National Library
of Canada

Canadian Theses Service

Ottawa, Canada
K1A 0N4

Bibliothèque nationale
du Canada

Service des thèses canadiennes

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.

UNIVERSITY OF ALBERTA

GEOCHEMICAL AND ISOTOPIC TRACING OF WATER/ROCK INTERACTIONS IN THE WESTERN CANADA SEDIMENTARY BASIN

by ©

Catherine A. Connolly

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF GEOLOGY

EDMONTON, ALBERTA
FALL, 1990

ISBN 0-315-64764-7

UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR: Catherine A. Connolly

TITLE OF THESIS: Geochemical and Isotopic Tracing of Water/Rock Interactions in the Western Canada Sedimentary Basin.

DEGREE: Doctor of Philosophy

YEAR THIS DEGREE GRANTED: Fall, 1990

Permission is hereby granted to THE UNIVERSITY OF ALBERTA LIBRARY to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly or scientific research purposes only.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

Cathy Connolly

University of Alberta
Department of Geology
Edmonton, Alberta

Date: July 27, 1990

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "Geochemical and Isotopic Tracing of Water/Rock Interactions in the Western Canada Sedimentary Basin" submitted by Catherine A. Connolly in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

F.J. Longstaffe
Dr. F.J. Longstaffe (Supervisor)

H. Baadsgaard
Dr. H. Baadsgaard (Supervisor)

Dr. J.F. Lerbekmo

M.J. Dudas
Dr. M. Dudas

Dr. K. Muehlenbachs

Dr. R.H. McNutt (External Examiner)

Date July...27 /90

To my friend Bruce Keffer and my parents, Tom and Teresa Connolly.

ABSTRACT

The Alberta Basin, a sub-basin of the Western Canada Sedimentary Basin, is a foreland basin that has been tectonically uplifted and experienced gravity-driven flow of meteoric fluids. The basin is composed of southwesterly dipping and thickening sedimentary rocks consisting of: (1) Cambrian shales and siltstones; (2) eroded Jurassic and Paleozoic carbonates, shales and evaporites; and, (3) Cretaceous shales and silstones interbedded with thin lenses of sandstone. Rocks and minerals were sampled from Precambrian to Upper Cretaceous formations, whereas associated formation waters were extracted from Upper Devonian to Upper Cretaceous reservoirs.

Integration of isotopic (Sr, O, D) and major/minor elemental fluid compositions delineate two distinct hydrochemical regimes. Dilute fluids from Upper Cretaceous clastic units have isotopic and chemical compositions indicative of modern meteoric waters and appear decoupled from lower more saline reservoir fluids; there is no evidence of a seawater or evaporated brine component. Strontium isotopic compositions of these waters are distinctly less radiogenic than those in samples from stratigraphically lower reservoirs. Alteration of plagioclase and clay minerals dominate current water/rock reactions.

Stratigraphically lower, more saline fluids hosted in Upper Devonian to Lower Cretaceous reservoirs have elemental concentrations and $^{87}Sr/^{86}Sr$ ratios which may be modelled by two-component mixing, indicating cross-formational fluid migration. Elemental relations in the saline end-member are consistent with seawater evaporated beyond halite saturation, rather than halite dissolution from evaporite deposits in the basin. The saline end member has been diluted (50 to 80%) by a Neogene meteoric water during a post-Laramide pulse that flushed Tertiary waters through the basin. Hydrochemical isolation from more recent meteoric waters and the establishment of a mixing regime with distinctive density stratification ensued. Fluid chemistry, $^{87}Sr/^{86}Sr$ values and equilibrium thermodynamics demonstrate water/rock interactions which are dependent on the lithologic

composition of the reservoir: (1) carbonate hosted fluids are dominated by carbonate mineral reactions, with ion exchange reactions between smectite phases metastable to illite in intercalated shaly units, moderating the water chemistry; and, (2) clastic hosted fluids are dominated by clay mineral reactions with clay mineral transformation (beidellite → illite) and ion exchange reactions controlling the water chemistry.

Evidence for the hydrochemical zones and water mixing is further substantiated by isotopic data for diagenetic illite in the basin. Stable isotope data and calculated model ages indicate that diagenetic illites from Precambrian to Upper Cretaceous formations formed at relatively equivalent (post-Eocene) times, late in the paragenetic sequence. Plotting of the diagenetic illites on mixing diagrams ($^{87}Sr/^{86}Sr$ *vs* 1/Sr and Sr) delineates several zones corresponding to those established for the waters, with the addition of a separate Cambrian zone, where the pore fluid environment and authigenic phases are isolated from stratigraphically higher formations by the Middle Devonian evaporites. Devonian through Cardium diagenetic illites form a mixing regime, where Jurassic carbonate and Devonian anhydrite form the low-$^{87}Sr/^{86}Sr$ high-Sr concentration end member and K-feldspar or Rb-rich clays resulting from Rb exclusion in carbonates form the high-$^{87}Sr/^{86}Sr$ and low-Sr concentration end member. Local environments result in distinct $^{87}Sr/^{86}Sr$ signatures in diagenetic phases but do not alter the effects of cross-formational fluid movement and mixing.

ACKNOWLEDGEMENTS

This work was carried out during the tenure of an NSERC scholarship and a Dissertation Fellowship. Financial support was provided by Texaco Resources Canada and Petroleum Aid to Education.

The following companies graciously granted permission to sample fluids on their leases: ESSO Resources Canada (Dave Todd, Chris Ford); Gulf Resources Canada (Ron Mader); Enron Oil Canada Limited (Tim McKay); Prophet Petroleum (Andy Graw); Columbia Gas Development of Canada (Ray Kashmir); Westhill Resources (John Rodgers); Cabre Exploration (Gary Mascant); and Wellore Resources (Ron Savage).

The author would like to thank the *Geochemistry Group* (Pat Cavell, John Duke, Steve Prevec, Paul Lhotka and Susan Atkinson) for taking me in, providing an excellent environment in which to conduct research, and for their patience, help and advice. Dragan Krstic and the mass spectrometry group for their instruction and help and Wayne Day and Al Stelmach for technical support.

During the work on the thesis I worked at many locations and in many different laboratories and I wish to thank all of these people.

Dr. Karlis Muehlenbachs at the University of Alberta for granting access to his laboratory facilities, for many stimulating discussions and unending encouragement. James Steer is thanked for obtaining the deuterium analyses on the water samples and help in the laboratory. I am grateful to the Department of Soil Science (Dr. Dudas and his students) at the University of Alberta for allowing me to use their SOLMINEQ.88 PC/SHELL software and for providing instruction along the way.

The people who helped with the fluid analyses at Washington University in St. Louis are gratefully acknowledged. Dr. Lynn Walter for allowing me to come work in her laboratory for six months and Ted Huston for methods development and with obtaining some of the organic acid analyses. Dave Sassani and Everett Shock for their time and patience in assisting with running the EQ3-NR software and for numerous discussions and

instruction in thermodynamics.

The people at the University of Western Ontario who helped with the diagenetic mineral separations are thanked for allowing me to work in their laboratories for 2 months and for their patience in explaining various techniques and instrumentation.

Dr. Hugh Abercrombie and the Institute of Sedimentary and Petroleum Geology are gratefully acknowledged for permitting me to come and use some of their GEO-CALC software, including some modifications made by Dr. Abercrombie for low-temperature geochemical systems. The time Dr. Abercrombie afforded me and his patience were extremely helpful.

Bruce Keffer, Pat Cavell, and Diane Caird merit special acknowledgements for all the time they donated towards my thesis, their unending enthusiasm and their friendship.

Special thanks to my supervisors Dr. F.J. Longstaffe and Dr. H. Baadsgaard for all the time and effort they put toward this project and my committee members for assistance throughout the thesis.

TABLE OF CONTENTS

APPENDIX

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1. INTRODUCTION

The term diagenesis includes all processes which affect a sediment from sedimentation until the constituent grains achieve chemical equilibrium during metamorphism. Diagenesis involves many interdependent elements and processes, including sediment composition and texture, degree of lithologic variation, burial rate, sedimentary and tectonic environment, hydrodynamic and geothermal gradients, chemical reaction rates, and a host of other factors (HUTCHEON, 1982). Furthermore, diagenesis is an ongoing attempt to attain equilibrium in an environment characterized by the transient behavior of temperature, fluid flow and fluid composition (e.g. connate water; meteoric water). Consequently, diagenetic studies tend to be interdisciplinary, drawing ideas, techniques, and concepts from many fields of geology.

Much of the early work in diagenesis concentrated on the volumetrically most important reactions which lead to the formation of authigenic phases and/or the alteration of minerals, such as: 1) quartz cementation; 2) calcite cementation; and 3) feldspar alteration. Shale/sandstone interaction was stressed; in particular how reactions in the former controlled or altered the formation of authigenic phases in the latter. Historically, the degree of mass transfer between these two lithologies has been a matter of ongoing debate. Many of these early investigations were concentrated in the Gulf Coast Basin, a juvenile basin with a simple compactional burial history, which allowed investigations of diagenetic trends to be correlated with increased depth and temperature in sandstones and shales. The following trends were noted: (1) the transformation of smectite to illite through an intermediary mixed layer illite/smectite (BURST, 1959, 1969; PERRY and HOWER, 1970; HOWER *et al.*, 1976; BOLES and FRANK, 1979); (2) the albitization of calcic plagioclase (LAND and MILLIKEN, 1981; BOLES, 1982); and (3) the enrichment of Mg and Fe in carbonate cements (BOLES, 1978). While these issues were being addressed in the field of clastic diagenesis, concurrent studies were occurring in the field of carbonate diagenesis, addressing problems such as the mechanisms of dolomitization, mass movement, biological influences, and porosity development.

The Western Canada Sedimentary Basin, and its sub-basin the Alberta Basin, are foreland basins that have been tectonically uplifted and characterized by gravity-driven flow of meteoric waters (HITCHON, 1969a, 1969b, 1984; GARVEN, 1985, 1989). Consequently this basin differs from juvenile basins where diagenetic trends were first established. This may result in distinctive diagenetic trends in the Alberta Basin when compared to trends established in other types of sedimentary basins. Furthermore, the Alberta Basin is composed of two distinct lithology types - clastic and carbonate, providing a scenario where both fields of diagenesis may be studied both individually and interdependently.

Many diagenetic studies have been conducted on the Alberta Basin since the initial work of LERBEKMO (1961a). However, most of these studies are confined to the textural, compositional and mineralogical aspects of basin rocks within a single formation and do not include an investigation of the associated fluids (Belly River Formation - LERBEKMO, 1961b, 1963; CAMPBELL and LERBEKMO, 1963; CARRIGY and MELLON, 1964; IWUAGWU and LERBEKMO, 1981, 1982, 1984; STOREY, 1982; LONGSTAFFE 1986; AYALON and LONGSTAFFE, 1988; Cardium Formation - THOMAS and OLIVER, 1979; GRIFFITH, 1982; STALEY, 1986; KRAUSE *et al.* 1987; MACHEMER and HUTCHEON, 1988; Viking Formation - THOMAS and OLIVER, 1979; FOSCOLOS *et al.*, 1982; ROBB, 1985; GRANT, 1985; DEAN 1986; REINSON and FOSCOLOS, 1986; STALEY, 1986; LONGSTAFFE and AYALON, 1987; Glauconitic Formation - TILLEY, 1982; TILLEY and LONGSTAFFE, 1984; YOUNG and DOIG, 1986; Devonian - WALLS, 1977, 1983; WALLS *et al.*, 1979; WALLS and BURROWS, 1985; MACHEL, 1985; STOAKES, 1980; CARPENTER and LOHMANN, 1989). Early studies of the formation waters have been conducted for the entire Western Canada Sedimentary Basin (BILLINGS *et al.*, 1969; HITCHON and FRIEDMAN, 1969; HITCHON *et al.*, 1971). While these reconnaissance studies have some associated detriments (several sub-basins and aquifer systems were combined and control over sampling techniques and procedures was not monitored), consolidation of all these mineral/rock and fluid studies has established an essential framework upon which it is now feasible to conduct, in the Alberta Basin, diagenetic studies which amalgamate water and rock data. Other than the study of ABERCROMBIE (1989) for the Cold Lake region in east-central Alberta, such works have not been undertaken anywhere in Alberta. It is the intent of this thesis to examine all of the formations from a vertical section in the Alberta Basin, in an attempt to define the extent and scale of water/rock interaction and to establish the authigenic mineral and porewater evolution.

LOCATION AND STRATIGRAPHY

The Alberta Basin is a foreland basin within the Western Canada Sedimentary Basin, bordered to the west by the Rocky Mountain Thrust Belt, to the northeast by the Precambrian Shield, and to the southwest by the Sweetgrass Arch (Fig. 1.1). The study area embodies approximately 20,000 km^2 in the Alberta Basin and is composed of a wedge of unfolded sedimentary rocks that thicken and dip toward the southwest, resting unconformably on a similarly tilted Precambrian basement (Fig. 1.2). The wedge of sedimentary rocks is composed of: (1) Cambrian basal sandstones and shales; (2) eroded Jurassic and Paleozoic carbonates, shales and evaporites; and (3) Cretaceous shales and siltstones interbedded with thin lenses of sandstone (Table 1.1). The Cretaceous clastic rocks are separated from stratigraphically lower units and the Cambrian units are separated from stratigraphically higher units by major regional unconformities. Silurian, Ordovician, Lower Devonian, Upper Mississippian, Pennsylvanian, Permian, Triassic and most of the

Jurassic strata are not found under the Central plains of Alberta (Fig. 1.3). The rocks and minerals studied were sampled from Precambrian to Upper Cretaceous formations, whereas, associated formation waters were extracted from Upper Devonian through to Upper Cretaceous reservoirs.

The tectonic history of the Western Canada Sedimentary Basin and its present day morphology are a product of orogenic forces active during Jurassic through Tertiary time. The Columbian Orogeny occurred near the end of the Jurassic as a result of subduction of the Pacific Plate beneath the margin of the North American Plate. Subsequent shortening across the orogen initiated formation of the Rocky Mountians (PRICE, 1973; DICKINSON and SNYDER, 1978; BEAUMONT, 1981; JORDON, 1981). Slow epeirogenic uplift and thrusting along the eastern Cordillera heralded the first pulse of the Laramide Orogeny during the Late Cretaceous. Culmination of the Laramide Orogeny occurred in Late Paleocene or Early Eocene and resulted in downwarping and burial of the foreland basin (PRICE, 1973; DICKINSON, 1974; PORTER *et al.*, 1982; HITCHON, 1984). Subsequent erosion of accumulated Tertiary and Upper Cretaceous rocks has occurred in the Central plains of Alberta.

OBJECTIVES

The primary objectives of this thesis are to contribute to the understanding of water/rock interactions in a sedimentary basin dominated by gravity-driven flow of meteoric waters and to examine the scale of diagenetic interdependence between formation waters and detrital and authigenic phases. Specifically, the goals are to elucidate the subsurface processes of: 1) mineral transformation, alteration, dissolution and precipitation; 2) fluid movement and mixing; and, 3) mass movement through shales to adjacent sandstones. The results of all of these processes are reflected in the present day chemical and isotopic (O, C, H, Sr) composition of the reservoir fluids and authigenic phases.

Porewaters record diagenetic reactions which have occurred during their residence time in the system and solid phases exhibit the cumulative effects of diagenesis. Thus, to obtain a complete representation of diagenesis, both phases were examined.

Hydrogeochemical models of the porewaters are established independent of hydrologic models, providing a separate method with which to examine basinal fluid flow. Based purely on chemical and isotopic trends, water origin and diagenetic evolution are evaluated in terms of water mixing and water/rock interaction. It is of significance to delineate the interface of mixing zones in sedimentary basins, as diagenetic processes are most active at these sites (KNAUTH, 1988). Specific reactions and minerals most influential in controlling the current water composition and contributing components to the mixing regime are indicated by equilibrium thermodynamics.

The rock reservoir is examined by analyzing both whole rocks and mineral separates. Allogenic (feldspars, mica, carbonate) and diagenetic (illite, chlorite, carbonate, apatite) mineral separates from Precambrian through Cretaceous rocks in the study area are analyzed isotopically (Sr, O, C) and for Sr and Rb concentration in order to: (1) establish diagenetic minerals in terms of water mixing and rock/water reactions; (2) help formulate, in conjunction with the fluid chemistry, the porewater evolution; (3) determine the degree of open versus closed system behavior in the basin with respect to cross-formational fluid flow; and, (4) establish the sequence or timing of diagenetic mineral formation and the scale over which this occurs or specific zones to which it is restricted. Strontium ratios are not measurably fractionated during sedimentary processes; the distribution of Sr isotopes in mineral phases is independent of temperature, pressure, distribution coefficients or Sr activity. Therefore, $^{87}Sr/^{86}Sr$ ratios and Sr concentrations of specific mineral phases constrain possible source minerals, because different minerals of the same rock have diverse Rb/Sr ratios, resulting in characteristic $^{87}Sr/^{86}Sr$ signatures of potential sources. Stable isotopes (O, C) of authigenic phases provide a record of conditions prevailing during their formation; porewater composition, temperature, and mineral/water ratio. Thus, by combining the two isotope systems, the origin of the water phase and the source of Sr can be determined, providing information on water mixing and migration, the extent and nature of water/rock interaction, and the chemical evolution of water and subsequent authigenic phases.

To attain these objectives, a range of interrelated disciplines are used to adequately evaluate the Alberta Basin *system*, including mineralogy (diagenetic mineral precipitation, alteration, transformation and dissolution), aqueous (brine) geochemistry, hydrogeology and hydrodynamics, thermodynamic modelling of aqueous species, organic geochemistry and isotopic (stable and radiogenic) geochemistry.

OUTLINE OF THESIS

The thesis has three major divisions and is composed of five main chapters, with a summary and conclusion chapter following these:

Chapter 2 provides the geological and geochemical framework for a study of the Alberta Basin by evaluating isotopically (O, C, Sr), the whole rocks and authigenic carbonate cements in the study area. These phases are examined to detemine meteoric influence and diagenetic modification to all of the formations. Whole rock Sr analyses are presented, establishing an overall strontium *signature* for the specific formations.

Chapters 3, 4 and 5 describe the present day formation water chemistry and isotopic (radiogenic and stable) systematics, in conjunction with the hydrochemical evolution and present day equilibrium. Each of these chapters deals with a specific aspect of the present day water composition and possible mechanisms to explain this composition:

I. Fluid chemistry - provides a brief description of the chemical and short chain aliphatic acid composition of the waters. A theory for the origin of the fluids and ensuing diagenetic modifications is presented;

II. Isotope systematics and fluid mixing - examines the O, H and Sr isotopic compositions of the waters to further distinguish the degree of fluid mixing and/or isolation. These relationships are explained in the context of the evolution of the Alberta basin and its provenance;

III. Geochemical equilibrium model - more clearly defines the degree of water/rock interaction by applying equilibrium thermodynamics to the waters to calculate the distribution of aqueous species at *in situ* temperatures and pressures and to model mineral/water equilibria.

Chapter 6 contains an isotopic (O and Sr) and Sr and Rb concentration study of the mineral separates (detrital and diagenetic) from the various formations in the Alberta Basin. A refined model for the paleoflow paths in the Alberta Basin and the origin of authigenic minerals and porewater composition is developed in the context of previous water studies.

SIGNIFICANCE OF STUDY

The results of this study illustrate the application of geochemical and isotopic systematics to classify water/rock interaction. Data unique to Alberta Basin studies at the present time include: 1) strontium analyses of sedimentary rocks, minerals, and formation waters; 2) short chain aliphatic acid analyses; 3) fluids collected at the wellhead with suitable techniques for the preservation of specific chemical species; 4) thermodynamic modelling of water/rock equilibrium; and, 5) chemical and isotopic tracing of water/rock interactions basinwide. The general contribution of this study is the clarification of chemical reactions active in sedimentary basins dominated by gravity-driven flow and the scale over which they are active (micro, meso, macro). The significance of cross-formational fluid flow in the Alberta Basin is illustrated and the degree of penetration of current meteoric fluids into the various formations and their importance to diagenetic processes is indicated. Constraining the fluid movement and water/rock interaction in the Alberta Basin may have later applications to the other water/rock studies and may be important to economic considerations, such as oil recovery and environmental geology.

REFERENCES

ABERCROMBIE H. (1989) Water-rock interaction during diagenesis and thermal recovery, Cold Lake, Alberta. Ph.D. Diss., Univ. of Calgary, Calgary, Alberta.

AYALON A. and LONGSTAFFE F.J. (1988) Oxygen isotope studies of diagenesis and pore-water evolution in the western Canada sedimentary basin: Evidence from Upper Cretaceous Basal Belly River sandstone, Alberta. *J. Sediment. Petrol.* **58**, 489-505.

BEAUMONT C. (1981) Foreland basins. *Geophys. J. Roy. Astron. Soc.* **65**, 291-329.

BILLINGS G.K., HITCHON B. and SHAW D.R. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin, 2. Alkali metals. *Chem. Geol.* **4**, 211-223.

BOLES J.R. (1978) Active ankerite cementation in the subsurface Eocene of southwest Texas. *Contrib. Mineral. Petrol.* **68**, 13-22.

BOLES J.R. (1982) Active albitization of Gulf Coast Tertiary. *Am. J. Sci.* **282**, 165-180.

BOLES J.R. and FRANK S.G. (1979) Clay diagenesis in Wilcox sandstones of southwest Texas: Implication of smectite diagenesis on sandstone cementation. *J. Sediment. Petrol.* **49**, 55-70.

BURST J.F. (1959) Post-diagenetic clay mineral environmental relationships in the Gulf Coast Eocene. In *Clays and Clay Minerals, Proceedings of the 6th National Conference on Clays and Clay Minerals* (ed. A. SWINEFORD), pp. 327-341. Intern. Ser. Mon. Earth Sci. **2**.

BURST J.F. (1969) Diagenesis of Gulf Coast clayey sediments and its possible relation to petroleum migration. *Am. Assoc. Petrol. Geol. Bull.* **53**, 73-93.

CAMPBELL F.A. and LERBEKMO J.F. (1963) Mineralogic and chemical variations between Upper Cretaceous continental Belly River shales and marine Wapiabi shales in western Alberta, Canada. *Sedimentol.* **2**, 215-226.

CARPENTER S.J. and LOHMANN K.C. (1989) $\delta^{18}O$ and $\delta^{13}C$ variations in Late Devonian marine cements from the Golden Spike and Nevis reefs, Alberta, Canada. *J. Sediment. Petrol.* **59**, 792-814.

CARRIGY M.A. and MELLON G.B. (1964) Authigenic clay mineral cements in Cretaceous and Tertiary sandstones of Alberta. *J. Sediment. Petrol.* **34**, 461-472.

DEAN M.E. (1986) Diagenesis of the Viking Formation, south-central Alberta. Unpub. M.Sc. Thesis, Univ. of Alberta, Edmonton, Alberta.

DICKINSON W.R. (1974) Plate tectonics and sedimentation. In *Tectonics and Sedimentation* (ed. W.R. DICKINSON), pp. 1-27. Spec. Pub. Soc. of Econ. Geol. Paleon.

DICKINSON W.R. and SNYDER W.S. (1978) Plate tectonics of the Laramide Orogeny. In *Laramide Folding Associated with Basement Faulting in the Western United States*. pp. 355-366. Geol. Soc. Am. Mem. **151**.

FOSCOLOS A.E., REINSON G.E. and POWELL T.G. (1982) Controls on clay-mineral authigenesis in Viking sandstone, central Alberta. 1. Shallow depths. *Can. Mineral.* **20**, 141-150.

GARVEN G. (1985) The role of regional fluid flow in the genesis of the Pine Point deposit, western Canada sedimentary basin. *Econ. Geol.* **80**, 307-324.

GARVEN G. (1989) A hydrogeologic model for the formation of giant oil sands deposits of the western Canada sedimentary basin. *Am. J. Sci.* **289**, 105-166.

GRANT S.K. (1985) Geologic study of the Viking Formation, Harmattan East Field. Unpub. M.Sc. Thesis, Univ. of Alberta, Edmonton, Alberta.

GRIFFITH L.A. (1981) Depositional environment and conglomerate diagenesis of the Cardium Formation, Ferrier Field, Alberta. Unpub. M.Sc. Thesis, Univ. of Calgary, Calgary, Alberta.

HITCHON B. (1969a) Fluid flow in the Western Canada Sedimentary Basin, 1. Effect of topography. *Water Resour. Res.* **5**, 186-195.

HITCHON B. (1969b) Fluid flow in the Western Canada Sedimentary Basin, 2. Effect of Geology. *Water Resour. Res.* **5**, 460-469.

HITCHON B. (1984) Geothermal gradients, hydrodynamics and hydrocarbon occurrence, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* **68**, 713-743.

HITCHON B. and FRIEDMAN I. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin, 1. Stable isotopes of hydrogen and oxygen. *Geochim. Cosmochim. Acta* **33**, 1321-1349.

HITCHON B., BILLINGS G.K. and KLOVAN J.E. (1971) Geochemistry and origin of formation waters in the western Canada sedimentary basin, III. Factors controlling chemical composition. *Geochim. Cosmochim. Acta* **35**, 567-598.

HOWER J., ESLINGER E.V., HOWER M.E. and PERRY E.A. (1976) Mechanisms of burial metamorphism of argillaceous sediments: 1. Mineralogical and chemical evidence. *Geol. Soc. Am. Bull.* **87**, 725-737.

HUTCHEON I. (1982) Diagenesis 3. Aspects of the diagenesis of coarse-grained siliciclastic rocks. *Geosci. Canada* **10**, 4-14.

IWUAGWU C.J. and LERBEKMO J.F. (1981) The role of authigenic clays in some reservoir characteristics of the basal Belly River sandstone, Pembina Field, Alberta. *Bull. Can. Petrol. Geol.* **29**, 479-491.

IWUAGWU C.J. and LERBEKMO J.F. (1982) The petrology of the basal Belly River sandstone reservoir, Pembina Field, Alberta. *Bull. Can. Petrol. Geol.* **30**, 187-207.

IWUAGWU C.J. and LERBEKMO J.F. (1984) Application of outcrop information to subsurface exploration for sandstone reservoirs; basal Belly River Formation (Upper Cretaceous), Alberta, Foothills. In *The Mesozoic of Middle North America.* (eds. D.F. STOTT and GLASS D.J.), pp. 387-400. Can. Soc. Petrol. Geol., Mem. **9**.

JORDON T.E. (1981) Thrust loads and foreland basin evolution, Cretaceous western United States. *Am. Assoc. Petrol. Geol. Bull.* **65**, 2506-2520.

KNAUTH L.P. (1988) Origin and mixing history of brines, Palo Duro Basin, Texas, U.S.A. *Appld. Geochem.* **3**, 455-474.

KRAUSE F.F., COLLINS H.N., NELSON D.A., MACHEMER S.D. and FRENCH P.R. (1987) Multi-scale anatomy of a reservoir: Geological characterization of Pembina-Cardium Pool west-central Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* **71**, 1233-1260.

LAND L.S. and MILLIKEN K.L. (1981) Feldspar diagenesis in the Frio Formation, Brazoria County, Texas Gulf Coast. *Geology* **9**, 314-318.

LERBEKMO J.F. (1961a) Porosity reduction in Cretaceous sandstones of Alberta. *J. Alberta Soc. Petrol. Geol.* **9**, 192-199.

LERBEKMO J.F. (1961b) Stratigraphic relationship between the Milk River Formation of the southern plains and the Belly River Formation of the southern Foothills of Alberta. *J. Alberta Soc. Petrol. Geol. Bull.* **9**, 273-276.

LERBEKMO J.F. (1963) Petrology of the Belly River Formation, southern Alberta Foothills. *Sedimentol.* **2**, 54-86.

LONGSTAFFE F.J. (1986) Oxygen isotope studies of diagenesis in the basal Belly River sandstone, Pembina I-Pool, Alberta. *J. Sediment. Petrol.* **56**, 78-88.

LONGSTAFFE F.J. and AYALON A. (1987) Oxygen-isotope studies of clastic diagenesis in the Lower Cretaceous Viking Formation, Alberta: Implications for the role of meteoric water. In *Diagenesis of Sedimentary Sequences* (ed. J.D. MARSHALL), pp. 277-296. Geol. Soc. Spec. Pub. **36**.

MACHEL H.G. (1985) Facies and diagenesis of the Upper Devonian Nisku Formation in the subsurface of central Alberta. Unpub. Ph.D. Diss., McGill Univ., Montreal, Quebec.

PERRY E. and HOWER J. (1970) Burial diagenesis in Gulf Coast pelitic sediments. *Clays and Clay Mins.* **18**, 165-177.

PORTER J.W., PRICE R.A. and McCROSSAN R.G. (1982) The Western Canada Sedimentary Basin. *Roy. Soc. Phil. Trans.* **305**, 169-192.

PRICE R.A. (1973) Large scale gravitational flow of supra-crustal rocks, southern Canadian Rocky Mountains. In *Gravity and Tectonics* (eds. K.A. DEGONG and R.S. CHOLTEN), pp. 491-502. Wiley.

REINSON G.E. and FOSCOLOS A.E. (1986) Trends in sandstone diagenesis with depth of burial, Viking Formation, southern Alberta. *Bull. Can. Petrol. Geol.* **34**, 126-152.

ROBB G.A. (1985) Sedimentology and diagenesis of the Viking Formation, Garrington Oil Field, south-central Alberta. Unpub. M.Sc. Thesis., Univ. of Alberta, Edmonton, Alberta.

STALEY G.H. (1986) The diagenesis of the Cretaceous Cardium and Viking Formations, Alberta Basin, Canada. *Terra Cognita* **6**, 107-108.

STOAKES F.A. (1980) Nature and control of shale basin fill and its effect on reef growth termination: Upper Devonian Duvernay and Ireton Formations of Alberta, Canada. *Bull. Can. Petrol. Geol.* **28**, 345-410.

STOREY S.R. (1982) Optimum reservoir facies in an immature, shallow lobate delta system: Basal Belly River Formation, Keystone-Pembina area. In *Depositional Environments and Reservoir Facies in Some Western Canadian Oil and Gas Fields* (ed. J.C. HOPKINS), pp. 3-13. Univ. of Calgary Core Conference.

THOMAS M.B. and OLIVER T.A. (1979) Depth-porosity relationships in the Viking and Cardium Formations of central Alberta. *Bull. Can. Petrol. Geol.* **27**, 209-228.

TILLEY B.J. (1982) Sedimentology and clay mineralogy of the Glauconitic sandstone, Suffield heavy oil sands, southeastern Alberta. Unpub. M.Sc. Thesis, Univ. of Alberta, Edmonton, Alberta.

TILLEY B.J. and LONGSTAFFE F.J. (1984) Controls on hydrocarbon accumulation in Glauconitic sandstone, Suffield heavy oil sands, southern Alberta. *Am. Assoc. Petrol. Geol. Bull.* **68**, 1004-1023.

WALLS R.A. (1977) Cementation history and porosity development, Golden Spike reef complex (Devonian) Alberta. Unpub. Ph.D. Diss., McGill Univ., Montreal, Quebec.

WALLS R.A. (1983) Golden Spike reef complex. In *Carbonate Depositional Environments* (eds. P.A. SCHOLL), pp. 445-453. Am. Assoc. Petrol. Geol. Mem. **33**.

WALLS R.A., MOUNTJOY E.W. and FRITZ P. (1979) Isotopic composition and diagenetic history of carbonate cements in Devonian Golden Spike reef, Alberta, Canada. *Geol. Soc. Am. Bull.* **90**, 963-982.

WALLS R.A. and BURROWES G. (1985) The role of cementation in the diagenetic history of Devonian reefs, Western Canada. In *Carbonate Cements* (eds. N. SCHNEIDERMANN and P.M. HARRIS), pp. 185-220. SEPM Spec. Paper **36**.

YOUNG H.R. and DOIG D.J. (1986) Petrography and provenance of Glauconitic sandstone, south-central Alberta, with comments on the occurrence of detrital dolomite. *Bull. Can. Petrol. Geol.* 34, 408-425.

SYSTEM	STRATIGRAPHIC UNIT	GENERAL LITHOLOGY AND DEPOSITIONAL SETTING
Upper Cretaceous	Basal Belly River	Carbonaceous sandstone interbedded with shale and sandstone.
	Lea Park	Shales becoming more marine toward base.
	Cardium	Three sandstone members separated by dark shales. Sandstone members may have conglomerate at the top and be interspersed with shale lenses.
Lower Cretaceous	Viking	Varies from fine salt and pepper sandstone to siltstone to silty shale; sandstone generally interspersed with shale.
	Glauconitic	Very fine to medium quartz sandstone mixed with coarser salt and pepper sandstone. Clay and calcareous cement vary.
	Ostracod	Predominantly shale that is partly calcareous, containing bands of argillaceous limestone.
	Basal Quartz	Essentially sandstone varying greatly in colour and texture. Upper beds are more calcareous. Contains lenses of shale.
Middle Jurassic	Rock Creek	Calcareous sandstone and rusty weathering shale; argillaceous limestone lenses.
	Poker Chip Shale	Black calcareous shales with thin limestone beds.
Lower Jurassic	Nordegg	Black limestone and black calcareous shales with abundant chert fragments; top highly fossiliferous.
	Fernie	Shale; commonly sandy, in places calcareous, and occasionally bituminous.
Mississippian	--	Massive coarse-grained limestone, alternating with beds of black fine-grained limestone; may contain chert nodules.
Upper Devonian	Wabamun	Limestone dominant in the upper part of the group and dolomite in the middle and lower parts; however, may consist of all one litholgy or the other.
	Nisku	Dolomite, variably silty and anhydritic.
	Leduc	Semi-fragmental and reeflike; crystalline dolomite with scattered vugs.
Middle/Lower Devonian	Elk Point	Anhydritic dolomite, fossiliferous
Cambrian	--	Calcareous grey to black shale. Buff to glauconitic sandstone; shale partings.
Precambrian	--	Crystalline basement.

Table 1.1. Stratigraphic column with lithologic descriptions for the study area in the Alberta Basin.

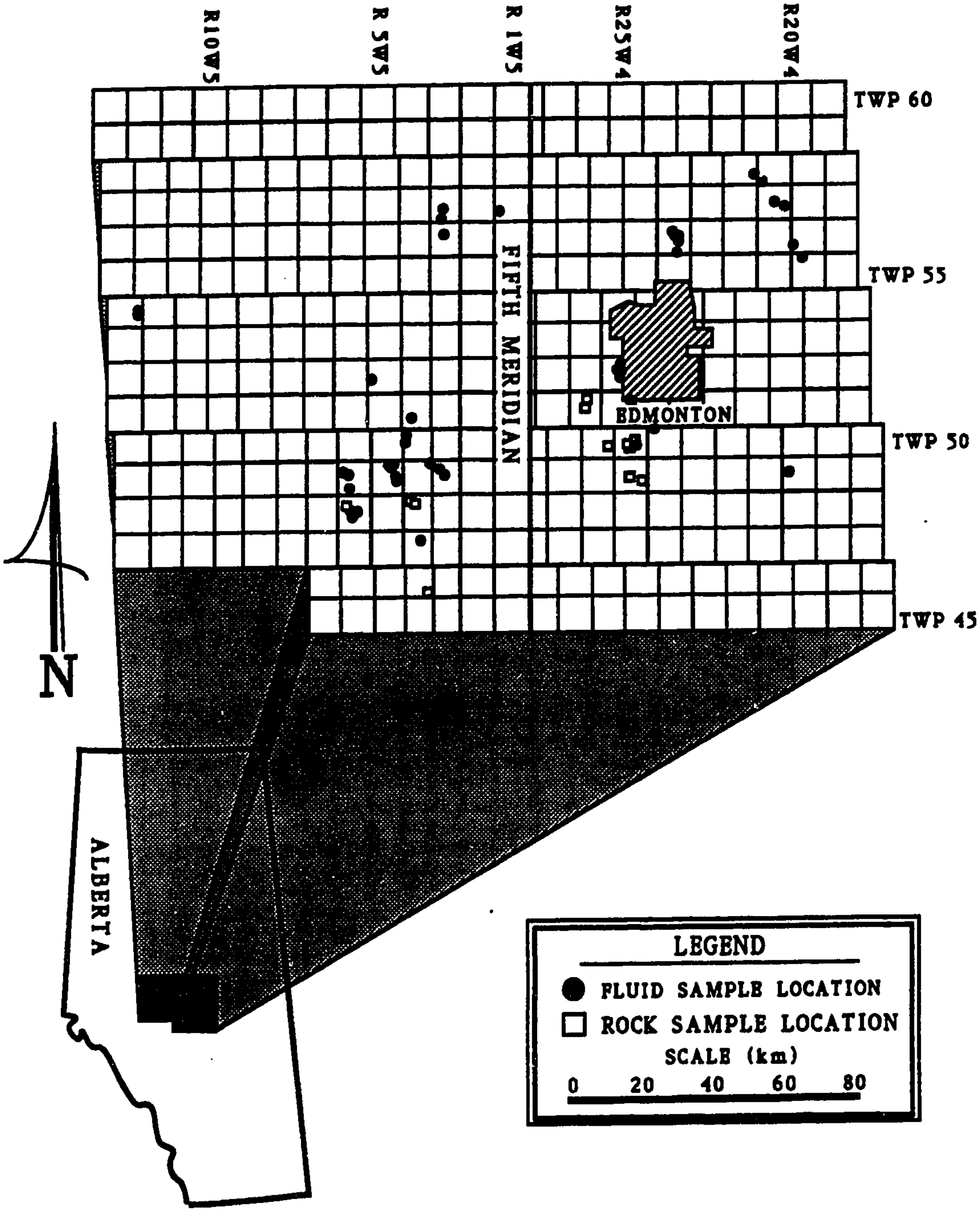


Fig. 1.1. Map of Alberta illustrating the location of the study area.

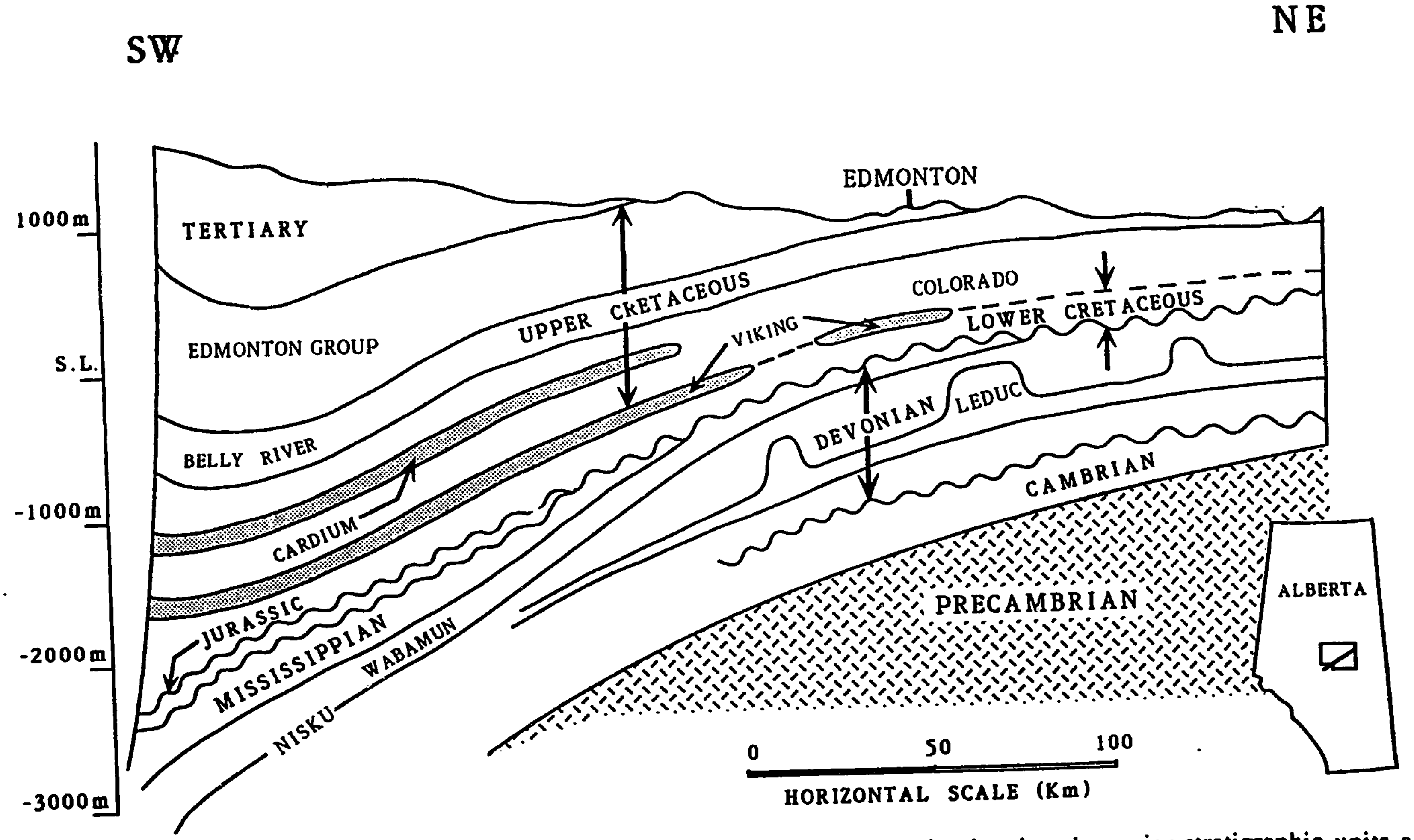


Fig. 1.2. Geological cross section from SW to NE through the Alberta Basin showing the major stratigraphic units and unconformities.

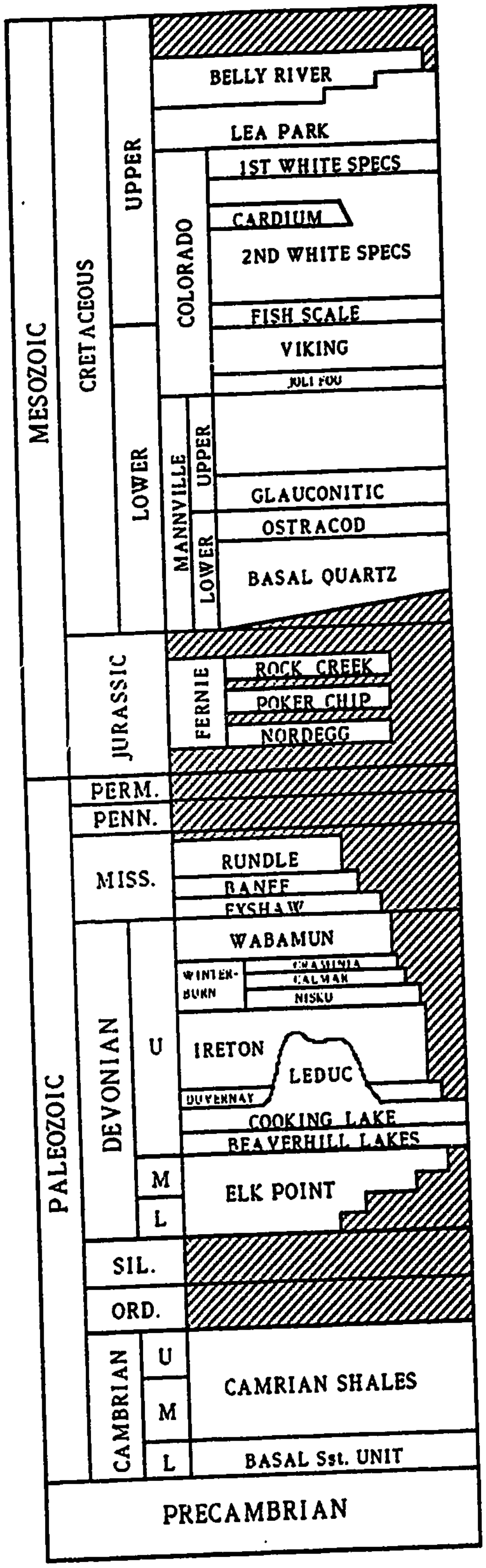


Fig. 1.3. Generalized stratigraphic column,Central Plains, Alberta, Canada (modified after *Energy Resources Conservation Board; Table of Formations*).

CHAPTER 2. STRONTIUM AND STABLE ISOTOPIC CHARACTERIZATION OF CLASTIC AND CARBONATE ROCKS IN THE ALBERTA BASIN, WESTERN CANADA SEDIMENTARY BASIN: WHOLE ROCKS AND CARBONATE CEMENTS

INTRODUCTION

Carbonate rocks and carbonate cements within clastic sedimentary rocks are volumetrically significant in the Alberta Basin, a sub-basin of the Western Canada Sedimentary Basin (Fig. 2.1). Carbonate phases occur in every formation from Precambrian to the Upper Cretaceous and are of interest because they are: (1) ubiquitous and have the potential to control pore fluid chemistry; (2) readily formed at various stages of diagenesis; and, (3) associated with many diagenetic reactions which occur in sedimentary environments (HAYES, 1979; MILLIKEN *et al.*, 1981; LAND, 1984; BOLES, 1987; SCHULTZ *et al.*, 1989). Some of the diagenetic reactions with which carbonate phases are directly or indirectly associated include: (1) albitization of calcic plagioclase (LAND and MILLIKEN, 1981); (2) pressure solution and dissolution of carbonates; and, (3) clay diagenesis, including illitization of smectite (BOLES and FRANK, 1979). These reactions may be focused within discrete stratigraphic intervals (LOUCKS *et al.*, 1977; BOLES and FRANK, 1979) or occur throughout a basin. Investigation of whole rock limestone/dolostone and shale and separated diagenetic carbonate cements in the clastic units should help to elucidate the importance of specific reactions and the scale (micro-; meso-; macro-) over which they are significant.

The $^{87}Sr/^{86}Sr$ ratios of unaltered marine carbonates provide a record of the $^{87}Sr/^{86}Sr$ composition of seawater over time, as these phases exclude Rb from their structure resulting in a static $^{87}Sr/^{86}Sr$ signature. Several Phanerozoic $^{87}Sr/^{86}Sr$ seawater curves have been constructed using unaltered carbonates (PETERMAN *et al.*, 1970; VEIZER and COMPSTON, 1974; FAURE, 1982; BURKE *et al.*, 1982). In the construction of these curves it is assumed that the Sr concentration and isotopic composition is uniform throughout the world's oceans at any given time (VEIZER and COMPSTON, 1974; FAURE, 1982). Deviation of carbonate $^{87}Sr/^{86}Sr$ values from established seawater curves suggests that either the carbonate samples did not obtain $^{87}Sr/^{86}Sr$ ratios from contemporaneous seawater, or that they were diagenetically contaminated by foreign Sr.

The $^{87}Sr/^{86}Sr$ ratios of minerals provide potential tracers of mineral-water interactions because of the mobility of Sr in surface and subsurface environments, and because different minerals of the same lithologic unit have diverse Rb/Sr ratios, resulting in considerably different Sr isotopic ratios. Unlike stable, lower mass isotopes, Sr isotopes are not measurably fractionated during sedimentary processes; the distribution of Sr isotopes in mineral phases is independent of temperature, pressure, distribution coefficients or Sr activity. Hence, $^{87}Sr/^{86}Sr$ ratios of authigenic carbonate cements in clastic rocks permit the identification of the major sources of Sr in the pore fluid and indicate the dimensions within which the fluid was isotopically homogeneous. Similarly, $^{87}Sr/^{86}Sr$ ratios in limestone/dolostone sequences can also be used to indicate diagenetic recrystallization and mineralogic stabilization reactions under varying flow conditions (CLAUER *et al.*, 1989).

$\delta^{18}O$ and $\delta^{13}C$ values of carbonate minerals provide a record of conditions prevailing during their crystallization and/or recrystallization (GIVEN and LOHMANN, 1985; O'NEIL, 1987) because of the characteristic fractionation of light stable isotopes, particularly in low-temperature sedimentary environments. Carbonate $\delta^{18}O$ values are useful for interpreting the porewater composition, temperature, and mineral/water ratio from which the solid phases precipitated; $\delta^{13}C$ values indicate the source of CO_2, delineating the relative effects of organic processes versus chemical exchange in carbonates (O'NEIL, 1987).

The purpose of this study is to define the intra-formational and cross-formational isotopic variability of $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and $\delta^{13}C$ in whole rocks, including carbonate (limestone/dolostone) and clastic rocks (shales), and carbonate cements within the Alberta Basin, in an attempt to establish the diagenetic reactions that are/were active in the basin and constrain the mineral phases or sedimentary units which are/were influential to these reactions. Such information indirectly provides insight into the origin and evolution of the waters, water/rock interactions, and water migration histories. A survey of $^{87}Sr/^{86}Sr$ ratios in whole rocks (clastic and carbonate) and authigenic carbonates from a complete vertical stratigraphic section in the Alberta Basin will also help define the significance of unconformities and lithological differences in controlling $^{87}Sr/^{86}Sr$ variability in pore fluids and resulting authigenic phases. By amalgamating data from radiogenic isotopes with stable isotopic systems, the diagenetic interdependence of the various formations and intermediary basinal fluids is delineated.

GEOLOGIC AND HYDRODYNAMIC FRAMEWORK

The Alberta Basin is part of the Western Canada Sedimentary Basin, bordered to the west by the Rocky Mountain Thrust Belt, to the northeast by the Precambrian Shield, and to the southeast by the Sweetgrass Arch (Fig. 2.1). The Alberta Basin is a foreland basin composed of essentially undeformed, southwesterly dipping Mesozoic and Paleozoic sedimentary rocks which rest unconformably on Precambrian rocks of the Canadian Shield (Fig. 2.2). The basin may be subdivided into three general lithologic units: (1) Cretaceous clastic rocks composed of thick shale and siltstone units interbedded with thin sandstones;

(2) Jurassic, Mississipian and Devonian carbonates, shales and evaporites; and (3) Cambrian green shales overlying a basal Cambrian sandstone. Upper Mississippian, Pennsylvanian, Permian, Triassic and sections of the Jurassic have been eroded from the Central Plains of Alberta.

Geometry of the Alberta Basin is largely a result of tectonism during the Jurassic to Tertiary (NELSON, 1970). The Rocky Mountains were initiated during the Columbian Orogeny near the end of the Jurassic, when subduction of the Pacific Plate beneath the margin of the North American Plate resulted in shortening across the orogen (PRICE, 1973; DICKINSON and SNYDER, 1978; BEAUMONT, 1981; JORDON, 1981). Subsequently, the first minor pulse of the Laramide Orogeny occurred during the Late Cretaceous, causing thrusting and uplift along the eastern Cordillera (TAYLOR *et al.*, 1964). This orogenic activity generated a downwarping of the western Alberta Plains, which filled with westerly sourced detritus. The major pulse of the Laramide Orogeny occurred in Late Paleocene or Early Eocene and caused maximum burial of the foreland basin. Extensive overthrusting occurred in the eastern Cordillera, accompanied by uplift of the Alberta Basin (TAYLOR *et al.*, 1964; PORTER *et al.*, 1982; HITCHON, 1984). Subsequent erosion of accumulated Tertiary and Upper Cretaceous rocks occurred. It is estimated that approximately 1900 m of overburden in the west of the Alberta Basin and 900 m in the east have been eroded since maximum burial (NURKOWSKI, 1984; BEAUMONT *et al.*, 1985; LONGSTAFFE, 1986).

The current hydrodynamic regime in the Alberta Basin was initiated by the second pulse of the Laramide Orogeny. Associated overthrusting effected a large hydraulic head in the eastern Foothills, creating a mechanism for deep penetration of cool, meteoric waters which discharged eastward (HITCHON, 1969a; HITCHON 1984). Prior to the Laramide Orogeny, it is doubtful that a hydraulic head greater than that generated by the present Canadian Cordillera ever existed (HITCHON and FRIEDMAN, 1969). It has been suggested that the Upper Devonian - Carboniferous carbonate rocks of the Alberta Basin channel flow throughout the basin toward the northeast and act as a low fluid potential drain for the basin (HITCHON, 1969b; HITCHON, 1984). Alternatively, GARVEN (1989) suggests that the regional flow system has undergone dissipation and partitioning, at least since the Pliocene, with younger, shallower formations developing smaller flow sub-systems.

HITCHON (1984), using the data of HACQUEBARD (1977), has attributed major shifts in the geothermal gradient of the Alberta Basin to the late stage of the Laramide Orogeny. HITCHON (1984) suggests that during the Late Paleocene, the gradient decreased from ~30°C/km in the western Alberta plains to ~23°C/km in the east, but that this trend was reversed after the second pulse of the Laramide Orogeny. By the Eocene, the geothermal gradient increased from ~21°C/km in the west to ~27°C/km in the east, a similar but subdued pattern to the modern gradient. BEAUMONT *et al.* (1985), in their lithospheric flexure model, demonstrated that the paleogeothermal gradient has probably increased systematically northeastward from the Foothills, at least since the early stages of the major Laramide Orogeny. However, their studies suggest that the gradients in the past were higher than those estimated by HITCHON (1984), and approximated those of present day (27°C/km in the Foothills to 40°C/km in the Edmonton area). The heat flow pattern has not changed since the Eocene (HITCHON, 1984; MAJORWICZ *et al.* 1985).

ANALYTICAL PROCEDURES

A total of 152 core samples representative of the stratigraphic units in the study area were obtained from 31 locations. Most of the samples were obtained from continuous cores over limited lateral extent, with the exception of samples from the Belly River and Viking Formations, which were part of earlier lateral studies (DEAN, 1986;

LONGSTAFFE, 1986; LONGSTAFFE and AYALON, 1987; AYALON and LONGSTAFFE, 1988). In addition, Mississippian and Jurassic samples were collected to the west of the main vertical section (~40 to 60 km) because these formations were eroded from the Central Plains of Alberta. Whole-rock samples and isolated diagenetic cements were studied using optical petrography, X-ray diffraction (XRD), stable isotope analyses (C and O) and radiogenic isotope analyses ($^{87}Sr/^{86}Sr$). The diagenetic cements were isolated by both chemical (acid leaching) and physical (micro-milling; PREZBINDOWSKI, 1980) techniques.

The oxygen and carbon isotope data are presented in the usual δ notation relative to Standard Mean Ocean Water (SMOW) for oxygen (CRAIG, 1961) and the *Belemnitella americana* from the Peedee Formation (PDB) for carbon (CRAIG, 1957). To calculate the oxygen isotope results for calcite and dolomite, 1.01025 and 1.01110, respectively were used for the total carbonate CO_2 fractionation factor (α) at 25°C (modified after SHARMA and CLAYTON, 1965). The calcite α was used in all calculations for siderite; the dolomite α was used in all calculations for ankerite. An oxygen isotope, CO_2-H_2O fractionation factor of 1.0412 at 25°C has been employed in all these calculations.

Oxygen and carbon stable isotope analyses for carbonate minerals were obtained by reacting organic-free, powdered rock samples (<44 μm) in anhydrous H_3PO_4 at 25°C, using the method of WALTERS *et al.* (1972), modified after McCREA (1950) and EPSTEIN *et al.* (1964). Carbonate content and mineralogy were confirmed by XRD prior to isotope analyses. Because of possible cross-contamination of CO_2 gas produced from calcite and dolomite, results for calcite are presented only when the calcite/dolomite ratio was greater than 0.5 in the sample; results for dolomite are recorded only when the calcite/dolomite ratio was less than 0.7 in the sample. These same restrictions were applied to ankerite/dolomite mixtures. These criteria were frequently satisfied by analyzing an isolated size fraction rather than a whole rock fraction. Siderite was analyzed only when it was the sole carbonate phase in the sample. CO_2 was obtained from siderite and ankerite by reaction at 25°C for 21 days. Replicate isotopic analyses of carbonate minerals are better than ±0.1‰ for oxygen and ±0.05‰ for carbon.

$^{87}Sr/^{86}Sr$ ratios were obtained for both whole rock and carbonate mineral separates. Dissolution of whole-rock carbonates and drilled out diagenetic carbonate separates were performed using dilute ultrapure HNO_3 (1:3) at room temperature; decomposition of carbonate cements within clastic rocks was accomplished by gentle dissolution using 2N HNO_3. To prevent substantial interlayer leaching of Sr from exchangeable sites within clay minerals that predominate in shales, the chemical decomposition of carbonate cements in clastic rocks was generally restricted to sandstones. Furthermore, for the $^{87}Sr/^{86}Sr$ ratio to be considered a valid estimate of a specific carbonate phase, this phase had to comprise >25% of the sample, a stipulation often requiring the use of an isolated size separate. Clastic whole rock dissolution was accomplished using ultrapure HF + HNO_3 and gentle heating in covered vessels. Strontium was separated from the dissolved solutions by coprecipitation with $Ba(NO_3)_2$ from a strong HNO_3 sample solution, and purified in cation-exchange columns. The Sr was loaded as $SrCl_2$ on a double Re-filament and analyzed on a VG-Micromass-30 mass spectrometer equipped with automatic peak-switching and an on-line computer for data processing. The within-run precision of a single $^{87}Sr/^{86}Sr$ analysis was ±0.00005; however, this value rose to ± 0.00010 for samples with a high organic content (Mississippian, Nordegg, Rock Creek Formations). Repeated runs of the NBS-987 standard yielded a mean $^{87}Sr/^{86}Sr$ ratio of 0.71024 ± 0.00005 (1σ). All measured $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$.

RESULTS

Stable ($\delta^{13}C_{(PDB)}$; $\delta^{18}O_{(SMOW)}$) and radiogenic isotope ($^{87}Sr/^{86}Sr$) results are given in Table 2.1. Sample locations, depths, lithologies from which the samples were obtained, and the composition of the analyzed samples are listed. Micromilling (PREZBINDOWSKI, 1980), rather than chemical leaching, was used to extract diagenetic components from some samples. These physically separated samples are denoted by a *D* after the sample names in Table 2.1. A *ND* follows the sample name if the corresponding *nondiagenetic* (i.e., groundmass) component from the same sample was analyzed. With the exception of some samples from the Viking and Belly River Formations, most of the samples are from a limited lateral extent (Table 2.1) so that vertical processes and variation can be examined largely independent of lateral perturbations.

Petrography of Formations

The mineralogy of specific formations in the Alberta Basin is significant to a study of $^{87}Sr/^{86}Sr$ ratios because different minerals are variably resistant to alteration and exchange. Hence, different minerals variably influence the chemical and isotopic composition of porewaters. Furthermore, distinctive Rb/Sr ratios and resulting $^{87}Sr/^{86}Sr$ ratios characterize different mineral phases. Diverse mineralogy, or even variation in the modal mineralogy within one formation, may potentially cause significant isotopic differences in the porewater composition. Strontium contributions to the porewaters from various minerals are reflected in the isotopic compositions of the authigenic cements precipitating from the porewaters, allowing hypotheses to be made regarding cross-formational fluid-flow in the basin.

Core samples from each of the formations shown in the stratigraphic column for the

Alberta Basin (Fig. 2.3) have been examined petrographically, by XRD and by SEM. These observations have been augmented with other petrographic studies to obtain a good average composition of the total mineral assemblage for each formation in the study area. Detailed descriptions of lithologic successions, detrital and authigenic mineralogy, and paragenetic sequences for individual formations are given in Appendix I; a brief overview/summary is provided here.

Altered muscovite biotite granites of the Precambrian basement are unconformably overlain by the basal Cambrian sandstones (~40 m) and shales (~185 m). The sandstones are clean quartz arenites containing early diagenetic chlorite, which is succeeded paragenetically by quartz overgrowths and kaolinite and then by illite/smectite (I/S) and illite. The Cambrian green shales contain intercalated sandstones. The diagenetic component of the shales consists of highly altered chlorite, some of which is being replaced by less altered kaolinite; I/S and illite are the last phases precipitated in the paragenetic sequence. Cambrian lithologies are unconformably overlain by Devonian sedimentary units (~975 m thick), which are composed of evaporites at the base, followed by generally one of two end member lithologies, limestone or secondary dolomite (ANDRICHUK, 1958). Intervening shale formations are composed of alternating carbonate and quartz/illite units. Eroded Mississippian carbonates (~40 m) and Jurassic mixed carbonate/clastic units (~40 m) overlie the Devonian. The principal diagenetic minerals observed in the Devonian through Jurassic formations are carbonate (calcite, dolomite, ankerite) and illite. The Cretaceous clastic rocks (highly variable thickness, increasing toward the southwest) unconformably succeed the Jurassic units in the western part of the study area and the Devonian units toward the east (Fig. 2.2). The Cretaceous assemblage is composed of shale units with interspersed sandstone lenses. The abundance of authigenic minerals is variable, even within a single formation, but similar phases are generally found throughout the Cretaceous formations. Diagenetic clay minerals include Fe-rich chlorite, kaolinite, dickite, smectite, illite and interstratified expandable phases including chlorite/smectite (C/S), smectite/illite (S/I) and illite/smectite (I/S). Diagenetic carbonates include calcite, dolomite, ankerite and siderite. There is a paucity of feldspar in the Cretaceous formations of the study area, with the exception of the Viking and Belly River Formations, where albite/oligoclase plagioclase feldspars are much more abundant (6-26 %) and altered than K-spar (1-8%). Paragenetic sequences for the main reservoirs of Cretaceous units are illustrated in Appendix I.

Carbonate Stable Isotopes

Cretaceous Clastic Rocks

Figure 2.4 is an illustration of the distribution of calcite cements and detrital dolomite phases within Cretaceous formations of the Alberta Basin. The characteristics of these cements and where they occur in the paragenetic sequence of the unit are described in Table 2.2. In general, the Cretaceous formations are characterized by one or two phases of calcite cementation: (1) an early poikilotopic phase that is found between uncompacted grains and characterized by relatively high (>+20‰) $\delta^{18}O$ values; and (2) a later phase that generally follows quartz formation, partially to completely replaces detrital grains, and is succeeded by kaolin and illitic minerals. This later calcite is characterized by lower $\delta^{18}O$ values (+8.5 to +17.5‰) relative to the early poikilotopic calcites. While the early calcite phases are not found in all the Cretaceous formations, the later phases are constituents of every Cretaceous formation. Furthermore, all of these late diagenetic phases appear to have precipitated at similar times in their respective paragenetic sequences, with a high percentage of the calcite replacing feldspar, such that the amount of calcite decreases with decreasing feldspar content in the rock. The $\delta^{18}O$ values for late authigenic calcite are relatively low in the continental sediments from the Belly River Formation (avg. +10‰), but increase, in decreasing increments, in the stratigraphically older formations. For the Viking Formation and stratigraphically lower Cretaceous formations, the $\delta^{18}O$ values of calcite cements from sandstones remain essentially constant. The $\delta^{13}C$ values of the Cretaceous carbonate cements are highly variable (-14.3 to +4.2‰), but do show a broad positive correlation with corresponding $\delta^{18}O$ values (Fig. 2.5). Those formations in which calcite was extracted from both shale and sandstone lithologies (i.e. Glauconitic and Basal Quartz Formations) show a pronounced variation in the $\delta^{18}O$ values of calcite phases from each lithology (Fig. 2.4). The $\delta^{18}O$ values from sandstone hosted calcites average +15.0 to +15.5‰, whereas those from the shale lithologies are much higher (~+18.5 to +19.4‰).

Dolomite in the Cretaceous formations is dominantly detrital, although it may also occur as an early void filling cement or as a replacement of calcite. The $\delta^{18}O$ values of dolomite lie between +19.5 and +23.9‰, which is within the range for the Paleozoic carbonate rocks of western Canada. Similar values to this study have been reported for dolomite grains from other Cretaceous clastic rocks in Alberta (HITCHON and FRIEDMAN, 1969; LONGSTAFFE, 1984, 1986, 1987).

Siderite and ankerite occur sporadically within the Cretaceous units. Siderite has been identified in the Viking Formation and analyzed isotopically. Siderite was also found in the Cardium (MACHEMER and HUTCHEON, 1988) and the Glauconitic Formations, but it is not abundant in the study area and therefore was not analyzed. Viking siderite most often occurs in finer grained sandstones where it appears to have formed early in the paragenetic sequence. The $\delta^{18}O$ and $\delta^{13}C$ values of siderite range from +18.5 to +24.3‰

and -0.8 to -4.6‰, respectively. The siderite phases with the lowest $\delta^{18}O$ values are from an area approximately 120 km south-southwest of the main vertical section for this study highlighted in Fig. 2.1. Here a rooted sedimentary facies has been identified (HEIN *et al.*, 1986). Such an environment is favorable to siderite precipitation as it is characterized by hydrochemical conditions of high bicarbonate activity, low oxidation potential and extremely low concentrations of dissolved sulfide (GARRELS and CHRIST, 1965; CURTIS, 1967; GAUTIER, 1982).

Ankerite has been recognized in both the Viking and Basal Quartz Formations. In the former formation, it is a relatively late diagenetic cement, often associated with dolomite and found replacing detrital feldspar and dolomite, coating authigenic quartz, and filling pores. DEAN (1986) determined this ankerite to be Ca-rich and postulated that the ankerite has directly replaced calcite. However, ankerite is more commonly associated with dolomite in the Viking Formation. A split peak on XRD charts, with d-spacings at both dolomite and ankerite locals, would suggest that instead of replacing calcite, ankerite may be replacing dolomite. Furthermore, using carbonate staining techniques (DICKSON, 1965), dolomite appears to be altering to ankerite. Due to the difficulty in physically separating dolomite and ankerite, mixtures were analyzed isotopically. With an increasing percentage of dolomite, the $\delta^{18}O$ value increased, up to a value of +22.2‰. The values of $\delta^{18}O$ and $\delta^{13}C$ for pure ankerite from the Viking Formation analyzed in this study are +16.5‰ and -5.9‰, respectively, well within the range of +16.3 to +17.9‰ and -12.4 to -3.5‰ reported for $\delta^{18}O$ and $\delta^{13}C$ respectively, by LONGSTAFFE and AYALON (1987) for the same area.

Ankerite in the Basal Quartz Formation is not as abundant as in the Viking Formation, but also occurs as a replacement of dolomite. The $\delta^{18}O$ and $\delta^{13}C$ values show little variation between the dolomite and ankerite phases. Together these carbonates range from +22.6 to +24.0‰ and -0.3 to +1.1‰, for $\delta^{18}O$ and $\delta^{13}C$ respectively.

Devonian – Jurassic Carbonate Rocks

The Devonian through Jurassic rocks in the Alberta Basin are dominantly carbonates that are interrupted by shale/carbonate units which range in composition from shaly carbonates to calcareous shales. There is less variation in $\delta^{18}O$ and $\delta^{13}C$ values in these formations relative to the Cretaceous units; however, some notable trends exist. Figure 2.6 is $\delta^{13}C$ versus $\delta^{18}O$ plot of samples from the Devonian Elk Point, Beaverhill Lake, Cooking Lake, Nisku and Leduc stratigraphic units, illustrating no particular trend of the data for these formations. This lack of correlation is also exhibited on Fig. 2.8. However, when $\delta^{13}C$ versus $\delta^{18}O$ data are plotted for the Wabamun and stratigraphically younger carbonate formations (up to the Cretaceous unconformity) a broad, positive correlation (Fig. 2.7 and 2.8) is exhibited.

Microdrilled diagenetic separates of sparry vug filling carbonates from the Devonian to Jurassic carbonates were also analyzed (Table 2.1). $\delta^{18}O$ and $\delta^{13}C$ values for diagenetic phases in the Cooking Lake and Leduc Formations are virtually identical to the whole rock carbonate values for these formations and exhibit no correlation on a $\delta^{13}C$ versus $\delta^{18}O$ plot. Conversely, Wabamun, Fernie, and Nordegg diagenetic carbonates (vug-filling spar) show a pronounced decrease in $\delta^{18}O$ values and a moderate decrease in $\delta^{13}C$ relative to whole rock data. Stable isotope data for these diagenetic separates also exhibit a positive correlation, which follows the trend established by the whole rock data in Fig. 2.7.

Siderite was not observed in any of the Devonian to Jurassic limestone/dolostone units; however, ankerite and partially ankeritized dolomite have been identified. These phases have an irregular distribution and stable isotopic values of ankerite are comparable to dolomite values within the same formation, although ankerite commonly has $\delta^{18}O$ and $\delta^{13}C$ values at the high end (i.e. $\delta^{18}O$>+23.0‰ and $\delta^{13}C$>-1.0‰) of the range exhibited by both phases.

Cambrian Clastic Rocks

Only one sample, a silty sandstone, contained sufficient calcite to be analyzed and yielded $\delta^{18}O$ and $\delta^{13}C$ values of +23.5‰ and -1.6‰, respectively. MACDONALD (1987) has reported values of +12.2‰ and -4.1‰ for $\delta^{18}O$ and $\delta^{13}C$, respectively, for a calcite sample from the Cambrian sandstone 325 km south of the study area. The sample from MACDONALD's (1987) study was extracted from the basal sandstone and is of uncertain paragenesis.

Ankerite and ankeritized dolomite samples have $\delta^{18}O$ and $\delta^{13}C$ values ranging from +18.6 to +19.6‰ and -3.7 to -3.4‰, respectively. These samples formed subsequent to quartz overgrowths, but prior to pronounced clay mineral formation. The stable isotope values of these phases are comparable to those for dolomite from MACDONALD's (1987) study ($\delta^{18}O$=+19.7‰; $\delta^{13}C$=-1.8‰), despite the ~450 km distance separating the dolomite/ankerite samples.

Radiogenic Isotopes - Whole Rock and Carbonate Cements

$^{87}Sr/^{86}Sr$ ratios were obtained for carbonate cements from the clastic sedimentary units (i.e. Cretaceous and Cambrian) using both chemical and physical extraction processes.

Experiments have shown that leaching carbonate phases from clay-bearing samples may yield an erroneous $^{87}Sr/^{86}Sr$ value for the carbonate phase if the Sr contribution made by exchangeable cations in the clay phase is substantial enough. Similarly, leaching experiments conducted by STUEBER *et al.* (1987) have shown that chemical leaching of clay minerals may significantly increase $^{87}Sr/^{86}Sr$ ratios in formation waters. In their study, STUEBER *et al.*, (1987) leached whole rock shales from the Illinois Basin ($^{87}Sr/^{86}Sr$ = 0.7279 - 0.7547) with 0.25N HCl and with 1N ammonium acetate and obtained leachates with $^{87}Sr/^{86}Sr$ values comparable to those of the formation waters (0.7102 - 0.7129). Precipitating diagenetic minerals, such as carbonate cements, would acquire these radiogenic $^{87}Sr/^{86}Sr$ formation water values. Similar results were shown by CHAUDHURI *et al.* (1987) for a Kansas shale, where an acid leachate with an $^{87}Sr/^{86}Sr$ ratio of 0.7140 was produced from a whole rock with an $^{87}Sr/^{86}Sr$ ratio of 0.7951.

In this study, gentle leaching of authigenic carbonates from various formations was necessary because these phases were often too small to be physically extracted. However, only sandstone samples with abundant (>20%) carbonate were analyzed. McNUTT *et al.*, (1987b) and CLAUER *et al.*, (1989) have used similar techniques with dilute acetic acid and 1N HCl, respectively on crystalline rocks that do not contain clay minerals and report the silicate phases to be unaffected. Thus, the Sr in acid leachates is likely from the Sr in exchangeable sites in clay minerals. However, the Sr concentration in these sites relative to that in carbonate phases is relatively small, particularly if carbonate comprises >20% of the rock (CLAUER, 1981; FAURE, 1986). Consistency of the data obtained for specific sandstone formations of the Alberta Basin suggests that exchangeable Sr from clay minerals is not affecting the carbonate $^{87}Sr/^{86}Sr$ ratios, as the modal clay mineralogy within a specific formation varies from sample to sample, but the $^{87}Sr/^{86}Sr$ ratio of the carbonate phase within the formation is relatively constant. It is noted in Table 2.1, where chemical leaching was used for shale lithologies or where the leached carbonate constituted a small percentage of the whole rock sample. The first situation yields variable $^{87}Sr/^{86}Sr$ values for the carbonate cement, all of which are more radiogenic than other carbonate samples extracted from sandstones within the same formation. Moreover, shale extracted carbonates have the highest $^{87}Sr/^{86}Sr$ ratios compared to any other diagenetic carbonates from the entire basin. In the second situation where leached carbonate constituted a small percentage of the whole rock, $^{87}Sr/^{86}Sr$ ratios were also high, but these samples have almost no clay component and exhibit good intra-formational consistency. Therefore, these values are likely representative of the porewaters from which they precipitated.

Figure 2.9 illustrates the $^{87}Sr/^{86}Sr$ results from the carbonate whole rocks and authigenic cements in the Alberta Basin, as a function of the age of the formations. The seawater curve of BURKE *et al.* (1982) is provided as a reference for (1) the original seawater values for the marine carbonates, or (2) the original porewater composition for marine clastic rocks at the time of deposition. During the Phanerozoic the isotopic composition of Sr in the oceans changed with time. However, throughout the world's oceans at any given time, the isotopic composition and concentration of Sr remained uniform (VEIZER and COMPSTON, 1974) because of the: (1) long residence time of Sr (~5 x 10^6 years); (2) rapid mixing in oceans (10^3 years); and (3) high concentration of Sr in the oceans (7676 ± 68 µg/kg; BRASS and TUREKIAN, 1974) compared to average river water (68.5 µg/l). Furthermore, it has been found that Sr in relatively isolated environments such as Hudson Bay (FAURE *et al.*, 1967) or the inland sea during Cretaceous time (WHITTAKER *et al.*, 1987) are isotopically indistinguishable from the major oceans for a specific time period. Thus, deviation of $^{87}Sr/^{86}Sr$ ratios from seawater values in limestone/dolostone rocks and carbonate cements from clastic formations deposited in seawater indicates changes in porewater chemistry that occurred during diagenesis.

Most of the carbonate cement or whole rock dolostones/limestone $^{87}Sr/^{86}Sr$ values are greater than that of seawater for their respective time periods. Furthermore, some of these values are greater than those of seawater for all Phanerozoic time, refuting the possibility that these porewaters with high $^{87}Sr/^{86}Sr$ ratios may be solely a result of fluid migration from reservoirs with high $^{87}Sr/^{86}Sr$ seawater values (i.e., Cambrian) to those with low values (i.e., Jurassic). Instead, water/rock interaction and diagenesis is also strongly indicated. However, none of the $^{87}Sr/^{86}Sr$ ratios are particularly high, when compared to those reported for other limestones, such as in the Bindley Field (0.72195-0.72300), central Kansas (CHAUDHURI, 1987). Samples with $^{87}Sr/^{86}Sr$ ratios that plot directly on or within error of the BURKE *et al.* (1982) seawater curve are a Cambrian calcite cement, Devonian dolostones of the Cooking Lake and Leduc Formations, limestones of the Beaverhill Lake Formation, and some Cretaceous calcite cements from the Viking Formation.

The Cambrian calcite is a poikilotopic cement that was physically extracted and yielded an $^{87}Sr/^{86}Sr$ value of 0.7094, which is close to the Cambrian seawater value at the time of deposition. Acid-leached Cambrian carbonate samples from shales give $^{87}Sr/^{86}Sr$ values of 0.7436 to 0.7492; higher values are obtained for acid leached samples from the basal sandstones (0.7492 to 0.7504). The carbonates leached from the Cambrian sandstones were extracted from almost pure quartz arenites, that are lithified by quartz cements and contain little to no detectable clay or potential Rb-high, radiogenic $^{87}Sr/^{86}Sr$ sources. However, these sandstones are located between the Precambrian basement and Cambrian shales, both of which have significantly high $^{87}Sr/^{86}Sr$ ratios.

The $^{87}Sr/^{86}Sr$ values for the Devonian Cooking Lake and Leduc Formations (0.7082 to 0.7083) and for a drilled out calcite from the Beaverhill Lake Formation

(0.7081) are within the error of the BURKE *et al.* (1982) seawater curve. The former two formations are composed of dolomite; however, dolomitization has not seemingly affected the Sr isotopic compositions. The Beaverhill Lake Formation contains pristine diagenetic calcite which plots on the seawater curve; however, the nondiagenetic fraction, which contains a trace of quartz/silt (illite dominated) does not plot on the curve. Similarly, the Devonian Elk Point Group, although texturally well preserved, has $^{87}Sr/^{86}Sr$ values higher than seawater for the time of precipitation. The higher values may be due to the small content of quartz/silt (illite dominated) in the matrix of the Elk Point Group, or it may be a result of interaction with the evaporite at its base. These deposits contain minerals with a significant amount of Rb and thus a radiogenic $^{87}Sr/^{86}Sr$ signature. The Nisku Formation has $^{87}Sr/^{86}Sr$ ratios (avg. 0.70871) higher than the seawater curve, but the lower end of the range of Nisku values intersects the seawater curve within error. The Wabamun Formation is characterized by two distinct groups of $^{87}Sr/^{86}Sr$ ratios (0.70857-0.70902; 0.70937-0.70977), both of which are higher than the seawater curve, and higher than any other Devonian carbonates.

The Mississippian carbonates are slightly more radiogenic (avg. 0.70854) than the seawater curve values at the time of precipitation; Jurassic carbonates are even more so considering the low $^{87}Sr/^{86}Sr$ ratios of seawater during Jurassic time.

A trend of decreasing $^{87}Sr/^{86}Sr$ values with increasing stratigraphic age is established in the Cretaceous carbonate cements. The Basal Quartz Formation has the highest values (0.7082-0.7107), with authigenic carbonates of the Viking and Belly River exhibiting pronounced decreases (0.70832-0.70747, 0.70697-0.70564, respectively) in $^{87}Sr/^{86}Sr$ ratios. Surprisingly, the $^{87}Sr/^{86}Sr$ ratios for the Belly River Formation carbonates are less radiogenic than seawater values for that time period. This is unusual because minerals comprising a sedimentary system contain variable Rb/Sr ratios and generally any diagenetic reactions that occur subsequent to deposition serve to increase the $^{87}Sr/^{86}Sr$ ratios in porewater and ensuing authigenic phases (VEIZER and COMPSTON, 1974).

The $^{87}Sr/^{86}Sr$ ratios of the various diagenetic phases within a specific formation, particularly in the Belly River and Viking Formations, are similar. For example, although the stable isotope values for ankerite, siderite, calcite and dolomite in the Viking Formation are significantly different (>10‰ variation in $\delta^{18}O$ in some situations), the $^{87}Sr/^{86}Sr$ ratios of these phases are extremely similar (Table 2.1), regardless of where the phases precipitated in the paragenetic sequence. Furthermore, not only are the intra-formational $^{87}Sr/^{86}Sr$ values similar, but the range in inter-formational $^{87}Sr/^{86}Sr$ ratios is not significantly large (0.7056 to 0.7107) for Devonian through Cretaceous units when the potential sources of Rb, hence radiogenic $^{87}Sr/^{86}Sr$ ratios, such as illite and K-feldspar and the span of time represented by these units are taken into account. Generally, more radiogenic values characterize authigenic phases and porewaters in other sedimentary basins (STUEBER *et al.*, 1987; CHAUDHURI *et al.*, 1987). The largest range in $^{87}Sr/^{86}Sr$ values of the formation carbonates between stratigraphic units, is that between the Viking Formation and the Upper Cretaceous Belly River Formation, with the exception of the shale rich Cambrian unit.

Whole rock $^{87}Sr/^{86}Sr$ ratios for shale formations situated between limestone/dolostone units or carbonate rich sandstones were determined in order to delineate potential sources of radiogenic $^{87}Sr/^{86}Sr$ to the porewaters and subsequent cements, and to further deduce the significance of intraformational or cross-formational fluid/mass movement. Most of the Cretaceous whole rock $^{87}Sr/^{86}Sr$ values are low compared to clastic rocks of other sedimentary basins (STUEBER *et al.*, 1987; McNUTT *et al.*, 1987; CHAUDHURI, 1987). For example, Lea Park shale samples have $^{87}Sr/^{86}Sr$ ratios of 0.7074. Shales from the Cardium Formation have higher, but still relatively low $^{87}Sr/^{86}Sr$ values (0.7184 to 0.7198). Whole rock values from the Basal Quartz Formation are highly variable and exhibit the highest values in the Cretaceous formations (0.7117 - 0.7219).

Considering the leachate values (0.7102-0.7129) obtained in STUEBER *et al.'s* (1987) leaching experiments of whole rock shales with $^{87}Sr/^{86}Sr$ values of 0.7279 - 0.7547, the Cretaceous shales are likely not significant contributers of radiogenic Sr to reservoir pore fluids. The highest $^{87}Sr/^{86}Sr$ value obtained for the Alberta Basin Cretaceous shales is 0.7212, much less than those for the New Albany shale in the study of STUEBER *et al.* (1987). By analogy, the leachate value or contributions to the formation waters must also be much less for the Alberta Basin Cretaceous waters. Radiogenic whole rock shale values are only characteristic of formations stratigraphically lower than the Mississippian formations in the study area. Devonian shales exhibit much higher $^{87}Sr/^{86}Sr$ values, although the data are highly variable (0.7087 - 0.7391), likely due to variable carbonate content in the shales. The Cambrian whole rock $^{87}Sr/^{86}Sr$ values (0.7436 - 0.7856) and the Precambrian whole rock $^{87}Sr/^{86}Sr$ values (1.1452 - 1.2487) are variable, but potentially significant sources of radiogenic Sr.

DISCUSSION

Meteoric diagenesis in an open system commonly results in a lowering of $\delta^{18}O$ and $\delta^{13}C$ values in marine carbonate rocks (GROSS, 1964;, LAND, 1970; ALLAN and MATTHEWS, 1977, 1982; O'NEIL, 1987). However, significant changes in the isotopic composition of diagenetic phases occurs only during reactions involving dissolution and reprecipitation (YEH and SAVIN, 1976, 1977; ESLINGER and YEH, 1981; reviews by O'NEIL, 1987; LONGSTAFFE, 1987). The shift toward lower stable isotopic values occurs because recrystallization takes place in waters depleted in ^{18}O relative to seawater (eg. meteoric water) and/or at elevated temperatures. Both of these processes are important in the Western Canada Sedimentary Basin because: (1) temperatures were once greater in most lithologic units because of increased burial depths in the Eocene, following the Laramide Orogeny when downwarping and infilling were occurring in the western Plains; and (2) meteoric waters were introduced by gravity-driven flow that flushed through the basin subsequent to the second pulse of the Laramide Orogeny. Hence, the stable isotopic composition of authigenic phases may indicate the relative importance of these processes to diagenesis in the Alberta Basin. Furthermore, the $^{87}Sr/^{86}Sr$ ratios of whole rocks and diagenetic carbonates may trace the origins of fluids responsible for the diagenesis of rocks and indicate characteristics of meteoric water dominated diagenesis.

Carbonate Cements in Cambrian Clastic Rocks

Carbonate phases are not common and have an irregular distribution in the Cambrian units within the study area. The micro-drilled poikilotopic calcite from a silty sandstone has a stable isotopic composition ($\delta^{18}O$=+23.5‰; $\delta^{13}C$=-1.6‰) indicative of relatively early, low temperature formation that has not been substantially affected by meteoric waters. The $^{87}Sr/^{86}Sr$ (0.7094) ratio of the calcite is within error of the $^{87}Sr/^{86}Sr$ value of seawater at the time of Cambrian deposition, further suggesting this phase has not been significantly altered. However, as already mentioned, MACDONALD (1987) reported a distinctly different stabe isotopic value for Cambrian calcite ($\delta^{18}O$=+12.2‰; $\delta^{13}C$=-4.1) from the basal sands. It is evident that the two calcite phases precipitated at different times in the paragenetic sequence for the Cambrian units, even when consideration is given to the distance separating the two units. To investigate these variations or bracket changes in porewater $\delta^{18}O$ and/or temperature, the relationship between the measured $\delta^{18}O$ of each diagenetic carbonate and the possible combinations of water $\delta^{18}O_{(SMOW)}$ and temperature are shown in Fig. 2.10, following CLAYTON *et al.* (1966) and LONGSTAFFE (1986). At present, conditions in the Cambrian provide an endpoint for the porewater evolution. The few available $\delta^{18}O$ values for formation waters average -2.6‰ (HITCHON and FRIEDMAN, 1969). Present day calculated Cambrian reservoir temperatures are ~110 to 120°C using an average surface temperature of 5°C (HITCHON, 1984) and a geothermal gradient of 40°C/km. During maximum burial following the Laramide Orogeny, the formation temperatures would have been in the range of 160 to 180°C for the samples in this study and 150 to 170°C for the samples in MACDONALD's (1987) study, as calculated using the data of BEAUMONT *et al.* (1985) and assuming a surface temperature of +16°C in the Eocene (PIEL, 1971).

Although the Lower Cambrian sediments were deposited originally in a nonmarine, brackish setting, they were reworked by the Sauk transgression prior to lithification. Hence, the initial $\delta^{18}O$ composition of the water was probably about 0‰ (±1‰), the current value for standard mean ocean water. Alternatively, the water may have been more ^{18}O depleted given the possible early contributions by meteoric waters or potential interaction with entrapped bottom waters (SAVIN and YEH, 1981). Early diagenetic processes generally cause a slight increase in porewater $\delta^{18}O$, as shown by the porewater evolution curve. Petrographic analysis of the Cambrian calcite from this study indicate early diagenetic formation and the $\delta^{18}O$ value of this calcite is compatible with such an origin (Fig. 2.10). Although recharge of meteoric fluids during a large scale regional exposure associated with an unconformity sometime after the Devonian has been suggested (CARPENTER and LOHMANN, 1989), it is unlikely that the early Cambrian calcite phase formed as a result of this event. The Middle Devonian evaporite sequence has been shown to be relatively closed to cross-formational fluid flow between Cambrian hosted fluids and those hosted in stratigraphically higher formations (CONNOLLY *et al.*, 1990b). Even if meteoric recharge had been influential to Cambrian porewaters sometime from Late Devonian to pre-Laramide time the reservoir temperatures and porewater isotopic compositions in the Cambrian would not likely have precipitated a calcite with an isotopic composition of +23.5‰. The $\delta^{13}C$ value of the early calcite (-1.6‰) is within the range typical for marine carbonates derived from CO_2 of inorganic origin (LAND, 1980; POPP *et al.*, 1986). Furthermore, the $^{87}Sr/^{86}Sr$ ratio is similar to that of seawater in the Cambrian. This value would likely have been much higher if the calcite formed later, such as in Devonian time, when Rb-rich mineral phases in the overlying Cambrian shales would likely have contributed ^{87}Sr to the porewaters increasing their $^{87}Sr/^{86}Sr$ ratios.

The ankerite and ankerite/dolomite phases formed relatively late in the paragenetic sequence, subsequent to quartz overgrowths and are found replacing detrital feldspar. With increasing burial depth, the $\delta^{18}O$ of the dominantly marine porewater can be expected to increase due to isotopic exchange with phases like calcite, dissolution of rock fragments and/or contributions from dewatering of clay minerals (CLAYTON *et al.*, 1966; HITCHON and FRIEDMAN, 1969; SUCHECKI and LAND, 1983). Furthermore, temperatures would be increasing toward the maximum value reached (160 to 180°C) for the ankerite containing reservoirs during burial diagenesis after the Laramide Orogeny. At these temperatures, it is possible for porewater $\delta^{18}O$ values to be enriched up to +4 to +5‰, but likely not higher due to the buffering reactions of clay minerals (SUCHECKI and LAND, 1983) in the Cambrian shales. Thus, the oxygen isotope requirements of the porewaters for ankerite formation with a $\delta^{18}O$ value of +19.1‰ may be satisfied at maximum burial (Fig. 2.10). At no other time does the ankerite curve intersect reasonable $\delta^{18}O_{H2O}‰_{(SMOW)}$ values. Even at present day calculated reservoir temperatures of 110 to 120°C, $\delta^{18}O$ values of greater than 0‰ for the porewaters, not -2.6‰, would be required in order for the ankerite (+19.1) curve to intersect the porewater evolution curve. In addition, it is possible that the porewaters may have once had an even more negative $\delta^{18}O$ composition than illustrated, immediately after the Laramide Orogeny; but the $\delta^{18}O$ composition of the porewaters may have increased since then because of dissipation of the regional flow system of gravity-driven meteoric waters (GARVEN, 1989), and subsequent burial diagenetic exchange reactions in the rock reservoir. This scenario would make ankerite formation after meteoric recharge even less likely.

$^{87}Sr/^{86}Sr$ ratios and mineralogy provide further evidence that ankerite formed at maximum burial and temperatures. Mineral reactions occur much more readily at higher temperatures and paragenetically late ankerite cement often forms at relatively higher temperatures (120 to 160°C) in a sedimentary basin (BOLES, 1978). In addition, the $^{87}Sr/^{86}Sr$ ratios of the ankerite and ankerite/dolomite phases are relatively high (0.7492-0.7504) and similar to the whole rock $^{87}Sr/^{86}Sr$ values of the Cambrian shales and sandstones, even though the carbonates were leached out of very clean quartz arenites that contained no to trace feldspar or mica in the quartz cemented lithology (i.e., no sample contamination). At maximum temperatures mineral reactions and ion exchange prevail; however, a significant amount of time would be required even for minerals with high Rb/Sr ratios to decay and modify the Cambrian porewater values from an original seawater value (0.709) to the authigenic carbonate cement value (0.750). The high $^{87}Sr/^{86}Sr$ ratios of the ankerite, ankerite/dolomite and their similarity to present day shale values suggests that these carbonate phases formed relatively recently with respect to geologic time, such as during maximum burial after the Laramide Orogeny, prior to the major influx of meteoric waters. The high $^{87}Sr/^{86}Sr$ ratios also imply that at this time the porewaters were near equilibrium with the rock column, possibly as a result of ion exchange reactions in the overlying shale and mass movement into the underlying sandstones. The Precambrian basement may also have been a contributing source. Regardless of which minerals/stratigraphic unit provided a source of $^{87}Sr/^{86}Sr$ to the porewaters and subsequent ankerite and ankerite/dolomite, isotopic ratios of the authigenic phases do suggest that these carbonates were formed prior to meteoric flushing in a relatively high temperature regime.

The $\delta^{18}O$ value of the calcite phase reported by MACDONALD (1987) cannot be explained unless significant lowering in porewater $\delta^{18}O$ occurred after maximum burial of the unit (Fig. 2.10). This change could only be accomplished by a pervasive influx of low $\delta^{18}O$ meteoric water, which is consistent with basin history. Prior to the Laramide Orogeny, it is doubtful that a hydraulic head greater than that generated by the present Canadian Cordillera ever existed. Maximum burial corresponded to maximum relief, which led to a major regional influx of fresh water ($\delta^{18}O \sim -15‰$; TAYLOR, 1974) into the unit; a net cooling effect resulting from the recharge of cold meteoric water occurred. This sequence of events is reflected in the deviation of the trend of the porewater curve on Fig. 2.10. The oxygen isotope results for the lower $\delta^{18}O$ calcite overlap the lower part of the curve and require an influx of meteoric fluid in order to intersect a porewater curve in a temperature regime compatible with current reservoir conditions. The $\delta^{13}C$ value is slightly more negative than the early calcite, but is still indicative of a dominantly inorganic reservoir. Meteoric water may have delivered some CO_2 generated from maturation of organic matter, but this was still dominated by inorganic marine carbonate.

Elk Point - Nisku Carbonates

Examination of the stable isotope data for the Devonian carbonates, with the exception of the Wabamun Group, illustrates a pronounced similarity between the diagenetic phases drilled out of the carbonate sequence and the whole rock ground mass. Such synonymity indicates neither temperature increase or meteoric water had significant influence on the diagenesis of these rocks.

During diagenesis, carbonates undergo stabilization from aragonite, high Mg-calcite and low Mg-calcite to diagenetic low-Mg calcite, usually in discrete micro-environments (O'NEIL, 1987). When this stabilization occurs early, the carbonates generally have well preserved textural components and $\delta^{18}O$ values similar to seawater carbonates. Conversely, later diagenesis/stabilization is usually characterized by texturally altered carbonates that have lowered $\delta^{18}O$ values (POPP *et al.*, 1986; CARPENTER and LOHMANN, 1989). Once stabilized, carbonates normally do not undergo perpetual dissolution/precipitation with younger diagenetic fluids, but maintain isotopic integrity (GIVEN and LOHMANN, 1985).

The Elk Point, Beaverhill Lake, Cooking Lake, Leduc and Nisku stratigraphic units in the Alberta Basin show little to no textural alteration within the study area. However, all of the rocks but the Beaverhill Lake are dolostones and it is unlikely that they originally precipitated as these phases. Recrystallization reactions must have occurred, allowing for re-equilibration of the carbonates with basin waters. POPP *et al.* (1986) suggest that precipitation of secondary calcite depleted in ^{18}O by less than 3‰ relative to original calcite, indicates that contemporaneous seawater was an important component of the diagenetic fluid. Thus, early marine diagenesis should result in little, if any, oxygen isotope shift in carbonate sediments. CARPENTER and LOHMANN (1989) have reported $\delta^{18}O$ and $\delta^{13}C$ values of +25.7‰ and +2.0‰, respectively for unaltered calcite in the Golden Spike reefs of the Leduc Formation, Alberta, and POPP *et al.* (1986) report values of +27.1‰ and +2.0‰, respectively for unaltered Middle Devonian limestones in eastern North America. The values in both these studies are reasonably close to those reported here for dolomite phases, even when consideration is given to the different oxygen fractionation effects between calcite and dolomite (2 to 4‰, based on Holocene calcite and dolomite (LAND, 1980; McKENZIE, 1984)). Furthermore, there is no correlation between $\delta^{18}O$ and $\delta^{13}C$ values in these Devonian units. As a result, these isotopic values would suggest that the temperature and isotopic composition of the waters during recrystallization were likely similar to the original formation waters, implying early dolomitization/marine diagenesis for the Elk Point, Beaverhill Lake, Cooking Lake, Leduc and Nisku stratigraphic units. The alternative is that diagenesis occurred at a low water/rock ratio, in which the oxygen isotopic composition of the fluid was buffered by dissolution/reprecipitation of the carbonates. Given the permeability of these Devonian carbonates and the observed dissolution zones (CARPENTER and LOHMANN, 1989), this latter suggestion is unlikely.

$\delta^{13}C$ values between -2 and +3‰ are typical for Phanerozoic marine limestones (KEITH and WEBER, 1964; VEIZER and HOEFS, 1976; VEIZER *et al.* 1982; POPP *et al.*, 1986). With the exception of the Wabamun Group, the $\delta^{13}C$ values for the Devonian limestones fall in this range and there is no indication that ^{13}C depleted biogenic carbon was an important source for the diagenetic carbonates of these units. The $\delta^{13}C$ values are most likely a result of redistributed marine carbonate.

The $^{87}Sr/^{86}Sr$ ratios of the Devonian carbonates further indicate these units experienced early dia[illegible] diagenetic fluids are, in general, variously enriched in ^{87}Sr (CLAUER *et al.*, [illegible] contrast, during early diagenesis, porewaters have nearly the same radiogenic isotopic composition as associated carbonate sediments (HOFMANN *et al.*, 1972). The Devonian (Beaverhill Lake - Nisku) carbonate $^{87}Sr/^{86}Sr$ ratios are similar to corresponding seawater values on the BURKE *et al.* (1982) seawater curve, with at least part of the range in carbonate $^{87}Sr/^{86}Sr$ ratios falling on the curve (Fig. 2.8). Thus, Sr coprecipitation with calcium carbonate occurred in seawater or porewater relatively unmodified from its original seawater ratios. Substantial meteoric diagenesis is not indicated.

The Devonian Beaverhill Lake and Elk Point units are the exceptions to the other Devonian units in that they have $^{87}Sr/^{86}Sr$ ratios which are more radiogenic than the corresponding seawater curve values, although their stable isotope values suggest minimal meteoric diagenesis. As mentioned earlier, the nondiagenetic component of the Beaverhill Lake and the Elk Point both contain a minor proportion of quartz/silt (illite) in the matrix of the carbonate. This minor component may be responsible for the observed increase in the $^{87}Sr/^{86}Sr$ values, but it would not alter the stable isotope values. In addition, evaporites form a large proportion of the base of the Elk Point Group, and these minerals may incorporate a substantial amount of Rb into their structure, resulting in increased $^{87}Sr/^{86}Sr$ ratios. However, these evaporites are impermeable and no evidence of their dissolution or interaction with Devonian hosted pore fluids has been found (SPENCER, 1987; CONNOLLY *et al.*, 1990a, 1990b). As a result, the Middle Devonian evaporites are not likely responsible for the elevated $^{87}Sr/^{86}Sr$ ratios relative to seawater at the time of deposition, observed in the Elk Point Group.

Wabamun - Jurassic Carbonates

Isotopic data for the Wabamun Group and stratigraphically younger carbonate formations up to the basal Cretaceous unconformity indicate a pronounced meteoric influence during diagenesis. Lower $\delta^{18}O$ values relative to the Elk Point - Nisku/platform carbonates characterize the overall whole rock data. Moreover, diagenetic carbonates from the Wabamun - Jurassic units have much lower stable isotopic values than associated whole rock material (i.e., Wabamun $\delta^{18}O = +16.0‰$; $\delta^{13}C = -6.1‰$). The lower $\delta^{18}O$ and $\delta^{13}C$ values may result from burial and associated temperature increase, or the introduction of an ^{18}O depleted meteoric fluid during a large scale regional exposure associated with an unconformity sometime after the Devonian or possibly associated with the Laramide meteoric influx. The correlation of $\delta^{18}O$ and $\delta^{13}C$ whole rock values of the Wabamun to Rock Creek carbonate units (Fig. 2.7 and 2.8) suggests a strong meteoric component is responsible, rather than a temperature increase. Although temperatures were significantly greater in these units during maximum burial subsequent to Laramide tectonism, increased temperatures fail to explain: (1) the correlation of $\delta^{18}O$ and $\delta^{13}C$ in these formations (Fig. 2.8) that is not observed in the stratigraphically lower formations; and (2) the pronounced variation of stable isotope values between diagenetic and whole rock values, even within one formation (i.e. Wabamun). In addition, at all times in the Alberta Basin history, the temperatures in the Wabamun and stratigraphically younger carbonate units would have been similar to or less than those in the Nisku and stratigraphically older formations where no lowering in isotopic values was observed. The $^{87}Sr/^{86}Sr$ ratios support the suggestion that Wabamun to Jurassic units were affected by relatively later, possibly meteoric diagenesis, by exhibiting converse trends to those established for the stable isotope data (Fig. 2.8). Due to Rb decay, late diagenetic fluids generally have more radiogenic $^{87}Sr/^{86}Sr$ ratios than original pore fluids. Therefore, most diagenetic reactions result in a decrease of stable isotope values and a corresponding increase in $^{87}Sr/^{86}Sr$ ratios.

The whole rock $\delta^{13}C$ values of the Wabamun through Jurassic rocks are lower than the Elk Point through Nisku Devonian units; however they may still be interpreted as being derived from a predominantly inorganic carbonate reservoir. The contribution of low ^{13}C CO_2, such as derived by thermal decarboxylation of organic matter, seems to have been relatively unimportant. In contrast, the micro-drilled Wabamun sample that appears to have precipitated in waters with a significant meteoric component, has a $\delta^{13}C$ value of -6.1‰, which requires the involvement of some organically derived CO_2. Maturation of organic matter likely released CO_2 into shale porewaters which was subsequently expelled into coarser grained units and carried by meteoric fluids.

Carbonate Cements in Cretaceous Clastic Rocks

The $\delta^{18}O$ values of the relatively late carbonate cements within the Cretaceous clastic sequence cannot be explained unless significant lowering of porewater $\delta^{18}O$ occurred, in a manner analogous to that shown for the Cambrian. The values from the shales are higher than those of the sandstones, which likely results from greater closed system behavior, less penetration of meteoric waters and increased water/rock reaction. There is an increase in $\delta^{18}O$ values of authigenic calcites in sandstones with increased stratigraphic age of the Cretaceous formations, which is accompanied by a narrowing of the gap between calcite values from shales and sandstone within a single formation. However, all formations still require a lowering of porewater $\delta^{18}O$ values to explain the $\delta^{18}O$ values of the authigenic carbonates. A similar relationship between Viking sandstones and Upper Cretaceous sandstones from the same locality was observed by LONGSTAFFE and AYALON (1987). They commented on the ^{18}O-rich nature (by 3 to 5‰) of both early and late diagenetic carbonate minerals from the Viking Formation when compared to similar phases in the Belly River Formation. Figure 2.4 illustrates this relationship but also shows that no further significant increase occurs in sandstone lithologies stratigraphically lower than the Viking Formation. The possible reasons for the distribution of $\delta^{18}O$ values in the Cretaceous may include (LONGSTAFFE and AYALON, 1987): (1) the starting porewater composition in the Viking and stratigraphically Lower Cretaceous units was dominantly seawater, whereas the Belly River was characterized by brackish to fresh water (IWUAGWU and LERBEKMO, 1982, 1984); (2) a greater degree of low ^{18}O meteoric water infiltrated and mixed with the waters of the Upper Cretaceous than mixed with the waters of the Lower Cretaceous; and/or (3) meteoric water which penetrated the Lower Cretaceous had a greater opportunity for water/rock interaction and subsequent ^{18}O enrichment than did fresh water entering stratigraphically higher units. It is of consequence that $\delta^{18}O$ values recorded for calcite of the basal Cambrian sandstone (MACDONALD, 1987) are comparable to values in the basal Belly River sandstones. Cambrian sandstones were originally deposited in a similar shoreline environment and likely were exposed to brackish waters. Furthermore, the Cambrian basal sands are permeable and may have directed a large proportion of low ^{18}O meteoric water. An isotopic study (radiogenic and stable) of the authigenic clay and detrital phases in the Alberta Basin may lead to increased understanding of these interdependent elements (Chapter 4).

