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An atmospheric $^{13}C/^{12}C$ reconstruction generated through removal of climate effects from tree-ring $^{13}C/^{12}C$ measurements

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ABSTRACT

An accurate reconstruction of past $^{13}C/^{12}C$ ratios of atmospheric CO_2 may provide key constraints on the historical activity of the biosphere as CO_2 source or sink. Tree rings appear to be a repository of this information but there is much noise in the collection of previous reconstructions, presumably associated with site selection, radial variability, choice of representative wood chemical constituent, and subtle effects of climate on fractionation. This study attempts to avoid these pitfalls and develop a 50-yr $\delta^{13}C_{ATM}$ record from juniper trees (genus *Juniperus*), in fact, by taking advantage of the influence of climate on fractionation. Trees were harvested from suitable sites in close proximity to weather stations with monthly records of temperature and precipitation, and ring material was separated from the sections in 5-year intervals around their full circumference. From each interval, relationships of $\delta^{13}C$ of the cellulose fraction with mean December temperature or precipitation of the respective sites emerged, showing nearly constant slopes from one interval to the next (averaging $-0.27‰$ °C^{-1} for temperature and $-0.04‰$ mm^{-1} for precipitation) but with different intercepts. The separation of these regression lines of different intervals is interpreted as the response of the trees to the changing $\delta^{13}C$ of atmospheric CO_2 so that $\delta^{13}C_{ATM}$ curves are constructed from this spacing.

The shape of the best-fit reconstruction suggests the biosphere has acted as a CO_2 source to about 1965 but has become a sink afterward. Although there are several recent studies whose results are compatible with this interpretation, the assumptions and statistical considerations in this study would still allow an exponentially decreasing curve through the data points from 1930–1979 and therefore, other interpretations are not excluded.

1. Introduction

Several types of historical information and observational data contribute to our understanding and modeling of the global carbon cycle, including fossil-fuel production, carbon-14 measurements in tree rings, direct P_{CO_2} measurements and $^{13}C/^{12}C$ ratios in tree rings. This last set of observations shows the greatest variability, but as a proxy record for $^{13}C/^{12}C$ ratios in the atmosphere it would be an important key to constraining carbon-cycle interpretations, particularly with regard to the role of the biosphere (Stuiver, 1978; Broecker et al., 1979). Much of the noise in these tree-ring $^{13}C/^{12}C$ reconstructions must be attributable to such factors as local pollution (Freyer, 1979b; Francey, 1981b), the "canopy" effect of respired CO_2 from neighboring biomass on a tree especially in the early stages of growth (Craig, 1954; Freyer, 1979a), choice of wood constituent for analysis (Tans and Mook, 1979), isotopic variation from one radius to another (Tans and Mook, 1979; Mazany et al., 1980), and climate effects on fractionation as carbon is fixed in the plant (see summary of coefficients in Long, 1982).

Our goal in the initial stage of research just completed was to generate a tree-ring $\delta^{13}C$ record relatively free of these effects. Notably, we took advantage of a relationship between $\delta^{13}C$ and climate parameters to generate a climate-free $\delta^{13}C$

Table 1. *Post-1930 changes in $\delta^{13}C$ derived from tree-ring studies*

Source	Trees (No.)	Location	Material*	Length of Record	Net $\delta^{13}C$ Change	General Trend
Francey (1981a)	2 species (7)	Tasmania	cell.	1930-1970	0 ‰	
Rebello and Wagener (1976)	Araucaria (1, 2 sections)	Brazil	cell. cell.	1930-1968 1930-1972	-0.8 -0.5	
Galimov (1976)	spruce (2)	USSR	ww	1930-1963	+1.3	
Farmer and Baxter (1974)	oak (1) larch (1)	England Scotland	ww ww	1930-1964 1930-1969	-0.9 +0.4	
Tans (1978)	3 species (4)	Netherlands	AAA	1930-1970	+0.7	
Farmer (1979)	elm (1)	Massachusetts	ww	1930-1968	+1.0	
Freyer (1979a)	13 species (26)	Europe, Azores, North Carolina	cell.	1930-1974	-0.8	
Pearman, Francey and Fraser (1976)	King Billy pine (2)	Tasmania	ww	1930-1970	+0.4	
Lerman (1974)	poplar (1)	Norway	AAA	1930-1951	-0.8	
Libby and Pandolfi (1974)	oak (1)	Germany	ww	1930-1950	+3.0	
Grinsted (1977)	bristlecone pine (1)	California	cell.	1930-1967	-0.02	
Lerman and Long (1980)	ponderosa pine (1)	Arizona	cell.	1930-1965	+1.0	
Dequasie and Grey (1971)	poplar	Utah	ww	1930-1965	-1.0	
Harkness and Miller (1980)	Norwegian pine (1)	Norway	cell.	1930-1970	-0.6	

*cell.=cellulose; ww=whole wood; AAA=acid-alkali-acid pretreatment.

reconstruction. This initial 50-year $\delta^{13}C$ record for the period 1930–1979 sheds new light on the conflicting 20th century $\delta^{13}C$ results from tree rings, summarized for the post-1930 period in Table 1.

