

**TRENDS OF  $^{13}\text{C}/^{12}\text{C}$  RATIOS IN PINYON TREE RINGS OF THE  
AMERICAN SOUTHWEST AND THE GLOBAL CARBON CYCLE**

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**ABSTRACT.** An accurate atmospheric  $^{13}\text{C}/^{12}\text{C}$  chronology can provide important constraints to models of the global carbon cycle. Trees accumulate carbon from atmospheric  $\text{CO}_2$  into growth rings and offer potential for  $^{13}\text{C}/^{12}\text{C}$  reconstructions, but results have not been reproducible. This paper presents  $\delta^{13}\text{C}$  curves from 5 sites, representing 20 pinyon (*Pinus edulis*) trees, where cores of 4 trees from each site have been pooled into a composite sample. Isotopic analysis of cellulose in 5-yr ring groups produces curves with a general trend of decreasing  $\delta^{13}\text{C}$  after 1800, but with pronounced short-term fluctuations superimposed upon the trend. Evidence indicates the fluctuations are strongly related to moisture availability (drought). A mean curve of the 5  $\delta^{13}\text{C}$  chronologies from which the fossil-fuel component is subtracted suggests a substantial biospheric  $\text{CO}_2$  contribution to the atmosphere since 1800.

INTRODUCTION

One of the important questions regarding the functioning of the global carbon cycle is whether fossil fuels have been the only source of excess  $\text{CO}_2$  contributing to the rise in atmospheric concentration. A net biospheric source in addition to fossil fuels would substantiate the extent of human impact on the biosphere (including soils) and would necessitate adequate sinks in the carbon cycle to accommodate this excess. A chronology of  $^{13}\text{C}/^{12}\text{C}$  ratios of atmospheric  $\text{CO}_2$  could help resolve this question because this ratio changes in response to inputs (or removal) of fossil-fuel and biospheric carbon. The fossil-fuel contribution can be differentiated on the basis of its "dilution" effect on atmospheric  $^{14}\text{C}$  activity, so that a residual  $^{13}\text{C}/^{12}\text{C}$  record representing biospheric activity can be isolated (Peng *et al*, 1983; Stuiver, Burk & Quay, 1984).

Although such an atmospheric  $^{13}\text{C}/^{12}\text{C}$  chronology is not available, isotopic measurements on tree rings are being studied as proxy indicators of these changes. Interferences such as climate effects, local pollution, local respired  $\text{CO}_2$  contributions, and natural variation of  $^{13}\text{C}/^{12}\text{C}$  ratios within and among individuals, however, may account for the non-concordant results generated in several studies (summary in Peng *et al*, 1983). Our research focuses on developing chronologies which account for the influences of these factors, especially climate, and we have previously reported results from individual juniper (Leavitt & Long, 1983) and pinyon (Leavitt & Long, 1985) trees collected at sites in Arizona. After recently demonstrating the value in pooling core samples from more than a single tree per site (Leavitt & Long, 1984), we now sample additional pinyon sites with greater density. This report contains results from 5 pinyon sites in the American Southwest which have been sampled to this greater depth so that 20 trees are effectively represented in this study.

## MATERIALS AND METHODS

During the summer of 1983 we sampled pinyon at 5 sites in rural areas of Utah, Colorado and New Mexico (Fig 1). The site elevations include 1965m (Kane Spring), 2080m (Aztec), 2150 (Dry Canyon), 2245 (Alton) and 2375 (Lower Colonias). The topography varied from site to site, but all were fairly typical pinyon-juniper, open-canopy-type woodlands. Where possible, isolated individuals were selected.

In an attempt to accurately represent the  $^{13}\text{C}/^{12}\text{C}$  trend and absolute values of all trees at the site, we employed pooling of samples (Leavitt & Long, 1984). We took 4 orthogonal increment cores from each of 8–12 trees within an area of typically 2–3ha. The Laboratory of Tree-Ring Research performed the dating of these cores, after which the 4 “best” trees were selected on the basis of the total length of tree-ring record, the number of missing rings, the relative isolation of the individual, etc. The final sample from each site thus contains 16 cores: 4 cores from each of 4 trees.

