A SINGLE-YEAR δ¹³C CHRONOLOGY FROM *PINUS TABULAEFORMIS* (CHINESE PINE) TREE RINGS AT HUANGLING, CHINA

STEVEN W. LEAVITT,[1] LIU YU,[2] MALCOLM K. HUGHES,[1] LIU RONGMO,[2] AN ZHISHENG,[2] GRACIELA M. GUTIERREZ,[1] SHELLEY R. DANZER[1] and SHAO XUEMEI[3]

ABSTRACT. Individual rings from 1899–1990 were pooled from four radii of four cross-sections obtained from trees at a managed forest site near Huangling, north of Xian in north central China. Splits of wood ground to 20-mesh were analyzed independently at both the Xian and Arizona laboratories, using their respective methods for cellulose isolation, combustion and mass-spectrometric analysis. The δ¹³C results were highly correlated ($r^2 = 0.66$) and absolute values typically within 0.2–0.3‰. Inter-tree variability was estimated as 1–1.5‰. The Huangling δ¹³C curve shows an overall downward trend with year-to-year fluctuations of up to 1.5‰ superimposed. A subset of δ¹³C maxima corresponded with below-normal precipitation and above-normal temperature in May and June, and minima were associated with above-normal precipitation and below-normal temperature in May and June, perhaps signaling early arrival of the East Asian Summer Monsoon. The generally poor climate correlations with all δ¹³C values, however, could be a consequence of the fairly mesic environment or of human disturbance. Chronologies of isotopic discrimination (Δ) and C_i/C_a had flat slopes, suggesting the δ¹³C trend was driven by global rather than local effects.

INTRODUCTION

Stable-carbon isotope (δ¹³C) chronologies have been established from tree rings in Europe (Freyer and Belacy 1983), North America (Leavitt and Long 1988, 1989c; Stuiver, Burk and Quay 1984), Australia (Francey 1981) and South America (Stuiver, Burk and Quay 1984; Leavitt and Lara 1994) in order to estimate past fluctuations of atmospheric δ¹³C of CO_2 (*e.g.*, Stuiver 1978; Peng *et al.* 1983), or as a means of reconstructing past climate (*e.g.*, Harkness and Miller 1980; Libby *et al.* 1976; Leavitt and Long 1989a). Isotopic dendrochronological studies in Asia have been limited (Liu, Liu and Sun 1990, 1993; Liu *et al.* 1988), but in 1990, a joint cooperative study was inaugurated between the National Key Laboratory of Loess and Quaternary Geology (NKLLQG) in Xian and the Laboratory of Tree-Ring Research (LTRR) in Tucson. In November 1990, a preliminary joint expedition was organized to investigate potential dendrochronological sites north of Xian. Ultimately, we gained access to a managed forest at Huangling for the purpose of sampling tree rings for an isotope study. Because of a major fire at the end of the last century, the length of our chronology is relatively short. However, it is sufficiently long to enable us to compare results to climate data and to isotopic results from other similar studies around the world.

METHODS

The Huangling site at Mt. Zi Wuling is located at 35°35′ N, 108°55′ E at an elevation of *ca.* 1200 m, *ca.* 30 km northwest of the town of Huangling in Shaanxi Province, 160 km north of Xian. The soils in these hills are developed on loess and sandstone, and the trees sampled were generally growing on west-facing aspects with slopes commonly from 20° to 40°. Chinese pine (*Pinus tabulaeformis*) was the dominant tree species at the site and constituted the tallest trees, but other trees included species of oak (*Quercus* sp.), cypress (*Cupressus* sp.) and trees of the honeysuckle family (Caprifoliaceae). The site was fairly "open", with 5–10 m between trees and a discontinuous canopy. We cored 20 trees to develop a tree-ring chronology, and cut 5 trees to obtain basal cross-sections for isotopic analysis.

