

AN O<sup>18</sup>/O<sup>16</sup> STUDY OF WATER FLOW  
IN NATURAL SNOW

by

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## Abstract

One of the most successful applications of oxygen isotope variations in nature has been their use in glaciology. Yearly isotopic variations in snowfall provide a means of determining past climatological trends from deep ice cores. The most notable example of this type of application would be the Greenland Ice Core discussed by Dansgaard et al. (1969).

When utilizing variations in stable isotope ratios as an indication of past climates two fundamental assumptions must be made. First, it is assumed that the isotopic ratio of precipitation falling in the area varies in some regular manner with a period of one year. The second assumption is that the isotopic composition of the snow does not change after it accumulates on the ground.

This thesis project was an attempt to study the interaction between the liquid and solid phases of water inside naturally occurring snow. One of the most reasonable methods of studying this interaction is by studying isotopic changes inside the snowpack when liquid water with an  $O^{18}/O^{16}$  ratio much greater than the snowpack is uniformly distributed on top of the snow.

It was found that water flow in several different types of sub-zero snow could be described quite satisfactorily in terms of isotopic, density and temperature variations. It was further concluded that accurate qualitative descriptions of flow would be extremely difficult without the isotopic

information.

The most unique result of this thesis project was the discovery that isotopic patterns in cold snow seemed to be manifestations of earlier water movement. That is to say, movement of the tracer through the snow tended to enhance the original isotopic pattern of the snow. The positions of the isotopic maxima and minima could usually be explained in terms of density variations.

The above result has definite implications for the use of oxygen isotope variations for the determination of past climates from ice cores. If liquid water, either from rain or surface melting, is present in the snowpack at any time we must conclude that isotopic variations may be introduced into the snowpack that are not related to climatological factors. Isotopic dating of such cores would obviously be in error. The conclusion reached by many researchers that liquid water movement inside a snowpack will tend to homogenize the snow isotopically does not seem to apply to sub-zero snowpacks.

In addition to the field project discussed above, this thesis presents a comprehensive description of the instrumentation and techniques used to measure the isotopic compositions of water samples with a precision of fourteen parts in one hundred thousand. A complete analysis of the exchange of oxygen isotopes between water and carbon dioxide is presented. A determination of factors that can introduce errors into the analysis of water samples is also given. It



is somewhat surprising that the non-zero voltage coefficients of resistance for the Victoreen Hi-meg resistors can be a major source of error in the analyses.

## TABLE OF CONTENTS

Abstract .....	i
Table Of Contents .....	iv
List Of Tables .....	vii
List Of Figures .....	viii
Acknowledgments .....	x
I. Introduction And Background .....	1
1.1 A Review Of Previous Isotopic Work On Glaciers And Snow .....	1
1.2 General Techniques Of Measuring The $O^{18}/O^{16}$ Ratio In A Water Sample .....	5
1.3 Motivations Of This Study .....	8
II. The Dual Beam Mass Spectrometer .....	10
2.1 General Features .....	10
2.2 The Dual Collector Assembly .....	13
2.3 The Measuring System .....	16
2.4 The Sample Inlet System .....	26
III. Experimental Technique Of Determining Del .....	35
3.1 Laboratory Procedures .....	35
3.1.1 Sample Preparation .....	35
3.1.2 The Equilibration Of Water And Carbon Dioxide .....	39
3.1.3 The Mass Spectrometer Analysis Of A Carbon Dioxide Sample .....	51
3.2 Correction Factors Applied To Mass Spectrometer Analyses .....	58
3.2.1 Switching Correction .....	60

3.2.2	Tank Carbon Dioxide Correction .....	63
3.2.3	Linear Correction To Force Agreement With World Standards .....	66
3.2.4	Corrections That Were Not Applied To These Data .....	73
IV.	Sources Of Error In Determining $O^{18}/O^{16}$ Ratios ...	77
4.1	Multiple Regression Analysis Of Mass Spectrometer Parameters .....	77
4.2	Equality Of Mass 46 Peak Heights .....	82
4.3	Sources Of Error In The Equilibration Of Water With Carbon Dioxide .....	85
4.4	Isotopic Fractionation Of A Carbon Dioxide Sample During Sample Preparation .....	87
4.5	Analytical Precision Of Analyses .....	90
V.	An Isotopic Study Of Water Flow In Natural Snow ...	95
5.1	Introduction .....	95
5.2	The Type Of Snowpacks Studied .....	98
5.3	Snowpack Parameters Measured .....	99
5.4	Experimental Procedure .....	100
5.5	Uncertainties In Sampling Technique .....	103
5.6	Difficulties Encountered And Disadvantages In Stable Isotope Methods In Snow Hydrology .....	106
VI.	The Isotopic Tracing Of Water Movement In Snow ...	109
6.1	Introduction .....	109
6.2	Tracing Experiment---P1 .....	110
6.3	Isotopic Tracing Experiment---T1 .....	118
6.4	Isotopic Tracing Experiment---T2 .....	123

6.5	Isotopic Tracing Experiment---T3 .....	126
6.6	Isotopic Tracing Experiment---PL2 .....	130
6.7	Isotopic Tracing Experiment---PL3 .....	136
6.8	Isotopic And Mass Balance In The Artificial Tracing Experiments .....	141
6.9	Conclusions .....	144
	List Of Works Consulted .....	147
	Appendix I-Property Of The DEL Function-Combination ...	155
	Appendix II- Property Of The DEL Function-Inversion ...	156
	Appendix III-Isotopic Mixing Of Two Water Samples .....	157
	Appendix IV-Isotopic Fractionation And Rayleigh Distillation .....	159
	Appendix V-Determination Of A "Best" Weighting Function .....	162
	Appendix VI-Property Of The DEL Function-Error Propagation .....	164

## LIST OF TABLES

3.1	Data Comparing Two Methods Of Sample Analysis .....	58
3.2	The Precision Of Two Methods Of Sample Analysis ..	59
3.3	Data Used To Check The Linearity Of Analyses .....	68
3.4	World Average Values Of Water Standards .....	70
3.5	U.B.C. Measurements Of The Water Standards .....	70
3.6	Machine Corrected Del Values Of World Standards ..	72
4.1	Results Of Regression Analysis .....	81
4.2	Error In DEL Caused By A Difference In Mass 46 Peak Heights .....	84
4.3	Gauge Reading VS Rayleigh Error In Del .....	90
4.4	Summary Of Errors Involved In Measuring Water Samples .....	93
5.1	Lateral Homogeneity In A Representative Snowpack .	105
6.1	Summary Of Data---P1 .....	112
6.2	Summary Of Data---T1 .....	120
6.3	Summary Of Data---T2 .....	124
6.4	Summary Of Data---T3 .....	128
6.5	Summary Of Data---PL2 .....	132
6.6	Summary Of Data---PL3 .....	138
6.7	Conservation Of Mass Considerations For Five Tracing Experiments .....	143
6.8	Isotopic Conservation In Tracing Experiments .....	144

## LIST OF FIGURES

2.1	Dual Collector System .....	14
2.2	Mass Spectrometer Measuring System .....	18
2.3	Block Diagram Showing Effect Of Gain And Offsets .	21
2.4	Determination Of Calibration Constant K .....	23
2.5	The Sample Introduction System .....	27
2.6	The Back Diffusion Problem .....	29
2.7	The Volume Rate Of Flow Into The Mass Spectrometer .....	31
2.8	The Operation Of The Magnetic Valves .....	33
3.1	Sample Flasks And Sample Tubes Used In This Study	36
3.2	The Sample Preparation Line .....	37
3.3	The Proposed Model For Water And Carbon Dioxide Equilibration .....	41
3.4	The Equilibration Of A Carbon Dioxide Sample .....	46
3.5	Equilibration Time For Samples Of Various Compositions .....	48
3.6	The Cubic Splines For A Typical Analysis .....	56
3.7	The Observed Switching Transient .....	60
3.8	The Linearity Of Isotopic Analyses Based On A Mixing Experiment .....	69
3.9	Electrical Analogue Of Magnetic Valves Of Inlet System .....	75
4.1	The Effect Of Peak Matching On The DEL Value Obtained .....	84
6.1	Sample Positions And Stratigraphic Features In Pit P1 .....	111

6.2	Isotopic Changes With Time Of Two Snow Layers .....	113
6.3	Isotopic Profile Of Pit In Experiment P1 .....	114
6.4	Variation Of Density With Depth---T1 .....	121
6.5	Isotopic Composition As A Function Of Depth---T1 .....	121
6.6	The Correlation Between Isotopic And Density Changes---T1 .....	122
6.7	Isotopic Composition As A Function Of Depth---T2 .....	125
6.8	Density AS A Function Of Depth---T2 .....	125
6.9	The Correlation Between Isotopic And Density Changes---T2 .....	126
6.10	The Variation Of Density With Depth---T3 .....	129
6.11	Isotopic Variations With Depth---T3 .....	129
6.12	Positions Of Samples Taken In Tracing Experiment PL2 .....	131
6.13	Temperature Profile For Experiment PL2 .....	133
6.14	Density Variations With Depth---PL2 .....	133
6.15	Isotopic Variations With Depth---PL2 .....	134
6.16	Correlation Between Isotopic Changes And Density Changes---PL2 .....	135
6.17	Snow Stratigraphy And Sample Location---PL3 .....	136
6.18	Isotopic Composition As A Function Of Depth---PL3 .....	139
6.19	Density Variations AS A Function Of Depth---PL3 .....	139
6.20	The Correlation Between Isotopic And Density Changes---PL3 .....	140
6.21	The Physical Model Used In The Study Of Water Flow .....	142

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## I. INTRODUCTION AND BACKGROUND

### 1.1 A Review Of Previous Isotopic Work On Glaciers And Snow

During the past fifteen years many researchers have studied the isotopic composition of polar glaciers, temperate glaciers and snow. Initial investigations by Dansgaard (1961), Epstein and Sharp (1967), Epstein Sharp and Gow (1965), and Merlivat et al. (1967b) were restricted to polar regions where the complicating effects of percolating water and ablation were minimized. They were thus able to identify a periodic variation in the ice cores preserved in the ice as changes in the isotopic composition. They were also able to find a direct correlation between the deuterium/hydrogen ratios ( $D/H$ ) and oxygen-18/oxygen-16 ratios ( $O^{18}/O^{16}$ ). In addition, some empirical evidence was found regarding the expected theoretical variation of isotopic ratios with altitude.

The work being done on temperate glaciers is still in a formative stage. Epstein and Sharp (1959), Sharp et al. (1960), Macpherson and Krouse (1967), Arnason (1969b), Ambach et al. (1971) and West (1972) are only a few who have studied the ice and snow from temperate glaciers in North America and Europe and, as expected, have found the isotopic data much harder to interpret than similar data from polar glaciers. According to these authors the great variation in

the winter layers of snow caused by the varying isotopic composition of the precipitation tends to be reduced as melting proceeds. The conclusion of these researchers was that as the melting process progressed, the glacier tended to become homogenized by the capture of freezing rain and snow in crevasses on the glacier surface. Sharp et al. (1960) also speculated that some of the homogenization was due to the existence of water trapped in the snow layers. As expected there was noticeable enrichment of oxygen-18 in the ice as the melting season progressed because the liquid phase, and thus the effluent, would be enriched in the lighter isotope. In these studies isotopic exchange between the liquid and solid phases of the water was neglected. Arnason (1969b) and Buason (1972) have since shown that this exchange should not be neglected in the case of hydrogen isotopes in temperate glaciers.

Isotopic methods applied to snow present even more difficulties than studies on the ice of temperate glaciers. Nevertheless, the importance of understanding the hydrological principles governing water storage and runoff has prompted several researchers to use isotopic data for studies of natural snow. Gonfiantini and Picciotto (1959) were among the first to study oxygen isotope variations in the polar regions. Deutsch et al. (1966) have used oxygen isotopes to determine net accumulation rates of snow on an alpine glacier using the distinct "isotopic seasons" encountered. They found poor correlation between analyses

of isotopic data of yearly accumulation rates when compared to stratigraphic studies, which normally form the basis of such investigations. This is in agreement with Gonfiantini et al. (1963) who concluded that snowpack metamorphism destroys yearly features in the stratigraphic sense. For this reason the yearly isotopic variation described by Epstein and Sharp (1967) is a more reliable indicator of accumulation rates. Dincer et al. (1970a) and Dincer et al. (1970b) used tritium and oxygen-18 analyses to calculate the ratio of the subsurface runoff to the total runoff from a snowpack with the constraint of conservation of isotopic species. They also studied the maturation process of a "typical" snowpack and have observed that percolation tends to homogenize the pack isotopically.

The final conclusion reached above is important. It implies that the most damaging effect that liquid water movement can have on a snowpack is the removal of the isotopic record. This is not what was found in the present study at all. This researcher has found that distinct isotopic variations can actually be caused by water movement and at times the original isotopic profile can even be enhanced. This of course means that isotopic peaks that were introduced by the percolation of water might be identified as a yearly isotopic peak and introduce errors in the interpretation of such data.

The project that is most closely associated with this study is that of Krouse and Smith (1972). Working in the

snowpacks of the Sierra Nevadas they were able to trace the movement of water in the snowpack with a profiling density gauge and isotopic analyses of representative samples. By introducing isotopic analyses into their study, Krouse and Smith were able to identify the source of water that existed at various levels in the snowpack. The ability to determine the origin of liquid water inside the snowpack seemed so important that an intensive study of water-snow interaction within a snowpack seemed desirable. Krouse and Smith used natural isotopic variations in the rain as the primary source of liquid water. In the present study all experiments were done with an artificial tracer of distilled seawater. Many different types of snow were studied in an effort to see if conclusions about water movement in snow hold true for various types of snow. It was found that the water flow within a specific snowpack was explainable using only density measurements, isotopic measurements and on some occasions temperature variations. Conclusions were finally made about water flow in very cold snowpacks but it is believed that careful measurements of many parameters are necessary to characterize the snow before conclusions can be stated with a high degree of confidence for isothermal snowpacks.

## 1.2 General Techniques Of Measuring The $O^{18}/O^{16}$ Ratio In A Water Sample

Water vapor itself is unsuitable for introduction into a mass spectrometer because of the long time required to pump it out on completion of the analysis. For this reason carbon dioxide is equilibrated with the water sample under investigation, as described by Epstein and Mayeda (1953). Carbon dioxide is readily analyzed in a mass spectrometer and from its isotopic composition the isotopic composition of the water sample can be determined.

It is difficult to measure absolute isotopic abundances with great precision. However, the difference in composition between two samples can be determined with a precision of better than two parts in ten thousand. For this reason, results of isotopic studies of oxygen are generally reported in terms of a DEL scale as follows:

$$\text{DEL}(X/S) = (R_X/R_S - 1) 10^3 \quad [1.1]$$

where  $R_X$  and  $R_S$  refer to the ratios of the intensities of the mass 46 and mass 44 ion beams for the carbon dioxide equilibrated with the unknown water sample and the standard carbon dioxide, respectively. The symbol 46/44 will be used in this thesis to refer to the ratio of the ion beam currents at mass 46 and mass 44. As shown by Epstein (1959), the DEL value thus obtained is the same as the DEL value obtained by direct measurement of the  $O^{18}/O^{16}$  ratio in the water sample.

The properties of the DEL function are subtle. For

instance, if a DEL value was measured relative to standard A and it was required to know the DEL value relative to another standard, standard B, the following relationship can be used:

$$\text{DEL}(X/B) = \text{DEL}(X/A) + \text{DEL}(A/B) + \text{DEL}(X/A)\text{DEL}(A/B)/10^3 \quad [1.2]$$

As another example, if one had the value of DEL(A/B) but needed the value of DEL(B/A) the following relationship is used:

$$\text{DEL}(B/A) = -\text{DEL}(A/B) \cdot 10^3 / [\text{DEL}(A/B) + 10^3] \quad [1.3]$$

Many other features of the DEL function exist and those pertinent to this study are derived in Appendices I, II, III and VI. The standard normally used in isotopic studies of oxygen in water samples is "Standard Mean Ocean Water" (SMOW) as defined by Craig (1961a). In fact no true samples of SMOW exist and so the International Atomic Energy Agency has distributed a standard referred to as IAEA SMOW which has a DEL value quite close to SMOW. The reference standard used in calculating all DEL values in this project was IAEA SMOW. By Craig's definition of SMOW it has an  $O^{18}/O^{16}$  ratio that is 1.008 times the  $O^{18}/O^{16}$  ratio of NBS1, another common laboratory standard. Many laboratories throughout the world have measured the value of NBS1 relative to IAEA SMOW and on the basis of these measurements the average value obtained for DEL(NBS1/IAEA SMOW) is -7.86. By using equations 1.2 and 1.3 and the average value of DEL(NBS1/IAEA SMOW) the following result is obtained.

$$\text{DEL}(\text{IAEA SMOW}/\text{SMOW}) = -0.08 \quad [1.4]$$

Measurements made relative to IAEA SNOW can easily be expressed relative to SNOW by using equations 1.2 and 1.4. It should be noted that the difference between these two standards is smaller than the present analytical precision of analyses made at most laboratories.

It is difficult to maintain constant operating conditions for a mass spectrometer and so if the unknown sample and the reference standard are measured at different times the resulting DEL will be in error. For this reason carbon dioxide that has been equilibrated with the unknown sample and carbon dioxide that serves as a working standard are admitted alternately into the mass spectrometer. The 46/44 ratio of the unknown is measured for a given period of time, then magnetic valves are switched and the working standard is analyzed for the same period of time. This process is repeated several times and in so doing any changes in the mass spectrometer will have less effect in the calculated DEL value.

Mass spectrometers used to measure oxygen isotope ratios are usually based on the design of A.O. Nier (1947). Modifications to this basic design are usually those proposed by McKinney et al. (1950) and Nier et al. (1947) which enable small differences in the 46/44 ratio to be measured. The essential features of such mass spectrometers are: a sample inlet system capable of alternately introducing small aliquots of unknown samples and working standard to the source region of the mass spectrometer; a

source capable of ionizing the carbon dioxide and accelerating the ions through several thousand volts; a magnetic analyzer, usually a 60° or 90° sector field electromagnet which separates the mass 46 and 44 ion beams; and a dual collector arrangement from which the ion currents can be used to determine the 46/44 ratio of the carbon dioxide. Specific features of the mass spectrometer used in this project are described in Chapter II.

### 1.3 Motivations Of This Study

The conversion of a mass spectrometer from one capable of analyzing lead tetramethyl to one capable of measuring oxygen isotope ratios in a sample of carbon dioxide was begun in the summer of 1972 under the direction of Dr. G.P. Erickson working on a temporary summer appointment. The system became operational in the spring of 1973. A great deal of testing and developing of procedures was required to reduce analytical uncertainties to an acceptable level. Much of the work of this project was to develop and analyze these procedures.

The more interesting portion of this thesis project was the field project originally proposed by Dr. Ken West. The investigations of Krouse and Smith had demonstrated the usefulness of stable isotopes in snow hydrology and Dr. West proposed an intensive study of the interaction between the liquid and solid phases of water in snowpacks. Surprisingly little had already been done in terms of an



artificial tracing experiment and so it was felt the information gained from such a project would be most useful to researchers utilizing more conventional methods in snow hydrology.

Chapter II deals with the actual changes made in the McKinney-Nier mass spectrometer used in this study. The use of inexpensive parametric amplifiers to replace conventional vibrating reed electrometers in the measuring system is described in detail. Chapter III deals with the actual technique of measuring the isotopic ratios of a water sample and would be useful to persons interested in how the DEL values are actually obtained in any study. The fourth chapter deals with possible sources of error existing in the isotopic analysis of water samples. Chapters V and VI deal with the results of the field experiment and have definite implications for studies in snow hydrology. Some entirely new concepts have been presented in this study and anyone using stable isotopes as a tool in studying water-snow or water-ice systems may find them useful.

## II. THE DUAL BEAM MASS SPECTROMETER

### 2.1 General Features

The mass spectrometer used in this study was designed and constructed by F. Kollar and R.D. Russell (Kollar, 1960) for the precise measurement of lead isotope ratios. It is essentially a McKinney-Nier mass spectrometer (Nier, 1947; McKinney et al. 1950; Nier et al. 1947) with some source modifications as described by Kollar and collector modifications made by the author with assistance from R.D. Russell. The deflection plates described by Kollar are normally grounded except when beam deflection is required to zero amplifiers in the measuring system. Electronic supplies are those described by Russell and Bellis (1971). A general discussion of the collector region and the associated measuring system is described by Russell and Ahern (1974) and in greater detail in this thesis. Some of the specific details of the machine are: a 90 degree sector magnet; 12 inch radius of curvature; source exit slit of 0.004 inches; collector slit widths of 0.070 inches and 0.140 inches for the beams of mass to charge ratio of 46 and 44 respectively; tungsten ribbon filament; accelerating potential variable from 1.5 kV to 5.0 kV; two Faraday cups that are "leakproof" from the point of view of the ion beams and secondary electrons; and a gas sample introduction system that is capable of allowing alternate admission of standard and unknown carbon dioxide samples to the source

region of the mass spectrometer (Nier, Ney, Inghram, 1947).

Since this mass spectrometer was initially used for measuring lead isotope ratios it has some properties that are superior to spectrometers with small radii of curvature. This is primarily its ability to resolve peaks so completely in the mass range 44 to 46. Using formulas derived in Duckworth (1958) the resolution of the mass spectrometer was found to be 157 for the 46 collector system and 82 for the 44 collector system. This means that the 44 collector is just able to separate mass 82 from mass 83 on the spectrogram. Since we are interested in collecting only the 46 and 44 ion beams this means that the beams are separated a substantial distance and the 45 beam can be eliminated by collision with the defining slits. The actual dispersion per unit mass at mass 46 is 0.261 inches and at mass 44 0.273 inches. With the elimination of the 45 beam the ratio we measure is directly proportional to the  $O^{18}/O^{16}$  ratio of the water if we make the first order approximation of neglecting ions of the form  $C^{13}O^{17}O^{16}$  and  $C^{12}O^{17}O^{17}$  flowing into the 46 cup and neglecting the loss of  $O^{18}$  atoms in molecules of the form  $C^{12}O^{18}O^{18}$ ,  $C^{12}O^{17}O^{18}$ ,  $C^{13}O^{16}O^{18}$ ,  $C^{13}O^{17}O^{18}$ ,  $C^{13}O^{18}O^{18}$  all of which are of low relative abundance. The above approximations introduce errors of less than the analytical uncertainty of the method and are justifiable. Since the 45 beam is not collected we do not make the corrections for  $C^{13}$  or for the 45 ion beam in the 44 collector, common in many laboratories.

The operation of the mass spectrometer during the data acquisition period is controlled by an Inderdata Model 4 computer (Blenkinsop, 1972; Russell et al. 1971). Analog signals proportional to the intensities of the ion beams in question are fed into a ratiometric digital voltmeter (RDVM). The Interdata computer reads several ratio estimates, performs digital filtering and passes back filtered data points to a teletype. After a specified period of time the computer switches two magnetic valves and analysis of the sample in the other side of the sample introduction system begins. This process is repeated until five data points exist for both the unknown sample and the working standard. Final data reduction was done by a Fortran IV program on the IBM 370 computer at the University of British Columbia.

Since most of the specific details of the mass spectrometer are found in the references above, it is sufficient to limit discussion to those modifications of the mass spectrometer made for the conversion from lead tetramethyl to stable isotope applications. The primary differences are in the collector assembly, the measuring system and the sample inlet system. Each of these will now be discussed in some detail.

## 2.2 The Dual Collector Assembly

The specific details of the collector assembly introduce two new practices to the mass spectrometry laboratory at UBC. These are:

1. The defining slits consist of two separate plates, one plate defining the y dimension of the ion beam and one plate defining the z dimension. The two plates forming the defining slits are physically separated in the collector assembly by a distance of 0.630 inches and this has caused no apparent complications in the operation of the mass spectrometer. The construction of the slits was found to be relatively simple when compared to previous methods of slit construction. Again the abundant resolution allowed this technique to be implemented.

2. The use of two parametric amplifiers (Philbrick Model 1702) for the first stage amplification of the ion beams enabled us to place the amplifiers inside the vacuum system thus eliminating the need to pass a high impedance lead into the vacuum system. Thus the signals are less susceptible to noise contamination than would otherwise be the case.

The specific construction of the collector region is shown in Figure 2.1. All collector slits are made of Nichrom V metal sheeting and milled to the specific dimensions by D. Schreiber of the Department of Geophysics and Astronomy. The y defining slit is held at a potential of +300 volts D.C. which prevents secondary electrons

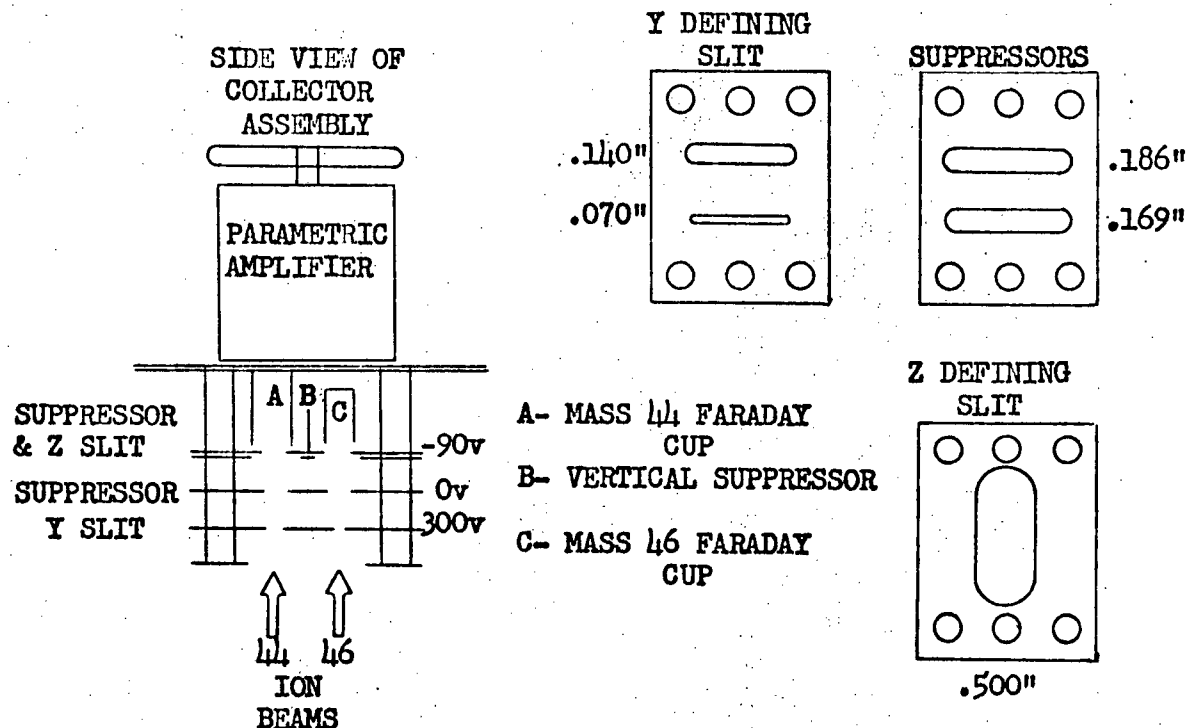


Figure 2.1 Dual Collector System

created by the collision of an ion beam with a slit edge from reaching the Faraday cups. The first suppressor is held at ground potential and serves as a mask that prevents the field on the y defining slit from influencing ion trajectories near the cups. The next combination of slits includes the z defining slit and a second suppressor. This combination is held at a potential of -90 volts D.C. and performs the task of preventing any secondary electrons created at the Faraday cups from escaping, and thus giving non-linear contributions to the ion beam currents. The two Faraday cups are situated approximately 0.05 inches immediately above the second suppressor and are separated by a vertical suppressor physically and electrically connected to the second suppressor. It was found that this suppressor

made it physically impossible for a scattered ion to enter the wrong collector. Since this suppressor was added it is felt that no serious problems can be attributed to secondary electrons. The Faraday cups are constructed from a single piece of Nichrome and the seams have been silver soldered to make them impermeable to ions. The two parametric amplifiers sit on a fiberglass circuit board through which all electrical connections are made. The mass 44 Faraday cup is attached by first spot welding a small piece of copper to the closed end and then soldering the combination to a copper plate on the bottom of the circuit board. Due to the larger feedback resistance in the 46 circuit more care was taken in this connection. A small hole was drilled through the center of the circuit board and a Teflon insulator placed in the hole. The 46 Faraday cup was then rigidly suspended from a 12 gauge Nichrome wire connected through the Teflon plug to the negative input of the 46 parametric amplifier. Leads to the circuit board and collector plates were insulated by putting Teflon tubing around the bare leads where possible. Connections were made with a wire wrapping tool. Use of solder was kept to a minimum. The Victoreen "hi-Meg" resistors were supported by a metal spring assembly attached to the tops of the parametric amplifiers using Araldite epoxy.

At the present time neither the 44 or 46 ion beams are focussed on the defining slits. Plans have been made to correct this in the near future. The apparatus has proven

to be satisfactory and no serious difficulties can be attributed to focal problems within the collector.

### 2.3 The Measuring System

When measuring oxygen isotopic ratios, one is confronted with the problem of converting ion beam currents in the neighborhood of one picoampere into manageable signals. This is usually accomplished by passing the current through a very high resistance in the feedback loop of an electrometer circuit. Such electrometers have typically been of the vibrating reed or vibrating capacitor type analyzed in detail by Palevsky et al. (1947). A vibrating capacitor electrometer has three favorable characteristics: it shifts the information to a more convenient frequency range; it can have an output impedance very much lower than the input impedance; and it has significant power gain. Excellence of such electrometers has prompted their application in many mass spectrometers throughout the world. Signal amplification and noise characteristics of such electrometers still set the standard in measuring systems for mass spectrometers.

An alternative approach to ion current measurement is that of the D.C. electrometer tubes described by Russell et al. (1964) and Stacey et al. (1965). They are characterized by a very high input impedance, a sufficiently short rise time to record the mass spectrum on a chart recorder, and relatively low noise. The main disadvantage of electrometer



tubes is their poor drift characteristics. Nevertheless the mass spectrometry laboratory at the University of British Columbia has used these amplifiers in mass spectrometers designed for measuring strontium isotope ratios and lead isotope ratios for fifteen years.

Within the past two years several manufacturers (including Teledyne-Philbrick and Analogic) have started producing parametric operational amplifiers. These amplifiers are small in size and are essentially the solid state equivalent of the vibrating reed electrometer. The effect of the mechanical vibrating reed is obtained by a varying potential distribution in a varactor diode. Thus the charge distribution can be modulated to effect a varying capacitance. If a constant or slowly varying charge exists on the modulated capacitance, a time-varying voltage results which can be amplified by a low noise A.C. amplifier. The output of this amplifier is then phase-sensitively demodulated to restore correct polarity and is then boosted by a conventional D.C. output stage. A more comprehensive description of a varactor bridge operational amplifier can be found in Analogic Devices Specification Sheet C016-50-1/69. For our purposes it is not necessary to understand the operation of the parametric amplifier but it is only necessary to take note of the important characteristics of such amplifiers. Two Teledyne-Philbrick parametric amplifiers model 1702 were used in the measuring system shown in Figure 2.2. The important characteristics

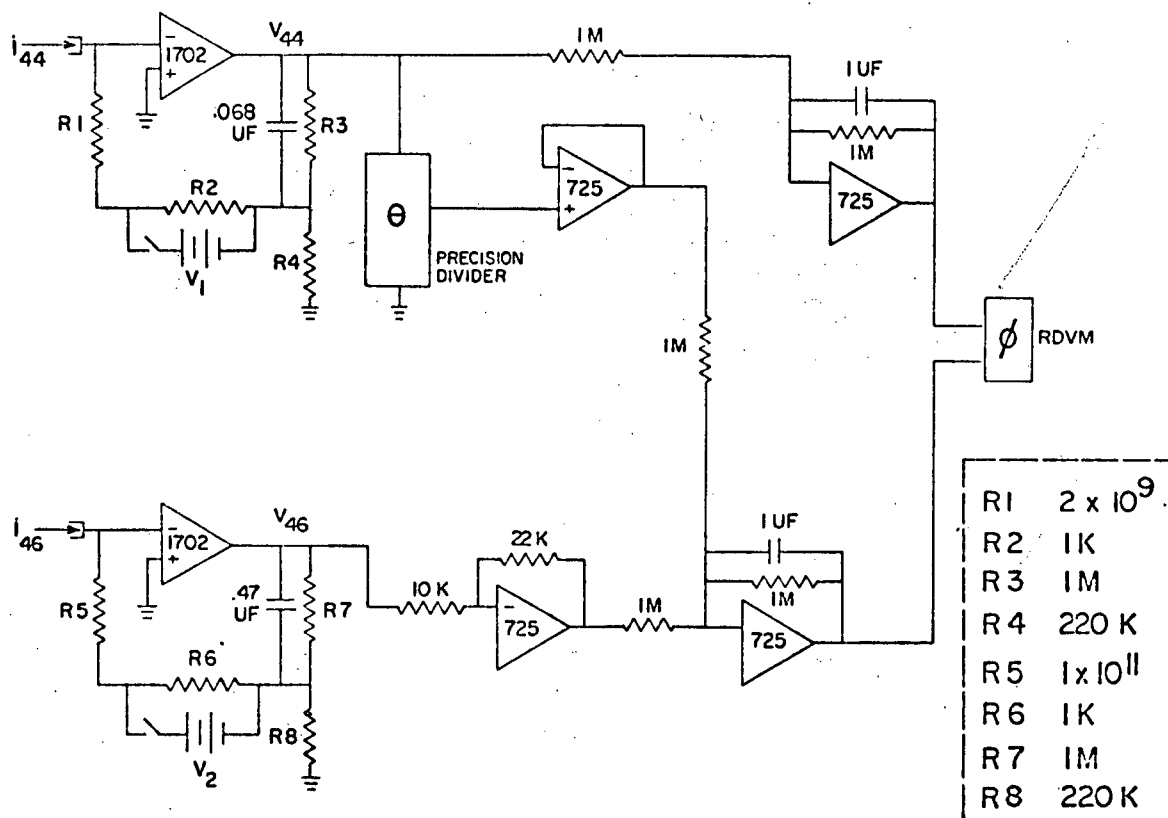


Figure 2.2 Mass Spectrometer Measuring System

of the Teledyne-Philbrick operational amplifiers are found in Teledyne-Philbrick Specification Sheet 12m 12-71 'Parametric Operational Amplifier 1702/170201'. Some of the most important characteristics are:

1. A minimum open loop voltage gain of  $10^5$ .
2. Maximum voltage offset without external trim 5 mV.
3. Maximum input bias current 5 fA.
4. A common mode input impedance of  $10^{14}$  ohms.

