

Interpreting Past Climate From Stable Isotopes in Continental Organic Matter

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The isotopic composition of fossil organic material from continental deposits contains myriad information about past environmental conditions. Much effort has been devoted to study of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ variations in organic matter, which depend strongly on isotopic effects occurring in the hydrologic cycle. Derivation of proxy temperature signals has been demonstrated in studies using $\delta^2\text{H}$ data from plant cellulose extracted from fossil wood, packrat middens, and peat, because plant tissues preserve isotopic signals inherited from the temperature-dependent signature of local meteoric water. More complex deconvolution of oxygen and hydrogen isotope data from terrestrial plant cellulose has also been undertaken using correlative or mechanistic models (calibrated through comparison of modern meteorological and isotopic data) that implicitly or explicitly consider the effects of secondary isotopic alteration of plant waters during evapotranspiration. Such models have been applied with notable success to isotopic studies of wood cellulose, which has proven to be a valuable source of quantitative proxy climate data, especially in the continuous time-series records offered by tree-ring sequences.

Promising results have also been obtained from isotopic study of oxygen in aquatic plant cellulose preserved in lake sediments, hydrogen in aquatic plant lipids, and oxygen and hydrogen in cellulose from peat deposits.

INTRODUCTION

Continental organic matter contains many potential paleoclimatic signals inherent in the isotopic composition of its constituent elements. Foremost among such isotopic signals are those preserved in the $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios in plant tissues, which contain information about the isotopic composition of past environmental water associated with tissue synthesis. Understanding and documentation of the temperature- and moisture-dependent oxygen and hydrogen isotope fractionations that occur as water passes through the hydrologic cycle sets the stage for quantitative reconstruction of paleoclimate. Valuable information may be gleaned also from variations in $^{13}\text{C}/^{12}\text{C}$ ratio in plant matter, although interpretation in climatically relevant terms is commonly less straightforward.

The following discussions focus rather narrowly on quantitative interpretation of isotopic signals from the cellulose fraction of fossil plant matter, rather than attempting to review the broad field of paleoenvironmental research in which isotopic data from continental organic matter are routinely applied. This focus has been chosen for practical reasons (to limit the length of the discussions) and to highlight the rich store of quantitative information available from careful consideration of precisely measureable isotopic variations in organic matter. The article emphasizes the interpretation of isotopic data from wood cellulose, with less detailed consideration of isotopic data from lake sediments and peat.

WOOD

Hydrogen and oxygen isotope data from terrestrial plant matter contain signals originating from local meteoric water (which may provide proxy temperature), as well as moisture-dependent signals from enrichment of plant water by evapotranspiration prior to tissue synthesis [e.g. Ferhi and Létolle, 1977; Burk and Stuiver, 1981; Yapp and Epstein, 1982a]. Carbon isotope composition is fundamentally controlled by photosynthetic pathway, resulting in the well-known differentiation of C_3 and C_4 plants [Bender, 1971; Smith and Epstein, 1971]. Humidity-dependent variations occur in the carbon isotope composition of tissues from C_3 plants, related to water use efficiency [Francey and Farquhar, 1982; Farquhar et al., 1988], whereas strongly invariant carbon isotope effects may occur in C_4 plants [Marino and McElroy, 1991].

Following early attempts to use whole wood [e.g. Libby et al., 1976], studies have mainly been conducted using α -cellulose extracted from finely ground wood powder [Green, 1963]. Oxygen isotope analysis of the purified cellulose is usually undertaken on carbon dioxide gas produced by pyrolysis in a nickel or quartz tube [Thompson and Gray, 1977; Hardcastle and Friedman, 1974] or by mercuric chloride combustion [Rittenberg and Ponticorvo, 1956; Sternberg, 1989]. Hydrogen isotope determinations are conducted on cellulose that has been nitrated to eliminate exchangeable, non-carbon-bound hydrogen [DeNiro, 1981]; hydrogen gas for analysis is produced by reduction of combustion water over hot zinc or uranium [Epstein et al., 1976; Sternberg, 1989]. Carbon isotope ratios may be determined on carbon dioxide gas produced by combustion of either type of cellulose. Isotope ratios are expressed as " δ " values relative to SMOW (standard mean ocean water) for oxygen and

hydrogen, and PDB (Pee Dee belemnite) for carbon, and have typical analytical uncertainties equal to or greater than ± 0.2 , ± 2 , and ± 0.1 ‰, respectively, depending on the method used and the natural inhomogeneity of the cellulose.

Oxygen, hydrogen, and carbon isotope data from terrestrial plant cellulose have been used as both qualitative and quantitative indicators of past environmental change. Qualitative interpretations may rely simply on correspondence between changes in isotopic composition and expected environmental change inferred from other sources of information. Examples include a study by Dubois and Ferguson [1985], which proposed that low cellulose $\delta^2\text{H}$ values in radiocarbon-dated pine from northern Scotland reflected "amount effects" on the isotopic composition of rainfall during Holocene wet phases. More recently Becker et al. [1991] attempted to identify post-Younger Dryas climatic amelioration in southern Germany on the basis of changing cellulose $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values from tree-ring sequences, arguing that increasing $\delta^{13}\text{C}$ reflected declining humidity (increasing water use efficiency) and increasing $\delta^2\text{H}$ reflected a temperature-dependent rise in meteoric water $\delta^2\text{H}$.

