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BULLETIN 262

THE ORIGIN AND MIGRATION OF PETROLEUM IN THE WESTERN CANADIAN SEDIMENTARY BASIN, ALBERTA A geochemical and thermal maturation study

G. Deroo, T. G. Powell, B. Tissot and R. G. McCrossan with contributions by P. A. Hacquebard



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PREFACE

This report records the results of a joint project between the Institut français du Pétrole and the Geological Survey of Canada. It consists of a detailed geochemical study of oils and their source rocks in the central part of the Alberta Basin and the relationship of heavy oils and tars at the margin of the basin to the conventional oils.

It represents one of the most comprehensive geochemical studies ever undertaken of a large petroleum province and is an important bench-mark both in international co-operation and the rapidly developing field of organic geochemistry as applied to petroleum geology.

Ottawa, September 15, 1976

D.J. McLaren Director General Geological Survey of Canada

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THE ORIGIN AND MIGRATION OF PETROLEUM IN THE WESTERN CANADIAN SEDIMENTARY BASIN, ALBERTA: A GEOCHEMICAL AND THERMAL MATURATION STUDY

Abstract

This report gives the results of organic geochemical and maturation studies of oil- and gas-bearing sedimentary rocks in the Albertan part of the Western Canadian Sedimentary Basin. The geochemical work comprises a study of 106 conventional oils, 63 heavy oil extracts and 189 extracts from Paleozoic and Mesozoic sediments. Samples were examined successively from two areas; the central part of the Alberta Syncline adjacent to the Foothills including the Leduc Woodbend-Homeglen Rimbey reefal trend, and the northeastern and eastern parts of the Alberta Syncline including the Athabasca Tar Sands and Lloydminster regions. The maturation study has determined the degree of organic metamorphism (DOM) of producing oil and gas pools in Alberta based on rank variations of subsurface and near-surface coals.

The rank of subsurface coals (Mannville Formation, Lower Cretaceous) was determined from vitrinite reflectance measurements of thirty samples collected from coreholes along a 338 km (210 mile) section across the eastern flank of the Ålberta Syncline. The coals lie at depths of from 600 to 3300 m (1968-10 826 ft.) and increase in rank from 0.4 to 1.6 per cent Ro from east to west. The near-surface coals, of younger formations, show a similar increase in rank, which is illustrated with an isomoisture contour map of Alberta. The east-west changes are from 30 to 5 per cent in moisture content.

The maximum depth of burial of the near-surface coals has been obtained from moistureoverburden correlations. By adding this depth to the present subsurface position of the Mannville coals, the original overburden of these coals is obtained also. When this depth is plotted against the reflectance data of the coals, a smooth curve results. Isoreflectance contours have been derived which permit rank assignments at various depth levels above and below the Mannville curve. Thus, by plotting the depth of petroleum zones at the moisture position of the overlying near-surface coals (obtained from isomoisture contour map), the Ro (or degree of organic metamorphism) of these zones has been determined. The corresponding paleotemperatures were derived from Karweil's (1956) diagram by using 35 m.y. as coalification time for the Mannville coals.

Results show that, in Alberta, 88 per cent of initial oil reserves have a DOM comparable with a coal rank of 0.5 to 0.9 per cent Ro (reflectance), or with high volatile C to middle of high volatile A bituminous coal; the corresponding paleotemperatures range from 68° to 116°C. No oil was found above 1.3 per cent Ro (medium volatile bituminous coal), or above 143°C. With regard to the DOM of initial gas reserves, biogenic methane occurs at a coal rank of 0.4 to 0.5 per cent Ro (subbituminous coal) or between 52° to 68°C; thermal gas ranges from 0.8 to 2.0 per cent Ro (middle of high volatile A bituminous coal to semianthracite), or between temperatures of 106° and 177°C.

A post-Paleozoic regional unconformity separates the detrital deposits of Cretaceous and Jurassic ages from the predominantly carbonate deposits of Mississippian and Devonian ages. In the central part of the basin, the oils occurring near the unconformity can be separated from the others on the basis of their gross properties. For the most part, they are derived from source rocks within the Mannville Formation. This formation was the source of the oil found in the Lower and Upper Mannville reservoirs throughout the region and the Jurassic, Mississippian and Upper Devonian (Wabamun Group) deposits adjacent to the unconformity. In these Paleozoic reservoirs, certain oils have lost the lightest fractions with a resulting increase in the percentage of sulphur and asphalts and an increase in viscosity and specific gravity. The reservoirs associated with the Cretaceous transgression, and occurring to the northeast of Leduc-Woodbend, have been partly supplied with oils from source rocks in the Devonian (Winterburn Group). Their affinity with the Devonian oils is evident from the isoprenoid distribution and is confirmed by detailed analysis of the thiophenic and aromatic compounds.

The source for the oils in the remaining Cretaceous and Devonian reservoirs is in the contemporaneous fine-grained sediments. The source rocks for these two groups of oils have undergone similar maturation histories and their organic content is similar in composition. Consequently, a clear distinction between the Cretaceous and Devonian oils was not apparent

until an advanced stage of analysis, namely the analysis of the aromatic fraction. At this stage, it is possible also to separate two groups of Devonian oils, those occurring in the Beaverhill Lake Formation from those found in the Woodbend Group.

In the northeastern and eastern part of the basin, the heavy oil extracts from Lower Cretaceous sandstones and some Devonian carbonates show a gradational change in composition northeastward toward the shallower part of the basin. Conventional pooled oils from the same general area fit into the same picture. Three stages of degradation are recognized departing from a normal oil: type "a", with a decrease in normal alkanes and an apparent increase in phytane and pristane; type "b", with the disappearance of the normal alkanes leaving only pristane and phytane; type "c", in which even the isoprenoids have disappeared leaving only other isoalkanes and cyclo-alkanes. The heavy oils, including those of the Athabasca deposits, are very similar in their cyclo-alkane content to the conventional Lower Cretaceous oils from the central part of the Alberta Basin. A study of the aromatic and thiophenic compounds reinforces that interpretation. Examination of rock extracts from the margin of the basin indicates that they have undergone little diagenesis. Thus, it is concluded that biodegradation and water washing with some possible inorganic oxidation are responsible for the progressive alteration of, primarily, normal Lower Cretaceous oil migrating updip where it encounters fresh water invading the basin from the outcrop area along the shield edge. Because of the huge quantities of bitumen in the heavy oil deposits, it is necessary to admit some contribution from the pre-Cretaceous sediments in the centre of the basin.

Comparative analysis of the aromatic fractions of oils from throughout the basin allows the relative effects of diagenesis, secondary migration, or alteration processes to be established.

Résumé

Ce rapport expose les résultats auxquels ont abouti des études sur la géochimie organique et la maturation des roches sédimentaires, pétrolifères et gazifères, recueillies dans le partie albertaine du bassin sédimentaire de l'Ouest canadien. La partie géochimique du travail comporte l'étude de 106 pétroles de type classique, de 63 extraits de pétroles lourds et de 189 extraits de sédiment du Paléozoïque et du Mesozoïque. Les échantillons à l'étude proviennent de deux régions: d'une part, la partie centrale du synclinal de l'Alberta en contact avec les Foothills, qui comprend l'axe récifal Leduc Woodbend-Homeglen Rimbey; et d'autre part les parties nord-est et est du synclinal de l'Alberta, qui comprennent les régions de Lloydminster et des sables bitumineux de l'Athabasca. L'étude de la maturation a permis de déterminer le degré de métamorphisme des matières organique, ou leur capacité de produire des gisements de pétrole et de gaz en Alberta, selon les variations observées du rang des charbons qui se trouvent dans le sous-sol ou à proximité de la surface.

Le rang des charbons de sous-sol (formation de Mannville, du Crétacé inférieur) a été déterminé on mesurant le pouvoir réflecteur des vitrinites dans trente échantillons provenant de sondages géologiques forés le long d'une coupe de 338 km (210 milles) en travers du flanc est du synclinal de l'Alberta. Les charbons reposent à des profondeurs variant entre 600 et 3300 m (entre 1968 et 10 826 pieds) et leur rang va on augmentant, d'est en ouest (Ro passant de 0.4 à 1.6 pour cent). En ce qui concerne les charbons superficiels, qui appartiennent à des formations plus récentes, on constate une augmentation de rang similaire qu'illustre une carte des courbes d'égale humidité de l'Alberta. La teneur en eau des charbons passe, d'est en ouest, de 30 à 5 pour cent.

On a pu déterminer la profondeur maximale d'enfouissement des charbons qui se trouvent aujourd'hui près de la surface, en mettant en corrélation la teneur en humidité et l'épaisseur des morts-terrains. En ajoutant cette profondeur à la position actuelle, en profondeur, des charbons de Mannville, on obtient aussi la profondeur d'enfouissement initiale de ces charbons. Lorsque l'on trace la courbe de cette profondeur en fonction du pouvoir réflecteur des charbons, on obtient une courbe régulière. On en déduit les courbes d'égal pouvoir réflecteur qui permettent d'attribuer aux charbons un rang en fonction de la profondeur à laquelle ils se trouvent au-dessus ou au-dessous de la courbe de Mannville. En traçant ainsi la courbe des profondeur des zones pétrolifères en fonction de la teneur en humidité des charbons qui les recouvrent à proximité de la surface (au moyen d'une carte des courbes d'égale humidité), le Ro (dégre de métamorphisme organique) de ces zones a pu être déterminé. Les paléotempératures correspondantes ont été calculées à l'aide du diagramme de Karweil (1956); on a utilisé, dans le cas des charbons de Mannville, 35 millions d'années comme période de houillification.

Les résultats démontrent qu'en Alberta, 88 pour cent des réserves initiales de pétrole ont un degré de métamorphisme organique comparable à un rang de charbon correspondant à une valeur de Ro (pouvoir réflecteur) allant de 0.5 à 0.9 pour cent, soit de charbon à haute teneur en matières volatiles allant de C aux valeur moyennes de A; les paléotempératures correspondantes s'échelonnent entre 68° et 116°. On n'a découvert aucun pétrole dont le Ro se situe au-delà de 1.3 pour cent (charbon bitumineux à moyenne teneur en matières volatiles), ou correspondant à une température supérieure à 143°C. En ce qui concerne le degré de métamorphisme organique dans le cas des réserves initiales de gaz, on rencontre du méthane d'origine biologique lorsque le rang du charbon se situe entre Ro = 0.4 pour cent et Ro = 0.5 pour cent (charbon subbitumineux) ou la température entre 52° et 68°C; le gaz d'origine thermique se rencontre entre Ro = 0.8 pour cent, Ro = 2.0 pour cent (à mi-chemin entre le charbon bitumineux à haute teneur en matières volatiles A et le charbon maigre anthraciteux), ou entre 106° et 177°C.

Une discordance régionale, postérieure au Paléozoïque, sépare les dépôts détritiques du Crétacé et du Jurassique des dépôts du Mississippien et du Dévonien où dominent les roches carbonatées. Dans la partie centrale du bassin, les hydrocarbures qui se rencontrent à proximité de la discordance peuvent être distingúes des autres en fonction de leurs caractères généraux. Ils proviennent pour la plupart de roches mères appartenant à la formation de Mannville. C'est également de cette formation que provient le pétrole qui a été découvert dans les roches réservoirs du Mannville inférieur et du Mannville supérieur dans toute la région, et dans les gisement du Jurassique, du Mississippien et du Dévonien supérieur (formation de Wabamun) de part et d'autre de la discordance. Dans ces roches réservoirs du Paléozoïque, certains hydrocarbures ont perdu leurs fraction les plus légères, ce qui a eu pour effet d'augmenter leur teneur en bitume et d'augmenter ainsi leur viscosité et leur densité. Les roches réservoirs que l'on associe à la transgression du Crétacé et qui se rencontrent au nordest de l'axe Leduc-Woodbend, doivent en partie leur pétrole à des roches mères qui datent du Dévonien (formation de Winterburn). Ce pétrole présente des affinités manifestes avec les hydrocarbures du Dévonien, de par la distribution des composés isopréniques, ce que confirme une analyse détaillée des éléments thiophéniques et aromatiques.

Les hydrocarbures qui se rencontrent dans les autres roches réservoirs du Crétacé et du Dévonien trouvent leur origine dans des sédiments à grains fins datant de la même époque. Les roches mères de ces deux groupes de pétroles ont subi des processus de maturation similaires et leurs matières organique présentent la même composition. C'est pourquoi une distinction nette entre les hydrocarbures du Crétacé et ceux du Dévonien n'a pu être établie qu'à la suite d'une analyse plus poussée, notamment celle de la fraction aromatique. A ce stade, il est possible également de distinguer deux groupes d'hydrocarbures appartenant au Dévonien, soit ceux qui se rencontrent dans la formation de Beaverhill Lake et ceux que l'on rencontre dans le groupe de Woodbend.

Dans la partie nord-est et est du bassin, les pétroles lourds extraits des grès du Crétacé inférieur et de certaines roches carbonatées du Dévonien présente une composition qui évolue graduellement en direction du nord-est, là où se trouve la partie moins profonde du bassin. Les pétroles qu'on trouve dans des champs de type classique et qui proviennent de cette même région présentent la même évolution. A partir d'un pétrole normal, on distingue trois stades de dégradation: le type "a", qui correspond à la diminution des alcanes normaux et augmentation apparente de la teneur en "phytane" et en "pristane" (alcanes ramifiés en C_{20} et C_{19}); le type "b", avec la disparition des alcanes normaux, ne laissant que de la "pristane" et le "phytane"; le type "c", où même les composés isopréniques ont disparu, ne laissant que d'autres isoparafiines et des cyclanes. Les pétroles lourds, notamment ceux des gisements de l'Athabasca, ressemblent beaucoup, par leur teneur en cyclanes, aux pétroles classiques du Crétacé inférieur que l'on rencontre dans la partie centrale du bassin de l'Alberta. Il suffit d'une étude des composés aromatiques et thioféniques pour corroborer cette interprétation. L'étude des fragments de roches extraits de la marge du bassin révèle qu'ils n'ont subi qu'une faible diagénèse. On en conclut donc qu'un processus de biodégradation et de lavage par l'eau, accompagné d'une oxydation de matières inorganiques, sont responsables de l'altération progressive du pétrole du Crétacé inférieur (à l'origine normal) lors de sa migration vers le haut, où ce pétrole a rencontré les eaux douces que envahissaient le bassin en provenance de la zone d'affleurements située le long de la bordure de Bouclier. En raison des énormes quantités de bitume dans les gisements de pétrole lourd, il faut bien admettre une certaine contribution des sédiments antérieurs au Crétacé qui se rencontrent au centre du bassin.

Grâce à une analyse comparative des constituants aromatiques des pétroles rencontres dans toute l'étendue du bassin, il est possible de déterminer les effets relatifs de la diagénèse, de la migration secondaire ou des processus d'altération.

THE ORIGIN AND MIGRATION OF PETROLEUM IN THE WESTERN CANADIAN SEDIMENTARY BASIN, ALBERTA: A GEOCHEMICAL AND THERMAL MATURATION STUDY

CHAPTER 1

INTRODUCTION

OUTLINE OF STUDY

This report presents the results of a joint project between the Institut Français du Pétrole (IFP) and the Geological Survey of Canada (GSC). The study was initiated to gain some understanding of the geochemical processes that have led to the generation and accumulation of petroleum and bituminous deposits using techniques developed by IFP. The Albertan part of the Western Canadian Sedimentary Basin was an obvious choice for this study since it is the major petroleum-bearing province of Canada and contains a wide variety of petroleum types in a range of geological conditions. In addition, it is perhaps the best-documented petroleum province in the world and samples are readily available through the Energy Resources Conservation Board of Alberta. The GSC has been responsible for the provision of geological information and samples, while the IFP has conducted the geochemical analyses and has made the appropriate geochemical interpretations. An additional project has been carried out in the GSC by P.A. Hacquebard on the use of corals to indicate the organic metamorphism in Alberta; it is extremely pertinent to the geochemical study since it provides an independent guide to the thermal history of the Alberta The results of this work, therefore, are Basin. incorporated into this report (see Chap. 3).

The areas for the geochemical study are outlined in Figure 1-1. The work was carried out successively in two main geographic areas. The first area is in the central part of the Alberta Basin adjacent to the Foothills. It includes the Leduc Woodbend-Homeglen Rimbey reefal trend extending as far as the Redwater field to the northeast; to the southwest, it extends as far as the Harmattan fields to the north of Calgary and, to the northwest, it includes the Swan Hills and Kaybob fields northwest of Edmonton (*see* Ball, 1970 for detailed distribution of pools). The second area consists of the 'heavy oil belt' extending from the Peace River region

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Authors' addresses:

- G. Deroo, B. Tissot:
- Institut Français du Pétrole, Rueil Malmaison, Paris T.G. Powell, R. G. McCrossan:
- Institute of Sedimentary and Petroleum Geology, 3303-33rd Street N.W., Calgary, Alberta T2L 2A7 P.A. Hacquebard:

Atlantic Geoscience Centre, Bedford Institute of Oceanography, P.O. Box 1006 Dartmouth, Nova Scotia B2Y 4A2 in the northwest through the Athabasca Tar Sands to Lloydminster in the southwest. Part of the work on the second area has been published already (Deroo *et al.*, 1974) but, for the sake of completeness, the results are repeated here.

In the following chapters, some geological considerations are outlined and the distribution of oil and gas reserves relative to the degree of organic metamorphism is discussed. The discussion of the geochemistry is laid out in the order that the studies were carried out and the problems resolved. Thus, the conventional oils and rock extracts in the central part of the basin are dealt with first followed by the problems associated with the heavy oil belt. During the course of the study, it was recognized that a number of the rock extracts were contaminated and many of the oils and extracts had undergone various forms of



FIGURE 1-1. Location of areas of study in Alberta.

alteration in the geological environment. These effects became critical to the study of the heavy oil belt but were found also in the central part of the basin. Separate subsections are devoted to the effects and recognition of the contamination and alteration.

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PREVIOUS WORK IN THE GEOCHEMISTRY OF PETROLEUM IN ALBERTA

The origin of petroleum deposits in Alberta and, in particular, the Athabasca Tar Sands has been debated extensively in the literature. One of the more comprehensive earlier studies is that of Hitchon (1964) who reviewed the composition of Albertan oils based on U.S. Bureau of Mines Routine Analyses. He separated the asphaltic and sulphur-rich Mannville oils from the others and suggested that the differences in composition reflected the different environment of deposition of the Mannville sediments. He also provides a comprehensive list of early papers (up to 1964) on geochemical aspects of petroleum deposits in Alberta. Subsequent papers have emphasized exploration aspects of petroleum geochemistry. Maturation studies using gas cuttings analysis and spore colouration have defined the oiland gas-bearing regions of Alberta (Staplin, 1969; Evans and Staplin, 1971; Evans et al., 1971). The effects of maturation, gas-deasphalting, water washing and biodegradation have been discussed extensively (Evans et al., 1971; Rogers et al., 1972; Rogers et al., 1974). The application of petroleum geochemistry to the search for oil has been illustrated also for the Western Canadian Sedimentary Basin (Bailey et al., 1974).

GENERAL GEOLOGY

STRUCTURE AND GEOLOGICAL HISTORY

The following sections are intended to provide a general geological background to the geochemical study and are drawn largely from "The geological history of western Canada", edited by McCrossan and Glaister (1964), and from Parsons (1973).

The Albertan part of the Western Canadian Sedimentary Basin comprises a broad belt of Mesozoic and Paleozoic sedimentary rocks which trends northwesterly through the province. A major regional unconformity separates the Paleozoic sediments from the more gently dipping Mesozoic strata. The western margin of the basin is the Rocky Mountain Thrust Belt and the northwestern margin is where the sediments lap onto the Precambrian Shield. To the southeast, the basin continues into Saskatchewan. Adjacent to the Foothills area, the sedimentary sequence exceeds 5700 m (19 000 ft.) (Fig. 2-1) but this sequence thins to the northeast and east owing to both depositional thinning and erosion. Paleozoic, Triassic and Jurassic rocks are mainly marine, whereas the Cretaceous strata are mixed continental and marine. The table of formations and the regional cross-sections showing the various stratigraphic relationships are shown in Figures 2-2 and 2-3.

Structurally, the Albertan section of the basin is a simple monocline which is extremely deformed at the western margin adjacent to the Rocky Mountain Front. The basin has been divided tectonically into three parts (McCrossan and Porter, 1973): Craton Centre, Craton Margin, and Deformed Craton Margin. The Craton Centre occupies the eastern part of the basin adjacent to the shield area where deformation consists only of gentle regional arches; this area incorporates the second stage of the geochemical study (Fig. 2-1). The Craton Margin consists of the central part of the basin adjacent to the Foothills; it includes the first area of study (Fig. 2-1) and again the amount of deformation is relatively small, comprising broad gentle arches with some normal faulting. The maximum depth of burial is much greater than at the Craton Centre. The Deformed Craton Margin constitutes the disturbed belt of the Foothills and falls outside the area of study.

Pre-Devonian rocks are not included in this study; the following outline is confined, therefore, to Devonian and younger strata. During the Devonian and Carboniferous, deposition of platform carbonates and evaporites predominated in eastern and southeastern Alberta whereas a deeper water facies was deposited in northwestern Alberta. Middle Devonian sediments were laid down in a shallow topographic basin created by post-Ordovician erosion. The boundaries of the basin were topographic highs, namely the Peace River Uplift, the West Alberta Ridge, and the Precambrian Shield (Fig. 2-4). Sedimentation throughout the Devonian and Carboniferous can be explained by a series of transgressive pulses of the sea from the northwest. Each transgressive pulse deposited shale, carbonate and evaporitic facies with or without reef development. The boundaries and areal extent of the facies vary with time. The West Alberta Ridge was submerged during the Middle Devonian but the Peace River Uplift remained emergent until the end of the Late Devonian.



FIGURE 2-1. Generalized basin fill isopach map of Alberta Basin showing main structural features (after Parsons, 1974).





FIGURE 2-2. Table of formations in Alberta (after Alberta Oil and Gas Conservation Board).

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Emergence of the shelf began in the Late Mississippian and was followed by erosion during the Permian with some sedimentation (mid-Permian) in the Peace River region. The Triassic and Jurassic rocks in the Alberta subsurface were deposited on a relatively stable shelf representing the eastern flank of a marine sedimentary basin whose depocentre was in British Columbia. During the Late Jurassic, orogenic movements to the west resulted in the deposition of thick continental clastic strata in the Foothills. In Alberta, epeirogenic movements in the Early and post-Jurassic resulted in the erosion of earlier rocks.

During the Early Cretaceous, uplift continued in the Cordillera and the resulting erosion supplied continental sediments that were transported and deposited on the western part of the gently subsiding shelf. At the same time, seas transgressing the shelf from both the northwest and southeast finally merged near the end of the Early Cretaceous to form the Colorado Sea.

Post-Colorado time began with the uplift of the eastern Cordillera and the deposition of coarse continental clastics in the Foothills area. On the plains, marine shales continued to be deposited for a time but, as orogenesis continued, continental debris was transported eastward and laid down across the plains as the sea retreated both to the northwest and southeast. Continued uplift of the Cordillera resulted in the deposition of thick continental sediments.

Continental deposition was continuous from the Late Cretaceous into the Tertiary, and Tertiary sediments consist entirely of continental sands and conglomerates. The Laramide Orogeny probably reached its peak in the Eocene resulting in deformation of the Rocky Mountains and Foothills Belt mainly by overthrusting. Simultaneously with this thrusting from southwest to northeast, downwarping of the region now known as the western plains formed the Alberta Syncline. Erosion of the Rockies during the Oligocene resulted in the deposition of large amounts of clastic sediment in the syncline. General uplift of the shelf continued through the Miocene and Pliocene and much of the Tertiary sediment was removed by erosion.

DESCRIPTION OF ROCK UNITS (OUTLINE)

The Middle Devonian in Alberta is divided into Lower and Upper Elk Point Groups. The Lower Elk Point Group is up to 300 m (1000 ft.) thick and is confined to central and northwestern Alberta (Fig. 2-4). The lower part consists of interbedded red beds and evaporites which change upward to limestones and, finally, thick evaporites. The Upper Elk Point Group [up to 300 m (1000 ft.) thick] extends from northwestern Alberta through eastern Alberta into Saskatchewan. The basal units, Keg River and Winnipegosis Formations, consist of reefal and non-reefal carbonates varying in thickness from 15 to 180 m (50-600 ft.). The Prairie Evaporite and Muskeg Formation, consisting primarily of evaporites, overlie and infill the depressions between the reefs. These are succeeded by the clastic-carbonateevaporite sequence of the Dawson Bay Formation which, in turn, is overlain by the dolomitic siltstones of the

Watt Mountain Formation. This formation contains coarse-grained sandstone (Gilwood Fm.) adjacent to the Peace River Arch. A thin tongue of the Slave Point platform carbonate occurs to the south of the Peace River Arch and forms the base for the Upper Devonian reefal development in that area.

The Beaverhill Lake Formation forms the basal unit of the Upper Devonian and is between 150 and 210 m (500-700 ft.) thick. In the type area, it consists of an alternating sequence of limestone and shale which changes along an irregular front to a shelf or platform carbonate facies to the east and west of Edmonton (Fig. 2-5). Coarsely crystalline dolomites occur along the shelf margin in southern Alberta and form the leading edge of a series of interbedded anhydrites and dolomites and, farther to the south and southeast, anhydrite is interbedded with dolomite. South of the Peace River Arch, a carbonate bank-reef complex (Swan Hills Member) developed on a broad shelf. The Swan Hills section is essentially a build up of successive carbonate layers consisting of lagoon limestones with a reef rim and enclosed within limestones or interbedded argillaceous limestones and shale. Northward, the Beaverhill Lake Formation grades into the basinal facies of the Waterways Formation.

The Beaverhill Lake Formation is overlain by the Woodbend Group, comprising reef-fringed platform carbonates and intervening shale basins (Fig. 2-6), reaching up to 300 m (1000 ft.) in thickness. A basal platform carbonate, the Cooking Lake Formation, forms the base of the areally restricted carbonate banks and reefs of the Leduc Formation. The economically important Homeglen-Rimbey-Morinville reefal trend developed on the edge of the underlying platform and forms the eastern boundary of a shale basin (Ireton and Duvernay Fms.) shaped like a great horseshoe plunging northwestward from north of Calgary. Its western boundary is formed by another carbonate shelf, the Cairn Platform. To the northeast, the Grosmont tabular reefs are equivalent to the Upper Leduc Reefs.

The Winterburn Group (Fig. 2-7) consists of up to 120 m (400 ft.) of dolomite, evaporite, and silty carbonate. Dolomitization of the Nisku Formation is particularly pronounced over the Leduc Reefs.

The Wabamun Group (Fig. 2-8) is made up predominantly of carbonates in western Alberta, grading into evaporites and red beds in eastern and southeastern Alberta. It forms a wedge-shaped unit which is less than 15 m (50 ft.) in northeastern Montana but thickens to 240 m (800 ft.) in northwestern Alberta and up to 540 m (1800 ft.) in the Rocky Mountains.

Much of the upper part of the Carboniferous was eroded from the Alberta Plains prior to the Cretaceous (Fig. 2-9), but thick sections [up to 300 m (1000 ft.)] are preserved in the Peace River and Foothills regions. The lower part is represented by the Exshaw and Banff shales which are up to 150 m (500 ft.) thick. These are succeeded by shales and limestones of the Rundle Group [75-150 m (250-500 ft.)] in the study-area. Permian sediments in Alberta comprise only a few erosional remnants which are found in the Peace River region.

Triassic and Jurassic rocks are confined to the Foothills and Peace River regions (Fig. 2-10). The sub-crop edge occurs to the east of Calgary and trends northward whilst the section thickens westward to 900 m (3000 ft.) in the Foothills. Lower Triassic sediments consist of thinly laminated, bituminous shales which become phosphatic in the Middle Triassic. An evaporitic facies, consisting of anhydrite, dolomite, dolomitized limestone, and red beds, forms the lower part of the Upper Triassic and is overlain by bioclastic limestones, siltstones, and shales. Lower Jurassic rocks are composed mainly of bituminous, phosphatic and partly calcareous shales and may contain substantial amounts of chert. These are overlain by interbedded sands and shales of Middle Jurassic age. The lower part of the Upper Jurassic is made up of marine shale and sandstone which grade up into the dominantly terrestrial sandstones, shales and coal seams of the Kootenay and Nikanassin Formations.

Cretaceous rocks unconformably overlie the earlier systems. The Lower Cretaceous incorporates both the Basal Cretaceous Sand, which rests on the unconformity surface, and the overlying units up to the base of the Fish Scale Zone. This sequence is divided into the Lower Mannville Group [up to 150 m (500 ft.) thick in study-area] and Upper Mannville Group [up to 180 m (600 ft.) thick in central Alberta, increasing to 450 m (1500 ft.) in the Foothills] (Fig. 2-11) and the overlying Lower Colorado Shale [90 m (300 ft.) thick in the study-area] (Fig. 2-12). The Lower Cretaceous rock types include a thick sand facies in the Foothills which trends in a northeasterly direction across the plains in the vicinity of Edmonton with a predominantly shale facies to the northwest and southeast. The sand facies decreases in areal extent in the Upper Mannville and Lower Colorado.

The Upper Cretaceous is subdivided at the First White Specks into a basal marine Upper Colorado section and an upper continental post-Colorado section. The Upper Colorado is dominantly a thick shale with some intervening sands (Cardium Fm.) and thickens regularly from less than 240 m (800 ft.) to the east of Edmonton to over 1200 m (4000 ft.) at the Alberta-British Columbia border (Fig. 2-13). The lower part of the post-Colorado Supergroup consists of marine shales but these are rapidly superceded by continental deposits of the Belly River and Edmonton Formations. The post-Colorado is approximately 300 m (1000 ft.) thick in the vicinity of Edmonton but reaches 1650 m (5500 ft.) in the Foothills (Fig. 2-14).

Tertiary sediments are present in the western plains in front of the Foothills; they are an entirely continental facies consisting of intermixed sands and conglomerates. Up to 900 m (3000 ft.) of Tertiary sediments are preserved in the Foothills but their original thickness is not known.

BURIAL HISTORY

The burial histories (to the end of the Cretaceous) of a number of samples from a section across the basin are shown in Figure 2-15. These burial histories were

computed using isopach maps of the various stratigraphic formations (from McCrossan and Glaister, 1964). An inherent assumption in this diagram is that the maximum depth of burial was achieved in post-Mannville time and that this depth exceeded the amount of overburden that was removed by erosion during the time represented by the unconformity.

The major unknown factor in these computations is the thickness of the Carboniferous in the vicinity of Leduc Woodbend. During the Late Carboniferous, considerable erosion of Mississippian rocks occurred. However, there is also considerable evidence of the thinning of Mississippian strata to the south and east. It is probable that the total thickness of Carboniferous strata in the vicinity of Leduc never exceeded 600 m (2000 ft.). Permian, Triassic and Jurassic strata probably were never present in the Leduc region or were very thin.

It can be seen that the maximum depth of burial for Devonian rocks was greatest in the western part of the basin and that it steadily decreased toward the eastern margin. The maximum depth of burial of sediments on the eastern shelf is difficult to determine because of erosion but was probably less than 1200 m (4000 ft.). The thickness of Tertiary sediments prior to erosion is not known. Some consideration of this aspect of sedimentation is given in Chapter 3. Maximum depths of burial for most of the samples examined are given in Appendix A.

HYDROLOGICAL CONSIDERATIONS

The fluid flow and geochemistry of formation waters in the Western Canadian Sedimentary Basin have been studied extensively by Hitchon and co-workers (see Billings et al., 1969; Hitchon, 1963, 1964, 1969a, 1969b; Hitchon and Friedman, 1969; Hitchon et al., 1969; Hitchon et al., 1971). They have demonstrated that the topography has a profound effect on the fluid flow in this area. Both the major and minor topographic features exert an important control on the distribution and recharge of the regional and local flow systems. Major regional recharge areas are indicated for the Disturbed Belt, Caribou Mountains, Swan Hills and Cypress Hills. Smaller hills are recharge areas of lesser importance. The major recharge areas correspond to high fluid potentials. Conversely, the major lowlands are the main regional discharge areas.

The theoretical model, based on topography, is modified to a major extent within the Alberta Basin by a thick succession of strata that acts as a low fluid potential drain which corresponds with highly permeable Upper Devonian and Carboniferous carbonate rock units. This drain essentially channels flow from the entire Alberta Basin and discharges it in the region of the Athabasca oil sands. Within the drain, channels of greater or lesser importance are indicated by low fluid potential and high fluid potential reef complexes, respectively, which are related to variations in permeability. The unconformity at the base of the Cretaceous does not appear to provide a barrier to fluid movement. Thus, there is a high degree of







FIGURE 2-16. Stratigraphic distribution of oil and gas reserves in Alberta (after Energy Resources Conservation Board, Alberta, 1973).

correlation between the composition of formation fluids from above and below the unconformity. The movement of fluids in proximity to the unconformity takes place in whichever set of strata offers the least resistance to movement, i.e. that having the greatest permeability.

A detailed study of the salinity variations in different stratigraphic units in Alberta has been made by Hitchon (1964). There is a gradual increase in the concentration of dissolved solids in the various formation waters with depth. Accompanying this trend, there is a gradual decrease in the proportion of sodium in the cations without any change in the essentially chloride-rich nature of the anions.

The regional distribution of salinities, particularly in the Devonian, shows a strong correlation with the lithology of the enclosing formation. Thus, in the Upper Devonian, notably in the Woodbend Group, high salinities prevail in the highly permeable reefal masses. The same pattern of salinities is found in the Winterburn Group as in the Woodbend, but the distribution in the Wabamun does not reflect that of the underlying reefal masses. Rather the fluid flow is essentially in an updip direction and the high permeability zones developed in the underlying Devonian are not apparent. In the Carboniferous rocks, extremely saline waters again are associated with high permeability regions of flow.

The salinity of formation waters from the Jurassic is generally low. In central and northern Alberta, the regional variations in chloride content are quite similar to the overlying Mannville. The general updip decrease in salinity is seen also in the overlying Mannville. In southern Alberta, there is some control of the salinity pattern by gross lithofacies changes and, in places, the salinity is controlled by the movement of formation waters across the sub-Cretaceous unconformity.

In the Viking, there is a close relationship between the chloride concentration and the regions of thick development of sandstone. Regions of low chloride are coincident with trends of thicker sand development. The gross lithology and not the direction of fluid flow is probably the controlling factor.

Finally, the distribution of salinity and flow patterns relative to the tar sands deposits are of interest to this study. Hydraulic head cross-sections of the Peace River (Hitchon, 1974) and Athabasca Tar Sands (Hitchon *et al.*, 1969) show that the deposits are within the near-surface groundwater regime at the present time. In the case of the Peace River deposits, the salinities of the waters are 500 mg per litre or less.

PETROLEUM OCCURRENCE

The general stratigraphic distribution of oil and gas is shown in Figure 2-16. The majority of the reserves are confined to the Devonian, but oil and gas are distributed throughout the stratigraphic column. It must be noted, however, that the heavy bitumen within the Mannville Group, notably the Athabasca Tar Sands, represents a considerable reserve which is not amenable to treatment by conventional reserve estimates.

Stratigraphic traps are characteristic of nearly all the hydrocarbon accumulations in Alberta with the notable exception of the Foothills region. In the Devonian, porous reefs constitute the main reservoirs whereas, in the post-Devonian sediments, the hydrocarbon accumulations may occur beneath an unconformity, in sand infills on the unconformity surface, in isolated sand lenses, or in sheet sands which pinch out laterally.

Approximately one half of the Middle Devonian reserves occur in the numerous Keg River pinnacle reefs of the Rainbow and Zama areas and fall outside the scope of this study. The other major accumulations (Mitsue and Nipisi) are located in outwash Gilwood Sands on the eastern flank of the Peace River Arch (Fig. 2-4). The Upper Devonian contains over 40 per cent of the total provincial reserves of oil and gas. More than 85 per cent of the hydrocarbons in this interval are in Leduc and Beaverhill Lake reservoirs; the Nisku and Wabamun account for the remainder. The Leduc and Beaverhill Lake accumulations are in stratigraphic traps of the reefal type (Figs. 2-5, 2-6); the Nisku traps are combination structural-stratigraphic types and those in the Wabamun are strictly stratigraphic in nature. The Nisku accumulations occur in porous carbonates which are draped over the underlying Leduc reefs (Fig. 2-7) whilst those in the Wabamun are located in porous carbonates underneath the Paleozoic unconformity (Fig. 2-8).

In spite of their limited areal extent, the Carboniferous rocks contain approximately 15 per cent of the total provincial hydrocarbon reserves. The accumulations are mainly in the Mississippian Rundle Group both in the Foothills and Plains areas (Fig. 2-9). On the Plains, the traps occur where porous Pekisko and Elkton carbonates are sealed at the Mississippian unconformity. In the Foothills, the hydrocarbon accumulations are in a relatively small number of large thrust-faulted and/or folded structures. The Permian sediments contain only a small reserve of hydrocarbons. These are mostly gas accumulations in the Belloy sand in the Peace River region.

The Triassic is productive in northeast British Columbia but only the Coquina Reservoir at South Kaybob and scattered localities in the Peace River region are productive in Alberta. The Jurassic reserves occur almost entirely in the Nordegg sands at Gilby and Medicine River where the sands pinch out to the east (Fig. 2-10).

Conventional hydrocarbons in the Manville and Lower Colorado (Lower Cretaceous) represent approximately 14 per cent of the proven reserves in the province. They occur in localized sand bodies, which either are infills on the eroded Paleozoic surface or are in the form of sand bars and lenses (Figs. 2-11, 2-12). In addition to the conventional accumulations, the Lower Cretaceous contains various "oil sands" deposits (Fig. 2-11b) where total reserves of bitumen in place are estimated at 895 billion barrels.

The Upper Colorado contains approximately 14 per cent of the provincial reserves, the majority of which are concentrated in two large stratigraphic sand traps (Figs. 2-13, 2-14) at Pembina and Medicine Hat. A few small pools occur in the post-Colorado part of the section. Only one small gas pool has been located in Tertiary rocks.

CHAPTER 3

RANK OF COAL AS AN INDEX OF ORGANIC METAMORPHISM FOR OIL AND GAS IN ALBERTA

by

P.A. Hacquebard

INTRODUCTION

Coal rank gives a measure of the degree of metamorphism to which vegetal matter has been subjected in the coalification series from peat to anthracite. Since organic matter is involved, it has become customary to refer to these generally low-grade alterations as organic metamorphism (Gutjahr, 1966; Staplin, 1969).

The agencies that control rank are pressure, heat, and duration of heat, all of which are related directly to the amount of overburden overlying the coal. Of these factors, heat is the most important; pressure is significant only in the early stages of diagenesis and results mainly in a loss of water due to compaction. Coal rank is an excellent measure of the degree of organic metamorphism because, once a specific rank has been attained, it cannot be reversed. An increase in heat will cause a corresponding increase in rank, but a lowering of heat will have no effect. It is for this reason that anthracite can be found at shallow depth, at a temperature that is much below that which existed during its formation. In this context, coal has been aptly described as a maximum-reading thermometer of paleotemperatures.



FIGURE 3-1. Regional geological cross-section through east flank of Alberta Syncline (after Gussow, 1962), showing coal-bearing formations and part removed by erosion since late Eocene time (for location, see Fig. 3-9, line C-D).

The objective, when correlating petroleum occurrences with coal rank, is to obtain their degree of organic metamorphism and, if possible, to find the corresponding paleotemperatures to which they were exposed. Previous studies, starting with the work of David White in 1915 (*see* Hacquebard and Donaldson, 1970, Table I), have indicated specific levels of coal rank beyond which hydrocarbons will not occur. In the present study, such levels have been determined for all the fields of Alberta that showed production in 1973, thus providing information that may be projected to new areas.