The low input bias current and high input impedance lend themselves quite well to picoampere current measurement. The basic features of the measuring system of Figure 2.2 are found in Russell and Ahern (1974). The treatment given there neglects zero offsets and this point warrants a more

complete analysis in this thesis as it is believed that offsets can be a significant source of error.

The D.C. circuit analysis given here will make the usual approximations that all the current flowing into the Faraday cup will flow through the feedback resistor, the input to each parametric amplifier is held at a virtual ground, and that the effect of all offsets can be represented by a constant voltage added to the output.

By using Kirchoff's laws and assuming all the ion current passes through the feedback resistors it is a straightforward calculation to show:

$$V_{44} = -V_1(1+R_3/R_4) - i_{44} (R_3 + R_1 R_3 / R_4 + R_2 R_3 / R_4 + R_1 + R_2) \quad [2.1]$$

and similarly

$$V_{44} = -V_2(1+R_7/R_8) - i_{46} (R_7 + R_5 R_7 / R_8 + R_6 R_7 / R_8 + R_5 + R_6) \quad [2.2]$$

where resistances and voltages are as shown in Figure 2.2.

In the actual circuit it has been found that amplifier offsets can be a significant source of error in the measured DEL value. For this reason it is important to understand how amplifier offsets affect the DEL value to be calculated. To a first approximation each amplifier can be represented by a black box that multiplies an input voltage by a gain ( $G_i$ ) and adds to that voltage some offset voltage ( $A_i$ ). By using the numbering convention given on Figure 2.2 the buffer amplifier following the precision divider will have gain  $G_5$  and offset  $A_5$ . With this notation the circuit analysis can be carried to the point where the relationship between the "true" DEL, assuming no measuring system

offsets, and the measured DEL can be obtained. Once this analysis is completed it becomes evident that a certain zeroing procedure will eliminate any errors due to amplifier offsets.

If we define P and Q as follows:

$$P = R_4 / (R_3 R_4 + R_1 R_3 + R_2 R_3 + R_1 R_4 + R_2 R_4) \quad [2.3]$$

$$Q = R_8 / (R_7 R_8 + R_5 R_8 + R_6 R_7 + R_5 R_8 + R_6 R_8) \quad [2.4]$$

and if we assume the amplifier test voltages V1 and V2 are zero, as is normally the case, then it is clear from Figure 2.3 the voltages given at the R.D.V.M. Will be:

$$E_{44} = -G_3 i_{44} / P + G_3 A_1 + A_3 \quad [2.5]$$

and

$$E_{46} = -G_4 G_6 i_{46} / Q + G_4 G_6 A_2 + G_6 A_4 - G_5 G_6 \theta i_{44} / P + G_5 G_6 \theta A_1 + G_6 A_5 + A_6 \quad [2.6]$$

where THETA is the reading of the precision divider. We can now solve equations 2.5 and 2.6 for the 44 and 46 ion beam currents:

$$i_{44} = (-E_{44} + G_3 A_1 + A_3) P / G_3 \quad [2.7]$$

$$i_{44} = \frac{(-E_{46} - G_5 G_6 \theta i_{44} / P + G_6 A_4 + G_4 G_6 A_2 + G_5 G_6 \theta A_1 + G_6 A_5 + A_6) Q}{G_4 G_6} \quad [2.8]$$

substituting equation 2.7 into 2.8 gives:

$$i_{46} = [-E_{46} - G_5 G_6 \theta (-E_{44} / G_3 + A_1 + A_3 / G_3) + G_4 G_6 A_2 + G_6 A_4 + G_5 G_6 \theta A_1 + G_6 A_5 + A_6] Q / G_4 G_6 \quad [2.9]$$

It is now clear that we can write an expression for the

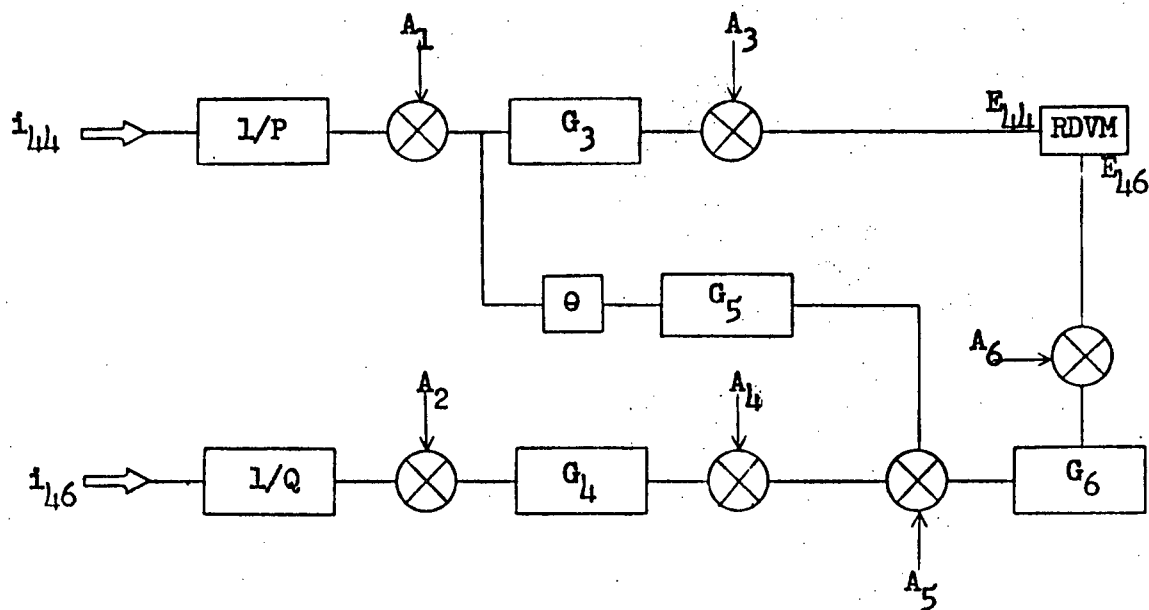


Figure 2.3 Block Diagram Showing Effect of Gain and Offsets

ratio of the 46 to 44 ion beam currents. By making the following definitions:

$$S = -G_5 G_6 \theta A_3 / G_3 + G_4 G_6 A_2 + G_6 A_4 + G_6 A_5 + A_6 \quad [2.10]$$

$$T = G_3 A_1 + A_3 \quad [2.11]$$

we find that:

$$R = i_{46} / i_{44} = Q G_3 / (P G_4 G_6) [E_{46} - G_5 G_6 \theta E_{44} / G_3 + S] / [E_{44} + T] \quad [2.12]$$

The RDVM produces a reading that is proportional to the true ratio of its inputs. That is:

$$\phi = U E_{46} / E_{44} \quad [2.13]$$

where  $\phi$  is the reading of the RDVM and  $U$  is a meter calibration constant. The validity of equation 2.13 was checked empirically by using a six digit precision divider and was shown to be valid to the most significant digit of the RDVM.

By using equations 1.1 and 2.12 we can now determine what the true DEL value is in terms of parameters we can measure. If we adopt the notation that parameters unique to the ratio appearing in the denominator of 1.1 will have a superscript "s" then the true DEL becomes:

$$\text{DEL}/10^3 = \frac{[(\phi - G_5 G_6 \theta U / G_3 + SU / E_{44}) / (1 + T / E_{44})]}{[(\phi^s - G_5 G_6 \theta U / G_3 + SU / E_{44}^s) / (1 + T / E_{44}^s)]} - 1 \quad [2.14]$$

At first this equation seems quite cumbersome to use but if we note equations 2.10 and 2.12 we find that a calibration constant K can be easily measured for the entire measuring system by just noting how PHI changes with a change in THETA for any fixed ratio.

$$d\phi/d\theta = K = G_5 G_6 U [1/G_3 - A_3 / (G_3 E_{44})] \quad [2.15]$$

since A3 can easily be set to zero before determination of K, equation 2.15 becomes:

$$K = G_5 G_6 U / G_3 \quad A_3 = 0 \quad [2.16]$$

One such determination of K is given in Figure 2.4. This and similar plots testify to the linearity of the measuring system. Rewriting equation 2.14 we obtain:

$$\text{DEL}/10^3 = \frac{[(\phi - K\theta + SU / E_{44}) / (1 + T / E_{44})]}{[(\phi^s - K\theta + SU / E_{44}^s) / (1 + T / E_{44}^s)]} - 1 \quad [2.17]$$

which involves only the approximation that A3=0.0 when K was determined.

In this form it now becomes evident how we may zero amplifiers before an analysis to make offset errors

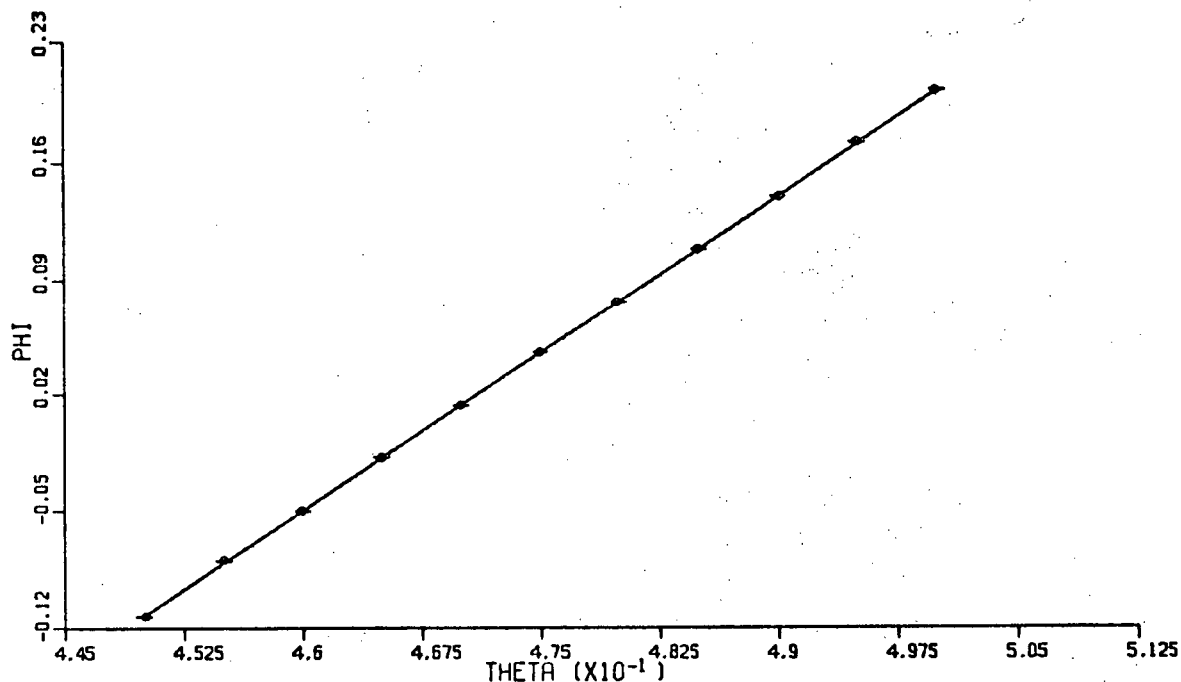


Figure 2.4 Determination of Calibration Constant  
K

insignificant in the calculation of DEL. By applying a sufficiently high voltage to the deflector plates in the source, ion beams can be deflected so that no current is flowing into the Faraday cups. By so doing the voltage at the 44 input to the RDVM given by equation 2.5 becomes:

$$E_{44} = G_3 A_1 + A_3$$

the voltage at the output of the two parametric amplifiers becomes:

$$V_{44} = A_1$$

$$V_{46} = A_2$$

From equation 2.6 the 46 input to the RDVM becomes:

$$E_{46} = G_6 (G_4 A_2 + A_4 + \theta G_5 A_1 + A_5) + A_6$$

The voltages at these four points ( $V^{44}, V^{46}, E^{44}, E^{46}$ ) are easily accessible and may be measured and nulled. If we first zero  $V^{44}$  then by definition  $A_1$  equals zero and  $E^{44}$

becomes equal to A3. If we now zero  $E^{44}$  both A1 and A3 are equal to zero and by equation 2.11 T is equal to zero. The next step is to zero the 46 parametric amplifier which makes A2 equal to zero. If next we zero  $E^{46}$  then we know from the above equation that:

$$E_{46} = G_6 A_4 + G_6 A_5 + A_6 = 0$$

Inserting this information into equation 2.10, remembering that A1, A2, and A3 are already zero, shows that S is now equal to zero.

With both S and T equal to zero equation 2.14 reduces to:

$$\text{DEL} = [(\phi - \phi^S) / (\phi^S - K\theta)] 10^3 \quad [2.18]$$

which is a simple formula easily applied since  $\phi$  is the RDVM reading when the unknown is being analyzed,  $\phi^S$  is the RDVM reading when the standard is being analyzed,  $\theta$  is the setting of the precision divider and K is found from equation 2.16.

In practice only A1 and A2 were set to zero before an analysis. Other offsets were periodically checked and were always less than 3 mV and thus introduced very small errors. Nevertheless, the simplicity of the zeroing procedure given above warrants its inclusion in future isotopic analyses.

The measuring system described has been used for the analysis of approximately seven hundred samples and only one severe drawback has been discovered. It is not uncommon for the parametric amplifiers used to have baseline



discontinuities of up to 15 mv in the 46 parametric amplifier and when this happens the resultant DEL can be in error by up to 0.3 DEL units. Such discontinuities are quite noticeable in the PHI values and such analyses are rerun immediately until an analysis free of gross discontinuities is obtained. This involves a great deal of time and so plans have been made to install a baseline compensation circuit in at least the 46 collector system. This has not yet been implemented.

The noise characteristics of this measuring system are controlled through analog filtering provided by amplifiers number three and number four. Further digital filtering is done by the Interdata Model 4 computer. The noise characteristics at the output of the parametric amplifiers is controlled primarily by the capacitors in parallel with resistors R3 and R7. The filtering thus provided is sufficient and no problems associated with noise in the measuring system are believed to exist.

The noise characteristics of the parametric amplifiers have been compared directly to a Carey Model No. 31 vibrating reed electrometer and a measuring system using the Analogic varactor bridge diode in a mass spectrometer used by Dr. P.H. Reynolds at Dalhousie University. It was found that the vibrating reed electrometer had an equivalent noise current of 1.31 femtoamperes. The Analogic varactor bridge diode had a noise current of 1.9 femtoamperes after much filtering. The Teledyne-Philbrick parametric amplifier had

a noise current of 3.6 femtoamperes. All of these were calculated with a  $10^{11}$  ohm feedback resistor and a time constant of 0.47 seconds. Such results seem quite satisfactory especially when relative costs are considered. The cost of a vibrating reed electrometer is approximately \$1500 for a total investment of about \$3000 for a complete measuring system. The measuring system of Figure 2.2 has a total cost of less than \$150 excluding the RDVM and labor costs.

#### 2.4 The Sample Inlet System

The sample introduction system in a gas source mass spectrometer must be capable of introducing representative aliquots of an unknown sample to the source region of the mass spectrometer. In a mass spectrometer designed to measure oxygen isotope ratios of a carbon dioxide sample it is also necessary that the sample introduction system be capable of alternately delivering samples of unknown and standard carbon dioxide.

The system shown in Figure 2.5 is a representation of the introduction system on the mass spectrometer used in this study. It consists of two complete inlet systems each featuring:

1. A 2-liter sample reservoir bulb.
2. Approximately 60 cm of 0.4 mm diameter capillary tubing.

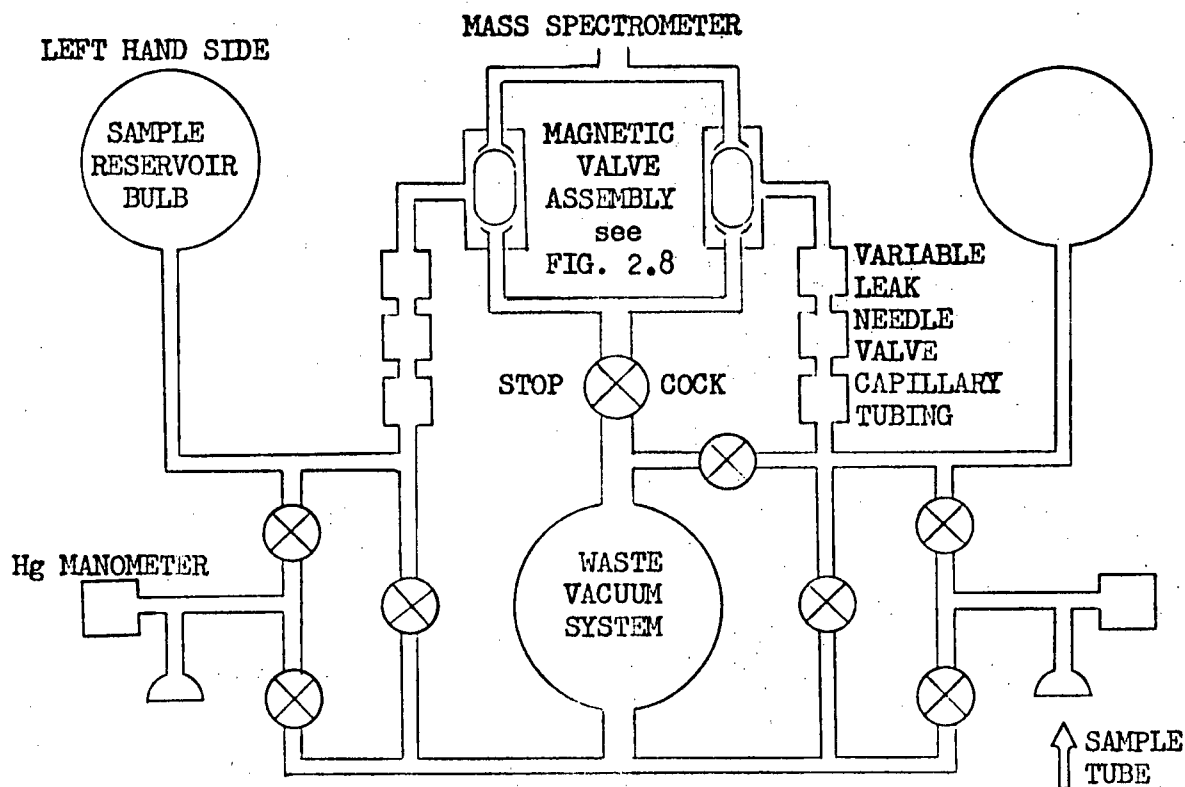


Figure 2.5 The Sample Introduction System

3. A set of magnetic valves which allow alternate analysis of standard and unknown carbon dioxide.

In addition the inlet system has an independent vacuum system allowing rapid removal and replacement of a new sample.

The 2-liter reservoir serves as a large volume containing the sample during the analysis. It should be of sufficient size so that the pressure on the high pressure side of the capillary does not change appreciably during the course of an analysis and thus alter the volume flow into the mass spectrometer. In addition to this it should be large enough to prevent significant changes in isotopic composition due to any fractionation of the sample.

The capillary tubing serves a very important function.

It prevents any compositional discontinuity at the leak itself from migrating as far as the sample reservoir. The importance of this feature cannot be over emphasized since it ensures that the isotopic ratio in the reservoir will not be altered by back diffusion. If flow through the inlet system toward the leak is viscous all molecular species of carbon dioxide (e.g.  $C^{12}O^{16}O^{18}$  and  $C^{12}O^{16}O^{16}$ ) will travel at the same velocity and therefore the isotopic composition will be uniform and constant in time. It is not uncommon to have molecular flow at the leak of a mass spectrometer. In this case the isotopic composition of the carbon dioxide passing through the molecular leak will be enriched in the lighter isotope. The result of this is that the region immediately before the leak will be enriched in the heavier isotope. It is intuitively obvious that if there is to be a steady state the isotopic ratio of the carbon dioxide leaving the molecular leak will equal the isotopic composition of the carbon dioxide in the reservoir. Since the 46/44 ratio of the carbon dioxide immediately behind the molecular leak is greater than the gas flowing into that region, a diffusion front will begin moving toward the reservoir. At some distance the diffusion front will become stationary due to the net mass flow towards the leak.

A steady state calculation, suggested by R.D. Russell, can be made for the location of the stationary diffusion front. By inserting measured values of the parameters, the length of the capillary tubing can be chosen so the

diffusion front occurs well within the length of the capillary and therefore never affects the isotopic ratio in the reservoir. The problem is described in Figure 2.6.

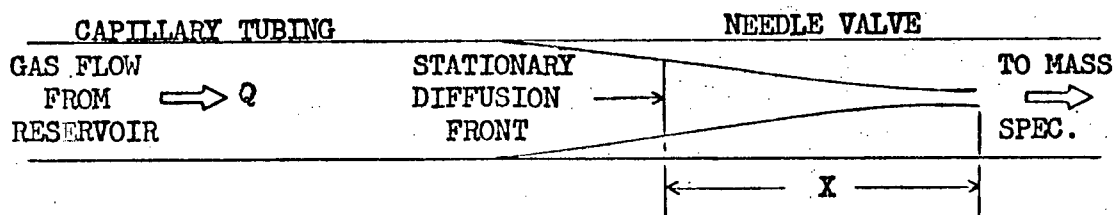


Figure 2.6 The Back Diffusion Problem

It was shown by Einstein (see for example Daniels and Alberty) that for a Brownian process the mean of the square of the displacements in a particular direction  $x$  is related to the diffusion coefficient  $D$  by:

$$D = \bar{x}^2 / (2t) \quad [2.20]$$

where  $t$  is the time taken to advance a distance  $x$ . From 2.20 it is clear that the velocity of the diffusion front is given by:

$$v = dx/dt = [D/2t]^{1/2} \quad [2.21]$$

Substituting 2.20 into 2.21 gives:

$$v = D/x \quad [2.22]$$

which is to say that the diffusion front moves toward the reservoir at a monotonically decreasing velocity. There is a net gas flow toward the leak which will exactly counteract the velocity of the diffusion front at some point. It is clear the velocity of the gas flow,  $c$ , is given by:

$$c = Q/A \quad [2.23]$$

where  $Q$  is the volume of gas flow past any given point per

second and  $A$  is the cross-sectional area of the capillary. To find the position of the stationary diffusion front the velocities given in 2.22 and 2.23 must be exactly equal and opposite in direction.

$$D/x = Q/A \quad [2.24]$$

$$x = DA/Q \quad [2.25]$$

Since the value of the diffusion coefficient is usually given at STP it is necessary to examine the dependence of  $D$  on pressure and temperature. It is commonly known (see Page, p. 351) that for self-diffusion of ideal gases:

$$D = \pi \mu s / 8 \quad [2.26]$$

where  $\mu$  is the mean free path and  $s$  is the average velocity of the molecule. It is also commonly known that:

$$\mu = kT / [\sqrt{2} \pi \sigma^2 p] \quad [2.27]$$

$$s = [(8kT)/(\pi m)]^{1/2} \quad [2.28]$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $\pi \sigma^2$  is the effective cross-sectional area of the molecule,  $P$  is the pressure of the gas in the system and  $m$  is the mass of the molecule.

From equations 2.26, 2.27 and 2.28 it is clear that:

$$D = D^0 (P^0/P) (T/T^0)^{3/2} \quad [2.29]$$

where the superscript  $^0$  represents values at STP. From the ideal gas law it is clear that:

$$Q = Q^0 (T/T^0) (P^0/P) \quad [2.30]$$

Substitution of 2.29 and 2.30 in equation 2.25 gives:

$$x = (D^0/Q^0)(T/T^0)^{\frac{1}{2}}A \quad [2.31]$$

where all parameters are now evaluated at STP.

The volume flow rate,  $Q$ , can be measured by noting the change in the pressure in the mass spectrometer as a function of time. Such a determination is shown graphically in Figure 2.7. From this figure we ascertain that 18.7% of

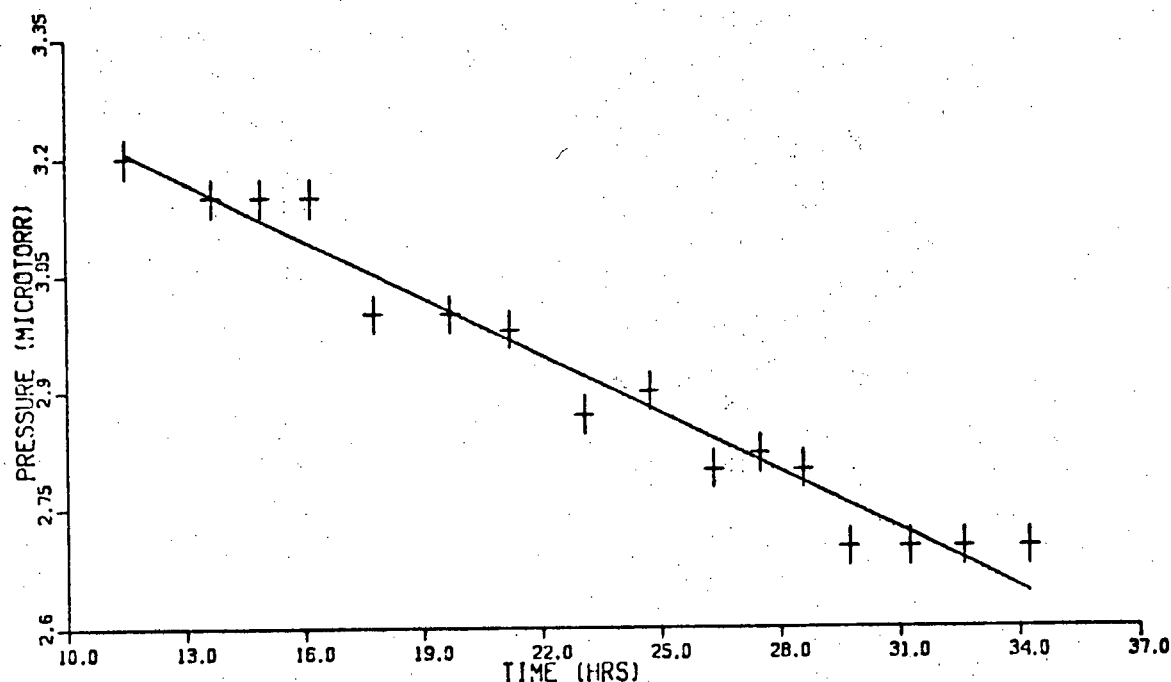


Figure 2.7 The Volume Rate of Flow into the Mass Spectrometer

the sample is consumed in 22 hours. Since the volume of the reservoir is 2.4 liters this corresponds to a volume flow equal to:

$$Q = 5.67 \times 10^{-3} \text{ cm}^3/\text{s}$$

with this information and noting that the sample line pressure equals 5 torr and  $T$  equals 295°K we can calculate  $Q^0$  from equation 2.30.

$$Q^0 = 4.03 \times 10^{-5} \text{ cm}^3/\text{s}$$

the diameter of the capillary tubing is 0.043 cm so

$$A = 1.45 \times 10^{-3} \text{ cm}^2.$$

The value of the diffusion coefficient of carbon dioxide diffusing into air was found in tables to be:

$$D = 0.139 \text{ cm}^2/\text{s}$$

The coefficient for self diffusion of carbon dioxide will be less than  $0.139 \text{ cm}^2/\text{s}$  and so the  $x$  calculated will be larger than the true  $x$ .

Inserting the above values into 2.31 gives:

$$x = 5.4 \text{ cm}$$

It is not known whether the leak used was viscous or molecular. The actual capillary tubing is approximately 60 cm long and so even if the leak is molecular the stationary diffusion front would occur well within the capillary. It has been observed empirically that the composition of the reservoir does not change with time (See Chapter IV).

Of course the diffusion front is not really a step function as assumed in the above calculation but instead a broader diffusion boundary. Calculations made by R.D. Russell from a numerical solution of the diffusion equation with net flow opposing the motion of the front give comparable results. More importantly such calculations show the validity of the assumption of stationarity of the front.

The magnetic valves (Figure 2.8) used in this inlet system are essentially the same as those proposed by McKinney et al. (1950) and Epstein (1953). The actual magnetic valves are available through Glass Instruments



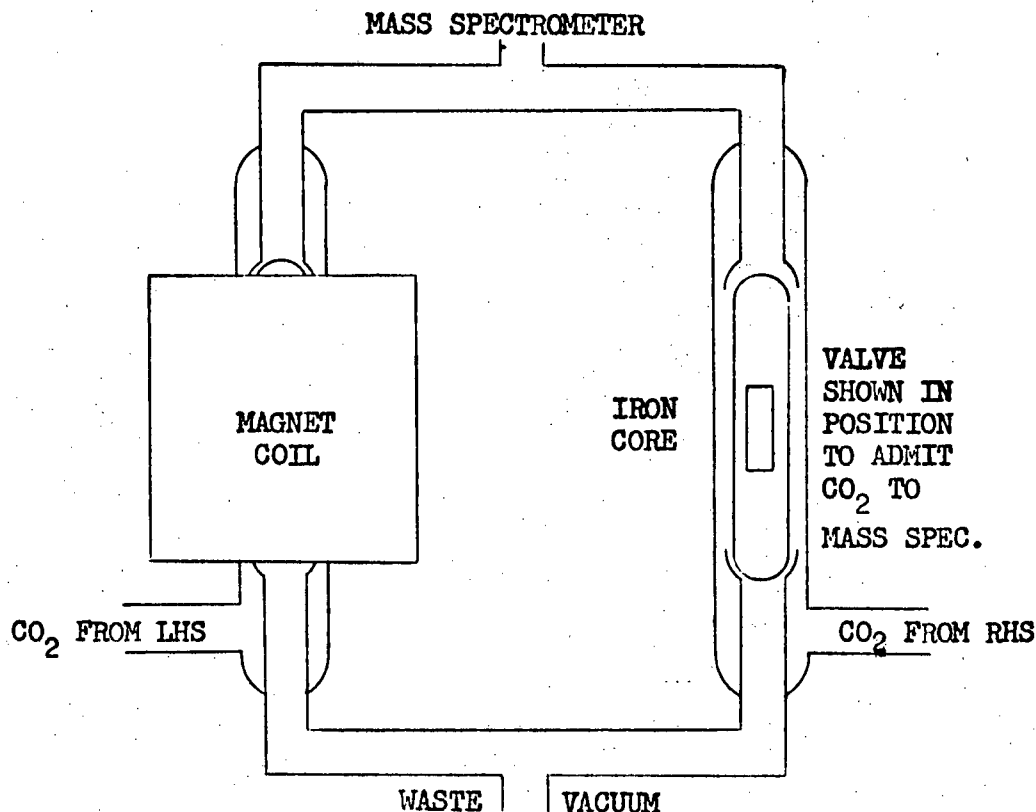


Figure 2.8 The Operation of the Magnetic Valves

Inc. Pasadena, California and have been found to be quite satisfactory. The small glass piston has an iron rod in its center so that it can be raised to divert gas flow into a waste vacuum system or lowered to allow gas flow into the mass spectrometer. The current flowing in the magnetic coils is such that when gas from one side of the sample inlet system is flowing into the mass spectrometer, gas from the other side is being pumped away.

The performance of similar magnetic valves has often been questioned as testified to by the presence of a valve mixing correction at many laboratories as indicated by Begbie et al. (1972). The adjustment is one that corrects for a "leaky" valve that allows a finite amount of gas to

pass when it is "closed". If this happens it is clear that a mixture of the two sides of the inlet system is being analyzed instead of only one side. Such corrections have not been found necessary with the magnetic valve system employed in this study. The validity of ever making such corrections will be examined in Chapter III.

### III. EXPERIMENTAL TECHNIQUE OF DETERMINING DEL

#### 3.1 Laboratory Procedures

Techniques for measuring oxygen isotope ratios vary considerably in laboratories around the world. Techniques must be developed at each laboratory for taking a water sample and determining its isotopic composition. The final test of the overall process is the reproducibility it yields. The procedure developed at the University of British Columbia has been shown to successfully reproduce measurements to 0.14 DEL units which is quite adequate for glaciological research. The analysis of a water sample involves two stages. The water sample must be equilibrated with carbon dioxide and the equilibrated carbon dioxide must be analyzed in the mass spectrometer.

