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THE UNIVERSITY OF ALBERTA

'Stable isotope systematics of heavy oil deposits, Lower Cretaceous, Alberta and Saskatchewan'

by

Kevin Lee Ringham

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

DEPARTMENT OF GEOLOGY

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled 'Stable isotope systematics of heavy oil deposits, Lower Cretaceous, Alberta and Saskatchewan' submitted by Kevin Lee Ringham in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE.

Supervisor

Frank W. Schwartz

H. Baadsgaard

Date Sept. 02, 1984

DEDICATION

Catherine Linda, for suffering two years of Edmonton on my behalf, for your patience and support;

To my parents, for their unquestioning support and trust of my academic pursuits, though sometimes the way was dark.

ABSTRACT

Cretaceous sediments in Alberta are a well known host of heavy oil deposits, containing upwards of 1000 billion barrels of crude oil. These deposits are considered remnants of super-giant, conventional oil pools that originated lower in the basin, migrated updip, and were trapped in their present positions. Exact ages of origin, migration, and entrapment are unknown but must be post-Cretaceous.

Following emplacement *in-situ* alteration by both inorganic, and organic processes commenced. Water washing, oxidation by dissolved oxygen, and microbial metabolism were the main mechanisms, which worked primarily on the lighter oil fractions. Alteration depended on the ease of removal from the parent oil. Using stable isotope analyses of formation waters, dissolved bicarbonate ion, methane, carbon dioxide, and carbonate cements the type and sequence of alteration becomes apparent.

Original biodegradation via aerobic bacteria metabolising crude oil (as an energy source), accompanied by inorganic alteration, resulted in production of various light weight organic byproducts. Due to the enormous amount of oil present all readily available sources of oxygen were consumed creating anoxic conditions. Anaerobic fermentation then dominated, as bacteria utilized the organic byproducts resulting from initial biodegradation. The fermentation produced carbon-13 enriched carbon dioxide, and carbon-13 depleted methane. The carbon dioxide eventually precipitated as 'heavy' carbonate cement. 'Light' methane and heavy bicarbonate still exist, suggesting the process continues at present. Oxygen isotope values in the cements yield information pertaining to the formation waters during precipitation. Deuterium ratios of methane and formation waters elucidate [illegible] process of methane formation. Carbon isotope ratios of methane, cement and bicarbonate ions clarify the type of biodegradation, and the sequence of microbial attack. This data supports an aerobic-anaerobic fermentation mechanism as responsible for the heavy oil.

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First and foremost to Karlis, my supervisor, for the opportunity, encouragement, and subject enabling me to 'roll back the frontiers', for putting up with delays, for his interest and motivation, for his critisms, and most importantly for never losing faith.

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I. INTRODUCTION

A. OBJECTIVE

Stable isotope ratios in giant, heavy oil deposits may reveal clues to, and the nature of the alteration processes affecting the original petroleum. By isotopically examining components such as carbonate cement, dissolved bicarbonate ion, water, methane, and carbon dioxide gas the genetic relationship between the components becomes clearer. The role of each component during biodegradation will become clear, and their importance determined.

The results of stable isotope techniques will elucidate the biodegradation process that led to the formation of heavy oil deposits. The carbonate cements, previously established as among the most enriched known (Dimitrakopoulous & Muehlenbachs 1985) can be investigated, and explained in light of biodegradation. The relationships of cement, dissolved bicarbonate and carbon dioxide will be examined. How does one phase relate to the others? Can a common origin be found?

The isotopic signature of methane should reveal whether it was biologically or thermally generated. If biogenic origins are indicated, any connection to carbon dioxide (and eventually heavy carbonate) will be traced. Does methane generation involve carbon dioxide? If so, in what way are the two gases related?

Are the isotopic signatures of formation waters mirrored by cements and/or methane? What type of equilibrium, or non-equilibrium, conditions exist? What ties all these phases and their isotopic compositions together? Can biodegradation account for this, or will another mechanism be needed to explain alteration of petroleum?

Answers for all these question will be found through stable isotope studies. The degree, timing and nature of the alteration can be determined, and comparisons to modern day activity made. A mechanism of formation for each phase will be proposed.

Previous Work

Crude oil alteration by subsurface waters is well known, and has been widely investigated (Welte 1967; Bailey et al. 1973; Evans et al. 1971; Jobson et al. 1972, 1979; and others.) Examination of alterated oils has revealed that bacterial, physical, and chemical processes of a widely varying nature can work alone or in complex combinations yielding the bitumen remaining today (Bailey et al. 1973). Alteration, which may occur at the site of petroleum origin, during migration, or after entrapment, results in higher specific gravity, viscosity and pour point; higher nitrogen and sulpher content; and higher optical activity than the precursor. Alteration may result from thermal maturation; gas deasphalting; water action via water washing (which removes light hydrocarbons), inspissation (evaporation of gases), or oxidation; and/or biodegradation (Milner et al. 1977).

Carbon-13 rich diagenetic carbonates have been reported by other authors (Murata et al. 1969; Nakai et al. 1975; Deuser 1970; and others), although not in association with heavy oil deposits. The Alberta deposits are the first reported case of heavy oils and carbon-13 rich carbonates occurring together. Diagenetic carbonates associated with conventional oil pools generally have very low $^{13}C/^{12}C$ ratios (Donovan 1974).

Stable isotope studies in Alberta have been confined primarily to the Athabasca deposit, but some Cold Lake carbonates were analyzed by Dimitrakopoulous and Muehlenbachs (1985). These authors related enrichment trends to depth through and spatial distribution surrounding heavy oil deposits. Alberta deposits have been compared to other world occurrences of heavy oil and found unique in their carbon-13 enrichment (Appendix I).

B. STUDY AREA

The Cretaceous sediments in Alberta, contained in the Western Canada Sedimentary Basin, are a well known host of heavy oil deposits. The deposits contain upwards of 1000 billion barrels of crude oil, and cover an area greater than 90,000 square kilometres (Hills 1974). Forming a broad discontinous arc across northern Alberta, the major deposits begin with Peace River, continue eastward through Wabasca and Athabasca before turning south through Cold Lake and Lloydminster. Several smaller deposits continue the trend along the Alberta-Saskatchewan border through Chauvin, Provost and Suffield until they peter out in northern Montana. (Fig. 1 after Hills 1974). The four largest contain the majority of the oil.

Nearly all the deposits are located in Cretaceous strata, mostly in the Mannville Group, with a few situated in the overlying Lower Colorado Group (Jardine 1974; Deroo et al. 1977) One or two pools in Saskatchewan are found in Mississippian (Bakken) sands. The deposits are all found at shallow depths and associated with topographic highs in the underlying Paleozoic unconformity. Original trapping occurred via stratigraphic and structural means (Fig. 2).

C. ORIGIN OF OIL

The bitumen presently comprising the heavy oil deposits is the remnants of supergiant conventional oil pools (Deroo et al. 1977; Rubenstein et al. 1977). The crude oil giving rise to these pools is thought to have originated deeper in the basin (Deroo et al. 1977), and migrated to its present position before being altered by various means to the bitumenuos tar seen today. Ages of origin, migration, and emplacement are unknown but obviously post-Cretaceous. The timing of degradation was after emplacement, although how closely remains unknown. Some clues can be gleaned to broadly fix alteration, but the exact age has not yet been

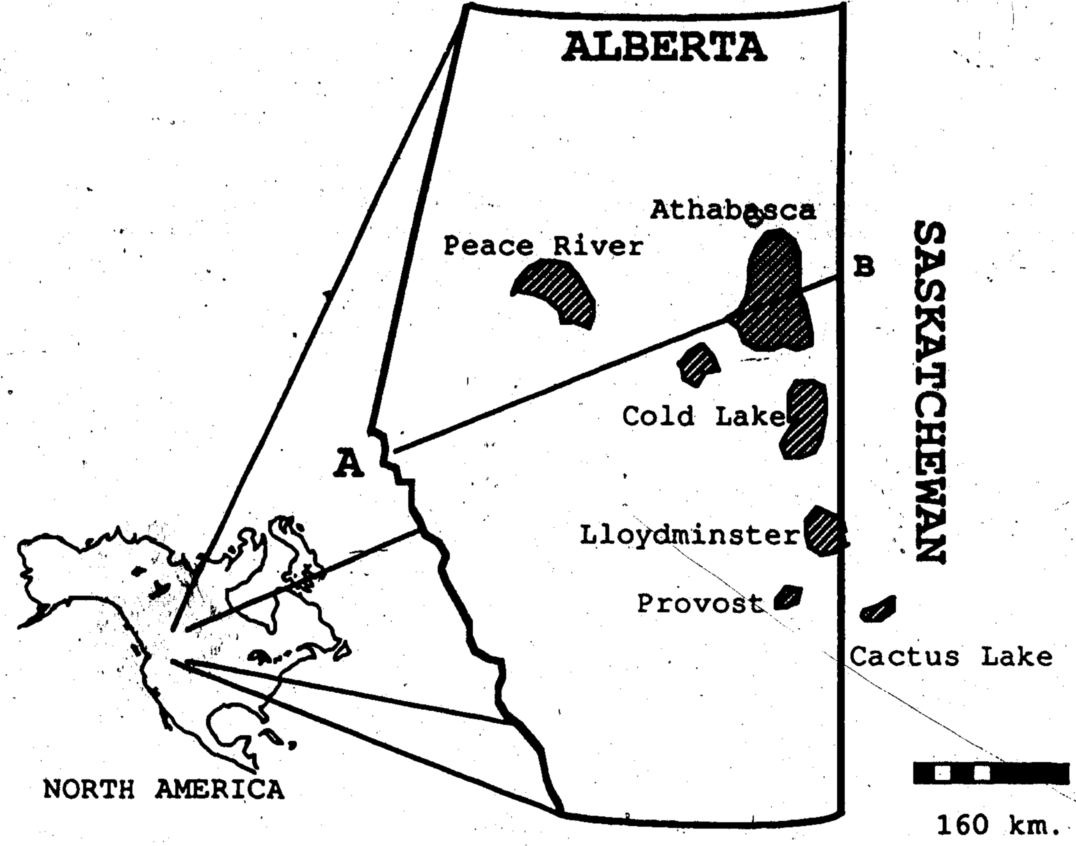


Figure 1: Location map showing Lower Cretaceous heavy oil deposits in Alberta and Saskatchewan.

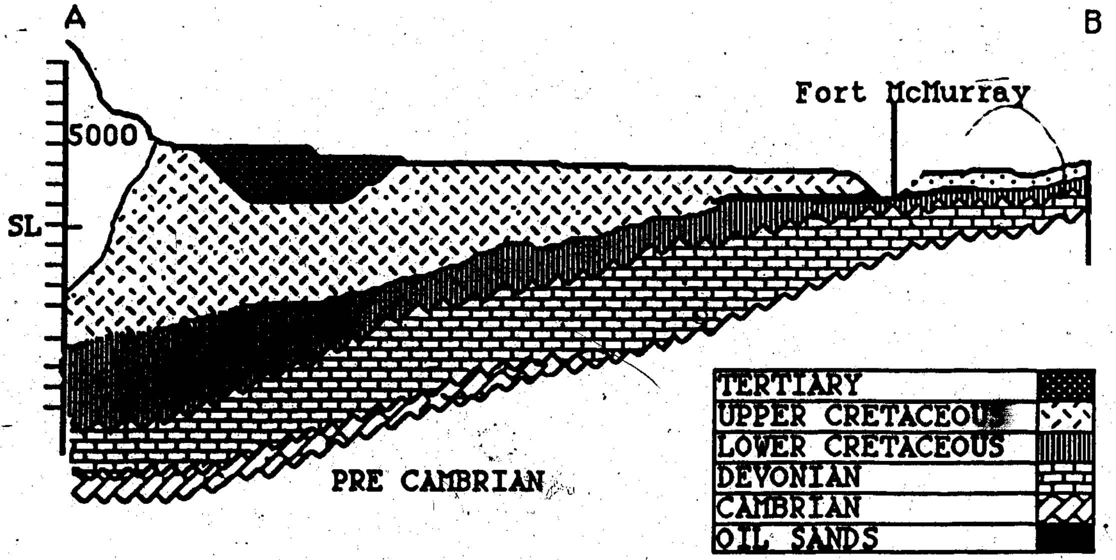


Figure 2: Cross section of Alberta through the Athabasca deposit.

determined.

D. GEOLOGICAL HISTORY

The tectonic setting responsible for the Lower Cretaceous sedimentation was established in the late Jurassic. Due to uplift of the Western Cordillera via the Nevadan orogeny, eastward drainage and sediment movement was initiated. Drainage was eastward across western Alberta, and northerly in eastern Alberta towards the Boreal Sea. Since most of the area west of the Canadian Shield was emergant a major erosional event started, resulting in removal of several thousand metres of sediment. A series of resistant topographic highs was created in the Devonian and Mississippian limestone covering most of the basin. These ridges trend northwest-southeast across northeastern British Columbia, north central Alberta, and southwestern Saskatchewan. Relief along them may reach 150 metres (Rudkin 1965; Jardine 1974).

By early Cretaceous sediment was supplied from the proto-Cordillera, and the emergant Canadian Shield to the east. Throughout the Cretaceous the ridges controlled an extensive river system which in turn enhanced relief and definition of the ridges. This drainage system was responsible for sediment transport and deposition.

In the Aptian, a slow eustatic rise of the oceans began, initiating interplay between fluvial, and marine deposition environments. This initial transgression was the forerunner of a complex transgressive-regressive series culminating with deposition of open marine shales in the Albian and Cenomanian.

E. STRATIGRAPHY AND SEDIMENTOLOGY

The rising marine influence and continued fluvial deposition have left the Lower Cretaceous sediments in Alberta a confusing and complicated sequence. There have been many attempts at unravelling and separating the various formations, groups, and members (Vigrass 1977; Putnam 1982). Basically the Lower Cretaceous is divided into the Lower and Upper Mannville, and the Lower Colorado Groups. In this report a simple stratigraphic column is employed. (Fig. 3 after Vigrass 1977; Putnam 1982; Gross 1982; Ducharme & Murray 1982).