2. Sampling and analysis

The foundation of this research was based upon the results of Arnold (1979) who found $\delta^{13}C$ of cellulose in juniper leaves was strongly correlated with the climate (temperature, precipitation) of the sites where they were sampled. Given such a $\delta^{13}C = f(\text{climate}) + C$ relationship, if the $f(\text{climate})$ portion remains constant in time then its position in space, represented by C, should change in response to changes in $\delta^{13}C$ of the tree's carbon source, i.e., the atmospheric reservoir. We chose to test this scheme using tree rings in order to track the relationship back into time. Because the leaf regressions were developed from juniper leaves in Arizona, this initial experiment was also conducted with juniper trees from Arizona.

We sampled 10 sites from Arizona (Fig. 1) at the end of the 1979 growing season, some duplicating locations where Arnold (1979) had sampled leaves. The samples represent a variety of elevations and a range of mean temperature and precipitation (Table 2). Although different species of juniper were harvested, Arnold (1979) had demonstrated no significant $\delta^{13}C$ differences in leaves of different juniper species at the same site. Samples were taken from open sites in rural localities in an effort to avoid major automotive and industrial influence. As discussed in the following section, however, difficulties in extending the analysis to all 10 sites may evidence the influence of mining and smelting

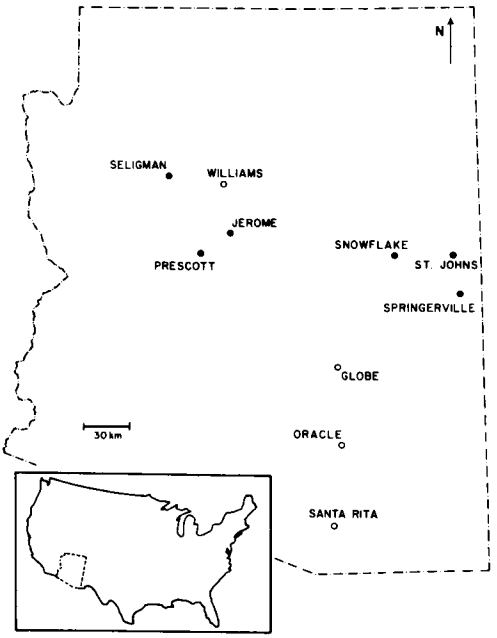

Fig. 1. Map of juniper sampling sites. Sites with open circles may be influenced largely by local effects (see text).

activities in the southern part of Arizona. The chosen sites were close to weather stations where representative climate data for 50 years could be obtained (Table 2). In fact, this proximity of sampling sites to weather stations is closer than any other $\delta^{13}C$ tree-ring study to date. Because of our interest in climate influence on tree $\delta^{13}C$, additional care was taken to avoid sampling sites which might experience microclimate other than that recorded at the weather stations, e.g., sites affected by cold-air drainage or sites where trees had access to near-surface groundwater thus decreasing the influence of precipitation.

Those individual trees selected were cut down to obtain complete sections from near the base of the tree. The sections were sanded smooth to bring out the ring pattern and dating was performed under the direction of Jeffrey S. Dean of the Laboratory of Tree-Ring Research at the University of Arizona. Because only the Prescott tree cross-dated, ring counting was necessary to date the other sections so that their dating is not absolute and errors of a few years are possible. Comparison of characteristics of the Prescott $\delta^{13}C$ trend with that of other trees, however, confirmed the general accuracy of the ring counting.

The tree rings were separated into 5-year intervals and milled from the full circumference of each of the sections. In this manner, the isotopic bias of a single radius was avoided. From this wood, cellulose was isolated in a method modified after Green (1963). Resins and oils were first removed with toluene/ethanol in a soxhlet extraction apparatus. This treatment was followed by bleaching of the material in an acidified, sodium chlorite solution.

