National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

Canada

UNIVERSITY OF ALBERTA

Organic Geochemistry of Oil and Sour Gas Reservoirs in the Upper Devonian Nisku Formation, Brazeau River Area, Central Alberta, Canada.

by

Bernadette Kim Manzano ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirement for the degree of Master of Science.

DEPARTMENT OF GEOLOGY

Edmonton, Alberta
Spring, 1995

National Library of Canada
Acquisitions and Bibliographic Services Branch
395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale du Canada
Direction des acquisitions et des services bibliographiques
395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

ISBN 0-612-01630-7

Canada

UNIVERSITY OF ALBERTA

Release Form

NAME OF AUTHOR: **Bernadette Kim Manzano**

TITLE OF THESIS: **Organic Geochemistry of Oil and Sour Gas Reservoirs in the Upper Devonian Nisku Formation, Brazeau River Area, Central Alberta, Canada.**

DEGREE: **Master of Science**

YEAR THIS DEGREE GRANTED: **1995**

Permission is hereby granted to the University of Alberta Library to reproduce single copies of this thesis and of lend or sell such copies for private, scholarly, or scientific research purposes only.

The author reserves all other publication rights in association with the copyright in the thesis, and except as herein before provided neither the thesis nor any substantial portion thereof may be printed or otherwise reproduced in any material form whatever without the author's prior written permission.

Bernadette K. Manzano

Bernadette Kim Manzano
La Baja Road,
Maracas, St. Joseph,
Trinidad, West Indies.

Date: 24th March 1995

UNIVERSITY OF ALBERTA

Faculty of Graduate Studies and Research

The undersigned certify that they have read, and recommended to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled: "**Organic Geochemistry of Oil and Sour Gas Reservoirs in the Upper Devonian Nisku Formation, Brazeau River Area, Central Alberta, Canada**", in partial fulfillment of the requirements for the degree of Master Of Science in Geology.

Hans-G. Machel

Dr. H. Machel (Supervisor)

Dr. B. Jones

Dr. K. Muehlenbachs

P. Fedorak

Dr. P. Fedorak

Date: 17/03/95

Abstract

Thermochemical sulfate reduction (TSR) involves the reduction of anhydrite to hydrogen sulfide by reaction with hydrocarbons. Information concerning the alteration of hydrocarbons during TSR has been obtained from organic geochemical and stable isotope analyses of hydrocarbon accumulations within the Upper Devonian, Nisku Formation in the Brazeau River area, Alberta, Canada. The Nisku Formation contains a series of oil and gas condensate pools that are located at depths of 3 - 4 km. Hydrogen sulfide reservoir concentrations range from <1 % to 31 % and reservoir temperatures range from 100 °C to 130 °C .

The eighteen oil and gas condensate pools sampled show a wide variation in thermal maturity and hydrogen sulfide content. Generally, oil pools are located updip in the study area with sweet gas condensate pools downdip, and then sour gas condensate pools still further downdip. The maturity parameter, Pr/nC$_{17}$, was not significantly affected by TSR and is used to determine the maturity level for each pool. Hydrogen sulfide concentrations in hydrodynamically 'isolated' pools gave a good estimate for the degree of TSR in these reservoirs. In constrast, hydrogen sulfide concentrations and hydrocarbon compositions in pools that were not 'isolated' reflect migration and mixing of gases.

With increasing TSR the following changes in the oils and gas condensates were noted:

(1) Decrease in saturate/aromatic ratio;
(2) increase in organo-sulfur compounds (e.g., benzothiophenes);
(3) decrease (small or no change) in API gravity;
(4) δ^{34}S values of oils and gas condensates approached the values for anhydrite of the Nisku Formation in the study area;
(5) increase in δ^{13}C in saturate fraction;
(6) decrease, in some cases, in normal heptane/methylcyclohexane ratio.

Acknowledgement

This thesis would not have been possible without the support (financial and otherwise) from a number of companies and individuals. The author would therefore like to acknowledge the following:

Financial Support

Amoco Canada
Natural Science and Engineering and Research Council of Canada

Supervisors

Dr. Hans Machel and Dr. Pat Cavell (University of Alberta, Edmonton)
Dr. Martin Fowler and Dr. Lyord Snowdon (Institute of Sedimentary and Petroleum Geology, Calgary)

Sampling

Core Laboratories, Edmonton
Bob Cantin (Field Assistance)
Dan Boutin and Tom Hoey (Amoco Canada)
Andre Chow, Frederic Monnier, John McMurray, John Miller (Chevron Canada)
Ron Lambie and Orlin Lavallie (Petro Canada)

Sample Analyses

Jesusa Pontoy, Maria Mihailescu and Nenita Lozano (Stable Isotope Laboratory, University of Calgary)
Sneh Achal, Brad Gorhom and Marg Northcott (Institute of Sedimentary and Petroleum Geology, Calgary)

Discussion and Thesis Editing

Martin Fowler, Lyord Snowdon, Hans Machel, Roy Krouse, Andre Chow, Frederic Monnier, Pat Cavell, Dene Tarkyth and committee members (Brian Jones, Karlis Muehlenbachs and Phillip Fedorak).

On a personal note, the author would like to thank her family, loved ones and friends for all their support and encouragement. Finally the author give thanks to God for providing for all her needs.

Table of Contents

Chapter Page

1 Introduction and Objectives 1

1.1 Study Area and Hydrocarbon Production 1

1.2 The Problem 6

1.3 Objectives 8

2 Geology and Diagenetic Evolution 9

2.1 General Geology 9

2.2 Diagenetic Evolution 11

3 Thermochemical Sulfate Reduction 14

3.1 Mechanism 14

3.1.1 Oxidation of Organic Compounds by Sulfur 16

3.1.2 Dehydrogenation of Organic Compounds by Sulfur 17

3.1.3 Incorporation of Sulfur into Organic Compounds 17

3.2 Minimum Temperatures for TSR 19

3.3 Organic Compounds 21

4 Materials and Methods 23

4.1 Sampling and Grouping 23

4.2 Analytical Methods 28

5 Results 31

6 Discussion 53

6.1 Correlation Studies 53

6.1.1 Oil-Oil Correlations 53

6.1.1.1 Isoprenoid/n-alkane Ratios 53

6.1.1.2 $\delta^{34}S$ Values 55

6.1.1.3 $\delta^{13}C$ Values 55

6.1.2 Oil-Source Correlations 57
6.2 Thermochemical Sulfate Reduction and Thermal Maturation 59
6.2.1 Isoprenoid/n-alkane Ratios 60
6.2.2 Gross Composition 62
6.2.3 Organo-sulfur Compounds 65
6.2.4 API Gravity 66
6.2.5 Carbon and Sulfur Stable Isotopes 68
6.2.6 Paraffin Index and $nC_7/MCYC_6$ 73
6.3 Biodegradation and Water washing 77
6.4 Migration and TSR 81
6.5 Temperature and Depth Boundaries for TSR 83
6.6 Implications for Exploration 83

7 Summary and Conclusions 85

8 Recommended Future work 87
8.1 Source Rock Identification 87
8.2 $\delta^{34}S$ Hydrogen sulfide in Natural Gas 87
8.3 Gasoline Range Hydrocarbons 89
8.4 Whole Oil 89

References Cited 90

List of Tables

		Page
Table 1	Physical reservoir conditions and hydrogen sulfide concentrations for the pools in the Nisku Formation in the Brazeau River area.	5
Table 2a	List of wells in 'isolated' oil pools	25
Table 2b	List of wells in 'isolated' gas condensate pools.	26
Table 2c	List of wells in bank edge reef pools.	27
Table 3	Gasoline compound identification list for peaks shown in Figure 8.	33
Table 4a	Normalized percentages of gasoline compounds in 'isolated' oil pools.	38
Table 4b	Normalized percentages of gasoline compounds in 'isolated' gas condensate pools.	39
Table 4c	Normalized percentages of gasoline compounds in bank edge reef pools.	40
Table 5	Gasoline ratios for the pool in the Nisku Formations in the Brazeau River area.	41
Table 6	Gross composition of oils and condensates in the Nisku Formation.	42
Table 7	Isoprenoid to normal paraffin ratios.	49
Table 8	Carbon and sulfur stable isotopic values.	50
Table 9	Classes of organo-sulfur compounds identified in crude oils.	52
Table 10	Geochemical changes indicating thermal maturation and/or TSR.	78

List of Figures

		Page
Figure 1	Location of the study area and paleogeography of Alberta in the late Devonian time.	2
Figure 2	Generalized geographical distribution of pools in the Nisku Formation in the Brazeau River, West Pembina and Bigoray areas.	3
Figure 3	Hydrocarbon pools in the Nisku Formation in the Brazeau River area (study area).	4
Figure 4	Generalized cross section through all the facies types in the Brazeau River area.	10
Figure 5	Paragenetic sequence of the Nisku Formation in the study area.	12
Figure 6	TSR reactions involving hydrocarbons in the gas-water interface of gas condensate reservoirs.	18
Figure 7	Generalized relationship of thermal maturity to phases of crude oil generation, crude oil destruction and Thermochemical Sulfate Reduction.	20
Figure 8	Typical gasoline gas chromatogram.	34
Figure 9a	Gasoline chromatograms for 'isolated' oil pools.	35
Figure 9b	Gasoline chromatograms for 'isolated' gas condensate pools.	36
Figure 9c	Gasoline chromatograms for bank edge reef pools.	37
Figure 10a	Whole oil gas chromatograms for 'isolated' oil pools.	43
Figure 10b	Whole condensate gas chromatograms for 'isolated' gas condensate pools.	45
Figure 10c	Whole condensate chromatograms for bank edge reef pools.	47

Figure 11	FPD-gas chromatograms for selected samples aromatic fractions.	51
Figure 12	Use of isoprenoid/n-alkane ratios as indicators of biodegradation, maturity and depositional environment.	54
Figure 13	Pr/nC$_{17}$ versus Ph/nC$_{18}$ for oils and condensates within the Nisku Formation in the Brazeau River area.	56
Figure 14a	Pr/nC$_{17}$ versus hydrogen sulfide.	61
Figure 14b	Pr/nC$_{17}$ versus mean formation depth.	61
Figure 15	Bar chart showing the gross composition of oils and condensates within the Nisku Formation in the study area.	63
Figure 16	Dehydrogenation of hexane with sulfur to benzene and H_2S.	64
Figure 17	API gravity versus Pr/nC$_{17}$ for oils and condensates within the Nisku Formation in the study area.	67
Figure 18	$\delta^{34}S$ permil CDT versus hydrogen sulfide.	69
Figure 19	$\delta^{13}C$ saturates permil PDB versus Pr/nC$_{17}$.	71
Figure 20	$\delta^{13}C$ saturates permil PDB versus hydrogen sulfide.	72
Figure 21	Paraffin Index 2 versus Pr/nC$_{17}$ for oils and condensates in the Nisku Formation in the Brazeau River area, Alberta.	74
Figure 22	n-Heptane/methylcyclohexane versus Pr/nC$_{17}$.	75
Figure 23	Dehydrogenation of heptane with sulfur to methylcyclohexane and H_2S.	77
Figure 24	Water washing parameter (MCYC$_6$/Tol) versus Pr/nC$_{17}$.	80
Figure 25	Mean formation depth versus reservoir hydrogen sulfide concentration.	82

Figure 26 Sulfur isotope composition of condensates and hydrogen sulfide in natural gas samples versus hydrogen sulfide concentration. 88

Abbreviations and Symbols

δ	delta
$\delta^{13}C$	delta ^{13}C (carbon isotopic composition)
$\delta^{34}S$	delta ^{34}S (sulfur isotopic composition)
$3MC_5/nC_6$	ratio of 3-methylpentane to normal hexane
$3MC_5$/Ben	ratio of 3-methylpentane to benzene
BP	bank edge reef pool
BSR	bacterial sulfate reduction
CDT	Canon Diablo Troilite Standard
CYC_6/Ben	ratio of cyclohexane to benzene
FD DATE	finished drilling date
FPD	flame photometric detector
GAS-INJ	gas injection pool
GAS-INJ	gas injection well
GC-FLOW	gas condensate well
GC-SUSP	gas condensate well, suspended
H2O-INJ	water injection well.
H2O-INJ	water injection pool
iC_5/nC_5	ratio of iso pentane to normal pentane
IP	'isolated' pool
$MCYC_6$/Tol	ratio of methylcyclopentane to toluene
MFD	mean formation depth
n-alkane(s)	normal alkane(s)
$nC_7/MCYC_6$	ratio of normal heptane to methylcyclohexane
NE	not enough sample
NES	not enough organo-sulfur compounds in sample
OIL-ABD	crude oil well, abandoned
OIL-FLOW	crude oil well
OIL-SUSP	crude oil well, suspended.
PDB	Peedee Belemnite Standard

Ph/nC_{18}	ratio of phytane to n-octadecane
PI 2	Paraffin Index 2
Pr/nC_{17}	ratio of pristane to n-heptadecane
Pr/Ph	ratio of pristane to phytane
SUSP	suspended pool
TOC	total organic carbon
TSR	thermochemical sulfate reduction
‰	permil (part per million)

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Study area and Hydrocarbon Production

The Upper Devonian Nisku Formation in the Brazeau River area of west central Alberta has been the focus of several geological and geochemical studies (Chevron Exploration Staff Ltd., 1979; Machel, 1983; Anderson and Machel, 1988; Machel et al., in press, b). Hydrocarbon [1] pools in the adjacent Bigoray and West Pembina areas are producing mainly crude oil, whereas, both oil and gas condensate (sweet and sour) are produced in the Brazeau River area (Figures 1 and 2).

The study area (Figure 3) is located between townships 45 and 48 and ranges 12 and 16 west of the fifth meridian. The mean subsurface depth of the Nisku Formation (Table 1) in the study area ranges from 3000 metres (2000 metres below sea level) in the northeast to greater than 4000 metres (2900 metres below sea level) in the southwest as a result of a regional structural dip of about 1-2° to the southwest. Reefal buildups (reservoirs) are generally 50-100m thick and 1-2 km in diameter (Machel and Anderson, 1988; Villeger and Webb, 1992). There are nine oil pools and seventeen gas condensate pools (Figure 3). Within the study area, oil pools are located updip with sweet gas condensate and then sour gas condensate pools occurring further downdip. Most of the hydrocarbon reservoirs in the study area are located in the Brazeau River area. Each pool is identified (Energy Resources Conservation Board, 1993a) by a single letter (for example, pool 'A' or pool 'S'). There are three pools located in the southwestern

---

[1] The term 'hydrocarbon' is used throughout this thesis to include all organic compounds in oils and gas condensates.

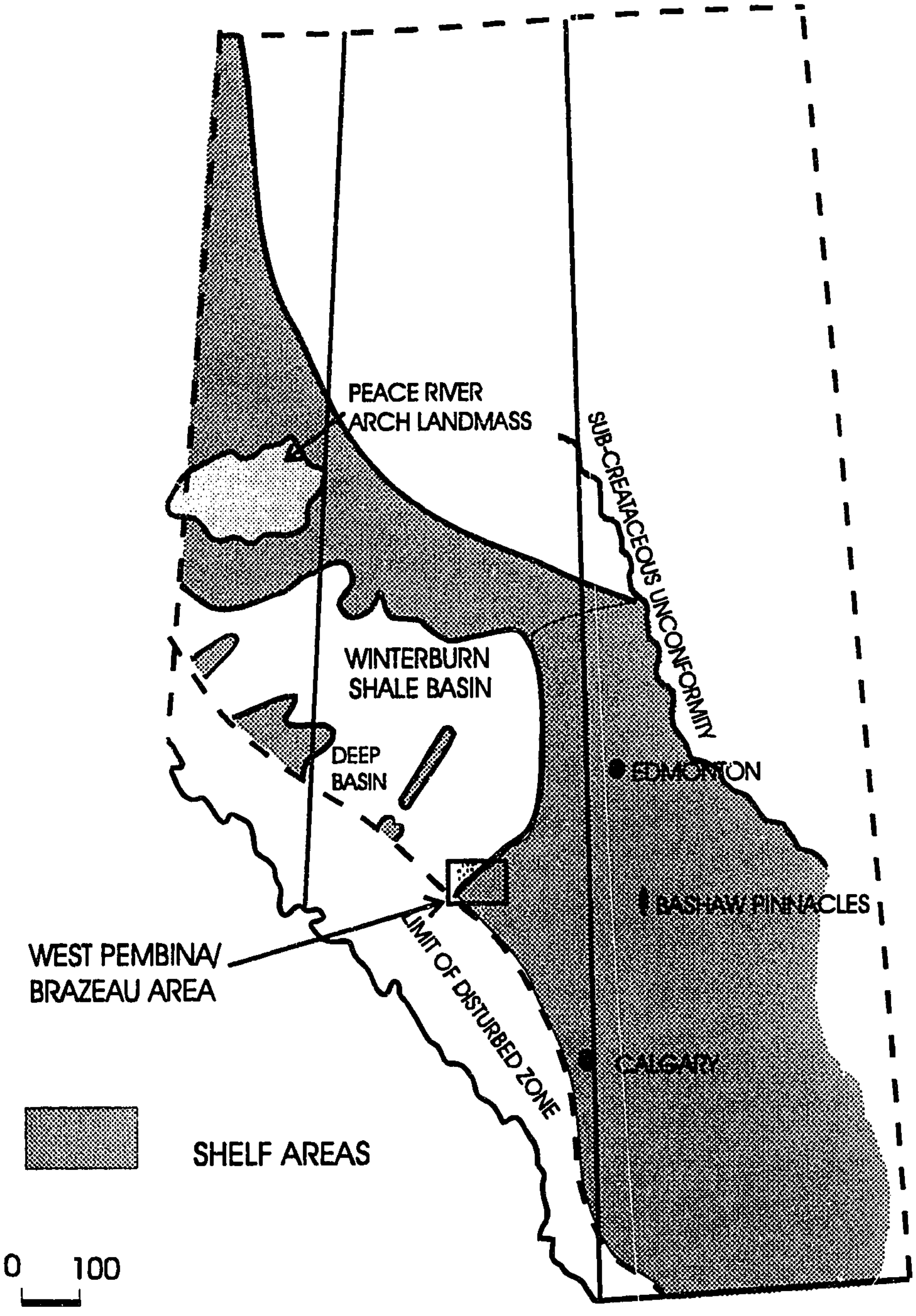


Figure 1: Location of the study area and paleogeography of Alberta in the late Devonian time. Framed area is shown expanded in Figure 2. (Modified from Stoakes, 1992).

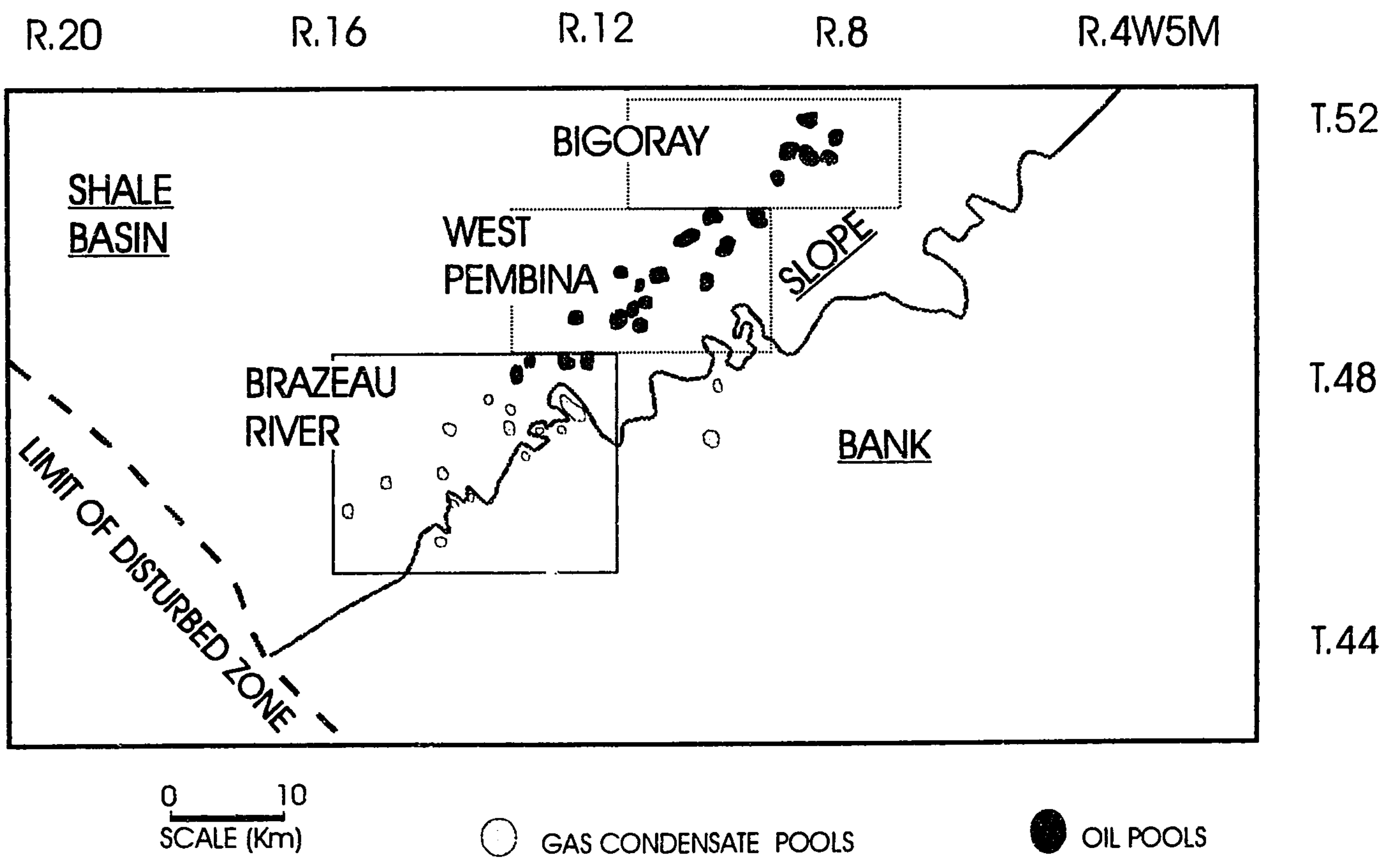


Figure 2: Generalized geographical distribution of the pools in the Nisku Formation in the Brazeau River, West Pembina, and Bigoray areas. Solid framed area is shown in Figure 3. (Adapted from Watts, 1987; Anderson and Machel,1988; and Switzer et at.,1994).

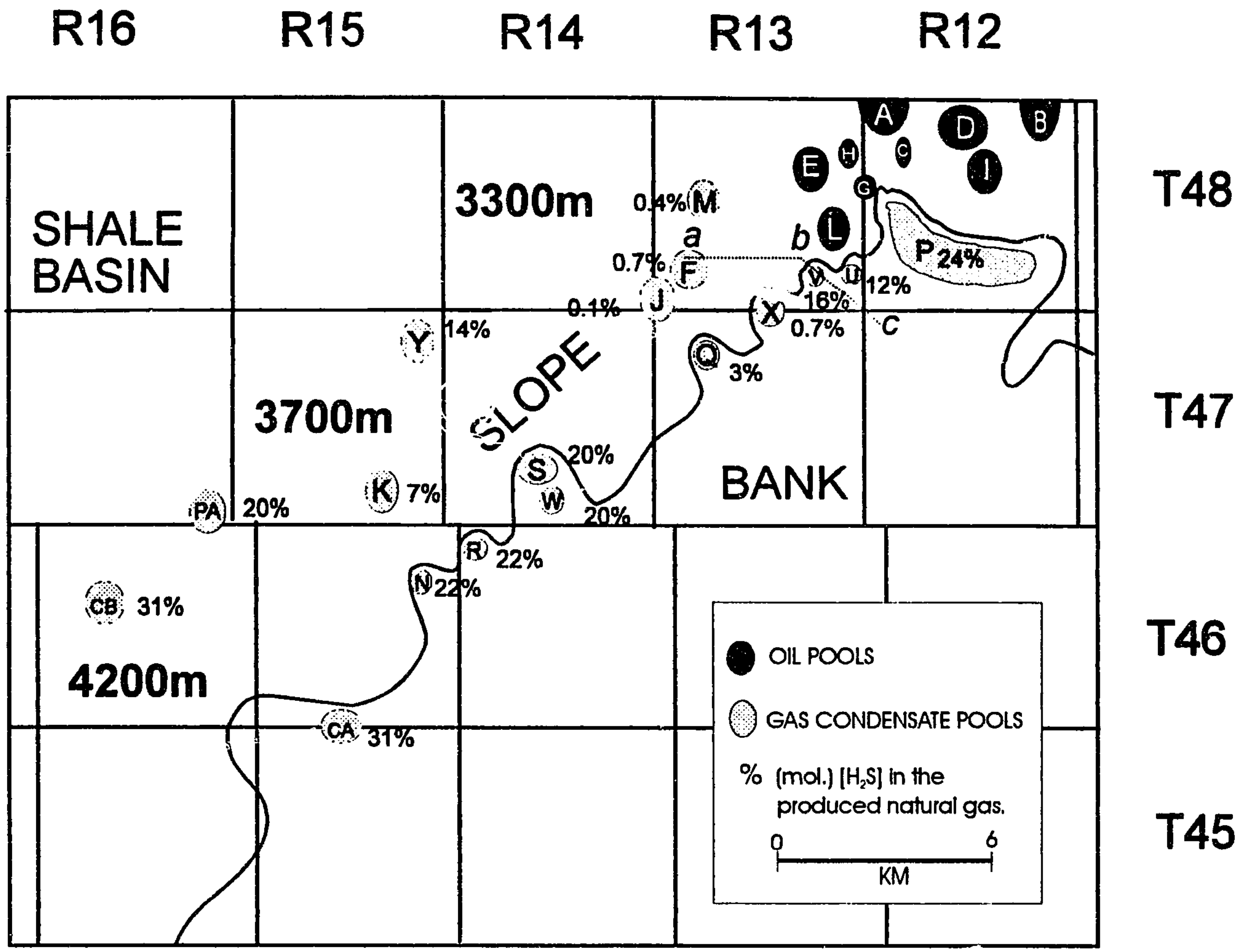


Figure 3: Hydrocarbon pools in the Nisku Formation in the Brazeau River area (study area). Pool size, identification and H_2S concentrations taken from Energy Resources Conservation Board (1993 a, b, c). Cross section a - c is shown in Figure 4.

Table 1: Physical reservoir conditions and hydrogen sulfide concentrations for the pools in the Nisku Formation in the Brazeau River area.

Pool	^Production	*IP/BP	H_2S	Temperature	Initial Pressure	Mean Formation Depth
	Type		mole Fraction	°C	Kilopascal	metres KB
A	OIL	IP	0.0073	107	46530	3107.4
B	OIL	IP	0.0073	102	32520	3070.1
C	OIL	IP	0.0073	107	33233	3101.1
D	OIL	IP	0.0073	102	34490	3068.8
E	OIL	IP	0.0073	108	46200	3200.0
L	OIL	IP	0.0073	105	40977	3221.8
F	G.C.	IP	0.007	107	46300	3355.1
J	G.C.	IP	0.0012	108	38390	3361.5
M	G.C.	IP	0.0044	104	50590	3271.8
K	G.C.	IP	0.0669	117	70730	3844.4
Y	G.C.	IP	0.1355	114	54510	3669.8
PECO A	G.C.	IP	0.2022	119	72120	3970.2
CB	G.C	IP	0.313	127	59770	4213.5
P	G.C.	BP	0.2435	99	35780	3117.5
V	G.C.	BP	0.1699	96	34760	3198.4
Q	G.C.	BP	0.0332	110	35860	3383.4
W	G.C.	BP	0.1983	113	37050	3727.8
S	G.C.	BP	0.1932	110	37880	3752.6

^G.C. : Gas condensate

***IP: 'Isolated' pool; BP: Bank edge reef pool**

part of the study area that are within the study area township and range boundaries but are not in the Brazeau River area. These are: the only pool in the Nisku Formation in the Peco area (officially called Pool 'A' and identified as Pool 'PA' in Figure 3) and the only two pools in the Nisku Formations in the Columbia area (officially called Pools 'A' and 'B' and identified as 'CA' and 'CB' respectively in Figure 3).

Reefs, which form the reservoir facies, occur as an elongated shelf margin complex (band edge reef) and as a series of small reefs on the slope towards the shale basin (Figure 3). These small reefs (reservoirs) in the shale basin are surrounded by relatively impermeable calcareous shales and appear to be hydrologically 'isolated' from each another as indicated by the virgin pressures listed in Table 1. The shallowest 'isolated' pools have pressures close to hydrostatic, whereas, the deepest 'isolated' pools in the shale basin have pressures far in excess of hydrostatic. Expected pressures are based on the present day depths at the normal hydrostatic gradient of about 10 MPa/km.

1.2 The Problem

Hydrogen sulfide concentrations in gas condensate pools in the study area range from <1% to 31% (Table 1, Figure 3). Most of the hydrogen sulfide in the pools with concentrations greater than 6%, was probably produced by thermochemical sulfate reduction (TSR). This process, as originally discussed by Orr (1974), essentially involves abiological reduction of sulfate ions by hydrocarbons to produce a relatively high concentration of hydrogen sulfide (>5% to 95%) in deep carbonate reservoirs (Orr, 1977; Machel et al., in press, a).

