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D/H ratios of environmental water recorded by D/H ratios of plant lipids

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Isotope ratios of chemical components are powerful tools in the interpretation of palaeoenvironments, particularly carbonates from foraminiferans[1,2], desert caliche[3], and desert pavements[4]. Isotope ratios of plant cellulose are also indicators of environmental variables such as temperature and relative humidity[5-7]. Several workers have reported climatic fluctuations based on hydrogen and oxygen isotope ratios of cellulose from tree trunks[8-10] and peats[11,12]. Here I present measurements that demonstrate that for submerged aquatic plants δD values of lipids record D/H ratios of environmental water, whereas cellulose does not. I further demonstrate that δD values of lipids in conjunction with δ^{18}O values of cellulose provide significant information on isotope ratios of environmental water.

Oxygen and hydrogen isotope ratios of plant cellulose were first proposed as palaeoclimatic indicators because isotope ratios of rainwater (meteoric water as defined by Craig[13]) are related to climate; that is, rainwater from warmer regions at lower latitudes or altitudes has high D/H and $^{18}O/^{16}O$ ratios, whereas in cooler regions at higher latitudes or altitudes these ratios are lower. Plants record the hydrogen and oxygen isotope ratios of water available for growth in their cellulose[5-7]. Thus deducing climate through isotope ratios of meteoric water is a matter of deciphering the isotopic fractionations that take place during water uptake, evapotranspiration and incorporation into cellulose. The major problems with the use of cellulose to interpret climate, however, are the effect of evapotranspiration in modifying isotopic ratios of leaf water relative to ground water[7,14], and species-specific variable isotopic fractionations that occur during metabolic processes responsible for incorporation of hydrogen in cellulose[15-20]. Particularly relevant to this paper is the latter problem. Large variability in δD values of non-exchangeable hydrogens from cellulose of different species of plants grown in a single site, exposed to the same climate and meteoric water, have been observed[15,16]. This variability also extends to aquatic plants, indicating that variable hydrogen isotopic fractionations during cellulose synthesis are primarily due to fractionations occurring during biochemical reactions[17,18]. In addition, fractionations occurring during biochemical reactions are influenced by environmental factors such as temperature[19] and light quality[20]. As a result of this variability, absolute δD values of water available during cellulose synthesis cannot be deduced from hydrogen isotope ratios of cellulose. Differences in hydrogen isotope ratios of plant cellulose through time can be due to changes in δD values of groundwater, to differences in isotopic fractionations particular to each species, or to environmental effects on the hydrogen isotope fractionations occurring during cellulose synthesis. Thus climatic information from hydrogen isotope ratios of cellulose cannot be precisely estimated.

