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Oxygen and carbon isotopic record of climatic variability in tree ring cellulose (*Picea abies*): An example from central Switzerland (1913-1995)

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Abstract. Stable isotopic data from terrestrial records spanning the last century provide an unique opportunity to test and calibrate how these systems respond to recent climatic change. Here we present an annual oxygen and carbon isotope record covering the period from 1913 to 1995 measured in tree ring cellulose of spruce trees (*Picea abies*) from central Switzerland. We compare these results with historical low- and high-frequency instrumental data. The isotopic data show high-frequency and spectral correlations, although long-term trends appear to be dissimilar. Our approach also uses constructed time series of these isotopic data with the different climate variables and demonstrates that not all parameters affect the record in the same manner. Additionally, we tested the trees' ability to record the isotopic composition of precipitation and thus changes in temperature and atmospheric circulation. Over the last 23 years, changes of up to 2‰ in the $\delta^{18}O$ value of precipitation have been recorded in the nearby Bern Global Network for Isotopes in Precipitation station, and our tree ring isotopic record shows similar changes as a result of moisture uptake during the growing season. Naturally, all biologic systems react differently to environmental perturbations, and correlation with other records will provide a means to validate how well these systems reflect actual climatic changes.

1. Introduction

A variety of terrestrial isotopic records can be exploited to provide continuous proxies of climatic change. Annually, laminated lake sediments and tree ring archives are particularly suitable because of their high-resolution potential [*McKenzie and Hollander*, 1993; *Robertson et al.*, 1997a; J.L. Teranes and J.A. McKenzie, Lacustrine Oxygen Isotope Record of 20th-Century Climate Change in Central Europe: New Interpretation of Paleo-Climatic Controls on Oxygen Isotopes in Precipitation, submitted to Geology, 1998] . Such records spanning the last 100 years can be validated and calibrated using historical instrumental databases, such as temperature, pressure, precipitation, solar variability, etc., and are thus valuable for interpreting longer time series from the geologic past. With an increased temporal and spatial resolution, terrestrial isotopic records can potentially be used to map changes in paleoprecipitation via calibration with the existing Global Network of Isotopes in Precipitation (GNIP) stations formerly referred to as International Atomic Energy Agency (IAEA) stations [*Rozanski et al.*, 1993]). The terrestrial proxy data can provide a record of isotopic changes in precipitation, which can be used to understand (1) changes in the dominance of different airmasses carrying precipitation to an area, and (2) changes in the spatial geometry of the westerly jet stream. The information extracted from the proxy data can be applied to validate and test present climate models, eventually leading to improved forward modeling.

The interpretation of terrestrial archives in temperate zones in terms of paleoclimate/environmental reconstructions is, however, not an easy task. For example, tree ring studies have demonstrated that trees located at the limit of their ecologic distribution are typically the best recorders of climatic change. This is because only one or few factors control their development and distribution, for example, temperature, precipitation, or/and elevation [*Schweingruber et al.*, 1990]. To improve our understanding of paleoclimatic change spatially, we need to investigate temperate regions. Here we present a spruce tree ring cellulose carbon and oxygen isotope chronology from a temperate setting, and show how these proxies respond to recent climate change via comparison with existing instrumental records. Presently, this study represents the longest annual oxygen isotopic tree ring record (1913-1995) from continental Europe.

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2. Background Theory

The oxygen and carbon isotopic composition of tree rings has been related to climatic variables such as temperature, relative humidity, water stress, anthropogenic CO_2 forcing, and even pollution [*Buhay and Edwards*, 1993; *Burk and Stuiver*, 1981; *DeNiro and Epstein*, 1979; *Edwards et al.*, 1985; *Freyer*, 1979; *Leavitt*, 1988; *Ramesh et al.*, 1986; *Robertson et al.*, 1997a; *Saurer et al.*, 1997b; *Saurer et al.*; 1995; *Switsur et al.*, 1996]. The ^{18}O signal contained in tree ring cellulose is generally considered to be controlled by (1) the isotopic composition of the water utilized in cellulose production and (2) the biologic fractionation between cellulose and water [*DeNiro and Epstein*, 1979; *Sternberg et al.*, 1986]. In terrestrial plants these controls are further complicated by transpiration of water through the leaves' stomata.

The model of *Dongmann et al.* [1974], modified by *Aucour et al.* [1996], can be used to calculate the oxygen isotopic value in leaf water and cellulose as described by the following equations:

$$\delta^{18}O_{\text{leaf water}} = (1-f)[\varepsilon_e + \varepsilon_k(1-h) + h\delta_{\text{atm}} + (1-h)\delta_{\text{sw}}] + f\delta_{\text{sw}} \quad (1)$$

$$\delta^{18}O_{\text{cellulose}} = \delta^{18}O_{\text{leaf water}} + \varepsilon \quad (2)$$

where f is the fraction of leaf water not subject to evaporation [*Allison et al.*, 1985]; ε_e is the liquid-vapor equilibrium fractionation for water [*Majoube*, 1971]; ε_k is the water liquid-vapor kinetic fractionation, dependent on airflow dynamics at the leaf boundary area [*Buhay et al.*, 1996]; h is atmospheric relative humidity; and δ_{atm} and δ_{sw} are the isotopic composition of atmospheric water vapor and soil water, respectively. Equation (1) can used to estimate the isotopic composition of cellulose, using the appropriate biologic fractionation factor ε, which is ~27‰ (±3‰) for a variety of plants [*DeNiro and Epstein*, 1979, *DeNiro and Epstein*, 1981]. The f factor in (1) is included to reduce the overestimation of evaporative effects of leaf water (estimated to be 0.2 [*Allison et al.*, 1985]). The f factor can also be viewed as a dampening factor accounting for the alteration of the isotopic composition of photosynthate due to exchange with stem water prior to cellulose formation (see below).