The cores were split into 5-yr ring groups and ground to 20 mesh. Conversion to cellulose resulted after several steps in a process modified after Green (1963). First, soxhlet extraction of the wood with 2:1 toluene-

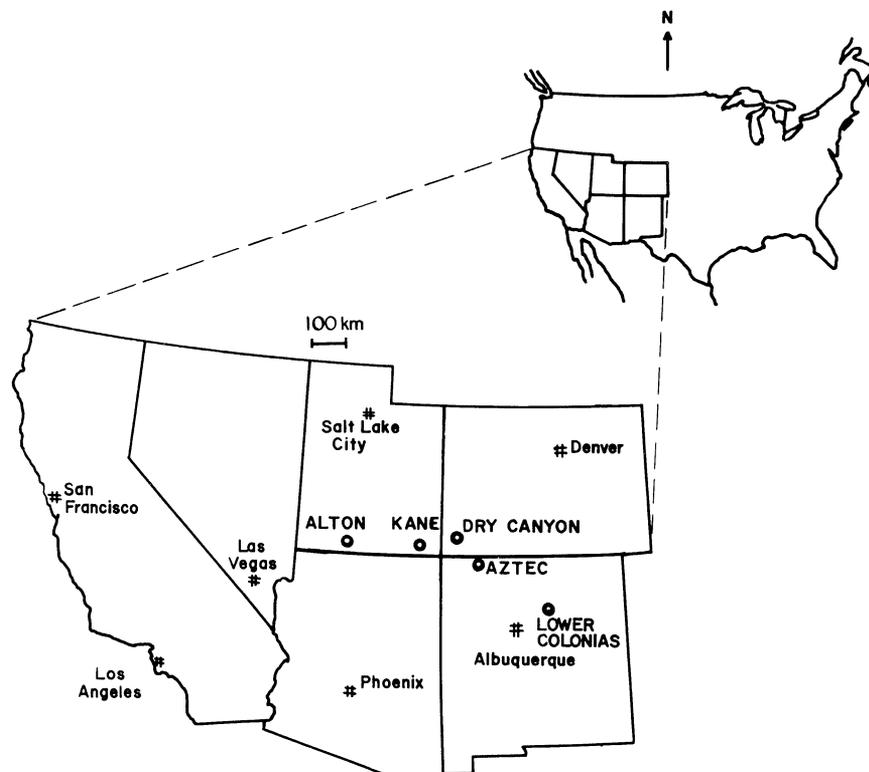


Fig 1. Location map of the 5 pinyon sites sampled in this study

ethanol followed by 100% ethanol removes oils and resins. Next, a solution of hot (70°C), acidified sodium chlorite solution decomposes lignin until a residual cellulose (holocellulose) remains. Combustion of cellulose at 800°C in the presence of oxygen within a recirculating microcombustion line provides CO<sub>2</sub> for isotopic analysis. The CO<sub>2</sub> sample is dried cryogenically (cold ethanol, -80°C) and collected with liquid nitrogen. Following mass-spectrometric analysis of the CO<sub>2</sub>, the <sup>13</sup>C/<sup>12</sup>C ratios are expressed as δ<sup>13</sup>C values (per mil units) with respect to the PDB calcite standard after the procedures of Craig (1957). Reproducibility tests suggest the overall precision for cellulose preparation, sample combustion, and isotopic analysis is ca ± 0.1‰.

#### RESULTS AND DISCUSSION

Figure 2 contains the δ<sup>13</sup>C curves from each site. The longest records, Alton and Kane Spring, extend back nearly 500 yr. The curves are far from "smooth" but rather show trends of decreasing δ<sup>13</sup>C (especially post-1800) upon which are superimposed short-term fluctuations. One of the remarkable features of these fluctuations is that they frequently appear synchronous from site to site, eg, the minima at 1825-29 and 1840-44, and the abrupt δ<sup>13</sup>C drop from 1675-79 to 1680-84. Such consistent behavior of tree-ring δ<sup>13</sup>C time series has already been reported between widely separated pinyon individuals (Leavitt & Long, 1985), and found inversely correlated to 5-yr mean standardized ring-thickness indices. Because dendro-