Evidence for TSR activity in the Brazeau River area includes petrographic features and stable isotope compositions ($\delta^{13}C$ and $\delta^{34}S$) of several solid phases (saddle and matrix dolomite, calcite, anhydrite and elemental sulfur) sampled from pool U (Machel et al., in press, b). Anhydrite is normally a reactant, whereas calcite, saddle dolomite and elemental sulfur can be formed as by-products during TSR. Saddle dolomite, which occurred only in the water bearing part of the pool, had $\delta^{13}C$ values of -12 ‰ to +2 ‰PDB. In contrast, $\delta^{13}C$ values of the grey matrix dolomite sampled ranged from -5 ‰ to +2 ‰PDB. The depleted $\delta^{13}C$ values of saddle dolomite against the background normal marine $\delta^{13}C$ values of the matrix dolomite were explained by the incorporation of organic carbon oxidized during TSR. Late diagenetic replacive calcite ($\delta^{13}C$ values: -12 ‰ to -18 ‰PDB) was present throughout pool U studied but occurred as a replacement of anhydrite only in the uppermost, gas-bearing upper part. In addition, elemental sulfur occurred only in the gas-water zone, with $\delta^{34}S$ values (24 ‰CDT) similar to those of anhydrite (24 to 28 ‰CDT).

Machel et al. (in press, b), interpreted these findings in conjunction with hydrogen sulfide concentrations and stable isotope compositions of gases and suggested (a) that TSR had occurred in the study area, (b) that it took place in the gas-water transition zone and (c) that it resulted in a spatial distribution of the inorganic solids relative to the gas-water contact. That study, however, was unable to explain the observed variation in reservoir hydrogen sulfide concentrations. Sour gas condensate pools located only a few kilometres apart display a wide variation in hydrogen sulfide concentrations (Figure 3, Table 1). Generally, however, there appears to be an increase in hydrogen sulfide content with increasing depth of 'isolated' gas condensate pools, whereas, pools along the bank edge reef display no apparent trend in hydrogen sulfide content with depth. The following questions, therefore, need to be answered:

1. **What factors control the distribution of hydrogen sulfide concentrations in both the 'isolated' pools and pools along the bank edge reef?**

2. **How have hydrocarbons in these pools been affected by TSR?**

3. **The increase in depth observed across the study area could cause an increase in thermal maturity of hydrocarbon pooled within the Nisku Formation. Maturation is known to alter the hydrocarbon compositions. Can the effects of thermal maturation be distinguished from those of TSR?**

Oils and gas condensates in the study area have not previously been analyzed in relation to TSR. Because hydrocarbons are the reducing agents during TSR, changes in hydrocarbon compositions (e.g., API gravity and sulfur content) should reflect the extent of TSR reactions in these reservoirs.

1.3 Objectives

The major objective of this study is to utilize organic geochemistry and stable isotopes to distinguish the effects of thermal maturation and TSR on the reservoir hydrocarbons pooled in the Nisku Formation in the study area. An attempt will be made to define changes in hydrocarbon distribution and relate these to TSR reactions and to provide some insights into the variations of reservoir hydrogen sulfide concentrations in the study area. Other processes, for example, biodegradation and water washing, which may also influence hydrogen sulfide distribution and gross composition of liquid hydrocarbons, will also be discussed. The result of this study will provide new insights into reactions involving TSR and the resulting changes in hydrocarbon distribution in sour gas reservoirs. These findings can assist in further sour gas exploration by providing information about hydrocarbon involvement and the changes in reservoir hydrocarbon quality during TSR. Estimation of the amount hydrogen sulfide generated, preserved and lost from hydrocarbon pools as result of open or close systems may be quantify from analysis of the reservoir hydrocarbons.

CHAPTER 2

GEOLOGY AND DIAGENETIC EVOLUTION

2.1 General Geology

The facies and stratigraphy of the Nisku Formation in the West Pembina and Brazeau River areas are discussed in detail in Chevron Exploration Staff Ltd. (1979); Machel (1983); Anderson and Machel (1988); and Watts (1987). Only the salient parts are summarized here.

The Nisku Formation, in the Brazeau River area, consists of a platform (called bank) facies, reefal facies, and off-reef facies (Figure 4). The Nisku Formation was deposited on top of the flat-lying Ireton Formation (shale) and is overlain by the Calmar Formation (shale). The reefal facies, called the Zeta Lake Member, in which hydrocarbons accumulated, is a fossiliferous mud-mound facies. It is present as an elongate body fringing the bank-edge reef and as numerous 'isolated' buildups on the slope towards the adjacent basin. The off-reef facies consist of the Lobstick, Bigoray, Cynthia and Wolf Lake members. The Dismal Creek Member, proposed by Machel (1984) for the outer shelf (bank) facies, is time equivalent to the Zeta Lake Member. The Cynthia Member lithology (argillaceous mudstone and calcareous shale) is a good seismic reflector and was used to define the outer bank (slope) boundary shown in Figures 2 and 3.

The depositional history of the Nisku Formation, discussed in detail in Watts (1987) and Anderson and Machel (1988) is based on a conventional litho-stratigraphic interpretation. More recently, Villeger and Webb (1992) and Villeger (1994) have proposed an alternative interpretation using a sequence stratigraphic approach. Hydrocarbon migration, maturation and TSR took place more than 300

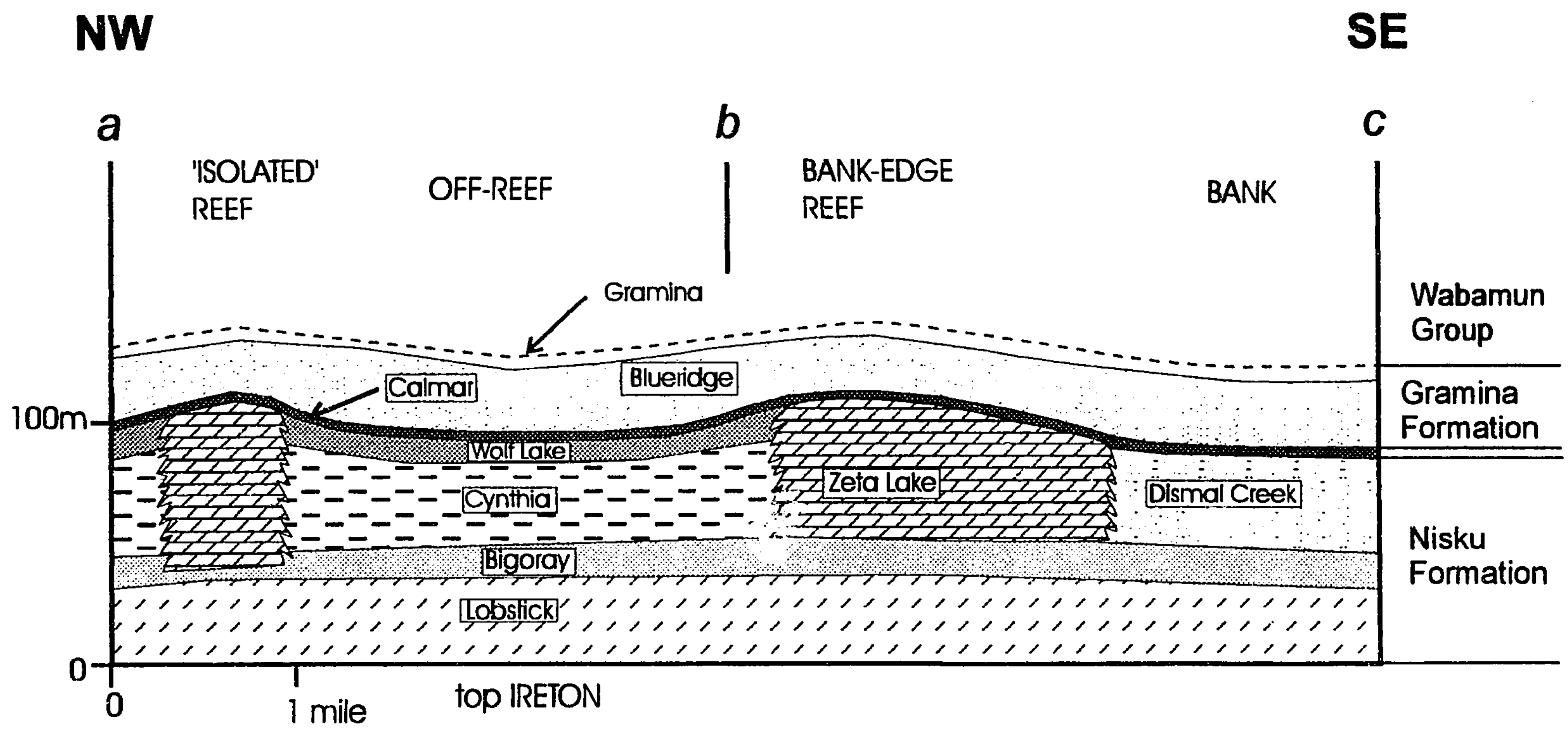


Figure 4: Generalized cross section (see dashed line in Figure 3) through all the facies types in the Brazeau River area. The top of the Ireton was taken as datum. (Modified from Machel, 1983).

million years after deposition, making any further discussion of the depositional history of the Nisku Formation irrelevant for the objectives of this study. For the purpose of this study, the present geometry of the Nisku system, as shown in Figures 2, 3 and 4, is the most important feature.

2.2 Diagenetic Evolution

In the study area, the Nisku Formation was affected by a complex sequence of diagenetic events. The paragenetic sequence (Machel, 1985; Anderson and Machel, 1988) involves six main diagenetic stages (Figure 5).

Diagenetic Stage I

Deposition and shallow burial up to a depth of about 300 metres, which was reached at the end of the Devonian period. All reefal and non-reefal strata were lithified.

Diagenetic Stage II

By the end of the Mississippian period the maximum burial depth was about 1100 metres. Major events during this stage were chemical compaction, matrix dolomitization and replacive anhydritization.

Diagenetic Stage III

From end of the Mississippian to lower Cretaceous period, the rock record contains no recognizable evidence of major diagenetic events during this period of non-deposition, erosion and minor sedimentation.

Diagenetic Stage IV

At the end of the Cretaceous period, the burial depths in the study area ranged from about 2000(NE) to 3400 metres (SW). The major events during this stage were oil generation and migration.

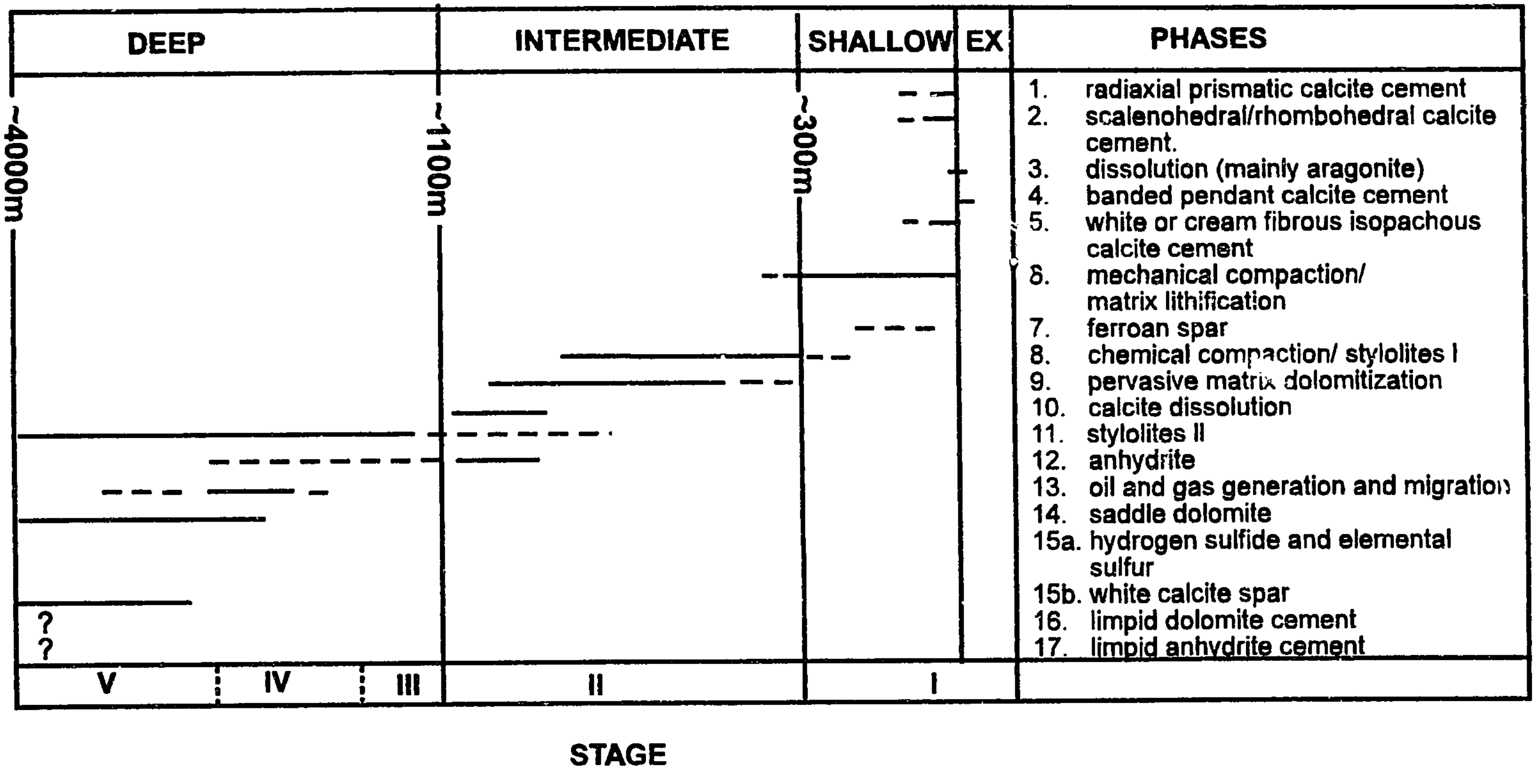


Figure 5 : Paragenetic sequence of the Nisku Formation in the study area (Anderson and Machel, 1988).

Diagenetic Stage V

Increasing burial depths during Stage V reached a maximum of about 4500-5000 m (maximum burial temperatures 135-150°C). The major events were TSR, and the formation of saddle dolomite and white calcite spar.

Diagenetic Stage VI

Stage VI from the Paleocene/Eocene to the Recent represents the period of erosion and relative uplift of the study area to its present burial depth of approximately 3500 m.

CHAPTER 3

THERMOCHEMICAL SULFATE REDUCTION

Thermochemical sulfate reduction was originally discussed by Orr (1974). The process basically involves abiological sulfate reduction of anhydrite by hydrocarbons. Significant products of TSR are hydrogen sulfide and elemental sulfur because of their economic value. Studies in TSR environments have shown that inorganic solids [late calcite cement (Sassen et al., 1987; Krouse et al., 1988; Heydari and Moore, 1989; Kaufman et al., 1990), saddle dolomite (Machel, 1987a; Kaufman et al., 1990; Machel et al., in press, b), sulfides (Macqueen and Powell, 1983) and elemental sulfur (Heydari and Moore, 1989; Machel, 1992)] are formed as by-products of TSR. Machel (1987, 1989), based on an extensive literature review, proposed a reaction scheme for bacterial sulfate reduction (BSR) and TSR to account for the formation of hydrogen sulfide, elemental sulfur, carbonates and sulfides in shallow and deep diagenetic environments. The reaction scheme proposed by Machel (1987, 1989) focused on the inorganic reactants and products involved in TSR. Given that the main objective of the present study is the analysis of the liquid hydrocarbons in relation to TSR, the reaction scheme proposed by Machel (1987, 1989) will not be discussed further. An overview of the TSR mechanism concentrating mainly on the organics, suggested minimum temperatures in TSR reactions, and a literature review of hydrocarbon alterations previously documented for TSR environments is discussed in sections 3.1, 3.2 and 3.3 respectively.

3.1 Mechanism

BSR is known to occur at shallow depths, under anaerobic conditions and at temperatures less than 80°C (Orr, 1977; Trudinger et al., 1985). BSR is a common source of low concentrations of hydrogen sulfide in petroleum reservoirs and in low-temperature diagenetic settings that are not hydrocarbons reservoirs. The amount of hydrogen sulfide accumulated from BSR normally does not exceed 2-5 % and has $\delta^{34}S$ values isotopically lower by 10 to 20 ‰CDT than those of the associated sulfate (Krouse, 1977; Orr, 1977; Machel et al., in press, a).

Orr (1974) was the first to provide an explanation for high hydrogen sulfide concentrations in deep carbonate reservoirs. Orr (1974, 1977) illustrated that with increasing depth, temperature and partial pressure of hydrogen sulfide, $\delta^{34}S$ of the hydrogen sulfide and organic sulfur approach that of reservoir sulfate in many deep carbonate reservoirs in several geological basins. High temperatures (>100°C), high hydrogen sulfide concentrations (>10%), and a small sulfur isotopic fractionation (from SO_4^{2-} to H_2S), eliminated the possibility of BSR as the source of the hydrogen sulfide in these reservoirs. Orr (1974) proposed that in deep carbonate reservoirs the hydrogen sulfide was formed abiologically from the reduction of anhydrite by hydrocarbons. The process, now generally called thermochemical sulfate reduction, involves three main steps.

Step 1

Hydrogen sulfide is generated by thermal cracking of organo-sulfur compounds in the oils. The amount of hydrogen sulfide produced is dependent on the sulfur content of the original (or source) kerogen and is generally less than 3% (Orr, 1977).

Step 2

The hydrogen sulfide produced from thermal cracking may initiate TSR reactions. H_2S probably reacts with sulfate ions present in the formation water to produce sulfur:

$$SO_4^{2-} + 3H_2S \text{ ----> } 4S + 2H_2O + 2OH^- \qquad (1)$$

Anhydrite ($CaSO_4$) is the main source of sulfate ions in the subsurface formation waters.

Step 3

The reduced sulfur (equation 1) reacts with hydrocarbons to generate H_2S. The reaction of sulfur with hydrocarbons is complex (Pryor, 1962). Sulfur can react with hydrocarbons in a variety of ways, of which three are identified below and discussed in sections 3.1.1, 3.1.2 and 3.1.3:

(1) In an aqueous medium, sulfur can oxidize hydrocarbons to carboxylic acids.
(2) In a non-aqueous medium, sulfur can react with hydrocarbons to form dehydrogenated products such as alkenes and aromatics.
(3) Sulfur can be incorporated into hydrocarbon molecules to form organo-sulfur compounds.

3.1.1 Oxidation of Organic Compounds by Sulfur

Toland (1960) demonstrated that in a basic aqueous medium, organic compounds react with sulfur to produce carboxylic acids at temperatures of 280-330°C by the general reaction equation:

$$R\text{-}CH_3 + 3S + 2H_2O \text{ -----> } R\text{-}COOH + 3H_2S \qquad (2)$$

Decarboxylation of carboxylic acids can produce carbon dioxide and reduced hydrocarbon species.

$$R\text{-}COOH \text{ -----> } R\text{-}H + CO_2 \qquad (3)$$

Reactions 2 and 3 result in the overall reduction in the length of the carbon chain, by one carbon atom.

The formation of sulfur via equation 1 is important for equation 2 since experiments conducted by Toland (1960) showed that sulfate does not directly oxidize organic species. When xylene (dimethylbenzene) was heated with aqueous ammonium sulfate, no reaction occurred. When the experiment was repeated, however, in the presence of hydrogen sulfide, phthalic acid ($C_6H_4(COOH)_2$) was produced. Hydrogen sulfide, therefore, was needed to initiate the oxidation reaction. Ammonium sulfate was the most efficient oxidant, because of its high solubility, while calcium sulfate had the least oxidizing potential. Paraffins and olefins were oxidized to carboxylic acids with yields falling off rapidly as the length of the carbon chain increased above about C_8. Alkylated aromatic hydrocarbons were oxidized with higher yields to their corresponding carboxylic acids. Oxidation of hydrocarbons by sulfur, to produce hydrogen sulfide and lower weight hydrocarbons, presumably occurs within the water column near the gas-water interface in subsurface reservoirs (Figure 6).

3.1.2 Dehydrogenation of Organic Compounds by Sulfur

Sulfur is also a powerful dehydrogenating agent. When sulfur is heated with hydrocarbons in a non-aqueous medium, dehydrogenation of hydrocarbons and hydrogen sulfide evolution commence at about 150°C (Pryor, 1962). Alkanes are dehydrogenated to alkenes:

$$RCH_2CH_3 + S \text{ -----> } RCH{=}CH_2 + H_2S \qquad (4)$$

Bryce and Hinshelwood (1949) showed that the reaction rates of sulfur with straight chain paraffins (C_2 - C_8) at 320°C to 349°C increase with increasing carbon number. Cyclic alkanes can be converted to aromatic compounds (Pryor, 1962):

$$C_6H_{12} + 3S \text{ ----> } C_6H_6 + 3H_2S \text{ (at 300°C)} \qquad (5)$$

3.1.3 Incorporation of Sulfur into Organic Compounds

Most of the organo-sulfur compounds present in oils are the result of early incorporation of sulfur into kerogen during diagenesis. The sulfur generated from TSR during catagenesis (equation 1, p.15) can react with hydrocarbons to form

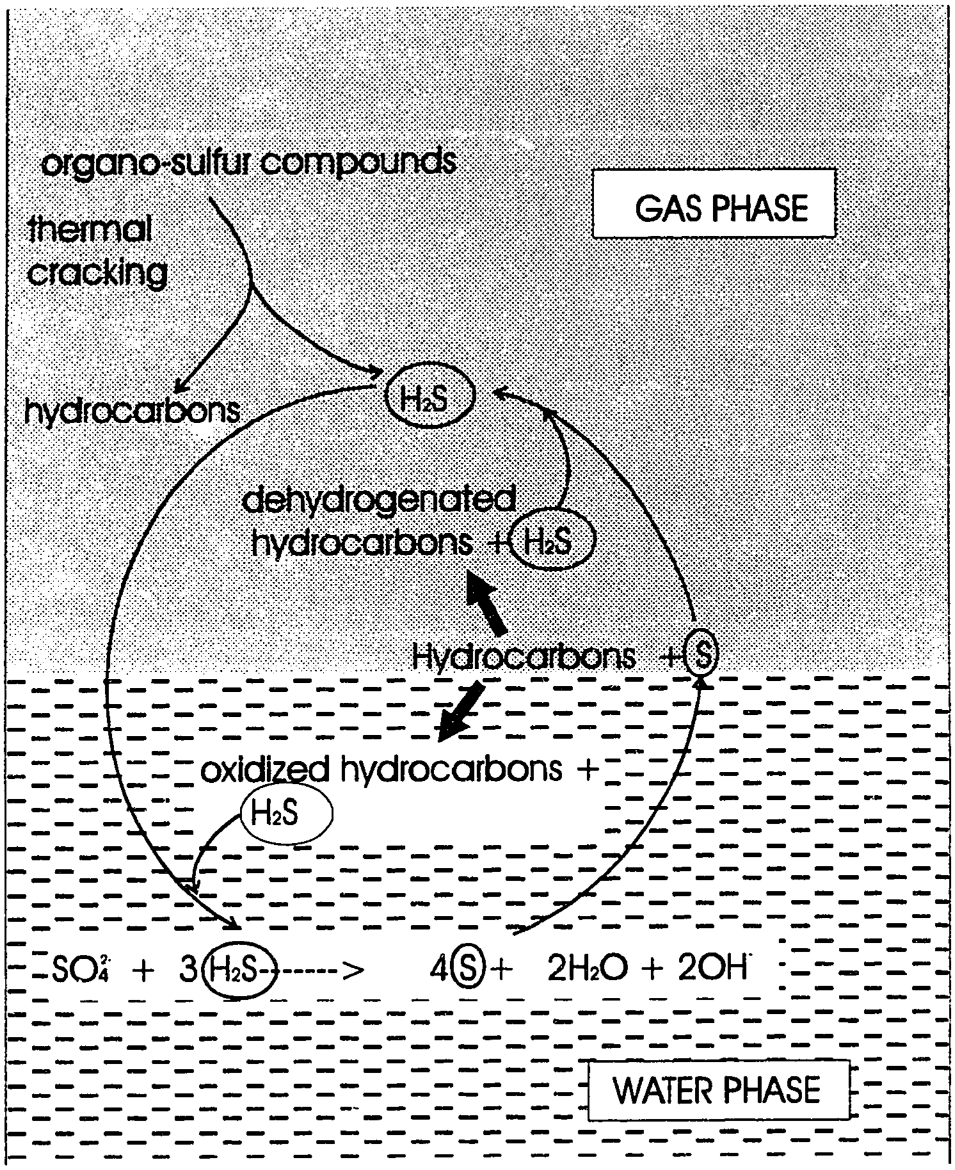


Figure 6: TSR reactions involving hydrocarbons in the gas-water interface of gas condensate reservoirs.

additional organo-sulfur compounds (Orr, 1974; Ho et al., 1974) as shown below:

$RH + S \longrightarrow RSH$ Mercaptans (6)

$2RH + 2S \longrightarrow RSR + H_2S$ Dialkyl sulfides (7)

$R\text{-}C_4H_9 + 2S \longrightarrow R\text{-}C_4H_7S + H_2S$ Cyclic sulfides (8)

$R\text{-}C_4H_9 + 4S \longrightarrow R\text{-}C_4H_3S + 3H_2S$ Thiophenes (9)

3.2 Minimum Temperatures for TSR

Feely and Kulp (1957); Dhannoun and Fyfe (1972); and Anisimov (1978) demonstrated that TSR reactions are exothermic based on thermodynamic calculations. Theoretically, therefore, a number of TSR reactions are possible. The minimum temperature, however, of the onset of TSR is uncertain and has stimulated much debate. Most TSR laboratory experiments have been conducted at temperatures above 250°C (Toland, 1960; Kiyosu, 1980). On the basis of thermodynamic calculations, Anisimov (1978) concluded that significant accumulation of hydrogen sulfide from the reduction of calcium sulfate by hydrocarbons in natural environments requires temperatures above 150°C. In a critical review, Trudinger et al. (1985) concluded that abiological sulfate reduction (or TSR) below 200°C has not been unequivocally demonstrated. Nevertheless, minimum temperatures of about 100-140°C are suggested for the onset of TSR (Machel, 1987; Krouse et al., 1988; Sassen, 1988; Sassen and Moore, 1988; Machel, in press, a). These temperatures were derived from fluid inclusion and maturity data from carbonate rocks, where TSR has been inferred to have occurred. Sassen (1988) estimated that the onset of TSR (Figure 7) is at level of thermal maturation at which crude oil is cracked to condensate (vitrinite

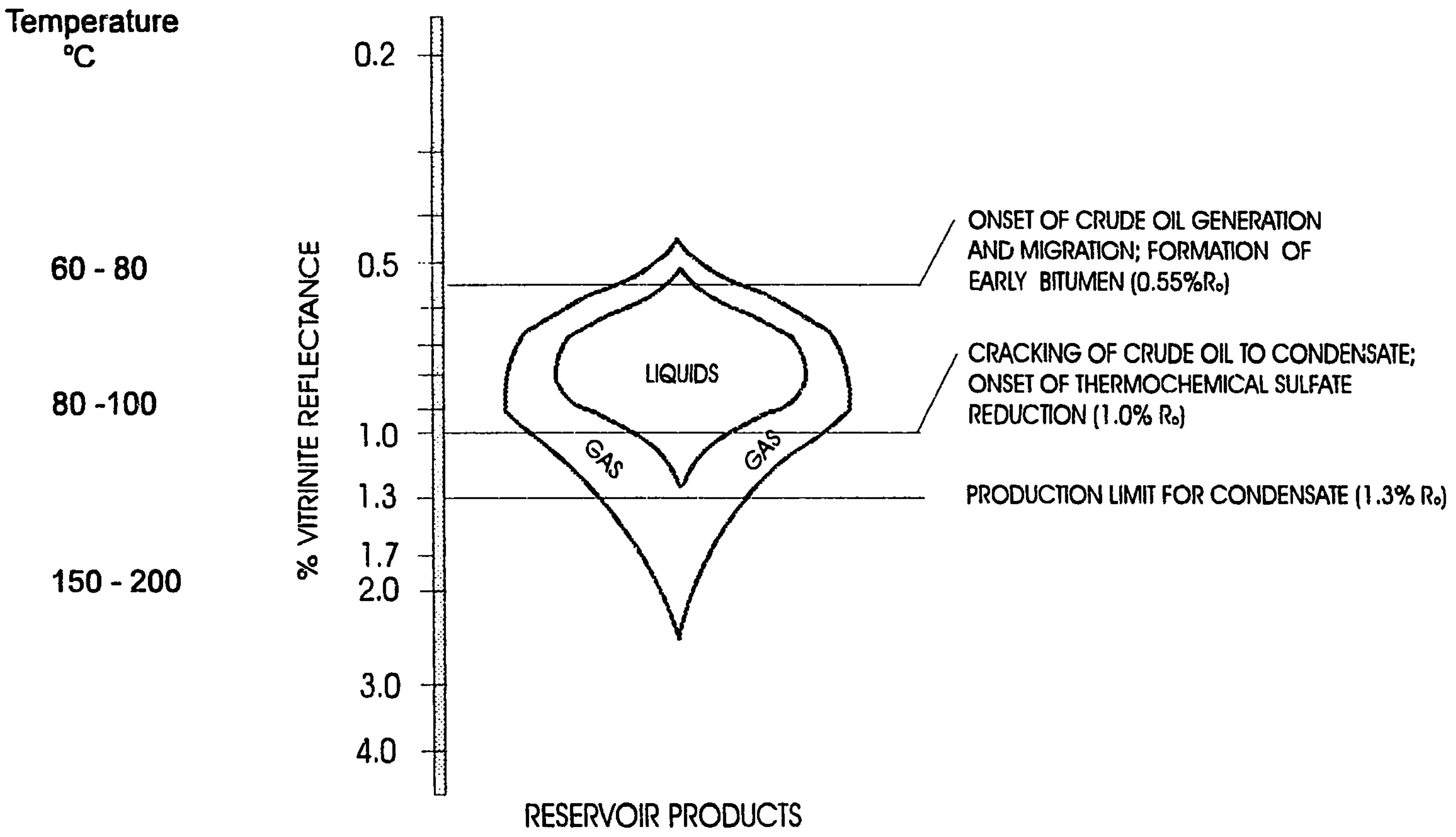


FIGURE 7: Generalized relationship of thermal maturity to phases of crude oil generation, crude oil destruction and TSR (modified from Sassen, 1988; Machel *et al.*, in press,a).

reflectance of 1% R_o, ≈120°C). Therefore, TSR probably occurs to a significant degree only in gas condensate and natural gas pools.

