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Climatic and environmental controls on the variation of C_3 and C_4 plant abundances in central Florida for the past 62,000 years

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Abstract

Lake Tulane provides one of the few continental sediment records beyond the late glacial period (~15,000 cal years B.P.) for eastern North America. Its continuous, organic-rich sediment has yielded pollen assemblages that date back 62,000 years. Here we report the first organic geochemical characterization of the sediment core from Lake Tulane based on compound-specific carbon isotopic analyses of higher plant leaf waxes. Our millennium-resolution carbon isotope data allow us to quantitatively assess the variations in the relative abundances of C_3 and C_4 plants in Central Florida under contrasting climate conditions and different atmospheric $p\mathrm{CO}_2$ levels during the last glacial–interglacial cycle. Specifically, our results indicate large changes in the relative abundance of C_3 and C_4 plants, with ~40% higher input from C_4 plants during the last glacial maximum (LGM) than during the Holocene. During the last glacial period, C_4 plant abundance decreased dramatically during the pine phases when precipitation increased, indicating that increasing precipitation overrode the impact of low atmospheric $p\mathrm{CO}_2$, leading to expansions of C_3 plants. Our results provide new insights on the forcing mechanisms and first quantitative estimates on the C_3 and C_4 plant variation in central Florida for the last 62,000 cal years.

Keywords: Lake Tulane; Sediment record; C_3 and C_4 plants; Leaf waxes; Compound-specific carbon isotope analysis

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1. Introduction

Understanding the forcing mechanisms and scales of vegetation response to global climate change requires long-term records from continental settings. Lake sediments provide excellent climatic and environmental records in diverse continental environments based on variations in lithological, biological, chemical and physical properties. Eastern North America is among the most highly studied regions in the world where lake sediments have been analyzed for multiple paleoclimatic and paleoenviornmental proxies (e.g., pollen assemblages). Unfortunately, few lake-sediment records from eastern North America extend much beyond the last 15,000 cal years because of glaciation or sediment desiccation during the last glacial interval. Lake Tulane, a sinkhole lake in the central Florida peninsula is the only site known to contain a continuous sediment record for the last 62,000 years (Grimm et al., 1993).

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High-resolution pollen and macrofossil studies from Lake Tulane reveal dramatic changes in vegetation in response to climatic and environmental changes in Florida (Grimm et al., 1993). High abundances of *Pinus* (pine) pollen during the middle to late Holocene are attributed to increased moisture availability, whereas high abundances of *Ambrosia* (ragweed), Poaceae (grass), and *Quercus* (oak) during the last glacial period resulted from drier climatic conditions. In addition, large oscillations of *Pinus* pollen during the last glacial period appear to correlate with the major Dansgaard–Oeschger (D–O) stadials that are terminated by Heinrich events in the North Atlantic. Based on analysis of pollen and macrofossil data, Grimm et al. (1993, in revision) conclude that the pine phases were wetter and warmer than the intervening ragweed–grass–oak phases. Grimm et al. (in revision) hypothesize that because thermohaline circulation, which transports heat from the subtropics, was reduced during cold D–O stadials and particularly during Heinrich events, the subtropics warmed when heat transport to the North Atlantic was diminished.

Compound-specific carbon-isotope analyses of plant leaf waxes in sediment cores provide more specific data on the past changes in C_3 and C_4 plant abundances on land than analyzing bulk organic matter which includes input from both terrestrial and aquatic sources (e.g., Street-Perrott et al., 1997; Huang et al., 1999a, 2000, 2001; Schefuß et al., 2003). Changes in the C_3 and C_4 plant ratios are affected by climatic and environmental factors such as temperature, aridity, and atmospheric $p\text{CO}_2$ levels, although the relative importance of these factors is a subject of considerable debate (Cerling et al., 1997; Pagani et al., 1999; Huang et al., 2001; Schefuß et al., 2003). Lake Tulane sediment is excellent for observing the resulting ecological consequences of low $p\text{CO}_2$ and the manner in which these consequences are mediated by fluctuations from low to high climatic moisture-balance. In particular, the multiple episodes of increased precipitation during last glacial period, when $p\text{CO}_2$ was about the lowest in the earth history (Petit et al., 1999), provide an excellent opportunity to evaluate the interactions between precipitation and $p\text{CO}_2$ for shaping C_3/C_4 plant ratios.

