Sr ISOTOPIC COMPOSITION OF SALINE WATERS AND HOST ROCK IN THE EYE-DASHWA LAKES PLUTON, ATIKOKAN, ONTARIO

Sr ISOTOPIC COMPOSITION OF SALINE WATERS AND HOST ROCK IN THE EYE-DASHWA LAKES PLUTON, ATIKOKAN, ONTARIO

By

Michael T. (Bone) Franklyn, Hons. B.Sc.

A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree
Master of Science

McMaster University
December 1987

MASTER OF SCIENCE (1987)
(GEOLOGY)

McMaster University
Hamilton, Ontario

TITLE: Sr isotopic composition of saline waters and host rock in the Eye-Dashwa lakes pluton, Atikokan, Ontario.

AUTHOR: Michael T. Franklyn, Hons. BSc., BSc. (McMaster University 1985, 1982).

SUPERVISOR: Dr. R.H. McNutt

NUMBER OF PAGES: XI; 108.

ABSTRACT

Groundwater samples from seven boreholes at the Atikokan research area, northwestern Ontario, have been analysed to determine their Sr content and isotopic composition. Whole rock and mineral separates have also been analysed. The groundwaters can be broadly divided into two groups. The 'shallow' waters have low Sr content and high and variable isotopic ratios (.705 - .728) while the 'deep' Sr-rich saline groundwaters have low and constant $^{87}Sr/^{86}Sr$ ratios (.706 - .707). The saline waters are in isotopic equilibrium with plagioclase and the role of other major rock forming minerals in controlling the isotopic and chemical composition of these waters is negligible. Gypsum is in isotopic equilibrium with the saline waters and appears to be 'young'.

The degree of water-plagioclase interaction appears to have been extensive implying low water/rock ratios (ie., 'closed' system. The chemistry of the Atikokan groundwaters is similar to several Shield mine waters. If seawater was a precursor of these waters, there is no evidence for it today. Some degree of mixing with surface waters is indicated in all samples.

The granites of the Eye-Dashwa lakes pluton are very Sr-rich. This is reflected in the low isotopic ratios of plagioclase and other minerals and in turn in the low ratios for the saline groundwaters, which are some of the lowest values yet reported.

ACKNOWLEDGEMENTS

I would like to express my appreciation, first and foremost to Bob McNutt. His guidance, insightful comments good humour and patience made this research experience both interesting and rewarding.

This work was made possible by Drs. D.C. Kamineni and M. Gascoyne of AECL who kindly provided core and waters samples for analysis in this study. The funding of this project by AECL is also greatly appreciated. I would like to thank Dr. S.K. Frape of the University of Waterloo for providing both valuable advice and a few precious samples that were used in this work and also for laying much of the groundwork on which studies such as this one are based.

Steve Zymela and Steve Prevec provided this neophyte with much appreciated help in the computer tasks carried out for this work. For their helpful comments and suggestions I would like to thank, Wang Xing Li, Steve Prevec, and Brent McInnes.

The assistance of Dave Jones, Jim McAndrews and Ota Mudroch, on the solid source mass spectrometer, ICP-MS and XRF, respectively, is very much appreciated. Jack Whorwood is responsible for the quality photographs and photo reductions contained in this thesis.

Many thanks to Brent and Noreen and my friends in the department, for providing the essential distractions and diversions that made the past two years memorable. And finally, for her undying support and confidence, I thank Karen.

TABLE OF CONTENTS

Page

CHAPTER ONE : INTRODUCTION

CHAPTER TWO : METHODOLOGY

2.3 Chemical Analyses

CHAPTER THREE : GROUNDWATERS

CHAPTER FOUR : PETROGRAPHY AND GEOCHEMISTRY OF THE HOST-ROCK MATERIAL

CHAPTER FIVE : DISCUSSION Page

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

CHAPTER ONE

INTRODUCTION

1.1 Purpose of Study

A number of granitic plutons in the Canadian Shield are currently being studied by the Canadian Nuclear Fuel Waste Management Programme (CNFWMP) of Atomic Energy of Canada Limited (AECL) in conjunction with the Geological Survey of Canada (GSC) to assess the feasibility of using igneous plutons as possible containment sites for high level nuclear waste. To this end, a thorough investigation of the geology of potential sites is required. Specific assessment of the relationship between the characteristics of the host rock formation and the groundwater regime in the area is needed. As one method of assessment, Sr isotopes have been used in this study to investigate the nature and extent of water-rock interaction. The Sr isotopic composition of both drillcore and groundwater samples, collected since 1979 from seven boreholes at the Eye-Dashwa Lakes pluton test grid near Atikokan, Ontario, have been determined.

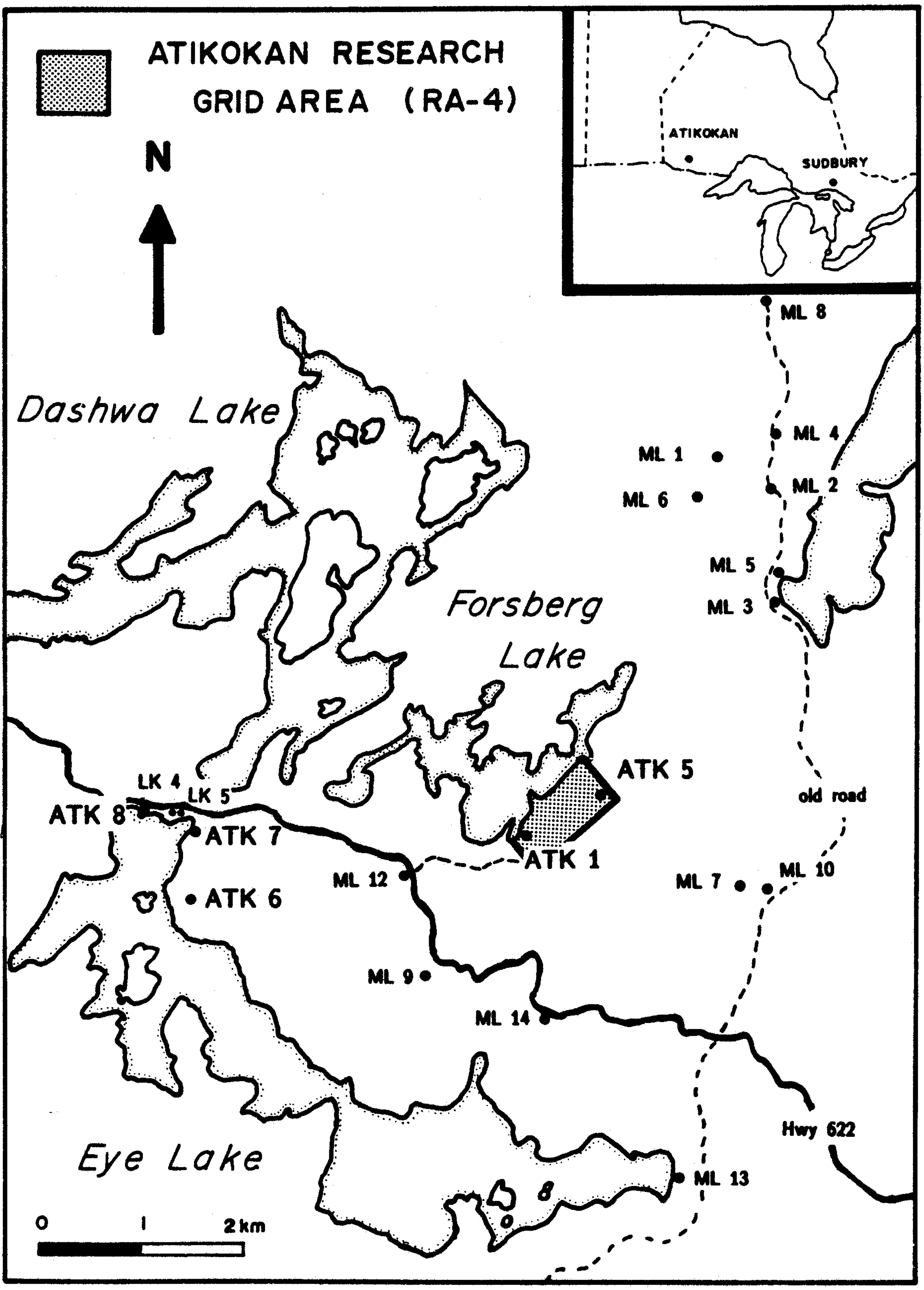
1.2 General Geology

The Eye-Dashwa lakes pluton is located in the Superior Structural Province of the Canadian Shield approximately 18 kilometres NNW of Atikokan, Ontario. The area is accessible by highway 622 which runs north from Atikokan (figure 1).

The pluton is intrusive to the Dashwa gneiss, a series of tonalitic to granodioritic gneisses. It is egg-shaped and consists of three distinct compositional, intrusive phases. The earliest is a medium to coarse grained syenodiorite which forms the border of the main 'granite', an intermediate phase, found only in the southern and eastern margins of the pluton, is a fine to medium grained, massive to foliated leucogranite. The last phase which constitutes the bulk of the Eye-Dashwa pluton is a medium to coarse grained, subporphyritic, biotite-hornblende granite. The test grid area in which boreholes ATK-1 through ATK-5 were drilled is located in this unit.

Subsequent faulting and intrusion of diabase dykes have affected both the intrusive granite and the surrounding Dashwa gneiss (Brown et al., 1980). Faults and fractures in the area contain a number of fracture filling minerals that broadly fall into two categories; high and low-temperature. Fracture filling minerals will be discussed in detail in a later section.

Figure 1: Map showing the location of the Atikokan research area, northwestern Ontario. Location of research area test grid, alternately known as Forsberg Lake test grid, in which boreholes ATK-1 through ATK-5 were drilled (for relative position of boreholes see figure 2). The site of ATK-6,7 and 8 as well as the LK and ML series shallow boreholes are also shown.


ATIKOKAN RESEARCH GRID AREA (RA-4)
N
ATIKOKAN
SUDBURY
Dashwa Lake
Forsberg Lake
Eye Lake
ML 8
ML 4
ML 1
ML 2
ML 6
ML 5
ML 3
ATK 5
old road
LK 4
LK 5
ATK 8
ATK 7
ATK 1
ML 12
ML 10
ML 7
ATK 6
ML 9
ML 14
Hwy 622
ML 13
0
1
2 km

1.3 Geochronology of Eye-Dashwa lakes pluton

In a study of the ages of fractures in the Eye-Dashwa lakes pluton, Kamineni and Stone (1983) reported a K-Ar age of 2658 ± 67 Ma for a hornblende from an undeformed granite sample taken from the east-central region of the pluton. This age is similar to those of other Archean plutons in the area, as determined by Birk and McNutt (1981). Peterman et al.(1985) have reported an age of 2674 ± 23 Ma from the Eye-Dashwa lakes pluton based on the U-Pb zircon method. Krogh and Turek (1982) have found ages slightly older at 2.68 to 2.75 Ga by U-Pb zircon dating from granitic intrusions in the Western Superior Province, indicating that perhaps a considerable length of time may have passed before the blocking temperature of the K-Ar and Rb-Sr systems was reached, resulting in the younger ages derived by these methods.

K-Ar dates from high temperature fracture filling materials range from 2,655 ± 31 Ma for an aplite to 2,472 ± 71 Ma for a chlorite filled fracture. Radiometric ages of aplite, epidote, hornblende-porphyry and chlorite filled fractures indicate that the fractures are ancient and formed shortly (maximum 300 Ma) after the pluton was emplaced (Kamineni and Stone, 1983). Diabase dykes within the pluton yield K-Ar ages of 1,132 ± 27 Ma, an age similar to that of the Duluth Gabbro and other diabase dykes in the Lake

Superior region (Douglas, 1980). This indicates renewed fracturing in the pluton following approximately 1300 Ma of quiescence. The most recent activity in the Eye-Dashwa lakes pluton probably reflects re-opening of pre-existing near surface fractures. Low temperature carbonates (i.e. calcite) are found as coatings in reactivated epidote and chlorite filled fractures and give ^{14}C ages of 54 ± 10 to 21 ± 8 Ka. K-Ar ages quoted were obtained at the Geochronology Laboratory of the GSC while the ^{14}C dates were determined at the Isotope Laboratory, University of Waterloo.

CHAPTER TWO

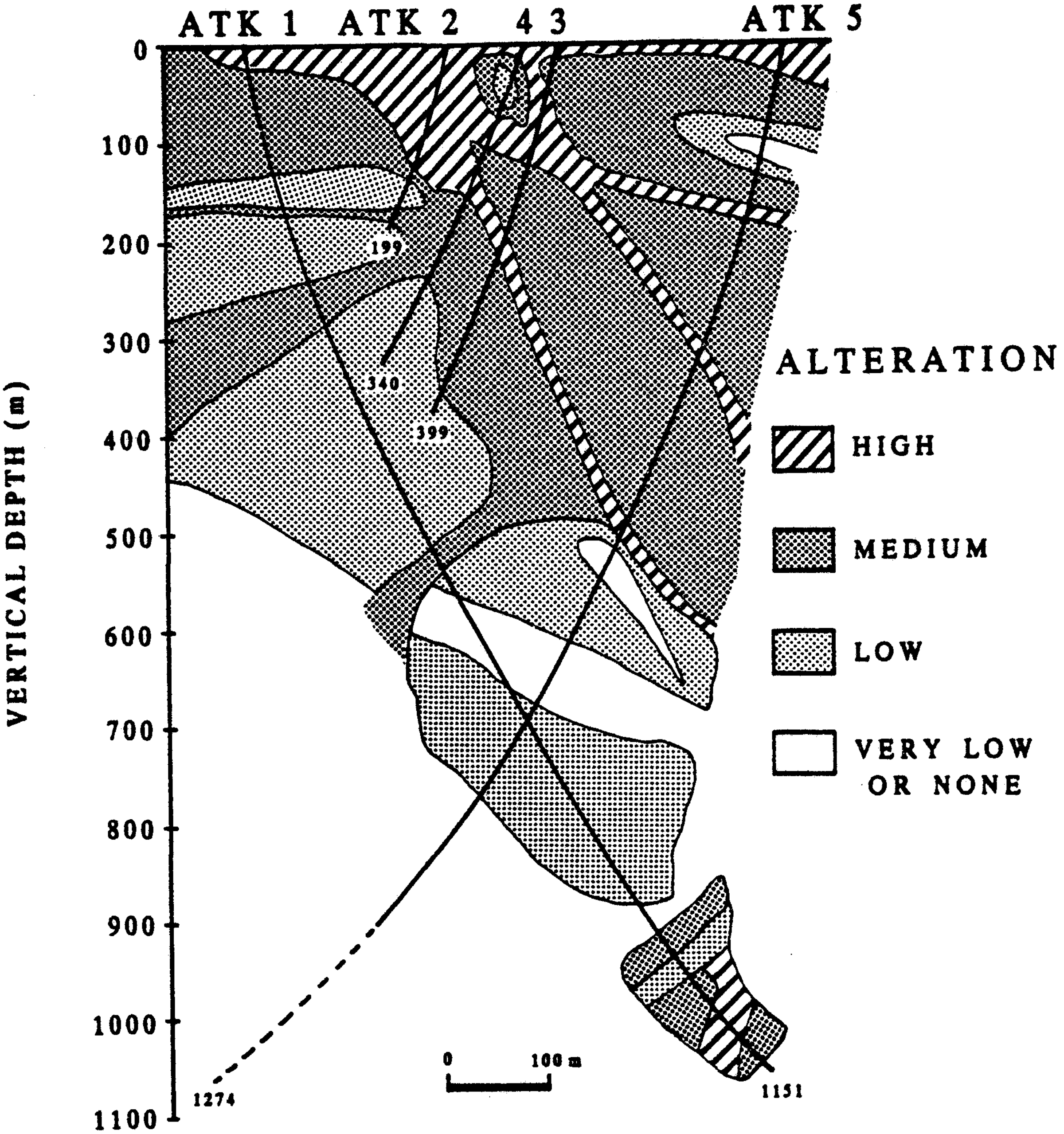
METHODOLOGY

2.1 Sample Collection

Core and water samples were kindly provided by Dr. D.C. Kamineni of AECL. Addition samples of saline waters were provided by Dr. S.K. Frape of the University of Waterloo. Core samples were made available from boreholes ATK -1,2,4, 5,6,7,8 (figures 1 and 2). Due to the number of engineering and chemical tests done on each section of drillcore, only a small portion of the recovered core is allocated to geological studies (for details the reader is referred to the standard sample distribution scheme: page 13, TR-278, Percival and Hume 1984). Because of the relative scarcity of core it was not possible to obtain samples that were uniformly distributed over the length of the boreholes. The core samples that were made available varied from a minimum of 48 g to split core sections ca. 30 cm in length. Most core available was from ATK-1. Fortuitously, several of the samples were from the immediate vicinity in which a highly concentrated brine sample had also been collected and made available to us.

Boreholes ATK-1 through ATK-5 were drilled in a test grid area on the east shore of Forsberg Lake (figure 1) in the fall of 1979. ATK-1 and -5 were drilled to a depth in

Figure 2: Alteration section across the Atikokan research area drill site showing the relative degree of alteration based upon macroscopic and mesoscopic observations such as the degree of discolouration of feldspars and ferromagnesian minerals (modified from Kamineni and Dugal, 1981).


ATK 1
ATK 2
4 3
ATK 5
VERTICAL DEPTH (m)
0
100
200
300
400
500
600
700
800
900
1000
1100
199
340
399
1274
1151
0
100 m
ALTERATION
HIGH
MEDIUM
LOW
VERY LOW OR NONE

excess of 1000m (1151 and 1274m, respectively) while ATK-2,3,4 were drilled to a maximum depth of 400m (199m, 399m and 340m respectively) (figure 2). All holes were NQ-3 type, diamond drilled boreholes (75.8 mm diameter) from which the 45mm diameter core samples were pulled. Following drilling, swabbing or high pressure air-lifting techniques were used to clear the borehole of drill water and rock chips.

Water samples were collected from boreholes by placing packers at various levels in the hole and allowing water to drain into the isolated zone over time (up to 18 months). The packers were sequentially penetrated from the top down and the water within each zone sampled. The packers used to isolate intervals for geochemical sampling are Lynes (2 5/8") Production Injection Packers (PIP s). Each PIP is ca. 0.9m long and is lowered into position and then inflated using a high pressure pump. These packers are capable of remaining sealed for periods in exceess of one year (Gartner-Lee 1983). Some chemical parameters are measured 'downhole' or in situ to avoid the affect of change in pressure, temperature and the time taken to pump the waters to the surface (ie. redox potential, temperature, dissolved oxygen,conductivity etc.). For such measurements, a series of sensors and samplers are mounted in a 'piggyback' fashion within an instrument called a Downhole Geochemical Probe that is lowered into the borehole (Bottomley et al, 1980).

The ATK holes were sampled using 44 mm. diameter I.D. tubing connected to rubber bladder 'squeeze pumps' attached to a 2 h.p. electric air compresssor. The PIPs were penetrated to allow sampling using a high pressure Alco water pump. Ideally, as short a section of the borehole as possible should be isolated between packers, thereby allowing the source of the incoming water to be as tightly constrained as possible. Sampling zones are selected on the basis of hydraulic conductivity data and on the degree of fracturing as determined from borehole acoustic televiewer (ATV) logs. In the absence of identifiable, high permeability zones, a long section or perhaps the entire hole was left open during testing/collection.

Water samples collected from the ATK holes represent a minimum of 10m and up to 700m between packers. The data for waters that represent several hundred metres of the borehole may reflect mixing between near surface (and drill water) and deep waters within that interval. Such mixing can be detected by the addition of a dye (Rhodamine WT) to the drilling water or by the presence of high levels of tritium.

On surface, samples are filtered through 0.45 µm membrane filters, acidified (8ml/L HNO_3) and stored in precleaned, high density polyethylene (HDPE) Nalgene bottles for subsequent analyses.

2.2 Sample Preparation

2.2.1 Water Samples

Most water samples were suitable for analysis as received from AECL because they had been filtered and acidified in the field. They were clear and free of sediments. Some samples however, were discoloured and were doubly filtered and reacidified at McMaster. The brown colour was due to the precipitation of iron hydroxides also called 'pipe scale', an unavoidable byproduct of the drilling process. The consequence of Fe-hydroxides on Sr isotopic analysis should be negligible since they contain no Sr. 'Pipe scale' is present in all samples as they are taken from the boreholes (J. Ross, pers. com.) and therefore, any effect would be the same for all samples. Prior to ion exchange column work and analysis on the Inductively Coupled Plasma mass spectrometer (ICP-MS), the water samples were acidified with 2.5 N HCl to convert Sr species to chlorides.

2.2.2 Core Samples

2.2.2.1 Crushing

Prior to crushing, all core samples were washed with Milli-Q water and any markings or oxidation products removed. The samples were then crushed in a chipmunk jaw crusher and ground in a BICO ceramic disc pulverizer with a minimal space setting between the plates. Following the crushing of each sample the apparatus was disassembled and cleaned with wire and soft bristle brushes, acetone and compressed air. Clean quartz was passed through the disc pulverizer between each sample to aid in the thorough cleaning of the plates. Whenever possible (based on sample availability) the equipment was pre-contaminated by passing a small amount of sample through the jaw crusher, disc pulverizer and shatterbox, this portion was then discarded. The result of the crushing procedure was a mixture of grains ranging in size from a fine powder to rock chips up to 3mm in diameter. This mixture of grain sizes was then mixed until homogeneous and quartered. One portion was ground to -300 mesh in a Spex Industries tungsten-carbide ring shatterbox. This pulverized aliquot was used for whole rock analyses. The remaining crushed rock was used for mineral separation work.

2.2.3 Mineral Separates

Very fine material (-200 mesh) was removed from the mineral separate fraction by washing the grains a minimum of six times (and as many as 13) with Milli-Q water. This was done by placing the crushed rock in a 1000 ml beaker and filling the beaker with Milli-Q water. The solution was stirred vigorously with a glass stirring rod, allowed to settle for ca. 30 seconds, the cloudy supernatant water was decanted off and the procedure repeated until the water remained clear after stirring. The 'cleaned' grains were rinsed twice with methanol, transferred to a large watch glass and oven dried at 100°C overnight. The cleaned samples were stored in large-mouthed Nalgene bottles.

Because brass sieves present a contamination problem (Hickson and Juras, 1986), new sieves were constructed using a piece of commercially available Nytex monofilament nylon mesh stretched between two polyethylene beakers with the top beaker's bottom removed. The nylon mesh material was secured between the beakers and a lid placed on top. The sample was shaken by hand until the required separation was achieved. Samples were passed through a series of progressively finer sieves. At each stage the sample was passed through the sieve twice. A new piece of mesh was used for each sample.

The first pass used a 21 mesh (0.84 mm diameter) nylon screen. Grains coarser than this (+21 mesh) were set aside or recrushed and the above procedure repeated. The -21 mesh fraction was then passed through a 64 mesh (0.22 mm), a 100 mesh (0.149mm) and finally a 150 mesh (0.09mm) screen. In this way, three different size fractions of each sample were isolated:

1. 21 to 64 mesh
2. 64 to 100 mesh
3. 100 to 150 mesh

It was found that the best results were achieved during density separation using either the 21 to 64 or 64 to 100 mesh fractions, the latter being more suitable for finer grained samples.

