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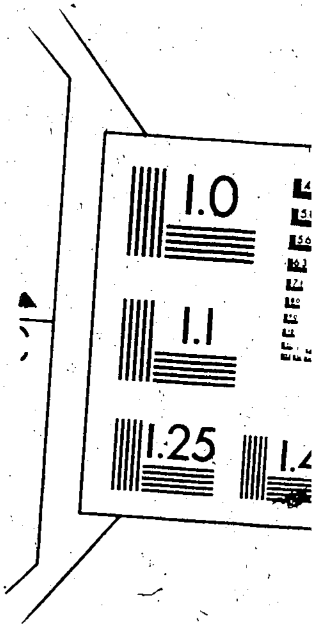

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FURTHER WORK ON THE OXYGEN-18 CONCENTRATION IN ATMOSPHERIC WATER SUBSTANCE IN CENTRAL ALBERTA

by

DAVID CHARLES ELLIS

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
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DEPARTMENT OF GEOGRAPHY

EDMONTON, ALBERTA
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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "Further Work on the Oxygen-18 Concentration in Atmospheric Water Substance in Central Alberta", submitted by David Charles Ellis in partial fulfilment of the requirements for the degree of Master of Science in Meteorology.

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Supervisor

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Edward Lozowski

Date April 2, 1979

ABSTRACT

During the 1970's at the University of Alberta, theses dealing with the oxygen-18 concentration in meteoric waters have been written by three previous authors. The present study is a direct continuation of the work of Sandhu (1978). Water vapour, rain, small hail and graupel were sampled on days with thundershowers in central Alberta. Oxygen-18 content was determined by mass spectrometry. The purpose of this thesis was to evaluate the collected data, and to test the feasibility of using these ground-level measurements, with a theoretical isotopic cloud model, to study the processes of precipitation formation.

A recapitulation of the cloud models is given in Chapter II. Table 2.1 on page 18 lists the models and summarizes their various constraints. A very simple model, defined by Equation (2.9) on page 23, has been used to convert the measured isotopic del-values to cloud condensation temperatures. These formation temperatures are contained in Table 4.3 for rain, and in Table 4.4 for graupel. A graphical comparison is shown in Figure 4.5 on page 68.

Short-term variations were discovered in the water vapour del-values so that the reliability of the vapour measurements became, and remains, an important question. Consequently the use of the theoretical models for individual showers was seriously hampered. The formation temperatures of the graupel

samples ranged from 0°C to -20°C with a fairly uniform distribution. The rain samples were more numerous than their graupel counterparts, but they suffered varying amounts of evaporative enrichment during their descent from cloud to ground. Possible corrective measures have been suggested in Chapter V for the rain del-values.

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A number of persons other than the author had worked on the research presented in this thesis before it came to my attention. I wish to acknowledge with gratitude Dr. R. B. Charlton and Dr. H. S. Sandhu for their sampling work during stormy weather in central Alberta. Dr. John Gray and his colleagues in the Physics Department of the University of Alberta did the laboratory preparations and the mass spectrometer analyses. The study was funded for 5 years by the National Research Council of Canada.

I wish to thank Dr. R. B. Charlton again, this time for the part he played as my supervisor. He accepted me when others did not, and, initially, it was he who proposed the use of the model specified by Equation (2.9). His belief that even simple surface measurements could yield information about precipitation formation was a constant source of encouragement to me as we developed the experimental data into a six-chapter thesis.

Dr. K. D. Hage should receive the credit for much of the work in Section 5.1. It was unpublished previous work by him which motivated me to attempt Chapter V. His predilection for statistics is reflected, in fact, throughout the thesis.
Dr. E. P. Lozowski supplied the initiative for organizing the oral examination.

The Geography Department and especially the Cartography Division, led by Mr. G. A. Lester, were extremely helpful in the preparation of the final draft. The Canadian Atmospheric Environment Service and members of the University's Extension Library also provided help for which I am truly grateful. Finally of course, I must thank my typist, Ms. Lynda Raffin, who typed and re-typed the manuscript, remained calm in the face of deadlines, and in my opinion, graduated with honours to the rank of "Mathematical Typist".

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a	radius of a spherical waterdrop
b	slope of a regression line
c	shape factor of a log-normal distribution, $c^2 = \text{var}\ (\ln x)$
c_p	specific heat capacity at constant pressure
c_v	specific heat capacity at constant volume
C	constant of integration in the approximate form of the Clausius-Clapeyron Equation
$\frac{d}{d\tau}$	time rate of change
D	diffusivity of water vapour, $H_2{}^{16}O$
D'	diffusivity of water vapour, $H_2{}^{18}O$
D4	an isotopic cloud model involving a purely hypothetical Rayleigh condensation (Dansgaard, 1964)
e	natural base of logarithms
f	a function
F_v	fraction of remaining water vapour
F_w	fraction of remaining water
F_{vent}	ventilation factor ≃ 1.1
h	relative humidity
H	height of cloud base above ground
i	index used in Equation (5.5); $i = \frac{1 - \alpha_{18}\alpha_K(1 - h)}{\alpha_{18}\alpha_K(1 - h)}$

j	sequential number of a sample
k	coefficient proportional to the ventilation factor F_{vent}
L	latent heat of condensation
L1, L2, L3, L4	labels of the "wet" models (Linton, 1972)
m	molecular weight
$\dot{m}$	rate of mass loss from an evaporating waterdrop
M1, M2, M3, M4	labels of the "dry" models (Miyake, 1968)
n	number of samples in a population
N	mass of water substance
N_c	mass of water substance in the form of condensed cloud droplets
N_v	mass of water substance in the vapour phase
$(N_v)_o$	initial mass of water vapour in a parcel of air
p'	partial saturated vapour pressure of a volatile liquid in solution
P	saturated vapour pressure of a pure liquid
q	quotient used to determine $\delta_e{}^{18}O$ in Equation (5.5); $q = \frac{\alpha_{18}h}{1 - \alpha_{18}\alpha_K(1 - h)}$
r	mixing ratio of water vapour in dry air
r_s	saturated mixing ratio of water vapour in moist air
R	isotopic concentration ratio, as for example, $\left[\frac{^{18}O}{^{16}O}\right]$

R_b	isotopic concentration ratio in the free atmosphere
R^*	universal gas constant; expressed in cal. mole^{-1} deg.$^{-1}$ in Equation (1.9)
R'_g	rainfall rate at the ground
s, s.d.	standard deviation
SM	a nearly linear isotopic cloud model, approximately the same as L1
t	temperature in degrees Celsius
t_c	cloud condensation temperature in degrees Celsius
t_d	temperature of the dew point in degrees Celsius
t_o	cloud-base or LCL-temperature in degrees Celsius
t_{air}	air-temperature at the surface in degrees Celsius
T	temperature in degrees Kelvin
T*	virtual temperature in degrees Kelvin
v	terminal fall speed of a waterdrop
V	volume
W	cloud liquid water content
x	independent variable of the log-normal probability density function, Equation (4.6)
x_{th}	threshold value of x
X	fractional part of the equilibrium fractionation factor α; $X = \frac{(\alpha - 1)}{10^{-3}}$
z	heavy-isotope enrichment defined by Equation (4.5)
Z	a generalized heavy isotope

α	a generalized equilibrium fractionation factor
α_D	equilibrium fractionation factor for Deuterium
α_K	kinetic fractionation factor
α_3	skewness coefficient
α_{18}	equilibrium fractionation factor for Oxygen-18
β	median value of x, a log-normal variate
γ	ratio of specific heats, $\frac{c_p}{c_v}$; $\gamma = 1.4$ for dry air
$\delta_c{}^{18}O$	estimated oxygen-18 del-value of condensed cloud droplets
$\delta_e{}^{18}O$	a theoretical limiting del-value for evaporating raindrops as $F_w \rightarrow 0$
$\delta_h{}^{18}O$	measured oxygen-18 del-value of a graupel sample
$\delta_v{}^{18}O$	measured oxygen-18 del-value of a water vapour sample
$\delta_w{}^{18}O$	measured oxygen-18 del-value of a rain sample
$(\delta_w{}^{18}O)_{cor}$	roughly calculated evaporative enrichment in falling rain
ε	ratio of molecular weights for water vapour and dry air; $\varepsilon = 0.622$
μ	arithmetic mean of a statistical population
ν	number of degrees of freedom
ρ	Pearson's correlation coefficient
ρ_a	density of water vapour at the surface of a waterdrop
ρ_b	density of water vapour in the free atmosphere

$\overline{\rho_c}$	mean saturation deficit in a vertical column of air
σ^2	variance of a statistical population
τ	time
χ^2_ν	chi-squared statistic with ν degrees of freedom

CHAPTER I

HISTORICAL SYNOPSIS

1.1 The Naturally Occurring Isotopic Forms of Water

Even before the dawn of the nuclear age, Gilfillan (1934) had measured a slight distinction between the "heavy" waters of the oceans and the "light" waters of terrestrial freshwaters. He attributed the observed difference in specific gravity to a difference in isotopic composition. Within the oceans of the world, however, the absolute variation of the relative concentrations of the isotopic forms of water is extremely small: 10°/₀₀ for deuterium, and 1°/₀₀ for oxygen-18 (Hoefs, 1973; Epstein and Mayeda, 1953; Friedman, 1953). The corresponding variation in meteoric waters is more than 20 times that of sea water (Craig, 1961a). Consequently, mean ocean water has been considered as a standard, designated SMOW (Standard Mean Ocean Water), where

$$\left[\frac{D}{H}\right]_{SMOW} = 0.15576 \times 10^{-3} \quad \text{(Hagemann et al., 1970), and}$$

$$\left[\frac{^{18}O}{^{16}O}\right]_{SMOW} = 1.9934 \times 10^{-3} \quad \text{(Craig, 1961b).}$$

In practice, isotopic abundance ratios are determined by mass spectrometry where an unknown sample ratio is compared with the appropriate standard ratio. The result, in parts per thousand, is expressed as a del-value:

$$\delta^{18}O_{sample} \equiv \frac{R_{sample}-R_{standard}}{R_{standard}} \times 10^{3} \qquad (1.1)$$

where $R = \left[\frac{^{18}O}{^{16}O}\right]$ for example (Craig, 1961a,b; Epstein and Mayeda, 1953). At the present time, precision is routinely of the order of ± 2.0°/₀₀ for deuterium, and ± 0.2°/₀₀ for oxygen-18 (Hage et al., 1975; Hoefs, 1973). SMOW is now the accepted world-wide standard for both hydrogen and oxygen isotopes.

The chemical behaviour of each isotope of a given element depends strongly on the extra-nuclear structure (Hoefs, 1973; Dansgaard, 1961). The nucleus is more influential in determining an isotope's physical properties. For this reason, isotopes can be separated relatively easily on the basis of some physical property such as density or boiling point. Table 1.1, taken from the work of Wahl and Urey (1935), lists the measured saturated vapour pressures for the isotopic forms of water at 5 temperatures. A control sample was used at the lowest temperature, and the entries in the Table are comparable to present-day values.

Isotopic effects are most pronounced amongst the lightest elements, and especially among the isotopes of hydrogen. In the case of water, the lightest isotope has the highest saturated vapour pressure at any specified temperature. Although $H_2{}^{18}O$ and $D_2{}^{16}O$ have nearly equal molecular weights, the heavy-hydrogen form shows the greater reduction in its saturated vapour pressure.

TABLE 1.1

SATURATED VAPOUR PRESSURES OF THE ISOTOPIC FORMS OF WATER AT VARIOUS TEMPERATURES

(WAHL AND UREY, 1935)

Temperature t (°C)	Saturated Vapour Pressures, P, (mm of Hg)			
	$P_{(H_2{}^{16}O)}$	$P_{(H_2{}^{18}O)}$	$P_{(HD^{16}O)}$	$P_{(D_2{}^{16}O)}$
11.25	10.0	9.86	9.23	8.53
11.25	10.0	9.89	9.18	8.53
23.0	21.0	20.82	19.51	18.25
35.6	43.5	43.15	40.80	38.50
46.35	77.0	76.41	72.53	69.07
100.0	760.0	757.7	740.7	722.8

The isotopic forms of water can thus be separated by fractional distillation both in the laboratory and in the Earth's atmosphere as suggested by Epstein and Mayeda (1953). The more volatile $H_2{}^{16}O$-component of sea water is preferentially removed from the oceans by evaporation, tends to remain in the vapour phase, but is eventually deposited as snow at high latitudes and altitudes. $\delta^{18}O \simeq -60°/_{\circ\circ}$ for snow near the South Pole (Aldaz and Deutsch, 1967).

1.2 Empirical Meteorological Relationships

In a trend similar to that of terrestrial freshwater, precipitation becomes isotopically lighter with increasing latitude, with increasing altitude, and from warm to cold season in non-tropical latitudes (Hage et al., 1975; Dincer, 1968; Epstein, 1956; Dansgaard, 1954; Riesenfeld and Chang, 1936). Dansgaard (1964, 1961) found an excellent correlation between the annual mean del-value of $H_2{}^{18}O$ in precipitation and the annual mean air-temperature at the surface. The regression line was given by the following equation:

$$\overline{\delta^{18}O} = (0.69\ \overline{t_{air}} - 13.6)°/_{\circ\circ} \qquad (1.2)$$

in which the temperature term was expressed in degrees Celsius. Also, for deuterium,

$$\overline{\delta D} = (5.6\ \overline{t_{air}} - 100.)°/_{\circ\circ} \qquad (1.3)$$

The averaging process was thought to smooth out the numerous fluctuations in the del-values recorded for individual storms, so that $\overline{t_{air}}$ could be considered as a direct link to the effective, annual mean condensation temperature. In general, the heavy isotope content of precipitation decreases with decreasing condensation temperature, t_c (Dansgaard, 1964). It should be possible, therefore, to deduce t_c from an observed del-value of a heavy isotope. Conversely, it should also be possible to predict, for an observed dew point, the range of del-values for cloud droplets produced by convective cooling.

Equations (1.2) and (1.3) can be combined so that $\overline{t_{air}}$ is eliminated. A relation between deuterium and oxygen-18 results.

$$\text{i.e., } \overline{\delta D} = (8\overline{\delta^{18}O} + 9)°/_{\circ\circ} \qquad (1.4)$$

This relationship has been called the precipitation line (Dincer, 1968). Since the isotopic species of water are fractionated during the processes of evaporation, condensation, and freezing, and since these processes apply equally well to both $HD^{16}O$ and $H_2{}^{18}O$, it seems quite logical for the fractionation of deuterium to parallel that of oxygen-18 (Hoefs, 1973). Equation (1.4) is usually written as an empirical equation proposed by Craig (1961a):

$$\delta D = (8\delta^{18}O + 10)°/_{\circ\circ} \qquad (1.5)$$

The relation was, however, originally suggested by Friedman (1953) who compared his own deuterium measurements with the early oxygen-18 measurements of Epstein and Mayeda (1953).

1.3 Fractionation Factors

For a quantitative study of isotopic fractionation in water, the fractionation factors, α_D and α_{18}, are required. Under equilibrium conditions, these factors, for evaporation and condensation, are given approximately by the ratios of the saturated vapour pressure of the light isotope to the saturated vapour pressure of the heavy isotope (Dansgaard, 1961):

$$\alpha_D \equiv \frac{\left[\frac{D}{H}\right]_{liq}}{\left[\frac{D}{H}\right]_{vap}} \simeq \frac{P_{(H_2{}^{16}O)}}{P_{(HD^{16}O)}} \qquad (1.6)$$

$$\alpha_{18} \equiv \frac{\left[\frac{^{18}O}{^{16}O}\right]_{liq}}{\left[\frac{^{18}O}{^{16}O}\right]_{vap}} \simeq \frac{P_{(H_2{}^{16}O)}}{P_{(H_2{}^{18}O)}} \qquad (1.7)$$

The ideal gas law is assumed to apply in the vapour phase, and Raoult's law for ideal solutions in the liquid phase. That is, the partial saturated vapour pressure, p', of an ideal liquid in solution, is equal to its pure saturated vapour pressure, P, times its mole-fractional concentration in the solution. In such a case, the fractionation factors depend on temperature only (Dansgaard, 1961).

Lewis and Cornish (1933) were the first to determine α_{18} experimentally, and the isotopic vapour pressures measured by Wahl and Urey (1935) also yielded values of α_D and α_{18}, at specified temperatures, via Equations (1.6) and (1.7). The integrated form of the Clausius-Clapeyron Equation, in which the latent heat of condensation is assumed constant, can be written as

$$P = C e^{-(mL/R^*T)} \qquad (1.8)$$

where C is a constant of integration, and R* is the universal gas constant. In Equation (1.8) the saturated vapour pressure is a function of molecular weight m, latent heat of condensation L, and absolute temperature T. $P_{(HD^{16}O)}$ and $P_{(H_2{}^{18}O)}$ can be calculated by Equation (1.8) as well as $P_{(H_2{}^{16}O)}$. The molecular weight is then the main variable, and the appropriate ratio of the saturated vapour pressures gives an expression for the fractionation factor which resembles Equation (1.8) but has a positive exponent.

Zhavoronkov et al. (1955) determined an equation for α_{18} in the temperature range, 15°C to 100°C,

$$\text{viz.,} \quad \alpha_{18} = 0.9822\, e^{(15.788/R^*T)} \qquad (1.9)$$

where R* must be expressed in calories $\text{mole}^{-1}\ {}^{\circ}\text{K}^{-1}$. Dansgaard (1964, 1961) had such confidence in this equation that he used it to extrapolate values of α_{18} down to -20°C. Table 1.2 contains these "classical" values of α_D and α_{18}, at various temperatures, and was originally prepared by Dansgaard (1964) from the work of Merlivat et al. (1963) and Zhavoronkov et al. (1955). These were the values used by Miyake et al. (1968) and by Linton (1972).

TABLE 1.2

EQUILIBRIUM FRACTIONATION FACTORS FOR DEUTERIUM (α_D) AND OXYGEN-18 (α_{18}) DURING A VAPOUR-LIQUID PHASE CHANGE

(DANSGAARD, 1964)

Temperature t (°C)	α_D	α_{18}
100	1.029	1.0033
80	1.037	1.0045
60	1.046	1.0059
40	1.060	1.0074
30	1.069	1.0082
20	1.079	1.0091
10	1.091	1.0101
0	1.106	1.0112
-10	1.124	1.0123
-20	1.147	1.0135

The fractionation factors, especially at sub-freezing temperatures, have proven difficult to obtain precisely even in controlled laboratory studies. Majoube (1971) determined empirically two improved relationships for α_D and α_{18}:

$$\ln \alpha_D = \frac{24.844 \times 10^3}{T^2} - \frac{76.248}{T} + 52.612 \times 10^{-3} \quad (1.10)$$

$$\ln \alpha_{18} = \frac{1.137 \times 10^3}{T^2} - \frac{0.4156}{T} - 2.0667 \times 10^{-3} \quad (1.11)$$

These curves were based on nearly 50 data-points, in the temperature range 0°C to 100°C, and give 4-decimal accuracy for the fractionation factors. Stewart (1975) confirmed Majoube's (1971) determinations for α_D but considered those for α_{18} slightly too large. Nevertheless he used them in his thesis as they appear in Figures 1.1 and 1.2 on pages 12 and 13, respectively.

Tables 1.3 and 1.4 list fractionation factors for deuterium and oxygen-18, respectively, and give an indication of the historical trend in their accuracy. Figures 1.1 and 1.2 show the corresponding, present-day curves. Evidently the fractionation factors, for equilibrium evaporation and condensation, are now quite well known in the normal temperature range of liquid water. Values for supercooled water may be extrapolated with a reasonable degree of confidence. Of course non-equilibrium conditions occur in the real, natural world, but the deviation from equilibrium may often be quite small (Stewart, 1975; Facy et al., 1963).

TABLE 1.3

A COMPARISON OF MEASURED FRACTIONATION FACTORS FOR DEUTERIUM (α_D)

t (°C)	(Vapour-Liquid) Wahl and Urey (1935)	Merlivat et al. (1963)	Merlivat et al. (1971)	Majoube (1971)	(Vapour-Ice) Merlivat and Nief (1967)
100	1.026	1.029	1.0253	1.0271	--
80	1.038	1.037	1.036	1.0366	--
60	1.051	1.046	1.048	1.0487	--
40	1.064	1.060	1.062	1.0645	--
30	1.071	1.069	1.072	1.0740	--
20	1.078	1.079	1.082	1.0850	--
10	1.086	1.091	1.094	1.0977	--
0	1.095	1.106	109	1.1123	1.132
-10	--	1.124	1.127	1.1293	1.151
-20	--	1.147	1.150	1.1492	1.173

TABLE 1.4

A COMPARISON OF MEASURED FRACTIONATION FACTORS FOR OXYGEN-18 (α_{18})

	(Vapour-Liquid)			(Vapour-Ice)
t (°C)	Wahl and Urey (1935)	Zhavoronkov et al. (1955)	Majoube (1971)	Matsuo and Matsubaya (1969)
100	1.0030	1.0033	1.0050	--
80	1.0050	1.0045	1.0059	--
60	1.0066	1.0059	1.0070	--
40	1.0080	1.0074	1.0082	--
30	1.0089	1.0082	1.0090	--
20	1.0099	1.0091	1.0098	--
10	1.0111	1.0101	1.0107	--
0	1.0125	1.0112	1.0117	1.0119
-10	--	1.0123	1.0129	1.0127
-20	--	1.0135	1.0142	1.0135

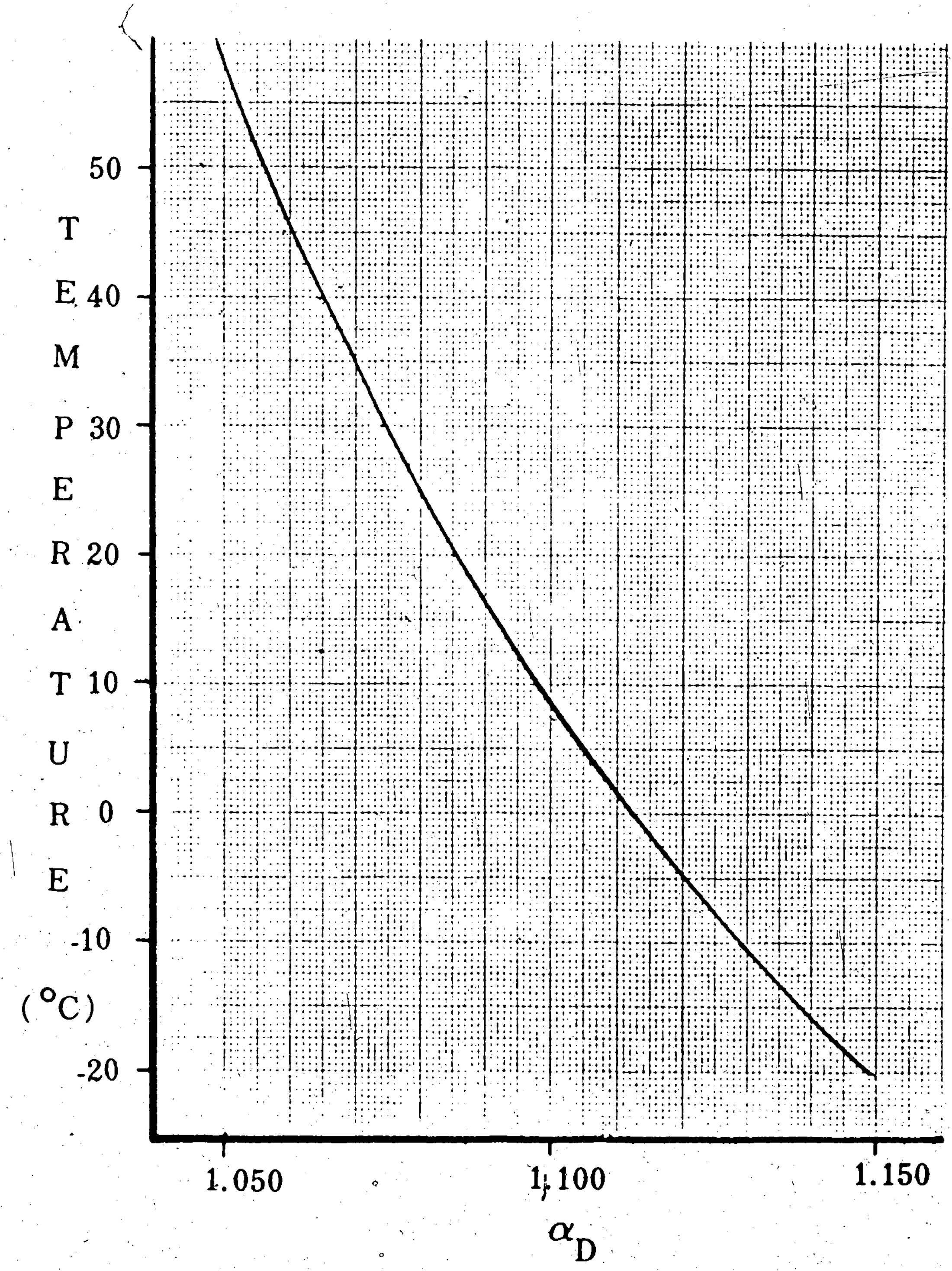


Figure 1.1 Equilibrium fractionation factor for deuterium as a function of temperature (Majoube, 1971).