Athabasca

As shown the Athabasca deposit contains four formations. The Lower Mannville Group unconformably overlies the Devonian limestone and constitutes the McMurray Formation. The McMurray Formation has been divided into Lower, Middle and Upper Members. Depositional environments are:

1. Lower McMurray Member - fluvial channels and floodplain;
2. Middle McMurray Member - estuary, marginal marine with fluvial influence;
3. Upper McMurray Member - estuary to nearshore marine

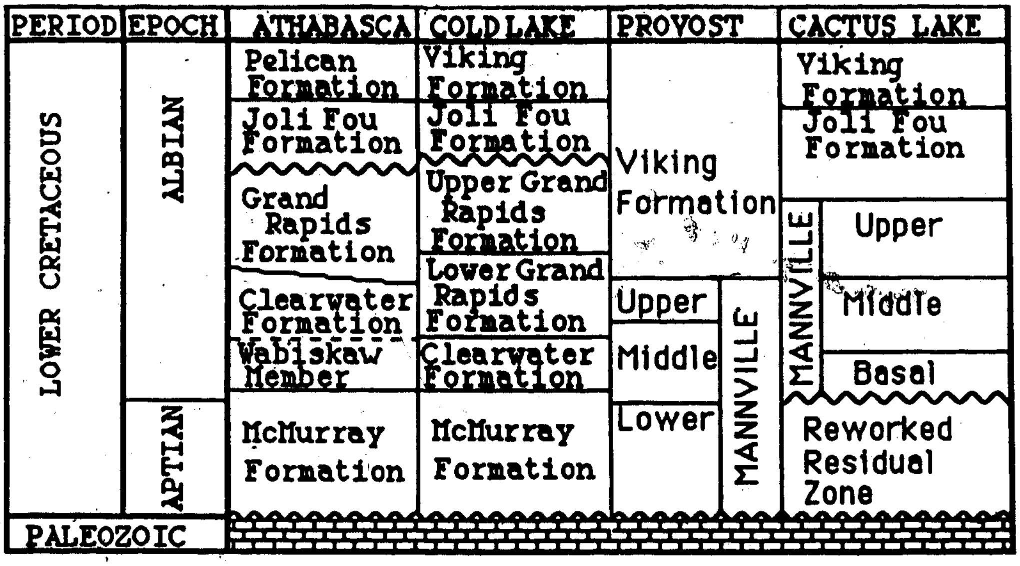


Figure 3: Stratigraphic column for the deposits studied (after Vigrass 1977).

varying from drowned channel to shoreface and offshore (Flach & Mossop 1985; O'Donnell & Jodrey 1984). The McMurray Formation has been investigated thoroughly as this is where most of the oil saturated zones occur. It shows an overall transgressive sequence with small transgression-regression cycles found throughout the formation.

Overlying the McMurray Formation is the Wabaskaw Member, a glauconitic, marine sand, and the shale Clearwater Formation. These are indicative of open marine conditions. The overlying Grand Rapids Formation is a mixture of marine and non-marine sands and shales. The entire succession is capped by the open marine Lower Colorado Group, the Joli Fou and Pelican Formations, a series of deep water shales.

During the transgression-regression sequences, the marine boundary seems to have been located in the Athabasca Tar Sands area. Indeed, great debate rages as to whether a fluvial, fluvio-lacusterine, fluvial esturine, or tidal channel-esturine environment dominated (Flach & Mossop 1985; Mossop & Flach 1983; Stewart 1981; and Nelson & Glaister 1978). Despite debate, a fluvial setting heavily influenced by marine conditions existed. Most of the heavy oil sands are closely associated with channels, bars, and (river) sand lenses of some type.

Cold Lake

At Cold Lake the Mannville sediments are divided into two parts, the Lower Mannville Group being comprised of the

McMurray Formation while the Upper Mannville Group is the Clearwater, Lower and Upper Grand Rapids Formations. The McMurray Formation, confined mostly to the Paleozoic lows, is discontinuous, sporadically distributed, and lens shaped. It is a non-marine sandstone.

The Clearwater Formation sands are massive, continuous, and contains most of the oil. It is a marine sequence ranging from 7 to 65 metres in thickness and may be interbedded with shales. The Upper and Lower Grand Rapids Formation each contain significant oil thicknesses. They are a non-marine sequence of coarse and fine grained sandstones interbedded with coal horizons.

Lloydminster

Although there are no samples from the Lloydminster area in this study, its geology is included because it has been studied in detail. Understanding this pool helps decipher the smaller, less-well studied pools located to the south and east.

In the Lloydminster area the Mannville Group is divided into nine informal formations. The Lower Mannville equates to the Dina Member. The Cummings, Lloydminster, Rex, General Petroleums (G.P.), and Sparky Members are the Middle Mannville, while the Waseca, MacLaren, and Colony Members comprise the Upper Mannville.

The geology of the Lloydminster area is very complicated due to the extreme lateral and vertical facies variations. The assemblege consists of seemingly random juxtaposed sandstones, siltstones, shales, and coals (Putnam 1982). Again, since the sandstones are the oil bearing horizons they have been studied carefully, especially the Sparky and G.P. Members. Lesser amounts of oil are found in the Cummings and Lloydminster Members (Middle Mannville Group), and the Upper Mannville Group.

The Lower Mannville Group sandstones are tabular bodies infilling lows in the Paleozoic unconformity. They are fairly widespread, coarse grained and generally interpreted as fluvial, valley-fill deposits (Putnam 1982).

The Middle Mannville Group is generally a series of medium grained sheet sandstones with thick, lenticular, and ribbon sandstones and shales randomly interspersed throughout. Shales become more prevalent near the top of the section, with the Sparky being primarily a shale unit with a few glauconitic sandstone interbeds. The Middle Manville is interpreted as a nearshore to offshore sequence (Vigrass 1977). The ribbon sandstones represent some type of tidal channel or tidal creek deposits (Putnam 1982). Most workers agree that maximum marine conditions occurred during Middle Mannville.

The Upper Mannville Group, comprised mainly of ribbon sandstones with fewer sheet sandstones is thought to indicate a return to mainly fluvial conditions (Vigrass 1977; Putnam 1982). This interpretation is based on the scoured erosional features presented by the sands. Topping the whole sequence are the Colorado Group Shales, a thick marine succession indicating yet another major transgression.

Provost

The portion of the Provost oil field studied is also contained in Mannville sediments. It is similar to the Lloydminster deposit, being a series of stacked channel fill and sheet sands. The Lower Mannville contains most of the oil in enormous sand filled channels incised into the Paleozoic bedrock. They are quite thick, and may stretch for several kilometres before being truncated.

There are channel and sheet sands at all levels, different 'members' are separated by thin coal beds. Relative proportions of channel to sheet sand bodies are also used to determine 'members' and depositional environments (Gross 1982). Rigorous use of the Lloydminster names is tenuous owing to the great facies variance, and distance separating the deposits.

The Provost sands are interpreted as successive erosional drainage channels, which cut into pre-existing paralic sands (ibid). This implies a series of transgressive-regressive episodes over the area repetitively drowning an established river system. If these marine events can be correlated to those in other deposits further north the whole area must be one of low relief and gradual slopes.

Cactus Lake

The Cactus Lake heavy oil pool is ninety kilometres south and east of Lloydminster. It is unique to this study as it is the only deposit located in both Mississippian and Cretaceous sediments. The heavy oil is located in the Bakken Formation, a three member Paleozoic sequence. The depositional environments envisaged are:

1. lowest (Exshaw) shale - shallow marine basin;
2. middle (Coleville) sandstone - tidal flat and sand ridge/bar;
3. top (Upper) shale - shallow offshore shale (Ducharme & Murray 1981).

Overlying the Bakken Formation is the Residual Zone, a detritus layer comprised of chert fragments intermixed with clasts of various other sedimentary rocks (White 1974). It is highly variable in both content and occurrence over this area. Designated as a non-marine deposit of reworked underlying material, it has not been transported for any great distance (White 1974).

The Basal Mannville sand sits unconformably above the Residual Zone. It is considered a marine coastal sand deposited on the Cretaceous unconformity (Ducharme & Murray 1981). They postulate the Basal Mannville Member may in fact be the G.P. Member of the Middle Mannville Group. Due to its stratigraphic position and sedimentary environment there is merit to this theory.

The Middle Mannville members, mostly absent due to non-deposition, are very thin and poorly described. The Upper Mannville members, though present, are not well documented. The Mannville Formation is overlain by the Lower Colorado Group as expected.

II. BACKGROUND AND PREPARATION

A. BACKGROUND OF ISOTOPES

Introduction to Isotopes

Stable isotope geochemistry has been focussed on light elements and their isotopes: hydrogen (^{1}H, ^{2}H), carbon (^{12}C, ^{13}C), nitrogen (^{14}N, ^{15}N), oxygen (^{16}O, ^{18}O), and sulfur (^{32}S, ^{32}S). There are several reasons these elements have been investigated so thoroughly:

1. they are the most commonly occurring elements,
2. they occur in relatively great abundance in nearly all terrestrial compounds,
3. they are very important in biological systems,
4. they participate in a wide variety of geochemical reactions,
5. their relative concentrations can be measured with analytic errors much smaller than natural variations (Fritz & Fontes 1980).

Measurement of isotopic concentrations coupled with comparisons to internationally recognized standards allows geochemists to reach conclusions based on isotopic analyses.

In order to measure isotopic concentrations geochemists employ ratios of the isotope of interest (the heavier one) versus the most commonly occurring (lighter) isotope. Ratios are used because measuring absolute amounts of isotopes is difficult owing to the very small amounts of heavy isotopes.

The ratios are expressed in the form:

$$R = N_1/N \qquad \text{Eqn. 1}$$

where N_1 = isotopes of interest, and N = the most commonly occurring isotope. In order to understand, and utilize, the isotope ratio of a substance under scrutiny a comparison expression is used:

$$\delta x = (R_2/R_3 - 1)1000 \qquad \text{Eqn. 2}$$

R_2 is the isotopic ratio of the sample and R_3 is the isotopic ratio of a suitable standard. The δ-value is expressed in per mill (°/₀₀ or parts per thousand) as the numbers are more convenient to use in this form. So, for a carbonate sample Equation 2 becomes:

$$\delta Car. = ((^{13}C/^{12}C_2)/(^{13}C/^{12}C_3) - 1)1000 \qquad \text{Eqn. 2a}$$

Oxygen isotopes are expressed $^{18}O/^{16}O$, while hydrogen isotopes are given D/H.

Standards

The standards used in stable isotope geochemistry are internationally recognized. Oxygen-18 and deuterium are reported versus v-SMOW, an artificial Standard Mean Ocean Water, distributed by the International Atomic Energy Agency in Vienna. By definition $\delta^{18}O$ = 0 °/₀₀, δD = 0 °/₀₀ in v-SMOW standard. Carbon-13 is reported versus PDB, a marine carbonate standard derived from a Bellemnite americana from the Pee Dee Formation found in the southern United States. Again by definition $\delta^{13}C$ = 0 °/₀₀ for the PDB standard, for $\delta^{18}O$, 0°/₀₀ on the PDB scale is +30.86 °/₀₀ on the v-SMOW scale, whereas 0°/oo v-SMOW is -29.94°/oo PDB.

The reason for the difference between the oxygen-18 in water and carbonate has to do with atomic kinetics, whe[illegible] the heavier isotopes tend to favour the more stable, ordered phase. Hence carbonate in isotopic equilibrium with water is enriched in oxygen-18 by approximately 30 °/oo, depending on the temperature of formation of the carbonate.

During the course of the thesis, all oxygen and deuterium isotope ratios are reported compared to the v-SMOW standard. All carbon isotope ratios are reported versus the PDB standard.

Fractionation of Isotopes

Obviously, since isotopic ratios and comparisons to standards are important, there must be some processes or reactions which alter isotope concentations within a medium of interest. Indeed all chemical reactions, and physical transformations involving minerals, water and organic species result in isotopic fractionation to some degree. The most important ones are kinetic effects during reactions or biological processes causing isotopic fractionation. Fractionation can occur in simple reactions, such as water evaporating from the ocean, yielding water vapour having $\delta^{18}O$ = -7 °/oo (v-SMOW), or in complex photosynthesis which leaves organic matter with $\delta^{13}C$ from -22 to -35 °/oo (PDB).

Similarily other processes like carbonate dissolution and/or reprecipitation, weathering of minerals into clays, rain or snow fall, coral and shellfish growth, transformation of organic debris into crude oil, biogenic formation of methane, breakdown of carbohydrates, and burning of fossil fuels all entail isotopic fractionation. By examining the range of fractionation between two (or more) phases of interest, the reactions giving rise to the fractionation can be determined. Since the extent of all commonly occurring fractionations have been measured, the reconstruction of past events, from an isotopic vantage, is possible.

B. ISOTOPES OF INTEREST

As mentioned, stable isotope studies of phases associated with heavy oil deposits help unravel their origin and history. Geochemical and isotopic studies are routinely performed in petroleum research in order to reconstruct the source, generation, migration and alteration history of hydrocarbons (Fuex 1977). Other useful information that may be gained from stable isotope techniques are recognition of bacterial degradation, maturity of methane producing sources, characterization of, and differentiation between various crude oils (Stahl 1977). So, since different processes affect different elements, through isotopic examination, the geologic history of an oil pool can be pieced together.

Analysis of three isotope pairs, $^{13}C/^{12}C$, $^{18}O/^{16}O$, and D/H will elucidate the history of the deposit under study.