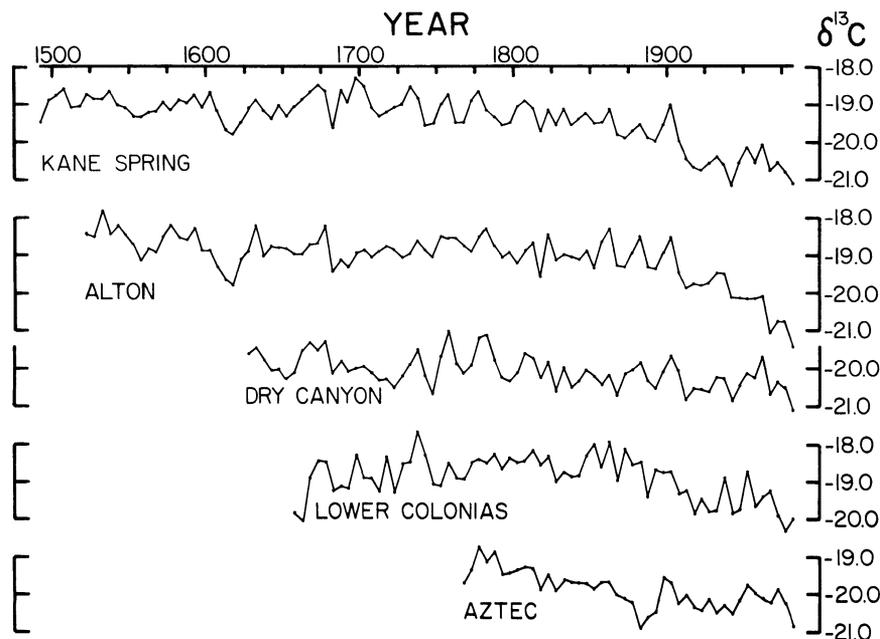


Fig 2. The δ<sup>13</sup>C curves from the 5 sites each derived from analysis of a composite sample produced by pooling 4 cores from each of 4 trees

climatology employs these ring indices for climate reconstruction, the isotopic fluctuations may also be linked to climate. The inverse ring index- $\delta^{13}\text{C}$  relation indicates that narrow rings (reduced growth due to low moisture and/or high temperature) have high  $\delta^{13}\text{C}$  values and wide rings have low  $\delta^{13}\text{C}$ .

The mechanism for this relationship may be contained in the plant carbon isotope fractionation model of Francey and Farquhar (1982):

$$\begin{aligned} \delta_{\text{plant}} &= \delta_{\text{atmosphere}} - a - (b - a) C_i/C_a \\ &\text{and} \\ C_i &= C_a - A/g, \end{aligned}$$

where  $C_i$  and  $C_a$  are internal plant and external atmospheric  $\text{CO}_2$  concentrations, respectively,  $a$ ,  $b$  are constants related to fractionation within the plant,  $A$  is the rate of assimilation of  $\text{CO}_2$ , and  $g$  is stomatal conductance for  $\text{CO}_2$ .

By this model, the positive deviations above the mean trend of the  $\delta^{13}\text{C}$  curves (Fig 2) imply that assimilation ( $A$ ) is high and/or conductance ( $g$ ) is low. Because the positive  $\delta^{13}\text{C}$  deviations occur in those years when the rings are relatively narrow, low conductance is more likely than high assimilation, implying some type of drought condition in which stomata are closed more frequently due to moisture stress. During years when assimilation is low and/or conductance is high, the  $\delta^{13}\text{C}$  curve deviates below the mean trend. Again, in this case the relatively large rings indicate assimilation is high so that it must be increased stomatal conductance which dominates to produce the lower  $\delta^{13}\text{C}$  values.

Verification of such a drought- $\delta^{13}\text{C}$  relationship requires a more direct drought parameter than ring thickness. Such parameters might include Palmer's (1965) drought severity index (PDSI) which measures moisture abnormality in terms of meteorologic drought and Palmer's (1965) hydrologic drought index (PHDI). We used PHDI in this analysis because PHDI reflects soil moisture whereas PDSI deals more with classification of weather. Karl (1983) describes in greater detail differences between hydrologic and meteorologic drought. PHDI values are available from the National Climatic Center, Asheville, North Carolina, for each month from 1931 through present. The climate data used to calculate the PHDI's are averaged over a region so that generally these indices in the southwestern US represent an area of several thousand  $\text{km}^2$ . PHDI values become increasingly negative with increasing drought severity, and more positive with moisture excess.