2.2.3.1 Magnetic Separation

After sieving, the next step in the mineral separation process was magnetic separation. Magnetite was first removed from the samples with a simple bar magnet. Samples were then passed through a Franz Isodynamic Magnetic Separator, model LI, with a side tilt of 15^{o} and a slope setting of 25^{o}. With increasing current, concentrates of epidote, biotite, and quartz and feldspars were obtained. At each stage the samples were passed through the separator a minimum of three times to increase the purity of that particular fraction. Plagioclase, K-feldspar and quartz are all collected together in the non-magnetic fraction. Epidote is difficult to purify using solely magnetic separation. The concentrates collected above (K-feldspar, plagioclase and epidote) were further separated using heavy liquids.

2.2.3.2 Density Separation

In light of the well documented health hazards and prohibitive cost of heavy liquids, a new and unique product was used for the density separations carried out in this study. Sodium polytungstate ($3Na_2WO_4.9WO_3.H_2O$) is a nontoxic, relatively inexpensive powder ($60 Can/2 kg) that when mixed with water can yield a heavy liquid with a density of between >1.0 and 3.0 g/ml.

One desirably feature of sodium polytungstate is that its density can be 'fine tuned' to suit ones needs. Since the density of plagioclase varies from a low of 2.63 g/ml for albite to a high of 2.76 for anorthite and that of microcline and orthoclase varies from 2.55 to 2.63 there is some overlap for the two types of feldspars. Using chip samples of pure reference minerals, a polytungstate solution was made with a density of ca. 2.63. Since the plagioclase in these rocks is oligoclase its density will be approximately 2.65. Therefore, when placed in this solution, the plagioclase sank, while the K-feldspar floated. Since the density of quartz is 2.65 it was collected along with the plagioclase fraction. In these analyses quartz is not considered a contaminant since it contains an insignificant amount of Sr.

A second sodium polytungstate solution with a density of ca. 3.1 g/ml was prepared for the separation of epidote. Other phases collected with epidote during magnetic separation could include hornblende, chlorite, sphene and possibly biotite. Hornblende, biotite and chlorite are all less dense than epidote, while sphene can be easily separated from epidote by hand picking. Therefore, the combination of magnetic and density separation followed by hand picking resulted in high purity epidote. Epidote was often seen as a coating on plagioclase grains and in these cases the grains were recrushed by hand in a steel mortar and the entire separation process repeated in order to obtain a high purity epidote separate.

The density separations were done in a 500 ml separatory funnel equipped with a Teflon stopcock. First, a small amount of the heavy liquid would be loaded into the flask. A maximum of ca. 15 g of mineral grains would then be added via a funnel followed by the remainder of the liquid (350 ml in total). The solution would then be thoroughly stirred to overcome any surface tension effects and to ensure that all mineral grains were coated with the solution. Care must be taken not to introduce air bubbles while stirring or adding the liquid as these will adhere to the grain surfaces and interfere with the separation. The mixture was then allowed to equilibrate from a period of 2-3 hours. During this time, the top of the flask must be sealed, either with a stopper or a piece of Parafilm to prevent evaporation and thus a change in the density of the solution.

After an obvious separation has been achieved and no grains are seen to be in motion (up or down), the plagioclase contents of the flask are slowly and carefully drained into a funnel lined with filter paper. Potassium feldspar is collected in a second filter-lined funnel. Several methods of filtration were experimented with. Flat filter paper placed in a Buchner funnel attached to a vacuum line was found to be unsatisfactory as some of grains were lost around the edges of the filter paper, even though it was pre-wetted. Finally, the slowest method was adopted, in which a cone was made from a circular piece of filter paper and the heavy liquid was left to drain through. Due to the relatively high viscosity of the sodium polytungstate solution (especially the higher density solution) little advantage was seen when a vacuum line was attached. Therefore the samples simply drained under gravity.

After filtration, the heavy liquid was recovered and could be reused. One effect however, of the lengthy filtration, is that the density of the solution can change considerably. Therefore it is strongly recommended that the density of the solution be tested between each sample, using a set of mineral standards.

The mineral separates were washed a minimum of 6 times with Milli-Q water, rinsed twice with acetone and left overnight in a drying oven. The sodium polytungstate is highly soluble in water and effectively removed from the surface of the grains by this method.

Between every sample, the density separation apparatus was disassembled, thoroughly washed, rinsed with Milli-Q water and dried in the oven. The sodium polytungstate solutions were kept in air-tight Teflon bottles. The density of the solution was tested before each use. The solutions were also frequently doubly filtered to assure their purity.

Following these steps the mineral separates were examined under a binocular microscope to determine their purity. In the case of the biotite and several epidotes, individual grains were handpicked from the final product of these separation steps.

2.3. Chemical Analyses

2.3.1 XRF

Rb and Sr concentrations for whole rock samples were determined by the Mo-Compton peak method using a Phillips 1450 AHP automatic sequential X-ray fluorescence spectrophotometer (XRF) located in the Department of Geology, McMaster University. A 5 g sample of whole rock powder (-300 mesh) was mixed with ca. 1 ml of Mowiol, a polyvinyl alcohol binder, placed in a 30 mm Chemplex aluminum cap and pressed into a pellet under a pressure in excess of 20 tons/ sq. inch. Raw data were corrected for absorption and enhancement effects according to the method outlined by Marchand (1973). USGS standards used in calibration include: G-2, GSP-1, AGV-1, W-1, BCR-1, MRG-1, SY-3, BE-N as well as NBS 70A. A comparison of values for three standards (G-2, GSP-1 and AGV-1) is shown in Appendix 2. The Rb and Sr data agree within ± 1% with the values reported by Flanagan (1986).

2.3.2 Sr Isotope Ratios

Whole rock and mineral separate samples were dissolved in a series of acids ($HF/HNO_3/HCl$) in Teflon bombs over a period of 4 days. The resulting solution was then split and the isotope dilution aliquot spiked with the appropriate spike. For this work ^{84}Sr and ^{87}Rb spikes were used. The samples were loaded onto ion exchange columns in 2.5 N HCl acid. Rb (ID), Sr (ID) and Sr(IR) aliquots were collected for analyses. The Sr samples were loaded (in phosphoric acid H_3PO_4) onto Ta single filaments and analysed in the VG 354 solid source mass spectrometer. The isotope ratio samples were run dynamically while the Sr isotope dilution samples were run statically. Details of the sample preparation procedure are provided in Appendix One. Replicate analyses of NBS 987 and several samples (both a dilute and a concentrated groundwater as well as one whole rock sample) gave a precision level of 0.003% for Sr isotopic analyses (details given in Appendix 2). The results of standard data for NBS 987 agree well within error with the VG value (.710211 vs .710232). The values of Pankhurst and O'Nions (1973) (.71039) and the NBS certificate (.71014) are considered to be outdated. Isotopic ratios for USGS standards G-2 and AGV-1 agreed within error with those of Pankhurst and O'Nions (1973) while that of GSP-1 did not, perhaps due to a slight heterogeneity in the standard.

2.3.3 Sr and Rb Isotope Dilution

The Rb concentration of mineral separates was determined by the method of isotope dilution (ID) on the Sciex-Elan Inductively Coupled Plasma mass spectrometer (ICP-MS) at McMaster. Based upon a single USGS standard, Rb isotope dilution samples appear to agree with those of Pankhurst and O'Nions (1973) to within ± 0.3% .

The Sr concentration of mineral separates was measured using isotope dilution on the VG 354 solid source ionizing mass spectrometer at McMaster. Sr ID values agree within ± 0.3% with those of Pankhurst and O'Nions (1973) for G-2, GSP-1 and AGV-1. Details of the Rb and Sr ID analyses are given in Appendix Two.

The $^{87}Rb/^{86}Sr$ ratio was calculated from the Rb and Sr concentrations determined above with the assistance of a BASIC programme kindly provided by a fellow graduate student, Steve Prevec.

2.3.4 Sr Determination in Groundwaters

The Sr concentration of the groundwater samples was determined using the Rh internal standard method on the ICP-MS. In this method a small aliquot (100 mg) of a Rh solution (400 ppb) is added to both the water samples and the Sr standard solutions. The counts are then normalized to the measured Rh response and a Sr concentration is calculated. This method was found to be particularly useful since it overcomes machine drift, the nemesis of the ICP-MS. Rh was chosen since it is an element not commonly found in groundwaters and has similar ionization characteristics to Sr.

The very high Ca content of some brines was found to 'throttle' the ICP-MS, a result of the photomultiplier being overwhelmed by the large Ca signal. For these samples, weight by weight dilutions were done until the Ca concentration was reduced to within the working range of the instrument.

The precision and accuracy of the ICP-MS method are discussed in Appendix Two.

CHAPTER THREE

GROUNDWATERS

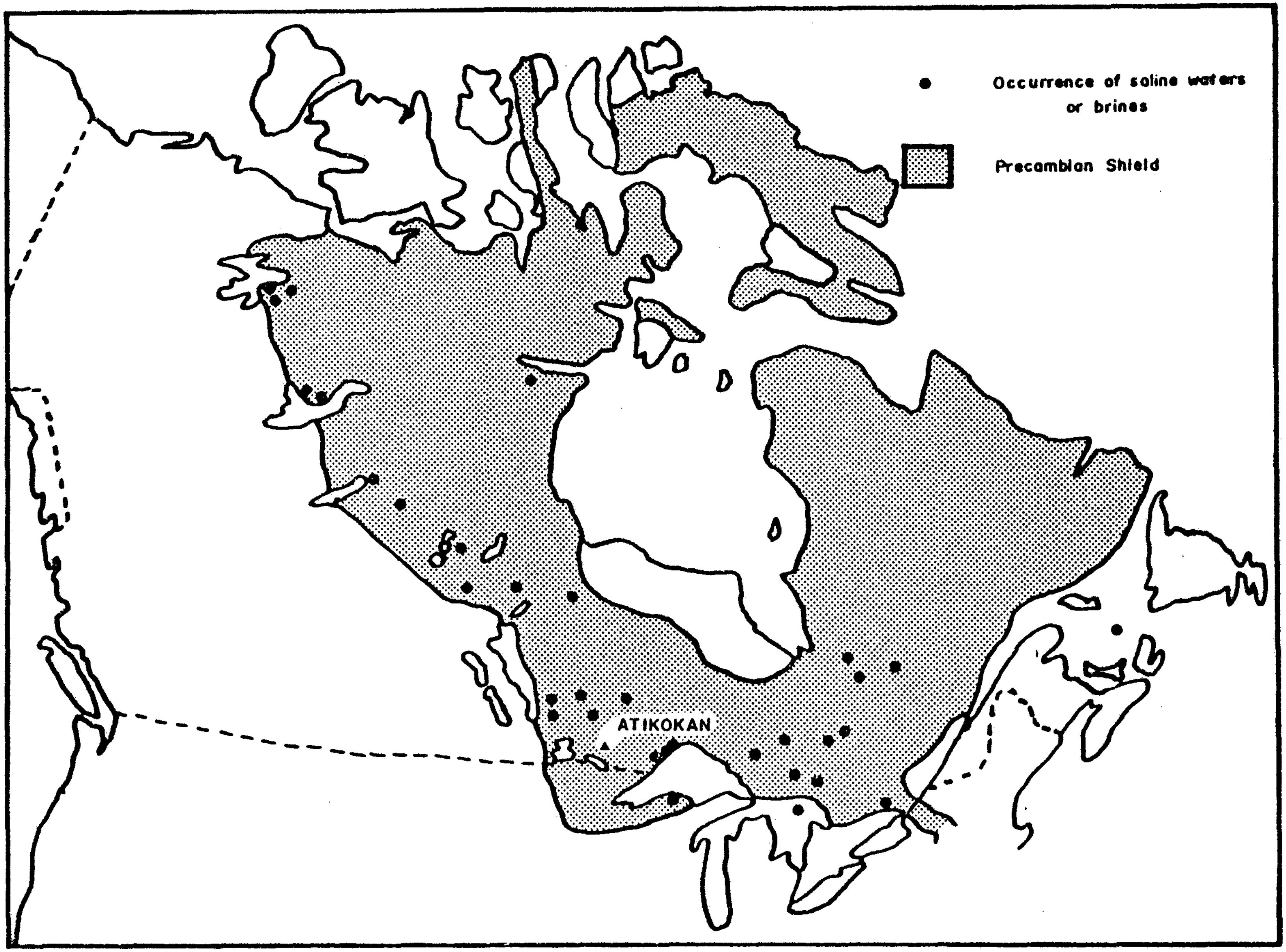
A. REVIEW OF CHEMICAL DATA

3.1 Elemental Chemistry

Brines have been found at over 30 localities in the PreCambrian Shield of Canada (figure 3) as well as in the Baltic Shield and younger rocks such as the Hercynian granites at Cornwall, England (Frape and Fritz, 1982, 1987, Edmunds et al., 1987). They are located in a variety of crystalline rock types. Early work on these Shield waters by Fritz and Frape (1982), Frape and Fritz (1982), Frape et al. (1984) and McNutt et al. (1984) at Sudbury, Ontario, Thompson, Manitoba and Yellowknife, Northwest Territories showed several significant similarities in their chemical compositions.

Groundwaters are described in terms of their total dissolved solids (TDS), which equals the sum of the cations and anions in solution. Waters with TDS < 1,000 mg/L are referred to as `fresh', while those with TDS < 10,000 are called `brackish'. `Saline' waters are those with TDS between 10,000 and 100,000 and `brines' have TDS > 100,000 mg/L. Frape et al. (1984) defined the fresh and brackish waters that occur above 650m as `shallow' groundwaters and those occurring below this level as `deep' groundwaters.

Figure 3: Location of sites on Canadian Shield where saline waters and brines have been sampled (modified from Frape and Fritz, 1987).


● Occurrence of saline waters or brines
▨ Precambian Shield
ATIKOKAN

They found that shallow groundwater major element chemistry reflects the local host rock composition, ie. Thompson, Manitoba where the elevated Mg content of the shallow waters reflects the Mg-rich nature of the ultramafic host rock. At other sites, the fresh to brackish waters are dominated by a Na-Ca-HCO_3 or Ca-Na-HCO_3 compositions.

In granitic terrains the shallow groundwater chemistry is dominated by Na, followed by Ca>Mg>K>Sr. Bicarbonate is the major anion, followed by SO_4>Cl. In shallow waters associated with mafic rocks Ca>Mg>Na with lesser amounts of K and Sr. Bicarbonate dominates the anionic composition with lesser Cl which is present in equal or greater concentrations than SO_4.

In contrast to the variable nature of fresh and brackish waters, the chemistry of deep groundwaters is very consistent across the Shield. The saline waters or brines that occur in isolated pockets below 650 metres are Ca-Na-Cl brines with TDS up to 325,000 mg/L and commonly greater than 100,000 mg/L. Some of the chemical contrasts between fresh waters and brines from the Canadian Shield are summarized in Table 1. The waters analysed in this study follow many of the geochemical trends noted by Frape and Fritz (1987) and Pearson (1987) that apply to groundwater samples from across the Canadian Shield. At Atikokan, as at other Shield localities, Cl is the major anion. The major cations are

TABLE 1: A comparison of chemical data for fresh waters and brines sampled on the Canadian Shield - data shown are taken from Table 1, Frape and Fritz, 1987.

SITE	SAMPLE	DEPTH (m)	pH	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L	HCO_3 mg/L	SO_4 mg/L	TDS mg/L
BRINES													
Thompson	4000-4	1500	5.00	64000	45000	5100	199	1080	207000	1760	19	284	324500
Sudbury	N3644b	1650	6.90	62000	22000	48.0	320	1700	168000	1530	-	213	255800
Sudbury	N3646A	1600	6.55	63800	18900	78.0	430	1580	162700	1250	58	223	249100
Sudbury	N3651	1600	6.80	65000	16880	12.0	122	1390	156000	1090	-	138	240700
Yellowknife	4500-6C	1372	5.55	57300	32600	920	495	1640	142000	1520	2	1	237100
Matagami	R36	1800	6.70	61300	14800	3400	338	1460	143581	1785	101	405	227200
Yellowknife	YK2041	1372	-	44700	30000	890	430	950	115000	1010	-	57	193100
Thompson	4000-5	1220	6.25	46300	17000	1960	126	910	115000	1110	9	107	182600
Yellowknife	YK2042	1372	-	39300	21700	820	164	910	109000	935	-	54	172900
Norita	4E-85 #1	-	-	29100	13300	4200	335	960	90000	1134	75.9	5	139100
Yellowknife	YK4500-6A	1372	-	28600	15000	550	118	530	73600	667	-	219	119300
Thompson	4000-6	1220	6.30	26800	8670	637	59.9	558	63800	793	15	2	101400
FRESH													
Yellowknife	14	130	7.40	80.0	107	42.3	4.3	-	51	0.41	341	227	853
Yellowknife	6	175	7.25	103	26	45.9	5.7	-	4	0.1	350	197	739
Thompson	400-1	100	7.50	23.6	119	21.6	6.2	0.6	123	1.4	264	9	579
Sudbury	DOW0002	152	-	21.0	30	6.0	1.8	<0.1	63	-	23	25	185
Sudbury	L26000	793	-	16.0	12	2.9	2.2	<0.1	7	-	32	43	126
Thompson	4000-7	1220	6.20	16.5	3.5	4.1	1.1	-	3	0.18	27	51	117

Ca and Na. Elements such as Sr, Ca and Na have been shown to define mixing trends (Fritz and Frape, 1982) while more labile elements such as K and Mg show highly variable concentrations which are poorly correlated with salinity due to several competing reactions that involve these elements, such as the formation of secondary clay minerals and chlorite, respectively. Still other elements such as F, Br, Li (and Mg) reflect the composition of the source rock in their concentrations, rather than mixing.

The origin of these brines is not understood since their initial chemical compositions have been dramatically altered through time by extensive low temperature water/rock interactions (Frape et al., 1982). Possible precursors of the shield brines include seawater, meteoric,'hydrothermal', metamorphic and glacial waters. The fact that all brines from across the Canadian Shield have very similar chemical composition implies that they are probably genetically related (Frape et al., 1984) or that they have reached their present composition as the result of a long history of exchange with a variety of host rocks and have come to 'equilibrium' under similar pressure and temperature conditions.

As an example of how the chemistry of a brine can be changed through water-rock interaction, consider seawater. Seawater has a higher Na/Ca ratio and lower Br/Cl and Ca/Mg ratios than many highly concentrated brines. Fritz and Frape (1982) discuss how the formation of secondary mineral phases during alteration can significantly effect brine chemistry. Albitization of feldspars will act as a sink for Na, while the formation of chlorite and illite clays will effectively incorporate significant amounts of Mg and K, respectively. Silicate hydrolysis of Ca-bearing minerals such as plagioclase serves to increase the Ca concentration of brines. Sulfate could be removed from seawater by precipitation of gypsum, a mineral that is ubiquitous in fractures below 500m at Atikokan (Kamineni and Dugal, 1982). Formation of calcite would also incorporate large amounts of bicarbonate and Ca. Chloride could be added to solution from the breakdown of biotite and hornblende. In this way, Na-Mg-Cl dominated seawater, could be transformed through time into a Ca-Na-Cl Shield brine via water-rock interaction at low temperatures. Although fossil seawater is only one possible precursor of the brines, this example demonstrates that the formation of secondary mineral phases can profoundly alter brine chemistry.

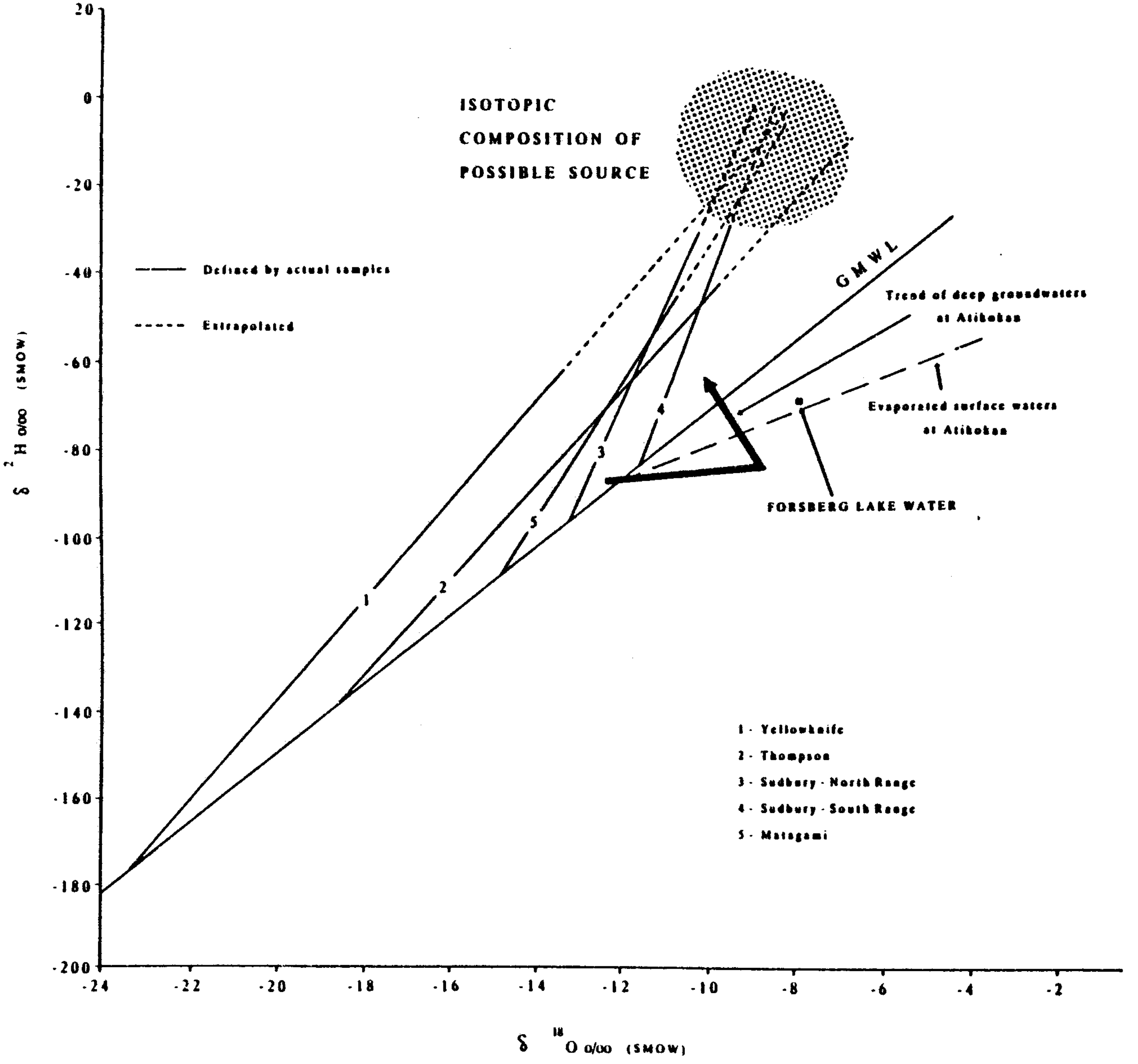
3.2 Stable Isotopes

Although the origin of the saline waters of the Canadian Shield remains uncertain, several lines of evidence now indicate that mixing is an important process in their formation. Frape and Fritz (1982) showed that the stable isotopic trends defined by high salinity samples from Sudbury, Thompson and Yellowknife reflected mixing between local, shallow meteoric groundwaters and a highly concentrated source brine with an unusual stable isotopic composition which lay above the GMWL (figure 4). The isotopic composition of this possible source brine ($\delta^{18}O$ = -10 to -7 ^{o}/oo, δD = -20 to 0 ^{o}/oo SMOW) is distinctly different from fluids found in sedimentary or hydrothermal environments.