3.3 Organic Compounds

Although few studies have investigated the alteration of hydrocarbons in the reservoir resulting from TSR (Orr, 1974; Sassen, 1988; Claypool and Mancini, 1989; Thompson, 1994; Machel et al., in press, a), several chemical processes have been documented:

(1) Krouse et al. (1988) showed, on the basis of $\delta^{13}C$ values, that propane is more susceptible than ethane to TSR oxidation and that methane is the least reactive. The increasingly negative $\delta^{13}C$ values of carbon dioxide in sour gas reservoirs were correlated with increasing TSR in that study.

(2) The $\delta^{34}S$ value of hydrogen sulfide in the natural gas and $\delta^{34}S$ value liquid hydrocarbons approach that of the reservoir sulfate (Orr, 1974; Claypool and Mancini, 1989).

(3) Reservoirs in which TSR have occurred display low C_{15+} saturated hydrocarbon contents and relatively low saturate/aromatic ratios (Sassen, 1988; Claypool and Mancini, 1989). Normal alkanes are preferentially removed during TSR and there is an increase in the gas/oil ratio.

(4) Sour gas condensates formed during TSR have more positive $\delta^{13}C$ values than low sulfur condensates at similar maturity (Claypool and Mancini, 1989).

(5) TSR is accompanied by the formation of organo-sulfur compounds during catagenesis. (Orr, 1974; Ho et al., 1974).

(6) High S/N ratios are observed in TSR-affected pools (Orr, 1974) with values generally greater than 25 (Thompson, 1994).

(7) TSR-affected condensates have lower API gravities than sweet condensates (Claypool and Mancini, 1989), although the molecular distribution is shifted significantly towards the lower molecular weight compounds in TSR-affected pools.

(8) Sulfur-rich bitumens are formed as by-products of TSR in geological environments (Powell and Macqueen, 1984; Sassen and Moore, 1988; Sassen, 1988). In laboratory experiments (Bryce and Hinshelwood, 1949) the reaction of hexane and sulfur at 320°C produced hydrogen sulfide, a small quantity of mercaptans and 'black-coloured involatile tar'.

CHAPTER 4

MATERIALS AND METHODS

4.1 Sampling and Grouping

Liquid hydrocarbons from eighteen selected Nisku Formation pools in the Brazeau River area were sampled from 29th November to 1st December 1993. For safety reasons, samples were taken by field operators from Amoco, Chevron or Petro Canada in steel 500 cc high pressure bombs, at the well head separators. Tables 2a, 2b, and 2c list the hydrocarbon pools in the study area, their present status (Energy Resources Conservation Board, 1993c) and which pools were sampled for geochemical analysis. Hydrocarbon reservoirs in the study area fall into one of three main categories based on their location within the basin and production type:

(1) 'isolated' oil pools (sweet),
(2) 'isolated' gas condensate pools (both sweet and sour), and
(3) bank edge reef gas condensate pools (sour).

'Isolated' oil pools are composed of a two-phase system where liquid hydrocarbons are overlain by a gas cap. These pools are 'sweet', i.e., their gas phases have less than one molar percent of hydrogen sulfide. Three of the 'isolated' gas condensate pools sampled are sweet and the remainder are sour pools (Table 1, Figure 3). In gas condensate pools, temperatures and pressures are high enough that the reservoir fluids form a single phase. Reservoir gas condensates separate at surface temperatures and pressures into two phases: gas and liquid (condensate).

Abbreviations used in Tables 2a, 2b and 2c.

Pool/Status Column

- GAS-INJ: Gas injection pool
- SUSP: Suspended pool
- H2O-INJ: Water injection pool

Well Status Column

- OIL-FLOW: Crude oil well
- GAS-INJ: Gas injection well
- OIL-SUSP: Crude oil well, suspended.
- OIL-ABD: Crude oil well, abandoned
- H2O-INJ: Water injection well.
- GC-FLOW: Gas condensate well
- GC-SUSP: Gas condensate well, suspended

FD DATE: Finished drilling date

Table 2a: List of wells in 'isolated' oil pools.

Pool/ Status	Well location/W5	Well Status	FD DATE/ yy-mm-dd	Operator	Sampled
A GAS INJ	*15-31-48-12 11-31-48-12 11-31-48-12	OIL-FLOW OIL-FLOW OIL-FLOW	80-01-22 91-01-22 77-09-28	Petro Canada Petro Canada Petro Canada	Yes
B GAS INJ	9-35N-48-12 *9-35-48-12 8-35-48-12 8-35-48-12	GAS-INJ OIL-FLOW OIL-FLOW OIL-FLOW	79-06-24 77-11-30 88-10-25 82-05-06	Chevron Chevron Chevron Chevron	Yes
C SUSP	*12-29-48-12 12-29-48-12	OIL-FLOW OIL-ABD	92-02-04 78-02-21	Corex Corex	Yes
D GAS INJ	*5-34-48-12 10-33-48-12 7-33-48-12 3-33-48-12 15-28-48-12	OIL-FLOW GAS-INJ OIL-ABD OIL-FLOW OIL-FLOW	79-08-22 80-01-05 78-05-01 92-11-06 83-02-02	Chevron Petro Canada Petro Canada Petro Canada Petro Canada	Yes
E GAS INJ	*5-26-48-13 2-26-48-13 15-23-48-13	OIL-FLOW GAS-INJ OIL-FLOW	78-12-05 78-07-03 78-09-23	Petro Canada Petro Canada Petro Canada	Yes
G SUSP	12-19-48-12	OIL-SUSP	78-07-08	Petro Canada	No
H PRIMARY	10-25-48-13	OIL-FLOW	78-07-03	Imperial Oil	No
I PRIMARY	*5-27-48-12 3-27-48-12 14-22-48-12	OIL-FLOW OIL-ABD OIL-FLOW	87-05-14 79-02-09 79-08-22	Chevron Chevron Chevron	Yes
L H2O-INJ	*12-13-48-13 5A-13-48-13	OIL-FLOW H2O-INJ	88-01-27 82-08-19	Petro Canada Petro Canada	Yes

* well location from which hydrocarbon sample was taken.

Table 2b: List of wells in 'isolated' gas condensate pools.

Pool/ Status	**Well location/W5**	**Well Status**	**FD DATE/ yy-mm-dd**	**Operator**	**Sampled**
J PRIMARY	9-1-48-12	GC-FLOW	79-12-14	Amoco	Yes
	*6-6-48-13	GC-FLOW	81-09-18	Amoco	
M GAS-INJ	7-20-48-13	GAS-INJ	79-09-23	Petro Canada	Yes
	*6-20-48-13	GC-FLOW	80-10-21	Petro Canada	
F GAS-INJ	5-8-48-13	GAS-INJ	78-04-26	Amoco	Yes
	4-8-48-13	GC-FLOW	80-06-10	Amoco	
	*8-7-48-13	GC-FLOW	81-05-07	Amoco	
K GAS-INJ	2-11-47-15	GAS-INJ	81-04-10	Amoco	Yes
	*14-2-47-15	GC-FLOW	79-08-01	Amoco	
Y PRIMARY	*6-36-47-15	GC-FLOW	81-11-28	Amoco	Yes
Peco A PRIMARY	*6-1-47-16	GC-FLOW	84-08-28	Amoco	Yes
Columbia B SHUT IN	9-20-46-16	GC-SUSP	80-02-0?	Husky	No

* well location from which hydrocarbon sample was taken.

Table 2c: List of wells in bank edge reef pools.

Pool/ **Status**	**Well location/W5**	**Well Status**	**FD DATE/ yy-mm-dd**	**Operator**	**Sampled**
P GAS-INJ	3-20-48-12	GAS-INJ	78-09-08	Petro Canada	Yes
	2-19-48-12	GC-SUSP	79-12-30	Petro Canada	
	*11-12-48-12	GC-FLOW	83-02-27	Petro Canada	
	7-10-48-12	GAS-INJ	77-12-06	Petro Canada	
	11-09-48-12	GC-FLOW	90-03-04	Petro Canada	
	9-7-48-12	GC-FLOW	81-02-21	Petro Canada	
	11-04-48-12	GAS-INJ	85-08-09	Amoco	
	11-3-48-12	GAS-INJ	92-03-22	Amoco	
	10-02-48-12	GC-FLOW	78-11-23	Petro Canada	
U GAS SUSP	2-12-48-13	GC-SUSP	79-11-17	Petro Canada	No
V PRIMARY	*2-11-48-13	GC-FLOW	78-06-13	Petro Canada	Yes
X H2O-INJ	6-3-48-13	OIL-FLOW	90-04-14	Petro Canada	No
	3-3-48-13	H2O-INJ	86-12-21	Petro Canada	
Q PRIMARY	*3-32-47-13	GC-FLOW	78-03-30	Amoco	Yes
	10-29-47-13	GC-FLOW	89-07-25	Amoco	
S GAS-INJ	*12-10-47-14	GC-FLOW	88-05-26	Amoco	Yes
	15-07-47-14	GAS-INJ	79-10-27	Amoco	
W GAS-INJ	*11-03-47-14	GC-FLOW	87-04-11	Amoco	Yes
	5-2-47-14	GAS-INJ	74-05-03	Amoco	
R PRIMARY	7-31-46-14	GC-FLOW	81-09-07	Amoco	No
N PRIMARY	8-26-46-15	GC-FLOW	80-02-0?	Husky	No
Columbia A PRIMARY	7-4-46-15	GC-FLOW	81-01-08	Husky	No

* well location from which hydrocarbon sample was taken.

Bank edge reef pools are also gas condensate pools and exist along the edge of the carbonate platform bounded on the west side by the Cynthia Member and on the east by the Dismal Creek Member. Mean formation depth, reservoir temperature, initial reservoir pressure and hydrogen sulfide concentration for each pool sampled were obtained from the Energy Resources Conservation Board (1993a) and are listed in Table 1.

4.2 Analytical Methods

Analyses of liquid hydrocarbon samples for $\delta^{13}C$ and $\delta^{34}S$ were conducted at the Stable Isotopes Laboratory of the University of Calgary. All other organic geochemical analyses were conducted at the Institute of Sedimentary and Petroleum Geology in Calgary.

Gasoline range hydrocarbons (C_5 - C_8) were analysed using the procedure described by Snowdon and Osadetz (1988); and Snowdon and Powell (1979). Samples were analysed on a HP5890 Gas Chromatograph connected to an OI Analytical 4460 Sample Concentrator. A small amount of the sample was mixed with deactivated alumina and transferred to the Sample Concentrator. The hydrocarbons were then swept onto the Gas Chromatograph 50m HP-1 column and separated using the following temperature program: 30°C to 45°C at a rate of 1°C/min. The initial and final temperatures were held for 10 and 25 minutes respectively.

The API gravity of each hydrocarbon sample was determined indirectly from its specific gravity using the equation:

$$\text{API} = [141.5/(\text{specific gravity @ } 16°\text{C})] - 131.5.$$

The specific gravity was obtained using a 10ml grade-A volumetric flask where:

$$\text{Specific gravity} = \frac{\text{weight of flask and sample - weight of flask}}{\text{weight of flask and water - weight of flask}}$$

Gas Chromatograms of the whole oil and condensate samples were obtained using procedures described by Fowler et al. (1991). Hydrocarbons samples were analysed on a Varian 3700 using 30m DB-1 fused silica column connected to a flame ionization detector. The following temperature program was used: 30°C to 300°C at rate of 6°C/min and held for 20 minutes at maximum temperature.

The samples were distilled to 160°C and gross composition and stable isotope analyses were performed on the residual fraction (>160°C). The distilled samples (>160°C) were fractionated using open column (1:3 mixture activated silica gel: alumina) liquid chromatography. Saturates were eluted with pentane, aromatics with a pentane, dichloromethane (1:1) mixture, resins with methanol and asphaltenes were recovered using a chloroform wash (Fowler et al., 1991).

Sulfur compounds, in the aromatic fractions of five selected condensate samples, were analyzed using conditions similar to those for the whole oil and condensate gas chromatography analysis except that the initial temperature was 60°C and a sulfur-selective flame photometric detector (FPD) instead of a flame ionization detector was used.

δ^{13}C values were determined for distilled unfractionated hydrocarbon samples and for saturate and aromatic hydrocarbon fractions. The procedure described in Sofer (1980) involved combustion of a small amount of the sample overnight in a closed pyrex tube with copper (II) oxide at 550°C. The carbon isotopic composition of the carbon dioxide produced from combustion was then analyzed on a mass spectrometer constructed around Micromass 903 components.

Sulfur in distilled samples was converted to SO_2 for $\delta^{34}S$ analysis. Approximately 1 - 4g of the liquid sample was first decomposed in a Parr Bomb, then barium chloride was used to precipitate barium sulfate. The dried $BaSO_4$ was then mixed with a 1:1 mixture of vanadium pentaoxide and silica and heated to 900°C to produce SO_2 (Yanagisawa and Sakai, 1983). The sulfur isotopic composition of the SO_2 produced was then measured on a mass spectrometer.

CHAPTER 5

RESULTS

Figure 8 shows a typical gasoline chromatogram. Peak numbers in Figure 8 refer to compounds identified in Table 3 that were chromatographically separated and integrated during gasoline analysis. Gas chromatograms for 'isolated' oil pools, 'isolated' gas condensate pools and bank edge reef pools are shown in Figures 9a, 9b and 9c respectively. Normalized gasoline range hydrocarbon concentrations for twenty eight (28) compounds for the oils and condensates sampled in the Nisku Formation in the study area are given in Tables 4a, 4b and 4c. The values given in Tables 4a, 4b, and 4c are normalized i.e., the sum of all the twenty eight compound percentages equals to 100. Selected ratios of the gasoline range hydrocarbons calculated for the oils and condensates analysed are given in Table 5. These ratios are used to indicate maturity levels, and the degree of water washing and biodegradation (see sections 6.2.6 and 6.3).

Table 6 gives the API gravities, weight percentages of boiling point fraction above and below 160°C and the normalized percentages of different fractions (saturates, aromatics, resins and asphaltenes) of the hydrocarbons samples. Insufficient amount of pool Y condensate sample was available for distillation. As a result, the relative percentages of boiling point fractions are not reported for the condensate sampled from pool Y. Weight percentages of hydrocarbon fractions (saturates, aromatics, resins and asphaltenes) for pool Y was determined using the undistilled sample.

Figures 10a, 10b, 10c shows gas chromatograms obtained for whole oil and condensate samples. Hydrocarbons below C_{11} gave poor resolution and are not shown on whole oil and condensate gas chromatograms. The ratios of pristane/phytane, pristane/n-heptadecane and phytane/n-octadecane (Table 7) were calculated from integrated peak areas obtained from gas chromatograms of oils and condensates.

FPD-gas chromatograms of aromatics from five selected condensate sample are shown in Figure 11. These chromatograms were compared to sulfur aromatics gas chromatograms in Hughes (1984). Table 9 lists the different types of sulfur compounds found in oils. Numbers shown in Figure 11 refer to types of sulfur compounds listed in Table 9.

The results obtained from stable isotope analyses ($\delta^{13}C$ and $\delta^{34}S$) of distilled (>160°C) hydrocarbon samples and saturates and aromatic fractions are given in Table 8. The carbon isotopic composition of whole distilled (>160°C) samples and saturate and aromatic fractions are expressed relative to the Peedee Belemnite standard (PDB) where:

$$\delta^{13}C\ (‰) = \frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{PDB}}{(^{13}C/^{12}C)_{PDB}} * 1000$$

Insufficient amount of pool Y condensate sample was available for distillation. As a result no stable isotopes analyses were conducted on the condensate sampled from pool Y. The sulfur isotopic composition of whole distilled (>160°C) sample are expressed relative to the Canon Diablo troilite standard (CDT) where:

$$\delta^{34}S\ (‰) = \frac{(^{34}S/^{32}S)_{sample} - (^{34}S/^{32}S)_{CDT}}{(^{34}S/^{32}S)_{CDT}} * 1000$$

The amount of organo-sulfur present in some oil and sweet condensate samples was not sufficient for $\delta^{34}S$ analysis and hence in these cases no results are reported in Table 8.

Table 3: Gasoline compound identification for peaks shown in Figure 8.

PEAK #	COMPOUND
1	Iso Pentane
2	Normal Pentane
3	2,2-Dimethylbutane
4	Cyclopentane
5	2,3-Dimethylbutane
6	2-Methylpentane
7	3-Methylpentane
8	Normal Hexane
9	Methylcyclopentane
10	Benzene
11	Cyclohexane
12	2-Methylhexane
13	1,1-Dimethylcyclopentane
14	2,3-Dimethylpentane
15	3-Methylhexane
16	1,cis,3-Dimethylcyclopentane
17	1,trans,3-Dimethylcyclopentane
18	1,trans,2-Dimethylcyclopentane
19	Normal Heptane
20	Methylcyclohexane
21	1,cis,2-Dimethylcyclopentane
22	2,5-Dimethylhexane
23	2,4-Dimethylhexane
24	2,2,3-Trimethylpentane
25	Toluene
26	3-Methylheptane
27	1,cis,4-Dimethylcyclohexane
28	Normal Octane

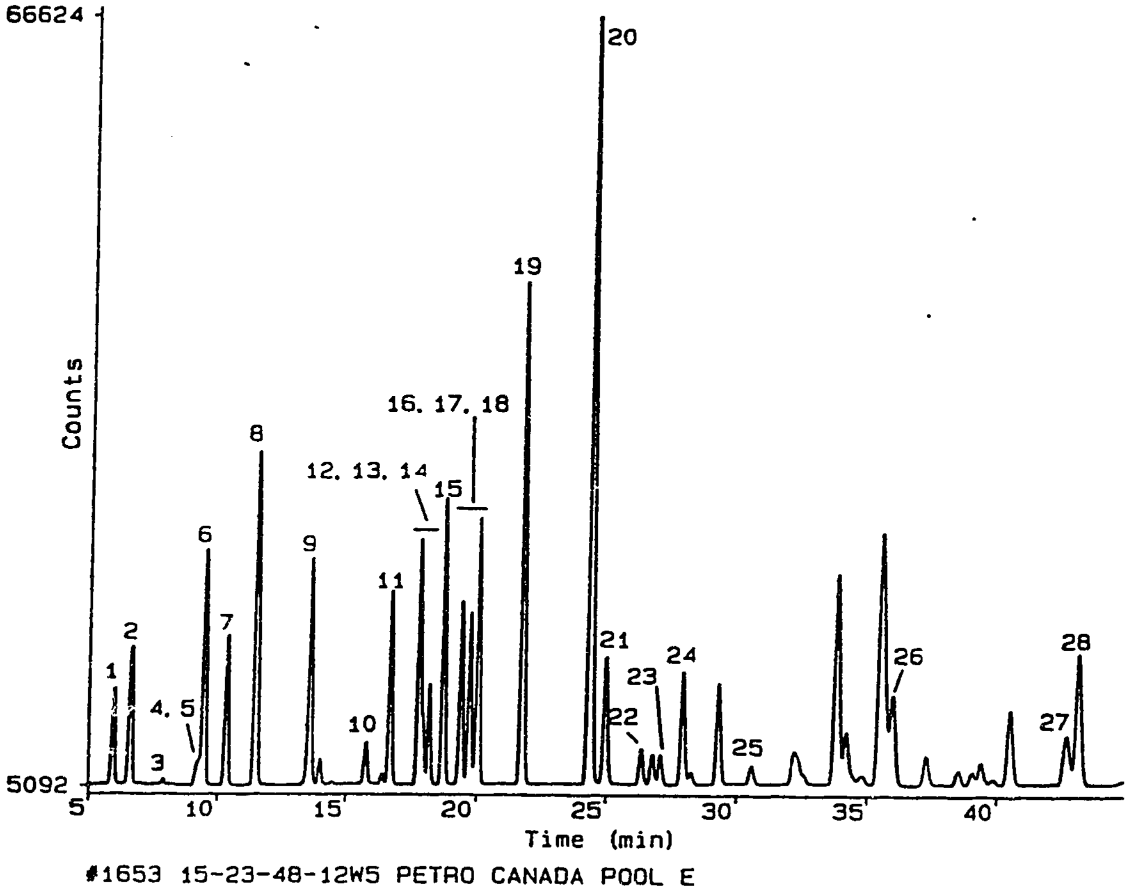


Figure 8: Typical gasoline gas chromatogram. See Table 3 for peak identifications.

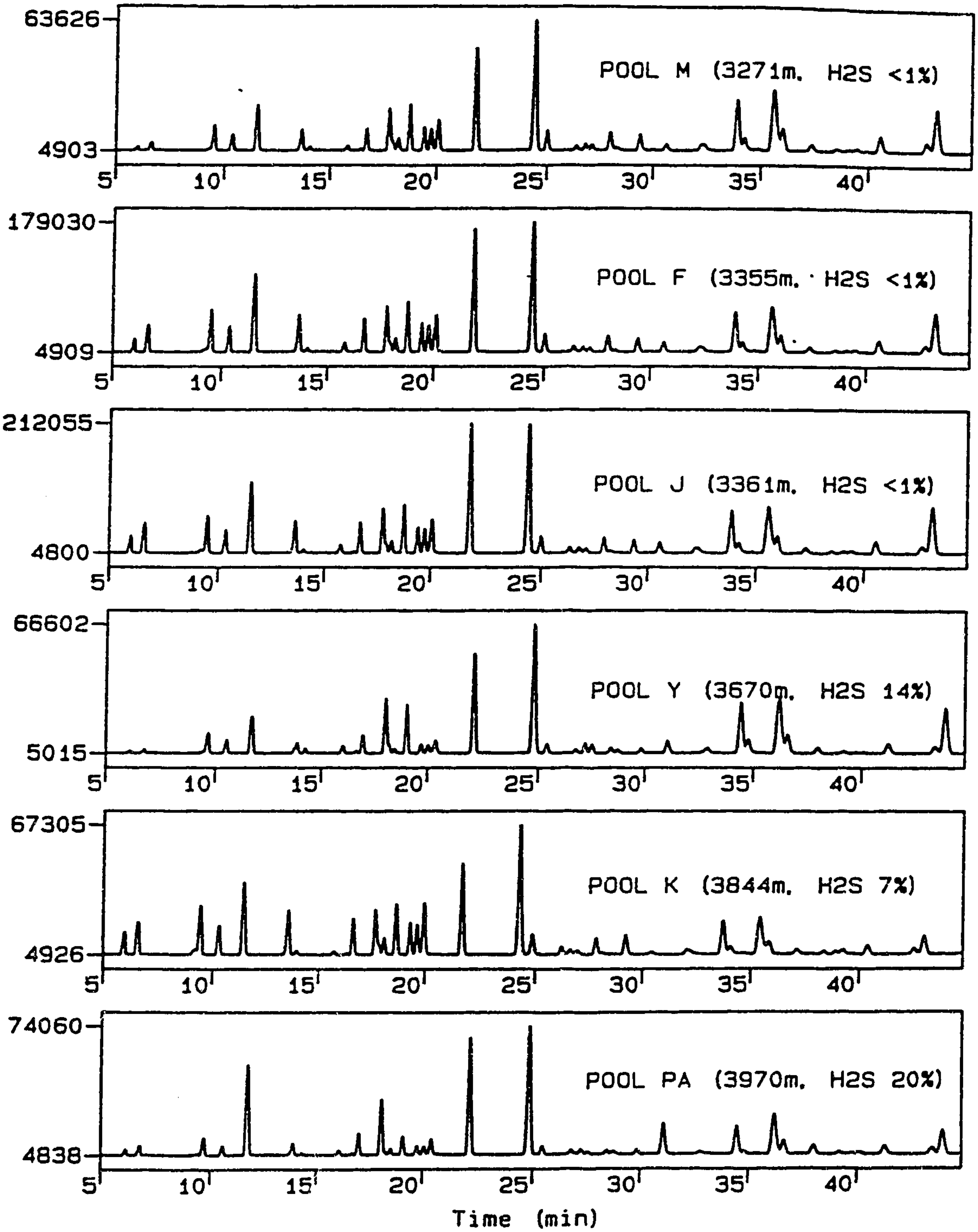


Figure 9a: Gasoline chromatograms for 'isolated' oil pools.

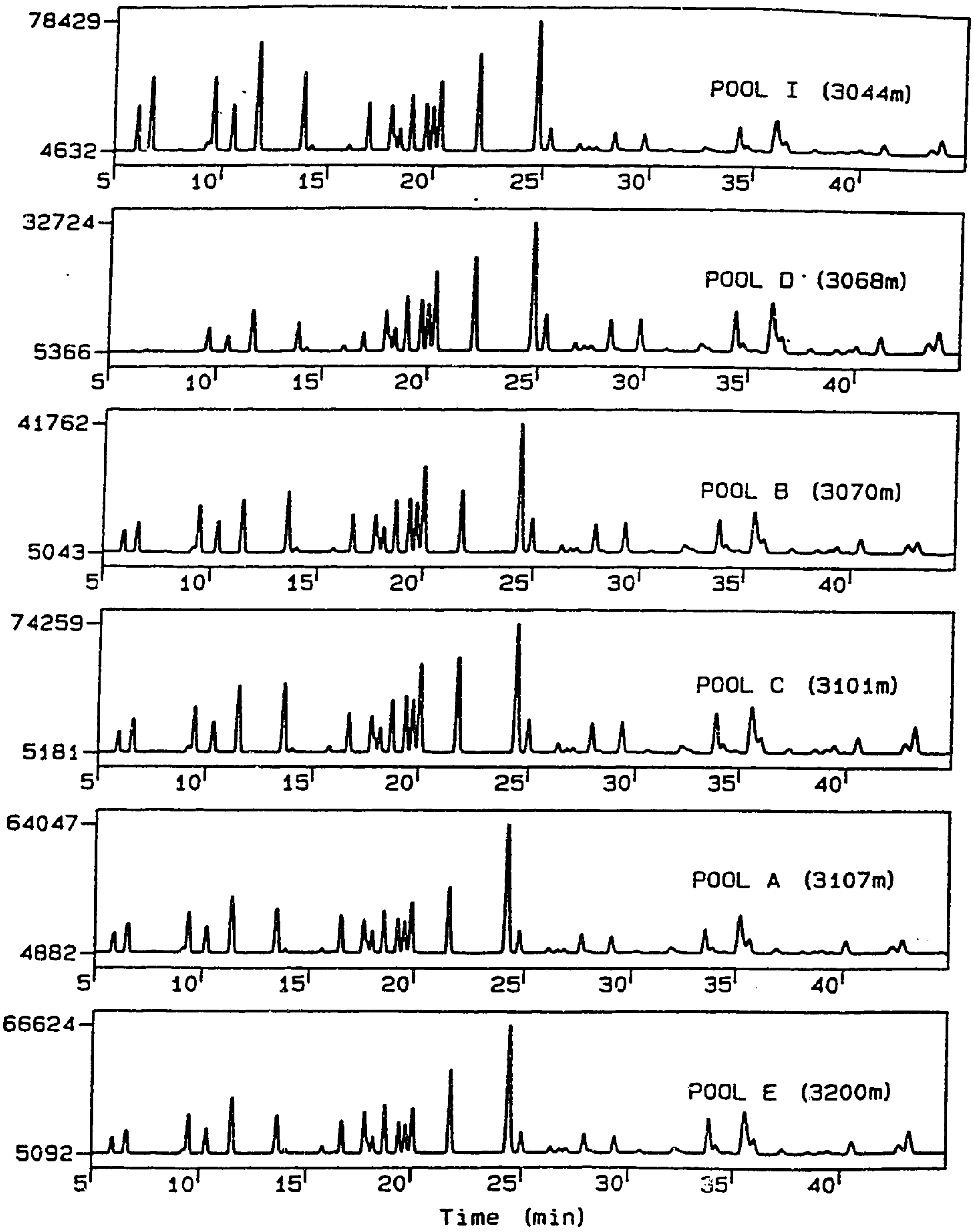


Figure 9b: Gasoline chromatograms for 'isolated' gas condensate pools.