Such efforts often place useful qualitative constraints on paleoenvironmental interpretations, but commonly have limited potential to support independent reconstruction of climatically relevant parameters. Of more interest in the present context are methods for deriving quantitative information from isotopic variations in terrestrial plant cellulose. Reported studies fall into two principal (although not necessarily mutually exclusive) categories, depending on whether reconstructions are based on transfer functions describing empirical correlations between isotopic and climatic parameters (analogous to traditional dendroclimatological analysis) or on semi-empirical models that attempt to account mechanistically for fractionations occurring in the plants.

"Transfer Function" Approach

The transfer function approach improves upon qualitative analysis by establishing statistically significant correlations between cellulose isotopic data and pertinent environmental parameters for plants at modern sites, that may be used in turn to interpret cellulose data from fossil or subfossil deposits. An early example using hydrogen isotope data was reported by Yapp and Epstein [1977], who identified a strong linear relation between $\delta^2\text{H}$ of cellulose and associated environmental water at modern North American sites and applied it to infer late-glacial meteoric water composition in eastern United States from a suite of radiocarbon-dated fossil wood samples. In subsequent investigations these authors also documented strong relations between cellulose $\delta^2\text{H}$ and mean annual temperature in ring increments from selected trees [Yapp and Epstein, 1982b], reflecting direct transfer of temperature-dependent isotopic signals from local meteoric water to cellulose, as well as identifying weak humidity-dependent variations in the hydrogen-isotope separation between cellulose and water [Yapp and Epstein, 1982a]. Epstein and Krishnamurthy [1990] also used this approach for interpretation of hydrogen isotope data from tree-ring sequences obtained at 23 sites around the world to assess recent global temperature change.

Such simple transfer functions must be applied to paleoclimate reconstruction with caution, as their applicability is constrained nat-

urally by the range of climatic conditions sampled within their respective analogue data sets. The existence of humidity-dependent effects within the set of data used by Yapp and Epstein [1982a] provides a good case in point; valid estimation of past meteoric water isotopic composition using their observed linear relation between $\delta^2\text{H}$ of water and cellulose (which implicitly averages out the humidity effects) is inherently limited to sites that experienced the same style of secular climatic variation as that exhibited geographically by their modern data set.

More sophisticated multiple regression analysis of isotopic data from wood cellulose has also been undertaken to disentangle and quantify the simultaneous influence of different environmental factors. Of particular note are investigations by Ramesh et al. [1985, 1986] using ring sequences from silver fir trees growing in the Kashmir Valley, India. These studies verified the existence of statistically significant correlations between cellulose $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$, and various meteorological parameters (temperature, precipitation, humidity, cloudiness, etc), as well as demonstrating strong coherence in the isotopic variations between and within trees at the same site. Such observations strengthen the basis for using isotopic data from trees for paleoclimate analysis, as well as providing valuable independent information about the parameters that should be considered in mechanistic models. In turn, application of transfer functions based on the results of statistical analysis must be undertaken with due consideration of the mechanistic basis for the derived relations.

"Mechanistic" Approach

Efforts to understand how cellulose obtains its isotopic composition have fostered derivation of models to account for the isotopic effects occurring as water and carbon dioxide are assimilated by plants. Francey and Farquhar [1982; see also Farquhar et al., 1988] showed that carbon isotope variations in plants could be modelled in terms of assimilation rate of carbon dioxide and stomatal conductance, which are influenced by environmental factors such as relative humidity, water stress, and light levels. Unfortunately, owing to the complexity of possible interactions among environmental factors and strongly species-specific physiological characteristics, quantitative paleoclimate reconstruction using carbon isotope variations in wood cellulose remains rather elusive [see Stuiver and Braziunas, 1987], except perhaps in cases where dominance by an individual environmental factor can be assured [Leavitt, this volume].

Attempts to apply models that account for oxygen and hydrogen effects in plants have met with notable success, on the other hand, because of simpler environmental influences on oxygen and hydrogen assimilation into plant tissues. Burk and Stuiver [1981] showed that wood cellulose $\delta^{18}\text{O}$ could be modelled in terms of input (soil) water $\delta^{18}\text{O}$, humidity- and temperature-dependent isotopic enrichment arising from evapotranspiration of plant water, and biochemical fractionation effects occurring during cellulose synthesis. Subsequent studies [Edwards et al., 1985; Edwards and Fritz, 1986] suggested that cellulose $\delta^{18}\text{O}$ or $\delta^2\text{H}$ could be modelled adequately using only input water $\delta^{18}\text{O}$ or $\delta^2\text{H}$ and relative humidity as variables, and assuming fixed values for isotopic fractionations during plant water evapotranspiration and cellulose synthesis. Edwards

and Fritz [1986] coupled independent equations of the form suggested by Yapp and Epstein [1982a] describing the oxygen and hydrogen isotopic relations between soil water and cellulose with a meteoric water line linking oxygen and hydrogen isotope content in the input water:

$$\delta^{18}\text{O}_{\text{cellulose}} = A\delta^{18}\text{O}_{\text{water}} + 1000(A - 1) \quad (1)$$

$$\text{where } A = \alpha_n\alpha_e\alpha_k - \alpha_n(\alpha_e\alpha_k - 1)h$$

$$\delta^2\text{H}_{\text{cellulose}} = B\delta^2\text{H}_{\text{water}} + 1000(B - 1) \quad (2)$$

$$\text{where } B = \beta_n\beta_e\beta_k - \beta_n(\beta_e\beta_k - 1)h$$

$$\delta^2\text{H}_{\text{meteoric water}} = C\delta^{18}\text{O}_{\text{meteoric water}} + D \quad (3)$$

The terms α and β represent equilibrium (α_e and β_e) and kinetic (α_k and β_k) fractionations during plant water evapotranspiration, and biochemical (α_n and β_n) fractionations between cellulose and plant water, and h is photosynthetic humidity (the mean relative humidity during growth of the wood). Equations (1) and (2) are based implicitly on the Craig and Gordon [1965] model for steady-state evaporation from a terminal reservoir for which input exactly balances vapour loss, assuming isotopic equilibrium between ambient atmospheric vapour and input water, and (3) is the appropriate local meteoric water line. Solution of this set of equations for a pair of cellulose $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values yields quantitative estimates of input water isotopic composition and photosynthetic humidity, which may be useful paleoclimate parameters. The model is shown graphically in Figure 1.

The Edwards and Fritz [1986] model was applied initially to interpret isotopic data from bulk fossil wood samples preserved in a kettle-fill sequence in southeastern Canada. The reconstructed postglacial climate history agreed closely with other independent sources of information, and was further reinforced by comparison with results of additional oxygen-isotope studies in lake sediments [Edwards and Fritz, 1988; Edwards and McAndrews, 1989].

In another application of the model Clague et al. [1992] compared present climate with that during the early Holocene period of elevated timberline at an alpine site in southwestern Canada, using samples of modern and fossil fir and pine. This study incorporated small modifications to the fractionation factors proposed by Edwards and Fritz [1986], adopted as a result of ongoing efforts to refine the characterization of the isotope effects occurring during plant water evapotranspiration [e.g. Buhay et al., 1991]. Edwards and Buhay [in press] also used the model in this form in a preliminary interpretation of recent climate history in southern Ontario (A.D. 1736-1968) from an elm ring-sequence, and presented an updated version of the postglacial climate reconstruction of Edwards and Fritz [1986] incorporating the small reductions in the magnitude of inferred shifts in water $\delta^{18}\text{O}$ and humidity resulting from use of altered fractionation factors.

Considerable scope for additional "fine-tuning" of the model exists to account for improved knowledge about plant physiology, such as possible species- or temperature-dependent variations in the biochemical fractionations, or to account for temperature-dependent variations in equilibrium exchange between plant water and atmospheric vapour or other factors affecting the evaporative-enrichment response of plant waters, etc. As noted by DeNiro et al.

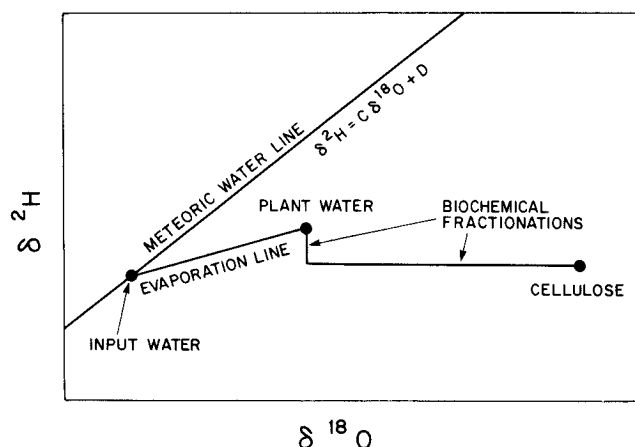


Fig. 1. Graphical representation of the Edwards and Fritz [1986] model. Potential paleoclimate signals exist in displacement along the meteoric water line (which may provide proxy temperature) and along the evaporation line (inverse to photosynthetic humidity). Note that the sensitivity of the model varies depending on the sense of climatic variation in meteoric water $\delta^{18}\text{O}$ versus h space, as the meteoric water and evaporation lines are not orthogonal.

[1988], and in spite of this inherent flexibility, such models continue to significantly understate the actual complexity of the system. Nevertheless, it is also apparent, even at the current state of development, that such models can effectively mimic the sum of the natural processes in order to derive useful paleoenvironmental information with a substantial degree of confidence. Ongoing development of the approach depends on incorporation of knowledge gained from studies of modern plants, especially better understanding of how isotopic signals are translocated within plants and the isotopic relations between plant water and cellulose [e.g. DeNiro and Cooper, 1989], kinetic isotope effects during evapotranspiration [e.g. Bariac et al., 1990; Flannagan et al., 1991a, b], and compartmentalization of water within plant tissues [e.g. Yakir et al., 1989].

