# A SINGLE-YEAR $\delta^{13}$ C CHRONOLOGY FROM *PINUS TABULAEFORMIS* (CHINESE PINE) TREE RINGS AT HUANGLING, CHINA

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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  $\delta^{13}$ C results were highly correlated (r<sup>2</sup> = 0.66) and absolute values typically within 0.2–0.3‰. Inter-tree variability was estimated as 1–1.5‰. The Huangling  $\delta^{13}$ C curve shows an overall downward trend with year-to-year fluctuations of up to 1.5‰ superimposed. A subset of  $\delta^{13}$ C maxima corresponded with below-normal precipitation and below-normal temperature in May and June, and minima were associated with above-normal precipitation and below-normal temperature in May and June, subset of  $\delta^{13}$ C unit the fairly mesic environment or of human disturbance. Chronologies of isotopic discrimination ( $\Delta$ ) and C<sub>i</sub>/C<sub>a</sub> had flat slopes, suggesting the  $\delta^{13}$ C trend was driven by glo-

#### INTRODUCTION

Stable-carbon isotope ( $\delta^{13}$ C) 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  $\delta^{13}$ C of CO<sub>2</sub> (*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  $35^{\circ}35'$  N,  $108^{\circ}55'$  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.

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#### 606 S. W. Leavitt et al.

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  $\alpha$ -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<sub>2</sub> 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<sub>2</sub> 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 <sup>13</sup>C/<sup>12</sup>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  $0.12 \pm 0.44\%$  ( $\pm 1 \sigma$ ) more <sup>13</sup>C-enriched than the corresponding NKLLQG values. Deines (1980) reports that holocellulose tends to be slightly more <sup>13</sup>C-enriched than  $\alpha$ -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 <sup>13</sup>C-depleted, whereas 2 and 4 were the most <sup>13</sup>C-enriched. The difference between most and least <sup>13</sup>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<sub>2</sub>. If the estimated chronology of  $\delta^{13}$ C of air CO<sub>2</sub> 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<sub>2</sub> concentration available for photosynthesis to atmospheric CO<sub>2</sub> concentration (C<sub>i</sub>/C<sub>a</sub>).



Fig. 1. China pine  $\delta^{13}$ C chronologies from Huangling, China, as measured on  $\alpha$ -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 ( $\Delta$ ) (upper line) and C<sub>i</sub>/C<sub>a</sub> (lower line) derived from the LTRR Huangling  $\delta^{13}$ C chronology, and measurements and estimates of  $\delta^{13}$ C of atmospheric CO<sub>2</sub> (see text).

#### 608 S. W. Leavitt et al.

If the trend seems to track changes in atmospheric  $\delta^{13}$ C of CO<sub>2</sub>, 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 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.

recipitation 3 2 1 0 --2 s a N D M A м J J A Temperature 2 0 -- 1 -2 -3 S D A 0 Ν J F м

MONTH

Departure from Mean (std. dev. units)

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 <sup>13</sup>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<sub>i</sub>/C<sub>a</sub> 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.

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