DISTRIBUTION AND RANK OF COAL DEPOSITS IN THE ALBERTA PLAINS REGION

In the Alberta Plains, the near-surface coals are of Late Cretaceous and Early Tertiary age. There are several coal-bearing formations and, since these dip gently to the west, coal lies close to the surface in many parts of the region (see Fig. 3-1). As a result, mining has been carried out in numerous localities and has provided a wealth of analytical data. These data show that the coals range in rank from lignite in the east to high volatile C bituminous in the west, but that by far the greatest part of the Plains region is occupied by coals of subbituminous rank.

Contour maps of equal calorific values and equal moisture contents have been published by the Alberta Research Council (see Stansfield et al., 1925; Stansfield and Lang, 1944) and show that coal ranks change across the Alberta Syncline in a regular manner. These maps have been updated and expanded recently by Steiner et al. (1972), and the moisture data used in Figure 3-1 were obtained from one of them. As can be seen in the cross-section (Fig. 3-1), the moisture content of the near-surface coals decreases in a regular fashion from 30 per cent in the east-northeast to 10 per cent in the west-southwest.

In the Alberta Plains, coal is present also in the upper part of the Mannville Formation, which is of Early Cretaceous age (Fig. 3-1). However, these coals have not been mined because they are thin and lie at appreciable depths below the surface. As a result, no rank data were readily available but, from old core samples, it still was possible to obtain the rank of some of these coals by means of vitrinite reflectance measurements.



FIGURE 3-2. Location, depth and rank of Mannville coal samples and isomoisture contours of near-surface coals of Edmonton and Paskapoo Formations (for location of section, *see* Fig. 3-9, line A-B).

RANK DETERMINATIONS OF MANNVILLE COALS BY REFLECTANCE MEASUREMENTS

In the Plains area north and northeast of Calgary (Fig. 3-9), it was possible to collect 54 core samples of Mannville coals that were intersected by old wells drilled in search of petroleum and natural gas. Of these, 34 samples gave reliable reflectance readings, but 20 samples did not because of oxidation of the coals. Table 3-1 gives the data on the 34 samples and Figure 3-2 shows their geographic locations, approximate subsurface depths and reflectance rank.

TABLE 3-1

Record of Mannville coal samples showing location, depth and reflectance rank

er er -2	Location of Well					Position of coal sample		ax lue)			
San Imbe						depth	sea level	al va			
well nu in F	Lsd.	Sec.	Tp.	R.	Mer.	in well elevation		%R mod			
1	9	19	46	5	W4	1979	+ 258	0.42			
2	10	34	36	4	W4	2368	- 175	0.41			
3	6	28	40	8	W4	2983	-482	0.44			
4	6	14	38	10	W4	3181	-648	0.47			
5	10	10	10	40	10		2911	-633	0.48		
5	10	18	42	12	VV4	2915	-637	0.49			
6	16	23	25	12	W4	3315	-878	0.58			
7	7	26	20	10	1414	4107	-1420	0.55			
	,	20	30	10	VV4	4133	-1446	0.59			
8	8	18	36	19	W4	4222	-1346	0.66			
9	12	14	38	21	W4	4287	-1597	0.62			
10	16	19	38	20	W4	4340	-1650	0.68			
11	8	26	39	20	W4	4235	-1547	0.67			
12	12	22	39	21	W4	4402	-1714	0.67			
13	6	29	39	22	W4	4507	-1886	0.68			
14	10	33	39	23	W4	4715	-2018	0.65			
15	4	32	38	22	W4	4617	-1881	0.61			
16	10	20	35	21	W4	4668	-1861	0.64			
17	6	6	6	6	6	32	21	wa	4606	-1878	0.60
17			32	21	¥¥4	4624	-1896	0.68			
18	8	20	32	17	W4	4103	-1280	0.58			
19	6	22	32	17	W4	4040	-1281	0.60			
20	7	17	30	18	W4	4176	-1353	0.62			
21	6	10	28	20	W4	4415	-1643	0.67			
22	10	28	26	21	W4	4696	-1740	0.66			
23	10	3	22	20	W4	3979	-1152	0.59			
24	11	15	42	4	W5	6875	-3737	0.81			
25	4	18	41	3	W5	6780	-3624	0.80			
26	3	36	37	3	W5	6911	-3900	0.80			
27	11	30	34	3	W5	7795	-4473	0.95			
28	6	15	33	3	W5	7899	-4499	0.96			
29	6	11	35	6	W5	9386	-5491	1.08			
30	12	31	37	9	W5	10790	-6481	1.31			
31	6	16	28	6	W5	11175	-6612	1.58			

The latter is given in V-types, which represent increments of vitrinite reflectance that range from 0.40 to 0.49 per cent for V4, from 0.50 to 0.59 per cent for V5, and so forth.

As can be seen in Figure 3-2, the rank of the Mannville coals increases from V4 in the east to V15 in the west. This rank increases with increasing depth of burial and is parallel to that observed for the near-surface coals (shown by the isomoisture contours). The increase in depth of the Mannville coal zone follows the general westerly inclination of the strata toward the axis of the Alberta Syncline (Fig. 3-1).

The changes in rank of the Mannville coals are only lateral in nature, because the same stratigraphic horizon is involved. That these changes are related to an increase in overburden is clearly indicated by Figure 3-2, but a true relationship can be obtained only when the rank is plotted against the original maximum depth of burial, rather than against present depth below the surface. Moreover, when the maximum depth of burial is known, it may be possible also to plot the vertical changes in rank above and below the determined values, and obtain a three-dimensional picture of the changes in organic metamorphism.

COAL RANK AND MAXIMUM DEPTH OF BURIAL

Moisture content versus depth of burial

The eroded thickness of overburden that was originally above the Mannville coals can be deduced from the rank of the overlying near-surface coals. These coals are lignites and subbituminous coals and, as such, are ranked by their moisture content. A correlation between moisture content and depth of burial is, therefore, required. For this it is necessary to have moisture data on vertical coal sequences through various rank stages. Such data do not exist in Canada, but they are available from German mines and boreholes in publications by Kutzner (1960) and Patteisky and Teichmüller (1960).

For the lowest rank material, the brown coal deposit near Cologne has provided the necessary analyses, while the higher rank moisture data were obtained from boreholes in the Upper Silesian coalfield. When the information of both areas is plotted in one diagram, it is found that the moisture content decreases logarithmically with depth (see Fig. 3-3).

It is interesting to point out that, on some British and New Zealand coal sequences, Suggate (1959) obtained a similar result, with a closely comparable logarithmic rate of decrease.

Eroded sediments of Alberta Syncline

In Figure 3-1, the maximum thickness of sediments originally present in the Alberta Plains has been plotted to scale in relation to the geological cross-section. The various eroded thicknesses were obtained from the moisture contents of the near-surface coals and their correlation with maximum depth of burial as shown in Figure 3-3.

Figure 3-1 indicates that the order of magnitude of the eroded overburden is not unreasonable.



FIGURE 3-3. Relationship of moisture content of coal and depth of burial, plotted logarithmically from data of Kutzner (1960) and Patteisky and Teichmüller (1960).

The Paskapoo Formation is known to reach a present thickness of more than 1524 m (5000 ft.) in the Porcupine Hills of southern Alberta (Taylor *et al.*, 1964), and an original thickness of at least 1829 m (6000 ft.) may, therefore, be acceptable. Like the underlying formations, the Paskapoo would have thinned toward the east but, starting with an optimum of 1829 m (6000 ft.), there is sufficient thickness available to make up the calculated overburden corresponding with 20, 25 and 30 per cent moisture. Moreover, the removed thicknesses of the Edmonton and Belly River Formations also contribute to this.

The required 2195 m (7200 ft.) of overburden for the 10 per cent moisture position are more difficult to interpret. An additional 914 m (3000 ft.) of overburden, probably also of Paskapoo age, are necessary because, following this period, the whole region was uplifted and subjected to erosion. These additional strata may well have occurred in the western region adjoining the Foothills because of its proximity to the area of greatest subsidence and aggradation, prior to the Laramide Orogeny. According to Taylor *et al.* (1964), the major source of the Paskapoo sediments was the Cordilleran geanticline, and especially the highlands of its eastern flank in the present Columbia Mountains (i. e. collectively the Purcell, Selkirk and Monashee Mountains). These deposits formed "a great series of coalescent, interfingering alluvial fans, fluvial sediments and basin deposits which fringed the highlands and reached across the Rocky Mountain geosyncline on the stable shelf" (Taylor *et al.*, ibid.).

Rank of Mannville coals versus maximum depth of burial

The maximum depth of burial of the Mannville coals is obtained by adding the thickness of eroded sediments to the present depth below the surface. This has been done in Figure 3-4, which shows the relationship between rank and maximum depth of burial of 30 Mannville coals across the eastern flank of the Alberta Syncline (Sec. A-B in Figs. 3-2, 3-4). The rank is shown on the abscissa in per cent reflectance and the

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FIGURE 3-4. Rank and maximum depth of burial of Mannville coals.

depth of burial on the ordinate at the left in both feet and metres. On the ordinate at the right, the per cent moisture of the near-surface coals is ruled off in relation to their corresponding depths of burial, as obtained from Figure 3-3.

The procedure followed in plotting the curve is illustrated with Mannville coal D, which has a reflectance of 0.62 per cent and lies 1402 m (4600 ft.) below the present surface, where near-surface coal E has 20 per cent moisture. A coal with 20 per cent moisture requires an overburden thickness of 1463 m (4800 ft.). The maximum depth of burial of coal D, therefore, is 1402 + 1463 = 2865 m (4600 + 4800 = 9400 ft.), which is shown on the ordinate.

The other 29 coals used for the diagram have been plotted in the same way. The resultant curve shows that a good correlation exists between rank and maximum depth of burial. However, the Mannville coalification curve relates only to lateral changes along an east-west section that is 338 km (210 miles) long. For an insight into the vertical changes in rank above and below the curve, additional information on coalification time and paleotemperature is required.

RANK, COALIFICATION TIME AND PALEOTEMPERATURE

Coalification diagrams of Karweil and Bostick

The diagram of Karweil, which was first published in 1956, shows the effect of time on the coalification process (see Fig. 3-5). When, for instance, vegetal matter is heated at 120°C for 10 m.y., a high volatile bituminous coal with 0.6 per cent Ro or 43.7 per cent V.M. will result. However, if the duration of heat is extended to 100 m.y., then a low volatile bituminous coal with 1.68 per cent Ro or 20 per cent V.M. will be formed. The diagram, which is based on reaction kinetics, also shows that long heating at relatively low temperature can produce coal of the same rank as short heating at higher temperature. For instance, $60^{\circ}C$ during 300 m.y., or $180^{\circ}C$ for 10 m.y. will both result in a bituminous coal with 35 per cent V.M.

From the diagram, it is obvious that, if the rank of coal and its coalification time are known, the paleotemperature can be read directly from the ordinate. For studies of organic metamorphism in relation to petroleum occurrences, this feature is of particular importance. Bostick (1973) used it to great advantage in his studies of phytoclasts and, since the rank of these dispersed coaly particles is obtained from reflectance measurements, he converted Karweil's diagram into one showing contours of equal reflectance (see Bostick, 1973, Fig. 8). In so doing, the Ro rank of coal can be translated readily into paleotemperatures once the coalification time has been determined.

Coalification history of Mannville coal with a rank of 0.74 per cent Ro

Bostick's diagram lends itself well to plotting the coalification history of particular samples. Following his guidelines, the history of a Mannville coal with 0.74 per cent Ro is portrayed in this manner in Figure 3-6 by the V-shaped curve.

The coal, which is Early Cretaceous in age, was initially deposited 104 m.y. ago. This is shown as 0 on the time scale marked on the abscissa. After its formation, the original peat bog was buried by younger sediments, and subsidence and deposition continued until late Eocene-early Oligocene time, when the region was uplifted, following the Laramide Orogeny. Therefore, at 72 m.y. after its initial deposition, the coal reached its maximum overburden and was subjected to the optimum temperature. After this, erosion took place until the present time, or for 32 m.y.

At present, the coal lies at a depth of 1829 m (6034 ft.) and has a rank of 0.74 Ro. The current temperature at this depth is 55° C. This value was obtained by interpolation from the Simonette oil pool, because it lies at the same relative rank position in the field as the Mannville coal under discussion, namely below the 17 per cent moisture contour. Oil with a



FIGURE 3-5. Relationships between rank, temperature and duration of coalification (after Karweil, 1956, simplified; with VM-Ro conversions according to Teichmüller, 1971 and Alpern and Lemos de Sousa, 1970).

measured temperature of 105° C occurs at a depth of 3534 m (11 662 ft.), which calculates to a geothermal gradient of 2.92°C/100 m. From this, a temperature of 55°C is obtained at a depth of 1829 m (6034 ft.).

Of the particular Mannville coal under discussion, the following data now are available: 72 m.y. until maximum overburden was reached; 32 m.y. of erosion until the present time; a rank of 0.74 per cent Ro; and a current temperature of 55°C.

When this information is entered in Bostick's and Karweil's coalification model, then the V-shaped curve shown in Figure 3-6 will result. It shows (through integration of the area above the curve with the total area of the rectangle) that a rank of 0.74 per cent Ro can be obtained only when, at 72 m.y., a temperature of 103°C has been reached. As the 0.74 per cent isoreflectance contour intersects the 103°C abscissa at 35 m.y. (point A in Fig. 3-6), it follows that this particular rank can be equated with a heating period of 35 m.v. This does not mean that the coal actually was heated for that length of time at that temperature. As the diagram shows, the temperature gradually increased to 103°C during 72 m.y., and then decreased to 55°C during the next 32 m.y. The result, however, is the same as is portrayed in Karweil's diagram by the 35 m.y. contour, at 103°C.



FIGURE 3-6. Coalification history of Mannville coal with a rank of 0.74% Ro and present subsurface temperature of 55°C [plotted according to Bostick's (1973, Fig. 8) coalification diagram with Ro contours based on Teichmüller's (1971) conversion].



FIGURE 3-7. Relationship of rank and paleotemperatures of Mannville coals, based on 35 m.y. contour of Karweil's (1956) coalification diagram (with VM-Ro conversions of Teichmüller, 1971).

Correlation of paleotemperatures and Ro rank of Mannville coals

With the establishment of a coalification period equal to the 35 m.y. contour, it now becomes possible to obtain the paleotemperatures of the various rank stages of the Mannville coals.

For each time contour in Karweil's diagram there is a logarithmic relationship between coal rank and paleotemperature. For the 35 m.y. contour, this relationship is shown in Figure 3-7. For example, a rank of 0.8 per cent Ro correlates with a temperature of 106° C.

CONSTRUCTION OF COALIFICATION DIAGRAM APPLICABLE TO ENTIRE ALBERTA PLAINS REGION

By returning to the Mannville coalification curve (Fig. 3-4) with the paleotemperatures corresponding to the various Ro readings, it is possible now to calculate the paleogeothermal gradient and determine the positions of the isoreflectance contours. The resulting diagram, shown in Figure 3-8, gives a three-dimensional picture of the changes in rank (or degree of organic metamorphism). Apart from the vertical changes, it also relates to regional changes, because the diagram is tied in with the isomoisture contours of Figure 3-2 and,





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FIGURE 3-9. Map of Alberta showing isomoisture contours of near-surface coals and locations of crude oil pools with reserves greater than 5 million barrels (after Steiner *et al.*, 1972, Fig. 5 and Energy Resources Conservation Board, Alberta, 1973).


FIGURE 3-10. Map of Alberta showing isomoisture contours of near-surface coals and locations of natural gas pools with reserves greater than 50 billion cubic feet (after Steiner *et al.*, 1972, Fig. 5 and Energy Resources Conservation Board, Alberta, 1973).





b) Oil reserves according to major stratigraphic discoveries

FIGURE 3-11. Coal rank assignments and paleotemperatures of initial petroleum reserves in producing fields of Alberta.

and, therefore, is applicable to the entire Alberta Plains region. This is considered acceptable because the agencies that controlled the coalification of the near-surface coals were the same as those affecting the underlying measures.

Calculation of paleogeothermal gradients

The procedure followed can best be explained by considering one particular coal of the Mannville curve, namely coal C (see Figs. 3-4, 3-8). Coal C has a depth of burial of 3810 m (12 573 ft.) and a rank of 0.8 per cent Ro, which corresponds to a paleotemperature of 106°C (from Fig. 3-7). The gradient over this depth, when using a surface temperature of 16°C, calculates to 2.4°C/100 m (or 1.30°F/100 ft.). A surface temperature of 16°C (or 60°F) was used because, during early Oligocene time (when the maximum depth of burial was reached), a mild climate prevailed in western Canada, with a much higher average annual temperature than at present (Piel, 1971).

Calculations, similar to the one explained above, have been made to obtain the gradients at the other principal Ro positions. The results, which are shown in the uppermost abscissa of Figure 3-8, indicate that the paleogeothermal gradient was not constant, but varied across the section. The highest gradient of 2.8°C/100 m occurred in the east, on the site of the Canadian Shield (left side of Fig. 3-8) and the lowest gradient of 2.2°C was obtained in the west, where the sedimentary column is thickest (these gradients are equal to 1.52°C and 1.23°F/100 ft., respectively).

This result conforms with present observations of the geothermal gradient, except that the current temperatures are higher, with gradients declining from 4. 3° C/100 m in the east to 2. 2° C in the west along the same line of section (or from 2. 4° to 1. 2° F/100 ft., respectively).

Determination of isoreflectance contours

The isoreflectance contours show the vertical and lateral changes in Ro rank in the subsurface in relation to the Mannville coalification curve (dashed lines in Fig. 3-8). Their position has been obtained from the geothermal gradients and the paleotemperatures. The procedure is as follows: in order to find the vertical position of 0.7 per cent Ro above the 0.8 per cent position on the curve (at C), one subtracts the two corresponding temperatures of 106° and 96° (from Fig. 3-7) and divides by the gradient of 2.4. As the latter is per 100 m, it is necessary to multiply by 100, which gives a distance of 417 m (1376 ft.).

In the same way, the positions of 0.6, 0.5 and 0.4 per cent Ro above the curve have been calculated, as well as those for 0.9 to 1.6 per cent Ro below the curve. The procedure was repeated for all principal Ro positions of the curve and, by connecting the corresponding Ro level, the isoreflectance contours were drawn. With these contours, the rank now can be obtained for every subsurface position above and below the Mannville coal horizon throughout the Alberta Plains region.

DISTRIBUTION OF OIL AND GAS POOLS IN RELATION TO ISOMOISTURE CONTOURS OF NEAR-SURFACE COALS

In Figures 3-9 and 3-10, the oil and gas pools have been plotted on the isomoisture contour map of the nearsurface coals present in the Alberta Plains region. Noteworthy is the observation that these maps already reveal a general correlation between coal rank and the known petroleum occurrences. Figure 3-9 shows that, with the exception of two fields, there are no oil pools west of the 10 per cent moisture contour. These exceptions are the Ricinus and Turner Valley fields, both occurring in structurally deformed areas. On the other hand, the gas pools (Fig. 3-10) extend as far west as the 4 per cent moisture contour, denoting a geographic demarcation with a higher rank of coal than the oil pools.

From the maps, the rank, in terms of moisture content of the near-surface coals immediately overlying the oil and gas pools, can be read directly. This is illustrated with the Judy Creek and Pembina oil fields in Figure 3-9. At J, the moisture content is 26 per cent and at P it lies between 15 and 20 per cent, averaging 17 per cent.

In Figure 3-10, the gas pools of Edson and Medicine Hat have been especially marked. At E, the moisture content of the near-surface coals is 14 per cent, while at M it lies between 25 and 35 per cent, averaging 30 per cent.

DETERMINATIONS OF DEGREE OF ORGANIC METAMORPHISM (DOM) OF PRODUCING PETROLEUM FIELDS IN ALBERTA

Procedure followed in obtaining the coal rank positions

The four petroleum occurrences especially indicated on the isomoisture contour maps are shown also in Figure 3-8, and have been marked 1, 2, 3 and 4. Their DOM in terms of coal rank are determined in the following manner.

The Judy Creek oil pool (1) is plotted at the 26 per cent moisture position to its producing depth of 2743 m (9000 ft.), where it lies at a rank level of 0.8 to 0.9 per cent Ro, or V8. The Pembina oil pool (2) is plotted at the 17 per cent moisture position. It produces from an average depth of 1524 m (5000 ft.), which correlates with a rank of V6. The Medicine Hat gas pool (3) at 30 per cent moisture and a depth of 610 m (2000 ft.) plots through to V4. The Edson gas field (4), which underlies the 14 per cent moisture contour by 3048 m (10 000 ft.), is correlated with a rank of V10.

Of these fields, those below the Mannville curve produce from the Paleozoic, while those that lie above it have production from the Cretaceous or Tertiary. Since the former are below the Paleozoic unconformity (see Fig. 3-1), the question arises: can their rank position be projected from the considerably younger Mesozoic coals? The answer to this question is related to the maximum depth of burial, because it controls the rank of coal. An increase in depth of burial can cause an increase in rank, but a decrease will not affect it, because the coalification process is irreversible; once a specific rank has been attained, it cannot be diminished.

It seems reasonable to assume that the maximum depth of burial took place in post-Mannville time, and that this depth exceeded the amount of overburden that was removed by erosion during the time represented by the unconformity. Rank projections from the Cretaceous into the underlying Paleozoic, therefore, appear to be in order.

<u>Coal rank assignments and paleotemperatures</u> of initial petroleum reserves in producing fields of Alberta

Rank assignments of all oil and gas pools known in Alberta in 1973 have been made in the same manner as was explained previously for the four selected fields shown in Figure 3-8. A total of 78 oil pools and 66 gas pools have been considered and, of each, the calculated initial reserves have been plotted against the projected coal rank, which is given in terms of reflectance by V types. For each V type, moreover, the corresponding paleotemperatures (obtained from Fig. 3-7) have been recorded also. The data on initial reserves, depth of producing zones and their geological age were obtained from the publication by the Energy Resources Conservation Board of Alberta (1973) on oil and gas reserves. The results are shown in Figure 3-11a and Appendices B and C.

The diagram reveals that, in Alberta, 88 per cent of the initial (in place) oil reserves have a DOM comparable to a coal rank of 0.5 to 0.9 per cent Ro (V5-V8), with about half (41%) of this occurring at V6. The paleotemperatures in this interval range from 68 to 116°C, with the bulk occurring between 82 and 96°C. No oil was found above V12, or above 143°C. These results conform rather well with published data of Landes (1966), Wassojewitch et al. (1969), Tissot et al. (1971) and Teichmüller (1974), which indicate that significant hydrocarbon generation begins about 65°C (0.5% Ro) and destruction of liquid hydrocarbons takes place above 135-150°C (1.2% Ro). This interval has been called the "liquid window" by Pusey (1973). In Alberta, the liquid window lies essentially between 52 and 131°C (or between 0.4 and 1.1% Ro). When expressed in thickness of potential sediments, the window averages about 3000 m (9900 ft.), as deduced from Figure 3-8).

An interesting observation is that, while the Paleozoic oil occurs in about the same quantities at the rank levels of V6, V7 and V8, the Cretaceous oil is found predominantly at V6.

Further distinctions can be made if the oil reserves are broken down according to their stratigraphic occurrence (Fig. 3-11b). The distribution of Devonian and post-Mannville (Cretaceous) reserves are symmetrical about modes at V7 and V6, respectively. This type of distribution to a large extent reflects the close association of the oil pools with their source rocks. In contrast, the distribution of Mannville and Jurassic reserves indicates the effects of secondary migration. These are the pools occurring in the V4 zone in the vicinity of Lloydminster and the more important Mannville accumulations occurring in the V5 zone. In contrast, only a small proportion of the Mannville reserves occur in the V6 and V7 classes which are the optimum zones for the occurrence of oil in the Devonian and post-Mannville sequences. The occurrence of oil in the V4 zone below the minimum generation temperature of 65°C indicates that up-dip migration has occurred. Organic geochemical studies of Alberta oils (see Chap. 6) give strong support to an eastern migration of oil derived from the Mannville. In the case of the Mississippian, the distribution of reserves is enlarged to include the V9 and V10 zones due to the fields in the Harmattan region adjacent to the Foothills.

As regards the DOM of natural gas pools, large quantities of biogenic methane occur at a coal rank of V4, or between temperatures of 52 and 68°C. Thermal gas ranges over a much larger rank interval; it is abundant particularly between V8 and V11 (47% of total thermal gas) and substantial quantities also lie at V15 (15%). The temperature range of the thermal gas is from about 106 to 177°C. According to Landes (1966), gas is found between 120 and 204°C. So, here also, the Alberta occurrences are within the broad temperature limitations previously published.

In general terms, it can be stated that, in Alberta, the DOM of most of the oil is comparable with a rank of V5 to V8, or with high volatile "C" to high volatile "A" bituminous coal. Gas compares with V8 to V19, or with middle of high volatile "A" bituminous coal to semi-anthracite.

In conclusion, it can be stated that the present comparative study of coal rank and petroleum occurrences supports the view that both oil and gas occur within specific ranges of organic metamorphism. These ranges are defined by the paleotemperatures and this temperature interval can be deduced from the rank of coal and also from the rank of dispersed coaly particles in associated sediments. Rank determinations, therefore, are an important tool in petroleum exploration. They can outline areas with a favourable degree of organic metamorphism, and also indicate the subsurface position of the petroleum "floor" beyond which exploration drilling should not be extended.

CHAPTER 4

ANALYTICAL METHODS AND SAMPLING PROCEDURES USED IN GEOCHEMICAL STUDY

ANALYTICAL PROCEDURE

The analytical methods used are described in detail by Oudin (1970) and Durand *et al.* (1970) and are summarized in Figure 4-1. The oils were distilled and the fraction boiling above 210° C retained. The fraction boiling below 210° C was not used in the analysis since its composition can be altered during sampling and storage (Poulet and Roucaché, 1970). The rocks were ground to <90 microns in an "aurec" pulverizer and the organic carbon determined. Selected samples were extracted in a soxhlet with chloroform in total darkness according to the method described by Durand *et al.* (1970).

The same procedure was then used on both the oils and rock extracts (Fig. 4–1), and is applicable when as little as 100 mg are available. Separation of asphaltenes was achieved by precipitation with hexane and saturated hydrocarbons; aromatic hydrocarbons and resins were separated by liquid chromatography on alumina and silica gel. This stage of the analysis gave information on the overall composition of the oil or extract and provided a basis for the selection of samples for more detailed study.

The saturated hydrocarbons were analyzed by capillary gas chromatography (CGC) and mass spectrometry (MS). The mass spectrometry was carried out on an AEI MS2 instrument. The volumetric percentage of normal + isoalkanes and cyclo-alkanes with 1, 2, 3, 4, 5 and 6 cycles (Fig. 4-2) were determined by the method of Hood and O'Neal (1959). Gas chromatography was carried out using a Perkin Elmer 900B gas chromatograph with a capillary column coated with OV-17. Normal alkanes ranging from nC₁₄ to nC₃₀ were analyzed (Fabre *et al.*, 1972) as well as isoprenoid alkanes ranging from C₁₅ to C₂₅ (Han and Calvin, 1969) (Fig. 4-2).

The aromatic hydrocarbons also were analyzed by gas chromatography. Both the distribution of true aromatics and thiophenic compounds were determined using a gas chromatograph equipped with both a flame ionization detector (FID) and a flame photometric detector (FPD). The results are illustrated in Figure 4-3. The upper chromatogram (FID) represents the data for both the aromatic and thiophenic compounds while the lower curve (FPD) shows only the thiophenic compounds. The lower curve represents the distribution of three main types of thiophenes: the benzothiophenes, the dibenzothiophenes and the naphthobenzothiophenes (Castex *et al.*, 1974). The range of each of these is shown in the lower part of Figure 4-3 with the structure characteristic of each group. Gas chromatographic analysis was used as a basis for selecting samples for a more detailed study of the aromatic hydrocarbons.

The aromatic hydrocarbons were then split by liquid chromatography into the mono-, di- and triaromatic fractions (Figs. 4-1, 4-4). A detailed study was made of each fraction using mass spectrometry at a low ionization voltage (10 eV). This analysis (Oudin, 1970) gave the distribution in mass per cent of the aromatic and thiophenic compounds in each aromatic fraction (Figs. 4-4, 4-5). The distribution of compounds can be determined as a function of:

- (a) Number of carbon atoms (Fig. 4-5a);
- (b) Mass family C_nH_{2n-p} (Fig. 4-5b, f);
- (c) Number of carbon atoms within each mass family for the successive aromatic compounds of p=6 to p=28 and for the sulphur compounds (benzo- and dibenzothiophenes), known as thiophenics, of the same molecular mass (Fig. 4-5c to e).

Sulphur analyses were made on both the total oil or extract and on the aromatic fraction.

SAMPLING AND PROGRAMME

The study has been made in two geographic areas as previously indicated (Fig. 1-1). The geographic locations of the oil and rock samples from each of the major stratigraphic intervals are plotted in Figures 2-4 to 2-14 and are cross-referenced to Appendices D and E. In each area, the analytical work has been carried out in four successive stages as follows:

- (a) Measurement of total organic carbon in rocks;
- (b) Extraction (or distillation to 210°C) and fractionation of the extracts (or the oils) followed by analysis of their saturated hydrocarbons by capillary gas chromatography (CGC) and mass spectrometry (MS);
- (c) Analysis of their aromatic hydrocarbons and thiophenic compounds by capillary gas chromatography (CGC);
- (d) Analysis of their aromatic hydrocarbons by MS after fractionation into mono-, di- and triaromatics.

Each of the stages a, b, and c have served for the selection of samples to be analyzed in the following stages. The numbers of samples from the two areas which have been analyzed in this manner follow on pages 26 and 27.





SAMPLE	M 62
LOCATION	FIGURE LAKE 6 · 24 · 63 · 18W4
DEPTH	2195
AGE	ALBIAN
FORMATION	GLAUCONITIC SS
IDENTIFICATION	O



- a) Distribution of cyclic compounds by ring number based on mass spectrometry.
- b) Distribution of n-alkanes and acyclic isoprenoids.
- c) Gas chromatogram showing n-alkanes, and acyclic isoprenoid alkanes.



FIGURE 4-3. Gas chromatograms of the aromatics and thiophenes. Aromatics and thiophenes are combined in upper curve (FID) and thiophenics alone in lower curve (FPD). Range of the three detected groups of thiophenic compounds included in curve showing below. Note difference in range of thiophenes in a conventional (Group 2) Mannville oil compared to a typical (Group 3) Devonian oil.

For the oils from the central part of the basin: 135 samples of which 25 samples stage b yielded insufficient extract to 79 samples stage b allow the total analysis outlined stage c 49 samples in b. stage d 25 samples 35 samples stage c 21 samples stage d

For the extracts from the central part of the basin:

stage a 545 samples of 200 g each. Of these, 125 were made up of 1000 g and 49 supplementary samples were analyzed because of contamination problems. For the oils from the margin of the basin:

stage b27 samplesstage c27 samplesstage d2 samples



FIGURE 4-4. Principal structural types of aromatic hydrocarbons. Monoaromatics occur in aromatic fraction 1, diaromatics in fraction 2, triaromatics in fraction 3. Benzothiophenes are eluted with fraction 2 and dibenzothiophes with fraction 3.

For the extracts from the margin of the basin:

stage a	241 samples with 36 supplemen
	tary samples.
stage b	54 samples of which 10 did not
	yield any extract and only 11
	samples had sufficient extract
	to complete the analysis out-
	lined in b.
stage c	24 samples
stage d	4 samples

For heavy oil extracts from the margin of the basin:

stage b	63 samples of which 35 were
	completely analyzed at this
	stage.
stage c	39 samples
stage d	3 samples

A detailed list of all samples giving locality and the different procedures carried out on each sample is given in Appendices D and E.

SAMPLE	Wb2		
LOCATION	GOLDEN SPIKE 12-24-51-27W4		
DEPTH	4602′		
AGE	FAMENNIAN		
FORMATION	WABAMUN (D1)		
IDENTIFICATION			





DISTRIBUTION BY



FAMILIES DISTRIBUTION IN THE MASS CnH2n-12 CnH2n-14 CnH2n-18 cent d e 2.25 4.50 2.25 F1 **F1** Aromatic hydrocarbons mass per 2.00 200 400 F2+3 F2+3 3.50 1.75 1.75 3.00 1.50 1.50 2.50 1.25 1.25 2.00 1.00 1.00 0.75 1.50 075 0.50 1.00 0.50 0.25 0.5 0.25 0.00 0.00 0.0 25 Carbon number Carbon number Carbon number GSC

FIGURE 4-5. Typical distribution of aromatic compounds based on mass spectrometry.

- a) Distribution of aromatic hydrocarbons by carbon number.
- b) Distribution by mass family in total aromatic fraction.
- c) Distribution by carbon number in the mass family C_nH_{2n-12} . Peak at C_{13} is attributed to the naphthalene family and the peak at C_{17} to dibenzothiophenes. F_1 =fraction 1, etc.
- d) Distribution by carbon number in the mass family C_nH_{2n-14} . Peak at C_{17} is attributed to true aromatics and plateau at C_{20} , C_{21} to dibenzothiophenes.
- e) Distribution by carbon number in the mass family C_nH_{2n-18} (phenanthrene). Peak at C_{18} is attributed to phenanthrene and secondary peak at C_{20} - C_{21} is attributed to dibenzothiophenes.
- f) Distribution by mass family in fraction 3, compounds at p=12, 14, 16 are equivalent to sulphur families 16S, 18S, 20S (see Fig. 4-4).



- B) Sample washed in chloroform.
- C) Interior of core sample. D) Exterior of core sample.



SAMPLE	LC19
LOCATION	SANDY LAKE 13-4-84-20W4
DEPTH	680′
AGE	ALBIAN
FORMATION	JOLI FOU
IDENTIFICATION	-•-



50

10

50



GROSS COMPOSITION



SaturatesS AromaticsA Asphaltenes and resins...L

SAMPLE	M41
LOCATION	MARTEN HILLS 6-19-75-24W4
DEPTH	2144′
AGE	ALBIAN
FORMATION	CLEARWATER
IDENTIFICATION	Ð

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SAMPLE	M76
LOCATION	TAWATINAW NORTH 10-34-60-21W4
DEPTH	2487'
AGE	ALBIAN
FORMATION	GLAUCONITIC SS
IDENTIFICATION	•







SAMPLE	M77
LOCATION	TAWATINAW NORTH 10-34-60-21W4
DEPTH	2487′
AGE	ALBIAN
FORMATION	GLAUCONITIC SS
IDENTIFICATION	•



FIGURE 4-7. Example of Type 1 contamination of rock extracts from the margin of the basin.

Amontal Company and Amontal Company	
SAMPLE	
LOCATION	DIESEL OIL
DEPTH	
AGE	
FORMATION	
IDENTIFICATION	

Saturates
Asphaltenes and resins





SAMPLELC 20LOCATIONWABASCA
10-5-83-21W4DEPTH719'AGEALBIANFORMATIONVIKINGIDENTIFICATION---











FIGURE 4-8. Examples of Type 2 contamination of rock extracts.

PROBLEM OF CONTAMINATION

In both areas of study, many of the rock extracts were found to be contaminated to a greater or lesser extent. For example, in the central part of the basin, 60 out of 110 samples have some anomaly in the distribution of normal alkanes. There is a maximum in the normal alkane distribution at nC_{20} (Fig. 4-6a) which occurs irrespective of the geological or geographic provenance of the samples. The anomaly was reduced by superficial washing of the core but there is no doubt that the contamination extended deeply into the samples. To check the extent of the contamination, the peripheral 7 to 8 mm of a core were removed and extracted separately from the central part of the core. The saturated hydrocarbons from the periphery show a prominent maximum at nC_{20} in the normal alkanes (Fig. 4-6d); in contrast, the saturated hydrocarbons extracted from the core interior do not show such a marked maximum at nC_{20} (Fig. 4-6c), but it is present nonetheless. Hence the contamination is deeply impregnated in the rock. It seems that the polluting agent is almost entirely composed of saturated hydrocarbons rich in normal and iso-alkanes. In the contaminated

TABLE 4-1

Composition of extracts from contaminated and uncontaminated rock

Sample No. LC10 Bingley 4-23-40-7W5 7560' Albian-Viking	Exterior Part (contaminated)	Interior Part (uncontaminated)		
Gross composition of ext	racts			
% resins + asphaltenes	45.50	41.10		
% HC aromatics	18.00	15.70		
% HC saturated	36.50	43.20		
Ratio HC saturated/HC aromatics	2.02	2.75		
% resins + asphaltenes % resins + asphaltenes + HC arom.	71	72		
% HC aromatics % resins + asphaltenes + HC arom.	29	28		
Composition of saturate	d HC			
% alkanes (iso + n)	53	61		
% cyclo-alkanes	47	39		
Distribution of cyclo-alkanes				
cyclo-alkanes with 1 ring	28.1	27.8		
cyclo-alkanes with 2 rings	25.0	25.9		
cyclo-alkanes with 3 rings	18.5	19.1		
cyclo-alkanes with 4 rings	17.7	16.7		
cyclo-alkanes with 5 rings	10.7	10.5		

GSC

samples, there is an increase in the proportion of saturated hydrocarbons (Table 4-1) and more particularly the iso- and normal alkanes. In comparison, the distribution of resins, asphaltenes and aromatic hydrocarbons remains unchanged and, also, the cycloalkanes are not affected. Examination of the aromatic hydrocarbons (CGC) does not show any difference between the hydrocarbon extracts of the periphery and those from the interior part. This contamination has been designated type 1. The 60 polluted samples were not contaminated to the same extent and the results obtained on 30 of them could be used.

Similar contamination problems were encountered in the study of the margin of the basin. In this region, those samples that had a low extract yield were contaminated to the greatest extent (Fig. 4-7a, b, c). This feature can be illustrated by two extracts from the same level at Tawatinaw North (Fig. 4-7c, d). The sample with the lowest extract (M76, 55 mg) was contaminated to a greater extent than the sample with a higher extract (M77, 150 mg). The polluted samples also are characterized by a low content and irregular distribution of isoprenoids. Many of the Devonian samples from this region also have been contaminated.

Another type of contamination (type 2) is illustrated by an extract from the Bohn Lake sample (M31) from the McMurray Formation (Fig. 4-8). This extract, which is anomalously low in asphaltenes and resins, has a large yield of saturated hydrocarbons (242 mg). The chromatogram of the saturated hydrocarbons shows a symmetrical hump of unresolved peaks in the vicinity of C_{18} (Fig. 4-8). This distribution is similar to that of diesel oil in which the compounds below C18 have been lost by evaporation. A similar hump in the same range was found in the chromatogram of the aromatic hydrocarbons. This feature was confirmed by the MS analysis where the distribution of aromatic hydrocarbons by carbon number shows a narrow and symmetrical distribution about a C₁₇ to C₁₈ mode; the same feature was found in the various aromatic and thiophenic mass families. In addition, the monoaromatics clearly are more abundant than the other mass families.

CHAPTER 5

GEOCHEMICAL ANALYSES OF CONVENTIONAL OILS (BASIN CENTRE) AND ROCK EXTRACTS

GEOCHEMISTRY OF OILS

Three groups of oils have been defined in the Western Canadian Sedimentary Basin.

- Group 1 occurring in Upper and Lower Cretaceous reservoirs (Belly River, Cardium, Viking Fms.)
- Group 2 occurring in the lowermost Cretaceous (Lower Mannville Gp.) Jurassic and Mississippian
- Group 3 occurring in the Upper Devonian (Nisku, Leduc Fms.) and Middle Devonian (Beaverhill Lake Fm.)