Examination of the system water-cement-dissolved bicarbonate -gas will reveal method of, conditions present during, and timing of alteration. Ultimately, greater understanding of formation and emplacement of tar sands will be gained.

Carbon

Analysis for $\delta^{13}C$ of cements, dissolved bicarbonate ions, carbon dioxide, and methane will help resolve several problems. Firstly, what is the source of carbon in the cement and dissolved bicarbonate? The $\delta^{13}C$ of each will distinguish between either dissolution of pre-existing carbonate, or a source of new carbon dioxide such as the biodeg[illegible]tion or inorganic oxidation, as giving rise to these phases. If the first case exists isotopic equilibrium between cement and bicarbonate will be recognizable; if the second case is true then no equilibrium will be found.

Secondly was carbon in the carbon dioxide and methane in isotopic equilibrium and, if so, were they generated simultaneously? If they are in equilibrium, differences in $^{13}C/^{12}C$ of methane and carbon dioxide may reflect the temperature of formation for the gases, and by extension the carbonate cements. Again, what is the source of carbon in the gases? Source of carbon in the gases will be indicated by their $\delta^{13}C$, The degree of the isotopic fractionation will pinpoint the process that gave rise to them.

Oxygen

Oxygen isotope ratios of the cements and formation waters indicate the history of the deposits. The $\delta^{18}O$ of waters will identify whether formation waters are predominantly connate or meteoric. By comparing the $^{18}O/^{16}O$ of the water and the cement, the state of equilibrium, or non-equilibrium, conditions is established. If equilibrium exists the cements formed late in the deposit's history. If non-equilibrium is found then the cements formed before the present waters infiltrated. This will give a rough idea of the timing of alteration. The changes, if any, in the source of the waters with time will also become apparent when the $\delta^{18}O$ of the cements are measured, since oxygen-18 incorporated into the carbonate is assumed to equilibrate with water prior to precipitation.

Deuterium

Deuterium ratios of water and methane are helpful in several ways. Firstly they help determine present day formation water origins. The δD of methane also indicates its origins. By comparing D/H of methane to D/H of formation water, the process of methane formation becomes clearer (Schoell 1980). Is biodegradation, sulfate reduction, or thermal cracking the formation process? What, if any, isotopic equilibrium conditions were present during methane formation? Measuring the D/H of the phases will answer these queries.

As is usual in isotopic studies comparisons with other workers data are included. In order to understand the ratios collected for this thesis the work of other authors is incorporated.

C. SAMPLE ACQUISITION

Source

In order to obtain samples for research several oil companies were approached. Of these Esso Resources, Murphy Oil and Gas, and Petro-Canada all of Calgary; and Syncrude Ltd. of Edmonton supplied material. Samples from Athabasca, Leming (Cold Lake), Lindbergh, Provost and Cactus Lake were provided. They consisted of:

1. primary formation waters, from wells that had been producing for several months in order to avoid drilling fluid contamination of the samples;
2. core samples from various wells, usually an attempt was made to match water samples and core;
3. gas samples which were obtained from heavy oil deposits with enough gas present to sample without difficulty.

In all over fifty samples of all types were received.

Esso Resources supplied water and gas samples from producing wells at their Cold Lake project. The water samples were collected in 250 millilitre bottles from dewatering drums at the well-head. Gas samples were collected in 500 millilitre gas cylinders at operating temperatures and pressures.

Murphy Oil provided water from separator tanks (near well-head) in sealed one litre bottles, from which bicarbonate ion was precipitated. They also sent plug samples (3 cm. by 3 cm. by 6 cm.) of oil sand ore. All samples were from Lindbergh, a southern extension of the Cold Lake deposit.

Petro-Canada sent suites of waters from both Provost and Cactus Lake (Saskatchewan Heavy Oil Project or SHOP) deposits. One litre bottles were used, with the samples taken from separator tanks. Bicarbonate ions were precipitated from both suites.

Syncrude's Edmonton office supplied powdered carbonate cement samples from several drill holes located on their oil lease in the Athabasca heavy oil deposit. In addition six water samples were collected by the author. Bicarbonate ions were precipitated from these samples also.

D. TREATMENT

Water

All water samples were treated in two ways. First they were analyzed for oxygen-18 according to the technique described by Epstein and Mayeda (1953). Approximately ten millilitres of water were pipetted into sample tubes. All gases originally present were removed by alternately freezing the samples in a dry ice/alcohol bath, evacuating the gases and thawing again. The cycle was repeated twice, excepting gas rich samples which required a third cycle, to ensure complete degassing.

Following degassing an aliquot of carbon dioxide, ranging from eight to twelve millilitres (3.59 X 10^{-4} to 5.39 X 10^{-4} M), of known isotopic composition was frozen in. The samples were placed in a shaker bath of water to equilibrate at 25.3°C for a minimum of twelve hours. After equilibration the carbon dioxide was extracted by freezing the gas into a sample tube. Isotopic ratios of oxygen-18 were measured on a V. G. Isotope (Model 602D) mass spectrometer.

Secondly D/H were determined using the method of Friedman (1953). Very small (10-20 microlitre) samples of water were injected into a vacuum line, and reduced by passing the vapor through an uranium oven at 800°C. The resulting hydrogen was pumped into sample tubes using a Toepler pump, and analyzed on a second V. G. Isotope mass spectrometer.

In addition 250 millilitres of each water sample were reacted with approximately 160 millilitres of 1.0 M barium chloride solution in order to precipitate any dissolved bicarbonate ion. Precipitation, in sealed vessels, was allowed to continue for six to fourteen hours depending on yield. Smaller yeilds were reacted longer in order to extract the maximum amount of bicarbonate from solution. The precipitate was filtered through 0.7 micron filter paper and dried in an oven at 110°C for four to six hours. After drying and degassing the samples were powdered, and portions weighed for reaction and analysis. Sample sizes of 0.5 to 1.5 grams were used.

The weighed samples were placed in two chambered reaction tubes with 100% phosphoric acid in one chamber, and precipitate in the other. Following twelve hours of outgassing on a vacuum line the tubes were placed in a 25.3°C bath, and the reactions started by mixing the acid and precipitate. Immersion of the reaction tubes in the bath ranged from eight to fourteen hours to ensure the complete reaction took place at constant temperature. The carbon dioxide released was frozen out via liquid nitrogen and the non-condensible gases purged. The carbon dioxide was transferred to sample tubes for analysis on the mass spectrometer. Both $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios were recorded.

Cements

The carbonate cements were contained in plug samples of heavy oil ore, necessitating separation of cement and bitumen prior to analysis. Ten gram portions were separated for cleaning and any consolidated samples were pulverized. Cleaning involved soaking weighed samples in organic solvents such as chloroform, acetone and/or methanol. Usually six and ten washings in chloroform removed all the bitumen. Samples containing more bitumen required two more washings. Clean samples were dried in a vacuum oven for at least twelve hours to remove any traces of chloroform.

After drying, two to three gram samples of sediment and cement were placed in reaction tubes as before. Experience dictated sample size as cement was poorly developed in most cores, resulting in low carbon dioxide yields. Reaction, immersion in a constant temperature bath, and collection followed described procedures.

Six powdered samples from Athabasca were treated simply by weighing 0.5 gram samples and treating them as above, since no cleaning or crushing was required. All carbonate samples were anaalyzed for both $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios.

Gases

The six gas samples were collected in 500 millilitre cylinders by the author. Three were from gas producing wells, two were vent gases from heavy oil wells undergoing steam injection, and one was from an observation well. Production well gas was assumed dry and combosted without treatment, whereas vent and observation well gases were passed through a dry ice/alcohol trap to ensure they were dry.

Gas samples were combusted in a flow-through oven at 800°C. A quartz tube was packed with copper oxide, and platinum to act as a catalyst. The ends were stoppered with glass wool. Samples of 50, or 75 millilitres were injected through a septum at one end, and a liquid nitrogen trap collected carbon dioxide and water vapor after combustion.

Samples were run to completion, monitored by a very accurate pressure gauge.

Once combustion was complete the water and carbon dioxide were separated and cleaned. The water was reacted with uranium while the carbon dioxide was analyzed without further treatment to measure the isotopes of interest.

III. RESULTS

In this chapter the data generated for this study are presented. The isotope data, listed area by area, will be explained, the significance of the ratios of different phases examined, relationships of phases to each other as highlighted by isotopic data are discussed. In addition other information gleaned, such as equilibrium conditions, timing of alteration and isotope sources are explained.

Athabasca

The Athabasca samples, provided by Syncrude, consisted of water, precipitated bicarbonate, and carbonate cement. The waters were colllected from dewatering wells around the open pit perimeter, bicarbonate ions were precipitated as described earlier. The powdered carbonate samples were provided by A. Brack.

The isotope ratios for the waters fall within two distinct groups each showing good internal consistancy. The first group, KLR TW 23 to 26 have average ratios of $\delta^{18}O = -24.2 \pm 0.4$ $^{o}/_{oo}$, $\delta D = -187.9 \pm 2.3$ $^{o}/_{oo}$, while the second, KLR TW 27 and 28, have averages of $\delta^{18}O = -21.0 \pm 0.2$ $^{o}/_{oo}$, $\delta D = -167.3 \pm 1.1$ $^{o}/_{oo}$. These are very close to ratios reported by Wallick and Dabrowski (1982) for two aquifers in the Athabasca deposit. They reported the Methy Aquifer, located beneath the Prairie Evaporite, as having average ratios of $\delta^{18}O = -24.1 \pm 0.4$ $^{o}/_{oo}$, $\delta D = -173.0 \pm 4.9$ $^{o}/_{oo}$. Waters in the Basal Aquifer, found in the McMurray

Formation, average $\delta^{18}O = -21.4 \pm 1.3$ °/oo, $\delta D = -158.3 \pm 8.2$ °/oo. It would seem samples from both flow systems were obtained for this study.

TABLE I: Isotopic analyses of samples from the Athabasca heavy oil deposit.

FORMATION WATER			Ba(OH)$_2$ PRECIPITATE	
Sample No.	$\delta^{18}O$	δD	Sample No.	$\delta^{13}C$
KLR TW 23	-23.91 -23.86	-186.2	KLR TC 23	+20.92
KLR TW 24	-24.07	-186.8 -186.6	KLR TC 24	+20.89
KLR TW 25	-24.24 -24.19	-188.3	KLR TC 25	+22.75
KLR TW 26	-24.92	-191.7	KLR TC 26	+20.24
KLR TW 27	-20.77 -20.86	-166.5	KLR TC 27	-- --
KLR TW 28	-21.21	-168.1	KLR TC 28	+15.90

Water reported vs. v-SMOW, precipitate vs. PDB standards.

The first group of waters (KLR TW 23 to 26) plot on the meteoric water line when a modified 'North American' equation is applied (Fritz & Fontes 1980, p.32). (Figure 4) These waters are substantially lighter in both oxygen-18 and deuterium than modern day meteoric water ($\delta^{18}O = -23$ °/oo, $\delta D = -165$ °/oo v-SMOW). This difference between the $\delta^{18}O$ and δD values in the two waters shows they are not related, that is the Methy Aquifer does not contain modern meteoric water. The depleted nature of waters KLR TW 23 - 26 imply the aquifer was recharged under colder climatic conditions, possibly during the the Pleistocene or earlier (Wallick &

Dabrowski 1982).

The other waters (KLR TW 27 and 28), presumeably Basal Aquifer samples, plot slightly off the meteoric water line. KLR TW 27 and 28 have $\delta^{18}O$ = -21.0 ± 0.2 °/oo, δD = -167.3 ± 1.1 °/oo, Basal Aquifer waters average $\delta^{18}O$ = -21.4 ± 1.3 °/oo, δD = -158.3 ± 8.2 °/oo, and present day meteoric water have $\delta^{18}O$ = -23 °/oo, δD = -165 °/oo (v-SMOW). These groundwater samples closely resemble meteoric water, so recharge is fairly rapid. The variation in isotope ratios could be due to seasonal variations of input, since winter precipitation is isotopically depleted compared to summer rainfall.

The $\delta^{13}C$ of dissolved bicarbonate are extremely high with KLR TC 23 to 26 having $\delta^{13}C$ ranging from +20.24 to +22.75 °/oo (PDB), and KLR TC 28 having $\delta^{13}C$ = +15.90 °/oo (PDB, TABLE I) The precipitated bicarbonate $^{13}C/^{12}C$ follows the same pattern as $\delta^{18}O$ of waters, showing different isotopic signatures depending on the water group examined. The $^{13}C/^{12}C$ of KLR TC 23 - 26 group is 5 - 6 °/oo higher than KLR TC 28.

These high ^{13}C waters are being pumped from the oil sands and the bicarbonate ratios reflect carbon dioxide produced in the deposit. The only source of carbon appears to be the bitumen ($\delta^{13}C \simeq -30$ °/oo) so a complex mechanism of formation is required for generation of enriched carbon dioxide from such a precursor.