Cellulose was converted to CO_2 in a microcombustion system. The CO_2 was analyzed in a Micromass 602C mass spectrometer and $\delta^{13}C$ was calculated with respect to the PDB standard (Craig, 1957). Repeated combustions of a cellulose

Table 2. *Tree and site characteristics of juniper sampling localities*

Site	Elevation	Species	Ring-counted age	Distance to weather station	Mean annual temp.	Mean annual precip.
Globe	1195 m	*Juniperus monosperma*	120	6.7 km	16.5°C	40.7 cm
Jerome	1845	*J. monosperma*	145	3.3	15.2	45.8
Oracle	1450	*J. deppeana*	145	1.2	16.7	51.9
Prescott	1705	*J. deppeana*	104*	5.8	11.7	48.6
St. Johns	1790	*J. monosperma*	380	5.0	11.7	27.9
Santa Rita	1370	*J. deppeana*	100	0.4	17.6	52.5
Seligman	1605	*J. osteosperma*	105	1.7	12.1	28.5
Snowflake	1735	*J. monosperma*	145	2.5	10.9	30.7
Springerville	2315	*J. monosperma*	380	6.7	9.2	30.4
Williams	2055	*J. osteosperma*	85	5.0	9.6	53.7

* Cross-dated age.

standard over several months indicated a precision of combustion and analysis of $\pm 0.1‰$.

3. Results

3.1. *The general $\delta^{13}C$ trends*

After the initial $\delta^{13}C$ analysis of the rings from all ten juniper sections, it became clear that all do not exhibit the same trend. Six of the stations (Jerome, Prescott, St. Johns, Seligman, Snowflake, Springerville) all show various degress of an overall decreasing $\delta^{13}C$ trend. The others show a generally flat $\delta^{13}C$ trend (Globe, Santa Rita, Williams) or an increasing $\delta^{13}C$ trend (Oracle) over the past 50 years. Because these non-decreasing trends are also reflected in cores from neighboring trees, this phenomenon appears to be related to the whole site and not simply to anomalous individuals. Some evidence indicates that these trends may manifest a local pollution effect in that three of these sites (Globe, Oracle, Santa Rita) are in the vicinity of copper-mining operations which require fossil fuels for their smelting and calcining activities. In addition to CO_2 from the fuels ($\delta^{13}C \leq -25‰$), a heavy CO_2 ($\delta^{13}C \simeq 0‰$) will also be released during calcining of limestone to lime, and SO_2 may additionally be released from the sulfide ores. This heavy CO_2 from calcining could counteract the downward global $\delta^{13}C$ trend, and experiments by Freyer (1979b) indicate that SO_2 may induce higher than normal $\delta^{13}C$ values in plants. The Oracle tree, which is closest to a copper smelter (12 km), actually shows a marked $\delta^{13}C$ increase approximately coincident with the opening of the smelter in 1956. Further difficulties with these three sites were encountered in attempting to include them in the analysis described below, lending support to the hypothesis that these sites are dominated by local effects. The Williams site is not near any such pollution sources, but is the youngest tree (Table 2) and may be showing a canopy effect. In the data analysis which follows, the Williams site may be included with similar results to the case when only the six sites with the decreasing $\delta^{13}C$ trends are used.

3.2 *δ versus climate relationships*

A variety of $\delta^{13}C = f(\text{climate})$ relations were explored in the search for those which have both significant correlations and constant coefficients from one interval to the next. Examples of such relationship include:

$$\delta = AT + BT^2 + CT^3 + DR + ER^2 + FR^3 + T \times R + K$$
$$\delta = A(T \times R) + K$$
$$\delta = A(T/R) + K$$
$$\delta = AT + K$$
$$\delta = AR + K$$

where T and R represent temperature and precipitation, respectively. From the weather records, the 5-year mean temperature and precipitation was calculated for each individual month, for groups of months (seasons), and for the full year, and all were tested in the regression search. With all 10 sites, only the polynomial relationship in T and R showed high correlation coefficients but, unfortunately, the sign and magnitude of the coefficients were extremely variable from one interval to the next. The simple regressions of δ versus T and δ versus R had uniformly low r^2 values. A typical example of the r^2 results for the δ versus T regressions with 10 stations is shown in Fig. 2, where r^2 is very low regardless of which 5-year mean monthly temperature was tested from the 1965–69 interval.

The four stations which did not show a $\delta^{13}C$ decrease over the 50-year period were then removed and the regressions retested. Results with the polynomials in T and R were similar to that from 10 stations: highly significant correlations but no consistency of coefficients. However, when the simple δ versus T and δ versus R relations were tested, a pattern of good correlations and consistency of coefficients from one interval to the next emerged. In Fig. 2 the r^2 values for individual months in the 1965–69 interval show a pattern of

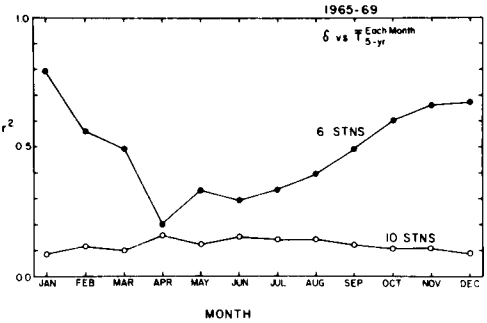

Fig. 2. Typical strengths of correlation (r^2) for $\delta^{13}C$ versus 5-year mean monthly temperature. The r^2 values for 10 stations and 6 stations are plotted for comparison.

highest values in winter months and lowest in summer months, but in all cases greater than the r^2 values for 10 sites. Patterns of r^2 of the δ versus R regressions were similar, but the r^2 values were typically lower by 0.1 and 0.2. The winter months in the south-western U.S. are generally considered an important preconditioning period with regard to tree-ring growth of the following growing season (Fritts, 1976), and these results might suggest formation of sugars during the winter months that are then assimilated into rings during the following growing season.