##### 3.1.1 Sample Preparation

The sample preparation involves the equilibration of carbon dioxide with the water sample as described by Epstein and Mayeda (1953). Some major alterations have been made to their basic procedure and so a detailed description of the preparation is given here. Ten milliliters of water is loaded into a 60 ml Pyrex sample flask (see Figure 3.1a) through the sidearm. The acidity of the sample is checked at this time and if the pH of the sample is greater than 8 a

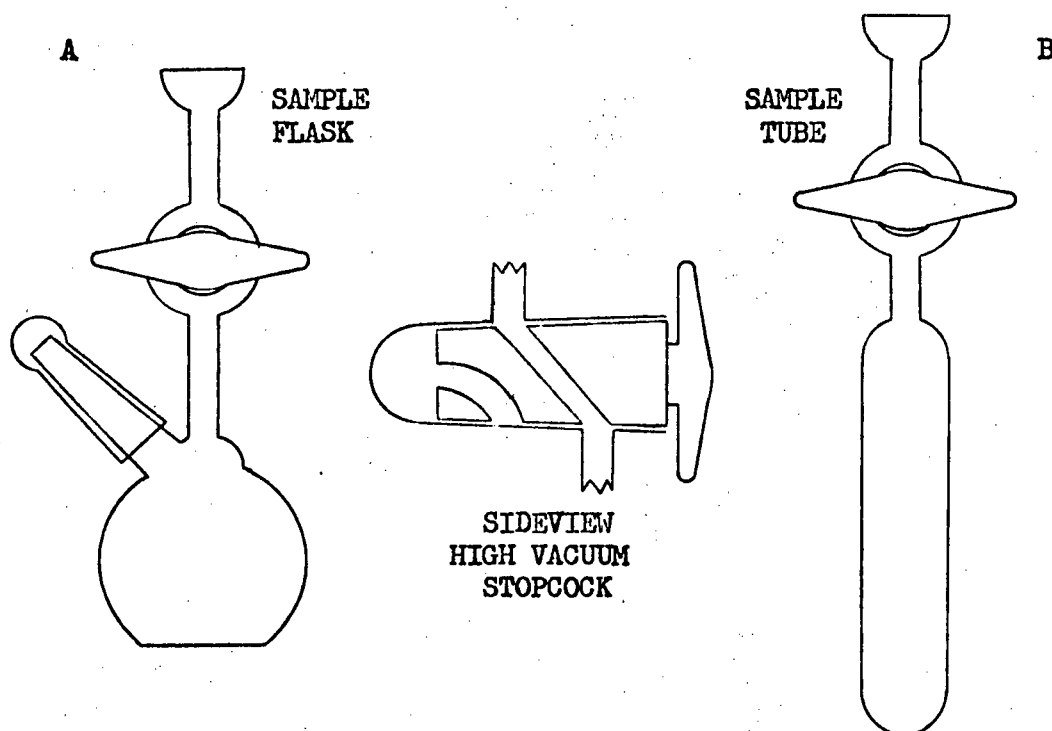


Figure 3.1 Sample Flasks and Sample Tubes Used in This Study

drop of nitric acid should be added to ensure rapid equilibration of the water and carbon dioxide as first noted by Faurholt (1924). In the water samples analyzed in this study the addition of nitric acid was never necessary. After being loaded, the sample flask is connected to the sample preparation line shown in Figure 3.2 using a Viton "O-ring" and a spring clamp. The interior of the high vacuum stopcock is then evacuated by the pumping system of the preparation line. To save time, seven to ten flasks are placed on the sample preparation line at the same time. Liquid nitrogen is then placed around each sample flask until the water samples are frozen, the stopcocks are opened and the air in the flasks is pumped away. After the stopcocks are closed the water samples are thawed with warm

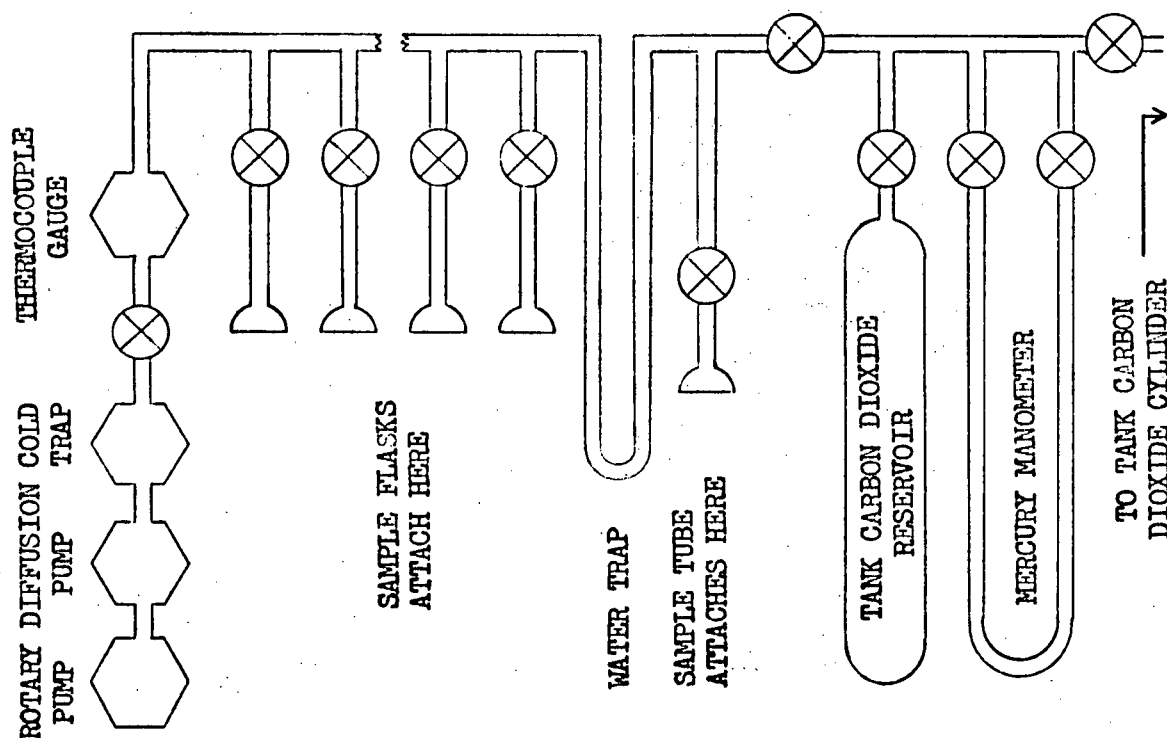


Figure 3.2 The Sample Preparation Line

water to remove any dissolved gases, primarily nitrogen and oxygen. The samples are then refrozen with liquid nitrogen and any remaining air is removed. The next step in the sample preparation is to allow the ice to melt and then to immerse the flasks in a mixture of dry ice and methanol, henceforth referred to as "slurry". The temperature of this mixture is 201°K which is sufficient to freeze water in the vacuum system but not carbon dioxide. After the water is completely frozen all stopcocks are opened and any carbon dioxide that was dissolved in the water samples is pumped away. A dewar of slurry is placed on the water trap and the mercury manometer is made ready for use by closing one stopcock. The connection to the vacuum system is then closed and carbon dioxide from the reservoir is transferred from the gas-pipet into the sample flasks to a pressure of

twenty centimeters mercury. The flask stopcocks are closed and the samples are placed in a constant temperature bath at  $25.3 \pm .1$  °C.

The equilibration of the carbon dioxide with the water is a process that has been studied in some detail. The reaction rate is not determined by the chemical reaction but is governed by the physical process of water transport from the bottom of the sample flask to the gas-liquid interface. This process will be discussed in detail in the next section. It is sufficient to say that after some period of time the isotopic composition of the carbon dioxide will reflect the composition of the water sample.

After the sample has been equilibrated, the sample flasks are taken from the bath and immediately placed in the slurry on the sample preparation line. After freezing no further equilibration takes place. The only step left in the sample preparation is the removal of the carbon dioxide from the sample flask and its transfer to a sample tube such as the one shown in Figure 3.1b. This is accomplished as follows. A dewar of slurry is placed on the water trap to ensure that only dry carbon dioxide is transferred to the sample tube. This step is important for two reasons; first, if any water vapor is in the sample tube the carbon dioxide will re-equilibrate with that vapor thus altering its composition over a period of time. Secondly, if water vapor is introduced into the mass spectrometer it will adsorb on the glass and metal surfaces. Carbon dioxide tends to

adsorb on the water molecules and thus the mass spectrometer acquires a memory since any new carbon dioxide samples will be contaminated by the previous sample. This memory was very noticeable until the step of drying the carbon dioxide was included in the sample preparation. After cooling the water trap with slurry and evacuating a sample tube, liquid nitrogen is placed around the sample tube. The stopcock to the pumps is closed, the stopcock on the sample flask is opened and the sample starts transferring. The pressure is monitored in the sample preparation line until it is less than  $1.2 \times 10^{-3}$  torr. This ensures that any fractionation of the sample due to selective freezing of the carbon dioxide will cause an error in DEL of less than 0.1 DEL units. A discussion of the above calculation is given in the next chapter. After transfer the stopcock of the sample tube is closed and the sample is ready for mass spectrometer analysis.

### 3.1.2 The Equilibration Of Water And Carbon Dioxide

Unless the amount of time it takes to equilibrate the carbon dioxide with the water sample is known, errors may result from insufficient reaction time. The chemical reaction of carbon dioxide with water was studied in detail by Mills and Urey (1939, 1940). They point out that it was Faurholt (1921, 1924) that first recognized that the reaction

process was determined by the pH of the solution. When the pH is less than 8 the reaction is one of simple hydration:



If the pH of the solution rises above 10 then a much slower bi-molecular reaction predominates:



The half-life of reaction 3.1 is approximately 17 minutes at 25°C but when the carbonate ion of 3.2 is present the time of half exchange was about 28 hours. For this reason it is clear that it is necessary to force reaction 3.1 to occur by having a pH less than 8.

If the isotopic equilibration between the water and carbon dioxide were the rate controlling step it is clear that the equilibration would be ninety-nine percent complete in less than two hours. The rate of equilibration was studied as part of this research and such was not the case. It appeared that the half reaction took approximately two hours instead of seventeen minutes and so some process other than the chemical reaction is the rate controlling step.

It seems reasonable that the increased time of equilibration is a result of inadequate mixing of water in the sample flask. It is probably true that the reaction between the carbon dioxide and the water at the surface takes place in the time suggested by Mills and Urey. However the water in the bottom of the flask circulates slowly and this circulation controls the overall reaction rate. Since no discussion of the equilibration mechanism



could be found the following model is proposed.

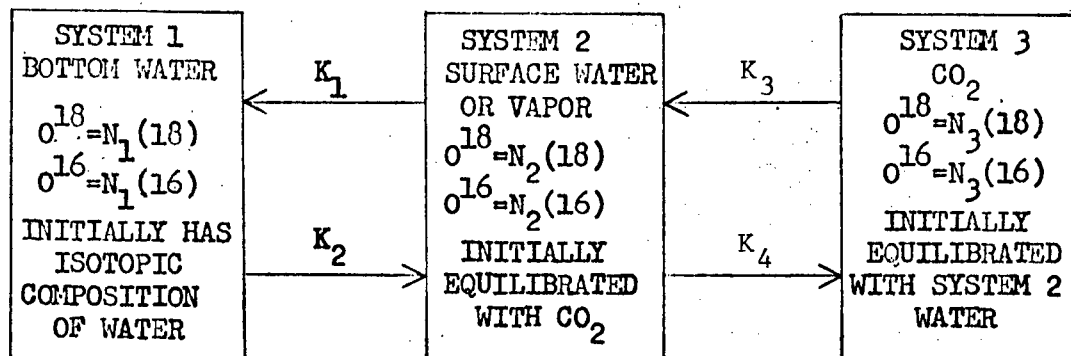


Figure 3.3 The Proposed Model for Water and Carbon Dioxide Equilibration

The physical description of the equilibration process involves three assumptions:

1. The equilibration time is controlled by the physical transport constants  $k_1$  and  $k_2$  and is essentially independent of the chemical rate constants  $k_3$  and  $k_4$ .
2. The number of  $O^{16}$  atoms in all three systems remains approximately constant and only changes in isotopic ratios due to variations in the  $O^{18}$  content need be considered.
3. The number of  $O^{18}$  atoms being transported from system  $i$  to system  $j$  is proportional to the number of  $O^{18}$  atoms in system  $i$ . (i.e. we assume a first order process as suggested by McKay, 1938)

If we let  $N_1(18)$  stand for the number of oxygen-18 atoms in system 1 and similar expressions for systems 2 and 3 we can write:

$$d[N_1(18)]/dt = k_1 N_2(18) - k_2 N_1(18) \quad [3.3]$$

$$d[N_2(18)]/dt = k_2 N_1(18) - k_1 N_2(18) \quad [3.4]$$

from equation 3.4

$$N_1(18) = [1/k_2] [d(N_2(18))/dt] + [k_1/k_2] N_2(18) \quad [3.5]$$

differentiating 3.5 gives

$$d[N_1(18)]/dt = [1/k_2] d^2(N_2(18))/dt^2 + [k_1/k_2] d(N_2(18))/dt \quad [3.6]$$

substitution of 3.5 and 3.6 into 3.3 gives

$$d^2[N_2(18)]/dt^2 + (k_1 + k_2) d[N_2(18)]/dt = 0 \quad [3.7]$$

The solution of 3.7 is given as follows:

$$N_2(18) = \frac{B}{k_1 + k_2} e^{-(k_1 + k_2)t} + \frac{A}{k_1 + k_2} \quad [3.8]$$

this in addition to equation 3.5 yields:

$$N_1(18) = A[1/k_2 - 1/(k_1 + k_2)] - B/[k_1 + k_2] e^{-(k_1 + k_2)t} \quad [3.9]$$

If the initial values of  $N_1(18)$  and  $N_2(18)$  are substituted into equations 3.8 and 3.9 we obtain:

$$N_2(18) = \left[ \frac{k_1 N_2^0(18) - k_2 N_1^0(18)}{k_1 + k_2} \right] e^{-(k_1 + k_2)t} + \frac{k_2}{k_1 + k_2} [N_1^0(18) + N_2^0(18)] \quad [3.10]$$

where the superscript  $^0$  indicates initial values. If we define

$$\rho_{12} = N_1(16)/N_2(16) \quad \rho_{23} = N_2(16)/N_3(16) \quad [3.11]$$

and define the  $O^{18}/O^{16}$  ratios as follows:

$$R_1 = N_1(18)/N_1(16) \quad R_2 = N_2(18)/N_2(16) \quad [3.12]$$

then it follows that

$$N_1^0(18)/N_2(16) = R_1^0 \rho_{12} \quad [3.13]$$

dividing both sides of equation 3.10 by  $N_2(16)$  will then give:

$$R_2 = \left[ \frac{k_1 R_2^0 - k_2 \rho_{12} R_1^0}{k_1 + k_2} \right] e^{-(k_1 + k_2)t} + \frac{k_2}{k_1 + k_2} [\rho_{12} R_1^0 + R_2^0] \quad [3.14]$$

Since we assume that the chemical equilibration between the carbon dioxide and the water in system 2 is rapid we can write:

$$R_3 = \alpha R_2 = \left[ \frac{k_1 R_3^0 - \alpha k_2 \rho_{12} R_1^0}{k_1 + k_2} \right] e^{-(k_1 + k_2)t} + \frac{k_2}{k_1 + k_2} [\alpha \rho_{12} R_1^0 + R_3^0] \quad [3.15]$$

where  $\alpha$  is the separation factor as given by Compston and Epstein (1958) to be equal to 1.0407 at 25°C.

As shown in section 3.2.2 there is a relationship between  $R_1^0$  and  $R_3^0$ . It is worthwhile to translate  $R_3^0$  into terms of  $R_1^0$  since it is possible to estimate  $R_1^0$  but  $R_3^0$  would depend upon the value of  $\rho_{23}$ .

From the tank carbon dioxide correction given in section 3.2.2 it is true that:

$$\alpha R_1^0 = R_3^0 (1 + \alpha / \rho_{23}) - \alpha \rho_{23} R_T \quad [3.16]$$

where the following assumptions have been made:

1. The isotopic ratio of system 2 is the same as system 1 before chemical equilibration begins, i.e. the water is well mixed.
2.  $R_3^0$  is the ratio of the carbon dioxide after the equilibration with the water in system 2 which corresponds to the final carbon dioxide ratio calculated in section 3.2.2
3.  $R_T$  is the ratio of the tank carbon dioxide.

Substitution of 3.16 into 3.15 gives:

$$R_3 = \left[ \frac{k_1 \rho_{23}}{\alpha + \rho_{23}} (\alpha R_1^0 + \frac{\alpha}{\rho_{23}} R_T) - \alpha k_2 \rho_{12} R_1^0 \right] \frac{e^{-(k_1+k_2)t}}{k_1+k_2} \quad [3.17]$$

It is clear that  $R_3$  is given by a function of the form

$$R_3 = c_1 e^{c_2 t} + c_3$$

by equation 1.1 the DEL will be

$$\text{DEL}(R_3/\text{SMOW}) = \frac{1000c_1}{R_{\text{SMOW}}} e^{c_2 t} + \left( \frac{c_3}{R_{\text{SMOW}}} - 1 \right) 1000$$

which is also of the form:

$$\text{DEL}(R_3/\text{SMOW}) = p_1 e^{p_2 t} + p_3 \quad [3.18]$$

The final dependance of DEL upon the parameters deserves some attention. It is clear from equation 3.17 that  $p_1$  is dependent upon the initial isotopic ratio of the water and upon the relative amounts of water and carbon dioxide ( $\rho_{12}$  and  $\rho_{13}$ ). The half-life of the reaction is

determined only by the transport constants  $k_1$  and  $k_2$  which are constant given any fixed conditions. The  $P_3$  term is also a function of  $R_1^0$ ,  $\rho_{12}$ , and  $\rho_{23}$ . The conclusion is that the values of  $p_1$  and  $p_3$  vary between samples but that  $p_2$  is constant. We therefore deduce that if we study the reaction time on any water sample we should be able to calculate the time necessary for the reaction of any other water samples.

The equilibration process was studied empirically by equilibrating a 10 ml water sample that was isotopically very different from the tank carbon dioxide initially placed over it. Representative aliquots of carbon dioxide were withdrawn at intervals of approximately one hour and their isotopic composition measured relative to IAEA SMOW. The results of this experiment are given in Figure 3.4. Figure 3.4 is a least squares fit to an exponential function of the form given by equation 3.18. Data points were weighted in proportion to the reciprocal of the analytical variance in determining the DEL value. Error bars on the graph are taken at the one-sigma level. The result of the fit is excellent and confidence in the estimate of the parameters is high. The value of  $p_2$  was found to be:

$$p_2 = (-0.52 \pm .01)\text{hr}^{-1} \quad [3.19]$$

In general water samples whose equilibrated carbon dioxide is very different isotopically from the tank carbon dioxide will take longer to be within a specified range of the steady state value than samples that have nearly the same isotopic composition in their equilibrated carbon

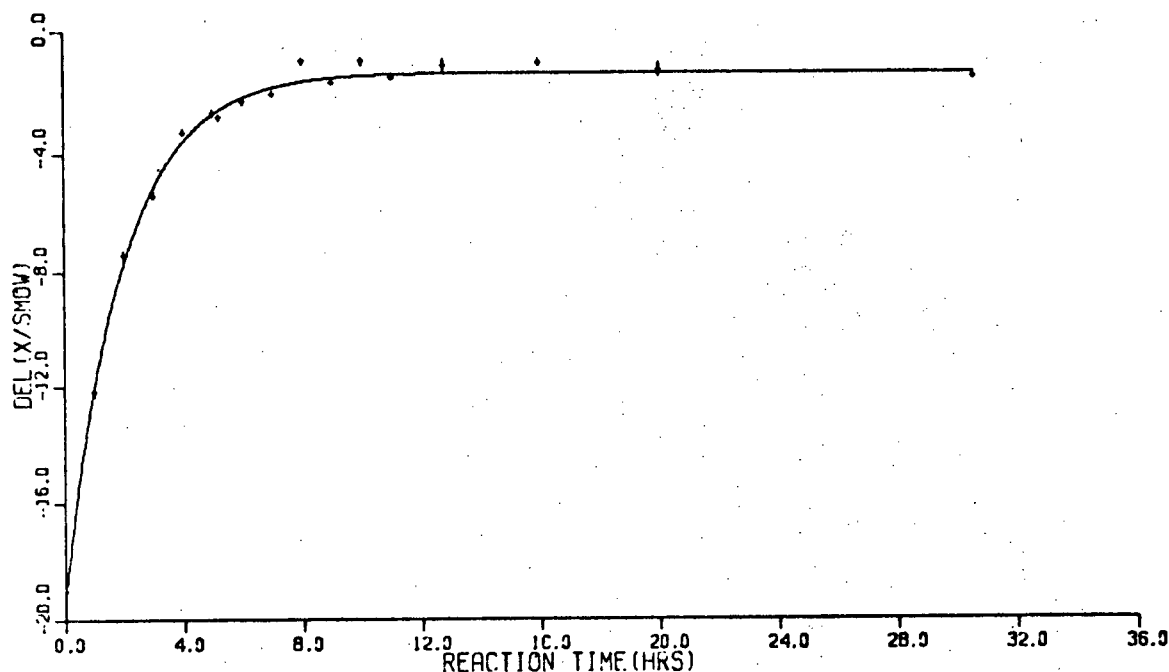


Figure 3.4 The Equilibration of a Carbon Dioxide Sample

dioxide. In fact it is clear that if the isotopic ratio of the carbon dioxide in final equilibrium with the water sample was identical to tank carbon dioxide it would take no time at all to equilibrate. Therefore if one wishes to know how long it takes a water sample to reach equilibrium with the carbon dioxide above it in the sample flask the equilibrium DEL value must be specified.

Using the value of  $p_2$  in equation 3.19, it is possible to determine the time necessary for the carbon dioxide to be within a given number of DEL units of the steady state value. The calculation is straightforward. Remembering the reaction proceeds according to equation 3.18 we write:

$$y = p_1 \exp(p_2 t) + p_3 \quad [3.20]$$

where  $p_3$  is the final equilibrium DEL value of the carbon dioxide ( $t$  infinite),  $p_1$  plus  $p_3$  is the DEL value of the

tank carbon dioxide (t equal to zero) and  $p_2$  is a constant as given in equation 3.19. If  $Q$  is the magnitude of the difference between the steady state value and the value at some time  $t$  it is clear that:

$$Q = |p_3 - y| = |-p_1 \exp(p_2 t)| \quad [3.21]$$

$$Q = |p_3 - \text{DEL}(\text{TANK}/\text{SMOW}) \exp(p_2 t)|$$

The value of  $\text{DEL}(\text{TANK}/\text{SMOW})$  is known very well where SMOW is the isotopic ratio of carbon dioxide in equilibrium with SMOW and is:

$$\text{DEL}(\text{TANK}/\text{SMOW}) = -18.75 \quad [3.22]$$

as mentioned previously:

$$\text{DEL}(\text{X}/\text{SMOW}) = p_3 \quad [3.23]$$

with this information equation 3.21 becomes:

$$Q = |\text{DEL}(\text{X}/\text{SMOW}) + 18.75| \exp(-.52t) \quad [3.24]$$

solving for  $t$

$$t = 0 \quad |Q| \leq \text{DEL}(\text{X}/\text{SMOW}) + 18.75 \quad [3.25]$$

$$t = (-1/.52) \ln |Q / [\text{DEL}(\text{X}/\text{SMOW}) + 18.75]| \quad \text{elsewhere}$$

Figure 3.5 is a plot of equation 3.21 for the three values of  $Q$  specified. For the samples analyzed in this project the error due to insufficient equilibration time must be less than .01 DEL units since the minimum equilibration time was fifteen hours.

Other laboratories have studied the equilibration of carbon dioxide and water. Several interesting and pertinent observations were made by the Institute for Thermal Spring

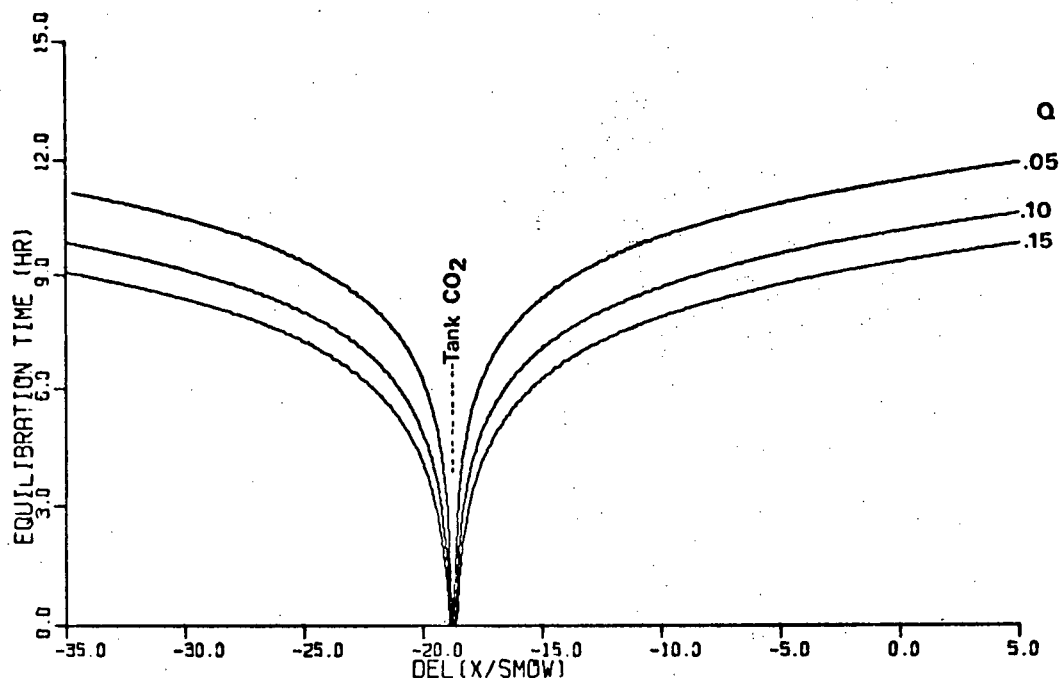


Figure 3.5 Equilibration time for samples of various compositions

Research of Okayama University. Matsubaya (1972) studied the effect of the pH of the water sample on the equilibrium DEL value. The result of this study was that pH values between 2 and 10 did not affect the DEL value obtained after overnight equilibration. There is no reason to suspect a different conclusion at U.B.C. although the equilibration time is longer than was Matsubaya's.

A more interesting result occurred when Matsubaya studied the effect of water sample size on the time necessary for equilibration. One would expect that equilibration time would increase with sample size because of increased mixing problems. Matsubaya found the converse was true and the time for equilibration increased for any given water sample if the volume of the water was decreased. A plausible explanation of this observation can be obtained



by re-examining equation 3.17. It is clear that only the parameter  $p_2$  affects the equilibration rate for any given water sample. Clearly the chemical environment does not change and so the increase in equilibration time must be attributed to the transport constants  $k_1$  and  $k_2$ . These transport constants are a measure of the efficiency of the mixing process. Matsubaya used round bottom equilibration flasks such that the angle of intersection between the water surface and the flask became more severe by adding more water. It is reasonable to assume mixing would therefore improve if sample size were increased, causing a decrease in reaction time. This effect is counteracted somewhat by increased sample size and it is hard to see intuitively which effect dominates. This provides a possible explanation of the empirical observation of Matsubaya.

The separation factor  $\alpha$  is a constant that has been precisely determined by O'Neil and Epstein (1966) and is  $1.04073 \pm .00005$  at 25°C. This is in close agreement with the much used value of 1.039 quoted by Craig (1957). Staschewski (1964) presents an extremely good analysis of the variation of  $\alpha$  with temperature and the effect of temperature variations in the water on the DEL value will be analyzed in Chapter IV.

There remains a final point of interest in the relationship given by equations 3.17 and 3.18. If one examines equations 3.3 and 3.4 at steady state he deduces that:

$$k_2/k_1 = N_2(18)/N_1(18)$$

but at steady state the water is well mixed and

$$R_2 = R_1$$

this leads to the fact that

$$k_2/k_1 = N_2(16)/N_1(16) = 1/\rho_{12}$$

By examining equations 3.17 and 3.18 we see that since  $p_1$  is known from the experimental equilibration and since  $R_1^0$  and  $R_T$  and  $\rho_{13}$  plus  $\rho_{23}$  can be estimated by knowing the amount of carbon dioxide and water inserted in the reaction vessel, an estimate of the value of  $\rho_{12}$  can be made. Similarly a second estimate can be obtained using the expression for  $p_3$ .

The calculations are tedious and will not be presented here since it is a minor point. The analysis was carried out and the value of  $\rho_{12}$  was estimated to be approximately 3500, which is probably better than an order of magnitude calculation. Therefore the system which we have defined to be system two corresponds to a layer of water about 2 microns deep on the surface of the water in the sample flask. At this point the question arises if the reaction between the carbon dioxide and water might actually occur in the gas phase. Knowing the vapor pressure of water and the volume of the vacuum above the water sample indicates that the ratio of water to water vapor in the equilibration flask is approximately 12,000. The difference between this number and the previous estimate of 3500 can not be shown with a high degree of confidence. We therefore conclude that it is quite possible that the reaction between carbon dioxide and water takes place entirely in the gas phase.

### 3.1.3 The Mass Spectrometer Analysis Of A Carbon Dioxide Sample

The final step in obtaining a DEL value is the mass spectrometer analysis of the equilibrated carbon dioxide. Mass spectrometer techniques vary between laboratories and so a description of the exact technique used in this study is necessary. Details of the mass spectrometer were given in Chapter II and so we are only concerned with the actual procedure employed.

At the beginning of each day on which analyses were to be made a background spectrum was obtained. After a few days of routine analyses the background would remain unchanged unless difficulties in the vacuum system existed. Principal concern was the magnitude of the background peak at mass 46. It can be shown numerically that background peaks at mass 46 would not affect results significantly if magnitudes were less than 10 mv. This was used as the primary criterion to determine whether analyses would be performed or not. Background was never higher than 10 mv at a case current of 300 microamps on days on which analyses were made.

After running the background spectrum, an aliquot of dry tank carbon dioxide was inserted into the left hand side (LHS) of the sample introduction system. Quantities were considered sufficient if the source pressure rose to between  $2 \times 10^{-6}$  and  $4 \times 10^{-6}$  torr as measured by an ion gauge

located several inches below the source. Experience showed that such pressures would give voltages of six to seven volts at mass 44 with a case current of 300 microamps and "optimum" source conditions. This tank carbon dioxide would then serve as a daily working standard and all measurements would be made relative to it.

After successful loading of the left hand side of the sample introduction system and optimization of source conditions, a slow magnetic scan was made in both directions over the mass 46 peak. Flatness of the mass 46 peak top was crucial unless no instabilities existed in the various power supplies. Peak shape could be altered by varying settings of the source parameters. Such parameters were manipulated until satisfactory peak tops were obtained. With completion of this step, analysis of the first unknown sample could begin.

A sample tube containing carbon dioxide of unknown composition was attached to the right hand side (RHS) of the sample introduction system with a "Viton" O-ring and spring clamp. The trapped air between the sample tube stopcock was removed using the sample line pumping system after the stopcock to the magnetic valves had been closed to prevent air flowing into the mass spectrometer. The unknown carbon dioxide was then transferred into the large reservoir bulb on the right hand side of the inlet system. This was accomplished by expanding the carbon dioxide in the sample tube into the large bulbs in a series of three to four small

aliquots. The amount of the sample in the reservoir would be increased or decreased until the mass 46 peak height of the sample was equal to the mass 46 peak height of tank carbon dioxide in the left hand side of the inlet system.

After accomplishing the peak matching, the magnetic valves would be cycled allowing the samples in the two sides of the inlet system to alternately flow into the mass spectrometer. This process would continue for approximately ten minutes. After this period of valve cycling the mass spectrometer high voltage supply would be adjusted such that the mass 46 ion beam was centered in the Faraday cup. Source potentials would be adjusted to give maximum sensitivity and important machine parameters would be recorded for the future analysis of data discussed in the following chapter.

When the operator was convinced no peculiarities existed with the mass spectrometer, it would be placed under the supervision of an Interdata Model 4 computer. The computer would initially switch the magnetic valves into the configuration allowing the daily working standard (tank carbon dioxide) to flow into the source of the mass spectrometer. It was found that a period of time was required after valve cycling for the isotopic ratio to reach steady state. For this reason the first five data points would be rejected and data analysis would begin with the sixth point. The switching correction described in the next section numerically compensates for non-steady state ratios

in both sides of the inlet system.

After collecting seven data points, the mean value and standard deviations of the PHI values are printed on a teletype, awaiting further data reduction. The magnetic valves were then cycled and the unknown sample was analyzed as described above. This process was repeated until five PHI values were collected for both the unknown and the working standard. If the analysis was of acceptable precision the unknown sample was then pumped away by the mechanical pumps and ten minutes later a new sample was loaded into the mass spectrometer.

If major difficulties were encountered in the analysis of any carbon dioxide sample, they would reflect themselves in the analytical precision obtained. Specifically if consecutive measures of PHI differences differed by more than 0.0010 it was found, in general, that the calculated uncertainty would exceed acceptable limits. Therefore if this occurred during an analysis the sample would be re-analyzed on the mass spectrometer. Thus with the same carbon dioxide in the right hand side of the mass spectrometer source conditions would be reoptimized and re-analysis would begin. This process would be repeated a maximum of four times or until an analysis with acceptable analytical precision was obtained. No data were rejected but rather the weighting function derived in Appendix V would be applied to all the DEL values obtained for the carbon dioxide sample in question. In this manner only one

DEL value would be obtained for each equilibration of carbon dioxide with water.