[1]Laboratory of Tree-Ring Research, The University of Arizona, Tucson, Arizona 85721 USA
[2]National Key Laboratory of Loess and Quaternary Geology, Xian 710061 China
[3]Institute of Geography, Academia Sinica, P.O. Box 771, Beijing 100101 China

The samples were dated at LTRR. The oldest cores dated to AD 1885, and the inside ages of the cross-sections ranged from AD 1893 to 1908. Four "radii" were cut from each of four cross-sections at orthogonal positions for isotopic analysis. Rings of these radii were separated with a razor knife under a binocular microscope and pooled for a site composite sample for each year. For specific years, however, the wood from each tree was processed separately to determine inter-tree variation. All samples were ground in a mill to 20-mesh size; one split was sent to the NKLLQG, and a second split was retained by LTRR. At LTRR, we processed samples to holocellulose using a modified acid-chlorite method described by Leavitt and Danzer (1993), using a sodium chlorite solution acidified by acetic acid in the final delignification step. The NKLLQG used the method described in Stuiver, Burk and Quay (1984) to isolate α-cellulose with delignification *via* a sodium hypochlorite solution acidified by sulfuric acid and a final sodium hydroxide step to eliminate hemicelluloses.

Samples were combusted to CO_2 at the LTRR in a recirculating microcombustion line in the presence of excess oxygen, cryogenically purified, and analyzed on a VG Micromass 602C mass spectrometer with modernized electronics. At the NKLLQG, samples were combusted to CO_2 in sealed quartz tubes in the presence of copper oxide and platinum wire, purified and analyzed on a Finnigan-MAT 251 mass spectrometer. At both laboratories, the measured $^{13}C/^{12}C$ ratios were calculated as $\delta^{13}C$ (‰) with respect to the PDB standard.

RESULTS

Figure 1 shows the $\delta^{13}C$ results from both laboratories. The two records are highly correlated with $r^2 = 0.66$ (p <.001). On average, each LTRR isotopic result is 0.12 ± 0.44‰ (± 1 σ) more ^{13}C-enriched than the corresponding NKLLQG values. Deines (1980) reports that holocellulose tends to be slightly more ^{13}C-enriched than α-cellulose because the small percentage of hemicelluloses in holocellulose are enriched by *ca.* 3‰ relative to the alpha-cellulose making up the balance of the holocellulose. These results indicate that the two laboratories produce highly compatible and largely interchangeable isotopic analyses. Therefore, further data analysis reported here is on the LTRR $\delta^{13}C$ chronology.

With respect to inter-tree variability, the tree-ring holocellulose from the four trees was analyzed separately for years 1900, 1910, 1920, 1930, 1940, 1950, 1960, 1970, 1980 and 1985. Trees 1 and 3 tended to be the most ^{13}C-depleted, whereas 2 and 4 were the most ^{13}C-enriched. The difference between most and least ^{13}C-enriched values for each of these years ranged from 0.7 to 3.1‰, with an average standard deviation of 0.64‰. These numbers are similar to those seen in other studies of inter-tree variability (Leavitt and Long 1989b).

The Huangling $\delta^{13}C$ chronology displays a negative slope with an overall decline of *ca.* 1.5–2‰. Because of possible juvenile effects associated with the early years of growth (Francey and Farquhar 1982), the decline after 1915, in the range of 1–1.5‰, may better reflect the real decline experienced by these trees at this site. There are substantial $\delta^{13}C$ fluctuations of up to 1.5‰ superimposed on the trend. The trend and fluctuations are similar to the chronologies developed at 14 pinyon pine sites in the American Southwest (Leavitt and Long 1989c) and one *Fitzroya* site in Chile (Leavitt and Lara 1994), which were developed from a sequence of 5-yr pooled tree-ring samples.

The pinyon pine and *Fitzroya* chronologies were believed to represent the changes in $\delta^{13}C$ of atmospheric CO_2. If the estimated chronology of $\delta^{13}C$ of air CO_2 from direct air measurements (Keeling, Mook and Tans 1979; Keeling *et al.* 1989) and air trapped in ice bubbles (Friedli *et al.* 1986) is subtracted from the measured $\delta^{13}C$ from the Chinese pine rings, a measure of discrimination is obtained ($\Delta = [\delta_{air} - \delta_{plant}] / [1 + \delta_{plant}]$) (Ehleringer 1991). We plotted this difference in Figure 2 (top). This algorithm has effectively removed any trend in the original data (slope not significantly different