There are exceptions to this stratigraphic classification for some oils occurring in the vicinity of the Lower Cretaceous unconformity.

Gross composition

The Group 2 oils can be distinguished from the other two groups on the basis of gross composition (Fig. 5-1). They are richer in aromatics ($\geq 20\%$) and asphalt (including resins) than the remaining oils.

Generally, analyses of the total oils (Fig. 5-1) show that the Group 2 oils are richest in aromatics (>20%) and asphalt (including resins). Similarly, analyses of the oil "residues" ($t^{\circ} > 210^{\circ}$ C) demonstrate that the Group 2 oils are richest in aromatics and poorest in saturated hydrocarbons (<55%) (Fig. 5-2). It is not possible, however to distinguish between the other two groups on the basis of gross composition alone. The difference between Group 2 and the other groups is shown more clearly by the distribution of hydrocarbons (acyclic alkanes, cyclic alkanes and aromatic hydrocarbons) (Fig. 5-3). The samples belonging to Group 2 have the highest aromatic content (>33%) and the lowest alkane content (<29%), but again the other two groups cannot be distinguished.

At this stage, it is worth noting the exceptions to the above classification. The Mississippian oils (Elkton Fm.) from Westward Ho (Sample 47, Appendix D and Fig. 2-9), Sundre (46), Harmattan East (49) and Harmattan Elkton (48) are clearly richer in saturated hydrocarbons (>65%) than the other oils of Group 2. The proportion of aromatic hydrocarbons in the total hydrocarbons is lower than (<30%) and the cyclic alkane contents are amongst the highest of the Group 2 oils. The Sylvan Lake (72, 73) and Medicine River (66-70) oils are richer in saturated hydrocarbons than most of the Group 2 oils but the distribution of hydrocarbons within the saturate fraction (acyclic and cyclic alkanes) is similar. The Niton (62) crude and the oils from northeast of Leduc-Woodbend (N. Leduc-Woodbend, 60), Armisie (59) and Acheson East (58) are richer in alkanes than most of the Group 2 oils and contain a higher proportion of branched and normal alkanes. In contrast, the Wabamun (38) oil (Devonian) is similar to the Group 2 oils.

The sulphur analyses (Fig. 5-4) show that the Group 2 oils are richest in sulphur (≥ 0.70 %). Note that the Group 2 oils, as a rule, occur in reservoirs that are close to the pre-Cretaceous unconformity.

Saturated hydrocarbons

Mass spectrometric analysis of the saturated hydrocarbons can be used to distinguish all 3 groups of oils. The distinctions are based on the distribution of acyclic (normal and branched) alkanes, cyclo-alkanes with one and two rings, and cyclo-alkanes with three or more rings (Fig. 5-5). The second group is characterized by a low acyclic alkane content ($\leq 49\%$). The third group is separated from the first by the high percentage of cyclo-alkanes with 1 and 2 cycles (<29%).

The Jurassic and Mississippian oils [Medicine River (66-70), Gilby (65), and Sylvan Lake (72, 73)] and the Wabamun (38) oil (Leduc-Woodbend pool) have characteristics of the second group. These oils, along with the oils from the "Ostracod and Glauconitic" zones of the Mannville are amongst the richest in polycyclic alkanes (>3 rings >22%). The Niton oil from the base of the Cretaceous is distinctly different from the remainder of the Group 2 oils; it has a very high percentage of alkanes (>65%) and a very small content of cyclo-alkanes (1 and 2 cycles <25%).

Analysis of the saturated hydrocarbons by capillary gas chromatography shows a similarity in the distribution of n-alkanes in the different groups (Fig. 5-6); the Niton oil containing a higher proportion of high molecular weight n-alkanes (>C₂₃) is an exception (Fig. 5-20). However, the acyclic isoprenoid content, expressed as a percentage of the n-alkanes, can be used to separate the three groups (Fig. 5-7). The second group has the lowest isoprenoid content (<18%) and the first and third groups have values of 18 to 26 and 23 to 44 per cent, respectively.

The Jurassic and most of the Mississippian and Mannville oils have similar saturated hydrocarbon contents. In contrast, the Lower Mannville oils from North Leduc (60), Campbell Namao (57), Morinville (56) and Armisie (59), as well as the Mississippian oil at Gilby (52), have values similar to those of the third group. Oils from the Lower Mannville at East Acheson (58), the Mississippian at Glenevis (41) and



FIGURE 5-1. Gross composition of conventional crude oils in terms of saturated hydrocarbons plus distillate (below 210°C), aromatic hydrocarbons and resins plus asphaltenes.

CRETACEOUS	AROMATIC
Belly Biver Lee Park	100.0
Badheart, Cardium, 2nd White Specks	\bigwedge
Basal Fish, Viking, Joli Fou, Pelican	90 / 10
Upper Mannville	
Glauconitic and Ostracod Zonese	80 / 20
Lower Mannville	
JURASSIC	
Δ	60 / / / / / / 40
MISSISSIPPIAN	
•••••••••••••••••••••••••••••••••••••••	50
DEVONIAN	
Stettler, Wabamun	
Calmar, Nisku	30
Ireton, Leduc, Grosmont 🖻	
Duvernay	20
Cooking Lake, Basal Reef, Beaverhill Lake, Swan Hills	
Gilwood, Watt Mountain	
Muskeg, Elk Point, Keg Hiver	0 / / / / / / / / / / / / / / / / / / /
Exception to classification92	ALKANES ASPHALTS
Impregnation*	AND RESINS
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AROMATIC

FIGURE 5-2a. Gross composition of oil fractions boiling above 210°C in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes. All oils.

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CRETACEOUS	
Belly River, Lea Park•	
Badheart, Cardium, 2nd White Specks	
Basal Fish, Viking, Joli Fou, Pelican	
Upper Mannville	
Glauconitic and Ostracod Zones	
Lower Mannville	
JURASSIC	
····· Δ	
MISSISSIPPIAN	
DEVONIAN	
Stettler, Wabamun	
Calmar, Nisku	
Ireton, Leduc, Grosmont	
Duvernay	
Cooking Lake, Basal Reef, Beaverhill Lake, Swan Hills	
Gilwood, Watt Mountain	
Muskeg, Elk Point, Keg River	
Exception to classification92	
Impregnation*	





FIGURE 5-2b. Gross composition of oil fractions boiling above 210°C in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes. Group 1.

CRETACEOUS	
Belly River, Lea Park	
Badheart, Cardium, 2nd White Specks	
Basal Fish, Viking, Joli Fou, Pelican	
Upper Mannville	
Glauconitic and Ostracod Zones	
Lower Mannville	
JURASSIC	
Δ	
MISSISSIPPIAN	
······ A	
DEVONIAN	
Stettler, Wabamun	
Calmar, Nisku	
Ireton, Leduc, Grosmont 🖻	
Duvernay 🖻	
Cooking Lake, Basal Reef, Beaverhill Lake, Swan Hills 💀	
<i>Gilwood, Watt Mountain</i>	
Muskeg, Elk Point, Keg River	
Exception to classification	

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FIGURE 5-2c. Gross composition of oil fractions boiling above 210°C in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes. Group 2.

CRETACEOUS
Belly River, Lea Park
Badheart, Cardium, 2nd White Specks
Basal Fish, Viking, Joli Fou, Pelican
Upper Mannville
Glauconitic and Ostracod Zones
Lower Mannville
JURASSIC
Δ
MISSISSIPPIAN
••••
DEVONIAN
Stettler, Wabamun
Calmar, Nisku
Ireton, Leduc, Grosmont
Duvernay
Cooking Lake, Basal Reef, Beaverhill Lake, Swan Hills
Gilwood, Watt Mountain ច
Muskeg, Elk Point, Keg River +
Exception to classification
Impregnation*
· · · · · · · · · · · · · · · · · · ·





FIGURE 5-2d. Gross composition of oil fractions boiling above 210°C in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes. Group 3.

CRETACEOUS Belly River, Lea Park	AROMATIC HYDROCARBONS 100 0 90 10 80 20 70 30
MISSISSIPPIAN	
DEVONIAN Stettler, Wabamun Calmar, Nisku Ireton, Leduc, Grosmont Duvernay Cooking Lake, Basal Reef, Beaverhill Lake, Swan Hills Gilwood, Watt Mountain Muskeg, Elk Point, Keg River Exception to classification 92 Impregnation *	50 40 40 40 40 40 40 40 40 40 4

FIGURE 5-3a. Composition of hydrocarbons isolated from oil fractions boiling above 210°C in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons. All oils.

-D-

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CRETACEOUS Belly River, Lea Park
JURASSIC
MISSISSIPPIAN
DEVONIAN
Stettler, Wabamun
Calmar, Nisku
Duvernay Cooking Lake, Basal Reef, Beaverhill Lake, Swan Hills
Gilwood. Watt Mountain
Muskeg, Elk Point, Keg River
Exception to classification

.





FIGURE 5-3b. Composition of hydrocarbons isolated from oil fractions boiling above 210°C in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons. Group 1.

GSC

CRETACEOUS	AROMATIC HYDROCARBONS
Belly River, Lea Park	
Glauconitic and Ostracod Zones	
MISSISSIPPIAN	50 50
DEVONIAN Stettler, Wabamun Calmar, Nisku Lettop Leduc Grosmont	40 30 30 70
Duvernay	
Exception to classification	100 90 80 70 60 50 40 30 20 10 ACYCLIC CYCLOALKANES ALKANES
• 59	
• 62	48 *
	V asc

FIGURE 5-3c. Composition of hydrocarbons isolated from oil fractions boiling above 210°C in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons. Group 2.

SC

PETACEOUS	
Polly Diver Lee Perk	
Belly Hiver, Lea Park	•
Badneart, Cardium, 2nd white Specks)
Basal Fish, Viking, Joli Fou, Pelican	•
Upper Mannville	ر
Glauconitic and Ostracod Zones	,
Lower Mannville	د
URASSIC	
	•
/ISSISSIPPIAN	
	1
DEVONIAN	
Stettler, Wabamun	
Calmar, Nisku	,
Ireton. Leduc. Grosmont	
Duvernav	
Cooking Lake. Basal Reef. Beaverhill Lake. Swan Hills	
Gilwood, Watt Mountain	
Muskeg, Elk Point, Keg River	
Exception to classification92	
Impregnation*	





FIGURE 5-3d. Composition of hydrocarbons isolated from oil fractions boiling above 210°C in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons. Group 3.

GSC

the Wabamun (38) at Leduc have values intermediate between the second and third groups, i.e. similar to Group 1. The Niton (62) oil has a very low value (<5%) even by comparison with those of Group 2.

The plot of the ratio of isoprenoids to n-alkanes against the percentage of acyclic alkanes in the saturated hydrocarbons (Fig. 5-8) shows precisely the same classification. Group 2 clearly is distinguished from the other two groups and the oils from the Lower Mannville sediments to the northeast of Leduc-Woodbend, namely North Leduc, Armisie, East Acheson, Campbell Namao and Morinville, are situated in the Devonian Group 3 envelope and the Wabamun oil in the Group 2 envelope.

Aromatic hydrocarbons

Results of the analyses of the aromatic and thiophenic compounds from 24 oil samples allow the following distinctions to be made.



FIGURE 5-4. Sulphur contents of conventional oils.

Group 1 oils

Group 1, in which the sulphur content of the oils is low (0.05-0.31%; Fig. 5-4), is depleted uniformly in thiophenic compounds (Table 5-1). In fact, examination of the aromatic hydrocarbons by MS shows that the benzothiophenes are rare and that the dibenzothiophenes are confined to compounds of low carbon number $(C_{13} \text{ to } C_{21})$. These latter compounds are recognized, in the distribution by carbon number of the mass family C_nH_{2n-12} (Fig. 5-9, Group 1), by a shoulder at C_{20}/C_{21} together with a mode at C_{13} in the alkylnaphthalenes. The monoaromatics (F₁) of the mass families C_nH_{2n-12} and $C_{n}H_{2n-14}$ are well represented and comprise steroids and triterpenoids. On the other hand, in the tri-aromatic fraction, the phenanthrene family (C_nH_{2n-18}) is the family most abundantly represented. The tricyclic sulphur compounds are not abundant and the polycyclic forms are present only in small amounts.

Group 2 oils

Group 2 is the richest in sulphur (0.65-4.15%; Fig. 5-4) because of its large content of thiophenic compounds. The dibenzothiophenes are the most abundant sulphur compounds (Table 5-1). Their presence (Fig. 5.9, Group 2) is indicated by a secondary peak at C_{16}/C_{17} beside the C_{13} mode of the alkylnaphthalenes in the distribution by carbon number of the mass family C_nH_{2n-12} . Similarly, in the mass family C_nH_{2n-18} , a secondary peak attributed to sulphur compounds occurs at C_{21} beside the mode at C_{17} . Molecules in the range C_{21} to C_{35} , which probably are sulphur bearing, are well represented in the mass families C_nH_{2n-12} and C_nH_{2n-14} .

In the triaromatic plus fraction, the distribution of mass families shows that the thiophenic compounds $(C_nH_{2n-16}S \text{ and } C_nH_{2n-18}S)$ are at least as abundant as the appropriate molecules of the phenanthrene family (C_nH_{2n-18}) . Note that the $C_nH_{2n-16}S$ sulphur-bearing family is equivalent to the aromatic hydrocarbon family C_nH_{2n-12} but is distinguished from the latter by its occurrence in Fraction 2 (Fig. 4-4). Furthermore, the monoaromatics with 4 and 5 cycles (Table 5-1) are poorly represented in the mass families C_nH_{2n-12} and C_nH_{2n-14} (Fig. 5-9, Group 2).

The Niton (62) oil resembles Group 2 oils in the large content of dibenzothiophenes (Table 5-1) and in the distribution of sulphur molecules in the penanthrene family (C_nH_{2n-18}). In contrast to the Group 2 oils, the Niton oil has a mode at C_{16} and not at C_{13} in the mass family C_nH_{2n-12} : the concentration of probable sulphur molecules in the range C_{21} to C_{35} in the mass families C_nH_{2n-12} and C_nH_{2n-14} is also lower (Fig. 5-21).

The Mississippian oils from the Harmattan region have a small content of sulphur in the total oil. Together with the Niton oil, they have the smallest aromatic, asphaltene and resin contents of the group. Mass spectrometric analysis of the oil from Harmattan East shows a distribution of aromatic compounds similar to that of the Niton oil, except that the monoaromatic compounds are in slightly greater concentration.





Group 3 oils

Group 3 can be divided into two sub-groups; the sulphur content of the two groups is noticeably different with values of 0. 22 to 0. 81 per cent and 0. 09 to 0. 26 per cent (Fig. 5-4) and this difference is reflected in their distribution of thiophenic compounds.

In sub-group 3a (Nisku and Leduc reservoirs), the distribution of aromatic and thiophenic molecules is similar to that of Group 2. As in Group 2, the naphthalene family (C_nH_{2n-12}) is the most important and the mode at C_{13} in the alkylnaphthalenes is followed by a less important peak at C_{16} attributed to the sulphur compounds (Fig. 5-9). However, the dibenzothiophenes of the mass families C_nH_{2n-12} and C_nH_{2n-14} are much less important than in Group 2 (Table 5-1), particularly beyond C_{20} (Fig. 5-9, Group 3a). The distribution by families in the triaromatic plus fraction shows that sulphur molecules with one thiophene cycle are of the same importance as the aromatics of the phenanthrene family (C_nH_{2n-18}) in those oils richest

in sulphur (Homeglen-Rimbey-Leduc Fm.; Leduc-Woodbend-Leduc Fm.). In contrast, in the oils with a lower sulphur content (Leduc-Nisku Fm.; Redwater-Leduc Fm.; Morinville-Leduc Fm.), the phenanthrene family is in greater concentration than the corresponding thiophenic compounds. Finally, the monoaromatics with 4 and 5 rings (C_nH_{2n-12} , C_nH_{2n-14}) are more abundant than in Group 2 and are typical of oils from less deeply buried reservoirs (Redwater and Morinville).

In sub-group 3b (Beaverhill Lake), the thiophenic molecules are less abundant than in Group 3a. This can be seen in the naphthalene family (C_nH_{2n-12}) by the absence of a secondary peak associated with the C_{13} mode or at best by a peak at C_{16} which is very weak by comparison with the C_{13} mode (Fig. 5-9, Group 3b); in the triaromatic plus fraction, the phenanthrene group (C_nH_{2n-18}) is clearly more abundant than the corresponding sulphur compounds with one thiophene cycle (Fig. 5-9, Group 3b). Also, the monoaromatics with 4 and 5 rings (C_nH_{2n-12}) and C_nH_{2n-14} generally are more abundant than in Group 3a

GR	OUP 1
SAMPLE	104
LOCATION	WILLESDEN GREEN 8 · 17 · 42 · 6W5
DEPTH	5150'-5167'
AGE	CAMPANIAN
FORMATION	BELLY RIVER
IDENTIFICATION	





GROUP 2				
GROOP 2				
SAMPLE	71			
LOCATION	WILLESDEN GREEN 6 · 22 · 39 · 5W5			
DEPTH	7514'-7522'			
AGE	ALBIAN			
FORMATION	GLAUCONITIC A			
IDENTIFICATION				

GR	OUP 3a
SAMPLE	32
LOCATION	HOMEGLEN RIMBEY 9-10-42-2W5
DEPTH	7854'-7862'
AGE	FRASNIAN
FORMATION	D3
IDENTIFICATION	









FIGURE 5-6. Distribution of saturated hydrocarbons in conventional oils.

(Table 5-1); these steroids and triterpenoids are typical of the oil from Snipe Lake (13).

The oils from the Leduc Formation at Redwater resemble the oils of Group 3a rather than those of Group 3b. This can be seen in the triaromatic fraction where there is a small proportion and narrow distribution of thiophenic compounds and a large proportion of phenanthrene hydrocarbons (C_nH_{2n-18}). In addition, there is a smooth distribution of aromatic mass families in the fractions having higher boiling points.

The oil from the Beaverhill Lake Formation at Kaybob differs from the oils from reservoirs of the same age because of the presence of high molecular weight benzo-thiophenes and also because of the importance of the monoaromatics in the families C_nH_{2n-12} and C_nH_{2n-14} .

In summary, MS analysis of the aromatic and thiophenic compounds can be used to differentiate the three



FIGURE 5-7. Distribution of isoprenoids as a function of n-alkane content in conventional oils.

groups of oils. Group 1, from Colorado and post-Colorado reservoirs, contains only a relatively small proportion of thiophenic compounds compared to the true aromatic molecules and the dibenzothiophenes are confined to compounds of low carbon number ($<C_{20}$). Group 2, from Lower Mannville Jurassic and Mississippian reservoirs, contains a large proportion of sulphur compounds. The dibenzothiophenes are distributed through a wide range of carbon numbers with substantial amounts in the higher range (C_{21} to C_{35}). Group 3, from the Upper and upper Middle Devonian, contains a smaller proportion of thiophenic compounds than Group 2. The dibenzothiophenes are distributed through a wide range of carbon numbers but with only relatively small amounts in the higher range (C_{21} to C_{35}). Group 3 can be separated into two sub-groups, namely Group 3a from the Nisku and Leduc reservoirs, and Group 3b from the Beaverhill Lake reservoir. In the former, the dibenzothiophenes are more abundant in the mass families C_nH_{2n-12} and C_nH_{2n-14} compared to the latter.

Comparisons of the gas chromatograms of the aromatics (FID) with the thiophenic compounds (FPD) lead to analogous conclusions. Group 1 oils have practically no benzothiophenes and very few dibenzothiophenes but those that are present are found in the low carbon number range. Group 2 oils are richer in benzo- and dibenzothiophenes, and these are present in both the low and high carbon number ranges. Group 3 oils have benzo- and dibenzothiophenes in the lower range.

Oils at the unconformity

As in the saturated hydrocarbons, the stratigraphic classification, based on the aromatic fraction, does not apply always for oils occurring in close proximity to the unconformity. Initially, the oils can be separated using the gas chromatograms (FID/FPD) of the aromatics and thiophenes. On this basis, oils from Jurassic and Mississippian strata in the Medicine River, Gilby and Sylvan Lake pools and from Wabamun strata in the Leduc pool belong to Group 2. In contrast, oils from the Lower Cretaceous at North Leduc-Woodbend and probably those of the same age at Morinville and Campbell Namao are similar to the Group 3 oils, although they are appreciably richer in sulphur compounds than those of Group 3.

Detailed examination of the aromatic fractions by MS confirms these conclusions. At Medicine River (Fig. 5-10), oils from the Jurassic and Mississippian rocks show a close relationship with those from the Lower Mannville (cf. Fig. 5-9, Group 2). At Leduc-Woodbend (Fig. 5-11), the oil from the Wabamun strata (Devonian) differs markedly from that from the Nisku reservoir (Devonian) and is related to the Jurassic and Mississippian oils from Medicine River. However, the oil from the Blairmore reservoir (Lower Cretaceous), lying to the north of the main Leduc pool, is similar to that from the Nisku reservoir (Devonian); the same applies to the oil occurring in the Mannville at Morinville.



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			DISTRI	BUTION E	BY ER	DISTRIBUTION BY MASS FAMILIES		
GROU	JP 1 (OIL)				40		225	_
SAMPLE	104						200	t
LOCATION	WILLESDEN GREEN 8-17-42-6W5				25		175	1
DEPTH	5150'-5167'		Λ		20		125	+
AGE	CAMPANIAN	er cent	$ \uparrow\rangle$	h	15		1 00 075	
FORMATION	BELLY RIVER	ass pt			5		050	
IDENTIFICATION	٠	m suo	0 15 2	0 25 30		6 8 10 12 14 16 10 20 22 24 26 2	0 000	_
GROU	JP 2 (OIL)	Irocart			40		225	_
SAMPLE	71 .	ic hyd			30		200	1
LOCATION	WILLESDEN GREEN 6-22-39-5W5	romat			25		150	Ą
DEPTH	7514'-7522'	A			20		125	1
AGE	ALBIAN	5		\mathbb{N}^+	15		100	_



 C_nH_{2n-12}

DISTRIBUTION IN THE MASS FAMILIES

CnH2n-14

2.25

C_nH_{2n-18}

4.50







FIGURE 5-9. Distribution of aromatics in oils from the central basin area based on mass spectrometry (see Fig. 4-5 for explanation).

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IDENTIFICATION

GLAUCONITIC A

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The oils from the Jurassic, Mississippian and Wabamun sediments are very similar to that found in Cadomin strata (Lower Cretaceous) at Kaybob. In all of these oils, the mode at C_{16}/C_{17} is more important than the mode at C_{13} in the distribution by carbon number of the mass family C_nH_{2n-12} (Figs. 5-10, 5-11); this indicates a very large content of sulphur compounds. Similarly, there is a large content of sulphur compounds in the range C_{21} to C_{35} in the mass families C_nH_{2n-12} and C_nH_{2n-14} . The triaromatic fractions also show a molecular distribution similar to the Group 2 oils.

The sample from the Lower Mannville at Morinville also shows a mode at $\rm C_{16}$ in the mass family $\rm C_nH_{2n-12}$ but the molecules in the range $\rm C_{21}$ to $\rm C_{35}$ form a less significant proportion of the families $\rm C_nH_{2n-12}$ and $\rm C_nH_{2n-14}$ which is more characteristic of Group 3 than

Group 2. The distribution of mass families in the aromatic fraction bears some resemblance to the Kaybob (Cadomin) oil but the phenanthrene family (C_nH_{2n-18}) is more important than the thiophene compounds with 4 and 5 cycles $(C_nH_{2n-18}S \text{ and } C_nH_{2n-20}S)$. The sample from the Lower Blairmore at North Leduc-Woodbend is the closest to Group 3 (Fig. 5-11); it has a mode at C_{13} in the alkylnaphthalenes (C_nH_{2n-12}) accompanied by a secondary peak at C_{16} attributed to sulphur compounds, a small content of heavy molecules (C_{21}^+) and a molecular distribution in the triaromatic fraction which is similar to the Nisku oil from the Leduc pool. In both the Morinville and North Leduc-Woodbend samples, the dibenzothiophenes are represented to a greater extent than is normal for Group 3 oils.

TABLE 5-1

	CAMPLE			P= 6(10S)		P = 8(12S)		P = 12(16S)			P = 14(18S)			S) oil
GROUP	No.	Field	FORMATION	Fr 1 monoaro	Fr 2 benzothio	Fr 1 monoaro	Fr 2' benzothio	Fr 1 monoaro	Fr 2 diaro	Fr 3 dibenzothio	Fr 1 monoaro	Fr 2 diaro	Fr 3 dibenzothio	Sulphur in aromatic hydrocarbon	Sulphur in tota (fraction above 210°C.
1	102	Pembina	Belly River	5.82	0.42	8.91	0.65	3.73	10.98	2.67	2.44	8.76	3.28	0.43	0.19
	104	Willesden Green	Belly River A	7.83	0.14	13.10	0.30	4.57	10.24	1.58	3.02	9.02	1.93	0.47	0.22
	95	Pembina	Cardium	6.98	0.17	12.08	0.00	5.21	8.04	1.86	3.42	9.11	1.42	0.60	0.22
	98	98 93 Ferrier	Cardium D	5.91	2.91	9.50	2.30	5.46	8.24	0.81	3.57	9.78	0.93	0.19	0.09
	93		Viking A	7.25	1.06	9.52	1.76	5.26	8.69	2.77	3.69	9.03	2.91	0.41	0.05
	90	Legal	Viking	5.00	0.46	8.39	0.45	3.95	7.24	0.89	2.19	10.68	2.13	0.41	0.31
2	68	Medicine River	Ostracod G	6.44	0.45	10.12	0.20	3.79	10.89	7.67	2.63	8.35	5.27	2.26	0.85
	71	Willesden Green	Glauconitic A	5.62	6.59	9.22	5.50	2.67	10.03	8.28	1.77	8.44	4.59	2.37	1.04
	63	Pembina	Basal Quartz	7.24	5.32	8.20	2.31	3.74	11.39	7.93	2.99	7.60	4.86	2.94	1.47
	55	Kaybob	Cadomin A	10.11	7.96	8.95	4.39	2.62	5.52	13.41	1.71	5.74	6.22	3.62	1.93
	76	Lloydminster*	Sparky	3.65	8.59	8.19	7.93	4.66	6.38	7.02	3.09	8.72	4.34	-	3.55
	89	Choice*	Upper Blairmore	7.48	6.32	8.37	3.84	5.24	5.91	6.55	5.32	7.75	3.95	-	2.55
	62	Niton	Basal Quartz B	7.13	1.16	7.90	0.25	4.29	8.14	10.08	3.54	9.09	5.54	2.20	0.83
	41	Glenevis	Banff	8.24	4.19	8.56	3.11	4.59	2.24	12.76	5.02	3.53	7.95	5.45	4.15
	49	Harmattan E	Elkton	7.67	3.11	11.33	1.73	5.86	5.77	10.68	4.37	7.40	4.40	2.09	0.63
	53	Medicine River	Jurassic D	4.36	6.67	7.05	4.06	3.80	5.79	11.38	2.56	6.20	7.67	3.70	1.77
	42	Gilby	Rundle K	3.67	10.57	5.62	6.58	2.65	4.40	12.88	1.51	5.11	9.08	5.05	2.44
	38	Leduc Woodbend	Wabamun	5.63	9.70	8.06	6.49	2.86	5.54	12.16	1.89	5.26	7.08	3.90	2.96
	45	Medicine River	Pekisko B	5.21	7.80	8.27	4.62	4.61	6.02	8.64	3.37	6.90	6.23	3.35	1.66
2+3	56	Morinville	Lower Mannville	5.09	4.47	8.82	3.85	3.48	4.61	10.81	1.87	5.27	8.31	2.00	1.12
	60	N Leduc Woodbend	Blairmore	6.91	1.44	10.48	0.48	4.97	5.54	8.33	3.72	6.91	7.14	1.54	0.45
За	35	Leduc Woodbend	Nisku	6.99	4.21	12.04	3.40	4.20	6.05	4.05	2.75	7.83	2.78	1.13	0.47
	32	Rimbey	Leduc	10.22	1.40	15.34	0.42	4.93	9.56	5.78	3.40	8.90	2.56	1.23	0.45
	23	Redwater		7.78	1.96	12.14	0.69	4.42	7.00	3.51	2.86	9.30	2.76	1.31	0.62
	26	Leduc Woodbend		7.50	1.44	13.40	0.36	4.41	8.95	6.30	3.22	7.74	4.74	0.70	0.31
	24	Morinville		8.32	0.94	10.52	0.40	4.30	7.95	3.00	3.20	9.01	3.20	0.74	0.30
Зb	21	Kaybob	Beaverhill Lk A	5.60	3.05	13.42	2.33	5.92	4.56	1.70	3.92	8.84	0.36	0.35	0.09
	15	Swan Hills	Beaverhill Lk B	6.74	0.74	12.62	0.62	4.41	10.12	2.87	3.23	8.55	2.53	0.57	0.20
	13	Snipe Lake	Beaverhill Lk	5.79	1.47	9.35	1.08	4.80	8.96	1.79	3.77	9.89	1.91	0.56	0.26

Oils - distribution	(weight per cent)	of monoaromatic,	diaromatic	compounds and
benzothiophenes in the	aromatic families	$C_{n}H_{2n-n}$ (p=6, 8,	12 and 14)	and sulphur content

*Oils from AREA 2

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FIGURE 5-10. Distribution of aromatics in Medicine River oils from near the pre-Cretaceous unconformity based on mass spectrometry (see Fig. 4-5 for explanation).



FIGURE 5-11. Distribution of aromatics in oils from the Leduc-Woodbend reservoirs based on mass spectrometry (see Fig. 4-5 for explanation).

Summary

Group 2 oils are distinguished clearly from those of the other two groups on the basis of gross composition and sulphur content, but Group 1 oils can only be distinguished from those of Group 3 after detailed analysis of the saturated hydrocarbons (MS CGC). Lastly, the division of Group 3 into the two sub-groups is achieved only after detailed analysis of the aromatic hydrocarbons.

Group 1 includes the oils from the Colorado and post-Colorado reservoirs. These oils have the lowest concentration of sulphur (Fig. 5-4) and aromatic hydrocarbons, are richest in saturated hydrocarbons, acyclic alkanes (Fig. 5-3, 5-5) and acyclic isoprenoids but have n-alkane distributions similar to those of Group 2. They can be distinguished from the Group 3 oils by the lower proportion of cyclo-alkanes with 1 and 2 rings (Fig. 5-5), and also on the basis of their benzothiophene content which is small and limited to the lower carbon number range (Fig. 5-9).

Group 2 comprises the majority of the Lower Mannville, Jurassic, Mississippian and Wabamun oils. These oils are the richest in sulphur (Fig. 5-4) and aromatics but are the poorest in saturated hydrocarbons (Figs. 5-1, 5-2), acyclic alkanes, and acyclic isoprenoids relative to n-alkanes. Their very high sulphur values are attributed to large amounts of benzothiophenes and dibenzothiophenes. The dibenzothiophenes have a wide carbon number range (C_{21} to C_{30}).

With the exception of oils from the Wabamun reservoirs, Group 3 corresponds to oils from the Upper Devonian (Nisku, Leduc and Beaverhill Lake reservoirs). These oils contain a higher proportion of thiophenic compounds than Group 1 and they have a smooth distribution over a wide range of carbon numbers. The Beaverhill Lake oils form Group 3b and generally contain a smaller proportion of thiophenic compounds than those from the overlying Devonian oils (Group 3a).

Exceptions to this classification are found in the reservoirs at the base of the Mannville, located to the northeast of the principal pools at Leduc-Woodbend, namely Acheson East, Armisie and North Leduc-Woodbend and at Campbell Namao and Mannville (Figs. 5-1 to 5-3). These oils have a lower content of cyclo-alkanes with 3, 4 and 5 rings than is present in the other Lower Cretaceous oils, and their ratio of isoprenoids to n-alkanes is similar to those of Group 3 (Figs. 5-7, 5-8). Also, the distribution of thiophenic components (N. Leduc, Morinville) in these oils differs from Group 2 in having a smaller proportion of high molecular weight dibenzothiophenes, but the total amounts of these compounds still exceed that found in the Group 3 oils. Thus, the oils from the base of the Mannville occurring northeast of the Leduc-Woodbend pools have a certain affinity with those of Group 3. They also have certain similarities with the anomalous Lower Mannville oil from Niton, but this latter oil differs from all the others in having a large content of heavy n-alkanes, which is characteristic of oils derived from nonmarine organic matter.

GEOCHEMISTRY OF SEDIMENTARY ORGANIC MATTER

Organic carbon

Organic carbon analyses of 543 samples of finegrained sediments show (Fig. 5-12) that Cretaceous sediments, between the Belly River Formation and the base of the Mannville Group, and the Devonian Duvernay sediments contain 1 per cent or more of organic carbon in more than 50 per cent of the samples. In the Belly River Formation and Mannville Group, a third of the samples have values greater than 3 per cent. In the Upper Devonian (Wabamun to Beaverhill Lake, inclusive, with the exception of the Duvernay), more than 80 per cent of the samples have less than 0.50 per cent organic carbon. In the case of sediments between the top of the Wabamun and the base of the Nisku, 60 per cent of the samples have values below 0.10 per cent.

Impregnations

The extract yield (extract/organic carbon) and yield of hydrocarbons (HC/org. C) can be used to distinguish those rocks which are abnormally rich in extract and hydrocarbons even though their organic carbon values occur in the same range (0.54-1.80%) as unimpregnated samples. The division is made in the Cretaceous samples where the extract yield (extract/ org. C) is greater than 10 per cent (Fig. 5-13a, b) and in the Devonian samples where the extract yield is greater than 20 per cent (Fig. 5-13c, d). The high extracts, which represent most of the organic carbon, suggest that the rocks containing these products are hydrocarbon reservoirs. These extracts have been defined, therefore, as impregnations. These impregnations are similar in composition to the oils (Fig. 5-14a, b) but tend to have higher resin and asphalt contents and correspondingly lower saturated hydrocarbon contents. Impregnations were found throughout the section (Devonian to Cretaceous) but were particularly common in the Mannville of eastern Alberta (see Chap. 6) in the Mississippian and the Wabamun. Impregnations from different stratigraphic intervals tend to have a similar hydrocarbon composition to the conventional reservoired oils from the same intervals. Thus, the impregnations from the Colorado and post-Colorado sediments have similar hydrocarbon compositions to the Group 1 oils; certain impregnations from the Upper Devonian are similar to the Group 3 oils, and certain samples from the base of the Mannville, the Wabamun and the Mississippian adjacent to the unconformity are like the Group 2 oils.



FIGURE 5-12. Organic carbon content of rock samples.





FIGURE 5-13b. Extract yields of rock samples as a function of maximum burial. Mannville Group.

Extract (mg per gram organic carbon)


Extract (mg per gram organic carbon)





Extract (mg per gram organic carbon)



FIGURE 5-14a. Gross composition of rock extracts in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes. Belly River to Viking Formations.

<u>Composition of extracts in relation to</u> stratigraphy and type of organic matter

In the remaining samples, the resin and asphalt contents (Fig. 5-14a to c) are always greater than in oils of the same age. The saturated hydrocarbon content is generally lower except for several Devonian (Beaverhill Lake) samples which have saturated hydrocarbon contents close to those of the oils. The extracts (Fig. 5-15) contain similar or higher amounts of acyclic alkanes than their contemporaneous oils with the exception of extracts from the Beaverhill Lake and Muskeg Formations where certain samples are poorer in both acyclic alkanes and cyclo-alkanes than the oils in contemporaneous reservoirs.

Based on the detailed analysis (CGC, MS) of their hydrocarbons, the extracts can be separated into the following geochemical groups which follow the stratigraphy: a) post-Colorado; b) Colorado; c) Mannville; d) Mississippian; e) Wabamun; f) Calmar/Leduc;
g) Duvernay; h) Cooking Lake/Beaverhill Lake; and
i) Middle Devonian. The geochemical characteristics of the extracts (excluding impregnations) from the various stratigraphic intervals are summarized in Table 5-2 and are illustrated in Figures 5-16, 5-18 and 5-19. Commonly, there is considerable variation within a particular stratigraphic interval: a detailed description of these variations is given in Appendix F.

There are a number of features in the rock extracts which persist through the different formations regardless of depth. In particular, there are a number of characteristics in the saturated hydrocarbons which can be related to the nature of the parent organic matter (Fig. 5-19).

In the Belly River, Lea Park, Cardium and Mannville Formations, there is an abundance of C_{20} plus n-alkanes with a pronounced odd carbon predominance in the range C_{23} to C_{31} which is characteristic of debris



FIGURE 5-14b.

4b. Gross composition of rock extracts in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes. Mannville Group.

derived from high forms of plant life. This type of distribution is accompanied commonly by a large content of acyclic alkanes in the saturate fraction and a low ratio of isoprenoid alkanes to normal alkanes.

In the Colorado and Mannville Groups, the Woodbend Group (Ireton, Calmar and Nisku Fms.) and Beaverhill Lake Formation, some samples show a sharp mode at C_{15} , or C_{15} and C_{17} , or exceptionally at C_{16} in the normal alkanes (Figs. 5-16, 5-19). These distributions resemble those found in living benthic algae. It must be emphasized, however, that this type of distribution does not seem to correspond to a single type of sedimentation or depositional environment. During Devonian time, sedimentation consisted mainly of carbonate with associated fine-grained clastic and evaporitic strata but, during Cretaceous time, the sediments were almost entirely clastic. In the Watt Mountain Formation (Middle Devonian), the n-alkane distribution resembles that of organic matter derived from higher forms of plant life. This original characteristic probably was very strong,

since it persists despite the present great depth of burial which should have resulted in considerable maturation.

Extracts containing a mode at C₁₅ in the n-alkane distributions frequently have a high content of steroid and triterpenoid hydrocarbons in the saturate and monoaromatic fractions (Figs. 5-16, 5-18 and 5-19). Other characteristics of the aromatic distributions can be related less readily to the type of parent organic matter. The dominant families in the aromatic hydrocarbons are the naphthalene and phenanthrene families (Fig. 5-18). The relative proportions of these two families in the aromatic fraction varies. Thus, in the post-Colorado and Mannville extracts, the naphthalene family predominates in the Colorado, Duvernay, Cooking Lake-Beaverhill Lake and Watt Mountain-Muskeg extracts, the naphthalene and phenanthrene families occur in roughly equal proportions. Only in the Calmar-Ireton series does the phenanthrene family predominate to any marked extent.



FIGURE 5-14c. Gross composition of rock extracts in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes. Mississippian to Wabamun Group.

The extracts from the Mannville are distinguished by their exceptionally large content of thiophenes (Table 5-3). Both benzothiophenes and dibenzothiophenes are abundant throughout a wide carbon number range $(C_{11} \text{ to } C_{29})$. The sulphur compounds in the triaromatic fraction are at least as abundant as the phenanthrene family. The extracts which contain such substantial amounts of n-alkanes above C_{20} are depleted in dibenzothiophenes in the range C_{21} to C_{29} in comparison with the other Mannville extracts. In this respect, they show the same variation as does the Niton oil with respect to the other oils of Group 2. In contrast, the thiophene content of the Colorado and post-Colorado extracts is lower. The benzothiophenes are in low concentration or absent and the dibenzothiophenes are confined to the lower carbon number range (below C_{20}). The thiophene distribution in one extract from the Mississippian resembles that of the Mannville Group.