The objectives of this study are: 1) to obtain the first 62,000 year record of carbon-isotope records of higher plant biomarkers for eastern North America from Lake Tulane sediments; 2) to quantify changes in the relative abundance of C_3 and C_4 plants around the site, and to assess the impact of precipitation vs. $p\text{CO}_2$ on the C_3/C_4 plant ratios; 3) to provide new insights on the vegetation and climate change in the study region based on isotopic measurements on biomarkers in Lake Tulane sediments.

2. Samples and experimental methods

2.1. Site and samples

Lake Tulane (Latitude 27°35′9″ N; Longitude 81°30′13″ W; longitude: −81.50361, 117 ft or 36.7 m a.s.l.) lies on the Lake Wales Ridge, which is composed of Pliocene beach sands overlying limestone at depth. The Lake Wales Ridge rises ~30 m above the surrounding lowlands. The lake is in the alluvial aquifer. Sediment core (TFG) used in this study is 17 m in length. A total of 73 samples (each sample is ~1 cm thick, ~1 cm^3 volume), were sub-sampled throughout the core at ~20 cm intervals. The chronology was established by 55 AMS radiocarbon dates on terrestrial macrofossils and bulk sediment (Grimm et al., in revision). The sediment is organic rich, with loss-on-ignition >10%, and up to 45%, and contains no carbonate minerals. The core is continuous through the last 62,000 cal years B.P., with no obvious hiatus.

Pine and oak leaves were collected from Kanapaha Botanic Gardens, in Gainsville, Florida 110 km north of Lake Tulane on Feb. 23, 2003. Leaves were taken from living trees with labeled identification and a description of its modern habitats. Slash pine (*Pinus elliottii*) is the fastest growing southern pine, and common in Florida and Gulf coast. Longleaf pine (*Pinus palustris*) was the dominant pine on the coastal plain. Both oaks (*Quercus hemispherica*, *Quercus virginiana*) are common in Florida.

2.2. Extraction and purification

Sediment samples were freeze-dried, and free lipids extracted using an Accelerated Solvent Extractor ASE200 (Dionex) using 2:1 (v/v) dichloromethane(DCM):methanol. Plant leaf samples were first cleaned with clean water to remove dust particles, freeze-dried, and then rinsed with DCM three times to obtain extracts of leaf waxes. Carboxylic acid fraction is isolated from the total extracts using solid phase extraction (Aminopropyl Bond Elute®), and is then methylated using anhydrous 2% HCl in Methanol. Methylated carboxylic acid fractions were further purified using a silica gel flash column chromtography with DCM as the eluant (removes hydroxyl-carboxylic acids). Aliphatic hydrocarbons were obtained by eluting the neutral fractions with hexane. Some alkenes were present in the aliphatic hydrocarbon fractions, which were removed by RuO_4 oxidation followed by a silica gel chromatograhpy (Huang et al., 1999b).

2.3. Gas chromatography

Hydrocarbons and fatty acid fractions were first analyzed using an Hewlett-Packard 6890 gas chromatograph, fitted with a 60 m fused silica column (HP-1 MS, 0.32 mm i.d., 0.25 μm film thickness), a flame ionization detector, a split/splitless injector (operated at a split ratio of 10:1), and an HP7683 auto-sampler. Helium was used as the carrier gas, with a flow rate of 1.7 ml min^{-1}. The temperature program was isothermal at 40 °C for 1 min, followed by heating to 300 °C at 10 °C min^{-1}.

