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$\delta^{13}C$ VARIATIONS IN C_3 PLANTS OVER THE PAST 50,000 YEARS

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ABSTRACT. We examined three sets of data to determine if there are consistent changes in $\delta^{13}C$ of C_3 plants through time, under the hypothesis that environmental changes from glacial to postglacial may have caused such isotopic changes over the last 50 ka. The records of $\delta^{13}C$ change in all types of plant data from *RADIOCARBON* and from the University of Arizona Radiocarbon Laboratory archives both reveal significant decline of 0.8–1.0‰ in $\delta^{13}C$ from pre- to post-10 ka BP averages. The $\delta^{13}C$ of wood data alone from *RADIOCARBON* shows a larger significant decline of 3.0‰, and twigs, leaves and *Juniperus* categories from the Arizona data individually show declines of 0.4–1.44‰. Peat and charcoal from both data sets show no significant mean $\delta^{13}C$ differences. A highly constrained set of wood samples from the Great Lakes region spanning the last 12 ka show isotopic changes of *ca.* 3‰, but most of that variation apparently does not reflect global environmental changes.

INTRODUCTION

Continuous sequences of tree rings going back hundreds of years have been studied to develop a record of recent anthropogenically and biospherically induced atmospheric changes of $\delta^{13}C$ (Peng *et al.* 1983; Stuiver, Burk & Quay 1984; Leavitt & Long 1988). Because $\delta^{13}C$ of atmospheric CO_2 is an important contributor to plant $\delta^{13}C$ (Farquhar, O'Leary & Berry 1982), it might be possible to reconstruct atmospheric $\delta^{13}C$ for periods well beyond the longest tree-ring chronologies by using isolated pieces of ^{14}C dated plant matter, *e.g.,* wood. For this purpose, Krishnamurthy and Epstein (1990) used wood, from which cellulose was isolated, up to 42 ka BP from all over the world. They attributed the glacial to postglacial shift in $\delta^{13}C$ of *ca.* 4‰ primarily to changes in atmospheric CO_2 $\delta^{13}C$.

The $\delta^{13}C$ of plants, however, is not only a function of the isotopic composition of environmental CO_2, but also depends on the ratio of internal to external CO_2 (C_i/C_a). The latter ratio will be governed by rates of carbon fixation *vs.* rates of stomatal conductance, and these in turn may be influenced by environmental effects, such as temperature, relative humidity and moisture stress. Thus, sorting out CO_2 from other environmental parameters in interpreting $\delta^{13}C$ of tree rings is not trivial. Marino and McElroy (1991) describe a greater potential of C_4 plants for atmospheric $\delta^{13}C$ reconstructions because of minimal influence of C_i/C_a ratios on C_4 carbon isotope fractionation.

We explore here the possibility that there are consistent, reproducible changes in $\delta^{13}C$ of C_3 plants through time by tabulating previously measured $\delta^{13}C$ values of ^{14}C-dated plant matter, and by analyzing a specific set of wood samples from the past 12 ka. The latter set of samples was tailored to avoid or limit obscuring effects of intrasite variability, latitude effects, altitude effects and species differences. The $\delta^{13}C$ chronologies derived from this exercise may contain multiple environmental influences, but if an atmospheric $\delta^{13}C$ chronology can be derived from C_4 plants, then by difference, other environmental changes may be gleaned from the C_3 record.

METHODS

We selected plant entries from Volumes 1 through 31 (1959–1989) of *RADIOCARBON*. All pre-10 ka BP plant-related values were tabulated from Volumes 1–31, but a sufficiently large and representative number (525) of post-10 ka BP values were obtained from Volumes 28–31. Of the total of 821 values in the final data base, 306 are wood, 146 are peat, 256 are charcoal, and the remaining 113 are miscellaneous entries, such as cellulose, string, leaves, moss, seeds, organic matter, organic carbon, acorns, pine cones and roots. Although most labs did not describe pre-

treatment methods, acid, acid-base and acid-base-acid pretreatments predominated among those that did.