The thiophene distribution in the Devonian extracts resembles that of the Colorado Group. In the Calmar-Nisku-Leduc-Ireton series, benzothiophenes occur only in small amounts or are absent; the dibenzothiophene content also is low and confined to the range below C_{20} . In the case of the Duvernay, the dibenzothiophene content is high and is spread through a wide carbon number range although those below C_{20} are dominant. The Beaverhill Lake series contains relatively small amounts of thiophenes. The benzothiophenes occur below C_{20} , whereas the dibenzothiophenes occur above C_{20} . The thiophene distribution in the Watt Mountain-Gilwood-Muskeg series resembles that of the Calmar-Nisku series.

It is of particular interest that the impregnations from the Mississippian and Wabamun contain a large content of thiophenes which have a distribution closely resembling that from the Mannville (Fig. 5-18).



FIGURE 5-14d. Gross composition of rock extracts in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes. Calmar to Beaverhill Lake Formations.

Role of burial in determining composition of extracts

The distribution of extract yields, as a function of depth of burial, permits the establishment of a productivity graph of the rock extracts. In a general fashion, the curves express the transformation of organic material to petroleum compounds. For a given organic material this transformation increases with diagenesis, and passes through a maximum before diminishing at great depths where advanced diagenesis favours cracking. This results in the formation of gas and light hydrocarbons at the expense of kerogen and higher molecular weight hydrocarbons. The analytical method does not permit the retention of the light fractions; therefore, what is observed is an apparent diminution of the quantities of extract at great depth.

In this study, one can illustrate conveniently the role of burial using Devonian samples since the extracts

are numerous and are distributed throughout a wide range of depth (1020-3900 m; $3400-13\ 000\ ft.$).

The Devonian samples can be divided into two groups which form separate series (Fig. 5-17). One group comprises samples from the Woodbend to Wabamun and the other those from the Beaverhill Lake. The difference in extraction yields between the two groups corresponds to differences either in the organic matter between the two groups of samples or in the geothermal history. In comparison with the Woodbend group, the extracts from the Beaverhill Lake group have undergone less cracking to gaseous hydrocarbons despite similar depths of burial; thus, the proportion of heavier hydrocarbons in the extracts from the most deeply buried Beaverhill Lake samples is higher than that from the Woodbend samples from corresponding depths. For a given group of samples, the extraction yield is of the order of 10 per cent at 1200 m (4000 ft.) and reaches a maximum 20 per cent through 2700 m (9000 ft.)

SATURATES			AROMATICS					
STRATIGRAPHIC UNIT (number of samples)	Acyclics%	n-alkanes	lsoprenoids % of n-alkanes	Ring distribution	Hydrocarbons Mass Spectrometry	Sulphur Compounds Comments on Gas Chromatography (FPD) (P = 6, 8, 12 & 1		hene content in CnH2n-p & 14) weight %
POST-COLORADO GROUP (9)	>60	High content above C ₂₀ and odd predominance C ₂₀ -C ₃₁	low	3 ring compounds dominant	Naphthalene and phenanthrene families dominate, naphthalene family most important	Benzothiophene content low, dibenzothiophenes confined to low molecular weight range, in triaromatic fraction phenanthrene family dominates	Benzothiophene 0.72	Dibenzothiophenes 6.13
COLORADO GROUP (40)	<60	Mixed distribution, some have maximum above C_{20} , some have maximum at C_{15} . Odd predominance slight at basin centre, marked at basin margin	high	3-4 ring compounds in largest concentration	Naphthalene and phenanthrene families prominent and in equal concentrations or phenanthrene family more important	Benzothiophene content low or absent, dibenzothiophenes confined to low molecular weight range ($\sim 2_{20}$), in triaromatic fraction phenanthrene family dominates with subsidiary plateau at CnH2n-20 to CnH2n-22	1.62 (0.00-4.02)	6.40 (4.34-9.92)
MANNVILLE Basin Centre Type 1 (9)	< 65	Mode at C ₁₅ /C ₁₆	high	ring analysis variable; maximum is at 2-3 or 3-4	Naphthalene and phenanthrene families prominent but naphthalene family dominates	Dibenzothiophenes and benzothiophenes very abundant throughout carbon range. Sulphur compounds in triaromatic fraction often as important as phenanthrene family. In Upper Mannville, benzothiophene content is low	4.4 (1.01-6.62)	23.05 (12.27-36.12)
Type 2 (4)	>65	High content above nC ₂₀ and odd predominance C ₂₃ to C ₃₁	low	2-3 rings maximum; low cyclo-alkane content	As Type 1 above	Similar to Type 1 but dibenzothioph- enes are in lower concentration in range C ₂₁ to C ₂₉		
Basin Margin Type 1 (7)	~40%	Mode at C_{15}	intermediate to high	2 rings dominate decreasing regularly to 6 rings	As Type 1 above	As Type 1 above		
Type 2 (4)	variable	Bimodal, high content above C_{20} , odd even predominance, peak at C_{15}	intermediate to low	2-3 rings predominate	As Type 1 above	Benzothiophene and dibenzothioph- enes occur in lower molecular weight range. Small amounts of heavy thiophenes		
MISSISSIPPIAN (1)	~40%	Mode at C_24 and plateau at C_16-C_19	low	2 rings predominante		As Mannville Basin centre Type 2. i.e. dibenzothiophenes depleted in range C21 to C29 relative to other Mannville types		
CALMAR NISKU LEDUC IRETON (21)	~50	Mode at C_{15} , slight odd predominance above C_{20} in shallow samples	high	Maximum at 2 rings, shallow samples have higher content of 3 and 4 rings	Phenanthrene family dominates, naphthalene family less prominent	Small amounts only or no benzothioph- enes, dibenzothiophenes occur only in the low carbon number range. Phenanthrene family very prominent in triaromatics	0.69	2.90
DUVERNAY (4)	40-50	Mode C_{15} to C_{20} , slight odd predominance above C_{20}	high shallow samples, lower in deeper samples	Maximum at 2 rings, shallow samples, high content 3-4 rings	Single mode at naphthalene family in shallow sample. Accompanied by high content of monoaromatic steroids and triterpenoids. Deeper samples have prominent naphthalene and phenanth- rene families in equal proportions	Widespread distribution of dibenzothiophenes with low carbon number range dominant. Variable benzothiophene content	7.94 1.08	13.76 14.20
COOKING LAKE BASAL LEDUC REEF BEAVERHILL LAKE (22)	>50	Mode C ₁₅ to C ₁₉ often with odd predominance in this range	intermediate to high	Maximum at 1, 2 decreasing to 6 rings. Shallow samples have maximum at 3-4 or 4-5	Mode at naphthalene family, equal or subsidiary peak at phenanthrene fam- ily. Monoaromatic steroids and triter - penoids present in shallower samples	Low content of benzothiophenes and dibenzothiophenes. Former confined to lower carbon number range; latter to higher range	0.75 2.05	5.23 3.63
WATT MOUNTAIN GILWOOD MUSKEG (6) Type 1	70	High content above nC20 with odd predominance in range C_{21} - C_{27}	low	Low content cyclo- alkanes and flat distribution	Naphthalene and phenanthrene families predominate, monoaromatic steroids and triterpenoids present	Low benzothiophene content and slightly higher dibenzothiophene content but confined to lower carbon number range	1.31	6.33
Туре 2	50-60	Mode C15-C19	intermediate to high	Maximum at 1, 2 decreasing to 6 rings		As Type 1 above		

-

TABLE 5-3

Rock extracts – distribution	(weight per cent)	of monoaromatic,	diaromatic and
benzothiophenes in the	aromatic families C	_n H _{2n-p} (p=6, 8,	12 and 14)

Ċ.			P = 6	5(10S)	P = 8	B(12S)	P = 12(16S)			P = 14(18S)		
SAMPLE NC	BOREHOLE	FORMATIONS	Fr 1 monoaro	Fr 2 benzothioph	Fr 1 monoaro	Fr 2 benzothio	Fr 1 monoaro	Fr 2 diaro	Fr 3 dibenzothio	Fr 1 monoaro	Fr 2 diaro	Fr 3 dibenzothio
PC1	Pembina	Belly River	4.75	0.42	6.01	0.31	2.67	21.59	2.24	1.73	7.93	3.89
UC17	Leslieville	Badheart	3.68	1.54	4.93	0.52	3.45	11.44	1.94	2.41	8.88	2.83
UC14	Baysel Bingley	Cordium	4.19	0.63	5.25	0.34	3.18	11.21	1.86	2.20	8.04	3.41
UC21	Garrington	Cardium	2.29	1.06	2.85	0.70	2.19	7.43	3.94	1.71	7.34	5.98
LC 14	Burnt Lake	Basal Fish	3.78	0.00	4.27	0.00	3.26	6.69	3.51	2.57	7.82	3.45
LC16	Caroline	Viking	4.39	2.25	4.45	1.77	3.00	7.70	2.61	1.93	7.34	1.73
LC7	Carbondale	Viking	3.31	0.65	5.51	0.28	5.27	5.02	3.26	3.41	9.00	3.88
M1	Vimy 1	Upper Blairmore	5.44	0.55	9.08	0.46	3.40	13.42	4.16	1.55	9.01	8.11
M12	Ferry Bank	Mannville	1.56	3.45	1.91	1.61	1.70	12.15	14.09	1.22	5.99	11.73
M7	Acheson		5.10	4.15	6.28	2.47	2.69	11.58	11.23	2.10	8.03	6.18
M10	Buck Lake		3.24	1.82	2.48	1.00	2.73	6.47	31.95	2.28	4.86	4.17
M14	Bentley	Lower Mannville	3.58	3.56	4.09	2.11	2.49	8.01	14.88	1.42	6.96	8.78
M16	Butte		6.08	0.38	7.40	0.06	5.06	6.11	10.51	4.19	8.10	5.10
M80	O'Hairy	Upper Blairmore	10.09	3.66	13.09	1.33	2.80	15.39	5.97	2.59	5.31	5.34
Wb2	Golden Spike	Wabamun	4.16	9.57	6.38	6.75	2.65	6.23	11.70	1.48	7.15	7.50
Wi4	Dickson	Nisku	5.38	0.45	7.79	0.24	5.07	6.48	1.63	3.80	8.32	1.27
W2	El Dorena	Dunnan	2.71	3.39	4.69	4.55	5.80	4.57	6.66	3.88	8.27	7.10
W11	Ferrybank	Duvernay	2.12	0.58	4.87	0.50	3.19	7.71	7.25	2.48	9.38	6.95
B11	NE Virginia Hills		7.49	0.25	11.10	0.05	3.52	10.85	2.56	2.20	10.25	2.67
B15	SwanHills	Beaverhill Lk	7.43	1.33	10.05	0.72	3.27	15.51	1.67	1.94	10.04	1.96
B18	Rock Island		4.99	1.79	7.38	1.11	5.53	7.67	2.16	6.20	11.07	1.19
MD4	Swan Hills	Watt Mountain	5.23	0.82	4.72	0.49	3.05	11.19	4.19	2.26	6.86	2.14
												GSC

then diminishes again at greater depths. The quantitative variation with depth is matched also by variations in the composition of the extracts. In the case of the Beaverhill Lake group, with increasing burial to a depth of 2700 m (9000 ft.), the samples show a progressive enrichment in normal and branched alkanes (acyclic alkanes) compared with the cyclo-alkanes. The n-alkanes, in turn, show an enrichment in the lighter components while the higher molecular weight n-alkanes diminish; the ratio of isoprenoids to n-alkanes also decreases. Cyclo-alkanes with 3 and 4 cycles commonly are present above a depth of 2250 m (7500 ft.) but are rarely found below this depth.

At depths of 3600 m (12 000 ft.), the extracts do not contain any high molecular weight components; this suggests that the hydrocarbons have been cracked to give low molecular weight hydrocarbons including gas.

At the margin of the basin, the petroleum potential, as indicated by rock extracts, is as follows. For the material at the base of the Colorado and the Upper Mannville, the possibilities for the genesis of liquid hydrocarbons in this region are limited. This conclusion is based on the low extraction yields, and the high proportion of light hydrocarbons by comparison with the more complex molecules in the saturated and aromatic fractions.

In the case of the Lower Mannville material located away from the pre-Cretaceous unconformity, the relatively high content of polycyclic and high molecular weight alkanes are characteristics favourable for the generation of hydrocarbons. However, the distribution of n-alkanes and monoaromatics of the steroid and triterpenoid type suggests that this organic matter has undergone little diagenesis in comparison with that from contemporaneous rocks in the central part of the basin. Likewise, Devonian sediments adjacent to the margin of the basin seem to be favourable for the genesis of hydrocarbons but, again, the level of diagenesis is low. Thus, the overall low diagenetic state of the organic matter in sediments of all ages at the basin margin precludes them from being source rocks at the present time.



FIGURE 5-15a. Composition of hydrocarbons from rock extracts in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons. Belly River to Viking Formations.



FIGURE 5-15b. Composition of hydrocarbons from rock extracts in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons. Mannville Group.



FIGURE 5-15c. Composition of hydrocarbons from rock extracts in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons. Mississippian to Wabamun Group.



FIGURE 5-15d. Composition of hydrocarbons from rock extracts in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons. Calmar to Beaverhill Lake Formations.

POST-COLORADO GROUP			
SAMPLE	PC 1		
LOCATION	PEMBINA 8 - 1 - 48 - 4W5		
DEPTH	3254′		
. AGE	CAMPANIAN		
FORMATION	BELLY RIVER		
IDENTIFICATION	•		





COLORADO GROUP			
SAMPLE	UC 3		
LOCATION	HOLBURN 10-33-50-1W5		
DEPTH	3300′		
AGE	TURONIAN		
FORMATION	CARDIUM SD		
IDENTIFICATION	0		















FIGURE 5-16a. Distribution of saturated hydrocarbons in rock extracts from central basin area. Colorado and post-Colorado Groups.

MANNVILLE GROUP				
SAMPLE	M 1			
LOCATION	VIMY 1 9-9-58-25W4			
DEPTH	2709′			
AGE	ALBIAN			
FORMATION	UPPER BLAIRMORE			
IDENTIFICATION	-0-			





MANNVILLE GROUP			
SAMPLE	M 12		
LOCATION	FERRY BANK 6-9-44-27W4		
DEPTH	5133'		
AGE	APTIAN		
FORMATION	LOWER MANNVILLE		
IDENTIFICATION	0		





MISSISSIPPIAN GROUP			
SAMPLE	Ms 1		
LOCATION	N GILBY 4-20-41-2W5		
DEPTH	6590'		
AGE	TOURNAISIAN		
FORMATION	PEKISKO		
IDENTIFICATION	A		







FIGURE 5-16b. Distribution of saturated hydrocarbons in rock extracts from central basin area. Mannville, Mississippian Formations and Wabamun Group.

CALMAR/LEDUC GROUP			
SAMPLE	Wi 1		
LOCATION	VOLMER 2 - 16 - 55 - 25W4		
DEPTH	4195′		
AGE	FRASNIAN		
FORMATION	CALMAR (D2)		
IDENTIFICATION			





CALMAR/LEDUC GROUP			
SAMPLE	Wi 3		
LOCATION	LEDUC 1 16 - 6 - 48 - 24W4		
DEPTH	5132'		
AGE	FRASNIAN		
FORMATION	NIKSU (D2)		
IDENTIFICATION			









FIGURE 5-16c. Distribution of saturated hydrocarbons in rock extracts from central basin area. Calmar/Leduc Formations.

DUVERNAY GROUP			
SAMPLE	W 2		
LOCATION	EL DORENA 1 4 - 27 - 57 - 20W4		
DEPTH	3592′		
AGE	FRASNIAN		
FORMATION	DUVERNAY (D3)		
IDENTIFICATION	۲		





DUVERNAY GROUP			
SAMPLE	W 16		
LOCATION	DICKSON 16 - 12 - 36 - 3W5		
DEPTH	6488'		
AGE	FRASNIAN		
FORMATION	DUVERNAY (D3)		
IDENTIFICATION			





DUVER	NAY GROUP
SAMPLE	W 9
LOCATION	FERRY BANK 2-8-44-27W4
DEPTH	7370′
AGE	FRASNIAN
FORMATION	DUVERNAY (D3)
IDENTIFICATION	8



FIGURE 5-16d. Distribution of saturated hydrocarbons in rock extracts from central basin area. Duvernay Formation.

BEAVERHILL LAKE GROUP			
SAMPLE	W 5		
LOCATION	EL DORENA 1 4-27-57-20W4		
DEPTH	3825′		
AGE	FRASNIAN		
FORMATION	COOKING LAKE		
IDENTIFICATION	-0-		





BEAVERHILL LAKE GROUP				
SAMPLE	B 15			
LOCATION	SWAN HILLS 4-7-67-8W5			
DEPTH	8076′			
AGE	FRASNIAN			
FORMATION	BEAVERHILL LAKE			
IDENTIFICATION	-0-			







BEAVERHILL LAKE GROUP			
SAMPLE	B 11		
LOCATION	NE VIRGINIA HILLS 4-33-65-12W5		
DEPTH	9030′		
AGE	FRASNIAN		
FORMATION	BEAVERHILL LAKE		
IDENTIFICATION	-0-		



FIGURE 5-16e. Distribution of saturated hydrocarbons in rock extracts from central basin area. Beaverhill Lake and Cooking Lake Formations.

COMPARISON OF OILS AND EXTRACTS

Group 1 oils

Oils from Group 1 occur in the Viking, Cardium, and Belly River reservoirs and differ from the Group 2 oils present in the adjacent Mannville reservoirs in a number of characteristics. In the saturated fraction, differences are found in the proportion of normal and branched alkanes, the ratio of isoprenoids to n-alkanes and the distribution of isoprenoids. The distribution of true aromatic compounds is similar but there are differences in the distribution of thiophenic compounds. In the first group of oils, the thiophenic compounds are scarce and are confined to compounds with less than 20 carbon atoms. In contrast, Group 2 oils contain abundant thiophenic compounds which extend up to C_{35} . Even in the Legal (Viking) oil, where there is the widest distribution of aromatic mass families in a Group 1 oil, the sulphur compounds are confined to the lower range of molecular weights.

The distribution of aromatic hydrocarbons in the rock extracts shows the same differences between the Colorado and post-Colorado samples and the Lower Mannville samples as is found for the Group 1 and Group 2 oils. However, analysis of the saturated hydrocarbons (notably the proportion of normal and branched alkanes in the saturate fraction and the n-alkane distribution) enables one to further distinguish the post-Colorado from the Colorado extracts. On the same basis, the post-Colorado extracts (Belly River, Lea Park) do not appear to be related to the oils reservoired in these formations. This leads to the conclusion that the source rocks for the first group of oils are the Cretaceous sediments between the top of the Mannville and the top of the Colorado (Figs. 5-20, 5-21). Any differences between the distribution of aromatic hydrocarbons between the Colorado Group extracts and the oils in adjacent reservoirs could be explained by absorption phenomena during migration: more of the triaromatic compounds (C_nH_{2n-18}) would tend to remain in the source rock compared with the monoaromatics (mainly C_nH_{2n-8}) which would tend to be expelled with the oil toward the reservoirs.

Group 2 oils

Oils occurring in Lower Mannville reservoirs, and certain oils associated with the unconformity, differ from other oils in their gross characteristics (overall composition, hydrocarbon composition, sulphur content). They differ also in the composition of their saturated hydrocarbons (cyclo-alkane content and distribution, and isoprenoid content and distribution). The distribution of aromatic hydrocarbons in the Group 2 oils is similar to that for Group 3 and both contain abundant thiophenic compounds. They differ in their content of higher molecular weight thiophenic compounds (C₂₅ to C₃₅).

One series of extracts from the Lower Mannville has the characteristics of organic matter derived from higher forms of plant life. As such, they are similar to the Niton oil (Figs. 5-20a, 5-21a). Other extracts from the Mannville (Fig. 5-20b) are similar to the Colorado extracts in the character of their saturated hydrocarbons. The distribution of aromatic hydrocarbons in all of the Mannville extracts shows the same distinctive features found in the Group 2 oils. One can assume, therefore, that the Mannville sediments have been the source for the oils reservoired in the Mannville. It is necessary, however, to emphasize the diversity of types of organic matter in the Mannville deposits and to note the existence of an oil (Niton) derived from nonmarine organic matter in this sequence (Figs. 5-20a, 5-21a).

Group 3 oils

Oils occurring in both the Upper Devonian and the upper Middle Devonian are very similar, particularly in the distribution of their saturated hydrocarbons. The recognition of two sub-groups (3a and 3b) is based solely on a study of their aromatic hydrocarbons. Group 3a corresponds to the Nisku and Leduc oils, Group 3b to the Beaverhill Lake oils; Group 3b has less thiophenic and more polycyclic aromatic compounds than Group 3a.



FIGURE 5-17. Yield of extract from Devonian rocks as a function of maximum depth of burial.



FIGURE 5-18a. Distribution of aromatics in rock extracts from central basin area based on mass spectrometry (see Fig. 4-5 for explanation). Colorado and post-Colorado Groups.



FIGURE 5-18b. Distribution of aromatics in rock extracts from central basin area based on mass spectrometry (see Fig. 4-5 for explanation). Mannville and Wabamun Groups.



FIGURE 5-18c. Distribution of aromatics in rock extracts from central basin area based on mass spectrometry (see Fig. 4-5 for explanation). Calmar/Leduc and Duvernay Formations.





BEAVERHILL LAKE GROUP					
SAMPLE B 11					
LOCATION	N.E. VIRGINIA HILLS 4-33-65-12W5	s mas			
DEPTH	DEPTH 9030'				
AGE	FRASNIAN	vdroc			
FORMATION	BEAVERHILL LAKE	atic h			
IDENTIFICATION	÷	Arom			









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FIGURE 5-18d. Distribution of aromatics in rock extracts from central basin area based on mass spectrometry (see Fig. 4-5 for explanation). Beaverhill Lake and Middle Devonian Formations.



SAMPLE

LOCATION

DEPTH

M 1

VIMY 1

9-9-58-25W4

2709'

DISTRIBUTION

BY FAMILY

50

DISTRIB. OF N-ALKANES

AND ISOPRENOIDS

15

10

33,13

DISTRIBUTION

BY FAMILY

50

DISTRIB. OF N-ALKANES

AND ISOPRENOIDS

15

10

FIGURE 5-19a. Variation in saturated hydrocarbon distributions with type of organic matter in rock samples. Nonmarine organic matter dominant.

SAMPLE

LOCATION

DEPTH

PC 8

KNOB HILL

10-25-46-2W5

3216′



DISTRIBUTION

BY FAMILY

DISTRIB. OF N-ALKANES

DISTRIB. OF N-ALKANES AND ISOPRENOIDS

DISTRIBUTION BY FAMILY

FIGURE 5-19b. Variation in saturated hydrocarbon distributions with type of organic matter in rock samples. Marine organic matter dominant.



FIGURE 5-20a. Correlation of source rocks with crude oils based on saturated hydrocarbons. Group 1.

GROU	UP 2 (OIL)		DISTRIBUTION BY		DISTRIB. OF N-ALKANES
SAMPLE	71				
LOCATION	WILLESDEN GREEN 6-22-39-5W5				
DEPTH	7514'-7522'	50			
AGE	ALBIAN	cent		cent	5
FORMATION	GLAUCONITIC A	ne per s		ht per	
IDENTIFICATION	•	ons volun	123455	oids weig	15 20 23 .
MANNVILLE	GROUP (ROCK)	ydrocarb		d isopren	
SAMPLE	M 12	ated h		esan	15
LOCATION	FERRY BANK 6-9-44-27W4	Satura		alkan	
DEPTH	5133'	50		Ė	
AGE	APTIAN				
FORMATION	LOWER MANNVILLE	10			
					15 20 25
DENTIFICATION	0		DISTRIBUTION BY		Carbon number DISTRIB. OF N-ALKANES
IDENTIFICATION GROU SAMPLE LOCATION DEPTH AGE	© JP 2 (OIL) 63 PEMBINA 6-32-48-4W5 5828' APTIAN	ent ø	DISTRIBUTION BY FAMILY	cent	Carbon number DISTRIB. OF N-ALKANE: AND ISOPRENOIDS
GROU SAMPLE LOCATION DEPTH AGE FORMATION	UP 2 (OIL) 63 PEMBINA 6-32-48-4W5 5828' APTIAN ELLERSLIE (BASAL QUARTZ)	le per cent ≅ s	DISTRIBUTION BY FAMILY	ht per cent	Carbon number DISTRIB. OF N-ALKANES AND ISOPRENOIDS
IDENTIFICATION GROU SAMPLE LOCATION DEPTH AGE FORMATION IDENTIFICATION	UP 2 (OIL) 63 PEMBINA 6-32-48-4W5 5828' APTIAN ELLERSLIE (BASAL QUARTZ) O	ons volume per cent ≅	DISTRIBUTION BY FAMILY	oids weight per cent	Carbon number DISTRIB. OF N-ALKANES AND ISOPRENOIDS
IDENTIFICATION GROU SAMPLE LOCATION DEPTH AGE FORMATION IDENTIFICATION MANNVILLE	UP 2 (OIL) 63 PEMBINA 6-32-48-4W5 5828' APTIAN ELLERSLIE (BASAL QUARTZ) GROUP (ROCK)	iydrocarbons volume per cent ≅ s	DISTRIBUTION BY FAMILY	d isoprenoids weight per cent	Carbon number DISTRIB. OF N-ALKANES AND ISOPRENOIDS
IDENTIFICATION GROI SAMPLE LOCATION DEPTH AGE FORMATION IDENTIFICATION MANNVILLE SAMPLE	UP 2 (OIL) 63 PEMBINA 6-32-48-4W5 5828' APTIAN ELLERSLIE (BASAL QUARTZ) GROUP (ROCK) M 10	ated hydrocarbons volume per cent ≈ s	DISTRIBUTION BY FAMILY	es and isoprenoids weight per cent	Carbon number DISTRIB. OF N-ALKANES AND ISOPRENOIDS
IDENTIFICATION GROI SAMPLE LOCATION DEPTH AGE FORMATION IDENTIFICATION MANNVILLE SAMPLE LOCATION		Saturated hydrocarbons volume per cent ≈	DISTRIBUTION BY FAMILY	alkanes and isoprenoids weight per cent	Carbon number DISTRIB. OF N-ALKANE: AND ISOPRENOIDS
IDENTIFICATION GROI SAMPLE LOCATION DEPTH AGE FORMATION IDENTIFICATION MANNVILLE SAMPLE LOCATION DEPTH	© JP 2 (OIL) 63 PEMBINA 6-32-48-4W5 5828' APTIAN ELLERSLIE (BASAL QUARTZ) © GROUP (ROCK) M 10 BUCK LAKE 10-7-46-6W5 6888'-6891'	Saturated hydrocarbons volume per cent s	DISTRIBUTION BY FAMILY	n-alkanes and isoprenoids weight per cent	Carbon number DISTRIB. OF N-ALKANES AND ISOPRENOIDS
IDENTIFICATION GROU SAMPLE LOCATION DEPTH AGE FORMATION IDENTIFICATION IDENTIFICATION MANNVILLE SAMPLE LOCATION DEPTH AGE	© JP 2 (OIL) 63 PEMBINA 6-32-48-4W5 5828' APTIAN ELLERSLIE (BASAL QUARTZ) © GROUP (ROCK) M 10 BUCK LAKE 10-7-46-6W5 6888'-6891' APTIAN	Saturated hydrocarbons volume per cent s	DISTRIBUTION BY FAMILY	n-alkanes and isoprenoids weight per cent	Carbon number DISTRIB. OF N-ALKANES AND ISOPRENOIDS
IDENTIFICATION GROI SAMPLE LOCATION DEPTH AGE FORMATION IDENTIFICATION MANNVILLE SAMPLE LOCATION DEPTH AGE FORMATION	O JP 2 (OIL) 63 PEMBINA 6-32-48-4W5 5828' APTIAN ELLERSLIE (BASAL QUARTZ) O GROUP (ROCK) M 10 BUCK LAKE 10-7-46-6W5 6888'-6891' APTIAN LOWER MANNVILLE	Saturated hydrocarbons volume per cent s s s	DISTRIBUTION BY FAMILY	n-alkanes and isoprenoids weight per cent	Carbon number DISTRIB. OF N-ALKANES AND ISOPRENOIDS

FIGURE 5-20b. Correlation of source rocks with crude oils based on saturated hydrocarbons. Group 2.

GROUP 3/S	ub-group 3a (OIL)
SAMPLE	32
LOCATION	HOMEGLEN RIMBEY 9-10-42-2W5
DEPTH	7854'-7862'
AGE	FRASNIAN
FORMATION	D3
IDENTIFICATION	
DUVERNAY (RO	CK IMPREGNATION)
SAMPLE	W 9
LOCATION	FERRY BANK 2-8-44-27W4
DEPTH	7370′
AGE	FRASNIAN
FORMATION	DUVERNAY (D3)
IDENTIFICATION	





n-alkanes and isoprenoids weight per cent

GROUP 3/Sub-group 3b (OIL)					
SAMPLE	15				
LOCATION	SWAN HILLS (Unit 1) 10-29-66-10W5				
DEPTH	8911'- 8920'				
AGE	FRASNIAN				
FORMATION	BEAVERHILL LAKE "B"				
IDENTIFICATION	DENTIFICATION -D-				
BEAVERHILL LAKE (ROCK)					
SAMPLE	B 15				
LOCATION	SWAN HILLS 4-7-67-8W5				
DEPTH	8076′				
AGE	FRASNIAN				
FORMATION	BEAVERHILL LAKE				
IDENTIFICATION	-0-				







Correlation of source rocks with crude oils based FIGURE 5-20c. on saturated hydrocarbons. Group 3.

Ring number

0.001		DISTRIBUTION BY CARBON NUMBER	DISTRIBUTION BY MASS FAMILIES	DISTRIBU CnH2n-12	TION IN THE MASS CnH2n-14	FAMILIES CnH2n-18	DISTRIB. BY MASS
GROU	104		40	225 F1	2.25 F 1	4.50	
LOCATION	WILLESDEN GREEN	10	30	200 - F2+3	²⁰⁰ — F2+3	3 50	30
DEPTH	5150'-5167'		25	125	1.25	2 50	25
AGE	CAMPANIAN	te ent	15	100	1.00	2 00	15
FORMATION	BELLY RIVER	ss ber		075	0.50	100	0
IDENTIFICATION	•		5 0 6 8 10 12 M K 6 20 22 24 26 28			0.50	5
COLORADO	GROUP (ROCK)	rocarb	40	225	225	4.50	40
SAMPLE	LC 17	ic hyd	35	200 F1 F2+3	200 F1 F2+3-	400	35
LOCATION	CAROLINE 10-27-35-6W5	oumat	25	1.50	1.75	3 50	25
DEPTH	8465′	Ξ.	20	125	125	2 50	20
AGE	ALBIAN	5	15	075	0.75	150	15
FORMATION	VIKING SS		s	050	0.50	1.00	5
IDENTIFICATION	-	0 0 0 20 20 30 30	0 6 8 10 12 14 16 8 20 22 24 25 25	0.00 15 20 25 30 35	0.00 6 20 25 30 35	0.00 15 20 25 30 35	0 6 6 10 12 ⁸ 14 ⁹ 16 ⁸ 6 20 22 24 38 28
NITO	ON (OIL)		40				40
SAMPLE	62		35	200 F1 F2+3	200 — F1 F2+3	400	35
LOCATION	NITON 4 - 19 - 34 - 12W5		25	175	1.50	3 50	30
DEPTH	6493'		20	1.25	1.25	2 50	20
AGE	APTIAN		15	075	0.75	2 00	15
FORMATION	BASAL QUARTZ B		10 5	050	0.50	100	
IDENTIFICATION	•		0 6 6 10 12 14 15 6 20 22 24 25 28	0 000 10 15 20 25 30 35		0.00 15 20 25 30 35	0 6 8 10 12 ⁴ 14 ⁶ 16 ⁶ 8 20 22 24 25 28
MANNVILLE	GROUP (ROCK)	Locart	40	225	225	4.50	40
SAMPLE	M 14		35	200 F1 F2+3	200 F 1 F2+3	400	35
LOCATION	BENTLEY 10-11-40-2W5	omat	25	175	1.50	3 50	25
DEPTH	6530'-6533'	ζ.	20	125	1.25	2 50	20
AGE	APTIAN			075	0.75	150	
FORMATION	LOWER MANNVILLE		5	0.50	0.50	100	s VL
IDENTIFICATION	0	0 0 15 20 25 30 30	0 6 8 10 12 H 16 18 20 22 24 26 28	0.00 15 20 25 30 35	000 0 15 20 25 30 35	0.00 15 20 25 30 35	0 6 8 10 12#14#16#16 20 22 24 25 28
		Carbon number	p of C _n H _{2n-p}	Carbon number	Carbon number	Carbon number	p of C _n H _{2n-p}

.

FIGURE 5-21a. Correlation of source rocks with crude oils based on aromatic hydrocarbons. Group 1.

GSC

GROUP 2 (OIL)			
SAMPLE	71		
LOCATION	WILLESDEN GREEN 6-22-39-5W5		
DEPTH	7514'-7522'		
AGE	ALBIAN		
FORMATION	GLAUCONITIC A		
IDENTIFICATION	•		
MANNVILLE	GROUP (ROCK)		
SAMPLE	M 12		
LOCATION	FERRY BANK 6-9-44-27W4		
DEPTH	5133′		
AGE	APTIAN		
FORMATION	LOWER MANNVILLE		
IDENTIFICATION	0		

DISTRIBUTION BY

DISTRIBUTION BY





DISTRIBUTION IN THE MASS FAMILIES

FIGURE 5-21b. Correlation of source rocks with crude oils based on aromatic hydrocarbons. Group 2.

GROUP 3/Su	ib-group 3a (OIL)				
SAMPLE	SAMPLE 32				
LOCATION	HOMEGLEN RIMBEY 9-10-42-2W5				
DEPTH	7854'-7862'				
AGE	FRASNIAN	r cent			
FORMATION	D3	ass pe			
IDENTIFICATION					
		1			
DUVERNAY (RO	CK IMPREGNATION)	rocar			
SAMPLE	W 9	ic hyd			
LOCATION	FERRY BANK 2 - 8 - 44 - 27W4	omat			
DEPTH	7370′	A			
AGE	AGE FRASNIAN				
FORMATION	DUVERNAY (D3)				
IDENTIFICATION]			





1.75

1.50

1.25

1.00

0.75

0.50

0.2

0.00



4.50

4.00

3.50

3.00

2.50

2 00

150

100

0.5 0.0

4.50

400

3.50

300

2.50

2 00

150

1.00

0.5

0.00





0.50

0.25

0.00

ю

20 25 30

15

6 8 10 12 14 16 18 20 22 24 26 28

Extracts from rocks of approximately the same age (Calmar, Nisku, Ireton, Leduc, Duvernay, Cooking Lake and Beaverhill Lake) have saturated hydrocarbons that are similar in distribution to the Group 3 oils apart from variations due to type of organic matter and to the diagenetic stage of the sediment (Fig. 5-20).

Gas chromatographic analyses of aromatic hydrocarbons from the Calmar, Nisku, Leduc, Ireton, Duvernay and Cooking Lake Formations show, for the most part, that the distribution of benzo- and dibenzothiophenes resembles that of Group 3a. Equally, they show that the Beaverhill Lake extracts are relatively depleted in thiophenic compounds and, in this respect, resemble the oils of Group 3b. The same results are obtained for the Beaverhill Lake extracts and oils when their aromatics are analyzed by mass spectrometry (Fig. 5-21c). It is apparent, therefore, that organic material of the Calmar, Nisku, Ireton, Leduc, Duvernay, Cooking Lake and Beaverhill Lake Formations must have contributed to the genesis of oils now pooled in reservoirs of the same age.

In the case of extracts from the oldest rocks examined (Watt Mountain Fm., Middle Devonian), the characteristics of both the aromatic hydrocarbons and the saturated hydrocarbons are different from those of the corresponding oils. The characteristics of the saturated hydrocarbons from the Mitsue oil, located in the Gilwood Sands of the Watt Mountain Formation, are similar to those of the Group 3 oils and to an extract from the Muskeg Formation (Grizzly).

Oils associated with the pre-Cretaceous unconformity

In general terms, oils occurring in proximity to the pre-Cretaceous unconformity resemble either Group 2 or Group 3.

In the region southwest of the Leduc-Woodbend pool, the oils located in Jurassic and Mississippian, and Upper Devonian (Wabamun) reservoirs are closely related to those of Group 2. The extracts obtained from Mississippian and Devonian rocks immediately under the unconformity are similar to the Group 2 oils. These extracts have all the characteristics of impregnations and differ from the Group 2 oils in their larger content of aromatic compounds which tend to concentrate in the fine-grained rocks because of absorption effects. This suite of oils and impregnations differ from the bulk of Devonian oils (Group 3) in the large content of heavy thiophenic compounds (benzothiophenes). These reservoirs, therefore, have been supplied from the same source as the Lower Mannville reservoirs.

In contrast, the oils located at the base of the Mannville to the northeast of the main Leduc-Woodbend pool, namely North Leduc, Armisie, Acheson East, Campbell Namao and Morinville are in many respects similar to the third group, yet their thiophene content, particularly dibenzothiophenes, is larger than in the Group 3 oils which suggests some derivation from oils of the second group and possibly of the Niton type. Thus, the reservoirs at the base of the Mannville to the northeast of Leduc-Woodbend are believed to have been supplied principally by source rocks of the underlying Devonian, but partly from the surrounding Cretaceous.

CHAPTER 6

GEOCHEMISTRY OF HEAVY OILS AND HEAVY OIL EXTRACTS

INTRODUCTION

This part of the report concerns the east-central region of Alberta, including the area limited by the oil sands of Athabasca, Wabasca and Peace River to the north, Cold Lake to the east, and the oil pools of Mitsue to the northwest and Lloydminster to the southeast (Fig. 1-1). Within this region, a number of alteration processes have affected profoundly the composition of the oils. These processes and their effects on the conventionally pooled oils and tar sands are discussed. Finally, variations in the composition of the Mannville oils across the basin are considered.

DEGRADATION PHENOMENA

Evans *et al.* (1971) have delineated a number of processes that can occur during the migration and accumulation of petroleum. These processes are biodegradation, water washing, inorganic oxidation, deasphalting/evaporation, and differential migration of the lighter fractions. Many of these processes have been recognized in the Western Canadian Sedimentary Basin, particularly in the shallow part in the direction of the Athabasca Tar Sands.

Biodegradation

Bacteria can utilize hydrocarbons as a carbon source for their metabolic processes. This process occurs in the subsurface where oxygen-bearing waters invade the reservoir; the hydrocarbons are attacked in the order of the ease with which they can be metabolized. This results in the progressive removal of n-alkanes followed by the acyclic isoprenoids and other branched alkanes. Thus, the greatest changes occur in the saturated hydrocarbons.

The effects of biodegradation are seen in a series of heavy oil samples from the Mannville Group; there is a progressive transformation of the saturated hydrocarbons from the central part of the basin toward the Athabasca Tar Sands. The stages in the transformation are illustrated in Figure 6-1 with type examples. The samples are arranged from south to north beginning with a conventional crude oil from the Bellshill Lake pool. The Edgerton sample is depleted in normal alkanes and there is a relative enrichment of the isoprenoids, especially pristane and phytane. At Flat Lake, the normal alkanes have almost disappeared and pristane and phytane are very prominent, although their absolute quantities also have decreased. At Pelican, adjacent to the McMurray area, even the isoprenoids have disappeared leaving only other iso-alkanes and the cyclo-alkanes. Thus, the results of biodegradation are

an enrichment in the acyclic and aromatic hydrocarbons, and in the non-hydrocarbon resins and asphaltenes. The various stages of degradation are classified into types a, b and c.