An example of the δ versus T regressions for three of the intervals, spaced 20 years apart, is shown in Fig. 3. Only the 1955–59 interval is actually significant at 95% (for 5 degrees of freedom, 95% significance occurs at $r = 0.81$), but there is a marked consistency of the slopes. In fact, the spacing between these lines seems generally consistent with the exponential consumption of fossil fuels, i.e., the $\delta^{13}C$ drop between 1955–59 and 1975–79 is greater than that between 1935–39 and 1955–59. However, because the standard error of the estimate associated with each of the regression lines in Fig. 3 is approximately 0.3 to 0.5‰, this apparent difference in spacing is not statistically significant.

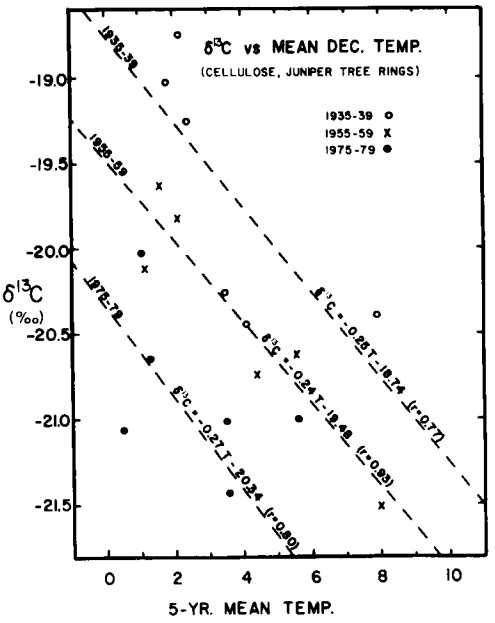

Fig. 3. Examples of the $\delta^{13}C$ versus 5-year mean December temperature for three of the intervals.

The scatter seen about these regression lines may arise from several sources beyond the possibility that other variables may be important. A single tree was harvested at each site, but the work of Arnold (1979) with juniper leaves suggests intra-site $\delta^{13}C$ variability of several tenths per mil among different individuals. Slight errors in the dating by ring counting could result in some scatter due to the non-coincidence of the $\delta^{13}C$ measured from five rings and the average climate for the period those rings are believed to represent. Despite their proximity, microclimatological differences may exist between the sites and the weather stations. Furthermore, the weather records were not complete and about 2% of the monthly mean temperature and precipitation values for the 50 years are missing. This led to calculated five-year means which were biased by these missing values.

For the three intervals given in Fig. 3, zero-order correlation coefficients are illustrated in Table 3 for δ versus T, δ versus R and T versus R, along with first-order partial correlations for δ versus T and δ versus R. A significant positive correlation of T and R does exist for two of the intervals and indicates the reliability of multiple linear regression of δ with both T and R will be limited by the non-independence of these "independent" variables. The

Table 3. *Zero-order and first-order correlation coefficients of $\delta^{13}C$ and December T and R for the three five-year intervals depicted in Fig. 3*

	Zero-order correlation coefficients		
	1935–39	1955–59	1975–79
δ versus T	−0.77*	−0.93†	−0.80*
δ versus R	−0.64	−0.83*	−0.52
T versus R	+0.58	+0.79*	+0.90†
	First-order partial correlation coefficients		
	1935–39	1955–59	1975–79
δ versus T	−0.63	−0.79	−0.89*
δ versus R	−0.37	−0.43	+0.77

* $P < 0.05$
† $P < 0.01$

first-order partial correlation coefficients are generally smaller than the respective zero-order values and in one case even the sign is different. We have used zero-order regressions in the analysis and found they satisfy our requirement for functions whose coefficients remain nearly constant from one interval to the next. Partial regression coefficients would probably be needed to determine truly independent T and R coefficients, but are not essential to this study.