The Arizona Radiocarbon Laboratory data contain similar categories of materials, but over 90% were treated with acid-base-acid prior to analysis. Out of 1067 relevant entries, 384 are charcoal, 283 plant fragments, 120 twigs, 174 wood, 67 peat and the balance are miscellaneous. More than 50% of these samples have not been reported in *RADIOCARBON*.

We obtained a set of cross-sections of old wood from six buried forests in the Great Lakes region (Fig. 1). Reported ^{14}C dates (in yr BP) for the sites are: Two Creeks: 11,850 ± 100 (Broecker & Farrand 1963); Green Bay: 11,940 ± 390 (F. T. Thwaites 1958, unpublished site report); Liverpool: 11,815 ± 640 (Schneider & Reshkin 1982); Gribben Basin: 9850 ± 300 (Hughes & Merry 1978); Olson: 8320 ± 70 (Chrzastowski, Pranschke & Shabica 1991); Southport: 6340 ± 300 (Schneider, Sander & Larsen 1979). Full cross-sections of four different trees from each site were separately ground to eliminate questions of site and circumferential variability (Leavitt & Long 1984). Oils and resins were leached from the ground wood with toluene-ethanol in a soxhlet extraction appara-

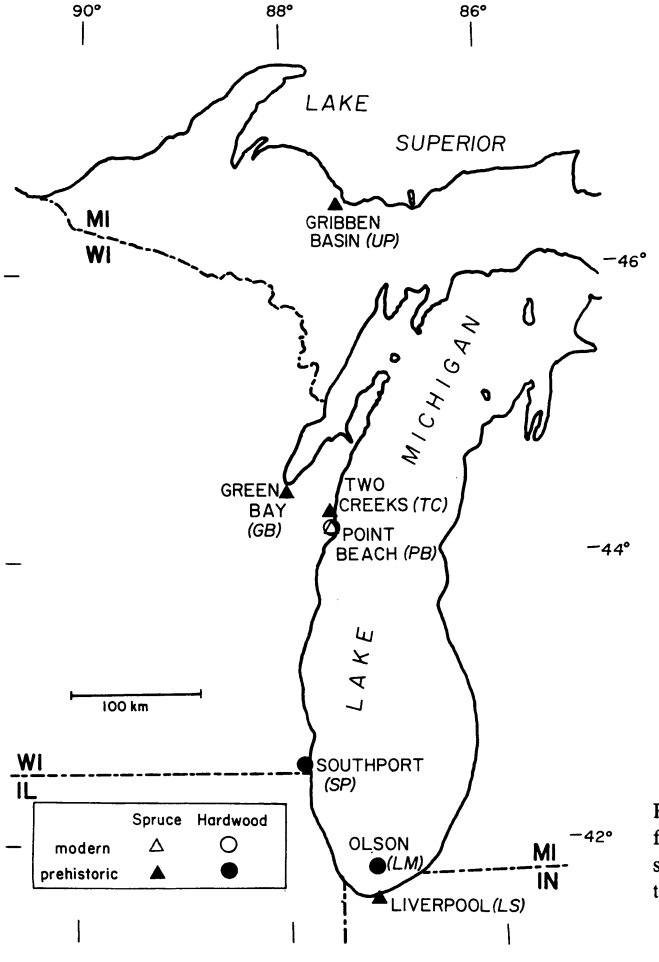

Fig. 1. Site locations where wood was obtained for isotopic analysis in this study. See text for site ages and Table 2 for sample characteristics.

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tus, and cellulose was isolated by bleaching the extracted wood in an acidified sodium chlorite solution (Green 1963). Samples were combusted to CO_2, analyzed mass-spectrometrically, and $\delta^{13}C$ results calculated with respect to the PDB standard. Cross-sections (hardwoods) and cores (white spruce, 4 cores per tree) were also obtained from modern trees at the Point Beach site just south of Two Creeks, and were processed in the same manner as the old wood.

Results and Discussion

Figure 2 contains the plot of all plant data points tabulated from *Radiocarbon*. As a first approximation, a major break in the data seems to appear at *ca.* 10 ka BP. The pre-10 ka BP mean of −25.0‰, in fact, is significantly heavier than the post-10 ka BP mean by 0.8‰. Figure 2 also contains the 5- and 11-point running means through the data. The $\delta^{13}C$ values slowly rise from 50 ka BP to just before 10 ka, after which they fall. There does not appear to be a singular peak in $\delta^{13}C$ values at 18–20 ka BP, as suggested by Krishnamurthy and Epstein (1990), but the magnitude of post-20 ka BP change is comparable.