The $^{87}Sr/^{86}Sr$ ratios characterizing the authigenic cements in the Cretaceous formations range from 0.7107 in the stratigraphically lowest unit to 0.7056 in the stratigraphically highest. The $^{87}Sr/^{86}Sr$ values (0.7101-0.7119) for calcite/dolomite or calcite/ankerite from the Basal Quartz Formation suggest that Sr dissolved in porewaters must have come from detrital source material; however, a pure calcite phase was not isolated and this radiogenic signature may be a result of the ankerite component in the calcite/ankerite mixtures. The relatively radiogenic ankerite/dolomites (0.7110-0.7112) have $\delta^{18}O$ values that indicate they formed during burial diagenesis, prior to the Laramide Orogeny and the influx of cold meteoric waters, when formation waters and diagenetic minerals in the reservoir rock were close to equilibrium. The $^{87}Sr/^{86}Sr$ values of both the ankerite/dolomite and the calcite are higher in the Basal Quartz Formation than in any other Cretaceous formations, independent of whether they are early or late in the paragenesis. It is likely that the relatively high $^{87}Sr/^{86}Sr$ values for the carbonate phases in this formation are partly a result of the lithology, which consists of channel sands surrounded by shale, resulting in less continuous permeability and increased water/rock interaction. In addition, if ankerite and dolomite/ankerite formed during burial diagenesis at higher temperatures, a higher degree of equilibrium between the whole rock and porewaters may have been attained.

The low $^{87}Sr/^{86}Sr$ values of carbonate cements in the Viking and particularly the Belly River Formations, corresponds well with the increased plagioclase (albite/oligoclase) and volcanic rock fragment content of these formations. Plagioclase, similar to carbonate, has very low Rb/Sr ratios; the Rb/Sr ratio of volcanic ash depends on its composition but may be less than 0.1 in basalt (STANLEY and FAURE, 1979). Therefore, these phases contribute Sr with low and time-invariant $^{87}Sr/^{86}Sr$ ratios to the porewaters. Furthermore, plagioclase and volcanic rock fragments in the Viking and Belly River Formations are highly altered, suggesting these phases likely contributed a significant proportion of their Sr to the pore fluids. Experimental data on feldspar hydrolysis (AAGARD and HELGESON, 1982; HELGESON and MURPHY, 1983, HELGESON *et al.*, 1984) also suggest an initial low temperature stage of extremely rapid exchange of cation species with the water, indicating rapid equilibration with Sr isotopes, with this equilibration being achieved more rapidly in an open system (HELGESON and MURPHY, 1983). Therefore, it would appear that plagioclase was/is controlling ^{87}Sr/^{86}Sr ratios of the Viking and Belly River carbonates.

The effect of local plagioclase dissolution on the strontium chemistry of porewater has been modelled by SCHULTZ *et al.* (1989) using two component mixing equations (FAURE, 1986). The results of SCHULTZ *et al.* (1989) are shown in Fig. 2.11, whereby a plagioclase of oligoclase/andesine composition, with an ^{87}Sr/^{86}Sr ratio of 0.7069 and 700 ppm total Sr, is progressively dissolved into porewater which fills 20% of the porosity in the rock and initially contains an estimated 25 ppm Sr and has an ^{87}Sr/^{86}Sr ratio of 0.7082. This situation is analogous to that of the Belly River and Viking Formations, which contain plagioclase of this oligoclase/andesine composition and are presently dominated by meteoric waters (CONNOLLY *et al.*, 1990b). Figure 2.11 shows the rapid change in porewater ^{87}Sr/^{86}Sr relative to the initial porewater composition, with very little dissolution of the plagioclase phase. If this leaching occurred early during feldspar hydrolysis, it would further explain the similarity in ^{87}Sr/^{86}Sr of various carbonate phases in the Belly River and Viking Formations. Regardless of where they occur in the paragenetic sequence, all of the authigenic carbonate phases would record the ^{87}Sr/^{86}Sr values contributed to the porewaters by plagioclase because of its rapid alteration.

$^{87}Sr/^{86}Sr$ Water/Rock Equilibration

In order to examine the degree of water/rock interaction in the Alberta Basin, the range of $^{87}Sr/^{86}Sr$ values for both the porewater (CONNOLLY *et al.*, 1990) and corresponding reservoir authigenic/allogenic phases have been listed in Table 2.3. By examining both porewater and rock systems, a comparison can be made between the existing system and the evolution of past water systems recorded in the $^{87}Sr/^{86}Sr$ ratios of authigenic minerals. A strong overlap between present day whole rock $^{87}Sr/^{86}Sr$ values and brine $^{87}Sr/^{86}Sr$ values would indicate that Sr exchange between the fluid and rock systems had achieved equilibrium. Such a scenario has been reported by McNUTT (1987a) for the brines from Precambrian age rocks in Canada. Conversely, a strong divergence of water and rock $^{87}Sr/^{86}Sr$ values would indicate disequilibrium, such as would occur during a relatively recent influx of meteoric water. Such a situation often characterizes sedimentary systems, which tend to be more transient and unstable than those of basement rocks. The data in Table 2.3 corroborate this observation. In general, most of the $^{87}Sr/^{86}Sr$ ratios for the formation waters are more radiogenic than the carbonate constituents of the reservoir in which they are residing, with the exception of the Leduc Formation and some of the stratigraphically younger Cretaceous units (i.e. Viking and Belly River Formations).

Occurrence of water/rock equilibration in the Leduc Formation is likely a result of this formation's unique hydrologic regime. Different Devonian reefal facies (platform, pinnacle) are characterized by varying fluid movement. Where water movement in platform reefs has a more dominant lateral component, similar to many of the formations in the Alberta Basin, porewater movement in pinnacle reefs is more restricted. Compacting shales drape the pinnacle reefs, directing pore fluids upward through the reef. This results in slow vertical brine movement and permeability zoning, which is more conducive to water/rock equilibration, as the influx of *outside* porewaters is restricted.

Some of the stratigraphically higher Cretaceous formations have equivalent $^{87}Sr/^{86}Sr$ ratios for authigenic carbonates and corresponding porewaters for reasons described earlier. Plagioclase is a significant component of these reservoirs and it exhibits alteration, with this dissolution likely occurring rapidly in a low temperature environment. Because of its high Sr concentration, the $^{87}Sr/^{86}Sr$ ratio of plagioclase tends to dominate the fluid system relatively quickly, particularly in reservoirs dominated by acidic meteoric waters. Hence, equilibration between the authigenic carbonates and reservoir waters in Belly River and Viking Formations reflects rapid equilibration of the pore fluids with plagioclase.

The more radiogenic $^{87}Sr/^{86}Sr$ character of most of the pore fluids relative to their reservoir rocks indicate porewater interaction with minerals characterized by relatively high Rb/Sr ratios, which subsequently yield high $^{87}Sr/^{86}Sr$ ratios. Although sources of radiogenic ^{87}Sr are abundant in portions of Albera Basin lithologies, the acquisition of such Sr by formation waters depends on mineral transformation reactions and the water/rock interactions which may release it. Reactions which are a consequence of burial diagenesis and have been suggested as sources of radiogenic ^{87}Sr (STUEBER *et al.*, 1987) are the dissolution and albitization of detrital feldspar (LAND and MILLIKEN, 1981; BOLES, 1982; LAND, 1984) and the decomposition of mica (HOWER *et al.*, 1976). However, these phases were likely not significant sources of radiogenic ^{87}Sr to the porewaters hosted in Devonian and stratigraphically higher formations. Potassium feldspar and mica are not abundant constituents of the Devonian through Cretaceous units in the basin, other than locally, and local enrichment does not explain the scale over which the radiogenic fluid values occur. Thus, radiogenic ^{87}Sr was most likely acquired through interactions between formation waters and clays. Some of the Cretaceous whole rock shale values suggest that they could provide radiogenic $^{87}Sr/^{86}Sr$ to the porewaters as well, providing that closed system behavior was active allowing for the attainment of equilibrium between the water and shale phases of the Cretaceous. However, water/rock equilibrium in the Cretaceous formations has been shown to be highly unlikely, primarily as a result of Laramide tectonism. If the formation fluid leaching processes are responsible for these radiogenic formation fluid values (STUEBER *et al.*, 1987), the only lithologic units with whole rock $^{87}Sr/^{86}Sr$ ratios high enough to likely produce the resulting radiogenic fluid values (Table 2.3) are the Devonian and Cambrian shales. The Middle Devonian evaporites provide an impermeable zone; however, making the Cambrian shales an unlikely source, as cross-formational fluid flow between waters in Cambrian reservoirs and those in stratigraphically higher units has been prevented(CONNOLLY *et al.*, 1990a; 1990b). Hence, ion exchange reactions of formation fluids with clay minerals in the Devonian shale formations likely provides a significant component of radiogenic Sr to the porewaters.

One last possibility to be considered to explain the radiogenic Sr values of the formation waters is the enrichment of $^{87}Sr/^{86}Sr$ as a result of exclusion of Rb in the carbonate phases. Carbonates do not readily accept Rb into their mineral structure, resulting in an enrichment of this element in associated pore fluids and its subsequent incorporation into exchangeable sites in clay minerals. Radioactive decay of Rb to Sr and subsequent cation exchange with the porewaters would provide a source of radiogenic Sr. If this process is responsible for the increased water $^{87}Sr/^{86}Sr$ ratios over $^{87}Sr/^{86}Sr$ ratios in diagenetic phases, this would suggest that the mineral/water reactions are ongoing, equilibration has not been reached and that the carbonate phases precipitated earlier in the paragenetic sequence, when water $^{87}Sr/^{86}Sr$ ratios were lower. Furthermore, the radiogenic porewaters have not seemingly dominated the carbonate whole rock $^{87}Sr/^{86}Sr$ values, as is also shown by some Devonian authigenic carbonate cements (i.e. CC70D) which are enriched in $^{87}Sr/^{86}Sr$ (0.7132).

The relatively uniform range of water $^{87}Sr/^{86}Sr$ ratios in the Alberta Basin formation fluids suggests that either the radiogenic source material is uniformly distributed through the geological column, which is clearly not true as shown by Table 2.1, or there has been considerable cross-formational flow of subsurface water. Exceptions to this are the Leduc Formation hosted waters, which have already been discussed, and the Upper Cretaceous hosted waters. The slight variation towards the Upper Cretaceous may reflect an isolated system characterized by different formation fluid movement and/or formation specific mineralogy dominating the fluid system.

The relative similarity in $^{87}Sr/^{86}Sr$ ratios between detrital and authigenic and between early and late authigenic phases for Devonian through Cretaceous units suggests a relative consistency in fluid $^{87}Sr/^{86}Sr$ ratios over time. Even whole rock shale $^{87}Sr/^{86}Sr$ values stratigraphically higher than the Devonian are never greater than 0.7212. This may be a result of (1) marine carbonates having a significant influence in stratigraphically lower reservoirs, and (2) plagioclase feldspar, which has similar $^{87}Sr/^{86}Sr$ ratios and Sr concentrations to the carbonates, dominating the fluid chemistry of stratigraphically higher reservoirs. The combination of these two mineral phases dominating the fluid chemistry (Sr) in the Alberta Basin apparently causes the relatively low $^{87}Sr/^{86}Sr$ ratios basinwide.

CONCLUSIONS

Stable and radiogenic isotopes were determined for limestone/dolostone whole rocks, shale whole rocks and authigenic carbonate cements from a Precambrian to Upper Cretaceous stratigraphic assemblage comprising a vertical section in the Alberta Basin, Western Canada Sedimentary Basin. The Cambrian clastic sedimentary rocks contain carbonate phases with isotopic compositions that indicate a wide range of formation conditions: (1) early calcite with $\delta^{18}O = +23.5‰$ and $^{87}Sr/^{86}Sr$ ratios equivalent to Cambrian seawater (0.709); (2) ankerite formed during maximum burial with $\delta^{18}O$ values of +19.1‰ and $^{87}Sr/^{86}Sr$ values (0.749-0.750) distinctly close to whole rock Cambrian shale values; and (3) calcite formed late in the paragenetic sequence, subsequent to meteoric flushing with a $\delta^{18}O$ value of +12.1‰.

Isotopic data for most of the Devonian carbonate assemblage, with the exception of the uppermost unit (Wabamun Group) show little to no meteoric water influence. The stable isotope data for these units do not necessarily imply that meteoric waters did not infiltrate them, rather recrystallization/diagenetic stabilization reactions occurred early in these reservoirs, prior to meteoric infiltration. Wabamun through Jurassic carbonate units start to exhibit a significant meteoric component, particularly in their diagenetic phases. $\delta^{18}O$ and $\delta^{13}C$ isotopic values exhibit a linear correlation and are inversely correlated to $^{87}Sr/^{86}Sr$. The inverse trend with $^{87}Sr/^{86}Sr$ ratios reflects an increased meteoric component in the diagenetic carbonate, which caused a release of ^{87}Sr, from radioactive decay of ^{87}Rb decay, to the porewaters.

Most of the carbonate phases in the Cretaceous formations have stable isotope values that indicate crystallization from formation water containing a sizable fraction of meteoric water. Furthermore, $^{87}Sr/^{86}Sr$ ratios of these authigenic carbonates decrease with decreasing stratigraphic age in the section; values as low as 0.706 are reported. These low $^{87}Sr/^{86}Sr$ ratios are likely a result of plagioclase alteration contributing a significant amount of Sr with low $^{87}Sr/^{86}Sr$ ratios to the porewaters.

There is a disparity between the $^{87}Sr/^{86}Sr$ ratios of authigenic phases and the porewaters residing in corresponding reservoirs for most of the formations in the Alberta Basin, indicating a dynamic system that has not acquired equilibrium. Ion exchange reactions with clay minerals in Devonian shale lithologic units appear to be the predominant source of radiogenic Sr. However, carbonate reservoirs in the stratigraphically lower part of the section and plagioclase found in predominantly Upper Cretaceous reservoirs provide a significant sources of Sr with low $^{87}Sr/^{86}Sr$ ratios. These sedimentary units appear to maintain $^{87}Sr/^{86}Sr$ ratios in the basin at relatively low values for both porewaters and authigenic carbonate phases (<0.712).

REFERENCES

AAGARD P. and HELGESON H.C. (1982) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solution. I. Theoretical considerations. *Am. J. Sci.* 282, 237-285.

ALLAN J.R. and MATTHEWS R.K. (1977) Carbon and oxygen isotopes as diagenetic tools: Surface and subsurface data, Barbados, West Indies. *Geology* 5, 16-20.

ALLAN J.R. and MATTHEWS R.K. (1982) Isotope signatures associated with early meteoric diagenesis. *Sedimentol.* 29, 797-817.

ANDRICHUK J.M. (1958) Stratigraphy and facies analysis of Upper Devonian reefs in Leduc, Stettler, and Redwater area, Alberta. *Am. Assoc. Petrol. Geol. Bull.* 42, 1-93.

AYALON A. and LONGSTAFFE F.J. (1988) Oxygen isotope studies of diagenesis and pore-water evolution in the western Canada sedimentary basin: Evidence from Upper Cretaceous basal Belly River sandstone, Alberta. *J. Sediment. Petrol.* 58, 489-505.

BEAUMONT C. (1981) Foreland basins. *Geophys. J. Roy. Astron. Soc.* 65, 291-329.

BEAUMONT C., BOUTILIER R., MACKENZIE A.S. and RULLKOTTER J. (1985) Isomerization and aromitization of hydrocarbons and paleothermometry and burial history of Alberta foreland basin. *Am. Assoc. Petrol. Geol. Bull.* 69, 546-566.

BOLES J.R. (1978) Active ankerite cementation in the subsurface Eocene of southwest Texas. *Contrib. Mineral. Petrol.* 68, 13-22.

BOLES J.R. (1982) Active albitization of plagioclase, Gulf Coast Tertiary. *Am. J. Sci.* 282, 165-180.

BOLES J.R. (1987) Six million year diagenetic history, North Coles Levee, San Joaquin basin, California. In *Diagenesis of Sedimentary Sequences* (ed. J.D. MARSHALL), pp. 191-200. Geol. Soc. Spec. Pub. 36.

BOLES J.R. and FRANK S.G. (1979) Clay diagenesis in the Wilcox sandstones of southwest Texas: Implications of smectite diagenesis on sandstone cementation. *J. Sediment. Petrol.* 49, 55-70.

BRASS G.W. and TUREKIAN K.K. (1974) Strontium distribution in Geosecs oceanic profiles. *Earth Planet. Sci. Letters* 23, 141-148.

BURKE W.H., DENISON R.E., HETHERINGTON E.A. KOEPNICK R.B., NELSON H.F. and OTTO J.B. (1982) Variation of seawater ^{87}Sr/^{86}Sr throughout Phanerozoic time. *Geology* 10, 516-519.

CARPENTER S.J. and LOHMANN K.C. (1989) δ^{18}O and δ^{13}C variations in Late

Devonian marine cements from the Golden Spike and Nevis Reefs, Alberta, Canada. *J. Sediment. Petrol.* 59, 792-814.

CHAUDHURI S., BROEDEL V. and CLAUER N. (1987) Strontium isotopic evolution of oil field waters from carbonate reservoir rocks in Bindley field, central Kansas, U.S.A. *Geochim. Cosmochim. Acta* 51, 45-53.

CLAUER N., CHAUDHURI S. and SUBRAMANIUM R. (1989) Strontium isotopes as indicators of diagenetic recrystallization scales within carbonate rocks. *Chem. Geol. (Isotope Geosci. Sec.)* 80, 27-34.

CLAYTON R.N., FRIEDMAN I., GRAF D.L., MAYEDA T.K., MEENTS W.F. and SHIMP N.F. (1966) The origin of saline formation waters, 1. Isotopic composition. *J. Geophys. Res.* 71, 3057-3067.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990a) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. I. Chemistry. *Appld. Geochem.* 5, 375-396.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990b) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. II. Isotope systematics and water mixing. *Appld. Geochem.* 5, 397-414.

CRAIG H. (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochim. Cosmochim. Acta* 12, 133-149.

CRAIG H. (1961) Standards for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* 133, 1833-1834.

CURTIS C.D. (1967) Diagenetic iron minerals in some British Carboniferous sediments. *Geochim. Cosmochim. Acta* 31, 2109-2123.

DEAN M.E. (1986) Diagenesis of the Viking Formation, south-central Alberta. M.Sc. Thesis, Univ. of Alberta, Edmonton, Alberta.

DICKINSON W.R. and SNYDER W.S. (1978) Plate tectonics of the Laramide Orogeny. In *Laramide Folding Associated with Basement Block Faulting in the Western United States*, pp. 355-366. Geol. Soc. Am. Mem. 151.

DICKSON J.A. (1965) A modified staining technique for carbonate in thin section. *Nature* 219, 587.

DUTTON S.P. and LAND L.S. (1985) Meteoric burial diagenesis of Pennsylvanian arkosic sandstones, southwestern Anadarko Basin, Texas. *Am. Assoc. Petrol. Geol.* [illegible] 69, 22-38.

EPSTEIN S., GRAF D.L. and DEGENS E.T. (1964) Oxygen isotope studies on the origin of dolomite. In *Isotopic and Cosmic Chemistry* (eds. H. CRAIG *et al.*), pp. 169-180. North Holland Publishing Company.

ESLINGER E.V. and YEH H.W. (1981) Mineralogy, $^{18}O/^{16}O$, and D/H ratios of clay-rich sediments from Deep Sea Drilling Project site 180, Aleution Trench. *Clays and Clay Mins.* **29**, 309-315.

FAURE G. (1982) The marine - strontium geochronometer. In *Numerical Dating in Stratigraphy* (ed. G. ODIN), pp. 73-79. John Wiley and Sons.

FAURE G. (1986) *Principles of Isotope Geology (2nd. Ed.).* John Wiley and Sons.

FAURE G., CROCKET J.H. and HURLEY P.M. (1967) Some aspects of geochemistry of strontium and calcium in the Hudson Bay and Great Lakes. *Geochim. Cosmochim. Acta* **31**, 451-461.

FRIEDMAN I. and O'NEIL J.R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. In *Data of Geochemistry* (6th Ed.) (ed. M. FLEISCHER). United States Geol. Surv. Prof. Pap. 440-KK.

GARRELS R.M. and CHRIST C.L. (1965) *Solutions, Minerals, and Equilibria.* Freeman, Cooper and Company.

GARVEN G. (1989) A hydrogeologic model for the formation of giant oil sands deposits of the western Canada sedimentary basin. *Am. J. Sci.* **289**, 105-166.

GAUTIER D.L. (1982) Siderite concretions: Indicators of early diagenesis in the Gammon Shale (Cretaceous). *J. Sediment. Petrol.* **52**, 859-871.

GIVEN R.K. and LOHMANN K.C. (1985) Derivation of the original isotopic composition of Permian marine cements. *J. Sediment. Petrol.* **55**, 430-439.

GROSS M.G. (1964) Variations in the $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios of diagenetically altered limestones in the Bermuda Islands. *J. Geology* **72**, 170-194.

HACQUEBARD P.A. (1977) Rank of coal as an index of organic metamorphism for oil and gas in Alberta. In *The Origin and Migration of Petroleum in the Western Canadian Sedimentary Basin, Alberta* (eds. G. DEROO, T.G. POWELL, B. TISSOT, R.G. McCROSSAN), pp. 11-22. Geol. Surv. Can. Bull. 262.

HAYES J.B. (1979) Sandstone diagenesis - the hole truth. In *Aspects of Diagenesis* (eds. P.A. SCHOLLE and P.R. SCHLUGER), pp. 127-139. Soc. Econ. Paleo. Mineral. Spec. Pub. 26.

HEIN F.J., DEAN M.E., DELURE A.M., GRANT S.K., ROBB G.A. and LONGSTAFFE F.J. (1986) The Viking Formation in the Caroline, Garrington and Harmattan East fields, western south-central Alberta: Sedimentology and paleogeography. *Bull. Can. Petrol. Geol.* **34**, 91-110.

HELGESON H.C. and MURPHY W.M. (1983) Calculation of mass transfer among minerals and aqueous solutions as a function of time and surface area in geochemical processes. I. Computational approach. *Math. Geol.* **15**, 109-130.

HELGESON H.C., MURPHY W.M. and AAGARD P. (1984) Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solution. II. Rate constants, effective surface area, and the hydrolysis of feldspar. *Geochim. Cosmochim. Acta* 48, 2405-2432.

HITCHON B. (1969a) Fluid flow in the Western Canada Sedimentary Basin, 1. Effect of topography. *Water Resour. Res.* 5, 186-195.

HITCHON B. (1969b) Fluid flow in the Western Canada Sedimentary Basin, 2. Effect of geology. *Water Resour. Res.* 5, 460-469.

HITCHON B. (1984) Geothermal gradients, hydrodynamics, and hydrocarbon occurrence, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* 68, 713-743.

HITCHON B. and FRIEDMAN I. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin – I. Stable isotopes of hydrogen and oxygen. *Geochim. Cosmochim. Acta* 33, 1321-1349.

HOFMANN A.W., HART S.R. and HARE P.E. (1972) $^{87}Sr/^{86}Sr$ ratios of pore-fluids from deep-sea cores. *Annu. Rep. Geophys. Lab.*, Carnegie Inst., 563-564.

HOWER J., ESLINGER E.V., HOWER M.E. and PERRY E.A. (1976) Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence. *Geol. Soc. Am. Bull.* 87, 725-737.

IWUAGWU C.J. and LERBEKMO J.F. (1982) The petrology of the basal Belly River sandstone reservoir, Pembina Field, Alberta. *Bull. Can. Petrol. Geol.* 30, 187-207.

IWUAGWU C.J. and LERBEKMO J.F. (1984) Application of outcrop information to subsurface exploration for sandstone reservoirs: Basal Belly River Formation (Upper Cretaceous), Alberta foothills. In *The Mesozoic of Middle North America* (eds. D.F. STOTT and D.J. GLASS), pp. 387-400. Can. Soc. Petrol. Geol. Mem 9.

JORDON T.E. (1981) Thrust loads and foreland basin evolution, Cretaceous western United States. *Am. Assoc. Petrol. Geol. Bull.* 65, 2506-2520.

KEITH M.L. and WEBER J.N. (1964) Carbon and oxygen isotopic compositions of selected limestones and fossils. *Geochim. Cosmochim. Acta* 28, 1787-1816.

LAND L.S. (1970) Phreatic versus vadose meteoric diagenesis of limestone: Evidence for fossil water table. *Sedimentolt.* 14, 175-185.

LAND L.S. (1980) The isotopic and trace element geochemistry of dolomite: The state of the art. *Soc. Econ. Paleon. Mineral. Spec. Publ.* 28, 87-110.

LAND L.S. (1984) Frio sandstone diagenesis, Texas Gulf Coast: A regional isotopic study. In *Clastic Diagenesis* (D.A. McDONALD and R.C. SURDAM), pp. 47-62. Am. Assoc. Petrol. Geol. Mem. 37.

LAND L.S. and MILLIKEN K.L. (1981) Feldspar diagenesis in the Frio Formation, Brazoria County, Texas Gulf Coast. *Geology* 9, 314-318.

LONGSTAFFE F.J. (1984) The role of meteoric water in diagenesis of shallow sandstones: Stable isotope studies of the Milk River aquifer and gas pool. In *Clastic Diagenesis* (eds. D.A. MACDONALD and R.C. SURDAM), pp. 81-98. Am. Assoc. Petrol. Geol. Mem. 37.

LONGSTAFFE F.J. (1986) Oxygen isotope studies of diagenesis in the basal Belly River sandstone, Pembina I-Pool, Alberta. *J. Sediment. Petrol.* 56, 78-88.

LONGSTAFFE (1987) Stable isotope studies of diagenetic processes. In *Stable Isotope Geochemistry of Low Temperature Fluids* (ed. T.K. KYSER), pp. 187-257. Mineral. Assoc. Canada Short Course 13.

LONGSTAFFE F.J. and AYALON A. (1987) Oxygen-isotope studies of clastic diagenesis in the Lower Cretaceous Viking Formation, Alberta: Implications for the role of meteoric water. In *Diagenesis of Sedimentary Sequences* (ed. J.D. MARSHALL), pp. 277-296. Geol. Soc. Spec. Pub. 36.

LOUCKS R.G., BEBOUT D.G. and CALLOWAY W.E. (1977) Relationship of porosity formation and preservation to sandstone consolidation history - Gulf Coast Lower Tertiary, Frio Formation. *Gulf Coast Assoc. Geol. Soc. Trans.* 27, 109-120.

MACDONALD J. (1987) The basal Cambrian sandstone: Mineralogy and diagenesis. B.Sc. Thesis, Univ. of Alberta, Edmonton, Alberta.

MACHEMER S.D. and HUTCHEON I. (1988) Geochemistry of early carbonate cements in the Cardium Formation, central Alberta. *J. Sediment. Petrol.* 58, 136-147.

MAJORWICZ J.A., RAHMAN M., JONES F.W. and McMILLAN N.J. (1985) The paleogeothermal and present thermal regimes of the Alberta basin and their significance for petroleum occurrences. *Bull. Can. Petrol. Geol.* 33, 12-21.

McCREA J.M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* 18, 849-857.

McKENZIE J. (1984) Holocene dolomitization of calcium carbonate sediments from the coastal sabkhas of Abu Dhabi, U.A.E.: A stable isotope study. *J. Geol.* 89, 185-198.

McNUTT R.H. (1987a) $^{87}Sr/^{86}Sr$ ratios as indicators of water/rock interactions: Application to brines found in Precambrian age rocks from Canada. In *Saline Water and Gases in Crystalline Rocks* (eds. P. FRITZ and S.K. FRAPE), pp.81-88. Geol. Assoc. Canada Spec. Pap. 33.

McNUTT R.H., FRAPE S.K. and DOLLAR P. (1987b) A strontium, oxygen and hydrogen isotopic composition of brines, Michigan and Appalachian Basins, Ontario and Michigan. *Appld. Geochem.* 2, 495-506.

MILLIKEN K.L., LAND L.S. and LOUCKS R.G. (1981) History of burial diagenesis determined from isotopic geochemistry, Frio Formation, Brazoria County, Texas. *Am. Assoc. Petrol. Geol. Bull.* 65, 1397-1413.

NELSON S.J. (1970) *The Face of Time, the Geologic History of Western Canada.* Alberta Soc. Petrol. Geol.

NURKOWSKI J.R. (1984) Coal quality, coal rank variation and its relation to reconstructed overburden, Upper Cretaceous and Tertiary Plains coals, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* 68, 285-295.

O'NEIL J.R. (1987) Preservation of H, C, and O isotopic ratios in the low temperature environment. In *Stable Isotope Geochemistry of Low Temperature Fluids* (ed. T.K. KYSER), pp. 85-128. Mineral. Assoc. Canada Short Course 13.

O'NEIL J.R., CLAYTON R.N. and MAYEDA T.K. (1969) Oxygen isotope fractionation in divalent metal carbonates *J. Chem. Phys.* 51, 5547-5558.

PETERMAN Z.E., HEDGE C.E. and TOURTELOT H.A. (1970) Isotopic composition in seawater throughout Phanerozoic time. *Geochim. Cosmochim. Acta* 34, 105-120.

PIEL K. (1971) Palynology of Oligocene sediments of central British Columbia. *Can. J. Bot.* 49, 1885-1920.

POPP B.N., ANDERSON T.F. and SANDBERG P.A. (1986) Textural, elemental and isotopic variations among constituents in Middle Devonian limestones, North America. *J. Sediment. Petrol.* 56, 715-727.

PORTER J.W., PRICE R.A. and McCROSSAN R.G. (1982) The Western Canada Sedimentary Basin. *Roy. Soc. Phil. Trans.* 305, 169-192.

PREZBINDOWSKI D. (1980) Microsampling technique for stable isotope analyses for carbonates. *J. Sediment. Petrol.* 50, 643-644.

PRICE R.A. (1973) Large scale gravitational flow of supra-crustal rocks, southern Canadian Rocky Mountains. In *Gravity and Tectonics* (ed. K.A. DEGONG and R.S. CHOLTEN), pp. 491-502. Wiley.

SAVIN S.M. and YEH H. (1981) Stable isotopes in ocean sediments. In *The Sea, The Oceanic Lithosphere* (ed. C. EMILIANI), pp. 1521-1554. Wiley.

SCHULTZ J.L., BOLES J.R. and TILTON G.R. (1989) Tracking calcium in the San Joaquin basin, California: A strontium isotopic study of carbonate cements at North Coles Levee. *Geochim. Cosmochim. Acta* 53, 1991-1999.

SHARMA T. and CLAYTON R.N. (1965) Measurements of O^{18}/O^{16} ratios of total oxygen of carbonates. *Geochim. Cosmochim. Acta* 29, 1347-1353.

SPENCER R.J. (1987) Origin of Ca-Cl brines in Devonian formations, Western Canada Sedimentary Basin. *Appld. Geochem.* 2, 373-384.

STANLEY K.O. and FAURE G. (1979) Isotopic composition and sources of strontium in sandstone cements: The High Plains sequence of Wyoming and Nebraska. *J. Sediment. Petrol.* **49**, 45-54.

STUEBER A.M., PUSHKAR P. and HETHERINGTON E.A. (1987) A strontium isotopic study of formation waters from the Illinois basin, U.S.A. *Appld. Geochem.* **2**, 477-494.

SUCHECKI R.K. and LAND L.S. (1983) Isotopic geochemistry of burial-metamorphosed volcanogenic sediments, Great Valley sequence, northern California. *Geochim. Cosmochim. Acta* **47**, 1487-1499.

TAYLOR H.P.Jr. (1974) The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Econ. Geol.* **69**, 843-883.

TAYLOR R.S., MATHEWS W.H. and KUPSCH W.O. (1964) Tertiary. In *Geological History of Western Canada* (ed. R.G. McCROSSAN and R.P. GLAISTER), pp. 190-194. Alberta Soc. Petrol. Geol.

VEIZER J. and COMPSTON W. (1974) ^{87}Sr/^{86}Sr composition of sea water during the Phanerozoic. *Geochim. Cosmochim. Acta* **38**, 1461-1484.

VEIZER J. and HOEFS J. (1976) The nature of ^{18}O/^{16}O and ^{13}C/^{12}C secular trends in sedimentary rocks. *Geochim. Cosmochim. Acta* **40**, 1387-1395.

VEIZER J., COMPSTON W., HOEFS J. and NIELSON H. (1982) Mantle buffering of early oceans. *Naturwissenschaften* **69**, 173-180.

WALTERS L.J., Jr., CLAYPOOL G.E. and CHOQUETTE P.W. (1972) Reaction rates and δ^{18}O variation for the carbonate-phosphoric acid preparation method. *Geochim. Cosmochim. Acta* **36**, 129-140.

WHITTAKER S.G., KYSER T.K. and CALDWELL W.G. (1987) Paleoenvironmental geochemistry of the Claggett marine cyclothem in south-central Saskatchewan. *Can. J. Earth Sci.* **24**, 967-984.

YEH H.W. and SAVIN S.M. (1976) The extent of oxygen isotope exchange between clay minerals and seawater. *Geochim. Cosmochim. Acta* **40**, 743-748.

YEH H.W. and SAVIN S.M. (1977) Mechanism of burial metamorphism of argillaceous sediments. 3. O-isotope evidence. *Geol. Soc. Am. Bull.* **88**, 1321-1330.

able 2.1. Stable and radiogenic isotope results for whole rocks and mineral separates from Precambrian to Upper Cretaceous formations in the Alberta Basin, south-central Alberta. Sample location, depth, lithology and composition of the analyzed whole rock / mineral separate are listed. Sample names with the letter D after them denote diagenetic separates that were physically drilled from the rock rather than removed by chemical means; ND denotes the groundmass or nondiagenetic component of the sample. * Small amount of carbonate in proportion to clay minerals, spurious values; ^ Very small percentage of carbonate in the total sample (<5%), but residing in a clean sandstone with no clay. Other abbreviations used in the table are the following: WR = whole rock; (-) = not analyzed; SST. = sandstone; SH. = shale; SLTST. = siltstone; LST. = limestone; CALC. = calcareous; CAL= calcite; DOL= dolomite; ANK = ankerite.

FORMATION	LOCATION	DEPTH (m)	SAMPLE NAME	LITHOLOGY	MINERAL/ROCK ANALYZED	RADIOGENIC ISOTOPES $^{87}Sr/^{86}Sr$	STABLE ISOTOPES $\delta^{18}O$ (SMOW)	$\delta^{13}C$ (PDB)
BELLY RIVER CONTINENTAL	6-19-46-5W5	1066.1	C91-A	SST.	CALCITE	–	+10.0	-5.4
	6-6-50-10W5	1247.7	C221-J	SST.	CALCITE	–	+11.0	-2.6
	6-16-42-6W5	1539.[illegible]	C56-J	SST.	CALCITE	–	+10.8	-4.8
	14-33-51-19W5	1593.5	C229-O	CGL	CALCITE	–	+8.5	-14.3
	"	1663.3	C229-S	SST.	CALCITE	–	+9.7	-9.8
BASAL BELLY RIVER	8-32-48-4W5	980.9	CC180.14	SST.	CALCITE	–	+15.1	+0.5
	"	"	"	"	DOL/ANK	–	+21.9	+0.2
	"	986.7	CC180.13	SST.	CALCITE	0.70614	–	–
	"	987.8	CC180.11	SST.	CALCITE	0.70586	+13.0	-4.7
	"	988.2	CC182	SST.	CALCITE	0.70623	+13.1	-4.0
	"	988.7	CC180.10	SST.	CALCITE	0.70697	–	–
	"	990.2	CC186	SST.	CALCITE	0.70572	+13.0	-6.2
	"	990.8	CC180.08	SST.	CALCITE	0.70508	+13.2	-5.0
	"	991.5	CC180.07	SST.	CALCITE	0.70582	+13.5	-4.9
	"	992.0	CC180.06	SST.	CALCITE	0.70604	+13.9	-4.4
	"	992.7	CC180.05	SST.	CALCITE	0.70594	+12.7	-6.7
	"	994.6	CC180.02	SST.	CALCITE	0.70607	–	–
	"	995.0	CC180.01	SST.	CALCITE	0.70615	+14.0	0.0
	4-20-43-2W5	1108.6	CC88A	SST.	CALCITE	0.70564	+11.7	-2.5
	"	1110.2	CC88B	SST.	CALCITE	0.70584	+11.7	-3.3
	15-27-35-9W5	2251.8	CC15	SST.	CALCITE	0.70586	+11.5	-6.0
LEA PARK	8-32-48-4W5	995.3	CC179.2	SH.	WR	0.70745	–	–
	"	997.0	CC179.01	SH.	WR	0.70744	–	–
CARDIUM	8-32-48-4W5	1306.5	CC170.04	SH.	WR	0.71893	–	–
	"	1308.7	CC170.03	SH.	WR	0.71962	–	–
	"	1310.3	CC170.02	SH.	WR	0.71843	–	–
	"	1389.4	CC170.01	SH.	WR	0.71583	–	–
VIKING	1-16-53-26W4	1149.1	CC160	SST.	CALCITE	–	+25.5	+1.5
	"	"	"	"	SIDERITE	–	+24.3	-1.7
	7-7-29-26W4	1280.0	CM500	SST.	DOL>>ANK	–	+20.0	-10.5
	16-1-46-4W5	1734.0	C726	CGL	CALCITE	–	+14.1	-7.2
	6-25-40-2W5	17[illegible]6.0	CM100	SST.	ANKERITE	–	+16.3	-2.4
	14-30-31-28W4	1884.0	CM519A	SST.	DOL>>ANK	–	+20.3	-2.6
	10-18-31-2W5	2199.8	C631	SST.	CALCITE	0.70781	+14.9	-7.2
	3-17-40-4W5	2160.2	CM51	SST.	SIDERITE	0.70730	+23.1	-1.7
	16-10-32-3W5	2221.0	C10/7	SST.	ANKERITE	0.70747	+16.5	-5.9
	6-16-35-5W5	2468.0	M218	SST.	DOL>>ANK	–	+22.1	-8.5
	2-30-38-7W5	2537.0	C140	SST.	SIDERITE	0.70808	+24.2	-0.8
	"	2537.0	C141	SST.	SIDERITE	0.70762	+21.2	-2.1
	10-24-33-8W5	3101.4	CC660	SST.	SIDERITE	0.70832	+18.5	-4.6
GLAUCONITIC	14-12-50-26W4	1295.6	CC146	SH.	CALCITE	–	+18.3	-0.4
	4-32-48-4W5	1754.3	CC142.04	SH.	DOLOMITE	0.70928	–	–
	"	1756.4	CC142.03	SH.	CALCITE	–	+18.4	+0.5
	"	"	"	"	DOLOMITE	–	+19.9	+0.6
	"	"	"	"	CAL 1.5X DOL1X	0.70785	–	–
	"	1757.8	CC142.02	SST.	CALCITE	0.70903	+14.4	-2.5
	"	1758.1	CC144	SST.	CALCITE	0.70803	+14.7	-2.5
	"	1758.6	CC142	SST.	CALCITE	0.70879	+15.5	-1.7
	"	1760.4	CC142.01	SH.	CALCITE	–	+19.3	+1.8
	"	"	"	"	DOLOMITE	–	+19.5	+1.0
	"	"	"	"	CAL 2.5X DOL 1X	0.70898	–	–
OSTRACODE	4-32-48-4W5	1764.2	CC130	SH. / LST	CALCITE	0.70867	+17.3	-2.6
BASAL QUARTZ II	1-16-50-26W4	1154.7	CC158	SH. / SLTST.	WR	0.71181	–	–
	14-12-50-26W4	1296.7	CC150.13	SST. / SLTST.	WR	0.71363	–	–
	"	1298.2	CC150.12	SST. / SLTST	WR	0.72187	–	–
	"	1302.3	CC150.09	SST.	CALCITE	–	+18.9	-0.1
	"	1302.7	CC150.08	SST.	CALCITE	–	+18.7	-0.3
	"	"	"	"	DOLOMITE	–	+23.5	+0.1
	"	"	"	"	CAL 1X DOL 2.5X	0.71006	–	–
	"	1303.3	CC152	SST.	CALCITE	–	+17.8	-1.3
	"	"	"	"	DOL/ANK	–	+22.6	-0.3
	"	1303.6	CC150.07	SST. / SLTST.	CALCITE	–	+19.0	-0.6
	"	"	"	"	DOLOMITE	–	+23.9	0.0
	"	"	"	"	CAL2X/DOL1X	0.71073	–	–
	"	1304.2	CC150.05	SH.	WR	0.71171	–	–
	"	"	"	"	CALCITE	–	+19.7	+4.2
	"	"	"	"	ANKERITE	–	+24.0	+1.1
	"	"	"	"	CAL1X/ANK1X	*0.71192	–	–
	"	1304.4	CC150	SST.	CALCITE	–	+19.0	-0.3
	"	1311.2	CC150.02	SH.	WR	0.71742	–	–
	8-31-48-4W5	1774.2	CC154	SH.	WR	0.71534	–	–
	"	"	"	"	ANK/DOL	*0.71449	+24.3	+0.2

FORMATION	LOCATION	DEPTH (m)	SAMPLE NAME	LITHOLOGY	MINERAL/ROCK ANAYLYZED	RADIOGENIC ISOTOPES $^{87}Sr/^{86}Sr$	STABLE ISOTOPES $\delta^{18}O$ (SMOW)	$\delta^{13}C$ (PDB)
BASAL QUARTZ I (DETRITAL)	1-16-50-26W4	1330.8	CC120 02	SST.	ANK/DOL	*0.71121	-	-
	"	1333.7	CC120.01	SST.	ANK/DOL	*0.71104	-	-
	"	1337.6	CC120	SST.	CALCITE	0.70820	+15.5	-1.5
ROCK CREEK	8-4-42-5W5	2337.5	CC110.03	SST.	CALCITE	*0.71282	-	-
	"	2341.9	CC110	SILTY LST.	CALCITE	-	+20.9	-0.4
	"	2343.5	CC110.02	LST. / SLTST.	CALCITE	-	+22.2	+6.4
	"	"	"	"	ANKERITE	-	+23.4	0.0
	"	"	"	"	CAL 1.7X ANK 1X	0.70916	-	-
	"	2344.8	CC114	LST. / SLTST.	CALCITE	-	+22.0	+1.0
	"	"	"	"	ANKERITE	-	+23.2	0.3
	"	"	"	"	CAL/ANK	0.70859	-	-
	"	2346.6	CC110.01	SLTST.	CALCITE	-	+23.0	0.0
	"	"	"	"	CAL 4X ANK 1X	0.70877	-	-
POKER CHIP SHALE	8-4-42-4W5	2349.6	CC1[illegible].01	SH.	WR	0.71171	-	-
	"	"	"	"	ANKERITE	-	+18.5	-5.6
NORDEGG	8-31-48-4W5	1776.7	CC102	LST.	WR / CALCITE	0.70831	+19.0	-1.8
	"	1776.9	CC100	LST.	WR / CALCITE	0.70803	+19.3	-1.2
	"	1777.0	CC99.02	LST.	WR / CALCITE	0.70795	+20.6	-0.7
	"	"	CC99.02D	"		-	+18.5	-0.9
	"	1778.5	CC101	LST.	WR / CALCITE	0.70885	-	-
	"	1780.3	CC99	LST.	WR / CALCITE	0.70842	+18.8	-1.4
	"	1782.2	CC99.01	LST.	WR / CALCITE	0.70892	+18.8	-1.6
FERNIE	8-32-48-4W5	1805.5	CC90	LST.	WR / CALCITE	0.70843	+22.2	-0.2
	"	"	CC90	LST.	DIA. CALCITE	0.70873	+17.0	-1.3
	"	806.2	CC92	LST.	WR / CALCITE	0.70903	+19.7	-2.9
MISSISSIPPIAN	4-32-48-4W5	1774.9	CC82.01	LST.	WR / CALCITE	0.70862	+18.7	-2.0
	"	1775.6	CC82	LST.	WR / CALCITE	0.70850	+19.3	-2.1
	8-31-48-4W5	1783.0	CC80.01	LST.	WR / CALCITE	0.70848	+21.0	-2.1
	"	1783.6	CC80	LST.	WR / CALCITE	0.70855	+21.2	-1.1
EXSHAW	14-29-48-6W5	6978.8	-	SH.	WR	0.71012	-	-
WABAMUN	1-16-50-26W4	1368.1	CC70.06	LST.	WR / CALCITE	0.70857	+22.4	-1.4
	"	1368.9	CC70.04	LST.	WR / CALCITE	0.70871	+22.5	-1.3
	"	1369.3	CC70.03	LST.	WR / CALCITE	0.70869	+22.6	-1.6
	"	1370.4	CC70	LST.	WR / CALCITE	0.70902	+22.6	-1.1
			CC70D	"	CALCITE	0.71318	-	-
	"	1373.4	CC70.02	LST.	WR / CALCITE	0.70977	+18.4	-2.9
	"	"	CC70.02D	"	CALCITE	-	+16.0	-6.1
		"	"	"	ANKERITE	-	+24.3	-0.7
	"	1374.0	CC70.01	LST.	WR / CALCITE	0.70937	+18.1	-2.9
	"	"	"	"	DOLOMITE	-	+22.5	-0.6
STETTLER	10-23-50-26W4	1510.9	-	CALC. SH.	DOLOMITE	0.71167	-	-
GRAMINEA	7-19-50-26W4	1533.1	-	CALC. SH.	WR	0.73939		
	"	1533.3	-	CALC. SH.	WR	0.73914		
CALMAR	1-16-50-26W4	1545.0	-	CALC. SH.	WR	0.73890		
	"	1549.6	-	CALC. SH.	WR	0.73407		
	1-12-50-27W4	1870.6	-	CALC. SH.	WR	0.72618		
NISKU	1-16-50-26W4	1551.1	CC60.04	DOLOSTONE	WR / DOLOMITE	0.70867	-	-
	"	1552.2	CC60.03	DOLOSTONE	WR / DOLOMITE	0.70857	-	-
	"	1553.6	CC60	DOLOSTONE	WR / DOLOMITE	0.70842	+26.7	-2.9
	"	1554.0	CC60.02	DOLOSTONE	WR / DOLOMITE	0.70895	-	-
	"	1554.8	CC60.01	DOLOSTONE	WR / DOLOMITE	0.7089	-	-
IRETON	4-15-50-26W4	1639.4	-	CALC. SH.	WR	0.73077		
LEDUC	8-17-50-26W4	1831.2	CC50.10	DOLOSTONE	WR / DOLOMITE	0.70834	+24.7	+1.8
	"	1831.7	CC50.09	DOLOSTONE	WR / DOLOMITE	0.70829	+25.0	+1.9
	"	1832.6	CC50.08	DOLOSTONE	WR / DOLOMITE	0.70832	+25.1	+1.9
	"	1833.2	CC50.07	DOLOSTONE	WR / DOLOMITE	0.70819	+24.8	+1.8
	"	1833.4	CC50.06	DOLOSTONE	WR / DOLOMITE	0.70823	+24.8	+1.7
	"	"	CC50.06D	"	DOLOMITE	-	+24.9	+1.0
	"	1834.6	CC50.05	DOLOSTONE	WR / DOLOMITE	0.70827	+24.7	+1.7
	"	1836.0	CC50.04	DOLOSTONE	WR / DOLOMITE	0.70817	+24.7	+1.7
	"	1839.9	CC50.03	DOLOSTONE	WR / DOLOMITE	0.70825	+24.6	+1.7
	"	1842.2	CC50.02	DOLOSTONE	WR / DOLOMITE	0.70830	+24.9	+1.8
	"	1843.3	CC50.01	DOLOSTONE	WR / DOLOMITE	0.70828	+25.0	+1.6
	"	1844.6	CC50	DOLOSTONE	WR / DOLOMITE	0.70825	+25.0	+1.7

FORMATION	LOCATION	DEPTH (m)	SAMPLE NAME	LITHOLOGY	MINERAL/ROCK ANALYZED	RADIOGENIC ISOTOPES $^{87}Sr/^{86}Sr$	STABLE $\delta^{18}O$ (SMOW)	ISOTOPES $\delta^{13}C$ (PDB)
DUVERNEY	9-22-51-27W4	1819.7	1819.7ND	CALC. SH.	CALCITE	0.71079		
	"	"	1819.7D	"	CALCITE	0.70798		
	"	1820.7	-	CALC. SH.	WR	0.70867		
	"	"		"	CALCITE	-	+25.3	+3.7
	14-29-48-6W5	2648.9	-	CALC. SH.	WR	0.71283		
COOKING LAKE	8-17-50-26W4	1845.3	CC40.02	DOLOSTONE	WR / DOLOMITE	0.70837	+25.5	+2.1
	"	"	CC40.02D	"	DOLOMITE	-	+24.8	+1.7
	"	1848.6	CC40.01	DOLOSTONE	WR / DOLOMITE	0.70833	+24.4	+2.8
	"	"	CC40.01D	"	DOLOMITE	0.70830	+24.5	+2.3
	"	1848.6	CC40	DOLOSTONE	WR / DOLOMITE	0.70819	+24.7	+2.6
BEAVERHILL LAKE	1-27-51-27W4	1955.9	1955.9ND	LST.	CALCITE	0.71083	+24.0	+3.0
	1-27-51-27W4	"	1955.9D	"	CALCITE	0.70810	-	-
	14-29-48-6W5	2888.4	-	LST.	WR	0.70872	-	-
ELK POINT	8-17-50-26W4	2251.6	CC32	DOLOSTONE	WR / ANKERITE	0.70862	+29.6	+3.4
	"	2252.1	CC30.03	DOLOSTONE	WR / DOLOMITE	0.70836	+27.6	+1.8
	"	2252.6	CC30	DOLOSTONE	WR / DOLOMITE	0.70825	+28.1	+0.9
	"	2253.2	CC30.04	DOLOSTONE	WR / DOLOMITE	0.70831	+28.7	+1.3
	"	2254.1	CC30.02	DOLOSTONE	WR / DOLOMITE	0.70826	+28.6	+1.9
	"	2254.8	CC30.01	DOLOSTONE	WR / DOLOMITE	0.70823	+28.8	+1.6
VARIABLE SHALE	14-29-48-6W5	3008.4	-	SH.	WR	0.72492	-	-
CAMBRIAN	8-17-50-26W4	2634.7	CC20	SH. / SLTST.	WR	0.74307	-	-
	"	[illegible]	CC16.14	SH. / SLTST.	CAL/ANK/DOL	0.74718	-	-
	"	[illegible]	CC1.	SH. / SLTST.	WR	0.77173	-	-
	"	2635.8	CC16.13	SH. / SLTST.	WR	0.77896	-	-
	"	"	"	"	CAL2X/ANKDOL1X	0.74365	-	-
	"	2636.1	CC16.12	SH. / SLTST.	WR	0.77658	-	-
	"	2637.7	CC16.11	SH. / SLTST.	WR	0.76180	-	-
	"	2637.8	CC16.10	SH. / SLTST.	WR	0.77876	-	-
	"	"	"	"	CAL 1.5X/ANKDOL1X	0.74822	-	-
	"	2638.5	CC16.09	SH. / SLTST.	WR	0.76364	-	-
	"	2639.2	CC16.08	SH. / SLTST.	WR	0.78577	-	-
	"	2640.1	CC16.07	SH. / SLTST.	WR	0.77686	-	-
	"	2640.9	CC16.06	SH. / SLTST.	WR	0.77161	-	-
	"	2641.7	CC16.05	SH. / SLTST.	WR	0.77959	-	-
	"	2642.0	CC16.04	SH. / SLTST.	WR	0.75689	-	-
	"	2643.2	CC16.03	SH. / SLTST.	WR	0.75101	-	-
	"	2643.6	CC16.02	SH. / SLTST.	WR	0.75410	-	-
	"	2644.1	CC16.01	SH. / SLTST.	WR	0.75625	-	-
		2701.4	CC14	SST.	DOL/ANK	-	+18.6	-3.7
	"	2701.8	CC11.03	SST.	ANKERITE	0.74823	+19.6	-3.4
	"	2733.9	CC11.01	SST.	ANK/DOL	0.75038	-	-
	14-29-48-6W5	3134.5	3134.5D	SST. / SLTST.	CALCITE	0.70836	+23.5	-1.6
	"	3134.5	3134.5ND	SST. / SLTST.	WR	0.76561	-	-
PRECAMBRIAN	8-17-50-26W4	2738.9	C1	GRANITE	WR	1.14523	-	-
	"	2740.0	CC0.01	"	WR	1.24867	-	-

Table 2.2. Summary of the various calcite phases in the Cretaceous formations of the Alberta Basin. Includes a general description of their location in the paragenetic sequence and indicates those phases extracted from sandstone as opposed to those extracted from shale. The average or range in $\delta^{18}O$ values is provided at the end of the descriptions.

FORMATION	CALCITE PHASES
Belly River	*Early phase: poikilotopic, in samples exhibiting limited compaction ($\delta^{18}O$ = +21‰; AYALON and LONGSTAFFE, 1988). Late phase: replaces detrital grains, primarily feldspar and volcanic rock fragments, together with clay minerals; subsequently overlain by clay minerals (Belly River Continental $\delta^{18}O$ = +10‰; basal Belly River $\delta^{18}O$ = +13.0‰).
Viking	Early phase: poikilotopic, between uncompacted grains ($\delta^{18}O$ = +25‰). Late phase: precipitated subsequent to siderite and quartz formation but prior to the formation of authigenic kaolin group minerals and illite ($\delta^{18}O$ = +14.5‰).
Glauconitic	Late phase: (Sst.) precipitated subsequent to diagenetic quartz, replacing detrital feldspars and other minerals and succeeded by clay minerals ($\delta^{18}O$ = +15.5‰). (Sh.) ($\delta^{18}O$ = +18.7‰).
Ostracod	Extracted from limestone lens within a shale horizon ($\delta^{18}O$ = +18.7‰).
Basal Quartz	Late phase: (Basal Sst.) precipitated subsequent to authigenic quartz but prior to clay authigenesis ($\delta^{18}O$ = + 15.5‰). (Channel Sst. and Sh.) $\delta^{18}O$ range from +17.8 to +19.7‰; Sst. avg. +18.6‰; Sh. avg. +19.4‰.

*observed in the study of AYALON and LONGSTAFFE (1988).

Table 2.3. Comparison of Sr isotopic analyses of formation water and reservoir authigenic cements or whole rock carbonates within the same formation or group.

		^{87}Sr/^{86}Sr	
Formation	**Reservoir Rock Mineral**	**Rock**	**Water**
Belly River	Calcite	0.70564-0.70623	0.70578-0.70634
Viking	Siderite	0.70762-0.70808	0.70768-0.70894
	Calcite	0.70781	
	Ankerite	0.70747	
Glauconitic	Calcite	0.70803-0.70903	0.70758-0.71024
	Dolomite/Calcite	0.70785-0.70898	
	Dolomite	0.70928	
Ostracod	Calcite	0.70867	0.70821-0.70859
Basal Quartz	Calcite	0.70820	0.70886-0.71137
	Dolomite/Calcite	0.71006-0.71073	
	Ankerite/Dolomite	0.71104-0.71121	
Rock Creek	Calcite/Ankerite	0.70859-0.70916	0.71220-0.71168
Nordegg	Limestone	0.70795-0.70892	0.71037-0.71170
Mississippian	Limestone	0.70848-0.70862	0.70966-0.71031
Wabamun	Limestone	0.70857-0.70902	0.71062-0.71285
	Limestone	0.70937-0.70977	
Nisku	Dolostone	0.70842-0.70895	0.70998-0.71206
Leduc	Dolostone	0.70817-0.70834	0.70872-0.70981

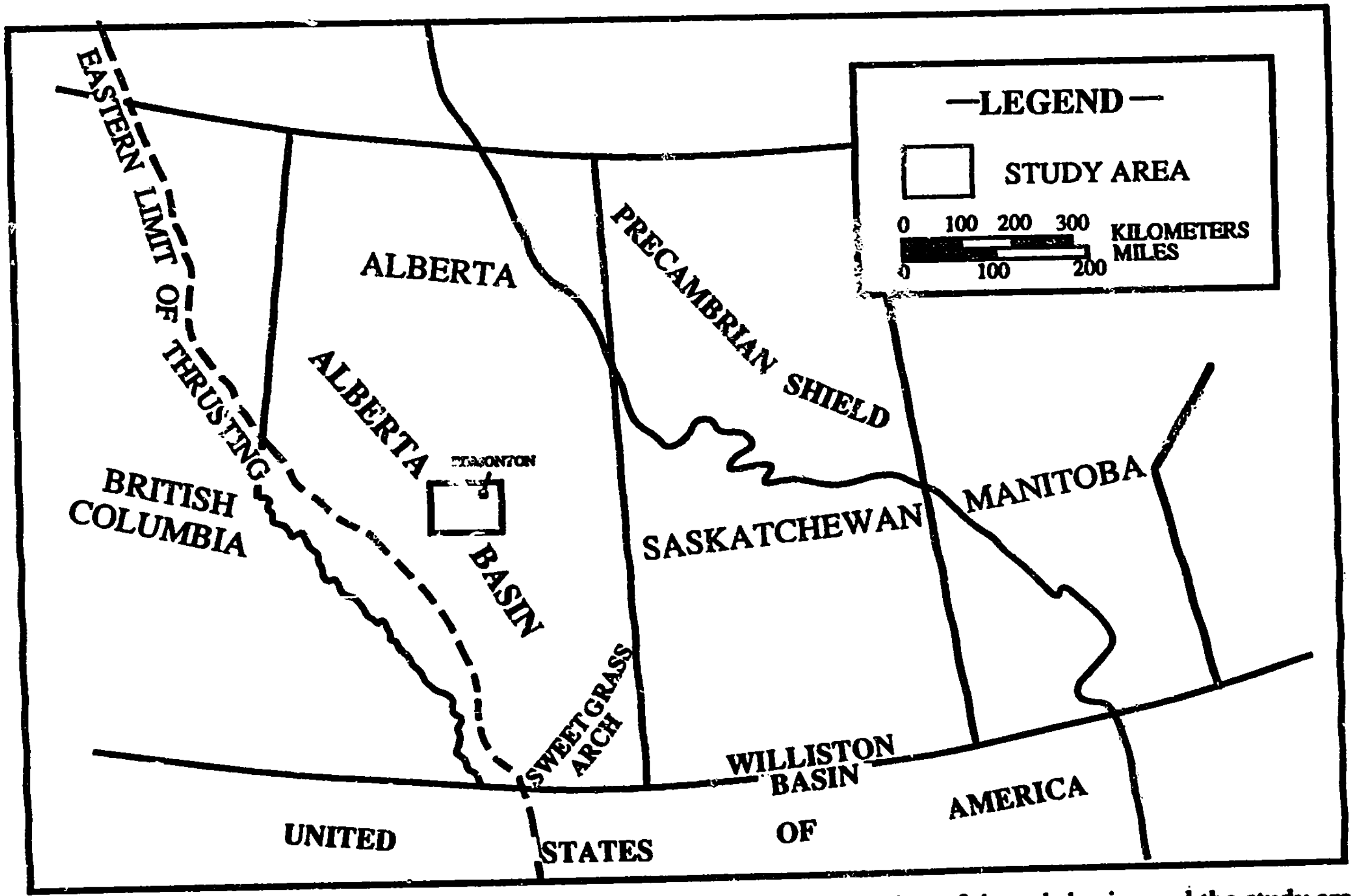


Fig. 2.1. Map of the Western Canada Sedimentary Basin, showing location of the sub-basins and the study area.

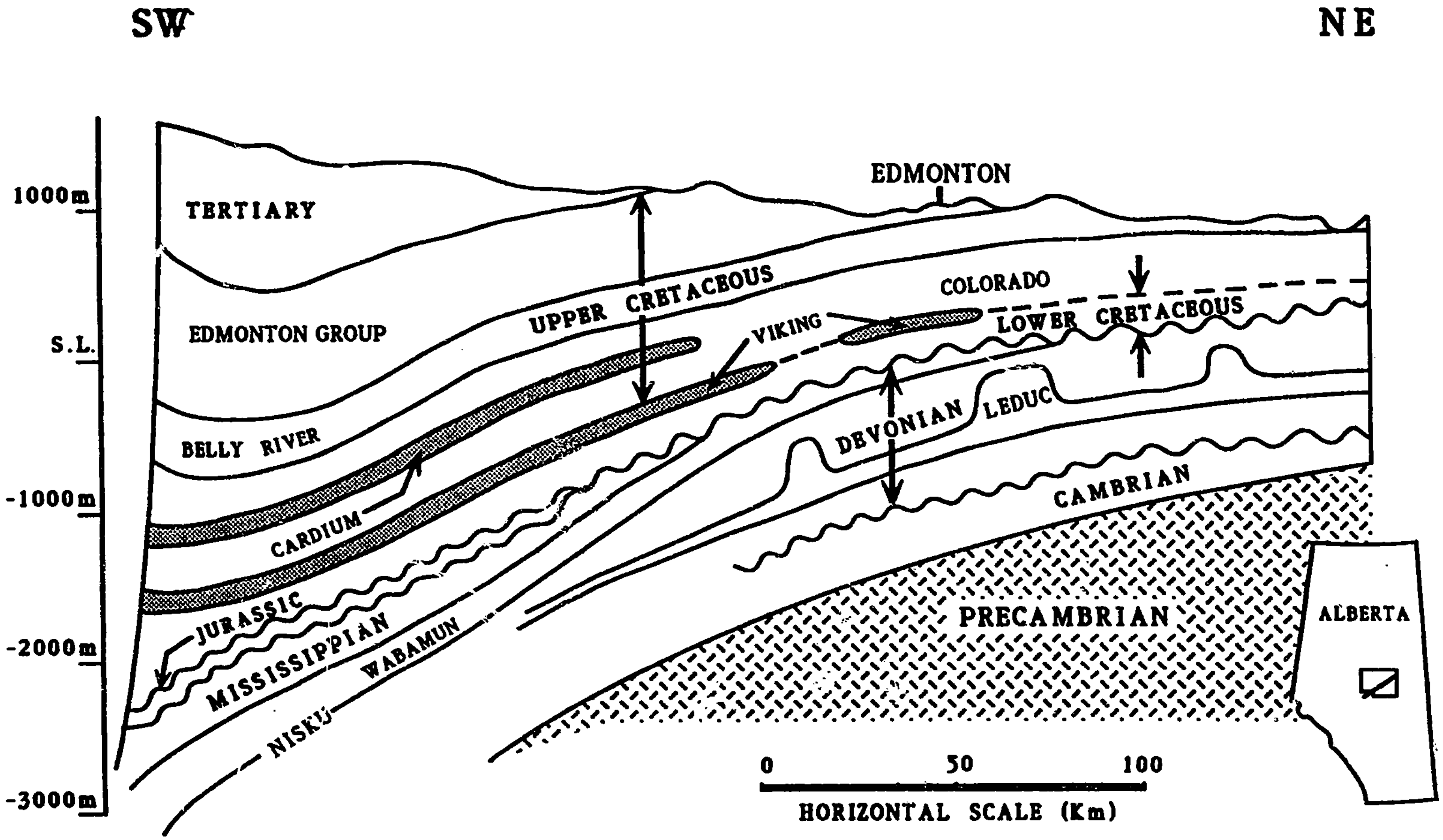


Fig. 2.2. Geological cross-section from SW to NE through the Alberta Basin showing the major stratigraphic units and unconformities.

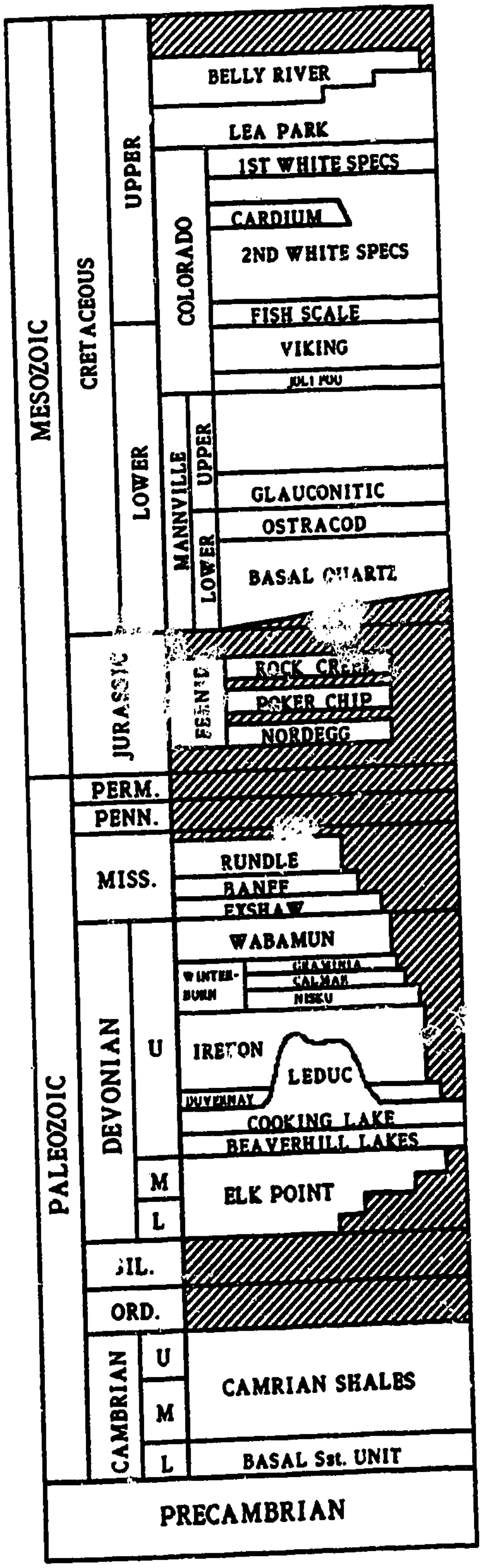


Fig. 2.3. Generalized stratigraphic column, Central Plains, Alberta Basin (modified after the *Energy Resources Conservation Board, Table of Formations*).

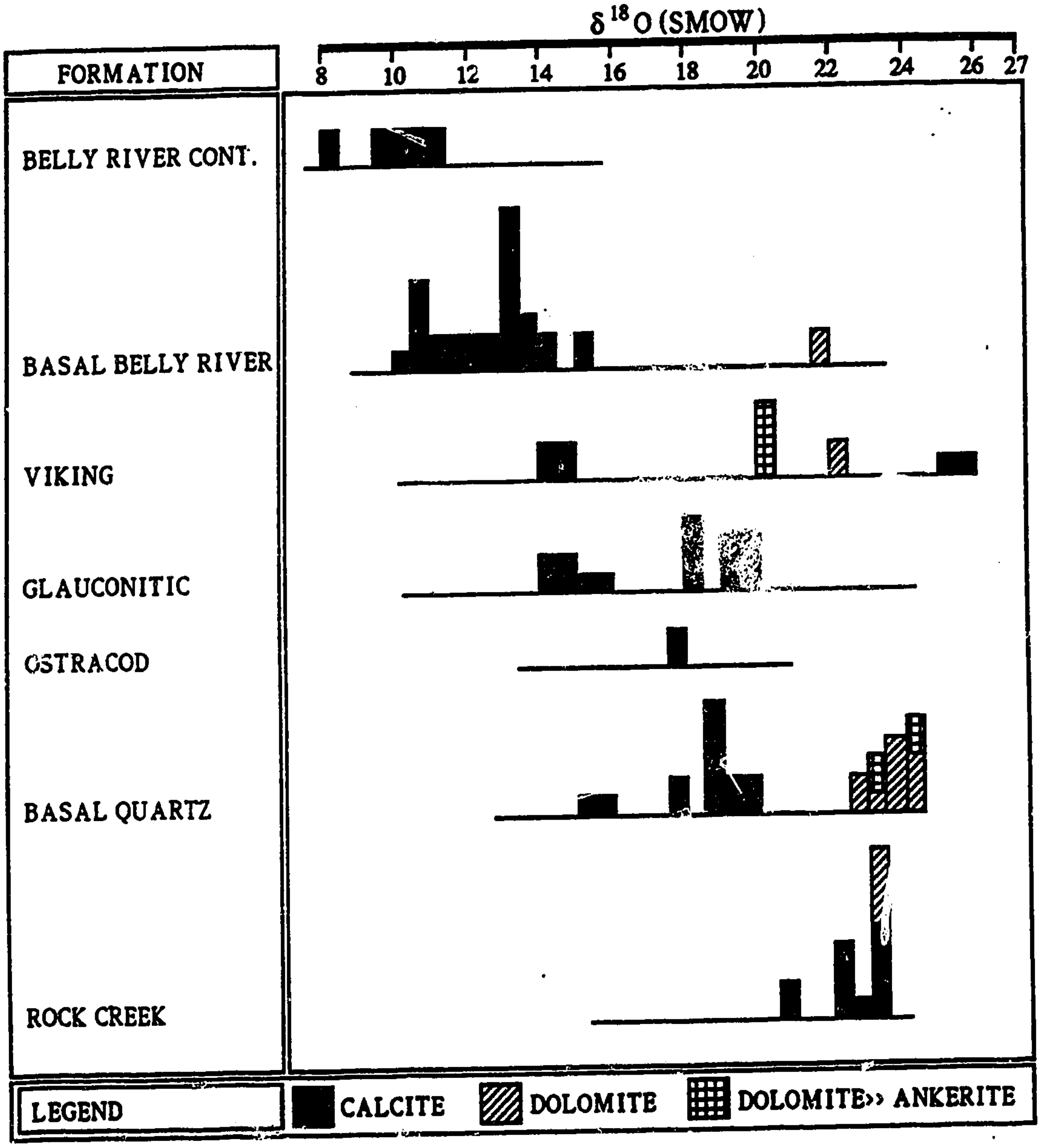


Fig. 2.4. Histogram of $\delta^{18}O_{(SMOW)}$ compositions of calcite and dolomite carbonate phases from sandstones and shales in the Cretaceous formations of the Alberta Basin, Western Canada Sedimentary Basin. Data was taken from Table 2.1; height of the bars for specific formations reflect relative abundances of carbonate at a specific isotopic composition. The uppermost Jurassic formation is provided at the base of the figure for reference.

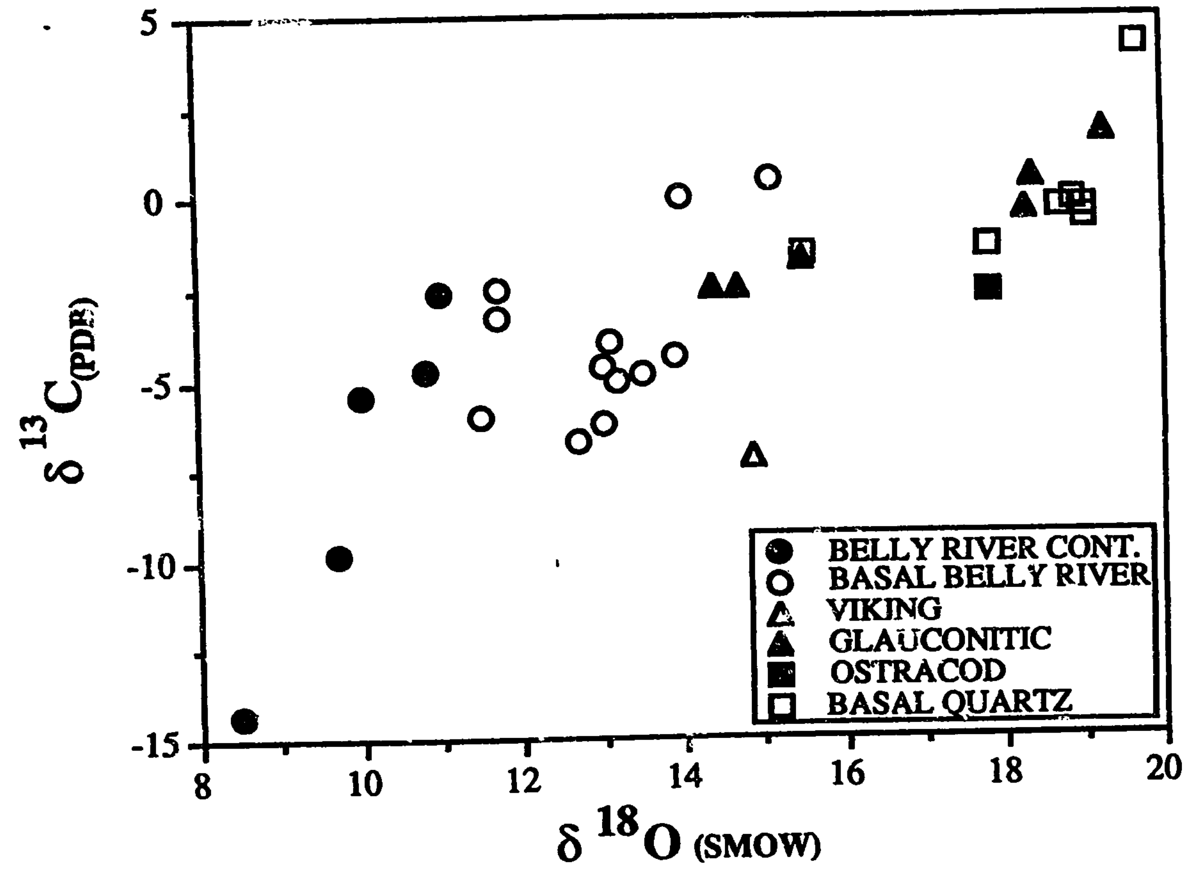


Fig. 2.5. $\delta^{13}C_{(PDB)}$ versus $\delta^{18}O_{(SMOW)}$ plot of authigenic calcite cements from Cretaceous formations in the Alberta Basin.

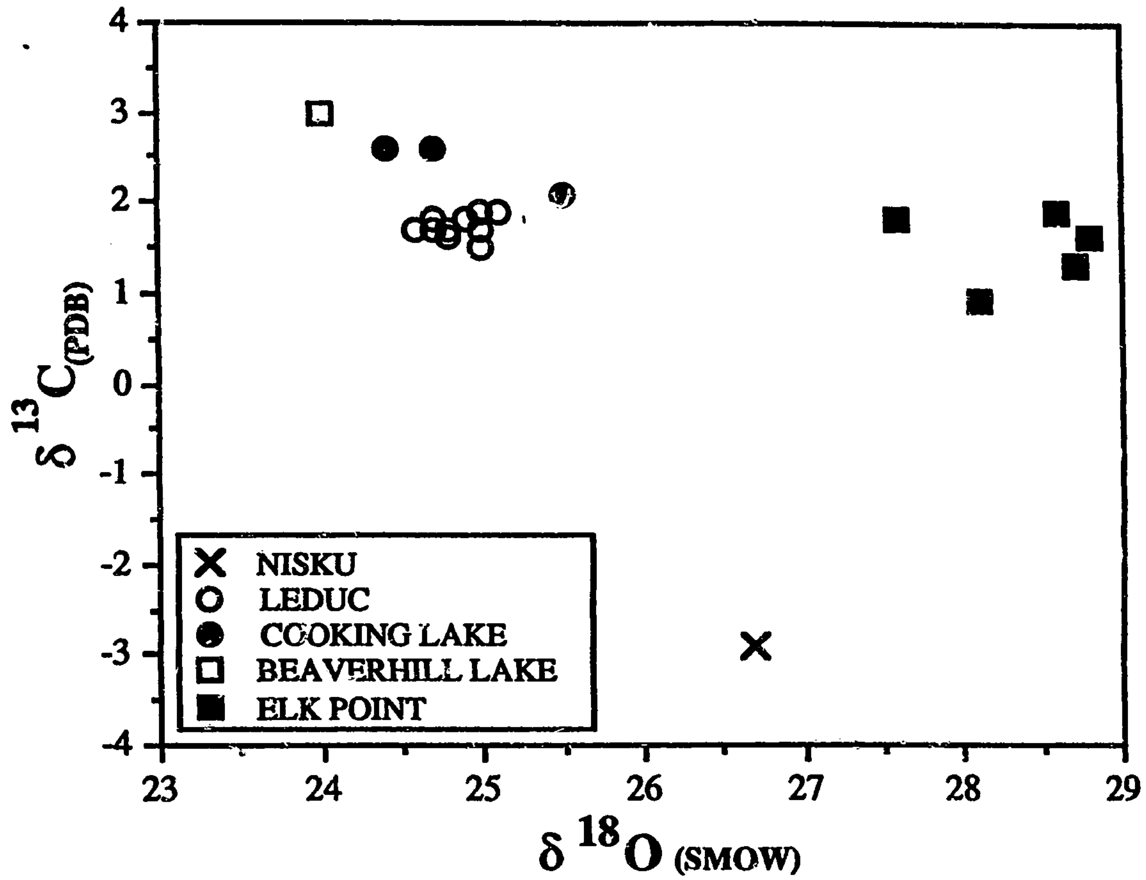


Fig. 2.6. $\delta^{13}C_{(PDB)}$ versus $\delta^{18}O_{(SMOW)}$ plot of the calcite and dolomite phases from the Devonian Nisku, Leduc, Cooking Lake, Beaverhill Lake and Elk Point stratigraphic units, in the Alberta Basin.

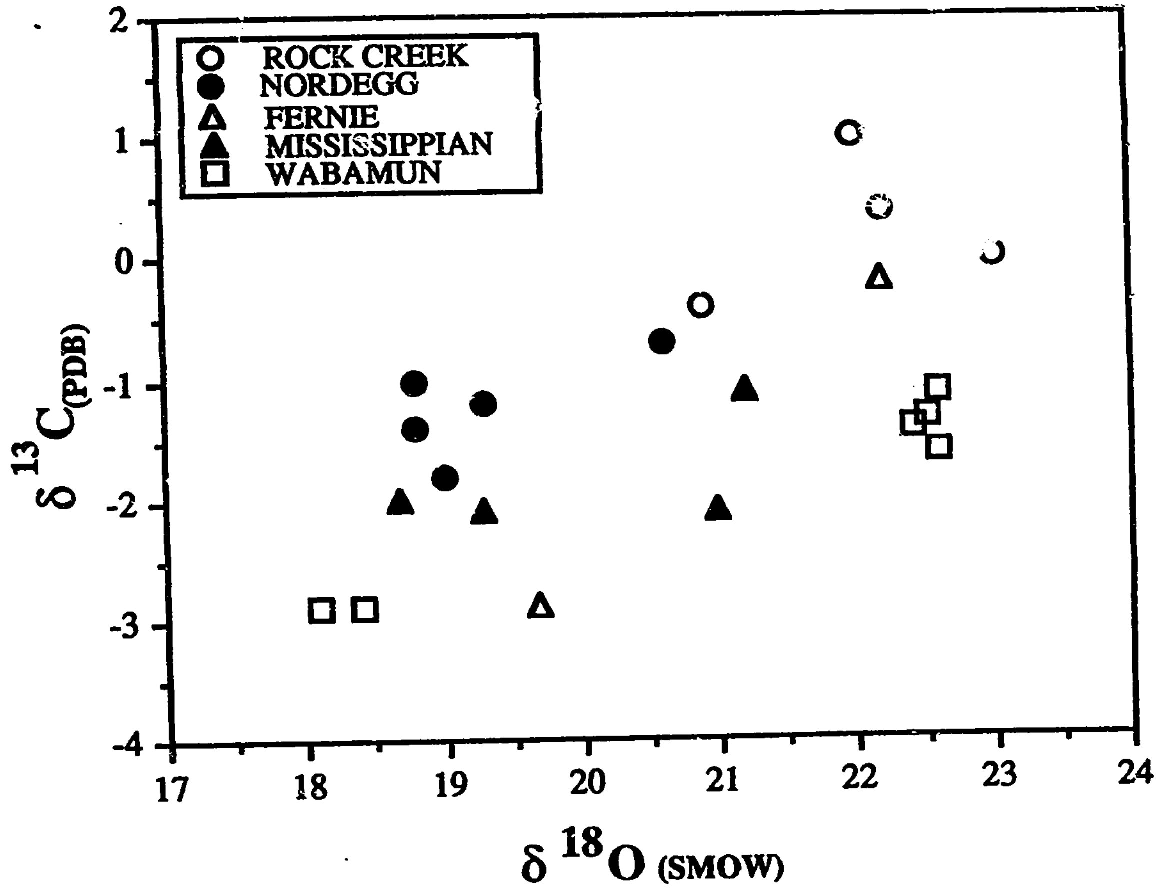


Fig. 2.7. $\delta^{13}C_{(PDB)}$ versus $\delta^{18}O_{(SMOW)}$ plot of the calcite phases from the Wabamun, Mississippian, Fernie, Nordegg and Rock Creek stratigraphic units in the Alberta Basin.

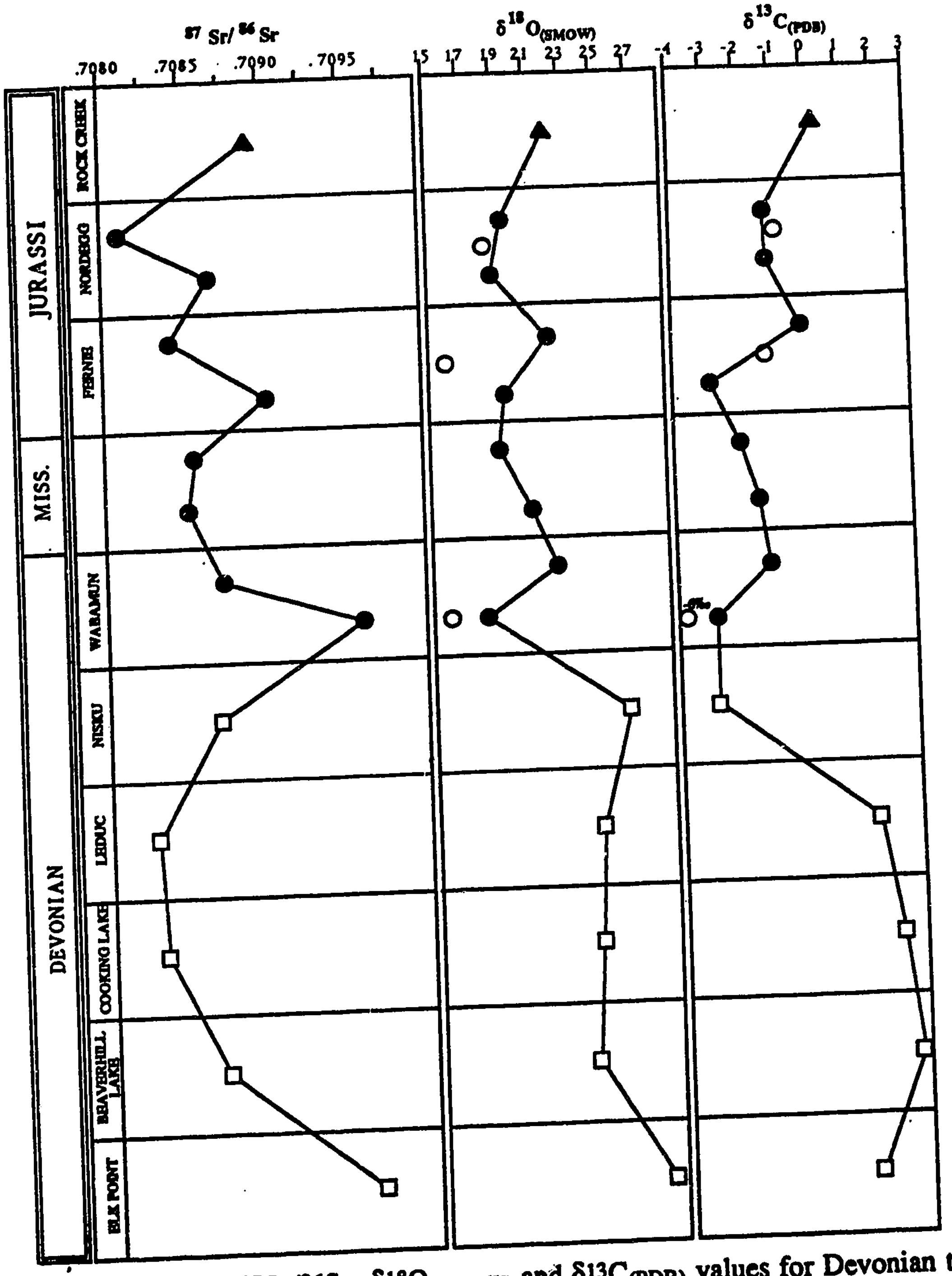


Fig. 2.8. Average $^{87}Sr/^{86}Sr$, $\delta^{18}O_{(SMOW)}$ and $\delta^{13}C_{(PDB)}$ values for Devonian through Jurassic carbonates. Each formation is represented by a spatially equivalent subdivision, which is not representative of the amount of time for each system or the thickness of the lithologic unit. Each point found at a correlative local horizontally across the figure represents an average value for the samples; data was taken from Table 2.1. Where there was an obvious disparity in the data with depth within a single formation, two averages were calculated for one formation. Symbols stand for the following: (□) W.R. Dolomite; (●)W.R. Calcite; (▲) W.R. Carbonate; (○) Diagenetic Calcite (Micro-drilled).

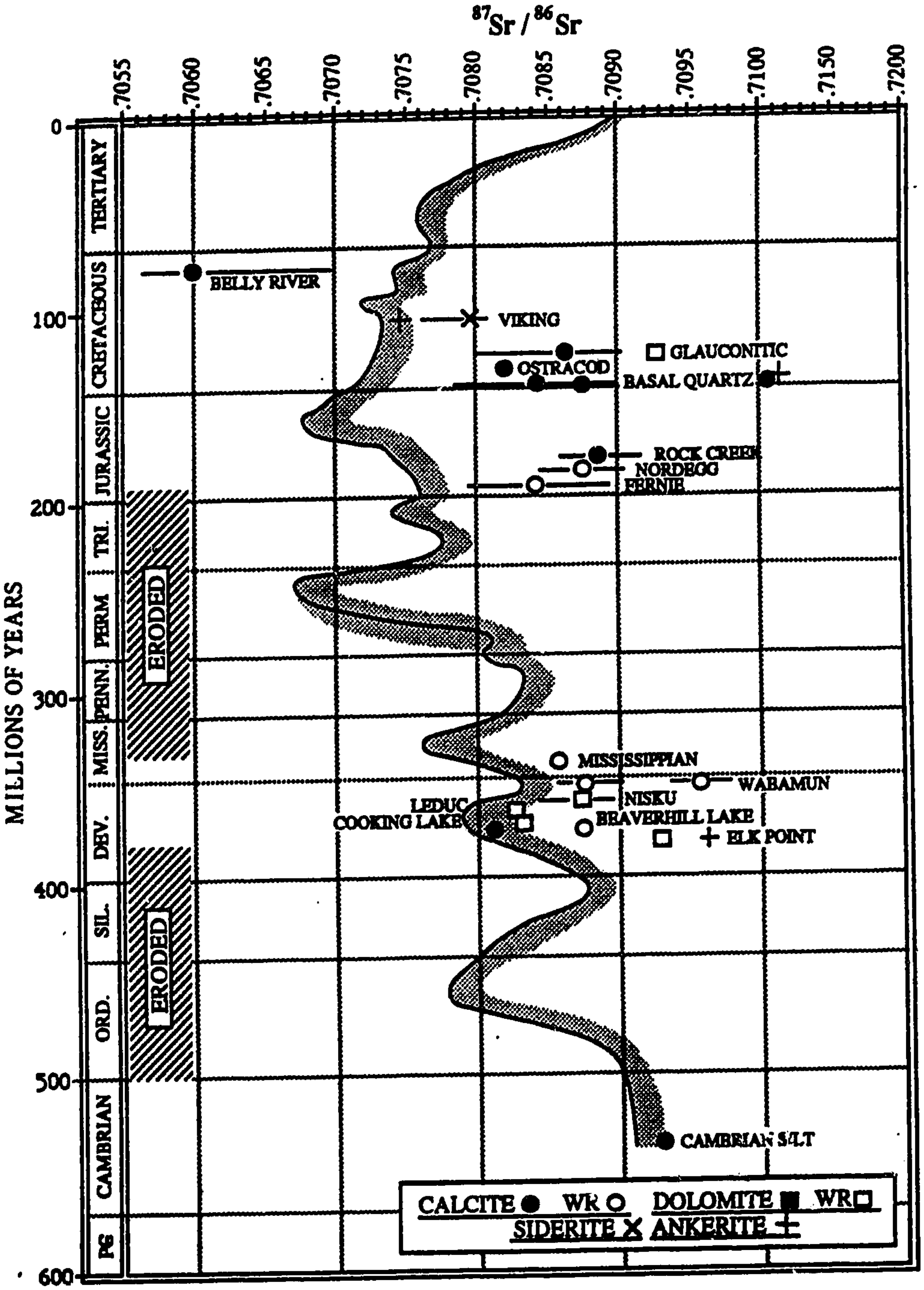


Fig. 2.9. Strontium isotopic composition of whole rock limestones, whole rock dolostones, detrital dolomites and authigenic calcites, siderites and ankerites from the Alberta Basin. The seawater curve is from BURKE *et al.* (1982). Note that most of the whole rocks and authigenic cements have a more radiogenic $^{87}Sr/^{86}Sr$ signature than seawater for a specific time period, with the exception of diagenetically early calcite in the Cambrian, some Devonian rocks and Upper Cretaceous cements.

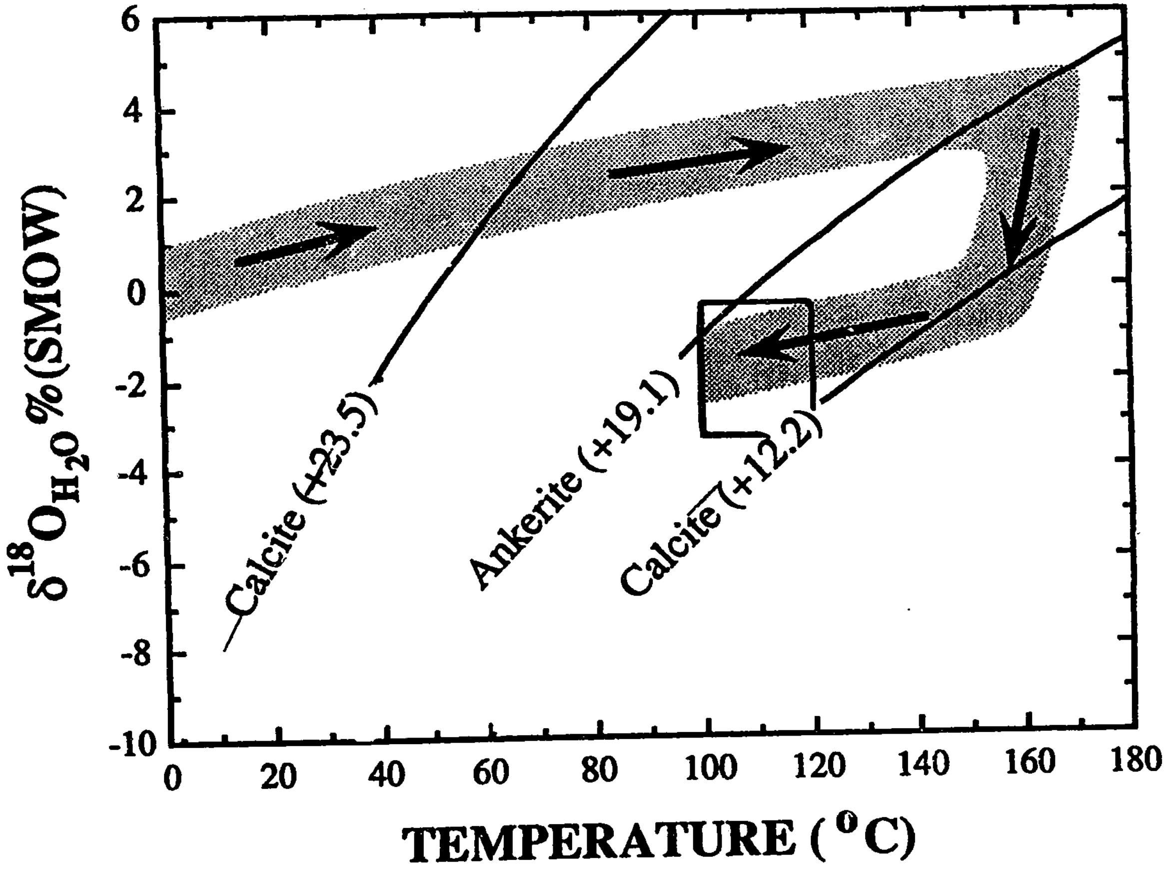


Fig. 2.10. $\delta^{18}O_{(SMOW)}$ of porewater versus temperature for diagenetic carbonates from Cambrian formations in the Alberta Basin, Western Canada Sedimentary Basin. The $\delta^{18}O_{(SMOW)}$ values of each phase was calculated using the following equations (T=degrees K): (1) $10^3\ln\alpha_{calcite\text{-}H2O}=2.78(10^6)T^{-2}-2.89$ (FRIEDMAN and O'NEIL, 1977 after O'NEIL *et al.*, 1969); (2) $10^3\ln\alpha_{ankerite\text{-}H2O}=2.78(10^6)T^{-2}+0.32$ (DUTTON and LAND, 1985). The field encompassing present day conditions for the Cambrian sandstone is outlined.

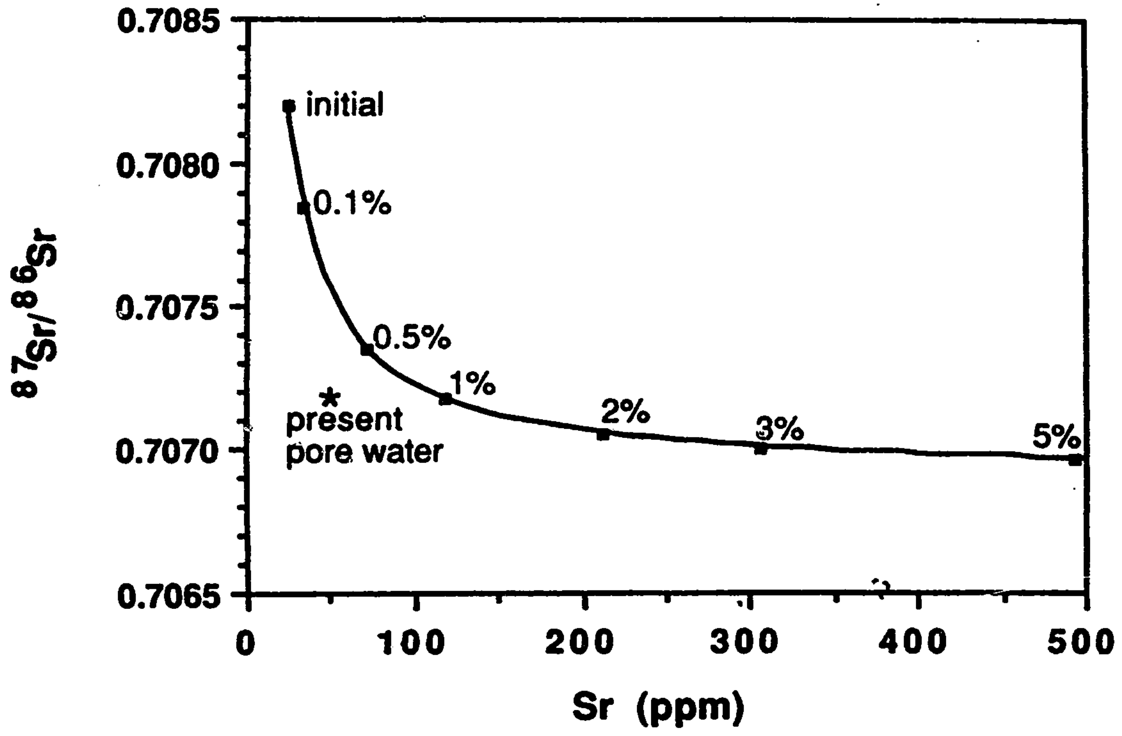


Fig. 2.11. $^{87}Sr/^{86}Sr$ *vs* Sr (ppm) mixing diagram illustrating the effect of plagioclase dissolution on pore water strontium. Percentages indicate the volume % of plagioclase dissolved into the pore fluid from the bulk rock, including porosity. Model assumes an inital rock with 20% porosity filled with pore water containing 25 ppm strontium ($^{87}Sr/^{86}Sr$ =0.7082) and plagioclase with 700 ppm strontium (0.7069). Precipitation of carbonate cement from evolving pore water would result in a decrease in total Sr in the water, with no change in the ratio (modified after SCHULTZ *et al.*, 1989).

CHAPTER 3. ORIGIN AND EVOLUTION OF FORMATION WATERS, ALBERTA BASIN, WESTERN CANADA SEDIMENTARY BASIN.

I. CHEMISTRY

INTRODUCTION

The origin of saline brines in sedimentary basins is a controversial topic. Early investigators advocated a simple connate origin (WHITE, 1965). More recently, the concept of complete flushing of sedimentary basins by meteoric waters was introduced in an attempt to explain isotopic data (CLAYTON *et al.*, 1966) and later, the importance of flushing of sedimentary basins by gravity driven flow was stressed by hydrodynamic flow models (TOTH, 1980; GARVEN, 1985; BETHKE, 1986). However, there is now growing chemical and isotopic evidence that in some settings, waters may still be present that have been hydrologically isolated since entrapment during sedimentation (KNAUTH and BEEUNAS, 1986; KHARAKA *et al.*, 1987; KNAUTH, 1988). Amalgamation of these two ideas has resulted in hypotheses that call for mixing of meteoric and modified connate waters (HITCHON and FRIEDMAN, 1969) and suggestions that a component of dense connate water may not be completely removed from an aquifer (DOMENICO and ROBBINS, 1985). As a result, a wide variety of interpretations for the provenance of basinal waters have been offered, with most discussions focusing on three mechanisms for the production of the basinal brines: shale membrane filtration, infiltration of subaerially evaporated seawater, and dissolution of evaporite deposits (GRAF *et al.*, 1966; CARPENTER, 1978; HANOR, 1979). Regardless of which model is favored, it is known that water undergoes chemical and isotopic changes through fluid movement and mixing, mineral dissolution and precipitation, diffusion from adjacent shales, and organic maturation reactions, all of which are reflected in the present chemical compositions of formation waters.

The Western Canada Sedimentary Basin is considered to be a classic example of a basin dominated by gravity driven flow, and many studies have been made on the basinal fluids. BILLINGS *et al.* (1969) examined the water chemistry and concluded that membrane filtration was the dominant control of salinity. In a more detailed investigation, HITCHON *et al.* (1971) used statistical analyses to arrive at a chemical model whereby original seawater evolved in composition and was influenced by recharged meteoric water, exchange with carbonates, membrane filtration, solution of evaporites, formation of new minerals and exchange with clays and organic matter. Recently, SPENCER (1987) speculated that residual evaporite brines played a major role in the evolution of Devonian brines in the basin and were modified by reaction with the Precambrian basement and subsequently diluted by meteoric waters. The study presented here examines formation waters from Devonian-Cretaceous reservoirs in the Alberta Basin and focuses on formational interdependence and water-rock interactions. The study is spatially restricted to the central region of the Alberta Basin so lateral variations inherent in some basin-wide studies are avoided.

This paper is the first of three and concentrates on the chemistry, origin and evolution of Alberta Basin formation waters. Forty-three water samples from Devonian through Cretaceous strata were analyzed for alkalinity, major, minor and trace cation compositions, anion compositions, H_2S content and S isotopes, and short-chain aliphatic acids (SCA). Other than the studies of KHARAKA *et al.* (1985) and KHARAKA and CAROTHERS (1986), no information has been hitherto reported on the distribution of SCAs in oil field waters from reservoirs older than Mesozoic. Furthermore, no SCA data exist for the Alberta Basin formation waters. Present water chemistries and late diagenetic events are discussed in terms of water mixing and water-rock interactions. Radiogenic and stable isotope data are discussed in the second paper (CONNOLLY *et al.*, 1990) and chemical thermodynamics are used in the third paper to calculate equilibrium mineral assemblages from the water chemistry. The existence of three distinct water groups in the basin and the degree of inter-relationship among them, is described in all three papers.

