokaryotic origin under highly reducing conditions (McKirdy et al., 1983; Reed et al. 1986). Low values of hopane/sterane show an influence of oxidizing depositional environments or maturity (PP4, CH10 and CH11).

Sterane distributions (Figure 4-13, Appendix C, peak designations in

Unit	C ₂₉	C ₂₉ (S)	C ₂₉ ^β S ₂₈	C ₂₉ ^{αβ} S ₂₈	C ₂₉ ^{αα} S ₂₈	C ₂₇ (H) C ₂₈ (H)	C ₂₉ ^{αα} S ₂₈	C ₂₇ R	Hopane Sterane
PP01	33.78	12.95	0.53	0.89	0.72	0.81	1.58	1.43	1.70
PP2	28.04	10.74	0.53	1.23	1.15	1.36	1.20	1.39	2.05
PP4			0.44	0.79	0.76	0.71	1.13	1.05	0.42
Ch6	31.87	11.63	0.55	1.08	1.24	1.20	1.41	1.48	1.21
CH10	24.08	6.99	0.56	1.11	1.27	2.53	1.56	1.22	0.75
CH11	20.84	5.95	0.54	1.08	1.16	2.90	1.47	1.45	0.88
SP14	21.83	7.24	0.52	1.86	1.08	1.94	0.92	1.47	1.67
SP15	28.10	9.56	0.52	1.17	1.08	1.51	1.35	1.29	2.20
BP17	41.87	14.87	0.52	1.23	1.10	0.36	1.10	1.04	4.87
BP18	49.17	18.34	0.54	1.39	1.18	0.48	1.03	0.95	8.54
WB20	32.47	9.44	0.48	2.38	0.93	0.43	0.61	1.13	2.23
MP21	35.50	11.28	0.44	3.07	0.88	0.34	0.48	1.36	2.39
GP24	40.93	14.00	0.47	1.84	0.90	0.55	0.59	1.06	2.59
GP25	38.12	14.53	0.49	2.03	0.96	0.31	0.64	1.36	2.46
GP26	34.20	14.82	0.48	1.81	0.94	0.37	0.61	0.91	2.00

after: Seifert and Moldowan, 1978; Ji-Yang et al., 1982; McKirdy et al., 1983; Copnan et al., 1986; Fowler and Brooks, 1987; Hofmann et al., 1987 and Longman and Palmer, 1987.

α = alpha, β = beta

Table 4-6: Sterane parameters.

Appendix C), are less uniform than terpane chromatograms and reflect the diversity of algal input in the original environment (McKirdy et al., 1983). The steranes are characterized by a predominance of C₂₉ (21-43%) relative to C₂₈ and C₂₇ (Table 4-6). A ternary plot of C₂₇, C₂₈ and C₂₉ αα steranes (Ji-Yang et al., 1982) reveals that the predominance of C₂₉αα can distinguish Ordovician marine shales from younger marine oils (Figure 4-14). The study suite (dashed window) is very similar to the Ordovician oil window proposed by Longman and Palmer (1987), and a general C₂₉ enrichment in Lower Palaeozoic hydrocarbons as reported by Moldowan et al., (1985). The dominance of C₂₉ may be an indicator of cyanobacteria or algae (Fowler and Douglas, 1984; Volkman et al., 1983), and is acceptable for Ordovician oils since this time predates the massive radiation of vascular plants (Volkman et al., 1983). Lower C₂₈ concentrations than those seen

in the Cow Head Group extracts and seep oils, are common in eukaryotic source. High concentrations of C_{28} are associated with the presence of the fossil algae *Gloeocapsomorpha priaca* (Hoffmann et al., 1987). Total distributions show strong correlations between the Green Point Formation shale extracts and Parsons Pond seep oils, although the oils have more mature distributions (Figure 4-13, Appendix C). Normal steranes are less abundant than rearranged steranes (diasteranes). The concentrations of rearranged steranes is not unusually large (Vlierboom et al., 1986; Longman and Palmer, 1987), and their dominance is common in Ordovician oils (Fowler and Brooks, 1987; Hoffmann et al., 1987). The difference between rearranged and normal steranes may be a result of influence of carbonate/anoxic depositional environments, as clastic environments prompt catalysis of steroid precursors for rearranged steranes, (McKirdy et al., 1983; Connan et al., 1986).

Maturation can be calculated from relative values of specific steranes (ratios calculated using peak height). Most ratios compare R (right) and S (left) stereoisomers or $\alpha\alpha$ and $\beta\beta$ steranes (Tables 4-6). The most reliable indicators of maturity are $C_{20\alpha\alpha} S/R$ and $C_{20\beta\beta} S/C_{20\alpha\alpha} S$. Equilibrium is reached when $S/S+R = 0.50$ or $S=R$, (Seifert and Moldowan, 1978; McKirdy et al., 1983). The oils and sample from the Green Point Formation at a more distal depositional setting are more mature (Table 4-6). The $C_{20\alpha\alpha} S/S+R$ ratio also nears isomerization at 0.75 or $\alpha\beta/\alpha\alpha > 1$, (Ji-Yang et al., 1982; Connan et al., 1986). The oils are more mature (0.53) than the extracts which average 0.51 (Table 4-6). An abundance of $C_{20\beta\beta} R$ relative to $C_{20\alpha\alpha} R$ indicates high maturity for the Parsons Pond seep oils and low maturity for the extracts. However, specific

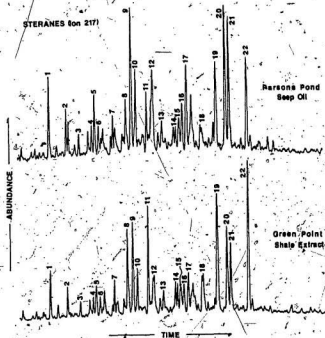


Figure 4-13: Distribution of steranes, m/z 217.
Peak designation in Appendix C.

steroidal precursors, strongly influence the occurrence of certain stereoisomers during early diagenesis, (ten Haven et al., 1986).

With maturity, $\alpha\alpha$ steranes are preferentially lost to $\beta\beta$ steranes through isomerization kinetic conversion (C. Walters, Pers. Com.). The ratio of $\beta\beta/\beta\beta+\alpha\alpha$ shows maturity with isomerization (0.50-0.60). The Green Point shales are more mature (0.61-63) than the oils, Parsons Pond and Cow Head shales (0.40-0.56) (Table 4-6). Rearranged steranes (m/z 218) can be used for the interpretation of maturation (Ji-Yang et al., 1982). $\alpha\alpha/\beta\beta$ for the oils is mature at approximately

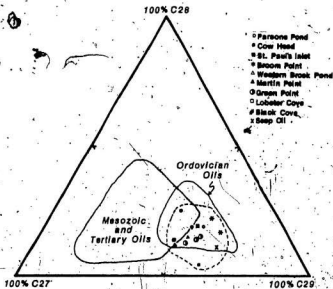


Figure 4-14: Ternary plot of selected steranes. Solid fields after Longman and Palmer, 1987. Dashed field encloses study samples.

0.29. Cow Head and Parsons Pond shales are immature (0.60-1.13), and the Green Point, Western Brook and Martin Point localities are marginally mature (0.31-0.47).

Samples from the Cow Head Group shales have less than 10% methyl steranes; (m/z 231), the oils have the highest at 9%. C_{30} steranes (m/z 414) were detected in all samples with the exception of CH₄ (samples size was too low for detection), and indicates a marine influence that is not common to Cambrian and older sediments (Moldowan et al., 1984; Peters et al., 1985). This lag has been interpreted as a result of the slow evolution of C_{30} steroids.

Steranes indicate that the oil and shale extracts are mature. Maturity is low

in Cow Head and Parsons Pond localities and increases slightly across the Allochthon from the Shallow Bay Formation to the Green Point Formation. The large concentrations of hopane to sterane indicates good preservation under anoxic conditions with some carbonate influence. The original biogenic material was probably diverse prokaryotic organisms (cyanobacteria/algae). Distributions are similar between the seep oils and Green Point Formation shale extracts.

4.2.8. Summary of Saturate Data

Analysis of saturated HC suggests that extracts and oils have all been derived from Early Paleozoic (Cambro-Ordovician) type oil. Normalized distribution curves reflect common Paleozoic marine type HC (Tissot and Welte, 1984). Odd predominance from nC_{13} to nC_{19} is common in Ordovician oils (Powell et al., 1984; Reed et al., 1986; Hoffmann et al., 1987). An abundance of hopanes relative to steranes and a dominance of rearranged to normal steranes is common to Ordovician oils and prokaryotic influence (Reed et al., 1986; Longman and Palmer, 1987). This suggests that the seep oil around Parsons Pond is not related to offshore Cretaceous/Tertiary sediments, or a local Carboniferous basin, but is in fact derived from shale found within the Ordovician Cow Head Group. OEP and CPI relationships indicate similarities between Green Point Formation extracts and seep oils ranging from early to mid maturity within the zone of potential source rocks (Scalan and Smith, 1969; Hunt, 1979). Isoprenoid data indicate Cambro-Ordovician type sediments (Powell et al., 1984) and a mid to late maturity with good petroleum potential. Bitumen, specific ions and fraction analysis indicate fair to excellent petroleum potential with low to moderate

maturity (Oudin, 1976; Leenheer, 1984; Powell et al., 1984). Maturity increases across the Allochthon and in the original depositional environment towards the Long Range Mountains. Due to the geological setting, so long as the samples are not overmature then it is possible that they may lie below the surface at a higher maturity, and have potential as a source rock.

Correlation to a source rock using saturates and TOC eliminates a number of samples that have too low a level of preserved organic matter to constitute a potential source. Extractable HC yield in one Green Point (GP27), two Cow Head (CH8 and CH11) and three St. Paul's samples (SP13, SP14 and SP16) exceed 50mg/g organic carbon (Table 4.1) and must be considered as good to excellent potential source rocks (Powell, 1978). OEP curves, Pr/Ph ratios, n-alkanes, hopanes and steranes indicate potential sources that includes shales from the Broom Point, Green Point and Martin Point locations.

4.3. Aromatic Hydrocarbons

The use of aromatic fractions in geochemical studies is limited as aromatics are extremely complex and difficult to characterize by conventional techniques (Radke and Welte, 1983). Chromatograms of bitumen aromatics consists of unevenly spaced peaks of identifiable naphthalenes, phenanthrenes and thiophenes resting on a slight hump of unresolved compounds (Figures 4-15,4-18). A decrease in the relative abundance of aromatic hydrocarbons with increasing number of benzene rings, and overlap of methyl groups is common to oil and extract profiles (Radke et al., 1984). A sophisticated technique of selected ion monitoring (SIM) provides more detailed profiles of specific compounds than conventional scanning

mass-spectrometry. GC-MS parameters were similar to saturate analysis. Specific ions (m/z) selected for this study are based on Palmer (1984), Radke et al. (1984), Philp and Gilbert (1985) and Connan et al. (1986), and include:

- 178 - phenanthrene (P)
- 192 - methylphenanthrene (MP)
- 206 - dimethylphenanthrene (DMP)
- 220 - trimethylphenanthrene (TMP)

- 184 - dibenzothiophene (DBTh)
- 198 - methyl dibenzothiophene (MDBTh)
- 212 - dimethyl dibenzothiophene (DMDBTh)
- 226 - trimethyl dibenzothiophene (TMDBTh)

Low molecular weight naphthalenes were undetectable as a result of weathering, common in outcrop samples (Tissot and Welte, 1984). Trimethyl and tetramethylnaphthalenes were observed associated with thiophenic compounds in the Cow Head extracts and oils.

4.3.1. Phenanthrenes

Aromatics are geochemically significant for their use as thermal maturation indicators. This "index of maturation" is derived from relative distributions of methyl and dimethyl phenanthrenes (Radke et al., 1982; Radke et al., 1984; Tissot and Welte, 1984; Connan et al., 1986) (Figure 4-15). Phenanthrenes are thought to be genetically related to steroids and triterpenoids and the parent ion is composed of 3 benzene rings (Tissot and Welte, 1984). The pattern of alkyl homologs (methyl isomers) changes with the increasing degree of thermal maturation (Radke et al., 1982). Interference from sulphur enriched compounds (thiophenes) can result in slightly higher maturation indices not corrected for in this study, due to low sulphur contents for the oils and extracts (Flemming, 1970).

Samples are considered for this type of analysis when migration is absent (Radke and Welte, 1983). Shales from the Cow Head are unaffected by migrated oils with the exception of St. Paul's samples which both isotopically and chemically appear to have been affected by associated seeps and are stained.

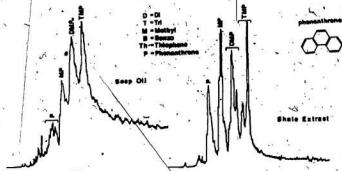


Figure 4-15: SIM chromatographic distribution of phenanthrenes and methyl isomers.