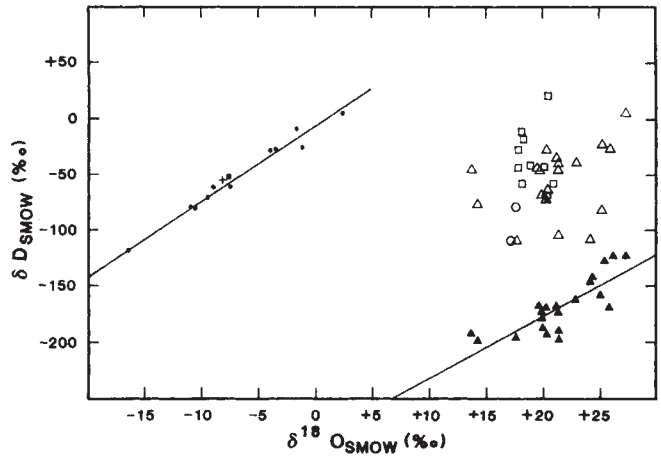

Fig. 1 The relationship between δD and δ^{18}O values of lake waters, δD values of non-exchangeable hydrogen of cellulose and δ^{18}O values of cellulose from submerged aquatic plants, and δD values of lipids and δ^{18}O values of cellulose. Symbols: ●, isotope ratios of lake water in this study; +, ■, isotope ratios of waters measured by DeNiro and Epstein[19] and Epstein *et al.*[5] respectively; △, isotope ratios of cellulose measured in this study; □, ○, isotope ratios of cellulose measured by DeNiro and Epstein[19] and Epstein *et al.*[5] respectively; ▲, δD values of lipids versus δ^{18}O values of cellulose. Correlation coefficients, *r*, were 0.95 for water values, 0.38 for cellulose values, and 0.80 for lipids versus cellulose values.

There are three possible solutions to this problem. The first and most difficult is a complete understanding of all isotopic fractionations occurring during water uptake through cellulose synthesis for different species. This knowledge can then be used to deduce δD values in meteoric water from isotope ratios of plant cellulose. The second is to find a single species whose isotopic fractionations do not vary between individuals of the same species or with environmental conditions. The third solution, specifically addressed here, is the analysis of a plant component that incorporates deuterium without the metabolic effects observed for cellulose. Previous D/H ratio measurements in lipids and cellulose from plants show that whereas cellulose has a large variation in δD relative to the δD of the available water, lipids have a relatively constant δD value[21,22]. Thus lipids may be a plant metabolic component that truly records the δD values of environmental waters.

The feasibility of using δD values of lipids in conjunction with δ^{18}O values of cellulose to deduce isotope ratios of meteoric water is demonstrated here. Submerged aquatic plants from several lakes of different geographical regions having water with different isotope ratios were collected and $^{18}O/^{16}O$ and/or D/H ratios of their cellulose and lipids, and the surrounding water, were determined (Table 1). Submerged aquatic plants are ideal organisms for this analysis because they do not transpire, and transpiration modifies the isotope ratio of water available for cellulose synthesis relative to the water source[14]. δD and δ^{18}O values of lake waters were highly correlated with each other ($r = 0.95$, $P < 0.01$, Fig. 1) and this relation is expressed by the regression equation

$$\delta D_{water} = 6.7\delta^{18}O_{water} - 6.9 \quad (1)$$

The slope of this regression line (6.7) is smaller than that of meteoric water (8.0) (ref. 13). As lakes of warmer regions at lower altitudes evaporate more rapidly, they may have a disproportionate increase in δ^{18}O values of the water relative to increases in δD values due to kinetic effects, thus decreasing the slope of the line. δD values of extracted and nitrated plant cellulose were not related to the δD values of lake water

Table 1 δD and $\delta^{18}O$ values of lake waters at different geographical locations and altitudes, δD and $\delta^{18}O$ values of cellulose and δD values of lipids from plants growing in the respective lakes