GEOLOGICAL SETTING OF THE ALBERTA BASIN

The Alberta Basin is part of the Western Canada Sedimentary Basin, bordered to the west by the Rocky Mountain Thrust Belt, to the northeast by the Precambrian Shield, and to the southeast by the Sweetgrass Arch (Fig. 3.1). The Alberta Basin is a simple monocline comprised of essentially undeformed, southwesterly dipping Mesozoic and Paleozoic sedimentary rocks which rest unconformably on Precambrian rocks of the Canadian Shield (Fig. 3.2). Adjacent to the Rocky Mountain Foothills, the sedimentary package exceeds 5,700 m, but thins to the east owing both to depositional thinning and erosion. Mesozoic strata include Cretaceous sedimentary rocks composed of thick shale and siltstone units interbedded with thin sandstones (Table 3.1). A major regional unconformity separates these rocks from eroded Jurassic and Paleozoic carbonates, shales and evaporites. A more subtle unconformity separates Mississippian from Jurassic rocks. Upper Mississippian, Pennsylvanian, Permian, Triassic, and most of the Jurassic have been eroded from the Central Plains of Alberta.

The tectonic history of the Western Canada Sedimentary Basin has been strongly influenced by the Canadian Cordillera, with the present day morphology originating via orogenic forces in the Jurassic-Cretaceous period (NELSON, 1970). The Columbian Orogeny occurred near the end of the Jurassic as a result of subduction of the Pacific Plate beneath the edge of the North American Plate, and shortening across the orogen initiated formation of the Rocky Mountains (PRICE, 1973; DICKINSON and SNYDER, 1978; BEAUMONT, 1981; JORDON, 1981). The Late Cretaceous was marked by the first pulse of Laramide tectonism, with thrusting and uplift occurring along the eastern Cordillera (TAYLOR *et al.*, 1964). The major pulse of the Laramide Orogeny occurred in

Late Paleocene or Early Eocene, resulting in maximum burial of the foreland basin (TAYLOR *et al.*, 1964; PORTER *et al.*, 1982; HITCHON, 1984). Subsequent erosion of accumulated Tertiary and Upper Cretaceous rocks has occurred.

The current hydrodynamic regime in the Alberta Basin was initiated by the second orogenic pulse of the Laramide Orogeny. Associated overthrusting produced a large hydraulic head in the eastern Foothills, creating a mechanism for deep penetration of meteoric waters which discharged eastward (HITCHON, 1969a; HITCHON, 1984). Prior to the Laramide Orogeny, it is doubtful that a hydraulic head greater than that generated by the present Canadian Cordillera ever existed (HITCHON and FRIEDMAN, 1969). It has been suggested that the Upper Devonian-Carboniferous carbonate rocks channel flow from most of the Alberta Basin toward the northeast in the role of low fluid potential drain for the basin (HITCHON, 1969b; HITCHON, 1984). However, GARVEN (1989) suggests that the regional flow system has undergone dissipation and partitioning, at least since the Pliocene, with younger, shallower formations developing smaller flow sub-systems.

SAMPLE COLLECTION AND ANALYSIS

Prior to sampling, care was taken to ensure that the oilfield waters collected were not exposed to water flood or other potential sources of anthropogenic contamination, such as swabbing or acidizing. All water samples were collected exclusively from oil fields to avoid dilution problems associated with gas wells. Oil-water emulsions were collected in large acid-cleaned bottles from the well-head of producing oil-wells and the two phases were allowed to separate. The waters were filtered through glass wool to remove any solids and oil droplets. If H_2S gas was present, two filtered aliquots were immediately collected in 500 ml glass jars containing excess cadmium acetate (1.5 g) to precipitate dissolved sulfide as CdS.

Water from the macroporous filter was subsequently passed through a 0.22-µm filter using a pressure-driven automated filtration device. A 125 ml aliquot was collected for pH, density, total alkalinity and Cl measurements, with the former three determinations being performed immediately in the field. The pH was measured using a combination electrode and portable pH meter, density with a portable densitometer, and total alkalinity potentiometrically by Gran titration (GIESKES and ROGERS, 1973). The Cl measurement was done by $AgNO_3$ potentiometric titration in the laboratory. A *reverse alkalinity* measurement was made by back-titrating the *forward total alkalinity* sample solution with a weak base (0.05N NaOH), using a potentiometric technique to select the endpoint. Reverse alkalinity is primarily contributed by short-chain aliphatic acids (SCA) (WILLEY *et al.*, 1975). Subtracting the reverse alkalinity from the total alkalinity provides a good estimate of the carbonate alkalinity because of the low concentration of other protolytic species at the low pH values of these brines.

Samples for SCAs were collected in 125 ml glass amber bottles containing a bactericide (cupric chloride; 0.5 g). These samples were immediately refrigerated until analysis. Concentration and identification of SCAs were conducted by ion exclusion chromatography (ICE) on a Dionex 4000i series ion chromatograph, using an ICE-AS1 column. Conditions selected do not differentiate between isomers of butyrate or valerate. Each water solution was diluted and pretreated with an On Guard-Ag cartridge containing a high capacity, strong acid cation exchange resin in Ag form, which removed Cl, Br and I (and other Ag insoluble species) from sample matrices. The sample was injected into the AS1 exchange column and eluted at 0.8 ml/min flow with 0.2 mN HCl eluant (2% 2-propanol). Suppressed background conductivity detection (anion micro-membrane suppressor; 6 mM tetrabutylammonium hydroxide, approximately 2 ml/min) was used. Retention times were approximately: acetate 13 min; propionate 15 min; butyrate 18 min; valerate 27 min. Recovery was > 98%, so no correction has been made to the data.

Precision was ± 5% for acetate and ±20% for propionate and butyrate.

A 250 ml aliquot was acidified to pH<2, using HNO_3, for analysis of cations by a Leeman Labs Plasma-Spec III inductively coupled plasma-atomic emission spectrometer (ICP-AES). The samples were analyzed in simultaneous mode and in two separate groups; (1) major elements (Ca, B, Ba, Mg, Na, Sr) at 1:100 and 1:50 dilution and (2) minor and trace elements (Fe, K, Li, Mn, Pb, Si, Zn) at 1:10 or undiluted. Replicate analyses of gravimetric standard solutions indicate a precision better than ±2%.

A 125 ml aliquot containing 0.5 g cadmium chloride was used for Br and SO_4 analysis by ion chromatography. Bromide was measured on an AS2 column at an eluant flow rate of 2.5 ml/min and SO_4 was measured on an AS5 column at an eluant flow rate of 1.5 ml/min. Suppressed background conductivity detection (anion micro-membrane suppressor; 25 mN H_2SO_4, ~4 ml/min) was used. The eluant was 2 mM NaOH; 4.5 mM Na_2CO_3; 2% CH_3CN and 0.8 mM 4-cyannophenol. Precision of anion analyses is better than ±2%.

Samples for S isotopic analyses of dissolved SO_4 and S were collected in a 250 ml bottle containing 1.5 g of cadmium acetate. The Cd-acetate present exceeded the molality of dissolved H_2S, thus all H_2S was trapped as CdS. The CdS was filtered and barium chloride added to the filtrate to precipitate sulfate as $BaSO_4$ (LONGINELLI and CRAIG, 1967).

The H_2S collected and precipitated with cadmium acetate at the wellhead was quantitatively converted in the laboratory to Ag_2S by acidification and sparging into a 1M $AgNO_3$ solution. The SO_2 gas for S isotope analyses was produced by combustion of Ag_2S with Cu_2O at 950°C under vacuum, and $BaSO_4$ was reacted with sodium metaphosphate at 950°C under vacuum. Sulfur isotope ratios were measured on a VG mass spectrometer and results are reported in the standard δ notation relative to Canyon Diablo troilite (CDT).

Depths and temperatures were determined from logs. Depths were set as the mid-point between perforations. Maximum bottomhole temperatures recorded from the logs were corrected for cooling by drilling processes (KEHLE, 1971) and extrapolated back to the depth of the formation of interest assuming a geothermal gradient of 30°C/km (HITCHON, 1984).

RESULTS AND DISCUSSION

General

Chemical compositions, densities, temperatures and depths of Alberta Basin formation waters are summarized in Table 3.2. Most samples have charge balance errors <±2%, as determined by direct analysis. Total dissolved solids (TDS) were calculated by summing the concentrations of all the major and minor ions, and are in the range from 4 - 235 g/l. The average TDS is 80 ± 47 g/l, making the waters relatively dilute and variable in salinity compared to waters in some other basins which have been extensively studied, such as the Palo Duro Basin (FISHER and KREITLER, 1987), the Appalachian and Michigan Basins (McNUTT *et al.*, 1987) and the Mississippi Interior Salt Basin (KHARAKA *et al.*, 1987). Formation water temperatures in the study area range from 35 to 75°C; the average temperature being 53±10°C. Samples were obtained from depths of 680 to 1970 m; the average depth is 1333 ± 312 m.

According to the water classification of HEM (1970), all of the waters are brines (TDS>35 g/l), except those from the Rock Creek, Belly River and Cardium stratigraphic units. The former two formational waters are classified as saline (TDS = 10 - 35 g/l) and the latter as brackish (TDS = 1 - 10 g/l). Location in the basin, stratigraphic position and lithologic composition of the reservoir rocks appear to be more important than depth in controlling the TDS. Most of the waters are Na - Cl brines, with Na comprising >90% of the total cations and Cl comprising >98% of the total anions. Exceptions to this are: (i) several Devonian samples, which are actually Na-Ca-Cl brines (CARPENTER, 1978) and are the most concentrated of all the samples; and, (ii) all of the Cardium waters which are HCO_3^- – Na waters and are the most dilute. Sodium and Cl are extremely well correlated in all the formation waters (r=0.98). Figure 3.3 shows a cross section through the study area illustrating the formation-water concentration distribution within the basin, with contours showing equal values of Cl concentration. The contour lines dip in accordance with the rocks, with more dilute waters extending to greater depths toward the southwest, closer to the potentiometric high for the basin. A <5 g/l concentration contour is shown towards the SW, which approximates the distribution of the Cardium Formation (Fig. 3.2). This formation is more porous than surrounding shale units and meteoric fluids are likely directed toward the Cardium in the direction of decreasing free energy.

Alkalinity and Short-Chain Aliphatic Acids

Short-chain aliphatic acid anions (SCA) are water-soluble volatile fatty acids with five or fewer C atoms (C_2-C_5) per molecule. The observed order of aliphatic acid anion abundance for most basin brines is acetate>>propionate>butyrate>valerate. Total SCA concentrations for Alberta Basin waters vary from 0 to 932 mg/l over a temperature range of 40 to 75°C (Table 3.3). As in other sedimentary basins, acetate is by far the most abundant SCA ranging from 0 to 844 mg/l. However, at low total SCA concentrations, the weight percent of acetate is more variable, with other SCA species commonly becoming more significant (Fig. 3.4). Propionate concentrations range from 0 to 74 mg/l, becoming more abundant in stratigraphically younger, though not necessarily lower temperature, units. Values up to 17.1 mg/l were obtained for butyrate. Valerate and dicarboxylic acid anion concentrations were below detection limits.

Influence of SCAs on Alkalinity

Alkalinity is a key parameter in controlling carbonate mineral saturation states and the pH buffer capacity of subsurface waters. Short-chain aliphatic acids may contribute significantly to the total titration alkalinity, as demonstrated in many other sedimentary basin brines, including those from the San Joaquin Valley, Houston and Corpus Christi (WILLEY *et al.*, 1975; CAROTHERS and KHARAKA, 1978; SURDAM and CROSSEY, 1985); south Louisiana (WORKMAN and HANOR, 1985; HANOR and WORKMAN, 1986); and offshore Texas (KHARAKA *et al.*, 1985).

The reverse alkalinity measurement was used as a reasonable approximation of the total SCA content in the waters. This value made it possible to compensate for SCA effects to the titration alkalinity measurement, thereby omitting pre-analytical sample treatment usually required to isolate organic from alkaline species. This is advantageous because SCAs are easily volatilized during the isolation procedure. The reverse alkalinity value agrees reasonably well with the summation of individual SCA species as determined by ion chromatography (Table 3.3). Figure 3.5 illustrates the variable influence of SCA concentration on total titration alkalinity measurements in the Alberta Basin. Short-chain aliphatic acid anions can constitute up to 91% of the total titration alkalinity in Alberta Basin waters.

Occurrence and Distribution of SCAs

In sedimentary basins, SCAs may be produced by bacterial SO_4 reduction and methanogenesis (HATTON and HANOR, 1984) or they may be formed abiotically during thermal maturation of organic matter (SURDAM *et al.*, 1984). Conversely, SCAs can also be consumed by bacteria or, if temperatures are >85°C, degraded by thermal decarboxylation into methane, ethane, propane or butane. CAROTHERS and KHARAKA (1978) suggested that concentrations of SCAs define three temperature zones. Zone 1 is characterized by temperatures <80°C and SCA concentrations <60 mg/l, consisting principally of propionate. Zone 2 corresponds to temperatures of 80-200°C and much higher concentrations of SCAs (up to 4900 mg/l). Acetate forms 90% or more of the total SCAs and the concentration of all SCAs decrease with increasing temperature. Zone 3 has temperatures >200°C and is inferred to have no aliphatic acid anions present. Microbiological degradation of acetate by methanogenic bacteria and dilution by mixing with meteoric waters were postulated to explain the composition and concentration of SCAs in zone 1; thermal decarboxylation of SCAs was thought to decrease the concentration of SCAs in zone 2.

Although the temperatures of the formation waters in the Alberta Basin (35° to 75°C) correspond to zone 1 of the classification of CAROTHERS and KHARAKA (1978), the predominant SCA is acetate, with concentrations often >60 mg/l. Bacterial action can alter the order of aliphatic acid anion dominance, with acetate preferentially degraded relative to propionate, and propionate preferentially degraded relative to butyrate and valerate. However, the general observation that longer chain aliphatic acid anions dominate in low temperature reservoirs (CAROTHERS and KHARAKA, 1978; WORKMAN and HANOR, 1985) is not substantiated by data for the Alberta Basin, or for some other basins (KHARAKA *et al.*, 1985; MEANS and HUBBARD, 1987; FISHER, 1987). High acetate concentrations can result from a lack of methanogenic bacteria (KASPER and WUHRMANN, 1978). Thus, acetate dominance, rather than suggesting a lack of bacterial activity, may indicate the type of bacteria that is or is not present. Propionate and butyrate appear to become more significant in Alberta Basin waters in stratigraphically younger units that have relatively lower total organic acid contents (Fig. 3.4b), but there are insufficient data to define distinct relations.

Short-chain aliphatic acid concentrations, within a given formation, are significantly lower in waters containing H_2S (see Table 3.3). Sulfate-reducing bacteria are likely depleting the SCA concentration (MEANS and HUBBARD, 1987) by reaction (1):

$$CH_3COO^- + SO_4^{-2} \leftrightarrow 2HCO_3^- + HS^- \qquad (1)$$

In support of this mechanism, those waters containing H_2S and lower SCA concentrations also have higher carbonate alkalinities (Table 3.3).

Both bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR) have been cited as mechanisms responsible for H_2S generation in Devonian reservoirs of the Alberta Basin (KROUSE, 1980; MACHEL, 1987; KROUSE *et al.*, 1988). Sulfur isotopic data obtained in this study (Table 3.3) can be used in concert with data from KROUSE (1980) for waters in the study area, to evaluate the relative importance of these mechanisms. KROUSE (1980) noted in a survey of $\delta^{34}S$ values for SO_4 and S, that there was a marked transition from BSR to TSR at present reservoir temperatures near 80°C. This is reflected in the $\delta^{34}S$ values for SO_4 in formation waters, which are approximately $+40‰_{CDT}$ at lower temperatures and $+20‰_{CDT}$ at higher temperatures. All of the water sampled in this study resided in low temperature reservoirs (<75°C). The few samples analyzed here are similar to those of KROUSE (1980) and corroborate the hypothesis that these waters are undergoing BSR as shown by equation (1). Furthermore, the $\Delta\delta^{34}S$ for SO_4^{-2} - H_2S are relatively high in the waters examined in this study, which is characteristic of the lower temperature, BSR zone.

The concentrations of SCAs in Alberta Basin formation waters are not directly interpretable in terms of temperature, depth, salinity, or geological age of the reservoir, but they do exhibit a strong relation with proximity to source rock, primarily the Jurassic, but also the Mississippian shales (Fig. 3.6). Jurassic and Devonian (Duvernay) shales are the most organic-rich shales in the Alberta Basin (DEROO *et al.*, 1977; MOSHIER and WAPLES, 1985); however, many Devonian waters contain H_2S, likely of bacterial origin. Thus, even if SCA generation had been important in Devonian source rocks, as it apparently is in Jurassic shales, SO_4 reducing bacteria would have utilized them. Reverse alkalinity measurements suggest that most of the Devonian waters, other than one sample with a low H_2S content, had extremely low SCA abundances (Table 3.3).

In other studies of oil field brines, $\delta^{18}O$ values and Br concentrations have been related to SCA concentrations (MEANS and HUBBARD, 1987). Little correlation between SCAs and these chemical parameters is observed for Alberta Basin formation waters. Anomalously high values of Br are observed in some of the high SCA waters, particularly those in the Jurassic and Mississippian. However, there is no consistent trend established, possibly because of variable amounts of bacterial degradation affecting the SCA concentration in a non-linear fashion. Values of $\delta^{18}O$ become slightly more positive with increasing total SCA content suggesting that water-washing and dilution may have decreased the total SCA concentrations.

High Alkalinity in the Cardium Formation

Anomalously high alkalinity values exist in the formation waters sampled from the Cardium Formation. These waters are dilute and are derived from fluid movement upwards into the formation through a shale membrane (Fig. 3.7), the Second White Speckled Shale. GRAF *et al.* (1966) and GRAF (1982) have proposed a model for shale membrane filtration that may be considered as a cause of the Cardium Formation water chemistry; however, this model necessitates $NaHCO_3^o$ passing through shale membranes to remove excess Na and aqueous carbonate from the input to effluent solutions and this complex is very weak and likely ineffective (NESBITT, 1980).

DEMIR (1988) has shown that the concentration drop of Na molality across a compacted smectite membrane is only 0.8 for a transient period and 0.3 molality units at steady state. A number of smectite-enriched bentonite beds in the Lower Cretaceous units of Alberta have been documented (AMAJOR, 1978, 1980; TIZZARD and LERBEKMO, 1975); however, these units are rare in the study area, with smectite being found in only one Blairmore and one Viking sample. Thus, shales in the study area would be much less efficient membranes than those in the study of DEMIR (1988). The difference in molality on the immediate influent and effluent sides of the Cardium Formation is a little more than 0.8 molality, which is too large a variation considering the shale mineralogy characterizing the formations does not provide the most efficient filtration. Furthermore, the shale unit containing the most smectite in the Lower Cretaceous (the Joli Fou Formation) is stratigraphically lower than the Viking Formation. This shale unit would provide the most efficient membrane in the study area. If membrane filtration is the significant cause of the Cardium Formation water chemistry, similar concentrations and alkalinities should then be observed in the waters of the Viking Formation, and such is not the case. Therefore, although membrane filtration may affect Cardium waters to a minor degree, the process does not effectively explain the chemistry observed, so other processes must be considered.

The Cardium alkalinity values are better understood when examined in conjunction with data on the existing flow regime and the geometry and distribution of lithologies (Fig. 3.7). The Cardium Formation is a marine sandstone bounded by low permeability shales. Meteoric waters flushing through the Cardium Formation, as indicated by hydrological, chemical and isotopic data, would cause oxidation of organic matter in surrounding shales to CO_2 (MACHEMER and HUTCHEON, 1988). Solution of this CO_2 would increase fluid buoyancy and CO_2-charged waters would migrate through the Cardium Formation and be trapped by overlying shales. The pH of the water should remain relatively constant, buffered by organic debris or mineral assemblages (BERNER, 1981) and high alkalinity values result. Furthermore, it has been demonstrated that dilute meteoric waters are dominated by Na, Ca and HCO_3^- and contain little Cl (GARRELS, 1967; GARRELS and MACKENZIE, 1967; NESBITT, 1985). Cardium Formation waters have compositions similar to meteoric waters, except for the Ca concentration. The lack of Ca is likely a result of calcite cementation and clay-mineral cation-exchange reactions. Dilute meteoric waters invoke cation exchange reactions on clay minerals causing increased concentration of Na in the fluid phase and Ca on the clays (CERLING *et al.*, 1989).

Solution - Mineral Equilibria

Thermodynamic controls on formation water composition must be investigated before evaluating potential sources of water molecules and solutes. Stability relations between subsurface waters and various mineral phases can be evaluated by calculating the ion activity product (IAP) of the minerals in each analyzed water and comparing this value to the equilibrium constants of the mineral (K_T) at a specific temperature. This is referred to as the saturation index (S.I.) and is technically defined as S.I. = log (IAP/K_T). A positive log S.I. value indicates supersaturation of the solution with respect to the mineral, a negative log S.I. value undersaturation, and zero indicates equilibrium. The degree of undersaturation or oversaturation is indicated by the magnitude of the logarithm.

Aqueous species distribution and mineral saturation states were computed using the computer code EQ3NR (WOLERY, 1983). In this program, the $\dot{B}$ equation (HELGESON, 1969) is used to approximate activity coefficients of aqueous species. These approximations should be limited to applications in which the *true* ionic strength is no greater than 1 molal. However, because of complexing, the true ionic strength is much less than the stoichiometric ionic strength and solutions having stoichiometric ionic strengths up to ~ 3 can be evaluated with confidence. Except for one Leduc (11-15-50-26W4) and one Nisku (15-29-49-26W4) sample, this stipulation is met by all the samples discussed here.

All Alberta Basin formation waters are saturated with respect to quartz (Fig. 3.8), regardless of the TDS value or whether they are from carbonate or clastic rocks. This confirms that the salinities represent *in situ* conditions and have not been diluted by condensed water vapor during sample collection.

Although the formation waters are predominantly of the Na - Cl type, they are several orders of magnitude undersaturated with respect to halite. Saturation indices range from -1.45 to -4.19 (mean value =-1.89), with values approaching saturation with increasing ionic strengths.

Saturation with respect to carbonate minerals cannot be calculated directly because measured pH values are affected both by degassing resulting from pressure release during sampling and by oxidation of Fe. The former effect results in an increase in pH and S.I. in the waters; the latter causes a decrease in these values (FISHER and KREITLER, 1987). Regardless of these uncertainties, equilibration of the formation waters with respect to calcite and some with respect to dolomite, is probably a reasonable assumption considering the following arguments.

First, carbonate minerals and groundwater exhibit rapid equilibration relative to the residence time of deep basin brines (PALCIAUSKAS and DOMENICO, 1976; PLUMMER *et al.*, 1978, 1979; BUSENBERG and PLUMMER, 1982). Correspondingly, the kinetics of calcite and dolomite dissolution suggest that if the brines have been in residence since the Pliocene (GARVEN, 1989), it is likely that saturation by dissolution has been attained, although water-carbonate oxygen isotopic equilibrium has not been reached (CONNOLLY *et al.*, 1990).

Second, the Paleozoic section of the Alberta Basin is dominated by carbonates and all of the Mesozoic clastic units contain calcite cements throughout the paragenetic sequence of their assemblage. Carbonate cements are found late in the paragenetic sequence in many of the clastic units, implying carbonate saturation. The oxygen isotopic compositions of these cements (LONGSTAFFE, 1986; AYALON and LONGSTAFFE, 1988) indicates that they were formed during and subsequent to the Laramide orogeny and concomitant flushing of meteoric waters. At this time the waters were at their most dilute in many parts of the basin, yet carbonate precipitation still occurred.

Finally, saturation indices estimated from measured parameters (Alk$_C$ and Ca) and activities determined using EQ3NR, show the brines to be generally saturated or oversaturated with respect to both calcite and dolomite, even when the pH values are manipulated to very low values. When the pH was set assuming calcite or dolomite equilibrium at the measured carbonate alkalinity, Ca concentration and temperature, the equilibrium pH value decreased from the field measured value by between 0.58 to 1.57 pH units (average = 1.04 ± 0.2). Hence, the assumption of saturation is supported, as it is unlikely that measured pH values are much more than a log unit higher than the true subsurface values.

Figure 3.8a shows the S.I. for some of the carbonate phases in the waters, with quartz plotted for reference. Equilibration of the waters with subsurface calcite was used to calculate pH, using the following equation:

$$CaCO_3 + H^+ \leftrightarrow Ca^{+2} + HCO_3^- \qquad (2)$$

with dolomite equilibration being similarly used in those formations where it is pervasive. Considering the uncertainty on the measured pH values, this appears the best way to represent *in situ* pH values. Examining the carbonate phases, magnesite is undersaturated in all the waters, whereas strontianite and particularly witherite are oversaturated.

Low levels of SO_4 (below the detection limit) characterize the stratigraphically highest, most dilute waters in the Alberta Basin (from Belly River, Cardium, and Viking units). When SO_4 is present in waters, they are saturated with respect to barite, but undersaturated with respect to celestite and anhydrite, with the degree of undersaturation becoming more significant in stratigraphically higher, more dilute clastic-hosted waters (Fig. 3.8b). Barite is extremely insoluble and only a low Ba concentration (0.2mg/l) is required to saturate and precipitate this phase. As a result, barite controls the S.I. of witherite to some extent. Witherite has very high S.I. in the dilute formation waters that lack SO_4. However, when SO_4 becomes significant, Ba is precipitated with SO_4 and witherite shows a corresponding decrease in S.I. Celestite is also a very insoluble mineral phase, but strontianite precipitates most of the Sr from solution and barite most of the SO_4, so celestite does not come close to saturation.

Feldspars and clay minerals are the most likely buffers of Na and K, but silicate mineral equilibria in saline brines at slightly elevated temperatures cannot be quantitatively evaluated at present (FISHER and KREITLER, 1987). Furthermore, Al is difficult to measure accurately in these waters. However, Al may be conserved in the reactions, as shown below:

$$2NaAlSi_3O_8 + H_2O + 2H^+ = Al_2Si_2O_5(OH)_4 + 2Na^+ + 4SiO_{2(aq)} \quad (3)$$

$$2KAlSi_3O_8 + H_2O + 2H^+ = Al_2Si_2O_5(OH)_4 + 2K^+ + 4SiO_{2(aq)} \quad (4)$$

By comparing brine ion activity ratios with those predicted by equilibria phase relations at *in situ* temperatures (SUPCRT data base; HELGESON *et al.*, 1978; SHOCK and HELGESON, 1988) the directions of reactions (3) and (4) can be evaluated. The IAP/K values derived for equation (3) suggest kaolinization of albite is occurring which is corroborated by thin section petrography. Kaolinization of K-feldspar (4) is not significant but the IAP/K values of equation (4) approach initiation of the reaction (IAP/K= 0.2). Albitization of plagioclase feldspar is indicated for all of the formation waters; however, albitization of K-feldspar is not suggested. The above reactions give only the direction of the reaction. Such representation is one dimensional and does not consider other reactions which are occurring concurrently. Thus, it is recognized that stability relations are more accurately portrayed on activity - activity diagrams (see Chapter 5).

Trace and Major Element Constraints on Water Origins

The formation water samples from the Alberta Basin can be divided into 3 groups based on isotopic (CONNOLLY *et al.*, 1990) and chemical composition of the waters (Fig. 3.9). Group I waters are dominantly carbonate-hosted (Devonian, Mississippian and lowermost Jurassic (Nordegg Formation) carbonates) but also include waters from the lowermost Cretaceous (Basal Quartz Formation) clastic assemblage. Group II waters are from dominantly clastic, partially carbonate reservoirs, comprised of the Middle Jurassic Fernie Group, and Lower Cretaceous Ostracod, Glauconitic and Viking Formations. Group III waters are from clastic rocks of the Rock Creek (Jurassic) and Upper Cretaceous Cardium Formation and Belly River Group.

The above groups do not necessarily follow the order of the stratigraphic units in the subsurface, with the Middle Jurassic being placed in Group II and the Rock Creek Formation in Group III, although they are stratigraphically lower than the Basal Quartz Formation of Group I. The Jurassic is represented by a small lens of sedimentary rocks in the western part of the basin that is not found at most of the sampling locations. The dip of Cl concentration contours (Fig. 3.3) and of the hydrologic groups towards the southwest (Fig. 3.9) indicate that dilute waters extend to greater depths in this direction. Thus, when water chemistry is considered, Jurassic waters, because of their more westerly sampling locations, are more akin to shallower, less saline waters to the east.

Because the sedimentary rocks in the Alberta Basin are predominantly marine deposited, seawater is an appropriate reference solution with which to compare the formation waters. Such a comparison is justified since seawater composition is considered to have been constant since the Cambrian (HOLLAND, 1984). To test the origin and modification of basinal waters, compositional relations were examined to help determine whether waters originated by one or more of the following: (1) subaerially evaporating seawater; (2) dissolution of evaporite deposits; (3) complete or partial flushing of meteoric waters by gravity driven flow; or, (4) interaction of formation waters with enclosing sedimentary rocks. Graphs illustrating these compositional relations are also useful to distinguish the degree of diagenetic reactions and subsequent water equilibration with host rocks. Osmotic and reverse osmotic processes (GRAF, 1982) are relatively ineffective in the Alberta Basin, for reasons that were addressed earlier in the paper. Thus, mixtures of water molecules and solutes and their sources are evaluated.

Component of Subaerially Evaporated Seawater or Dissolution of Evaporites

During evaporation of seawater, the ratio Cl:Br is constant until halite saturation is reached, at which point Cl is preferentially removed from the fluid and Br is concentrated in the residual solution. The seawater evaporation trajectory (S-E-T) (CARPENTER, 1978) in Fig. 3.10 depicts this relation. The distribution of formation waters on this graph, relative to the S-E-T, can indicate the different origins and processes which have affected water chemistry. Waters which plot directly on the log Cl versus log Br S-E-T, at concentrations greater than seawater, can be tentatively interpreted as subaerially evaporated brines. Waters affected by halite dissolution have an excess of Cl relative to Br and plot above the S-E-T. If waters plot below the S-E-T, they may have evaporated past the onset of halite precipitation and been subsequently diluted by meteoric water or seawater.

Meteoric water is the most likely diluting solution in the Alberta Basin

(CONNOLLY *et al.*, 1990). Addition of meteoric water to seawater evaporated past the point of halite precipitation causes the mixture to move off the evaporation trajectory along a straight line parallel to the sloping portion of the S-E-T (CARPENTER, 1978). Such dilution reduces Br and Cl concentrations in percentages shown by the isopleths in Fig. 3.10. Therefore, formation waters which plot to the right and below the S-E-T may be interpreted as having an evaporite brine component. Recently, the conservative nature of Br in sedimentary basins and its utility in determining the origin of formation water has been questioned. Reverse partitioning of Br can cause an enrichment of Br relative to Cl during halite recrystallization (LAND and PREZBINDOWSKI, 1981; STOESSELL and CARPENTER, 1986). Hence, it is possible that waters derived from halite recrystallization can plot to the right and below the S-E-T.

KHARAKA *et al.* (1987) have also suggested that waters derived from the dissolution of halite and mixed with meteoric or marine waters could result in a water plotting beneath the S-E-T. This possibility was considered by examining the chemistry of some shallow waters in the Alberta Basin (HOLYSH, 1989) and some Belly River formational waters (HITCHON *et al.*, 1971), both of which are dominated by a meteoric fluid component. Hypothetical mixing lines joining these waters with those derived from salt dissolution indicate that the hypothesis of KHARAKA *et al.* (1987) is a highly unlikely explanation for Alberta Basin waters. Greater than 85% meteoric water is required to have the dissolution of halite-meteoric water mixture reach the S-E-T, let alone to have it plot to the right of the S-E-T. Furthermore, if the mixture did plot beneath the S-E-T, it would be extremely dilute and require additional mixing with unreasonably large volumes of seawater which had passed the onset of halite precipitation in order to explain the present position of the waters (Fig. 3.10).

Formation waters from the Alberta Basin cluster in several distinct groups in Fig. 3.10. None of the water samples plot above the S-E-T, suggesting that none of them are derived from congruent halite dissolution despite abundant salt deposits found in the Middle Devonian within and to the east of the study area. HITCHON *et al.* (1971) suggest that halite dissolution in the subsurface accounts for the high salinity of some formation waters, but that this effect is minimized by the development of channel flow in the low fluid potential drain lying above Middle Devonian strata. Whether this channel flow is presently active or not remains controversial (HITCHON *et al.*, 1971; DEROO *et al.*, 1977; HITCHON, 1984; GARVEN, 1985; 1989). Nevertheless, dissolution of underlying salt does not appear to be affecting the chemistry of the overlying formation waters, regardless of the presence of the salt edge in many of the underlying evaporite units is in the study area.

Most of the waters from the dominantly carbonate rocks of Group I plot to the right of the S-E-T, with some plotting directly on it. Although congruent dissolution of halite cannot explain these trends, it is important to consider whether these waters have resulted from reverse partitioning of Br during recrystallization of halite. In addition to the unreasonably large rock/water ratio required (greater than 5; see STOESSELL and CARPENTER, 1986, Table 2) to generate the existing Br concentrations (STOESSELL and CARPENTER, 1986; SPENCER, 1987) additional chemical evidence argues against halite recrystallization.

First, increasing Br concentrations via halite recrystallization can be recognized by decreasing K/Br ratios (STOESSELL and CARPENTER, 1986) and increasing Na/Br ratios (FISHER and KREITLER, 1987) because of the variable distribution coefficients of these elements in this scenario. A plot of log K versus log Br (Fig. 3.11a) illustrates that Group I waters, which demonstrate the largest degree of evaporation, have some of the highest K/Br ratio of the groups and show no evidence of decreased ratios relative to the other fluid groups. Thus, waters with largest Br enrichments are similarly enriched in K, contrary to what would result from halite recrystallization. Similarly, on a log Na versus log Br plot (Fig. 3.11b), all the water groups plot under the S-E-T. Sodium depletion is unlikely if the waters were derived from the recrystallization of halite.

Second, the summation of divalent cations charge-balanced with respect to Cl (denoted CF on the graph) versus log Br (CARPENTER, 1978), plotted in Fig. 3.12, shows waters from Group I plot above, not below, the S-E-T. Bromide enrichment from halite recrystallization would force waters below the S-E-T, exhibiting an enrichment in Br and a corresponding depletion in divalent cations (STOESSELL and CARPENTER, 1986).

Finally, the oxygen isotopic composition of the waters (CONNOLLY *et al.*, 1990) exhibit a positive, though not pronounced, relation with Br. Values of $\delta^{18}O$ enriched in ^{18}O cannot be achieved by simple salt dissolution at low temperatures but require initial evaporative processes to enrich the water in the heavy isotope. Waters in the Alberta Basin which exhibit the highest degrees of evaporation on Fig. 3.10 are the most enriched in ^{18}O.

From the above discussion, it appears reasonable to suggest that Group I waters originated by varying degrees of seawater evaporation to beyond halite saturation, and subsequent mixing with meteoric waters introduced to the Alberta Basin in response to gravity-driven flow during the Laramide Orogeny. Although Group II waters were sampled from stratigraphically higher units than Group I, some of these waters plot to the right of the S-E-T in Fig. 3.10. This behavior is likely the result of desorption of Br from organics (MEANS and HUBBARD, 1987), as these waters are closest to the dominant source rocks in the basin, the Jurassic shales, and have the highest SCA concentrations. It is unlikely that these waters were evaporated past the onset of halite saturation and subsequently diluted, since stratigraphically lower, more concentrated waters from Group I, located directly beneath and closer to halite deposits, plot on the S-E-T. Other Group II waters plot directly on the S-E-T, suggesting that they migrated up the S-E-T, never reaching halite precipitation and then were subsequently diluted back down the trajectory.

The proximity of the Group II waters to those from Group I on the graph (Fig. 3.10), suggests that the former waters were close to halite saturation, prior to dilution. Based on the approximate maximum degrees of evaporation of Group I and II waters, the majority of these brines have experienced about 50 to 80% dilution by meteoric water.

Together, Groups I and II exhibit a strong correlation in Fig. 3.10 at a slight angle to the S-E-T, which seems to define the waters as two component mixtures between a Br-enriched brine and a more dilute water. Conservative mixing phenomena yield straight line relations on linear scales that can develop curvature on log-log plots (HANOR, 1987). However, over the concentration range in these plots, a linear relation would be maintained regardless of scale (Fig. 3.10, inset). Log scales are used here to be consistent with the original work on compositional trends of seawater (CARPENTER, 1978).

Cretaceous formation waters (5 samples) from Group III form a linear relation beneath the S-E-T and are more dilute than seawater. Group III Rock Creek water samples (2 samples) plot slightly above the S-E-T and are also more dilute than seawater. All of the waters from Group III appear chemically unrelated to Group I or II, and the Cl/Br ratio cannot be used to establish the identity of dilute end members, because meteoric waters are known to be compositionally distinct from dilute formation waters (GARRELS, 1967; GARRELS and MACKENZIE, 1967; NESBITT, 1985).

Diagenetic Modifications of Waters

The chemistry of divalent cations in waters can be monitored by considering the concentration of divalent cations charge balanced by Cl. This relation is also referred to as the Carpenter Function (CF) (CARPENTER, 1978), and is defined below as:

$$CF = Ca + Mg + Sr - SO_4 - HCO_3 \text{ (in meq/l)}$$

Dolomitization of calcite, reduction of SO_4 and precipitation of gypsum or halite are common reactions in evaporite settings. Despite the effect that these processes have on individual ionic concentrations, the CF relative to Br remains unchanged during the specified reactions as seawater is evaporated (Fig 3.12). Furthermore, dilution by meteoric water or seawater does not displace a brine from the S-E-T. Hence, the relation of CF to Br can be used, in conjunction with log Cl versus log Br relations, as a basis for determining whether a brine originated from evaporation of seawater and subsequently underwent (i) water-rock interaction or (ii) mixing with waters of different origins. The relation of CF versus log Cl (Fig. 3.13) is also useful because Cl is a conservative element in sedimentary basins.

Elemental plots also maintain standard compositional trends during evaporation (Figs 3.11 and 3.14). If a solution containing several different ions is concentrated by evaporation, the ratios of the various ions, with respect to each other, remain constant except in cases where ions are precipitating or reacting with the substrate in which the brine is contained. Thus, various diagenetic reactions may be inferred by examining ion ratios relative to seawater evaporation trajectories in conjunction with Figs 3.10, 3.12 and 3.13.

Some of the formation waters in Group III are characterized by negative CF values and are not represented in Figs. 3.12 and 3.13. These include all of the waters from Cardium and Rock Creek reservoirs, and one from the Belly River (16-22-47-4W5). These waters are classified as Na - HCO_3 waters and are of meteoric origin. The extremely high alkalinity and high proportions of Na relative to divalent cations (i.e. Na/Ca > 34) particular to these formation waters results in negative CF values; therefore, these waters are not represented on the graphs in Figs. 3.12 and 3.13.

Most of the Alberta Basin formation waters from Group I plot slightly above the S-E-T on the log CF versus log Br plot (Fig. 3.12). This suggests that these waters are slightly enriched in divalent cations because they are not depleted in Br (see Fig. 3.10). Divalent cations must be a result of other reactions occurring in Devonian and Cambrian shales, adjacent to and underlying Devonian carbonate reservoirs. For example, silicate hydrolysis reactions (HUTCHEON, 1989), in which a clay mineral, such as kaolinite, reacts to form illite, obtaining K from coexisting porewater and releasing protons, provide a potential source of acid (reaction 5):

$$3Al_2Si_2O_5(OH)_4 + 2K^+ \leftrightarrow 2KAl_3Si_3O_{10}(OH)_2 + 2H^+ + 3H_2O \qquad (5)$$

(BJØRLYKKE,1984)

Clay-carbonate reactions provide another potential source of acid, via CO_2, in sedimentary systems (HUTCHEON, 1989; HUTCHEON *et. al.*, 1980). Reactions such as the conversion of kaolinite and dolomite to chlorite and calcite (reaction 6) are likely occurring in Devonian and Cambrian shales:

$$5CaMg(CO_3)_2 + Al_2Si_2O_5(OH)_4 + SiO_2 + 2H_2O \leftrightarrow$$

$$Mg_5Al_2Si_3O_{10}(OH)_8 + 5CaCO_3 + 5CO_2 \qquad (6)$$

(SKIPPEN and TROMSDORFF, 1986)

Numerous reactions of this kind, including those that involve smectite or illite, may also occur. Similarly, chlorite, ankerite and calcite may contain Fe and Mg, and a parallel reaction to (6) can be written for the Fe end members:

$$5FeCO_3 + Al_2Si_2O_5(OH)_4 + SiO_2 + 2H_2O \leftrightarrow Fe_5Al_2Si_3O_{10}(OH)_8 + 5CO_2 \qquad (7)$$

Other reactions providing a source of CO_2 to formational fluids would be decarboxylation reactions in Devonian hydrocarbons.

Reactions such as 6 and 7 generate CO_2 in solution, a source of acid for the dissolution of carbonate in Group I reservoirs, which would cause a corresponding increase in divalent cations through dissolution of the reservoir rock not compensated for by the CF. These reactions are indicated on elemental plots (Figs. 3.11 and 3.14) used in conjunction with Fig. 3.12. Potassium and Mg are depleted relative to the S-E-T, whereas Ca is enriched in most of the waters with the exception of Group III. Thus, rather than attributing Group I water chemistry solely to dolomitization reactions (SPENCER, 1987), Fig. 3.12 indicates other processes are influencing the water composition. Ion exchange reactions in shales surrounding carbonate reservoirs may also explain an excess of divalent cations as is discussed below.

Ankeritization of the dolomite and calcite in the Devonian carbonate assemblages may provide a further explanation for the excess of divalent cations. BOLES (1978) and BOLES and FRANKS (1979) suggested ankeritization occurred via the following reaction

$$4CaCO_3 + Fe^{+2} + Mg^{+2} \leftrightarrow 2CaFe_{0.5}Mg_{0.5}(CO3)_2 + 2Ca^{+2} \qquad (8)$$

They also noted that adjacent shales could provide the Fe and Mg necessary for the reaction. Much of the dolomite in the study area has been identified to be Fe-rich (ankerite) (see Chapter 2 and Appendix I) and reaction (8) would cause an increase in the CF value relative to S-E-T, as Fe is not compensated for in the function.

Samples from Group II fall below the S-E-T suggesting that along with minimal enrichment in Br (Fig. 3.10), these waters also have a marked depletion in divalent cations. This depletion is further indicated by the high Na/Ca ratios for all of these brines. Albitization or the formation of K-feldspar removes monovalent cations from solution and replaces them with divalent cations, causing an increase in the CF. However, processes such as kaolinization of feldspar and clay mineral stabilization reactions are indicated by a depletion of divalent cations in Group II waters. These processes are typical in sedimentary zones penetrated by meteoric water (HURST and IRWIN, 1982). Meteoric waters are dilute and acidic, and kaolinization reactions (e.g. of albite) would generate high Na contents, particularly because a relatively high fraction of volcanic fragments and Na-plagioclase are present in these reservoirs (CONNOLLY *et al.*, 1990).

Cation exchange processes may also explain the water chemistry of Group I and Group II waters. CERLING *et al.* (1989) noted that when clay minerals in shales and sandstones are weathered by meteoric waters, a release of Na ions, previously held as exchangeable ions, occurs. To examine the potential for cation exchange processes, the parameter mCl-mNa (molality of Cl minus molality of Na), defined as the Na deficiency (FISHER and KREITLER, 1987), is used (Figs. 3.15a and 3.15b). High Na concentrations in basin brines, such as those of the Alberta Basin, would promote ion-exchange reactions such as simple exchange on clays, conversion of calcic plagioclase to albite, and alteration of detrital clays to Na-clays. Clays equilibrated with waters of high ionic strength have higher Na/Ca ratios than do those equilibrated with waters of low ionic strength (CERLING *et al.*, 1989). Charge balance requires that for each divalent cation released to solution, two monovalent ions are removed from solution. Sodium exchange is indicated by the relation between Na deficiency and the sum of major divalent cations (Fig. 3.15). All samples shown in Fig. 3.15a fall on or above the S-E-T, with the most saline waters from Group I exhibiting the greatest degree of Na removal. This suggests that in addition to the processes described earlier, ion-exchange may account for high concentrations of divalent cations in Group I.

If Na and Cl behave relatively conservatively during evaporation, waters having high Cl contents probably had high initial Na contents. However, high Na concentrations would more effectively drive exchange reactions and cause Na loss. Figure 3.15b shows that many of the Group I waters have lost Na, indicating exchange processes may have been active. Both Group II and III waters show enrichment rather than removal of Na. This is likely because these waters are dilute, resulting in Ca being removed from solution (Fig. 3.14b) and replaced by Na. Figure 3.10 clearly illustrates that Group II waters are all ~ 80% diluted, with Group I being much more concentrated. This difference in ionic strength may be sufficient to divide the ion-exchange processes.

A strong linear relation between Group I and Group II is observed in Figs. 3.10, 3.11, and 3.12, and maintained on linear molar scales. Plotting log Cl versus CF (Fig.

3.13) more clearly demonstrates a distinct break between Group I and Group II. Group I waters plot predominantly under the S-E-T providing additional evidence that these waters are concentrated seawater that has been diluted by meteoric water. Group II plot above the S-E-T, confirming a depletion in divalent cations and exhibiting a strong meteoric component responsible for altering the original seawater composition of the deposited sediments. Samples of Group III are distinct from the trend established by the other two groups.

Mixing Relations-Elemental Relations

Figures 3.10 through 3.15 strongly suggest a mixing relation between Group I and Group II waters, while Group III waters appear unrelated to them. The principles governing mixing systematics are reviewed by FAURE (1986). Briefly, when a brine of constant composition is mixed with dilute meteoric water, concentrations of elements (Na, Ca, K, Mg, Sr) on an x - y plot form a linear array directed toward the origin. When two brines of differing composition mix, a similar relation is observed on an x - y plot, but with a non-zero intercept. When the two-brine mixture is diluted with meteoric water, a triangle of mixing is introduced encompassing a scatter of points, with the three end-member components forming the apices of a triangle (LOWRY *et al.*, 1988). However, these relationships occur only during closed system behavior and do not consider diagenetic disturbance of any kind.

Cation cross-plots were constructed to determine whether mixing relations could be distinguished among Alberta Basin waters. Figure 3.16a is such a plot of Ca versus K and exhibits a linear array directed toward the origin. Waters of Group II plot closer to the origin than Group I; Group III waters are so dilute relative to the other two groups that they can barely be observed at the scale of the graph. This behavior suggests that Alberta Basin formation waters are composed of a single brine of constant composition diluted by meteoric water. Most elemental plots are similar to Fig. 3.16a, with correlation coefficients >0.91, both with and without plotting the two most concentrated waters. However, if Na is plotted versus other elements (e.g. K, Mg, Ca, Sr), a somewhat different relationship is observed (Fig. 3.16b). A linear relation between Group I and Group II is apparent with a non-zero intercept; Group III is completely removed from the trend. A mixing triangle is not indicated. Rather, mixing between two brines, Group I and Group II is observed, with Group III waters apparently acting as an independent, much more dilute system. Plots of Na versus other elemental concentrations provide a more accurate indication of the mixing relations because Na is the most abundant cation in the waters, and the least likely to be masked by diagenetic reactions, and it is a very conservative element in sedimentary systems.

Diagenetic reactions affect water chemistry in the Alberta Basin (Figs. 3.12 and 3.13), but linearity of all x-y plots for major elements of the waters (Na, Ca, K, Mg, Sr) suggests that mixing occurred subsequent to these reactions. Many of the diagenetic reactions, particularly in the clastic rocks, were driven by meteoric recharge in response to Laramide tectonism. Because Group I and II waters appear to have mixing relations, this suggests that mixing occurred after this major flushing event. The regional flow system underwent dissipation and partitioning in the Pliocene (GARVEN, 1989) and this is probably when the Group I and Group II waters became isolated from Group III (CONNOLLY *et al.*, 1990). If meteoric waters were still influential today in the stratigraphically lower fluid system, all of the major element x-y plots would have intersections at the origin.

CONCLUSIONS

Formation waters from Devonian through Cretaceous carbonate and clastic reservoirs in the Alberta Basin were examined for SCAs and major and minor elements. The abundance and distribution of SCAs in Alberta Basin formation waters do not appear influenced by or related to reservoir temperature, sampling depth or geological age. However, a strong association between SCA concentration and proximity to the Jurassic shales is evident, with water-washing and meteoric flushing providing a contributing influence.

Three distinct water groups are evident in the Alberta Basin: Group I waters are dominantly carbonate-hosted and are stratigraphically the lowest; Group II waters are primarily from clastic reservoirs; and Group III waters are completely clastic-hosted and comprise the stratigraphically highest zone. Group I and II form a distinct hydrochemical regime, which is decoupled from the dilute waters of Group III.

Group III water chemistry is dominated by Na and HCO_3^- (alkalinity) and there is no evidence of a seawater or an evaporated brine end-member. Reservoirs containing these waters were primarily deposited in seawater; however, the dilute nature of these Na - HCO_3^- waters argue for complete flushing of any residual marine waters in these reservoirs by meteoric waters.

Formation waters from Group I and Group II form two component mixtures of (i) a residual evaporite brine and (ii) post-Laramide but pre-present day meteoric water. The brine end-member was formed by evaporation of seawater beyond the point of halite saturation and was not influenced by congruent dissolution of evaporite deposits. These carbonate-hosted waters were subsequently influenced by silicate hydrolysis and clay-carbonate reactions in surrounding shales and ankeritization reactions of reservoir carbonates. The clastic-hosted waters of Group II were affected by feldspar-clay mineral leaching reactions initiated by gravity driven flow of meteoric waters, resulting from Laramide orogenesis. Both Group I and Group II waters may also have been altered by ion exchange processes. Group I and Group II waters define a two component mixture, which was established subsequent to hydrochemical isolation in the Pliocene. At this point cross-formational flow began to become significant relative to lateral flow.

REFERENCES

AMAJOR L.C. (1978) Some Viking bentonites, south-central Alberta. Unpub. M.Sc. Thesis, Univ. Alberta, Edmonton, Alberta.

AMAJOR L.C. (1980) Chronostratigraphy, sedimentary environments, of Lower Cretaceous Viking Sandstones, Alberta. Unpub. Ph.D. Diss., Univ. Alberta, Edmonton, Alberta.

AYALON A. and LONGSTAFFE F.J. (1988) Oxygen isotope studies of diagenesis and pore-water evolution in the western Canada sedimentary basin: Evidence from the Upper Cretaceous Basal Belly River sandstone, Alberta. *J. Sediment. Petrol.* 58, 489-505.

BEAUMONT C. (1981) Foreland basins. *Geophys. J. Roy. Astron. Soc.* 65, 291-329.

BERNER R.A. (1981) A new geochemical classification of sedimentary environments. *J. Sediment. Petrol.* 51, 359-365.

BETHKE C.M. (1986) Hydrologic constraints on the genesis of the Upper Mississippi Valley mineral district from Illinois Basin brines. *Econ. Geol.* 81, 233-248.

BILLINGS G.K., HITCHON B. and SHAW D.R. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin, 2. Alkali metals. *Chem. Geol.* 4, 211-223.

BJØRLYKKE K. (1984) Formation of secondary porosity: How important is it? In *Clastic Diagenesis* (eds. D.A. McDONALD and R.C. SURDAM), pp. 277-286. Am. Assoc. Petrol. Geol. Mem. 37.

BOLES J.R. (1978) Active ankerite cementation in the subsurface Eocene of southwest Texas. *Contrib. Mineral. Petrol.* 68, 13-22.

BOLES J.R. and FRANKS S.G. (1979) Clay diagenesis in Wilcox sandstones of southwest Texas: Implications of smectite diagenesis on sandstone cementation. *J. Sediment. Petrol.* 49, 55-70.

BUSENBERG E. and PLUMMER L.N. (1982) The kinetics of dissolution of dolomite in CO_2 - H_2O systems at 1.5 to 65°C and 0 to 1 atm P_{CO_2}. *Am. J. Sci.* 282, 45-78.

CAROTHERS W.W. and KHARAKA Y.K. (1978) Aliphatic acid anions in oil-field waters - implications for origin of natural gas. *Am. Assoc. Petrol. Geol. Bull.* 62, 2441-2453.

CARPENTER A.B. (1978) Origin and chemical evolution of brines in sedimentary basins. *Okla. Geol. Surv. Circ.* 79, 60-77.

CERLING T.G., PEDERSON B.L. and VON DAMM K.L. (1989) Sodium-calcium ion exchange in the weathering of shales: Implications for global weathering budgets. *Geology* 17, 552-554.

CLAYTON R.N., FRIEDMAN I., GRAF D.L., MAYEDA T.K., MEENTS W.F. and SHIMP N.F. (1966) The origin of saline formation waters, I. Isotopic composition. *J. Geophys. Res.* 71, 3869-3882.

CONNOLLY C.A, WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. II. Isotope systematics and water mixing. *Appld. Geochem.* 5, 397-414.

CREANEY S. and ALLAN J. (in press) Hydrocarbon generation and migration in the Western Canada Sedimentary Basin. In *Classic Petroleum Provinces*. Geol. Soc. of London Spec. Pub.

DEMIR I. (1988) Studies of smectite membrane behavior: Electrokinetic, osmotic and isotopic fractionation processes at elevated pressure. *Geochim. Cosmochim. Acta* 52, 727-737.

DEROO G., POWELL T.G., TISSOT B. and McCROSSAN R.G. (1977) The origin and migration of petroleum in the Western Canada Sedimentary Basin, Alberta. A geochemical and thermal maturation study. *Geol. Surv. Can. Bull.* 262.

DICKINSON W.R. and SNYDER W.S. (1978) Plate tectonics of the Laramide Orogeny. In *Laramide Folding Associated with Basement Block Faulting in the Western United States* (ed. V. MATHEWS III), pp. 355-366. Geol. Soc. Am. Mem. 151.

DOMENICO P.A. and ROBBINS G.A. (1985) The displacement of connate waters from aquifers. *Geol. Soc. Am. Bull.* 96, 328-335.

FAURE G. (1986) *Principles of Isotope Geology* (2nd Ed.). John Wiley & Sons.

FISHER J.B. (1987) Distribution and occurrence of aliphatic acid anions in deep subsurface waters. *Geochim. Cosmochim. Acta* 51, 2459-2468.

FISHER R.S. and KREITLER C.W. (1987) Geochemistry and hydrodynamics of deep-basin brines, Palo Duro Basin, Texas, U.S.A. *Appld. Geochem.* 2, 459-476.

GARRELS R.M. (1967) Genesis of some ground waters from some igneous rocks. In *Researches in Geochemistry,* 2 (ed. P.H. ABELSON), pp. 405-420. New York, John Wiley and Sons.

GARRELS R.M. and MACKENZIE F.T. (1967) Origin of the chemical compositions of some springs and lakes.In *Equilibrium Concepts in Natural Water Systems*, pp. 222-242. Washington, D.C., Am. Chem. Soc. 67.

GARVEN G. (1985) The role of regional fluid flow in the genesis of the Pine Point deposit, western Canada sedimentary basin. *Econ. Geol.* 80, 307-324.

GARVEN G. (1989) A hydrogeologic model for the formation of giant oil sands deposits of the western Canada sedimentary basin. *Am. J. Sci.* 289, 105-166.

GIESKES J.M. and ROGERS W.C. (1973) Alkalinity determination in interstitial waters of marine sediments. *J. Sediment. Petrol.* 43, 272-277.

GRAF D.L. (1982) Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines. *Geochim. Cosmochim. Acta* 46, 1431-1448.

GRAF D.L., MEENTS W.F., FRIEDMAN I. and SHIMP N.F. (1966) The origin of saline formation waters - II. Calcium chloride waters. *Illinois State Geol. Survey Circ.* 393.

HANOR J.S. (1979) Sedimentary genesis of hydrothermal fluids. In *Geochemistry of Hydrothermal Ore Deposits* (ed. H.L. BARNES), pp. 137-168. Wiley.

HANOR J.S. (1987) *Origin and Migration of Subsurface Sedimentary Brines.* Soc. Econ. Paleon. Mineral. Short Course 21.

HANOR J.S. and WORKMAN A.L. (1986) Dissolved fatty acids in Louisiana oil-field brines. *Appld. Geochem.* 1, 37-46.

HATTON R.S and HANOR J.S. (1984) *Dissolved Volatile Fatty Acids in Subsurface Hydropressured Brines: A Review of Published Literature on Occurrence, Genesis, and Thermochemical Properties.* Technical Report for Geopressured Geothermal Activites in Louisiana. DOE Report No. DOE/NV/10174-3.

HELGESON H.C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci.* 267, 729-804.

HELGESON H.C., DELANY J.M., NESBITT H.W. and BIRD D.K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. *Am. J. Sci.* 178-A, 1-229.

HEM J.D. (1970) Study and interpretation of the chemical characteristics of natural water. *U.S. Geol. Surv. Water - Supply Paper* 1473.

HITCHON B. (1969a) Fluid flow in the Western Canada Sedimentary Basin, 1. Effect of topography. *Water Resour. Res.* 5, 186-195.

HITCHON B. (1969b) Fluid flow in the Western Canada Sedimentary Basin, 2. Effect of geology. *Water Resour. Res.* 5, 460-469.

HITCHON B. (1984) Geothermal gradients, hydrodynamics, and hydrocarbon occurrence, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* 68, 713-743.

HITCHON B. and FRIEDMAN I. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin, I. Stable isotopes of hydrogen and oxygen. *Geochim. Cosmochim. Acta* 33, 1321-1349.

HITCHON B., BILLINGS G.K. and KLOVAN J. E. (1971) Geochemistry and origin of formation waters in the western Canada sedimentary basin, III. Factors controlling chemical composition. *Geochim. Cosmochim. Acta* 35, 567-598.

HOLLAND H.D. (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press.

HOLYSH S. (1989) Regional groundwater flow and petroleum related geochemical signatures, Chauvin area east-central Alberta. Unpub. M.Sc. Thesis, Univ. Alberta, Edmonton, Alberta.

HURST A. and IRWIN H. (1982) Geological modeling of clay diagenesis in sandstones. *Clay Min.* 17, 5-22.

HUTCHEON I. (1989) Application of chemical and isotopic analyses of fluids to problems in sandstone diagenesis. In *Burial Diagenesis* (ed. I. HUTCHEON), pp. 279-310. Min. Assoc. Canada Short Course 15.

HUTCHEON I., OLDERSHAW A. and GHENT E. (1980) Diagenesis of sandstones of the Kootenay Formation at Elk Valley (southeastern British Columbia) and Mount Allan (southwestern Alberta). *Geochim. Cosmochim. Acta* 44, 1425-1435.

JORDON T.E. (1981) Thrust loads and foreland basin evolution, Cretaceous western United States. *Am. Assoc. Petrol. Geol. Bull.* 65, 2506-2520.

KASPER H.F. and WUHRMANN K. (1978) Kinetic parameters and relative turnovers of some important catabolic reactions in digesting sludge. *Appld. Environ. Microbiol.* 36, 1-7.

KEHLE R.C. (1971) Geothermal survey of North America; 1971 annual progress report. *Am. Assoc. Petrol. Geol. Bull.* unpublished report, 37p.

KHARAKA Y.K., HULL R.W. and CAROTHERS W.W. (1985) Water-rock interactions in sedimentary basins. In *Relationships of Organic Matter and Mineral Diagenesis* (eds. D.L. GAUTIER, Y.K. KHARAKA and R.C. SURDAM), pp. 79-124. SEPM Course No. 17.

KHARAKA Y.K. and CAROTHERS W.W. (1986) Oxygen and hydrogen isotope geochemistry of deep basin brines Chap. 2. In *Handbook of Environmental Isotope Geochemistry,* II (eds. P. FRITZ and J.C. FONTES), pp. 305-360.

KHARAKA Y.K., MAEST A.S., CAROTHERS W.W., LAW L.M., LAMOTHE P.J. and FRIES T.L. (1987) Geochemistry of metal-rich brines from central Mississippi Salt Dome basin, U.S.A. *Appld. Geochem.* 2, 543-561.

KNAUTH L.P. (1988) Origin and mixing history of brines, Palo Duro Basin, Texas, U.S.A. *Appld. Geochem.* 3, 455-474.

KNAUTH L.P. and BEEUNAS M.A. (1986) Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters. *Geochim. Cosmochim. Acta* 50, 419-433.

KROUSE H.R. (1980) Stable isotope geochemistry of non-hydrocarbon constituents of natural gas. In *Storage, Transport, Processing,* World Petrol. Congr. Proc. 4, 85-92.

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* 333, 415-419.

LAND L.S. and PREZBINDOWSKI D.R. (1981) The origin and evolution of saline formation water. Lower Cretaceous carbonates, south-central Texas, U.S.A. *J. Hydrol.* 54, 51-74.

LONGINELLI A. and CRAIG H. (1967) Oxygen - 18 variations in sulfate ions in seawater and saline lakes. *Science* 156, 56-69.

LONGSTAFFE F.J. (1986) Oxygen isotope studies of diagenesis in the basal Belly River sandstone, Pembina I-Pool, Alberta. *J. Sediment. Petrol.* 56, 78-88.

LOWRY R.M., FAURE G., MULLET D.I. and JONES L.M. (1988) Interpretation of chemical and isotopic compositions of brines based on mixing and dilution, "Clinton" sandstones, eastern Ohio, U.S.A. *Appld. Geochem.* 3, 177-184.

MACHEL H.G. (1987) Saddle dolomite as a by-product of chemical compaction and thermochemical sulfate reduction. *Geology* 15, 936-940.

MACHEMER S.D. and HUTCHEON I. (1988) Geochemistry of early carbonate cements in the Cardium Formation, Central Alberta. *J. Sediment. Petrol.* 58, 136-147.

McNUTT R.H., FRAPE S.K. and DOLLAR P. (1987) The strontium, oxygen and hydrogen isotopic composition of brines, Michigan and Appalachian basins, U.S.A. *Appld. Geochem.* 2, 495-505.

MEANS J.L. and HUBBARD N.J. (1987) Short-chain aliphatic acid anions in deep subsurface brines: A review of their origin, occurrence properties and importance and new data on their distribution and geochemical implications in the Palo Duro Basin, Texas. *Org. Geochem.* 11, 177-191.

MOSHIER S.O. and WAPLES D.W. (1985) Quantitative evaluation of Lower Cretaceous Mannville Group as source rock for Alberta's oil sands. *Am. Assoc. Petrol. Geol. Bull.* 69, 161-172.

NELSON S.J. (1970) *The Face of Time, the Geologic History of Western Canada*, pp. 56-67. Alberta Soc. Petrol. Geol.

NESBITT H.W. (1980) Characterization of mineral-formation water interactions in Carboniferous sandstones and shales of the Illinois sedimentary basin. *Am. J. Sci.* 280, 607-630.

NESBITT H.W. (1985) A chemical equilibrium model for the Illinois Basin formation waters. *Am. J. Sci.* 285, 436-458.

PALCIAUSKAS V. and DOMENICO P.A. (1976) Solution chemistry, mass transfer, and the approach to chemical equilibrium in porous carbonate rocks and sediments. *Geol. Soc. Am. Bull.* 87, 207-214.

PLUMMER L.N., WIGLEY T.M. and PARKHURST D.L. (1978) The kinetics of calcite dissolution in CO_2 - water systems at 5 to 60°C and 0.0 to 1.0 atm CO_2. *Am. J. Sci.* **278**, 179-216.

PLUMMER L.N., PARKHURST D.L. and WIGLEY T.M. (1979) Critical review of the kinetics of calcite dissolution and precipitation. In *Chemical Modeling in Aqueous Systems* (ed. E.A. JENNE), pp.537-573. Am. Chem. Soc. Symp. Ser. **93**.

PORTER J.W., PRICE R.A. and McCROSSAN R.G. (1982) The Western Canada Sedimentary Basin. *Roy. Soc. Phil. Trans.* **305**, 169-192.

PRICE R.A. (1973) Large scale gravitational flow of supra-crustal rocks, southern Canadian Rocky Mountains. In*Gravity and Tectonics* (eds. K.A. DEGONG and R.S.CHOLTEN), 491-502. Wiley.

SHOCK E.L. and HELGESON H.C. (1988) Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C. *Geochim. Cosmochim. Acta* **52**, 2009-2036.

SKIPPEN G. and TROMMSDORFF V. (1986) The influence of NaCl and KCl on phase relations in metamorphosed carbonate rocks. *Am. J. Sci.* **286**, 81-104.

SPENCER R.J. (1987) Origin of Ca-Cl brines in Devonian formations, Western Canada Sedimentary Basin. *Appld. Geochem.* **2**, 373-384.

STOESSELL R.K. and CARPENTER A.B. (1986) Stoichiometric saturation tests of $NaCl_{1-x}Br_x$ and $KCl_{1-x}Br_x$. *Geochim. Cosmochim. Acta* **50**, 1465-1474.

SURDAM R.C., BOESE S.W. and CROSSEY L.J. (1984) The chemistry of secondary porosity. In *Clastic Diagenesis* (eds. D.A. McDONALD and R.C. SURDAM), pp. 127-149. Am Assoc. Petrol. Geol. Mem. **37**.

SURDAM R.C. and CROSSEY L.J. (1985) Mechanisms of organic/inorganic interactions in sandstone/shale sequences. *S.E.P.M. Short Course Notes* **17**, 177-232.

TAYLOR R.S., MATHEWS W.H. and KUPSCH W.O. (1964) Tertiary. In *Geological History of Western Canada* (ed. R.G. McCROSSAN and R.P. GLAISTER), pp. 190-194. Alberta Soc. Petrol. Geol.

TIZZARD P.G. and LERBEKMO J.F. (1975) Depositional history of the Viking Formation, Suffield area, Alberta, Canada. *Bull. Can. Petrol. Geol.* **23**, 715-752.

TOTH J. (1980) Cross-formational gravity flow of ground-water: A mechanism of the transport and accumulation of petroleum (the generalized hydraulic theory of petroleum migration). In *Problems of Petroleum Migration* (eds. W.H. ROBERTS III and R.J. CORDELL), pp. 121-167. Am. Assoc. Petrol Geol. Studies in Geology **10**.

WHITE D.E. (1965) Saline waters of sedimentary rocks. In *Fluids in Subsurface*

Environments (eds. A. YOUNG and J.E. GALLEY), pp. 342-366. Am. Assoc. Petrol. Geol. Mem. 4.

WILLEY L.M., KHARAKA Y.K., PRESSER T.S., RAPP J.B. and BARNES I. (1975) Short-chain aliphatic anions in oilfield waters and their contribution to the measured alkalinity. *Geochim. Cosmochim. Acta* 39, 1707-1711.

WOLERY T.J. (1983) EQ3NR: A computer program for geochemical aqueous speciation-solubility calculations, users guide and documentation, UCRL - 53414. Lawrence Livermore Lab., *Univ. Calif.*

WORKMAN A.L. and HANOR J.S. (1985) Evidence for large-scale verticle migration of dissolved fatty acids in Louisiana oil field brines: Iberia field, south-central Louisiana. *Trans. Gulf Coast Assoc. Geol. Soc.* 35, 293-300.

SYSTEM	STRATIGRAPHIC UNIT	GENERAL LITHOLOGY AND DEPOSITIONAL SETTING
Upper Cretaceous	Basal Belly River	Carbonaceous sandstone interbedded with shale and sandstone.
	Lea Park	Shales becoming more marine toward base.
	Cardium	Three sandstone members separated by dark shales. Sandstone members may have conglomerate at the top and be interspersed with shale lenses.
Lower Cretaceous	Viking	Varies from fine salt and pepper sandstone to siltstone to silty shale; sandstone generally interspersed with shale.
	Glauconitic	Very fine to medium quartz sandstone mixed with coarser salt and pepper sandstone. Clay and calcareous cement vary.
	Ostracod	Predominantly shale that is partly calcareous, containing bands of argillaceous limestone.
	Basal Quartz	Essentially sandstone varying greatly in colour and texture. Upper beds are more calcareous. Contains lenses of shale.
Middle Jurassic	Rock Creek	Calcareous sandstone and rusty weathering shale; argillaceous limestone lenses.
	Poker Chip Shale	Black calcareous shales with thin limestone beds.
Lower Jurassic	Nordegg	Black limestone and black calcareous shales with abundant chert fragments; top highly fossiliferous.
	Fernie	Shale; commonly sandy, in places calcareous, and occasionally bituminous.
Mississippian	--	Massive coarse-grained limestone, alternating with beds of black fine-grained limestone; may contain chert nodules.
Upper Devonian	Wabamun	Limestone dominant in the upper part of the group and dolomite in the middle and lower parts; however, may consist of all one litholgy or the other.
	Nisku	Dolomite, variably silty and anhydritic.
	Leduc	Semi-fragmental and reeflike; crystalline dolomite with scattered vugs.
Middle/Lower Devonian	Elk Point	Anhydritic dolomite, fossiliferous
Cambrian	--	Calcareous grey to black shale. Buff to glauconitic sandstone; shale partings.
Precambrian	--	Crystalline basement.

Table 3.1. Stratigraphic column for the study area in the Alberta Basin. Waters were collected from Upper Devonian - Upper Cretaceous formations.

Table 3.2. Sample locations, depths, temperatures and chemical compositions of Alberta Basin waters. All ionic concentrations are in mg/l. *nd* = below detection limit; (-) = not analyzed. Lead analyses were conducted, but levels were below detection in all the formation water samples.

SYSTEM	STRATIGRAPHIC UNIT	LOCATION	DEPTH (m)	TEMP (C)	TDS (g/l)	pH	DENSITY (g/l)	Na	Ca	Mg	K	Sr	Ba	Li	B	Cl	SO4	Br	Fe	Mn	Zn	H_2S
Upper Cretaceous	Belly River	6-5-49-6W5	1078	35	15	7.9	1.008	5690	163	47	72	17	43	1	5	8890	nd	118	0.01	0.34	nd	
	Belly River	8-29-48-6W5	1090	49	16	7.5	1.009	6050	179	50	33	21	47	1	21	9590	nd	126	0.02	0.42	0.69	
	Belly River	2-28-48-6W5	1076	45	16	8.4	1.008	5990	186	52	47	21	41	1	5	9500	nd		0.21	0.34	nd	
	Belly River	16-22-47-4W5	884	46	11	8.0	1.005	4210	125	30	34	15	27	1	3	6250	nd	72	2.46	0.17	0.01	
	Cardium	3-24-49-5W5	1245	43	5	8.8	1.002	2450	32	11	28	7	5	1	6	2140	nd	31	0.03	nd	nd	
	Cardium	14-20-48-6W5	1426	54	4	8.3	1.002	2040	8	3	9	1	4	1	5	1860	nd	28	0.11	0.01	nd	
	Cardium	16-30-49-6W5	1304	47	4	8.5	1.002	2150	9	3	22	1	4	1	5	1930	nd	26	0.02	0.03	nd	
Lower Cretaceous	Viking	12-20-49-21W4	898	41	55	7.4	1.036	20800	431	233	107	104	175	5	8	33300	nd	181	30.11	0.50	nd	
	Viking	15-21-56-24W4	1050	47	60	7.3	1.040	22000	1070	416	102	182	365	5	7	36100	nd	172	7.13	0.62	0.04	
	Viking	8-32-55-20W4	703	40	74	7.1	1.050	25100	2020	884	209	230	203	8	8	44700	nd	191	8.20	1.19	0.93	
	Viking	6-7-56-20W4	676	44	74	7.9	1.049	25200	2040	942	275	217	189	9	8	44500	nd	184	0.21	0.41	0.18	
	Glauconitic	4-36-49-4W5	1630	59	67	7.1	1.044	24700	1030	280	348	234	350	11	5	39700	nd	123	58.94	2.64	0.02	
	Glauconitic	12-16-51-4W5	1574	65	65	6.9	1.043	24800	510	207	489	88	7	12	7	38900	36	153	20.19	0.21	0.05	
	Glauconitic	14-4-51-25W4	1293	-	96	-	1.063	31900	4040	867	576	360	176	19	8	58300	-		0.50	1.55	0.18	
	Ostracod	16-20-49-3W5	1609	65	72	7.1	1.048	25900	1350	390	330	264	395	12	5	42700	10	137	36.74	0.99	0.07	
	Ostracod	5-30-49-3W5	1640	67	62	7.7	1.041	22600	888	236	354	151	72	11	7	37200	17	129	0.21	1.03	0.06	
	Basal Quartz	10-29-56-24W4	1067	46	73	6.2	1.048	23100	2100	795	478	180	83	-	17	44100	102	174	65.94	2.35	0.06	
	Basal Quartz	13-21-56-24W4	1060	-	91	6.8	1.061	30600	2870	1178	740	199	14	16	27	54400	268	211	16.39	0.60	0.02	
	Basal Quartz	14-23-52-26W4	1253	-	111	7.2	1.075	35000	5780	1307	844	375	3	27	37	67400	215	280	0.26	5.11	nd	122
	Basal Quartz	15-33-51-25W4	1358	56	113	6.9	1.078	35900	4030	1344	1050	376	2	30	39	69500	281	267	0.18	6.59	nd	54
	Basal Quartz	2-25-52-26W4	1237	52	94	7.6	1.069	24900	4570	1154	818	289	2	24	32	61700	339	242	0.20	4.01	nd	38
	Basal Quartz	16-34-49-5W5	1700	63	60	7.1	1.040	22900	626	150	390	64	27	11	7	35900	-	-	93.05	1.69	0.44	
Middle Jurassic	Rock Creek	10-25-54-13W5	1969	75	22	7.5	1.014	8470	123	46	119	26	14	4	15	12700	11	28	0.15	0.09	0.06	
	Rock Creek	16-24-54-13W5	1984	64	21	7.1	1.014	8440	240	49	134	38	36	4	11	12300	20	30	52.20	0.70	0.02	
	Middle Jurassic	8-34-49-5W5	1699	57	59	7.0	1.040	22300	698	155	395	60	2	11	8	34800	170	100	129.17	1.42	0.01	
	Middle Jurassic	6-34-49-5W5	1706	61	62	7.9	1.042	23600	793	179	555	54	2	16	8	36800	295	113	0.25	1.02	0.03	
Lower Jurassic	Nordegg	14-13-49-5W5	1703	-	107	6.9	1.072	35300	4240	1039	1050	239	2	33	37	64100	520	225	0.24	1.87	nd	
	Nordegg	1-16-52-5W5	1647	67	100	6.8	1.066	33800	3180	1038	573	483	105	17	13	60700	-	237	63.59	1.25	2.88	
Mississippian	Banff	6-31-50-4W5	1621	58	103	8.5	1.068	36900	2180	800	924	323	2	25	14	61700	273	224	0.16	0.15	nd	
	Banff	14-30-50-4W5	1640	62	87	8.1	1.057	31100	1250	568	659	208	2	19	10	52500	222	181	1.76	0.19	nd	
Upper Devonian	Wabamun	9-16-57-3W5	1340	50	93	7.0	1.063	30700	3550	1051	714	325	4	18	17	55900	87	467	2.18	2.46	0.03	
	Wabamun	2-4-57-3W5	1334	50	102	7.1	1.070	33200	3890	1292	714	359	5	22	15	62900	56	244	11.87	1.30	0.02	
	Wabamun	13-20-56-3W5	1399	52	137	6.8	1.093	41200	7380	2071	1480	446	4	36	53	84100	140	335	9.34	0.66	nd	5
	Wabamun	3-7-57-1W5	1247	44	108	6.9	1.074	33600	4810	1498	992	393	2	26	43	66100	151	269	0.27	0.26	nd	20
	Nisku	15-29-49-26W4	1596	69	178	6.9	1.119	50600	12200	2545	3200	365	2	55	103	106000	624	514	0.26	0.15	nd	136
	Nisku	14-3-56-24W4	1179	45	113	6.4	1.076	33300	6720	184[illegible]	1930	187	1	37	66	67600	1080	354	0.27	0.19	nd	199
	Nisku	16-10-56-24W4	1170	45	111	6.0	1.075	32700	6400	1768	1840	184	1	36	62	67000	1000	335	0.34	0.27	nd	252
	Leduc	11-14-57-21W4	972	41	106	6.2	1.070	34200	4380	1870	896	219	1	20	43	63100	880	241	0.31	0.07	nd	367
	Leduc	6-20-57-21W4	978	39	99	6.5	1.067	31100	4260	1582	842	168	1	19	35	60000	1280	227	0.28	0.07	nd	415
	Leduc	7-6-58-21W4	979	42	108	6.1	1.073	33000	4850	1862	1000	187	1	22	42	65100	1170	258	0.28	0.08	nd	367
	Leduc	11-12-58-22W4	985	42	111	6.0	1.074	34900	5220	1987	1080	198	1	23	48	66100	1240	274	0.27	0.08	nd	347
	Leduc	11-15-50-26W4	1623	63	235	6.2	1.161	50000	30000	5035	3640	1190	7	50	142	144000	294	1260	17.48	0.49	0.83	
	Leduc	6-23-52-26W4	1536	65	129	6.7	1.088	34500	11100	2109	1580	397	3	28	56	78300	837	485	0.62	1.42	nd	4

Table 3.3. Alkalinities and organic acid content of Alberta Basin brines. A_T = titrated alkalinity; A_R = reverse alkalinity; A_C = carbonate alkalinity; ORG ACIDS = total short chain aliphatic acids; FORM = formate; ACE = acetate; PROP = propionate; BUT = butyrate. The alkalinities are presented in meq/l and the organic acids in mg/l and meq/l. *nd*= below detection limit; (-) not analyzed.

SYSTEM	FORMATION	LOCATION	A_T	A_R	%A_T	A_C	ORG ACIDS (mg/l)	FORM (mg/l)	ACE (mg/l)	PROP (mg/l)	BUT (mg/l)	ORG ACIDS (meq/l)	SO_4 ‰(CDT)	H_2S ‰(CDT)
Upper Cretaceous	Belly River	6-5-49-6W5	10.42	0.23	2.21	10.19	—	—	—	—	—	—		
	Belly River	8-29-48-6W5	6.11	0.10	1.64	6.01	0.5	0.5	ND	ND	ND	0.01		
	Belly River	2-28-48-6W5	5.17	0.02	0.39	5.14	—	—	—	—	—	—		
	Belly River	16-22-47-4W5	13.98	0.76	5.44	13.22	18.2	ND	17.9	0.3	ND	0.31		
	Cardium	3-24-49-5W5	41.44	0.06	0.14	41.38	44.2	2.6	41.1	0.5	ND	0.76		
	Cardium	14-20-48-6W5	32.43	0.06	0.19	32.37	—	—	—	—	—	—		
	Cardium	16-30-49-6W5	43.24	0.30	0.69	42.95	16.8	0.9	13.6	2.3	ND	0.28		
Lower Cretaceous	Viking	12-20-48-21W4	9.91	0.45	4.54	9.46	60.0	ND	18.6	41.4	ND	0.88		
	Viking	15-21-56-24W4	18.29	16.73	91.47	1.57	931.8	1.4	843.5	71.2	17.1	15.49		
	Viking	8-32-55-20W4	5.41	3.63	67.10	1.78	151.4	ND	77.4	74.0	ND	2.32		
	Viking	6-7-56-20W4	3.18	1.48	46.54	1.71	97.4	2.5	27.9	67.0	ND	1.45		
	Glauconitic	4-36-49-4W5	13.86	6.68	35.42	7.18	296.1	ND	245.2	46.4	4.5	4.84		
	Glauconitic	12-16-51-4W5	26.70	0.97	3.63	25.73	—	—	—	—	—	—		
	Glauconitic	14-4-51-25W4	7.54	4.87	64.59	2.67	284.2	6.3	238.8	30.4	8.7	4.70		
	Ostracod	16-20-49-3W5	11.90	5.16	43.36	6.74	377.8	9.1	336.3	26.9	5.5	6.33		
	Ostracod	5-33-49-3W5	12.91	8.52	66.00	4.39	496.1	7.1	452.1	28.6	8.3	8.31		
	Basal Quartz	10-29-56-24W4	8.17	5.69	69.65	2.48	—	—	—	—	—	—		
	Basal Quartz	13-21-56-24W4	15.10	0.01	0.07	15.09	—	—	—	—	—	—		
	Basal Quartz	14-23-52-26W4	6.82	0.25	3.67	6.58	15.7	0.8	9.7	5.2	ND	0.25	37.2	17.8
	Basal Quartz	15-33-51-25W4	7.59	0.44	5.80	7.16	11.0	0.2	5.7	5.1	ND	0.27		
	Basal Quartz	2-25-52-26W4	6.11	1.10	18.00	5.01	—	—	—	—	—	—		
	Basal Quartz	16-34-49-5W5	23.60	10.03	42.50	13.57	542.2	1.5	535.0	5.7	ND	9.18		
Middle Jurassic	Rock Creek	10-25-54-13W5	34.67	5.14	14.83	29.54	327.6	4.3	278.9	37.5	6.9	5.42		
	Rock Creek	16-24-54-13W5	26.55	8.07	30.40	18.48	433.6	0.9	391.3	30.1	11.3	7.06		
	Middle Jurassic	8-34-49-5W5	27.02	12.91	47.78	14.11	708.1	2.2	627.6	62.0	16.4	11.72		
	Middle Jurassic	6-34-49-5W5	29.49	13.76	46.66	15.73	—	—	—	—	—	—		
Lower Jurassic	Nordegg	14-13-49-5W5	11.80	4.91	41.61	6.90	296.9	1.6	259.1	30.9	5.3	4.91		
	Nordegg	1-18-52-5W5	29.03	7.43	25.59	21.60	425.6	1.2	389.0	32.1	3.3	7.09		
Mississippian	Banff H	6-31-50-4W5	9.98	8.11	81.26	1.87	446.4	1.1	394.7	45.6	5.0	7.39		
	Banff H	14-30-50-4W5	10.29	8.91	86.59	1.38	511.2	1.3	461.2	43.8	4.9	8.50		
Upper Devonian	Wabamun	9-16-57-3W5	9.52	0.66	6.93	8.86	36.3	1.0	33.0	2.3	ND	0.31		
	Wabamun	2-4-57-3W5	8.35	2.65	31.74	5.70	—	—	—	—	—	—		
	Wabamun	13-20-56-3W5	3.55	0.66	18.59	2.89	30.1	1.2	23.3	5.6	ND	0.50		
	Wabamun	3-7-57-1W5	8.71	0.97	11.14	7.74	—	—	—	—	—	—		
	Nisku	15-29-49-26W4	5.81	—	—	—	29.9	1.7	20.0	8.2	ND	0.49		
	Nisku	14-3-56-24W4	12.79	0.21	1.64	12.58	7.5	ND	ND	7.5	ND	0.10	42.2	14.3
	Nisku	16-10-56-24W4	10.32	1.07	10.37	9.25	—	—	—	—	—	—		
	Leduc	11-14-57-21W4	9.61	0.10	1.04	9.51	—	—	—	—	—	—		
	Leduc	6-20-57-21W4	9.02	0.03	0.33	8.99	—	—	—	—	—	—	37.7	20.8
	Leduc	7-8-58-21W4	9.59	0.06	0.63	9.53	—	—	—	—	—	—		
	Leduc	11-12-58-22W4	8.45	0.55	6.51	7.90	—	—	—	—	—	—		
	Leduc	11-19-60-26W4	4.76	3.20	67.23	1.56	—	—	—	—	—	—		
	Leduc	6-23-62-26W4	4.29	2.23	51.98	2.07	120.6	0.3	116.3	4.0	ND	2.03		

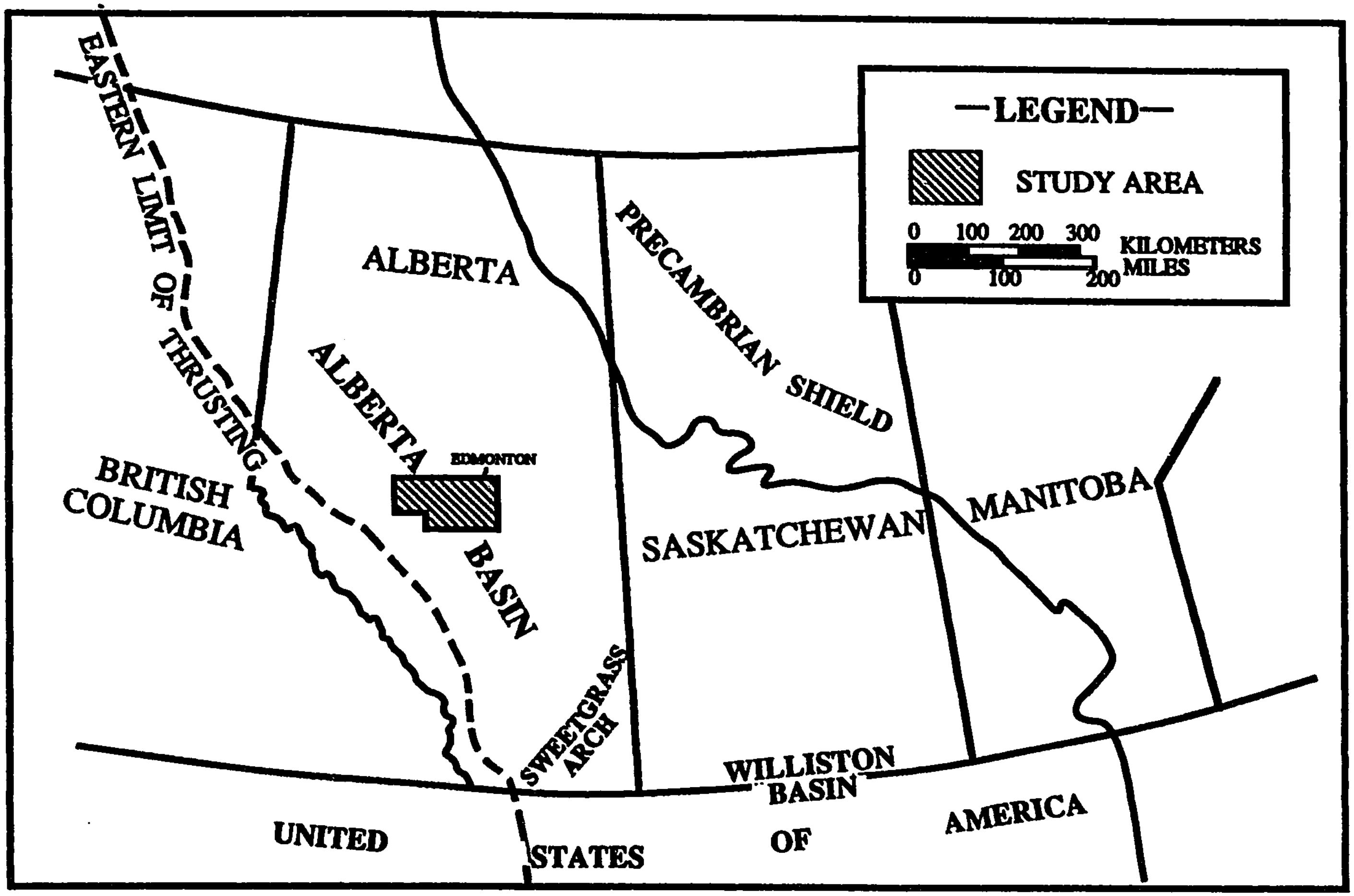


Fig. 3.1. Map of the Western Canada Sedimentary Basin, showing the location of the study area.

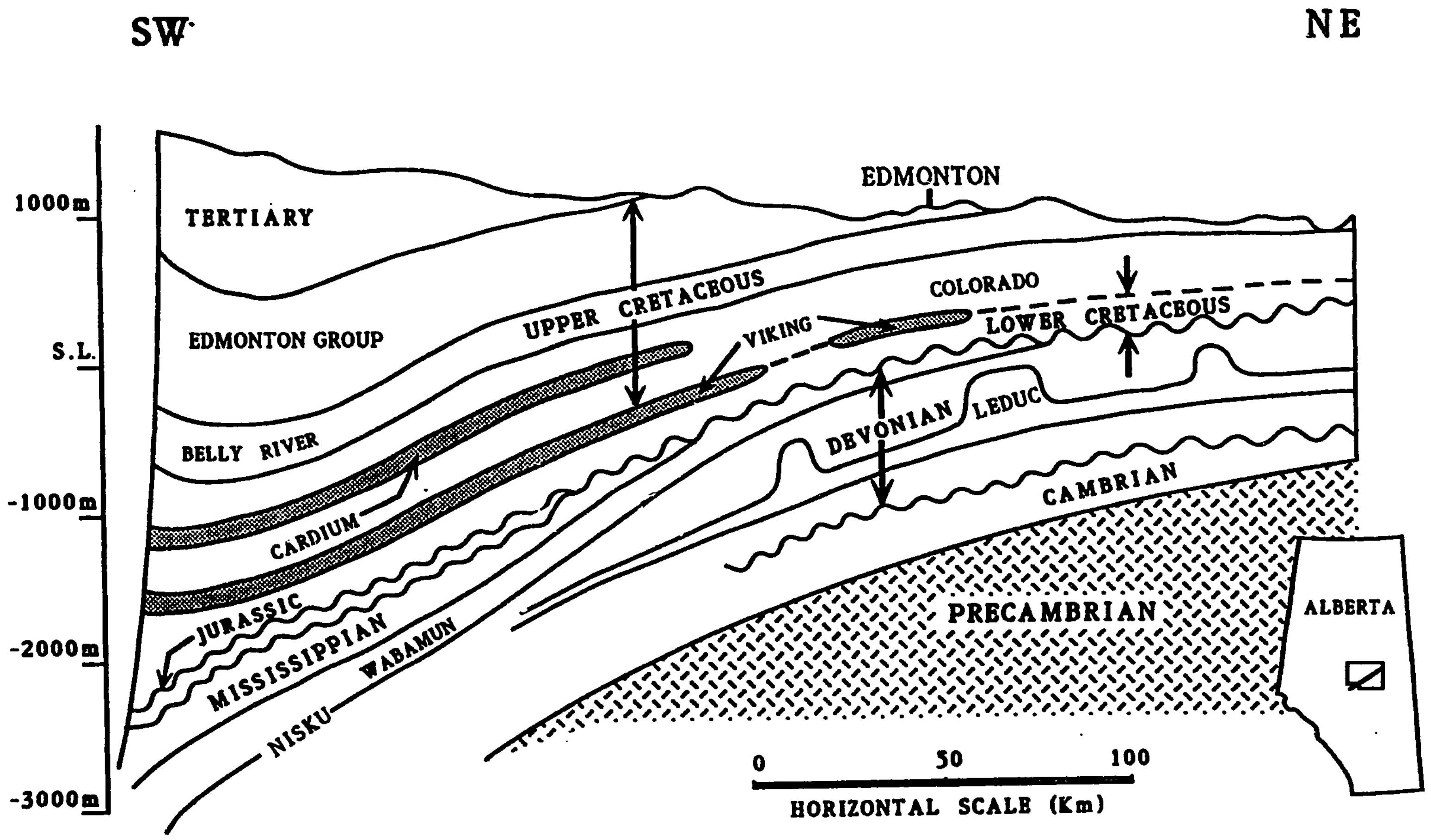


Fig. 3.2. Geological cross section from SW to NE through the Alberta Basin showing the major stratigraphic units and unconformities.

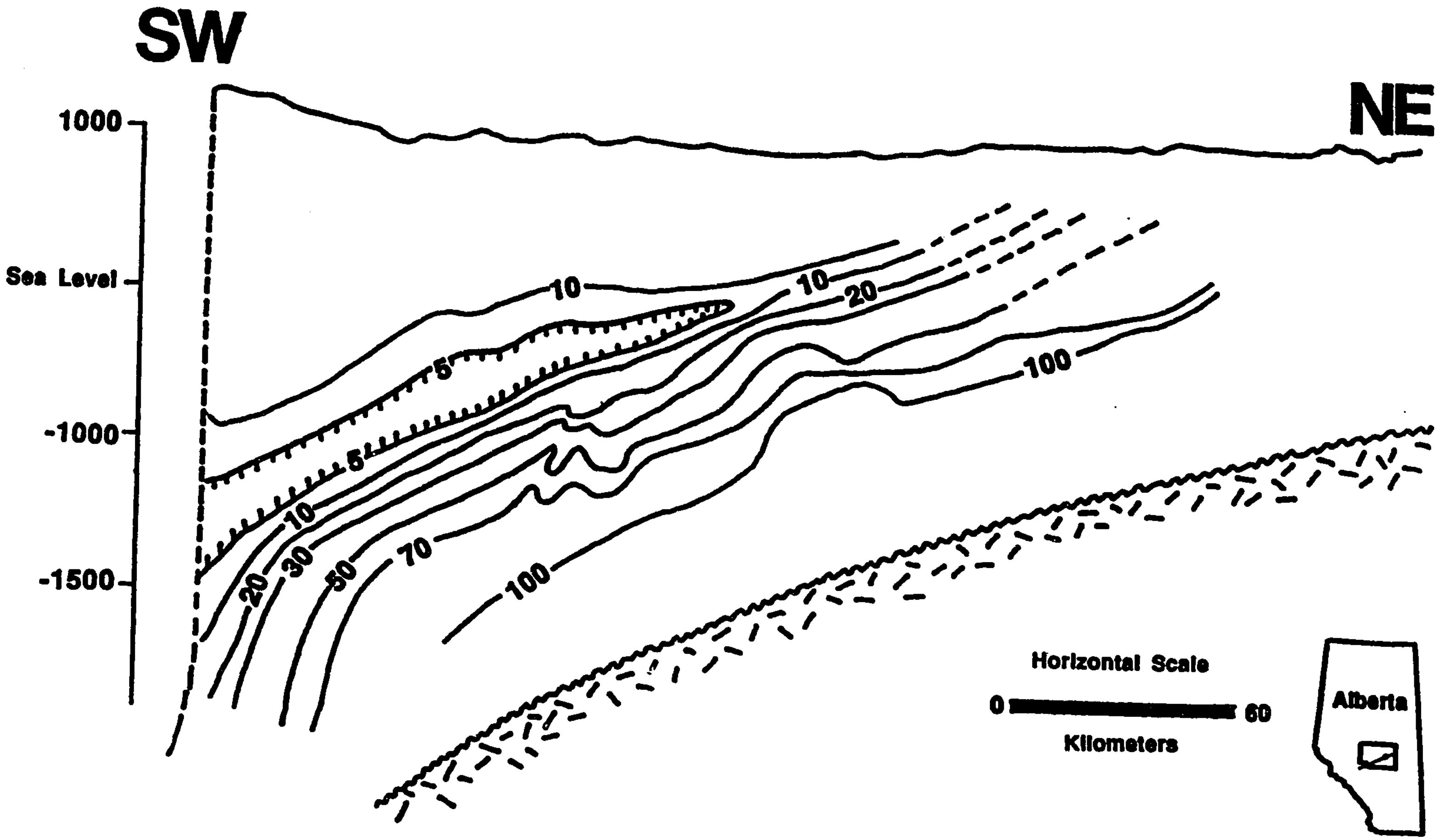
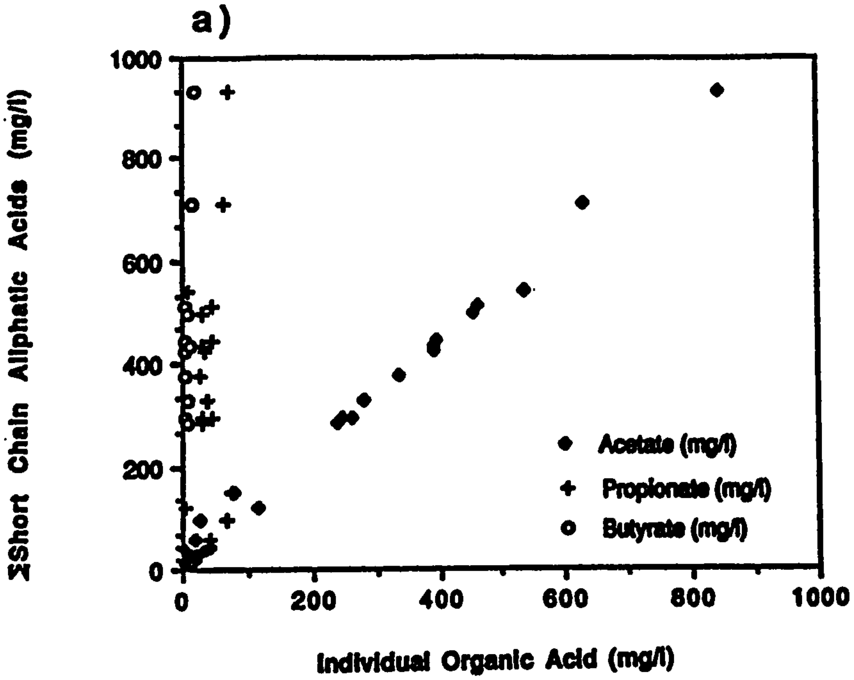


Fig. 3.3. Cross section from SW to NE through the Alberta Basin with contours showing equal values of Cl concentration (g/l).



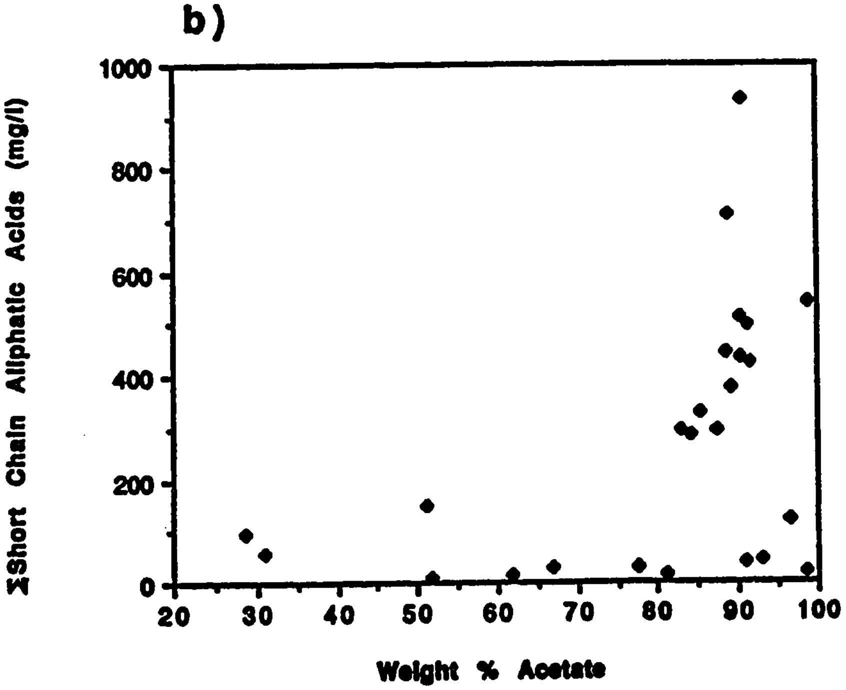


Fig. 3.4. a) Distribution of total SCA versus the individual species. The correlation coefficient of total SCAs versus acetate is 0.996, illustrating the dominance of acetate concentration. (b) Total SCA versus weight % acetate. Acetate is generally the dominant anion as shown in Fig. 3.4a, but at lower total SCA concentrations, acetate comprises less of the total weight % of the SCAs.

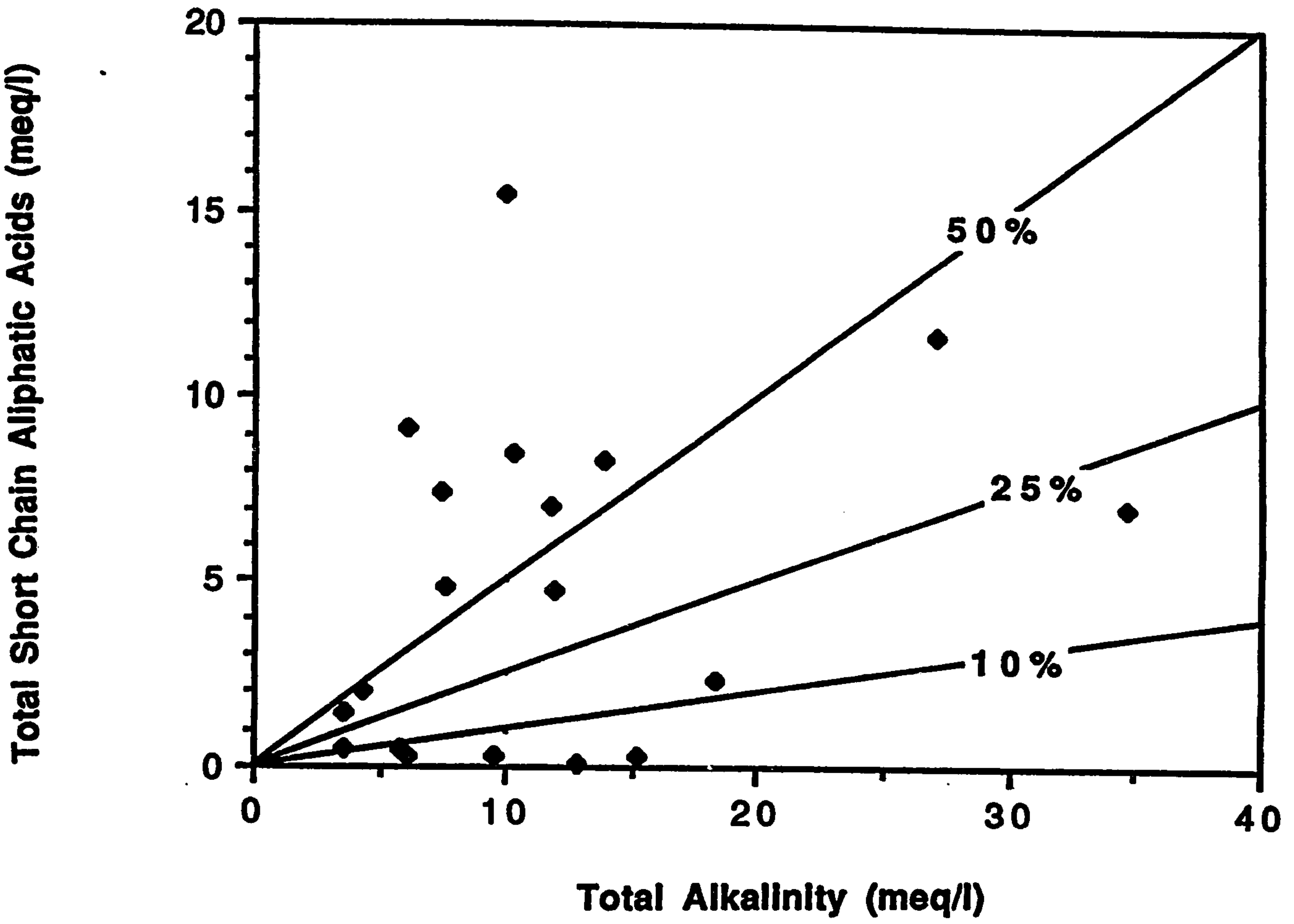


Fig. 3.5. Plot of SCA alkalinity versus total titration alkalinity for Alberta Basin brines. The SCAs comprise a widely varying percentage of the total alkalinity.