Type a is typified by the Edgerton sample (Mannville) in which there is a decrease in the normal alkane content with an apparent increase in the proportion of isoprenoid compounds.

Type b comprises degraded oils in which the normal alkanes have disappeared totally but in which the isoprenoids pristane and phytane are relatively unaffected, e.g. Flat Lake (Colony Fm.).

Type c oils contain no normal alkanes or isoprenoids, as illustrated by the Pelican example from the Wabiscaw Formation.

Water washing, inorganic oxidation and deasphalting-migration

In practice, it is extremely difficult to separate the relative effects of water washing, inorganic oxidation and deasphalting-migration since all of these affect the aromatic fraction to a greater or lesser extent. Although deasphalting and subsequent migration of the lighter fractions depletes the residue in light saturated hydrocarbons, similar effects can be produced by evaporation during the analytical procedure. The effects of these various phenomena can be seen best in the aromatic fraction and particularly in the aromatic mass families C_nH_{2n-8} , C_nH_{2n-12} , and C_nH_{2n-14} and the equivalent thiophenic families $C_nH_{2n-10}S$, $C_nH_{2n-12}S$, $C_nH_{2n-16}S$ and $C_nH_{2n-18}S$. At a given level of diagenetic alteration in the Mannville oils, the following variations attributable to alteration can be seen.

In the monoaromatic hydrocarbons:

- 1. In the mass family C_nH_{2n-8} , a shift in the mode to higher carbon numbers;
- 2. In the mass families C_nH_{2n-12} and C_nH_{2n-14} , an overall enrichment of compounds above C_{20} or C_{25} , particularly in the first-named family.

In the diaromatic hydrocarbons of the families $\rm C_nH_{2n-12}$ and $\rm C_nH_{2n-14}$:

- 3. A decrease in the total percentage;
- 4. A decrease in the mode; or/and
- 5. A displacement of the mode to higher carbon numbers.

In the thiophenic compounds of families $C_nH_{2n-10}S$, $C_nH_{2n-12}S$, $C_nH_{2n-16}S$, and $C_nH_{2n-18}S$:

6. An increase in their concentration;



FIGURE 6-1. Effects of biodegradation on composition of saturated hydrocarbons from heavy oils.

- 7. An enrichment of compounds in the higher molecular weight range; and
- 8. A decrease in the concentration of compounds in the lower molecular weight range.

All of the Mannville oils do not show all of the above changes. Specific instances are given in the following sections.

GEOCHEMISTRY OF POOLED OILS

Fourteen samples have been examined from reservoirs within the Mannville Group (Wainwright, Sparky and Blairmore Fms.) in the Lloydminster region (Appendix D; Fig. 4-11).

Gross composition of oils

The oils from the Lloydminster region have similar sulphur contents (>2%) and are similar in composition to the Group 2 oils (Figs. 5-1, 5-2); they are richer in polycyclic molecules than the oils from Groups 1 and 3. The oils from the Upper Mannville in this region differ from the majority of the Group 2 oils in the composition of the residue ($t^{\circ}>210^{\circ}C$). They, together with those from the Pekisko at Gilby, the Wabamun at Leduc, and the Banff at Alexis, Glenevis and Cherhill, are richer in resins and asphaltenes.

In the case of the unaltered oils (Wainwright, Bellshill Lake, Thompson Lake and Choice), mass spectrometric analysis of the hydrocarbons shows that the acyclic alkane contents are of the same order as those of Group 2 (Fig. 5-3) but the altered oils are depleted in alkanes (≤ 17 %) and richer in aromatic hydrocarbons (≥ 52 %) than those of Group 2.

Saturated hydrocarbons

Analysis by gas chromatography reveals that a number of samples have undergone biodegradation. This degradation can be appreciated by means of an examination of the chromatograms and, particularly, by comparison of the isoprenoids, pristane and phytane, with normal alkanes that elute at approximately the same time. If the proportion of these isoprenoids is compared with that of the C_{17} and C_{18} n-alkanes (Table 6-1), the following classification is established. Those oils with a ratio of pristane plus phytane to nC₁₇ plus nC₁₈ of less than 0.60 are unaltered, namely Wainwright (Lloydminster Fm.), Bellshill Lake, Thompson Lake and Choice. Those with ratios between 0.60 and 1.00 have had some n-alkanes removed, namely Wainwright (Wainwright Fm.) and David. A ratio of 1.00 corresponds to type a, as previously defined (Fig. 6-1); ratios between 1.00 and 2.00 (Baxter Lake, Chaurin South-Lloydminster Fm., and Hayter) and those above 2.00 (Aubundale, Chauvin and Chauvin South-Sparky Fm.) indicate progressive removal of n-alkanes. Finally, in the Wildmere and Lloydminster samples, only the isoprenoids remain and are equivalent to type b (Fig. 6-1).

TABLE 6-1

Pooled heavy oils – ratios of isoprenoids to n-alkanes (C_{17} and C_{18})

SAMPLE NO.	BOREHOLE	FORMATION	Pristane C ₁₇	Phytane C18	$\frac{Pr+Ph}{C_{17}+C_{18}}$	<u>x</u> Isoprenoids n-alkanes	Alkanes HC saturated	Biodegradation
87	Bellshill Lake		0.39	0.39	0.39	15.65	46.03	
88	Thomson Lake	Blairmore	0.57	0.33	0.45	19.06	44.68	
89	Choice		0.60	0.41	0.50	19.00	48.65	
81	Wainwright	Lloydminster A	0.66	0.50	0.58	22.15	41.84	
86	David	Lloydminster	0.70	0.50	0.60	27.43	30.54	
80	Wainwright	Wainwright	1.16	0.68	0.92	37.15	39.26	
79	Baxter Lake	Wainwright	1.68	1.10	1.39	66.17	30.50	
83	Chauvin South	Lloydminster C	2.14	1.26	1.70	63.64	31.90	
85	Hayter	Sparky A	2.15	1.27	1.71	77.05	32.29	type a
78	Auburndale	Wainwright A	2.76	1.43	2.10	89.54	29.27	.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
82	Chauvin	Upper Sparky	2.67	1.61	2.14	103.23	31.33	
84	Chauvin South	Sparky G	3.17	1.94	2.55	89.08	31.98	
77	Wildmere	Lloydminster	indeterminable				28.83	type b
76	Lloydminster	Sparky S					25.98	
								GSC

The effects of biodegradation can be illustrated in a more general manner (Fig. 5-8) by plotting the ratio of total acyclic isoprenoids to n-alkanes against the percentage of acyclic alkanes in the saturated hydrocarbons. This relationship shows the same successive stages of degradation as are outlined above. When the isoprenoid to n-alkane ratio exceeds 40 per cent, the oils are similar to type a; at 100 per cent, they are similar to type b. Unaltered oils from this region have a slightly higher isoprenoid content than the Group 2 oils. Consequently, unaltered oils from the eastern margin of the basin have isoprenoid to n-alkane ratios of above 30 per cent, whereas Group 2 oils from the basin centre have values between 10 and 20 per cent.

Degradation of saturated hydrocarbons has occurred in the Upper Mannville oils between the Wainwright-David and Lloydminster pools but it has not affected those from Bellshill Lake, Thompson Lake and Choice lying to the southwest. This degradation never reaches the level of type c found in nearly all the heavy oil impregnations and oil sands located between Lloydminster and the Athabasca and Wabasca deposits. In these heavy oil impregnations, the loss of gaseous and light liquid hydrocarbons has resulted in an increase in specific gravity of the oil rendering them non-producible by conventional methods.

As the alkanes are susceptible to degradation, they cannot be used to compare oils of the Upper Mannville in this area with those of Groups 1, 2 and 3. Rather, saturated compounds which are little affected by bacterial activity, such as the acyclic alkanes with 2, 3 and 4 rings, must be considered. Their distribution in Mannville oils is similar to those of the Group 2 oils. However, certain of the oils do have a slightly lower content of 3-ring cyclo-alkanes than the typical Group 2 oils.

Aromatic hydrocarbons

With the exception of the Bellshill Lake sample, gas chromatograms show that the polyaromatic compounds from the Mannville oils in this area are poorly resolved, particularly in the range above C_{20} . These oils are rich in benzothiophenes of all ranges (C12-C30); this is expressed as an upward drift of the chromatogram. The dibenzothiophenes (C_{11} - C_{20}) are relatively less important. The distribution of thiophenic compounds is similar to that in oils from other areas such as from the Pekisko Formation at Gilby, the Banff Formation at Alexis, Cherhill and Glenevis, and the impregnations from the Wabamun Formation at Golden Spike. It is similar also to that in some of the less altered impregnations from this area, namely Sandy Lake (McMurray Fm.), Lloydminster (Sparky Fm.), Provident Prospect (Leduc Fm.) and Edgerton (Lloydminster Fm.). In contrast, the oil from Bellshill Lake is similar to the unaltered Group 2 oils in that it contains polyaromatics which are better resolved.

Two oil samples from the Upper Mannville have been analyzed by mass spectrometry (Table 5-1). These are an unaltered oil from the Choice pool and the Lloydminster oil which is the most extensively biodegraded conventional oil encountered. The Choice oil has all the characteristics of the Group 2 oils. The distributions of aromatics by carbon number and monoaromatics by family are similar to those of the Glenevis oils. The Choice oil has higher modes at C_{13-14} and C_{16-17} in the C_nH_{2n-12} and C_nH_{2n-14} mass families respectively and a higher content of steroid and triterpenoid monoaromatics than the Glenevis oil. The distribution of thiophenic compounds is similar to that of the Pembina (63) oil.

In the Lloydminster oil, the distribution of aromatics by carbon number is characterized by the importance of compounds between C_{20} and C_{30} and the low proportion of compounds below C_{20} ; this is typical of the Group 2 oils. The low concentration of compounds below C_{20} is observed in all three aromatic fractions (F₁F₂F₃+) in the mass families $\mathrm{C_{n}H_{2n-8}},~\mathrm{C_{n}H_{2n-12}},~\mathrm{C_{n}H_{2n-14}}$ and C_nH_{2n-18} . The higher concentrations of compounds above C_{20} are confined to the last three families listed. The monoaromatics of the steroid and triterpenoid type $(C_{25}+)$ are particularly important in the families $\mathrm{C}_{n}\mathrm{H}_{2n-12}$ and $\mathrm{C}_{n}\mathrm{H}_{2n-14};$ the diaromatic hydrocarbons beyond C_{20} and the benzothiophenes are equally as important. The benzothiophenes are well represented in the range C₂₀-C₃₂ and naphthobenzothiophenes (C₂₀+) are present in the mass family C_nH_{2n-18} .

The results of the gas chromatography and mass spectrometry show that Lloydminster oil is similar to the Mississippian oils at Gilby and Glenevis in most respects except for the high steroid and triterpenoid content and the presence of benzothiophenes and nonthiophenic compounds beyond C_{20} in the families C_nH_{2n-12} and C_nH_{2n-14} . It remains to be seen whether the relative abundance of these compounds is due to enrichment as a result of loss of light compounds or an immature level of diagenesis or a combination of these processes.

GEOCHEMISTRY OF HEAVY OIL EXTRACTS

This section of the report is concerned with the heavy oils and impregnations extracted from rocks in the study-area. Some 63 samples have been examined (Appendix D) both from above and below the unconformity although the majority are from the Mannville. All have the characteristics of impregnations of heavy tars. Nine samples were from the Athabasca Tar Sands and 3 others were from the Peace River area.

Mannville impregnations

Gross composition

It has been shown in the previous section that the Cretaceous Mannville oils are readily distinguished from both the post-Mannville and Devonian oils on the basis of gross composition alone. The heavy oil extracts form a distinct group in the diagram of gross composition (Figs. 6-2, 6-3). They all have higher resin and asphaltene contents and lower saturated hydrocarbon contents than the pooled oils from the central part of the basin and, as such, resemble the pooled oils in the Lloydminster region discussed above.

Saturated hydrocarbons

Type samples of heavy oils have been selected to show the systematic changes that appear to take place with progressive geographic approach toward the oil sands or the heavy oil area in the shallower parts of the basin (Fig. 6-1). These stages have been discussed in the previous section. Evans *et al.* (1971) have shown that a similar change has taken place in oils from Mississippian strata in southeastern Saskatchewan. They explained that the changes were caused largely by bacterial action.

In the present case, the distribution of the saturated hydrocarbons shows that the dominant process operating in the McMurray deposit was a biodegradation rather than a low thermal maturation. The phenomenon of degradation explains the progressive change from an unaltered oil (Bellshill Lake) to a strongly altered one (Pelican). The reverse hypothesis with a Bellshill Lake oil coming from a heavy and immature oil of the Pelican type through thermal maturation -- as Connan (1972) had shown by laboratory experiment with heavy oils of Aquitaine -- cannot be retained for the McMurray oil. Upon thermal maturation, a heavy and immature oil produces normal and branched alkanes from the breaking of chains linked to heavy and polycyclic molecules. There is no reason to suppose that such cracking would favour either normal alkanes or branched alkanes. In a supposed succession of thermal maturation going from Pelican, Flat Lake, Edgerton to Bellshill Lake, the isoprenoids appear first and selectively, and only later do the normal alkanes appear. That successive appearance of isoprenoids and normal


FIGURE 6-2. Gross composition of heavy oil extracts in terms of saturated hydrocarbons, aromatic hydrocarbons and resins plus asphaltenes.

alkanes does not fit with a natural cracking process so that the thermal evolution theory is unacceptable. The observed variations in oil composition from Bellshill Lake to Pelican corresponds to a natural succession that would be expected to result from biodegradation. The isoprenoids are more resistant to biodegradation than the normal alkanes so that the ratio of isoprenoids to n-alkanes would be expected to increase and become very large as the last traces of normal alkanes were removed from an oil, leaving a reduced absolute, but non-zero concentration of isoprenoids. Ultimately, both the n-alkanes and the isoprenoids are removed and the ratio becomes undefined. As can be seen in Figure 6-1, the ratio of isoprenoids to alkanes is about one for type a oils but very large for type b oils and undefined for type c oils, indicating that the dominant or exclusive process must have been biodegradation.

All 63 of the samples can be classified by gas chromatography into three stages of degradation compared to the pooled oils. All of the more extremely altered samples (types b and c; Fig. 6-3) are poor in alkanes, but there is only slight variation in cycloalkane content. The hydrocarbon composition of the type a samples falls within the Group 2 triangle indicating the similarity to the Mannville-type oils. The heavy oils from the Peace River region fall in the type b category.

Since the cyclo-alkane compounds are relatively stable, they can be used to establish the relationship of the heavy oils of eastern Alberta, both above and below the unconformity, with the unaltered oils occurring throughout the basin. Figure 6-4 shows the distribution of 2-, 3- and 4-ring cyclo-alkanes for all oil samples. Almost all of the heavy oil samples fall within the area of the Group 2 or Lower Mannville type oils containing



FIGURE 6-3. Composition of hydrocarbons in heavy oil extracts in terms of acyclic alkanes, cyclo-alkanes and aromatic hydrocarbons.



FIGURE 6-4. Distribution of cyclo-alkanes (2, 3 and 4 rings) in heavy oil extracts in relation to those of pooled oils.

a somewhat higher amount of tricyclic alkanes than either the Upper Cretaceous (Group 1) or Devonian (Group 3) oils. This relationship suggests a common origin for both the conventional and heavy Lower Cretaceous oils.

Relationship of formation water type to hydrocarbon type

The Mannville pooled oils and most of the type a samples (those that show the least alteration) occur with waters of greater than 80 parts per thousand total salinity (Fig. 6-5). The more altered oils of the b and c types are all located in zones of lower salinity. This same relationship has been observed previously by Evans *et al.* (1971) for oils in Mississippian strata of southeastern Saskatchewan.

Aromatics and thiophenics

The aromatic and associated thiophenic compounds are degraded only partially by bacterial activity. The comparative chromatograms of aromatic and thiophenic compounds can be used, therefore, as a guide to the relationships and classification of the oils.

Thirty-nine samples analyzed by GLC have a wide distribution of thiophenic compounds in the range from C_{12} to C_{30} . The two examples in Figure 6-6 show a faintly altered oil from Edgerton in the top chromatograms and below this an altered sample from the Nisku





Formation, beneath the unconformity at Skaro. The FID curves record non-sulphur-bearing aromatics, and the FPD curve the thiophenes (Fig. 4-3). The right-hand portion of the FPD curve is at a noticeably lower level in the Skaro example, and indicates a lower amount of benzothiophenes compared with the Edgerton sample.

The peaks just before the centre of the FPD curve (lower curve) in the Skaro diagram (Fig. 6-6) are less intense than the same peaks in the Edgerton diagram and this indicates a lower content of dibenzothiophenes in the former. These differences can be seen better in Figures 6-7 and 6-8 where the curves for each of these groups of compounds are shown separately. In the benzothiophene curve (Fig. 6-7), the lower molecular weight and less complex benzothiophenes at the right-hand part of the curve are present only in small amounts in the Skaro example. Similarly, in Figure 6-8, the dibenzothiophene peaks in the central part of the curve are less intense in the Skaro sample. Various stages of this alteration process were observed in all 39 samples analyzed. The decrease in amounts of lower molecular weight ring compounds can be seen also in the aromatic hydrocarbons (Fig. 6-6). It can be explained partly by biodegradation, partly by water washing, and possibly by some inorganic reactions throughout geologic time.

Reference samples are shown at the top and bottom of Figure 6-9; these are Mannville oils. One, a heavy oil typical of the Lloydminster area, is relatively unaltered and the other, a very heavy oil from the McMurray Formation, is extremely altered. The McMurray oil differs from the Lloydminster sample only in the lower molecular weight aromatics and thiophenics. These are compared with an oil from the Viking at Legal (type 1) which, lacking a significant content of thiophenics, is totally different. A Redwater oil from the Leduc Formation is compared with the two reference samples in Figure 6-10. It may be seen that the Redwater Devonian (type 3) oil is richer in thiophenic compounds than the Group 1 oil, but the more complex thiophenic compounds of higher molecular weight are not well represented.

The reference samples are compared with a typical Group 2 oil from the Glauconitic Formation at Glen Park in Figure 6-11. It can be seen that the Glen Park oil contains a wider range of thiophenic molecules than either the Group 1 or Group 3 oils and that this example does resemble both the altered and relatively unaltered reference samples from the Mannville, particularly in the left side of the chromatograms. The strongest similarity is between the oils of Lloydminster pool and the Mississippian Banff sample from Glenevis (Fig. 6-12) which illustrates the geochemical similarity of the unconformity oils to the slightly altered heavier oils of the Mannville.

Two nondegraded oils, one from the Mannville and the other from the Devonian, in the Glen Park field, are compared (Fig. 4-3). The Glauconitic (Glen Park) oil shows the typically wide distribution of the thiophenics in the Mannville oils. In contrast, the Leduc oil from the same field shows only a weak representation of the lower molecular weight dibenzothiophenes.

There is some variation in the sulphur content of the high gravity oils of the Mannville Group. This variation is due to concentration brought about by selective removal of compounds such as n-alkanes and low molecular weight aromatics. To support this hypothesis, it is pointed out that:

- 1. When compared with other oils having the same burial depth range, it is apparent that the nondegraded Mannville oils and unconformity oils belong to the same group as the higher sulphur crudes of the basin (see above).
- 2. A linear relation exists between the sulphur content and the aromatic-polycyclic (aromatic hydrocarbons, resins, asphaltenes) contents of the pooled oils of Mannville or of the unconformity (Fig. 6-13).

The additional incorporation of sulphur during the biodegradation, as a result of sulphate reduction by anaerobic bacteria, is certainly possible but is likely to be a subordinate factor.



FIGURE 6-6. Gas chromatograms of aromatics and thiophenes from heavy oils. Note poorly resolved peaks before the centre of Skaro (FPD) chromatogram compared to that of Edgerton indicating a diminution in dibenzothiophenes.



FIGURE 6-7. Chromatogram (FPD) for the benzothiophenes isolated from samples shown in Figure 6-6.



FIGURE 6-8. Chromatogram (FPD) for the dibenzothiophenes and naphthobenzothiophenes isolated from samples shown in Figure 6-6.



FIGURE 6-9. Chromatograms (FID, FPD), conventional Viking oil (Group 1) compared with a degraded McMurray Formation oil and a partly altered oil at Lloydminster.



FIGURE 6-10. Chromatograms (FID, FPD), conventional Devonian oil (Group 3) compared with the same references as shown in Figure 6-9.

Mass spectrometric examination of the aromatic fraction of heavy oil extracts (Table 6-2) confirms the characteristics observed using gas chromatography. The heavy oil extract from the McMurray sands (GCOS Plant M24), for example, shows a large content of sulphur which is typical of all Group 2 oils. This large sulphur content can be attributed to abundant thiophenic compounds (Table 6-2), particularly dibenzothiophenes in the range C_{21} to C_{35} . The thiophenic compounds with one thiophene cycle families ($C_nH_{2n-16}S$ and $C_{n}H_{2n-18}S$) are more abundant than the true aromatics of the phenanthrene family (C_nH_{2n-18}) . The heavy oil extracts differ from the Group 2 oils in that monoaromatics of the steroid and triterpenoid type clearly are represented. The degradation phenomena already observed by gas chromatography are confirmed by mass spectrometry, particularly the absence or reduced quantities of compounds with low carbon numbers $(C_{12} \text{ to } C_{17})$. These degradation characteristics will be discussed more fully in a later section. Mass spectrometric analysis of aromatic hydrocarbons from a heavy oil at Peace River (M48) shows that it is similar to the Group 2 oils. In particular, it resembles the Flat

Lake (M59) sample which has undergone approximately the same amount of biodegradation.

Colorado Group impregnations

A single impregnation has been analyzed from the Colorado Group sediments; it occurs at Wabasca (LC20/ LC21) in the Viking Formation, 6 m (20 ft.) above the Mannville. The distribution of saturated hydrocarbons shows a small amount of normal and branched alkanes (<20%) and a large content of 3- and 4-ring cycloalkanes. This latter feature resembles the impregnations and heavy oils of the underlying Mannville; the similarity is re-enforced upon examination of the aromatic hydrocarbons by gas chromatography and mass spectrometry (Fig. 6-14). Both the true aromatics and the thiophenes contain heavy molecules beyond C25. The concentration of dibenzothiophenes and the presence of naphthodibenzothiophenes resemble those found in the GCOS oil sands (M24) and Flat Lake (M59) samples. Similarly, monoaromatics of the steroid and triterpenoid types are found in the mass families C_nH_{2n-12} and C_nH_{2n-14}, and lower molecular weight compounds



FIGURE 6-11. Chromatograms (FID, FPD), conventional Mannville oil (Group 2) compared with the same references as shown in Figure 6-9.

TABLE 6-2

Heavy oils extracts – distribution (weight per cent) of monoaromatic, diaromatic compounds and benzothiophenes in the aromatic families C_nH_{2n-p} (p = 6, 8, 12 and 14)

ġ			P = 6	(10S)	P = 8	s(12S)	F	P=12(165	5)	F	P≈14(185	5)
BOREHOLE		FORMATION	Fr1 monoaro	Fr 2 benzothio	Fr1 monoaro	Fr2 benzothio	Fr1 monoaro	Fr2 diaro	Fr3 dibenzothio	Fr1 monoaro	Fr2 diaro	Fr 3 dibenzothio
M24	G.C.O.S. Plant	McMurray	4.19	5.38	7.51	5.86	4.80	2.66	* 9.74	3.61	5.25	7.78
M37	Pelican	Wabiskaw	5.91	7.40	7.98	5.31	3.30	2.42	13.02	3.16	4.25	7.70
M42	Marten Hills		6.16	6.05	9.46	5.16	4.89	4.16	9.53	4.40	6.95	4.69
M59	Flat Lake	Colony	7.27	7.01	9.63	4.38	4.90	3.42	11.14	4.51	4.92	6.93
M89	Edgerton	Lloydminster	8.94	6.78	11.37	3.93	5.04	5.26	9.60	3.53	6.31	5.85
M78	Skaro	Niksu	3.89	6.64	8.55	4.23	5.56	4.84	7.87	3.73	6.42	5.31
LC21	Wabasca	Viking	6.65	3.90	10.17	2.97	4.86	2.42	13.82	3.87	3.27	8.24
M48	Peace River	Bullhead	6.25	9.69	7.44	7.49	3.28	2.75	13.56	3.14	4.31	8.05
										-		GSC



FIGURE 6-12. Chromatograms (FID, FPD). Strongest similarity is between heavy oil from Lloydminster and a Mississippian conventional oil at Glenevis illustrating geochemical similarity of unconformity oils with slightly altered Mannville oils.

(below C_{17}) are present in low concentrations. It would appear that this basal Colorado impregnation is derived from the Wabasca oil sands of the underlying Mannville.

Extracts from Devonian rocks adjacent to and away from the unconformity

Eight Devonian rock samples were extracted originally; subsequently, a further 6 samples were extracted of which 5 were supplementary samples. Samples taken from within 12 m (40 ft.) of the pre-Cretaceous unconformity [Wabamun (W105), Nisku (Wi9), Grosmont (W24/W25), and Beaverhill Lake (B19)] have been compared with samples taken from between 90 and 660 m (300-2200 ft.) beneath the unconformity [Ireton (W20, W21, W22, W23), Beaverhill Lake (B17, B18), and Muskeg (MD6, MD5)]. Only one of the Muskeg (MD6) samples yielded any extract. A number of extracts are affected by contamination, notably Vegreville (Wi9-Nisku) by the second type oil and Craigend (W25-Grosmont), Wappau (B19-Beaverhill Lake), Meadowbrook (W22/ W23-Ireton) and Plum Lake (W21-Ireton) by the first type (see Chap. 4). In all of these cases, the extracts yielded only small quantities of saturated hydrocarbons. The following observations can be made for the nonpolluted samples.

Samples directly under the unconformity

The Marten Hills (Wb5-Wabamun) sample has a high extract yield (extract/org. C) and has normal alkane and isoprenoid distributions similar to the Upper Devonian oil samples. The sample from Craigend (W24-Grosmont) has an n-alkane mode at C_{17} - C_{19} and abundant n-alkanes above C_{20} with a slight odd predominance between C_{23} and C_{29} ; the supplementary extract (W25) in which the saturated hydrocarbons are contaminated has an aromatic distribution (CGC) similar to an impregnation which has undergone alteration by water washing.





The Wappau (B19-Beaverhill Lake) extract is similar; the saturated hydrocarbons are contaminated and the aromatic distribution (CGC) is characteristic of heavy oil impregnations. The absence of the lighter fractions is attributed to evaporation.

Samples away from the unconformity

In contrast to the samples discussed above, the extracts from Meadowbrook (W23-Ireton) and Plum Lake (W21-Ireton), in which the saturated hydrocarbons are contaminated, have aromatic (CGC, FID) and thiophenic (FPD) distributions similar to the Duvernay extract from Ferrybank (W9).

The only extract from the Muskeg (MD6) sample shows a loss of alkanes below C_{20} . This loss may have been caused during the analytical procedure, based on the low quantity of saturated hydrocarbons (45 mg) obtained from this extract (250 mg). This extract is similar in some ways to one from the Watt Mountain Formation at Swan Hills (Fig. 5-19b), particularly in

the distribution of thiophenic compounds ignoring the loss of the lighter compounds in the Muskeg sample.

The Beaverhill Lake sample (B18-Rock Island) was taken from the vicinity of the Marten Hills pool and has an irregular distribution of n-alkanes with an odd predominance between C_{15} and C_{21} and between C_{25} and C_{29} ; the isoprenoids and particularly pristane and phytane are abundant.

Origin of gas associated with heavy oil deposits

Before summarizing this part of the study, it is interesting to note that the heavy oil zone includes a number of fields of dry gas which are situated within the Mannville or immediately under the unconformity. For purposes of comparison, gases from both studyareas have been divided into four groups (A to D) on the basis of composition (Fig. 6-15). The dry gases from the basin margin comprise 95 per cent or more of methane (Fig. 6-15, Group A); the other components are chiefly represented by nitrogen ($\leq 3\%$), whereas the higher hydrocarbon homologues C₂ to C₆ form less than 2 per cent. As such, these gases are similar in composition to those occurring in post-Colorado reservoirs at Medicine Hat in the extreme southeast of Alberta, whereas the closer Colorado fields (Fig. 6-15, Group B) are richer in higher homologues (C_2+) . The content of higher hydrocarbons is clearly higher in the gas fields along the Redwater Homeglen-Rimbey reefal trend (Fig. 6-15, Group D) and the Lower Mannville and Mississippian (Fig. 6-15, Group C). Moreover, these gases are associated with or adjacent to pools of liquid hydrocarbons.

Two hypotheses can be proposed to explain the origin of the dry gas fields at the margin of the basin. In the first, dry gas would be formed by cracking of hydrocarbons in the deeper parts of the basin; a migration across the transgressive deposits of the Mannville in contact with the unconformity would then occur, followed by accumulation in the structures at the margin of the basin. In the second hypothesis, dry gas would accumulate in situ; it would have a biogenic origin and would form at an early stage of diagenesis. The preservation of this diagenetic methane suggests an origin from a sedimentary sequence which has not been disturbed since deposition. This excludes the formations which have been truncated and eroded by the Mesozoic unconformity and particularly the Paleozoic formations.

The second hypothesis appears to be the most plausible since long distance migration cannot explain the observed variations in gas composition between groups A to D.

Summary

The McMurray oil and the other heavy oils of eastern Alberta, including Peace River, are degraded as the result of the activity of micro-organisms, water washing and probably some inorganic oxidation. The micro-organisms are responsible particularly for the loss of alkanes and possibly some of the cyclo-alkanes and aromatic molecules. Water washing probably is

SAMPLE	M 24
LOCATION	G.C.O.S. PLANT 92-10-W4
DEPTH	
AGE	APTIAN
FORMATION	McMURRAY
IDENTIFICATION	O



SAMPLE	LC 21
LOCATION	WABASCA 10-5-83-21W4
DEPTH	719′
AGE	ALBIAN
FORMATION	VIKING
IDENTIFICATION	•

FIGURE 6-14. Composition of impregnation in Lower Colorado Group combined with GCOS oil sand.

responsible for the impoverishment of the most soluble cyclo-alkanes and aromatics with the fewest rings. Oxidation of lower molecular weight compounds of the cyclo-alkane, aromatic and thiophenic fractions probably occurred also. The loss of the lower molecular weight compounds as a result of degradation causes a relative enrichment in the heavier molecules. Ignoring the effect of alteration, the Athabasca oils and the other heavy oils of eastern Alberta show a close relationship with the pooled oils of the Lloydminster area as well as the conventional Mannville oils. Similarities, based on the polycyclic fraction (saturated and unsaturated), suggest a common origin for all these oils.

The Devonian samples that are adjacent to the unconformity generally contain impregnations of heavy oil which may or may not be affected by contamination. These samples, taken at a distance from the unconformity, namely from the Ireton and Beaverhill Lake Formations, are similar to the types of extracts found in the Duvernay Formation (e.g. El Dorena), which have undergone little maturation.

RELATIONSHIP BETWEEN HEAVY OILS AND CONVENTIONAL OILS

Introduction

Conclusions reached in the previous section were that the heavy oils of eastern Alberta have been more or less degraded by the activity of microorganisms, by water washing, and probably by some inorganic oxidation. Microbial activity causes the loss of normal or branched alkanes and certain molecules among the cyclo-alkanes and aromatics. Water washing causes a depletion of the simplest and most soluble cyclic molecules and oxidation affects the lower molecular weight polycyclic compounds.

Apart from the degradation phenomena, the heavy oils resemble the conventional oils of the Lloydminster region and the oils of the Mannville Group. The similarity is based on the saturated and aromatic polycyclic compounds and suggests a common or related origin for all of these oils. The comparisons of the aromatic fractions have been based on gas chromatographic analyses; in this section, a more detailed comparison based on MS analysis is summarized.

Aromatic composition of heavy oil extracts

The following heavy oil extracts have been analyzed; the choice has been made on the basis of locality, age of reservoir and state of degradation. Type c:

CGOS Athabasca	McMurray Fm.	Sample M24
Type b:		
Marten Hills	_	Sample M42
Type a:		
Edgerton	Lloydminster Fm.	Sample M89

Detailed examination of the aromatic hydrocarbons confirms the similarity of the heavy oils with those of Group 2 (Table 6-2). The characteristic features are the importance of the thiophenic compounds and particularly the dibenzothiophenes between C_{21} and C_{35} in the mass families $C_nH_{2n-16}S$ and $C_nH_{2n-18}S$ (Fig. 6-14). In the triaromatic plus fraction, the distribution of families shows that the sulphur molecules with one thiophene cycle ($C_nH_{2n-16}S$, $C_nH_{2n-18}S$) clearly are present in greater concentration than the true aromatic molecules of the phenanthrene family (C_nH_{2n-18}).

The general similarity does not exclude completely certain variations within Group 2; notably in the mass families C_nH_{2n-8} , C_nH_{2n-12} , and C_nH_{2n-14} and the equivalent thiophenes of $C_nH_{2n-10}S$, $C_nH_{2n-12}S$, $C_nH_{2n-16}S$ and $C_nH_{2n-18}S$. These variations may be related to varying degrees of diagenesis and/or alteration.

Variation in aromatic compositions with increasing alteration in heavy oils and conventional oils

For the Group 2 oils, the diagenetic state is known, or is known for a comparable example, so the listed compositional variations which are produced by nonthermal alteration can be related to a given level of maturation.

In the aromatics:

- 1. In the mass family $C_{n}\mathrm{H}_{2n-8},$ a shift in the mode to higher carbon numbers;
- 2. In the mass families C_nH_{2n-12} and C_nH_{2n-14} , an overall enrichment, particularly beyond C_{20} or C_{25} in the former family.

In the diaromatics of the families ${\rm C}_n{\rm H}_{2n-12}$ and ${\rm C}_n{\rm H}_{2n-14}{\rm :}$

- 3. A decrease in the total percentage;
- 4. A decrease in the mode; or/and
- 5. A displacement of the mode to higher carbon numbers.

In the thiophenic families $C_nH_{2n-10}S$, $C_nH_{2n-12}S$, $C_nH_{2n-16}S$ and $C_nH_{2n-18}S$:

- 6. An increase in their concentration;
- 7. An enrichment in the heavy ranges (C_{20} +) accompanied by/or
- 8. A decrease of the concentration of compounds in the low boiling ranges.

The term alteration is used here to designate both the consequence of secondary migration and bacterial degradation, water washing and inorganic oxidation; the last three processes may be associated. Only in the geological context can the relative effects of maturation and alteration be distinguished. As a first approximation, the relative stages of maturation can be estimated

	Р				OTH	IER GAS	GASES		
				POOLS	C2+	^{CO} 2	SH ₂		
	1	Cr	Ľ١	Craigend	0.17	0.96			
	2	F	-0-	Flat	1.15				
	3	FL	۵	Figure Lake	0.33	1.04			
	4	MH	-0-	Marten Hills	0.13	1.61			
	4	MН		Marten Hills	0.12	1.46			
A	5	CL		Calling Lake	0.35	1.51			
	6	Ba		Baptiste	1.97				
	7	F		Flat	0.26	1.73			
	8	Ab	•	Abee	1.76	0.72			
	9	Т	•	Thorhild (1st GI)	0.76	0.72			
	10	Т	•	Thorhild (2nd GI)	1.27	2.02			
	1	Be	O	Bellis	1.97	0.35			
	2	Be	-0-	Bellis	3.15				
	3	FS	-	Ft Saskatchewan	3.16	0.12			
в	3	BL	-•-	Beaverhill Lake	3.16	0.12			
	4	FB	-•-	Ferrydell-Bon Accord	3.46	0.06			
	5	W	•	Westlock	5.77	0.25			
	6	Т	-0-	Thorhild	5.30	0.70			
	1	AI	0	Alexander	11.64	1.84			
	2	G	Δ	Gilby	12.19	3.61	0.07		
	3	SL		Sylvan Lake (P.)	12.42	3.49	0.07		
	4	SL	•	Sylvan Lake	14.40	3.15			
C	5	G	O	Gilby (BQ"b")	13.14	4.28	0.06		
	6	G	•	Gilby (P.)	13.82	4.38	—		
	7	SL		Sylvan Lake (Elk)	15.11	3.59			
	8	G	Ð	Gilby (BQ"a")	14.67	4.36	0.01		
	9	SL	•	Sylvan Lake	18.26	2.65	—		
	1	L	0	Leduc Woodbend	13.05	0.22			
	2	GS		Golden Spike	11.46	2.21	1.89		
n	3	Н		Homeglen Rimbey	10.58	2.12	3.16		
	4	М		Malboro	2.56	2.60	14.39		
	5	SL		Sylvan Lake	13.33	1.81	4.78		
1	6			Leduc Woodbend	25.27	0.50			

A





FIGURE 6-15. Composition of gases from producing fields in the study-area.



FIGURE 6-16. Map showing variation in present geothermal gradient (in °C/km) in Alberta.

A. MEDICINE RIVER-HARMATTAN REGION Geothermal gradient 30°C/km

aboutterman 8									
SAMPLE	49								
LOCATION	HARMATTAN EAST 7-18-32-3W5								
DEPTH	8484'-8488'								
AGE	TOURNAISIAN								
FORMATION	RUNDLE								
IDENTIFICATION									





ILIES	3													
	C _n H _{2n-14}													
2.50														
2.25				E.	1									
2.00				_ Fr.	2 -									
1.75				Fr.	3									
1.50														
1.25		<u>۸</u>												
1.00		Ĥ												
0.75	-	+												
0.50	-1	h X												
0.25	-#		Æ	/	-									
0,	<u></u>													
1	UI	5 2	0 2	53	0 35									

Fr. 3

30

35

SAMPLE	68
LOCATION	MEDICINE RIVER 4-28-38-4W5
DEPTH	7484'
AGE	ALBIAN
FORMATION	OSTRACOD G
IDENTIFICATION	٠



SAMPLE	45					
LOCATION	MEDICINE RIVER 16-32-39-3W5					
DEPTH	7093′					
AGE	TOURNAISIAN					
FORMATION	PEKISKO B					
IDENTIFICATION	A					



FIGURE 6-17a. Distribution of aromatics in oils at various levels of diagenesis. Medicine River-Harmattan region.

by considering the present geothermal gradients and maximum burial of the different oils under consideration (Fig. 6-16). It allows us to make a comparison of crude oil composition within successive maturation zones. The results are summarized in Figure 6-17.

Zone of present geothermal gradient 30°C per 1000 m

This domain includes the oil pools adjacent to the Foothills and also the Alexis, Cherhill and Glenevis pools. Comparison can be made readily since the oils are in production and the gradients and burial depths are well known. In the case of the Medicine River fields (Fig. 6-16), the Jurassic (53) and Pekisko (45) oils have a shallower depth of burial than the oil from the Lower Mannville (Ostracod G68) because of their more northerly structural position. This is reflected in the composition of the hydrocarbons which generally indicate a relatively low level of maturation. The aromatic hydrocarbons have variations 1, 3 and 4, as listed above, and they are accompanied by a higher proportion of benzothiophenes. These two oils are in reservoirs of comparable depths of burial and have similar gas to oil ratios (GOR) (Fig. 6-18) which are lower than that for the Mannville reservoir. The observed variations can be related jointly to differences in the degree of maturation and to the effects of secondary migration.



FIGURE 6-17b. Distribution of aromatics in oils at various levels of diagenesis. Pembina-Leduc Woodbend region.

