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Paleoclimatic significance of δD and $\delta^{13}C$ values in piñon pine needles from packrat middens spanning the last 40,000 years

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Abstract

We compared two approaches to interpreting δD of cellulose nitrate in piñon pine needles (*Pinus edulis*) preserved in packrat middens from central New Mexico, USA. One approach was based on linear regression between modern δD values and climate parameters, and the other on a deterministic isotope model, modified from Craig and Gordon's terminal lake evaporation model that assumes steady-state conditions and constant isotope effects. One such effect, the net biochemical fractionation factor, was determined for a new species, piñon pine. Regressions showed that δD values in cellulose nitrate from annual cohorts of needles (1989–1996) were strongly correlated with growing season (May–August) precipitation amount, and $\delta^{13}C$ values in the same samples were correlated with June relative humidity. The deterministic model reconstructed δD values of meteoric water used by plants after constraining relative humidity effects with $\delta^{13}C$ values; growing season temperatures were estimated via modern correlations with δD values of meteoric water. Variations of this modeling approach have been applied to tree-ring cellulose before, but not to macrofossil cellulose, and comparisons to empirical relationships have not been provided. Results from fossil piñon needles spanning the last ~40,000 years showed no significant trend in δD values of cellulose nitrate, suggesting either no change in the amount of summer precipitation (based on the transfer function) or δD values of meteoric water or temperature (based on the deterministic model). However, there were significant differences in $\delta^{13}C$ values, and therefore relative humidity, between Pleistocene and Holocene. Published by Elsevier Science B.V.

Keywords: paleoecology; stable isotopes; C-13/C-12; D/H; Pleistocene; Holocene; New Mexico

1. Introduction

The hydrogen isotopic composition of cellulose from tree rings, bog mosses, and other sources, is generally regarded as a temperature proxy (Yapp and Epstein, 1982a; Brenninkmeijer et al., 1982; Feng and Epstein, 1994, 1995b; Long et al., 1990; Lipp et al., 1993). The D/H ratio (δD [1]) in source water for plants, ultimately meteoric water, has been shown to be linearly related to the δD value of the nonexchangeable, carbon-bound hydrogens in nitrated cel-

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[1] $\delta D = [(D/H_{sample}/D/H_{standard}) - 1] \times 1000$. Results are expressed in permil, ‰, using VSMOW as the standard for δD and VPDB as the standard for $\delta^{13}C$ (Craig, 1957, 1961; Coplen, 1994).

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lulose (Epstein and Yapp, 1977; Yapp and Epstein, 1982b; White et al., 1994). Variations in δD value of meteoric water are correlated with variations in temperature over space and time (Dansgaard, 1964; Gat, 1980; Rozanski et al., 1993). These correlations serve as the basis for temperature reconstructions from cellulose isotopes. Further justification for the use of the cellulose δD value as a temperature proxy comes from spatial correlations between mean annual temperature and nitrated cellulose of modern plants growing near weather stations; slopes of the cellulose δD — temperature best-fit line have been found to be very similar to the meteoric water δD–temperature relationship (Yapp and Epstein, 1982a; Long et al., 1990).

However, neither δD values in meteoric water nor in cellulose are linked exclusively to temperature variations. Processes that change the meteoric water isotopic composition from what would be predicted based on a long-term temperature–δD relationship include isotopic depletion by long storm tracks and consequent Rayleigh distillation effects, and isotopic enrichment by recycling of continental evaporated moisture (Gat, 1980; Ingraham and Taylor, 1986). Thus, the meteoric source water does not necessarily provide an unambiguous temperature signal (Lawrence and White, 1991).

A deterministic model for hydrogen isotope effects in leaf water and cellulose, based on Craig and Gordon's (1965) lake water evaporation model, predicts that both δD value of meteoric water and relative humidity will influence δD values of cellulose (Edwards and Fritz, 1986; White et al., 1994). Indeed, correlations between δD values in tree-ring cellulose nitrate with summer rainfall amount and relative humidity have been found (Lawrence and White, 1984; Ramesh et al., 1986; Edwards and Fritz, 1986; Yakir et al., 1990; Lipp et al., 1993, 1996b). In some locations, we hypothesize that evaporative effects related to relative humidity may dominate source water effects from δD values in meteoric water. Proxy records for relative humidity and precipitation seasonality are rare; the possibility of developing such a proxy from stable isotopes in plant cellulose has motivated our current research.

The $\delta^{13}C$ of plant cellulose has been used to estimate the concentration and isotopic composition of atmospheric CO_2 on time scales from centuries to millennia (Peng et al., 1983; Stuiver et al., 1984; Leavitt and Long, 1983, 1989a; Van de Water et al., 1994; Feng and Epstein, 1995a). Other environmental conditions that may influence $\delta^{13}C_{cell}$ include relative humidity (Ramesh et al., 1986; Saurer and Siegenthaler, 1989; Lipp et al., 1996a,b), drought and moisture stress (Leavitt and Long, 1989b; Feng and Epstein, 1995b), soil water status (Dupouey et al., 1993) and nutrient levels (Francey and Farquhar, 1982). If $\delta^{13}C$ values of atmospheric CO_2 are constrained, $\delta^{13}C_{cell}$ values may be used to infer other environmental changes, particularly moisture conditions.

In this paper we assess the relative influence of temperature, relative humidity and precipitation amount on δD and $\delta^{13}C$ values in needles from piñon pine (*Pinus edulis*) in central New Mexico, and interpret changes in δD and $\delta^{13}C$ values in needles from packrat middens spanning the last 40,000 years. We compare two approaches to reconstructing climate from the isotopic composition of macrofossils: (1) a transfer function approach, derived from linear regressions between interannual variations in climate parameters and δD and $\delta^{13}C$ values of annual needle cohorts; and (2) a deterministic modeling approach that accounts for physical and biochemical isotopic fractionation between source water and cellulose. While many transfer functions using cellulose stable hydrogen (and oxygen) isotopes have been developed, mainly in tree rings, few have been utilized to reconstruct long-term climate change (e.g., Feng and Epstein, 1994; Lipp et al., 1996a). The deterministic model has been applied before, but the assumptions implicit to the model have not been adequately tested (e.g., Clague et al., 1992; Buhay and Edwards, 1995). A detailed comparison between the two methods has not been done.

The 40,000-year midden record represents the richest archive of plant macrofossils available for isotopic studies (Betancourt et al., 1990). Yet, only three other studies have used δD values in macrofossils to deduce past climate (Siegel, 1983; Long et al., 1990; Jennings and Elliott-Fisk, 1993). These reconstructions were limited because (1) they have lacked mechanistic exploration of the source of the climate signal, (2) spatial correlations between δD values and climate parameters have not been supported by temporal correlations at specific sites, and

(3) δD values from several different species were pooled for reconstruction.

2. Isotopes in plant matter: theory

2.1. Deterministic modeling of hydrogen isotopes in plant cellulose

The relationship between δD of meteoric water (δD_{mw}) and plant cellulose nitrate (δD_{cell}) can be described by the model:

$$(\delta D_{cell} + 1000)/(\delta D_{mw} + 1000) =$$

$$\alpha_B \alpha_\epsilon \alpha_K - \alpha_B(\alpha_\epsilon \alpha_K - 1)RH \quad (1)$$

where α_B, α_ϵ, and α_K are net biochemical, equilibrium and kinetic fractionation factors, respectively; and RH is relative humidity (Yapp and Epstein, 1982b; Edwards and Fritz, 1986; White et al., 1994; Terwilliger and DeNiro, 1995). Cellulose is nitrated for δD analysis to remove exchangeable, hydroxyl hydrogens (Epstein et al., 1976). Eq. 1 accounts for enrichment of leaf water by steady-state evapotranspiration and is derived from the Craig and Gordon (1965) model of evaporation from a terminal lake. It assumes that local atmospheric vapor is in isotopic equilibrium with meteoric water. Thus, both temperature (via the δD_{mw}–T relation) and humidity theoretically should influence values of δD_{cell}.

Relative humidity exerts an influence on leaf water δD values as transpiration through leaf stomata causes evaporative enrichment of the heavy isotopic species of leaf water (HDO and $H_2^{18}O$) (Yakir, 1992; Pendall, 1997). To the degree that this isotopically enriched leaf water is used during carbon assimilation and incorporated into cellulose precursors, a humidity signal may be transferred to the δD value of cellulose nitrate. In avocado seedlings, a humidity signal was present in leaf δD_{cell} values, but not in wood δD_{cell} values (Terwilliger and DeNiro, 1995), suggesting that biochemical fractionation pathways may be different for leaves and wood. Net biochemical fractionation of hydrogen isotopes also varies among species, and has not been studied in detail except in a few species (DeNiro and Epstein, 1981; White et al., 1994). It represents the largest source of uncertainty in Eq. 1, because it must be evaluated for each species, and assumed to be constant through time. For wood, a heterotrophic tissue, α_B may include biochemical fractionation during photosynthesis in the leaf as well as post-photosynthetic exchange that might occur between cellulose precursors and stored starch (DeNiro and Cooper, 1989; Terwilliger and DeNiro, 1995). In autotrophic tissue such as conifer needles, it is likely that α_B will be less complicated by post-photosynthetic processes (Terwilliger and DeNiro, 1995).