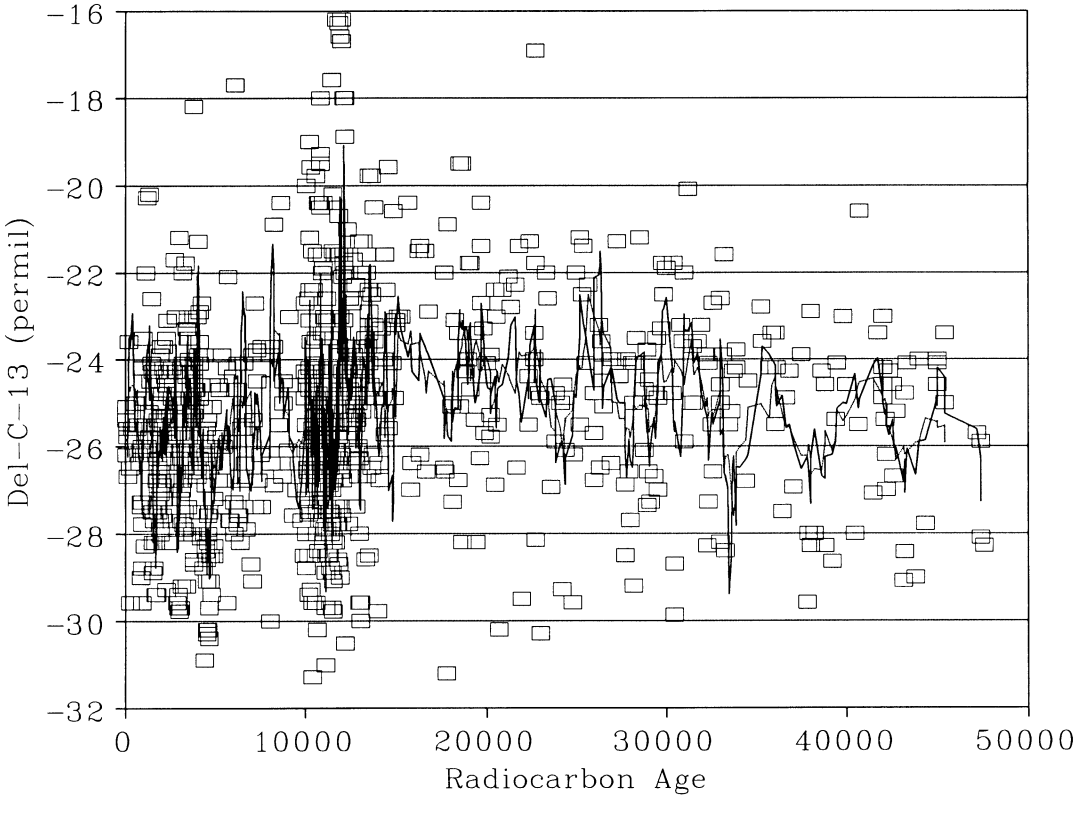

Fig. 2. $\delta^{13}C$ values (□) for all plant categories tabulated from *Radiocarbon*. Five- and 11-point running means are drawn to infer trends.

Figure 3 contains only the wood data from *Radiocarbon*. $\delta^{13}C$ drops dramatically at *ca.* 10 ka BP. The pre-10 ka BP mean of −24.1‰ is significantly heavier than that of the post-10 ka mean by 3‰. The 5- and 11-point running means chart progress of the $\delta^{13}C$ changes, and likewise show a rise in values from 50 ka BP to *ca.* 14–15 ka BP, followed by the decline. It is this sharp drop that