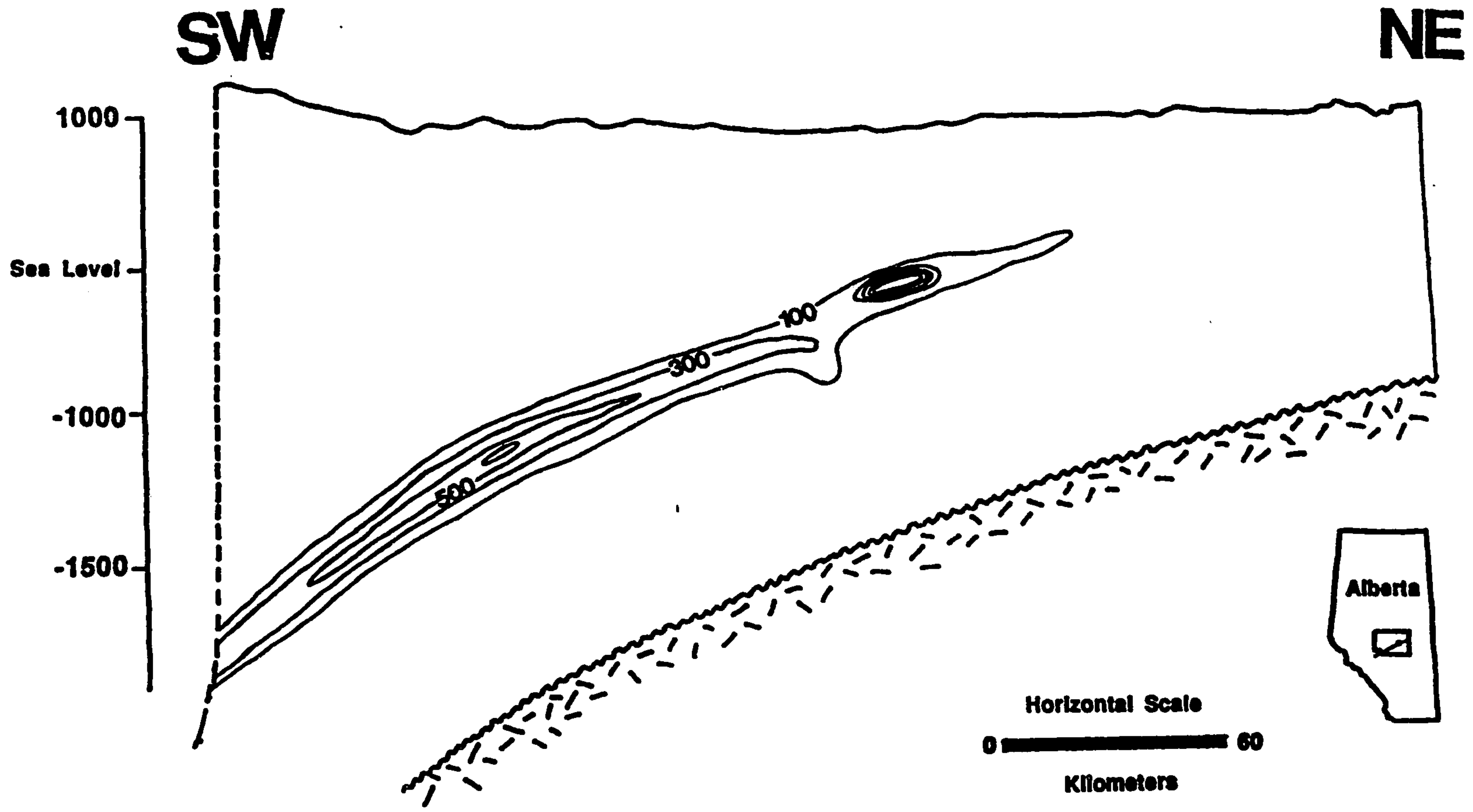


Fig. 3.6. Cross section from SW to NE through the Alberta Basin with contours showing equal values of total SCA concentration. Contour interval is 200 mg/l.

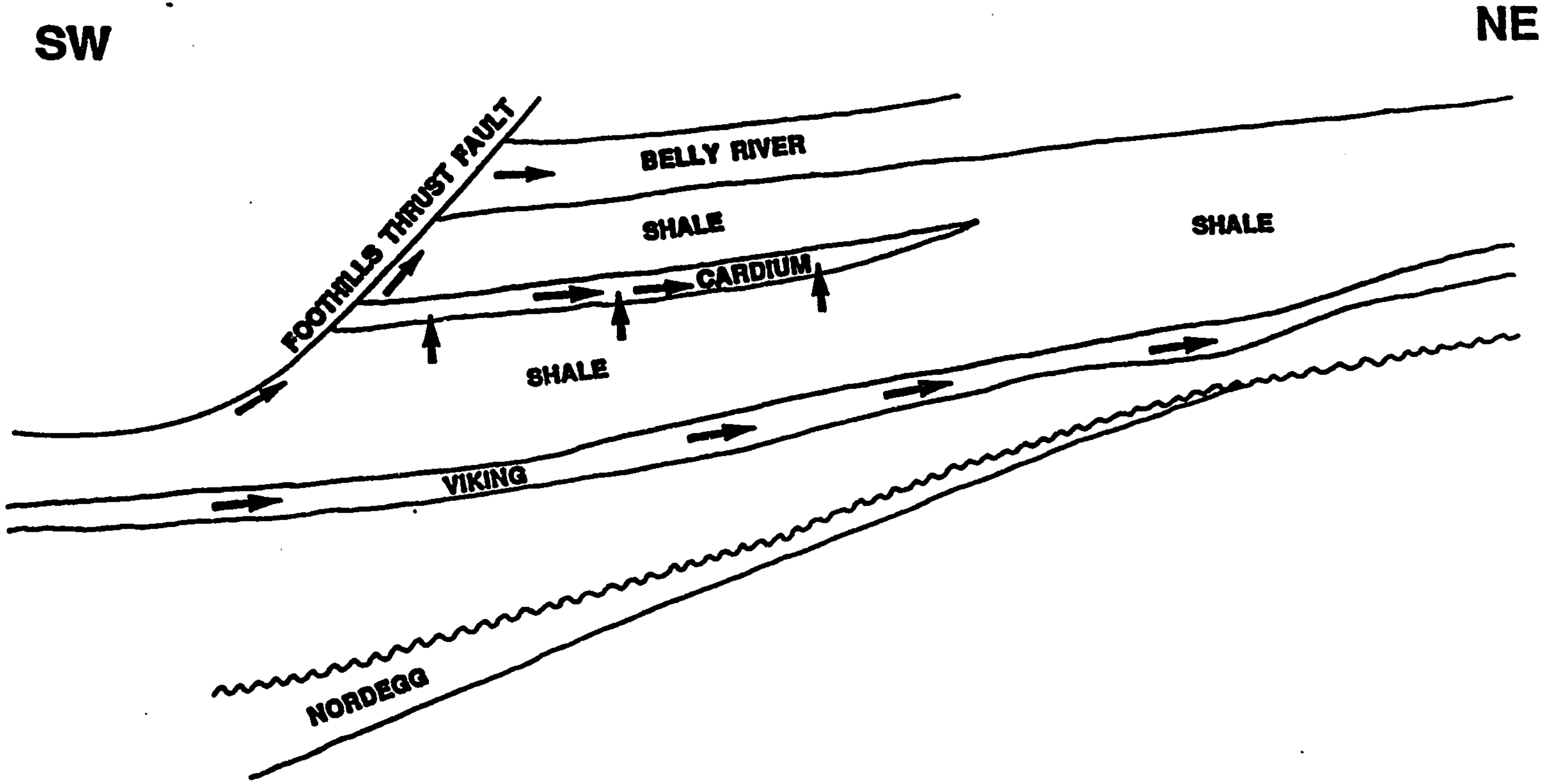


Fig. 3.7. Schematic cross section from SW to NE in the Alberta Basin illustrating proposed migration pathways for oil and gas derived from source rocks for the Cretaceous Jurassic section (modified from CREANEY and ALLAN, in press).

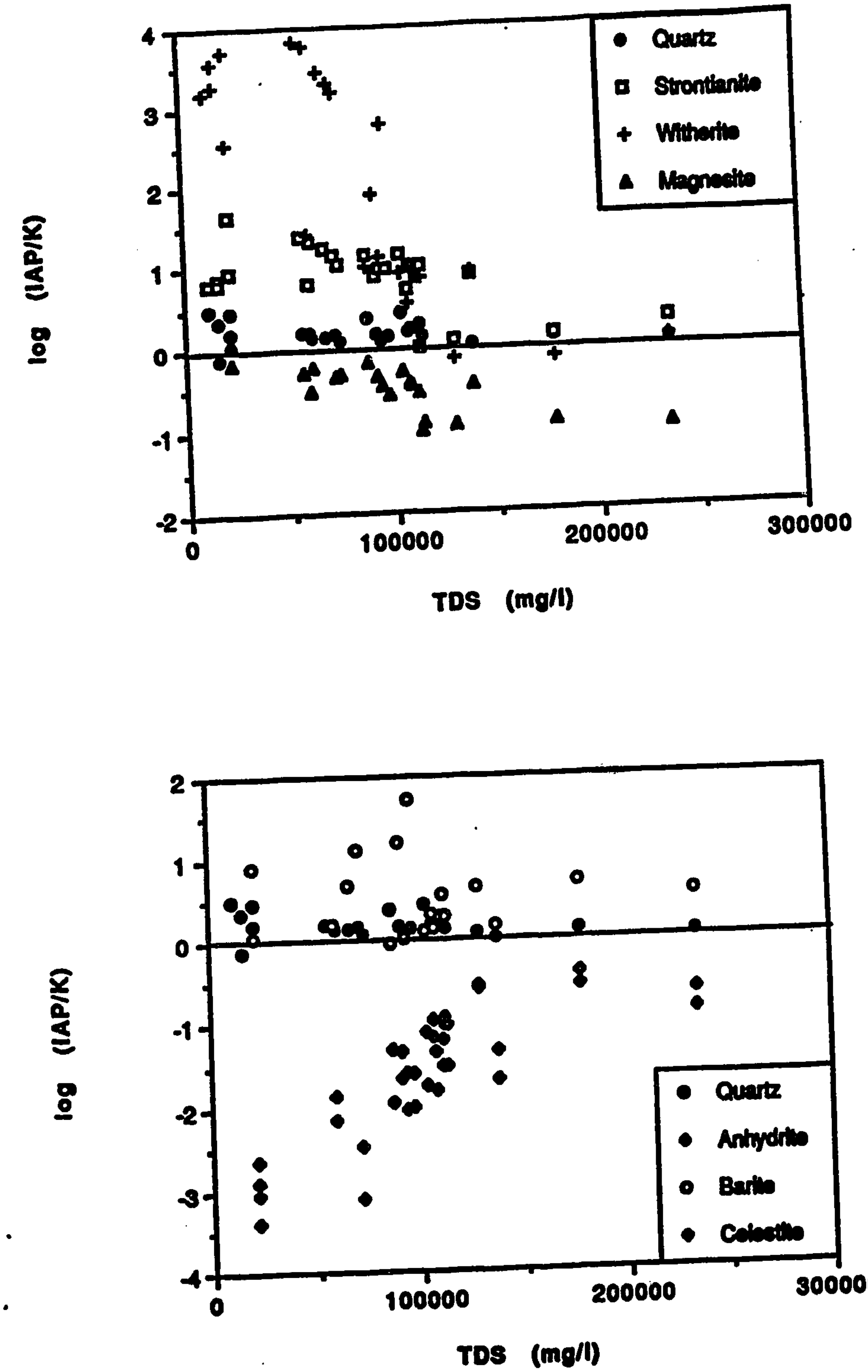


Fig. 3.8. Saturation index (S.I. = log (IAP/K)) vs total dissolved solids. Quartz is on plots (a) and (b) for reference. (a) Depicts saturation states of the carbonate minerals for Alberta Basin waters assuming pH is set by calcite phases in the host lithology. (b) Depicts saturation states of sulfate minerals in Alberta Basin waters.

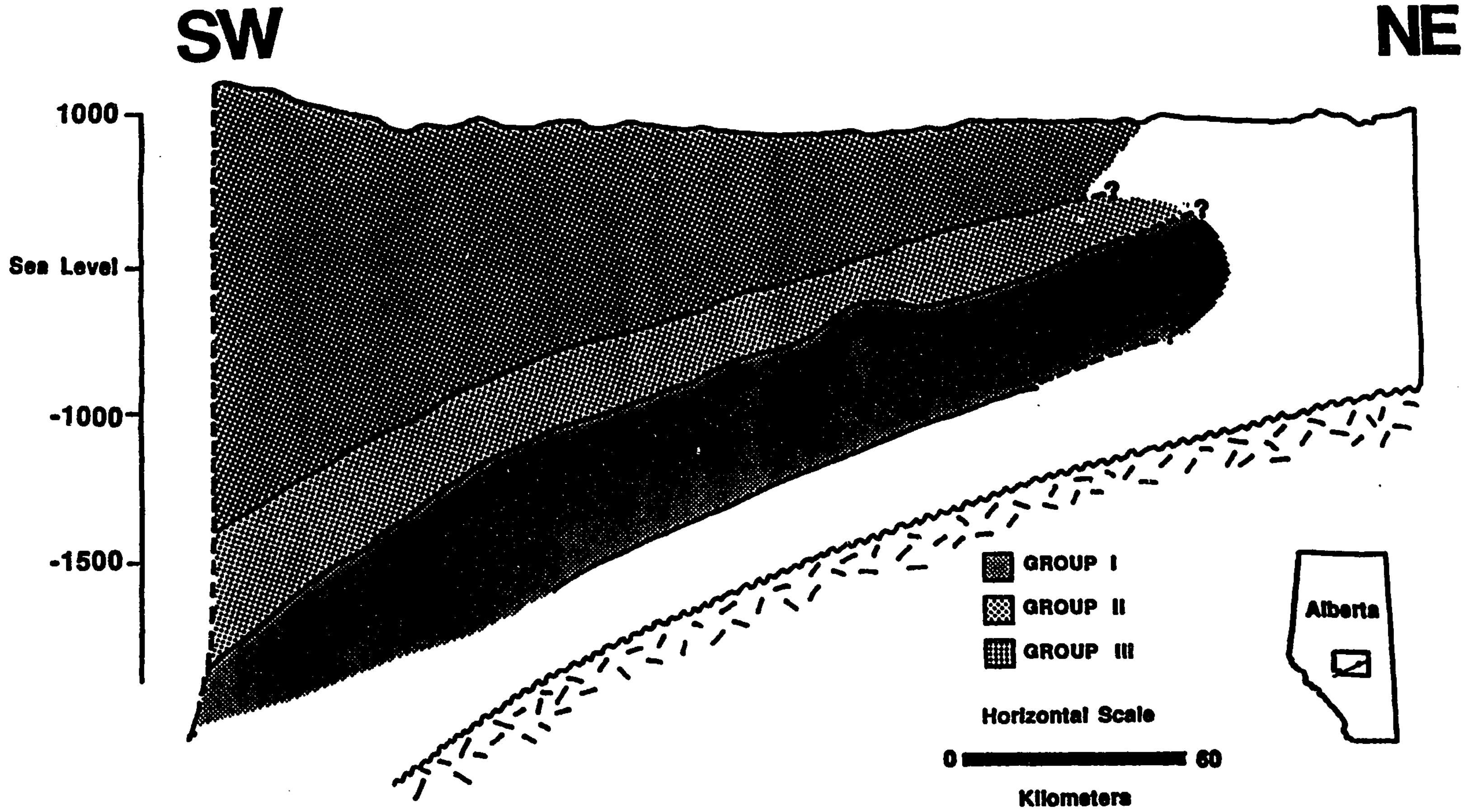


Fig. 3.9. Geological cross section from SW to NE through the Alberta Basin illustrating the division of formation waters into Groups I, II and III.

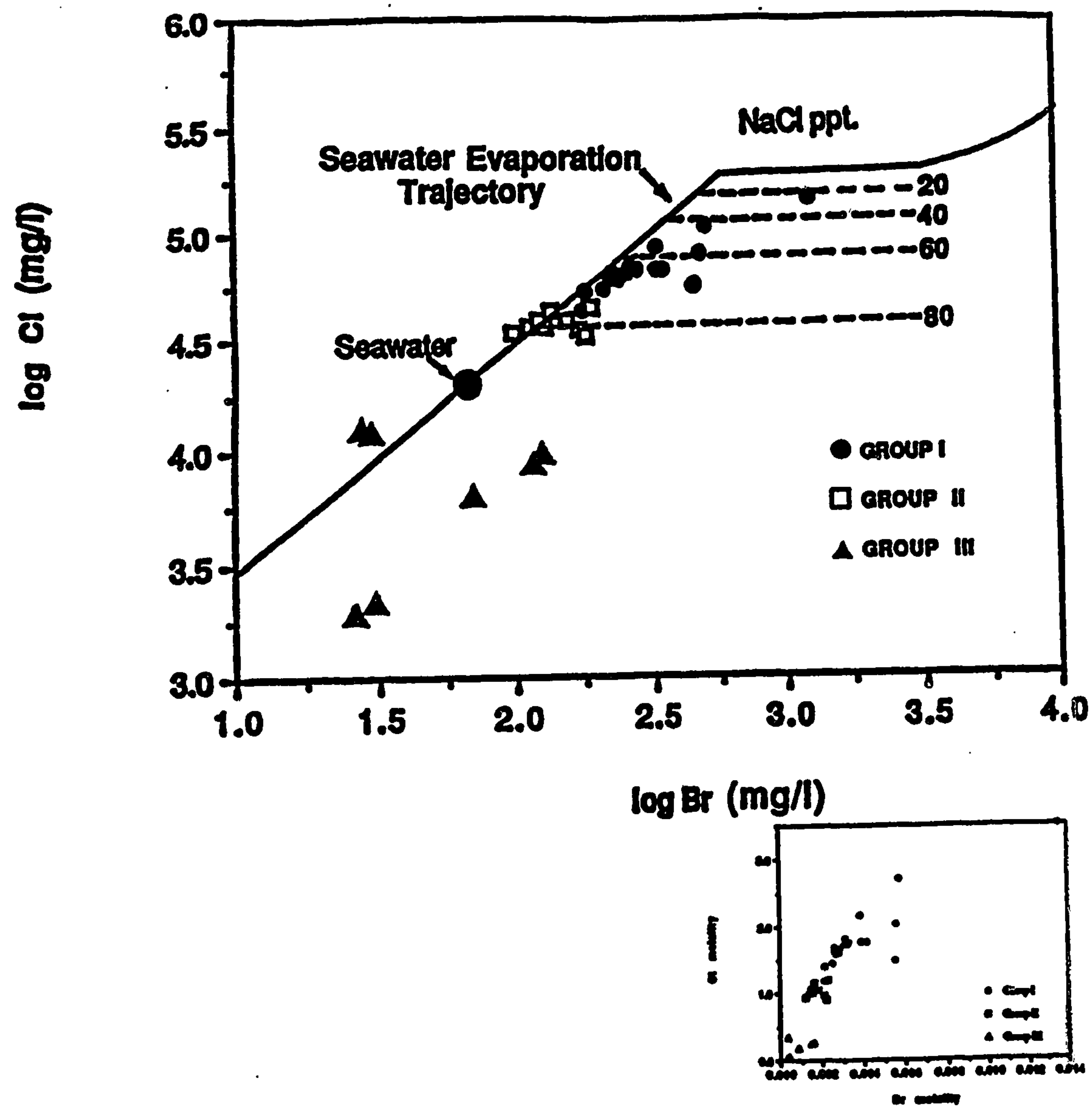


Fig.3.10. Log Cl vs log Br for Alberta Basin formation waters with the seawater evaporation trajectory for reference (CARPENTER, 1978). None of the samples plot above the S-E-T indicating salinity was not achieved by dissolution of halite. Group I brines plot to the right of the S-E-T indicating they have a seawater component that reached halite precipitation and was subsequently diluted with meteoric water. Isopleths showing remixing proportions of 20, 40, 60, and 80% are given for reference. Most of the brines for Groups I and II plot between 50 and 80% dilution. Group III waters are all more dilute than seawater. Inset provides a graph of the molality of Cl versus the molality of Br.

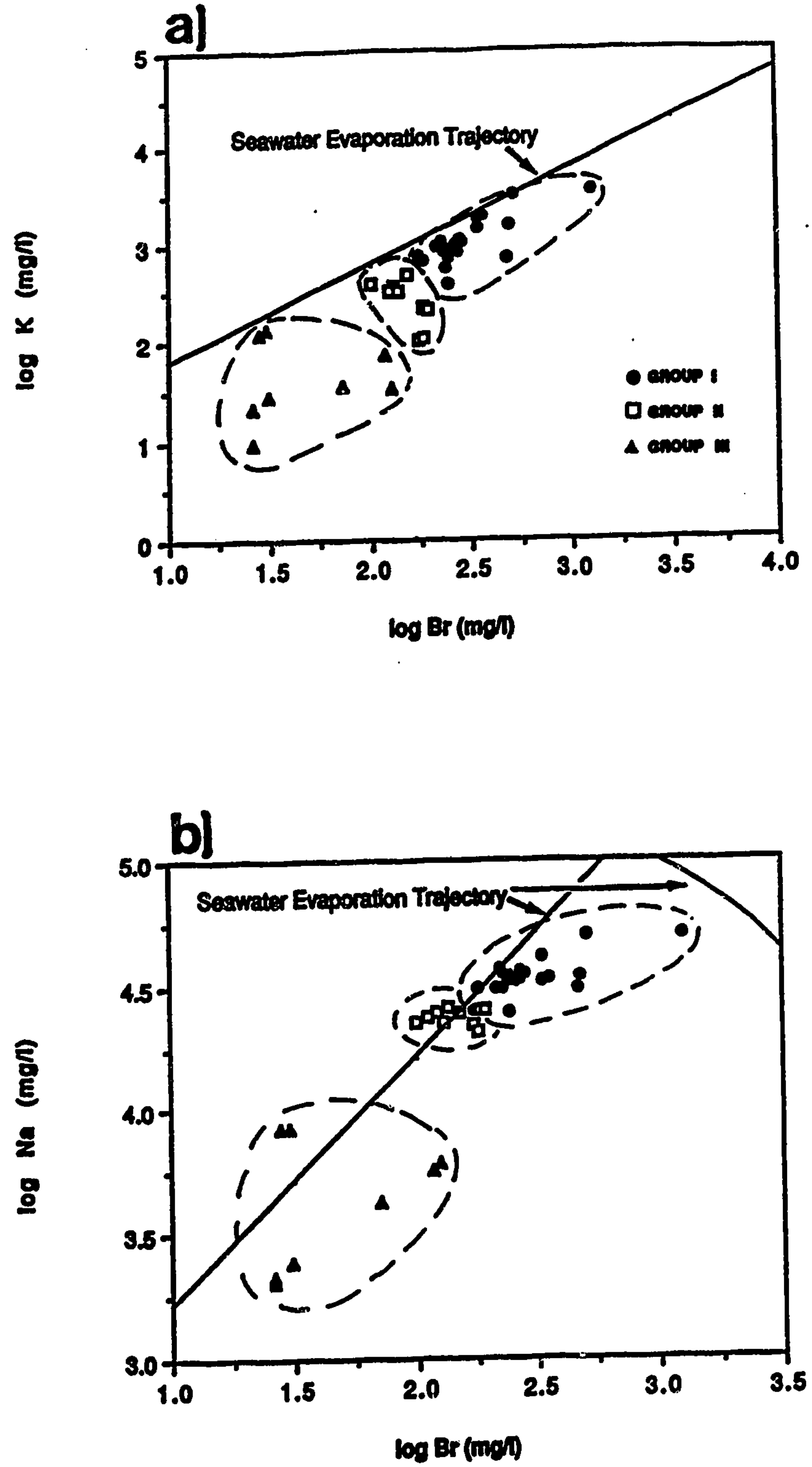


Fig.3.11. (a)Log K vs log Br for Alberta Basin brines. Fluids which show the greatest enrichment in NaCl from seawater evaporation plot closest to the S-E-T in this figure. Note that Group I waters plot closest to the S-E-T. (b) Log Na vs log Br for Alberta Basin brines.

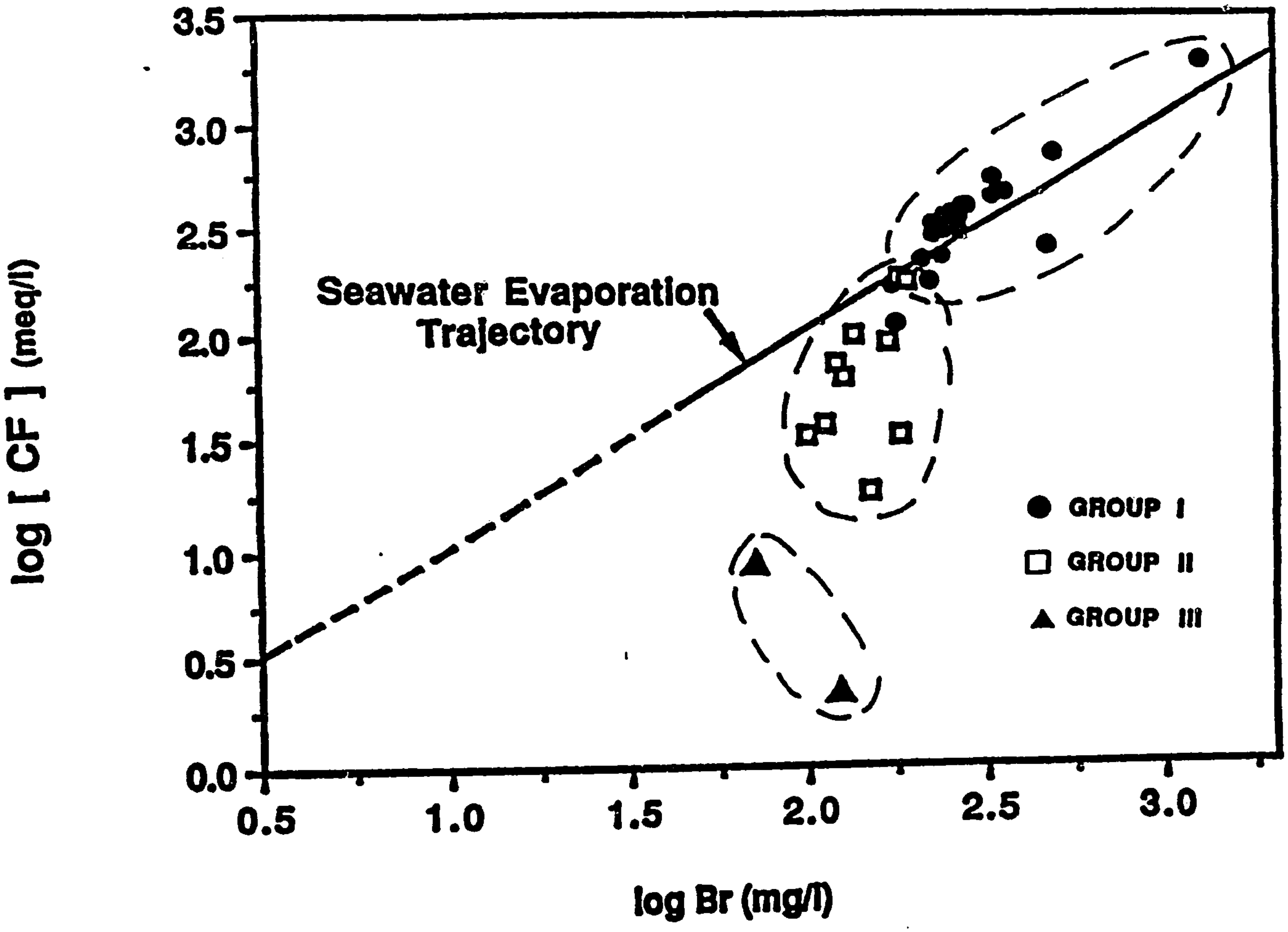


Fig.3.12. Log CF vs log Br for Alberta Basin formation waters.

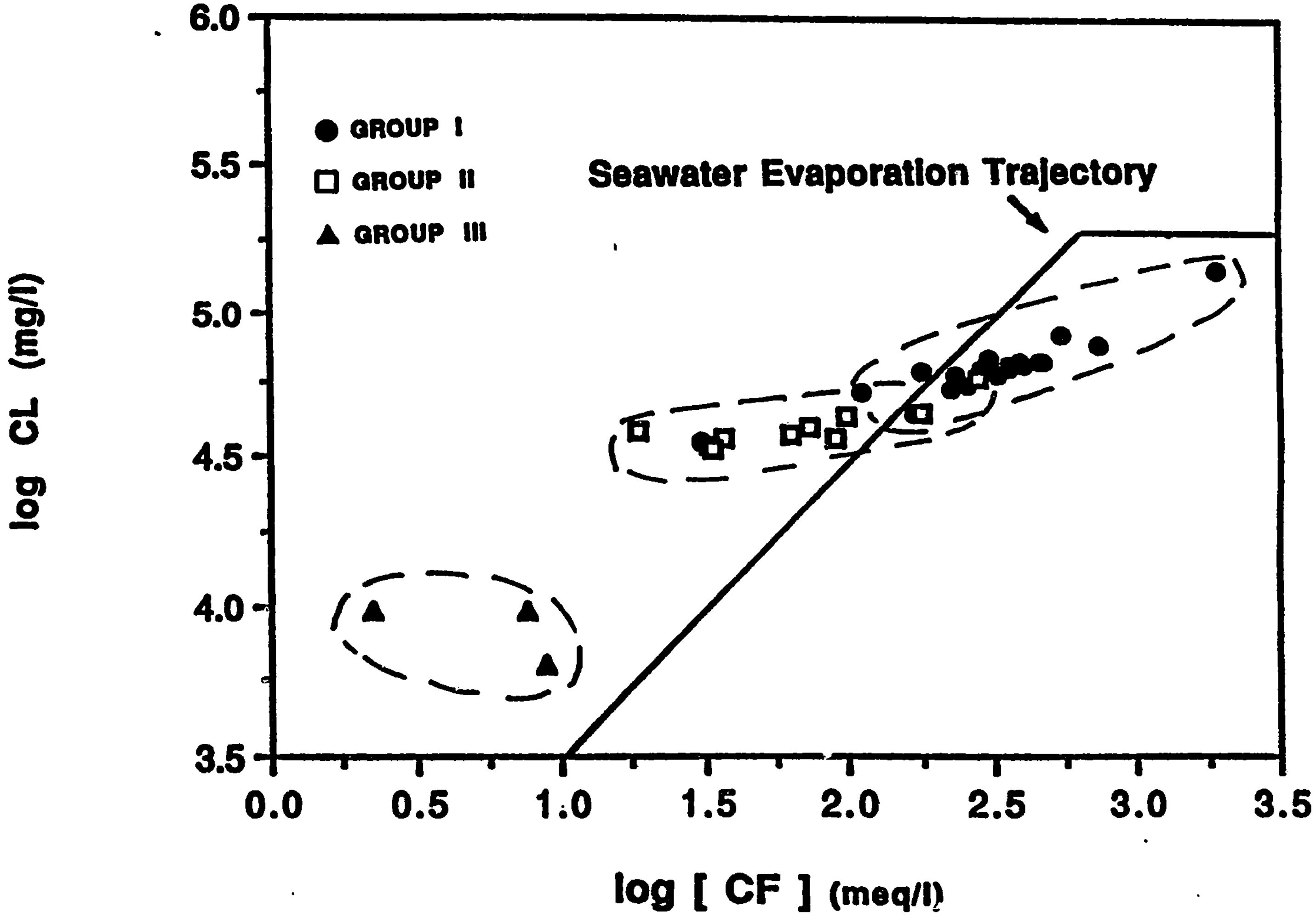
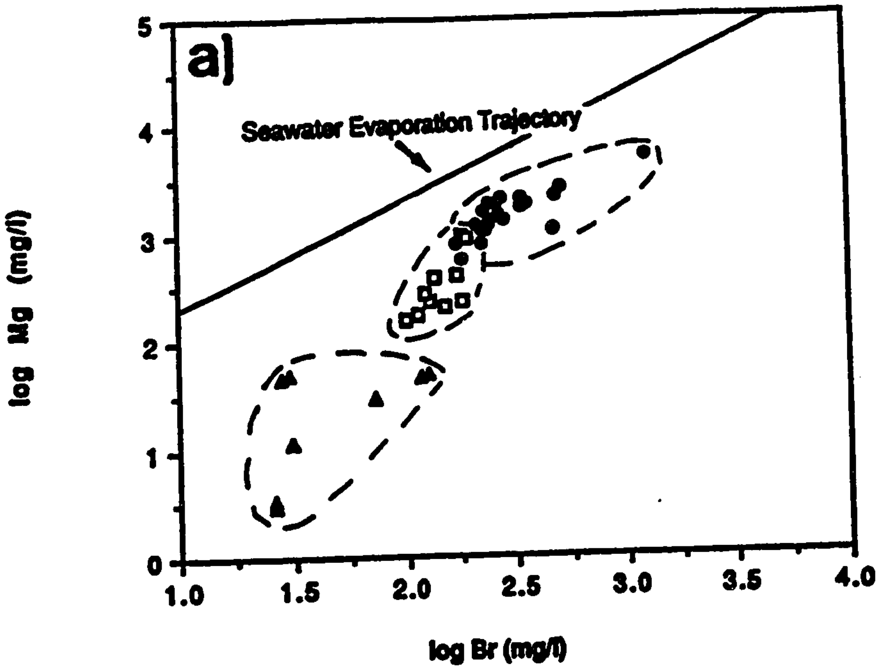


Fig.3.13. Log Cl vs log CF for Alberta Basin formation waters.



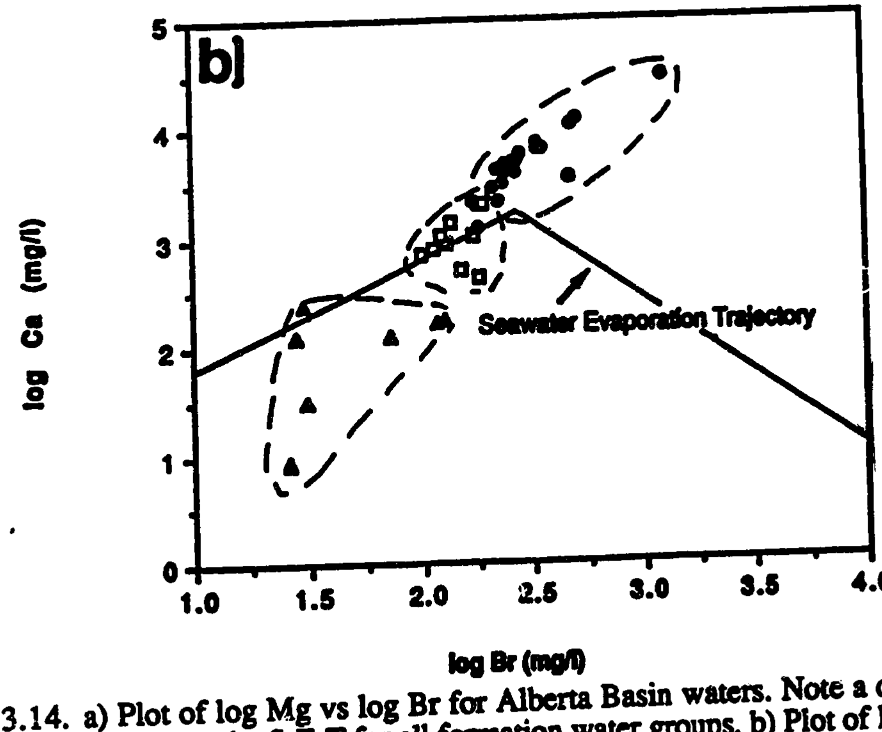


Fig.3.14. a) Plot of log Mg vs log Br for Alberta Basin waters. Note a depletion of Mg relative to the S-E-T for all formation water groups. b) Plot of log Ca vs log Br for Alberta Basin waters. There is a significant increase in Ca relative to S-E-T, for Group I waters.

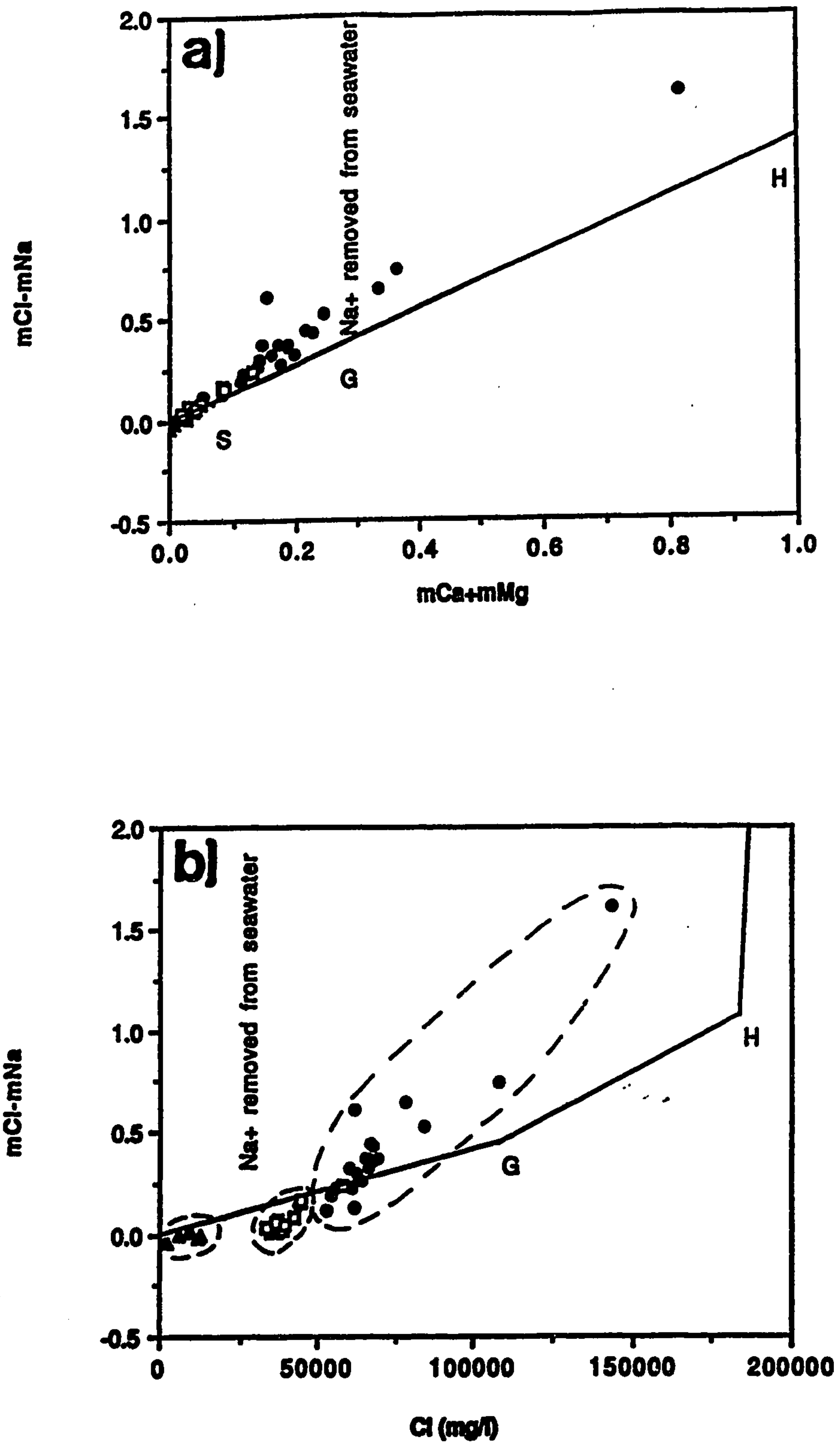


Fig.3.15. (a) Plot of (mCl-mNa) vs (mCa + mMg) for Alberta Basin brines. (b) Plot of (mCl - mNa) vs Cl. Line SGH shows the evaporating seawater trajectory: S = seawater, G = start of gypsum precipitation, H = start of halite precipitation.

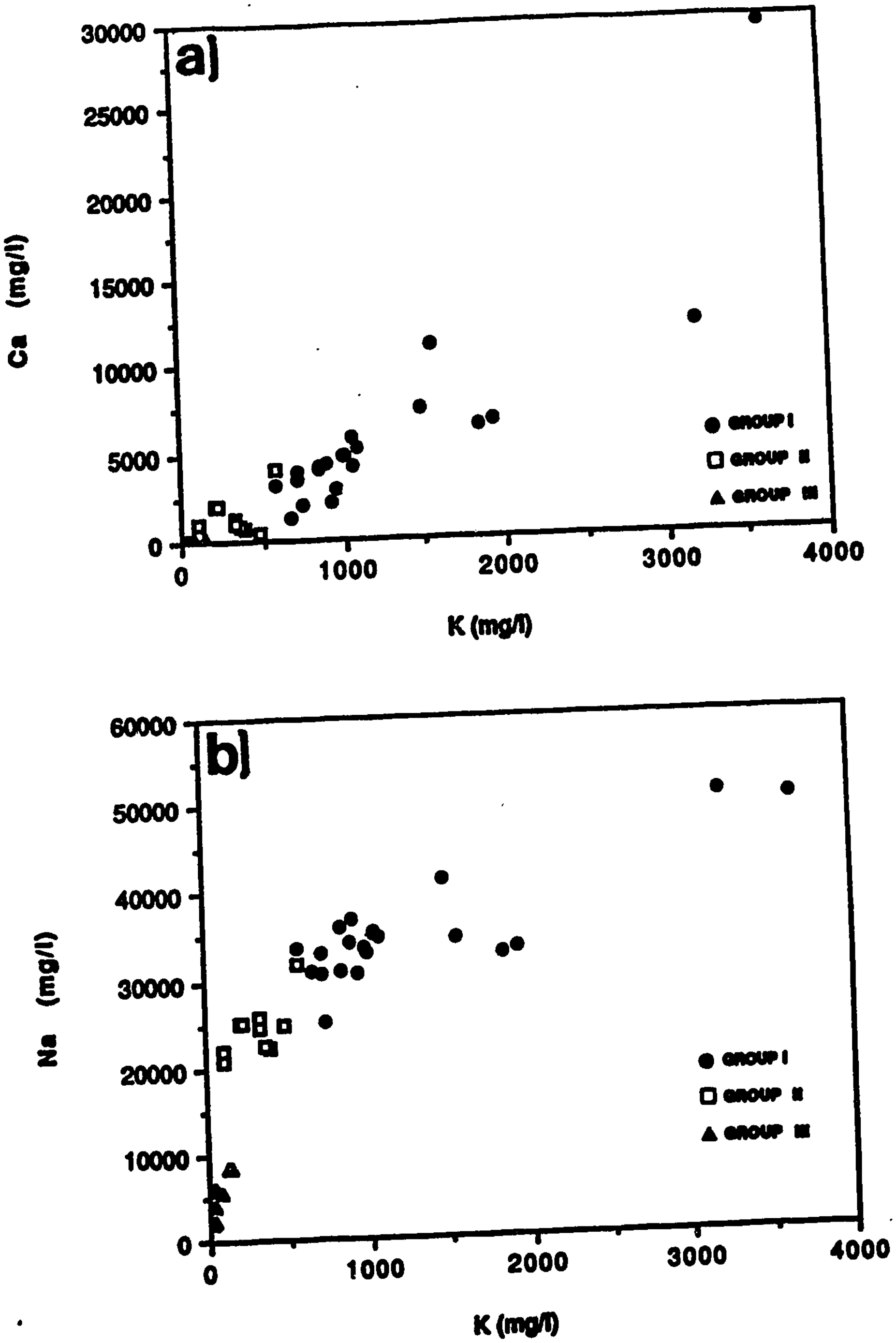


Fig.3.16. (a) Plot of Ca vs K which form a linear array intersecting close to the origin. A least squares fit to the data yields r=0.91. (b) Na vs K in Alberta Basin brines. A linear array is observed between Group I and Group II; however, Group III belongs to a separate system.

CHAPTER 4. ORIGIN AND EVOLUTION OF FORMATION WATERS, ALBERTA BASIN, WESTERN CANADA SEDIMENTARY BASIN.

II. ISOTOPE SYSTEMATICS AND WATER MIXING

INTRODUCTION

Many formation water studies have focused on the Western Canada Sedimentary Basin. The pioneer work establishing the character of groundwater flow is reported by HITCHON (1969a, 1969b) and recently, further evaluation has been completed by the hydrogeological modelling of GARVEN (1985, 1989). Preliminary isotopic and chemical characteristics are reported for 78 formation waters from oil and gas fields in the basin (BILLINGS *et al.*, 1969; HITCHON and FRIEDMAN, 1969; HITCHON *et al.*, 1971). Although these studies provide an excellent reconnaissance of the whole Western Canada Sedimentary Basin, they do not address separate aquifer systems or interformational variation throughout the basin.

Formation waters may originate as meteoric water recharged through and reacting with the rock column, or as connate water trapped during sediment deposition. Subsequent isotopic changes to formation waters may result from dilution by meteoric water, mixing of brines with contrasting chemical and isotopic composition, and/or water-rock interaction. The use of Sr isotopic measurements of formation waters, in conjunction with stable isotopes, can constrain the extent of water-rock interaction and clarify migration pathways. Oxygen and D values are important indicators for the origin of the water, whereas $^{87}Sr/^{86}Sr$ ratios reflect sources of dissolved Sr and can provide information regarding water mixing and migration, the extent and nature of water-rock interaction, and the chemical evolution of waters. CHAUDHURI (1978) was the first to apply $^{87}Sr/^{86}Sr$ ratios to the investigation of oil field brines in sedimentary basins in his study of brines in central Kansas. Since then this technique has been applied to many other oilfield waters, including those in Ohio (SUNWALL and PUSHKAR, 1979), Israel (STARINSKY *et al.*, 1983), Arkansas (STUEBER *et al.*, 1984), Mississippi (RUSSEL and COWART, 1985), Illinois (STUEBER *et al.*, 1987), southern Louisiana (POSEY *et al.*, 1985) and the Michigan and Appalachian basins (McNUTT *et al.*, 1984, 1987). No Sr isotopic analyses have yet been reported for the Alberta Basin.

The work reported here is the second of a three part study on the isotopic, chemical and equilibrium thermodynamic properties of a suite of oil field waters from the Alberta Basin. The purpose of this research is to determine, independent of hydrological models, the extent of interformational water mixing and the significance of water-rock interaction in a spatially restricted area of the Alberta Basin. Forty-three formation waters were sampled from different geographical locations and formations (Fig. 4.1). The stratigraphic and structural framework of the basin has been described in CONNOLLY *et al.* (1990). Briefly, the study area is part of the Western Canada Sedimentary Basin and comprises a wedge of unfolded sedimentary rocks that thicken toward the west-southwest and rest unconformably on Precambrian basement. The wedge of sedimentary rocks is composed of thick units of: (1) Cretaceous shale and siltstone interbedded with thin lenses of sandstone; and (2) eroded Jurassic and Paleozoic carbonates, shales and evaporites. The Cretaceous clastic rocks are separated from stratigraphically lower units by a major regional unconformity. Upper Mississippian, Pennsylvanian, Permian, Triassic and most Jurassic strata are not found in the Central Plains of Alberta.

All of the brine samples were analyzed chemically (CONNOLLY *et al.*, 1990) and for $^{87}Sr/^{86}Sr$ ratios; isotopic compositions of D and O were determined for a representative subset of brine samples. Isotopic analyses of mineral phases and rock samples from various stratigraphic units have also been determined to establish the extent of isotopic equilibration with the formation water. Thermodynamic modelling of the aqueous species was applied to the waters in a separate third study, in an attempt to elucidate the importance of water/rock interactions in controlling water compositions and mineral precipitation.

SAMPLE COLLECTION AND ANALYSIS

Procedures for brine collection are described in CONNOLLY *et al.* (1990). A total of 43 core samples representative of the stratigraphic units in the study area from which waters were sampled, were obtained from 14 different locations. Mineral compositions of the whole-rocks and diagenetic cements were studied petrographically and by X-ray diffraction. Whole rock samples and diagenetic cements were obtained for isotopic analyses (C, O, Sr), using a slow-speed, hand-held drill.

Untreated 125 ml aliquots of formation water for O and D analyses were collected in glass bottles filled to overflowing and capped with air-tight lids. Oxygen isotope ratios were determined by the CO_2 equilibration method (EPSTEIN and MAYEDA, 1953), but the equilibration period was extended to 7 to 10 days to overcome kinetic effects inherent in isotopic equilibration of CO_2 with saline brines. The equation of SOFER and GAT (1972) was used to convert the O isotope analyses from activity to concentration units. The D isotopic values were determined by the method of COLEMAN *et al.* (1982). Deuterium and O isotopic ratios were measured by conventional gas-source mass-spectrometry. Results are reported in concentration units using the usual δ notation with respect to the SMOW standard (CRAIG, 1961). The precision is ±0.13‰ and ±2.3‰ for $\delta^{18}O$ and δD, respectively.

Stable isotope analyses of carbonate minerals were obtained by reacting organic-free, powdered rock samples (<44 μm) in phosphoric acid using the method of WALTERS *et al.* (1972), modified after McCREA (1950) and EPSTEIN *et al.* (1964). All $\delta^{13}C$ values are given in permil notation relative to the Peedee belemnite (PDB) standard. Carbonate content and mineralogy were confirmed by XRD prior to isotope analyses; replicate isotopic analyses of carbonate minerals were better than ± 0.2‰.

A 125 ml aliquot of formation water, acidified to pH<2 using HNO_3, was collected for determination of the $^{87}Sr/^{86}Sr$ ratios. The $^{87}Sr/^{86}Sr$ ratios in formation waters and mineral phases were measured on a VG-MM 30 mass spectrometer, following separation by standard ion exchange techniques. Dissolution of carbonate, both whole-rock and isolated diagenetic phases, was performed using dilute (2N), ultrapure HNO_3 at room temperature; dissolution of shales was accomplished using ultrapure HF and HNO_3 and gentle heating. The within-run precision of a single analysis of the ratio was ±0.00003; repeated runs of the NBS-987 standard gave 0.71022 (± 0.00005). The Sr concentration was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES); the exact conditions of analysis are described in CONNOLLY *et al.* (1990).

RESULTS AND DISCUSSION

General

Sample locations, temperatures, depths and isotopic compositions of Alberta Basin formation waters are summarized in Table 4.1. Complete chemical analyses for these waters are reported and discussed elsewhere (CONNOLLY *et al.*, 1990). In brief, the principal ionic species of Alberta Basin waters are Na and Cl, with Ca becoming more significant in the waters from the Devonian reef strata. Although the average total dissolved solids (TDS) is relatively low (80 ± 47 g/l), the range in total concentration is large (4 to 235 g/l). Temperatures in the study area range from 35 to 75°C (average = 53°±10°C) and depths range from 680 to 1970 m (average = 1333±312 m). The samples cover a large stratigraphic interval, but the depths and temperatures are relatively similar because of the dip of the basin and availability of sample locations for specific formations.

Dilute waters extend to greater depths in the western part of the basin, closer to the Canadian Cordillera, a potentiometric high.

The water samples from the Alberta Basin have been divided into three groups based on chemistry and reservoir lithology (see discussion in CONNOLLY *et al.*, 1990). Group I waters are from Devonian, Mississippian and lowermost Jurassic (Nordegg Formation) carbonates and the lowermost Cretaceous (Basal Quartz Formation) clastic assemblage. Group II waters are hosted by the Middle Jurassic carbonates and the Cretaceous Ostracod, Glauconitic, s [illegible] lastic assemblages. Group III includes waters in the clastic rocks of the Rock [illegible] rdium, and Belly River stratigraphic units. Group I and Group II waters are separated from those of Group III by the Second White Speckled Shale, a regional transgressive shale. The results discussed below demonstrate that the division of waters into these three groups is further suggested by the brine isotopic compositions.

Oxygen and Deuterium Isotopes

Basic Relations

Oxygen and D isotopic analyses for the Alberta Basin formation waters are plotted in Fig. 4.2. Most samples from Group I and Group II have very similar δD values. Group III waters have δD values which are more negative and slope toward the meteoric water line (MWL). A least squares fit to all data intersects the meteoric water line at $\delta D = -121‰_{(SMOW)}$ and $\delta^{18}O = -16.3‰_{(SMOW)}$, close to the current weighted mean annual values for present day rainfall in Edmonton, Alberta ($\delta D = -125‰_{(SMOW)}$; $\delta^{18}O = -16.3‰_{(SMOW)}$; DANSGAARD, 1964) (see Fig. 4.1 for location). Regression of the isotopic data from

HITCHON and FRIEDMAN (1969), results in a meteoric water intercept of δD= -144‰(SMOW) and δ18O= - 19.3‰(SMOW). This is actually in reasonably good agreement with the data presented here given that (i) the samples of HITCHON and FRIEDMAN (1969) covered a broader geographical range, and (ii) techniques for determining D isotopic values in saline waters have evolved and are more accurate than those in use in the 1960's (HORITA and GAT, 1989).

Waters from the Jurassic Rock Creek Formation from Group III are relatively dilute and plot closer to the MWL than many stratigraphically higher samples. These samples, located in the middle of the stratigraphic section (Fig. 4.1), are the deepest and most westerly waters sampled (Table 4.1). Salinity contours increase in dip toward the west with proximity to the Canadian Cordillera (CONNOLLY *et al.*, 1990). Thus, dilute, meteoric waters extend to greater depths in the western part of the Alberta Basin and the position of the Jurassic samples on Fig. 4.2 may be attributed to increased meteoric water influences resulting from the location of the reservoir from which the waters were sampled. Similar values for Jurassic waters from southern Alberta have been reported by HITCHON and FRIEDMAN (1969); however, these were ascribed to meteoric recharge from the Sweetgrass Hills.

Significance of Water-Rock Interactions

The distribution of stable isotopes in waters from the Alberta Basin can be interpreted in several ways. Simple mixing of meteoric water and ocean water will form a mixing line joining surface rainwater and SMOW (standard mean ocean water). However, the brines from the Alberta Basin fall to the right of such a line, showing a large ^{18}O enrichment relative to meteoric water, but a comparatively small enrichment in D. Water-rock interactions have often been called upon to explain the isotopic composition of waters in sedimentary basins. Albitization (LAND and PREZBINDOWSKI, 1981) and equilibration with calcite (CLAYTON *et al.*, 1966; HITCHON and FRIEDMAN, 1969) can alter the O isotopic composition of waters, and processes such as membrane filtration can affect both O and H isotopes (GRAF *et al.*, 1966; KHARAKA *et al.*, 1973).

Of these phenomena, O isotopic equilibration between the formation waters and the carbonate rocks, as a function of temperature, can be most readily tested, using the approach of CLAYTON *et al.* (1966). Oxygen and carbon isotopic analyses for the reservoir carbonate samples are given in Table 4.2. The carbonate samples were usually obtained from cores within several kms (≤3) of the location of the comparable water samples.

Most of the Devonian carbonates are dolomites with the exception of the Wabamun Group, which is composed of calcite in the study area (Table 4.2). Although no waters could be sampled from the Middle Devonian Elk Point Group, rock samples were collected and analyzed because they lie beneath the Leduc Formation and potentially could have interacted with overlying formation waters. Diagenetic minerals drilled out of Devonian whole rock samples were generally characterized by $\delta^{18}O$ values similar to, but at the low end of the range of isotopic values for whole-rock samples. In contrast to the Devonian rocks, the Jurassic and Mississippian show a pronounced discrepancy between $\delta^{18}O$ values for whole-rock samples and diagenetic calcite cements, with the cements being as much as 5‰ lighter for some samples.

Authigenic carbonate cements are the only carbonate phases within the clastic rocks, with the minor exception of detrital dolomite grains in some units. Some of these rocks contain more than one generation of cement, with each generation having a distinct isotopic composition. For example, the Viking Formation contains siderite ($\delta^{18}O$ = +18 -

+26‰(SMOW)), calcite ($\delta^{18}O$ = +14‰(SMOW)) and ankerite ($\delta^{18}O$ = +16.3 - +16.7‰(SMOW)) cements (see Chapter 2) and dolomite grains ($\delta^{18}O$ = +19.3 - +22.1‰ (SMOW)). Many of the values reported here for the authigenic carbonates in the Cretaceous clastics disagree with those reported by HITCHON and FRIEDMAN (1969) for similar formations. However, their values are within the range of values reported here and the variation between the two data sets is probably because HITCHON and FRIEDMAN (1969) obtained whole-rock carbonate isotope values for sandstones without isolating cement generations.

The calcite-water fractionation factor of FRIEDMAN and O'NEIL (1977) and the dolomite-water fractionation factor of MATTHEWS and KATZ (1977) were used to calculate the O isotopic composition of formation water in equilibrium with calcite and dolomite, respectively, as a function of subsurface temperature. Figure 4.3 a-c shows the isotopic composition of waters in the Alberta Basin relative to the carbonate values at the present temperature of each water sample for the different water groups (I - III).

Group I waters are plotted in Fig. 4.3a. These waters are dominantly from carbonate reservoirs (Devonian), but also include waters from a clastic unit (Basal Quartz Formation). One water sample plots slightly above the Dol 26‰ curve, suggesting it is in equilibrium with dolomite. However, most of the waters from dolomitic reservoirs are depleted in ^{18}O relative to O isotopic equilibrium values. In general, waters from calcitic reservoirs are also not equilibrated isotopically with the carbonate host at present temperatures, but are variably enriched or depleted in ^{18}O relative to equilibrium values. Enrichment relative to calcite likely indicates reaction with dolomitic limestone and depletion suggests remnants of the effect of the regional influx of fresh water through the basin, subsequent to the Laramide Orogeny. The waters from the clastic reservoirs in Group I (small solids dots) are enriched in ^{18}O relative to the carbonate cements present.

Waters from Group II reservoirs are dominantly clastic, but contain reservoir waters from one carbonate unit (Jurassic). These waters are plotted in Fig. 4.3b. Most of the waters from this group have isotopic compositions which are in equilibrium or slightly enriched relative to the cement compositions. HITCHON and FRIEDMAN (1969) suggest that because extensive volumes of carbonate are only found at depth, enrichment of ^{18}O in shallower formation waters probably results from exchange with carbonate cements or less likely, from exchange with CO_3^{-2} or HCO_3^- in water. However, as in the case of D isotopes, the $\delta^{18}O$ signatures of the Group II waters are similar to those of Group I and thus are not consistent with separate sources of ^{18}O. Furthermore, the carbonate cements in Group II reservoirs were predominantly formed subsequent to the pervasive influx of low-^{18}O meteoric water after the Laramide Orogeny (LONGSTAFFE and AYALON, 1987), indicating that water reactions with stratigraphically lower carbonate rocks may better explain the slight enrichments.

Waters from the low salinity clastic reservoirs of Group III are shown in Fig. 4.3c. Half of the waters are depleted in ^{18}O relative to equilibrium values, and half are near equilibrium with the authigenic calcite cements at present reservoir temperatures. Considered in the context of the tectonic history of the basin, the data suggest that the low ^{18}O waters are largely influenced by local meteoric waters and and have not reacted significantly with earlier formed calcite cements.

In summary, most of the waters in the Alberta Basin do not appear to be in isotopic equilibrium with the carbonate phases present in the reservoir in which they reside. Furthermore, the waters are not biased toward ^{18}O depletion or enrichment but exhibit both traits, suggesting some communication between the waters of different stratigraphic units. Enrichment relative to equilibrium values likely results from waters derived from stratigraphically lower carbonate rocks in the basin (Devonian carbonates); depletion relative to equilibrium is probably the result of regional flushing of meteoric waters subsequent to the Laramide Orogeny. In addition, the data suggest that the waters are, or were in the recent past, actively moving in the basin. If not, a greater degree of equilibration would be observed, particularly with the carbonate phases which are generally more reactive than silicate minerals. Enriched isotopic values of formation waters have been attributed to the effects of membrane filtration (HITCHON and FRIEDMAN, 1969); however, the chemical data (CONNOLLY *et al.*, 1990) and shale abundance and composition in the Alberta Basin dispute this. Albitization is also unlikely to have been a significant influence on the isotopic composition of the waters, because carbonate phases are more abundant and more reactive than albite, and carbonate equilibration is not obvious. Furthermore, albitization is not a very significant process in the Alberta Basin (Appendix I).

Relations With Conservative Chemical Constituents

Although the data are not conclusive, extensive rock buffering of $\delta^{18}O$ values in Alberta Basin waters is not apparent from equilibrium modelling presented above. Alternatively, D is less prone to diagenetic alteration. The δD values of formation waters plotted against geochemical constituents which largely behave conservatively (Na, Cl) is a useful technique to distinguish chemical variations in subsurface waters which might result from mixing of subsurface brines, as opposed to those explainable by water/rock interactions. Formation waters, clay minerals, and hydrocarbons are the main reservoirs of H in a sedimentary basin; however, hydrocarbons do not tend to readily exchange H. If the amount of H in clay minerals is large in a sedimentary basin relative to the amount of formation water, then H-isotope exchange with clay minerals could significantly affect the water δD values. However, the amount of exchangeable H in clay minerals, relative to water H, is generally small. Furthermore, the effective water-rock ratio is also increased if formation waters mainly flow through aquifers (KNAUTH, 1988), which is likely the case in the Alberta Basin (MAJOROWICZ *et al.*, 1985; TOTH, 1989). Therefore, δD is largely conservative and well suited for distinguishing chemical variations. The $\delta^{18}O$ composition of a water is more ambiguous because it may be influenced by both water and rock reservoirs. However, when used in conjunction with δD data, $\delta^{18}O$ values can be used to indicate the relative proportion of water-rock interaction.

Figure 4.4 illustrates a series of plots of Cl and Na *vs* δD, and Cl and Na *vs* $\delta^{18}O$. On both δD plots (Figs. 4.4a and 4.4c) a good linear relation is observed; regression of the data results in x-intercepts similar to the δD value indicated on Fig. 4.2, with the Cl *vs* δD = -118‰$_{(SMOW)}$ and the Na *vs* δD = -120‰$_{(SMOW)}$. Separation of the waters into the 3 groups recognized from chemistry alone (CONNOLLY *et al.*, 1990) is very pronounced. Comparing Figs. 4.4a and 4.4c with the $\delta^{18}O$ *vs* δD plot (Fig. 4.2), a meteoric water influence can be logically inferred. Group I is the most saline and enriched in deuterium in Fig. 4.4, with some samples showing some deviation from the main cluster. Many of the Group I samples are from variable Devonian reefal facies (platform, pinnacle), with fluid movement differing in these two environments. The pinnacle reefs (Leduc Formation) direct porewaters from surrounding compacting shales upwards through the reef resulting in vertical brine movement and permeability zoning (DAVIS, 1972), whereas fluid movement in the platform reefs have a more dominant lateral component. This variation may cause some of the scatter observed on the plots (Fig. 4.4). Group II waters have lower Na and Cl concentrations, but have similar δD values to Group I. Group III is by far the most dilute, with a significant gap separating it from Group I and II. Group III waters also have the lowest δD values; several samples have δD values very similar to present rainfall.

The Na and Cl *vs* $\delta^{18}O$ graphs were plotted to assess the impact of water-rock interaction (Figs. 4.4b and 4.4d). The x-intercepts, determined by regression of the data, for both the O graphs are notably greater than on Fig. 4.2, with the Cl *vs* $\delta^{18}O$ plot = -14‰$_{(SMOW)}$ and the Na *vs* $\delta^{18}O$ plot = -15.5‰$_{(SMOW)}$. These values deviate from meteoric water values slightly more than the δD values, when the amount of error associated with the two analyses (i.e. 0.13‰ for $\delta^{18}O$ and 2.3‰ for δD) is considered. This is likely because of some O-isotope exchange between the water and rock, particularly the carbonate phases. Thus, Figs. 4.4b and 4.4d corroborate the lack of ^{18}O equilibration in host carbonates (Fig. 4.3). Although processes such as albitization and O-isotope exchange with carbonate minerals have likely occurred to some degree in the basin, they have not significantly affected the $\delta^{18}O$, δD isotope systematics of the present formation waters.

Evaporated Seawater Component

If water-rock interaction is not shown to dominate the stable O and H isotopic composition of the waters in a sedimentary basin, mixing of evaporated brines with meteoric water can, in many cases, account for the isotopic compositon of the formation waters (KNAUTH and BEEUNAS,1986). Highly evaporated seawater can have negative δ-values similar to some meteoric waters, given the hooked-shaped isotope trajectory of evaporated brines (Fig. 4.5; KNAUTH and BEEUNAS, 1986). DOMENICO and ROBBINS (1985) also show that meteoric waters do not completely flush out dense, residual brines, but rather mix with these brines. Such behavior will produce linear mixing trends on a δD - $\delta^{18}O$ diagram similar to those observed earlier by CLAYTON *et al.* (1966).

In the Alberta Basin, the δD and $\delta^{18}O$ values of formation water increase with increasing salinity, indicating a meteoric or mixed meteoric-marine origin. Because a residual seawater component associated with marine evaporite deposits is consistent with formation water chemistry (CONNOLLY *et al.*, 1990) the possibility of a hooked-shaped seawater evaporation trajectory should be evaluated.

During seawater evaporation, residual waters at first become enriched in ^{18}O and D, but then become depleted as evaporation proceeds, resulting in a hooked-shaped trajectory (Fig. 4.5). Two seawater evaporation trajectories are shown on Fig. 4.5: the curve of HOLSER (1979), which is based on laboratory data; and the curve of PIERRE *et al.* (1984) which is based on the evaporation of the Ojo de Liebre waters. The curve proposed by PIERRE *et al.* (1984) closely approximates the evaporation curve of the Black Sea (GUTSALO, 1980), and both curves show a more rapid and pronounced decrease in δD than the curve of HOLSER (1979), for equivalent increases in concentration. Furthermore, the PIERRE *et al.* (1984) curve closely parallels the meteoric water line after it recurves. This parallelism likely reflects conditions close to equilibrium which exist after the isotope evaporation curve hooks around when phase transitions in hydration spheres are occurring (GUTSALO, 1980).

Even the most saline Alberta Basin formation waters have very negative δD values. If an evaporite brine is an end-member, an extremely negative δD value is required to produce a mixing line between a brine and meteoric waters with the orientation of the trajectory for Alberta Basin formation waters on a δD *vs* $\delta^{18}O$ plot (Fig. 4.5). Halite precipitation begins at 11X and continues to 65X evaporated concentration of seawater (CARPENTER, 1978). CONNOLLY *et al.* (1990) have shown that waters in Group I have experienced extensive evaporation and gone beyond halite precipitation. Their data indicate that the more concentrated waters could have evaporated to a concentration of 45X. However, extrapolation of the PIERRE *et al.* (1984) curve to 45X concentration does not produce sufficiently negative δD values representative of the Alberta Basin waters. Measured δD values for the Black Sea (GUTSALO, 1980) are close to the curve of PIERRE *et al.* (1984) and come close to a likely evaporite brine end member composition for the Alberta Basin formation waters. However, this δD value for the Black Sea (Fig. 4.5) represents 80X concentration, which exceeds the field of halite precipitation and the degree of concentration likely experienced by Group I fluids.

Most likely, the isotopically heavy end member of the brine had a more complicated origin. One scenario would involve an evaporating brine subjected to intermittent incursions of meteoric water. The various marine incursions in the Devonian were separated by periods of uplift, during which the hydrodynamic situations allowed the influx of fresh water (GORRELL and ALDERMAN, 1968). The influence of episodic meteoric recharge into an evaporated pan is shown in Fig. 4.6. Here, sea water evaporates along a positive slope towards point A and is subsequently subjected to mixing with meteoric water. This process drives the isotopic composition of the brine from point A downward back toward the MWL, with the amount of displacement depending on the relative proportions of the waters being mixed. During the Devonian the study area was progressively migrating toward higher latitudes and lower temperatures, so that recharging meteoric water would have had an increasingly negative stable isotopic composition. In addition, uplift to the west would have caused a decrease of the isotopic values of meteoric waters, because of altitudinal effects. The zig-zag pattern on Fig. 4.6 depicts hypothetical incursions of progressively isotopically depleted waters into the basin. Although the exact path over which the water evolved is highly speculative, the end members, an evaporated seawater component (CONNOLLY *et al.*, 1990) mixing with a meteoric water, is reasonably well constrained and compatible with the tectonic history. Thus, the very negative δ-values of Alberta Basin waters do not rule out an evaporated seawater component.

δD Homogeneity Between Water Groups

Previous arguments suggest that all of the rocks in the Alberta Basin have been affected by meteoric recharge, and that Group III waters are chemically and isotopically distinct from those of Group I and Group II. The waters in Group I and Group II have relatively constant δD values (-82.2 ± 6.3‰) regardless of depth or stratigraphic unit; a regression line of the stable isotope results for these two groups intersects the MWL at δD = -96‰$_{(SMOW)}$ and $\delta^{18}O$ = -13.3‰$_{(SMOW)}$. These values are greater than modern rainfall δD and $\delta^{18}O$ values by 25‰ and 3‰, respectively.

Group I and Group II waters have a large lateral and vertical extent over which δD values are consistent. The lack of significant variation in the δD values of waters from Group I and II (Devonian-Lower Cretaceous), and the fact that they differ from present meteoric values, indicate minimal influence from the overlying flow subsystems which are flushed with modern meteoric waters. GARVEN (1989) has suggested that gravity driven flow in the Western Canada Sedimentary Basin, initiated by the Laramide Orogeny, was probably active until dissipation of the regional flow system in the Miocene-Pliocene.

To evaluate whether the Group I and Group II waters represent formations waters retained since the Neogene, conditions at that time must be examined. Paleolatitude studies indicate essentially the same latitude situation for western Canada during the post-Laramide period (HITCHON and FRIEDMAN, 1969); however, the mean annual temperature in the Neogene was approximately 9°C (WOLFE, 1980). This is at least 4°C warmer than the present average surface temperature of 5°C (HITCHON, 1984) for the study area. DANSGAARD (1964) has shown that current meteoric waters change in δD by 5.6‰ and $\delta^{18}O$ by 0.7‰ for every 1°C change in temperature. Deviations from these values resulting from kinetic effects such as altitude and lateral migration of weather inland across the continent should not have been any different then than they are today. Topographic relief of the Rocky Mountains was at a maximum in early Eocene time (BEAUMONT, 1981; HITCHON, 1984), with uplift and erosion being the strongest during the Oligocene and Miocene. However, towards the end of the Miocene and in the Pliocene, the altitude of the Rocky Mountains was similar to the present day (BEAUMONT, 1981). The lateral distance of rain and weather eastward across Canada was also similar in the Pliocene to present day. Thus, the changes in δD and $\delta^{18}O$ values for meteoric waters resulting solely from temperature may be applied in this situation. The Pleistocene glaciations were not considered to be a contributing influence to the isotopic composition of the Group I and Group II waters because these events occurred subsequent to the proposed time of dissipation of the regional flow regime (GARVEN, 1989).

Considering the temperature effect, δD and $\delta^{18}O$ values of rainwater in the Neogene would have been higher by 22‰ and 2.8‰, respectively, relative to modern meteoric waters. Both values are similar to the differences noted above between the actual Group I and Group II intersection with the MWL and the present rainfall values. Therefore, the isotopic composition of Group I and Group II waters indicate that meteoric waters in the Pliocene are one end member of a two component mixing system, with an evaporated brine component being the other member. Hydrochemical isolation of Group I and Group II waters since the Neogene would be required to preserve the mixing relations. This isolation was likely a result of the dissipation of the regional flow system into local flow systems (GARVEN, 1989).

Strontium Isotopes

General Stratigraphic Trends

The $^{87}Sr/^{86}Sr$ ratios for formation waters and diagenetic cements from the Alberta Basin are shown in Fig. 4.7 as a function of age of the reservoir rock (as opposed to the age of a given diagenetic cement which could be much younger) relative to the Sr isotope age curve for seawater (BURKE *et al.*, 1982). This curve reflects a balance between the input of Sr with low $^{87}Sr/^{86}Sr$ ratios from mid-ocean ridge basalts and of Sr with high $^{87}Sr/^{86}Sr$ ratios from continental erosion, for a given time period. Strontium has a long residence time in the ocean; therefore, its concentration and isotopic composition is uniform throughout the world's oceans at any given time (VEIZER and COMPSTON, 1974). Thus, Sr is a useful indicator of the changes that occur in water chemistry during the diagenesis of marine sediments.

. Deviation of formation water $^{87}Sr/^{86}Sr$ ratios from the Burke curve indicates a contribution of Sr from sources other than seawater or marine minerals (carbonates or evaporites) in the host rock. Most of the waters are more radiogenic than coeval seawater values until the Upper Cretaceous. Waters extracted from Upper Cretaceous reservoirs have significantly less radiogenic signatures than Upper Cretaceous seawater. The large excursion in brine $^{87}Sr/^{86}Sr$ from the seawater age curve precludes a Sr source from seawater of any age and indicates water-rock interaction must have altered the formation water chemistry in the Alberta Basin.

All of the formation waters are more radiogenic than the corresponding diagenetic cements for a specific stratigraphic unit until the upper Lower Cretaceous to Upper Cretaceous reservoirs, when their values begin to overlap. The $^{87}Sr/^{86}Sr$ values for the waters and minerals in the oldest Devonian formation (Leduc) sampled are also reasonably close to each other. The general lack of comparable water-rock $^{87}Sr/^{86}Sr$ ratios indicates that the diagenetic carbonates were formed earlier in the burial history and that the water Sr isotopic composition subsequently evolved, with little Sr-isotope re-equilibration between the waters and the cements. This is consistent with some relatively rapid changes in basin configuration, hydrodynamics and geothermal gradients induced by the Laramide Orogeny.

Whole-rock and diagenetic fractions from all stratigraphic units in the study area have been analyzed for $^{87}Sr/^{86}Sr$, except for the Devonian shales (Table 4.2). The only stratigraphic units that have $^{87}Sr/^{86}Sr$ ratios greater than any of the formation waters are Cambrian shales and the Precambrian basement. Most of the other units in the stratigraphic column, particularly the shales (e.g. Poker Chip Shale), have $^{87}Sr/^{86}Sr$ ratios similar to the highest $^{87}Sr/^{86}Sr$ values from the waters. However, rock Sr ratios must be higher than those of the waters in order for the former to raise the Sr isotopic ratio of the latter. Strontium is more mobile during weathering than Rb, and the $^{87}Sr/^{86}Sr$ ratio of the Sr that goes into solution is generally lower than the $^{87}Sr/^{86}Sr$ ratio of the rock (STANLEY and FAURE, 1979). STUEBER *et al.* (1987) conducted leaching experiments on shales with whole-rock values of 0.75472, where the leachate yielded values of only 0.71229 and 0.71178, depending on the leaching reagent. It is apparent, then, that the clastic and carbonate rocks are in hydraulic communication because the $^{87}Sr/^{86}Sr$ ratios of some waters in the Jurassic and Lower Cretaceous contain highly radiogenic Sr. However, Devonian and/or Cambrian shales are the only apparent source for these more radiogenic Sr isotopic ratios.

There appears to be a discrepancy between the degree of water-rock interaction indicated by the stable O versus the radiogenic Sr isotopic data. This may be explained by considering the differences in relative concentrations of O and Sr in water and solid phases. A large reservoir of O is present in both the rock and water phase, resulting in the O isotopic composition of the water changing toward equilibration with the rock at relatively low water-rock ratios. However, owing to low Sr concentrations in waters relative to rocks, the Sr isotopic composition of the water is reset at a water-rock ratio an order of magnitude higher than that required to reset its O isotopic composition (BANNER *et al.*, 1989) and a variation in the apparent degree of equilibration occurs.

Mixing Relations

The linear trends observed in the Na and Cl *vs* δD and $\delta^{18}O$ plots (Figs. 4.4a-d) suggest possible mixing relations among waters of the Alberta Basin which may be best described by the processes of diffusional upward flow (HANOR, 1984) or density stratification (LAND, 1987). Linear relations observed for these waters on seawater evaporation curves and elemental plots (CONNOLLY *et al.*, 1990) suggest that the waters in different stratigraphic units composing Group I and Group II are in contact with one another and are not behaving as isolated hydrological systems.

Potential mixing relations can also be tested using a plot of $^{87}Sr/^{86}Sr$ ratios *vs* reciprocal Sr concentrations (Table 4.1). The goodness of fit of the data points to a straight line tests the strength of the mixing hypothesis and the assumption that the waters were not altered in some way after mixing (FAURE, 1986). A plot of $^{87}Sr/^{86}Sr$ *vs* 1/Sr (Fig. 4.8) for all of the Alberta Basin formation waters displays several trends or groups. First, the extremely dilute samples from the Cardium and Belly River units in Group III are also extremely depleted in Sr. As with other chemical components (CONNOLLY *et al.*, 1990), the Sr isotopic systematics of the Group III waters attest to their lack of association with the rest of the brines in the basin. Second, with the exception of a couple of Group II brine samples, most Group I and II water samples form a near-vertical array with a slightly negative slope. The dominantly carbonate hosted brines of Group I generally have higher $^{87}Sr/^{86}Sr$ ratios than formation waters from the clastic rocks of Group II, but Sr concentration of both groups is quite similar. This behavior is unusual because carbonate rocks generally have high average Sr concentrations (610 ppm; FAURE, 1986) and relatively low isotopic ratios (0.708-0.709), whereas shales and sandstones generally have much lower average Sr concentrations (sandstone 20 ppm; shale 300 ppm; FAURE 1986) and much higher $^{87}Sr/^{86}Sr$ ratios; these characteristics result in the positive slope usually observed on $^{87}Sr/^{86}Sr$ *vs* 1/Sr plots.

The contribution of Sr from the rock to the fluid phase is controlled by mineral reactivity and solubility, both of which tend to be greater for carbonates than for clastic rocks. Carbonate minerals, plagioclase and volcanic ash are important sources of Sr. Clay, microcline, mica, apatite and ferromagnesium minerals contribute less Sr, either because they are more resistant to chemical weathering, have low Sr concentrations, or both (STANLEY and FAURE, 1979).

. When waters have interacted with rocks of two completely different lithological compositions, (e.g. carbonate and clastic rocks) and two completely different Sr concentrations and $^{87}Sr/^{86}Sr$ ratios, two end member components can frequently be observed. In the Alberta Basin two different rock groups are present, the Paleozoic carbonates and the Cretaceous clastic rocks. From previous discussion it has been determined that the waters from these units, Group I and Group II, are in communication; therefore, a two component mixing line is expected. However, Fig. 4.8 indicates that the clastic rocks have high Sr concentrations, similar to the carbonates, and that a vertical trend is generated rather than a mixing line with a definable slope. When Fig. 4.8 is enlarged, a non-random mixing trend becomes definable with a negative slope. This negative slope is unique; a mixing line with such an orientation has not been previously published, although low $^{87}Sr/^{86}Sr$ values similar to those from the Alberta Basin have been reported in the San Joaquin Basin (BOLES, pers. comm.).

The positive slope on the right side of Fig. 4.8 between some Group II and Group III waters represents waters sampled from the Rock Creek Formation and Middle Jurassic units. Both of these waters, particularly that from the Rock Creek, have been shown by stable isotopes and chemical concentrations to have been diluted by meteoric waters. The Middle Jurassic was sampled reasonably close to the Rock Creek sampling locations and may be affected by downward flow from the Rock Creek unit. Both waters are displaced to the right because of dilution, which would affect their Sr concentration but not their $^{87}Sr/^{86}Sr$ ratios.

In summary, the waters in Groups I and II appear to be an open chemical system with each other, with the Group II waters in stratigraphically higher units having lower Sr concentrations than those from Group I. It would appear that diffusional flow has been an active process between the high $^{87}Sr/^{86}Sr$, carbonate-hosted waters and the low-$^{87}Sr/^{86}Sr$ clastic-hosted waters; a tentative *density stratification* has been established. Density stratification is characterized by a regular increase in salinity commonly observed in sedimentary basins. Barring forced flow or hydrothermal convection, which are unlikely processes in the study area, basins become stratified in their salinity distribution until displaced by meteoric recharge. This corroborates the previous argument that waters from Group I and II have not experienced meteoric recharge since at least the Pliocene.

Provenance of Clastic Sedimentary Rocks

The concentration of Sr in sandstones and waters may be directly proportional to the abundance of a given mineral phase. STANLEY and FAURE (1979) show that 88.5 - 98.5% of the Sr in authigenic cements from the High Plains sequence of Nebraska and Wyoming originated from sources having low $^{87}Sr/^{86}Sr$ ratios (0.706 - 0.709). The concentration of Sr in the sandstones from this sequence is directly proportional to the abundance of plagioclase, suggesting it is the principal source of Sr in the formation water and the control on formation water $^{87}Sr/^{86}Sr$ ratio. The study emphasized the dominance of plagioclase and volcanic ash, both of which are characterized by low $^{87}Sr/^{86}Sr$ ratios, as prevalent sources of Sr dissolved in porewaters.

Petrographic analysis of rocks in the study area in the Alberta Basin indicate that igneous and sedimentary terrains have contributed detritus to the Lower Cretaceous formations, with minor contributions from metamorphic sources. Previous studies dealing with Cretaceous rocks in the Alberta Basin have suggested that the sediment source was the Precambrian Shield to the east (CAMERON, 1965; ORR *et al.*, 1977), the Canadian Cordillera to the west (MELLON, 1967; VIGRASS, 1977), or a combination of these two. In contrast, PUTNAM (1982) and SUTTNER (1969) have suggested a more southerly source of sediment for the basin.

Toward the end of the Lower Cretaceous, the regional dip of the Alberta Basin was to the north or northeast because of the rising mountain chain to the southwest. The Cretaceous river systems were draining toward the north (Fig. 4.9) (WILLIAMS and STELCK, 1975; PUTNAM, 1982). This inferred stream orientation and flow direction contrasts with sediment dispersal patterns previously proposed for the upper Lower Cretaceous in the study area. The distribution of sediments has been interpreted as having emanated eastward from the Canadian Cordillera in response to mountain building triggered by the Columbian Orogeny (EISBACHER *et al.*, 1974; MIALL, 1978). However, EISBACHER *et al.* (1974) also inferred a northward paleoflow direction subparallel to the mountain front. This theory eliminated high $^{87}Sr/^{86}Sr$ constituents from the Canadian Shield as a major source of detritus to the Alberta Basin during Cretaceous time and pointed to the northwest U.S.A. as a likely source of sediment.

The Rocky Mountains of western Montana and Idaho, which were either present or forming during Lower Cretaceous (PUTNAM, 1982; GARVEN, 1989), are the main highlands to the southwest of the study area. Associated with these units was an eastward migrating volcanic regime. This volcanic belt was associated with regional orogenesis which originated in Oregon during the Middle to Late Jurassic and migrated as far east as western Montana during the Late Cretaceous and Early Tertiary. Culmination of this period of continuous mobility occurred in west-central Montana with the onset of Laramide tectonism. Thus, the decrease in $^{87}Sr/^{86}Sr$ of both rocks and waters of the study area throughout the Cretaceous may be accounted for by the increasing influence of volcanic sediments, as the locus of deposition moved closer to the Alberta Basin in response to the migration of orogenic movements. Plagioclase and volcanic ash are dominant constituents of these volcanics, both of which could have contributed considerable Sr to the water because of their reactivity, regardless of the fact that they were not the most abundant mineral constituents present. The $^{87}Sr/^{86}Sr$ ratios of volcanic rocks in continental environments tend to range from 0.703 - 0.708 with a mean of 0.70577 (FAURE, 1986). Detritus from these volcanic rocks, plus ^{87}Sr-poor sedimentary rocks from the same region, may be the origin of the low and decreasing $^{87}Sr/^{86}Sr$ ratios in the waters, particularly if these solids provide >80% of the Sr to the waters, as is the case in other basins (STANLEY and FAURE, 1989).

A volcanic contribution to the Cretaceous sediments would help to explain the negatively sloped *mixing* trend observed between the dominantly carbonate (Group I) and clastic rocks (Group II) (Fig. 4.8). Volcanic rocks have an average Sr concentration of 465 ppm (FAURE, 1986) which is relatively similar to the average carbonate concentration of 610 ppm for carbonates. If the former minerals release slightly less Sr than the latter, with different $^{87}Sr/^{86}Sr$ ratios, the negative slope in Fig. 4.8 could result.

CONCLUSIONS

Formation waters in the Alberta Basin form three hydrochemical groups: (1) Group I is composed of waters from the Devonian and Mississippian carbonates and the Cretaceous Basal Quartz Formation; (2) Group II is composed of waters from Cretaceous clastic rocks of the Ostracod, Glauconitic, and Viking Formations, together with the Jurassic waters; (3) Group III is composed of waters from the Belly River, Cardium and Rock Creek stratigraphic units.

Plots of stable isotopes (δD *vs* $\delta^{18}O$), combined stable isotope and elemental data (Cl *vs* δD; Cl *vs* $\delta^{18}O$) and $^{87}Sr/^{86}Sr$ *vs* 1/Sr, suggest that two hydrological regimes are present in the basin. One regime is dominated by flushing of modern meteoric waters through the upper portion of the sedimentary succession and is represented by Group III waters. The second regime is isolated from the first and is characterized by association between Group I and II waters. This regime is composed of a mixture of meteoric waters that flushed through the basin as a result of Laramide tectonism and original connate brines. Group I and II formation waters became isolated from present day meteoric water recharge during the Pliocene; upward diffusional flow and density stratification followed, resulting in stratigraphically lower formations becoming more saline than the formations located stratigraphically higher in the section.

Variation in water $^{87}Sr/^{86}Sr$ ratios indicate that different water-rock interactions and changes in provenance have occurred in the basin. The $^{87}Sr/^{86}Sr$ ratios in Group I waters (0.7076 - 0.7129) are strongly influenced by Devonian and Cambrian shales. The $^{87}Sr/^{86}Sr$ ratios for waters and diagenetic minerals in the upper Lower and Upper Cretaceous are relatively low (0.7058) suggesting that a volcanic source to the southwest (Montana) was a significant source of detritus for the study area.

REFERENCES

BANNER J.L., WASSERBURG G.J., DOBSON P.F., CARPENTER A.B. and MOORE C.H. (1989) Isotopic and trace element constraints on the origin and evolution of saline groundwater from central Missouri. *Geochim. Cosmochim. Acta* **53**, 383-398.

BEAUMONT C. (1981) Foreland basins. *Geophys. J. Roy. Astron. Soc.* **65**, 291-329.

BILLINGS G.K., HITCHON B. and SHAW D.R. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin. 2. Alkali metals. *Chem. Geol.* **4**, 211-223.

BURKE W.H., DENISON R.E., HETHERINGTON E.A., KOEPNICK R.B., NELSON H.F. and OTTO J.B. (1982) Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time. *Geology* **10**, 516-519.

CAMERON E.M. (1965) Application of geochemistry to stratigraphic problems in Lower Cretaceous of western Canada. *Am. Assoc. Petrol. Geol. Bull.* **49**, 62-80.

CARPENTER A.B. (1978) Origin and chemical evolution of brines in sedimentary basins. *Okla. Geol. Surv. Circ.* **79**, 60-77.

CHAUDHURI S. (1978) Strontium isotopic composition of several oilfield brines from Kansas and Colorado. *Geochim. Cosmochim. Acta* **42**, 329-331.

CLAYTON R.N., FRIEDMAN I., GRAF D.L., MAYEDA T.K., MEENTS W.F. and SHIMP N.F. (1966) The origin of saline formation waters, I. Isotopic composition. *J. Geophys. Res.* **71**, 3869-3882.

COLEMAN M.L., SHEPHERD T.J., DURHAM J.J., ROUSE J.E. and MOORE G.R. (1982) Reduction of water with zinc for hydrogen isotope analysis. *Anal. Chem.* **54**, 993-995.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. I. Chemistry. *Appld. Geochem.* **5**, 375-396.

CRAIG H. (1961) Isotopic variations in meteoric waters. *Science* **133**, 1702-1703.

DANSGAARD W. (1964) Stable isotopes in precipitation. *Tellus* **16**, 436-468.

DAVIS T.L. (1972) Velocity variations around Leduc Reefs Alberta. *Geophys.* **17**, 548-604.

DOMENICO P.A. and ROBBINS G.A. (1985) The displacement of connate waters from aquifers. *Geol. Soc. Am. Bull.* **96**, 328-335.

EISBACHER G.H., CARRIGY M.A. and CAMPBELL R.B. (1974) Paleodrainage pattern and late orogenic basins of the Canadian Cordillera. In *Tectonics and Sedimentation* (ed. W.R. DICKINSON), pp. 143-146. S.E.P.M. Spec. Pub. 22.

EPSTEIN S. and MAYEDA T. (1953) Variation of 0-18 content of waters from natural sources. *Geochim. Cosmochim. Acta* **4**, 89-103.

EPSTEIN S., GRAF D.L. and DEGENS E.T. (1964) Oxygen isotope studies on the origin of dolomite. In *Isotopic and Cosmic Chemistry* (ed. H. CRAIG *et al.*), pp. 169-180. North Holland Publishing Company.

FAURE G. (1986) *Principles of Isotope Geology* (2nd Ed.). John Wiley and Sons.

FRIEDMAN I. and O'NEIL J.R. (1977) Compilation of stable isotope fractionation factors of geochemical interest. In *Data of Geochemistry* (6th Edn.) (ed. M. FLEISCHER) U. S. Geol. Surv. Prof. Paper **440-KK**.

GARVEN G. (1985) The role of regional fluid flow in the genesis of Pine Point deposit. *Econ. Geol.* **80**, 307-324.

GARVEN G. (1989) A hydrogeologic model for the formation of giant oil sands deposits of the western Canada sedimentary basin. *Am. J. Sci.* **289**, 105-166.

GORRELL H.A. and ALDERMAN G.R. (1968) Elk Point Group saline basins of Alberta, Saskatchewan, and Manitoba, Canada. *Geol. Soc. Am. Spec. Paper* **88**, 291-317.

GRAF D.L., MEENTS W.F., FRIEDMAN I. and SHIMP N.F. (1966) The origin of saline formation waters - III Calcium chloride waters. *Illinois State Geol. Surv. Circ.* **393**.

GUTSALO L.K. (1980) Trends and factors governing isotope shifts in evaporating brines and the criteria for underground brine production. *Geokhimiya* **11**, 1734-1744.

HANOR J.S. (1984) Variation in the chemical composition of oil-field brines with depth in northern Louisiana and southern Arkansas: Implication for mechanisms and rates of mass transport and diagenetic reaction. *Gulf Coast Assoc. Geol. Trans.* **34**, 55-61.

HITCHON B. (1969a) Fluid flow in the Western Canada Sedimentary Basin, 1. Effect of topography. *Water Resour. Res.* **5**, 186-195.

HITCHON B. (1969b) Fluid flow in the Western Canada Sedimentary Basin, 2. Effect of geology. *Water Resour. Res.* **5**, 460-469.

HITCHON B. (1984) Geothermal gradients, hydrodynamics, and hydrocarbon occurrence, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* **68**, 713-743.

HITCHON B. and FRIEDMAN I. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin. I. Stable isotopes of hydrogen and oxygen. *Geochim. Cosmochim. Acta* **33**, 1321-1349.

HITCHON B., BILLINGS G.K. and KLOVAN J.E. (1971) Geochemistry and origin of formation waters in the western Canada sedimentary basin, III. Factors controlling chemical composition. *Geochim. Cosmocim. Acta* **35**, 567-598.

HOLSER W. (1979) Trace elements and isotopes in evaporites. In *Marine Minerals* (ed. R.G. BURNS), pp. 246-295. Reviews in Mineralogy, Mineral. Soc. Amer. 6.

HORITA J. and GAT J.R. (1989) Deuterium in the Dead Sea: Remeasurement and implications for the isotopic activity correction in brines. *Geochim. Cosmochim. Acta* 53, 131-133.

KHARAKA Y.K., BERRY F.A. and FRIEDMAN I. (1973) Isotopic composition of oil field brines from Kettleman North Dome oil field, California, and their geological implications. *Geochim. Cosmochim. Acta* 37, 1899-1908.

KNAUTH L.P. (1988) Origin and mixing history of brines, Palo Duro Basin, Texas, U.S.A. *Appld. Geochem.* 3, 455-474.

KNAUTH L.P. and BEEUNAS M.A. (1986) Isotope geochemistry of fluid inclusions in Permian halite with implications for the isotopic history of ocean water and the origin of saline formation waters. *Geochim. Cosmochim. Acta* 50, 419-433.

LAND L.S. (1987) The major ion chemistry in sedimentary basins. In *2nd International Symposium on Physics and Chemistry of Porous Media*, 160-179.

LAND L.S. and PREZBINDOWSKI D.R. (1981) The origin and evolution of saline formation water. Lower Cretaceous carbonates, south-central Texas, U.S.A. *J. Hydrol.* 54, 51-74.

LONGSTAFFE F.J. and AYALON A. (1987) Oxygen-isotope studies of clastic diagenesis in the Lower Cretaceous Viking Formation, Alberta: implications for the role of meteoric water. In *Diagenesis of Sedimentary Sequences* (ed. J.D. MARSHALL), pp. 277-296. Geol. Soc. Spec. Pub. 36.

MAJOROWICZ J.A., RAHMAN M., JONES F.W. and McMILLAN N.J. (1985) The paleogeothermal and present thermal regimes of the Alberta Basin and their significance for petroleum occurrences. *Bull. Can. Petrol. Geol.* 33, 12-21.

MATTHEWS A. and KATZ A. (1977) Oxygen isotope fractionation during dolomitization of calcium carbonate. *Geochim. Cosmochim. Acta* 41, 1431-1438.

McCREA J.M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* 18, 849-857.

McNUTT R.H., FRAPE S.K. and FRITZ P. (1984) Strontium isotopic composition of some brines from the Precambrian Shield of Canada. *Isotop. Geosci.* 2, 205-215.

McNUTT R.H., FRAPE S.K. and DOLLAR P. (1987) The strontium, oxygen and hydrogen isotopic composition of brines, Michigan and Appalachian basins, U.S.A. *Appld. Geochem.* 2, 495-505.

MELLON G.B. (1967) Stratigraphy and petrology of the Lower Cretaceous Blairmore and Mannville Groups, Alberta foothills and plains. *Research Council Alberta Bull.* 21.

MIALL A.D. (1978) Tectonic setting and syndepositional deformation of molasse and other nonmarine - paralic sedimentary basins. *Can. J. Earth Sci.* **15**, 1613-1632.

ORR R.D., JOHNSTON J.R. and MANKO E.M. (1977) Lower Cretaceous geology and heavy oil potential of the Lloydminister area. *Bull. Can. Petrol. Geol.* **25**, 1187-1221.

PIERRE C., ORTLIEB L. and PERSON A. (1984) Supratidal evaporitic dolomite at Ojo de Liebre lagoon: Mineralogical and isotopic arguments for primary crystallization. *J. Sediment. Petrol.* **54**, 1049-1061.

POSEY H.H., WORKMAN A.L., HANOR J.S. and HURST S.D. (1985) Isotopic characteristics of brines from three oil and gas fields, southern Louisiana. *Gulf Coast Assoc. Geol. Soc. Trans.* **35**, 261-267.

PUTNAM P.E. (1982) Fluvial channel sandstones within Upper Mannville (Albian) of Lloydminister area, Canada - geometry petrography, and paleogeographic implications. *Am. Assoc. Petrol. Geol. Bull.* **66**, 436-459.

[illegible] C.W. and COWART J.B. (1985) Strontium isotope geochemistry of oil-field [illegible]rs in southeastern Mississippi: Evidence for fluid rock interaction and [illegible]cation as a hydrologic tracer. *Geol. Soc. Am. Abstracts with Programs* 17, [illegible]5.

SOFER Z. and GAT J.R. (1972) Activities and concentrations of oxygen-18 in concentrated aqueous salt solutions: Analytical and geophysical implications. *Earth Planet. Sci. Lett.* **15**, 232-238.

STANLEY K.O. and FAURE G. (1979) Isotopic composition and sources of strontium in sandstone cements: The high plains sequence of Wyoming and Nebraska. *J. Sediment. Petrol.* **49**, 45-54.

STARINSKY A., BIELSKI M., LAZAR B., STEINITZ G. and RAAB M. (1983) Strontium isotope evidence on the history of oilfield brines, Mediterranean Coastal Plain, Israel. *Geochim. Cosmochim. Acta* **47**, 687-695.

STUEBER A.M., PUSHKAR P. and HETHERINGTON E.A. (1984) A strontium isotopic study of Smackover brines and associated solids, southern Arkansas. *Geochim. Cosmochim. Acta* **48**, 1637-1649.

STUEBER A.M., PUSHKAR P. and HETHERINGTON E.A. (1987) A strontium isotopic study of formation waters from the Illinois basin, U.S.A. *Appld. Geochem.* **2**, 477-494.

SUNWALL M.T. and PUSHKAR P. (1979) The isotopic composition of strontium in brines from petroleum fields of southeastern Ohio. *Chem. Geol.* **24**, 189-197.

SUTTNER L.J. (1969) Stratigraphic and petrologic analysis of Upper Jurassic - Lower Cretaceous Morrison and Kootenai Formations, southwest Montana. *Am. Assoc. Petrol. Geol. Bull.* **53**, 1391-1410.

TOTH J. (1989) Large-scale characteristics of pore-fluid potential fields in the Alberta Basin, Canada. *EOS Trans., Am. Geophys. Union* **70**, 1096.

VEIZER J. and COMPSTON W. (1974) $^{87}Sr/^{86}Sr$ composition of seawater during Phanerozoic time. *Geochim. Cosmochim. Acta* **36**, 1461-1484.

VIGRASS L.W. (1977) Trapping of oil at intra-Mannville (Lower Cretaceous) disconformity in Lloydminister area, Alberta and Saskatchewan. *Am. Assoc. Petrol. Geol. Bull.* **61**, 1010-1028.

WALTERS L.J., Jr., CLAYPOOL G.E. and CHOQUETTE P.W. (1972) Reaction rates and $\delta^{18}O$ variation for the carbonate - phosphoric acid preparation method. *Geochim. Cosmochim. Acta* **36**, 129-140.

WILLIAMS G.D. and STELCK C.R. (1975) Speculations on the Cretaceous palaeogeography of North America. In *The Cretaceous System in the Western Interior of North America* (ed. W.G. CALDWELL), pp. 1-20. Geol. Assoc. Can. Special Paper **13**.

WOLFE J.A. (1980) Tertiary climates and floristic relations at high latitudes in the northern hemisphere. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **30**, 313-323.

Table 4.1. Sample locations, depths, temperatures and isotopic compositions of Alberta Basin brines; – = not analyzed.