from zero); thus, air $\delta^{13}C$ must have dominated the original downward $\delta^{13}C$ trend. Using the Farquhar, O'Leary and Berry (1982) model for carbon isotope fractionation in plants, we calculated and plotted in Figure 2 (bottom) the ratio of plant internal CO_2 concentration available for photosynthesis to atmospheric CO_2 concentration (C_i/C_a).
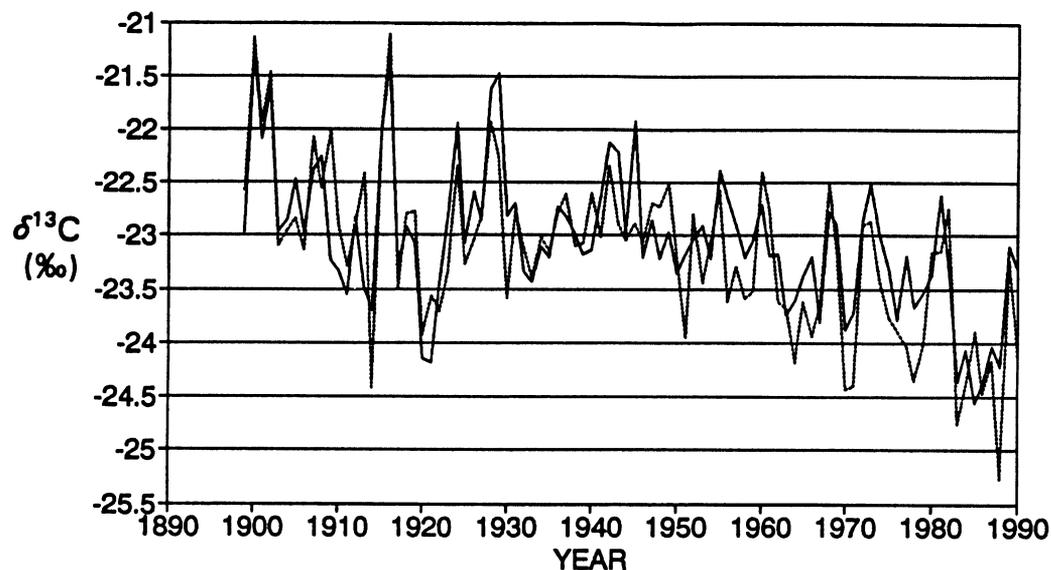
Fig. 1. China pine $\delta^{13}C$ chronologies from Huangling, China, as measured on α-cellulose by NKLLQG (gray dotted line) and holocellulose by LTRR (dark line). Both laboratories started chemical and isotopic preparation from splits of the same ground wood samples.
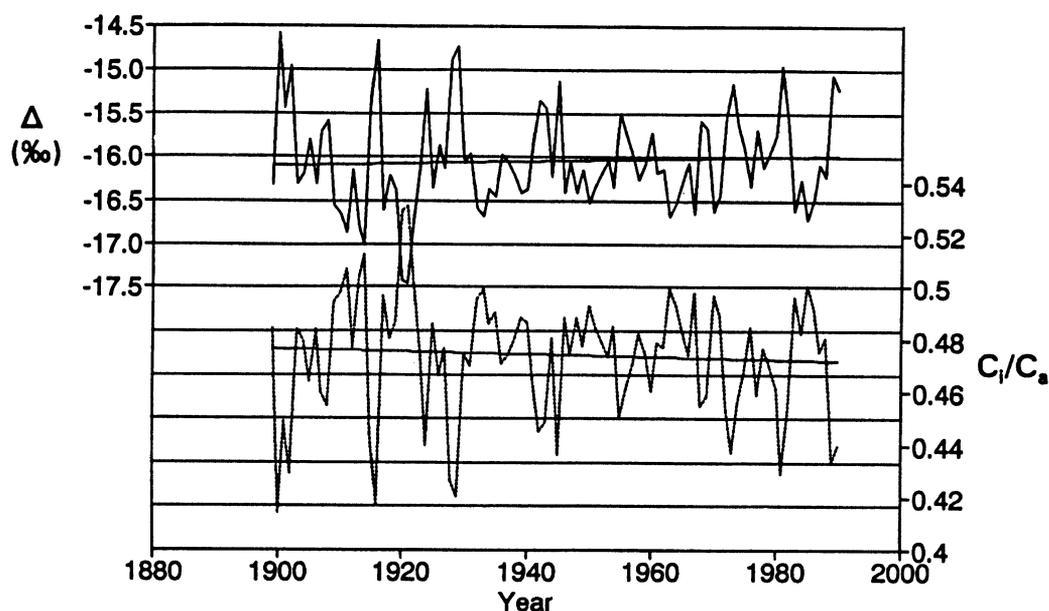
Fig. 2. Chronologies of discrimination (Δ) (upper line) and C_i/C_a (lower line) derived from the LTRR Huangling $\delta^{13}C$ chronology, and measurements and estimates of $\delta^{13}C$ of atmospheric CO_2 (see text).

