LATE PLEISTOCENE-RECENT ATMOSPHERIC δ^{13}C RECORD IN C$_4$ GRASSES[1]

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ABSTRACT. Samples of *Setaria* species from packrat middens, herbarium specimens and modern plants preserve a record of δ^{13}C of atmospheric CO_2 from 12,600 BP to the present. No secular trend is detected between 12,600 and 1800 BP, when the mean value of δ^{13}C during that period was $-6.5 \pm 0.1‰$ (the error is the standard deviation of the mean). Our value agrees with δ^{13}C averages of pre-industrial CO_2 from polar ice cores, and differs significantly from modern regional ($-8.2 \pm 0.1‰$) and global ($-7.7‰$) values, which are higher because of fossil fuel burning.

INTRODUCTION

Recently, Marino and McElroy (1991) showed that carbon isotope ratios in a C$_4$ grass, *Zea mays* (cultivated corn) tracked changes in the carbon isotope ratios of atmospheric CO_2 from the years 1948–1987. Here, we present δ^{13}C and ^{14}C age data for species of the C$_4$ grass genus, *Setaria*. C$_4$ plants have advantages over C$_3$ plants as proxies for atmospheric carbon isotope studies. Briefly, in C$_3$ plants, the fractionation of C isotopes that occurs during photosynthesis is affected by environmental factors, such as temperature and atmospheric CO_2 concentrations. Fractionation in C$_4$ plants is little influenced by such factors and is more uniform (O'Leary 1988). Tiezen and Boutton (1989) confirm reduced variation in C$_4$ grasses. Henderson, von Caemmerer and Farquhar (1992) explore details of photosynthetic fractionation in C$_4$ dicots and monocots.

Two *Setaria* species, *S. macrostachya* and *S. leucopila*, are common today across the southwest USA and into central Mexico (Rominger 1962). Both respond to summer rains, growing and flowering from July to October. These species are commonly preserved in middens constructed by packrats (*Neotoma*). Packrat middens are well-known reservoirs of paleoecological information and have been the subject of intensive study (Betancourt, Van Devender & Martin 1990). Packrats forage up to 50 m from their dens for plants for food and den-building, sampling the local vegetation. In dry shelters in arid climates, middens of plant matter and fecal pellets at the den may become indurated with crystallized urine, and persist for tens of thousands of years.

One of us (L. J. T.) has studied grasses preserved in dozens of packrat middens from sites across the American Southwest (*e.g.*, Betancourt 1984; Van Devender & Toolin 1983; Van Devender, Toolin & Burgess 1990). Floral parts of *Setaria macrostachya* have been found in many midden assemblages from Arizona to Mexico (Fig. 1). The fragments studied for identification include the distinctive, indurated floral bracts (lemma and palea) that enclose the reproductive organs.

METHODS AND RESULTS

All samples were given standard acid-base-acid treatment to remove carbonate and humic contaminants, and combusted to CO_2. Values of δ^{13}C of the CO_2 were measured with a 1σ analy-
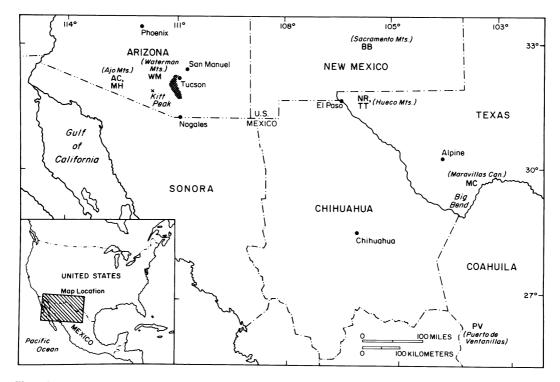
Fig. 1. Sample location map. Locations of Holocene packrat middens are indicated by letters (*e.g.*, BB, Big Boy). Locations of modern (1990) specimens are within the cross-hatched area near Tucson.