Data reduction at the University of British Columbia has been done in two different ways. The data reduction essentially involves the translation of the PHI values into a DEL value using equation 2.18 derived in Chapter II. Samples analyzed for the Polar Continental Shelf Project were reduced using a Fortran IV program written by R.D. Russell. This method does a least squares fit of a Tchebychev polynomial to the PHI values of the unknown and standard samples. It essentially constructs two parallel curves through the data points where the difference between curves is PHIDIF used in the equation. The value of PHISTD is taken to be the average PHI value obtained when analyzing the working standard in the left hand side.

The reduction program used in this study does not place the constraint of parallel curves on the data. Instead cubic spline curves are drawn through the data points. It can be shown that the functions thus determined are continuous through the first derivative. These curves are piecewise solutions but this seems adequate since there is no reason to expect that high order derivatives are continuous when the method of sample measurements is considered. Figure 3.6 shows a typical example of the curves used in the determination of DEL.

After determining the form of the cubic splines the difference between the two curves is evaluated numerically

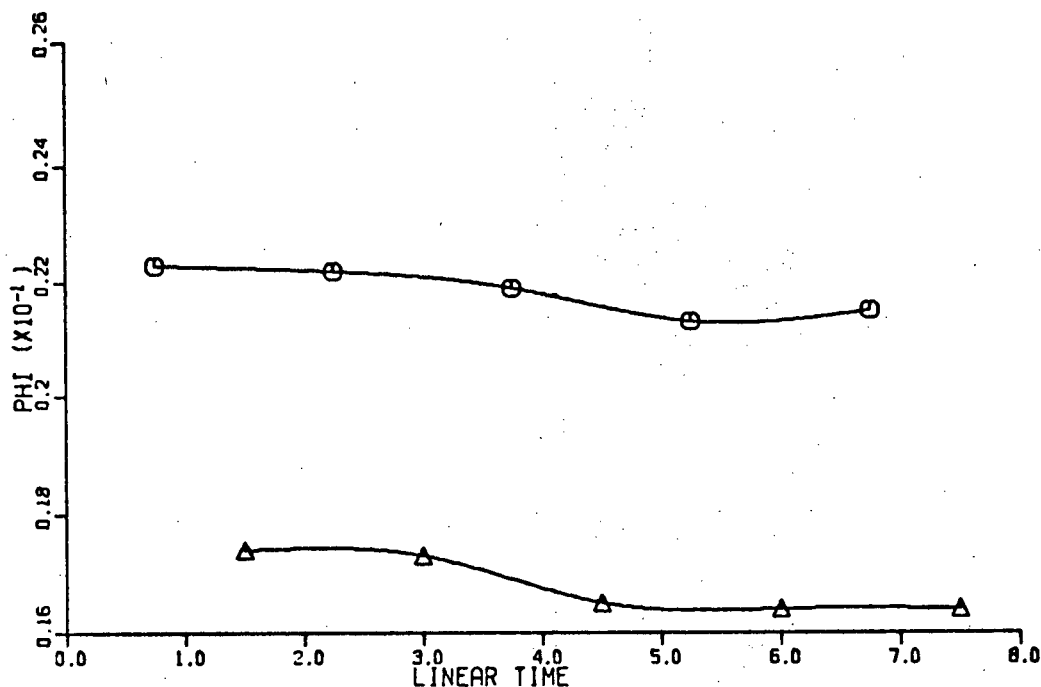


Figure 3.6 The Cubic Splines for a Typical Analysis

five-hundred times. Therefore a good estimate of PHIDIF is obtained in addition to determining its standard deviation. The same process is used in determining PHISTD. The DEL value is then calculated using the equation derived in Chapter II. The advantage of this method is that a more reliable estimate of the analytical error is obtained.

The DEL values obtained are of course relative to the working standard for that day. At least twice a day samples of the UBC LTW standard (distilled local tap water) are analyzed in the mass spectrometer. By using equations derived in Appendices I and II the DEL values can be altered such that the DEL values of all unknowns are made relative to UBC LTW. After applying several corrections discussed in the next section the values can then be made relative to IAEA SMOW.



A more straightforward method of analysis would be to place UBC LTW in the left hand side of the mass spectrometer and make measurements directly to it. This method would assume perfect symmetry on both sides of the sample inlet system. As it happens this is a bad assumption as indicated in Table 3.1 below.

The most logical way of comparing the two methods of sample analysis is to compare the standard deviation of the values obtained by each method. Table 3.2 provides a summary of the two methods.

In seven out of ten cases the standard deviation of the measurements is less when using a dummy working standard in the left hand side of the inlet system. It was primarily this result which led to the adoption of this procedure.

The precision based on duplicate analyses is much better if sample line symmetry is not assumed. There exist two drawbacks with the method used. First an extra analysis of UBC LTW is required every day and second, each analysis of an unknown sample is based upon two individual analyses. This fact means that the resultant error in measurements is increased by something less than the square root of two. The method employed was copied from the Institute of Thermal Spring Research, Misasa, Japan.

	NBS1	NBS1A	SLAP	UBC LTW
SMOW	-7.87	-24.45	-56.39	-17.58
	-7.81	-24.44	-56.17	-17.39
	-8.04	-24.52	-55.94	-17.51
	(-8.07)	(-24.54)	(-57.04)	(-18.09)
	(-7.70)	(-24.25)	(-56.40)	(-17.52)
NBS1		-16.60	-49.37	-10.10
		-16.76	-48.68	-9.59
		-16.62	-48.29	-9.78
		(-16.88)	(-49.07)	(-9.96)
		(-16.50)	(-48.97)	(-9.56)
NBS1A			-33.32	6.61
			-32.74	7.04
			-32.21	7.10
			(-32.72)	(7.03)
			(-32.76)	(7.18)
SLAP				41.31
				41.13
				41.09
				(41.21)
				(40.70)

TABLE 3.1 DATA COMPARING TWO METHODS OF SAMPLE ANALYSIS

The figures enclosed in ( ) are values obtained assuming perfect sample line symmetry. The unbracketed values were obtained by the method used in this study. The names of the standard in the right hand side of the inlet system is in the first row. The standard in the left hand side is found in the left hand box.

### 3.2 Correction Factors Applied To Mass Spectrometer Analyses

Errors in measurements always exist. Some errors are random in nature and can never be completely eliminated,

sample measured	DEL method 1	DEL method 2	sigma 1	sigma 2
NBS1/SMOW	-7.91	-7.88	.12	.26
NBS1A/SMOW	-24.47	-24.40	.04	.20
SLAP/SMOW	-56.17	-56.72	.22	.45
LTW/SMOW	-17.49	-17.80	.10	.40
NBS1A/NBS1	-16.66	-16.69	.09	.27
SLAP/NBS1	-48.78	-49.02	.55	.07
LTW/NBS1	-9.82	-9.76	.26	.28
SLAP/NBS1A	-32.76	-32.74	.55	.03
LTW/NBS1A	-6.92	7.11	.27	.11
LTW/SLAP	41.18	40.96	.12	.36

TABLE 3.2 THE PRECISION OF TWO METHODS OF SAMPLE ANALYSIS

The means and standard deviations of all boxes in Table 3.1 are presented here. Method 1 refers to the method employed in this study while method 2 refers to the method assuming perfect sample line symmetry.

only reduced by multiple measurements and sound experimental design. Many systematic errors also exist in measurements and great effort should be taken to remove this unwanted bias. In this research project four corrections were applied to all data. The corrections (in the order applied) are; switching correction, tank carbon dioxide correction, a linear correction to force agreement with world averages, and a correction to make measurements relative to IAEA SMOW. Each of these corrections will now be discussed.

### 3.2.1 Switching Correction

A switching transient follows each cycling of the magnetic valves. It is an empirical observation that the PHI values do not reach their steady state value for a significant period of time after valve cycling. However, the behavior of the PHI values as they approach their steady state value is so consistent that a correction can be made to compensate for the incorrect values obtained. If one plots the variation of the PHI values with time the pattern observed approximates the exponential curves represented in Figure 3.7.

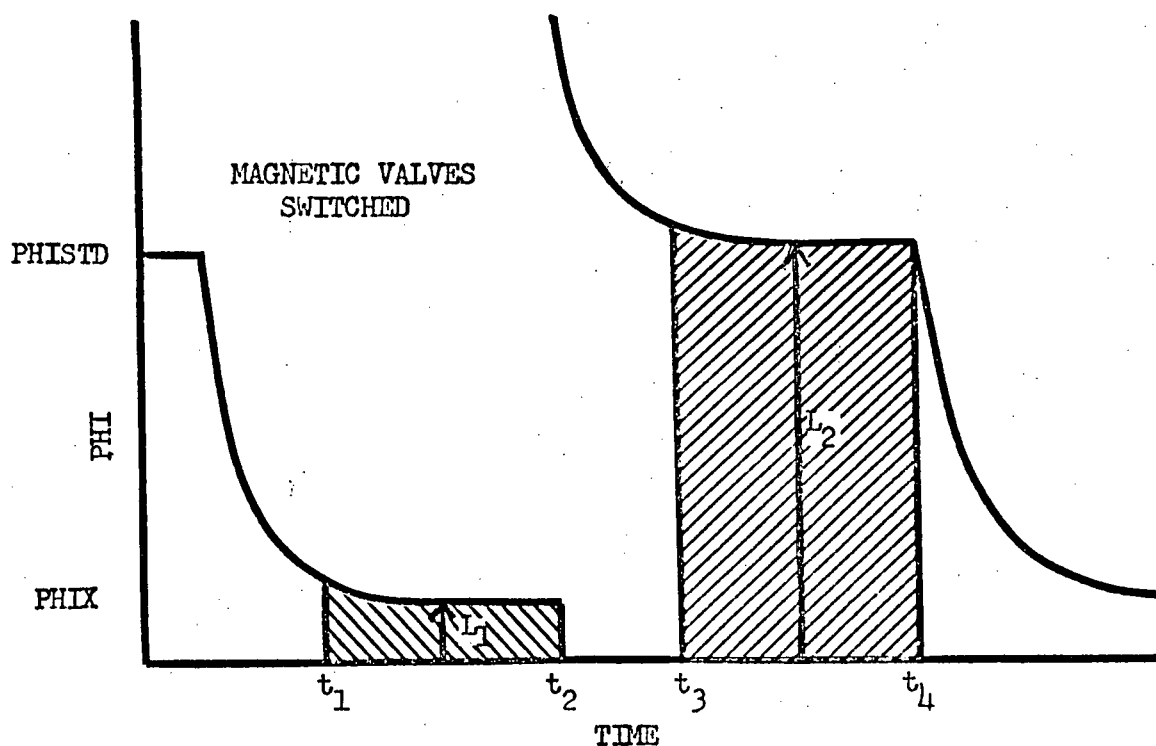


Figure 3.7 The Observed Switching Transient

Data are only taken in the shaded area of each curve

and it can be seen that each estimated PHI value will be too large. This means that the estimated PHIDIF should be multiplied by some correction factor and this correction factor can be made arbitrarily close to one by waiting a sufficiently long period of time before collecting data. Obviously a correction factor should be inserted into the equation to determine DEL.

Each of the curves in Figure 3.7 can be approximated by an exponential function.

$$PHI_x = p_1 \exp(p_2 t) + p_3$$

$$PHI_{STD} = p_4 \exp(p_5 t) + p_6$$

It is clear that initially ( $t=0$ ):

$$PHI_x = p_1 + p_3$$

$$PHI_{STD} = p_4 + p_6$$

and at steady state ( $t$  infinite) the PHI values are:

$$PHI_x = p_3$$

$$PHI_{STD} = p_6$$

therefore the steady state estimate of PHIDIF is:

$$PHIDIF(T) = p_3 - p_6$$

however we make measurements at times  $t_1$  and  $t_2$ . Therefore, in general, the measured PHIDIF;  $PHIDIF(M)$  will not be equal to the true PHIDIF;  $PHIDIF(T)$ . If the quantities  $L_1$  and  $L_2$  are as shown in Figure 3.7, we can estimate the average values of them as follows:

$$\overline{L_1} = \frac{p_1}{p_2} \frac{1}{t_2 - t_1} (e^{p_2 t_2} - e^{p_2 t_1}) + p_3$$

similarly

$$\overline{L2} = \frac{p_4}{p_5} \frac{1}{t_4 - t_3} (e^{p_5 t_4} - e^{p_5 t_3}) + p_6$$

With these stipulations the measured value of PHIDIF becomes:

$$\begin{aligned} \text{PHIDIF}(m) = \overline{L1} - \overline{L2} &= \frac{p_1}{p_2} \frac{1}{t_2 - t_1} (e^{p_2 t_2} - e^{p_2 t_1}) \\ &+ p_3 - \frac{p_4}{p_5} \frac{1}{t_4 - t_3} (e^{p_5 t_4} - e^{p_5 t_3}) - p_6 \end{aligned}$$

therefore PHIDIF should be multiplied by:

$$\frac{\text{PHIDIF}(T)}{\text{PHIDIF}(M)}$$

From the preceding arguments it should be clear that the value of PHIST used in equation 2.18 is also in error and should be multiplied by:

$$\frac{p_6}{\frac{p_4}{p_5} \frac{1}{t_4 - t_3} (e^{p_5 t_4} - e^{p_5 t_3}) + p_6}$$

The two corrections above were measured by doing a least squares fit of empirical data to exponential curves. It was found that PHIDIF should be multiplied by  $0.998 \pm .002$  and PHIST should be multiplied by  $0.999 \pm .001$  to remove the systematic error observed when the magnetic valves are cycled. The corrected values of the two parameters are then placed in the proper places in equation 2.18 to determine the switching asymmetry corrected DEL value.

### 3.2.2 Tank Carbon Dioxide Correction

If the mass of water placed in the sample flask is very much greater than the mass of carbon dioxide placed over the water sample then the isotopic ratio of the water would remain unchanged during the equilibration process. If one wishes to be realistic he must admit that for finite amounts of water a correction must be applied to the measured DEL value to compensate for the isotopic shift of the water towards that of the carbon dioxide as equilibration takes place. Craig (1957) was the first to present a formula that corrects for this effect. This writer has derived Craig's relationship independently and it will now be presented.

At equilibrium the isotopic ratios between the water and the carbon dioxide are related to each other by the separation factor:

$$r_{\text{CO}_2} = \alpha r_{\text{H}_2\text{O}} \quad [3.26]$$

We now define " $\rho$ " to be the ratio of the number of  $\text{O}^{16}$  atoms in the water to the number of  $\text{O}^{16}$  atoms in the carbon dioxide. If the superscript 0 denotes quantities before equilibration and  $N(18)$  stands for the number of oxygen-18 atoms we can write:

$$N^0(18)_{\text{H}_2\text{O}} + N^0(18)_{\text{CO}_2} = N(18)_{\text{H}_2\text{O}} + N(18)_{\text{CO}_2} \quad [3.27]$$

Dividing by  $N(16)_{\text{CO}_2}$ , assumed to be constant during the equilibration process, gives:

$$\frac{N^0(18)_{\text{H}_2\text{O}}}{N(16)_{\text{CO}_2}} + \frac{N^0(18)_{\text{CO}_2}}{N(16)_{\text{CO}_2}} = \frac{N(18)_{\text{H}_2\text{O}}}{N(16)_{\text{CO}_2}} + \frac{N(18)_{\text{CO}_2}}{N(16)_{\text{CO}_2}} \quad [3.28]$$

$$\rho r_{H_2O}^0 + r_{CO_2}^0 = \rho r_{H_2O} + r_{CO_2} \quad [3.29]$$

substituting 3.26 into the above equation gives:

$$\rho r_{H_2O}^0 + r_{CO_2}^0 = \frac{\rho}{\alpha} r_{CO_2} + r_{CO_2} = \frac{\rho+\alpha}{\alpha} r_{CO_2} \quad [3.30]$$

$$\alpha r_{H_2O}^0 = \frac{\rho+\alpha}{\rho} r_{CO_2} - \frac{\alpha}{\rho} r_{CO_2}^0 \quad [3.31]$$

dividing by  $r_{CO_2}^{ST}$  and subtracting one from both sides gives:

$$\frac{\alpha r_{H_2O}^0}{r_{CO_2}^{ST}} - 1 = \frac{\rho+\alpha}{\rho} \left( \frac{r_{CO_2}}{r_{CO_2}^{ST}} - 1 \right) - \frac{\alpha}{\rho} \left( \frac{r_{CO_2}^0}{r_{CO_2}^{ST}} - 1 \right) \quad [3.32]$$

assuming  $r_{CO_2}^{ST}$  refers to a standard carbon dioxide sample we can substitute into the left hand side of 3.32 to have the equivalent water standard by using 3.26.

$$\left( \frac{r_{H_2O}^0}{r_{H_2O}^{ST}} - 1 \right) = \frac{\rho+\alpha}{\rho} \left( \frac{r_{CO_2}}{r_{CO_2}^{ST}} - 1 \right) - \frac{\alpha}{\rho} \left( \frac{r_{CO_2}^0}{r_{CO_2}^{ST}} - 1 \right) \quad [3.33]$$

$$DEL(true) = \frac{\rho+\alpha}{\rho} DEL(measured) - \frac{\alpha}{\rho} DEL(TANK CO_2) \quad [3.34]$$

Since the carbon dioxide placed in the left hand side of the mass spectrometer was tank carbon dioxide the last term will be equal to zero.

$$DEL(true) = \frac{\rho+\alpha}{\rho} DEL(measured) \quad [3.35]$$



where DEL(measured) is the value obtained from the mass spectrometer after applying the switching correction.

The value of  $\rho$  is easily obtained. Assuming 10 ml water samples with 50 cm<sup>3</sup> of carbon dioxide at 20 cm Hg pressure and a temperature of 201.15°C (dry-ice methanol) a value of 348 is obtained for  $\rho$ . The separation factor  $\alpha$  has been determined by many people including Compton and Epstein (1958), Craig (1957), O'Neil and Epstein (1966) and Staschewski (1964). The value obtained by O'Neil and Epstein seems most reliable. At 25°C the value of  $\alpha$  they obtained was  $1.04073 \pm .00005$ .

The tank carbon dioxide correction used in this study is simply one of multiplication. From 3.35 it is clear that:

$$\text{DEL(true)} = 1.0030 \text{ DEL(measured)} \quad [3.36]$$

After applying the switching correction and the tank carbon dioxide correction we have the best estimate of the DEL value of the unknown relative to tank carbon dioxide. At least two times each day a sample of carbon dioxide that has been equilibrated with UBC-LTW is analyzed on the mass spectrometer. The only corrections applied to the UBC-LTW measurements are the switching correction and tank carbon dioxide corrections. By knowing the weighted average of the UBC-LTW values (see Appendix V) relative to the tank carbon dioxide and the value of each unknown relative to tank carbon dioxide we can use the equations derived in

Appendices I and II to calculate the DEL values of the unknowns relative to UBC-LTW.

By using this method of obtaining data we are assuming that the isotopic composition of the tank carbon dioxide remains constant during the course of a day. We make no assumptions about symmetry between the two sides of the sample inlet system since all samples of importance are placed in the right hand side of the inlet system and therefore all asymmetries cancel out in the final data reduction.

### 3.2.3 Linear Correction To Force Agreement With World Standards

The International Atomic Energy Agency (IAEA) and the National Bureau of Standards (NBS) distribute four standard water samples which serve as the basis for intercomparisons between laboratories measuring isotopic ratios in water samples. Since these standards serve as the only intercomparison, the author adopted the philosophy that measurements of the world standards made at the University of British Columbia should be constrained to agree with the average world measurements of these standards. Other laboratories have adopted similar methods and multiply all data by a linear constant such that differences between laboratory measurements and world average values are minimized. It was felt that justification of a linear

correction factor was necessary and for this reason a mixing experiment was performed.

If one mixes two liquids of different isotopic composition, the isotopic ratio of the mixture will lie between the isotopic ratios of the two liquids. Appendix III gives a complete derivation of the mixing problem. For our purposes we can use the small ratio approximation presented in the appendix since  $O^{18}/O^{16}$  ratios are typically of the order of 1:500. Therefore:

$$\text{DEL}(\text{MIX}) = (x \text{ DEL}(\text{A}) + y \text{ DEL}(\text{B})) / (x+y) \quad R \ll 1 \quad [3.37]$$

where  $x$  is the number of milliliters of liquid A and  $y$  is the number of milliliters of liquid B in the mixture. For the case of oxygen isotopes the error in treating the  $x$  and  $y$  values as masses instead of volumes is less than six parts per million and this introduces no measurable error.

Two isotopically different water samples (approximately 25 DEL difference) were used in this experiment. Aliquots of each liquid were accurately weighed and then mixed together. By arbitrarily assigning the isotopic composition of one liquid to 0 and the isotopic composition of the other to 1 an experiment could be performed to test the linearity of oxygen analyses at U.B.C. Table 3.3 gives the results of the experiment.

The errors presented in the fourth column of Table 3.3 are the analytical errors in mass spectrometer analysis and do not include errors in sample preparation, if any. Figure

Mass of liquid A	mass of liquid B	theoretical composition	experimental DEL
54.8306 g	0.0 g	0.0	-26.04 $\pm$ .03
49.8474	4.9721	0.09070	-24.02 $\pm$ .09
44.8181	9.9735	.18203	-21.67 $\pm$ .16
39.9056	14.9266	.27222	-19.46 $\pm$ .10
34.8734	19.8431	.36265	-12.23 $\pm$ .10
29.9101	24.8703	.45400	-15.00 $\pm$ .06
24.9053	29.8912	.54549	-12.67 $\pm$ .08
19.9559	34.7858	.63545	-10.49 $\pm$ .11
14.9422	39.8185	.72714	-8.30 $\pm$ .05
9.9615	44.8328	.81820	-6.19 $\pm$ .09
4.9854	49.8316	.90905	-4.11 $\pm$ .11
0.	54.7651	1.0	-1.58 $\pm$ .05

TABLE 3.3 DATA USED TO CHECK THE LINEARITY OF ANALYSES

3.8 is a graphical representation of the data in Table 3.3. The line drawn is the least squares line as defined by York (1969). The slope of the given line is  $0.04095 \pm .00009$ . Therefore one can conclude that the data fit a straight line as well as possible given analytical precisions of 0.14 DEL. Therefore a linear correction factor is justified in forcing agreement with the world averages.

A total of 18 laboratories around the world have made measurements of the four water standards SMOW, NBS1, NBS1A and SLAP. The average values of the standards relative to SMOW are:

$$\text{DEL}(\text{NBS1}/\text{SMOW}) = -7.86 \pm .04$$

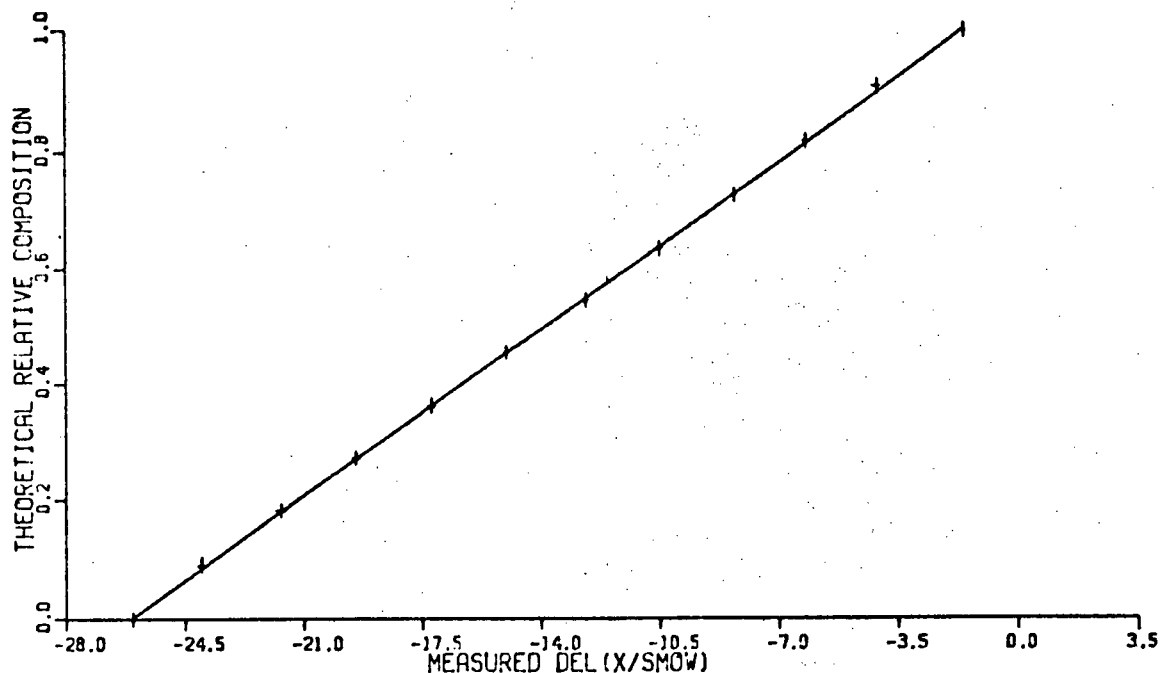


Figure 3.8 The Linearity of Isotopic Analyses  
Based on a Mixing Experiment

$$\text{DEL (NBS1A/SMOW)} = -24.21 \pm .08$$

$$\text{DEL (SLAP/SMOW)} = -55.38 \pm .14$$

From the above values and the results found in Appendices I and II the matrix in Table 3.4 can be constructed:

It should be pointed out that the world measurements of the above values do not appear to have normal distributions and for this reason caution should be exercised in using them. However, due to the large number of independent measurements, the average values must be known quite well as reflected in the quoted errors of the mean.

The measurements in Table 3.5 were made at the University of British Columbia using the technique described in this manuscript. Direct comparison can be made between Tables 3.4 and 3.5. It should be noted that the data in Table 3.5 have been corrected for the switching asymmetry

	SMOW	NBS1	NBS1A	SLAP
SMOW	0.0	-7.86	-24.21	-55.38
NBS1	7.92	0.0	-16.49	-47.90
NBS1A	24.81	16.76	0.0	-31.94
SLAP	58.62	50.31	32.99	0.0

TABLE 3.4 WORLD AVERAGE VALUES OF WATER STANDARDS

The water standard in the top row indicates the standard whose ratio appears in the numerator of the definition of DEL, while the water standards in the first column represent the standard in the denominator.

and tank carbon dioxide.

0.0	-7.91	-24.47	-56.17	-17.49
7.97	0.0	-16.66	-48.78	-9.82
25.08	16.94	0.0	-32.76	6.92
59.51	51.28	33.87	0.0	41.18
17.81	9.92	-6.87	-39.55	0.0

TABLE 3.5 U.B.C. MEASUREMENTS OF THE WATER STANDARDS

The values in this table are the same type as in Table 3.4. The fifth column and fifth row contain values for the UBC LTW Standard.

The entries in the two tables can be compared by the

use of equation 1.2. Specifically it is observed that  $DEL(i/j) = DEL(i/k) + DEL(k/j) + DEL(i/k)DEL(k/j)/1000$  where the subscripts represent the specific rows and columns. For instance one can now calculate the value of  $DEL(NBS1/SMOW)$  if he knows the value of  $DEL(NBS1/LTW)$  and  $DEL(LTW/SMOW)$ . Eighty comparisons of this type can be made between Tables 3.4 and 3.5. If one takes the difference between the entry in Table 3.4 and the equivalent calculated entry in Table 3.5 and sums the square of the differences for all possible intercomparisons he has obtained a quantity which is a measure of the amount of agreement between the two tables. The objective of this exercise is to find a constant multiplication factor by which one should multiply the entries in Table 3.5 so that the sum of the squares of the differences between the two tables is minimized. Performing the necessary calculus yields a cubic equation, the three roots of which are the values of the desired constant. In practice it has been found that for any data set the calculation gives one real root very close to one and two conjugate complex roots whose real parts and magnitudes are very much different from one. The calculations were made using the data of Tables 3.4 and 3.5. The real root obtained was:

$$W = 0.9827$$

[3.38]

Using the initial data it was found that the average difference squared between the entries in Tables 3.4 and 3.5 was 0.327. After applying the linear correction to Table

3.5 it was found that we had reduced the average difference squared to 0.03, which is an impressive improvement. The correction seems very useful and also very justifiable in light of the above fact.

All measurements in this study were multiplied by this linear correction factor. Multiplying the data in Table 3.5 by the linear correction factor,  $W$ , gives the data in Table 3.6.

0.0	-7.77	-24.05	-55.20	-17.19
7.83	0.0	-16.37	-47.94	-9.65
24.65	16.65	0.0	-32.19	6.8
58.48	50.39	33.28	0.0	40.47
17.50	9.75	-6.75	-38.87	0.0

TABLE 3.6 MACHINE CORRECTED DEL VALUES OF WORLD STANDARDS

The table entries correspond exactly to the entries of Table 3.5.

After applying the linear correction it is seen that we now have the necessary information to change measurements relative to UBC-LTW to measurements relative to IAEA SMOW. Specifically we note:

$$\text{DEL(UBC-LTW/IAEA SMOW)} = -17.19 \quad [3.39]$$

All DEL values listed in this study have been treated identically using the procedure presented in this chapter.



### 3.2.4 Corrections That Were Not Applied To These Data

Several corrections which are made by many laboratories were not made to these data. A brief explanation of why it was not deemed necessary to make these corrections is useful.

Many laboratories collect both the mass 44 and 45 peaks in the same Faraday cup. The main constituent in the 45 beam is  $C^{13}O^{16}O^{16}$  and therefore the ratios must be corrected using the known  $C^{13}/C^{12}$  ratio of the sample. Since we collect only the mass 44 beam in one cup and mass 46 ion beam in the other it was not necessary to make a correction for the mass 45 beam flowing into the mass 44 collector.

A small fraction of the mass 46 ion beam comes from ions of the form  $C^{13}O^{16}O^{17}$  and  $C^{12}O^{17}O^{17}$ . Similarly some small fraction of the oxygen-18 is not measured in molecules of the form  $C^{12}O^{17}O^{18}$ ,  $C^{12}O^{18}O^{18}$ ,  $C^{13}O^{18}O^{18}$  and  $C^{13}O^{17}O^{18}$ . Craig (1957) derived correction factors for such molecules and using any reasonable estimates of carbon and oxygen isotope ratios it can be shown that neglecting corrections of the above type contribute an error much less than the analytical precision.

Another common correction applied to oxygen isotope measurements is commonly referred to as a leak correction. Putting the same sample in both sides of the mass spectrometer should produce a DEL value of zero. In general such is not the case and this is attributed to

non-symmetrical leaks. A correction factor is calculated to remove this discrepancy. When using the method employed in this study such corrections are not necessary since all critical carbon dioxide samples are placed in the same side of the inlet system.

Another common correction applied to analyses is usually called the "valve mixing correction". This attempts to correct for the fact that the magnetic valves may not be completely closed when they are intended to be. That is the gas flowing into the mass spectrometer is really a mixture of the gas in the two sides of the inlet system. The correction is usually made by noticing any decrease in the mass 44 peak height as the sample in the side of the inlet system not being analyzed is pumped away. If a decrease in the peak height is noticed, it is assumed that it is caused by the fact that there is no more gas in the "closed" side of the inlet system to flow through the "leaky" valve.

The author has searched for this effect on many occasions and it has never been detected. Furthermore it is felt that such corrections can never be made with confidence because the decreased peak height could be attributed to either the loss of flow from the "closed" side of the inlet system or more efficient removal of the gas in the "open" side of the inlet system. An electrical analogue is helpful. The magnetic valves can be treated as a network of resistors as shown in Figure 3.9.

Points in the system where the pressure is very low can

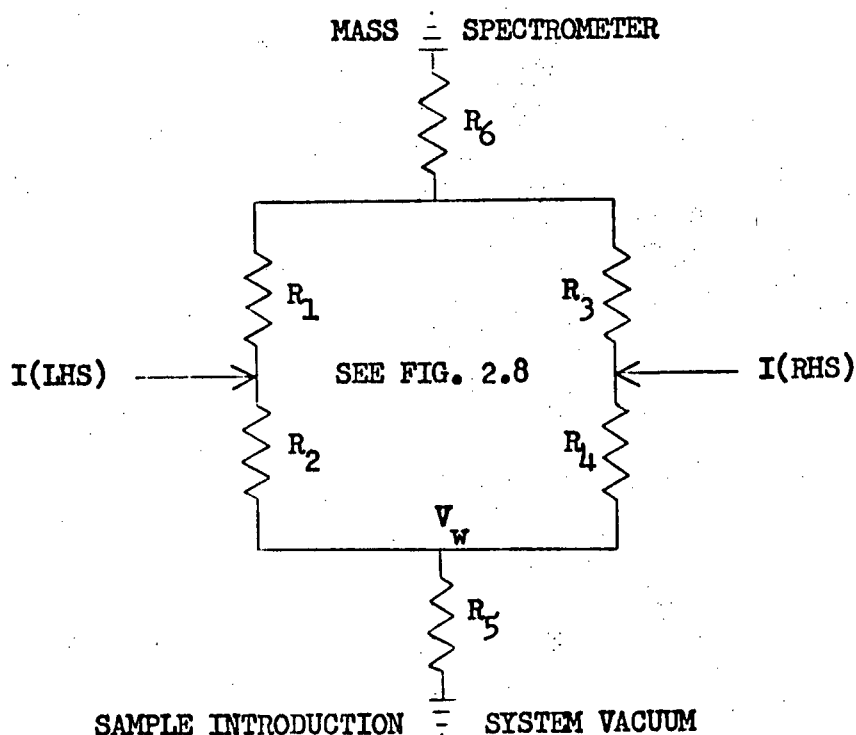


Figure 3.9 Electrical Analogue of Magnetic Valves of Inlet System

be treated as virtual grounds. The resistances represent impedance to the gas flow,  $I(LHS)$  and  $I(RHS)$ . If we wish to analyze the gas in the left hand side the resistances  $R1$  and  $R4$  are made small while the resistances  $R2$  and  $R3$  are made larger. It is clear that if  $R2$  and  $R3$  are not many times greater than  $R1$  and  $R4$  respectively, then some of the gas in the right hand side will flow into the mass spectrometer and some of the gas in the left hand side will flow into the waste vacuum system. It should also be pointed out that the potential above  $R5$  will be approximately equal to:

$$V_W \approx I(RHS)(R_3+R_6)R_5 / (R_3+R_6+R_4+R_5)$$

If the gas in the right hand side is now pumped away,

$I(RHS)=0$ , the flow into the mass spectrometer will decrease for one of two reasons:

1. The flow from the right hand side through R3 will become zero.
2. The potential at Vw will decrease and therefore the flow from the left hand side through R2 and R5 into the waste vacuum system will increase causing a decrease in the flow through R1.