The equilibrium and kinetic fractionation factors are fairly well known. Equilibrium fractionation is slightly temperature dependent (Majoube, 1971; Friedman and O'Neill, 1977). Kinetic fractionation values were determined over a range of turbulence (Merlivat, 1978; Merlivat and Jouzel, 1979); although turbulence in leaf boundary layers is dependent upon transpiration rates, leaf shape and size, α_K is likely to be fairly consistent within a species (Farquhar et al., 1989; Buhay et al., 1996).

2.2. Carbon isotopes in plant cellulose

The $\delta^{13}C$ of plant cellulose is influenced by the ratio of intercellular p_{CO_2} (C_i) to atmospheric p_{CO_2} (C_a) and $\delta^{13}C$ value of the atmosphere (atm). C_i/C_a is regulated by diffusion through stomata and uptake by carboxylating enzymes, processes resulting in fractionation of carbon isotopes. Francey and Farquhar (1982) modeled the $\delta^{13}C$ of plant matter as:

$$\delta^{13}C_{plant} = \delta^{13}C_{atm} - a - (b - a)C_i/C_a \quad (2)$$

where a is kinetic fractionation caused by diffusion through stomata (4.4‰) and b represents biochemical fractionation by the photosynthetic enzyme Rubisco (~29‰). When C_i/C_a is high the plant shows the greatest ^{13}C depletion; this occurs when stomatal conductance is high and photosynthetic rates are low (Farquhar et al., 1982). Eq. 2 illustrates that the influence of climate parameters on $\delta^{13}C_{cell}$ values is not as direct as on δD_{cell} values. The main influence that we are concerned with in our semi-arid pines is stomatal response to moisture availability or relative humidity. Drier conditions induce stomatal closure, fewer $^{12}CO_2$ molecules are available for assimilation, and $\delta^{13}C$ values of cellulose increase, relative to when moisture conditions are optimal (Leavitt and Long, 1989b).

3. Methods and site description

3.1. Plant material

Packrat middens were collected from limestone cliffs across an elevational range from 1700 to 1920 m near the Sevilleta Long Term Ecological Research (LTER) site south of Albuquerque, New Mexico (Fig. 1). The Sevilleta record represents the northern and upper elevational limits of *P. edulis* during the last glacial, and its lower limits during the Holocene (Betancourt et al., 1993). About 30 needles of *P. edulis* were combined from each midden containing sufficient material for preparation of cellulose nitrate. In addition, individual twigs (mainly *Juniperus monosperma*) were obtained from several of the middens for isotopic analysis.

Bulk samples (ca. 10 g) of fecal pellets from individual middens were dated using the conventional beta-decay radiocarbon technique, and provide a good estimate of the average age of the midden (Webb and Betancourt, 1990). However, mixing of plant fragments of different age occurs within the same middens, so the age of a particular taxon (or

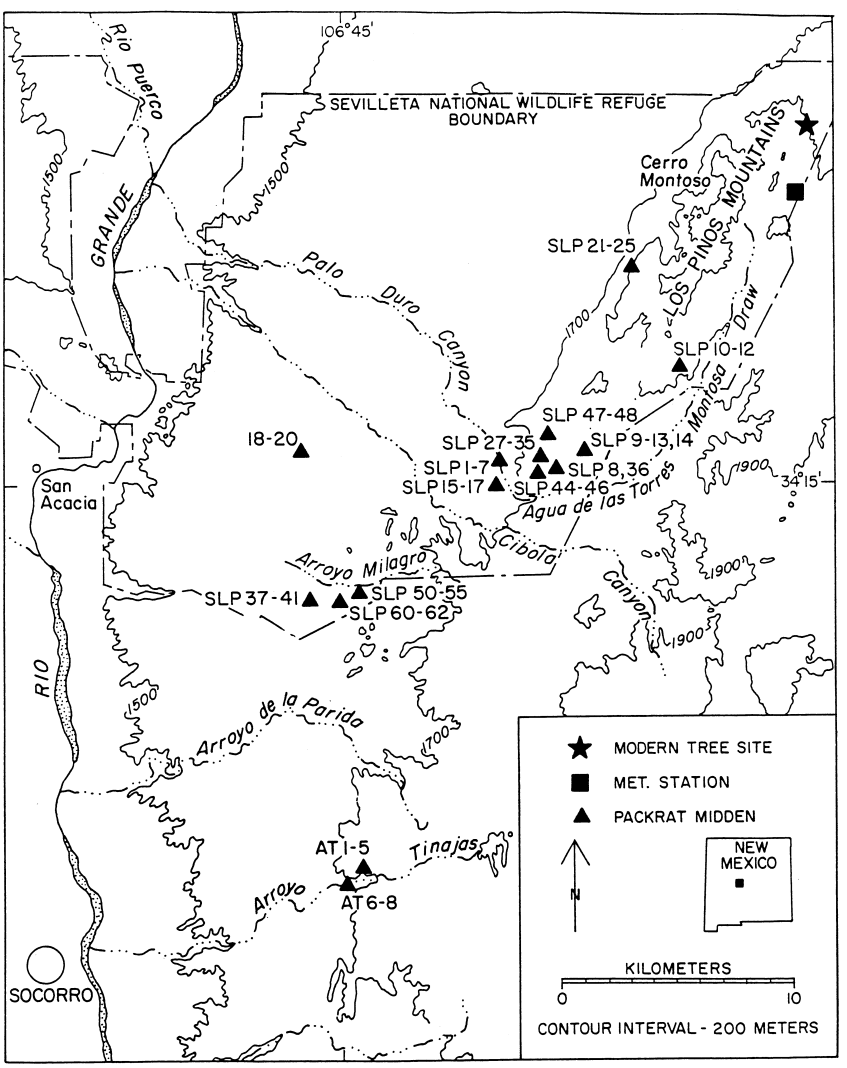


Fig. 1. Site map for Sevilleta midden locations in central New Mexico (inset). Modern piñon site and the Cerro Montoso meteorological (met) station are located at the north end of the Los Pinos Mountains.

individual fragments) may differ from the average age of the midden (Van Devender et al., 1985). For most of the piñon needles analyzed in this study, CO_2 generated from combustion of the needle samples for stable isotopic analysis was analyzed by tandem accelerator mass spectrometry at the University of Arizona NSF Accelerator Facility (Donahue, 1995). These AMS ^{14}C dates represent the average age of the needles themselves, and reduce but do not eliminate the potential for temporal mixing. We therefore use the AMS dates, where available, rather than the conventional dates, in climate reconstruction. Radiocarbon dates younger than 18,400 ^{14}C yr B.P. were corrected to calendar years before present using calibration curves developed from tree rings and U–Th-dated corals (Stuiver and Reimer, 1993; Bartlein et al., 1995).

The 30 piñon needles extracted from each packrat midden for this study hypothetically could have come from one tree in one year or several trees over 10 or more years. Given that middens are probably occupied by packrats for several years, the pooled needles likely represent an average isotopic value across several individuals over several years. Thus, they represent the average climatic conditions over several years, and are less likely to be strongly influenced by a single anomalous tree or year. The duration of the depositional episode for each midden, however, remains uncertain.

We note that we lack replication (e.g., several middens of the same age, within $\pm$ ~500 years) in the time series from the Sevilleta LTER. For this preliminary work, we assumed that the value for a single midden represents a population of middens for that particular time period. We recognize the inherent weakness in this assumption, which is a common flaw in many fossil studies, but nevertheless use this exercise to show how our isotopic models can be applied.

Modern plant material was obtained from four individual trees on the Sevilleta LTER. The collection site was on a north-facing hillslope at ~1900 m elevation. The trees had access only to water stored in the shallow soil, not deep groundwater, maximizing the potential response to seasonal and interannual changes in the isotopic composition of meteoric water. Annual cohorts were collected from four sides of each tree for the years 1989–1996. During 1996, fresh samples of needles were collected four times throughout the year for water extraction and isotopic analyses. Fresh leaf samples were kept frozen until water was extracted by cryogenic distillation (Ehleringer and Osmond, 1989).