Independent work by Pearson (1987) using the chemical composition of concentrated samples extrapolated to halite saturation, defines a source brine of similar isotopic composition. By extrapolating the concentrations of major ions versus the estimated isotopic composition (described above), Pearson was able to calculate a composition of the source brines at Sudbury, Thompson and Yellowknife. The composition of all three is essentially the same, the only different being the high Mg content at Thompson, reflecting the Mg-rich host rock at that locality discussed earlier.

These two lines of evidence, the unique stable isotopic composition and consistent major ion composition for three widely separated Shield sampling locations, argues strongly in favour of a Shield source brine of uniform composition.

Figure 4: Stable isotopic trend of deep groundwaters at Atikokan plotted on a ^{18}O and deuterium plot with other Canadian Shield groundwaters showing possible isotopic composition of source brine or brines from major sites on the Shield. The deepest samples which are correspondingly also the most concentrated plot toward the head of the heavy arrow. (modified from Gascoyne et al., 1987 and Frape and Fritz, 1987).


20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-24
-22
-20
-18
-16
-14
-12
-10
-8
-6
-4
-2
$\delta\ ^{2}H$ o/oo (SMOW)
$\delta\ ^{18}O$ o/oo (SMOW)
ISOTOPIC
COMPOSITION OF
POSSIBLE SOURCE
Defined by actual samples
Extrapolated
GMWL
Trend of deep groundwaters
at Atikokan
Evaporated surface waters
at Atikokan
FORSBERG LAKE WATER
1
2
3
4
5
1 - Yellowknife
2 - Thompson
3 - Sudbury - North Range
4 - Sudbury - South Range
5 - Matagami

It is now widely accepted (by Frape et al., 1982, Frape and Fritz, 1982, McNutt et al., 1987 and others) that all saline groundwaters sampled on the Canadian Shield represent a mixture of at least two isotopically distinct endmembers, one being a concentrated brine, the other being local fresh to brackish meteoric waters. At Atikokan, a three component mixing system may exist where, in addition to the forementioned components, an evaporated surface water, the drill water from Forsberg Lake may be involved (pers. comm. S. Frape). This explanation would be consistent with the direction of the ^{18}O and D shift seen for the saline samples at Atikokan (figure 4).

Low temperature secondary mineral exchange reactions can also explain the unique stable isotopic composition of the shield brines (Fritz and Frape, 1984). The hydration of primary silicates would result in the formation of clays which, in a closed system, would be enriched in ^{18}O and depleted in deuterium. The residual fluid would therefore become correspondingly depleted in ^{18}O and enriched in deuterium. This reaction would thus shift the residual water (brine) above the GMWL, a shift in the direction of the Shield brines. Such reactions would occur in closed systems such as sealed fractures and shear zones where the brines are isolated. Maximum water-rock exchange would be favoured by conditions of low water-rock ratios where flow rates are also low, conditions which exist in deep sealed fractures. Such structural features are common in the deep boreholes (ATK-1 and -5) at Atikokan (Kamineni and Dugal, 1982).

3.3 Strontium Isotopes

McNutt et al. (1984) have shown that Sr isotopes can be used as tracers of water-rock interactions and mixing processes. The geochemically similar behaviour of Sr and Ca further enhances the usefulness of Sr isotopes since they 'trace' Ca, a major component of shield brines and several rock forming minerals (McNutt, 1987).

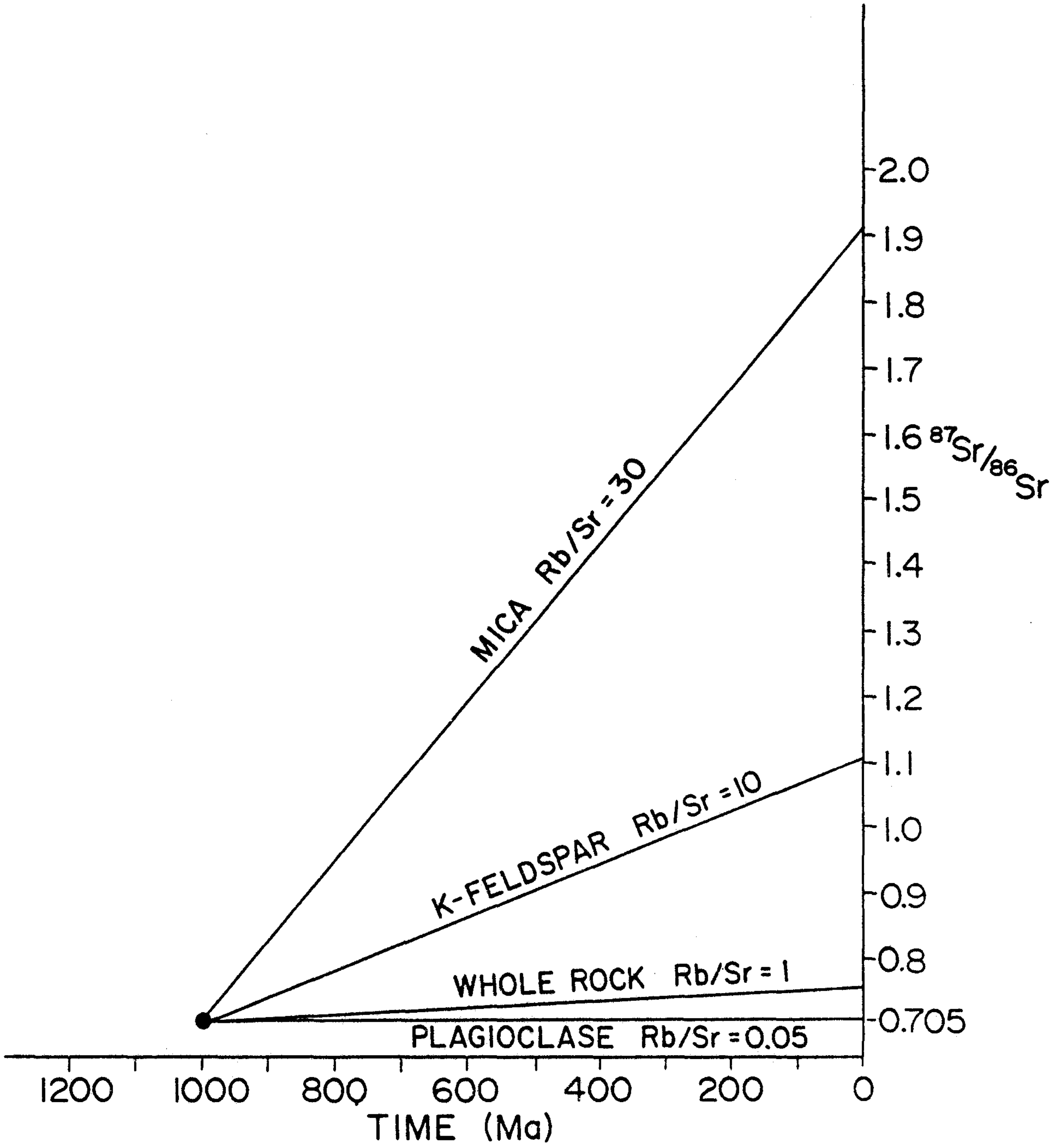
Strontium has four naturally occurring isotopes - ^{84}Sr (0.56%), ^{86}Sr (9.9%), ^{87}Sr and ^{88}Sr (83.8%). While the abundance of the stable isotopes ^{84}Sr, ^{86}Sr and ^{88}Sr remains constant, ^{87}Sr increases in abundance with time through the radioactive β-decay of ^{87}Rb to ^{87}Sr ($T_{1/2}$ (^{87}Rb) = 4.88×10^{10} years).

In mass spectrometric analysis, the ^{87}Sr/^{86}Sr ratio is measured, as it is easier to determine a ratio than the absolute abundance of ^{87}Sr. The value is normalized to ^{86}Sr/^{88}Sr = .1194 to correct for fractionation of the sample in the mass spectrometer. The measured ^{87}Sr consists of two components, the initial ^{87}Sr contained in the rock or mineral at the time of its formation plus the radiogenic

^{87}Sr component that has resulted from the decay of ^{87}Rb over time (t). The greater the Rb content (ie. the higher the Rb/Sr ratio) of a mineral, the greater the rate of increase of the ^{87}Sr/^{86}Sr ratio of that mineral (figure 5). The whole rock value is the product of its constituent minerals. Therefore, for decay in a given time, a mineral such as a mica (ie. muscovite) with a very high Rb/Sr ratio will have a significantly higher ^{87}Sr/^{86}Sr ratio than a Rb-poor (ie. very low Rb/Sr) mineral such as plagioclase. Rubidium free minerals such as epidote, gypsum and calcite will gain very little radiogenic Sr with time and therefore their ^{87}Sr/^{86}Sr ratios will increase even more slowly than that of plagioclase.

If groundwater reacts with a rock and isotopic equilibrium is reached, then the ^{87}Sr/^{86}Sr ratio of the two phases would be equal. If however, equilibrium was reached with a single mineral phase, perhaps due to kinetic effects, then the water would attain a Sr isotopic ratio equal to that of the mineral. If no water-rock interaction takes place, the ^{87}Sr/^{86}Sr of the water should reflect its source. In this way, Sr can be used as a powerful tool in the study of water-rock interactions (McNutt, 1987). This argument is best applied to a 'closed' system, one in which water can exchange with a host rock (or a given mineral) over a prolonged period. If however, large volumes of water are 'flushed' through a rock with a short residence time for any

Figure 5: Strontium evolution diagram showing relative rate of increase of the $^{87}Sr/^{86}Sr$ ratio of constituent minerals. A rock formed 1000 Ma with an initial $^{87}Sr/^{86}Sr$ value of 0.705 evolves to a present-day $^{87}Sr/^{86}Sr$ ratio of 0.748. Note that each mineral evolves in proportion to its Rb/Sr ratio. Rb-poor minerals such as epidote, calcite and gypsum would evolve even more slowly than plagioclase and would therefore have a lower slope than the plagioclase evolution line shown (taken from McNutt, 1987).


MICA Rb/Sr = 30
K-FELDSPAR Rb/Sr = 10
WHOLE ROCK Rb/Sr = 1
PLAGIOCLASE Rb/Sr = 0.05
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.705
87Sr/86Sr
1200
1000
800
600
400
200
0
TIME (Ma)

given water volume (ie. an 'open' system), then the use of Sr as a tracer will be more limited.

Early work by McNutt et al. (1984) using Sr isotopes to investigate water-rock interactions that at Sudbury, showed that isotopic values from a given borehole were constant and that distinct values existed for each site studied, indicating equilibration with the local host rock. Secondary minerals (gypsum) were found to be in equilibrium with the associated brines. Sr isotopic data from Sudbury also supported the concept of 'isolated' pockets of brines. At the North Range, samples located immediately adjacent to a major vertical fault zone in the North mine showed distinctly different $^{87}Sr/^{86}Sr$ ratios of approximately .716 west of the fault and .711 east of the fault. These two distinct waters, in close proximity, appeared to be completely isolated from one another (McNutt et al., 1984).

Recent work (McNutt et al., 1986,1987, McNutt, 1987, Fritz et al., 1987 and Edmunds et al., 1987) has shown that equilibration with whole rock may be the exception rather than the rule. At East Bull Lake (EBL) dilute waters are in equilibrium with secondary minerals (ie. laumontite) and the waters are more radiogenic than the bulk of the host rock (McNutt et al., 1987). Calcium-Na-Cl brines from Matagami appear to be in equilibrium with calcite and the waters in the area have the same isotopic value over large distances in contrast to the situation at Sudbury (McNutt et al., 1986). Evidence for equilibration with plagioclase has been found at Cornwall by Edmunds et al. (1987) and with chlorite and other low Rb/Sr minerals at Stripa, Sweden (Fritz et al., 1987).

Sr isotopes can also be used to demonstrate mixing between isotopically distinct endmembers such as dilute surface waters and concentrated brines at depth. McNutt (1987) has illustrated this for the Nipigon `Moose licks' (brackish waters that seep to the surface). In general, as the waters become more dilute (ie. TDS and Sr content decrease) their isotopic ratio increases.

Secondary minerals precipitated from the brines (ie. gypsum) often have the same isotopic value as the brine with which they are associated (McNutt et al., 1987). This could indicate that fracture-filling is a `recent' event, although how recent is unknown or, that isotopic equilibrium has been maintained between the mineral and the water. The strontium isotopic analyses of such secondary mineral phases is a potentially very useful way to determine the relative `age' of a brine. As has been shown, brines undergo extensive exchange with the host rock minerals and therefore the brine cannot be considered to behave as a `isolated' system, one of the criteria for radiometric dating. As a result, no unique `age' can be assigned the brines since they are continually undergoing change through the degradation of primary minerals in the host rock, and the formation of secondary mineral phases.

However, fracture-filling minerals such as gypsum ($CaSO_4.2H_2O$), epidote [$CaFeAl_2O.OH(Si_2O_7)(SiO_4)$] and calcite ($CaCO_3$) all of which contain Sr in the Ca^{2+} site, should be analysed to determine the role that they play (if any) in controlling the isotopic composition of the brine.

B. Sr Isotopic Results for Atikokan

Water samples from seven of the eight holes drilled at Atikokan were analysed in this study, the results are shown in Table 2 (a and b). The majority of samples analysed were from the deep boreholes ATK-1 and -5 (Table 2a). The results reflect an astonishing consistency in the $^{87}Sr/^{86}Sr$ ratios of the water samples collected. Eleven samples from depths of 550-1150m in ATK-1 yield an average ratio of .7063 +/- .0008 (2 sigma). Eleven samples from ATK-5 give an average of .7074 +/- .005. If one sample (ATK 5-1A) which is open to the surface and very dilute (ie. <0.1 mg/L Sr, and therefore susceptible to groundwater contamination), is eliminated from the ATK-5 series, the average ratio for the groundwaters from this hole becomes .7066 +/- .0005 . Therefore, the Sr ratios of the waters from the two deep boreholes are equal within error.

Table 2a : Sr isotopic ratios, Sr and tritium content, and TDS of water samples taken from deep boreholes ATK -1, 5 and 7.

SAMPLE NUMBER	1 BOREHOLE from (m)	INTERVAL to (m)	Sample Depth (m)	[Sr] mg/L	2 Tritium (TU's)	87Sr/86Sr ratio	ERROR (2 sigma) x10^{-6}	3 TDS ‡ mg/L
ATK1-760	760	open	-	53	42	0.706045	4	7810
ATK1-1089	1089	1099	-	172	135	0.706136	13	23080
ATK1-4A	553	610	-	-		0.706687	11	-
-4B	553	610	570	6	66	0.706331	13	1040
-5B	610	676	-	-		0.706715	13	-
-6A	676	746	-	-		0.707255	13	-
-6B	676	746	680	9	101	0.705749	11	1555
-8B	852	943	790	24	106	0.706391	10	4115
-9A	943	1003	880	308	86	0.706134	13	40100
-9B	943	1003	-	-		0.706208	14	-
-10B	1003	1151	-	-		0.706148	10	-
ATK5-6	382.2	406.5	-	2.2	40	0.706645	13	560
ATK5-775-3	775	1274	-	68	67	0.706430	14	10030
ATK5-1A	0	229	100	<0.1	52	0.714759	10	146
-2A	229	425	320	1.6	69	0.706959	14	417
-3A	425	744	420	4	41	0.706652	14	1020
-3B	425	744	680	24	112	0.706349	13	3025
-4A	744	1144	700	31	86	0.706432	17	4100
-4B	744	1144	980	220	62	0.707003	16	28500
-5A	1144	1217	-	-		0.706838	10	-
-6A	-	-	-	-		0.706676	16	-
-6B	1217	1274	1050	205	72	0.706143	10	21000
ATK7-2-48	150	350	-	6.0	15	0.706117	30	1315
-4-41	365	580	-	5.6	34	0.705751	31	1035
-3-42	580	780	-	5.3	24	0.705966	37	2080

1 samples labelled with suffix A and B do not indicate duplicate analyses: A indicates that sample was collected with production injection packer (PIP) inflated while B indicates that the sample was collected with the PIP deflated. Note also that the sampling depths of A and B samples are not equal.

2 tritium analyses done at the Isotope Laboratory, University of Waterloo (TU = tritium units) reported by Gartner-Lee (1983) and AECL (see Appendices 4 & 5)

3 TDS values calculated by author from data from AECL and Gartner-Lee

‡ data shown is a compilation of work done by the author, AECL and Gartner-Lee Associates (1983) samples labelled with A & B suffix are from Gartner-Lee (1983) remainder of data from AECL

Table 2b : Sr isotopic ratios, Sr and tritium content, and TDS of water samples taken from boreholes ATK -2,4,6 and 8 as well as LK and ML series.

SAMPLE NUMBER	BOREHOLE from (m)	INTERVAL to (m)	[Sr] mg/L	Tritium (TU's)	87Sr/86Sr Ratio	ERROR (2 sigma) x 10^{-6}	TDS mg/L
ATK2-3	126.2	199	0.50	58	0.708551	11	397
ATK4-13	160.6	340	0.63	6	0.708253	10	332
ATK6-6-13	150	350	0.33	20	0.706473	14	171
ATK8-1	0	716	0.36	44	0.709348	31	144
ATK8A-5	0	137	0.12	24	0.715561	13	100
ATK8B-2	137	716	9.62	7	0.705266	13	1630
ATK8A-2	0	137	0.11	68	0.716096	30	106
LK4	20.8	88.1	0.21	52	0.708253	10	154
LK5	18.6	20.1	0.50	76	0.746594	13	83
ML9-1	45	BOH	0.34	43	0.708513	10	174
ML9-2	33.5	44.1	0.25	6	0.709443	3	154
ML9-3	24	32.6	0.23	71	0.709800	17	151
ML9-4	14	23.1	0.12	71	0.710429	16	125
ML9-5	7.5	13.1	0.06	74	0.727748	10	90
ML9-6	0	6.6	0.05	59	-		70
ML12-OB1	0	7.6	0.07	17	0.726426	19	135
ML12-2	39	47.1	0.40	6	0.706877	34	216
ML12-3	27.5	38.1	0.24	-	0.708157	16	168
ML12-4	14.5	26.6	0.26	18	0.708136	10	176
ML12-5	8.5	13.6	0.17	-	0.711714	14	136

* comments are the same as those for Table 2a.

BOH = bottom of hole

The $^{87}Sr/^{86}Sr$ ratios of the shallow borehole samples are more variable, with most values falling in the range .706 to .708 (Table 2b). Considerably higher values are however noted for samples which were open to the surface, such as ATK 5-1A (previously mentioned), ATK 8A-5 and 8A-2 all of which have very high ratios (ca. .715) . These samples contain very little Sr and the values likely reflect the influence of surface waters, be they drill water from Forsberg Lake or local precipitation. The anomalously high value of .746 for LK 5 is somewhat puzzling. The sample is described as an artesian well (J. Ross pers. comm.) and was drilled immediately adjacent to LK 4, although at a higher level. Unfortunately, the author was unable to obtain a sample of surface water which would have proven very useful in determining a high $^{87}Sr/^{86}Sr$ end member for mixing of these waters.

The LK and ML (multiple level) series samples are shallow, percussion drilled boreholes. The waters in these holes were collected less than 90 metres below the surface and show considerable variability in their Sr ratios, typical of the shallow , fresh to brackish waters described earlier.

The trend of decreasing $^{87}Sr/^{86}Sr$ ratios with increasing Sr content and TDS described by McNutt et al., (1984) for other Shield localities is evident for the

Atikokan samples (figure 6). At higher Sr concentrations the trend approaches a constant value (ca. .706).

In the deeper boreholes there is a clear trend seen where TDS increases with depth (figures 7,8). A corresponding increase in Ca, Sr (figures 7,8), Na, Cl and Br is noted, while Mg, Si and HCO_3 show decreasing concentrations with depth, though the change is less dramatic. An apparent exception to this trend is sample ATK 1-1089. This sample was collected from a small, 10 metre, interval (1089 to 1099m). Both its TDS (23,080 mg/L) and Sr concentration (172 mg/L) are significantly lower than those of ATK 1-9A (40,077 and 308 mg/L respectively) which was collected 200 m above it, at 880 m. Sample dilution is the probable cause, based upon two lines of evidence. A hydrogeological study done in 1983 (Gartner-Lee, 1983) found that between 900 and 1150 m in ATK-1, that a "significant subhorizontal fracture zone" existed, with a localized decrease in the geothermal gradient. This fracture zone was not intersected by ATK-5 and no decrease in the geothermal gradient was found. Analyses of tritium levels, done at the University of Waterloo, show that of the 43 samples tested, ATK 1-1089 has the highest tritium count at 135 T.U. (tritium units). Values greater than 15 T.U. are taken to indicate dilution by fresh waters for samples deeper than 100 m (Gascoyne et al., 1987). This is compelling evidence that in addition to localized, insitu dilution that

Figure 6: Strontium isotopic ratio vs Sr content for groundwaters from Atikokan research area. Note that the $^{87}Sr/^{86}Sr$ ratio of more concentrated samples becomes constant at a value of approximately .706 while the more dilute waters demonstrate a rapid increase in their isotopic ratio as Sr content decreases.