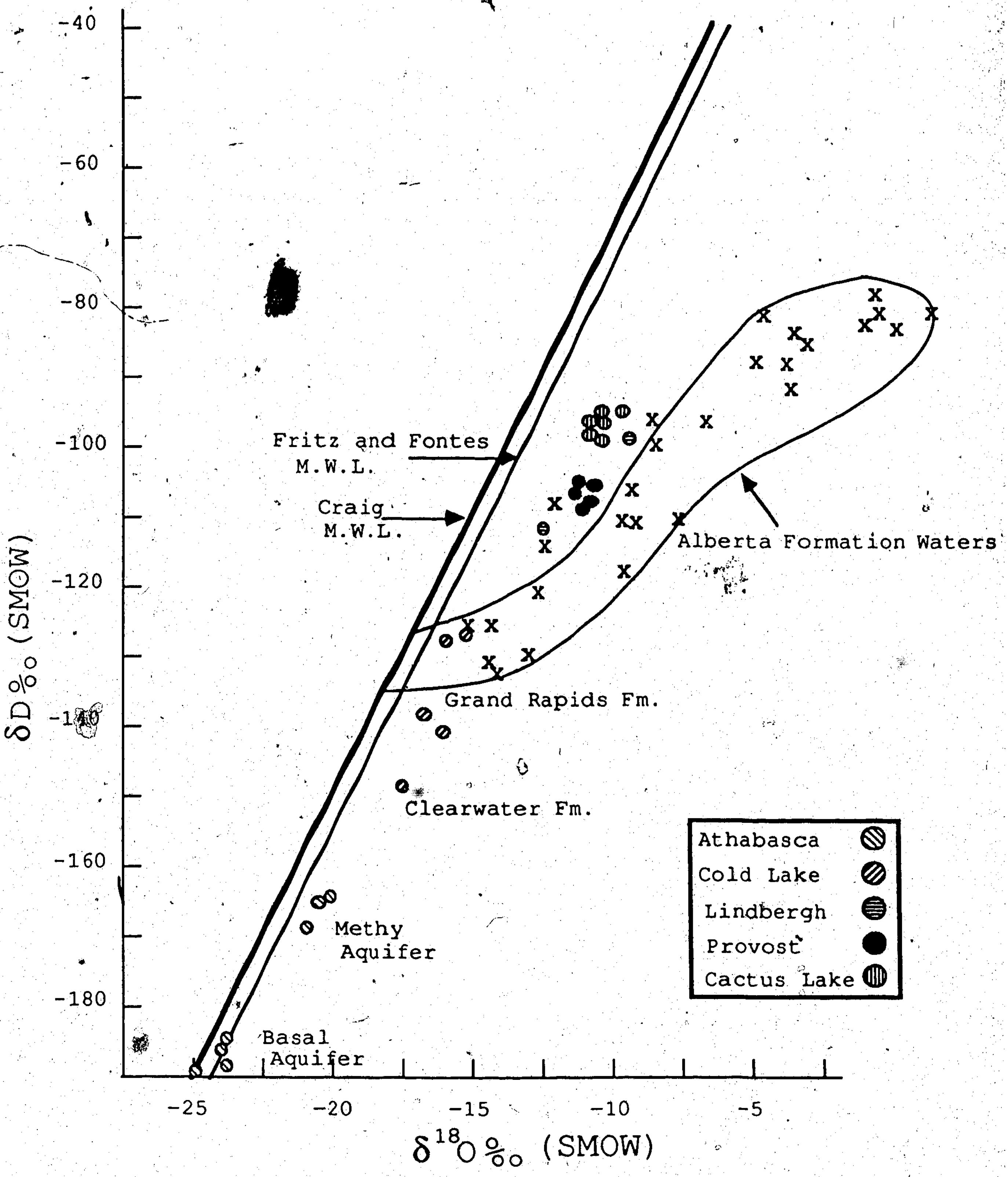


Figure 4: Plot of meteoric water lines of Craig (1961) and Fritz & Fontes (1980), with isotopic ratios of formation waters from this study.

The first group of precipitated carbonate, KLR TC 23-26, are (if the assumption of ancient waters is correct) strong evidence that the process responsible for enrichment of carbon-13 has been occurring for a long time. The lower ratio of KLR TC 28 probably result from the mixing of bicarbonate from two sources. Modern recharge, while replenishing the groundwater, has to pass through a considerable thickness of muskeg, which is largely composed of rotting organic matter. Carbon dioxide derived from organics has a $\delta^{13}C$ of -25 to -30, so mixing this carbon dioxide with petroleum derived carbon dioxide will lower the $^{13}C/^{12}C$ of the dissolved bicarbonate. If any precipitation is occurring the resultant carbonate will be isotopically heavier than its predecessor, while the remaining dissolved bicarbonate will be lighter than the ions infiltrating originally.

TABLE II: Isotopic analyses of carbonate cements from the Athabasca heavy oil deposit.

Sample No.	$\delta^{13}C$	$\delta^{18}O$
KLR TC 17	+15.63 +15.08	+19.27 +19.02
KLR TC 18	+12.98	+19.01
KLR TC 19	+15.39	+19.24
KLR TC 20	+2.91 +2.94	+24.01 +23.42
KLR TC 21	+16.03	+18.91
KLR TC 22	+18.92	+18.54

$\delta^{13}C$ reported vs. PDB, $\delta^{18}O$ reported vs. v-SMOW standard.

The carbonate cements removed from core are also isotopically enriched but display lower $^{13}C/^{12}C$ than present day bicarbonate ions. Using calcite-bicarbonate equilibrium data (Emrich et al. 1970), at 10°C calcite should [illegible] 2.5 $^{o}/_{oo}$ enriched compared to co-existant bicarbonate. The difference at Athabasca is -5.53 $^{o}/_{oo}$, signifying the bicarbonate is heavier. Obviously the dissolved bicarbonate and cement are not in isotopic equilibrium, yet their uniquely high ^{13}C nature implies a common source.

Not only is the carbon not in equilibrium, but the oxygen-18 found in the cement is not in equilibrium with the oxygen-18 in the waters. Again using published data (O'Neil [illegible] al. 1971), the cements present in the Athabasca deposit formed in equilibrium with water with isotopic ratios of $\delta^{18}O = -12$ to -9 $^{o}/_{oo}$ depending on the temperature (from 5 to 20 °C). This is obviously neither seawater ($\delta^{18}O = 0$ $^{o}/_{oo}$) nor meteoric water presently found in the Athabasca area. The water is envisaged as connate, or modified seawater incorporated during sedimentation so these are diagenetic, not depositional, cements.

This implies the cements formed fairly early during the history of the Athabasca oil deposit. This is consistant with the model of biodegradation proposed for oil sand formation discussed later. In addition there seems to be no (or very limited) cement dissolution-reprecipitation in this area, or the two sets of $^{13}C/^{12}C$ data would be closer in value.

There is one anomolous carbonate sample, KLR TC 20, showing much different isotope ratios for both oxygen-18 and carbon-13. This particular sample, from both sedimentological (Brack pers. comm.) and isotopic data, must have formed from a mixture of bicarbonate ions. One source is the enriched bicarbonate, while the majority are bicarbonate ions derived from the underlying Devonian limestone. Mixing would lower the $^{13}C/^{12}C$ compared to the other samples. The anomolous $^{18}O/^{16}O$ ratio is due to the higher oxygen-18 of formation water which carried the dissolved limestone into its present position. Formation waters from the underlying Methy Aquifer are postulated as the carrier of the dissolved Paleozoic limestone.

Cold Lake

The Cold Lake samples, next most numerous, are water, precipitated bicarbonate, and methane, which reveal even more about the nature of heavy oil formation. The methane was collected from two sources, natural gas production wells and (enhanced recovery) heavy oil wells. The latter are called vent gases, and were taken from steam injection sites. Samples were taken from both the Clearwater and Grand Rapids Formations.

Oil field waters from Cold Lake also reveal two flow systems. This is not suprising since KLR TW 33 and 35 are from the Clearwater Formation; KLR TW 31 originated in the Grand Rapids. What is curious is that KLR TW 1 and KLR TW

35, being from the same well, show depletion with time of both oxygen-18 and deuterium. The samples were collected about two years apart. Bearing in mind the steam injection occurring in this area it would seem the formation waters have been mixing with the steam.

TABLE III: Isotopic analyses of samples from the Cold Lake heavy oil deposit.

FORMATION WATER Sample No.	$\delta^{18}O$	δD	$Ba(OH)_2$ PRECIPITATE Sample No.	$\delta^{13}C$
KLR TW 1 Clearwater	-17.31 -17.28 -17.23	-139.6	KLR TC 23	+19.53 +19.60
KLR TW 31 Grand Rapids	-17.48 -17.55	-149.3		
KLR TW 33 Clearwater	-15.65 -15.63	-129.6		
KLR TW 35 Clearwater	-15.44	-127.8		

Water reported vs. v-SMOW, precipitate vs. PDB standards.

Taken together, oxygen and deuterium data indicate water slightly shifted from the meteoric water line. Formation waters are generally shifted, so this is not unexpected. Cold Lake formation waters are just off the meteoric water line, close to the Alberta basin trend (Hitchon & Friedman 1969). Evolved formation waters generally plot quite far off the meteoric water line, since they tend to become enriched in both oxygen-18 and deuterium with time. In this case there must be a strong influence of 'evolved' formation water, mixing with injection steam which leads to greater depletion. As a result the waters plot close to the meteoric water line.

Unfortunately there was not enough water to precipitate bicarbonate ion, excepting the first sample, KLR TC 1. This sample shows extremely high ^{13}C enrichment, although not as high as the Athabasca deposit. Again a link to petroleum as the source of carbon in the dissolved bicarbonate must be postulated.

TABLE IV: Isotopic analyses of samples from the Cold Lake heavy oil deposit.

METHANE			FORMATION WATER	
Sample No.	$\delta^{13}C$	δD	Sample No.	δD
KLR TG 1	-61.69	-295.4	KLR TW 1	-139.6
Clearwater		-269.7	Clearwater	
		-269.2		
KLR TG 29	-48.11	-309.5		
Clearwater		-310.0		
KLR TG 34	-60.21	-323.6	KLR TW 35	-127.8
Clearwater	-57.48	-319.9	Clearwater	
KLR TG 36	-26.57	-316.6		
Clearwater	-24.90	-311.8		
KLR TG 37	-59.01	-337.6		
Clearwater		-60.80		
KLR TG 30	-58.85	-268.4	KLR TW 31	-149.3
Grand Rapids	-55.52	-269.8	Grand Rapids	

^{13}C ratios reported vs. PDB, D ratios reported vs. v-SMOW.

The $^{13}C/^{12}C$ and D/H in the methanes place them very close to depleted biogenic methanes reported by Schoell (1980). He proposed a $\delta^{13}C$ of -64 $^{o}/_{oo}$ as the defining value for pure, biogenic methane. There is, however, a scatter in

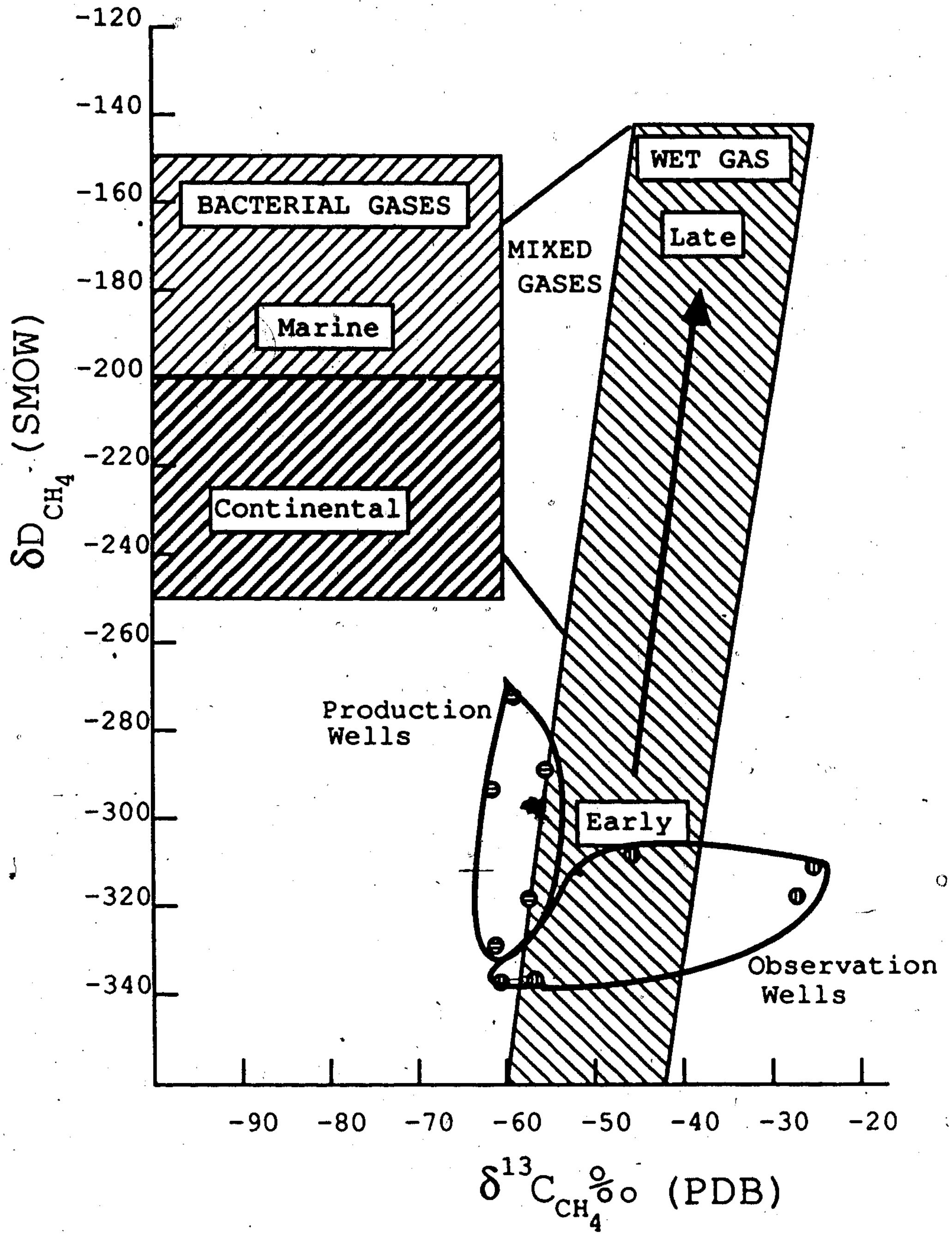


Figure 5: Plot of carbon and hydrogen variations in methane in natural gases from different origins (after Schoell 1980). Cold Lake data plotted for comparison.

the data, approximately 35 $^{o}/_{oo}$ for carbon-13 and 65 $^{o}/_{oo}$ for deuterium. The production wells (KLR TG 1, 30, 34) all lie very close to 'pure biogenic' gas values (Fig. 5 after Schoell 1980). Vent gases (KLR TG 29, 36) on the other hand, show a wider range of ratios. Vent gases generally have greater depletion of deuterium than production gases, and have relatively enriched $^{13}C/^{12}C$.

