

Stable isotopes in tree ring cellulose and climatic change*

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ABSTRACT

Relationships between the stable isotope contents ($\delta^2\text{H}$, $\delta^{13}\text{C}$) in dendrochronologically dated tree rings of firs (*Abies alba*, Black Forest) and air temperature, relative humidity, as well as precipitation rate were investigated for the period 1959 to 1980. Only the late wood of each ring was used, since isotope data from early wood, grown during spring, does not unambiguously reflect the climate of the respective growth season. The $\delta^{13}\text{C}$ -values, but not the $\delta^2\text{H}$ -values show significant correlations with temperature, humidity, and precipitation. Based on this observation, $\delta^{13}\text{C}$ -values were used to construct a paleoclimatic record for the past millenium. This required correction for anthropogenic ^{13}C -inputs since about 1850. The reconstructed temperatures are largely in agreement with presently-accepted variations in the recent past, whereby a "climatic optimum" appears during the Early Middle Ages with August temperatures about 0.5°C higher than today.

1. Introduction

The isotopic composition of carbon stored in the growth rings of trees may document a record of $^{13}\text{C}/^{12}\text{C}$ variations in atmospheric CO_2 , represent physiological responses to environmental changes, or a combination of both. In the first category, a decrease in $^{13}\text{C}/^{12}\text{C}$ in tree rings over the period 1850–1950 was attributed to an increasing component of ^{13}C -depleted CO_2 , released into the global atmosphere by increasing fossil fuel combustion and/or by deforestation and expanding agriculture. Furthermore, tree-ring $^{13}\text{C}/^{12}\text{C}$ variations are caused by the physiological response to increasing global atmospheric CO_2 concentrations such as from increased natural biospheric carbon releases (Stuiver, 1978; Wilson, 1978; Freyer 1979). In the second category, some authors have sought an explanation of $^{13}\text{C}/^{12}\text{C}$ variations in tree

rings through correlation with temperature (Libby et al., 1976; Pearman et al., 1976). In this case, it is normally assumed that the $^{13}\text{C}/^{12}\text{C}$ ratio remained constant in the atmosphere and, instead, a temperature-sensitive metabolic process within the plants is implied. In the third category, it is suggested that $^{13}\text{C}/^{12}\text{C}$ in air is influenced by respiration from surrounding vegetation, which in turn responds to environmental factors such as temperatures and water availability (Mazany et al., 1980). Thus, climatologic variables such as relative air humidity and precipitation rate may also affect the $\delta^{13}\text{C}$ -values in tree ring cellulose.

The $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of meteoric water at any location are mostly related to temperature but atmospheric circulations may also have a considerable effect. Thus it is to be expected, and has been documented, that climatic conditions influence the $^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$ -compositions of tree ring cellulose (Epstein and Yapp, 1976; Francey and Farquhar, 1982; Rundel et al., 1988). In general, under warm and dry conditions enrichment of heavier isotopes takes place.

This study deals with the possible impact of temperature, relative air humidity, and precipitation

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rate on ^2H and ^{13}C accumulation in the cellulose of tree rings of fir trees (*Abies alba*) from the Black Forest (FRG). It covers the time of about the past 1000 years BP. Only nitrated cellulose from the late wood of the tree rings was used, since the early wood does not reflect the climate situation of the respective year (spring) unambiguously (Wilson and Grinsted, 1977). In the early wood, carbon of organic matter from the previous year may be included.

2. Materials and methods

Dendroclimatological studies including tree ring width measurements and scanning electron microscopy show that, at the subalpine timberline in Black Forest, late wood of fir trees forms primarily during August (Fritts, 1976; Loris, 1981). The transition from early to late wood is microscopically distinguishable. Thus, it was possible to sample with the aid of a dental drill the late wood of the tree rings from 19 fir trees (*Abies alba*) from the Black Forest (48°33'N, 8°20'E; 880 m a.s.l.). The time span of AD 1004–1980 was covered by the 19 trees as follows: Fir 1: 1004–1125; Fir 2: 1100–1200; Fir 3: 1180–1285; Fir 4: 1265–1400; Fir 5: 1295–1420; Fir 6: 1399–1440; Fir 7: 1435–1480; Fir 8: 1460–1520; Fir 9: 1513–1545; Fir 10: 1565–1704; Fir 11: 1662–1742; Fir 12: 1737–1800; Fir 13: 1800–1880; Fir 14: 1780–1920; Fir 15: 1879–1980; Fir 16: 1879–1979; Fir 17: 1845–1980; Fir 18: 1879–1979; Fir 19: 1880–1980. For calibration with measured climatic data (1959–1980, meteorological station Hornisgrinde, Black Forest), the late wood of Fir 15–19 was sampled.