Species	Locations	Water		Cellulose		Lipid
		δD	$\delta^{18}O$	δD	$\delta^{18}O$	δD
Myriophyllum sp.	Villeperdue, France, 100 m	−25	−1.2	−107	+24.2	−146
Alisma plantago	Lespuau, France, 300 m	−27	−3.5	−81	+25.0	−158
Potamogeton crispus	Lespuau, France, 300 m	−27	−3.5	−39	+22.8	−162
Myriophyllum sp.	Lago Calzado, Peru, 4,425 m	−119	−16.4	−77	+14.3	−199
Eleocharis acicularis	Lago Calzado, Peru, 4,425 m	−119	−16.4	−46	+13.7	−192
Eleocharis acicularis	Imbabura, Ecuador, 3,650 m	−62	−7.4	−104	+21.3	−173
Elatina sp.	Imbabura, Ecuador, 3,650 m	−62	−7.4	−46	+19.9	−178
Potamogeton sp.	Imbabura, Ecuador, 3,650 m	−62	−7.4	−41	+21.4	−197
Eleocharis maculosa	Cotapaxi, Ecuador, 4,100 m	−62	−8.9	−63	+20.4	−170
Equisetum boyotensis	Cotapaxi, Ecuador, 4,100 m	−62	−8.9	−68	+19.8	−174
Myriophyllum quitensis	Cotapaxi, Ecuador, 4,100 m	−62	−8.9	−45	+19.6	−168
Potamogeton panamensis	Cotapaxi, Ecuador, 4,100 m	−62	−8.9	−71	+20.2	−189
Calitriche nubigena	Junin, Peru, 4,425 m	−71	−9.5	−108	+17.7	−196
Isoetes palmerii	Junin, Peru, 4,425 m	−80	−11.0	−27	+20.4	−193
Crassula palludosa	Lago Chisaca, Colombia, 3,620 m	−79	−10.6	−35	+21.2	−168
Hydrilla verticillata	Lago Gatun, Panama, 165 m	−28	−3.9	−45	+21.4	−190
Utricularia sp.	Florida, USA, ≤1 m	+5	+2.4	—	+26.2	−123
Eleocharis acicularis	Florida, USA, ≤1 m	−8	−1.6	+6	+27.2	−122
Cabomba caroliniana	Florida, USA, ≤1 m	−8	−1.6	0	+24.3	−141
Hydrilla verticillata	Florida, USA, ≤1 m	−8	−1.6	−26	+25.8	−170
Najas guadalupensis	Florida, USA, ≤1 m	−8	−1.6	−21	+25.3	−127

Isotope ratios of water, cellulose and lipids were determined as previously described[18,19,22] and reported in δ units, where δ (‰) = $[(R_{sample}/R_{standard})-1]\times 1{,}000$, and R is ratio of rare to common isotope. The standard used here for δD and $\delta^{18}O$ values is standard mean ocean water (SMOW).

($r=0.36$, $P>0.05$). This result contradicts the reported constant 22‰ difference between δD values of extracted and nitrated cellulose from terrestrial plants and the δD values of water available for plant growth[6]. δD values of lipids and $\delta^{18}O$ values of cellulose were highly correlated with the respective isotope ratios of lake waters ($r=0.79$, $P<0.01$ for lipids; $r=0.94$, $P<0.01$ for cellulose). However, interpretation of these relations is difficult because the δD and $\delta^{18}O$ values of the water when cellulose and lipids were synthesized could have been different from those at the time of water sampling. A way of overcoming this problem is to determine whether δD values of lipids or cellulose correlate with $\delta^{18}O$ values of cellulose and whether the relation between δD and $\delta^{18}O$ values of these plant metabolites is similar to the relation observed between δD and $\delta^{18}O$ values of water available for growth.

δD values of non-exchangeable hydrogen of cellulose and $\delta^{18}O$ values of cellulose for several submerged aquatic plants measured here and reported elsewhere[5,19] are not correlated ($r=0.38$, $P>0.05$, Fig. 1). In contrast, δD values of lipids are correlated with $\delta^{18}O$ values of cellulose at a highly significant level ($r=0.80$, $P<0.01$, Fig. 1) with the linear regression equation

$$\delta D_{lipid} = 5.5\delta^{18}O_{cell} - 286‰ \quad (2)$$

The slope of this regression line (5.5) is less than that of lake water (6.7). The relation between δD of lipids and $\delta^{18}O$ of cellulose of submerged aquatic plants, including a lower slope, can be explained by deriving a theoretical equation relating the δD values of lipids to $\delta^{18}O$ values of cellulose. Consider the two equations showing the isotopic labelling of lipids and cellulose by deuterium and oxygen-18 respectively from the water available to the plant,

$$\delta D_{lipid} = \alpha_d \delta D_{water} + (\alpha_d - 1)\times 1{,}000 \quad (3)$$

and

$$\delta^{18}O_{cell} = \alpha_o \delta^{18}O_{water} + (\alpha_o - 1)\times 1{,}000 \quad (4)$$