The above-noted study by DeNiro and Cooper [1989] is worthy of special mention because it revealed particularly intriguing evidence from potato sprouts grown under controlled conditions that the oxygen isotope composition of cellulose precursors may be reset by equilibration with cell water prior to cellulose synthesis. If shown to be true for other plant cellulose, this would have potential to greatly simplify paleoclimate interpretation by eliminating the need to account for the effect of evapotranspiration on cellulose $\delta^{18}\text{O}$, and perhaps (by extension) cellulose $\delta^2\text{H}$ [DeNiro and Cooper, 1989]. Although many questions remain unanswered, the weight of empirical evidence presently favours the existence of significant moisture-dependent effects on both oxygen and hydrogen isotope ratios in wood cellulose [see discussions of Edwards, 1990, and DeNiro and Cooper, 1990]; however, ongoing studies may conceivably discover that other mechanisms could at times imitate such effects.

Another source of potential uncertainty in the application of such a model is the possibility of species-dependent effects, either in the biochemical reactions producing cellulose, or in the physical

processes accompanying evapotranspiration. Although strong evidence of such complications is presently lacking, this problem can be circumvented effectively by using mono-specific sample suites or tree-ring sequences. Calibration of model parameters using recent ring sequences and instrumental meteorological data also permits indirect assessment of such effects to complement results from physiological study and growth experiments, as discussed below.

Interpretation of Model Output

Interpretation of input water isotopic composition, photosynthetic humidity, or other meteorological factors inferred from analysis of cellulose isotopic data (by whatever means) requires careful consideration of the conditions under which the plant lived. Trees using well-mixed groundwater having a relatively long subsurface residence time may be expected to incorporate isotopic signals representative of local weighted mean annual precipitation (and thus proxy temperature). In contrast, trees in more active hydrogeologic settings characterized by shorter groundwater residence times (such as talus slopes or other rapidly draining systems) may incorporate short-term seasonal fluctuations in isotopic composition that provide alternative information such as changing seasonal proportions [e.g. Yapp and Epstein, 1985; Clague et al., 1992] or rainfall amount [e.g. Lawrence and White, 1984].

Similarly, the relation between moisture conditions during the growth period, as indicated by photosynthetic humidity values (or, for example, precipitation inferred from transfer functions) and the local synoptic moisture regime may not be straightforward. Modelled humidity will be biased naturally toward periods of more rapid growth, which may be unrepresentative of average growth season conditions. The potential effects of such opportunism on the part of trees will be most marked in extreme climates, in which growth may be limited to short daily or periodic episodes, and least marked in temperate climates, in which favorable conditions persist over longer intervals. Even in temperate climates, isotopic composition of cellulose is likely to vary between early and late wood in a single annual ring [Epstein and Yapp, 1976; Luckman and Gray, 1990], in response to changing growth season conditions. As well, neighbouring trees at the same site could possibly sample different parts of the growing season because of differing periods of photosynthetic activity [Friedman et al., 1988].

Models like that of Edwards and Fritz [1986] also harbour potential for misrepresentation of past meteoric water $\delta^{18}\text{O}$ and humidity if water used by a tree did not lie on a known meteoric water line (i.e. if equation (3) is unknown or incorrect). A possible example of this occurs in a silver fir ring sequence reported by Ramesh et al. [1985]. Shown in Figure 2 is a comparison of oxygen and hydrogen isotope data and inferred input water $\delta^{18}\text{O}$ and photosynthetic humidity from two radii of a tree having a notably asymmetric cross-section. Ramesh et al. [1985] demonstrated that strong coherence existed between the isotopic signals from the normal and stunted radii, in spite of systematic differences in the $\delta^2\text{H}$ values. They attributed the uneven growth to internal physiological effects, and speculated that circumferential isotope variability reflected varying seasonal bias in wood around the trunk. These data were merged with $\delta^2\text{H}$ and $\delta^{13}\text{C}$ data from a third radius of the same tree