Following the extraction of lipids by Soxhlett (Northfelt et al., 1981), cellulose was extracted and nitrated (Alexander and Mitchell, 1949). Such nitration is necessary to eliminate the exchangeable hydroxyl hydrogens present in cellulose (Epstein et al., 1976). Cellulose nitrate samples were combusted (Northfelt et al., 1981; Stump and Frazer, 1973), carbon and hydrogen isotope ratios were determined on CO_2 and H_2 . Isotopic data are reported as δ (‰)-values with respect to SMOW for $\delta^2\text{H}$ and with respect to PDB for $\delta^{13}\text{C}$ values. Precision of preparation plus mass-spectrometric measurements was better than ± 2 ‰ for $\delta^2\text{H}$ and ± 0.3 ‰ for $\delta^{13}\text{C}$.

3. Results and discussion

3.1. Calibration of tree ring cellulose δ -values with measured climatic parameters

In an attempt to derive a relationship between the isotopic composition of late wood ($\delta^2\text{H}$ and $\delta^{13}\text{C}$) and basic climatological parameters such as August temperature (T), August relative humidity (H), and August precipitation rate (P), simple and multiple linear regression analyses were performed for data obtained on the 1959 to 1980 samples.

When simple regressions were applied for $\delta^2\text{H}$ values and climatic variables, the following equations are obtained:

$$\delta^2\text{H} = 2.2 T(^{\circ}\text{C}) - 89.1,$$

$$r = 0.36;$$

$$\delta^2\text{H} = -0.02 P(\text{mm}) - 58.9,$$

$$r = -0.23;$$

$$\delta^2\text{H} = -0.8 h(\%) + 4.7,$$

$$r = -0.38.$$

These relationships are non-significant (95% -level). Thus, deuterium contents in cellulose do not indicate any simple, linear relationship between either temperature, relative humidity or amount of precipitation. This contrasts with $\delta^{13}\text{C}$ -data of late wood cellulose, as shown in Figs. 1, 2, and 3; simple linear regression analyses yield correlations significant at the 95% -level. To eliminate the human impact on $\delta^{13}\text{C}$, caused by combustion of fossil fuel, the $\delta^{13}\text{C}$ -values were corrected for each year by a linear interpolation between end-points: $+0.0136$ ‰ for the 1959 samples to $+0.3$ ‰ in 1980. This slope was estimated by combination of data from Freyer, 1979 and Siegenthaler 1978, who found a linear $\delta^{13}\text{C}$ decrease of 1.5 ‰/100 years (according to 0.3 ‰/20 years).

In addition, however, multiple regression was applied to account for the fact that stable isotope contents in tree rings are affected by more than one climatic variable. In these analyses, values of $\delta^2\text{H}$ and $\delta^{13}\text{C}$ are taken as dependent variables and are correlated with several independent variables using linear equations of the type:

$$\delta^2\text{H}(\delta^{13}\text{C}) = a_0 + a_1 T + a_2 H + a_3 P.$$

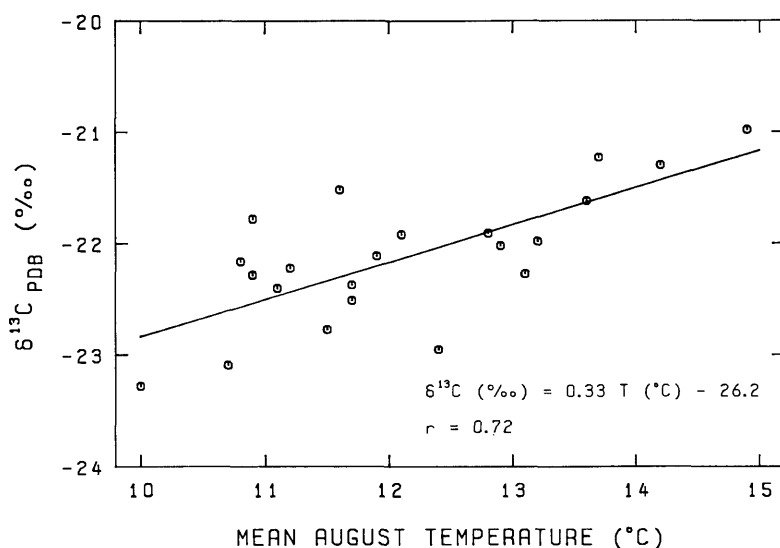


Fig. 1. Relationship of mean August temperatures (meteorological station Hornisgrinde, Black Forest) and $\delta^{13}\text{C}$ values in late wood cellulose (average of five firs from Black Forest) during the period 1959–1980.

In this equation, T represents the average August temperature ($^{\circ}\text{C}$), H the average relative air humidity in August (%), and P the average August precipitation (mm). Again, the $\delta^{13}\text{C}$ values are corrected for fossil fuel contributions. Regression equations are computed for three, two and one

independent variable. The results of these analyses are summarized in Table 1.

These analyses clearly show that, in comparison to ^2H , ^{13}C variations in cellulose are a much better tracer for climatic variations, at least as far as August temperatures are concerned. The reason

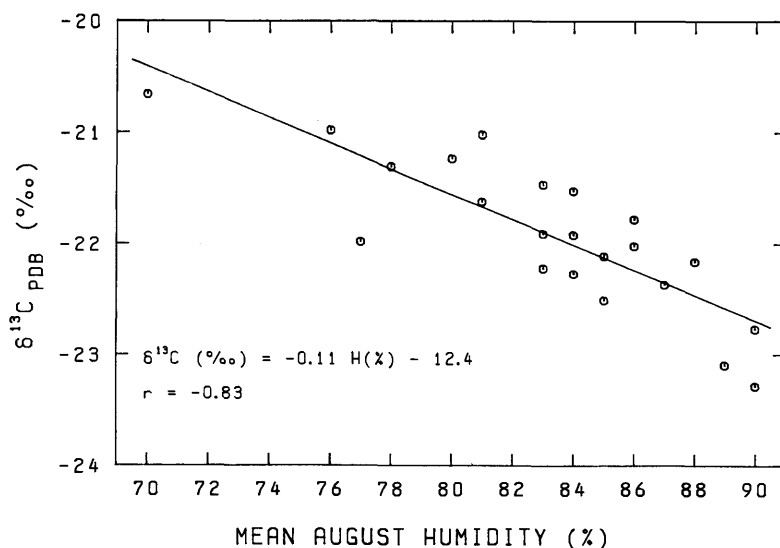


Fig. 2. Relationship of mean August relative humidity (meteorological station Hornisgrinde, Black Forest) and $\delta^{13}\text{C}$ values in late wood cellulose (average of five firs from Black Forest) during the period 1959–1980.

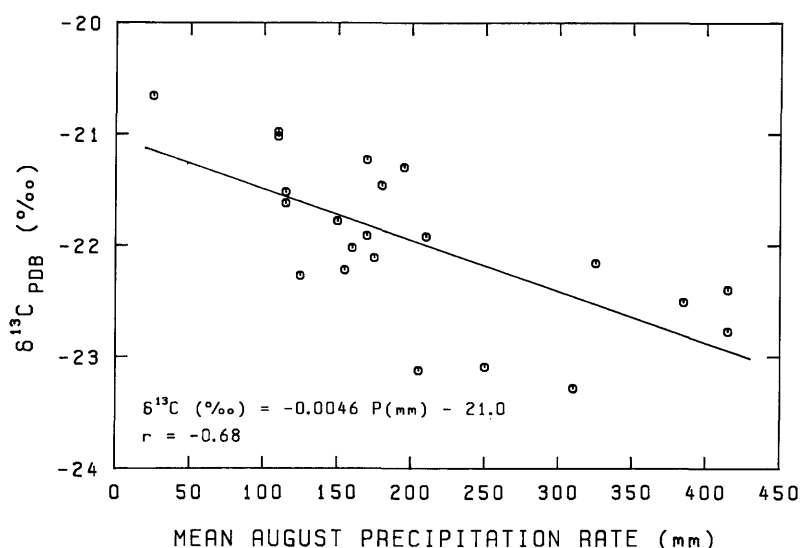


Fig. 3. Relationship of mean August precipitation rate (meteorological station Hornisgrinde, Black Forest) and $\delta^{13}\text{C}$ values in late wood cellulose (average of five firs from Black Forest) during the period 1959–1980.