3.2. Laboratory methods

Dry needle and twig samples (modern and fossil) were ground in a Wiley mill and processed to holocellulose (Leavitt and Danzer, 1993). Exchangeable, hydroxyl hydrogens were removed from cellulose by nitration using the fuming nitric acid and acetic anhydride method described in Sternberg (1989). Cellulose nitrate was combusted in pyrex tubes with excess cupric oxide at 520ºC for 3–4 hours. H_2O and CO_2 were purified cryogenically under vacuum (Sternberg, 1989) and collected into separate vials for carbon and hydrogen analysis. Samples were analyzed at three different laboratories. At the University of Arizona, zinc reduction of water was used to produce H_2 (Coleman et al., 1982). H_2 and CO_2 were analyzed on VG-602C and Finnigan Delta S mass spectrometers with reproducibility of $\pm$4.5‰ for δD_{cell}, and $\pm$0.2‰ for $\delta^{13}C_{cell}$. Needles from modern trees GDR2 and GDR5 were analyzed in the laboratory of Dr. S. Epstein, at California Institute of Technology, using similar methods (Sternberg, 1989), but with uranium reduction of H_2, giving reproducibility of $\pm$3‰. Needles from modern tree GDR1 and all 1996 needles were analyzed for δD in the laboratory of Dr. J. White at the University of Colorado, using uranium reduction, with reproducibility $\pm$2.8‰. δD_{cell} values were adjusted to a common nitrocellulose standard measured at all three laboratories (a difference of <8‰). δD of leaf water and precipitation was determined at University of Arizona with reproducibility of $\pm$2‰ (Coleman et al., 1982). Despite the fact that we corrected values to a common standard, we recognize that a portion of the variability in our data set may stem from interlaboratory differences.

3.3. Climatic seasonality and piñon phenology

Climate data and precipitation samples were obtained from the Cerro Montoso weather station, located ~3 km from the modern tree sampling location

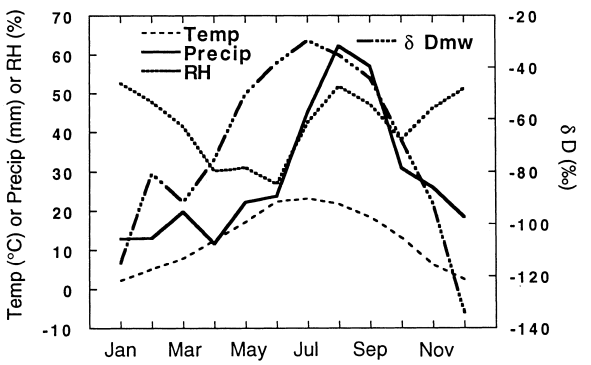


Fig. 2. Monthly average climate conditions for the period of record (1989–1996) and δD_{mw} values of precipitation samples collected at monthly intervals from 1994 to 1996 at the Cerro Montoso meteorological station on the Sevilleta LTER, elevation 1980 m.

at an elevation of 1980 m. This weather station was located in piñon–juniper woodland and had detailed records of relative humidity, temperature and precipitation. The Cerro Montoso record encompasses an eight-year period (1989–1996) during which the prolonged El Niño episode of 1991–1994 was bracketed by the La Niña events of 1989 and 1996 (D. Moore, pers. commun., 1997). Mean annual temperature and precipitation for the period of record are 12.7°C and 345 mm, respectively. Fig. 2 shows the seasonal variations of temperature, precipitation and relative humidity. Seasonal precipitation is characterized by a highly variable winter–early spring (December–March), an arid late spring and foresummer (April–June), monsoonal rains from July to September, and a dry autumn (October–November). Precipitation falling between July and September in the form of convective thunderstorms associated with the Mexican monsoon is responsible for 50% of the average total (Douglas et al., 1993). High relative humidity is associated with monsoonal rains in summer, but low temperatures (low saturation vapor pressure) in winter also produce high relative humidity.

Currently, δD_{mw} is strongly correlated with temperature at the Sevilleta, both for the entire year and for the May–August growing season; no correlation with amount was found in any season (Fig. 2; Pendall, 1997). We utilize the relationship between growing season temperature and δD_{mw} (standard errors of coefficients in parentheses):

$$\text{GS Temp} = 0.16\,(\pm 0.05)\,\delta D_{mw} + 26.9\,(\pm 2.22) \quad (P < 0.005) \tag{3}$$

in a later section.

The greatest stress for plant growth occurs in the arid foresummer (May–June), when soil moisture becomes depleted by high evaporative demand before the onset of monsoonal rains. On the average, bud swelling and needle elongation begin in mid-April at our modern piñon site, and the annual cohort of needles develops well into August. During years with abundant soil moisture, needle elongation is vigorous during May and June, but after dry winters, such as in 1996, initiation of needle growth may be delayed until the onset of the monsoonal rains, with fewer fascicles and shorter needles produced (Pendall, 1997). Thus, recharge of soil moisture by late winter and spring precipitation appears to be critical for piñon growth during the arid months of May and June. This ability to respond to precipitation events and soil moisture conditions early and late in the growing season illustrates considerable phenological plasticity in piñon pines.

4. Evaluation of the climatic significance of δD_{cell} and $\delta^{13}C_{cell}$

4.1. Modern relationships: hydrogen

Values of δD_{cell} in annual cohorts of piñon needles from four trees from 1989 to 1996 are shown in Table 1. Similar temporal trends are evident from tree to tree, but absolute values differ from tree to tree. Variations in δD_{cell} values between years are significant; variations within years are not significant (one-way ANOVA, Model II, calculated following Snedecor and Cochran, 1981; Table 2). This indicates that we have a representative sample of the population of trees, and that interannual variability is more important than inter-tree variability for δD_{cell} values. We examined whether δD_{cell} values were related to several climate parameters, including mean annual temperature, precipitation and relative humidity; growing season temperature, precipitation, relative humidity (mean, minimum, and maximum) and vapor pressure; and the same parameters averaged over different combinations of months. The

Table 1
δD_{cell}, $\delta^{13}C_{cell}$ and Δ in needles from modern piñon trees in central New Mexico

Year	GDR1	GDR2	GDR3	GDR5	Average	Std Error	Average Δ, ‰
δD (‰) vs. V-SMOW							
1989	na	−32.2	−31.6	−17.8	−27.2	4.7	
1990	na	−22.4	−35.8	−16.4	−24.9	5.7	
1991	−52.7	−43.4	−33.9	−29.9	−40.0	5.1	
1992	−56.3	−43.3	−55.6	−39.1	−48.6	4.3	
1993	−46.9	−33.7	−47.8	−46.9	−43.8	3.4	
1994	−17.9	−13.9	−27.9	−1.8	−15.4	5.4	
1995	−31.7	−31.9	−17.9	−4.9	−21.6	6.5	
1996	−52.4	−34.6	−42.2	−32.7	−40.5	4.5	
$\delta^{13}C$ (‰) vs. V-PDB							
1989	−18.80	−17.60	−19.79	−19.40	−18.90	0.48	12.7
1990	−18.52	−17.89	−20.22	−19.14	−18.94	0.50	12.8
1991	−20.21	−18.83	−20.27	−19.89	−19.80	0.33	13.6
1992	−19.67	−18.08	−20.27	−19.51	−19.38	0.46	13.1
1993	−20.07	−18.96	−20.29	−21.70	−20.26	0.56	14.0
1994	−19.54	−18.07	na	−20.15	−19.25	0.62	13.0
1995	−19.77	−19.27	na	−19.71	−19.58	0.16	13.3
1996	−21.62	−19.73	−21.27	−20.99	−20.90	0.41	14.7

Averages and standard error of the mean are calculated for each year. Δ was calculated from Eq. 6 using $\delta^{13}C_{atm} = -8.0$.

Table 2
Analysis of variance for δD and Δ in cellulose from modern piñon needles

Source of variation	df	SS	MS	*F*
δD				
Between years	7	3912.51	558.93	5.86
Within years	22	2099.21	95.42	
Total	29	6011.73		
Δ				
Between years	7	12.87	1.84	2.26
Within years	22	17.89	0.81	
Total	29	30.75		

Variation between years (interannual) is significant in both cases ($P < 0.05$ for δD; $P < 0.10$ for Δ), and variation within years (inter-tree) is not. df = degrees of freedom; SS = sum of squares; MS = mean square; *F* (variance ratio) = $MS_{between}/MS_{within}$.

strongest relationships are shown in Table 3. Average δD_{cell} was more strongly correlated with climate parameters than was δD_{cell} for individual trees, with the exception of GDR1 (Table 3). This suggests that averaging the δD_{cell} values increased the signal-to-noise ratio (Fritts, 1976). In reporting the regression equations, we use the average value because it probably represents an assemblage of needles gathered by a packrat over a period of time. Assemblages of packrat midden fossils can span several years, but to best define the climatic sensitivity we used annual cohorts from several trees and monthly climate data.