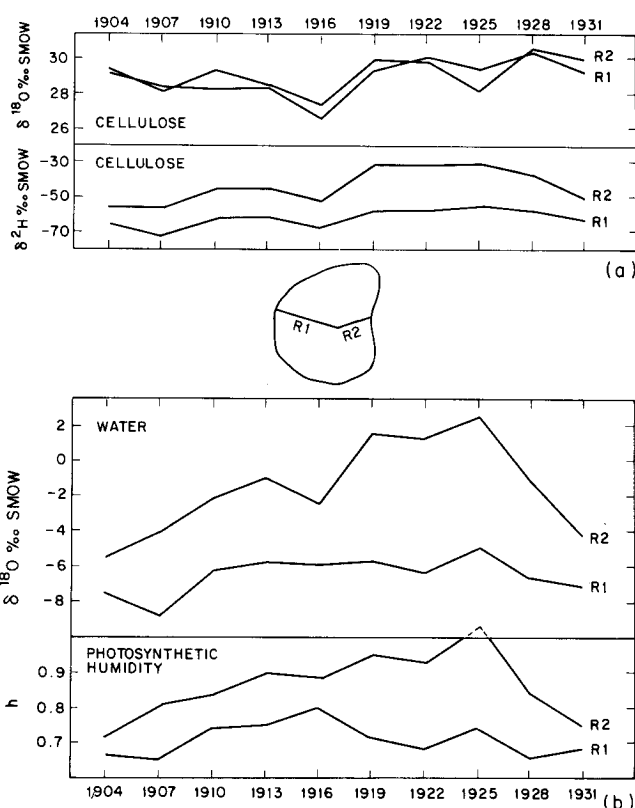


Fig. 2. a. Cellulose $\delta^{18}\text{O}$ and $\delta^2\text{H}$ profiles from a 30-year silver fir (*Abies pindrow*) ring-sequence [data from Ramesh et al., 1986]. The original ring-by-ring data are expressed here as three-year averages for simplicity.

b. Inferred meteoric water $\delta^{18}\text{O}$ and photosynthetic humidity, derived using the model of Edwards and Fritz [1986] with modified fractionations in equations (1) and (2) as suggested by Buhay et al. [1991; $\alpha_n = 1.0264$; $\alpha_e = 1.0095$; $\alpha_k = 1.0210$; $\beta_n = 0.9520$; $\beta_e = 1.0797$; $\beta_k = 1.0185$] and the Kashmir meteoric water line [Ramesh et al., 1986; $\delta^2\text{H} = 6.8\delta^{18}\text{O} + 2$] for equation (3). Note that both inferred parameters fall within expected ranges for R1, but not for R2.

and a radius from a neighbouring silver fir for the statistical comparison with growing season meteorological parameters mentioned previously [Ramesh et al., 1986].

As revealed in Figure 2, model-derived values for radius R1 (normal growth) fall within the ranges reported by the original authors, and thus provide plausible climate records, whereas values for radius R2 (stunted growth) range well beyond realistic values. The simplest explanation to account for this significant discrepancy is that water used by the R2 side of the tree did not fall on the Kashmir meteoric water line, and hence the model is not accounting correctly for isotopic effects during evapotranspiration. The isotopic enrichment of cellulose in R2 relative to R1 and the underestimation of isotopic enrichment during evapotranspiration (i.e. excessively high inferred water $\delta^{18}\text{O}$ and humidity) could occur if a portion of the cellulose on the R2 side of the tree had been derived from "pre-evaporated" soil water lying off the meteoric water line, perhaps as a result of shallower rooting on this side of the tree.

Moreover, the discrepancy between model-derived data from R1 and R2 varies over time, which may in itself constitute an additional climate signal; maximum divergence occurs during the latter half of the 30-year period represented by the ring sequence, which was slightly warmer and drier than the early part of the record [Ramesh et al., 1986; Table 1] and hence perhaps even more likely to foster isotopic differences between the radii by the postulated mechanism. It is tempting to speculate whether differential growth of the tree is not also a straightforward signal of recurrent moisture stress on the stunted side.

Climatic correlations derived by Ramesh et al. [1986] are broadly consistent with equivalent correlations inherent in both the Burk and Stuiver [1981] and Edwards and Fritz [1986] models. For example, Ramesh et al. [1986] found cellulose $\delta^{18}\text{O}$ to be most strongly influenced by relative humidity, with a regression coefficient of about -0.2‰ per 1% relative humidity, as opposed to -0.3‰ per 1% predicted for steady-state evaporation by both the Burk and Stuiver [1981] model and the Edwards and Fritz [1986] model, as configured here. Underestimation of sensitivity to humidity would be expected given the use of average growth season relative humidity, which is naturally biased by consistently high humidity at night, rather than average daytime relative humidity (i.e. photosynthetic humidity) considered in calibration of the models.

Cellulose $\delta^2\text{H}$ from the Kashmir site correlated most strongly (and negatively) with rainfall amount, which Ramesh et al. [1986] argued was an indirect confirmation that cellulose $\delta^2\text{H}$ reflected the $\delta^2\text{H}$ of associated meteoric water, in light of "amount effects" noted by previous authors for precipitation and cellulose [e.g. Dansgaard, 1964; Lawrence and White, 1984]. A positive correlation with temperature, of similar magnitude to that observed globally for precipitation, was taken as further indirect evidence of the isotopic link between cellulose and water. Their analysis did not reveal strong dependence on humidity, but could not discount a weak relation. These observations are consistent qualitatively with relations predicted by the modified Edwards and Fritz [1986] model, which suggests that variation in cellulose $\delta^2\text{H}$ is controlled primarily by changing water $\delta^2\text{H}$, and secondarily by changing humidity (with a coefficient of about -1‰ per 1% change in photosynthetic humidity).

Carbon isotope variations in the Kashmir sample suite were strongly correlated with both humidity and cloudiness, in agreement with the expected influence of moisture and light levels as originally modelled by Francey and Farquhar [1982; see discussion of Ramesh et al., 1986].