where α_d and α_o are defined as $(D/H)_{lipid}/(D/H)_{water}$ and $(^{18}O/^{16}O)_{cellulose}/(^{18}O/^{16}O)_{water}$ respectively. Although these terms are usually reserved for equilibrium fractionation processes, I use them here in the same sense as that used by Epstein and colleagues[5,7]. Their use is in part justified by recent evidence that oxygen isotope ratios of cellulose may be determined by fractionations occurring during the equilibrium between hydrated carbonyl groups in carbohydrate intermediates and water during cellulose synthesis[23]. Merging equations (1), (3) and (4) the following equation expressing the relation between δD of lipids and the $\delta^{18}O$ values of cellulose is derived:

$$\delta D_{lipid} = (6.7(\alpha_d/\alpha_o)\delta^{18}O_{cell}) + [1{,}000(\alpha_d - 1) - (6.9\alpha_d) - 6{,}700(\alpha_d/\alpha_o)(\alpha_o - 1)] \quad (5)$$

having a slope of $6.7\alpha_d/\alpha_o$ and intercept at $[1{,}000(\alpha_d-1) - 6.9\alpha_d - 6{,}700(\alpha_d/\alpha_o)(\alpha_o-1)]$. Thus the slope of a plot of δD values of lipids against $\delta^{18}O$ values of cellulose is not only a function of the slope of the line described by plotting δD against $\delta^{18}O$ values of water, but of the fractionation constants α_d and α_o. Accordingly, the greater the discrimination against deuterium during the formation of plant lipid or the smaller the discrimination against oxygen-18 during cellulose synthesis, the lower the slope of this line should be. Using the α_d of 0.870 as reported for saponifiable lipids of green algae[21], and the α_0 of 1.027 as previously reported for cellulose[5,19] in equation (5), the following is derived:

$$\delta D_{lipid} = 5.7\delta^{18}O_{cell} - 289‰ \quad (6)$$

nearly identical to the regression equation (2) obtained for the observed values.

The determination of absolute δD values of environmental water by analysis of plant lipids will allow a more precise estimation of palaeotemperatures, because it can be used to confirm the estimation of oxygen isotope ratios of water from oxygen isotope ratios of cellulose. Furthermore, with the method described here, it will be possible to determine the relation between δD and $\delta^{18}O$ values of water from lakes, which may be an important indicator of relative humidity. Because the lipid fraction of plants tends to be preserved longer it may be possible to determine climate further back in time than with cellulose.

This will be possible once it has been shown that isotopic ratio alterations due to diagenetic effects are minimal. If the results reported here can be extrapolated to terrestrial plants, then the technique of using δD values of lipids along with $\delta^{18}O$ values of cellulose may be applicable in determining the D/H and $^{18}O/^{16}O$ ratios of environmental water from δD and $\delta^{18}O$ values of lipids and cellulose from peats, where there is a large variation in isotopic ratios due to species composition[11,12].

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Glacial tunnel valleys and Quaternary history of the outer Scotian shelf

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High-resolution seismic reflection data indicate the presence of huge sub-surface channel networks on the outer Nova Scotian continental shelf. Channel axes extend to over 450 m below present sea level (b.s.l.). Channel walls average 2–3 km in width. Mechanisms capable of producing such channels include fluvial, submarine canyon or glacial erosion. Considerable debate has focused on the positions of the Tertiary/Quaternary (T/Q) and Pleistocene/Holocene (P/H) boundaries[1–4] in this region and the relationship of the T/Q boundary to the unconformity at the base of the channel networks. Uncertainty also surrounds the extent of Pleistocene ice sheets on the south-east Canadian continental margin[4–7]. Here we present a new stratigraphy for the Sable Island region (Fig. 1) based on seismic profiles, with lithologic and biostratigraphic control provided by two strategically placed boreholes. This stratigraphic analysis establishes the positions of the T/Q and P/H boundaries outside the valleys at 51 m and 220 m b.s.l. respectively. Our analysis also implies that the large channel systems are tunnel valleys, cut by a sub-ice meltwater process under a pre- to early Wisconsinan ice sheet which extended close to the shelf edge.