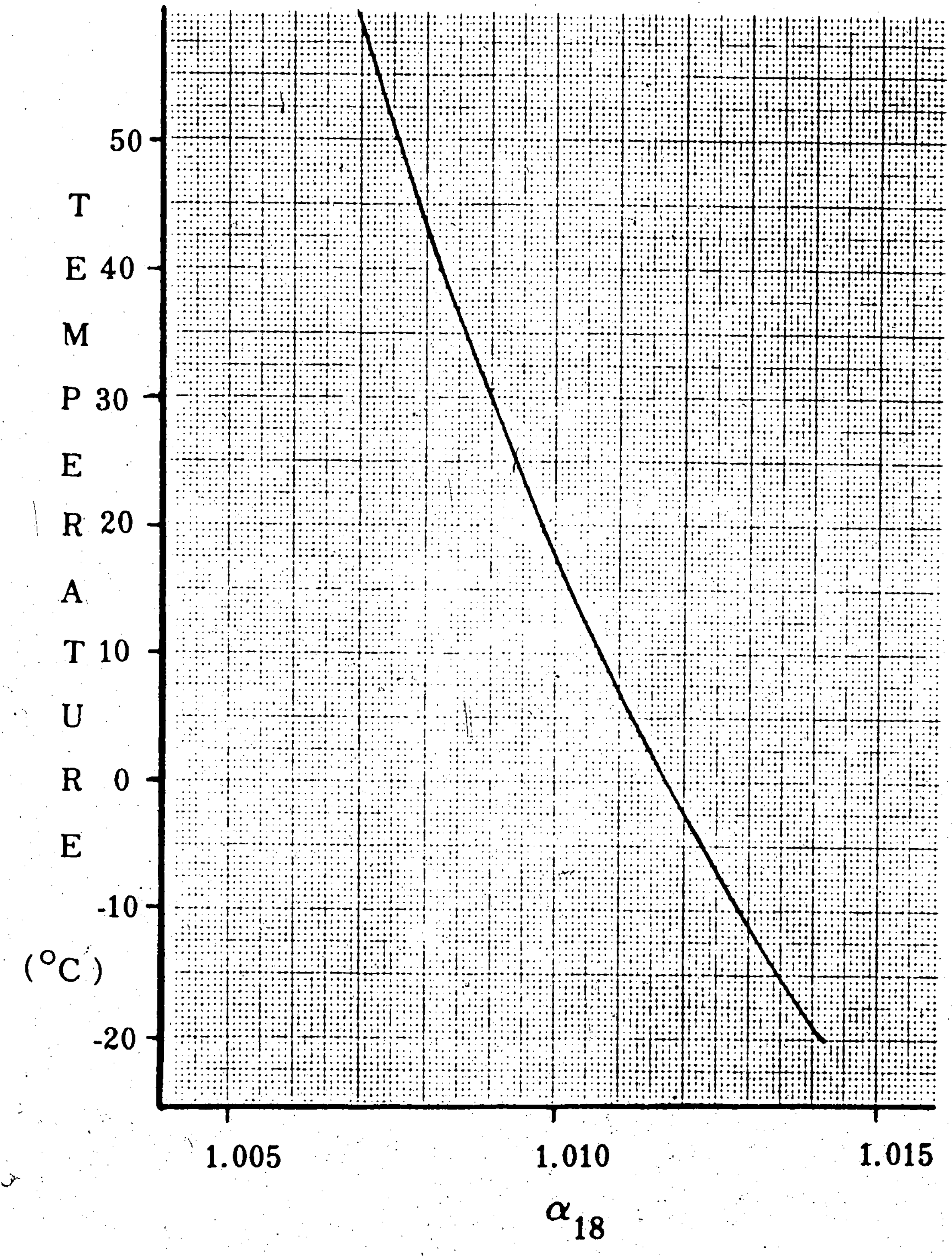


Figure 1.2 Equilibrium fractionation factor for oxygen - 18 as a function of temperature (Majoube, 1971).

1.4 Oxygen-18 Studies at the University of Alberta

The idea of using oxygen-18 as an atmospheric tracer and climatic indicator has been discussed by meteorologists and physicists at the University of Alberta for about a decade. For example, Gray and Thompson (1976) have recently demonstrated a correlation between an annual mean air-temperature and the ^{18}O-abundance in the cellulose of tree rings. A number of precipitation sampling experiments have been carried out since 1970, and the results have led to three previous theses. The present study is a continuation of the work of Sandhu (1978).

West (1972) and Linton (1972) gave the first comprehensive reports on the oxygen-18 work at the University of Alberta. Linton (1972) described the theoretical studies of Dansgaard (1964, 1961) and modified the four cloud models of Miyake et al. (1968), but he restricted his discussion of experimental results to the summer rainfall data of 1970 and 1971 at Edmonton. He did not attempt to sample water vapour. He was particularly concerned with the change in $\delta^{18}O$ with time during periods of sustained rain, and, to account for the observed trends in his data, he estimated some enrichment in oxygen-18 during the rain's descent from cloud to ground.

The work of Linton (1972) was continued by Hage et al. (1975) until 205 precipitation samples had been collected. In addition, these authors attempted to sample water vapour by drawing air slowly through a coiled condenser embedded in a slushed carbon-dioxide-and-ethanol freezing mixture. They confirmed that nearly complete recovery of the vapour was accomplished by this method. However, vapour del-values were not published, and their discussion concentrated on the marked distinction between the results for rain and snow. An unusually large variation in $\delta^{18}O$ was found within and between individual snowstorms. The descent phenomena described by Linton (1972) were thought to be inapplicable to falling snow. It was concluded, therefore, that, in winter, the effective condensation temperature was highly variable at Edmonton, and that the water vapour feeding the snowstorms had at least two different origins and/or histories.

In the present study precipitation samples were collected, this time in association with the Alberta Hail Project of Penhold, Alberta. Field sampling took place during three summer hail seasons in central Alberta. Unlike liquid precipitation, when cloud droplets are completely frozen into snow pellets or hailstones, the oxygen-18 content is not appreciably enriched during the descent from cloud to ground. Some enrichment may occur, however, during the freezing or wet-growth process (Bailey et al., 1969). This novel feature of fixation by freezing has made the isotopic analysis of hailstones a popular area of research since about the time of Facy et al. (1963).

CHAPTER II

OXYGEN-18 STUDIES AND CLOUD PHYSICS

2.1 Cloud Modelling

Perhaps the first step in understanding cloud structure and precipitation development is to identify the water vapour source. It is here that oxygen-18 in vapour form may be used as a tag or trace element. Then, if the ^{18}O-content in the water vapour entering the cloud is known, the corresponding ^{18}O-abundance in the condensed droplets can be calculated as a function of cloud temperature by means of a numerical model. Thus it would seem that vapour sampling should receive considerable attention, and this concept formed a tacit premise of the study.

Miyake et al. (1968) described four isotopic cloud models based on cloud type and condensation process. The mathematical equations were derived from the mass conservation of the isotopic species. Conservation of bulk mass was rigidly retained in the closed models, but not in the open ones where cloud droplets were allowed to precipitate out of a cooling parcel of air. Liquid condensation was considered to be an equilibrium process for cloud-droplet formation, but non-equilibrium conditions were encountered during the growth of ice crystals by deposition. Frozen condensate was essentially isolated from the remaining vapour and did not influence any subsequent condensation.

The four models can be most easily interpreted as follows:

- M1, a closed system with equilibrium between the total vapour and total condensed phases;
- M2, a closed system with deposition on to ice crystals;
- M3, an open system with equilibrium between total vapour and the remaining cloud droplets, some water removed as rain;
- M4, an open system with deposition on to ice crystals, some of which precipitate.

The models have been listed in Table 2.1 along with Linton's (1972) basic equation for each one. R is an atomic abundance ratio as used in Equation (1.1). N represents the amount of water substance in grams in a parcel of air. For the closed systems, $N = N_c + N_v = (N_v)_o$. The subscript, o, denotes the initial condition at the lifting condensation level or cloud base. Other subscripts are used to indicate the following:

water vapour by v,
liquid water by w,
hail or graupel by h,
unspecified condensate by c.

Although Miyake et al. (1968) set out to describe mathematically the process of adiabatic condensation followed by precipitation, they nevertheless used in their models the dry adiabatic law, or Poisson's Equation, in the form:

TABLE 2.1

THE FOUR ISOTOPIC CLOUD MODELS AND THEIR DEFINING EQUATIONS

Miyake's (1968) Label	Linton's (1972) Label	Description of Model	Mathematical Equation Used to Derive $\delta_c{}^{18}O = f(t)$
M1	L1	Closed system with equilibrium between the total vapour and condensed phases.	$R_c = \frac{(N_v R_v)_o}{\left(\frac{1}{\alpha} - 1\right) N_v + (N_v)_o}$
M2	L2	Closed system with equilibrium at the vapour-liquid condensate interface only; some condensate frozen.	$R_c = \frac{(N_v R_v)_o - N_v R_v}{(N_v)_o - N_v}$
M3	L3	Open system with equilibrium between the vapour and condensed phases remaining in the cloud.	$\frac{dR_v}{R_v} = \frac{(\alpha - 1) dN_v - N_c d\alpha}{N_v + \alpha N_c}$
M4	L4	Open system with equilibrium at the vapour-condensate interface only.	$\frac{dR_c}{dN_v} = \frac{R_c - \alpha R_v}{N_c}$

$$V = V_o \left[\frac{T_o}{T}\right]^{1/(\gamma - 1)} \qquad (2.1)$$

where V was the total volume of the system, and γ, the ratio of specific heats, $\frac{c_p}{c_v}$, for dry air. Linton (1972) substituted a pseudoadiabatic cooling process and worked with the virtual temperature,

$$T^* = \left[\frac{1 + \frac{r_s}{\varepsilon}}{1 + r_s}\right] T, \qquad (2.2)$$

where r_s was the saturated mixing ratio for air at temperature T, and $\varepsilon = 0.622$. His models were otherwise very similar to those of Miyake et al. (1968), and he introduced the terms "wet" and "dry" to distinguish the two sets of models.

Figure 2.1 has been compiled from Linton's (1972) thesis for the sake of comparison. The curves are labelled according to columns 1 and 2 of Table 2.1. SM is a nearly linear, simplified form of model L1, to be discussed in the next section. The cloud parameter, W or LWC, equals $\frac{N_w}{V}$, and is called the liquid water content of the cloud. It was held constant by Linton (1972) during the calculations for any, particular, open model.

2.2 The Simplified Model (SM)

When Facy et al. (1963) introduced isotopic analysis

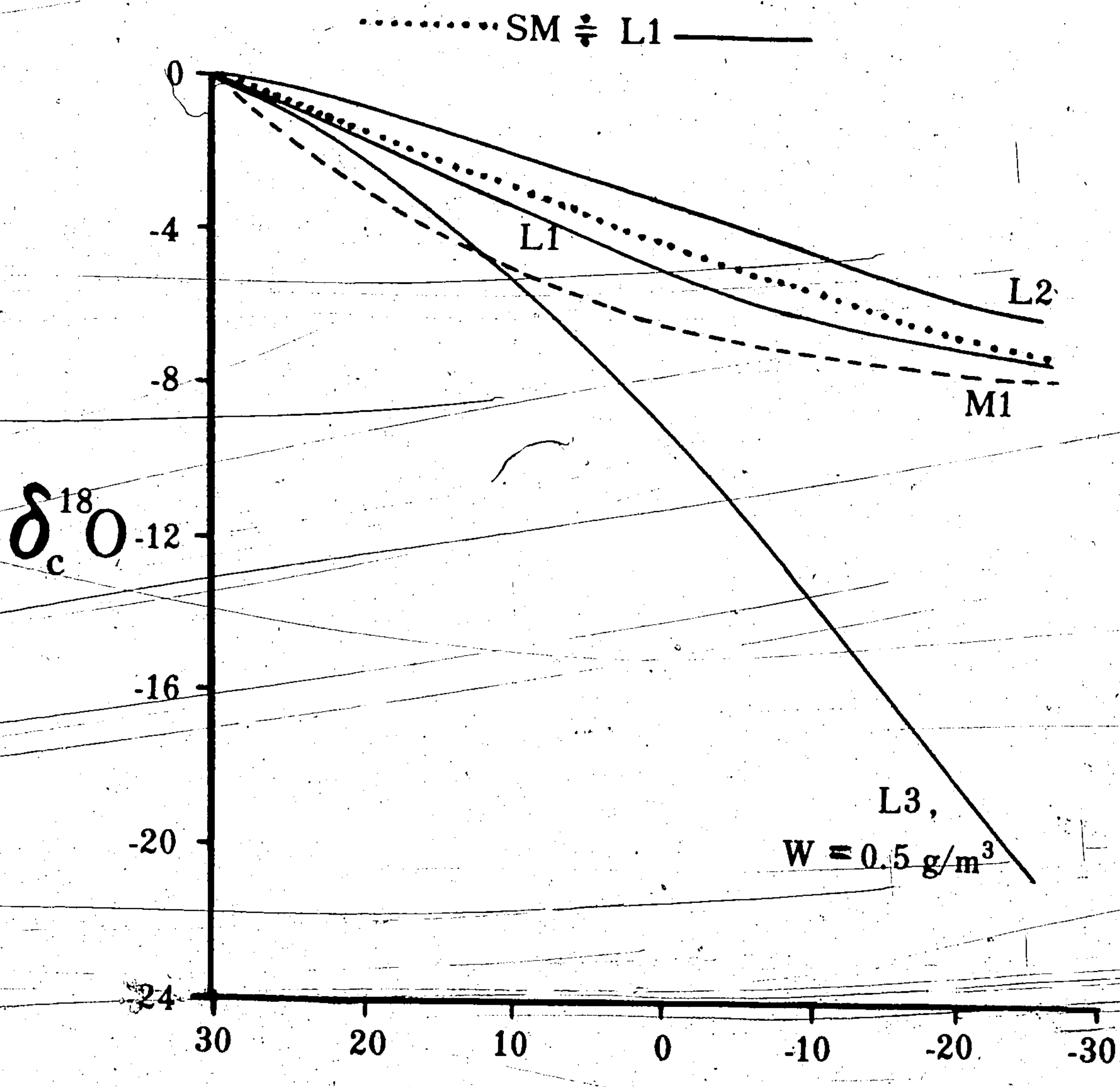


Figure 2.1 Differing isotopic cloud models which relate $\delta_c{}^{18}O$ to cloud temperature. SM was calculated using values of α_{18} from Table 1.2.

to the study of hailstone formation, they chose L1, as a first model, to describe the adiabatic updraft region of a hail-generating cumulonimbus. Since they did not collect any vapour samples, they had to estimate the initial value of $\left[\frac{D}{H}\right]$ in the air mass feeding the storm. Even so, they were able to plot $\left[\frac{D}{H}\right]$ against hailstone radius and to correlate the deuterium concentration with temperature and height. Thus they deduced a rough growth history for their hailstone without the benefit of the more elaborate models.

Miyake et al. (1968) defined the model M1 by the equation:

$$R_c = \frac{(N_v R_v)_o}{\left(\frac{1}{\alpha} - 1\right) N_v + (N_v)_o} \qquad (2.3)$$

The fraction of remaining vapour, F_v, can now be introduced to give

$$R_c = \frac{(R_v)_o}{\left(\frac{1}{\alpha} - 1\right) F_v + 1} \qquad (2.4)$$

$$\text{where } F_v = \frac{N_v}{(N_v)_o} = \frac{r_s}{(r_s)_o} \qquad (2.5)$$

The subscript, o, referred to cloud base, and the absence of subscript, o, implied a general height above the cloud base. The saturated mixing ratio, r_s, and hence F_v, could simply be read from a tephigram by following a moist-adiabat. In the case of oxygen-18, the fractionation factor, α_{18}, could be taken from Figure 1.2 or calculated from Equation (1.11). $(R_v)_o$, therefore, constituted a crucial measurement, and, in the present work, $\delta_v{}^{18}O$ for water vapour was assumed to be constant from the ground up to cloud base. This assumption was also made by Facy et. al. (1963).

Equation (2.4) can be expressed in terms of del-values by using the defining Equation (1.1).

$$\text{i.e.} \quad \delta_c{}^{18}O = \left[\frac{R_c - R_{standard}}{R_{standard}}\right] \times 10^3$$

$$(\delta_v{}^{18}O)_o = \left[\frac{(R_v)_o - R_{standard}}{R_{standard}}\right] \times 10^3$$

Subtracting gives

$$\delta_c{}^{18}O - (\delta_v{}^{18}O)_o = \left[R_c - (R_v)_o\right] \times \frac{10^3}{R_{standard}} \qquad (2.6)$$

Substituting Equation (2.4) to eliminate R_c yields

$$\delta_c{}^{18}O - (\delta_v{}^{18}O)_o = \left[10^3 + (\delta_v{}^{18}O)_o\right]\left[\frac{(\alpha - 1)\ F_v}{\alpha + (1 - \alpha)\ F_v}\right] \qquad (2.7)$$

The denominator, $\left[\alpha + (1 - \alpha)\ F_v\right]$, ranges from 1.0 when $F_v = 1$, to α when $F_v = 0$.

$$\text{i.e.}\quad 1 \le \left[\alpha + (1-\alpha)F_v\right] \le \alpha \qquad (2.8)$$

Since α is never much greater than 1.0, the denominator in Equation (2.7) is also approximately 1.0. The term, $(\delta_v{}^{18}O)_o$, on the right hand side of (2.7) can be set equal to -26°/₀₀, an average value for water vapour during summer in Alberta (Sandhu, 1978). If the fractionation factor is written as $\alpha = 1 + \frac{X}{10^3}$, Equation (2.7) becomes, approximately,

$$\delta_c{}^{18}O \simeq (\delta_v{}^{18}O)_o + 0.974XF_v \qquad (2.9)$$

which defines the simplified model SM.

2.3 The Applicability of the Cloud Models

When Miyake et al. (1968) proposed their four basic models, they also suggested the conditions under which each model could be applied. The open models, M3 and M4, represented frontal, stratiform precipitation. Extensive rain or snow of this type has been discussed since Dansgaard's (1953) observation that $\delta_w{}^{18}O$ distinctly increased with time during the passage of a strong warm front over Denmark.

The closed models, M1 and M2, were thought to correspond to convective showers where the precipitation efficiency was low. In these models, the growing reservoir of cloud condensate and the diminishing vapour source were never separated from the cloud. As the adiabatic cooling proceeded, the increasing volume of bulk condensate permitted only a slow change of $\delta_c{}^{18}O$ with temperature or time.

The distinction between equilibrium and non-equilibrium models turned out to be rather academic in the case of cloud formation. Equilibrium condensation was always considered to apply, at least at the microphysical vapour-condensate interface. According to Miyake et al. (1968) M1 and M2 differed by only about 2 del-units at most, and M3 was practically identical to M4. A comparison of L1 and L2 can be seen in Figure 2.1 on page 20 In the case of fractionation via deposition in a vapour-ice system, however, the non-equilibrium models seemed especially applicable. The fractionation factors for such a model have been included in Tables 1.3 and 1.4 under the heading of "Vapour-Ice".

As mentioned in the preceding section, Facy et al. (1963) found L1 to be quite satisfactory for a qualitative description of the growth of a large hailstone. The simplified model, SM, given by Equation (2.9), was an approximate form of L1. Miyake et al. (1968) preferred model M2 for the growth of large hailstones. Dansgaard (1964) incorporated the Rayleigh condensation formulae into a precipitation model to be designated D4 in Figure 2.2, and specified by

$$1 + \frac{\delta_c Z}{10^3} = \frac{\alpha}{\alpha_o} F_v^{(\overline{\alpha} - 1)} \qquad (2.10)$$

where Z has been used to designate any general isotope. The quantities, α_o, α, and $\bar{\alpha}$ were fractionation factors referring to the initial condensation temperature, an instantaneous condensation temperature, and the mean condensation temperature, respectively. $\delta_c Z$, in this case, denoted an infinitesimal element of condensate.

Figure 2.2 has been assembled to illustrate the potential variations which can occur among the different models. D4 was calculated from Equation (2.10), and, as for Figure 2.1, the values of α_{18} were taken from Table 1.2. M2, L1 and SM all turned out to be practically identical. In the limiting case of the open models when W = 0, L3, L4, and D4 were all equivalent and represented a theoretical Rayleigh condensation with no intermediate cloud.

The ^{18}O-concentration of the condensate, $\delta_c{}^{18}O$, represents the entire condensed phase in the closed models. On the contrary, in the open models, it represents only that portion of the total condensate which remains in the cloud. When W = 0, as in D4, it applies, in fact, to an infinitesimally small portion which is immediately isolated after formation. In the open models, some of the condensate is removed via precipitation and can then be sampled at ground level.

According to Dansgaard (1964), the Rayleigh condensation process D4 leads to much more fractionation, for small quantities, than the closed equilibrium process manages for the entire condensed phase. In nature, the growth of liquid cloud droplets by coalescence, and the equilibration of condensate and cloud

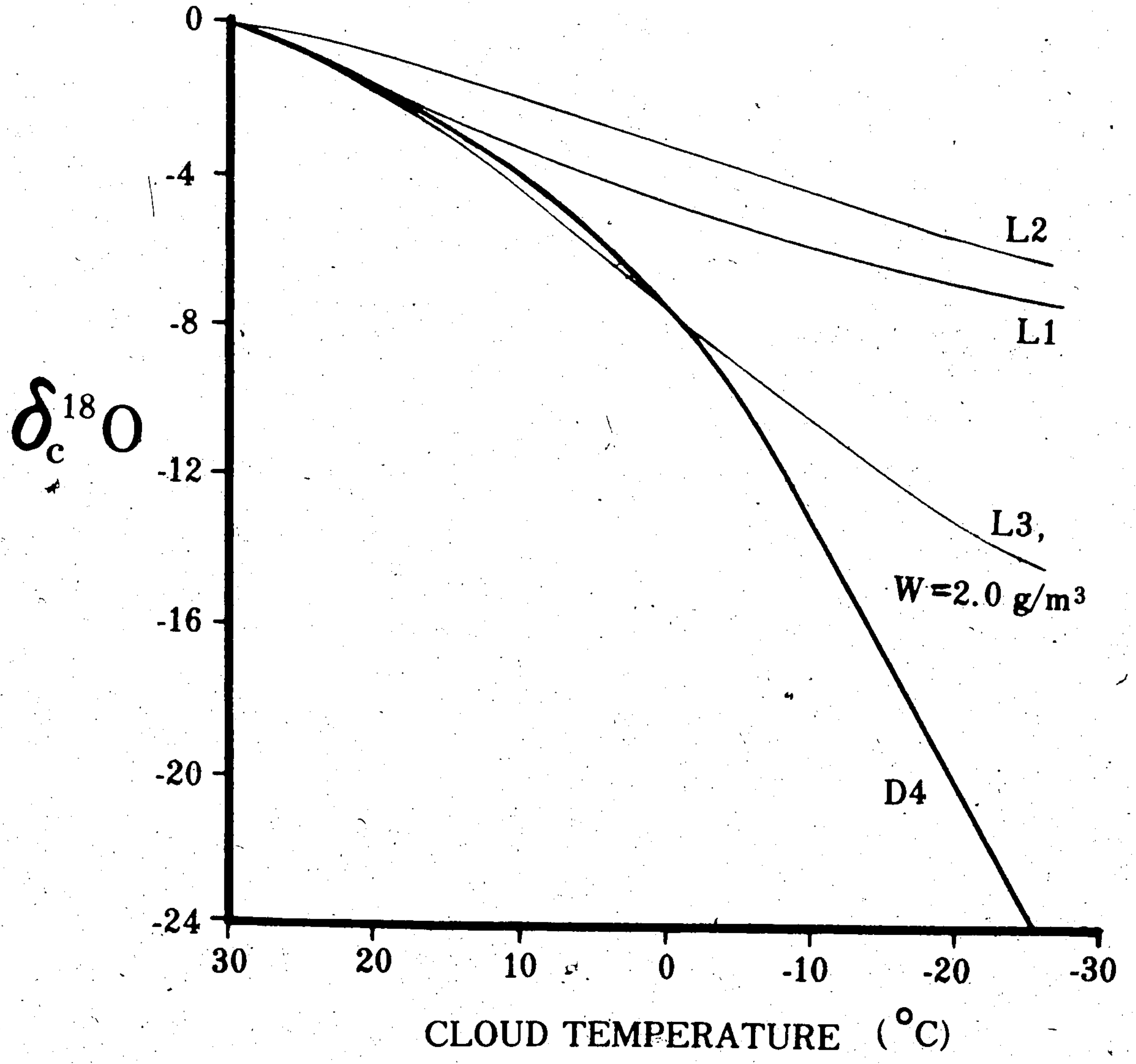


Figure 2.2 The range of the isotopic cloud models. L2 shows the least fractionation, L3 is the open model favoured by Linton (1972), and D4 is the Rayleigh limit when W = 0.0 g/m^3

vapour by isotopic exchange will prevent dramatic fractionation. In most cases, then, the del-values of precipitation samples collected in the field can be expected to follow the curve of model L1. Equilibrium conditions will tend to be the rule, not the exception, and deviations should be small. D4 is the ultimate limit of fractionation, and might perhaps be detectable as a function of hailstone radius in regions of dry growth.

Linton's (1972) model L3, with W = 2.0 grams of liquid cloud water per m^3, has been included in Figure 2.2 because it fits D4 closely for about 40°C of cooling. It was the model he favoured for general use. Its variable liquid water content gives flexibility to the model, but from a practical viewpoint, the cloud parameter W is just one more numerical quantity to be estimated for each shower. The precise variation of W with space and time during a shower would be a further complication. When $W \leq 2.0$ grams of liquid water per m^3, L3 would not represent the del-values of precipitation samples much better than D4.