ORGANIC LAKE SEDIMENTS AND PEAT

Lake Sediments

Carbon isotope analysis of organic matter in lake sediments has been used extensively to provide qualitative indications of paleolimnologic change, which may in turn provide indirect paleoclimatic information [e.g. see Stuiver, 1975; Håkansson, 1985; McKenzie, 1985]. Potential isotopic signals include productivity-driven enrichment of ^{13}C in dissolved inorganic carbon due to preferential uptake of ^{12}C by phytoplankton in the water column, which may lead to preservation of a proxy DIC $\delta^{13}\text{C}$ record in offshore or deep-water sediments. Carbon isotope variations related to chang-

ing proportions of allochthonous (e.g. terrestrial) and autochthonous organic matter can also provide qualitative information about local environmental change in nearshore sediments.

Studies have also been undertaken using the cellulose fraction of organic matter from lake sediments in order to resolve isotopic variations within a specific organic constituent. Cellulose is extracted from the fine fraction ($< 149\ \mu\text{m}$) of the sediments using a technique similar to that used for purification of wood cellulose [Green, 1963], with additional washing and decanting or heavy liquid separation to remove detrital sediment particles [Edwards and McAndrews, 1989; Edwards and Elgood, 1992]. Investigations using cores from several Canadian lakes [Edwards and McAndrews, 1989; MacDonald et al., in prep; Edwards, unpublished data] suggest that cellulose in the fine fraction of offshore (profundal) sediments is commonly derived entirely from aquatic plants and algae, possibly because of rapid sedimentation and burial of phytoplankton in fecal pellets with little opportunity for oxidation [Schradler, 1971; Ferrante and Parker, 1977], compared to longer residence times of terrestrial organic matter in the oxic zone. Lake water $\delta^{18}\text{O}$ and DIC $\delta^{13}\text{C}$ histories from sediment cellulose have potential to provide qualitative paleohydrologic information analogous to that obtained from primary lacustrine carbonates [see Talbot, 1990]. Edwards and McAndrews [1989] and Edwards and Fritz [1988] showed that quantitative deconvolution of $\delta^{18}\text{O}$ profiles from sediment cellulose and carbonate (respectively) from lake sediment cores could be undertaken to reconstruct residual changes in lake water $\delta^{18}\text{O}$, independent of changing input water isotopic composition, using the regional meteoric water $\delta^{18}\text{O}$ history derived by Edwards and Fritz [1986].

Figure 3 illustrates an example of carbon and oxygen isotope stratigraphy for a sediment core from a small tundra lake in central Canada. A notable lack of correspondence exists between the whole organic and cellulose $\delta^{13}\text{C}$ profiles in this core, demonstrating that isotopic variations within undifferentiated organic material may mask more subtle $\delta^{13}\text{C}$ variations in aquatic cellulose. Cellulose $\delta^{18}\text{O}$ variations were apparently inherited from changing lake water $\delta^{18}\text{O}$, which was controlled primarily by varying evaporative enrichment of lake waters, signifying changing hydrologic balance related to advance and retreat of the Arctic Front (MacDonald et al., in prep.).

Considerably more climatically relevant information could be obtained if both oxygen and hydrogen isotope contents of lake water could be inferred from aquatic plant cellulose, since evaporative enrichment of lake waters relative to local meteoric water constitutes a possible climate signal, analogous to that for plant water enrichment in terrestrial cellulose [e.g. see Edwards and McAndrews, 1989]. Attempts to obtain useful hydrogen isotope data from aquatic plant cellulose have met with little success, apparently owing to substantial species-dependent variability in the biochemical fractionation effects between water and phytoplankton and aquatic plants [Stiller and Nissenbaum, 1980; Sternberg et al., 1984a, b; Sternberg, 1988; Edwards, unpublished data]. As shown by Sternberg [1988], however, consistent hydrogen isotope fractionation does occur between water and lipids in various aquatic plant species, permitting coupling of cellulose $\delta^{18}\text{O}$ with lipid $\delta^2\text{H}$ in a model that could be used to reconstruct $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of associ-