Laboratories making the valve mixing correction assume the first case is true and neglect the second case. Placing reasonable estimates as to the magnitudes of the various resistances shows their assumption to be invalid.

It should be noted that a mixing correction could be applied correctly if the isotopic ratio of the gas flowing into the mass spectrometer is monitored as the gas in one side of the sample system is pumped away. If the gases were of significantly different isotopic composition one could make the correction with confidence since it would be possible to determine which of the above two phenomena was occurring.

Due to the good agreement between the U.B.C. data and the world standards there is strong justification for not making the three corrections mentioned above. Continual caution should be maintained to ensure that changes in the sample inlet system with time do not make our assumptions invalid.

#### IV. SOURCES OF ERROR IN DETERMINING $O^{18}/O^{16}$ RATIOS

During the course of obtaining isotopic compositions of samples from the field project to be discussed in the next two chapters, approximately three hundred mass spectrometer analyses were performed. Of these analyses approximately one-hundred ten were replicate analyses of water samples whose isotopic composition had been previously determined. By recording various mass spectrometer parameters associated with an analysis it is possible to identify probable sources of error in an analysis. An alternative method is to hold all but one of the parameters constant and study the effect it has on the measured DEL value. This technique is time consuming and difficult to accomplish at times. A third approach used in identifying possible sources of error is to make theoretical calculations to ascertain if various factors are important in an analysis. All three of the above methods were used in this study and the results of each will be presented here.

##### 4.1 Multiple Regression Analysis Of Mass Spectrometer Parameters

It is difficult to determine whether altering mass spectrometer potentials, pressures, currents, etc. affects the measured isotopic ratios. Such a determination is extremely useful because it allows the operator to know which variable he can alter without affecting the DEL value

he determines.

For each mass spectrometer analysis of a water sample the values of seven different mass spectrometer variables were recorded. These variables were:

1. The number of analyses already made that day.
2. The time since the first analysis of the day was made.
3. The total filament emission current.
4. The operating pressure in the mass spectrometer when the unknown sample is being analyzed.
5. The DEL value of the sample analyzed immediately before the present analysis.
6. The magnitude (in volts) of the mass 46 peak for the unknown sample.
7. The magnitude (in volts) of the mass 46 peak for the tank carbon dioxide working standard.

By noting the DEL values and associated analytical uncertainties it is possible to determine if any of the seven variables above affect the measured DEL values by performing a multiple regression analysis.

The data used for this analysis were obtained over the course of five months. The approach was to perform a multiple regression on the data with DEL values being the dependent variables. Normally a multiple regression is performed when all values of the dependent variables are from the same distribution. In our problem it is clear that we are sampling distributions with many different means

since the data are from the analysis of many different water samples. For this reason we must construct as many "dummy" variables as there are water samples with duplicate analyses. Say there are  $m$  samples that have been analyzed two or more times. The  $K$ th dummy variable is assigned the value 1 for the  $K$ th sample and 0 otherwise. In this manner the difference between water samples will be manifest by the coefficients of the appropriate dummy variable and in principle the average value of the  $K$ th dependent variable minus the coefficient of the  $K$ th dummy variable should be constant. The success of the regression analysis was confirmed by checking the above relationship.

In performing the multiple regression analysis it is necessary to make three assumptions:

1. The effect of random error is small compared to the effect of variations in the seven independent variables. This assumption is realized if the number of duplicates is much greater than the number of independent variables. The ratio in this analysis was eight to one.
2. The relationships between the dependent variables and the independent variables is the same except for an additive constant, the coefficient of the appropriate dummy variable.
3. The effect of an error in an independent variable

is not a function of the magnitude of that variable. This is to say that the dependent variable is a linear combination of the independent variables.

The regression analysis of data was performed using a multiple regression program supported by the University of British Columbia Computing Centre. In this manner the coefficients in the regression equation 4.1 are all determined:

$$\text{DEL} = b_0 + b_1 v_1 + \dots + b_n v_n \quad [4.1]$$

where the  $v$ 's are the independent variables and the dummy variables. From 4.1 it follows directly that:

$$v_i = -(b_0 + b_1 v_1 + \dots + b_n v_n) / b_i + \text{DEL} / b_i \quad [4.2]$$

To obtain estimates of allowable variations in the machine parameters in question we must insert average values of the variables into 4.2. In addition if we insist that the measured DEL value must be within some value "e" of the optimum value we rewrite 4.2 as follows:

$$v_i = -(b_0 + b_1 \bar{v}_1 + \dots + b_n \bar{v}_n) / b_i + (\overline{\text{DEL}} \pm e) / b_i \quad [4.3]$$

By allowing  $e$  to vary from 0.05 to 0.15 we obtain the limits of variations permissible in the machine parameters. Comparing these values with the actual variations in the parameters indicates which variables may affect the measured DEL value and are therefore possible sources of error.



Table 4.1 summarizes the results of the multiple regression analysis.

	ACTUAL SIGMA	ALLOWED VARIATION BY REGRESSION ANALYSIS		
		e=.05	e=.10	e=.15
Prior No. of Runs	3.62	4.02	8.02	11.70
Net Time (Hours)	5.06	120.6	240.6	351.0
Emission Current	85.68	132.5	264.4	385.8
Pressure	.4387	.4513	.9005	1.314
Previous DEL	7.67	87.77	175.2	255.6
Sample Peak Height	.0728	.0145	.0288	.0421
Std. Peak Height	.0736	.0165	.0329	.0481

TABLE 4.1 RESULTS OF REGRESSION ANALYSIS

The first column gives the actual standard deviation of the corresponding machine parameter. If any of the entries in the last three columns are smaller than the actual standard deviation then an error in DEL will result and the magnitude of the error will be greater than or equal to e.

It is clear from the table that the first five variables cause little error in the measured DEL values but the magnitudes of the mass 46 peaks of both the sample and standard seem to affect the outcome. Calculations based on the voltage coefficient of resistance for the Victoreen resistors (Whittles, 1960) used in the measuring system indicate that non-linearities in the resistors can actually account for an error in DEL of 0.14 when the magnitude of

the mass 44 peak decreases from seven to five volts. Future analyses should attempt to hold peak heights constant since non-zero voltage coefficients of resistance may explain the unexpected result obtained in the regression analysis.

#### 4.2 Equality Of Mass 46 Peak Heights

Many arguments can be made for constraining either the mass 44 or mass 46 peak heights to be equal for the two sides of the mass spectrometer inlet system. If one believes he has a large background in the mass spectrometer or if he is worried about non-zero baselines it is best to equalize the smaller of the two peaks, i.e. the mass 46 peaks. If these problems are negligible then it would be advantageous to match the mass 44 peaks to ensure a constant gas flow into the mass spectrometer which in turn would cause a constant pressure in the source region.

The parametric amplifiers used in the mass spectrometer measuring system can drift sufficiently to alter the measured isotopic values obtained. During the course of an analysis the mass 46 baseline can drift as much as 10 mv from the initial zero. In addition to this, discontinuities as large as 15 mv have been observed. To minimize such problems it was decided that all analyses in this study would be carried out with equal mass 46 peak heights.

It is necessary to know how the DEL value varies with the magnitude of the peak height difference so we know how closely we should match the mass 46 peak heights. A 10 mv

baseline offset will cause less than 0.1% error for samples differing by 20 DEL units, if its 46 peaks are matched within 20 mv.

An experiment was performed where the initial amount of carbon dioxide placed in the unknown side of the mass spectrometer was sufficient to cause the mass 46 peak height of the unknown sample to exceed the corresponding peak height of the working standard by 100 mv. The DEL value was measured and the analytical precision noted. The peak height of the sample side was then decreased, by removing a portion of the carbon dioxide through a viscous leak, and the DEL redetermined. This process was repeated several times. The results are displayed in Figure 4.1. The slope of the least squares line was determined to be  $1.22 \pm .42$ . Difficulties are believed to exist with the circled point and so it was discarded, even though the apparent precision was high, and the slope was redetermined as  $2.31 \pm .39$ . With these values it is possible to estimate the allowable variation in peak height difference for a given error in the DEL value. It is clear that if we use the second slope determined we will obtain a more severe constraint than is probably necessary. The results are given in Table 4.2. It is clear from the table that if the peaks are matched to within 20 mv the resulting error in DEL will be less than 0.05. In practice peaks were normally matched within 10 mv and rarely differed by more than 20 mv. It can therefore be concluded that the error in measurements due to unequal peak

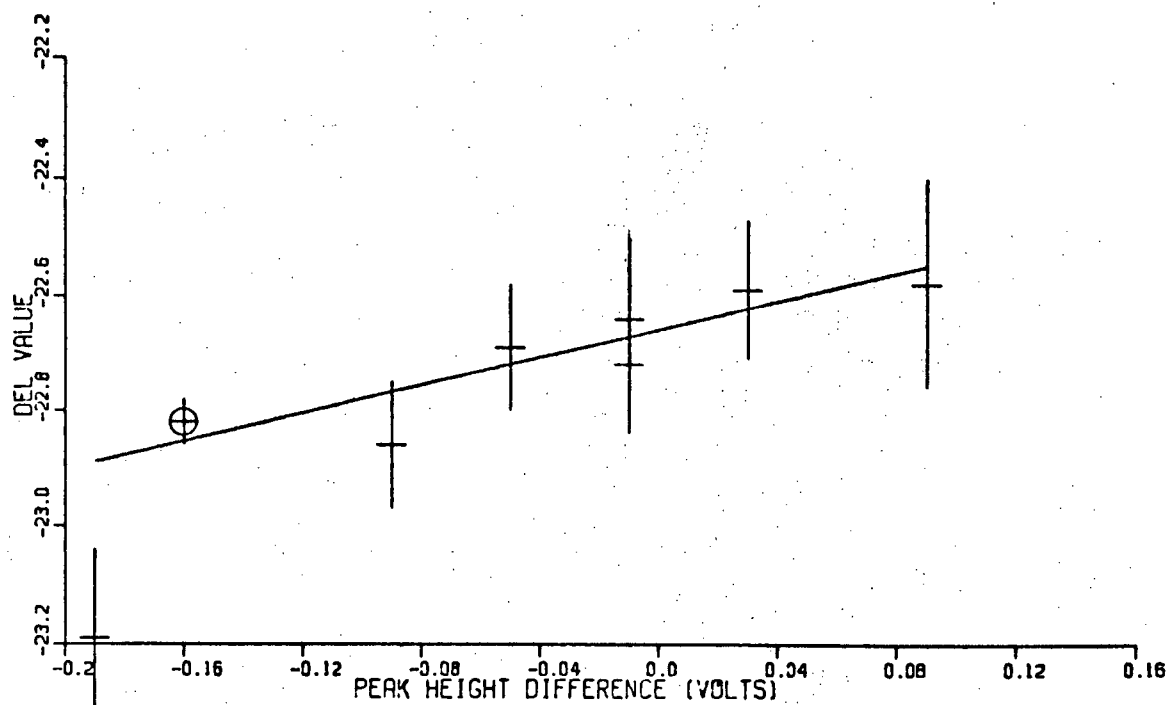


Figure 4.1 The Effect of Peak Matching on the DEL Value Obtained

	Error in DEL			
	.05	.10	.15	.20
All Points Included	.041 volts	.082	.123	.164
One Point Excluded	.022 $\pm$ .004	.043	.065	.087

TABLE 4.2 ERROR IN DEL CAUSED BY A DIFFERENCE IN MASS 46 PEAK HEIGHTS

heights is acceptable.

### 4.3 Sources Of Error In The Equilibration Of Water With Carbon Dioxide

In addition to errors that exist in the mass spectrometer analysis of unknown samples difficulties can exist in the equilibration of water and carbon dioxide. It is clear from the discussion presented in Chapter III that errors can result from insufficient equilibration time. For the isotopic compositions of samples in this study it was shown (Figure 3.5) that equilibration times greater than twelve hours would ensure errors less than 0.05 DEL units. All samples analyzed in this study met this criteria.

An additional source of error is related to the constancy of the temperature in the water bath. Errors arise because the separation factor defined in equation 3.15 of the previous chapter, is not independent of temperature. A complete investigation of the effect was made by Staschewski (1964). Staschewski empirically determined the following relationship:

$$\log_{10}(\alpha) = 8.247/T - 0.00969 \quad [4.4]$$

converting to Napierian logarithms yields:

$$\ln(\alpha) = 18.989/T - 0.02231 \quad [4.5]$$

$$\alpha = .9779 e^{18.989/T} \quad [4.6]$$

We wish to determine what effect changing the bath temperature has on the measured DEL value. Let us assume that the isotopic equilibration of the standard took place at the optimum temperature of 25.3°C but the unknown sample

was equilibrated at some other temperature. If we define K as follows:

$$K = \alpha_t / \alpha_{25.3} \quad [4.7]$$

it follows from Appendix VI that:

$$\text{DEL}(m) = K \text{ DEL}(T) + (K-1)10^3 \quad [4.8]$$

where  $\text{DEL}(m)$  is the measured value and  $\text{DEL}(T)$  is the true value of DEL obtained if T is equal to 25.3°C.

Combination of 4.6 and 4.7 gives:

$$K = .9384 \exp(18.989/T) \quad [4.9]$$

substituting 4.9 into 4.8 gives:

$$\text{DEL}(m) = .9384 \exp(18.989/T) [\text{DEL}(T)+1000] - 1000 \quad [4.10]$$

Since we are interested in the variation of  $\text{DEL}(m)$  with changes in temperature, we differentiate 4.10 with respect to T.

$$\frac{d[\text{DEL}(m)]}{dT} = \frac{-18.989(.9384 \text{ DEL}(T)+938.4)e^{18.989/T}}{T^2} \quad [4.11]$$

For the DEL values measured in this study we can assume that  $0.9384 \text{ DEL}(T)$  is much smaller than 938.4 and we obtain the approximate expression:

$$\Delta \text{DEL} = (-17819/T^2) \exp(18.989/T) \Delta T \quad [4.12]$$

where  $\Delta \text{DEL}$  is measured in DEL units and T is measured in °K. We are normally very close to a temperature of 25.3°C and in this region equation 4.12 reduces to:

$$\Delta \text{DEL} = -0.21 \Delta T \quad [4.13]$$

The water bath in this study was regulated to  $\pm .13^{\circ}\text{C}$  which translates into a maximum error in DEL of less than 0.03 DEL units. We therefore conclude that error contributions from variable equilibration bath temperatures are negligible.

#### 4.4 Isotopic Fractionation Of A Carbon Dioxide Sample During Sample Preparation

The process of equilibrating a water sample with carbon dioxide was described in Chapter III. The last step in that process involved transferring the equilibrated carbon dioxide from over the water sample into a sample tube. During this exchange the pressure in the preparation line is monitored to ensure adequate sample transfer.

It is most probable that the gas flow in the sample preparation line obeys viscous flow laws during most of the sample transfer. However it is possible that the lighter carbon dioxide molecule ( $\text{C}^{12}\text{O}^{16}\text{O}^{16}$ ) migrates at a faster rate than the heavier isotopic species ( $\text{C}^{12}\text{O}^{16}\text{O}^{18}$ ). Such a process would indeed be true if the carbon dioxide had to diffuse through a background of some gas that did not freeze in a vacuum at liquid nitrogen temperatures (e.g. nitrogen, oxygen). Other processes could also introduce isotopic fractionation. For instance the fact that the heavier isotopic species may freeze faster than the lighter molecule could alter the isotopic composition of the carbon dioxide

collected in the sample tube.

The problem before us is, assuming that fractionation does indeed take place, what fraction of the sample must be transferred to guarantee acceptable errors in the isotopic ratio? This problem can be solved using the results of the Rayleigh distillation found in Appendix IV. The only unknown quantity is  $\alpha$ , the fractionation factor. It seems reasonable that the greatest source of fractionation would be from unequal diffusion rates in the sample line and so  $\alpha$  will be equal to the square root of the mass ratio of the two isotopic species of carbon dioxide in question. We therefore write:

$$\alpha = (44/46)^{1/2} = 0.978 \quad [4.14]$$

From Appendix IV we write:

$$q/r_0 = [1-f^{1/\alpha}]/(1-f) \quad r \ll 1 \quad [4.15]$$

where  $q$  is the isotopic ratio of the carbon dioxide molecules that have reached the sample tube,  $r$  is the true isotopic ratio of the unfractionated carbon dioxide, and  $f$  is the fraction of the gas molecules that have not yet undergone fractionation (i.e. the ratio of the current pressure to the original pressure in the sample line).

We again must use the result derived in Appendix VI to estimate the error resulting in the DEL value as a function of  $f$ . It should be noted that if  $f=0$  (i.e. all the sample has transferred) then  $q/r_0=1$  and no error will result in the measured DEL value. From the appendix:



$$\text{DEL}(\text{measured}) = q/r_0 \text{ DEL}(\text{TRUE}) + (q/r_0 - 1)10^3 \quad [4.16]$$

Since the DEL values are much less than 1000 we can write:

$$\text{DEL}(\text{ERROR}) = \text{DEL}(\text{measured}) - \text{DEL}(\text{TRUE}) = (q/r_0 - 1)10^3 \quad [4.17]$$

combining 4.15 and 4.17 gives:

$$\text{DEL}(\text{ERROR}) = [(1-f^{1/\alpha})/(1-f) - 1]10^3 \quad [4.18]$$

The transfer is monitored using a thermocouple pressure gauge. The initial pressure in the system is 16.46 torr. Using equation 4.18 and the value of  $\alpha$  in equation 4.14 we obtain Table 4.3.

Normally samples would transfer to gauge readings greater than 65, meaning errors would be less than .04 DEL. Samples that pulled over to gauge readings of less than 60 would be equilibrated and analyzed again. Such redeterminations seldom gave differences larger than the analytical precision and so we conclude that, if the sample is being fractionated, the degree of fractionation is less than that assumed in this analysis. It is important to note that even assuming the worst case, contributions to the error of the analysis are extremely small.

In many of the instances when the pressure would not decrease to a gauge reading of 60 it would stabilize in the 46 to 50 range. It is possible that in these cases we are seeing the effect of outgassing of stopcock grease or the

Gauge Reading	pressure torr	$f \times 10^3$	Correction	DEL (error)
30	.1	6.075	1.000662	.662
40	.06	3.645	1.000433	.433
50	.032	1.944	1.000255	.255
58	.017	1.033	1.000148	.148
59	.015	.9113	1.000132	.132
60	.014	.8505	1.000125	.125
61	.012	.7290	1.000109	.109
62	.010	.6075	1.000093	.093
63	.0078	.4739	1.000075	.075
64	.0010	.3645	1.000059	.059
65	.0042	.2552	1.000043	.043
66	.0031	.1883	1.000033	.033
67	.0023	.1397	1.000025	.025
68	.0017	.1033	1.000019	.019
69	.0012	.0729	1.000014	.014
70	.0010	.0608	1.000012	.012

TABLE 4.3 GAUGE READING VS RAYLEIGH ERROR IN DEL

partial pressure of some contaminant. It was observed that duplicate analyses of such samples always agreed within analytical error.

#### 4.5 Analytical Precision Of Analyses

The final test of experimental technique lies in how well isotopic ratios can be reproduced. Ideally, many measurements would be made of a single water sample and the standard deviation of those analyses calculated in the normal way. Alternatively many different samples can be analyzed two or more times and give an equivalent estimate of the precision. Confidence in the estimate of precision

requires nearly twice as many measurements of duplicate pairs compared to measurements of a single sample. The method of determining the precision of analyses from replicate pairs is found in Youden (1951). Basically, one calculates the sum of squares difference for each different sample of water and evaluates the number of degrees of freedom for that sample by subtracting one from the number of replicate analyses. We finally obtain the variance estimate of the measurements by dividing the total sum of squares by the total number of degrees of freedom for the data set.

The calculation of precision was carried out and proved to be very informative. On the basis of 52 water samples that were analyzed twice, 4 water samples analyzed three times and one sample that was analyzed five times, the analytical precision taken at the one-sigma level is 0.14. Many laboratories state their precision as 0.1 and so the measurements at the University of British Columbia are of comparable quality.

As discussed in Chapter III, each measured value of an unknown water sample was based on two mass spectrometer analyses, a measurement of the unknown sample relative to the tank carbon dioxide and a determination of the local working standard (UBC LTW) relative to the same tank carbon dioxide. For this reason one would expect that our analytical precision would not be as high as laboratories that make only a single mass spectrometer measurement per

sample.

The above proposition was checked by determining the analytical precision based on the daily determinations of UBC LTW to the tank carbon dioxide working standard. On the average two and one-quarter determinations of a UBC-LTW standard were made daily. From these duplicate analyses the precision of a single mass spectrometer measurement was found to be .125. Assuming that an average of 2.23 UBC LTW standards were analyzed daily we would deduce that the error in the measurement of an unknown sample would be:

$$(\text{error})^2 = (.125)^2 + (.125)^2 / 2.23 \quad [4.19]$$

$$\text{error} = 0.15$$

This estimate of precision agrees extremely well with the actual analytical precision of 0.14. We can therefore conclude that the method used in this study (i.e. each DEL value based on two mass spectrometer analyses) increases the standard deviation very little. Its most serious disadvantage is that it requires one additional analysis of a standard each day.

The estimates of analytical error above include both errors in sample preparation and errors in the mass spectrometer analysis of a sample. The data reduction method used in this study gives an estimate of the latter error for each sample analyzed. The average analytical error of a mass spectrometer analysis is 0.12. This implies that the error in sample preparation must be approximately

sample preparation error of a single sample	.06*
analytical error in mass spectrometer analysis	.10
total error in measuring a single sample	.12
sample preparation error for method used	.07*
analytical error in mass spectrometer analysis	.12
total error for method used in this study	.14

\* these numbers are quite uncertain

TABLE 4.4 SUMMARY OF ERRORS INVOLVED IN  
MEASURING WATER SAMPLES

0.07. We therefore conclude that the largest source of error in this study is the analytical error associated with the mass spectrometer and not with sample preparation.

Analytical errors are often dependent upon the magnitude of the quantity being measured. That is to say the fractional error is constant but not the absolute error. The errors determined in this project seemed to be independent of the magnitude of the DEL value. This observation was substantiated by determining the correlation coefficient between DEL values and their associated analytical error. The correlation was found to be 0.16. This implies near independence between DEL values and associated errors. We thus conclude that errors in measurements are constant within the range of isotopic compositions in this project.

Table 4.4 summarizes what is known about errors in

measurement in this study.

## V. AN ISOTOPIC STUDY OF WATER FLOW IN NATURAL SNOW

### 5.1 Introduction

Understanding of the physics of waterflow in snowpacks has increased considerably in the past five to ten years. Much of the work has been done by S. Colbeck of the U.S. Army Corp of Engineers Cold Regions Research and Engineering Laboratory (CRREL). Colbeck has presented a physical model that describes the bulk water flow through both homogeneous and stratified snow. Experimental data support the simple gravity flow model proposed for homogeneous snow (Colbeck and Davidson, 1972) but at present the effect of impermeable layers in the snow remains a theoretical supposition. (Colbeck, 1973)

It is unfortunate that the studies of Colbeck reveal nothing about the actual processes an "average" water molecule undergoes. Quantitative studies only reveal net flow at any given depth and cannot unambiguously determine the source of the water. Therefore if one is interested in studying the interaction between the liquid and solid phases of water, which was the purpose of the present study, different techniques must be brought to bear on the problem. Gerdel (1948,1954) was among the first to study water movement in natural snowpacks for which attempts to study the interaction between the liquid and solid phases were made. The experiments he conducted were done utilizing dyes in varying concentration. Two difficulties exist in dye

tracing experiments. First, the introduction of the dye alters the physical characteristics of the snowpack and therefore an unnatural situation is studied. Second, it is quite conceivable that dye suspended in liquid water does not behave the same as water. An example of this would be the case in which a water wave encounters a layer of high density snow. The dye may come out of solution and freeze in the dense layer but water formed by melting in the layer may continue to flow. It would be much better to study the actual water molecules.

The first difficulty has been addressed by Langham (1973). He has devised a method of introducing the dye into the snowpack so that its introduction does not alter the properties of the snowpack. However, it is probable that the migration of dye throughout the lower part of the snowpack actually alters physical properties of the snow. Even neglecting this argument it is still true that data from dye tracing experiments express facts about the distribution of the dye in the snowpack and not the water itself. Therefore from a purely philosophical point of view, dye tracing experiments have inherent difficulties.

Stable isotopes provide an internal label for water that cannot alter the physical properties of the snowpack to any significant degree. Therefore, the most logical method of studying water percolation in snowpacks would be through changes in the stable isotope distribution. In fact several researchers have pursued studies related to stable isotope



distributions in natural snowpacks. These include Judy et al. (1970), Friedman and Smith (1972) and Meiman et al. (1972) who studied the natural variation, both in time and space, of hydrogen isotopes in seasonal snowpacks. Krouse and Smith (1972) conducted a study in the Sierra Nevada Mountain Range in which water movement was actually monitored with a density profiling gauge as well as oxygen isotope variations. They used natural isotopic variations in the precipitation as the tracer and so were apparently looking at isotopic changes smaller than the present study. Arnason et al. (1972) and Buason (1972) have conducted similar investigations in both natural and artificial snowpacks and have been able to gain empirical support for a numerical model proposed by Buason. Agreement between the theory and experiments is exceptionally good but unfortunately the theory is over-parameterized and difficult to apply to natural snowpacks.

Krouse and Smith point out that the study of water flow in snowpacks would lend itself quite well to artificial tracing using distilled sea water to simulate rainfall. To the knowledge of this writer the present study is the first attempt to apply this idea to natural snow and therefore the observations are unique. An obvious advantage is the high degree of control in parameters allowing access to information that is often extremely difficult to obtain.

The purpose of this field project is to investigate the interaction between the liquid and solid phases of water in

the snowpack. The method to be used is an artificial tracer enriched in the isotope oxygen-18 introduced on the top of the snowpack. Temporal changes in the isotopic and density profiles of the pack will give insight into the exchange of tracer and snow.

## 5.2 The Type Of Snowpacks Studied

It is often difficult to make generalizations about physical properties of snowpacks because of the interrelationships that exist between characteristic parameters. One must clearly state the physical properties of the snowpack being studied and conclusions reached must be qualified as applying to that specific type of snow. In addition to this West (personal communication) points out that the geographical location seems to alter snow properties and so even the study area may affect conclusions.

Recognizing the above difficulties, experiments were designed such that snow characteristics varied a great deal between successive tracing experiments. Therefore some generalizations can be made if the same phenomenon is observed in different types of snow. However it is important to note that all tracing experiments were conducted on Mt. Seymour, British Columbia and therefore little can be said about the validity of the conclusions reached in this experiment in other locations. It is the author's subjective opinion that the snowpacks studied were

sufficiently different that results are most likely applicable to many other localities. It is felt that the conclusions reached for cold, sub-zero snowpacks are valid in general but the study of the one isothermal situation yields little information.

### 5.3 Snowpack Parameters Measured

The list of physical parameters that must be specified to characterize a snowpack is extremely long (Colbeck, 1974b). It was recognized from the beginning that measurement of all these parameters would require so much effort that the number of individual tracing experiments would be limited to one or two. It was judged more important to limit the parameters studied and increase the number of tracing experiments to six. For this reason the parameters recorded, both before and after the tracer was applied, were:

1. temperature
2. density
3. isotopic composition
4. positions and characteristics of stratigraphic layers and a general description of snow texture

It would have been beneficial to measure the ratio of liquid water to snow at various times and depths, and indeed the information is useful, but the calorimetry used would have

been extremely time consuming and so was neglected.

#### 5.4 Experimental Procedure

When studying water movement in snow, horizontal layers that are impermeable to water can drastically alter flow patterns (Colbeck, 1973). For this reason experimental technique was varied sufficiently to detect the relative amounts of directional flow. The different methods of monitoring the water flow were:

1. Unconstrained flow in natural snow with layering.
2. Flow in non-stratified snow constrained to remove any horizontal flow component.
3. Flow in layered snow constrained to the vertical direction.

The most effective method of studying the isotopic distribution in the snow was found to be through the use of snow pits as described by West (1972). Slight modifications were made to West's procedure. The sampling tubes consisted of a stainless steel tube approximately 36" long and one-half inch in diameter. These sampling tubes were inserted perpendicularly into the working face of the snow pit with a twisting motion to prevent freezing and compaction. The unusual dimensions of the tubes allowed us to obtain an extremely long snow sample and thus short period variations were filtered out in the actual sampling. The diameter was chosen so that the required amount of

sample was obtained with a single tube insertion. It was not unusual to observe compaction in the sampling tube but this did not seem to cause complications, as will be shown by the mass balance studies.

The pit was normally dug less than one hour before the time the tracer was applied and so the edge effect of the open pit was assumed minimal. A perpendicular line was marked on the pit wall and samples taken at four to six inch intervals. Densities and isotopic compositions of these samples were later determined in the laboratory. Temperatures were taken and a general description of snow structure and stratigraphy was made. The isotopically enriched tracer was then sprinkled on the surface of the snow above the working face. After two to five hours, and at intermediate times, the snowpit was resampled and the same information recorded.

In two of the three pit sampling experiments a forty-four inch square lysimeter was placed approximately five feet below the surface of the snow and in the working face of the pit. The tracer never reached the lysimeter in the case of the sub-zero snowpack and so we conclude that it either had a strong horizontal velocity component or it froze before reaching the lysimeter. Another difficulty exists in the method of lysimeter insertion used in this study. When the slot was cut into the working face the normal flow that existed in the snow was interrupted. In fact, what probably happens is that any water flow that was

taking place before the introduction of the opening stops and the water begins accumulating above the slot until the potential energy of the water column can overcome the potential barrier. During this time the water probably flows around the lysimeter. It may require a day to reach a steady state (Wanciewicz, personal communication) and therefore it is not surprising that no effluent was collected in the lysimeter. Mass balance considerations indicate that the tracer probably did not reach the level of the lysimeter anyway.

The importance of horizontal flow in natural snow was studied by comparing results from snowpits and snow tubes. The snow tubes were square, white acrylic tubes, seven feet long with a cross-sectional area of one square foot. Access ports drilled every six inches allowed insertion of a stainless steel sample tube and removal of a snow sample. The tubes were inserted into the snow by force from the top. In this manner water flow was constrained to the vertical. The conclusions reached in this portion of the field project were essentially the same as the unconstrained results obtained from the pits. Therefore we conclude that flow in cold snow, with limited layering, is essentially vertical. This supposition will be investigated in the next chapter.

In two cases water flow through homogeneous snow without layering was studied. In these instances the seven foot long tubes were filled from the top with fresh snow that had fallen within the last two days. The snow was

thoroughly mixed before being introduced into the tube. The isotopically enriched tracer was sprinkled on the top of the column of snow and was sampled after two or three hours. Original isotopic composition was assumed to be constant (measured by taking four aliquots of the snow as it was inserted in the tube). Initial densities were calculated by assuming a constant density gradient and by assuming conservation of mass. Results from these experiments show the interaction between the liquid and solid phases of water extremely well. Unfortunately, it was not practical to measure temperature variations in these cases.

In all, six independent tracing experiments were conducted in the snow on Mt. Seymour during the months of January through March, 1974. The variety of snow encountered enables one to make general statements about the interaction of snow and percolating water in sub-zero snowpacks. The individual experiments are discussed in the next chapter.

### 5.5 Uncertainties In Sampling Technique

The method of sampling the snowpack was destructive; that is, the snow collected before applying the tracer was removed from the system. When the snowpack was sampled at a later time it was necessary to take a sample of snow one to two inches away from the original sampling point. Therefore the lateral variations in density and isotopic compositions would necessarily have to be smaller than the variations we

wished to measure. For this reason a short sampling experiment was conducted.

A layer of apparently homogeneous snow six inches thick was selected for the experiment. A sample was collected every three inches along a horizontal line in this layer. If variations existed in any given horizontal layer we would expect to see them manifest in the data obtained as long as the scale of the variations was less than a few feet. Since we are interested in variations in the order of inches, the experiment should yield the required information.