Linton (1972) was concerned about the high del-values given by model L2. He would have predicted greater fractionation to occur under non-equilibrium conditions. He attributed the dilemma to the closed nature of the models L1 and L2. The removal of condensate via precipitation would invalidate the closed models. Consequently, he concluded that a closed system was not a realistic approach to the atmosphere. He then favoured the generality of the open model L3, with equilibration between cloud droplets and vapour, and with some allowable precipitation.

Miyake et al. (1968) also seemed to favour the open system with equilibrium between cloud water and remaining vapour. In such a model, relatively large changes in del-value can be predicted and then verified by taking consecutive samples during prolonged periods of precipitation. Under natural conditions, no cloud can be expected to obey a mathematical model exactly. In fact natural clouds evolve, from closed to open systems, and from equilibrium to non-equilibrium conditions when freezing occurs. Thus each model is somewhat applicable some of the time, but none is completely so.

2.4 The Appropriateness of Cloud Model and Local Weather

The various numerical models were defined and constrained by their mathematical equations. Experimental evidence must be observed in the field to support any one model's suitability at a given time and under specific weather conditions. It is puzzling, in hindsight, to justify the "dry" models of Miyake et al. (1968) as valid predictors of condensation and precipitation phenomena.

The experimental evidence for the present study came from vapour and precipitation samples collected in central Alberta and reported by Sandhu (1978). The theoretical models described heretofore often assumed the source water vapour to be in equilibrium with SMOW, and so implicated warm maritime climates with $(\delta_v{}^{18}O)_o = -8.1°/_{\circ\circ}$ at $t_o = 30°C$. Such a condition would be completely irrelevant to Alberta's cool, semi-arid climate where, according to Sandhu (1978),

$$(\delta_v{}^{18}O)_o \simeq -26°/_{\circ\circ} \text{ and } t_o < 15°C.$$

Lowering the initial condensation temperature, t_o, was shown by Linton (1972) to increase the slope of $\delta_c{}^{18}O$ against cloud temperature, but the del-value of the initial condensate remained unchanged.

From Figure 2.1 on page 20, it is clear that a relatively large difference exists between the closed and open models. If the closed models correspond to convective showers and the open models to frontal precipitation (Miyake et al., 1968), the open model L3 will be inappropriate most of the time during the summer months in central Alberta. It is known from climatic records that Edmonton experiences a pronounced summer maximum of convective precipitation and falls well below Dansgaard's (1964) linear regression line (Hage et al., 1975). Because of the difference between the closed and open models, it may be possible to distinguish these two major types of precipitation from the measured del-values of collected samples.

The present work was concentrated on summer convective precipitation. So the open models were disregarded, at least at the outset. Relevant synoptic weather maps were consulted, however, to search for warm frontal activity. The model SM was used to estimate a tentative condensation temperature for each precipitation sample.

2.5 Experimental Procedure

The water vapour and precipitation samples were collected in the field by a number of workers other than the author. The work was conducted during the summers of 1974, 1975, and 1976 in central Alberta east of the Rocky Mountains. A roving collection vehicle was often used so that the samples could be taken under showers, the location of which had been previously identified by the weather radar of the Alberta Hail Project at Penhold Airport.

Surface air-temperature and wet-bulb temperature were recorded on location before the beginning of rainfall, when the ambient air was thought to be representative of the air feeding the cloud. The prevailing weather conditions were compared with those at neighbouring weather stations: Penhold, Rocky Mountain House, Calgary, and Edmonton. Synoptic weather maps, radiosonde profiles, and satellite photographs were assembled as additional reference material.

The vapour samples were collected as described by Hage et al. (1975). The freezing-out temperature ranged from -55°C to -70°C (Sandhu, 1978). The standard deviation of the resulting del values, a crucially important quantity, was 0.6°/₀₀ for the vapour samples. It was thus three times the experimental error expected for the solid and liquid samples.

2 or 3 ml. of water were required for a single laboratory measurement. Consequently, liquid samples could be collected in just a few minutes of rain, whereas vapour samples required more than an hour unless they were taken in plastic bags and

condensed later. The laboratory analysis for ^{18}O-content was carried out in the Physics Department of the University of Alberta at Edmonton. The total time for one analytic run in the laboratory was of the order of a few days.

The laboratory procedure consisted of two parts: first, the equilibration of the water sample with a standard carbon dioxide gas, and second, the isotopic analysis of the carbon dioxide on a ratio mass spectrometer. Both Linton (1972) and Sandhu (1978) have described the laboratory technique in some detail. The originators of the method, however, were Epstein and Mayeda (1953). West (1972) gave the first account of the modern equilibration procedure at the University of Alberta, and it was this part of the laboratory work which took 24 hours or more to establish equilibrium between the water and carbon dioxide. Sandhu (1978), who supervised the laboratory reductions, suggested an equilibration time of 30 to 70 hours at 26°C. On the mass spectrometer, the final stage of the analysis, Coleman and Gray (1972) obtained del-values with a precision better than ± 0.2°/₀₀.

CHAPTER III

EXPERIMENTAL RESULTS AND SOME DISCUSSION

3.1 Unusually High Del-Values

The numerical data for this study have recently been tabulated by Sandhu (1978) who discussed the results on a daily basis. Tables of the measured del-values have been compiled in Appendix C for reference. In Appendix D, all the raw data-points are presented in graphical form.

A careful examination of the figures in Appendix D will reveal a few spurious results. The most obvious is the graupel sample taken on 5 August 1975, with $\delta_h{}^{18}O = +6.8°/_{\circ\circ}$. Positive del-values in precipitation samples are rare and have been attributed to heavy-isotope enrichment from partial evaporation of falling raindrops near the oceans.

Ehhalt et al. (1963) reported values of $\delta_w D$ up to $+44°/_{\circ\circ}$ and simultaneous measurements of $\delta_w{}^{18}O$ up to $+8°/_{\circ\circ}$ in rain samples collected in semi-arid regions of South Africa. The oxygen-18 enrichment in rain may be as high as 8 or 9 del-units under extreme conditions, but Linton's (1972) calculations showed that enrichments of 2 or 3 del-units were more typical estimates. Ehhalt et al. (1963) measured a decrease in $\delta_w{}^{18}O$ of $1.7°/_{\circ\circ}$ on one occasion during the first hour of a thunderstorm in Heidelberg.

For solid precipitation, such as graupel, evaporative enrichment during descent has been assumed in the past to be negligibly small. However, Bailey et al. (1969) calculated and measured heavy-isotope enrichment during the freezing of supercooled water droplets accreted by growing hailstones. The maximum observed increase, in an icing tunnel, was about 6°/oo for deuterium and 1.5°/oo for oxygen-18.

The graupel sample of 5 August 1975, with $\delta_h{}^{18}O = +6.8$°/oo, was apparently formed from vapour with $\delta_v{}^{18}O = -18$°/oo or lower. The graupel del-value was, therefore, much too large to be derived from the observed vapour, but the source of the error was not obvious. The collection and laboratory procedures were intended to be identical for all samples. Consequently, although this spurious sample was very evident and easily culled from the data, its occurrence made all the other precipitation measurements slightly more suspect than the quoted error of ±0.2°/oo in the mass spectrometry.

No positive del-values were noted for liquid or vapour samples. The highest ones recorded were about -4°/oo for rain. Because of the relatively large enrichment possible in falling raindrops, all the liquid samples were considered to be valid. As a consequence, enrichments of the order of 6 del-units, on 5 June 1974 for example, had to be accepted and accounted for.

There were 3 vapour samples which were thought by the author to be somewhat doubtful, namely those with the highest del-values on: 23 May 1974, 24 May 1974, and 30 June 1976. The first vapour sample of 23 May 1974 was collected during a snow-and-rain shower under saturation conditions. Liquid fog droplets may have been incorporated with the condensed vapour. If so, the measured del-value would lie between that of the pure vapour and that of pure rain. Such a result is indeed evident in Figure D.1 of the Appendix.

The bottle containing the vapour condensed on 24 May 1974 was the only sample collected on this date. Evaporative enrichment was suspected, and the del-value, -18.5°/oo, was probably too high. On 23 May 1974, less than 18 hours previously, the measured vapour del-value was -30.9°/oo, one of the lowest on record.

On 30 June 1976, four vapour samples were taken within 6 hours at the University of Alberta. Three gave concurrent del-values lower than -20°/oo. The odd exception was found to have $\delta_v{}^{18}O$ = -9.5°/oo. This value looked distinctly out of place, but no explanation for the discrepancy was apparent. Sandhu (1978) noticed the close proximity of virga which could account for some enrichment, but not likely so much as 10°/oo.

When these 3 spurious vapour samples were disregarded, the remaining 66 had an arithmetic mean of -26.2°/oo. Sandhu's (1978) mean of -25.8°/oo was based on 69 samples. The standard deviation of an individual measurement was 3.3°/oo. Thus, if the distribution of del-values were Gaussian or normal, measurements higher than -16°/oo would be exceedingly rare, about three in a thousand. Values lower than -36°/oo could be expected to occur with the same frequency. The lowest recorded del-value was

-33.1°/oo on 15 June 1976.

Evidently the distribution is not symmetrical, for high del-values are more probable than low ones. On occasion, maritime air with $\delta_v^{18}O \geq -10$°/oo may reach Alberta. Such an occasion is shown by the weather maps centered around 30 June 1976, and reproduced in Figures 3.1 to 3.4 (U.S.A. Department of Commerce, 1976). On that date, an upper flow of maritime Pacific air was established across the Rocky Mountains at about latitude 40°N. Very little water vapour was removed by precipitation on the mountains, and the air must have reached Alberta practically undepleted in heavy isotopes.

The maritime air was detected at ground level by del-values significantly higher than average. Even $\delta_v^{18}O = -9.5$°/oo, the highest del-value observed for water vapour, cannot be completely ignored in this case. Deuterium measurements would be extremely valuable in substantiating these unusually high del-values which are rare but still possible.

3.2 Statistical Results for Water Vapour

Nearly half of the vapour samples came from the field work of 1976. Mean del-values were calculated for each season as follows:

(-25.7 ± 0.9)°/oo for 1974 based on 16 samples,

(-26.7 ± 0.8)°/oo for 1975 based on 18 samples,

2 ± 0.5)°/oo for 1976 based on 32 samples.

The 1976 season was apparently quite representative with respect

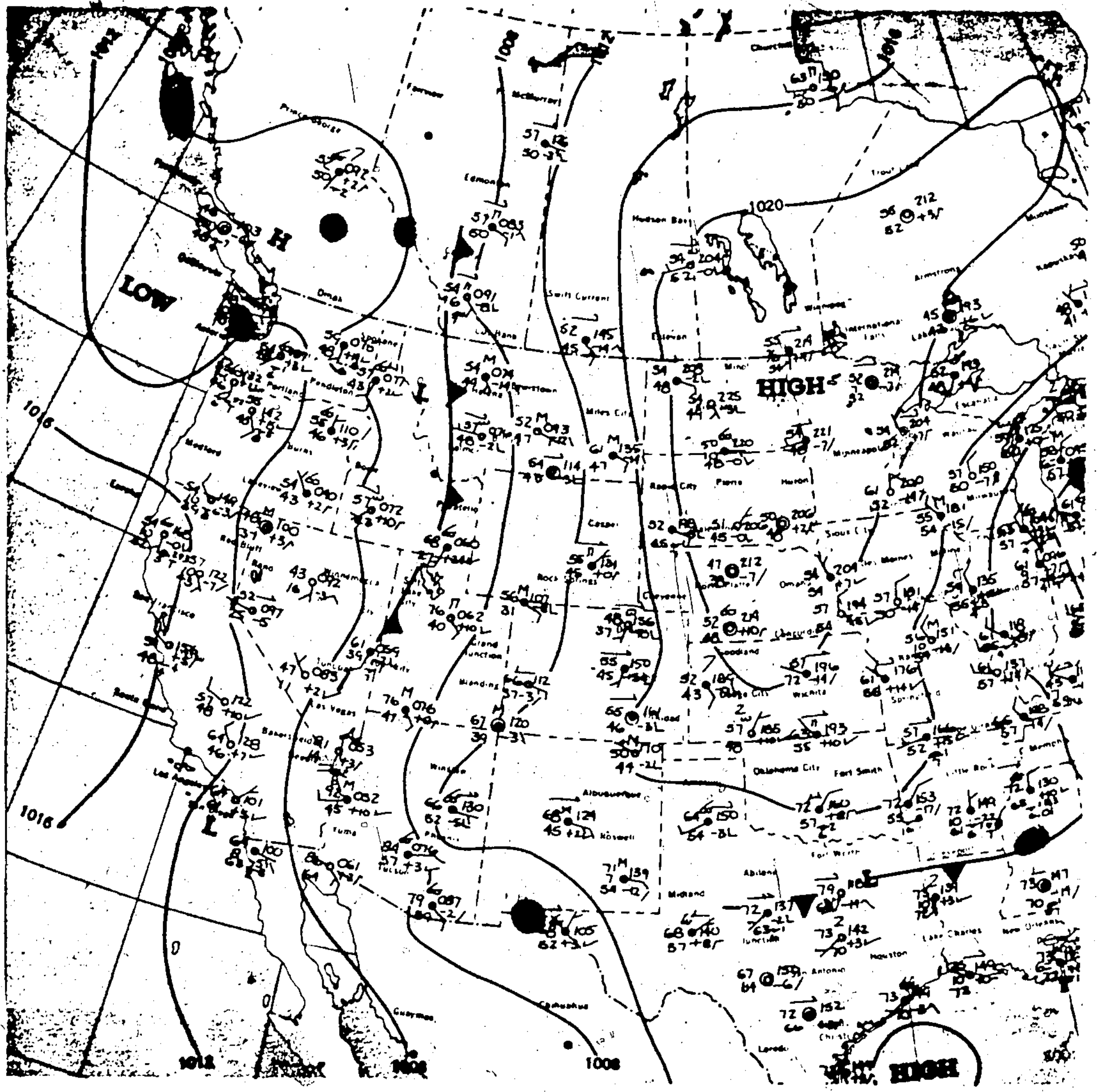


Figure 3.1 Surface weather map for western North America showing very little rain at 6:00 a.m., M.D.T., on 30 June 1976.

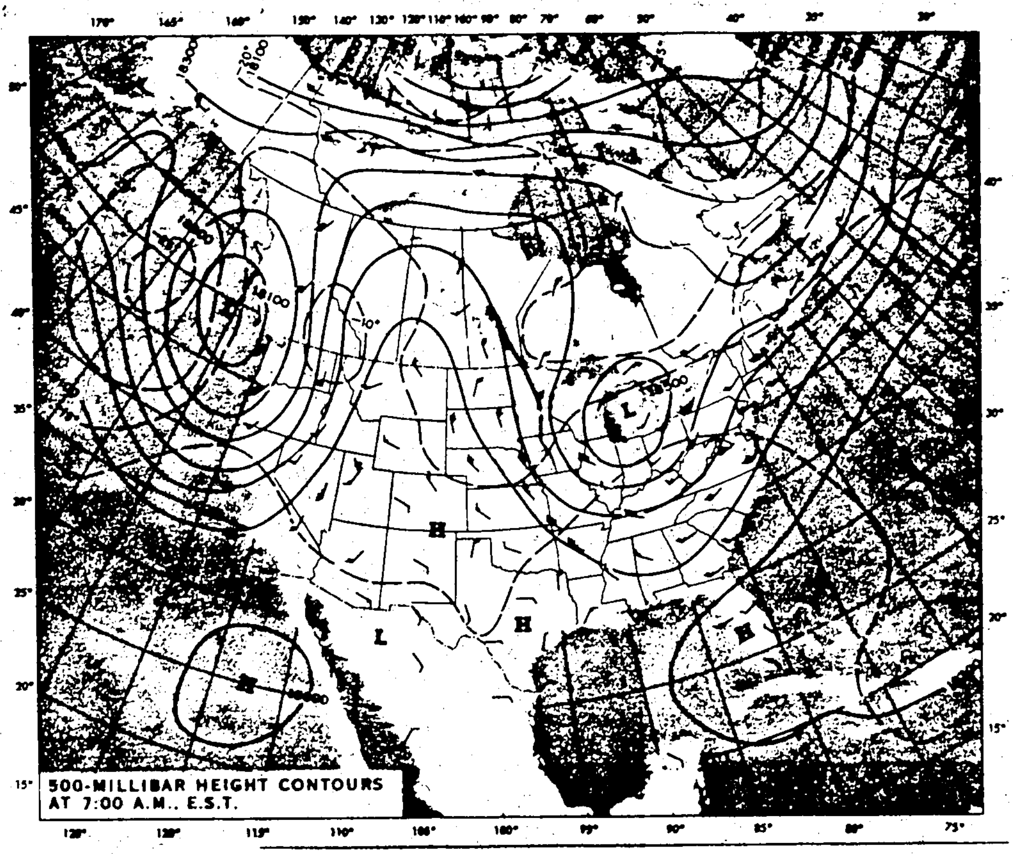


Figure 3.2 500-millibar weather map for western North America at 6:00 a.m., M.D.T., 30 June 1976. Pacific vortex was prominent, and southerly winds aloft were strong.

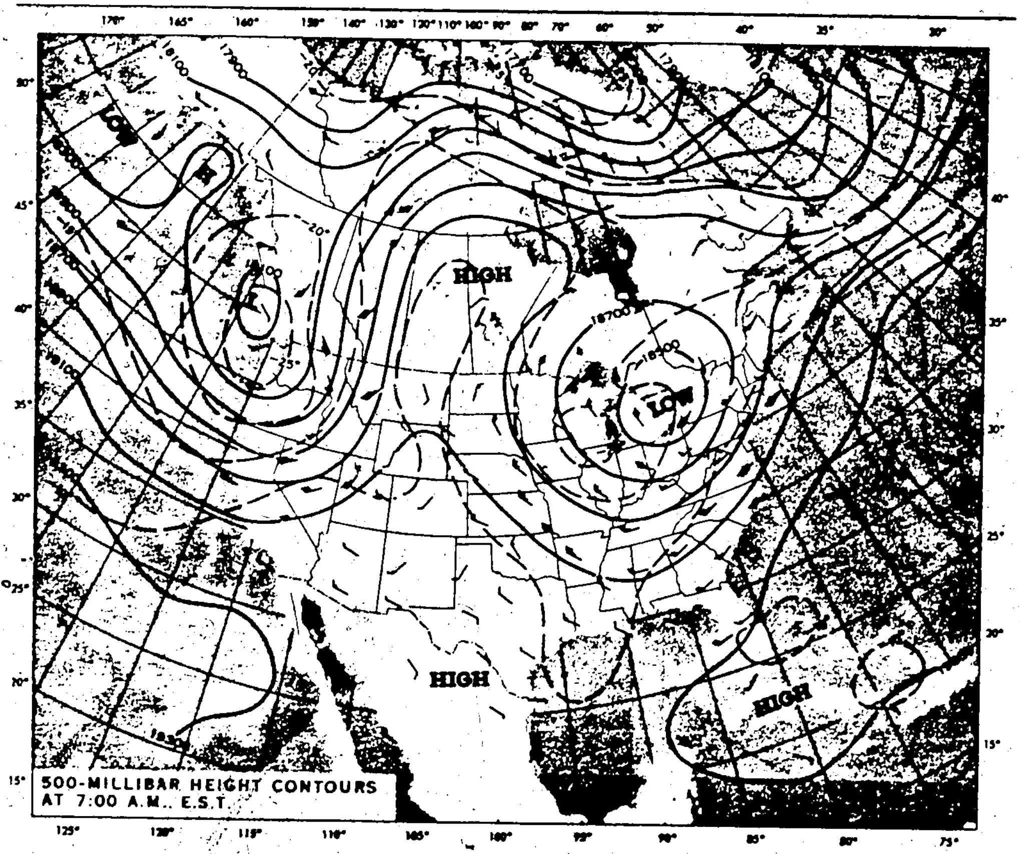


Figure 3.3 500-millibar map for western North America at 6:00 a.m., M.D.T., 1 July 1976 . Southerly flow over Alberta was still well established.

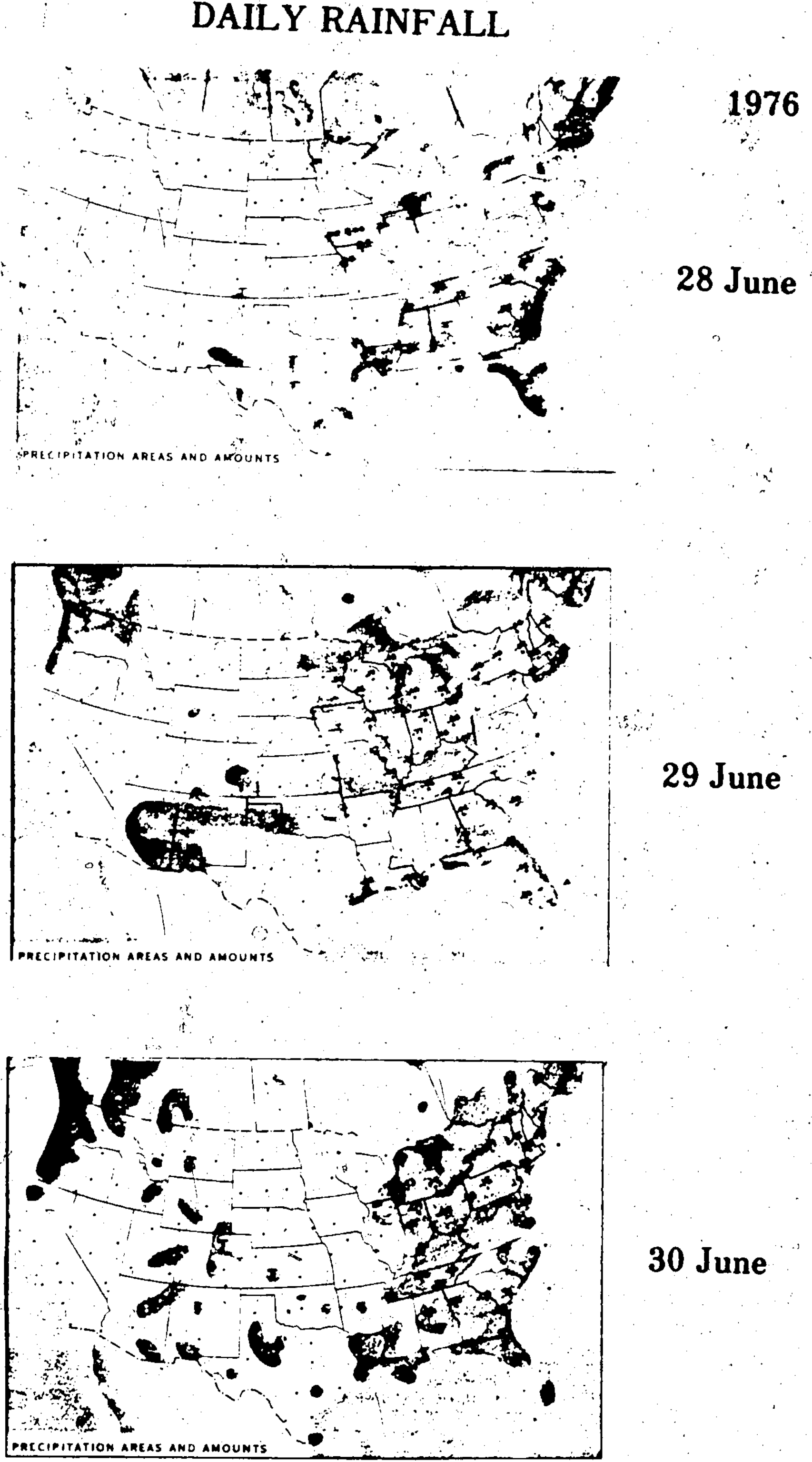


Figure 3.4 Successive daily rainfall charts for: 28 June (top), 29 June (middle), and 30 June (bottom), 1976. Amounts measured in 0.01 inches.

to measurements of $\delta_v{}^{18}O$. The indicated errors are standard deviations of the mean and are inversely proportional to the square root of the number of samples. They are proportional, as well, to the standard deviation of the del-value population which was estimated as 3.3°/₀₀ based on all 66 samples.

The seasonal trend in ^{18}O-content reported by Dansgaard (1961) for the semi-continental location of Copenhagen was expected to be modified in central Alberta. The Copenhagen tendency had been equally conspicuous in both rain and vapour samples. Ehhalt et al. (1963), however, found the trend in rain suppressed, or even reversed, for the interior regions of South Africa, but presumably it was still believed to occur in the atmospheric water vapour. In Alberta, it was found to be present in water vapour, graupel, and rain, with statistically the same magnitude for each case.

In the lower half of Figure 3.5, the del-values of the vapour samples are plotted against calendar date. The least-squares regression line represents the seasonal trend during May, June, and July, but not August. The upper line in Figure 3.5 is the corresponding regression line for small hail. The data for rain are summarized in Figure 3.6 on page 49. The slopes of the various regression lines are included in Table 3.1 on page 43.