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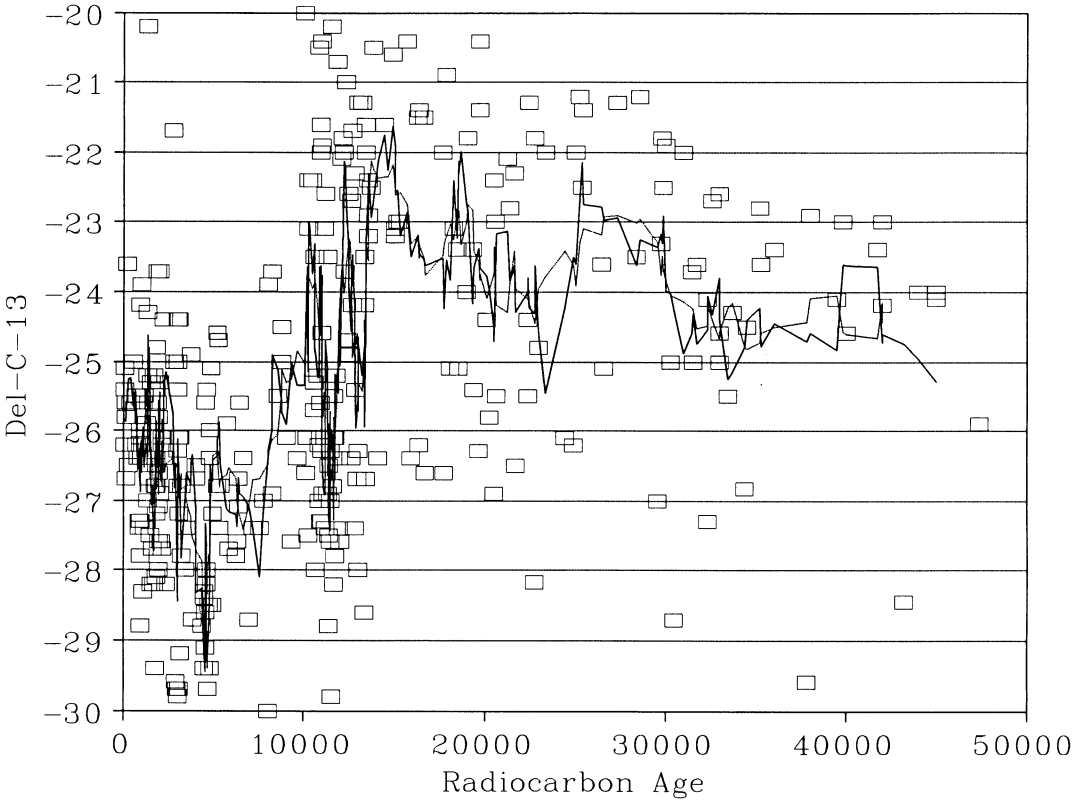

Fig. 3. $\delta^{13}C$ values for wood samples tabulated from *RADIOCARBON*. Lines are 5- and 11-point running means.

motivated closer scrutiny of $\delta^{13}C$ changes in plants over the last 12 ka with a special set of wood samples from the Lake Michigan area. Examination of the peat and charcoal subsets, however, revealed no major dislocations in $\delta^{13}C$. One of the problems with this data set, overall, is that the $\delta^{13}C$ values may have been obtained by the respective ^{14}C laboratories more as an estimate of the fractionation occurring during their processing rather than as the exact value of the original sample.

The Arizona Radiocarbon Laboratory data base was used for further examination of temporal plant $\delta^{13}C$ changes because of expected consistency in preparation and analysis inherent in samples treated by one lab. Further, their CO_2 samples for $\delta^{13}C$ analysis are routinely taken after quantitative combustion, and should therefore provide high assurance of being representative of the original organic matter. Figure 4 depicts all plant data (including peat, charcoal, wood and twigs) along with 5- and 11-point running averages. Despite the paucity of data prior to 30 ka BP, $\delta^{13}C$ gradually rises to *ca.* 22 ka BP, and declines after *ca.* 12 ka BP. Pre- and post-10 ka BP means are again statistically different by *ca.* 1.0‰ (Table 1).

Unlike wood samples from *RADIOCARBON*, the Arizona Laboratory data show no significant difference in post- and pre-10 ka BP values of wood. *Juniperus* samples (primarily twigs and leaves), nearly exclusively from packrat middens of the American Southwest, are plotted separately (Fig. 5). The pre-10 ka BP average is significantly heavier than the post-10 ka BP average by *ca.* 0.4‰, and the pre-10 ka BP trend, on average, is fairly flat back to 30 ka BP.