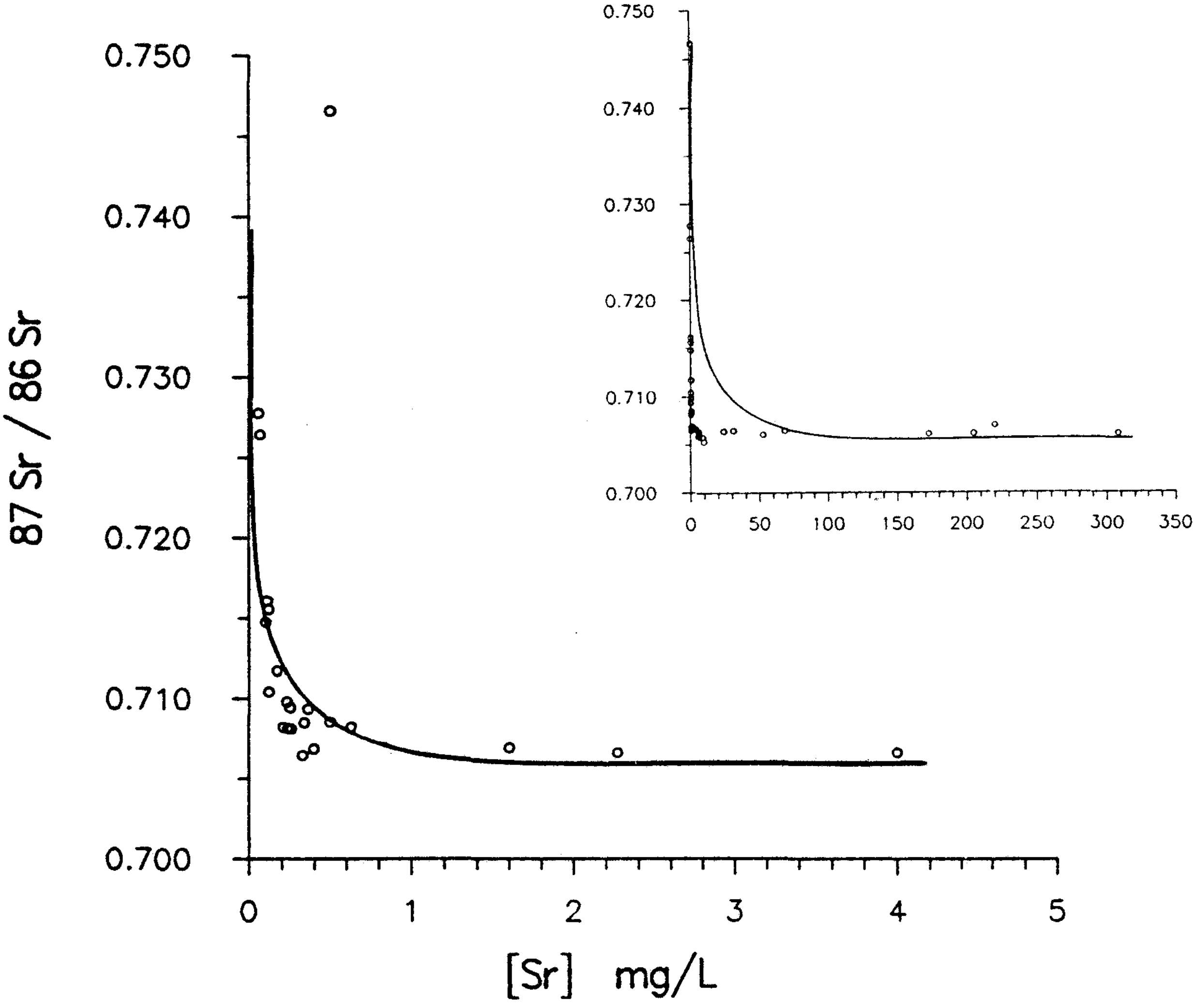

0.750
0.740
0.730
0.720
0.710
0.700
87 Sr / 86 Sr
0
1
2
3
4
5
[Sr] mg/L
0.750
0.740
0.730
0.720
0.710
0.700
0
50
100
150
200
250
300
350

Figure 7: Plot of concentrations of various components vs depth for groundwater samples from ATK-1 borehole. Note subparallel trend of increasing concentration with depth for Sr, Na, Ca and TDS. Increase is more subtle for K while bicarbonate deceases with depth. (data from Gartner-Lee, 1983)

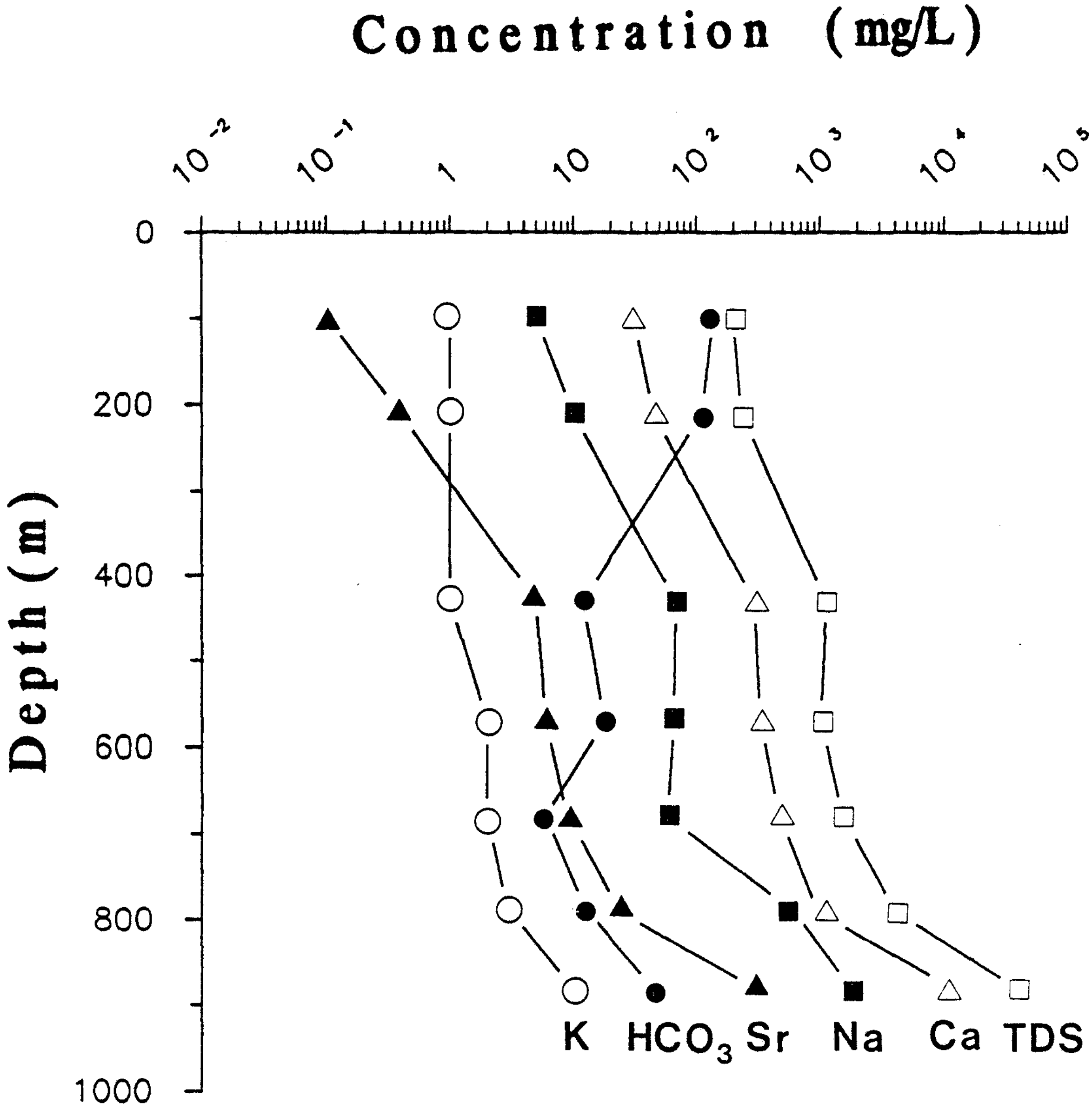
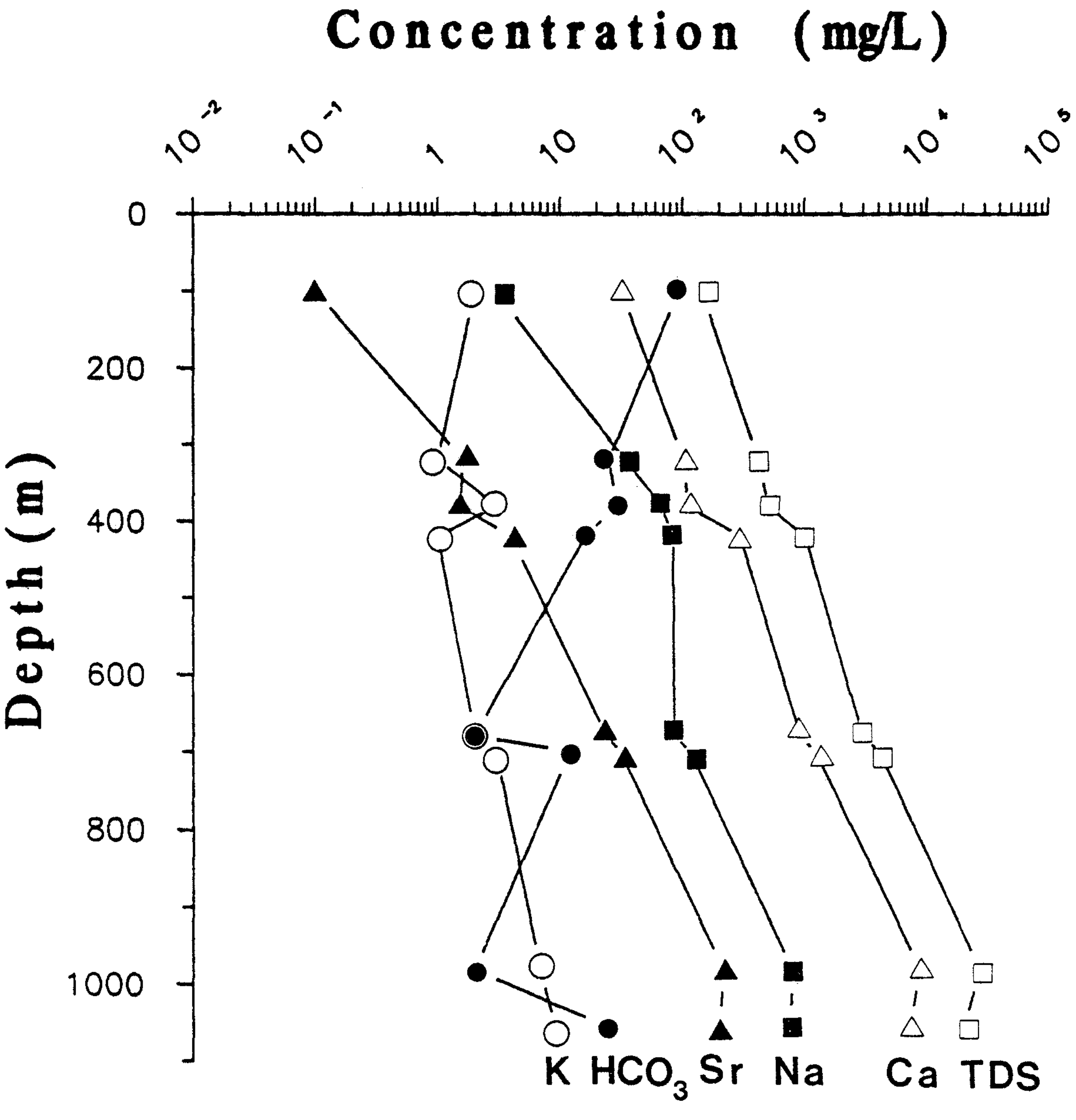

Concentration (mg/L)
10^{-2}
10^{-1}
1
10
10^{2}
10^{3}
10^{4}
10^{5}
Depth (m)
0
200
400
600
800
1000
K
HCO_3
Sr
Na
Ca
TDS

Figure 8: Plot of concentrations of various components vs depth for groundwater samples from ATK-5 borehole. Trends are the same as those described for ATK-1 (figure 7). (data from Gartner-Lee, 1983)


Concentration (mg/L)
10⁻²
10⁻¹
1
10
10²
10³
10⁴
10⁵
Depth (m)
0
200
400
600
800
1000
K
HCO3
Sr
Na
Ca
TDS

significant amounts of drill/surface water must have entered the zone during sampling. Frape and Fritz (1987) have found similar situations (ie Bob's Lake Fault, Sudbury) where the presence of young tritiated waters at depths of 1000m indicate that some large vertical fault systems can be hydraulically connected to the surface. Once disturbed by drilling, the waters often show progressive dilution over a period of years. This does not appear to be the case at Atikokan. Dilution effects are due to the introduction of surface water during drilling and not the result of migration of surface waters downward along fractures. Hydrological testing showed interconductivity to be very low at deeper levels in ATK-1 and 5 and resampling over a two year period indicated ... "increasing salinities with time in the deep, low permeability zones presumably due to replacement of drilling waters by saline formational waters" (Gartner-Lee, 1983). The Sr content of surface/drill water is extremely low (ng/L level) while that of the deep saline waters is very high (>100 mg/L). Therefore, contamination of deep saline waters by drill water is reflected in elevated tritium levels, but the effect on the $^{87}Sr/^{86}Sr$ ratios of the saline groundwater is insignificant.

CHAPTER FOUR

PETROGRAPHY AND GEOCHEMISTRY OF THE HOST-ROCK MATERIAL

4.1 Background

The Eye-Dashwa lakes pluton consists of three compositionally distinct phases. The pluton margin consists of an early, medium to coarse grained syenodiorite. A leucogranite-granodiorite comprises the intermediate phase and the bulk of the pluton is a late, porphyritic, biotite-hornblende granite (sl) in which the ATK boreholes are located. Some compositional zoning is reflected in the higher biotite concentration in the center of the pluton while hornblende is more abundant towards the margin of the pluton.

The major phenocrystic phases seen in core are microcline, plagioclase and hornblende. Biotite is seen in unaltered samples but it is usually at least partially chloritized. A slight increase in the ferromagnesian minerals (hornblende + biotite + sphene) is seen in the lower section of the ATK-1 borehole but overall, the core from boreholes ATK-1, 4 and 5 is similar and very homogeneous. Modal analyses of approximately 300 samples from these three boreholes plot within the granitegranodiorite field of Strecheisen (1976) (Stone and Kamineni, 1982).

4.2 Alteration of the Host Rock

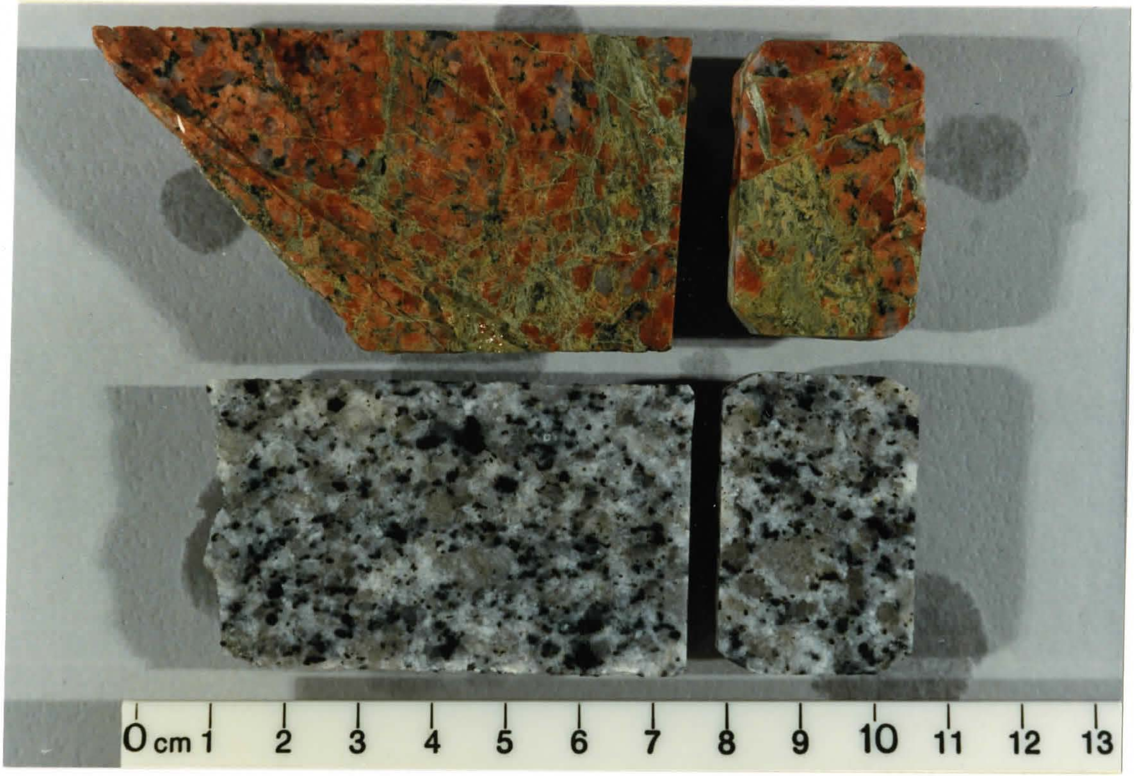
The following is a brief summary of the salient points made by Kamineni and Dugal (1982) in an exhaustive study of fracturing and alteration in the ATK core. Some degree of alteration is apparent in all core studied. Macroscopically, the degree of alteration is readily judged by the intensity of pink discolouration of the originally grey granite. Kamineni and Dugal identified six alteration types seen in core based upon the macroscopic and mesoscopic discolouration of feldspars and ferromagnesian minerals. The alteration types are (from most to least altered):

1. pink feldspar
2. yellow feldspar
3. green feldspar
4. diffused green feldspar
5. bleaching of feldspars to pink and white cream colour
6. alteration of ferromagnesian minerals

Pink alteration is the most abundant type, and a deep pink discolouration (Plate 1) is always associated with areas of intense fracturing. Core that is grey in colour (Plate 1) is usually associated with unfractured and

Plate 1: Photograph contrasting macroscopic differences between 'fresh' and altered core. Top core is a highly altered pink granite (ATK 1-137). Note the total pink discolouration of feldspar (contrasted against colourless quartz) and the abundance of epidote filled fractures. Note the 'splayed' nature of some epidote fractures (centre) and offset in small piece at right.

Bottom core is a sample of a 'fresh', grey granite (ATK 5-120). Very minor discolouration of feldspars and abundance of relatively fresh ferromagnesian minerals as well as the absence of fractures characterize this sample. 'Fresh' core tends to be somewhat more massive and competent than highly altered core.


0 cm 1 2 3 4 5 6 7 8 9 10 11 12 13

relatively unaltered zones, distant from major fracture systems.

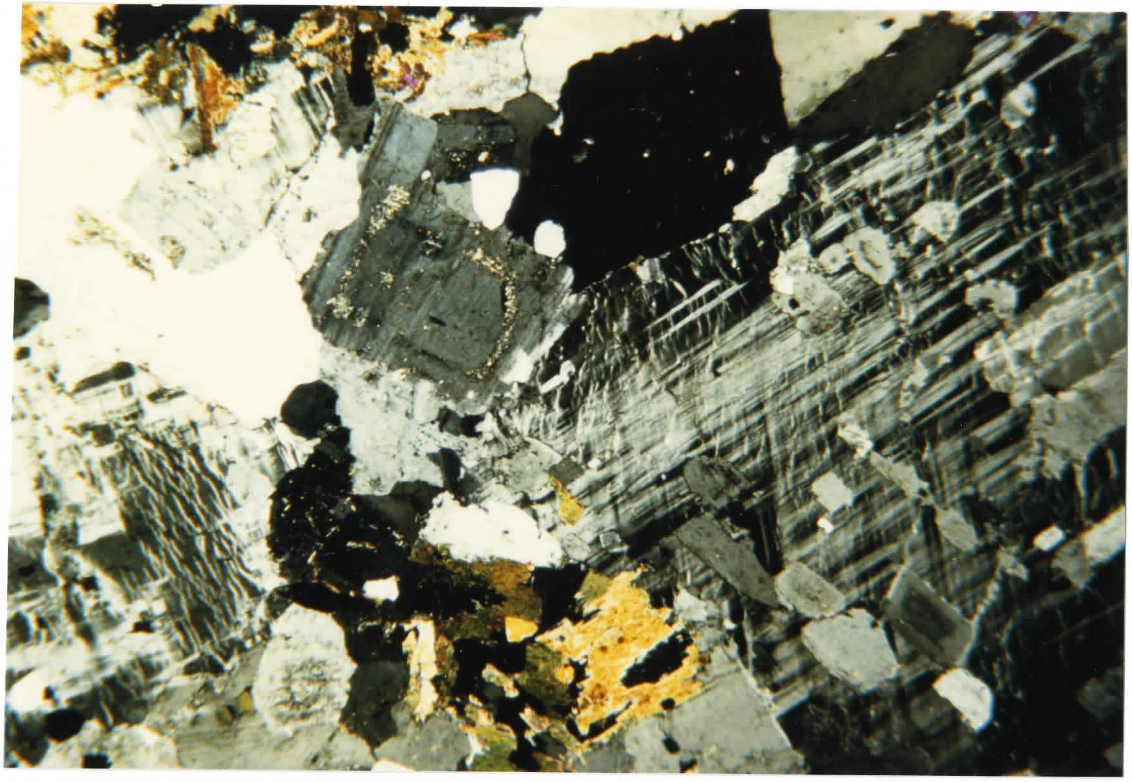
Microscopically, the diffuse green, yellow and green alteration types are indistinguishable from the least altered grey and pinkish-grey granite. Kamineni and Dugal (op. cit.) suggest that the yellow and green colouration of feldspar may be a primary feature, related more to a concentration of trace elements in those feldspars, than to alteration.

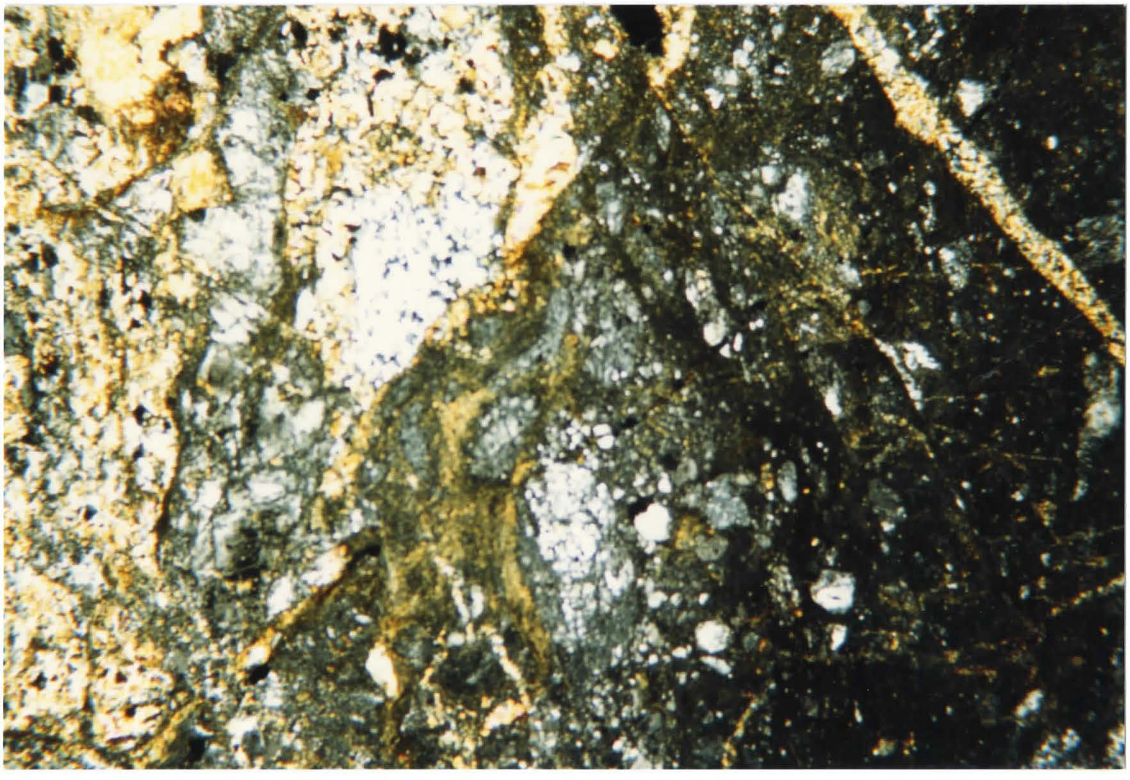
On the microscopic scale, alteration can be seen to occur in two different environments; either as distinct alteration minerals enclosed in their host grains, or as stringers around and across primary quartz and feldspar grains. The first type of association is more common, the second is found in highly altered rocks. Among the more abundant alteration minerals are epidote, chlorite, sericite and hematite.

In all thin sections examined in this study, plagioclase phenocrysts are all altered to some degree (Plates 2 and 3). Sericite flakes are ubiquitous. Other common alteration products associated with plagioclase are epidote, calcite, hematite and occasionally chlorite. These results are consistent with the description by Kamineni and

Plate 2 : A photomicrograph of sample ATK 5-120, a 'fresh', grey granite. Although this is the 'freshest' sample studied, alteration is apparent in the central plagioclase and highlights the compositional zoning of the oligoclase. K-feldspar is unaffected by alteration while plagioclase inclusions often contain sericite. Relatively unaltered biotite at bottom and upper left indicate minimal alteration.