SYSTEM	STRATIGRAPHIC UNIT	LOCATION	DEPTH (m)	TEMP (C)	$\delta^{18}O$	δD	$^{87}Sr/^{86}Sr$	1/Sr
Upper Cretaceous	Belly River	6-5-49-6W5	1078	35	-10.3	-96	0.70634	6.03E-02
	Belly River	8-29-48-6W5	1090	49	-10.4	-100	0.70628	4.88E-02
	Belly River	2-28-48-6W5	1076	45	—	—	0.70616	4.75E-02
	Belly River	16-22-47-4W5	984	48	-10.0	-101	0.70578	6.52E-02
	Cardium	3-24-49-5W5	1245	43	—	—	0.70738	1.53E-01
	Cardium	14-20-48-6W5	1426	54	-15.6	-127	0.70690	9.07E-01
	Cardium	16-30-49-6W5	1304	47	-15.8	-116	0.70639	9.62E-01
Lower Cretaceous	Viking	12-20-49-21W4	999	41	-8.0	-83	0.70787	9.60E-03
	Viking	15-21-56-24W4	1050	47	-9.4	-88	0.70768	5.49E-03
	Viking	8-32-55-20W4	703	40	-9.5	-92	0.70852	4.35E-03
	Viking	6-7-56-20W4	676	44	—	—	0.70694	4.60E-03
	Glauconitic	4-36-49-4W5	1630	59	-5.5	-82	0.70758	4.28E-03
	Glauconitic	12-16-51-4W5	1574	65	—	-82	—	—
	Glauconitic	14-4-51-25W4	1293	—	—	—	0.71024	2.78E-03
	Ostracod	16-20-49-3W5	1609	65	-6.7	-85	0.70621	3.79E-03
	Ostracod.	5-30-49-3W5	1640	67	—	-82	0.70659	6.64E-03
	Basal Quartz	10-29-56-24W4	1067	46	—	-85	0.70686	5.57E-03
	Basal Quartz	13-21-56-24W4	1060	—	-6.9	-86	0.71008	5.02E-03
	Basal Quartz	14-23-52-26W4	1253	—	-4.6	-118	0.71131	2.66E-03
	Basal Quartz	15-33-51-25W4	1359	56	-5.5	-74	0.71137	2.66E-03
	Basal Quartz	2-25-52-26W4	1237	52	-5.9	-84	0.71061	3.46E-03
	Basal Quartz	16-34-49-5W5	1700	63	—	—	0.70945	—
Middle Jurassic	Rock Creek	10-25-54-13W5	1969	75	-10.4	-103	0.71220	3.79E-02
	Rock Creek	16-24-54-13W5	1964	64	—	—	0.71168	2.66E-02
	Middle Jurassic	8-34-49-5W5	1699	57	-4.0	-77	0.70966	1.66E-02
	Middle Jurassic	6-34-49-5W5	1706	61	—	—	0.70978	1.86E-02
Lower Jurassic	Nordegg	14-13-49-5W5	1703	—	-3.3	-69	0.71170	4.18E-03
	Nordegg	1-16-52-5W5	1647	67	-4.0	-78	0.71037	2.16E-03
Mississippian	Banff	6-31-50-4W5	1621	58	—	—	0.71031	3.09E-03
	Banff	14-30-50-4W5	1640	62	-3.4	-125	0.70966	4.81E-03
Upper Devonian	Wabamun	9-16-57-3W5	1340	50	-5.6	-82	0.71072	3.06E-03
	Wabamun	2-4-57-3W5	1334	50	-6.2	-75	0.71062	2.78E-03
	Wabamun	13-20-58-3W5	1399	52	—	-73	0.71235	2.24E-03
	Wabamun	3-7-57-1W5	1247	44	-5.0	-81	0.71128	2.55E-03
	Nisku	15-29-49-26W4	1596	69	—	-58	0.71206	2.74E-03
	Nisku	14-3-56-24W4	1179	45	—	—	0.70998	5.35E-03
	Nisku	16-10-56-24W4	1170	45	-5.3	-77	0.71005	5.43E-03
	Leduc	11-14-57-21W4	972	41	-5.4	-88	0.70964	4.57E-03
	Leduc	6-20-57-21W4	978	39	-7.2	-82	0.70975	5.94E-03
	Leduc	7-6-58-21W4	979	42	-6.1	-82	0.70937	5.34E-03
	Leduc	11-12-58-22W4	985	42	-4.5	-98	0.70959	5.06E-03
	Leduc	11-15-60-26W4	1623	63	+2.4	-104	0.70972	8.43E-04
	Leduc	6-23-52-26W4	1536	65	-6.8	-87	0.70961	2.52E-03

Table 4.2. Isotopic composition of Alberta Basin carbonates. Abbreviations on the table are: D = diagenetic; DET = detrital; WR = whole-rock, – = not analyzed.

SYSTEM	STRATIGRAPHIC UNIT	LOCATION	DEPTH (m)	MINERAL / ROCK TYPE	TYPE	$\delta^{13}C$	$\delta^{18}O$	$^{87}Sr/^{86}Sr$
Upper Cretaceous	Belly River	8-32-48-4W5	981	calcite	D	0.51	+15.13	0.70804
		8-32-48-4W5	988	calcite	D	-4.71	+12.98	0.70586
		8-32-48-4W5	992	calcite	D	-4.98	+13.34	0.70590
		8-32-48-4W5	994	calcite	D	-5.24	+12.53	0.70578
		8-32-48-4W5	995	calcite	D	-0.34	+13.99	0.70815
	Lea Park	8-32-48-4W5	996	shale	WR	–	–	0.70745
	Cardium	8-32-48-4W5	1309	shale	WR	–	–	0.71938
Lower Cretaceous	Viking	3-17-40-4W5	2160	siderite	D	-1.74	+23.14	0.70776
		11-21-36-2W5	1903	siderite	D	-2.81	+23.55	–
		2-30-38-7W5	2537	siderite	D	-2.13	+21.20	0.70762
		13-8-35-6W5	2727	siderite	D	-2.23	+24.24	–
		16-1-48-4W5	1734	calcite	D	-7.18	+14.09	–
		1-16-50-26W4	1149	calcite	D	1.60	+25.27	–
		6-16-35-5W5	2468	dolomite	DET	-8.50	+22.10	–
		6-25-40-2W5	1776	ankerite	D	-2.43	+16.30	–
	Glauconitic	14-12-50-26W4	1296	calcite	D	-0.44	+16.29	0.71094
		4-32-48-4W5	1758	calcite	D	-2.52	+14.90	0.70803
		4-32-40-4W5	1759	calcite	D	-1.72	+15.41	0.70879
	Ostracod	4-32-48-4W5	1764	calcite	D	-2.51	+17.78	0.70865
	Blairmore	1-16-50-26W4	1338	calcite	D	[illegible]	+15.05	–
		14-12-50-26W4	1303	shale	WR	–	–	0.71171
		14-12-50-26W4	1304	calcite	D	[illegible]	+18.79	–
Lower Jurassic	Nordegg	8-31-48-4W5	1777	[illegible]	WR	[illegible]	+20.61	0.70795
		8-31-48-4W5	1780	calcite	D	-1.40	+16.77	0.70842
		8-31-48-4W5	1782	calcite	WR	-0.99	+18.82	0.70892
	Poker Chip	8-4-42-5W5	2350	shale	WR	–	–	0.71167
	Jurassic	8-32-48-4W5	1805	calcite	WR	-0.19	+22.24	0.70844
				calcite	D	-1.32	+17.00	0.70874
		8-32-48-4W5	1806	calcite	WR	-2.99	+19.69	0.70903
Mississippian	Banff	4-32-48-4W5	1776	calcite	WR	-2.23	[illegible]	[illegible]
		8-31-48-4W5	1784	calcite	WR	-1.09	[illegible]	[illegible]
Upper Devonian	Wabamun	1-16-50-26W4	1370	calcite	WR	-1.27	+22.69	0.70902
		1-16-50-26W4	1374	calcite	WR	-2.93	+18.08	0.70937
	Nisku	1-16-50-26W4	1554	dolomite	WR	-2.87	+26.68	0.70842
	Leduc	8-17-50-26W4	1832	dolomite	WR	[illegible]	[illegible]	0.70830
		8-17-50-26W4	1833	dolomite	WR	1.61	+25.71	0.70819
Middle Devonian	Elk Point	8-17-50-26W4	2252	dolomite	WR	3.41	+29.59	0.70922
		8-17-50-26W4	2254	dolomite	WR	1.51	+27.30	–
Cambrian	Cambrian	8-17-50-26W4	2635	shale	WR	–	–	0.74307
		8-17-50-26W4	2638	shale	WR	–	–	0.77570
		8-17-50-26W4	2643	shale	WR	–	–	0.75627
		8-17-50-26W4	2645	sst/calcite	D	–	–	0.75038
Precambrian	Precambrian	8-17-50-26W4	2739	greenstone	WR	–	–	1.09317
		8-17-50-26W4	2740	greenstone	WR	–	–	1.30972

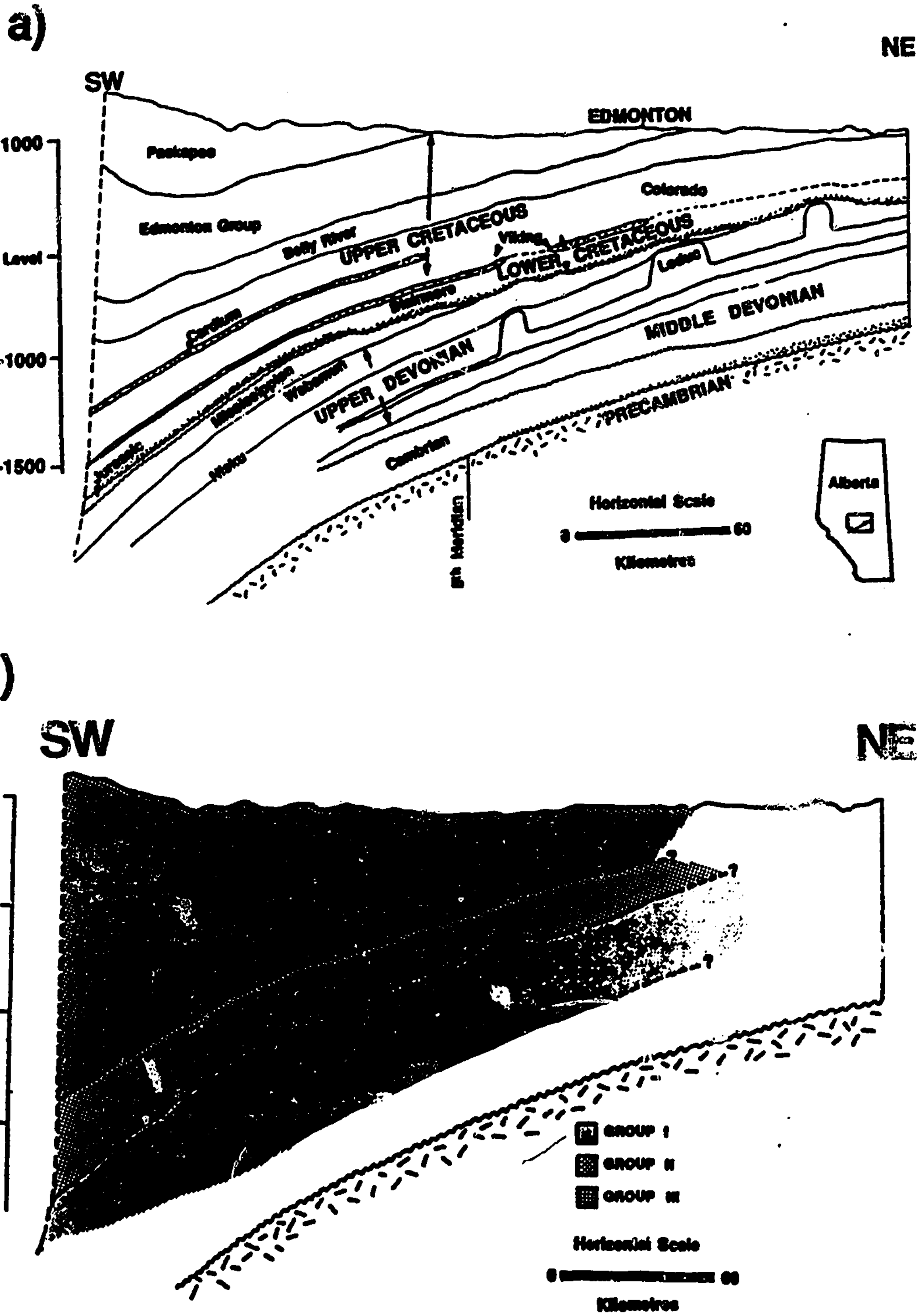


Fig. 4.1. (a) Geological cross section from SW to NE through the Alberta Basin showing the major stratigraphic units and unconformities. The study area is highlighted in the reference map. (b) Same geological cross section as (4.1a) illustrating the division of the formation waters into Groups I, II and III.

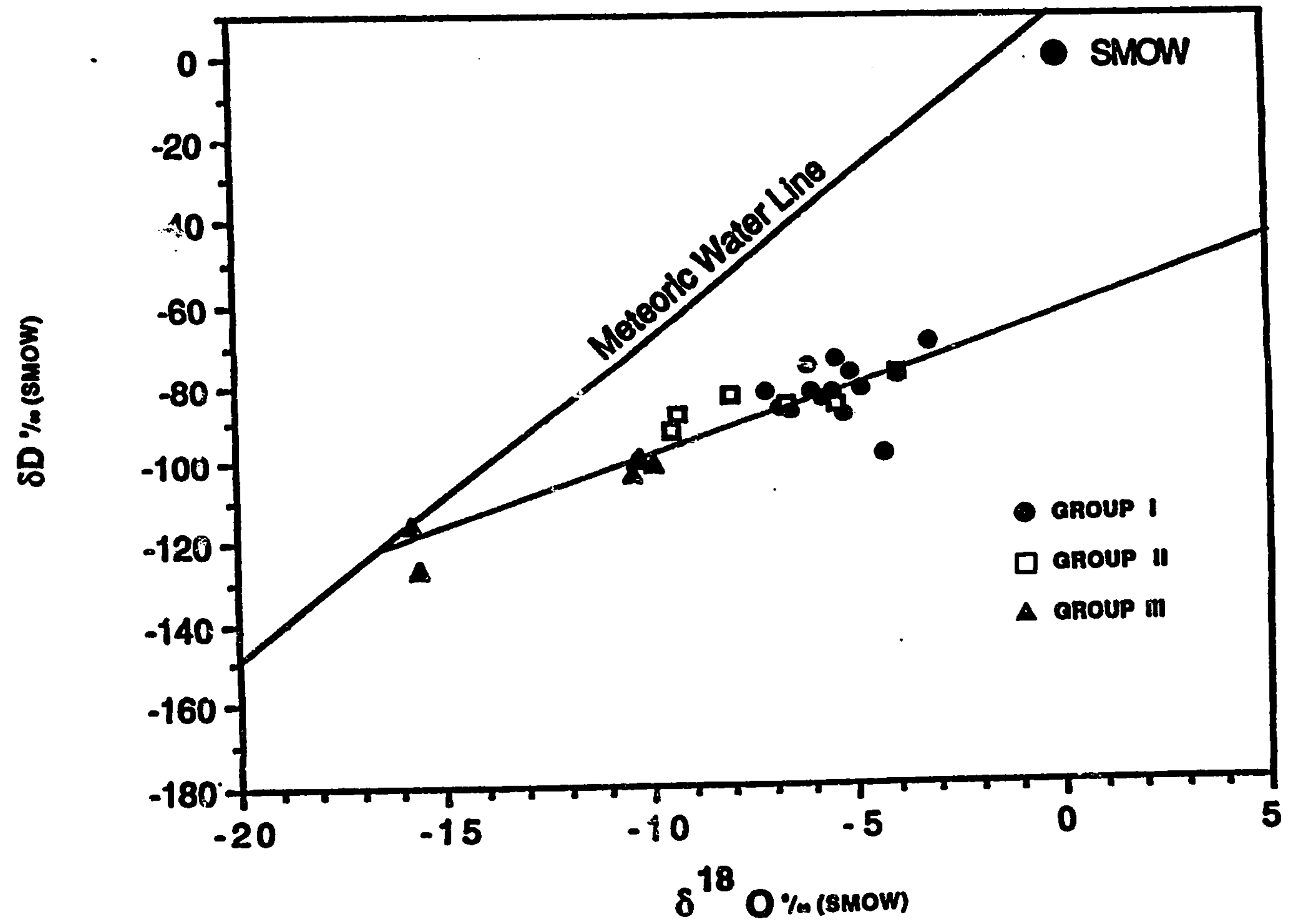


Fig. 4.2. Stable isotopic composition of Alberta Basin formation waters, with the Meteoric Water Line (MWL) and standard mean ocean water (SMOW) plotted for reference. All water samples plot to the right of MWL. Intersection of the formation waters with the MWL occurs at $\delta D_{(SMOW)}$= -121‰ and $\delta^{18}O_{(SMOW)}$= -16.3‰.

Fig. 4.5. Plot of isotope equilibrium between formation waters and carbonate in the Alberta Basin. (a). Group I: the large solid dots represent waters extracted from dolomite with $\delta^{18}O$ = +25 to +30 ‰$_{(SMOW)}$; the open dots represent waters in limestones with $\delta^{18}O$ = +18 to +22 ‰$_{(SMOW)}$; the small dots represent calcite cements from clastic rocks with $\delta^{18}O$ = +15 to +16‰$_{(SMOW)}$. (b). Group II: solid squares represent waters extracted from whole rock limestone with $\delta^{18}O$ = +18 to +22‰$_{(SMOW)}$; open squares represent calcite cements from sandstones with $\delta^{18}O$ = +14 to +16‰$_{(SMOW)}$. (c) Group III: triangles represent waters extracted from rocks with authigenic calcites ranging from $\delta^{18}O$ = +12 to +14‰$_{(SMOW)}$. Line Dol 28 represents combinations of $\delta^{18}O$ water and temperature in equilibrium with dolomite of $\delta^{18}O$ = +28%‰$_{(SMOW)}$, etc. Similarly, line Cal 21 represents combinations of $\delta^{18}O$ water and temperature in equilibrium with calcite of $\delta^{18}O$ = +21‰$_{(SMOW)}$, *etc*. The thicker lines represent the dolomite equilibrium relation with temperature and the thinner lines the calcite equilibrium relation. Horizontal lines on all three graphs depict the range in isotopic composition of the waters for the particular group illustrated.

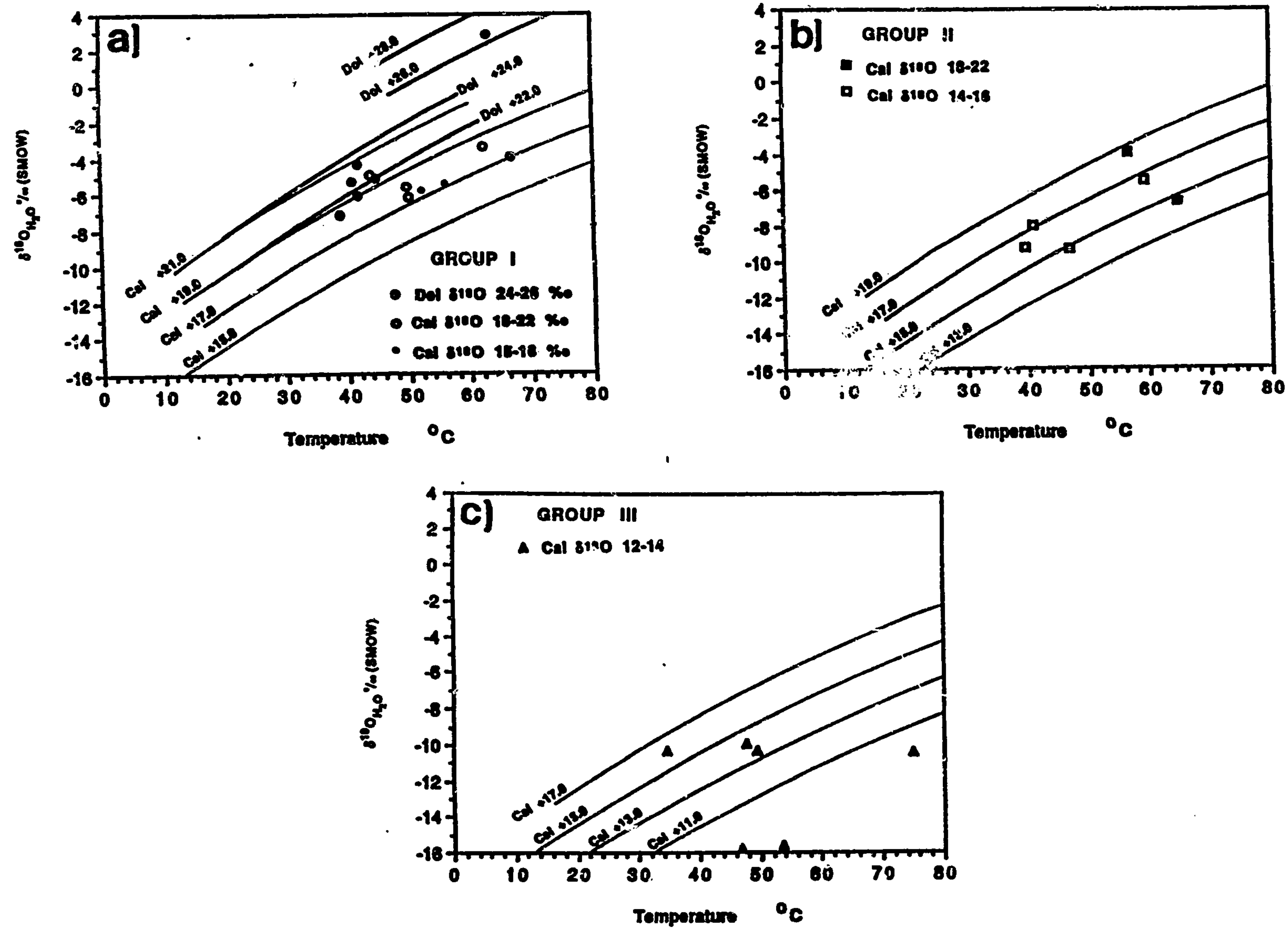
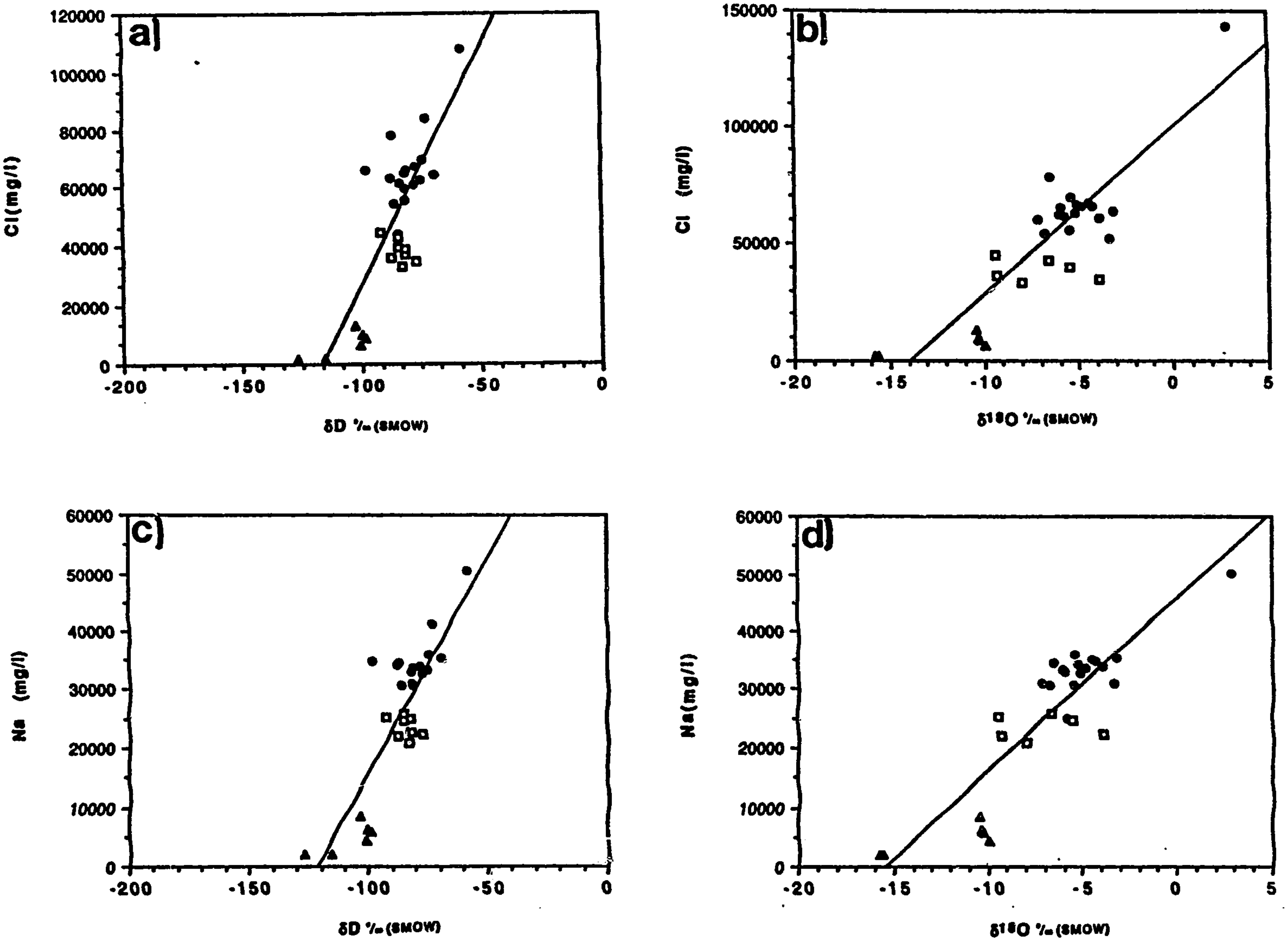

a)
GROUP I
● Dol δ18O 24-26 ‰
○ Cal δ18O 18-22 ‰
• Cal δ18O 15-18 ‰
Dol +28.0
Dol +26.0
Dol +24.0
Dol +22.0
Cal +21.0
Cal +19.0
Cal +17.0
Cal +15.0
δ18OH2O ‰ (SMOW)
4
2
0
-2
-4
-6
-8
-10
-12
-14
-16
0
10
20
30
40
50
60
70
80
Temperature °C
b)
GROUP II
■ Cal δ18O 18-22
□ Cal δ18O 14-16
Cal +19.0
Cal +17.0
Cal +15.0
Cal +13.0
δ18OH2O ‰ (SMOW)
Temperature °C
c)
GROUP III
▲ Cal δ18O 12-14
Cal +17.0
Cal +15.0
Cal +13.0
Cal +11.0
δ18OH2O ‰ (SMOW)
Temperature °C

Fig. 4.4. (a) Cl vs $\delta D_{(SMOW)}$; (b) Cl vs $\delta^{18}O_{(SMOW)}$; (c) Na vs $\delta D_{(SMOW)}$; and (d) Na vs $\delta^{18}O_{(SMOW)}$. A near linear correlation is observed in all of the plots; however, on all of the plots Group III appears detached from Groups I and II. These graphs are interpreted largely in terms of mixing. The scale of the plots were designed to encompass the range of isotopic values common in sedimentary basins. The correlation of each of the plots was better than r=0.8; (●) Group I; (◻) GroupII; (▲) Group III.


a)
Cl(mg/l)
120000
100000
80000
60000
40000
20000
0
-200
-150
-100
-50
0
δD ‰ (SMOW)
b)
Cl (mg/l)
150000
100000
50000
0
-20
-15
-10
-5
0
5
δ18O ‰ (SMOW)
c)
Na (mg/l)
60000
50000
40000
30000
20000
10000
0
-200
-150
-100
-50
0
δD ‰ (SMOW)
d)
Na(mg/l)
60000
50000
40000
30000
20000
10000
0
-20
-15
-10
-5
0
5
δ18O ‰ (SMOW)

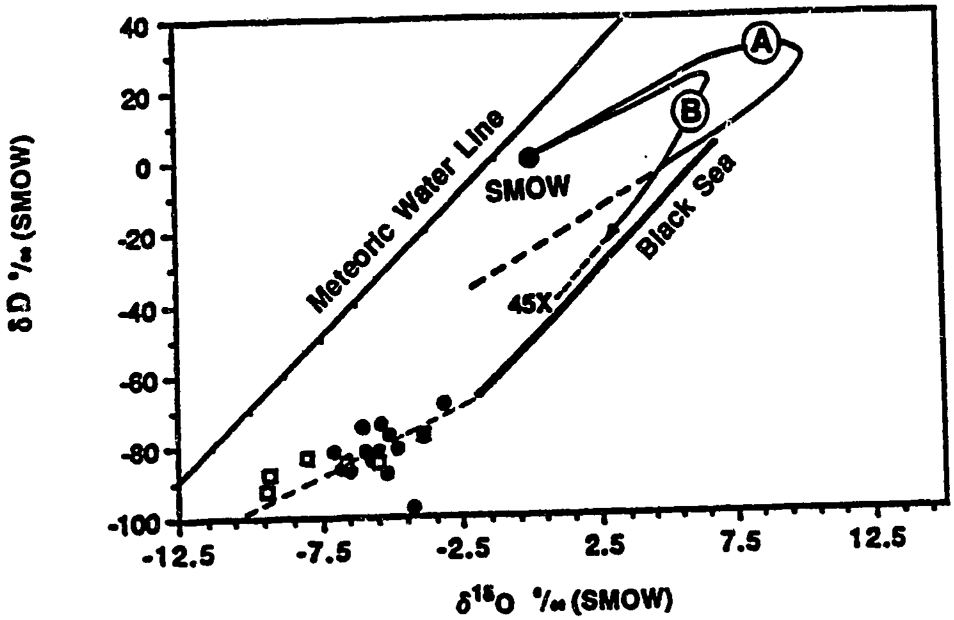


Fig. 4.5. Stable isotopic compositions of D and O in Group I (●) and Group II (□) formation waters with the trajectories for seawater undergoing evaporation superimposed on them. Curve A is the estimate of HOLSER, (1979) of evaporating seawater through a concentration of 10X. Curve B is given by PIERRE *et al.* (1984) and is based on field evidence from the Ojo de Liebre waters. Halite facies corresponds to approximately 11X - 65X. (modified from KNAUTH and BEEUNAS, 1986). The thick black line represents the Black Sea trend after it has hooked around to a concentration of 80X (GUTSALO, 1980).

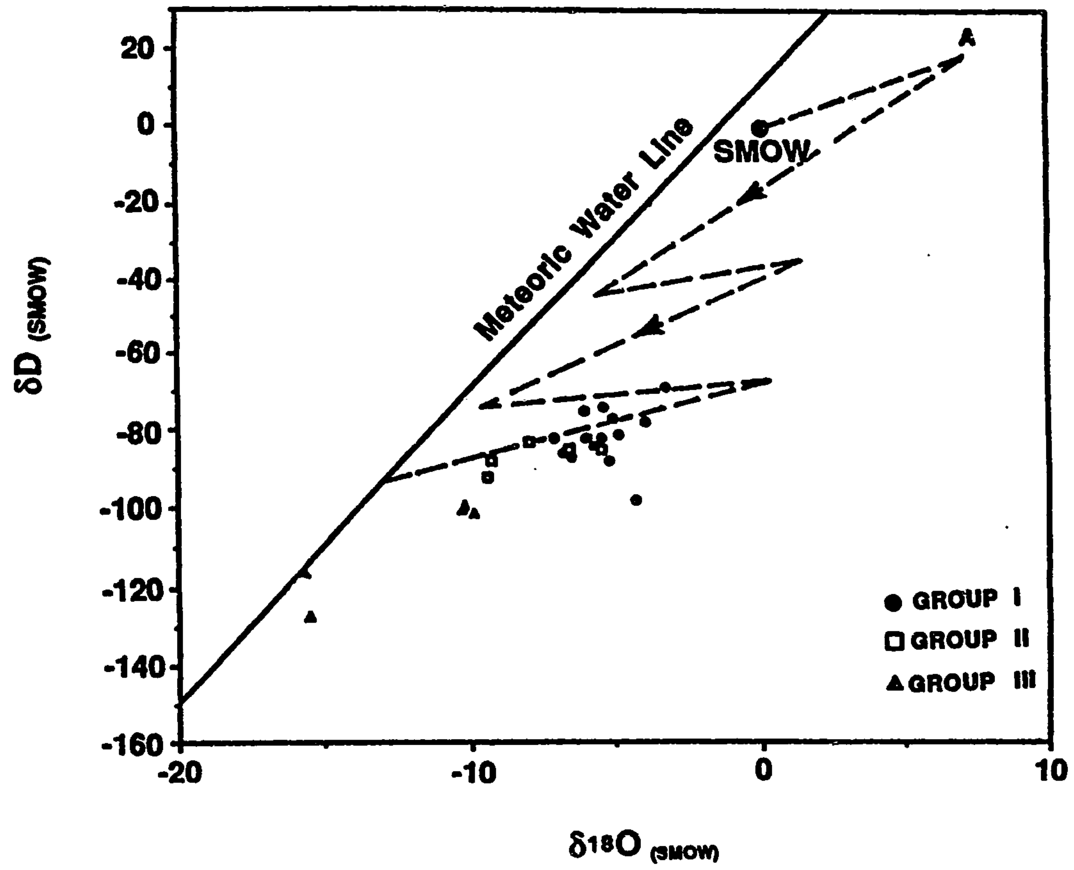


Fig. 4.6. Possible combination of evaporation-mixing steps to produce the observed isotopic compositions; arrows illustrate the direction in which the fluids are evolving.

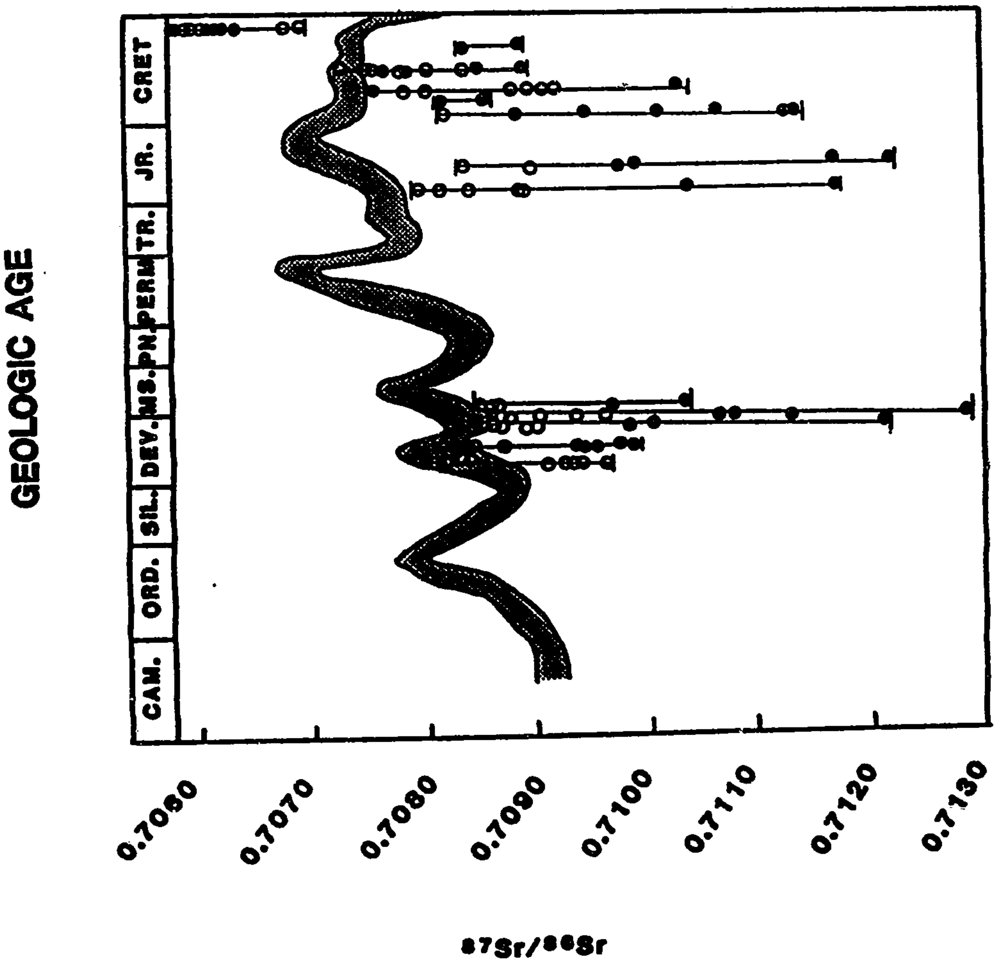


Fig. 4.7. Strontium isotopic composition of waters (●) and carbonates (○) from the Alberta Basin. The seawater curve is from BURKE *et al.* (1982). Note that most of the rocks and waters are radiogenic with respect to seawater for the time in question except the Upper Cretaceous where waters and rocks become less radiogenic. All of the waters are more radiogenic than the rocks until the Upper Cretaceous when they start to overlap.

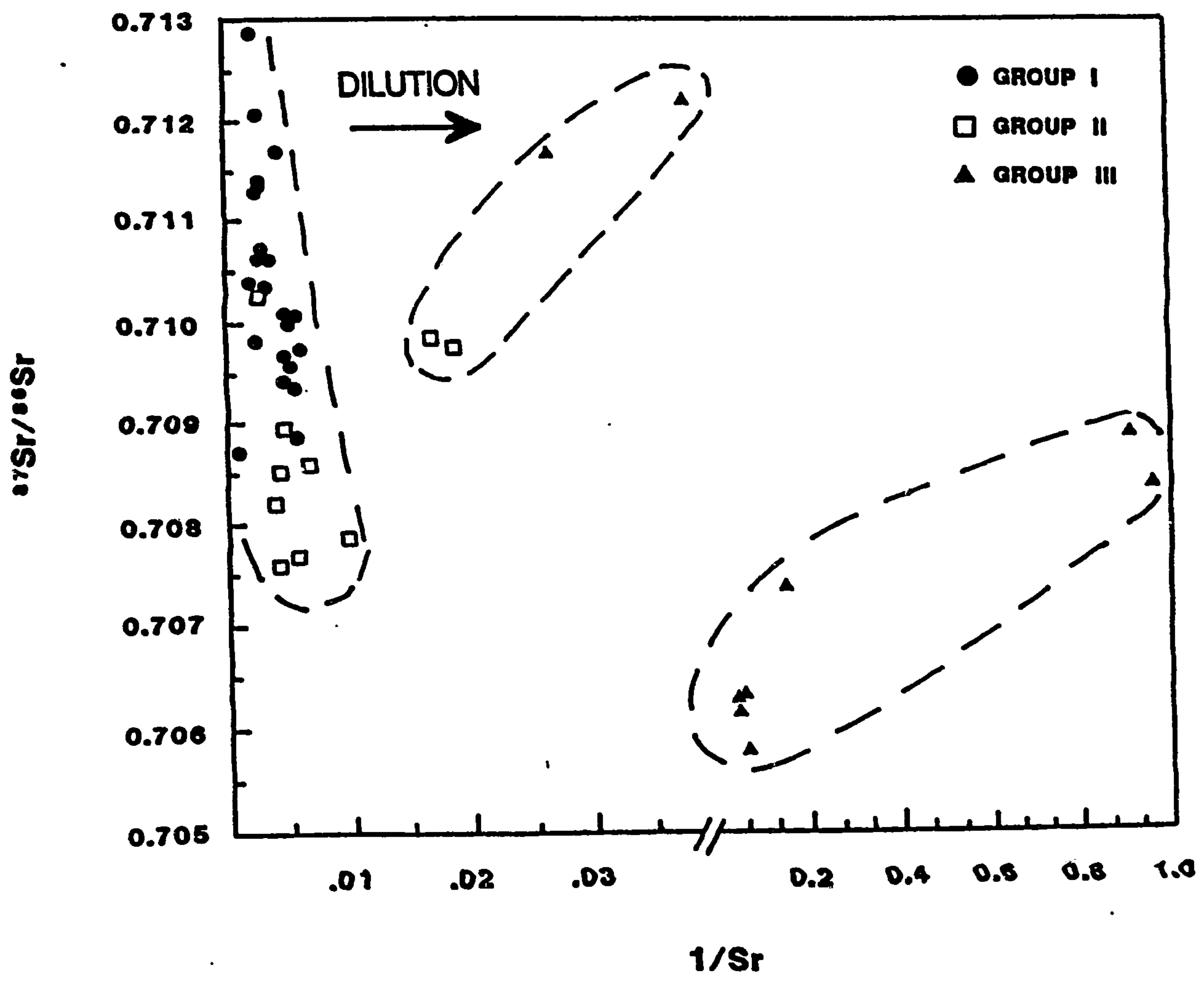


Fig.4.8. ^{87}Sr/^{86}Sr vs 1/Sr plot of Alberta Basin waters. The scale has been broken to accommodate the Cardium and Belly River water samples from Group 3 on the plot.

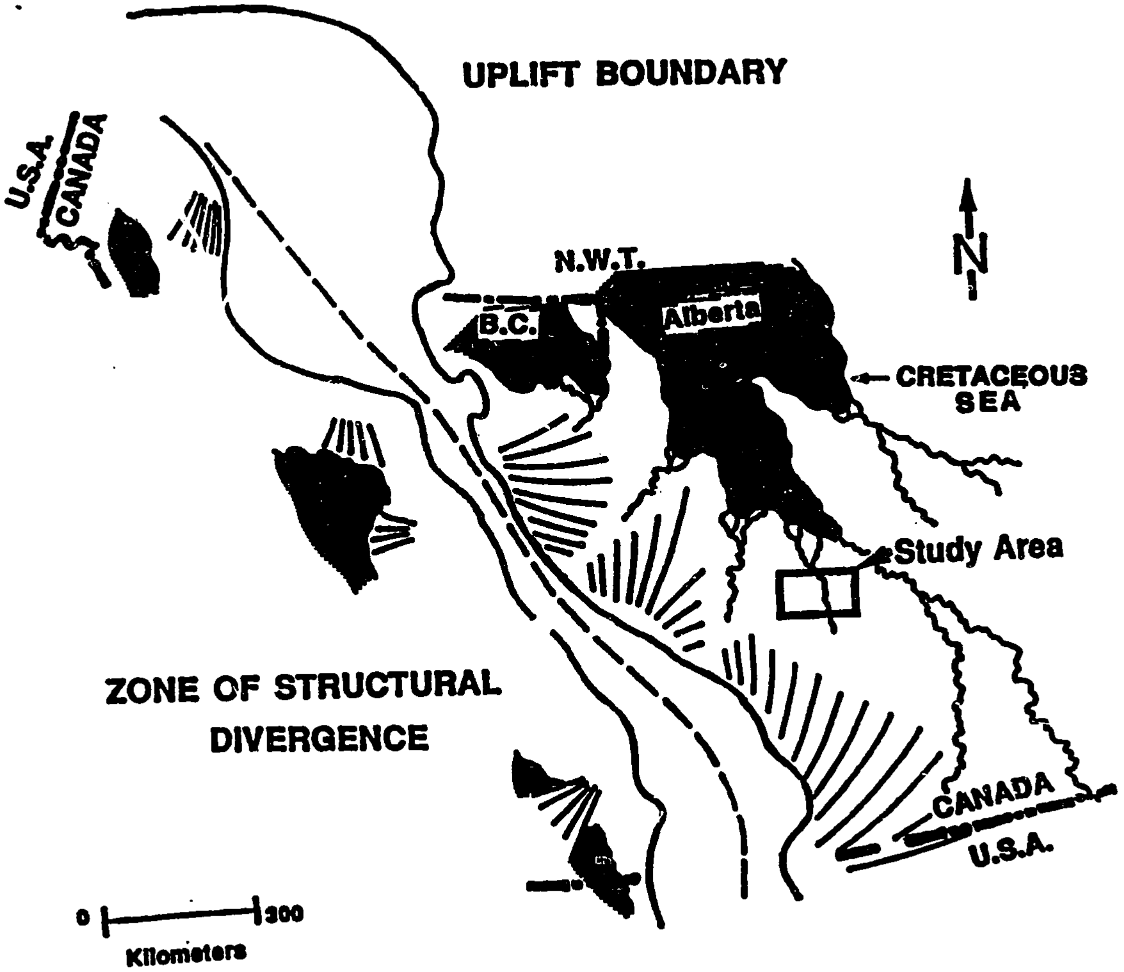


Fig.4.9. Paleotectonic map of the Upper Mannville showing paleodrainage relative to the axis of the Columbian Orogeny (modified from EISBACHER *et al.*, 1974).

CHAPTER 5. ORIGIN AND EVOLUTION OF FORMATION WATERS, ALBERTA BASIN, WESTERN CANADA SEDIMENTARY BASIN

III. GEOCHEMICAL EQUILIBRIUM MODEL

INTRODUCTION

Diagenetic processes in sedimentary basins are most commonly investigated using the textural, mineralogical and compositional aspects of basin rocks. However, to fully understand diagenetic processes, information regarding mineral precipitation, dissolution, and ion transport is required. Equilibrium thermodynamics provides the necessary theoretical framework to establish the importance of water/rock interactions in controlling water compositions and mineral precipitation under the temperatures and pressures of interest (ABERCROMBIE, 1989). Porewater composition is one of the main controlling factors in diagenetic reactions, particularly in sandstones, and has two possible contrasting, primary sources; 1) meteoric (dilute and acidic); and, 2) seawater (concentrated and alkaline) (HURST and IRWIN (1982). During burial unstable minerals equilibrate with these porewaters. As a result, diagenetic processes are reflected in the composition of the formation waters. Comparison of fluid and mineral compositions obtained from natural systems with thermodynamic stability data from experiments, strongly indicates the degree of water/rock interaction that has occurred during diagenesis because of the independent nature of the two data sets (NESBITT, 1980, 1985; ABERCROMBIE, 1989).

The study of rock/brine interaction in sedimentary basins using a thermodynamic equilibrium approach has been successfully applied by KRAMER (1969), MERINO (1975), PALCIAUSKAS and DOMENICO (1976), NESBITT (1980, 1985), HUTCHEON (1981), and LAND and PREZBINDOWSKI (1981). Recently, the understanding of water/rock interactions during burial diagenesis has been enhanced by the study of processes at *in situ* recovery sites, where artificial diagenesis caused by cyclic steam injection provides an environment analogous to that of burial diagenesis (ABERCROMBIE, 1989; ABERCROMBIE *et al.*, 1989).

The purpose of this paper is to apply both thermodynamic principles and data to the geochemical aspects of diagenesis, facilitating an interpretation of the chemical environment during diagenesis. No studies have yet applied thermodynamic modelling to the waters in the Alberta Basin. In this study, water compositions from 13 formations in the Alberta Basin are examined in an attempt to identify important mineral-solution interactions that have occurred in the subsurface. Forty-three oil-field waters, that were previously analyzed chemically (CONNOLLY *et al.*, 1990a) and isotopically (CONNOLLY *et al.*, 1990b) are examined using chemical thermodynamics to calculate the distribution of aqueous species at *in situ* temperatures and pressures. The calculated distributions are used to examine the state of the water sample with respect to an equilibrium state under identical conditions. Previous work (CONNOLLY *et al.*, 1990a, 1990b) has suggested that many of the formation waters in the Alberta Basin are in communication and a mixing regime has been established. Furthermore, many chemical reactions, such as mineral transformation and cation exchange reactions, were identified as potentially influential to the Alberta Basin waters (CONNOLLY *et al.*, 1990a). The use of equilibrium phase diagrams will help indicate which of these reactions are currently active. Therefore, all of the aqueous species and diagenetic and detrital phases present in a vertical section in the basin were examined because water/rock interaction is not confined to one formation but involves cross-formational fluid flow and mixing. This involves the modelling waters hosted in both carbonate and clastic stratigraphic units which has not been previously done.

GEOLOGICAL SETTING

Location and Stratigraphy

The Alberta Basin is a foreland basin within the Western Canada Sedimentary Basin in south-central Alberta, Canada (Fig. 5.1). Undeformed, southwesterly dipping Paleozoic and Mesozoic sedimentary rock are represented, with the exception of eroded Upper Mississippian, Pennsylvanian, Permian, Triassic and most of the Jurassic strata (Figs. 5.2 and 5.3). The Cambrian sandstone rests unconformably on the Precambrian basement and the sandstone gives way to shale in the Upper Cambrian. Carbonate rocks, interspersed with shale formations dominate the Devonian, with some formations containing substantial anhydrite. Mississippian and Jurassic rocks are dominantly carbonates. These rocks are overlain unconformably by the Cretaceous clastic succession, which dominated by shales with intercalated sandstones.

The tectontic history of the Western Canada Sedimentary Basin and its present day morphology are a result of orogenic forces active during Jurassic through Tertiary time. At the end of the Jurassic, during the Columbian Orogeny, subduction of the Pacific Plate beneath the North American plate caused shortening across the orogen resulting in the formation of the Rocky Mountains (PRICE, 1973; DICKINSON and SNYDER, 1978; BEAUMONT, 1981; JORDON, 1981). Slow epeirogenic uplift and thrusting along the eastern Cordillera heralded the first pulse of the Laramide Orogeny during the Late Cretaceous. Culmination of the Laramide Orogeny occurred in Late Paleocene or Early Eocene and resulted in downwarping and burial of the foreland basin (PRICE, 1973; DICKINSON, 1974; KAUFFMAN, 1977; PORTER *et al.*, 1982, HITCHON, 1984). Subsequent erosion of accumulated Tertiary and Upper Cretaceous rocks has occurred.

The present hydrodynamic regime was initiated by the second pulse of the Laramide Orogeny. The uplifting and thrusting of the Canadian Cordillera is seen as the mechanism responsible for generating the deepest penetration of meteoric water that the basin has ever experienced (HITCHON and FRIEDMAN, 1969). Dissipation and partitioning of this regional flow system, with younger shallower formations developing smaller flow sub-systems, has been suggested (GARVEN, 1989; CONNOLLY *et al.*, 1990a, 1990b).

Petrography of Formations

All of the formations shown in the stratigraphic column of Fig. 5.3 have been examined petrographically and by X-ray diffraction. Twenty-six individual cores were examined from a limited lateral extent in the Alberta Basin, defined by the study area in Fig. 5.1. From these core samples, more than 150 thin secions representative of formations from Precambrian to Upper Cretaceous were examined. These observations are augmented by other petrographic studies in order to obtain a good average composition of the total mineral assemblage for each formation over the study area (Appendix I). Furthermore, forty-three water samples hosted in thirteen formations from Upper Devonian to Upper Cretaceous were obtained. A description of units stratigraphically lower than the studied waters and of the shales dividing the reservoirs has been included to better assess all possible water/rock interactions. The petrography of the Alberta Basin formations is described in Appendix I, with a brief summary/overview given below.

Altered muscovite biotite granites of the Precambrian basement are unconformably overlain by the basal Cambrian sandstones (~40 m thick) and shales (~185 m thick). The sandstones are mature quartz arenites and the shales/siltstones overlying the basal unit contain highly altered authigenic chlorite, which is succeeded by less altered kaolinite followed by illite/smectite (I/S) and illite. Cambrian lithologies are unconformably overlain by Middle Devonian evaporites, which are succeeded by the Upper Devonian carbonates (~975 m thick). These carbonate units are typically dominated by one of two end member lithologies, limestone or secondary dolomite (ANDRICHUK, 1958). Intervening shale formations are composed of alternating carbonate and quartz/illite horizons. Mississippian (~30 m thick) carbonates and Jurassic carbonate/clastics (~40 m thick) overlie the Devonian. Authigenic phases in the Devonian through Jurassic carbonate/shale formations include carbonate (calcite, dolomite and ankerite) and illite. The Cretaceous clastic rocks (highly variable thickness, increasing toward the southwest) unconformably succeed the Jurassic in the western part of the study area and the Devonian in the east, and are composed of shale horizons with interspersed sandstone lenses. Authigenic components in the Cretaceous are variable in abundance, even within a single formation, but similar phases are generally found throughout the Cretaceous. Diagenetic clay minerals include Fe-rich chlorite, kaolinite, dickite, smectite, illite and interstratified expandable phases including chlorite/smectite (C/S), smectite/illite (S/I) and illite/smectite (I/S); diagenetic carbonates include calcite, dolomite, ankerite and siderite. There is a paucity of feldspar in the Cretaceous formations of the study area, with the exception of the Viking and Belly River Formations, where albite/oligoclase plagioclase feldspars are much more abundant (6-26 %) and altered than K-spar (1-8%). Paragenetic sequences for the main reservoirs of Cretaceous are illustrated in Appendix I.

Formation Waters

Sample collection, analytical procedures and chemical and isotopic data for the formation waters are discussed and reported in CONNOLLY *et al.* (1990a, 1990b). The principal ionic species of Alberta Basin waters are Na and Cl, with Ca becoming more significant in the waters from Devonian reef strata. Variations in the content of major and minor elements in the waters are illustrated by examining changes in Na/Cl, Ca/Cl, Mg/Cl and K/Cl ratios with increasing correlative Cl concentrations (Fig. 5.4). Figure 5.4a is a plot of Na/Cl *vs* Cl and illustrates that for very dilute fluids Na/Cl is greater than 1, but approaches values of 0.4 at 100 000 mg/l Cl. Figure 5.4b, 5.4c and 5.4d show that Ca/Cl, Mg/Cl and K/Cl ratios respectively, increase with increasing Cl; however, the K/Cl versus Cl plot displays considerable scatter. The total dissolved solids in waters from the Alberta Basin range in concentration from 4 to 235 g/l (avg. = 80 ± 47 g/l), with the resulting ionic strengths ranging from 0.1 to 2.4 (avg. = 1.3).

Pressures and measured formation temperatures were obtained from the Energy Resources Conservation Board. Pressure data represent an average value of measurements taken over a two year period at three month intervals, disregarding the first three month period to allow for equilibration of formation pressure. Measured bottom-hole temperatures in the study area range from 40 to 80°C (average = 58° ± 12°C).

A variety of chemical geothermometers incorporated into the program SOLMINEQ.88 PC/SHELL (WIWCHAR *et al.*, 1988; KHARAKA *et al.*, 1988) were also used to provide independent values of subsurface temperatures. These geothermometers are based on geothermal systems, but modified versions are incorporated into the program so that they are relevant to the higher water salinities and hydraulic pressures found in sedimentary basins.

FOURNIER *et al.* (1974) have suggested three basic requirements for the use of aqueous geothermometers: 1) the chemical species involved must be present; 2) equilibrium between these species and the minerals controlling their abundance must be attained; and, 3) re-equilibration between the minerals and aqueous species cannot occur prior to sampling. Numerous geothermometers exist and most are based on cation concentrations that have been empirically fit to systems where temperatures have been measured directly (KHARAKA and MARINER, 1988); however, most of these geothermometers are useful only in higher temperature reservoirs (>75°C). Magnesium-Li geothermometers and chalcedony geothermometers are considered to render the most accurate temperature estimates for reservoirs ranging from 30°C to 70°C (KHARAKA *et al.*, 1988; KHARAKA and MARINER, 1988). The chalcedony geothermometer was selected because: 1) chalcedony gives the most reasonable values correlative with measured values; 2) the activities of silica for all of the formation waters are log normally distributed and exhibit negligible variation between formations; the cation concentrations exhibit a more scattered distribution; 3) the Mg-Li geothermometer is based on the premise that Mg^{+2} and Li^{+3} commonly substitute for each other in amphibole, pyroxenes, micas and clay minerals; such a geothermometer may not be widely applicable to both dolomite/carbonate and clastic formations; and 4) the predominance of clays in the basin, particularly within the Cretaceous units, suggest that more than one exchange reaction may control cation concentrations. With the exception of a few samples from the Devonian, the chalcedony geothermometer was within 10°C, usually 5°C, of the measured temperature. The geothermometer consistently gave higher temperatures than the measured temperature, likely due to inaccuracies inherent in the direct measurement of bottomhole fluids (i.e., circulation of drilling mud). The measured bottomhole temperature is a function, in part, of the time lapse between the cessation of drilling and time of logging (HANOR, 1987), whereas chemical geothermometers reflect the reservoir temperatures at the time of sampling. As there are uncertainties associated with both methods of obtaining temperature, the temperature value used for the thermodynamic modelling represents an average of the chemical and measured temperatures.

The water samples from the Alberta Basin have been divided into three groups based on chemistry and isotopic composition of the formation fluids, and reservoir lithology (CONNOLLY *et al.*, 1990a, 1990b). Group I waters are from Devonian, Mississippian and lowermost Jurassic (Nordegg Formation) carbonates and the lowermost Cretaceous (Basal Quartz Formation) clastic assemblage. Group II waters are hosted by the Middle Jurassic carbonates and the Ostracod, Glauconitic, and Viking clastic assemblages. Group III includes waters from the clastic rocks of the Rock Creek, Cardium and Belly River stratigraphic units. The above classification is adhered to in this paper based on the aforementioned characteristics and to be consistent with the other two studies (CONNOLLY *et al.*, 1990a, 1990b). Furthermore, the division of the formation waters into these groups is reflected in the distribution of ionic strengths in the waters (Fig. 5.5).

Group I and II are reasonably distinct, but do overlap; these two Groups have previously been described in terms of a mixing regime (CONNOLLY *et al.*, 1990a; 1990b). Group III fluids have much lower ionic strengths than Group I and II, reflecting the diluting meteoric component in these waters.

EQUILIBRIUM BETWEEN MINERALS AND FORMATION WATERS

Prior to meaningful water/rock calculations, three requirements must be met. First, reliable chemical data for the waters being examined must be available. Second, an appropriate conceptual model of solution behavior is required for the types of waters being studied, one which allows the calculation of thermodynamic activities of dissolved species. Third, thermodynamic data are needed for the water/rock reactions of interest at the temperatures of interest. Furthermore, interpretation of the speciation-solubility calculations is dependent on a thorough knowledge of basin-rock mineralogy.

The chemical data used in this study are available in CONNOLLY *et al.* (1990a) and include a complete representation of most chemical species found in formation waters in sedimentary basins. The waters and data were obtained using the most modern techniques available at present (modified from LICO *et al.*, 1982). The speciation solubility calculations were accomplished using the computer codes EQ3NR (WOLERY, 1983; WOLERY *et al.*, 1984) and SOLMINEQ.88 PC/SHELL (WIWCHAR *et al.*, 1988; KHARAKA *et al.*, 1988). EQ3NR computed aqueous speciation and mineral saturation states using ion pair assumptions and the $\dot{B}$ equation (an extended Debye-Huckel equation) to approximate activity coefficients (HELGESON, 1969). Calculations provided by EQ3NR were not the primary values used in the study but provided a comparison for the speciation calculations computed by SOLMINEQ.88 PC/SHELL. SOLMINEQ.88 PC/SHELL is based on a PC version of the computer code SOLMINEQ.88 (KHARAKA *et al.*, 1988) and advanced versions of SOLMINEQ (AGGARWAL et al., 1986;

KHARAKA and BARNES, 1973), and provides the option of using either the $\dot{B}$ equation or Pitzer equations to compute the activity coefficients of aqueous species. The model used was dependent on the ionic strength of the formation water. The $\dot{B}$ equation (HELGESON, 1969), the same as used in the EQ3NR code, was considered preferable for waters with ionic strengths <1 molal. Assumptions employed by the $\dot{B}$ equation are maintained up until 1 molal; however, the equation yields significantly lower activity coefficients than the true values at ionic strengths >1 molal. Hence, for these more concentrated waters Pitzer equations were employed.

Pitzer equations (PITZER, 1973, 1981; SILVESTER and PITZER, 1978; HARVIE *et al.*, 1984) were used to compute the activity coefficients of aqueous species in solutions greater than 1 molal. These equations are based on an ion interaction or virial coefficient model that assumes no ion associations or complexing. Tests of the Pitzer coefficients in concentrated brines (HARVIE *et al.*, 1984) have shown that second virial coefficients give reliable results up to ionic strengths of about 4 and the use of higher coefficients can give reliable results up to ionic strengths of 6. However, there are drawbacks that should be considered when using Pitzer equations in SOLMINEQ.88 PC/SHELL. First, the program distributes aqueous species based on ion association; a set of mass balance and mass action equations are built which are iteratively solved to yield the distribution of species that best satisfies the constraints of the ion-association model under *in situ* conditions. This discrepancy between the ion-interaction equations in the Pitzer model and the distribution of species by ion association is resolved by incrementing ion activity coefficients obtained from Pitzer equations for these species. The second problem associated with using Pitzer equations is the lack of completely reliable data for some key components, such as CO_3^{-2}. As there are drawbacks with both models, both $\dot{B}$ and Pitzer equations were used to provide complementary insights into the chemical nature of Alberta Basin waters.

Both EQ3NR and SOLMINEQ.88 PC/SHELL were used to calculate speciation solubility calculations. The EQ3NR program used was not written with Pitzer equations, so data calculated using it is not presented here. However, EQ3NR was used as a basis for comparison because the two speciation models use different iteration techniques and have a slight variation in the complexes contained in their data bases. The two programs gave approximately the same distribution of data. Activities, saturation states, and distributions on activity phase diagrams were very similar, with more scatter being exhibited by the EQ3NR generated data. This is to be expected as the ion association model breaks down at higher ionic strengths.

Input for SOLMINEQ.88 PC/SHELL consisted of *in situ* temperatures (avg. chalcedony and measured temperatures), pressure, carbonate alkalinity, the concentrations of major and minor ions and pH. However, rather than use the measured pH value, a pH option was invoked. Credible pH values representative of *in situ* formation waters are required to study sub-surface reactions between aqueous solutions, carbonate and silicate minerals (NESBITT, 1980). Field measurements yield spurious data because of degassing due to pressure release during sampling and/or oxidation of Fe. Consequently, *in situ* pH values were obtained by calculating the pH values of individual waters from carbonate equilibria using the following equation (NESBITT, 1980):

$$CaCO_3 + H^+ \leftrightarrow Ca^{+2} + HCO_3 \qquad (1)$$

This was accomplished by assuming saturation of the formation waters with respect to primarily calcite, but dolomite was used when it dominated the formation mineralogy. Only for the Cardium Formation was saturation with respect to siderite implemented to calculate pH because siderite is a dominant and relatively late phase in the paragenesis of the Cardium (Fig. 5.3) and siderite was the only carbonate phase to yield realistic pH values in this formation. The use of carbonate minerals to set pH was considered reasonable because: 1) carbonate minerals and groundwater exhibit rapid equilibration

(PALACIAUSKAS and DOMENICO, 1976; PLUMMER *et al.*, 1978, 1979; BUSENBERG and PLUMMER, 1982); 2) carbonate cements are principal constituents throughout most paragenetic sequences (Appendix I) and solutions have most likely maintained continual contact with carbonate; and 3) saturation of formation waters with respect to calcite and dolomite was achieved even when pH values were manipulated to very low values. The pH values calculated with respect to carbonate saturation are realistic for these waters.

The concepts of buffer intensity and infinite buffers have been presented by STUMM and MORGAN (1981) and are discussed by ABERCROMBIE (1989) as possible mechanisms for controlling pH. Candidates for pH buffers include aqueous carbonate species, aqueous organic species, carbonate minerals and silicate hydrolysis, with the last two mechanisms being the most significant to the Alberta Basin. However, the reservoirs discussed in this study are characterized by much lower temperatures than those present where these processes are active (i.e., cyclic steam injection sites). Furthermore, the relative volume of carbonate relative to phases involved in silicate hydrolysis reactions makes the asumption of pH based on carbonate saturation reasonably accurate.

Stability Relations

Stability relations between subsurface waters and various mineral phases can be evaluated by calculating the ion activity product (IAP) of the minerals in each analyzed water and comparing this value to the equilibrium constants of the mineral (K_T) at a specific temperature. This is referred to as the saturation index (S.I.) and is technically defined as S.I. = log (IAP/K_T). A positive log S.I. value indicates supersaturation of the solution with respect to the mineral, a negative log S.I. value undersaturation, and zero indicates equilibrium. The degree of under- or supersaturation is indicated by the magnitude of the logarithm.

Preliminary results of the saturation state of Alberta Basin formation waters with respect to various minerals have been reported in CONNOLLY *et al.* (1990a) but are reviewed here for those cases where Pitzer equations were used to speciate >1 molal solutions.

Halite

Halite is not saturated in any of the waters examined (Fig. 5.6a); however, with increasing ionic strength (>1.5), saturation indices are concentrated between -1 and -2 for Alberta Basin formation waters.

Sulfates

The ion activity products for the sulfate minerals were not calculated for all of the Alberta Basin waters as the concentration of sulfate in some waters hosted by Cretaceous sedimentary rocks were below detection limits. Saturation with respect to sulfate was presented in CONNOLLY *et al.* (1990a), but the activities were determined using the $\dot{B}$ equation. Because this method is very inaccurate when modelling sulfate in solution, there are in fact significantly more sulfate minerals approaching saturation than was originally indicated by CONNOLLY *et al.* (1990a).

Of the waters with measurable sulfate, those with increasing ionic strength approach saturation with respect to gypsum and anhydrite (Fig. 5.6b). The two phases have very similar S.I. values for a specific sample, with anhydrite generally more saturated than gypsum. Plotting the gypsum - anhydrite equilibrium relations in a manner analagous to HARDIE (1967) and NESBITT (1980), Alberta Basin waters span the stability fields of gypsum and anhydrite (Fig. 5.7). This explains the variable saturation state with respect to gypsum or anhydrite between samples and the roughly equal S.I. values. Most of the samples plot relatively close to the line of gypsum/anhydrite equilibrium when consideration is given to the scale at which temperature is plotted. The temperature of gypsum/anhydrite equilibrium is near 56°C (LANGMUIR and MELCHIOR, 1985), but this temperature of transition is lowered considerably by the presence of NaCl and increased pressure, two characteristics typical of Alberta Basin waters. These arguments suggest that waters in the Alberta Basin should generally be more saturated with respect to anhydrite. Anhydrite, but not gypsum, was the only phase observed in the reservoir rocks.

Two different processes may be responsible for the approach toward saturation of anhydrite and gypsum with increased ionic strength (NESBITT, 1980): 1) the concentrations of Ca and SO_4 increase and approach saturation levels in waters of increasing ionic strength; or, 2) successively more concentrated brines approach anhydrite and gypsum saturation through anhydrite and gypsum dissolution. The latter explanation is most likely for Alberta Basin waters, as the fluids approaching or exceeding saturation with respect to anydrite and gypsum are only from Leduc and Nisku reservoirs. These formations contain the highest content of anhydrite in the Alberta Basin and although these fluids are among the most concentrated in the basin, there are other waters of equal ionic strength (i.e. Wabamun Group) that are not saturated with respect to gypsum or anhydrite and correspondingly contain no observed sulfates in their mineral assemblage.

Figure 5.6(c) illustrates the saturation state of Alberta Basin formation waters with respect to barite and celestite. These minerals form a complete solid solution series with one another; however, barite is more insoluble (LANGMUIR and MELCHIOR, 1985). Most of the waters are supersaturated with respect to barite, with the waters of greater ionic strength being less so. An opposite trend is established by celestite, where the S.I. increases with increasing ionic strength. These distributions may be explained by the fact that barium is much more abundant in dilute solutions and seizes most of the sulfate available in solution. However, there is less barium and more strontium in solutions of higher ionic strength, as these solutions generally indicate a longer residence time whereby barite would have already precipitated, resulting in increased celestite saturations and the observed trends. In addition, KUSHNIR (1982) has shown that dehydration of primary gypsum to anhydrite at depth expels Sr which supersaturates the water of dehydration with respect to celestite. There is evidence of gypsum dehydration processes in the Devonian of the Alberta Basin (GORRELL and ANDERSON, 1968) and such a process may also be partially responsible for the observed trends.

Carbonates

The stability of dolomite has been obtained using pH values calculated with respect to calcite saturation, except for the Nisku and Leduc Formations for which dolomite saturation was used and the Cardium Formation, for which used siderite saturation was used. All of the waters exhibit supersaturation with respect to dolomite (Fig. 5.7d), regardless that some of these stratigraphic units, particularly the Mississippian and Jurassic, contain little to no observable dolomite. The distribution in Fig. 5.7d indicates either: 1) concentration of the brines and precipitation of dolomite; or, 2) dissolution of dolomite with successively more concentrated brines approaching dolomite saturation. The latter mechanism is the most likely, as there is no trend observed with ionic strength for the Alberta Basin waters and dolomite is a dominant phase in the Devonian formations of the Alberta Basin. Since the fluids of Group I and Group II form a mixing relationship (CONNOLLY *et al.*, 1990a, 1990b), the effects of dolomite dissolution, if prevalent in Group I, are likely to be observed in Group II. In addition, dolomite is consistently observed in Cretaceous sequences, although present as only a minor, normally detrital phase.

Although the waters are supersaturated with respect to dolomite, relatively little authigenic dolomite has been observed in the stratigraphic column, although ankerite of very dolomitic composition is found in some of the formations (i.e. Viking Formation, Basal Quartz Formation; see Chapter 2). The lack of dolomite formation is likely the result of kinetic inhibition of dolomite crystallization at the lower temperatures common in sedimentary basins (LAND, 1982; HARDIE, 1987). Dolomite is well known for its reluctance to nucleate and grow, thus supersaturation of dolomite without crystallization is common in sedimentary basins, as it is in seawater (BROECKER and PENG, 1982).

The supersaturation of dolomite may imply that pH values should have been set with respect to this phase in many cases rather than calcite. However, as stated, dolomite is commonly supersaturated in waters saturated with calcite. On a plot of temperature versus log a_{Ca}/a_{Mg}, an equilibrium line between disordered dolomite and calcite can be drawn (Fig. 5.8). All of the Alberta Basin waters plot on the calcite side, suggesting calcite is the mineral phase with which the waters are in equilibrium. However, the waters do plot close to the equilibrium line between disordered dolomite and calcite.

Siderite is variably saturated but predominantly undersaturated in Alberta Basin waters. Iron is very difficult to measure accurately and although the waters were collected, filtered and acidified to a $pH<2$ immediately at the wellhead, some iron may have precipitated from solution during collection. Furthermore, iron is difficult to model thermodynamically. Hence, these data are not considered further.

Silicates

Silica activities are reported for all of the samples (Table 5.1). The data for $a_{SiO2(aq)}$ are log normally distributed and regardless of ionic strength, the silica activites are relatively constant, with Group I exhibiting slightly more variability than the other two groups (Table 5.1). This regular distribution is reasonable because quartz is found in all of the stratigraphic sequences, even the carbonate megasequence. RIMSTIDT and BARNES (1980) have shown that the precipitation rate of silica is identical for three different silica phases, quartz, cristobalite, and amorphous silica. This would suggest that the time required to reach equilibrium silica concentrations is independent of the silica polymorph controlling precipitation but is dependent on the precipitation rate and the ratio of the effective mineral surface area to fluid mass. This provides a large number of possible sources of silica that would yield similar equilibrium concentrations. Approximately one month is required for silica to reach equilibrium at 100°C for fine- to medium-grained sandstones (RIMSTIDT and BARNES, 1980; ABERCROMBIE, 1989).

The logarithm of the ratio of cation activity (Na, Ca, Mg, and K) divided by the hydrogen activity is another important variable with respect to mineral/clay stability. Examination of the data for the Alberta Basin (Table 5.1) indicates that the controls on $a_{cation/H+}$ values are disparate for Group I versus Group II and III, except possibly for K+/H+ activity ratios. Thus, it would appear that separate reactions/exchange processes are responsible for the cation content in Group I as opposed to those in Group II and III. This corresponds to a pronounced variation in lithologies between the groups, with primarily carbonate reservoirs hosting Group I waters as opposed to the dominantly clastic hosted waters of Group II and III. The clustering of Group II and III activity ratios and their variation from Group I differs from the mixing patterns and groupings established in CONNOLLY *et al.* (1990a), based on trends of major ion chemistry. Group III was removed from Group I and II mixing relations because of its extremely low elemental concentrations and high content of meteoric water. However, when ion activities are calculated and the cation activity divided by the hydrogen activity, it can be observed that the mineral reactions/exchange processes influencing the water composition are very different between the carbonate (Goup I) and clastic reservoirs (Groups II and III).

Transient behavior in a diagenetic system precludes the attainment of time invariant equilibrium. Minerals equilibrate with porewaters very quickly, on the order of days or weeks, at temperatures as low as 70°C (HUTCHEON, 1989). Conversely, mixing processes, which result in similar trends of major ionic species, are established over a relatively long period of time. However, the analyzed concentrations of the major elements present in the produced waters used to determine mixing regimes do not account for the distribution of each element among all potential species in solution (HUTCHEON, 1989). Therefore, differing equilibrium states may be established over short periods within the immediate reservoir, while maintaining the overall mixing zones reflected in the trends for the major ion chemistry. This would result in differing clusters or trends of data depending on the process being examined.

The capacity of a given rock to control the water composition is dependent on the mass of the reacting material, both water and rock, and the form of the equilibrium constant for potential buffering reactions. Other variables influencing the capacity of minerals to control water composition are temperature, fluid flow rates, and mineral dissolution and precipitation rates.

The composition of the system under consideration can be represented by the components Na_2O-K_2O-CaO-MgO-SiO_2-Al_2O_3-H_2O-CO_2. The component FeO was not included in the system because the thermodynamic properties of iron bearing minerals are not well known, although HUTCHEON (1989) has suggested that Fe in chlorite does not affect the thermodynamics of this phase substantially. The evaluation of silicate stabilities in formation waters in the above system requires a large body of information regarding the composition of various aqueous and mineral phases. Some mineral saturation states were determined by the program SOLMINEQ.88 PC/SHELL using congruent dissolution reactions; however, aluminosilicate saturation states could not be determined in such a manner because aluminum was not measured in the formation waters. This problem was resolved by making equilibrium phase diagrams on which all of the reactions were written to conserve aluminum. These diagrams are used to establish the state of the formation waters with respect to *in situ* conditions and were constructed using the program PTAsystem, part of the GEOCALC software package (BROWN *et al.*, 1987, 1988). Thermodynamic data used for minerals, water and aqueous species involved in the reactions described in this study are from BERMAN and BROWN (1985), BERMAN *et al.* (1985), HELGESON *et al.* (1981) and HARR *et al.* (1984). Absent from these compilations are the thermodynamic properties for clay minerals and certain other minerals (chalcedony) characteristically formed in low temperature sedimentary environments.

Clay minerals are generally not present in thermodynamic data bases because they are not considered to be thermodynamically homogeneous. This is a result of their : 1) micrometre to sub-micrometre size; 2) two dimensional habit; and, 3) heterogeneity resulting from interlayering and variations in chemical composition (ABERCROMBIE, 1989). The difficulties in determining the thermodynamics of clay minerals has resulted in two contrasting models to describe mixed layer smectite/illites solid solution (AAGAARD and HELGESON, 1983) or two distinct phases (GARRELS, 1984). In this paper the latter model is used. GARRELS (1984) has shown that illite and smectite behave as separate phases in terms of their stability with respect to coexisting solutions at low temperatures and a two phase system appears to better explain the calculated characteristics of equilibrium aqueous solutions.

A number of methods are available for estimating the thermodynamic properties of clays (TARDY and GARRELS, 1974; TARDY and FRITZ, 1981). ABERCROMBIE (1989), using the free energies for the lattice oxide clay components and interchangeable cations from BERMAN *et al.* (1985), estimated the thermodynamic properties of real clays. These are the values incorporated into this study.

Smectite is included as a separate phase and has been modelled using Na, K, Ca and Mg beidellite components. Iron may also be a very dominant constituent in such clays; however, it is not included in the system for the reasons already mentioned. Following NESBITT (1980), HUTCHEON (1981) and ABERCROMBIE (1989), smectites are modelled without interlayer or hydration waters, as the amount of this water under diagenetic conditions is unknown. Beidellite is the smectitic phase modelled thermodynamically, but the mineral phase will also be referred to as smectite. Activities of individual smectite components were estimated, through necessity, because compositions and activity-composition relationships are unavailable. However, estimation of the activities of individual smectite components considered the following: 1) the XRD observations of ABERCROMBIE (1989), whereby the position of collapsed smectite peaks indicates that smectite in the Clearwater Formation is dominated by Ca and Mg varieties. ABERCROMBIE's (1989) study was east of the study area examined here, but both areas had similar sources of sediment during Clearwater time; 2) the chemical analyses of MAIKLEM (1962) in which Cretaceous smectites from various locations in the Alberta basin, were analyzed by XRF; 3) the source and precursor phases of smectite in the Alberta Basin; and, 4) the most common exchangeable cations, their order of abundance and their valence. Based on these observations, Ca and Mg varieties of beidellite were considered to be dominant with the activities of Ca- and Mg- beidellite set at 0.4. The activities for Na- and K- beidellite were set at 0.1. In addition to the smectite, the thermodynamic properties of illite were calculated by ABERCROMBIE (1989) and chalcedony was added to the data base.

Equilibrium Activity Diagrams. Stability relations between silicates and aqueous phases are best shown on activity diagrams (GARRELS and CHRIST, 1965). Phase diagrams have been constructed in terms of Na^+/H^+, K^+/H^+, $Ca^{+2}/(H^+)^2$, and $Mg^{+2}/(H^+)^2$ activity ratios versus silica activity, in order to establish the minerals most likely involved in water/mineral interactions (Figs. 5.9a-d). All of the phase diagrams were calculated at 100 bars pressure and 60°C temperature, the average *in situ* values for the waters. Because of the low original dip of the Alberta Basin and the location of the sampling sites, deviation from these average values for specific water samples is insignificant.

Figure 5.9a illustrates Alberta Basin water compositions superimposed on phase relations for the Na system. Gibbsite, kaolinite, smectite (Na-beidellite) and albite are the mineral phases considered in the system and all of the Alberta Basin waters plot in the smectite stability field, toward the boundary with kaolinite and albite. HELGESON *et al.* (1969) and EBERL (1984) have calculated reaction paths of solutions when reacting with minerals and have found that dilute groundwater generally equilibrates first with gibbsite, then kaolinite and a second clay mineral before equilibrating with feldspars, and during these reactions it is conceivable to have conversion of one phase to a second (i.e. gibbsite to kaolinite, kaolinite to montmorillonite). Providing these conversions are rapid, the solution composition may be controlled by clay reactions, as has been shown for the Illinois Basin in the study by NESBITT (1985). Importantly, all of the waters from the Alberta Basin, even those from Group III, which have demonstrated a strong meteoric component, indicate mineral-fluid interactions have been significant and are reasonably evolved in their reaction paths.

Some waters from the Alberta Basin display distinctive trends which correspond to theoretical slopes on the phase diagram. Group I waters do not exhibit such a trend or slope on Fig. 5.9a, because illite is the only clay mineral found in many of the systems of Group I and the waters are not dominated by phases in the Na system. The high carbonate content in Group I waters suggest that they should be dominated by carbonate reactions. Group II and III form more distinctive trends in Fig. 5.9a, particularly the Group III. Both trends are parallel to the slope corresponding to the smectite/albite equilibrium reaction, consistent with the mineral assemblage in the reservoirs in this group.

The trends exhibited by Group II and III also show increasing Na^+/H^+ activity ratios with decreasing silica activities (Fig. 5.9a). This trend of decreasing silica activities corresponds to one of decreasing temperatures. As described by ABERCROMBIE (1989), such a distribution would be expected for isothermally invariant equilibrium between kaolinite, albite and smectite with decreasing temperature, and such a system may be partially controlling the composition of Group II and Group III waters.

Figure 5.9b illustrates Alberta Basin formation waters with respect to equilibrium K phase relations. All of the waters plot near the phase boundaries of K-spar, illite and smectite, and relatively close to kaolinite, but are in the illite field. In this figure, none of the water groups have well defined slopes or trends suggesting that possibly the activity of potassium for all of the waters is being controlled by more than one reaction.

Figures 5.9c and 5.9d augment the other activity diagrams by showing phase diagrams of $Ca^{+2}/(H^{+})^{2}$ and $Mg^{+2}/(H^{+})^{2}$ versus silica activities, respectively. With the large volume of carbonate rock characterizing the Devonian through Jurassic formations in the Alberta Basin, it may seem relatively impractical to construct plots such as in Fig. 5.9c and 9d when carbonate units may be acting as open system donors of Ca and Mg to the formation waters. However, CONNOLLY *et al.* (1990b) have shown through the use of Sr ratios and concentrations that the formation waters hosted in these reservoirs appear to be dominated by reactions other than carbonate reactions, such as ion exchange with clay minerals. Therefore, it was considered advantageous to examine the waters with respect to silicate diagenesis/thermodynamic equilibrium models. Phase relations for the Ca system illustrate that all of the fluids plot in the smectite field, except one Group III water. The Alberta Basin waters are very much removed from the anorthite stability field because all the plagioclase feldspars in the basin contain Na. Incorporation of Na into the anorthite component (i.e., toward albitic composition) would tend to enlarge the anorthite stability field, shifting it down toward the Alberta Basin waters. The Mg activity diagram shows that most of the Group II and III waters plot in the chlorite region while most of the Group I waters plot in the smectite zone. Group II and III reservoirs contain increased chlorite contents in stratigraphically higher formations, corresponding to waters farther within the chlorite field. Group I waters have much higher magnesium contents than the other two groups; however, they plot in the smectite field and contain no chlorite in their mineral assemblage. This may attest to a strong carbonate component controlling equilibrium in Group I.

CONTROLS ON FORMATION WATER COMPOSITION

Single cation activity ratios versus silica activity plots indicate which minerals are most influential in controlling the water composition in the Alberta Basin. All four activity diagrams (Figs. 5.9a-9d) have some notable similarities. All show a slight increase in cation/H^+ activity ratios with decreasing silica activities for Groups II and III, which is accompanied by a decrease in temperature. The observed trends and location of water samples with respect to equilibrium mineral phases on the activity-activity diagrams are corroborated by similar trends and locations on activity ratio-temperature diagrams.

Examination of the separate groups shown Figs. 5.9a-5.9d illustrates that Group I exhibits no significant trends on the phase diagrams, but is a clustering of points, Group II displays a slight trend and Group III exhibits a well defined trend. The high degree of correlation demonstrated by Group III as opposed to the poor correlation shown by Group I may reflect the relative complexity of the system(s) involved and the relative importance of carbonate mineral reactions. Group III waters do not contain a component of the original seawater that may have been present when the reservoirs were deposited (CONNOLLY *et al.*, 1990a). The relatively early waters with which the sediments hosting the Group III waters originally equilibrated have been subsequently flushed from the system by gravity-driven modern meteoric water. Thus, all previous records of reactions held by early waters have been eliminated, yielding a very simple system. Group II and particularly Group I have maintained an original seawater component in their systems (CONNOLLY *et al.*, 1990a) and their overall water chemistry is likely the result of a series of equilibrium reactions, rather than one dominating reaction. The complexity of these systems detracts from a well defined trend for one reaction, but represents a current equilibrium state that is a culmination of previous systems and reactions. Furthermore, carbonate mineral reactions are likely important to Group I waters which would not be reflected on Figs. 5.9a-5.9d.

Sodium concentrations in the Alberta Basin waters are controlled either by plagioclase feldspar or sodic-clay minerals. It is observed in Fig. 5.9a that clay minerals control the Na^+/H^+ ratios, although plagioclase is present in most of the formations, from trace amounts in the carbonate sequence to relatively abundant in the Upper Cretaceous units. Feldspar has been observed to react rapidly with groundwaters and is one of the first species to alter completely in a weathering environment (i.e., meteoric waters) (GARRELS and MACKENZIE, 1967), indicating that kinetic inhibition is not a likely explanation for the feldspar solution disequilibria. Rather, the lack of feldspar solution equilibria may be a result of two other factors. First, plagioclase is not very abundant in some formations, such as the carbonate megasequence. Clay minerals are much more prevalent in these units and likely have more control on the aqueous species. Second, in formation waters from reservoirs where plagioclase is abundant, such as the upper Lower to Upper Cretaceous, the waters have likely evolved beyond the point of plagioclase equilibrium in their reaction paths, to the point where plagioclase is altered and the waters are in equilibrium with the resulting sodic clay. This hypothesis is supported in the stratigraphically higher formations of the Upper Cretaceous, where plagioclase rock fragments exhibit significant alteration.

The potassium concentrations of the formations also appear to be controlled by clay minerals. Potassium feldspar may also be contributing to the K concentration; however, K-feldspar is less reactive in a weathering or leaching (meteoric water) environment than plagioclase (GARRELS and MACKENZIE, 1967) and does not show any significant signs of alteration in the mineral assemblage. Furthermore, K-spar is present in such small amounts relative to clay minerals that the clay minerals more likely control K^+/H^+ activities.

The lack of equilibrium with K-spar may result from both low abundances and kinetics. Illite is a much more reactive mineral and appears to be controlling K concentrations (Fig. 5.9b).

The $Ca^{+2}/(H^+)^2$ and $Mg^{+2}/(H^+)^2$ activity diagrams both indicate that Alberta Basin waters are controlled by a Ca- and Mg-beidellite respectively, with the latter diagram showing the waters extending into the chlorite field. Importantly, if ideal mixing had not been invoked, and the activities of beidellite not set as they were (i.e. Ca and Mg at 0.4 and Na and K at 0.1), all of the waters on both graphs would have plotted in the kaolinite stability field, causing misleading interpretations with regard to equilibrium relationships. Although kaolinite is a very prevalent phase in the rock column, particularly in the Cretaceous, if these rocks are examined petrographically (Appendix I) and by SEM (Chapter 4), kaolinite is not the last phase formed in the paragenetic sequences (LONGSTAFFE, 1986; LONGSTAFFE and AYALON, 1987; AYALON and LONGSTAFFE, 1988). Petrographic investigations suggest kaolinite is undergoing some alteration or transformation. This combined with the fact that the waters often plot in the fields corresponding to the last observed phase in their respective paragenetic sequence gives credence to the manner in which the beidellite activities were divided. Furthermore, a strict division between most of the Group I fluids plotting in the smectite field with most of the Group II and III plotting in the chlorite field corresponds to the authigenic mineralogy in the reservoir rocks.

The Group I waters show equilibration with respect to smectite on all of the activity diagrams, except Fig. 5.9b; however, smectite has not been observed in the reservoir rocks. This is likely a result of the absence of illite on the other phase diagrams and the similarity between illite and beidellite. The idealized formulas chosen for illite ($K_{0.8}Al_{1.9}Si_4O_{10}(OH)_2$) and beidellite ($(Me^{n+})_{0.3/n}Al_{1.9}Si_4O_{10}(OH)_2$), are comparable, particularly since beidellite is modelled without any interlayer water. Thus, as modelled in this study, K-beidellite and illite are almost the same thermodynamically except that beidellite has a lower layer charge per formula unit resulting in fewer interlayer cations. Thus, when illite is not present, the Group I waters plot within the field closest thermodynamically to illite and are metastable within the smectite fields.

In summary, the formation waters of the Alberta Basin appear to segregate into the three groups indicated. Group I is very much different from Group II and Group III, suggesting the variation in lithologies is likely the cause. Formation waters from Group I are equilibrated with smectite, illite, calcite and dolomite, with gypsum and anhydrite becoming more significant for waters with ionic strengths >2.0. Group II and Group III are equilibrated with respect to calcite, dolomite, illite, smectite and chlorite. Carbonate minerals appear to control equilibrium reactions in Group I waters, with some moderation by potassic clay (illite) minerals. Feldspars and micas are variably abundant in all the formations, but exert little control on basin water compositions (see also Chapter 4). Clay minerals appear to have a significant control on the formation water composition within the Cretaceous clastic units (Groups II and III). Clay minerals have been shown to control groundwater compositions in other sedimentary basins (BRICKER and GARRELS, 1966; GARRELS, 1967; NESBITT, 1977, 1980, 1985; ABERCROMBIE, 1989). Significantly, kaolinite was not involved in any of the reactions that control the water compositions. Kaolinite is a large component of many of the clastic reservoirs but examination of the paragenetic sequence suggests kaolinite alteration is occurring and kaolinite is no longer dominant in mediating water compositions. This supports the conclusions of CONNOLLY *et al.* (1990a; 1990b), in which they suggest, based on the chemistry and isotopic compositions of the formation waters, that a mixing zone has been established between Devonian through Lower Cretaceous hosted waters which is unaffected by meteoric waters, allowing for the establishment of density stratification and the formation of illite.

The reactions by which cation/H+ activities are controlled is uncertain. It may be by the conversion of one mineral to another (i.e. kaolinite to illite) or may result from cation exchange reactions. The importance of these reaction types will be evaluated in the next section.

MECHANISMS AFFECTING THE COMPOSITION OF ALBERTA BASIN BRINES

A wide variety of interpretations have been generated to explain the composition of waters in sedimentary basins, with most discussions focusing on: 1) dissolution of evaporite deposits; 2) complete or partial flushing by meteoric waters; or, 3) interaction of formation waters with enclosing sedimentary rocks. These processes may be investigated using some of the techniques described by NESBITT (1985). The preliminary investigation addressing the provenance of Alberta Basin waters (CONNOLLY *et al.*, 1990a; 1990b) can be further clarified by a thermodynamic evaluation.

Dissolution of Evaporites

High Cl contents in the Alberta Basin have been attributed to the dissolution of soluble chloride salts (HITCHON *et al.*, 1971). Halite is the most common soluble chloride salt and upon dissolution, equal molar proportions of Na and Cl are released to solution, resulting in Na/Cl = 0.65g/g. The dissolution of halite into solution can be calculated such that as consecutively greater amounts of halite dissolve in solutions, Na/Cl values change toward the value of 0.65g/g. Dissolving halite into Alberta Basin formation waters of differing concentrations (i.e. the starting point of curves A, B and C) produces the various hypothetical trends (A, B, C) shown on Fig. 5.4a. Regardless of the starting concentration of the formation water, none of these produced trends are compatible with the overall distribution shown by Alberta Basin formation waters. Thus, dissolution of evaporites is not a viable explanation for the current chemistry of the formation waters.

Mixing of Dilute Meteoric Groundwaters with Formation Waters

Gravity driven flow of meteoric water has dominated many of the diagenetic reactions that have occurred in the Alberta Basin (LONGSTAFFE, 1986; LONGSTAFFE and AYALON, 1987; AYALON and LONGSTAFFE, 1988). GARRELS (1967) and GARRELS and MACKENZIE (1967) have shown that dilute meteoric waters are dominated by Na, Ca and HCO_3, and contain very little Cl. Examination of groundwaters (HOLYSH, 1989) and meteoric waters (CONNOLLY *et al.*, 1990a) in the Alberta Basin verify this observation and show that these waters often have Na/Cl , Ca/Cl and $HCO_3 + CO_3$ / Cl values greater than 1.0. Thus, meteoric groundwaters are compositionally distinct from dilute formation waters and mixing of the two compositions should result in a characteristic orientation on a graph.

Curve D on Fig. 5.4a illustrates a mixing relationship between dilute meteoric groundwaters and Alberta Basin formation waters with 20 g/l Cl. Some formation waters from Group III have a Na/Cl ratio greater than 1 and plot extremely close to the y-axis. These waters were sampled from the Cardium Formation and contain a high content of meteoric water (CONNOLLY *et al.*, 1990a; 1990b). Following trend D, intersection of three points occurs, prior to intersection with the formation waters. All of these points are from Belly River Formation reservoirs, confirming the strong meteoric component attested to these Group III waters. Two Group III points plot just below the Belly River Foramtion samples, representing the Rock Creek Formation waters. These also have a strong meteoric component but were likely of higher concentration(~30 g/l) prior to the influx of meteoric waters, as indicated by their location on the graph. Besides the Group III waters, mixing of formation waters with dilute modern meteoric waters does not explain the trends of Group I and Group II lending support to the hypothesis that these waters were isolated from meteoric influence since the Pliocene (CONNOLLY *et al.*, 1990b).

Ion Exchange Versus Dissolution / Precipitation Reactions

The transient behavior of temperature, fluid flow, and water composition is typical of sedimentary basins and precludes the attainment of time invariant equilibrium. Nevertheless, equilibrium thermodynamics allows the state of the system under consideration at any one time to be compared to an equilibrium state under the same conditions. It is understood that original seawater and depositional waters in sedimenatary basins interact with the surrounding mineral assemblage, modifying the original water composition. Depositional waters in the Alberta Basin were altered by early diagenetic reactions; however, it is likely that equilibrium has been upset numerous times since. For example, the second pulse of the Laramide Orogeny cast the sediments and fluids of the Alberta Basin into disequilibrium. This would have resulted in variable reactions between minerals and fluids, providing they were kinetically favorable.

Whereas cation/H^+ activity ratios versus silica activities indicate the minerals most likely involved in water/mineral interactions, phase diagrams of cation/H^+ activity ratios versus cation/H^+ activity ratios provide more information on the types of reactions that might be occurring between the various minerals and aqueous phases. Figures 5:10a and b illustrate some cation/H^+ versus cation/H^+ activity diagrams with the waters of the Alberta Basin superimposed on them. Once again the activity diagrams are plotted at 100 bars pressure and 60°C temperature.

A unit slope for the activity ratios on the diagrams implies that mineral reactions are controlled by exchange reactions between minerals of similar composition. The slopes of the boundaries in Fig. 5.10 are controlled by the stoichiometry of the minerals involved and a unit slope requires that both minerals have the same stoichiometric coefficients for the species involved in the exchange. Two such reactions are possible for K^+/H^+ and Na^+/H^+ activity ratios in Fig. 5.10a: Na^+ and K^+ exchange between albite and K-feldspar or Na^+ and K^+ exchange between smectite components. Any other reaction likely results from the conversion of one mineral phase to another. Fig. 5.10a illustrates the location of the various water groups with respect to the equilibrium mineral phases. Regression analysis through Group I waters yields a slope of 0.92 at a correlation coefficient of 0.93, suggesting that exchange processes are dominating the composition of these waters. Plotting these same fluids on Fig. 5.10b for $Ca^{+2}/(H^+)^2$ and $Mg^{+2}/(H^+)^2$ activity ratios, a similar relationship is observed between the smectites. Because Group I waters exhibit identical behavior on both graphs, it appears that the cation activity ratios in these waters are likely controlled by exchange processes between smectite components.

Examining the phase relations for Na^+ and K^+ on Fig. 5.10a, the water compositions for Group I reflect exchange reactions involving Na- and K- beidellite components; however, almost all of the samples lie within the illite field. A similar situation exists on Fig. 5.10b for Ca^{+2} and Mg^{+2}, in that exchange reactions between Ca- and Mg-beidellite components appear to be controlling the water chemistry, although illite is the only clay mineral phase that has been identified in these reservoirs. This would suggest that smectite controls these activity ratios, but is metastable with respect to illite.

Group II and Group III trends on Fig. 5.10a are not as well correlated as Group I and have slopes which dismiss ion exchange as being the sole processes controlling the activity ratios for Na^+/H^+ and K^+/H^+ for Alberta Basin waters. Separate regression analyses for each of these groups indicates a reasonably close parallelism with the regression line representing the reaction between smectite (Na-beidellite) and illite, with most of the waters plotting in the illite field. These observations corroborate those for mineral phases observed in the basin, where paragenetic sequences (Appendix I) reflect illitization of smectite and kaolinite is currently active, particularly in the Cretaceous. It has been demonstrated by HURST and IRWIN (1982), that a hydraulic head that causes meteoric water to penetrate deep into sedimentary basins typically generates kaolinite cements, while a decrease in hydraulic head causes concentrated brines to rise within the basin, generating an environment conducive to the formation of illitic cements. The Alberta Basin documents an analogous history. Meteoric waters flushed through the basin as a result of the hydraulic head generated by the Laramide Orogeny. Abundant kaolinite was formed, particularly in the Cambrian units and the Cretaceous sequence. Dissipation of the hydraulic head subsequently occurred (GARVEN, 1989; CONNOLLY *et al.*, 1990b), likely resulting in the conversion of kaolinite to Na-beidellite, to illite, with Na-beidellite being an intermediary phase.

Figure 5.10b indicates that different types of reactions are controlling the $Ca^{+2}/(H^+)^2$ and $Mg^{+2}/(H^+)^2$ activity ratios for Group II and Group III waters than are controlling Na^+/H^+ and K^+/H^+ activity ratios. Group II and III have slopes of 0.85 and 0.82 respectively on Fig. 5.10b and these fluids plot in the chlorite stability field. The waters are probably dominantly controlled by metastable smectite exchange reactions; however, other reactions are also affecting the waters to a lesser degree, preventing the attainment of a unit slope.

Numerous reactions were referred to in CONNOLLY *et al.* (1990a) as possibilities for providing an excess of divalent cations to the formation waters of Group I. These processes, such as silicate hydrolysis reactions and clay carbonate reactions may once have been active, particularly

$$\text{Kaolinite} + K^+ \leftrightarrow \text{Illite} + H^+ \quad (2).$$

Kaolinite may have been very abundant in these stratigraphic units after the Laramide Orogeny, but has been subsequently illitized. This process could have yielded the current excess of divalent cations. However, at present the formation waters do not indicate that these phase changes are active, but are shown to be dominated by cation exchange processes.

Exchange reactions were not as prevalent in Group II and Group III. Initially, meteoric recharge resulted in the formation of kaolinite, as observed by petrographic relationships and isotope analyses (LONGSTAFFE and AYALON, 1987), then the alteration of plagioclase feldspar and equilibration with Na-beidellite likely occurred as shown in the following equation:

$$7NaAlSi_3O_8 + 6H^+ \leftrightarrow NaAl_7Si_{11}O_{30} + 10SiO_2 + 6Na^+ \qquad (3)$$

Subsequently, illite was probably formed from the conversion of smectite. Either of the commonly accepted illitization reactions (transformation - HOWER *et al.*, (1976); cannibalization - BOLES and FRANK, (1979)) would result in excess cations, particularly Na^+, being released. Combining either illitization reaction with that of (3) would explain the excess of Na^+ Alberta Basin waters, particularly in the Cretaceous units and the observed mineral assemblage.

The linear relationship maintained between Group I and Group II waters on mixing, elemental, and isotopic plots shown in CONNOLLY *et al.* (1990a, 1990b) is not repeated here on activity phase diagrams (Figs. 5.9 and 5.10). This suggests that although on a large scale, Groups I and II are mixing and have possibly established density stratification, current chemical reactions occurring in the different groups are defined by the surrounding lithology. Because Group II and Group III are characterized by clastic reservoirs, they plot and form similar trends on the activity diagrams as the distribution of each element among potential species in their waters is similar, whereas waters from Group I are from predominantly carbonate reservoirs where currently active mineral reactions are distinct from those in clastic reservoirs.

CONCLUSIONS

Equilibrium thermodynamics was used to establish the importance of water/rock interactions in controlling water compositions and mineral precipitation in the Alberta Basin. Three distinct formation water groups, which were previously established based on chemical (CONNOLLY *et al.*, 1990a) and isotopic (CONNOLLY *et al.*, 1990b) compositions, were similarly used in this study based on ionic strength (Fig. 5.5) and major ion/Cl versus Cl plots. These groups are: Group I, which are dominantly carbonate-hosted and are stratigraphically the lowest; Group II, which are primarily from clastic reservoirs; and Group III, which are completely clastic-hosted and comprise the stratigraphically highest zone.

Stability relations and activity diagrams of cation/H^+ activity ratios versus silica activities for the formation waters of the Alberta Basin show distinct trends for the three water groups. Group I are equilibrated with smectite, illite, calcite, and dolomite, with gypsum and anhydrite becoming increasingly significant for waters with ionic strengths >2.0. Carbonate minerals appear to dominate the equilibrium reactions with moderation by illite. Group II and III waters are equilibrated with respect to calcite, dolomite, illite, smectite and chlorite, with the distribution of Group II waters indicating a more complex origin (i.e., more reactions contributing to the water chemistry) than those for Group III. Clay minerals dominate water/rock reactions in these groups, distinguishing them from Group I.

Potential mechanisms for altering the composition of Alberta Basin waters are: (1) dissolution of evaporites; (2) flushing by meteoric waters; and/or, (3) interaction of formation waters with enclosing sedimentary rocks. The first mechanism is not currently active and only Group III waters are affected by modern meteoric flushing. Water/rock interaction is a predominant mechanism affecting the current composition of basinal fluids. Ion exchange reactions between smectite phases, metastable to illite, characterize Group I waters. Groups II and III waters are controlled by the conversion of beidellite to illite, but are partially controlled by ion exchange reactions between Ca- and Mg-beidellite, metastable to chlorite.

Equilibrium mineral reactions/exchange processes responsible for aqueous speciation are different for Group I waters when compared to Groups II and III, suggesting lithologic variation (i.e. clastic *vs* carbonate rocks) is the likely cause. This distinction indicates the various reactions contributing to the overall mixing regime established between Groups I and II in the Alberta Basin (CONNOLLY *et al.*, 1990a; 1990b), as equilibrium thermodynamics considers the distribution of each species among potential species in solution. All of the water groups indicate relatively evolved reaction paths (kaolinite → montmorillonite → illite), despite being part of a basin thought to be dominated, as recently as the Pliocene, by gravity-driven flow.