The average δD_{cell} values of piñon needles were significantly inversely related to growing season precipitation amount (Table 3), yielding the regression (standard errors of coefficients in parentheses):

$$\delta D_{cell} = -0.210\,(\pm 0.06)\left[\text{GS Pptn (mm)}\right] - 0.596\,(\pm 9.58) \quad (P = 0.013) \tag{4}$$

δD_{cell} values were also significantly related to the proportion of growing season precipitation relative to the entire year (Table 3). Less significant relationships were found with May–August mean relative humidity and May–August minimum relative humidity. No correlation was found between average δD_{cell} and any temperature variable, although individual GDR2 showed a better (not significant) correlation with growing season temperature than with precipitation amount.

Interannual variations in average δD_{cell} values and growing season precipitation are shown for 1989–1996 in Fig. 3a. The inset shows the correlation between the two parameters. Extreme years, such as the very dry 1989 and very wet El Niño years of

Table 3
Results from correlations of δD_{cell} or $\delta^{13}C_{cell}$ values in needles from individual trees and values averaged for all trees with climate parameters

		GDR1	GDR2	GDR3	GDR5	Average
δDcell vs.						
May–Aug Ppt/Tot Ppt	multiple r	−0.905	−0.757	−0.676	−0.788	−0.823
(%summer)	adj. r^2	0.773	0.502	0.367	0.558	0.623
	P	0.013 *	0.030 *	0.066	0.020 *	0.012 *
May–Aug Ppt	multiple r	−0.824	−0.542	−0.760	−0.753	−0.818
(mm)	adj. r^2	0.599	0.176	0.507	0.494	0.615
	P	0.044 *	0.165	0.029 *	0.031 *	0.013 *
May–Aug mean RH	multiple r	−0.608	−0.584	−0.611	−0.630	−0.708
(%)	adj. r^2	0.212	0.232	0.268	0.297	0.419
	P	0.201	0.128	0.108	0.094	0.049 *
May–Aug min RH	multiple r	−0.633	−0.693	−0.303	−0.489	−0.612
(%)	adj. r^2	0.251	0.393	0.000	0.112	0.375
	P	0.177	0.057	0.466	0.219	0.107
Growing Season Temp	multiple r	0.496	0.589	0.252	0.304	0.392
(ºC)	adj. r^2	0.057	0.238	0.000	0.000	0.013
	P	0.317	0.125	0.547	0.464	0.337
Avg $\delta^{13}C_{cell}$	multiple r	na	na	na	na	0.744
(‰)	adj. r^2	na	na	na	na	0.465
	P	na	na	na	na	0.055
$\delta^{13}C_{cell}$ vs.						
June min RH	multiple r	−0.910	−0.767	−0.787	−0.435	−0.804
(%)	adj. r^2	0.786	0.521	0.525	0.054	0.646
	P	0.012 *	0.026 *	0.063	0.281	0.016 *

Multiple r = Pearson correlation coefficient; adj. $r^2 = r^2$ adjusted for sample size; P = significance level. na = not analyzed.
* Significant relationship at $P \leq 0.05$.

1992–1993, are well represented (inversely) by the δD_{cell} in all trees. This time series is too short to test for significant autocorrelation. However, we believe that since the needles are fully autotrophic shortly after initiation of needle development, relatively little biological autocorrelation should be present in the stable isotope values.

4.2. Modern relationships: carbon

$\delta^{13}C_{cell}$ values were obtained on CO_2 from the same samples of cellulose nitrate combusted for δD_{cell} analysis. As for δD, trends from year to year are similar among the four trees, but values from individual trees vary (Table 1). Interannual variations in $\delta^{13}C_{cell}$ values are significantly greater than variations among trees, but inter-tree variability is somewhat higher than for δD_{cell} (one-way ANOVA; Table 2). Interannual variations in the average value of $\delta^{13}C_{cell}$ are significantly correlated with June minimum relative humidity (Table 3) yielding the regression (standard errors of coefficients in parentheses):

$$\delta^{13}C_{cell} = -0.18\,(\pm 0.05)\,[\text{Jun Min RH (\%)}] - 17.15\,(\pm 0.77) \quad (P = 0.016) \tag{5}$$

June minimum relative humidity represents the average daytime relative humidity during June, commonly a period of maximum leaf elongation (Pendall, 1997). We did not find significant correlations between $\delta^{13}C_{cell}$ and any other climate parameter.

In order to use δD_{cell} values for reconstructing climate with the deterministic model, we constrain relative humidity with $\delta^{13}C_{cell}$ values. But first, variations in the $\delta^{13}C$ value of atmospheric CO_2 must be controlled for. We correct $\delta^{13}C_{cell}$ values to whole-plant values by subtracting 1.5‰ (Leavitt and Long, 1991), and then apply the expression

$$\Delta = (\delta^{13}C_{atm}/1000 - \delta^{13}C_{whole\ plant}/1000)/(1 + \delta^{13}C_{whole\ plant}/1000)1000 \tag{6}$$

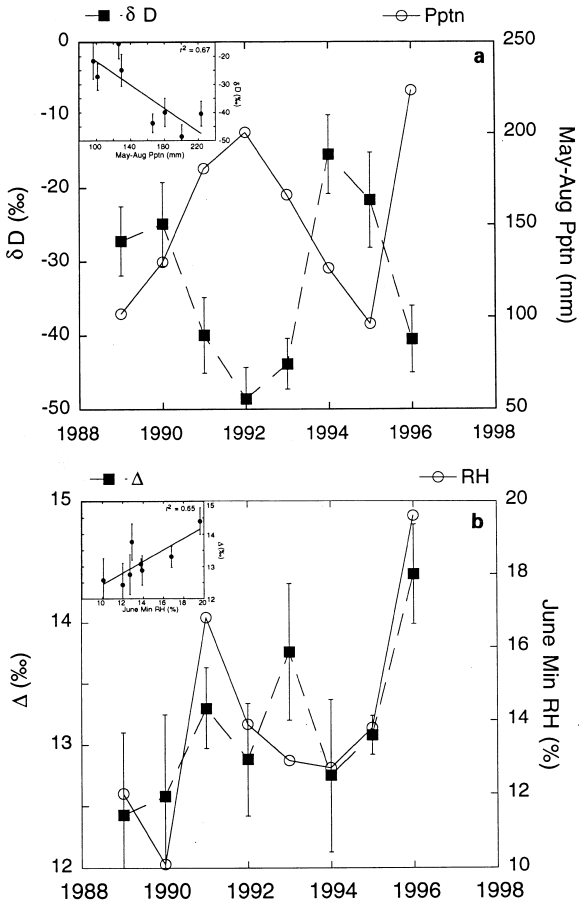


Fig. 3. (a) Time series of average modern δD_{cell} values (■) and amount of precipitation occurring between May and August (○) recorded at Cerro Montoso meteorological station. Error bars on δD values represent standard error of the mean. Inset illustrates regression between δD_{cell} values and growing season precipitation. (b) Time series of average modern discrimination (Δ) values (■) and June minimum relative humidity (○). Error bars on Δ represent standard error of the mean. Inset illustrates regression between Δ values and June minimum relative humidity.

to obtain carbon isotope discrimination in per mil (Farquhar and Lloyd, 1993). Modern $\delta^{13}C_{atm}$ is about −8.0‰ and palaeo-$\delta^{13}C_{atm}$ values were obtained from Leuenberger et al. (1992). Relative humidity was determined from the regression equation

$$\Delta = 0.18\,(\pm 0.05)(\text{Jun Min RH}) + 10.65\,(\pm 0.77) \quad (P = 0.016) \tag{7}$$

Interannual variations in Δ values and June minimum relative humidity are shown in Fig. 3b, with correlation shown in the inset. Relative humidity is inversely related to $\delta^{13}C_{cell}$ values, but directly related to Δ values, because of subtracting $\delta^{13}C_{cell}$ from $\delta^{13}C_{atm}$ values.

4.3. Parameterization of deterministic isotope model

If δD_{cell} is measured, a relationship between δD_{mw} and relative humidity can be determined from Eq. 1 only if the biochemical, equilibrium, and kinetic fractionation factors are known. If these factors and relative humidity are well constrained, Eq. 1 can be solved for δD_{mw}, which can then be related to local climate parameters such as temperature. A major uncertainty in using Eq. 1 is the biochemical fractionation factor, which is evaluated below. Before proceeding, however, assumptions made in Eq. 1 require consideration.

First, it is assumed that source water for plants is meteoric water. In some cases, meteoric water is isotopically altered by evaporation from soil profiles (Zimmerman et al., 1967; Barnes and Allison, 1983). Below about 50 cm in soils at the modern tree site, moisture reflects the average annual isotopic value of meteoric inputs (Pendall and Leavitt, 1996). Piñon trees in New Mexico are not able to use soil water that has been evaporatively enriched, presumably because it is held at too high a tension to be extracted by the roots; xylem sap isotopic values cluster around the local meteoric water line (Pendall and Leavitt, 1996).