Plate 3 : In sharp contrast to photograph above, this sample (ATK 1-137) is highly altered. Dark area at right is plagioclase which is now obscured by a mass of alteration products (epidote, sericite and opaques). Though not visible here, K-feldspar is still recognizable and much less affected by alteration. Note the high concentration of epidote (yellow), sericite (white) and quartz at left. This sample shows cataclastic textures and many cross-cutting epidote veinlets (ie. top right). The field of view for both photographs is ca. 3 mm.





Dugal (1982) of the 4 alteration assemblages seen in plagioclase:

1. sericite + epidote
2. sericite + calcite
3. sericite, epidote, calcite + hematite
4. sericite + chlorite

In the thin sections studied here, the first assemblage is by far the most common, although all types are seen. Microprobe data by Kamineni and Dugal (opcit) indicate that all but the most pristine plagioclase grains show Ca depletion in the cores with even greater depletion near their margins. Indeed, microprobe analysis shows that the bulk composition of plagioclases from bleached and pink alteration zones are close to that of pure albite. Significantly less alteration is seen in the potassium feldspars. Microprobe data on K-feldspars from altered zones show them to be rich in the albite component with high Ba contents.

The most common ferromagnesian minerals seen in thin section are biotite and hornblende. Biotite is readily chloritized and therefore is seen only in the 'fresh' grey (plate 2) and greyish pink core. In samples that are more extensively altered (ie. pink granites), biotite has been completely replaced by chlorite, epidote and hematite. In these rocks hornblende is more stable than biotite. In altered samples, hornblende often contains epidote, chlorite, sphene and carbonate inclusions. If alteration is less pronounced, as in greyish-pink core, the most common alteration product is epidote, found as a rim around the hornblende, or at the contact of the hornblende and plagioclase grains.

In addition to being a common alteration product of both plagioclase and hornblende, epidote occurs as a fracture filling mineral. Kamineni and Dugal (1982) have identified and characterised three types of occurrences in the less altered grey and pinkish-grey ATK core. The first is as the growth of Fe-poor, Al-rich epidote crystals on the surface of plagioclase grains. The second is as large epidote crystals surrounding ferromagnesian minerals. This type of epidote is Fe-rich and Al-poor reflecting the composition of the biotite and hornblende from which it formed. Surrounding these large yellow grains, fine colourless epidote is often seen forming. Microprobe data show this third type of epidote to be Fe-poor and Al-rich.

In the more altered pink core, the epidote has a uniform chemical composition and is the Fe-rich type found as fracture filling mineral (Plates 1 and 3). Kamineni and Dugal (1982) contend that epidote found in rocks with low to medium degrees of alteration is formed by local reactions, while that found in highly altered rocks is formed during more widespread reactions.

Analyses of chlorites show that they are progressively enriched in Fe and depleted in Mg, as the degree of alteration increases from the grey through to pink granites whereas for similar degrees of alteration, both the Fe and Mg content of sericite is seen to increase (Kamineni and Dugal, 1982).

4.3 Fracturing in the Host Rock

Fractures, joints and faults can be of great importance in the context of nuclear waste storage. Such structural features can have a major influence on the transport of radionuclides in solution, while secondary, fracture-filling minerals play a role in the sealing of fractures and have sorptive properties and stabilities very different than those of the host rock.

A detailed examination of fracture systems in the Eye-Dashwa lakes pluton by Kamineni and Stone (1980) and Kamineni (1982) revealed that four distinct fracture-filling stages can be identified. The four stages represent a sequence of decreasing age and temperature of circulating fluids. They are:

1) pegmatite-aplite (600-650°C)
2) epidote (300-500°C)
3) chlorite (200-450°C)
4) low-temperature minerals (<100°C)
(Fe-oxides,gypsum,carbonates,clays)

The pegmatite-aplite filled fractures are magmatic in origin and represent hydraulic fracturing related to deuteric activity during the final phases of crystallization of the pluton. This type of fracture has remained sealed and is seldom seen to have been reactivated. In sharp contrast, the epidote, chlorite and low-temperature mineral filled fractures are commonly reactivated, perhaps several times throughout the history of the pluton. Fracture frequency histograms of boreholes ATK -1 through 5 showed that the most highly altered core samples were always associated with the highest fracture frequencies (up to 200 fractures/m). Based upon these observations Kamineni and Dugal (1982) proposed a four stage model involving fracturing, rock alteration, fracture filling and subsequent deformation of the filling materials. These phases have a post-emplacement origin and were formed at temperatures between ca. 100°C (meteoric waters) and 600°C (hot magmatic fluids). Replacement textures indicate that many of these fracture-filling minerals are derived largely from wall rock alteration by hydrothermal fluids.

The significance of reactivation and sealing of pre-existing fractures with respect to the migration of radionuclides will be discussed later.

4.4 Selection of Core

The isotopic analyses were concentrated on core that could be correlated with isotopic data for waters collected form the same depth in a given borehole. Whenever possible an effort was made to match the core to a well constrained water sample (ie. one collected over a short interval). This was only possible in one instance. Water sample ATK 1-1089 was collected from a 10m interval in the ATK -1 borehole (1089 - 1099m). Eight core samples analysed were from 1067 to 1127 metres in that same borehole and only one of these (ATK 1-57) at 1089.15m fell within the interval of the water. While, due to its mobility, water may be homogenized over a large volume, the host rock can be highly variable on the metre scale, ie. the whole spectrum of alteration types (grey through pink granites) can be seen in a 10m interval.

4.5 Results of Isotopic Analyses

Eight whole rock samples from ATK-1 and one from ATK-5 were analysed for Sr content and Sr isotopic ratio. Table 3 lists the results of these analyses and shows a comparison

Table 3 : Correlation of Sr data for water and core samples from boreholes ATK - 1 and 5.

SAMPLE	DEPTH (m)	[Sr] mg/L	87Sr/86Sr Ratio	ERROR (2 sigma x 10^{-6})	
ATK 1-1089	1089 - 1099	172.3	0.706136	18	Water
1-45	1066.6	3558	0.706779	13	Core
1-52	1088.15	3253	0.706957	13	"
1-57	1089.65	905	0.713958	13	"
1-137	1105.9	1567	0.707993	11	"
1-74	1107.15	904	0.710018	11	"
1-75	1107.85	939	0.710030	16	"
1-78	1120	545	0.717194	16	"
1-81	1127	992	0.710004	16	"
ATK 5-6	382 - 406.5	2.3	0.706645	13	Water
5-5	407.40	974	0.711188	11	Core
ATK 5-775-3	775 - 1274	68.4	0.706430	7	Water
5-120	868.8	1115	0.709221	10	Core

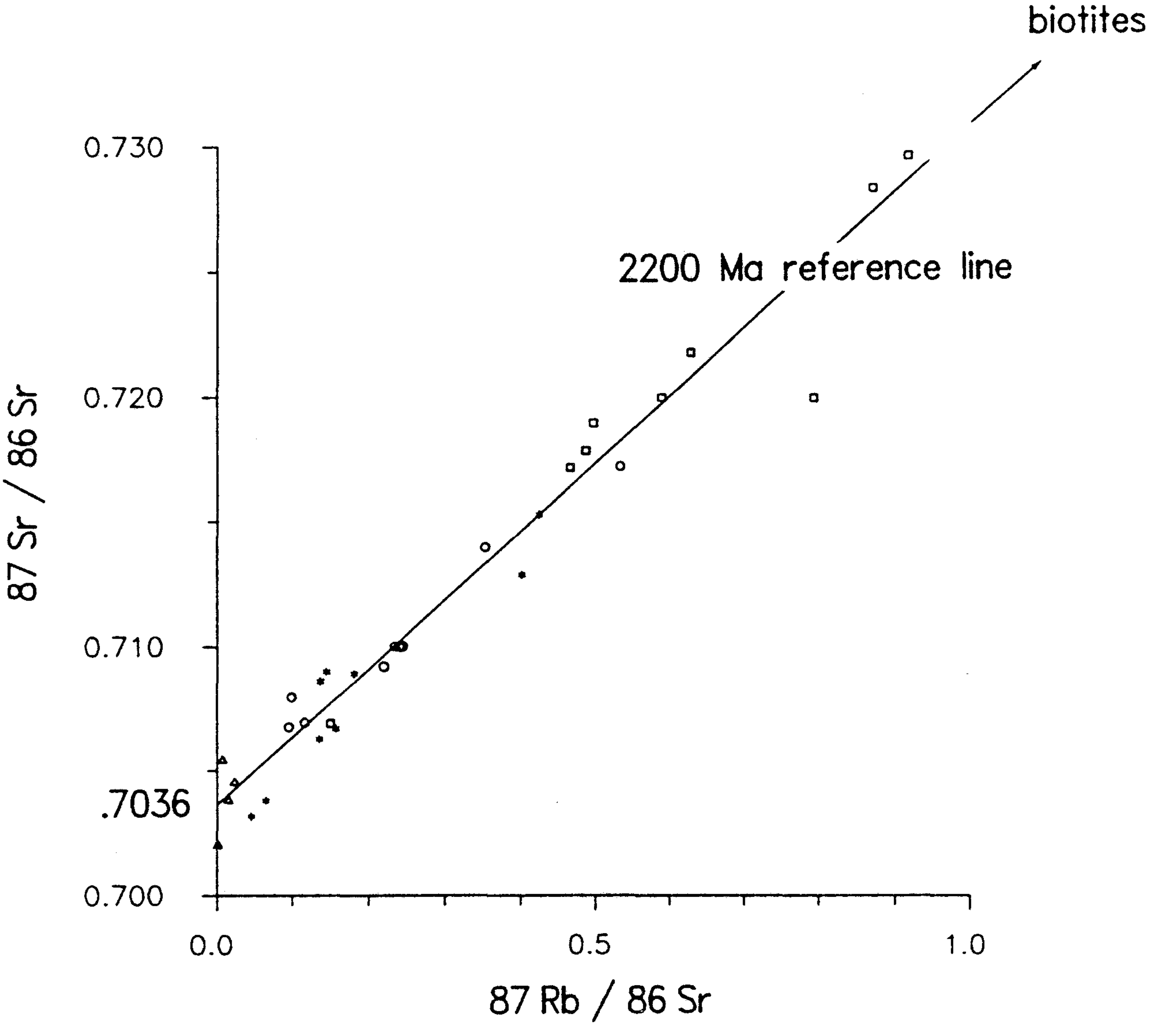
of the rock and water values. It is evident that the Sr ratios of the core samples are more variable (.707 to .717) than those of the water samples (discussed in Chapter 3). As well, the Sr ratios of all whole rock samples are higher than the water collected in their vicinity. ATK-1 core samples from 1067m to 1127m vary in their isotopic ratios from .707 to .717. Samples ATK 1-52 and 1-57 correspond closely to the location of the upper packer for water sample ATK 1-1089. The ratio of that brine is .7061 while the two core samples have ratios of .707 and .714, and are separated by only 1.5m. This example highlights the limited use of a comparison of water and whole rock data and therefore, to gain further insight, mineral separates were prepared for the core samples collected near brine sample ATK 1-1089. The results are shown in Table 4.

Plagioclase and potassium feldspar separates were prepared from each sample, and where present in sufficient quantities, biotite and epidote separates were also analysed. When plotted on a Rb-Sr isochron diagram, all whole rock-mineral results gave errorchrons with ages ranging from 1410 to 2615 Ma. Sr initial ratios ranged from .701 to .705. Figure 9 is an isochron diagram on which all mineral and whole rock data have been plotted (n=31). The data scatter about the 2200 Ma reference line and give an initial ratio of .7036 (errorchron age = 2177 ± 82 Ma). These results are similar to those of Peterman (pers. com.,

Table 4 : Rb and Sr data for whole rock and mineral separate samples from Atikokan

CORE	MINERAL	SAMPLE #	[Rb] ppm	[Sr] ppm	87Rb/86Sr Ratio	87Sr/86Sr Ratio	Errors (2 sigma x 10^{-6})
1-45	epidote	S-13	45	8997	0.015	0.703864	13
	plag	S-16	42	896	0.136	0.708624	11
	kspar	S-17	132	609	0.626	0.721808	12
	whole rock		118	3558	0.095	0.706779	13
1-52	kspar	M-4	338	1121	0.870	0.728396	10
	plag	S-4	51	811	0.180	0.708928	11
	epidote	S-11	59	7266	0.023	0.704574	11
	whole rock		131	3253	0.116	0.706957	13
1-57	plag	S-6	56	380	0.423	0.715274	11
	kspar	S-7	287	903	0.916	0.729679	13
	whole rock		111	905	0.353	0.713958	13
1-74	kspar	F-9	165	1020	0.465	0.717149	11
	plag	F-11	35	640	0.157	0.706709	10
	whole rock		73	904	0.233	0.710018	11
1-75	kspar	F-1	176	1046	0.486	0.717819	14
	plag	F-3	29	623	0.135	0.706283	14
	whole rock		80	928	0.244	0.710030	16
1-78	kspar	S-1	81	295	0.793	0.719993	13
	plag	S-2	26	189	0.401	0.712871	13
	whole rock		101	545	0.532	0.717194	16
1-81	biotite	S-24	456	267	5.015	0.893898	13
	kspar	S-25	53	1021	0.150	0.706922	14
	plag	S-26	13	575	0.064	0.703808	13
	whole rock		83	992	0.240	0.710004	16
1-137	plag	S-9	27	540	0.144	0.709013	11
	kspar	M-1	143	699	0.588	0.719999	10
	epidote	S-22	14	5895	0.007	0.705462	13
	whole rock		54	1562	0.099	0.707993	11
5-120	biotite	S-27	464	626	2.147	0.782797	11
	kspar	F-4	230	1334	0.496	0.718947	17
	plag	F-6	15	963	0.045	0.703172	11
	whole rock		85	1110	0.219	0.709221	10
1-255	gypsum	546.6 m	-	-	-	0.706305	11
1-M-8	epidote	550 m	4	11877	0.001	0.702066	13
7-C	calcite	236.8 m	-	-	-	0.705466	13

Figure 9: Rubidium-Sr isochron plot of rock and mineral separate samples from Eye-Dashwa lakes pluton. The 2200 Ma line is for reference only. Whole rock samples (○), K-feldspar (□), plagioclase (*) and epidote (△).


biotites
2200 Ma reference line
87 Sr / 86 Sr
0.730
0.720
0.710
.7036
0.700
0.0
0.5
1.0
87 Rb / 86 Sr

1986) who got an age of 2300 Ma (initial ratio = .7030) for an epidotized granite from Atikokan. In light of the limited hand specimen size available for analysis coupled with the existence of pore fluids at all depths, the results would be expected to reflect some degree of open system behaviour. Therefore, the ages listed have no true geological meaning.

The analysis of mineral separates is however instructive. We see that the plagioclases have low $^{87}Sr/^{86}Sr$ ratios ranging from .703 to .715. The higher values undoubtedly reflect the presence of trace amounts of either potassium feldspar or other more Rb-rich phases. Sr ratios for microcline range from a low of .707 to a high of .728. Quartz was collected along with the plagioclase fraction (due to their similar densities), but since it contains essentially no Sr, its presence will decrease the measured Sr concentration of the plagioclase but does not affect the $^{87}Sr/^{86}Sr$ ratio.

Four epidote separates gave the lowest Sr ratios (.702 - .706). The lowest one, sample M8 from ATK-1 (255m) provided by Kamineni is a deep green, translucent, granular, primary epidote, taken from a non-reactivated epidote vein 3-4mm in diameter (D.C. Kamineni pers. comm.). All other epidote separates were prepared from crushed core samples. Many grains that initially appeared to be epidote to the naked eye, actually were plagioclase grains coated with a thin layer of epidote as an alteration product. These samples were recrushed and reprocessed to increase their purity. It is possible however, that these epidote separates had trace amounts of plagioclase and hornblende as inclusions.

A single gypsum sample from ATK-1 had a $^{87}Sr/^{86}Sr$ ratio (.7063) essentially equal to that of the brine from which it precipitated (see ATK 1 -4A and 4B, Table 2a) . A large calcite vein (ca. 2 cm in diameter) from ATK-7 (237m) gave a slightly lower ratio of .7055 compared to the water samples from that hole of .7058 - .7061.

The Sr content of the Atikokan granite is very high. Whole rock values are as high as 3500 ppm, while Rb levels are no higher than 130 ppm. Mineral separates reflect this high Sr content, ie. plagioclases contain as much as 1000 ppm Sr, while the maximum Sr content of an epidote was an astonishing 11,877 ppm (ca. 1.0% SrO). When compared to analyses of whole rock and mineral separates done by Fritz et al., (1987) for their Stripa granites, the Atikokan samples have much lower Rb/Sr ratios. The average whole rock $^{87}Rb/^{86}Sr$ ratio at Atikokan is .237 compared to 26.14 at Stripa. A plagioclase from Stripa has a $^{87}Rb/^{86}Sr$ ratio of 21.12 ($^{87}Sr/^{86}Sr$ = .735) compared to an average $^{87}Rb/^{86}Sr$ of .186 ($^{87}Sr/^{86}Sr$ = .706) at Atikokan. The Sr rich nature of the Eye-Dashwa granite is also reflected in the high Sr concentration of the ATK brines relative to the deep brines at Stripa (308 vs 1.5 ppm, respectively).

CHAPTER FIVE

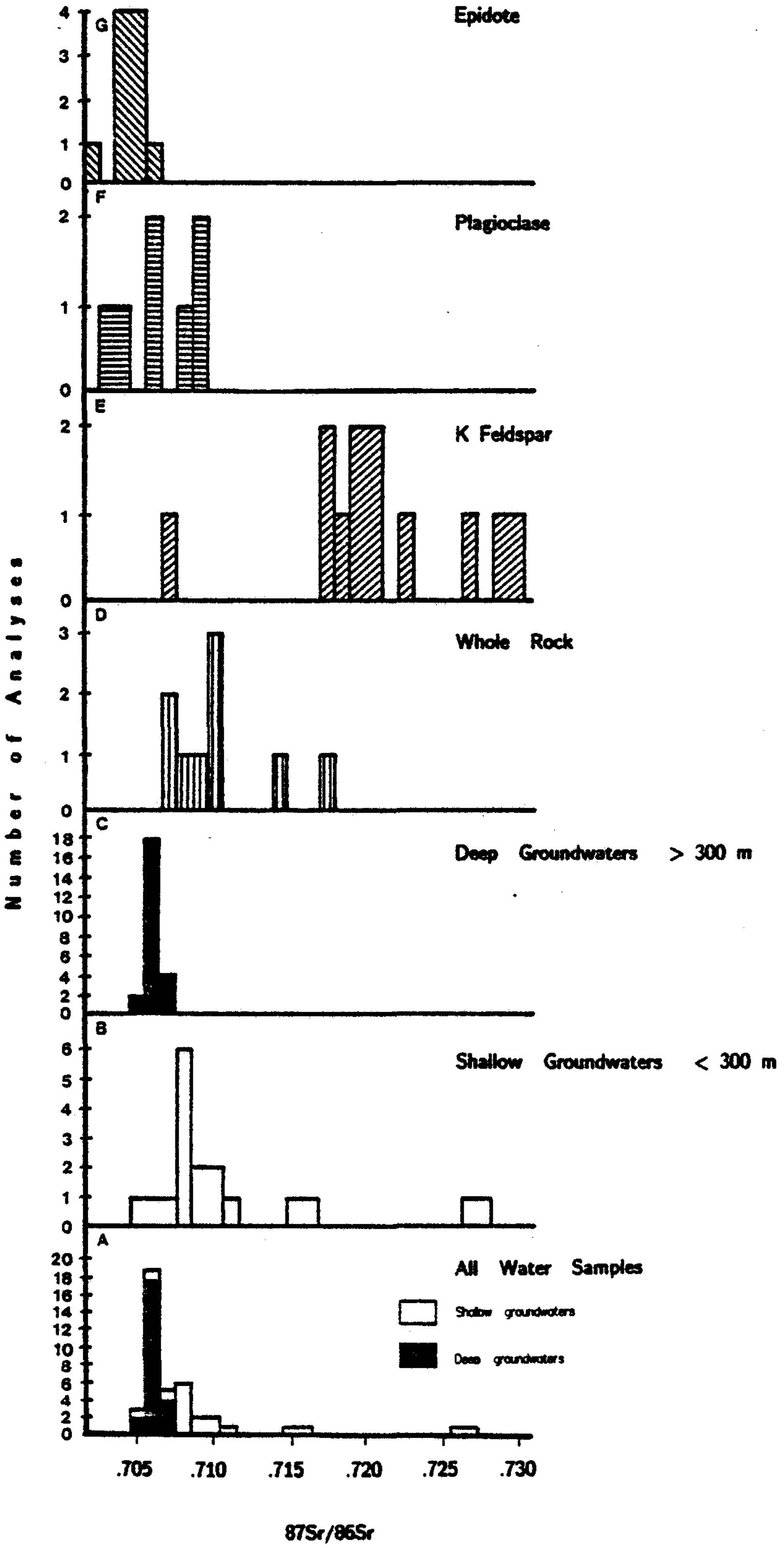
DISCUSSION

5.1. Groundwaters

5.1.1 Shallow Groundwaters

The Sr isotopic ratios of the shallow dilute waters at Atikokan are higher and more variable than those of the deeper, more concentrated groundwaters (figure 10). A similar situation exists at East Bull Lake (McNutt et al., 1987). Most fresh waters at Atikokan have ratios between .706 and .709 with several greater than .715. Groundwaters in the upper 300m are Ca-HCO_3-rich with very low TDS. The water chemistry changes to a Ca-Na-Cl-SO_4 type from approximately 400 to 800m (Appendix 4). Below 800m the saline waters are Ca-Na-Cl type. Three flow regimes were defined by hydrogeological testing in the Eye-Dashwa lakes pluton test grid area (Gartner-Lee, 1983). First, a local groundwater flow regime exists to a depth of 150m. From 150 to 600m the intermediate flow regime is related to discrete fracture zones and below 600m a regional, deep flow regime exists. Gascoyne et al. (1987) have defined 2 discrete zones at Atikokan based upon a decrease in hydraulic conductivity and corresponding increases in salinity and chlorinity that occur below approximately 300m. They state that above 300-500m, groundwater mixing is driven by surface

Figure 10: Frequency diagram showing present-day $^{87}Sr/^{86}Sr$ values for rock, mineral and groundwater samples at Atikokan research area. (a) all groundwater samples; (b) shallow groundwater samples; (c) deep groundwater samples; (d) whole rock data; (e) K-feldspar; (f) plagioclase; (g) epidote. Note the change in scale of the frequency axis.


G
Epidote
F
Plagioclase
E
K Feldspar
D
Whole Rock
C
Deep Groundwaters > 300 m
B
Shallow Groundwaters < 300 m
A
All Water Samples
Shallow groundwaters
Deep groundwaters
Number of Analyses
0
1
2
3
4
4
6
8
10
12
14
16
18
20
.705
.710
.715
.720
.725
.730
87Sr/86Sr

recharge-discharge controls while below this level sharp increases in salinity reflect diffusion controlled processes.

The variability seen in the shallow water samples could therefore be the result of several factors. Drillwater contamination is certainly important. Contamination effects are far more significant for the low TDS (very low Sr), shallow waters than for deeper more saline (Sr-rich) brines. Local recharge waters, rich in bicarbonate would leach overburden material which could vary both in thickness (depth) and mineralogy, and therefore would yield highly variable $^{87}Sr/^{86}Sr$ ratios. Input from surface waters, lakes and streams as well as the abandoned 350m deep Steep Rock open pit mine to the southeast all would affect the groundwaters sampled in the upper 300-500m. In light of all of the possible sources, each with its own isotopic signature the variability in the shallow groundwaters is not surprising.