For water vapour, the slope of the regression line is (+0.054 ± 0.017)°/₀₀ per day. Thus the seasonal trend is small but still significantly different from zero. The calculated

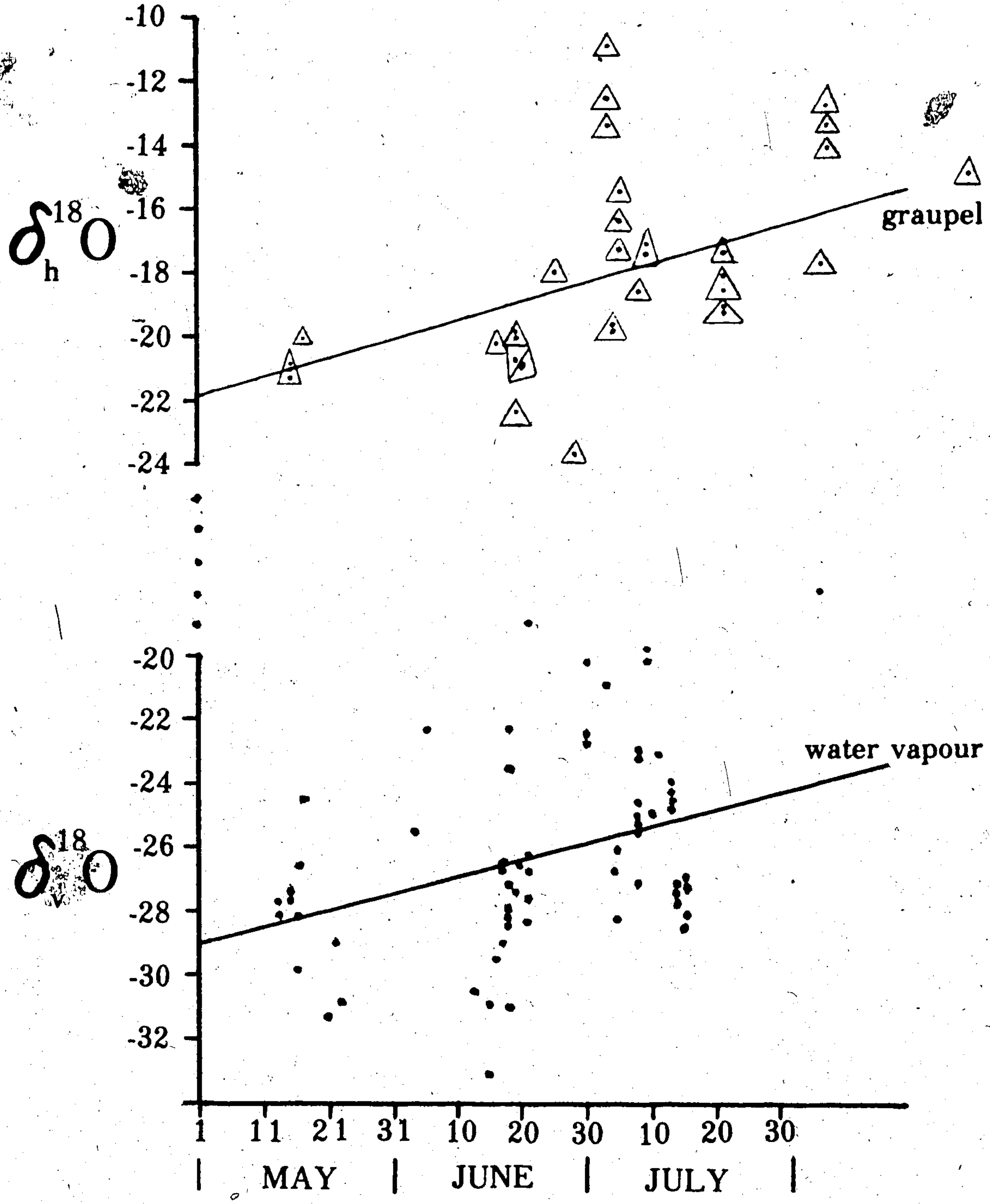


Figure 3.5 Oxygen-18 concentration in graupel (top), and atmospheric water vapour (bottom) during May, June and July in central Alberta.

correlation coefficient, ρ, is $(+0.37 \pm 0.13)$. According to Keeping (1962), the quantity, $\rho\left[\frac{n-2}{1-\rho^{2}}\right]^{\frac{1}{2}}$, has the Student-t distribution with $(n - 2)$ degrees of freedom and can be used to test the null hypothesis that $\rho = 0$. n is the total number of samples or trials. Because of the large number of vapour samples collected over the three years, the correlation between the vapour del-values and calendar date is different from zero with greater than 99% confidence. It is nevertheless small in magnitude because of the large intrinsic scatter in the measured del-values.

The standard error of estimate (Keeping, 1962) is a measure of the variance about the regression line and is less than the standard deviation of the del-value population. For the vapour samples, it is 2.8°/oo, compared with 3.3°/oo for the standard deviation of an individual del-value. The regression line is thus a better predictor than the mean del-value of the observations, but, because of the large uncertainty remaining, it still cannot be relied upon to estimate $(\delta_v{}^{18}O)_o$ in the atmosphere on a specified date. The water vapour feeding any one particular storm or shower must be sampled, as before, to get the best estimate of $(\delta_v{}^{18}O)_o$.

The samples used to compile Figure 3.5 were all collected at ground level. The variation of $\delta_v{}^{18}O$ with height above ground is still an open question. It may not be large since the

TABLE 3.1

STATISTICAL RESULTS FOR SAMPLES COLLECTED DURING 1974, 1975, and 1976

Item of Interest	Atmospheric Water Substance		
	Vapour	Rain	Hail
Number of samples	66	52	33
Standard deviation of a single sample (°/oo)	3.3	4.4	3.1
Mean del-value (°/oo)	-26.2	-14.7	-17.9
Standard deviation of the mean (°/oo)	0.4	0.6	0.5
Correlation coefficient with respect to calendar date	+0.37	+0.28	+0.42
Slope of regression line with respect to calendar date	+0.054	+0.057	+0.059
Correlation coefficient with respect to $\delta_v {}^{18}O$	+1.0	+0.60	+0.50
Slope of regression line with respect to $\delta_v {}^{18}O$	+1.0	+0.75	+0.87

atmosphere is often well mixed by winds and thermal turbulence. Miyake et al. (1968) measured a lapse rate of approximately -2‰ per km on one occasion during rain on the slopes of Mount Fuji. They also recorded a drop in $\delta_v{}^{18}O$ of 8‰ in less than two hours. A steep gradient of $\delta_v{}^{18}O$, at a front for example, or near a thunderstorm, may be of special interest for it will indicate a discontinuity and identify the associated weather.

Ehhalt (1974) has published vertical profiles of $\delta_v D$ from water vapour samples taken during aircraft flights over North America and the Pacific Ocean. More often than not, $\delta_v D$ decreased with height up to the tropopause. On flights over land masses, however, the profiles showed ground-level inversions in $\delta_v D$ nearly 50% of the time. In these cases, $\delta_v D$ increased slightly with height in the surface layer before it resumed the typical lapse rate of -32‰ per km. Most of the sampling was done over Scotts Bluff, Nebraska, where the standard deviation of an individual deuterium lapse rate was 12‰ per km. Knight et al. (1975) published a typical, June profile for deuterium in clear air. $\delta_v D$ was practically constant at -140‰ from the ground up to a height of 2 km.

3.3 Statistical Results for Small Hail and Graupel

Because of the fixation of the ^{18}O-concentration in ice by freezing, it was expected that the graupel samples would be the most reliable. The mean of 33 measured del-values covering the three years was (-17.9 ± 0.5)‰ (Sandhu, 1978). The number of small hail samples was about half the number for water vapour, but the scatter was about the same in the two groups. The standard deviation of the graupel population was estimated as 3.1°/₀₀. The value of -17.9°/₀₀ was precisely the del-value given by Hage et al. (1975) for the annual mean of all precipitation at Edmonton.

The individual, seasonal means for graupel were:

(-18.7 ± 0.6)°/₀₀ for 1974 based on 11 samples,
(-15.9 ± 1.2)°/₀₀ for 1975 based on 12 samples,
(-19.3 ± 0.5)°/₀₀ for 1976 based on 10 samples.

These means showed more year-to-year variability than the corresponding ones for water vapour. The year 1975 in particular had relatively large fluctuations in $\delta_h{}^{18}O$. Both the highest (-10.8°/₀₀) and lowest (-23.6°/₀₀) del-values for hail occurred in 1975.

In addition, it was rather surprising to discover that the seasonal means for hail and vapour changed in opposite directions from one year to the next. This out-of-phase variation suggested that the del-values for hail and vapour might not be so well correlated after all. Table 3.2 has been constructed, therefore, to illustrate the lack of a strong correlation between $\delta_h{}^{18}O$ and $\delta_v{}^{18}O$.

Column 1 contains the nine dates on which samples of both graupel and water vapour were collected. Columns 2 and list the measured del-values. The regression lines of Figure 3.5 were used to calculate the residuals which are given in

TABLE 3.2

DEL-VALUES FOR 15 SIMULTANEOUS SAMPLES OF GRAUPEL AND WATER VAPOUR COLLECTED MAINLY IN 1974

Date of Sample	$\delta_h{}^{18}O$	$\delta_v{}^{18}O$	Deviation of $\delta_h{}^{18}O$ from its Regression Line	Deviation of $\delta_v{}^{18}O$ from its Regression Line
74/05/15	-20.8	-27.7	+0.2	+0.65
"	-20.9	-27.7	+0.1	+0.65
"	-21.2	-27.7	-0.2	+0.65
74/05/17	-20.0	-24.5	+0.9	+3.75
74/07/04	-19.6	-26.8	-1.5	-1.15
"	-19.7	-26.8	-1.6	-1.15
74/07/05	-15.4	-26.2	+2.6	-0.60
"	-16.3	-26.2	+1.7	-0.60
"	-17.2	-26.2	+0.8	-0.60
74/07/09	-17.4	-20.2	+0.4	+5.20
"	-17.0	-20.2	+0.8	+5.20
75/06/16	-20.1	-29.5	-1.0	-2.86
75/06/20	-20.8	-26.6	-1.9	-0.17
75/08/05	-17.6	-18.0	-1.4	+5.92
76/07/08	-18.5	-26.0	-0.7	-0.55

columns 4 and 5 for graupel and vapour, respectively. It can be seen that the large vapour residuals are not paired with large hail residuals, and, on 5 occasions out of 15, the members of a pair have opposite signs.

According to Equation (2.9) for the simplified model, $\delta_h{}^{18}O$ should be directly proportional to $(\delta_v{}^{18}O)_o$. Since both the graupel and vapour del-values were found to be significantly correlated with calendar date, they would also be correlated, to some extent, with each other. Actual regression analysis of the 15 simultaneous vapour and graupel samples in Table 3.2 yielded a correlation coefficient of (+0.50 ± 0.28), and a slope, b, of (+0.87 ± 0.42). In Equation (2.9), b = 1.0. The partial correlation coefficient for the graupel and vapour del-values, with calendar date held constant, was +0.37.

A correlation coefficient of 0.37 does not imply strong correlation, but it is not zero either. Since the graupel del-values are likely to be the more reliable, the vapour measurements must be carefully scrutinized. Yet both the graupel and the vapour results, taken in their entireties, have statistically the same variance and show the same seasonal trend. Evidently $\delta_v{}^{18}O$, measured at ground level, is not always a reliable estimate of $(\delta_v{}^{18}O)_o$ at cloud base. On the other hand, since the correlation is significantly different from zero, the surface measurements do represent the vapour feeding the cloud some of the time. The slope of the graupel-vapour regression line, 0.87, is quite satisfactory and provides a degree of confidence in the experimental technique and in the measured del-values on the whole.

3.4 Statistical Results for Rain

Figure 3.6 was prepared in order to compare all available rain data for May, June, and July in central Alberta. The global survey of the International Atomic Energy Agency - World Meteorological Organization included Edmonton as a continental weather station of North America. The IAEA-WMO del-values were precipitation-weighted, monthly means and were tabulated for 5 years (IAEA, 1970, 1969). The numerical data have been reproduced in Appendix B. The lowest line of Figure 3.6 was deduced from Linton's (1972) data for the spring and summer rainfall of 1971 in Edmonton.

The regression line, with respect to calendar date, for the 1974-1976 rain del-values appeared to be very representative in spite of the large variance of the del-value population. The standard deviation of 4.4°/₀₀ was distinctly larger than the 3.3°/₀₀ for water vapour. The slope of the regression line, however, was practically identical with the graupel and vapour values.

The excessive variance was caused in large part by 5 or 6 dramatically high values of $\delta_w{}^{18}O$. In 1971, Linton (1972) did not find any del-values for rain higher than -10°/₀₀, but during the summers of 1974 and 1975, they occurred at a rate of about 3 per season. In the case of water vapour, the unusually

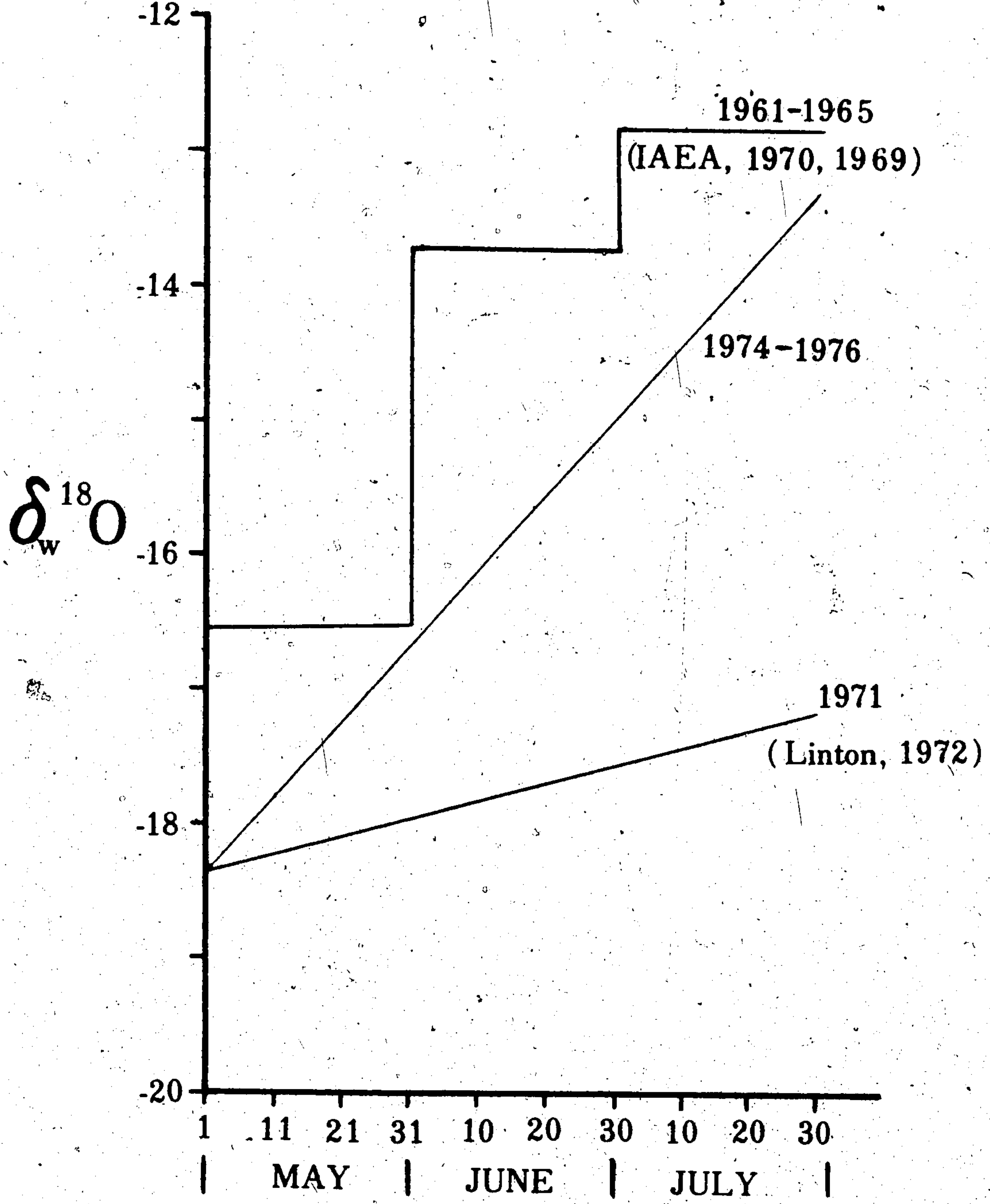


Figure 3.6 Oxygen-18 concentration in rain samples collected during May, June and July in central Alberta.

high del-values were considered to be spurious, and, with a little hesitation, were disregarded. Dealing with the rain samples was not so easy. All the samples were retained because, in theory at least, evaporative enrichment could amount to 10°/₀₀ or even more (Dansgaard, 1964, 1961).

The very high del-values also contributed to the overall mean of -14.7°/₀₀ which was not particularly abnormal when compared with the IAEA-WMO data (IAEA, 1970, 1969). It was nevertheless 3.0°/₀₀ higher than the 1971 mean (Linton, 1972), and 3.2°/₀₀ higher than the corresponding mean of the graupel samples. No doubt some of this difference can be attributed to the partial evaporation of falling raindrops, but it is also likely that, on the average, summer rain in Alberta is composed of water droplets condensed nearer to the cloud base than the constituents of small hail. The relative importance of these two explanations is not yet clear.

The individual, seasonal means for rain were:

(-15.7 ± 0.8)°/₀₀ for 1974 based on 23 samples,
(-13.3 ± 1.2)°/₀₀ for 1975 based on 19 samples,
(-14.8 ± 0.9)°/₀₀ for 1976 based on 10 samples.

These means varied in parallel with those for graupel. The correlation with vapour del-value was also similar to the graupel value and was given near the bottom of Table 3.1 on page 43. Simultaneous values of $\delta_w{}^{18}O$ and $\delta_h{}^{18}O$ were strongly correlated; $\rho = (0.72 \pm 0.34)$ for these two forms of precipitation.

CHAPTER IV

THE EFFECTIVENESS OF THE MODELS

4.1 The Observational Data and the Closed Models

Until the onset of precipitation from a cooling cloud, a closed isotopic model should provide an adequate description of the fractionation processes. Stewart (1975) came to the conclusion that atmospheric condensation, to form cloud droplets, led approximately to isotopic equilibrium between the cloud liquid water and the remaining water vapour. In the case of hail formation, Miyake et al. (1968) suggested the use of model L2, which was identical to L1 until the first occurrence of freezing.

Equation (2.9), which defined the simplified form of L1, can be written as the difference between the del-values of the condensate and the original vapour.

$$\text{i.e.}\quad \delta_c{}^{18}O - (\delta_v{}^{18}O)_o = 0.974 \times F_v \qquad (4.1)$$

An initial, precipitation sample, taken at cloud base, would be a good estimate of $\delta_c{}^{18}O$. A small hail or graupel sample would represent the cloud conditions at the time of freezing.

The non-equilibrium closed model, L2, differs from L1 and SM because of its step-by-step condensation process. Each step is terminated by the freezing of the outer shell of condensate surrounding a growing precipitation particle. In this way, the frozen ice becomes isolated from the remaining vapour and is no longer in isotopic equilibrium with it.

The differential equation for Rayleigh condensation (Dansgaard, 1961) is assumed to apply to the remaining vapour, and to the condensing outer liquid shell, rather than to the total condensed and frozen water. As the steps become smaller and smaller, this model describes the growth of precipitation by a vapour-solid mechanism. So, at the vapour-condensate interface,

$$\frac{dR}{R_v} = (\alpha - 1)\frac{dF_v}{F_v} \tag{4.2}$$

Or, in terms of del-values as defined by Equation (1.1),

$$d(\delta_v{}^{18}O) = (10^3 + \delta_v{}^{18}O)\ (\alpha - 1)\frac{dF_v}{F_v} \tag{4.3}$$

R_c, the isotopic abundance ratio for the total condensed phase, was given in Table 2.1. It can be derived from the conservation of mass conditions, for the entire system is still closed. Therefore,

for oxygen-18, $N_cR_c + N_vR_v = (N_vR_v)_o$,

and for oxygen-16, $N_c + N_v = (N_v)_o$.

Solving for R_c gives $$R_c = \frac{(N_vR_v)_o - N_vR_v}{N_c},$$

or alternatively, $$R_c = \frac{(N_vR_v)_o - N_vR_v}{(N_v)_o - N_v},$$ as in Table 2.1.

Introducing the fraction of remaining vapour F_v leads to

$$(1 - F_v)\delta_c{}^{18}0 = (\delta_v{}^{18}0)_o - F_v\delta_v{}^{18}0 \qquad (4.4)$$

In practice, the initial conditions at cloud base are observed, or estimated, and then used in the right hand side of Equation (4.3) to calculate the change in $\delta_v{}^{18}0$ corresponding to a small condensation dF_v. This gives a corrected value of $\delta_v{}^{18}0$ to be used in Equation (4.4) to determine $\delta_c{}^{18}0$. The process is repeated, and condensations are thus calculated according to the steps of dF_v.

If the fractionation factor were known as a simple function of the remaining fraction F_v, Equation (4.2) could be integrated. Such a function could be obtained by selecting pairs of F_v's and t's from the appropriate moist-adiabat on a tephigram. The temperatures would then be converted to α's by means of Figure 1.1 or 1.2, or by the corresponding Equation (1.10) or (1.11).

Tables 4.1 and 4.2 group together the various days which provided measurements suitable for model testing. In all, 16 dates have been tabulated. Simultaneous estimates of t_o, $(\delta_v{}^{18}0)_o$, and $\delta_c{}^{18}0$ were made for the dates specified in column 1.

TABLE 4.1

INVENTORY OF THE OBSERVATIONAL DATA FOR 1974

Date of Samples	Number of Samples Vapour	Number of Samples Precipitation	Type of Weather
74/05/15	1	6	Upslope showers in cold air
74/05/17	1	1	Orographic showers during Arctic outbreak
74/05/23	2	3	Cold-frontal showers
74/06/03	1	2	Widespread thundershowers in extensive low pressure
74/06/05	1	3	Light convective showers
74/07/04	1	7	Post-frontal, convective, evening showers in cool maritime air
74/07/05	2	6	Convective evening showers in unstable air aloft
74/07/09	2	3	Post-frontal light showers in lee trough
74/07/11	1	2	Stratiform cyclonic rain, 2 cm.

TABLE 4.2

INVENTORY OF THE OBSERVATIONAL DATA FOR 1975 AND 1976

Date of Samples	Number of Samples		Type of Weather
	Vapour	Precipitation	
75/06/16	1	4	Pre-cold-frontal showers
75/06/17	1	1	Light convective shower
75/06/20	1	4	Moderate convective shower
75/06/21	2	3	Cold-frontal showers
75/08/05	1	3	Cold-frontal showers
76/07/08	7	9	Widespread convective showers with extensive low pressure over western North America
76/07/14	4	1	Convective afternoon shower in cold polar air

Only occasionally was there more than one vapour sample on a given date. The number of precipitation samples, however, was on the average 3 or 4 per day.

Figure 4.1 shows the results for 9 July 1974. The temperature, t_o, at the lifting condensation level was 11°C. The del-value of the vapour feeding the cloud was estimated at -20.2°/₀₀, and consequently the del-value of the initial condensate was calculated to be -9.8°/₀₀. The curves of Figure 4.1 all originate at this point, $(\delta_c{}^{18}O = -9.8°/_{oo},\ t = 11°C)_o$, the point of initial condensation.

Nearly linear curves represent the isotopic cloud models SM and L2. The non-equilibrium model, L2, indicates that precipitation of an observed del-value must have been condensed at a colder cloud temperature, t_c, than would have been the case under total equilibrium. The open models give condensation temperatures which are warmer than those of SM. Thus the model SM serves at least as a reasonable compromise, and can be used with some confidence to estimate condensation temperatures, especially near the cloud base. From the curve for SM, the condensation temperatures were found to be: +0.8°C for the rain sample, and -16.4°C and -20.0°C for the graupel samples.

