THE VARIATIONS AND CLIMATIC SIGNIFICANCE OF D/H RATIOS IN THE CARBON-BOUND HYDROGEN OF CELLULOSE IN TREES

Thesis by

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to Marilea

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Abstract

The δD values of nitrated cellulose from a variety of trees covering a wide geographic range have been measured. These measurements have been used to ascertain which factors are likely to cause δD variations in cellulose C-H hydrogen.

It is found that a primary source of tree δD variation is the δD variation of the environmental precipitation. Superimposed on this are isotopic variations caused by the transpiration of the leaf water incorporated by the tree. The magnitude of this transpiration effect appears to be related to relative humidity.

Within a single tree, it is found that the hydrogen isotope variations which occur for a ring sequence in one radial direction may not be exactly the same as those which occur in a different direction. Such heterogeneities appear most likely to occur in trees with asymmetric ring patterns that contain reaction wood. In the absence of reaction wood such heterogeneities do not seem to occur. Thus, hydrogen isotope analyses of tree ring sequences should be performed on trees which do not contain reaction wood.

Comparisons of tree δD variations with variations in local climate are performed on two levels: spatial and temporal. It is found that the δD values of 20 North American trees from a wide geographic range are reasonably well-correlated with the corresponding average annual temperature. The correlation is similar to that observed for a comparison of the δD values of annual precipitation of 11 North American sites with annual temperature. However, it appears that this correlation is significantly disrupted by trees which grew on poorly-

drained sites such as those in stagnant marshes. Therefore, site selection may be important in choosing trees for climatic interpretation of δD values, although proper sites do not seem to be uncommon.

The measurement of δD values in 5-year samples from the tree ring sequences of 13 trees from 11 North American sites reveals a variety of relationships with local climate. As it was for the spatial δD vs climate comparison, site selection is also apparently important for temporal tree δD vs climate comparisons. Again, it seems that poorly-drained sites are to be avoided. For nine trees from different "well-behaved" sites, it was found that the local climatic variable best related to the δD variations was not the same for all sites.

Two of these trees showed a strong negative correlation with the amount of local summer precipitation. Consideration of factors likely to influence the isotopic composition of summer rain suggests that rainfall intensity may be important. The higher the intensity, the lower the δD value. Such an effect might explain the negative correlation of δD vs summer precipitation amount for these two trees. A third tree also exhibited a strong correlation with summer climate, but in this instance it was a positive correlation of δD with summer temperature.

The remaining six trees exhibited the best correlation between δD values and local annual climate. However, in none of these six cases was it annual temperature that was the most important variable. In fact annual temperature commonly showed no relationship at all with tree δD values. Instead, it was found that a simple mass balance model incorporating two basic assumptions yielded parameters which

produced the best relationships with tree δD values. First, it was assumed that the δD values of these six trees reflected the δD values of annual precipitation incorporated by these trees. Second, it was assumed that the δD value of the annual precipitation was a weighted average of two seasonal isotopic components: summer and winter. Mass balance equations derived from these assumptions yielded combinations of variables that commonly showed a relationship with tree δD values where none had previously been discerned.

It was found for these "well-behaved" trees that not all sample intervals in a δD vs local climate plot fell along a well-defined trend. These departures from the local δD vs climate norm were defined as "anomalous". Some of these anomalous intervals were common to trees from different locales. When such widespread commonalty of an anomalous interval occurred, it was observed that the interval corresponded to an interval in which drought had existed in the North American Great Plains.

Consequently, there appears to be a combination of both local and large scale climatic information in the δD variations of tree cellulose C-H hydrogen.

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Introduction

The use of light element stable isotopes in the study of past climates had its beginnings in the theoretical work of Urey (1947). He showed for certain cases that the equilibrium partitioning of isotopes between coexisting substances can be expected to be temperature dependent. With the advent of mass spectrometers capable of measuring these small, temperature-induced variations in isotope ratios (McKinney, et al, 1950), an experimental study of systems which might record paleoclimate became possible (Epstein, et al, 1953). The bulk of subsequent paleoclimatic studies involved measurements of $^{18}O/^{16}O$ ratios of the carbonate tests of marine invertebrates (Savin, 1977). Consequently, it is the past climate as reflected by ocean water temperatures and volume changes that has received the greatest attention.

Within the past decade there has been an increasing interest in the use of stable isotope variations in terrestrial systems to study continental climatic change. The successful application of stable isotope methods to the investigation of past continental climatic variations requires the existence of natural systems that meet several criteria. Firstly, the system should contain a chronological record of isotopic variations. This implies that the initially acquired isotopic composition is unchanged through time and that the time of its fixation can be ascertained. Furthermore, this chronology should extend far enough into the past to provide information that predates instrumental climatic records. Secondly, the relationship of the isotopic variations in the system to variations in climate should be well-defined. Thirdly, the system should be widespread in order to provide a diverse sample of different climate regimes. Finally, it must be possible to accurately measure that part of the isotopic composition of the system which is climatically meaningful. This is of particular importance, if the system is a complex mixture of components of differing isotopic compositions.

The existence of tree chronologies that have been dated to a particular calendar year for several thousand years into the past (Fritts, 1976) has made them attractive candidates for stable isotopic investigation of past climate. To date, the isotopes of three elements in trees (carbon, hydrogen, and oxygen) have been studied from this standpoint.

The basis for expecting a correlation between carbon isotope ratios in trees and local climate is unclear, although at least two groups claim to have detected such a correlation (Pearman, et al, 1976; Wilson and Grinsted, 1977). However, for hydrogen and oxygen, there is a reason to expect, a priori, that the stable isotope ratios will vary in response to climatic change. This expectation is based on the observation that the hydrogen and oxygen isotope ratios of cellulose in plants will reflect the isotopic variations of the local meteoric waters (Epstein, et al, 1976; DeNiro and Epstein, 1979). As will be discussed in a subsequent section, the isotopic composition of meteoric water seems to vary in response to such climatic variables as temperature. Consequently, the D/H and $^{18}O/^{16}O$ ratios in trees can vary in response to climate via the variations in local precipitation.

It is only in the past six years that hydrogen or oxygen isotope measurements have been made on tree materials in an attempt to ascertain any relationship to local climate. For oxygen only one such study is in the literature (Gray and Thompson, 1976), while for hydrogen, only four papers on the subject have been published (Libby and Pandolfi, 1974; Schiegl, 1974; Wilson and Grinsted, 1975; Epstein and Yapp, 1976). It is this work on the hydrogen isotopes which is of interest here, principally because of its largely unsatisfactory nature.

For example, Libby and Pandolfi (1974) attempted to analyze the D/H ratios in a tree ring sequence of an oak that grew in Germany. They analyzed the whole wood tissue. Analysis of whole wood tissue has been shown by Epstein, et al (1976) to yield D/H ratios which depend not only on the D/H ratio of the environmental water, but also on the varying proportions of the various chemical constituents in the wood. Consequently, the climatic significance of whole wood hydrogen isotope ratios is suspect. Furthermore, Libby and Pandolfi employed an analytic method for hydrogen isotope determinations that is untested and whose validity has been questioned (Epstein and Yapp, 1977). This method produced a range in the δD values of the oak analyzed by Libby and Pandolfi (1974) of about 190 per mil. This δD range for a single tree is greater than the total δD range of about 180 per mil observed by Epstein, et al (1976) for plants which grew in climates ranging from sub-tropical to sub-arctic. Therefore, it seems quite probable that both the data and the conclusions in the work of Libby and Pandolfi (1974) are of doubtful validity.

This skepticism about the soundness of the Libby and Pandolfi (1974) study is supported by the work of Schiegl (1974). This latter investigation involved the measurement of D/H ratios of whole wood tissue from a spruce, also in Germany. Over the entire span of tree rings analyzed by Schiegl, the total δD range is only about 12 per mil.

This contrasts with a range of about 170 per mil obtained by Libby and Pandolfi over the same interval in their oak. Schiegl (1974) used a standard combustion method for analyzing the D/H ratios in the wood tissue. Thus, it is easier to accept the validity of the data obtained by him. This acceptance makes the order-of-magnitude larger δD range of Libby and Pandolfi (1974) appear even less plausible.

Although Schiegl (1974) did analyze whole wood tissue, his δD data exhibit a measure of correlation with the local annual temperature. However, as implied by the work of Epstein, et al (1976), such a correlation is not to be generally expected for whole wood tissue, if the climatic "signal" arises from the variation of the D/H ratio of the local meteoric water.

Wilson and Grinsted (1975) subdivided two rings from a Monterey pine that grew in New Zealand. They extracted the cellulose in these samples and measured its D/H ratios. From these measurements they concluded that there is a negative temperature coefficient for D/H variations in trees. However, it is difficult to accept their conclusion. First of all, the analysis of cellulose hydrogen involves the measurement of a composite D/H ratio arising from contributions of both C-H and OH hydrogen. The latter is readily exchangeable and may make it difficult to obtain good reproducibility of analyses (Epstein, et al, 1976). In this context, it is noted that Wilson and Grinsted (1975) do not report their analytical error. Furthermore, these authors do not plot the cellulose δD values against the temperatures which they used to determine the temperature coefficient. Thus, it is not possible to judge how good the correlation is or whether they have employed all the pertinent δD. A general criticism of the Wilson and Grinsted (1975) study has been published by Epstein (1978).

From the work which has been published to date, it is apparent that the optimal manner in which to analyze D/H ratios in trees for possible climatic interpretation is to both isolate "pure" cellulose and remove its exchangeable hydroxyl hydrogens. This has been accomplished by extracting nitrated cellulose from trees for D/H analysis (Epstein, et al, 1976). Epstein and Yapp (1976) employed this method to measure δD values in a tree ring sequence from a pine which grew in Scotland. The 40-year moving average of these δD values was compared with the 40-year moving average of winter temperatures in Edinburgh, Scotland. A definite correlation between these variables was found to exist, but the details of the relationship are hidden by the use of the 40-year moving averages.

Thus, as outlined above, there are presently no studies in the literature which provide a convincing, fairly detailed comparison between the δD variations of tree cellulose C-H hydrogen and local climate. In addition, given the complex and dynamic nature of the interaction between tree, water, atmosphere and soil, it is possible that other factors may superimpose isotopic "signals" on those expected from climate alone. Most of these possible complications have not been considered in the limited literature extant in this new area of research. Therefore, it is apparent that the problem of hydrogen isotope variations in trees requires better definition.

The problem is twofold. First, it is necessary to identify and develop those concepts which are likely to provide the framework on which interpretations of D/H variations will be made. Second, it is important to acquire a body of analytical data which can be used to substantiate or refute those concepts, or to contribute to the development of new ideas. The acquisition of such data is a significant part of the problem, because the proper analytical method involves a great deal of work. For this work about 550 combustions have been performed with the attendant, advance chemical preparation of the samples. With this foundation it is the intent of this thesis to more clearly define the problem of isotope variations in the cellulose C-H hydrogen of trees.

The overall approach is divided into five parts. These constitute five separate sections of this thesis. Each section contains an introduction pertinent to the subject which follows. In the first section, improvements in the analytical procedure for measuring hydrogen isotopes in tree cellulose are discussed. The second section consists of a characterization of the plant-water hydrogen isotope relationship. This characterization involves consideration of the possible effects that the various steps in the pathway leading from meteoric precipitation to cellulose C-H hydrogen might have on the isotope ratio finally recorded by the tree. Section three discusses the role that tree physiology may play in producing some fraction of the year-to-year isotopic variation in a tree. In addition the association of hydrogen isotope heterogeneities around the circumference of a tree with reaction wood is examined. In Section four and Appendix I, a simple transport model is developed which delineates some of the variables that might influence the isotopic composition of precipitation. The relationships that are actually observed between the hydrogen isotope composition of precipitation and such variables as temperature and precipitation intensity are then examined. Comparisons of the hydrogen isotope compositions of trees from a wide geographic range with various local climatic variables are made in section five. These comparisons are of both a spatial and temporal nature. Interpretations of these comparisons are made in the context of the discussions of sections two through four.

All the samples analyzed for this thesis are described in Appendix II. They are listed by the identification letters and numbers that are referred to in the text. Sample locations for this thesis were limited to the North American continent, because it contains a wide range of climates within which trees commonly grow, and because the availability of samples and meteorological data for this work was greatest for North America.

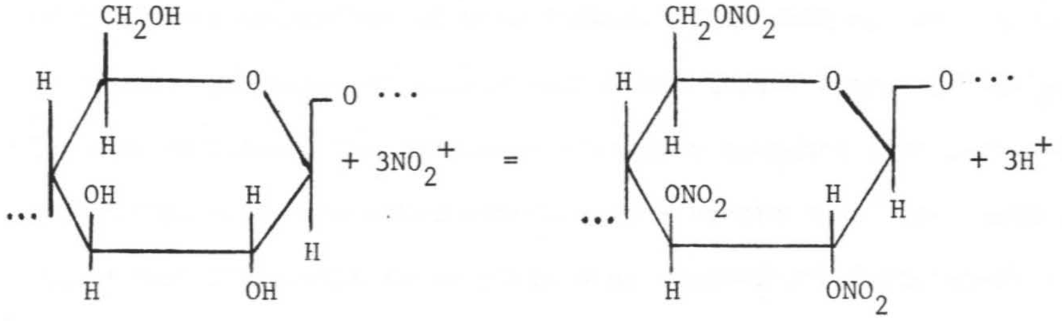
Section 1

Analytical Procedure

All δD values reported for trees and other plants in this thesis were obtained from nitrated cellulose extracted from the plant tissue. The rationale for seeking to isolate a single, relatively pure chemical component from wood is as follows. Firstly, cellulose appears to be common to all photosynthesizing plants. Secondly, in the case of trees, it is the single most abundant chemical constituent, usually comprising from 40 up to 60 weight percent of the dry, solvent-extracted wood (Timell, 1957; Meier, 1964). Thirdly, cellulose is a structural component of the cell wall, and as long as the wood and its constituent cells are intact, it can be presumed that the cellulose has remained immobile. This is a particularly important feature if one is concerned with the examination of isotopic variation in trees through time. Finally, the different chemical constituents of trees have been shown to be isotopically different. In some cases this can amount to a δD difference of 100 per mil or more (Smith and Epstein, 1970; Epstein, et al, 1976). The relative proportions of these constituents can also vary, even within a single tree. Coupled with the isotopic differences, it is important that these possible complexities be avoided.

Nevertheless, many of the earlier analyses of δD variations in trees were performed on whole wood tissue. Some of this work (Libby and Pandolfi, 1974; Libby, et al, 1976) has been questioned on methodological and conceptual grounds (Epstein and Yapp, 1977), while other work has shown that whole wood tissue δD analyses may in some instances yield results that can be interpreted without apparent ambiguity (Scheigl, 1974). However, the comparatively large number of additional uncertainties to be expected in the interpretation of whole wood δD analyses argue in favor of the isotopic analysis of purified chemical species - in this instance, cellulose.

Unfortunately, the isolation of essentially pure cellulose is not only difficult, but insufficient. Cellulose, as a carbohydrate polymer of glucose units, contains two classes of bound hydrogen (OH and CH). Exchange experiments with D_2O (Mann, 1971) have shown that most of the hydroxyl hydrogen in cellulose exchanges readily with water, whereas the carbon-bound hydrogen is non-exchangeable. Epstein, et al (1976) sought both to extract purified cellulose and to remove exchangeable hydroxyl hydrogen with the use of an esterification technique that produced cellulose nitrate. After solvent extraction with 1:1 benzene-methanol, then acetone, Epstein, et al (1976) directly nitrated powdered wood using a nitric-phosphoric acid mixture (Alexander and Mitchell, 1949). The net fully substituted reaction of pure cellulose is:



The direct nitration of solvent-extracted wood produces a mixture of nitrated cellulose, hemicelluloses, and lignin. Hemicelluloses are a collection of various non-cellulose polysaccharides present in intimate association with cellulose as structural units of the cell wall (Meier, 1964). Lignin is a general term for a variety of compounds of high molecular complexity that constitute the matrix of the cell - i.e., the material in which the cellulose is imbedded. Lignin molecules are characterized by a large proportion of aromatic groups (Freudenberg, 1964).

The separation of cellulose nitrate from this mixture was accomplished by dissolution of the cellulose nitrate in acetone, centrifugation of the insoluble nitrated lignin and hemicelluloses, decantation of the supernatant solution, and precipitation of cellulose nitrate from the acetone solution by rapid addition of distilled water (Epstein, et al, 1976). The resultant "purified" cellulose nitrate was the material which was analyzed for its D/H ratio.

Subsequent work by DeNiro and Epstein (in preparation) has found that the method of Epstein, et al (1976) produces, in some instances, δD values that are significantly different from those obtained by an alternative method of preparing cellulose nitrate. DeNiro and Epstein purified cellulose using a sodium chlorite delignification technique adapted from the method of Wise (1944). They then nitrated this purified α-cellulose to obtain cellulose nitrate which was analyzed for its δD value. Two different nitration reagents (one using nitric-phosphoric acid, the other nitric acid - acetic anhydride) were employed, but it was found that these yielded no significant differences in δD values. Furthermore, DeNiro and Epstein noted that a second nitration of the cellulose nitrate prepared by the method of Epstein, et al (1976) produced a product whose δD values agreed with those obtained from the single nitration of the previously delignified cellulose. In addition they found that the cellulose nitrate from the second nitration had infrared spectra identical to the cellulose nitrate obtained from the nitrated, delignified cellulose.

Since the original method of Epstein, et al (1976) requires somewhat less time and material for the actual manipulation of the various steps in the procedure, it was decided to further investigate the renitration technique in an attempt to ascertain more generally its applicability.

The principal steps in the renitration procedure used in this work are depicted in Figure 1-1.

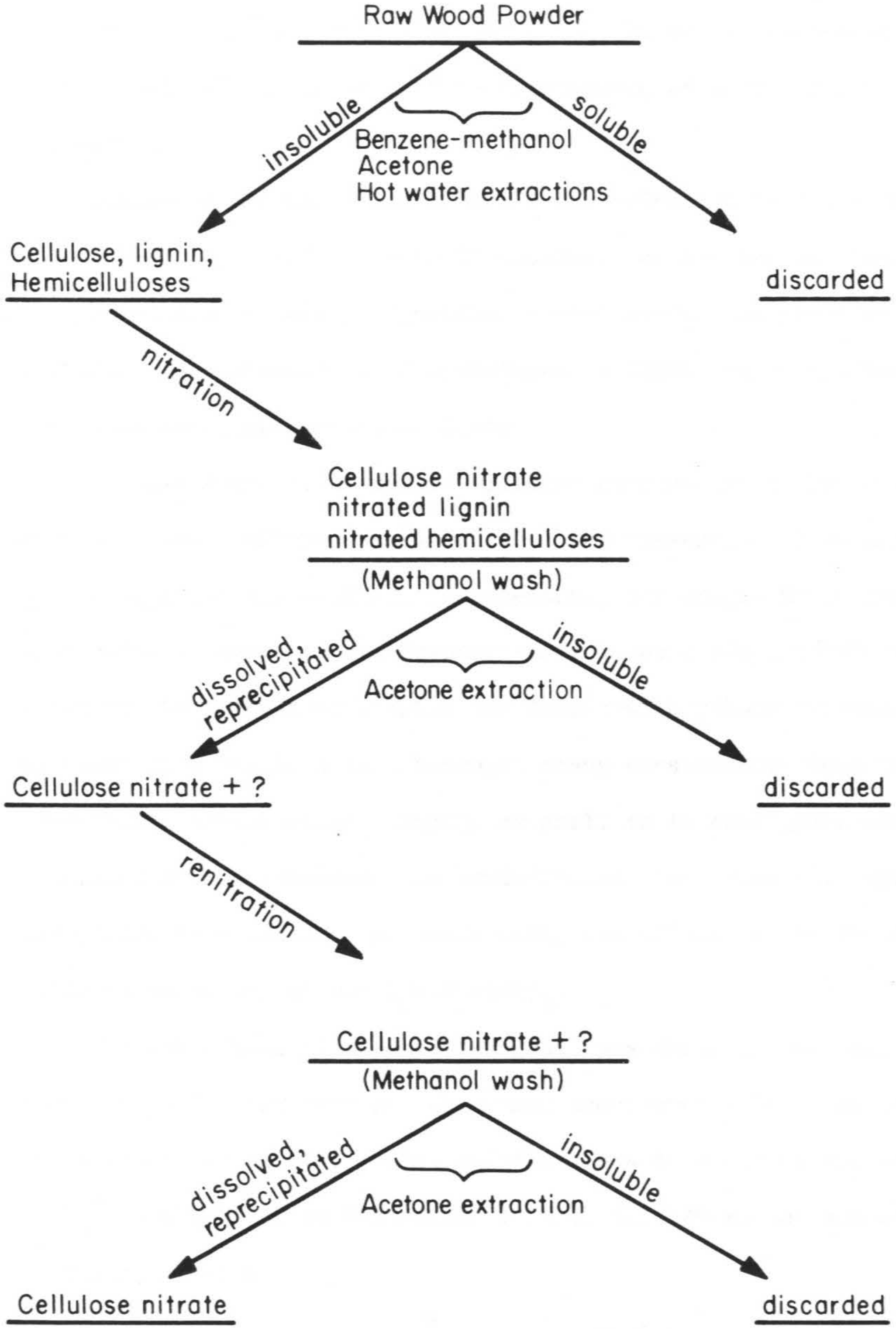
All cellulose nitrate samples regardless of method of preparation were analyzed for their D/H ratios by combustion in a static atmosphere of pure oxygen at 850°C. The combustion chamber is a horizontal quartz tube approximately 70 cm in length and 2 cm in diameter. A resistance furnace encloses the tube over about one-third of its length and is positioned at the end opposite that at which the sample is loaded. A ground glass joint provides access to the system for sample loading and is thoroughly cleaned between each combustion. Additionally, the minimum amount of Apiezon N grease necessary to maintain a high vacuum is applied to the joint -i.e.,it is applied only at the basal end.

After loading, a sample is pumped for a minimum of 10 minutes while positioned at the cool end of the tube. Dry 0_2 gas from a liquid 0_2 reservoir is then introduced to the combustion chamber at a pressure of about 15 cm of mercury. The sample is quickly moved into the furnace-enclosed part of the tube by the use of a hand-held magnet which acts on a small piece of iron completely encased in its own quartz sheath that is, in turn, attached to the quartz sample boat. The cellulose nitrate oxidizes explosively. However, with the exception of the ground glass joint, the portions of the combustion tube outside the resistance furnace are torched to avoid a long term buildup of carbon in the interior walls.

When such a buildup occurs, it has been found that it will produce a substantial isotopic "memory effect". In other words the hydrogen

Figure 1-1

Flow diagram showing the principal steps in the preparation of cellulose nitrate by the renitration method. The procedure outlined in the figure commonly requires about seven days to complete.


Raw Wood Powder
insoluble
soluble
Benzene-methanol
Acetone
Hot water extractions
Cellulose, lignin,
Hemicelluloses
discarded
nitration
Cellulose nitrate
nitrated lignin
nitrated hemicelluloses
(Methanol wash)
dissolved, reprecipitated
insoluble
Acetone extraction
Cellulose nitrate + ?
discarded
renitration
Cellulose nitrate + ?
(Methanol wash)
dissolved, reprecipitated
insoluble
Acetone extraction
Cellulose nitrate
discarded

isotope composition of a sample will be affected by the hydrogen isotope composition of the sample that immediately preceded it in the combustion chamber. As was implied above, however, the problem of a "memory effect" can be avoided by maintenance of a very clean combustion chamber.

Subsequent to the initial explosion, oxidation of the product gases is allowed to proceed for 8 to 10 minutes. At the end of this time they are passed slowly through a multiple-coil liquid nitrogen trap and the procedure is continued as in Epstein, et al (1976) to obtain hydrogen gas for mass spectrometric analysis.

Because there is no mercury Toepler pump to cycle the combustion products, the problems associated with the presence of hygroscopic mercury nitrate are avoided. Furthermore, all stopcocks in the extraction system that are downstream from and exposed to the oxidizing gases of the combustion chamber are Teflon with rubber O-rings. These features have resulted in a hydrogen blank consistently less than one micromole. Consequently, samples as small as 10 milligrams can be combusted with a background contamination of less than 1%. Hydrogen gas yields were measured manometrically and calculated on the basis of fully nitrated cellulose: $C_6H_7O_2(ONO)_3$.

The D/H ratios of the hydrogen gas thus obtained were measured on a double-collecting isotope ratio mass spectrometer based on the design of McKinney, et al (1950) with modifications to minimize the contribution of H_3^+ to the HD^+ beam (Friedman, 1953). All D/H ratios are expressed in the δ notation.

$$\delta D \text{ (in per mil)} = \frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} \times 1000$$

Where R = D/H and the standard is Standard Mean Ocean Water (SMOW) as defined by Craig (1961a). All δD values have been corrected for valve mixing, background, and H_3^+ contributions (Friedman, 1953; Craig, 1957).

The hydrogen isotope reproducibility of the combustion process is indicated by 99 individual cellulose nitrate preparations from each of which at least two aliquots were combusted and analyzed for their δD values. The average deviation of different combustions for all 99 preparations is one per mil with a maximum difference of 6 per mil between different combustions of a specific cellulose nitrate preparation. The 6 per mil maximum occurs in only one instance. Furthermore, in 96% of the cases, the duplicate combustions of a cellulose nitrate preparation differ from one another by 4 per mil or less for the population of cellulose nitrate samples being considered. In view of this and the small average deviation, it does not seem unreasonable to state that the experimental error (in δD) of the combustion process is about ± 2 per mil. Hydrogen yields in these cases are variable, but do not correlate with δD as will be discussed below.

It now becomes important to determine the reproducibility of independent renitrations of pairs of raw wood from the same parent sample. Table 1-1 lists the δD values and hydrogen yields from independent renitrations of wood pairs from 21 different samples. The average deviation of the δD values of these 21 pairs is one per mil. The maximum δD difference between any two members of a pair is 5 per mil and occurs only once.

Table 1-1: δD and H_2 Yields of Independent Renitration Procedures

Sample		Nitration - Renitration #1		Nitration - Renitration #2	
		δD	H_2 yield (%)	δD	H_2 yield (%)
BCT-12	(1926-30)	-111 (2)*	101	-112 (1)	100
BCT-12	(1931-35)	-116 (2)	104	-116 (1)	104
BCT-12	(1936-40)	-126 (1)	103	-130 (1)	100
Col-DF-1	(1881-85)	- 71 (1)	99	- 70 (1)	100
Col-DF-1	(1916-20)	- 64 (2)	99	- 64 (1)	100
Col-DF-1	(1971-74)	- 54 (1)	98	- 51 (1)	101
Col-DF-16	(1881-85)	- 78 (2)	104	- 77 (1)	99
Col-DF-16	(1916-20)	- 78 (1)	104	- 78 (1)	98
KSA-As-1a	(1941-45)	-162 (2)	102	-159 (1)	102
SNF-LP-1	(1956-60)	- 77 (3)	101	- 78 (1)	105
SNF-LP-1	(1966-70)	- 79 (2)	99	- 75 (2)	101
OPW-DF-1	(1971-75)	- 47 (1)	100	- 48 (1)	102
MNY-BO-7	(1811-15)	- 78 (2)	106	- 76 (1)	101
MNY-BO-7	(1821-25)	- 68 (2)	108	- 70 (1)	111
MNY-BO-7	(1846-50)	- 56 (2)	107	- 55 (1)	105
MNY-BO-7	(1881-85)	- 56 (2)	104	- 55 (1)	103
MNY-BO-7	(1941-45)	- 50 (2)	100	- 48 (2)	102
SAS-JP-1	(1956-60)	-175 (1)	103	-172 (1)	106
PRE-2		+ 26 (1)	105	+ 22 (1)	104
BrPn	(1581-90)B	- 90 (1)	103	- 88 (1)	98
BrPn	(1761-70)B	- 81 (2)	104	- 86 (1)	101

*Number in parenthesis indicates number of separate combustions contributing to listed δD analysis

The high yields obtained for some of the samples of Table 1-1, particularly MNY-BO-7 (1821-1825), are worrisome because they represent the possibility of incomplete nitration. This eventuality would mean that some hydroxyl hydrogen was contributing to the analyzed δD value. Since the bulk of cellulose hydroxyl hydrogen is readily exchangeable (Mann, 1971) and may be very different, isotopically, from the cellulose C-H hydrogen (Wilson and Grinsted, 1975; Epstein, et al, 1976), its effect on total sample isotopic variability during processing may not be readily predicted, or controlled. Consequently, the presence of exchangeable hydroxyl hydrogen in a partially nitrated sample may not bode well for the attainment of a high level of cellulose nitrate δD reproducibility.

At this point a comparison of the δD values of cellulose nitrates obtained from the renitration and sodium chlorite methods is useful. Table 1-2 presents the results of δD and hydrogen yield measurements on 16 pairs of samples with one member of each pair representing nitration by one of the two methods. In both methods nitric-phosphoric acid was the nitrating reagent. The average deviation between corresponding pairs of the two methods is about 1.5 per mil. A maximum δD difference of 5 per mil is observed between the two methods for the 16 trials of Table 1-2, and this maximum difference occurs only once. The similarities of the average and maximum deviations for the cases of reproducibility of the combustion process, reproducibility of a single method (Table 1-1) and reproducibility (or comparability) of two different methods (Table 1-2) suggests that the differences in the latter case may be due to random experimental error, if indeed that is the cause

Table 1-2: δD and H_2 Yields of Different Nitration Methods

		Nitration of wood + Renitration		Nitration of delignified cellulose	
Sample		δD	H_2 yield (%)	δD	H_2 yield (%)
AW-BO-1	(1891-95)	- 30 (2)*	105	- 32 (2)	100
AW-BO-1	(1896-1900)	- 27 (1)	99	- 29 (1)	101
AW-BO-1	(1906-10)	- 31 (1)	104	- 27 (1)	101
AW-BO-1	(1941-45)	- 27 (1)	104	- 30 (2)	101
BrPn	(1601-10)B	- 91 (2)	98	- 95 (1)	103
BrPn	(1581-90)B	- 89 (2)	100	- 92 (1)	
BrPn	(1761-70)B	- 83 (3)	103	- 86 (1)	
PRE-2		+ 24 (2)	104	+ 23 (2)	98
SAS-JP-1	(1931-35)	-181 (1)	101	-178 (2)	101
SAS-JP-1	(1956-60)	-174 (2)	104	-173 (2)	100
SAS-JP-1	(1971-75)	-158 (1)	105	-159 (2)	102
AW-BO-1	(1931-35)	- 14 (2)	101	- 18 (3)	101
AW-BO-1	(1886-90)	- 37 (2)	103	- 41 (2)	99
RE-CO-2	(1921-25)	- 60 (2)	104	- 55 (1)	101
BCT-12	(1921-25)	-104 (2)	100	-100 (1)	98
MNY-BO-7	(1821-25)	- 68 (3)	109	- 69 (1)	99

*Number in parenthesis indicates number of separate combustions contributing to listed δD analysis of the differences in the two former cases. With this line of reasoning it may be said that the methods of renitration and nitration of delignified α-cellulose are isotopically equivalent for hydrogen.

Turning to the question of yields, it is apparent that the yields of hydrogen from cellulose nitrate obtained via the renitration method (Fig. 1-1) are generally equal to or greater than those of the cellulose nitrate of delignified α-cellulose origin. In the extreme, the sample MNY-BO-7 (1821-1825) has a hydrogen yield that is 10 percentage units greater for the renitration case than for the nitrated α-cellulose case, yet the δD difference between the two methods for this sample is only one per mil (Table 1-2). If the entire difference in yields is due to incomplete nitration only, then hydroxyl hydrogen will comprise about 5% of the hydrogen sample. On the assumption that all the hypothesized hydroxyl hydrogen is exchangeable, the δD value of the hydroxyl hydrogen, after pumping in the combustion chamber, may be about + 48‰ in Pasadena (Epstein, et al, 1976). At a 5% level of contamination this could change the δD value of the cellulose nitrate by about 6 per mil when the δD value of C-H hydrogen is around -70 per mil. The fact that this has not occurred suggests that there is an alternative explanation for both the high hydrogen yields and the companion fact that these yields seem to have no influence on the agreement of δD values - at least within the limits of both yield and accepted experimental error discussed for the data of Tables 1-1 and 1-2. However, at this juncture it is not apparent what that explanation is.

The agreement between the δD values of the two methods of Table 1-2, as well as the observation that the hydrogen yields are generally higher for cellulose nitrate obtained from the renitration method, is consistent with the results of DeNiro and Epstein in this regard. The hydrogen isotope equivalency of the two methods also supports the contention that a simple extension of the method of Epstein, et al, (1976) by addition of a second nitration and acetone dissolution step (Fig. 1-1) yields a technique that, at least for hydrogen, has the same general applicability as does the method of nitrating delignified cellulose (DeNiro and Epstein, in preparation). Consequently, it is this amended method of Epstein, et al (1976) which has been adopted for this work.

In view of the generally unstable nature of cellulose nitrate, there is some concern for the possibility that its hydrogen isotope ratios will vary during long term storage. Table 1-3 contains the δD values and H_2 yields of combustions of various cellulose nitrate samples before and after long term storage. For the bulk of the storage time, the samples were kept in clear plastic vials with snap caps. These vials were stored on an open laboratory shelf at the ambient room temperature. In all examples of Table 1-3 the cellulose nitrate was prepared by the renitration method of Figure 1-1. The significant feature of the combustion pairs of Table 1-3 is the agreement, within the experimental error of ± 2 per mil, of all the δD values. Such agreement, coupled with the comparatively small deviations of the hydrogen yields, suggests that there has been little chemical alteration of the cellulose nitrate during storage; or that any such alteration has not had important hydrogen isotope consequences.

In summary, the method of cellulose nitrate preparation employed for this work seems to yield a product of substantial chemical stability with respect to hydrogen isotope variations. This stability is probably

Table 1-3: δD and H_2 Yields of Combustions Performed Before and After Long Term Storage of Cellulose Nitrate

	1st Combustion		Elapsed storage time between combustions	2nd Combustion	
Sample	δD	H_2 yield (%)		δD	H_2 yield (%)
SNF-LP-1 (1931-35)	- 84	102	13 months	- 80	100
SAS-JP-1 (1951-55)	-169	104	15½ months	-169	105
Col-DF-1 (1951-55)	- 61	100	10½ months	- 59	100
Col-DF-1 (1926-30)	- 74	103	11 months	- 71	100
FCA-WS-1 (1916-20)	-130	100	11 months	-131	104
FCA-WS-1 (1936-40)	-137	100	11 months	-136	104
MO-O-2 (1941-45)	- 45	105	13 months	- 47	104
SNF-LP-1 (1961-65)	- 82	102	13 months	- 84	100
MNY-BO-7 (1931-35)	- 31	102	12½ months	- 33	97

an important factor in the capability of the overall procedure to measure δD variations to within ± 2 per mil.

A δD comparison of samples prepared by the single nitration method of Epstein, et al (1976) and the renitration method employed herein has been made to determine if the differences noted by DeNiro and Epstein (in preparation) are generally evident. Epstein et al (1976) have published δD analyses of 25 different plants from a wide range of environments and have correlated these cellulose nitrate δD values with those of the local environmental waters. Twenty-three of these original 25 samples were available as the raw, powdered plant tissue and were reanalyzed by the renitration method. The results of these reanalyses together with the published results of the single nitration method of Epstein, et al, are listed in Table 1-4.

The differences in δD values between the two groups are basically along the lines noted by DeNiro and Epstein for other plants. The grasses (PR-TG, Phy-III, UBLM-1, OM-1, WR-1, and NLS) generally show smaller δD differences between the two methods than plants with woody tissue. The latter tend to yield more positive δD values by the renitration method. DeNiro and Epstein have attributed these differences to the removal of an impurity by the renitration and delignified cellulose methods that is apparently not always removed by the single nitration of solvent-extracted, powdered wood. The identity of this suspected impurity remains unknown, but the results of Table 1-4 support the conclusion of DeNiro and Epstein that it has a more negative δD value than the coexisting cellulose C-H hydrogen.

The differences in δD values obtained by the two methods of Table 1-4 imply that the original plant-water isotopic relationship

Table 1-4: Comparison of δD and H_2 Yields for Samples Prepared by the Renitration Method of this Work vs the Single Nitration Method of Epstein, et al (1976).

	Renitration Method		Published * values of single nitration		δD Environmental
Sample	δD	H_2 Yield (%)	δD	H_2 Yield (%)	Water
PR-TG	- 5	96	- 4	100	+ 7
MRM	- 10	103	- 7	91	+ 7
Phy-III	- 42	104	- 40	98	- 3
H-2	- 41	105	- 45	102	- 24
PW-CP	- 59	103	- 66	96	- 28
SW-CP	- 54	99	- 60	98	- 28
UBLM-1	- 40	105	- 44	93	- 32
UBLM-2	- 37	104	- 44	91	- 32
PS-LAS	- 49	100	- 63	103	- 42
LM	- 65	99	- 71	106	- 51
OM-1	-101	99	-104	100	- 65
OM-2	- 80	104	- 92	98	- 65
WR-1	- 87	102	- 85	100	- 69
WR-2	- 76	101	- 84	100	- 69
BCT-10	- 98	102	-103	100	- 97
NLS	-136	95	-140	96	-104
BCT-9	-141	99	-142	98	-106
BCT-5	-122	104	-134	96	-113
BCT-7	-138	104	-140	98	-117
BCT-11	-146	102	-154	100	-136
BCT-3	-148	103	-153	97	-139
BCT-1	-143	99	-154	93	-144
Yuk-W-1	-165	101	-181	100	-174

* Source of published data: Epstein, et al (1976)

derived by Epstein, et al (1976) should be reexamined. Using the 23 points available for comparison by the two nitration methods, the linear regression of the published data of Epstein et al (1976) is:

$$\delta D_{\substack{\text{cellulose}\\ \text{nitrate}}} = 0.984\ \delta D_{\substack{\text{environmental}\\ \text{water}}} - 24$$

with a linear correlation coefficient of 0.976. The linear regression of the 23 analyses obtained by the renitration method is:

$$\delta D_{\substack{\text{cellulose}\\ \text{nitrate}}} = 0.907\ \delta D_{\substack{\text{environmental}\\ \text{water}}} - 22$$

with a linear correlation coefficient of 0.970.

Thus, the differences in methods with the apparent removal of an isotopically "light" impurity by the renitration method has not produced a dramatic change in the published plant-water isotopic relationship. A more general discussion of this relationship appears in a subsequent chapter of this work.

Summary

The δD value of the C-H hydrogen of cellulose can be measured by analysis of properly prepared cellulose nitrate. Two somewhat different methods of cellulose nitrate preparation result in a product whose δD value is the same by either method. One of these methods (renitration) is an extension of the method of Epstein, et al (1976) by addition of a 2nd nitration and acetone dissolution step. The other method involves a single nitration of delignified cellulose (DeNiro and Epstein, in preparation). Both methods yield cellulose nitrate with δD values different from those obtained by the original method of

Epstein, et al (1976). These differences are thought to be due to the removal of an impurity or impurities that were not completely removed by the Epstein, et al, procedure. All subsequent cellulose nitrate δD values reported for the work herein were prepared by the renitration method as described in the foregoing section.

Section 2

Plant-water Hydrogen Isotope Relationships

Central to the problem of using hydrogen isotope variations in tree cellulose to study continental climate is the question of the degree to which the D/H ratios of the cellulose reflect the D/H ratio of the meteoric water in the tree's environment. As previously mentioned, it is the isotopic composition of this meteoric water which is thought to vary in response to climatic change.

After falling as rain or snow on the continents, water has three principal paths to follow: (1) runoff into lakes or streams; (2) penetration into the soil to become part of the ground water reservoir; (3) evaporation directly back into the atmosphere. Of course none of these paths is completely independent. Water does evaporate after penetrating the soil, and certainly there is a great deal of evaporation from lakes and streams. Furthermore, ground water not uncommonly can contribute to the flow of river systems, etc.

Trees act as a kind of intermediary in this larger hydrological cycle. Water is withdrawn from the soil via the roots, passes up through the stem and transpires from the leaves in often prodigious quantities. Kozlowski (1964) has cited work which found that a single tree (in this case a silver maple) was capable of transpiring up to 58 gallons of water per hour in July. Kozlowski also notes that forests have been observed to transpire 8,000 gallons of water per acre per day, or more, depending presumably on the site conditions.

Such large losses might imply that trees induce more loss of soil water to the atmosphere than would occur in their absence. In this vein Lull and Axley (1958: cited by Kozlowski, 1964) found that the uppermost 5 feet of a forest soil in New Jersey experienced 30% greater water loss than the equivalent zone in a bare soil. Wilde (1958) has noted the results of several workers which show that the levels of water tables can be depressed in the presence of a stand of trees. While the actual magnitudes are probably dependent on the site of interest, these results do indicate the significant role that trees can play in the loss of soil meteoric water back to the atmosphere.

This leads to the question of the effect of this water movement on its isotopic composition. Assuming that the precipitation has fallen to the ground with some isotopic composition characteristic of the meteorological conditions that spawned it, what steps in the sequence of events leading finally to its transpiration from tree leaves are likely to alter the original isotopic composition?

If the precipitation does not immediately infiltrate into the soil, it will likely undergo evaporation while on the surface. The evaporation of water from a well-mixed reservoir open to the air will commonly produce an increase in the D/H ratio of the residual liquid (Craig, et al, 1963; Friedman, et al, 1964; Craig and Gordon, 1965). Gat and Tzur (1967) have examined the expected enrichment for the case of water which is evaporating as it infiltrates into the soil. Using a modified version of the isolated reservoir model of Craig and Gordon (1965), they found that the average isotopic composition of the precipitation would not be appreciably modified by above-ground evaporation if the infiltration rates were sufficiently high. In fact the rates characteristic of a large spectrum of soils (greater than 7 mm/hour) were found by these authors to result in predicted $\delta^{18}O$ increases of less than one per mil for a relative humidity of 75% and evaporation rates of 200 mm/month or less. Craig (1961b) has found that companion δD and $\delta^{18}O$ values of precipitation commonly vary in accordance with the relationship $\delta D = 8\ \delta^{18}O + 10$. For waters undergoing evaporation the slope of this relationship is generally less than 8 (Craig and Gordon, 1965). Thus, the expected increase in δD is less than 8 per mil for the infiltrating waters of the Gat and Tzur model.

The case of waters infiltrating into heavy or poorly drained soils at very slow rates of less than 1 mm/hour will be considered later in this section. For the usual cases, however, it seems reasonable to conclude that precipitation falling onto well-drained soils will enter the soil with very little isotopic modification due to evaporation while on the soil surface.

The potential for isotopic modification of water once it is in the soil must now be examined. Zimmermann, et al, (1967) have addressed this question with a number of field and laboratory studies. During the course of one year they made measurements of the δD values of two field soils:one grass-covered, the other bare. Samples were taken from two depth intervals in each field: 0-10 cm and 10-20 cm. It was found that the water from the bare field was consistently enriched in deuterium by an average of 10 per mil compared to the grass-covered field. This average enrichment was characteristic of both the 0-10 cm samples and the 10-20 cm samples considered as separate groups.

Tritium tracer studies by this group (Zimmermann, et al, 1967) seem to indicate that water moves downward through soil in a layer-by-layer fashion. From these tracer studies, it was concluded that the total water loss due to evaporation was the same in each of the two fields. Since the soil water from the grass-covered field was less enriched in deuterium than soil water from the bare field, there is an implication that two different evaporative processes were in operation with each process having a different effect on the isotopic composition of soil water.

In this same work Zimmermann, et al, (1967) showed with laboratory experiments that transpiring plants do not produce an isotopic enrichment in the reservoir from which they withdraw water. However, for the case of bare soil, laboratory experiments with water evaporating from sand showed that water in the uppermost layer of sand can become enriched in deuterium. The depth to which isotopic enrichment occurs for the water in the sand seems to depend on the rate of evaporation -- the greater the evaporation rate the shallower will be the level to which isotopic enrichment penetrates in the steady state. However, even low evaporation rates are not likely to have a significant effect since, as modeled by Zimmermann, et al, a low evaporation rate on the order of 0.04 cm/day with an enrichment depth of 15 cm will require 150 days to approach 1/e of this steady-state depth. Consequently, they state that this depth of enrichment will not likely occur, since it seems probable that there will be a new precipitation event in that interval to push down the uppermost layer of water and begin the process anew.

Thus, in the absence of extreme drought it seems that water in bare soil will undergo a comparatively small degree of isotopic enrichment due to evaporation. Furthermore, for plant-covered soils this enrichment will be even less since much of the evaporative loss in this instance would be due to transpiration -- a process that does not appear to isotopically enrich soil water. In central Europe this bare soil evaporative deuterium enrichment is estimated to be 10 per mil with an estimated, resultant plant-covered soil enrichment of less than 5 per mil (Zimmermann, et al, 1967). This latter value is not very different from a deuterium enrichment of 4 to 6 per mil observed by Gat and Tzur (1967) for soil water obtained from an irrigated alfalfa field, although in this instance a significant amount of evaporation had occurred in the precursor rain as it fell through very dry air.

In summary, it appears that the waters of soils with "normal" infiltration rates are likely to preserve the isotopic composition of the precursor meteoric water with very little modification due to evaporation. Since plants transpire this water and incorporate some of it during photosynthesis, the potential for plants to record isotopic variations of the original precipitation is apparent.

The realization of this potential, however, depends on the nature of the isotopic fractionation of water as it moves from the soil through the plant and into the atmosphere. Wershaw, et al, (1966) and Zundel, et al, (1978) have performed isotopic analyses on water at several different stages in its passage through trees. In the former work the subjects were trees from Colorado and Washington and in the latter several species of tropical trees in Brazil. In both works water samples were collected in situ. Wershaw, et al, found that the δD values of soil water, root water, and xylem and phloem water were essentially the same. Zundel, et al, recorded the same result -- no difference between soil water and branch water -- for $\delta^{18}O$. This means that there is virtually no isotopic fractionation associated with the passage of water from the soil, to the roots and through the stem.

However, when it reaches the leaves, water undergoes significant isotopic modification (Gonfiantini, et al, 1965; Wershaw, et al, 1966; Epstein, et al, 1977; Farris and Strain, 1978; Zundel, et al, 1978; DeNiro and Epstein, 1979). Both δD and $\delta^{18}O$ values are increased in leaf water compared to stem water due to evaporation of water from the leaves. Measurements of leaf water δD values have found it to be as much as 80 per mil more positive than the precursor stem water (Wershaw, et al, 1966).

Dongman, et al, (1974) and Farris and Strain (1978) have modeled leaves in terms of a well-mixed reservoir with a source of liquid input, and evaporation as the only output. These models predict that, among other things, the steady-state δD (or $\delta^{18}O$) value of leaf water will depend on the relative humidity of the environmental air. Lower relative humidities will result in greater isotopic enrichments, if other variables remain constant. In fact measurements of leaf water have shown that diurnal variations in its isotopic composition probably are directly related to variations in humidity (Dongman, et al, 1974; Zundel, et al, 1978), although other parameters were not constant in these experiments.

Thus, under many commonly expected conditions, meteoric water will have followed a circuitous path from precipitation to soil water to root and stem water with little or no isotopic change, only to be significantly modified within the environs of the leaf. Because they carry out their photosynthetic processes in the leaves, it is likely to be the isotopic composition of the leaf water that is being recorded by trees.

Yet, the relationship of the δD value of carbon-bound hydrogen in tree cellulose to the leaf water δD value is also going to depend on the isotopic fractionation associated with the biochemical processes leading to the synthesis of cellulose. Therefore, it is instructive to consider the pathway of hydrogen in this overall process.

At some point in the "light" reaction (Rabinowitch and Govindjee, 1969) water is split into its constituent hydrogen and oxygen components with energy provided by light. Since this step involves a change in the bonding of the hydrogen atoms, there is an opportunity for significant hydrogen isotopic fractionation to occur (Buddenbaum and Shiner, 1977). A portion of these hydrogen atoms (ions ?) are then bound as the hydride to $NADP^+$ (nicotinamide adenine dinucleotide phosphate) to form NADPH. Again, the change in bonding of the hydrogen signals the possibility of isotopic fractionation. The hydrogen enters the carbon pathway via transfer from NADPH to 3-phosphoglyceric acid to form glyceraldehyde-3 phosphate (Calvin and Bassham, 1962). Several steps in the transformation of this substance to glucose monophosphate appear to involve the intramolecular transfer of carbon-bound hydrogen (Rabinowitch and Govindjee, 1969). All represent at least the possibility of exchange with the hydrogen of water. The remaining steps leading to cellulose appear to offer less opportunity for isotopic fractionation (Hassid, 1971).

It is the overall fractionation rather than the fractionation associated with any one step that is of interest here. It should be possible to determine the magnitude of the overall fractionation of hydrogen isotopes in the transformation from water to cellulose. Furthermore, the extent to which this fractionation differs from one plant species to another can also be examined.

Aquatic plants represent the simplest systems to examine in this context, since they will not have undergone leaf water isotopic fractionation due to transpiration. Therefore, it can be assumed that the isotopic composition of the leaf water is the same as that of the ambient water. Furthermore, aquatic plants growing in natural environments can be utilized if the water reservoir in which they are growing is sufficiently large to insure that its isotopic composition has not changed appreciably during the plant's lifetime. Seven of the plants listed in Table 2-1 appear to fit these criteria. All seven are listed below together with their cellulose nitrate δD values, δD values of the ambient water, approximate water temperatures at the time of collection, and calculated net fractionation factor. Sample descriptions are in Appendix II.

Sample	Cellulose Nitrate δD	Ambient Water δD	Approximate Water Temp. (°C)	α (net)
PR-TG	-5	+7	27	0.988
Phy-III	-42	-3	16	0.961
PW-CP	-59	-28	17	0.968
SW-CP	-54	-28	17	0.973
LM	-65	-51	21	0.985
OM-1	-101	-65	16	0.961
NLS	-136	-104	15	0.964

$$\text{Where } \alpha \text{ (net)} = \frac{1 + \dfrac{\delta D \text{ (cell nit.)}}{1000}}{1 + \dfrac{\delta D \text{ (leaf water)}}{1000}}$$

These plants have been analyzed previously (Epstein, et al, 1976), but the tabulated data herein represent reanalysis by the renitration method. The most striking feature of these data is that the cellulose carbon-bound hydrogen is depleted in deuterium with respect to the water in all cases. The magnitudes of the depletions vary somewhat but the similarities in kind for these fractionations seem to require that the biochemical processes which produced them are themselves very similar for the species examined here. Of these seven samples the five that were collected from waters with temperatures in the range of 15 to 17°C exhibit very similar α's. Furthermore, the α's of the

Table 2-1: δD Values of Cellulose Nitrate and Associated Meteoric Water, Approximate Growing Season Relative Humidity.

Sample	Cellulose Nitrate δD	Approx. Ave. Annual meteoric H_2O δD	Approx. growing season relative humidity h	$\frac{1+\frac{\delta D_{CN}}{1000}}{1+\frac{\delta D_{MW}}{1000}}$
PR-TG(PR-3)	-5	+7	1.00	0.988
MRM	-10	+7	0.77	0.983
Phyllospadix	-42	-3	1.00	0.961
H-2	-41	-24	0.70	0.983
PW-CP	-59	-28	1.00	0.968
SW-CP	-54	-28	1.00	0.973
UBLM-1	-40	-32	0.68	0.992
UBLM-2	-37	-32	0.68	0.995
MO-0-2	-39	-45	0.64	1.006
RE-CO-2	-46	-50	0.66	1.004
LM	-65	-51	1.00	0.985
AW-BO-1	-23	-60	0.68	1.039
MNY-BO-7	-42	-60	0.70	1.019
MNY-GA-2	-33	-60	0.70	1.029
MNY-RM-5	-45	-60	0.70	1.016
OM-1	-101	-65	1.00	0.961
OM-2	-80	-65	0.75	0.984
WR-1	-87	-69	0.68	0.981
WR-2	-76	-69	0.68	0.992
UAZ-PP-1	-31	-75	0.40	1.048
PO-DF-1	-57	-75	0.60	1.019
WM-B-1	-87	-90	0.66	1.003
BCT-10	-98	-97	0.70	0.999
Col-DF-1	-62	-100	0.50	1.042
NLS	-136	-104	1.00	0.964
BCT-9	-141	-106	0.75	0.961
SNF-LP-1	-75	-110	0.50	1.039
BCT-5	-122	-113	0.70	0.990
BCT-7	-138	-117	0.75	0.976
NT-1	-100	-119	0.50	1.022
BrPn	-80	-130	0.45	1.057
FCA-WS-1	-137	-135	0.72	0.998
BCT-12	-125	-135	0.70	1.012
MT-1	-130	-135	0.60	1.006
MT-2	-122	-135	0.60	1.015
BCT-11	-145	-136	0.70	0.990
BCT-3	-148	-139	0.70	0.990
BCT-1	-143	-144	0.70	1.001
SAS-JP-1	-165	-155	0.65	0.988
FA-As-1	-159	-165	0.69	1.007
Yuk-W-1	-166	-174	0.62	1.010
OPW-DF-1	-54	-54	0.75	1.000

two from warmer waters are more similar to one another than to the remaining five. Consequently, it seems possible that some of the variance of the α's in the sample set is due to the effects of temperature.

One literature value is of interest in this discussion. DeNiro and Epstein (1979) published the results of experiments which confirm the existence of CO_2 and H_2O oxygen isotope exchange prior to incorporation of the oxygen in the synthesis of carbohydrates. Included in their results, although not discussed, are analyses of both leaf water and cellulose nitrate δD values. The analyses are from wheat plants- i.e. a transpiring, terrestrial plant species. The average α (net) calculated from their two sets of experiments run at 25°C is 0.990 ± 0.001; where only the leaf water δD is used to calculate α (net). This value compares to the values for the aquatic species from 21°C and 27°C waters of 0.985 and 0.988 respectively. The similarities between the α's for the terrestrial and the aquatic plants at comparable temperatures favors the conclusion that the biochemistry associated with hydrogen isotope fractionation is similar for these two groups of plants.

There are, however, suggestions that the situation may be somewhat more complex for terrestrial plants. Ziegler, et al, (1976) claim to have demonstrated a correlation between degree of hydrogen isotope fractionation in land plants and the pathway of carbon fixation. Unfortunately, their hydrogen isotope analyses were made on untreated plant or water-washed plant tissue and this casts doubt on the validity of the interpretations made from these analyses (Epstein, et al, 1976).

Nevertheless, the trees that are of interest in the present work all have a common pathway of carbon fixation: the so-called C-3, or Calvin cycle (Calvin and Bassham, 1962), as does wheat. Thus the similarities of hydrogen isotope fractionation between cellulose carbon-bound hydrogen and leaf water noted for wheat and the preceding aquatic species can probably be extended to trees as well.

Two pairs of samples in Table 2-1 may provide additional information on this point. UBLM-1 and UBLM-2 are a grass and a willow tree respectively which grew subaerially side-by-side in a marsh adjacent to Lake Mendota, Wisconsin. Both plants incorporated water from the same source. As can be seen in Table 2-1, the δD values of these different species agree within experimental error. This seems to suggest an absence of different biochemically induced net fractionations between cellulose C-H hydrogen and leaf water for the two plants.

Similar arguments can be made for WR-1 and WR-2, a grass and a maple tree respectively, that grew side-by-side in sandy soil immediately adjacent to the Wisconsin River near Spring Green. Their cellulose C-H hydrogen δD values differ by only 11 per mil, again suggesting the probable similarity of the net biochemical fractionations for two morphologically very different plant species.

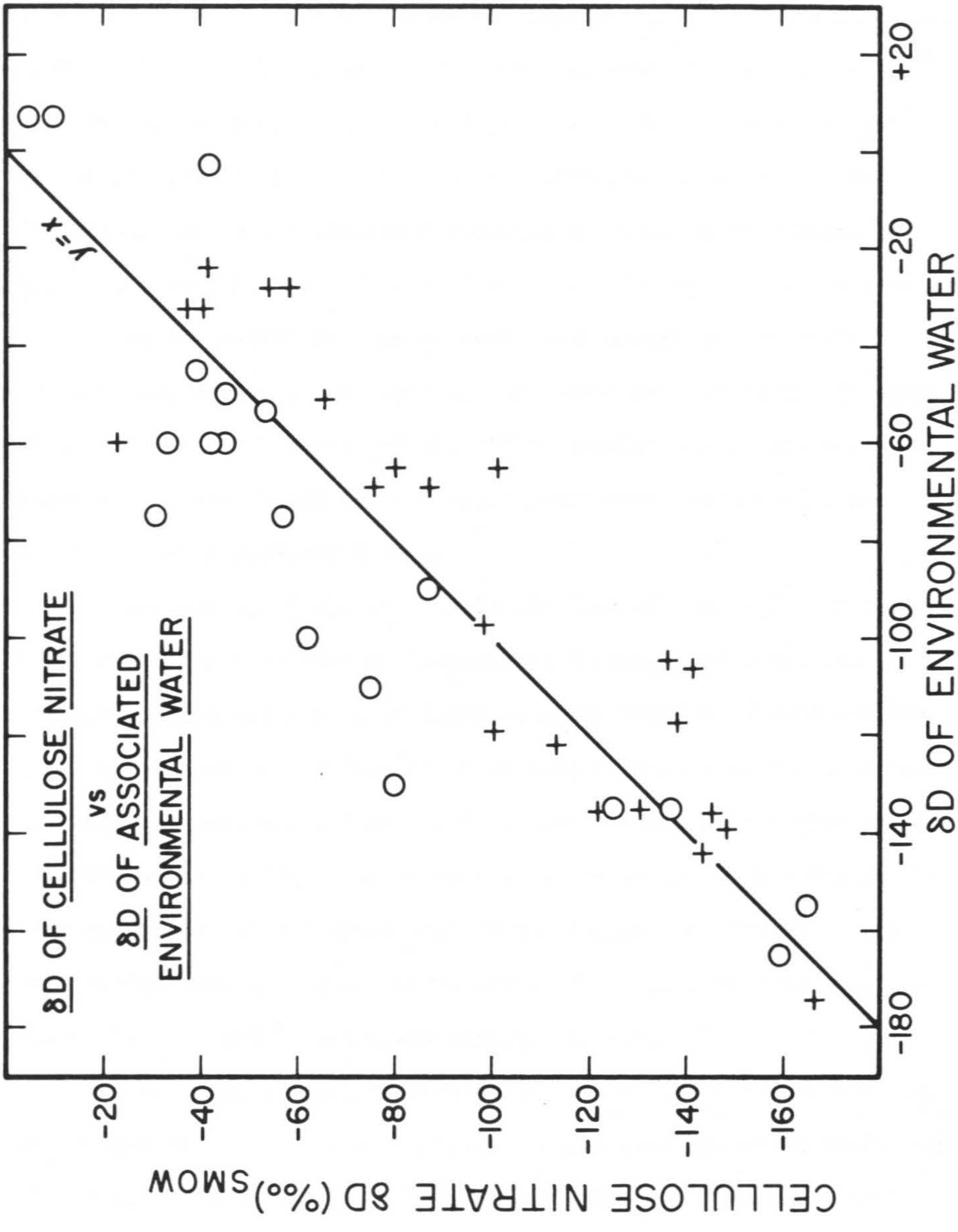
Comparisons of measured δD values of cellulose nitrate extracted from trees and other terrestrial and aquatic species with the δD values of the associated meteoric waters are presented in Table 2-1 and plotted in Figure 2-1. There is a fairly strong correlation between the two variables, but a large amount of scatter is obvious. Furthermore, the depletion in deuterium of cellulose C-H hydrogen compared to water that was observed for the aquatic plants and wheat is not generally

Figure 2-1

A plot of the δD value of the nitrated cellulose from a variety of plants from a wide geographic range against the δD value of the associated environmental water. The open circles depict points for which the δD value of the environmental water was obtained from the literature (Wershaw, et al, 1966; Friedman, et al, 1964; Taylor, 1974). The crosses indicate those points for which the δD value of the water was analyzed in this laboratory. The linear regression of these data yields the expression:

$$\delta D_{CN} = 0.87\ \delta D_{H_2O} - 11$$

The linear correlation coefficient is 0.891.


δD OF CELLULOSE NITRATE
vs
δD OF ASSOCIATED
ENVIRONMENTAL WATER
y = x
δD OF ENVIRONMENTAL WATER
-180
-140
-100
-60
-20
+20
CELLULOSE NITRATE δD (‰)SMOW
-20
-40
-60
-80
-100
-120
-140
-160

seen in Figure 2-1. This lack of universal depletion also contrasts with the results of Epstein, et al, (1976), even though some of the data of Figure 2-1 represent samples first analyzed by Epstein, et al, (1976). If only the re-analyzed samples of Epstein, et al, are considered, the overall level of depletion which they observed for cellulose nitrate δD is still apparent although the magnitude has diminished due to the different analytical methods (see section on analytical procedures). It should be noted that most of their samples originated in regions of comparatively high humidity. From the previous discussion about isotopic enrichment of leaf water, it seems apparent that the Epstein, et al, (1976) samples simply did not experience a high level of leaf water enrichment because of these higher relative humidity levels.

Consequently, if the scatter in the data of Figure 2-1 is not due to isotopic fractionation differences reflecting differences in biochemistry, then the effect of local relative humidity should explain some of the observed enrichment of cellulose nitrate δD values compared to the local meteoric waters. This follows from the fact that the local meteoric waters being used for comparison in Table 2-1 and Figure 2-1 have generally not undergone significant isotopic enrichment due to evaporation, and thus the leaf waters of the plants in these regions should be enriched in deuterium compared to them.

The leaf water model of Farris and Strain (1978) can be employed to examine the role that transpiration might have played in producing the scatter of Figure 2-1. For manageability, the isotopic steady-state for leaf water is assumed, although this is only approximately correct (Zundel, et al, 1978). The steady-state expression for the isotopic composition of leaf water is:

$$(2\text{-}1)\quad \delta D_L = \alpha_{eq}\ \alpha_k\ (1-h)\ (1000 + \delta D_i) + \alpha_{eq} h(1000 + \delta D_a) - 1000$$

where, δD_L = leaf water δD

δD_i = stem or imput water δD

δD_a = ambient atmospheric water vapor δD

α_{eq} = equilibrium fractionation factor between liquid and vapor

α_K = kinetic fraction factor between liquid and vapor

h = relative humidity

Farris and Strain have incorporated many refinements into their model, including normalization of relative humidity to leaf temperature and consideration of the effects of turbulent and laminar flow on the fractionation factor. For the natural samples being considered here, there is too little information to quantitatively incorporate these parameters, so the simplest case has been employed - ie. static conditions and relative humidity at the temperature of the air.

Now, some additional assumptionsare made. Firstly, it is assumed that δD_i is the same as the δD of the local unenriched meteoric waters. Secondly, δD_a is assumed to have the value of water vapor in isotopic equilibrium with δD_i. Thirdly, α_{eq} and α_k are assumed to be constant. Finally, δD_L is assumed to be related to the cellulose nitrate δD value (δD_{CN}) by α (net) as defined for the wheat and aquatic plants previously, then

$$\frac{1 + \frac{\delta D_{CN}}{1000}}{1 + \frac{\delta D_i}{1000}} = \alpha_{net}\ \alpha_{eq}\ \alpha_k - \alpha_{net}\ (\alpha_{eq}\ \alpha_k - 1)h \qquad (2\text{-}2)$$

A plot of the quotient on the left side of the preceding equation vs the local relative humidity should yield a linear array, if all of the assumptions which went into the derivation are valid. The relative humidities used for this plot are listed in Table 2-1. They were obtained from data in Landsberg (1974) and the National Atlas of the United States of America (1970). These relative humidity data are estimates of the daily (24 hr) average humidity during the growing season. Trees, however, photosynthesize during the daylight hours (Kramer and Kozlowski, 1960) and relative humidity can undergo large diurnal fluctuations commonly reaching minimum values in the afternoon (Ruffner and Bair, 1977; Zundel, et al, 1978). Thus, the average daytime relative humidity is likely to be lower than the average humidity for an entire 24 hour cycle. As a result, the relative humidity data of Table 2-1 are probably an overestimate of the actual relative humidities extant during the daytime transpiration that accompanies photosynthesis.

Nonetheless, these 24 hr. averages were employed, because data on the diurnal fluctuations of relative humidity during the growing season at each of the sample sites of Table 2-1 have not been obtained. It has been assumed that the average daylight relative humidity in a particular locale will be proportional to the 24 hr. average relative humidity with a proportionality constant that is independent of the locale.