Second, isotopic equilibrium between meteoric water and atmospheric vapor is assumed. Atmospheric vapor samples collected in 1995 and 1996 were very close to isotopic equilibrium with recent precipitation (Pendall, 1997). On average, measured δD values of vapor were 5‰ more depleted than values estimated from equilibrium with meteoric water at growing season temperatures. The isotopic values were not correlated with relative humidity, or with any other climate parameter. White et al. (1994) found that in New York, relative humidity and the δD value of vapor were correlated such that the two effects cancelled each other out in Eq. 1. This is not the case for our study area, so relative humidity should have an influence on δD_{cell} values. In regions where relative humidity and δD value of vapor approximately cancel, strong correlation between δD_{mw} and δD_{cell} values has been observed (White et al., 1994).

Finally, Eq. 1 assumes steady state between source water entering the leaves and water evaporating from leaf surfaces (Craig and Gordon, 1965; Flanagan and Ehleringer, 1991). Derivation of Eq. 1 from Craig and Gordon's model of lake evaporation treats the leaf water as a closed basin, with water entering only from the stem and leaving only via transpiration, and retaining a steady state isotopic composition (White et al., 1994). Steady state conditions have been achieved in controlled experiments after about one hour, and steady state may be approached under field conditions (White, 1983; Flanagan and Ehleringer, 1991). However, few field studies have confirmed this assumption. At the Sevilleta, measured values of δD in leaf water (LW) were strongly correlated with values calculated with the steady-state model, using a diffusive boundary layer (Pendall, 1997):

$$\delta D_{LWmodel} = 0.84\,\delta D_{LWmeas} + 17.0 \quad (P = 0.0001) \tag{8}$$

Measured δD_{LW} values that are more depleted than predicted, such as we have observed, may reflect exchange with depleted organic matter, or they may reflect the existence of more than one pool of leaf water (White, 1983, 1989; Yakir et al., 1989; Buhay et al., 1996). Regardless of the source of the observed depletion in δD_{LW} values, this offset is taken into account in the deterministic model.

The next step, then, is to quantify the fractionation factors. Equilibrium fractionation (α_ϵ) is temperature dependent, and results from the phase change between liquid and vapor. If the tolerance of average growing season temperatures for piñon is 18–23ºC, α_ϵ can be constrained to 1.084–1.077, a range of 7‰ (Friedman and O'Neill, 1977). We will use $\alpha_\epsilon = 1.087 \pm 0.0035$ in Eq. 1, accounting for the 5‰ depletion of vapor from precipitation equilibrium, and the estimated range of growing season temperatures.

Kinetic fractionation has been evaluated in detail by Buhay et al. (1996). Although α_K varies depending on the relative degree of molecular and turbulent transport, most often maximum kinetic enrichment is assumed, due to transfer across the leaf boundary layer by diffusion (Flanagan and Ehleringer, 1991; Buhay et al., 1996). Pines have stomata that are recessed in pits in the epidermis and are likely to have leaf boundary layers dominated by diffusion (Kozlowski et al., 1991; White et al., 1994). Comparison of measured and modeled leaf water δD and $\delta^{18}O$ values suggests that diffusive transport dominates for piñon pine (Pendall, 1997). Buhay et al. (1996) describe an apparent dependence of kinetic fractionation of hydrogen isotopes on temperature. However, this effect is more likely biochemical rather than physical in nature, and is probably related to isotopic exchange between leaf water and leaf organic constituents, before cellulose synthesis occurs. Rather than include the offset observed between measured and modeled δD_{LW} values in the kinetic effect, as Buhay et al. (1996) have done, we include the offset in the net biochemical fractionation factor. Merlivat (1978) determined α_K to be 1.025 for D/H under purely molecular conditions; with increased turbulence this value will approach unity (White et al., 1994). We take $\alpha_K = 1.025$ in Eq. 1.

Leaf water, not stem water, is the primary source water for cellulose synthesis, because photosynthesis takes place in leaves (Yakir, 1992). Net biochemical fractionation, i.e., the fractionation between source water and cellulose, was defined by Yapp and Epstein (1982b) as

$$\alpha_B = R_{cell}/R_{leaf\ water} \tag{9}$$

where $R = (D/H_{sample})/(D/H_{standard})$. It should be evaluated on a species-by-species basis (DeNiro and Epstein, 1981). In Table 4 we show measured δD_{LW} and δD_{cell} values from 1996, and δD_{LW} values corrected for the offset from steady state, using Eq. 8. Net biochemical fractionation was estimated using Eq. 9 and the corrected δD_{LW} values (Table 4). The primary assumption made by Eq. 9 is that leaf water is isotopically homogeneous and that cellulose is synthesized from this pool. Yakir et al. (1989) provided evidence for at least 2 pools of isotopically distinct water in leaves. White (1983) modeled δD_{LW} as a mixture of evaporatively enriched water plus depleted water that was hypothetically bound in semi-crystalline state, and unavailable for use in photosynthesis. Our leaf water extraction technique removed all the water from the leaves, homogenizing any variations that might have existed in different pools. Terwilliger and DeNiro (1995) showed that under controlled conditions, leaf water of avocado behaved as a single pool and relative humidity variations were recorded in leaf δD_{cell}. As a first approx-

Table 4
Net biochemical fractionation (α_B) calculated from δD in 1996 leaf water (LW) and cellulose nitrate in individual trees from Eq. 9

Tree (#)	δD_{LW} (‰, V-SMOW)	$\delta D_{LW\text{-}CORR}$ (‰, V-SMOW)	δD_{cell} (‰, V-SMOW)	α_B	α_{B-CORR}
GDR 1	−2.36	15.02	−52.42	0.9476	0.9336
GDR 2	−2.64	14.78	−34.58	0.9654	0.9513
GDR 3	−3.32	14.21	−42.24	0.9578	0.9444
GDR 5	−1.00	16.16	−32.66	0.97673	0.9519
Average				0.9605	0.9453

Leaf water values are growing season averages measured on three dates (23/4/96, 12/8/96, and 5/10/96). Values of leaf water were corrected to values modeled from steady-state (Eq. 8). Average corrected α_B was used in Eq. 1 to reconstruct δD_{mw}.

imation, we use the α_B value (corrected to steady state) of 0.9453 ± 0.0085 (average of four trees ± standard deviation), in modeling climate with Eq. 1 (Table 4). The average value of α_B is comparable to the range of 0.945 to 0.927 determined from modeled leaf water and measured δD_{cell} in white pine wood (White, 1983).

5. Packrat Midden data: results and interpretation

5.1. Variations in δD_{cell} and Δ values over the last 40,000 years

The range of values in δD_{cell} in piñon needles over the past 40,000 years is similar to that over the years 1989–1996 (−50 to −17‰ in fossil material vs. −49 to −15‰ in average values of modern material; Table 5 and Table 1). There is no significant difference between Holocene (<10,000 yr B.P.) and Pleistocene (>10,000 yr B.P.) means (*t*-test, $P > 0.05$); there is no significant trend in piñon needle δD_{cell} values over time (Fig. 4a). However, there are variations in twig δD_{cell} values over time, with low values occurring 10,000–15,000 yr B.P., a high value in the middle Holocene, and low to intermediate values approaching the present (Fig. 4a).

The range of discrimination (Δ) values in middens is 12.55 to 16.64‰ (Table 5); in modern needles the average range is 12.43 to 14.40‰ (Table 1). There is a small but significant difference between Holocene and Pleistocene Δ means, with Pleistocene values ∼1.1‰ more positive (*t*-test, $P = 0.048$) (Fig. 4b). Discrimination values remove trends caused by changing atmospheric $\delta^{13}C$

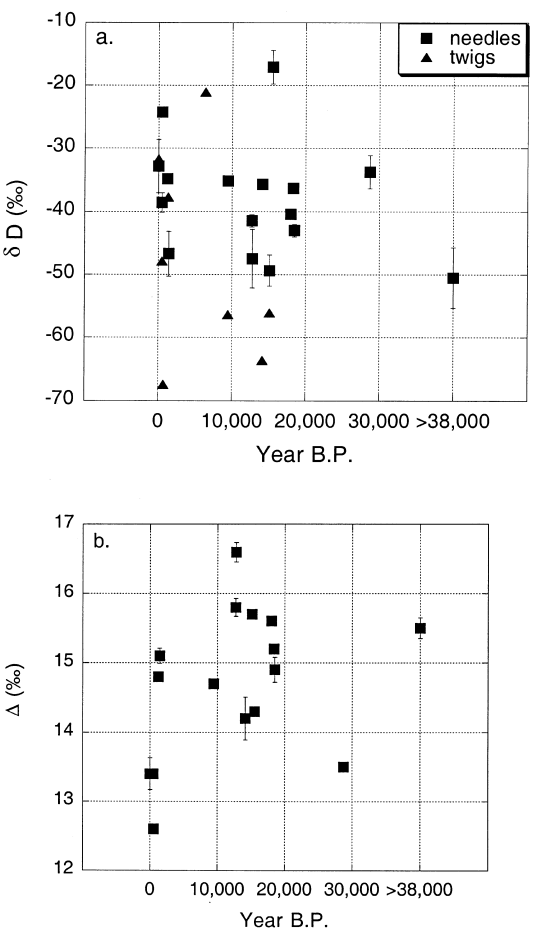


Fig. 4. (a) Time series of δD_{cell} in fossil piñon needles (■) and juniper twigs (▲) from packrat middens. Error bars on piñon needle samples represent 1σ where more than one sample was analyzed. Dates younger than 18,400 are corrected to calendar years B.P. (Stuiver and Reimer, 1993) but older dates are plotted as uncorrected ^{14}C yr B.P. (b) Time series of Δ in the same fossil piñon needles that were analyzed for δD_{cell} (a).