3.3 *New $\delta^{13}C$ curves generated from the δ versus climate relationships*

If the slopes of these δ versus T or δ versus R regressions were identical from interval to interval, simply plotting the intercepts would then be a valid representation of the $\delta^{13}C$-spacing between intervals and thus the change in $\delta^{13}C$ through time. The upper curves with the error bars in Figs. 4 and 5 represent such plots of the intercepts of δ versus mean December temperature and δ versus mean December precipitation, respectively. However, because the slopes are not identical, the lines may diverge or converge toward the $\delta^{13}C$ ordinate. The extreme effect of such non-parallel lines is evidenced in the 1930–34 interval which has positive T and R coefficients when all other intervals are negative.

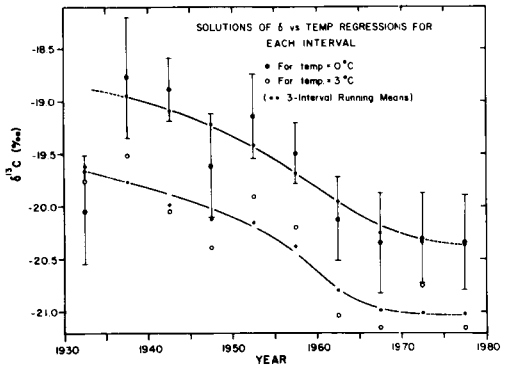

Fig. 4. Straight plot of the intercepts of the $\delta^{13}C$ versus mean December temperature of the 5-year intervals (solid circles) and plot of the position of these same regressions for $T = 3\,°C$ (open circles), i.e., near the average temperature of all six stations. The three-interval running mean weights the three successive points equally, except for the first or last point which is weighted twice that of the adjacent point. "Error bars" represent one s.d. of scatter about the regression line of the respective interval. Error bars on lower curve are identical to upper curve.

A more representative record of the spacing between the regression lines may therefore be made by calculating near the mean of the December temperature and precipitation of all six stations, about 3 °C and 27 mm, respectively. Because the curves in each figure (4 and 5) are obtained from the same regression equations, the error bars in the lower curves are the same as in the upper, actually representing the standard error of the estimate. Given the $\delta^{13}C_{ATM}$ drop of 0.65‰ from 1956 to 1978 calculated from direct $\delta^{13}C_{ATM}$ and P_{CO_2}

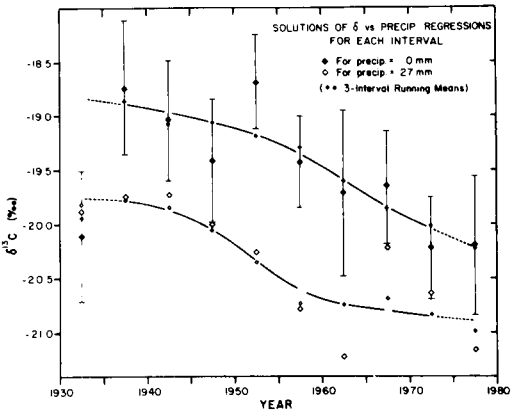

Fig. 5. Plot of the intercepts of the $\delta^{13}C$ versus mean December precipitation regressions of the 5-year intervals (solid diamonds) and plot of the position of these same regressions for $R = 27$ mm (open diamonds), i.e., near the average precipitation of all 6 stations. "Error bars" represent 1 s.d. of scatter about the regression line of the respective interval. Error bars on lower curve are identical to upper curve.

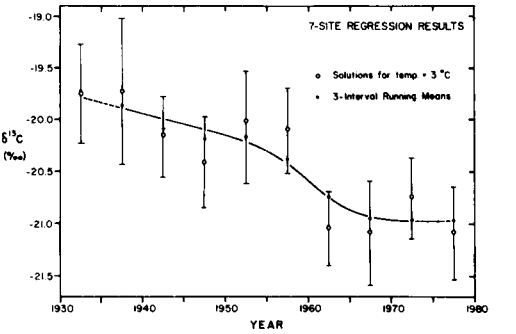

Fig. 6. Plot of the $\delta^{13}C$ values of the $\delta^{13}C$ versus mean December temperature regression for $T = 3\,°C$, when seven sites (including Williams) are used in the analysis. The trend is similar to Fig. 4 where six sites are included.

measurements (Keeling et al., 1979, 1980), the $\delta^{13}C$ reconstruction derived from the temperature curve (for $T = 3\,^{\circ}C$) more faithfully reproduces this atmospheric $\delta^{13}C$ change. It is worth noting that when this analysis was performed with seven stations, including the Williams site, a nearly identical $\delta^{13}C$ was reproduced but with somewhat larger error bars (see Fig. 6).

Similar results were also obtained when equal slopes were forced to the points of each interval. This was accomplished by rearranging the standard linear regression equation so that a slope (m) could be substituted and an apparent $\delta^{13}C$ intercept could be calculated. Again, the $\delta^{13}C$ reconstructions obtained from the δ vs T set of regressions better reproduced a 1956–1978 $\delta^{13}C_{ATM}$ drop of about 0.65‰.