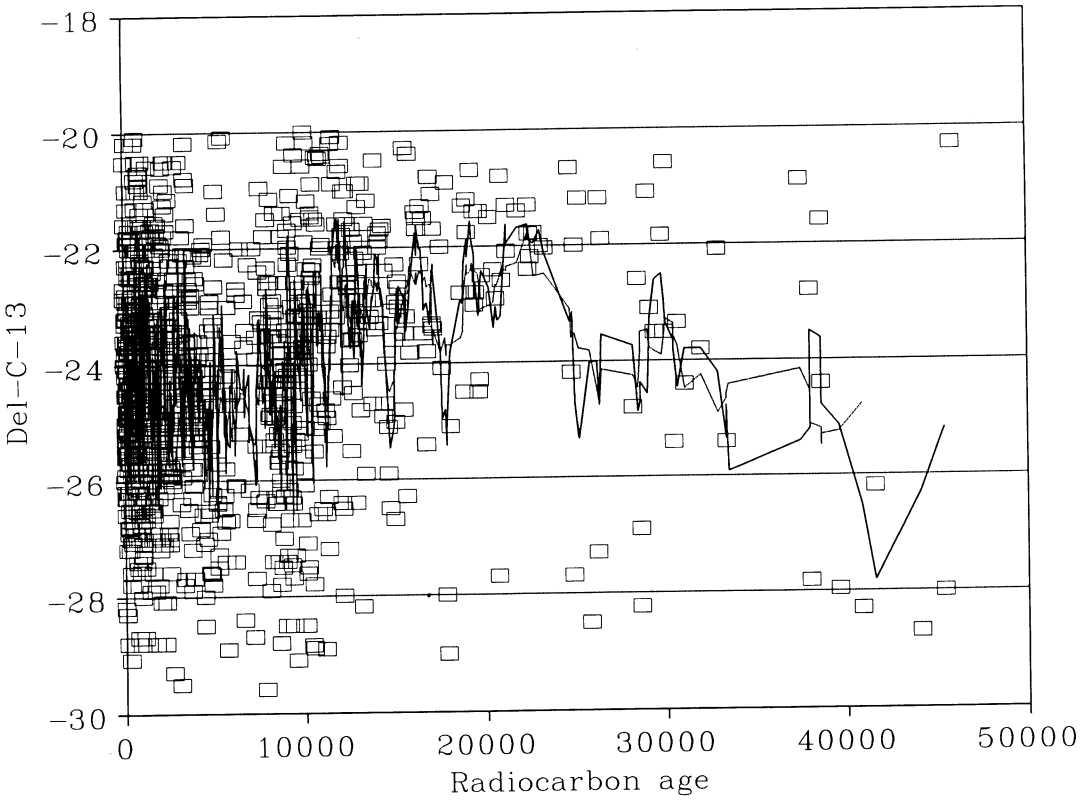

Fig. 4. $\delta^{13}C$ values for all plant categories tabulated from data of the University of Arizona Radiocarbon Laboratory. Lines are 5- and 11-point running means.

TABLE 1. Comparison of Pre- and Post-10 ka BP $\delta^{13}C$ Values

Material	Post-10 ka BP(n) (‰)	Pre-10 ka BP(n) (‰)	Difference (‰)	t-test significance
Radiocarbon Data Set				
Charcoal	−24.40 (127)	−24.10 (129)	−0.3	ns
Peat	−27.60 (103)	−27.90 (43)	−0.3	ns
Wood	−27.1 (192)	−24.1 (114)	3.0	<.001
All data	−25.80 (525)	−25.0 (296)	0.8	<.01
University of Arizona Data Set				
Charcoal	−24.60 (357)	−24.55 (27)	0.05	ns
Leaves	−23.19 (12)	−21.75 (7)	1.44	<.01
Peat	−27.08 (51)	−26.68 (16)	0.40	ns
Plant frag.	−23.70 (208)	−23.30 (75)	0.40	ns
Twigs	−23.08 (37)	−22.22 (82)	0.86	<0.02
Wood	−24.44 (142)	−24.66 (32)	−0.22	ns
*Juniperus**	−22.41 (55)	−21.97 (98)	0.44	<.05
All data	−24.40 (823)	−23.41 (244)	0.99	<.01

*This includes genus-specific data for other categories such as wood, needles, leaves, plant fragments.