Five maturity sensitive parameters have been derived from the calculation of phenanthrene indices. The methylphenanthrene indices (MPI_1 , MPI_2 , MPI_3 and MP/P), are based on three or four isomers of methylphenanthrene and/or phenanthrene (Table 4-7), and dimethylphenanthrene index (DPI) is calculated from phenanthrene and two groups of dimethylphenanthrene isomers (Radke et al., 1982; Connan et al., 1986). Precision for DPI is lower than MPI due to its more difficult separation on the gas-chromatogram.

Values for MPI_1 ranging from 0.4 to 0.6 are immature, 0.6 to 0.9 moderately mature, and >0.9 highly mature (Connan et al., 1986). Generally extracts for this

UNIT	MPI ₁ [*]	MPI ₂ [*]	MPI ₃ [†]	MP/P [‡]	DPI	R c	maturity
PP5	0.91	0.87	0.92	1.80	1.37	0.95	moderate
CH10	0.46	0.50	0.82	2.18	-	0.68	low
SP12 [§]	0.42	0.47	0.79	2.10	0.33	0.65	low
BP18	0.83	0.90	1.11	2.09	0.75	0.90	moderate
WB20	0.51	0.52	0.87	1.20	0.42	0.71	low
MP21	0.52	0.49	0.77	1.30	0.45	0.71	low
GP25	0.75	0.70	0.92	3.73	0.92	0.85	moderate
GP28	0.73	0.80	0.90	2.92	1.05	0.84	moderate
SPoil	1.10	1.24	1.06	2.25	-	1.06	high
PPoil	1.15	1.39	1.20	3.59	1.09	1.09	high
TH37	1.25	1.49	1.51	3.98	1.72	1.15	high

$$MPI_1 = \frac{1.5(2-MP + 3-MP)}{P + (1-MP + 9-MP)} \quad \frac{MP}{P} = \frac{1-MP + 2-MP + 3-MP + 4-MP}{P}$$

$$MPI_2 = \frac{3(2-MP)}{P + (1-MP + 9-MP)} \quad DPI = \frac{4(1,2,3,4-DMP)}{P + (5,6,7-DMP)}$$

$$MPI_3 = \frac{(2-MP + 3-MP)}{(1-MP + 9-MP)} \quad R c = \frac{0.60(MPI_1) + 0.40}{(0.65 \leq MPI \leq 1.35)}$$

- * = Radke et al., 1982
- † = Radke and Welte, 1983
- ‡ = Connan et al., 1986

Table 4-7: Maturation indices based on phenanthrene and methyl isomers.

study have a low to moderate maturity (0.42 - 0.91) with the exception of the Table Head and seep oil which are high to over matured (> 1.10) (Table 4-7). As maturity increases, 9-MP and 1-MP isomers decrease in abundance relative to 2-MP and 3-MP isomers. Separation between 9 and 1-MP and 2 and 3-MP is limited on the GC used, and the use of indices combining these homolog groups are the most desirable (MPI₁, MPI₃, MP/P). MPI₂ is higher than MPI₁ and MPI₃ due to domination of 2-MP over 3-MP. MP/P (methylphenanthrene/phenanthrene) increases with maturity to >10.

A linear increase up to 135%, followed by a systematic linear decrease between MPI₁ and vitrinite reflectance data collected by Radke and Welte (1983) has been used for the calculation of a maturation parameter associated with the

oil window (Figure 4-16). That calculated parameter (equation below Table 4-7) will herein be referred to as Rc. Irregular variations in the Rc have been interpreted to be a result of influences from specific organic facies and dependant on Type I and Type II organic matter. (Radke et al., 1986). Isomers with lower thermal stabilities (thiophenes) will be more useful in Type II determination at early maturity (Radke et al., 1986). Extracts must also be indigenous to accurately represent the source rock thermal history (Radke et al., 1982). Calculated maturities (Rc) are low to moderate for all the extracts with the exception of the Table Head Group. Seep oils lie near the top of the oil window and are mature ($Rc \sim 1.07$) (Table 4-7).

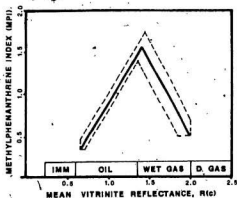


Figure 4-16: Maturation based on MPI indices, broken line represents standard error, (after Radke and Welte, 1983).

Comparisons between carbon isotope values and maturity parameters indicated that there is a restriction on the distribution of these factors in association with environment (Stahl, 1977). In relation to location and age, no

trends are observed in the Cow Head Group shales. This type of a study can be masked by degradation, migration and mixing (Fuex, 1977; Stahl, 1977). The seep oils and Table Head extract are of the highest maturity and have the lowest carbon isotope values, whereas those extracts with the highest isotopic values have the lowest maturity (Figure 4-17). Correlation of MPI to $\delta^{13}\text{C}$ shows a parabolic relationship (Figure 4-17) resulting from constant $\delta^{13}\text{C}$ with higher maturity. No relationship is observed within the depositional environment, but a trend to a higher maturity is observed with age. Samples that are younger (St. Paul's and Martin Point) are less mature.

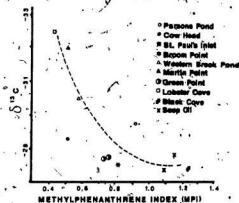


Figure 4-17: Comparison of $\delta^{13}\text{C}$ to MPI.

4.3.2. Thiophenes

An examination of saturated hydrocarbons is sometimes not sufficient to characterize different types of oils. Crude oils become increasingly similar with maturation and the saturates particularly lose their character (Deroo, 1976; Palmer, 1984). Typical signs of biodegradation observed in saturates (loss of

normal alkanes and isoprenoids) are not common in aromatic hydrocarbons (Tissot and Welte, 1984). Aromatics have been used successfully to aid in correlation of mature and immature hydrocarbons (Tissot et al., 1974; Deroo, 1976). Thiophenic compounds have a lower stability than phenanthrenes and in Type II organic matter are more useful for the determination of maturity (Radke et al., 1986), especially when catagenesis is strong or oils are altered (Deroo, 1976). Relative distribution of dibenzothiophenes (DBTh) and methyl isomers can be used for correlation. Both the SPoil and PPoil have larger unresolved aromatic complex mixture than the extracts (partially due to methylnaphthalenes), with a much lower percent of high molecular weight methyl isomers (Deroo, 1976).

Comparison of thiophene distributions indicates similarity in composition between Cow Head and Table Head extracts and seep oils, and an overall richness in thiophenic compounds in the extracts. The strongest correlation is observed between BP18 and SPoil with similar chromatograms from GP25 and GP28, although these have lost more of their lower molecular weight compounds (Figure 4-17).

Thiophenes are also useful for maturation, and may be more useful than MPI for Type II organic matter. Relationships of DBTh to specific methyl isomers can be used to determine thermal maturity (Hughes, 1984; Palmer, 1984; Radke et al., 1986; Connan et al., 1986). The abundance of 1-MDBTh should decrease with maturity relative to 2,3,4-MDBTh, and the ratio of 4-MDBTh/1-MDBTh should increase with maturity. Four methyl dibenzothiophene ratios (MDR_4 , $MDR_{1,4}$, MDR_3 , MDR_2 ; see Table 4-8 for calculations) have been determined to

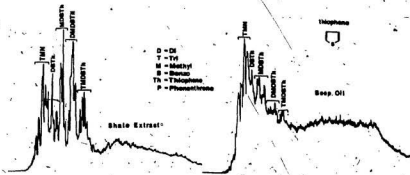


Figure 4-18: SIM chromatographic distributions of benzothiophenes and methyl isomers.

assess maturation using DBTh and MDBTh. Radke et al. (1986) suggested that MDR can be used for maturation (immature: <0.5 , mature: $0.5-1.0$, overmature: >1.0) and to determine organic type. MDR for Type II organic matter is 1.5% less than MDR for Type III organic matter, ranging from 0.2 to 1.0. Samples from this study range from 0.38 to 1.06 within the range of Type II organic matter. MDR , MDR_1 and MDR_4 are immature to marginally mature for all samples with the exception of the seep oil which is mature, and the Table Head extract which is overmature (Table 4-8). MDR_4 of 0.6 to 0.7 is moderately mature; <0.6 , immature to low maturity and >0.7 , high to overmature. Similar maturity is observed in MPI's for all samples. MDR_1 is not as effective an indicator due to the inverse relation with DBTh which may be lost with weathering, creating values ≥ 1 .

UNIT	MDR ₄ *	MDR ₁ *	ΔMDR*	MDR [†]
PP5	1.19	1.49	2.68	0.80
CH10	0.71	1.47	2.18	0.48
SP12	0.55	0.62	1.14	0.49
BP18	0.88	1.23	2.08	0.70
WB20	0.42	0.81	1.23	0.52
MP21	0.57	0.65	1.22	0.87
GP25	0.63	1.33	1.96	0.47
GP28	0.66	1.73	2.46	0.38
PPo11	0.72	0.89	1.61	0.81
SPo11	0.83	0.98	1.81	0.85
TH37	2.00	1.89	3.89	1.06

$$MDR_4 = \frac{4-MDBTh}{DBTh} \quad \Delta MDR = \frac{1,2,3,4}{DBTh} \frac{MDBTh}{DBTh}$$

$$MDR_1 = \frac{1-MDBTh}{DBTh} \quad MDR = \frac{4-MDBTh}{1-MDBTh}$$

* = Connan et al., 1986

† = Radke et al., 1985

Table 4-8: Maturation parameters based on benzothiophene and methyl isomers.

4.4. Carbon Isotopes

Carbon is comprised of a mixture of 2 stable isotopes, ^{12}C and ^{13}C , with the ratio $\text{C}^{12}/\text{C}^{13}$ being approximately 99:1 (Hoefs, 1980). The use of variations in this ratio can indicate age, source and environment. In petroleum studies, $\delta^{13}\text{C}$ isotopes are particularly useful as $^{12}\text{C}/^{13}\text{C}$ concentrations are not significantly altered during maturation (Schoell, 1984). Petroleum has always been assumed to reflect the variability of the source organic matter during deposition (Schoell, 1984). However the variation within a suite of petroleums may be considerable and cannot be differentiated simply with $\delta^{13}\text{C}$. The most reliable correlations are applied in conjunction with other techniques (Williams, 1974; Welte et al., 1975; Fuex, 1977), or between individual fractions (Stahl, 1977; Stahl, 1980). Stahl

(1980) and Sofer (1984) suggest a linear increase in $\delta^{13}\text{C}$ with maturity, perhaps obvious only in overmature and immature stages (Fuex, 1977; Schoell, 1984). An increase in $\delta^{13}\text{C}$ has been used to indicate thermal and tectonic features (Clayton and Bostick, 1985; Vlierboom et al., 1986). Diagenesis will preferentially eliminate ^{13}C enriched fractions (primary fractionation) and concentrate ^{12}C in organic residue (Degens, 1969). This is observed in fossil biomass, which is 6 ‰ lower in ^{13}C as compared to recent sediments (-26 to -20 ‰). Secondary fractionation effects such as biodegradation and water washing have little influence on $\delta^{13}\text{C}$ (Schoell, 1984). An important point to stress for all $\delta^{13}\text{C}$ studies is that variations between HC fractions gives a more distinctive isotopic character than individual value of an oil, kerogen or bitumen (Fuex, 1977). Fluctuations between fractions of a single oil are related to carbon number, OEP and molecular structures (Degens, 1969). Oils with similar $\delta^{13}\text{C}$ may have extremely different fraction isotopic characters, separating them categorically into different families.

4.4.1. Age Variations

Isotopic composition can be used for paleogeographical reconstructions (Schoell, 1984). General variations in $\delta^{13}\text{C}$ have been observed throughout geological time and may be associated with a variety of causes (Figure 4-19). The emergence of land plants in the Devonian through Carboniferous saw a trend towards heavier isotopic values (Welte et al., 1975). A general enrichment of ^{12}C with increasing age is evident, possibly associated with variations in photosynthetic activity that changed atmospheric CO_2 (Junge et al., 1975; Stahl, 1977). Lighter $\delta^{13}\text{C}$ values in both the Triassic and Pre-Devonian oils may be

caused by increases in atmospheric CO_2 pressure (Degens, 1969) (Figure 4-10). The $\delta^{13}\text{C}$ values indicate consistently that the biological source for these oils is dominantly marine. Age variations can be attributed to water temperature, photosynthesis or pH (Degens, 1969; Williams, 1974; Fuex, 1977; Stahl, 1977).

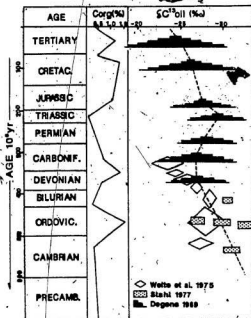


Figure 4-10: Variations in carbon isotope compositions with geological time, after Stahl, 1977.