4.2 The Evaporation Problem

Most of the rain samples were enriched to some extent by evaporation below cloud base. The exact amount has been difficult to state quantitatively, and Sandhu (1978) did not

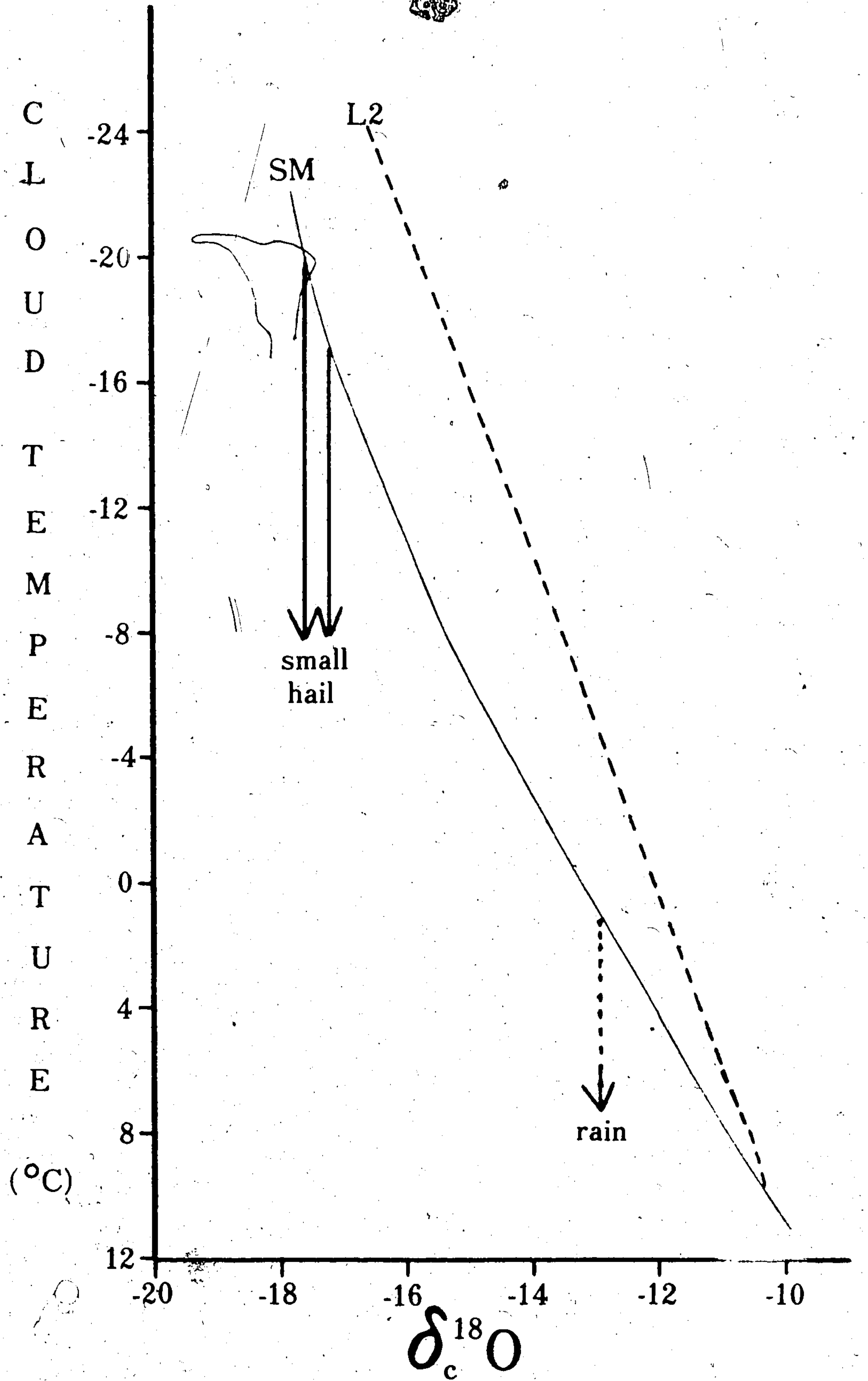


Figure 4.1 Cloud models SM and L2 for 9 July 1974.

postulate any numerical corrections. During periods of prolonged rain, it has been thought in the past that, as the atmospheric humidity increased to 100%, evaporative enrichment decreased towards zero (Dansgaard, 1964; Ehhalt et al., 1963).

Two separate showers were observed on 8 July 1976. Nine sequential precipitation samples were collected as well as 7 vapour samples, some of which were taken immediately before the start of the showers. The empirical data have been plotted in Figure 4.2 for the shower at Alder Flats, Alberta, and in Figure 4.3 for the later shower at Winfield.

At Alder Flats, the afternoon air-temperature was 21°C, and the relative humidity at the surface was 47%. The height of the cloud base was about 1 km above the ground. Five rain samples were collected during the first shower, and, when placed in sequence, showed a distinct "amount effect" (Dansgaard, 1964). That is, the observed del-values of the rain samples decreased with time. The initial del-value was about 3°/oo higher than the following ones, as the samples became progressively less enriched with time. The minimum enrichment, $\delta_w{}^{18}O - (\delta_c{}^{18}O)_o$, was 0.7°/oo for the first sample. The actual enrichment, as estimated from the other 4 samples, was about 3.2°/oo under the prevailing weather conditions.

The evening hailstorm at Winfield, about 35 km east of Alder Flats, occurred two hours later on the same day. The results shown in Figure 4.3, however, are more difficult to interpret. At ground level before the storm, the air-temperature

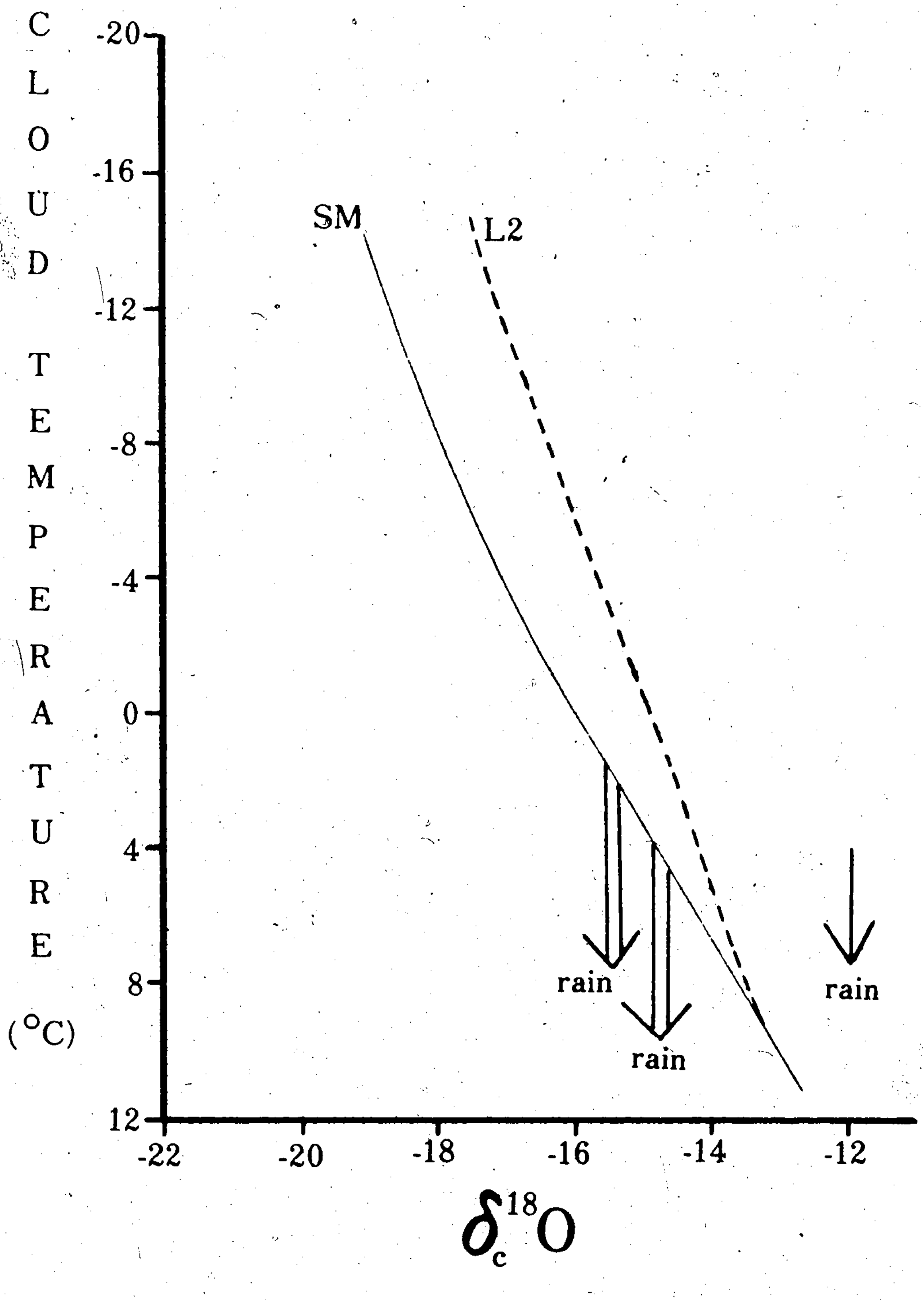


Figure 4.2 Cloud models SM and L2 for 8 July 1976 at Alder Flats, Alberta.

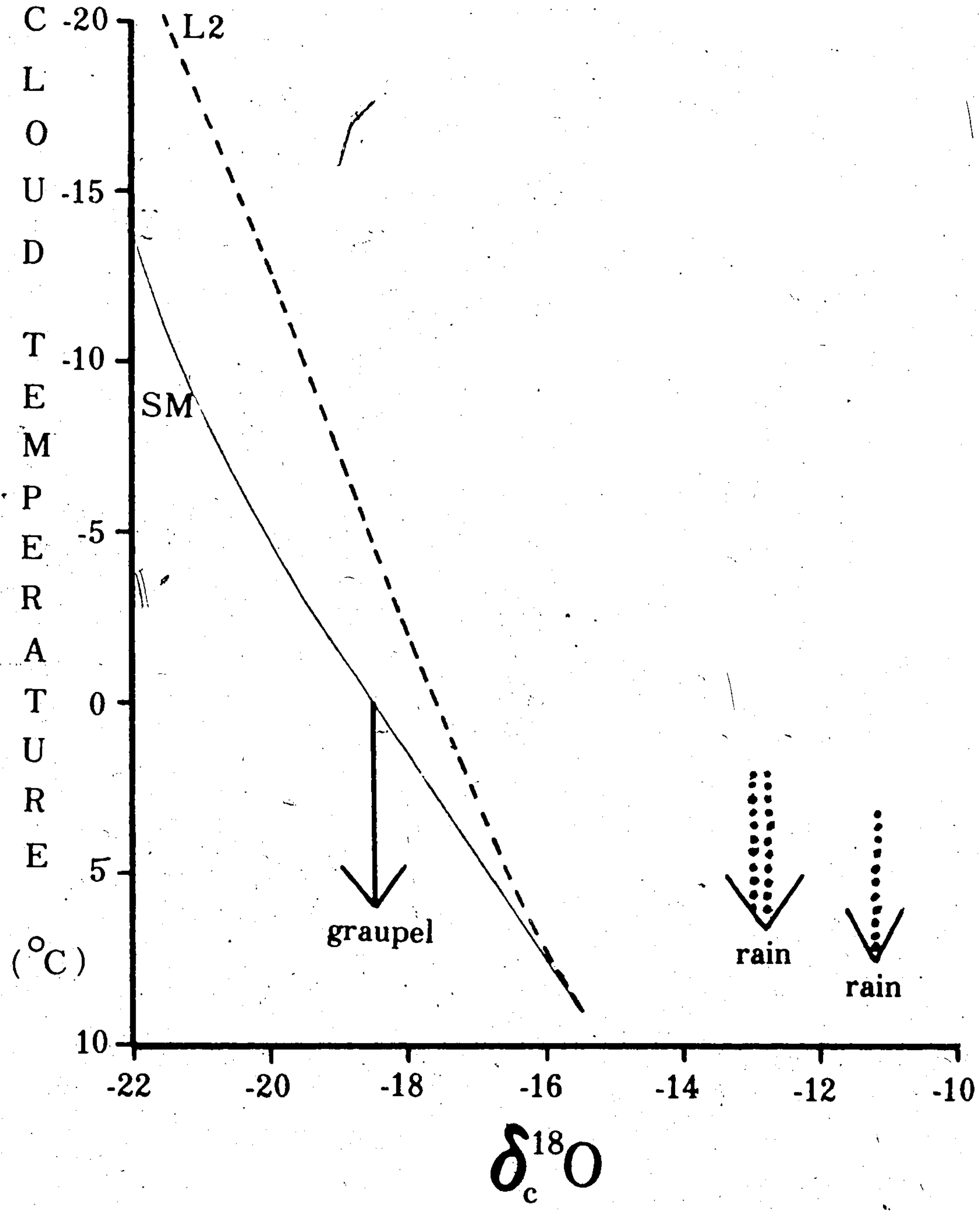


Figure 4.3 Cloud models SM and L2 for 8 July 1976 at Winfield, Alberta.

was 20°C, the relative humidity 53%, and the del-value of water vapour was fluctuating around -26°/oo. Three vapour samples were bagged before the rain began, but their del-values, -27.2, -25.6, and -25.1°/oo, were consistently lower than those at Alder Flats by 5°/oo. The arithmetic mean, -26.0°/oo, was adopted in Figure 4.3.

The "amount effect" (Dansgaard, 1964) was evident again, and the earliest rain sample had the highest del-value. If -26.0°/oo were a true estimate of $(\delta_v{}^{18}O)_o$, then the calculated value of $(\delta_c{}^{18}O)_o$ would be -15.5°/oo, and consequently all 3 rain samples would lie well to the right of the point of initial condensation. Evaporative enrichment could be invoked to account for the high del-values, but the amount of enrichment would be much greater than that observed at Alder Flats even though the weather conditions were not much different. As an alternative hypothesis, the reliability of the vapour measurements should be challenged. Similar measurements on 30 June 1976 were observed to be highly variable.

At the end of the storm, a graupel shower was encountered, and a sample of small, "shot size" hail was collected. Its measured del-value was -18.5°/oo. The corresponding cloud temperature of condensation, according to model SM, was close to 0°C. According to model L2, it was -4.6°C, but even so, this temperature seemed too warm for graupel.

Rogers (1976) cites a model of a single-celled convective shower which was observed with radar by Browning et al. (1968)

on 2 May 1967 at Pershore, England. The shower was thought to be representative of many such showers with a single, mature, weak updraft confined to the upper part of the cloud where the temperature was about -30°C. The ice crystals which formed there grew to graupel-sized particles until they could no longer be balanced by the weak updraft. Some further growth by accretion must have occurred at warmer temperatures during the descent, but downdrafts were predominant at low levels and quickly developed a precipitation streamer. Most of the growth, therefore, must have occurred in the cold, upper regions of the cloud.

In a review paper, Braham (1968) described the condensation-precipitation process in terms of a vertical continuity principle for stratified clouds. The cold, upper levels provided the initial ice crystals which then served as precipitation embryos for lower regions. Growth by diffusion and deposition had a maximum rate when the temperature was around -15°C. Consequently, if the shower studied by Browning et al. (1968) is typical of summer showers in central Alberta, and if the graupel is removed quickly from the lower and warmer cloud levels, then the condensation temperatures would be expected to range from -30°C to -15°C. In actual fact, very few samples were found in this range.

However, in the case of convective clouds with strong updrafts, Braham (1964) detected graupel particles by the time the clouds had reached top temperatures of -10°C. The research concentrated on the summer cumulus clouds of Missouri, U.S.A., a more humid area than Alberta. Nonetheless, it was a surprise to discover ice pellets and snow pellets in virtually every cloud which reached a top temperature between -5°C and -10°C, provided the cloud had first developed large liquid drops by coalescence, that is by the "warm-rain" mechanism.

The temperature of a hailstone growing by the accretion of supercooled cloud droplets is elevated towards 0°C because of the heat of fusion released by the freezing droplets (Ludlam, 1958, 1950; Schumann, 1938). If the cloud temperature is near 0°C as well, freezing proceeds slowly, some evaporation occurs from the liquid surface, and isotopic fractionation takes place [illegible] hailstone slightly enriched. Bailey et al. (1969) have [illegible]ated isotopic fractionation during the wet growth of [illegible]stone in an icing tunnel. The maximum enrichment in oxygen-18 was found to be 1.5°/₀₀.

Thus the graupel sample collected at Winfield on 8 July 1976 may have been enriched to a del-value of -18.5°/₀₀. At Alder Flats, however, such a del-value would have corresponded to a condensation temperature near -10°C, where enrichment would have been negligible. As a general rule in Alberta's climate, snow pellets probably result from dry growth so that their isotopic concentrations are preserved and can be used as experimental controls. On 8 July 1976, the vapour samples collected at Alder Flats seem to be more representative of the cloud vapour than the ones taken later at Winfield.

4.3 The Distribution of the Rain Samples

Because of the common occurrence of enriched rain in Alberta, let a variable z now be introduced to represent enrichment.

$$\text{i.e.} \quad z \equiv \delta_w{}^{18}O - (\delta_c{}^{18}O)_o \qquad (4.5)$$

$\delta_w{}^{18}O$ is the measured oxygen-18 content of a rain sample, and $(\delta_c{}^{18}O)_o$ is the oxygen-18 content of the initial condensate as estimated from an appropriate vapour sample. When z is positive, the observed del-value at ground level has become so enriched that it exceeds the del-value of the condensate at cloud base.

The distribution of z about zero is shown in Figure 4.4. Out of 39 rain samples on 14 dates, there were 11 cases with $z > 0$, and 5 of these had del-values which exceeded that of the initial condensate by more than 4°/₀₀. The distribution has, therefore, positive skewness most of which can be attributed to evaporative enrichment.

If the del-values of the rain samples could be corrected to cloud base, then their distribution would become narrower than the one shown in Figure 4.4. Perhaps the crudest possible correction would be simply to disregard the samples with $z > 0$. The remaining 28 samples would then form a population with a mean, $\bar{z}$, of -2.3°/₀₀, a standard deviation of 1.3°/₀₀, and skewness, -0.17. This is the population contained in Table 4.3.

Although the negative skewness agrees with intuition,

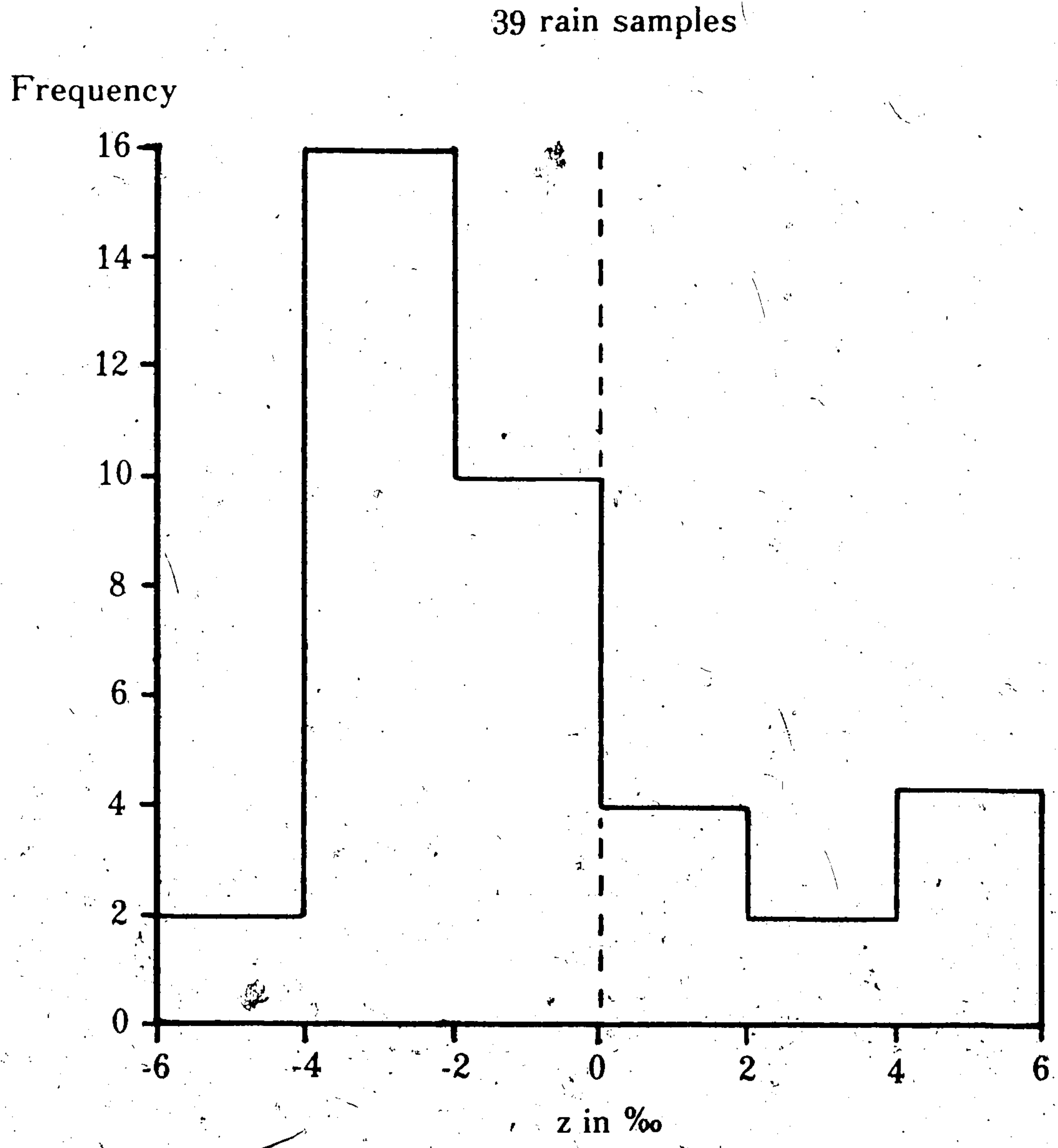


Figure 4.4 Frequency distribution of $z = \delta_w^{18}O - (\delta_c^{18}O)_o$.

TABLE 4.3

UNCORRECTED CONDENSATION TEMPERATURES, t_c, FOR 28 SUMMER RAIN SAMPLES WITH z < 0, ACCORDING TO THE MODEL SM

Date of Sample	t_o (°C)	$(\delta_c{}^{18}O)_o$ (°/₀₀)	z (°/₀₀)	t_c (°C)	$t_o - t_c$ (°C)
74/05/15	0.0	-16.3	-2.8	-6.6	6.6
"	0.0	-16.3	-2.6	-6.0	6.0
"	0.0	-16.3	-2.3	-5.3	5.3
74/06/03	1.5	-14.2	-2.1	-3.4	4.9
"	1.5	-14.2	-2.0	-3.2	4.7
74/06/05	1.5	-11.0	-1.2	-1.1	2.6
74/07/04	4.0	-15.8	-0.9	+1.8	2.2
"	4.0	-15.8	-2.1	-1.0	5.0
"	4.0	-15.8	-3.1	-3.8	7.8
"	4.0	-15.8	-2.9	-3.2	7.2
"	4.0	-15.8	-4.8	-8.9	12.9
74/07/05	4.0	-15.2	-0.6	+2.6	1.4
"	4.0	-15.2	-1.9	-0.6	4.6
74/07/09	11.0	- 9.8	-2.9	+0.8	10.2
74/07/11	10.0	-12.6	-0.2	+9.8	0.2
75/06/16	3.5	-18.5	-0.3	+3.0	0.5
75/06/17	7.5	-15.9	-2.5	+1.5	6.0
75/06/20	9.0	-16.1	-1.7	+4.3	4.7
"	9.0	-16.1	-5.1	-7.1	16.1
"	9.0	-16.1	-3.1	-0.2	9.2
75/06/21	6.0	-15.5	-3.8	-4.7	10.7
"	6.0	-15.5	-0.7	+4.2	1.8
75/08/05	6.0	- 7.1	-3.6	-2.0	8.0
76/07/08	11.0	-12.7	-2.2	+3.7	7.3
"	11.0	-12.7	-2.8	+1.7	9.3
"	11.0	-12.7	-2.8	+1.7	9.3
"	11.0	-12.7	-2.1	+4.0	7.0
76/07/14	10.0	-17.1	-0.1	+9.9	0.1

the exact nature of the distribution may be difficult to determine. A log-normal distribution of $(-z)$ is a plausible, first suggestion because of its strong peak near the cloud-base region where $z=0$. The accuracy of the del-values will become extremely critical, for the variable z is the difference between two of them. The mean, $\bar{z}$, was $-2.3^{\circ}/_{\circ\circ}$ for the 28 rain samples of Table 4.3, and such a value may be typical of summer rain in Alberta. If so, more than half of the collected samples can be expected to have values of z between $-2.3^{\circ}/_{\circ\circ}$ and $0.0^{\circ}/_{\circ\circ}$.

4.4 The Condensation Temperatures and Their Distribution

The model SM was used to determine a roughly averaged, condensation temperature, t_c, for each of the 28 rain samples with $z < 0$. Column 5 of Table 4.3 lists these temperatures, the mean of which is -0.3°C. The distribution of t_c is related to the del-values of Figure 4.4 with $z < 0$, and it forms the histogram shown at the top of Figure 4.5. The smooth comparison curve represents a normal distribution having a mean, 0°C, and a standard deviation of 4.5°C. The actual standard deviation of the temperatures in column 5 of Table 4.3 is 4.7°C.

At the bottom of Figure 4.5, the analogous distribution of 14 graupel samples is shown. This diagram is based on the numerical measurements recorded in Table 4.4. The extraneous sample collected on 5 August 1975 has not been included in the diagram.