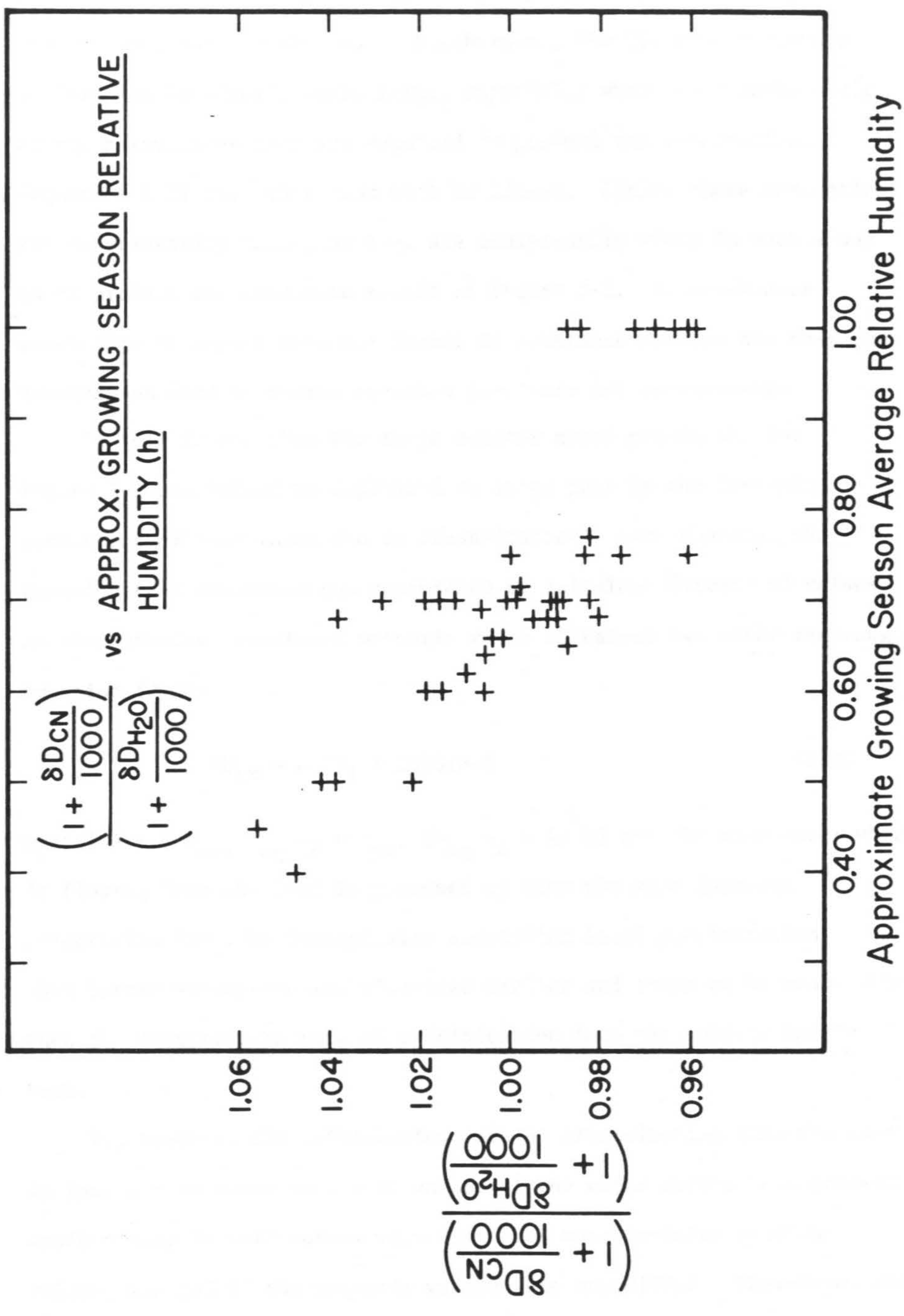
The plot of the apparent cellulose nitrate-meteoric water hydrogen isotope fractionation vs the 24 hr. average growing season relative humidity is in Figure 2-2. Since $\alpha_{eq}\ \alpha_k$ is greater than one (Majoube, 1971; Merlivat, 1978), equation (2-2) predicts that the slope of a

Figure 2-2

A plot of the apparent fractionation factor between cellulose nitrate and local meteoric water against the approximate growing season relative humidity. Those points indicating a relative humidity of one represent aquatic plants. The linear regression of these data yields the equation:

$$\frac{1 + \frac{\delta D_{CN}}{1000}}{1 + \frac{\delta D_{MW}}{1000}} = -0.124\ h + 1.089$$

The correlation coefficient is -0.793.


$\frac{\left(1+\frac{\delta D_{CN}}{1000}\right)}{\left(1+\frac{\delta D_{H_2O}}{1000}\right)}$ vs APPROX. GROWING SEASON RELATIVE HUMIDITY (h)
1.06
1.04
1.02
1.00
0.98
0.96
0.40
0.60
0.80
1.00
Approximate Growing Season Average Relative Humidity
$\frac{\left(1+\frac{\delta D_{CN}}{1000}\right)}{\left(1+\frac{\delta D_{H_2O}}{1000}\right)}$

straight line defined by the points of Figure 2-2 should be negative, and in fact, this is the case. Furthermore, the linear correlation coefficient is significantly large, especially when one remembers all of the assumptions that are required to produce the expectation (equation 2-2) that this plot will be linear. Either these assumptions are substantially valid, or they are individually wrong in such a way as to produce the composite result of Figure 2-2. It seems more reasonable to expect that the former circumstance obtains and that the assumptions used to derive equation (2-2) are not unreasonable.

If this is so, then the large scatter noted previously for Figure 2-1 can indeed be explained in large part by the isotopic enrichment of leaf water due to transpiration. Consequently, the equation that describes the dependence of cellulose nitrate δD values on isotopically unenriched meteoric water δD values is, after rearranging equation (2-2):

$$\delta D_{CN} = A\ \delta D_i + 1000(A-1) \qquad (2\text{-}3)$$

where, $A = [\ \alpha_{net}\ \alpha_{eq}\ \alpha_K - \alpha_{net}\ (\alpha_{eq}\ \alpha_K - 1)\ h]$ and the stem water which is flowing into the leaf is presumed to have the same isotopic composition (δD_i) as isotopically unmodified local precipitation. This latter assumption was discussed earlier and found to be reasonable when the infiltration rate of precipitation into the soil is fairly high.

If, however, the infiltration rate of precipitation into the soil is low, the increase in the δD values of the water during this process would result in soil waters with δD values more positive than the values expected if the meteoric waters were unmodified. Therefore, the value of δD_i in the preceding equation would be more positive and so in turn would the value of the analyzed cellulose nitrate (δD_{CN}). This can be illustrated by considering the extreme cases. At one extreme will be the situation in which the infiltration of the precipitation is delayed and it remains on the surface long enough to reach an isotopic steady state during evaporation. This condition may be modeled as evaporation from an isolated reservoir; the equation for which is:

$$\delta D_{ss} = \left[\frac{(1 + \frac{\delta D_a}{1000})\ \alpha_{eq}\ h}{1 - \alpha_{eq}\ \alpha_K\ (1-h)} - 1 \right] 1000 \qquad (2\text{-}4)$$

All the symbols have the same meaning as in the preceding leaf water model equations. δD_{ss} is the steady-state δD value of the reservoir liquid (Eriksson, 1965). After reaching steady-state, the residual liquid is presumed to infiltrate into the soil. For a hypothetical case, let

$h = 0.65$

$\alpha_{eq} = 1.090$ (from Majoube, 1971)

$\alpha_K = 1.0249$ (from Merlivat, 1978)

$\delta D_a = -190‰$

$\delta D_{MW} = -117‰$

δD_{MW} is the δD value of the original precipitation that would be in isotopic equilibrium with δD_a. Although δD_{MW} does not enter into the isolated reservoir expression, it will be important for the calculation of the leaf water δD value. Then, for the aforementioned hypothetical parameters:

$$\delta D_{ss} = -58‰$$

If it is assumed that this δD_{ss} value is transmitted to a tree and ultimately transpired, the δD of the leaf water (δD_L) for the same humidity, α's and δD_a would be, from equation (2-4):

$$\delta D_L = -58‰$$

In other words the δD value of the leaf water would be the same as that of the highly enriched soil water, since both are presumed to be at isotopic steady-state under the same environmental conditions and no additional enrichment can occur in the leaf.

However, if the precipitation should infiltrate into the soil with sufficient rapidity to avoid evaporative isotopic enrichment, then the δD value of the soil water passing into the tree to be ultimately transpired will be:

$$\delta D_{MW} = -117‰$$

Thus, the δD value of the leaf water in this circumstance would be, from equation (2-1):

$$\delta D_L = -81‰$$

These calculations illustrate the point that evaporation of precipitation while on the surface can produce isotopic enrichments which, when coupled with transpiration, result in a greater net increase in δD of leaf water than would occur from transpiration alone. This is in spite of the fact that both processes occur under the same environmental conditions. The difference lies in the fact that leaf water steady-state δD values represent a balance between an incoming liquid and exchange with atmospheric vapor, while the steady-state δD values of precipitation evaporating as a well-mixed isolated reservoir at the surface are determined by exchange with atmospheric vapor alone. Although the steady state is not likely to be achieved during infiltration (Gat and Tzur, 1967), the previous calculations do show the comparative impacts of transpiration and surface evaporation on the δD value of leaf water.

Thus, they indicate the possible effects that changes in soil drainage characteristics during the lifetime of a tree might have on the isotopic record contained in the cellulose. Yet, according to Wilde (1958), soils generally tend to become better drained with the establishment and growth of a forest. Since progressive deterioration of soil drainage capacity will probably not occur during the lifetime of a tree, the possibility that the tree ring cellulose isotopic record will be thereby altered is also minimized.

Up to this point, most of the variables that could affect the isotopic composition of water passing through trees have been considered, except one: the seasonal variability of the isotopic composition of precipitation. The existence of this variation for temperate and colder climates has been well-established by numerous δD and $\delta^{18}O$ measurements of monthly precipitation performed by the International Atomic Energy Agency (IAEA). The impact of this variation on the cellulose nitrate δD values measured in trees probably depends on a number of factors: (1) is the water in soils isotopically well-mixed over the course of at least one year; (2) if the water is not isotopically well-mixed, how does it migrate through the soil and what is the pattern of soil water uptake established by the root system; (3) does water from the saturated zone below the water table represent a significant component of the total water passing through a tree during the growing season?

The answer to the first of these three questions probably depends, in degree, on the type of soil and its drainage characteristics as well as on the amount and distribution of precipitation in the course of a year. Eichler (1966) measured the deuterium profiles of soil water from soils in Germany and observed variations in the δD values to depths of 3 meters. The patterns between different cores varied somewhat, but may have represented the seasonal variations in precipitation. The amplitudes of the soil water variations, however, were considerably attenuated compared to those of central European precipitation. The soil water δD values exhibited a range of about 20 per mil, while the seasonal range of central European precipitation is on the order of 100 per mil (Knott, 1964; cited by Zimmermann, et al, 1967). Consequently, either (1) the variations in soil water δD values are due to something other than the seasonal variation of precipitation, (2) there is considerable mixing of the soil water from different precipitation events, and/or (3) the degree of isotopic enrichment due to evaporation shows a seasonal preference for winter, when the precursor precipitation values are most negative. The latter explanation is favored by Zimmermann, et al, (1967) and may be possible, if for example, the ground is frozen in winter with an accumulated snow cover. This would mean that in spring the snow could melt and evaporate while only slowly infiltrating into the still frozen ground. However, evaporation rates would probably be low as well, and would thus minimize the degree of isotopic enrichment (Gat and Tzur, 1967).

The data of Zimmermann, et al, (1967) show that the average isotopic composition of a year's accumulation of soil water in a plant-covered soil in Germany has a δD value of -62 per mil, which is very close to the average annual δD value of precipitation from this region (about -60 per mil). The accumulation of soil water for the same span of time in a bare soil was -52 per mil which does reflect the effects of evaporation. The δD profiles obtained for these two cases showed some variation, with a greater amplitude for the bare soil than the plant-covered (Zimmermann, et al, 1967). In both cases the amplitude was considerably smaller than that of the seasonally varying precipitation, thus confirming the observations of Eichler (1966). In view of the similarity of the plant-covered annual soil water δD value to the average annual δD value of local precipitation, it seems probable that vertical mixing of soil water is of primary importance in reducing the amplitudes of soil water deuterium profiles.

The preservation of any type of seasonal variation of δD values in soil water implies a particular kind of soil water movement. Using tritium tracers Zimmermann, et al, (1967) have characterized this movement as a layer-by-layer process. A new precipitation event infiltrates the soil and forms a layer which pushes down the layers from earlier events. Thus, the seasonal character of the original precipitation can presumably be preserved in the soil profile, if vertical soil water mixing is incomplete.

The fact that the roots of trees can have a significant vertical extension into the soil implies that they will take up water from more than one of these postulated seasonal layers. This implication will be used to develop a simple model of the expected isotopic composition of water passing through a tree during the growing season.

Firstly, it is assumed that the volume occupied by a root system is approximated by a cylinder with uniform root density throughout. Secondly, it is assumed that the downward movement of the layers of water is approximated by a sine wave of the form:

$$\delta\ (t,z) = \delta_o \sin \frac{2\pi}{T} (t - \frac{z}{a}) + K$$

$\delta\ (t,z)$ = the δ value of the soil water at any particular t and z

δ_o = the amplitude of the δ variation

T = the period of variation; in this case 12 months

t = some time during the period in fractional units of T

z = the vertical distance below the soil surface with z positive and increasing as one moves downward from the surface

a = phase velocity of sine wave

K = average annual isotopic composition of soil water

To obtain the average isotopic composition of water passing through a tree during the growing season it is first necessary to find the instantaneous average δ value of water being absorbed by the cylinder of roots. Thus:

$$\delta_{\text{instantaneous}} = \frac{\int_o^d \delta\ (t,z)\ \pi r^2 dz}{\int_o^d \pi r^2 dz}$$

Where r = the radius of the cylinder of roots. The limits of integration are the soil surface (z = o) and the base of the cylinder of roots (z = d). The average instantaneous δ value of the water absorbed by the cylinder of roots must then be integrated over the length of the growing season to get the average δ value of water passing through the tree during this time. Thus:

$$\delta_{gsa} = \frac{\int_{t_1}^{t_2} \delta_{inst}\, dt}{\int_{t_1}^{t_2} dt}$$

Where δ_{gsa} = the average δ value of the water passing through the tree during the growing season. The limits of integration are determined by which portion of the year represents the growing season. t = 0 is taken to be the spring - i.e. about April. For a constant cylinder radius the expressions obtained for three different growing seasons are as follows:

for, $0 \leq t \leq T/4$ (April to June)

$$\delta_{gsa} = \frac{aT}{\pi^2 d} \left[\sin(\frac{2\pi d}{aT}) + \cos(\frac{2\pi d}{aT}) - 1\right] \delta_o + K$$

for, $T/4 \leq t \leq T/2$ (July to September)

$$\delta_{gsa} = \frac{aT}{\pi^2 d} \left[\sin(\frac{2\pi d}{aT}) - \cos(\frac{2\pi d}{aT}) + 1\right] \delta_o + K$$

for, $0 \leq t \leq T/2$ (April to September)

$$\delta_{gsa} = \frac{aT}{\pi^2 d} \left[\sin\ (\frac{2\pi d}{at})\right] \delta_o + K$$

Plots of (δ_{gsa} - K) vs d/a are found in Figure 2-3. d/a is plotted in units of months since "d" is measured in meters and "a" in meters per month. Values of "a" taken from Zimmermann, et al, (1967) are on the order of from 0.1 to 0.3 meters per month. Consequently, a tree with roots about one meter deep will have a d/a ratio of from 3.3 to 10 months. For a "normal" growing season from April to September, the average isotopic composition of the water passing through the tree will be anywhere from 35% of the amplitude more positive to 15% of the amplitude more negative than the average isotopic composition of the soil water. However, it should be remembered that the amplitude of the δD values of soil water variations are greatly attenuated at depth. In fact they may have as little as 20% of the value of the precursor precipitation amplitude (Eichler, 1966). Therefore, the fluctuations predicted by Figure 2-3 for the preceding tree example are likely to represent actual δD variations on the order of no more than 5 per mil, for conditions analogous to those in central Europe.

At this stage it is important to note the possible failures of the assumptions of this model. First, the precipitation-mimicking sinusoidal variation of soil water δD values may not occur, especially if precipitation only falls at certain times of the year. Second, the root geometry will probably not be cylindrical, or even if it were, the root density and water-absorbing capacities would probably not be uniform (Kramer and Kozlowski, 1960). Third, the water from any given layer may be depleted by the tree soon after it has moved below the surface and consequently, it will not be available for absorption by roots at a lower level. Finally, the layer-by-layer downward movement of soil water may not exist in soil which is disturbed by the very presence of the roots.

The various caveats notwithstanding, the model represented by the curves of Figure 2-3 does provide some qualitative predictions about the isotopic composition of water passing through trees. It does not

Figure 2-3

A plot of the average isotopic composition of water passing through a tree during various growing seasons according to the model described in the text. The various symbols are defined as follows:

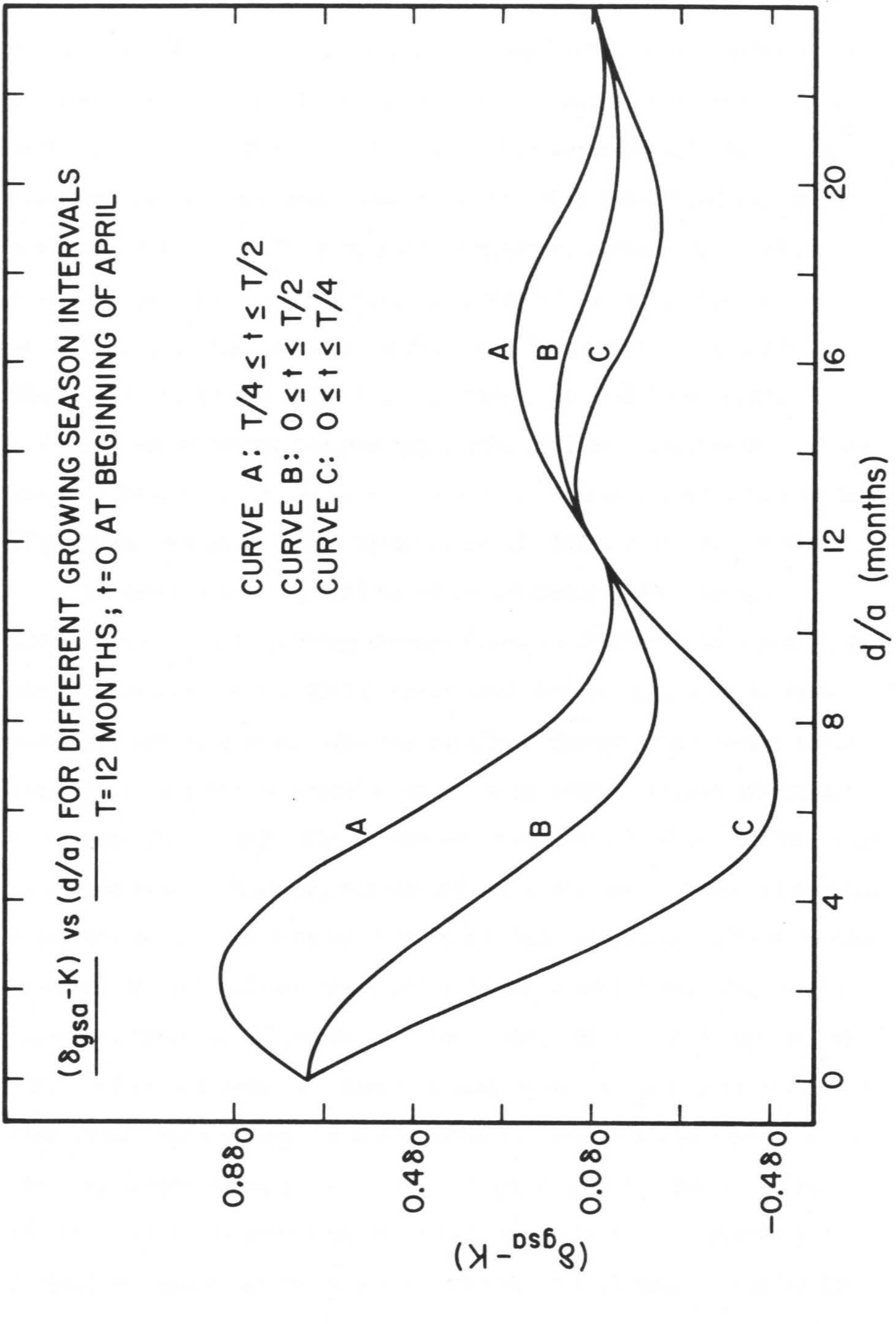
δ_{gsa} = average isotopic composition of the water passing through a tree during the growing season

K = the value of the average annual precipitation

δ_o = the amplitude of the seasonal variation of the δ values of the precipitation

d = the depth of the root system of the tree (in meters)

a = the rate of downward movement of the various water layers (in meters per month)


(δgsa-K) vs (d/a) FOR DIFFERENT GROWING SEASON INTERVALS
T=12 MONTHS; t=0 AT BEGINNING OF APRIL
CURVE A: T/4 ≤ t ≤ T/2
CURVE B: 0 ≤ t ≤ T/2
CURVE C: 0 ≤ t ≤ T/4
A
B
C
0.880
0.480
0.080
-0.480
(δgsa - K)
0
4
8
12
16
20
d/a (months)

presume vertical mixing of soil water, yet it indicates that even in the absence of such mixing trees might commonly "see" a growing season average isotopic composition of soil water that is very close to the soil water average for a single year. With the vertical mixing, or attenuation, that actually seems to occur, this likelihood becomes a strong probability. The reasonably consistent results obtained by using the average annual δD value of meteoric waters in Figures 2-1 and 2-2 tend to support this conclusion. Furthermore, the model of Figure 2-3 provides a basis for expecting that cellulose formed at different times during the growing season will have different isotopic compositions, e.g. earlywood and latewood. In fact, they commonly do (Wilson and Grinsted, 1975; Epstein, et al, 1976; Epstein, 1978).

The importance of ground water in determining the isotopic composition of water passing through trees is difficult to assess. In general, however, Wilde (1958) has stated that in upland soils tree roots are not in contact with the capillary fringe of the water table. Thus, in this instance there seems to be no need to assess its impact. Tree roots in lowland soils on the other hand are said to be "influenced" by ground water. However, the ground water may have limited influence, since the root systems of many trees in these environments tend to have the greatest fraction of their total volume near the surface, in the uppermost meter or so (Kramer and Kozlowski, 1960). Consequently, the uptake of ground water by trees in lowland soils seems most likely to predominate either when the water table is very near the surface or in times of severe drought. Depending on the origin and residence time of its waters, the ground water in either of the two aforementioned lowland circumstances could act to "dampen" any climatic response in the hydrogen iwotopes in the cellulose of lowland trees.

Summary

The hydrogen isotopic relationship between plants and environmental waters is determined by the sequential interaction of several different processes. The major steps in each of the sequences can be examined to determine their individual impact before the net result itself is examined, and thus, the net result can be better understood.

Such examinations in this work and others have led to the following conclusions:

(1) In many circumstances the hydrogen isotopic composition of soil water can be expected to be very nearly the same as the precursor precipitation over the course of a year.

(2) Water passes from the soil into a tree and up to the leaves without measurable fractionation.

(3) In the leaves there is commonly a significant increase in δD values of the water due to vigorous transpiration.

(4) The average isotopic composition of water passing through a tree during the growing season will quite probably be close to the average annual isotopic composition of the soil water, and therefore to the average annual isotopic composition of the local precipitation.

(5) The δD value of cellulose nitrate extracted from trees will reflect the δD value of this local precipitation. However, the cellulose nitrate δD value will also reflect the transpiration of leaf water and the effect of humidity on the resulting isotopic enrichment. Additionally, the hydrogen isotope composition of the cellulose C-H hydrogen will be different by a biochemically originated fractionation

factor (α_{net}) from the leaf water isotopic composition. These effects are summarized for the isotopic steady state by equation (2-3). For $\alpha_{eq} = 1.090$, $\alpha_K = 1.0249$, and $\alpha_{net} = 0.978$, the value of A in equation (2-3) does not deviate from one (1) by more than about 7% over a humidity range of 20 to 90%. Thus, humidity has little impact on the slope of equation (2-3). For these same values of the various α's, the intercept, 1000(A-1), varies by about one per mil in δD for an incremental change in relative humidity of 1%.

The implication is that unless the growing season average relative humidity changes by more than a few percent from year to year at any single site, the δD variations of cellulose nitrate extracted from a sequence of tree rings will directly reflect the δD variations of the soil water passing through the tree and thus, quite probably, the variations of the local precipitation. However, it should be remembered that the validity of this conclusion may depend on the degree to which equation 2-3 actually characterizes the hydrogen isotope composition of cellulose C-H hydrogen.

Section 3

Some Effects of Tree Physiology on the Variations of Hydrogen Isotope Ratios in Cellulose

From the discussion in Section 2, it is apparent that the isotopic composition of the C-H hydrogen in the cellulose of a tree ring can, in principle, reflect the hydrogen isotopic composition of the water that has passed through the tree during the same growing season. In practice this relationship will depend on a number of factors related to plant physiology.

Foremost among these factors is the time lag between synthesis of glucose in the tree leaves and its subsequent polymerization as cellulose in the cell walls of a newly forming ring. If the growing cells of the ring incorporate only glucose from that current year, the δD relationships between cellulose C-H hydrogen and water will probably be that much simpler. In fact the degree to which this condition will obtain appears to be dependent on the type of tree under consideration.

Kramer and Kozlowski (1960) have summarized some of the pertinent observations on this point. They cite several studies which concluded that for conifers and ring-porous hardwoods radial growth commonly begins in the spring at about the same time as the development of new buds. Diffuse-porous hardwoods on the other hand typically do not begin radial growth at lower levels of the main trunk until well after the significant expansion of new leaves. These differences have different isotopic implications.

Since ring-porous hardwoods in temperate regions generally shed their leaves in the fall, they will lack a photosynthesizing capacity in the spring until new leaves have developed. Therefore, in order for radial growth to occur at the onset of bud development--ie. before the new leaves have formed, the tree must be using stored material to generate the initial cells of the new growth ring. These stored substances are probably carbohydrates which were formed during the latter part of the preceding growing season, since that is the time when the concentration of these reserve materials typically increases in trees (Kramer and Kozlowski, 1960; Kramer, 1964). Thus, the earliest formed wood in the ring of a ring-porous tree is likely to contain cellulose whose hydrogen isotope composition is representative of conditions that existed in the preceding summer and/or early fall. In contrast, wood formed in this ring after the leaves have developed will probably contain cellulose formed principally from precursors that were synthesized during the current growing season. As discussed in the preceding section (see Figure 2-3), the carbohydrates synthesized in the late summer and early fall will reflect the more positive δD values of water likely to be passing through the tree during this time. Therefore the earliest ring-porous wood to be formed in the subsequent year will have the comparatively more positive δD values of this summer carbohydrate, while the wood formed after the leaves have extended and begun to photosynthesize will have a more negative, growing season-integrated δD value (see Figure 2-3).

Ring-porous trees contain two distinguishable regions within any single ring (earlywood and latewood). Earlywood is generally characterized by a high density of large diameter vessels and is lighter in color than latewood. These physical differences make these two regions of a ring convenient subdivisions for isotopic analysis. Table 3-1 lists δD values for earlywood and latewood in two bur oaks from two different locales. For all the oak samples in this table the δD value of the earlywood cellulose nitrate is more positive than the δD value of the corresponding latewood. Therefore, the earlywood that was sampled

Table 3-1: δD and H_2 Yield of Cellulose Nitrate Extracted from Earlywood and Latewood of Some Oak and Pine Trees.

	Earlywood		Latewood	
Sample	δD	H_2 yield (%)	δD	H_2 yield (%)
AW-BO-1 (Bur Oak)				
1966	-3	100	-26	102
1967	-5	105	-31	103
1968	-6	106	-29	105
1969	-20	106	-40	104
1970	-16	104	-34	104
1971	-8	101	-31	101
1972	-16	100	-40	102
1973	-16	103	-40	104
1974	-19	103	-37	104
1975	-18	99	-36	105
MNY-BO-7 (Bur Oak)				
1807	-29	102	-70	106
OIO-VP-1 (Pine)				
1949	-33	99	-42	98
1969	-36	98	-26	98
BCT-12 (Pine)				
1972	-137	100	-143	100
1973	-140	99	-129	101

here must have contained a significant proportion of cellulose formed from carbohydrates synthesized the preceding summer. The latewood of these samples may have contained some of this "preceding summer" cellulose as well, but in significantly smaller proportions.

As was previously mentioned, the timing of the formation of new wood in conifers and ring-porous trees is similar. However, the pattern of hydrogen isotopic variation within the ring of a conifer may not necessarily be the same as that of a ring-porous hardwood. Conifers generally retain their leaves (needles) through the winter and thus are capable of some photosynthesis simultaneously with or even prior to the onset of radial growth (Fritts, 1976). Consequently, while the earliest formed wood in the ring of a conifer may contain some cellulose formed from stored carbohydrates, it is also possible that this will be a smaller proportion of the initial wood than was true for the ring-porous hardwoods. If so, the conifer wood formed earlier in the growing season may have more negative δD values than the later formed wood (see Figure 2-3).

As with ring-porous woods, it is possible to conveniently subdivide conifers on the basis of earlywood and latewood. In this case a color change was employed--the latewood being darker than the earlywood. Two pairs of earlywood-latewood δD analyses from each of two different pine trees are listed in Table 3-1. The δD differences between earlywood and latewood cellulose nitrate are not consistent for either of the two trees. This might have been anticipated from the preceding discussion, and it dovetails with similar observations of Epstein, et al., (1976) on other conifers.

It was mentioned earlier that diffuse-porous trees such as maple do not begin radial growth in the lower trunk at the onset of bud development. In fact radial growth initiation seems to spread as a wave from the region around the buds down to the base of the trunk possibly following the pattern of growth hormone movement. The elapsed time between the start of this wave at "bud burst" and its arrival in the lower trunk can be on the order of several weeks (Kramer and Kozlowski, 1960, p. 40). Thus, the earliest formed wood in the new ring near the top of a ring-diffuse tree may contain some carbohydrate from the preceding summer in its cellulose, since the new leaves are not yet extended. The earliest formed wood in the ring at the lower trunk, however, may only contain cellulose formed from carbohydrates synthesized during the current growing season. This would follow from the fact that by the time growth begins in the lower trunk, the leaves have extended (Kramer and Kozlowski, 1960). Nevertheless, it is also possible that the first-formed wood of the lower trunk incorporated locally stored carbohydrates. As a result it could contain carbohydrates from the preceding summer as well.

An investigation of some of the isotopic consequences of this diffuse-porous behavior would include a continuous series of samples of a growth ring from the top of the tree to its base. Such a study is beyond the scope of the present work. However, it seems that even in the extreme, diffuse-porous wood will probably incorporate no more preceding-summer carbohydrate than would ring-porous wood under the same environmental conditions. Consequently, the δD value of a diffuse-porous ring will probably reflect that current season's water δD value to at least the same degree as a ring from a ring-porous tree.

Wigley, et al, (1978) have suggested that the intra-ring isotopic differences exemplified by the data in Table 3-1 could have implications for the nature of any climatic response of the δD value of cellulose nitrate in tree ring sequences. They base this argument on an assumption that the isotopic composition of a single tree ring is determined by the mass balance between two isotopically distinct components--earlywood and latewood. From this premise they go on to show that a correlation between δD (or $\delta^{18}O$) values and the reciprocal of total ring width necessitates the conclusion that the δD variations are not responding independently to climate. This follows from the fact that ring widths themselves may vary in response to climatic variables (Fritts, 1976). If one accepts their assumption that a tree ring is isotopically a two-component system, the conclusion about ring width-isotope correlations may be reasonable.

However, the "distinctive" things about earlywood and latewood are physical in nature. It was these physical differences which originally made them a convenient choice to use as guides for subdividing tree rings for isotopic analysis (Epstein, et al, 1976). In fact the physical traits of earlywood and latewood <u>grade</u> into one another, albeit sometimes with a large gradient (Fritts, 1976). The same appears to be true of intraring isotopic variations.

Wilson and Grinsted (1975) and Epstein (1978) have found that if a tree ring is divided on a finer scale than just earlywood and latewood, there is a more discernibly continuous isotopic variation throughout the ring. Thus, the apparent two-component isotopic nature of earlywood and latewood is more an artifact of the imposed two-component sampling method than anything else. Furthermore, a continuously varying isotopic composition of cellulose formed throughout the growing season is what would be expected, since the isotopic composition of the ambient precipitation varies during this time (IAEA).

The rate at which a ring is growing may not affect its final, composite cellulose isotopic composition, so long as the rate is relatively uniform throughout the growing season. This follows from the numerous observations of Section 2 that indicate that it is the isotopic composition of the water passing through the tree during the growing season that determines the average isotopic composition of the cellulose. Thus, as long as the cambium is forming new cells at some approximately constant rate from beginning to end of the growing season, it won't matter, isotopically, how wide or narrow the ring is.

Yet, the width of the ring might be controlled by some climatic parameter which is also influencing the δD value of the water that the tree "sees". It would be hard to argue that the isotopic composition of the water was controlled by ring width. Rather, it seems more probable that the water δD value and ring width could vary independently in response to the same variable. Since the cellulose δD value reflects the water δD value, there could be a correlation between cellulose nitrate δD and ring width. However, it would have nothing to do with the influence of ring width on δD of cellulose *per se*. Consequently, a correlation of δD values with ring width would not in itself be sufficient evidence to say that ring width variations are controlling δD variations.

The only thing about variations in isotopic composition between different rings that might have a truly two-component nature in the climatic sense is the possible presence of cellulose derived from carbohydrates synthesized in the preceding summer. Thus, the relative proportions of the components from two different seasons might influence the isotopic behavior of the ring. However, for this to be significantly related to ring width, the cellulose formed from the preceding season carbohydrates would have to constitute an important fraction of the current ring. This "preceding-season" cellulose would also have to be of constant isotopic composition from year to year and represent a constant mass of cellulose from one year to the next. Even if all of these conditions are met, in order to be able to use the isotopic patterns of the physically defined earlywood and latewood to explain ring width vs δD correlations, one must assume that the presumed constancy of ring-porous earlywood and conifer latewood is somehow related to the presence of the cellulose formed from stored, preceding-season carbohydrates. The existence of this last relationship has not been established.

The proposed test of Wigley, et al, (1978) for determining whether or not a climatic response of cellulose δD is dependent on ring width is beguilingly simple. However, it offers little insight, because the assumptions on which it is based are either unproven or contradicted by the data. Thus, the mere existence of a correlation of cellulose nitrate δD variations with ring width would not unambiguously indicate that some of the climatic response of the former is controlled by the latter. Instead, it may suggest that the variables affecting δD of the water are also independently affecting ring width and thus introducing a parametric correlation between cellulose nitrate δD and ring width.

Thus, the intra-ring isotopic variations characterized by the published data of Wilson and Grinsted (1975), Epstein, et al, (1976), and Epstein (1978), as well as the earlywood-latewood data in Table 3-1 of the present work, suggest that for some trees (especially ring-porous hardwoods) a portion of the cellulose in a ring will have an isotopic composition representative of a season other than the one of interest. However, it does not appear that a simple comparison of ring widths with the corresponding cellulose nitrate δD values will yield a result that conclusively shows whether or not this second isotopic component is important in determining the year to year variations in δD values of tree rings. At present, there does not seem to be any isotopic test that can be applied to ascertain the importance of the role of this hypothesized second component.

The relationships between the cellulose nitrate δD variations in a tree ring sequence and climate are considered in Section 5. Any correlations between δD values and ring width are noted therein on a case-by-case basis. However, at this point it is appropriate to consider an additional line of investigation on the relationship between ring width and δD variations.

It is a common observation that any single ring is quite often not of uniform thickness around the circumference of a tree. In fact the patterns of tree ring sequences in cross section frequently display radial asymmetry due to the predominance of wide rings in one direction and narrow rings in another (Fritts, 1976). This asymmetry raises the possibility of isotopic heterogeneity in different radial directions. If such heterogeneity exists and produces different patterns in the variation of δD values for sequences measured in different directions, it would pose a serious impediment to efforts to obtain climatic information from hydrogen isotopes in trees.

One way to examine the possible effects of tree radius asymmetry on the pattern of hydrogen isotope variations would be to analyze diametrically opposed ring sequences from a number of trees with different degrees of asymmetry. Degree of asymmetry is defined in this work as the difference between the maximum and minimum radii divided by one-half of their sum. Thus,

$$\text{degree of asymmetry (a.d.)} = \frac{\Delta r}{0.5(r_a + r_b)}$$

where,

r_a = maximum radius

r_b = minimum radius

$\Delta r = r_a - r_b$

By using this normalization procedure it is possible to compare the magnitude of asymmetry for trees of different absolute dimensions. Four trees whose ring patterns span a wide range of asymmetry were obtained for isotopic analysis. The trees together with their measured degree of asymmetry are listed below.

Sample	(a.d.)
KSA-As-1 (Aspen)	0.012
MNY-GA-2 (Green ash)	0.193
Col-DF-1 (Douglas Fir)	0.242
SNF-LP-1 (Lodgepole pine)	0.486

Sample MNY-GA-2 was provided to this laboratory as a section of wood about 2 cm wide and 2 cm thick cut across the diameter of the tree. It is assumed that this chosen diameter was at, or near, the diameter of maximum asymmetry (R. L. Phipps, personal communication). The other three samples were originally obtained as cross-sectional slabs of wood. KSA-As-1 and Col-DF-1 were both sampled by removing sections about 3 cm wide and 2 cm deep from nearly diametrically opposed radii of maximum and minimum dimension. The minimum radius of SNF-LP-1 however appeared to be missing some rings, so a section at right angles to the diameter of maximum asymmetry was obtained to serve as the "pseudo-minimum". The measured maximum radius of SNF-LP-1 was sampled with no difficulty. Thus, the a.d. value for SNF-LP-1 listed in the preceding table is actually the value obtained by using the maximum and the sampled, intermediate radius.

Each of the radial sections was subdivided into groups of 5 growth rings. The time-equivalence of these growth rings for the radial section pairs of three of the trees was verified by physically tracing the rings around their circumference. In the case of MNY-GA-2 the rings of the opposing radial sections were dated by R. L. Phipps of the U.S.G.S. and these dates were used to group time-equivalent 5-year intervals. The five-year samples were analyzed for the δD value of the cellulose C-H hydrogen (see analytical procedures section). The differences between the δD values (ΔD) of corresponding time intervals for the two radial sections of a tree were then compared with the differences in the aggregate 5-year ring widths (ΔRW) of those intervals. With the exception of MNY-GA-2, the ring widths were measured using a hand-held micrometer under a binocular microscope. With care, a precision no worse than ± 0.1 mm could be attained. The ring widths of MNY-GA-2 were measured by R. L. Phipps.

Figure 3-1 and Table 3-2 depict the results obtained from the two radial sections of KSA-As-1, a coastal Alaskan aspen. All 8 available

Figure 3-1

A plot of the differences in δD against the differences in aggregate ring widths for corresponding 5-year intervals from two radial sections of KSA-As-1. "a" is the maximum radius, while "b" is the minimum. The δD values and ring widths of "b" are subtracted from those of "a".

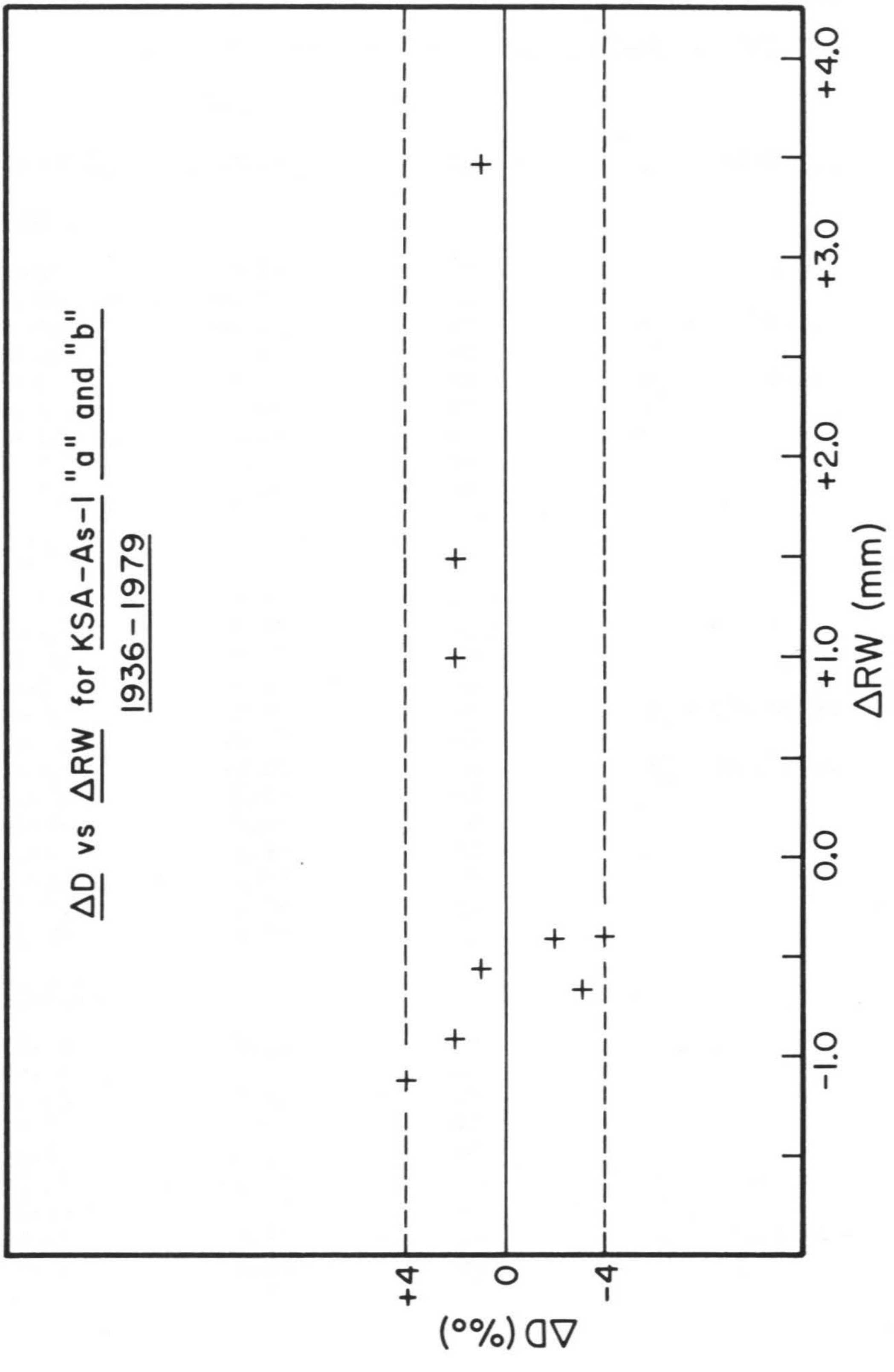

ΔD vs ΔRW for KSA-As-1 "a" and "b"
1936-1979
ΔD (%)
+4
0
-4
-1.0
0.0
+1.0
+2.0
+3.0
+4.0
ΔRW (mm)

Table 3-2: ΔRW and ΔD Values for Corresponding 5-Year Intervals from Different Radial Sections in KSA-As-1, MNY-GA-2, Col-DF-1, and SNF-LP-1.

Interval	ΔRW(mm)	ΔD	Comments
KSA-As-1			
1936-40	-0.66	-3	
1941-45	-0.39	-2	
1946-50	-0.54	+1	r_a = 165.8 mm
1951-55	-0.35	-4	
1956-60	3.47	+1	r_b = 163.8 mm
1961-65	1.49	+2	
1966-70	-0.93	+2	
1971-75	-1.14	+4	
1976-79	1.00	+2	
MNY-GA-2			
1906-10	1.39	-1	
1911-15	0.94	-2	
1916-20	0.50	-4	
1921-25	0.51	-2	
1926-30	0.40	-5	r_a = 174.46 mm
1931-35	-0.43	-3	
1936-40	-0.15	-1	r_b = 143.79 mm
1941-45	0.10	-3	
1946-50	1.48	0	
1951-55	2.33	+2	
1956-60	1.89	-4	
1961-65	1.31	-4	
1966-70	2.78	-3	
Col-DF-1			
1866-70	-0.21	+8	
1871-75	0.91	+3	
1876-80	0.77	+1	
1881-85	0.56	+7	
1886-90	-0.10	+5	
1891-95	2.49	-3	r_a = 180.2 mm
1896-1900	1.27	-1	
1901-05	-0.78	+3	r_b = 141.2 mm
1906-10	2.77	+4	
1911-15	3.11	-1	

Table 3-2 (continued)

Interval	ΔRW(mm)	ΔD	Comments
1916-20	-0.05	+14	
1921-25	2.92	0	
1926-30	3.92	-2	
1931-35	2.16	-3	
1936-40	3.02	-1	
1941-45	0.08	+3	
1946-50	1.02	+7	
1951-55	0.67	+9	
1956-60	2.82	+2	
1961-65	1.11	+1	
1966-70	2.46	-4	
1971-74	-0.03	+4	
SNF-LP-1			
1921-25	-0.89	-4	
1926-30	-0.38	-3	
1931-35	2.89	-3	
1936-40	2.77	-5	r_a = 85.7 mm
1941-45	0.10	0	
1946-50	3.28	-10	r_b = 52.2 mm
1951-55	7.04	-5	
1956-60	3.66	-11	
1961-65	4.52	-8	
1966-70	4.90	-7	

$\Delta RW = RW_a - RW_b$

where RW_a and RW_b are the aggregate ring widths (in mm) of corresponding 5-year intervals in the "a" and "b" directions respectively.

Similarly,

$\Delta D = \delta D_a - \delta D_b$

r_a and r_b are the lengths of the radii from the center of the tree to the outermost ring in the maximum and minimum directions respectively, as defined in the text.

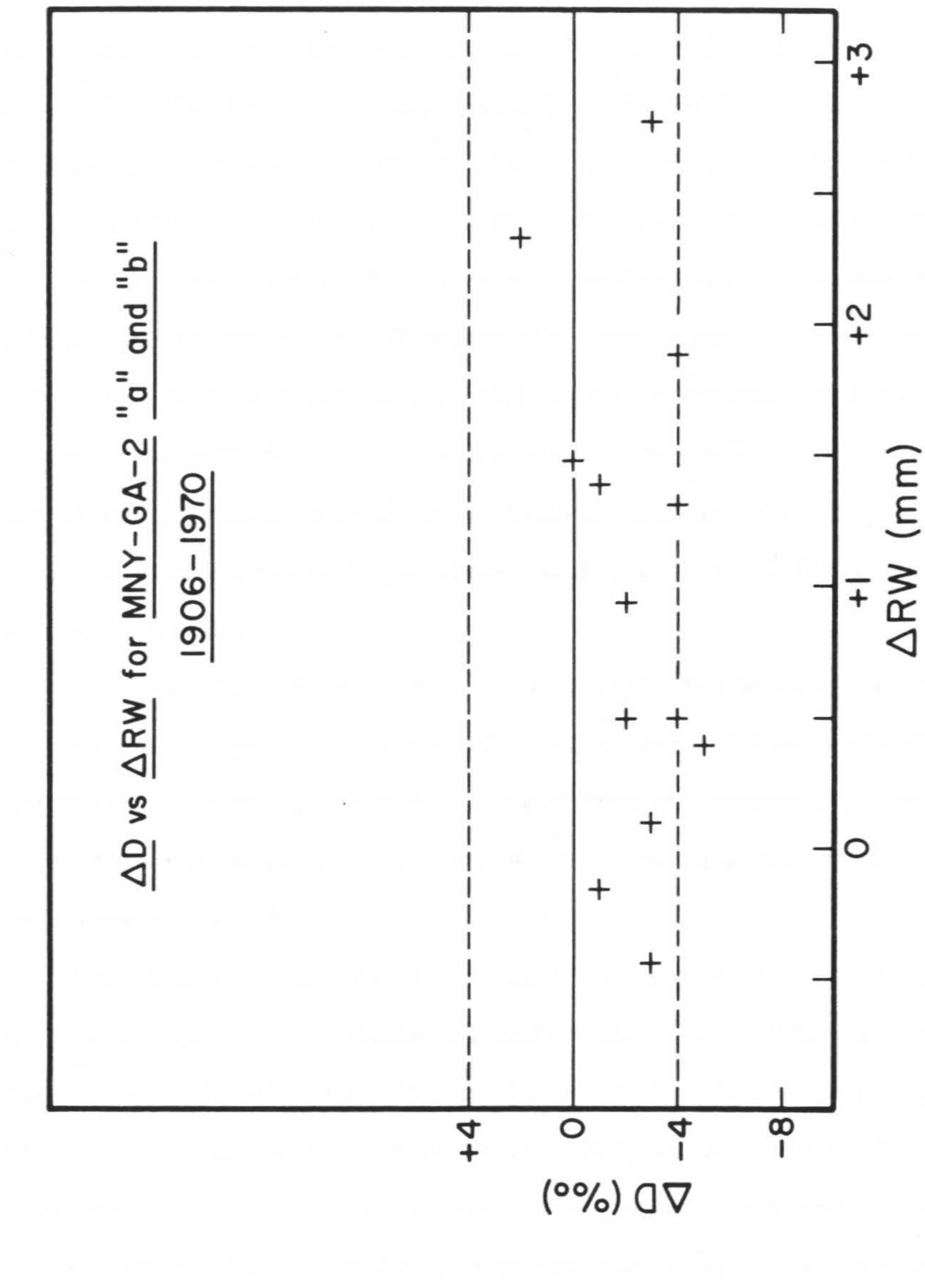
5-year samples from both sections were analyzed as well as an outermost 4-year sample. It is apparent that even for a tree with a very low overall degree of asymmetry, the detailed pattern of ring width variations diverges markedly from that expected of a perfect circle. In fact not only are there significant differences in aggregate 5-year widths between the two sections, but the sign of the difference varies. For this example, however, there is no significant difference in δD values between the two sections--all samples agree within the accepted limits of experimental error. Thus, there appears to be no important heterogeneity in the hydrogen isotope distribution of the ring sequences.

Of a possible twenty 5-year samples in each of the radial sections of MNY-GA-2, the outermost 13 were analyzed for their cellulose nitrate δD value in one section while all 20 were analyzed in the other section for subsequent attempts at correlation with climatic variables. The ΔD and ΔRW data for the two sections are listed in Table 3-2 and plotted in Figure 3-2. As was the case with the Alaskan aspen, this comparatively symmetric New York ash reveals a range in the ΔRW values of the 5-year interval pairs both in sign and magnitude. Here, again, however, the corresponding δD values of the two sections agree within experimental error with one exception. Yet, even this exception is only one per mil removed from being within the limits of the precision of measurement. Consequently, the general pattern of hydrogen isotope behavior in this tree is also one of homogeneity.

Twenty-two of the outermost 5-year samples were isotopically analyzed for one of the radial sections of Col-DF-1. For the other section, all 32 of the 5-year samples were analyzed for possible subsequent climatic interpretation. These 22 pairs of data for ΔD

Figure 3-2

A plot of the differences in δD against the differences in aggregate ring widths for corresponding 5-year intervals from two radial sections of MNY-GA-2. "a" is the maximum radius, while "b" is the minimum. The δD values and ring widths of "b" are subtracted from those of "a".


ΔD vs ΔRW for MNY-GA-2 "a" and "b"
1906-1970
ΔD (%)
+4
0
-4
-8
0
+1
+2
+3
ΔRW (mm)

and ΔRW are in Table 3-2 and Figure 3-3. Col-DF-1 has a comparatively high degree of asymmetry and the expected variation of ΔRW values of the corresponding 5-year samples is evident. Furthermore, there is a considerable scatter in the ΔD values of the sample pairs. In fact 6 of the 22 pairs have ΔD values that are different by amounts greater than those attributed to experimental error. Interestingly, the sign of the difference is the same for all those cases in which the ΔD value exceeds the error limit of 4 per mil. Furthermore, the excessive ΔD values tend to occur for ΔRW values that are no greater than about 1mm. Hence, the largest deviations in ΔRW are not associated with hydrogen isotope heterogeneities in this instance. Nevertheless, the presence of significantly large δD differences between corresponding 5-year samples from the same tree raises questions about the kinds of interpretations that can be made.

It should be pointed out that the abbreviated sampling of one of each of the two radial sections of MNY-GA-2 and Col-DF-1 probably did not introduce a bias. This is apparent from the observation that there is no discernible trend of ΔD or ΔRW with time in either of these data sets (see Table 3-2).

The ΔD and ΔRW values for the most asymmetric of the four trees (SNF-LP-1) are found in Table 3-2 and Figure 3-4. The magnitude of the maximum ΔRW value (+7.04) in SNF-LP-1 is larger than the maximum ΔRW in either of the other tree trees. This is in spite of the fact that SNF-LP-1 has a smaller diameter than any of the other trees. Such a large ΔRW maximum is probably attributable to the very high degree of asymmetry in SNF-LP-1. In fact, if the true minimum radius had been

Figure 3-3

A plot of the differences in δD against the differences in aggregate ring widths for corresponding 5-year intervals from two radial sections of Col-DF-1. "a" is the maximum radius, while "b" is the minimum. The δD values and ring widths of "b" are subtracted from those of "a".

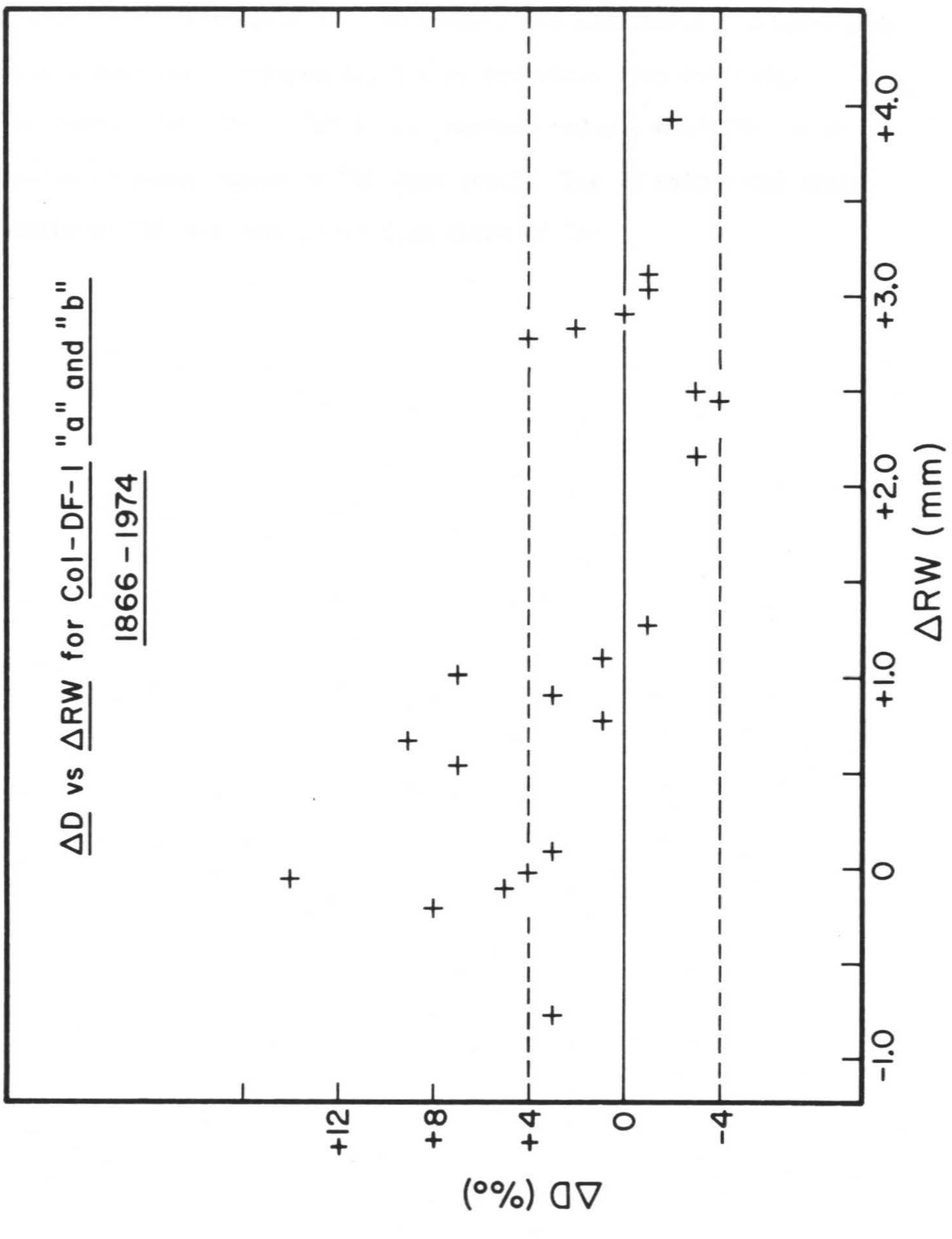
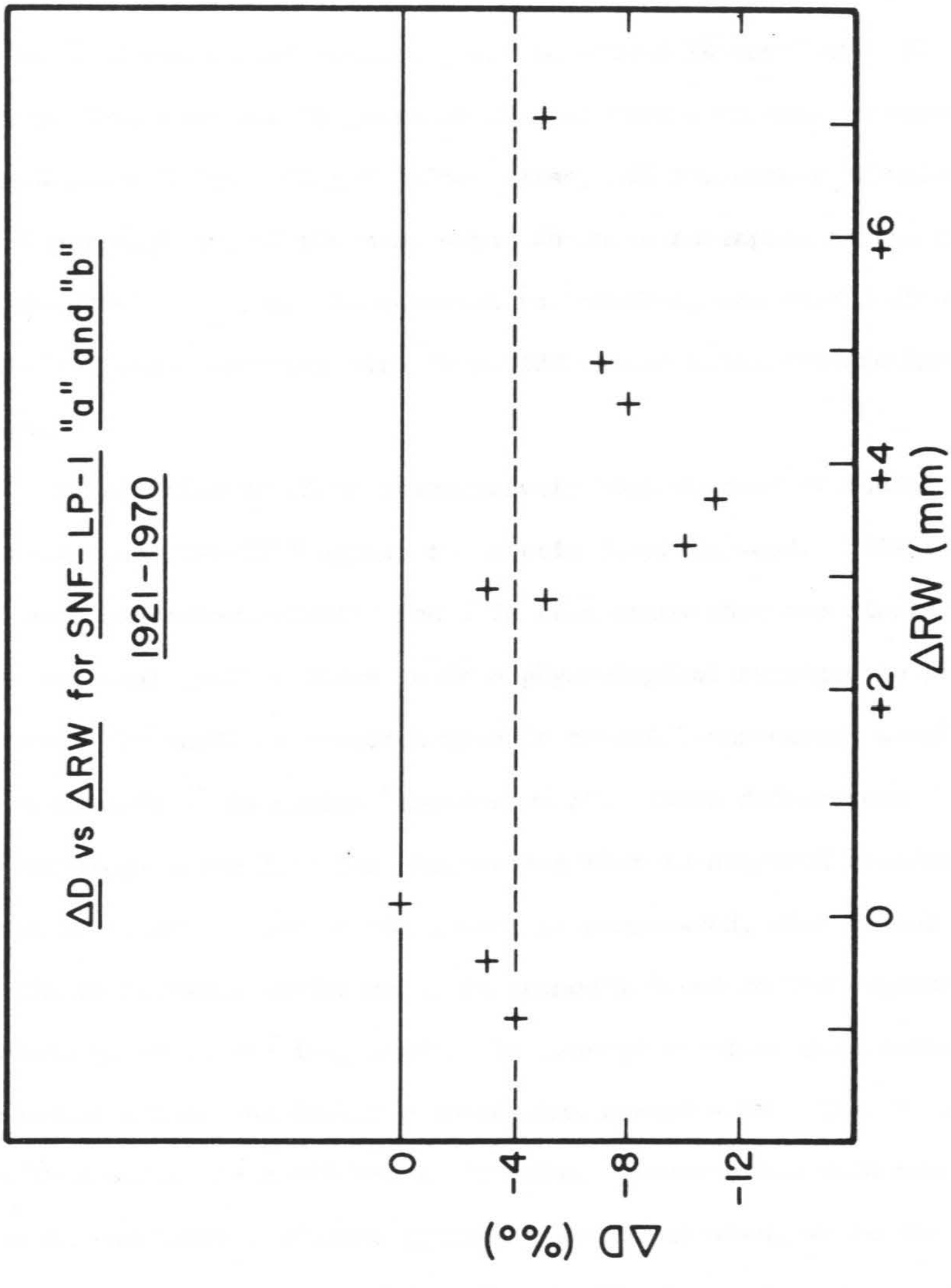

ΔD vs ΔRW for Col-DF-1 "a" and "b"
1866-1974
ΔD (%)
+12
+8
+4
0
-4
ΔRW (mm)
-1.0
0
+1.0
+2.0
+3.0
+4.0

Figure 3-4

A plot of the differences in δD against the differences in aggregate ring widths for corresponding 5-year intervals from two radial sections of SNF-LP-1. "a" is the maximum radius, while "b" is a radius at right angles to "a" (see text). The δD values and ring widths of "b" are subtracted from those of "a".


ΔD vs ΔRW for SNF-LP-1 "a" and "b"
1921-1970
ΔD (%)
0
-4
-8
-12
ΔRW (mm)
0
+2
+4
+6

used to calculate the a.d. value instead of the radius of the sampled "pseudo-minimum", the a.d. value would have been 1.013.

All 10 of the 5-year samples available in SNF-LP-1 were analyzed in each of the radial sections, so the record is complete. As seen in Figure 3-4, 6 of the 10 pairs of samples have ΔD values in excess of the 4 per mil limit of precision. Also, all the excess ΔD values (> 4 per mil) are of the same sign, which is analagous to the circumstance of Col-DF-1. However, in contrast to Col-DF-1, the excess ΔD values in SNF-LP-1 are associated with those ΔRW values which deviate most from zero.

In addition to their comparatively high degrees of radial asymmetry, SNF-LP-1 and Col-DF-1 appear to contain reaction wood. This is a type of wood characteristically found in tree stems that are displaced from the vertical, and it seems to be a physiological response to gravitational stress. In conifers reaction wood is termed "compression wood", while in hardwoods it is called "tension wood". These differences in terminology arise from the observation that in stressed conifers reaction wood is usually found on the lower, or compressed, side of the tree, while in stressed hardwoods it is commonly found on the extended side. (Wardrop, 1964; Westing, 1968). In general reaction wood seems to be somewhat denser and darker colored than normal wood. Its cells have thicker walls and a different chemistry. Compression wood has a higher lignin and lower cellulose content than normal wood, while the opposite is true of tension wood (Meier, 1964). The formation of reaction wood in trees often produces a radially asymmetric pattern in the growth rings. Commonly, the reaction wood is concentrated in the widest portions of the rings (Wardrop, 1964; Westing, 1968). Judging by the generally darker color of the wood along the maximum radii of SNF-LP-1 and Col-DF-1, it is indeed the wider portions of the rings that contain most of the reaction wood in these trees. Thus, the radial asymmetry of the growth ring pattern in these two conifers can probably be attributed to the presence of compression wood, although the indications are less distinct for Col-DF-1 than for SNF-LP-1, as might be expected from their different degrees of asymmetry.

However, for MNY-GA-2 (an ash tree) there is no indication of any tension wood in the tree ring sequence that might explain the measured radial asymmetry. The decrease in size and number of vessels that is characteristic of earlywood in tension wood (Wardrop, 1964) was not found in this tree. This difference between MNY-GA-2 and the asymmetric conifers may be significant with respect to the problem of hydrogen isotope heterogeneity.

As was noted previously, both Col-DF-1 and SNF-LP-1 exhibit considerable hydrogen isotope heterogeneity, while MNY-GA-2 does not. The difference in the degree of asymmetry between MNY-GA-2 and Col-DF-1 is not very large, yet only one of the 13 pairs of time-equivalent samples from the two radial sections of MNY-GA-2 differed in δD value by more than 4 per mil, while 27% of the samples from Col-DF-1 differed by more than this limit of precision. This seems to imply that it is not the asymmetry in the variation of ring widths alone that is related to a high degree of hydrogen isotope heterogeneity, but rather that the presence of reaction wood in the tree is somehow connected with such nonuniformity. The fact that KSA-As-1 exhibits a very homogeneous hydrogen isotope pattern reinforces this conclusion, since KSA-As-1 does

does not appear to contain reaction wood, but does contain some variations in the patterns of ring widths.

One factor which may be contributing to the difference in degree of isotopic heterogeneity between MNY-GA-2 and Col-DF-1 is the method of sampling. The δD values were determined for 5-year intervals. Consequently, the δD value obtained is a weighted average of the isotopic composition of each of the rings in the interval that was sampled. Thus,

$$\delta D_{ave.} = \sum_{i=1}^{5} X_i \; \delta D_i$$

X_i = the fraction of the aggregate 5-year width contributed by the width of the i'th ring

δD_i = δD value of the i'th ring

It is assumed that the density and cellulose content of all rings are the same and that only their widths vary.

If the δD value of any single ring is constant around the tree, δD_{ave} will only be different for different time-equivalent 5-year sections when the corresponding X_i values are different. Therefore, a comparison of the corresponding individual ring widths from each of two time-equivalent 5-year samples might provide some insight into the nature of variations in δD_{ave} around a tree.

Such comparisons are made for six different 5-year intervals from both MNY-GA-2 and Col-DF-1 in Table 3-3. These intervals cover most of the range of ΔD and ΔRW values in each of the trees. The correlation coefficients from the linear regressions of the five pairs of X_i values in each 5-year interval are listed. If the corresponding X_i values were

Table 3-3: X_i Ranges, Correlation Coefficients for $X_i(b)$ vs $X_i(a)$, ΔD and ΔRW for Corresponding 5-Year Intervals from Different Radial Sections in MNY-GA-2 and Col-DF-1

Interval		Range of X_i Values	Linear Correlation Coefficient for $X_i(b)$ vs $X_i(a)$	5-Year Interval (a-b) ΔD	ΔRW
MNY-GA-2					
1906-10	(a)	0.15 to 0.28	0.974	-1	1.39
	(b)	0.14 to 0.28			
1926-30	(a)	0.16 to 0.23	0.852	-5	0.40
	(b)	0.12 to 0.27			
1931-35	(a)	0.12 to 0.37	0.910	-3	-0.43
	(b)	0.10 to 0.47			
1941-45	(a)	0.15 to 0.24	0.715	-3	0.10
	(b)	0.17 to 0.25			
1951-55	(a)	0.15 to 0.25	0.437	+2	2.33
	(b)	0.16 to 0.24			
1966-70	(a)	0.17 to 0.24	0.697	-3	2.78
	(b)	0.15 to 0.25			
Col-DF-1					
1881-85	(a)	0.14 to 0.30	-0.033	+7	0.56
	(b)	0.14 to 0.29			
1901-05	(a)	0.14 to 0.25	-0.802	+3	-0.78
	(b)	0.16 to 0.26			
1916-20	(a)	0.16 to 0.24	-0.740	+14	-0.05
	(b)	0.17 to 0.28			
1921-25	(a)	0.17 to 0.26	-0.077	0	2.92
	(b)	0.18 to 0.25			
1941-45	(a)	0.13 to 0.36	0.052	+3	0.08
	(b)	0.15 to 0.33			
1946-50	(a)	0.14 to 0.27	-0.098	+7	1.02
	(b)	0.15 to 0.24			

the same in each time-equivalent 5-year sample, they would be linearly correlated with a slope and correlation coefficient of + 1. In no instance is this observed in Table 3-3. However, it is noteworthy that the correlation coefficients for the X_i pairs in the six 5-year samples from MNY-GA-2 are all positive and of sufficient magnitude to suggest that the contribution of any one ring to an aggregate sample is likely to be approximately the same around the tree. Thus, much of the homogeneity of the hydrogen isotope composition around MNY-GA-2 can probably be attributed to this factor.