5.1.2 Deep Groundwaters

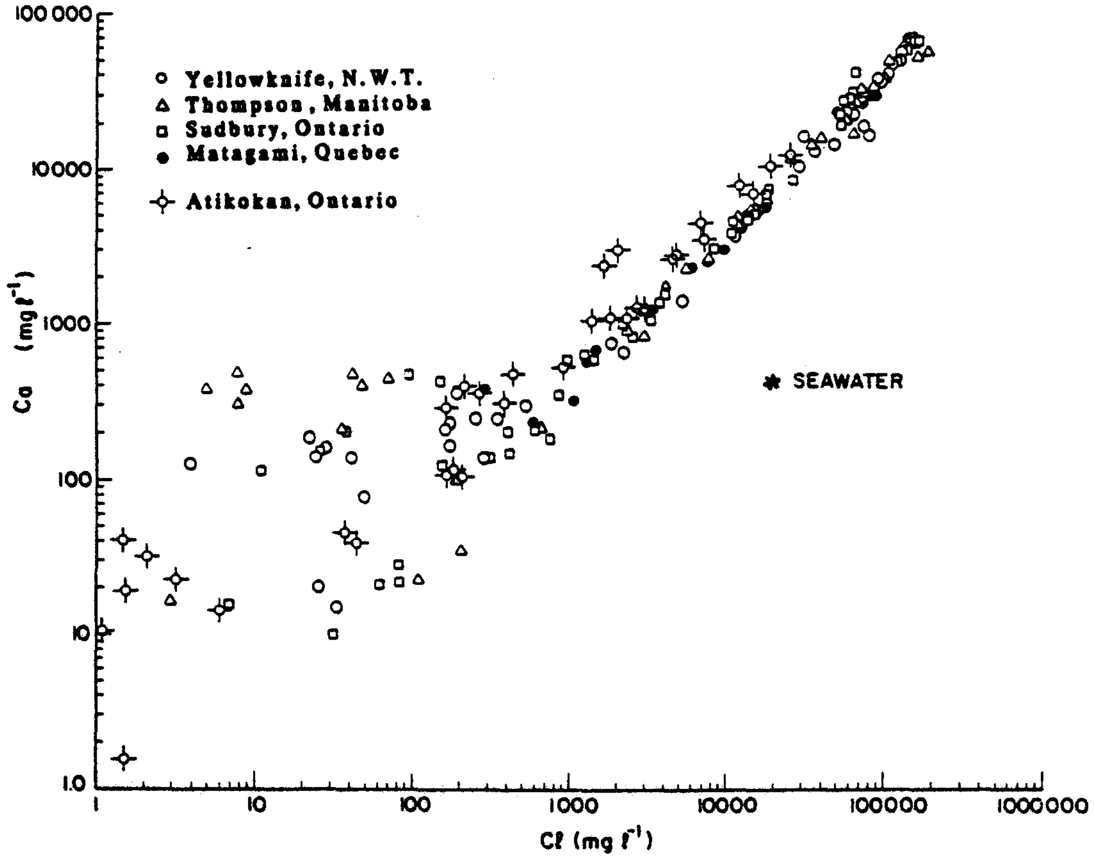
The situation for the deeper groundwater at Atikokan is less variable, however, the elevated tritium content of many of the ATK samples is an indication that some mixing has taken place at depth. The TDS values given in Tables 2a and b should be considered as minimum values since many contain significant tritium (an indication of mixing with surface/recent waters). Gascoyne et al. (1987) have shown that a simple correction (used to estimate an approximate source brine composition, before dilution with tritiated surface waters) applied to sample ATK 1-9A (^3H=86 TU) increases the true salinity from 40 g/L to give an end-member brine with a TDS of 140 g/L. A similar correction applied to the rest of the Atikokan samples would, in many cases, double or triple their TDS values. These calculations fail to account for the untraceable effects of dilution by nontritiated waters from fracture systems above and below the sample zone, the result of which would further increase the true salinity of these samples. Therefore, although saline waters collected at Atikokan have the highest salinities of the four research areas to date, their true salinities are higher than those reported here.

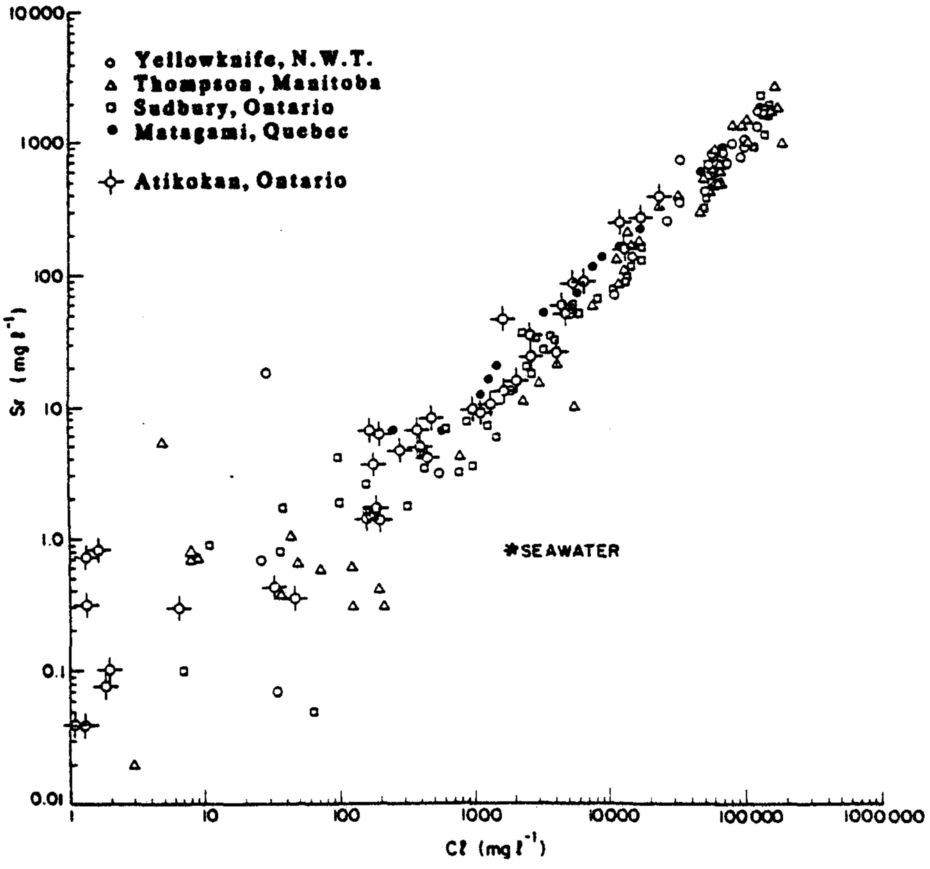
5.1.3 Groundwater Geochemistry

Frape and Fritz (1987) have shown that an excellent correlation exists between Ca and Cl concentrations for groundwaters from the Canadian Shield. Cl is typically used as the basis for comparison due to its conservative nature in solution. The use of Cl is also convenient since it is the most abundant ion in these groundwaters and its concentration increases as a function of depth and salinity. Figure 11a shows that at high Ca concentration (ie. below

Figure 11a: The relationship of Ca concentration and Cl concentration for Atikokan groundwaters shown with other groundwaters from the Canadian Shield. Note linear relationship between Ca and Cl at higher concentrations (modified from Frape and Fritz, 1987).

Figure 11b: The relationship of Sr concentration and Cl concentration for Atikokan groundwaters shown with other groundwaters from the Canadian Shield. Note linear relationship between Sr and Cl at higher concentrations. The high Sr content of Atikokan groundwaters is reflected in the small displacement of the linear trend, ie. higher Sr/Cl ratio (modified from Frape and Fritz, 1987).


Yellowknife, N.W.T.
Thompson, Manitoba
Sudbury, Ontario
Matagami, Quebec
Atikokan, Ontario
SEAWATER
Ca (mg l⁻¹)
Cl (mg l⁻¹)
1.0
10
100
1000
10000
100 000
1
10
100
1000
10000
100000
1000000


Yellowknife, N.W.T.
Thompson, Manitoba
Sudbury, Ontario
Matagami, Quebec
Atikokan, Ontario
SEAWATER
Sr (mg l⁻¹)
Cl (mg l⁻¹)
0.01
0.1
1.0
10
100
1000
10000
1
10
100
1000
10000
100000
1000000

700m at Atikokan) a linear relationship exists between Ca and Cl. Frape and Fritz (op. cit.) state that the relatively uniform Ca concentration of the most concentrated brines may reflect equilibration with Ca-bearing secondary minerals, which are common at Atikokan, such as calcite (found in upper 500m), gypsum (below 500m) and epidote (found at all depths).

Frape et al. (1984) first demonstrated that a linear relationship exists between Sr and Cl content for saline waters and brines from the Canadian Shield, and that the trend appears very similar to that of Ca (fig. 11b). This is what would be expected based upon the similar geochemical behaviour of Sr and Ca. Turekian (1956) found that a strong correlation existed between Sr and Ca for felsic rocks but that this was often not the case for mafic rocks. As shown in chapter three, both the Ca and Sr content of the ATK groundwaters show a consistent increase with depth (and therefore chlorinity). The point is also made by Frape and Fritz (1987) that Sr/Cl ratios are very similar for all sites across the shield (ca .008).

Edmunds et al. (1985) argue that Br and Cl assume a geochemically conservative role only after they are added to solution. Once in solution they are not likely to be incorporated into new low temperature minerals and as such they are excellent indicators of mixing or dilution. Br/Cl ratios can also be useful in assessing the role of fossil seawater and sedimentary brines as possible sources of shield brines. The relationship between major element ratios and Br/Cl have been used by Frape et al. (1984) and more recently Gascoyne et al. (1987) to assess the role of seawater in the brines at several sites in the Canadian Shield.

Data from Atikokan is shown in Figure 12 along with results from other research areas and mines in the Canadian Shield. Distinct differences in the Br/Cl and Ca/Mg ratios of several areas are clearly illustrated. Atikokan groundwaters are highly enriched in Ca relative to Mg, with similar values to those of Sudbury and Stripa. The Ca/Mg ratio of saline waters from Atikokan are up to five orders of magnitude greater than that of seawater. The Br/Cl ratio of the ATK samples is also considerably greater than that of seawater and similar to values for the minewaters, Stripa and Chalk River (CRNL). Some data for East Bull Lake (EBL) and the Whiteshell Nuclear Research Establishment and Underground Research Laboratories (WN/URL) appear to reflect the influence of sedimentary brines (ie. Manitoba brines or Western Canada Sedimentary brine WCSB) or seawater, while others are similar to Atikokan, Sudbury, etc. Both the URL and EBL research areas have either sedimentary formations or basin brines located within 40 km of the sampling sites.

Figure 12: Relationship of Ca/Mg and Br/Cl ratios of Atikokan groundwaters with samples from other research areas, Shield mines, Stripa, Western Canada Sedimentary Basin (WCSB), Manitoba Paleozoic rock brines and seawater. Note the similarity of ATK, Sudbury and Stripa data in contrast to seawater and sedimentary brines. Ratios are expressed as molar ratios. All waters shown have TDS > 3000 mg/L. ATK = Atikokan, CRNL = Chalk River Nuclear Laboratories, EBL = East Bull Lake, URL/WN = Whiteshell/Underground Research Laboratory. (modified from Gascoyne et al., 1987).

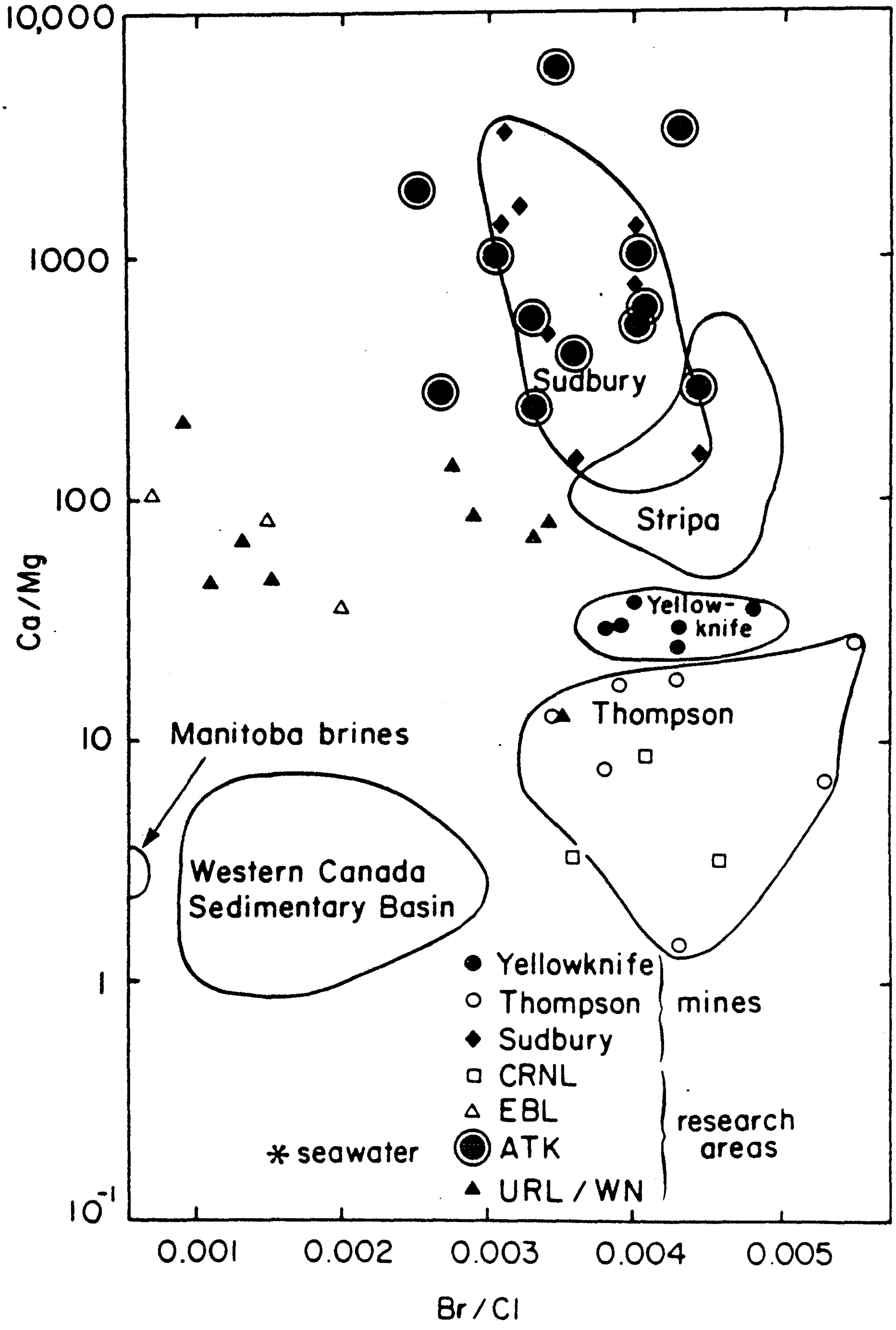

10,000
1000
100
10
1
10^{-1}
Ca/Mg
0.001
0.002
0.003
0.004
0.005
Br / Cl
Sudbury
Stripa
Yellow-knife
Thompson
Manitoba brines
Western Canada Sedimentary Basin
● Yellowknife
○ Thompson
◆ Sudbury
mines
□ CRNL
△ EBL
◉ ATK
▲ URL / WN
research areas
* seawater

Figure 13: Relationship between Atikokan groundwaters and samples from other research areas and Shield mines. Note the distinct cluster of ATK data near mine waters field which differs radically from the positions of seawater and sedimentary brines. Na/Ca and Br/Cl values shown are molar ratios. URL/WN = Whiteshell/Underground Research Laboratory, CRNL = Chalk River Nuclear Laboratory, EBL = East Bull Lake, WCSB = Western Canada Sedimentary Basin. (modified from Gascoyne et al., 1987).

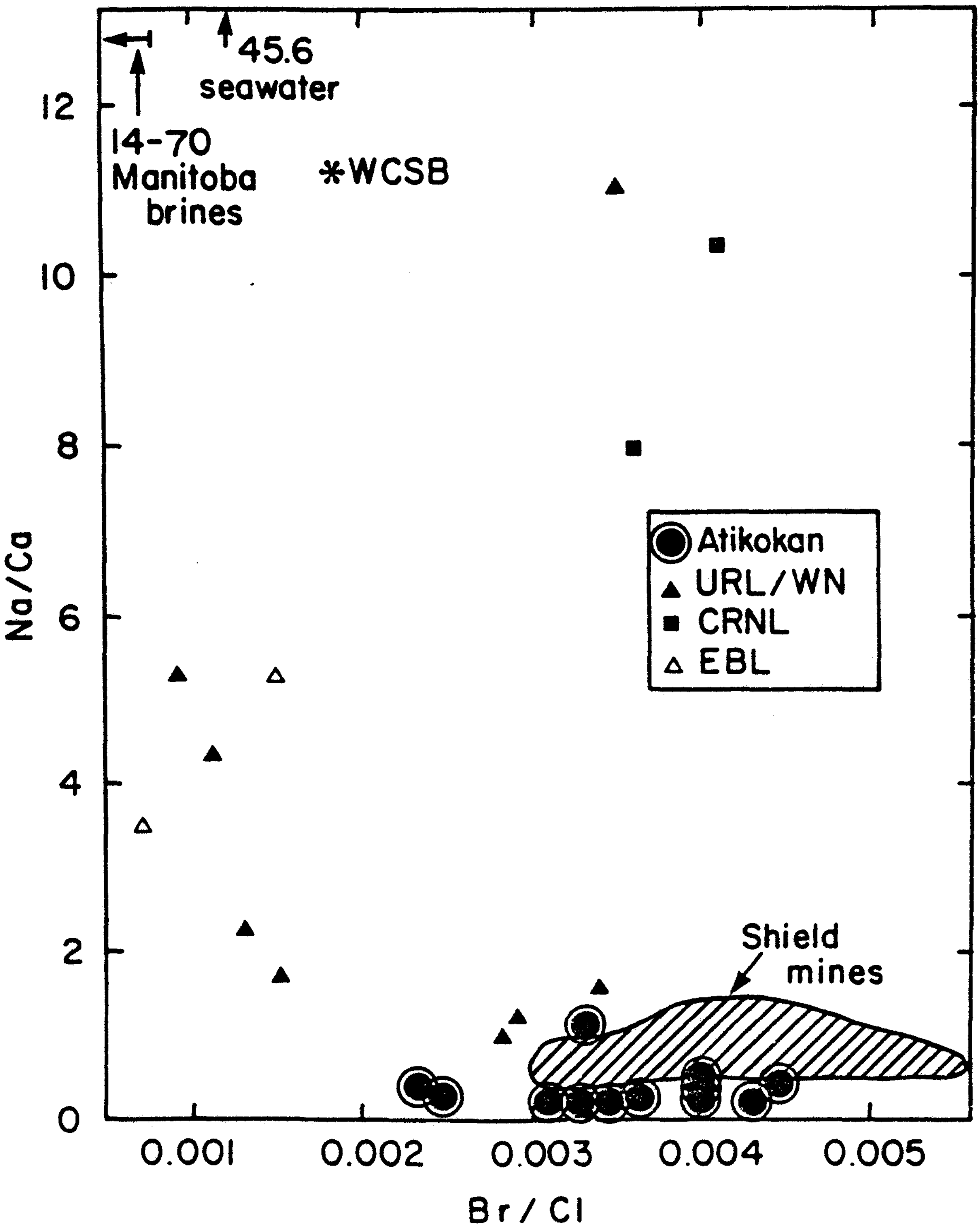

45.6
seawater
14-70
Manitoba
brines
*WCSB
Atikokan
URL/WN
CRNL
EBL
Shield
mines
Na/Ca
0
2
4
6
8
10
12
0.001
0.002
0.003
0.004
0.005
Br / Cl

Figure 13 also reflects the distinctive composition of the Atikokan groundwaters. The very low Na/Ca molar ratios of the ATK saline waters are similar to those of shield mine waters and dramatically different from that of seawater or sedimentary brines. Evidence for the role of sedimentary brines and/or seawater at EBL and URL is again seen in figure 13 where high Na/Ca and low Br/Cl ratios of those sources are reflected in some of the saline samples. Inspite of fairly similar lithologies at Atikokan and Pinawa (both are felsic intrusions) groundwater samples from the former have high Br/Cl and low Na/Ca ratios (similar to mine waters) while the latter have low Br/Cl and high Na/Ca ratios (similar to seawater).

It is generally agreed (Frape and Fritz, 1987, Gascoyne et al., 1987, Pearson, 1987) that the saline waters of the Canadian Shield have a complex history and that the 'solute' and 'water' components of these brines have different histories. The primary origin of the solute component is very difficult to identify since it is obscured by subsequent water-rock interactions which almost certainly play a major role in many areas.

Frape and Fritz (1987) point out that there are two schools of thought on the origin of the salinity of shield brines. The first is that the origin of the salinity is due to the emplacement of sedimentary/basinal brines or modified

Paleozoic seawater. This external origin of salinity is supported by Kelly et al. (1986) and Guha and Kanwar (1987). The second possible source of salinity proposed by several workers (Edmunds et al., 1984, Nordstrom et al., 1985, Kamineni, 1987, McNutt, 1987) is an in situ source. These workers argue that the present composition of the deep shield brines was reached through a process of intense water-rock interaction and/or leaching of fluid inclusions which have obscured the original source of the brines, be it sedimentary, metamorphic, etc.

Although a seawater signature is probably preserved and therefore explains some of the trends at WN/URL and EBL, no such signature is preserved at the Atikokan research area. This could be due to the fact that both the WN/URL and EBL sites are located near the margin of the Canadian Shield while Atikokan is centrally located. It also implies less water-rock interaction at EBL and URL. Strontium evidence does not support a seawater source at either EBL or URL (McNutt et al., 1987, W. Li, pers. comm.).

Frape and Fritz (1987) have stated that the geochemical similarity of brines from across the shield indicates that the extent of water-rock interaction is "extreme". Evidence for the role of water-rock interaction at Atikokan will now be reviewed.

5.2 Water-Rock Interaction

Several tools are available to assess the degree of water-rock interaction between groundwaters and the rocks in which they are found. McNutt (1987) has shown that Sr is a powerful tracer of this process. When coupled with other evidence such as kinetic studies on mineral dissolution, stable isotopes and major elements chemistry, a convincing argument can be made for the role of water-rock interaction at Atikokan.

5.2.1 Kinetic Evidence

In a study of the kinetics of dissolution rates of silicate minerals, Lasaga (1984) found that the rate of release of silica at low temperature was two orders of magnitude faster for anorthite than for albite. The weathering index discussed by Lasaga becomes very important in considering the partial equilibration of groundwaters with certain rock forming minerals at low temperature. Lasaga carried out his experiments at 25°C and pH=5, conditions similar to those measured at depth in the Eye-Dashwa lakes pluton (Gartner-Lee, 1983). The approximate mean lifetime of a 1-mm radius crystal in continuous contact with a sufficiently undersaturated solution was calculated and the results are shown in Table 5.