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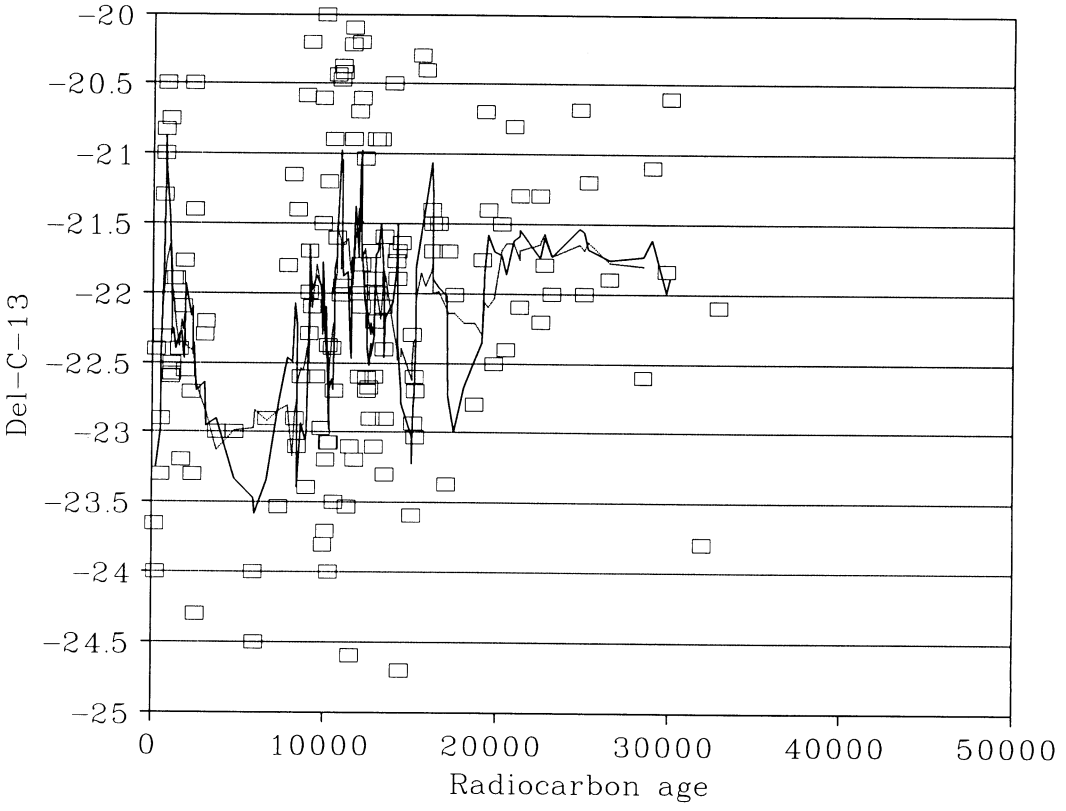

Fig. 5. $\delta^{13}C$ values for *Juniperus* data from the Arizona Laboratory. Lines are 5- and 11-point running means.

Perhaps the most interesting test was the analysis of old wood from a relatively limited geographic area (Fig. 1) with maximum elevational differences of *ca.* 60–70 m. The raw $\delta^{13}C$ results on cellulose from four trees at each site are listed in Table 2 and plotted in Figure 6. Scatter among trees at each site is *ca.* 1–2‰. Notably, the Two Creeks and Green Bay spruces have nearly identical means, yet are distinguished from the Liverpool site of the same age by *ca.* 2‰. The latitude coefficient of 0.16‰ °latitude^{-1} of Stuiver and Braziunas (1987) would actually predict that the lower