Carbon isotopic data from the Cow Head Group have kerogen and whole oil values ranging from -28.0 to -33.8 ‰ (Table 4-9). These lie within the observed range of Ordovician oils (-25 to -34 ‰), and are more negative on average than $\delta^{13}\text{C}$ from Cretaceous and Tertiary sediment values. Individual fraction isotopes from the Cow Head Group samples range from -26.9 to -34.2 ‰ for saturates,

-26.5 to -33.9 ‰ for aromatics, -26.9 to -33.2 ‰ for NOS and -26.5 to -31.9 ‰ for asphaltenes (Table 4-9). These ranges lie within the accepted range of normal marine Ordovician crude oils, although the range is large for oils from a similar source (Hatch et al., 1987).

The idea of using carbon isotopes to place an oil within a specific geological time frame is limited by the fact that $\delta^{13}\text{C}$ values between different ages are fairly similar and may overlap (Figure 4-19). A comparison of the mean $\delta^{13}\text{C}$ for oils and extracts for this study (-29.6‰), and observed $\delta^{13}\text{C}$ for Ordovician oils (-30‰) is surprisingly similar (Degens, 1969).

4.4.2. Environmental Assessment

One of the most useful aspects of carbon isotopes is in determining depositional environment. The average $\delta^{13}\text{C}$ composition of whole crude is identical to lipids from living marine and nonmarine organisms (Silverman, 1963; Fuex, 1977) and marine plankton (Degens, 1969). Isotope variations between recent marine and nonmarine sediments have been interpreted on the basis of distance from the shoreline, showing a gradual trend to more positive $\delta^{13}\text{C}$ values as marine organic matter increases (Silverman and Epstein, 1958; Hunt, 1967; Tissot and Welte, 1984). General trends in $\delta^{13}\text{C}$ are recognized (Figure 4-20), including: 1) organic carbon is lower than atmospheric CO_2 , marine carbonates and inorganic carbon by 10 to 30‰, 2) $\delta^{13}\text{C}$ gradually decreases from living organisms to recent sediments to sedimentary rocks, 3) methane has a naturally large range of $\delta^{13}\text{C}$ and, 4) petroleum has a narrower range from -20 to -34‰ (Silverman, 1963; Degens, 1969; Galimov, 1976; Fuex, 1977).

UNIT NUMBER	$\delta^{13}C$ SATURATE	$\delta^{13}C$ AROMATIC	$\delta^{13}C$ NOS	$\delta^{13}C$ ASPHALT	$\delta^{13}C$ KEROGEN
PP2	-30.2	-29.3	-31.7	-29.4	-29.4
PP3	-29.4	-28.8	-29.3	-28.3	-29.1
PP4	-30.6	-30.1	-29.7	-29.5	-29.4
PP5	-28.1	-27.2	-28.4	-28.4	-29.7
PP6	-30.8	-30.6	-27.6*	-28.6	-29.4
PP7	-34.2	-32.9	-33.8	-21.8	-32.3
CH8	-33.6	-33.9	-30.0	-29.7	-29.4
CH9	-31.7	-30.7	-29.9	-27.9	-30.1
CH10	-32.1	-31.4	-30.0	-29.6	-29.2
CH11	-31.4	-32.1	-31.2	-30.4	-30.3
SP12	-31.6	-29.9	-30.2	-30.0	-32.5
SP13	-30.1	-28.5	-27.8	-29.4	-31.0
SP14	-34.0	-32.7	-33.2	-31.9	-32.7
SP15	-31.9	-30.8	-29.9	-30.2	-33.8
SP16	-30.4	-29.6	-30.8	-28.6	-28.5
SP17	-31.2	-30.2	-31.7	-28.5	-28.2
SP18	-30.7	-29.6	-30.8	-28.6	-28.4
WH19	-30.9	-30.7	-31.0	-29.9	-30.2
WH20	-29.7	-28.8	-27.1	-28.5	-30.6
MP21	-31.2	-30.8	-30.9	-31.3	-32.0
MP22	-30.5	-29.1	-30.2	-29.2	-28.9
MP23	-30.4	-29.9	-30.8	-29.8	-30.7
GP24	-29.9	-29.9	-29.6	-29.5	-28.9
GP25	-29.6	-29.5	-29.3	-28.9	-28.7
GP26	-30.4	-30.2	-30.1	-29.8	-28.9
GP27	-30.8	-30.9	-30.4	-29.8	-28.6
GP28	-30.0	-29.9	-29.6	-29.5	-28.5
LC29	-27.6	-27.3	-28.1	-27.3	-28.4
LC30	-27.6	-26.8	-26.9	-27.1	-28.0
LC31	-26.8	-26.4	-27.0	-26.5	-28.2
TH1	-26.9	-27.3	-28.1	-27.3	-28.0
TH3	-27.4	-27.8	-27.8	-26.9	-28.4
SPoil	-30.9	-30.5	-29.7	-29.5	-28.8*
PPoil	-30.5	-29.9	-29.3	-29.1	-28.5*

* extrapolated kerogen values

Table 4-9: Carbon isotopic values for kerogens and individual fractions.

Distributions of carbon isotopes associated with various types of oils (Type I, II and III) can be used to separate organic matter into classes. Williams (1974) assessed a suite of 184 samples from the Triassic to the Ordovician for $\delta^{13}C$.

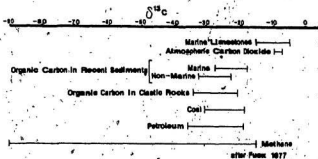


Figure 4-20: The distribution of carbon isotopes in some natural materials.

variations. His study found that Ordovician samples were limited to Type I organic matter and were slightly more positive than Type II and Type III organic matter (Figure 4-21). The Cow Head Group shales span the boundaries between Type I and Type II organic matter based on isotopic data. This correlates with Rock-Eval results to be presented later in this chapter (Section 4.6). Cow Head samples can thus be interpreted as an admixture of Type I and II organic matter, or a poor quality Type I organic matter (Macauley et al., 1987).

In an effort to determine the environmental importance of carbon isotopes, Sofer (1984) used a suite of 339 oils plus individual fractions to develop an effective depositional interpretation technique. The oils were divided into waxy and nonwaxy based on n-alkane distributions. Waxy oils have abundant $n\text{C}_{22}$ to $n\text{C}_{30}$ n-alkanes (terrestrial); and nonwaxy oils are most abundant around $n\text{C}_{17}$

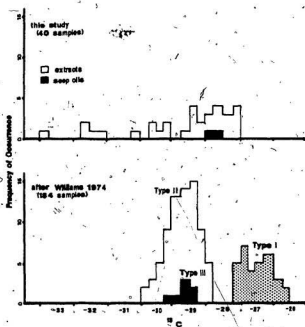


Figure 4-21: Frequency histograms of carbon isotopes for whole oils in relation to organic matter type.

(marine) (Sofer, 1984). It is important to reiterate that all oils and extracts from the Cow Head Group exhibit a non-waxy n-alkane distribution with a maximum of 18% n-alkane at nC_{17} and higher chain n-alkanes parabolically less abundant (see Section 4.2.1).

Variations between individual fractions are more useful than individual isotopes from whole oil. Biological and geochemical conditions will effect the isotopic compositions of each fraction differently (Sofer, 1984). Saturates and aromatics are useful in $\delta^{13}C$ interpretations as they are most easily obtained

(Fuex, 1977). Aromatics are the most enriched in $\delta^{13}\text{C}$, and saturates are most depleted (Fuex, 1977). Stahl (1978) suggests a general trend as follow:

$$\delta^{13}\text{C}_{\text{ker}} > \delta^{13}\text{C}_{\text{asp}} > \delta^{13}\text{C}_{\text{nos}} > \delta^{13}\text{C}_{\text{aro}} > \delta^{13}\text{C}_{\text{sat}}$$

$\delta^{13}\text{C}_{\text{aro}}$ versus $\delta^{13}\text{C}_{\text{sat}}$ are found in Table 4-9 and Figure 4-23a. These two isotopes have a linear relationship (Sofer, 1984). Samples that are waxy show a terrigenous isotopic value and plot in the lower right hand corner of the graph (Figure 4-23a). Cow Head Group extracts lie above the boundary determined for waxy (terrigenous) organic matter, and scatter around the non-waxy (marine) relation (Figure 4-23a). Some overlap exists between marine and nonmarine shales (Sofer, 1984). The differences between marine and nonmarine categories can better be described statistically (Table 4-11). Values calculated for terrigenous bitumens (Ter*) and marine bitumens (Mar*) from $\delta^{13}\text{C}_{\text{aro}}$ and $\delta^{13}\text{C}_{\text{sat}}$ and the canonical variable (CV) can be used to determine environment. The best fit equation for the Cow Head shales should be the equation for marine oils (Mar*) or an equivalent $\text{CV} < 0.47$ (Sofer, 1984). In Table 4-10 almost all Cow Head Group extracts and oils fit the marine/nonwaxy equation, with a few being terrestrial, however, still nonwaxy according to CV. Anomalous samples are from St. Paul's Inlet (SP12, SP13, SP14 and SP15) and contain high HC/extract when compared to other samples (Figure 4-1). Distributions of n-alkane shows an increase in $n\text{C}_{24}$ to $n\text{C}_{27}$ (Figure 4-7), and indicates these samples have been biodegraded or contaminated. Relatively high $\delta^{13}\text{C}$ from kerogen and individual fractions indicate some degree of biodegradation has taken place (Table 4-9).

UNIT	$\delta^{13}\text{C}_{\text{Caro}}$ $\delta^{13}\text{C}_{\text{Cest}}$	Ter*	Mar*	CV	Class	QC
PF1	0.9	1.8	0.7	-0.29	M/N	-
PF2	0.6	1.9	0.8	-1.20	M/N	0.077
PF3	0.5	1.8	0.7	-0.90	M/N	-
PF4	0.9	2.1	0.9	-0.94	M/N	0.064
PF5	0.2	1.7	0.7	-1.65	M/N	-
PF7	1.3	1.3	0.3	-1.84	T/N	0.033
CH8	-0.3	1.4	0.4	-1.90	M/N	0.067
CH9	1.0	1.6	0.6	0.40	M/N	-
CH10	0.7	1.6	0.5	-0.15	M/N	0.016
CH11	0.7	1.7	0.6	-3.45	M/N	0.040
SP12	1.7	1.7	0.6	-1.92	T/N	0.030
SP13	1.6	1.8	0.7	-1.23	T/N	-
SP14	1.3	1.4	0.3	-1.78	T/N	0.032
SP15	1.3	1.6	0.6	-1.12	T/N	0.009
SP16	0.6	1.8	0.7	-0.89	M/N	-
BP17	1.1	1.7	0.6	-0.46	M/N	0.010
BP18	1.1	1.8	0.7	-0.31	M/N	0.036
WB19	0.2	1.7	0.7	-1.63	M/N	0.096
WB20	0.9	1.9	0.8	-0.45	M/N	0.027
MP21	0.4	1.7	0.6	-1.09	M/N	0.044
MP22	0.8	1.8	0.7	-0.42	M/N	-
MP23	0.5	1.8	0.7	-1.18	M/N	0.003
GP24	0.0	1.9	0.8	-2.38	M/N	0.060
GP25	0.1	1.8	0.8	-2.25	M/N	0.080
GP26	0.3	1.8	0.7	-1.56	M/N	0.074
GP27	-0.1	1.7	0.7	-2.32	M/N	0.033
GP28	0.1	1.9	0.0	-2.13	M/N	0.077
LC29	0.3	2.1	1.0	-2.43	M/N	-
LC30	0.8	2.1	1.0	-1.34	M/N	-
LC31	0.4	2.2	1.2	-2.45	M/N	-
TH1	-0.3	2.2	1.1	-3.98	M/N	-
TH37	-0.4	2.2	1.0	-4.04	M/N	-
SFO11	0.3	1.7	0.7	-1.41	M/W	0.021
FFO11	0.6	1.8	0.7	-0.86	M/W	0.063

$$\delta^{13}\text{C}_{\text{Caro}} - \delta^{13}\text{C}_{\text{Cest}} = \text{Ter}^* = 0.12 \times \delta^{13}\text{C}_{\text{Cest}} + 5.45$$

$$= \text{Mar}^* = 0.10 \times \delta^{13}\text{C}_{\text{Cest}} + 3.74$$

$$\text{CV} = -2.53 \times \delta^{13}\text{C}_{\text{Cest}} + 2.22 \times \delta^{13}\text{C}_{\text{Caro}} - 11.65$$

N = nonwaxy, M = marine, T = terrestrial

Table 4-10: Environmental indicators using carbon isotopic compositions, (after Sofer, 1984).

An accurate measure for environmental determination uses CV and quadratic coefficients (QC) (Sofer, 1984). QC is calculated from the best fit quadratic curve for $n\text{C}_{10}$ to $n\text{C}_{33}$ for each sample: $\% \text{ n-alkane} = A(\text{carbon \#})^2 +$

$B(\text{carbon } \#) + C$, where A is the QC (Table 4-10). Sofer determined a linear correlation between the QC and CV (Figure 4-22). A vertical line corresponding to 0.47 divides the graph into marine and terrestrial, and a horizontal line divides the graph into waxy and non-waxy. The upper left corner would then be common to marine samples. Samples from this study are within these boundaries and are of marine origin, as expected for Ordovician hydrocarbons.