For Col-DF-1 there are no significant positive correlations of corresponding X_i values in any two equivalent 5-year samples. Therefore, when agreement is observed for δD values of corresponding 5-year intervals, it must be in spite of the variation of corresponding X_i values in the two aggregate samples.

In the extreme, the X_i values for the interval 1901-1905 in Col-DF-1 show a strong negative correlation, but a ΔD value of only +3 per mil. Coupled with the fact that the aggregate 5-year ring widths of the two sections are only different by 0.78 mm, this suggests the kind of behavior associated with reaction wood, for which a relative increase of ring width in one radial direction can be accompanied by a relative decrease in the opposite radial direction (Wardrop, 1964). The fact that this behavior has not caused any significant difference in δD values between the two time-equivalent 5-year samples suggests either that there is minimal difference between the δD values of the different individual rings, or that there are δD heterogeneities around any single ring that when combined with the other rings, compensate for the variations in the X_i values. Although it may occur, the latter happenstance seems less probable than the former, particularly when it is noticed that a similar strong, negative correlation for the X_i values of the interval 1916-1920 is associated with the largest ΔD value in the whole sequence (see Fig. 3-3).

It is possible that a small range of X_i values within each of two corresponding 5-year samples in Col-DF-1 is contributing to small ΔD values. However, some intervals such as 1941 to 1945, with a ΔD of only +3 per mil, exhibit larger ranges in X_i values for each of the two 5-year sections than do intervals with large ΔD such as 1946-1950. Thus, again, there is no consistent sampling effect to be perceived.

It seems plausible that different combinations of the preceding phenomena are contributing to varying degrees in each case. Thus, the overall effect is to produce a departure from experimental isotopic homogeneity in about 27% of the 5-year samples from Col-DF-1 (see Figure 3-3).

Hence, the use of aggregate samples -- ie. 5 year, is capable of producing apparent isotopic heterogeneity in theory, but in practice it does not appear to do so for a symmetric tree (KSA-As-1) or for an asymmetric tree that lacks reaction wood (MNY-GA-2). For a tree that contains reaction wood, however, multiple-ring sampling may induce some heterogeneity, but at present the distinction between sampling effects and inherent isotopic heterogeneity has not been made.

The differences in the ΔD vs ΔRW patterns (Figs. 3-3 and 3-4) of Col-DF-1 and SNF-LP-1 that were mentioned previously are not readily explained. As noted, the largest ΔD values of Col-DF-1 tend to be associated with the smallest deviations of ΔRW, while for SNF-LP-1, the maximum deviations in both ΔD and ΔRW tend to be affiliated. This may be related to the fact that the two sections from Col-DF-1 were separated by about 180°, while those from SNF-LP-1 were at right angles. However, in view of the differences in species, locale, etc., it is not possible at present to provide a plausible speculation.

In spite of the differences in location, climate, and species of the four preceding trees, it does appear to be reasonable to conclude that trees which contain reaction wood are likely to exhibit significant hydrogen isotope heterogeneities between different radial sections of time-equivalent samples. An absence of reaction wood, on the other hand, seems to offer the strong possibility that the temporal patterns of hydrogen isotope variation displayed by one radial section will be the same as those displayed by another radial section from that tree.

This question of the influence of tree physiology on the distribution of hydrogen isotopes around a growth ring, and the mechanisms involved, is too complex to be resolved here. However, from the evidence obtained to date, it seems that in choosing trees to be isotopically analyzed for climatic study, those containing reaction wood should be avoided until more is known about their isotopic behavior. With the exception of the two conifers discussed above (Col-DF-1 and SNF-LP-1), the tree ring sequences which have been analyzed in this work are free of any obvious reaction wood, although its presence in small, undetected amounts may be possible.

Summary

It seems probable that the cellulose contained in any single growth ring was formed predominantly from precursor sugars that were synthesized during the current growing season. However, it is likely that at least some carbohydrate synthesized during the preceding growing season has been incorporated as well. The magnitude of the contribution of preceding-season carbohydrate to the cellulose of any one ring probably varies from season to season, and the role of this "second component" in producing year to year δD variations of growth rings is difficult to assess. Correlations of δD values with ring width along a radial section do not appear to be unambiguously related to varying proportions of this second component, since it is equally possible that both δD and ring width are varying independently in response to the same climate parameters.

Hydrogen isotope heterogeneities in time-equivalent samples around a tree constitute a potentially serious impediment to the interpretation of δD variations in tree ring sequences as climatic signals. However, the available evidence suggests that the problem of hydrogen isotope heterogeneities is likely to be limited to, or most severe in, trees which contain reaction wood. In the absence of reaction wood, there does not seem to be any significant problem with such heterogeneities. Consequently, at present, only trees which lack reaction wood should be isotopically analyzed for climatic interpretation until more is known about the isotopic behavior of those trees that contain it.

Section 4

The Variation of Hydrogen and Oxygen Isotopes in Precipitation

The response of the isotopic composition of precipitation to climatic variables has been alluded to in previous sections. At this point the evidence for this climatic dependence will be examined in the light of existing concepts and some modifications thereto.

Some of the earliest investigations of the variations in the isotopic composition of fresh water to be carried out using precision mass spectrometry were those of Epstein and Mayeda (1953), Friedman (1953) and Dansgaard (1953). The variations observed by these groups were characterized in terms of the fractionations accompanying condensation and evaporation processes. Epstein and Mayeda envisioned a multiple-still condensation process, while Dansgaard formulated a mass balance equation that directly related the isotopic composition of the precipitation to the condensation temperature. The two characterizations are not independent and depend for their validity on the fact that the partial saturation vapor pressures of the different isotopic species of water are different.

Subsequent work established that the isotopic composition of precipitation can vary on a seasonal basis at a single site (Epstein, 1956), on a glacial to interglacial scale (Epstein, et al, 1970; Dansgaard, et al, 1971) and, in a comparatively systematic way, on a broad geographic scale (Friedman, et al, 1964; Dansgaard, 1964). The 1964 study by Dansgaard is of particular interest to the work herein, because it established a definite, empirical relationship between the isotopic variation of annual precipitation from a wide geographic range and the associated annual mean surface temperature.

For a number of coastal, or near-coastal, North Atlantic sites, as well as sites in Greenland and Antarctica, Dansgaard found that the deuterium temperature coefficient was 5.6‰ per °C. He points out that this is very similar in magnitude to the value expected if the condensation processes are characterized by a Rayleigh-type model (Rayleigh, 1896).

The intriguing implication of this result is that it suggests that if δD values of precipitation are single-valued functions of temperature, then perhaps the converse is true. Thus, δD variations in precipitation might be used as indicators of surface temperature variation. That the converse might not always be true is suggested by Dansgaard's δ vs T relationship. There are a number of points which lie well off the best fit curve and appear to suggest that there may be more variables involved than just local surface temperature. In fact, Dansgaard discusses the possibility that varying air mass histories might play a role in producing some of the largest positive deviations from the best-fit curve of δ vs T. An additional and related possibility is the role that clouds might play in influencing the isotope vs temperature trajectory.

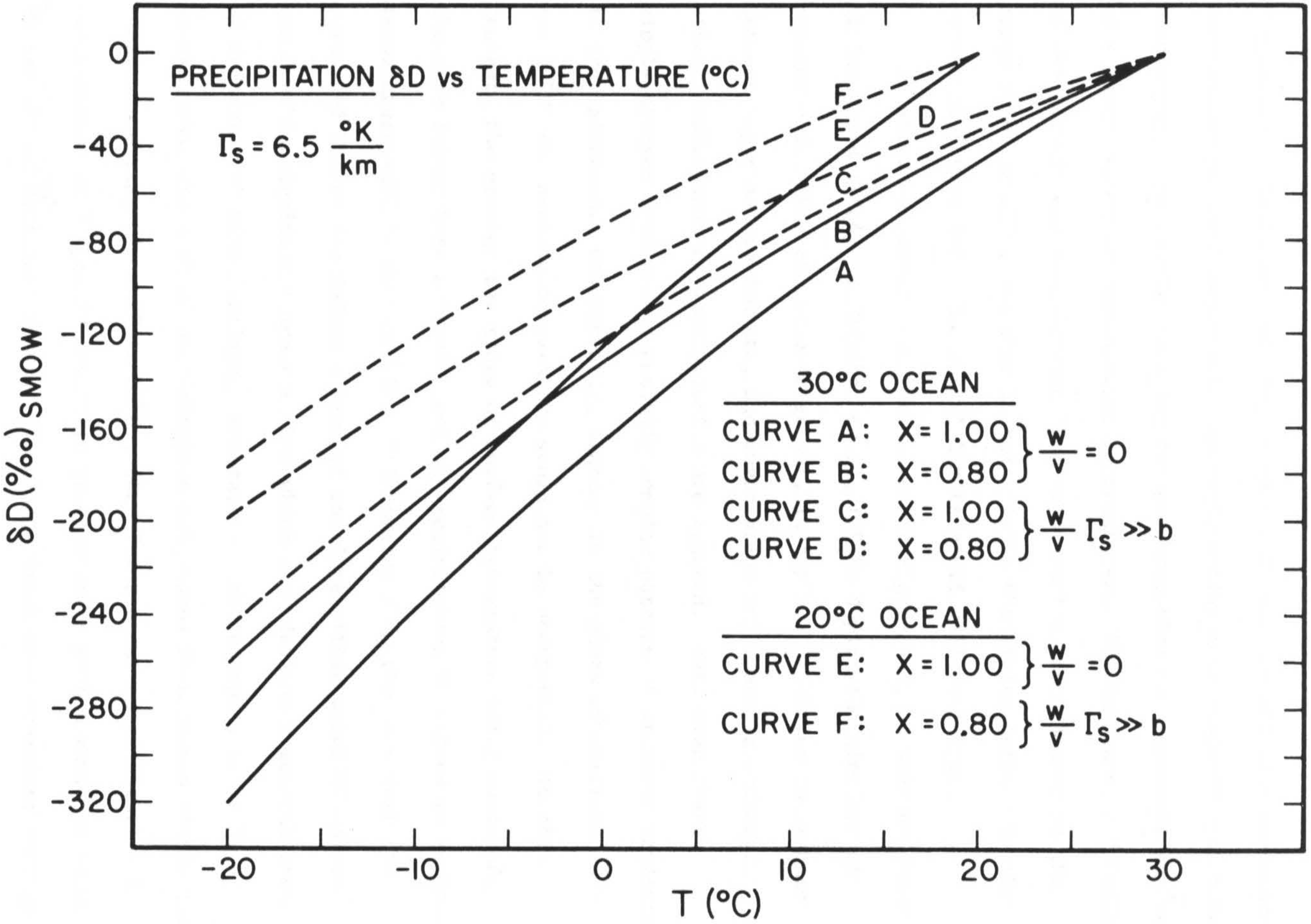
In the simplest form of the Rayleigh model, as employed by Dansgaard (1964), the water that condenses is assumed to be removed immediately from the air mass as precipitation. At the other extreme, no precipitation is removed and the vapor and condensate are presumed to be in continuous equilibrium isotope exchange. It is apparent that the real world lies somewhere in between, since it is observed that without clouds there is no precipitation, while a continual increase in cloud density will ultimately result in some loss of condensate as precipitation (Rogers, 1979).

Miyake, et al, (1968) have presented an oxygen isotope condensation model which incorporates the continuous presence of cloud during precipitation. Their model assumes a constant density of condensate within the confines of the cloud during the continuous cooling of the cloud parcel. The incorporation of a cloud presence in models characterizing the fractionation of isotopes during condensation seems a reasonable step toward improved understanding of the relative importance of different variables in influencing the isotopic composition of precipitation. A relationship between the δD value of precipitation and its condensation temperature has been derived from the continuity equation in Appendix I. In this derivation the fractional amount of water vapor in the vapor-condensate system has been specified, rather than the absolute density of cloud condensate. The calculated curves are found in Figure 4-1.

In spite of the different approaches, the results of Figure 4-1 are qualitatively the same as those of Miyake, et al, (1968). Figure 4-1 shows that the δD vs T coefficient is smaller for greater amounts of cloud. For example, the average isobaric temperature coefficient in the absence of clouds, for precipitation originating from a 30°C ocean is, in the interval 0 to 20°C, 6.0‰ per °C. However, if 20% of the vapor-condensate system is comprised of clouds which are assumed to be in continuous equilibrium exchange with the vapor (curve B), then the average temperature coefficient in the interval 0 to 20°C is 4.8‰ per °C. The curves of Figure 4-1 depict isobaric and non-isobaric cooling. If the process is non-isobaric, the temperature coefficients will be even smaller. This was noted by Dansgaard (1964) for the case of no clouds, and is implicit in the oxygen isotope curves of Miyake, et al, (1968).

Figure 4-1

A plot of precipitation δD values vs condensation temperature as calculated from the transport model in Appendix I. The solid curves are those calculated for isobaric cooling in the case of wholly horizontal transport. The dashed curves are those calculated for non-isobaric cooling in the case of wholly vertical transport. X is the fraction of the total moisture that is in the vapor phase.


PRECIPITATION δD vs TEMPERATURE (°C)
$\Gamma_s = 6.5 \frac{°K}{km}$
30°C OCEAN
CURVE A: X = 1.00
CURVE B: X = 0.80
$\frac{w}{v} = 0$
CURVE C: X = 1.00
CURVE D: X = 0.80
$\frac{w}{v} \Gamma_s \gg b$
20°C OCEAN
CURVE E: X = 1.00 $\frac{w}{v} = 0$
CURVE F: X = 0.80 $\frac{w}{v} \Gamma_s \gg b$
A
B
C
D
E
F
δD(‰) SMOW
0
-40
-80
-120
-160
-200
-240
-280
-320
T (°C)
-20
-10
0
10
20
30

When one considers the additional factor of different source temperatures, it is apparent from Figure 4-1 that a particular condensation temperature does not necessarily uniquely define a corresponding δD value. Conversely, a particular δD value for precipitation may represent any one of a large number of condensation temperatures. For instance, a δD value of -95 per mil may have derived from condensation temperatures in the range of -5 to 11°C, and that is only within the limits defined by the curves of Figure 4-1. The actual limits could well be larger.

It should be noted that the curves of Figure 4-1, as well as those of Dansgaard (1964) and Miyake, et al, (1968) depict the simplest of systems - ie, they are time-invariant, isotopic equilibrium is assumed between vapor and condensate, and evaporation and isotopic exchange effects subsequent to precipitation are ignored. Yet, even these simple systems depict a potentially complex pattern of isotopic variation in precipitation. Consequently, scatter in the plots of observed δD (or $\delta^{18}0$) vs. surface temperature would not be unexpected. In this context, the greater the range of surface temperature being examined, the more likely that a broad trend of precipitation δD values vs surface temperature will be discernible. This arises from the fact that the curves of Figure 4-1 define a kind of envelope within which δD values can exhibit significant scatter, but which also defines a general trend of declining δD with declining temperature. For example, if it is assumed that the bulk of precipitation originates from oceans within the temperature range from 20 to 30°C., then for the curves of Figure 4-1 condensation at 5°C could result in precipitation with a range of about 80 per mil at different times or locales. Since an approximate average temperature coefficient for these curves in the region of 5°C is about

5‰ per °C, a temperature range significantly greater than 16 degrees might have to be spanned to insure that the overall relationship of δD vs T defined by the envelope could in fact be observed. Of course this is a hypothetical, and possibly extreme example, but it does serve to illustrate the point that a distinctive precipitation δD vs T relationship is more likely to be evident when a large range of temperature is considered.

The derivation of the curves in Figure 4-1 from the continuity equation (see Appendix I) suggests the possibility that the isotopic composition of precipitation could be related to precipitation rates. This follows from the fact that the net isotopic composition of precipitation measured at the surface is some weighted average of the isotopic composition of precipitation condensed at different heights (temperatures) in the atmosphere. Since the condensation and precipitation processes are dynamic, the degree of weighting of any portion of precipitation in the final ensemble will depend on its rate of formation compared to the rates of formation of precipitation from other levels. The weighted vertically integrated isotopic composition of precipitation at any particular moment during a precipitation event will then be given by:

$$\delta D_{\text{vertical}} = \frac{\int_{z_1}^{z_2} \delta D\,(z)\; p(z)\; dz}{\int_{z_1}^{z_2} p(z)\; dz} \tag{4-1}$$

p(z) = the precipitation rate at any specified height arising from water condensed at that height (mass per unit volume per unit time)

$\delta D(z)$ = δD value of the precipitation at its height of condensation

z = vertical height

It is assumed in this expression that there is no isotopic exchange of precipitation subsequent to its condensation. This is not a realistic assumption (Friedman, et al, 1962; Miyake, et al, 1968; Stewart, 1975).

However, equation (4-1) will be employed as a useful first approximation to the real world, with the caution that any departures from isotopic behavior predicted by equation (4-1) might be a consequence of the neglected post-condensation exchange.

It should be noted that the denominator in the expression for $\delta D_{vertical}$ has the units of mass per unit area per unit time. Consequently, it represents the vertical flux of precipitation - ie. the precipitation intensity. If the value of the numerator is not greatly dependent on the precipitation intensity and does not vary significantly for a range of integration limits, then the measured δD value of precipitation may be related to the reciprocal of precipitation intensity. In fact Matsuo and Friedman (1967), Miyake, et al, (1968) and Mook, et al, (1974) have reported a rough relationship between the isotopic composition of rainfall and rain intensity. Generally, the greater the intensity the more negative the δD or $\delta^{18}O$ value. These studies were of individual storm systems with precipitation collected throughout the course of the storm.

Little information on the longer term relationship between δ values and precipitation intensity is available. Dansgaard (1964) discussed an apparent relationship between monthly $\delta^{18}O$ values of precipitation and rainfall amount. He found that for low latitude locations there is a negative correlation between $\delta^{18}O$ and amount. In one instance, Dansgaard used hourly rainfall values from an African station to compute monthly weighted rainfall intensity. A comparison between these 16 monthly intensity data and monthly $\delta^{18}O$ values of precipitation revealed no correlation between the two parameters. Dansgaard concluded that the relationship between $\delta^{18}O$ values and amount of precipitation was probably influenced most importantly by humidity - ie. evaporation. Thus, for smaller amounts of rainfall it is to be expected that the degree of isotopic enrichment due to evaporation would be greater, and therefore a plot of $\delta^{18}O$, or δD, vs rainfall amount should show a negative correlation.

This negative correlation between monthly $\delta^{18}O$ precipitation values and rainfall amount was found by Dansgaard to be generally absent at higher latitudes. However, he did observe some evidence for the correlation in summer months at midlatitude sites such as Tokyo.

From the standpoint of trying to understand the relative importance of evaporation in producing a so-called "amount effect", the relationship between δD and $\delta^{18}O$ could be crucial. Craig (1961b) found that for a wide range of freshwaters there is a strong correlation of δD vs $\delta^{18}O$. His best fit linear equation for these data is:

$$\delta D = 8\ \delta^{18}O + 10$$

Work by Dansgaard (1964) and Miyake, et al, (1968) has shown that if condensation temperature is important in determining the δ value of precipitation, the slope of δD vs $\delta^{18}O$ should be about 8 for equilibrium between condensate and vapor. There is some theoretical expectation of variation above and below this value, but these deviations are not appreciably different from the observed value of 8 over a substantial range of temperature (at least -20° to 30°C, Dansgaard, (1964).

However, if evaporation acts to isotopically enrich water, the measured slope of δD vs $\delta^{18}O$ is usually significantly different from 8 (Craig, 1961b; Craig and Gordon, 1965). Observed values of the slope for evaporated water are commonly 5 or less. The lower values are due to the fact that evaporation normally proceeds under nonequilibrium isotopic conditions. The kinetic isotopic fractionation factor for oxygen is significantly greater than the corresponding equilibrium value, while the difference between the kinetic and equilibrium fractionation for hydrogen is not very large (Craig and Gordon, 1965; Stewart, 1975; Merlivat, 1978). Consequently, during nonequilibrium evaporation there tends to be a greater relative loss of ^{16}O compared to H than occurs in the equilibrium case. Thus, the δD and $\delta^{18}O$ values of the residual liquid increase along a trajectory whose slope has values less than 8 (see Dansgaard, 1964; Craig and Gordon, 1965).

This is an important result from the standpoint of examining the relationships between δD values of precipitation and precipitation intensity. If it is accepted that the Craig "meteoric water line" accurately reflects the array of δD and $\delta^{18}O$ values to be expected from isotopic equilibrium precipitation processes then this represents an appropriate criterion for identifying those water samples which have undergone evaporative isotopic enrichment. Any samples whose δD vs $\delta^{18}O$ plot lies significantly to the right of the meteoric water line can be identified as probably having experienced such isotopic enrichment. In the comparison of precipitation δD values with intensity it is important that secondary effects such as those due to evaporative enrichment be filtered out. This removes the possibility of interpreting relatively positive δD values in terms of evaporative enrichment from a small amount of rainfall rather than as a consequence of low precipitation intensity and its possible relationship to the condensation process (equation 4-1). Dansgaard (1964) did not apply the evaporative enrichment criterion to the samples which he examined for an "amount effect", or for the African station for which monthly $\delta^{18}O$ was compared to monthly precipitation intensity.

It was decided that the possibility of a relationship between precipitation intensity and δD values is sufficiently important that it merits further examination. In the context of the bearing of such a relationship on climatic interpretation of δD values in precipitation, it would be desirable to have annual values of δD and precipitation for a large succession of years from a single locale. Unfortunately, such data have not been collected long enough or completely enough at any one locale to enable such a comparison. Monthly δD and $\delta^{18}O$ values, however, have been measured by the International Atomic Energy Agency (IAEA) for several years at a number of sites worldwide. In terms of looking for a relationship between δD values and precipitation intensity, monthly values are not adequate for temperate or colder climates. This is because there are large seasonal variations in temperature at such sites, and the temperature differences between the low latitude ocean waters and the sites of precipitation are greater in winter than in summer (Landsberg, 1974). It is immediately apparent from Figure 4-1 that large seasonal differences in condensation temperature can result in seasonal isotope differences which reflect the different seasonal condensation histories of the air masses. Consequently, a relationship between precipitation intensity and δD values on a month-to-month basis within any year at temperate and colder sites will probably be masked by the significant differences due to large temperature changes on that same month-to-month time scale.

However, tropical oceanic sites offer the possibility that month-to-month δD and precipitation intensity correlations will be meaningful. As indicated by equation (4-1), a relationship between δD and precipitation intensity is likely to depend on the vertical extent of condensation - ie. the degree of vertical uplift and cooling. If all air masses involved in such condensation at a site on a month-to-month basis have entered with a common isotopic composition and similar temperatures and relative humidities, then the degree of vertical uplift, cooling and condensation alone will determine the vertically averaged δD value of the precipitation. The seasonal temperature uniformity of tropical island sites and their proximity to the isotopically "constant" oceans makes them attractive choices for comparison of the available month-to-month δD and precipitation intensity data.

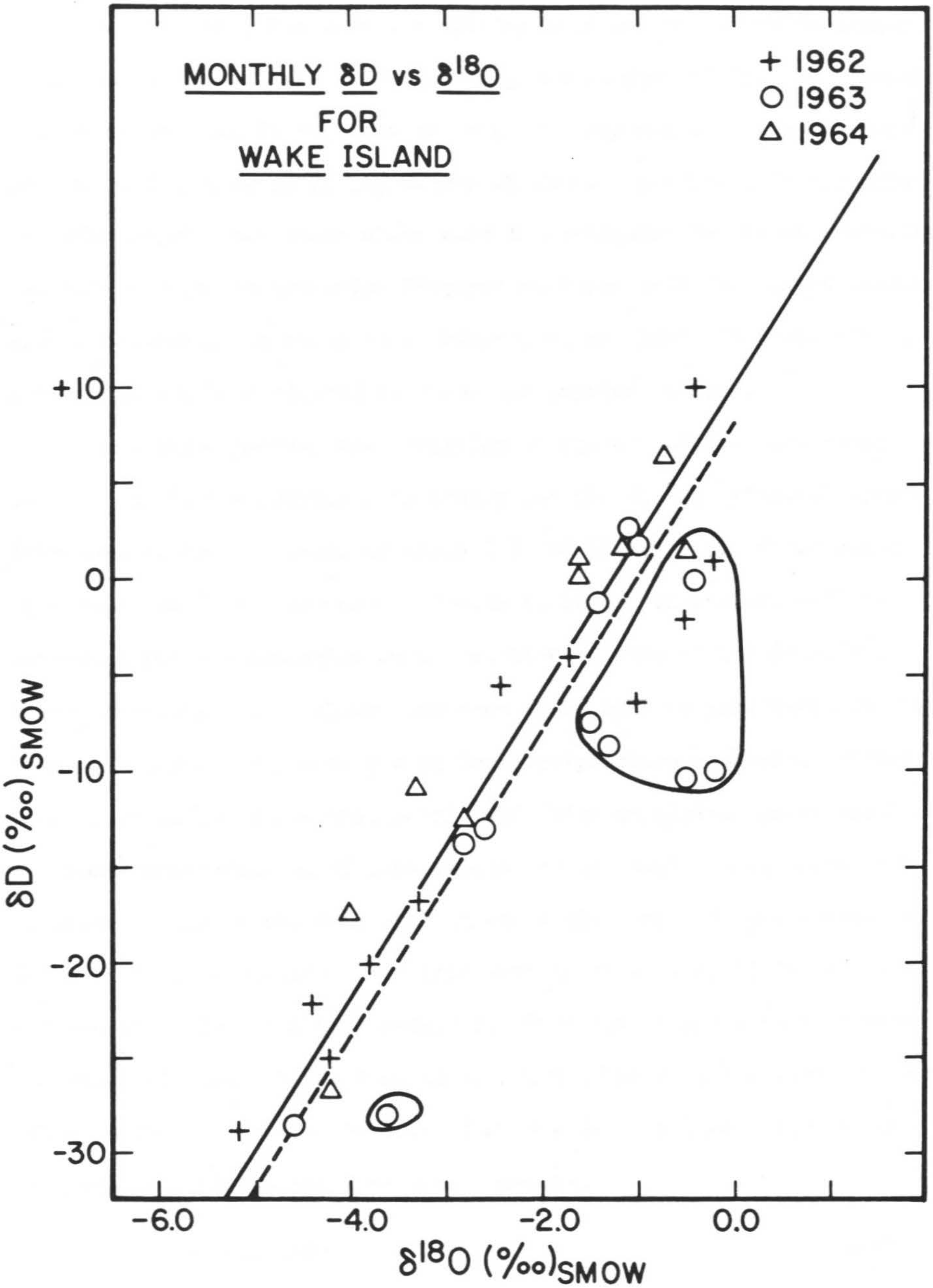
Wake Island in the tropical Pacific Ocean (Lat. 19.28° N.; Long. 166.65° E; altitude above sea level: 3 m) was chosen as a site for such a comparison. Monthly δD and $\delta^{18}O$ values for precipitation at this site are reported in the IAEA, World Survey of Isotope Concentrations in Precipitation for portions of the years 1962, 1963 and 1964. Average monthly temperatures for the sample interval range from a low of 24.8°C to a high of 28.3°C. Consequently, there is very little seasonal variation of temperature. There is a range of average monthly relative humidities from a low of 67% to a high of 83%, but it exhibits no significant correlation with season over the sample interval. The monthly average isotopic compositions of the vapor are unknown.

The start and stop times of individual precipitation events for Wake Island in the years 1962, 1963, and 1964 were obtained from the Environmental Data Service, National Climatic Center, Asheville, North Carolina. From these data, total elapsed time during which rain was actually falling in a given month could be determined. The unweighted average monthly precipitation intensity was then calculated by dividing the total monthly rainfall amount by the total elapsed time.

Prior to comparison of the monthly δD vs precipitation intensity values, all the available 1962-1964 δD and $\delta^{18}O$ data were plotted to determine which should be eliminated as being highly probable representatives of evaporative isotopic enrichment. This δD vs $\delta^{18}O$ plot is in Figure 4-2. The "meteoric water" line $\delta D = 8\ \delta^{18}O + 10$ was drawn to establish a frame of reference. Points whose $\delta^{18}O$ values were more than about 0.3 per mil to the right of the meteoric water line were rejected as probably having undergone significant evaporative enrichment. These rejected points are enclosed by the circles in Figure 4-2. All other points on or to the left of the meteoric water line were assumed to represent waters which had undergone little or no evaporative enrichment of D or ^{18}O. This assumption may not be correct if some of the points to the left of the line represent waters which have evaporated into an atmosphere of very negative δD and $\delta^{18}O$. Such a happenstance could result in decreases in the δD and $\delta^{18}O$ values of

Figure 4-2

A comparison of the δD and $\delta^{18}O$ values of monthly precipitation at Wake Island for the years 1962, 1963 and 1964. The values are taken from IAEA data. The solid straight line represents the meteoric water line defined as $\delta D = 8\ \delta^{18}O + 10$ (Craig, 1961b). The dashed line is a curve displaced approximately 0.3 per mil in $\delta^{18}O$ to the right of the meteoric water line. The points enclosed by the circles are considered to have undergone significant evaporation as indicated by their displacement to the right of the meteoric water line by more than about 0.3 per mil in $\delta^{18}O$ (see text).


MONTHLY δD vs δ18O
FOR
WAKE ISLAND
+ 1962
○ 1963
△ 1964
+10
0
-10
-20
-30
δD (‰)SMOW
-6.0
-4.0
-2.0
0.0
δ18O (‰)SMOW

the evaporating water due to exchange with the very negative vapor (see equation 2-4), but such a condition does not appear to be common in nature (Friedman, et al, 1964; Craig and Gordon, 1965). As a result, the points on, and to the left of, the meteoric water line are regarded as most probably representing waters which have condensed in isotopic equilibrium with the vapor phase with no subsequent important evaporation. The role of post-condensation isotopic exchange under saturated conditions may be important for these data (Miyake, et al, 1968; Stewart, 1975), but it can not be evaluated from the information on hand.

The average monthly precipitation δD values and the reciprocal of the monthly precipitation intensity for the 22 "equilibrium" waters from Wake Island are found in Table 4-1 and Figure 4-3. Remembering that equation (4-1) provides no reason to expect that there will be constancy for the numerator on the right-hand side of the equation, it is interesting that there does seem to be some overall trend to the data. In general the months with low precipitation intensity exhibit more positive δD values than months with high precipitation intensity. A linear representation of this general result would be expected from equation (4-1), if the numerator on the right hand side were constant and negative. The latter condition must be true since δD is negative and precipitation intensity positive. That the former condition might be approximately true on the time scale examined here is indicated by the aforementioned trend to the data of Figure 4-3. A linear regression of these data yields the following equation:

$$\delta D = 29.4 \left(\frac{1}{I}\right) - 27 \qquad (4-3)$$

The linear correlation coefficient is 0.803 and I = precipitation

Table 4-1: Monthly Precipitation Total (W), Reciprocal of Monthly Precipitation Intensity ($\frac{1}{I}$) and Monthly δD Value of Precipitation.

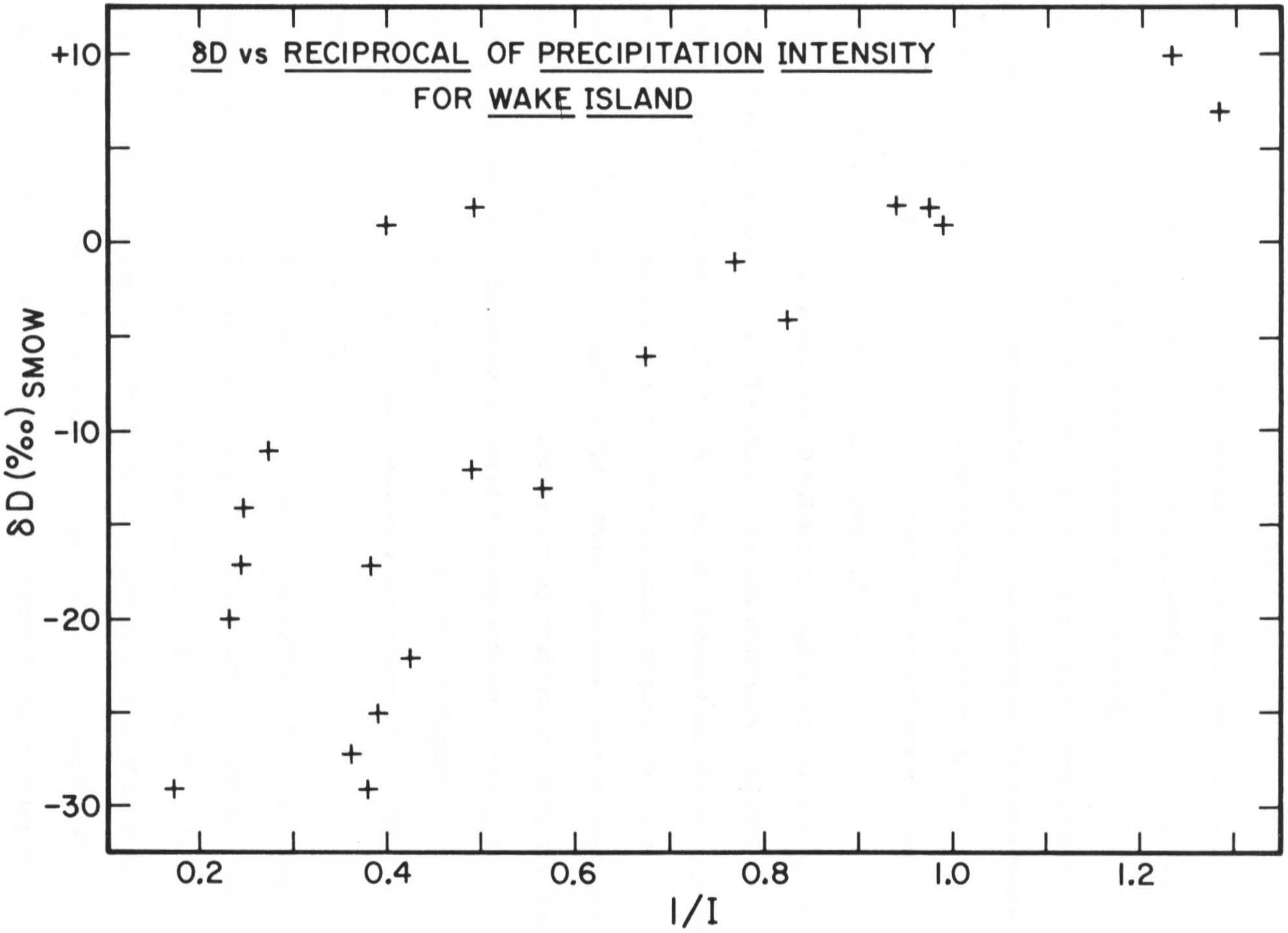
Month	W(m)	$\frac{1}{I}$	δD
1962			
Feb.	0.041	0.673	-6
Mar.	0.025	1.232	+10
June	0.132	0.387	-17
July	0.216	0.380	-29
Aug.	0.217	0.235	-20
Sept.	0.160	0.389	-25
Oct.	0.297	0.427	-22
Nov.	0.030	0.827	-4
1963			
Mar.	0.028	0.768	-1
May	0.093	0.495	+2
July	0.035	0.563	-13
Sept.	0.053	0.247	-14
Nov.	0.079	0.173	-29
Dec.	0.044	0.941	+2
1964			
Jan.	0.023	0.987	+1
Feb.	0.015	1.287	+7
Mar.	0.027	0.974	+2
April	0.093	0.397	+1
June	0.133	0.277	-11
July	0.113	0.488	-12
Aug.	0.149	0.364	-27
Sept.	0.176	0.246	-17

Figure 4-3

A plot of the monthly δD value of precipitation at Wake Island vs the reciprocal of rainfall intensity for the years 1962, 1963 and 1964. The rainfall intensity data are in units of meters per month and were obtained from rainfall start-stop times provided by the Environmental Data Service, National Climatic Center, Asheville, North Carolina. The δD values are from IAEA data and exclude those points which are circled in Figure 4-2. The linear regression of the δD and reciprocal intensity data yields the expression:

$$\delta D = 29.4(1/I) - 27$$

The correlation coefficient is 0.803.


δD vs RECIPROCAL OF PRECIPITATION INTENSITY
FOR WAKE ISLAND
δD (‰) SMOW
+10
0
-10
-20
-30
0.2
0.4
0.6
0.8
1.0
1.2
1/I

intensity (meters per month).

If this equation is extrapolated to infinite intensity -ie. $1/I = 0$, the δD value to be expected is -27 per mil. Physically, infinite intensity would imply that all the available water vapor was being condensed. Thus, the precipitation in such a hypothetical case would be of the same isotopic composition as the vapor, because there can be no net isotopic fractionation if all the material in one reservoir is transferred to another. This hypothetical value for the average vapor is much greater than the δD values of about -70 to -90 per mil measured for oceanic water vapor (Craig and Gordon, 1965).

As was discussed above, the δD values of Figure 4-3 are most likely unmodified by evaporation. Therefore, the comparatively positive δD value for the intercept could be interpreted to mean that the assumption of linear isotopic variation with the reciprocal of precipitation intensity is not theoretically valid. Thus, the numerator on the right-hand side of equation (4-1) is probably not approximately constant, but rather may vary as a function of precipitation intensity and/or δD. Such inconstancy might explain some of the scatter of Figure 4-3, particularly the two comparatively positive δD values of May, 1963 and April, 1964 (see Table 4-1).

Nevertheless, in spite of the lack of theoretical justification for assuming that δD values of precipitation are linearly related to the reciprocal of precipitation intensity, it is an empirical "fact" that the two variables are correlated in precipitation at Wake Island. Furthermore, this relationship may be approximately and empirically characterized by a linear "best-fit" line, although some scatter is evident. The implication is that if there is a correlation between precipitation amount and precipitation intensity at any single site, there could then be a correlation between δD values and the reciprocal of the total amount of the corresponding precipitation. Dansgaard (1964) found an amount effect for the precipitation at Wake Island in the year 1962. However, he did not attempt to eliminate data from waters that had been isotopically enriched by evaporation as was done in this work. For the 22 "unmodified" points of Table 4-1, linear regression yields the equation:

$$\delta D = 0.529\left(\frac{1}{W}\right) - 21 \qquad (4\text{-}4)$$

The regression coefficient is 0.731 and W = the monthly total precipitation (meters), Consequently, there does seem to be some correlation between total amount of monthly precipitation and δD value at this site. Interestingly, the correlation of monthly precipitation amount and precipitation intensity for the 22 months in Table 4-1 is not very good. The linear regression is:

$$W = 8.42(I) + 1.516 \qquad (4\text{-}5)$$

The correlation coefficient is only 0.495. Thus, either the correlation of δD vs precipitation amount is fortuitous for these data, or the truly nonlinear character of the δD vs precipitation intensity relationship acts in some manner to induce the observed δD vs reciprocal amount correlation.

The significance of these results lies in the implication that δD (or $\delta^{18}O$) values in precipitation may vary from year to year at a site in response to varying precipitation intensity as much as to temperature change. Furthermore, because precipitation amount and precipitation intensity could be correlated, it is possible that precipitation δD values will vary in response to variations in the precipitation amount. As previously mentioned, Dansgaard (1964) has demonstrated the existence of an "amount effect" on monthly $\delta^{18}O$ values of precipitation from low latitude sites on an annual basis and for some coastal mid-latitude sites during summer months. Thus, the δD values of summer precipitation may be correlated from one year to the next with the total amount of summer precipitation. However, this is a tentative supposition, because the relationship between δD (or $\delta^{18}O$) values of precipitation and precipitation intensity needs to be examined for a much larger number of appropriately chosen sites to better determine just how commonly a good correlation is observed.

In summary the interpretation of δD variations of meteoric water in climatic terms may require consideration of temperature, precipitation, or both as the variables of dominant importance. While intensity may be the variable of choice when considering precipitation-related δD variations, it is a variable which has not been recorded for any great length of time at a single site. Thus, the precipitation amount must generally be used as a surrogate when looking at temporal variations of δD values of meteoric water such as recorded by tree ring sequences.

A point of conceptual interest is raised by some of the data of Table 4-1. In particular the δD values of precipitation in March, 1962 and February, 1964 are sufficiently positive (+10 and +7 per mil respectively) to raise the question of just how they achieved these values without undergoing isotopic enrichment due to evaporation. That the latter process has not affected these waters appears to be supported by the position of their δD vs $\delta^{18}O$ plots adjacent to the meteoric water line (Figure 4-2). Furthermore, if the isotopic compositions of the oceans are near the value of SMOW, Figure 4-1 suggests that the unmodified equilibrium precipitation from initially saturated air should have δD values no greater than zero. However, the evaporating surface waters of the low latitude oceans have δD values greater than zero and in fact they can be as positive as about +10 per mil (Friedman, et al, 1964; Craig and Gordon, 1965). Acting in the opposite sense, oceanic water vapor commonly has more negative δD values than the theoretically expected equilibrium vapor, because the actual evaporation is of a nonequilibrium character (Craig and Gordon, 1965).

One factor which quite probably can explain the comparatively positive δD values of Table 4-1 is the unsaturated nature of non-precipitating air masses. One scenario which incorporates this fact is as follows. Assume that an oceanic air mass has water vapor with a δD value of -85 per mil. If this air were saturated and had evaporated from an ocean at $30^{\circ}C$, it would, upon cooling, initially condense water with a δD value of -17 per mil, since the equilibrium value of α at $30^{\circ}C$ is 1.074 (Majoube, 1971). However, if the air mass were sufficiently unsaturated at $30^{\circ}C$ that condensation could not begin until it reached, by adiabatic cooling, a temperature of $10^{\circ}C$, the δD value of the initial condensate would be +5 per mil, because the equilibrium α value at this temperature is 1.098. Thus, there is a theoretically possible way to achieve positive δD values for low latitude precipitation without calling on evaporative enrichment of the precipitation. The actual numbers used in this hypothetical example may not be generally applicable, but they do serve to illustrate the point that low latitude equilibrium condensation can produce precipitation with positive δD values.

The overall sense of the preceding discussion about factors likely to influence the δD values of precipitation has been that in detail and over narrow ranges of temperature, there are likely to be many perturbations of a δD vs temperature relationship. However, the expectation is that such a relationship will exist and be reasonably unambiguous for annual precipitation sampled from a wide range of locales with a correspondingly large range of average annual temperatures. Dansgaard (1964) has, as was noted, observed such a relationship for $\delta^{18}O$ values from precipitation at North Atlantic coastal sites and some Greenland and Antarctic stations. Since the trees analyzed herein for their δD values were limited to North American sites, the annual IAEA precipitation data for the 11 available North American sites were assembled and compared with the corresponding average annual temperature. These data are listed in Table 4-2 and plotted in Figure 4-4. The total annual temperature range is about 24°C, and there is a definite relationship between the δD values of annual precipitation and the annual temperature at these sites. If a least squares straight line is fitted to these data it yields the equation:

$$\delta D = 5.60T(^{\circ}C) - 120 \qquad (4\text{-}6)$$

The linear correlation coefficient is 0.903. The North American waters that comprise this sample population are from both continental and coastal sites. The value of 5.60‰ per °C. for the temperature coefficient of these data is the same as that found by Dansgaard (1964) although the intercept is more negative by 20 per mil. However, if the data from Bethel, Alaska are left out of the regression, the temperature coefficient for the plot of Figure 4-4 is 6.27‰ per °C and the linear correlation coefficient is 0.946. Bethel is located in western Alaska and may not be significantly affected by the large scale moisture transport systems that are probably affecting the other sites (Benton and Estoque, 1954). Thus, Bethel may be somewhat more "decoupled" in an isotopic sense from these sites than the balance of the sites are from each other.

The temperature coefficient of 6.27‰ per °C obtained when Bethel, Alaska is excluded from the regression of the data of Figure 4-4 is comparatively large for the temperature interval involved. For the temperature range of -4 to 20°C at the locales of Figure 4-4, the maximum average temperature coefficient that occurs for any of the curves of Figure 4-1 is about 6.0‰ per °C. This latter value is calculated for a condensation trajectory with no clouds and from an ocean of 20°C. From the observed patterns of moisture transport over the North American continent (Benton and Estoque, 1954) it is apparent that most of the precipitation at such stations as Waco, Texas and Chicago, Illinois must have originated from the Gulf of Mexico, which is warmer than 20°C.

Thus a single condensation trajectory is inadequate for explaining the temperature coefficient defined by the data of Figure 4-4. Rather, it seems more probable, as discussed earlier, that the overall trend observed in Figure 4-4 is a consequence of the fact that the various δD values lie within the "envelope" of condensation trajectories delineated by the extremum curves of Figure 4-1. Therefore, the temperature coefficient obtained for the North American IAEA precipitation data is most probably an artifact of the particular combination of condensation histories exhibited by precipitation at each of the sites. This ensemble of condensation histories may in itself be an indicator

Table 4-2: Average δD Value of Annual Precipitation and Average Annual T(^{o}C)

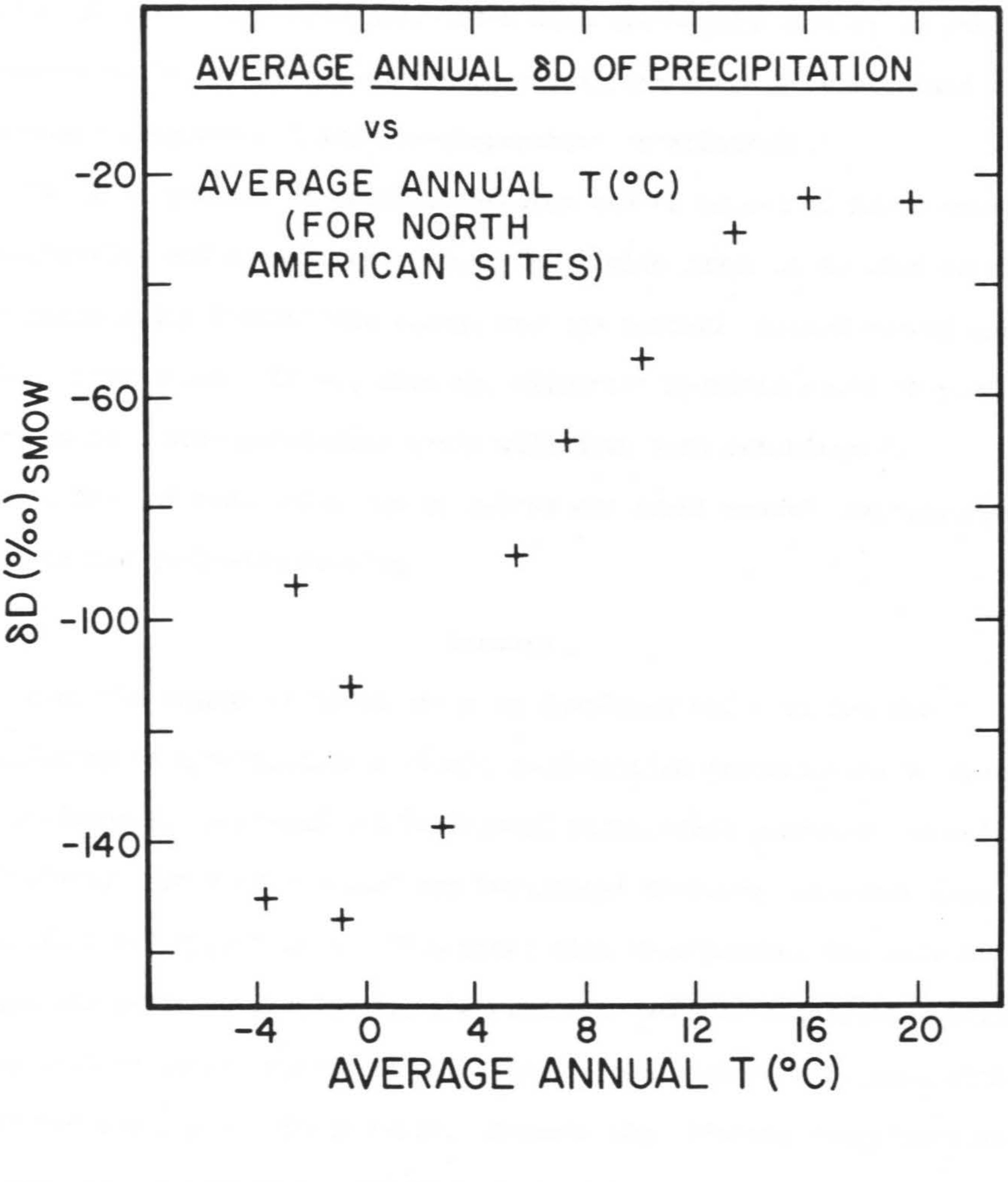
Location	Average Annual T(^{o}C)	Average Annual δD
Bethel, Alaska (1962-1965)	-2.4	-94
Waco, Texas (1962,1964,1965)	19.8	-25
Cape Hatteras, N.C. (1962-1965)	16.1	-24
Flagstaff, Ariz. (1962-1963)	7.4	-68
Santa Maria, Calif. (Mar., 1963 to Feb., 1964)	13.5	-30
Chicago, Illinois (1962)	10.1	-53
Goose Bay, Newfoundland (1962-1964)	-0.5	-112
Edmonton, Alberta (1963-1965)	3.0	-137
Fort Smith, N.W.T. (1964, 1968)	-3.6	-150
Whitehorse, Yukon (1962-1965)	-0.9	-154
Ottawa, Ontario (1968)	5.5	-88

Figure 4-4

A plot of the δD values of annual precipitation against annual temperature for eleven available North American IAEA stations. The linear regression of these data yields the equation:

$$\delta D = 5.60\ T(^{o}C) - 120$$

The correlation coefficient is 0.903.


AVERAGE ANNUAL δD OF PRECIPITATION
VS
AVERAGE ANNUAL T(°C)
(FOR NORTH
AMERICAN SITES)
δD (‰) SMOW
-20
-60
-100
-140
-4
0
4
8
12
16
20
AVERAGE ANNUAL T (°C)

of the general climatic patterns prevailing across the continent. Hence, the measured temperature coefficient obtained by comparing different geographic sites probably characterizes in some complex fashion, the overall dynamics of the continental climate. However, many more sites and the climatic variables associated with them would have to be studied to determine if any definite dynamic significance could be attached to an average geographical isotope-temperature relationship.

The good overall correlation between the δD values of North American precipitation and annual temperature for a wide range of locales implies that trees which incorporate annual average meteoric waters should exhibit such a correlation. If so, then the climatic significance of δD variations in trees on a wide geographic scale will have been established. A comparison of tree cellulose δD values and local annual temperature is found in the following section.

Summary

A simple transport model has been developed which allows the calculation of hypothetical isotopic condensation trajectories by specifying atmospheric vertical and horizontal temperature gradients as well as the relative rates of vertical and horizontal moisture transport (see Appendix I and Figure 4-1). This model also incorporates the role of clouds and produces results for the extremum cases of transport (wholly horizontal or wholly vertical) which are in qualitative agreement with published results for these cases. Because the relative contributions of vertical and horizontal moisture transport to the condensation trajectory can be specified in this model, it is not limited to calculation of the extremum cases.

This model indicates that the δD values of precipitation may vary in response to a number of factors including ocean source temperature, isotopic composition of the initial vapor, cooling process, condensation temperature, amount of cloud, and precipitation intensity. Additionally, isotopic exchange and/or evaporation subsequent to condensation can be expected to influence the δD value of precipitation.

Notwithstanding the multiplicity of these potentially important parameters, it is observed that over a wide range of temperature and geography the annual precipitation δD values are indeed reasonably well-correlated with average annual surface temperature. This correlation seems to imply that in many instances variations of the annual average weighted condensation temperature are reasonably well-represented by variations of annual average surface temperature. In addition to the δD vs T correlation, there is a possibility that the δD value of summer precipitation in temperate climates could be correlated with the average precipitation intensity, or its possible approximate equivalent--precipitation amount. Thus, the climatic variables temperature and precipitation seem to be strong candidates for correlation with δD variations in tree ring sequences, because as has been demonstrated in a previous section of this work, tree δD values commonly reflect the δD values of ambient meteoric waters.

Section 5

Comparisons of Isotopic Variations of Cellulose C-H Hydrogen in Trees with Variations in Climate

In addressing the question of the climatic significance of δD variations in trees, it is important to keep in mind that there are actually two scales of climatic change which are of interest--spatial and temporal. The δD variations in trees offer the possibility that both spatial and temporal climatic signals can be discerned, because trees are geographically widespread and also contain an internal chronology which may isotopically record local climatic change. The observations of the preceding sections that (1) δD values in trees commonly reflect δD values of local meteoric waters and (2) the δD values of meteoric waters can vary spatially in concert with temperature suggest that a spatial comparison of tree δD values and temperature might be the best first step toward ascertaining the extent of climatic sensitivity of this parameter.

Spatial Variations

Twenty-five trees from 22 sites throughout North America were obtained and analyzed for their cellulose C-H hydrogen δD value (see analytical section). The outermost 4 or 5 rings were analyzed. Because of the different times at which the various trees were felled, the total sample interval spanned is from 1961 to 1975. Sample locations and descriptions can be found in Appendix II. The locations of the tree samples as well as the North American sites of the International Atomic Energy Agency (IAEA) precipitation stations are plotted in Figure 5-1. It can be seen in Figure 5-1 that the tree samples cover much the same range of geography and climate as the IAEA stations.

The δD values measured for the trees and the average annual temperatures of nearby meteorological stations are listed in Table 5-1

Figure 5-1

The geographic distribution of the δD values of tree samples analyzed for this work. In addition, the δD values of annual precipitation at the eleven North American IAEA stations are depicted. The crosses indicate tree sites, while the open circles are the IAEA stations. δD values of the trees are underlined, while the δD values of the precipitation at the IAEA stations are enclosed in parentheses. Note that there is a general decrease in δD values of both the trees and the precipitation from coastal to inland sites and from south to north.

Geographic Distribution of Tree δD Values

___ Underlined number is δD value of tree

( ) Number in parentheses is δD value of annual precipitation at the indicated IAEA station.

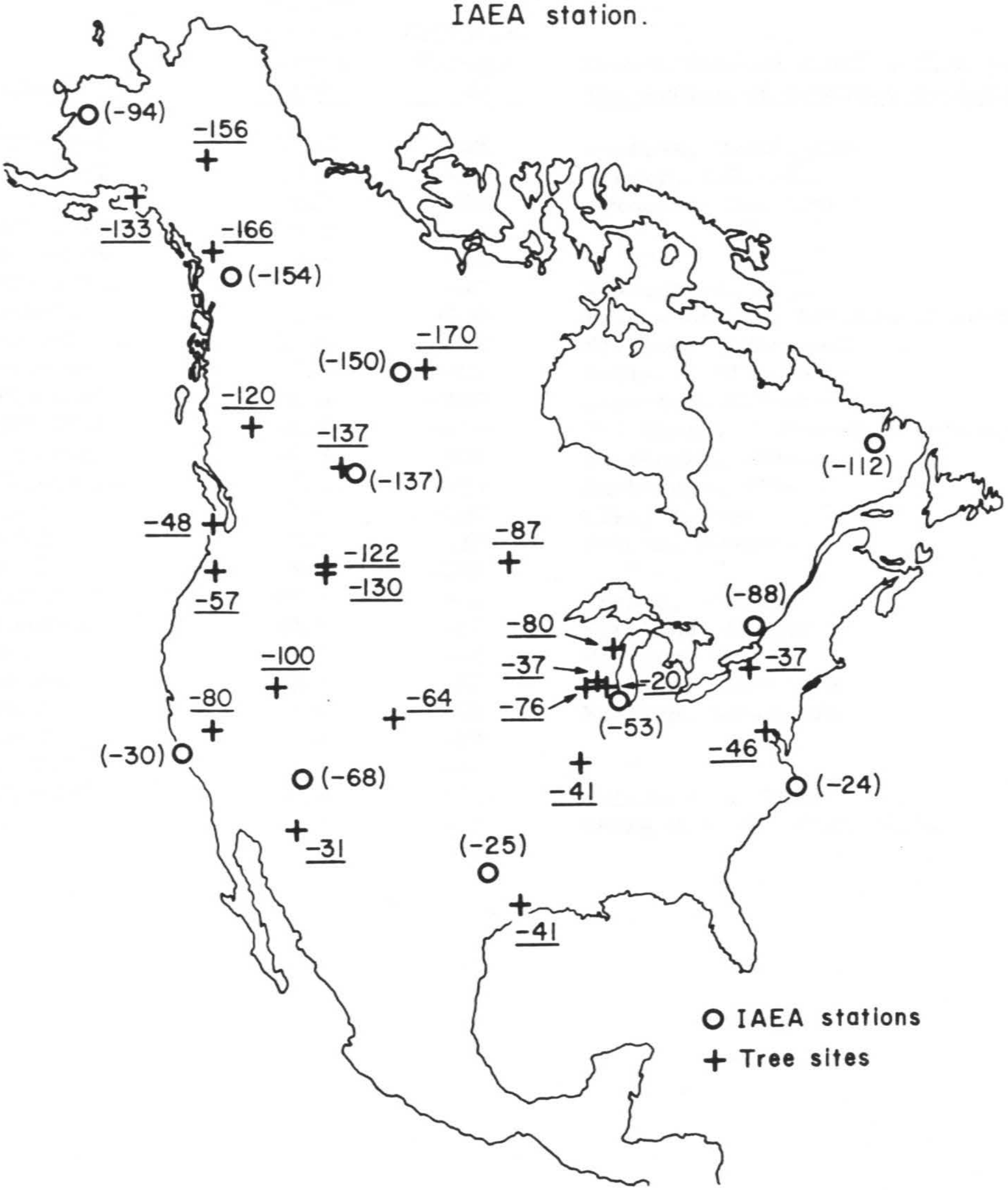


Table 5-1: δD of Cellulose Nitrate and Approximate Average Annual Temperature in Region of Growth Site.

Sample	Surface Average Annual T (°C)	Cellulose Nitrate δD	Meteorological station that is the source of temperature data
OPW-DF-1	11.3	-48	Seattle, Washington
Col-DF-1	10.5	-64	Denver, Colorado
MNY-GA-2	8.2	-33	Syracuse, New York
MNY-BO-7	8.2	-34	" " "
MNY-RM-5	8.2	-45	" " "
RE-CO-2	14.0	-46	Washington, D.C.
BCT-12	3.4	-120	Prince George, British Columbia
MO-0-2	12.6	-41	St. Louis, Missouri
AW-BO-1	7.0	-20	Madison, Wisconsin
FCA-WS-1	0.9	-137	Edmonton, Alberta
SAS-JP-1	-3.5	-170	Ft. Smith, Northwest Territory
FA-As-1	-3.3	-156	Fairbanks, Alaska
KSA-As-1a	2.1	-133	Anchorage, Alaska
NT-1	7.4	-100	Elko, Nevada
MT-1	5.7	-130	Helena, Montana
MT-2	5.7	-122	" "
UAZ-PP-1	19.3	-31	Tucson, Arizona
PO-DF-1	12.6	-57	Portland, Oregon
H-2	20.2	-41	Houston, Texas
WM-B-1	2.5	-87	Winnipeg, Manitoba
WR-2	7.0	-76	Madison, Wisconsin
OM-2	7.0	-80	" "
UBLM-2	7.0	-37	" "
Yuk-W-1	-0.7	-166	Whitehorse, Yukon
BrPn	0.7	-80	White Mts. #1, California

and plotted in Figure 5-2. It is apparent from Figure 5-2 that there is a relationship between the δD values and annual temperature. However, some scatter is also evident. The circled points in Figure 5-2 seem to lie significantly above the general "trend line" of the data and may be unusual from the standpoint of the conditions in their environments of growth. For example, UBLM-2 is a willow tree which grew in a marsh in Madison, Wisconsin. The waters in the saturated soil in which this tree grew were analyzed and found to have a δD value of -32 per mil (see Table 2-1). This value is considerably more positive than the average annual precipitation in the area, the latter of which has a δD value of about -60 per mil. Consequently, either the meteoric water incorporated by the tree had undergone significant evaporation as it slowly infiltrated into the poorly drained soil, or the water represented predominantly summer precipitation which is commonly more positive than the average annual precipitation (IAEA). In either case, the δD value recorded by the tree would not be representative of average annual precipitation and therefore would probably not reflect average annual temperature.

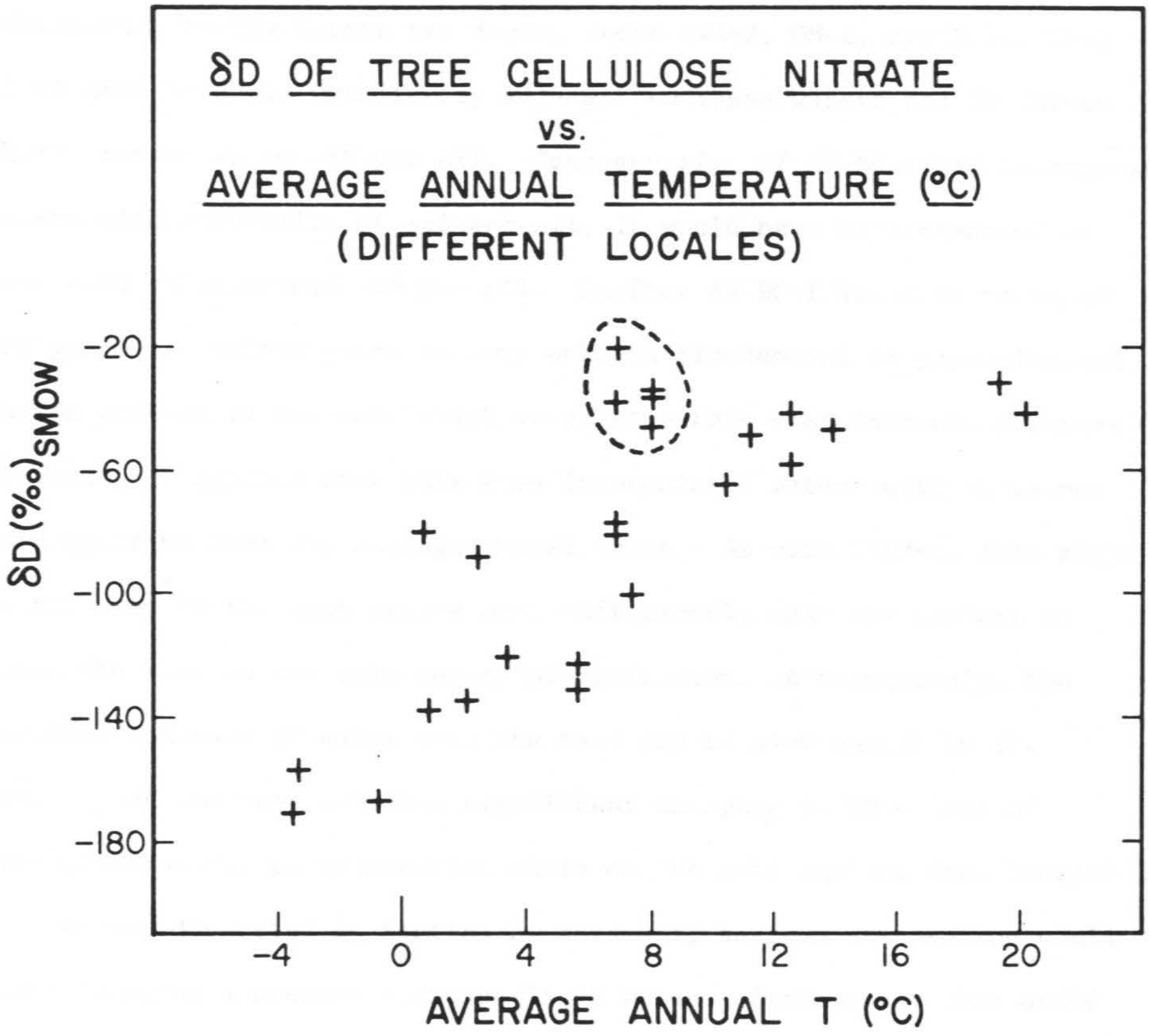
Samples MNY-GA-2, MNY-RM-5, and MNY-BO-7 which are also enclosed in the circle in Figure 5-2 grew in a marsh in New York. The waters utilized by these plants were not available for analysis, but it is possible that conditions similar to those noted for the UBLM-2 site were present at the site of these three trees. Thus, they may have incorporated waters with δD values which were somewhat more positive than the average annual δD values in the area and therefore the trees do not have δD values representative of the average annual local temperature.

Figure 5-2

A plot of the δD values of trees from a wide range over North America against the average annual temperature. The tree samples represent various intervals within the span 1961-1975. The five points enclosed in the dashed circle represent trees which may have grown under conditions that could obscure a climatic interpretation of their δD values. The remaining twenty points define a trend with the following linear regression equation:

$$\delta D = 5.81\ T(^{o}C) - 134$$

The correlation coefficient is 0.884.


δD OF TREE CELLULOSE NITRATE
vs.
AVERAGE ANNUAL TEMPERATURE (°C)
(DIFFERENT LOCALES)
δD (‰)SMOW
-20
-60
-100
-140
-180
-4
0
4
8
12
16
20
AVERAGE ANNUAL T (°C)

The fifth point enclosed by the circle of Figure 5-2 is AW-BO-1. This is a bur oak which grew in a pasture in Southeastern Wisconsin amidst a small stand of oaks. The analyzed δD value of water from a nearby stream was -62 per mil. This water value is similar to δD values measured for water from the Wisconsin River and from a river near Oconto, Wisconsin. In the latter two cases, trees (WR-2, OM-2, see Table 2-1) which grew in soils immediately adjacent to these waters had δD values in the range -76 to -80 per mil. Consequently, if AW-BO-1 had incorporated waters with a δD value of -62 per mil, it would have been expected to have a δD value around -75 per mil. In fact AW-BO-1 has a δD value of -23 per mil. Unless there is some unknown biochemical or physiological factor present in bur oaks which is causing this comparatively positive δD value, it appears that this tree incorporated waters with δD values more positive than the average annual value. As with UBLM-2, this might be the case if the root system were sufficiently near the surface to cause the tree to use only summer precipitation. Alternatively, the infiltration rate of water into the soil may be slow enough in the environs of the tree to allow significant increase in δD values of precipitation due to evaporation while on the soil surface (see Section 2).

As was discussed in Section 2, this soil surface evaporation would probably cause a greater increase in δD values of the water than would occur from transpiration alone. Thus, significant above-ground evaporation of precipitation would cause tree δD values to be more positive than otherwise expected. The relationship of these more positive tree δD values to annual temperature would probably be altered in a spatial δD vs T plot compared to other sites at which no above-ground evaporation of precipitation had occurred.