Recent work has demonstrated that leaf water is compartmentalized, and not all of it is subject to evapotranspiration through the stomata [*Yakir et al.*, 1994]. In an equivalent approach to equation (1), *Saurer et al.* [1997a] recommend using a dampening factor of 0.3 to 0.5. This factor corresponds to a f=0.5 to 0.7, that is, a very distinct reduction of the leaf water enrichment would be reflected in the stem cellulose. Additionally, there is evidence that 45% of the leaf water isotopic signal transferred to the sucrose produced in the chloroplasts is exchangeable with stem water before it is synthesized into cellulose [*DeNiro and Cooper*, 1989; *Farquhar et al.*, 1998; *Sternberg et al.*, 1986]. The exchange of stem water with sucrose results in a further reduction of the leaf water enrichment.

The carbon isotopic signature in plants is regulated by photosynthetic fixation of CO_2 via stomatal transfer. This isotopic fractionation is controlled predominantly by two factors in C_3 plants: (1) the CO_2 concentration in the atmosphere and inside the leaf, respectively c_a and c_i ; and (2) biologic fractionation due to the isotopic discrimination of ribulose-1,5-bisphosphate carboxylase enzyme. The model of *Francey and Farquhar* [1982] is described as

$$\delta^{13}C_{\text{plant}} \approx \delta^{13}C_{\text{atm}} - a - (b - a)c_i/c_a \quad (3)$$

where $\delta^{13}C_{\text{atm}}$ is the $\delta^{13}C$ value of atmospheric CO_2, a is the diffusion fractionation across the boundary layer and the stomata (≈4.4‰), and b is the enzymatic biologic fractionation (≈27‰). It is important to note that according to *Francey and Farquhar* [1982]:

$$c_i = c_a - A/g \quad (4)$$

where A is the CO_2 assimilation rate and g is the boundary layer/stomatal resistance for diffusion of CO_2. This relationship demonstrates the importance of the stomatal pores, as a control on the $\delta^{13}C$ value of plants. Equation (3) only holds true, however, for bulk plant material. The relationship between the $\delta^{13}C$ values of the plant and its cellulose is described by *White et al.* [1993]:

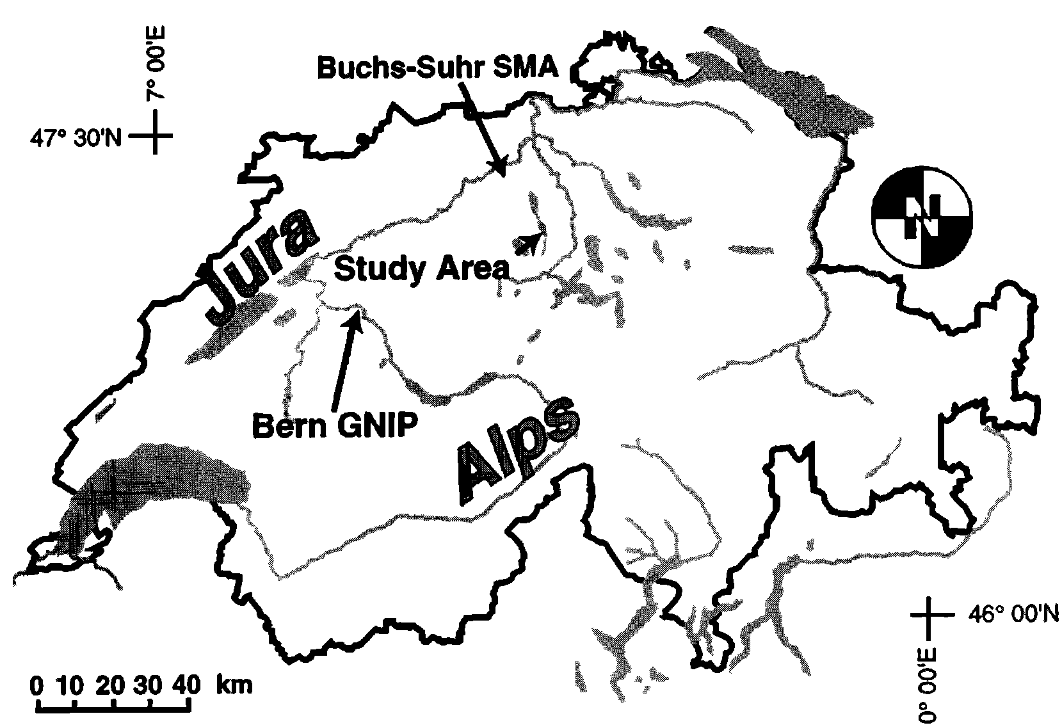

Figure 1. Map of Switzerland showing the location of the Eigentobel study area in relation to meteorologic stations, the Bern GNIP/SNIHC station, and the significant geographic barriers.

$$\delta^{13}C_{cellulose} = \delta^{13}C_{plant} + \delta_{c\text{-}p} \quad (5)$$

where $\delta_{c\text{-}p}$ is the difference between the bulk plant $\delta^{13}C_{plant}$ and the cellulose $\delta^{13}C_{cellulose}$ values and is ~1.4‰ for *Picea abies* [*Saurer et al.*, 1997a].