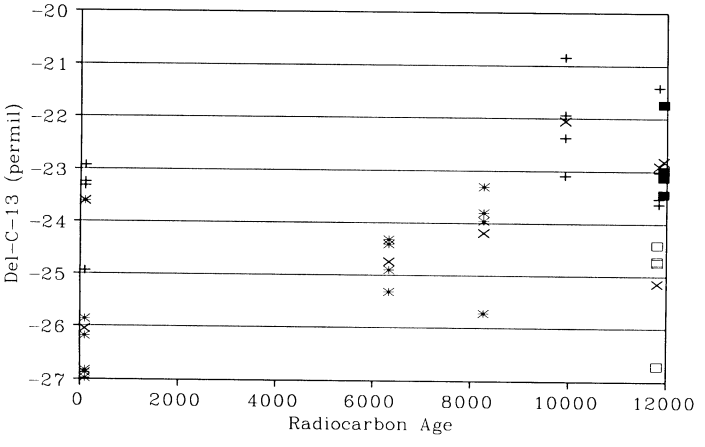

Fig. 6. $\delta^{13}C$ of wood from six buried forest localities and a modern site. Site locations and abbreviations are shown in Figure 1, and site ages are given in text. ■ = GB spruce; + = TC, UP, PB spruce; ✳ = LM, SP, PB hardwoods; □ = LS spruce; × = averages.

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TABLE 2. Characteristics of Wood Samples from Great Lakes Sites

Sample	No. of rings	Diameter (cm)	Species	$\delta^{13}C$ (‰)
Southport				
SP-20	*Ca.* 50	*Ca.* 7	Oak	−25.32
SP-21	72	5.6	Hickory	−24.42
SP-33	22	3.7	Oak	−24.32
SP-35	*Ca.* 27	*Ca.* 6	Hickory or ash	−24.90
Olson				
LM-128	117	13.5	Hickory	−23.80
LM-56	69	16.0	Ash	−23.31
LM-126	65	8.5	Oak	−25.73
LM-57	73	23	Oak	−23.97
Liverpool				
LS-44	23+	7.5	Spruce	−24.41
LS-46	24	7.0	Spruce	−24.72
LS-45	56	11.5	Spruce	−24.75
LS-47	48	10.7	Spruce	−26.72
Green Bay				
GB-107	*Ca.* 65	9.0	W. spruce	−22.99
GB-109	57	7.7	W. spruce	−23.44
GB-118	97	8.2	W. spruce	−21.74
GB-120	*Ca.* 80	8.2	W. spruce	−23.12
Two Creeks				
TC-38	*Ca.* 150	11.5	W. spruce	−23.63
TC-73	*Ca.* 171	14.0	W. spruce	−23.53
TC-85	*Ca.* 150	13.0	W. spruce	−23.02
TC-86	*Ca.* 135	8.0	W. spruce	−21.43
Gribben Basin				
UP-101	102	8.6	W. spruce	−20.85
UP-102	82	16.2	W. spruce	−21.95
UP-103	82	12.0	W. spruce	−23.10
UP-104	105	*Ca.* 13	W. spruce	−22.37
Point Beach				
PB-1 (4 cores)	24	11.3	W. spruce	−23.26
PB-2 (4 cores)	20	8.7	W. spruce	−24.95
PB-3 (4 cores)	21	17.8	W. spruce	−23.32
PB-4 (4 cores)	*Ca.* 22	11.5	W. spruce	−22.90
PB-10	17	5.8	Oak	−26.20
PB-11	18	4.5	Basswood?	−25.87
PB-12	36	7.8	Basswood?	−23.62
PB-13	31	6.2	Oak	−26.83
PB-14	*Ca.* 23	6.3	Poplar	−26.98
PB-15	44	10.7	Oak	−26.87

latitude Liverpool site should be *ca.* 0.3‰ heavier than the Two Creeks site. However, the Two Creeks and Green Bay sites were relatively close to a glacier that eventually overrode them, whereas the Liverpool site remained hundreds of kilometers south of the farthest glacial extent, so that the great difference may be attributable to unusual (dry?) climatic conditions at those northerly sites. For the modern trees from Point Beach, the hardwood mean is *ca.* 2.5‰ lighter than that of conifers with minor overlap of values, quite comparable to the average difference between these wood groups found by Stuiver and Braziunas (1987) of 3.0‰.