Since only 14 cases were available, and since 3 of these

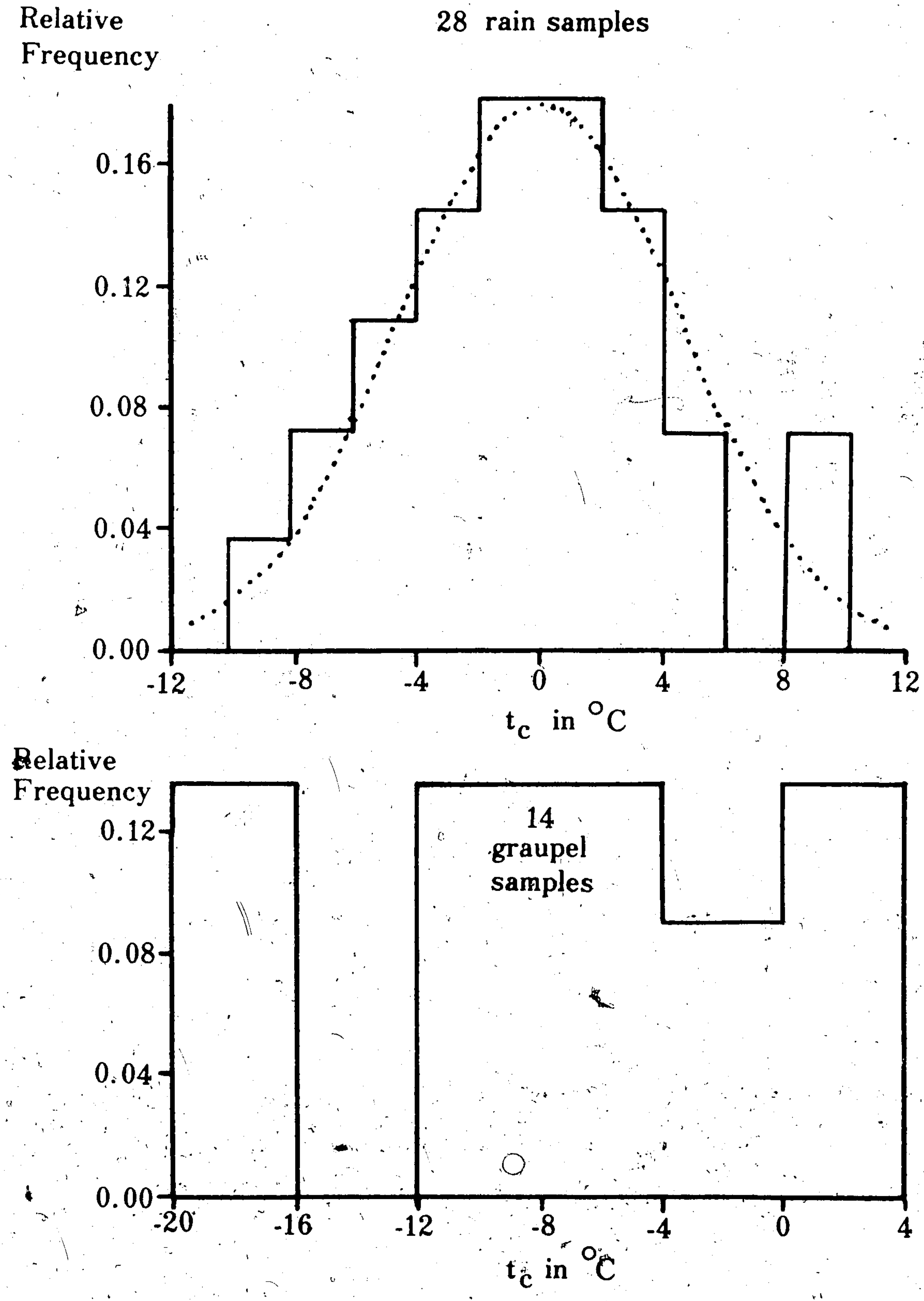


Figure 4.5 Frequency distribution of the condensation temperatures, t_c for rain (top), and for graupel and small hail (bottom).

TABLE 4.4

UNCORRECTED CONDENSATION TEMPERATURES, t_c, FOR 14 SUMMER HAIL SAMPLES FROM CENTRAL ALBERTA ACCORDING TO THE MODEL SM

Date of Sample	$\delta_h{}^{18}O$ (°/∘∘)	$(\delta_c{}^{18}O)_o$ (°/∘∘)	t_o (°C)	t_c (°C)
74/05/15	-20.8	-16.3	0.0	-10.5
"	-20.9	-16.3	0.0	-10.7
"	-21.2	-16.3	0.0	-11.9
74/05/17	-20.0	-13.1	0.0	-16.2
74/07/04	-19.6	-15.8	4.0	- 5.9
"	-19.7	-15.8	4.0	- 6.1
74/07/05	-15.4	-15.2	4.0	+ 3.6
"	-16.3	-15.2	4.0	+ 1.4
"	-17.2	-15.2	4.0	- 0.8
74/07/09	-17.4	- 9.8	11.0	-20.0
"	-17.0	- 9.8	11.0	-16.4
75/06/16	-20.1	-18.5	3.5	+ 0.2
75/06/20	-20.8	-16.1	9.0	- 5.0
76/07/08	-18.5	-15.5	9.0	0.0

had condensation temperatures above freezing, it was not possible to calculate a very significant mean value of t_c for the graupel population. The positive condensation temperatures did not exceed their respective cloud-base temperatures, however, and so these cases were retained in Figure 4.5. They almost certainly indicate a doubtful del-value for the vapour feeding the cloud and considerable uncertainty in the point of initial condensation. The shower at Winfield on 8 July 1976 was a well documented, similar example discussed in Section 4.2.

The actual distribution for graupel was surprisingly uniform, in marked contrast with that of the rain samples. Evidently the formation of graupel, at least in these few instances, was not closely dependent on cloud temperature. All condensation temperatures between 0°C and -20°C seemed to occur with nearly equal frequency.

Braham (1958) reached a similar conclusion more than 20 years ago when he used radar data to study summer cumulus clouds in Arizona, U.S.A. He observed a wide range of heights and temperatures at which the precipitation echoes first appeared. He reasoned, therefore, that the microphysics of convective clouds was strongly controlled by the macroscopic variables of synoptic meteorology which characterized the atmosphere in which the clouds formed.

4.5 The Variation of Temperature at the Lifting Condensation Level

Figure 4.5 on page 68 indicated that the condensation temperatures for rain were well represented by a normal distribution when the excessively enriched samples were ignored. It was thought that t_o might also be an approximately normal variate, largely independent of t_c. Figure 4.6 was prepared to illustrate the closeness of the fit of a normal curve to different populations of t_o.

At the top of the figure is shown the t_o-population for the 16 dates of Tables 4.1 and 4.2. These were the days for which the convective cloud models were calculated. The diagram in the middle is the distribution of all cloud-base temperatures recorded by Sandhu (1978). The mean has dropped only half a degree to 5.0°C and the standard deviation is unchanged even though the number of observations has more than doubled. The 16 dates, considered in the top diagram, form a representative subpopulation of the middle group.

At the bottom of Figure 4.6, a distribution of completely independent data has been plotted. During the spring and summer of 1978, from May 8th to July 31st, mid-afternoon (2200 G.M.T.) cloud-base temperatures were determined from the Edmonton International Airport's hourly reports. The bottom histogram is thus an actual record of 85 consecutive days centered around the sampling seasons used by Sandhu (1978). The arithmetic mean, $\bar{t}_o = 4.9°C$, is statistically the same as those of the

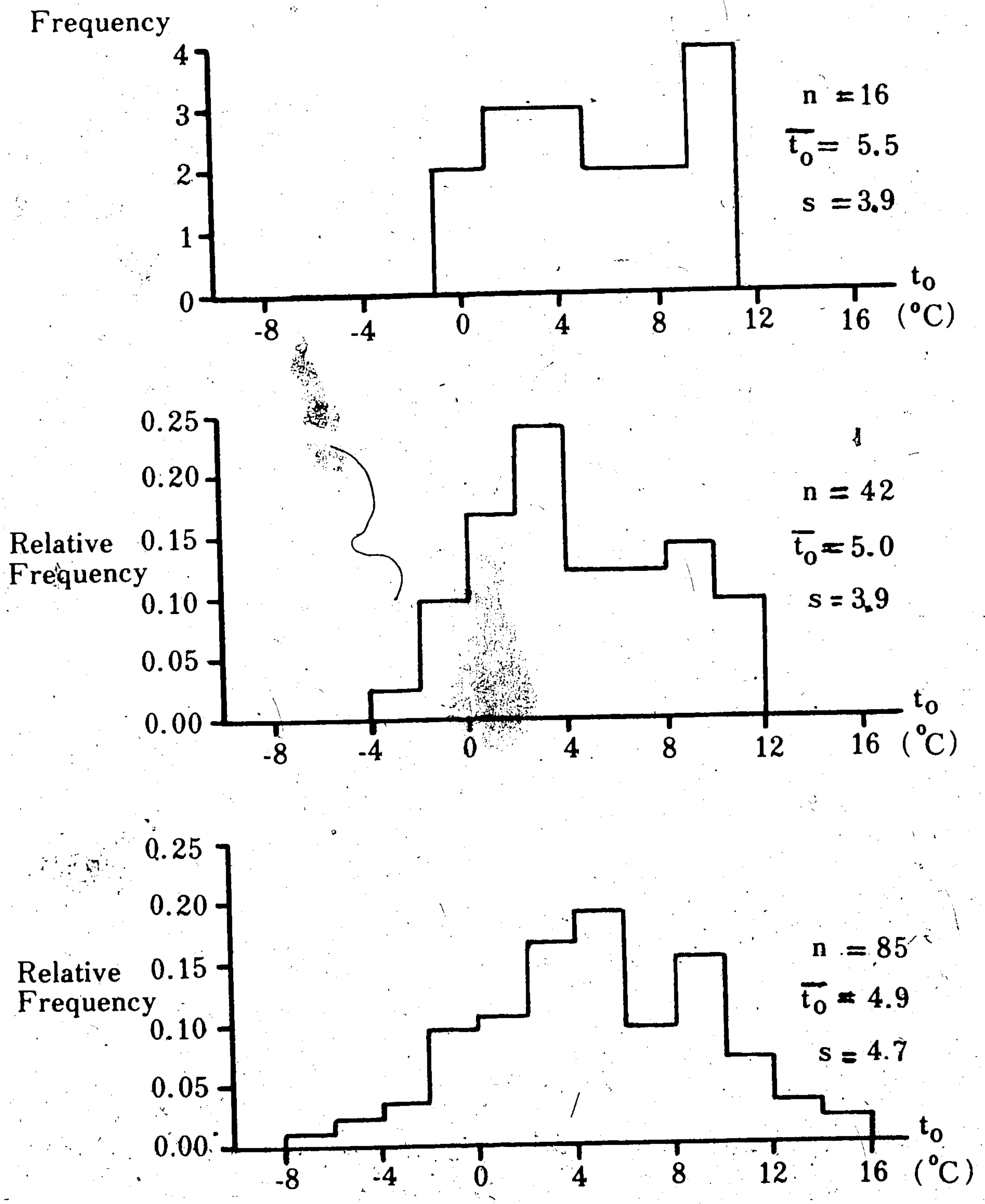


Figure 4.6 Frequency distributions of the cloud-base temperatures, t_o, from May to July in central Alberta.

smaller, previous groups, compiled during 1974, 1975 and 1976. The corresponding 85 measurements for Penhold, Alberta had a mean of 5.7°C, and the same standard deviation, 4.7°C, as the Edmonton population. These numerical data are tabulated in Appendix A.

In order to obtain a numerical statistic which would evaluate the goodness-of-fit, a chi-squared test was performed on each distribution of Figure 4.6. $\chi_{\nu}^{2} = 0$ would imply a perfect fit, and the subscript ν was used to indicate the number of degrees of freedom in the test. In general, the chi-squared statistic is a positive rational number which increases with ν.

The goodness-of-fit is then expressed by the probability of getting a higher value of χ_{ν}^{2}, by the random selection of samples, than the value actually calculated from an experimental population. If $\text{Prob}(\chi_{\nu}^{2} > \text{calculated value}) \simeq 50\%$ or higher, the fit is adequately good under the assumption that the experimental errors are truly random. The results of the tests have been collected into Table 4.5. The hypothesis that t_0 approximates a normal variate is well supported by the chi-squared tests, and the goodness-of-fit improves as the number of samples increases.

4.6 The Skewed Distributions

In Section 4.3, the variable z was defined as a difference between two del-values. The frequency distribution

TABLE 4.5

STATISTICAL PARAMETERS FOR THE POPULATIONS OF t_o SHOWN IN FIGURE 4.6

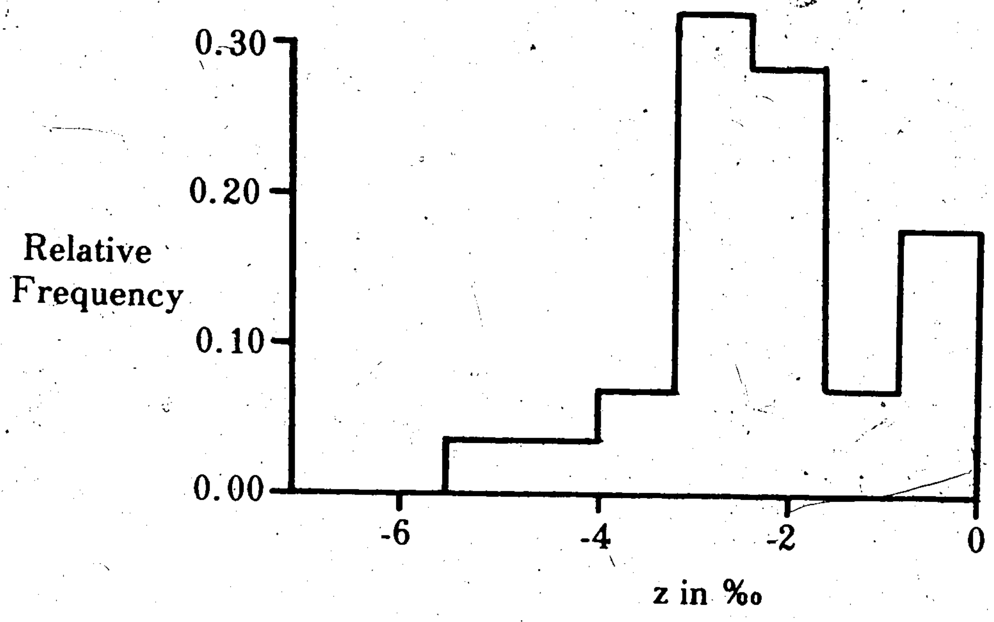
Statistical Parameter	Populations of t_o Cloud Modelling Dates Only	 Sandhu's (1978) Data of 1974, 1975, 1976	 Consecutive Mid-afternoons in 1978
n	16	42	85
Mean, $\overline{t_o}$ (°C)	5.5	5.0	4.9
Standard Deviation (°C)	3.9	3.9	4.7
Degrees of Freedom	2	4	7
Calculated χ^2_ν (normal curve)	1.71	1.79	3.78
Goodness-of-fit (normal curve)	44%	77%	81%

of z, shown in Figure 4.4, had positive skewness which was attributed to large amounts of evaporative enrichment in about one quarter of the rain samples. If the del-values could be corrected to cloud base, it might be possible to evaluate the change by the skewness of the resulting, adjusted population.

The temperature-equivalent to z is the difference, $(t_c - t_o)$. Positive values of $(t_o - t_c)$ are listed in the last column of Table 4.3 for the 28 rain samples with $z < 0$. When the condensation temperature t_c is thought of as the sum of t_o and $(t_c - t_o)$, its distribution can be seen as an intermediate between the normal distribution of t_o and the skewed distribution of $(t_c - t_o)$. When the excessively enriched samples were ignored, the skewness of both the z and the $(t_c - t_o)$ populations approached zero. The actual values were, in fact, -0.17 for z, and -0.43 for $(t_c - t_o)$. A nearly symmetrical distribution of t_c might, therefore, have been expected.

The distributions of z and $(t_c - t_o)$ for the 28 rain samples of Table 4.3 are compared in Figure 4.7. At the top is the compact distribution of z expressed in parts per thousand. The lower diagram is derived from the condensation temperatures deduced by means of the model SM. The difference $(t_c - t_o)$ appears to have a more spread out distribution than z, and to be a closer approximation to a log-normal variate. The goodness-of-fit between the observed and calculated distributions at the bottom of Figure 4.7 is roughly 78%.

In its most general form, the log-normal distribution



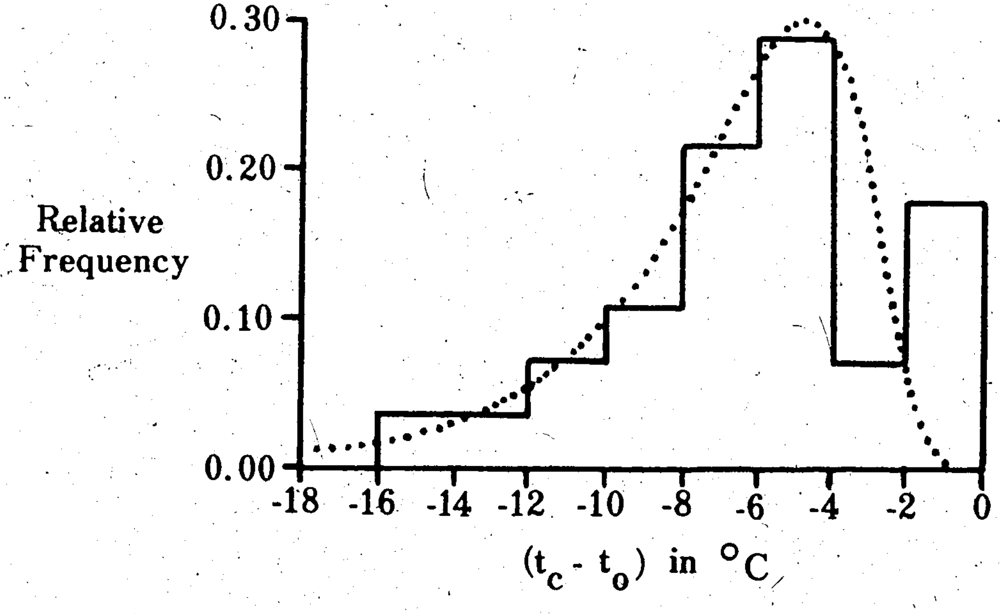


Figure 4.7 Frequency distributions for the 28 rain samples. A log-normal curve (bottom) has been fitted to the distribution of $(t_c - t_o)$.

of a variable x is specified by its probability density function for all $x > 0$:

$$f(x\,;\,x_{th},\,\beta,\,c) = \frac{(x-x_{th})^{-1}}{c(2\pi)^{\frac{1}{2}}} \times e^{-\frac{1}{2c^2}\left[\ln(x-x_{th})-\ln\beta\right]^2} \qquad (4.6)$$

The location parameter, x_{th}, also called the threshold value, was arbitrarily assumed to be zero for $(t_c - t_o)_{th}$ in Figure 4.7. In reality, at cloud base, it should be somewhat greater than zero since cloud droplets must grow to a threshold of drizzle-sized drops before they can fall from the cloud as rain. The growth process ensures a non-zero value for $(t_c - t_o)_{th}$.

The parameters, β and c, pertain to the normally distributed population of ln x; $\ln\beta$ is the median and c^2 the variance. In Figure 4.7, $\ln\beta = 1.8$ and $c = 0.5$. If the usual symbols, μ and σ^2, are retained for the variable x itself rather than for ln x, then the various parameters are related by the following set of equations (Moshman, 1953):

$$\omega = e^{c^2} = e^{\mathrm{var}(\ln x)}$$

$$x_{th} = \mu - \frac{\sigma}{(\omega - 1)^{\frac{1}{2}}}$$

$$\beta = \frac{\sigma}{(\omega^2 - \omega)^{\frac{1}{2}}}$$

$$\text{Skewness, } \alpha_3 = (\omega + 2)(\omega - 1)^{\frac{1}{2}}$$

$$\mu = x_{th} + \beta(\omega)^{\frac{1}{2}}$$

$$\sigma^2 = \beta^2\omega(\omega - 1) \qquad (4.7)$$

Although the log-normal distribution was chosen to represent the observations of $(t_c - t_o)$ mainly for convenience, the choice was not entirely unjustifiable. Moshman (1953) listed a large variety of diverse variates which appeared to be log-normally distributed, and Bury (1975) indicated some of the necessary conditions under which the log-normal distribution could be predicted in advance. He described the problem rather qualitatively, however, in terms of "a measurable characteristic of a Black Box".

In the case of cloud physics, a cumulus congestus cloud might be regarded as the proverbial Black Box. ^{18}O-concentration in the ensuing precipitation would be a measurable characteristic of this Black Box which would result from causes that could not be measured directly or even identified perhaps. Nevertheless, if:

(i) the measurable characteristic were the multiplicative, rather than additive, effect of underlying causes,

(ii) the causes were independent random variables, and

(iii) the number of causes were large,

then the measurable characteristic should be log-normally distributed (Bury, 1975). The complex mechanisms of droplet growth, freezing and splintering, along with isotopic fractionation and exchange, provide a whole gamut of possibly multiplicative effects which eventually determine the value of $\delta_w{}^{18}O$.

CHAPTER V

CORRECTIVE MEASURES

5.1 Mass Loss from Falling Waterdrops

In Section 4.2 of the preceding Chapter, the problem of evaporative enrichment below cloud base was discussed in some detail. The variable z was defined in Section 4.3, and samples with $z > 0$ were said to be excessively enriched. When these samples were disregarded, the skewness of the del-value population changed its sign from positive to negative. It may be possible to calculate numerical corrections which could be subtracted from the rain del-values to compensate for evaporative enrichment. The revised del-values would then be more useful to studies of precipitation formation.

In theory the amount of enrichment in the oxygen-18 content of a falling waterdrop may range up to tens of del-units (Stewart, 1975; Dansgaard, 1961). Actual measurements, however, suggest that it rarely exceeds 10°/₀₀. Stewart (1974) made an extensive study of the evaporation problem, both in the laboratory and during a Colorado rainstorm. An enrichment of 4°/₀₀ per kilometer of descent is probably a typical average which agrees with Linton's (1972) calculations and the estimated 3.2°/₀₀ enrichment at Alder Flats, Alberta, on 8 July 1976. Ehhalt et al. (1963) reported a total enrichment of 8.0°/₀₀ at one of their stations in the South African interior.

An exact expression for the rate of evaporation from a single drop of radius, a, was formulated by Kinzer and Gunn (1951) and updated by Stewart (1974). The mass loss per unit time is given by:

$$\dot{m} = 4 \pi a (\rho_a - \rho_b) (D + F_{vent} \sqrt{Dav/2\pi}) \qquad (5.1)$$

where ρ_a and ρ_b are the densities of water vapour at the drop's surface and in the free atmosphere, respectively. D is the diffusivity of water vapour in air, and v is the fall speed for a raindrop of radius a. The ventilation factor, F_{vent}, is dimensionless and very nearly equal to 1.1. Stewart (1974) used experimental data to show that Equation (5.1) can be written approximately as

$$\dot{m} \simeq 4 \pi a (\rho_a - \rho_b) (kD^{0.58}) \qquad (5.2)$$

where $k = F_{vent} (av/2\pi)^{\frac{1}{2}}$

Let the humidity of the air relative to the drop surface be $h = \frac{\rho_b}{\rho_a}$, so that (5.2) becomes

$$\dot{m} \simeq 4 \pi a \rho_a (1 - h) (kD^{0.58}) \qquad (5.3)$$

It can now be seen that the rate of mass loss for each individual drop depends on the radius, drop temperature, and humidity. The bulk mass loss would depend, as well, on the frequency distribution of raindrop size. Integration of the mass loss equation must be performed over a vertical column from the cloud base to the ground.

Such an integration would be difficult to verify experimentally, but Kessler (1969), using a kinematical approach, managed to obtain a relatively simple alternative expression. Based on ground-level measurements of rainfall rates, he determined an equation for the fraction of remaining water, F_w.

i.e.,

$$F_w \simeq \frac{R'_g}{R'_g + H \frac{d}{d\tau} (\overline{\rho_c})} \tag{5.4}$$

where R'_g is the rainfall rate at the surface, H is the height of the cloud base above the ground, $\frac{d}{d\tau} (\overline{\rho_c})$ is the time rate of change of the "mean saturation deficit" between cloud base and ground.

Equation (5.4) would be especially useful during long periods of rain when a number of sequential samples could be collected easily. However, it should be applied, in future, to all rain sampling experiments, for it allows F_w to be calculated from rather simple observations of: rainfall rate, height of cloud base, initial relative humidity, and the elapsed time since the beginning of the rain. The accuracy of F_w would depend mainly on the precision of $\frac{d}{d\tau} (\overline{\rho_c})$

Once determined, F_w could be inserted into Stewart's (1974) equation for the correction to cloud base of a measured del-value:

$$(\delta_w{}^{18}O)_{cor} = \delta_w{}^{18}O - (\delta_w{}^{18}O)_o$$

$$= \left[\delta_e{}^{18}O - (\delta_w{}^{18}O)_o\right]\left[1 - (F_w)^i\right] \qquad (5.5)$$

where the index $i = \dfrac{1 - \alpha_{18}\alpha_K(1 - h)}{\alpha_{18}\alpha_K(1 - h)}$,

and $\delta_e{}^{18}O = \dfrac{qR_b - R_{SMOW}}{R_{SMOW}}$,

with $q = \dfrac{\alpha_{18}h}{1 - \alpha_{18}\alpha_K(1 - h)}$.

α_K is the kinetic fractionation factor, $(D/D')^{0.58}$. In the present case, D' is the diffusivity of $H_2{}^{18}O$. For an evaporating waterdrop, $\delta_e{}^{18}O$ is the theoretical limiting del-value which is approached as $F_w \to 0$. The quotient, q, determines $\delta_e{}^{18}O$ for a given bulk atmosphere where

$$\left[\frac{^{18}O}{^{16}O}\right]_{vap} = R_b.$$

5.2 An Order-of-Magnitude Correction for the Rain Del-values

Equation (5.5) provides a potentially accurate method of converting rain del-values at the surface to their corresponding values at cloud base. Unfortunately the data assembled by Sandhu (1978), and reproduced in Appendix D, did not include rainfall rates or changes in the "mean saturation deficit" (Kessler, 1969). Precise measurements of temperature and humidity were recorded, however, and from these, a very crude correction formula has been concocted:

$$\frac{(\delta_w{}^{18}O)_{cor}}{H} = -\frac{t - 5.0}{10.0} - \frac{7.0}{2^{(j-1)}}\left(1 - \frac{r}{r_s}\right) \qquad (5.6)$$

The magnitude of $(\delta_w{}^{18}O)_{cor}$, in parts per thousand, is the adjustment to be subtracted from the measured del-value of a particular rain sample to get its cloud-base del-value. H is the height of the cloud base above the ground in kilometers. It places a lower limit on the radius of a cloud waterdrop. Drops with radii smaller than this limit will evaporate completely while falling through the atmosphere.