In short, the circled points in Figure 5-2 are interpreted to be representative of sites at which trees incorporated soil water that was more positive than the δD value of average annual precipitation. Thus, these samples suggest that site conditions may be very important in choosing trees for possible interpretation of geographical climatic variation. The scatter in Figure 5-2 that is not accounted for by the circled points will be discussed somewhat later.

If the circled points in Figure 5-2 are eliminated from consideration in spatial δD vs T plots, the balance of the data produces an array of points for which a linear regression yields the expression:

$$\delta D = 5.81\ T(^{\circ}C) - 134 \qquad (5\text{-}1)$$

The linear correlation coefficient is 0.884. The slope of this curve is very similar in magnitude to the slope of 5.60 obtained in Section 4 for the regression of the North American IAEA precipitation data. Since the tree sites and IAEA stations do extend over much the same range of geography and climate (Figure 5-1), it might be expected that a regression of the two sets of δD data against temperature would produce a similar slope, providing that the δD values of the tree samples employed in the comparison reflect the δD values of annual precipitation at these sites. Furthermore, the very good correlation between tree δD values and annual temperature in Figure 5-2 indicates that trees from properly chosen sites may be isotopically analyzed to interpret spatial patterns of climatic change.

Seven of the "well-behaved" tree samples in Figure 5-2 have chronologies that extend back in time to at least 1931 A.D. These trees are OPW-DF-1, Col-DF-1a, RE-CO-2, BCT-12, MO-0-2, FCA-WS-1, and SAS-JP-1.

They range in location from as far south as St. Louis, Mo. and Reston, Va. to as far north as Ft. Smith, N.W.T. In addition these trees are near meteorological stations whose instrumental temperature records also date from at least 1931. This suggests the possibility of plotting spatial tree δD variations vs annual temperature for five-year intervals from 1931-1970. Such plots could determine whether or not there have been any important changes over this interval in the character of the δD vs T relationship as defined by the seven trees. These data are in Figures 5-3 and 5-4.

Because there are far fewer sites included in Figures 5-3 and 5-4, it is statistically possible that the linear regressions of these data will not produce the same slope as that obtained from the regression of the data of Figure 5-2. Thus, it does not seem to be possible to attach physical significance to any differences in slope between the large data group (Figure 5-2) and its subset (Figures 5-3 and 5-4). However, changes of slope between different 5-year intervals in Figures 5-3 and 5-4 may have a physical interpretation.

The equations for the linear regressions of the different five-year intervals are found in the various plots of Figures 5-3 and 5-4. The analytical error of ± 2 per mil for the measurement of δD values imposes an error on the regression slopes of Figures 5-3 and 5-4 of about ± 0.3‰ per °C. Thus, with the exception of 1941-45 all the five-year intervals exhibit within experimental error the same spatial δD temperature coefficients. The large 1941-45 temperature coefficient of 8.65‰ per °C seems to be a consequence of something other than normal analytical error.

It seemed possible that the δD value of the reaction wood in Col-DF-1a might be influencing the temperature coefficient.

Figure 5-3

Comparisons of the δD values of seven trees from a wide range over North America (OPW-DF-1, Col-DF-1a, RE-CO-2, BCT-12, MO-0-2, FCA-WS-1, and SAS-JP-1, see Appendix II) with average annual temperature. The comparisons are made for different corresponding five-year intervals. The equations of the linear regressions of the data are shown within the plots of each of the five-year intervals. The pattern of declining δD values with declining temperature is remarkably consistent for the trees and the intervals depicted in this figure.

SPATIAL δD vs. T(°C) FOR DIFFERENT 5-YEAR INTERVALS

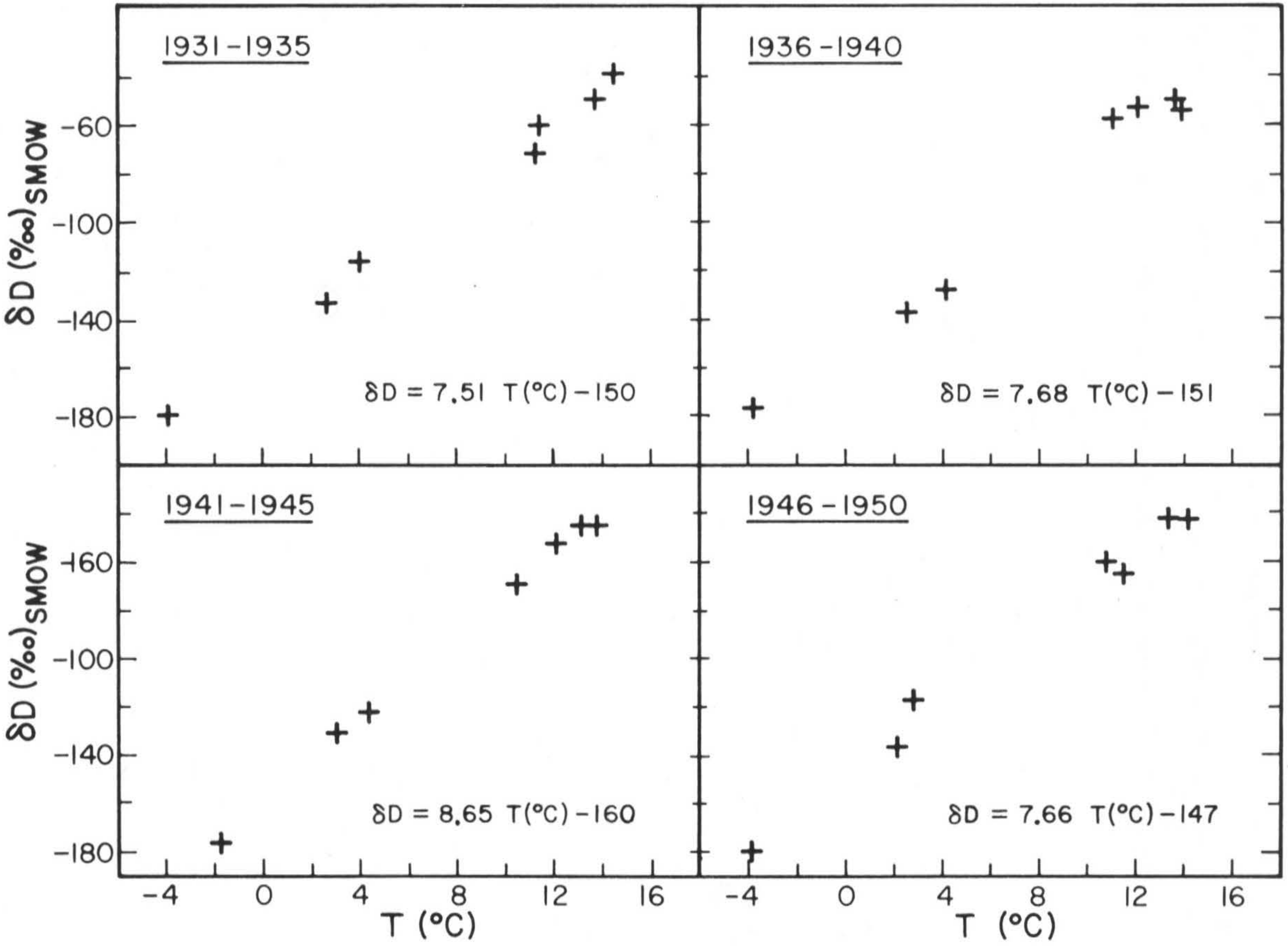
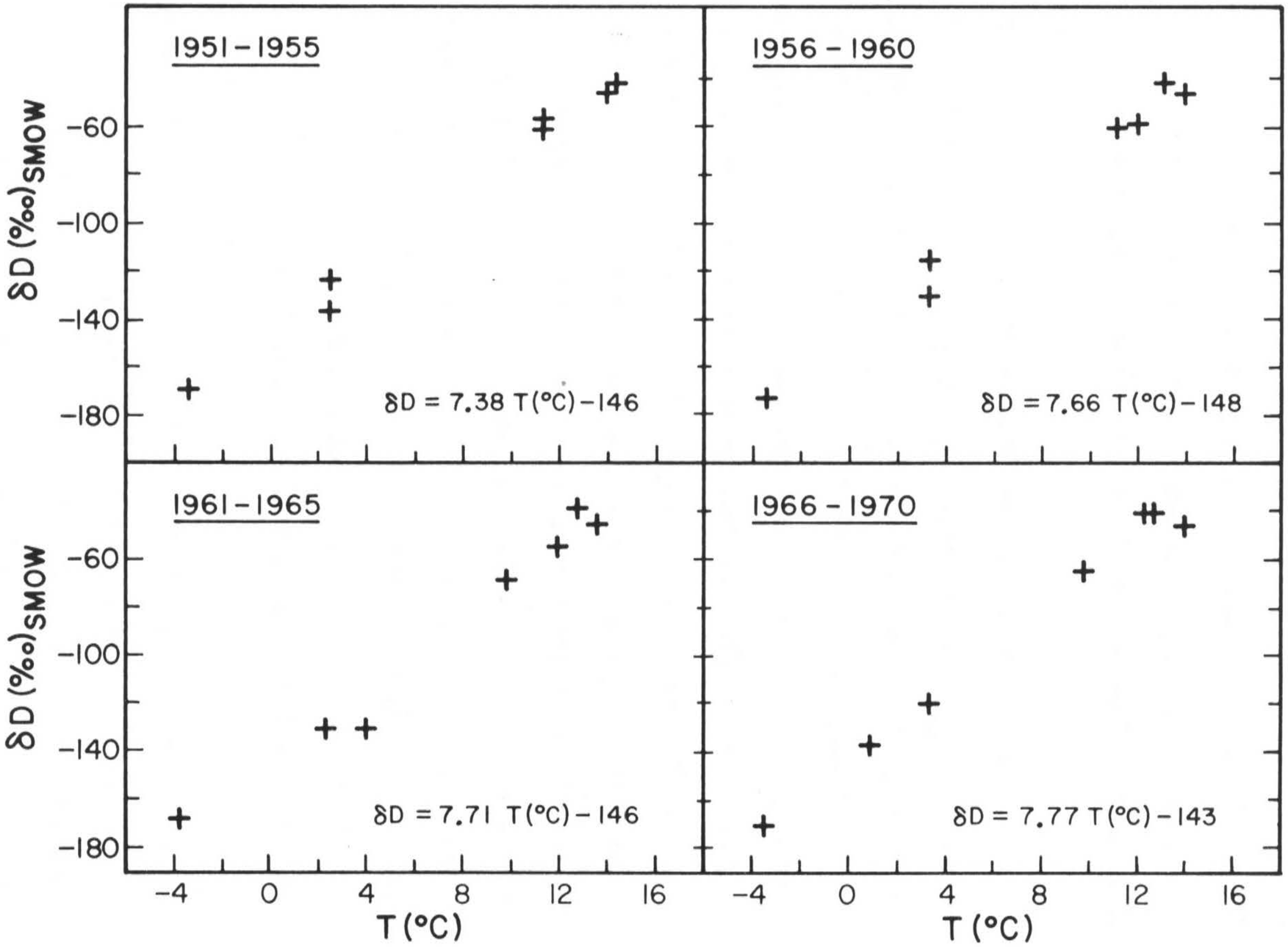


Figure 5-4

Same trees as in Figure 5-3 except that four different five-year intervals are compared. Again, the overall pattern of declining δD with declining temperature is maintained throughout these intervals in spite of the differences in species and relative ages of the trees.



SPATIAL δD vs. T(°C) FOR DIFFERENT 5-YEAR INTERVALS

This was checked by comparing 1941-45 δD values of the "a" and "b" samples (see Section 3, Table 3-2). The δD value from the "b" sample is only 3 per mil more negative than the δD value of the "a" sample. Thus, the presence of reaction wood in Col-DF-1a does not seem to have had a role in producing the large 1941-45 temperature coefficient, because the latter still has a value of 8.62‰ per °C if the 1941-45 "b" δD value is not used.

An alternative explanation could involve the small sample size - ie. only seven trees. For example, a comparison of data in the 1936-40 interval with data in the 1941-45 interval reveals that for MO-0-2 the average annual temperature decreased between the earlier and later intervals while the δD value increased. Conversely, for the same two intervals the temperature for SAS-JP-1 increased while the δD value decreased slightly. Since MO-0-2 has a relatively more positive δD value, while SAS-JP-1 is very negative, these two changes alone could have acted to increase the spatial temperature coefficient of the 1941-45 interval. However, a linear regression of the five samples exclusive of MO-0-2 and SAS-JP-1 still results in a temperature coefficient of 8.31‰ per °C. Consequently, large fluctuations of δD value and/or temperature for only one or two points in the small sample population do not appear to have produced the large 1941-45 temperature coefficient.

Thus, one is left with the prospect of interpreting the relatively large 1941-45 spatial temperature coefficient in terms of a climatic pattern between these seven sites which was in some manner different from the patterns of the other five-year intervals. Since these plots present a weighted five-year average δD value vs an unweighted five-year average annual temperature, it is possible that any climatic signal inherent in the large temperature coefficient is linked with a change in the relative δD weightings at the various sites. For instance, if annual δD values of precipitation are being recorded by the trees, the relative proportions of summer and winter precipitation could have changed at the various sites in such a way as to produce an increase in the spatial δD vs T slope.

In addition, varying contributions of moisture from different oceanic sources different surface temperature - condensation temperature relationships, or possibly even differential changes in growing season length could have acted individually or in combination to produce a larger 1941-45 spatial temperature coefficient between these seven sites. At present, the small number of sites allow only speculative guesses about the meaning of the magnitude of the 1941-45 slope. However, a larger number of sites spanning a longer time interval could determine whether or not this "anomaly" is a geographically general characteristic of 1941-45, and whether or not it has analogs in other five-year intervals.

Notwithstanding the possibility that the spatial 1941-45 δD vs T slope is truly different, the fundamental observation to be drawn from Figures 5-3 and 5-4 is that over this entire 40 year period, an impressively consistent pattern of declining tree δD values with declining spatial temperature has been maintained. This has occurred in spite of the differences in tree species and different relative ages of the trees. Thus, it enhances the conclusion that the δD values of trees from properly chosen sites can indeed be indicators of spatial climatic differences.

Some of the possible causes of the scatter in the 20 "well-behaved" data points of Figure 5-2 should be considered at this point. It is possible, for example, that trees growing in regions of low humidity may exhibit comparatively positive δD values due to a high degree of deuterium enrichment in the leaf water during transpiration. This would tend to shift the tree δD value above the general trend of the data of Figure 5-2, even if the tree is using soil water whose isotopic composition is equal to that of the average annual precipitation (see Section 2 of this thesis). The relatively positive position of the BrPn point in Figure 5-2 may be explained by this effect, since the growing season relative humidity in the region of BrPn is only about 45% (see Table 2-1).

A second source of scatter may arise from the fact that the surface temperatures used for comparison with the tree δD values are unweighted average annual temperatures. If the trees are incorporating annual precipitation, the δD value of this precipitation will probably be a weighted average of varying proportions of the various seasonal precipitations. Consequently, the unweighted temperature and weighted δD values may not always be uniformly related. Furthermore, the compared temperatures are those of meteorological stations which are not located at the exact site of tree growth. Thus, the pattern of geographic temperature variation of these stations may not be exactly analogous to that of the growth sites.

Biochemical or physiological differences between these 20 different "well-behaved" trees could produce some, as yet, unrecognized differences in the net hydrogen isotope fractionation between leaf water and cellulose C-H hydrogen. Such differences might contribute to the scatter in Figure 5-2.

There may be trees among the 20 "well-behaved" samples that have not incorporated average annual precipitation. Instead, some trees may have utilized water predominantly from a single season. When plotted against annual temperature, the δD values of these trees might produce some scatter such as appears in Figure 5-2.

Finally, as was discussed in Section 4, there is likely to be scatter in the primary precipitation δD vs temperature relationship (see Figure 4-4). This scatter would be manifested in Figure 5-2, if the δD values of the trees reflected the δD values of the local meteoric waters.

In spite of the aforementioned possible perturbations of a spatial relationship between tree δD values and annual temperature, it is apparent from Figure 5-2 that such a relationship does exist. Furthermore, for the 20 "well-behaved" samples of Figure 5-2, the relationship is quite close to that which might be expected if the δD variations of the trees mimic those of the local annual precipitation.

Thus, as has been noted previously, trees from the proper sites seem to record δD values that correspond to geographic climatic differences. In this vein, it is worth pointing out that the samples analyzed for this work were collected by individuals who did not evaluate the site conditions from the standpoint of their isotopic suitability. Consequently, the fact that 20 out of 22 sites do delineate a definite relationship between tree δD values and annual temperature suggests that appropriate sites are probably not uncommon.

Summary

A comparison of the geographic variation of the δD values of trees with the associated average annual temperature reveals an overall correlation for many sites and species of trees. The spatial linear temperature coefficient obtained for δD values from 20 widely separated tree samples in North America is 5.81‰ per °C. This compares to a temperature coefficient of 5.60‰ per °C obtained from annual precipitation δD values at 11 North American IAEA sites (see Section 4). The similarity of these two coefficients is consistent with the idea that the δD variations of the trees are reflecting the δD variations of the local precipitation. The latter conclusion is supported by the spatial distribution of the tree δD values (Figure 5-1). These δD values decrease from the coast to the interior and from south to north. This pattern of variation is analogous to that observed for meteoric waters over North America (Taylor, 1974).

The geographical temperature vs tree δD correlation for seven widely separated North American trees shows a remarkable consistency over the interval from 1931 to 1970. This consistency is maintained in spite of the differences in both species and relative ages of the seven tree samples involved. There is a somewhat larger temperature coefficient evident for the interval 1941-45 than for the other 5-year intervals in this 40 year span, but the limited number of sites prevents any strong assessment of the large scale climatic significance of the "anomaly".

Site conditions seem to be important in determining the δD values recorded by trees. It appears, for example, that trees in poorly-drained marsh soils may incorporate waters with δD values that are more positive than those of average annual precipitation (see also Section 2).

In general, however, it is apparent that the δD values of trees from a variety of sites will provide information about geographic variations of climate. Thus, for a large number of time-equivalent samples from a wide range of locales it may be possible to reconstruct a former pattern of meteoric water δD distributions. This pattern may in turn provide information about a composite of interacting, dynamic climatic phenomena.

Temporal Variations

A kind of temporal variation of tree δD values was examined in the plots of Figures 5-3 and 5-4. In those instances it was the variation through time of the geographical δD temperature coefficient that was investigated. At this juncture, however, it is the temporal relationship of δD variations to climate at a single location that is of interest.

This is a very new field involving a difficult analytical method. Consequently, there has been essentially no work done to quantitatively examine the relationship between climatic variables and δD variations of cellulose C-H hydrogen in tree ring sequences.

Libby and Pandolfi (1974) claimed to have demonstrated a relationship between δD values in a central European oak and English winter temperatures. However, they performed their analyses on whole wood tissue which seems capable of producing ambiguous results (Epstein, et al, 1976). At the same time, Libby and Pandolfi (1974) employed untested analytical techniques that seem to be of doubtful validity (Epstein and Yapp, 1977).

Scheigl (1974), on the other hand, employed recognized methods to analyze δD variations in a European spruce. Although whole wood tissue was analyzed, for 10 to 20 year sample intervals Scheigl found indications of a correlation between δD values and average annual temperature. However, Scheigl did not publish a value for the δD - temperature coefficient which would have arisen from this correlation.

Epstein and Yapp (1976) published results from the δD analysis of cellulose C-H hydrogen in a Scots pine from Loch Affric, Scotland. They found that comparisons of 40 year moving averages of tree δD values and winter temperatures from a station over 100 km from the tree site indicated a long term similarity in trend. The temperature coefficient derived from this correlation is about 22.8‰ per °C. This high value may be related to the fact that the tree was located in mountainous terrain where temperature variations can be quite large, while the weather station used for comparison was at a sea level coastal location where temperatures are commonly more moderated.

Wilson and Grinsted (1975) subdivided two rings from a New Zealand Monterey pine and measured the cellulose δD values. Their samples contained not only C-H hydrogen, but also the exchangeable OH hydrogen. The validity of their data has been challenged (Epstein, et al, 1976). However, for the record, it should be stated that Wilson and Grinsted interpreted their data in terms of a negative δD - temperature coefficient with a value of -5‰ per °C.

Aside from these few, and sometimes methodologically unsatisfactory efforts, no work has been done to directly compare δD variations in tree ring sequences with associated instrumental climatic data. In view of the fundamental importance of such comparisons to improved understanding of δD variations in trees, it seems absolutely necessary that additional and more satisfactory investigations be undertaken. To this end, several tree ring sequences from different species and a wide range of locales were obtained for isotopic analysis.

Thirteen of the samples in Table 5-1 from eleven locations contain chronologies of 25 years or more. Furthermore, they were located near meteorological stations which have recorded both temperature and precipitation that can be used for comparison with the δD variations in the tree ring sequences. The chronologies were sampled in five-year intervals. This was done both to facilitate the isotopic analysis of a larger number of chronologies from different locales and to smooth out possible short term isotopic vicissitudes in favor of longer term variations that might more probably reflect climatic change.

The δD value of a five-year interval will obviously be weighted by the relative proportions of cellulose contributed to the aggregate sample by each of the constituent rings. However, such weighting by the tree really can not be avoided, even when individual rings are analyzed. The individual rings are weighted by the varying proportions of cellulose contributed during different portions of the growing season (Kramer and Kozlowski, 1960; Fritts, 1976). Furthermore, the isotopic compositions of celluloses formed at different times of the growing season can be different (Epstein, 1978). Thus, isotopic analysis of individual rings does not solve the weighting problem; it merely shifts the time scale. Therefore, while acknowledging that an indeterminate weighting problem may exist for all isotopic analyses of tree ring sequences, it is recognized that this feature is inherent in the system being studied and cannot presently be circumvented.

The thriteen chronologies studied for this thesis are individually examined below. Instrumental records of climatic data were obtained from the Weather Almanac, the Smithsonian Institute's <u>World Weather Records</u> and the Environmental Data Service, Asheville, N.C.

MO-0-2

This oak tree grew near Owensville, Missouri. The nearest meteorological station is St. Louis about 120 km to the east-northeast of the tree site. Five-year samples were obtained for the entire radius of the tree from 1926 to 1975. In addition the three outermost rings 1976-1978 were analyzed as a single sample. The plot of the δD analyses vs age is in Figure 5-5. There appears to be a long term increase in the δD values of the tree from 1926 to 1978. A singular increase in δD is noted between the intervals 1926-30 and 1931-35 with a similar sharp δD decrease going to 1936-40. The total range of δD values in this 53 year sequence is 17 per mil.

The initial comparison of the δD sequence of this tree was with St. Louis average annual temperature. This comparison is shown in Figure 5-6. It is apparent that there is no significant correlation of δD values with annual temperature in this tree. The linear regression of the data of Figure 5-6 yields the expression:

$$\delta D = -3.28\ T(^{\circ}C) + 0.8 \qquad (5\text{-}2)$$

The linear correlation coefficient is only -0.351.

Comparisons of the tree δD variations with the temperatures of various seasons yield similar fruitless results. However, if one considers the role of seasonal precipitation in determining the average annual δD value of the local meteoric water, there appears to be a

Figure 5-5

The variation of the δD values of MO-0-2 with age. The δD values were measured for consecutive sequences of five rings, with the exception of the interval 1976-78, for which only three rings were analyzed.

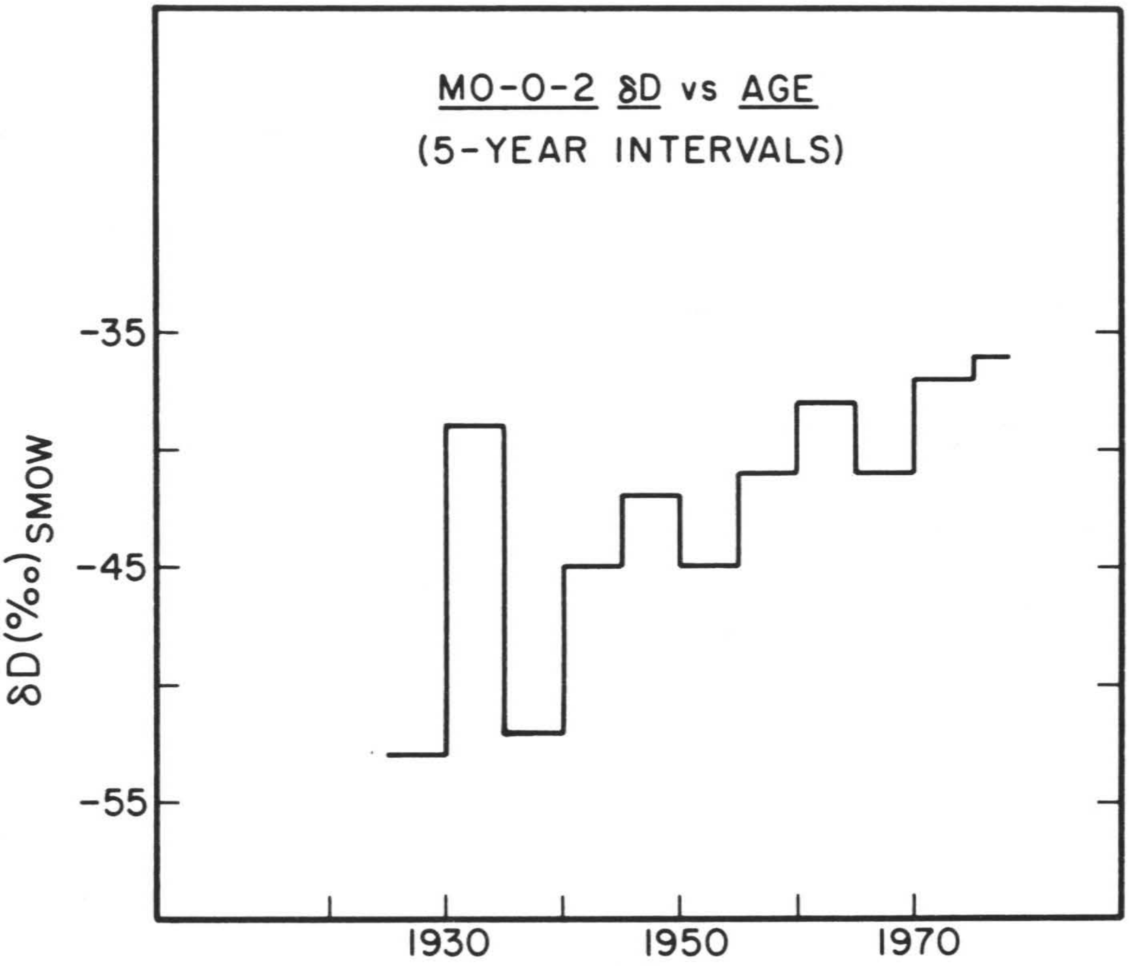
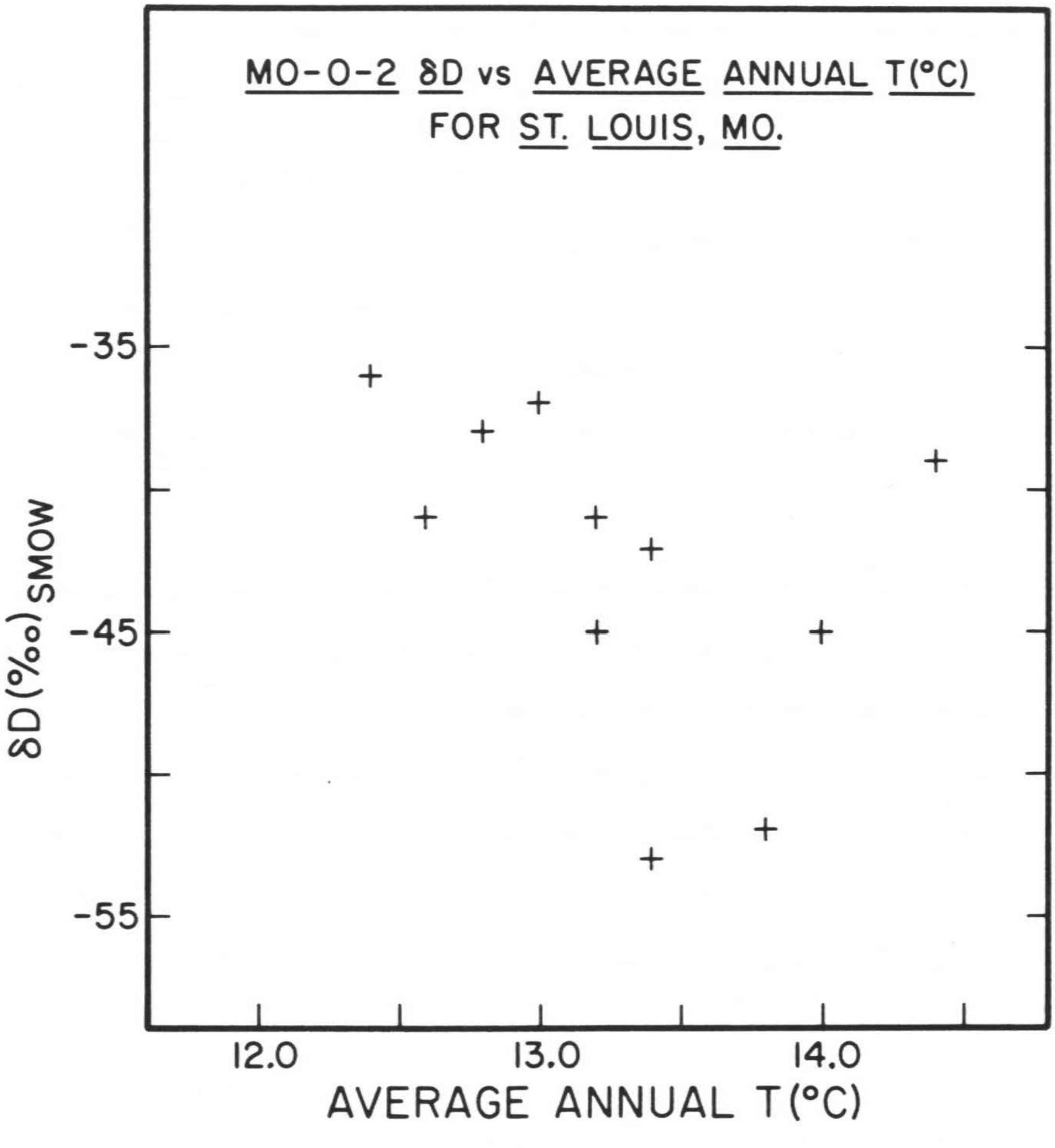

MO-O-2 δD vs AGE
(5-YEAR INTERVALS)
-35
-45
-55
δD(‰)SMOW
1930
1950
1970
DATE (A.D.)

Figure 5-6

A comparison of the δD values of MO-0-2 with the corresponding average annual temperature of St. Louis, Missouri, for five-year intervals. The comparison spans the years 1926-1978. It is apparent that there is no significant relationship between the two variables.


MO-O-2 δD vs AVERAGE ANNUAL T(°C)
FOR ST. LOUIS, MO.
-35
-45
-55
δD (‰)SMOW
12.0
13.0
14.0
AVERAGE ANNUAL T(°C)

somewhat more systematic relationship between the tree δD variations and climate. The reasoning is as follows.

If the isotopic composition of average annual precipitation is regarded as being comprised of two components (summer and winter), the δD value of the annual precipitation must be a weighted average of the δD values of these two components. Thus,

$$\delta D_{Ann} = X_s\ \delta D_s + X_w\ \delta D_w \qquad (5\text{-}3)$$

δD_{Ann} = δD value of total annual precipitation

δD_s = δD value of summer precipitation

δD_w = δD value of winter precipitation

X_s = fraction of total annual precipitation that falls in the summer

$X_w = 1-X_s$

There is some precedent for regarding annual precipitation δD values as being made up of two components. Friedman, et al, (1964) found that the δD value of average annual precipitation in the eastern half of the United States was approximately correlated with the ratio of snow to total precipitation. As was noted by Friedman, et al, (1964), such a correlation could be expected if the winter snow and summer rain represented the isotopic end members of a two component system. Thus, it may not be too unrealistic to express the δD value of annual precipitation as in equation (5-3) above.

Furthermore, if it is assumed that the δD value of precipitation is some linear function of temperature (Dansgaard, 1964), then:

$$\delta D_s = k_s T_s + K_s \qquad (5\text{-}4)$$

$$\delta D_w = k_w T_w + K_w \qquad (5\text{-}5)$$

where k_s and k_w were generally expected to be positive (see Section 4).

k_s = the summer temperature coefficient

k_w = the winter temperature coefficient

K_s = the summer constant

K_w = the winter constant

T_s = summer temperature (monthly average)

T_w = winter temperature (monthly average)

If $k_s = k_w = k$ and $K_s = K_w$, then the preceding equations can be used to express δD_{Ann} in three ways:

$$\delta D_{Ann} = X_s \, (\delta D_s - \delta D_w) + \delta D_w \tag{5-6}$$

$$\delta D_{Ann} = k \; X_s \, (T_s - T_w) + \delta D_w \tag{5-7}$$

$$\delta D_{Ann} = k \left[X_s \, (T_s - T_w) + T_w \right] + K_w \tag{5-8}$$

Equations (5-7) and (5-8) are equivalent, because both depend for their derivation on the equality of the summer and winter temperature coefficients and constants.

With the assumption that the water incorporated by a tree during the growing season can have the δD value of average annual precipitation (see Section 2), it is possible to apply the preceding equations to the problem of δD variations in tree ring sequences. For the aforementioned case of MO-0-2, values of X_s for the various five-year intervals were calculated from St. Louis precipitation by defining several isotopic summers. Correlations between the tree δD values and the parameters X_s, $X_s(T_s - T_w)$, and $X_s \, (T_s - T_w) + T_w$ were made for the variously defined summers and winters. It was found that the best correlation was achieved for an isotopic summer defined as May, June, July, August, and September. The balance of the year was then defined as isotopic winter. Interestingly, of the three parameters mentioned above, the δD values of the tree correlated best with $X_s\ (T_s - T_w)$. The plot of the MO-0-2 δD values vs $X_s\ (T_s - T_w)$ is found in Figure 5-7 and the data are listed in Table 5-2. Note that in contrast with annual temperature, there appears to be a definite relationship between δD and the parameter $X_s\ (T_s - T_w)$. The equation of the regression is:

$$\delta D = 6.26\ X_s\ (T_s - T_w)\ - 92 \qquad (5\text{-}9)$$

The linear correlation coefficient is 0.623.

There is some scatter in the data. In particular the plot of the interval 1971-75 lies well off the apparent δD vs $X_s\ (T_s - T_w)$ trend. With reference to the discussion in Section 4 about the possible variations in the δD values of precipitation, it is not surprising that there is scatter in the plot of Figure 5-7. This is particularly true in view of the small range of temperature (about $2^{\circ}C$). It should be pointed out that there is no indication from the variations of δD values of this tree sequence with time that 1971-75 is a particularly anomalous interval. As can be seen in Figure 5-5, the δD value of this five-year period shows no abrupt changes from the δD values of the intervals on either side. Thus, if the δD value of the 1971-75 interval signals some anomalous climatic behavior, it cannot be deduced from the δD time sequence alone.

If the ring widths respond to the same climatic parameters as does the δD value of the precipitation, ring widths could theoretically provide some insight into this question. The ring widths would probably vary in response only to the local climatic conditions (Fritts, 1976),

Figure 5-7

A comparison of the δD values of MO-0-2 with the parameter $X_s\ (T_s - T_w)$ as calculated from St. Louis meteorological data (see text). The linear regression of these variables yields the expression:

$$\delta D = 6.26\ X_s\ (T_s - T_w) - 92$$

The linear correlation coefficient is 0.623. The point representing the interval 1971-75 is regarded as "anomalous" and is discussed in the text. It is apparent that there is a stronger overall relationship between the variables in this figure than between δD and annual T(°C) as depicted in Figure 5-6.

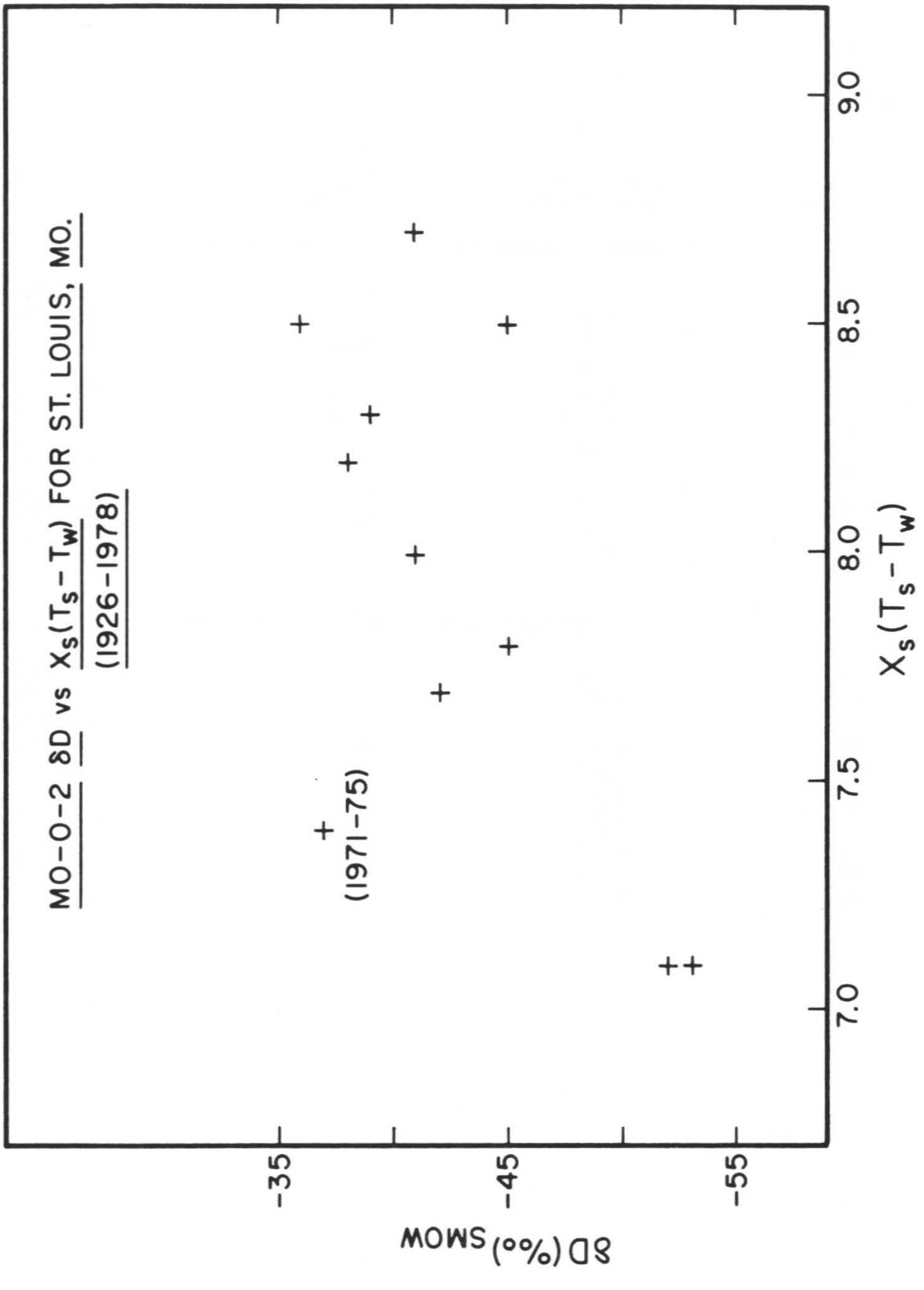

MO-O-2 δD vs X_s(T_s - T_w) FOR ST. LOUIS, MO.
(1926-1978)
(1971-75)
-35
-45
-55
δD (‰) SMOW
7.0
7.5
8.0
8.5
9.0
X_s(T_s - T_w)

Table 5-2: δD Values, Annual Temperature and $X_s(T_s - T_w)$ for MO-0-2 and SAS-JP-1

Interval	T_{Ann} (°C)	$X_s(T_s - T_w)$	δD
MO-0-2	Summer = (May, June, July, August, September)		
1926-30	13.3	7.1	-53
1931-35	14.5	8.3	-39
1936-40	13.6	7.1	-52
1941-45	13.3	8.5	-45
1946-50	13.4	7.7	-42
1951-55	14.0	7.8	-45
1956-60	13.2	8.7	-41
1961-65	12.7	8.2	-38
1966-70	12.7	8.0	-41
1971-75	12.9	7.4	-37
1976-78	12.4	8.5	-36
SAS-JP-1	Summer = (May, June, July, August)		
1926-30	-	-	-182
1931-35	-3.9	10.4	-179
1936-40	-	-	-176
1941-45	-1.8	9.3	-178
1946-50	-3.9	10.4	-179
1951-55	-3.4	9.8	-169
1956-60	-3.4	10.3	-173
1961-65	-3.8	12.3	-167
1966-70	-3.5	11.7	-170
1971-75	-3.3	13.7	-159

while the δD values of the precipitation can vary in response to both local climatic variables and the history of the condensation process (see Section 4). To the extent that the latter process is invariant, the ring width and tree δD values might indeed be responding to the same climatic variables and thus, would be parametrically correlated with one another. If this were true, deviations of points from a general δD vs ring width trend could signal that the condensation history of the precipitation has changed, because all other things being equal, only the δD value would respond to such a change. Of course such a scenario would not work if the ring width variations are not climatically sensitive, or if they are responding to a different set of climatic variables than are the δD values.

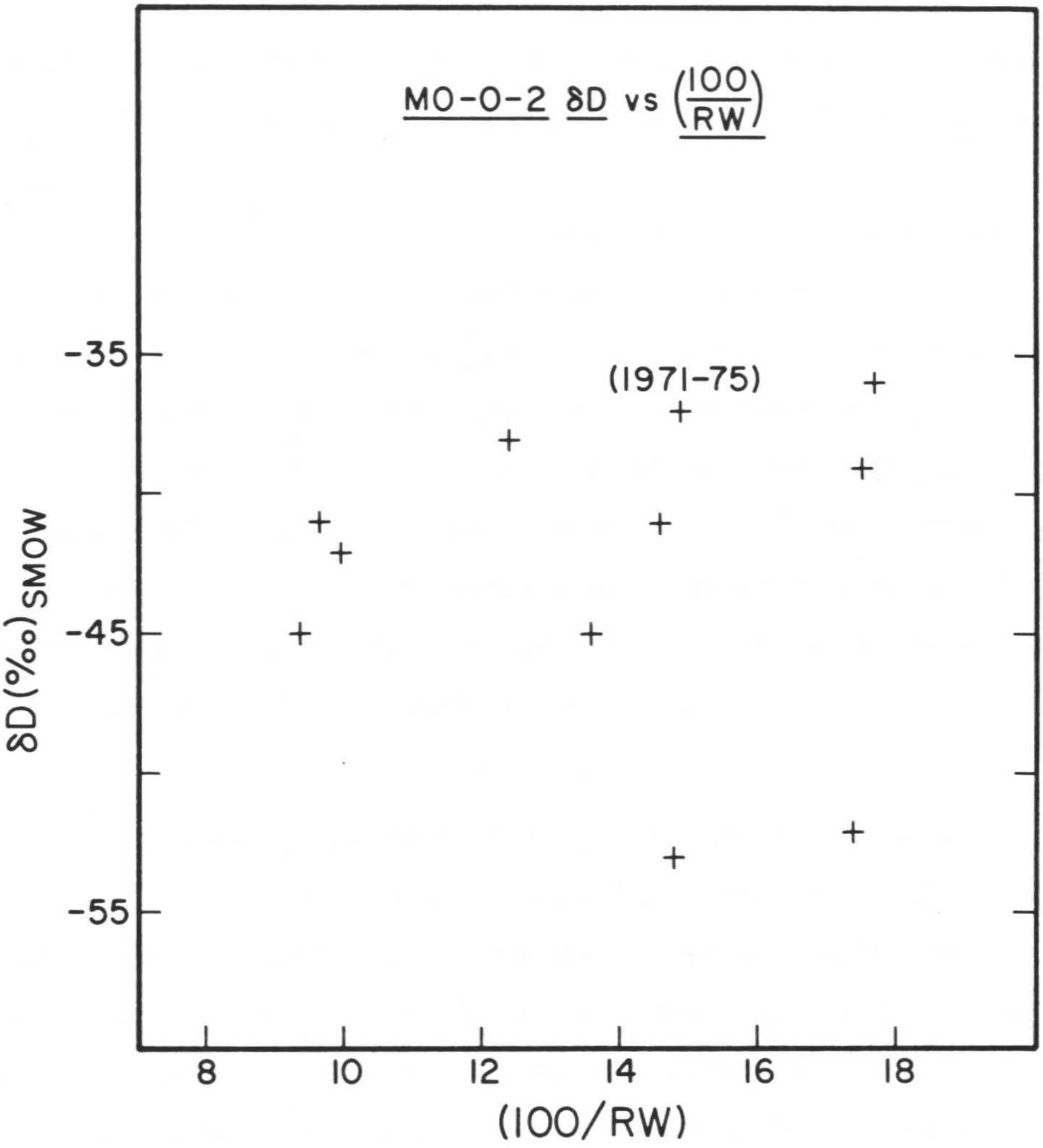
Since aggregate ring widths of five-year intervals were routinely measured for this work, they are included in plots of δD vs reciprocal ring width for each of the tree ring sequences. The reciprocal of ring width was employed to maintain consistency with literature discussions of this variable (Wigley, et al, 1978; also see Section 3 of this thesis).

The plot of MO-0-2 δD values vs reciprocal ring width is found in Figure 5-8. Firstly, there is no general trend to the data and secondly, because of this, the 1971-75 point does not stand out. Thus, in the case of MO-0-2, there is no information from the internal data available at present that could point to the "anomalous" δD value of 1971-75.

However, it should be reiterated that even though the temperature range is small, for MO-0-2 there is a remarkably improved correlation of δD values with climate when the seasonally weighted δD values of the local precipitation are considered. Thus, MO-0-2 δD values seem to be

Figure 5-8

A plot of the δD values of MO-0-2 against the reciprocal of the aggregate ring width of the corresponding five-year intervals. There is no relationship between these variables in this tree and consequently, no information about the "anomalous" interval 1971-75.


MO-0-2 δD vs (100/RW)
(1971-75)
-35
-45
-55
δD (‰)SMOW
8
10
12
14
16
18
(100/RW)

varying for the most part in response to the difference between summer and winter temperatures as weighted by summer precipitation. Furthermore, the tree δD vs X_s $(T_s - T_w)$ temperature coefficient is positive which is to be expected if the local annual weighted precipitation varies with temperature (see Section 4). Therefore, the conclusion that the tree is recording δD variations of the local meteoric water is further enhanced.

The concept of precipitation-weighted temperature that was applied to MO-0-2 δD variations will be used in the same fashion for tree sequences to be subsequently discussed. Furthermore, the δD vs reciprocal ring width relationship will be plotted for all of these samples to determine if the previously mentioned theoretical criterion for identifying climatically anomalous δD values has application in any specific cases. Unless average annual unweighted temperature was found to correlate significantly with tree ring δD values, plots of these two parameters are not included with each subsequent tree sequence.

Col-DF-1

This Douglas Fir grew in Mt. Vernon Canyon, Jefferson County, Colorado. Consequently, the weather data from nearby Denver, Colorado were employed for comparison with the tree δD values. Col-DF-1 was discussed in Section 3 of this thesis. It contains reaction wood, and apparently as a consequence of this, it exhibits hydrogen isotopic heterogeneity for some five-year samples around the circumference of the tree. Therefore, two different radial sections from this tree may produce different patterns of δD variation through time. The plots of δD variation vs age for two diametrically opposed radial sections are found in Figure 5-9. The "a" section represents the direction of the maximum radius in this asymmetric tree, while the "b" section represents the minimum (see Section 3). The "a" section was analyzed for virtually all of its radial extent (from 1816 to 1974). δD analysis of section "b" commenced with the year 1866. The total range in δD for Col-DF-1a is 44 per mil over the 159 year span of the sequence.

It is apparent from Figure 5-9 that there are some significant differences in detail between the isotopic patterns of the two sections. However, there are also some overall similarities. For example, there is a long term increase in δD values from 1871 to 1974 evident in both sections.

Denver weather records have only been kept since the middle 1870's. Consequently, the comparison of δD values in the Col-DF-1 a and b sequences with Denver climatic variables commences with the 1876-80 interval. Both annual and seasonal temperature and precipitation variations were compared with the δD variations. In no instance was a good overall correlation found. The best of these bad correlations as measured by the magnitude of the linear correlation coefficient is of δD vs average annual temperature. For Col-DF-1a the linear regression equation for comparison with annual temperature is:

$$\delta D = 4.84\ T(^{\circ}C) - 116 \qquad (5\text{-}10)$$

The linear coefficient is 0.471.

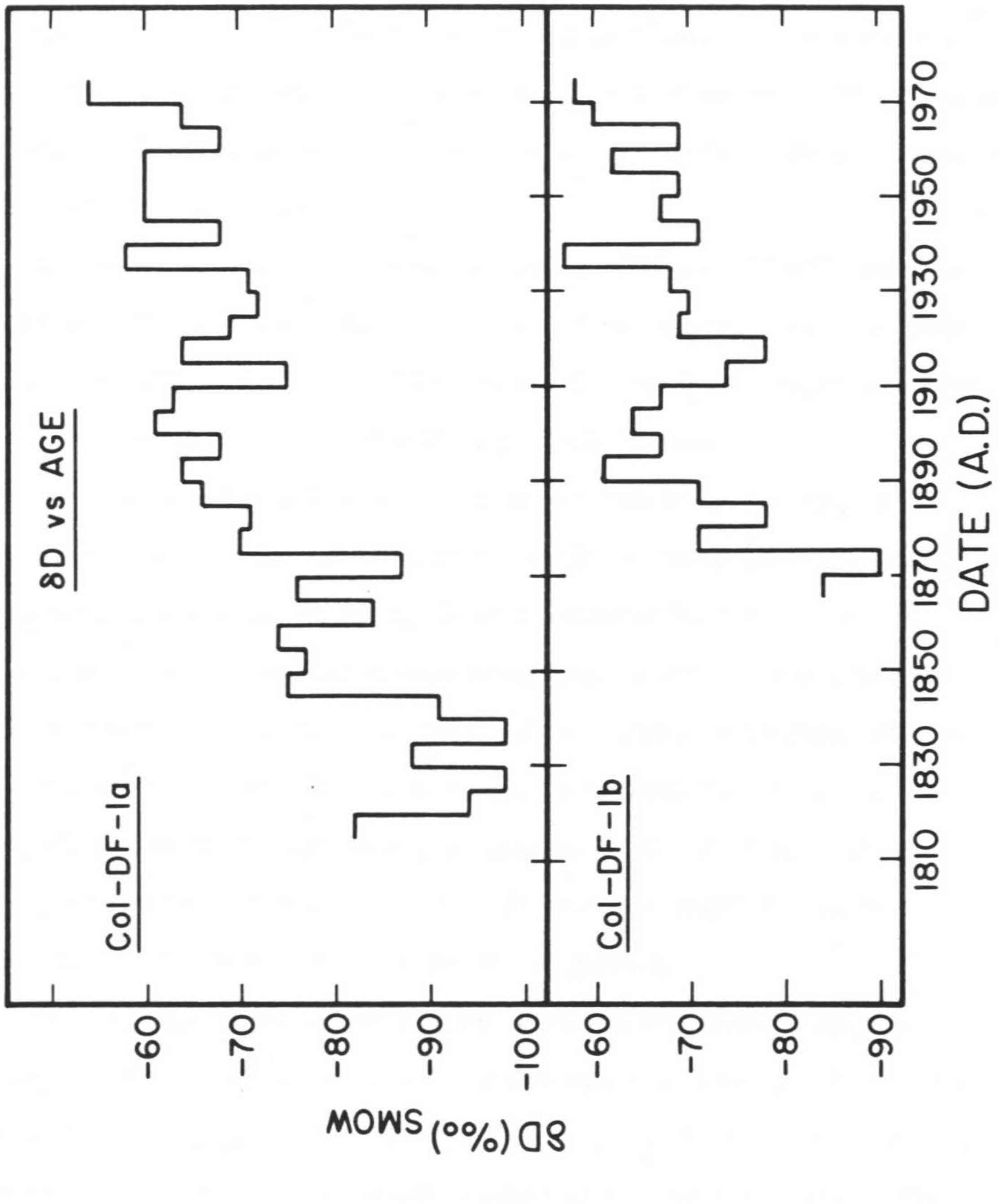
An analogous regression for Col-DF-1b yields:

$$\delta D = 2.48\ T(^{\circ}C) - 93 \qquad (5\text{-}11)$$

The linear correlation coefficient is 0.236. It was decided to apply the same two component climatic weighting approach to Col-DF-1 as was applied to MO-O-2. The isotopic summer was again defined as May, June,

Figure 5-9

The variations of the δD values of Col-DF-1a and Col-DF-1b with age. These time sequences represent two different radial directions within the same tree. It is noted that there are some differences in detail between the δD values of the two sequences. This may be due to the presence of reaction wood in this tree (see Section 3 of this thesis). Over the long term, however, the two sequences show similar trends.


δD vs AGE
Col-DF-Ia
Col-DF-Ib
-60
-70
-80
-90
-100
-60
-70
-80
-90
δD (‰) SMOW
1810
1830
1850
1870
1890
1910
1930
1950
1970
DATE (A.D.)

July, August, and September. Of the three parameters defined in equations (5-6, 5-7, and 5-8), the $X_s\ (T_s - T_w) + T_w$ expression exhibited the best correlation. The plots of δD vs $\left[X_s\ (T_s - T_w) + T_w\right]$ for the "a" and "b" sections of Col-DF-1 are found in Figure 5-10 and the data are listed in Table 5-3. Even though the plots of Figure 5-10 represent an "improved" correlation, it is obvious that they still do not represent well-correlated parameters.

Interestingly, in both plots of Figure 5-10 the 1971-74 interval exhibits a distinctly positive δD shift off the approximately defined general "trend" of the data. This is similar to the behavior observed for the interval 1971-75 in the Missouri oak (MO-0-2).

Because Col-DF-1 exhibits isotopic heterogeneity for <u>27%</u> of the five-year intervals in the two radial sections, it is possible that a portion of the scatter in Figure 5-10 is induced by this property. Without knowing the precise causal relationship between the presence of reaction wood in a tree and the resulting hydrogen isotope heterogeneity, it is not possible to know how to correct for the latter. However, it was felt that taking an average of the δD values of each five-year interval from the "a" and "b" sections might partially compensate for some of the existing heterogeneity.

The average δD values of the two sections are plotted against $X_s\ (T_s - T_w) + T_w$ in Figure 5-11. Again, the interval 1971-74 is clearly distinct from the general trend of the data. Furthermore, the interval 1891-95 also appears to be somewhat displaced above the overall data trend. Because both the 1971-74 and 1891-95 samples have δD values which agree within experimental error for the "a" and "b" sections

Figure 5-10

Comparisons of the δD values of Col-DF-1a and Col-DF-1b with the parameter $X_s (T_s - T_w) + T_w$ as calculated from Denver, Colorado, meteorological data (see text). The linear regression of these variables for Col-DF-1a yields the equation:

$$\delta D = 2.63 \left[X_s (T_s - T_w) + T_w \right] - 98$$

The correlation coefficient is 0.358.

A linear regression of the data for Col-DF-1b results in the equation:

$$\delta D = 2.74 \left[X_s (T_s - T_w) + T_w \right] - 101$$

The linear correlation coefficient is 0.350. The two equations are similar, but neither represents a good correlation between the variables. The compared data span the interval 1876-1974 and in each instance except one, five-year intervals are compared. The one exception is the four-year interval 1971-74.

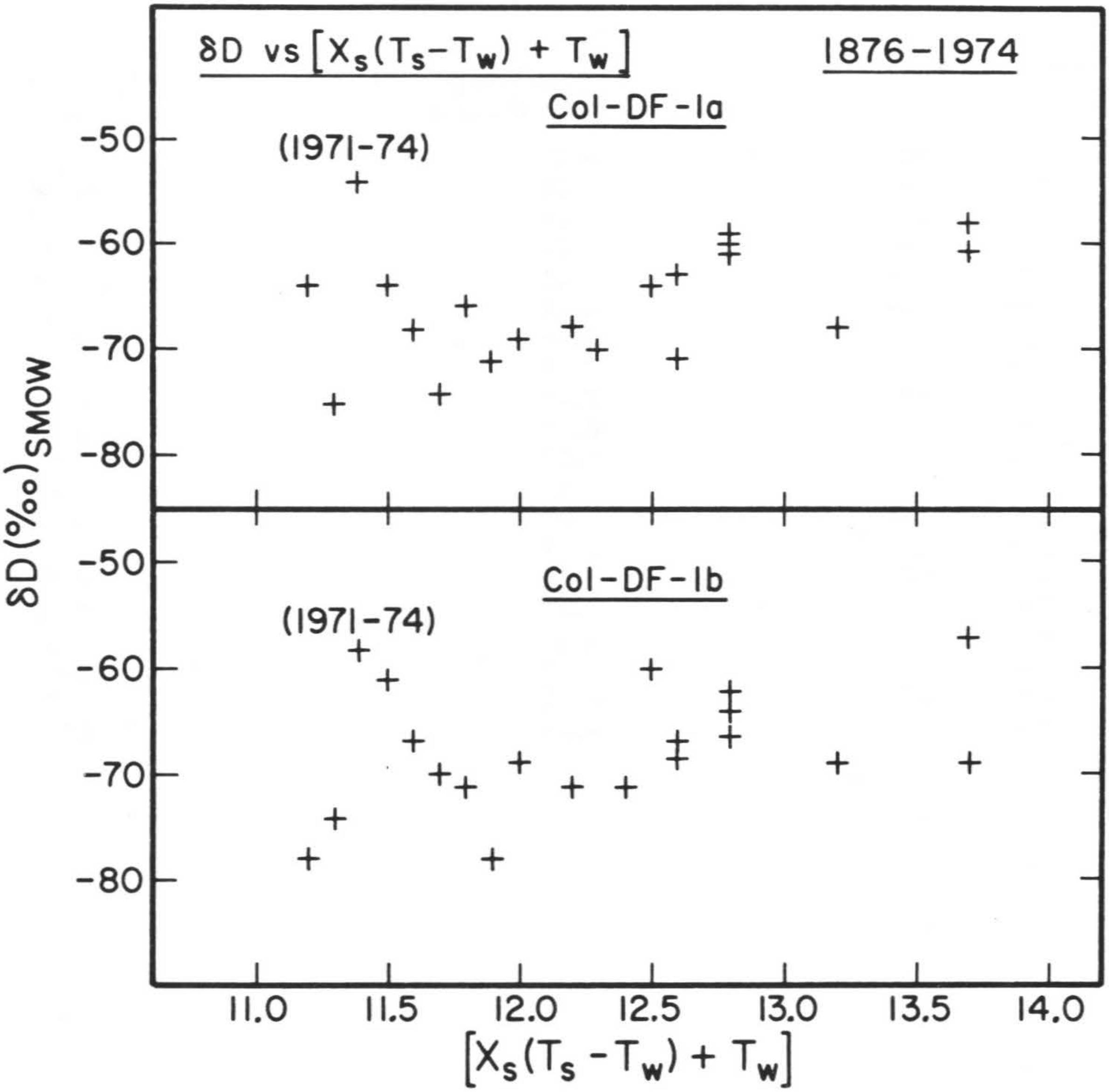

δD vs [X_s(T_s−T_w) + T_w]
1876−1974
Col-DF-1a
(1971-74)
Col-DF-1b
(1971-74)
-50
-60
-70
-80
δD (‰)SMOW
11.0
11.5
12.0
12.5
13.0
13.5
14.0
[X_s(T_s − T_w) + T_w]

Table 5-3: δD Values and $X_s(T_s - T_w) + T_w$
for Col-DF-1a and Col-DF-1b
S = (May, June, July, August, September)

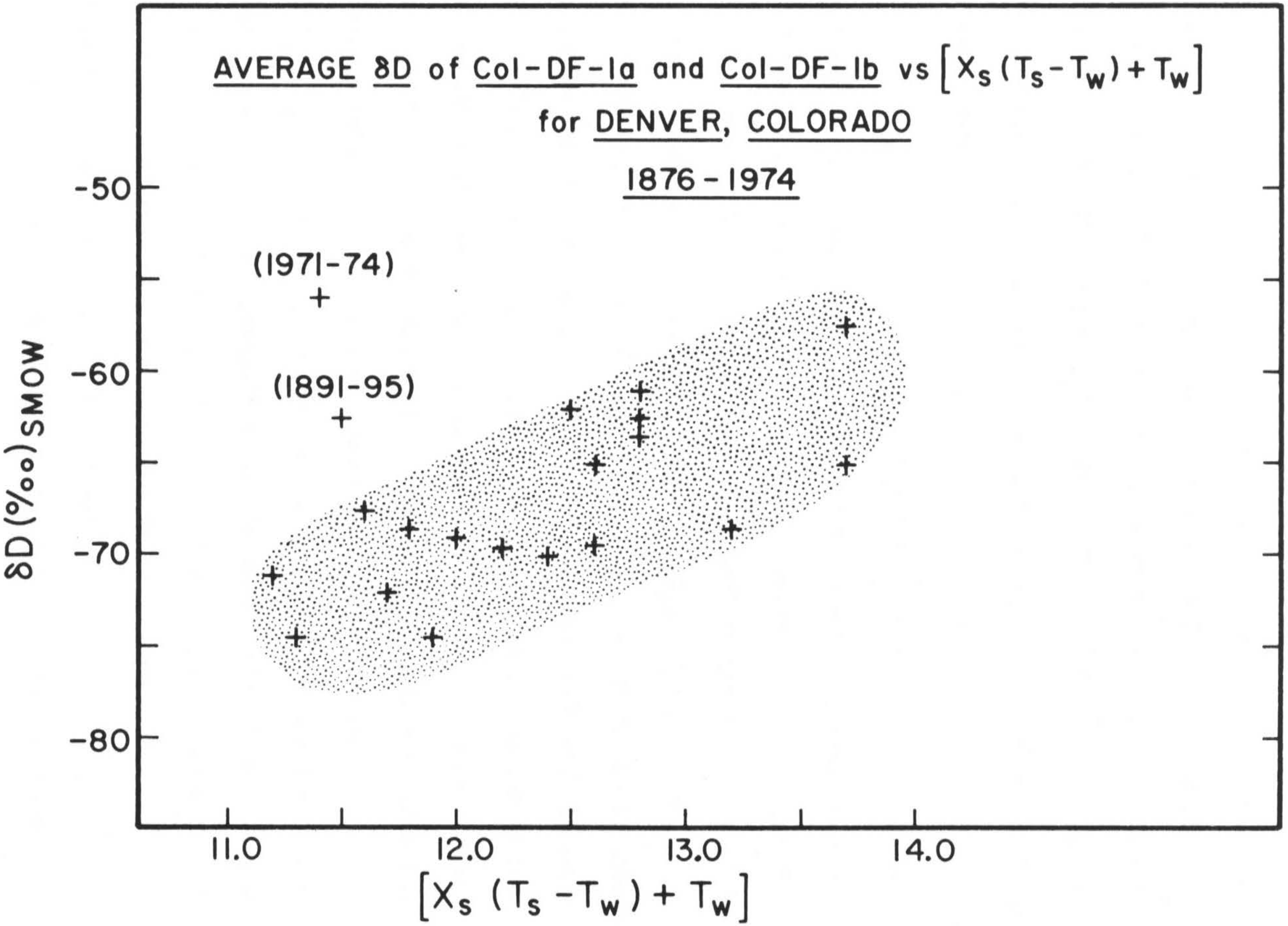
Interval	$X_s(T_s - T_w) + T_w$	δD	
		"a"	"b"
1876-80	12.4	-70	-71
1881-85	11.9	-71	-78
1886-90	11.8	-66	-71
1891-95	11.5	-64	-61
1896-1900	11.6	-68	-67
1901-05	12.8	-61	-64
1906-10	12.6	-63	-67
1911-15	11.3	-75	-74
1916-20	11.2	-64	-78
1921-25	12.0	-69	-69
1926-30	11.7	-74	-70
1931-35	12.6	-71	-68
1936-40	13.7	-58	-57
1941-45	12.2	-68	-71
1946-50	12.8	-60	-67
1951-55	13.7	-61	-69
1956-60	12.8	-60	-62
1961-65	13.2	-68	-69
1966-70	12.5	-64	-60
1971-74	11.4	-54	-58

Figure 5-11

The average δD values for corresponding five-year intervals of Col-DF-1a and Col-DF-1b plotted against $X_s\ (T_s - T_w) + T_w$ as calculated from Denver, Colorado, meteorological data (see text). The stippled region in the figure is interpreted to be the general trend of the data in the diagram. The linear regression of the data in the stippled region yields the expression:

$$\delta D = 4.64 \left[X_s\ (T_s - T_w) + T_w \right] - 125$$

The correlation coefficient is 0.723. The points representing the intervals 1891-95 and 1971-74 are interpreted to be "anomalous" and are discussed in the text.


AVERAGE δD of Col-DF-Ia and Col-DF-Ib vs $[X_s(T_s-T_w)+T_w]$
for DENVER, COLORADO
1876-1974
(1971-74)
(1891-95)
δD (‰) SMOW
-50
-60
-70
-80
11.0
12.0
13.0
14.0
$[X_s(T_s-T_w)+T_w]$

(Table 5-3), it does not seem likely that the positive shifts observed in Figure 5-11 are a consequence of the isotopic heterogeneity phenomenon.

It is apparent that the general trend defined by the averaged δD data of Figure 5-11 is "tighter" than those of the separate sections of Figure 5-10. A linear regression of the averaged δD vs $X_s (T_s - T_w) + T_w$ data of Figure 5-11, exclusive of the 1891-95 and 1971-74 points, yields the expression:

$$\delta D = 4.64 \left[X_s (T_s - T_w) + T_w \right] - 125 \qquad (5\text{-}12)$$

The linear correlation coefficient is 0.723. Similar regressions for the "a" and "b" sections separately yield correlation coefficients of 0.644 for "a" and 0.652 for "b", again with 1891-95 and 1971-74 excluded. When these regressions of δD against $X_s (T_s - T_w) + T_w$ were compared with the regression of the "a" and "b" average δD vs annual temperature, the latter yields a correlation coefficient of only 0.486 with 1891-95 and 1971-74 excluded. Thus, although one must exercise caution in the interpretation of these correlation coefficients, it does seem probable that the δD values of the Col-DF-1 sequence are responding to variations in the δD values of average annual precipitation, since the $X_s (T_s - T_w) + T_w$ parameter was derived from a characterization of the isotopic behavior of the precipitation. It should be mentioned that the temperature coefficient of equation (5-12) has a value (4.64) which is well within the range of temperature coefficients expected for precipitation (see Section 4 of this thesis).