Because of this *ca.* 2.5‰ species difference, we have chosen to look simply for $\delta^{13}C$ trends in the spruce and hardwood results separately. Before considering trends, however, another potentially important problem with which to contend is that of the so-called "juvenile" effect, when tree rings tend to be $\delta^{13}C$-depleted in the early life of many trees (Francey & Farquhar 1982). The reported magnitude of this effect of increasing $\delta^{13}C$ in early rings ranges from *ca.* 1.4‰ over the first 30 years of Douglas fir and chestnut (Freyer 1979) to *ca.* 2‰ over the first 150 years of sequoia (Craig 1954). Of the pinyon pine reported by Leavitt & Long (1988), about half did not show a noticeable juvenile effect, and the others showed increases of 1–1.5‰ over the first 25–40 years. Because of the variable ages of the trees, this effect is plausible, but its presence in these trees is far from certain. For example, the youngest tree (22 yr) at the Southport site (SPSL-33) has the heaviest $\delta^{13}C$, whereas the second oldest has the lightest. Likewise, the youngest tree from the Two Creeks site (TCSL-86) is isotopically the heaviest. Further, $\delta^{13}C$ isotope time series developed from tree rings of Two Creeks trees (Leavitt & Kalin 1992) generally do not show a juvenile effect. Because of these uncertainties, we have not included a correction for juvenile effect in this treatment.

For hardwoods, if *ca.* 1‰ is added to the Point Beach hardwood mean to correct it back to a preindustrial value (Friedli *et al.* 1986), and if the Southport and Olson means are normalized to the latitude of Point Beach with the Stuiver-Braziunas coefficient, then the fully normalized mean $\delta^{13}C$ values for Point Beach, Southport and Olson are *ca.* −25.1, −25.0 and −24.5‰, respectively. Thus, changes in these hardwoods over the past 8200 years appear to be minor. Applying the same +1‰ correction to the Point Beach spruce mean, and a +0.32‰ correction to the Gribben Basin (UP) mean to normalize it to the Two Creeks latitude, the normalized mean $\delta^{13}C$ for Point Beach spruce, Gribben Basin and Two Creeks are *ca.* −22.6, −21.8 and −22.9‰, respectively. Again, this represents a very limited $\delta^{13}C$ change in these trees over the past 12 ka BP. In this case, however, the large $\delta^{13}C$ difference between Liverpool and Two Creeks suggests we may not have adequately accounted for severe environmental effects on the older northernmost sites.

Conclusions

We have examined three $\delta^{13}C$ data sets, each with its own qualities, but none without potential complications. Despite much scatter, the full plant data sets from *Radiocarbon* and the Arizona ^{14}C Laboratory both show a statistically significant mean $\delta^{13}C$ difference from pre- to post-10 ka BP. This displacement is not universal, because no similar significant decline is observed in peat or charcoal, and although a strong $\delta^{13}C$ decline is seen in the *Radiocarbon* data of wood only, no such significant change occurs in the Arizona wood data. The pattern of change observed in the *Radiocarbon* wood data, however, is similar to the change reported by Krishnamurthy and Epstein (1990). General problems with the *Radiocarbon* and/or Arizona data include mixing of latitudes, altitudes, species, plant organs, species, *etc.* Where only material of the genus, *Juniperus,* was examined from the Arizona data, we found a significant decline of *ca.* 0.4‰.

For a set of wood samples spanning the last 12 ka from one region (Great Lakes), the cellulose values suggest a lack of environmentally induced $\delta^{13}C$ change. Perhaps the biggest problem of interpretation is accounting for the influence of severe climate effects, *e.g.*, dry air associated with nearby continental glaciers that may have caused inordinately isotopically heavy cellulose at the Gribben Basin and Two Creeks sites.

In summary, no uniformly consistent pattern of $\delta^{13}C$ change in plants emerges, but where there is change, it appears to occur between *ca.* 15 ka and 10 ka BP. There is no evidence that the observed changes are artifacts of the data sets. Further planned research includes examination of the high-frequency fluctuation of all plots to determine synchroneity, and isotopic analysis of additional wood samples.

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