for this differential behaviour is explained as follows: The $\delta^{13}\text{C}$ value of cellulose in C_3 -plants is mainly influenced by diffusion of atmospheric CO_2 through the stomatal pore into the intercellular spaces and the discriminating activity by the CO_2 accepting enzyme RuDP-carboxylase. The width

of the stomatal pore which affects the diffusion rate, is dependent on local climatic conditions such as temperature and humidity (Farquhar and Caemmerer, 1982).

The situation appears more complex for the $\delta^2\text{H}$ -values of plant cellulose. These are impacted

Table 1. Results of multiple linear regression analyses. The relationships hold true for five fir trees investigated; the confidence level is set as 95%

Dependent variable	Independent variables used	Regression equation	Multiple correlation coefficient	Standard error of estimate [‰]
$\delta^2\text{H}$	T, H, P	$\delta^2\text{H} = -36.62 + (0.80 \pm 1.27) T - (0.67 \pm 1.18) H - (0.03 \pm 0.01) P$	0.19	4.3
	T, H	$\delta^2\text{H} = -25.61 + (0.83 \pm 1.38) T - (0.56 \pm 0.88) H$	0.12	4.86
	T, P	$\delta^2\text{H} = -84.50 + (1.96 \pm 1.71) T - (0.007 \pm 0.01) P$	0.20	4.17
	H, P	$\delta^2\text{H} = -14.85 - (0.53 \pm 0.28) H - (0.03 \pm 0.01) P$	0.14	4.46
	T	$\delta^2\text{H} = -89.08 + (2.22 \pm 1.50) T$	0.07	7.67
	H	$\delta^2\text{H} = -25.31 - (0.80 \pm 0.56) H$	0.07	8.04
	P	$\delta^2\text{H} = -54.44 - (0.01 \pm 0.009) P$	0.02	4.63
$\delta^{13}\text{C}$	T, H, P	$\delta^{13}\text{C} = -12.81 + (0.03 \pm 0.12) T - (0.11 \pm 0.05) H - (0.001 \pm 0.001) P$	0.74	0.32
	T, H	$\delta^{13}\text{C} = -16.76 + (0.13 \pm 0.12) T - (0.08 \pm 0.04) H$	0.64	0.36
	T, P	$\delta^{13}\text{C} = -25.06 + (0.28 \pm 0.08) T - (0.002 \pm 0.001) P$	0.61	0.38
	H, P	$\delta^{13}\text{C} = -13.16 - (0.10 \pm 0.02) H - (0.002 \pm 0.001) P$	0.76	0.34
	T	$\delta^{13}\text{C} = -26.22 + (0.34 \pm 0.06) T$	0.58	0.37
	H	$\delta^{13}\text{C} = -12.41 - (0.11 \pm 0.02) H$	0.68	0.38
	P	$\delta^{13}\text{C} = -21.04 - (0.004 \pm 0.001) P$	0.41	0.55

by other additional factors: Important are evapotranspiration of leaf water through the more or less open stomata, exchange of ^2H -isotopes between atmospheric air humidity and leaf water pools, as well as the direct uptake of soil- and precipitation water through the roots (White, 1988; Brenninkmeijer, 1983).

Thus, it appears possible that trees growing on a well "irrigated" soil (e.g., the Black Forest) may not use average August precipitation but utilize more water from preceeding months. Under these conditions comparison of August temperatures with $\delta^2\text{H}$ -values might produce a scatter of data points such as seen in Table 1. Exchange processes of $^1\text{H}/^2\text{H}$ between the leaf water pool and the air humidity contribute to the $\delta^2\text{H}$ of celluloses. Thus varying atmospheric circulations which bring vapour with different deuterium contents in contact with the needles might cause a high scatter of the relations between cellulose deuterium and relative humidity at the subalpine timberline encountered in the Black Forest. Finally, there is likely to be scatter in the primary precipitation $\delta^2\text{H}$ /temperature relationship (Yurtsever and Gat, 1981). This scatter would be manifested also in possible relations between $\delta^2\text{H}$ of tree ring cellulose and $\delta^2\text{H}$ of local meteoric waters.