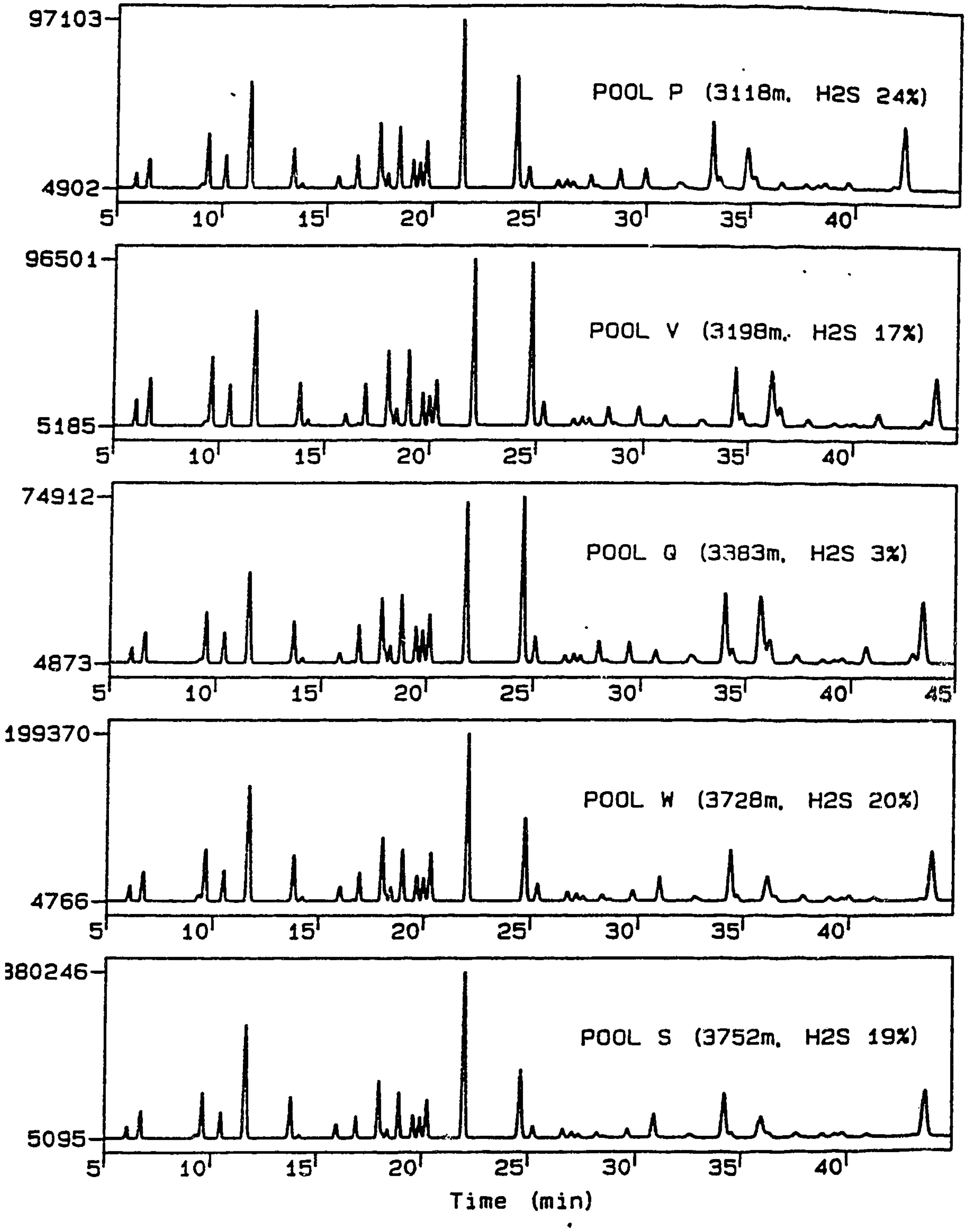


Figure 9c: Gasoline chromatograms for bank edge reef pools.

Table 4a: Normalized percentages of gasoline compounds in 'isolated' oil pools.

COMPOUND	*TYPE	`C#	POOL DESIGNATION				
			B	D	E	A	C
Iso pentane	B	5	2.12	0.11	1.70	1.87	1.75
Normal pentane	N	5	3.44	0.34	3.00	3.62	3.47
2,2-Dimethylbutane	B	6	0.05	0.03	0.09	0.04	0.04
Cyclopentane	C	5	0.64	0.00	0.42	0.61	0.66
2,3-Dimethylbutane	B	6	0.00	3.32	0.00	0.00	0.00
2-Methylpentane	B	6	5.35	0.00	5.26	5.07	4.68
3-Methylpentane	B	6	3.37	2.04	3.08	3.13	2.98
Normal hexane	N	6	6.28	5.78	7.63	7.56	7.19
Methylcyclopentane	C	6	6.67	3.86	5.00	5.89	6.92
Benzene	A	6	0.41	0.75	0.87	0.64	0.59
Cyclohexane	C	6	3.79	2.19	3.72	3.71	3.52
2-Methylhexane	B	7	5.00	6.11	5.89	4.92	4.42
1,1-Dimethylcyclopentane	C	7	0.00	0.00	0.00	0.00	0.00
2,3-Dimethylpentane	B	7	2.40	2.50	1.83	2.09	2.06
3,Methylhexane	B	7	5.16	6.28	5.50	5.02	4.71
1c3Dimethylcyclopentane	C	7	5.24	5.78	3.50	4.37	4.98
1t3-Dimethylcyclopentane	C	7	4.90	5.37	3.29	4.02	4.70
1t2-Dimethycyclopentane	C	7	8.68	9.43	5.31	6.85	8.07
Normal heptane	N	7	6.35	11.19	10.04	9.09	8.91
1c2-Dimethylcyclopentane	C	7	3.83	4.83	2.84	3.22	3.36
Methylcyclohexane	C	7	15.01	17.47	17.08	14.97	13.72
2,5-Dimethylhexane	B	8	0.84	1.11	0.80	0.80	0.97
2,4-Dimethylhexane	B	8	0.55	0.74	0.70	0.60	0.50
2,2,3-Trimethylpentane	B	8	3.54	0.23	2.74	3.12	3.25
Toluene	A	7	0.22	0.41	0.51	0.40	0.35
3-Methylheptane	B	8	2.20	3.04	2.83	2.59	2.19
1c4-Dmethylcyclohexane	C	8	1.86	2.57	1.87	1.72	1.78
Normal octane	N	8	2.10	4.55	4.52	4.10	4.25

* B: Branched N: Normal (Straight) C: Cyclic (Naphthenes)

` C#: Number of carbon atoms

Table 4b: Normalized percentages of gasoline compounds in 'isolated' gas condensate pools.

COMPOUND	*TYPE	`C#	POOL DESIGNATION					
			M	F	J	K	Y	PA
Iso pentane	B	5	0.44	1.24	1.60	2.16	0.27	0.67
Normal pentane	N	5	1.11	3.11	3.50	3.97	0.53	1.34
2,2-Dimethylbutane	B	6	0.03	0.04	0.05	0.07	0.04	0.02
Cyclopentane	C	5	0.00	0.38	0.39	0.60	0.00	0.16
2,3-Dimethylbutane	B	6	3.81	4.84	4.35	5.93	3.24	2.51
2-Methylpentane	B	6	0.00	0.00	0.00	0.00	0.00	0.00
3-Methylpentane	B	6	2.16	2.78	2.50	3.39	1.93	1.34
Normal hexane	N	6	6.84	9.66	8.97	9.36	6.27	14.60
Methylcyclopentane	C	6	3.10	4.35	3.82	5.40	1.92	1.96
Benzene	A	6	0.69	1.06	0.96	0.41	1.15	0.67
Cyclohexane	C	6	2.77	3.47	3.21	3.93	2.50	2.93
2-Methylhexane	B	7	6.37	5.72	5.65	6.07	8.95	7.97
1,1-Dimethylcyclopentane	C	7	0.00	0.00	0.00	0.00	0.00	0.00
2,3-Dimethylpentane	B	7	1.49	1.35	1.22	1.76	0.52	0.77
3,Methylhexane	B	7	5.86	5.31	5.19	5.56	7.00	2.52
1c3Dimethylcyclopentane	C	7	2.94	3.02	2.73	3.51	1.24	1.24
1t3-Dimethylcyclopentane	C	7	2.72	2.80	2.55	3.31	1.15	1.15
1t2-Dimethycyclopentane	C	7	4.09	4.00	3.69	5.82	2.01	2.15
Normal heptane	N	7	13.60	13.79	14.84	10.42	15.32	17.44
1c2-Dimethylcyclopentane	C	7	3.01	2.22	2.13	2.57	1.63	1.48
Methylcyclohexane	C	7	18.81	15.88	15.85	16.63	21.16	20.63
2,5-Dimethylhexane	B	8	0.72	0.72	0.73	0.95	0.64	0.69
2,4-Dimethylhexane	B	8	0.93	0.61	0.65	0.51	1.52	0.45
2,2,3-Trimethylpentane	B	8	0.33	0.21	0.23	0.18	0.59	0.50
Toluene	A	7	1.10	1.39	1.55	0.36	2.39	5.80
3-Methylheptane	B	8	4.68	2.95	3.01	2.28	4.36	3.19
1c4-Dimethylcyclohexane	C	8	2.35	1.45	1.50	1.24	1.71	1.73
Normal octane	N	8	10.04	7.68	9.13	3.63	11.96	6.10

*** B: Branched N: Normal (Straight) C: Cyclic (Naphthenes)**
` C#: Number of carbon atoms.

Table 4c: Normalized percentages of gasoline compounds in bank edge reef pools.

COMPOUND	*TYPE	`C#	POOL DESIGNATION				
			P	V	Q	W	S
Iso pentane	B	5	1.14	1.71	1.05	1.31	1.01
Normal pentane	N	5	2.70	3.90	2.63	3.06	2.94
2,2-Dimethylbutane	B	6	0.05	0.06	0.03	0.05	0.03
Cyclopentane	C	5	0.43	0.37	0.31	0.71	0.47
2,3-Dimethylbutane	B	6	5.20	5.76	4.49	5.39	4.89
2-Methylpentane	B	6	0.00	0.00	0.00	0.00	0.00
3-Methylpentane	B	6	3.00	3.22	2.57	3.06	2.71
Normal hexane	N	6	11.06	10.48	8.78	12.99	13.66
Methylcyclopentane	C	6	3.99	3.79	3.82	4.82	4.65
Benzene	A	6	1.15	0.99	0.90	1.52	1.63
Cyclohexane	C	6	2.87	3.17	3.04	2.67	2.28
2-Methylhexane	B	7	6.65	6.78	6.25	6.66	6.59
1,1-Dimethylcyclopentane	C	7	0.00	0.00	0.00	0.00	0.00
2,3-Dimethylpentane	B	7	1.26	1.24	1.32	1.24	0.90
3,methylhexane	B	7	5.39	5.82	5.55	4.83	4.84
1c3Dimethylcyclopentane	C	7	2.48	2.53	2.92	2.36	2.39
1t3-Dimethylcyclopentane	C	7	2.25	2.31	2.68	2.17	2.19
1t2-Dimethycyclopentane	C	7	4.32	3.70	4.17	4.68	4.18
Normal heptane	N	7	15.66	13.81	14.02	16.98	19.16
1c2-Dimethylcyclopentane	C	7	2.19	2.16	2.54	1.90	1.54
Methylcyclohexane	C	7	11.45	14.73	15.77	9.37	8.67
2,5-Dimethylhexane	B	8	0.83	0.65	0.78	1.05	1.13
2,4-Dimethylhexane	B	8	0.71	0.72	0.76	0.52	0.47
2,2,3-Trimethylpentane	B	8	0.31	0.25	0.27	0.25	0.21
Toluene	A	7	2.35	1.12	1.41	3.15	3.45
3-Methylheptane	B	8	1.60	2.52	3.18	0.47	0.44
1c4-Dmethylcyclohexane	C	8	0.62	1.06	1.50	0.31	0.27
Normal octane	N	8	10.35	7.16	9.25	8.49	9.34

*** B:Branched N:Normal(Straight) C:Cyclic(Naphthenes)**
` C#:Number of carbon atoms.

Table 5: Gasoline ratios for the Nisku pools in the Brazeau River area.

Pool	Maturity		Water Washing			Biodegradation	
	PI 2	$nC_7/MCYC_6$	$3MC_5/Ben$	$MCYC_6/Tol$	CYC_6/Ben	iC_5/nC_5	$3MC_5/nC_6$
B	11.24	0.42	8.15	67.61	9.16	0.61	0.54
D	16.88	0.64	2.74	42.70	2.94	0.33	0.35
E	17.88	0.59	3.54	33.82	4.28	0.57	0.40
A	16.51	0.61	4.94	37.42	5.85	0.52	0.41
C	16.81	0.65	5.07	39.54	5.99	0.50	0.41
M	23.18	0.72	3.13	17.08	4.01	0.40	0.32
F	24.93	0.87	2.61	11.47	3.27	0.40	0.29
J	27.01	0.94	2.61	10.23	3.35	0.46	0.28
K	18.29	0.63	8.34	46.18	9.64	0.54	0.36
Y	25.83	0.72	1.68	8.87	2.17	0.51	0.31
PA	31.12	0.85	2.01	3.56	4.40	0.50	0.09
P	29.91	1.37	2.62	4.88	2.50	0.42	0.27
V	26.13	0.94	3.24	13.14	3.19	0.44	0.31
Q	25.16	0.89	2.84	11.15	3.37	0.40	0.29
W	34.16	1.81	2.00	2.98	1.75	0.43	0.24
S	37.44	2.21	1.66	2.51	1.40	0.35	0.20

PI 2: Paraffin Index 2
nC_7: normal hexane, $MCYC_6$: methylcyclohexane,
$3MC_5$: 3-methylpentane, Ben: benzene,
Tol: toluene, CYC_6: cyclohexane,
iC_5: iso pentane, nC_5: normal pentane.

Table 6: Gross composition of Nisku oils and gas condensates

Pool	^Production Type	*IP/BP	H_2S mole fraction	`MFD (meters)	API gravity	<160°C %	>160°C %	Saturates %	Aromatics %	Resins %	Asphaltenes %
A	OIL	IP	0.0073	3107.4	44.0	44.5	49.7	83.80	14.12	1.88	0.20
B	OIL	IP	0.0073	3070.1	43.5	37.4	55.6	81.65	15.65	2.18	0.52
C	OIL	IP	0.0073	3101.1	42.8	30.8	60.6	81.51	15.97	2.27	0.25
D	OIL	IP	0.0073	3068.8	39.4	31.6	66.3	81.46	15.29	2.57	0.68
E	OIL	IP	0.0073	3200.0	42.0	37.8	57.0	84.72	12.68	2.39	0.21
F	G.C.	IP	0.0070	3355.1	48.4	44.6	52.6	89.23	9.72	0.58	0.47
J	G.C.	IP	0.0012	3361.5	53.6	67.7	30.2	95.05	3.94	0.65	0.36
M	G.C.	IP	0.0044	3271.8	48.6	40.0	56.7	97.99	1.10	0.61	0.31
K	G.C.	IP	0.0669	3844.4	48.2	45.8	50.9	83.97	14.94	0.97	0.12
Y	G.C.	IP	0.1355	3669.8	47.5	``N.E.	``N.E.	90.13	9.11	0.70	0.06
Peco A	G.C.	IP	0.2022	3970.2	46.7	80.1	17.4	64.61	34.17	1.15	0.07
P	G.C.	BP	0.2435	3117.5	48.7	48.3	47.3	74.12	24.34	1.34	0.20
V	G.C.	BP	0.1699	3198.4	48.8	45.1	50.0	80.73	18.11	1.10	0.06
Q	G.C.	BP	0.0332	3383.4	47.1	40.4	57.8	89.16	9.48	1.25	0.11
W	G.C.	BP	0.1983	3727.8	42.3	69.2	28.2	65.33	30.90	3.32	0.45
S	G.C.	BP	0.1932	3752.6	52.4	65.6	29.7	68.66	30.06	1.11	0.17

^G.C. : Gas condensate

***IP: 'Isolated' pool BP: Bank edge reef pool**

`MFD: Mean Formation Depth

``NE: Not enough sample of pool Y to distill; whole oil (instead of distilled sample) fractionated.

Percentages of hydrocarbon fractions are normalized, i.e., the sum of the percentages of saturates, aromatic, resins and asphaltenes in a sample equals 100%.

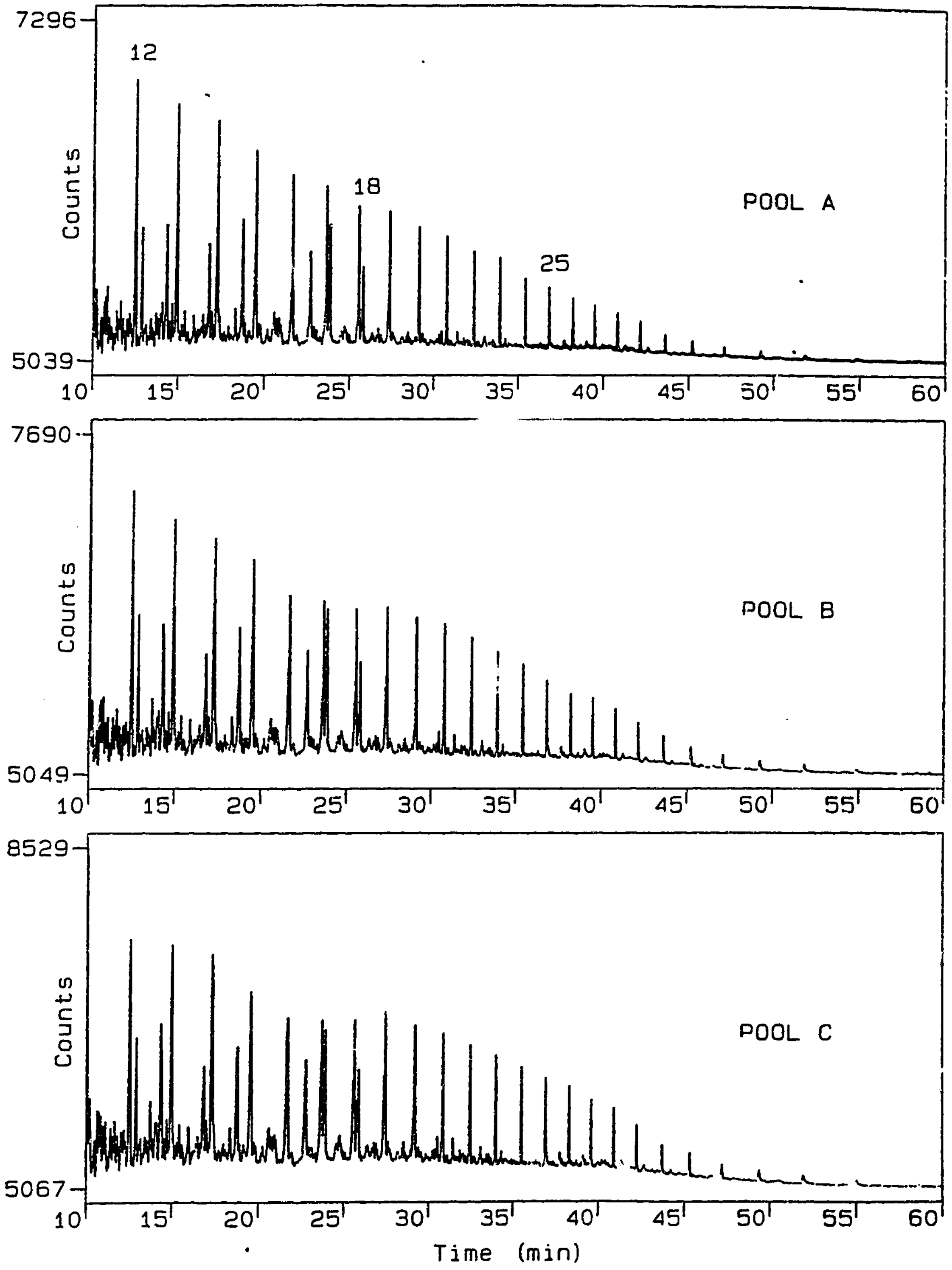


Figure 10a: Whole oil gas chromatograms for 'isolated' oil pools.

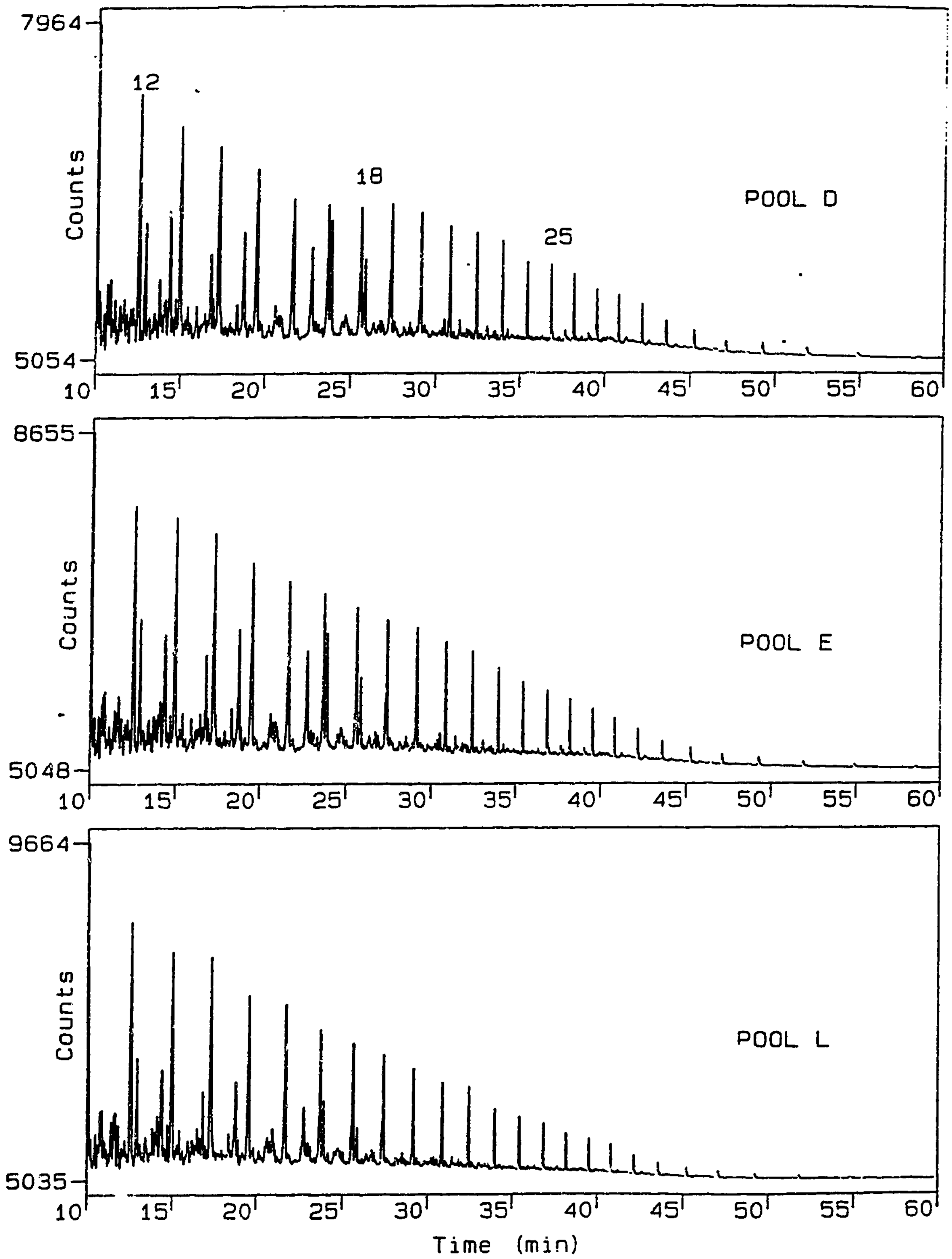


Figure 10a: Continued.

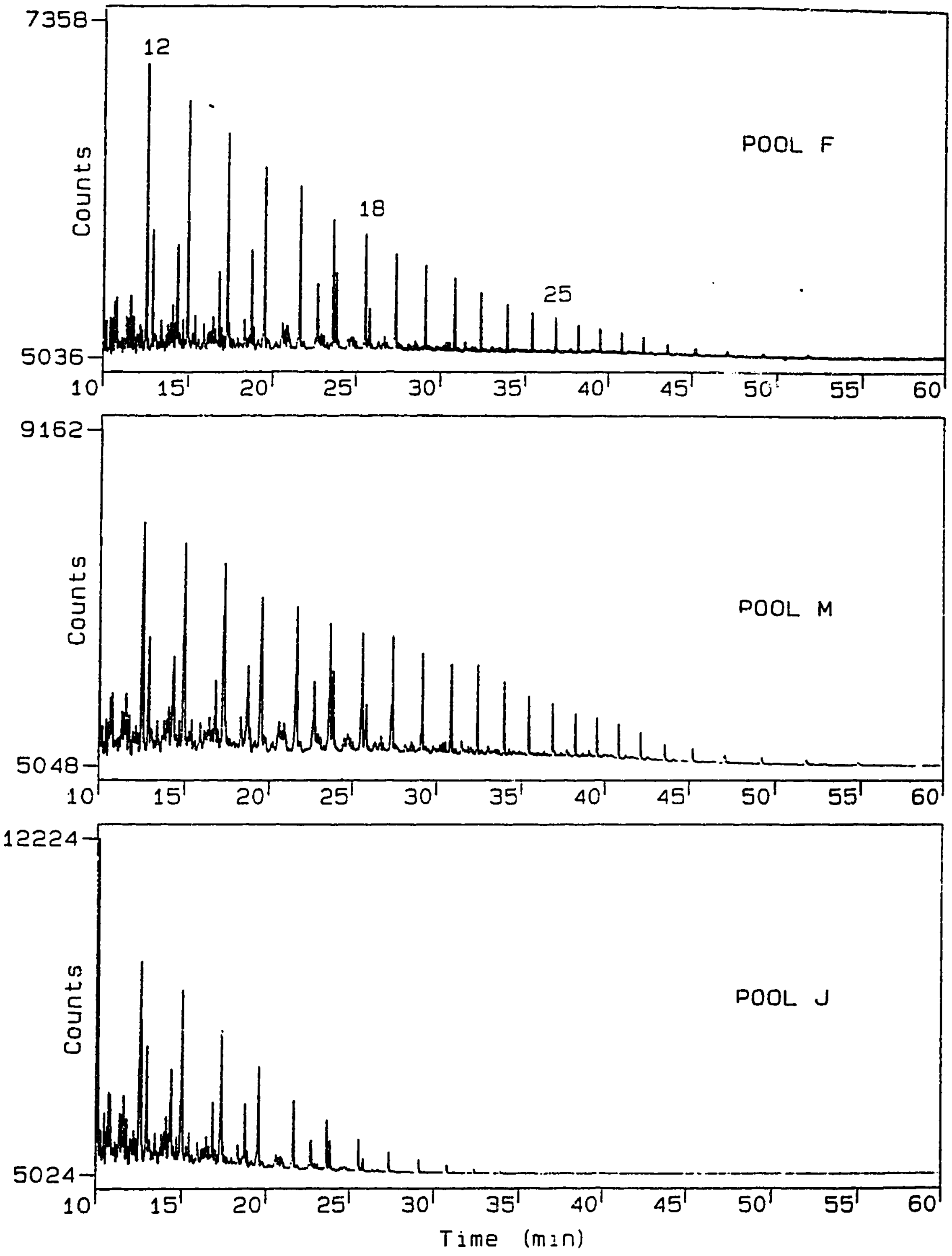


Figure 10b: Whole condensate gas chromatograms for 'isolated' gas condensate pools.

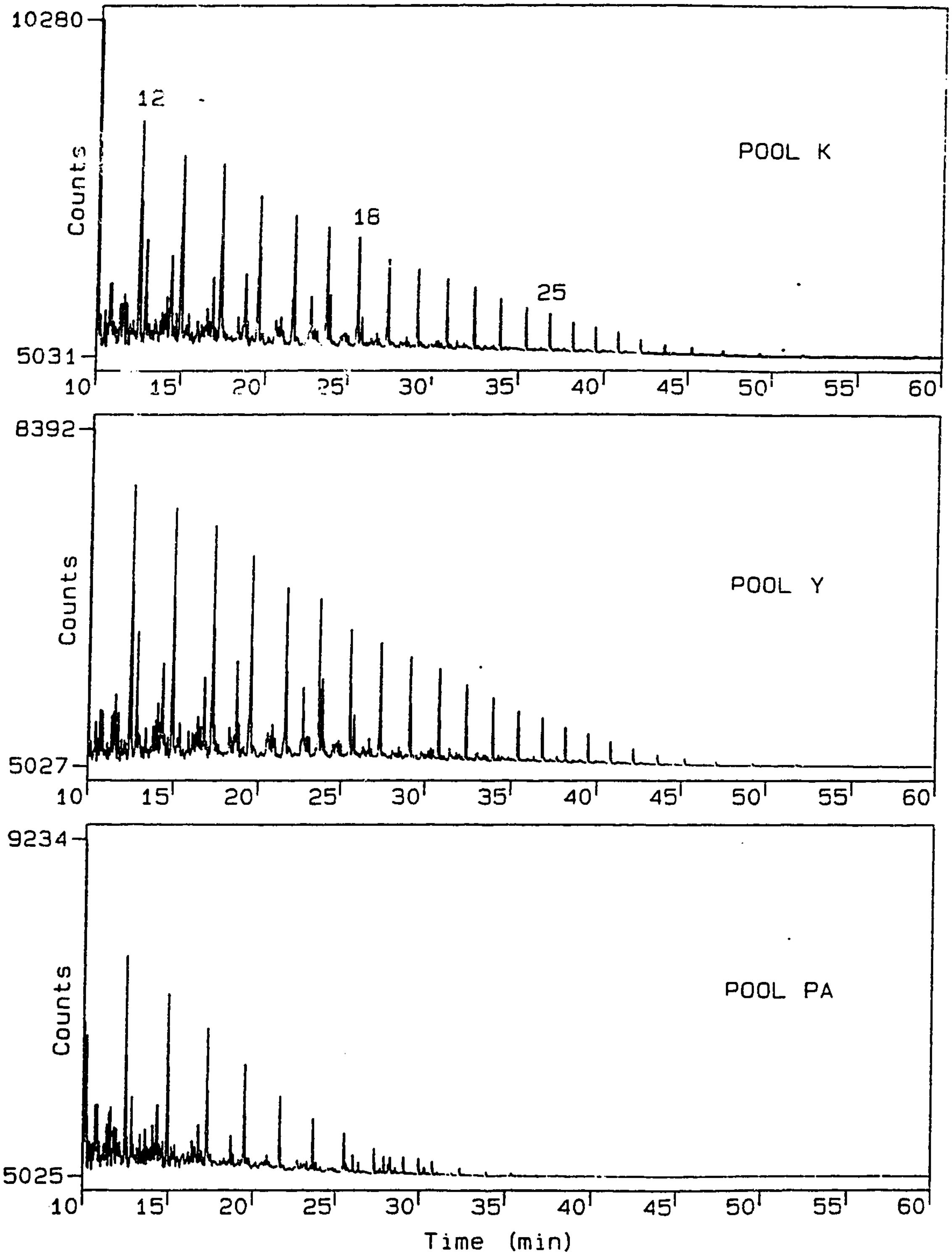


Figure 10b: Continued.