In the first term on the right hand side of Equation (5.6), t is the air-temperature at the surface in degrees Celsius, provided $t > 5°C$. For colder temperatures, t is arbitrarily set equal to 5 so that the temperature-dependent term does not contribute to $(\delta_w{}^{18}O)_{cor}$. The second term on the right is the relative humidity component with j = 1, 2, 3,...

for samples collected sequentially and numbered 1, 2, 3, ..., respectively. It is thus a crude function of time, and $2^{(j - 1)}$ acts in the same direction as increasing humidity during prolonged rain.

The relative importance of kinetic evaporation and isotopic exchange in the enrichment of a falling raindrop has been studied by a number of workers (Stewart, 1975; Linton, 1972; Miyake et al., 1968; Friedman et al., 1962). When the atmosphere is saturated there is no net evaporation, but isotopic exchange will still occur if the drop and the atmospheric vapour are not in isotopic equilibrium. Under dry conditions, on the other hand, when evaporation is rapid, the kinetic effect probably dominates (Ehhalt et al., 1963). In Equation (5.6), the relative humidity term tends to become more and more dominant as $\frac{r}{r_s}$ decreases.

It must, of course, be remembered that Equation (5.6) is not intended to be a physically rigorous formula. It cannot take the place of Equation (5.5), but it should provide a zero-order adjustment to the rain del-values to correct for evaporative enrichment. It should give results which are somewhat improved over those obtained by just ignoring all excessively enriched samples, as was done in the preceding Chapter.

The corrections determined by means of Equation (5.6) are listed in the last column of Table 5.1 under the heading $(\delta_w{}^{18}O)_{cor}$. Based on 39 rain samples, the mean adjustment is

TABLE 5.1

THE ROUGH CALCULATIONS OF ISOTOPIC ENRICHMENT BY MEANS OF EQUATION (5.6)

Date of Sample	j	t (°C)	$\frac{r}{r_s}$	H (km)	$(\delta_w{}^{18}O)_{cor}$ (°/oo)
74/05/15	1	11.5	0.52	1.2	-4.8
"	2	11.5	0.52	1.2	-2.8
"	3	11.5	0.52	1.2	-1.8
74/06/03	1	10.0	0.77	0.5	-1.1
"	2	10.0	0.77	0.5	-0.7
74/06/05	1	18.0	0.41	1.6	-8.7
"	2	18.0	0.41	1.6	-5.4
"	3	18.0	0.41	1.6	-3.7
74/07/04	1	17.5	0.48	1.4	-6.7
"	2	17.5	0.48	1.4	-4.2
"	3	17.5	0.48	1.4	-3.0
"	4	17.5	0.48	1.4	-2.3
"	1	8.0	1.00	0.0	0.0
74/07/05	1	16.0	0.50	1.2	-5.5
"	2	16.0	0.50	1.2	-3.4
"	3	16.0	0.50	1.2	-2.4
74/07/09	1	24.0	0.53	1.3	-6.7
74/07/11	1	16.0	0.73	0.6	-1.8
"	2	16.0	0.73	0.6	-1.2
75/06/16	1	16.0	0.51	1.2	-5.4
"	2	16.0	0.51	1.2	-3.4
75/06/17	1	10.0	0.88	0.4	-0.5
75/06/20	1	14.0	0.76	0.5	-1.3
"	2	14.0	0.76	0.5	-0.9
"	3	14.0	0.76	0.5	-0.7
75/06/21	1	23.0	0.40	1.7	-10.2
"	2	23.0	0.40	1.7	-6.6
"	3	23.0	0.40	1.7	-4.8
76/07/08	1	21.0	0.59	0.9	-4.0
"	2	21.0	0.59	0.9	-2.7
"	3	21.0	0.59	0.9	-2.1
"	4	21.0	0.59	0.9	-1.8
"	5	21.0	0.59	0.9	-1.6
"	1	20.0	0.56	1.0	-4.6
"	2	20.0	0.56	1.0	-3.0
"	3	20.0	0.56	1.0	-2.3
76/07/14	1	12.0	0.87	0.3	-0.5

$(-3.7 \pm 0.5)°/{\circ\circ}$, and values of $(\delta_w{}^{18}O)_{cor}$ range from 0.0 to -14.2°/∘∘. If the samples collected on 5 August 1975 are omitted, as in Table 5.1, the mean correction is then -3.3°/∘∘, or approximately the average difference between the hail and rain del-values treated in Chapter III.

The numerical data for 5 August 1975 have been suspect ever since the mass spectrometer results were available (Sandhu, 1978). On that date, however, evaporation must have taken place at an extreme rate. The surface air-temperature, 28°C, was the highest of any sampling date, and the relative humidity, 0.31, was the lowest. The calculated correction to cloud base, -14.2°/∘∘, was also an extremum.

It seems likely, in retrospect, that Equation (5.6) actually over-corrects when the air is very dry. Isotopic exchange would operate against kinetic evaporation and would tend to re-establish the equilibrium del-values of liquid and vapour. Adjustment times would be of the order of a few minutes (Stewart, 1975). Nevertheless extreme conditions and large enrichments can be expected occasionally during an Albertan summer. In future experiments therefore, Equations (5.4) and (5.5) should be used to obtain quantitatively accurate corrections and to evaluate Equation (5.6).

5.3 The Revised Frequency Distributions

Once the corrections to cloud base have been determined, by whatever means, a whole new set of adjusted populations becomes available. Table 5.2 contains four such populations, designated by the subscript, adj. The corresponding uncorrected distributions were given in Table 4.3. The two rain samples collected on 5 August 1975 have been omitted so that the total number of samples is now 37.

The population of del-values, $(\delta_w {}^{18}O)_{adj}$, adjusted to approximate conditions at cloud base, has a mean of -18.8°/oo and a standard deviation of 3.0°/oo. Both values are somewhat lower than their respective ground-level measurements. The numerical values tabulated for $(z)_{adj}$ are all negative, and, although this is an obvious improvement, it must be remembered that Equation (5.6) was specifically devised to reduce the number of excessively enriched samples having $z > 0$.

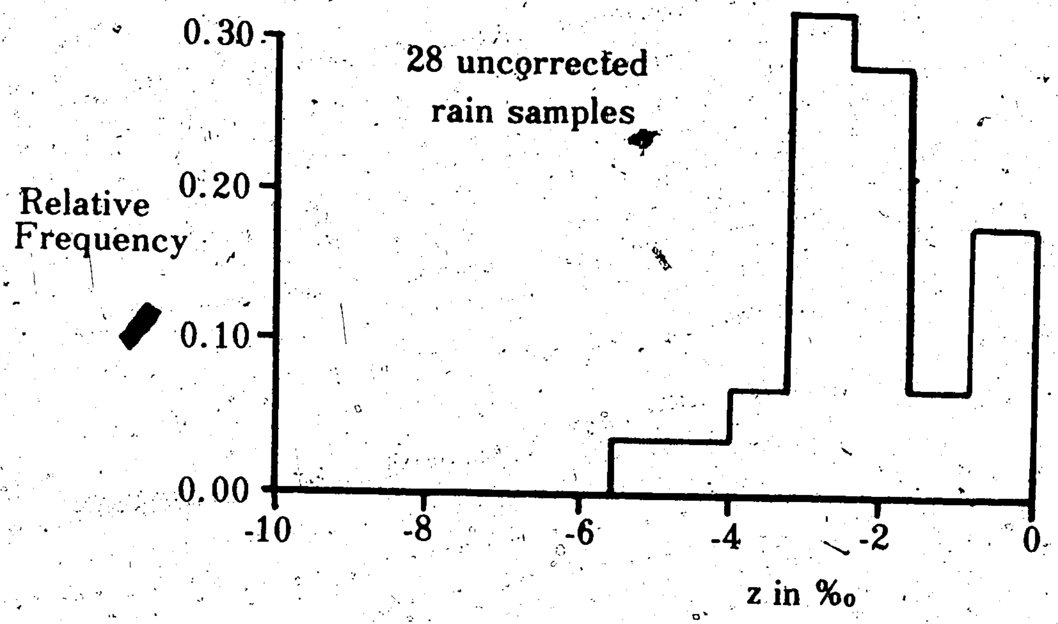
More substantial evidence of improvement is shown in Figure 5.1, where the actual distributions are compared. The upper histogram represents the uncorrected values of z exactly as in Figure 4.7 on page 76. The lower histogram is the revised version based on the 37 adjusted values. The mean has changed from -2.3°/oo to -4.6°/oo, and the skewness from -0.17 to -0.24. Moreover, it is now possible to fit a log-normal curve to the adjusted data so that the goodness-of-fit is better than 90%. Apparently the correction formula has some merit in spite of its lack of rigour, and, in addition, the log-normal hypothesis provides a satisfactory overall description of the rain del-values.

The step from del-values to cloud condensation

TABLE 5.2

ADJUSTED DISTRIBUTIONS OF 37 RAIN SAMPLES CORRECTED ACCORDING TO EQUATION (5.6)

Date of Sample	$(\delta_w{}^{18}O)_{cor}$ (°/₀₀)	$(\delta_w{}^{18}O)_{adj}$ (°/₀₀)	$(z)_{adj}$ (°/₀₀)	$(t_c)_{adj}$ (°C)	$(t_c - t_o)_{adj}$ (°C)
74/05/15	-4.8	-23.9	-7.6	-21.0	-21.0
"	-2.8	-21.7	-5.4	-13.5	-13.5
"	-1.8	-20.4	-4.1	- 9.4	- 9.4
74/06/03	-1.1	-17.4	-3.2	- 5.3	- 6.8
"	-0.7	-16.9	-2.7	- 4.2	- 5.7
74/06/05	-8.7	-13.8	-2.8	- 4.8	- 6.3
"	-5.4	-17.6	-6.6	-14.7	-16.2
"	-3.7	-13.6	-2.6	- 4.4	- 5.9
74/07/04	-6.7	-23.4	-7.6	-19.6	-23.6
"	-4.2	-22.1	-6.3	-14.2	-18.2
"	-3.0	-21.9	-6.1	-13.7	-17.7
"	-2.3	-21.0	-5.2	- 9.8	-13.8
"	0.0	-20.6	-4.8	- 8.9	-12.9
74/07/05	-5.5	-16.3	-4.3	+ 1.4	- 2.6
"	-3.4	-19.2	-7.2	- 6.5	-10.5
"	-2.4	-19.5	-7.5	- 7.4	-11.4
74/07/09	-6.7	-19.4	-9.6	-30.7	-41.7
74/07/11	-1.8	-14.6	-2.0	+ 4.1	- 5.9
"	-1.2	-13.1	-0.5	+ 8.7	- 1.3
75/06/16	-5.4	-19.6	-1.1	+ 1.5	- 2.0
"	-3.4	-22.2	-3.7	- 6.0	- 9.5
75/06/17	-0.5	-18.9	-3.0	+ 1.0	- 8.5
75/06/20	-1.3	-19.1	-3.0	+ 0.1	- 8.9
"	-0.9	-22.1	-6.0	-10.9	-19.9
"	-0.7	-19.9	-3.8	- 2.3	-11.3
75/06/21	-10.2	-21.5	-6.0	-12.4	-18.4
"	-6.6	-22.8	-7.3	-18.8	-24.8
"	-4.8	-24.1	-8.6	-26.2	-32.2
76/07/08	-4.0	-16.0	-3.3	+ 0.6	-10.4
"	-2.7	-17.6	-4.9	- 5.1	-16.1
"	-2.1	-17.6	-4.9	- 5.1	-16.1
"	-1.8	-17.3	-4.6	- 4.0	-15.0
"	-1.6	-16.4	-3.7	- 0.9	-11.9
"	-4.6	-15.9	-3.3	- 0.8	- 9.8
"	-3.0	-15.9	-3.3	- 0.8	- 9.8
"	-2.3	-15.3	-2.7	+ 1.0	- 8.0
76/07/14	-0.5	-17.7	-0.6	+ 8.0	- 2.0



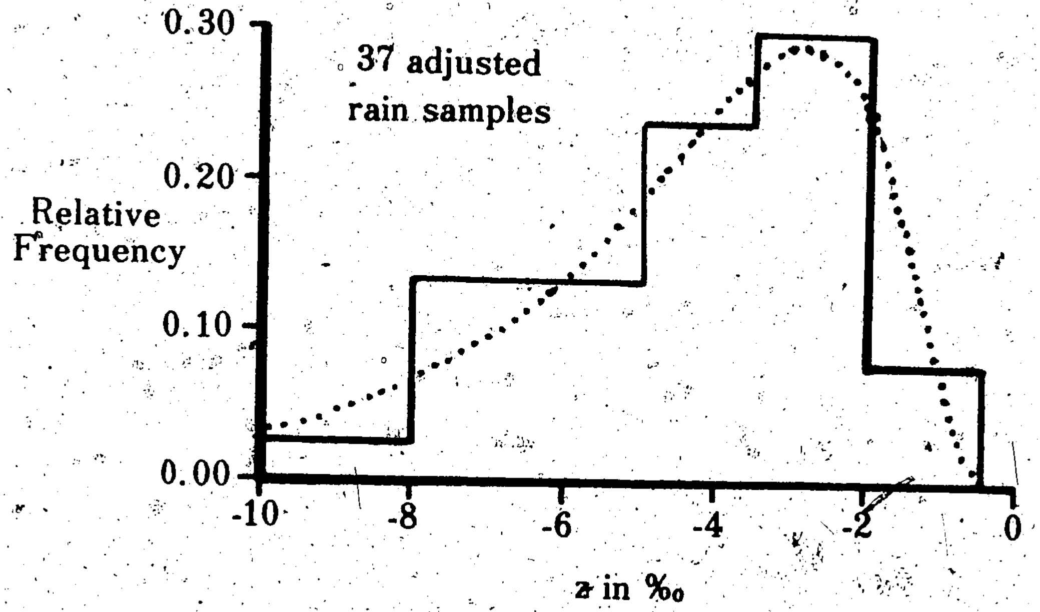


Figure 5.1 Frequency distributions of z in ‰ : 28 uncorrected rain samples (top), and 37 adjusted samples (bottom). A log-normal curve has been fitted

temperatures depends on the specified isotopic cloud model. Unfortunately a small error in $(\delta_w{}^{18}O)_{adj}$ leads to a comparatively large error in t_c. Therefore, an exact equation must be established to correct for evaporative enrichment, before it will be possible to test the accuracy of the hypothesized, numerical cloud models. At the present time, the experimental data are not sufficiently reliable to distinguish between the specific models updated by Linton (1972). The empirical results discussed in this study have thus been treated mainly in bulk, and the simplified model, SM, has been used as a general approximation for all cases.

The simplified model was used again to produce the last two columns of Table 5.2 on page 89, where the adjusted del-values have been converted to adjusted condensation temperatures. Like Figure 5.1, the histograms of Figure 5.2 show the effect of the correction to cloud base. The range of temperatures, $(t_c - t_o)$, has become more extensive, and the distribution is more skewed. The mean condensation temperature, measured from the cloud-base temperature $\bar{t}_o$, has changed from -6.1°C to -12.9°C, and the skewness, from -0.43 to -1.34. A few of these resultant temperatures could now support the shower model of Browning et al. (1968) discussed in Section 4.2.

As before, a quantitative evaluation of the general improvement can be deduced by fitting a log-normal curve to the adjusted distribution and calculating the numerical goodness-of-fit. The best fit heretofore, shown in Figure 4.7, was

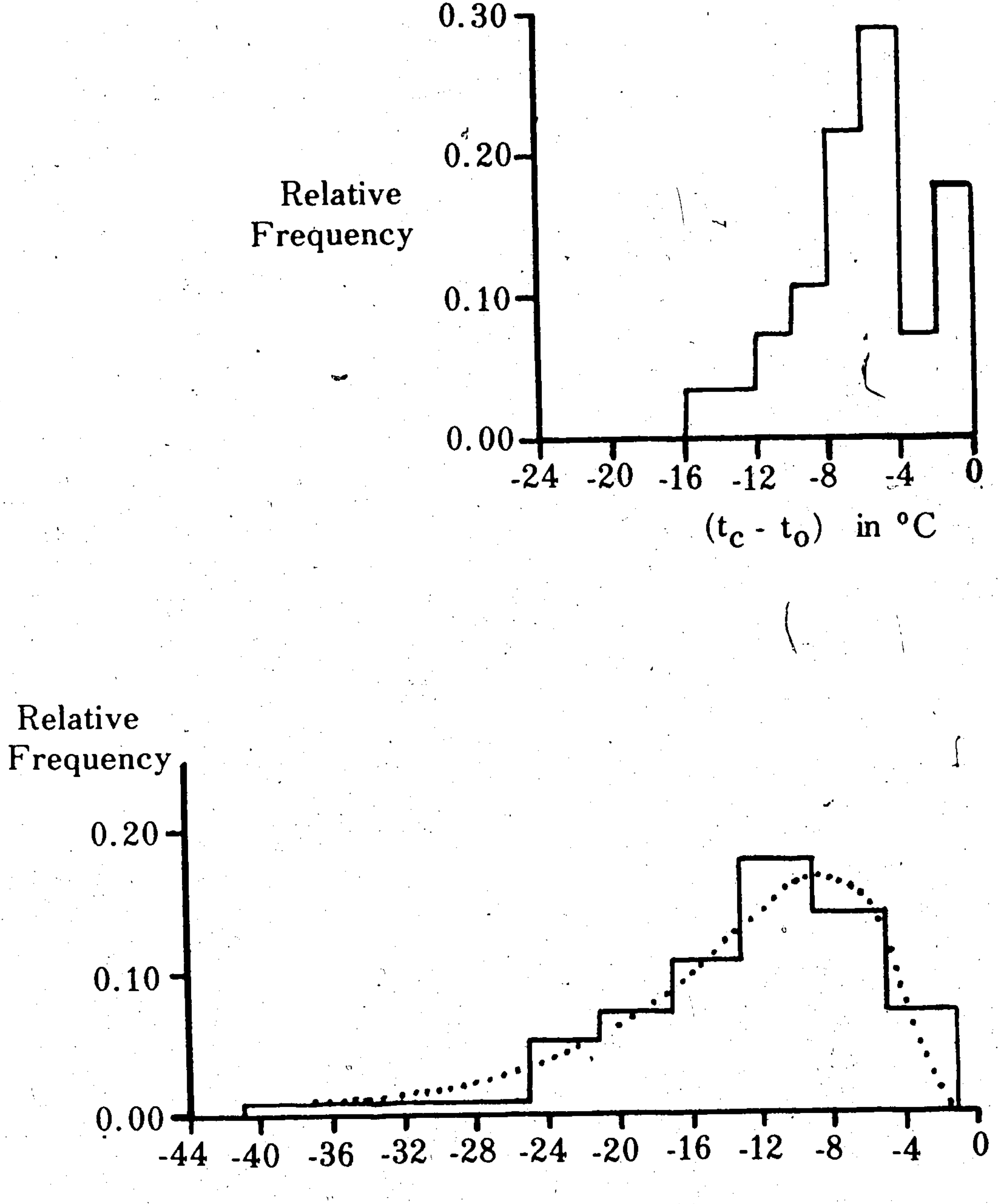


Figure 5.2 Frequency distributions of $(t_c - t_o)$: 28 uncorrected rain samples (top), and 37 adjusted samples (bottom). A log-normal curve has been fitted to the $(t_c - t_o)_{adj}$ distribution.

about 78%. In Figure 5.2 the fit is only slightly worse than that of the adjusted del-values, and is close to 90%. Evidently then, the observed del-values of rain samples can be improved by correcting for evaporation. The exact equation still remains to be verified, but Stewart's (1974) thesis and Kessler's (1969) kinematic model surely indicate the next attempt.

CHAPTER VI

ENDGAME

6.1 Final Synopsis

The collection of precipitation samples must be one of the easiest techniques of present-day environmental studies. Laboratory analysis for deuterium and oxygen-18 concentrations, though tedious, has become a routine procedure following the method introduced by Epstein and Mayeda (1953). Modern mass spectrometers routinely yield isotopic del-values accurate to ±2°/₀₀ for deuterium, and ±0.2°/₀₀ for oxygen-18. These experimental errors are one to two orders of magnitude smaller than the changes in the measured del-values of atmospheric water substance (Hage et al., 1975).

In the present decade at the University of Alberta, research work has, for convenience, been restricted to the oxygen-18 isotope. West (1972) further confined his studies to snow and ice samples from Canadian glaciers and took advantage of the "locked-in" premise for isotopic content in ice. Even so, he noticed some discrepancies between the stratigraphic and the isotopic variations, especially in the Ellesmere glacier, and he urged that caution be exercised in the interpretation of experimental data in glaciology.

Linton (1972) extended the study to summer rainfall samples at Edmonton, Alberta. He also revised the theoretical isotopic cloud models of Miyake et al. (1968) so that the numerical modelling would be as accurate as possible. The four types of models have been described in Table 2.1. The evaporation problem became obvious to Linton during the course of his work, and he recommended that the sampling technique should try to minimize evaporative enrichment. Subsequently, Stewart (1975) published a quantitative review of the effects of kinetic evaporation and isotopic exchange on the fractionation of falling waterdrops.

Sandhu (1978) continued the oxygen-18 studies in central Alberta. This time, water vapour as well as precipitation samples were collected in association with the Alberta Hail Project. The work concentrated on convective showers, some of which produced small hail or graupel, during the spring and summer of 1974, 1975, and 1976. The measured del-values are tabulated in Appendix C, and the entire data-bank, in compact format, is given in Appendix D (Sandhu, 1978).

In the present thesis, Equation (2.9), a simplified form of Linton's (1972) closed model with total vapour and condensate in equilibrium, was used to calculate cloud condensation temperatures. These temperatures were deduced from the measured del-values of "simultaneous" vapour and precipitation samples. For rain, condensation temperatures which have not been corrected for evaporation are listed in Table 4.3. A rough attempt was made to eliminate some of the evaporative enrichment, and consequently, adjusted values appear in Table 5.2.

For the small hail and graupel samples, formation temperatures, again based on Equation (2.9), are given in Table 4.4. Graphical distributions of the condensation temperatures for rain and graupel are shown in Figure 4.5. When the variates, del-values or temperatures, are measured from their appropriate cloud-base values, the distributions become distinctly skewed. A population of 37 rain samples is well represented by a log-normal curve in Figures 5.1 and 5.2.

6.2 Final Conclusions

1. A seasonal trend in atmospheric oxygen-18 content was confirmed for central Alberta in all three phases of atmospheric water substance. For the period May to July, del-values increased by 0.06°/oo per day in samples of graupel, rain, and water vapour. Since the scatter about the regression line was large, however, the seasonal norm cannot be relied upon to estimate $(\delta_v{}^{18}O)_o$. Vapour samples are still needed and should be taken as close as possible to cloud base.

2. Short-term variations were discovered in the vapour del-values, but they appeared to be random, and in the long run, they did not contribute appreciably to the overall variance of the del-value population. They did, however, make the estimated point of initial condensation considerably uncertain for an individual shower. Evidently vapour samples, collected at the surface before the onset of precipitation, provide reliable

estimates of $(\delta_v{}^{18}O)_o$ only part of the time.

3. The isotopic cloud models have all been well computed in the laboratory, but their use is hampered by the uncertainty in the point of initial condensation. The problem is complicated even further by the partial evaporation of rain during its descent from cloud to ground. Unless the rain del-values can be corrected to account for evaporative enrichment, they will not be very useful in the substantiation of any cloud model. The work of Stewart (1974) and Kessler (1969) offers a potentially accurate correction formula based on precipitation rates and changes in relative humidity.

4. The results for small hail and graupel were thought to be the most trustworthy. The formation of graupel particles, and possibly hailstone embryos, was not observed to be overwhelmingly temperature dependent. The generation and growth of graupel occurred over a temperature range from 0°C to -20°C with perhaps a fairly uniform distribution. This last conclusion has yet to be confirmed by a large number of simultaneous vapour and graupel samples.

6.3 Final Recommendations

1. The obvious need for deuterium measurements has already been stressed by Sandhu (1978) who also pointed out the critical role that the water vapour samples play with respect to cloud modelling. The reliability of the vapour

del-values is perhaps the most pressing concern. Simultaneous and instantaneous vapour samples should continue to be collected, their del-values determined, and their repeatability verified. The inflation of a large balloon, for example, could provide 5 to 10 identical samples.

2. The variation of $\delta_v{}^{18}O$ horizontally, vertically, and with respect to time, should be investigated further. Ehhalt (1974) has already published some vertical profiles for $HD^{16}O$. Although Hage et al. (1975) were the first to collect vapour samples at the University of Alberta, the condensing-freezing technique has been used for two decades at least (Dansgaard, 1961). Until now, however, short-term variations of $\delta_v{}^{18}O$ were not suspected. All the isotopic cloud models updated by Linton (1972) required a true estimate of $(\delta_v{}^{18}O)_o$. It was thought that such an estimate would be sufficient throughout the lifetime of a convective shower. It appears unlikely now that a single vapour sample can be relied upon for this estimate.

3. West (1972) confined his research to ice and snow samples of mountain glaciers. Isotopic analysis of falling snow might be the most satisfying area of the heavy-isotope work. Ice-crystal habit offers an additional clue to the formation temperature, and in particular, dendritic growth by deposition is known to occur most rapidly around -15°C (Braham, 1968). This growth process should be described by a non-equilibrium model with vapour-ice fractionation factors.

A number of snowbelt regions exist in Canada, such as those in the lee of the Great Lakes where the del-value of the source water can be measured easily. The contribution of large lakes, in general, to the heavy-isotope content of atmospheric water substance has yet to be determined. In Alberta, much summer precipitation is thought to be derived from continental freshwater (Hage et al., 1975).