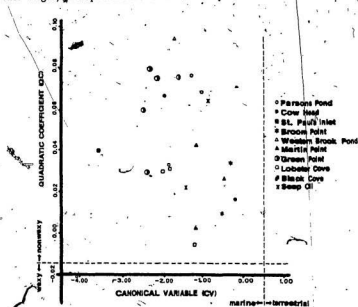


Figure 4-22: Environmental assessment using the quadratic coefficient and canonical variable, (after Sofer, 1984).

4.4.3. Isotopic Correlation

Carbon isotopes can be used as a tool in oil/oil and oil/source correlations (Stahl, 1978; Grizzle et al., 1979; Peters et al., 1985; Galimov and Frik, 1986; Fuex, 1987). Carbon in a rock is made up of kerogen, bitumen and dead carbon (charcoal). To eliminate differences between an oil and source rock, it is best to use isotopic values of extracted bitumens (Fuex, 1977), or pyrolyzed kerogen (Fuex, 1987). Geographically related oils correlate positively when the equivalent fractions differ by less than 1‰ (Fuex, 1977; Stahl, 1978; Sofer, 1984), the kerogen is within 1‰ of the oil at equal maturities (Fuex, 1977) or the extract is within 0.6‰ of the oil (Stahl, 1978). A linear relationship has been observed to exist between $\delta^{13}\text{C}_{\text{ker}}$ of the shales and $\delta^{13}\text{C}_{\text{asp}}$ from the extracts (Macko and Quick, 1986). The $\delta^{13}\text{C}$ of asphaltenes are generally more negative than $\delta^{13}\text{C}_{\text{ker}}$ (Figure 4-23c), and scatter about the linear relationship.

Two oils may have similar isotopes but distinctive fraction compositions. An isotopic type curve technique applies these variations showing that $\delta^{13}\text{C}$ increases with increasing polarity within the fractions (Silverman, 1971; Galimov, 1973). Stahl (1977) has applied the systematic variation in carbon isotopes from fraction to fraction to determine oil/oil and oil/source correlations using regression analysis, and estimated kerogen values based on $\delta^{13}\text{C}$ of each fraction. When the estimated kerogen is within -0.5‰ of an associated oil/extract, the oils are genetically linked (ΔK , Table 4-11). When estimated kerogen is within 0.6‰ of asphalt isotopes from a related extract or oil, the crudes can again be genetically linked ($\Delta\text{K-asp}$, Table 4-11). Table 4-11 shows estimated kerogens for St. Paul's

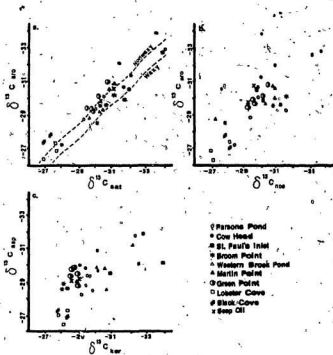


Figure 4-23: a. depositional determination (after Sofer, 1984); b. aromatic-verses NOS, (after Schoell, 1983); c. asphalt versus kerogen, (after Macko and Quick, 1986).

Inlet (SPoil) and Parsons Pond (PPoil) in relation to the shale extracts. Variations between the two different oils (SPoil, PPoil) which are themselves genetically related are not significant. Both ΔK -asp and ΔK indicate that samples most likely to be associated to the oils are from Green Point (GP24, GP25, GP26 and GP27), Parsons Pond (PP3), St. Paul's Inlet (SP16) and Martin Point (Mf-22). are found in St. Paul's and Broom Point Member shales.

UNIT	ΔK		$\Delta K\text{-asp}$	
	SPoll	FPoll	SPoll	FPoll
PP2	-0.6	-0.9	0.1	-0.3
PP3	-0.13	-0.6	0.4	0.0
PP4	-0.6	-0.9	0.1	-0.3
PP5	-0.9	-1.2	-0.2	-0.6
PP6	-0.6	-0.9	0.1	-0.3
PP7	-3.5	-3.8	-2.8	-3.2
CH8	-0.6	-0.9	1.0	-0.3
CH9	-1.3	-1.6	-0.6	-1.0
CH10	-0.4	-0.7	0.3	-0.1
CH11	-1.5	-1.8	-0.8	-1.2
SP12	-3.7	-4.0	-3.0	-3.4
SP13	-2.2	-2.5	-1.5	-1.9
SP14	-3.9	-4.2	-3.2	-3.6
SP15	-5.0	-5.3	-4.3	-4.7
SP16	0.3	0.0	1.0	0.6
SP17	0.6	0.3	1.3	0.9
SP18	0.4	0.1	1.1	0.7
WB19	-1.4	-1.7	-0.7	-1.1
WB20	-1.6	-2.1	-1.1	-1.5
MP21	-3.2	-3.5	-2.5	-2.9
MP22	-0.1	-0.4	0.6	0.2
MP23	-1.9	-2.2	-1.2	-1.6
GP24	-0.1	-0.4	0.6	0.2
GP25	0.1	-0.2	0.8	0.4
GP26	-0.1	-0.4	0.6	0.2
GP27	0.2	-0.1	0.9	0.5
GP28	0.3	0.0	1.0	0.6
LC29	0.4	0.1	1.1	0.7
LC30	0.8	0.5	1.5	1.1
LC31	0.6	-0.3	1.3	0.9
TH1	0.8	0.5	1.5	1.1
TH37	0.4	0.1	1.1	0.7

$$\Delta K = \delta^{13}\text{C Kerogen} - \delta^{13}\text{C Kexk}$$

Kexk = Extrapolated Kerogen from Stahl's curves (1977)

$$\Delta K\text{-asp} = \delta^{13}\text{C Kerogen} - \delta^{13}\text{C Asphalt}$$

Table 4-11: Correlation parameters based on Stahl, 1978.

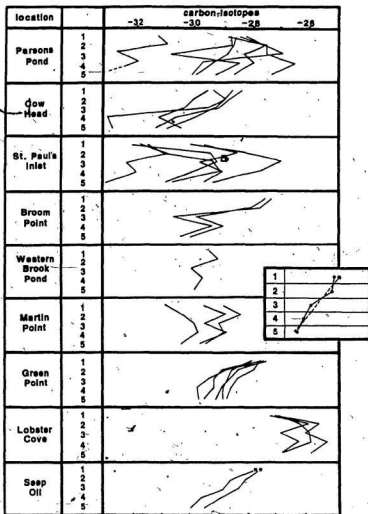
Visual inspection of isotope curves can be used to characterize oils. Distribution of $\delta^{13}\text{C}$ between fractions of increasing polarity is effective as a correlation tool (Stahl, 1978; Galimov and Frik, 1986). The curves are based on $\delta^{13}\text{C}$ ratios of saturates (5), aromatics (4), NOS (3), asphaltenes (2) and kerogens (1: both measured and extrapolated), plotted according to their polarity (Figure

4-24). Equal spacing along the Y axis is arbitrary and the X axis show increasing isotopic values. Extrapolated kerogens are a result of the best linear fit calculated by linear regression. Curve morphologies are a distinguishing feature and advantage of this approach. There are three type of curves found in this study, sublinear, arched (also recorded by Galimov and Frik, 1986) and irregular. Curves that are sublinear or arched have a small range between fraction isotopes (2 to 3°/oo), curves that are irregular have a larger range (>3°/oo). Similar measured kerogen and extrapolated kerogens are found in Green Point, Broom Point and Lobster Cove samples. Variations between fractions, or total curve morphologies, are similar for the Green Point and seep oils, both showing sublinear curves.

The general use of isotopes to interpret source correlations using isotopic type curves and ΔK , ΔK_{asp} calculations indicate an excellent correlation between samples from the Green Point type locality and local seep oils.

4.4.4. Isotopic Maturation

The effect of maturation on isotopic composition is controversial. Isotopes are useful in correlation studies because they are unaffected by maturation (Fuex, 1977; Schoell, 1983). However, some increase in $\delta^{13}C$ with maturity has been observed (Stahl, 1980; Sofer, 1984), and the isotopic composition of each fraction is internally consistent with the degree of maturation (Chung et al, 1981). Variations between whole oils and fractions can best be explained by maturation. The heavier the isotopic composition, the more mature the samples. In relation to individual fractions, the carbon isotopic composition of saturates increases as weight percent increases. For all other fractions, the isotopic composition increases



* extrapolated kerogen value
 1 - Kerogen 2 - Asphalt 3 - NGS 4 - Aromatic 5 - Saturate

Figure 4-24: Isotopic type curves, (after Stahl, 1978).
 Inset is a typical marine oil curve.

as the weight percent decreases. Figure 4-25b shows the Cow Head Group saturates have the opposite relation and are immature. Aromatic relationships

show no trend and form a scatter (Figure 4-25c). The isotope composition of asphaltene plotted to weight percent is asymptotic (Chung et al., 1981) (Figure 4-25a). Isotopic compositions of asphaltenes become heavier as weight percent decreases and maturity increases, possibly indicating asphalt as being a source for other fractions (Chung et al., 1981). The gross composition and isotopic variations indicate that maturation has slightly influenced the individual fractions and effects are only observed in the asphaltenes.

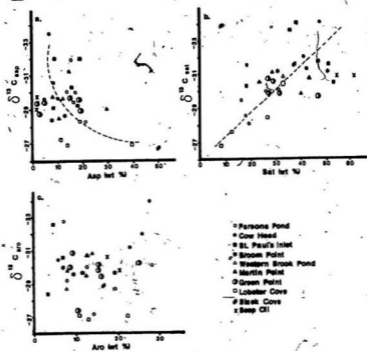


Figure 4-25: Weight percent versus carbon isotopes for individual fractions, (after Chung et al., 1981).

4.5. Nitrogen Isotopes

The distribution of nitrogen in natural biogenic material has been used for interpretation of environments, hydrocarbon migration and sedimentary cycling (Hoering and Moore, 1958; Wada et al., 1975; Grizzle et al., 1979; Macko and Parker, 1983; Robertson, 1988). Nitrogen applications to isotopes in geochemical exploration or source rock evaluation are limited (Grizzle et al., 1979; Macko and Quick, 1986). Some natural abundance of ^{15}N in organic and inorganic substances are summarized in Figure 4-26. The $\delta^{15}\text{N}$ varies from -12 to +25 ‰ relative to atmospheric nitrogen. Stahl (1977) suggested a range in crude oils of approximately -9 to +9 ‰, which is the largest distribution found in the literature and on average is much lower than $\delta^{15}\text{N}$ for crudes proposed by Hoering and Moore (1958; +1 to +7 ‰), Wada et al. (1975; 0 to +7 ‰), Grizzle et al. (1979; +3 to +13 ‰) and Hoefs (1980; 0 to +15 ‰). Total range for crude oils encompassing all the literature is from -9 to +15. Sources for petroleum can be associated with terrestrial, marine and atmospheric nitrogen having similar ranges based on reported data (Figure, 4-26).

4.5.1. Nitrogen Source Correlation

Stahl (1977) and Macko and Parker (1983) suggested $\delta^{15}\text{N}$ ratios would be useful in petroleum exploration and source correlations due to their wide range in values (20 ‰) as compared to $\delta^{13}\text{C}$ (10 ‰). Limited amounts of nitrogen are found in hydrocarbons and are usually as low or lower than 0.1 % (Macko, 1981).

The $\delta^{15}\text{N}$ for the Cow Head Group extracts and oils range from -6.9 ‰ to

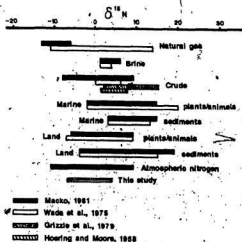


Figure 4-26: Variations in nitrogen isotopes in some natural materials.

+4.4‰ (Table 4-12). Fractionation during migration and maturation causes a decrease in $\delta^{15}N$, favoring the lighter ^{15}N isotope in natural gas (Stahl, 1977). Migration may mask the effect of maturation (Stahl et al., 1976). Oils are slightly more mature than extracts from the Cow Head Group, and have a light $\delta^{15}N$ (-1.5). Lobster Cove (LC29, LC30 and LC31) and Table Head (TH1 and TH37) show more positive $\delta^{15}N$ due to their high maturity. Samples most similar to the oils include Green Point Formation shales (PP4; SP16, BP18, MP22, MP23, GP24, GP25, GP26 and GP27). Grizzle et al. (1979) suggested that $\delta^{15}N$ values of extracts within -1.5‰ of an associated oil can be used for genetic relation, although oils became more negative with maturation. Those samples from the Cow Head Group that are within -1.5 ‰ of the oil include PP4, SP16, BP18,

GP25, GP26 and GP27. This suggests a correlation between the Green Point Formation and the seep oils.