The scatter of both $\delta^2\text{H}$ - and $\delta^{13}\text{C}$ -values could

also be influenced by the fact that the meteorological station is not located at the exact sampling locality. Thus, the pattern of geographical climate variation of this station may not be exactly analogous to that of the growth sites. This is obviously only of minor importance because otherwise the good correlation of the $\delta^{13}\text{C}$ values with increasing temperature, decreasing humidity and decreasing precipitation rate could not be accounted for.

The correlation between $\delta^{13}\text{C}$ contents and temperature amounts to an increase of $+0.33\text{‰}/^\circ\text{C}$ (Fig. 1). This value is in good agreement with relations found by Wilson and Grinsted (1977) for *Pinus radiata* ($0.2\text{‰}/^\circ\text{C}$), by Freyer and Belacy (1983) for *Pinus Sylvestris* ($0.18\text{‰}/^\circ\text{C}$), by Tans (1978) for *Quercus* sp. (0.27 to $0.39\text{‰}/^\circ\text{C}$), and by Stuiver and Braziunas (1987) for some coniferous trees ($0.32\text{‰}/^\circ\text{C}$).

3.2. Reconstruction of paleoclimatic data

Generally, the aging of the Firs 1–19 was accompanied by steadily increasing $\delta^{13}\text{C}$ -values with time (see Fig. 4). The increase was different among the trees and accounted for a minimum of 0.2‰ (Fir 6) and a maximum of 2.2‰ (Fir 2), and averaged $1.0\text{‰} \pm 0.6\text{‰}$ (Fir 1–19). This trend is

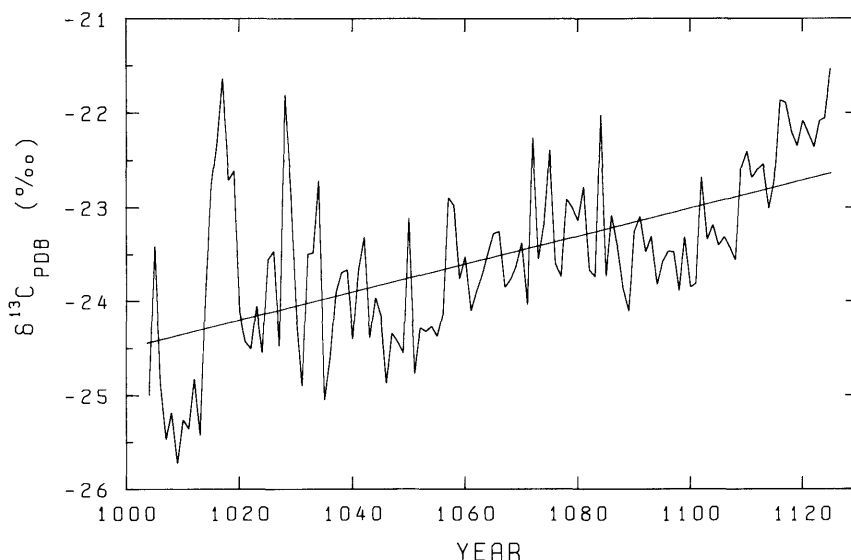


Fig. 4. Original $\delta^{13}\text{C}$ -values of Fir 1 (Black Forest), covering the period 1004–1125.

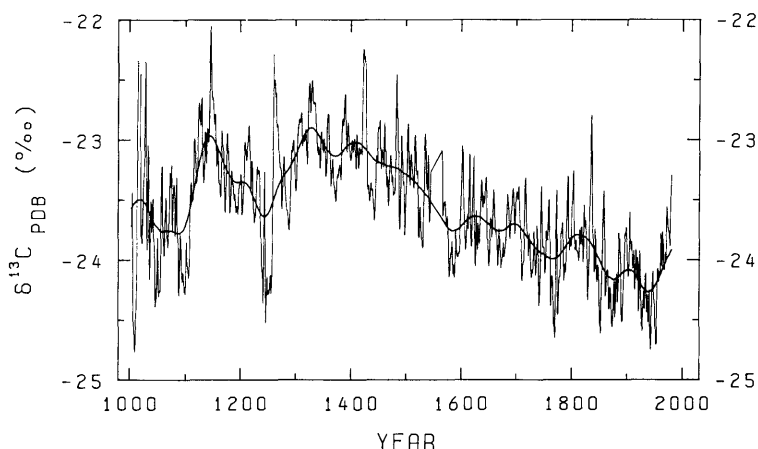


Fig. 5. $\delta^{13}\text{C}$ -values of cellulose extracted from late wood of firs (*Abies alba*) at Black Forest during the period from AD 1004 to AD 1980. The ^{13}C series is smoothed by Gaussian low pass filters over 3 and 100 years.