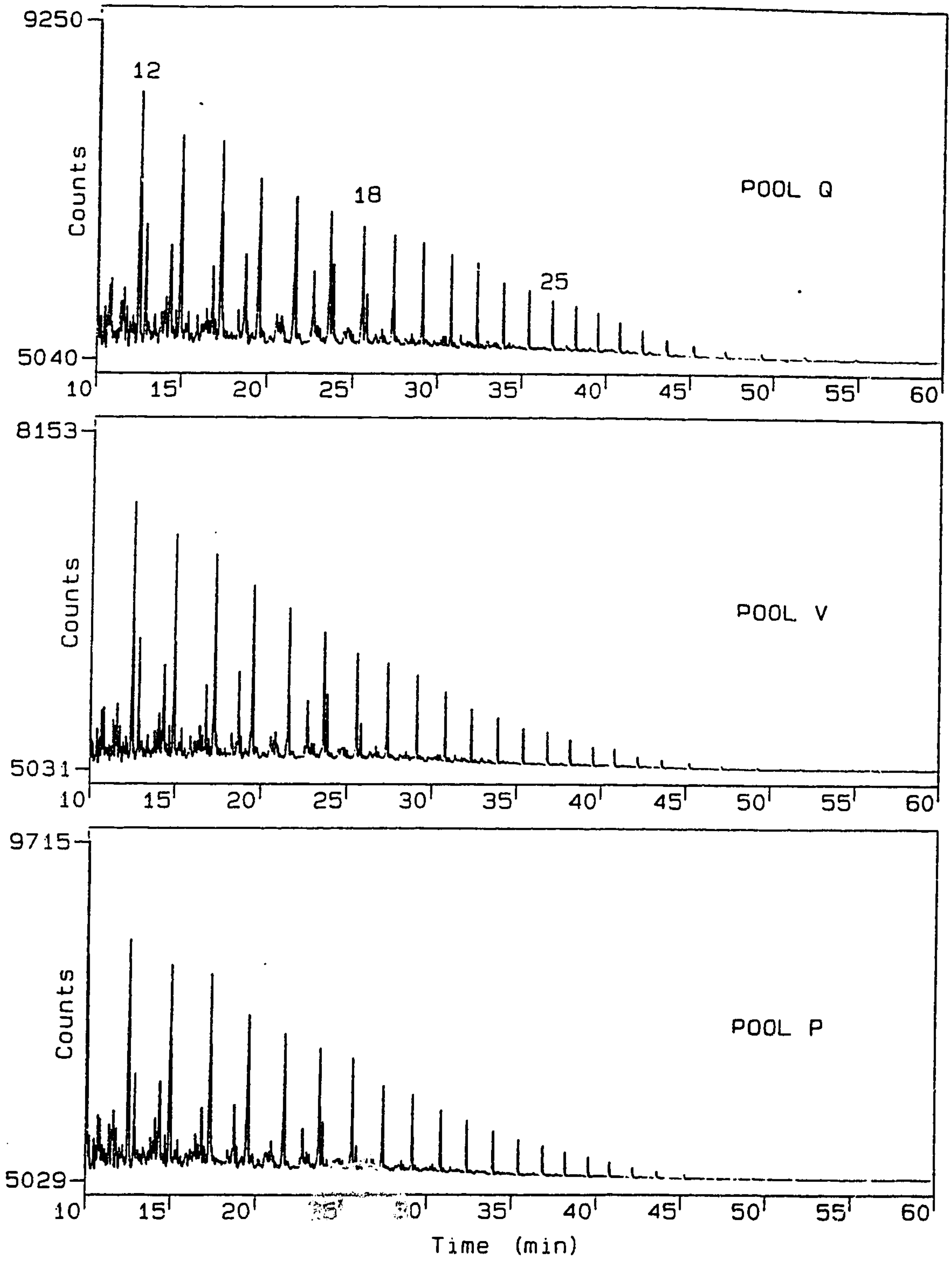


Figure 10a: Whole condensate chromatograms for bank edge reef pools.

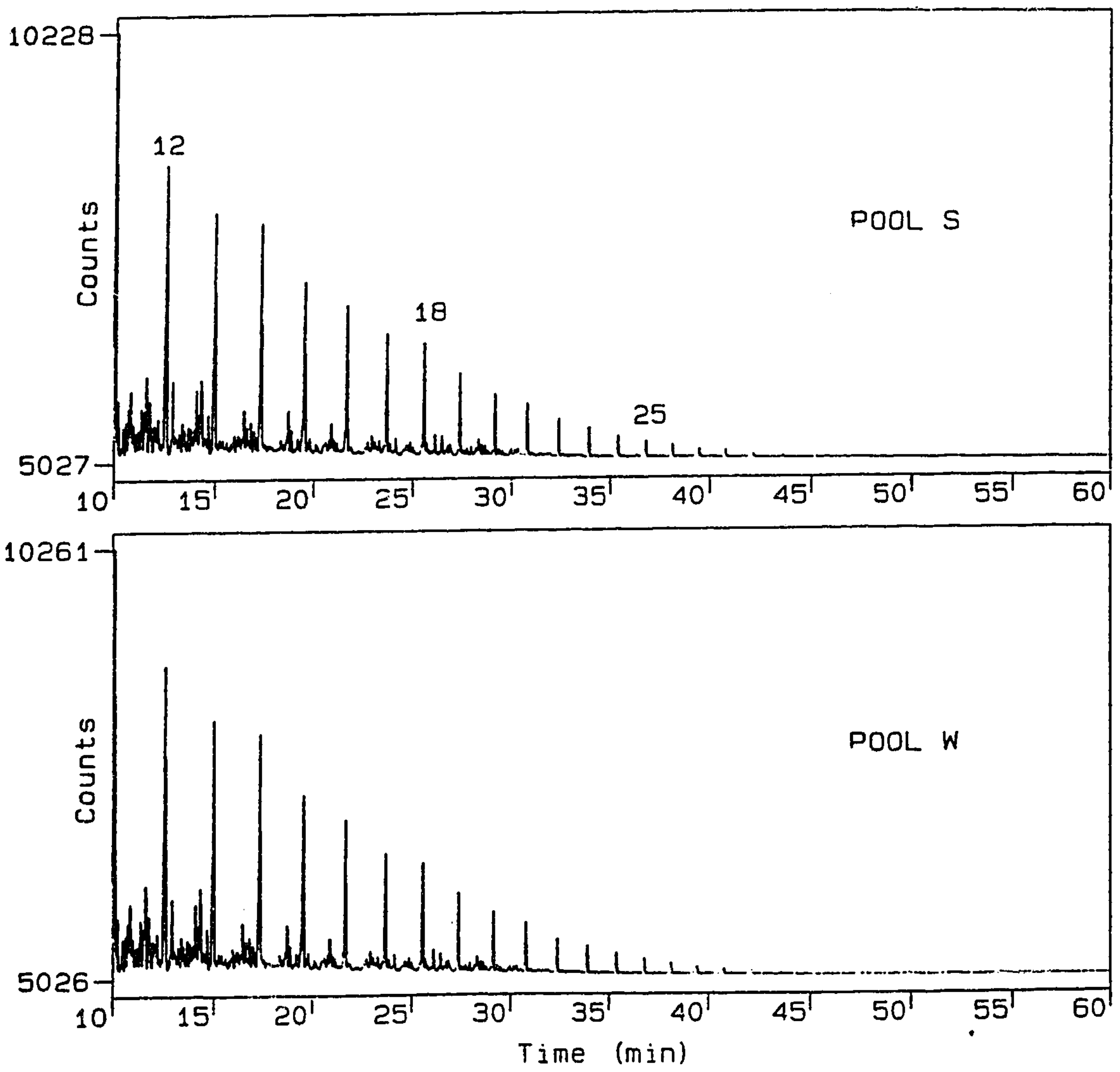


Figure 10c: Continued.

Table 7: Isoprenoid to normal paraffin ratios.

Pool	\`Production	*IP/BP	H_2S	\`\`MFD	^Pr/Ph	^Pr/nC$_{17}$	^Ph/nC$_{18}$
	Type		mole fraction	metres			
A	OIL	IP	0.0073	3107.4	1.56	0.77	0.56
B	OIL	IP	0.0073	3070.1	1.57	0.91	0.62
C	OIL	IP	0.0073	3101.1	1.37	0.93	0.67
D	OIL	IP	0.0073	3068.8	1.51	0.87	0.60
E	OIL	IP	0.0073	3200.0	1.58	0.72	0.52
F	G.C.	IP	0.007	3355.1	1.83	0.59	0.36
J	G.C.	IP	0.0012	3361.5	2.27	0.59	0.39
M	G.C.	IP	0.0044	3271.8	1.69	0.62	0.40
K	G.C.	IP	0.0669	3844.4	1.81	0.43	0.25
Y	G.C.	IP	0.1355	3669.8	1.68	0.50	0.34
Peco A	G.C.	IP	0.2022	3970.2	2.24	0.24	0.12
P	G.C.	BP	0.2435	3117.5	1.99	0.39	0.22
V	G.C.	BP	0.1699	3198.4	1.78	0.51	0.34
Q	G.C.	BP	0.0332	3383.4	1.91	0.61	0.43
W	G.C.	BP	0.1983	3727.8	1.81	0.08	0.05
S	G.C.	BP	0.1932	3752.6	1.74	0.08	0.05

Ratios are calculated from samples gas chromatogram peak areas.

\`G.C. : Gas Condensate

***IP: 'Isolated' pool BP: Bank edge reef pool.**

\`\`MFD: Mean Formation Depth

Pristane: 2,6,10,14 tetramethyl pentadecane; Phytane: 2,6,10,14 tetramethyl hexadecane

^Pr/Ph: Pristane/Phytane; ^Pr/nC$_{17}$: pristane/n-heptadecane; ^Ph/nC$_{18}$: phytane/n-octadecane

Table 8: Carbon and sulfur stable isotopic values.

Pool	^Production Type	*IP/BP	H2S mole fraction	`MFD metres	$\delta^{13}C$ >160°C	$\delta^{13}C$ saturates	$\delta^{13}C$ aromatics	$\delta^{34}S$ >160 °C
A	OIL	IP	0.0073	3107.4	-28.78	-29.45	-27.41	NES
B	OIL	IP	0.0073	3070.1	-29.29	-29.60	-25.34	NES
C	OIL	IP	0.0073	3101.1	-28.98	-29.46	-27.44	12.7
D	OIL	IP	0.0073	3068.8	-28.99	-29.44	-27.25	10.9
E	OIL	IP	0.0073	3200.0	-29.11	-29.58	-27.50	NES
F	G.C.	IP	0.0070	3355.1	-28.45	-28.55	-26.42	17.7
J	G.C.	IP	0.0012	3361.5	-28.19	-28.62	-25.99	NES
M	G.C.	IP	0.0044	3271.8	-28.44	-28.62	-26.41	NES
K	G.C.	IP	0.0669	3844.4	-27.53	-28.06	-26.02	22.2
Y	G.C.	IP	0.1355	3669.8	NE	NE	NE	NE
PECOA	G.C.	BP	0.2022	3970.2	-25.99	-26.51	-23.54	25.3
P	G.C.	BP	0.2435	3117.5	-27.43	-28.05	-25.99	26.1
V	G.C.	BP	0.1699	3198.4	-28.24	-28.24	-26.96	26.7
Q	G.C.	BP	0.0332	3383.4	-28.36	-28.80	-26.63	22.1
W	G.C.	BP	0.1983	3727.8	-25.75	-26.12	-25.77	26.2
S	G.C.	BP	0.1932	3752.6	-25.86	-26.04	-25.34	26.3

^G.C. : Gas condensate

***IP: 'Isolated' pool ; BP: Bank edge reef pool.**

`MFD: Mean Formation Depth

$\delta^{13}C$ results are expressed relative to PDB. Accuracy of measurements: +/-0.25 permil

$\delta^{34}S$ results are expressed relative to CDT. Accuracy of measurements: +/- 0.3 permil

NE: Not enough sample of pool Y to distil

NES: Not enough organo-sullfur compounds in the sample for analysis.

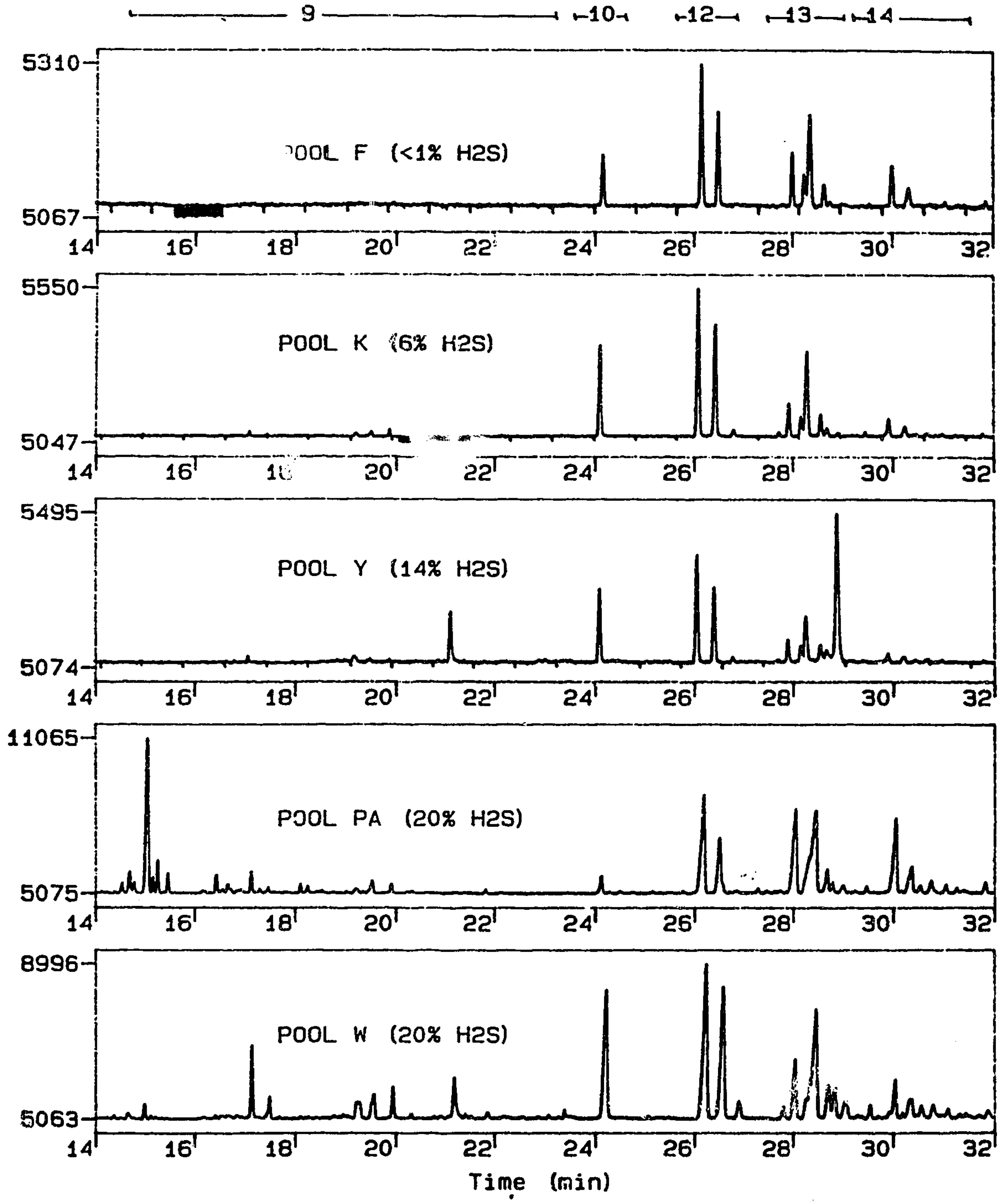


Figure 11: FPD-gas chromatograms for selected samples aromatic fractions. Refer to Table 9 for compound identification.

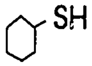
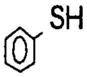
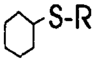
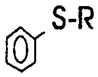
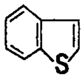
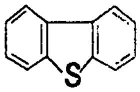
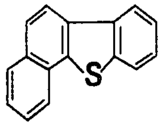
	Class		General Formula
1	Alkyl thiols	Mercaptans	R-SH
2	Cyclic thiols		
3	Aromatics thiols		
4	Dialkyl sulfides		R-S-R
5	Disulfides		R-S-S-R
6	Alkyl cycloalkyl sulfide		
7	Alkyl aryl sulfides		
8	Thiophenes		
9	Benzothiophenes		
10	Dibenzothiophenes		
11	Benzonaphthothiophenes		
12	Methyldibenzothiophenes		
13	C_2-dibenzothiophenes		
14	C_3-dibenzothiophenes		

Table 9: Classes of organo-sulfur compounds identified in crude oils. (Ho *et al.*, 1974 ; Hughes, 1984)

CHAPTER 6

DISCUSSION

6.1 Correlation Studies

Establishing a common source for all of the hydrocarbon pools sampled is essential in order to eliminate source variation as a factor influencing the hydrogen sulfide concentrations in the study area. This problem was addressed in two phases. First the oils and condensates were analyzed to determined if they could be correlated (i.e., if oils and gas condensates have a common source). Secondly, a possible source rock(s) for these hydrocarbons was investigated.

6.1.1 Oil-Oil Correlations

Several correlation parameters used in previous studies (as listed below) were employed in this thesis to determine if the oils and condensate sampled had a common source. These correlation parameters include isoprenoid to n-alkane ratios and stable isotopes ($\delta^{13}C$ and $\delta^{34}S$). Geochemical alteration of oils and condensates by thermal maturation and TSR in the study area hinders the use of other probably more useful correlation parameters. Correlation using biomarker analysis, for example, was not possible. Steranes and hopanes were not detected in condensate samples and are present only in very low concentrations (results not reported) in the oil samples because of their high level of thermal maturity.

6.1.1.1 Isoprenoid/n-alkane Ratios

A plot of pristane/n-heptadecane (Pr/nC_{17}) versus phytane/n-octadecane (Ph/nC_{18}) ratios (Figure 12) can indicate maturity levels, biodegradation, and

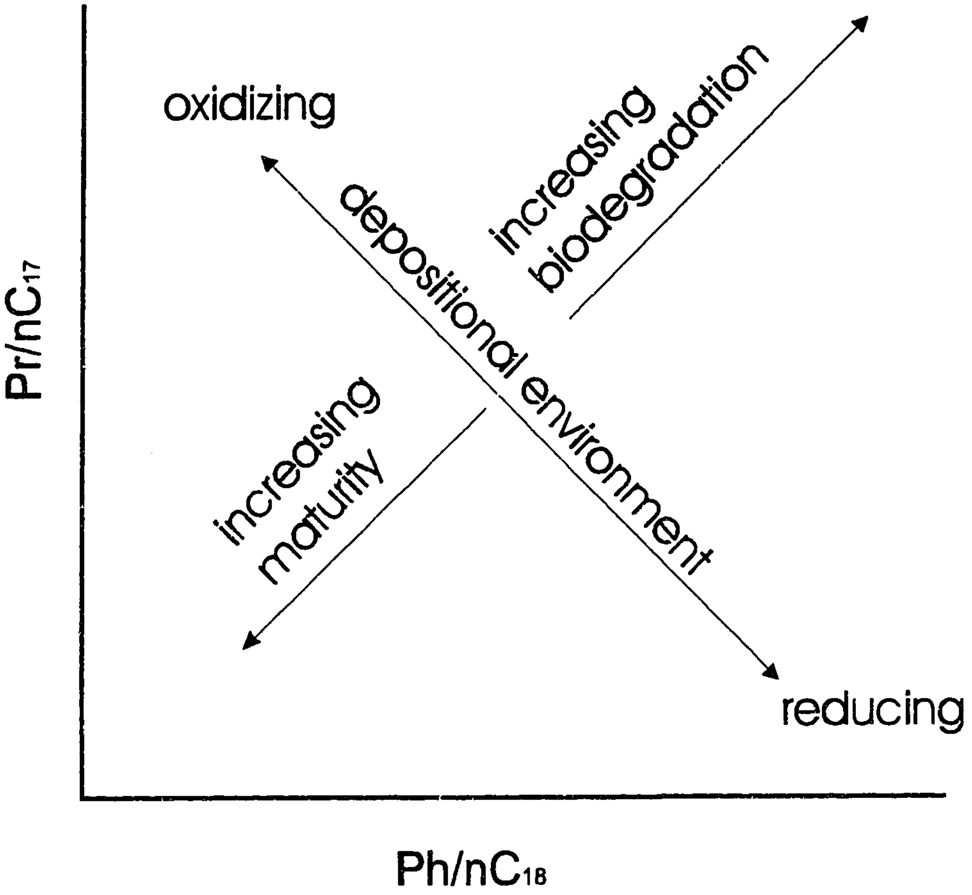


Figure 12: Use of isoprenoid/n-alkane ratios as indicators of biodegradation, maturity and depostional environment (modified from Waples, 1985).

depositional environment (Talukdar et al., 1985; Waples, 1985; Saban et al., 1987; Osadetz et al., 1992). Oils from different sources tend to plot along different maturity lines. A similar plot for the oils and condensates in the study area (Figure 13) shows that the samples follow one maturity trend ($Pr/nC_{17} = 1.3(Ph/nC_{18}) + 0.09$) and, therefore, probably belong to one family.

6.1.1.2 $\delta^{34}S$ Values

Sulfur isotopic compositions and sulfur concentrations have been used as a bulk parameter in oil-oil correlation studies (e.g., Tissot and Welte, 1984). The isotopic composition of sulfur in oils is dependent on that of the source rock. The $\delta^{34}S$ values of oils sampled are about 10 ‰CDT (Table 8, p. 50). This value, however, increases with increasing molar concentration of hydrogen sulfide in gas condensate pools. Such a change in sulfur isotopic composition is common in TSR-affected pools (Orr, 1974; Claypool and Mancini, 1989). $\delta^{34}S$ was, therefore, not a reliable correlation parameter in this study.

6.1.1.3 $\delta^{13}C$ Values

Carbon isotopic compositions of liquid hydrocarbons have also been used to correlate oils (e.g., Stahl, 1978; Sofer, 1984). Maturation increases the $\delta^{13}C$ values of oils, but the change is not expected to exceed 2 ‰PDB. Therefore, oils that differ by more than 2 - 3 ‰PDB are commonly interpreted to be from different sources (Sofer, 1984). There are exceptions to this rule. Orr (1974) and Chung et al. (1981) reported a 3.6 ‰PDB range from the least to most mature oils from the Big Horn Basin, Wyoming which had a common source. The maximum difference in $\delta^{13}C$ obtained for the oils and condensates sampled was 3.54 ‰PDB (Table 8, p. 50) which is probably a reflection of not only maturation but also TSR. Claypool and Mancini (1989) demonstrated that TSR also increases

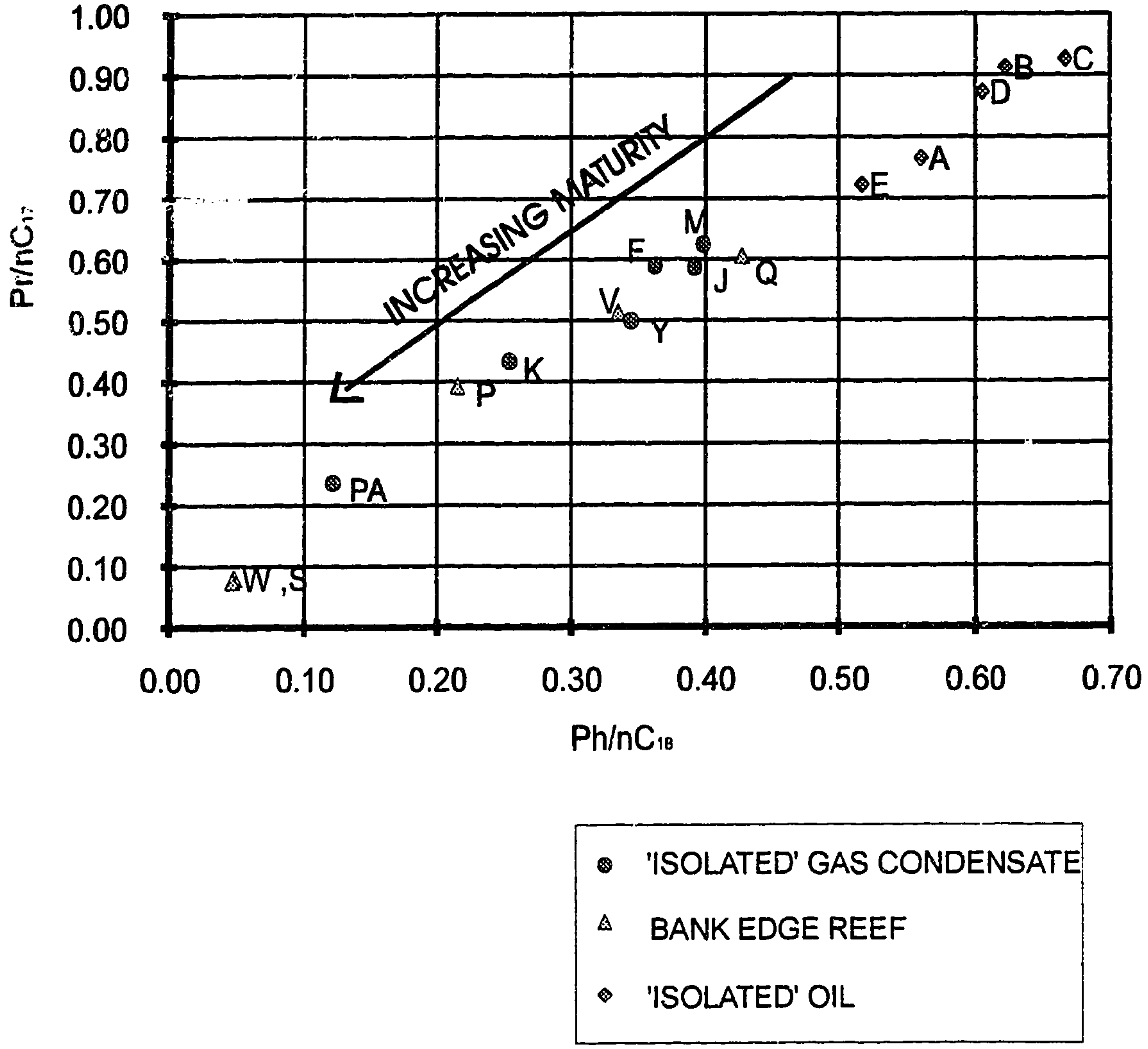


Figure13: Pr/nC$_{17}$ versus Ph/nC$_{18}$ for oils and condensates within the Nisku Formation in the Brazeau River area.

$\delta^{13}C$ values of hydrocarbons in sour gas condensates pools. Therefore, hydrocarbon correlation using $\delta^{13}C$ was also not reliable in this study.

Whole oil and condensate gas chromatograms of hydrocarbon sampled which have similar maturity levels show similar distributions (e.g., oil samples B and D, Figure 10a, p. 43 - 44 and condensate samples V, Figure 10c, p.47 and Y, Figure 10b, p. 46). This observation, together with the isoprenoid to n-alkane ratios, is consistent with the interpretation that the hydrocarbons in this study probably belong to one family. Previous organic geochemical studies in the study area have implied that the Nisku pinnacle reefal reservoirs in the Bigoray, West Pembina and Brazeau River areas all have one source (Allan and Creaney, 1991; Creaney et al., 1994). However the actual source rock(s) for the hydrocarbons in the Nisku Formation in the study area is still controversial (Chevron Exploration Staff Ltd., 1979; Creaney et al., 1994).

6.1.2 Oil-Source Correlations

Pristane/phytane ratio has been used in previous oil-source correlation studies (e.g., Snowdon and Powell, 1979; Clayton et al., 1987; Allan and Creaney, 1991). Sweet oils analyzed have pristane/phytane ratios (Table 7, p. 49) ranging from 1.37-1.58 (average: 1.52). Mature condensate ratios are higher ranging from 1.69-2.27 (average: 1.89). These values indicate that the oils and condensates are derived from a marine source rock (Tissot and Welte, 1984; Peters and Moldowan, 1993). The increase in pristane/phytane ratio from oils to condensates is expected since the ratio has previously been shown to increase with increasing maturity (Hunt, 1979; Tissot and Welte, 1984). Suggested source rocks for the hydrocarbons in the Nisku Formation in study area are the Duvernay Formation and the Cynthia shale Member (Chevron Exploration Staff Ltd., 1979; Allan and Creaney, 1991; Creaney et al., 1994).