The 5 pinyon sites each fall into a different region for which PHDI's have been tabulated. We calculated 5-yr mean PHDI's from the monthly values and compared them with  $\delta^{13}\text{C}$  curves of the corresponding site. Figure 3 illustrates a striking inverse relationship between  $\delta^{13}\text{C}$  of the Kane Spring site and PHDI from the southwest Utah region ( $r = -0.93$ ). Correlations for the other pinyon sites with their respective regional PHDI were not as pronounced (Alton,  $r = -0.50$ ; Dry Canyon,  $r = -0.47$ ; Lower

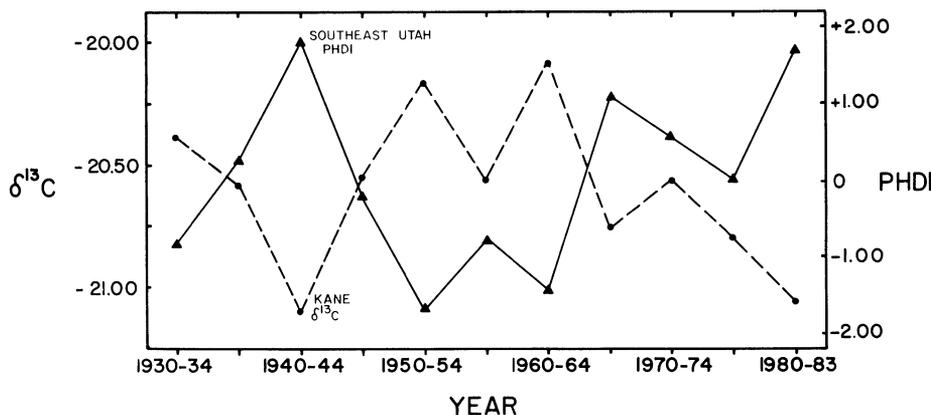


Fig 3. Plot of Kane Spring  $\delta^{13}\text{C}$  data (●) and the 5-yr mean Palmer hydrologic drought indices (PHDI) (▲) for the post-1930 period. The first point on the PHDI curve is actually 1931–34 and the last point is 1980–82.

Colonias,  $r = -0.10$ ; Aztec,  $r = -0.84$ ). Only the Kane Spring and Aztec correlations were significant at 95%. However, when first differences of  $\delta^{13}\text{C}$  and PHDI were correlated at each site, all relationships were significant at 95% or better except that for Dry Canyon (Kane Spring,  $r = -0.91$ , Alton,  $r = -0.75$ , Dry Canyon,  $r = -0.60$ ; Lower Colonias,  $r = -0.62$ ; Aztec,  $r = -0.77$ ). Thus a clear relationship between  $\delta^{13}\text{C}$  fluctuations and moisture conditions for these southwestern US sites emerges. However, it would be inappropriate to attribute the long-term decreasing  $\delta^{13}\text{C}$  trend at each site to this moisture effect, because that would imply the unlikely occurrence of decreasing drought frequency (increasing PHDI's) from ca 1800 to present.

Figure 4 contains the average  $\delta^{13}\text{C}$  curve for the 5 sites (upper curve). This has been calculated after first normalizing each curve to a sequence of differences from its respective pre-1830 mean  $\delta^{13}\text{C}$ . The vertical bars represent the scatter ( $\pm 1\text{s}$ ) among normalized values of the 5 sites. This curve shows a substantial  $\delta^{13}\text{C}$  drop of ca 1.5‰, higher than the ca 1‰ drop found by Stuiver, Burk & Quay (1984), but lower than the ca 2‰ drop determined mainly in European trees by Freyer & Belacy (1983). The middle curve in Figure 4 represents the fossil-fuel  $\delta^{13}\text{C}$  contribution to the atmosphere as modeled by Peng *et al* (1983). Subtraction of this fossil-fuel contribution from the upper curve yields the lower residual curves (unsmoothed and smoothed). Assuming the upper curve represents a chronology of changes in atmospheric  $\delta^{13}\text{C}$ , then the lower curve reflects the biospheric  $\text{CO}_2$  contribution to the atmosphere, presumably derived mainly through land-use changes. The smoothed, 5-yr running mean residual curve suggests biospheric contributions beginning near 1800 but with the largest contribution occurring at the beginning of the 20th century. This latter change, however, may in part reflect climate-induced  $\delta^{13}\text{C}$  changes in the transition from drought-dominated pentads 1895–99 and