However, in the case of Col-DF-1, there is a variation due to isotopic heterogeneity within the tree that appears to be superimposed on the variation induced by precipitation. Therefore, it would be best to avoid trees with reaction wood, if one is seeking to isotopically analyze tree ring sequences for possible climatic interpretation (see Section 3 of this thesis). Except for Col-DF-1, the tree ring sequences that are compared with climatic variables in this work seem to be free of reaction wood.

The fact that the 1971-74, 75 interval is apparently shifted off the general data trend of δD vs local climatic for both Col-DF-1 and MO-O-2 suggests that it may be a consequence of more than just local site or tree physiology effects. The additional fact that the δD shift is positive at both locations further implies the possibility of a link between the isotope effects at the two sites.

The plots of δD vs reciprocal ring width for Col-DF-1a and Col-DF-1b are found in Figures 5-12 and 5-13 respectively. In neither case is there a clear correlation between the two variables. However, in both cases, but especially in the "a" section, 1971-74 lies at an extremum position. Thus, to the extent that the ring widths and δD values in this tree are responding to coupled, but possibly different, climatic variables, the "anomalous" position of the 1971-74 point in Figure 5-12 may foreshadow its behavior in Figure 5-11. It should be pointed out that the aggregate ring width of the 1971-74 interval has been normalized to a "5-year" value by assuming that the measured width is 4/5 of the value it would be if there were five years in the sample.

FCA-WS-1

FCA-WS-1 is a white spruce from a forest approximately 150 Km west-northwest of Edmonton, Alberta. The tree was old enough to be sampled over the time span from 1891 to 1975. The nearest meteorological

Figure 5-12

A plot of the δD values of Col-DF-1a against the reciprocal of the aggregate ring width of the corresponding five-year intervals. The point representing the interval 1971-74 is clearly distinct from the general cluster of the data. There does not appear to be any overall relationship between δD and reciprocal ring width.

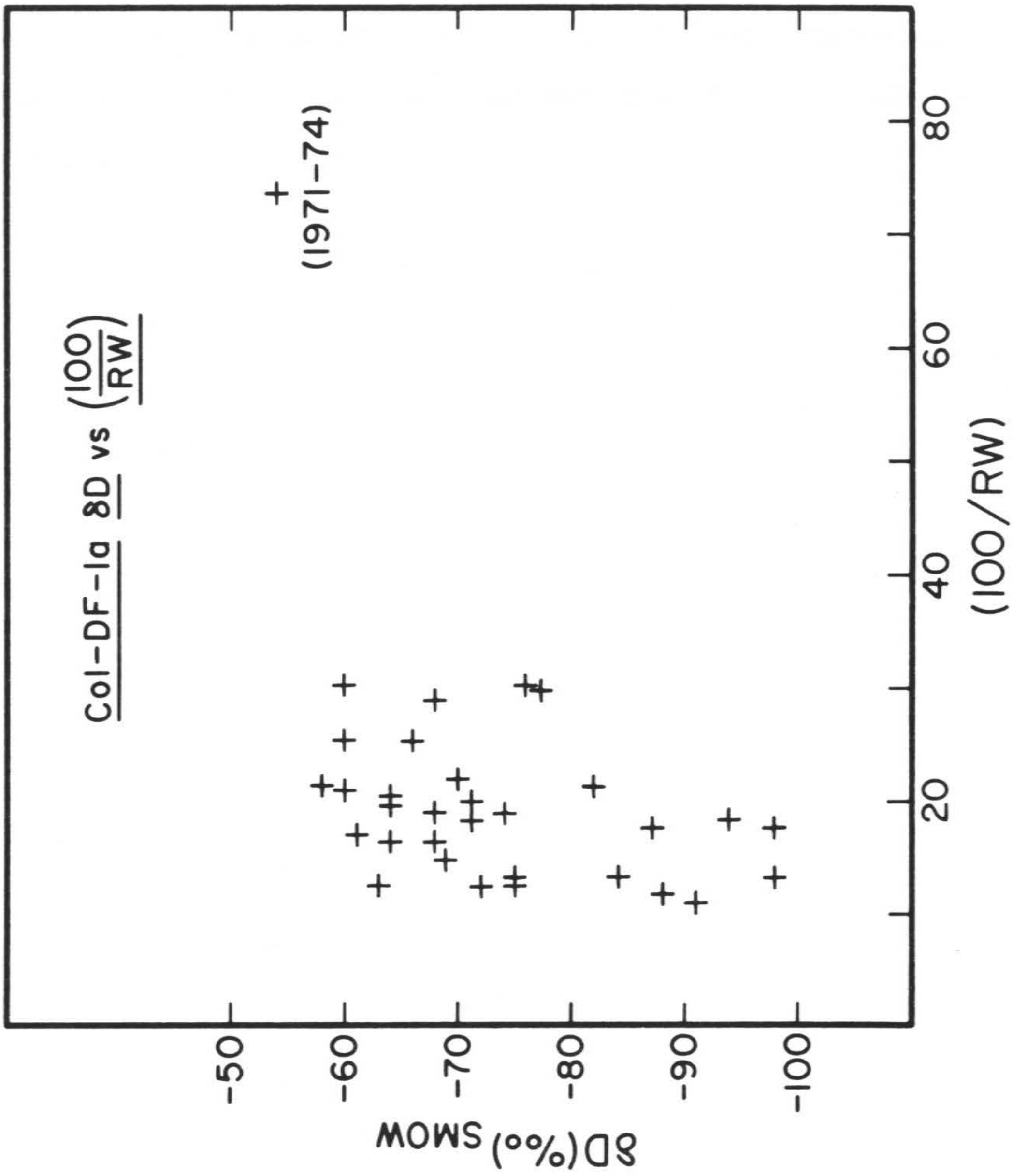
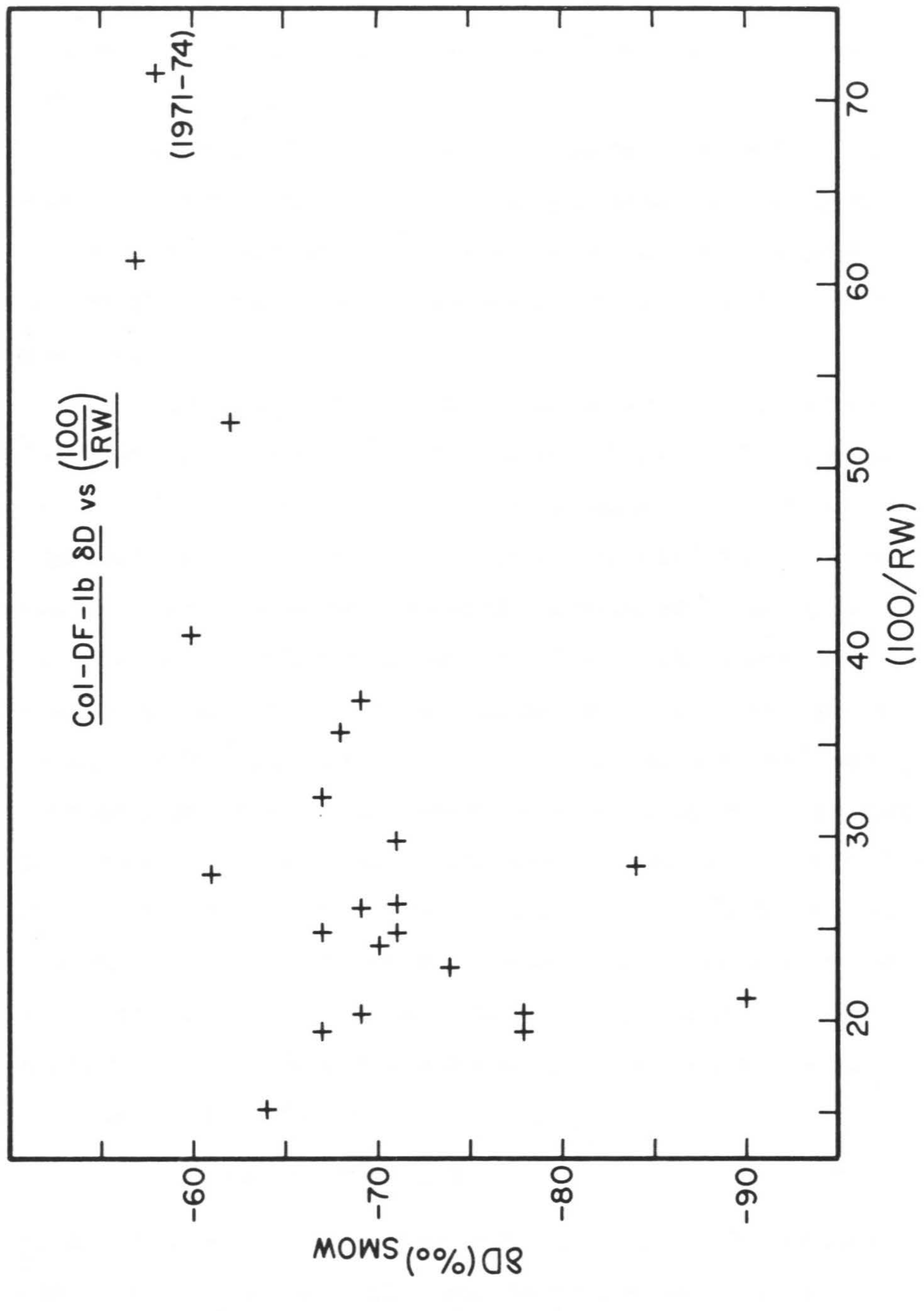

Col-DF-1a δD vs (100/RW)
(1971-74)
δD(‰) SMOW
-50
-60
-70
-80
-90
-100
20
40
60
80
(100/RW)

Figure 5-13

A plot of the δD values of Col-DF-1b against the reciprocal of the aggregate ring width of the corresponding five-year intervals. There is a larger degree of scatter for these data then was evident for the data of Col-DF-1a in Figure 5-12. However, the point representing the interval 1971-74 also occupies an extremum position in the plot of Col-DF-1b.


Col-DF-Ib δD vs (100/RW)
(1971-74)
20
30
40
50
60
70
(100/RW)
-60
-70
-80
-90
δD(‰) SMOW

station with instrumental records of this age is Edmonton, Alberta. Therefore, the Edmonton climatic records were obtained for comparison with the δD variations in the spruce.

The plot of the FCA-WS-1 δD values vs age is in Figure 5-14. The range of δD values over the age of the tree is 33 per mil. However, the bulk of this range is produced by the very negative δD value of -163 per mil. There is no overall trend with time of the δD values in this tree.

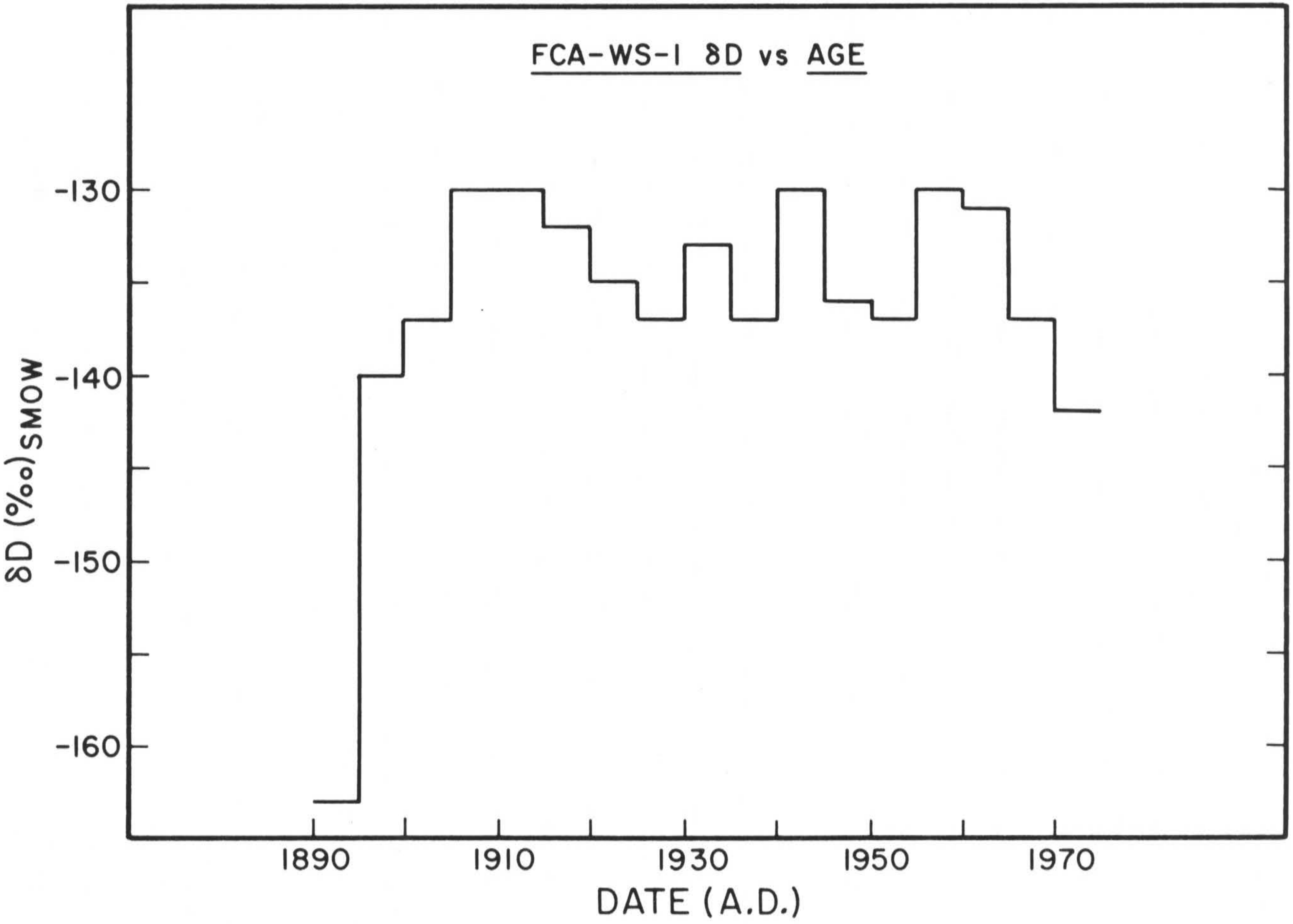
Gray and Thompson (1976, 1977) analyzed a different spruce from the Edmonton area for the $\delta^{18}O$ values of its cellulose. They found an exceptionally good correlation of tree $\delta^{18}O$ values with average annual temperature over the interval 1882 to 1969. Their tree was sectioned into five-year samples, but these sample intervals are offset by one year from the intervals used to subdivide FCA-WS-1 for δD analysis in this thesis. Thus, whereas a five-year sample from FCA-WS-1 would span the interval 1951-55, a similar sample from Gray and Thompsons' tree would cover the years 1950-54. Consequently, there is only an 80% overlap in time of five-year samples from the two trees. Nevertheless, it is of interest to compare the δD values measured in FCA-WS-1 for this thesis with the published $\delta^{18}O$ values of the Edmonton spruce analyzed by Gray and Thompson (1977). If the very negative δD value of 1891-95 is eliminated from the comparison, a linear regression of the five-year intervals that have 80% overlap yields the equation:

$$\delta D = 3.97\ \delta^{18}O - 230 \tag{5-13}$$

The linear correlation coefficient is 0.778 for the 15 compared samples. When the small range of δD values and the differences in isotopes,

Figure 5-14

The variation of the δD values of FCA-WS-1 with age over the interval 1891-1975. The largest fraction of the total variance of δD in this tree arises from the difference between the δD value of the 1891-95 interval and the δD values of the balance of the sample intervals in the tree.


FCA-WS-1 δD vs AGE
-130
-140
-150
-160
δD (‰) SMOW
1890
1910
1930
1950
1970
DATE (A.D.)

sample locale, and five-year sample intervals are considered, the level of correlation between the δ values in the two trees is relatively high. However, the correlation is severely disrupted when the δD value for 1891-95 is included in the compared data. Thus, there are also some apparently important differences in the nature of the δD and $\delta^{18}O$ variations in the two trees.

For example, a plot of the δD values of FCA-WS-1 vs average annual Edmonton temperature does not result in a well-defined linear trend (Figure 5-15). Even if the 1891-95 point is eliminated, the linear regression of δD values vs annual temperature has a correlation coefficient of only 0.587.

With the assumption that FCA-WS-1 incorporated waters whose δD values reflected those of the average annual precipitation, the seasonally weighted, isotopic two component model (Equation 5-3) can be applied to attempt to characterize the δD variations. The various parameters of equations (5-6) through (5-8) were calculated and compared with the δD variations of FCA-WS-1. Examination of the IAEA isotopic data for monthly precipitation in Edmonton suggests that appropriate choices of isotopic summer months in this region are May, June, July, and August. It is found that overall, none of the parameters of equations (5-6) through (5-8) are better correlated with the δD variations than is the average annual temperature. However, the plot of δD vs $X_s (T_s - T_w) + T_w$ produces an interesting array of points. This plot is in Figure 5-16. The data are compiled in Table 5-4.

With the exception of the 1891-95 sample, the data in Figure 5-15 have been divided into two domains as indicated by the stippling. This division is based on both a visual perception of the data trends and

Figure 5-15

A comparison of the δD values of FCA-WS-1 with the corresponding average annual temperatures of Edmonton, Alberta. There is no overall relationship apparent in these data. The compared data span the years from 1891-1975.

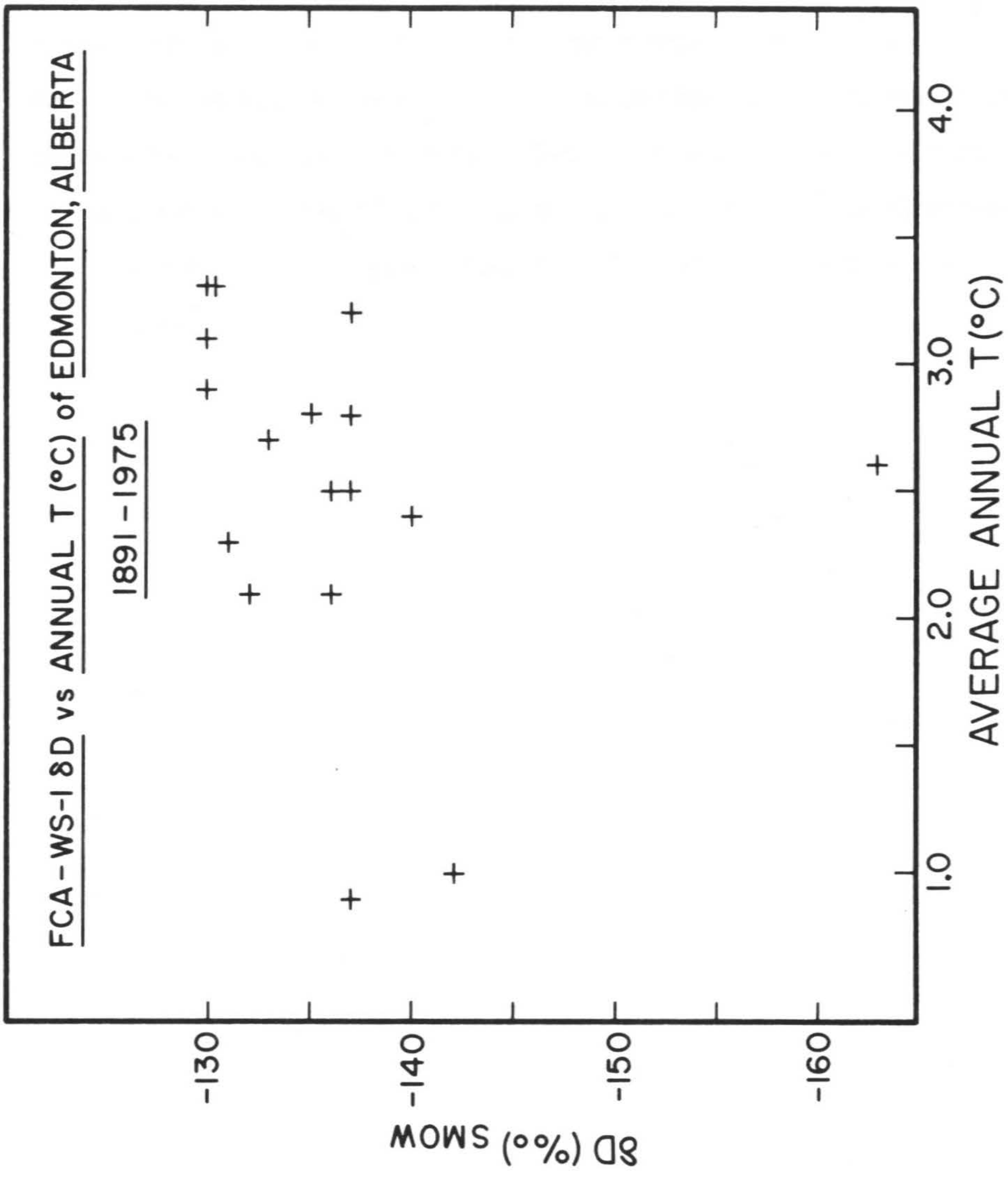

FCA-WS-1 δD vs ANNUAL T (°C) of EDMONTON, ALBERTA
1891-1975
δD (‰) SMOW
-130
-140
-150
-160
AVERAGE ANNUAL T (°C)
1.0
2.0
3.0
4.0

Figure 5-16

A comparison of the δD values of FCA-WS-1 with $X_s (T_s - T_w) + T_w$ as calculated from Edmonton, Alberta, meteorological data. The overall correlation between these data is not significant. However, there appear to be two dominant domains within which there is a more systematic relationship between the variables. This could be interpreted to mean that there are two types of large scale climatic patterns that alternately prevail in the Edmonton region. The 1891-95 interval seems to be in a class by itself.

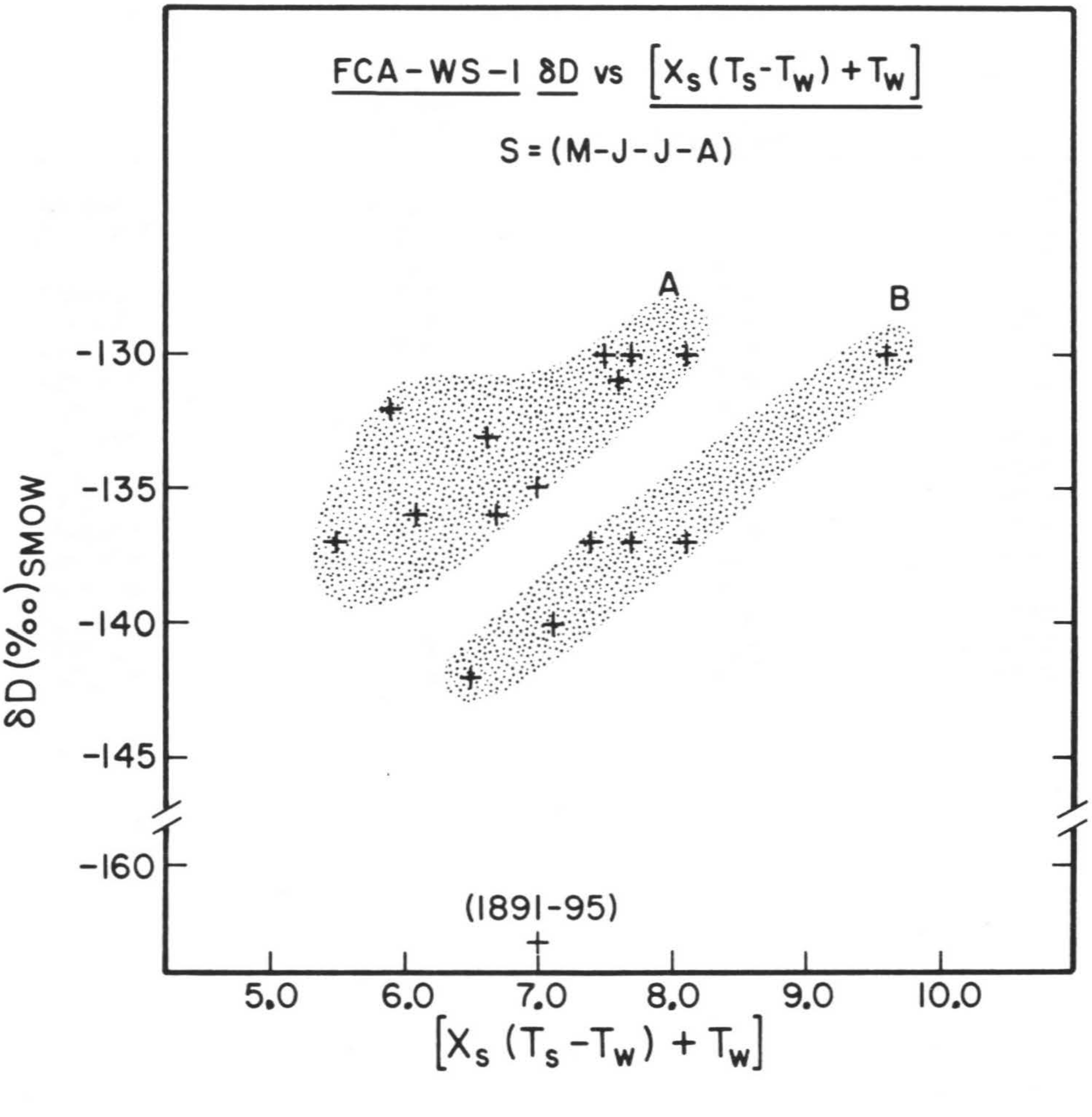

FCA-WS-1 δD vs [$X_S(T_S-T_W)+T_W$]
S = (M-J-J-A)
A
B
-130
-135
-140
-145
-160
δD (‰) SMOW
(1891-95)
5.0
6.0
7.0
8.0
9.0
10.0
[$X_S(T_S-T_W)+T_W$]

Table 5-4: Average Annual Temperature, $X_s(T_s - T_w) + T_w$ and δD Values for FCA-WS-1

s = (May, June, July, August)

Interval	Annual T(°C)	$X_s(T_s - T_w) + T_w$	δD
1891-95	2.6	7.0	-163
1896-1900	2.4	7.1	-140
1901-05	3.2	8.1	-137
1906-10	2.9	7.7	-130
1911-15	3.3	9.6	-130
1916-20	2.1	5.9	-132
1921-25	2.8	7.0	-135
1926-30	2.8	7.4	-137
1931-35	2.7	6.6	-133
1936-40	2.5	6.7	-136
1941-45	3.1	8.1	-130
1946-50	2.1	6.1	-136
1951-55	2.5	7.7	-137
1956-60	3.3	7.5	-130
1961-65	2.3	7.6	-131
1966-70	0.9	5.5	-137
1971-75	1.0	6.5	-142

an expectation of the behavior these trends might exhibit (equation 5-8). Region B in Figure 5-16 contains points representing the sample intervals 1896-1905, 1911-15, 1926-30, 1951-55, and 1971-75. A linear regression of the six points of region B yields the expression:

$$\delta D = 3.74 \left[X_s \; (T_s - T_w) + T_w \right] - 166 \qquad (5\text{-}14)$$

The correlation coefficient is 0.977. The regression of the ten points of region A produces the equation:

$$\delta D = 2.49 \left[X_s \; (T_s - T_w) + T_w \right] - 150 \qquad (5\text{-}15)$$

The correlation coefficient is 0.769.

Although a limited number of data with a small range of δD values have been used to define these regions, there is some support for this division in the data of Figure 5-16. It is observed that most data points in region B of Figure 5-16 represent local δD minimums in the time sequence of Figure 5-14. Thus, there is some reason to expect that the region B points could have been identified as a distinct group independently of a comparison with local climatic data. However, both the 1936-40 and 1946-50 intervals represent local δD minimum in Figure 5-14, and neither of these samples plots in region B of Figure 5-16. Therefore, the inherent distinguishability of the region B points in a time sequence is imperfect.

If the trends defined by the A and B regions of Figure 5-16 are real, they suggest that the δD values of the waters incorporated by the tree have varied in response to more than just local climatic changes. The likelihood of such a circumstance was discussed in Section 4 of this thesis.

The A and B domains in Figure 5-16 seem to imply that in the

Edmonton region there are only two large scale climatic patterns which commonly superimpose δD variations on those that would normally be associated with local climatic change. Interestingly, the intervals represented by the points of region B are generally similar to the intervals associated with drought in the Great Plains of North America. For example, the region B sample years 1896-1905, taken as a single group, follow closely on the heels of the Great Plains drought of the early 1890's (Roberts and Olson, 1975). Furthermore, the 1926-30 interval in region B immediately precedes the mid-1930's "Dust Bowl".

The preceding associations between Great Plains drought and the occurrence of points in region B of Figure 5-16 are not precise. However, there was a drought condition in the Great Plains centered on the year 1912 (Roberts and Olson, 1975). The interval 1911-15 in FCA-WS-1 encompasses this year and is also located in region B. Thus, the possible association between Great Plains drought and points in region B is accentuated by this example. Further evidence is provided by the interval 1951-55. It is represented by a point in region B and was also a time of drought in the Great Plains (Roberts and Olson, 1975).

The association of the 1971-75 point in region B with Great Plains drought is still somewhat tentative, but there appear to be indications from 1974 onward that episodic dry spells were occurring in various portions of this area (Roberts and Olson, 1975).

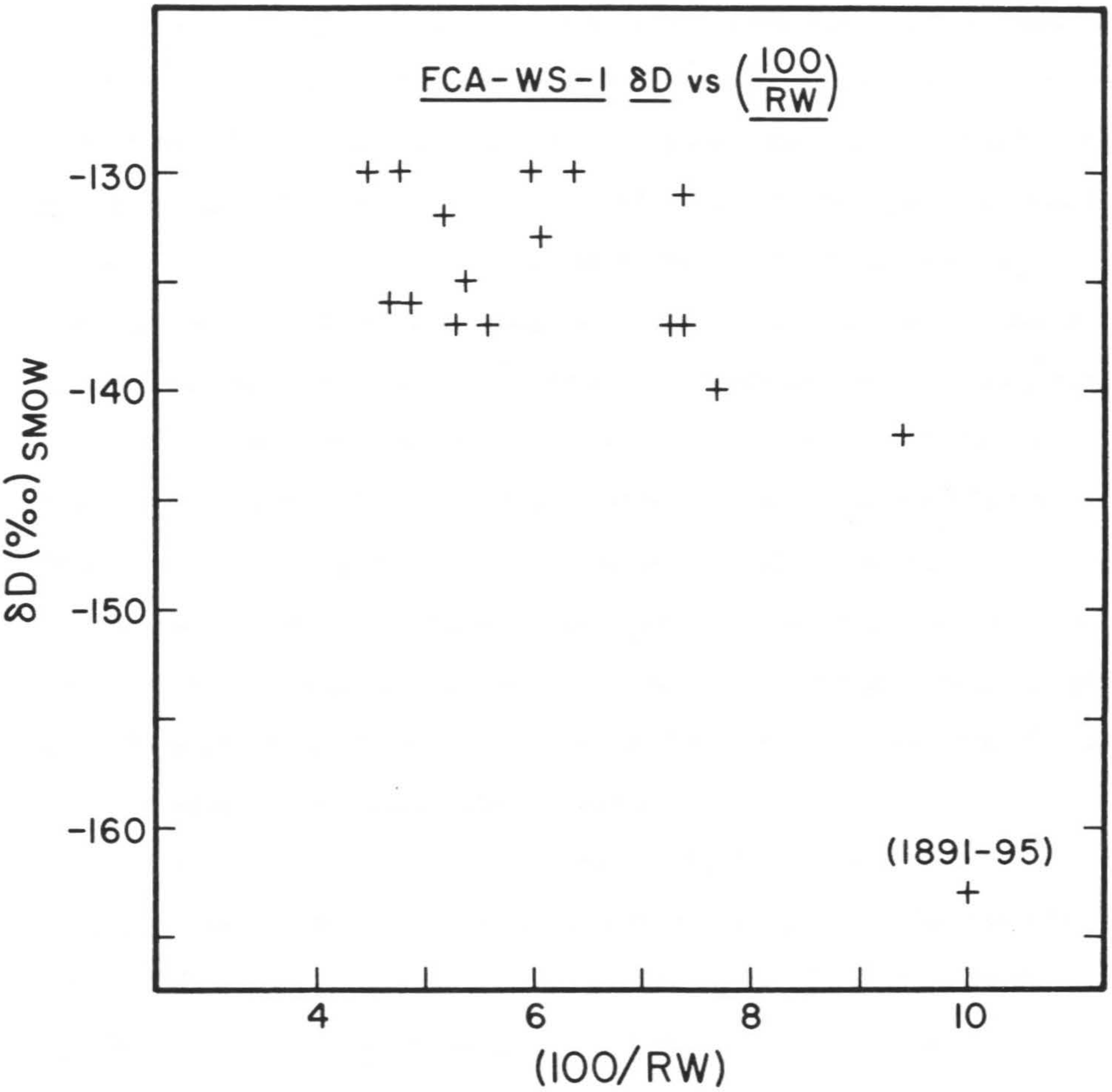
Up to now, the 1891-95 interval in FCA-WS-1 has been ignored. It falls well outside either of the two domains of Figure 5-16. It is not known if this is a consequence of physiological and/or local site conditions, or if it represents a bona fide large decrease in the δD value of precipitation during that time. That it might be the latter is indicated by two observations: (1) the δD values of region B represent relative decreases compared to A. Furthermore, the region B sample intervals may be associated with climatic patterns of drought in the Great Plains. It is obvious that the δD value of the 1891-95 sample is greatly decreased compared to samples in region A. Also, a Great Plains drought was centered in the 1891-95 interval. Thus, the δD value of the 1891-95 sample may be a reflection of climatic patterns that prevailed during this drought period. (2) There is a suggestion in the data of Col-DF-1 (see Figure 5-11) that the δD value of the 1891-95 interval is displaced from the general trend of δD vs local climate. Since both Denver and Edmonton are in physical proximity to the North American Great Plains and the climatic systems that dominate them, the anomalous δD values of 1891-95 at the two sites may be more than coincidence. Additional analyses of properly selected trees from these and other locations might help to resolve this question.

The plot of FCA-WS-1 δD values vs reciprocal ring width is found in Figure 5-17. There seems to be a trend of decreasing δD values with decreasing ring width, but it is ill-defined. However, the 1891-95 sample is clearly distinct from the balance of the samples in Figure 5-17. Thus, this plot may serve to signal the possibly complex climatic meaning of the 1891-95 δD value.

Returning to the question of the $\delta^{18}O$ variations measured by Gray and Thompson (1976, 1977) in an Edmonton spruce, it is not apparent why they should find that $\delta^{18}O$ values correlate only with local temperature, while the δD values measured in FCA-WS-1 for this thesis seem to be

Figure 5-17

A plot of the δD values of FCA-WS-1 against the reciprocal of the aggregate ring widths of the corresponding five-year intervals. There may be a weak relationship between these variables with δD decreasing as ring width decreases. The point representing 1891-95 appears to be set apart from the general cluster of the data points.


FCA-WS-1 δD vs (100/RW)
δD (‰) SMOW
-130
-140
-150
-160
4
6
8
10
(100/RW)
(1891-95)

responding to both local and large scale climatic changes. An explanation of this difference depends on more information than is presently available.

SAS-JP-1

SAS-JP-1 is a jack pine which grew near Porter Lake in the Canadian Northwest Territories. The growth site is approximately 250 Km northeast of Fort Smith, N.W.T., which represents the nearest long term source of meteorological data. The tree was felled in its 51st year and could be sectioned into five-year samples spanning the interval 1926-75. The climatic data from Fort Smith only date from 1931. Furthermore, there are some months in the interval 1936-40 for which no data are available.

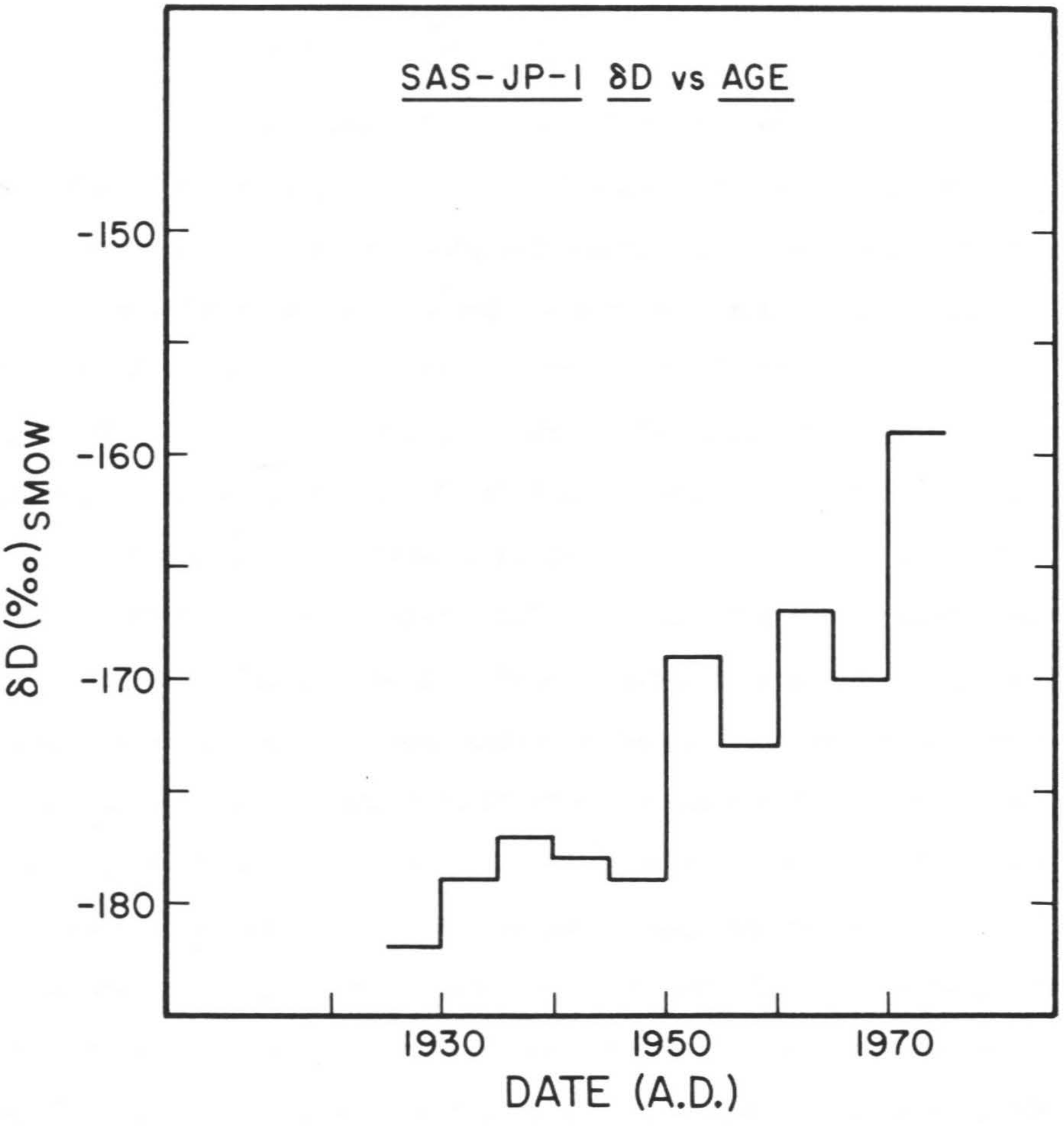
The δD variations through the tree ring sequence of SAS-JP-1 are depicted in Figure 5-18. Over the 50 year length of the record, there is a δD range of 23 per mil. Additionally, the δD values exhibit a long term increase from oldest to youngest samples. Both the 23 per mil δD range and the long term δD increase are in contrast to the small (12 per mil) δD range and absence of a time trend found in FCA-WS-1 about 950 Km to the southwest over this same 50 year interval.

Correlations of the δD variations in SAS-JP-1 with a variety of annual and seasonal temperature data were attempted. In addition the seasonally weighted, isotopic two-component model of equation (5-3) was applied to the local climatic data and compared to the SAS-JP-1 δD variations.

It was found that there is no correlation of δD values with the average annual temperature. The linear correlation coefficient for the regression of δD against annual temperature is only -0.107. Of all the other variables compared with the δD variations of SAS-JP-1, the best

Figure 5-18

The variation of the δD values of SAS-JP-1 with age over the interval from 1926 to 1975. There is a definite long term increase in the δD values with time from older to younger samples, with a total range in δD of 23 per mil.


SAS-JP-1 δD vs AGE
-150
-160
-170
-180
δD (‰) SMOW
1930
1950
1970
DATE (A.D.)

correlation was obtained with X_s $(T_s - T_w)$. Isotopic summer was defined as May, June, July and August. The variation of δD with X_s $(T_s - T_w)$ is plotted in Figure 5-19 and the data are listed in Table 5-2. The linear regression of these data produces the expression:

$$\delta D = 3.91 \; X_s \; (T_s - T_w) \; - 215 \qquad (5\text{-}16)$$

The correlation coefficient is 0.820. Thus, an assumption that the tree δD value is reflecting the δD value of annual precipitation and that the precipitation δD value is a weighted average of two seasonal components has again shown that there is order where, on first examination, none had seemed to exist. It should be noted that the δD value of the interval 1936-40 is not plotted in Figure 5-19, because as was previously mentioned, there are no Fort Smith temperature or precipitation data for several of the months in this interval.

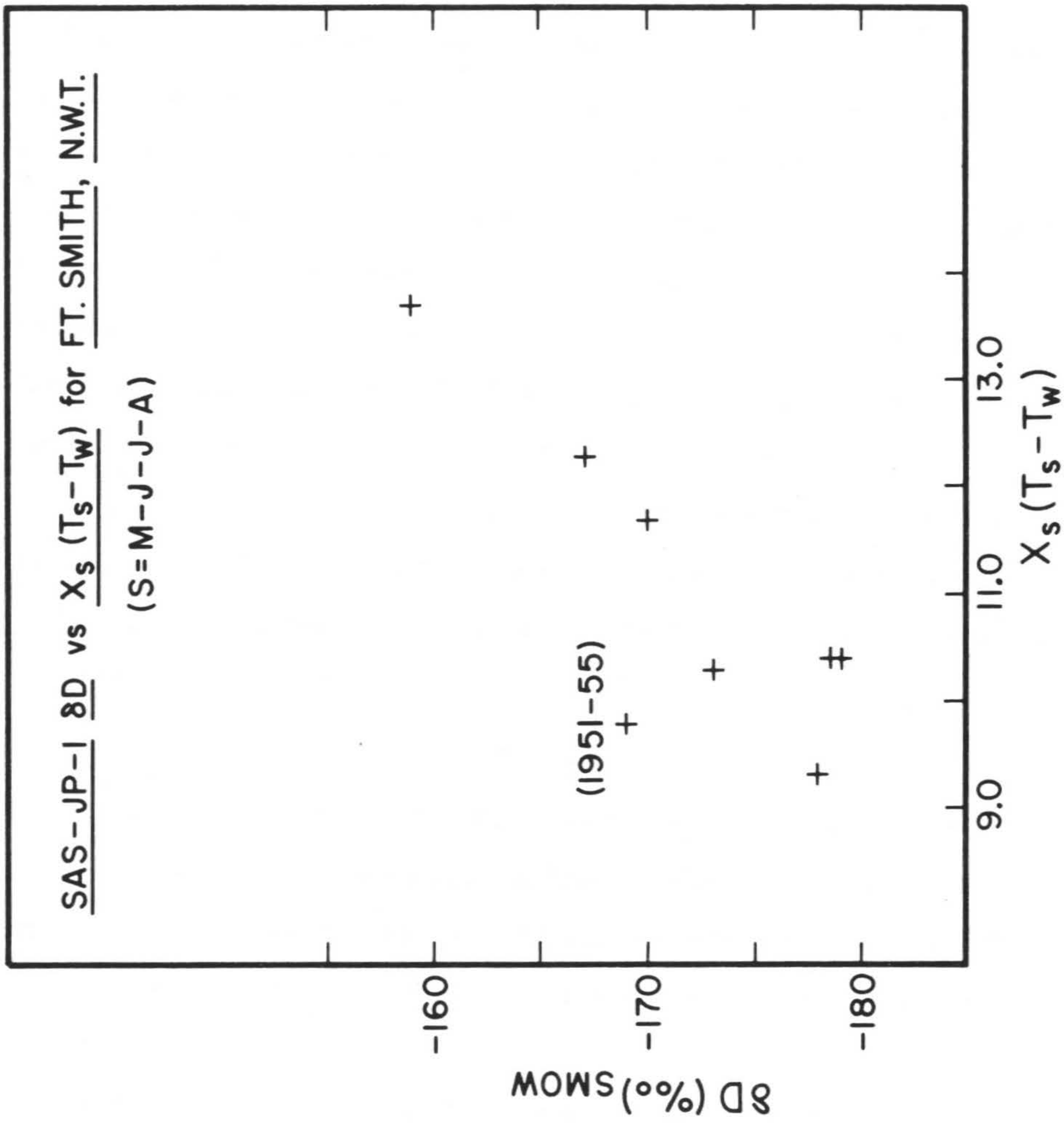
The displacements of individual δD values from the general trend of δD vs local climate that have been observed in the preceding three trees are not as strongly manifested in SAS-JP-1. There does seem to be a positive shift of the 1951-55 δD value off the local trend line. However, the trend of Figure 5-19 is defined by such a limited number of data that it is not possible to assess the significance of the 1951-55 departure. Consequently, for the 45 years from 1931 to 1975 (with the possible unknown exception of 1936-40) the δD values of precipitation at the site of SAS-JP-1 seem to have varied predominantly in response to local climate as represented by the parameter X_s $(T_s - T_w)$. Furthermore, the largest fraction of this response to X_s $(T_s - T_w)$ appears to arise from the variation of the ratio of summer precipitation to total annual precipitation. This follows from the fact that the correlation

Figure 5-19

A comparison of the δD variations of SAS-JP-1 with $X_s\ (T_s - T_w)$ as calculated from the meteorological data of Ft. Smith, Northwest Territory (see text). The linear regression of these data yields the equation:

$$\delta D = 3.91\ X_s\ (T_s - T_w) - 215$$

The correlation coefficient is 0.820. This strong correlation contrasts with the lack of a relationship between annual temperature and the δD values of SAS-JP-1. The point representing the interval 1951-55 is interpreted to be possibly "anomalous" (see text). The meteorological records for Ft. Smith are missing data for a number of months in the interval 1936-40. Consequently, this interval is not included in the data plotted in the figure.


SAS-JP-I δD vs X_S (T_S-T_W) for FT. SMITH, N.W.T.
(S=M-J-J-A)
(1951-55)
9.0
11.0
13.0
X_s (T_s-T_w)
-160
-170
-180
δD (‰) SMOW

coefficient for a linear regression of δD against X_s is 0.785. This latter value is not much smaller than the value of 0.820 for the correlation coefficient of equation (5-16).

The plot of the δD values of SAS-JP-1 vs reciprocal ring width is in Figure 5-20. In this instance any attempt to use this plot to deduce which δD values are not likely to be representative of local climate would lead to a spurious conclusion. The greatest departure of any δD value from the apparent δD vs ring width trend is for the 1966-70 sample. However, as can be seen from Table 5-2 and Figure 5-19 this interval falls quite nicely within the overall δD vs X_s (T_s - T_w) trend. Therefore, in this instance the δD vs reciprocal ring width plot was not merely inconclusive; it in fact provided the wrong information.

SAS-JP-1 provides the best example so far of temporal δD variations in trees responding to a climatic parameter other than temperature alone. In fact in this instance, average annual temperature showed no relationship whatsoever with the δD variations.

KSA-As-1

This aspen grew about 150 meters above the Knik River on the north side of West Twin Peak near Anchorage, Alaska. The tree was of sufficient age to yield five-year samples extending from 1936 to 1975 A.D. Meteorological records from Anchorage extend from 1941 to the present.

The δD variations of the tree ring sequence from KSA-As-1 are found in Figure 5-21. In the 40 year period spanned by this tree the δD values display a range of 28 per mil. There is also a persistent trend of increasing δD values from older to younger samples in this tree.

Figure 5-20

A plot of the δD values of SAS-JP-1 against the reciprocal of the aggregate ring widths of the corresponding five-year intervals. There seems to be a broadly defined relationship between these variables. This may indicate that both are varying in response to the same or related climatic variables.

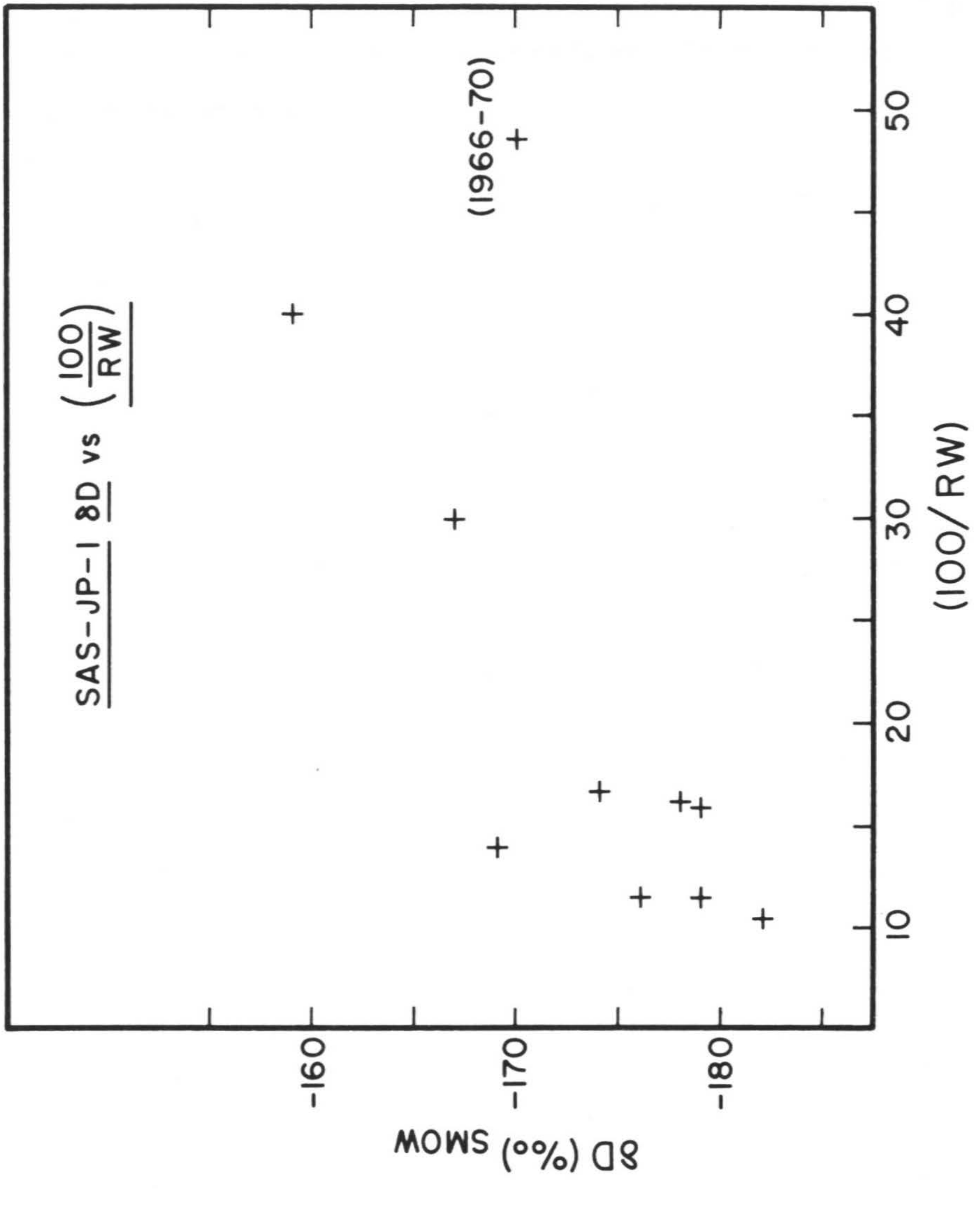
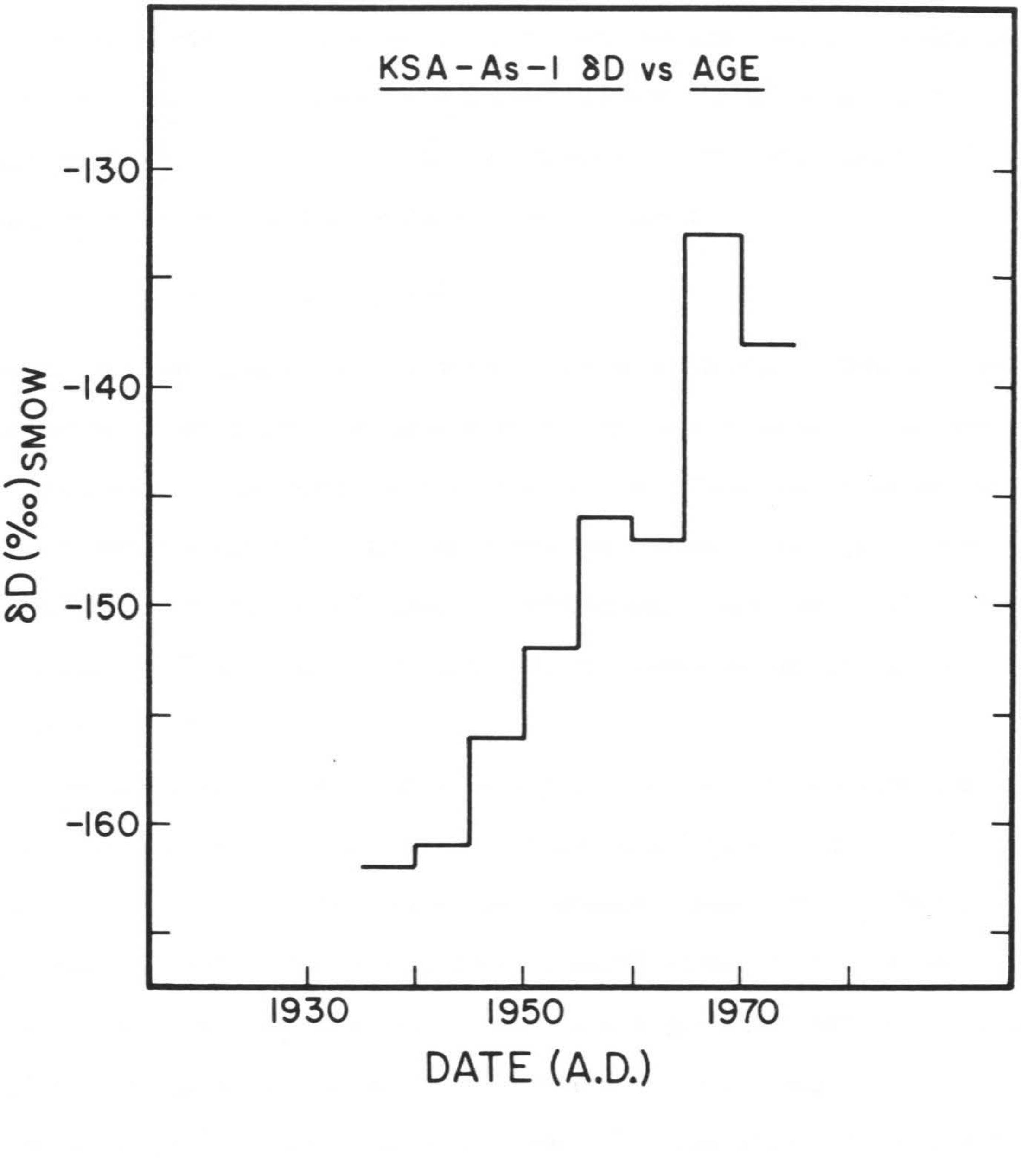

SAS-JP-1 δD vs $\left(\frac{100}{RW}\right)$
(1966-70)
-160
-170
-180
δD (‰) SMOW
10
20
30
40
50
(100/RW)

Figure 5-21

The variation of the δD values of KSA-As-1 with age over the interval from 1936 to 1975. Over this 40 year period, there is a distinct long term increase in δD values from older to younger samples. The total δD range is 28 per mil.


KSA-As-1 δD vs AGE
-130
-140
-150
-160
δD (‰) SMOW
1930
1950
1970
DATE (A.D.)

The comparison of the δD variations with average annual Anchorage temperature indicates that there is no relationship between these two variables. The linear correlation coefficient is only -0.013. Except for X_s, none of the parameters which assume that the tree is incorporating precipitation with average annual δD values correlate well with KSA-As-1 δD variations. In the case of X_s, the relationship has a negative slope with a correlation coefficient of -0.719. The equation for this regression is (with summer = June, July, August):

$$\delta D = -151.5 X_s - 93 \tag{5-17}$$

The physical meaning of the negative slope is entirely unclear if the tree is actually incorporating annual precipitation, because in temperate climates summer precipitation has more positive δD values than winter precipitation essentially without exception (IAEA). Thus, increases in the relative proportion of summer to winter precipitation should cause increases in δD values, rather than the decreases indicated by the preceding equation.

The resolution of this dilemma may lie in the rejection of the assumption that the tree is incorporating annual precipitation. If the water incorporated by the tree is predominantly summer rain, then it is possible that rainfall amount will be related to the δD variations. The greater the amount of rain, the greater the likelihood that its δD value will be more negative. Whether this is due to lesser degrees of evaporative isotopic enrichment when there is more rain, or to an effect of precipitation intensity on the weighted average δD value of the rainfall, or both, is uncertain at this time (see Section 4 of this thesis and Dansgaard, 1964). However, the expectation that rainfall amount can be negatively related to precipitation δD values suggests that such a relationship be examined for the KSA-As-1 δD variations.

A comparison of average monthly precipitation amounts for June, July, and August in Anchorage with KSA-As-1 δD values is shown in Figure 5-22. The data are listed in Table 5-5. Although there are only seven points defining the relationship, the trend does seem to be one of declining δD value with increasing amount of summer rain. The linear regression of these data results in the expression:

$$\delta D = -758.8\ W_s - 113 \tag{5-18}$$

W_s = average monthly summer precipitation in meters

The correlation coefficient is -0.674. Thus, the negative slope of the δD vs X_s relationship can be explained by assuming that the tree is incorporating only summer rain and that the δD value of this rain is "controlled" by a rainfall "amount effect".

Additional comparisons of KSA-As-1 δD variations were made with rainfall amounts for summers of various lengths. However, it was found that the best correlation was with the average monthly rainfall of June, July, and August.

Consequently, the variations of the δD values in KSA-As-1 may be evidence for the existence of a relationship between the amount of summer precipitation and its isotopic composition. However, there is no information to be gained on whether this relationship is tied to precipitation intensity, evaporation, or some combination of the two.

In addition this tree adds to the growing weight of evidence that tree δD variations can be related to local climatic variables other than temperature *per se*.

Figure 5-22

A comparison of the δD values of KSA-As-1 with the average monthly amount of summer precipitation. The "best-fit" definition of summer in this case is for the months June, July and August. The summer precipitation data are from Anchorage, Alaska. A linear regression of these data results in the expression:

$$\delta D = -758.8\ W_s - 113$$

The correlation coefficient is -0.674. The point representing the interval 1946-50 is considered to be "anomalous" (see text). The precipitation amounts are expressed in meters.

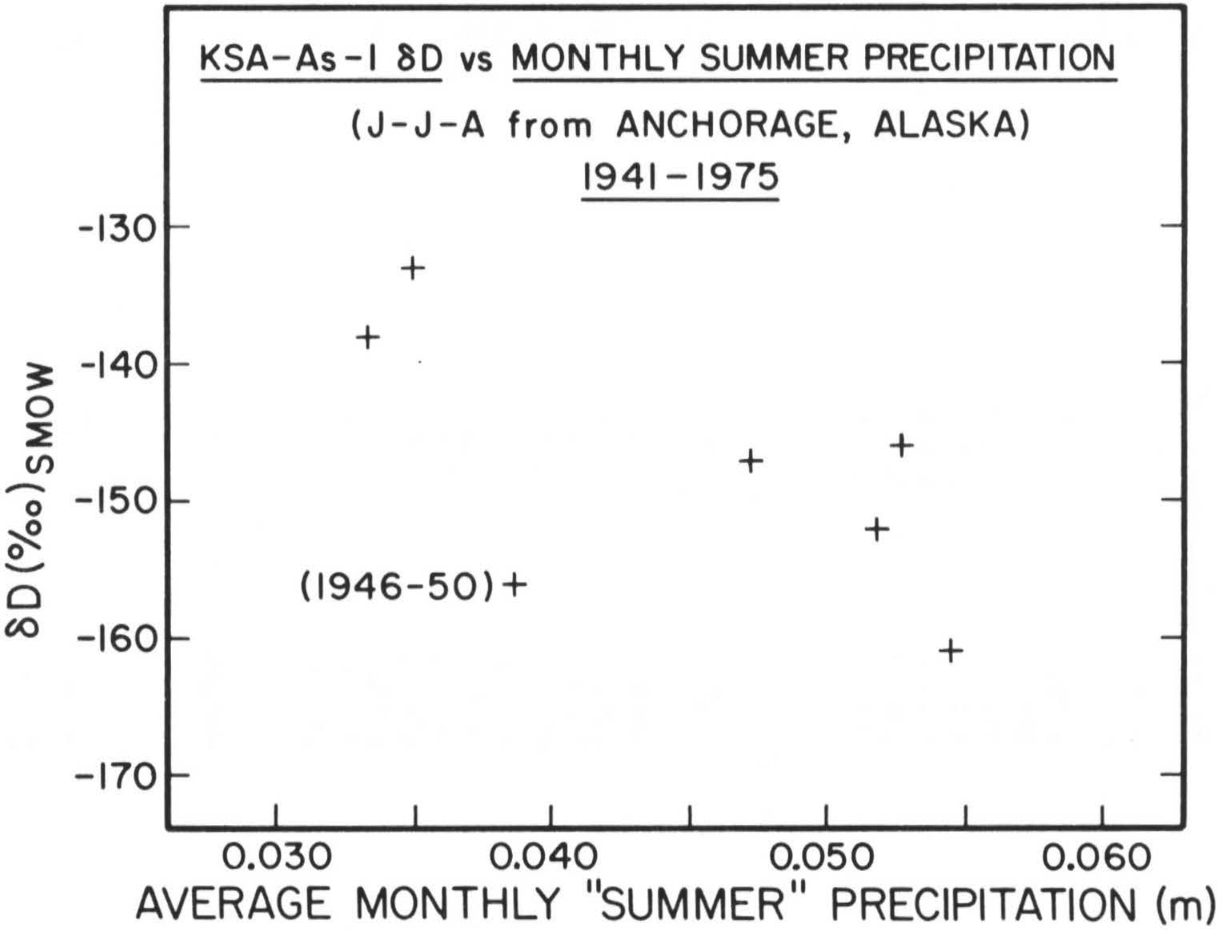

KSA-As-I δD vs MONTHLY SUMMER PRECIPITATION
(J-J-A from ANCHORAGE, ALASKA)
1941-1975
(1946-50)
-130
-140
-150
-160
-170
δD (‰) SMOW
0.030
0.040
0.050
0.060
AVERAGE MONTHLY "SUMMER" PRECIPITATION (m)

Table 5-5: X_s, W_s, and δD Values of KSA-As-1

T_s, W_s, and δD Values of BCT-12

Annual T, T_s, and δD Values of FA-As-1

Interval	S = June, July, August		
KSA-As-1	X_s	W_s	δD
1941-45	0.415	0.0546	-161
1946-50	0.357	0.0388	-156
1951-55	0.397	0.0519	-152
1956-60	0.414	0.0528	-146
1961-65	0.331	0.0473	-147
1966-70	0.320	0.0351	-133
1971-75	0.299	0.0336	-137

	S = April, May, June, July, August		
BCT-12	T_s (°C)	W_s	δD
1916-20	11.0	0.0364	-114
1921-25	11.6	0.0321	-104
1926-30	11.9	0.0357	-111
1931-35	11.7	0.0483	-116
1936-40	12.0	0.0553	-128
1941-45	11.9	0.0504	-121
1946-50	10.8	0.0555	-117
1951-55	10.3	0.0516	-123
1956-60	11.3	0.0544	-116
1961-65	11.3	0.0573	-130
1966-70	11.2	0.0483	-120

	S = June, July, August		
FA-As-1	Annual T(°C)	T_s (°C)	δD
1951-55	-3.7	14.5	-173
1956-60	-3.3	15.0	-167
1961-65	-4.0	14.3	-166
1966-70	-3.3	15.5	-156
1971-75	-3.7	15.9	-156
1976-77	-2.4	16.1	-145

The trend of δD vs rainfall amount in Figure 5-22 seems to be disrupted somewhat by the 1946-50 interval, although for such a small number of data points it is difficult to be certain just which, if any, are anomalous. The plot of δD vs reciprocal ring width is in Figure 5-23. There is no basic trend in the data that could be used to determine which points might represent δD values that were responding to some factor other than local climate. Hence, ring width measurements of this aspen have proved to be of no value in singling out "anomalous" isotopic values.

FA-As-1

FA-As-1 is an aspen that grew on Chena Ridge near Fairbanks, Alaska. The tree was quite young when felled. Its chronology extends from 1951-1977. Five 5-year samples were removed from the tree, as well as a sample comprised of the outermost two years of growth (1976-77). Meteorological records from Fairbanks cover the entire span of the tree's chronology.

The δD variations of the tree ring sequence are displayed in Figure 5-24. The δD range over the 27 year history of FA-As-1 is 28 per mil. As with KSA-As-1, there is strong trend to the δD data of FA-As-1. They tend to become more positive from younger to older samples. Furthermore, there is a strong correlation between the δD variations in FA-As-1 and KSA-As-1. The linear regression of the five corresponding sample intervals yields the expression:

$$\delta D\ (\text{FA-As-1}) = 0.934 \quad \delta D\ (\text{KSA-As-1}) - 30$$

The correlation coefficient is 0.977. Since there is such a high degree of correlation between the δD values of the two trees, and since

Figure 5-23

A plot of the δD values of KSA-As-1 against the reciprocal of the aggregate ring widths of the corresponding five-year intervals. There is no evidence of an overall relationship.