3. Methods

3.1. Site Selection

Our study area is located on the central Swiss plateau (47° 10' 47"N, 8° 15' 26"E, 600 meters above sea level, between two significant physical barriers, the Jura mountains to the northwest and the Alps to the south (Figure 1). The four different weather systems, which converge over central Switzerland controlling climate, include Mediterranean, continental, Atlantic, and polar regimes [*Beniston et al*, 1994]. A stand of spruce tress (*Picea abies*) located at a semi-dry to medium-dry site on a 10-20° southernly facing slope was selected for sampling (F.H. Schweingruber, personal communication, 1996). Based on previous studies with similar classification, this site, named Eigentobel, should be sensitive to moisture changes [*Saurer et al.*, 1995]. This particular location was selected because of its immediate proximity to a small lake, Baldeggersee, located 1 km to the northeast of the tree stand, which contains a varved sediment record spanning the last hundred years. Based on results of an earlier isotope study of lacustrine varves in nearby Lake Greifen [*McKenzie and Hollander*, 1993], Baldaggersee has been the focus of a recent paleoclimate/calibration study, which has provided an unique record of annual climate change (Teranes and McKenzie, submitted manuscript, 1998). A comparison between the response to climatic forcing of these two terrestrial archives will be undertaken.

The Eigentobel site (Figure 1) lies 25 km south of the Schweizerische Meteorologishe Anstalt (SMA) weather station in Aarau, which was relocated in 1984 to Buchs-Suhr (<5 km distance). Additionally, a SMA precipitation station is located 6 km northwest of the study area at Beromuenster. These combined stations provide a continuous record of climatological data (precipitation, relative humidity, temperature, etc.) since the beginning of the 20th century, which are made available through the SMA electronic data bank (H. Bantle personal communication, 1997). The GNIP station at Bern (60 km to the southwest of Eigentobel) operated in conjunction with the Swiss Network for Isotopes in the Hydrological Cycle (SNIHC) has produced a continuous monthly record of the oxygen isotopic composition of rainfall since the early 1970's [*International Atomic Energy Agency/World Meteorological Organization*, 1998] Isotopic measurements collected during the growing season, defined as May-September, are used in this study to evaluate the ability of these trees to record the isotopic signature of the precipitation. All oxygen isotope ratios of precipitation from the Bern GNIP/SNIHC station, which is operated by the Swiss National Hydrological and Geological Survey, were measured at the Stable Isotope Laboratory of the Physics Institute, University of Bern.

3.2. Sampling

At the Eigentobel site, four spruce trees were selected for dendrochronology and isotopic analysis. Four is considered the number of trees required to produce a well-representative isotopic record [*Robertson et al*, 1997b; *Saurer et al.*, 1995]. Each tree was located within less than 10 m of each other, and care was taken to select trees with similar growth histories. All trees are estimated to be older than 90 years, as determined by core intersection with the inner-most rings. Each tree was cored 3 times with a 5 mm borer. The first two cores were recovered from the same bearing, one of which was reserved as an archive. The subsequent core was taken at 90° from the original orientation. The two opposing cores were used for geochemical analysis. Ring widths were measured on each sampled tree, and from these a relative tree ring index (Figure 2) was constructed. Some rings (>10%) appeared to be missing resolvable early wood/late wood boundaries, or were simply too small (<1 mm) to make a clear distinction, and thus whole rings had to be used. Whole annual ring samples from all trees were separated and pooled together from corresponding years in equal weights in order to balance the influence of each individual. The $^{13}C/^{12}C$ ratios of the whole rings should have a "smoothing" effect on the data, due to the utilization of the previous years carbohydrate in the early wood. Oxygen isotopes are not affected in the same way as carbon isotopes in tree rings and should represent the water used by the plant during that year. A previous experimental study with oak by *Hill et al* [1995] has documented that the $\delta^{18}O$ value of early wood does not have an affinity with the previous years' late wood.

3.3. Geochemical Analysis

Pooled annual whole wood samples were first milled and then αcellulose was extracted using a method modified after *Green* [1963] for smaller (up to 80 mg) amounts of material. For oxygen isotope analysis, the $^{18}O/^{16}O$ ratios were measured on CO gas produced via an elemental analyzer coupled to a stable isotope ratio mass spectrometer (EA-IRMS), following the method of *Werner et al.* [1996] and *Saurer et al.* [1998]. Cellulose (1.3-1.5 mg) enclosed in a tin cup is introduced into a glassy-carbon filled reaction furnace at 1080°C under a continuous flow of ultra pure He gas, where it undergoes pyrolysis forming CO (95% conversion). The CO is then transferred to the mass spectrometer after removal of H_2O and CO_2 in a chemical trap and passes through a gas chromatographic column under continuous flow via an open split valve. The sample's relative isotopic ratio is measured against a reference gas pulse of CO from a gas injector system. All isotopic measurements are reported in the standard delta notation:

$$\delta\,(‰) = \{(R_{sample}/R_{standard})-1\} \times 1000$$

The $\delta^{18}O$ values for each sample run is standardized to Vienna SMOW (VSMOW) using internal cellulose standards, which have been measured as CO_2 produced by the standard nickel pyrolysis method in operation at the University of Bern [*Saurer et al.*, 1997b]. Samples from years 1968-1995 and 1913-1967 were analyzed for oxygen isotope composition on an EA coupled to a Delta-S Finnigan MAT mass spectrometer at the Paul Scherrer Institute, and an EA coupled to a Micromass Optima mass spectrometer at the Stable Isotope Laboratory of the Geological Institute, ETH-Zürich, respectively. The intercalibration of both mass spectrometers was verified by the measurement of both an internal standard (Merck cellulose, 28.67±0.3‰), and the IAEA C3 cellulose standard with a value reported by University of Bern of 32.2±0.11‰ [*Buhay et al.*, 1995]. Analytical reproducibility for this method is about ±0.30‰ (1σ) based on measurements of an internal cellulose standard. All carbon isotope analysis were conducted using

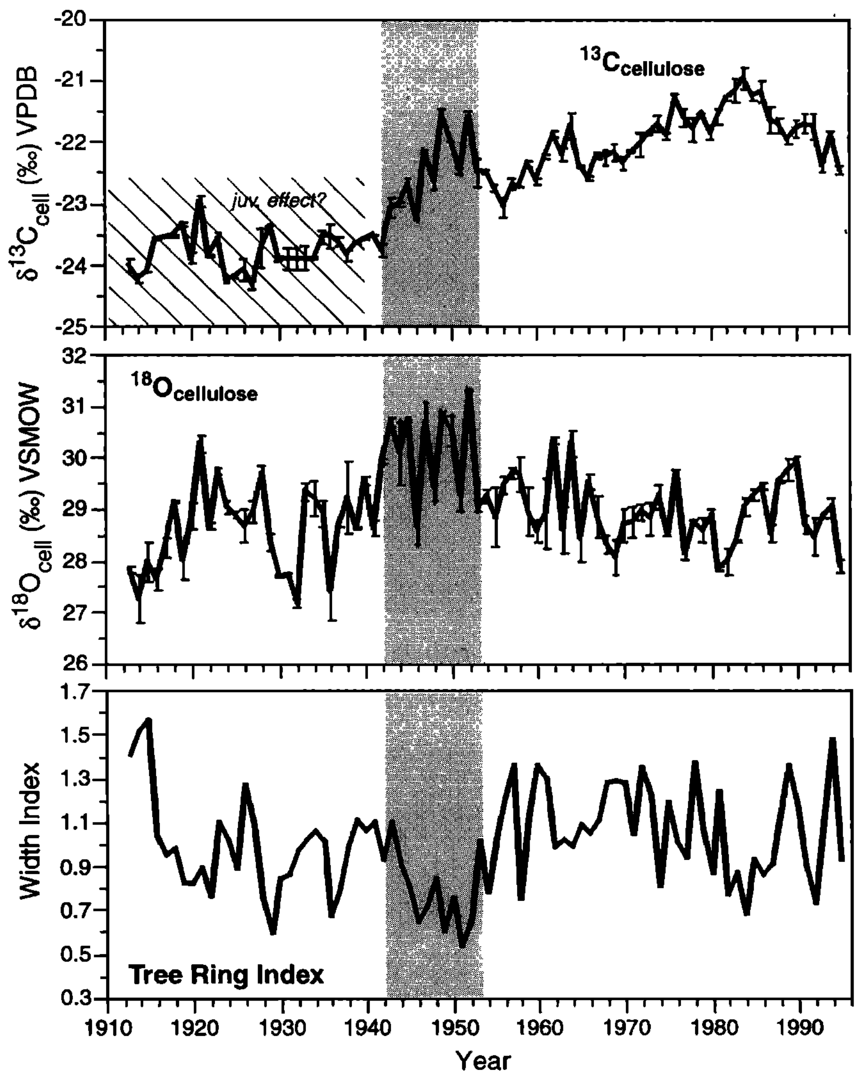

Figure 2. Three graphs showing the raw data for $\delta^{13}C_{cellulose}$ and $\delta^{18}O_{cellulose}$ values (with error bars, 1σ) and tree ring index (a relative index constructed from all trees). The hatched lined section in the $\delta^{13}C_{cellulose}$ plot indicates the area where the data appear to show a juvenile effect from soil-respired CO_2. The shaded area indicates the warmest period in Switzerland within the last 100 years, which occurred between 1940 and 1950 [*Beniston et al.*, 1994]. Note how all three records respond at this time with increased isotopic values and decreased tree ring widths reflecting an extreme warm climatic event.

standard EA-IRMS procedures and CO_2 gas measured on an EA coupled to a Micromass Optima mass spectrometer calibrated with NBS-22 standard for $\delta^{13}C$ reported relative to Vienna Pee Dee belemnite (VPBD). Sample reproducibility, based on 70 analyses of an internal standard, is ±0.09 (1σ). Both oxygen and carbon isotope analyses were duplicated for each yearly cellulose sample, from which mean values were calculated (Figure 2).