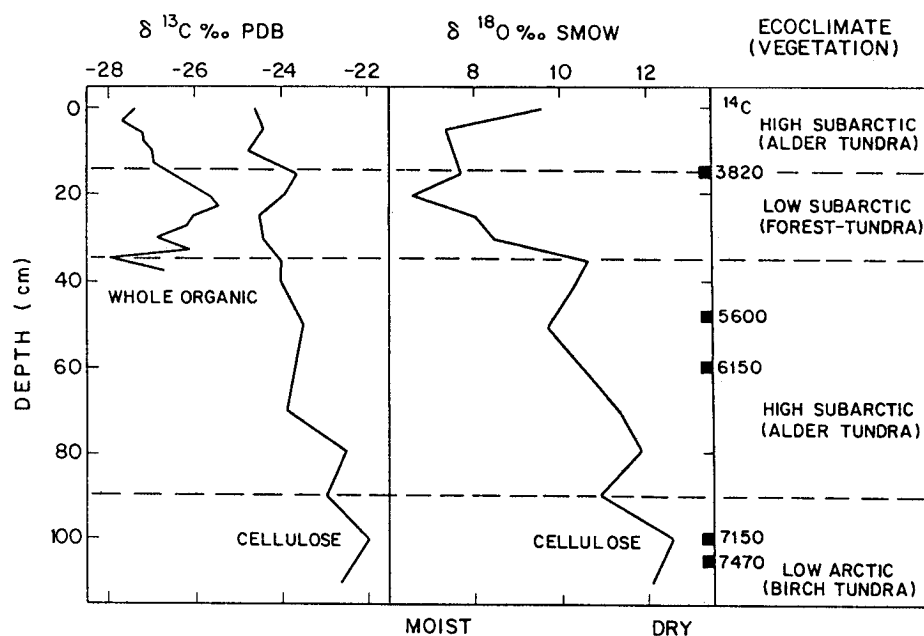


Fig. 3. Carbon and oxygen isotope data from a sediment core, Queen's Lake, Northwest Territories, Canada. Cellulose $\delta^{18}\text{O}$ mainly responded to varying evaporative enrichment, reflecting changing water balance. Covariance of cellulose $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the lower part of the core is consistent with closed-basin hydrology under dry climatic conditions [cf. Talbot 1990]. Covariance disappears in sediments deposited after about 6000 B.P. as open-basin conditions developed in response to climatic amelioration [MacDonald et al., in prep.]. Discrepancy between $\delta^{13}\text{C}$ of undifferentiated organic matter [Edwards, unpublished data] and cellulose $\delta^{13}\text{C}$ in the upper part of the core shows the influence of abundant non-cellulose organic material, probably of both aquatic and terrestrial origin.

ated water. Significant opportunities for paleoenvironmental reconstruction exist if further studies verify that aquatic plant lipids can be derived from sediments along with aquatic plant cellulose.

Peat

Plant matter preserved in peat deposits derives from a range of microenvironments, from terrestrial conditions inhabited by trees and emergent vegetation, subject to variable evaporative isotopic enrichment of oxygen and hydrogen in plant water, to fully saturated conditions that are essentially aquatic. Isotopic studies of peat include attempts to derive quantitative information from whole organic matter or cellulose [e.g. Schiegl, 1972; Dupont and Mook, 1987; Chatwin, 1981], relying on temperature-dependent isotopic signals inherited from local meteoric water, as well as more qualitative examinations of $\delta^{18}\text{O}$, $\delta^2\text{H}$, and $\delta^{13}\text{C}$ of the whole organic or cellulose fractions, to better understand environments of peat formation or to seek other paleoenvironmental signals [e.g. Brenningmeijer et al., 1982; Dupont and Brenningmeijer, 1984; Gouze et al., 1987; Aucour et al., this volume].

Possible species-dependent variations in biochemical isotope effects during cellulose synthesis could be especially significant for peat, because of the variety of plants (and photosynthetic pathways) that may be represented in a single sample. Varying carbon isotope effects may provide broad indications of changing climate, as reflected by changing ratio of C_3 to C_4 plants [see Aucour et al., this volume], but are unlikely to record more subtle environmental signals like those that appear to be preserved in tree cellulose. Biochemical fractionation effects for oxygen in peat plants (as in

other plants and algae) seem to be remarkably invariant, in contrast to the suspected variability in the hydrogen isotope effects [Sternberg, 1988]. Brenningmeijer et al. [1982] concluded that covariant (but seemingly excessive) fluctuations in cellulose $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from a core of an ombrotrophic bog in The Netherlands reflected fundamental control by meteoric water isotopic composition (\approx proxy temperature), overprinted by noise from varying biochemical effects on hydrogen, and evaporative enrichment effects on both hydrogen and oxygen from plant water transpiration. Dupont and Mook [1987] later derived tentative "relative deuterium temperature" records using hydrogen isotope data from several Dutch peat cores, by correcting for varying taxonomic composition of the peat.

If biochemical fractionation effects were similar for different plants in a particular peat assemblage, or specific plants could be selectively subsampled, then estimates of meteoric water isotopic composition could be derived from cellulose $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data, using a model like that of Edwards and Fritz [1986] to filter out residual enrichment arising from evapotranspiration (which would indicate a spurious apparent humidity). Carrying out this exercise using the data reported by Brenningmeijer et al. [1982], for example, yields highly reasonable values for $\delta^{18}\text{O}$ of water in the Engbertsdijksveen bog around the time of the Subboreal/Subatlantic transition (Figure 4). Reconstructed water $\delta^{18}\text{O}$ values are further supported by the observation that cellulose $\delta^{18}\text{O}$ and $\delta^2\text{H}$ obtained on two separates of a single sample (taken at 105 cm), which was chosen by the authors to illustrate species-dependent isotopic differences, produce identical estimates of water $\delta^{18}\text{O}$