Table 5
δD_{cell} and δ^3C_{cell} in fossil piñon needles and δD_{cell} in juniper twigs from packrat middens in central New Mexico

Midden ID	Conv. date (^{14}C yr B.P.)	Conv. (Lab. No.)	AMS date (^{14}C yr B.P.)	AMS (Lab. No.)	Calib. date (yr B.P.)	δD (‰ V-SMOW)	Stand. dev. (‰)	δ^{13}C (‰ PDB)	Stand. dev. (‰)
Piñon needles									
Modern trees	na		na	na	na	−32.8	4.23(8)	−19.64	0.23 (8)
SLP35	405 ± 75	GX15922	na	na	480	−38.6	1.53 (2)	−18.15	
SLP27	370 ± 75	GX15921	472 ± 90	AA11186	512	−24.3		−17.31	
SLP11	2450 ± 70	A5503	1550 ± 90	AA11184	1207	−34.8		−19.74	
SLP52	1285 ± 65	GX17496	1604 ± 140	AA11416	1409	−46.7	3.56 (2)	−19.51	0.11 (2)
SLP8	9200 ± 160	A5462	8500 ± 75	AA11418	9480	−35.2		−19.38	
AT5	10795 ± 115	GX17630	na	na	12723	−41.4	0.98 (3)	−20.73	0.13(3)
AT7B	11220 ± 125	GX18031	10855 ± 140	AA11417	12780	−47.5	4.65 (3)	−21.58	0.14 (3)
SLP1	11560 ± 220	A5458	12137 ± 150	AA11187	14160	−35.7		−19.42	0.31 (2)
AT7A	11520 ± 145	GX18030	12813 ± 100	AA11189	15134	−49.3	2.50 (3)	−20.84	0.06 (3)
AT2	12270 ± 145	GX17627	13044 ± 120	AA11185	15507	−17.1 [a]	2.68 (2)	−19.50	0.01 (2)
AT8	11725 ± 135	GX18033	15080 ± 160	AA11190	17999	−40.4	0.19 (2)	−20.73	0.02 (2)
BB3	16260 ± 350	A2065	15465 ± 125	AA15003	18377	−36.3		−20.35	
BB2	18300 ± 420	A2064	15610 ± 125	AA15002	18511	−43.0	0.99 (2)	−20.11	0.18 (2)
AT3	33600 ± 1450	GX17628	28722 ± 390	AA11188	nc	−33.7	2.61 (2)	−18.69	0.00 (2)
AT1	>38000	GX17626	na	na	nc	−50.5	4.79 (2)	−20.62	0.15 (2)

Midden ID	Conv. date (^{14}C yr B.P.)	Conv. (Lab. No.)	AMS date (^{14}C yr B.P.)	Calib. date (yr B.P.)	δD (‰)
Twigs					
SLP2	0 ± 0	A5497	na	0	−31.7
SLP35	405 ± 75	GX15922	na	480	−47.8
SLP46	680 ± 60	GX17000	na	700	−67.4
SLP4	1420 ± 60	A5459	na	1350	−37.7
SLP29B	5485 ± 80	GX16979	na	6340	−21.1
SLP8	9200 ± 160	A5462	8500	9480	−56.4
SLP1	11560 ± 220	A5458	12137	14160	−63.6
AT7A	11520 ± 145	GX18030	12813	15134	−56.1

Conventional dating was done on *Neotoma* sp. fecal pellets associated with the needles; AMS dating was done on CO_2 generated from combustion of the same needles analyzed for δD_{cell} and $\delta^{13}C_{cell}$. AMS dates (or conventional dates if AMS was not available) were calibrated following Stuiver and Reimer (1993) back to ca. 18,400 yr B.P. Calibrated dates were rounded to the nearest 10 yr B.P. for plotting. Standard deviations (standard error for modern samples) are shown where multiple samples (number in parentheses) were analysed for δD_{cell} or $\delta^{13}C_{cell}$. Individual juniper twigs (and a root in one case) were analyzed for δD_{cell}. Dates on twigs are from pellets or piñon needles from the corresponding middens. Na = not analyzed; nc = not calibrated. Samples BB2 and BB3 provided by Dr. T. van Devender, from Sacramento Mountains, NM.
[a] Probable analytical outlier on δD_{cell}.

values, so the difference probably reflects a response to climatic changes.

Δ and δD_{cell} values were correlated in both the middens (adj. $r^2 = 0.338$, $P = 0.014$) and the modern samples (adj. $r^2 = 0.465$, $P = 0.055$, one outlier excluded; Fig. 5). The mechanism responsible for fractionation of both these isotopes is likely to be related to stomatal conductance, which is regulated to some degree by relative humidity (Mott and Parkhurst, 1991; Aphalo and Jarvis, 1991). Fig. 5 shows that modern needles can be separated into two groups based on summer precipitation: dry summers favor high δD_{cell} and low Δ values, while wet summers favor low δD_{cell} and high Δ values. The majority of midden needles is clustered near modern samples from wet summers (growing season precipitation >160 mm). A single midden data point falling above the trend line ($\delta D_{cell} = -17.1$; $\Delta = 14.3$; midden AT2) contains an anomalous δD_{cell} value (* in Fig. 5).

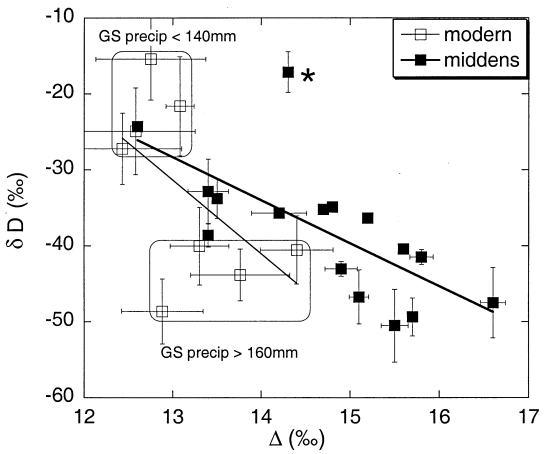


Fig. 5. Correlations between δD_{cell} and Δ values in modern and fossil piñon needles. Modern needles appear to cluster into two groups, one with growing season precipitation (*GS precip*) <140 mm, and one with growing season precipitation >160 mm. * = probable analytical outlier for δD_{cell} value in midden AT2.

Differences between conventional ^{14}C dates on bulk pellets and AMS dates on piñon needles range from 100 to nearly 5000 ^{14}C years, and generally increase with increasing age (Table 5). Because packrat middens can become mixed during habitation, as well as post-depositionally, they may be dated less precisely than other proxy records, such as tree rings and lake sediments. The differences between conventional and AMS dates do not change any interpretations we make from the stable isotope results.

Below, we present two alternative approaches to interpreting the stable isotope values from the fossil cellulose. First, we use linear regressions developed from δD_{cell} and Δ values in modern needles to form transfer functions for reconstructing summer precipitation and relative humidity. We then compare the climate reconstruction based on these transfer functions to a deterministic reconstruction of δD_{mw}, and thus temperature, utilizing Eqs. 1–3.

5.2. Reconstruction of summer moisture based on transfer functions

Relationships established between modern needles and climate using linear regression showed that both δD_{cell} and Δ values in piñon needles are strongly influenced by summer moisture. These regression relationships are robust, both with r^2 values ~0.65, because analysis of variance determined that interannual variability was significant relative to inter-tree variability (Table 2). Few paleoclimatologists using stable isotopes analyze replicate samples from their modern proxies. Although this necessary practise is becoming more common, analysis of variance is generally neglected, and therefore the relative variance among replicate samples is not determined (e.g., Lipp et al., 1996b; Saurer et al., 1997).