REFERENCES

AAGAARD P. and HELGESON H.C. (1983) Activity/composition relations among silicates and aqueous solutions: II. Chemical and thermodynamic consequences of ideal mixing of atoms on homological sites in montmorillonites, illites and mixed-layer clays. *Clays and Clay Mins.* 31, 207-217.

ABERCROMBIE H.J. (1989) Water-rock interaction during diagenesis and thermal recovery of heavy oil, Cold Lake, Alberta. Ph.D. Thesis, Univ. of Calgary, Calgary, Alberta.

ABERCROMBIE H.J., SHEVALIER M. and HUTCHEON I. (1989) Natural diagenesis: A model for artificial diagenesis during steam assisted recovery of heavy oil, Cold Lake, Alberta, Canada. *Water/Rock Interaction* VI.

AGGARWAL P.K., HULL R.W., GUNTER W.D. and KHARAKA Y.K. (1986) SOLMINEQ: A computer code for geochemical modelling of water-rock interactions in sedimentary basins. *Proc. Third Canadian-American Conference on Hydrogeology-Hydrogeology of Sedimentary Basins, Application to Exploration and Exploitation* (ed. B. HITCHON, S. BACHU, and C.M. SAUVEPLANE), pp. 196-203. Nat. Water Well Assoc. 3.

ANDRICHUK J.M. (1958) Stratigraphy and facies analysis of Upper Devonian reefs in Leduc, Stettler, and Redwater area, Alberta. *Am. Assoc. Petrol. Geol. Bull.* 42, 1-93.

AYALON A. and LONGSTAFFE F.J. (1988) Oxygen isotope studies of diagenesis and pore-water evolution in the western Canada sedimentary basin: Evidence from Upper Cretaceous basal Belly River sandstone, Alberta. *J. Sediment. Petrol.* 58, 489-505.

BEAUMONT C. (1981) Foreland basins. *Geophys. J. Roy. Astron. Soc.* 65, 291-329.

BERMAN R.G. and BROWN T.H. (1985) The heat capacity of minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2: Representation, estimation, and high temperature extrapolation. *Contrib. Mineral. Petrol.* 85, 168-183.

BERMAN R.G., BROWN T.H. and GREENWOOD H.J. (1985) A thermodynamic data base for minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. *Atom. Ener. of Canada Ltd., Tech. Report* TR-377.

BOLÈS J.R. and FRANK S.G. (1979) Clay diagenesis in the Wilcox sandstones of southwest Texas: Implications of smectite diagenesis on sandstone cementation. *J. Sediment. Petrol.* 49, 55-70.

BRICKER O.P. and GARRELS R.M. (1966) Mineralogical factors in natural water chemistry. In *Principles and Applications of Water Chemistry* (eds. S.D. FAUST and J.V. HUNTER), pp. 449-469. John Wiley and Sons.

BROECKER W.S. and PENG T.H. (1982) *Tracers in the Sea*. Lamont-Doherty Geological Survey.

BROWN T.H., BERMAN R.G. and PERKINS E.H. (1987) GEO-CALC: A software package for rapid calculation of stable pressure-temperature-activity diagrams. *Geol. Soc. Am. Annual Meeting* 19, 603.

BROWN T.H., BERMAN R.G. and PERKINS E.H. (1988) GEO-CALC: Software package for calculation and display of pressure-temperature-composition phase diagrams using an IBM compatible personal computer. *Computers and Geosciences* 14, 279-289.

BUSENBERG E. and PLUMMER L.N. (1982) The kinetics of dissolution of dolomite in CO_2 - H_20 systems at 1.5 to 65°C and 0 to 1 atm P_{CO2}. *Am. J. Sci.* 282, 45-78.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. I. Chemistry. *Appld. Geochem.* 5, 375-396.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. II. Isotope systematics and water mixing. *Appld. Geochem.* 5, 397-414.

DICKINSON W.R. (1974) Plate tectonics and sedimentation. In *Tectonics and Sedimentation* (ed. W.R. DICKINSON), pp. 1-27. Special Publication Soc. of Econ. Geol. Paleon.

DICKINSON W.R. and SNYDER W.S. (1978) Plate tectonics of the Laramide Orogeny. In *Laramide Folding Associated with Basement Faulting in the Western United States*. pp. 355-366. Geol. Soc. Am. Mem. 151.

EBERL D. (1984) Clay mineral formation and transformation in rocks and soils. *Phil. Trans. Roy. Soc., London.* A311, 241-257.

FOURNIER R.O., WHITE D.E. and TRUESDELL A.H. (1974) Geochemical indicators of sub-surface temperatures - Part 1, basic assumptions. *U.S. Geol. Sur., J. of Res.* 2, 259-262.

GARRELS R.M. (1967) Genesis of some ground waters from some igneous rocks. In *Researches in Geochemistry*, 2, (ed. P.H. ABELSON), pp. 405-420. Wiley.

GARRELS R.M. (1984) Montmorillonite/illite stability diagrams. *Clays and Clay Mins.* 32, 161-166.

GARRELS R.M. and CHRIST C.L. (1965) *Solutions, Minerals and Equilibria*. Harper and Row.

GARRELS R.M. and MACKENZIE F.T. (1967) Origin of the chemical compositions of some springs and lakes. In *Equilibrium Concepts in Natural Water Systems*, pp. 222-242. Washington, D.C., Am. Chem. Soc. 67.

GARVEN G. (1989) A hydrogeologic model for the formation of giant oil sands deposits of the western Canada sedimentary basin. *Am. J. Sci.* **289**, 105-166.

GORRELL H.A. and ALDERMAN G.R. (1968) Elk Point Group saline basins of Alberta, Saskatchewan, and Manitoba, Canada. *Geol. Soc. Am. Spec. Pap.* **88**, 291-317.

HANOR J.S. (1987) *Origin and Migration of Subsurface Sedimentary Brines*. Soc. Econ. Paleon. Mineral. Short Course **21**.

HARDIE L.A. (1967) The gypsum-anhydrite equilibrium at one atmosphere pressure. *Am. Mineral.* **52**, 171-200.

HARDIE L.A. (1987) Dolomitization: A critical view of some current views. *J. Sediment. Petrol.* **57**, 166-183.

HARR C., GALLAGHER J.S. and KELL G.S. (1984) *NBS/NRC Steam Tables. Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in S.I. Units.* Hemisphere Publishing Co.

HARVIE C.E., MOLLER N., and WEARE J.H. (1984) The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_2-H_2O system to high ionic strengths at 25°C. *Geochim. Cosmochim. Acta* **48**, 723-751.

HELGESON H.C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *Am. J. Sci.* **267**, 729-804.

HELGESON H.C., GARRELS R.M. and MACKENZIE F. (1969) Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions. *Geochim. Cosmochim. Acta* **33**, 455-481.

HELGESON H.C., KIRKHAM D.H. and FLOWERS G.C. (1981) Theoretical prediction of the thermodynamic properties of aqueous electrolytes at high temperatures and pressures. IV. Calculations of activity coefficients, osmotic coefficients, and apparent molal and standard and relative and partial molar properties to 600°C and 5Kb. *Am. J. Sci.* **281**, 1249-1516.

HITCHON B. (1984) Geothermal gradients, hydrodynamics and hydrocarbon occurrence, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* **68**, 713-743.

HITCHON B. and FRIEDMAN I. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin, I. Stable isotopes of hydrogen and oxygen. *Geochim. Cosmochim. Actu* **33**, 1321-1349.

HITCHON B., BILLINGS G.K. and KLOVAN J.E. (1971) Geochemistry and origin of formation waters in the western Canada sedimentary basin, III. Factors controlling chemical composition. *Geochim. Cosmochim. Acta* **35**, 567-598.

HOLYSH S. (1989) Regional groundwater flow and petroleum related geochemical signatures, Chauvin area, east-central Alberta. Unpub. M.Sc. Thesis., Univ. of Alberta, Edmonton, Alberta.

HOWER J., ESLINGER E., HOWER M.E. and PERRY E.A. (1976) Mechanism of burial metamorphism of argillaceous sediments: 1. Mineralogical and chemical evidence. *Geol. Soc. Am. Bull.* **87**, 725-737.

HURST A. and IRWIN H. (1982) Geological modeling of clay diagenesis in sandstone. *Clay Mins.* **17**, 5-22.

HUTCHEON I. (1981) Applications of thermodynamics to clay-mineral and authigenic mineral assemblages. In *Clays and the Resource Geologist* (ed. F.J. LONGSTAFFE), pp. 169-193. Min. Assoc. Canada Short Course **7**.

HUTCHEON I. (1989) Application of chemical and isotopic analyses of fluids to problems in sandstone diagenesis. In *Burial Diagenesis* (ed. I. HUTCHEON), pp. 279-310. Min. Assoc. Canada Short Course **15**.

JORDON T.E. (1981) Thrust loads and foreland basin evolution, Cretaceous western United States. *Am. Assoc. Petrol. Geol. Bull.* **65**, 2506-2520.

KAUFFMAN E.G. (1977) Geological and biological overview: Western interior basin. *The Mountain Geologists* **69**, 75-99.

KHARAKA Y.K. and BARNES I. (1973) SOLMINEQ. Solution-mineral equilibrium computations. *U.S. Geol. Surv. Computer Contributions*, NTIS #PB-215 899, 81p.

KHARAKA Y.K., GUNTER W.D., AGGARWAL P.K., PERKINS E.H. and DeBRAAL J.D. (1988) SOLMINEQ.88: A computer Program Code for Geochemical Modeling of Water-Rock Interactions. *U.S. Geol. Surv. Water Invest.* Report 88-4227, 420pp.

KHARAKA Y.K. and MARINER R.H. (1988) Chemical geothermometers and their application to formation waters from sedimentary basins. In *The Thermal History of Sedimentary Basins. Methods and Case Histories* (eds. N.D. NAESER and T.H. McCULLOH), pp. 99-117. Springer-Verlag.

KRAMER J.R. (1969) Subsurface brines and mineral equilibria. *Chem. Geol.* **4**, 37-50.

KUSHNIR J. (1982) The partitioning of seawater cations during the transformation of gypsum to anhydrite. *Geochim. Cosmochim. Acta* **46**, 433-446.

LAND L.S. (1982) Dolomitization. *Am. Assoc. Petrol. Geol. Educ. Course Notes* **24**.

LAND L.S. and PREZBINDOWSKI D.R. (1981) The origin and evolution of saline formation water. Lower Cretaceous carbonates, south-central Texas, U.S.A. *J. Hydrol.* **54**, 51-74.

LANGMUIR D. and MELCHIOR D. (1985) The geochemistry of Ca, Sr, Ba and Ra sulfates in some deep brines from the Palo Duro Basin, Texas. *Geochim. Cosmochim. Acta* **49**, 2423-2432.

LICO M.S., KHARAKA Y.K., CAROTHERS W.W. and WRIGHT V.A. (1982) Methods of collection and analysis of geopressured, geothermal and oil field waters. *U. S. Geol. Sur. Water Supply Pap.* **2194**, 21pp.

LONGSTAFFE F.J. (1986) Oxygen isotope studies of diagenesis in the basal Belly River sandstone, Pembina I-Pool, Alberta. *J. Sediment. Petrol.* **56**, 78-88.

LONGSTAFFE F.J. and AYALON A. (1987) Oxygen-isotope studies of clastic diagenesis in the Lower Cretaceous Viking Formation, Alberta: Implications for the role of meteoric water. In *Diagenesis of Sedimentary Sequences* (ed. J.D. MARSHALL), pp. 277-296. Geol. Soc. Spec. Pub., **36**.

MAIKLEM W.R. (1962) Clay minerals from some Upper Cretaceous bentonites, southwestern Alberta. M.Sc. Thesis, Univ. of Alberta, Edmonton, Alberta.

MERINO E. (1975) Diagenesis in Tertiary sandstones from Kettleman North Dome, California - II. Interstitial solutions: Distribution of aqueous species at 100°C and chemical relation to the diagenetic mineralogy. *Geochim. Cosmochim. Acta* **39**, 1629-1645.

NESBITT H.W. (1977) Estimation of the thermodynamic properties of Na- Ca- and Mg-beidellites. *Can. Mineral.* **15**, 22-30.

NESBITT H.W. (1980) Characterization of mineral-solution interactions in Carboniferous sandstones and shales of the Illinois sedimentary basin. *Am. J. Sci.* **280**, 607-630.

NESBITT H.W. (1985) A chemical equilibrium model for the Illinois basin formation waters. *Am. J. Sci.* **285**, 436-458.

PALCIAUSKAS V.V and DOMENICO P.A. (1976) Solution chemistry, mass transfer, and the approach to chemical equilibrium in porous carbonate rocks and sediments. *Geol. Soc. Am. Bull.* **87**, 207-214.

PITZER K.S. (1973) Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **77**, 268-277.

PITZER K.S. (1981) Characteristics of very concentrated aqueous solutions. In *Chemistry and Geochemistry of Solutions of High Temperatures and Pressures*. Phys. and Chem. of the Earth. **13-14**, 249-272.

PLUMMER L.N., WIGLEY T.M. and PARKHURST D.L. (1978) The kinetics of calcite dissolution in CO_2 - water systems at 5 to 60°C and 0.0 to 1.0 atm CO_2. *Am. J. Sci.* **278**, 179-216.

PLUMMER L.N., PARKHURST D.L. and WIGLEY T.M. (1979) Critical review of the kinetics of calcite dissolution and precipitation. In *Chemical Modelling in Aqueous Systems* (ed. E.A. JENNE), pp. 537-573. Am. Chem. Soc. Symp. Ser. **93**.

PORTER J.W., PRICE R.A. and McCROSSAN R.G. (1982) The Western Canada Sedimentary Basin. *Roy. Soc. Phil. Trans.* **305**, 169-192.

PRICE R.A. (1973) Large scale gravitational flow of supra-crustal rocks, southern Canadian Rocky Mountains. In *Gravity and Tectonics* (eds. K.A. DEGONG and R.S. CHOLTEN), pp. 491-502. Wiley.

RIMSTIDT J.D. and BARNES H.L. (1980) The kinetics of silica-water reactions. *Geochim. Cosmochim. Acta* 44, 1683-1699.

SILVESTER K.S. and PITZER K.S. (1978) Thermodynamics of electrolytes. S. Enthalpy and the effect of temperature on the activity coefficients. *J. Soltn. Chem.* 7, 327-337.

STUMM W. and MORGAN J.J. (1981) *Aquatic chemistry, 2nd edition.* John Wiley & Sons.

TARDY Y. and GARRELS R.M. (1974) A method of estimating the Gibbs energies of formation of layer silicates. *Geochim. Cosmochim. Acta* 38, 1101-1116.

TARDY Y. and FRITZ B. (1981) An ideal solid solution model for calculating solubility of clay minerals. *Clay Mins.* 16, 361-373.

WIWCHAR B., PERKINS E.H. and GUNTER W.D. (1988) SOLMINEQ.88 PC/SHELL Manual.

WOLERY T.J. (1983) EQ3NR: A computer program for geochemical aqueous speciation-solubility calculations, user's guide and documentation, UCRL - 53414. Lawrence Livermore Lab., *Univ. Calif.*

WOLERY T.J., SHERWOOD D.J., JACKSON K.J., DELANEY J.M. and PUIGDOMENECH I. (1984) EQ3/6: Status and applications, UCRL-91884. Lawrence Livermore Lab., *Univ. Calif.*

Table 5.1. The minimum, maximum, mean and standard deviation values for the activities of silica, Na^+/H^+, $Ca^{+2}/(H^+)^2$, $Mg^{+2}/(H^+)^2$, and K^+/H^+. For each activity, a value is given for all of the groups combined, in addition to values for the individual groups, which are based on the ionic strength of the water samples from the Alberta Basin.

ACTIVITIES	GROUPS	MINIMUM	MAXIMUM	MEAN	STANDARD DEVIATION
SiO_2 (aq)	All	-3.71	-3.02	-3.25	0.14
	I	-3.34	-3.11	-3.22	0.09
	II	-3.44	-3.12	-3.28	0.10
	III	-3.71	-3.02	-3.27	0.24
Na^+/H^+	All	5.16	6.85	5.97	0.45
	I	5.16	6.16	5.63	0.32
	II	5.90	6.81	6.34	0.30
	III	5.80	6.85	6.18	0.37
$Ca^{+2}/(H^+)^2$	All	8.81	11.80	10.29	0.86
	I	8.81	10.79	9.72	0.66
	II	9.80	11.80	10.82	0.71
	III	9.84	11.75	10.74	0.71
$Mg^{+2}/(H^+)^2$	All	8.59	12.05	10.07	0.91
	I	8.59	10.53	9.47	0.62
	II	9.40	11.64	10.59	0.83
	III	9.61	12.05	10.60	0.84
K^+/H^+	All	3.35	4.40	3.91	0.30
	I	3.35	4.40	3.80	0.32
	II	3.86	4.38	4.13	0.17
	III	3.52	4.38	3.86	0.28

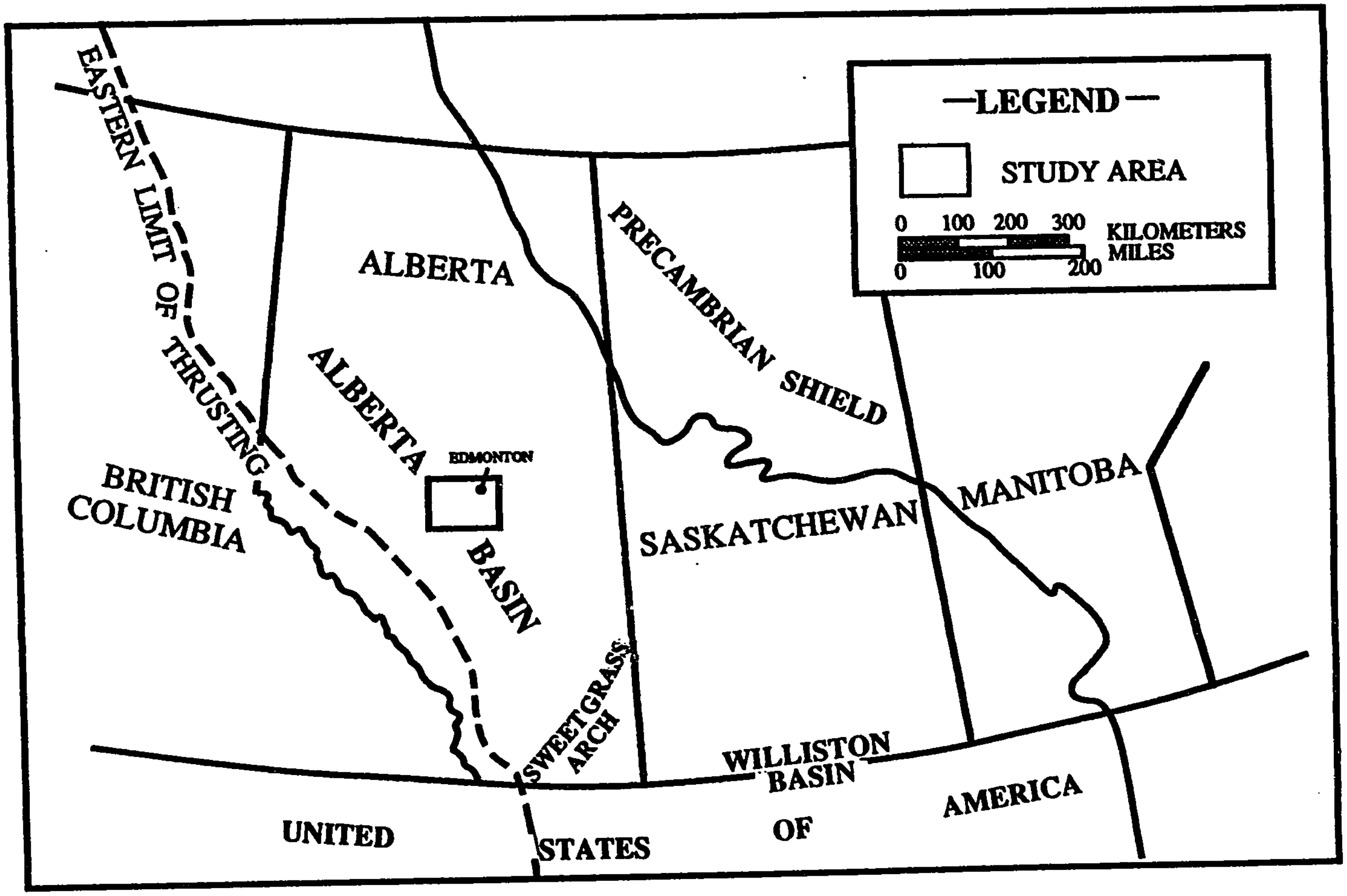


Fig.5.1. Map of the Western Canada Sedimentary Basin, showing the location of the sub basins and the study area.

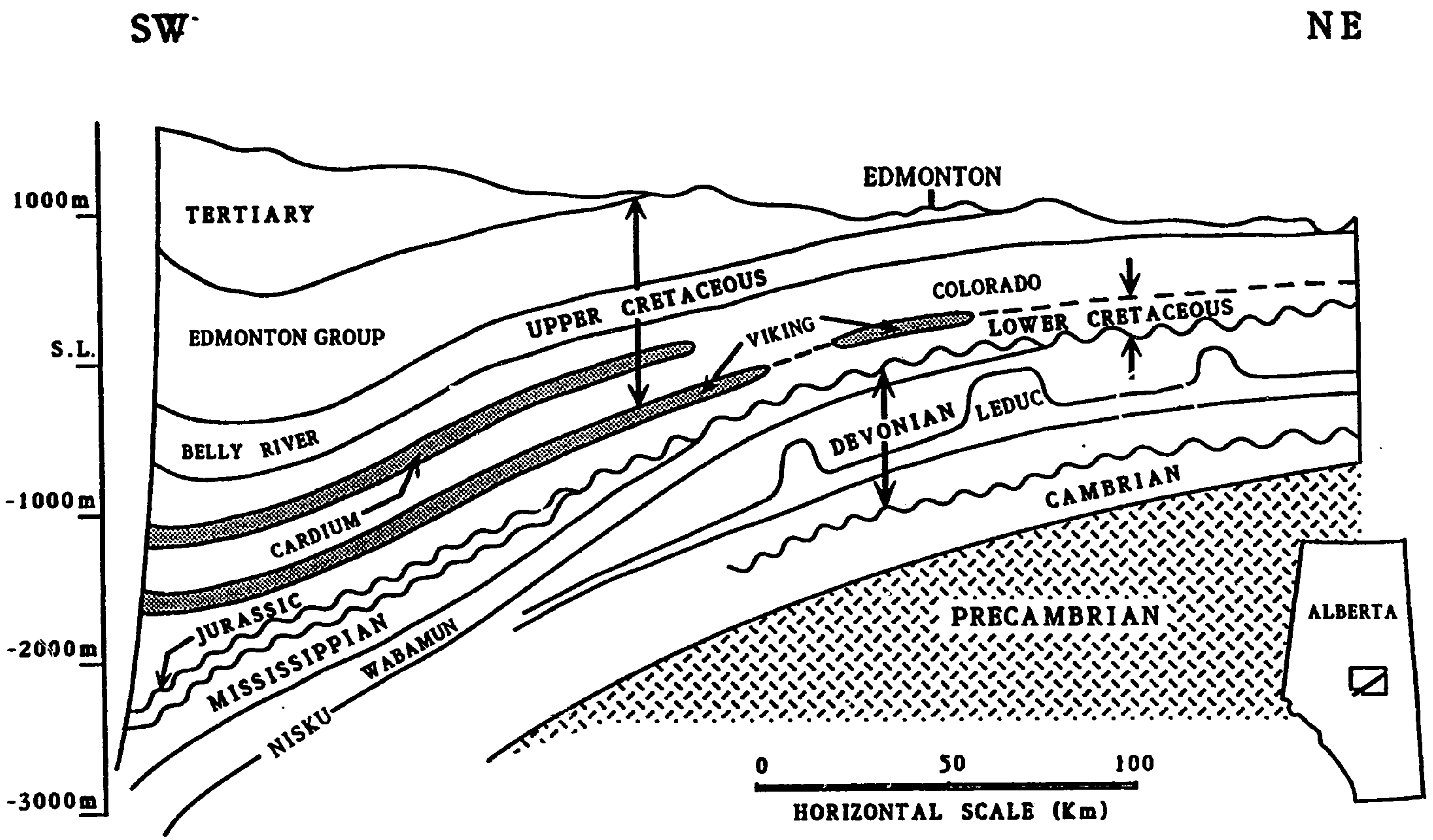


Fig. 5.2. Geological cross section from SW to NE through the Alberta Basin showing the major stratigraphic units and unconformities. Reference map identifies the location of the study area.

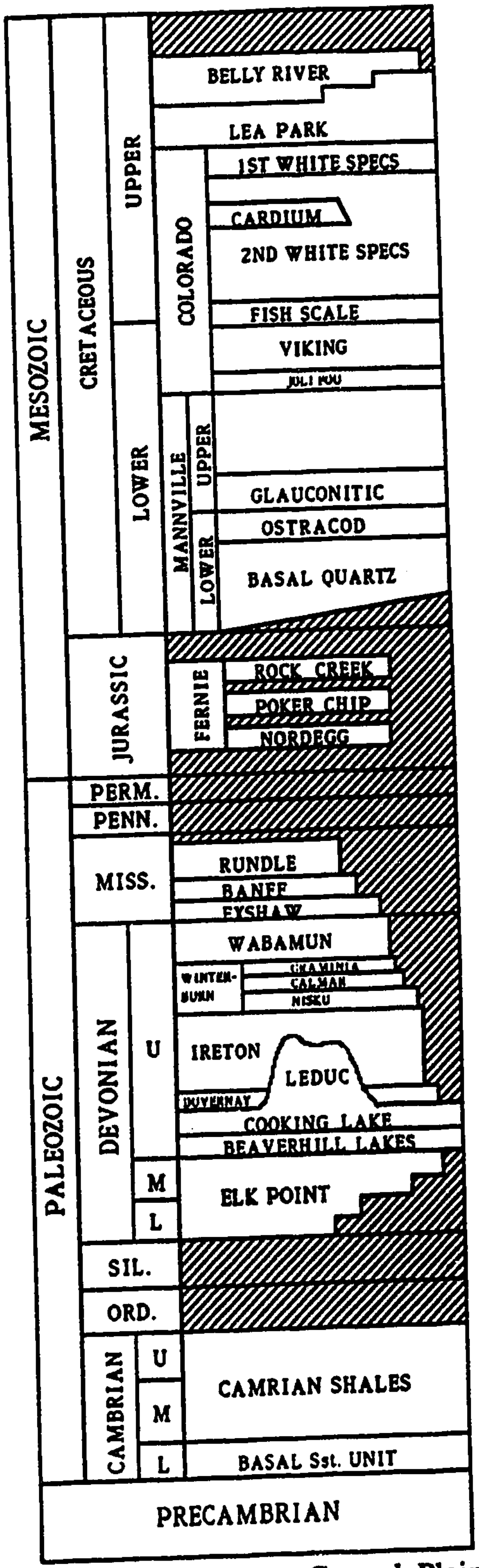


Fig. 5.3. Generalized stratigraphic column, Central Plains, Alberta, Alberta Basin (modified after *Energy Resources Conservation Board* Table of Formations).

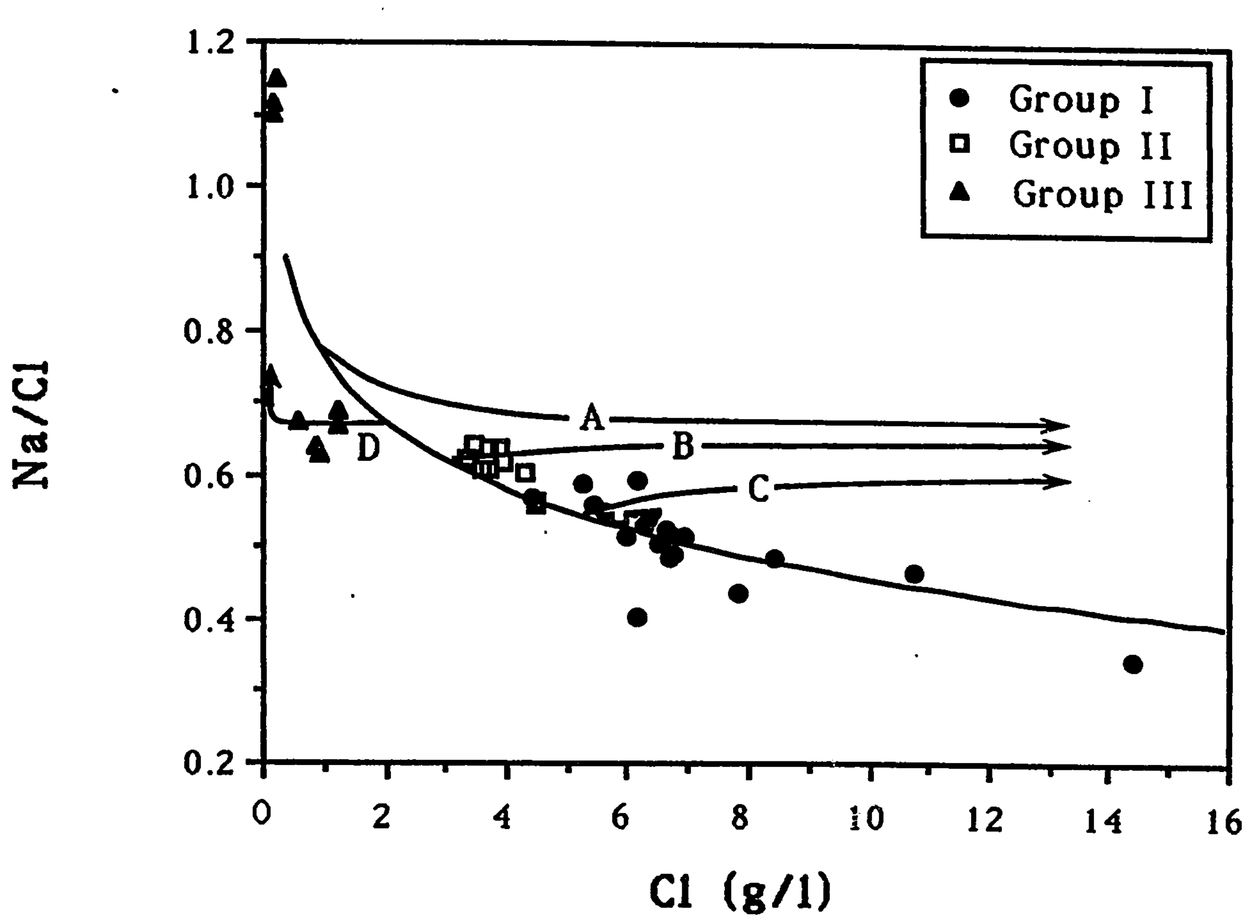


Fig. 5.4. (a) Plot of Na/Cl versus Cl ratios for Alberta Basin formation waters. Curves A, B, and C represent changes to Na/Cl ratios and Cl concentration upon dissolution of halite in waters of 10 g/l Cl, 20 g/l Cl, and 50 g/l Cl, respectively. Curve D represents the mixture of dilute meteoric groundwaters with formation waters of approximately 20 g/l Cl.

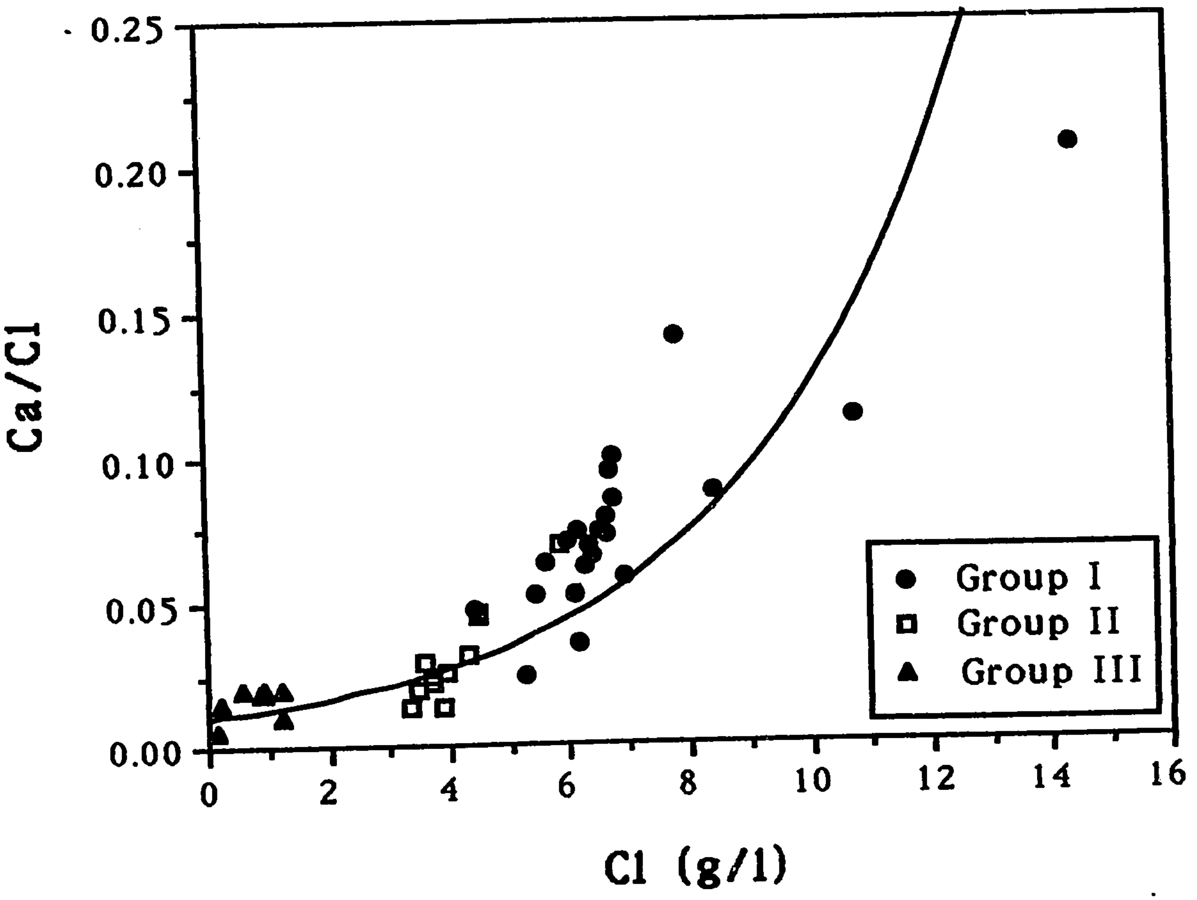


Fig. 5.4. (b) Plot of Ca/Cl versus Cl ratios for Alberta Basin formation waters.

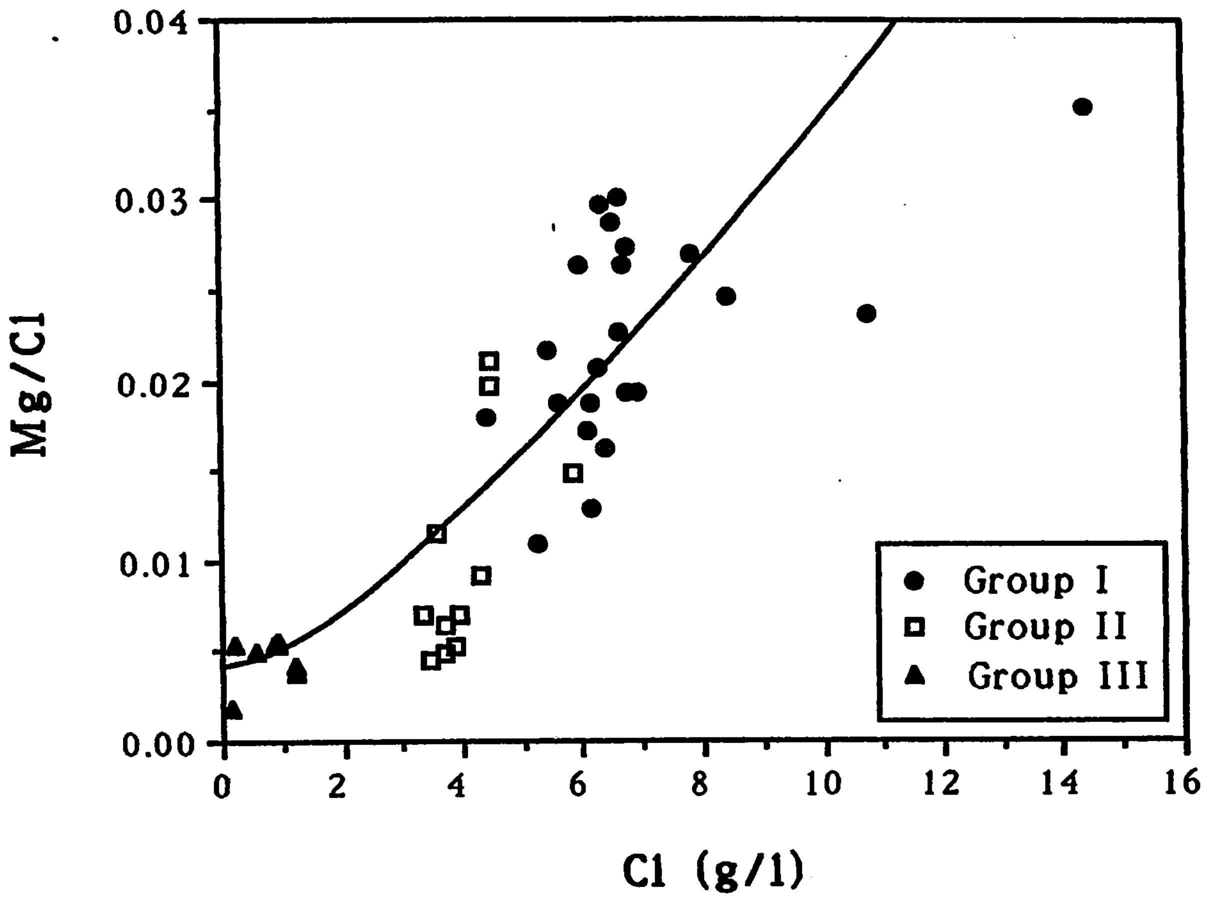


Fig. 5.4. (c) Plot of Mg/Cl versus Cl ratios for Alberta Basin formation waters.

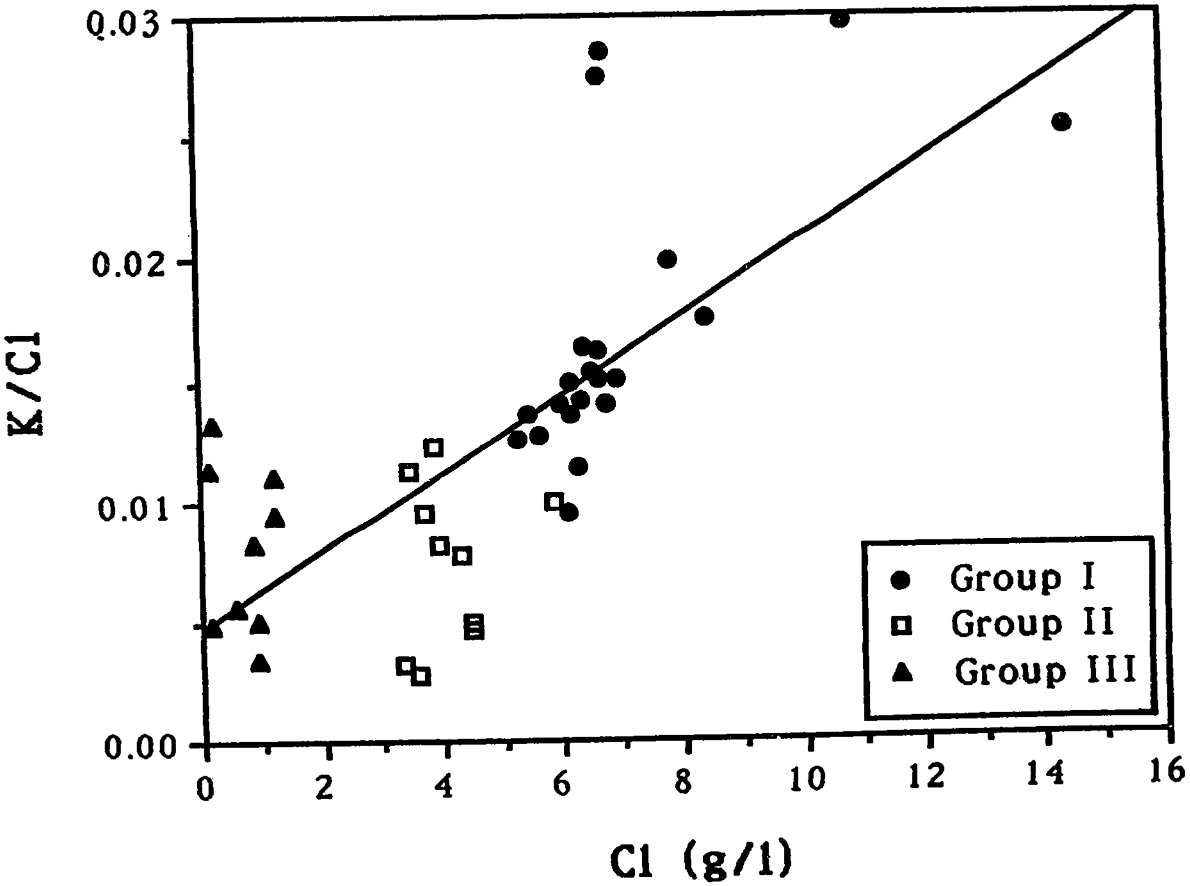


Fig. 5.4. (d) Plot of K/Cl versus Cl ratios for Alberta Basin formation waters.

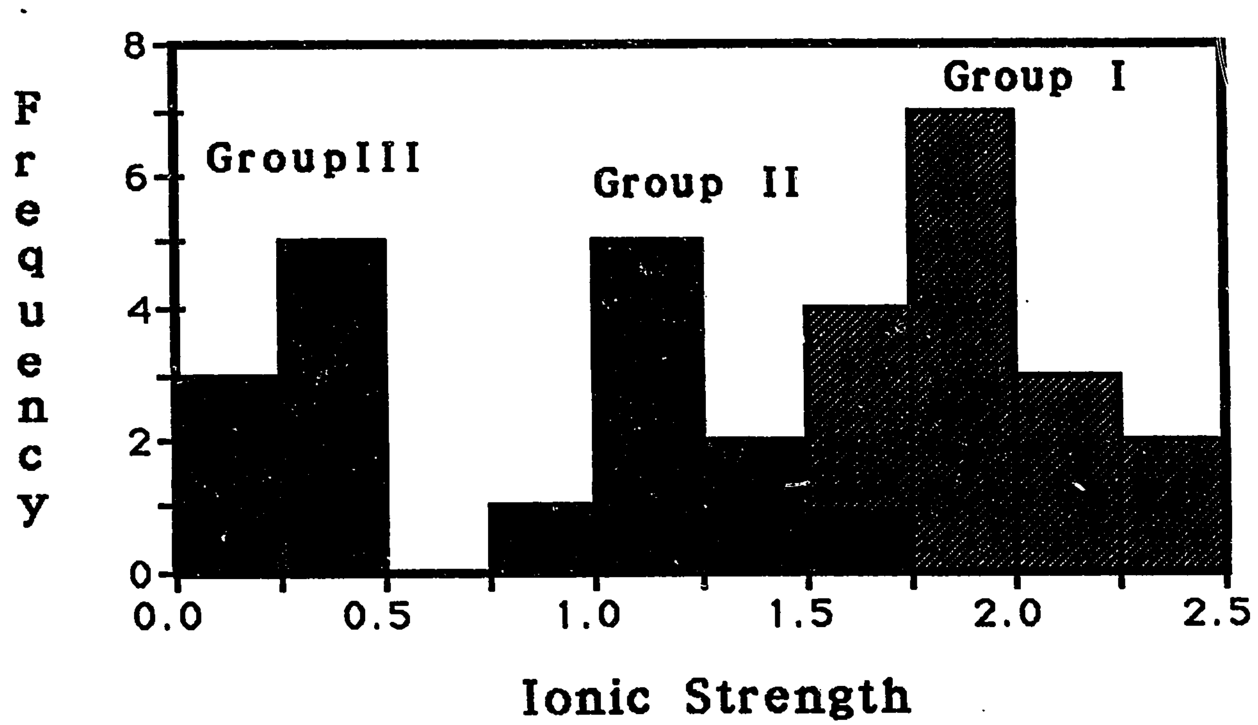


Fig. 5.5. Histogram of ionic strength values. Waters in the Alberta Basin show a distinct segregation into three separate groups.

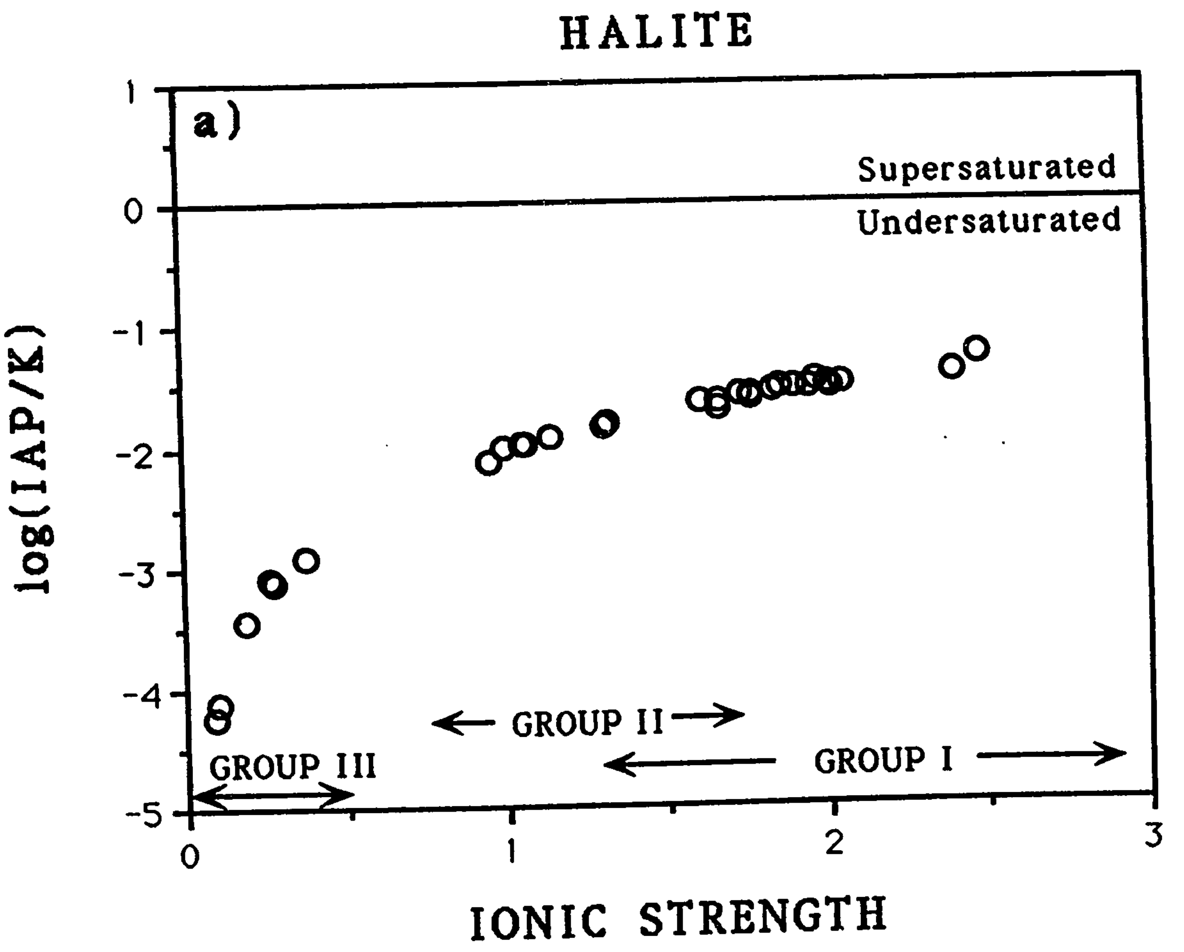


Fig. 5.6. Saturation index of various mineral species in the Alberta Basin versus the ionic strength of the solution. On all of the graphs the range in ionic strength of Group I, II, and III are shown. (a) Halite; note, one sample with an S.I. of -8.2 is missing from the graph in order to reduce the scale of the graph.

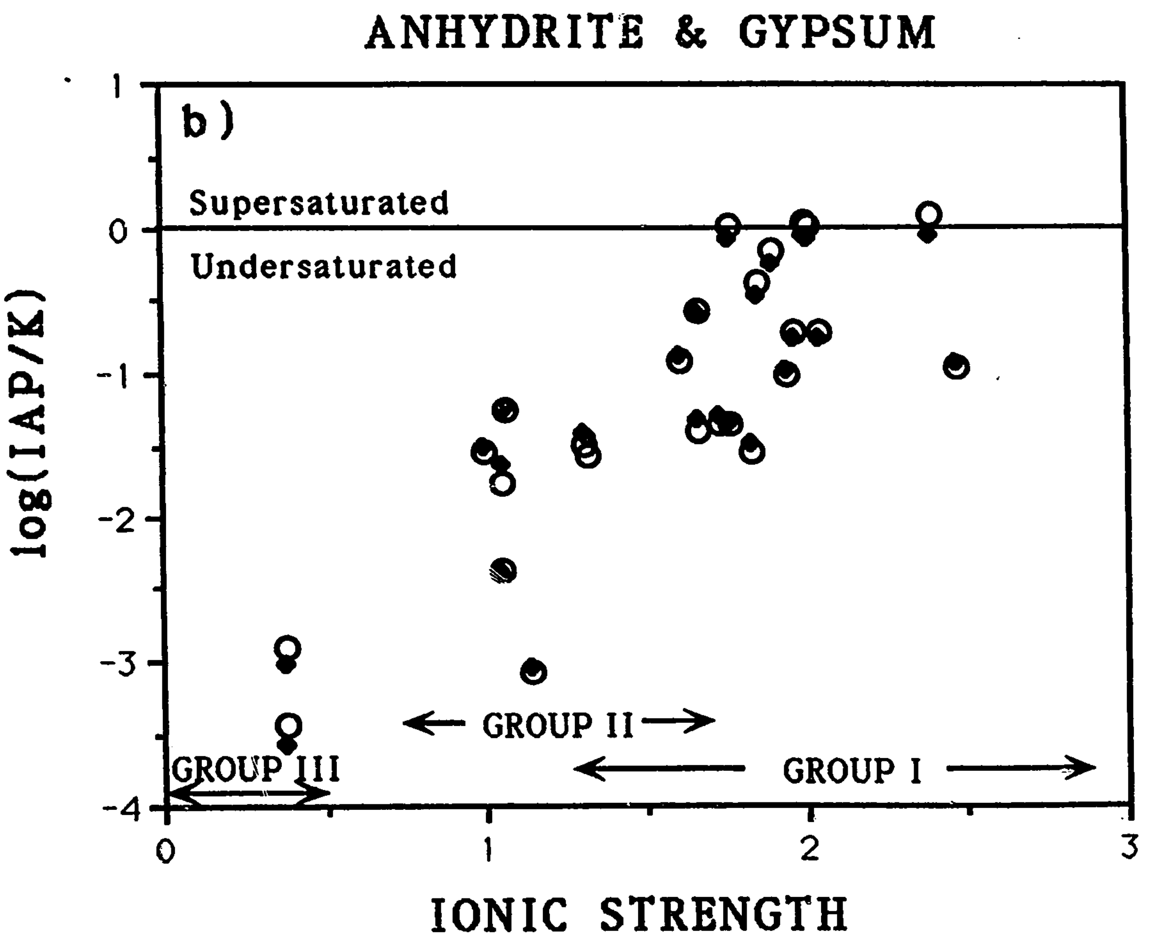


Fig. 5.6. (b) Anhydrite ○ and Gypsum (●).

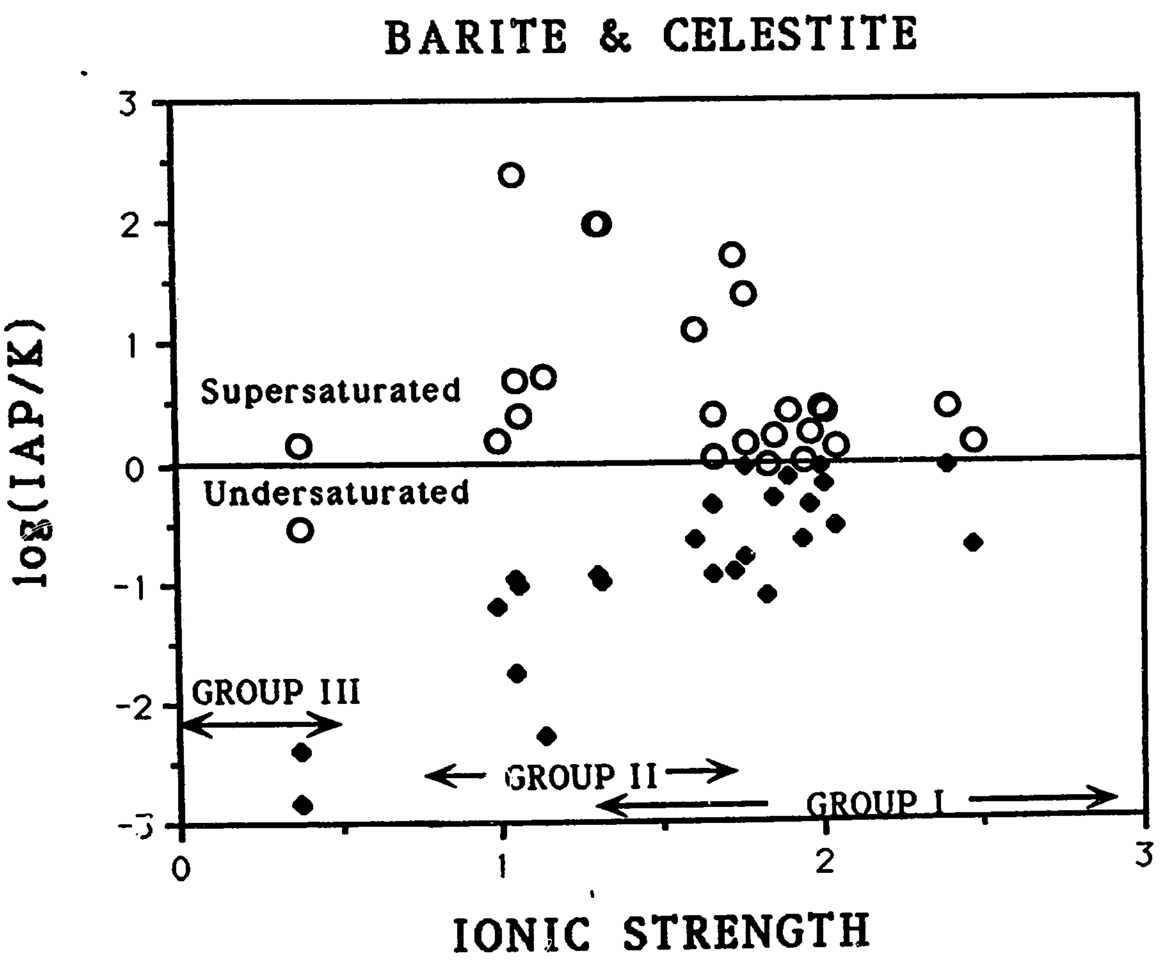


Fig. 5.6. (c) Celestite (●) and Barite ○.

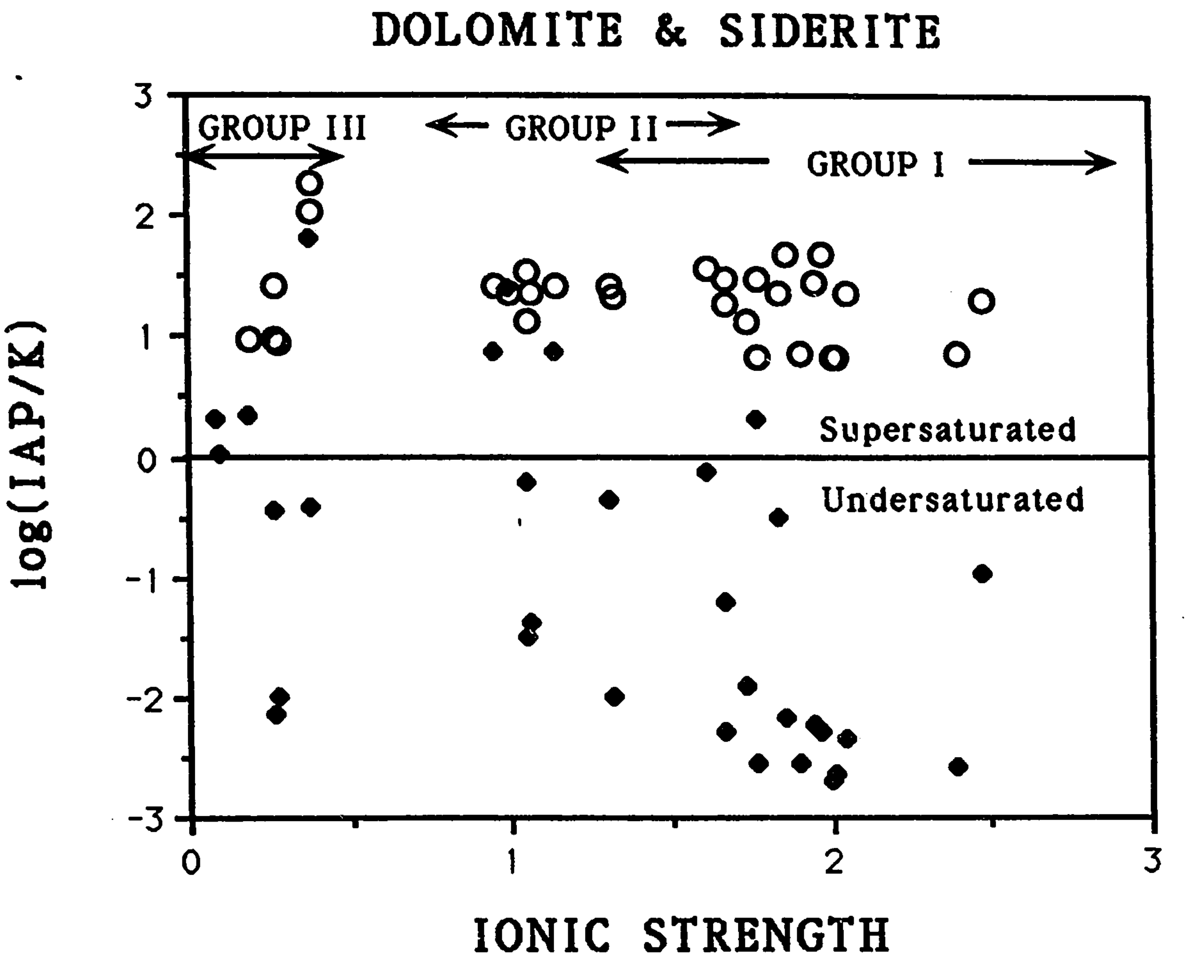


Fig. 5.6. (d) Carbonates; Dolomite ○ and Siderite (◆).

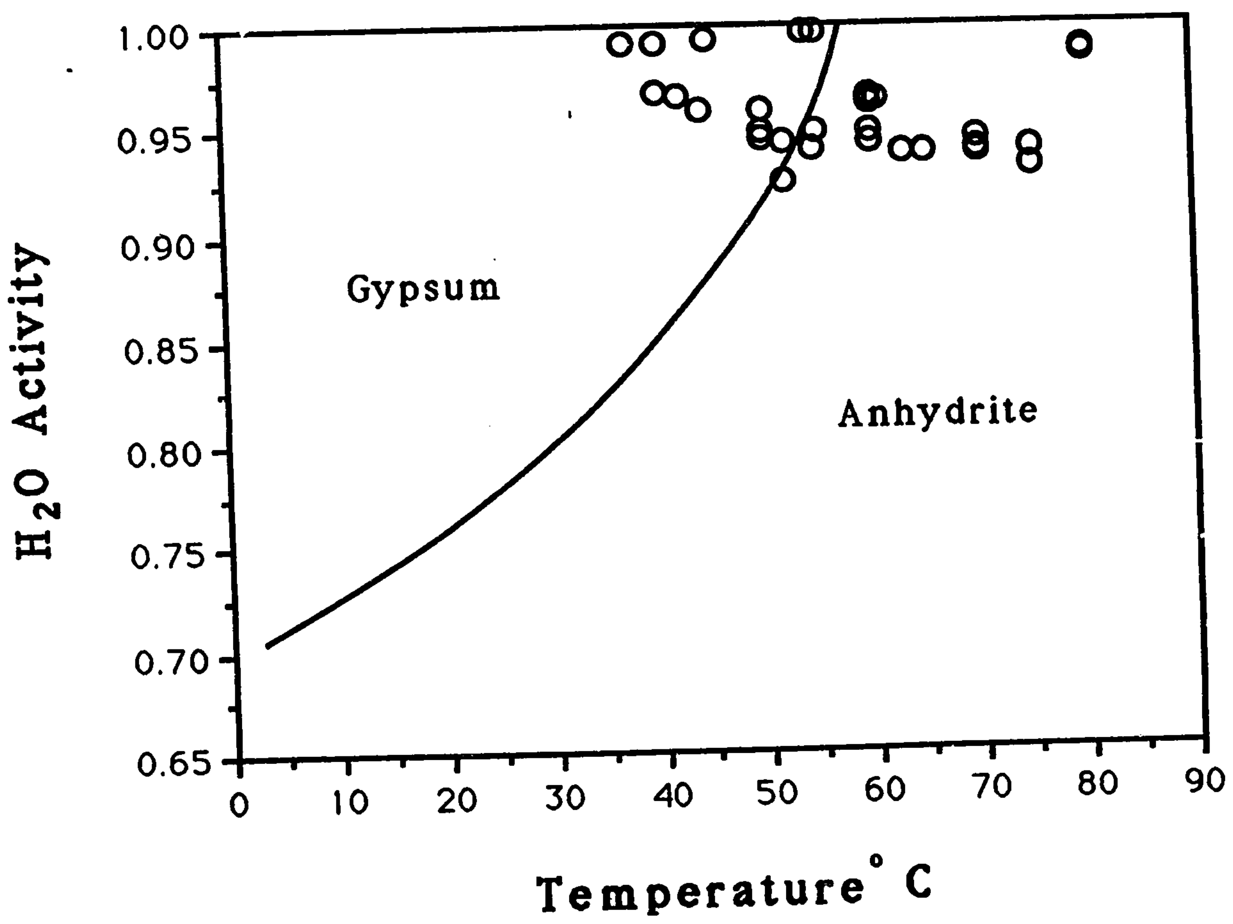


Fig. 5.7. Activity of water versus temperature (°C), illustrating the stability fields of gypsum and anhydrite (modified after HARDIE, 1967). Alberta Basin waters are plotted on the graph. If waters plot in the gypsum stability field, anhydrite is the more soluble phase and will dissolve upon contact with the water and vice versa.

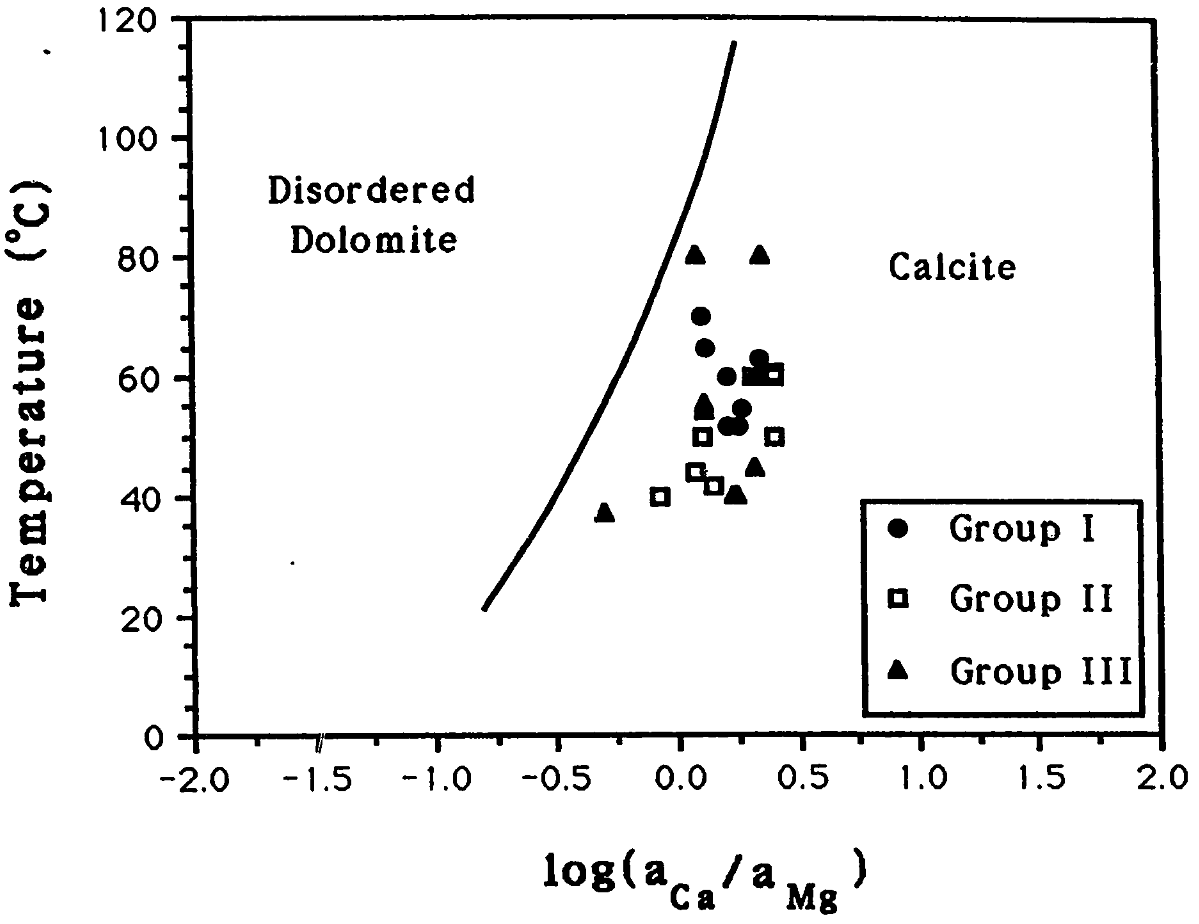


Fig. 5.8. Plot of temperature (°C) versus log a_{Ca}/a_{Mg} for Alberta Basin waters. The mineral phase boundaries were estimated using data from HELGESON *et al.* (1978).

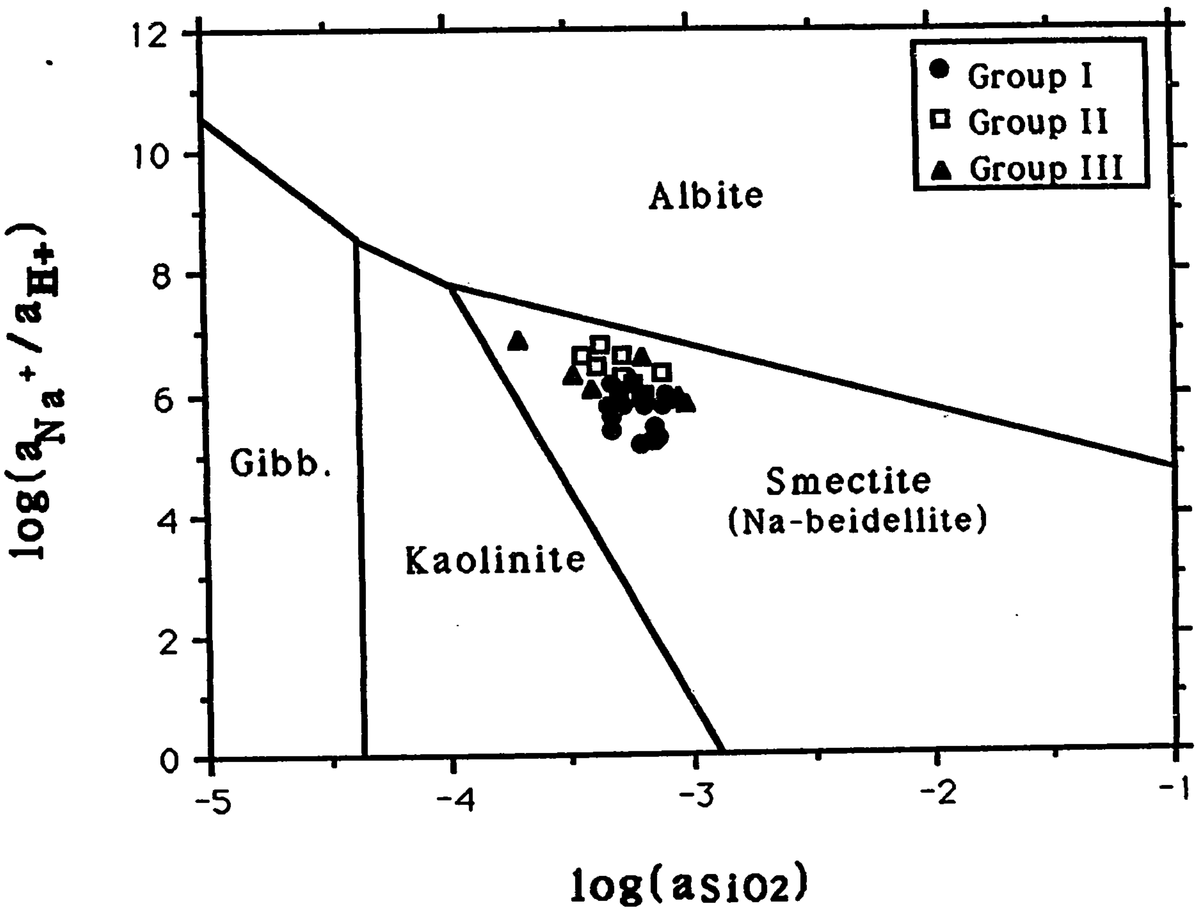


Fig. 5.9. Activity diagrams for some Alberta Basin waters. Phase boundaries were calculated at 100 bars pressure and 60°C, the average values for all the samples of Alberta Basin waters. Individual water samples were calculated at specific temperatures and pressures with the program SOLMINEQ.88 PC/SHELL. (a) log Na+/H+ activity ratios versus log silica activities at Na-beidellite activity of 0.1.

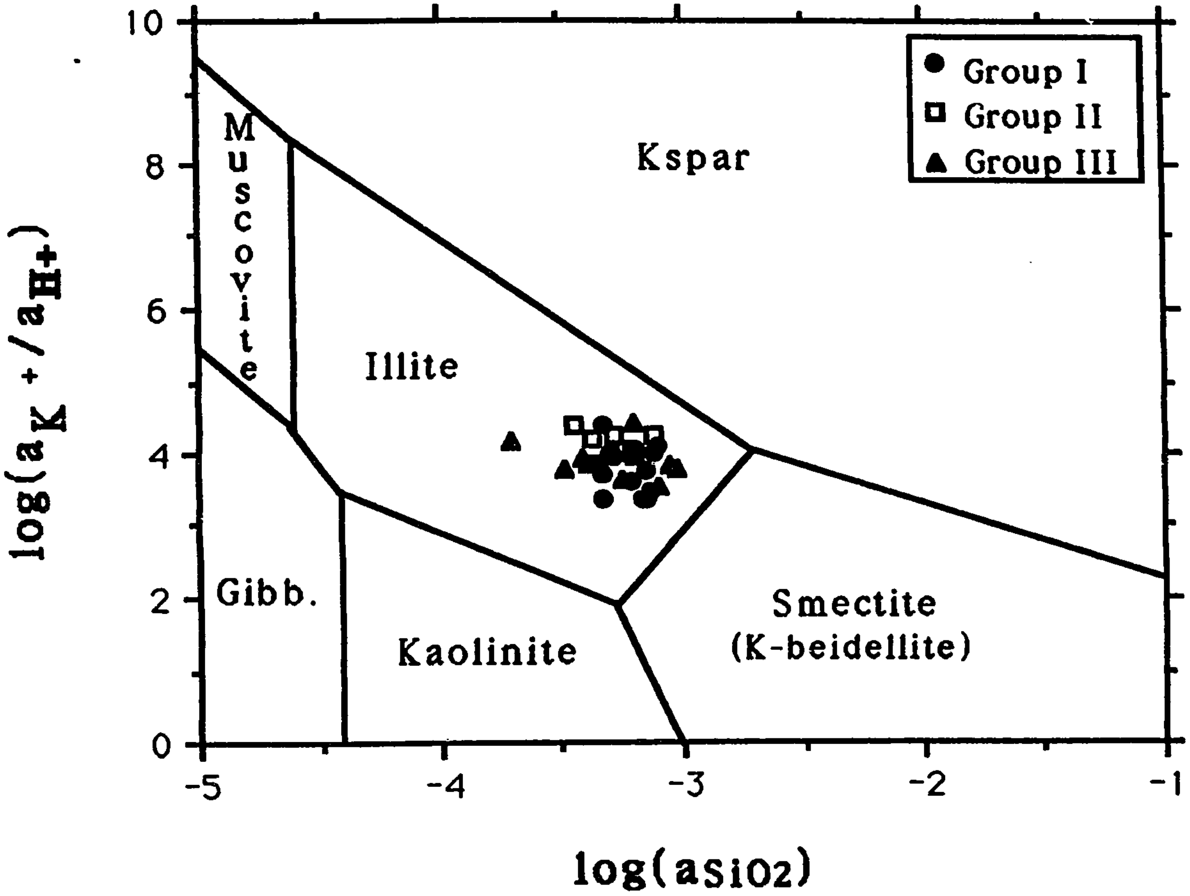


Fig. 5.9. (b) log K+/H+ activity ratios versus log silica activities at K-beidellite activity of 0.1.

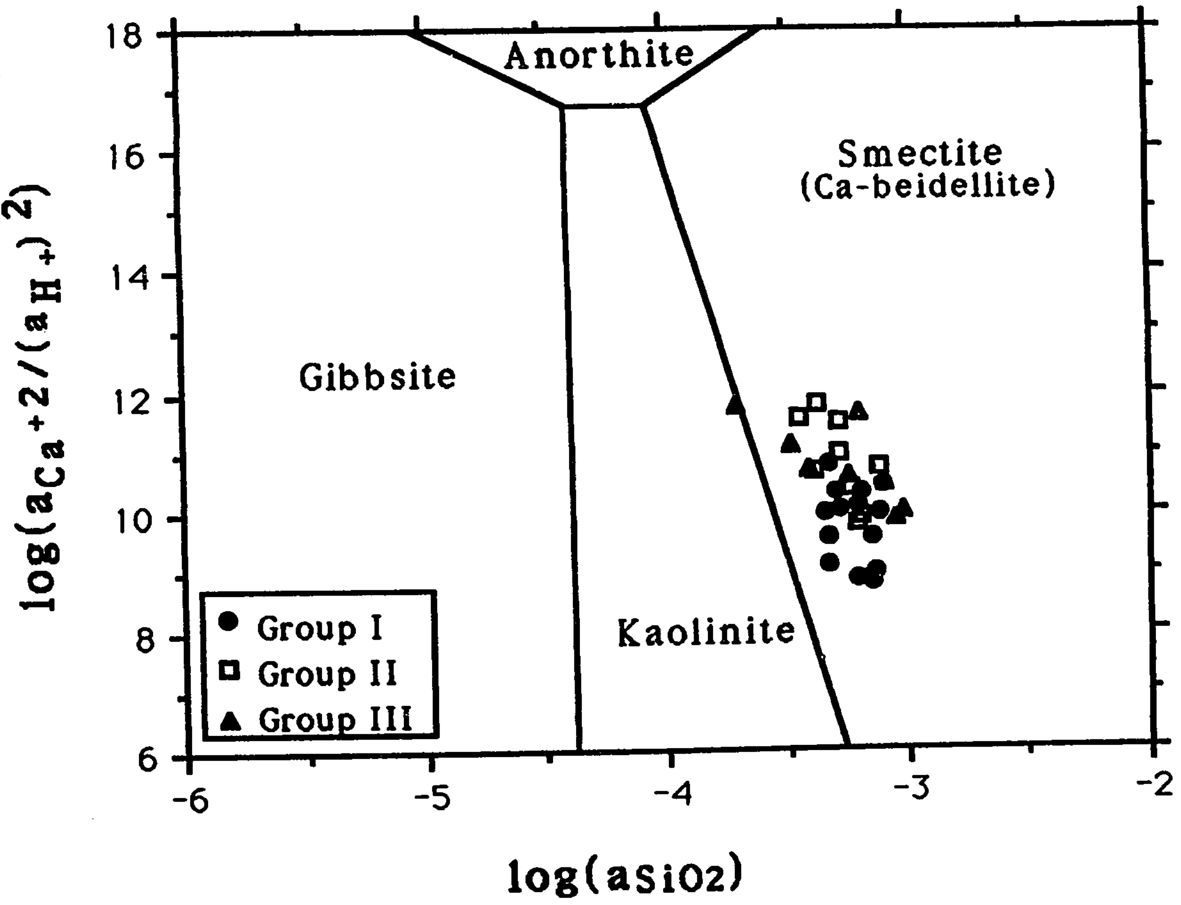


Fig. 5.9. (c) log $Ca^{+2}/(H^{+})^{2}$ activity ratios versus log silica activities at Ca-beidellite activity of 0.4.

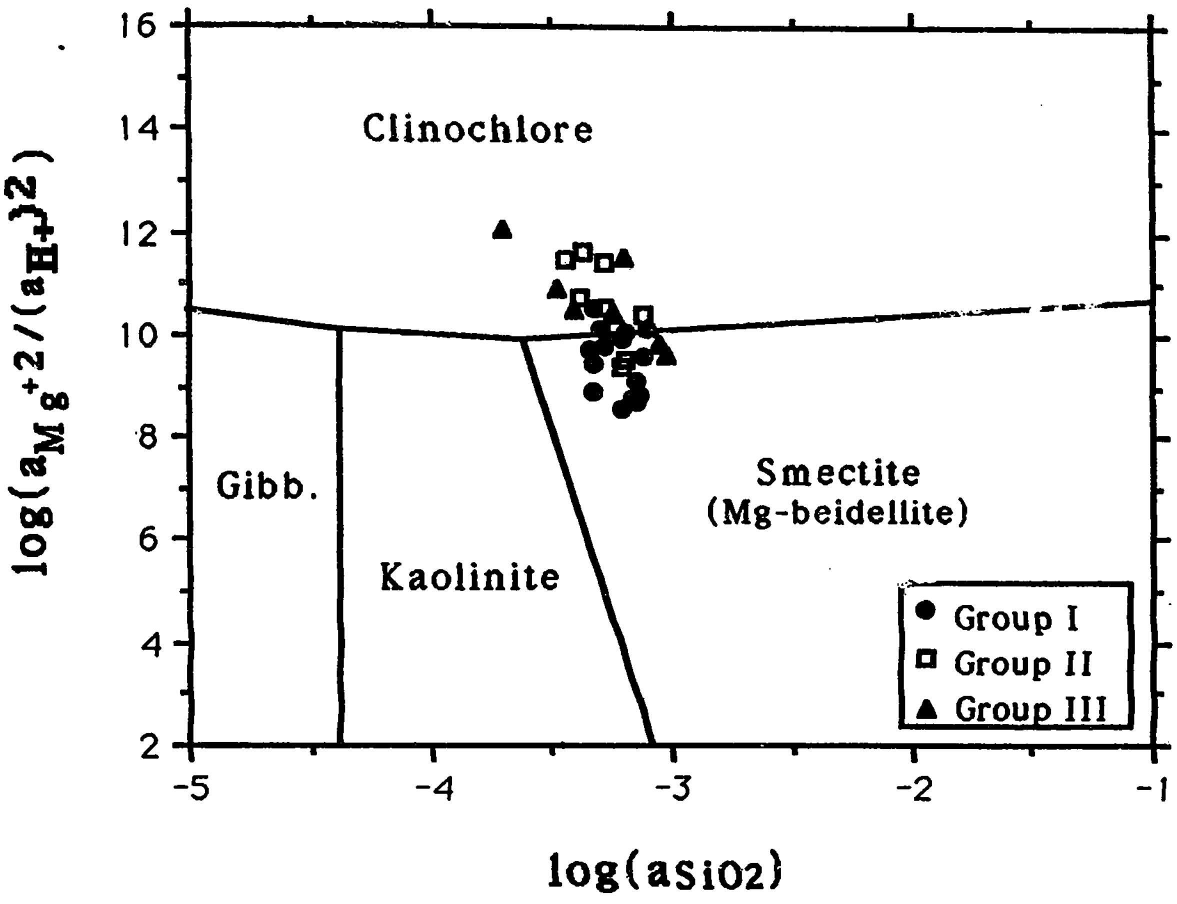


Fig. 5.9. (d) log $Mg^{+2}/(H^{+})^{2}$ activity ratios versus log silica activities at Mg-beidellite activity of 0.4.

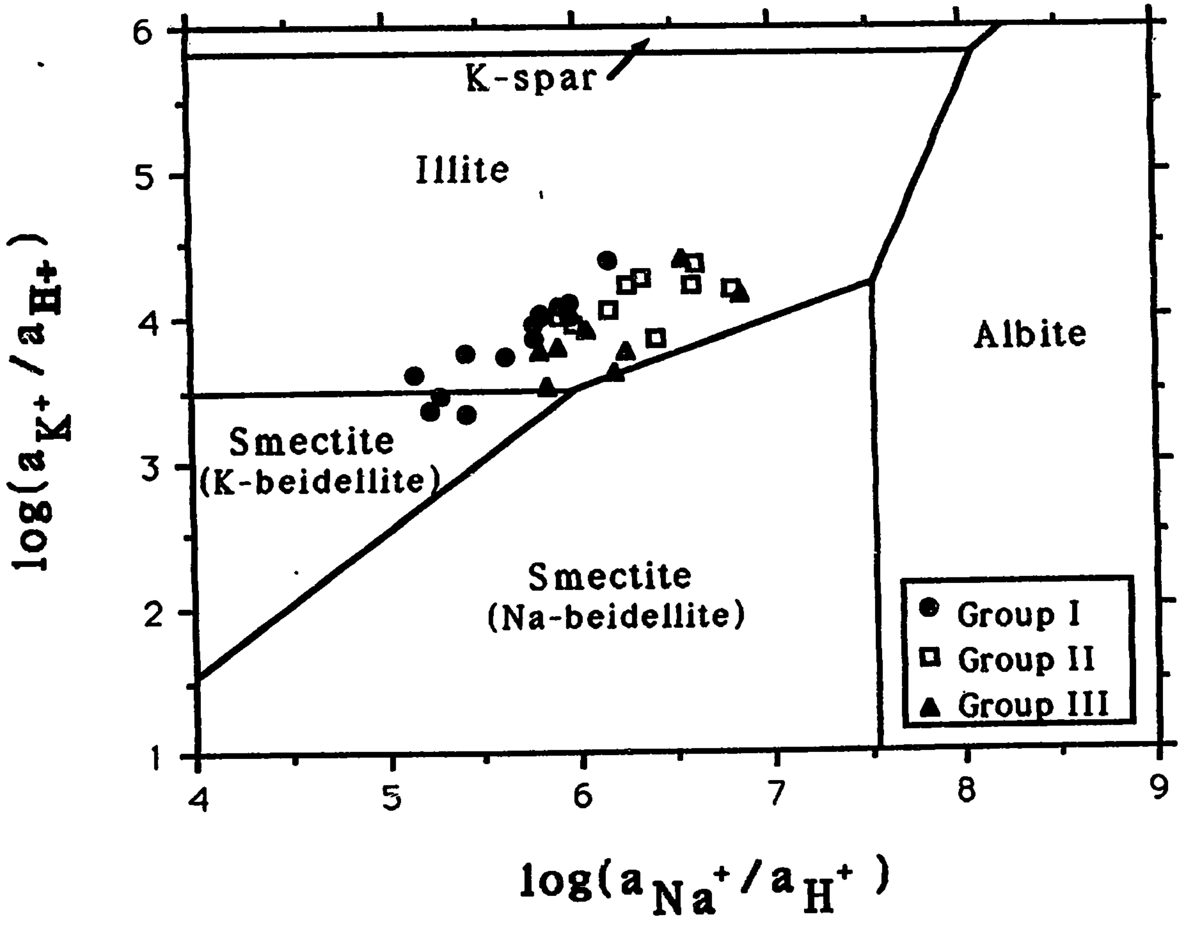


Fig.5.10. Activity diagrams for some Alberta Basin waters. Phase boundaries were calculated at 100 bars pressure and 60°C, the average values for all the samples of Alberta Basin waters. Individual water samples were calculated at specific temperatures and pressures with the program SOLMINEQ.88 PC/SHELL. (a) log Na^+/H^+ activity ratios versus log K^+/H^+ activity ratios; the activity of the Na-beidellite component is 0.05 and the activity of the K-beidellite component is 0.015.

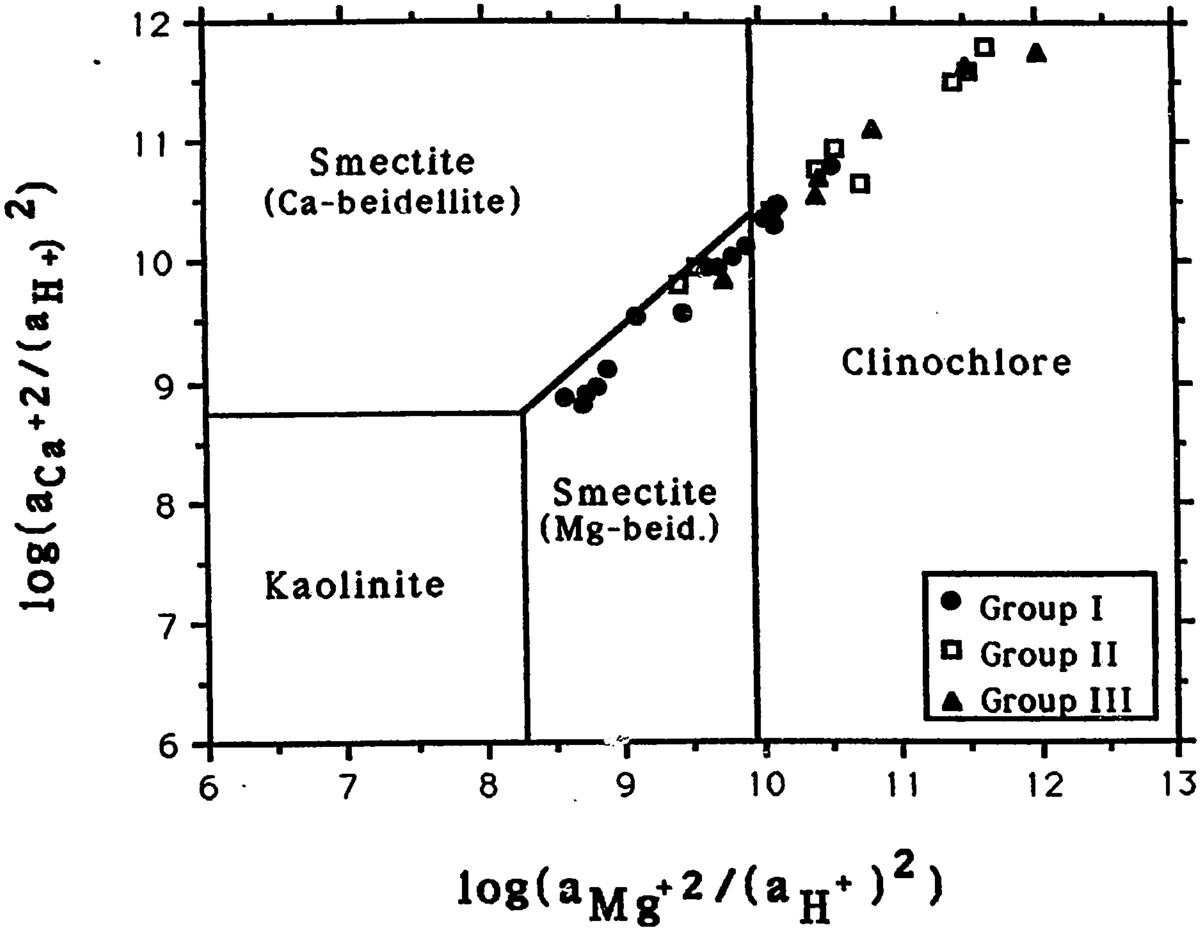


Fig. 5.10. (b) log $Mg^{+2}/(H^+)^2$ activity ratios versus $Ca^{+2}/(H^+)^2$ activity ratios; the activity of the Mg-beidellite component is 0.40 and the activity of the Ca-beidellite component is 0.40.

CHAPTER 6. STRONTIUM AND STABLE ISOTOPIC CHARACTERIZATION OF CLASTIC AND CARBONATE ROCKS IN THE ALBERTA BASIN, WESTERN CANADA SEDIMENTARY BASIN: DIAGENETIC AND DETRITAL PHASES

INTRODUCTION

The study of Rb/Sr systematics in sedimentary rocks helps constrain the diagenetic history of sedimentary units by: (1) providing a chronology of diagenetic events through dating of diagenetic phases; and (2) indicating elemental mass transfer and the source of diagenetic pore fluids, providing information on mixing relationships and cross-formational fluid dynamics.

Clay minerals are the most ubiquitous constituents of sedimentary rocks. These minerals are of major interest in Rb-Sr studies of sedimentary systems because they equilibrate with the porewater environment during neoformation and transformation and can subsequently remain as closed systems. Furthermore, clay minerals, particularly illite and glauconite, are enriched in Rb, resulting in a sufficient spread in Rb/Sr ratios for obtaining geologically valid isochrons. Such isochrons have been obtained for diagenetic illite (CLAUER, 1979, 1982; MORTON, 1985a), allowing inferences to be made regarding the scale of diagenesis and whether it was a gradual or episodic event (MORTON, 1985a). Because waters/solutions are the chief agents of mass transfer and chemical change during diagenesis and changes in porewater composition often result in alteration/precipitation of the mineral assemblage, dating the diagenetic component may provide constraints on porewater evolution. Moreover, the extent to which orogenic activity was influential to porewaters and resulting authigenic phases may be discerned. For example, foreland basins are generally dominated by gravity-driven flow of meteoric waters. The timing of this influx and the scale over which it was significant may be discriminated by dating the authigenic component of the formations.

The isotopic composition of Sr in carbonate and silicate cements from non-marine and marine sandstones can provide information about the source of Sr in aqueous solutions from which authigenic minerals precipitate during diagenesis. To be present in circulating fluids, Sr must be released from mineral constituents by processes such as dissolution (feldspars, carbonates), mineral alteration (albitization of plagioclase, recrystallization of smectite to illite) and ion exchange reactions (largely involving clay minerals). Diagenetic studies of mineralogical relationships through observations of progressive paragenesis/authigenesis in a sedimentary unit have been used to imply the occurrence of these reactions (HOWER *et al.*, 1976; BOLES and FRANK, 1979 LAND and MILLIKEN, 1981; BOLES, 1982; LAND, 1984). However, whether these reactions actually occur and the scale over which they are significant has only been hypothesized, not actually demonstrated using a geochemical tracer. Strontium provides an excellent geochemical tracer as it is not measurably mass fractionated during chemical reactions and its isotopic composition changes because of the radioactive decay of ^{87}Rb to ^{87}Sr; variable ^{87}Sr/^{86}Sr ratios occur due to diverse Rb contents in different minerals. This variability can result in authigenic phases with very different isotopic *signatures* depending on their source or precursor phases. Hence, if the paragenetic history has been determined and the diagenetic phases characterized isotopically (^{87}Sr/^{86}Sr), it is possible to define the evolution of basinal/formational porewaters and the scale to which the processes defining them are homogeneous.

. In this paper, diagenetic and detrital phases for clastic and carbonate formations from the Alberta Basin, Western Canada Sedimentary Basin were analyzed for radiogenic isotopes (^{87}Sr/^{86}Sr), stable isotopes (C and O), and elemental (Rb and Sr) concentrations. The primary goals are: (1) to date diagenetic clay minerals; (2) to establish water mixing and water-rock interaction processes by examining the diagenetic phases that crystallized from or were altered in these waters; (3) to determine the degree of open versus closed system behavior in the basin with respect to cross-formational fluid flow and water mixing; and, (4) to establish the sequence of diagenetic mineral formation and the scale over which it occurred, or the specific zones to which it has been restricted. Focus is placed on clay minerals, particularly illite, as they are prevalent and the only datable primary alkali silicates able to grow, equilibrate and stay in equilibrium during sedimentary processes. Combined with previously obtained data on the carbonate minerals (Chapter 2), whole rocks (Chapter 2) and formation fluids (Chapters 3, 4 and 5) in the Alberta Basin, water/rock interaction and fluid mixing processes are demonstrated.

GEOLOGIC BACKGROUND

The Alberta Basin is part of the Western Canada Sedimentary Basin and is bordered to the northeast by the Precambrian Shield, to the west by the Rocky Mountain Thrust Belt and to the southeast by the Sweetgrass Arch (Fig. 6.1). This study examines an assemblage of sedimentary rocks which form a vertical section from the Precambrian basement to Upper Cretaceous in the Alberta Basin. The basin is a foreland basin comprised of a wedge of essentially undeformed sedimentary rocks that dip and thicken towards the southwest, resting unconformably on the Precambrian basement (Fig. 6.2). The basin may be subdivided into three general lithologic units: (1) Cambrian shales overlying a basal Cambrian sandstone; (2) Jurassic and Paleozoic carbonates, shales and evaporites; and (3) Cretaceous clastic rocks composed of thick shale and siltstone units interbedded with thin sandstone lenses. Upper Mississippian, Pennsylvanian, Permian, Triassic, and most of the Jurassic have been eroded from the Central Plains of Alberta (Fig. 6.3).

Present day morphology of the Western Canada Sedimentary Basin was initiated during the Jurassic-Cretaceous period Toward the end of the Jurassic, subduction of the Pacific Plate beneath the western edge of the North American Plate occurred as a result of the Columbian Orogeny (PRICE, 1973; DICKINSON and SNYDER, 1978; BEAUMONT, 1981; JORDON, 1981). Shortening across the Columbian Orogen generated thrust sheets toward the east initiating the formation of the Rocky Mountains. Northeasterly and easterly movements progressed from Early Jurassic to mid-Lower Cretaceous, with deformation being confined to the core orogenic zone and western ranges. During the Late Cretaceous, slow epeirogenic uplift along the eastern Cordillera was initiated by the first pulse of the Laramide Orogeny (TAYLOR *et al.*, 1964; DICKINSON and SNYDER, 1978). Consequently, during the Paleocene a thick sequence of continental clastics were deposited in the Foothills and across Alberta causing maximum downwarping in the basin. In the Early Eocene, the second pulse of the Laramide Orogeny occurred creating a period of maximum subaerial relief and subsequent burial (PORTER *et al.*, 1982; HITCHON, 1984). Positive movement of the continental plate ensued, resulting in erosion and additional southwest tilting of the sedimentary column in the foreland basin. It has been estimated that approximately 1900 m of overburden in the western part of the Alberta Basin and 900 m in the east have been eroded since maximum burial (NURKOWSKI, 1984; BEAUMONT *et al.*, 1985; LONGSTAFFE, 1986).

During the 600 Ma history of the Western Canada Sedimentary Basin, the hydrodynamic regime has likely changed several times, locally and basin wide, in response to various tectonic movements. The current hydrodynamic regime in the Alberta Basin originated subsequent to the second orogenic pulse of the Laramide Orogeny. Associated overthrusting created a large hydraulic head in the eastern Foothills, creating a mechanism for deep penetration of cool, meteoric waters which discharged eastward (HITCHON, 1969a, 1984). It is doubtful that a hydraulic head greater than that generated by the present Canadian Cordillera ever existed prior to the Laramide Orogeny, (HITCHON and

FRIEDMAN, 1969). It has been suggested that the Upper Devonian - Carboniferous carbonate rocks of the Alberta Basin channel flow throughout the basin toward the northeast, and act as a low fluid potential drain for the basin (HITCHON, 1969b, 1984; DEROO *et al.*, 1977). Alternatively, GARVEN (1989) suggests that the regional flow system has undergone dissipation, at least since the Pliocene, with younger, shallower formations developing smaller flow sub-systems. This latter hypothesis is supported by the chemical and isotopic composition of the waters (CONNOLLY *et al.*, 1990a, 1990b).

Shifts in the geothermal gradient of the Alberta Basin, as a result of the second pulse of the Laramide Orogeny, have been postulated by HITCHON (1984) using the data of HACQUEBARD (1977). HITCHON (1984) suggests that during the Late Paleocene, the gradient decreased from ~30°C/km in the western Alberta plains to ~23°C/km in the east, but that this trend was reversed after the second pulse of the Laramide Orogeny. By the Eocene the geothermal gradient increased from ~21°C/km in the west to ~27°C/km in the east, a similar but subdued pattern to that which exists today. BEAUMONT *et al.* (1985), in their lithospheric flexure model, demonstrated that the paleogeothermal gradient has probably increased systematically northeastward from the Foothills at least since the early stages of the major Laramide Orogeny. However, their studies suggest that the gradients in the past were higher than those estimated by HITCHON (1984), and approximated those of present day (27°C/km in the Foothills to 40°C/km in the Edmonton area). The heat flow pattern has not changed since the Eocene (HITCHON, 1984; MAJOROWICZ *et al.*, 1985).

STRONTIUM IN SEDIMENTARY ROCKS

Sources of Strontium

The concentration and isotopic composition of Sr in pore fluids migrating through a sequence of basinal sediments is controlled by the mineral or rock particles with which the solution interacts (STANLEY and FAURE, 1979). The fraction of Sr in solution derived from a particular mineral is dependent upon the abundance of that mineral, its Sr concentration and its relative susceptibility to dissolution and chemical weathering. When present, carbonate minerals, volcanic ash and plagioclase are important sources of Sr. Microcline, mica, clay, apatite and ferromagnesian minerals are less important because of their lower Sr concentrations and/or greater resistance to weathering. Important sources of *radiogenic* Sr are those minerals which contain significant amounts of Rb, such as micas, K-feldspar, certain clays and some evaporite minerals.

Variations in $^{87}Sr/^{86}Sr$ determined for porewaters and diagenetic minerals indicate variations in Sr sources to interstitial waters, because Sr does not fractionate isotopically under conditions prevailing in the crust. Low, unradiogenic Sr isotope ratios are generally associated with rocks of low Rb contents, but may also occur in relatively young, high-Rb rocks and minerals. Higher radiogenic isotope ratios are characteristic of older rocks and/or those with high Rb contents. Calcium carbonate and plagioclase have very low Rb/Sr ratios but high Sr concentrations; therefore, they contribute substantial amounts of Sr with low and time-invariant $^{87}Sr/^{86}Sr$ ratios. The contribution of radiogenic Sr from volcanic ash is extremely variable, depending on whether it is of basaltic (low Rb/Sr) or felsic (high Rb/Sr) composition. Apatite and ferromagnesian minerals are generally not abundant in sedimentary systems and have low Rb/Sr ratios and low Sr concentrations respectively, resulting in the release of Sr with relatively low $^{87}Sr/^{86}Sr$ ratios. Microcline and mica are potential sources of very radiogenic ^{87}Sr, but because these phases are resistant to chemical weathering, with the exception of biotite, and generally have low Sr concentrations, their contribution of radiogenic Sr to porewaters is variable depending on the physical/chemical conditions (temperature, acid versus basic porewaters *etc.*) in the sedimentary unit. Detrital clay minerals contribute Sr predominantly through cation exchange, but alteration of the phases can result in the release of Sr from the structure. Illite and smectite derived from weathering of older Rb-bearing rocks may contain mobile radiogenic ^{87}Sr; conversely, the exchangeable ^{87}Sr may be unradiogenic, common Sr.

Isotopic Dating of Clays

Isotopic dating of sediments has been attempted using two separate methods: (1) the whole rock method (COMPSTON and PIDGEON, 1962; HART and TILTON, 1966; OBRADOVICH and PETERMAN, 1968; BOFINGER *et al.*, 1968, 1970); and, (2) the separated fine fraction method (BONHOMME *et al.*, 1965; BONHOMME *et al.*, 1968; BONHOMME and CLAUER, 1972; CLAUER and BONHOMME, 1974; CLAUER *et al.*, 1975; CLAUER, 1981). The dates determined from the whole rock method are difficult to interpret because isotopic homogeneity and closure of the system to loss or gain of Rb and Sr cannot be inferred. Isotopic homogeneity is not necessarily associated with the time of deposition and the initial isotopic heterogeneity inherited at the time of deposition may be enhanced or diminished by later diagenesis, structural deformation, recrystallization during incipient metamorphism or a combination of these.