tical precision of 0.13‰, based on repeated measurements of a laboratory standard calibrated to PDB. The CO_2 was then reduced to graphite (Slota *et al.* 1987) for ^{14}C dating by accelerator mass spectrometry (AMS) (Linick *et al.* 1986; Donahue, Jull & Toolin 1990). Although it is preferable to measure δ^{13}C on plant cellulose rather than on a mix of tissues, the small mass of *Setaria* fragments found in most samples (<1mg–5mg) precludes further loss of datable material that would occur on cellulose extraction. Direct dating of the *Setaria* was imperative because all plant species in a given midden may not be contemporaneous (Van Devender *et al.* 1985). In fact, in the course of this study, we found that the ^{14}C age of the *Setaria* differed greatly from previous measurements on other plants from the same middens. For example, Waterman Mountains #2 was originally dated on juniper twigs at 21,510 BP, whereas the *Setaria* from this midden dated to 9895 BP. The lack of contemporaneity of different plant species in a single midden calls into question the value of results in which the age of one plant, or of bulk materials, is assumed to be the same as for other plants. This situation appears to have been overlooked by Marino *et al.* (1992).

Five midden samples were large enough to compare cellulose (method modified after Green (1963)) and mixed-tissue values for δ^{13}C (Table 1). These results can be compared to those from modern (AD 1990) *Setaria* samples. Modern samples were collected in eastern Pima and adjacent Santa Cruz counties, Arizona, and from The University of Arizona (ARIZ) herbarium. Cellulose *versus* mixed-tissue values for midden fragments differed less in the older specimens than in modern material (Table 1). We believe this is because the modern material contained more varied tissues (anthers, pistils, *etc.*) than the midden samples, where only the indurated, higher-cellulose-content lemmas and paleas remain. This effect is consistent with variations in different tissues of maize kernels (Tiezen & Fagre 1993).

TABLE 1. Mixed-Tissue *versus* Cellulose $\delta^{13}C$ (PDB)

Sample no.	Mixed-tissue (‰)	Cellulose (‰)	Difference (‰)
Modern Samples			
AA-6630	−11.8	−11.0	0.8
AA-6631	−11.9	−11.4	0.5
AA-6646a	−11.7	−10.9	0.8
AA-6646b	−11.7	−10.9	0.8
AA-6342a	−11.8	−11.1	0.7
AA-6342b	−11.6	−11.1	0.5
AA-6864	−12.4	−11.5	0.9
AA-6644	−11.6	−10.9	0.7
AA-6343	−11.4	−10.8	0.6
			Mean = 0.7
Holocene Samples			
AA-6634	−9.9	−9.6	0.3
AA-7056	−9.7	−9.5	0.2
AA-7058	−9.5	−9.1	0.4
AA-7059	−10.3	−10.1	0.2
AA-7061	−10.3	−10.0	0.3
			Mean = 0.3

TABLE 2. Herbarium and Modern Samples

Arizona county	Year	Herbarium no. (ARIZ)	AA-no.	$\delta^{13}C$ (‰, PDB)
Pima	1939	23344	7704	−10.4
Pima	1949	77865	7648	−9.8
Pima	1957	123359	7649L*	−10.4
Pima	1968	169494	7650L	−11.9
Pima	1978	211886	7651L	−11.8
Pima	1986	285825	7652M	−11.9
Pima	1990	290001	6644L	−11.6
Pima	1990	289153	6343L	−11.4
Pima	1990	---	6864M	−12.4
Pima	1990	---	6630L	−11.8
Pima	1990	290010	6631M	−11.9
Santa Cruz	1990	289593	6646aL	−11.7
Santa Cruz	1990	289593	6646bL	−11.7
Santa Cruz	1990	289594	6342aM	−11.8
Santa Cruz	1990	289594	6342bM	−11.6

*Sample no. suffixes: L = *S. leucopila*; M = *S. macrostachya*; a, b indicate different plants collected under the same field number.