Table 6 and Fig. 6a and c show growing season rainfall amount and June daytime relative humidity reconstructed using Eqs. 4 and 7, respectively. The reconstructed values in Fig. 6a and c are plotted with the 95% confidence intervals determined from the modern regressions, corrected by a factor of $t = 5.53$ for 15 predictions; this accounts for the increased chance of predicting a value that is outside the 95% confidence interval as more reconstructed values are determined (Snedecor and Cochran, 1981). According to δD_{cell} values, summer rainfall amount has not changed drastically over the past 40,000 years at this site (*t*-test, $P > 0.05$). Because δD_{cell} values in modern needles are also correlated with proportion of summer rain (Table 3), midden δD_{cell} values suggest relatively small changes in precipitation seasonality over this time period. However, June daytime relative humidity is significantly higher during the late Pleistocene than during the Holocene (*t*-test, $P = 0.037$). The transfer functions suggest that early summers may have been moister than they are currently, with little change in total growing season precipitation.

5.3. Reconstruction of δD_{mw} and temperature from a deterministic model

A modeling approach, where Eq. 1 is coupled with the empirical relation between Δ and relative humidity, provides an alternative interpretation of the climatic significance of δD_{cell}. After calculating Δ in the fossil needles to remove the $\delta^{13}C_{atm}$ signal, Eq. 7 can be used to reconstruct June daytime relative humidity. This latter parameter is correlated with growing season (May–August) relative humidity at the Sevilleta (GS RH = 0.51 Jun Min RH + 13; adj. $r^2 = 0.298$). We use this estimate of growing season relative humidity (±6% from 95% confidence interval) and fractionation factors given in Section 4.3 in solving Eq. 1 for δD_{mw}. Table 6 and Fig. 6b show

Table 6
Reconstructions of growing season precipitation amount, δD_{mw}, estimated error on δD_{mw} and growing season temperature, calculated from δD_{cell}; and June daytime relative humidity calculated from Δ, over the past 40,000 years in central New Mexico

Midden ID	Date (yr B.P.)	GS Pptn [a] (mm)	δD_{mw} [b] (‰ V-SMOW)	Est. error [c] (‰)	GS Temp [d] (ºC)	Δ [e] (‰)	June Min RH [f] (%)
Modern trees	0	153	−62.0		16.7	13.4	14.9
SLP35	480	172	−67.6	±18.0	15.8	13.4	14.9
SLP27	512	126	−55.3	±16.8	17.8	12.6	11.8
SLP11	1207	160	−61.1	±16.6	16.9	15.1	20.9
SLP52	1409	198	−73.0	±19.8	14.9	14.8	20.0
SLP8	9480	161	−62.0	±16.6	16.7	14.7	19.5
AT5	12723	181	−66.3	±17.4	16.0	15.8	23.4
AT7B	12780	200	−70.6	±20.9	15.3	16.6	26.6
SLP1	14160	162	−63.4	±16.6	16.5	14.2	17.8
AT7A	15134	206	−74.1	±18.8	14.7	15.7	23.1
AT2	15507	103 [g]	−45.2 [g]	±19.5	19.5 [g]	14.3	18.1
AT8	17999	178	−65.6	±16.7	16.1	15.6	22.6
BB3	18377	164	−62.3	±16.6	16.7	15.2	21.2
BB2	18511	186	−69.3	±17.4	15.5	14.9	20.3
AT1	28722	156	−62.7	±19.1	16.6	13.5	15.4
AT3	>38000	210	−75.5	±21.0	14.5	15.5	22.6

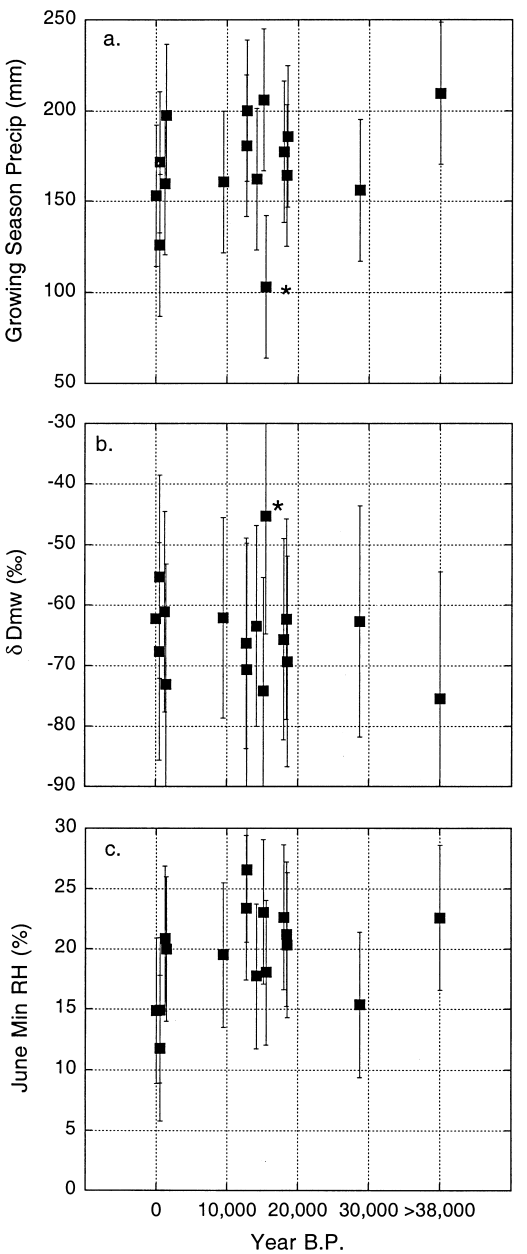
[a] Growing Season Pptn (mm) $= -3.19\delta D_{cell} + 48.6$. 95% confidence interval $= \pm 39$ mm.
[b] Calculated from $(\delta D_{cell} + 1000)/(\delta D_{mw} + 1000) = \alpha_B\alpha_\epsilon\alpha_K - \alpha_B(\alpha_\epsilon\alpha_K - 1)RH$, using $\alpha_B = 0.9453$; $\alpha_\epsilon = 1.087$; $\alpha_K = 1.025$; RH was reconstructed from Δ, see below.
[c] Estimated error using $\alpha_B = 0.9453 \pm 0.0085$; $\alpha_\epsilon = 1.087 \pm 0.0070$, and RH ±6% in Eq. 1.
[d] Growing Season Temp $= 0.164\delta D_{mw} + 26.9$.
[e] Calculated from Eq. 6, using $\delta^{13}C_{atm}$ values from Leuenberger et al. (1992).
[f] Calculated from $\Delta = 0.18$ (Jun Min RH) + 10.65. 95% confidence interval = ±6%.
[g] Probable analytical outlier on δD_{cell}.

reconstructed δD_{mw} values in central New Mexico during times when packrat middens with piñon needles were preserved. Average estimated error was ±18‰ for δD_{mw} values, and varied from sample to sample because we incorporated the varying standard deviations of the original δD_{cell} analyses. The reconstructed modern value is similar to measured values of groundwater in the area of the Sevilleta (Pendall, 1997). However, there is no significant change over time in δD_{mw} values, despite accounting for changes in relative humidity.

Because needles rely on summer precipitation, we take the relation between modern May–August δD_{mw} and average growing season temperature (Eq. 3) to reconstruct growing season temperature in the fossil material. Growing season temperature reconstructed from δD_{mw} using Eq. 3 did not change significantly over the past 40,000 years (Table 6). Apparently, δD_{mw} as calculated from δD_{cell} in fossil piñon needles is not an accurate recorder of growing season temperature changes; we do not believe that Pleistocene growing season temperatures were the same as today's. However, it is possible that the relation between δD_{mw} and temperature has changed since the Pleistocene. The error estimated on δD_{mw} values represents a range of ~6ºC, similar to the probable magnitude of Pleistocene–Holocene temperature changes in the Southwest (Stute et al., 1992, 1995).

Juniper twigs were present in a minority of the middens. We selected individual, woody twigs from a few middens for δD_{cell} analysis (Table 5). Fig. 4a shows that δD_{cell} values in twigs are lower during the glacial maximum than δD_{cell} in needles. A mid-Holocene twig value (6340 yr B.P., Table 5) is higher than the modern average for juniper twigs (piñons were not present in middens at this time). Apparently, δD_{cell} values in juniper twigs are recording climate differently than δD_{cell} values in piñon needles at the Sevilleta. δD_{cell} values of woody tissue are more directly influenced by changes in δD_{mw} and less affected by relative humidity than δD_{cell} values of leaves (White, 1983; Terwilliger and DeNiro,

1995). Spatial correlations across the southwestern USA have shown δD_{cell} values in juniper twigs reflect local temperature (Long et al., 1990). These results show that δD_{cell} values from different species or fossil plant tissues should not be combined in transfer functions or deterministic modeling of paleoclimate interpretations.