UNIT	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
PP3	-28.3	3.0
PP4	-29.5	-2.5
PP5	-28.4	2.0
PP6	-28.6	2.3
CH8	-29.7	-1.3
CH9	-29.7	0.1
CH11	-30.8	0.3
SP14	-31.9	-1.1
SP15	-30.2	0.2
SP16	-29.2	3.0
BP18	-28.6	-2.6
WB19	-29.9	4.4
MP22	-29.2	-5.1
MP23	-29.8	-6.9
GP24	-29.5	-5.2
GP25	-28.9	-2.3
GP26	-29.8	-1.5
GP27	-29.8	-2.1
LC29	-26.9	-5.2
LC30	-27.1	-6.3
LC31	-27.2	-4.6
TH1	-27.3	2.6
TH37	-26.9	-1.3
Oil	-29.6	-1.5

Table 4-12: Nitrogen isotopes from selected Cow Head Group kerogens and oils.

The values of $\delta^{15}\text{N}$ change throughout the geological record (Grizzle et al., 1979). The Permian was enriched in $\delta^{15}\text{N}$ compared to pre-Permian and post-Permian crudes. The most striking result of the N_2 analysis is that many of the Cow Head samples have $\delta^{15}\text{N}$ much lower than those of most forms of modern and recent nitrogen. The Cow Head shales are the oldest recorded $\delta^{15}\text{N}$ on extractable material reported to date. The oldest samples previously had been from the Silurian (Grizzle et al., 1979). By superimposing $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ data from this study onto a proposed relation with determined age windows, Cambro-Ordovician samples fall independently in the upper left (Figure 2-27). This

indicates a lighter isotopic influence in organic matter in ancient depositional sequences associated with variations in biogenic and atmospheric cycles at that time.

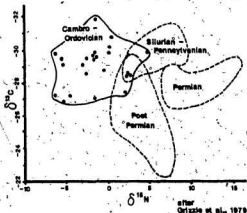


Figure 4-27: Nitrogen isotope composition of kerogen versus carbon isotope asphaltene values, (dashed boundaries after Galimov and Frik, 1986).

The distribution of nitrogen isotopes can be used to evaluate the original depositional environment in relation to oxygen depletion and ocean circulation. In stratified oceanic conditions lower $\delta^{15}\text{N}$ values are often found as a result of reduced nutrient supply and increased N_2 fixation. Stratified oceans produce abundant nutrients during periods of upwelling or land plant input and favor NO_3^- and NH_4^+ production, tending to result in a heavier isotopic composition of the organics (Saino and Hattori, 1987; N. Ostrom, pers. com.).

In applying these ideas to the Cow Head Group, at least three changes in circulation can be determined (Figure 4-28). Consistent negative $\delta^{15}\text{N}$ through

Cow Head Bed Nos. 8 and 11 indicate stratified conditions and intermediate or bottom anoxic conditions. This correlates well with high levels of TOC for these intervals. Extreme negative values in beds 6 and 15 may indicate maximum extent of the anoxic event and a large input of nutrient material that produced maximum primary fractionation. Debris flows that are common in the Cow Head Group would supply the quantity of nutrients required. Bed 13 has more positive $\delta^{15}\text{N}$ and perhaps indicates a change in ocean circulation to an unstratified event with open circulation. This coincides well with the increase in abundance of red/green shales (Figure 4-28).

Finally a general trend to more negative values from proximal to distal could indicate more limited nutrients in the deep offshore environment when oxygen levels appear to be lower and encouraged preservation:

Isotope information from both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ indicate Cambro-Ordovician type oils. Original depositional environments are marine (non-waxy). Maturity can be associated only on a relative basis and indicates the seep oil is more mature. Variation in total isotope distribution show maturation trends across the Humber Arm Allochthon (discussed in Chapter 5) and strong oil/source correlation between the seep oils and the Broom Point and St. Paul's Member shales from the Green Point Formation.

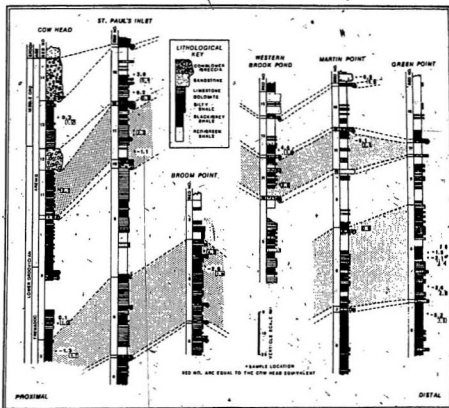


Figure 4-28: Distribution of nitrogen within the Cow Head Samples. Small numbers in boxes indicate TOC, Large are $\delta^{15}\text{N}$.

4.6. Rock-Eval. Pyrolysis

Determination of maturity using more than one technique is recommended for accuracy, especially with marine-organic matter because it is lipid rich. Rock-Eval pyrolysis provides a final assessment for this study. Pyrolysis was carried out on 25 extracted samples (Table 4-13), using a Rock-Eval II pyrolysis instrument.

Extracted samples are rarely used though bitumen does contribute slightly to the P2 peak (Snowden, 1984; Peters, 1986).

Sample name	TOC %	Concentration, ppm			Tmax	PI	HI	OI	GP
		P1	P2	P3					
PP2	0.66	220	590	-	444	.24	105	-	910
PP4	1.54	540	3810	-	440	.14	247	-	4450
PP5	2.56	2510	10590	-	442	.19	414	-	13100
CH8	1.10	210	3990	-	442	.05	363	-	4200
CH9	0.57	220	1170	-	434	.16	205	-	1390
CH10	0.66	300	1710	-	439	.15	259	-	2101
CH11	0.88	180	1980	-	443	.08	248	-	2160
SP12	1.25	340	4850	-	442	.07	388	-	5290
SP15	0.15	70	530	-	439	.12	353	-	600
BF17	1.34	570	5670	-	441	.09	423	-	6240
BF18	2.73	850	14550	-	442	.06	533	-	15400
WB19	1.52	490	6270	-	440	.07	413	-	6760
WB20	1.48	760	6730	-	438	.10	481	-	7490
MP21	0.95	350	3120	-	436	.10	328	-	3470
MP22	1.46	900	4420	-	436	.17	303	-	5320
GP25	1.95	940	10180	-	442	.08	522	-	11120
GP26	1.72	860	6860	-	439	.11	394	-	7520
GP27	1.82	640	8120	-	435	.07	446	-	8760
GP28	1.49	440	6590	-	438	.06	442	-	7030
LC32	2.58	1540	310	-	571	.83	12	-	1850
TH37	1.43	1210	100	-	450	.92	-	-	1310

PI = Production Index = P1/(P1+P2)

HI = Hydrogen Index = P2/TOC

OI = Oxygen Index = P3/TOC*

* = P3 less than 10 and thus not recorded

GP = Generation Potential = P1+P2

other abbreviations explained in the literature

Table 4-13: Results from Rock-Eval analysis.

Source rocks of petroleum are characterized by generation and migration of hydrocarbons. Standard laboratory pyrolysis or artificial heating of samples (Figure 4-20) can help determine the amount of free or generated hydrocarbons present in the rock (P1) at 300°C. Heating of the kerogen at 25°/min generates potential or pyrolytic hydrocarbons (P2). Trapped CO₂ and water are released during thermal cracking up to 390°C (P3) (Barker, 1974; Tissot and Welte, 1984). Measurement of P1 and P2 are done with a flame ionization detector (FID). P3 is limited to a narrow temperature window and is difficult to collect (Tissot and

Welte, 1984). In this study, P3 was extremely low in concentration and resulting oxygen indices (OI) were <10 (Table 4-13).

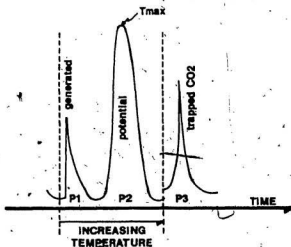


Figure 4-29: Generation products from programmed Rock-Eval pyrolysis, (after Tissot and Welte, 1984).

A fourth factor, "Tmax", corresponds to a maximum hydrocarbon generation temperature during pyrolysis and is useful for evaluation of maturation. Hoffmann et al. (1987) have suggested that Tmax is perhaps related to organic matter type rather than maturity. Tmax is useful for organic matter maturation if the organic type is uniform and Type III (Hoffmann et al., 1987). Type I and II organic matter (ordovician organics) is not as useful as a maturation index. Tmax for the Cow Head Group shales averages 441 ranging from 435 - 444, or low to early maturity (Figure 4-30). This is similar to Tmax values determined by Macauley et al., (1987) for the same area. Notable exceptions are the Lobster Cove and Table Head Tmax values that are overmature (571) and highly mature (450).

MATURITY						
		PI	Tmax	HI (I)	HI (II)	Ro
immature	low	0.02	435	900	600	0.3
		0.05	438			0.4
		0.10	443			0.5
mature	high			700		0.6
		0.25	455	500	400	0.7
		0.40	465	200	200	0.8
overmature		0.50		0	0	0.9
						1.0
						1.2
						1.35
						2.0
						3.0

after Macauley et al., 1985

Figure 4-30: Maturation parameters based on organic matter type and Rock-Eval data.

4.6.1. Genetic Potential

Typical Rock-Eval data can indicate economic potential, maturation, and organic matter type. Parameters used are based on the previous mentioned factors (P1, P2, P3 and Tmax) and TOC. Genetic Potential (GP) = (P1 + P2), also referred to as Hydrocarbon Potential, represents the total of all HC available in the rock for pyrolysis, or the economic capability (Macauley et al., 1985). Qualities of organic matter for a given deposit are determined by a ratio of GP to TOC. The Cow Head Group shales all contain relatively small percentages of TOC in relation to GP (Figure 4-31). Qualities of the Cow Head Group shales are 10.1 kg/t as compared to lower values of 9.2 kg/t for the Table Head, and 7.2 kg/t for Lobster Cove shales. Converted into average yield potential based on an average specific gravity of 0.85 (Flemming, 1970), Cow Head Group shales have a potential of 59.5 kg/t (70 l/t), considered a high yield. Lobster Cove and Table Head are considerably lower, 18.5 kg/t (21.8 l/t) and 13.2 kg/t (15.5 l/t) respectively. Minimum required yield for economic consideration is 41.8 l/t (Macauley et al., 1985). The Cow Head samples fall within this range, with the highest potential from Green Point and Broom Point localities and one sample from Parsons Pond (RP5) (Table 4-13).

Tissot and Welté (1984) determined an acceptable GP for potential source rock. Shales with genetic potential values <2000 ppm are a non-source rock with some potential for gas production. PP2, CH2, SP15 and the Lobster Cove and Table Head shales are the only shales that are <2000 ppm (Table 4-13). GP from 2000 - 6000 is considered to be a moderate source rock and found in PP4.

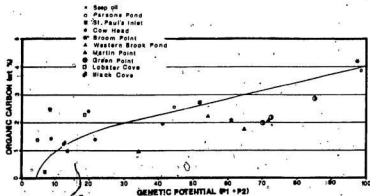


Figure 4-31: Economic potential based on TOC and genetic potential:

CH8, CH10, CH11, SP12, MP21 and MP22. Samples with good potential as source rocks (>6000) include shales from Green Point, Broom Point, Western Brook Pond and PP5. Samples with high genetic potential (PP5, BP18, GP25) originate from the Broom Point Member of the Green Point Formation and indicate increasing Type I/II organic matter concentrations (Tissot and Welte, 1984).

4.6.2. Organic Matter Type

The Hydrogen Indices (HI) = (P2/TOC) can be used in conjunction with Tmax or the Oxygen Indices (OI) = (P3/TOC) to determine kerogen type and maturation (Espitalie et al., 1977). HI verses OI lie near the Y axis (Figure 4-32). OI is negligible and indicates low oxidation during deposition with good organic preservation. The Cow Head Group shales are composed of Type I organic matter that is moderately mature or immature Type II based on HI and OI relations. Lobster Cove and Table Head samples lie near the origin showing high maturity.

It is common in Ordovician samples to have reduced amounts of oxygen indicating good generation potential (M. Fowler, Pers. Com.).

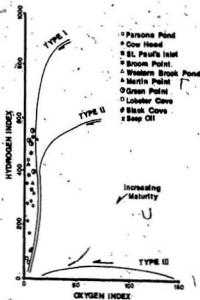


Figure 4-32: Organic matter types in relation to hydrogen and oxygen indices.

Tmax and HI compositions (Figure 4-33) exhibit a slight inverse relation and indicate low maturity at the petroleum generation stage (Macauley et al., 1985). In comparing Tmax to Type I and II organic matter, the Cow Head Group shales are low to moderately mature, poor quality Type I organic matter or good quality

Type II organic matter (Figure 4-30). Lobster Cove shales are overmature and Table Head are highly mature for both Type I and II organic matter. Samples from Green Point, Broom Point and Western Brook Pond are enriched average Type I organic matter or excellent Type II organic matter (Figure 4-30).