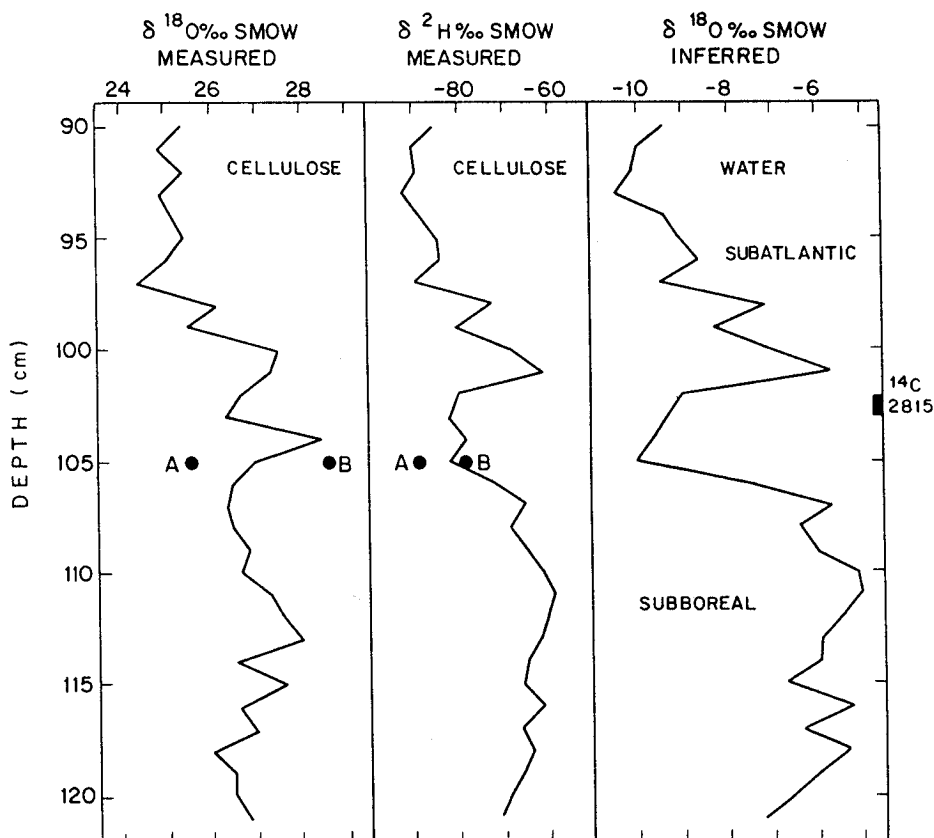


Fig. 4. Cellulose oxygen and hydrogen isotope data from Brenningkmeijer et al. [1982; Figure 2] for part of a core from Engbertsdijksveen bog, The Netherlands. The core interval represents about 350 years of accumulation, spanning the Subboreal-Subatlantic climatic deterioration. Bog water $\delta^{18}\text{O}$ was inferred using the Edwards and Fritz [1986] model, using the global meteoric water line of Craig [1961] as equation (3) and the fractionation factors listed in the caption of Figure 2. B and A refer to splits of the sample from 105 cm, containing and lacking *Eriophorum* plant matter, respectively. Both subsamples yield the same inferred input water $\delta^{18}\text{O}$ value, as would be expected if *Sphagnum* (the major constituent of the peat) and *Eriophorum* have similar biochemical isotope effects. The difference in the apparent discrepancies between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for A and B illustrates the much larger relative influence that humidity-dependent effects have on cellulose $\delta^{18}\text{O}$ compared to cellulose $\delta^2\text{H}$.

(while yielding, predictably, differing apparent humidities). Both of these observations are, in fact, consistent with isotopic data reported from plants in a modern Dutch bog [Brenningkmeijer et al., 1982; Figure 1]. Cellulose $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data for various species of *Sphagnum* moss and other vascular plants that occur in the peat fall along a linear trend similar in slope to that of the evaporation line implicit in the Edwards and Fritz [1986] model as here configured. This suggests that biochemical effects may, after all, be rather similar in the major species within this taxonomic assemblage (although this exercise does not confirm that correct values for the biochemical fractionation factors are being used).

More conclusive information about possible species-dependent effects on cellulose $\delta^2\text{H}$ could be obtained by comparison with lipid $\delta^2\text{H}$, as suggested by Sternberg [1988], and as discussed in the previous section.

CONCLUDING COMMENTS

Numerous isotopic signals exist in other types of continental organic matter, yet few offer potential for detailed quantitative

time-series paleoclimate reconstruction equivalent to that obtainable from wood cellulose, and cellulose (and perhaps lipids) of sediments and peat. Promising exceptions may include isotopic data from plant remains in packrat middens [e.g. Long et al., 1990], mammal bone collagen [e.g. Cormie, 1991], insect chitin [Miller et al., 1988], or other substrates that may be preserved in fossil deposits.

Both qualitative and quantitative information about past environmental conditions may be obtained from isotopic study of continental organic matter. Although qualitative data may place useful constraints on interpretations based on other sources of information, the greatest value of isotopic studies is realized by the ability to make quantitative estimates of climatically relevant parameters independently of other data.

The most useful climatically relevant isotopic parameter is the isotopic composition of meteoric water. Aside from possibly providing paleotemperature, this parameter can afford a fundamental baseline at regional spatial scale for assessment of paleomoisture variations. Isotopic signals preserved in terrestrial cellulose provide

one of the least ambiguous sources of information about changes in past meteoric water composition, which can in turn be used to deconvolute isotopic signals preserved in other materials.

Finally, it is clear that the existing models used to interpret such data remain first approximations that need to be continually tested and refined as new data become available from study of modern plants.

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