The higher $^{13}C/^{12}C$ of vent gas are attributed to steam injection. Injection probably triggers two processes. The first is thermolysis, whereby light gaseous hydrocarbons are driven off from heavy oil sands by heat. Laboratory experiments on tar sands have shown themolysis is effective at tempreatures as low as 25°C (Strausz et al. 1977, Jha et al. 1979). Methane produced had $\delta^{13}C$ = -39.3 and -43.0 $^{o}/_{oo}$ respectively in the studies. Both dealt with Athabasca tar sand bitumen with an average $\delta^{13}C$ = -29.6 $^{o}/_{oo}$.

In the Cold Lake deposit, steam injection could produce methane by thermolysis. Jha et al. (1979) state as time passed the kinetic isotope effect (between gases and bitumen) will lessen, so the methane should become progressively enriched. This mechanism may account for the relatively high $^{13}C/^{12}C$ seen in KLR TG 29 and 36, since the Leming Cold Lake deposit undergoes steam injection for as long as two months before the wells are pumped out. Such a long heating episode could free 'enriched' methane or other gases, which would raise the $^{13}C/^{12}C$ of the gases present.

Steam injection also seems to cause a release of carbon dioxide (See Table V). This carbon dioxide must be derived from either the carbonate cement (via dissolution), or from the dissolved bicarbonate ion, both of which are enriched in carbon-13. This enriched carbon dioxide mixes with the depleted carbon dioxide produced from methane combustion, leading to the relatively high carbon-13 ratios of the vent gases (KLR TG 29, 36).

TABLE V: Mole percentages of gas samples with $\delta^{13}C$ ratios from the Cold Lake deposit.

Sample No.	^{13}C	CH_4	CO_2	C_2+	O_2,N_2,CO
PRODUCTION GASES					
KLR TG 1	-61.69	98.01	0.49	0.05	1.46
KLR TG 30	-58.85	95.39	0.13	1.85	2.63
KLR TG 34	-60.25	91.25	0.45	0.13	8.18
KLR TG 37	-60.80	98.58	0.08	0.34	0.00
VENT GASES					
KLR TG 29	-48.11	76.72	18.09	~~0~~.47	4.73
KLR TG 36	-24.90	22.14	68.91	8.74	0.22

All $\delta^{13}C$ ratios reported vs. PDB standard.

Schoell (1980) states significant amounts of C_2+ gaseous hydrocarbons will raise $^{13}C/^{12}C$ and lower D/H in methane. The C_2+ factions are produced by abiogenic means. The mixture of carbon dioxide from different sources will also change the isotopic ratios, as explained. Some contamination of the methane is probable, accounting for the ratios listed in Table IV.

Lindbergh

The Lindbergh deposit, located eighty kilometres south of the Leming, Cold Lake area, is considered part of the same deposit. Unfortunately far fewer samples were received for analysis from this area.

TABLE VI: Isotopic analyses of water samples from the Lindbergh heavy oil pool.

Sample No.	$\delta^{18}O$	δD
KLR TW 2	-12.61	-110.6
KLR TW 3	-9.31	-98.6

Water ratios reported vs. v-SMOW standard.

The waters in this deposit lie slightly off the meteoric water line, again among the Alberta Basin formation waters (Hitchon & Friedman 1969). These have not been significantly affected by either meteoric water or steam injection as at Leming, but are envisaged as more or less typical Alberta formation waters.

TABLE VII: Isotopic analyses of carbonate samples from the Lindbergh heavy oil pool.

CARBONATE CEMENT			$Ba(OH)_2$ PRECIPITATE	
Sample No.	$\delta^{13}C$	$\delta^{18}O$	Sample No.	$\delta^{13}C$
KLR TC 4 (2)	+13.88	+17.91	KLR TC 2	+10.53
KLR TC 4 (4)	-2.71	+19.89		
KLR TC 5 (4)	+17.54	+18.32	KLR TC 3	-2.47
KLR TC 5 (5)	+10.31	+22.08		
KLR TC 5 (6)	+15.01	+19.81		

^{13}C ratios reported vs. PDB standard, ^{18}O reported vs. v-SMOW. Numbers in brackets indicate samples taken from the same core, but at differing depths. For exact locations see

Appendix 1.

The precipitated bicarbonate ions (Table VII) show two very different ratios. KLR TC 2 is moderately enriched, while KLR TC 3 is depleted. It would seem that in the Lindbergh area a greater amount of bicarbonate derived from inorganic or primary carbonate is present and mixing with the high carbon-13 bicarbonate. The $\delta^{13}C$ show the precipitated bicarbonate and cement the two phases are not in isotopic equilibrium. The cements, with one exeption, all show moderate to high enrichment in carbon-13 and oxygen-18. As in the case of Athabasca, these probably formed fairly early during the deposit's history.

The wide variation in $^{13}C/^{12}C$ probably reflect incorporation of some earlier carbonate either from the Paleozoic unconformity or carbonate that was formed during the Cretaceous. KLR TC 4 (4) shows a possible marine carbonate.

The $^{18}O/^{16}O$ of the cements are similar to those found in Athabasca. They precipitated in the same type of water; a brackish connate water or a meteorically modified connate water. Precipitation occurred relatively quickly after deposition, and emplacement of the oil.

Provost and Cactus Lake

The Provost and Cactus Lake deposits are examples of heavy oil pools that have isotopic ratios widely varient from the previously discussed deposits. Both deposits are smaller and located at deeper depths than the other deposits. They make an interesting comparison to the larger pools.

TABLE VIII: Isotopic analyses of samples from the Provost heavy oil deposit.

FORMATION WATER Sample No.	$\delta^{18}O$	δD	$Ba(OH)_2$ PRECIPITATE Sample No.	$\delta^{13}C$
KLR TW 12	-11.45 -11.46	-107.3	KLR TC 12	-21.31
KLR TW 13	-11.55	-107.3	KLR TC 13	-19.93
KLR TW 14	-11.40	-108.0	KLR TC 14	-20.63
KLR TW 15	-11.41 -11.28	-109.5	KLR TC 15	-20.16
KLR TW 16	-11.16	-107.5	KLR TC 16	-20.06

Water reported vs. v-SMOW, precipitate vs. PDB standard.

The waters from Provost lie off the meteoric water line, as discussed earlier near Alberta Basin formation waters (Hitchon & Friedman 1969). The $^{18}O/^{18}O$ are considerably enriched compared to the Athabasca and Cold Lake samples, showing less influence from Recent meteoric water, and more 'evolution' (Clayton et al. 1966; Hitchon & Friedman 1969). This is expected con~~sidering the~~ deeper source of the formation waters.

The precipitated bicarbonate values, in marked contrast to all other observed, show remarkably consistant, depleted ratios. This is the usual trend that has been reported in sediments surrounding conventional oil pools (Donovan 1974). Petroleum is considered the source of the carbon, but the type of degradation is different. This accounts for the lower values.

TABLE IX: Isotopic analyses of samples from the Cactus Lake oil deposit.

FORMATION WATER Sample No.	$\delta^{18}O$	δD	$Ba(OH)_2$ PRECIPITATE Sample No.	$\delta^{13}C$
KLR TW 6	-10.64	-95.1	KLR TC 6	-8.52
KLR TW 7	-9.58 -9.72	-94.2	KLR TC 6	-8.56
KLR TW 8	-10.65	-95.6	KLR TC 8	-5.88
KLR TW 9	-10.22 -10.33	-93.5	KLR TC 9	-15.66
KLR TW 10	-10.47 -10.56	-95.8	KLR TC 10	----
KLR TW 11	-10.47	-95.3	KLR TC 11	-10.01

Water reported vs. v-SMOW, precipitate vs PDB standard.

The Cactus Lake samples exhibit a similiar contrast to the larger deposits. The water samples show the most enriched $^{18}O/^{16}O$ and D/H of the samples studied. This water has been unaffected by meteoric water and plots well off the meteoric water line (Craig 1961) within the Alberta Basin ratios. As is the case with the Provost water, this is an evolved formation water (Hitchon & Friedman 1969).

The $^{13}C/^{12}C$ of precipitated bicarbonate show a wide range (from $\delta^{13}C$ = -15.66 to -5.88 °/₀₀ PDB) and relative depletion when compared to other data generated for this study. This deposit is a small oil field contained within Mississipian and Cretaceous sediments. There is plenty of

Mississippian limestone available for dissolution, and a mixing of carbonate-derived bicarbonate and depleted carbon dioxide could easily give rise to the isotopic ratios measured. The depleted carbon dioxide is thought to have originated from petroleum in the same manner as that at Provost, but via a different pathway than the large tar sands.

IV. DISCUSSION

A. BIODEGRADATION

Having presented isotope data collected from heavy oil deposits, and having referred to biodegradation as responsible, the need to describe this process arises. What is biodegradation? How does it proceed? What are its effects?

Simply stated, biodegradation is a process whereby various types of bacteria metabolize crude oil as an energy source to sustain life, grow and reproduce. In reality biodegradation is a very complex subject, not fully understood, needing specific criteria and environments to succeed. These criteria are: asuitable temperature, between 20° and 65° C; an oxygen supply; and petroleum containing no poisons to bacteria, such as H_2S. An obvious prerequisite is a steady influx of water to transport both bacteria, and nutrients once the bacteria become established. Harwood (1973) also asserts aerobic as opposed to anaerobic, bacteria are responsible for petroleum biodegradation. Aerobic bacteria require oxygen in order to survive, whereas anaerobic bacteria cannot tolerate its presence.

Bacteria consume crude oil components sequentially, depending on their ease of removal from the parent. The sequence is:

Normal Paraffins C_{10}-C_{19}

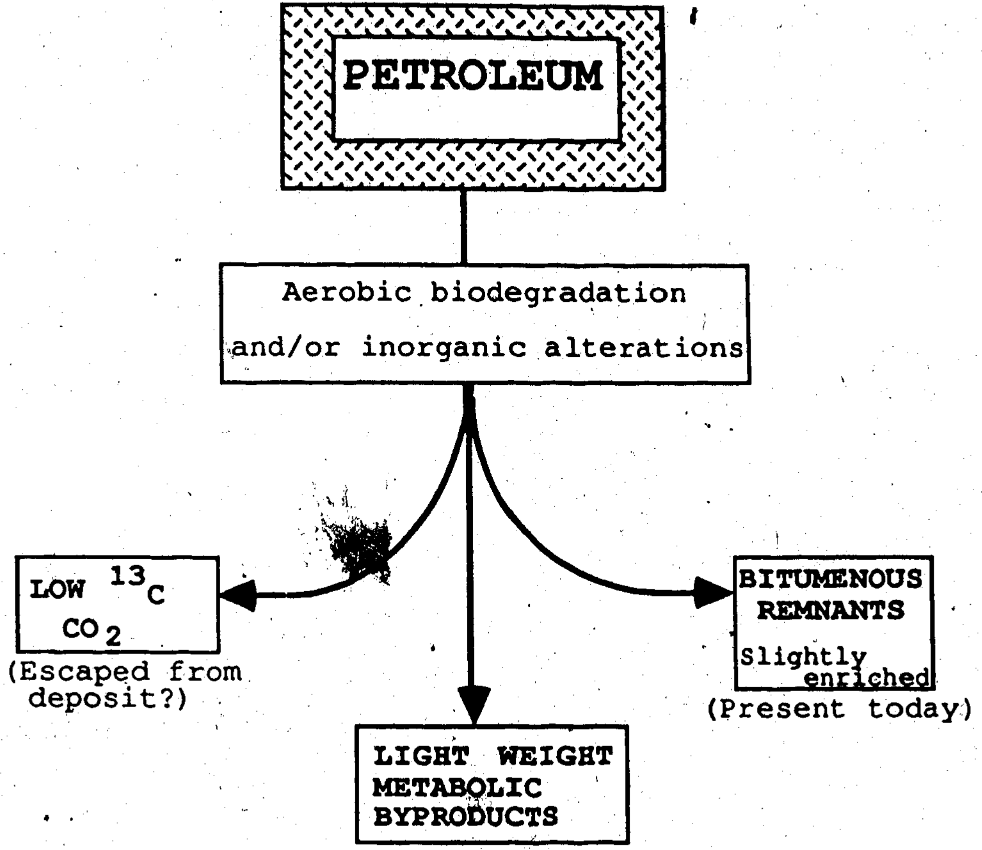
Gases C_2-C_4

Paraffins C_5-C_9
Iso-paraffins C_1-C_{12}
Aromatics
Cycloalkanes
N-S-O Compounds
Isoprenoids
Cyclic Isoprenoids

(Perry & Cerniglia 1973; Hunt 1979).

Bacterial consumption results in metabolic byproducts including organic acids, hydroperoxides, aldehydes, alcoho~~ls, ketones~~, esters, and carbon dioxide (Harwood 1973; ZoBell 1973). A non-degraded portion also remains, usually consisting of carbon-13 enriched aromatic [illegible] cyclic isoprenoid compounds.

During biodegradation microbes preferentially attack the smaller chain members of each faction, working toward the larger molecules (Stahl 1980). They also preferentially consume isotopically lighter molecules so the byproducts, and any carbon dioxide produced at this juncture is isotopically depleted (Stahl 1980; see Figure 6, a). More durable (and larger) alkanes are eventually consumed so byproducts and carbon dioxide become increasingly heavy with time (see Figure 6, b) The N-S-O compounds (including asphaltic and naphthaltic faction) left are slightly enriched in carbon-13 as the isotopically lighter aromatic to N-S-O fraction are consumed.