The Cynthia Member was described by the Chevron Exploration Staff Ltd. (1979) and suggested to be the source of the oils in the Nisku reefs in the study area. This conclusion was based on total organic carbon (TOC) values and comparison of $\delta^{13}C$ values of oils in the Nisku Formation in the West Pembina area to those of kerogens extracted from several possible source rocks. Cores from the Cynthia Member were not sampled for the present study and therefore data to corroborate the potential of the Cynthia as the source rock for the Nisku hydrocarbons in the study area is lacking. Chevron Exploration Staff Ltd. (1979) reported only 28% of the Cynthia shale sampled had TOC greater than 0.5% with a maximum of 1.0%. The Cynthia Member based on TOC values has poor to fair source rock qualities (Peters, 1986). Creaney et al. (1994) have, therefore, noted that the correlation of the Cynthia Member to the Nisku reef oils is not definite.

The Duvernay Formation was eliminated as a possible source rock by Chevron Exploration Staff Ltd. (1979) based on the guideline that source kerogens have $\delta^{13}C$ values 1.5 to 2.0 ‰PDB higher than those of the generated oils. This conclusion, however, may be based on a restricted premise. Bitumen (soluble portion of kerogen) $\delta^{13}C$ values are generally about 0.5 to 1.5 ‰PDB lower than those of their source kerogens and $\delta^{13}C$ values of oils are further depleted by 0 to 1.5 ‰PDB compared to those of the corresponding bitumens (Peters and Moldowan, 1993). A negative correlation between oils and kerogens, therefore, is generally accepted if $\delta^{13}C$ values of oils and kerogens differ by more than 2 to 3 ‰PDB and when oils have $\delta^{13}C$ values higher than those of kerogens (Hunt, 1979; Tissot and Welte, 1984). The carbon isotopic data reported by Chevron Exploration Staff Ltd. (1979) showed that $\delta^{13}C$ values for the Duvernay kerogens (-28.1 to -27.4 ‰PDB) are higher than those of oils in the Nisku Formation (-29.0 to -27.7 ‰PDB), and the difference is less than 2 ‰PDB. Hence, $\delta^{13}C$ values suggest that the Duvernay Formation is a possible source rock for the Nisku reef hydrocarbons.

Allan and Creaney (1991) indicated that the oils derived from the Duvernay Formation and the oils in the Nisku Formation are very similar. Both are low sulfur oils (<0.5%) and have pristane/phytane ratios of about 1.5. Biomarker analyses reported by Allan and Creaney (1991), however, showed that the distribution of tricyclic terpanes and hopanes of the oils that were derived from the Duvernay Formation and oils in the Nisku Formation were dissimilar. The authors suggested that these differences may be due to a subtle difference in the original bacterial population in the two source facies. It is also possible that the oils which were derived from the Duvernay Formation and oils in the Nisku Formation in the study area have a common source (i.e., Duvernay Formation) and that the differences may be due to small changes in the bacterial population of the Duvernay Formation at different parts of the basin or that the oils compared were at different maturity levels.

Additional organic geochemical analyses are, therefore, needed to identify positively the source rock(s) for the hydrocarbons in the Nisku Formation in the Bigoray, West Pembina and Brazeau River areas. As stated earlier, based on isoprenoid to n-alkane ratios, there is a high possibility that the hydrocarbons sampled have a common source. Although the evidence is not conclusive, the assumption is made for further interpretations in this study that the oils and condensates sampled do have a common source.

6.2 Thermochemical Sulfate Reduction and Thermal Maturation

TSR is acknowledged to take place at temperatures and thermal maturities commensurate with those at which the cracking of crude oil to condensate occurs (Sassen, 1988; Machel et al., in press, a). The changes in hydrocarbon distribution in the reservoir resulting from TSR are similar to those caused by thermal maturation. Thermal maturation results in a decrease in heavier hydrocarbons accompanied by an increase in natural gas (e.g., Hunt, 1979; Tissot and Welte, 1984). Similar effects are seen in TSR-affected pools (Sassen, 1988; Claypool and Mancini, 1989, Machel et al., in press, a). The effects of TSR on hydrocarbons may, therefore, be difficult to distinguish from the effects of thermal maturation.

In the study area, thermal maturation is probably the main factor controlling the hydrocarbon distribution in 'isolated' oil and 'isolated' gas condensate pools at depths shallower than 3360 m (<110°C). These reservoirs are 'sweet' and hence TSR has not occurred, at least not to any significant degree, within these pools. However, 'isolated' pools which lie deeper than 3360 m (Figure 3, Table 1) are sour and, therefore, the hydrocarbon distribution observed at present probably reflects both thermal maturation and TSR effects. Changes to the hydrocarbons in the Nisku Formation in the study area reflecting either thermal maturation or/and TSR are discussed in the following sections.

6.2.1 Isoprenoid/n-alkane Ratios

Based on Pr/nC_{17} and Ph/nC_{18} ratios (see section 6.1.1.1), hydrocarbon pools in the Nisku Formation in the study area follow a distinct thermal maturation trend (Figures 12 and 13). As expected, maturity increases from oil to gas condensate pools. The maturation parameter (Pr/nC_{17}) does not show a direct correlation with hydrogen sulfide reservoir concentrations (Figure 14a). The ratio of Pr/nC_{17} can, therefore, be used as an independent maturation parameter that is not significantly affected by TSR.

Pr/nC_{17} versus depth relations (Figure 14b) suggest that migration (and possibly mixing) of hydrocarbons occurred along the bank edge reef pools. 'Isolated' pools follow the expected trend of increasing maturity with increasing depth. All pools sampled along the bank edge reef except pool Q, however, have higher Pr/nC_{17} values than expected for their present depths. The horizontal lines extrapolated from pools S, W, V, and P in Figure 14b suggest possible source

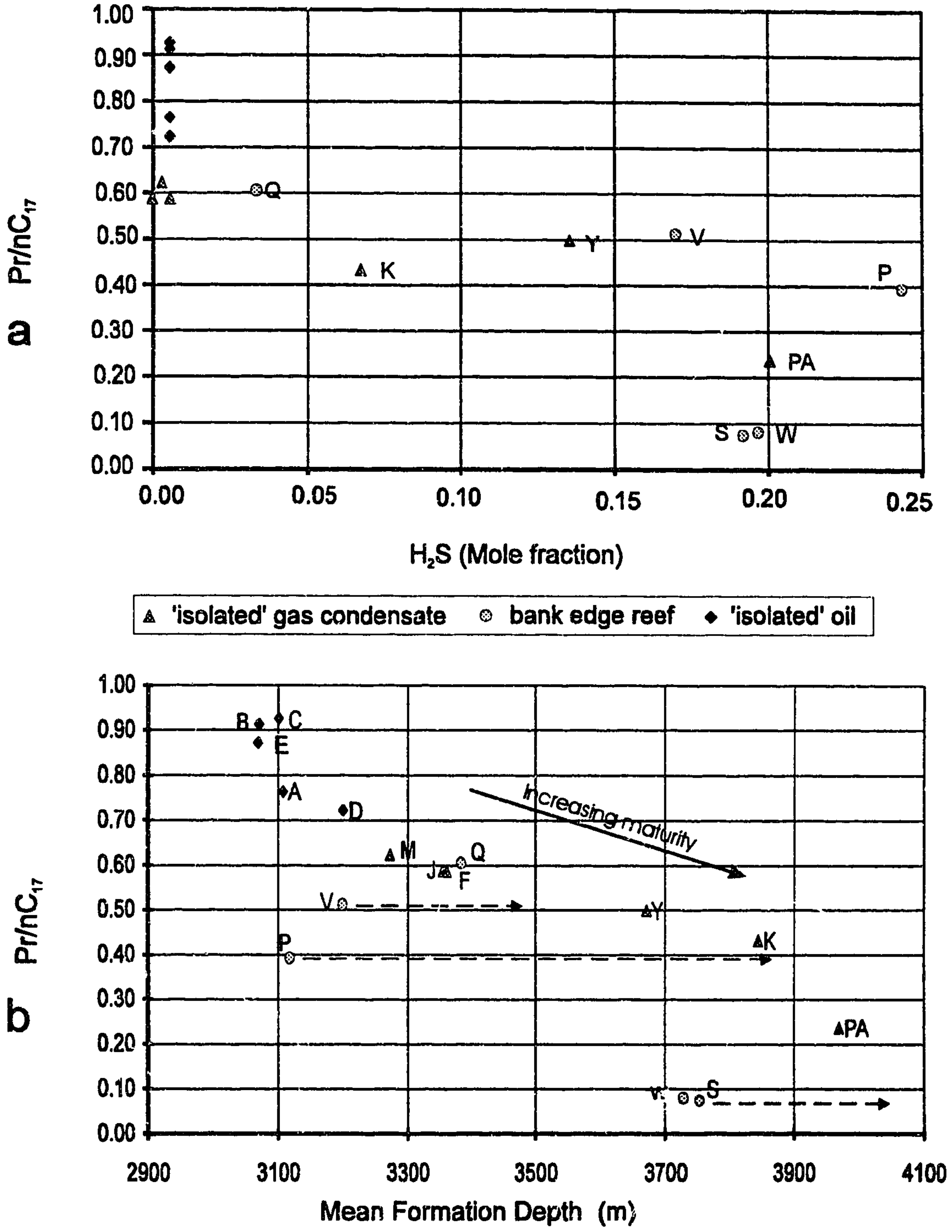


Figure 14: Pr/nC_{17} versus (a) H_2S and (b) mean formation depth.

depths for the pooled hydrocarbons, implying updip migration and mixing of hydrocarbons in the bank edge reef pools.

6.2.2 Gross Composition

The gross compositions of distilled hydrocarbon samples have probably been affected by both thermal maturation and TSR. As an oil matures, the relative amount of saturated hydrocarbons increases with a corresponding decrease in aromatics (Tissot and Welte, 1984; Hunt, 1979). This trend is observed in oils and sweet condensates with increasing thermal maturation (Figure 15. The opposite trend is observed in sour gas condensate pools with increasing hydrogen sulfide content and, to some degree, with thermal maturation. Thus, in sour gas condensate pools, with increasing hydrogen sulfide reservoir content, the ratio saturate/aromatic decreases. Similar trends have been previously observed in other sour gas condensate pools and were attributed to the preferential removal of saturated hydrocarbons during TSR (Sassen, 1988; Claypool and Mancini, 1989). Bryce and Hinshelwood (1949); Pryor (1962); and Valitov and Valitov (1975) showed that the reaction of paraffins with sulfur can produce aromatic compounds with alkenes as intermediates. An example of this dehydrocyclization reaction is shown in Figure 16 for the conversion of hexane to benzene. Valitov and Valitov (1975) showed that some of these reactions with gasoline hydrocarbons can occur at temperatures as low as 50°C, and that reaction rates increase with an increase in temperature and in the presence of limestone. Dehydrocyclization of paraffins to aromatics by reaction with sulfur provides one explanation for the decrease in saturates with a corresponding increase in aromatics in sour gas condensate pools.

Saturates can also be removed from TSR-affected pools by sulfur oxidation reactions. Generally, the length of a paraffin chain is shortened by such oxidation reactions (equations 2 and 3, p.16). The rates of sulfur oxidation reactions,

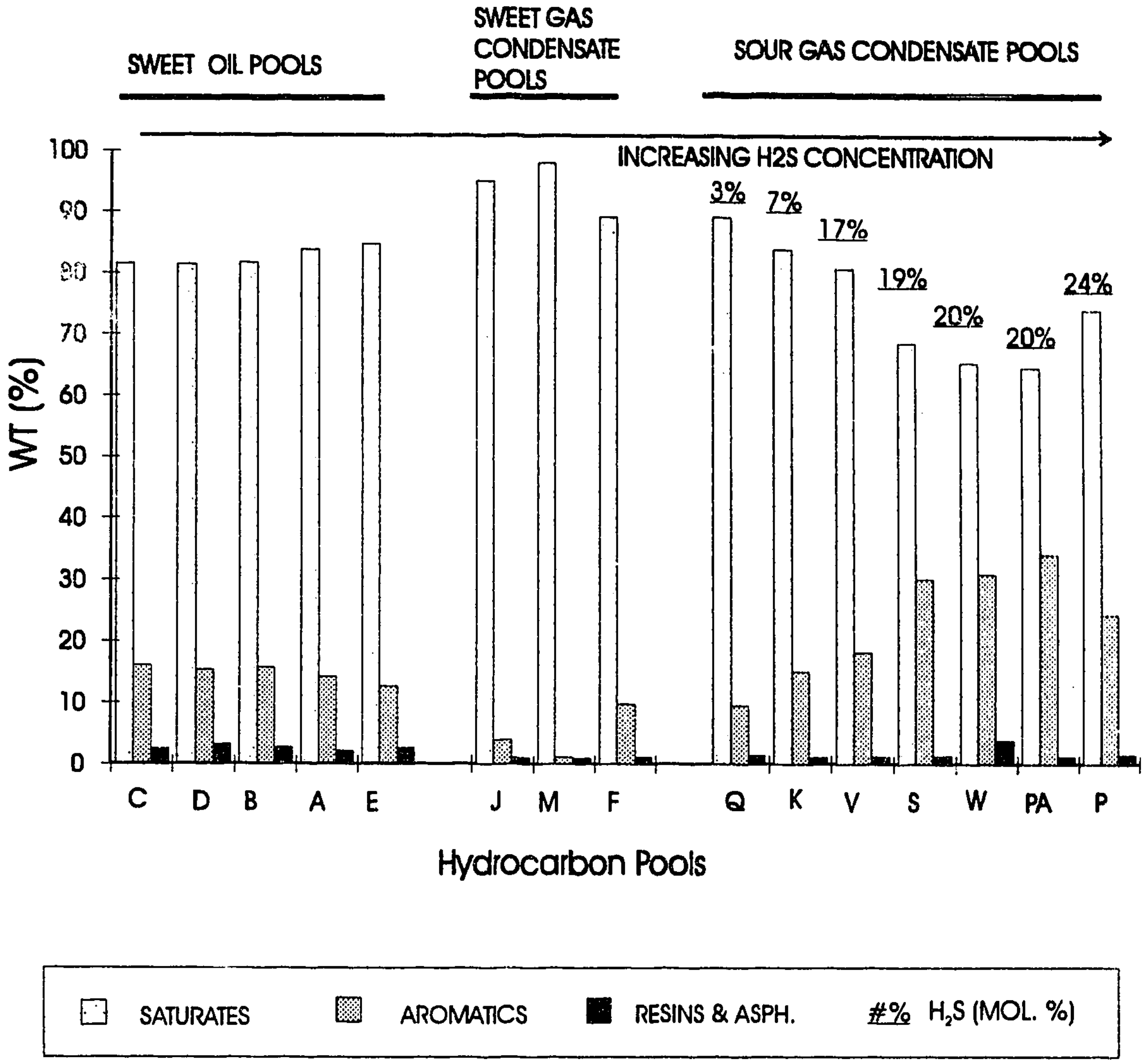
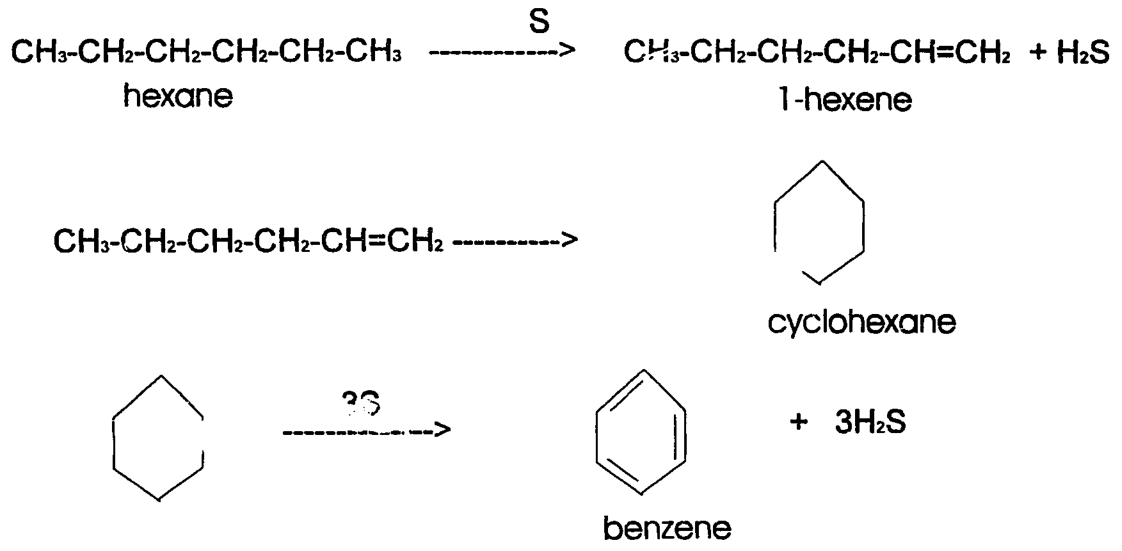


Figure 15: Bar chart showing the gross composition of oils and condensates within the Nisku Formation in the study area.



Overall reaction: C_6H_{14} + 4S -----------> C_6H_6 +$4H_2S$

Figure 16: Dehydrogenation of hexane with sulfur to benzene and H_2S.

however, decrease with increasing carbon number (Toland, 1960) and therefore, gasoline compounds are probably more prone to oxidation than are heavier hydrocarbons. The decrease in saturate content via oxidation reactions can, therefore, also result in an increase in aromatics content of sour gas condensate pools.

Whole oil and condensate gas chromatograms provide additional evidence that saturates have been removed from sour gas condensate pools. With increasing thermal maturation and hydrogen sulfide content in the gas condensate pools (particularly in 'isolated' pools), heavier n-alkanes decrease and lighter hydrocarbons ($<C_{10}$) increase (Figure 10b, p. 45 - 46). This trend can be the result of both thermal maturation and TSR. Thermal maturation results in the cracking of heavier hydrocarbons to produce lighter hydrocarbons, while TSR removes heavier hydrocarbons via oxidation reactions to produce lower molecular hydrocarbons and via dehydrocyclization reactions to produce aromatic compounds.

6.2.3 Organo-sulfur Compounds

Expected products from the reactions of sulfur with hydrocarbons are organo-sulfur compounds. The different aromatic sulfur compounds detected in selected gas condensate pools in the study area are shown in Figure 11. Prior to TSR, the aromatic sulfur compounds present in an oil are wholly dependent on its source and maturity level (Ho et al., 1974; Hughes, 1984). In an immature oil, the source rock alone determines the type and distribution of organo-sulfur compounds in the oil. Increasing thermal maturation causes a prominent decrease in benzothiophenes relative to dibenzothiophenes. Carbonate-derived oils are generally characterized by a significant content of benzothiophenes (Hughes, 1984).

The absence of benzothiophenes in gas condensate from pool F (Figure 11, p. 51) suggests a high level of thermal maturity. However, with increasing hydrogen sulfide and thermal maturity, these compounds are seen in pools PA and W (Figure 11, p. 51). There is also an overall increase in aromatic sulfur compounds in these pools with increasing hydrogen sulfide content. The occurrence of benzothiophenes and heavier aromatic sulfur compounds in these thermally mature pools is probably due to the reaction of sulfur (from reduced anhydrite, see equation 1 p. 15) with the hydrocarbons, i.e., these compounds were probably formed as by-products of TSR. The formation of organo-sulfur compounds during catagenesis has been reported by Ho et al. (1974) in condensates associated with high hydrogen sulfide content. The authors suggested that the mercaptans present in condensates were formed by the reaction of hydrogen sulfide with light hydrocarbons. Whereas, the presence of mercaptans were not determined in the hydrocarbon samples, the formation of benzothiophenes in sour gas condensates suggests that other lower molecular weight sulfur compounds, including mercaptans, may also be present. TSR, therefore, can alter the distribution of sulfur compounds in oils during catagenesis.

6.2.4 API Gravity

The incorporation of sulfur into liquid hydrocarbons (e.g., equations 6-9, p. 19) during catagenesis may be one factor contributing to the variation in API gravity in hydrocarbon pools sampled. Thermal maturation results in the cracking of heavier hydrocarbons and in an increase in gas content in reservoirs (e.g., Hunt, 1979). Therefore, an increase in thermal maturation results in a decrease in the density of liquid hydrocarbons in reservoirs. This change was observed for oils to sweet condensates in this study. Figure 17 shows that there is an increase in API gravity (decrease in density) from oils to sweet condensates with increasing thermal maturation. However, in most sour gas pools, there appears to be a no significant change (e.g., pool Y) or a possibly decrease in API gravity (e.g., pool

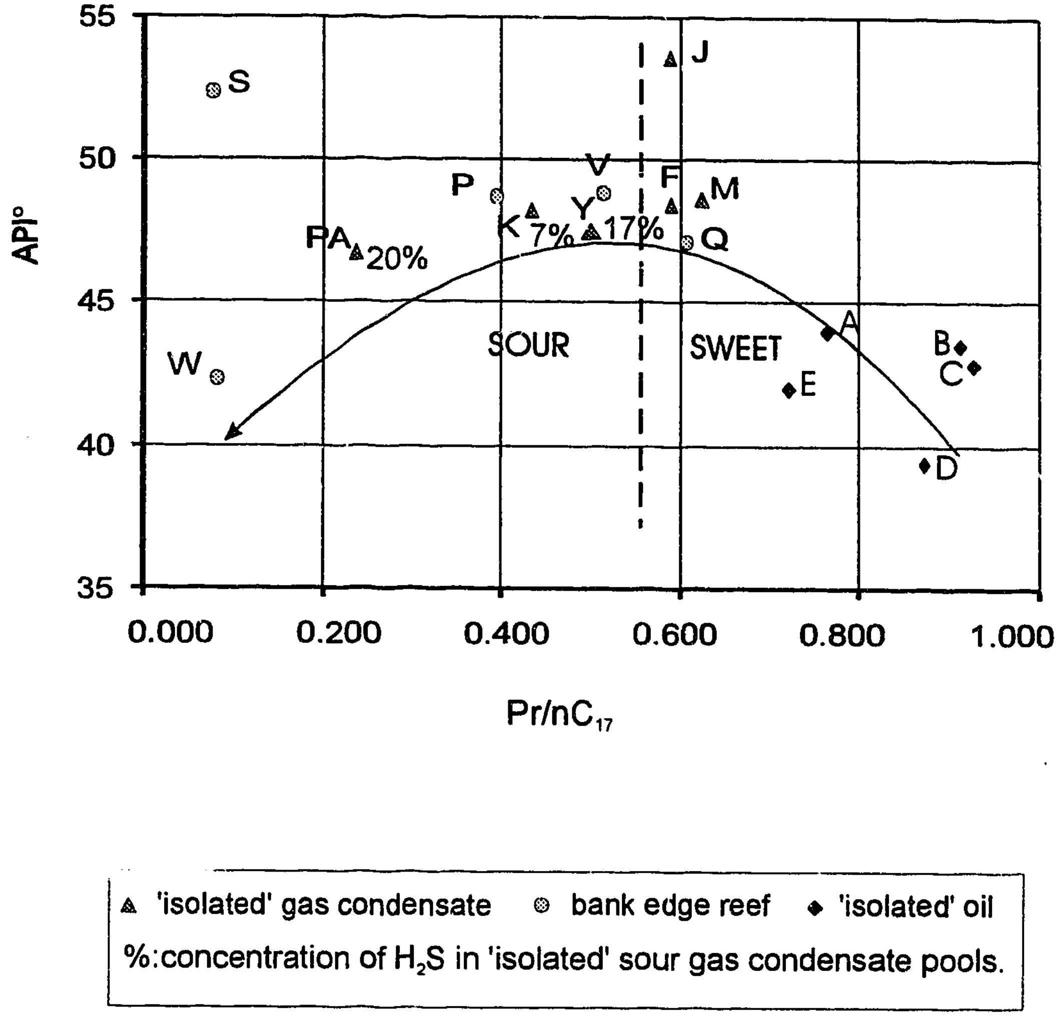


Figure 17: API gravity versus Pr/nC$_{17}$ for oils and condensates within the Nisku Formation in the study area.

W) with increasing maturity, although there is a shift towards lower molecular weight compounds in the sour gas condensate pools relative to sweet gas condensates (Figures 10b, p. 45 and 10c, p. 47).

Claypool and Mancini (1989) report a similar decrease in API gravity for sour gas condensates relative to sweet gas condensates. The anomalies in API gravities for hydrocarbon samples can possibly be explained by the incorporation of the heavy sulfur atom (atomic weight 32) into hydrocarbon molecules. The expected increase in API gravity (decrease in density) in liquid hydrocarbons with increase in thermal maturation as a result of removal of heavier hydrocarbons is probably balanced by the increase in density resulting from the incorporation of sulfur into liquid hydrocarbons. The net effect, therefore, results in either no significant change (e.g., pool Y) or a decrease in API gravity in sour gas condensate pools (e.g.,pool W) relative to sweet gas condensate pools. The decrease in API gravity is not directly correlative with hydrogen sulfide reservoir concentrations (Figure 17). Other factors (e.g., sampling and storage) may have influenced the API gravity of hydrocarbon samples.

6.2.5 Carbon and Sulfur Isotopes

The $\delta^{34}S$ values of liquid hydrocarbons in the Nisku Formation in the study area should increase with increasing hydrogen sulfide content because the sulfur source for the formation of organo-sulfur compounds during catagenesis is inferred to be from the reduction of anhydrite (see equation 1, p. 15). As indicated by Figure 18, this appears to be the case. In oil pools with low hydrogen sulfide concentrations, $\delta^{34}S$ values obtained are probably similar to those of the source kerogen. With increasing hydrogen sulfide concentration in the reservoir, $\delta^{34}S$ values quickly approach the $\delta^{34}S$ values of the Nisku Formation subsurface anhydrite (+24 to +28 ‰CDT) reported by Machel (1985); and Machel and Burton (1991). These results are consistent with the observations made by Orr

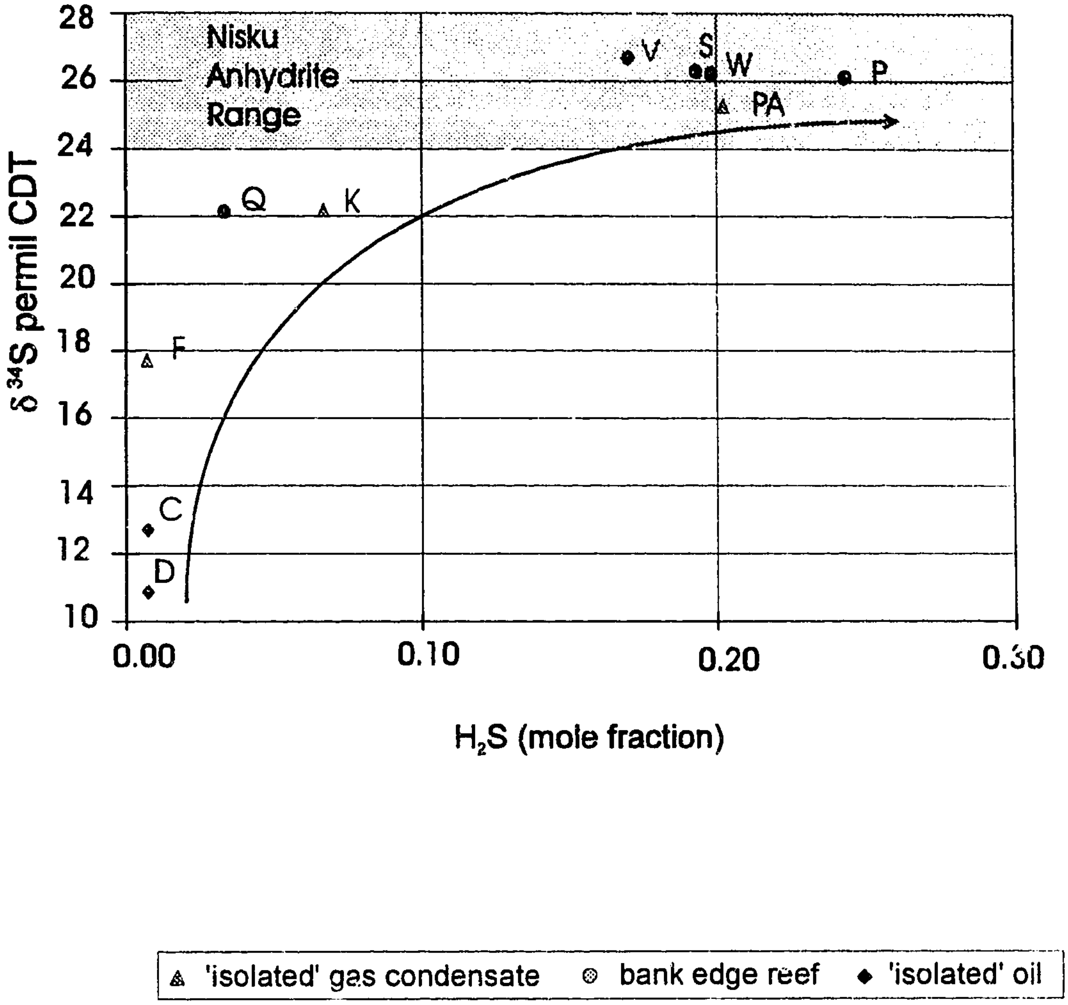


Figure 18: $\delta\,^{34}S$ permil CDT versus hydrogen sulfide

(1974) who noted that the shift in $\delta^{34}S$ values of hydrocarbons towards that reservoir anhydrite in the Big Horn Basin, Wyoming was compelling evidences for abiological sulfate reduction (or TSR).