Both the density and the isotopic composition were measured in the laboratory for each of the ten samples collected. The results are given in Table 5.1. The experimental uncertainty in sampling the isotopic composition of the horizontal snow layer was found to be 0.17. This is not significantly different than the analytical precision of the mass spectrometer analyses of 0.14. We can therefore conclude that the sampling technique does not introduce errors into the isotopic measurements greater than 0.1 DEL. This is less than the magnitude of the isotopic changes we wish to study.

The experimental uncertainty in measuring the density of the horizontal layer was found to be 0.017 for densities in the neighborhood of .245 gm/cm<sup>3</sup>. Due to the consistency of the isotopic results the variation in the density measurements is probably not a real feature of the snow but instead is caused by our method of taking snow samples. As



Sample	Density (gm/cm <sup>3</sup> )	DEL (x/SMOW)
H1	.265	-14.70
H2	.270	-14.82
H3	.225	-14.76
H4	.223	-14.94
H5	.234	-14.84
H6	.246	-14.71
H7	.233	-14.95
H8	.251	-15.13
H9	.260	-14.98
H10	.242	-14.53
Mean	.245	-14.84
Sigma	.017	0.17

TABLE 5.1 LATERAL HOMOGENEITY IN A REPRESENTATIVE SNOWPACK

previously stated, it was not uncommon to observe compaction of the snow inside the stainless steel sampling tubes. It seems reasonable to assume that the amount of compaction is linearly related to the mass of snow in the sample tube which in turn is directly related to the density of the snow. If compaction of the snow is the source of variation in density measurements as is suspected, then it follows

that uncertainties in density measurements can be represented as having a constant percentage error rather than constant absolute error. From the figures in Table 5.1 we note that densities are in error by seven percent. This is in agreement with uncertainties obtained by other workers (Church, personal communication).

#### 5.6 Difficulties Encountered And Disadvantages In Stable Isotope Methods In Snow Hydrology

As it turns out, snow is an extremely difficult substance in which to make measurements. Insertion of any apparatus into the snowpack alters flow patterns, physical characteristics of the snow and even stratigraphy. Digging snow pits exposes the working face to abnormal temperatures and edge effects can be sensed up to one foot away from the wall. Cross country skiers easily alter surface densities of snowpacks.

Even if one could study water-snow interaction without altering its natural state he would find it an extremely complicated system. Horizontal layering can disturb vertical flow to such an extent that artificial tracing experiments become impossible. Insertion of lysimeters suffers from the difficulty discussed in section 5.4. Short days and harsh weather also hamper field measurements.

In addition to the above problems the researcher using stable isotopes encounters unique difficulties. Compared to dye tracing experiments, the laboratory time and cost of

analyzing a water sample are extremely high. It was estimated that every sample obtained for this project took an average of three to four hours field and laboratory time compared to much less than an hour for dye tracing samples. The cost of an oxygen analysis is normally about twenty-five dollars if done commercially.

A more serious drawback to stable isotope techniques in snow hydrology is that one has no indication of what his results will be until after he has left the sampling site. For this reason he can not adjust his sampling technique to compensate for unexpected phenomena. He must blindly proceed, collecting samples assuming nothing is going wrong. Therefore errors in sampling that become evident after mass spectrometer analysis cannot be corrected by additional sampling. This is probably its most serious drawback.

A final difficulty one encounters in field sampling is that the amount of tracer one must apply to the surface of the snow must be sufficient to cause appreciable isotopic changes. Typically the large mass of snow within a few feet of the surface required sixty pounds of tracer to cause isotopic shifts of five DEL units. This is a serious drawback when the sampling area must be reached on foot, as it was in this experiment.

Even considering the disadvantages inherent to stable isotope tracking of water percolation in snow, it is felt that the additional information one can gain from it warrants its use. Certainly many of the conclusions of the

next chapter could not have been reached by any other method. Careful introduction of a tracer on the surface of the snowpack is unlikely to introduce changes into the snowpack that normal rain or meltwater would not have introduced anyway. It still remains the most natural method that can be used in snow hydrology and for this reason alone its use is justified.

## VI. THE ISOTOPIC TRACING OF WATER MOVEMENT IN SNOW

### 6.1 Introduction

A total of six isotopic tracing experiments were made near Brockton Knoll on Mt. Seymour, British Columbia during the months of January, February and March in 1974. The site was selected due to the proximity of a remote weather station operated by Dr. M. Church of the University of British Columbia and Dr. B. Sagar of Simon Fraser University. The data from this meteorological station were made readily available. The specific site of the tracing experiments was on the southern side of Brockton Knoll in a relatively flat meadow. Extremely high winds were often encountered at this site and the amount of drifting and snow depths were much greater than those at the weather station. In spite of the drifting at the project site, stratigraphic layers were nearly always horizontal (an exception to this is in experiment PL3).

All samples were taken using the stainless steel tubes described in the previous chapter. These tubes were sharpened on the leading edge in such a manner as to prevent loss of snow or collection of unwanted snow. Holes in the snowpack were always checked to ensure complete removal of the snow sample. Snow densities were calculated by weighing the mass of snow in each sample and dividing by the volume of the specific sampling tube used. The isotopic composition was determined from the same sample for which

the density was measured. Temperatures of the snowpack were taken with a mercury-in-glass thermometer, calibrated at the ice point and the boiling point. A general description of the position and characteristics of stratigraphic layers was recorded for later reference. Snow texture was categorized in broad categories; light powder, medium packed, compact, and ice. The data obtained for each tracing experiment will be presented in the following sections.

## 6.2 Tracing Experiment---P1

On January 19, 1974, an initial tracing experiment was carried out at the Mt. Seymour site. The main purpose of this experiment was to study the magnitude of isotopic changes that would be encountered. For this reason no density data were obtained but the densities were probably within the range of 0.2 to 0.3 gm/cm<sup>3</sup>. This experiment gave some very interesting results showing the possible effects which could be monitored isotopically. To perform the experiment a pit six and one-half feet deep, eight feet long and four feet wide was dug. Samples representing the initial isotopic composition of the snow were taken immediately. The positions of the sample holes are shown by the closed circles on Figure 6.1. The relationships between their location and the stratigraphic layers is clearly shown.

Distilled seawater with an isotopic composition of -1.02 DEL relative to IAEA SMOW was placed on top of the

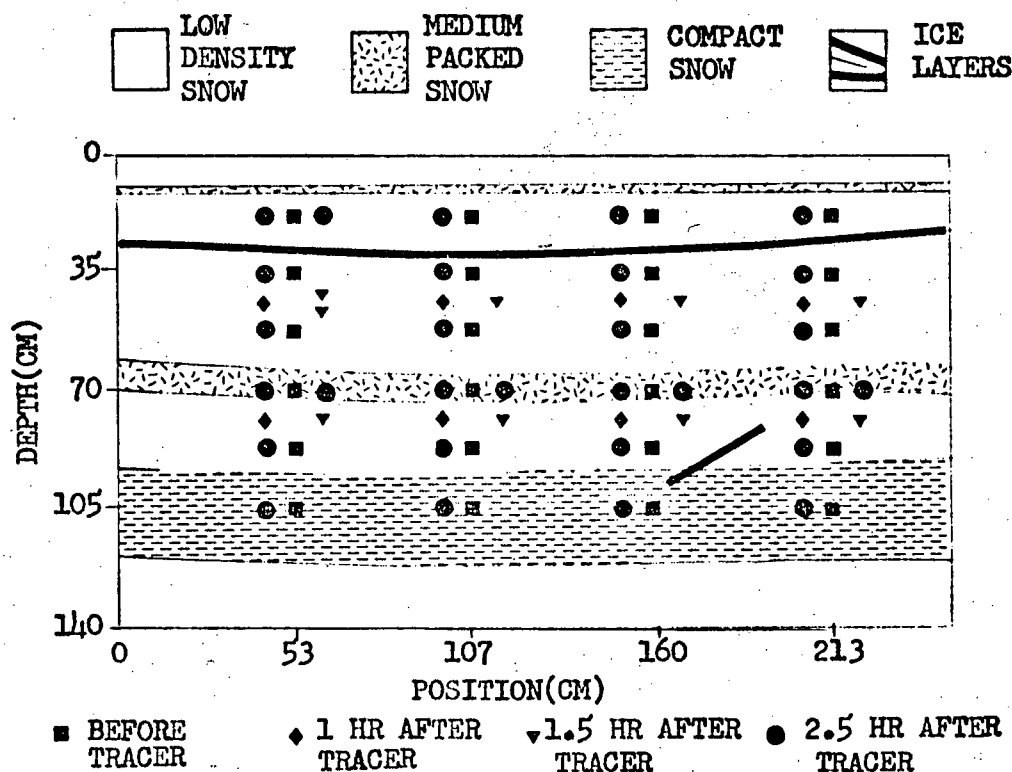


Figure 6.1 Sample positions and Stratigraphic Features in Pit P1

pack. Approximately 15140 ml was dispersed uniformly over an eight foot by three foot area. In addition to this, 1890 ml of the tracer was sprinkled on a one foot diameter circle one-half foot back from the pit wall and over each of the four sampling columns shown in Figure 6.1. It is a straightforward calculation to show that, assuming vertical flow, the application of the tracer in this manner is equivalent to distributing 34400 ml of tracer uniformly over the eight foot by three foot area.

Snow samples were taken approximately one hour, one and one-half hours, and two and one-half hours after the tracer application. The results of the isotopic analyses are given in Table 6.1.

Depth	Time	DEL Before	DEL After
0.	-	-13.81	-13.12
17.78	2.24	-13.53	-12.95
35.56	2.30	-13.38	-13.08
44.45	0.94	-13.91	-13.42
44.45	1.44	-13.91	-13.39
44.45	2.33	-13.91	-13.90
53.34	2.36	-14.26	-14.49
71.12	2.41	-13.34	-13.47
80.01	1.04	-13.18	-12.89
80.01	1.54	-13.18	-12.93
80.01	2.44	-13.18	-13.02
88.90	2.47	-13.29	-12.96
106.68	2.53	-13.53	-13.64

TABLE 6.1 SUMMARY OF DATA---P1

There are basically two things that can be studied from these data; the temporal change in isotopic composition at depths of 45 cm and 80 cm and the variation of the isotopic composition with depth due to the tracer application. Both effects were easily seen in this experiment.

Figure 6.2 shows how the isotopic composition of two layers of snow responded to passage of liquid water. The lower curve represents the isotopic composition of the snow at a depth of 45 cm while the upper curve represents the



isotopic composition at 80 cm. The definite peaks show the retention of liquid water for some time in the two layers before it percolated to lower layers. Normally one would

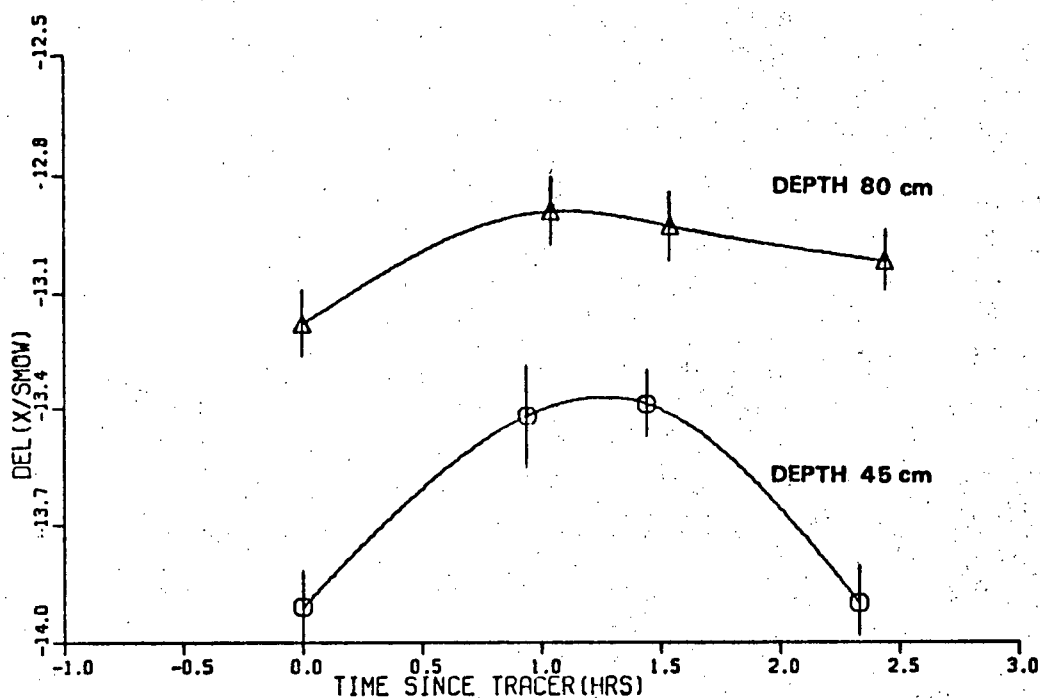


Figure 6.2 Isotopic Changes with Time of Two Snow Layers

expect the peak at 80 cm to lag the peak closer to the surface. In fact, with the broadness of the peak it is difficult to either prove or disprove this fact. Referring to the stratigraphic profile one sees that the average flow rate between the surface and 45 cm was probably less than the flow rate between 45 cm and 80 cm. Therefore it would not be at all surprising to find that the peak flow at 80 cm lags the peak flow at 44.45 cm by less than 0.5 hours. The main conclusion to be reached from Figure 6.2 is that oxygen isotopes can clearly demonstrate the presence of liquid water in the snowpack and indeed can be used to determine

when water content reaches a maximum at any given layer.

The three curves in Figure 6.3 show the original isotopic composition of the snowpack (circles), the isotopic composition of the snow two and one-half hours after tracer application (triangles), and the net change in isotopic composition (plus signs). Initially the DEL values ranged

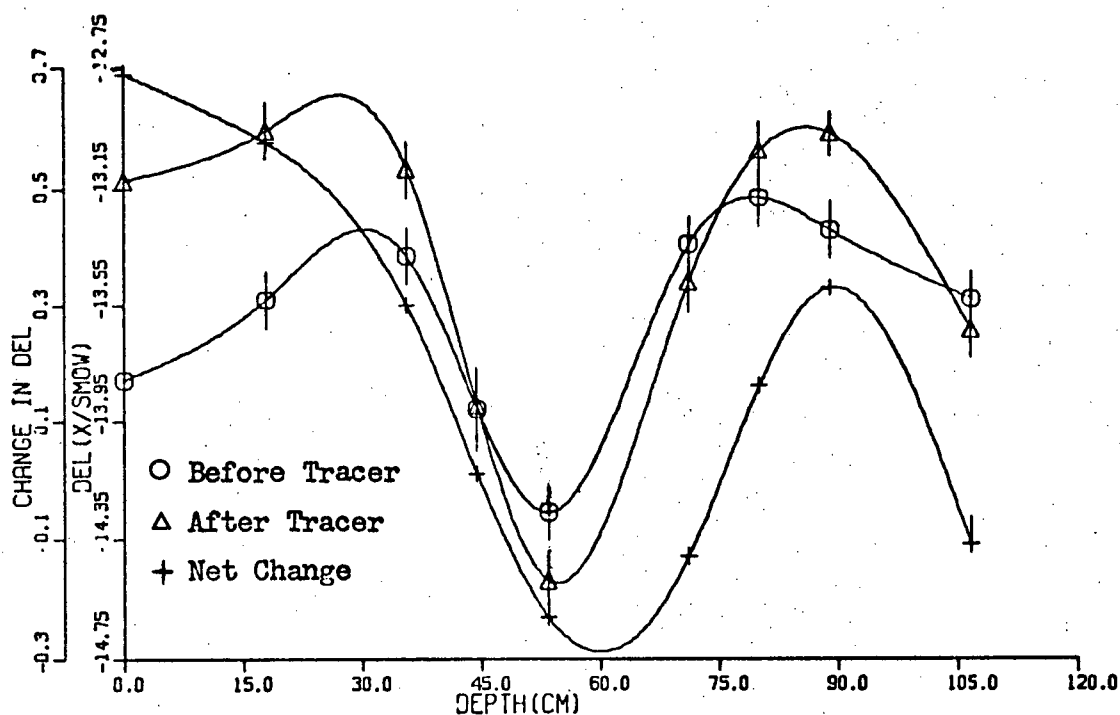


Figure 6.3 Isotopic Profile of Pit in Experiment P1

between -14.26 and -13.18. This difference could easily be attributed to isotopic variations within the snow as it accumulated on Mt. Seymour. After the tracer has percolated through the snowpack the isotopic variation lies between -14.49 and -12.89 DEL. What is even more interesting is that the change in isotopic composition with depth follows the same general pattern as the original

isotopic variation.

It should be noted that the curve representing the change in isotopic composition is independent of both the original composition and final composition of the snowpack. What this feature is essentially telling us is that the passage of liquid water through the snowpack has enhanced the isotopic variations in the snowpack. This is an exact contradiction to the observations of the researchers referred to in Chapter I which indicated that meltwater tends to decrease isotopic variations in the pack. The solution to this dilemma may be that meltwater tends to create isothermal snowpacks at 0°C, whereas this project was conducted in sub-zero snow. It is believed the isotopic enhancement observed in this tracing experiment was the first such case ever found.

Due to the high correlation between the initial isotopic profile and the change in isotopic composition after application of the tracer, it seems reasonable that the original isotopic variation was a result of water flow in the snowpack and not of isotopic variations in the snow as it was deposited.

During the week preceding this tracing experiment heavy precipitation was recorded at the meteorological station and was most likely in the form of rain based on temperature readings. Therefore, it is reasonable to assume that a great deal of water had passed through the snowpack since the snow had fallen. The original isotopic pattern found in

the snow could well have been caused by water passage.

One can speculate as to what is causing the isotopic variation with passage of water. The best example of the high correlation between initial and net change in isotopic compositions is near the isotopic minimum at 55 cm depth. The question then arises: Is there some underlying physical feature of the snowpack that could cause the observed isotopic patterns. Referring to Figure 6.1 shows that a three inch layer of medium packed snow does indeed separate the samples taken at 53 cm and 71 cm. Therefore we conclude that either stratigraphic horizons or snow compaction seem to have an effect on isotopic distributions in cold snow.

The curve representing the change in isotopic composition has several features which can be explained. The initial portion of the curve does not have high correlation with the initial isotopic profile. This could very well be a result of disturbing the initial stratigraphic features of the snowpack when applying the tracer. The disturbance could well reach to the 15 cm depth. Another possible explanation is that since the point at 0 cm depth is an extrapolation of measured data, our extrapolation may have been in error.

The portion of the difference curve above 60 cm is decreasing monotonically with depth. Since the isotopic composition of the tracer was -1.02 DEL we would expect the snow to be shifted towards more positive DEL values. As the liquid percolates through the snow two things happen; one, a

substantial portion of the original tracer freezes and cannot affect snow at lower depths and two, the liquid phase becomes contaminated with the original snow and becomes isotopically lighter. Both of these effects help explain the initial monotonically decreasing characteristic encountered in many of the tracing experiments.

The portion of the difference curve between 45 cm and 75 cm is negative. A natural question to ask is how can the snow become isotopically lighter when the tracer applied was enriched in the heavy isotope? The solution to this dilemma lies in the fractionation of isotopic species as water freezes or conversely as snow melts. The heavier isotopic species ( $H_2O^{18}$ ) tends to freeze before the lighter species. Conversely the lighter isotopic species ( $H_2O^{16}$ ) will melt at a higher rate than the heavy species. Suzuoki and Kimura (1973) show that the fractionation can be as large as 3 DEL units for an equilibrium system. Since the heavy isotope is preferentially removed from the liquid phase it follows that the liquid phase gets progressively lighter with increasing depth. Therefore isotopic changes in the negative direction are realizable.

The isotopic minimum at 55 cm probably occurs because of the medium packed snow layer. The amount of liquid that is frozen per centimeter of snow increases in compact snow layers. Therefore a substantial portion of the remaining isotopically light liquid phase is removed in the packed snow causing the isotopic minimum.

The enrichment of the snow in the heavy isotope between 75 cm and 90 cm is difficult to explain. One can speculate that the downward continuation of the heat wave encountering the low density snow causes substantial melting to occur depleting the snow in the light isotope. This could also explain the inflection point at 90 cm as the point where the released liquid phase begins refreezing. Isotopic conservation does exist in the snow between 70 cm and 105 cm depth which supports the above speculation. Density measurements would have added more weight to this argument.

The following tracing experiments will more clearly demonstrate the features of the curve discussed. In fact, the arguments presented here include information from the other tracing experiments. The feature most characteristic of experiment P1 is the high correlation between the initial isotopic profile and the change in isotopic composition. The implications of this will be discussed later.

### 6.3 Isotopic Tracing Experiment---T1

Two tracing experiments were performed in unnatural conditions. The white acrylic tubes described in the previous chapter were filled with snow that had fallen within the last day. The snow was thoroughly mixed before being placed in the tube.

An interesting observation was made concerning the isotopic uniformity within the snow from a single storm. The snow that went into the tubes was sampled four times

before mixing. It is most probable that all the snow came from a single storm since only the upper six inches of snow was used and it had been snowing heavily immediately before the experiment. Normally one would expect that the snow over the fifty square foot area from which the snow was collected would have uniform isotopic composition. Such was not the case. The isotopic composition of the four snow samples collected varied from  $-14.95$  to  $-17.88$  DEL. The most reasonable explanation of this observation is that the isotopic composition of the precipitation changes due to the depletion of the reservoir and fractionation between the system and the precipitation. Such observations have been made by other researchers who were studying the problem more closely (Judy et al., 1970). The amount of tracer used was 7070 ml. Its DEL value was  $-1.47$  and its temperature at the time of application was  $+4.0$  °C.

The results of this artificial tracing experiment are given in Table 6.2. As expected the unnatural situation gives results that are more straightforward than the natural situation discussed in the previous section.

The initial densities were calculated by assuming conservation of mass and a constant density gradient that paralleled the deep portion of the density curve (after tracer). Both the density measured after the tracer was applied and the calculated initial density curves are shown in Figure 6.4.

The + curve represents the change in density. The

Depth cm	Time Hrs.	Density Before	Density After	DEL Before	DEL After
0.	-	.137	.325	-16.25	-12.99
15.24	1.85	.153	.295	-16.25	-13.18
45.72	2.01	.184	.211	-16.25	-13.70
76.20	2.10	.215	.225	-16.25	-14.65
106.68	2.16	.247	.245	-16.25	-15.89
137.16	2.23	.278	.312	-16.25	-15.99
167.64	2.30	.309	.331	-16.25	-16.68
213.36	-	.356	.37	-16.25	-16.25

TABLE 6.2 SUMMARY OF DATA---T1

large density increase in the first 45 cm implies that the tracer did not penetrate past that point in the snow. However, the isotopic data tell quite a different story. Figure 6.5 is a graphical presentation of the isotopic measurements.

It is quite clear that the tracer affected the snow column to a depth of over one meter. Therefore it seems evident that a portion of the snow in the upper part of the column melted as the tracer percolated through it. At the same time some of the isotopically heavy tracer froze. As it turns out the amount of original tracer freezing and snow melting between 45 and 95 cm was nearly equal resulting in only a small density increase but a sizable isotopic



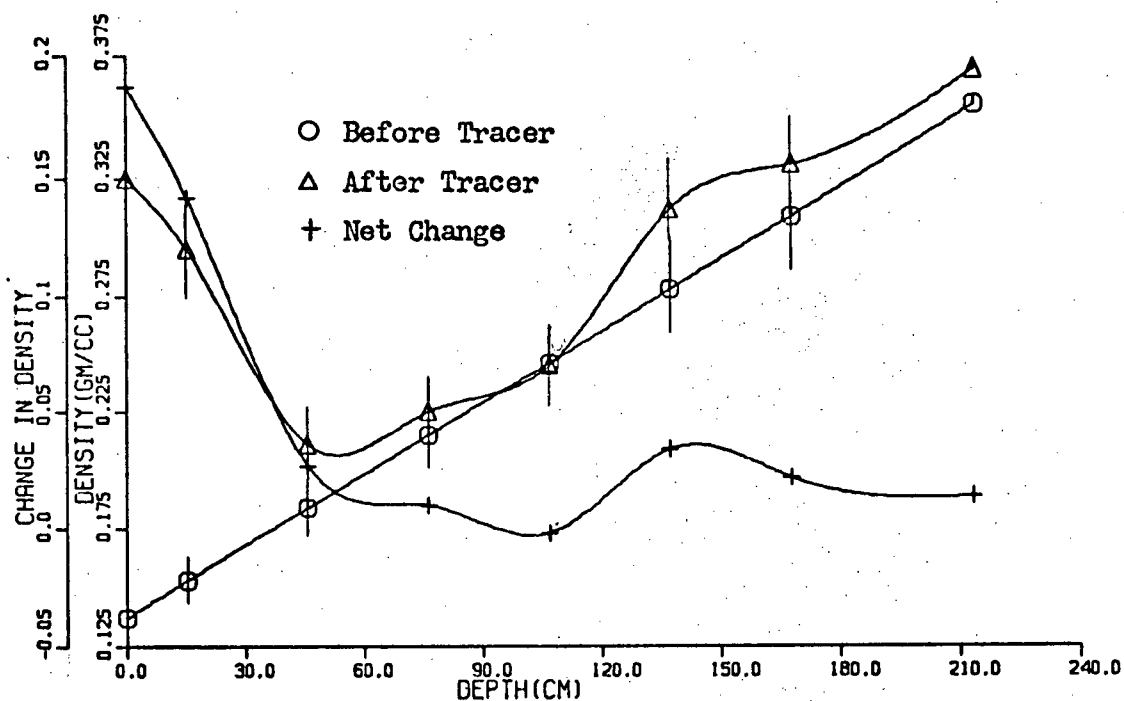


Figure 6.4 Variation of Density with Depth---T1

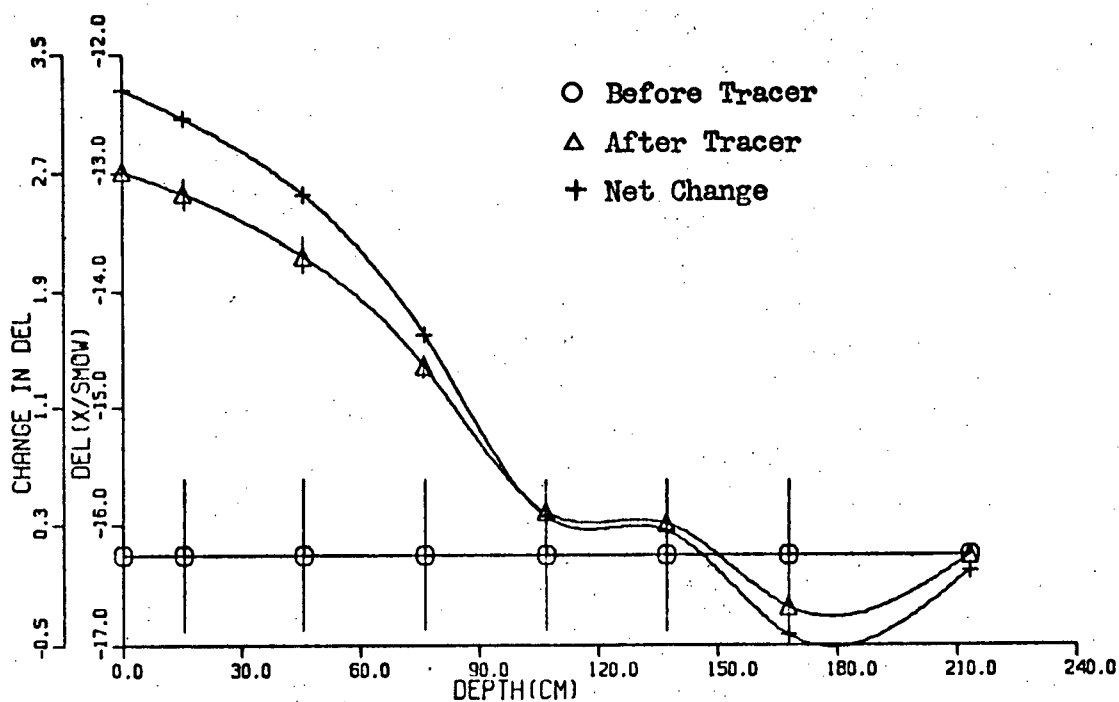


Figure 6.5 Isotopic Composition as a Function of Depth---T1

enrichment. Essentially all the original tracer had mixed with the snow in the first meter. The water that was

originally in the snowpack still existed at a depth of one meter and continued to percolate through the lower portion of the tube accounting for the small increase in density.

Figure 6.6 presents two of the curves in the previous two graphs in a manner that is more suitable for comparing density and isotopic changes. It is evident that some of the change in density is due to the tracer freezing. The

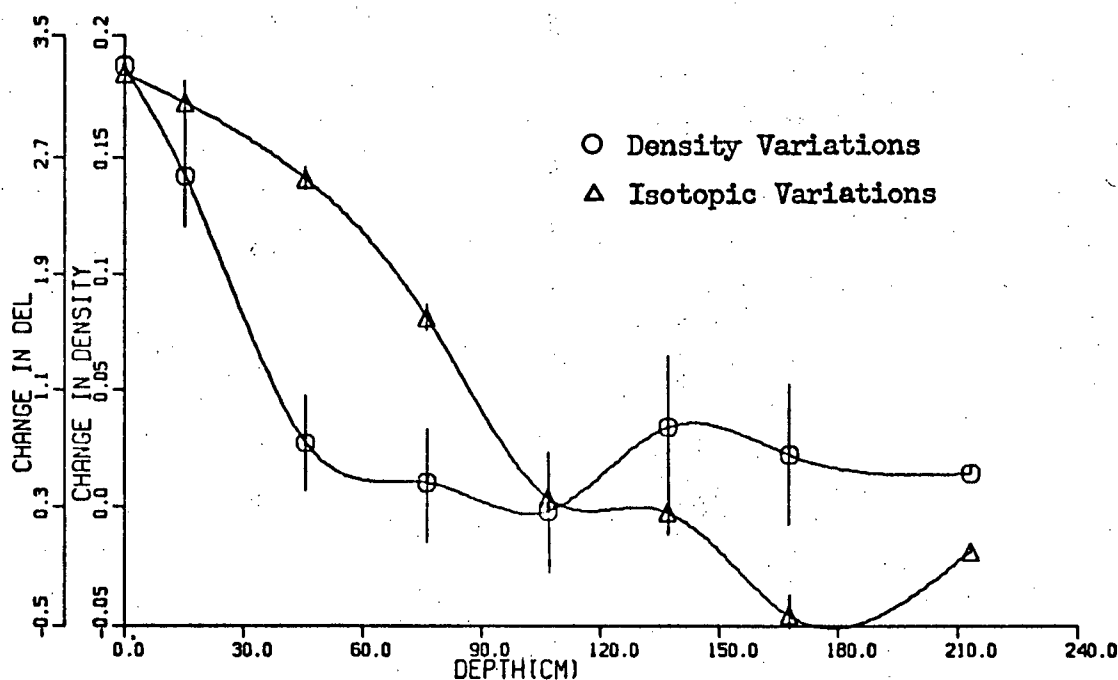


Figure 6.6 The Correlation Between Isotopic and Density changes---T1

correlation coefficient between the two curves is 0.76 which is fairly high, meaning that over half the change in density can be attributed to a simple freezing of the tracer. It does indicate a more complicated process is also occurring since otherwise a higher correlation would have been obtained. This tends to support the arguments presented above.

#### 6.4 Isotopic Tracing Experiment---T2

An experiment very similar to experiment T1 was conducted a week later on February 1, 1974. The sampling interval was decreased to six inches from twelve. Snow temperatures of  $-2.5^{\circ}\text{C}$  were substantially colder than the  $-1.0^{\circ}\text{C}$  temperatures of experiment T1. This should lead to higher correlations between isotopic and density changes. The tracer employed had a DEL value of  $-1.31$  and a temperature of  $4.5^{\circ}\text{C}$  when applied. Again 7070 ml of tracer was used. Initial densities were calculated as in the previous section. Large isotopic variations between  $-14.36$  and  $-18.65$  again existed in the four samples of snow collected as the tube was filled.

The results of the experiment are found in Table 6.3. The isotopic pattern obtained is in Figure 6.7. It appears that the tracer only reached a depth of 45 cm which is considerably less than obtained for the previous experiment. The colder snow temperatures probably account for this observation. The large discontinuity in isotopic composition below 90 cm is cause for concern. It seems real since the trend continues for three sampling intervals. It probably is a manifestation of inadequate mixing of the snow before insertion in the sampling column. It is most likely not a result of water flow.

The density information, found in Figure 6.8, indicates sizable density changes exist up to 30 and 60 cm from the top of the snow column. This agrees reasonably well with

Depth cm	Time Hrs.	Density Before	Density After	DEL Before	DEL After
0.	-	.140	.351	-16.61	-11.84
15.24	2.03	.152	.312	-16.61	-12.70
30.48	2.15	.163	.178	-16.61	-14.81
45.72	2.20	.175	.176	-16.61	-15.89
60.96	2.25	.187	.241	-16.61	-15.52
76.20	2.27	.198	.218	-16.61	-15.99
91.44	2.32	.210	.222	-16.61	-15.61
106.68	2.33	.222	.211	-16.61	-17.80
121.92	2.43	.233	.220	-16.61	-17.68
137.16	2.47	.245	.231	-16.61	-17.17
167.64	2.52	.268	.324	-16.61	-16.16
213.36	-	.303	.295	-16.61	-16.61

TABLE 6.3 SUMMARY OF DATA---T2

our estimate from the isotopic profile. It would seem that the colder snow simplifies the interaction between solid and liquid phases in the snow. Simple freezing of the tracer predominates and little snow seems to be raised enough in temperature to bring about melting.