6. Discussion

We developed transfer functions between time series of δD_{cell} and $\delta^{13}C_{cell}$ values and climate parameters at a single site. The time series were limited to eight years because piñon pine only holds its needles for 8–10 years; longer time series can be obtained using tree rings. However, leaves are much more common than woody material in packrat middens, and our aim was to investigate the paleoclimatic potential of the long midden record at the Sevilleta. Transfer functions showed that 67 and 65% of the interannual variability in piñon needle δD_{cell} and $\delta^{13}C_{cell}$ values was attributable to interannual variations in summer precipitation and relative humidity, respectively. These correlation coefficients are larger than determined for time series correlations between δD_{cell}, $\delta^{18}O_{cell}$ and $\delta^{13}C_{cell}$ and various climate parameters in some studies, where r^2 values were on the order of 0.15 to 0.45 (Lipp et al., 1996b; Saurer et al., 1997), but similar to r^2 values of 0.57 to 0.86 for correlations between δD_{cell} and summer rainfall amounts (Lawrence and White, 1984). Despite the strong correlations, the range of climatic conditions that occurred during our 1989–1996 calibration period does not necessarily represent the range of conditions that occurred over the Pleistocene–Holocene transition. This potential weakness is inherent to all proxy records calibrated based on time series. Another approach for deriving transfer functions is based on a single analysis of the proxy, e.g., δD_{cell}, and mean annual climate parameters at an array of locations (Yapp and Epstein,

Fig. 6. (a) Growing season precipitation reconstructed from δD_{cell} values using the transfer function described by Eq. 4. Error bars (±39 mm) show 95% confidence interval, corrected for 15 predictions (Snedecor and Cochran, 1981). * = probable analytical outlier for δD_{cell} value in midden AT2. (b) δD_{mw} values reconstructed using the deterministic model described by Eq. 1 coupled with RH estimated by Eq. 7. See text for values of parameters. Error bars reflect accumulated errors in biochemical and equilibrium fractionation factors and relative humidity (Table 6). * = probable analytical outlier for δD_{cell} value in midden AT2. (c) June daytime relative humidity reconstructed from Δ values using the transfer function described by Eq. 7. Error bars (±6%) show 95% confidence interval, corrected for 15 predictions (Snedecor and Cochran, 1981).

1982a; Long et al., 1990). These spatially based transfer functions usually have the advantage of covering a wide range of climatic conditions, but they do not apply to any specific place, and it is not clear that the same function would be derived for temporal changes. This is particularly true for proxies ultimately derived from δD or $\delta^{18}O$ values in meteoric water, as distance from the coast and seasonality of precipitation can cause large local deviations from a regionally or globally averaged δD — or $\delta^{18}O$ — temperature trend (Rozanski et al., 1993). Despite the possibility of calibrating a proxy during a period that is not truly analogous to the past climate, we believe that temporal transfer functions using δD_{cell} and $\delta^{18}O_{cell}$ values are more appropriate than spatial transfer functions, because of the potential for large local differences in hydrology, storm tracks, and the mixing of species that usually is necessary in spatial transfer functions.

Our transfer functions suggest that summers during the LGM at the Sevilleta were as moist as today, but that early summers may have been responsible for a greater portion of the summer's precipitation than currently. The relative importance of monsoonal precipitation in the southwestern USA during the last glacial period is currently being debated; there is some consensus that summers were drier than today (Betancourt et al., 1990; Thompson et al., 1993). Monsoonal circulation would be undermined by boundary conditions dramatically different than today (Douglas et al., 1993). Direct evidence for dry summers is meagre in the southwest, but decreased monsoonal circulation is suggested by the presence of juniper savannah where tropical forest grows today in the Peten region of Guatemala (Leyden et al., 1993; Bradbury, 1997). By contrast, possible evidence for wet glacial summers in New Mexico and Arizona comes from enriched $\delta^{13}C$ values of Pleistocene-age pedogenic carbonates and herbivore tooth enamel (Cole and Monger, 1994; Liu et al., 1996; Connin et al., 1998). It is conceivable that abundant late spring precipitation compensated for decreased monsoon rainfall during the LGM, but additional evidence is required to support this contention.

The deterministic modeling approach realistically accounts for complex isotopic fractionations involved in cellulose manufacture, and describes basic biophysical and biochemical processes that should not change over time or space. However, there are several sources of error inherent to this approach. Our reconstruction of δD_{mw} is contingent on calculated humidity changes based on $\delta^{13}C_{cell}$, which could be problematic because (1) there is uncertainty in paleo-$\delta^{13}C_{atm}$, (2) June minimum relative humidity accounts for only 30% of the variation in growing season relative humidity, and (3) 35% of the variation in modern $\delta^{13}C_{cell}$ is unrelated to humidity. Eq. 1 involves assumptions of values for equilibrium, kinetic, and net biochemical fractionation factors. The equilibrium fractionation factor can be constrained to within ±0.0035 (3.5‰), allowing for a range of 18–23ºC in average growing season temperatures. Piñons growing during the Pleistocene at the Sevilleta may have experienced lower growing season temperatures than these, but how much lower is speculative (Van Devender, 1990a,b). The kinetic fractionation factor is assumed to be 1.025 for the fully diffusive condition, but would be lower if turbulent conditions were more important in the past than they are thought to be currently.

Net biochemical fractionation is more uncertain than kinetic or equilibrium factors. We estimated α_B by measuring δD values in leaf water over a growing season and cellulose from that year in four trees, and correcting the leaf water to steady-state values; this produced an average of 0.9453 ± 0.0085 for the four trees. This standard deviation represents inter-tree variability, and is on the order of natural variability in δD_{cell} values. Our value of α_B incorporates possible effects of leaf water heterogeneity, exchange with organics, and post-photosynthetic metabolism (DeNiro and Cooper, 1989; Yakir et al., 1989). In stems, photosynthates made with enriched leaf water may undergo isotopic exchange with depleted stem water or stored starch, removing the leaf water signal from stem cellulose (Yakir, 1992). In this case the biochemical fractionation factor would be insignificant, or at least not related to δD_{LW} values. Strong 1 : 1 correlations observed between wood δD_{cell} and δD_{mw} values may be explained by such exchange (Yakir, 1992; White et al., 1994). Our piñon needles have very long leaf water residence times (up to several days) as a result of low stomatal conductance, increasing the possibility of exchange between leaf water and depleted organic matter (Pendall, 1997). Furthermore, it is impossible to assess the degree

that such effects may alter α_B values through time or under different climatic regimes.

Uncertainties associated with the deterministic model could be reduced with a tighter reconstruction of relative humidity, and better understanding of how α_B values might be influenced by climate changes. If δD_{mw} values did change at the Sevilleta, those changes were not represented in δD_{cell} values. Temperature reconstructions based on reconstructed δD_{mw} values must assume that the temperature–δD_{mw} relationship holds through time. If storm tracks or precipitation seasonality changes, this relation may well shift. We therefore put little emphasis on the temperature reconstructions presented in Table 6. More independent data are needed to determine how well the model reconstructs δD_{mw} values.

7. Conclusions

At our site in central New Mexico, δD_{cell} values in piñon needles are correlated with growing season precipitation amount rather than temperature, and $\delta^{13}C_{cell}$ values are correlated with June daytime relative humidity. We have more confidence in summer moisture reconstructions based on the transfer functions than in the δD_{mw} and temperature reconstructions from the deterministic model. However, additional independent evidence for relatively moist Pleistocene summers in the southwestern USA is required to corroborate our limited data set.

We believe that we have constrained the parameters used in the deterministic modeling approach more fully than other researchers who have applied this model to paleoclimate reconstruction (e.g., Edwards and Fritz, 1986; Clague et al., 1992; Saurer et al., 1997). However, if the possibility for non-analog situations is ignored, the transfer function approach appears to be more straightforward, at least for this study. Although transfer functions are favored by many researchers using δD_{cell} and $\delta^{18}O_{cell}$ values, in many instances they may be applied by default, when not enough information is available to apply the deterministic model (Lawrence and White, 1984; Feng and Epstein, 1994; Lipp et al., 1996a,b; Switsur et al., 1996).

The deterministic model incorporates more quantifiable uncertainty into paleoclimate reconstruction than do the transfer functions, because it defines the system more explicitly. While a transfer function may be statistically robust, it incorporates uncertainty of unknown magnitude related to the possibility of using a non-analog calibration period or location. The use of these two approaches is not mutually exclusive; indeed, we rely on the $\delta^{13}C_{cell}$–RH transfer function to constrain the deterministic model. The two approaches reconstruct different climate parameters, all of which contribute significantly to understanding the past environment. We have quantified estimates of uncertainties involved in both approaches, and suggest that this be standard practice for all palaeoenvironmental reconstructions based on stable isotopic proxies.

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