The $\delta^{13}C$ values of saturated hydrocarbons reflect the effects of both thermal maturation and TSR. With increasing thermal maturation, the ^{12}C content of hydrocarbons increases in the gas phase and decreases in the liquid phase. Consequently, $\delta^{13}C$ values of liquid hydrocarbons increase with increasing thermal maturity (Fuex, 1977). The changes in the carbon isotopic composition of saturated hydrocarbons of distilled hydrocarbon samples are consistent with this observation, i.e., the $\delta^{13}C$ values are less negative with increasing thermal maturity (Figure 19).

As stated earlier (see sections 3.3, p. 21 and 6.2.2, p. 62), saturates are preferentially removed during TSR. Therefore, $\delta^{13}C$ values of the saturated hydrocarbons are affected not only by thermal maturation but also by TSR. Claypool and Mancini (1989) illustrated that high-sulfur condensates had higher $\delta^{13}C$ values than did low-sulfur condensates of similar maturity. The shaded region in Figure 20 shows the suggested change for $\delta^{13}C$ with increasing hydrogen sulfide content (or TSR). Both bank edge reef pools P and V have lower $\delta^{13}C$ values than may be expected. This suggests that the hydrocarbons in these two pools were probably not the main reactants used to reduce anhydrite to hydrogen sulfide during TSR. If so, the degree of TSR which has occurred in pools V and P may be overestimated based on hydrogen sulfide content. Updip migration of hydrogen sulfide (with hydrocarbons) is probably the main factor controlling the hydrogen sulfide concentrations in pools V and P.

In a closed system where hydrogen sulfide is neither removed or introduced, the concentration of this gas in the reservoir can be a useful parameter in determining the extent of TSR. In an open system, however,

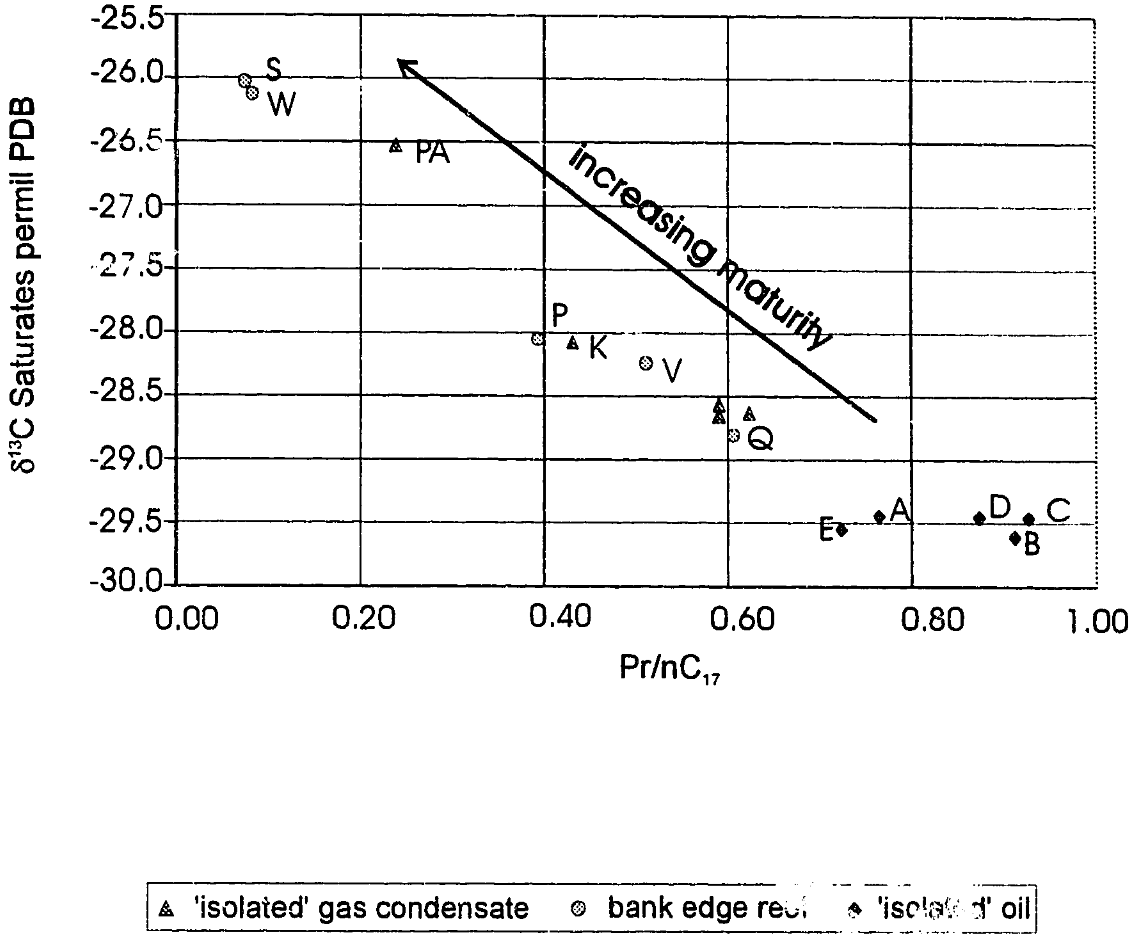


Figure 19: $\delta^{13}C$ saturates permil PDB versus Pr/nC_{17}

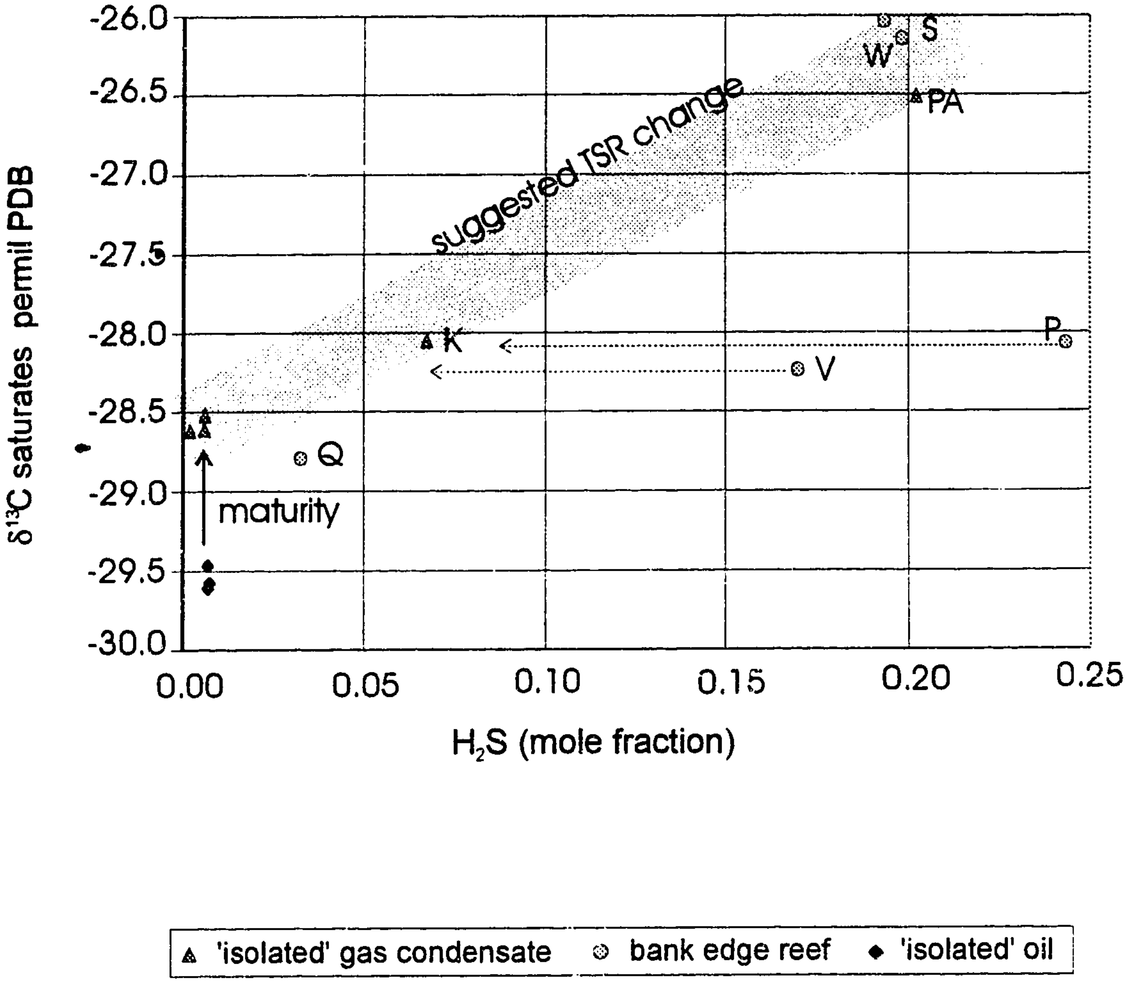


Figure 20: $\delta^{13}C$ saturates permil PDB versus hydrogen sulfide.

hydrogen sulfide content may not be a reliable parameter for estimating the extent of TSR. $\delta^{13}C$ values of saturates can probably be a useful parameter to show the extent of TSR, but it should be remembered that this parameter is also affected by thermal maturation.

6.2.6 Paraffin Index and $nC_7/MCYC_6$

Paraffin Index 2 (also called heptane value) is broadly defined as the percentage of normal heptane in a group of C_7 compounds that are predominantly cyclic alkanes. Paraffin Index 2 and the ratio of normal heptane to methylcyclohexane ($nC_7/MCYC_6$) are parameters using gasoline range hydrocarbons (C_5 - C_8) that have been used previously as thermal maturation indicators (Thompson, 1983 and 1987). Naphthenes or cyclic alkanes are believed to play a dual role in maturation; some molecules split open to form paraffins, while others form aromatics by yielding hydrogen to paraffins (Hunt, 1979). With increasing thermal maturation, therefore, cyclic alkanes decrease relative to straight-chained hydrocarbons. Consequently, Paraffin Index 2 increases with increasing thermal maturation. This change is observed for the oils and condensates in the Nisku Formation in the study area (Figure 21). Generally with increasing thermal maturation (relative to Pr/nC_{17}), Paraffin Index 2 increases. Pool K and to a lesser extent pool B, however, have lower values for this parameter than expected suggesting that water washing or biodegradation may have occurred in these reservoirs. The possibility of water washing and biodegradation is discussed in section 6.3, p. 76.

For reasons similar, as to those outlined above for Paraffin Index 2, $nC_7/MCYC_6$ also increases with increasing thermal maturation. A plot of $nC_7/MCYC_6$ versus Pr/nC_{17} (Figure 22) suggests that both thermal maturation and TSR may be affecting this gasoline maturity parameter. 'Isolated' sour gas condensate pools (PA, Y and K) show lower $nC_7/MCYC_6$ values than expected

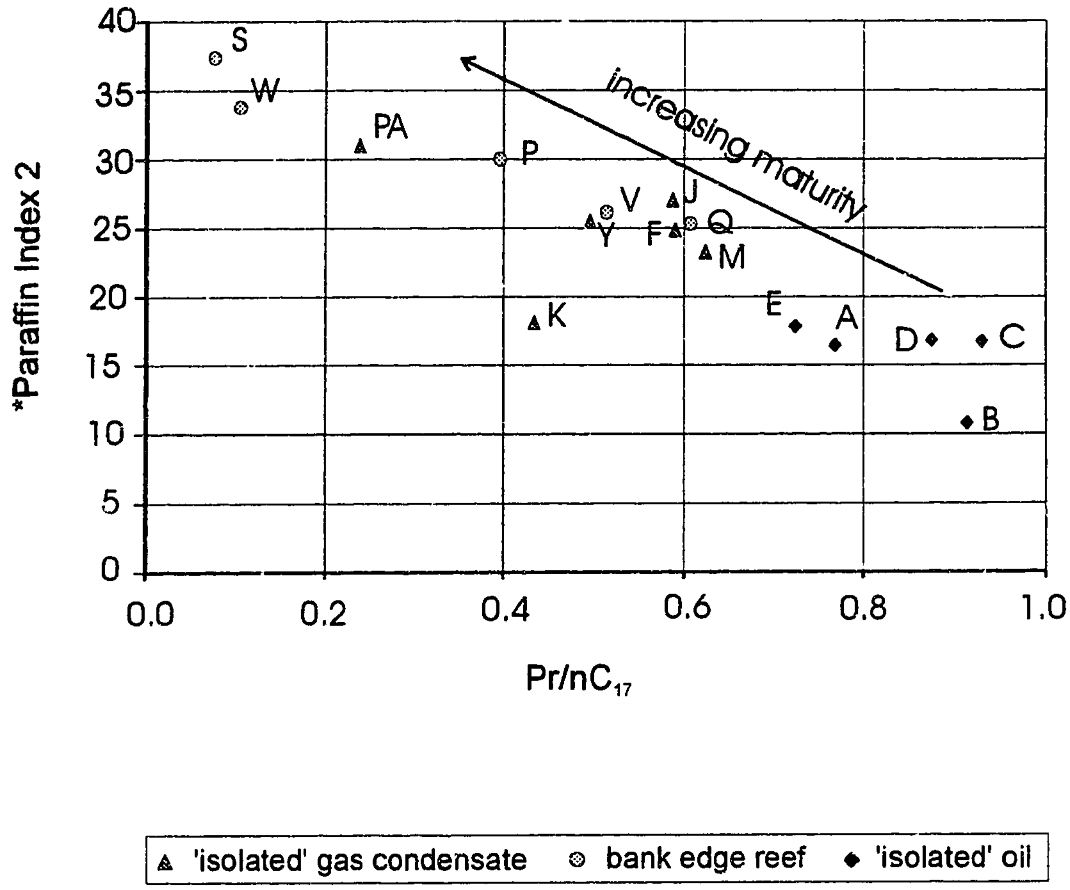


Figure 21: Paraffin Index 2 versus Pr/nC$_{17}$ for oils and gas condensates in the Nisku Fomation in the Brazeau River area, Alberta.

*Paraffin Index 2 = (normal heptane × 100) / A

where A = sum (cyclohexane, methylhexane, 1,1-dimethylcyclopentane,
3-methylhexane, 1,cis-3-dimethylcyclopentane,
1,trans-2-dimethylcyclopentane, n-heptane and methylcyclohexane)

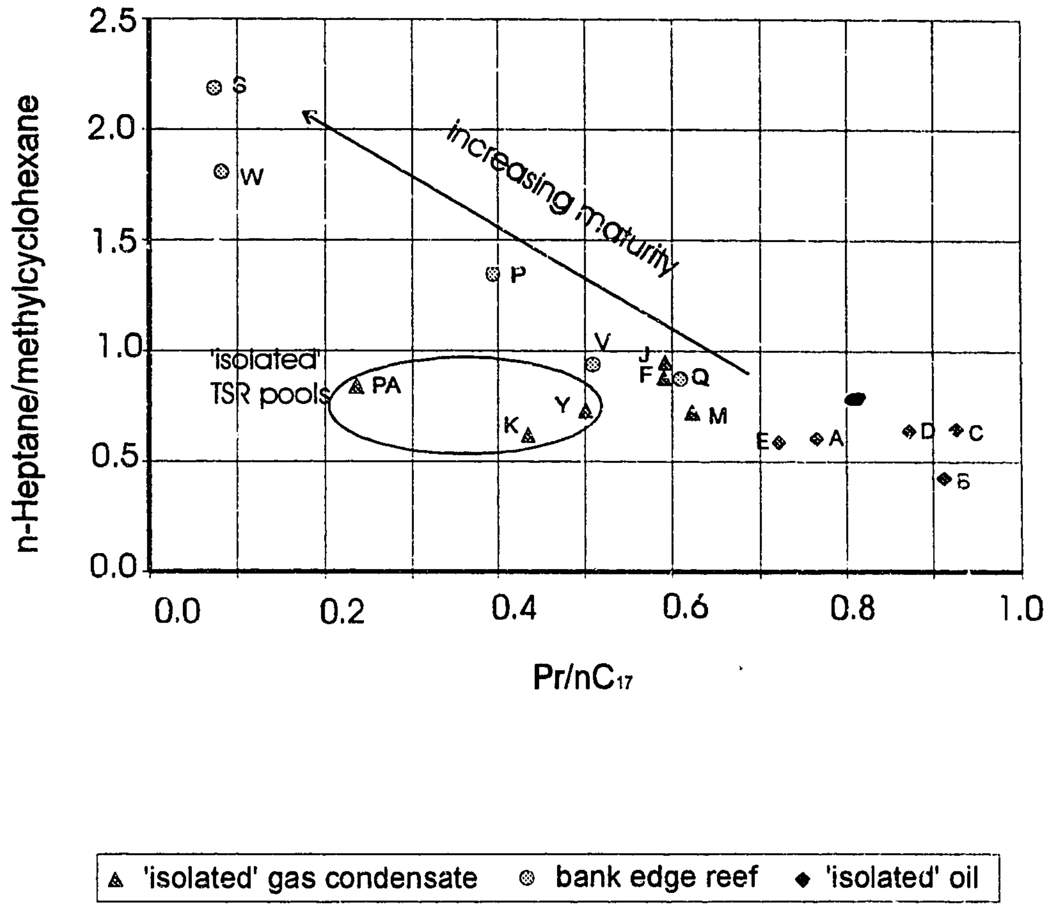


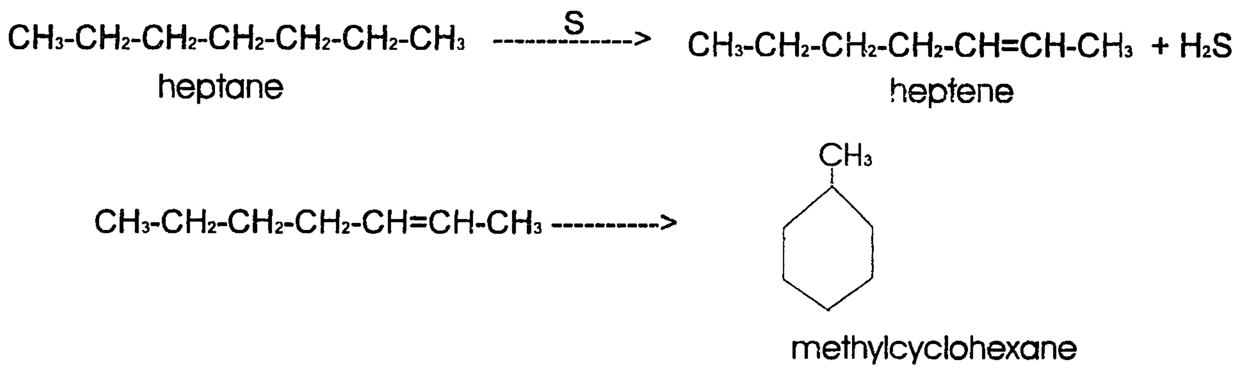
Figure22: n-Heptane/methylcyclohexanen ($C_7/MCYC_6$) versus Pr/nC_{17}

based on their maturity levels. Other TSR-affected pools, S and W, however, along the bank edge reef trend, give the values expected for their maturity level. The decrease in normal heptane relative to methylcyclohexane in 'isolated' sour gas condensate pools can be explained by the reaction of sulfur with heptane. Valitov and Valitov (1975) reacted heptane with sulfur at 250°C in the present of limestone for 10 hours. Methylcyclohexane, hydrogen sulfide and organo-sulfur compounds were produced. The formation of methylcyclohexane from normal heptane can be represented by the series of reactions shown in Figure 23. Previously reported studies have not documented the effects of TSR on maturity parameters that utilize gasoline range hydrocarbon composition (in particular $nC_7/MCYC_6$). More studies of in the gasoline range hydrocarbons in other sour gas condensates pools are needed before one can attribute a decrease in $nC_7/MCYC_6$ to TSR.

Table 10 summarizes the changes in oils and condensates in the study area resulting from both thermal maturation and thermochemical sulfate reduction.

6.3 Biodegradation and Water Washing

Biodegradation and water washing reduce the overall quality of oils. Biodegradation occurs at shallow depths, within the temperature limits (<80°C) for bacterial activity (Bailey et al., 1973). Microorganisms can metabolize most types of hydrocarbons, including aromatics and cyclic paraffins, but normal paraffins are preferentially attacked (Tissot and Welte, 1984). Bacterial activity, therefore, commonly reduces the overall paraffinicity of oils. The ratios of light hydrocarbons [iso-pentane/normal pentane (iC_5/nC_5) and 3-methylpentane/normal hexane ($3MC_5/nC_6$)] are useful biodegradation indicators (Welte et al., 1982; Thompson, 1983; Osadetz et al., 1992). These ratios increase with increasing biodegradation. The values obtained for the hydrocarbons in the Nisku Formation in the study area (Table 5) provide no evidence that any of the oils or



Overall reaction: $C_7H_{16} + S \text{ -------------> } CH_3.C_6H_{12} + H_2S$

Figure 23: Dehydrogenation of heptane with sulfur to methylcyclohexane and H_2S (Valitou and Valitou, 1975).

Table 10 : Geochemical changes indicating thermal maturation and/or TSR.

Parameter	**Thermochemical Sulfate Reduction**	**Thermal Maturation**
Saturate/Aromatic	Decreases	Increases
Organo-sulfur compounds	Increases	Decreases
API	Slight decrease	Increases
$\delta^{34}S$	Approaches $CaSO_4$ value	Little change
$\delta^{13}C$ saturates	Increases	Increases
Paraffin Index 2	Increases	Increases
$nC_7/MCYC_6$	Closed system: decreases	Increases

condensates in this study have been biodegraded. This conclusion is supported by the whole oil and condensate gas chromatograms. Normally severely degraded oils' gas chromatograms show removal of n-alkanes, an increase in isoprenoid hydrocarbons (e.g., pristane and phytane) and an increase in the unresolved napthenic hump (Bailey et al., 1973). Gas chromatograms of the oils and condensates sampled show normal distributions i.e., the disappearance of heavy hydrocarbons with increasing thermal maturation (Figures 10a, 10b and 10c, p. 43 - 48).

Biodegraded oils are usually water washed but not all water washed oils are biodegraded. Water washing removes soluble hydrocarbons by the flow of water under-saturated with respect to these hydrocarbons. Generally lighter hydrocarbons are more soluble than heavier hydrocarbons. The solubility of hydrocarbons in water can been used as a guide to the expected sequence of compound removal with progressive washing. For a given carbon number, ring formation and unsaturation, increase hydrocarbon solubility. Therefore, aromatics are more soluble than paraffins; branched and cyclic paraffins have intermediate solubility (Price, 1976). More recent water washing experiments (Lafargue and Barker, 1988) suggested that in the gasoline range hydrocarbons, normal paraffins are more affected by water washing than cyclic paraffins.

Light hydrocarbon ratios [3-methylpentane/benzene (3MC$_5$/Ben); methylcyclohexane/toluene (MCYC$_6$/Tol) and cyclohexane/benzene (CYC$_6$/Ben)] increase with increasing degree of water washing. They can be used as parameters to assess the degree of water washing. Figure 24 demonstrates that with increasing degree of thermal maturation, the water washing parameter, MCYC$_6$/Tol, decreases. Overall, most of the pools in the study, with the exception of pool K, show no significant effects of water washing (Table 5, p. 41).

Higher values for water washing ratios for pool K than are expected based

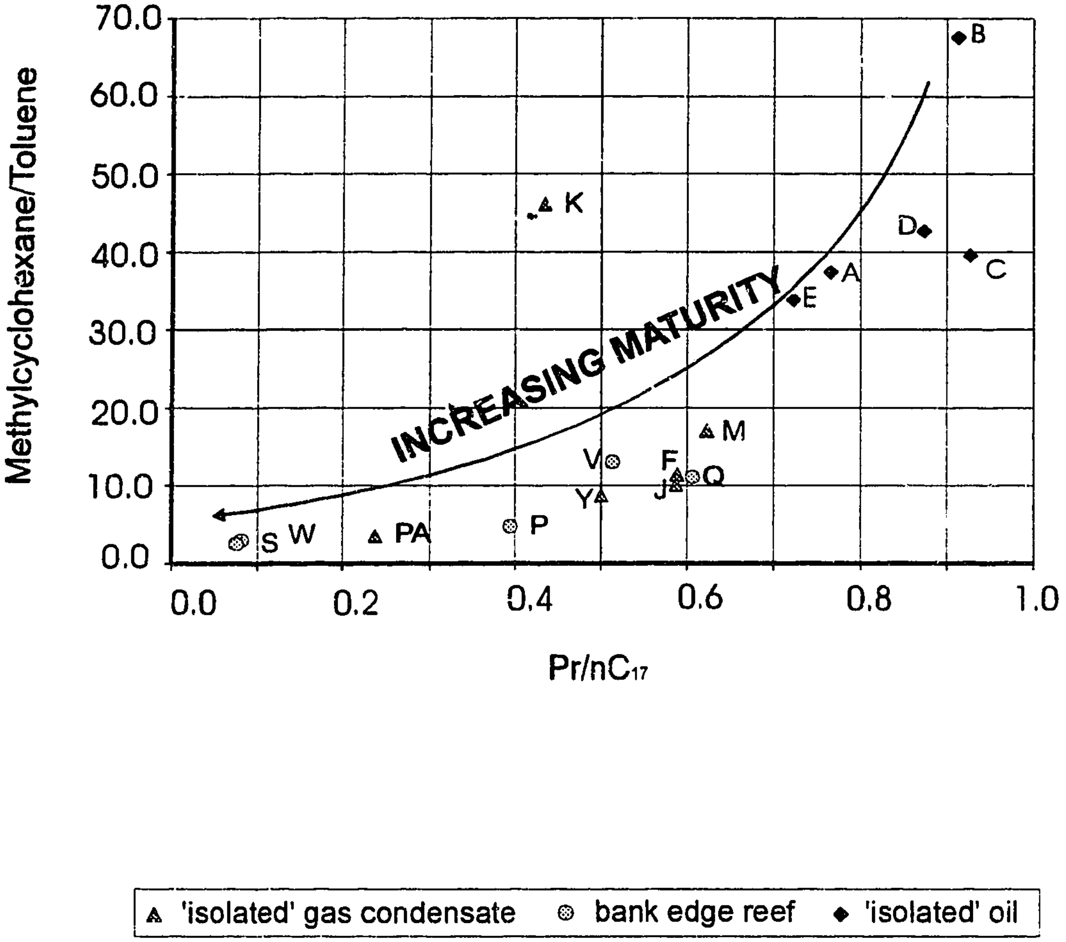


Figure 24: Water washing parameter (MCYC$_6$/Tol) versus Pr/nC$_{17}$

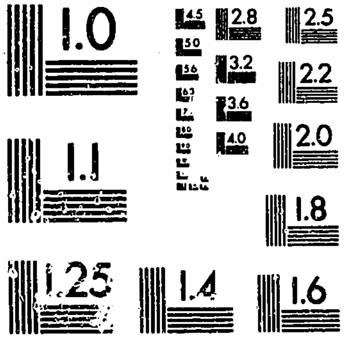
solely on its maturity level (Table 5; Figure 24) suggest that this pool has been affected by water washing. Pool K also has relatively lower hydrogen sulfide concentration than expected for its depth (Figure 25). If water washing occurred simultaneously with or after TSR, hydrogen sulfide would have been easily removed from the reservoir, as a result of its high solubility in water. Water washing, therefore, provides one possible explanation for the relatively low hydrogen sulfide content of pool K in relation to its depth. Based on initial reservoir pressures (Table 1, p. 5), however, this pool appears to be 'isolated' (sealed off from fluid flow). An understanding of the migration of formation water and the geology of the study area are important to support the organic geochemical evidence that pool K hydrocarbons have been affected by water washing. This is, however, beyond the scope of the thesis.

6.4 Migration and TSR

The geochemical data obtained in this study do not clearly define the migration pathway and the extent of mixing of hydrocarbons along the bank edge reef pools. The hydrocarbon m [illegible] is in pools P and V and, to a lesser degree, in pools S and W r [illegible] resent depths (Figure 14b, p. 61), suggest that these hydroc [illegible] ted from deeper sources or are the product of migrated hy [illegible] ndigenous reservoir hydrocarbons. Hydrogen sulfide from [illegible] could readily migrate updip along the bank edge reef tren [illegible] oncentration of hydrogen sulfide in shallower pools (e.g., [illegible] migrated hydrogen sulfide could then react with the indigenous reservoir hydrocarbons and sulfate ions in the formation water to increase the hydrogen sulfide and the gas content in these reservoirs. The rate of TSR reactions in these pools may be slower than those in deeper pools since the shallower pools are at lower temperatures.