If the trend seems to track changes in atmospheric $\delta^{13}C$ of CO_2, then the fluctuations may be correlated to climate, as was the case with the southwestern U.S. pinyon pine (Leavitt and Long 1989a). To test this possibility, we regressed the $\delta^{13}C$ values with climate data from Tongchuan, China (*ca.* 80 km north of Xian and midway between Xian and Huangling), available from 1957 to the present. Correspondence of tree-ring $\delta^{13}C$ with average annual temperature and average growing season temperature ($r^2 = 0.08$ and 0.16, respectively) and with total annual precipitation and growing season precipitation ($r^2 = 0.002$ and 0.001, respectively) was not significant.

Thus, we concentrated on those years of $\delta^{13}C$ maxima and minima to determine if certain distinctive climate conditions could produce the $\delta^{13}C$ deviations. Within the 1932–1990 period of the longer Xian climate record, the $\delta^{13}C$ maxima were chosen as 1945, 1973, 1981 and 1989, and the minima were 1970, 1983 and 1985. For these years, we compared the difference between the average temperature and total precipitation of each month averaged over the period 1932 to 1990 to the monthly precipitation and mean temperature for the years of specific maxima and minima. Figure 3 shows the results for the four $\delta^{13}C$ maxima (first bar is average of all 4 yr), using a scale of standard deviation units above or below the 1932–1990 means. Lower-than-average precipitation in the months of May and June of the growing season (and December of the year preceding the growing season) seem to contribute to the high $\delta^{13}C$. High temperatures in May and June (and in November of the previous year) also occur for the $\delta^{13}C$ maxima. This correspondence of high $\delta^{13}C$ and high growing-season temperature and reduced moisture is suggestive of the influence of drought seen in pinyon pine of the U.S. Southwest (Leavitt and Long 1989a). The 1929 ring also has a pronounced $\delta^{13}C$ peak, but it precedes the Xian climate record. However, historical evidence confirms extreme drought in central China in 1929.
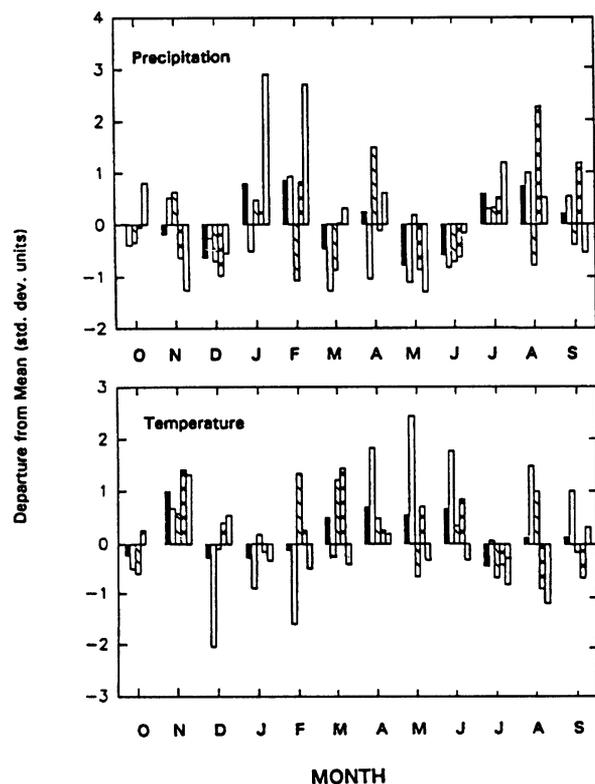

Fig. 3. Monthly average temperature and total precipitation for the 4 yr of $\delta^{13}C$ maxima plotted as deviations from the monthly averages for the full period of record, 1932–1990. From left to right, the 5 bars for each month indicate deviations from the long-term mean for: 1) the mean of the four maxima; 2) 1945; 3) 1973; 4) 1981; and 5) 1989, respectively.