not yet understood in detail, but may be caused by individual intrinsic age-related physiological effects and/or local canopy-effects (Francey and Farquhar 1982). Since this trend was observed to be quite linear with time, it was corrected by subtracting the slope of the simple regression line from their $\delta^{13}\text{C}$ values. Thus, the various individual "aging effects" of the trees could be eliminated and thus equalized. When connecting the individual firs, the overlaps agree quite well, which may document a common climatic signal on formation of

late wood cellulose in various stages of the tree's life. However, because the measured $\delta^{13}\text{C}$ -values of the single trees showed different levels, each pattern was shifted in order to correspond the overlaps at the end and at the beginning of each tree, respectively. For example, the pattern of Fir 1 (1004–1125) shows an increasing trend at the end of the curve (see Fig. 4, 5). Fir 2 (1100–1200) also shows an increasing trend at the beginning of the curve (see Fig. 5). Now, Fir 2 was shifted to match the regression lines of the overlaps between

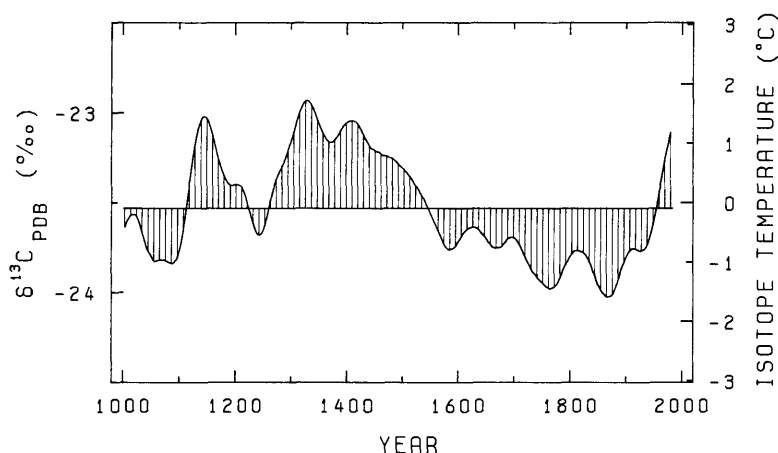


Fig. 6. $\delta^{13}\text{C}$ -values (smoothed by Gaussian low pass filter over 100 years) of cellulose extracted from late wood of firs (*Abies alba*) at Black Forest during the period from AD 1004 to AD 1980. Values from 1850 up to 1980 are corrected for input of human fossil fuel CO_2 (see text). Temperatures are reported as deviations from their mean value.

Fir 1 and Fir 2 (25 years). Subsequently Fir 3 was shifted and so on. Thus, connection of the different trees was carried out according to the "fine structures" enclosed within each tree. The record in Fig. 5 is consistently characterized by these "fine structures" (compare Fig. 4 to Fig. 5).

The de-trended and shifted $\delta^{13}\text{C}$ values of the late wood of tree rings from 19 firs covering the time span from 1004 AD to 1980 AD are shown in Fig. 5. In this Fig., two fir trees are part of the average isotopic "medieval warm phase" (Fir 1, 2: 1004–1200) and four fir trees are part of the "Little Ice Age" (Fir 10–13: 1565–1880). The post 1850-epoch is covered by an average of the five recent fir trees (Fir 15–19: 1845–1980).

Based on the temperature correlation presented in Table 1, paleotemperatures were reconstructed and are shown in Fig. 6. From correlations given in Table 1 it also would be possible to reconstruct relative air humidity and precipitation rate but temperature has been regarded as the basic meteorologic parameter other parameters depend on. The curve in Fig. 6 should be interpreted with some caution because the climatic causes of short-term isotopic changes during the past 21 years may be different from the causes of isotopic changes during the past thousand years. Thus, in order to evaluate this reconstruction, comparison with other climate reconstructions is necessary.