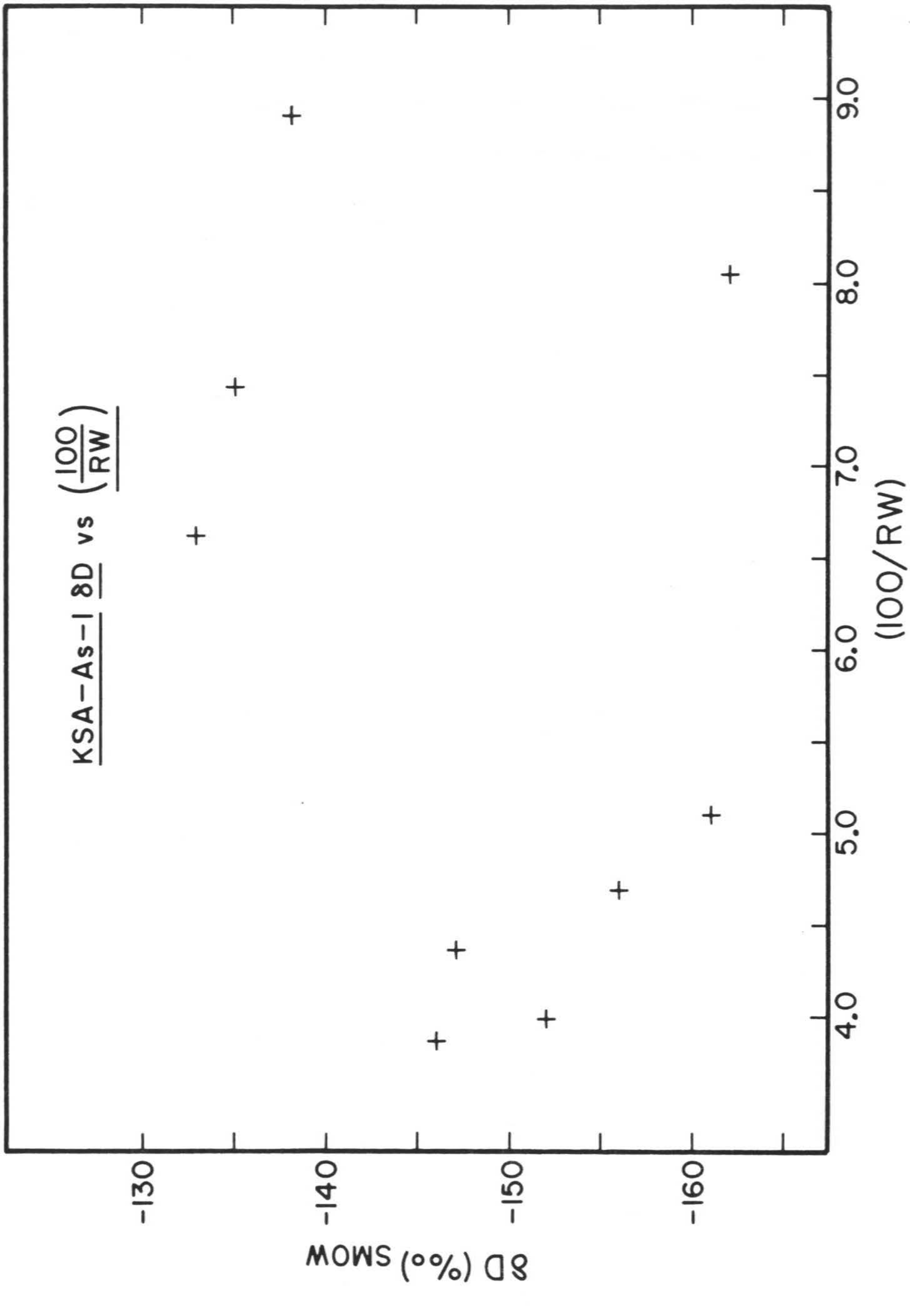
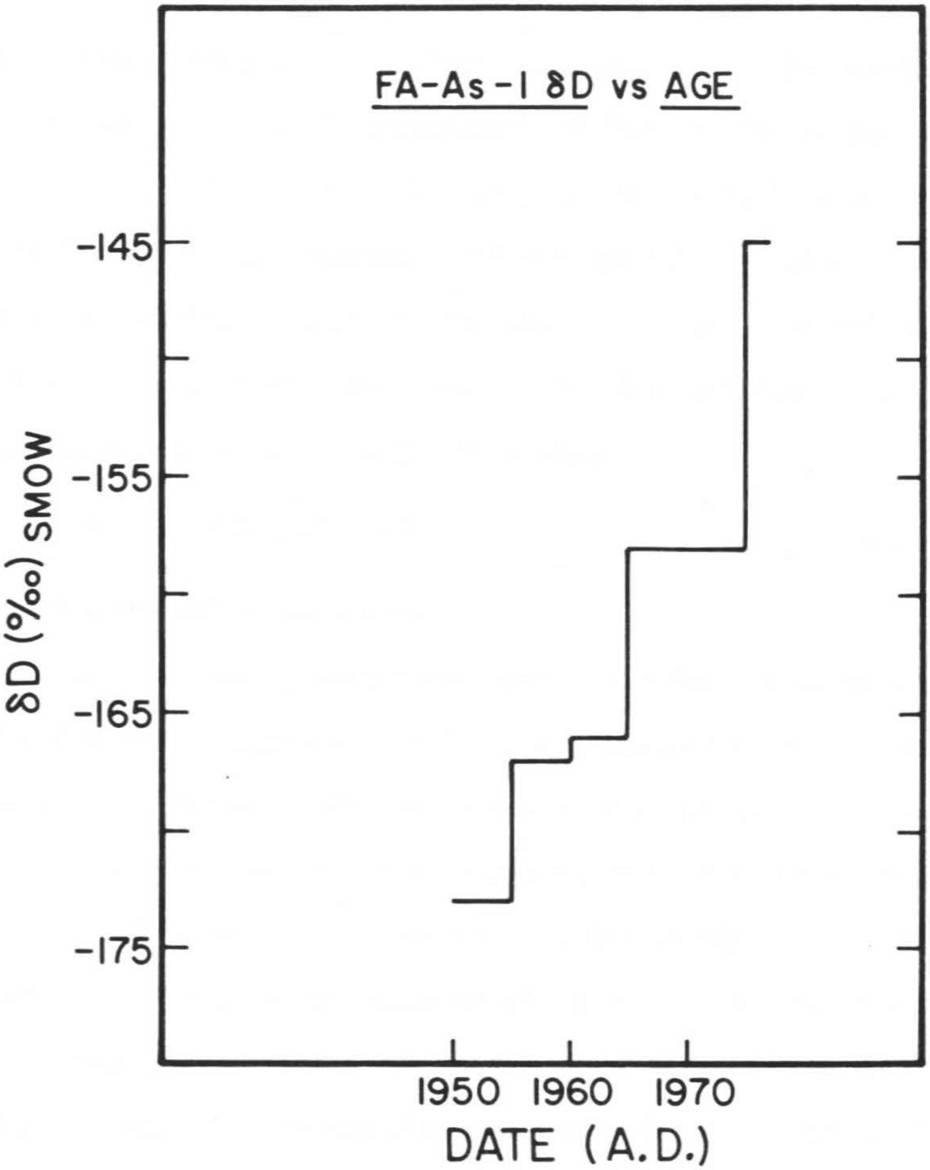

KSA–As–1 δD vs $\left(\frac{100}{RW}\right)$
-130
-140
-150
-160
δD (‰) SMOW
4.0
5.0
6.0
7.0
8.0
9.0
(100/RW)

Figure 5-24

The variation of the δD values of FA-As-1 with age for the interval from 1951-1977. The total δD range of this 27 year period is 28 per mil with a distinct long term increase in δD values from older to younger samples.


FA-As-1 δD vs AGE
δD (‰) SMOW
-145
-155
-165
-175
1950
1960
1970
DATE (A.D.)

the δD variations of KSA-As-1 are related to summer rainfall, it seems reasonable to assume that FA-As-1 δD values might also be correlated with summer precipitation.

However, a comparison of δD variations of FA-As-1 with several monthly combinations of Fairbanks summer rainfall produced a correlation coefficient no better than -0.462. This was obtained for the months of June, July, and August. Annual temperature was better correlated with the δD values of FA-As-1 and yielded a correlation coefficient of 0.745. The best relationship of all, however, was obtained for a summer (June, July, August) temperature comparison with the δD values. The data are listed in Table 5-5 and plotted in Figure 5-25. The regression of the data in Figure 5-25 results in the equation:

$$\delta D = 12.3\ T_s(^{o}C) - 347 \qquad (5\text{-}19)$$

The correlation coefficient is 0.897.

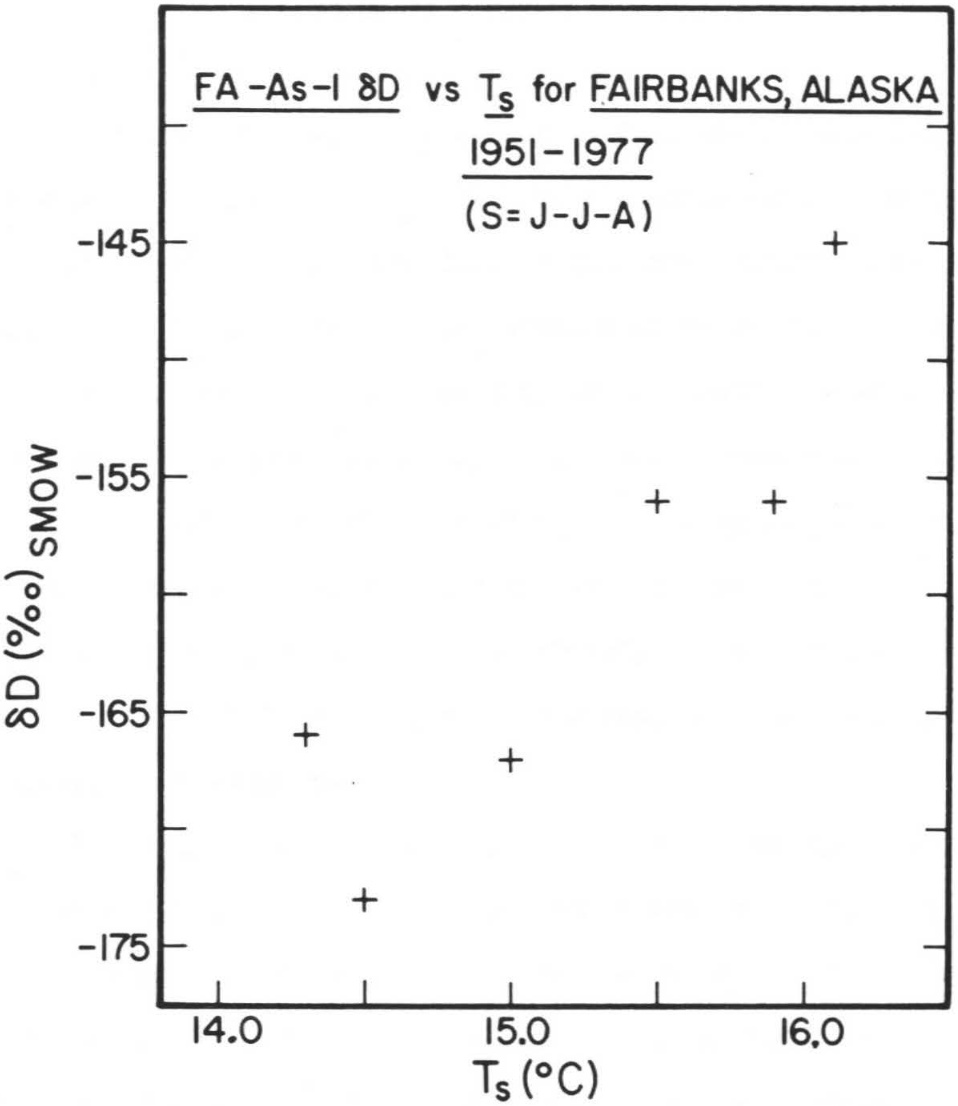
The high level of correlation noted previously for the δD values of KSA-As-1 and FA-As-1 suggests that the precipitation processes at these two sites are linked. This conclusion is reinforced by the fact that the δD values of FA-As-1 are more negative than those of KSA-As-1. More negative δD values are to be expected for inland sites compared to coastal locations, because by the time an air mass reaches the inland site it will probably have cooled and lost some of its moisture as precipitation. Thus, the moisture that remains to be precipitated at the inland site will have more negative δD values than it had at the coastal location (see Section 4 of this thesis). For Anchorage and Fairbanks this will be especially true, because the moisture must pass over the Alaska Range to get from Anchorage to Fairbanks (Benton and

Figure 5-25

A comparison of the δD values of FA-As-1 with the average summer temperature of Fairbanks, Alaska. The "best-fit" definition of summer includes the months June, July and August. The linear regression of these data yields the equation:

$$\delta D = 12.3\ T_s(^{o}C) - 347$$

The correlation coefficient is 0.897.


FA -As-I δD vs T_s for FAIRBANKS, ALASKA
1951-1977
(S= J-J-A)
-145
-155
-165
-175
δD (‰) SMOW
14.0
15.0
16.0
T_s (°C)

Estoque, 1954). Thus, to the extent that the precipitation processes at the two sites are actually coupled, not only will increased precipitation amount (or intensity) result in more negative δD values at Anchorage, but it could also tend to produce more negative δD values in Fairbanks precipitation by enhanced depletion of the moisture in the air mass.

Therefore the large temperature coefficient arising from the correlation of FA-As-1 δD values with Fairbanks summer temperature may be a consequence of both the local temperature effect on the condensation process and the preceding condensation history of the moisture as evidenced by the amount of precipitation at coastal locations such as Anchorage. Consequently, a very large δD vs temperature coefficient may signal that the local temperature is varying sympathetically with another factor or factors in the climatic system that are in themselves capable of producing variations in δD values. As discussed in Section 4, such factors might include cooling process, ocean temperature or precipitation intensity.

Thus, the aspens, FA-As-1 and KSA-As-1, appear to provide evidence for direct, long term isotopic linkage between a coastal and an interior precipitation site. In this instance the straightforward nature of the relationship is probably enhanced by the comparatively simple pattern of moisture transport (Benton and Estoque, 1954). Furthermore, both trees seem to have used only summer precipitation, so the effects of different combinations of seasons have also been eliminated. In short these trees represent a good natural experiment. The principal shortcoming is the brief time span represented by the tree chronologies. Similar, but older trees from each of these locations could provide a more statistically satisfying test of the reality of the isotopic, and hence, climatic coupling.

The small number of data points in FCA-As-1 and their relatively unambiguous behavior seems to obviate the need for a plot of δD vs reciprocal ring widths.

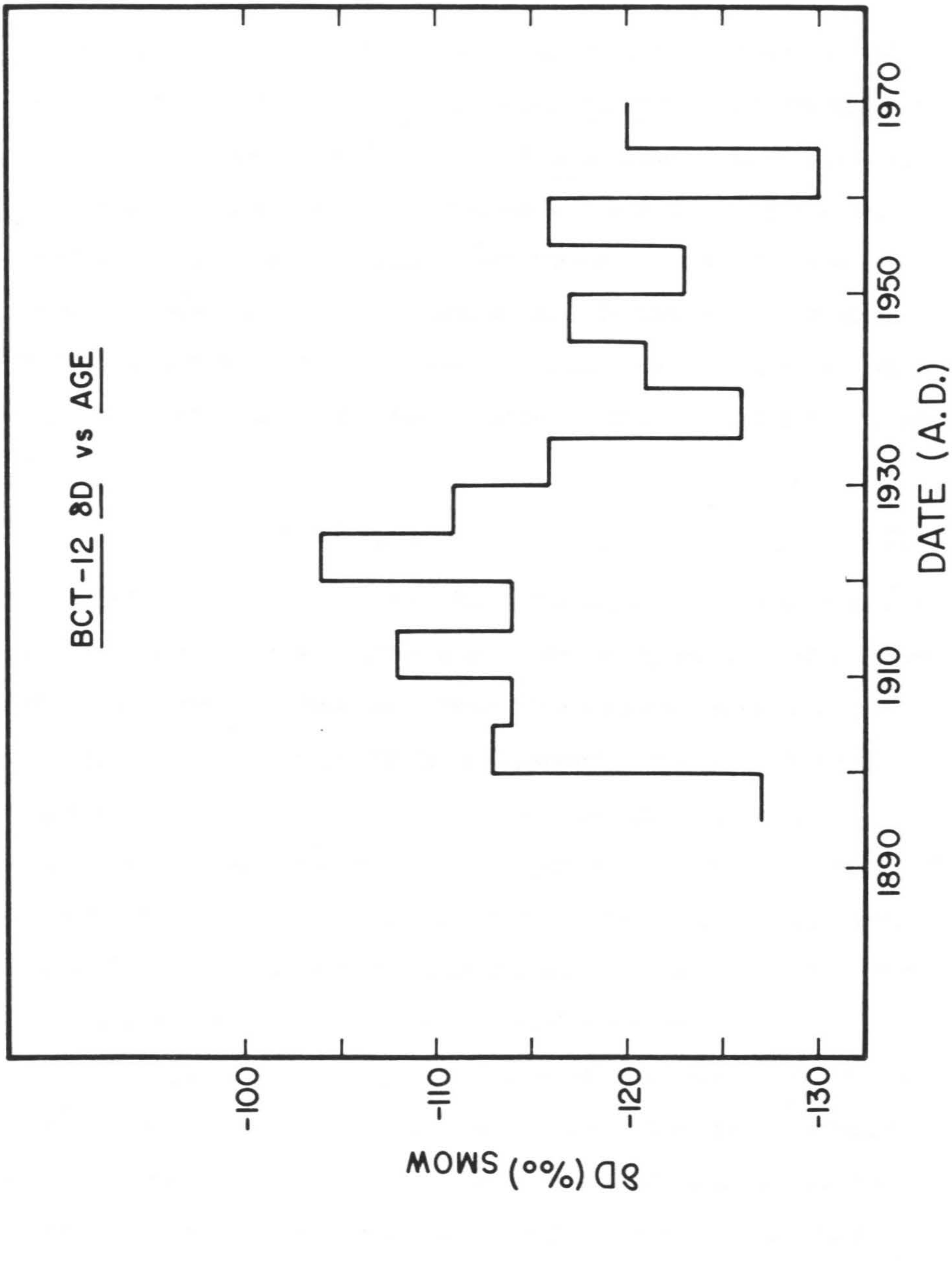
BCT-12

This pine tree grew in the vicinity of Seeley Lake, British Columbia about 100 kilometers west-northwest of Prince George, B.C. The tree provided five-year samples extending from 1896 to 1970. Meteorological data have been recorded at Prince George from 1916 to the present. The δD variations of the BCT-12 tree ring sequence are depicted in Figure 5-26. Over the 75 year length of the record, the δD values display a range of 26 per mil. There does not appear to be any overall trend to the δD values in the sequence, although there is the suggestion of a long term decrease in δD values from 1921 to 1970. For the period from 1941 to 1970, the δD values of BCT-12 show no systematic trend with time. This is in contrast to the persistent increase in δD values noted for the Alaskan aspens (KSA-As-1 and FA-As-1) during this period.

A comparison of BCT-12 δD variations with average annual Prince George temperatures indicates that there is no direct relationship -- the correlation coefficient is only -0.012. Similar comparisons of δD values with seasonal temperatures also indicate no correlation. Furthermore, none of the parameters derived from an assumption of seasonally-weighted average annual precipitation (equation 5-3), is well-correlated with BCT-12 δD values. This lack of correlation and the examples of KSA-As-1 and FA-As-1 suggest the possibility that only summer rain is

Figure 5-26

The variations of the δD values of BCT-12 with age over the interval from 1896 to 1970. There is no general trend to the δD values with time. The total range in δD over this period of 75 years is 26 per mil.


BCT-12 δD vs AGE
DATE (A.D.)
1890
1910
1930
1950
1970
δD (‰) SMOW
-100
-110
-120
-130

incorporated by the tree. However, as noted above, seasonal temperatures (including summer) do not show a relationship with BCT-12 δD variations. Thus, summer precipitation amounts were compared with the δD values.

Several combinations of summer months as well as average annual precipitation were tried, and it was found that the best correlation was obtained for a "summer" defined as April, May, June, July and August. As so defined, the average monthly amounts of summer precipitation, together with the average summer temperature and BCT-12 δD values are listed in Table 5-5. A plot of average monthly summer precipitation vs δD is in Figure 5-27. It is apparent that there is a strong relationship between these two variables for BCT-12. The best-fit linear curve is:

$$\delta D = -686.6\ W_s - 85 \qquad (5\text{-}20)$$

The correlation coefficient is -0.824. The negative slope is consistent with the observed patterns of summer, or tropical, rainfall δD vs rainfall amount patterns (Dansgaard, 1964; also Section 4 of this thesis).

Thus, the δD value of BCT-12 is apparently varying in direct response to a <u>local</u> climatic parameter over the interval 1916-1970. Furthermore, as was the case for the Alaskan aspens (KSA-As-1 and FA-As-1), the "controlling" climatic variable is not an annual average quantity. Instead, BCT-12 δD variations are related to a local summer climatic variation -- in this case, precipitation amount.

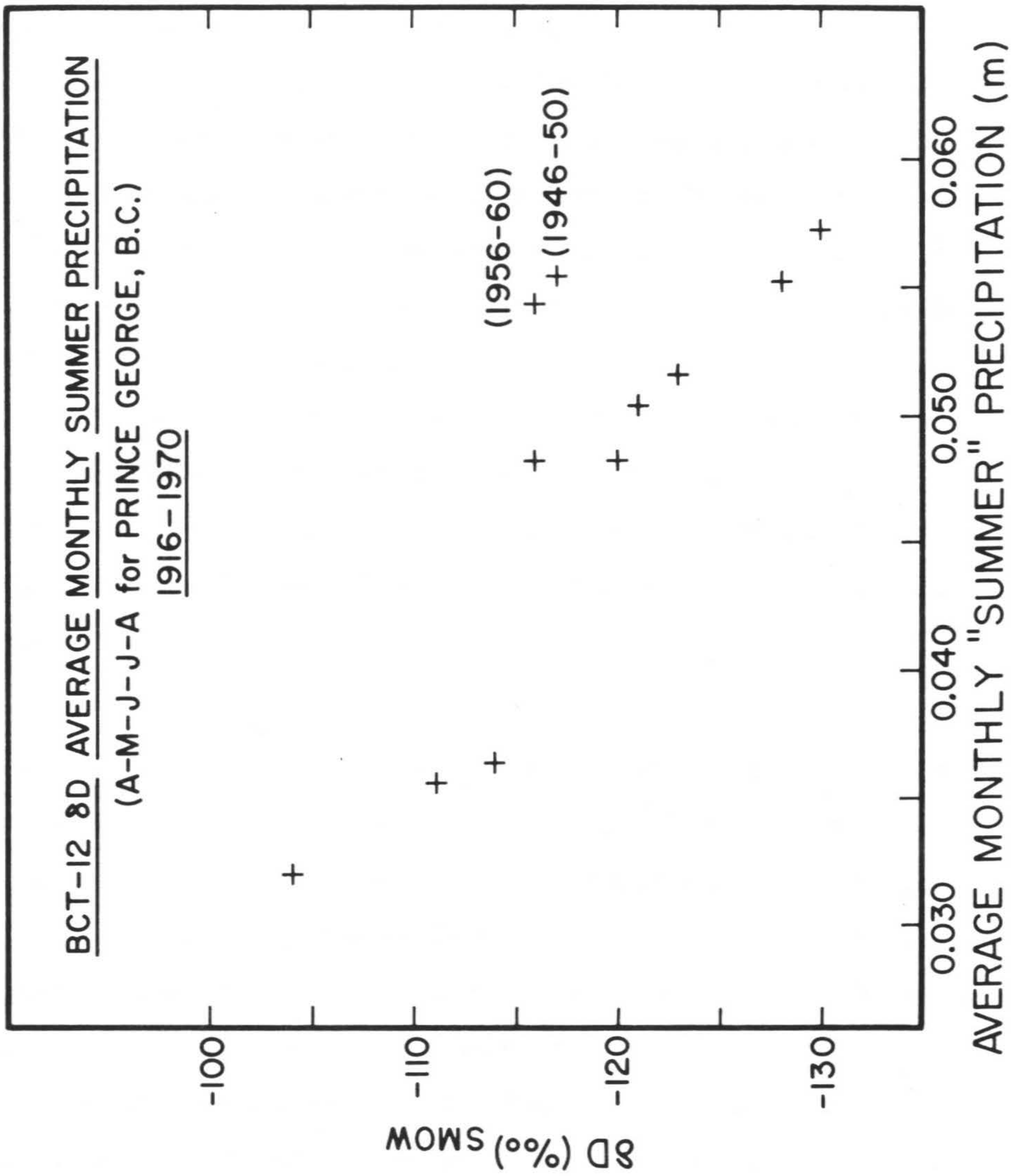
It is interesting to note that for BCT-12 the best correlation of a local summer climatic variable with δD was obtained for a "summer" extending from April to August, while for the Alaskan aspens the best correlations were for a summer defined to be June to August. This

Figure 5-27

A comparison of the δD values of BCT-12 with the average monthly amount of summer precipitation at Prince George, British Columbia. The "best-fit" definition of summer for this case includes the months April, May, June, July and August. The meteorological data span the period from 1916 to 1970. The linear regression of the δD and precipitation data for this interval results in the equation:

$$\delta D = -686.6\ W_s - 85$$

The correlation coefficient is -0.824. The points representing the intervals 1946-50 and 1956-60 are regarded as "anomalous" (see text). The precipitation amounts are expressed in meters.


BCT-12 δD AVERAGE MONTHLY SUMMER PRECIPITATION
(A-M-J-J-A for PRINCE GEORGE, B.C.)
1916–1970
(1956-60)
(1946-50)
-100
-110
-120
-130
δD (‰) SMOW
0.030
0.040
0.050
0.060
AVERAGE MONTHLY "SUMMER" PRECIPITATION (m)

seems to imply that BCT-12 had a longer growing season than KSA-As-1 and FA-As-1, and/or that the root geometries and soil water movement patterns for BCT-12 allowed it to sample a larger fraction of a year's precipitation (see Figure 2-3 in Section 2).

Inspection of the data in Figure 5-27 leads to the conclusion that two points (1946-50 and 1956-60) may lie significantly above the generally well-defined trend. At this juncture, it cannot be ascertained whether or not this represents a physiological phenomenon, or if it us linked to some change in the relationship between local climate and δD values of the precipitation.

The plot of BCT-12 δD values vs the reciprocal of ring width is in Figure 5-28. There is an apparent relationship between these variables. However, the trend is too ill-defined to provide any insight about the "anomalous" δD values of 1946-50 and 1956-60 in Figure 5-27.

OPW-DF-1

OPW-DF-1 is a Sitka spruce which grew in the Hoh River Valley on the Olympic Peninsula, Washington. Consecutive five-year samples spanning the interval 1856-1975 were obtained from the tree, and the δD values of this sequence are displayed in Figure 5-29. There is a distinct long term increase in δD values from 1856 to 1975. The total range of δD values over this 120 year interval is 37 per mil.

Seattle, Washington is about 100 km southeast of the tree site. Its meteorological records for temperature span the interval from 1890 to the present, although there are no data for some months in the years 1890 and 1891. The Seattle precipitation record extends unbroken from 1879 to the present.

Figure 5-28

A plot of the δD values of BCT-12 against the reciprocal of the aggregate ring widths of the corresponding five-year intervals. There seems to be a broadly defined overall relationship between these variables. This could mean that the two are varying in response to the same, or related, climatic variables.

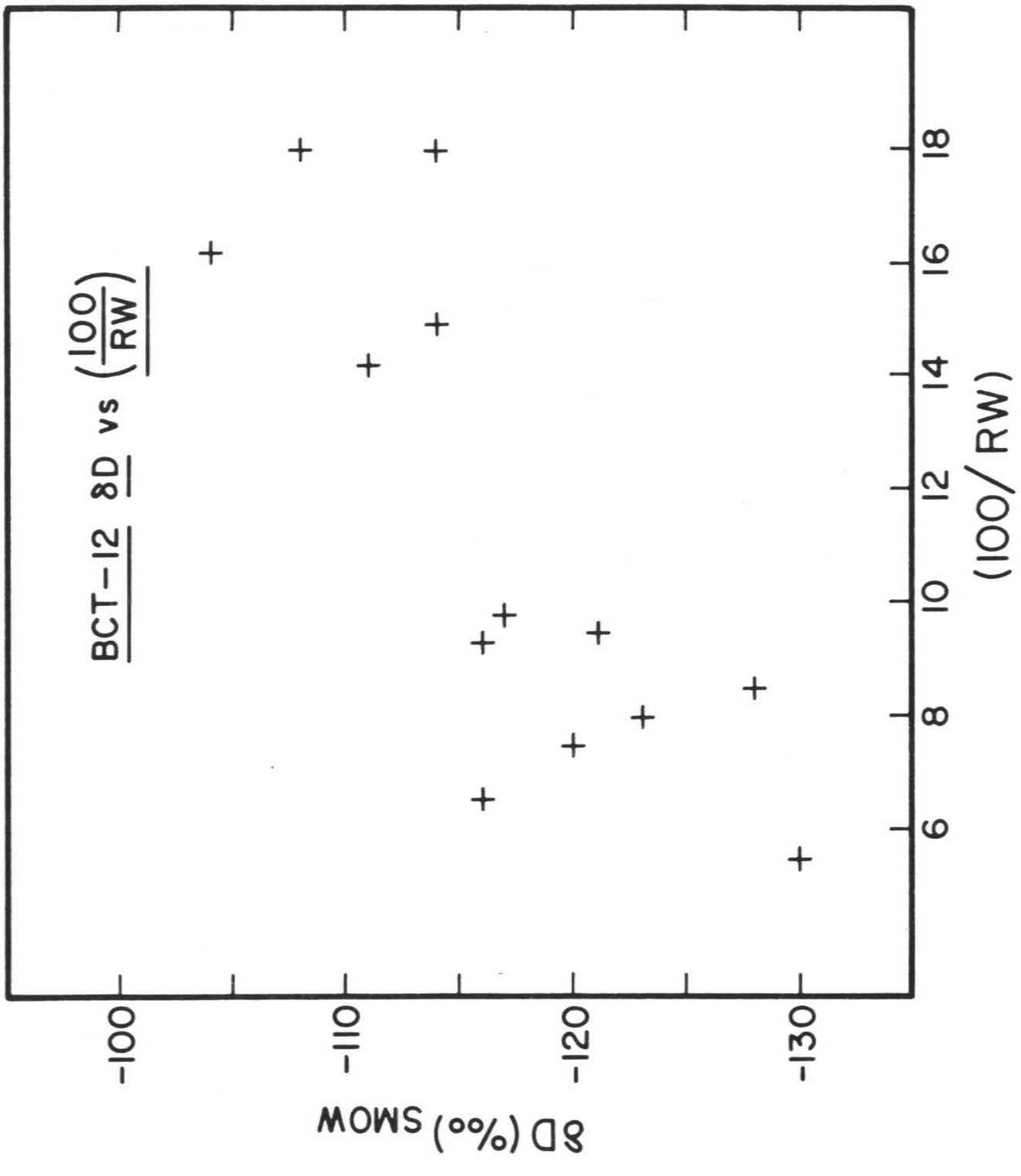
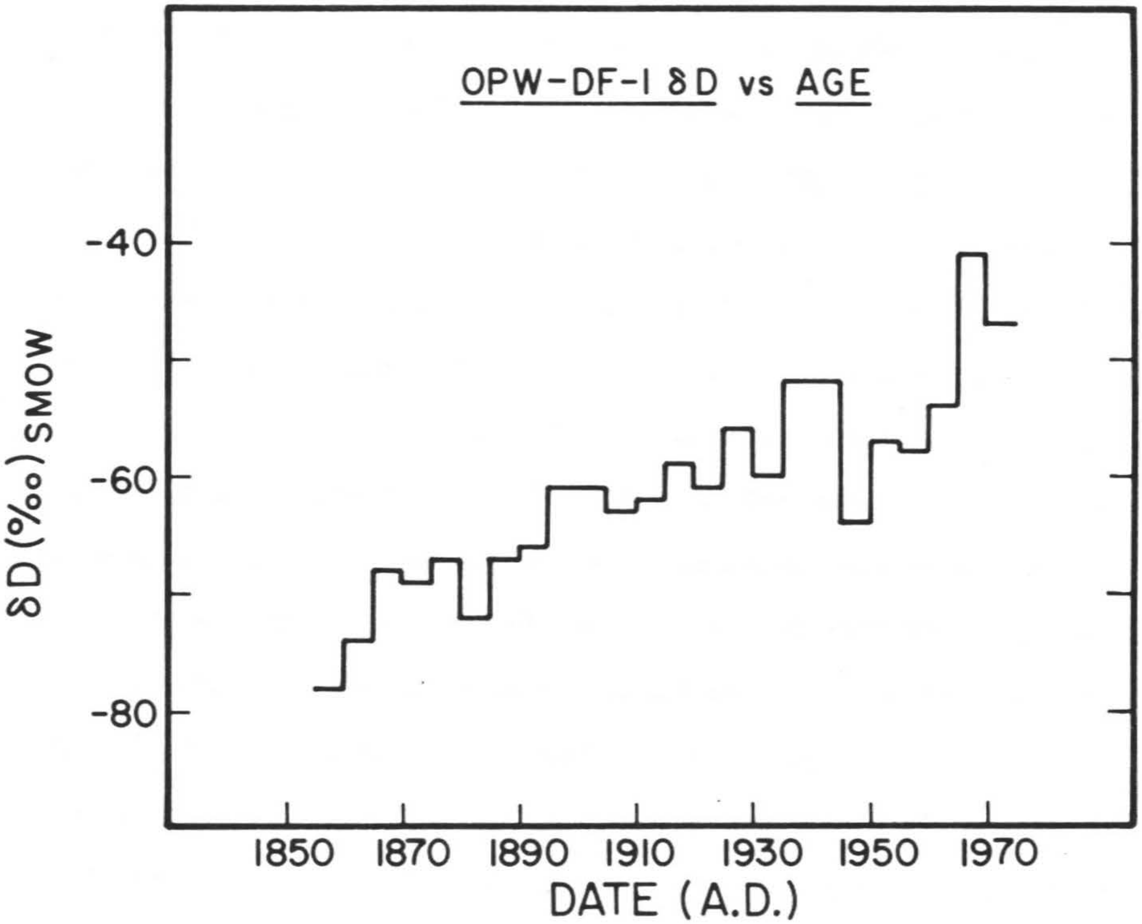

BCT-12 δD vs $\left(\frac{100}{RW}\right)$
δD (‰) SMOW
-100
-110
-120
-130
6
8
10
12
14
16
18
(100/RW)

Figure 5-29

The variation of the δD values of OPW-DF-1 with age over the interval from 1856 to 1975. There is a general increase in the δD values from older to younger samples with a total range in δD of 37 per mil for this 120 year period.


OPW-DF-1 δD vs AGE
δD (‰) SMOW
-40
-60
-80
1850
1870
1890
1910
1930
1950
1970
DATE (A.D.)

Victoria, B.C., about 80 km north of the tree site, represents another nearby station for which meteorological data have been recorded for a reasonably long period of time. Its climatic records date from 1891 to the present.

An attempt was made to decide which of these meteorological stations represented the better choice for comparison with the δD variations of OPW-DF-1. The best course seemed to be to compare data from both stations with the δD values of OPW-DF-1. The station showing the better correlation would then represent the optimal choice ipso facto.

The first choice for comparison was average annual temperature. The linear correlation coefficient of the Victoria, B.C. vs OPW-DF-1 regression for the years 1891-1975 is 0.017. Thus, there is no correlation whatsoever between the annual temperature at Victoria, B.C. and δD values in OPW-DF-1 for these years. The correlation coefficient for the regression of Seattle average annual temperature against OPW-DF-1 δD variations is 0.669 for the interval 1891-1975. Consequently, while the Seattle average annual temperature is not well-correlated with OPW-DF-1 δD variations, it certainly exhibits, as measured by the correlation coefficient, a much stronger relationship with isotopic conditions at the growth site than does Victoria annual temperature. Neither site exhibits any correlation of either annual or summer precipitation with the δD variations of OPW-DF-1. However, based on the fact that over the interval 1891-1975 the annual Seattle temperature shows some relationship to OPW-DF-1 δD values, while Victoria annual temperature does not, it was decided to employ Seattle data exclusively in subsequent δD vs climate comparisons.

Figure 5-30 contains the plot of OPW-DF-1 vs average annual Seattle temperature. The best-fit linear equation of these data is:

$$\delta D = 7.13\ T(^{o}C) - 138 \qquad (5\text{-}21)$$

As was mentioned previously, this regression has a correlation coefficient of 0.669. There is considerable scatter in the data of Figure 5-30. However, with one exception which will be discussed below, it was found that various seasonal temperature and precipitation amount comparisons result in even less significant correlation with OPW-DF-1 δD values. Thus, it appears that to the extent that the δD values of OPW-DF-1 vary sympathetically with local climatic change, it is probably the average annual climatic conditions that are important. This conclusion suggests that the seasonally weighted δD value of annual precipitation might be an important parameter. Equations (5-6) through (5-8) again serve as the model for the climatic characterization of annual precipitation δD values.

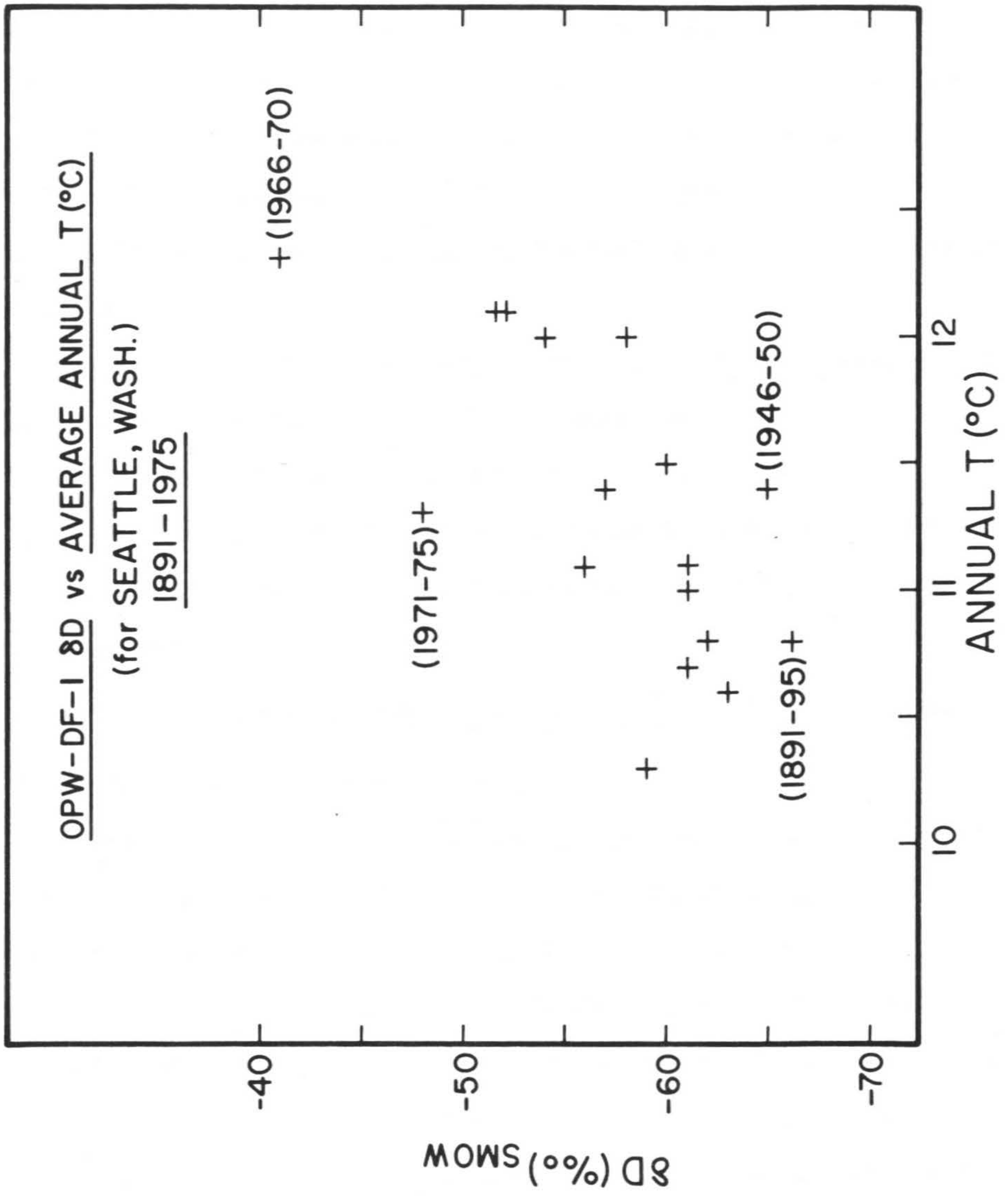
As was true for previous tree δD variations characterized in this manner, a principal difficulty involves defining an isotopic summer. For Seattle, it was felt that the best way to accomplish this would be to first define the isotopic winter and take the remainder of the year as summer. An a priori choice of the isotopic winter in Seattle was made with the aid of a criterion implied by the previously mentioned data of Friedman, et al, (1964). These authors noted that the ratio of snow to total annual precipitation was rather well-correlated with the δD value of the local meteoric water. This implies that snow may be one end-member of the postulated two component isotopic system. For Seattle, this suggests that those months which most commonly experience

Figure 5-30

A comparison of the δD values of OPW-DF-1 with the average annual temperatures of Seattle, Washington. The linear regression of these data yields the expression:

$$\delta D = 7.13\ T(^{\circ}C) - 138$$

The correlation coefficient is 0.669. The points representing the intervals labeled in the figure are considered to be "anomalous" (see text). Meteorological data from Seattle are available from 1891 to 1975.


OPW-DF-I δD vs AVERAGE ANNUAL T (°C)
(for SEATTLE, WASH.)
1891-1975
(1966-70)
(1971-75)
(1946-50)
(1891-95)
-40
-50
-60
-70
δD (‰) SMOW
10
11
12
ANNUAL T (°C)

measurable snowfall might be defined as the isotopic winter. The tabulated Seattle snowfall data in Ruffner and Bair (1977) were examined. From these data it seems apparent that November, December, January and February are the months in which measurable snow most commonly falls in Seattle. Hence, these months were defined as the isotopic winter with the balance of the year constituting the isotopic summer. Interestingly, over 50% of the annual Seattle precipitation falls in these four months.

The parameters X_s, $X_s\ (T_s - T_w)$, and $X_s\ (T_s - T_w) + T_w$ were compared with the δD variations of OPW-DF-1 (see equations 5-6, 5-7 and 5-8). It was found that the best correlation is between δD and $X_s\ (T_s - T_w) + T_w$. The latter data are listed in Table 5-6 and plotted in Figure 5-31. The linear regression of the data in Figure 5-31 yields the expression:

$$\delta D = 6.25 \left[X_s\ (T_s - T_w) + T_w \right] - 117 \qquad (5\text{-}22)$$

The correlation coefficient is 0.623.

There is a dramatic difference between the correlation coefficients for the regressions of OPW-DF-1 δD values vs the preceding three parameters (see equations 5-6 through 5-8). For the comparison of δD with X_s, the correlation coefficient is almost zero (-0.003), while for comparison with $X_s\ (T_s - T_w)$ it is almost as small (-0.062). Thus, the much larger correlation coefficient of 0.623 for the comparison of δD with $X_s\ (T_s - T_w) + T_w$ must be a consequence of the winter temperature.

With this in mind OPW-DF-1 was plotted against T_w in Figure 5-32. The linear regression of this plot yields the equation:

$$\delta D = 7.11\ T_w\ (^{o}C) - 102 \qquad (5\text{-}23)$$

Table 5-6: Annual T, T_w, $X_s(T_s - T_w) + T_w$, and δD Values of OPW-DF-1

S = March, April, May, June, July, August, September, October

Interval	Annual $T(^{o}C)$	$T_w(^{o}C)$	$X_s(T_s - T_w) + T_w$	δD
1891-95*	10.8	5.7	9.5	-66
1896-1900	11.0	6.1	9.1	-61
1901-05	11.1	6.3	9.5	-61
1906-10	10.6	5.4	8.1	-63
1911-15	10.8	5.7	8.9	-62
1916-20	10.3	5.4	9.0	-59
1921-25	10.7	5.6	8.6	-61
1926-30	11.1	5.8	9.6	-56
1931-35	11.5	6.5	9.7	-60
1936-40	12.1	6.7	10.1	-52
1941-45	12.1	7.0	10.5	-52
1946-50	11.4	5.9	9.5	-65
1951-55	11.4	6.6	9.4	-57
1956-60	12.0	6.7	10.1	-58
1961-65	12.0	7.1	10.0	-54
1966-70	12.3	7.4	10.5	-41
1971-75	11.3	6.0	9.4	-48

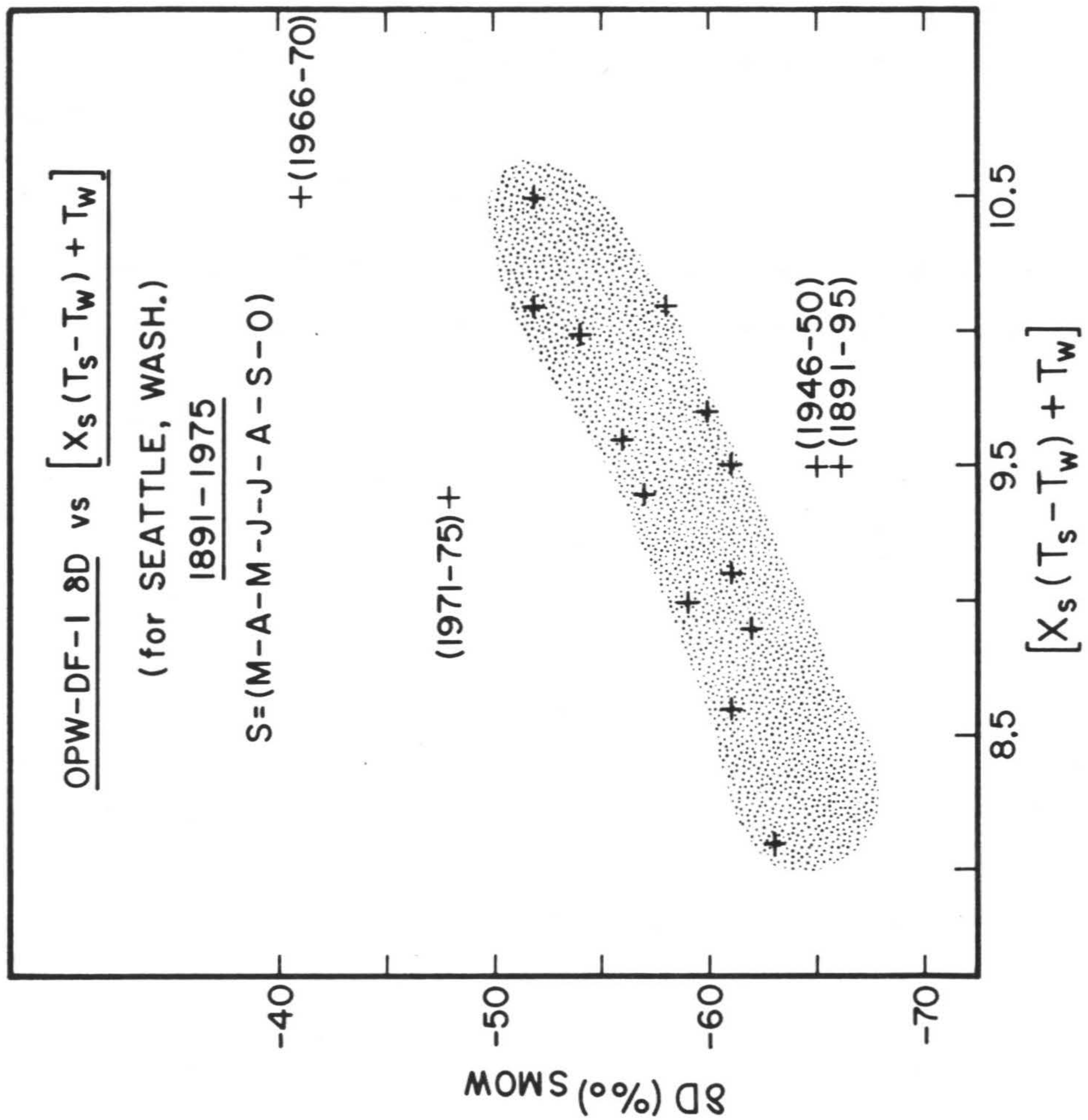
* The Seattle temperature records are missing data for several months in 1891. Consequently, the temperature and precipitation data which are compared with OPW-DF-1 in this first 5-year interval only span the years 1892-95, while the tree sample covers the complete interval.

Figure 5-31

A comparison of the δD values of OPW-DF-1 with $X_s \, (T_s - T_w) + T_w$ over the interval from 1891 to 1975. The linear regression of these data results in the equation:

$$\delta D = 6.25 \left[X_s \, (T_s - T_w) + T_w \right] - 117$$

The correlation coefficient is 0.623. The stippled region in the diagram is interpreted to be the domain of the "normal" variation of δD values with local climate. The points representing the labeled intervals in the figure are considered to be "anomalous" (see text). The meteorological data are from Seattle, Washington.



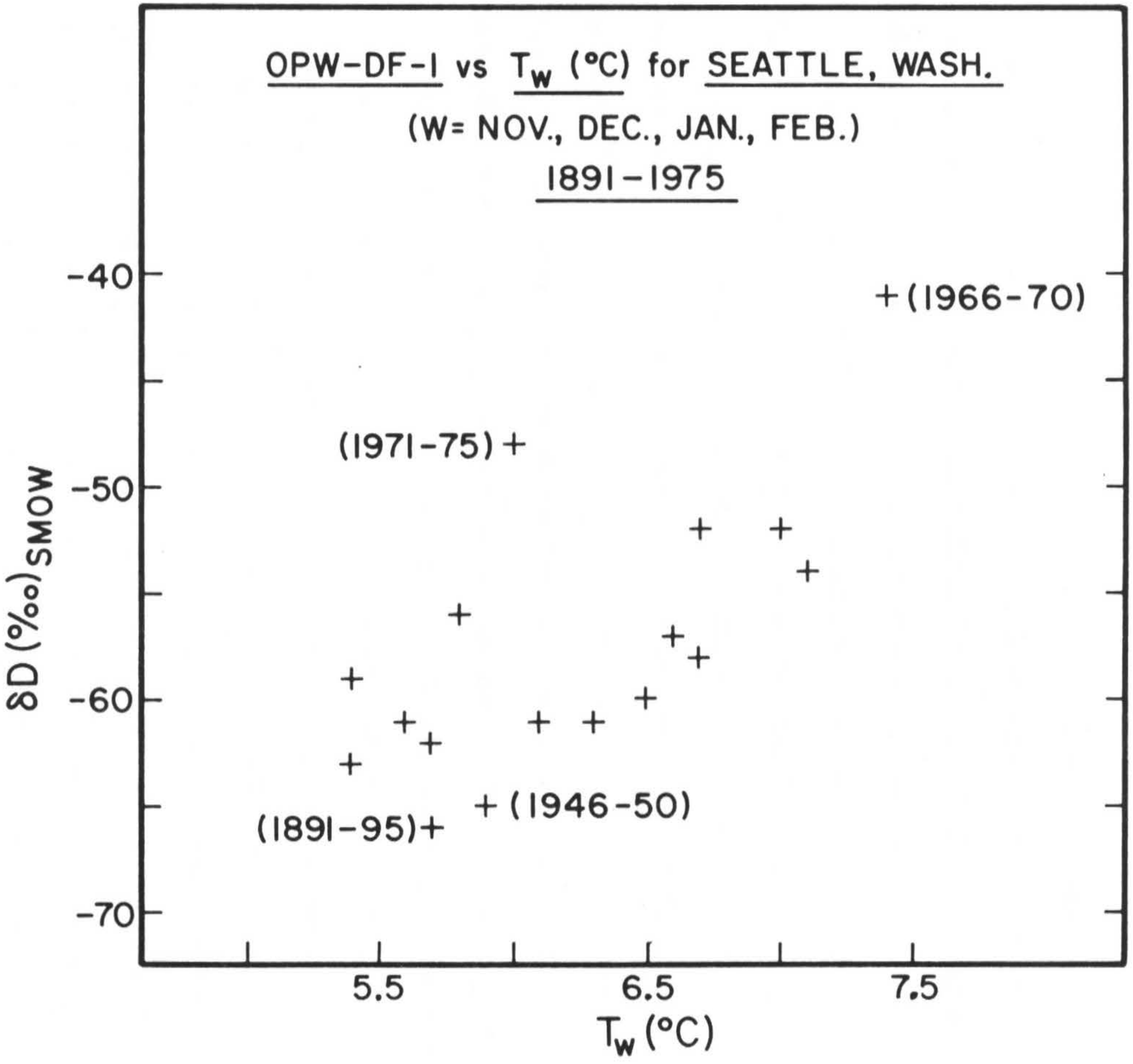
OPW-DF-I δD vs [X_s (T_s - T_w) + T_w]
(for SEATTLE, WASH.)
1891-1975
S=(M-A-M-J-J-A-S-O)
+(1966-70)
(1971-75)+
+(1946-50)
+(1891-95)
δD (‰) SMOW
-40
-50
-60
-70
8.5
9.5
10.5
[X_s (T_s - T_w) + T_w]

Figure 5-32

A comparison of the δD values of OPW-DF-1 with the average winter temperatures of Seattle, Washington, over the interval from 1891 to 1975. Winter is defined to include November, December, January and February. The linear regression of these data results in the expression:

$$\delta D = 7.11\ T_w\ (^{o}C) - 102$$

The correlation coefficient is 0.681. The points representing the labeled intervals in the figure are regarded as "anomalous" (see text).


OPW-DF-I vs T_W (°C) for SEATTLE, WASH.
(W= NOV., DEC., JAN., FEB.)
1891-1975
-40
-50
-60
-70
δD (‰)SMOW
(1966-70)
(1971-75)
(1946-50)
(1891-95)
5.5
6.5
7.5
T_W (°C)

The correlation coefficient is 0.681. While still not indicating a high degree of correlation, the magnitude of this coefficient is comparable to and, in fact, slightly larger than the correlation coefficient for δD vs annual temperature. While not negating the conclusion that the δD variations in OPW-DF-1 are probably related to annual climatic conditions, the data comparison in Figure 5-32 suggests that winter temperature plays a significant, perhaps dominant, role in the relationship. This seems to be a physically reasonable notion, since as was noted previously, over 50% of the annual precipitation falls in these four winter months (November, December, January and February).

The general patterns of the data in Figures 5-30, 5-31, and 5-32 are similar. However, there appears to be some discernible "fine structure" in the δD vs X_s $(T_s - T_w) + T_w$ plot of Figure 5-31. The δD values of the intervals 1966-70 and 1971-75 are clearly shifted in a positive sense from the general trend of the data. This is evident in all three of the figures. However, Figure 5-31 also seems to show that the δD values of the intervals 1891-95 and 1946-50 may be somewhat "anomalous". Such an interpretation would be difficult to make from the plots of δD vs T_w in Figure 5-32 and δD vs annual temperature in Figure 5-30. The absence of any clear-cut anomalous behavior of the 1891-95 and 1946-50 intervals in Figures 5-30 and 5-32 could imply that the apparently anomalous δD behavior of these intervals in Figure 5-31 is an accident of the particular choice of variables. Such an argument would be quite reasonable except that of the three, X_s $(T_s - T_w) + T_w$ appears to be the best choice of variables. This seems to follow from the observation that if the 1891-95, 1946-50, 1966-70, and 1971-75 intervals are excluded, the best data trend is defined by the δD vs

$X_s\ (T_s - T_w) + T_w$ plot. This can be illustrated by comparing the correlation coefficients for these three regressions as follows:

Compared parameters	Correlation coefficient
δD vs Annual T	0.780
δD vs T_w	0.717
δD vs $X_s\ (T_s - T_w) + T_w$	0.826

Thus in all three of the plots, there is a more clearly defined general trend to the data when the four "anomalous" intervals are not considered. However, the most distinct "residual" trend in this instance is that defined by the δD vs $X_s\ (T_s - T_w) + T_w$ plot. Thus, it may be that this parameter best characterizes the relationship of δD variations in OPW-DF-1 to local climatic variations. The "normal" δD vs local climate trend as interpreted here is indicated by the stippling in Figure 5-31. The best-fit linear equation of the data in the stippled region is:

$$\delta D = 4.53\ \left[X_s\ (T_s - T_w) + T_w\right]\ -101 \qquad (5\text{-}24)$$

The conclusion that $X_s\ (T_s - T_w) + T_w$ is the best choice of variables to describe δD vs local climate relationships depends on the assumption that the "anomalous" δD values of 1891-95 and 1946-50 in Figure 5-31 are in fact a product not only of local climatic change, but also of large scale climatic change that may have altered the "normal" condensation trajectories (see Figure 4-1 in Section 4 of this thesis). If this assumption is not valid, T_w is the better choice of variable to characterize the relationship of δD values to local climate. This follows, because the plot of OPW-DF-1 δD values vs T_w in Figure 5-32 gives no indication that there is anything isotopically unusual about the intervals 1891-95 and 1946-50. They simply appear to be part of the larger scatter of the δD vs local climate trend. This would be expected if they are related to local climatic change only.

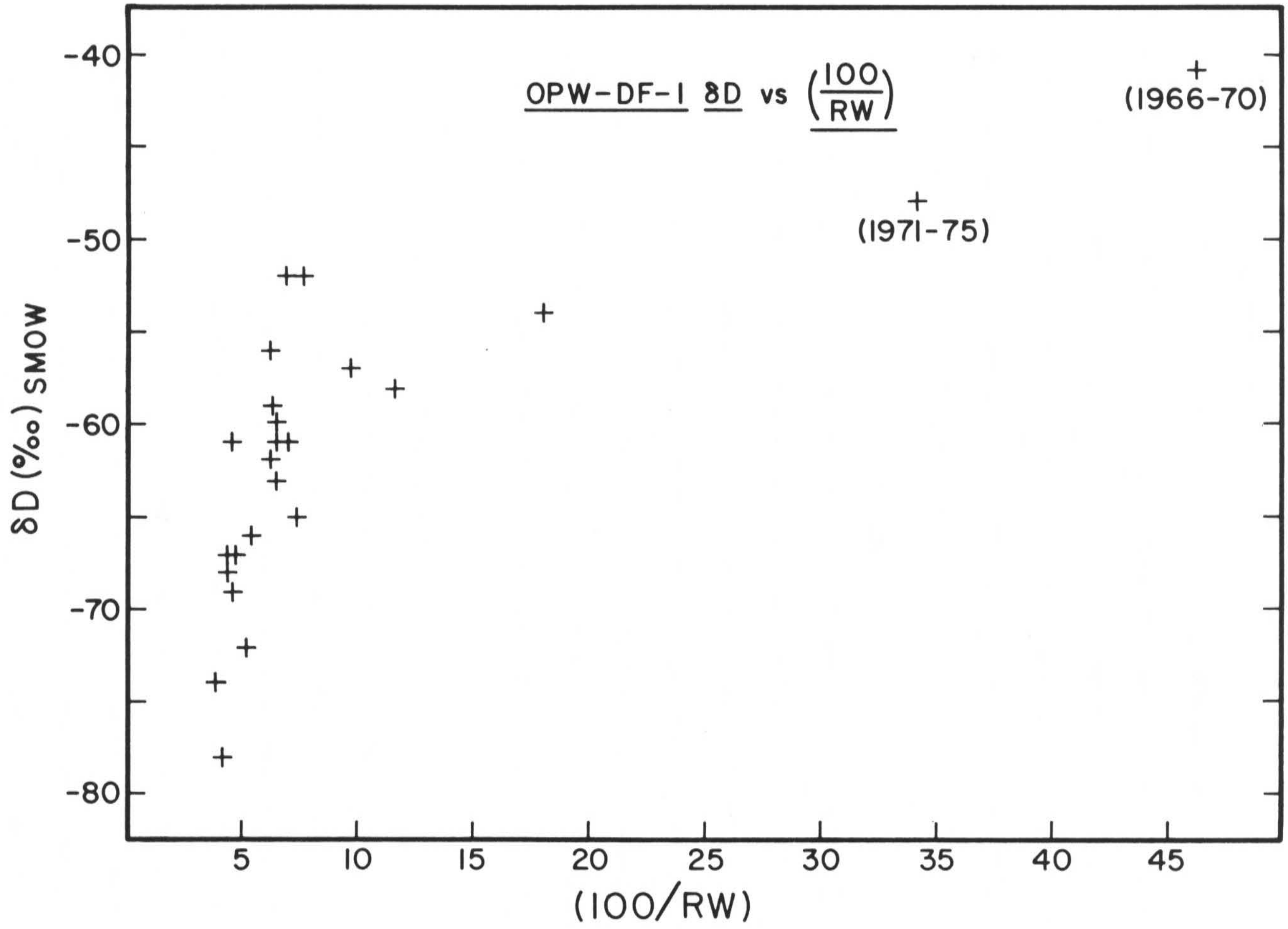
That the δD values of 1891-95 and 1946-50 may be reflecting large scale climatic changes in isotopic condensation trajectories rather than local climate or tree physiology effects is indicated by the δD data from trees in other locales. It is recalled that both KSA-As-1 and BCT-12 had general trends of δD vs local climate which suggested that the interval 1946-50 might be isotopically "anomalous". Furthermore, there was some indication from the δD vs local climate trends of FCA-WS-1 and Col-DF-1 that 1891-95 could be an isotopically "anomalous" interval. These coincidences provide only very tenuous support for the contention that large scale climatic changes in isotopic condensation trajectories occurred during these intervals, but they are intriguing.

The very large positive shifts in the δD values of the 1966-70 and 1971-75 intervals in OPW-DF-1 are difficult to characterize. The plot of δD values vs reciprocal ring width in Figure 5-33 reveals that the 1966-70 and 1971-75 intervals are not a part of the dominant grouping of data. Thus, this plot might have been used to signal some caution in trying to interpret the δD values of these intervals strictly in terms of local climatic change. However, one is still left with the question of the nature of the positive δD shift.

There is some suggestion in the MO-O-2, Col-DF-1, and FCA-WS-1 δD sequences that 1971-75 was a time of large scale change in isotopic condensation trajectories. However, there is no evidence for this in the limited number of data from KSA-As-1, while the BCT-12 sequence does not encompass this interval. Conclusions about the 1966-70 interval

Figure 5-33

A plot of the δD values of OPW-DF-1 against the reciprocal of the aggregate ring widths of the corresponding five-year intervals. There is no easily defined trend to the data. However, the points representing the intervals 1966-70 and 1971-75 appear to be significantly displaced from the general cluster of the data.


OPW-DF-1 δD vs $\left(\frac{100}{RW}\right)$
(1966-70)
(1971-75)
-40
-50
-60
-70
-80
δD (‰) SMOW
5
10
15
20
25
30
35
40
45
(100/RW)

in OPW-DF-1 would be prematurely drawn until more data can be obtained from other trees in that location.

The general thrust of the information about OPW-DF-1 seems to be that its δD variations are probably a reflection of the δD variations of the annual precipitation in the region. Because of this, the δD record in the tree is likely to represent not only local climatic change, but also large scale changes which might affect the condensation history of moisture that reaches the growth site.

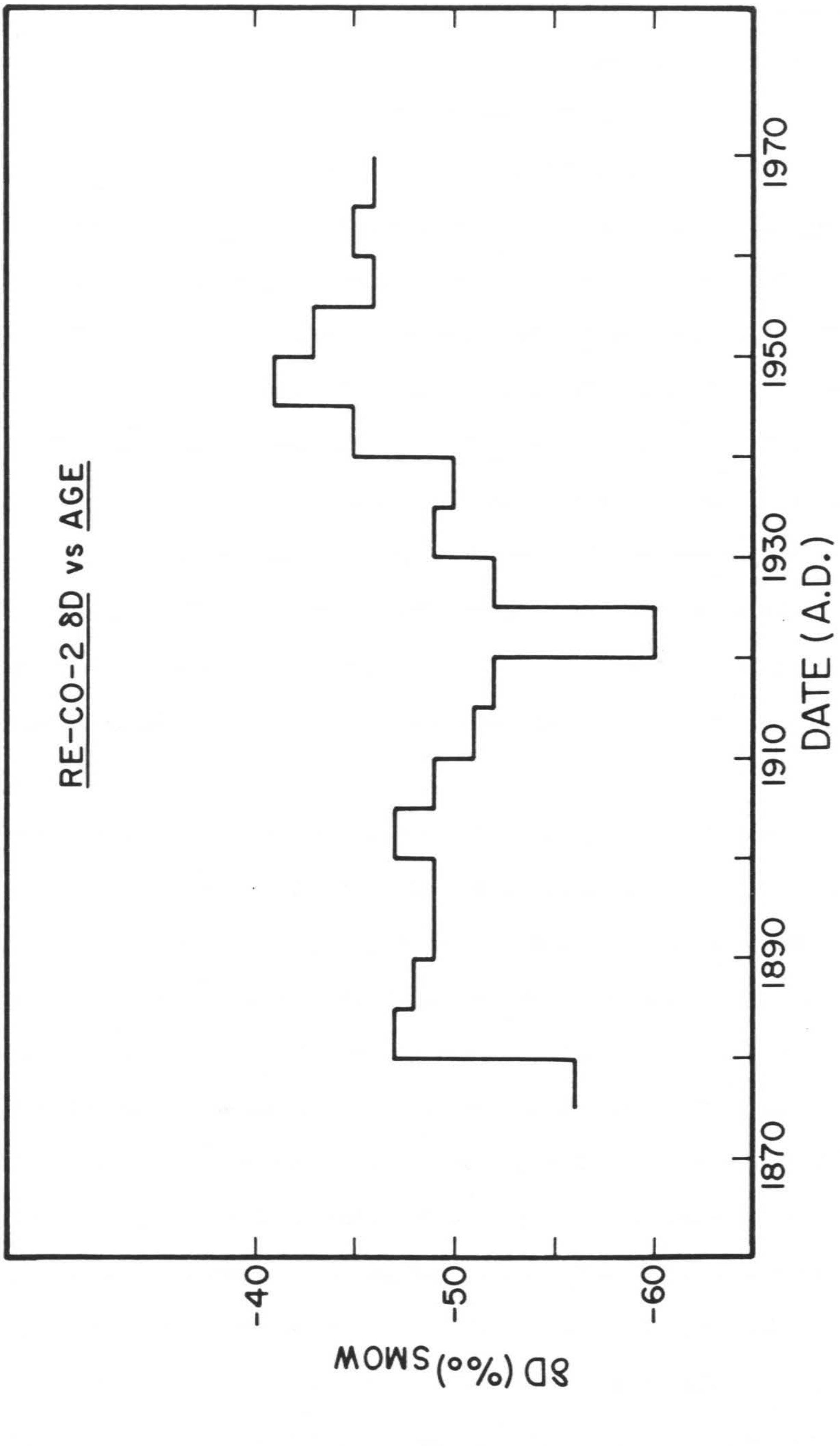
RE-CO-2

This chestnut oak is located a continent away from OPW-DF-1. RE-CO-2 grew on a site presently occupied by the United States Geological Survey in Reston, Virginia. The oak spans the interval from 1876 to 1971. Thus, it was sectioned into nineteen samples each of which spanned a five-year interval. The δD values of the dated tree ring sequence are found in Figure 5-34. The long term trend of the δD data is almost sinusoidal in character. Over the 95 year age of the tree the total δD range is 18 per mil.

