TREE-RING BULLETIN, *Vol. 42, 1982*

RESEARCH REPORT

STABLE CARBON ISOTOPES AS A POTENTIAL SUPPLEMENTAL TOOL IN DENDROCHRONOLOGY

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INTRODUCTION

Tree rings provide an important resource of past environmental information, accessible through established dendroclimatological techniques and more recently through stable isotope analysis. Long (1982) has summarized the current state of climate retrieval from tree rings using oxygen, carbon, and hydrogen stable isotopes. Most of these isotope studies use a series of single rings or groups of rings in exploring such isotope-climate relationships. However, the isotopic signal within the ring may provide important information on seasonal changes in environment and might even furnish a powerful new tool to dendrochronology under favorable circumstances.

The basis of such an application lies in a consistent seasonal pattern of variation of an environmental parameter which directly or inversely affects the carbon isotopic composition laid down in the xylem tissue. For stable carbon isotopes such parameters might include temperature, precipitation, sunlight, and atmospheric carbon dioxide concentration. For example, at mid-latitudes the temperature trend would consist of cool temperatures at initiation of growth, temperature increase to a July-August maximum, then cooling in September and October. Several *in vivo* and *in vitro* studies with various plants and plant enzymes have shown good correlations of carbon isotopic composition* with temperature, having coefficients ranging from -1 to +1.2 °/oo $\delta^{13}C/°C$ (Long 1982). Light intensity could affect rate of photosynthesis and in turn influence the carbon isotopic composition. The driving seasonal pattern might then be associated with day length and sun angle. Park and Epstein (1960), however, found no apparent effect of light intensity on the carbon isotopic composition of tomato plants grown under controlled conditions. Precipitation (or water stress) may also have a seasonal character, and could influence both stomatal opening for carbon dioxide and the water available for photosynthesis. In the southwestern U. S. the pattern might typically be abundant moisture at initiation of growth, moisture stress in late May and June, then abundant moisture in July and August with the onset of summer rains.

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* Isotopic composition, δ, is calculated as the ratio of heavy to light isotopes in a sample relative to the same ratio in a standard, and is expressed in per mil units. For carbon,

$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C)\ \text{unknown}}{(^{13}C/^{12}C)\ \text{standard}} - 1 \right) \times 1000$$

Lastly, a seasonal pattern in atmospheric carbon dioxide concentration results in lower concentration in summer than winter. The carbon isotopic composition of the carbon dioxide also changes seasonally, and is related to the CO_2 concentration by an approximate coefficient of -0.053 °/oo $\delta^{13}C$/ppm CO_2 (Pearman and Hyson 1980). Because seasonal CO_2 concentrations are latitude-dependent, the seasonal $\delta^{13}C$ variation at Hawaii is about 0.4 °/oo while at Point Barrow, Alaska, is about 1.0 °/oo (Broecker at al. 1979).

Experimental results described in this paper support a consistent, repeating variation of $\delta^{13}C$ within growth rings of juniper, perhaps common to all tree species. Although it is not clear which of the above environmental factors, if any, is the primary influence, the pattern seems unaffected by "false" ring boundaries.

BACKGROUND AND EXPERIMENTAL PROCEDURE

Several studies with leaves and tree rings have provided evidence for intra-annual variation of $\delta^{13}C$. Lowden and Dyck (1974) analyzed $\delta^{13}C$ of maple leaves and grass in Canada, collected at various times during several growing seasons. Their analysis was on whole-tissue and shows a decrease of $\delta^{13}C$ as the growing season progresses, typically about 2-3 °/oo. Wilson and Grinsted (1977) examined the $\delta^{13}C$ changes in cellulose and lignin in large rings of *Pinus radiata* from New Zealand which grew nearly year-round. Two, 2cm-wide rings were each subdivided into six segments. $\delta^{13}C$ analysis indicates a 1.5 °/oo increase at the beginning of the growing season and a rapid 1.5 °/oo decrease at the end. Because this fluctuation is much greater than that associated with atmospheric carbon dioxide and because of abundant rainfall at the site, they consider the $\delta^{13}C$ variation to be a temperature effect with a coefficient of +0.2 °/oo/°C. Finally, Freyer (1980) examined $\delta^{13}C$ of cellulose from the earlywood and latewood of 50 individual tree rings. In the mean, $\delta^{13}C$ of the earlywood was "lighter" (more negative) than the latewood.