2.4. Compound-specific carbon-isotope analysis

Carbon-isotope analyses of higher plant biomarkers were performed using a gas chromatograph-combustion-isotope ratio mass spectrometer (GC-C-IRMS, Thermo Finnigan). An HP 6890 GC, equipped with an AS 200 auto-sampler, was connected to a Finnigan MAT Delta$^+$-XL mass spectrometer via the combustion interface. The temperature program and capillary column used were identical to those used for GC analysis. Helium (UHP 5.5 grade) was used as the carrier gas operating at constant flow mode with a rate of 1.5 ml/min. Compounds separated by the GC column were converted to CO_2 and H_2O through the combustion furnace (0.5 mm i.d. × 1.5 mm o.d. × 34 cm) operated at 940 °C and loaded with CuO and Pt wires as oxidants and catalyst, respectively. Six pulses of CO_2 reference gas with known $\delta^{13}C$ values were injected via the interface to the IRMS, for the computation of sample $\delta^{13}C$ values. Typical standard deviation of duplicate analyses is about. ±0.2–0.3‰. For n-fatty acids, the added carbon as a result of derivatization has been corrected for its carbon isotopic contribution to the fatty acid methyl esters (Huang et al., 1999a). Values of $\delta^{13}C$ are reported in the usual δ notation relative to the Vienna Pee Dee Belemnite (VPDB) standard.

3. Results

We determined the carbon isotope ratios of individual long chain n-alkanes (C_{27}, C_{29} and C_{31}, total 61 samples) and n-fatty acids (C_{26}, C_{28} and C_{30}, total 72 samples) extracted from the Tulane sediment core at approximately millennial resolution for the last 62,000 years. These long carbon chain compounds are leaf waxes produced by land plants (Eglinton and Hamilton, 1967). The difference in the number of samples analyzed for n-alkanes and n-acids resulted from low concentrations and/or compound coelutions in some of the samples analyzed. Fatty acids are generally more abundant than alkanes, and were analyzed in more samples. The carbon-isotope values of C_{27}, C_{29} and C_{31} n-alkanes and C_{26}, C_{28} and C_{30} n-fatty acids show generally parallel downcore variations and are plotted along with pollen and loss-on-ignition data in Fig. 1. The data are plotted against sample age in Fig. 2, along with factor 1 scores of

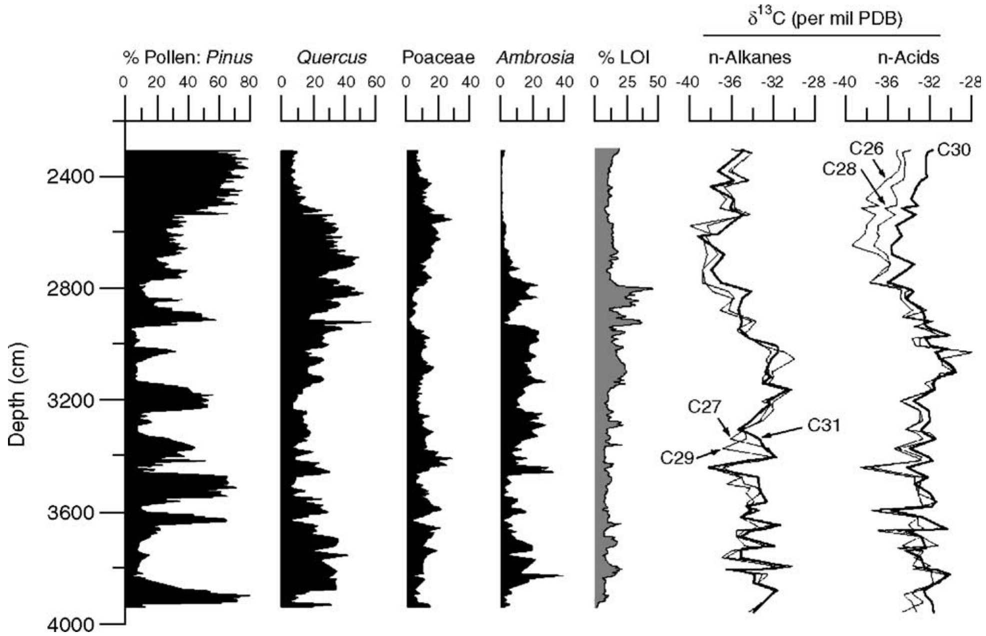

Fig. 1. Carbon isotope ratios of individual long chain leaf wax n-alkanes and n-acids, plotted against depth (including water depth), along with percentage pine, oak and ragweed pollen, as well as loss-on-ignition.