4. In the case of rain samples, evaporation below the cloud base has been bothersome in the past. An accurate calculation of the exact amount of evaporative enrichment is urgently needed in arid or semi-arid climates such as Alberta's. Recent work by Stewart (1974) and Kessler (1969) has put the required correction formula within reach.

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APPENDIX A

TABLE A.1

MID-AFTERNOON SURFACE TEMPERATURES, DEW POINTS AND LCL-TEMPERATURES FROM 8 MAY TO 31 JULY 1978 AT EDMONTON INTERNATIONAL AIRPORT

(ALL TEMPERATURES IN DEGREES CELSIUS)

Day of Month	MAY			JUNE			JULY		
	t	t_d	t_o	t	t_d	t_o	t	t_d	t_o
1				22	7	3.9	22	4	0.6
2				25	5	0.9	25	8	4.6
3				27	6	1.5	27	9	5.5
4				30	6	1.1	27	9	5.5
5				26	6	2.0	23	12	9.9
6				16	2	-0.7	12	4	2.6
7				22	3	-0.8	12	9	8.5
8	20	-1	-5.0	23	9	6.0	17	5	2.5
9	13	5	3.3	12	10	9.4	20	10	8.0
10	8	3	2.0	16	4	1.6	20	14	12.9
11	7	4	3.2	15	4	2.1	12	10	9.6
12	16	0	-3.1	21	6	2.8	24	13	10.8
13	16	-4	-7.8	22	9	6.2	20	12	10.3
14	20	3	-0.3	14	7	5.6	23	12	9.9
15	11	8	7.0	18	9	7.0	25	13	10.4
16	11	9	8.7	17	6	3.5	22	15	13.6
17	18	2	-1.4	25	8	4.6	16	5	2.6
18	17	-1	-4.6	9	4	3.1	14	10	8.8
19	22	2	-2.1	17	2	-1.0	20	8	5.7
20	26	3	-1.5	23	9	6.0	20	8	5.7
21	25	4	-0.1	23	12	9.9	22	12	10.2
22	18	8	6.0	18	11	9.7	26	11	7.9
23	13	-1	-3.8	16	7	5.2	28	12	8.7
24	9	2	0.6	23	9	6.0	25	12	9.3
25	6	5	4.8	22	7	3.9	26	9	5.3
26	13	5	3.5	23	8	5.0	31	12	8.1
27	20	2	-1.6	24	10	7.1	15	14	13.9
28	14	4	2.0	29	10	6.0	22	13	11.3
29	6	3	2.3	29	17	14.5	20	13	11.7
30	12	8	7.2	24	16	14.2	20	11	9.3
31	16	5	2.6				23	10	7.0

TABLE A.2

MID-AFTERNOON SURFACE TEMPERATURES, DEW POINTS AND LCL-TEMPERATURES FROM 8 MAY TO 31 JULY 1978 AT PENHOLD AIRPORT, ALBERTA

(ALL TEMPERATURES IN DEGREES CELSIUS)

Day of Month	MAY			JUNE			JULY		
	t	t_d	t_o	t	t_d	t_o	t	t_d	t_o
1				21	6	3.0	21	9	6.5
2				23	7	3.6	23	12	9.8
3				26	7	3.0	22	11	8.5
4				28	5	0.1	24	13	10.7
5				23	6	2.5	21	12	10.1
6				14	7	5.6	12	7	6.0
7				22	9	6.1	12	6	4.8
8	18	-2	-6.0	23	8	5.0	16	9	7.4
9	14	0	-2.8	10	6	5.2	19	12	10.7
10	10	3	1.7	14	8	6.8	21	16	14.9
11	8	5	4.3	15	7	5.3	16	10	9.0
12	14	1	-1.7	18	9	7.0	23	11	8.4
13	16	1	-2.1	22	9	[illegible].1	24	13	10.7
14	19	-1	-5.0	17	3	0.9	27	13	10.2
15	14	3	1.0	15	10	9.0	27	12	9.0
16	8	6	5.6	12	10	9.7	23	13	10.9
17	16	4	1.4	22	10	7.2	17	9	7.2
18	16	1	-2.0	10	4	2.7	17	11	9.9
19	21	3	-0.6	16	6	4.0	19	9	6.9
20	24	4	-0.1	24	9	5.8	23	10	7.3
21	24	5	1.0	21	11	9.0	19	10	8.1
22	21	7	4.0	17	11	9.9	26	14	11.3
23	13	-1	-4.0	14	8	6.8	27	15	12.4
24	6	2	1.1	21	9	6.5	28	14	11.1
25	7	5	4.5	20	9	6.7	26	13	10.6
26	16	3	0.3	21	9	6.5	31	13	9.7
27	18	3	0.2	23	9	6.0	21	12	10.1
28	9	-1	-3.0	27	14	11.4	21	14	12.8
29	13	-1	-4.0	28	16	13.4	22	12	9.9
30	10	7	6.4	23	14	12.2	17	11	9.9
31	14	7	5.6				21	10	7.9

TABLE A.3

MID-AFTERNOON SURFACE TEMPERATURES, DEW POINTS AND LCL-TEMPERATURES
FROM 8 MAY TO 31 JULY 1978 AT
ROCKY MOUNTAIN HOUSE, ALBERTA

(ALL TEMPERATURES IN DEGREES CELSIUS)

Day of Month	MAY			JUNE			JULY		
	t	t_d	t_o	t	t_d	t_o	t	t_d	t_o
1				22	5	1.4	22	6	2.7
2				24	3	-1.4	24	7	3.2
3				27	4	-0.6	22	11	8.8
4				29	2	-3.3	25	5	1.0
5				25	8	4.5	21	13	11.2
6				12	5	3.6	11	7	6.1
7				22	3	-0.8	10	9	9.8
8	18	-3	-7.2	22	6	2.7	14	8	6.9
9	13	0	-2.8	12	8	7.5	16	11	10.0
10	8	2	0.7	11	6	5.3	20	12	10.4
11	6	4	3.4	13	6	4.8	13	9	8.2
12	13	-3	-6.2	19	5	2.1	23	6	2.7
13	15	-3	-6.6	21	4	0.7	22	12	10.0
14	19	-3	-7.5	15	7	5.2	26	8	4.2
15	9	7	6.5	16	10	9.1	26	10	6.7
16	9	6	5.7	13	10	9.4	20	12	10.4
17	17	3	0.0	22	5	1.4	12	9	8.4
18	16	-2	-5.9	10	2	0.3	14	8	6.9
19	22	0	-4.5	17	2	-1.0	19	5	2.1
20	23	-2	-7.0	21	6	3.0	22	4	0.3
21	23	2	-2.2	22	10	7.3	21	14	12.5
22	14	7	5.4	13	11	10.8	22	14	12.2
23	12	-3	-6.0	15	7	5.2	26	11	8.1
24	6	4	3.7	22	3	-0.8	26	12	9.0
25	5	4	3.9	20	5	1.9	24	8	4.6
26	14	-2	-5.2	22	2	-1.9	29	11	7.1
27	18	-2	-6.0	24	5	1.1	19	10	8.0
28	12	2	0.0	26	8	4.2	19	12	10.6
29	13	-5	-8.5	25	13	10.6	21	12	10.1
30	8	6	5.6	22	13	11.3	17	9	7.2
31	5	1	-1.7				22	9	6.2

TABLE A.4

MID-AFTERNOON SURFACE TEMPERATURES, DEW POINTS AND LCL-TEMPERATURES FROM 8 MAY TO 31 JULY 1978 AT CALGARY INTERNATIONAL AIRPORT

(ALL TEMPERATURES IN DEGREES CELSIUS)

Day of Month	MAY			JUNE			JULY		
	t	t_d	t_o	t	t_d	t_o	t	t_d	t_o
1				19	2	-1.5	20	5	1.7
2				22	6	2.7	22	11	8.8
3				25	5	0.7	18	10	8.4
4				27	5	0.2	21	12	10.0
5				26	3	-1.6	19	11	9.5
6				9	3	2.0	10	9	8.8
7				20	8	5.5	17	9	7.5
8	19	-3	-7.3	25	5	0.7	12	7	6.2
9	10	3	1.5	11	8	7.4	21	12	10.0
10	11	2	0.0	11	7	6.2	23	11	8.2
11	7	3	2.2	15	6	4.0	15	5	2.9
12	14	-5	-8.7	18	4	1.3	24	6	2.1
13	16	0	-3.5	22	4	0.4	26	8	4.3
14	18	0	-3.7	18	-4	-8.3	27	9	5.3
15	16	3	0.4	9	7	6.7	28	7	2.9
16	8	6	5.4	17	9	7.4	22	8	5.2
17	15	2	-0.7	22	5	1.3	16	9	7.7
18	16	2	-1.0	6	4	3.5	14	8	7.0
19	20	1	-3.0	15	1	-1.8	17	7	5.2
20	23	0	-4.6	22	3	-0.9	22	6	2.7
21	22	2	-2.0	23	6	2.4	22	10	7.3
22	20	-5	-9.7	17	13	12.1	24	11	8.2
23	9	0	-1.8	14	9	8.0	28	10	6.2
24	4	3	2.7	22	3	-0.9	29	2	-3.4
25	12	-2	-5.0	19	8	6.0	27	8	4.1
26	15	-3	-6.8	20	6	3.2	31	9	4.4
27	18	0	-3.7	22	7	1.4	24	12	9.3
28	15	2	-0.7	28	5	0.0	21	11	8.9
29	12	-4	-7.3	26	12	9.0	23	10	7.5
30	7	5	4.3	25	9	5.8	12	11	10.8
31	11	5	3.5				22	9	6.4

APPENDIX B

TABLE B.1

PRECIPITATION WEIGHTED, MONTHLY MEAN DEL-VALUES RELATIVE TO SMOW FOR BULK RAINWATER AT EDMONTON, ALBERTA.

RAINFALL AMOUNTS, IN CM, GIVEN IN PARENTHESES (IAEA, 1970, 1969)

YEAR	MAY		JUNE		JULY	
1961	-13.2	(2.5)	-11.4	(4.7)	-14.8	(9.5)
1962	-17.8	(5.7)	-15.1	(7.8)	-11.6	(8.0)
1963	-21.3	(3.2)	-15.8	(5.5)	-12.8	(6.5)
1964	-13.1	(5.4)	-13.8	(2.6)	-11.6	(7.5)
1965	-17.0	(7.4)	-13.1	(19.0)	-12.4	(5.4)

APPENDIX C

TABLE C.1

OXYGEN-18 DEL-VALUES, RELATIVE TO SMOW, FOR SAMPLES COLLECTED IN 1974 (Sandhu, 1978)

	Date of Sample	Type of Sample	Vapour	Rain	Small Hail and Graupel
1	74/05/15	Vapour	-27.7		
2	"	Graupel			-20.8
3	"	Graupel			-20.9
4	"	Graupel			-21.2
5	"	Rain		-19.1	
6	"	Rain		-18.9	
7	"	Rain		-18.6	
8	74/05/16	Vapour	-29.9		
9	74/05/17	Graupel			-20.0
10	"	Vapour	-24.5		
11	74/05/21	Vapour	-31.3		
12	74/05/22	Vapour	-29.0		
13	74/05/23	Vapour	-22.3		
14	"	Vapour	-30.9		
15	"	Rain		-19.0	
16	74/05/24	Vapour	-18.5		
17	74/06/03	Vapour	-25.5		
18	"	Rain		-16.3	
19	"	Rain		-16.2	
20	74/06/05	Vapour	-22.3		
21	"	Rain		-5.1	
22	"	Rain		-12.2	
23		Rain		-9.9	
24	74/06/06	Rain		-16.7	
25	74/06/08	Rain		-19.1	
26	74/07/03	Vapour	-20.9		
27	74/07/04	Vapour	-26.8		
28	"	Rain		-16.7	
29	"	Rain		-17.9	
30	"	Rain		-18.9	
31	"	Hail			-19.6
32	"	Rain		-18.7	
33	"	Hail			-19.7
34	"	Rain		-20.6	

TABLE C.1 (continued)

	Date of Sample	Type of Sample	Vapour	Rain	Small Hail and Graupel
35	74/07/05	Vapour	-28.3		
36	"	Vapour	-26.2		
37	"	Rain		-15.8	
38	"	Rain		-10.8	
39	"	Hail			-15.4
40	"	Hail			-16.3
41	"	Hail			-17.2
42	"	Rain		-17.1	
43	74/07/07	Rain		-16.5	
44	74/07/09	Vapour	-19.8		
45	"	Vapour	-20.2		
46	"	Hail			-17.4
47	"	Rain		-12.7	
48	"	Hail			-17.0
49	74/07/10	Vapour	-24.9		
50	74/07/11	Vapour	-23.1		
51	"	Rain		-12.8	
52	"	Rain		-11.9	

TABLE C.2

OXYGEN-18 DEL-VALUES, RELATIVE TO SMOW, FOR SAMPLES COLLECTED IN 1975 (Sandhu, 1978)

	Date of Sample	Type of Sample	Vapour	Rain	Small Hail and Gtaupel
1	75/05/13	Vapour	-28.1		
2	"	Vapour	-27.7		
3	75/05/15	Vapour	-27.7		
4	"	Vapour	-27.5		
5	75/05/16	Vapour	-26.6		
6	"	Vapour	-28.2		
7	75/06/12	Vapour	-30.5		
8	75/06/16	Vapour	-29.5		
9	"	Rain		-14.2	
10	"	Rain		-18.8	
11	"	Hail			-20.1
12	75/06/17	Vapour	-26.6		
13	"	Rain		-18.4	
14	75/06/18	Vapour	-28.2		
15	"	Vapour	-22.3		
16	"	Vapour	-28.5		
17	"	Vapour	-31.1		
18	75/06/19	Vapour	-27.4		
19	75/06/20	Vapour	-26.6		
20	"	Rain		-17.8	
21	"	Graupel			-20.8
22	"	Rain		-21.2	
23	"	Rain		-19.2	
24	75/06/21	Vapour	-26.3		
25	"	Vapour	-19.0		
26	"	Rain		-19.3	
27	"	Rain		-11.3	
28	"	Rain		-16.2	
29	75/06/25	Graupel			-17.9
30	75/06/28	Graupel			-23.6

TABLE C.2 (continued)

	Date of Sample	Type of Sample	Vapour	Rain	Small Hail and Graupel
31	75/07/03	Rain		-5.3	
32	"	Rain		-3.9	
33	"	Graupel			-10.8
34	"	Graupel			-13.3
35	"	Graupel			-12.5
36	75/08/05	Vapour	-18.0		
37	"	Rain		-10.0	
38	"	Graupel			+6.8
39	"	Rain		-14.3	
40	"	Graupel			-17.6
41	75/08/06	Rain		-14.5	
42	"	Graupel			-13.3
43	"	Graupel			-14.0
44	"	Graupel			-12.5
45	75/08/28	Rain		-12.5	
46	"	Rain		-5.7	
47	"	Rain		-12.7	
48	"	Rain		-4.3	
49	"	Rain		-12.4	
50	"	Graupel			-14.8

TABLE C.3

OXYGEN-18 DEL-VALUES, RELATIVE TO SMOW, FOR SAMPLES COLLECTED IN 1976 (Sandhu, 1978)

	Date of Sample	Type of Sample	Vapour	Rain	Small Hail and Graupel
1	76/06/15	Vapour	-30.9		
2	"	Vapour	-33.1		
3	76/06/17	Vapour	-26.7		
4	"	Vapour	-29.0		
5	76/06/18	Vapour	-27.3		
6	"	Vapour	-23.6		
7	"	Vapour	-28.0		
8	76/06/19	Graupel			-22.3
9	"	Graupel			-20.7
10	"	Rain		-20.9	
11	"	Graupel			-19.8
12	"	Graupel			-19.9
13	76/06/21	Vapour	-27.7		
14	"	Vapour	-26.8		
15	"	Vapour	-28.4		
16	76/06/30	Vapour	-22.8		
17	"	Vapour	-22.5		
18	"	Vapour	-9.5		
19	"	Vapour	-20.2		
20	76/07/08	Vapour	-25.3		
21	"	Vapour	-24.6		
22	"	Vapour	-23.2		
23	"	Vapour	-23.0		
24	"	Vapour	-27.2		
25	"	Vapour	-25.6		
26	"	Vapour	-25.1		
27	"	Rain		-12.0	
28	"	Rain		-14.9	
29	"	Rain		-15.5	
30	"	Rain		-15.5	
31	"	Rain		-14.8	
32	"	Rain		-11.3	
33	"	Rain		-12.9	
34	"	Rain		-13.0	
35	"	Graupel			-18.5

TABLE C.3 (continued)

	Date of Sample	Type of Sample	Vapour	Rain	Small Hail and Graupel
36	76/07/13	Vapour	-24.6		
37	"	Vapour	-24.3		
38	"	Vapour	-24.7		
39	"	Vapour	-24.0		
40	76/07/14	Vapour	-27.2		
41	"	Vapour	-27.7		
42	"	Vapour	-27.4		
43	"	Vapour	-27.8		
44	"	Rain		-17.2	
45	76/07/15	Vapour	-28.2		
46	"	Vapour	-28.6		
47	"	Vapour	-27.2		
48	"	Vapour	-27.0		
49	76/07/21	Hail			-17.3
50	"	Hail			-19.0
51	"	Hail			-18.0
52	"	Hail			-18.5
53	"	Hail			-19.2

APPENDIX D

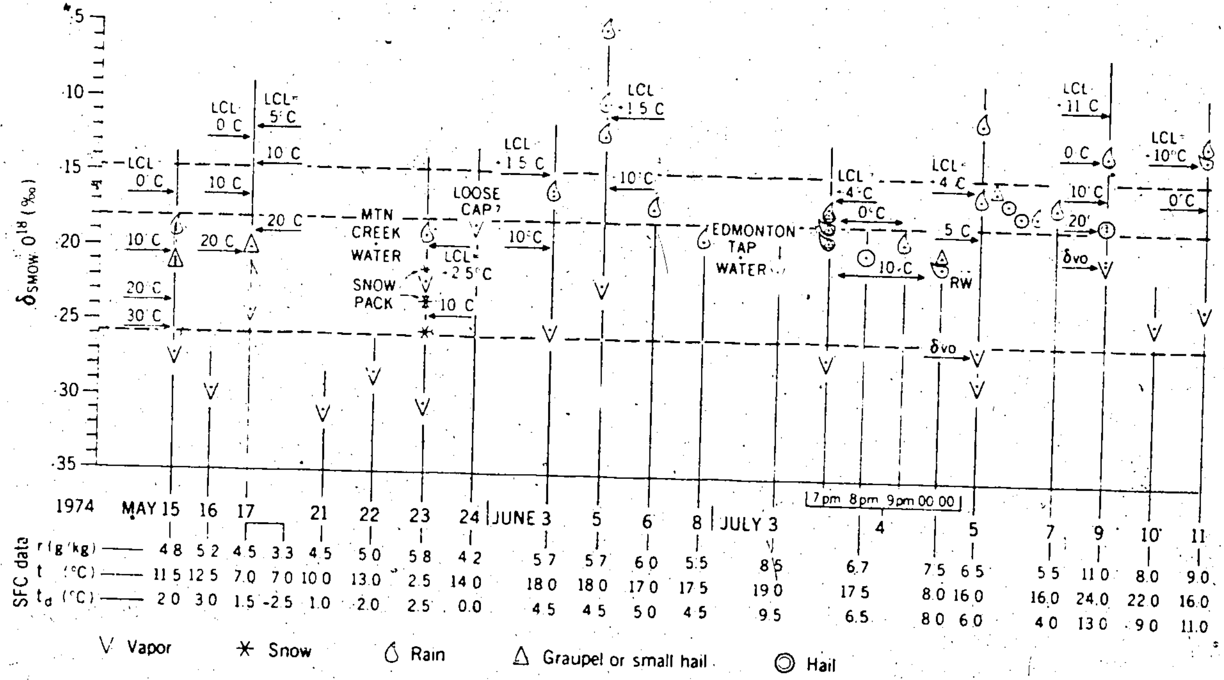

Figure D.1 Experimental isotopic data for 1974 in compact format (Sandhu, 1978).

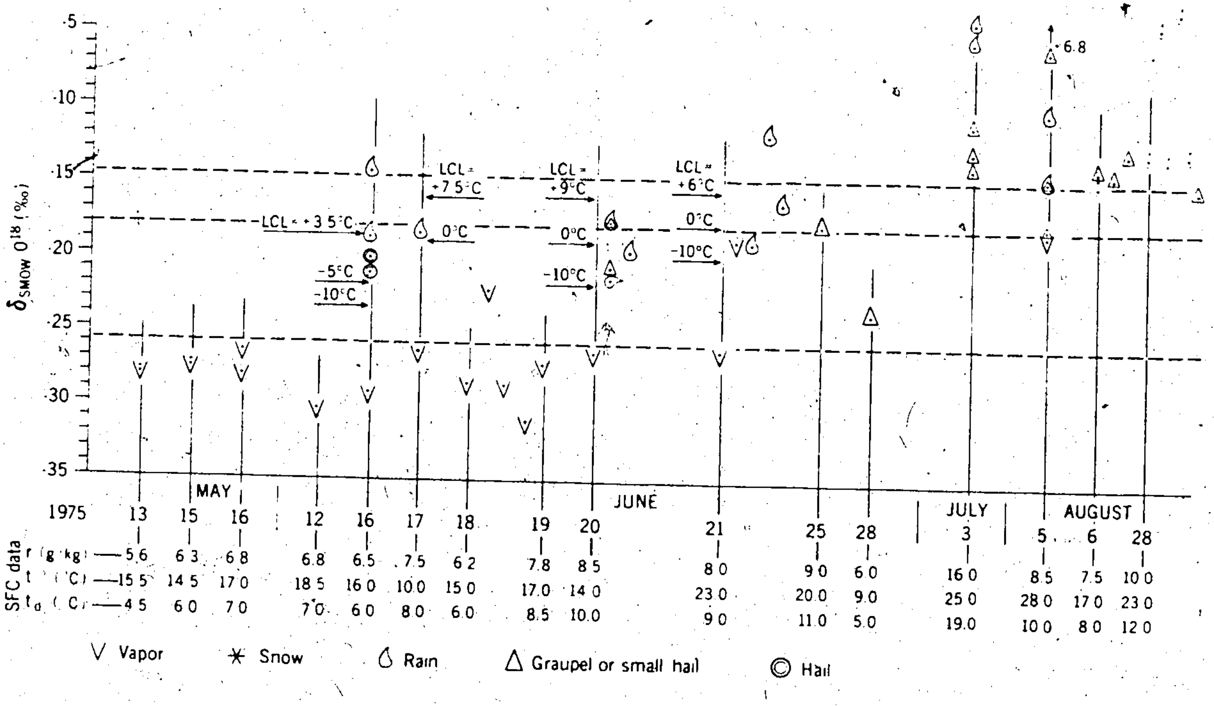

Figure D.2 Experimental isotopic data for 1975 in compact format (Sandhu, 1978).

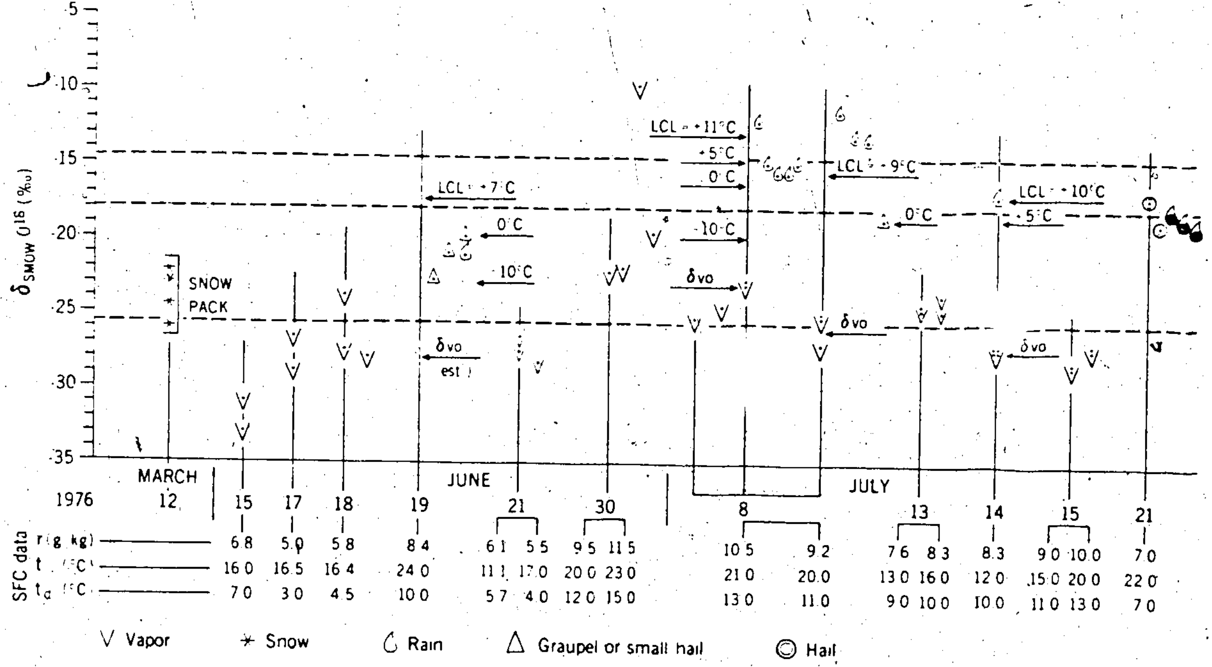

Figure D.3 Experimental isotopic data for 1976 in compact format (Sandhu, 1978).