We examined growth rings from an alligator juniper tree (*Juniperus deppeana*) harvested in January 1980 at a site near Prescott, Arizona. This choice has practical overtones in that the genus *Juniperus* has been important to southwestern U.S. dendrochronology. However, the rings of juniper are generally much smaller than the *Pinus radiata* growth rings used by Wilson and Grinsted (1977), due to shorter growing season and other limiting factors. The relatively large 1978 and 1979 growth rings of the Prescott juniper were subdivided into 3 and 4 approximately equal subsections, respectively (Figure 1). The latewood proportion of each ring was very small, and is represented by the thick ring boundaries in Figure 1. Even the subsections containing the latewood were dominated by earlywood cells, in contrast to the Wilson and Grinsted (1977) study where latewood occupied one full subsection of each ring. The existence of a diffuse, discontinuous false latewood band contained in subdivision III of the 1979 ring allowed a test of continuity of the $\delta^{13}C$ trend when growth was partially interrupted, presumably by early summer drought.

One split of each subsection was retained for a whole-tissue analysis. Cellulose was isolated from the second split of each subdivision by first extracting oils and resins with toluene and ethanol in a soxhlet extraction apparatus. This was followed by removal of lignins with an acidified sodium chlorite solution in a procedure modified after Green (1963). $\delta^{13}C$ analysis of the resulting cellulose could then be compared with the results of whole-tissue analysis to determine if these extra steps might be avoided in routine preparation. All samples were burned to CO_2 in a microcombustion system, collected, and analyzed on a Micromass 602C mass spectrometer. All $\delta^{13}C$ results are reported with respect to the commonly accepted PDB standard (Craig 1957), with precision of combustion and analysis estimated at 0.1 °/oo based upon repeated analysis of a laboratory cellulose standard.