4. Results

4.1. General Trends

The tree ring index and corresponding $\delta^{18}O$ and $\delta^{13}C$ values of the pooled cellulose from the Eigentobel tree rings are plotted versus year for the study period 1913 to 1995 in Figure 2. There is no statistically significant correlation (>95% confidence level) between the tree ring index and the isotopic data. The three data sets do not show a strong degree of covariance, except during the 1940s, when all parameters display excursions (Figure 2). Between 1940 and 1952 the isotopic values increased and correlate with a decrease in relative ring width. These years were the warmest sustained period in Switzerland within the last 100 years [*Beniston et al.*, 1994]. Apart from this period, the tree ring index shows no significant correlation with the historical record of climatological parameters, such as temperature, relative humidity, and precipitation. The $\delta^{13}C_{cellulose}$ record displays a first-order enrichment trend of ~3‰ from 1940 to 1995 (Figure 2). Superimposed on this first-order trend are up to four second-order enrichment-depletion trends, most notably the abrupt increase followed by a decrease of 2‰ from 1940 to 1955. First-order $\delta^{18}O_{cellulose}$ trends consist of two predominant enrichment-depletion cycles (Figure 2). The first one occurs between 1913 anf 1932 with a total shift magnitude of ~2.5‰. This cycle is followed by the second enrichment-depletion trend reaching a maximum of 31.3‰ in 1952; afterwards the data show a continuous depletion trend of ~2‰. Many second-order variations varying from 2 to 7 years are superimposed on the first-order trends.

Table 1. Correlation of Eigentobel's Carbon and Oxygen Isotope Data With Environmental Parameters.

	$\delta^{13}C$ VPDB, ‰			$\delta^{18}O$ VSMOW, ‰		
	r	*m*	significance†	*r*	*m*	significance†
			Raw Environmental Variables			
Temperature						
Average daily	0.28	0 27 ‰/°C	3.74×10^{-2}	0.39	0.35 ‰/°C	2.63×10^{-4}
Average maximum	na			0 49	0 27 ‰/°C	3.93×10^{-5}
Relative humidity						
Average daily	na			-0 37	-0.07 ‰/%	7.72×10^{-6}
Average midday	na			-0 47	-0 10 ‰/%	3.14×10^{-4}
Precipitation total	-0.30	-0.03 ‰/cm	2.33×10^{-2}	-0 41	-0.04 ‰/cm	9.48×10^{-5}
			High-Frequency Environmental Variables			
Temperature						
Average daily	0 67	0 23 ‰/°C	$1\ 20\times10^{-8}$	0 44	0 38 ‰/°C	$3\ 38\times10^{-5}$
Average maximum	0 72	0.17 ‰/°C	$6\ 26\times10^{-10}$	0 41	0 25 ‰/°C	$6\ 48\times10^{-4}$
Relative humidity						
Average daily	-0.60	-0.05 ‰/%	1.23×10^{-6}	-0.50	-0.10 ‰/%	$1\ 79\times10^{-6}$
Average midday	-0.62	-0.04 ‰/%	3.29×10^{-7}	-0.50	-0.08 ‰/%	1.41×10^{-6}
Precipitation	-0.77	-0 02 ‰/cm	2.64×10^{-12}	-0 62	-0.11 ‰/cm	2.92×10^{-8}

Climate data are mean values for June, July, and August (JJA) and *m* is the slope of the regression curve. Abbreviation na, not applicable.

† Significance as determined by the *F* test

4.2. Approach

To test if the stable isotopic variations measured in the cellulose were a response to climatic change, the data were compared via linear regression with a subset of raw and high-frequency environmental variables for the summer months (June, July, and August = JJA; Table 1). These months were selected because they had the highest degree of correlation with the Eigentobel isotopic data. High-frequency is defined as the first differences of the data set (one year minus the previous year), which allows for the rate of change to be determined and removes long-term trends without altering or modifying the existing data [*Loader and Switsur*, 1995; *Robertson et al.*, 1997b; *Saurer et al.*, 1995]. Times series of the high-frequency cellulose isotopic values and the historical climatic parameters are plotted together in Figures 3 and 4. The *r* values and slope coefficients (*m*) are noted. The direct comparison of these climatic and isotopic times series gives a better graphical representation of the temporal response of these isotopic proxy indicators versus a simple bivariant plot. Additionally, the carbon isotope data used for statistical comparison with environmental variables have been corrected for the change in the isotopic composition of atmospheric CO_2 (Table 1 and Figure 3), which has decreased by ~1‰ during the study period [*Francey and Allison*, 1996; *Friedli et al.*, 1986; *Mook et al.*, 1983].

4.3. Carbon Isotopes and Climatic Parameters

The constant and highly depleted $\delta^{13}C_{cellulose}$ values prior to 1940 are attributed to a juvenile effect [*Francey and Farquhar*, 1982] and only post 1940 data were used for the statistical analysis of this study (Table 1 and Figure 3). The direct correlation of the raw data yields only two significant relationships with average daily temperature (0.28) and total precipitation (-0.30). The rest of the parameters, including average maximum temperature, relative humidity daily average and mid-day average, show no significant correlation, whereas the high-frequency comparisons all yield statistically significant relationships. The total amount of precipitation for JJA has the highest degree of high-frequency inverse correlation with the $\delta^{13}C_{cellulose}$ value of -0.77.