The Mississippian oils from Harmattan East (49, Rundle), to the southwest of the Medicine River pools, clearly are more deeply buried. The high distillate content, distribution of n-alkanes, cyclic alkanes and aromatic compounds indicate a higher degree of maturation than the Medicine River (68) oil. However, as well as being richer in monoaromatics than the previous oils, it also shows variations 1, 3 and 4 for the mass family C_nH_{2n-12} . This anomaly can be explained by secondary migration; the more mobile aromatics are partially lost to higher reservoirs. In the Harmattan East field, the oils in the Mannville reservoirs have a higher GOR (Fig. 6-17) [1000 at a depth of 2413 m (8042 ft.)] than that in the underlying Mississippian [965 at 2887 m (9625 ft.)].

The Mississippian oil from Gilby (42, Pekisko) has the same conditions of burial as the Jurassic and Pekisko oils at Medicine River. However, it appears to be less mature, as indicated by the overall composition of the hydrocarbons and the fact that saturated hydrocarbons resemble the unaltered oils from the Lloydminster regions. The aromatic distribution shows variations 1, 3, 4 and 6 in contrast to the Jurassic and Pekisko oils at Medicine River. Since the conditions of burial are similar, these variations must be due to secondary migration of light compounds which, in this case, is accompanied by an enrichment of thiophenic compounds in the remaining oil. Although the GOR of this particular reservoir is not known, adjacent Mississippian reservoirs at Gilby have a GOR similar to those of the Jurassic and Pekisko oils at Medicine River.

The Mississippian oil from Glenevis (41), lying to the north of the oils discussed above, has been the least buried of the oils from this zone. It shows variations 1, 2, 3, and 4 in the mass family C_nH_{2n-14} , a relative increase in the proportion of dibenzothiophenes beyond C_{20} , and a lower maturation state than the Medicine River oils. Thus, within the limits of this geothermal gradient (30°C/1000 m), the Glenevis oil (41) has undergone the least maturation whilst that from Harmattan East (49) has suffered the most maturation. This conclusion is consistent with the paleotemperatures derived from coal rank studies (Appendices B, C). The estimated paleotemperatures of the Alexis, Cherhill and Glenevis reservoirs is 76°C while those of the Medicine River, Gilby and the Harmattan East pools are 111°C, 111°C and 127°C, respectively. The oils from Harmattan East (49), Medicine River (53 and 45) and, to a lesser degree, Gilby (42) have been affected by secondary migration; the lighter hydrocarbons have a tendency to escape from the reservoirs under the unconformity to reservoirs which are higher laterally and vertically, leaving in place the less mobile products.



FIGURE 6-17c. Distribution of aromatics in oils at various levels of diagenesis. Lloydminster region.



FIGURE 6-17d. Distribution of aromatics in oils at various levels of diagenesis. Athabasca region.



FIGURE 6-18. Gas/oil ratios of oil fields containing Group 2 oils as function of depth.

Zone of present geothermal gradient 40°C per 1000 m

This zone includes most of the oils in production and contains altered oils such as Lloydminster (76) or unaltered oils as at Leduc (38) and Pembina (63); it also includes heavy oil extracts which may be altered (Flat Lake, M59) or unaltered (Golden Spike, W62; Edgerton, M89; Skaro, W66). For the most northerly samples (M59, M89, W66 and 76), the maximum depth of burial is not known; but, for comparison purposes, it is estimated to be equivalent to that of the Glenevis (41) oil. The Pembina (63) sample, which has been buried the deepest of this group, has characteristics similar to the Medicine River (68) sample, which is more deeply buried but in a zone with a lower geothermal gradient. The oil from Leduc-Woodbend (38) and the impregnation from Golden Spike (W62) are both from the Wabamun Formation and are at the same maturation level. They show variations 1, 3 and 4 in the aromatic compounds and variation 6 in the thiophenic compounds. The Leduc-Woodbend (38) oil has a lower GOR (Fig. 6-17) [400 at a depth of 1345 m (4482 ft.)] than oils from reservoirs above the unconformity in the same field [525 to 550 at 1438-1363 m (4795-4545 ft.)]. Here again, the variations can be attributed to secondary migration, particularly since there is a strong similarity between this oil and the impregnation at Golden Spike.

Impregnations consisting of concentrations of heavy fractions could be the residue from migration or the residue left after evaporation of the light fractions after drilling, a product of alteration processes, or could be an original oil which has undergone little alteration. The samples of heavy oils from Edgerton (M89) and Skaro (Wi6) were extracted under the same conditions as the Golden Spike (W62) sample. Although they were less deeply buried, the Edgerton and Skaro samples can be distinguished from the Golden Spike sample only by their higher content of monoaromatics (mass families C_nH_{2n-8} , C_nH_{2n-12} and C_nH_{2n-14}) and particularly the compounds beyond C₂₅. The difference can be attributed to the lower degree of maturation of the former. The Edgerton and Skaro oils, as well as the Golden Spike sample, tend to contain a few light monoaromatic compounds (<C_{20}) in the mass family $\mathrm{C}_{n}\mathrm{H}_{2n-8}$ and even less in the families C_nH_{2n-12} and C_nH_{2n-14} ; this could be the result of secondary migration.

The heavy oil from the Lloydminster (76) pool is, in turn, compared with the Edgerton (M89) sample since the geothermal gradients and depths of burial are similar. The relative importance of the monoaromatics beyond C_{25} in the mass families C_nH_{2n-12} and C_nH_{2n-14} can be interpreted as due to a low degree of maturation, but the effect of concentration due to alteration must also be considered. The effects of alteration are manifested in the aromatic and thiophenic compounds by variations 1, 5, 7 and 8. These changes are more important than those attributed to secondary migration. A certain degree of degradation of the aromatic fraction accompanies the bacterial removal of normal alkanes in the saturate fraction (type b oil): it is attributable to water washing of the relatively soluble aromatic compounds and to inorganic oxidation of weakly soluble or insoluble compounds. The heavy oil extracted from the Flat Lake (M59) sample shows the same bacterial degradation of normal alkanes as at Lloydminster and variations 1 and 5 in the aromatics but without any modification of heavy monoaromatic compounds (C $_{25}$ +) or thiophenic compounds. In this case, the degradation of the aromatic fraction is less advanced than at Lloydminster since the thiophenic compounds are not affected.

Zone of unknown geothermal gradient

This part concerns the heavy oils extracted from samples located in the most northerly part of the studyarea, the region of the Athabasca (M24), Wabasca (LC21, base of Viking Fm.), Pelican (M37, Wabiscaw Fm.) and Marten Hills (M42, Wabiscaw Fm.). The present geothermal gradients are unknown but the burial depths are estimated to be equivalent to those of the preceding samples; this assumption is supported by the parallel importance of the heavy monoaromatics (C_{25} +) in the families C_nH_{2n-12} and C_nH_{2n-14} . These oils are considered in order of the known alteration (types a-c) of their saturated hydrocarbons.

The aromatics from the Marten Hills (M42, type b) extract show the same alteration effects observed in the Lloydminster oil which were attributed to water washing and inorganic oxidation. The Wabasca (LC21, types b, c, i.e. the beginning of the alteration of the isoprenoids) extract has the same characteristics as were found in the Flat Lake (M59) sample. Assuming that it has a history of secondary migration similar to that of the Marten Hills and Lloydminster samples, it is obvious that the oil is severely degraded.

The two remaining heavy oils, Pelican (M37) and GCOS Plant (M24), have the most degraded saturated hydrocarbons (type c). The same changes occur with regard to the aromatics as were observed in the Marten Hills and Lloydminster oils, but variation 5 is particularly significant. These samples represent the most advanced stage of alteration of the aromatics by water washing and inorganic oxidation.

Summary

Comparative analyses of the aromatic hydrocarbons of the Group 2 oils show that:

1. In the main oil field area, all oils located beneath the unconformity (Jurassic, Mississippian or Devonian) are altered as a result of secondary migration of the lightest components from the reservoir to vertically or laterally higher reservoirs. The geochemically defined maturation state of the oils in zones with comparable geothermal gradients correspond well to their respective depths of burial.

2. In the heavy oil zone, to the north of the main field area, all oils have undergone less maturation than the preceding oils. In addition to the effects of secondary migration, the aromatics from these oils have undergone degradation by water washing and inorganic oxidation which are associated with the biodegradation of the alkanes. These effects are at a maximum in the reservoirs closest to the Cretaceous unconformity even if the biodegradation of the normal alkanes has not reached the most advanced stage. In all probability, the unconformity corresponds to an aquifer and controls the distribution and alteration of hydrocarbons in its vicinity.

GENERAL CONCLUSIONS

Maturation studies based on coal rank have shown that, in Alberta, 88 per cent of the initial (in place) oil reserves have a degree of organic metamorphism comparable to a coal rank of 0.5 to 0.9 per cent Ro. The paleotemperatures in this interval range from 68° to 116°C. No oil was found above a paleotemperature of 143°C. While Paleozoic oil occurs in about the same quantities at the rank levels of V6, V7 and V8 (0, 60-0, 69% Ro to 0.80-0.89% Ro), the post-Mannville Cretaceous oil is found predominantly at V6 (0.60-0.69% Ro). Furthermore, heavy Mannville Cretaceous oil is found at V4, a level at which one normally does not expect oil to be present since it lies below the minimum generation temperature of 65°C. These results are consistent with the conclusion of the geochemical study which indicates that the heavy Cretaceous oils had migrated updip from the more central part of the basin.

As regards the natural gas pools, large quantities of biogenic methane occur at a coal rank of V4, or between temperatures of 52 and 68°C. Thermal gas ranges over a much larger rank interval; it is abundant particularly between V8 and V11 (0.80–0.89% Ro and 1.10-1.19% Ro) and substantial quantities also are present at V15 (1.50–1.59% Ro). The temperature range of the gas is from about 106° to 177°C.

Analysis of crude oils from the central part of the Western Canadian Sedimentary Basin has distinguished three groups of oils, one of which can be divided into two subgroups. The Group 2 oils can be separated from the other two groups on the basis of their gross composition, but the Group 1 oils can be distinguished from the Group 3 oils only after detailed analysis of the saturated hydrocarbons. Group 3 has been divided into two sub-groups only after detailed analysis of the aromatic hydrocarbons.

Group 1 includes the Colorado and post-Colorado oils. These oils have the lowest concentration of sulphur and aromatic hydrocarbons; they are richer in saturated hydrocarbons, especially the normal and branched alkanes, but have n-alkane distributions similar to Group 2. They can be separated from the Group 3 oils by the lower proportion of cyclo-alkanes with 1 and 2 rings; the quantities of benzothiophenes also are lower and are limited to the lower carbon number range.

Group 2 comprises the majority of the Lower Mannville, Jurassic, Mississippian and Wabamun oils with the exception of oils occurring in the Mannville to the northeast of the main pool at Leduc-Woodbend. These oils are the richest in sulphur and aromatics and the poorest in saturated hydrocarbons of all the oils examined; the n-alkane content and the ratio of isoprenoids to n-alkanes are also the lowest in the three groups. The very high sulphur values correspond to large amounts of benzothiophenes and dibenzothiophenes; the latter occur as relatively high molecular weight compounds $(C_{21}-C_{30})$.

Group 3 corresponds to oils from the Upper Devonian, excluding the Wabamun strata, and includes the Nisku, Leduc, Beaverhill Lake and Elk Point reservoirs. This group contains a higher proportion of thiophenic compounds than Group 1 with a smooth distribution over a wide range of carbon numbers. The Beaverhill Lake oils form Group 3b and are generally poorer in thiophenic compounds than those from the overlying Devonian corresponding to Group 3a.

The post-Colorado reservoirs (base of Belly River Gp.) and the Cardium and Viking reservoirs (Colorado Gp.) probably have been fed by source rocks from within the Colorado Group. The oils in the Lower Mannville reservoirs, which are effectively separated from those of the Colorado and post-Colorado by the nonmarine Upper Mannville sequence, have originated from the surrounding rocks in which the organic matter may be marine or nonmarine in origin. In the area to the northeast of Leduc-Woodbend, the Lower Mannville reservoirs have been fed mainly by rocks in the underlying Devonian (Calmar, Leduc Fms.). In contrast, the Jurassic and Mississippian reservoirs near the unconformity have taken their oils from the Lower Mannville sediments. The Beaverhill Lake, Cooking Lake, Duvernay and Ireton to Calmar Formations are considered to be the more favourable sediment sources for the Devonian reservoirs; and, of these, the Beaverhill Lake, Cooking Lake and Duvernay Formations constitute the most likely sources from a geochemical standpoint.

If the yield of the Devonian samples is considered as a function of maximum burial (Fig. 5-21), the principal zone of petroleum formation is seen to be situated between 1200 and 2700 m (4000-9000 ft.) for the Upper Devonian and almost to 3600 m (12 000 ft.) for the upper Middle Devonian (Beaverhill Lake). These depth ranges correspond to the depths of burial reached in the Upper Cretaceous and can be applied in the El Dorena-Redwater-Leduc region for the Upper Devonian and in the Swan Hills-Virginia Hills-Waskahigan for the Beaverhill Lake rocks (Fig. 5-13e). In the latter region, hydrocarbon genesis occurred in Devonian source sediments as early as the Carboniferous and proceeded through the Cretaceous whereas, in the Redwater-Leduc region, little hydrocarbon genesis occurred in Devonian rocks prior to the Cretaceous Period. In both cases, on the basis of the burial histories, the principal phase of genesis did not occur until the Cretaceous and probably the Late Cretaceous. In source rocks of Cretaceous age, oil genesis probably occurred approximately at the same time or a little later since this is probably the period of maximum burial of these rocks.

A major consequence of the timing of oil genesis (Late Cretaceous) was that a group of favourable traps was in place at the time of the generation phase. Thus, the trapping of oil and gas was a function of the degree of communication between the source rocks, the porous rocks and the reservoir traps. Another consequence is that the Cretaceous source rocks have undergone approximately the same degree of evolution as the Devonian source rocks, which may account for the similarities in the composition of the saturated hydrocarbons in the different oils.

The heavy Lower Cretaceous oils from the Lloydminster region are similar with respect to their aromatic content to the contemporaneous oils of the central part of the basin. The same can be said for all of the oils from the Wabasca, Cold Lake, Athabasca and Peace River areas. This statement applies to the more scattered localities between the main accumulations whether the reservoirs are above or below the unconformity. The aromatic characteristics of these oils are comparable to those of the least diagenetically altered oils (e.g. Glenevis) and are all the more marked since degradation favours the concentration of the heavy fractions which exhibit these diagenetic features. The effects of degradation include removal of n-alkanes and isoprenoids by biodegradation, loss of light hydrocarbons by secondary migration/ deasphalting, removal of the most soluble hydrocarbons by water washing, and inorganic oxidation of the most insoluble fractions, particularly the thiophenes. The degradation is particularly advanced adjacent to aquifers bearing relatively fresh water. Comparative analysis of oils of the Mannville type from the Foothills to the margin of the basin allows the effects of segregation/ migration to be determined, but the effect of primary migration on the composition of these oils is not definable.

At the margin of the basin, characteristics of rock extracts, whether they are Devonian or Mannville, indicate a low level of diagenesis for the organic material. The rock extracts contain n-paraffins, which supports considerably the idea that the heavy oils in contemporaneous reservoirs are biodegraded conventional oils and do not represent very immature oil. All the remaining geochemical characteristics of the heavy oils are comparable with the extracts of the Lower Mannville type encountered in the contemporaneous shales. As a first step, one can suppose that the heavy oil accumulations were formed in situ. However, the low level of diagenesis of the organic matter in the shales correlates with a low yield of hydrocarbons. Thus, the less deeply buried sediments at the margin of the basin could not have contributed, by themselves, the enormous accumulations of oil found at Athabasca. It is necessary to admit some contribution from source rocks located in the deeper parts of the basin.

It is difficult to delineate the roles of the various potential source rocks in supplying oil to the oil sands area, particularly the Paleozoic series under the unconformity. In fact, we have seen that communication across the unconformity exists in the region to the northeast of the main pool of Leduc-Woodbend since the oils at the base of the Mannville have affinities with those in the Paleozoic rocks under the unconformity. However, if the Paleozoic oils have contributed to the heavy oils at the margin of the basin, then distinctive geochemical characteristics of their saturate fraction will be masked by the dominant characteristics of the Group 2 oils; this means that the contribution of the Devonian oils to the heavy oil accumulations cannot be assessed readily. Geological considerations indicate that there is no obstacle to the migration of fluids from the deep parts of the basin to the basin margin. Such fluids could have moved readily through the detrital rocks at the base of the Mannville Group at the time of the Laramide Orogeny (Late Cretaceous to early Oligocene) when upward tilting to the northeast occurred in the easterly converging Paleozoic horizons.

Migration must have been facilitated also by the presence of methane of possible biogenic origin in the Mannville series at the margin of the basin. Its existence is known from fields which could have been exploited (e.g. Tweedie, Craigend) and it is possible that its former distribution was more widespread. The methane could have been a supplementary factor in the migration of the oil. It must have caused deasphalting of the oils resulting in a segregation of the heavy products from the more mobile compounds; these more mobile compounds then migrated. Thus, there is an association of heavy oils having geochemical characteristics diagnostic of a low level of diagenesis with more mobile products. The limit of migration is the margin of the basin at the Athabasca oil sands. It is likely that, at one time, the Clearwater and possibly subsequent formations extended across the shield area and may have formed a cap rock for oil accumulation. Under these conditions, the methane and light hydrocarbons may have formed a gas cap for the precursor oils of the "oil sands" as they accumulated; degradation processes were particularly active since the accumulations were relatively close to the surface and resulted in an increased gravity of the oils. The gas cap disappeared with the erosion of the cap rock but the oils, which were already degraded, did not escape from the reservoir because of their high viscosity. Clean white sands, exposed along the Clearwater River, occupy the updip pinchout of the tar sands and provide supporting evidence of a pre-existing gas cap which has since been breached (Gussow, 1955, p. 1628, 1629). The closure of the eroded zone would be assured by plugs of asphalt formed by oxidation of the surrounding oil as degradation continued to increase the gravity.

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APPENDICES

- A. Oils depth of burial of presumed source rocks at the end of the Cretaceous
- B. Record of crude oil pools in Alberta with assignment of level of organic metamorphism in terms of coal reflectance rank, and corresponding paleotemperatures
- C. Record of natural gas pools in Alberta with assignment of level of organic metamorphism in terms of coal reflectance rank, and corresponding paleotemperatures
- D. Location of oils and extent of analysis
- E. Location of extracts and extent of analysis
- F. Variations in composition of rock extracts

LE NO.	FIELD	LOCALITY OF	DEPTHS A	T END OF CRETACE	DUS TIME	
SAMP		BOREHOLE	GROUP 1	GROUP 2	GROUPS 3 AND (3a)	
		то	P OF MANNVILLE			
100	Lanaway	7-31-36-3-W5	5380			
93	Ferrier	10-4-41-8-W5	5880			
95	Pembina	16-12-47-6-W5	4660			
101	Ricinus	10-29-37-5-W5	5740			
99	Sylvan Lake	13-13-37-4-W5	5240			
97	Willesden Green	1-33-39-5-W5	5280 + 120 = 5400			
91	Gilby	14-15-41-2-W5	4700			
98	Ferrier	4-23-40-7-W5	5680			
90	Legal	14-18-56-25-W4	3820			
92	Willesden Green	1-33-39-5-W5	5400			
96	Bonnie Glen	16-30-46-27-W4	4640			
		т	OP OF CARDIUM			
103	Gilby	14-15-41-2-W5	4700 - 1120 = 3580			
102	Pembina	8-1-48-4-W5	3600			
105	Ferrier	4-10-42-8-W5	5600 - 1120 = 4480			
104	Willesden Green	6-35-43-7-W5	5120 - 1200 = 3920			
		BASE OF CRET	TACEOUS		TOP OF IRETON	
63	Pembina	10-25-46-2-W5		5100		
68	Medicine River	6-10-38-5-W5		6280		
69	Medicine	6-10-38-5-W5		6280		
71	Willesden Green	1-33-39-5-W5		6100		
69	Medicine River	10-10-39-2-W5		5600		
74	Lanaway	1-28-36-3-W5		6040		
72	Sylvan Lake	13-13-37-4-W5		5240 + 640 = 5880		
70	Medicine River	6-10-38-5-W5		6280		
38	Leduc Woodbend	4-31-49-25-W5		5000	5600 to 5680	
57	Campbell Namao	5-7-54-23-W4		4560	5080 5760*	
56	Morinville	7-10-55-24-W5		4760	5240 5740*	
55	Kaybob	2-14-64-18-W5		6940 + 160 = 7100		
66	Medicine River	6-28-39-3-W5		5720		
53		4-15-39-3-W5		5820		
65	Gilby	14-21-40-3-W5		5820		
52		14-19-40-3-W5		5660	6000	
61	Gien Park	13-35-48-27-W4		5100	6000 5600 6130*	
60	N Leduc Woodbend	4-31-49-25-W4		5000	2000 0150	
54	Sylvan Lake	10-20-38-3-W5		5960		
62	Niton	4-19-54-12-W5		5350		
64	Samson	9-9-44-24-W4		4000	5680	
58	Acheson East	4-32-52-25-W4		4900	5000	

SAMPLE N	FIELD	LOCALITY OF REFERENCE BOREHOLE	DEPTHS A GROUP 1	GROUPS 3 AND (3a)					
		BASE OF CRET	ACEOUS	TOP OF IRETON					
54	Armisie	7-4-52-25-W4		4960	5740				
67	Medicine River	4-28-39-3-W5		5920					
75	Three Hills	9-9-31-23-W4		4720					
		тс	OP OF DEVONIAN						
43	Sylvan Lake	2-9-38-3-W5		5740	6440				
42	Gilby	7-29-40-2-W5		5600	6020				
45	Medicine River	16-32-39-3-W5		5600	6420				
44	Sylvan Lake	10-36-37-4-W5		5800	6540				
40	Alexis	14-31-55-4-W5		4420	4920				
41	Glenevis	3-35-55-4-W5		4340	4840				
39	Cherhill	13-13-56-5-W5		4370	4870				
58	Acheson East	4-32-52-25-W4		4900	5680				
59	Armisie	7-4-52-25-W4		4960	5740				
47	Westward HO	5-8-33-4-W5		6620	7700				
51	Rowley	4-16-32-20-W4		4020	4450				
46	Sundre	14-14-34-5-W5		7140	8140				
49	Harmattan East	7-18-32-3-W5		6660					
50	Twining	6-3-32-24-W4		4660	5260				
48	Harmattan Elkton	1-31-32-4-W5		6660	7800				
			TOP OF IRETON						
33	Excelsior	7-10-55-24-W4			(5240)				
35	Leduc Woodbend	7-22-50-26-W4			(5600)				
34	Golden Spike	12-24-51-27-W4			(5740)				
37	Wizard Lake	10-9-48-27-W4			(5820)				
36	Leduc Woodbend	12-13-49-27-W4			(5800)				
		В	ASE OF IRETON						
31	Hemesley Dischou	3-29-43-1-W5			(7100 + 300)				
32	Homegien Rimbey	3-29-43-1-W5			(7100 + 300)				
23	Redwater	13-22-57-23-W4			(5480)				
26	Leduc Woodbend	4-31-49-25-W4			(6120 + 200)				
29	Bonnie Glen	16-30-46-27-W4			(6360)				
28	Wizard Lake	14-8-48-26-W4			(6500)				
30	Westerose	12-34-45-28-W4			(6320 + 400)				
25	Golden Spike	12-24-51-27-W4			(6220 + 0)				
24	Morinville	7-10-55-24-W4			(5760)				
27	Glen Park	14-35-48-27-W4			(6570 + 0)				
		BASE C	F BEAVERHILL LAKE						
12653	Skaro	4-27-57-20-W4 and 13-22-57-23-W4			(5220 + 1080 = 6300)				

base Ireton

APPENDIX A. Oils - depth of burial of presumed source rocks at the end of the Cretaceous.

									_								
INDEX NO. ON FIG. 3-9	NAME OF OIL POOL	INITIAL OIL IN PLACE IN 1000 STOCK TANK BARRELS	GEOLOGIC AGE 1	AVERAGE WELL DEPTH IN FEET	% MOISTURE OF NEAR-SURFACE COALS	COAL RANK IN V-TYPES OF REFLECTANCE	PALEOTEMPERATURE	DIAGRAM AT 35 M.Y.	INDEX NO. ON FIG. 3-9	NAME OF OIL POOL	INITIAL OIL IN PLACE IN 1000 STOCK TANK BARRELS	GEOLOGIC AGE 1	AVERAGE WELL DEPTH IN FEET	% MOISTURE OF NEAR-SURFACE COALS	COAL RANK IN V-TYPES OF REFLECTANCE	BALEOTEMPERATURE	DIAGRAM AT 35 M.Y.
1	Boundary I k	85.443	т	4 366	15	VG	°С 89	°⊢ 192	24	Redwater	1 300 000	D	3 208	29	V5	76	168
2	Red Farth	3,482		4,769	33	V5	76	168	25	Peco	10.000	T	6,953	12	V8	111	232
3	Loon	26,100	D	4.616	32	V5	76	168	26	Brazeau R	782	К	7,780	12	٧9	119	247
Ť	Utikuma Lk	62.300	D	5,663	32	V6	89	192			458,425	T	3,209	15-20	V5	76	168
4	Nipisi	739,000	D	5,604	32	V6	89	192	27	Pembina	7,440,000	к	5,081	15-20	V6	89	192
	Sturgeon Lk	44,400	Ð	8,853	21	V9	111	232		Golden Spike	327,680	D	5,800	23	V6	89	192
5		37,560	τ	5,000	22	V6	89	192		Glen Park	29,300	D	6,305	22	٧7	101	214
	Sturgeon Lk S'th	298,160	D	8,500	22	V8	111	232	28	Wizard Lk	385,000	D	6,460	22	٧7	101	214
	Gilwood	2,780	D	8,111	24	٧8	101	214			22,278	К	4,422	23	V6	89	192
6	Snipe Lk	198,000	D	8,534	24	V8	111	232		Leduc-Woodbend	522,874	D	5,315	23	V6	89	192
7	Simonette	105,000	D	11,593	17	V12	134	274			35,160	К	4,025	25	V5	76	168
8	Ante Ck	47,390	D	11,200	20	V12	134	274		Acheson	153,360	D	5,078	25	V6	89	192
9	Kaybob S'th	210,000	K	6,875	20	٧7	101	214		St- Albert - Big Lk	35,340	D	4,802	25	V6	89	192
10	Kaybob	301,310	D	9,780	22	V10	119	247	29	Morinville	1,250	К	3,584	27	٧5	76	168
11	Goose R	292,360	D	9,185	23	٧9	111	232		O amakali Namaa	38,600	К	3,700	27	V5	76	168
12	Meekwap	56,000	D	7,700	25	٧7	101	214		Campbell-Namao	20,522	D	5,276	27	V6	89	192
10	Virginia Hills	450,000	D	9,286	26	٧9	111	232		Durais Olan	25,000	K	3,951	21	٧5	89	192
13	Freeman	40,400	D	9,184	27	٧9	111	232	30	Bounie Gien	643,000	D	7,105	21	٧7	101	214
	Judy Ck	1,065,000	D	8,700	27	V8	101	214		Westerose	159,000	D	7,233	20	V8	101	214
14	Judy Ck S'th	19,550	D	8,931	26	V8	111	232	31	Joarcam	221,000	К	3,248	26	٧5	76	168
	Carson Ck N'th	357,600	D	3,769	25	٧5	76	168			11,570	T	5,621	12	٧7	101	214
14A	Windfall	102,000	D	8,620	22	V8	111	232	32	Ferrier	299,130	K	6,868	12	٧8	111	232
1.5	Swan Hills	2,479,000	Ð	8,000	30	٧7	101	214			20,000	К	8,199	12	V9	119	247
15	Swan Hills S'th	898,000	D	8,345	28	٧8	101	214			12,000	T	5,147	13	٧7	101	214
16	Mitsue	811,000	D	5,651	33	V6	89	192	33	Willesden Green	695,000	К	6,225	13	٧7	111	232
17	Edson	22,200	К	6,049	16	V7	101	214			12,610	К	6,995	13	٧8	111	232
18	Niton	56,442	К	6,493	20	٧7	101	214			1,800	Т	4,209	16	V6	89	192
10	Carrot Ck	12,550	К	5,450	17	¥7	89	192			49,557	К	5,856	16	٧7	101	214
19	Cyn - Pem	82,160	ĸ	5,395	20	V6	89	192	34	Gilby	37,000	K	7,045	16	٧8	111	232
20	Bigoray	16,300	К	5,891	20	٧7	101	214			91,600	J	7,051	16	٧8	111	232
21	Paddle R	38,000	М	5,146	23	V6	89	192			4,790	м	7,091	16	V8	111	232
	Cherhill	60,000	М	4,335	25	V5	76	168	35	Homeglen-Rimbey	93,500	D	7,925	17	V8	111	232
22	Alexis	47,700	М	4,495	25	V5	76	168		Wood R	4,000	D	5,558	22	V6	89	192
	Glenevis	24,200	М	4,350	25	V5	76	168	36	Malmo	7,330	К	4,713	23	V6	89	192
22	Fairydell-Bon Accord	28,120	D	3,760	29	V5	76	168			25,730	D	5,200	23	V6	89	192
23	Excelsior	33,800	D	3,879	29	V5	76	168		New Norway	14,000	D	4,800	24	V6	89	192
																	GSC

1 Re. Geologic age: T - Tertiary; K - Cretaceous; J - Jurassic; K - Triassic; M - Mississippian; D - Devonian

APPENDIX B. Record of crude oil pools in Alberta with assignment of level of organic metamorphism in terms of coal reflectance rank and corresponding paleotemperature.

INDEX NO. ON FIG. 3-9	NAME OF OIL POOL	INITIAL OIL IN PLACE IN 1000 STOCK TANK BARRELS	GEOLOGIC AGE ¹	AVERAGE WELL DEPTH IN FEET	% MOISTURE OF NEAR-SURFACE COALS	COAL RANK IN V-TYPES OF REFLECTANCE	PALEOTEMPERATURE	DIAGRAM AT 35 M.Y.	NDEX NO. ON FIG. 3–9	NAME OF OIL POOL	INITIAL OIL IN PLACE IN 1000 STOCK TANK BARRELS	GEOLOGIC AGE ¹	AVERAGE WELL DEPTH IN FEET	% MOISTURE OF NEAR-SURFACE COALS	OAL RANK IN V-TYPES OF REFLECTANCE	PALEOTEMPERATURE	FROM KARWEIL'S DIAGRAM AT 35 M.Y.
						<u> </u>	°C	°F							0	°C	°F
37	Duhamel	26,400	D	4,650	25	V5	76	168	55	W. Drumheller	53,500	D	5,600	20	V6	89	192
38	Ricinus	15,760	K	6,000	7	V8	119	247		Drumheller	5,500	K	4,280	20	V6	89	192
		38,451	K	8,850	7	V11	134	274		Wayne-Rosedale	28,010	D	5,300	20	V6	89	192
	Sundre	100,400	M	9,052	11	V10	127	261	56		30,579	К	4,450	19	V6	89	192
39	Westward Ho	35,000	K	8,854	11	V10	127	261		Hussar	73,357	К	4,650	18	V6	89	192
	Harmattan-Elkton	188,000	M	9,128	11	V10	127	261	57	Provost	408,400	K	2,946	30	V4	60	141
	Harmattan E.	206,000	M	8,625	12	V9	127	261	58	Bellshill Lk	258,000	К	3,017	29	V4	60	141
40	Garrington	189,000	K	6,634	12	V8	111	232		Thompson Lk	21,400	K	3,100	30	V4	60	141
		12,260	ĸ	5,900	13	V7	101	214	59	Hughenden	20,530	K	2,700	32	V4	60	141
	Sylvan Lk	45,760	J	7,200	13	V8	111	232	60	Wainwright	169,000	К	2,098	33(?)	٧4	60	141
41		123,572	м	7,500	13	V8	111	232	61	Wildmere	28,200	К	1,969	34(?)	٧4	60	141
	Medicine R	276,941	К	7,200	13	V8	111	232	62	Lloydminster	450,000	К	1,955	35(?)	٧4	60	141
		86,370	м	7,000	13	V8	111	232	63	Chauvin S'th	66,100	К	2,143	34(?)	V4	60	141
12	loffro	80,100	К	4,979	17	V6	89	192	03	Chauvin	38,400	К	2,067	34(?)	V4	60	141
42	Joine	166,000	D	7,003	17	V8	101	214	64	Hayter	55,810	К	2,735	34(?)	V4	60	141
13	Clive	131,279	D	6,227	19	٧7	101	214	65	Turner Valley		Not inc	luded; stru	cturally o	listurbed		
45	Alix	10,200	D	5,984	20	٧7	101	214	66	Wintering Hills	19,270	К	4,200	22	٧5	89	192
44	Nevis	17,520	D	5,800	21	V6	89	192	67	Cessford	133,229	к	3,051	26	٧5	76	168
45	Ewing Lk	9,210	D	5,380	20	V6	89	192	67	Matziwin	6,860	М	3,330	25	V5	76	168
16	Buffalo Lk	12,380	D	5,529	22	٧6	89	192	68	Little Bow	28,187	К	3,700	16	V6	89	192
40	Erskine	40,200	D	5,387	22	٧6	89	192	69	Lathom	21,000	К	3,837	18	V6	89	192
	Stettler	96,700	D	5,300	22	٧6	89	192	70	Countess	182,481	К	3,500	19	V5	76	168
47	Stettler S'th	12,488	D	5,300	22	V6	89	192	71	Bantry	202,200	ĸ	3,250	22	V5	76	168
4/	Fenn - Big Valley	379,400	D	5,289	22	V6	89	192	72	Princess	16,750	К	3,335	24	٧5	76	168
	Febb W.	16,000	Ð	5,577	21	V6	89	192	73	Jenner	74,640	К	3,122	26	V5	76	168
48	Wimborne	94,700	D	7,487	16	٧8	111	232	74	Hays	30,460	К	3,128	19	٧5	76	168
49	Innisfail	124,000	D	8,582	14	٧9	119	247	75	Alderson	35,359	K	3,300	23	٧5	76	168
50	Twining	121,000	м	5,406	17	V7	101	214	76	Grand Forks	115,000	К	2,984	19	V5	76	168
		162,000	к	6,673	12	V8	111	232		Taber	57,320	к	3,200	15	٧5	89	192
51	Crossfield	14,200	м	6,914	12	V8	111	232		Taber N'th	14,560	К	3,200	15	V5	89	192
52	Lone Pine Ck	7,656	D	8,011	15	V8	111	232	77	Taber S'th	100,070	K	3,200	15	V5	89	192
	Swalwell	10.900	D	6,452	17	V7	101	214		Horsefly Lk	29.400	K	3,155	15	V5	89	192
53	Three Hills	10,900	к	5,127	18	V6	89	192	78	Manyberries	17.120	К	3.620	28	V5	76	168
54	Rowley	19,700	M	4.480	21	V6	89	192		,			.,				GSC
- T	,			.,													

1 Re. Geologic age: T - Tertiary; K - Cretaceous; J - Jurassic; K - Triassic; M - Mississippian; D - Devonian

APPENDIX B. Continued.

INDEX NO. ON FIG. 3-10	NAME OF GAS POOL	INITIAL GAS IN PLACE IN BILLION CUBIC FEET	GEOLOGIC AGE ¹	AVERAGE WELL DEPTH IN FEET	% MOISTURE OF NEAR-SURFACE COALS	COAL RANK IN V-TYPES OF REFLECTANCE	8 PALEOTEMPERATURE	FROM KARWEIL'S	INDEX NO. ON FIG. 3-10	NAME OF GAS POOL	INITIAL GAS IN PLACE IN BILLION CUBIC FEET	GEOLOGIC AGE ¹	AVERAGE WELL DEPTH IN FEET	% MOISTURE OF NEAR-SURFACE COALS	COAL RANK IN V-TYPES OF REFLECTANCE	PALEOTEMPERATURE	FROM KARWEIL'S DIAGRAM AT 35 M.Y.
1	Dunvegan	990	M	4 800	20	VG	80	102	27	Brazogu P	1 420	M	0 800	12	V11	124	-F
2	Marten Hills	1 1 1 0	K	2 300	38(2)	VA	60	141	28	Lovett R	1,430	M	11 870	10	V12	1/6	2/4
3	Kaybob	370	ĸ	4,800	22	V6	89	192	29	Stolberg	86	M	12 730	5	¥13	140	235
-	Kaybob S'th	4.340	D	10.560	20	V11	127	261	30	Minnehich - Buck I	811	M	7 100	16	V8	111	232
4	Fox Ck	97	K	5.620	21	VG	89	192	31	Westerose S'th	1.850	D	7,640	18	V8	111	232
		52	к	6,480	18	V7	101	214			94	ĸ	6,830	16	V7	111	232
5	Bigstone	390	D	11,080	18	V11	134	274	32	Gilby	551	J	7,000	16	V8	111	232
6	Berland R	440	D	12,290	16	V13	141	285			497	м	7,250	16	V8	111	232
	Pine Ck	1,110	D	11,000	17	V11	134	274	33	Strachan	2,505	Ð	13,490	8	V16	162	324
7	Pine Ck - N.W.	350	D	10,670	18	V11	134	274	. 34	Ricinus W	2,140	Ð	14,710	6	V19(?)	175	346
	Marlboro	170	D	12,150	16	V13	141	285		Wildhorse Ck	160	M	7,380	4	V11	141	285
8	Obed	257	D	13,150	14	V14	152	305	35	Burnt Timber	440	м	10,590	4	V15	162	324
9	Virginia Hills	63	К	6,140	25	V6	89	192		Hunter Valley	78	м	8,690	4	V13	146	295
10	Judy Ck	85	К	4,610	26	٧5	76	168	36	Benjamin	208	м	11,000	5	V15	157	315
	Carson Ck	320	D	8,600	24	٧8	111	232	37	Harmattan-Elkton	430	D	11,000	11	V12	141	285
11	Whitecourt	69	1	5,070	25	V6	89	192		Olds	110	D	8,680	13	V9	119	247
	Millecourt	59	М	5,220	25	V6	89	192		Lone Pine Ck	490	D	7,920	14	V9	119	247
12	Big Bend	73	К	2,610	34	٧4	60	141	38	Orana field C	185	м	7,590	13	V8	119	247
13	Tweedie	63	К	1,440	38(?)	٧4	60	141	1	Grossfield E	1,280	D	8,780	13	V10	119	247
14	Craigend	92	К	1,830	36(?)	V4	60	141	39	Huxley	55	K	4,850	18	٧6	89	192
15	Edean	210	K	8,420	14	٧9	119	247	10	Neurie	68	К	4,570	21	V6	89	192
10	Luson	2,395	М	9,380	14	V10	127	261	40	INGALS	1,040	D	5,580	21	V6	89	192
16	Paddle R	280	J	5,020	23	V6	89	192	41	Provost	53*	К	2,950	28-35	V4	60	141
17	Westlock	437	К	2,600	30	٧4	60	141	42	Jumping Pound W	1,861	М	11,100	5	V15	157	315
1/	Fairy Dale - Bon Accord	128	К	2,680	28	٧4	60	141		Jumping Pound	840	М	9,940	6	V13	146	295
.18	Alexander	140	К	3,830	27	٧5	76	168	43	Sarcee	190	м	9,750	7	V12	141	285
19	Morinville	88	К	3,600	27	V5	76	168		Wildcat Hills	1,050	м	9,880	6	V13	146	295
20	St. Albert - Big Lake	130	К	3,800	25	V5	76	168	44	Moose	86	М	7,570	4	V12	141	285
21	Ft. Saskatchewan	617	ĸ	2 590	27	VA	60	141	45	Whiskey	160	М	11,820	5	V16	162	324
22	Beaverhill Lk	017	n	2,000	2/	74	00	141	45	Quirk Ck	460	М	6,340	5	V10	127	261
23	Plain	67	К	2,220	34	٧4	60	141			98	K	7,330	12	V8	119	247
24	Viking - Kinsella	1,080	К	2,080	33	V4	60	141	46	Crossfield	2,180	м	8,220	12	V9	119	247
25	Bittern Lk	87	ĸ	4,010	25	٧5	76	168			1,600	D	8,500	12	V9	119	247
26	Pembina	264	К	5,970	19	٧7	101	214	* Only	free gas is included, and	gas in solutio	n and i	n associati	on is omi	tted		GSC

1. Re. Geologic age: T - Tertiary; K - Cretaceous; J - Jurassic; M - Mississippian; D - Devonian

APPENDIX C. Record of natural gas pools in Alberta with assignment of level of organic metamorphism in terms of coal reflectance rank and corresponding paleotemperature.