TABLE 3. Specimens from Packrat Middens

Midden	Locality*	AA-no.	^{14}C age (BP)	δ^{13}C
Waterman Mts 1A	Pima, AZ	7058	2990 ± 55	−9.5
Waterman Mts 1C	Pima, AZ	7313	1795 ± 70	−10.6
Waterman Mts 1E	Pima, AZ	7059	2080 ± 55	−9.6
Waterman Mts 2	Pima, AZ	6862	9895 ± 160	−9.4
Waterman Mts 9A2	Pima, AZ	7049	10335 ± 75	−9.6
Waterman Mts 9B	Pima, AZ	7050	10415 ± 70	−9.6
Waterman Mts 9C	Pima, AZ	7033	9485 ± 120	−9.4
Waterman Mts 9D	Pima, AZ	7051	5610 ± 70	−10.0
Waterman Mts 10	Pima, AZ	7034	8935 ± 105	−9.5
Waterman Mts 12A	Pima, AZ	7035	6015 ± 75	−9.0
Waterman Mts 12A	Pima, AZ	7060	6125 ± 70	−9.4
Waterman Mts 13A1	Pima, AZ	6863	9340 ± 90	−8.8
Ajo Mts AC1B	Pima, AZ	6951	11100 ± 175	−9.6
Ajo Mts MH1D	Pima, AZ	6953	11240 ± 115	−11.0
Big Boy 3	Otero, NM	6952	10365 ± 255	−9.7
Tank Trap 2	El Paso, TX	6860	9825 ± 175	−9.5
Navar Ranch 1C1	El Paso, TX	7056	6005 ± 65	−9.7
Navar Ranch 4B	El Paso, TX	7061	10065 ± 85	−10.0
Navar Ranch 11	El Paso, TX	7047	9785 ± 75	−9.9
Navar Ranch 12	El Paso, TX	7048	9560 ± 85	−9.7
Navar Ranch 14D	El Paso, TX	7037	9885 ± 90	−10.5
Navar Ranch 18C	El Paso, TX	7038	7950 ± 60	−8.9
Navar Ranch 19C	El Paso, TX	7036	9125 ± 60	−9.6
Maravillas Canyon 13	Brewster, TX	7046	2790 ± 50	−10.2
Maravillas Canyon 16	Brewster, TX	7055	6800 ± 60	−9.4
Puerto de Ventanillas	Coahuila, Mex.	7314	12605 ± 190	−9.4

*AZ = Arizona; NM = New Mexico; TX = Texas: Mex. = Mexico. No county given for Mexican sample.

Table 2 presents mixed-tissue values of δ^{13}C for all recent samples. δ^{13}C measurements for modern *S. macrostachya* and *S. leucopila* (indicated by M or L in the table) were essentially the same, ranging from −11.6 to −12.4‰ and −11.5 to −12.8‰, respectively. For nine modern (1990) plants, δ^{13}C averages −11.90 ± 0.14‰.

Table 3 presents the results of our measurements on *Setaria* specimens from fossil packrat middens. The two species cannot be distinguished in this material. We show the values of δ^{13}C of florets (δ^{13}_p). The data for 26 midden samples of *Setaria* (12,600–1800 BP) average −9.67 ± 0.10‰, and the data from the herbarium samples (AD 1939–1986) range between the data for ancient and 1990 samples (Table 2).

Farquhar (1983) and Henderson, von Caemmerer and Farquhar (1992) have established a function for relating the δ^{13}C of C_4 plants (δ^{13}_p) to δ^{13}_a, the δ^{13}C of the atmospheric CO_2 fixed by the plant. For our *Setaria*, the relation between δ^{13}_p of florets and δ^{13}_a (Farquhar, personal communication) is

$$\delta^{13}_a = 2.9 + \delta^{13}_p \tag{1}$$

To account for the offset between mixed-tissue and cellulose δ^{13}_p values, we added the mean difference of the Holocene samples, 0.3‰ from Table 1, to Equation (1); thus the relation for midden florets becomes

$$\delta^{13}_a = 3.2 + \delta^{13}_p \qquad . \tag{2}$$

For the AD 1939–1990 samples, we added the mean differences for 1990 samples (0.7, from Table 3) to Equation (1) and applied the relation