Carbon-13 depleted byproducts were produced initially. As the light fractions were consumed, more and more ^{13}C enriched byproducts resulted.

Figure 6: Initail aerobic biodegradation of conventional oil as envisaged for Alberta heavy oil deposits.

Since no low carbon-13 carbonates were observed in the heavy oil deposit studied there appears to have been no carbonate precipitation from the carbon dioxide produced from aerobic degradation of the crude oil (see Figure 6). Possibly this is due to low pH (3 or 4) conditions resulting from the oxidation of petroleum by bacteria (ZoBell 1973), or from the pH conditions of any connate brines present. If connate brine was present and mixed with infiltrating meteoric water, then the newly formed formation water would be undersaturated in bicarbonate, not permitting precipitation of carbonate.

The effect of biodegradation is to lower API gravity, raise N-S-O ratios, and increase viscosity (Evans et al. 1971; Milner et al. 1977). Biodegradation has been associated with the formation of most of the heavy oil deposits in Alberta (Deroo et al. 1977). Since biodegradation entails such large scale alteration of petroleum, evidence of its occurrance should be apparent in the host sediment. In particular, stable isotopes of carbonate cement, dissolved bicarbonate ion, and formation fluids should reflect the alteration process.

The results presented earlier (Table II, VI) seem contradictary. As seen in Figure 6, isotopically depleted carbon dioxide should have been produced but was not. Even large carbon fractionation during precipitation cannot account for the enrichment actually measured. A method, therefore, of increasing the carbon-13 fraction must be proposed.

B. ENRICHMENT MECHANISMS

Isotopically heavy carbonate have been reported from around the world. They are mostly, but not exclusively, diagenetic, or secondary in nature. As such they reflect the $^{13}C/^{12}C$ of ancient carbon dioxide, or other parent material. Several mechanisms have been proposed as causing enrichment.

Gaseous Exchange

Isotopic exchange between carbon dioxide and methane has been suggested by several investigators as a means of carbon-13 enrichment of carbonates, especially within organic rich sediments. Miocene shales of the Monteray Formation (California) designated as oil source rocks, have $\delta^{13}C = -25$ to $+21$ ‰ (Murata et al. 1969). Organic rich shales of the Permian Irati Formation (Brazil) have $\delta^{13}C = -17.4$ to $+18.3$ ‰ (DeGiovani et al. 1974). Permian carbonates in Australian coals have reported $\delta^{13}C = -26.5$ to $+24$ ‰ (Gould & Smith 1979). These (and others) are attributed to isotopic exchange.

Although $^{13}C/^{12}C$ of naturally occurring, co-existant carbon dioxide and methane follow theoretical fractionation curves (Bottinga 1969), Galimov (1969) stated this exchange did not occur. High temperature work (Sackett & Chung 1979), and further low temperature studies (Claypool & Kaplan 1974; and others) have shown no exchange between the two gases, even in long duration experiments. Hence, this mechanism could not have caused high carbon-13 carbonates.

Dissolution-Reprecipitation

Dissolution of pre-existing marine carbonate, mixing of bicarbonate ions from different sources, and reprecipitation has been proposed as another method of enriching carbonates (Deines et al. 1974; Nakai et al. 1975; Allan & Matthews 1977). This mechanism involves an initial invading water, with an isotopically depleted bicarbonate ion derived from reduced organic matter or atmospheric carbon dioxide, coming into contact with a carbonate sequence. Dissolution of the pre-existing carbonate leads to mixing, with attendant enrichment of the dissolved bicarbonate. Subsequent reprecipitation enriches the surrounding rock in carbon-13. Problems with this mechanism arise in determining how a formation water already saturated in bicarbonate ion can dissolve, and then reprecipitate carbonate (Carothers & Kharaka 1980).

Dissolution-reprecipitation leading to enrichment is dealt with in different ways. Deines et al. (1974) measured bicarbonate in infiltrating surface, and local spring and well, waters. Infiltrating waters carried bicarbonate with $\delta^{13}C = -27\ ^{o}/_{oo}$, whereas spring/well waters had bicarbonate $\delta^{13}C = -12$ to $-13\ ^{o}/_{oo}$.

After recharge water reached the water table, it dissolved metastable marine carbonates ($\delta^{13}C = 0$ to $+2$

$^{o}/_{oo}$), thereby facilitating isotope exchange. Reprecipitation of bicarbonate as stable carbonate occurred, with the remaining aqueous bicarbonate enriched relative to the infiltrating ions, seen by comparing the two $\delta^{13}C$ values.

Nakai et al. (1975) invoke a similiar mechanism for enriched carbonates found in Antarctic lake sediments, but with an important difference. Periodic drying and flooding of the lake is involved. An initial drying allowed deposition of an original carbonate, which was partially dissolved by the next flooding. Isotopic exchange between atmospheric carbon dioxide, and dissolved bicarbonate occurred before the second evaporation initated precipitation of (now) heavier carbonate. Repeated flooding-evaporation events and atmospheric exchange are thought to have enriched the carbonate to a maximum of $\delta^{13}C = +12$ $^{o}/_{oo}$.

Allan & Matthews (1977) present data from the vadose and phreatic zones in Holocene carbonate terrane, Barbados. As meteoric water invades the vadose zone it acquires dissolved bicarbonate with an isotopic signature similiar to reduced organic matter. The water continues infiltration, dissolving metastable marine aragonite and/or high magnesium calcite, and precipitating stable, low magnesium calcite. Near the top of the vadose zone there was isotopic exchange with atmospheric carbon dioxide which helped 'buffer' the slightly depleted $^{13}C/^{12}C$. As the water percolated deeper, atmospheric exchange ceased so the $^{13}C/^{12}C$ of the dissolved bicarbonate increased. Once the vadose-phreatic boundary was reached, the water was in contact with groundwater saturated with dissolved marine bicarbonate, exchange occurred, and dissolved bicarbonate acquired a slight positive $\delta^{13}C$ of up to 5 °/oo.

This process cannot be responsible for the heavy carbonates found in this study because:

1. it cannot account for the large enrichment ratios seen without a pre-existing, very enriched carbon source;
2. there is not enough carbonate in the deposits to undergo extensive exchange with dissolved bicarbonate;
3. waters already saturated in bicarbonate will not be prone to dissolve more;
4. the measured isotopic ratios (of the deposits) does not support establishment of equilibrium between cements and bicarbonate at present.

Migration Effects

Isotopic fractionation during migration or diffusion of gases from the source area to its trapped position was considered a dominant feature in isotopic enrichment (Colombo et al. 1965). Isotopically lighter molecules were thought to move through the porous media more quickly than the heavier fractions, thereby creating fractionation. Although experimental evidence supported this hypothesis, actual field studies found the reverse is true (Galimov

1969). This mechanism could not be operative in this study, as the gas present has not undergone long distance migration.

Limited Carbon Reservoir

Quaternary dolomites from the continental margin of the northeastern United States have range of $\delta^{13}C$ from -64 to +21 $^{o}/_{oo}$ (Deuser 1970). The mechanism for producing such vastly different $^{13}C/^{12}C$, often found in the same rock, involves bacterial decomposition of a limited carbon reservoir. Initially the bacteria consumed isotopically light material, producing depleted carbon dioxide (and eventually carbonate) while enriching the residual matter. As time passed more of this residue was consumed, leading to the precipitation of heavier and heavier carbonates. This process, able to account for extremely depleted and enriched carbonates in close proximity, has limited application to the Alberta oil sands. It provides a mechanism of producing more enriched carbonates as time passes, this seems to occur at both Athabasca, and Cold Lake especially when $^{13}C/^{12}C$ of cement and bicarbonate ion are compared. It cannot, however, be applied outright.

As well as the individual problems discussed in each mechanism above, they all share one trait which makes them unsuitable for explaining the enriched carbonates reported. All involve cogeneration of depleted carbonate as an integral part of the process. Since no depleted carbonates are found in the large deposits, the mechanisms cannot be applied. The two smaller deposits, Provost and Cactus Lake, are thought to have different geologic histories, and therefore have undergone less complicated alteration. This is described fully later.

C. PREFFERRED MECHANISM

As mentioned the large tar sand deposits under investigation have undergone biodegradation which preferentially removed both isotopically light, and easily metabolized alkanes, in sequential order. This process has as an end result:

1. Bitumenous remnants,
2. Light weight metabolic byproducts,
3. Low carbon-13 carbon dioxide.

In order to produce methane gas, fermentation of the byproducts by anaerobic bacteria is envisaged. Fermentation yields isotopically fractionated carbon-13, with depleted methane and enriched carbon dioxide. The fractionation factor varies depending on the byproduct, and fermentation pathway involved (Rosenfeld & Silverman 1959; Games et al. 1978; Fuchs et al. 1979; and others). Temperature will also affect the size of the fractionation.

There are several reasons for accepting fermentation as a viable means of alteration. Given the vast size and petroleum content of the Alberta heavy oil deposits, aerobic bacteria utilized equally vast amounts of oxygen during initial biodegradation. Anoxic conditions suitable for anaerobic microbes likely resulted. Secondly, anaerobic microbial metabolism is the only means of producing biogenic methane (Brock et al. 1984) in large quantities as seen in large oil sand deposits. As stated, bacterial fermentation causes large carbon isotope fractionations in the resulting carbon dioxide and methane. A fourth, less important, factor is that anaerobic bacteria cannot directly attack and utilize hydrocarbons as an energy source (ZoBell 1973; Harwood 1973), although aerobic bacteria can and do. Since aerobic bacteria cannot produce methane, a two step process is needed to account for the large heavy oil deposits and biogenic methane seen.

The first step is biodegradation by aerobic bacteria as outlined earlier. The second step involves fermentation of the byproducts by anaerobic bacteria to produce the methane and bicarbonate (via carbon dioxide), and to create the carbon fractionations encountered.

D. METHANOGENESIS vs. SULFATE REDUCTION

Anaerobic sulfate reducing bacteria utilizing hydrocarbons as an energy source also produce carbon dioxide that is isotopically heavier than the material being consumed. Studies in southeastern Saskatchewan (Bailey et al. 1973), have reported sulfate reducing bacteria associated with biodegraded petroleum. Bicarbonate ion is 8 $^{o}/_{oo}$ enriched compared to the crude oil from which it was formed. Interstial bicarbonate data from marine sediments (Presley & Kaplan 1968), has been interpreted by others (Carothers & Kharaka 1980), as 5 to 6 °/₀₀ enriched in carbon-13 over the original organic matter. Could this process be responsible for the enrichment in heavy carbon measured in the tar sands?

Sulfate reducing and methanogenic bacteria compete for usable byproducts, and hydrogen within the same ecological niches (Brock et al. 1984, p. 418). Since the sulfate reducers are more efficient, and can scavage and utilize hydrogen at much lower concentrations than methanogens, the former grow at the expense of the latter. In addition, H_2S is produced, a poison to most methanogenic bacteria (Claypool & Kaplan 1974). Hence if sulfate reducers are present, methanogens are not.

So, as methanogenic and sulfate reducing bacteria are mutually exclusive, and if large amounts of methane are present with little or no H_2S (as is the case in large Alberta tar sands), then the methane (and the incumbant isotopic fractionation) must be a product of methanogenic, anaerobic bacteria metabolically utilizing byproducts and producing methane. This seems plausible since high methane concentrations have not been reported in sediments containing dissolved sulfate (Claypool & Kaplan 1974). The Athabasca deposit contains sulfate levels of 14 mg/l or less in the Basal Aquifer, and according to sulfur-34 ratios shows no sign of sulfur reducing bacteria (Wallick &

Dabrowski 1982).

E. THE FERMENTATION MECHANISM

Carbon

Carbon isotope fractionation during methane production was initially investigated by Rosenfeld and Silverman (1959). They reported anaerobic bacteria, metabolizing methanol, produced a very carbon-13 depleted methane, and a very carbon-13 enriched carbon dioxide. Beginning with methanol of $\delta^{13}C$ = -16.3 $^{\circ}/_{oo}$, anaerobic bacteria yielded methane, as depleted as -83.8° [illegible], and carbon dioxide with $\delta^{13}C$ = -1.2 $^{\circ}/_{oo}$ at 30° C. The fractionation recorded was roughly 80 $^{\circ}/_{oo}$.

Susequent work was undertaken by other investigators. Nakai (1961) found a 76 $^{\circ}/_{oo}$ fractionation between carbon dioxide and methane when acetate was anaerobically metabolized. Two sets of workers found a carbon-13 fractionation of close to 40 $^{\circ}/_{oo}$ in methane produced via carbon dioxide reduction (Fuchs et al. 1979; Games et al. 1978). In all cases the fractionation effect will increase at low temperature and decrease at higher temperatures.

The actual pathway of fermentation depends on the byproducts and bacteria available (Brock et al. 1984, p. 417). Very few light weight organic molecules have been identified as suitable for direct methanogenesis by bacteria (ibid, p. 715). They include formate (HCO_2H), methylamine

(CH_3-NH_2), dimethylamine ((CH_3)$_2$-NH), trimethylamine ((CH_3)$_3$-N), carbon monoxide, carbon dioxide, acetate (CH_3CO_2H), and methanol (CH_3OH) (ibid, p. 715). Over 200 plus species of micro-organisms are known to degrade petroleum (including yeasts and fungi), with bacteria comprising four families containing a total of twelve genera (Brock et al. 1984, p. 716). A large variety of bacteria, therefore, are capable of methanogenesis. Despite this morphological diversity all methanogenic bacteria seem very similiar in physiology and biochemistry (ibid.).

Three main pathways of methanogenesis have been identified. One is the conversion of methanol to methane via the reaction:

$$4CH_3OH = 3CH_4 + CO_2 + 2H_2O \qquad \text{Eqn. 3}$$

with a corresponding carbon fractionation value of 80 $^o/_{oo}$ (at 30°C) between carbon dioxide and methane (Rosenfeld & Silverman 1959).