Figure 6.9 shows the relationship between isotopic changes and density changes. The correlation coefficient between the two sets of data is 0.92, implying that essentially all the interaction that occurred between the

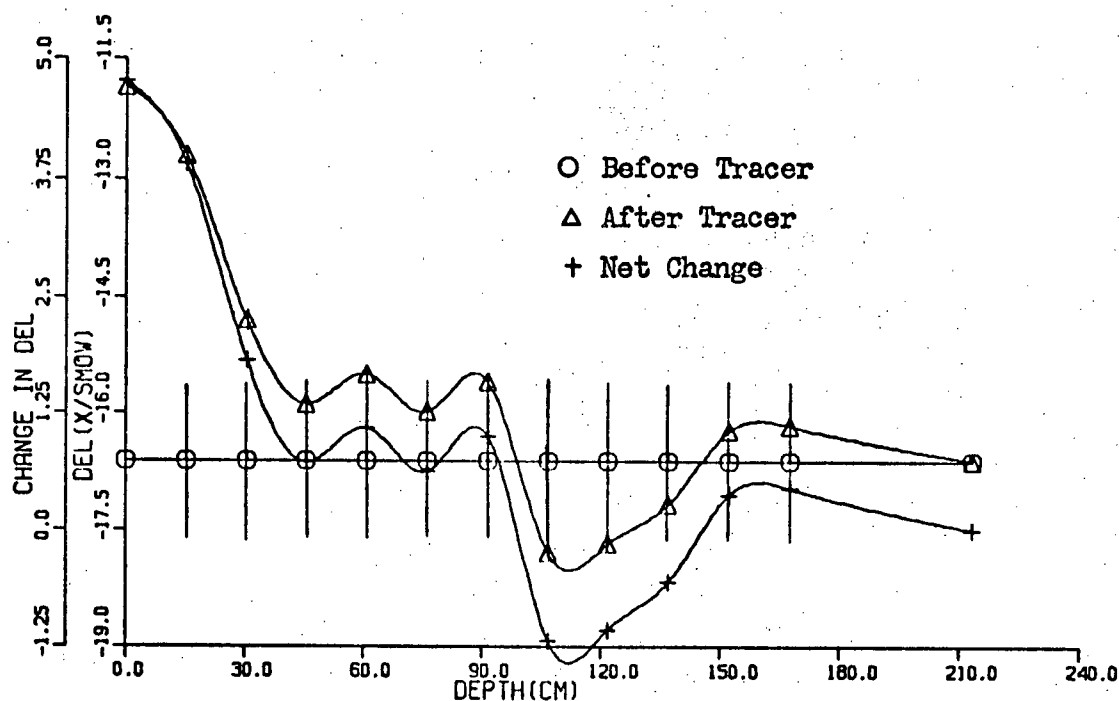


Figure 6.7 Isotopic Composition as a Function of Depth---T2

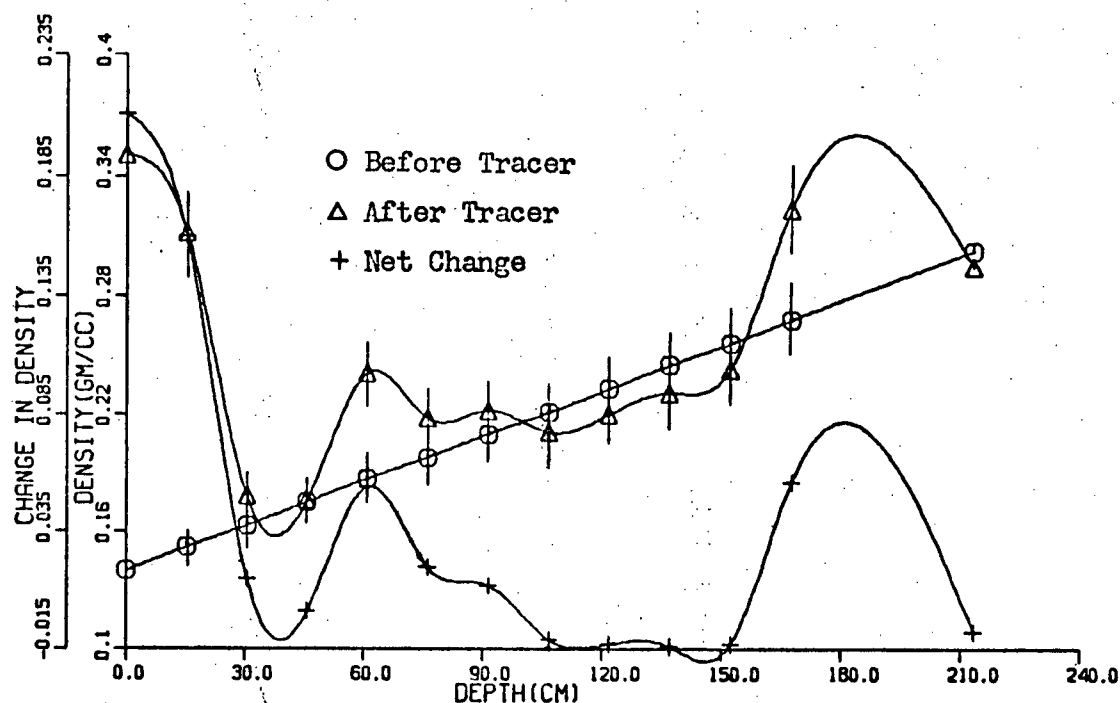


Figure 6.8 Density as a Function of Depth---T2

solid and liquid phase was the freezing of the tracer.

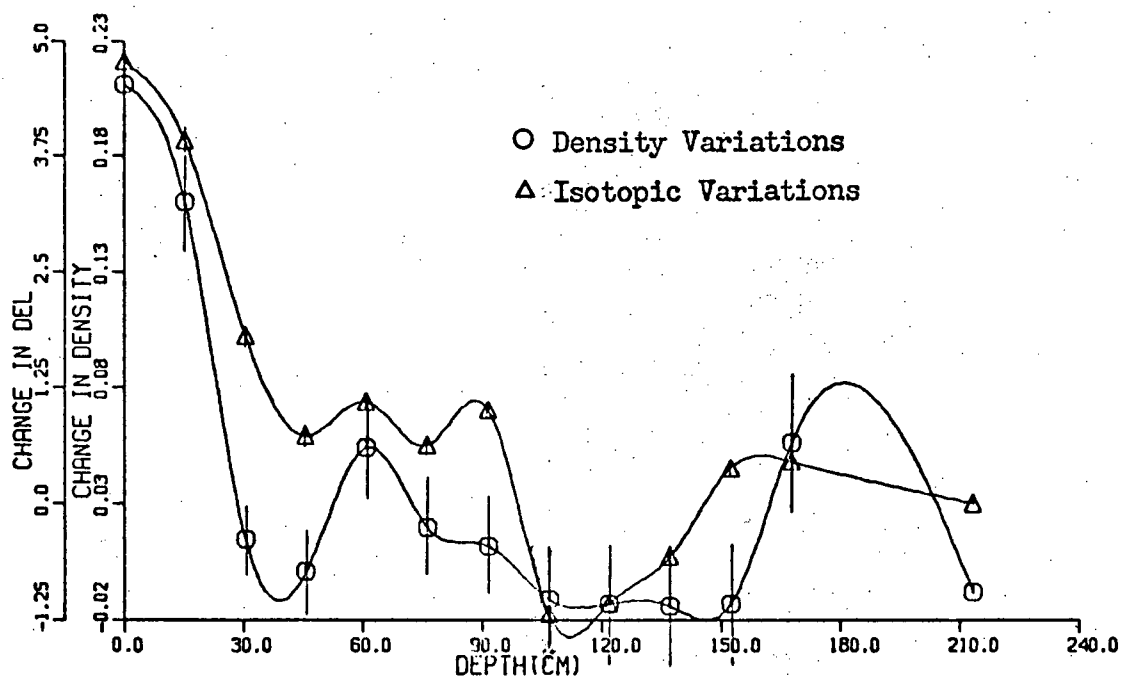


Figure 6.9 The Correlation Between Isotopic and Density Changes---T2

We conclude from the two tracing experiments in homogeneous, unlayered snow that, neglecting complicating effects of rapid density changes or stratigraphic features, the tracer simply freezes into the snowpack with little of the original pack melting. The colder the snowpack the more dominant is the effect. As snow approaches warmer temperatures the interaction between liquid and solid phases increases and displacement of material originally in the snowpack begins.

### 6.5 Isotopic Tracing Experiment---T3

The insertion of the acrylic snow tubes into the natural snow proved most difficult. By welding the stainless steel knife edges on the leading edge of the tubes, enough strength was obtained to allow the insertion

of the snow tube into natural snow. It should be noted that the acrylic tubes used in this portion of the experiment become quite brittle at sub-zero temperatures and therefore are probably not the best material to use in studies of this kind.

The original isotopic composition and densities were sampled by taking four aliquots of snow immediately outside the acrylic column at the depths corresponding to the locations of the access ports in the snow tubes. The retrieval of the snow samples from the stainless steel tubes normally required the use of a plunger to force the snow out into the collection bottle. This did not seem to affect the snow densities measured. It is possible that some systematic error was made in calculating the densities but this is only a supposition. It is important to note that the initial densities in experiment T3 are questionable. It is felt that the trend shown in the initial densities is correct but that the magnitudes are in error by some constant factor.

The data from this experiment are presented in Table 6.4. Since the initial densities were unrealizably small and difficulties existed in their determination, all initial densities were multiplied by 6.56 to force conservation of mass. These are probably the most realistic densities that can be obtained from the data.

The density and isotopic profiles are given in Figures 6.10 and 6.11 respectively. The initial density profile is

Depth cm	Time Hrs.	Density Before	Density After	DEL Before	DEL After
12.7		.190	.195	-18.00	-16.62
27.94	2.60	.210	.229	-15.40	-13.08
43.18	2.63	.249	.355	-14.84	-11.92
58.42	2.67	.236	.260	-20.72	-21.12
73.66	2.70	.262	.345	-11.47	-11.39
88.90	2.73	.295	.363	-12.14	-11.66
104.14	2.77	.295	.272	-11.39	-11.08
119.38		.308	.240	-10.00	-9.62

TABLE 6.4 SUMMARY OF DATA---T3

that obtained after multiplying by the scaling factor of 6.56.

The initial density profile shows a nearly linear density increase with depth. The density inversion near 60 cm may not be real if one considers magnitudes of the errors. The density profile after the tracer was applied clearly accentuates both the density increase at 45 cm and the density minimum at 60 cm. The isotopic profile indicates that essentially all the tracer froze out before reaching 60 cm depth, in very good agreement with the density data. The density decrease near 105 cm depth has no clear explanation and may be an error in sampling.

Two points need to be made concerning the results of



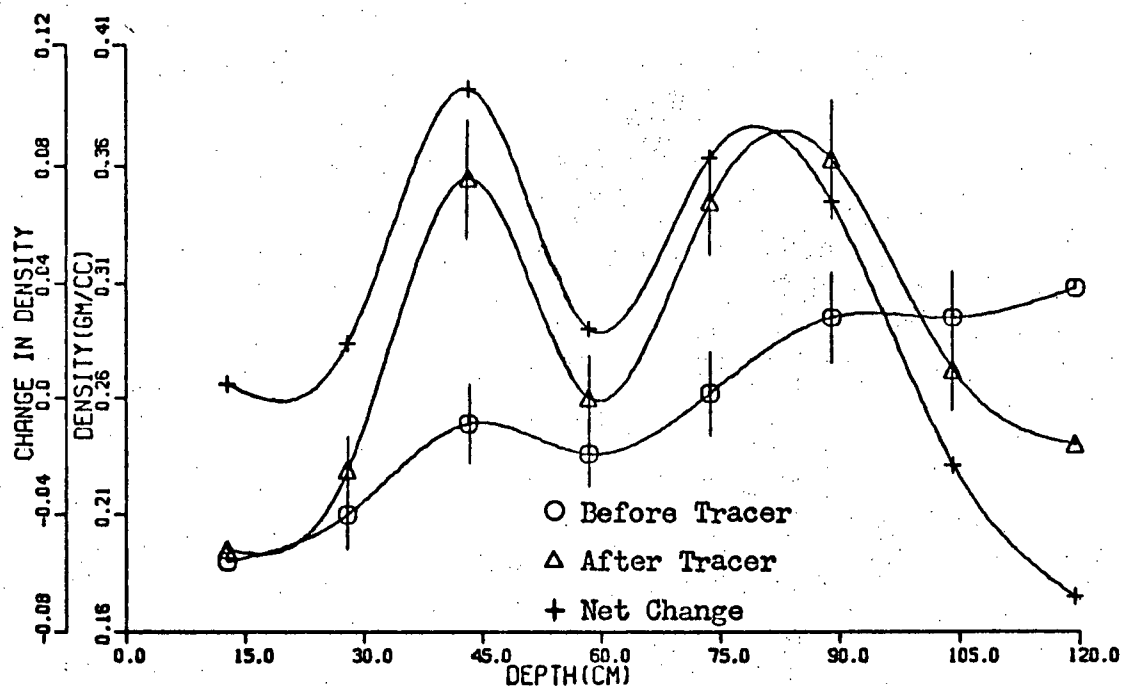


Figure 6.10 The Variation of Density with Depth---T3

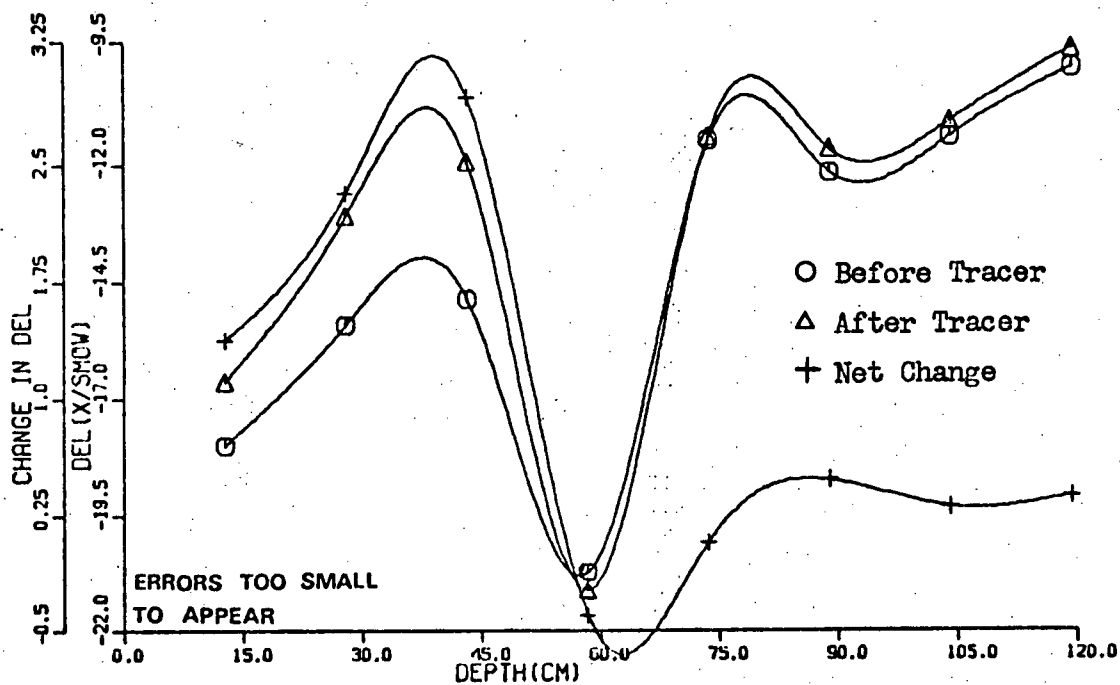


Figure 6.11 Isotopic Variations with Depth---T3

this experiment. First, it is evident that again density variations are causing enhancement of initial isotopic

features of the snow. The second point is that the isotopic results in cold snow consistently give very believable results, whereas it is much more difficult to obtain good density measurements using density tubes. It would seem easier to obtain isotopically good snow samples than samples with correct density information. This would support the use of stable isotopes in snow hydrology.

#### 6.6 Isotopic Tracing Experiment---PL2

A most informative experiment was conducted on March 3, 1974. By this time procedures had been developed and tested to such an extent that samples could be reliably collected. The snow being studied had fallen during the preceding week. It was apparently uniform in texture and no visible layering was found. By this time it had become obvious that water flow in this type of snow was predominately vertical and so sampling was done only in a single vertical column. The samples were collected at the positions shown in Figure 6.12. As is shown up to four aliquots were taken in some instances. The pit for this experiment had been dug the previous day to enable a longer interval of time to pass between application of the tracer and final sample collection.

March 3, 1974 was an extremely harsh day with temperatures of  $-8^{\circ}\text{C}$ , extremely high winds and heavy snows. For this reason the tracing experiment had to be cut short as conditions became unbearable for the researchers.

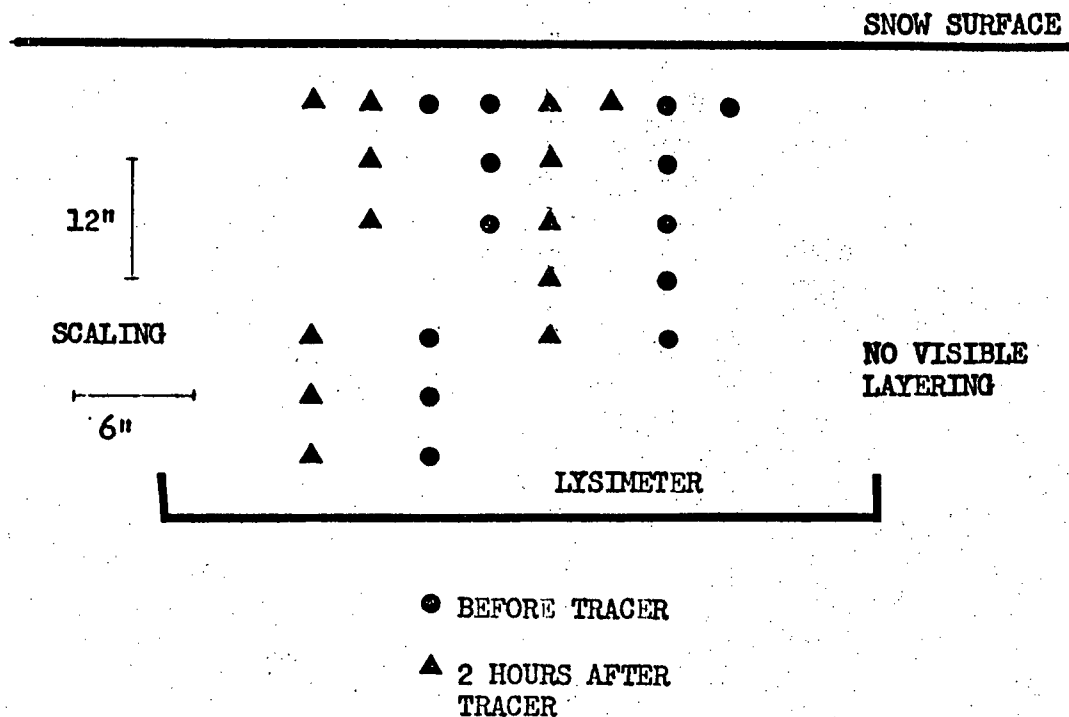


Figure 6.12 Positions of Samples Taken in Tracing Experiment PL2

Nevertheless results obtained from this experiment were extremely good.

The data collected in this experiment are presented in Table 6.5.

For the first time, temperatures were recorded before and after the tracer was applied. They proved to be a very useful indication of the progress of the liquid in the snowpack. The temperature profile from this experiment is given in Figure 6.13 and would seem to imply that a great deal of the tracer has accumulated in the top 40 cm of the snow.

The density information is displayed in Figure 6.14. As can be seen the initial density profile clearly manifests the homogeneity of the snowpack. The correlation

Depth cm	Time Hrs.	Density Before	Density After	DEL Before	DEL After
0.	-	.038	0.	-15.98	-17.18
15.24	1.65	.051	.034	-14.82	-15.04
30.48	1.72	.085	.153	-12.84	-9.07
45.72	1.82	.141	.119	-13.60	-10.89
60.96	1.92	.174	.247	-14.78	-14.78
76.20	2.04	.156	.196	-12.37	-11.73
91.44	2.14	.166	.233	-10.85	-11.03
106.68	2.25	.262	.340	-14.63	-15.49
124.46	-	.350	.423	-16.52	-17.72

TABLE 6.5 SUMMARY OF DATA---PL2

coefficient between initial density and depth is 0.95, which implies simple compression and few inhomogeneities. The most notable feature in the density profile after the tracer was applied is the abnormality at 45 cm depth. This is certainly unexpected since the composition of the snow was originally so uniform. Above 45 cm the correlation between initial and final densities is 0. Below 45 cm the correlation is quite high and the curves parallel each other extremely well. This high correlation implies errors in density measurements are much less than the accepted 7 percent.

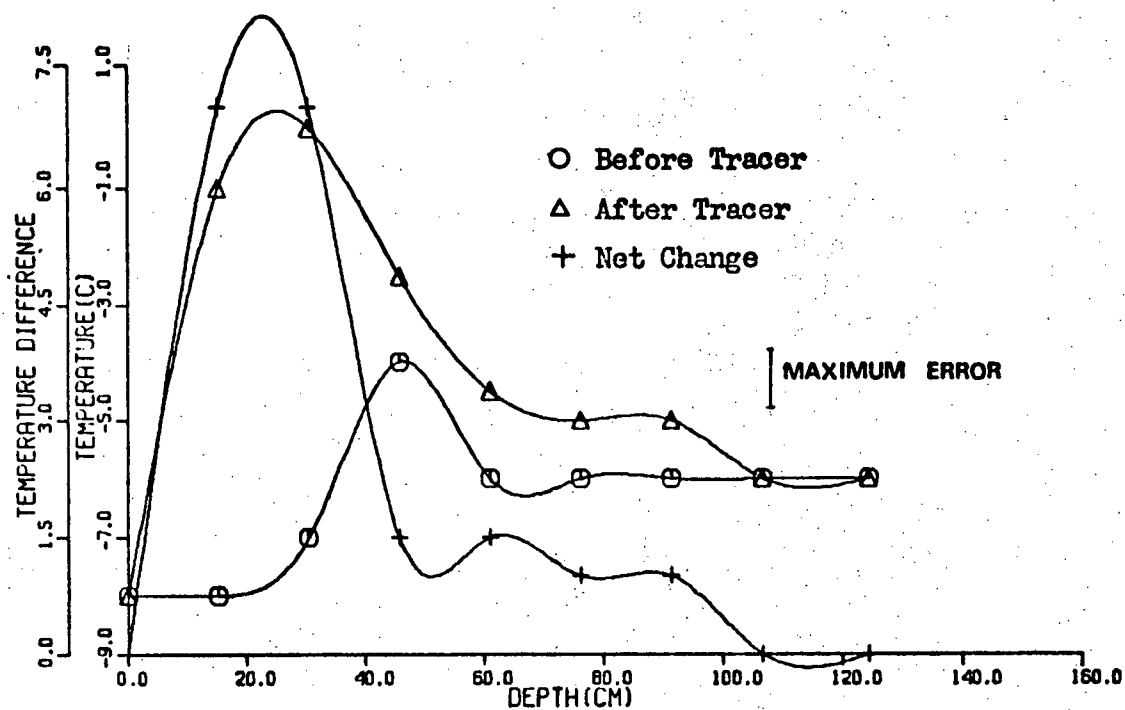


Figure 6.13 Temperature Profile for Experiment PL2

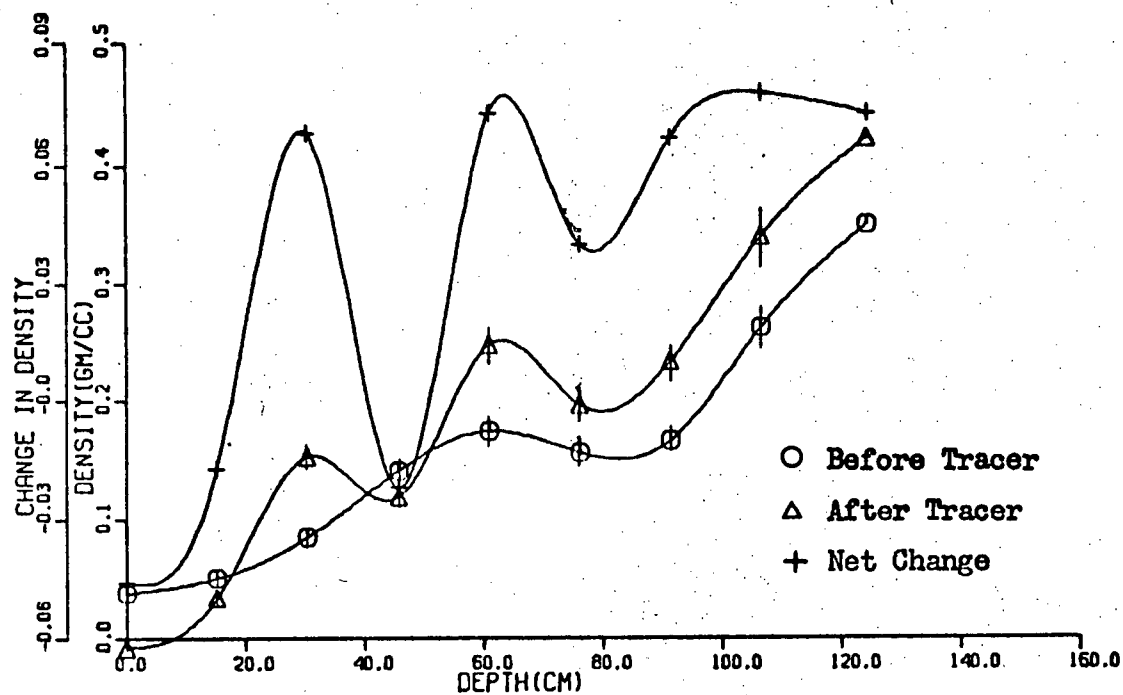


Figure 6.14 Density Variations with Depth---PL2

The isotopic results of this experiment are displayed

in Figure 6.15. Relatively large isotopic changes are

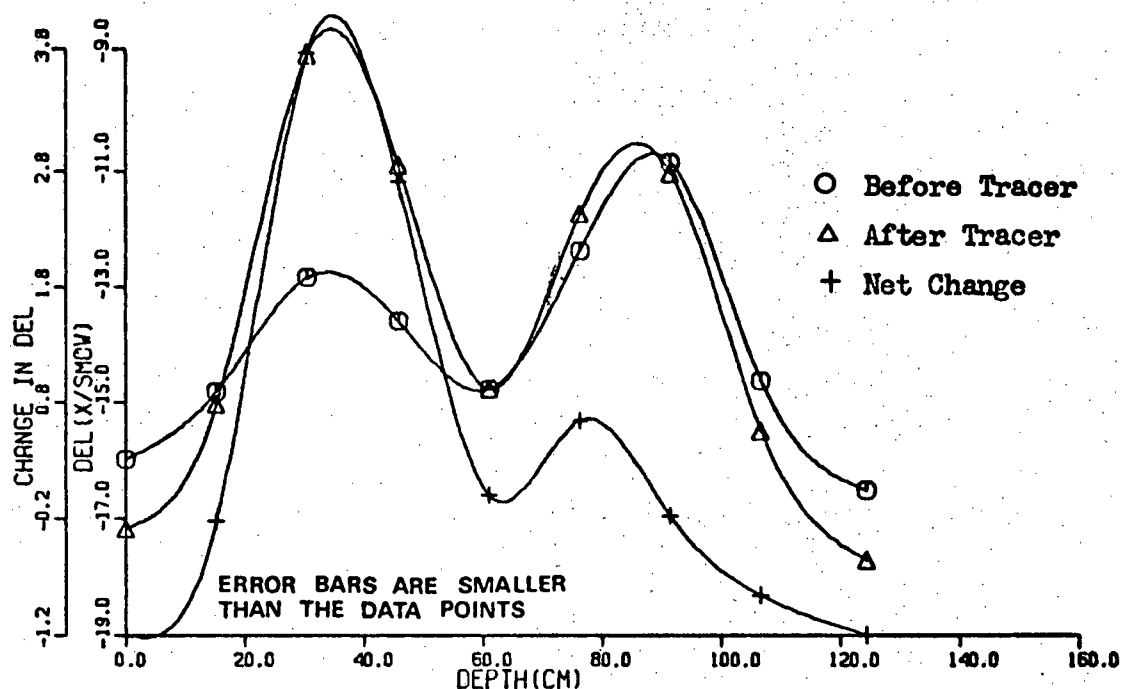


Figure 6.15 Isotopic Variations with Depth---PL2

evident in the first 50 cm of the snow column. Below 60 cm isotopic changes are smaller and, in general, negative. It would seem that the discontinuity in the density profile at 45 cm is indeed affecting the distribution of the isotopes. As in the other experiments isotopic peaks were enhanced when water passed through the snowpack. It is interesting that the isotopic maximum at 30 cm is enhanced much more than the maximum at 90 cm even though the latter peak was initially twice as large as the upper peak. This seems to indicate that some parameter must have been different during the tracing experiment than during the percolation that caused the original profile. The temperatures encountered on this day were much lower than most temperatures of the

previous week and therefore reduced penetration of the pack is to be expected.

Figure 6.16 allows easy comparison of isotopic changes and density changes. Again something peculiar happens at 45

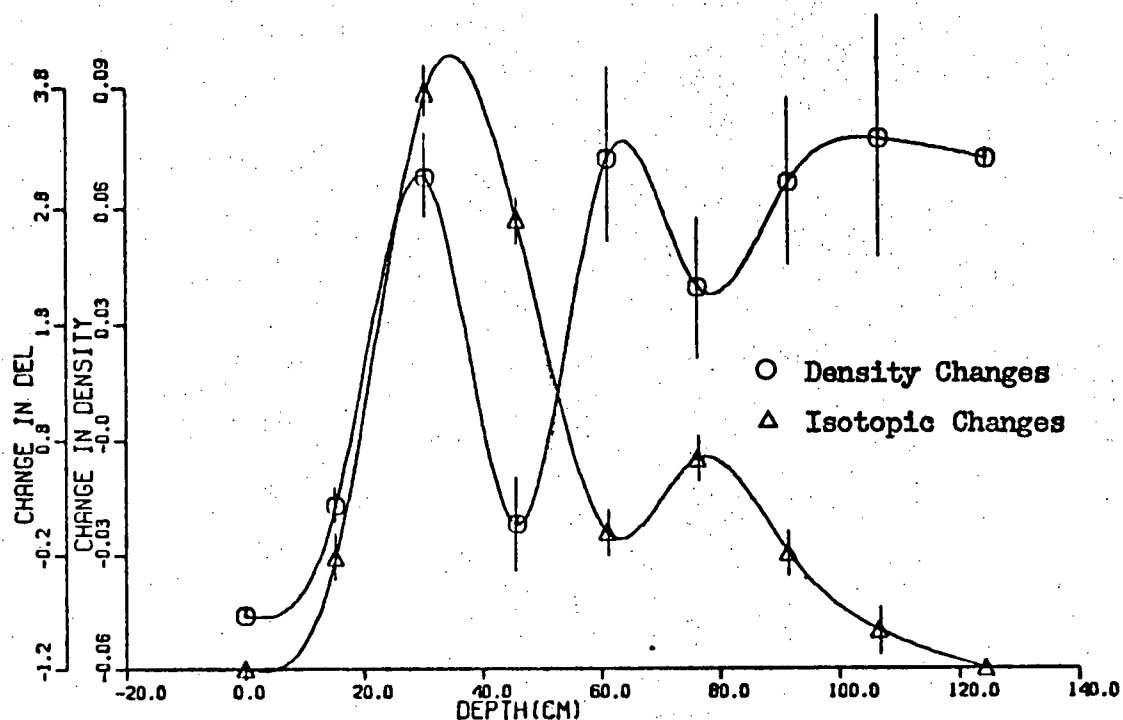


Figure 6.16 Correlation Between Isotopic Changes and Density Changes---PL2

cm depth. Above 45 cm the correlation between the two curves is 0.79 implying that most of the increase in density is a result of the original tracer freezing. Below 45 cm depth the correlation is -0.80. This means that isotopically light water generated in the upper 45 cm of snow is refreezing at the lower depths causing increased density but a smaller  $O^{18}/O^{16}$  ratio. The temperature profile tends to support this observation since heat was transported below the 45 cm depth. The source of the heat could easily be that given off as the liquid freezes.