Time series comparisons of the $\delta^{13}C_{cellulose}$ data show that the climatological parameters "force" the isotopic records differently at different periods. The $\delta^{13}C_{cellulose}$ responds to all of the parameters from 1944 to 1955, but, afterwards, not every change is represented in the isotopic record (Figure 3). For example, the isotopic record between 1982 and 1986 correlates with relative humidity but not with temperature and precipitation. Additionally, $\delta^{13}C_{cellulose}$ high-frequency values between 1970 and 1975 appear to correlate only with changes in precipitation, but not with the other parameters. With regard to the slopes of these linear regressions with $\delta^{13}C_{cellulose}$, the average daily and midday relative humidity for JJA have similar values, -0.05 and -0.04 ‰/%, respectively. In contrast, the values for the average maximum and daily temperatures are not exactly the same, 0.17 and 0.23 ‰/°C, respectively.

4.4. Oxygen Isotopes and Climatic Parameters

Oxygen isotope data do not exhibit the juvenile effect as the carbon isotopic data. Thus the $\delta^{18}O_{cellulose}$ values are compared with the climatic data for the entire study period, 1913-1995 (Table 1 and Figure 4). All linear regressions with $^{18}O_{cellulose}$ yielded statistically significant correlations (Table 1). The regressions with the high-frequency variables typically yielded higher degrees of correlation than the raw environmental variables (Table 1). Yet these correlations are lower than with the $\delta^{13}C_{cellulose}$ values and the high-frequency variables. The lower-frequency average maximum temperature displays a moderate correlation of 0.49 with the oxygen isotope data, but this is also the highest relationship for the raw data. A visual correlation between these parameters is obvious in Figure 5. The other raw parameters show a slightly weaker correlation/inversecorrelation (Table 1). The first-order correlation/inversecorrelation values are similar between the two different measurements of temperature (average daily and maximum) and relative humidity (average daily and midday). Precipitation changes display the highest relationship with the