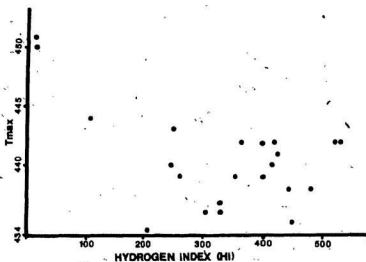


Figure 4-33: Tmax verses hydrogen indices.

4.6.3. Production Index

The Production Index (PI) or Transformation Ratio (Tissot and Welte, 1984) represents the ratio of volatile HC (P1) to Genetic Potential (P1 + P2) and indicates thermal maturation or migration. PI values for Cow Head Group Shales range from 0.06 - 0.24 which cover a broad range compared to PI values from Macauley et al. (1987), for a similar suite of samples (0.15 - 0.18) and a smaller range than another study by Macauley (1987) of 0 - 0.48. The range of PI in this study covers low to moderate maturity (Figure 4-30) and correlates to Tmax and

HI. Both the Lobster Cove (0.83) and Table Head (0.92) samples are overmature, similar to Macauley et al. (1987). Tmax should increase with the value of PI and maturity (Barker, 1974). PI to Tmax show a slight linear relationship at extreme values (Figure 4-34).

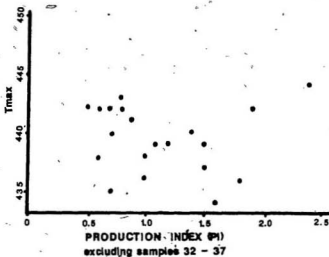


Figure 4-34: Tmax versus the production index.

Rock-Eval data indicate Cow Head Group extracts are low to marginally mature, with the exception of the Lobster Cove and Table Head which are high to overmature. The organic matter is either a poor quality Type I or good-quality Type II and may be an admixture. Isotopic values for kerogen also indicate mixed Type I and II kerogen (Figure 4-21). Lastly, the potential for the Cow Head Group shales has been assessed as good "economically" for samples from Green Point and Broom Point localities within the Broom Point Member shales and

below economic values for the rest of the sample suite including Lobster Cove and Table Head. This economic capability is viable only when assessed in conjunction with geological setting, source rock volume, organic matter quality and type.

Chapter 5

Summary and Conclusions

5.1. Environment of Deposition

The use of geochemistry to reconstruct depositional environments is relatively new (Tissot and Welte, 1984). Generally, migration lowers the content of geochemical material but does not alter the character of the geochemical fossils. Relative distributions of chemical compounds can indicate the amount of preservation and environment of deposition.

5.1.1. Carbonate/Clastic

Pure carbonates usually contain little organic matter, and a lower minimum TOC is proposed for carbonate rich source rocks (Hunt, 1967). The abundance of either carbonate or shale in the environment is determined by the type of organic matter present in the seep oils. Carbonate/evaporite sourced hydrocarbons have low CPI's (<0.8), high isoprenoid/n-alkane ratios (>1), low pristane/phytane, low C_{34}/C_{29} hopane (<0.1), hopane concentrations are greater than those of the steranes, and normal steranes are relatively more abundant than rearranged steranes and Tm/Ts is high. The Cow Head Group extracts have relatively high CPI (>1.00); low isoprenoid/n-alkane (<<1), high pristane/phytane and high C_{34}/C_{29} (>0.17) indicating clastic deposition. The environment is dominantly

clastic (shale) with local carbonate influences. This interpretation is strengthened by the sedimentology found within the Cow Head Group which is comprised of interbedded breccias, limestones and carbonate rich shales.

5.1.2. Anoxic/Oxic

Anoxic (anaerobic) low oxygen conditions aid preservation of a high percentage of organic matter. Where marine autochthonous organic matter is preserved in abundance usually indicates anoxic conditions (Tissot et al., 1970). The predominance of easily degraded organic material occurs where conditions are strongly reducing. Types of easily degraded material that indicate reducing conditions in the Cow Head Group shales are; high concentrations of hopanes (peaked at nC_{30}) relative to steranes, relative abundance of normal steranes, extreme negative $\delta^{15}N$, pristane/phytane < 0.75 and pristane/ $nC_{17} > 1.0$. These characteristics coincide with bulk chemistry (high HC and TOC in deeper depositional settings) and abundance of fine grained, black shales. Low oxygen index (OI) from Rock Eval analyses strengthens these types of conditions. Oxidizing conditions and/or biodegradation are observed where the amount of saturate is $> 25\%$ and NHC is $> 60\%$ (found only in Lobster Cove shales). Abundant C_{24} to C_{27} and high pristane/ nC_{17} can also indicate oxidation and/or biodegradation (SP13, SP14 and SP15).

Zones of anoxia can be determined by the amount and distribution of preserved organic matter with relation to original sedimentary deposition. Figure 5-1 proposes a hypothetical environment, based on preservation of organic matter, geochemical biomarkers and $\delta^{15}N$. The proposed environment favors a medial

anoxic zone with oxygen rich surface and bottom waters. A cycling sequence from stratified (anoxic) to unstratified (oxic) conditions may or can be inferred from the nitrogen data (Figure 4-28).

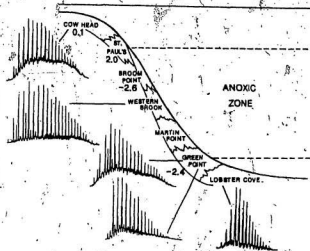


Figure 5-1: Anoxic conditions associated with the original continental shelf margin, numbers indicate nitrogen isotopes.

The preservation of organic matter for the shales is under anoxic to dysaerobic conditions; the influence of oxygen is indicated by biodegradation in some samples. Preservation is best along the lower shelf of the original margin. Interpretation of extreme distal facies is difficult as Lobster Cove shales are overmatured, however lower Green Point extracts (GP28) show an oxygen

influence, and are less preserved. Stratified oceans can be assumed from relation of $\delta^{15}\text{N}$, sedimentology and geochemical fossil preservation.

5.1.3. Marine/Terrestrial

One of the first determinations in organic geochemistry is the type of dominant organic material, either marine or non-marine in character. Marine organic matter comprises amorphous sapropelic material deposited in an aquatic regime, corresponding to Type II (non-waxy) kerogen. Saturated hydrocarbons are generally from 30-70%, aromatics from 25-60% and isoprenoids are abundant relative to normal n-alkanes. Steranes and terpanes are abundant but decrease with depth and maturation (Tissot and Welte, 1984). Sources for organic matter are algae (sterols) and prokaryotes (hopanes) containing abundant lipid material. This type of organic matter occurs in areas of high productivity and is preserved in sediments under anoxic conditions (Tissot et al., 1979).

In contrast, non-marine or terrestrial organic matter corresponds to Type III (waxy) kerogen, which is gas prone. Saturates are >60% with abundant n-alkanes, aromatics are <30%, isoprenoids and steranes are abundant (Hunt, 1979). Continental organic matter is mainly composed of higher land plants and is rich in cellulose and lignin.

Determination of the origin of organic matter for the Cow Head Group shales was done using n-alkanes, steranes and isotopic distributions. The most distinguishing geochemical feature that separates marine and terrestrial environments are n-alkane distributions. Maximum n-alkane concentration in low

molecular weight hydrocarbons from nC_{12} to nC_{20} , followed by a systematic decrease indicate marine organic matter. In contrast abundant nC_{22} to nC_{29} , and odd dominance in the nC_{29} region are common for terrestrial organic matter (Scalan and Smith, 1970). The Cow Head Group shale extracts are abundant in the low molecular weight range and decrease in the higher ranges with odd dominance from nC_{15} to nC_{21} , common in marine shales. A low percent of methyl-steranes (<10%) and dominant C_{29} sterane indicates low terrestrial input and marine dominance.

Carbon isotopes have been extremely useful in environmental interpretation (Sofer, 1984). Equations for marine and terrestrial organic matter using saturate and aromatic $\delta^{13}C$ coupled with CV (<0.47), and QC indicate a marine origin for all Cow Head Group shale extracts. These results are not surprising as the Ordovician predates the development of vascular land plants, and studies for marine/terrestrial organic material have been useful for verification.

5.2. Organic Matter

5.2.1. Kerogen Type

Of the types of organic matter proposed in Chapter I (Introduction), two are frequently observed in nature (Type II and III). Distinction of these Types is essential for a source rock assessment, as different types have different hydrocarbon potentials. A source rock must contain sufficient oil-prone organic matter. Comparisons of bitumen must be between rocks of similar organic matter type.

Both optical and physicochemical methods are applied. Physicochemical methods used in this study also include Rock Eval pyrolysis. Comparisons of the amount of hydrogen to oxygen generated in relation to carbon during pyrolysis applied to the "Van Krevlan" diagram determine organic matter type (Figure 4-32). Samples with a high percent of hydrogen and low oxygen are Type I and II kerogens. Type III (terrestrial) kerogen has a low Hydrogen index and high Oxygen index. All Cow Head Group shales are low in oxygen and high in hydrogen content, interpreted as Type I or admixed Type I and II kerogen. Carbon isotopes strengthen this interpretation. $\delta^{13}\text{C}$ is slightly more positive for Type I than Type II and III kerogen. Cow Head shales lie between Type I and II kerogen ranges. Aromatics, or more specifically methylthiophene (MDBTh) can be useful for kerogen interpretation, and suggests Type II organic matter for the Cow Head Group shales (MDR is 1.5% less than Type III).

Type III kerogen has been eliminated as it represents terrestrial organic matter not occurring in Ordovician oils. All the Cow Head Group shales are either Type I or II organic matter. It has been suggested that Ordovician organic matter is derived from Type I kerogen (Connan et al., 1986). Type II or admixed II and I kerogens have been proposed by others (Macauley et al., 1985). The Cow Head Group samples favor Type II organic matter with some influence from Type I.

5.2.2. Original Biogenic Material

Environmental and organic matter studies, emphasize the importance of the original biomass. Geochemical fossils are particularly useful as they retain the character of the original material. The Cow Head Group samples can be interpreted as containing abundant prokaryotic organisms. This is substantiated by a large amount of hopanes, high C_{34}/C_{24} diterpanes (>1.02), and high relative percent of rearranged steranes to normal steranes.

The influence of algae in the Cow Head Group is evident in the dominance of nC_{13} to nC_{19} , rich isoprenoids, abundant terpanes and dominance of C_{29} sterane over C_{28} . A dominance at nC_{17} observed in the Cow Head shale extracts corresponds to a fossil algae suggested as a precursor to many Ordovician marine shales (Hoffmann et al., 1986). This eliminates the influences by photoplankton which require a minimum at nC_{17} . These studies agree strongly with petrographic work by Macauley et al., (1987). These authors interpreted the Cow Head as containing abundant algal cysts, *Gloeoecapsomorpha prisca* Zalesky 1917, and fluorescing bitumen.

5.3. Maturation

Maturation in the Humber Arm Allochthon region can be determined by geochemical analyses and may be interpreted in relation to both burial and regional tectonics. In source determinations the most important factor is the location of the shale in relation to the oil window. Source rocks must undergo catagenesis at some point in time or at some location to be considered a source for the seep oils in the Parson Pond area. It is important to reiterate, that in outcrop,

the Humber Arm Allochthon shales are immature and only a few have entered the upper limit of the oil window (Table 5-1). Unfortunately, this study is limited to surface sampling and therefore it can only be assumed that with depth or perhaps associated with thrust faults, that maturation has reached an extent sufficient to have generated oil.

METHOD	NATURATION RESULTS AND RELIABILITY*
$\delta^{15}N$	● More positive for oils, high maturity or effect of migration.
Isoprenoid	● Pr/C ₁₈ = 0.3 for extracts = moderately mature.
Amount HC	● HC/EXT = 50 = low maturity. Lobster Cove and Table Head = 10 = high maturity.
n-Alkane	● Extracts are within the oil window. Low molecular weight preserved in Cow Head, St. Paul's and Broom Point localities.
Sterane/ Terpane	● Cow Head, Parsons Pond and St. Paul's are immature. Broom Point, Western Brook, Martin Point and Green Point are highly mature (based on stereo-isomers).
$\delta^{13}C$	● Maturity increases across allochthon from -32.3 to -28.4.
Aromatic	● MPI is immature at Cow Head and St. Paul's, and moderate for the rest of the samples.
Rock Eval	● Tmax = 411 for the extracts (low to early), and more than 450 for Lobster Cove and Table Head (over to high).

* Levels of reliability:

low = ● fair = ● good = ●

Table 5-1: Summary of maturation results.

Regional trends in maturation indicate an increase from the coastal exposures towards the Long Range Mountains, and across the coastal platform (Table 5-1). Carbon isotopes range from -32.3‰ along the coast to -24.4‰ near the Long Range Mountains (Figure 5-2). This increase in the heavier ¹³C isotope represents an increase in maturation. Similar patterns are observed with MPI, Tmax and Specific Ions (Figure 5-3). Retention of low molecular weight n-

alkanes and light aromatics decrease across the Allochthon. Northerly trends along the coast have not been noted.