Another is the fermentation of acetate by the reaction:

$$CH_3CO_2H = CH_4 + CO_2 \qquad \text{Eqn. 4}$$

with a carbon fractionation of 76 $^o/_{oo}$ at 30°C between the carbon dioxide and methane (Nakai 1961).

The third mechanism is carbon dioxide reduction, another two step process. One set of anaerobic bacteria ferment the byproducts to hydrogen and carbon dioxide (and acetate depending on the starting material). Methanogenic bacteria then reduce the carbon dioxide via:

$$CO_2 + 4H_2 = CH_4 + H_2O \qquad \text{Eqn. 5}$$

The accompanying carbon fractionation is 40 °/₀₀ at 40°C between carbon dioxide and methane (Games et al. 1978). At low temperatures the authors expect the fractionation would be greater. During the last reaction, the amount of carbon dioxide reduced is governed by the availability of hydrogen. If, for some reason, hydrogen generation is suppressed the other two processes may become more important. Hydrogen becomes available from the reduction of the byproducts into forms suitable for methanogenesis.

Other fermentation pathways have also been suggested such as:

$$CH_3COO^- + H_2O = HCO_3^- + CH_4 \qquad \text{Eqn. 6}$$

with an attendant enrichment of carbon-13 in the bicarbonate ion of 60 °/₀₀ at 60°C (Carothers & Kharaka 1980). This reaction, however, was derived on the basis of formation waters being depleted in acetate, and biologically may not be strictly valid.

At this point, the biodegradation envisaged for large Alberta tar sands is presented in Figure 7.

There appears to have been no carbonate precipitated from the early carbon dioxide. If every alteration step initially uses isotopically light material, the residual gets heavier and heavier until a maximum enrichment is reached. Based on the isotopic ratios measured for methane and bicarbonate (-60 °/₀₀ and +17 °/₀₀) the carbon dioxide in equilibrium with the bicarbonate must have a $\delta^{13}C = 10$ °/₀₀ (Mook et al. 1974). This is a 70 °/₀₀ shift

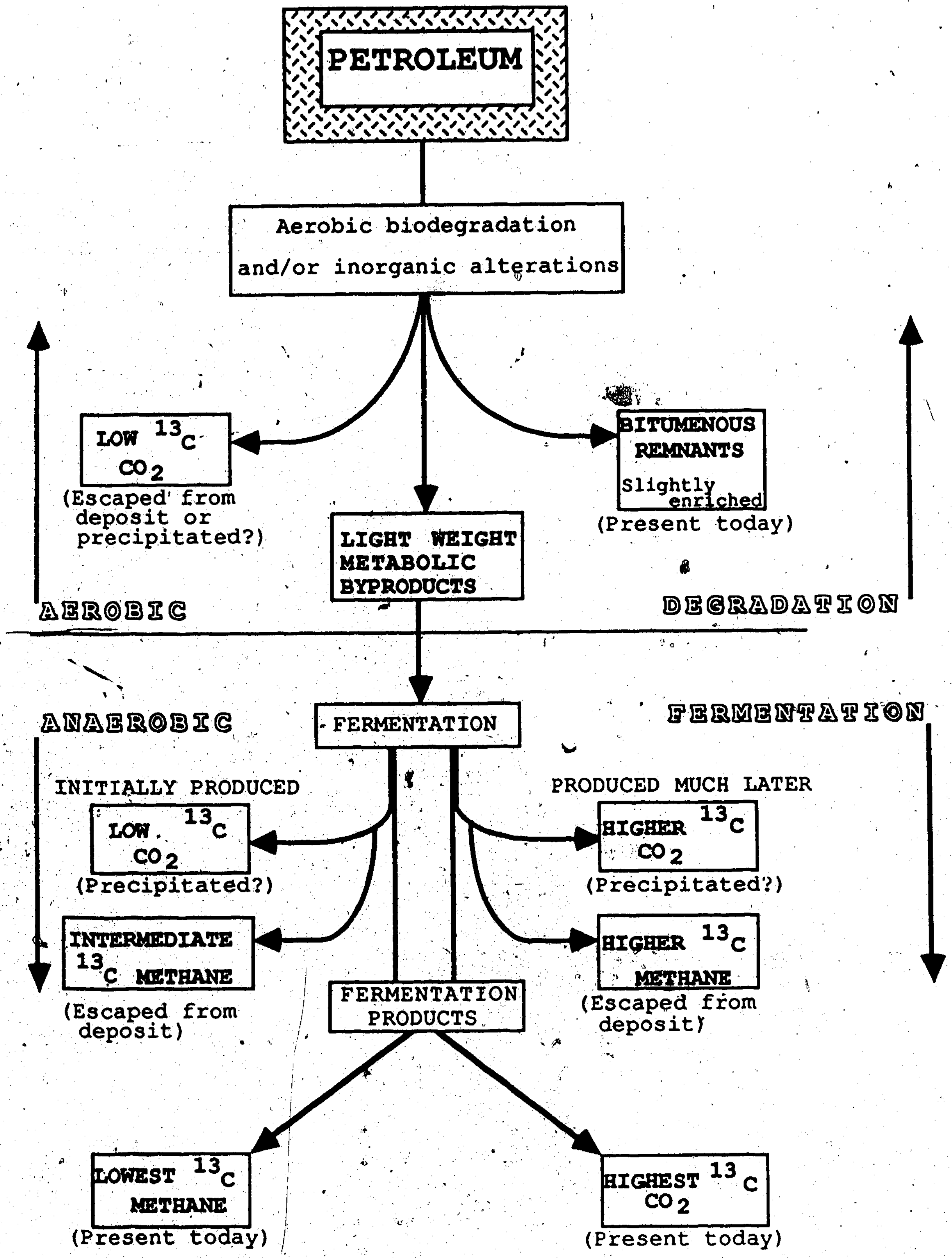


Figure 7: Proposed biodegradation history of the Athabasca and Cold Lake heavy oil deposits, showing products and relative isotopic depletion or enrichment.

during methanogenesis, which is within the range discussed earlier.

There has been an attempt in the literature to pinpoint one exclusive methanogenic process responsible for biogenic methane deposits, be it carbon dioxide reduction, or direct anaerobic fermentation. Each has an attendant carbon-13 fractionation. Methanogenesis, for this report, is considered the metabolic conversion of a precursor into methane, and some other products, as shown in Equations 3 to 5. The processes have an equal chance of occurring, dependent on the type of microbes, and the environment present. The products of methanogenesis will, of course, reflect the isotopic composition of the precursor.

Fermentation may breakdown the light weight organic molecules listed above into carbon dioxide, via the reaction:

$$2H_2O + CH_3CO_2H = 2CO_2 + 4H_2 \qquad \text{Eqn. 7}$$

Methanogenesis, through carbon dioxide reduction takes place via:

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad \text{Eqn. 5}$$

This creates another two step process during fermentation and methanogenesis, one generating carbon dioxide, the other generates methane. Methane produced directly through fermentation requires a single step. In order to differentiate between the two types of methanogenesis, D/H ratios must be carefully examined.

Deuterium

Although the isotopic fractionation of deuterium has not been investigated as thoroughly as that of carbon, some important trends have been established. Most of the work has been done by Schoell (1980), and Whiticar et al. (1986). Those papers form the basis of this section.

Schoell (1980) observed deuterium is fractionated approximately three to four times (3-4X) more than carbon in biogenic methane. He was thus able to outline 'maximum' $\delta^{13}C$ and δD of -64 and -150 °/₀₀ respectively, as boundaries for biogenic gas. These limits can be applied to 'pure' biogenic gas that has not been contaminated by, or mixed with either methane from other sources, other hydrocarbons, or carbon dioxide as mentioned in the previous chapter.

Further investigation revealed an equilibrium relationship between deuterium of biogenic methane and water present during methanogenesis. This relationship is expressed:

$$\delta D_1 = \delta D_2 - 160\ (\pm 10)\ {}^{o}/_{oo} \qquad \text{Eqn. 8}$$

where 1 = CH_4 and 2 = H_2O. The slope of the equation shows all the hydrogen in the methane is derived from associated water, or that during metabolism interreactive groups (within bacteria) are in isotopic equilibrium with water. Based on previous information (Brock et al. 1984), about methanogenesis, the latter is probably true.

Cold Lake gas and water samples originating in the same wells, which were collected for this study follow this relationship in only one case - KLR TG 1 and KLR TW 1. In the other two cases of methane and water originating in the same well (KLR TG 30 - gas, KLR TW 31 - water, and KLR TG 34 - gas, KLR TW 35 - water), the relationship is invalid. This implies, as explained, an impure biogenic methane (see Figure 8,9 after Schoell 1980; 1982), with steam injection triggering thermolysis of low deuterium, gaseous hydrocarbons.

Interestingly, if Equation 8 is valid (that is slope = 1), then all the hydrogen in bacterially produced methane has equilibrated with, or been derived directly from, the surrounding formation waters. Schoell (1980) proposes, if Equation 8 holds, that carbon dioxide reduction must be the prominant process of methanogenesis, since all the hydrogen in the reaction:

$$CO_2 + 4H_2 = CH_4 + H_2O \qquad \text{Eqn. 5}$$

is derived from sources 'external' to the precursor.

Noncompliance with Equation 8, where the slope is less than 1, indicates fermentation dominates such that:

$$CH_3CO_2H = CH_4 + CO_2 \qquad \text{Eqn. 4}$$

$$4CH_3OH = 3CH_4 + CO_2 + 2H_2O \qquad \text{Eqn. 3}$$

In these two cases hydrogen required to produce methane is contained within the precursor material, and methane formation occurs via hydrogenation of CH_3^- radicals. Thus only one hydrogen atom from 'external' sources is needed. In [illegible] later paper (Whiticar et al. 1986) Equation 8 is used to differentiate between methane formed by fermentation and

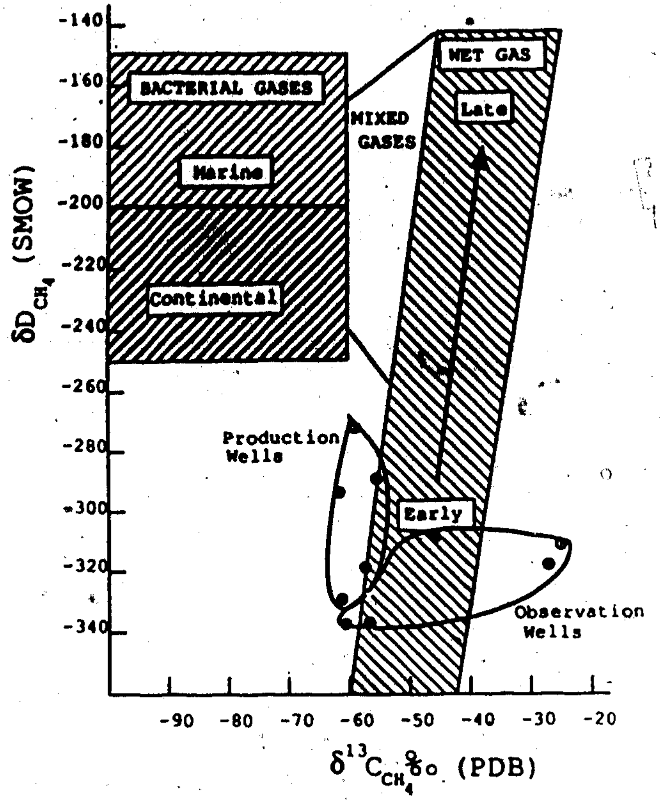


Figure 8: Plot of carbon and hydrogen variations in methane in natural gases from different origins (after Schoell 1980). Cold Lake data plotted for comparison.

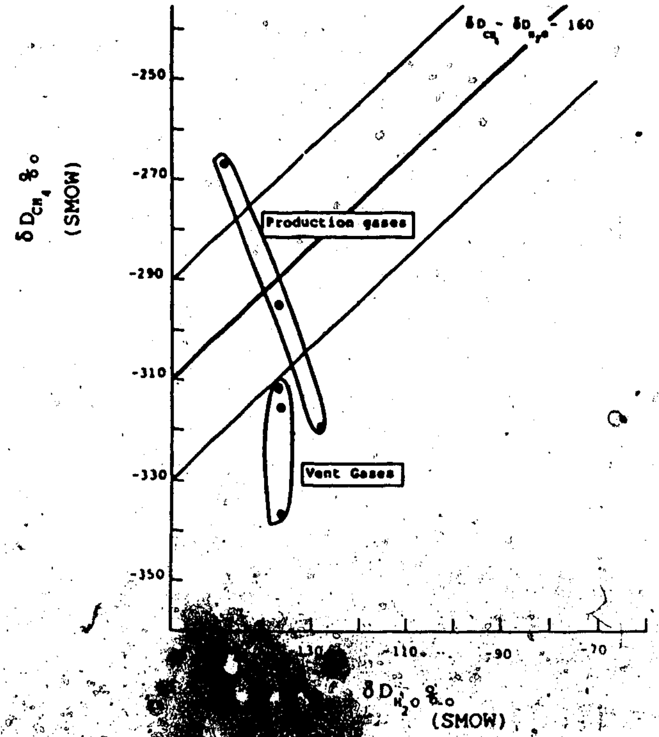


Figure 9: Plot [illegible]um ratios of water vs. methane coexisting in the same deposits (from Schoell 1980). Cold Lake data plotted for comparison.

methanogenesis through carbon dioxide reduction. In this case, measurement of δD can point out not only boigenic methane, but the process of methanogenesis.

In areas where fermentation is the only methanogenic process Equation 8 will have a slope of 0.25 (from 1 of 4 hydrogens). So, if Equation 8 is applied to data gathered from a methane in a heavy oil pool, and the slope is between 0.25 and 1 both types of methane formation are occurring. The closeness to one endpoint or another is indicative of which process dominates. Isotopic ratios outside the maximum limits indicate methane production by abiogenic means, with thermolysis being likely in the Cold Lake deposit.