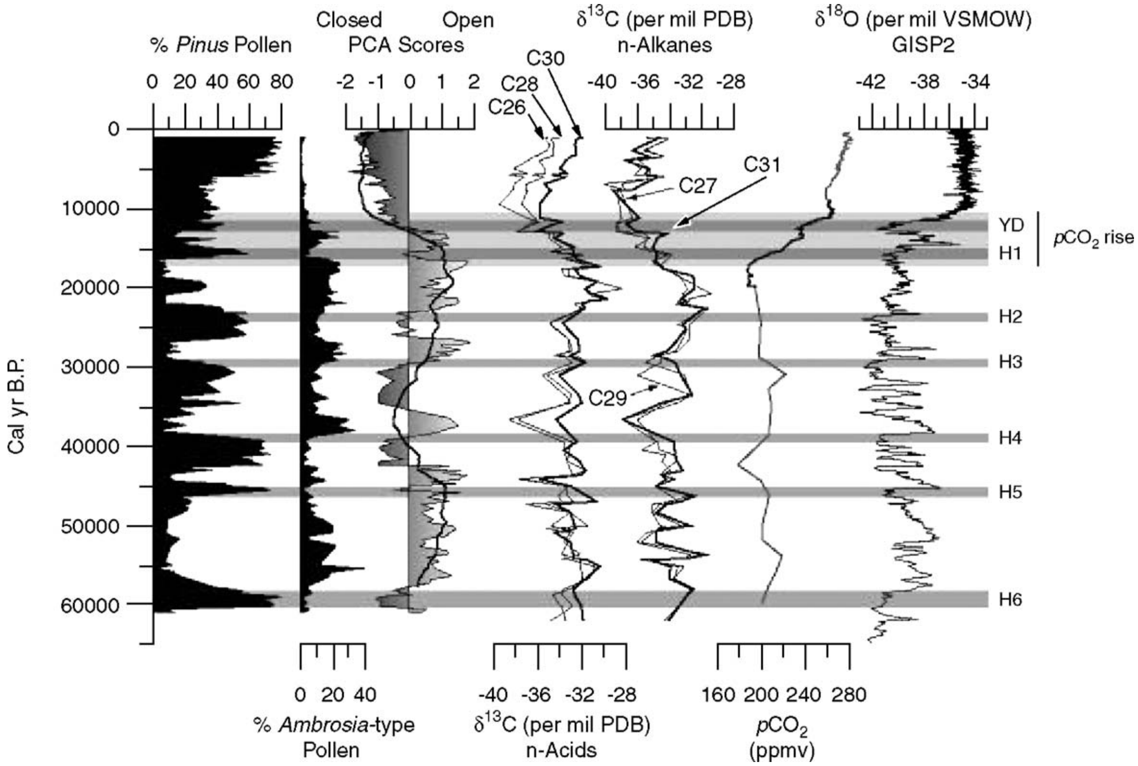

Fig. 2. Carbon isotope ratios of individual long chain leaf wax n-alkanes and n-acids plotted against age, along with percentage pine and ragweed pollen, PCA factor 1 scores, atmospheric pCO_2 and GISP $\delta^{18}O$ record.

principle component analysis of pollen, atmospheric pCO_2 level (Petit et al., 1999) and Greenland ice core $\delta^{18}O$ data (Grootes et al., 1993) for comparison.

Between 62,000 and 25,000 cal years B.P. (3900–3200 cm), the mean $\delta^{13}C$ values for the leaf waxes were about −33‰ to −34‰, with a slight trend towards lower $\delta^{13}C$ values with time (~1‰ decrease overall). However, there were significant oscillations with amplitudes up to 6‰ in this interval, especially from 58,000–30,000 cal years B.P. (3800–3300 cm). From 25,000–18,000 cal years B.P. (3200–3000 cm depth), the $\delta^{13}C$ values increased significantly, reaching a maximum of about −29‰ to −30‰ around 21,000 cal years B.P. (i.e., LGM). Between 18,000 and 10,000 cal years B.P. (3000–2600 cm), the $\delta^{13}C$ values rapidly decreased by up to 10‰. From 10,000–7000 cal years B.P. (2600–2550 cm), the $\delta^{13}C$ values remain relatively stable at around −38‰ to −40‰. From 7000 cal years B.P. to modern (2,550 cm to the surface), a clear trend existed towards higher $\delta^{13}C$ values (up to 5‰ increase).