2 of/de 2

PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT



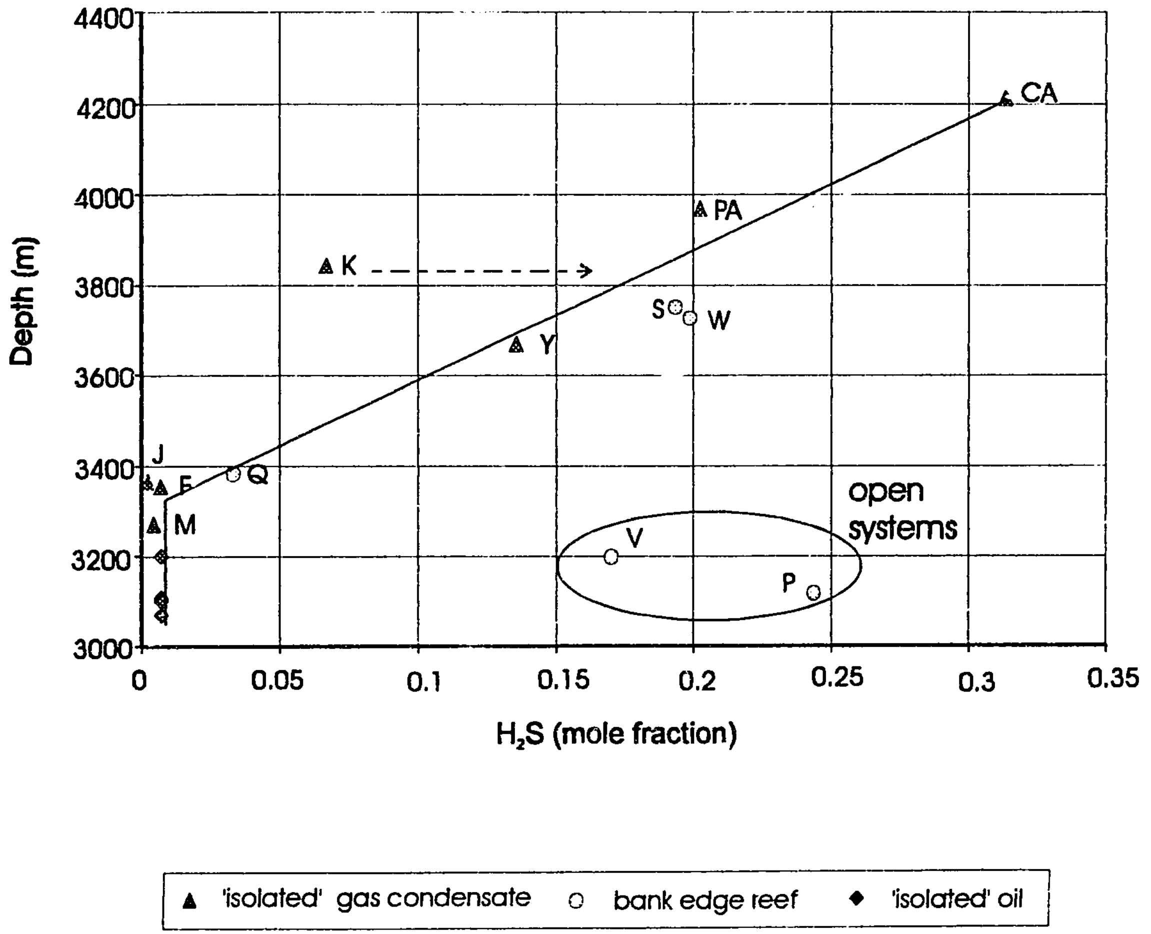


Figure 25: Mean formation depth versus reservoir hydrogen sulfide concentration.

6.5 Temperature and Depth Boundaries for TSR.

In the study area, 'isolated' pools provide some means for estimating the minimum depth and temperature boundaries for TSR. Up-dip migration along the bank edge reef gives a false indication of the extent of TSR, when estimates are based solely on hydrogen sulfide concentrations. In the 'isolated' gas condensate pools, with increasing depth, hydrogen sulfide generally increases (Figure 25). Using pool Y as the shallowest 'isolated' TSR-affected pool (Figure 25), the minimum temperature and depth for TSR in the study area are 114°C and ≈3670 metres, respectively (Table 1, p. 5). This temperature is consistent with previously reported minimum TSR temperatures (Orr, 1974; Macqueen and Powell, 1983; Machel, 1987).

The Winterburn Basin (including the study area) was buried much deeper than its present depth (see section 2.2, p. 11) and thus the rate of TSR reactions, at present, are much slower than at earlier geological time. Maximum burial temperatures were estimated to be around 135°C to 150°C (Anderson and Machel, 1988). TSR reactions were probably initiated during this period of maximum burial and highest temperatures and then continued at a slower rate during and after uplift.

6.6 Implications for Exploration

It is estimated that 95% of all Alberta sulfur production is derived from the processing of sour natural gas (Trollope, 1989). Once a stock piled 'waste product' dotting the Canadian landscape, world demand for sulfur in the 1980s, however, has seen the drawdown of Canadian inventory from 20Mt to under 3.5 Mt in 1990 (Hyne, 1991). The hydrocarbon component of deep sour gas reservoirs (natural gas and condensate) also contributes significantly to the economics of deep gas projects by providing additional revenue. These two factors, therefore, will ensure continued exploration for other deep sour gas reservoirs.

The findings from this thesis can assist in explorations by providing some insights into depth and temperature boundaries for TSR. For example, in the study area, high hydrogen sulfide concentrations were found in pools deeper than 3670 metres. The results obtained in this thesis can also help in distinguishing TSR from BSR environments in areas where the concentrations of hydrogen sulfide is less than 10%. Also, some of the documented changes in liquid hydrocarbons (e.g., increase in aromatic content and organo-sulfur compounds) may assist in evaluating the quality of reservoir hydrocarbons in other sour gas condensate reservoirs.

CHAPTER 7

SUMMARY AND CONCLUSIONS

The following conclusions can be drawn from the organic geochemistry, isotopic compositions ($\delta^{13}C$ and $\delta^{34}S$) and physical conditions of oil and gas condensate reservoirs in the Nisku Formation in the Brazeau River area, Alberta:

(1) Liquid hydrocarbons in the eighteen reservoirs sampled in the Brazeau River, Nisku Formation probably belong to one family, but further geochemical analyses are needed to identify the source rock(s) for the hydrocarbons.

(2) Both TSR and thermal maturation reduce the proportion of saturated hydrocarbons in liquid hydrocarbons. However, TSR results in a decrease in the saturate/aromatic ratio, whereas thermal maturity results in an increase the same ratio.

(3) TSR removes saturates via oxidation reactions to produce lower molecular weight hydrocarbons and via dehydrocyclization reactions to produce aromatic compounds.

(4) Organo-sulfur compounds are formed during catagenesis in TSR-affected pools.

(5) The formation of organo-sulfur compounds during catagenesis may result in a decrease in API gravity of condensates.

(6) The $\delta^{34}S$ of oils and condensates sampled approaches that of subsurface

anhydrite with increasing TSR.

(7) Both thermal maturity and TSR result in an increase in $\delta^{13}C$ values for saturates in oil and condensate samples.

(8) $\delta^{13}C$ values for saturates from the bank edge reef pools V and P indicate that the degree of TSR in these pools may be overestimated if hydrogen sulfide content alone is used.

(9) Migration of hydrogen sulfide from deeper pools is probably the controlling factor for present hydrogen sulfide concentrations in updip bank edge reef pools P and V.

(10) In 'isolated' sour gas condensate pools, the ratio of normal heptane/methylcyclohexane is lower than expected based on their maturity level. This may be due to the reaction of normal heptane with sulfur to produce methylcyclohexane.

(11) There is no evidence for biodegradation of any of the oils or condensates in this study.

(12) The composition of light hydrocarbons in pool K suggests that water washing may have reduced the hydrogen sulfide content in this pool.

CHAPTER 8

RECOMMENDED FURTHER WORK

The complexity of TSR reactions makes it almost impossible to understand fully all the different hydrocarbon alterations observed in this study. Liquid hydrocarbons were the main focus of the present study, however, analysis of other phases, for example, natural gas may provide additional insights into mechanisms of TSR reactions. Recommendations for further work directly related to the study area are listed below.

8.1 Source Rock Identification

The source rock for the hydrocarbons in the Nisku Formation in the study area needs to be properly identified. Previously reported studies have suggested the Duvernay Formation and the Cynthia Member as possible source rocks. Biomarker analysis was not possible in this study because of the high level of thermal maturity in the samples. Oil pools updip in the study area, in the West Pembina and in the Bigoray areas are at lower maturity levels and hence probably suitable for oil-source correlation studies using biomarker techniques. Source rock samples should be taken from the West Pembina or Bigoray areas, since the Duvernay may have slightly different characteristics than those previously reported for other parts of the Western Canada Sedimentary basin.

8.2 δ^{34}S Hydrogen Sulfide in Natural Gas

δ^{34}S of hydrogen sulfide in natural gas was measured. The results suggest that δ^{34}S values for liquid hydrocarbon samples were higher than those for the hydrogen sulfide in the natural gas (Figure 26). This is not consistent with results

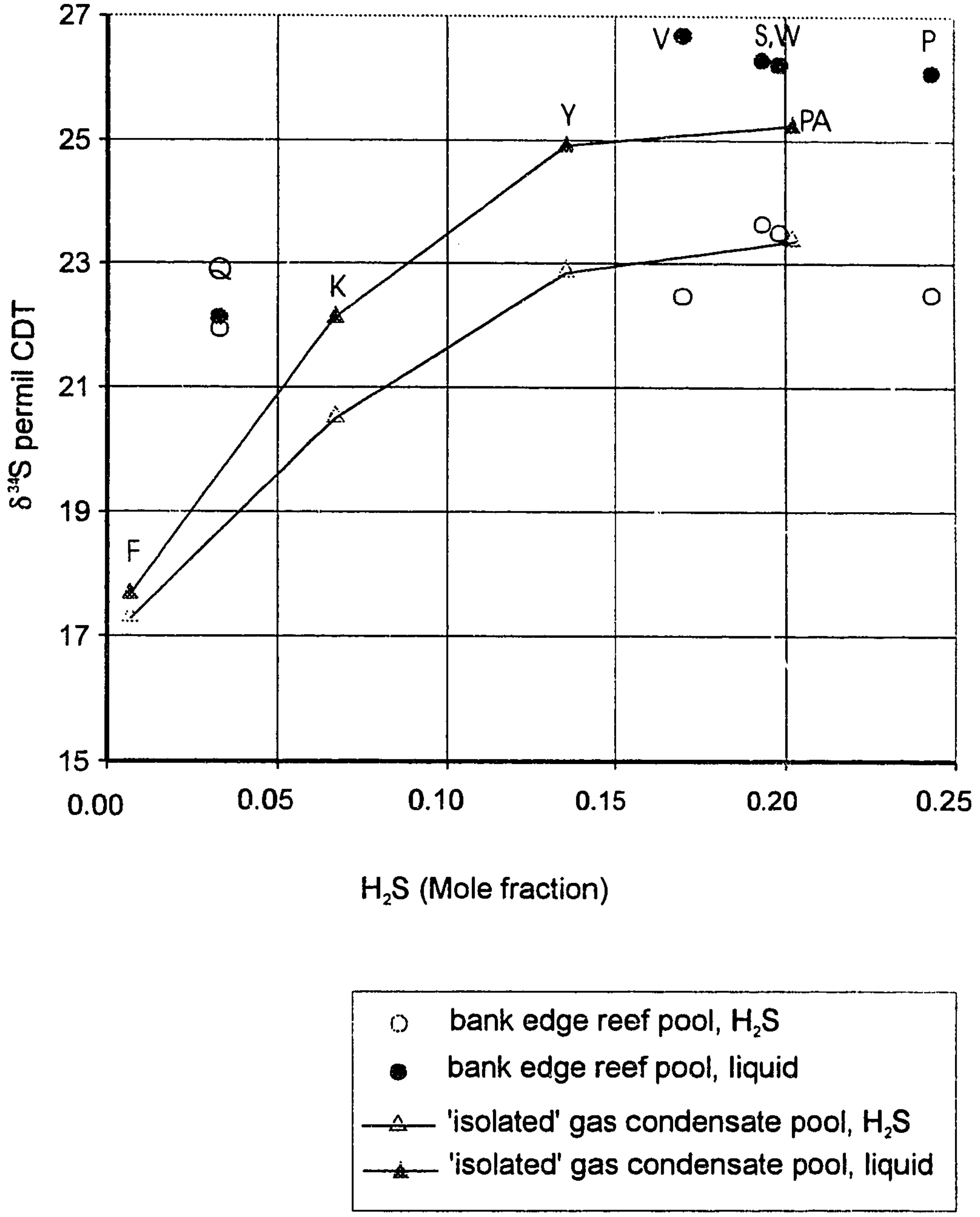


Figure 26: Sulfur isotope for condensates and hydrogen sulfide in natural gas versus reservoir hydrogen sulfide concentration.

reported in other TSR studies (Orr, 1974 and 1977; Krouse, 1977). Whereas the results do show that the $\delta^{34}S$ values for hydrogen sulfide and organic sulfur in oils and condensates approach the reservoir sulfate values with increasing hydrogen sulfide concentration, the exchange is expected to be faster for hydrogen sulfide than for oils. Previous studies have reported $\delta^{34}S$ for hydrogen sulfide in natural gas to be higher than that of accompanying for oils (Orr, 1974; Krouse, 1977). Sampling and determination of sulfur isotopic compositions should be repeated to ensure that the data reported herein are not erroneous.

8.3 Gasoline Range Hydrocarbons

Compound specific isotopic analyses for the gasoline range hydrocarbons can provide useful information about the relative reactivity of these compounds (C_5 - C_{10}) during TSR. It may also support the conclusion made in this study that n-heptane is converted to methylcyclohexane in closed TSR systems.

The formation of lower molecular weight sulfur compounds in TSR-affected pools suggests that $\delta^{34}S$ and percentage sulfur of the boiling point fraction below 160°C should be investigated to determine if it is possible to recognize effects of TSR on these organo-sulfur compounds. The volatility of this fraction, however, would make these procedures cumbersome.

8.4 Whole Oil

The high volatility of the hydrocarbon examined in this study made it difficult to obtain reliable analyses for C, H, N, and S. Samples were analyzed on the Perkin Elmer 240A Elemental Analyzer. Improved data should be obtained for oils and condensates in the study area in order to compare S/N ratios to results (>25) reported by Thompson (1994) for TSR-affected pools.

Percentages of different types of organo-sulfur compounds (e.g., mercaptans, benzothiophenes, dibenzothiophenes etc.) should be determined to assess variations in their concentrations at different stages of TSR.

REFERENCES CITED

Allan, J. and Creaney, S., 1991. Oil families of the Western Canada Basin. Bulletin of Canadian Petroleum Geology, Vol. 39, p. 107-122.

Anderson, J.H. and Machel, H.G., 1988. The Upper Devonian Nisku trend in central Alberta. In: Geldsetzer, H.H. J., James, N.P., and Tebbutt, G. E., (eds.), Reefs, Canada and adjacent area. Canadian Society of Petroleum Geologist Memoir, No. 13, p. 391-398.

Anisimov, L.A., 1978. Conditions of abiogenic [illegible]ion of sulfates in oil-and-gas bearing basins. Geochemistry Internat[illegible], Vol. 15, No. 6, p. 63-71.

Bailey, N.J.L., Krouse, H.R., Evans, C.R., and Rogers, M.A., 1973. Alteration of crude oils by waters and bacteria - evidence from geochemical and isotope studies. American Association of Petroleum Geologists Bulletin, Vol. 57, p. 1276-1290.

Bryce, W.A. and Hinshelwood, C., 1949. The reaction between paraffin hydrocarbons and sulphur vapour. Journal of Chemical Society, p. 3379-3387.

Chevron Exploration Staff Ltd., 1979. The geology, geophysics, and the significance of the Nisku reef discoveries, West Pembina area, Alberta, Canada. Bulletin of Canadian Petroleum Geology, Vol. 27, p. 326-359.

Chung, H.M., Brand, S.W. and Grizzle, P.L., 1981. Carbon isotope geochemistry of Paleozoic oils from Big Horn basin. Geochimica et Cosmochimica Acta, Vol. 45, p. 1803-1815.

Claypool, G.E. and Mancini, E.A., 1989. Geochemical relationships of petroleum in Mesozoic reservoirs to carbonate source rocks of Jurassic Smackover Formation, southwestern Alabama. American Association of Petroleum Geologists Bulletin, Vol. 73, p. 904-924.

Clayton, J.L., King, J.D., Threlkeld, C.N. and Vuletich, A., 1987. Geochemical correlation of Paleozoic oils, northern Denver Basin-Implications for exploration. American Association of Petroleum Geologists Bulletin, Vol. 71, p. 103-109.

Creaney, S., Allan, J., Cole, K.S., Fowler, M.G., Brooks, P.W., Osadetz, K.G., Macqueen, R.W., Snowdon, L.R. and Riediger, C.L., 1994. Petroleum generation and migration in the Western Canadian Sedimentary Basin. In: Mossop, G.D. and Shetsen, I., (comps.), Geological Atlas of the Western Canadian Basin. Calgary, Canadian Society of Petroleum Geologists and Alberta Research Council, p. 455-468.

Dhannoun, H.Y. and Fyfe, W.S., 1972. Reaction rates of hydrocarbons with anhydrite. Progress in Experimental Petrology, Vol. 2, p. 69-71.

Energy Resources Conservation Board, 1993a. Alberta reserves of gas, complete listing. ERCB Serial Publication 35, Alberta, Canada.

Energy Resources Conservation Board, 1993b. Pool Boundary. ERCB Board Orders (G), Alberta, Canada.

Energy Resources Conservation Board, 1993c. List of Wells in Alberta. ERCB Serial Publication 37, Alberta, Canada.

Feely, H.W. and Kulp, J.L., 1957. Origin of Gulf coast salt-dome sulphur deposits.

American Association of Petroleum Geologists Bulletin, Vol. 41, p. 1802-1853.

Fowler, M.G., Thomas, G., Goodarzi, F. and Foscolos, A., 1991. The petroleum potential of some tertiary lignites from northern Greece as determined using pyrolysis and organic petrological techniques. Organic Geochemistry, Vol.17, No. 6, p. 805-820.

Fuex, A.N., 1977. The use of stable carbon isotopes in hydrocarbon exploration. Journal of Geochemical Exploration, Vol. 7, p. 155-188.

Heydari, E. and Moore, C., 1989. Burial diagenesis and thermochemical sulfate reduction, Smackover Formation, southeastern Mississippi salt basin. Geology, Vol. 17, p. 1080-1084.

Ho, T.Y., Rogers, M.A., Drushel, H.V. and Kroons, C.B., 1974. Evolution of sulfur compounds in crude oils. American Association of Petroleum Geologists Bulletin, Vol. 58, p. 2338-2348.

Hughes, W.B., 1984. Use of thiophenic organosulfur compounds in characterizing crude oils derived from carbonate versus siliciclastic sources. In: Palacas, J.G., (ed.), Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks. American Association of Petroleum Geologists, Studies in Geology, No. 18, p. 181-196.

Hunt, J.M., 1979. Petroleum Geochemistry and Geology. W.H. Freeman, San Francisco, 617p.

Hyne, J.B., 1991. Producing and processing sour gas in the 1990s. Journal of Canadian Petroleum Technology, Vol. 30, p. 72-78.

Kaufman, J., Meyers, W.J. and Hanson, G.N., 1990. Burial cementation in the Swan Hills Formation (Devonian), Rosevear Field, Alberta, Canada. Journal of Sedimentary Petrology, Vol. 60, p. 918-939.

Kiyosu, Y., 1980. Chemical reduction and sulfur-isotope effects of sulfate organic matter under hydrothermal conditions. Chemical Geology, Vol. 30, p. 47-56.

Krouse, H. R., 1977. Sulfur isotope studies and their role in petroleum exploration. Journal of Geochemical Exploration, Vol.7, p. 189-211.

Krouse, H.R., Viau, C.A., Eliuk, L.S., Ueda, A. and Halas, S., 1988. Chemical and isotopic evidence of thermochemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs. Nature, Vol. 333, p. 415-419.

Lafargue, E. and Barker, C., 1988. Effects of water washing on crude oil compositions. American Association of Petroleum Geologists Bulletin, Vol. 72, p. 263-276.

Machel, H.G., 1983. Facies and diagenesis of some Nisku buildups and associated strata, Upper Devonian, Alberta, Canada. In: Harris, P.M., (ed.), Carbonate buildups - a core workshop. Society of Economic Paleontologists and Mineralogists Core Workshop, No. 4, p. 144-181.

Machel, H.G., 1984. Facies and dolomitization of the Upper Devonian Nisku Formation in the Brazeau, Pembina, and Bigoray areas, Alberta, Canada. In: Eliuk, L.S., (ed.), Carbonates in the subsurface and outcrop. Canadian Society of Petroleum Geologists Core Conference 1984, p. 191-224.

Machel, H.G., 1985. Facies and diagenesis of the Upper Devonian Nisku

Formation in the subsurface of central Alberta. Unpublished Ph.D. Thesis, McGill University, Montreal, 392p.

Machel, H.G., 1987. Some aspects of diagenetic sulphate-hydrocarbon redox-reactions. In: Marshall, J.D., (ed.), Diagenesis of Sedimentary Sequences. Geological Society Special Publication, No. 36, p. 15-28.

Machel, H.G., 1987a. Saddle dolomite as a by-product of chemical compaction and thermochemical sulfate reduction. Geology, Vol. 15, p. 936-940.

Machel, H.G., 1989. Relationships between sulphate reduction and oxidation of organic compounds to carbonate diagenesis, hydrocarbons accumulations, salt domes, and metal sulfide deposits. Carbonates and Evaporites, Vol. 4, p. 137-151.

Machel, H.G., 1992. Low-temperature and high-temperature origins of elemental sulfur in diagenetic environments. In: Wessel, G.R. and Wimberly, B.H., (eds.), Native Sulfur - Developments in Geology and Exploration. Society for Mining, Metallurgy and Exploration, p. 3-22.

Machel, H.G. and Burton, E.A., 1991. Burial-diagenetic sabkha-like gypsum and anhydrite nodules. Journal of Sedimentary Petrology, Vol. 61, No. 3, p. 394-405.

Machel, H.G., Krouse, H.R. and Sassen, R., in press, a. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. Applied Geochemistry.

Machel, H.G., Krouse, H.R., Riciputi, L.R. and Cole, D.R., in press, b. The Devonian Nisku sour gas play, Canada - A unique natural laboratory for study of thermochemical sulfate reduction. In: Vairavamurthy, M. and Schoonen, M.A.A., (eds.), Geochemical transformations of sedimentary sulfur. American Chemical Society Symposium Series 1995.

Macqueen, R.W. and Powell, T.G., 1983. Organic geochemistry of Pine Point lead-zinc ore field and region, Northwest Territories, Canada. Economic Geology, Vol. 78, p. 1-25.

Orr, W.L., 1974. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation - study of Big Horn Basin Paleozoic oils. American Association of Petroleum Geologists Bulletin, Vol. 58, p. 2295-2318.

Orr, W.L., 1977. Geologic and geochemical controls on the distribution of hydrogen sulphide in natural gas. In: Campos, R. and Goni, J., (eds.), Advances in Organic Geochemistry, Enadisma, Madrid, Spain, p. 571-597.

Osadetz, K.G., Brooks, P.W. and Snowdon, L.R., 1992. Oil families and their sources in Canadian Williston Basin, (southeastern Saskatchewan and southwestern Manitoba). Bulletin of Canadian Petroleum Geology, Vol. 40, p. 254-273.

Peters, K.E., 1986. Guidelines for evaluating petroleum source rocks using programmed pyrolysis. American Association of Petroleum Geologist Bulletin, Vol. 70, p. 318-329.

Peters, K.E. and Moldowan, J.M., 1993. The Biomarker Guide - Interpreting Molecular Fossil in Petroleum And Ancient Sediments. Prentice Hall, New Jersey, 363p.

Powell, T.G. and Macqueen, R.W., 1984. Precipitation of sulfide ores and organic matter: sulfate reactions at Pine Point, Canada. Science, Vol. 224, p. 63-66.

Price, L., 1976. Aqueous solubility of petroleum as applied to its origin and primary migration. American Association of Petroleum Geologists Bulletin, Vol. 60, p. 213-244.

Pryor, W.A., 1962. Mechanisms of Sulfur Reactions. McGraw-Hill, New York, NY. 241p.

Saban, M., Jovancicevic, B.S., Saracevic, S., Hollerbach, A. and Vitorovic, D., 1987. Correlative geochemical study of crude oils from southeastern and southern parts of the Pannonian Basin. Organic Geochemistry, Vol. 13, p. 325-333.

Sassen, R., 1988. Geochemical and carbon isotopic studies of crude oil destruction, bitumen precipitation, and sulfate reduction in the deep Smackover Formation. Organic Geochemistry, Vol. 12, p. 351-361.

Sassen, R., Moore, C.H., Nunn, J.A., Meendsen, F.C. and Heydari, E., 1987. Geochemical studies of crude oil generation, migration and destruction in the Mississippi salt basin. Gulf Coast Association of Geological Societies Transactions, Vol. 37, p. 217-224.

Sassen, R. and Moore, C.H., 1988. Framework of hydrocarbon generation and destruction in eastern Smackover trend. American Association of Petroleum Geologist Bulletin, Vol. 72, p. 649-663.

Snowdon, L.R. and Powell, T.G., 1979. Families of crude oils and condensates in the Beaufort-Mackenzie basin. Bulletin of Canadian Petroleum Geology, Vol. 27, p. 139-162.

Snowdon, L.R. and Osadetz K.G., 1988. Gasoline range (C_5 to C_8) data and C_{15+} saturate fraction gas chromatograms for the crude oils from SE Saskatchewan portion of the Williston basin. Geological Survey of Canada Open File #1785.

Sofer, Z., 1980. Preparation of carbon dioxide for stable carbon isotope analysis of petroleum fractions. Analytical Chemistry, Vol. 52, p. 1389-1391.

Sofer, Z., 1984. Stable carbon isotopic compositions of crude oils: Application to Source Depositional Environments and Petroleum Alteration. American Association of Petroleum Geologists Bulletin, Vol. 68, p. 31-49.

Stahl, W.J., 1978. Source rock-crude oil correlation by isotopic type-curves. Geochimica et Cosmochimica Acta, Vol. 42, p. 1573-1577.

Stoakes, F.A., 1992. Winterburn megasequence. In: Wendte, J., Strokes, F.A. and Campbell, C.V., (eds.), Devonian-Early Mississippian Carbonates of the Western Canada Sedimentary Basin: a Sequence Stratigraphic Framework. Society of Economic Paleontologists and Mineralogists Short Course No. 28, p. 207-224.

Switzer, S.B., Holland, W.G., Christie, D.S., Graf, G.C., Hedinger, A.S., McAuley, R.J., Wierzbicki, R.A. and Packard, J.J., 1994. Devonian Woodbend-Winterburn strata of the Western Canadian Sedimentary Basin. In: Mossop, G.D. and Shetsen, I., (comps.), Geological Atlas of the Western Canada Sedimentary Basin. Calgary, Canadian Society of Petroleum Geologists and Alberta Research Council, p. 165-202.

Talukdar, S., Gallango, O. and Chin-A-Lien, 1985. Generation and migration of hydrocarbons in the Maracaibo basin, Venezuela: An integrated basin study. Organic Geochemistry, Vol. 10, p. 261-279.

Thompson, K.F.M., 1983. Classification and thermal history of petroleum based on light hydrocarbons. Geochimica et Cosmochimica Acta, Vol. 47, p. 303-316.

Thompson, K.F.M., 1987. Fractionated aromatic petroleums and the generation of gas-condensates. Organic Geochemistry, Vol. 11, p. 573-590.

Thompson, K.F.M., 1994. A classification of petroleum on the basis of the ratio of sulfur to nitrogen. Organic Geochemistry, Vol. 21, p. 877-890.

Tissot, B.P. and Welte, D.H., 1984. Petroleum Formation and Occurrence. Berlin, Springer-Verlag, New York, 699p.

Toland, W.G., 1960. Oxidation of organic compound with aqueous sulfate. Journal of the American Chemical Society, Vol. 82, p. 1911-1916.

Trollope, F., 1989. Deep sections of Alberta Basin hold a much-sought sulphur treasure. Oilweek, April 24, 1989, p. 20-21.

Trudinger, P.A., Chambers, L. A. and Smith, J.W., 1985. Low-temperature sulphate reduction: biological versus abiological. Canadian Journal of Earth Science, Vol. 22, p 1910-1918.

Valitov, N.B. and Valitov, R.B., 1975. The role of temperature in the formation of sulfur-bearing petroleums and catagenic hydrogen sulfide in carbonate reservoirs (experimental investigations). Geochemistry International, Vol 12, No. 5, p. 73-81.

Villeger, M., 1994. Diachronism of Upper Devonian Nisku Formation (Alberta, Canada): geometry and sequence stratigraphy. Comptes Rendus des Seances. Academie des Sciences (Paris), Series 2 Geologie, Vol. 318, p. 1527-1533.

Villeger, M. and Webb, T.K., 1992. Upper Devonian diachronous reef generation (Alberta, Canada). Comptes Rendus des Seances. Academie des Sciences (Paris), Series 2 Geologie, Vol. 315, p. 1381-1387.

Waples, D.W., 1985. Geochemistry in Petroleum Exploration. International Human Resources Development Corporation, Boston, 232p.

Watts, N.R., 1987. Carbonate sedimentology and depositional history of the Nisku Formation (within the western canadian sedimentary basin) in the south central Alberta. In: Krause, F.F., and Burrows, O.G., (eds.), Devonian lithofacies and reservoir styles in Alberta. Second International Symposium on the Devonian System, and 13th Canadian Society of Petroleum Geologists Core Conference and Display, p. 87-152.

Welte, D.H., Kratochvil, H., Rullkotter, J., Ladwein, H. and Schaefer, R.G., 1982. Organic geochemistry of crude oils from the Vienna basin and an assessment of their origin. Chemical Geology, Vol. 35, p. 33-68.

Wendte, J., Strokes, F.A., and Campbell, C.V., 1992. Devonian-Early Mississippian carbonates of the Western Canada Sedimentary Basin: a sequence stratigraphic framework. Society of Economic Paleontologists and Mineralogists Short Course No. 28, 255p.

Yanaglsawa, F. and Sakal, H., 1983. Thermal decomposition of barium sulfate-vanadium pentaoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements. Analytical Chemistry, Vol. 55, p. 985-987.