A 50-year atmospheric $\delta^{13}C$ curve was generated by combining the running-mean $\delta^{13}C$ curve in Fig. 4 from the δ versus T regressions at $T = 3\,^{\circ}C$, with a running-mean $\delta^{13}C$ curve obtained from the intercepts of the δ versus T curves when a slope of -0.27‰ $^{\circ}C^{-1}$ was forced to the points of each interval. This value of -0.27 is approximately the mean coefficient of all of the δ versus December T linear regressions from all ten 5-year intervals. (For the δ versus R curves, the coefficients averaged -0.04‰ mm^{-1}.) The data and calculations from this procedure are given in Table 4. A record of relative $\delta^{13}C$ change for each $\delta^{13}C$ reconstruction was first obtained as the difference $\delta^{13}C$ of each interval from the 1975–1979 value. These $\delta^{13}C$ difference records were then averaged and added to the actual $\delta^{13}C_{ATM}$ value for the period 1975–1979 taken as -7.34‰ (Keeling et al., 1980). This atmospheric $\delta^{13}C$ reconstruction is plotted as the upper curve in Fig. 7. The vertical bars estimate error associated with each of these

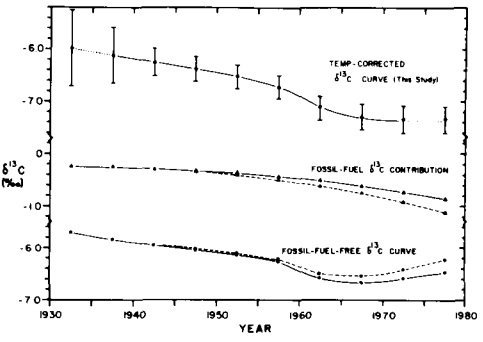

Fig. 7. Removal of fossil-fuel contribution to atmospheric $\delta^{13}C$. Solid diamonds are the temp.-corrected atmospheric $\delta^{13}C$ record developed in this study. Estimated error (1 s.d.) associated with each point is given by vertical bars in top curve. Triangles indicate the fossil-fuel $\delta^{13}C$ contribution according to Stuiver (1978) (solid) or the Mulholland (1979) modification of the Stuiver approximation (open). Circles represent the removal of the fossil-fuel $\delta^{13}C$ contribution from the upper atmospheric $\delta^{13}C$ curve.

Table 4. *An atmospheric $\delta^{13}C$ reconstruction using $\delta^{13}C$ values obtained from two sets of δ versus T regressions. Relative $\delta^{13}C$ deviations from each set were first calculated with respect to their respective 1975–79 $\delta^{13}C$ values and then the deviations were averaged. These deviations were added to the 1975–79 atmospheric $\delta^{13}C$ value of -7.34‰ to obtain the full 50-year reconstruction*

Interval	$\delta^{13}C$ from δ versus T regressions where $T = 3\,^{\circ}C$		$\delta^{13}C$ from δ versus T regressions where slope of -0.27 has been forced		Mean relative $\Delta\delta$	Absolute atmospheric $\delta^{13}C$
	Absolute δ	Relative $\Delta\delta$	Absolute δ	Relative $\Delta\delta$		
1930–34	−19.65‰	1.35‰	−18.86‰	1.36‰	1.36‰	−5.98‰
1935–39	−19.80	1.20	−18.97	1.25	1.22	−6.12
1940–44	−19.93	1.07	−19.11	1.11	1.09	−6.25
1945–49	−20.06	0.97	−19.27	0.95	0.96	−6.38
1950–54	−20.20	0.80	−19.38	0.84	0.82	−6.52
1955–59	−20.38	0.62	−19.59	0.63	0.62	−6.72
1960–64	−20.80	0.20	−20.00	0.22	0.21	−7.13
1965–69	−20.98	0.02	−20.17	0.05	0.04	−7.30
1970–74	−21.00	0.00	−20.20	0.02	0.01	−7.33
1975–79	−21.00	0.00	−20.22	0.00	0.00	−7.34

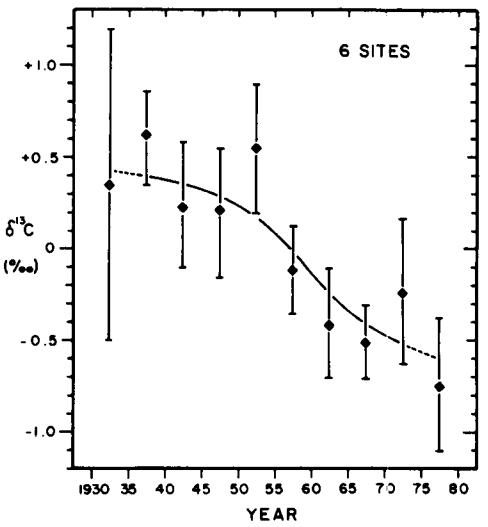

Fig. 8. The simple average $\delta^{13}C$ trend of the six sites after each individual curve has first been normalized to its mean value. This may be compared to the "climate-free" upper curve in Fig. 7 to judge the magnitude of temperature effect.

points Although the best-fit trend has been drawn in, it is clear that other downward trends are not disallowed by the data.