		-	_		-			
NDEX NO. ON FIG. 3-10	NAME OF GAS POOL	INITIAL GAS IN PLACE N BILLION CUBIC FEET	GEOLOGIC AGE ¹	AVERAGE WELL DEPTH IN FEET	% MOISTURE OF NEAR-SURFACE COALS	COAL RANK IN V-TYPES OF REFLECTANCE	PALEOTEMPERATURE	DIAGRAM AT 35 M.Y.
=		_					°C	۴
47	Okotoks	500	D	8,690	11	V10	12/	261
48	Ghost Pine	272	ĸ	4,700	20	V6	89	192
49	Drumheller	61	К	4,380	21	V6	89	192
	Wavne-Rosedale	220	К	3,890	19	V5	89	192
50		205	ĸ	4,370	19	V6	89	192
	Carbon	140	К	4,740	17	V6	89	192
51	Hussar	128	K	4,000	18	V6	89	192
		358	К	4,600	18	V6	89	192
52	Countess	270	К	2,860	20	V5	76	168
52	obuntess	61	K	4,280	20	V6	89	192
53	Connorsville	64	K	3,650	22	V5	76	168
r 4	Oracland	275	K	2,970	25	٧4	76	168
54	Gesstora	290	К	3,400	25	٧5	76	168
	Deinesse	67	К	2,190	24	٧4	60	141
55	Princess	66	К	3,190	24	٧5	76	168
		72	Т	1,640	28	٧4	60	141
56	Atlee-Buttalo	73	К	2,600	28	٧4	60	141
57	Bindloss	400	К	2,250	31	٧4	60	141
58	Sedalia	110	К	2,650	33	٧4	60	141
59	Oyen	62	К	2,520	32	٧4	60	141
60	Savanna Ck	230	М	8,480	5	V12	141	285
	Bantry	130	T	960	21	٧4	60	141
61		670	τ	960	20-25	٧4	60	141
	Alderson	500	К	1,970	20-25	٧4	60	141
		570	Т	1,330	25-32	٧4	60	141
62	Medicine Hat	2,550	T	1,600	25-32	٧4	60	141
		975	М	10,200	4	V15	76	168
63	Waterton	3,062	D	10,250	4	V15	157	315
	Pincher Creek	1,840	М	12,500	5	V17	166	331
64	Lookout Butte	420	М	11,910	4	V17	166	331
65	Etzikom	68	К	2,230	23	٧4	60	141
		254	ĸ	2,100	20-25	٧4	60	141
66	Pendant d'Oreille	100	ĸ	2,700	20-25	V5	76	168
1 80	Geologic age: T-T	ortiary K.	Creta		, luraee	ic.		GSC

1 Re. Geologic age: T-Tertiary; K-Cretaceous; J-Jurassic; M-Mississippian; D-Devonian

APPENDIX C. Continued.

	CE		EC	7	ET	C+ondord	Application	Allalysis	Detailed	Analysis
SAMPLE NC	IFP REFEREN	MELL/FIELC	GEOGRAPHI CO-ORDINAT	FORMATIO	DEPTH IN FE	Composition	Cotton too	Salurates	Acmotice	AIUIIIduce
						Gross	CGC	MS	CGC	MS
Α.			MIDDLE D	EVONIAN						
1	14630		10-6-88-8W5	Slave Point A	4216	-	-	-	-	
2	14631	Red Earth	10-12-87-8W5	Granite Wash B	4719	-	-	-	-	
3	14636	Lubicon	2-9-87-10W5	Granite Wash A	4750	-	-	-	-	
4	14639	Golden	7-7-87-14W5		5247	-	-	-	-	
5	14637		10-17-85-9W5	Slave Point A	4616	-	-	-	-	
6	14638	Loon	12-10-85-9W5	Granite Wash A	5008	-	-	-	-	
7	14629	1021 Laba	4-26-81-9W5	Keg River	5663	-	-	-	Ι	
8	14630	Utikama Lake	11-11-81-10W5	Gilwood B	5685	-	-	-	Ι	
9	14633		2-29-81-8W5	Keg River A	5749	-	-	-	I	
10	14634	Nipisi	4-13-79-8W5	Gilwood A	5604	-	-	-	-	
11	14635		6-25-77-8W5	Gilwood C	5889	-	-	-	-	
12	13435	Mitsue	10-16-12-4W5	Gilwood A	5651	-	-	-	-	
в.		BEAVER	HILL LAKE -	UPPER DEVONIA	N					
13	12683	Snipe Lake	4-13-70-18W5	Beaverhill Lake	8731	-	-	_	_	-
14	12684	Swan Hills South	4-12-66-11W5	Beaverhill Lake A	9119	-	-	-	-	
15	12677	Swan Hills Unit 1	10-29-66-10W5	Beaverhill Lake B	8911	-	-	-	_	-
16	12682	Judy Creek	4-5-64-10W5	Beaverhill Lake A	8450	-	-	-		
17	12692	Virginia Hills	12-16-65-13W5	Beaverhill Lake	9225	-	-	-		
18	12681	Carson Creek	6-12-62-12W5	Beaverhill Lake B	8728	-	-	-		
19	12679	Goose River	4-4-67-18W5	Beaverhill Lake	9194	-	-	-		
20	12695	Ante Creek	10-26-65-24W5		11,302	-	-	-		
21	12676	Kaybob	4-21-64-19W5	Beaverniii Lake A	9780	-	-	-		-
C.		WOODB	END GROUP	- UPPER DEVONIA	AN					
22	12653	Skaro	9-29-57-19W4	Cooking Lake (D3)	3662	-	-	-		_
23	12667	Redwater	10-29-57-21W4	Leduc (D3)	3208	-	-	-	-	-
24	12699	Morinville	1-14-54-26W4	Leduc (D3-B)	5094	-	-	-	-	-
25	12696	Golden Spike	9-22-51-27W4		5770	-	-	-		
26	12675	Leduc Woodbend	16-15-50-26W4	Loduo (Da)	5321	-	-	-	-	-
27	13164	Glen Park	14-35-48-27W4	Leauc (D3)	6300	-	-	-	-	
28	12690	Wizard Lake	2-16-43-27W4		6073	-	-	-		
29	12689	Bonnie Glenn	14-6-47-27W4	Leduc'(D3A)	7213	-	-	-		
30	12693	Westerose	12-34-45-28W4		7280	-	-	-		
31	12651	Homeglan Pimbou	1-1-43-2W5	Leduc (D3)	7908	-	-	-		
32	12652	nomegien knindey	9-10-42-2W5		7843	-	-	-		-
D.		WINTERB	URN GROUP	S-UPPER DEVON	IIAN					
33	12654	Excelsior	16-3-56-24W4		3822	-	-	-		
34	12687	Golden Spike	1-27-51-27W4	Nisku (D2)	5073	-	-	-		
35	12680	t a des Mile Sales a f	7-22-50-26W4		5019	-	-	-	-	-
36	13166	reanc wooapeug	12-18-49-27W4	Nisku (D2C)	5380	-	-	-		
37	12697	Wizard Lake	10-9-28-27W4	Nisku (D2)	5846	-	-	-		
E.			WABA	MUN						
38	12678	Leduc Woodbend	6-22-50-26W4	Wabmun (D1)	4475	-	-	-		

APPENDIX D. Location of oils and extent of analysis.

	ш						nalysis	etailed	naiysis		ш				F	0.000	nalysis	etailed
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F.			MISSISS	SIPPIAN						н		MANN	VILLE-LOW	FR CRETACEOUS				
	Tranca	a	10.10.00.000	í	42.25				-									
39	13390	Chernin	13-13-00-0900		4335	F			-				AREA	A 2				
40	13388	Alexis	14-31-55-4₩5	Banti	4495	-	_	_	_	76	14618	Lloydminster	16-3-50-1W4	Sparky S	1952	-		
41	13389	Glenevis	3-35-55-4W5		4350	-			_	77	14628	Wildmere	12-24-47-5W4	Lloydminster	2100	_		
42	13162	Gilby	7-29-40-2W5	Rundle K = Pekisko	6776	-			-	78	14623	Auburndale	9-15-47-6W4	Wainwright A	2070	-		- - -
43	13159	Svlvan Lake	2-9-37-3W5	Pekisko B	7256	-			_	79	14624	Bayter Lake	1-5-47-5W4	3	2190	_		
. 44	13169		10-36-37-4W5	Elkton C	7423	-				90	14614	Dunter Cuilo	15.22.45.6WA	Wainwright	2008	_		
45	13167	Medicine River	16-32-39-3W5	Pekisko B	7093	-			-	00	14014	Wainwright	15-22-45-0W4	L la valancia a tan A	2030			
46	13438	Sundre	14-14-34-5W5	Rundle B Elkton	8909	-	- -	- -		81	14615		15-23-45-6444	Lioyaminster A	2147	F		
47	13434	Westward Ho	5-8-33-4W5	Rundle A Elkton	8941	-				82	14626	Chauvin	11-23-43-1W4	Upper Sparky	2020	-		
48	13442	Harmattan Elkton	1-31-32-4W5	Rundle C Elkton	9079	-				83	14622	Chauvin South	4-26-42-2W4	Lloydminster C	2159	-		
49	13440	Harmattan Fast	7-18-32-3W5	Rundle Elkton	8484				_	84	14625		14-31-42-2W4	Sparky G	2035	-		
50	13//1	Twining	6.3.32.24WA	Rundle A = Pekisko	5406	_			-	85	14619	Hayter	14-16-41-1W4	Sparky A	2598	-		
50	10441	Davidavi	4 16 22 2014	Dehieko A	1400		_			86	14620	David	2-11-41-3W4	Lloydminster	2552	-		
- 51	13430	Rowley	4-10-32-20114	PERISKOA	4400				-	87	14616	Bellshill Lake	15-28-41-12W4		2970	-		
G.			JURA	SSIC						88	14617	Thompson Lake	9-32-40-11W4	Blairmore (Lower)	3100	-		
52	13161	Gilby	14-19-40-3₩5	Jurassic B	7077	-				89	14621	Choice	3-27-40-10₩4		2346	-		
53	13158	Medicine River	4-15-39-3W5	luna a la D	7006	-			-			LOWER C	OLORADO - I	OWER CRETACEC	us			
54	13168	Sylvan Lake	10-20-37-3W5	Jurassic D	7301	1				<u> </u>								
н		MANN		FR CRETACEOUS									ARE	A 1				
<u> </u>				En onemoro					-	90	12686	Legal	15-16-57-25W4	Viking	2798	-		- -
			ARE	A 1						91	12668	Gilby	4-34-41-4W5	Viking B	6362	-		-
55	12698	Kaybob	12-28-63-18W5	Cadomin A	5960	_			-	92	12691	Willesden Green	12-6-40-5W5		7010	-		-
56	12688	Morinville	6-20-55-24W4	Lower Mannville	3560	-			-	93	12656	Ferrier	6-28-39-8W5	Viking A	8375	-		- -
57	12685	Campbell Namao	4-25-54-25W4	Blairmore	3649								405				I I	
58	13393	Acheson East	4-32-52-25W4	Blairmore B	3996	-		_					AREA	4 2		-		
59	13394	Armisie	7-04-52-25W4		4062	_		_	-	94	14613	Joarcam	11-03-49-21W4	Viking	3248	-		
60	13165	N Leduc Woodbend	1-28-51-26W4	Blairmore	4281	-		_ _ .	_	J.		UPPER C	OLORADO - I	JPPER CRETACEC	US			
61	13163	Glen Park	13-35-48-27W4	Glauconitic B	4681	-			-	95	12658	Pembina	12-29-48-8W5		5134	_		
62	12201	Niton	A 10 54 12W5	Rapal Quartz R	6493	_		_	-	06	12000	Pennia Clan	4 9 56 27₩4	Cardium	2025	_		
02	10000	D 1	4-13-54-12W5	Dasai Quartz D	5000		_		_	90	12034	Willia day Oray	10.15.40 EWE	Openditions A	5071			++
03	12000	Pemoina	6-32-46-4445	Enersite	1000	H			-	97	12004	willesden Green	10-10-40-5005	Cardiulli A	0371	F		
64	13392	Samson	9-9-44-24W4	Blairmore A	4808	-			-	98	12672	Ferrier	10-13-40-8W5	Cardium D	6/3/	-		
65	13160	Gilby	14-21-40-3W5	Mannville B	/0/6	-			_	99	12663	Sylvan Lake	4-30-37-3W5		5754	-		-
66	13157		6-28-39-3W5	Basal Quartz P	7064	-			_	100	12650	Lanaway	10-19-36-3W5	Cardium A	5922	-		
67	13437		4-28-39-3W5	Basal Quartz B	7140	-			_	101	12661	Ricinus	12-18-36-8W5		9061	-		-
68	12662	Medicine River	4-28-38-4W5	Ostracod G	7484	-			_	ĸ.		POST-CC	LORADO - U	PPER CRETACEOL	JS			
69	12269		14-10-39-3W5	Ostracod A	6842	-		-		100	10050	Pombine	14 6 40 200	Bolly Pivo-	2000			
70	12674		4-4-39-4W5		7371	-		-		102	12659	Peniuma	10-20-41-495	belly hiver	3200			
71	12666	Willesden Green	6-29-39-5W5	Giauconitic A	7514	-			-	103	12656	GIIDY	10-32-41-4₩5	D-III Dive 1	419/	-		
72	12673		2-33-36-4W5	Ostracod B	7750	-		-	1	104	12671	Willesden Green	8-1/-42-6W5	Belly Hiver A	5150		- -	
73	12665	Sylvan Lake	11-22-38-4W5	Glauconitic E	7347	_		_	1	105	12660	Ferrier	4-7-41-8W5		5545			-
74	12670	Lanaway —	4-27-36-3W5	Mannville	7442	_		_	-	• Ave	rage de	pth						GS
75	13/130	Three Hills	9.9.31.23WA	Ostracod A	5127	_			-									
1 ''	1.0100		0.001 20114	1				11	_									

I.

°.	ACE	P	ES	z	ET		Standard	Analysis	Detailed	Analysis			ACE	0	ES	z	ET		Standaru Analysis	Alidiysis	Detailed	Analysis
SAMPLE N	IFP REFERED	MELL/FIEL	GEOGRAPH CO-ORDINAT	FORMATIO	DEPTH IN FE	Extract	s Composition	Saturates		Aromatics		SAMPLE N	IFP REFERE	WELL/FIEL.	GEOGRAPH CO-ORDINAT	FORMATIO	DEPTH IN FE	Extract	ss Composition	Saturates		Aromatics
							Gros	C C C C C C C C C C C C C C C C C C C		S≊									Gros	NS CCC	CGC	MS
Α.			MIDD	LE DEVONIAN							E	Ε.		WA	BAMUN GROU	IP-UPPER DEVONIA	AN					
				Area 1												Area 1						
MD1	12509	Cataralu	C 25 70 OWE	Watt Mountain	6918	-	-				۷	Wb1	12326	Volmer	2-16-55-25W4	Wabamun	3965	-			·	
MD2	12512	Grizzly	6-30-70-9WD	Muskeg	5973	-	-	- ·	-		. V	Wb2	12351	Golden Spike	12-24-51-27W4	Wabamun	4602	-			· -	-
MD3	13034	Goose River	12-23-67-18W5	Gilwood	9432	-	-		-		1	Wb3+	12410+	Leduc 1	5-22-50-26W4	"Devonian"	4541	_			-	
MD4	12570	Swan Hills	10-2-67-8W5	Watt Mountain	7871	-	-	- -	- -	-	\ \	Wb4+	12202+		16-6-48-24W4		4683			- -	-	<u> </u>
				Area 2							-	Wb5+	12210+	Netook	2-1-34-2W5	Wabamun	8807	-			·	
MD5	14489	Wappau	2-34-75-11W4	Keg River (?)	3202	-										Area 2				_		
MD6	14712	Christiana River	6-7-78-11W4	Keg River	3186	-	-		-		1	Wb6	13963	McMullen Lake	10-21-78-26W4		1769			-	-	
В.		BE	AVERHILL LAI	KE-UPPER DEVONI	AN							Wb7+	14100+	Marten Hills	6-19-75-24W4	Wabamun	2203			-	/	
				Area 1								Wb8+	14115+	Flat Lake	10-8-66-19W4		1838	H	_		_	
	12524	laussard	11 25 72 1214/5	Swap Hills	6900			_			W	WD9+	14118 +	likalta	7-22-66-20994	Wahamun (Nisku?)	2157	H		_		-
B2	12024	JOUSSAID	11-35-72-15₩5	Swall Hills Beaverbill Lake	7175-84	_	_	_			VV	- 010	14547	UKdita	7-24-37-17/14		2157				/	
B3	13019	Yellowstone	4-15-72-13W5	Swan Hills	7215-21	-	-	-	_			۲. 		[M155	ISSIPPIAN					-	
B4	12534			Beaverhill Lake	9193	1-	-	-	-			Ms1+	12196 +			Pekisko	6590	-			- -	-
B5	13031	Goose River E	10-15-67-18W5		9364	-	-		-			Ms2+	12200+	N. Gilby	4-20-41-2W5	Banff	6657	H	<u> </u>			
B6	12544		12-23-67-18W/5	Swan Hills	9163	-	-	-	-		-	Ms3+ Ms4	12490+		10-25-59-9W5		5282.90	H			-	+
87	12550	Goose River	12-23-07-16113		9383	-	-	-	-		-	Ms5+	18064 +	Lombell	10-16-59-6W5		4070-97		<u>-</u>	_	+_	
B8	12591	0	4-34-67-18W5	Beaverhill Lake	9024	-	-	-	-			Ms6	18059	Paddle River	11-3-56-8W5		5282-90	-	-		1-	1
B 9	12636	Waskahigan	10-5-65-24W5	Swan Hills	11,726	-	-	-	-	+		Ms7+	18063 +	Glenevis	2-24-56-5W5		4270-88	-		- -		1
B10	12555		14-5-64-24W5	Beaverhill Lake	11,891	-	-	_	-	+		Ms8+	18062	Cherhill	10-6-56-5W5		4486-512	-	-;	-	-	
B11	12573	N.E. Virginia Hills	4-33-65-12W5	Curee Hille	9030	-	-	_				Ms9	18056	Chip Lake	10-10-54-9W5	Mississippian	5892-915	-	-		-	
B12	125/4			Swan mills Resverbill Lake	9030	1-	_	_	_		M	As10	18057	Bigoray	11-1-51-8W5		6386-90	-	_		-	
B14	12566	 Swan Hills	10-2-67-8W5	Swan Hills	7470	-	-	-	_		N	Ms11	18055	E. Pembina	8-30-47-6W5		6722-42		-		-	-
B15	12641		4-7-67-8W5		8076	-	_	-			N	/s12	18053	Wilson Creek	6-15-44-5W5		7258-72	-	-		-	
B16	12435	Ferrybank	2-8-44-27W4	Beaverhill Lake	7716	-	-	-	-		N	Ms13	18054		10-27-43-4W5	-	7067-90	-				-
		, L ,		Area 2							N	As14	18049	Sanchild	6-11-43-10W5		9385-430	\vdash	4			+
	14105										N	Ws15+	12196	N Gilby	1.20.41.2005	Pekisko	6590	E				+
B17	14105	- Rock Island	14-31-74-23W4	Reaverbill Lake	4330	-	-	_			N	VIS10+	12200	N. GILDY	4-20-41-2445	Banff	6656				_	+
B19+	15285 4	+ Wappau	2-34-75-11W4	Source and	1644	+_	-	_	/-	-		us18+	18061	Medicine River	10-7-40-3W5	Mississippian	7137-47	-			+-	.†
		1				1	<u> </u>				N	Ms19+	18050				6380-90	-		- -	- -	
U.		WU	ODBEND GRU	JUP-UPPER DEVON							N	/ls20 +	18051	Prevo	11-14-39-1W5	Mississippian	6457-74	-	- ·		-	
				Area 1							N	Ms21	18052	Medicine River	8-28-38-3W5]	7261-93	-	-		-	

APPENDIX E. Location of extracts and extent of analysis.

APPENDIX E. Continued.

W1	13443	Fedorah	13-22-57-23W4	Cooking Lake	4485-88	-	-	-	-			G.			N	IANNVILLE - L	OWER CRETACEOU	S						
W2	12224		1-27-57-20W4	Duvernay	3592	-	-	-	-	- -	_													
₩3	12226	El Dorena		Cooking Lake	3825		-	-	- ·	-							Area 1							
W4	12239		4-27-57-20W4	Ireton	3161	-	-	-		-		MI	12	2398	Vimu	9-9-58-25WA	Lloper Blairmore	2709	-	-				-
W5	13039			Cooking Lake	3825	-	-	-	-			M2	13	3038	villy	5-3-36-23114	opper blaimbre	7709	-	-		-		
W6	12332	Volmer	2-16-55-25W4	Ireton	4450	-	-	-	-			M3	+ 12	2314 +	Manawan	14-18-56-25W4	Basal Quartz	3635-	-	-			-	
W7	12335			Leduc	5335	-	-	-	-			M4	+ 13	3044 +					-	-		-		
W8	12420			Ireton	7282	-	-	-	-			MS	13	3027	Volmer	2-16-55-25W4	Upper Blairmore	3325-30	-	-		-		
W9+	12423 +	Ferrybank	2-8-44-27W4	Duvernav	7370	-	-	-	-	-		ME	13	3395	Acheson	12-19-52-25W4		3963-66	-	-		-		
W10	12427				7461	-		-	-	\rightarrow	_	M7	13	3396				3992-94	-	-				-
W11	12432			Basal Leduc Reef	7618	-	-	-	-			M	+ 13	3398 +	Pembina	6-18-47-6W5	Lower Mannville	6769-72	-	-		-		
W12	13445	Alhambra	16-11-38-5W5		10,022	-	-					MS	13	3399	Minnehik-Bucklake	10-7-46-6W5		6883-86	-	-		-		
W13	13446			Leduc	10,025	-	-					M10	13	3400	Internet Bucklake	10740-0113		6888-91	-	-		-	-	-
W14	13444	Bailey Raven	13-13-37-4W5	20000	9635-39	-	-					M11	13	3407	Brazeau	6-14-45-9W5		7824-27	-	-	- ·	-		
W15	12445	Dickson	1-28-36-3W5		9906	-	-	-	-	-		M12	12	2158	Ferrybank	6-9-44-27W4	Mannville	5133	-	-	- ·			-
W16	12219	Dickson	16-12-36-3W5	Duvernay	6488	-	-	-	- ·	-		M13	13	3401				6517-20	-	-		-		
				Area 2								M14	13	3402	Bentley	10-11-40-2W5		6530-33	-	-	-			-
W17+	13929+	Grand Ranids	9.34.84.17WA		876		_	_	_	_	_	M15	13	3403			Lower Mannville	6538-42	-	-	- /	-		
W18+	14500 +	Pelican	10-16-78-17W4	Grosmont	1130		_†	_	_		-	M16	+ 13	3406 +	Butte	10-23-37-5W5		8130-33	-	-		-	-	-
W19+	14158+	Kikima	10-17-64-14W4	Groomont	1711	-	_	_	_		-	M17	13	3409	Strachan	10-31-37-8W5		10,150-55	-	-	-	-		
W20	14469		10 17 01 1111			\square		-		+							Area 2							
W21	15279	Plum Lake	14-26-64-21W4	Ireton (Base)	2685	_	-	_	1	-	-	MIE	+ 14	4673+	McIvor	9-35-102-12W4		322		_				-
W22	14164				2195	-	/	-	-	+		M19	+ 14	4677+	Tenn South	15-29-99-13W4	-	1803	-	_	_		_	-
W23	14715	Meadowbrook	5-24-63-25W4	Ireton	3348	-	_	-	-1.			M20	+ 14	4681+	W. Athabasca OSTH	6-21-95-16W4		970	-	-	-		_	-
W24	14463					1	/	-	1	+		M2	+ 1	4686+	Tenn South	6-12-95-7W4	1	894	-	-	-		-	-
W25+	15278+	Craigend	6-4-63-12W4	Grosmont	1851	-	_	-	1	_1		M22	+ 14	4697+	Steepbank	12-20-92-9W4	McMurray	180	-	-	-		_	_
W26+	14337+	Warwick	6-14-52-14W4	Ireton	2438	-1	-1	-		-		M23	+ 1	4700+	Ft. McMurray	4-26-88-9W4	ŕ	275	_	-	_			-
W27+	14263+	Provident Prospect	6-10-45-3W4	Leduc	2307		-1	-				M24	+ 13	3432+	GCOS. Pit		-		-	-	-			_
		1										M25	13	3912	Sandy Lake	16-5-86-21W4		1227	-	-	-1		_	-
<i>D</i> .		WIN	IERBORN GR	OUP-OPPER DEVO			_					M28	+ 1	4703+	Cadotte	3-20-84-17W4	-	2055	1_1	-	_		-	
				Area 1								M27	+ 1	3923+	Grand Rapids	9-34-84-17W4	Wabiscaw	751	-	-	_	-	-	-
Wi1	12328	Volmer	2-16-55-25W4	Calmar	4195	-	-	-	-	-		M28	+ 14	4709+	Pony Creeks	10-32-79-7W4		1215	-	-	-		-	_
Wi2	12349	Leamac Merland	15-7-49-25W4		5160	-1	-	-	-			M29	+ 13	3934+	Many Lakes	10-8-82-10W4	1	1439	-	-	-		-	_
Wi3	12206	Leduc 1	16-6-48-24W4	Nisku	5132	-	-	-	-	-	_	M30	1	3957		15 00 70 504	McMurray	0.05	-	1	-	+	1	
Wi4	13014	Distance	1 29 20 2005	1	9213-75	-	-	-	-	-	-	M33	14	4719	Bohn Lake	15-29-79-5W4		962	-	-	-			_
Wi5	13015	Dickson	1-28-36-3₩5	Nisku/Ireton	9275-301	-	-	-				M32	+ 1	3969+	Christiana River	6-7-78-11W4	1	1566	-	-	-	-	-	
				Aros 2								M33	+ 1	3917+	Mr. 1	10 5 00 01 114	Colony	776	-	-		-	-	
1410	14150	New Count	10.10.04.10		1001			_	r	_	_	M34	+ 1	3922 +	wabasca	10-5-83-21W4	McMurray	1395	-	-	-	-	-	
WID	14156	Noral South	10-12-64-16W4	-	1861	-	-	-	-	_		M35	+ 1	3943+	Devil Rapids	10-18-80-23W4		1408	-	-	-	1	1	-
W1/+	14181+	Figure Lake	0-18-03-1/W4	Nisku	2203	-	-	-	-	-	_	M36	+ 13	3954 +	Wabasca	10-30-79-23W4	Wabiscaw	1372	-	-	-	-	-	-
W18+	14352+	Skaf0	10.1.52.1584	-	2098	-	_	-	_	-		M37	+ 1	3965+	Pelican A3	10-25-78-23W4		1355	-	-	-		-1-	_
M19	14339	vegreville	10-1-53-15W4		2415	-	-	-	1										-			<u> </u>	G	ŝc

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APPENDIX E. Continued.

.0	NCE	Q	IIC	Z	E.		Standard	Analysis	Detailed	Analysis		VCE	٩	ES	z	ET		Standard	Analysis	Detailed Analysis
SAMPLE N	IFP REFERE	MELL/FIEL	GEOGRAPH CO-ORDINA	FORMATIC	DEPTH FEI	Extract	s Composition	Saturates	Aromatics		SAMPLE N	IFP REFERED	MELL/FIEL	GEOGRAPH CO-ORDINA1	FORMATIO	DEPTH FE	Extract	Composition	Saturates	Aromatics
							Gros	CGC M	CGC	ΣN					-			Gross	CGC	CGC
G.		N	IANNVILLE - L	OWER CRETACEOUS	3						н.		LOW	ER COLORADO	- LOWER CRETACE	OUS				
				Area 2											Area 1					
M38+	13960+	McMullen Lake	10-21-78-26W4	Wabiscaw	1588	-	-	-	-		LC1	12234	Calmette	6-33-58-25WA	Ioli Fou	2621	-	-		•
M39+	14493+		10-7-76-23W4	mabiooum	2442		-	-	1		LC2	13045	bannette	0-55-50-25114	5011 00	2021	-	-		•
M40	14098	Marten Hills	6-19-75-24W4	Clearwater	2144	-		-			LC3	12140			Viking	2500	-	-		· -
M41	14717					-	-	- -	- -		LC4	12144	Vimy	9-9-58-25W4	Viking/Joli Fou	2613	-	1		· -
M42+	1410/+		10-18-73-24W4	Wabiscaw	1877	-	-		- -	_	LC5	13001			Viking	2500-28	-	-		· _
M43+	14/11+		10-6-76-11W4	McMurray	1668	-	-			_	LC6	13005			Joli Fou	2640-44	-	-		·
M44	15283			Clearwater	1462	-	-	- [/	-	_	LC7	13000	Carbondale	7-10-55-24W4	Viking	2699-709	-	-		
M45+	14482+	wappau	2-34-75-11W4		1501		-	_		_	LC8	13025	Volmer	2-16-55-25W4	White Specks/Viking	2863-80	-	-		•
M46	14487			McMurray	1628	-		-		_	LC9	12409	Ferrier	10-4-41-8W5		7870	-			·
M4/+	15284+					-	-	-1/	1-1	_	LC10	12380	Baysel Bingley	4-23-40-7W5	Viking	7569	-	-		· -
M48+	16484+	Peace River	1-16-85-21W5	Bullhead	1615-20		-				LC11	13041					-	-		·
M49 +	16485+	Harmon	10-23-82-18W5		2260-300	-	-				LC12	12279		10-36-37-2W5		6247	-	-		•
M50 +	16486+	Kiminwum	15-21-78-20W5	Gething	2608-37		-				LC13	12281	Burnt Lake		Viking/Joli Fou	6295	-			·
M51+	14464+		10-27-67-25W4	McMurray	2547	-	-		\square		LC14	12298		10-26-37-2W5	Basal Fish	6165	-	-		
M22+	15280+			Colony	1950	-	-		-	_	LC15	12300				6194	-			·
M53+	144/2+	Dis Dand			1985		-	-		_	LC16	12301	Caroline	10-27-35-6W5	Viking	8440	-	-		-
NCC 1	15001	Big benu	11-8-67-26W4		2659	-				-	1017	12302				8465	-	-	-1-	
WEC NEC	102017			Basal Quartz		-	_		-	_	3.5				Area 2					
OCIVI ME7	144/0				2682	-		_			LC18	14496	Oractical	12 4 94 20044	1-11 5-1	690	-	1	-	
NEO.	15262				1005	-			-	_	LC19	15286	Sandy Lake	13-4-84-20004	Joli Fou	680	-	-	- /	1-
+8CM	14109+			Colony	1335	-	-	-			LC20+	13915+		10 5 00 0100			-	1		- /
M59+	14110+	Flat Lake	10-8-66-19W4		1352	-	-			_	LC21+	14721+	Wabasca	10-5-83-21W4	Viking	719	-	-		
M60	14/2/			McMurray	1788	-	-			_	LC22	14108	Flat Lake	10-8-66-19W4		1307	-			
M61	14113				1789				-	_	LC23	14119	-				-	1		-
M62	14171	Figure Lake	6-24-63-18W4	Glaucontic	2195	-	$ \land$			_	LC24	14725	lent Lake	10-7-65-13W4	Pelican	1006	1	\square		
M63+	141/5+		6-18-63-1/W4	Upper Mannville	1783	-	-	-	-	_	LC25 +	14240		10 5 50 000		1001	-	1		-
M64	14460	Craigend	6-4-63-12W4	Glauconitic	1782			-		_	LC26	14713	Muriel Lake	10-5-59-4W4	Viking	1291	-	1	-	
MCC	152//	Madlau	C 00 CC 044		1500		-	-/		_						20115				
100+	14123	wedley	0-22-00-2W4	J	1502	-	/								OTTER ORETAGE	.005				GSC

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M67+	14135+	Leming	14-3-65-4W4	Upper Mannville	1866	-	-	-	1		UC1	12294			Pad Heart	2000	-	-	- ·	-	
M68+	14140+	Marie	10-31-65-3W4		1190	-	-	-	1		UC2	13046	Holburn	10-33-50-1W5	Dau neart	3220	-	-	-	-	
M69	14214	Cold Lake	4-25-62-3W4	Llovdminster	1350	-	/	-			UC3	12997				3300	_	-	- ·	-	
M70	14990		1 20 02 0111	Lioyanniatar	1000	-	-	- -	-		UC4 -	12168	Round Valley	2-20-50-6W5		4118	-	-	- ·	-	
M71+	14215+	Ardmore	15-28-62-3W4	Lloner Mannville	1062	-	-		-		UC5	12311	Knob Hill	12-19-46-2W5	Cardium	4437	-	-	- ·	-	
M72+	14248+	Muriel Lake	2-23-59-3W4	opper mannine	1574	-	-	-	1		UC6	12479	Pigeon Lake	1 14 46 1945		4159	-	-	- -	-	
M73+	14359+	Lindberg	10-13-58-5W4	Lloydminster	1682	-	-	-	-		UC7+	12481	Figeon Lake	4-14-40-1115		4205	-	-		-	
M74+	14364+	Saddle Lake	1-35-58-12W4	Upper Mannville	1621	-	-	-			UC8	13043	Minnihik	16-12-47-6W5	Bad Heart	4850	-	-	-	-	
M75	14238	Bass A4	10-25-60-17W4	Glauconitic	2075	-	-		-	/	UC9	12483	O'Chiese	12-23-44-9W5		6151	-	-	- ·	-	
M76	14230	Tawatinaw N	10-34-60-23W4	First Glauconitic	2487	-	/	-			UC10	12344	Willesdon Groon	6 25 42 7WE		5750	-	-		-	
M77	14720	Tanatinan II	10-34-00-23114	That Gladeonnie	2489	-	-		-		UC11+	12347	willesden dieen	0-35-45-7405		5826	-	-	- ·	-	
M78+	14350+	Skaro	7-11-57-19W4	Basal Quartz	2628	-	-		-		UC12	12404	Formion	10 4 41 0005	0	6825	-	-			-
M79	14341	0'Hairy	11 26D 55 14MA	Upper Plairmare	1752	-	/				UC13-	12406	renner	10-4-41-8₩5	Cardium	7792	-	-		-	
M80	14992	onany	11-200-33-14114	opper Blainhore	1755	-	-		-	-	UC14	12373	Baysel Bingley	4-23-40-7₩5		6530	-	-			
M81+	14343+	Eliza	6-4-56-8W4	Colony 2	1615	-	-		-		UC15	12376	Dayser Dingley	4-25-40-7115		6614	-	-	- ·		•
M82+	14330+				2982	-	-		-		UC16	12230	Leafland	8-35-40-6W5		6109	-	-	-	-	
M83+	14346+	Beaverhill Lake	12-6-51-16W4	Basal Quartz	3016	-	-	-	/		UC17	13012			Bad Heart	5930-80	-	-	-		
M84+	14331+				2995	-	-		/		UC18	12369	Leslieville	1-33-39-5W5		5951	1	-	-	-	
M85+	14255+	Lloydminster	10A-33-48-1W4	Lower Sparky	1909	-	-		-		UC19	13013				6027-30	-	-	-	-	
M86+	14458+	Rayter Lake	1B-5-47-5W4	Sparky	2214	-	-	-			UC20 -	12317	Lanaway	7-31-36-3W5	Cardium	5880	-	-		-	
M87+	14258+	Daxter Lake	2-29-46-5W4	Lloydminster	2209	-	-	-	1		UC21	12468	Carrington	11.07.05.5145		6931	-	-	- 1		
M88+	14259+	McLaughin	10-10-46-2W4	GP-Rex	2013	-	-	-	1		UC22	12472	Garrington	11-27-35-5₩5		7103	-	-	-	-	
M89+	14264 +	Edgerton	7-7-45-3W4	Lloydminster	2506	-	-		-	-			POS	T-COLORADO	- UPPER CRETACEO	ous					
M90+	14266+	Chauvin	10-22-43-1W4	Sparky/GP	2088	-	-		-												
M91	14454	Ribstone Lake	6-29-43-5W4	Sparky	2218	-	1	-							Area 1						
M92+	15276+			opany		-	-	- /	' -		PC1	12157	-	8-1-48-4W5	Belly River	3254	-	-	-		
M93+	14268+	Greenglade	9-17-41-1W4	Dina	2790	-	-		1		PC2	12393	Pembina	10-3-48-4W5		3231	-	-	-		-
M94+	14271+	Hughenden	12-27-40-7W4	Sparky	2700	-	-		· -		PC3	13047			Lea Park		-	-	-	-	
M95+	14273+			Basal Quartz	2743	-	-		· /		PC4	12269	Minnehik	16-12-47-6W5		3955	-	-	-	-	
+ impre	egnations	5									PC5 13008 Minnehik	10 12 47 0110		3946-49	-	-	-		•		
🖊 analy	sis not co	ompleted									PC6 ·	PC6 + 12477 Pigeon Lake	- Pigeon Lake	4-14-46-1W5	Belly River	3156	-	-	-	-	
				~							PC7 12478 Pigeon Lake		Lea Park	3185	-	-	-	-			
											PC8	12286		10-25-46-2W5	Belly River	3216	-	-	-	-	
											PC9	12308	Knob Hill	12-19-46-2W5	2 shy river	3440	-	-	-	-	
											PC10	12310		12-13-40-2413	Lea Park	3500	-	-		-	

GSC
VARIATIONS IN COMPOSITION OF ROCK EXTRACTS

In the following discussion, samples from both the central part of the basin and the basin margin are considered.

> Post-Colorado Group (Belly River, Lea Park Fms.)

Central part of the basin

These samples have undergone shallow burial. They have small extract yields (extract/org. C <5%) and a high proportion of acyclic alkanes in the saturate fraction (>60%). The n-alkane distribution typically shows an abundance of n-alkanes above C_{20} with an odd carbon number predominance in the range C_{23} to C_{31} which is characteristic of higher plants (Fig. 5-16). The odd number predominance may be associated with a dominance of compounds containing 3 rings in the cyclo-alkane fraction (e.g. Knob Hill, PC8, Fig. 5-19); these compounds probably are derived from diterpenoid resin acids such as the abietic and agathic acids. Samples having the strongest odd number predominance also have the lowest isoprenoid content, although pristane is always well represented.