$\delta^{13}C$ values of leaf waxes show significant correlation with PCA factor 1 based on pollen data. The higher scores (representing more open vegetation) are related to higher $\delta^{13}C$ values, and vise versa. Surprisingly, however, the negative $\delta^{13}C$ spikes did not correlate with pine phases, but instead occur during pine troughs between 50,000 and 35,000 cal years B.P. (Fig. 2). During the Holocene, the $\delta^{13}C$ values were the lowest when oak pollen dominated and increased when pine pollen percentages increased after 7000 cal years B.P. During LGM, high abundance of ragweed and low abundance of pine correspond to the highest $\delta^{13}C$ values throughout the core. During the Pleistocene, large oscillations of pollen (such as pine) corresponded to high variability in $\delta^{13}C$ values of leaf waxes (Fig. 2).

4. Discussion

4.1. Carbon isotope ratios of leaf waxes in C_3 vs. C_4 plants and evergreen vs. deciduous trees

Carbon isotope values for C_3 and C_4 plant leaf waxes have been determined from plants grown in green house environments (Rieley et al., 1993; Collister et al., 1994). Long chain leaf wax n-alkanes show lower $\delta^{13}C$ values than bulk plant tissues (on average, C_4 plants 9.9‰ lower and C_3 plants 5.9‰ lower than the bulk values; Collister et al., 1994). Biosynthetically related n-alkyl lipids (such as n-aldehydes, n-acids) have similar values as n-alkanes (Collister et al., 1994). Long chain leaf waxes from C_3

and C_4 plants have non-overlapping δ^{13}C values ($C_4 \sim -20$‰, $C_3 \sim -33$‰, assuming bulk δ^{13}C values of −10‰ and −27‰ for C_4 and C_3 plants, respectively) and can be used to reconstruct past changes in the relative abundance of C_3 and C_4 plants from lake and marine sediment cores (Huang et al., 1999b, 2000, 2001; Schefuß et al., 2003).

δ^{13}C values of evergreen trees have also been reported to have higher δ^{13}C values than the co-occurring deciduous trees (both are C_3 plants). In a study of plant samples collected over 2 years, Brooks et al. (1997) show that δ^{13}C values of evergreen trees were 3–4‰ higher than deciduous trees. Similarly, 2–4‰ higher carbon-isotope discrimination occurs in oak (*Quercus gambelii*) than in pine (*Pinus edulis*) (Williams and Ehleringer, 1996). Stuiver and Braziunas (1987) show that δ^{13}C values of wood in gymnosperm trees are ~3‰ higher than those in angiosperm trees. Leaf wax *n*-alkanes from angiosperms have δ^{13}C values of −36.1 ± 2.7‰, 4.5‰ lower than those of gymnosperms (−31.6 ± 1.7‰) (Chikaraishi and Naraoka, 2003). No published data exist for the carbon isotopic compositions of leaf waxes from pine and oak trees in Florida. We therefore collected two pine-leaf and two oak-leaf samples (all common in Florida) from Kanapaha Botanic Garden in Gainsville, Florida, ~110 km north of Lake Tulane. The carbon isotopic values of leaf waxes of both species of pine are on average 4–5‰ higher than the oak trees (Table 1). We take this isotopic difference into consideration in our subsequent discussions.