### 6.7 Isotopic Tracing Experiment---PL3

The final tracing experiment was conducted on March 23, 1974. Relatively warm weather occurred just before this date and as a result a great deal of meltwater had penetrated into the snowpack. The meltwater created several stratigraphic layers of substantial size as shown in Figure 6.17. The liquid content of the snowpack was high enough to

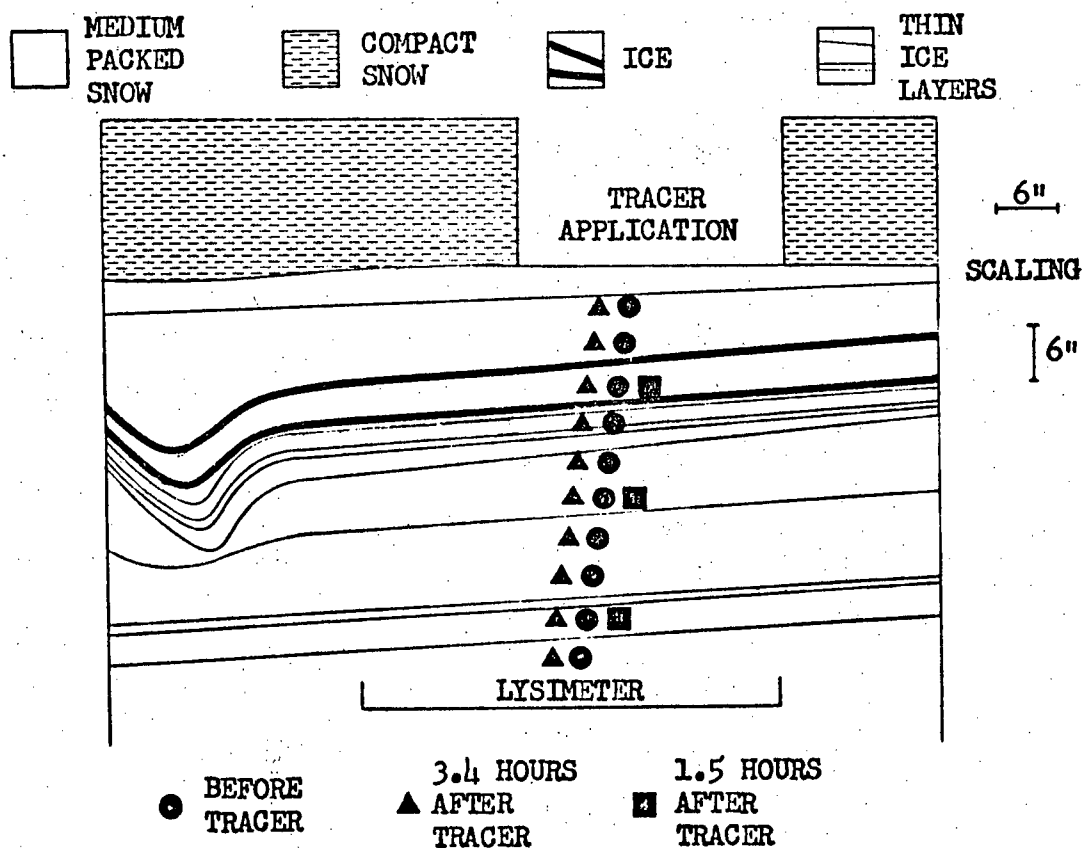


Figure 6.17 Snow Stratigraphy and Sample Location---PL3

create an isothermal snowpack at  $0^{\circ}\text{C}$ . The stratigraphic horizons were not horizontal but were oriented in such a way as to cause water to move away from the pit wall and to the left of the figure. For this reason the samples were taken



at an angle to the vertical.

The densities encountered in this final experiment far exceeded any of the previous experimental values. The densities were typically  $.45 \text{ gm/cm}^3$  and this introduced a problem with the amount of tracer applied. Approximately 150 kilograms of snow existed in the portion of the snowpack studied. The amount of tracer applied was only 14 kilograms. This ratio of nearly eleven times more snow than tracer should be compared with experiment PL2 where the ratio was a more reasonable five and one-half.

The results of this experiment are nearly uninterpretable. The data are presented in Table 6.6. The isotopic and density variations with depth are shown in Figures 6.18 and 6.19 respectively. Initially the isotopic composition tends to decrease with depth which is what one would expect if meltwater (isotopically light) formed in the upper part of the snow column, percolated to lower depths and refroze. At depths greater than 50 cm the net isotopic change is near zero implying that little of the original tracer percolated past that depth.

The initial density profile shows a gradual increase in density with depth. The density profile after application of the tracer oscillates erratically and displays no obvious characteristics. Possibly some insight into the water flow pattern is found by direct comparison of the density and isotopic variations shown in Figure 6.20. The correlation between the two curves above 45 cm is  $-0.83$ . Below that

Depth cm	Time Hrs.	Density Before	Density After	DEL Before	DEL After
0.	-	.469	.528	-10.92	-10.79
10.16	3.10	.416	.411	-11.59	-11.20
20.32	3.16	.334	.239	-12.57	-11.59
30.48	1.46	.352	.427	-12.10	-12.48
30.48	3.21	.352	.345	-12.10	-11.13
40.64	3.26	.402	.557	-13.17	-15.40
50.80	3.33	.417	.494	-13.39	-12.98
60.96	1.56	.431	.472	-14.06	-14.62
60.96	3.41	.431	.397	-14.06	-14.26
71.12	3.48	.333	.384	-13.01	-13.08
81.28	3.53	.378	.448	-12.67	-12.26
91.44	1.61	.444	.552	-14.05	-14.13
91.44	3.58	.444	.269	-14.05	-13.97
101.60	3.63	.437	.367	-14.04	-14.14

TABLE 6.6 SUMMARY OF DATA---PL3

depth the correlation reduces to +0.3. The stratigraphic profile shows the presence of many closely packed ice layers just above 45 cm depth which can possibly explain the abrupt change in correlation. Since the correlation coefficient in the upper 45 cm is negative it means that the isotopic tracer never penetrated into the pack. The quarter inch

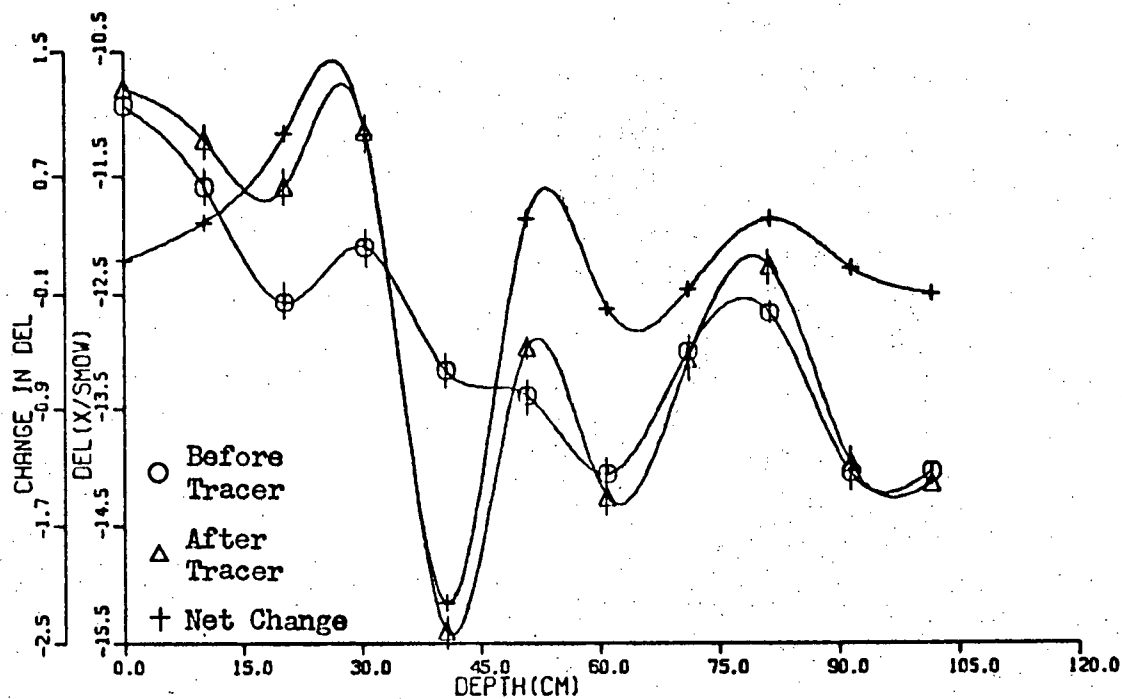


Figure 6.18 Isotopic Composition as a Function of Depth---PL3

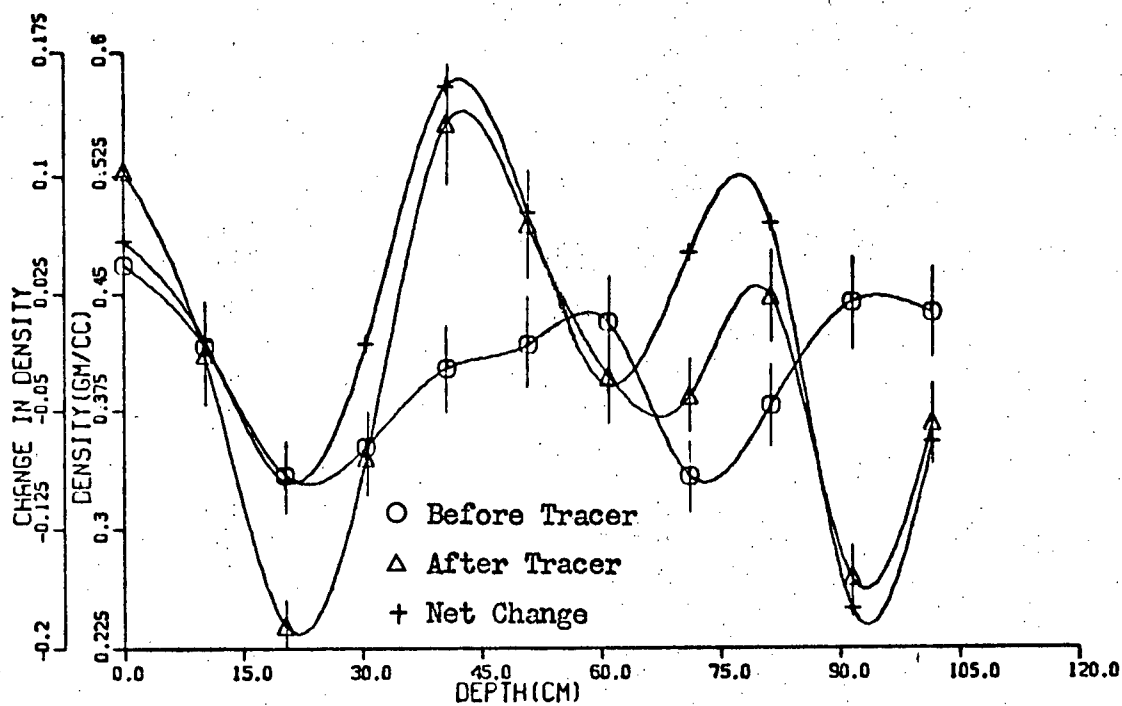


Figure 6.19 Density Variations as a Function of Depth---PL3

thick ice layer four inches below the surface of the snow

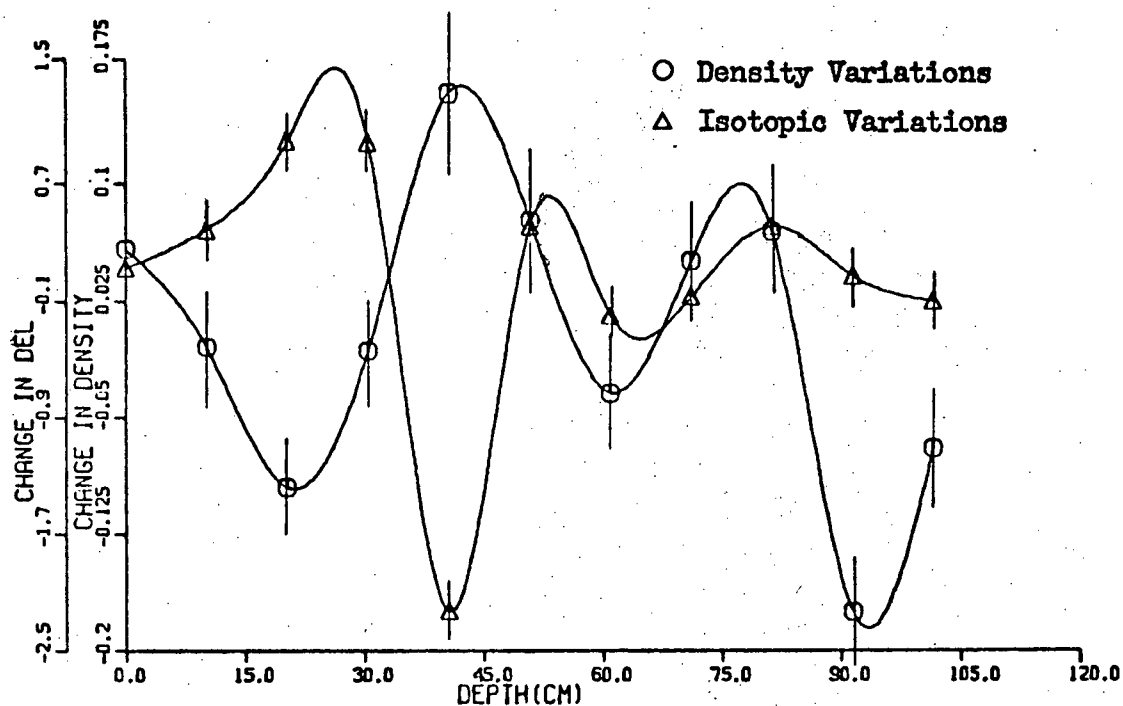


Figure 6.20 The Correlation Between Isotopic and Density Changes---PL3

most probably caused the tracer to flow horizontally and therefore the tracer did not penetrate into the sampled snow. The observed isotopic differences in the upper 45 cm of snow must still be explained.

The temperature of the applied tracer was  $+4^{\circ}\text{C}$ , higher than usual. Since the snowpack was already at  $0^{\circ}\text{C}$  the heat from this tracer most likely melted a portion of the original snow. This would result in 700 grams of liquid that could be as much as 3 DEL units lighter than the original snow. The large minimum near 40 cm may be a result of this water refreezing.

The conclusions reached in this experiment are highly speculative but do seem to indicate that very little tracer penetrated the snowpack. The presence of horizontal layers

would seem to make artificial tracing experiments inappropriate.

#### 6.8 Isotopic And Mass Balance In The Artificial Tracing Experiments

An important consideration in any tracing experiment is to see if the tracer can be accounted for. In an isotopic tracing experiment one should be able to account for both the mass and the isotopic species if he has chosen the correct physical model.

The model used in this experiment was as simple as possible. The tracer was assumed to flow downward, diverging in all directions at an angle,  $\theta$ . Since the tracer was distributed over a rectangular area the snow affected by the tracer occupies the lower portion of a rectangular pyramid. The cross-sectional view of the model is shown in Figure 6.21.

When the diverging tracer intersects the pit wall, it is assumed that the tracer stays within the snowpack and is not lost. It is clear that the sample tubes collect some snow that has not been altered by the tracer. For this reason a mixing correction was applied to data where applicable. In this manner the isotopic composition and densities actually correspond to the snow within the pyramid.

To test for conservation of mass it is only necessary to compute the mass of snow within the pyramid both before

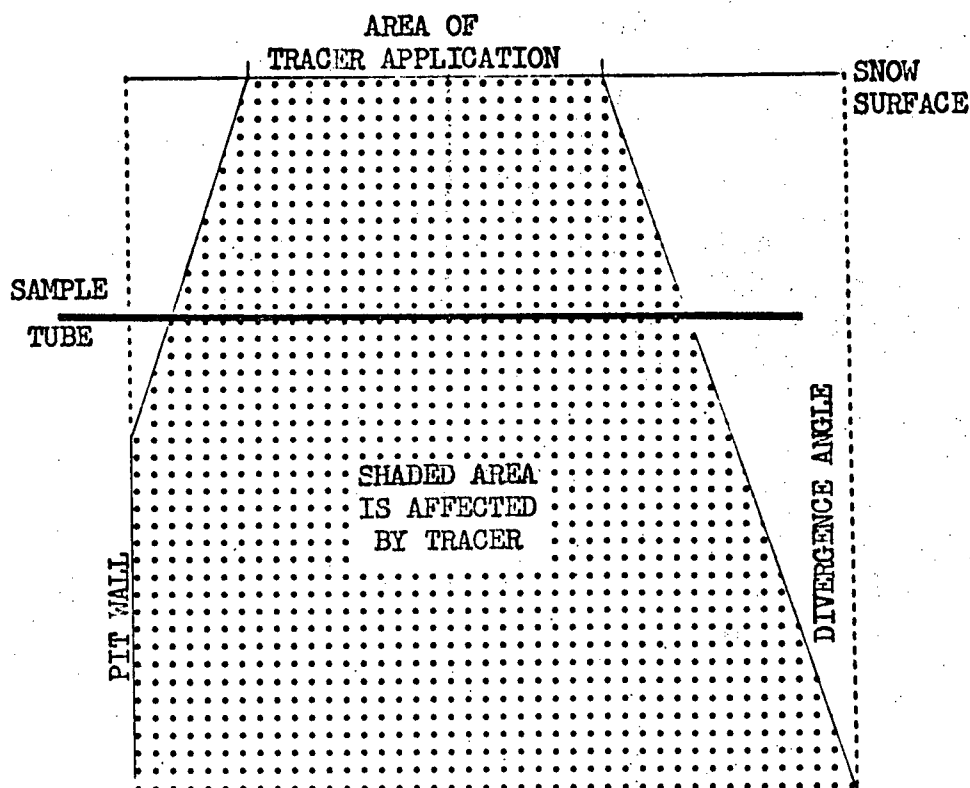


Figure 6.21 The Physical Model Used in the Study of Water Flow

and after the tracer was applied. The computation was done using a cubic spline integration of the density data. Since the initial densities in the three experiments utilizing the acrylic sample columns were either not measured or questionable, conservation of mass was forced. The results of the mass balance calculations are presented in Table 6.7.

As can be seen, the mass in experiment PL2 is within 5% of the expected value. Since it was a more complicated system than any of the acrylic tube experiments (T), it seems reasonable to make the assumption of conservation of mass in those cases to obtain initial densities. As can also be seen, only 2.6% of the tracer stayed within the closed system in experiment PL3. The above calculations are

	T1	T2	T3	PL2	PL3
initial mass	48.9	43.9	25.5	113.0	148.4
final mass	55.9	51.1	28.9	140.7	148.8
tracer mass	7.07	7.07	3.43	20.37	14.00
% mass yield	100	100	100	105	92

\*all masses are in kilograms

TABLE 6.7 CONSERVATION OF MASS CONSIDERATIONS  
FOR FIVE TRACING EXPERIMENTS

those obtained assuming no divergence of the tracer, (i.e. vertical flow).

The demonstration of conservation of isotopic species is slightly more complicated. Using the result of Appendix III we see that if isotopic species are conserved:

$$\text{DEL(AFTER)} = \frac{\text{MASS(TRACER)}\text{DEL(TRACER)} + \text{MASS(SNOW)}\text{DEL(SNOW)}}{\text{MASS(TRACER)} + \text{MASS(SNOW)}} \quad [6.1]$$

The mass and DEL value of the tracer were measured directly. The mass of snow was determined by integrating the initial densities. The initial DEL of the snow is calculated by integrating the product of initial density, cross-sectional area and DEL over all depths. The integral is normalized by dividing by the initial mass. The average DEL value after the tracer was applied was calculated in a similar manner.

The results of the above calculations are presented in Table 6.8.

The results indicate that the proposed model is too simple. Neglecting PL3, an average of one-third of the

	T1	T2	T3	PL2	PL3
tracer mass	7.07	7.07	3.43	20.37	14.00
DEL tracer	-1.47	-1.31	-1.30	-0.73	-1.02
initial mass	48.9	43.9	25.5	113.0	148.4
initial DEL	-16.25	-16.61	-13.93	-13.95	-12.94
final DEL	-15.36	-15.80	-13.06	-13.63	-12.93
DEL eqn. 6.1	-14.38	-14.49	-12.43	-11.93	-11.91
O <sup>18</sup> yield	47.3%	38.2%	58.3%	16.2%	1.0%

\* all masses in kilograms

\*\* all DEL values relative to IAEA SMOW

TABLE 6.8 ISOTOPIC CONSERVATION IN TRACING EXPERIMENTS

tracer can be accounted for. This implies that a large fraction of the tracer must run down the edge of the acrylic sampling tubes and flow horizontally in the case of PL2. It is interesting that the results of PL3 indicate nearly complete loss of the tracer as was inferred in the previous section. It is important to note that the low yield does not change any of the conclusions reached but only means the model chosen was too simple. Use of the correct model would not change the qualitative description of water flow in snow.

## 6.9 Conclusions

Several different types of snow were studied in this project. The results of five tracing experiments in sub-zero snowpacks gave consistent results and several conclusions can be reached. In the three situations where natural snow with layering was studied, the isotopic peaks



were enhanced, which implies, the original isotopic profile was a manifestation of earlier water movement in the pack. The locations of these isotopic peaks can be explained in terms of density variations and/or locations of stratigraphic layers.

The above point is very important. Seasonal variations in the isotopic composition of precipitation have been used to study yearly accumulation of snow and climatological changes over many centuries (Morner, 1972 Dansgaard et al., 1969). However this project indicates that either rain or meltwater on a sub-zero snowpack can produce isotopic maxima and minima that could be falsely identified as yearly snowfall.

The power of tracing water movement with stable isotopes was clearly demonstrated. In conjunction with density changes and temperature changes, the stable isotopes provide insight into what actually happened in the snowpack. Density measurements alone could not have distinguished what effects were due to the original tracer and what effects were caused by liquid released by the heat in the tracer. It is also clear that dye experiments are incapable of clearly identifying effects caused by melted snow from the snowpack.

It can be speculated that the horizontal component of water flow cannot be neglected even in uniform snow. The loss of a portion of the tracer in all the experiments indicates substantial horizontal flow.

Although isotopic measurements require much more time and effort than density measurements, they seem to be much more reliable. It is relatively easy to obtain a good isotopic sample but it was found difficult to acquire reliable densities. Further investigations into the problem of water flow in snow would be well advised to monitor densities with a profiling density gauge rather than with density tubes.

Much remains to be done in the study of water flow in natural snow. This project has demonstrated the importance of using stable isotopes if complete understanding is desired.

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## APPENDIX I Property of the DEL Function-Combination

Given DEL (A/B) and DEL (B/C) find DEL (A/C)

where A, B and C represent different water standards with  $O^{18}/O^{16}$  ratios of  $R_a$ ,  $R_b$  and  $R_c$  respectively.

$$\text{DEL (A/B)} = (R_a/R_b - 1)10^3 \quad [\text{A1.1}]$$

$$\text{DEL (B/C)} = (R_b/R_c - 1)10^3 \quad [\text{A1.2}]$$

from A1.1 and A1.2 it is clear that:

$$R_a = R_b [\text{DEL (A/B)} + 10^3] / 10^3 \quad [\text{A1.3}]$$

$$R_b = R_c [\text{DEL (B/C)} + 10^3] / 10^3 \quad [\text{A1.4}]$$

from A1.4 we obtain the following:

$$R_c = 10^3 R_b / [\text{DEL (B/C)} + 10^3] \quad [\text{A1.5}]$$

from A1.3 and A1.5 we obtain:

$$R_a/R_c = [\text{DEL (A/B)} + 10^3] [\text{DEL (B/C)} + 10^3] / 10^6 \quad [\text{A1.6}]$$

$$\text{DEL (A/C)} = (R_a/R_c - 1) 10^3 \quad [\text{A1.7}]$$

$$\text{DEL (A/C)} = [(\text{DEL (A/B)} + 10^3) (\text{DEL (B/C)} + 10^3) / 10^6 - 1] 10^3 \quad [\text{A1.8}]$$

$$\text{DEL (A/C)} = \text{DEL (A/B)} + \text{DEL (B/C)} + \text{DEL (A/B)} \text{DEL (B/C)} / 10^3 \quad [\text{A1.9}]$$

## APPENDIX II Property of the DEL Function-Inversion

Given DEL(A/B) find DEL(B/A)

$$\text{DEL}(A/B) = (R_a/R_b - 1) 10^3 \quad [A2.1]$$

$$R_a/R_b = [\text{DEL}(A/B) + 10^3] / 10^3 \quad [A2.2]$$

$$R_b/R_a = 10^3 / [\text{DEL}(A/B) + 10^3] \quad [A2.3]$$

$$(R_b/R_a - 1) 10^3 = \{ [-\text{DEL}(A/B)] / [\text{DEL}(A/B) + 10^3] \} 10^3 \quad [A2.4]$$

$$\text{DEL}(B/A) = -10^3 \text{DEL}(A/B) / [\text{DEL}(A/B) + 10^3] \quad [A2.5]$$

## APPENDIX III Isotopic Mixing of Two Water Samples

If one combines two isotopically different water samples, the isotopic composition of the mixture will lie between the isotopic compositions of the original liquids. The question before us then is to determine the isotopic ratio of the mixture, given the relative amounts of the original liquids and their isotopic compositions.

Define the following quantities:

$x$  = number of milliliters of liquid A in mixture

$y$  = number of milliliters of liquid B in mixture

$p$  = number of  $O^{18}$  atoms per milliliter in liquid A

$q$  = number of  $O^{16}$  atoms per milliliter in liquid A

$r$  = number of  $O^{18}$  atoms per milliliter in liquid B

$s$  = number of  $O^{16}$  atoms per milliliter in liquid B

The  $O^{18}/O^{16}$  ratios of liquids A and B are then:

$$R(A) = p/q \quad [A3.1]$$

$$R(B) = r/s \quad [A3.2]$$

Now assume that the number of water molecules is constant in any given volume of water:

$$p+q=r+s \quad [A3.3]$$

The isotopic ratio of the mixture is:

$$R(M) = (xp+yr)/(xq+ys)$$

dividing numerator and denominator by  $q$  gives:

$$R(M) = (xa+yb)/(x+yc) \quad [A3.4]$$

where  $a=p/q$ ,  $b=r/q$  and  $c=s/q$ . From equations A3.1, A3.2 and

A3.3 it follows that:

$$R(A)=a, \quad R(B)=b/c \quad \text{and} \quad a=b+c-1 \quad [A3.5]$$

Equations A3.5 can be solved for a, b and c giving

$$a=R(A)$$

$$b=R(B)[R(A)+1]/[R(B)+1] \quad [A3.6]$$

$$c=[R(A)+1]/[R(B)+1]$$

inserting equations A3.6 into A3.4 gives:

$$R(M) = \frac{\{xR(A)[R(B)+1] + yR(B)[R(A)+1]\}}{\{x[R(B)+1] + y[R(A)+1]\}} \quad [A3.7]$$

which is the desired result.

A useful approximation for  $R(M)$  can be made if the ratios are small as in the case of  $O^{18}/O^{16}$  (i.e.  $R \leq 1/450$ ). Making this approximation we obtain:

$$R(M) = [xR(A) + yR(B)]/[x+y] \quad [A3.8]$$

since we normally determine DEL values relative to a standard having isotopic ratio  $R(S)$  we can rewrite A3.8 in terms of  $DEL(A)$ ,  $DEL(B)$  and  $DEL(M)$  where:

$$DEL(A) = [R(A)/R(S) - 1]10^3$$

with similar expressions for  $DEL(B)$  and  $DEL(M)$ . From A3.8

$$R(M)/R(S) - 1 = \{x[R(A)/R(S) - 1] + y[R(B)/R(S) - 1]\}/[x+y]$$

multiplying both sides by  $10^3$  gives:

$$DEL(M) = [xDEL(A) + yDEL(B)]/[x+y] \quad R \ll 1 \quad [A3.9]$$

## APPENDIX IV Isotopic Fractionation and Rayleigh Distillation

In many cases where molecules are being transported from one system to another, it is possible for the molecular species to be transferred at different rates. This often results in changes in isotopic ratios between systems.

If we let  $x$  represent the number of one species of molecule and  $y$  represent the number of another type of molecule in the original sample we can make the following definitions:

$$s = x + y \quad [A4.1]$$

where  $s$  is the number of molecules in the system at any time and:

$$r = y/x \quad [A4.2]$$

where  $r$  is the isotopic ratio in the system.

If we assume one molecular species leaves at a different rate than the other species it is clear that the isotopic ratio of the molecules leaving the system at any instant will not be equal to the isotopic ratio in the system. Mathematically this can be written as:

$$y/x = f \, dy/dx \quad [A4.3]$$

where  $dy/dx$  is the isotopic ratio of the molecules leaving the system and  $f$  is the separation constant.

It should be clear that due to fractionation the isotopic composition of the original system will change as

molecules are removed from the system. Using equations A4.1, A4.2 and A4.3 it is a straightforward calculation to solve for the isotopic ratio of the molecules in the system as a function of the fraction of the original number of molecules remaining in the system:

$$\ln[s/s^0] = f \ln[r/r^0]/[1-f] + \ln[(r+1)/(r^0+1)] \quad [A4.4]$$

where the superscript <sup>0</sup> indicates initial values. The above equation can be solved for  $r$  numerically using the Newton-Raphson method. If the ratios in equation A4.4 are much less than unity then A4.4 reduces to:

$$(r/r^0)^{\alpha/(1-\alpha)} = s/s^0 \quad r \ll 1 \quad [A4.5]$$

For oxygen isotopes this approximation is valid and equation A4.5 tells us what  $r$  is as a function of  $s/s^0$ , the fraction of molecules remaining in the system. This calculation was first suggested by R.D. Russell.

Often we are interested in determining the isotopic ratio of the molecules that have left the original system instead of the ratio of those that have remained.

If we let  $q$  represent the isotopic ratio of all molecules that have left the original system we can use the result of Appendix III (A3.8) to write:

$$[sr + (s^0 - s)q]/s^0 = r^0 \quad r \ll 1 \quad [A4.6]$$

which is merely a statement of conservation of isotopic species. From A4.6 we write:

$$q/r^0 = [1 - sr/(s^0 r^0)]/[1 - s/s^0] \quad r \ll 1 \quad [A4.7]$$



substituting A4.5 into A4.7 gives:

$$q/r^0 = [1 - (s/s^0)^{1/\alpha}] / [1 - s/s^0] \quad r \ll 1 \quad [A4.8]$$

which is the final result.

Equations A4.5 and A4.8 can be used in many different situations one of which would be a Rayleigh Distillation process where the isotopic ratio of water vapor may be calculated as a function of the amount of the original reservoir that has evaporated.

## APPENDIX V Determination of a "Best" Weighting Function

In many studies several experimental estimates of a single value are obtained. Often it is felt that some of these estimates are more reliable than others and for this reason more importance should be given to them. The logical thing to do is to apply some weighting function to the data that is related to the analytical precision of the various estimates.

In this study we wanted to maximize the precision of the DEL values obtained, which is the same thing as minimizing the variance of the estimates. The weighting function to be applied was determined as follows.

It is commonly known (p. 168 Hogg and Craig) that if we define the weighted mean  $Y$  as follows:

$$Y = \sum w_i x_i \quad [A5.1]$$

where the  $w$ 's are the weights and the  $x$ 's the individual estimates, then the variance of  $Y$  is:

$$\sigma^2 = \sum (w_i \sigma_i)^2 \quad [A5.2]$$

if the correlation coefficient between the  $x$  estimates is zero (i.e. random sampling).

Making the usual constraint that the sum of the weights is equal to unity we write:

$$H(w_i, \lambda) = \sum (w_i \sigma_i)^2 - \lambda (\sum w_i - 1) = 0 \quad [A5.3]$$

where  $\lambda$  is a Lagrangian multiplier. Minimizing 5.3 with

respect to the weights and the multiplier will give an expression for  $W$  that minimizes the variance of the weighted DEL value determined by equation A5.1. Performing the necessary calculus gives:

$$W_K = [1/(\sigma_K)^2] / [\sum (1/\sigma_i)^2] \quad [A5.4]$$

which is the weighting function that maximizes the precision of the weighted DEL value.

In the case where all  $\sigma$ 's are equal we see that:

$$W_i = 1/n \quad [A5.5]$$

where  $n$  is the number of estimates. Likewise the variance of the weighted DEL value will be:

$$\sigma^2(Y) = (\sigma_i)^2/n \quad [A5.6]$$

which is just the standard error of the mean.

The weighting function of equation A5.4 was used for all estimates of DEL in this project. The  $\sigma_i$ 's were taken to be the analytical standard deviations of the mass spectrometer analyses.

APPENDIX VI Property of the DEL Function-Error Propagation  
Due to Errors Existing in the Apparent Ratios

At times it is possible for some factor to affect only one of the ratios in the determination of DEL, resulting in an error. That is to say that the measured DEL is given by:

$$\text{DEL (M)} = [kR_x/R_s - 1]10^3 \quad [\text{A6.1}]$$

when the true DEL value should have been:

$$\text{DEL (T)} = [R_x/R_s - 1]10^3 \quad [\text{A6.2}]$$

from A6.2 we see that:

$$R_x/R_s = \text{DEL (T)} / 10^3 + 1 \quad [\text{A6.3}]$$

$$kR_x/R_s = k\text{DEL (T)} / 10^3 + k \quad [\text{A6.4}]$$

$$\text{DEL (M)} = [k\text{DEL (T)} / 10^3 + (k-1)]10^3 \quad [\text{A6.5}]$$

$$\text{DEL (M)} = k\text{DEL (T)} + (k-1)10^3 \quad [\text{A6.6}]$$

$$\text{DEL (T)} = \text{DEL (M)} / k - (k-1)10^3 / k \quad [\text{A6.7}]$$

Equations A6.6 and A6.7 can often be used to determine the error that results in measuring isotopic ratios incorrectly. These results are most useful in determining the effect that various errors in analyses have on the resulting DEL values.