Figure 4 depicts a similar plot for the three $\delta^{13}C$ minima. Low tree-ring $\delta^{13}C$ values seem to be influenced by high precipitation and low temperatures during May and June of the growing season (and low precipitation during October and January, and low temperature in December and March preceding the growing season). The extreme ^{13}C-depleted years could represent years of early onset of the East Asian summer monsoon in May and June, and the extreme $\delta^{13}C$-enriched years could represent protracted delay of the monsoon.
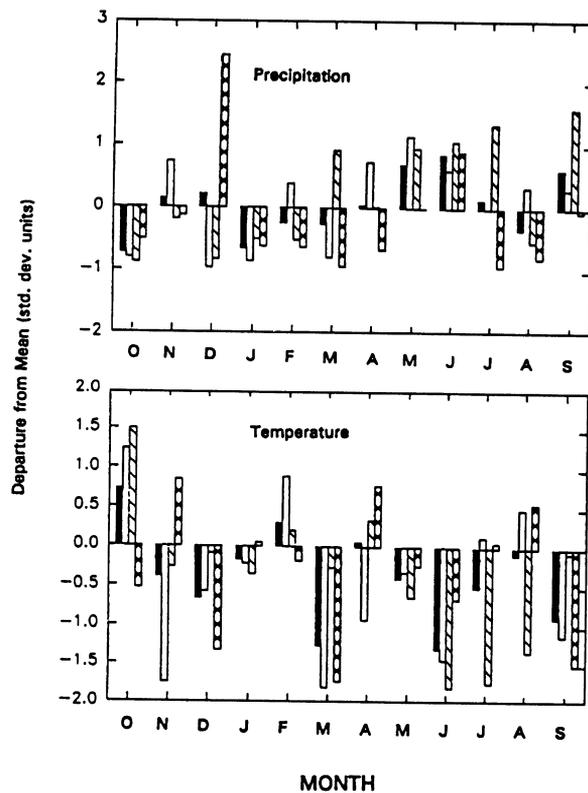

Fig. 4. Monthly average temperature and total precipitation for the 3 yr of $\delta^{13}C$ minima plotted as deviations from the monthly averages for the full period of record, 1932–1990. From left to right, the 5 bars for each month indicate deviations from the long-term mean for: 1) the mean of the three minima; 2) 1970; 3) 1983; and 4) 1985, respectively.

CONCLUSION

The $\delta^{13}C$ trend in the *ca.* 100-yr $\delta^{13}C$ record from Huangling is similar to the downward trends observed in other studies on other continents; it may reflect a shift in atmospheric $\delta^{13}C$. The flat trend of C_i/C_a suggests that disturbances (*e.g.*, sulfur dioxide pollution from coal burning) is not a factor in the $\delta^{13}C$. The substantial $\delta^{13}C$ fluctuations, however, do not correlate well with precipitation and temperature over the full length of climate record. This lack of sensitivity, compared to pinyon pine tree rings from the semi-arid southwestern U.S., may be a consequence of the Huangling area being much more mesic on average. When the $\delta^{13}C$ maxima and minima are scrutinized more closely, they seem to be associated with low precipitation/high temperature and high precipitation/ low temperature of the growing season, respectively. It is possible that these isotopic measurements may supplement rather than duplicate tree-ring width measurements: years with the smallest rings (1932, 1945, 1955, 1981) tend to correspond to low precipitation/high temperature of the months of March, April, May and June. Additional studies are in progress to develop longer $\delta^{13}C$ records from trees in the Qinling Mountains south of Xian.

REFERENCES

Deines, P. 1980 The isotopic composition of reduced organic carbon. *In* Fritz, P. and Fontes, J.-Ch., eds., *Handbook of Environmental Isotope Geochemistry*, Vol. 1. New York, Elsevier: 329–405.

Ehleringer, J. R. 1991 $^{13}C/^{12}C$ fractionation and its utility in terrestrial plant studies. *In* Coleman, D. C. and Fry, B., eds., *Carbon Isotope Techniques*. San Diego, Academic Press: 187–200.

Farquhar, G. D., O'Leary, M. H. and Berry, J. A. 1982 On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves. *Australian Journal of Plant Physiology* 9: 121–137.

Francey, R. J. 1981 Tasmanian tree rings belie suggested anthropogenic $^{13}C/^{12}C$ trends. *Nature* 290: 232–235.

Francey, R. J. and Farquhar, G. D. 1982 An explanation of $^{13}C/^{12}C$ variations in tree rings. *Nature* 297: 28–31.