Analysis of the aromatic hydrocarbons (CGC) shows that there is a similarity in the distribution of sulphur compounds (FPD) with the Colorado Group; in particular, the benzothiophenes are present only in the lower molecular weight range. The MS data (Fig. 5-18a) show the dominance of the naphthalene (C_nH_{2n-12}) and phenanthrene ($C_{n}H_{2n-18}$) families in the aromatic fraction. The importance of the naphthalene family is shown by a dominant mode at C_{13} (trimethyl or ethyl methyl naphthalene) in the distribution of mass families with carbon number; there is only a slight shoulder at C₂₀ representing the sulphur-bearing forms. The $\tilde{C_{nH_{2n-18}}}$ family has a C_{15} mode attributed to methyl phenanthrene. The dibenzothiophenes are well represented in the range of carbon number below C₂₀ but the benzothiophenes are particularly absent (Table 5-2). Steroids and triterpenoids are present in the monoaromatic fraction. The distribution by mass families in the triaromatic fraction is characterized by an important mode at C_nH_{2n-18} , a shoulder at C_nH_{2n-20} and C_nH_{2n-22} , and low values for the extreme families.

Impregnation

A sample from Pigeon Lake (Belly River Fm., PC6) has a very high extract yield (extract/org. C = 51%). The composition of the extract and distributions of saturated hydrocarbons and acyclic alkanes are similar to the Group 1 oils.

Colorado Group (Badheart, Cardium, Second White Specks, Fish Scale Zone, Viking and Joli Fou Fms.)

Central part of the basin

All samples taken from strata adjacent to the Cardium and Viking reservoirs have ratios of acyclic alkanes to saturated hydrocarbons of less than 60 per cent. The n-alkane distributions generally have a maximum in the higher carbon number range but a number of samples have a strong mode at C_{15} (e.g. Holburn, UC3, Fig. 5-16a) which can be related to the distribution of n-alkanes found in benthic algae (C_{15} and C_{17} modes). In these cores, the ratios of isoprenoids to n-alkanes are high and there is a slight odd number predominance in the range C_{23} to C_{29} . These samples come from the region between Leduc and Redwater, slightly to the northeast of the main study-area. Two samples (Garrington, UC21; Leafland, UC16) are particularly rich in alkanes above C_{20} suggesting that the organic matter is of nonmarine origin (Fig. 5-19a). In the majority of samples, the cyclo-alkanes with 4 rings are present in greater concentration than those with 3 and 5 rings and are particularly dominant in the samples from shallow depths. The ratio of isoprenoids to n-alkanes tends to decrease as the depth of burial of the sample increases.

Analyses (MS) of the aromatic hydrocarbons from 6 samples from the Viking and Cardium Formations show a certain relationship between these samples and those from the Belly River Formation (Fig. 5-18). However, the naphthalene family is dominant except for one sample from Carbondale (Viking Fm., LC7) and the phenanthrene family (C_nH_{2n-18}) is as important or more important than the naphthalene family (C_nH_{2n-12}) . The benzothiophenes are less well represented (Table 5-3) or may even be absent. The concentration of dibenzothiophenes is low (except Garrington, UC21) and these compounds occur only in the low molecular weight range below C_{20} ; this is typical of the Group 1 oils. Their presence is indicated in the family C_nH_{2n-12} by a slight shoulder at C_{18} and C_{19} which is more prominent in the Carbondale extract than in others from this group.

The Carbondale sample also shows a secondary peak at C_{19} in the mass family C_nH_{2n-14} , beside a mode at C_{15} ; this secondary peak is attributed to sulphur compounds. Generally, the distribution of mass families in the triaromatic fraction is characterized by a mode representing the C_nH_{2n-18} phenanthrene family and an inflexion at C_nH_{2n-20} and C_nH_{2n-22} . The concentrations of these families are greater than they are for the sulphur-bearing families C_nH_{2n-16} and C_nH_{2n-18} (Fig. 5-18a); again the Carbondale sample is the

exception in having the lowest concentration of the phenanthrene family (C_nH_{2n-18}) in this group. The dominance of the tricyclic phenanthrene family (C_nH_{2n-18}) (e.g. Garrington, UC21) indicates a derivation from higher plant forms which agrees with the previous interpretation based on the n-alkane distribution.

Analysis by gas chromatography (FID/FPD) of the aromatic hydrocarbons from 9 samples, including the 6 discussed above, shows that they are poor in benzothiophenes and that the dibenzothiophenes are confined to low carbon numbers.

Impregnation

Five samples, one from the Second White Specks and others from the Cardium Formation, have high extract yields and the characteristics of the saturated hydrocarbons are similar to the Group 1 oils. These samples are from Round Valley (UC4), Lanaway (12317), Willesden Green (UC11), Ferrier (UC13), and Pigeon Lake (UC7).

Margin of the basin

Of the nine examples examined from the basin margin, all of which are from the Lower Colorado Group, one has not yielded any extract (UC24), two have the characteristics of impregnations (LC20/LC21) and three others are clearly affected by contamination. The samples yielding less than 35 mg of extract are depleted in n-alkanes below C_{17} (evaporation) and the C_{19} , C_{20} and C_{21} n-alkanes form a particularly dominant mode; the isoprenoids are present in low concentration and are distributed irregularly (Fig. 4-8).

The Tent Lake (LC23, Pelican Fm., Fig. 1) sample, on the other hand, has a bimodal distribution of n-alkanes with a maximum at C15 and a more important maximum at C₂₉. The total distribution is marked by a predominance of n-alkanes with an odd number of carbon atoms. These characteristics are indicative of a low degree of catagenesis and a derivation from the debris of higher plant forms as is found in the Belly River Formation (Fig. 5-19). The sample from Muriel Lake (LC25, Viking Fm.) and Sandy Lake (LC18, Joli Fou Fm.) have a strong mode at C_{15} or C_{16} and a slight odd number predominance above C25 in the n-alkanes distribution. The isoprenoid alkanes are well represented with phytane predominant over pistane. At similar depths, these characteristics have been found in the Viking Formation at Carbondale (LC7, Fig. 5-16a) and in the Upper Mannville Group at Vimy (Mi, Fig. 5-16b). The distribution of cyclo-alkanes in the Muriel Lake sample is similar to that found in the Vimy sample (Fig. 5-16). This type of distribution is found also in the Tent Lake (LC23) sample.

Impregnation

The Wabasca (LC20/LC21) sample was taken from the Viking Formation only 6 m (20 ft.) above the Mannville. It shows a high yield of extract and hydrocarbons. The

hydrocarbons contain only a small proportion of acyclic alkanes (20%) and the large proportion of 3- and 4-cycle alkanes resembles the heavy oils and impregnations found in the underlying Mannville (see below and Chap. 6 for detailed discussion).

Mannville Group

Central part of the basin

This series is represented by 17 extracts. In the Upper Mannville Group, 3 samples, 2 from the same borehole at Vimy, suggest a certain heterogeneity in the deposits. The n-alkane distribution of one sample from Vimy (M2) resembles the distributions in samples from the Belly River Formation with a well-defined odd number predominance in the range nC_{23} to nC_{31} (Fig. 5-19a). In addition, it yields only a small amount of saturated hydrocarbons; asphaltenes represent more than 90 per cent of the extract and aromatics more than 95 per cent of the hydrocarbons. These features probably are related to coaly material in the parent rock. The other sample from the same level at Vimy (M1, Fig. 5-16b) and the Volmer (M5) sample both yield normal amounts of extracts, and hydrocarbons contain cyclo-alkanes in which 2 and 3 rings are the most abundant and display a C15/C16 mode in their n-alkane distributions which is typical of benthic algae.

Mass spectrometric analysis of the aromatic hydrocarbons from a Vimy (M1) sample shows a small benzothiophene content (Table 5-3) and a large dibenzothiophene content compared with the Colorado and post-Colorado sediments. The dibenzothiophenes are represented in the family C_nH_{2n-12} by a plateau at C_{16} - C_{17} in the distribution by carbon number and in the family C_nH_{2n-12} by a peak at C_{14} beside the C_{15} mode. As in the samples from the Colorado Group (Fig. 5-18a), the distribution of families in the triaromatic plus fraction shows a mode at C_nH_{2n-18} and a plateau between C_nH_{2n-20} and C_nH_{2n-22} but the sulphur-containing families C_nH_{2n-16} and C_nH_{2n-18} are more abundant (Fig. 5-18b).

The gas chromatogram (FPD) of this sample shows the relative importance of the dibenzothiophenes among the compounds in the lower range but the chromatogram is spoilt by the presence of free sulphur.

In the Lower Mannville Group, the rocks are generally rich in organic carbon (Fig. 5-12a) but the extract yields (extract/org. C) are lower than in the Colorado Group (Fig. 5-13). As in the Upper Mannville Group, there appears to be a certain heterogeneity in the deposits. One group of extracts (Ferrybank, M12; Buck Lake, M9 and M10; Brazeau, M11; Strachan, M17; and Acheson, M7) has a distribution of n-alkanes with a maximum at C15, C15-16 or C17, which is characteristic of organic material derived from benthic algae. With the exception of the Ferrybank sample, the ratios of acyclic alkanes to saturated hydrocarbons are generally higher than in oils of Group 2 (Fig. 5-15). The second group of extracts (Bentley, M13-M15) is characterized by a high proportion of n-alkanes above C_{20} . In this range (C_{21} - C_{31}), there is a pronounced



FIGURE 1. Distribution of saturated hydrocarbons in Lower Colorado rock extracts from the margin of the basin.

odd number predominance which is typical of organic material derived from higher plant forms. In addition, with similar depths of burial, the ratios of acyclic alkanes to saturated hydrocarbons are higher (67-77%) than in the first series. In the first series of extracts, the ratios of isoprenoids to n-alkanes are similar to the values for the Colorado extracts. In the second series, the ratios are the lowest recorded in the extracts and are similar to the value obtained from the Niton (62) oil which, in turn, is the lowest recorded from all of the oils.

Mass spectrometric analysis of the aromatic hydrocarbons from the Ferrybank (M12) sample, representing the first series of extracts, shows the first occurrence of abundant thiophenes (particularly dibenzothiophenes) in the extracts (Table 5-3). Again, the diaromatics, comprising trimethyl or ethyl naphthalene, form an important mode at C_{13} in the mass family C_nH_{2n-12} and a mode at C_{15} in the mass family $C_{n}\mathrm{H}_{2n-14}.$ Monoaromatics are poorly represented. Dibenzothiophenes and high molecular weight sulphur compounds (C21-C28) are represented by a secondary peak at C_{16-17} and a plateau at C_{20-21} in the first family and a peak at C_{19} in the second family. Dibenzothiophenes are particularly important and are distributed between C13 and C_{28} with an appreciable proportion between C_{21} and C_{28} . Benzothiophenes are abundant also between C_{11} and C_{29} . The distribution by families in the triaromatic fraction shows a mode for the phenanthrene family (C_nH_{2n-18}) but the peaks for the sulphur families $C_nH_{2n-16}S$ and $C_nH_{2n-18}S$ are equally important.

The same characteristics are found in the Acheson (M7) extract, with the difference that the modes in the mass families C_nH_{2n-12} and C_nH_{2n-14} occur at C_{16} and

 $\rm C_{19},$ respectively (attributed to dibenzothiophenes), and not at $\rm C_{13}$ and $\rm C_{15}$ (Fig. 5-21b). The Buck Lake (M10) extract is similar but, in this case, the $\rm C_{16}$ mode in the mass family $\rm C_nH_{2n-12}$ represents only 12.6 per cent of the total aromatics.

In the second series of extracts, the Bentley (M14) sample (Fig. 5-21a) has an aromatic distribution similar to those of the first series. The dibenzothiophenes are very abundant (Table 5-3) with a particularly pronounced mode at C_{16} in the mass family C_nH_{2n-12} but they are in lower concentration in the heavy range (C_{21} to C_{29}) than in the Ferrybank and Acheson samples (Fig. 5-21b). The same difference is found between the Niton oil and the other oils of Group 2.

Gas chromatography (FPD/FID) of the aromatic hydrocarbons also shows that the Acheson, Bentley and Ferrybank samples have a broad distribution of benzoand dibenzothiophenes in the higher carbon number range and as such resemble the Group 2 oils.

Impregnation

Four other samples, Acheson (M6), Pembina (M8), Butte (M16), and Manawan (M3 and M4), have higher extract ratios (extract/org. C) than the others ranging between 13 and 70 per cent (Fig. 5-13). The cycloalkane distributions and ratios of acyclic alkanes to saturated hydrocarbons (<50%) are similar to the Group 2 oils. The n-alkane mode falls between C₁₅ and C₁₇ (except Manawan) and the isoprenoids are fairly abundant. In the Acheson and Pembina extracts, the pristane and phytane contents are similar to those from the Mississippian extracts.

SAMPLE	M 80		
LOCATION	O'HAIRY 11-26B- 55-14W4		
DEPTH	1753′		
AGE	ALBIAN		
FORMATION	UPPER BLAIRMORE		
IDENTIFICATION	O		

DISTRIBUTION BY FAMILY								
50	-	-		-	-	-	-	
				-		-		
	Δ							
iO								
	_	1	2 1			5		



SAMPLE	M 62		
LOCATION	FIGURE LAKE 6-24-63-18W4		
DEPTH	2195'		
AGE	ALBIAN		
FORMATION	GLAUCONITIC SS		
IDENTIFICATION	O		

SAMPLE	M 44
LOCATION	WAPPAU 2-34-75-11W4
DEPTH	1462'
AGE	ALBIAN
FORMATION	CLEARWATER
IDENTIFICATION	O

SAMPLE	M 75
LOCATION	BASS A-4 10-25-60-17W4
DEPTH	2075′
AGE	ALBIAN
FORMATION	GLAUCONITIC SS
IDENTIFICATION	•

SAMPLE

LOCATION DEPTH

AGE

FORMATION

IDENTIFICATION



ĸ







25

20

15





FIGURE 2. Distribution of saturated hydrocarbons in Mannville extracts from the margin of the basin.

Mass spectrometric analysis of the aromatic hydrocarbons from the Butte (M16) sample shows the characteristics of the Group 2 oils, particularly the high content of heavy molecules (C_{21} to C_{30}) in the mass families C_nH_{2n-12} and C_nH_{2n-14} .

Margin of the basin

In addition to the oil sands, which are discussed in the section on heavy oils (Chap. 6), 9 samples from the Lower Mannville Group and 8 samples from the Upper Mannville have been extracted. Four of these samples did not yield any extract and the majority of the others have yielded only small quantities. Fourteen additional samples, 8 from the Lower Mannville and 6 from the Upper Mannville, have been extracted.

A number of the samples, particularly those yielding only a small amount of saturated hydrocarbons, have gas chromatograms which show the absence of compounds below C_{18} . This may be due to natural processes, such as deasphalting and migration of the light fraction, or to evaporation during the course of analysis. It can also be due to the first type of contamination as previously discussed (Fig. 4-7). This type of contamination affects samples from the Clearwater Formation at Marten Hills (M40/M44) and Wappau (M44). A sample from the McMurray Formation at Bohn Lake (M31) is affected by the second type of contamination (Fig. 4-8).

If the contaminated samples and the impregnations are set aside, the remaining Mannville extracts generally show an odd number predominance in the normal alkanes beyond C_{25} (Fig. 5-20). This predominance is stronger where there are few normal alkanes below C_{20} .

Two types of extracts can be distinguished. The saturated hydrocarbons of the first type (Fig. 2) are characterized by a low content of cyclo-alkanes with the concentration decreasing regularly from 2-ring compounds to 6-ring compounds, few normal alkanes beyond C_{20} , and a prominent maximum at C_{15} . The C₁₆ isoprenoid is at least as abundant as phytane or pristane. In the aromatic fraction, the distribution of thiophenic compounds (FPD) is characteristic in that light benzo- and dibenzothiophenes (<C20) predominate over heavy thiophenes as indicated by the absence of a prominent unresolved hump of compounds above C₂₀. Mass spectrometric analysis of the aromatic hydrocarbons from this type of extract (e.g. O'Hairy, M80; Fig. 3) confirms the absence of heavy thiophenes. It also shows a low concentration or absence of aromatic molecules above C_{20} , particularly in the mass families $\mathrm{C}_{n}\mathrm{H}_{2n-8},\ \mathrm{C}_{n}\mathrm{H}_{2n-12}$ and $\mathrm{C}_{n}\mathrm{H}_{2n-18}.$ The monoaromatic steroids and triterpenoids of the families $\mathrm{C}_{n}\mathrm{H}_{2n-12}$ and $C_{n}H_{2n-14}$ are well represented. All these characteristics are typical of the Upper Mannville sediments (cf. Vimy, M1, discussion, p. 136; Fig. 5-17).

The second type of extract (Fig. 2) contains abundant polycyclic alkanes and the C_{16} isoprenoid is less abundant than pristane or phytane. The maximum in the n-alkane distribution is at C_{16} and there is a second mode at C_{25} or higher. Again, the distribution of thiophenic compounds in the aromatic fraction (FPD) is characteristic but this time both light benzo- and dibenzothiophenes and higher molecular weight thiophenes, including naphthobenzothiophenes are present. Unresolved humps of compounds occur beneath the benzothiophenes ($<C_{20}$) and the naphthobenzothiophenes. All of these characteristics are similar to those of the Ferrybank (M12) extract described above and are typical of the Lower Mannville.

On the basis of these criteria, the Mannville extracts from the margin of the basin can be classified as follows. The first type, termed the "Upper Mannville type", includes the extracts from O'Hairy (M80, uppermost Blairmore Gp.), Marten Hills (M41, Clearwater Fm.), Cold Lake (14990, Lloydminster Fm.), Figure Lake (14171, Glauconitic unit), Craigend (M70, Glauconitic unit), Big Bend (M52, Basal quartz unit) and Flat Lake (M60, McMurray Fm.). In the last sample, the normal alkanes below C_{20} have been affected by bacterial degradation but the aromatic fraction is not affected (see Chap. 6).

The second type, termed the "Lower Mannville type", consists of extracts from Wappau (M44, Clearwater Fm.), Bass A-4 (M75, Glauconitic unit), Tawatinaw North (M77, First glauconitic unit), and Wappau (M47, McMurray Fm.).

Impregnation

Two samples from Big Bend (M52, Colony Fm.; M55, Basal quartz unit) and one sample from Ribstone Lake (M92, Sparky Fm.) contained impregnations. This was recognized in the Big Bend samples by the high extract yields but the condition could be identified in Ribstone Lake only after examination of the aromatic fraction (see Chap. 6).

Mississippian group

Eighteen samples have been examined from this group. Nine of the samples have organic carbon values between 0.24 and 1.13 per cent and extract ratios between 250 and 900 mg per gm organic carbon (Fig. 5-13c); they represent impregnations (Ms1-3, Ms5, Ms15-20). All the remaining samples have lower extract ratios (~120 mg/gm org. C) but only one sample has an organic carbon content above 0.30 per cent (Wilson Creek, Ms13, 1.52% org. C).

In the impregnations, the resins and asphaltenes form less than 50 per cent of the extract (Fig. 5-14c). The proportion of normal and branched alkanes in the saturated hydrocarbons is less than 40 per cent and the distribution of cyclo-alkanes shows a decrease in concentration with increasing ring number; the n-alkane distributions show important modes at C_{16} - C_{17} with a rapid decrease in the n-alkanes with increasing carbon number; pristane and phytane occur in equal concentrations. The abundance of monocyclic alkanes is similar to that of the dicyclics. There are two exceptions to these generalizations. The Prevo (Ms19, Ms20) samples, in spite of their high extract yields and large hydrocarbon contents, have a low proportion of normal and



FIGURE 3. Distribution of aromatics based on mass spectrometry (see Fig. 4-5 for explanation) in Mannville extracts from the margin of the basin.

			AROMATICS		
	DISTRIBUTION BY	DISTRIBUTION BY	DISTRI	BUTION IN THE MASS	FAMILIES
	CARBON NUMBER	MASS FAMILY	C _n H _{2n-12}	C _n H _{2n−14}	С _n Н _{2n-18}
B 18	Der cent		225 — F1 200 — F2 —	228 F1 200 F2 -	4.50
ROCK ISLAND 14 - 31 - 74 - 23W4	mass	30	L75 F3	175 - F3	3 50
4330′	r pours	20	1.25	125	2 50
FRASNIAN	droca	15	0.75	00	2 00
BEAVERHILL LAKE			0.50	0.50	100
-D-					0.00
	Carbon number	p of C _n H _{2n-p}	Carbon number	Carbon number	Carbon number
	SA	TURATES			
	Saturated HCS volume per cent MASS FAMILY B B B B B B B B B B B B B B B B B B B	DISTRIB. OF N-ALKANE AND ISOPRENOIDS	s 		

GSC

Carbon number FIGURE 4. Distribution of saturates and aromatics in a Devonian sample from the margin of the basin.

Ring number

SAMPLE LOCATION DEPTH AGE FORMATION

IDENTIFICATION

branched alkanes (≤ 20 %) in their saturated hydrocarbons and a mode of C₂₁ in their n-alkane distributions. The displacement of the mode to C₂₁ can be explained by a loss of low boiling temperature components. A similar loss was observed in both the saturated and aromatic hydrocarbons. The distribution of aromatics in the unaltered samples is similar and resembles the oils from the Mississippian reservoirs and in particular the Glenevis (41) oil.

With the exception of the Wilson Creek (Ms13) samples, the proportion of resins and asphaltenes in the remaining samples is always higher than 50 per cent and the aromatic hydrocarbons represent only 12 to 17 per cent of the extract which is clearly lower than the impregnations. Only the Wilson Creek (Ms13) sample yielded sufficient saturated hydrocarbons for a full analysis. The isoprenoid and cyclo-alkane distributions in this sample are similar to those of the impregnations except that the monocyclics are few in comparison with the dicyclics. In contrast, the normal alkanes show a mode at C_{24} and a plateau at C_{16} to C_{19} . This suggests the superposition of two types of distributions: one analogous to the preceding samples; the other as is found in the Niton (62) oil from the Mannville Group and the contemporaneous extracts from Bentley (M14), in which organic material of nonmarine origin is dominant. The aromatic distribution in the Wilson Creek sample resembles that from the Mannville. The remaining extracts are distinguished from the Wilson Creek extract by the poor resolution of peaks in the lower range of gas chromatograms of the aromatics.

Wabamun Group (Upper Devonian)

Central part of the basin

Of the five samples examined, three of them at least are impregnations (Leduc, W64, W63; Golden Spike, W62). They have extract yields above 35 per cent and the n-alkane distribution decreases regularly with increasing carbon number (Fig. 5-18b). In two of them (Golden Spike, W62; Leduc, W63), the ratios of acyclic alkanes to saturated hydrocarbons (<40%) and the distribution of cyclo-alkanes are similar to the Mississippian impregnations, but the Golden Spike sample has similar pristane and phytane contents. The third sample (Leduc, W64) has a higher ratio of acyclic alkanes to saturated hydrocarbons (>50%) with a regularly increasing cyclo-alkane disstribution from 2 to 4 cycles. All these impregnations have ratios of isoprenoids to n-alkanes in between those of the Upper Devonian oils and those of the basal Cretaceous oils and as such are similar to the Leduc-Woodbend oil from the same stratigraphic interval.

A sample from Netook (W65) was buried more deeply than the other samples and has a lower extract yield but a greater proportion of saturated hydrocarbons and alkanes. The distribution of cyclo-alkanes and the ratio of isoprenoids to n-alkanes are similar to those of Devonian oils. This sample is considered also to be an impregnation.

Analyses by gas chromatography of the aromatic hydrocarbons (FID/FPD) from two impregnations (Golden Spike, W62; Leduc, W63) show features of both Mississippian and Lower Mannville samples. Mass spectrometric analysis of the aromatics from the Golden Spike sample shows a larger content of sulphur compounds than in the Mannville samples (about 30% of the total aromatic fraction). In contrast to the Lower Cretaceous samples, these compounds are equally distributed between benzo- and dibenzothiophenes in the range C_{13} to C_{35} (Table 5-3). In the mass family $C_{nH_{2n-12}}$ (Fig. 5-18a), the C_{17} mode (dibenzothiophenes) is more important than the C_{13} peak (naphthalenes). There is also a plateau between C_{21} and C_{25} beyond the true aromatic mode in the mass family C_nH_{2n-14} . The phenanthrene family (C_nH_{2n-18}) shows a C_{17} mode and an inflexion at C_{21} attributed to sulphur compounds. The distribution of families in the triaromatic plus fraction shows that the $\mathrm{C}_{n}\mathrm{H}_{2n-16}\mathrm{S}$ and $\mathrm{C}_{n}\mathrm{H}_{2n-18}\mathrm{S}$ families are at least as important or more important than the phenanthrene family C_nH_{2n-18} (Fig. 5-18).

Margin of the basin

A single extract sample (W65) was examined from the Wabamun Group near the basin margin. It has a high extract yield and can be classed as an impregnation. The alkane and isoprenoid distributions are similar to those of Upper Devonian oil samples. The analysis, which was limited to CGC of the saturated hydrocarbons, does not permit an unequivocal correlation.

Calmar, Nisku, Ireton and Leduc Formations (Upper Devonian)

Central part of the basin

In this series, the extract yields (extract/org. C) range from 3 to 15 per cent. The proportion of acyclic alkanes in the saturated fraction is close to 50 per cent and the distribution of cyclo-alkanes shows a regular decrease in concentration toward the 4- and 5-ring compounds (Fig. 5-16). The deepest Leduc sample (Dickson, W15) has a small proportion of acyclic alkanes in the saturated fraction (<40%) and a high ratio of isoprenoids to n-alkanes.

The less deeply buried samples from the El Dorena-Volmer-Leduc area (Fig. 5-16c) have n-alkane distributions with a prominent C_{15} mode which is characteristic of material derived from benthic algae. In addition, two samples from the Volmer borehole (Ireton and Leduc Fms.) have features that indicate a low level of diagenesis: a large content of resins and asphaltenes (>50%), a predominance of cyclo-alkanes with 3 and 4 rings and a slight odd number predominance of n-alkanes in the range C_{27} to C_{29} . The ratios of acyclic alkanes to saturated hydrocarbons and isoprenoids to n-alkanes are similar to the other samples.

Gas chromatographic analysis (FID/FPD) of the aromatic hydrocarbons from the Calmar (Volmer, Wi1), Nisku (Leduc, Wi3) and Leduc (Dickson, W15) Formations show very few or no benzothiophenes, and dibenzothiophenes only in the low carbon number range. One sample from the Ireton Formation (El Dorena, W4) has benzo- and dibenzothiophenes extending throughout the carbon range, but most of these compounds occur below C_{20} .

Impregnation

A sample from the Nisku Formation (Dickson, Wi4) has a high extract yield (>45%), a ratio of alkanes to saturated hydrocarbons and distribution of n-alkanes characteristic of the oils, and a relatively high ratio of isoprenoids to n-alkanes (Fig. 5-16c). Gas chromatographic (FID/FPD) examination of the aromatics shows a certain similarity to the previous samples: few benzothiophenes and dibenzothiophenes and these are present only in the low carbon number range. Analysis by mass spectrometry (Fig. 5-18c) indicates the importance of the phenanthrene family (C_nH_{2n-18}) , especially phenanthrene itself (C_{14}) and trimethyl or ethyl methyl phenanthrene (C_{17}) . The monoaromatics in the mass families CnH2n-12 and CnH2n-14 are fairly abundant but, overall, these families are less important than the more condensed aromatics. Thiophenic compounds occur in small quantities (Table 5-3), but only in the C₁₄-C₁₆ range as indicated by a plateau of C₁₆ in the distribution of mass family C_nH_{2n-12} . The distribution according to families of the triaromatic fraction is dominated by a very strong C_nH_{2n-18} mode and is accompanied by very low values for other families, particularly the sulphur families CnH2n-16S and $C_nH_{2n-18}S.$

Margin of the basin

Samples from the Nisku (Vegreville, Wi9), Grosmont (Craigend, W24/W25) and Ireton (Meadowbrook, W22, W23; Plum Lake (W20/W21) Formations have been examined. The Vegreville (Wi9) sample shows a contamination of the second type (Fig. 4-3), whereas the samples from Craigend (W25), Meadowbrook (W22/W23) and Plum Lake (W21) contain contaminants of the first type.

Apart from the contaminated samples, a sample from Craigend (W24, Grosmont Fm.) has a mode of $C_{17}-C_{19}$ in the n-alkanes and abundant n-alkanes above C_{20} with a slight odd number predominance between C_{23} and C_{29} . A supplementary extract (Craigend, W25) has an aromatic distribution (FID/FPD) similar to an impregnation which probably has been altered by water washing (see Chap. 6). In contrast, the contaminated Meadowbrook (W23, Ireton Fm.) and Plum Lake (W21) samples have aromatic (FID) and thiophenic (FPD) distributions similar to the Ferrybank (W9) extract from the Duvernay Formation. However, the Plum Lake sample has an important component of cycloalkanes with 3 and 4 cycles indicating a lower level of diagenesis.

Duvernay Formation (Upper Devonian)

Central part of the basin

Samples from this formation have high extract yields (>10%). The extract from the shallowest sample at El Dorena (W2) indicates a low level of diagenesis (Fig. 5-16d) as is shown by the following: the predominance of resins and asphaltenes; acyclic alkane contents less than 40 per cent of the saturate fraction; a significant content of cyclo-alkanes with 4 and 5 rings; a strong odd number predominance of n-alkanes in the range C₁₇ to C₁₉; and a high ratio of isoprenoids to n-alkanes (especially pristane and phytane).

Two samples from greater depths (Dickson, W16; Ferrybank, W10) have more than 50 per cent acyclic alkanes in the saturated hydrocarbons, a lower ratio of isoprenoids to n-alkanes and a cyclo-alkane distribution similar to that found in oils (Fig. 5-16d).

Mass spectrometric analysis of the aromatic hydrocarbons from the El Dorena sample (Fig. 5-18c) shows a fairly widespread distribution of aromatic families. In the mass families C_nH_{2n-12} and C_nH_{2n-14} , there is an unusual abundance of monoaromatic steroids and triterpenoids, especially between C_{27} and C_{29}. The dibenzothiophenes also are abundant, but the phenanthrene family (C_nH_{2n-18}) is poorly represented. The distribution of the families in the triaromatic fraction shows low contents for both the phenanthrene family (C_nH_{2n-18}) and sulphur families ($C_nH_{2n-16}S$ and $C_nH_{2n-18}S$).

Gas chromatography (FPD) indicates a wide range of thiophenic compounds including the higher molecular weight range.

Impregnation

A sample from Ferrybank (W9) has a high extract ratio (>35%) and n-alkane and cyclo-alkane ratios similar to the oils. However, the ratio of acyclic alkanes to saturated hydrocarbons is low (<40%) and the ratio of isoprenoids to n-alkanes is high compared with the Upper Devonian oils.

Mass spectrometry reveals a wide distribution of aromatic hydrocarbon families (Fig. 5–18c). The C_nH_{2n-18} family is abundant, particularly the C_{17} compounds (trimethyl or ethyl methyl phenanthrene). The C_nH_{2n-12} and C_nH_{2n-14} mass families also are well represented. The former has a mode at C_{12} and a peak at C_{17} representing the dibenzothiophenes; the latter has a mode at C_{16} and a plateau at C_{19} – C_{21} due to dibenzothiophenes. Steroids and triterpenoids are not well represented in the monoaromatic fraction. The distribution of families in the triaromatic fraction shows that the phenanthrene family (C_nH_{2n-18}) is in greater concentration than the sulphur families $C_nH_{2n-16}S$ and $C_nH_{2n-18}S$.

Gas chromatographic (FID/FPD) analysis shows a widespread distribution of dibenzothiophenes with an emphasis on the lower carbon number range.

Cooking Lake Formation, basal Leduc Reef and Beaverhill Lake Formation

Central part of the basin

With the exception of the Cooking Lake samples (El Dorena, W3, W5), these samples are from greater depths than the remainder of the suite and the extract yields (extract/org. C) are the highest [6-20% for samples from 2100-3000 m (7000-10 000 ft.)]. The proportion of acyclic alkanes in the saturated hydrocarbons is usually over 50 per cent and the ratios of isoprenoids to n-alkanes are in the same range as the oils. The distribution of cyclo-alkanes is similar to the oils (Fig. 5-16e) yet, with increasing depth of burial, the proportions of saturated hydrocarbons in the extract and alkanes in the saturated fraction become progressively higher. Two very deep (3300 m; 11 000 ft.) samples from Waskahigan (B9, B10) yielded principally asphaltenes (85% of the extract). The hydrocarbons probably have been cracked to lighter fractions which have been lost by migration or during the analysis.

Among the different samples, there are a number of common features in the alkane distributions which can be related to the nature of the parent organic matter. Neglecting the polluted samples from Goose River (B7, B5), Yellowstone (B2, B3) and Waskahigan (B9), the following observations can be made.

- (a) There is a very strong mode at C_{15} or C_{17} in the alkanes from the Swan Hills (B15) and El Dorena (W3) samples which can be related to a derivation from benthic algae as in previous samples; there is also a slight predominance of nC_{19} .
- (b) There is a predominance of nC_{15} and nC_{17} and a slight predominance of nC_{19} in the alkanes from samples from Goose River (B6, B8) and northeastern Virginia Hills (B11, B12).
- (c) There is a predominance of C_{15} , C_{17} and C_{19} in extracts from Swan Hills (B13, B14).

The three types a, b, and c do not form a diagenetic succession since, in the same depth range [above 2400 m (8000 ft.)], both types a and c are found although type b is generally found at great depths [2700-3000 m (900-10 000 ft.)].

Gas chromatographic (FPD) analysis of the aromatic hydrocarbons from a Cooking Lake sample (El Dorena, W3) shows the presence of benzothiophenes in the low molecular weight range and dibenzothiophenes in the higher range. Mass spectrometric analysis of a Beaverhill Lake sample (Swan Hills, B15) shows a small content of benzo- and dibenzothiophenes (Table 5-3). The naphthalene family (C_nH_{2n-12}) is the most prominent mass family and shows a C13 mode, but there is no secondary peak of dibenzothiophenes or plateau at C_{16} - C_{17} . Steroids and triterpenoids are present in the $\mathrm{C}_{n}\mathrm{H}_{2n-12}$ and $\mathrm{C}_{n}\mathrm{H}_{2n-14}$ mass families in the monoaromatic fraction. There is a strong C_{17} mode in the phenanthrene family (C_nH_{2n-18}) . The distribution of mass families in the triaromatic fraction has a maximum at the phenanthrene family (C_nH_{2n-18})

and very low values for the sulphur-containing compounds (Fig. 5-18d). The corresponding gas chromatograms show a small content of thiophenic compounds and those that are present are confined to the lower molecular weight range.

Another Beaverhill Lake sample (northeastern Virginia Hills, B11) is similar to the previous sample, i.e. the naphthalene family (C_nH_{2n-12}) has a C_{13} mode and the phenanthane family (C_nH_{2n-18}) a C_{17} mode. There is also a similar distribution of mass families in the triaromatic fraction (Fig. 5-18d). Gas chromatographic analysis confirms the small content of thiophenic compounds.

Margin of the basin

Two samples from the Beaverhill Lake Formation at the margin of the basin have been examined; these are from Wappau (B19) and Rock Island (B17/B18). The extract from Wappau (B19) contains saturated hydrocarbons that have been contaminated, and the aromatic fraction has characteristics of an impregnation of heavy oil (see Chap. 6). In contrast, the sample from Rock Island (B18, Beaverhill Lake; Fig. 4) has an irregular distribution of normal alkanes with an odd number predominance between C_{15} and C_{21} and between C_{25} and C₂₉; the isoprenoids, particularly pristane and phytane, are very abundant. These characteristics are similar to a sample from the Duvernay Formation at El Dorena (W2) which has not been buried deeply. In both cases (Figs. 5-22, 5-16d), the chromatograms show the presence of sterane and triterpane compounds beyond C27 but the distributions differ. The difference is clarified by mass spectrometric analysis: the cycloalkanes with 3 and 4 cycles are more common in the Rock Island sample whereas, in the El Dorena sample, the mode is at 4 and 5 cycles. The distribution of thiophenic compounds by gas chromatography (FPD) is similar apart from a larger content of unresolved compounds in the El Dorena sample. This point can be supported by comparing MS analyses of the aromatic fractions (Figs. 5-18c, 5-22). The mass family CnH2n-14 is dominant and there is a large content of monoaromatic steroids and triterpenoids in the mass families C_nH_{2n-12} and C_nH_{2n-14}. There is also a similarity in the irregular distribution of diaromatic compounds, particularly in the family C_nH_{2n-14} . The benzo- and dibenzothiophenes, which are less abundant in the Rock Island sample, are represented over a wide range of carbon numbers but those occurring below C_{20} are more abundant. In both cases, the mass family C_nH_{2n-18} is equally rich in heavy molecules (C_{25+}) but does not contain any naphthobenzothiophenes. These two samples, at all stages of analysis, show characteristics that suggest they have undergone little catagenesis.

<u>Watt Mountain, Gilwood and</u> Muskeg Formations (Middle Devonian)

Central part of the basin

Two of the four samples studied in this group, one from Goose River (MD3, Gilwood Fm.) and the other

from Grizzly (MD2, Muskeg Fm.) have a cyclo-alkane distribution similar to the samples from the Beaverhill Lake sequence. However, the sample from Goose River, which had been deeply buried, has a low organic carbon content (0.06%), an abnormally low ratio of normal and branched (acyclic) alkanes to saturated hydrocarbons, and a very high ratio of isoprenoids to normal alkanes. In these respects, this sample differs from the Grizzly sample, which is similar to the Beaverhill Lake material, but for a higher ratio of normal and branched alkanes to saturated hydrocarbons.

The other samples from the Watt Mountain Formation, one from Grizzly (MD1) and one from Swan Hills (MD4), have very different features. A high ratio of normal and branched alkanes to saturated hydrocarbons (0.70) and a low ratio of isoprenoids to n-alkanes accompany a very specific n-alkane distribution. Normal alkanes above C_{20} are very prominent and have a predominance of odd carbon number molecules (Fig. 5-19a). This type of n-alkane distribution has been encountered in rock extracts and oils of nonmarine origin (Jurassic and Cretaceous of the Magellan Basin, Chile and Eocene of the Uinta Basin, Utah).

Mass spectrometric examination of the aromatic hydrocarbons from one of these extracts (Swan Hills, MD4; Fig. 5-18d) shows that the phenanthrene (C_nH_{2n-18}) and the naphthalene (C_nH_{2n-12}) families predominate, whereas the C_nH_{2n-6} and C_nH_{2n-8} families are poorly represented. In the phenanthrene family (C_nH_{2n-18}) , the mode at C_{17} is accompanied by a peak at C_{14} and a weaker one at C_{21} . In the C_nH_{2n-12}

and C_nH_{2n-14} mass families, monoaromatics and particularly monoaromatic steroids and triterpenoids are present, but the thiophenic compounds are not abundant (Table 5-3). A C₁₃ mode dominates the naphthalene (C_nH_{2n-12}) family and the sulphur compounds are represented only by a weak plateau between C_{15} and C_{20} . The distribution of mass families in the triaromatic fraction resembles one of the Devonian samples previously discussed (Dickson; Fig. 5-18d).

Gas chromatographic examination of the aromatic hydrocarbons from two samples from the Watt Mountain Formation (MD1, MD4) shows very small benzothiophene contents and slightly higher dibenzothiophene contents. The latter compounds are located almost exclusively in the lower molecular weight range.

Margin of the basin

Two samples from the Muskeg Formation (MD6, MD5) at the basin margin have been examined. Only one sample (Christina River, MD6) has yielded any extract. The saturated hydrocarbons have a large content of cyclo-alkanes with 2, 3 and 4 cycles and show a possible loss of components below C_{20} . This loss is not unreasonable considering the low yield of saturated hydrocarbons (45 mg) obtained from this extract (250 mg). In some ways, this sample resembles a sample from the Watt Mountain Formation at Swan Hills (MD4) in the distribution of thiophenic compounds (FPD) but, in the Christina River sample, the light hydrocarbons have been lost from both the saturate and aromatic fractions.