Figure 5-2: Average carbon isotope values across the Allochthon.

The observed increase in maturation toward the Mountains is here interpreted as a result of the remobilization of the Long Range Inlier during the Devonian (Williams et al., 1985). The effects of maturation are slight and the entire region is immature to low maturity. Exceptions to these regional patterns are the Lobster Cove shales that are extremely mature and interpreted as a floudering melange block (James and Stevens, 1986). The Table Head samples have a high maturation and lie at the base of the oil window.

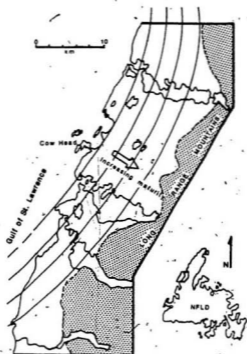


Figure 5-3: Regional trends in maturation.

An interpretation of regional changes in association to the seeps indicates that the oil (which itself is moderately mature) has been generated by: 1) more easterly portions of the allochthon or 2) as a result of the generation of HC from thermal stress which occurred associated with thrust surfaces. Faults may also serve as a path for migration of the oil:

5.4. Source Rock Characterization

Interpretation of source rocks is most reliable when more than one geochemical method is applied. The techniques used in this study are not equally reliable and must be treated on a relative scale. Table 5-2 indicates the relative reliability of selected methods (Tissot and Welte, 1984), and results of correlation studies.

Results obtained from the shales in the Cow Head Group indicate that the most probable source (or that with the most similar chemistry to the oils that has not undergone severe biodegradation or alteration), are samples from the Green Point type locality. Sedimentologically, this formation represents the more favorable sequence. The average grain size is finer than sediments found within the Shallow Bay Formation and at more proximal localities. This feature is desirable for the best preservation of organic matter, and high HC/TOC. Distal facies of the Cow Head Group are the source of detrital material under the presence of reduced oxygen conditions favoring increased organic content.

Chemically, the distribution of lipids (n-alkane and geochemical biomarkers) indicate that there is a good correlation to seep oils, from the Green Point type locality. The Broom Point Member of the Green Point Formation is liklied at the Green Point and Martin Point outcrops (Table 5-2). These outcrops have adequate organic content and a higher portion of bituminous organic material. One of the most striking similarities between the oils and extracts is from carbon isotopic studies, which indicate a positive correlation between the oils and the Green Point Formation. Bed Number 8 of the Cow Head Equivalents (James and Stevens, 1986) is the most acceptable source based on present data.

Samples		HC/TOC	Adipic AC17	Is-alkane chromat.	DBP	Pr/PC17	Ph/C18	Pr/Ph	hopanes	steranes	Aromatics	Δ ¹⁴ C _{org}	GC curves	GC curves	GC curves	Basalts
		●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
PP2	GP	+	-	-	+	+	+	+	+	+	+	+	+	+	+	+
PP3	SP	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PP4	GP	-	-	-	+	+	+	+	+	+	+	+	+	+	+	+
PP5	BP	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PP6	SP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
PP7	SB	-	+	+	+	+	+	+	+	+	+	+	+	+	+	+
CH8	SI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH9	FC	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH10	FC	+	-	+	+	+	+	+	+	+	+	+	+	+	+	+
CH11	FC	+	+	-	-	+	+	+	+	+	+	+	+	+	+	+
SP12	SP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
SP13	SP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
SP14	SP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
SP15	SP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
SP16	SP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
BP17	BP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
BP18	BP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
MB19	SP	+	-	-	+	+	+	+	+	+	+	+	+	+	+	+
MB20	SP	+	-	-	+	+	+	+	+	+	+	+	+	+	+	+
MP21	SP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
MP22	SP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
MP23	BP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GP24	BP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GP25	BP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GP26	BP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GP27	BP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GP28	BP	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

Reliability of method:
 low = ● fair = ● good = ●

Correlation to source:
 none = - low = + fair = * good = *

Table 5-2: Source determination from various methods.

5.5. Petroleum Resource Assessment

The potential of a proposed basin can be assessed using any relevant level or type of data (Master, 1984). To determine the resources available, four main factors must be looked at (Ulmishek and Harrison, 1984). These include: 1) source, 2) trap, 3) reservoir and 4) seal.

Basins are generally assessed as a unit when bounded on all sides to produce an enclosed system (Ulmishek and Harrison, 1984). The Humber Arm Allochthon is an independent system since it is separated horizontally by structural boundaries; vertically the Humber Arm Allochthon is partly opened upward (hence the oil seeps).

Resource estimates of the source, based on geochemistry are reliable (Momper, 1984). Within an independent system, migration factors are not taken into account as the system is interpreted as a closed unit (Ulmishek and Harrison, 1984). Minimum acceptable TOC for good potential sources is >1.5 and more than half of the shales from this study fall into this range (Table 4-1). Exceptions are MP21, MP23, PP3, PP6, CH9, CH11 and all St. Paul's samples except SP12. Samples interpreted to have excellent potential based on hydrocarbon yield (>50) and high TOC (Oudin, 1976; Powell, 1978; and Hunt, 1979) include GP24, GP26, BP17, CH8 and CH10. Genetic potential generated from Rock Eval data indicates that the Cow Head Group extracts have good potential, with the exceptions of PP2, CH9, SP15 and Lobster Cove and Table Head samples. Those with excellent potential include PP5, BP17, BP18, WB19, WB20, BP26, GP27 and GP28. On average, the Cow Head shales have a potential yield of 59.5 kg/t (70 l/t), well above the economic minimum of 41.8 l/t (Powell et al., 1984).

The volume of shales is a limiting factor as the Cow Head Group shales are thin and dispersed sapropel Type I/II organic matter. The Humber Arm Allochthon itself represents a rather large basin 1200 km² (4800 km³) which is substantially larger than the average size of a continental multicycle basin of 266

km² (693 km³) (Klemme, 1984). This type of basin is a result of crustal collision on a convergent plate margin and is commonly mixed clastic and carbonate (Klemme, 1984). The overall volume of black shales however is limited and thermal history suggests a large portion of these shales are not yet within the oil window.

Traps for petroleum must be of exploitable size. Only a small portion of organic matter is converted to hydrocarbons and well sealed traps are necessary to contain any produced oil. The Cow Head is an extensively deformed region that may contain abundant traps, though of limited size.

Reservoir rocks themselves need to be porous to retain the hydrocarbons necessary. The Humber Arm region is highly fractured, with narrow bedding intervals and stratified units. Massive units, absent in the Cow Head, are most conducive to good reservoir conditions.

Seals for reservoirs are necessary to contain migrated or free hydrocarbons. The Cow Head possesses good permeable migration pathways along zones of faulting, but these zones are open to the surface in many cases allowing hydrocarbons to escape.

Other factors that may have influenced the preservation of reservoirs include water recharge (minimal in the Allochthon), post migration tectonism (also minimal), escape migration (no seal present allowing hydrocarbons to escape), hydrothermal activity (not evident in outcrop) and biodegradation (minimal in both seep oils and extracts).

5.6. Conclusions

Study of the bitumen and seep oil from the Cow Head Group shale extracts within the geologic region known as the Humber Arm Allochthon reveal that:

1. Chemical properties of the oil resemble most closely those of the shales from bed number 8 of the Cow Head equivalents within the Broom Point Member of the Green Point Formation and Cow Head Group.
2. The source rock quality shows good potential for the production of economic amounts of hydrocarbons. Trap, reservoir and seal capabilities are low.
3. The majority of maturation indices show the section to be at early or immature stage of oil generation, just above to within the oil generation "window". Maturation increases across the coastal platform towards the Long Range Mountains.
4. Organic matter is of Type II with perhaps admixed Type I and II kerogen originating mainly from prokaryotic (algal) sources and deposited in an anoxic marine environment with clastic and minor carbonate input.
5. The oil and extracts are typical Ordovician early Paleozoic marine oils, classed as non-waxy normal clastic sourced hydrocarbons.
6. Methods most acceptable for source correlation include n-alkane distributions, specific ions and $\delta^{13}\text{C}$, corresponding well to the bitumens, indicating that extensive alteration does not occur in early and low maturation stages.

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Appendix A

Saturates, n-alkanes

Saturated chromatograms are run on a GC-MS in "scan" mode. Distributions are based on ion m/z 99. The y axis represents relative abundance of individual peaks, and the x axis represents retention times. Peak designations from 15 to 35 correlate to the specific number of carbon the make up that specific carbon chain represented by that peak. Isoprenoid insets have an x axis 10 times that in the regular n-alkane chromatograms and are designated pr = pristane, and ph = phytane.

Liquid chromatography separations were verified by ion scanning for di and trimethylnaphthalenes (m/z 156 and 170) and di and trimethylphenanthrenes (m/z 206 and 220).

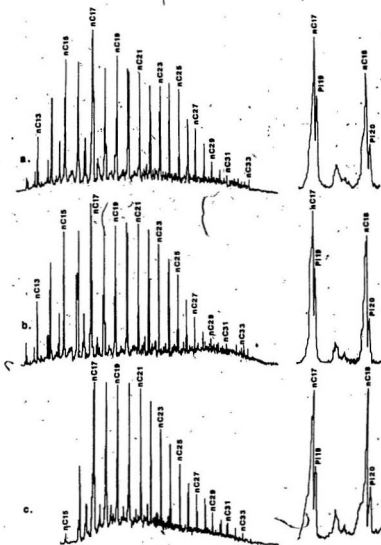


Figure A-1: n-alkane and isoprenoid distributions
 a. = SPoil, b. = PPOil, c. = PP5.

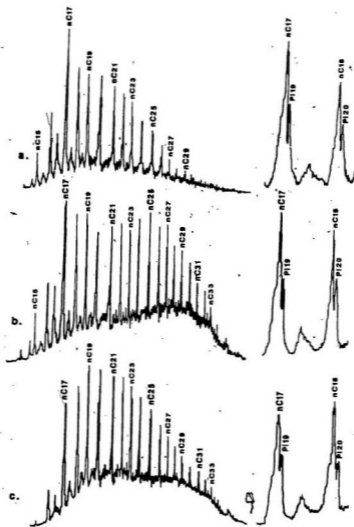


Figure A-2: n-alkane and isoprenoid distribution
 a. = PP6, b. = PP7, c. = CH8..

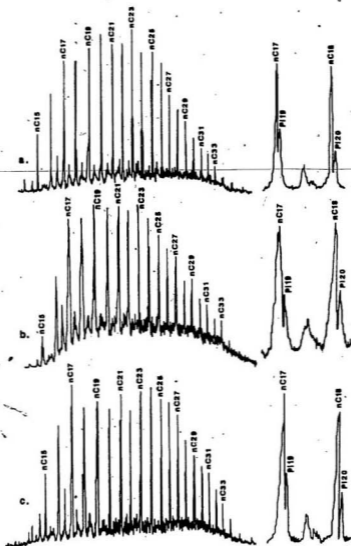


Figure A-3: n-alkane and isoprenoid distribution
 a. = CH10, b. = CH11, c. = SP12.

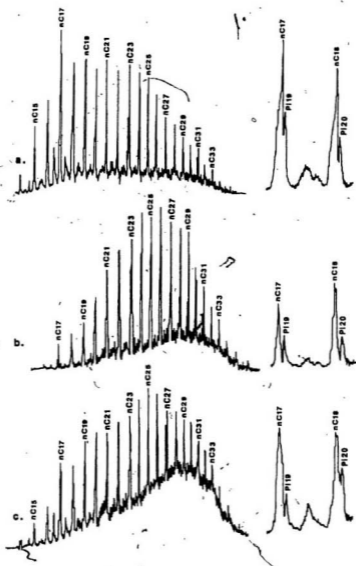


Figure A-4: n-alkane and isoprenoid distributions
a. = SP14, b. = SP15, c. = BP17.

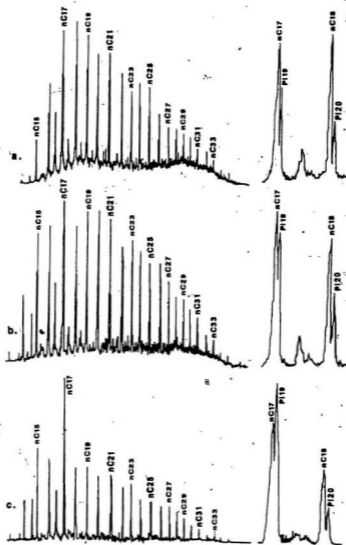


Figure A-5: n-alkane and isoprenoid distributions
 a. = BP18, b. = WB20, c. = MP21.