$$\delta^{13}_a = 3.6 + \delta^{13}_p \qquad . \tag{3}$$

We applied these corrections (Eq. 2, 3) to relate all of our δ^{13}_p measurements to a common datum, independent of variability in the character of the mixed tissues, following Marino and McElroy (1991). Figure 2 presents the resulting δ^{13}_a data for all samples, derived with the above equations.
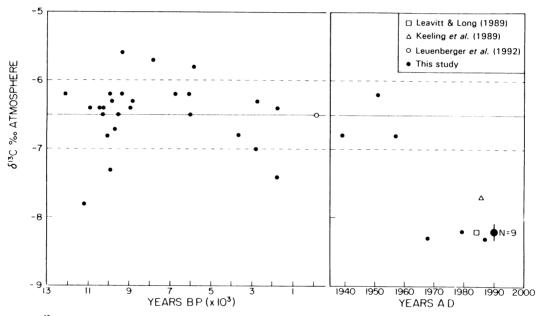

Fig. 2. $\delta^{13}C$ values of Holocene atmospheric CO_2. • = *Setaria* data; ⸺ = mean ± 1 σ of pre-1939 samples. --- = scatter of individual measurements about the mean; ● = mean of data for samples collected in 1990; the error bar = 1σ. Direct measurements: ∆, □; o = the mean of Arctic and Antarctic ice core pre-industrial $\delta^{13}C$ measurements.

The mean δ^{13}_a from nine 1990 *Setaria* samples is −8.2 ± 0.14‰, lower than the 1986 global mean of −7.7‰ (Keeling *et al.* 1989), but in line with differences between $\delta^{13}C$ values from clean-air and inland sites (Keeling 1961). Our value is empirically supported by comparison with an N_2O-corrected, seasonally averaged, mean atmospheric $\delta^{13}C$ value of −8.2‰, measured in 1983–1984 at Kitt Peak, southern Arizona (Leavitt & Long 1989).

From Equation (2), the mean value of δ^{13}_a for all 26 midden samples is −6.5 ± 0.1‰, which differs significantly from the modern and global values. Our Holocene mean agrees with $\delta^{13}C$ data for CO_2 in pre-industrial ice from Antarctica (Siple, −6.5 ± 0.07‰; South Pole −6.70 ± 0.13‰; Byrd, −6.49 ± 0.05‰, and Dye 3, Greenland, −6.41 ± 0.09‰) (Leuenberger, Siegenthaler & Langway 1992). The scatter of each of our Holocene measurements (0.5‰) is close to that of the modern samples

samples (0.42‰). This suggests that long-term changes in δ_a^{13} from 12,600–1800 BP could not have exceeded a few tenths of 1‰. Although our data indicate no secular trend in δ_a^{13} during the Holocene, events of short duration or small amplitude might remain undetected.

The nearly step-wise drop of 1.8‰ between 1957 and 1968 may be real, the few data notwithstanding. This interval of time corresponds approximately with a surge in the burning of fossil fuels in the southwestern USA, as a result of urban growth and ore smelting, and to a global increase in fossil fuel CO_2 production (Marland 1990). We plan to make more measurements on 20th century specimens to determine this segment of the δ_a^{13} vs. time curve with better precision.

Recently, Martinelli *et al.* (1991) showed that large outputs of biogenically fractionated CO_2 from the Amazon River produced a gradient in δ_a^{13} that could mimic secular changes produced, for example, by changes in atmospheric CO_2 concentration. In our region, there is no such large biogenic effect today, and none appears to have operated in the past. If our Holocene samples are grouped by region, there is no distinction between the western group (Arizona) with mean δ_p^{13} = –9.6 ± 0.15‰ and the eastern group (Texas and New Mexico) with mean δ_p^{13} = –9.7 ± 0.13‰.

CONCLUSION

Our results provide the first measurements of C-isotope values of Holocene atmospheric CO_2, constrained by AMS ^{14}C dating of the carbon used for the stable-isotope measurements. Reconstructions of δ_a^{13} such as ours may help clarify the interpretation of δ_p^{13} changes in C_3 plant tissues (*e.g.*, tree rings) in which C-isotope fractionation is strongly influenced by environmental factors (Leavitt & Danzer 1991; Krishnamurthy & Epstein 1990).

ACKNOWLEDGMENTS

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