4.2. Quantitative estimates of C_3 and C_4 plant changes in Central Florida

Carbon-isotope ratios of leaf waxes can be used to quantitatively reconstruct the percentage changes in C_3 and C_4 plants from ocean and lake sediments (Huang et al., 1999b, 2000, 2001; Schefuß et al., 2003). Because long chain leaf waxes in lake sediments are unambiguously derived from land plants (both C_3 and C_4 plants), but not algae and submerged aquatic organisms, analysis of δ^{13}C values of leaf waxes eliminates the uncertainty of terrestrial and aquatic sources that exists in the analysis of bulk-sediment δ^{13}C values. Endmember values for C_3 and C_4 plants can be based on general values for C_3 and C_4 plants, or they can be based on the extreme carbon-isotope values in the sediment core if the extreme values exceed the range of commonly assumed values (Collister et al., 1994). In the case of Lake Tulane, however, three endmembers must be assigned because carbon-isotope ratios of pines are different from oaks, despite both being C_3 plants. In order to quantitatively estimate the changes in C_3 and C_4 plants from Tulane, we use the following equations:

Table 1
Carbon isotope compositions (‰ VPDB) of individual leaf waxes in pine and oak samples from Florida

	Longleaf pine	Slash pine	*Quercus hemispherica*	Quercus virginians
n-Alkanes				
C_{27}	−31.4	−31.3	−40.4	−36.9
C_{29}	−29.2	−30.1	−40.2	−37.5
C_{31}	−29.3	−30.3	−36.7	−35.5
Mean	−30.0	−30.6	−39.1	−36.6
n-Acids				
C_{26}	−29.6	−29.9	−32.8	−32.7
C_{28}	−29.7	−32.7	−37.9	−34.3
C_{30}	−29.8	−31.2	−37.1	−34.2
Mean	−29.7	−31.3	−35.9	−33.7

$$\delta_p F_p + \delta_{C3}\left(F_{C3} - F_p\right) + \delta_{C4} = \delta_m \tag{1}$$

$$F_{C3} + F_p + F_{C4} = 1 \tag{2}$$

$$F_p = \text{Fine pollen fraction} \tag{3}$$

where F_{C3} and F_{C4} are estimated C_3 and C_4 plant abundance (expressed in fractions). F_p is the fraction of pine as a special category of C_3 plants and is taken to be equivalent to the pine-pollen fractions in order to provide enough equations to solve for the F_{C3} and F_{C4}. δ_p, δ_{C3} and δ_{C4} are endmember δ^{13}C values for leaf waxes of pine, C_3 (excluding pine, including oak and other C_3 trees and grasses), and C_4 plants, respectively. δ_m is the measured δ^{13}C value of leaf waxes downcore. We choose two endmember sets to test the sensitivity of the model: a) $\delta_{C4} = -20$‰, $\delta_p = -33$‰ and $\delta_{C3} = -38$‰; and b) $\delta_{C4} = -23$‰, $\delta_p = -33$‰ and $\delta_{C3} = -39$‰. The C_4 plant fraction is then

$$\text{a)}\quad F_{C4} = \left(\delta_m + 38 - 5F_p\right)/18 \tag{4}$$

$$\text{b)}\quad F_4 = \left(\delta_m + 39 - 6{*}F_p\right)/16. \tag{5}$$

Because the δ^{13}C trend in individual leaf waxes is generally similar (Figs. 1 and 2), we used the δ^{13}C value of C_{28} *n*-acid as the input value for δ_m, and computed the F_{C4} for the last 62,000 years (Figs. 3 and 4). Our results indicate the highest fraction of C_4 plant input was at LGM (~0.4). The fraction is relatively small and stable during the Holocene, with a