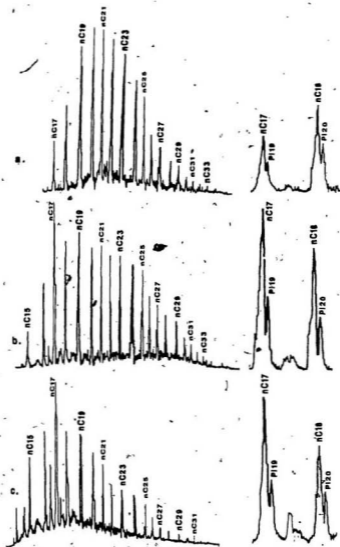


Figure A-6: n-alkane and isoprenoid distributions
 a. = MP22, b. = MP23, c. = GP24.

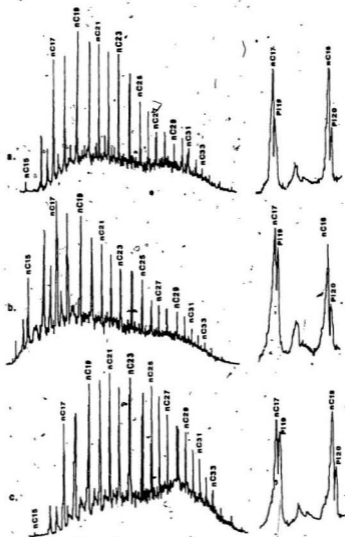


Figure A-7: n-alkane and isoprenoid distributions,
 a. = GP25, b. = GP26, c. = GP27.

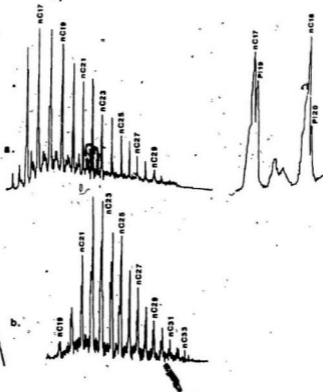


Figure A-8: n-alkane and isoprenoid distributions
a. = GP28, b. = LC30.

Appendix B

Terpanes, hopanes

Hopane distributions were collected in the select ion monitoring (SIM) mode of the GC-MS. Ion m/z 191 was monitored and peak heights were used in the calculation of relative ratios. The y axis represents relative abundance and the x axis represents retention time. Peak designations are noted in the following table.

PEAK DESIGNATION	MOLECULAR WEIGHT	TERPENE IDENTIFICATION
C23	318	tricyclic terpenes
C24	332	tricyclic terpenes
C25	346	tricyclic terpenes
C27 T _a	370	18a(H) 21b(H) trisnorhopane
C27 T _m	370	18a(H) 21b(H) trisnorhopane
C29	398	17a(H) 21b(H) norhopane
C30	412	17a(H) 21b(H) hopane
C30 M	412	17b(H) 21a(H) noretane
C31 S	426	17a(H) 21b(H) homohopane (22S)
C31 R	426	17a(H) 21b(H) homohopane (22R)
G	412	gamacerane
C32	440	17a(H) 21b(H) bisnorhopane (22S)
C32	440	17a(H) 21b(H) bisnorhopane (22R)
C33	454	17a(H) 21b(H) trisnorhopane (22S+R)
C34	468	17a(H) 21b(H) tetrano-hopane (22S+R)

R = right stereo isomer:
 17a(H), 21b(H) : a=alpha, b=beta
 (rr) = rearranged steranes
 S = left stereo isomer

Table B-1: Designation for hopane distributions.

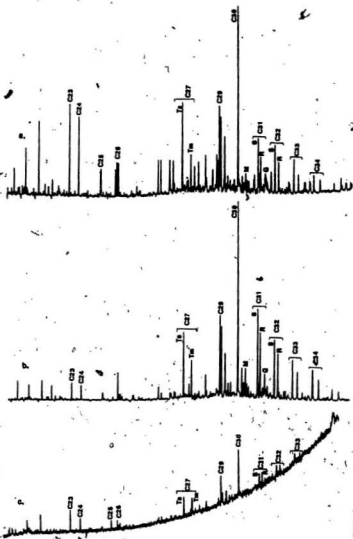


Figure B-1s. Hopane and tricyclic distributions
 a. = PPoil, b. = PP2, c. = PP4.

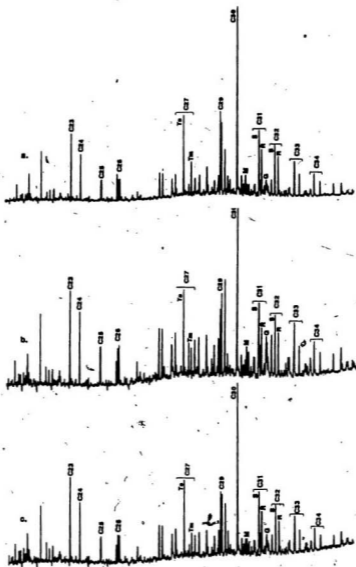
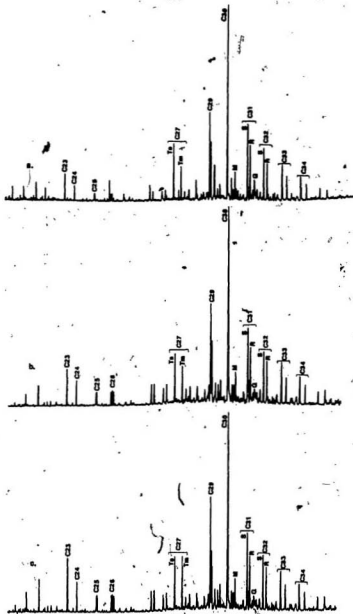


Figure B-2: Hopane and triacyclic distributions
a. = CH8, b. = CH10, c. = CH11.



1 **Figure B-3: Hopane and tricyclic distributions**
a. = SP14, b. = SP15, c. = MP21.

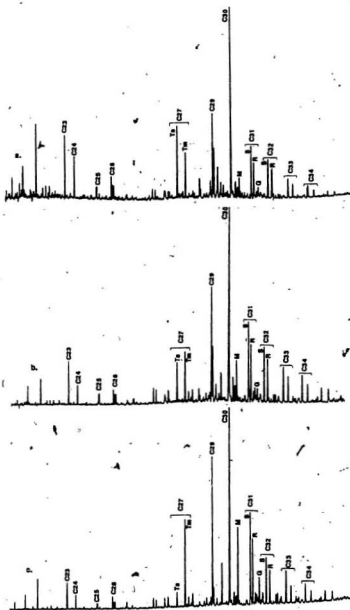


Figure B-4: Hopane and tricyclic distributions
 a. = BP17, b. = BP18, c. = WB20.

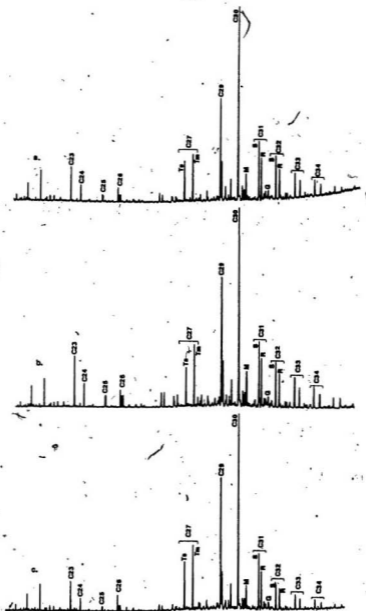


Figure B-5: Hopane and tricyclic distributions
a. = GP24, b. = GP25, c. = GP26.

Appendix C

Steranes

Sterane distributions are collected in SIM mode and calculated based on peak heights. The y axis represents relative abundance and the x axis represents retention times. Selected ions monitored included m/z 217, 218, 231 and 414. This appendix represents only the total (217) ion chromatogram. Specific peak designations from 1 to 22 are interpreted in the following table.

PEAK DESIGNATION MOLECULAR WEIGHT STERANE IDENTIFICATION

1 C27 (rr)	372	13b(H)17a(H) diacholestane (20S)
2 C27 (rr)	372	13b(H)17a(H) diacholestane (20R)
3 C27 (rr)	372	13a(H)17b(H) diacholestane (20S)
4 C27 (rr)	372	13a(H)17b(H) diacholestane (20R)
5 C28 (rr)	386	rearranged C28 steranes
6 C28 (rr)	386	rearranged C28 steranes
7 C28 (rr)	386	rearranged C28 steranes
8 C27	372	14a(H)17a(H) cholestane (20S)
9 C27/C29	372/400	14b(H)17b(H) cholestane (20R)
		rearranged C29 sterane
10 C27	372	14b(H)17b(H) cholestane (20S)
11 C27	372	14a(H)17a(H) cholestane (20R)
12 C29 (rr)	400	rearranged C29 steranes
13 C29 (rr)	400	rearranged C29 steranes
14 C29 (rr)	400	rearranged C29 steranes
15 C28	386	14a(H)17a(H) ergostane (20S)
16 C28	386	14b(H)17b(H) ergostane (20R)
17 C28	386	14b(H)17b(H) ergostane (20S)
18 C28	386	14a(H)17a(H) ergostane (20R)
19 C29	400	14a(H)17a(H) stigmastane (20S)
20 C29	400	14b(H)17b(H) stigmastane (20R)
21 C20	400	14b(H)17b(H) stigmastane (20S)
22 C21	400	14a(H)17a(H) stigmastane (20R)

Table C-1: Sterane peak designations.

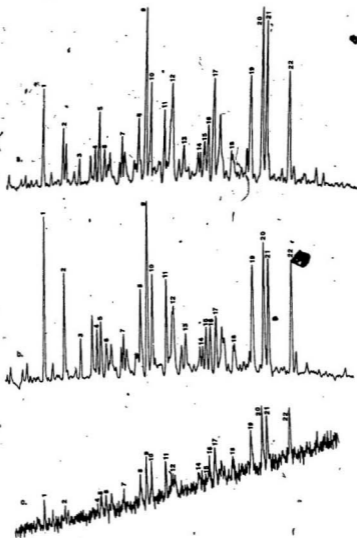


Figure C-1: Sterane distributions
a. = PPol, b. = PP2, c. = PP4.

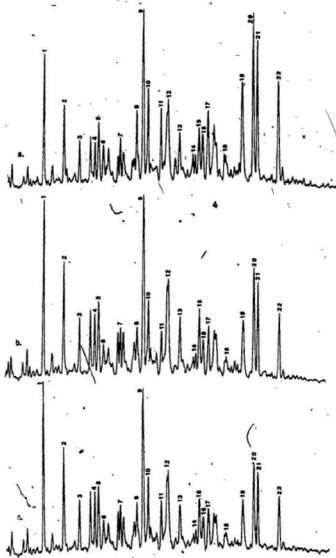


Figure C-2: Sterane distributions
a. = CH8; b. = CH10; c. = CH11.

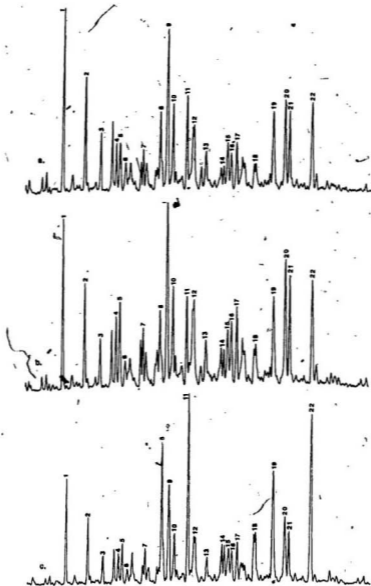


Figure C-3: Sterane distribution
a. = SP14, b. = SP15, c. = WB20.

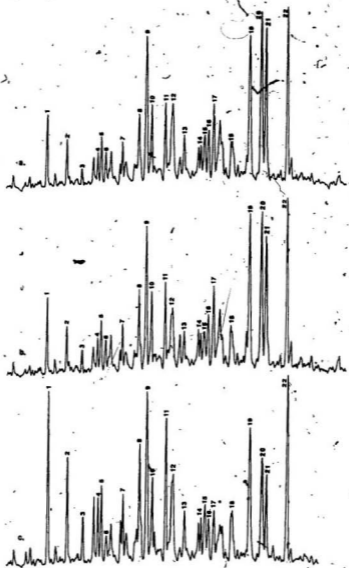


Figure C-4: Sterane distributions^a
a. = BP17, b. = BP18, c. = MP21.

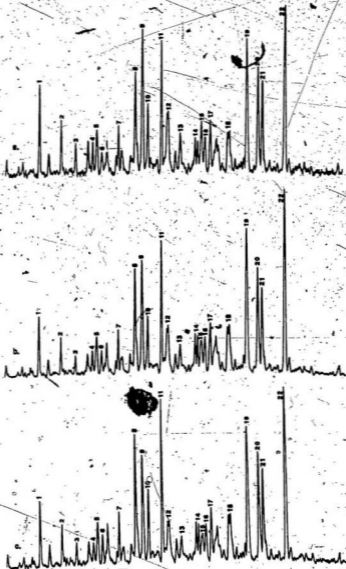


Figure C-5: Sterane distributions
a. = GP24, b. = GP26, c. = GP28.