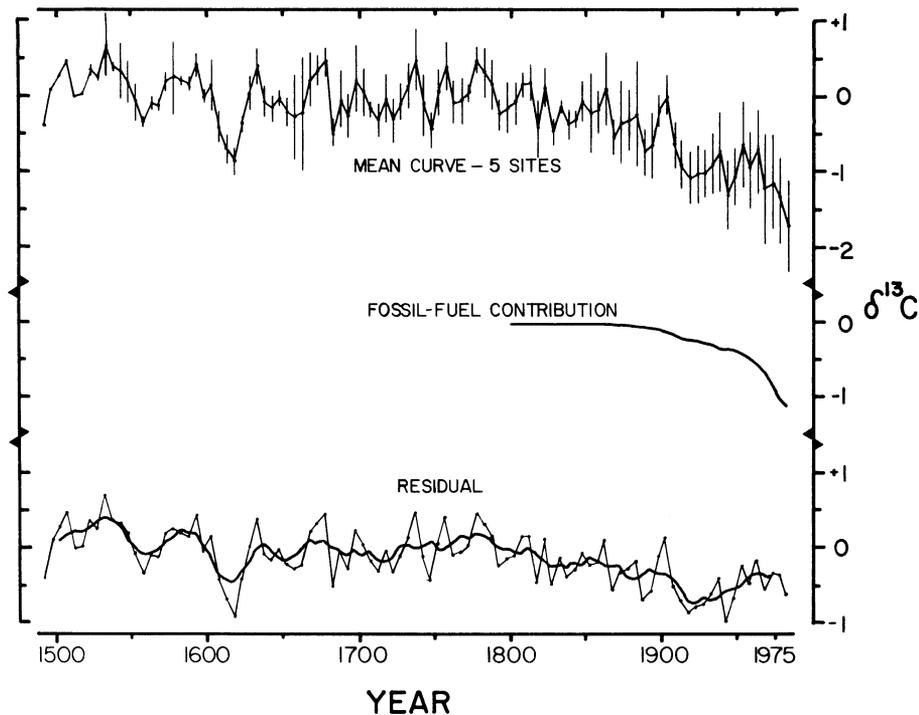


Fig 4. The mean  $\delta^{13}\text{C}$  curve from the 5 sites (upper curve), the portion of atmospheric  $\delta^{13}\text{C}$  trend attributed to fossil-fuel consumption (middle curve after Peng *et al*, 1983), and the residual difference representing apparent biospheric activity (lower curves, unsmoothed and smoothed)

1900–04 (narrow rings) to the more favorable growth pentad of 1905–09. The biospheric contribution appears to be about half the size of that calculated by Peng *et al* (1983) of 264 GT carbon.

#### CONCLUSIONS

Each new  $\delta^{13}\text{C}$  chronology from tree rings offers hope that the atmospheric trend will be accurately reproduced. The primary new feature of this study is that the  $\delta^{13}\text{C}$  of each tree is accurately represented by taking 4 orthogonal cores, and the  $\delta^{13}\text{C}$  of each site is accurately determined by pooling cores from 4 trees. Thus, there is a high degree of confidence that the site  $\delta^{13}\text{C}$  trends are representative of the overall site.

The similarity of chronologies among sites is embodied in the numerous short-term fluctuations that they have in common, and the decreasing post-1800  $\delta^{13}\text{C}$  trends. However, the similarity in the short-term fluctuations does not appear to be a common response to changes in atmospheric  $\delta^{13}\text{C}$ , but rather they appear climatically induced and strongly related to drought as represented by Palmer's hydrologic drought indices. This find-

ing offers potential for developing long drought chronologies from tree-ring  $\delta^{13}\text{C}$  measurements in the southwestern U S.

Although the  $\delta^{13}\text{C}$  trends are all decreasing, they decrease various absolute amounts and in different fashions. They cannot all be atmospheric trends, so we are now examining ring areas and standardized ring thickness indices for evidence as to why they differ. Taking the mean of the 5 sites, the record indicates a biospheric contribution intermediate between that found by Stuiver, Burk & Quay (1984) and that of Peng *et al* (1983). A major biospheric input ca 1900 appears consistent with the Peng *et al* (1983) results, but again we have yet to apply climate corrections as related to standardized ring indices. We are currently at various stages in processing 5 more pinyon sites in order to produce a 10-site network over a much wider area of the Southwest. We then hope to smooth out the  $\delta^{13}\text{C}$  fluctuations by accounting for the influence of drought by using ring-width indices in lieu of PHDI values which are only available for the last 50–100 years.

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