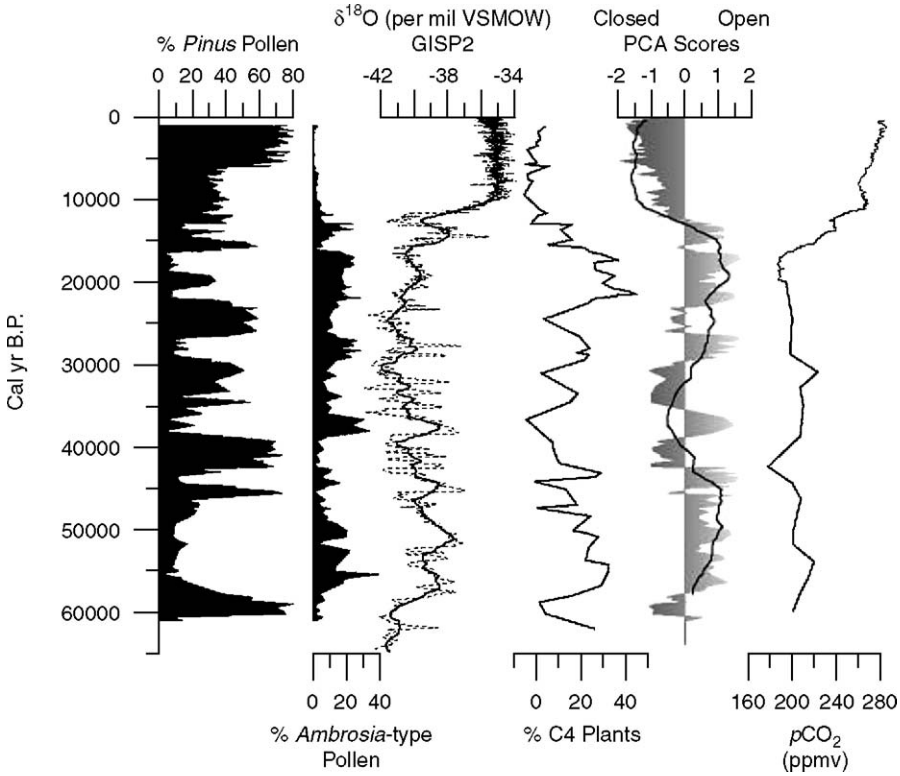

Fig. 3. Comparisons of computed percentage input from C_4 plants to the lake, Pine and Ambrosia-type pollen, PCA factor 1 scores and $p\text{CO}_2$ level.

small increase towards recent times. Changes in endmember δ^{13}C values resulted in little change in the relative percentage of C_3 and C_4 estimates (Fig. 4). It is interesting to note that changes in the C_3 and C_4 plants during the Holocene are small despite the ~5‰ shift in δ^{13}C values of leaf waxes (Figs. 2 and 3). Our results indicate that the Holocene carbon isotopic shift is primarily a result of changes in the relative abundance of pine and oak, rather than changes in C_3 and C_4 plant abundances.

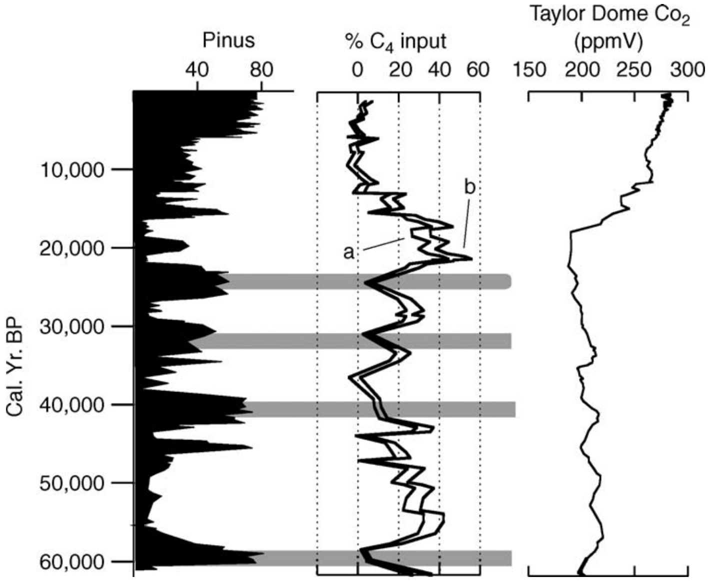

Fig. 4. Computed percentage input from C_4 plants with two different isotopic endmember assumptions.