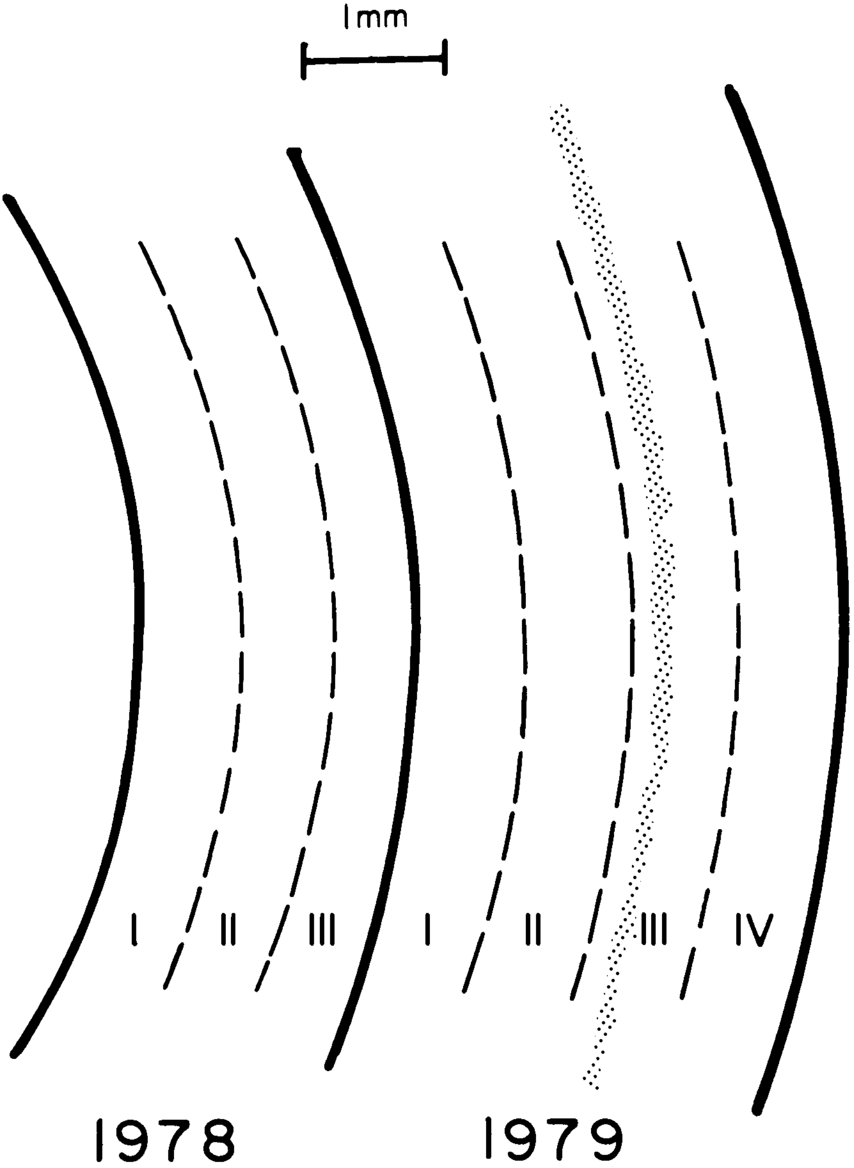

Figure 1. Subdivisions of the 1978 and 1979 growth rings from a section of *Juniperus deppeana* from Prescott, Arizona. Latewood is shown as the thick-lined ring boundaries, and a diffuse, "false" latewood band is shown in subdivision III of the 1979 ring.