TABLE 5: Dissolution rates of various silicate minerals

Mineral	Lifetime	$^{87}Sr/^{86}Sr$ Ratio of mineral
Quartz	43,000,000 years	-
Muscovite	2,700,000 years	very high
K-Feldspar	520,000 years	high
Albite	80,000 years	moderate
Enstatite	8,800 years	very low
Diopside	6,800 years	very low
Nepheline	211 years	moderate
Anorthite	112 years	very low

- modified from Lasaga, 1984 (Table 5, p. 1404)

The sequence is the same as that of Goldich (1938) for the stability of minerals at the earth's surface. Early formed high temperature minerals are least stable under low temperature weathering conditions while late crystallizing, lower temperature are most stable.

This kinetic evidence for the reactivity of plagioclase has important implications for the Sr isotopic systematics of water-rock interaction. The plagioclase in the Eye-Dashwa lakes pluton is oligoclase, therefore its dissolution rate would be somewhere between 112 years (anorthite) and 80,000 years (albite), but still its kinetics would be considerably faster than K-feldspar or muscovite. Since oligoclase is Sr-rich and Rb-poor, it has a low $^{87}Sr/^{86}Sr$ ratio. Muscovite and K-feldspar, by contrast, are K-bearing minerals and therefore Rb-rich, with correspondingly high $^{87}Sr/^{86}Sr$ ratios. Therefore, when in contact with low temperature groundwaters, the less stable plagioclase would begin to react with the water, readily exchanging its Sr with the water. `Equilibration' with muscovite would occur at a rate four orders of magnitude slower, with K-feldspar being somewhat intermediate. The implications of this are obvious. When groundwaters gain access to the host rock, plagioclase in that rock would react most rapidly changing both the ionic and isotopic composition of the water. No unique `age' can be assigned to the water since exchange reactions are continually occurring, ie., the composition of the groundwater is changing and evolving through time.

As kinetic arguments favour a preferential exchange between plagioclase and water, this should be reflected in similar present-day Sr isotope ratios for the plagioclase and groundwater. This is the case for the saline samples at Atikokan. The average $^{87}Sr/^{86}Sr$ ratio of 24 water samples from ATK-1,5 and 7 (collected below 300m) is .7064. The average Sr ratio for the 9 plagioclase analyses from ATK-1 and 5 is .7079. Furthermore, if two plagioclase separates (ATK1-78 and 1-57) are rejected due to the possible presence of impurities (indicated by Rb/Sr ratios three times higher than those of all other plagioclase separates) the isotopic value of the water and plagioclase are virtually identical, .7064 and .7065, respectively. The $^{87}Sr/^{86}Sr$ value of all the groundwaters range from .705 to .727 (figure 10A). The deep groundwaters (those below 300m) show a distinct peak at .706 (figure 10C). The plagioclase value (figure 10D) overlap this value with a range of .703 to .708. The Sr isotopic ratios of both potassium feldspar at .707 - .729 (figure 10E) and whole rock at .706 - .717 (figure 10D) are higher than that of the plagioclase and any significant degree of equilibration with either of these phases would be reflected in considerably higher ratios than those that are seen for the deep groundwaters. Therefore, plagioclase is the only primary, major mineral phase that could contribute any significant amount of Sr and Ca to the brines.

At Atikokan, as at East Bull Lake and Stripa, Sweden, the saline waters have achieved isotopic equilibrium, not with the whole rock, but rather with a particular mineral phase(s). At East Bull Lake both the shallow Na-HCO_3 and deeper Na-Cl waters are in isotopic equilibrium with late secondary fracture-filling minerals, predominantly laumontite (an alteration product of plagioclase) as well as calcite and gypsum. The isotopic values of the waters overlap only with the highest whole rock ratios, and those of primary minerals, plagioclase, orthopyroxene and clinopyroxene are all lower than the observed groundwater ratios of .713 to .714 (McNutt et al., 1987). Fritz et al. (1987) found similar results at Stripa, where Sr leaching and isotopic equilibration with low Rb/Sr fracture-filling minerals (ie. chlorite) was proposed to explain the observed $^{87}Sr/^{86}Sr$ ratio of the groundwater there.

5.2.2 Chemical Evidence

Evidence for isotopic equilibration with plagioclase is not unique to Atikokan. Edmunds et al. (1987) suggests that acid hydrolysis of plagioclase feldspar and biotite is responsible for the salinity and geochemistry of the saline waters of the Carnmenellis granite. Supported by field and petrographic evidence, Edmunds et al. propose two possible reactions involving the alteration of plagioclase to the secondary minerals laumontite and kaolinite, to explain the high Ca/Na ratio of the saline waters.

$$5\ Na_{0.8}Ca_{0.2}Al_{1.2}Si_{2.8}O_8 + 6H^+ + 19H_2O \text{ ------->\ } 3Al_2Si_2O_5(OH)_4 + 4Na^+ + Ca^{2+} + 4H_4SiO_4$$

Oligoclase Kaolinite

$$5\ Na_{0.8}Ca_{0.2}Al_{1.2}Si_{2.8}O_8 + 16H_2O + 2Ca^{2+} \text{ ------->\ } 3CaAl_2Si_4O_{12}.4H_2O + 4Na^+ + 2H_4SiO_4$$

Oligoclase Laumontite

Much of the Na released in both reactions would be incorporated into albite. Microprobe analyses by Kamineni and Dugal (1982) showed that much of the feldspar in the ATK core to be albitic. The molar Na/Ca ratio of the saline groundwaters both at Atikokan (0.2 - 1.1) and the Carnmenellis granite (1.3 - 4.0) are much lower than the average bulk composition of the oligoclase. Therefore Edmunds et al. (1987) would evoke preferential leaching of Ca-rich plagioclase (as has been demonstrated at Atikokan) or incongruent dissolution of the plagioclase. Both of these processes are plausible. Preliminary results indicate that the saline groundwaters at South Crofty in the Carnmenellis granite approach isotopic equilibrium with the plagioclase ($^{87}Sr/^{86}Sr$ = .735).

What does appear to be unique about the ATK waters amongst published Sr isotopic data on Shield brines is the low $^{87}Sr/^{86}Sr$ ratio that these saline waters have achieved. Table 6 lists some of the published ranges for groundwater Sr ratios.

5.2.3 Stable Isotopic Evidence

Further evidence of the role of plagioclase feldspar is offered from stable isotope geothermometry. Although mineral reactions at lower temperatures occur very slowly, the very long residence times of shield brines would allow sufficient time so that the composition of the brines could be profoundly affected by low temperature water-rock interactions (Savin, 1980). Unlike high temperature systems where isotopic fractionation between silicate minerals and water is minimal and isotopic equilibrium with rock is reached rapidly, at low temperature, mineral-water isotopic fractionation can become significant.

Low temperature 'equilibration' is also suggested by stable isotopes. Using O isotopes, Pearson (1987) has estimated equilibrium temperatures for quartz-water to be between 100° and 200°C, for alkali feldspars-water, 70° to 160°C and for the plagioclase-water system, 15° to 70°C. These calculations are only approximations since high temperature mineral-water data must be extrapolated to low

TABLE 6: ^{87}Sr/^{86}Sr Ratios of groundwaters in the Canadian Shield and Cornwall, U.K.

Atikokan	.706 - .707	this study
East Bull Lake	.712 - .713	McNutt et al., 1987
Sudbury - North Range	.710 - .717	McNutt et al., 1984
- South Range	.725 - .740	"
Yellowknife	.711 - .714	"
Thompson	.719 - .725	"
Matagami	.708 - .709	McNutt et al., 1986
Elliot Lake	.725 - .755	McNutt, Pers. Comm.
URL	.714 - .730	W. Li, Pers. Comm.
South Crofty, Cornwall	.728 - .732	Kay & Darbyshire 1986

temperatures, for which experimental data does not exist. The temperatures given above do at least seem to be reasonable.

Jessop and Lewis (1978) reported that the geothermal gradient of the shield is ca. 13°C per kilometre. If the average annual surface temperature is taken as 8°C, the temperature at a depth of 1000m would be 21°C and at 2000m would be 34°C, rising to 60°C at a depth of 4 km. The estimated plagioclase-water equilibrium temperatures of 15-70°C therefore coincide with temperatures in the upper 2-5 kilometres of the Shield. Thus it would appear that water-rock interactions involving groundwater and plagioclase would be the favoured reactions at these temperatures, lending further support to the role of plagioclase in determining the isotopic and chemical composition of the shield brines.

5.3 Secondary Minerals

5.3.1 Low Temperature Secondary Minerals

The isotopic value of secondary minerals are often found to be equal to the to the groundwater with which they are associated (McNutt, 1987). Unfortunately, the availability of low temperature secondary mineral samples from the ATK core was very limited and only two samples were analysed. Both samples do however have ratios similar to those of the saline waters. A gypsum sample from ATK-1 (550m) has a $^{87}Sr/^{86}Sr$ ratio of .7063 which is essentially identical to the surrounding groundwater (.7064). The second sample from ATK-7 is a calcite and has a slightly lower ratio of .7055 and is a bit puzzling. This sample was taken from a carbonate filled vein located at 237m in borehole ATK-7. Regrettably, this zone was not isolated following drilling and therefore no corresponding water samples are available. The nearest water sample is ATK 7-4-41 which represents the interval from 365 to 580m and has a vale of .7058. Although the calcite and the groundwater are separated by approximately 130m, their values are similar, further sampling would be required to make a definitive statement on whether the two are in isotopic equilibrium. The sample consists of several rhombs of calcite that were scrapped from a vein, crushed and dissolved in HCl. It is therefore possible that the value of the calcite represents a mixture of an outer coating which has equilibrated with the water and a more pristine, unaltered centre that preserved its less radiogenic signature. The resulting mixture would yield a value which would lie between the two.

Kamineni (1983) found that gypsum is ubiquitous below 500m in the ATK core, due in part to the high Ca content of the deeper saline waters. It is difficult to determine whether the secondary minerals are controlling the Sr isotopic composition of the groundwater or whether they simply reflect the isotopic ratio of the water from which they crystallized. Unlike the EBL groundwaters which are more radiogenic than the primary mineral phases found in the host rock (McNutt et al., 1987), at Atikokan a strong argument has been made in this thesis for the extensive water-rock interaction between the deep groundwaters and plagioclase, i.e. this reaction is controlling the Sr isotopic composition of the waters. Secondary minerals do not appear to play a role in controlling the isotopic composition of the deep groundwaters at Atikokan. Depending upon the availability of bicarbonate or sulphate, calcite and gypsum have crystallized from the brackish and saline waters respectively, in isotopic equilibrium with these waters. Therefore, they do not control, but rather reflect, the isotopic composition of the water from which they crystallized.

5.3.2 Epidote

Epidote in the Eye-Dashwa lakes pluton have Sr contents ranging from 1300 to 12,000 ppm (average = 6900 ppm). The Sr isotopic ratio of epidotes from ATK-1 range from .702 to .706 (average = .705)(figure 10G), which is considerably lower than the saline water found in associated fractures. In particular, sample M-8 which is a pure (Rb/Sr = .001), primary, crystalline epidote, that appears to have an Archean signature of .7021 . The gypsum sample previously mentioned is from the same location and is in isotopic equilibrium with the water with a value of .7063 . It would appear that this epidote formed early in the pluton's history, by the alteration of plagioclase, and that the $^{87}Sr/^{86}Sr$ ratio has remained unchanged since that time due to the very low Rb content of the epidote. Isotopic exchange with groundwater does not appear to have occurred during this time. However, the remainder of the epidote samples have higher $^{87}Sr/^{86}Sr$ ratios (.704 to .706) and probably represent a second type of epidote. These were also formed by the alteration of plagioclase, probably during hydrothermal activity later in the pluton's history. The higher Sr isotopic ratios of this group of epidotes reflects the increased ratio of the plagioclase at the time of epidote formation. We therefore have at least two types of epidote with two distinct ages.

5.4 Implications for Radioactive Waste Disposal

The role of secondary mineral phases is very significant in the context of disposal of high level nuclear waste in the plutonic rocks of the Canadian Shield. Frape and Fritz (1987) have noted that boreholes which penetrate some of the most concentrated brines are essentially `self-sealing' where the boreholes actually show decreasing flows from rates of 100's litres/min. to zero flow due to plugging of the borehole by precipitation of secondary minerals such as gypsum. This same 'self-sealing' property could play a major role by restricting access of groundwaters to the storage vault while at the same time limiting the migration of radionuclides which are transported by groundwaters. Hydraulic pumping tests indicate no discernable hydraulic conductivity in gypsum filled fractures at Atikokan (Gartner-Lee, 1983).

The sorptive properties of secondary minerals have also been shown to be quite different from those of the primary minerals in the rock matrix. The extent of sorption of various radionuclides on alteration and fracture filling minerals can be considerable. Kamineni (1986) has found that low temperature secondary minerals such as gypsum can concentrate analogue elements (REE's). Analysed core from Atikokan indicates significant depletion of LREE (plus Ca and Sr) from altered samples relative to the unaltered granitic cores (Kamineni, 1986). Sphene, epidote, gypsum, clay minerals and iron oxides appear to act as sinks for the LREE leached from the rock matrix adjacent to fractures (Kamineni, 1985). Several fission products are analogous to the LREE in their geochemical behaviour (La≡Am, Nd≡Cm) and U and Th behave similarly to Np and Pu. In an experimental study using thin sections prepared from ATK core, Kamineni et al., 1983 found that ^{137}Cs is sorbed on sericite and altered plagioclase while titanite, epidote and chlorite sorb ^{90}Sr, ^{147}Pm and ^{241}Am. Iron oxide filled fractures were also found to sorb ^{95}Tc which under laboratory conditions exists as a non-sorbing anionic species.

Hydraulic conductivity tests and televiewer logs have shown that fractures exist at all depths at Atikokan, many of which contain groundwaters. Since fractures will play a dominant role in the transport of radionuclides through the geosphere, this evidence of the retardation of radionuclide migration by secondary mineral phases is encouraging. The sealing function of secondary minerals coupled with their ability to impede the transport of radionuclides to the biosphere means that they will play a central role in the overall scheme of high level nuclear waste disposal. Since nuclear fuel waste materials will be stored in relatively fresh, unaltered rocks (below 1000m), groundwaters that enter the vicinity of the vault will be heated by the waste material, inducing hydrothermal alteration in the area (Kamineni and Dugal, 1982). Geothermal gradients in the rock adjacent to the storage vault are estimated at 50 - 200°C/km (Bird and Fyfe, 1982). Kamineni and Dugal (op. cit.) have shown that, compared to unaltered rocks, altered rocks at Atikokan have lower porosities and permeabilities and greater sorptive capacities. Therefore, the alteration halo generated around the storage vault would act as a barrier to prevent the further penetration of groundwaters and reduce the transport of contaminants away from the storage area. The heat released during the decay high level nuclear waste could affect pre-existing secondary minerals in a very different way. The elevated temperatures could initiate gypsum dissolution or shrinkage due to dehydration. This would, in effect, create open pathways for radionuclide migration. Kamineni (1983) suggests that one possible answer would be to pump highly concentrated mineralising solutions into the fractures until supersaturation is achieved, effectively re-sealing the fractures and making them impermeable. This study has shown that gypsum has likely crystallized from the present-day groundwaters at Atikokan, therefore the gypsum (and other low-T secondary minerals) is 'young'. In light of their importance, further work is needed to assess the stability of these low-temperature minerals.

CHAPTER SIX

SUMMARY AND RECOMMENDATIONS FOR FUTURE STUDY

Water-rock interactions have played a major role in determining the chemical and isotopic composition of the groundwaters at Atikokan. In all likelihood this process has been occurring over much of the pluton's history and continues today. Strontium isotopes have been successfully employed in this study to determine the nature of the water-rock exchange. Isotopic equilibration has been reached with plagioclase feldspar and the role of K-feldspar, biotite and hornblende appear to be limited and insignificant relative to that of plagioclase. This mineral-water equilibration is supported by kinetic, stable isotopic and geochemical evidence. The use of Sr isotopes to eliminate several mineral phases from further consideration greatly simplifies reaction path calculations of the type used by Plummer et al. (1983) for modelling the chemical composition of groundwater systems. Gypsum is in isotopic equilibrium with the saline waters and has crystallized from them 'recently', but further work is needed to determine the role of other secondary minerals. The $^{87}Sr/^{86}Sr$ ratio of the saline waters at Atikokan is the lowest yet reported, reflecting the Rb-poor, Sr-rich nature of the plagioclase.

Geochemical trends at Atikokan are similar to those at several other PreCambrian Shield sites. The Ca/Mg, Na/Ca and Br/Cl ratios of the ATK groundwaters are similar to those of mines located in the Shield and indicate that seawater was not a precursor of these saline waters. Evidence exists for mixing of surface waters with groundwaters at all depths.

Further investigations should be concentrated on the secondary mineral phases. A greater number of analyses are required for both calcite and gypsum (as well as clay minerals, etc.) and an attempt should be made to analyse different 'generations' of these minerals within a given crystal or veinlet. In this way the isotopic evolution of the brines could be evaluated. Fluid inclusion work would be very useful. If different generations of inclusions could somehow be decrepitated separately, a great deal of insight into the history of the groundwaters would be gained.

REFERENCES

Bird, G.W. and Fyfe, W.S. 1982. The nuclear waste disposal problem - an overview from a geological and geochemical perspective. Chemical Geology, 36: 1-13.

Birk, D. and McNutt, R.H. 1981. Geochronology of Wabigoon belt granitoids, northwestern Ontario: Rb/Sr isochrons for seven late-tectonic plutons. Canadian Journal of Earth Sciences, 18: 157-175.

Bottomley, D., Graham, B. and Ross, J. 1980. Investigations into the geochemistry of groundwater in PreCambrian crystalline rocks. At. Energy Can. Ltd., Pinawa, Man., Tech. Rec. TR-122.

Brown, P.A., Kamineni, D.C., Stone, D. and Thivierge, R.H. 1980. General geology of the Eye-Dashwa lakes pluton, Atikokan, Ontario. GSC Paper 80-1A: 379-384.

Dence, M.R. 1979. Mineral stabilities and rock properties in relation to nuclear waste disposal. At. Energy Can. Ltd., Pinawa, Man., Tech. Rec. TR-1.

Douglas, R.J.W. 1980. Proposals for time classification and correlation of Precambrian rocks and events in Canada and adjacent areas of the Canadian Shield. GSC Paper 80-24: 19.

Edmunds, W.M., Andrews, J.N., Burgess, W.G., Kay, R.L.F. and Lee, J.D. 1984. The evolution of saline and thermal groundwaters in the Carnmenellis granite. Mineralogical Magazine, 48: 407-424.

Edmunds, W.M., Kay, R.L.F. and McCartney, R.A. 1985. Origin of saline groundwaters in the Carnmenellis granite: natural processes and reaction during Hot Dry Rock reservoir circulation. Chemical Geology, 49: 287-301.

Edmunds, W.M., Kay, R.L.F., Miles, D.L., Cook, J.M. 1987. The origin of saline groundwaters in the Carnmenellis granite, Cornwall (U.K.): Further evidence from minor and trace elements. in Saline waters and gases in crystalline rocks. GAC Special Paper 33. Ed. by P. Fritz and S. Frape. 127-144.

Fleer, V.N. and Johnston, R.M. 1985. The dissolution behaviour of minerals in granitic and gabbroic systems. At. Energy Can., Ltd., Pinawa, Man., Tech. Rec. TR-328-1.

Flanagan, F.J. 1986. Reference samples in geology and geochemistry. Geostandards Newsletter, 10: 191-256.

Frape, S.K. and Fritz, P. 1982. The chemistry and isotopic composition of the saline groundwaters from the Sudbury basin, Ontario. Canadian Journal of Earth Sciences, 19: 645-661.

Frape, S.K., Fritz, P. and McNutt, R.H. 1982. The origin and evolution of saline groundwaters in the Canadian Shield. 4th International Symposium on Water-rock Interactions. Japan. 141-144.

Frape, S.K., Fritz, P. and McNutt, R.H. 1984. The role of water-rock interaction in the chemical evolution of groundwaters from the Canadian Shield. Geochimica et Cosmochimica Acta, 48: 1617-1627.

Frape, S.K. and Fritz, P. 1987. Geochemical trends from groundwaters from the Canadian Shield. in Saline waters and gases in crystalline rocks. GAC Special Paper 33. Ed. by P. Fritz and S. Frape. 19-38.

Fritz, B., Clauer, N. and Kam, M. 1987. Strontium isotopic data and geochemical calculations as indicators for the origin of saline waters in crystalline rocks. in Saline waters and gases in crystalline rocks. GAC Special Paper 33. Ed. by P. Fritz and S. Frape. 121-126.

Fritz, P. and Frape, S.K. 1982. Saline groundwaters in the Canadian Shield - a first overview. Chemical Geology, 36: 179-190.

Garrels, R.M. 1967. Genesis of some groundwaters from igneous rocks. in Researches in Geochemistry, v. 2, Ed. by P.H. Abelson. 405-420.

Gartner-Lee Associates Ltd. 1983. Hydrogeological studies Forsberg Lake site (RA-4) for Atomic Energy of Canada Ltd. Project 82-3000. Gartner-Lee Assoc. Ltd. Internal Report: 82 pp.

Gascoyne, M., Davison, C.C., Ross, J.D. and Pearson, R. 1987. Saline groundwaters and brines in plutons in the Canadian Shield. in Saline waters and gases in crystalline rocks. GAC Special Paper 33. Ed. by P. Fritz and S. Frape. 53-68.

Goldich, S.S. 1938. A study of rock weathering. Journal of Geology, 46: 17-58.

Guha, J. and Kanwar, R. 1987. Vug brines-fluid inclusions: a key to the understanding of secondary gold enrichment processes and the evolution of deep brines in the Canadian Shield. in Saline waters and gases in crystalline rocks. GAC Special Paper 33. Ed. by P. Fritz and S. Frape. 95-102.

Hickson, C.J. and Juras, S.J. 1986. Sample contamination by grinding. Canadian Mineralogist, 24: 585-589.

Jessop, A.M. and Lewis, T. 1978. Heat flow and heat generation in the Superior Province of the Canadian Shield. Tectonophysics, 50: 55-77.

Kamineni, D.C. and Dugal, J.J.B. 1982. A study of rock alteration in the Eye-Dashwa Lakes pluton, Atikokan, Northwestern Ontario, Canada. Chemical Geology, 36: 35-57.

Kamineni, D.C. 1983. Sulfur-isotope geochemistry of fracture-filling gypsum in an Archean granite near Atikokan, Ontario, Canada. Chemical Geology, 39: 263-272.

Kamineni, D.C. and Stone, D. 1983. The ages of fractures in the Eye-Dashwa lakes plutons, Atikokan, Canada. Contributions to Mineralogy and Petrology, 83: 237-246.

Kamineni, D.C., Vandergraaf, T.T., Ticknor, K.V. 1983. Characteristics of radionuclide sorption on fracture-filling minerals in the Eye-Dashwa lakes pluton, Atikokan, Ontario. Canadian Mineralogist, 21: 625-636.

Kamineni, D.C. 1985. Significance of the distribution of rare-earth elements (REE) in the Eye-Dashwa lakes pluton to the migration of radionuclides. At. Energy Can. Ltd., Pinawa, Man., Tech. Rec. TR-299, Vol. II: 508-527.

Kamineni, D.C. 1986. Distribution of uranium, thorium and rare-earth elements in the Eye-Dashwa lakes pluton - a study of some analogue elements. Chemical Geology, 55: 361-373.