Oxygen

Oxygen isotope ratios of cemetns will indicate the history of heavy oil deposits. Since oxygen-18 in the cements will have equilibrated isotopically with the formation water present during precipitation the source and type of formation water become appearant. Oxygen ratios of present day waters can be used to determine its source.

The oxygen isotope ratios for the carbonate cements are within the range of diagenetic, or secondary carbonate. Since Athabasca cements have $\delta^{18}O = +18.54$ to $+19.27$ (except one sample), and Lindbergh cements have $\delta^{18}O = +17.91$ to $+22.08$, they are outside the range of marine carbonates (Figure 10). The carbonate cements precipitated in an environment with a strong fresh water influence, and are not

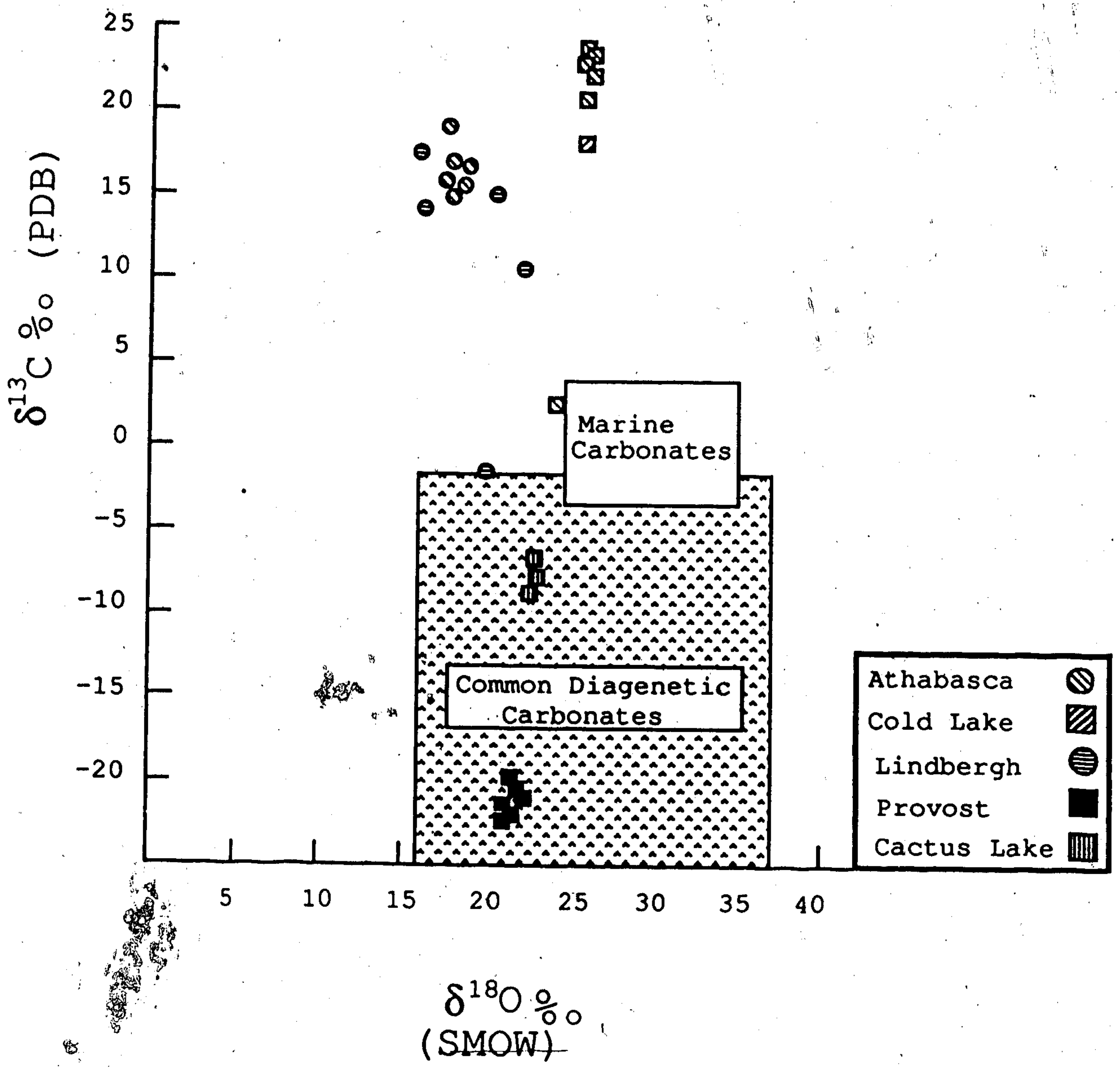


Figure 10: Plot of $\delta^{13}C$ and $\delta^{18}O$ of carbonates worldwide, showing compositions of marine, terrestrial and diagenetic carbonates. Also included are data from this study.

marine. The carbonates have a very restricted oxygen-18 range, but the formation waters examined range from $\delta^{18}O$ = -9 to -24 °/₀₀. It seems the carbonates formed under particular conditions, at about the same time in each deposit's history. The water present was likely a modified connate water, so the carbonate formed fairly early after oil entrapment, once biodegradation was established.

The only exceptions, KLR TC 20 (Athabasca) and KLR TC 4 (4) Cold Lake) have a marine $^{13}C/^{12}C$ and possibly a matching $^{18}O/^{16}O$. The most likely explanation for these ratios is a mixture of primary and enriched bicarbonate has been incorporated during the cement formation.

F. PROVOST AND CACTUS LAKE

These deposits are very different in isotopic and volumetric terms from the other deposits studied. They are envisaged as having undergone different alteration pathways. Like carbonates associated with other heavy oil deposits world wide (Ringham Appendix I), and conventional oil pools (Donovon 1974), Cactus Lake and Provost show carbon-13 depletion in their carbonates. Although these pools have undergone aerobic biodegradation, there is no isotopic evidence suggesting fermentation was established. Either anoxic conditions failed to develop, due to the deposits being too small or recharge (of oxygenated formation water) too rapid, or sulfate reduction dominated. Isotopic signatures of water, however, do not indicate rapid recharge of meteoric waters.

Other possibilities include inorganic processes such as water washing, inspissation and inorganic oxidation as degrading the oil in association with aerobic bacteria (Milner et al. 1977). These processes would yield heavy oil without the enriched carbonate of the larger deposits. Although the latter processes seem more likely, based on isotopic information, without further sampling it is difficult to postulate greater detail about the formation of the smaller deposits.

V. CONCLUSIONS

A. SUMMARY

Isotopic study of heavy oil deposits in Alberta allows several conclusions to be drawn. Examination of the phases, utilizing three isotopic pairs traces history and formation processes of each deposit. Biodegradation, the envisaged process, leaves distinct isotopic signatures as it progresses. Using isotopes the biodegradation model can be refined, and the process delineated with greater clarity. In addition, stable isotopes offer an elegant and precise means of the monitoring progression of biodegradation.

The heavy oil pools of the Lower Cretaceous are conventional oils biodegradated by aerobic bacteria, followed by anaerobic microbes. Aerobic bacteria metabolize the crude oil beginning with easily removed, and isotopically light fractions. Metabolic products are light weight organic compounds, bitumenous remnants, extremely carbon-13 depleted carbon dioxide, and an isotopically enriched residue. As time passes the isotopically enriched residue is consumed, leading to heavier byproducts and carbon dioxide. Since aerobic bacteria consume oxygen during biodegradation, anoxic conditions result in the large deposits.

Fermentation of the byproducts occurs after anoxic conditions develop, with methanogenesis occurring via three main pathways. These are methanol or acetate conversion, or carbon dioxide reduction. The final products are carbon-13 depleted methane, and carbon-13 enriched carbon dioxide. The carbon dioxide eventually precipitates as heavy carbonate cement. Fermentation, as opposed to other formation processes, is likely, as evidenced by the large quantities of methane present in the major deposits.

Pure biogenic methane as defined by Schoell (1980) was not obtained. Cold Lake samples showed $^{13}C/^{12}C$ outside the limits proposed. Contamination by C_2+ fractions is postulated. Other workers (Jha et al. 1979; Strausz et al. 1977), have shown thermolysis releases carbon-13 rich gaseous hydrocarbons from bitumenous sand at low temperatures. Schoell (1980) states C_2+ gases are isotopically enriched relative to methane, hence this mechanism could give rise to the data generated.

Throughout biodegradation isotopic enrichment of the remaining material occurs. This is illustrated by the dissolved bicarbonate in the Athabasca deposit showing a 5.6 $^{o}/_{oo}$ enrichment over the carbonate cement. The non-equilibrium would indicate the cement formed relatively early in the deposit's history, before enrichment took place. Further support is given by non-equilibrium between the oxygen-18 of the cements and formation waters, lending credence to the earlier formation of diagenetic cements. Presence of very enriched bicarbonate and depleted methane indicate fermentation continues at present.

Comparison of smaller deposits to major ones shows a different biodegradation history. There were no enriched bicarbonates found. Reasons for this may include failure of anoxic conditions to develop due to rapid recharge, or the small size of the deposits, so only aerobic bacteria flourished. Presence of sulfate reducing bacteria dominating petroleum degradation or inorganic alteration may have played an important role. Isotopic signatures of components in small deposits are similiar to those of conventional pools.

B. PRACTICAL APPLICATIONS

This work should have practical spin-offs. Recently the use of bacteria to clean up refined and crude petroleum spills has gained popularity. Use of stable isotopes to monitor the amount and level of biodegradation is very easy, especially in cases where the contamination has reached the water table. The $^{13}C/^{12}C$ of dissolved bicarbonate would be an elegant indicator of the biodegradation process.

Companies involved in heavy oil recovery could use stable isotope data to help monitor and model reservoir conditions. Certain useful questions may be answered. Does the bitumen undergo further chemical transformation as steam is injected? If so what gases are produced, or exsolved, and could they be used advantageously? Carbon dioxide gas may affect viscosity. Isotope data, especially from waters, could indicate cross formation leakage, revealing effectiveness of pressure induced fracture of host rock. In addition changes in reservoir characteristics may be predicted. Will carbon dioxide gas eventually precipitate, clogging pore throats and reducing permeability? Will, in fact, permeability be enhanced by carbonate dissolution? Stable isotope data could address these problems.

C. FURTHER WORK

Although this thesis has unravelled some of the mystery surrounding microbial degradation, much further work is needed. This work could approach the problem from several directions. The nature of aerobic alteration of crude oil is of interest. The isotopic fractionations, order of removal of light weight fractions, and the degradation pathways all need investigation. The bacteria, and/or biomass of present day tar sands could be identified for use in this step.

Fermentation of any aerobically produced byproducts, the carbon fractionations, and various types of the fermentation need determining on a local basis. Again isotopic and chemical changes need charting, and more data for gas-water-bicarbonate systems is needed. Ideally a long term study of the biodegradation of conventional oil through to bitumen, with attendant isotopic changes, chemical phases involved with alterations, and the physical parameters required would help decipher the formation of heavy oil deposits.

More investigation into thermolysis, the gases it produces, and the role they may play is appropriate. An indepth, long term stable isotope study, alone or in conjuntion with the other ideas mentioned, coupled with gas chromatography and microbiology, of each stage of alteration from conventional oil to bitumen would go a long way to resolving this fascinating problem.

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VII. APPENDIX I

This table contains isotopic data presented at the Canadian Society of Petroleum Geologists Annual Meeting, 1985, in a paper entitled "Biodegradation-Fermentation: A mechanism for ^{13}C-rich secondary carbonates associated with heavy oils of the Lower Cretaceous of Alberta" by R. Dimitrakopoulos, K. Muehlenbachs, and L. Ringham.

TABLE X: Isotopic analyses of carbonates associated with heavy oil deposits outside Alberta.

Sample Location	$\delta^{13}C$	$\delta^{18}O$
Canadian Arctic	3.57	25.24
Canadian Arctic	3.91	25.04
Canadian Arctic	-1.84	23.55
Zaire	-11.37	33.44
Brazil	-18.41	23.75
California	1.79	22.85

Samples analyzed by L. Ringham.
All carbon-13 reported vs. PDB, oxygen-18 vs. v-SMOW standards.

Isotopic data listed below were reported in Dimitrakopoulos & Muehlenbachs (1985). These are mean values calculated from individual wells, in three different deposits.

TABLE XI: Mean values of carbonates from individual wells in Cretaceous heavy oil deposits, Alberta.

Sample Location	Well Name	$\delta^{13}C$	$\delta^{18}O$
Athabasca (7-21-90-9W4)	FL 5-2	8.07	22.62
	PC 110	5.20	22.66
[illegible]d Lake (8-1-64-3W4)	NWR Co.		
	McWood Cold	3.50	23.88
	Ethel Lake	5.46	21.86
Lloyd. (2-26-51-1W4)	H. Durness 1	2.23	24.38
	Ohio #1	1.89	23.26

All carbon-13 reported vs. PDB, oxygen-18 vs. v-SMOW standards.

The isotopic ratios of the heavy oil fractions listed below were measured in 1982 by the German Geologic Survey for Dr. K. Muehlenbachs.

TABLE XII: Isotopic analyses of heavy oil fractions from Alberta heavy oils.

Sample Location	Fraction	$\delta^{13}C$
Mobil Ethel Lake	Saturates	-30.4
	Aromatics	-30.5
	Resins	-30.4
Athabasca	Saturates	-30.5
	Aromatics	-30.5
	Resins	-30.4
Aberfeldy	Saturates	-30.4
	Aromatics	-30.1
	Resins	-29.8
	Asphaltenes	-29.9
Buffalo Creek	Saturates	-30.7
	Aromatics	-30.3
	Resins	-30.3

All isotopic ratios reported vs. PDB standard.