For example, Lamb (1968) presents variations

of temperature over central England obtained by various methods including evaluation of historical data for about the same time scale as shown in Fig. 5. The agreement is surprisingly good, despite some divergence between Lamb's data (Fig. 7) and data presented here. This is possibly caused by non-climatic trends in the environment of the trees (e.g., shading).

Both data sets show a temperature increase at about 1100 AD, which reflects the beginning of the medieval warm phase. According to Lamb (1968), the high temperature plateau was sustained until about 1280 AD. In the tree ring curve, the decrease occurred earlier with a clear minimum at about 1240 AD, followed by a temperature increase which reached a maximum at about 1330 AD. From the middle of the 14th century, both curves show a decreasing temperature trend of comparable magnitude, terminating at about 1550 AD. The so called Little Ice Age from about 1550 AD to 1850 AD is also recognizable in both curves. Using the mentioned anthropogenic correction for post-1959 (0.3‰), and a non-linear correction for the pre-1959 epoch of a total of about 0.6‰ (see Friedli et al., 1986), the data of Lamb (1968) and the tree ring curve (Fig. 6) show the documented 19th and 20th century warming. Note, that uncorrected data (Fig. 5) do not show this warming as clearly.

It should also be noted that Kitagawa et al.

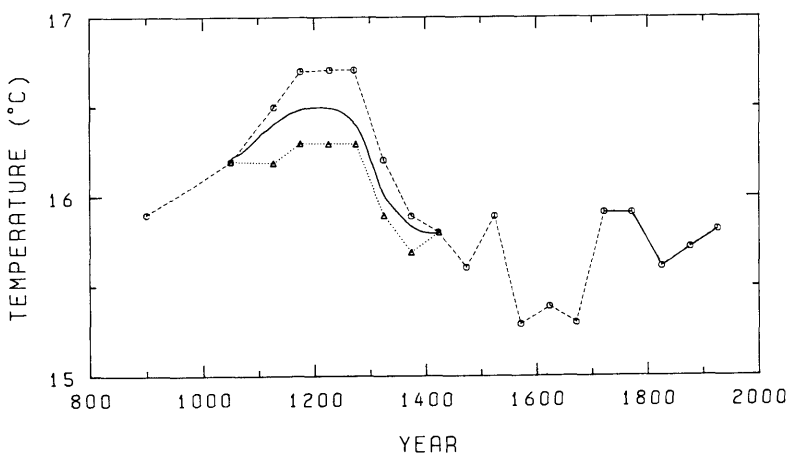


Fig. 7. Summer temperatures (July and August) prevailing in central England during the past millenium, 50-year averages. ○—○ Observed values. ○--○ Preferred values including temperatures adjusted to fit botanical indications. △...△ Unadjusted values based on purely meteorological evidence. — Analyst's opinion (after Lamb, 1968).

(1989) analysed the $\delta^{13}\text{C}$ -contents of tree rings from Japanese cedars (*Cryptomeria japonica*) and found for Japan $\delta^{13}\text{C}$ - and temperature records very similar to those recorded here for southern Central Europe.

4. Conclusions

Late wood ^{13}C and ^2H measurements in tree rings during the last millenium have been performed on several Black Forest fir trees (*Abies alba*). It has been found that $\delta^{13}\text{C}$ -values (and not $\delta^2\text{H}$) reflect the local temperature regimes despite some dependence on climatic factors such as humidity, temperature, and precipitation during August. Based on this observation, it was possible to reconstruct the paleoclimate for the past 1000

years. However, the $\delta^{13}\text{C}$ data must be corrected after 1850 AD (beginning of the industrialization) in order to provide a clear pattern of climatic change. Comparing these tree ring data with historical paleodata (Lamb, 1968), a general agreement does exist. Of course, local environmental conditions influence the picture and it is always problematic to retrieve paleoclimatic information from single trees. In spite of this, the investigation shows that $\delta^{13}\text{C}$ values of tree rings could provide a helpful tool to evaluate long term changes in paleotemperatures. The picture is less clear for $\delta^2\text{H}$ -values from nitrated cellulose, although it too must depend on local climatic parameters. However, based on the data available on fir trees from the Black Forest, it was not possible to provide a climatic interpretation of $\delta^2\text{H}$ data.

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