4.3. Vegetation change and forcing mechanism

The relative importance of climatic (precipitation, temperature) and atmospheric (pCO_2) conditions on the natural abundance of C_4 and C_3 plants is an important topic in earth system history and is widely debated (Cerling et al., 1997; Pagani et al., 1999; Huang et al., 2001; Schefuß et al., 2003). Because C_4 plants possess a CO_2 concentrating mechanism and have very low level (2% to 5% of those in C_3 plants) of photorespiratory inhibition of photosynthesis (von Caemmerer and Furbank, 1982), they have an important advantage over C_3 plants at times of low pCO_2/O_2 ratios in earth history (Sage et al., 1999). A widespread expansion of C_4 plants in the late Miocene may be primarily a result of significant reduction of atmospheric pCO_2 levels (Cerling et al., 1997). Because the physiological mechanisms that provide an advantage to C_4 plants under low pCO_2 to mitigate moisture loss, aridity is also an important factor in controlling the relative ratios of C_3/C_4 plants and the regional timing of C_4 expansion (Pagani et al., 1999; Huang et al., 2001; Schefuß et al., 2003). C_3 plants can increase in abundance relative to C_4 plants at low atmospheric pCO_2 levels of the last glacial period if precipitation is sufficiently high (Schefuß et al., 2003). Conversely, low pCO_2 levels can prohibit C_3 success under the precipitation levels that they tolerate today (Cowling and Sykes, 1999), and change the plant water use efficiencies (Polley et al., 1993). The sensitivity of C_3 and C_4 plants toward environmental factors likely differs in different natural ecosystems. Lake Tulane offers a unique opportunity to further understand the dynamics of C_3 and C_4 plants in the natural ecosystem of eastern North America.

The $\delta^{13}C$ values of leaf waxes were the highest ($-28‰$ to $-30‰$) during the LGM. The minimum $\delta^{13}C$ values ($-39‰$ to $-40‰$) were reached in the early Holocene 10,000–9000 cal years B.P. The results support higher abundances of C_4 plants in the LGM when climate was significant drier (based on both pollen data) and atmospheric pCO_2 was ~30% lower. Large oscillations of C_4 fractions occurred during the Pleistocene, with relatively high C_4 fractions interrupting pine expansions (Fig. 4). The estimated fraction of C_3 plants nearly reached the Holocene levels when pine expanded and precipitation increased. Because pCO_2 is generally low during the early part of the record, our data indicate that precipitation plays an essential role in modulating the natural abundance of C_3 and C_4 plants in central Florida (i.e., more important than pCO_2).

Based on species numbers, 63–80% of modern grasses in Florida use C_4 photosynthetic pathway (Sage et al., 1999). The low $\delta^{13}C$ values of leaf waxes during the early Holocene indicate a relatively small fraction of C_4 plants, contrasting with an increase in the grass pollen (Figs. 1 and 2). Although a higher ratio of C_3 to C_4 grasses during the early Holocene would explain the $\delta^{13}C$ values, it is unlikely that C_3 grasses were dominant members of the upland vegetation in Florida. Given the low percentages of *Ambrosia* and other herb pollen during the early Holocene, the $\delta^{13}C$ values may indicate that high grass pollen percentages derive from local emergent or damp–ground grasses growing near the lake. Thus, the $\delta^{13}C$ values may help to confirm that the presence of closed woodlands (rather than oak–grass savannas) on the upland during the early Holocene.

5. Conclusions

We have obtained a 62,000 year record of changes in the relative abundance of C_3 and C_4 plants from Lake Tulane, Central Florida. The record is so far the longest continental vegetation and isotopic record for eastern North America. Carbon-isotope data of individual leaf waxes from Lake Tulane sediments indicate substantially more abundant C_4 plants during LGM than the Holocene, as a result of the physiologically drier conditions and lower atmospheric pCO_2 level. Leaf waxes of pine have a few per mil higher $\delta^{13}C$ values than other C_3 angiosperms, leading to the ~4–5‰ positive carbon isotopic excursion from the early Holocene to the present. By using pine pollen fraction as an added input parameter, a quantitative estimate on the input of C_3 and C_4 plant leaf waxes to the lake sediments can be made, taking into consideration of different $\delta^{13}C$ values of evergreen and deciduous trees. Large decreases in C_4 plants during Pleistocene pine phases (and corresponding increases in C_3 plants to near Holocene levels) suggest that precipitation increases counteracted the physiological advantage of C_4 over C_3 plants in central Florida even when pCO_2 was at its minimum level in recent earth history. Therefore, the importance of precipitation on the natural balance of C_3 and C_4 plant must be carefully considered in vegetation models.

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the World Data Center for Paleoclimatology: http://www.ncdc.noaa.gov/paleo/data.html.

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