Long term meteorological records are available from nearby Washington, D.C. These records are complete for temperature and precipitation over the entire length of time spanned by the tree. The δD values of RE-CO-2 were compared initially with the average annual Washington, D.C. temperature. There was no significant relationship between the two variables as is indicated by the small correlation coefficient of 0.374. Furthermore, comparisons of RE-CO-2 δD values with seasonal temperatures and annual and seasonal amounts of precipitation revealed no correlations. However, the δD values of RE-CO-2

Figure 5-34

The variations of the δD values of RE-CO-2 with age over the interval from 1876 to 1970. There is no apparent long term trend to the data. The total range in δD values is 18 per mil.


RE-CO-2 δD vs AGE
δD (‰) SMOW
-40
-50
-60
DATE (A.D.)
1870
1890
1910
1930
1950
1970

(about -45 per mil) are consistent with those expected for a tree which is incorporating waters with a δD value around that expected for annual precipitation in this region (about -50 per mil as inferred from the δD isopleths of Taylor (1974); see Section 2 of this thesis for a discussion of the plant-water relationship). Consequently, it may be the seasonally weighted isotopic composition of the annual water which is varying in response to the local climate. The three parameters of equations (5-6), (5-7) and (5-8) were compared with the δD variations of RE-CO-2. Isotopic summer was defined as May, June, July, August and September. This is the same definition that was found to yield optimal comparisons for MO-0-2. Since MO-0-2 and RE-CO-2 are at similar latitudes with similar average annual temperatures and seasonal temperature extremes, it was felt that the definition of isotopic summer that was "successfully" applied to MO-0-2 could also be usefully applied to RE-CO-2.

Comparisons of RE-CO-2 δD values with X_s, $X_s\ (T_s - T_w)$, and $X_s\ (T_s - T_w) + T_w$ indicate no overall correlation in each case. Yet, the plot of δD vs $X_s\ (T_s - T_w)$ appears to contain the type of "fine structure" that has been described for other trees in this thesis. The data are listed in Table 5-7 and plotted in Figure 5-35. The lack of a general relationship between the δD values of RE-CO-2 and $X_s\ (T_s - T_w)$ is readily apparent. However, the stippled regions in Figure 5-35 are interpreted to be separate domains of isotopic variation within which there may be a correlation between δD values and local climate as represented by the parameter $X_s\ (T_s - T_w)$. The highly tentative nature of this interpretation of the data of Figure 5-35 precludes any general statements at this time about its possible implications. However, it

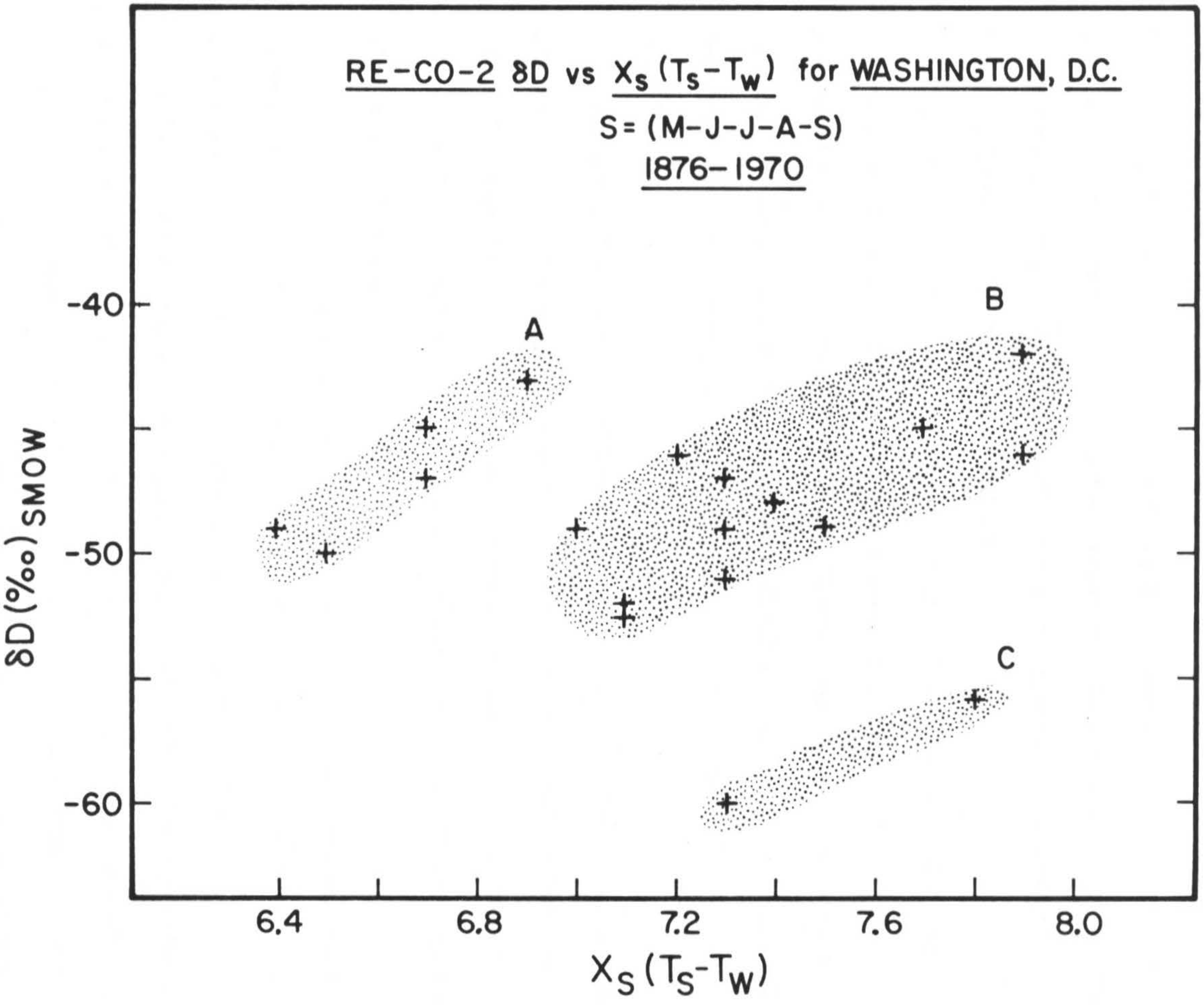
Table 5-7: $X_s(T_s - T_w)$, X_s, W_s, and δD Values of RE-CO-2

S = May, June, July, August and September

Interval	X_s	$X_s(T_s - T_w)$	W_s(m)	δD
1876-80	0.495	7.8	0.1168	-56
1881-85	0.420	6.7	0.0979	-47
1886-90	0.497	7.4	0.1218	-48
1891-95	0.411	6.4	0.0822	-49
1896-1900	0.483	7.5	0.0974	-49
1901-05	0.467	7.3	0.1060	-47
1906-10	0.498	7.3	0.1054	-49
1911-15	0.482	7.3	0.0992	-51
1916-20	0.472	7.1	0.0944	-52
1921-25	0.501	7.3	0.1022	-60
1926-30	0.471	7.1	0.0877	-52
1931-35	0.517	7.0	0.1191	-49
1936-40	0.433	6.5	0.0930	-50
1941-45	0.495	7.7	0.0964	-45
1946-50	0.560	7.9	0.1226	-42
1951-55	0.466	6.9	0.0992	-43
1956-60	0.470	7.2	0.0888	-46
1961-65	0.426	6.7	0.0740	-45
1966-70	0.501	7.9	0.0986	-46

Figure 5-35

A comparison of the δD values of RE-CO-2 with X_s (T_s - T_w) as calculated from Washington, D.C. meteorological data (see text). The stippled regions in the figure are interpreted to be domains within which the tree δD varies in response to local climate change as manifested by the model parameter X_s (T_s - T_w). If real, these three domains might mean that there are three types of large scale climatic patterns that alternately prevail in the Washington, D.C. area. The meteorological data from Washington, D.C., span the entire age of the tree from 1876 to 1970. The points in regions A and C are considered to be "anomalous", while those in region B are interpreted to be "normal" (see text).


RE-CO-2 δD vs X_S (T_S-T_W) for WASHINGTON, D.C.
S= (M-J-J-A-S)
1876-1970
A
B
C
-40
-50
-60
δD (‰) SMOW
6.4
6.8
7.2
7.6
8.0
X_S (T_S-T_W)

it may be worthwhile to examine some of the details of these "domains".

The grouped data designated as region B represent 12 of the 19 samples. Therefore, to the degree that these regions are real, the B domain seems to be the area of most probable occurrence of δD values. The data points contained within the domain of "intermediate" probability of occurrence (region A) represent the following intervals: 1881-85, 1891-95, 1936-40, 1951-55, and 1961-65.

Two of these intervals (1891-95 and 1951-55) have shown distinctive isotopic behavior in other trees from different locales. Both have exhibited isotopic characteristics in FCA-WS-1 that seem to mark them as being possibly different from the local norm. Furthermore, the 1891-95 interval has also shown possibly "anomalous" behavior in OPW-DF-1 and Col-DF-1.

The intervals 1881-85, 1936-40, 1961-65 have not appeared to display any significantly anomalous isotopic behavior in the trees (other than RE-CO-2) which have been examined thus far. Additionally, neither of the points (1876-80, 1921-25) of region C in Figure 5-35 have analogs in the other trees discussed to this point.

If region A in Figure 5-35 is considered to be a departure from the norm as represented by B, the occurrence of sample intervals in A that have also appeared to be isotopically "anomalous" in other trees at sites far removed from Reston suggests that perhaps the domains defined as in Figure 5-35 are real. If so, they could represent three different large scale climatic patterns which episodically dominate the climate at Reston, and which alter the isotopic condensation trajectories each time there is a change from one pattern to another. In this context some of the scatter, particularly in region B could arise as a consequence of the five-year sample intervals. Thus, a five-year sample might overlap a shift in large scale climatic patterns and contain isotopic information from both. Two possible examples of such samples are the intervals 1931-35 and 1956-60 both of which appear to lie at the left extreme of region B and both of which are neighbors in time with samples that lie within region A.

If the tree domains defined in Figure 5-35 are real and if the preceding interpretation of their meaning is correct, it implies that the δD variations in RE-CO-2 quite probably reflect not only variations in local climate, but also much larger scale climatic change.

The δD vs reciprocal ring width plot is located in Figure 5-36. It is readily apparent that there is little information to be gleaned from it that has any bearing on the preceding discussion. The one strong point that it does make, however, is that the tree δD value and ring width are not responding in concert with the same, or similar, climatic variables.

The MNY Sample Group

This group consists of three different trees: a red maple (MNY-RM-5), a bur oak (MNY-BO-7) and a green ash (MNY-GA-2). These three trees grew in the same general vicinity. The growth sites were scattered throughout a swamp-like environment in the Montezuma National Wildlife Refuge, New York. The chronologies of MNY-GA-2 and MNY-RM-5 extend from 1871 to 1970, while that of MNY-BO-7 covers the period from 1807 to 1970. The δD variations of these three tree ring sequences are displayed in Figures 5-37, 5-38, and 5-39. MNY-GA-2 (Figure 5-37) exhibits a roughly sinusoidal variation of δD values from 1871-1970 with a δD range of

Figure 5-36

A plot of the δD values of RE-CO-2 against the reciprocal of the aggregate ring width of corresponding five-year intervals. There is no apparent relationship between these variables for this tree.

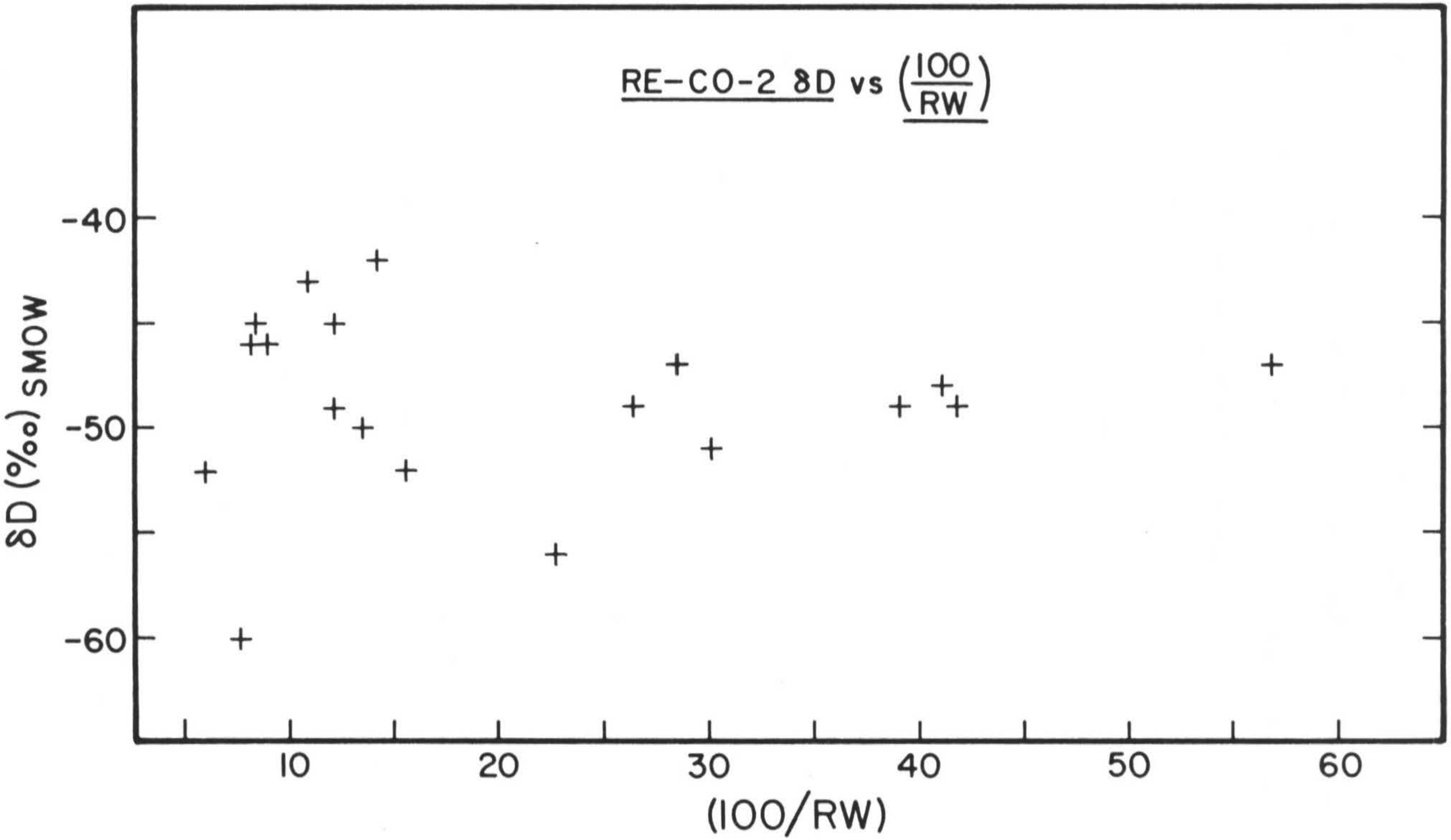

RE-CO-2 δD vs $\left(\frac{100}{RW}\right)$
δD (‰) SMOW
-40
-50
-60
10
20
30
40
50
60
(100/RW)

Figure 5-37

The variations of the δD values of MNY-GA-2 with age over the interval from 1871 to 1970. The δD range for this interval is 22 per mil. There is no monotonic long term trend to the δD values although they do seem to exhibit a crudely sinusoidal variation.

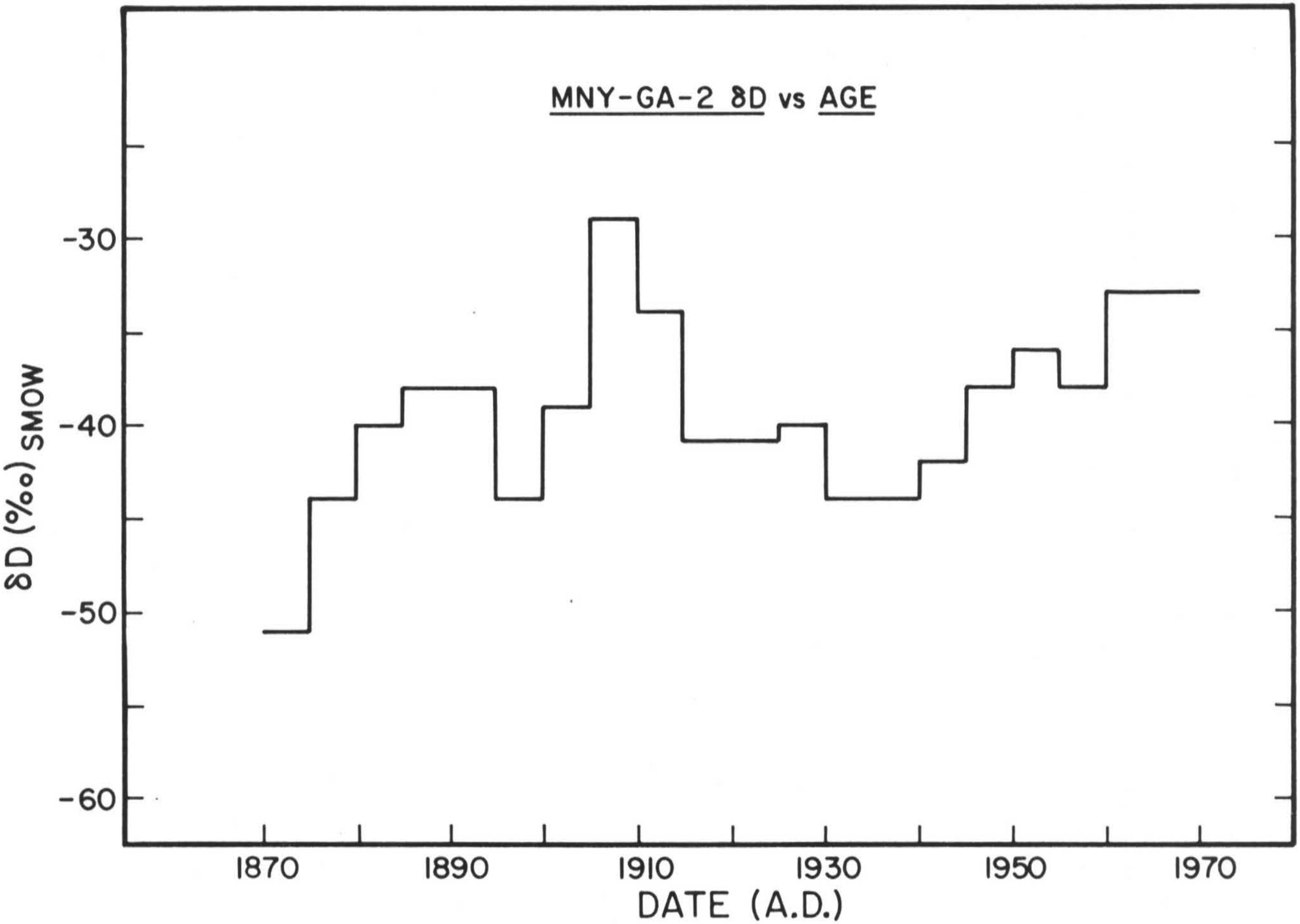

MNY-GA-2 δD vs AGE
δD (‰) SMOW
-30
-40
-50
-60
1870
1890
1910
1930
1950
1970
DATE (A.D.)

Figure 5-38

The variation of the δD values of MNY-RM-5 with age over the interval from 1871 to 1970. The total δD range over this period is 28 per mil. The δD values exhibit a long term increase from older to younger samples over this 100 year span of time.

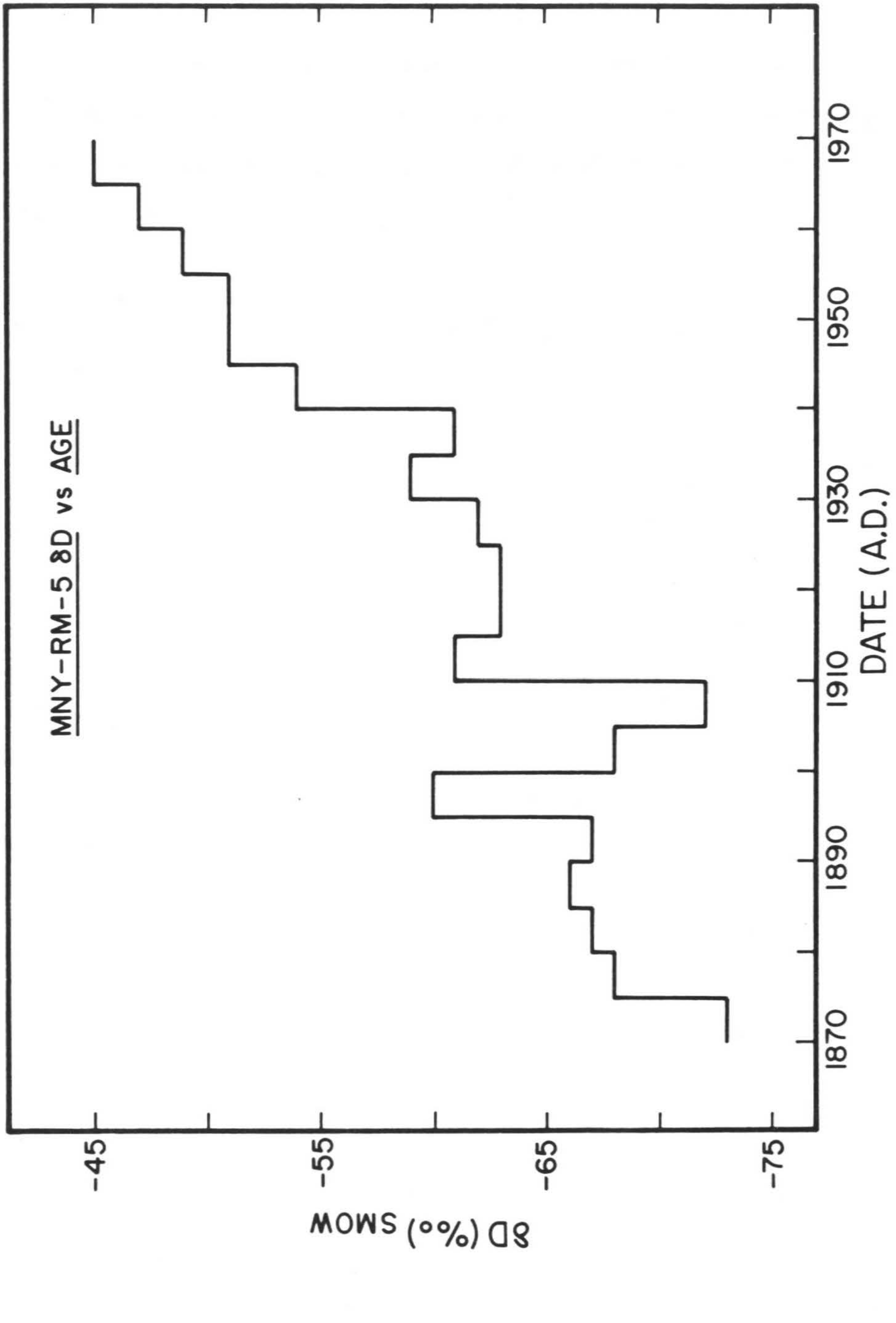
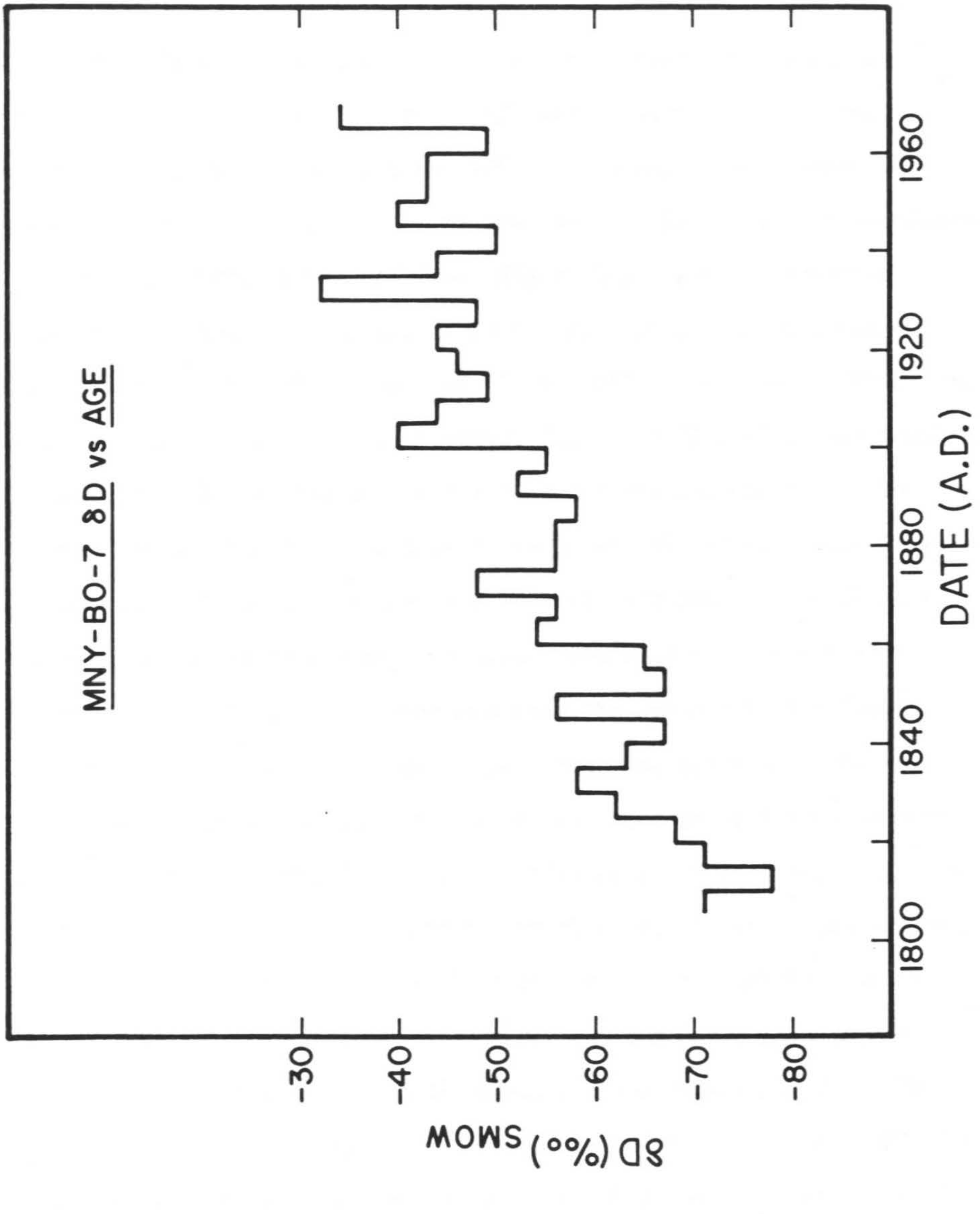

MNY-RM-5 δD vs AGE
δD (‰) SMOW
-45
-55
-65
-75
1870
1890
1910
1930
1950
1970
DATE (A.D.)

Figure 5-39

The variation of the δD values of MNY-BO-7 with age over the interval from 1807 to 1970. There appears to be a long term increase in the δD values from older to younger samples. The total δD range for this 164 year period is 46 per mil.


MNY-BO-7 δD vs AGE
δD (‰) SMOW
-30
-40
-50
-60
-70
-80
DATE (A.D.)
1800
1840
1880
1920
1960

22 per mil over this interval. The maximum and minimum δD values are -29 and -51 per mil respectively. MNY-RM-5 (Figure 5-38) reveals a distinctly different pattern of δD variation. There is a long term increase in δD values from 1871 to 1970 with a particularly sharp, monotonic rise from about 1936 to 1970. The maximum and minimum δD values in the 1871 to 1970 interval are -45 and -73 per mil respectively.

The δD record from MNY-BO-7 (Figure 5-39) shows a long term increase in δD values from 1807 to 1970. The maximum and minimum δD values in this interval are -32 and -78 per mil respectively. Thus, the total δD range is 46 per mil. However, for the 1871-1970 interval which it has in common with MNY-GA-2 and MNY-RM-5, MNY-BO-7 displays a δD range of 26 per mil with a maximum δD value of -32 per mil and a minimum δD value of -58 per mil. Within the 1871 to 1970 interval there is a continuation of the long term δD increase observed for the MNY-BO-7 chronology as a whole, but departures from the trend are significant.

The salient features of the three δD records depicted in Figures 5-37 through 5-39 are as follows: (1) there are significant differences in the patterns of isotopic change recorded by the three trees; (2) the total δD ranges exhibited by each of the trees in the 1871-1970 interval are similar and on the order of 22 to 28 per mil; (3) MNY-GA-2 and MNY-BO-7 are characterized by similar maximum and minimum δD values in the 1871-1970 interval. The maximum and minimum δD values of MNY-RM-5, on the other hand, are significantly more negative than those of MNY-GA-2 and MNY-BO-7. In fact the maximum δD value of MNY-RM-5 in the 1871-1970 interval is not much greater than the minimum δD values of the other two trees; (4) this feature is linked with the first feature above, but it is worth noting. The maximum and minimum δD values within each tree sequence are not coincident with those of the other sequences.

The swamp-like nature of the MNY growth area is a distinctive characteristic that may have important isotopic consequences. In the context of the geographic relationship between tree δD and temperature that was characterized in the first part of this section, it was noted that the MNY samples seemed to belong to a group that was displaced in a positive δD sense from the general trend of the data. Furthermore, it was pointed out that a tree from another marshy environment was incorporating water with a measured δD value more positive than that of the average annual precipitation.

As would be expected, the water table in the swampy growth area of the MNY trees is very shallow (R. L. Phipps, personal communication). Consequently, the root systems of the trees will also be shallow (Wilde, 1958; Kramer and Kozlowski, 1960). Because of the former condition, ground water may play a significant part in the water regimes of some trees. Shallow root systems, however, favor the incorporation of water which has recently infiltrated into the soil. Thus, a complex and quite probably highly variable balance may exist between the relative contributions of ground water and summer rain to the isotopic composition of water passing through a tree. The reason why summer rain is thought to be of importance in this case is because all of the presumably shallow-rooted MNY trees are deciduous and will only photosynthesize and grow during the summer months (see Section 2).

Since groundwater in temperate climates seems to have an isotopic composition which reflects that of the annual precipitation (Eichler, 1966), the groundwaters of MNY sites will probably have δD values that are more negative than the δD values of the summer rain. Thus, if trees from the MNY sites have water regimes which are dominated by groundwater, they will probably have more negative δD values than those trees for which summer rain plays a larger role.

Therefore, the comparatively more negative δD values of MNY-RM-5 suggest that it has incorporated a higher proportion of groundwater than have the other two trees from this area. If the ratio of the ground water to summer rain incorporated by this tree has been consistently high throughout its lifetime, the δD variations in the tree may be related to the variations of local annual temperatures. This of course assumes that the residence time of groundwater is short compared to the length of the sample interval of five years.

The meteorological station nearest to the MNY-RM-5 growth site is Syracuse, N.Y. It is located about 50 Km northeast of the Montezuma National Wildlife Refuge. The weather data from Syracuse are complete from 1903 to the present. However, there have been several station shifts which appear to have introduced inhomogeneities into the record. This is suggested by comparison of the average annual temperatures from Syracuse with those of Toronto, Ontario. During those intervals in which there were no station relocations, the correlation between Syracuse and Toronto annual temperatures is very good. But, a Syracuse station shift coincides with a shift in the Syracuse vs Toronto temperature curve. Consequently, the use of Syracuse annual temperatures would likely yield spurious comparisons with δD variations.

The good correlation of Toronto annual temperatures with Syracuse annual temperatures in the absence of a station relocation suggested that the former could be used for comparison with the δD values from the MNY samples. Toronto is located about 250 km northwest of the growth sites. Meteorological data have been recorded there continuously since 1841.

The Toronto average annual temperature and MNY-RM-5 δD data are listed in Table 5-8 and plotted in Figure 5-40. Although significant scatter is evident, there does seem to be a definite overall relationship between the two variables. The best-fit linear equation for these data is:

$$\delta D = 7.28\ T(^{o}C) - 118 \qquad (5\text{-}25)$$

The linear correlation coefficient is 0.789. Thus, the validity of three assumptions may have been established by this comparison: (1) groundwater is probably the dominant component in the water regime of MNY-RM-5; (2) the δD variations of annual precipitation in this area, as represented by the groundwater, are related to variations in "local" temperature; (3) the residence time of the local groundwater is short compared to the sample interval. Of course, if the water incorporated by the tree has a groundwater to summer rain ratio that is negatively correlated with annual temperature, this condition alone could induce a relationship of the type observed in Figure 5-40. However, such a fortuitous condition seems unlikely. It is possible, though, that some of the scatter of Figure 5-40 could be a consequence of a changing groundwater to summer rain ratio in the water incorporated by the tree.

Of the three trees from this area, MNY-GA-2 has, on the average, the most positive δD values. Thus, if one is searching for the tree which is most likely to have incorporated water with a dominant summer

Table 5-8: δD Values of MNY-RM-5, MNY-BO-7 and MNY-GA-2, Toronto, Ont. Annual Temperature and Syracuse, N.Y. Summer Precipitation S = April, May, June, July, August, September.

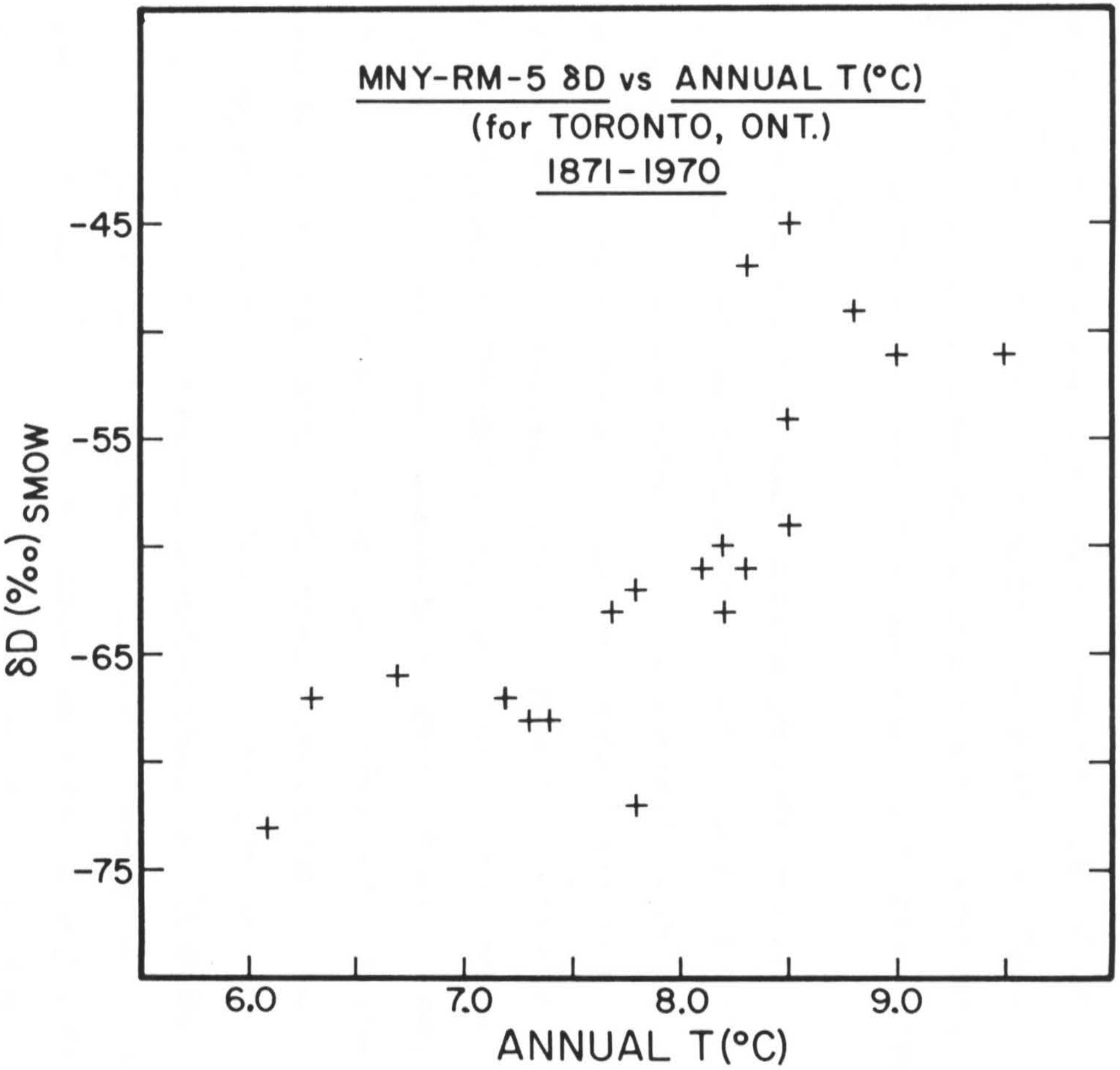
	Syracuse	Toronto	δD		
Interval	W_s(m)	T(°C)	MNY-RM-5	MNY-BO-7	MNY-GA-2
1841-45	-	6.9	-	-67	-
1846-50	-	6.7	-	-56	-
1851-55	-	6.4	-	-67	-
1856-60	-	6.2	-	-65	-
1861-65	-	7.1	-	-54	-
1866-70	-	6.8	-	-56	-
1871-75	-	6.1	-73	-48	-51
1876-80	-	7.4	-68	-56	-44
1881-85	-	6.3	-67	-56	-40
1886-90	-	6.7	-66	-58	-38
1891-95	-	7.2	-67	-52	-38
1896-1900	-	8.2	-60	-55	-44
1901-05	-	7.3	-68	-40	-39
1906-10	0.0724	7.8	-72	-44	-29
1911-15	0.0773	8.1	-61	-49	-34
1916-20	0.0776	7.7	-63	-46	-41
1921-25	0.0892	8.2	-63	-44	-41
1926-30	0.0840	7.8	-62	-48	-40
1931-35	0.0718	8.5	-59	-32	-44
1936-40	0.0734	8.3	-61	-44	-44
1941-45	0.0835	8.5	-54	-49	-42
1946-50	0.0798	9.0	-51	-40	-38
1951-55	0.0755	9.5	-51	-43	-36
1956-60	0.0841	8.8	-49	-43	-38
1961-65	0.0623	8.3	-47	-49	-33
1966-70	0.0843	8.5	-45	-34	-33

Figure 5-40

A comparison of the δD values of MNY-RM-5 with the average annual temperature of Toronto, Ontario, over the interval from 1871 to 1970. The linear regression of these data yields the expression:

$$\delta D = 7.28\ T(^{\circ}C) - 118$$

The correlation coefficient is 0.789.

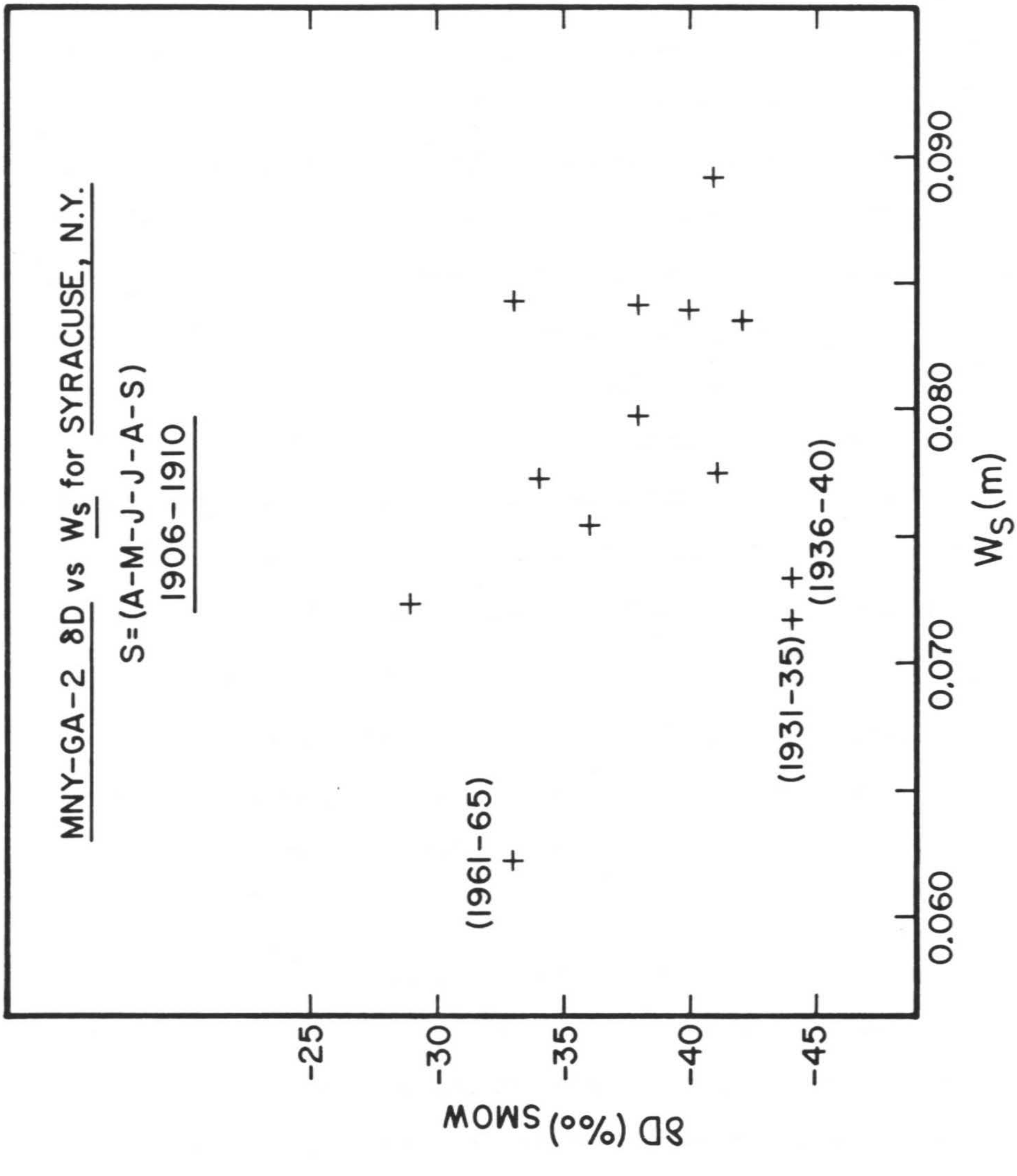

MNY-RM-5 δD vs ANNUAL T(°C)
(for TORONTO, ONT.)
1871-1970
-45
-55
-65
-75
δD (‰) SMOW
6.0
7.0
8.0
9.0
ANNUAL T(°C)

rain component, MNY-GA-2 is the best candidate. A comparison of the δD variations of MNY-GA-2 with variously defined Toronto summer temperatures reveals no correlation. Comparisons of δD values with Toronto summer rainfall amounts also yield no relationships. However, this may be in part because Toronto is on the "windward" side of Lake Ontario, while the MNY-GA-2 site is on the leeward side of the lake. Thus, the Syracuse precipitation data would represent the better choice for comparison even though there may be some possibility of inhomogeneity in that record.

Various combinations of "summer" Syracuse precipitation were compared with MNY-GA-2 over the interval 1906-1970. A basic pattern was evident for those "summers" which included the months of the normal growing season, but the best-defined pattern was for a summer that included April, May, June, July, August and September. The Syracuse precipitation data and MNY-GA-2 δD values are listed in Table 5-8 and plotted in Figure 5-41. There seems to be a diffuse, but nevertheless, discernible trend to 10 of the 13 data points in Figure 5-41. The three which appear to be distinct from this "trend" represent the intervals 1931-35, 1936-40 and 1961-65. The latter two intervals appeared to exhibit anomalous isotopic behavior in RE-CO-2 from Reston, Virginia. Consequently, there may be more than "local effects" causing the isotopic scatter in Figure 5-41. If so, then MNY-GA-2 may indeed be incorporating dominantly summer precipitation, because the negative slope which is apparent for the "general trend" of the data in Figure 5-41 is consistent with the possible presence of an "amount effect" on the isotopic composition of summer rainfall.

Figure 5-41

A comparison of the δD values of MNY-GA-2 with the average monthly amount of summer precipitation recorded at Syracuse, New York. The precipitation amount is in meters and the meteorological record for Syracuse extends from about 1906 to 1970. Inhomogeneities may exist in the Syracuse weather data (see text). The "best-fit" summer is defined as April, May, June, July, August and September. There is no well-defined "normal" trend. Thus, it is difficult to identify isotopically "anomalous" intervals. However, the points which are labeled in the diagram may qualify as such anomalies.


MNY-GA-2 δD vs W_S for SYRACUSE, N.Y.
S=(A-M-J-J-A-S)
1906-1910
(1961-65)
(1931-35)
(1936-40)
-25
-30
-35
-40
-45
δD (‰) SMOW
0.060
0.070
0.080
0.090
W_S (m)

The average δD value of MNY-BO-7 in the interval 1871-1970 is intermediate between those of MNY-RM-5 and MNY-GA-2. Therefore, it may be possible that the δD values of MNY-BO-7 are not generally dominated by either groundwater or summer rain, but by some varying combination of the two. A comparison of the Syracuse summer precipitation data with MNY-BO-7 δD data in the 1906-1970 interval shows no indication of the "fine structure" that was interpreted to be present for MNY-GA-2. Thus, it does not appear that summer precipitation exercises a controlling influence over MNY-BO-7 δD values in the 1906-1970 interval.

The MNY-BO-7 δD values and Toronto annual temperatures for the period 1841 to 1970 are listed in Table 5-8 and plotted in Figure 5-42. There is a great deal of scatter in the data, but the suggestion of a trend seems to be there. For the complete interval 1841 to 1970, the linear regression of the data of Figure 5-42 yields the expression:

$$\delta D = 6.90\ T(^{o}C) - 102 \qquad (5\text{-}26)$$

The linear correlation coefficient is 0.707. If only the interval corresponding to overlap with MNY-GA-2 and MNY-RM-5 is considered (1871 to 1970), the best fit equation is:

$$\delta D = 4.46\ T(^{o}C) - 82 \qquad (5\text{-}27)$$

The linear coefficient for the regression in this interval is 0.549. In either case the correlation of MNY-BO-7 δD values with annual temperature is not as good as that of MNY-RM-5. This is particularly true if one only considers the years which the two trees have in common (1871-1970).

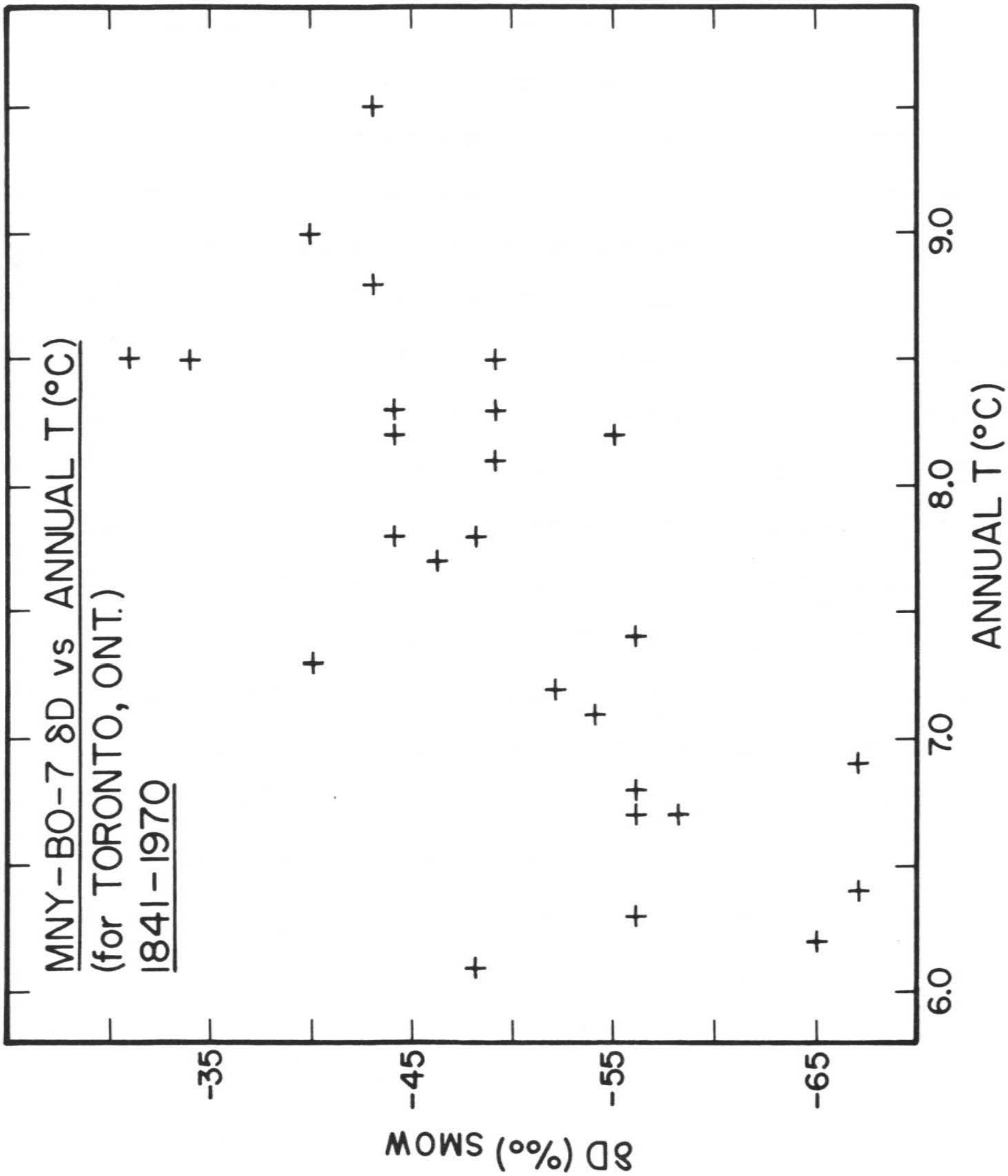
The lower degree of correlation of MNY-BO-7 δD values with annual temperature is consistent with the idea posited previously that

Figure 5-42

A comparison of the δD values of MNY-BO-7 with the average annual temperature of Toronto, Ontario, over the interval from 1841 to 1970. The linear regression of these data results in the equation:

$$\delta D = 6.90\ T(^{o}C) - 102$$

The correlation coefficient is 0.707.


MNY-BO-7 δD vs ANNUAL T (°C)
(for TORONTO, ONT.)
1841-1970
ANNUAL T (°C)
6.0
7.0
8.0
9.0
δD (‰) SMOW
-35
-45
-55
-65

this tree incorporated water which was not commonly dominated by either summer rain or groundwater. However, it seems probable that groundwater did play some role, because there is a measure of correlation between the MNY-BO-7 δD values and annual temperature.

The possible roles of varying tree biochemistries and/or physiologies in producing the different average δD values and patterns of temporal variation in these trees have not been considered for two reasons: (1) there are no quantitative tests that can presently be applied to these samples that would yield conclusive information about a biochemical effect; (2) much in the character of the differences can be explained in terms of the isotopic variations of the water incorporated by the trees.

The choice of swamp, or marsh-grown trees for the purpose of climatic interpretation of δD values does not appear to be an optimal one. The combination of shallow water tables and shallow root systems tends to enhance the possibility that variable mixing ratios of groundwater and summer rain will superimpose a nonclimatic δD variation on that which might otherwise be obtained from the precipitation-weighted δD value alone. However, with this caveat in mind, it does seem that under certain conditions a climatic signal can be forthcoming from the δD values of marsh-grown trees. It is just that there are no good criteria to apply at present to decide which marsh-grown trees are likely to be climatically "well-behaved". A choice based on the species analyzed for this work might be possible, but the particular interrelationships observed here may not, and probably do not, apply to all individuals of these species.

The δD vs reciprocal ring width plots for each of these trees are found in Figures 5-43 through 5-45. There are only the slightest suggestions of correlations for MNY-GA-2 and MNY-BO-7 and none whatsoever for MNY-RM-5. Furthermore, the climatically "anomalous" intervals of MNY-GA-2 exhibit no distinctive behavior in the ring width comparison of Figure 5-44.

AW-BO-1

AW-BO-1 is a bur oak which grew near Albion, Wisconsin. δD measurements were made on sample increments of five-years over the interval from 1851 to 1975 A.D. The plot of these δD values is in Figure 5-46. There seems to be a very slight trend toward increasing δD values from younger to older samples within the sequence. The total δD range over the 125 year record of Figure 5-46 is 24 per mil. However, the overall δD variance is small. The maximum δD value is -14 per mil, while the minimum is -38 per mil. The magnitude of these δD values is of interest, because as was discussed in the context of the geographic temperature vs δD relationship, AW-BO-1 appears to have incorporated waters with δD values which are more positive than those of the local annual precipitation.

The foregoing discussions of temporal δD variations in a variety of trees have suggested that in some instances the δD values recorded by trees may be those of summer rain. The relatively positive δD values of AW-BO-1 imply that such might be the case for this tree.

Meteorological data were obtained for Madison, Wisconsin which is situated about 30 km northwest of the growth site. The temperature and precipitation records are continuous from 1871 to the present. With

Figure 5-43

A plot of the δD values of MNY-RM-5 against the reciprocal of the aggregate ring widths of corresponding five-year intervals. There is no apparent relationship between these variables.

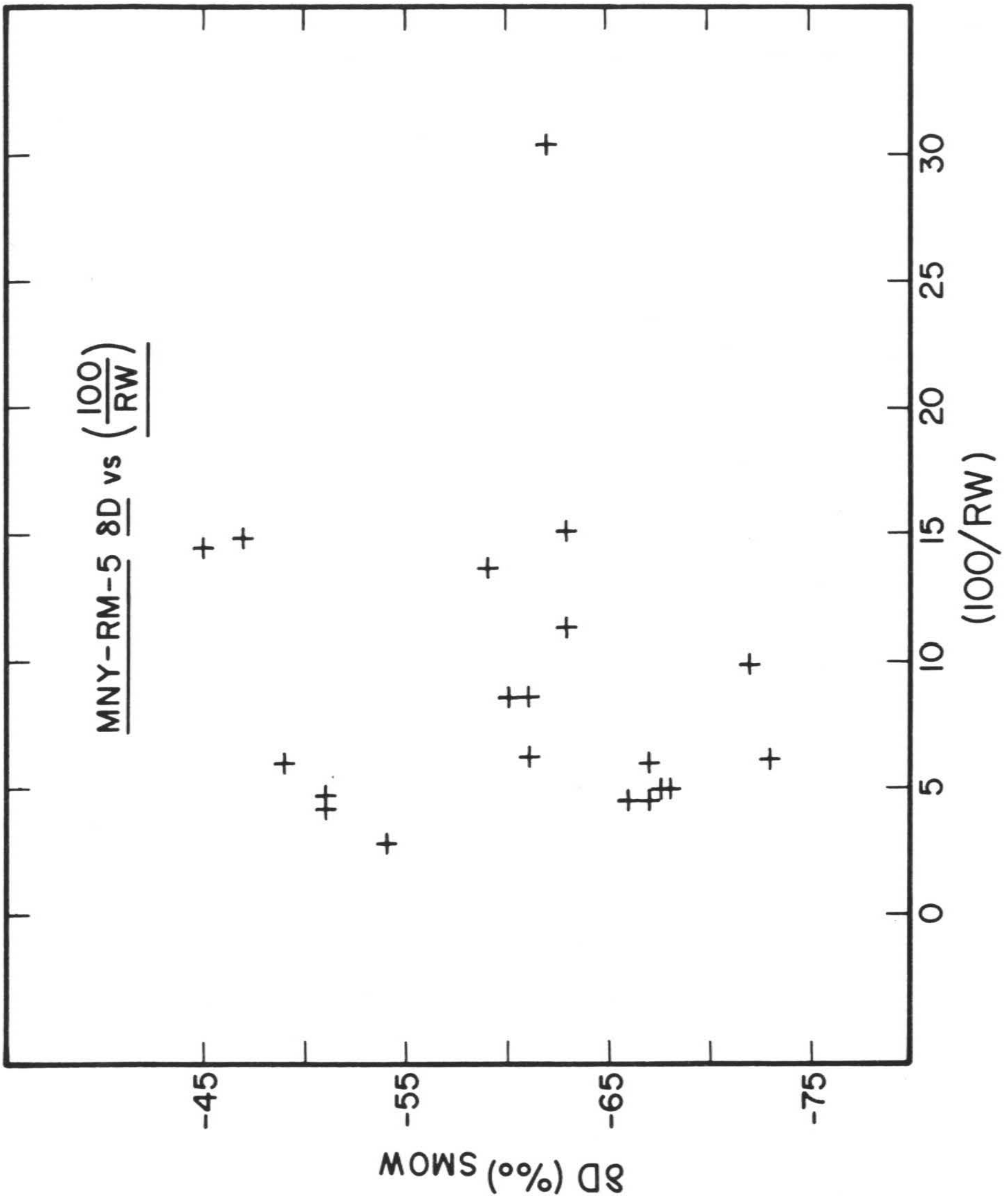

MNY-RM-5 δD vs $\left(\frac{100}{RW}\right)$
δD (‰) SMOW
-45
-55
-65
-75
(100/RW)
0
5
10
15
20
25
30

Figure 5-44

A plot of the δD values of MNY-GA-2 against the reciprocal of the aggregate ring widths of corresponding five-year intervals. There is only the slightest suggestion of a relationship between these variables.

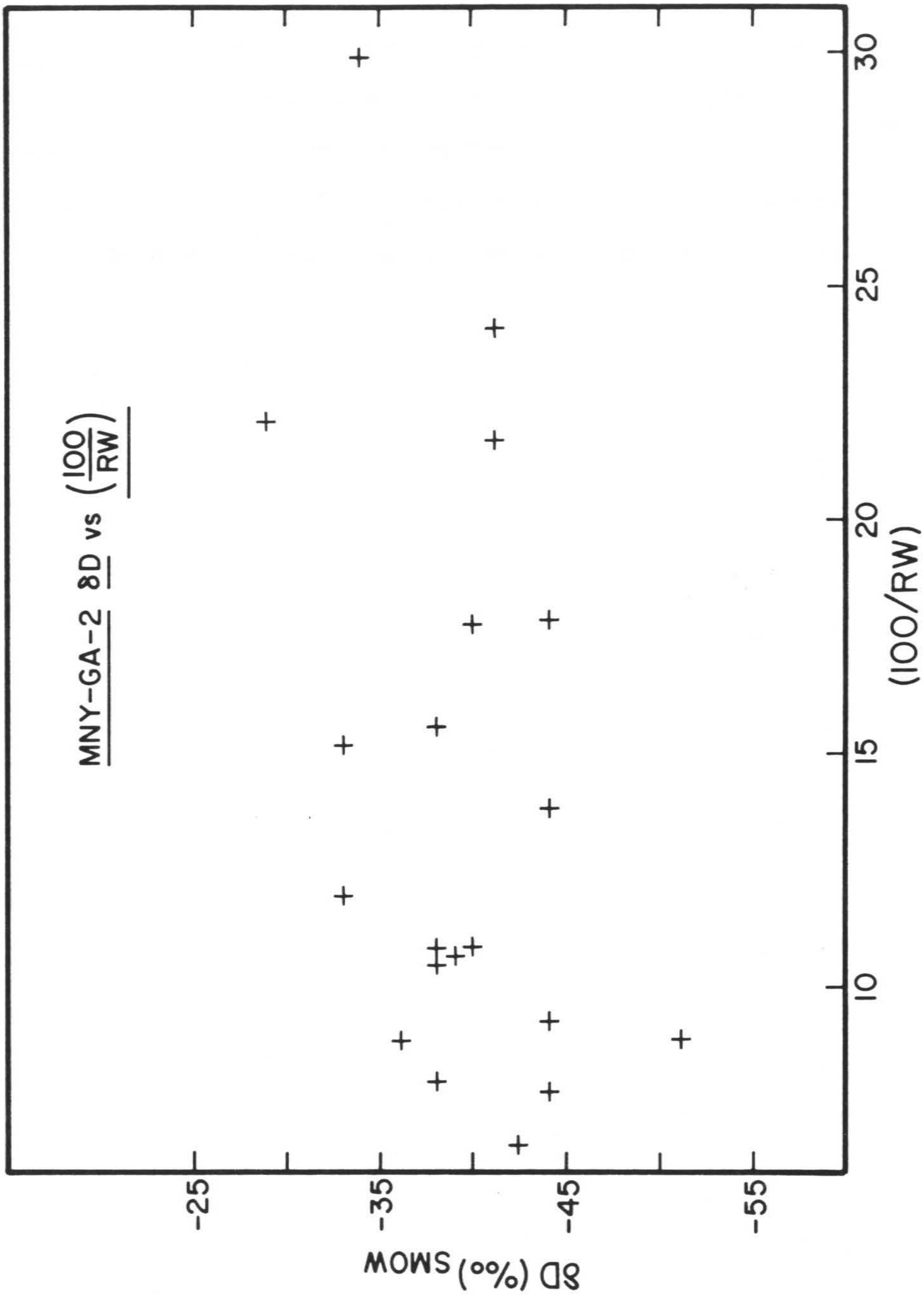

MNY-GA-2 δD vs $\left(\frac{100}{RW}\right)$
-25
-35
-45
-55
δD (‰) SMOW
10
15
20
25
30
(100/RW)

Figure 5-45

A plot of the δD values of MNY-BO-7 against the reciprocal of the aggregate ring widths of corresponding five-year intervals. The comparison is for the period from 1807 to 1970. There seems to be a slight suggestion of a relationship between these variables with a tendency for the δD values to increase as the ring widths decrease.