Kamineni, D.C. 1987. Halogen-bearing minerals in plutonic rocks: a possible source of chlorine in saline groundwater in the Canadian Shield. in Saline waters and gases in crystalline rocks. GAC Special Paper 33. Ed. by P. Fritz and S. Frape. 69-80.

Kay, R.L.F. and Darbyshire, D.P.F. 1986. A strontium isotope study of groundwater-rock interaction in the Carnmenellis granite. 5th International Symposium on Water-Rock Interaction (WRI-5). Reykjavik, Iceland, August 1986. Extended Abstracts. International Assoc. of Geochemistry and Cosmochemistry. pp 329-332.

Kelly, W.C., Rye, .O. and Livnat, A. 1986. Saline minewaters of the Keweenaw Peninsula, Northern Michigan: their nature, origin and relation to similar deep waters in Precambrian crystalline rocks of the Canadian Shield. American Journal of Science, 286: 281-308.

Krogh, .E. and Turek, A. 1982. Precise U-Pb zircon ages from the Gamitagma greenstone belt, southern Superior Province. Canadian Journal of Earth Sciences, 19: 859-867.

Lasaga, A.C. 1984. Chemical kinetics of water-rock interactions. Journal Geophysical Research, 89: 4009-4025.

Marchand, M. 1973. Determination of Rb, Sr and Rb/Sr by XRF. McMaster University Tech. Memo. 73-2, pp 16.

McNutt, R.H., Frape, S.K., Fritz, P. 1984. Strontium isotopic composition of some brines from the Precambrian Shield of Canada. Isotope Geoscience, 2: 205-215.

McNutt, R.H., Frape, S.K., Jones, M., Fritz, P. 1986. The $^{87}Sr/^{86}Sr$ values of brines in rocks of Archean age, Matagami area, Quebec: a contrasting behaviour to other Canadian Shield brines. 5th International Symposium on Water-Rock Interaction (WRI-5). Reykjavik, Iceland, August 1986. Extended Abstracts. International Assoc. of Geochemistry and Cosmochemistry. 379-381.

McNutt, R.H. 1987. $^{87}Sr/^{86}Sr$ ratios as indicators for water-rock interactions: applications to brines found in PreCambrian age rocks from Canada. in Saline waters and gases in crystalline rocks. GAC Special Paper 33. Ed. by P. Fritz and S. Frape. 81-88.

McNutt, R.H., Gascoyne, M., Kamineni, D.C. 1987. $^{87}Sr/^{86}Sr$ values in groundwaters of the East Bull Lake pluton, Superior Province, Ontario, Canada. Applied Geochemistry 2: 93-101.

Nordstrom, D.K., Andrews, J.N., Carlsson, L., Fontes, J.C., Fritz, P., Moser, H. and Olssen, T. 1985. Hydrogeological and hydrogeochemical investigations in boreholes - final report of the phase I geochemical investigations of the Stripa groundwaters: SKB Stripa Project, Swedish Nuclear Fuel and Waste Management Company, Report 85-06, 250p.

Pankhurst, R.J. and O'Nions, R.K. 1973. Determination of Rb/Sr and $^{87}Sr/^{86}Sr$ ratios of some standard rocks and evaluation of X-ray fluorescence spectrometry in Rb-Sr geochemistry. Chemical Geology, 12: 127-136.

Pearson, F.J. Jr. 1987. Models of mineral controls on the composition of saline groundwaters of the Canadian Shield. in Saline waters and gases in crystalline rocks. GAC Special Paper 33. Ed. by P. Fritz and S. Frape. 39-52.

Percival, J.,B. and Hume, J., P. 1984. Lithological and density data on ATK-5 standard core samples from the Forsberg Lake site near Atikokan, Ontario. At. Energy Can. Ltd., Pinawa, Man., Tech. Rec. TR-278.

Peterman, Z.E., Goldich,S.S., Doe, B.R., Naeser, C.W., Rosholt, J.N., Zartman, R.E. and Kamineni, D.C. 1985. Isotopic studies of core samples from the Eye-Dashwa lakes pluton, Atikokan, Ontario. Proc. 17th Info. Meet., Nuclear Fuel Waste Management. At. Energy Can. Ltd., Pinawa, Man., Tech. Rec. TR-299.

Plummer, L.N., Parkhurst, D.L. and Thorstenson, D.C. 1983. Development of reaction models for ground-water systems. Geochimica et Cosmochimica Acta, 47: 665-686.

Savin, S.M. 1980. Oxygen and hydrogen effects in low-temperature mineral-water interactions: in Fritz, P. and Fontes, J. Ch. eds., Handbook of environmental isotope geochemistry. v.I The terrestrial environment A. Elsevier Scientific Publishing Co., Amsterdam, 283-327.

Stone, D. and Kamineni, D.C. 1982. Fractures and fracture infillings of the Eye-Dashwa Lakes pluton, Atikokan, Ontario. Canadian Journal of Earth Sciences, 19: 789-803.

Streckeisen, A. 1976. To each plutonic rock its proper name. Earth Science Review, 12: 1-33.

Turekian, K. 1956. The geochemistry of strontium. Geochimica et Cosmochimica Acta, 10: 145-196.

APPENDIX ONE

Sample Dissolution:

Approximately 200 mg of rock powder (-300 mesh) or 20-150 mg of mineral separates (+64 mesh) were accurately weighed (± 5µg) in a clean, Savillex PFA Teflon dissolution bomb of known weight. To this ca. 10 ml of 42 wt.% HF were added. The bombs were then tightly sealed and placed inside an outer FEP Teflon jacket and placed in a dry oven at ca. 120°C for 3 days. The bombs were removed from the oven and taken to incipient dryness on a hot plate, a few drops of 16N HNO_3 added and, the sample was evaporated to dryness. All evaporations were carried out in a laminar-flow exhausted fume hood using glass drying chimneys to isolate each sample container thereby avoiding cross-contamination due to splattering. Five millilitres of 16N HNO_3 were added to dissociate any fluorides and/or sulphides present in the sample. Once again the samples were taken to dryness. Following the addition of ca. 5 ml of 6N HCl, the bombs were placed in the oven for 24 hours. The samples were removed from the oven, taken to dryness and redissolved in 4-10 ml (depending on the analyses to be done) of 2.5N HCl. Some of the coarser grained mineral separates required a greater period of time in the HF digestion stage, upto 7 days. If it was discovered that undissolved material, usually in the form of clear, colourless grains (especially for epidote) remained after the HCl stage, the procedure was repeated.

In this way, all samples were successfully and completely digested.

Spiking:

Due to the relative scarcity of several mineral separates (as little as 23 mg), Sr and Rb concentrations were determined by the method of isotope dilution (ID). Upon completion of the sample dissolution described above, the samples were split. If ID was to be done, 3 splits were made; one for Rb and Sr ID, one for Sr isotopic ratio analysis (IR) and a third split was set aside in case re-analysis was required.

Sample splitting for ID analysis was carried out according to the following procedure. The ID split weight and that of the dissolved sample must be measured accurately in order to determine the fraction of the initial sample weight that is represented by the ID split. Therefore, the entire dissolved sample was weighed in the dissolution bomb. Approximately 30-50% of this solution was then transferred to a tared, precleaned 15 ml Teflon vial and its weight was measured accurately (± 5 µg). Rubidium and Sr spikes were then added to the ID split and their precise weights recorded.

The spikes used were ^{87}Rb (99.20%) and ^{84}Sr (97.46%). An optimum amount of spike was estimated such that the

$^{84}Sr/^{86}Sr$ ratio of the sample would approximate one (this also served to conserve the spike). To this end, a dilute ^{84}Sr spike was made by the author and calibrated against 3 USGS rock standards; G-2, AGV-1 and GSP-1. The results are given in Table 1-1.

TABLE 1-1: Calibration of dilute ^{84}Sr spike.

Standard	Calculated Spike Concentration
G-2	5.697709
	5.728322
	5.691276
AGV-1	5.628937
	5.615302
	5.612017
GSP-1	5.647047

^{84}Sr spike concentration = 5.66 ± .091 (2σ) ppm

The concentration of the ^{87}Rb spike used was 1.668 ± 0.11 (2σ) ppm. In preparation for column work, the ID splits were dried after spiking and redissolved in ca. 1 ml of 2.5N HCl.

Column Chemistry:

Prior to being loaded onto the cation exchange columns, all samples were centrifuged for 5 minutes in polystyrene centrifuge tubes to remove any suspended particulate matter that could contaminate the columns. The exchange resin used for this work was Dowex Bio-Rad AG50W, 200-400 mesh, hydrogen form.

Groundwater samples were gently evaporated and re-acidified with ca. 2 ml of 2.5 N HCl before being centrifuged and loaded onto the columns. The method of Sr separation is the same for both groundwater and rock/mineral samples. The acid used for all elutions was quartz, sub-boiling, doubly distilled 2.5N HCl. For Sr IR analyses the sample was collected in an 8 ml aliquot. For ID analyses, Rb was first eluted in a 6 ml aliquot, followed by Sr in a 8 ml aliquot (after an intermediate 12 ml elution). The samples were collected in pre-cleaned 8 or 15 ml Teflon vials and gently evaporated to dryness on a hot plate. Samples were then stored, awaiting analysis on the mass spectrometers.

Analysis:

Strontium samples were dissolved in ca. 1 µL of 0.3 or 0.4M H_3PO_4 (the former resulting in better loads due to less spreading of sample) and loaded onto pre-conditioned, single Ta filament beads. The samples were then analysed on the VG 354 solid source mass spectrometer at McMaster. This is a five collector machine with a 27 cm radius and 90° magnetic sector. Magnetic field shifting and data analysis are controlled by a Hewlett-Packard 9121 computer using software programmes prepared by VG. Sr isotope ratios samples were run using the SrsT (normal) programme (150 scans) with an aiming current of 2V. Isotope dilution samples were run statically using a 1V aiming current (non-normalized) also consisting of 150 repeats. At least one NBS 987 standard was run in each barrel and the values are shown in Appendix Two.

Rubidium ID samples were analysed on the Sciex-Elan ICP-MS at McMaster using Sciex prepared software (isotope dilution programme). Prior to analysis, the dried Rb ID samples were dissolved in ca. 10 ml of 0.5N HCl. Unspiked USGS rock standards were also analysed to monitor Rb fractionation during analysis.

APPENDIX TWO

Precision and Accuracy

Table 2-1: Strontium Isotope Ratios of Standard NBS 987 run during the course of this thesis.

All values are normalized to $^{86}Sr/^{88}Sr = .1194$.

DATE	$^{87}Sr/^{86}Sr$ Ratio	Error [$2\sigma(x10^{-6})$]
01/05/86	.710213	14
25/09/86	.710152	11
04/12/86	.710206	14
26/02/87	.710218	9
	.710181	7
	.710198	9
06/03/87	.710227	13
	.710208	16
20/03/87	.710225	10
	.710236	14
	.710223	14
02/04/87	.710229	11
	.710243	13
	.710241	14
27/05/87	.710215	14
	.710192	13
	.710195	13
04/06/87	.710204	13
	.710200	10
18/06/87	.710255	11
10/07/87	.710181	13
06/08/87	.710207	10

Mean = .710211 ± 16 (2σ)

Published Values:

VG Value (1986)	.710232
Pankhurst and O'Nions (1973)	.71039 ± 56 (2σ x 10^{-6})
NBS Certificate	.71014

These results reflect only the precision and accuracy of the mass spectrometer analyses and not that of the chemical procedure.

Table 2-2: Replicate Analyses of Samples for $^{87}Sr/^{86}Sr$ ratios

SAMPLE	$^{87}Sr/^{86}Sr$	Error [$2\sigma(x10^{-6})$]	Description
ATK 1-1089	.706136	6	Water sample
	.706124	6	(172 ppm Sr)
	.706084	6	
Mean = .706115 ± .003 %			
LK-5	.746594	7	Water sample
	.746557	11	(0.5 ppm Sr)
Mean = .746576 ± .002 %			
1-78	.717166	6	Whole Rock
	.717194	6	(545 ppm Sr)
Mean = .717180 ± .002 %			

% error calculated from $[((x_1 - x_2)/2)X] \times 100$

These replicate analyses reflect the reproducibility (precision) of the entire sample preparation procedure. They represent both dilute and concentrated waters, as well as a relatively low Sr whole rock sample. The average error of these analyses is 0.003% a value equal to that of replicate analyses on the NBS standard. Therefore 0.003% is used as a blanket error on all Sr isotopic analyses.

Table 2-3: XRF and Isotope Dilution Results for some USGS standards.

XRF:

	Rb	Sr	Rb/Sr	Reference
G-2	169.5	480.9	.35238	this work
	169.3	479	.35351	1
% error	± .049	± .198		
GSP-1	254.2	239.4	1.06168	this work
	252.7	235.7	1.07198	1
% error	± .092	± .779		
AGV-1	67.3	654.9	.10281	this work
	67	659	.10167	1
% error	± .223	± .312		

Isotope Dilution:

	Rb		Sr	Reference
G-2	-		471.45	
			477.03	
			477.48	
		Mean =	475.32 ± 6.72	this work
			476.3	2
GSP-1	256.02		233.45	this work
	254.7		233.1	2
AGV-1			660.59	
			661.11	
			659.09	
		Mean =	660.26 ± 0.86	this work
			662.0	2

(all values in ppm)
1 Flanagan, 1986
2 Pankhurst and O'Nions, 1973

Table 2-4: Accuracy of Sr isotopic ratio analyses:

Standard	$^{87}Sr/^{86}Sr$	$^{87}Sr/^{86}Sr$ [1]
G-2	.709864 ± 11	.70988 ± 8
GSP-1	.769034 ± 12	.76887 ± 7
AGV-1	.704029 ± 13	.70409 ± 7

[1] Pankhurst and O'Nions, 1973
all errors reported as 2σ

These values represent the accuracy of the Sr isotopic analyses throughout the entire sample preparation procedure. The values for G-2 and AGV-1 agree within error with those of Pankhurst and O'Nions (1973). The agreement is not as good for GSP-1 perhaps reflecting some slight heterogeneity of the GSP-1 standard aliquot.

Table 2-5: Sr concentration analysis on ICP/MS using Rh as an internal standard.

NBS standard 1643b = 236.5 ppb
230.4

mean = 233 ± 3 ppb

NBS certificate = 227 ± 6

The Rh internal standard and NBS values agree within error.

APPENDIX THREE

SAMPLE DESCRIPTION OF CORE

Sample No.	Depth (m)	Sample Description
ATK 1-45	1066.90	- moderately altered, medium-coarse grained pink granite - several fine grained, epidote-rich crosscutting veinlets (<<3 mm in diameter) - plagioclase moderately altered to sericite + epidote - chloritised biotite, no hornblende
ATK 1-52	1088.15	- moderately altered, medium-coarse grained pink granite - many epidote-rich veinlets (25%) - plagioclase altered to sericite + epidote - chloritised biotite, no hornblende - similar to 1-45
ATK 1-57	1089.15	- similar to 1-45 and 1-52 but with high proportion of fine grained cataclastic material - epidote veinlets (10%) - chloritised biotite
ATK 1-74	1107.15	- coarse grained, quartz-rich pink granite - large chloritised biotites with haloes - biotite altered to chlorite + calcite - plagioclase is moderately sericitized
ATK 1-75	1107.85	- medium grained pink granite - plagioclase moderately sericitized - chloritised biotite with Fe-oxide rims - several small calcite and hematite veinlets (<<100 μ)
ATK 1-78	1120.00	- medium grained pink granite - large chloritised biotite (up to 2 mm) with minor epidote - plagioclase 'dusted' with sericite though twins still visible - large unaltered microcline contains inclusions of altered plagioclase - no hornblende
ATK 1-81	1127.00	- medium grained, massive grey granite - large 'fresh' hornblende crystals (up to 3mm) with minor alteration to epidote and calcite - minimal alteration of biotite to chlorite - hornblende and biotite present in equal abundance - minimal sericitization of plagioclase (+calcite) no epidote - degree of alteration similar to 5-120

ATK 1-137	1105.90	- medium grained pink granite - highly altered - plagioclase appears as dark 'clots' of fine grained alteration minerals (epidote, calcite, calcite, kaolin, hematite and other opaques) - abundant, small, randomly oriented, crosscutting veinlets, rich in epidote and fine grained polycrystalline quartz - rare biotite is completely chloritised, no hornblende - most highly altered sample
ATK 5-120	868.80	- medium grained grey granite - minor sericitization of plagioclase highlights compositional zoning - very minor alteration of biotite with epidote at plag/bio contacts - pleochroic haloes clearly visible in biotite - hornblende is also fresh with only minor alteration to epidote - 70% biotite, 30% hornblende - freshest sample

Appendix 4: Summary of groundwater analysis for Forsberg Lake Research Area, Atikokan, Ontario
Data taken from a report prepared by Gartner-Lee Associates Ltd., 1983

SAMPLE	Depth (m)	pH	Eh (mV)	Ca	K	Mg	Na	Sr	HCO_3	SO_4	Cl	Br	^3H (TU)	TDS
ATK 1 -1	100	6.0	+350	31	1	5	5	.1	137	7	2	<0.2	+64	199
-2A	210	6.4	+270	45	1	5	10	.4	112	20	31	<0.2	+83	232
-2B	430	5.5	+200	293	1	1	68	5	12	337	400	3.4	+74	1125
-4B	570	6.8	+220	332	2	1	66	6	18	240	365	3.6	+66	1040
-6B	680	6.2	+220	480	2	2	59	9	6	89	895	7.4	+101	1553
-8B	790	6.0	+220	978	3	2	613	24	13	80	2380	18	+106	4114
-9A	880	7.3	+10	11900	10	4	1830	308	45	430	25400	141	+86	40077
ATK 5 -1A	100	6.9	+180	32	2	4	3	<.1	92	3	2	<.1	+52	146
-2A	320	6.6	+170	102	1	2	34	1.6	25	53	193	1.2	+69	417
-int.	380	7.0	-	110	3	2	67	1.5	29	126	170	1.6	+27	513
-3A	420	6.8	+190	297	1	1	84	4	16	184	428	3.3	+41	1021
-3B	680	6.6	+100	940	2	1	86	24	<2	91	1860	17	+112	3027
-4A	700	5.7	+150	1240	3	1	116	31	12	114	2560	19	+86	4098
-4B	980	5.5	+160	8980	7	1	816	220	<2	263	18100	137	+62	28531
-6B	1050	5.5	-210	7460	9	1	779	205	21	186	12200	119	+72	20984
Forsberg Lake Drill Water		5.0	-	1.8	0.5	0.6	0.6	-	<10	2.5	<0.5	-	+129	26

- all concentrations listed are in mg/L

Appendix 5: Summary of groundwater analysis for Forsberg Lake Research Area, Atikokan, Ontario
Data taken from preliminary AECL results.

SAMPLE	BOREHOLE INTERVAL (m)	pH	Ca	K	Mg	Na	Sr	HCO_3	SO_4	Cl	Br	^3H	TDS
ATK 1-3	566 - 608	6.5	1120	1.8	1.2	308	13.5	3.0	770	1750	16.1	37	3991
-4	"	6.5	1180	1.5	0.7	331	15	<2.0	880	1910	17.8	8	4343
-5	"	4.5	930	2.2	2.6	240	9.6	<2.0	620	1390	13.7	17	3328
-760	760 - open	6.2	2500	3.6	3.8	493	48	50	129	4480	36.7	42	7810
-1089	1089 - 1099	4.6	6800	5.0	4.4	1400	160	4.0	630	13950	93.0	135	23080
ATK 2-3	126 - 199	7.8	66	0.9	7.1	20.6	0.4	285.0	2.4	0.9	<0.1	58	397
ATK 4-13	161 - 340	7.9	39	0.9	3.8	51	0.4	73	109	43.1	0.5	<6	332
ATK 5-6	382 - 407	7.3	101	2.4	2.8	82	1.2	16	149	199	1.3	40	558
-775-3	775 - 1274	4.9	3300	5.1	7.8	450	78.0	3.0	38.4	6100	36.1	67	10030
ATK 6-6-13	150 - 350	6.7	15	1.5	2.6	24.1	0.03	75.0	11.9	6.4	<0.1	20	171
ATK 7-4-41	365 -580	6.3	280	3.2	2.0	138	3.7	4.0	490	170	2.8	43	1034
-3-42	580 - 780	6.7	460	3.1	1.2	160	7.9	16.0	700	430	4.1	34	1685
-2-48	780 - 963	7.0	350	3.3	1.4	94	4.7	10.0	500	271	3.2	15	1315
ATK 8-1	0 - 716	8.2	23	3.6	2.8	8.9	0.1	60	33.6	5.2	0.2	44	-
8A-2	0 - 137	6.3	13	2.6	3.8	5.2	<0.05	66	2.0	0.9	<0.1	68	106
8A-5	0 - 137	7.6	14	2.6	3.7	5.6	<0.7	68	3.0	1.4	<0.1	24	100
8B-2	137 - 716	7.2	407	1.6	2.2	110.0	6.5	7	890.0	196.0	2.8	7	1628
LK 4	21 - 88	8.4	11	2.0	4.6	20.8	0.1	98.0	9.6	0.7	<0.1	52	154
LK 5	19 - 20	7.3	8	1.8	3.4	3.6	<0.03	55.0	0.9	0.7	<0.1	76	83
ML 9-1	45 - BOH	7.4	23	1.1	5.4	6.4	0.16	114.0	4.6	0.6	<0.1	43	173
-2	33.5 - 44.1	7.7	17	2.3	4.4	7.6	<0.03	110.0	3.8	0.4	<0.1	<6	154
-3	24 - 32.6	7.9	19	1.4	4.8	4.3	<0.03	108.0	4.2	0.3	<0.1	71	151
-4	14 - 23.1	7.2	14	1.8	4.1	3.8	<0.03	87.0	4.6	0.3	<0.1	71	125
-5	7.5 - 13.1	6.6	5	1.5	2.2	8.4	<0.03	49.0	12.8	1.4	<0.1	74	91
-6-OB1	0 - 6.6	6.6	4	1.3	12.8	2.9	<0.03	41.0	4.6	0.4	<0.1	59	70
ML 12-2	39.0 - 47.1	7.9	16	1.4	7.0	27.0	0.05	142	9.3	0.8	<0.1	<6	216
-3	27.5 - 38.1	7.9	11	1.4	5.7	16.7	<0.03	116	7.6	1.0	<0.1	-	168
-4	14.5 - 26.6	7.9	14	2.4	7.4	13.6	<0.03	122	6.4	0.9	<0.1	18	176
-5	8.5 - 13.6	7.6	14	2.6	4.9	5.4	<0.03	92	5.2	0.9	<0.1	-	136
-OB1	0 - 7.6	7.3	11	1.4	3.6	8.9	<0.03	94	2.8	1.0	<0.1	17	135

- all concentrations are in mg/L
- data released by Mel Gascoyne, AECL

APPENDIX SIX

Rb Content of ATK Groundwaters

Sample No.	[Rb] ppb
ATK 1-760	291.8
1-1089	140.9
ATK 5-6	6.8
5-775-3	10.1
ATK 7-2-48	16.2
7-4-41	23.8
7-3-42	18.5
ATK 2-3	4.5
ATK 4-13	4.0
ATK 6-6-13	6.1
ATK 8-1	6.5
8A-2	4.3
8A-5	4.2
8B-2	27.0
LK 4	5.0
LK 5	28.9
ML 9-1	17.7
9-2	10.5
9-3	3.7
9-4	4.1
9-5	26.5
9-6	6.6
ML 12-0B1	6.4
12-2	21.1
12-3	3.4
12-4	4.0
12-5	3.8