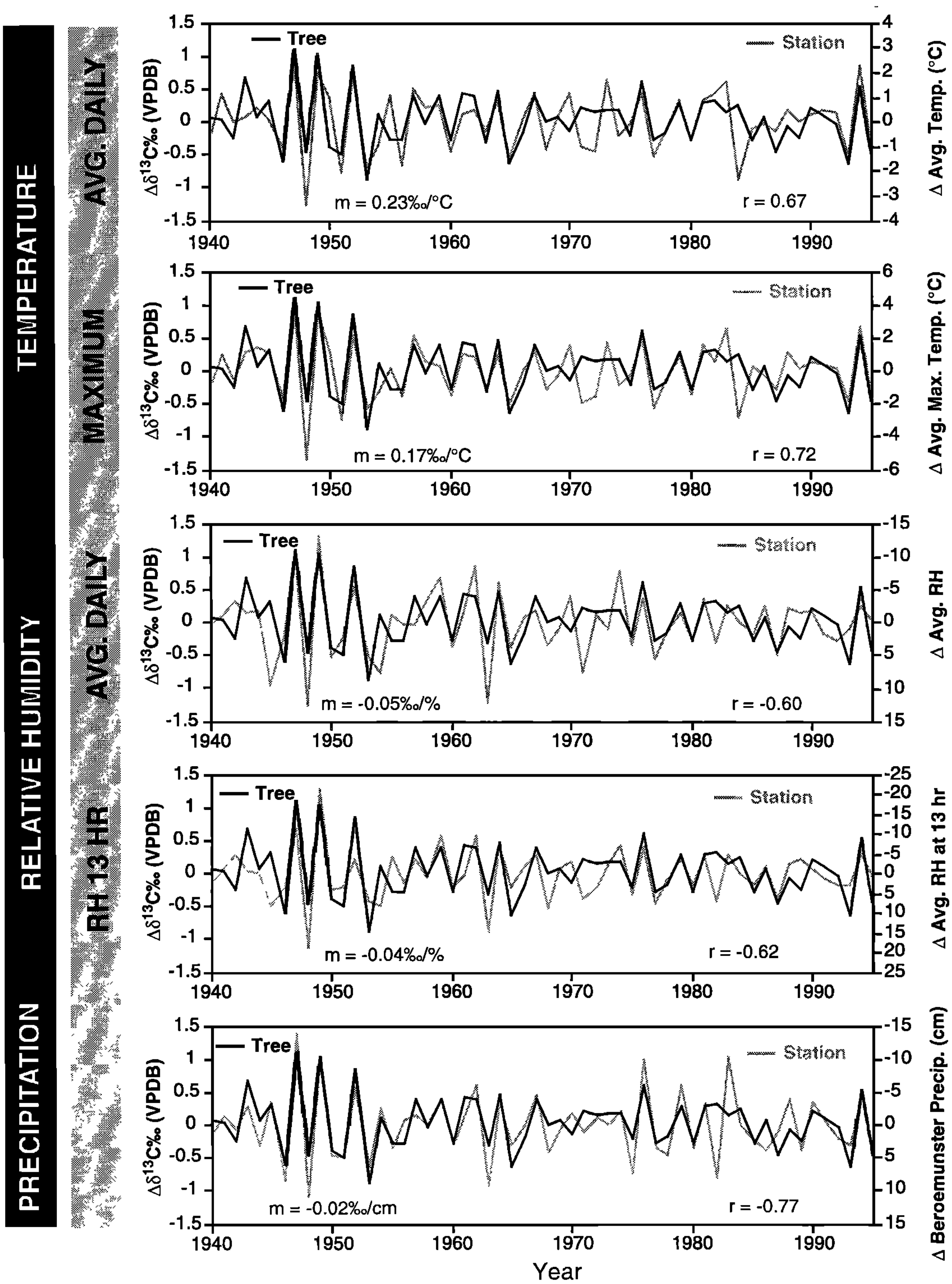

Figure 3. Time series of $^{13}C_{cellulose}$ high-resolution record (first differences) plotted separately with instrumental records of temperature (daily average and average maximum), relative humidity (RH, average daily and 13 hour or midday relative humidity), and total precipitation for summer months defined as June, July, and August (JJA). Note only data from samples younger than 1939 are compared due to the presence of the juvenile effect between 1913 to 1939 and the data have been corrected for the ~1‰ change in atmospheric CO_2 since 1940 [*Francey and Allison*; 1996, *Friedli et al.*; 1986, *Mook et al.*, 1983]. The axes for relative humidity and precipitation are reversed to emphasize the inverse relationship with the isotopic data.

$\delta^{18}O_{cellulose}$ values with an inversecorrelation of -0.62. The slope values of both low- and high-frequency environmental variables are similar except for precipitation, which shows a twofold increase in slope between the low- and high-frequency values (-0.04 to -0.11‰/%).

Time series evaluation of $\delta^{18}O_{cellulose}$ data indicates that, as with the $\delta^{13}C_{cellulose}$ times series, not all the parameters correspond to changes in the isotopic record during the same year (Figure 4). The highest levels of correlation/inversecorrelation between all parameters occur for the periods 1921-1923, 1945-

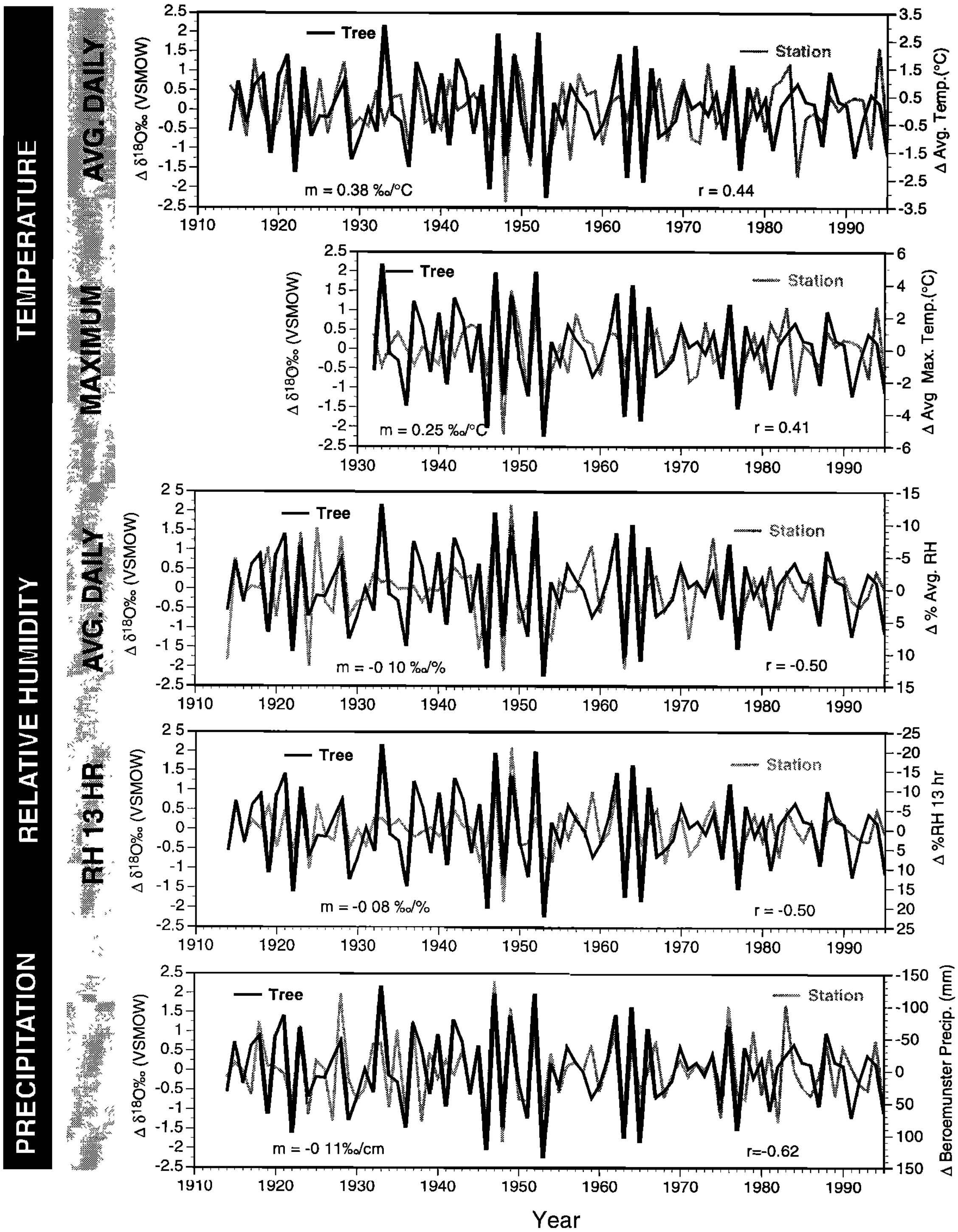

Figure 4. Time series of $\delta^{18}O_{cellulose}$ high-resolution record (first differences) plotted separately with instrumental records of temperature (daily average and average maximum), relative humidity (RH, average daily and 13 hour or mid-day relative humidity), and total precipitation for summer months defined as June, July, and August (JJA). Note that average maximum temperature data are only available from SMA station Aarau/Buchs-Suhr since 1930. The axes for relative humidity and precipitation are reversed to emphasize the inverse relationship with the isotopic data.