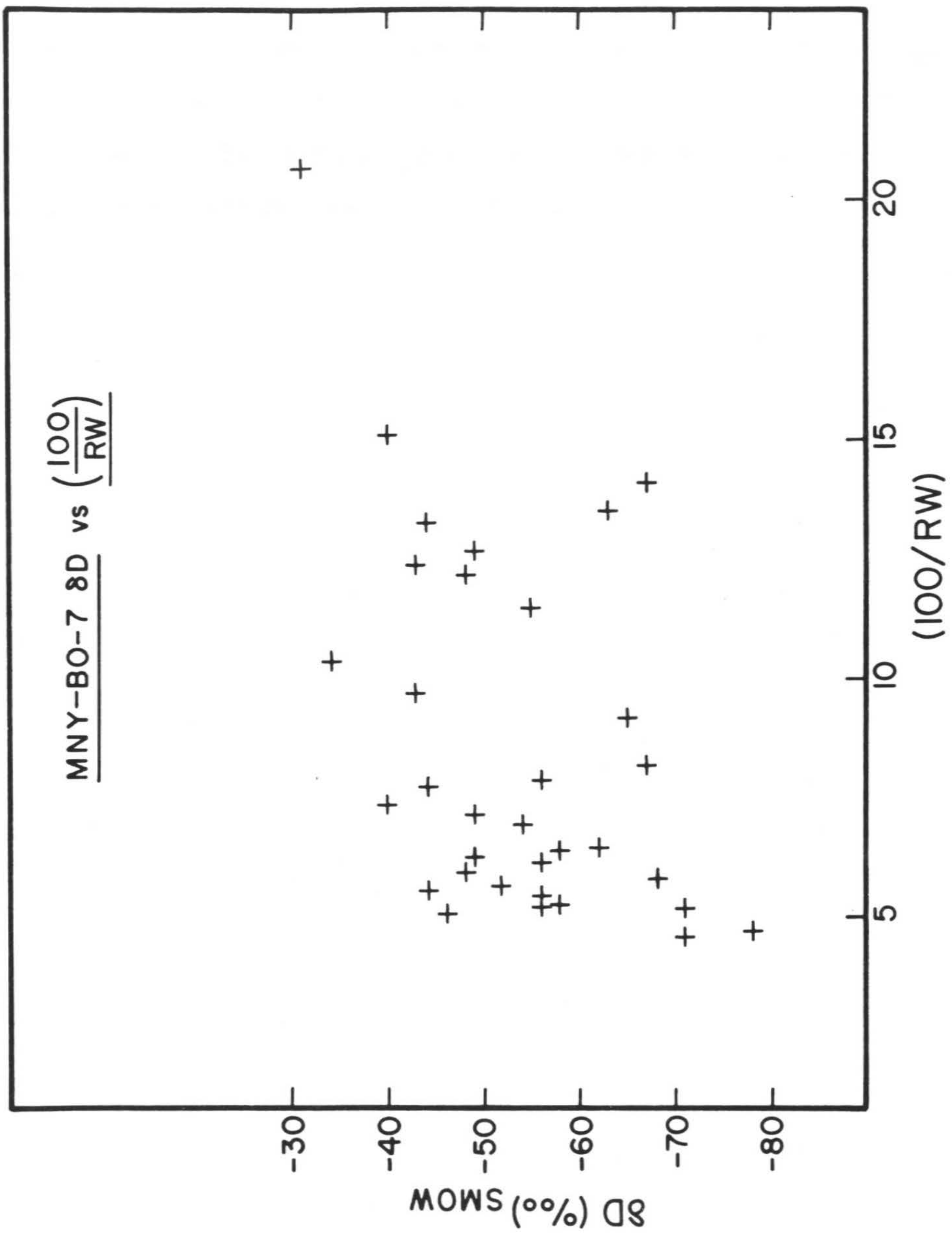
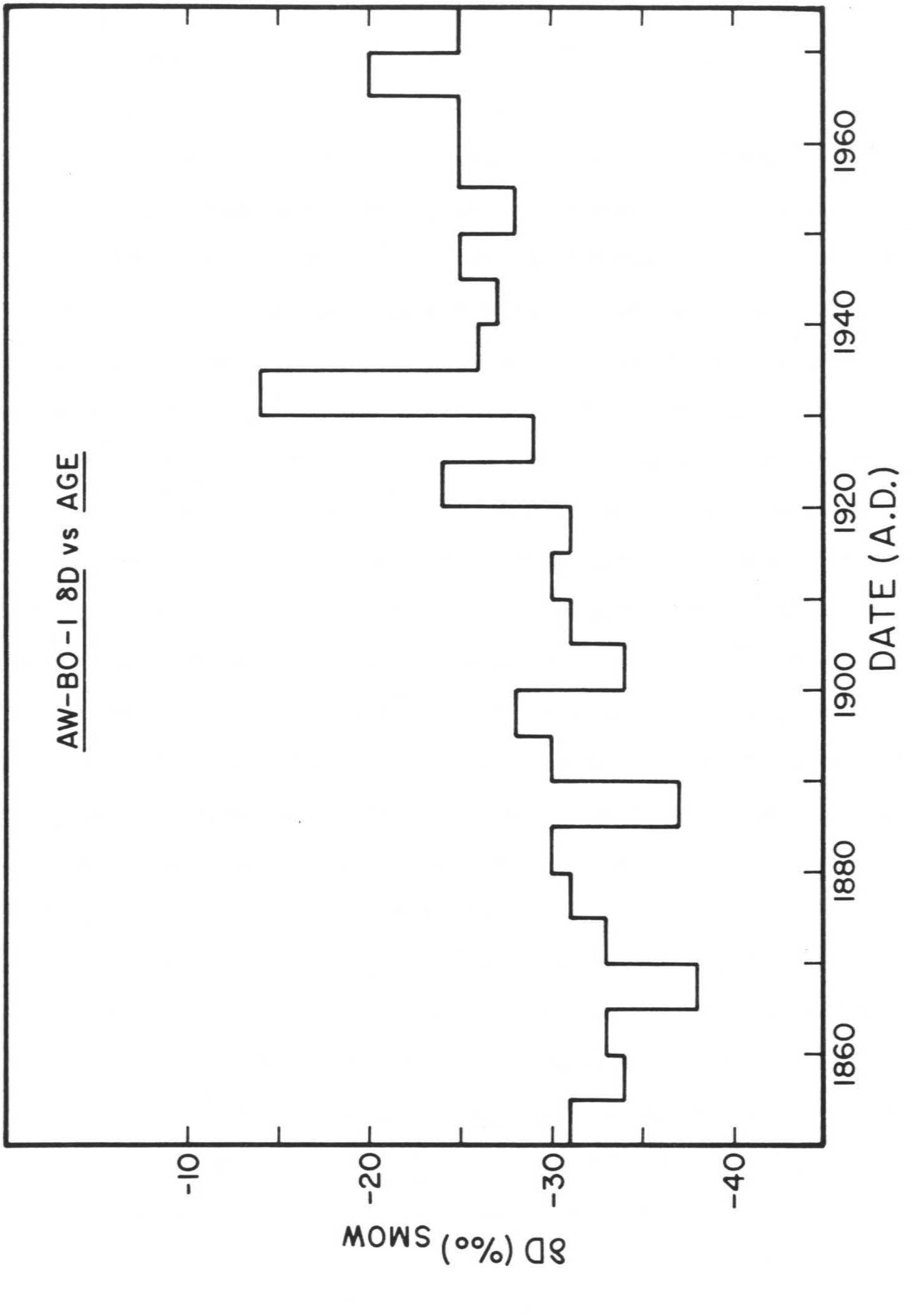

MNY-BO-7 δD vs (100/RW)
δD (‰) SMOW
-30
-40
-50
-60
-70
-80
5
10
15
20
(100/RW)

Figure 5-46

The variations of the δD values of AW-BO-1 with age over the interval from 1851 to 1975. The total range of δD for this period is 24 per mil, although the overall variance of the δD values is comparatively small. There appears to be a slight tendency for the δD values to generally increase from older to younger samples.


AW-BO-1 δD vs AGE
DATE (A.D.)
δD (‰) SMOW
-10
-20
-30
-40
1860
1880
1900
1920
1940
1960

the assumption that AW-BO-1 δD values reflect those of the summer precipitation and that the δD values of the latter vary in response to local climate, comparisons were made between AW-BO-1 δD variations and both summer temperature and precipitation amounts. The temperatures and precipitation amounts from a number of variously defined "summers" were utilized. In no instance was there any correlation between AW-BO-1 δD values and the summer temperatures or precipitation amounts. The linear correlation coefficients between these variables were only on the order of 0.100 for all the differently defined summers.

Rather than abandon the search for a local climate vs δD relationship, it was decided to compare the AW-BO-1 δD values with annual temperature. The linear correlation coefficient of the regression of these data is only 0.386, but it suggests that perhaps the δD variations in AW-BO-1 may be related to some climatic variable or variables other than those associated with summer. If it is assumed that in spite of the comparatively positive δD values of AW-BO-1, the tree has incorporated water whose δD variations reflect those of annual precipitation, then it is possible that the seasonally weighted annual precipitation δD values influence the isotopic record of the tree.

The parameters X_s, $X_s\ (T_s - T_w)$ and $X_s\ (T_s - T_w) + T_w$ of equations (5-6) through (5-8) were calculated on the basis of several differently defined summers and compared with the δD variations of AW-BO-1. The best correlation, as measured by the magnitude of the linear correlation coefficient, was for a comparison of δD values with $X_s\ (T_s - T_w) + T_w$ for a summer defined as April, May, June, July, August and September.

The equation of the linear regression is:

$$\delta D = 2.67 \quad \left[X_s\ (T_s - T_w) + T_w\right] \ - 56 \qquad (5\text{-}28)$$

The linear correlation coefficient is only 0.443, but, as was mentioned above, it is the largest obtained from any of the comparisons. As might be expected in such a case, the corresponding winter temperature correlates with the δD values to about the same degree as $X_s\ (T_s - T_w) + T_w$, but the correlation is still quite poor as is indicated by a correlation coefficient of only 0.480. The equation of the linear regression of δD against T_w is:

$$\delta D = 3.06\ T_w(^{o}C) - 24 \qquad (5\text{-}29)$$

Plots of AW-BO-1 δD values against $X_s\ (T_s - T_w) + T_w$ and T_w are found in Figures 5-47 and 5-48 respectively, while the data are listed in Table 5-9. Examination of these figures suggests that there may be some "fine structure" in the δD vs local climate relationship. However, this detail seems to be more clearly discernible in the plot of δD vs $X_s\ (T_s - T_w) + T_w$ in Figure 5-47. There is a suggestion in Figure 5-47 that the intervals 1931-35 and 1966-70 are isotopically "anomalous" in the sense that they are the points most greatly displaced from the general trend line defined by equation (5-28). If these two points are not considered in a linear regression of the data, the best-fit equation is:

$$\delta D = 2.50 \quad \left[X_s\ (T_s - T_w) + T_w\right] \ - 55 \qquad (5\text{-}30)$$

The correlation coefficient of this regression is 0.607.

The δD vs T_w relationship yields the following regression equation if 1931-35 and 1966-70 are omitted:

$$\delta D = 2.06\ T_w - 26 \qquad (5\text{-}31)$$

Figure 5-47

A comparison of the δD values of AW-BO-1 with $X_s\ (T_s - T_w) + T_w$ as calculated from the meteorological data from Madison, Wisconsin (see text). The stippled region in the figure is interpreted to be the domain of "normal" variation of δD with local climate. The labeled points may represent "anomalous" intervals, although the considerable scatter of the data within the stippled region could preclude such an interpretation. The meteorological data span the period from 1871 to 1975.

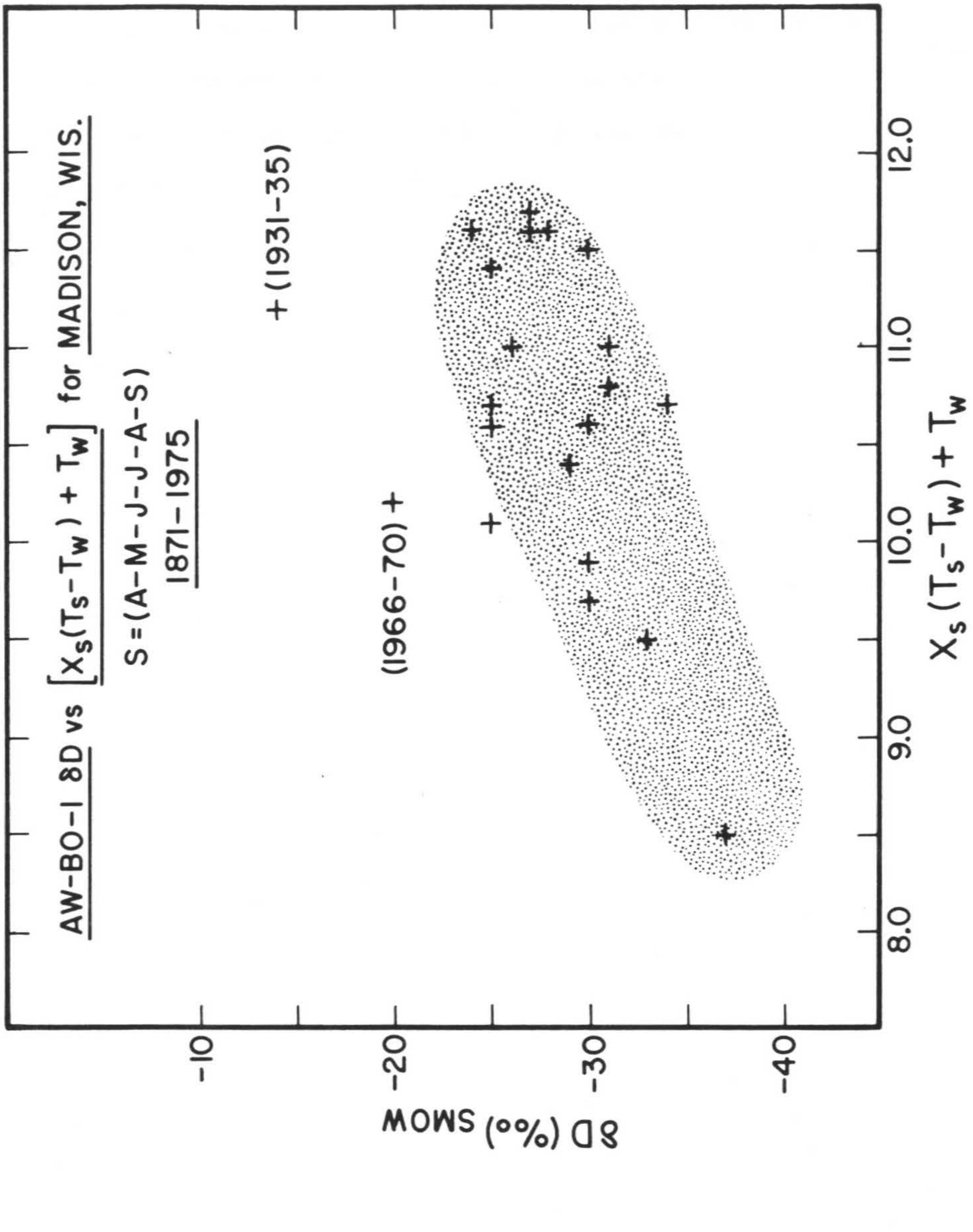

AW-BO-I δD vs $\left[X_s(T_s - T_w) + T_w\right]$ for MADISON, WIS.
S=(A-M-J-J-A-S)
1871–1975
+ (1931-35)
(1966-70) +
-10
-20
-30
-40
δD (‰) SMOW
8.0
9.0
10.0
11.0
12.0
$X_s(T_s - T_w) + T_w$

Figure 5-48

A comparison of the δD values of AW-BO-1 with the average winter temperature of Madison, Wisconsin. The meteorological data cover the interval from 1871 to 1975. Winter is defined as October, November, December, January, February and March. See text for discussion of the data in this figure.

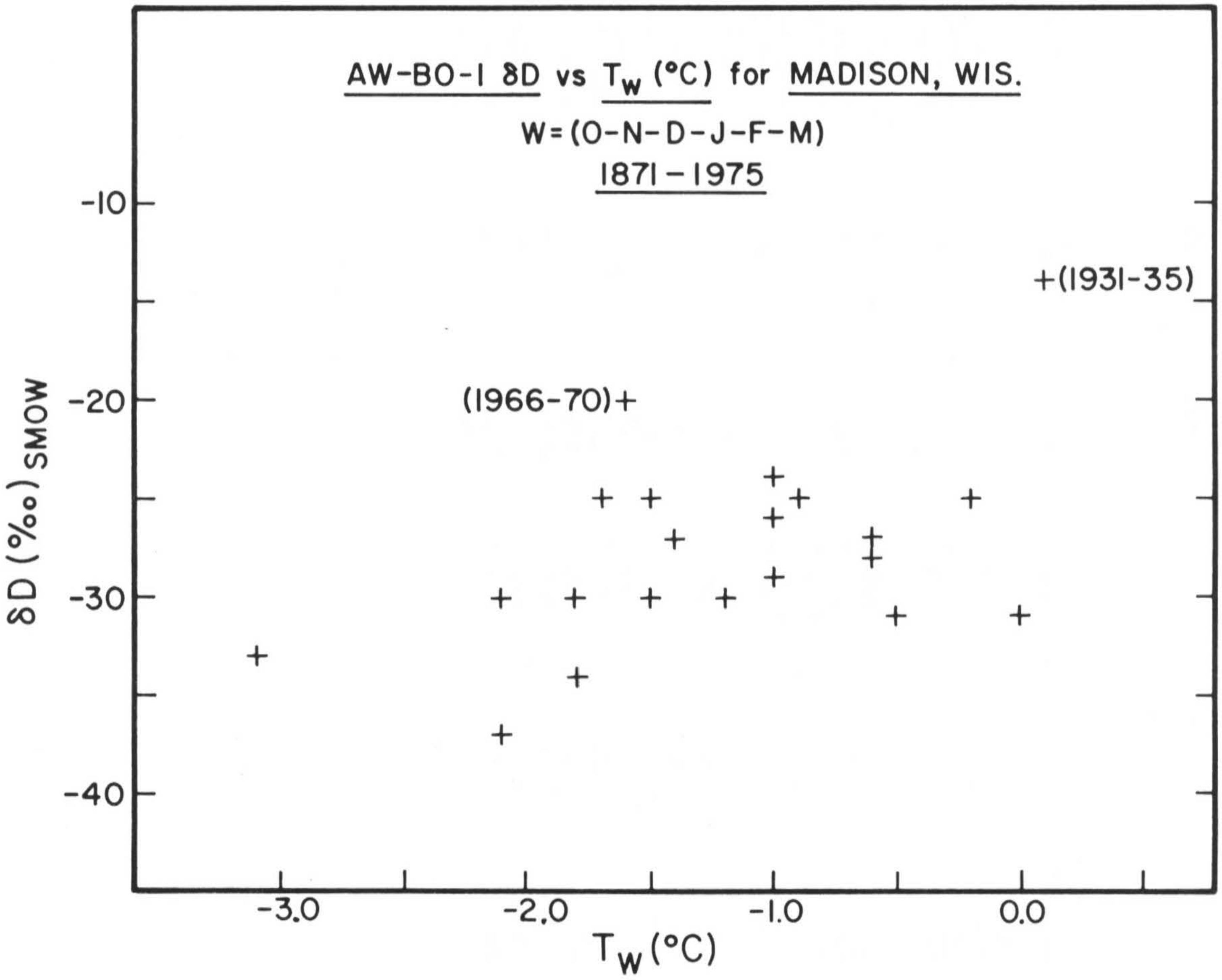

AW-BO-1 δD vs T_W (°C) for MADISON, WIS.
W=(O-N-D-J-F-M)
1871 – 1975
+(1931-35)
(1966-70)+
-10
-20
-30
-40
δD (‰) SMOW
-3.0
-2.0
-1.0
0.0
T_W (°C)

Table 5-9: T_s, T_w, W_s and $X_s(T_s - T_w) + T_w$ for Madison, Wisconsin and δD Values of AW-BO-1

S = April, May, June, July, August, September

Interval	T_s(°C)	T_w(°C)	W_s(m)	$X_s(T_s - T_w) + T_w$	δD
1871-75	17.1	-3.1	0.0688	9.5	-33
1876-80	17.6	0.0	0.0986	11.0	-31
1881-85	16.5	-1.5	0.1220	9.9	-30
1886-90	16.9	-2.1	0.0699	8.5	-37
1891-95	17.1	-2.1	0.0734	10.6	-30
1896-1900	17.6	-1.4	0.0815	11.7	-27
1901-05	16.6	-1.8	0.0824	10.7	-34
1906-10	16.1	-0.5	0.0828	10.8	-31
1911-15	16.8	-1.2	0.1000	11.5	-30
1916-20	16.4	-1.8	0.0833	9.7	-30
1921-25	17.2	-1.0	0.0937	11.6	-24
1926-30	16.4	-1.0	0.0892	10.4	-29
1931-35	17.7	0.1	0.0781	11.2	-14
1936-40	17.6	-1.0	0.0790	11.0	-26
1941-45	17.2	-0.6	0.0881	11.6	-27
1946-50	17.0	-0.2	0.0844	10.7	-25
1951-55	17.4	-0.6	0.0854	11.6	-28
1956-60	16.9	-1.5	0.0977	11.4	-25
1961-65	16.3	-1.7	0.0812	10.6	-25
1966-70	15.6	-1.6	0.0882	10.2	-20
1971-75	16.3	-0.9	0.0892	10.1	-25

The correlation coefficient is 0.441.

Thus, there is little substantial change in the value of the slope or intercept for the regression of δD vs $X_s (T_s - T_w) + T_w$ when 1931-35 and 1966-70 are omitted, but there is a significant increase in the value of the correlation coefficient. Conversely, omission of 1931-35 and 1966-70 from the δD vs T_w regression results in a considerably different slope and lower correlation coefficient. These results confirm the qualitative conclusions that might be reached by inspection of Figures 5-47 and 5-48.

As was stated previously, the relatively positive δD values of AW-BO-1 make it somewhat difficult to accept the idea that this tree has incorporated water whose δD values reflect those of annual precipitation. However, the little relationship that can be discerned between AW-BO-1 δD values and local climate is optimized if both winter temperature and precipitation amount are considered to be contributing, along with the corresponding summer quantities, to the δD value of the water used by this tree. Thus, there is more evidence for the incorporation of water whose δD variations at least mimic those of seasonally weighted annual precipitation than against it.

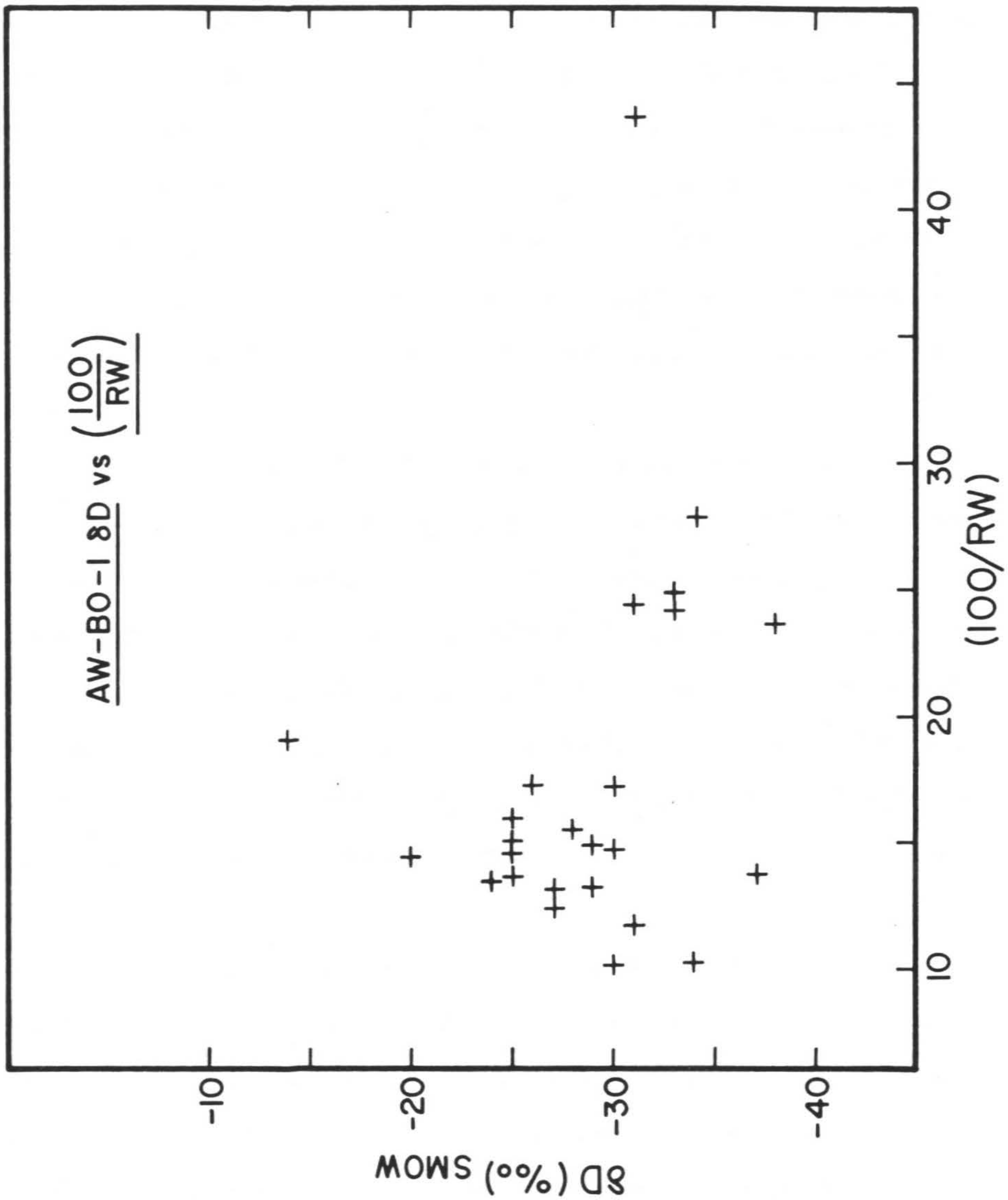
The more positive δD values of AW-BO-1 compared to those of other trees from this region which are known to incorporate "annual" precipitation (see Section 2) may mean that (1) AW-BO-1 experiences biochemical and physiological isotopic fractionation effects that are different from those trees; (2) local site conditions such as slow infiltration rate into the soil and consequent high level of evaporative isotopic enrichment have caused increases in the δD value of the precipitation prior to that normally occurring during transpiration (see Section 2); (3) the root geometry of AW-BO-1 has favored the preferential incorporation of summer rainfall although some winter (or average annual precipitation as in the groundwater) has also been incorporated. Any one or all of these factors could be important in producing the relatively positive AW-BO-1 δD values, but no information exists at present which might allow one to either choose between them or propose others.

In view of the many possible explanations for the generally deuterium-enriched nature of AW-BO-1, the surprising feature of Figure 5-47 is not the scatter, but the fact that there is <u>any</u> suggestion of a relationship between δD and local climate. This is particularly true when the low variance of the overall δD record is considered. Consequently, it seems that trees which have <u>both</u> a positive overall δD bias compared to other trees in the region and a generally low degree of δD variance should be avoided if climatic interpretations are to be attempted.

To complete the record, the plot of AW-BO-1 δD variations against reciprocal ring width is found in Figure 5-49 for the entire sample sequence (1851-1975). The high degree of scatter in Figure 5-49 is typical of that observed for many of the trees analyzed for this thesis and seems to imply that the δD values and ring widths are not varying in response to the same factors.

Figure 5-49

A plot of the δD values of AW-BO-1 against the reciprocal of the aggregate ring widths of corresponding five-year intervals. There is no apparent relationship between these variables. The compared data span the period from 1851 to 1975.


AW-BO-1 δD vs $\left(\frac{100}{RW}\right)$
-10
-20
-30
-40
δD (‰) SMOW
10
20
30
40
(100/RW)

Summary and Conclusions

The temporal variations of δD values that have been compared with local climatic variables for the thirteen preceding trees have revealed a variety of relationships. Three of these trees (KSA-As-1, BCT-12 and to a lesser extent MNY-GA-2) contain δD variations which seem to record the variations in amount of summer precipitation at each respective site. However, the "best fit" definition of summer is different at each of the sites. Furthermore, there are significant departures (anomalies) from the general trends of δD vs summer precipitation at each of these sites.

The δD values of a fourth tree (FA-As-1) appear to be varying in concert with local summer temperature. In addition the δD variations of FA-As-1 correlate well with the δD variations of KSA-As-1. The former tree is from an inland site (Fairbanks, Alaska) which is on the leeward side of the Alaska Range, while the latter is on the coastal side near Anchorage. As might be expected for coastal and inland sites which receive precipitation from a common transport system, the inland tree (FA-As-1) has more negative δD values than the coastal tree (KSA-As-1).

The other nine trees (MO-0-2, Col-DF-1, FCA-WS-1, SAS-JP-1, OPW-DF-1, RE-CO-2, MNY-BO-7, MNY-RM-5, and AW-BO-1) exhibit varying degrees of correlation between δD values and parameters derived from an assumption that the trees incorporate waters whose δD values reflect those of annual precipitation. Three of these nine trees (MNY-RM-5, MNY-BO-7, AW-BO-1) apparently grew under conditions which may preclude an a priori assumption that the δD variations represent climatic changes.

This is particularly true for inter-regional comparisons (see Section 5) and may be true for the interpretation of the internal chronologies as well. Although in the latter case, there was some evidence for a local temporal climatic signal in each of these three trees. The remaining six of these nine trees demonstrate a good geographic δD vs annual temperature relationship as was shown in Section 5. The details of their separate temporal δD vs local climate trends are, however, commonly somewhat complex.

It appears for instance that certain intervals within a given chronology will exhibit significant departures in δD values from those of the general trend. In fact in at least two trees (FCA-WS-1 and RE-CO-2), these departures are common enough that they seem to define separate domains of variation of δD vs local annual climate. While these departures from the "norm" could serve to complicate the local isotopic climate record, they may also contain implications about larger scale climatic patterns. With the exception of the MNY and AW-BO-1 trees, whose unusual local conditions may induce significant nonclimatic δD change, the isotopic departures from the locally defined "normal" δD vs climate trend are compiled in Table 5-10. Each interval for which an isotopic anomaly was recorded in any of these trees is listed. If a particular tree exhibits an anomaly for that interval the word "yes" is written in the appropriate space. The word "yes" is then followed by a plus or minus sign in parentheses. This indicates whether the δD departure from the norm is positive or negative in that tree. The word "no" indicates that there is no isotopic departure from the normal trend in that interval for that tree. A horizontal bar indicates either no δD or no meteorological data for that interval.

Table 5-10: Indication of Presence of "Anomalous" Departures of δD Values from the "Normal" Trend of δD vs Local Climate in Various Trees for Different Intervals

Sign in parentheses indicates the positive or negative character of the anomaly

Sample	1876 to 1880	1881 to 1885	1891 to 1895	1896 to 1905	1911 to 1915	1921 to 1925	1926 to 1930
MO-0-2	-	-	-	-	-	-	no
Col-DF-1	no	no	Yes(+)	no	no	no	no
FCA-WS-1	-	-	Yes(-)	Yes(-)	Yes(-)	no	Yes(-)
SAS-JP-1	-	-	-	-	-	-	-
KSA-As-1	-	-	-	-	-	-	-
FA-As-1	-	-	-	-	-	-	-
BCT-12	-	-	-	-	-	no	no
OPW-DF-1	-	-	Yes(-)	no	no	no	no
RE-CO-2	Yes(-)	Yes(+)	Yes(+)	no	no	Yes(-)	no

	1936 to 1940	1946 to 1950	1951 to 1955	1956 to 1960	1961 to 1965	1966 to 1970	1971 to 1975
MO-0-2	no	no	no	no	no	no	Yes(+)
Col-DF-1	no	no	no	no	no	no	Yes(+)
FCA-WS-1	no	no	Yes(-)	no	no	no	Yes(-)
SAS-JP-1	-	no	Yes(+)	no	no	no	no
KSA-As-1	-	Yes(-)	no	no	no	no	no
FA-As-1	-	-	no	no	no	no	no
BCT-12	no	Yes(+)	no	Yes(+)	no	no	-
OPW-DF-1	no	Yes(-)	no	no	no	Yes(+)	Yes(+)
RE-CO-2	Yes(+)	no	Yes(+)	no	Yes(+)	no	-

As can be seen in Table 5-10, for many of the intervals there is a local isotopic anomaly in only one tree. Consequently, from the present number, distribution, and ages of the analyzed tree samples, it is not always possible to ascertain the large scale significance of many of the anomalies in these intervals. Where it has seemed possible, it has been done within the context of the discussions of the individual trees, eg. FCA-WS-1.

Four intervals in Table 5-10, however, are of particular interest because of the number of trees whose δD values exhibit departures from the "normal" local δD vs climate trend. These four intervals are 1891-95, 1946-50, 1951-55, and 1971-75. At least three trees from the presently analyzed sample population exhibit "anomalous" δD values in each of these intervals. All the other intervals of Table 5-10 are represented by only one tree.

All four trees which contain data for 1891-95 exhibit anomalous δD values for this period. The trees are from Reston, Virginia; Jefferson County, Colorado; the Edmonton, Alberta region; and the Olympic Peninsula, Washington. Thus, there is a wide range of both geography and climate represented by these trees. This wide representation suggests that the changes in the δD vs local climate relationships which occurred at these sites may have been a response to large scale rather than local isotopic perturbations. It is of interest that drought conditions prevailed in the Great Plains of North America during this interval (Roberts and Olson, 1975). Thus, it may be that large scale changes in isotopic condensation trajectories occurred at this time in conjunction with changes in atmospheric circulation patterns that produced the drought. The signs of the isotopic departures at the various sites may provide some insight into the pattern of change, if a larger number of them can be obtained.

The three trees which display isotopic anomalies in the 1946-50 interval are all located at, or comparatively near, the upper western margin of North America. The two distinctly maritime sites (Anchorage and the Olympic Peninsula) exhibit negative anomalies while the inland site (near Prince George, B.C.) displays a positive anomaly. This may indicate higher than normal precipitation intensities at the coastal sites, while the opposite might have been true at Prince George (see Section 4 on the possible relationship between precipitation intensity and the isotopic composition of rain).

The 1951-55 interval appears to represent a shift in the pattern of anomalous isotopic behavior from the west coast to western Canadian sites and a site on the eastern seaboard of the United States. Interestingly, the signs of the anomalies exhibited by FCA-WS-1 and RE-CO-2 in the 1951-55 interval are the same as those which they displayed for the 1891-95 period. If 1946-50 and 1951-51 are taken to represent different phases of the same climatic pattern, then OPW-DF-1 also shows the same sign of departure for the 1946-50 and 1891-95 periods. Col-DF-1 which exhibited an anomaly in 1891-95 does not appear to do so in 1946-50 or 1951-55. However, it should be recalled that there is considerable scatter in the trend of Col-DF-1 δD values vs local climate possibly due to the presence of reaction wood. Therefore, such an anomaly could be present, but obscured. The interval 1951-55 was also one of significant drought in the North American Great Plains. The similarities of both occurrence and sign of isotopic anomalies for different trees during the 1891-95 interval and the 1946-55 interval suggest that the large scale patterns of climate change associated with drought at these times may have been similar.

Four trees exhibit anomalous isotopic behavior in the interval 1971-75. They represent the Olympic Peninsula, Washington; central Missouri; Jefferson County, Colorado; and the Edmonton, Alberta region. The sign of the departure is negative for the Edmonton tree (FCA-WS-1) as it was in the preceding two intervals. Col-DF-1 (Colorado) also shows the same positive departure that it showed in the 1891-95 interval. OPW-DF-1, however, is anomalous in a positive sense in the 1971-75 interval, whereas it was negative in 1891-95 and 1946-50. It is interesting that when OPW-DF-1, which appears to reflect changes in the δD value of annual precipitation, displays a <u>positive</u> anomaly in 1971-75, there is no anomalous behavior evident in the other near-coastal sample that seems to incorporate only summer rain (KSA-As-1). This is in contrast to the 1946-50 period. At this latter time the OPW-DF-1 anomaly was negative. Associated with the <u>negative</u> OPW-DF-1 anomaly was a negative anomaly in KSA-As-1. This association may be mere coincidence, but it could be tested with more tree samples.

It happens that there were more episodes of significant drought in the North American Great Plains (Roberts and Olson, 1975) than would be indicated by the isotopic anomalies of Table 5-10. In particular, the "dust bowl" years of the 1930's do not exhibit widespread isotopic anomalies in the nine trees of Table 5-10. This may suggest that more than one climatic pattern is capable of producing Great Plains drought.

The foregoing discussion about the possible large scale climatic implications and causes of isotopic departures from "normal" local δD vs climate trends depends on the actual existence of such anomalies in precipitation. Climatic comparisons of more than one tree sequence from a single locale as well as trees from multiple locales will be required to verify the general existence of these anomalies as a precipitation rather than a physiological phenomenon. However, the consistency of the association of several geographically distinct isotopic anomalies with known large scale climatic phenomena (drought) favors the conclusion that these isotopic departures can have empirical significance no matter how they specifically originate.

Furthermore, the existence of these anomalies in plots of tree ring δD variations vs local climatic parameters implies that the isotopic variations in older sequences can not always be unambiguously interpreted on short time scales of the order of five years. However, longer sample intervals may allow a more straightforward interpretation, because such anomalies will tend to be "smeared out" in the larger average.

One of the most potentially powerful applications of tree ring isotopic analysis to climate studies is suggested by the existence of these anomalies. The regional correlations of tree δD values with local temperature noted in Section 5 imply that tree δD values could be utilized to compile isotopic maps of continental scale. Thus , the spatial variations in the patterns of δD values could possibly be ascertained for different intervals of time extending as far back as the available samples would allow. In this context the "anomalous" δD values might prove of great worth, because the sign of the departure can be different at different locales for the same interval (as suggested by the data of Table 5-10). Therefore, the "anomalies" might contribute to significant changes in the spatial pattern of δD distributions and thus delineate possible large scale changes in climate.

However, if such an approach is to be viable, the work in this thesis suggests that sample selection may be very important both from the standpoint of site hydrology and possible physiological perturbations of the isotope record.

Appendix I

Ericksson (1965) has considered the fractionation of hydrogen and oxygen isotopes in precipitation in the context of simple atmospheric transport processes. He presented a theoretical treatment of the isotopic fractionations that might be expected of both eddy and advective transport processes in a saturated atmosphere. His resulting expressions for the isotopic composition of precipitation give the concentration of the heavy isotope as a function of specific humidity or, for the vertically integrated transport, "precipitable" water. The variables specific humidity and precipitable water are not as widely recorded as is temperature. Consequently, in studies of the relationships between variations in the isotopic composition of precipitation and climate, temperature is likely to be the more useful variable from a practical standpoint.

Therefore, it was decided to investigate the functional relationship between the isotopic composition of precipitation and condensation temperature in a simple transport model. Instead of assuming a particular functional dependence of specific humidity on height as was done by Ericksson (1965), it is assumed that the atmosphere possesses a specified temperature structure. In addition, it is assumed that a saturated parcel of air moving through this atmosphere has the same temperature as its surroundings.

For simplicity, only a two dimensional atmosphere is considered. The temperature is presumed to decrease from the surface upward and from south to north. The transport and precipitation of water in this atmosphere is described by the continuity equation. Thus, the principal constraint on the water at any point in the atmosphere is that mass be conserved.

A fraction of the total water present in a parcel of air is specified as condensate which is present as a cloud. This condensate is assumed to be in isotopic equilibrium with the associated vapor. In addition the water precipitating from the cloud at any level is assumed to have the same isotopic composition as the cloud at that level. Thus, there is a presumption that no isotopic exchange occurs subsequent to condensation and precipitation.

The mathematical derivation of a functional relationship between the isotopic composition of precipitation and temperature based on the preceding assumptions is found on the following pages. Any additional approximations or assumptions are indicated therein.

Definitions of Symbols

α = r_c/r_v = equilibrium fractionation factor

a = L/R

b = $\partial T/\partial Y$ = horizontal temperature gradient

E = saturation water vapor pressure = $E_o\ e^{a/T_o - a/T}$, from the Clausius-Clapeyron equation

g = gravitational acceleration

Γ_s = $-\frac{\partial T}{\partial Z}$ = vertical lapse rate

L = latent heat of condensation (or vaporization)

M_a = molecular weight of dry air

M_w = molecular weight of water

M^* = molecular weight of isotopic species

N = total mass (grams) of water vapor plus condensate in the system of interest

n_a = moles of dry air in the system

n_v = moles of water vapor in the system

p = precipitation rate (mass per unit volume per unit time)

P_a = partial pressure of dry air

r_c = (D/H) or $(^{18}0/^{16}0)$ of condensate

r_v = (D/H) or $(^{18}0/^{16}0)$ of vapor

R = ideal gas constant

ρ = total density (mass/volume) of water vapor plus condensate

ρ_c = density (mass/volume) of condensate

ρ_v = density (mass/volume) of water vapor

t = time

T = temperature (^{o}k)

v = horizontal wind velocity in y direction

$\vec{V}$ = resultant velocity of air

w = vertical velocity of air

x = fraction of total water in a system that is present as vapor

y = horizontal north-south distance. Positive and increasing toward the north from the equator

Z = vertical distance. Positive and increasing upward from the surface of the earth.

In the absence of evaporation, the continuity equation for water in the earth's atmosphere is:

$$\vec{\nabla} \cdot \rho \vec{V} = - \frac{\partial \rho}{\partial t} - p \tag{1}$$

for steady-state, $\frac{\partial \rho}{\partial t} = 0$

if only a two-dimensional system in y and z is considered, then

$$v \frac{\partial \rho}{\partial y} + w \frac{\partial \rho}{\partial z} + \rho \left(\frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right) = - p \tag{2}$$

if the Boussinesq approximation is applicable to the atmosphere as a whole - i.e. including nitrogen, oxygen, argon, etc. - then

$$\frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \approx 0 \tag{3}$$

and,

$$v \frac{\partial \rho}{\partial y} + w \frac{\partial \rho}{\partial z} = - p \tag{4}$$

but,

$$\rho = \rho_v + \rho_c \tag{5}$$

and,

$$\frac{\rho_v}{\rho_v + \rho_c} = X \tag{6}$$

thus,

$$\rho_c = \left(\frac{1}{x} - 1\right) \rho_v \tag{7}$$

and,

$$\rho = \frac{\rho_v}{x} \tag{8}$$

substituting for ρ from equation (8) into equation (4):

$$v \left[\rho_v \frac{\partial \left(\frac{1}{x}\right)}{\partial y} + \left(\frac{1}{x}\right) \frac{\partial \rho_v}{\partial y} \right] + w \left[\rho_v \frac{\partial \left(\frac{1}{x}\right)}{\partial z} + \left(\frac{1}{x}\right) \frac{\partial \rho_v}{\partial z} \right] = - p \tag{9}$$

For an isotopic species of water,

$$v \frac{\partial \rho^*}{\partial y} + w \frac{\partial \rho^*}{\partial z} = - p^* \tag{10}$$

(11) $\rho^* = \rho_v{}^* + \rho_c{}^*$

let $r = (\frac{D}{H}) = \frac{[HDO]}{2[H_2O] + [HDO]} \sim \frac{[HDO]}{2[H_2O]}$ since $[HDO] << [H_2O]$

(12)

$$r = \frac{\frac{\rho^*}{M^*}}{2\frac{\rho}{M}} = \frac{1}{2}\,\frac{M}{M^*}\,\frac{\rho^*}{\rho}$$

(13) $\rho^* = 2\,\frac{M^*}{M}\,\rho_v r_v + 2\,\frac{M^*}{M}\,\rho_c r_c$

similarly,

(14) $p^* = 2\,\frac{M^*}{M}\,p\ r_c$

also, for isotopic equilibrium between water vapor and condensate,

(15) $\frac{r_c}{r_v} = \alpha$, or $r_v = \frac{r_c}{\alpha}$

substituting for r_v in (13) from (15) and for ρ^* and p^* in (10) from (13) and (14) yields:

(16)

$$v\left[\rho_v r_c\,\frac{\partial(\frac{1}{\alpha} + \frac{1}{x} - 1)}{\partial y} + (\frac{1}{\alpha} + \frac{1}{x} - 1)\,\frac{\partial(\rho_v r_c)}{\partial y}\right] + w\left[\rho_v r_c\,\frac{\partial(\frac{1}{\alpha} + \frac{1}{x} - 1)}{\partial z} + (\frac{1}{\alpha} + \frac{1}{x} - 1)\,\frac{\partial(\rho_v r_c)}{\partial z}\right] = -\,r_c\,p$$

if α is assumed to be constant, then

(17)

$$v\left[\rho_v r_c\,\frac{\partial(\frac{1}{x})}{\partial y} + (\frac{1}{\alpha} + \frac{1}{x} - 1)\quad(\rho_v\,\frac{\partial\ r_c}{\partial y} + r_c\,\frac{\partial\rho_v}{\partial y})\right] + w\left[\rho_v r_c\,\frac{\partial(\frac{1}{x})}{\partial z} + (\frac{1}{\alpha} + \frac{1}{x} - 1)\ (\rho_v\,\frac{\partial\ r_c}{\partial z} + r_c\,\frac{\partial\rho_v}{\partial z})\right] = -\,r_c\,p$$

dividing through equation (17) by $\rho_v r_c$ and substituting for p in (17) from equation (9) yields, after rearranging terms:

(18)

$$\frac{\partial\ \ln\ r_c}{\partial y} + \frac{w}{v}\,\frac{\partial\ \ln\ r_c}{\partial z} = \frac{(x - \frac{x}{\alpha})}{(\frac{x}{\alpha} + 1 - x)}\,\frac{\partial\ \ln\ \rho_v}{\partial y} + \frac{w}{v}\,\frac{(x - \frac{x}{\alpha})}{(\frac{x}{\alpha} + 1 - x)}\,\frac{\partial\ \ln\ \rho_v}{\partial z}$$

assume that $\ln r_c = f\ (T, V)$

remembering that the water vapor is saturated and E is then a function of temperature only.

The amount of water vapor in the system does not constitute an independent variable since

$$EV = n_v RT$$

Thus, when T and V are specified, E and n_v are immediately determined.

Furthermore, X is considered to be independent of T and dependent only on V.

Now, if T can be assumed to be dependent on the position variables y and z, then by the chain rule for partial derivatives:

$$\frac{\partial \ln r_c}{\partial y} = \frac{\partial \ln r_c}{\partial T} \frac{\partial T}{\partial y} \tag{19}$$

$$\frac{\partial \ln r_c}{\partial z} = \frac{\partial \ln r_c}{\partial T} \frac{\partial T}{\partial z} \tag{20}$$

These expressions follow from equation (18), because the saturation vapor density ρ_v is a function of temperature only.

Since it is the purpose of this derivation to seek a functional relationship between $\ln r_c$ and temperature, and furthermore, since the temperature will be considered to vary in more than one direction, it is the total derivative of $\ln r_c$ with respect to temperature that is of interest.

Thus,

$$d \ln r_c = \frac{\partial \ln r_c}{\partial T}\, dT + \frac{\partial \ln r_c}{\partial V}\, dV \tag{21}$$

or,

(22) $$\frac{d \ln r_c}{dT} = \frac{\partial \ln r_c}{\partial T} + \frac{\partial \ln r_c}{\partial V} \frac{dV}{dT}$$

if V is a function of the position variables y and Z,

(23) $$\frac{dV}{dT} = \frac{\partial V}{\partial y} \frac{dy}{dT} + \frac{\partial V}{\partial Z} \frac{dZ}{dT}$$

substituting for $\frac{dV}{dT}$ in equation (22) from equation (23) and rearranging terms yields:

(24) $$\frac{\partial \ln r_c}{\partial T} = \frac{d \ln r_c}{dT} - \frac{\partial \ln r_c}{\partial V} \left[\frac{\partial V}{\partial y} \frac{dy}{dT} + \frac{\partial V}{\partial Z} \frac{dZ}{dT}\right]$$

substituting equation (24) into equation (19) and remembering that Z is constant in (19) - i.e. dZ = 0, yields:

(25) $$\frac{\partial \ln r_c}{\partial y} = \frac{d \ln r_c}{dT} \frac{\partial T}{\partial y} - \frac{\partial \ln r_c}{\partial V} \left[\frac{\partial V}{\partial y} \frac{dy}{dT}\right] \frac{\partial T}{\partial y}$$

now,

(26) $$\frac{dy}{dT} = \frac{\partial y}{\partial T} + \frac{\partial y}{\partial Z} \frac{dZ}{dT}$$

but in equation (25), dZ = 0

and,

(27) $$\frac{dy}{dT} = \frac{\partial y}{\partial T}$$

thus,

(28) $$\frac{\partial \ln r_c}{\partial y} = \frac{d \ln r_c}{dT} \frac{\partial T}{\partial y} - \frac{\partial \ln r_c}{\partial V} \frac{\partial V}{\partial y}$$

by analogy with the derivation of equation (28):

(29) $$\frac{\partial \ln r_c}{\partial Z} = \frac{d \ln r_c}{dT} \frac{\partial T}{\partial Z} - \frac{\partial \ln r_c}{\partial V} \frac{\partial V}{\partial Z}$$

(30) $$r_{total} = (1 - x)\, r_c + x\, r_v$$

(31) $$r_c = \frac{r_{total}}{(\frac{x}{\alpha} + 1 - x)}$$

(32) $\ln r_c = \ln r_{total} - \ln (\frac{x}{\alpha} + 1 - x)$

if r_{total} = constant at constant T

then,

(33) $$\frac{\partial \ln r_c}{\partial V} = - \frac{(\frac{1}{\alpha} - 1)}{(\frac{x}{\alpha} + 1 - x)} \frac{\partial X}{\partial V} = \frac{(1 - \frac{1}{\alpha})}{(\frac{x}{\alpha} + 1 - x)} \frac{\partial X}{\partial V}$$

now,

(34) $X = \frac{\rho_v}{\rho_c + \rho_v} = \frac{\rho_v}{\frac{N}{V}}$ where N = the total mass of vapor plus condensate

and,

(35) $$\frac{\partial X}{\partial V} = \frac{\rho_v}{N} = \frac{x}{V}$$

where it is assumed that N does not depend on V at constant T. This assumption does not appear to be unreasonable for the case of volume expansion, since at constant T, some of the condensate would have to be converted to vapor to maintain a constant value of E. With a smaller amount of condensate it is less likely that precipitation would occur. Thus, N could possibly remain unchanged.

Hence,

(36) $$\frac{\partial \ln r_c}{\partial V} = \frac{(1 - \frac{1}{\alpha})}{(\frac{1}{\alpha} + \frac{1}{x} - 1)} \frac{1}{V}$$

from the ideal gas law for saturated water vapor:

(37) $$V = \frac{n_v RT}{E}$$

Applying the chain rule for partial derivatives to V and remembering that E is a function of T only:

(38) $$\frac{\partial V}{\partial Z} = \frac{\partial V}{\partial T} \frac{\partial T}{\partial Z} + \frac{\partial V}{\partial n_v} \frac{\partial n_v}{\partial Z}$$

from equation (37) and the Clausius - Clapeyron expression for E

$$(39) \quad \frac{\partial V}{\partial T} = \frac{n_v R - n_v \left(\frac{aR}{T}\right)}{E}$$

from equation (37)

$$(40) \quad \frac{\partial V}{\partial n_v} = \frac{RT}{E} = \frac{V}{n_v}$$

Substituting from equations (39) and (40) into equation (38) and multiplying equation (36) by equation (38) yields:

$$(41) \quad \frac{\partial \ln r_c}{\partial V} \frac{\partial V}{\partial Z} = \frac{\left(1 - \frac{1}{\alpha}\right)}{\left(\frac{1}{\alpha} + \frac{1}{x} - 1\right)} \left[\left(\frac{1}{T} - \frac{a}{T^2}\right) \frac{\partial T}{\partial Z} + \frac{1}{n_v} \frac{\partial n_v}{\partial Z} \right]$$

Considering the last term on the right-hand side of the equation (41)

$$(42) \quad \frac{1}{n_v} \frac{\partial n_v}{\partial Z} = \frac{n_a}{n_v} \frac{\partial \left(\frac{n_v}{n_a}\right)}{\partial Z}$$ where n_a = moles of dry air in a parcel

= constant

but,

$$(43) \quad \frac{n_v}{n_a} = \frac{\frac{EV}{RT}}{\frac{P_a V}{RT}} = \frac{E}{P_a}$$

thus,

$$(44) \quad \frac{1}{n_v} \frac{\partial n_v}{\partial Z} = \frac{1}{E} \frac{\partial E}{\partial Z} - \frac{1}{P_a} \frac{\partial P_a}{\partial Z}$$

but,

$$(45) \quad \frac{\partial E}{\partial Z} = \frac{\partial E}{\partial T} \frac{\partial T}{\partial Z} = \frac{a}{T^2} E \frac{\partial T}{\partial Z}$$

and, with the hydrostatic approximation:

$$(46) \quad \frac{\partial P_a}{\partial Z} = - \rho_a g = - \frac{P_a M_a g}{RT}$$

therefore,

$$(47)\quad \frac{1}{n_v}\frac{\partial\, n_v}{\partial Z} = \frac{a}{T^2}\ \frac{\partial T}{\partial Z} + \frac{M_a g}{RT}$$

and,

$$(48)\quad \frac{\partial\ \ln\ r_c}{\partial V}\ \frac{\partial V}{\partial Z} = \frac{(1 - \frac{1}{\alpha})}{(\frac{1}{\alpha} + \frac{1}{x} - 1)}\ \left[\frac{1}{T}\ \frac{\partial T}{\partial Z} + \frac{M_a g}{RT}\right]$$

finally, substituting equation (48) into equation (29) yields:

$$(49)\quad \frac{\partial\ \ln\ r_c}{\partial Z} = \frac{d\ \ln\ r_c}{T}\ \frac{\partial T}{\partial Z} - \frac{(1 - \frac{1}{\alpha})}{(\frac{1}{\alpha} + \frac{1}{x} - 1)}\ \left[\frac{1}{T}\ \frac{\partial T}{\partial Z} + \frac{M_a g}{RT}\right]$$

Now,

$$(50)\quad \frac{\partial V}{\partial y} = \frac{\partial V}{\partial T}\ \frac{\partial T}{\partial y} + \frac{\partial V}{\partial n_v}\ \frac{\partial\, n_v}{\partial y}$$

and substituting from equations (50), (36), (39) and (40) into equation (28) yields:

$$(51)\quad \frac{\partial\ \ln\ r_c}{\partial y} = \frac{d\ \ln\ r_c}{dT}\ \frac{\partial T}{\partial y} - \frac{(1 - \frac{1}{\alpha})}{(\frac{1}{\alpha} + \frac{1}{x} - 1)}\ \left[(\frac{1}{T} - \frac{a}{T^2})\frac{\partial T}{\partial y} + \frac{1}{n_v}\ \frac{\partial\, n_v}{\partial y}\right]$$

by analogy with equation (42), the last term on the right-hand side of equation (51) is:

$$(52)\quad \frac{1}{n_v}\ \frac{\partial\, n_v}{\partial y} = \frac{1}{E}\ \frac{\partial E}{\partial y} - \frac{1}{P_a}\ \frac{\partial\, P_a}{\partial y}$$

but,

$$(53)\quad \frac{\partial E}{\partial y} = \frac{\partial E}{\partial T}\ \frac{\partial T}{\partial y} = \frac{a}{T^2}\ \frac{E\ \partial T}{\partial y}$$

and, P_a is assumed to be independent of y at constant Z, thus

(54) $$\frac{\partial P_a}{\partial y} = 0$$

therefore,

(55) $$\frac{\partial \ln r_c}{\partial y} = \frac{d \ln r_c}{dT} \frac{\partial T}{\partial y} - \frac{(1 - \frac{1}{\alpha})}{(\frac{1}{\alpha} + \frac{1}{x} - 1)} \left[\frac{1}{T} \frac{\partial T}{\partial y}\right]$$

now,

(56) $$\frac{\partial \ln r_c}{\partial y} + \frac{w}{v} \frac{\partial \ln r_c}{\partial Z} = \frac{d \ln r_c}{dT} \frac{\partial T}{\partial y} - \frac{(1 - \frac{1}{\alpha})}{(\frac{1}{\alpha} + \frac{1}{x} - 1)} \left[\frac{1}{T} \frac{\partial T}{\partial y}\right]$$
$$+ \frac{w}{v} \left[\frac{d \ln r_c}{dT} \frac{\partial T}{\partial Z} - \frac{(1 - \frac{1}{\alpha})}{(\frac{1}{\alpha} + \frac{1}{x} - 1)} (\frac{1}{T} \frac{\partial T}{\partial Z} + \frac{M_a g}{RT})\right]$$

Substituting for the left-hand side of equation (56) from equation (18) and remembering that:

$$\ln \rho_v = \ln (\frac{M_w E_o}{R}) + (\frac{a}{T_o} - \frac{a}{T}) - \ln T$$

yields, after rearranging terms:

(57) $$\frac{d \ln r_c}{dT} = \frac{(\frac{1}{\alpha} - 1)}{(\frac{1}{\alpha} + \frac{1}{x} - 1)} \left[(\frac{-a}{T^2}) - \frac{(\frac{w}{v} \frac{M_a g}{R})}{(b - \frac{w}{v} \Gamma_s)} (\frac{1}{T})\right]$$

where $b = \frac{\partial T}{\partial y}$ and $\Gamma_s = - \frac{\partial T}{\partial Z}$

If α, X, b, Γ_s, w, and v are assumed to be independent of the temperature, then equation (57) can be integrated between the limits r_{ci} and r_{cf}, and T_i and T_f

The final expression is:

(58) $$\ln \frac{r_{cf}}{r_{ci}} = \frac{(\frac{1}{\alpha} - 1)}{(\frac{1}{\alpha} + \frac{1}{x} - 1)} \left[(\frac{a}{T_f} - \frac{a}{T_i}) - \frac{(\frac{w}{v} \frac{M_a g}{R})}{(b - \frac{w}{v} \Gamma_s)} (\ln \frac{T_f}{T_i})\right]$$

The assumption of temperature independence for the various parameters noted above may not be completely valid for all. In particular, the assumption of constant α is only approximately true for small temperature intervals. However, it should be noted that:

$$\ln \frac{r_{cf}}{r_{co}} = \ln \frac{r_{c1}}{r_{co}} + \ln \frac{r_{c2}}{r_{c1}} + \ln \frac{r_{c3}}{r_{c2}} + \ . \ . \ . + \ln \frac{r_{cf}}{r_{cf-1}}$$

Thus, the isotopic composition at temperature T_f can be determined from equation (58) by taking the sum of the natural logarithms for small temperature increments up to the temperature of interest, where the appropriate α is employed for each increment.

Equation (58) has been used to calculate the variation of the δD value of precipitation with condensation temperature. Temperature increments of five degrees Centigrade were employed for the calculations. The average values of α within these temperature intervals were determined by extrapolation of the curves of Majoube.

The isotopic variation of precipitation in terms of δD is calculated from equation (58) by remembering that:

$$r_c = r_{st} \ (1 + \frac{\delta D}{1000})$$

Where r_{st} = D/H ratio of an arbitrary standard.

Condensation trajectories were calculated for the following cases:

(1) $X = 1.00$

(A) $\frac{w}{v} = 0$

(B) $\frac{w}{v} \Gamma_s >> b$

(2) $X = 0.80$

(A) $\frac{w}{v} = 0$

(B) $\frac{w}{v} \Gamma_s >> b$

The cases 1(A) and 2(A) represent purely horizontal, isobaric cooling. Cases 1(B) and 2(B) represent essentially vertical, non-isobaric cooling. Note that case 1(A) results in a reduction of equation (58) to the Rayleigh expression for isobaric condensation. The various curves calculated for the four preceding cases are found in Figure 4-1 of Section 4 in this thesis. The implications of these curves are discussed therein.

An additional feature of equation (58) is that it predicts that the slope of a δD vs $\delta^{18}O$ plot will depend on both the values of the α's and the value of X (where X is the fraction of the total moisture which is present as vapor). Craig and Gordon (1965) have also stated that such a dependency is to be expected.

Appendix II
(Sample Descriptions)

AW-BO-1: A wedge of wood from the outermost approximately 130 years of growth of a bur oak (Quercus macrocarpa). The tree grew in a small stand of oaks in pasture land near Albion, Wis. (elev. about 250 m.). The sample was provided by M. M. Bender and A. Berge. The ring sequence was dated at the Center for Climatic Research, University of Wisconsin-Madison.

BCT-1: A sample of wood from the branches of a quaking aspen which grew next to Stuart Lake, British Columbia. Collected by H. P. Taylor, Jr.

BCT-3: A sample of wood from branches of a quaking aspen which grew adjacent to Stuart Lake, British Columbia. Collected by H. P. Taylor, Jr.

BCT-5: A sample of wood from branches of a white spruce which grew adjacent to Lac des Roches, British Columbia. Collected by H. P. Taylor, Jr.

BCT-7: A sample of wood from branches of a poplar growing next to Naltesby Lake, British Columbia. Collected by H. P. Taylor, Jr.

BCT-9: A sample of wood from the branches of a Lombardy poplar which grew adjacent to Okanagan Lake, British Columbia. Collected by H. P. Taylor, Jr.

BCT-10: A sample of wood from branches of a Coulter pine (Pinus coulteri) which grew next to Kalamalka Lake, British Columbia. Collected by H. P. Taylor, Jr.

BCT-11: A sample of wood from branches of a lodgepole pine which grew adjacent to Seeley Lake, British Columbia. Collected by H. P. Taylor, Jr.

BCT-12: A section of wood from a pine tree which grew in the vicinity of Seeley Lake, British Columbia, Canada. The sample was collected by H. P. Taylor, Jr. The ring sequence was counted at Caltech by the author. H. P. T. believes the tree to have been cut down in early 1974. Therefore, the youngest ring is dated 1973.

BrPn: A section of wood from the bole of a Bristlecone pine which grew at an elevation of about 3000 m in the White Mts. of California. The sample was provided by C. W. Ferguson.

Col-DF-1: A 3/4 circular section of wood from the bole of a Douglas fir (Pseudotsuga menziesii) which grew in Mt. Vernon Canyon, Jefferson Co., Colorado (approx. elev. 2130 m). The sample was provided by I. Friedman. He has indicated that the youngest ring in the sequence is dated 1974 A.D. The ring sequence was counted at Caltech by the author with this date as the starting point.

FA-As-1: Circular cross section of wood from an aspen which grew near Rosie Creek Rd., Chena Ridge near Fairbanks, Alaska. The sample was collected and transmitted to Caltech by B. Kamb. The ring sequence was counted at Caltech by the author. The youngest ring is dated as 1977, because the sample was cut in early 1978.

FCA-WS-1: A section of wood from a white spruce (Picea glauca) which grew in a forest near Fox Creek, Alberta, Canada (54° 30 N. Lat.; 116° 45 W. Long.) at an approximate elevation of 880 m. The sample was provided by J. Soos of the Alberta Forest Service. The sample was cut in late September, 1978. The ring sequence was dated at Caltech by the author using the 1978 date for the youngest ring.

KSA-As-1: A circular section of wood from the bole of an aspen which grew on the north side of West Twin Peak (61° 28 N. Lat.; 149° 12 W. Long.) near Anchorage, Alaska. The tree grew at an approx. elevation of 150 m. The sample was provided by S. Spearrow via N. Brugman. The youngest ring is dated as 1979, because the tree was cut down in September, 1979. Ring sequences were counted at Caltech by the author.

LM: A sample of the aquatic Eurasian water milfoil which grew in Lake Mendota, Wisconsin. The sample was provided by H. D. Bruhn.

MO-O-2: A circular section of wood from an oak tree which grew in a small woodlot near Owensville, Mo. (approx. elev. 225 m). The sample was provided by S. L. Burner. The ring sequence was counted at Caltech by the author. The tree was cut down in October, 1978. Therefore, the youngest ring is dated as 1978.

MNY-BO-7: A section of wood from the bole of a bur oak (*Quercus macrocarpa*) which grew in a swamp in the Montezuma National Wildlife Refuge, New York (approx. elev. 140 m). The ring sequence was provided and dated by R. L. Phipps of the U.S.G.S., Reston, Va. and transmitted to Caltech by C. Kendall.

MNY-GA-2: A section of wood from the diameter of the bole of a green ash (*Fraxinus pennsylvania*). The tree grew in a swamp in the Montezuma National Wildlife Refuge, New York (approx. elev. 140 m). The ring sequence was provided and dated by R. L. Phipps of the U.S.G.S., Reston, Va. and transmitted to Caltech by C. Kendall.

MNY-RM-5: A section of wood from the bole of a red maple (Acer rubrum) which grew in a swamp in the Montezuma National Wildlife Refuge, New York (approx. elev. 140 m). The ring sequence was provided and dated by R. L. Phipps of the U.S.G.S., Reston, Va. and transmitted to Caltech by C. Kendall.

MRM: Sample of wood from a red mangrove which grew in the open ocean off Miami, Florida. Sample was provided by C. Emiliani.

MT-1: A sample of wood from branches of a birch which grew next to Flathead Lake, Montana (approx. elev. 910 m). Collected by H. P. Taylor, Jr.

MT-2: A sample of wood from branches of a maple which grew next to Flathead Lake, Montana (approx. elev. 910 m). Collected by H. P. Taylor, Jr.

NLS: An aquatic sedge which grew in Nymph Lake, Colorado. Collected by S. J. Lambert.

NT-1: A sample of wood from branches of an aspen which grew next to Brown Creek, Ruby Mts., Nevada. Collected by H. P. Taylor, Jr.

OM-1: An unidentified aquatic "grass" which grew in a marsh adjacent to the Oconto River near Oconto, Wis. Collected by C. Yapp.

OM-2: A sample of wood from the branches of a white birch which grew in a marsh adjacent to the Oconto River near Oconto, Wis. Collected by C. Yapp.

OPW-DF-1: A section of wood from the bole of a Sitka spruce (Picea sitchensis) which grew in the rain forest of the Hoh River Valley about 1.5 km S.W. of the Hoh River Ranger Station in the Olympic National Park, Wash. The tree grew at an approximate elevation of 170 m. The tree was felled in Feb., 1979 and the sample collected by H. Yanish. It was transmitted to Caltech by M. Brugman and K. Echelmeyer. The ring sequence was counted at Caltech by the author and the youngest ring dated as 1978.

Phyllospadix: A sample of an aquatic "grass" which grew in the open ocean off Santa Catalina Island, California. The sample was collected by E. Meyers.

PO-DF-1: A sample of wood from branches of a Douglas Fir (Pseudotsuga menziesii) which grew in Portland, Oregon. The sample was collected by J. H. Hall.

PR-TG: A sample of turtle grass growing completely submerged in the open ocean off Puerto Rico. Sample supplied by C. E. Cutress.

PW-CP: An aquatic pondweed which grew in Crespi Pond on the Monterey Peninsula, California. Collected by S. Epstein.

RE-CO-2: A section of wood from the bole of a chestnut oak (Quercus prinus) which grew on the present site of the U.S.G.S. National Headquarters at Reston, Va. The ring sequence was provided and dated by R. L. Phipps and transmitted to Caltech by C. Kendall.

SAS-JP-1: A circular section of wood from the bole of a jack pine (Pinus banksiana). The tree grew in the area around Porter Lake, Northwest Territories, Canada (61° 41 N. Lat.; 108° 10 W. Long.) at an approximate elevation of 60 m. The sample was collected and dated by S. Rowe of the Univ. of Saskatchewan and transmitted to Caltech by R. W. Forester.

SNF-LP-1: A circular section of wood from the bole of a lodgepole pine (Pinus contorta) which grew near the West Fork of Long Meadow

Creek in the Sierra National Forest, Calif. (approx. elev. 2200 m). The sample was collected and transmitted to Caltech by S. Wood. The ring sequence was counted at Caltech by the author. The youngest ring is dated as 1973, because the tree was cut on Sept. 20, 1973.

SW-CP: An aquatic silverweed which grew in Crespi Pond on the Monterey Peninsula, California. Collected by S. Epstein.

UAZ-PP-1: A circular section of wood from a Ponderosa Pine (*Pinus Ponderosa*) which grew on Radio Ridge in the Catalina Mts., Arizona. The sample was provided by V. C. LaMarche.

UBLM-1: An unidentified terrestrial grass which grew in a marsh adjacent to University Bay in Madison, Wisconsin. Collected by C. Yapp.

UBLM-2: A sample of wood from the branches of a willow tree which grew in a marsh adjacent to University Bay in Madison, Wisconsin. Collected by C. Yapp.

WM-B-1: A sample of wood from branches of a birch tree which grew in Winnipeg, Manitoba. Collected by S. Epstein.

WR-1: An unidentified terrestrial grass which grew in sandy soil adjacent to the Wisconsin River near Spring Green, Wisconsin. Collected by C. Yapp.

WR-2: A sample of wood from branches of a maple tree which grew in sandy soil adjacent to the Wisconsin River near Spring Green, Wisconsin. Collected by C. Yapp.

Yuk-W-1: A sample of wood from a branch of white spruce which grew in the vicinity of Kluane Lake, Yukon Territory. Sample collected by J. H. Hall.

H-2: A section of wood from an oak tree which grew in an open field near the NASA Space Center, Houston, Texas. The sample was collected by S. Epstein.

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