Freyer, H. D. and Belacy, N. 1983 $^{13}C/^{12}C$ records in northern hemisphere trees during the past 500 years—anthropogenic impact and climatic superpositions. *Journal of Geophysical Research* 88: 6844–6852.

Friedli, H., Lotscher, H., Oeschger, H., Siegenthaler, U. and Stauffer, B. 1986 Ice-core record of the $^{13}C/^{12}C$ ratio of atmospheric CO_2 in the past two centuries. *Nature* 324: 237–238.

Harkness, D. D. and Miller, B. F. 1980 Possibility of climatically induced variations in the ^{13}C and ^{14}C enrichment patterns as recorded by 300-yr old Norwegian pine. *In* Stuiver, M. and Kra, R. S., eds., Proceedings of the 10th International ^{14}C Conference. *Radiocarbon* 22(2): 291–298.

Keeling, C. D., Mook, W. M. and Tans, P. 1979 Recent trends in the $^{13}C/^{12}C$ ratio of atmospheric carbon dioxide. *Nature* 277: 121–123.

Keeling, C. D., Bacastow, R. B., Carter, R. F., Piper, S. C., Whorf, T. P., Heinman, M., Mook, W. G. and Roeloffzen, H. 1989 A three dimensional model of atmospheric CO_2 transport based on observed winds. 1. Analysis of observational data. *In* Peterson, D. H., ed., Aspects of Climate Variability in the Pacific and the Western Americas. Washington, D.C., American Geophysical Union, *Geophysical Monograph* 55: 165–236.

Leavitt, S. W. and Danzer, S. R. 1993 Method for batch processing small wood samples to holocellulose for stable-carbon isotope analysis. *Analytical Chemistry* 65: 87–89.

Leavitt, S. W. and Lara, A. 1994 South American tree rings show declining $\delta^{13}C$ trend. *Tellus* 46B: 152–157.

Leavitt, S. W. and Long, A. 1988 Stable carbon isotope chronologies from trees in the southwestern United States. *Global Biogeochemical Cycles* 2: 189–198.

____1989a Drought indicated in carbon-13/carbon-12 ratios of southwestern tree rings. *Water Resources Bulletin* 25: 341–347.

____1989b Inter-tree variability of $\delta^{13}C$ in tree rings. *In* Rundel, P. W., Ehleringer, J. R. and Nagy, K. A., eds., *Stable Isotopes in Ecological Research*. New York, Springer-Verlag: 95–104.

____1989c The atmospheric $\delta^{13}C$ record as derived from 56 pinyon trees at 14 sites in the southwestern United States. *In* Long, A., Kra, R. S. and Srdoč, D., eds, Proceedings of the 13th International ^{14}C Conference. *Radiocarbon* 31(3): 469–474.

Libby, L. M., Pandolfi, L. F., Payton, P. H., Marshall, J., Becker, B. and Giertz-Sienbenlist, V. 1976 Isotope tree thermometers. *Nature* 261: 284–288.

Liu, R., Zhou, W., Liu, Y., Sun, F. and Zhou, M. 1988 $\delta^{13}C$ measurements of tree rings from ancient *Abies* in Xian Yang. *China Quaternary Research* 8(1): 26–30 (in Chinese).

Liu, Y., Liu, R. and Sun, F. 1990 $\delta^{13}C$ analysis of tree rings from Mt. Qinling and its climatic implications. In *Environmental Geochemistry and Health*. Guizhou Science and Technology Press, pp. 12–14 (in Chinese).

____1993 $\delta^{13}C$ variations in tree rings from part of Shaanxi Province. In *Proceedings of the Fourth National Chinese Conference on Quaternary Geology*, Guangzhou Science and Technology Press (in Chinese).

Peng, T. H., Broecker, W. S., Freyer, H. D. and Trumbore, S. 1983 A deconvolution of the tree-ring based $\delta^{13}C$ record. *Journal of Geophysical Research* 88: 3609–3620.

Stuiver, M. 1978 Atmospheric carbon dioxide and carbon reservoir changes. *Science* 199: 253–258.

Stuiver, M., Burk, R. L. and Quay, P. D. 1984 $^{13}C/^{12}C$ ratios in tree rings and the transfer of biospheric carbon to the atmosphere. *Journal of Geophysical Research* 89: 11731–11748.