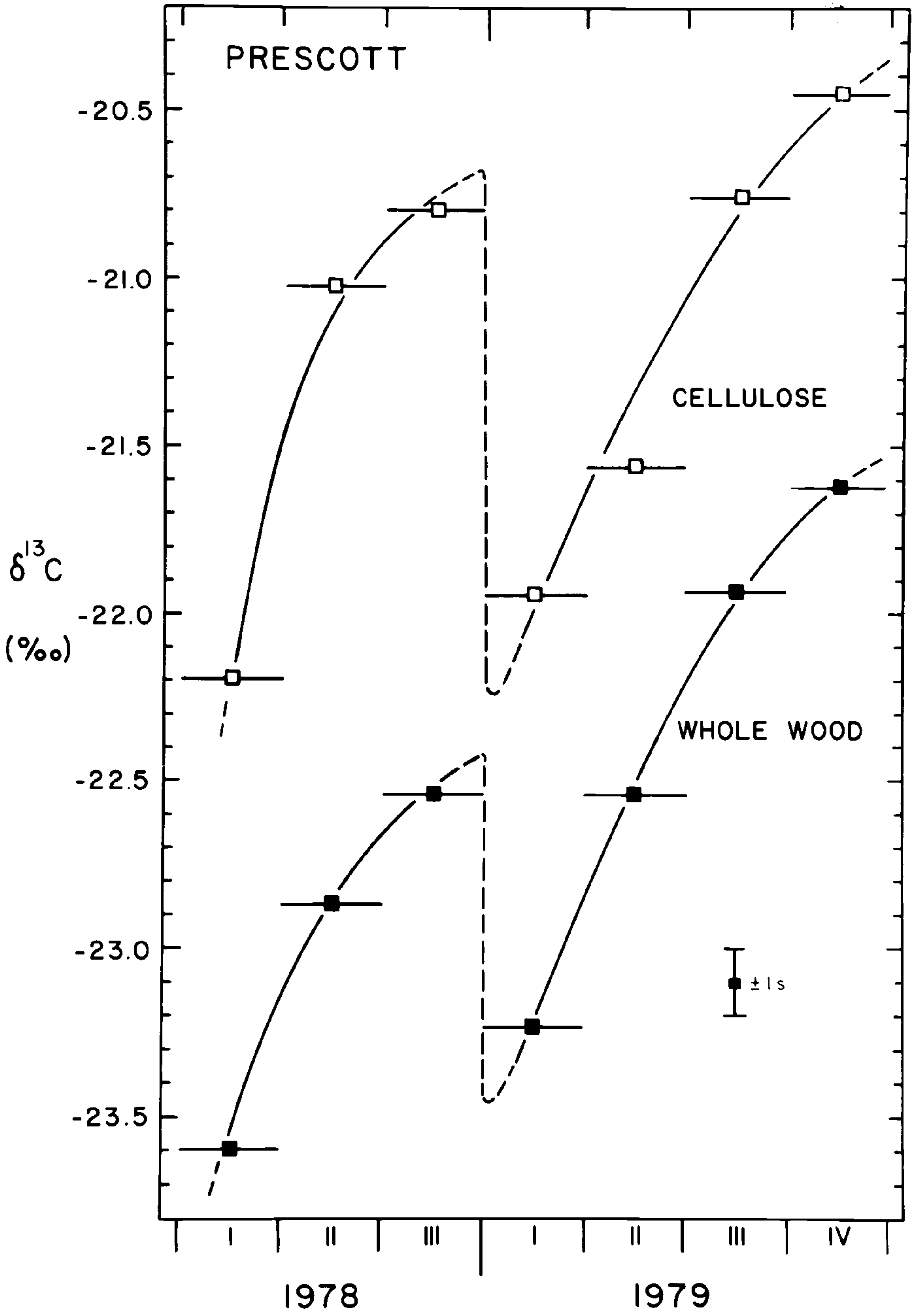

Figure 2. Pattern of $\delta^{13}C$ values for whole wood (solid squares) and cellulose (open squares) in the subdivisions of the 1978 and 1979 juniper rings.

RESULTS AND DISCUSSION

Whole wood and cellulose $\delta^{13}C$ analyses of these two rings are presented in Figure 2. For both rings, $\delta^{13}C$ increases (enrichment of ^{13}C) as the growing season progresses. A $\delta^{13}C$ difference of about 1 °/oo between subdivision III of the 1978 ring and subdivision I of the 1979 ring clearly marks the ring boundary for both cellulose and whole wood. $\delta^{13}C$ of wood and of cellulose show similar patterns, although the whole-wood values are generally about 1.5 °/oo lower than their cellulose counterparts. This difference may be attributable to the lignin component of whole wood which tends to have a "light" isotopic character (low $\delta^{13}C$ values) relative to the average of all wood components (Park and Epstein 1961). The $\delta^{13}C$ trend in the 1979 ring seems unaffected by the presence of the diffuse latewood band in subdivision III.

The cause of these fluctuations is not clear. The seasonal $\delta^{13}C$ fluctuation of atmospheric CO_2 is estimated to be about 0.4 °/oo on the basis of measurements at several "Pacific" sites from Arizona and California to Washington (Keeling 1961), approximately identical to the seasonal fluctuation estimated for Hawaii (Broecker et al. 1979). The magnitude of fluctuation in these tree rings is 2-3 times as great, although the direction of change is the same as that expected in the atmosphere.

The trend would also be reflective of a positive relationship between $\delta^{13}C$ in the plant and ambient air temperatures. Although an accurate temperature coefficient cannot be calculated directly because the exact timing of wood deposition and corresponding temperatures are unknown, an approximation may be made if we assume the diffuse latewood band in the 1979 ring occurred at about the end of June and that growth initiated at the beginning of April. The mean April and June temperatures at the nearby weather station at Prescott were 9.7 and 18.9°C, respectively, so that a linear temperature response of $\delta^{13}C$ over that period would be +0.13 °/oo/°C. However, if final cessation of growth is assumed to be at the beginning of October, then the July, August and September mean temperatures of 22.7, 20.2 and 20.4°C, respectively, appear to be almost independent of the increasing $\delta^{13}C$ trend after the false latewood band.

At the scale of ring subdivision, precipitation does not appear to have a major influence on the 1979 $\delta^{13}C$ trend. Precipitation was somewhat irregular with 1979 April through September monthly rainfall values of 3.3, 26.7, 4.1, 10.9, 56.9 and 13.2 mm, respectively. Within the limits of precision of $\delta^{13}C$ analysis, the trend shows no major changes related to moisture or drought. Length of day increases to the summer solstice in June, then progressively decreases. Likewise, during the late July and August rainy season, cloud cover could have reduced the total sunlight. Neither of these sunlight effects seems to be evidenced in the $\delta^{13}C$ trends.