The separated fine fraction (<2 μm) method relies on more specific criteria than the whole rock method and can be applied to date and hence identify source rocks (i.e., provenance) or individual events (i.e., diagenesis). During diagenesis or metamorphism, isotopic exchange and equilibration of mineral Sr with porewater may occur. Detrital and diagenetic minerals of sedimentary rocks are commonly concentrated in different size fractions, with the diagenetic component in the finer (<2 μm) clay material. It is this fine fraction of pelitic rocks that may be used to date diagenetic occurrences (HOFMANN *et al.*, 1974; MORTON, 1985a, 1985b). The preferred phases for dating in sediments are clay minerals, in particular illite, because they are the most common diagenetic constituents of sedimentary rocks, they are readily crystallized in equilibrium with the environment and they subsequently remain as closed systems after formation. Other clay minerals, including the chlorite, kaolinite, smectite and mixed-layer groups, are not enriched in Rb and are not as readily dated. GAUDETTE *et al.* (1966) considered illite to have a coherent core surrounded by an incoherent shield which serves as a locus for sorption and cation exchange. Precipitation of illite commences with the formation of fundamental particles (NADEAU and BAIN, 1986) or nuclei, which grow larger by accreting additional K and aluminosilicate layers. Therefore, when diagenetic illite forms over an extended period, the finest fraction (<0.2 μm) should contain the highest proportion of fundamental particles. This fine fraction would most reliably yield the age of formation of the illite, rather than a larger fraction whose age reflects the average effects of accretionary processes over time.

Providing mineralogical, sedimentalogical and chemical criteria formulated in relation to requirements of Rb/Sr geochronology (CLAUER, 1981, 1982) are consistently applied, geologically significant Rb-Sr data are more readily obtained from illitic clays. These criteria provide a means of identifying the clay phases in the sediment, determining the origin and genesis of the clay (detrital or authigenic), and establishing the origin and isotopic composition of Sr from different phases. Unfortunately, the most careful sample selection and preparation cannot remove fundamental uncertainties from Rb/Sr dating of sedimentary rocks, such as whether isotopic homogeneity was attained at closure, possible modification of the clay mineral, and analytical uncertainties.

When interpreting Rb-Sr data in sedimentary systems, it is important to realize the difference between diagenesis and regional metamorphism, a distinction often not made when studying sedimentary rocks (MORTON, 1983). The term diagenesis signifies any chemical and/or mineralogical change that occurs in a sediment after burial up to the onset of metamorphism. The transition from diagenesis to metamorphism is gradational, but is arbitrarily set at a temperature of 200°C. During metamorphism, heat is the chief agent of chemical change, the water/rock ratio is very small and in most instances recrystallization is isochemical; whole rock samples remain chemically isolated (MORTON, 1983; FAURE, 1986). Because of migrating solutions, diagenesis works in the opposite sense. Waters are the chief agents of chemical change in an environment where the water/rock ratio may be substantial. Diagenesis may be highly selective, promoting isotopic exchange and homogenization among particles that are spatially distant from one another, while neighboring but mineralogically different particles in the same sample may fail to exchange.

ANALYTICAL PROCEDURES

Fifty-two conventional core samples from Precambrian through Upper Cretaceous formations were studied (Fig. 6.3). All samples were prewashed with distilled water to remove excess drilling fluid. Standard petrographic thin sections of core samples were prepared after impregnating the samples with blue-dyed epoxy. Calcite was stained according to the method of DICKSON (1965). Final core sample selection was based on a petrographic and XRD study. Both detrital and diagenetic minerals were examined using optical petrography, X-ray diffraction (XRD), scanning electron microscopy (SEM), stable (O and C) isotope and radiogenic (Rb/Sr) isotope analyses.

Mineral/Size Separation

Core samples were disaggregated by gentle crushing and ultrasonication using a high frequency probe. Care was taken to avoid grinding of samples to minimize the introduction of clay-size feldspar and quartz. Clay mineral suspensions were washed into individual settling columns, dispersed in distilled water and allowed to settle for the appropriate period of time required to obtain a <2 μm size fraction. This procedure was repeated at least three times to ensure effective separation of clay minerals; however, if the sample contained a high percentage of clay, the procedure was repeated until the supernatant liquid was relatively clear. The mineralogical content of the <2 μm size fraction was determined by XRD using oriented sample mounts (glass slides) and a Rigaku X-ray diffractometer with Co-Kα radiation (30kV, 25mA).

The clay size fraction was further divided into 2.0 - 0.5 μm; 0.5-0.2 μm; 0.2-0.1 μm; and, <0.1 μm size fractions by conventional slow-speed centrifugation using spin times calculated for the settling of spherical particles (JACKSON, 1979). The centrifuge times were maximized, within reasonable time limits (approximately one hour), to minimize errors associated with acceleration and deceleration (CONNOLLY, 1985). The procedure was repeated a minimum of 5 times per size fraction to ensure effective separation.

The >5μm size fraction was separated into the following size fractions: 5-30 μm; 30 - 125 μm; and 125 - 250 μm using a combination of sonication and sieving techniques in an attempt to concentrate specific minerals (feldpar, kaolinite). The mineralogy of each size fraction was determined by XRD using randomly oriented samples.

Authigenic Minerals

Authigenic minerals are concentrated in the finest size fraction. Following standard chemical procedures for removal of organic matter (JACKSON, 1979) and subsequent thorough washing with distilled water using a high speed centrifuge, illite, chlorite and occasionally illite/smectite (I/S) were concentrated in the <0.2 μm size fraction. Use of a <0.2 μm size fraction removed contaminating phases, such as carbonate, feldspar, quartz and detrital clay phases (because of their larger sizes), so further chemical treatments to remove these phases were not required. Other studies have shown, using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), that the clay minerals in the <0.2 μm size fraction are almost entirely of authigenic origin (NADEAU and BAIN, 1986; AYALON and LONGSTAFFE, 1988; GLASMANN *et al.*, 1989).

Scanning electon microscopy was used on selected samples in this study and corroborates these observations. Detrital micas and chlorite observed in these samples occur in larger flakes, usually much greater than 2 μm.

Chlorite was separated chemically, usually from the <0.2 μm fraction; however, in samples where chlorite was less abundant, a larger range in size had to be used. Separation was accomplished by digesting the sample in dilute two times vapour distilled HCl (0.6 N) at 80°C for one hour. Leaching was followed by boiling the residue in a 3 percent Na_2CO_3 solution for ten minutes to remove silica associated with the decomposition of chlorite. This illitic residue was then thoroughly washed with distilled water. All samples were examined by XRD after the acid treatment/chlorite removal and were observed to be composed entirely of illite, or occasionally I/S. No appreciable affect on the oxygen isotope composition of the residual material (authigenic illite or I/S) results from this treatment (LONGSTAFFE, 1986).

Illite crystallinity indices were determined for all the <0.1 μm illites by: (1) measuring the peak width at half maximum of the diffraction peak corresponding to the plane (001) of the illite in an oriented clay smear; (2) converting CoKα values to CuKα values; and, (3) comparing these values to known standards (Fig. 6.4; KUBLER, 1966; THOREZ, 1976). These values are used to distinguish high temperature, well crystallized 2M illite polymorphs from the low temperature diagenetic 1M and 1Md polymorphs. All of the samples had indices >8, well above the defined minimum of 5.5 (KUBLER, 1966; THOREZ, 1976) for diagenetic illite. All of the <0.1μm illites in this study are interpreted as being diagenetic. The Devonian illites were the most crystalline, with illite crystallinity indices of 8, and these too were confirmed to be diagenetic by SEM analysis (Fig. 6.5).

Diagenetic kaolin group minerals were not isolated. However, they are not active participants in Rb-Sr systematics (unpub. data). In a manner similar to quartz, kaolinite is a very pure phase and does not readily exchange or incorporate Rb or Sr.

Apatite and Feldspars

When present, apatite always occurred with calcite and quartz. Calcite was removed by leaching with dilute acetic acid (1:10); the resulting quartz/apatite phases were isolated from one another using the heavy liquid tetrabromoethane.

For feldspar-containing samples, the clay component was first removed and then the feldspar phases were isolated using heavy liquids. Because of the small grain size of these samples, hand-picking was not a viable alternative to heavy liquids. Aqueous sodium polytungstate ($3Na_2WO_4.9WO_3.H_2O$) was used in preference to the halogenated hydrocarbons because specific densities could be achieved and easily maintained for individual samples. The densities of plagioclase feldspar and quartz commonly overlapped completely and isolation of these phases was not achieved. However, K-feldspar was separated from some samples.

The purity of apatite and feldspar fractions was confirmed by XRD analysis.

Stable Isotope Analyses

The oxygen and carbon isotope data are presented in the usual δ notation relative to Standard Mean Ocean Water (SMOW) for oxygen (CRAIG, 1961) and the *Belemnitella americana* from the Peedee Formation (PDB) for carbon (CRAIG, 1957). To calculate the oxygen isotope results for calcite and dolomite, 1.01025 and 1.01110 were used, respectively, for the total carbonate CO_2 fractionation factor (α) at 25 °C (modified after SHARMA and CLAYTON, 1965). The calcite α was used in all calculations for siderite; the dolomite α was used in all calculations for ankerite. An oxygen isotope, CO_2-H_2O

fractionation factor of 1.0412 at 25°C has been employed in these calculations.

Stable isotope analyses of carbonate minerals were obtained by reacting organic-free powdered rock samples (<44 µm) in anhydrous H_3PO_4 at 25°C, following procedures described by WALTERS *et al.* (1972), modified after McCREA (1950) and EPSTEIN *et al.* (1964). Carbonate content and mineralogy were confirmed by XRD prior to isotope analyses. Because of possible cross-contamination of CO_2 gas produced from calcite and dolomite, results for calcite are presented only when the calcite/dolomite ratio in a sample is greater than 0.5; results for dolomite are recorded only if the calcite/dolomite ratio in a sample is less than 0.7. These same restrictions were applied to ankerite/dolomite mixtures. These criteria were frequently satisfied by analyzing an isolated size fraction rather than using a whole rock fraction. Siderite was only analyzed when it occurred as the sole carbonate phase in the sample. CO_2 was obtained from siderite and ankerite by reaction at 25°C for 21 days. Replicate isotopic analyses of carbonate minerals were better than ± 0.1‰ for $\delta^{18}O$.

Oxygen was extracted from silicate minerals according to the BrF_5 method of CLAYTON and MAYEDA (1963), and quantitatively converted to CO_2 over a hot graphite rod. Replicate analyses were better than ±0.2‰. Over the period of experiments, NBS-28 was determined for every set of five samples and gave an average value of +9.65 ± 0.21‰. Precision and accuracy of data were monitored daily using an internal lab standard and the carbonate standard NBS-20.

Radiogenic Isotope Analyses

Using a combination isotope dilution (ID)/ isotope ratio (IR) procedure, Sr and Rb concentrations and $^{87}Sr/^{86}Sr$ ratios were determined for carbonates, both leached and unleached fractions of illite, chlorite removed by dilute acid leaching, feldspar, apatite and anhydrite. In order to minimize contamination associated with ion exchange reactions with clay minerals, illite was generally leached with dilute (0.6N) two times vapour distilled HCl. This leaching procedure also removed chlorite from the illite phase providing a leachate/chlorite sample for analysis. Homogeneous samples of each separated mineral were spiked with a mixed solution of ^{87}Rb and ^{84}Sr, and then equilibrated by HF- HNO_3 decomposition in closed vessels (carbonate samples were equilibrated with only dilute HNO_3). Strontium was separated by co-precipitation with $Ba(NO_3)_2$ from a strong HNO_3 sample solution and purified on a cation exchange column. The Sr was loaded as $SrCl_2$ on the side filament of a Re double filament. The alkalies from the supernatant liquid of the $Ba(NO_3)_2$-precipitation were concentrated and Rb was coprecipitated with $KClO_4$ by the addition of $HClO_4$ to the aqueous extract. The $(K,Rb)ClO_4$ was loaded on the side filament of a double-Re filament. Isotope ratios of both the Sr and Rb were measured on a VG-MM 30 mass spectrometer in semi-automatic mode with on-line data collection and processing. The within-run precision of a single analysis of the $^{87}Sr/^{86}Sr$ ratio was ±0.00003; repeated runs of the NBS-SRM 987 standard over the duration of the study yielded a mean $^{87}Sr/^{86}Sr$ ratio of 0.71027 ± 0.00004 (1σ). All measured $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$.

RESULTS AND DISCUSSION

General

Stable ($\delta^{13}C_{(PDB)}$; $\delta^{18}O_{(SMOW)}$) and radiogenic ($^{87}Sr/^{86}Sr$) isotope results and Sr and Rb concentrations are shown in Table 6.1. Listed are the locations, depths and lithologies from which the samples were obtained, and the composition of the analyzed samples (whole rock versus mineral separate). Some of the carbonate data listed have already been reported in Chapter 2, but average values are given again here in order to provide a comparison with the data obtained in this study.

Petrography

Core samples from each of the formations shown in the stratigraphic column for the Alberta Basin (Fig. 6.3) have been examined petrographically and by XRD; SEM analysis was conducted on a representative subset of Devonian and Cambrian samples. Extensive SEM analyses have been conducted on many of the Cretaceous formations in the Alberta Basin in other studies (LONGSTAFFE, 1986; LONGSTAFFE and AYALON, 1987; AYALON and LONGSTAFFE, 1988). Detailed descriptions of the lithologic successions, the detrital and diagenetic mineralogy and the paragenetic sequences of individual formations are given in Appendix I; a brief overview/summary is provided here.

Altered muscovite biotite granites of the Precambrian basement are unconformably overlain by basal Cambrian sandstones (~40m) and shales (~185m). The sandstones are clean quartz arenites containing early diagenetic chlorite which is succeeded paragenetically by quartz overgrowths and kaolinite, all of which are overlain by illite/smectite (I/S) and illite. The Cambrian green shales succeed the basal sandstones. The diagenetic component in the shales consists of highly altered early chlorite, some of which is being replaced by less altered kaolinite; I/S and illite are the last phases formed in the paragenetic sequence. The Cambrian units are unconformably overlain by Devonian sedimentary units (~975m), which are composed of evaporites at the base, followed by generally one of two end member lithologies, limestone or secondary dolomite (ANDRICHUK, 1958). Intervening shale formations are composed of alternating carbonate and quartz/illite units. Eroded Mississippian carbonates (~40m) and Jurassic mixed carbonate/clastic rocks (~40m) overlie the Devonian. The principal diagenetic minerals observed in the Devonian through Jurassic formations are carbonate (calcite, dolomite, ankerite) and illite. The Cretaceous clastic rocks (highly variable in thickness, increasing toward the southwest) unconformably succeed the Jurassic units in the western part of the study area and the Devonian units toward the east (Fig. 6.2). The Cretaceous sequence is dominated by shale units with interspersed sandstone lenses. Authigenic minerals are variable in abundance, even within a single formation, but similar phases are generally found throughout the Cretaceous formations. Diagenetic clay minerals include Fe-rich chlorite, kaolinite, dickite, smectite, illite and interstratified expandable phases, including chlorite/smectite (C/S), smectite/illite (S/I) and illite/smectite (I/S). Diagenetic carbonates include calcite, dolomite, ankerite and siderite. There is a paucity of feldspar in the Cretaceous formations within the study area, with the exception of the Viking and Belly River Formations, where albite/oligoclase plagioclase feldspars are much more abundant (6-26%) and altered than K-spar (1-8%). Paragenetic sequences for the main reservoirs of the Cretaceous units are illustrated in Appendix I.

Stable Isotope Constraints

The petrographic data for the formations of the Alberta Basin can be combined with oxygen-isotope results for the diagenetic minerals to deduce changes in porewater $\delta^{18}O$ that occurred during deposition, burial, uplift and erosion of the formations. As has already been discussed, maximum depths of burial and associated maximum temperatures can be approximated using erosional and paleogeothermal gradient data from BEAUMONT *et al.* (1985) and by assuming a surface temperature of +16°C in the Eocene (PIEL, 1971). Such an evaluation has already been illustrated for the Belly River (LONGSTAFFE, 1986; AYALON and LONGSTAFFE, 1988) and Viking (LONGSTAFFE and AYALON, 1987) Formations, whereby changes in porewater $\delta^{18}O$ values that accompanied diagenesis were determined and related to basinal tectonics, providing a relative timing of formation for diagenetic phases.

Cretaceous Clastic Rocks

The stable isotopic data for illites is relatively consistent among the Cretaceous formations; however, a wider range in values is noted for the I/S minerals. The relationship between the measured $\delta^{18}O$ of diagenetic illite, I/S and the possible combinations of water $\delta^{18}O$ and temperature were calculated and representative curves (i.e., *isotope curves*) are plotted on Fig. 6.6. Also shown is a porewater evolution curve, which is fitted to the graph in a manner that intersects the range of possible temperatures and water $\delta^{18}O$ values in an order consistent with the observed paragenetic sequences and the calculated isotope curves for individual diagenetic phases for the Cretaceous formations (Fig. 6.6). Illustrated on the porewater evolution curve are the various authigenic phases comprising the general paragenetic sequence for most of the Cretaceous formations. Present reservoir conditions in the various Cretaceous formations provide end points for the porewater evolution curve and are highlighted by the different boxes for individual formations. Figure 6.6 is a schematic illustration encompassing all of the Cretaceous formations in the Alberta Basin within the study area showing the likely range of temperatures and $\delta^{18}O_{H2O}$ values experienced by the reservoirs. Individual formations may have slight modifications to the porewater evolution curve or additional authigenic phases not illustrated here, but the general trend and paragenetic sequence of diagenetic minerals exhibited is adhered to by all Cretaceous formations.

The initial composition for the porewater exhibits a wide range of $\delta^{18}O$ values to include all possible values compatible with the various depositional environments. For example, if a formation was deposited under seawater conditions or in a shallow marine setting, the $\delta^{18}O$ value may be approximated by 0‰, which is the current value for standard mean ocean water. Alternatively, the water may have been more ^{18}O depleted given possible early contributions by meteoric water or potential interaction with entrapped bottom waters (SAVIN and YEH, 1981). WHITTAKER *et al.* (1987) have suggested that values as low as *-4‰* may have occurred in the bottom waters of the Cretaceous inland sea. A brackish water environment, such as the Belly River depositional environment, would be even more ^{18}O-depleted (possibly as low as ~ *-8‰*). Low temperature formation of early diagenetic phases, such as chlorite, occurred in these brackish to seawater environments. Regardless of the $\delta^{18}O$ values of the depositional waters, with increasing depth of burial it is likely that the $\delta^{18}O$ value of the porewaters increased due to water/rock interactions (Fig. 6.6). Processes such as isotopic exchange with phases like calcite, dissolution of rock fragments and/or contributions from the dewatering of clay minerals (CLAYTON *et al.*, 1966; HITCHON and FRIEDMAN, 1969; SUCHECKI and LAND, 1983) would all serve to increase $\delta^{18}O$ values of the porewaters to values possibly as high as +4 to *+6‰*, as indicated by fluid inclusions in the Alberta Deep Basin (TILLEY and LONGSTAFFE, 1989). However, the porewater $\delta^{18}O$ values likely did not exceed *+6‰*, due to the buffering reactions of clay minerals (SUCHECKI and LAND, 1983) in the Cretaceous shales. With increasing burial and temperature, chlorite may have continued to form and calcite precipitation started to occur.

During maximum burial in the Early Eocene, maximum temperatures in the basin were achieved and the isotopic composition of quartz indicates that the precipitation of this phase was occurring prior to and during maximum burial (Fig. 6.6). Topographic relief attained as a result of uplift of the Canadian Cordillera at this time (Eocene) led to a major regional influx of meteoric water ($\delta^{18}O$~-15‰; TAYLOR, 1974) into the Alberta Basin. The isotopic composition of relatively later diagenetic calcite in the paragenetic sequences of Cretaceous formations may only be explained by a decrease in the isotopic composition of the reservoir fluids; hence, this calcite likely precipitated during this recharge event. A decrease in reservoir temperatures accompanied the influx of meteoric waters, as illustrated by the bend on the porewater evolution curve (Fig. 6.6); temperature and $\delta^{18}O$ decreases are coincident with kaolinite precipitation. The influx of meteoric water and post-Eocene erosion continued, with the influence of meteoric waters becoming less pronounced in the Lower Cretaceous formations during the Pliocene (CONNOLLY *et al.*, 1990a; 1990b). Porewaters evolved toward present day conditions and moved into the I/S and illite fields toward the end of the porewater evolution (Fig. 6.6). In summary, chlorite, carbonates, quartz overgrowths and kaolinite almost always precede illite or I/S in the paragenetic sequences of Cretaceous formations (Fig. 6.6). Therefore, although the isotope curves for illite, I/S on the $\delta^{18}O$ porewater versus temperature graph appear to be consistent with burial diagenetic temperatures (i.e. >100°C) and pore fluid compositions (i.e. >~1‰), when consideration is given to the paragenetic sequence and isotopic curves for the other authigenic phases in the sedimentary units, illitic phases were more likely formed after flushing of meteoric waters and in a lower temperature regime. Hence, in Cretaceous units, illite and I/S are late diagenetic phases in the paragenetic sequence and have likely formed relatively recently and perhaps are still forming under present day conditions (Fig. 6.6).

Devonian Carbonate Rocks

The stable isotopic data for the Devonian illites are consistent among the formations, but not free from ambiguity. Constructing a porewater curve analogous to that of Cretaceous waters (Fig. 6.7), the illite isotopic data indicate the illite phases could have formed either relatively early in the history of the sedimentary units (i.e., prior to significant lowering of porewater $\delta^{18}O$ values) and/or very late, almost at present day conditions; it is possible that the illite component is a result of both early and late formation. There are fewer diagenetic phases in the carbonate dominated Devonian units than in the clastic units (e.g., Cretaceous, Cambrian), making it more difficult to clearly establish the relative timing of authigenic mineral formation. Furthermore, since these units are older than the Cretaceous formations, they have likely been subject to earlier tectonic events and have been influenced by more isotopically divergent porewater environments. However, the Devonian units did experience maximum burial and temperatures subsequent to the Laramide Orogeny. Moreover, maximum $\delta^{18}O$ values of the porefluids likely occurred at approximately this time, due to water/rock interactions and are relatively well constrained as a result of clay buffering reactions (SUCHECKI and LAND, 1983) and fluid inclusion data (TILLEY and LONGSTAFFE, 1989). As a result, the latter part of the curve is reasonably well constrained. Thermodynamic data and high $\delta^{18}O$ values of the Devonian reservoir fluids (>2‰) (Fig. 6.7; HITCHON and FRIEDMAN, 1969) together suggest that present day fluid characteristics are conducive to illite formation. Furthermore, SEM photographs exhibit various types of illite morphologies (Fig. 6.5), with the smallest diagenetic component (<0.1 μm) being filamentous, hairy illite. These diagenetic illites exhibit no alteration, are overlying the carbonate phases, and are the last phases growing into pore spaces. However, XRD patterns for Devonian illites exhibit relatively sharp peaks, although they are still well within the diagenetic field for illite crystallinity (KUBLER, 1966; THOREZ, 1976), suggesting that these Devonian illites are more crystalline than those in any other stratigraphic units. The relatively crystalline nature of Devonian illites, when compared to diagenetic illites from other Alberta Basin lithologic units, may indicate that the <0.1 μm size fraction that enriches the diagenetic component that was observed using the SEM also incorporated some of the early, more crystalline illite phases.

The relative timing of Devonian illite formation should also be considered in the context of the tectonic history and hydrodynamics of the Alberta Basin (HITCHON and FRIEDMAN, 1969). The Laramide Orogeny provided the largest hydraulic head ever experienced in the Alberta Basin. Initially during this event Devonian and Carboniferous carbonates provided a low fluid potential drain for these fluids (HITCHON, 1969b; HITCHON and FRIEDMAN, 1969; DEROO *et al.*, 1977). Although it has been suggested, based on Devonian erosional surfaces, that meteoric waters have penetrated these reservoirs prior to the Laramide Orogeny (CARPENTER and LOHMANN, 1989), it is unlikely that the Devonian hosted fluids ever had lower stable isotopic values than after the Laramide flushing event. Hence, it is unlikely that illite formation occurred progressively, subsequent to pre-Laramide incursions of meteoric fluids into the reservoir, as the isotopic composition of the porewaters would not accommodate such a hypothesis. Rather, the illites formed recently, toward the end of the paragenetic sequence and likely during burial diagenesis.

Cambrian Clastic Rocks

The stable isotope values of the Cambrian diagenetic (<0.1 μm) illites are compatible with two stages of formation of the illite phases in the paragenetic sequence if a simple porewater evolution curve, analogous to the Devonian and Cretaceous, is used. Uncertainties as to the validity of such a curve are recognized considering the Cambrian was deposited over 500 Ma providing a large time frame for diagenetic reactions and porewater changes. However, the evaporite sequence at the base of the Devonian has been shown to be a relatively impermeable barrier to fluid flow that is not contributing significantly to the water chemistry (CONNOLLY *et al.*, 1990a). As a result, vertical infiltration of meteoric fluids into the Cambrian would not have been significant after the Middle Devonian. This lack of vertical infiltration and cross-formational fluid flow is still consistent with the infiltration of low $\delta^{18}O$ meteoric water that occurred subsequent to the Laramide Orogeny, as these fluids were directed along fault systems in the Rocky Mountain foothills and had a southwesterly source and lateral component. Prior to this, the basinal morphology was such that meteoric waters would not likely have affected the Cambrian porewaters (PORTER *et al.*, 1982). In addition, as was described for the Devonian reservoirs, maximum temperatures and burial of the Cambrian unit would have occurred subsequent to the Laramide Orogeny and would likely have been succeeded by flushing of meteoric waters, constraining the latter part of the porewater evolution curve. Thus, it is possible that the porewater evolution curve drawn for the Cambrian is valid for most of the diagenetic reactions/phases that can be observed today.

In the shale lithologic units the $\delta^{18}O$ values of illite indicate that these minerals may have formed under conditions close to maximum burial and temperature in the Eocene, or relatively late in the paragenetic sequence - after the influx of meteoric waters. Scanning electron microscopy analysis indicates, by the filamentous morphology of illite and its location in the pore (Fig. 6.5), that illite found in the fine fraction formed very late in the paragenesis of the unit. The isotopic composition of the Cambrian shale porewaters is unknown, but if it was higher than in the sandstones (>-2‰), which is possible due to increased water/rock interactions in shales, it is reasonable that relatively late formation of illite is occurring in the Cambrian shales. The paragenetic sequence of the Cambrian sandstones is better defined than that of the shales. Chlorite, quartz overgrowths, and kaolinite formed prior to illite, narrowing the possible times of illite formation to relatively late to almost present day formation, analogous to the timing of illite formation in the Cretaceous units (Fig. 6.8). Scanning electron microscopy of these sandstones shows that very fine fraction (<0.2 μm) contains morphologically well defined hairy, filamentous illite growing into pore spaces (Fig. 6.5); altered illite is present as well, but in the larger (>1 μm) size fraction.

Rb-Sr Geochronology

Most of the illite samples were leached with 0.6 N HCl, both to extract chlorite and to rid the illite of common Sr generally found in exchangeable sites in clay minerals. Illite tends to fix relatively large and less hydrated ions, such as K and Rb, tightly in interlayer sites, making them less readily exchangeable, whereas illite holds smaller, more hydrated ions, such as Ca and Sr weakly in these sites, rendering them more readily exchangeable. The difference in size and hydration energy between Rb and Sr ions results in variable Rb/Sr ratios in exchangeable sites. Furthermore, the isotopic composition of Sr from exchangeable sites is strongly influenced by the isotopic composition of Sr from circulating formation water, with this *common* Sr generally lowering the total Rb-Sr ratios in illitic phases (MORTON, 1985b). Removal of Sr and Rb from exchangeable sites in illite facilitates an isotopic investigation of Rb and Sr in the non-exchangeable or core portions of the mineral, which is more valid for a geochronologic interpretation.

Although dilute HCl has commonly been used as a leaching reagent for clay minerals prior to Rb-Sr analysis (BOFINGER *et al.*, 1968; CHAUDHURI and BROOKINS, 1969, 1979; CORDANI *et al.*, 1978; KRALIK, 1984; MASSEY, 1984), it has been suggested that H^+ ions may be capable of not only replacing exchangeable cations, but of disrupting layer charge (NEWMAN, 1970; MORTON and LONG, 1980;

MORTON, 1985a, 1985b). Therefore, ammonium acetate (NH_4OAc) has been recommended as an alternative to HCl (MORTON, 1985). However, HCl has been shown to yield consistent data, regardless of acid concentration or duration of leaching (CHAUDHURI and BROOKINS, 1979), indicating that while it is an effective agent for removing Rb and Sr from exchangeable sites, it does not disrupt the illite core material. Geologically significant isochrons have been obtained when HCl has been used to leach clay minerals. Therefore, in this study, HCl was used because it was readily available in a pure, vapour distilled form.

Dating Diagenetic Minerals

The Rb-Sr method has been applied to the sedimentary rocks in this study in an attempt to date post-depositional events related to the formation of authigenic phases or the recrystallization of minerals. In order to obtain a geologically valid isochron, the following criteria must be met (FAURE and POWELL, 1972): (1) a uniform initial $^{87}Sr/^{86}Sr$ value; (2) a sufficient spread of Rb/Sr ratios to define a line; and, (3) closed system behavior after deposition/formation. Diagenesis of clay minerals in the Alberta Basin, especially in Cretaceous units, has been attributed to a change in porewater composition, particularly that associated with the influx of meteoric waters instigated by the Laramide Orogeny (LONGSTAFFE, 1986; LONGSTAFFE and AYALON, 1987; AYALON and LONGSTAFFE, 1988). Furthermore, it is suggested here and in other studies (TOTH, 1980) that sedimentary units as stratigraphically low as the Cambrian were also affected by this same influx of gravity-driven meteoric waters. Therefore, this major orogenic event has seemingly resulted in flushing meteoric waters through all the sedimentary units in the Alberta Basin as a result of the large hydraulic head generated by the uplift of the Canadian Cordillera (HITCHON and FRIEDMAN, 1969). Subsequent to this flushing, kaolinization followed by illitization appears to have prevailed in most Alberta Basin formations. Studies of diagenetic illite (BOLES and FRANK, 1979) have shown that it forms in chemical equilibrium with porewaters and behaves as a closed chemical system under subsequent sedimentary/diagenetic conditions. The sedimentary rocks of the Alberta Basin have never been exposed to temperatures greater than diagenetic (>200°C), so the illitic phases likely remained as closed systems with respect to Rb/Sr in the core material. If all of the diagenetic illite (<0.1 µm, HCl leached fraction) from the Alberta Basin was formed as a result of porewater change instigated by the Laramide Orogeny, then in the most simplistic model, the Rb/Sr data for these samples should form a single isochron whose age is coincident with the post-tectonic porewater change when density stratification and hydrochemical isolation was initiated (CONNOLLY *et al.*, 1990a, 1990b). However, the data did not yield a line on a standard isochron plot.

The absence of an isochron when considering Rb-Sr analyses for diagenetic minerals (illite, chlorite) from all formations in the Alberta Basin is clear evidence that these minerals did not form simultaneously in a system isotopically homogeneous with respect to Sr. Thus, smaller systems, such as individual formations, were considered. A single formation would be more likely to have attained a homogeneous initial $^{87}Sr/^{86}Sr$ ratio, potentially allowing valid isochrons to be drawn for the diagenetic minerals within a formation. For each formation for which there was a sufficient spread in Rb/Sr among the illite and chlorite, the calculation of an isochron was attempted. Only the Belly River Formation yielded an apparently valid isochron, with a mean square weighted deviance of 0.92 (Fig. 6.9). The slope age of this line is 75.7 ± 4.6 Ma, or Campanian, the depositional age of the Belly River sediments.

The correspondence of the data from Belly River diagenetic minerals with the time of deposition would appear to support MORTON's (1985a) theory of punctuated illite/smectite diagenesis, whereby illitization of smectite is an early, episodic and datable event, brought about by a change in porewater chemistry. However, as already discussed, the $\delta^{18}O$ values for the diagenetic illites in the Belly River Formation constrain the relative time of formation of the authigenic I/S component to relatively late in the paragenetic sequence. While illitization may have occurred soon after deposition, as indicated by the apparent isochron data, most of these phases would no longer be present in the diagenetic fraction (<0.2μm). A major flushing of the formation by acidic meteoric water would likely have resulted in alteration and kaolinization of many of the earlier formed phases. Such a gravity induced influx of meteoric waters was initiated approximately 40 to 57 Ma ago as a result of the Laramide Orogeny. Therefore, the linear relationship of the Belly River results on the isochron plot in Fig. 6.9 is more likely a pseudo-isochron or mixing line. Replotting the data for the Belly River on $^{87}Sr/^{86}Sr$ *vs* Sr and $^{87}Sr/^{86}Sr$ *vs* 1/Sr plots (Figs. 6.10a and 6.10b), a hyperbola and a line typical of mixing are generated, respectively. One chlorite point on both plots is removed from the trends illustrated, but this may be a result of: (1) the variable proportion of exchangeable common Sr which is included in the chlorite analysis when they are leached from the illite; and/or, (2) a *local* precursor phase to the chlorite altering the Sr component. Such a pseudo-isochron (Fig. 6.9) and mixing relationship (Fig. 6.10) might be expected for the Belly River chlorite and illite phases, partly because the chlorite analyzed was leached from the illite phases and such a chemical leaching procedure is often expected to generate a pseudo-isochron and mixing. However, $^{87}Sr/^{86}Sr$ *vs* $^{87}Rb/^{86}Sr$ plots for the illite and chlorite phases from the other formations in the basin showed no such linear relationships (i.e., pseudo-isochrons). This lack of correlation may suggest that: (1) the core Sr from the illite and chlorite minerals of the Belly River and the exchangeable Sr component were all part of a mixing regime, which was not the case for the other formations; (2) the Belly River chlorite and illite phases were formed relatively close together in the paragenetic sequence with respect to the total time frame since deposition, whereas in stratigraphically lower formations there was a greater length of time between the formation of the two phases, increasing the potential for variable water $^{87}Sr/^{86}Sr$ ratios during each mineral formation; and/or (3) the illites were formed by gradual illitization (HOWER *et al.*, 1976; BOLES and FRANK, 1979), resulting in different closure times for the various illites and variation with respect to chlorite.

Importantly, it was observed that many samples within a few meters of each other, primarily within the clastic units, yielded data which were completely incompatible with similar isochron dates. Such variability, when the environment and timing of formation were so similar, is most likely a result of different initial $^{87}Sr/^{86}Sr$ ratios, due to local environments and varying precursor phases, rather than gradual illitization. For example, the Cambrian shales are composed of siltstones and shales intercalated with sandy lenses, resulting in a highly variable modal mineralogy. Over time, with the decay of ^{87}Rb to ^{87}Sr, variations in porewaters in different parts of the section would occur, particularly if water movement was more restricted in some parts of the unit (the shales) than in others (the sandstones). Thus, it is likely that the Alberta Basin sediments are incompatible with the criteria required for obtaining geologically significant ages, even within individual formations. Variability in mineralogy over relatively short distances in the Alberta Basin formations results in a lack of homogeneous initial $^{87}Sr/^{86}Sr$ ratios.

Although not successful in the Alberta Basin, the Rb-Sr dating technique has been successfully applied in the Gulf Coast (MORTON, 1985a, 1985b). However, the Gulf Coast has a simple basin history and is in its first cycle of burial (GALLOWAY, 1984). The Gulf Coast Basin is characterized by large masses of internally consistent shale (>1km) that are/were primarily influenced by compactional fluids; substantial meteoric influx has not occurred. Therefore, when compared to the comparatively thin, heterogeneous units characterizing the Alberta Basin, diagenetic minerals in the Gulf Coast Basin are more likely to fit the criteria of an initially homogeneous, closed system required for an isochron.

Improved data for chlorite samples could, in future, be obtained by removal of exchangeable Sr from the mixed chlorite/illite phases prior to separation of the clays by leaching. An alternative method to that used here might be leaching the chlorite/illite samples with NH_4OAc first, to remove exchangeable cations, and then proceeding with the 0.6 N HCl acid treatment for chlorite removal.

Rb/Sr Model Ages

To constrain the timing of illitization in many of the formations the stable isotope data (Table 6.1) were correlated with calculated model ages (Table 6.2). Although it is difficult to put an upward limit on the $^{87}Sr/^{86}Sr$ initial value assumed in these calculations, because of potentially high variability in mineral Rb/Sr ratios, a relatively reasonable lower limit may be established. A good minimum estimate of the $^{87}Sr/^{86}Sr$ ratio of the porewater is the $^{87}Sr/^{86}Sr$ value of seawater at the time of deposition of the formation. Most of the formations in the Alberta Basin were deposited in seawater and because of the radioactive decay of ^{87}Rb, the $^{87}Sr/^{86}Sr$ ratios in formation porewaters likely increase over time from this initial seawater value. The varying $^{87}Sr/^{86}Sr$ values for seawater over the Phanerozoic time period are provided by BURKE *et al*. (1982). These values are likely valid estimates for all seawater environments at a particular time, even those that are/were somewhat isolated from the open ocean, such as the present day Hudson Bay (FAURE, 1986) or the Cretaceous inland sea (WHITTAKER *et al*., 1987). Decreasing $^{87}Sr/^{86}Sr_i$ values result in increased ages. Therefore, by using as the initial $^{87}Sr/^{86}Sr$ ratio, the seawater $^{87}Sr/^{86}Sr$ value at the time of deposition for a particular unit, the maximum possible age of an illite phase is calculated. This is particularly useful for some of the stratigraphically lower units (i.e. Devonian, Cambrian), where proof of meteoric water influence and porewater/tectonic disturbance has not been as clearly defined or placed within a time reference as those from stratigraphically higher units.

Model ages were calculated for an illite phase in most of the formations using the following formula:

$$t = 1/\lambda \ \ln \left[\left[\left({}^{87}Sr/{}^{86}Sr - {}^{87}Sr/{}^{86}Sr_i \right) / (Rb/Sr) \right] + 1 \right] \qquad (1)$$

where t is the time elapsed in years since the time of formation of the mineral, λ is the decay constant of ^{87}Rb (1.42×10^{-11}) in units of reciprocal years, $^{87}Sr/^{86}Sr$ is the measured $^{87}Sr/^{86}Sr$ value, $^{87}Sr/^{86}Sr_i$ is the assumed initial $^{87}Sr/^{86}Sr$ ratio and Rb/Sr is the measured concentration of Rb/Sr. Model ages were calculated for all of the <0.1 μm illite fractions which were interpreted to be authigenic following SEM examination and determination of illite crystallinity indices. Model ages for some <2.0 μm samples were also calculated to determine if there was a significant difference in age with size fraction. No model ages were calculated for the Belly River Formation because the present $^{87}Sr/^{86}Sr$ ratio for illite is lower than the corresponding seawater value at the time of deposition, likely due to early plagioclase alteration dominating the porewater $^{87}Sr/^{86}Sr$ ratios (Chapter 2; CONNOLLY *et al.*, 1990b).

The model ages calculated for Cretaceous rocks are variable (140 to 180 Ma) and usually older than the depositional age of the sedimentary unit, even when current water $^{87}Sr/^{86}Sr$ values are used for the $^{87}Sr/^{86}Sr_i$. The seawater value used for an initial $^{87}Sr/^{86}Sr$ ratio in equation (1) is probably too low an estimate for the initial $^{87}Sr/^{86}Sr$ value. There are many Rb-bearing minerals within the Cretaceous formations, more than in carbonate units, creating a high potential for increased initial $^{87}Sr/^{86}Sr$ ratios for the illitic phases in these units. However, because these systems are relatively complex mineralogically and have been studied extensively using petrography and stable isotopes

(LONGSTAFFE, 1986; LONGSTAFFE and AYALON, 1987; AYALON and LONGSTAFFE, 1988), it is easier to establish a paragenetic sequence for them than for stratigraphically lower formations. Hence, as already described, petrography and stable isotope systematics more clearly define the relative timing of illite formation to relatively late.

There is a high variability in the model ages calculated for the illite phases of the Devonian system. A similar situation was observed by MORTON (1985b) for two core samples from the Gulf Coast Upper Devonian Woodford Shale that were only 1.2 m depth apart. One Gulf Coast sample, a carbonate free black shale, plotted on a 302 my isochron with all the other Devonian shales analyzed in his study; however, the other sample, a greenish gray, finer grained and slightly dolomitic shale gave an age of 241 ± 2 my. Correspondingly, all of the Alberta Basin Devonian shales which had relatively younger model ages when compared to the range calculated, contained a higher percentage of carbonate. Thus, the age discrepancies observed for the illite minerals in the Devonian formations of the Alberta Basin should be evaluated with respect to variable carbonate mineral content which may affect the illitization reaction. Porewater in equilibrium with dolomite would be expected to contain a high Mg and Ca content. ROBERSON and LAHANN (1981) have shown that Mg^{+2}, Ca^{+2} and Na^{+} greatly inhibit the conversion of smectite to illite by both blocking the entry of K^{+} into the mineral structure and impeding the substitution of Al^{+3} for Si^{+4}. The relative inhibitory strength of these cations is $Mg^{+2}>Ca^{+2}>Na^{+2}$, so that a Mg - Ca rich mineral, such as dolomite, may be capable of strongly influencing the course of diagenesis of associated clays. NADEAU and REYNOLDS (1981) provide further evidence by demonstrating that the presence of carbonates inhibits the formation of I/S in the early stages of diagenesis. Such a hypothesis would require that illite samples which exhibit younger ages in the Devonian reflect a time when the rock was deeply buried and the inhibitory cation effect was overcome by higher temperatures of diagenesis. These higher temperatures would have occurred subsequent to the Laramide Orogeny, in a relatively narrow time frame, which is not exhibited by the highly random ages calculated here. In addition, all of the Devonian formations, even the shales, contain carbonate, only the relative amounts vary and stable isotope curves (Fig. 6.7) and SEM analysis also indicate that most of the diagenetic illite (<0.2 μm) formed reasonably late in the paragenetic sequence at approximately the same time. Therefore, the above explanation, although it should be considered and may apply to some of the relatively early illitic phases found in the Devonian, does not likely apply to the relatively late (<0.2 μm separate) diagenetic illite separates. Rather, more likely explanations for anomalous age patterns are: (1) discrepancies in initial $^{87}Sr/^{86}Sr$ ratios; (2) many of these shales were not leached with dilute HCl prior to analysis, so a large proportion of common strontium may be altering the results; and, (3) some of the earlier formed illite may have been incorporated into the separate comprising the relatively late formed phase. It is significant however, that when an initial $^{87}Sr/^{86}Sr$ value representative of some of the formation waters currently residing in the Devonian reservoirs is used (0.712), some of the illite model ages begin to become quite low within the realm of relatively recent illite formation (~80Ma).

Model ages calculated for the Cambrian <0.1 μm illites indicate that a porewater change/modification affected the Cambrian at least 200Ma (Table 6.2). It is unlikely that the $^{87}Sr/^{86}Sr_i$ value was ever lower than 0.709, the value of seawater at the time of deposition. Given that the maximum time calculated for formation of some of the illite phases was 200 Ma, using an initial $^{87}Sr/^{86}Sr$ ratio of 0.709, this assumed $^{87}Sr/^{86}Sr_i$ value is probably much too low, considering the >300 million year time period prior to this that the Cambrian was deposited and becoming increasingly more radiogenic. Thus, a higher

$^{87}Sr/^{86}Sr_i$ value of 0.720 was assumed to render a more accurate, though not necessarily correct, estimate of the age of formation for diagenetic illite. Calculated model ages using 0.720 for $^{87}Sr/^{86}Sr_i$ yielded a value as low as 70 Ma for the sandstone, with the shales having relatively higher values (Table 6.2), placing these illitic phases in the realm of relatively recent formation.

The shale units toward the top and the base of the Cambrian have lower $^{87}Sr/^{86}Sr$ whole rock values and lower model ages than those units toward the center. This is likely a result of the degree of closed versus open system behavior experienced by different localities in the formation. Toward the top and base of the Cambrian, the unit is porous and a larger proportion of water containing *common* Sr flows through these units relative to the shales. Conversely, in the shaly parts of the formation, the radioactive decay of ^{87}Rb results in a continued increase in the porewater $^{87}Sr/^{86}Sr$ ratios with little outside influence or input of *common* Sr. The variable model ages in the Cambrian is evidence of local conditions affecting the formation of illite rather than complete basinal or formational homogeneity. That the Cambrian illites yield such young ages is significant; however, in that it indicates that these units were likely affected by meteoric waters during the Laramide Orogeny, as this is the only major tectonic event that occurred during the time frame suggested by Cambrian model ages. Prior to this study, meteoric influence in the Cambrian as a result of this orogenic event has only been hypothesized through the use of hydrologic modelling (TOTH, 1980).

Mass Transfer and Mixing

Mixing relations explain many geological processes and are generally described mathematically by two component models. The validity of the mixing hypothesis is tested by plotting both an $^{87}Sr/^{86}Sr$ *vs* Sr plot and an $^{87}Sr/^{86}Sr$ *vs* 1/Sr plot and fitting the data to a hyperbolic curve on the former and a linear array on the latter; both plots must be satisfied to substantiate mixing. The assumptions applied to the mixing model is that neither the Sr concentrations nor the $^{87}Sr/^{86}Sr$ ratios were modified subsequent to mixing. The latter constraint may be violated if mixing is discontinued for a significantly long period of time, as ^{87}Rb continues to decay to ^{87}Sr, the amount of ^{87}Sr formed depending on the Rb content of the mixture. Thus, $^{87}Sr/^{86}Sr$ ratios will always be modified after mixing, the degree of alteration becoming more significant with the length of time elapsed since mixing and with increased Rb/Sr ratios. For this reason mixing models are most often applied to currently active or simple systems such as basinal fluids (STUEBER *et al.*, 1987; CONNOLLY *et al.*, 1990b), mixing of sediment components in oceans (BOGER and FAURE, 1974, 1976; BOGER *et al.*, 1980; SHAFFER and FAURE, 1976; FAURE and TAYLOR, 1983) and diagenetic studies of relatively young sediments (BRUECKNER and SNYDER, 1985; HURST, 1986; SCHULTZ *et al.*, 1989). It is possible to obtain a mixing relation for a mixing event that occurred in the past, provided the time of closure is accurately known, by calculating age corrections to account for increased $^{87}Sr/^{86}Sr$ values over time. However, as is evident, the potential for mixing and the number of end members increase with time so that age corrections may further complicate rather than elucidate past systems.

The geochemistry and isotope systematics of formation fluids in Devonian - Lower Cretaceous reservoirs of the Alberta Basin indicate cross-formational upward water migration, superimposed on a lateral water flow system (CONNOLLY *et al.*, 1990a, 1990b). Strontium isotope ratios and Sr contents suggest a two component mixing relation for these waters, with one end member having δD values characteristic of meteoric waters in the Neogene. This Neogene δD end-member reflects post-Laramide flushing of Tertiary meteoric waters throughout the basin and subsequent hydrochemical isolation from more modern waters. Assuming this hypothesis is correct, and from preceding arguments that illite was often one of the last phases to form in the paragenetic sequence after the change in porewater composition brought about by the Laramide Orogeny, the diagenetic illite phases in the Alberta Basin should reflect this mixing event. Plotting Cambrian through Upper Cretaceous authigenic illite phases on a graph of $^{87}Sr/^{86}Sr$ *vs* 1/Sr (Fig. 6.11), three distinct trends or clusters are observed. All of the Cambrian samples plot in a distinct field with the values from the shales exhibiting a consistent $^{87}Sr/^{86}Sr$ value, but a range in Sr concentration, whereas the value from the basal sandstone has a comparatively lower $^{87}Sr/^{86}Sr$ value, but a similar Sr concentration to the shales. Such a distribution for the Cambrian samples indicates that the shales were isotopically homogenized, but that this occurred separately from the sandstone; mixing was not a recently active process among Cambrian units, with the sandstone and shale lithologies behaving as reasonably distinct units. The distribution of Cambrian data indicates that these illites were either: (1) not formed at the same time as illites in stratigraphically higher formations; or, (2) not a result of mixing with formation waters hosted in stratigraphically higher formations in the basin, but were precipitated from waters that are/were relatively isolated. From previous arguments it is likely that the diagenetic illites in the Cambrian formed at approximately the same time as diagenetic illites in other formations in the Alberta Basin, particularly the illites within the Cambrian basal sandstone. Hence, it would appear that waters in the Cambrian formation are relatively isolated. This hypothesis is reasonable when considered in the context of the basinal lithology. Evaporite deposits of the Middle Devonian overlie the Cambrian shales and it has been previously suggested that these evaporite units are non-interactive and in effect impermeable to basinal fluids (CONNOLLY *et al.*, 1990a). This would result in a lack of vertical cross-formational fluid flow between the fluids in the

Cambrian and fluids hosted in stratigraphically higher units. However, the spatial occurrence of lithologic units is still compatible with the influx of meteoric waters into the Cambrian as a result of Laramide tectonism. These waters were sourced or recharged from the southwest where no Devonian evaporites occur; it is the cross-formational fluid flow between the Devonian and Cambrian in the center of the basin that does not appear to be occurring.

The illites from the Belly River also form a distinct trend on Fig. 6.11, deviating from the Cardium through Devonian trend toward lower Sr concentrations. These samples have been shown to form their own mixing regime (Figs. 6.10a and 6.10b), and that the illite phases are isotopically distinct from stratigraphically lower formations is reasonable when considered in the context of the basin hydrology. As already stated, the regional recharge system of gravity-driven meteoric waters throughout the Alberta Basin has dissipated since the Pliocene (GARVEN, 1989; CONNOLLY *et al.* 1990b), resulting in hydrochemical isolation of stratigraphically older formations but continued meteoric flushing of some parts of the Cardium Formation and all stratigraphically younger formations. If the illitic phases formed relatively late in the paragenetic sequence of all the formations in the Alberta Basin, a significantly different fluid environment would characterize the Upper Cretaceous reservoirs when compared to stratigraphically lower formations. This would be reflected in the isotopic composition of authigenic phases such as illite.

Illitic phases from Devonian through Cardium formations show a distinct, positive trend on Fig. 6.11, which is better illustrated on Fig. 6.12. These illites fulfil both criteria of mixing by exhibiting a hyperbolic curve on the $^{87}Sr/^{86}Sr$ *vs* Sr plot in Fig. 6.12a and a straight line with a correlation coefficient of 0.94 on the $^{87}Sr/^{86}Sr$ *vs* 1/Sr plot in Fig. 6.12b. Both plots suggest that all of these diagenetic illite phases were part of a mixing regime that is either currently active or was active in the recent past. It has been suggested that flushing of Tertiary meteoric waters throughout the Alberta Basin terminated in the Neogene for units stratigraphically lower than the Cardium Formation (CONNOLLY *et al.*, 1990b). Kaolinite was the first diagenetic phase to form in the Cretaceous in response to the meteoric waters that flushed through the Alberta Basin. Kaolinization is often an active process when gravity-driven, acidic meteoric waters penetrate deep into a sedimentary basin (HURST and IRWIN, 1982). However, if this influx of meteoric fluids dissipated during the Neogene (~5 Ma), as suggested by GARVEN (1989) and CONNOLLY *et al.* (1990a, 1990b), concentrated brines would have been able to rise within the basin, a process which typically results in the formation of illitic cements (HURST and IRWIN, 1982; HUANG *et al.*, 1986). If the formation of illite occurred ~ 5 Ma, this mixing event would still be observable on mixing diagrams, even if it was not currently active, as a significant variation in $^{87}Sr/^{86}Sr$ ratios could not develop over a 5 million year time period. Age corrections for the samples shown on Fig. 6.12 were calculated to test this hypothesis. A correction for 40 Ma, toward the end of the Eocene, and one for 5 Ma were calculated; however, both corrections increased the scatter of the data in Fig. 6.12.

One point which requires clarification is the components of the mixing regime in Fig. 6.12. Previous studies have suggested that the Cardium Formation is part of a meteoric flushed zone (CONNOLLY *et al.*, 1990a; 1990b), while in this study the clay mineral content suggests it is part of the stratigraphically lower mixing regime. This is a result of sampling restrictions for the waters and rocks in the Cardium. The clay minerals sampled for this study are from the stratigraphically lower shales, whereas the waters sampled were taken from stratigraphically higher aquifers in the Cardium. This would suggest that the mixing regimes established in both studies are still consistent with one another, with the division between the two systems being within the Cardium Formation.

Examining Fig. 6.12 in conjunction with Table 6.1, potential end member components may be established for the mixing regime from which illite formed. Looking first at the low $^{87}Sr/^{86}Sr$ high Sr concentration end, there are a limited number of mineral phases which could satisfy this role directly. Calcite and apatite from the Jurassic Nordegg Formation and anhydrite from the Devonian formations all have high enough Sr concentrations and low enough $^{87}Sr/^{86}Sr$ ratios to be reasonable candidates (Fig. 6.13), although apatite is resistant to alteration so is an unlikely candidate. It is possible that dilution of the Sr contributed by these phases could have occurred during meteoric infiltration; however, these phases, particularly apatite and anhydrite, are so enriched in Sr that they would still be able to fall on the mixing line as legitimate end members. Another possible end member to be considered is plagioclase feldspar, a significant component in the Viking (2 to 30%) and stratigraphically higher formations. It has been suggested that the source for this phase was volcanism and tectonically emplaced deposits in Idaho and Montana during Cretaceous time (EISBACHER *et al.*, 1974; CONNOLLY *et al.*, 1990b). An average Sr concentration for these deposits can be assumed to be 1050 to 1200 ppm based on an oligioclase composition (EISBACHER *et al.*, 1974; CRISS and FLECK, 1987), and the $^{87}Sr/^{86}Sr$ ratio is approximately 0.7055, based on the lowest $^{87}Sr/^{86}Sr$ values obtained for water and calcite cements, which are thought to incorporate Sr released from plagioclase alteration (CONNOLLY *et al.*, 1990b). Although the Viking plagioclase has the correct Sr concentration and $^{87}Sr/^{86}Sr$ ratio to be a potential end member, the illites from the Viking Formation are relatively removed from the low $^{87}Sr/^{86}Sr$ ratio, high Sr concentration end member location on the graph (Fig. 6.12a). If plagioclase was an end member component, the Viking illites would likely be closer to the end member position.

The high $^{87}Sr/^{86}Sr$, low Sr concentration end of the mixing regime is more difficult to establish. Geologically reasonable end member components with appropriate $^{87}Sr/^{86}Sr$ ratios can be chosen to fit mixing curves; however, it has been shown that diagenetic illite has formed after a major influx of meteoric water, therefore, a range in concentration, illustrated by the stipled area of Fig. 6.13, may represent the end member concentrations. For example, isolated K-feldspars from stratigraphically lower formations (i.e. Cambrian, Variable Shale) were all likely derived from the Precambrian Shield to the east of the study area and thus have high $^{87}Sr/^{86}Sr$ ratios from 0.77604 to 0.94428. Although these Cambrian units are apparently not in the same mixing regime as the Devonian through Cretaceous system, the provenance for K-feldspar did not change from Cambrian to at least the Lower Cretaceous. Therefore, these isolated K-feldspars can be used to approximate feldspar compositions as end-members for stratigraphically higher formations. The mixing regime shown in Fig. 6.13, illustrates that the Sr concentration of these K-feldspar phases is too high to form a direct end member. However, the infiltration of meteoric waters that occurred in the Alberta Basin, although not active at the time when the mixing regime was formed in these formations, would still have caused a dilution of the Sr concentrations, as determined by direct analysis, of the potential end members. This dilution would not significantly change the $^{87}Sr/^{86}Sr$ ratio of these minerals and would likely cause the $^{87}Sr/^{86}Sr$ ratios to be pushed toward lesser Sr concentrations and located in the end member position on the mixing diagram. This is illustrated by the horizontal arrows in Fig. 6.13. The mica group often has Rb/Sr and $^{87}Sr/^{86}Sr$ ratios similar to feldspar, but these minerals were not examined in this study because they are resistant to alteration and they are not an abundant constituent in any of the stratigraphic units where the proposed mixing regime is active.

Another possible radiogenic $^{87}Sr/^{86}Sr$ end member for the Devonian - Cambrian mixing regime is the indirect contribution by the carbonate phases. Because carbonate does not accept Rb into its structure, but readily accepts Sr, carbonate porewaters become enriched in Rb which becomes significant where a large volume of carbonate exists, such as the Devonian through Jurassic stratigraphic units. However, Rb is very stable in clay mineral cation exchange sits where it replaces K and sits in 12-fold coordination. As a result authigenic minerals precipitating from associated waters, particularly K-bearing phases such as illite, incorporate a large proportion of this Rb into their structure. Furthermore, cation exchange with already existing clay minerals will result in the incorporation of Rb into the clay and a resulting increase in $^{87}Sr/^{86}Sr$ ratios. Over time, and subsequent to recrystallization of carbonate, a highly radiogenic source is created which is readily available to the fluid component and may provide sources of high $^{87}Sr/^{86}Sr$. Figure 6.12 illustrates that the leached illite phases of the Devonian are closest to this radiogenic end-member, supporting this hypothesis.

Illite $^{87}Sr/^{86}Sr$ Values Versus Water $^{87}Sr/^{86}Sr$ Values

Comparison of $^{87}Sr/^{86}Sr$ ratios and Sr concentrations between diagenetic illite and current reservoir waters provides a means to interpret the degree of closed versus open system behavior in the sedimentary units of the Alberta Basin (Table 6.1). Without exception, illite is more radiogenic and generally much more more so, than associated reservoir waters. Moreover, diagenetic illite from shales show a larger deviation from the reservoir fluid toward higher $^{87}Sr/^{86}Sr$ ratios, than those from the sandstones. Strontium isotopes are not measurably mass fractionated during chemical reactions and the diagenetic minerals formed reflect the $^{87}Sr/^{86}Sr$ ratio of the fluids in which they precipitated, providing mineral formation was recent. Therefore, the discordance between water and illite $^{87}Sr/^{86}Sr$ ratios suggests that the local environment of formation has a strong influence on $^{87}Sr/^{86}Sr$ ratios of individual illitic phases, with the local mineralogic/lithologic environments being more influential in the shales. Because of the relatively high permeability in sandstones, authigenic phases forming in this environment are controlled more by solution compositon than the rock composition. Conversely, in shales the solution composition is largely controlled by the chemistry of the solids (HURST and IRWIN, 1982), which is demonstrated by the higher $^{87}Sr/^{86}Sr$ ratios in shale hosted illites when compared to those in sandstones. It has been shown that cross-formational fluid flow is occurring in the Alberta Basin (CONNOLLY *et al.*, 1990b), and this movement is apparently affecting the isotopic composition of diagenetic illites in Cardium through Devonian formations; however, it is also apparent that local environments are also significant to the mineral $^{87}Sr/^{86}Sr$ isotopic signature and that Sr from precursor phases is not carried far before authigenic phases are formed.

Local environments are established within the carbonate regime as well as in the clastic rocks. Carbonate phases do not readily incorporate Rb into their structure and the very small amount that may be incorporated is lost during recrystallization. This Rb is readily accepted into illite phases, in replacement of K, as is evidenced by the higher Rb/Sr ratios in Devonian shales than in stratigraphically higher clastic units. Local chemical/elemental environments are established that may differ from the overall reservoir fluid, as is observed in the $^{87}Sr/^{86}Sr$ ratio of later diagenetic calcite (Wabamun - 0.71388). This is also reflected in the radiogenic signature of the reservoir fluids of these formations, although the overall $^{87}Sr/^{86}Sr$ ratio of the carbonate is not much higher than the seawater at the time of deposition.

Calculated model ages (Table 6.2) further support the existence of locally distinct environments. A variety of ages are often obtained for diagenetic illites which are stratigraphically and spatially close in the basin. The only possible explanation for this deviation in ages is the significantly different initial $^{87}Sr/^{86}Sr$ ratios and Rb/Sr contents in these phases, resulting from distinct precursor mineral phases.

CONCLUSIONS

Whole rock and mineral separates (detrital and diagenetic) from the Alberta Basin, Western Canada Sedimentary Basin, were examined isotopically ($^{87}Sr/^{86}Sr$, $\delta^{18}O$) and for elemental (Rb and Sr) concentrations in an attempt to: (1) constrain water/rock interaction; (2) define mixing regimes; and (2) establish the degree of closed versus open system behavior with respect to cross-formational water flow. In addition, the relative timing of illite formation and scale over which it occurred in the Alberta Basin has been defined.

Illite was the primary diagenetic mineral examined because it is ubiquitous and the most amenable to study using Rb-Sr systematics. Petrographic, SEM, and stable isotope data suggest that the diagenetic illites sampled from Cambrian to Upper Cretaceous units are compatible with relatively recent to present day formation.

Dating diagenetic clay minerals, including both illite and chlorite, was unsuccessful in the Alberta Basin, probably because of the inhomogeneity of initial $^{87}Sr/^{86}Sr$ ratios. Instead model ages were calculated by assuming the minimum $^{87}Sr/^{86}Sr_i$ values to be those for seawater (BURKE *et al.*, 1982) at the time of deposition. Using these minimum $^{87}Sr/^{86}Sr$ ratios, maximum ages were calculated for the illite, which were particularly useful for illites sampled from the Cambrian and Devonian, where the paragenetic sequences are not yet well constrained and lack of varied diagenetic phases in the latter make it difficult to establish a paragenetic sequence. The model ages corroborated earlier stable isotopic data suggesting illite formed late in the paragenetic sequences of formations in the Alberta Basin or is currently still forming.

Mixing diagrams ($^{87}Sr/^{86}Sr$ *vs* 1/Sr and Sr) for all diagenetic illites in the Alberta Basin delineate several distinct zones of late diagenesis. The Cambrian formations are isotopically removed from stratigraphically higher formations, likely because evaporites deposits in the Middle Devonian impede cross-formational fluid flow. The diagenetic components from the Upper Cretaceous Belly River Formation also plot in a distinct region on the mixing diagrams, coincident with the separate hydrologic regime established in this formation relative to that for waters in stratigraphically lower formations. The Devonian through Cardium diagenetic illite phases form a mixing regime, where Jurassic apatite and carbonate and Devonian anhydrite form the low-$^{87}Sr/^{86}Sr$ high-Sr concentration end member and K-feldspar or illite minerals enriched in Rb as a result of exclusion of this element by carbonate form the high-$^{87}Sr/^{86}Sr$ and low-Sr concentration end member. The diluting effect of meteoric waters on the end member concentrations of specific minerals is unknown, making it difficult to establish specific phases as end members. Local mineralogic/lithologic environments are shown to be significant to the isotopic ($^{87}Sr/^{86}Sr$) composition of diagenetic phases, but do not alter the mixing regime, indicating cross-formational water movement is active and the influence of *common* Sr in the waters is important to all of the illite phases.

REFERENCES

ANDRICHUK J.M. (1958) Stratigraphy and facies analysis of Upper Devonian reefs in Leduc, Stettler, and Redwater area, Alberta. *Am. Assoc. Petrol. Geol. Bull.* **42**, 1-93.

AYALON A. and LONGSTAFFE F.J. (1988) Oxygen isotope studies of diagenesis and pore-water evolution in the western Canada sedimentary basin: Evidence from the Upper Cretaceous basal Belly River Sandstone, Alberta. *J. Sediment. Petrol.* **58**, 489-505.

BEAUMONT C. (1981) Foreland basins. *Geophys. J. Roy. Astron. Soc.* **65**, 291-329.

BEAUMONT C., BOUTILIER R., MACKENZIE A.S. and RULLKOTTER J. (1985) Isomerization and aromatization of hydrocarbons and paleothermometry and burial history of Alberta foreland basin. *Am. Assoc. Petrol. Geol. Bull.* **69**, 546-566.

BOFINGER V.M., COMPSTON W. and VERNON M.J. (1968) The application of acid leaching to the Rb-Sr dating of Middle Ordovician shale. *Geochim. Cosmochim. Acta* **34**, 5087-5096.

BOFINGER V.M., COMPSTON W. and GULSON B.L. (1970) A Rb-Sr study of the Lower Silurian Stage Circle Shale, Canberra, Australia. *Geochim. Cosmochim. Acta* **34**, 433-445.

BOGER P.D. and FAURE G. (1974) Strontium isotope stratigraphy of a Red Sea core. *Geology* **2**, 181-183.

BOGER P.D. and FAURE G. (1976) Systematic variations of sialic and volcanic detritus in piston cores from the Red Sea. *Geochim. Cosmochim. Acta* **40**, 731-742.

BOGER P.D., BOGER J.L. and FAURE G. (1980) Systematic variations of $^{87}Sr/^{86}Sr$ ratios, Sr concentrations, and mineral abundances in piston cores from the Red Sea. *Chem. Geol.* **29**, 13-38.

BOLES J.R. (1982) Active albitization of plagioclase, Gulf Coast Tertiary. *Am. J. Sci.* **282**, 165-180.

BOLES J.R. and FRANK S.G. (1979) Clay diagenesis in the Wilcox sandstones of southwest Texas: Implications of smectite diagenesis on sandstone cementation. *J. Sediment. Petrol.* **49**, 55-70.

BONHOMME M., WEBER F. and FAURE-MERCURET M. (1965) Age par la methode rubduim-strontuim des sediments du Bassin de Frannoeville. *Serv. Carte Geol. Als. Lorr. Bull.* **18**, 243-252.

BONHOMME M., VIDAL P. and COGNE J. (1968) Determination de l'age tectonique de la Series Ordovicenne et Siurienne de l'anse du Veryac'h (Presq'ile de Crozen, Linistere). *Serv. Carte Geol. Als. Lorr. Bull.* **21**, 249-252.

BONHOMME M. and CLAUER N. (1972) Possibilities d'utilisation stratigraphique des datations directes rubidium-strontium sur les roches sedimentaire: Colloque sur les Methodes et Tendancies de la Stratigraphie. *Science de la Terre* **3**, 539-565.

BRUECKNER H.K. and SNYDER W.S. (1985) Chemical and Sr isotopic variations during diagenesis of Miocene siliceous sediments of the Monterey Formation, California. *J. Sediment. Petrol.* **55**, 553-568.

BURKE W.H., DENISON R.E., HETHERINGTON E.A., KOEPNICK R.B., NELSON N.F. and OTTO J.B. (1982) Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time. *Geology* **10**, 516-519.

CARPENTER S.J. and LOHMANN K.C. (1989) $\delta^{18}O$ and $\delta^{13}C$ variations in Late Devonian marine cements from the Golden Spike and Nevis Reefs, Alberta, Canada. *J. Sediment. Petrol.* **59**, 792-814.

CHAUDHURI S. and BROOKINS D.G. (1969) The isotopic age of the Flathead sandstone (Middle Cambrian) Montana. *J. Sediment. Petrol.* **39**, 364-368.

CHAUDHURI S. and BROOKINS D.G. (1979) The Rb-Sr systematics in acid-leached clays. *Chem. Geol.* **24**, 231-242.

CLAUER N. (1981) Rb-Sr and K-Ar dating of Precambrian clay and glauconies. *Precamb. Res.* **15**, 331-352.

CLAUER N. (1982) The rubidium-strontium method applied to sediments: Certitudes and uncertainties. In *Numerical Dating in Stratigraphy: Timing of the Geochemical Evolution* (ed. G.S. ODIN), pp. 245-276. John Wiley and Sons.

CLAUER N. and BONHOMME M. (1974) Isotopic homogenization of strontium in clays. *Intern. Meet. Geochron. Cosmochem. Isotope Geol.* 26-31.

CLAUER N., HOFFER M., GRIMAUD D. and MILLOT G. (1975) Composition isotopique du strontium d'eaux interstitelles extraited de sediments recents: Un argument in faveur de l'homogenesation isotopique des mineralaux argileus. *Geochim. Cosmochim. Acta* **39**, 1579-1582.

CLAYTON R.N. and MAYEDA T.K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochim. Cosmochim. Acta* **27**, 43-52.

CLAYTON R.N., FRIEDMAN I., GRAF D.L., MAYEDA T.K., MEENTS W.F. and SHIMP N.F. (1966) The origin of saline formation waters, 1. Isotopic composition. *J. Geophys. Res.* **77**, 3057-3067.

COMPSTON W. and PIDGEON R.T. (1962) Rubidium strontium dating of shales by the whole-rock method. *J. Geophys. Res.* **67**, 3493-3502.

CONNOLLY C.A. (1985) Shale diagenesis of the Wilrich Member, Spirit River Formation, northwest Alberta. B.Sc. Thesis, Univ. of Alberta, Edmonton, Alberta.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990a) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. I. Chemistry. *Appld. Geochem.* 5, 375-396.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990b) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. II. Isotope systematics and water mixing. *Appld. Geochem.* 5, 397-414.

CORDANI U.G., KAWASHITA K. and THORNAZ-FILHO A. (1978) Applicability of the rubidium-strontium method to shales and related rocks. In *Contributions to the Geologic Time Scale* (eds. G.V. COHEE *et al.*), pp. 93-117. Am. Assoc. Petrol. Geol.

CRAIG H. (1957) Isotopic standards for carbon and oxygen and correction factors for mass-spectrometer analysis of carbon dioxide. *Geochim. Cosmochim. Acta* 12, 133-149.

CRAIG H. (1961) Standards for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* 133, 1833-1834.

CRISS R.E. and FLECK R.J. (1987) Petrogenesis, geochronology, and hydrothermal systems of the northern Idaho batholith and adjacent areas based on $^{18}O/^{16}O$, $^{87}Sr/^{86}Sr$, K-Ar and $^{40}Ar/^{39}Ar$ studies. In *Geology of the Blue Mountains Region of Oregon, Idaho, and Washington: The Idaho Batholith and its Border Zone* (eds. T.L. VALLIER and H.C. BROOKS), pp. 95-138. U.S. Geol. Surv. Pap. 1436.

DEROO G., POWELL T.G., TISSOT B. and McCROSSAN R.G. (1977) The origin and migration of petroleum in the western Canadian sedimentary basin, Alberta - A geochemical and thermal maturity study. *Geol. Surv. Can. Bull.* 262.

DICKINSON W.R. and SNYDER W.S. (1978) Plate tectonics of the Laramide Orogeny. In *Laramide Folding Associated with Basement Block Faulting in the Western United States*, (ed. MATHEWS V. III), pp. 355-366. Geol. Soc. Am. Mem. 151.

DICKSON J.A. (1965) A modified staining technique for carbonates in thin section. *Nature* 219, 587.

EISBACHER G.H., CARRIGY M.A. and CAMPBELL R.B. (1974) Paleodrainage pattern and late orogenic basins of the Canadian Cordillera. In *Tectonics and Sedimentation* (ed. W.R. DICKINSON), pp. 143-146. S.E.P.M. Spec. Pub. 22.

EPSTEIN S., GRAF D.L. and DEGENS E.T. (1964) Oxygen isotope studies on the origin of dolomite. In *Isotopic and Cosmic Chemistry* (eds. H. CRAIG *et al.*), pp. 169-180. North Holland Publishing Company.

FAURE G. (1986) *Principles of Isotope Geology (2nd Ed.).* John Wiley and Sons.

FAURE G. and POWELL J.L. (1972) *Strontium Isotope Geology.* Springer-Verlag.

FAURE G. and TAYLOR K.S. (1983) Sedimentation in the Ross Embayment: Evidence from RISP core 8(1977/78). In *Antarctic Earth Science* (eds. R.L. OLIVER, P.R. JAMES and J.B. JAGO), pp. 546-549. Australian Academy of Science, Canberra.

GALLOWAY W.E. (1984) Hydrogeologic regimes of sandstone diagenesis. In *Clastic Diagenesis* (eds. D.A. McDONALD and R.C. SURDAM), pp. 3-13. Am. Assoc. Petrol. Geol. Mem. 37.

GARVEN G. (1989) A hydrogeologic model for the formation of giant oil sands deposits of the western Canada sedimentary basin. *Am. J. Sci.* **289**, 105-166.

GAUDETTE H.E., GRIM R.E. and METZGER C.E. (1966) Illite, a model based on the sorption behavior of cesium. *Am. Mineral.* **51**, 1649-1656.

GLASMANN J.R., CLARK R.A., LARTER S., BRIEDIS N.A. and LUNDEGARD P.D. (1989) Diagenesis and hydrocarbon accumulation, Brent Sandstone (Jurassic), Bergen High Area, North Sea. *Am. Assoc. Petrol. Geol. Bull.* **73**, 1341-1360.

HACQUEBARD P.A. (1977) Rank of coal as an index of organic metamorphism for oil and gas in Alberta. In *The Origin and Migration of Petroleum in the Western Canadian Sedimentary Basin, Alberta* (eds. G. DEROO, T.G. POWELL, B. TISSOT, R.G. McCROSSAN), pp. 11-22. Geol. Surv. Can. Bull. **262**.

HART S.R. and TILTON G.R. (1966) The isotopic geochemistry of strontium and lead in Lake Superior sediments and water. In *The Earth Beneath the Continents* (J.S. STEINHART and T.S. SMITH), pp. 127-137. Am. Geophys. Union. Geophys. Mono. **10**.

HITCHON B. (1969a) Fluid flow in the Western Canada Sedimentary Basin, 1. Effect of topography. *Water Resour. Res.* **5**, 186-195.

HITCHON B. (1969b) Fluid flow in the Western Canada Sedimentary Basin, 2. Effect of geology. *Water Resour. Res.* **5**, 460-469.

HITCHON B. (1984) Geothermal gradients, hydrodynamics, and hydrocarbon occurrence, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* **68**, 713-743.

HITCHON B. and FRIEDMAN I. (1969) Geochemistry and origin of formation waters in the western Canada sedimentary basin – I. Stable isotopes of hydrogen and oxygen. *Geochim. Cosmochim. Acta* **33**, 1321-1349.

HOFMANN A., MAHONEY J.W. and GILETTI J. (1974) K-Ar and Rb-Sr data on detrital and post-depositional history of Pennsylvanian clay from Ohio and Pennsylvania. *Geol. Soc. Am. Bull.* **85**, 639-644.

HOWER J., ESLINGER E.V., HOWER M.E. and PERRY E.A. (1976) Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence. *Geol. Soc. Am. Bull.* **87**, 725-737.

HUANG W.L., BISHOP A.M. and BROWN R.W. (1986) The effect of fluid/rock ratio on feldspar dissolution and illite formation under reservoir conditions. *Clay Mins.* **21**, 585-601.

HURST A. and IRWIN H. (1982) Geological modelling of clay diagenesis in sandstones. *Clay Mins.* **17**, 5-22.

HURST R.W. (1986) Discussion: Chemical and Sr isotopic variations during diagenesis of Miocene siliceous sediments of the Monterey Formation, California - Discussion of the Sr isotopic data and its relevance to the timing of Monterey Formation fracturing. *J. Sediment. Petrol.* **56**, 569-573.

IWUAGWU C.J. and LERBEKMO J.F. (1981) The role of authigenic clays in some reservoir characteristics of the basal Belly River sandstone, Pembina Field, Alberta. *Bull. Can. Petrol. Geol.* **29**, 479-491.

JACKSON M.L. (1979) *Soil Chemical Analysis - Advanced Course (2nd ed.).* Madison, Wisconsin, published by the author.

JORDON T.E. (1981) Thrust loads and foreland basin evolution, Cretaceous western United States. *Am. Assoc. Petrol. Geol. Bull.* **65**, 2506-2520.

KRALIK M. (1984) Effects of cation-exchange treatment and acid leaching on the Rb-Sr system of illite from Fithian, Illinois. *Geochim. Cosmochim. Acta* **48**, 527-533.

KUBLER B. (1966) La cristallinite de l'illite et les zones tout a fait superieures du metamorphisme. *Colloque sur les etages tectoniques*. Univ. Neuchatel, A la Baconniere Ed., Neuchatel, 105-122.

LAND L.S. (1984) Frio sandstone diagenesis, Texas Gulf Coast: A regional study. In *Clastic Diagenesis* (D.A. McDONALD and R.C. SURDAM), pp. 81-98. Am Assoc. Petrol. Geol. Mem. 37.

LAND L.S. and MILLIKEN K.L. (1981) Feldspar diagenesis in the Frio Formation, Brazoria County, Texas Gulf Coast. *Geology* **9**, 314-318.

LONGSTAFFE F.J. (1986) Oxygen isotope studies of diagenesis in the basal Belly River sandstone, Pembina I-Pool, Alberta. *J. Sediment. Petrol.* **56**, 78-88.

LONGSTAFFE F.J. and AYALON A. (1987) Oxygen-isotope studies of clastic diagenesis in the Lower Cretaceous Viking Formation, Alberta: Implications for the role of meteoric water. In *Diagenesis of Sedimentary Sequences* (ed. J.D. MARSHALL), pp. 277-296. Geol. Soc. Spec. Pub. 36.

MAJORWICZ J.A., RAHMAN M., JONES F.W. and McMILLAN N.J. (1985) The paleogeothermal and present thermal regimes of the Alberta basin and their significance for petroleum occurrences. *Bull. Can. Petrol. Geol.* **33**, 12-21.

MASSEY K.W. (1984) Rubidium-strontium geochronology and petrography of the Hammamat Formation in the Northeastern desert of Egypt. M.Sc. Thesis, University of Texas at Dallas, Dallas, Texas.

McCREA J.M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.* **18**, 849-857.

MORTON J.P. (1983) Rubidium-strontium dating of clay diagenesis. Unpublished Ph.D. Diss. Univ. of Texas at Austin, Austin, Texas.

MORTON J.P. (1985a) Rb-Sr evidence for punctuated illite/smectite diagenesis in the Oligocene Frio Formation, Texas Gulf Coast. *Geol. Soc. Am. Bull.* **96**, 114-122.

MORTON J.P. (1985b) Rb-Sr dating of diagenesis and source age of clays in Upper Devonian black shale of Texas. *Geol. Soc. Am. Bull.* **96**, 1043-1049.

MORTON J.P. and LONG L.E. (1980) Rb-Sr dating of Paleozoic glauconite from the Llano region, central Texas. *Geochim. Cosmochim. Acta* **44**, 663-672.

NADEAU P.H. and BAIN D.C. (1986) Composition of some smectites and diagenetic illitic clays and implications for their origin. *Clays and Clay Mins.* **34**, 455-464.

NEWMAN A.C. (1970) The synergetic effect of hydrogen ions on the cation exchange of potassium in micas. *Clay Mins.* **8**, 361-373.

NURKOWSKI J.R. (1984) Coal quality, coal rank variation and its relation to reconstructed overburden, Upper Cretaceous and Tertiary Plains coals, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* **68**, 285-295.

OBRADOVICH J.D. and PETERMAN Z.E. (1968) Geochronology of the Belt Series, Montana. *Can. J. Earth Sci.* **5**, 737-747.

PERRY E.A., Jr. and TUREKIAN K.K. (1974) The effects of diagenesis on the redistribution of strontium isotopes in shales. *Geochim. Cosmochim. Acta* **38**, 929-936.

PIEL K. (1971) Palynology of Oligocene sediments of central British Columbia. *Can. J. Bot.* **49**, 1885-1920.

PORTER J.W., PRICE R.A. and McCROSSAN R.G. (1982) The Western Canada Sedimentary Basin. *Roy. Soc. Phil. Trans.* **305**, 169-192.

PRICE R.A. (1973) Large scale gravitational flow of supra-crustal rocks, southern Canadian Rocky Mountains. In *Gravity and Tectonics* (ed. K.A. DEGONG and R.S. CHOLTEN), pp. 491-502. Wiley.

ROBERSON H.E. AND LAHANN R.W. (1981) Smectite to illite conversion rates: Effects of solution chemistry. *Clays and Clay Mins.* **21**, 249-259.

SAVIN S.M. and YEH H. (1981) Stable isotopes in ocean sediments. In *The Sea, The Oceanic Lithosphere* (ed. C. EMILIANI), pp. 1521-1554. 7, Wiley.

SAVIN S.M. and LEE M. (1988) Isotopic studies of phyllosilicates. In *Hydrous Phyllosilicates (exclusive of micas)* (ed. S.W. BAILEY), pp. 189-223. Reviews in Mineralogy.

SCHULTZ J.L., BOLES J.R. and TILTON G.R. (1989) Tracking calcium in the San Joaquin basin, California: A strontium isotopic study of carbonate cements of North Coles Levee. *Geochim. Cosmochim. Acta* 53, 1991-2000.

SHAFFER N.R. and FAURE G. (1976) Regional variation of ^{87}Sr/^{86}Sr ratios and mineral composition of sediment in the Ross Sea. *Geol. Soc. Am. Bull.* 87, 1491-1500.

SHARMA T. and CLAYTON R.N. (1965) Measurements of O^{18}/O^{16} ratios of total oxygen of carbonates. *Geochim. Cosmochim. Acta* 29, 1347-1353.

STANLEY K.O. and FAURE G. (1979) Isotopic composition and sources of strontium in sandstone cements: The High Plains sequence of Wyoming and Nebraska. *J. Sediment. Petrol.* 49, 45-54.

STUEBER A.M., PUSHKAR P. and HETHERINGTON E.A. (1984) A strontium isotopic study of Smackover brines and associated solids, southern Arkansas. *Geochim. Cosmochim. Acta* 48, 1637-1649.

SUCHECKI R.K. and LAND L.S. (1983) Isotopic geochemistry of burial-metamorphosed volcanogenic sediments, Great Valley sequence, northern California. *Geochim. Cosmochim. Acta* 47, 1487-1499.

TAYLOR H.P. Jr. (1974) The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. *Econ. Geol.* 69, 843-883.

THOREZ J. (1976) Practical identification of clay minerals. G. Lelolte B 4820 Dison, Belgique.

TILLEY B.J. and LONGSTAFFE F.J. (1989) Diagenesis and isotopic evolution of porewaters in the Alberta Deep Basin: The Falher Member and Cadomin Formation. *Geochim. Cosmochim. Acta* 53, 2529-2546.

TOTH J. (1980) Cross-formational gravity-flow of groundwater: A mechanism of the transport and accumulation of petroleum (the generalized hydraulic theory of petroleum migration). In *Problems of Petroleum Migration* (eds. W.H. ROBERTS and R.J. CORDELL), pp.121-167. Am. Assoc. Petrol. Geol. Stud. in Geol., 10.

WALTERS L.J.,Jr., CLAYPOOL G.E. and CHOQUETTE P.W. (1972) Reaction rates and δO^{18} variation for the carbonate-phosphoric acid preparation method. *Geochim. Cosmochim. Acta* 36, 129-140.

WHITTAKER S.G., KYSER T.K. and CALDWELL W.G. (1987) Paleoenvironmental geochemistry of the Claggett marine cyclothem in south-central Saskatchewan. *Can. J. Earth Sci.* 24, 967-984.

YEH H. and SAVIN S.M. (1977) Mechanism of burial metamorphism of argillaceous sediments: 3. O-isotope evidence. *Geol. Soc. Am. Bull.* 88, 1321-1330.

Table 6.1. Stable and radiogenic isotopes and Rb and Sr concentrations for whole rocks and mineral separates from Precambrian to Upper Cretaceous formations in the Alberta Basin, south-central Alberta. Sample location, depth, lithology and composition of the analyzed separate are listed. Abbreviations used in the table are the following: * Illite leached with 0.6N two times vapour distilled HCl; ^ Illite treated with citrate bicarbonate to remove iron; WR = whole rock; SST. = sandstone; SH. = shale; SLTST. = siltstone; LST. = limestone; CALC. = calcareous; CAL = calcite; DOL = dolomite; ANK = ankerite. In addition to rock and mineral data, the range of $^{87}Sr/^{86}Sr$ ratios for modern fluids in corresponding reservoirs are listed (CONNOLLY *et al.*, 1990b).

SYSTEM	FORMATION	SAMPLE NAME	DEPTH (m)	LITHOLOGY	SIZE FRACTION	MINERAL ANALYZED	^{87}Sr/^{86}Sr RATIO	^{86}Sr (ppm)	TOTAL Sr (ppm)	^{87}Rb (ppm)	TOTAL Rb (ppm)	^{87}Rb/^{86}Sr	δ^{18}O	WATER ^{87}Sr/^{86}Sr AVERAGE
UPPER CRETACEOUS	BELLY RIVER	AVE. 8 SAMPLES	986.7-995	SST.	WR	CALCITE	0.70599						+13.0	0.70578-0.70634
		CC180.14	980.0	SST.	<0.1 Um	*ILL/SM	0.70899	10.92	112.95	24.95	88.15	2.26	+12.6	
					0.1-2.0 Um	CHLORITE	0.70650	26.14	270.33	4.30	15.18	0.16		
		CC180.10	988.7	SST.	WR	DOLOMITE	0.70697							
		CC180.05	992.7	SST.	WR	CALCITE	0.70584						+12.7	
					<0.1 Um	*ILL/SM	0.70880	11.88	122.80	25.88	91.43	2.15		
					<0.1 Um	CHLORITE	0.70663	110.28	1140.30	9.50	33.56	0.09		
		CC180.02	994.6	SST.	WR	CALCITE	0.70697							
					<0.1 Um	*ILL/SM	0.70818	18.26	188.85	27.18	96.03	1.47		
					0.1-2.0Um	CHLORITE	0.70887	58.66	606.53	7.60	26.84	0.13		
						MICROCLINE	0.71059	28.57	244.85	65.41	231.09	2.26		
	LEA PARK	CC179.2	995.3	SH.	WR	WR	0.70745							
					<0.1 Um	*ILL/SM								
					<0.1 Um	CHLORITE	0.70654	71.27	736.88	15.86	56.03	0.22	+13.3	
	CARDIUM	CC170.06	1303.8	SH.	<0.1 Um	*ILLITE	0.73168	7.31	75.81	73.25	258.81	9.90	+15.3	0.70738-0.70839
					<0.1 Um	CHLORITE	0.71040	57.16	519.24	33.83	119.53	0.59		
					0.1-2.0 Um	CHLORITE	0.71079	41.23	426.47	25.84	91.28	0.82		
		CC170.04	1306.5	SH.	WR	WR	0.71893							
		CC170.03	1308.7	SH.	WR	WR	0.71938							
					<0.1Um	*ILLITE	0.73157	7.82	81.08	74.56	263.41	9.42	+15.6	
					<0.1 Um	CHLORITE	0.71036	71.44	738.92	39.13	138.24	0.54		
					0.1-0.2 Um	CHLORITE	0.71087	53.91	557.65	38.09	134.57	0.70		
					0.2-2.0 Um	CHLORITE	0.71105	31.80	328.91	16.49	58.25	0.51		
		CC170.02	1310.3	SH.	WR	WR	0.71843							
		CC170.01	1309.4	SH.	WR	WR	0.71981							
LOWER CRETACEOUS	VIKING	CC162	1147.9	SST.	<0.1 Um	*ILLITE	0.71578	18.59	192.40	53.52	189.10	2.85	+15.6	0.70768-0.70894
					<0.1 Um	CHLORITE	0.70804	100.00	1034.11	22.18	78.37	0.22		
					0.1-2.0 Um	CHLORITE	0.70851	80.83	835.90	20.07	70.92	0.25		
		C631	2199.8	SST.	WR	CALCITE	0.70781						+14.9	
		Ciu/	2221.0		WR	ANKERITE	0.70747						+16.5	
		AVE. 4 SAMPLES	2160.2-3101.4	SST.	WR	SIDERITE	0.70796						+21.8	
	GLAUCONITIC	AVE. 3 SAMPLES	1757.8-1758.6	SST.	WR	CALCITE	0.70862						+14.9	0.70758-0.71024
		CC142.04	1754.3	SH.	WR	DOLOMITE	0.70928							
		CC142.03	1756.4	SH.	WR	CAL 1.5X/DOL1X	0.70785							
		CC142.01	1760.4	SH.	WR	CAL2.5X/DOL1X	0.70898							
		CC140	2285.9	SST.	<0.1 Um	*ILLITE							+15.9	
					<0.1 Um	CHLORITE	0.76254	11.63	121.05	35.27	124.62	3.00		
					<0.1 Um	ILLITE	0.71507	21.39	221.34	67.17	237.32	3.10	+14.1	
					0.2-2.0 Um	CHLORITE	0.71233	148.67	1538.13	27.86	98.44	0.19		
	OSTRACODE	CC130	1764.2	SH. / LST.	WR	CALCITE	0.70867						+17.8	0.70821-0.70859
	BASAL QUARTZ	CC156	1154.7	SH. / SLTST.	WR	WR	0.71181							0.70886-0.71131
					<0.1 Um	*ILL/SM	0.71449	16.64	172.14	39.78	140.56	2.36	+14.9	
					<0.1 Um	CHLORITE	0.70815	100.48	1039.14	22.32	78.87	0.22		
		CC150.13	1296.7	SST. / SLTST.	WR	WR	0.71363							
		CC150.12	1298.2	SST. / SLTST.	WR	WR	0.72187							
		CC150.08	1302.7	SST.	WR	CAL1X/DOL2.5X	0.71006							
		CC150.07	1303.6	SST. / SLTST.	WR	CAL2X/DOL1X	0.71073							

SYSTEM	FORMATION	SAMPLE NAME	DEPTH (m)	LITHOLOGY	SIZE FRACTION	MINERAL ANALYZED	^{87}Sr/^{86}Sr RATIO	^{86}Sr (ppm)	TOTAL Sr (ppm)	^{87}Rb (ppm)	TOTAL Rb (ppm)	^{87}Rb/^{86}Sr	δ^{18}O	WATER ^{87}Sr/^{86}Sr AVERAGE
LOWER CRETACEOUS	BASAL QUARTZ	CC150.65	1304.2	SH.	WR	WR	0.71171							
					<0.1 UM	' ILLITE	0.71170						+15.7	
					<0.1 Um	CHLORITE	0.71047	106.95	1106.28	31.60	111.64	0.29		
					0.1-2.0 Um	CHLORITE	0.71056	83.51	863.86	19.28	68.13	0.23		
		CC150.02	1311.2	SH.	WR	WR	0.71742							
					<0.1 Um	ILLITE	0.71802	21.84	226.03	72.60	256.51	3.29	+15.2	
	BASAL QUARTZ SAND	CC126	1320.9	SST.	0.1-0.2 Um	ILLITE							+15.9	
					0.1-0.2 Um	CHLORITE	0.71046	85.08	880.01	48.32	170.72	0.56		
		CC122	1324.5	SST.	0.1-2.0 Um	CHLORITE	0.71240	26.50	274.16	20.33	71.84	0.76		
		CC120.02	1330.8	SST.	WR	ANK/DOL	0.71121							
					0.1-2.0 Um	CHLORITE	0.71111	36.58	378.35	21.30	75.24	0.58		
		CC120.01	1333.7	SST.	WR	ANK/DOL	0.71104							
		CC120	1337.6	SST.	WR	CALCITE	0.70820						+15.5	
JURASSIC	ROCK CREEK	CC110.06	2331.2	SLTST.	<0.1 Um	*ILLITE	0.71857	45.01	465.90	49.32	174.24	1.08	+14.6	0.71220-0.71168
		CC110.03	2337.5	SST.	WR	CALCITE	0.71282							
					<0.1 Um	ILLITE	0.71311	31.96	330.64	60.83	214.93	1.88	+14.3	
		CC110.02	2343.5	LST. / SLTST.	WR	CAL1.7X /ANK1X	0.70916							
					<0.1-0.2 Um	ILLITE	0.72154	8.94	92.56	58.79	207.70	6.50		
		CC114	2344.8	LST. / SLTST.	WR	CAL/ANK	0.70859							
		CC110.01	2346.6	SLTST.	WR	CAL4X/ANK1X	0.70877							
	POKER CHIP SHALE	CC108.01	2349.6	SH.	WR	WR	0.71171							
					<0.1 Um	*ILLITE	0.71329	41.16	425.86	76.14	269.02	1.83	+16.3	
					<0.1 Um	CHLORITE	0.71334	46.33	479.32	21.14	74.70	0.45		
	NORDEGG	AVE. 6 SAMPLES	1776.7–1806.2	LST.	WR	CALCITE	0.70836						+19.2	0.71037-0.71170
		CC101	1778.5	LST.	WR	CALCITE	0.70885	50.75	524.12	0.33	1.16	0.01		
					30-125 Um	APATITE	0.70883	103.65	1071.99	0.41	1.45	0.00		
		CC99.01	1782.2	LST.	WR	CALCITE	0.70892							
					30-125 Um	APATITE	0.70877	103.65	1071.91	0.40	1.43	0.00		
	FERNIE	CC90	1805.5	LST.	WR	CALCITE	0.70843						+22.2	
		CC92	1806.2	LST.	WR	CALCITE	0.70905						+19.7	
MISSISSIPPIAN	MISSISSIPPIAN	AVE. 3 SAMPLES	1774.9–1783.6	LST.	WR	CALCITE	0.70856						+19.7	0.70966-0.71031
		CC80.01	1783.0	LST.	WR	CALCITE	0.70848	25.95	268.05	0.48	1.70	0.02	+21.0	
						DOLOMITE	0.70916	56.39	583.26	1.47	5.19	0.05		
	EXSHAW	–	6978.8	SH.	WR	WR	0.71012							
UPPER DEVONIAN	WABAMUN	AVE. 3 SAMPLES	1368.1–1369.3	LST.	WR	CALCITE	0.70866						+22.5	0.71062-0.71128
		CC70	1370.4	LST.	WR	CALCITE	0.70902	21.80	225.25	2.54	8.96	0.12	+22.6	
					0.1-0.2 Um	*ILLITE	0.79783	4.20	43.81	101.46	358.46	23.98		
						D CALCITE	0.71388	70.28	727.26	45.52	150.83	0.64		
		AVE. 2 SAMPLES	1373.4–1374.0	LST.	WR	CALCITE	0.70957						+18.3	
	STETTLER	–	1510.9	CALC. SH.	WR	DOLOMITE	0.71167	29.41	304.28	7.36	26.01	0.25		
					<2.0 Um	*ILLITE	0.78839	3.43	35.78	67.38	238.07	19.40		
	GRAMINEA	–	1533.3	CALC. SH.	WR	WR	0.79914							
					<0.1 Um	*ILLITE	0.76410	3.70	38.44	71.94	254.18	19.23	+20.3	
					<0.1 Um	ILLITE	0.74073	6.78	70.29	66.71	235.60	9.73	+19.4	

SYSTEM	FORMATION	SAMPLE NAME	DEPTH (m)	LITHOLOGY	SIZE FRACTION	MINERAL ANALYZED	^{87}Sr/^{86}Sr RATIO	^{86}Sr (ppm)	TOTAL Sr (ppm)	^{87}Rb (ppm)	TOTAL Rb (ppm)	^{87}Rb/^{86}Sr	δ^{18}O	WATER ^{87}Sr/^{86}Sr AVERAGE
UPPER DEVONIAN	CALMAR	-	1545.0	CALC. SH.	WR	WR	0.73890							
					<0.1 Um	ILLITE	0.73869	7.16	74.25	45.64	161.25	6.30	+20.0	
		-	1870.6	CALC. SH.	WR	WR	0.72816							
					<0.1 Um	ILLITE	0.72836	8.83	91.46	67.11	237.10	7.52	+20.2	
	NISKU	AVE. 4 SAMPLES	1551.1-1554.8	DOLOSTONE	WR	DOLOMITE	0.70878							0.70898-
		CC60	1553.6	DOLOSTONE	WR	DOLOMITE	0.70842	24.27	250.69	0.29	1.01	0.01	+26.7	0.71206
						ANHYDRITE	0.70992	412.88	4270.59	0.03	0.12	0.00		
	IRETON	-	1639.4	CALC. SH.	WR	WR	0.73077							
					<0.1 Um	ILLITE	0.73534	9.03	93.60	66.87	236.27	7.32	+19.8	
	LEDUC	AVE. 10 SAMPLES	1831.2-1843.3	DOLOSTONE	WR	DOLOMITE	0.70826						+24.8	0.70872-
		CC50	1844.6	DOLOSTONE	WR	DOLOMITE	0.70825	8.09	83.59	0.08	0.27	0.01	+25.0	0.70981
	DUVERNEY	-	2648.9	CALC. SH.	WR	WR	0.71283							
					<0.1 Um	ILLITE							+16.0	
					0.1-2.0 Um	*ILLITE	0.75206	5.01	52.06	45.54	160.89	8.98	+19.8	
	COOKING LAKE	AVE. 4 SAMPLES	1845.3-1848.6	DOLOSTONE	WR	DOLOMITE	0.70830						+24.9	
	BEAVERHILL LAKE	-	1955.9UD	LST.		CALCITE	0.71893						+24.0	
		-	1955.9D			CALCITE	0.75810							
		-	2088.4	LST.	WR	WR	0.70872							
MIDDLE DEVONIAN	ELKPOINT	CC32	2251.6	DOLOSTONE	WR	ANKERITE	0.70962						+29.6	
		CC30.03	2252.1	DOLOSTONE	WR	DOLOMITE	0.70936	9.50	98.22	1.61	5.68	0.17	+27.6	
		AVE. 4 SAMPLES	2252.6-2254.8	DOLOSTONE	WR	DOLOMITE	0.70926						+28.6	
	VARIABLE SHALE			SH.	WR	WR	0.72492							
					<0.1 Um	*ILLITE	0.82989	1.83	19.10	65.42	231.12	35.40		
					<0.1 Um	CHLORITE	0.71776	9.09	94.13	11.22	39.65	1.22		
						FELDSPAR	0.77604	22.58	235.01	63.88	225.70	2.80		
UPPER/MIDDLE CAMBRIAN	CAMBRIAN	CC20	2634.7	SH. / SLTST.	WR	WR	0.74307							
		CC16.14	2635.3	SH. / SLTST.	WR	CAL/ANK/DOL	0.74716							
		CC18	2635.6	SH. / SLTST.	WR	WR	0.77173							
					0.1-0.2 Um	*ILLITE	0.76893	1.60	16.66	47.58	168.10	29.37		
		CC16.13	2635.8	SH. / SLTST.	WR	WR	0.77995							
					WR	CAL2X/ANKDOL1X	0.74365							
		CC16.12	2636.1	SH. / SLTST.	WR	WR	0.77658							
					<0.1Um	*ILLITE	0.76916	2.89	30.06	57.32	202.51	19.61	+13.7	
					0.1-0.2Um	ILLITE	0.75087	4.66	48.42	49.48	174.80	10.49	+13.8	
					<0.1 Um	CHLORITE	0.74576	16.16	167.72	24.45	86.39	1.50		
		CC16.11	2637.7	SH. / SLTST.	WR	WR	0.76180							
					<0.1 Um	*ILLITE	[illegible]	2.18	22.69	50.52	178.48	22.89		
					0.1-0.2 Um	CHLORITE	0.75320	6.66	69.18	21.30	75.24	3.16		
		CC16.10	2637.8	SH. / SLTST.	WR	WR	0.77876							
					WR	CAL1.5X/ANKDOL1X	0.74922							
		CC16.09	2638.5	SH. / SLTST.	WR	WR	0.76364							
		CC16.08	2639.2	SH. / SLTST.	WR	WR	[illegible]							
					<0.1 Um	*ILLITE	0.74037	0.76	7.92	53.13	187.71	68.83	+13.9	
					0.2-2.0 Um	CHLORITE	0.76386	9.77	101.60	14.90	52.63	1.51		
		CC16.07	2640.1	SH. / SLTST.	WR	WR	0.77655							
		CC16.06	2640.9	SH. / SLTST.	WR	WR	0.77161							

SYSTEM	FORMATION	SAMPLE NAME	DEPTH (m)	LITHOLOGY	SIZE FRACTION	MINERAL ANALYZED	$^{87}Sr/^{86}Sr$ RATIO	^{86}Sr (ppm)	TOTAL Sr (ppm)	^{87}Rb (ppm)	TOTAL Rb (ppm)	$^{87}Rb/^{86}Sr$	$\delta^{18}O$	WATER $^{87}Sr/^{86}Sr$ AVERAGE
UPPER/MIDDLE CAMBRIAN	CAMBRIAN	CC16.05	2641.7	SH. / SLTST.	WR	WR	0.77959							
					<0.1Um	*ILLITE	0.73009							
					0.1-0.2 Um	*ILLITE	0.74357							
					<0.1-0.2 Um	CHLORITE	0.74330	20.85	216.36	26.51	93.67	1.26		
		CC16.04	2642.0	SH. / SLTST.	WR	WR	0.75689							
		CC16.03	2643.2	SH. / SLTST.	WR	WR	0.75101							
		CC16.02	2643.6	SH. / SLTST.	WR	WR	0.75410							
		CC16.01	2644.1	SH. / SLTST.	WR	WR	0.75625							
LOWER CAMBRIAN		CC14	2701.4	SST.	<0.1 Um	*ILLITE							+12.0	
					0.1-0.2 Um	*ILLITE	0.74263	1.96	20.33	46.43	164.05	23.42		
					0.2-2.0 Um	*ILLITE	0.74549	12.95	134.42	40.50	143.10	3.09		
		CC11.05	2701.8	SST.	WR	ANKERITE	0.74923						+19.6	
		CC11.01	2733.9	SST.	WR	ANK/DOL	0.75038							
PRECAMBRIAN/ CAMBRIAN		CC10		SST.	<0.1Um	*ILLITE	0.77748							
					<0.1-0.1 Um	CHLORITE	0.76306	20.36	211.45	57.86	204.42	2.81		
					0.1-0.2Um	*ILLITE	0.79140							
					30-125 Um	FELDSPAR	0.94428	13.13	138.88	130.47	460.95	9.82		
PRECAMBRIAN	PRECAMBRIAN	C1	2738.9	GRANITE	WR	WR	1.14523							
			2738.9		<0.1 Um	*ILLITE	0.96429						+14.4	
					0.1-0.2 Um	*ILLITE	1.01094						+13.8	
					0.1-2.0 Um	CHLORITE	0.70933	311.20	3218.60	37.70	133.19	0.12		

Table 6.2. Calculated Rb/Sr model ages of diagenetic illite in Precambrian to Cretaceous formations in the Alberta Basin. Those samples highlighted with a * denote a >0.2 μm size fraction, all others were <0.1 μm. Samples with an L after their sample name denote leached samples. Several initial ^{87}Sr/^{86}Sr ratios were selected for each sample. The first is the seawater ^{87}Sr/^{86}Sr value, taken from the BURKE *et al.* (1982) seawater curve, for the time of deposition of the sample; in general higher values were also selected, as generally the ^{87}Sr/^{86}Sr ratio of authigenic minerals and porewater increase over time, due to the decay of ^{87}Rb to ^{87}Sr.