For comparison, the upper "climate-free" curve in Fig. 7 may be compared with the simple, normalized mean $\delta^{13}C$ curve of the six sites shown in Fig. 8. The main differences are a somewhat larger overall $\delta^{13}C$ drop and a flatter post-1965 $\delta^{13}C$ in the Fig. 7 curve.

3.4. *Removal of fossil-fuel $\delta^{13}C$ contribution*

Stuiver (1978) devised an approximation to determine the fossil-fuel contribution to the atmospheric $\delta^{13}C$ curve from a measure of the dilution of radiocarbon activity in the atmosphere by fossil fuels. He reasoned that the difference in radiocarbon activity of the atmosphere (100%) and fossil fuels (0%) is 100%, and that the difference in $\delta^{13}C$ of the atmosphere ($-7‰$) and that of fossil fuels ($-25‰$) is about 18‰, so that the measured changes in atmospheric radiocarbon activity would be scaled to the corresponding change in $\delta^{13}C$ by the factor 18/100:

$$\Delta(\delta^{13}C) = (18/100)S$$

where S is the dilution of radiocarbon. Using the S-values from a model by Oeschger et al. (1975), the fossil-fuel $\delta^{13}C$ contribution to the atmosphere is given as the solid curve in the center of Fig. 7.

Mulholland (1979) suggested a modified version of this relationship of the form

$$\Delta(\delta^{13}C) = (\gamma/100)S$$

where the variable γ is used to represent a variable difference between $\delta^{13}C$ of the atmosphere and of fossil fuels as the usage patterns have shifted from coal ($\delta^{13}C \simeq -25‰$) to isotopically lighter petroleum and natural gas. Recalculation of the fossil-fuel $\delta^{13}C$ contribution using the mean $\delta^{13}C$ curve for fossil fuels of Mulholland (1979) yielded the dashed curve in the center of Fig. 7. This curve might actually represent an extreme fossil-fuel contribution in that the $\delta^{13}C$ values assumed by Mulholland for the categories of fossil fuels were slightly lighter than those of a similar tabulation by Freyer (1979c). Further, Mulholland apparently did not include the isotopically-heavy CO_2 release from cement production ($\delta^{13}C \simeq 0‰$) in his calculations.

The fossil-fuel $\delta^{13}C$ contributions to the atmosphere were subtracted from the atmospheric $\delta^{13}C$ curve in Fig. 7 to produce the fossil-fuel-free $\delta^{13}C$ curves at the bottom of Fig. 7. The solid $\delta^{13}C$ curve results from using the Stuiver approximation and the dashed curve from using the Mulholland modification. These curves are characterized by decreasing $\delta^{13}C$ to the late 1960's and then a reversal of the trend. This is in contrast to the results of Stuiver (1978) who found the post-1920 portion of his fossil-fuel-free $\delta^{13}C$ curve to be relatively flat, and interpreted it as a consequence of no major biospheric injections since the turn-of-the-century "pioneer agricultural revolution".

It bears mentioning that the validity of the Stuiver approximation has been questioned by Keeling (1979). He notes that the Stuiver approximation neglects isotopic fractionation during redistribution of industrial CO_2 and preserves an 18‰ δ^{13} difference between atmosphere and fossil-fuel. Modeling by Keeling (1979) suggests this approximation may only be useful for very coarse estimates, although he also found that if the $^{13}C/^{12}C$ fractionation factor between atmosphere and ocean is close to unity, then the Stuiver approximation better fits his model results which include fractionation during redistribution. Recent evidence cited by Keeling et al. (1980) suggests this

air–sea fractionation factor may, indeed, be closer to unity than the commonly quoted value of 0.986.

4. Interpretation and discussion

The fossil-fuel-free $\delta^{13}C_{ATM}$ curve generated in this study (Fig. 7), in contrast to that of Stuiver (1978), may reflect a significant amount of post-1930 biospheric activity. If we assume this curve indeed represents the global trend, the early portion of the curve could reflect a net biospheric CO_2 release as maintained by some authors primarily as the result of large-scale tropical deforestation and agriculture. Bolin (1977) has calculated that the biosphere may be releasing an amount of CO_2 equivalent to about one-fourth of the fossil-fuel contribution, although Pankrath (1979) estimates the net biospheric input to be as much as one-half of the fossil-fuel input. Woodwell et al. (1978) allow for a net biospheric input which may even be up to three times greater than that from fossil fuels.