Although the cause of the intra-annual $\delta^{13}C$ change is not evident, a characteristic, repetitive seasonal $\delta^{13}C$ signature does appear. This circumstance could be of importance in several dating applications. Because the trend does not appear to be interrupted by false latewood, $\delta^{13}C$ analysis could be useful in distinguishing a single ring with a false latewood band from two annual rings. In the former case the apparent double ring would show only a single annual $\delta^{13}C$ signature, and in the latter the two rings would show two annual signatures. This test might be particularly useful where sufficient materials from different individuals are not available for routine dendrochronological determination of false rings, e.g., in the extension of the bristlecone pine chronology.

Additionally, this $\delta^{13}C$ technique may be useful in dating complacent samples where standard dendrochronological methods fail. These may include samples from temperate sites with abundant moisture throughout the growing season, or perhaps tropical sites where growing seasons may be nearly year-long. Ultimately, just as ring widths are used in dendrochronology to reconstruct annual climate, if the cause of the $\delta^{13}C$ variation is found to be environmental, then the magnitude of seasonal variation of this parameter(s) may be reconstructed.

There are some limitations of this technique which would relegate it to only supplementary status relative to standard dendrochronology. First and foremost, the method would not be able to locate missing rings. Secondly, the size of the ring would limit both the number of subdivisions which could be reliably, physically separated, and the amount of material for analysis. At least two such subdivisions would be required for each ring under consideration in order to detect the $\delta^{13}C$ signature. From a standard 5 mm core, a ring 2 mm in width would be near the limit of providing sufficient quantity of carbon for mass spectrometric analysis of cellulose from the two 1 mm subdivisions. Of course, with larger cores or complete sections, problems of separation are more limiting than the amount of material available. Finally, although the yearly growth rings from complacent series could be delineated by this method, a knowledge of the true date of one ring would be required in order to assign absolute dates to all others. This might restrict absolute dating by this method to cores or sections from trees living at the recorded time of collection. However, if certain years have unusual $\delta^{13}C$ patterns found on a regional basis, then these may become the key signatures for dating all specimens, equivalent to the role of narrow rings from sensitive series in standard dendrochronology. Presently, the time required for preparation and analysis would probably prohibit large-scale, routine intra-annual analysis. Micro-combustion and analysis of a single sample take about 45 minutes, and cellulose isolation might add another 15-30 minutes.

CONCLUSIONS

The stable carbon isotopic analyses of subdivisions of two consecutive rings of a juniper tree from Prescott, Arizona, show a trend of increasing $\delta^{13}C$ within each ring. The ring boundary between the two is marked by a high $\delta^{13}C$ value at the end of one growing season and a relatively low $\delta^{13}C$ value at the beginning of the next season. Because this trend is seen in both whole wood and in the cellulose component, preparation time could be minimized by analyzing whole wood alone. Although the cause of the trend is not clear, its existence may provide an additional tool in tree-ring dating and may ultimately be the source of important seasonal environmental information.

Because the $\delta^{13}C$ trend does not appear to be altered by false latewood bands, its greatest utility may lie in testing for false rings in materials datable by standard dendrochronological techniques. It may also be useful in dating complacent ring series provided no rings are missing and that at least one ring has a known true age. This method could not be used to identify missing rings and would be constrained by physical separation of sufficient material for analysis.

Further groundwork is needed to expand our knowledge on this phenomenon. Tests are needed to determine the intra-annual signature from different species and from different localities and climates. Circumferential variability and $\delta^{13}C$ signatures of heartwood and sapwood rings should be examined. Controlled-environment growth chamber experiments may be necessary to determine the contributing effects and their order of importance.

ACKNOWLEDGEMENTS

We wish to thank Jeffrey S. Dean, Laboratory of Tree-Ring Research of The University of Arizona, for his assistance in crossdating the juniper section. This research was funded in part under DOE Contract DE-AC02-81EV10687.

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