Seismic reflection profiles were acquired with minisleeve exploder and 12-kJ sparker sources recording twelvefold coverage down to 2 s of two-way acoustic travel time. Wave-equation migration techniques were applied to lines near the borehole giving a maximum vertical resolution of 2 m. Seismic stratigraphic methods[8] were used to define seismic sequences and facies. Seismic lines spaced 400 m apart were run parallel to the northern shoreline of Sable Island, with the closest line ranging 1–3 km from the island and 2 km from the C67 and SAB 85 boreholes (Fig. 2). The SAB 85 borehole was drilled on Sable Island along the axis of a major channel observed on marine seismic profiles north of the island and correlated under the island using exploration land seismic profiles. The C67 borehole was drilled outside the channel, 3 km east of SAB 85. Coring and continuous sampling were conducted to a total depth of 152 m in SAB 85. The C67 borehole was a standard oil exploration well with samples recovered every 3 m through the Cenozoic section. Cores from SAB 85 were split on site, described, photographed and tested for geotechnical properties[9]. Borehole samples from C67 were mainly used for foraminiferal

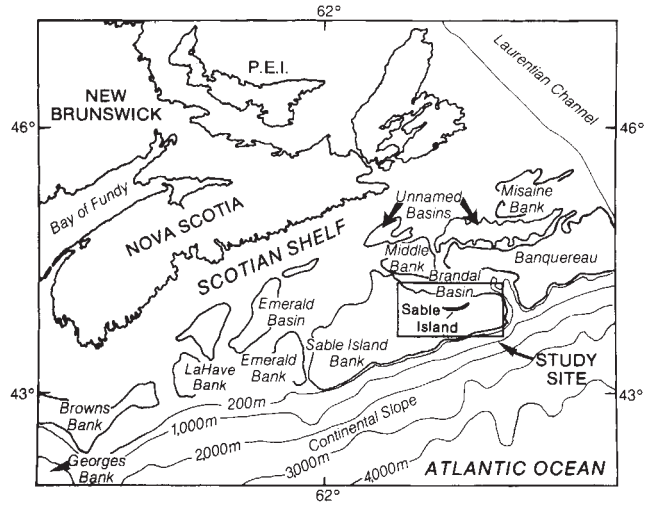

Fig. 1 The Scotian shelf is located on the south-east Canadian continental margin. Topography is dominated by a series of mid-shelf basins and outer shelf banks, one of which is Sable Island Bank, the site of a sub-surface glacial tunnel valley network and several recent boreholes.

analysis, sediment grain size and composition. Gamma logging was performed on both boreholes and electric logs were also available from C67. Identification of sedimentary units employed a standard facies logging method supplemented for SAB 85 by sieve grain size analyses and X-radiographs. Benthic foraminifera were used as palaeoenvironmental indicators[10,11].

The stratigraphy of the two boreholes and the area around Sable Island was derived from a combination of biostratigraphy, lithostratigraphy, seismic stratigraphy and radiocarbon-dating techniques (Table 1). Micropalaeontological analysis of C67 samples indicates that the T/Q boundary lies at a depth of 220 m (Fig. 3). This boundary was picked on the basis of the first downgoing occurrence (K. MacKinnon and F. Gradstein personal communication) of the Tertiary marker species *Astergerina guruchi*[12]. The position of the boundary coincides with a decrease in the number of reworked pre-Quaternary microfauna and lies within the uppermost extreme of several coarsening upward sequences inferred from gamma logs and lithology. These sequences are within seismic facies 1 (Table 1) which is characterized by parallel-to-divergent and occasionally shingled clinoforms. The shingled clinoforms and associated small channels indicate deltaic conditions. Additional support for such