SYSTEM	FORMATION	SAMPLE NUMBER	LITHOLOGY	^{87}Sr/^{86}Sr	I MODEL AGE Ma
CRETACEOUS	CARDIUM	CC170.06L	SH.	0.7074	170
				0.7090	160
		CC170.03L	SH.	0.7074	180
				0.7090	170
	VIKING	CC162L	SST.	0.7072	160
	GLAUCONITIC	CC140L	SH.	0.7072	180
				0.7090	140
	BASAL QUARTZ	CC156	SH. / SLTST.	0.7072	220
				0.7090	160
JURASSIC	ROCK CREEK	CC110.05L	SLTST.	0.7070	750
				0.7090	620
	POKER CHIP SHALE	CC108.01L	SH.	0.7070	240
DEVONIAN	WABAMUN	CC70L	LST.	0.7082	260
				0.7200	230
	STETTLER*	-L	CALC. SH.	0.7080	290
				0.7200	250
	GRAMINEA	-	CALC. SH.	0.7080	240
				0.7200	150
	CALMAR	1545	CALC. SH.	0.7080	340
				0.7200	210
		1870.6	CALC. SH.	0.7080	190
				0.7200	80
	IRETON	-	CALC. SH.	0.7080	260
				0.7200	150
	DUVERNEY*	-L	CALC. SH.	0.7090	340
				0.7200	250
CAMBRIAN	CAMBRIAN	CC18L	SH. / SLTST.	0.7090	140
				0.7200	120
		CC16.12L	SH. / SLTST.	0.7090	220
				0.7200	180
		CC16.11L	SH. / SLTST.	0.7090	170
				0.7200	140
		CC14L	SST.	0.7090	100
				0.7200	70

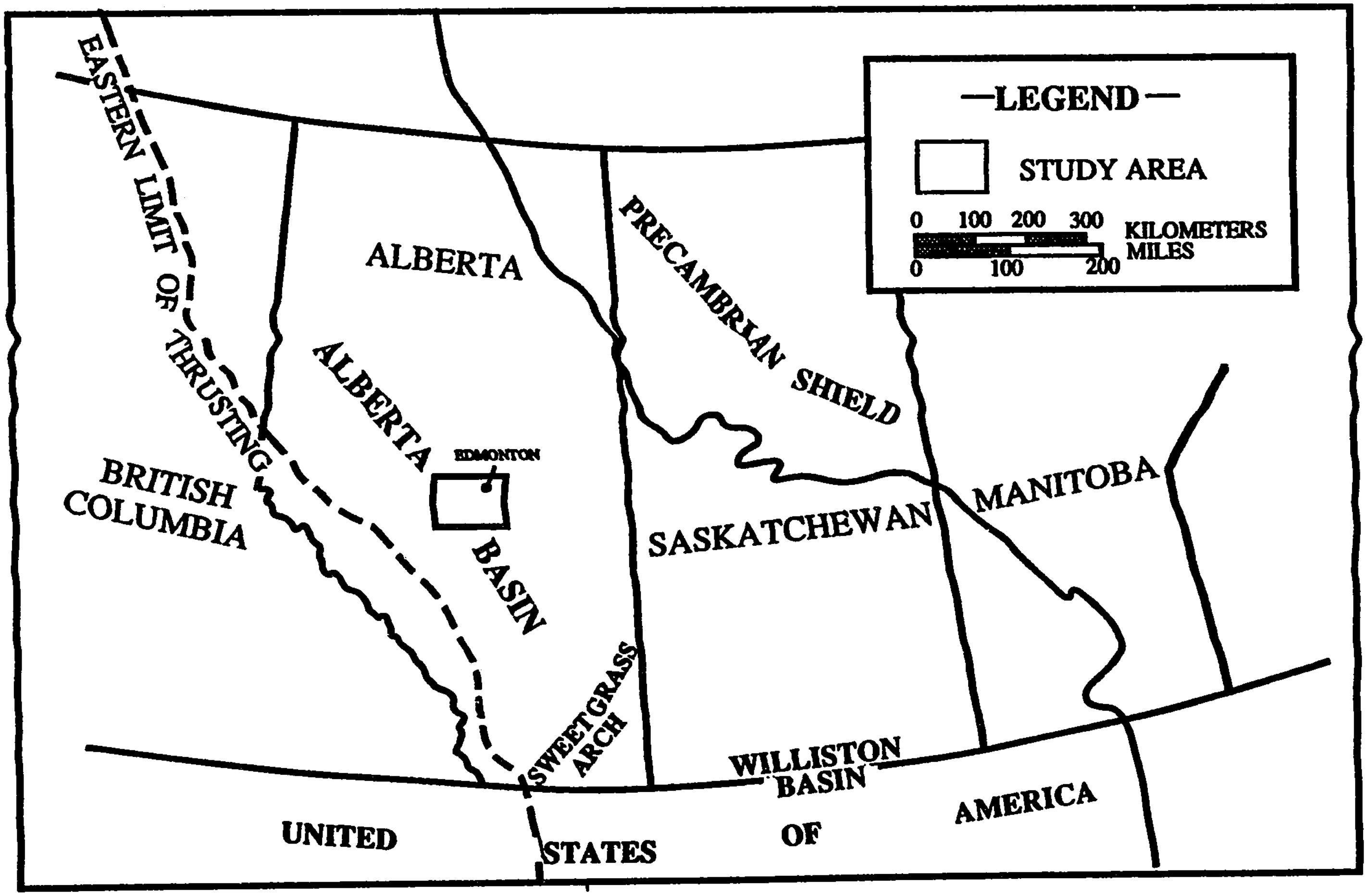


Fig. 6.1. Map of the Western Canada Sedimentary Basin, showing the location of the sub basins and the study area.

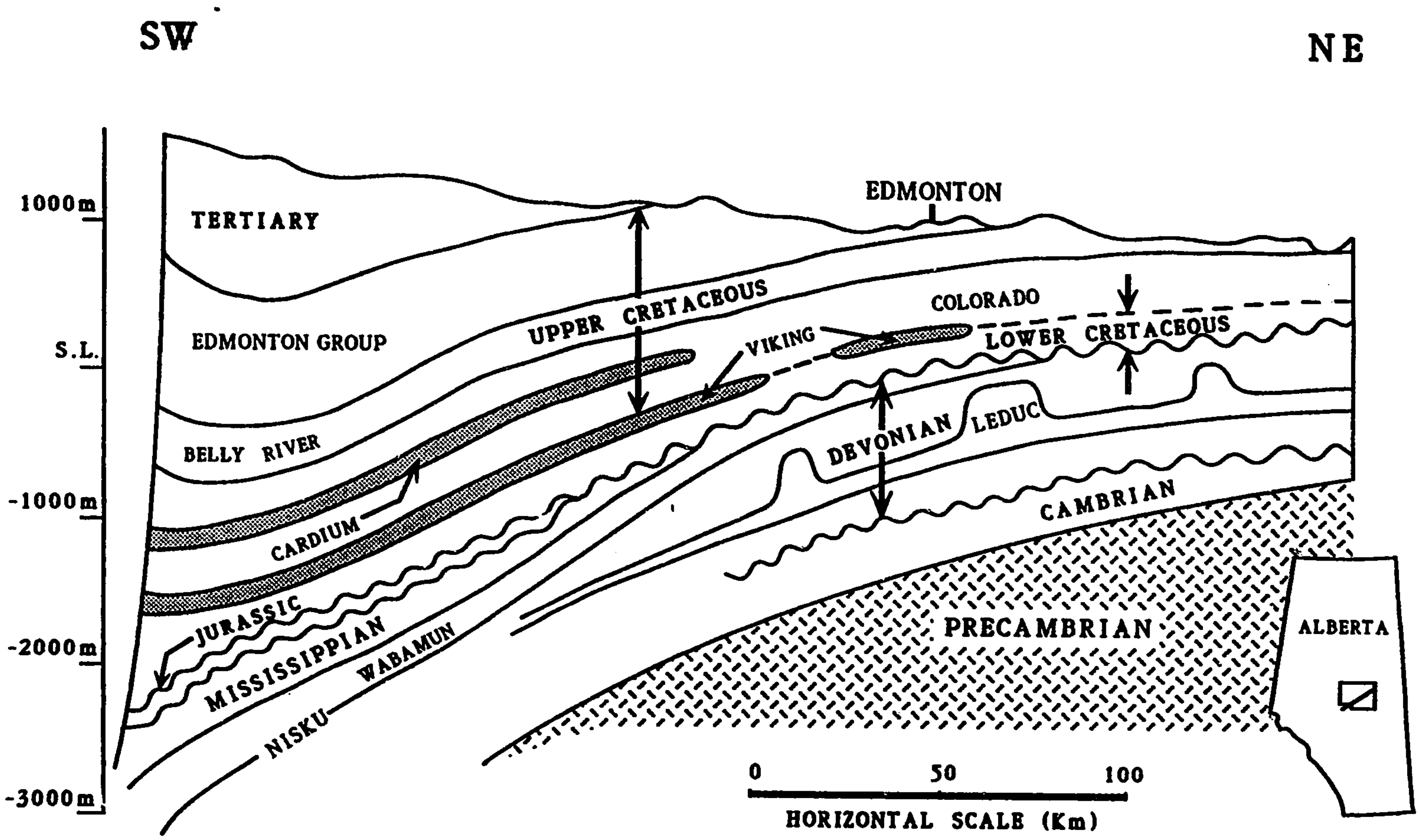


Fig. 6.2. Geological cross-section from SW to NE through the Alberta Basin, illustrating the major stratigraphic units and unconformities.

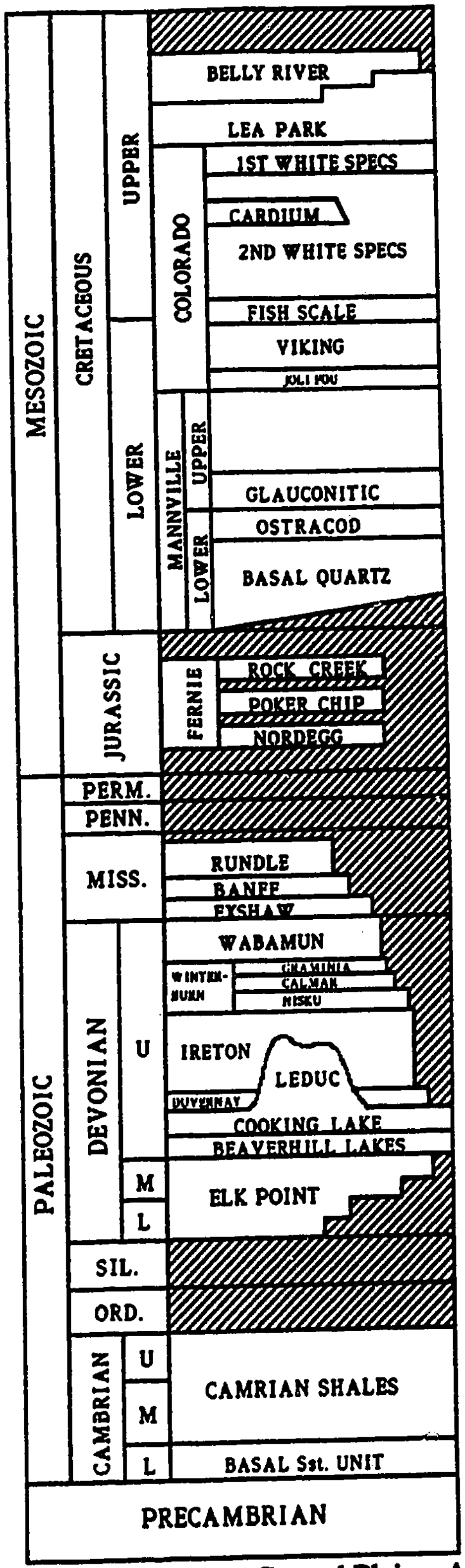


Fig. 6.3. Generalized stratigraphic column, Central Plains, Alberta Basin (modified after the *Energy Resources Conservation Board, Table of Formations*).

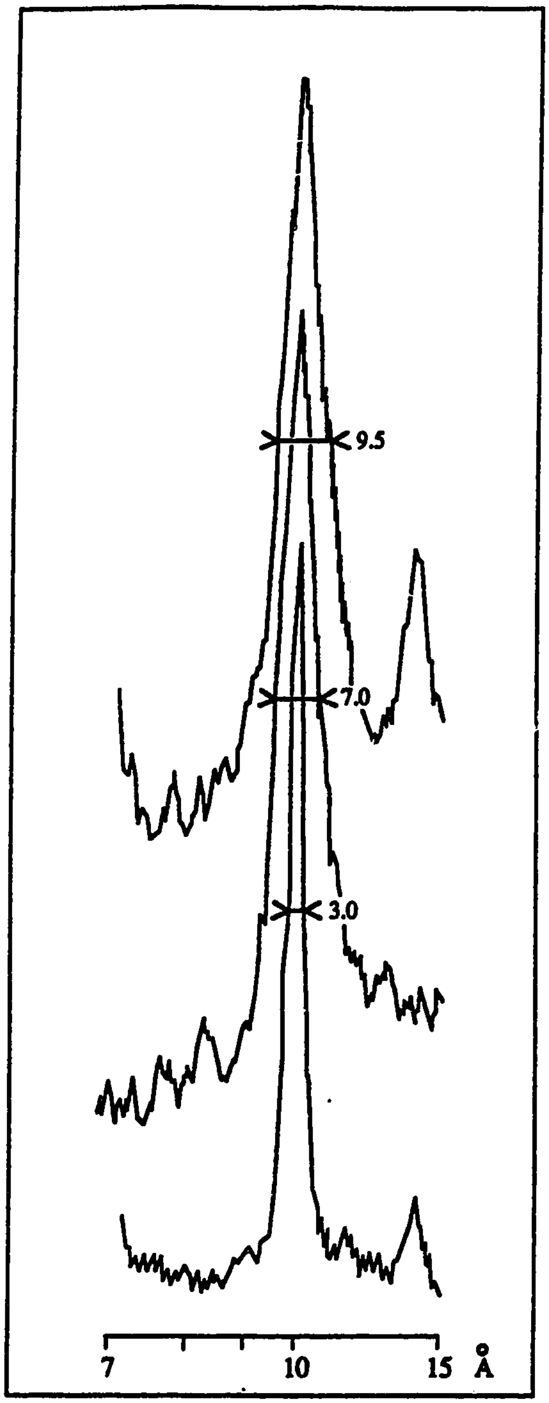


Fig. 6.4. Different standard illite crystallinity indices defined by Kubler (1966). These indices were established using CuKα radiation; therefore the data in this study had to be converted from CoKα radiation to CuKα values. Illite crystallinity values <3.0 characterize greenschist facies and values >5.5 correspond to diagenetic domains. Values between 3.0 and 5.5 are an overlap zone.

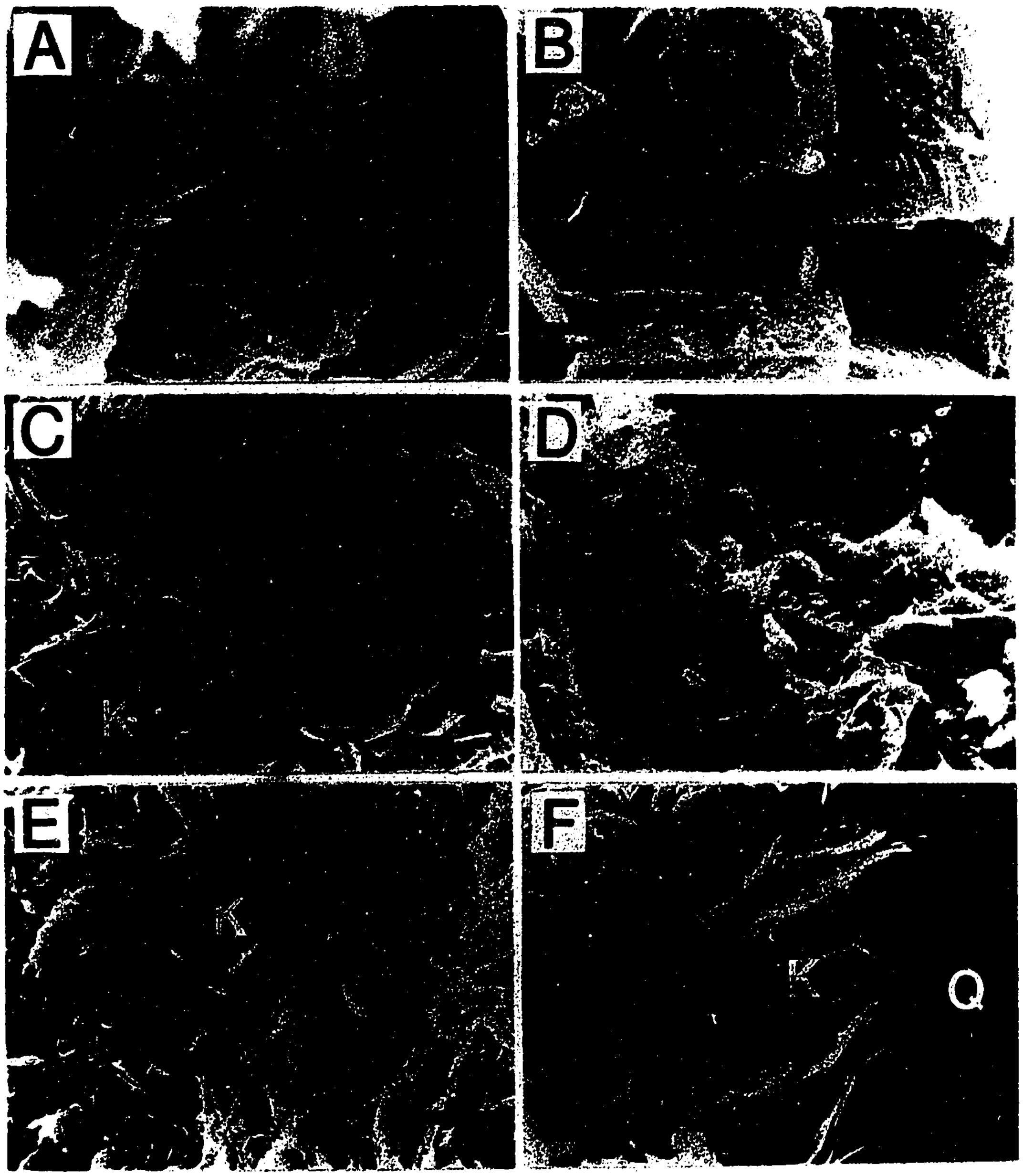
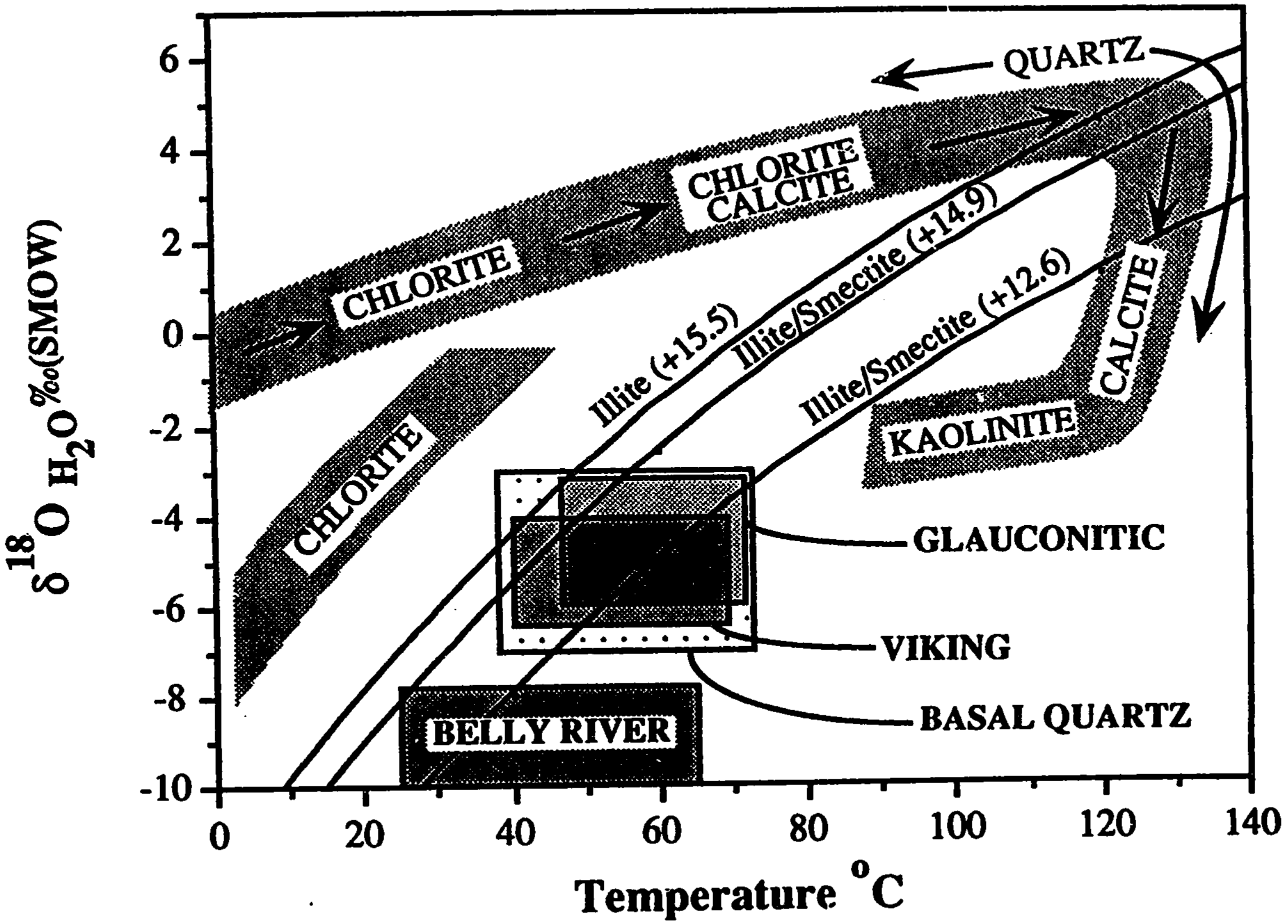


Fig. 6.5. (a) Devonian - filamentous illite (I) overlying carbonate (C) and growing into pore space. Scale bar = 1μm. (b) Devonian - authigenic illite (I) mat overlying carbonate (C). Scale bar = 1μm. (c) Cambrian shale - filamentous hairy illite (I) growing into pore space. Illite overlying and altering kaolinite (K). Scale bar = 2μm. (d) Overview of picture (c) illustrating the whole pore and the distribution of filamentous illite. Scale bar = 10μm. (e) Cambrian sandstone - altered kaolinite (K) with filamentous illite (I) overlying. Scale bar = 4μm. (f) Cambrian sandstone - kaolinite (K) filling in pore and overlying quartz grain (Q). Filamentous illite (I) overlying kaolinite. Scale bar = 2μm.

Fig. 6.6. $\delta^{18}O_{(SMOW)}$ of porewater versus temperature (°C) for diagenetic illite and illite/smectite minerals in Cretaceous formations. The curves for the minerals represent the average illite value and the maximum and minimum values for the illite/smectites in the Cretaceous rocks. The curves shown for each phase were calculated using the following equation (T = degrees K): $10^3\ln\alpha_{Illite\text{-}H2O} = [(2.58 - 0.19 \times I)] (10^6)T^{-2}$-4.19 (YEH and SAVIN, 1977; SAVIN and LEE; I = fraction of illite in illite/smectite. An I value of 75% was used for the Belly River Formation for I/S with $\delta^{18}O$ = +12.6‰. An I value of 80% was used for the Basal Quartz Formation for I/S with $\delta^{18}O$ = +14.9‰. The fields encompassing present day conditions for the primary reservoirs in Cretaceous rocks are outlined. A schematic representation of the general paragenesis and porewater evolution curve for Cretaceous formations is shown. A high degree of variability is exhibited for the initial pore fluid composition of the various formations, depending on whether the formations were deposited under brackish (-4 to -8‰) or marine (0 to -4‰) conditions. However, all the Cretaceous formation fluids followed a similar trend of increasing $\delta^{18}O$ values with burial diagenesis and increasing temperature followed by a decrease in pore fluid $\delta^{18}O$ values and temperature with the ensuing Laramide Orogeny. The minerals shown on the pore water evolution curve imply the general paragenetic sequence for all the formations; however, slight modifications within separate formations occur.


QUARTZ
CHLORITE CALCITE
CHLORITE
CHLORITE
Illite (+15.5)
Illite/Smectite (+14.9)
Illite/Smectite (+12.6)
CALCITE
KAOLINITE
GLAUCONITIC
VIKING
BASAL QUARTZ
BELLY RIVER
6
4
2
0
-2
-4
-6
-8
-10
0
20
40
60
80
100
120
140
Temperature °C
$\delta^{18}O\ H_2O$ ‰(SMOW)

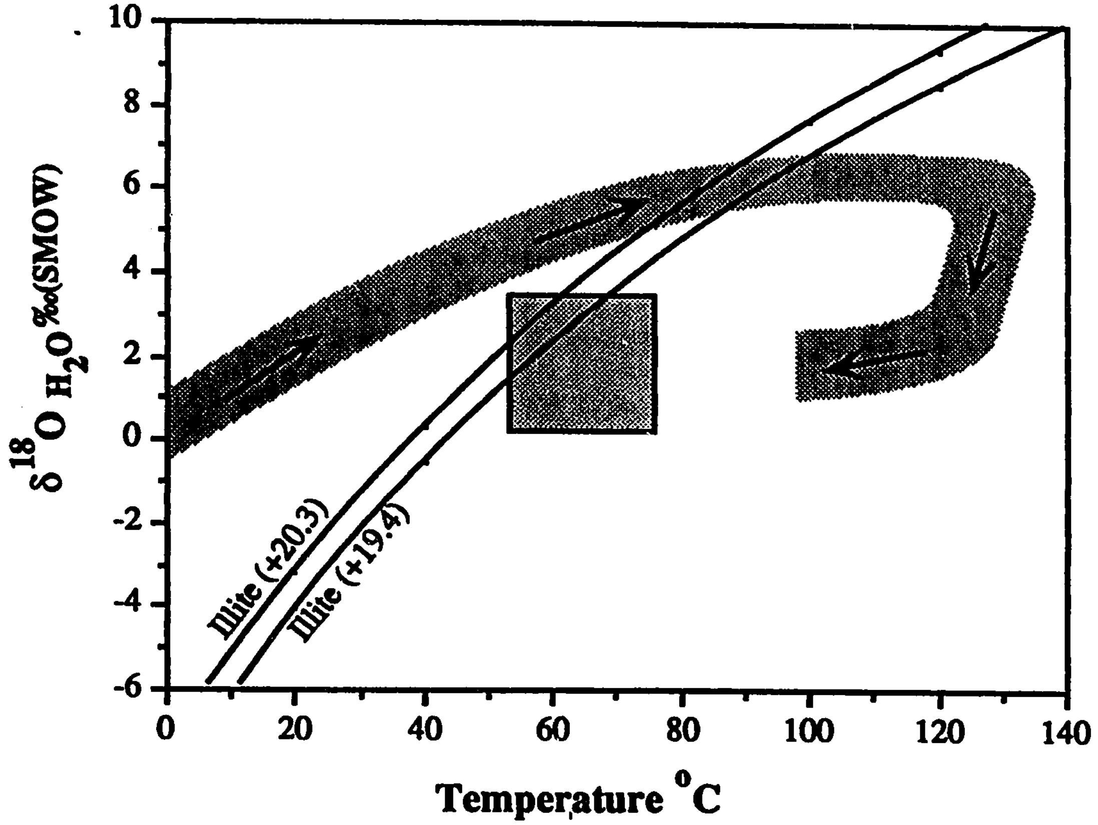


Fig. 6.7. $\delta^{18}O_{(SMOW)}$ of porewater versus temperature (°C) for diagenetic minerals in the Devonian carbonates. The curve illustrated for illite was calculated using the following equation (T = degrees K): $10^3 \ln\alpha_{Illite\text{-}H2O} = 2.39(10^6)T^{-2} - 4.19$ (YEH and SAVIN, 1977; SAVIN and LEE, 1988). The general pore water evolution curve, similar those shown for the Cretaceous, is illustrated here. Meteoric incursions, prior to that following the Laramide Orogeny may have been possible during the history of the Devonian; however, these would not have been as extensive or as significant to the pore fluids in the reservoirs.

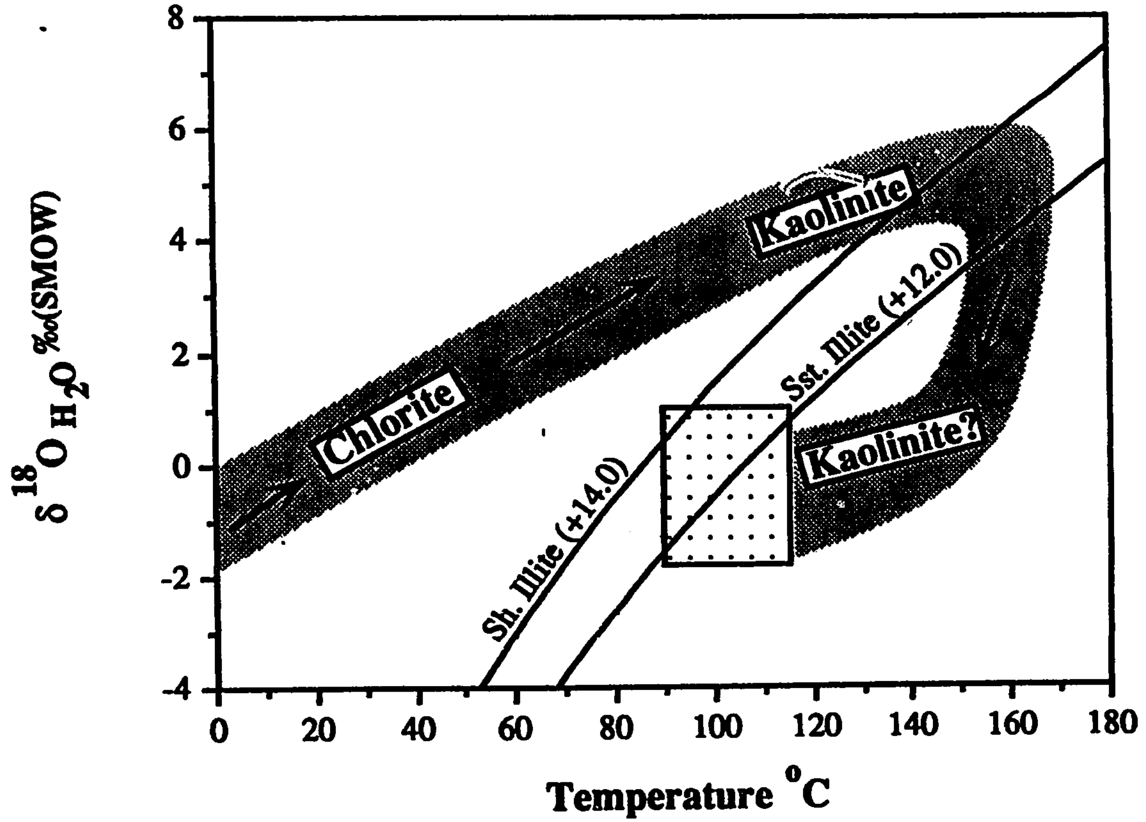


Fig. 6.8. $\delta^{18}O_{(SMOW)}$ of porewater versus temperature (T°C) for diagenetic illites (<0.1 µm) in the Cambrian formations of the Alberta Basin. The curve illustrated for illite was calculated using the following equation (T = degrees K): $10^3 \ln\alpha_{Illite-H_2O} = 2.39(10^6)T^{-2} - 4.19$ (YEH and SAVIN, 1977; SAVIN and LEE). The paragenetic sequence for the basal sandstone is partially outlined and constrains the illite curve for this unit (+12.0‰) to relatively late to present day formation in the paragenetic sequence, analogous to the Cretaceous illites. Present day pore fluid conditions for the shales are not well constrained and the corresponding illite phases (+14.0‰) may have formed during maximum burial or relatively late in the paragenetic sequence.

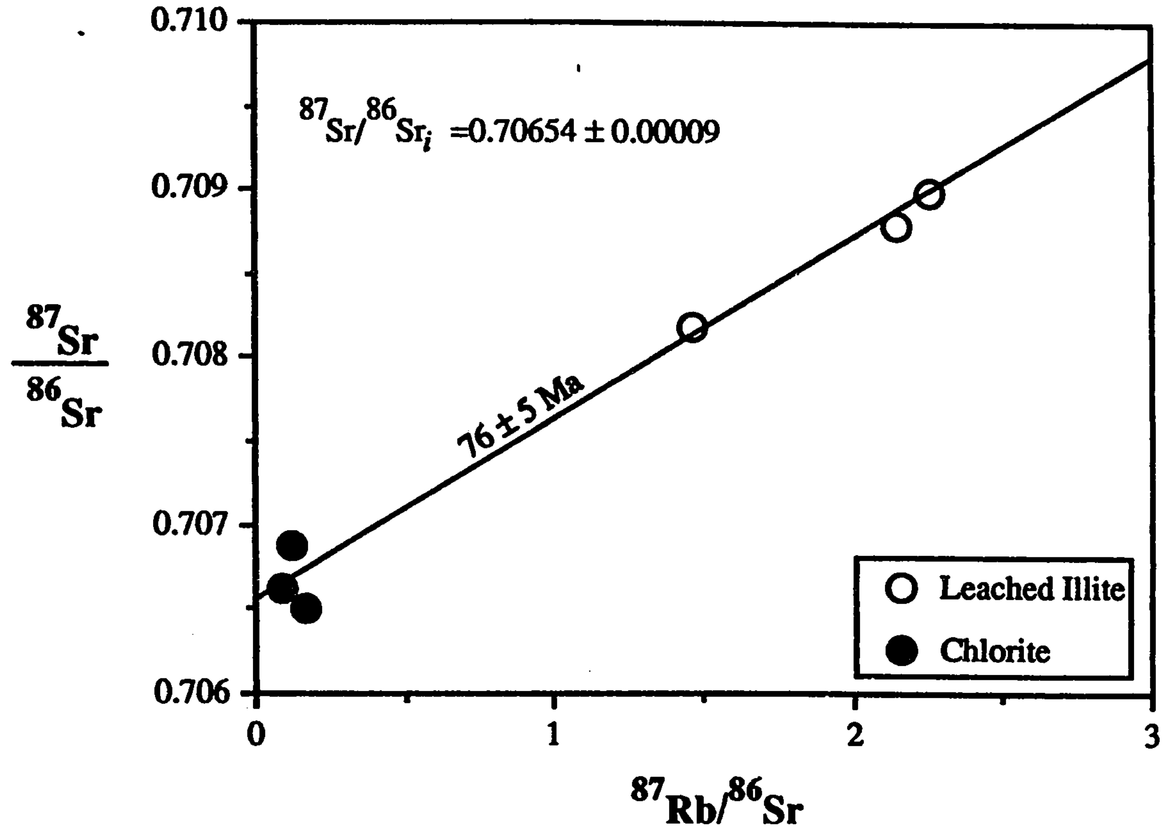


Fig. 6.9. Rb-Sr isochron formed by a suite of <0.1 μm illite phases and leached chlorites from the Belly River Formation, Alberta Basin. The age represented by the isochron is 76 ± 5 Ma, with an initial $^{87}Sr/^{86}Sr$ ratio of 0.70654 ± 0.00009 and a mean square weighted deviance of 0.919.

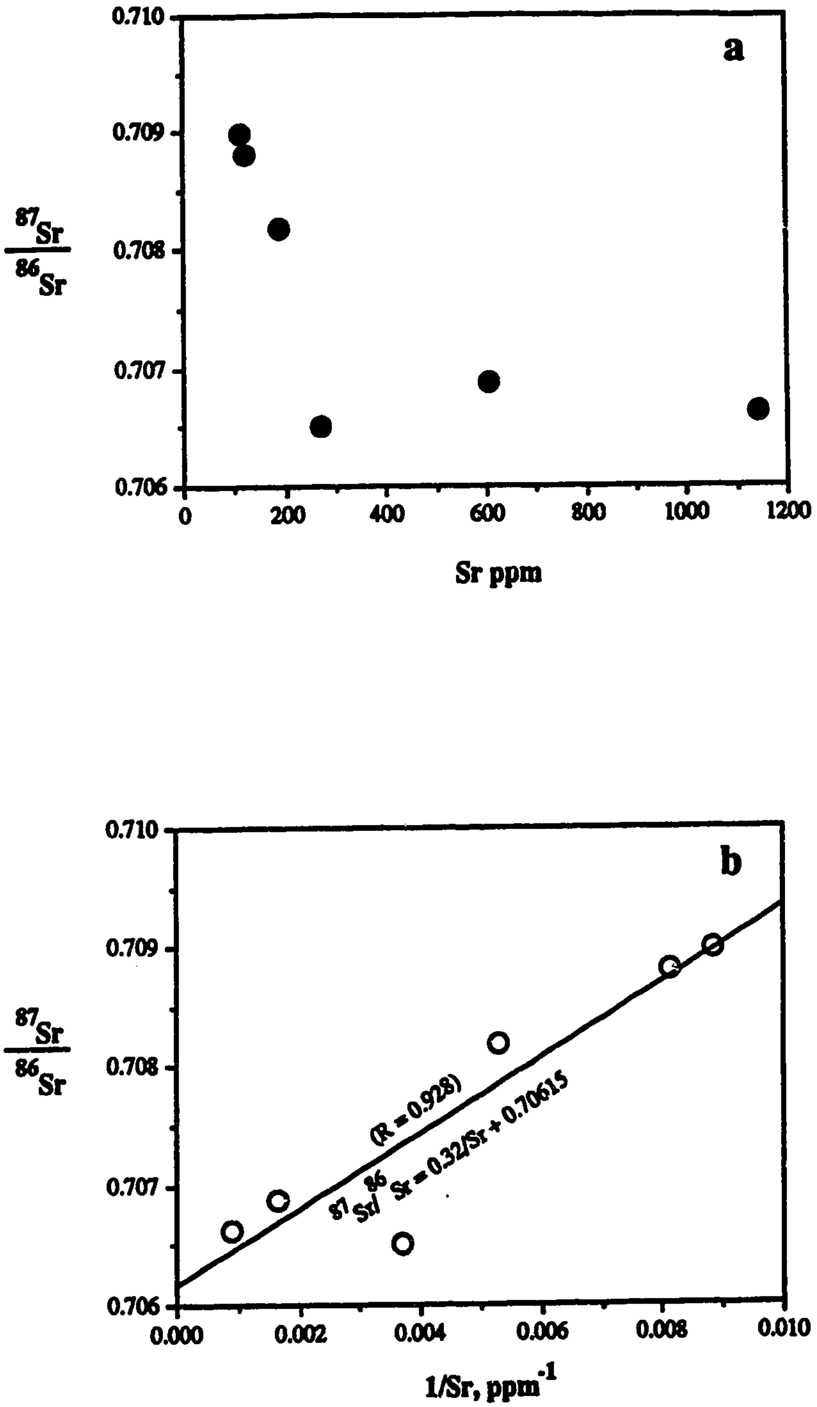


Fig. 6.10.a) An ^{87}Sr/^{86}Sr versus Sr plot showing a mixing hyperbola formed by the diagenetic chlorites and illites extracted from the Belly River Formation.

b) Transformation of the mixing hyperbola into a straight line by plotting the ^{87}Sr/^{86}Sr ratios versus the reciprocals of the Sr concentrations. The line has a slope of 0.32 and a y-intercept of 0.70615. The correlation coefficient is 0.93.

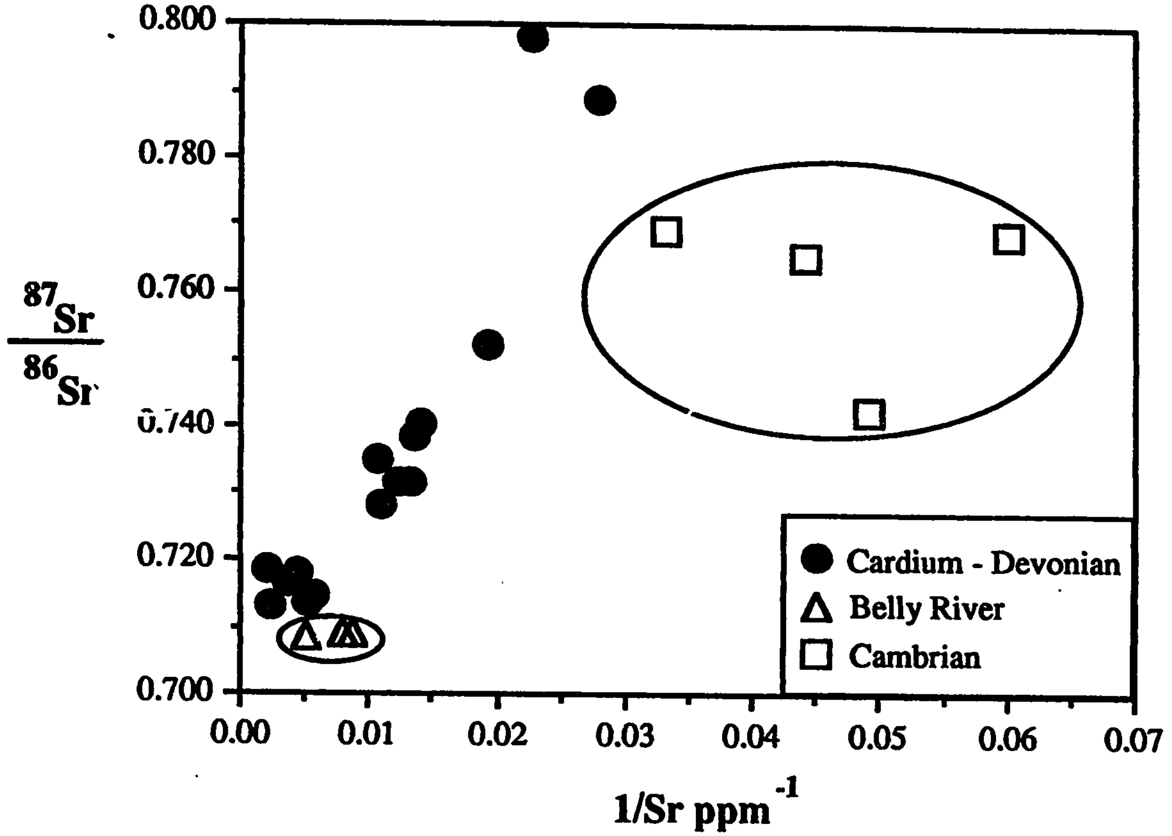


Fig. 6.11. $^{87}Sr/^{86}Sr$ versus 1/Sr (ppm^{-1}) graph of all of the <0.1 μm diagenetic illite phases from Cambrian to Upper Cretaceous formations in the Alberta Basin. Several distinct trends are shown on the graph. Cambrian and Belly River (Upper Cretaceous) illites form separate fields; the illites from Devonian through Cambrian formations, comprised of both leached and unleached samples, form a linear array.

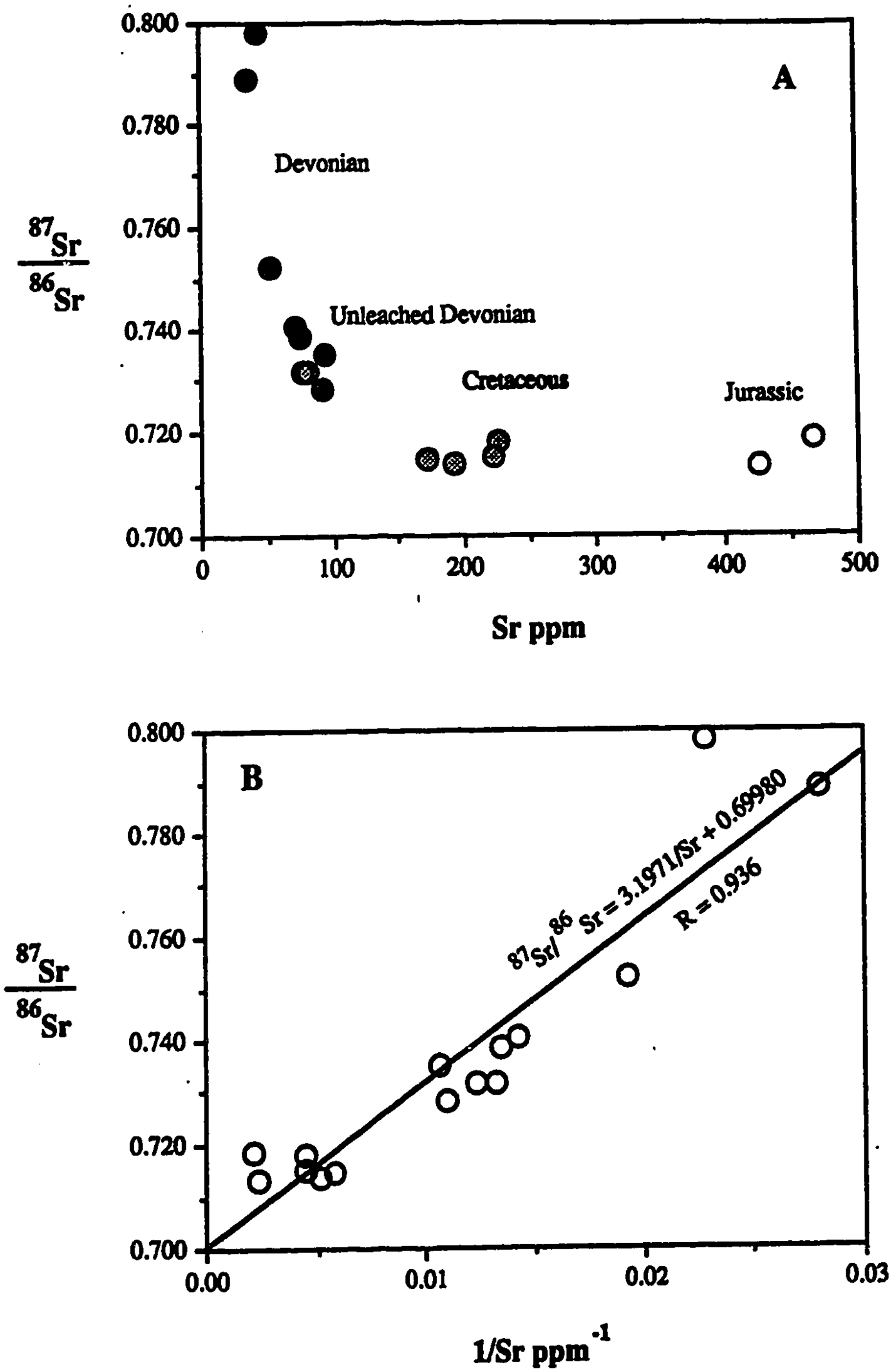


Fig. 6.12. a) ^{87}Sr/^{86}Sr versus Sr plot illustrating a mixing hyperbola formed by <0.1 μm leached and unleached illites from Cardium through Devonian formations in the Alberta Basin. Symbols are coded to reflect the various stratigraphic units in the basin. b) ^{87}Sr/^{86}Sr versus 1/Sr plot of data shown in Fig. 6.11a. Regression through the data yields a mixing equation of ^{87}Sr/^{86}Sr = 3.1971/Sr + 0.69980, with a correlation coefficient of 0.94.

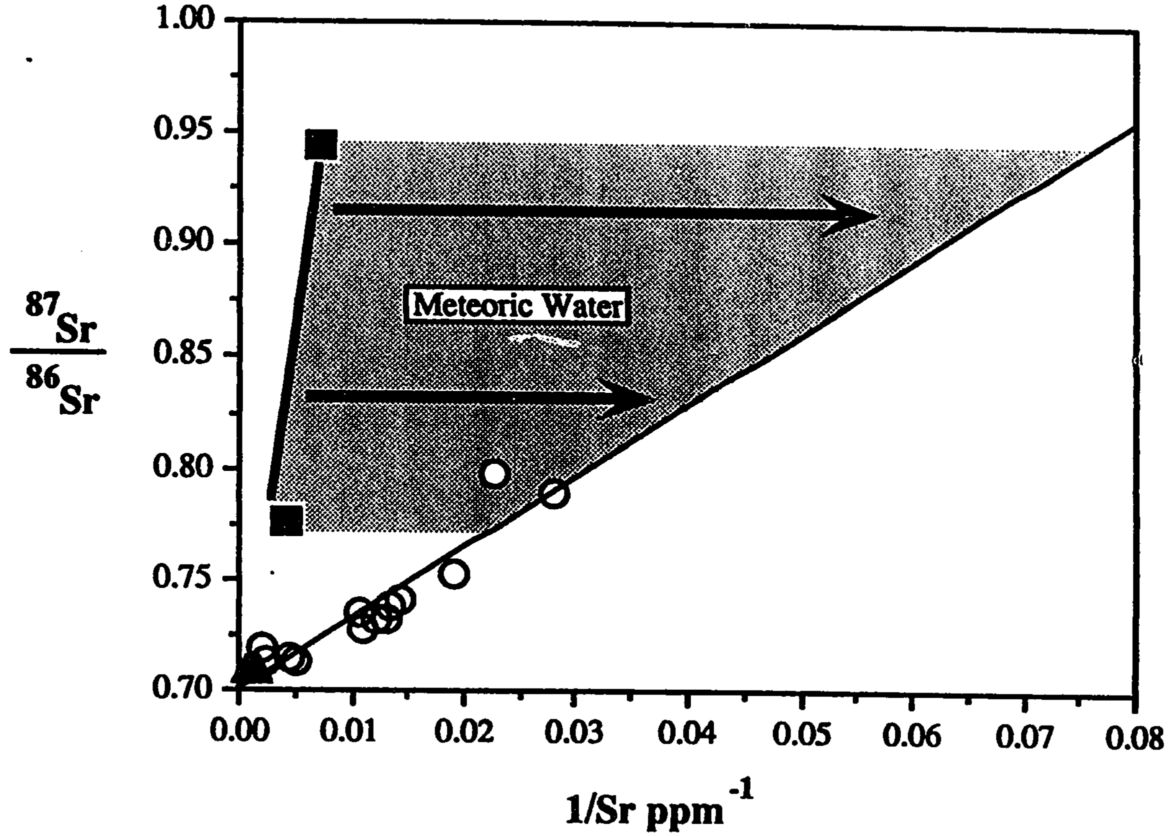


Fig. 6.13. Plot shown in Fig. 6.12b, illustrating potential end member components for the mixing regime. The stippled area outlines the region of potential feldspar end members. The solid squares represent the feldspar compositions and these minerals are potential end members at the high $^{87}Sr/^{86}Sr$, low Sr concentration end of the mixing regime. This area is large due to a diluting meteoric influence which will decrease the relative concentration of Sr contributed from the mineral end member in the direction of the arrows. The solid triangles represent the location of anhydrite, apatite and carbonate as potential end-members at the low $^{87}Sr/^{86}Sr$, high Sr concentration of the mixing regime.

CHAPTER 7. GENERAL DISCUSSION AND CONCLUSIONS

The primary objectives of this thesis were to determine: (1) the extent and nature of water/rock interaction in the Alberta Basin; (2) the scale of diagenetic interdependence between formation waters and detrital and authigenic mineral phases; and, (3) the chemical and isotopic evolution of the formation waters and resulting authigenic phases.

Initial studies of the whole rock and isolated carbonate cements indicated both a high degree of interaction among the formations and a strong meteoric component affecting the diagenesis of most of the formations from the Upper Cretaceous to the Precambrian basement. Several diagenetic zones were tentatively established and potential sources or precursor phases to diagenetic mineral reactions in the basin were highlighted. Subsequent geochemical, isotopic ($\delta^{18}O$, δD, $^{87}Sr/^{86}Sr$), and thermodynamic studies of the Upper Devonian to Upper Cretaceous formation waters delineated two hydrochemical regimes in the Alberta Basin: (1) a dilute, meteoric water flushed zone primarily restricted to the Upper Cretaceous; and, (2) a two component mixing zone consisting of fluids hosted in Upper Devonian to Lower Cretaceous units, where the saline end-member, a subaerially evaporated brine, is diluted (50 to 80%) by Neogene meteoric waters. The establishment of these zones was corroborated by the isotopic ratios ($\delta^{18}O$, $^{87}Sr/^{86}Sr$) and Rb and Sr concentrations of the diagenetic illite phases that precipitated from these fluids in Precambrian to Upper Cretaceous reservoirs. Major conclusions of the previous five chapters are summarized here.

WHOLE ROCKS AND CARBONATE CEMENTS

Stable ($\delta^{18}O$, $\delta^{13}C$) and radiogenic isotopes ($^{87}Sr/^{86}Sr$) for limestone/dolostone and shale whole rocks, and authigenic carbonate cements from a Precambrian to Upper Cretaceous stratigraphic assemblage in the Alberta Basin, indicate a meteoric influence in most of the formations. The Cambrian clastic rocks contain several generations of carbonate depicting the varied conditions (chemical, isotopic, temperature) that characterized the formation over its history. Early calcite phases have $\delta^{18}O$ values of +23.5‰ and $^{87}Sr/^{86}Sr$ ratios equivalent to Cambrian seawater (0.709). Ankerite phases formed later in the paragenetic sequence, and have $\delta^{18}O$ values (+19.2‰) indicating that these phases precipitated at temperatures associated with maximum burial of the basin, subsequent to the Laramide Orogeny. The $^{87}Sr/^{86}Sr$ values of the ankerites (0.749-0.750) are close to whole rock Cambrian shale values, suggesting equilibration between the formation waters and rock reservoir was attained at this time. A generation of calcite formed relatively late in the paragenetic sequence and has $\delta^{18}O$ values of +12.1‰, suggesting a significant lowering of the porewater $\delta^{18}O$. It is probable that this lowering was the result of flushing of gravity-driven meteoric waters subsequent to the Laramide Orogeny. Prior to this event, basin geometry was not conducive to a major flushing event and meteoric waters in the basin would not have had sufficiently negative $\delta^{18}O$ values to account for the $\delta^{18}O$ values of the late calcite phase. Hence, post-Laramide meteoric waters likely permeated formations as stratigraphically low as the Cambrian.

Most of the Devonian carbonate assemblages, with the exception of the uppermost unit (the Wabamun Group), show little to no meteoric water influence. This does not mean that meteoric waters failed to infiltrate these carbonate units, but rather that recrystallization/stabilization reactions occurred relatively early within the reservoirs, prior to meteoric infiltration. Wabamun and stratigraphically higher carbonate units, up to the

Jurassic, show a significant meteoric influence, both in the whole rock analyses and in the diagenetic separates. $\delta^{18}O$ and $\delta^{13}C$ values of the whole rock carbonates exhibit a linear correlation, but are inversely correlated with respect to $^{87}Sr/^{86}Sr$. The stable isotope trend indicates a meteoric influence. The inverse trend of the stable isotopes with $^{87}Sr/^{86}Sr$ suggests an increased diagenetic component resulting from the release of ^{87}Sr produced by the radioactive decay of ^{87}Rb in Rb/Sr rich minerals.

Most carbonate phases in the Cretaceous formations have stable isotope values that indicate a significant meteoric influence. Furthermore, $^{87}Sr/^{86}Sr$ ratios of authigenic carbonates decrease with decreasing stratigraphic age, with values as low as 0.706 being measured. These $^{87}Sr/^{86}Sr$ ratios of the authigenic carbonates are likely the result of plagioclase alteration releasing significant amounts of Sr with relatively low $^{87}Sr/^{86}Sr$ ratios to the porewaters.

There is a disparity between the $^{87}Sr/^{86}Sr$ ratios of authigenic phases and corresponding reservoir waters for most formations in the Alberta Basin, indicating a dynamic system that has not reached equilibrium. Devonian shale units appear to be the only stratigraphic units with $^{87}Sr/^{86}Sr$ ratios sufficiently high to account for the radiogenic component in some of the diagenetic phases in the Alberta Basin.

FORMATION WATERS

Integration of isotopic (Sr, D, O) and major/minor elemental fluid compositions provides a basis for dividing the formation waters into three distinct groups, here designated I, II, and III. Group I waters are dominantly carbonate-hosted and are stratigraphically the lowest; Group II waters are primarily from clastic reservoirs; and Group III waters are completely clastic-hosted and comprise the stratigraphically highest zone. Groups I and II form a distinct hydrochemical regime, which is decoupled from the dilute waters of Group III.

Chemistry

The abundance and distribution of short chain aliphatic acids (SCAs) in Alberta Basin formation waters increase with proximity to the Jurassic shales, the dominant source rocks in the basin, but decrease with increasing effects of water-washing and meteoric flushing. Contrary to what is observed in other sedimentary basins (CAROTHERS and KHARAKA, 1978; WORKMAN and HANOR, 1985; MEANS and HUBBARD, 1987), the abundance and distribution of SCAs in the Alberta Basin do not appear to be influenced by, or related to, reservoir temperature, sampling depth, salinity, or geological age. However, further analyses are necessary to establish more complete hypotheses concerning the occurrence of SCAs.

Formation water chemistry shows that Group III waters are dominated by Na and HCO_3^- (alkalinity), and display no evidence of a seawater or an evaporated brine component. The majority of reservoirs containing Group III waters were deposited in seawater; however, the dilute nature and chemical composition of these waters suggest complete flushing of any residual marine water in these reservoirs by meteoric water.

Formation waters from Group I and Group II form two component mixtures of a residual evaporite brine and a dilute meteoric water, indicating that complete flushing of these reservoirs by meteoric waters did not occur as has been previously suggested by CLAYTON *et al.* (1966). The brine end-member was formed by evaporation of seawater beyond the point of halite saturation and was not influenced by congruent dissolution of Middle Devonian evaporite deposits. The Group I predominantly carbonate-hosted waters are enriched in divalent cations, which may only be accounted for by silicate hydrolysis, clay-carbonate and/or ion-exchange reactions in surrounding shales, and/or ankeritization reactions of reservoir carbonates. The clastic-hosted waters of Group II are enriched in monovalent cations indicating that they were affected by either ion-exchange processes or feldspar-clay mineral leaching reactions initiated by gravity-driven flow of meteoric waters, as a result of Laramide orogenesis.

Isotopic Composition

Both stable ($\delta^{18}O$, δD) and radiogenic ($^{87}Sr/^{86}Sr$) isotopic analyses were conducted on the fluid samples. Plots of stable isotopes (δD *vs* $\delta^{18}O$), combined stable isotope and elemental data (Cl *vs* δD; Cl *vs* $\delta^{18}O$), and $^{87}Sr/^{86}Sr$ *vs* 1/Sr, indicate two hydrological regimes in the basin, analogous to those established based on water chemistry. One regime, represented by Group III waters, is dominated by the flushing of modern meteoric waters through the upper portion of the sedimentary succession. The second regime is isolated from the first and is characterized by association/mixing between Group I and II waters. This regime is composed of original connate brines and a meteoric water, demonstrated by stable isotopes to be of Neogene origin. Thus, it would appear that Group I and II formation waters became isolated from present day meteoric water recharge during the Pliocene as a result of dissipation of the regional recharge-discharge system (GARVEN, 1985); the establishment of upward diffusional flow (HANOR, 1984) and density stratification (LAND, 1987) followed. As a result, cross-formational fluid flow became significant relative to the lateral fluid flow, which dominated during meteoric recharge.

Variation in water $^{87}Sr/^{86}Sr$ ratios indicate that different water-rock interactions and changes in provenance have occurred in the basin. The $^{87}Sr/^{86}Sr$ ratios of Group I waters (0.7076 - 0.7129) appear to be strongly influenced by Devonian shales. The relatively low $^{87}Sr/^{86}Sr$ ratios (0.7058) for waters and diagenetic minerals in the upper

Lower and Upper Cretaceous stratigraphic units indicate that the volcanic rock fragments and plagioclase, observed petrographically, are a significant (dominant) source of Sr to the pore fluids. A southwest (Montana), rather than an western source for the volcanic detritus for the study area is likely (SUTTNER, 1969; EISBACHER *et al.*, 1974; PUTNAM, 1982).

Equilibrium Thermodynamics

Equilibrium thermodynamics was employed to establish the degree and type of water/rock interactions in the Alberta Basin. As alluded to in the chapters on the chemical and isotopic composition of the waters, these reactions are important in controlling water compositions and mineral precipitation in basinal waters. Thermodynamic analysis provides information by accounting for the distribution of each species among all potential species in solution (HUTCHEON, 1989). Hence, as different equilibrium states may be established over short periods of time within immediate reservoirs, reactions *currently* active and supplying components to the established fluid regime were evaluated.

Stability relations and activity diagrams of cation/H^+ activity ratios versus silica activities for the formation waters of the Alberta Basin exhibit distinct trends. Group I waters have equilibrated with smectite, illite, calcite, and dolomite. Gypsum and anhydrite become increasingly significant for waters with ionic strengths >1.5. Carbonate minerals appear to dominate the equilibrium reactions, with some influence by illitic phases. Group II and III waters are in equilibrium with calcite, dolomite, illite, smectite and chlorite, with the distribution of Group II waters indicating a more complex origin than Group III (i.e., more than one reaction contributing to the chemistry of the Group II waters). Clay minerals dominate water/rock reactions in Group II and III, distinguishing them from Group I. Ion exchange reactions between smectite phases, metastable to illite, characterize Group I waters. The water chemistry of Groups II and III is controlled by the conversion of beidellite to illite, but is also partially controlled by ion exchange reactions between Ca- and Mg-beidellite, metastable to chlorite.

Equilibrium mineral reactions/exchange processes responsible for aqueous speciation are different for Group I waters compared to Groups II and III, suggesting lithological variations (i.e., clastic *vs* carbonate) are the likely cause. Each of the water groups indicate relatively evolved reaction paths (kaolinite → montmorillonite → illite) (HELGESON *et al.*, 1969; EBERL, 1984), despite being hosted in a basin that has been dominated by gravity-driven flow of dilute meteoric waters.

ISOLATED DIAGENETIC AND DETRITAL PHASES

Detrital and diagenetic mineral separates from the Alberta Basin were examined isotopically ($^{87}Sr/^{86}Sr$, $\delta^{18}O$) and chemically (Rb and Sr concentrations) in an attempt to (a) further constrain water/rock interaction and mixing regimes in the basin, and to (b) subsequently establish the degree of closed versus open system behavior with respect to cross-formational fluid flow. In addition, the relative timing of illite formation, and scale over which it occurred in the Alberta Basin has been defined.

Illite was the main diagenetic mineral examined because it is ubiquitous and the most amenable to study using Rb-Sr systematics. Petrographic, SEM, and stable isotope data were used to determine the conditions of formation of illite in the stratigraphic units of the Alberta Basin. All of the formations indicated relatively recent to present day illite formation.

Dating the diagenetic component of the Alberta Basin, including both illite and chlorite, was unsuccessful most likely because of inhomogeneity of initial $^{87}Sr/^{86}Sr$ ratios. Consequently, model ages were calculated instead using minimum $^{87}Sr/^{86}Sr_i$ values which were assumed to be seawater $^{87}Sr/^{86}Sr$ ratios for the time of deposition and were taken from the BURKE *et al.* (1982) seawater curve. This assumption is valid as most of the formations were deposited in seawater. Using these minimum $^{87}Sr/^{86}Sr$ ratios, maximum ages were calculated for the illite. In general, the model ages support petrographic and stable isotopic data suggesting illite formation occurred relatively late in the paragenetic sequence.

Mixing diagrams ($^{87}Sr/^{86}Sr$ *vs* 1/Sr and Sr) for all the diagenetic illites in the Alberta Basin delineate several zones of diagenesis. The Cambrian formations form a separate region from stratigraphically higher formations on the diagrams, likely because Middle Devonian evaporites impede cross-formational fluid flow. Diagenetic components from the Upper Cretaceous Belly River Formation also plot in a distinct region on mixing diagrams, harmonious with the different hydrologic system established in this formation from stratigraphically lower formations. The Devonian through Cardium diagenetic illite phases form a mixing regime, where Jurassic carbonate and Devonian anhydrite likely form the low-$^{87}Sr/^{86}Sr$ high-Sr concentration end member, and K-feldspar or a carbonate excluded Rb-rich fluid/Rb-rich clay likely form the high-$^{87}Sr/^{86}Sr$ and low-Sr concentration end member. Local (lithological, mineralogical) environments are shown to influence the radiogenic signature of diagenetic illite phases, but these environments do not result in deviation of any of the Devonian through Cardium illites on the mixing diagram. The fluid regime deduced using authigenic illite further substantiates the mixing system and cross-formational fluid flow independently proposed from isotopic and chemical studies of the formation waters.

MAJOR CONCLUSIONS

This study demonstrates that there is a pronounced mixing regime and cross-formational fluid flow in the Alberta Basin that is hydrochemically isolated from significant infiltration of present day meteoric waters. The existence of this mixing regime is supported by the fluid chemistry, stable isotopes and radiogenic isotopes of the formation waters, and the stable and radiogenic isotopes of authigenic phases precipitating within the fluid regime. Independent of hydrologic models (GARVEN, 1985; 1989), chemical and isotopic data indicate dissipation of the regional flow system, instigated by the Laramide Orogeny, into smaller more local sub-systems (CONNOLLY *et al.*, 1990a; 1990b). These local systems primarily influence Upper Cretaceous reservoirs; however, they do extend to greater depths toward the southwest of the study area, the potentiometric high for the basin. The results of this study suggest that although gravity-driven meteoric circulation/flushing is important in modelling the hydrogeochemistry of the Alberta Basin, the chemical and isotopic composition of stratigraphically older and deeper reservoir fluids may be consistent with retention of a significant portion (20-50%) of subaerially evaporated fluid.

REFERENCES

BURKE W.H., DENISON R.E., HETHERINGTON E.A., KOEPNICK R.B., NELSON H.F. and OTTO J.B. (1982) Variation of seawater $^{87}Sr/^{86}Sr$ throughout Phanerozoic time. *Geology* **10**, 516-519.

CAROTHERS W.W. and KHARAKA Y.K. (1978) Aliphatic acid anions in oil-field waters - implications for origin of natural gas. *Am. Assoc. Petrol. Geol. Bull.* **62**, 2441-2453.

CLAYTON R.N., FRIEDMAN I., GRAF D.L., MAYEDA T.K., MEENTS W.F. and SHIMP N.F. (1966) The origin of saline formation waters, I. Isotopic composition. *J. Geophys. Res.* **71**, 3869-3882.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990a) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. I. Chemistry. *Appld. Geochem.* **5**, 375-396.

CONNOLLY C.A., WALTER L.M., BAADSGAARD H. and LONGSTAFFE F.J. (1990b) Origin and evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin. II. Isotope systematics and water mixing. *Appld. Geochem.* **5**, 397-414.

EISBACHER G.H., CARRIGY M.A. and CAMPBELL R.B. (1974) Paleodrainage pattern and late orogenic basins of the Canadian Cordillera. In *Tectonics and Sedimentation* (ed. W.R. DICKINSON), pp. 143-146. S.E.P.M. Spec. Pub. 22.

GARVEN G. (1985) The role of regional fluid flow in the genesis of the Pine Point deposit. *Econ. Geol.* **80**, 307-324.

GARVEN G. (1989) A hydrogeologic model for the formation of giant oil sands deposits of the western Canada sedimentary basin. *Am. J. Sci.* **289**, 105-166.

HANOR J.S. (1984) Variation in the chemical composition of oil-field brines with depth in northern Louisiana and southern Arkansas: Implication for mechanisms and rates of mass transport and diagenetic reaction. *Trans. Gulf Coast Assoc. Geol. Soc.* 34, 55-61.

HUTCHEON I. (1989) Application of chemical and isotopic analyses of fluids to problems in sandstone diagenesis. In *Burial Diagenesis* (ed. I. HUTCHEON), pp. 279-310. Min. Assoc. Can. Short Course **15**.

LAND L.S. (1987) The major ion chemistry in sedimentary basins. In *2nd Intern. Sym. on Phys. and Chem. of Porous Media*, 160-179.

MEANS J.L. and HUBBARD N.J. (1987) Short-chain aliphatic acid anions in deep subsurface brines: A review of their origin, occurrence properties and importance and new data on their distribution and geochemical implications in the Palo Duro Basin, Texas. *Org. Geochem.* **11**, 177-191.

PUTNAM P.E. (1982) Fluvial channel sandstones within Upper Mannville (Albian) of

Lloydminister area, Canada - geometry, petrography and paleogeographic implications. *Am. Assoc. Petrol. Geol. Bull.* 66, 436-459.

SUTTNER L.J. (1969) Stratigraphic and petrologic analysis of Upper Jurassic - Lower Cretaceous Morrison and Kootenai Formations, southwest Montana. *Am. Assoc. Petrol. Geol. Bull.* 53, 1391-1410.

WORKMAN A.L. and HANOR J.S. (1985) Evidence for large-scale vertical migration of dissolved fatty acids in Louisiana oil field brines: Iberia Field, south central Louisiana. *Trans. Gulf Coast Assoc. Geol. Soc.* 35, 293-300.

APPENDIX I

Petrography of Formations in the Alberta Basin

Formations from the Precambrian basement to Upper Cretaceous (Fig. A.1) in the Alberta Basin, Western Canada Sedimentary Basin, were examined petrographically and by X-ray diffraction. Twenty-six individual cores were examined from a limited lateral extent in the Alberta Basin, defined by the study area (Fig. A.2), and from these core more than 150 thin sections, representative of all the formations were examined. These observations are augmented by other petrographic studies in order to obtain a good average composition of the total mineral assemblage for each specific formation over the study area. A brief summary of the petrography of all the formations is given below.

The Precambrian basement in the study area is an altered muscovite-biotite granite, exhibiting chloritization of biotite and kaolinization and seritization of feldspar (BURWASH, 1951). The primary minerals are quartz (30%), orthoclase (20-35%), and plagioclase (albite to andesine; 20-40%). Varietal and secondary minerals include muscovite, biotite, kaolinite, chlorite and sericite.

The basal Cambrian sandstones unconformably overlie the Precambrian and are very mature quartz arenites. Quartz is the primary phase (70%) and the dominant cementing phase (8-28%). Anhydrite, kaolinite, chlorite, calcite and dolomite all occur as minor to trace cements, although anhydrite may occupy up to 20% of the volume. Porosity ranges from 0 to 6%. Cambrian shales overly the basal sandstone and are volumetrically more significant. The primary constituents are quartz (~50%, but variable), feldspar - dominantly K-feldspar (up to 10%), and clay minerals (~40%) with kaolinite, illite and chlorite occurring in decreasing abundance. Carbonate phases (calcite and ankerite) occur in trace amounts. Alteration includes chlorite replacement of biotite and kaolinization of feldspar and chlorite, with subsequent illitization of some of the kaolinite. Diagenetic illite/smectite (>70% illite) is very abundant and sericite is concentrated in organic rich laminae.

The Devonian Elk Point Group unconformably overlies the Cambrian shales and denotes the beginning of a marine megasequence (HITCHON, 1984). This formation is composed of halite and anhydrite deposits at its base, becoming predominantly dolomitic with trace amounts of quartz, calcite and mica, toward the top. The Beaverhill Lake Group overlie the Elk Point Group and is composed of an alternating sequence of limestone and shaley (quartz and illite) limestone. The Bearverhill Lake Group is succeeded by the reservoir rocks of the Devonian - the Leduc, Nisku, and Wabamun stratigraphic units. These three reservoir rocks are all composed of carbonate, with the gross lithologic character typified by two end-members, limestone and secondary dolomite. Various gradations occur between the two mineralogies, but a relatively pure end-member (particularly dolomite) predominates (ANDRICHUK, 1958a). In the study area, the Leduc and Nisku Formations are predominantly dolomite, while the Wabamun Group is composed of calcite. Much of the dolomite in the study area has been partially ankeritized and trace calcite and mica (illite) are present in the rocks. Anhydrite has been recorded as very prevalent in all the reservoir rocks (ANDRICHUK, 1958a, 1958b; McCROSSAN, 1961), but predominates in the Nisku Formation.

The intervening shale units of the marine megasequence are the Duverney, Ireton, Calmar, and Graminea Formations (Fig. A.1), all of which are composed of alternating carbonate and shaly units. The former two formations are very similar with calcite/dolomite grains in a groundmass of quartz (up to 50%), clay (illite, up to 15%), finer carbonate (30 to 90%) and trace pyrite. Anhydrite has been identified in these formations (McCROSSAN, 1961), but was not observed in the core studied. The Duverney Formation differs from the Ireton Formation in its higher organic content, resulting in its generally black color. The Calmar and Graminea Formations are differentiated from the preceding two shaley formations be their greater quartz/silt content. The Calmar Formation is a light green argillaceous siltstone with some red mottling. The Graminea Formation consists of white quartzose fine grained sandstones and siltstones and interbedded dolomites. Both formations have a high carbonate content, usually greater than 50%, and illite (up to 10%) is the sole clay mineral present.

The black cherty shales of the Exshaw Formation record the beginning of the Mississippian and are composed of calcite (~50%), quartz and chert (40%) and ankerite (8%), with trace pyrite, illite and feldspar. The Banff Formation is primarily calcite (50 to 60%), with quartz (5 to 30%) and trace to minor dolomite. Collophane, a cryptocrystalline variety of apatite may compose up to 10% of the rock. The Jurassic Nordegg Formation, unconformably overlies the Banff Formation and is similar in composition, but is more fossiliferous, containing slightly less quartz and more collophane (up to 20%).

The primarily clastic units of the Jurassic, the Poker Chip Shale and Rock Creek Formations, overlie the Nordegg Formation. The essential components of the former are chert and quartz (60 to 70%), ankerite (up to 20%), illite (10%) and kaolinite (5%), with trace pyrite and chlorite. The Rock Creek Formation is very similar to the Poker Chip Shale; however, the Rock Creek Formation has a higher content of calcite (up to 50%) at the base of the formation and overall a greater kaolinite (up to 10%) content. The Rock Creek Foramtion is composed of up to 90% quartz at the top, with no carbonate phase present.

Cretaceous rocks unconformably overlie the aforementioned strata. The Cretaceous units are composed dominantly of shale interspersed with sandstone lenses. Authigenic minerals in the Cretaceous rocks are variable in concentration, even within one formation, but similar phases are generally found throughout the Cretaceous. The Lower Cretaceous Mannville Group is composed of shales and reservoir rocks of the Basal Quartz, Ostracod and Glauconitic Formations. The Lower Mannville shales consist of quartz and chert (30 to 50%), K-feldspar (1 to 6%), calcite (0 to 20%), and clay minerals (up to 40%) consisting of variable kaolinite, illite, chlorite and smectite. Mica, pyrite, carbonaceous and bituminous material occur in small but persistant amounts (WILLIAMS, 1960). The Basal Quartz Formation is composed of primarily quartz (50 to 85%) at the base of the formation, with quartz being the primary cementing agent, with trace kaolinite. Higher up in the formation the quartz content varies (50 to 70%) and the lithologic unit contains rock fragments- primarily sedimentary (1 to 15%), orthoclase (<2%) and trace mica and pyrite. Authigenic calcite and quartz (2-20%) are the dominant cementing agents (WILLIAMS, 1960; MELLON, 1967). The overlying Ostracod Formation are limey shales that contain bands of argillaceous limestone. The proportions of the constituents in the Ostracod are highly variable but consist of chert (up to 70%) and quartz (12 to 22%), calcite (up to 60%), and trace pyrite and mica. The Glauconitic Formation is a litharenite composed of quartz (20-70%), chert (10-50%), sedimentary rock fragments (5-30%), feldspar - dominantly K-feldspar (0-10%) and detrital dolomite (0-15%). Clay minerals (2-18%) are composed of dominantly kaolinite, but chloritized illite, interstratified illite/smectite and glauconite occur in minor amounts. Porosity averages 2.5%, and cements include quartz, chert and void filling calcite and dolomite (YOUNG and DOIG, 1986). The Glauconitic paragenetic sequence is shown in Fig. A.3(a).

The Joli Fou Formation, which contains the thickest deposits of bentonite in the stratigraphic column, marks the beginning of the Colorado Group. The Colorado Group transects the Lower and Upper Cretaceous boundary and contains the reservoir rocks of the Viking and Cardium Formations. The shales of the Colorado Group are similar to the Mannville, but contain bentonite horizons variably enriched in smectite. The Group is divided by the speckled shales which contain a high content of chalk derived from phytoplankton shells. Chlorite becomes more significant toward the top of the Colorado Group.

Rock types present in the Viking Formation are conglomerates, coarse and fine grained sandstones and shales (DEAN, 1986; LONGSTAFFE and AYALON, 1987). Detrital minerals in the conglomerates and sandstones consist of quartz (5 - 60%), chert (5 - 80%), rock fragments (0 - 24%) and feldspar (0 - 30%). Flakes of kaolinite occur in some samples and the dominant cements are quartz and clay minerals with kaolinite > illitic clay minerals >smectite. Minor siderite, dolomite and ankerite cements are also present. Cements and illite become more significant in the finer grained rocks. The Viking shales consist of mostly illite (60 - 85%) and lesser amounts of illite/smectite (5 - 25%), kaolinite (trace - 20%), chlorite (trace - 10%) and smectite (not detected - 5%). The generalized paragenetic sequence is shown in Fig. A.3(b). The Cardium Formation is composed of three sandstone members separated by dark shales. These members may have a chert pebble conglomerate at the top and be separated by shale lenses. The sandstones are litharenites to sublitharenites, with the predominant framework grains being quartz (45-65%) and chert (5-15%), with lesser mica (0-3%), feldspar (0-1%), siderite (5-12%), shale and metamorphic rock fragments (0-5%). Cementing agents are quartz, kaolinite, illite, siderite, calcite and trace pyrite and chlorite. Clays constitute 10-30% of the sandstones (KRAUSE *et al.*, 1987). The general paragenetic sequence is shown in Fig. A.3(c).

The marine shales of the Lea Park Formation stratigraphically overlie the Colorado Group. These shales contain quartz (20 - 30%), feldspar (up to 30%) and clay minerals (30 - 60%). Clays consist of illite, kaolinite, chlorite and smectite. The basal Belly River sandstone interfingers the Lea Park shale and is a litharenite consisting of approximately 90% sand size grains and 10 % clay size material. The sandstone is composed mostly of rock fragments (50 to 80%), quartz (15 to 40%) and feldspars (2 to 30%) (LERBEKMO 1961, 1963; IWUAGWU and LERBEKMO, 1981, 1982; LONGSTAFFE, 1986; AYALON and LONGSTAFFE, 1988). Plagioclase feldspar is more abundant (6 - 26%; avg., 19%) and more altered than detrital K-feldspar (1 - 8%; avg., 2.5%). Mudstone and chert are the most abundant rock fragments, but carbonate, volcanic, metamorphic and plutonic rock fragments are also common. Most pores have been partially or totally filled by diagenetic clay minerals. The general paragenetic sequence is shown in Fig. A.3(d).

REFERENCES

ANDRICHUK J.M. (1958a) Stratigraphy and facies analysis of Upper Devonian reefs in Leduc, Stettler, and Redwater area, Alberta. *Am. Assoc. Petrol. Geol. Bull.* 42, 1-93.

ANDRICHUK J.M. (1958b) Cooking Lake and Duvernay (Late Devonian) sedimentation in the Edmonton area of Central Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* 42, 2189-2222.

AYALON A. and LONGSTAFFE F.J. (1988) Oxygen isotope studies of diagenesis and pore-water evolution in the western Canada sedimentary basin: Evidence from Upper Cretaceous Basal Belly River sandstone, Alberta. *J. Sediment. Petrol.* 58, 489-505.

BURWASH R.A. (1951) The Precambrian under the central plains of Alberta. M.Sc. Thesis. Univ. of Alberta, Edmonton, Alberta.

DEAN M.E. (1986) Diagenesis of the Viking Formation, south-central Alberta. M.Sc. Thesis. Univ. of Alberta, Edmonton, Alberta.

HITCHON B. (1984) Geothermal gradients, hydrodynamics, and hydrocarbon occurrence, Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* 68, 713-743.

IWUAGWU C.J. and LERBEKMO J.F. (1981) The role of authigenic clays in some reservoir characteristics of the basal Belly River sandstone, Pembina Field, Alberta. *Bull. Can. Petrol. Geol.* 29, 479-491.

IWUAGWU C.J. and LERBEKMO J.F. (1982) The petrology of the basal Belly River sandstone reservoir, Pembina Field, Alberta. *Bull. Can. Petrol. Geol.* 30, 187-207.

KRAUSE F.F., COLLINS H.N., NELSON D.A., MACHEMER S.D. and FRENCH P.R. (1987) Multiscale anatomy of a reservoir: Geological characterization of Pembina-Cardium Pool west-central Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* 71, 1233-1260.

LERBEKMO J.F. (1961) Stratigraphic relationship between the Milk River Formation of the southern plains and the Belly River Formation of the southern Foothills of Alberta. *J. Alta. Soc. Petrol. Geol.* 9, 273-276.

LERBEKMO J.F. (1963) Petrology of the Belly River Formation, southern Alberta Foothills. *Sedimentol.* 2, 54-86.

LONGSTAFFE F.J. (1986) Oxygen isotope studies of diagenesis in the basal Belly River sandstone, Pembina I-Pool, Alberta. *J. Sediment. Petrol.* 56, 78-88.

LONGSTAFFE F.J. and AYALON A. (1987) Oxygen-isotope studies of clastic diagenesis in the Lower Cretaceous Viking Formation, Alberta: Implications for the role of meteoric water. In *Diagenesis of Sedimentary Sequences* (ed. J.D. MARSHALL), pp. 277-296. Geol. Soc. Spec. Pub. 36.

MACHEMER S.D. and HUTCHEON I. (1988) Geochemistry of early carbonate cements in the Cardium Formation, central Alberta. *J. Sediment. Petrol.* **58**, 136-147.

McCROSSAN R.G. (1961) Resistivity mapping and petrophysical study of Upper Devonian inter-reef calcareous shales of central Alberta, Canada. *Am. Assoc. Petrol. Geol. Bull.* **45**, 441-470.

MELLON G.B. (1967) Stratigraphy and petrology of the Lower Cretaceous Blairmore and Mannville Groups, Alberta Foothills and Plains. *Research Council of Alberta*. **21**, 270 p.

WILLIAMS G.D. (1960) The Mannville Group, central Alberta. Unpub. Ph.D. Dissert. Univ. Alberta, Edmonton, Alberta.

YOUNG H.R. and DOIG D.J. (1986) Petrography and provenance of the Glauconitic sandstone, south-central Alberta, with comments on the occurrence of detrital dolomite. *Bull. Can. Petrol. Geol.* **34**, 408-425.

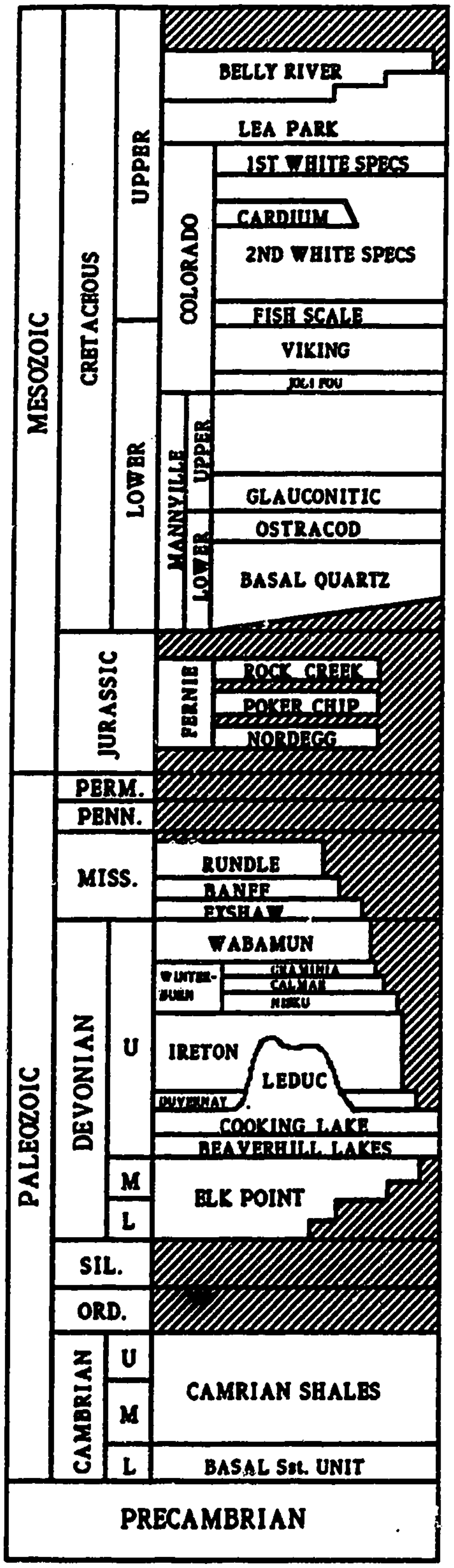


Fig.A.1. Generalized stratigraphic column, Central Plains, Alberta, Alberta Basin (modified after *Energy Resources Conservation Board Table of Formations*).

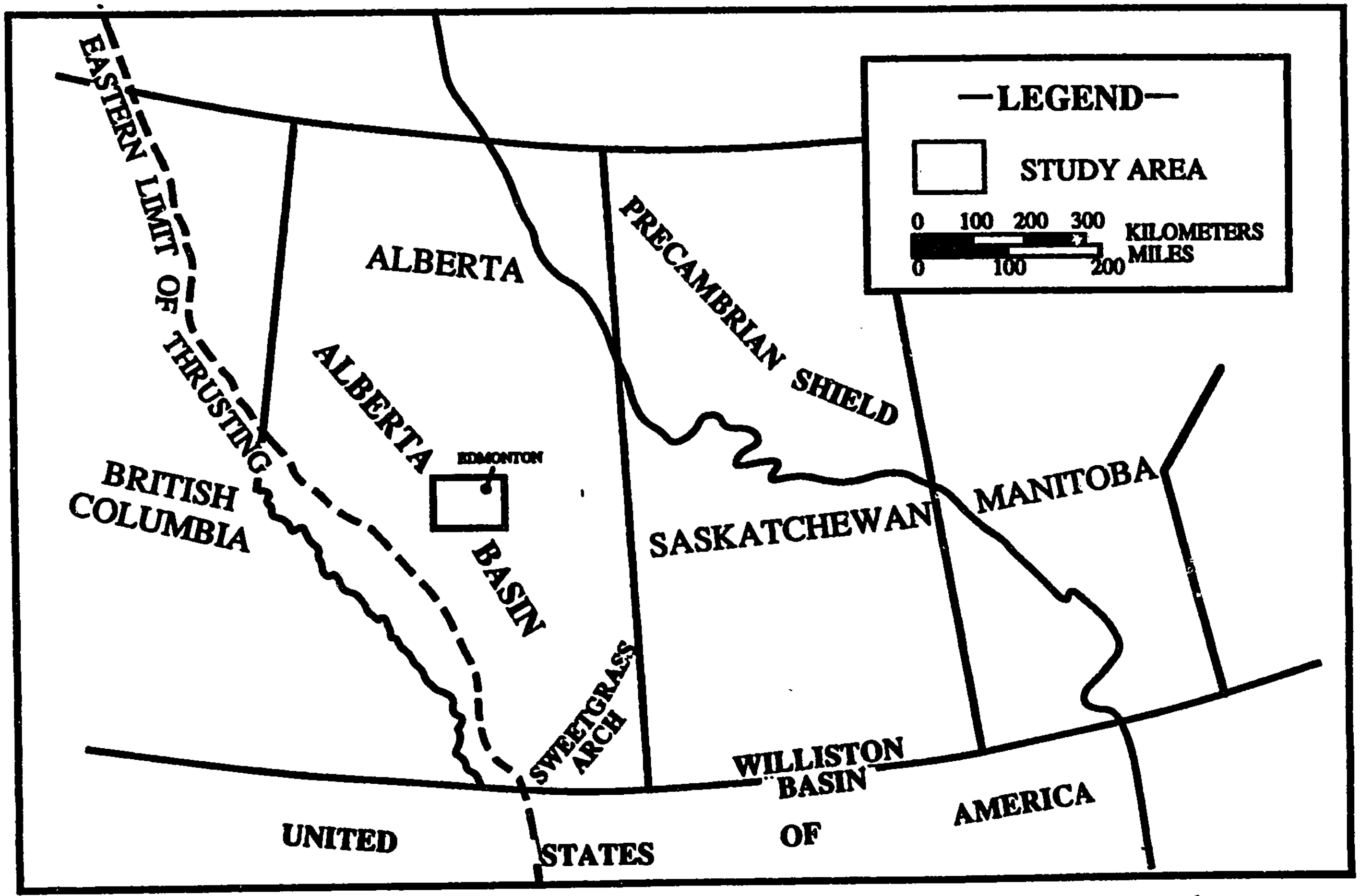


Fig. A.2. Map of the Western Canada Sedimentary Basin, showing the location of the sub-basins and the study area.

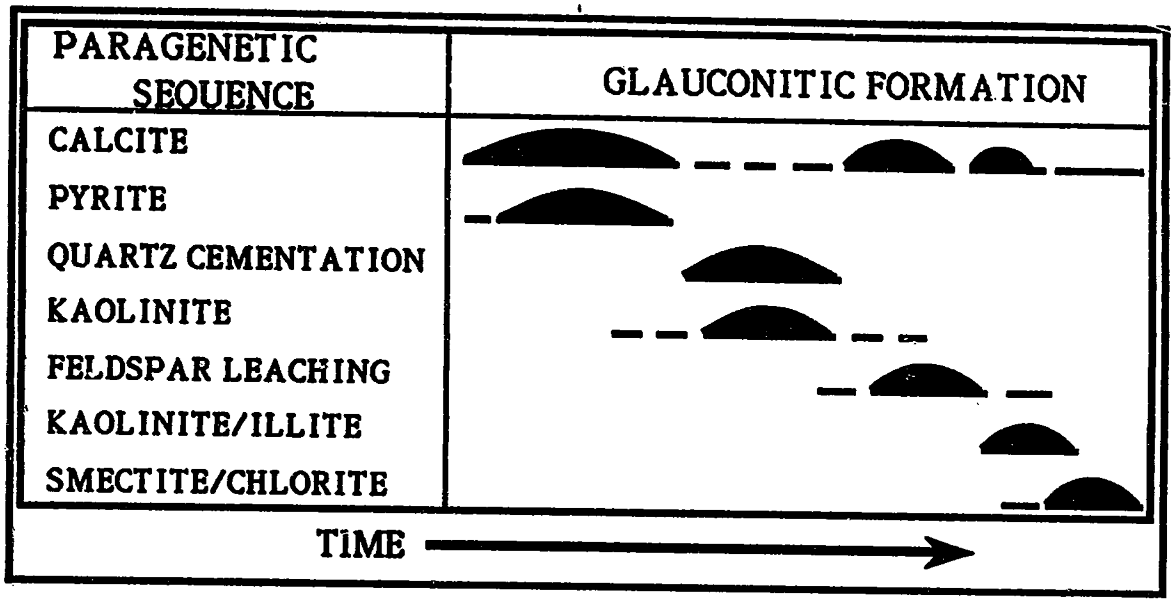
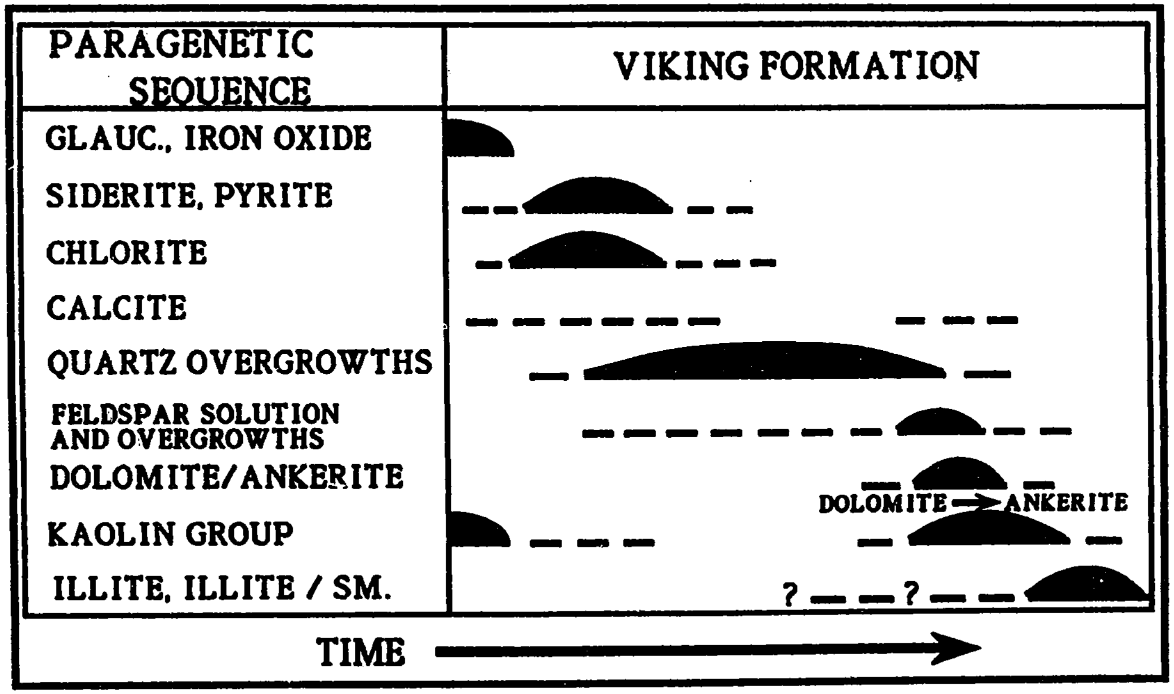
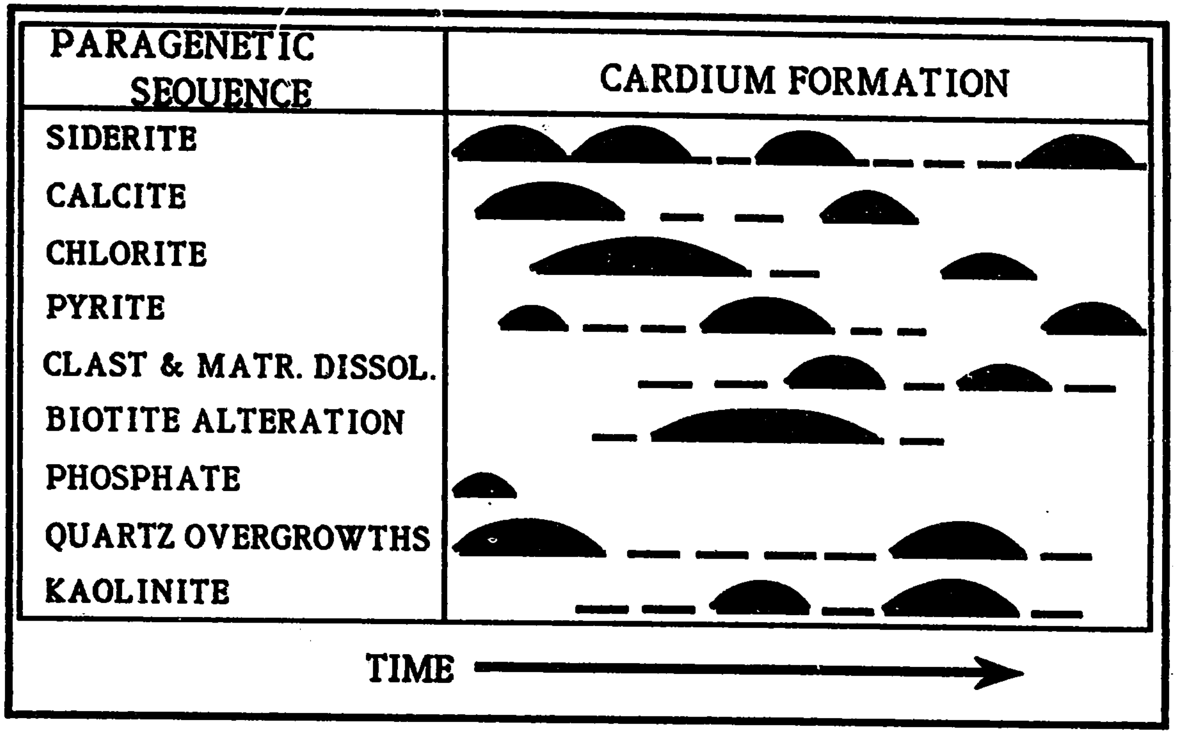


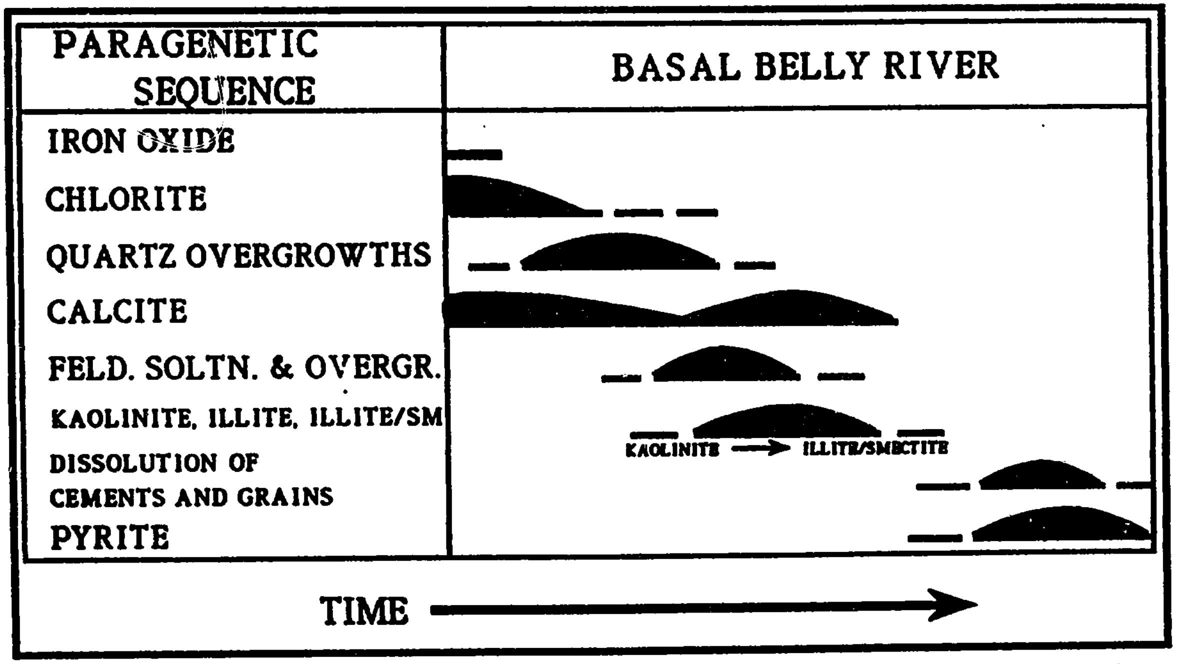
Fig. A.3. General paragenesis of diagenetic minerals for some of the Cretaceous reservoir rocks. (a) Glauconitic Formation



(b) Viking Formation (modified after DEAN, 1986; LONGSTAFFE and AYALON, 1987)



(c) Cardium Formation (modified after MACHEMER and HUTCHEON, 1988)



(d) basal Belly River Formation (modified after AYALON and LONGSTAFFE, 1988).