The reversal of this $\delta^{13}C$ trend of the fossil-fuel-free curve in the 1960's suggests a transition of the biosphere from net CO_2 source to sink. Broecker et al. (1979) maintain that any recent accelerated deforestation could be compensated by forest regrowth. There are several lines of evidence which lend various degrees of support to an increasingly important role of the sink aspects of the biosphere over the past few decades.

Forest regrowth has apparently been important in some areas. Regrowth of 10–20% has been observed in some parts of the Amazon (Adams et al., 1977) and there is evidence of it in forests of New England and northern Europe as well (Bolin, 1977; Woodwell et al., 1978). The magnitude of this effect, however, must be tempered by the lower biomass of this secondary regrowth. There is also evidence of a net carbon sink in the commercial forests of the southeastern U.S. (Delcourt and Harris, 1980). In fact, the biospheric carbon inventory of Armentano and Ralston (1980) indicates temperate-zone forests may have been a major net sink over the past three decades equivalent to 20–60% of the annual fossil-fuel release over that period. Furthermore, Bohn (1978) finds that organic peat soils are currently net accumulators of carbon, although it is not clear if the net carbon content of mineral soils is increasing or decreasing. A study of the seasonal amplitude of P_{CO_2} measurements at several monitoring stations by Pearman and Hyson (1981) suggests there has been a net carbon accumulation in the seasonal biosphere equivalent to 0.5×10^{15} gC yr^{-1} in recent years. Lastly, Killough and Emanuel (1981) examined ocean carbon models of various degrees of complexity, and find that in the more detailed models the biosphere could be accommodated as a net CO_2 source prior to about 1960, but after 1965 the ocean's capacity for CO_2 storage has been exceeded so that the biosphere must function as a net sink.

Thus a growing body of evidence lends credence to the possibility that the atmospheric $\delta^{13}C$ curves derived in Fig. 7 may indeed be an accurate representation of activity of the global biosphere. At this stage of research, however, caution must be exercised. Even though this analysis with up to seven of ten of the sites yielded essentially similar $\delta^{13}C$ curves, omission of three sites due to apparent pollution effects is a cause for concern. Furthermore, examination of the error bars on the $\delta^{13}C$ curve in Fig. 7 reveals that it would indeed be possible to draw some form of exponentially decreasing $\delta^{13}C$ curve over the full length of the 50-year period. Such a curve would have been the *a priori* expectation of most researchers, probably including us. Our curve was drawn as the best fit to the data points, and therefore our interpretations have been made with respect to that curve.

5. Conclusions

Many factors may contribute to the noise in $\delta^{13}C_{ATM}$ reconstructions from tree rings, including local pollution, effects of respired CO_2, the choice of wood constituent for analysis, and variation of isotopic composition from one radius to another. Careful site selection and laboratory procedure may minimize these effects. However, the effect of climate on fractionation is much more difficult to account for.

We have attempted to minimize these factors and, in fact, to remove the effects of climate from the $\delta^{13}C$ reconstruction. The temperature (and precipitation) coefficients necessary to factor out climate were obtained not by serial correlation of the $\delta^{13}C$ values of a tree with weather data, but rather by correlating the $\delta^{13}C$ values of several trees from a particular interval with the respective

climate of their sites. Problems in applying this technique to all ten of the sites we harvested may be a consequence of local point sources of pollution related to copper-smelting activities, in spite of the rural setting of all the sites. Although exclusion of three of these sites from the analysis was not done lightly, given the known decreasing global atmospheric $\delta^{13}C$ trend (Keeling et al., 1979), the non-decreasing trends at these sites suggest the global changes are being masked by some other influence(s).

The best-fit $\delta^{13}C$ reconstruction reproduced the $\delta^{13}C$ drop of about 0.65‰ that Keeling et al. (1979, 1980) found between 1956 and 1978, but the curve indicates a deceleration rather than an acceleration of the atmospheric $\delta^{13}C$ decrease. Examination of other current evidence on the recent capabilities of the biosphere as a carbon sink indicate that this new $\delta^{13}C_{ATM}$ curve may be a fair representation of reality. However, sufficient noise remains in this reconstruction, probably due to intra-site variability, missing climate data and possible dating errors, so that other interpretations cannot be excluded.

We have embarked on a program with pinyon pine (*Pinus edulis*) to verify these results and to develop a $\delta^{13}C$ record back into the 19th century with this technique. Dating of these samples is absolute, and climate is being reconstructed beyond the range of historic records using dendroclimatological techniques.

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