1953, 1961-1965, and 1976-1979. The high-frequency changes in $\delta^{18}O_{cellulose}$ have the highest degree of response with JJA precipitation changes, as is also the case for $\delta^{13}C_{cellulose}$. Each time series comparison, whether complied for $\delta^{13}C$ or $\delta^{18}O$, generates its own unique visual correlations, although some perturbations can be observed in all plots.

4.5. Comparison Between Carbon and Oxygen Isotopes

The linear regression of $\delta^{13}C_{cellulose}$ and $\delta^{18}O_{cellulose}$ values, excluding values prior to 1940, have no significant correlation (Figure 6a). In contrast with the lower-resolution data (Figure 2), the high-frequency variance between $^{13}C_{cellulose}$ and $^{18}O_{cellulose}$

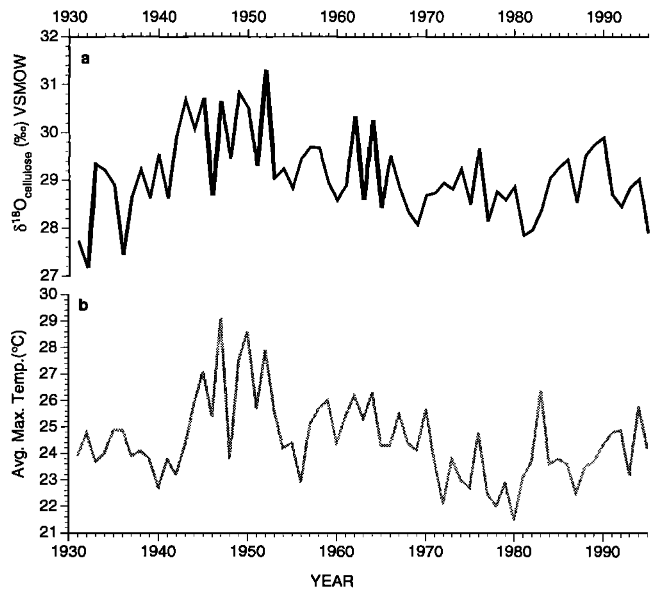

Figure 5. (a) Plot of $\delta^{18}O_{cellulose}$ (raw data) versus year from 1931 to 1995, and (b) plot of average maximum temperature data versus year for the same time period. Temperatures are from the Aarau/Buchs-Suhr SMA station. There is general visual correlation, confirmed by a linear regression of r =0.49. The most enriched isotopic values coincide with the period of sustained high temperatures from 1940 to 1955.

does display a significant correlation of r = 0.64 (Figure. 6b). Additionally, spectral analysis of both $\delta^{13}C_{cellulose}$ and $\delta^{18}O_{cellulose}$ time series reveals the same major periodicities at both 4.9 and 2.4 years, and a smaller non-significant cycle at 3.1

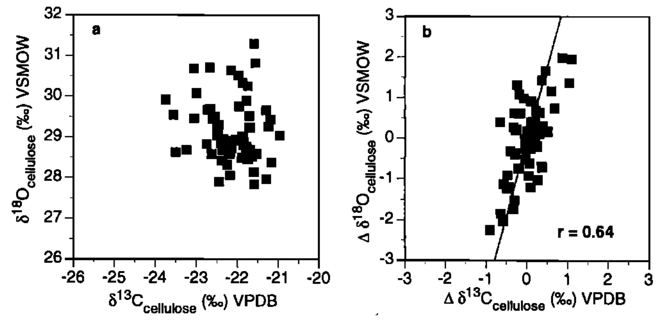

Figure 6. Bivariate plots of $\delta^{18}O_{cellulose}$ and $\delta^{13}C_{cellulose}$ values for the period of 1940 to 1994. (a) Plot of $\delta^{18}O_{cellulose}$ versus $\delta^{13}C_{cellulose}$ shows no correlation, only scatter. (b) In contrast, the bivariate plot of the high-resolution (first differences) isotopic data yields a correlation of 0.64 (>99% confidence level).

years (Figure 7). Thus the high-frequency changes in both carbon and oxygen isotopes ratios correlate and occur with the same timing.

4.6. Correlating Cellulose and Precipitation Isotopic Compositions

The monthly isotopic composition of precipitation from the Bern GNIP/SNIHC station was compared with $\delta^{18}O_{cellulose}$ record from 1973 to 1995 in Figure 8. The strongest correlation between the two $\delta^{18}O$ records was found for the months of May to September, which are considered to be the growing season for spruce. A similar observation was made for beech trees growing near Bern [*Saurer et al.*, 1997b]. Following the same approach as *Saurer et al.* [1997b], a relationship between the Eigentobel

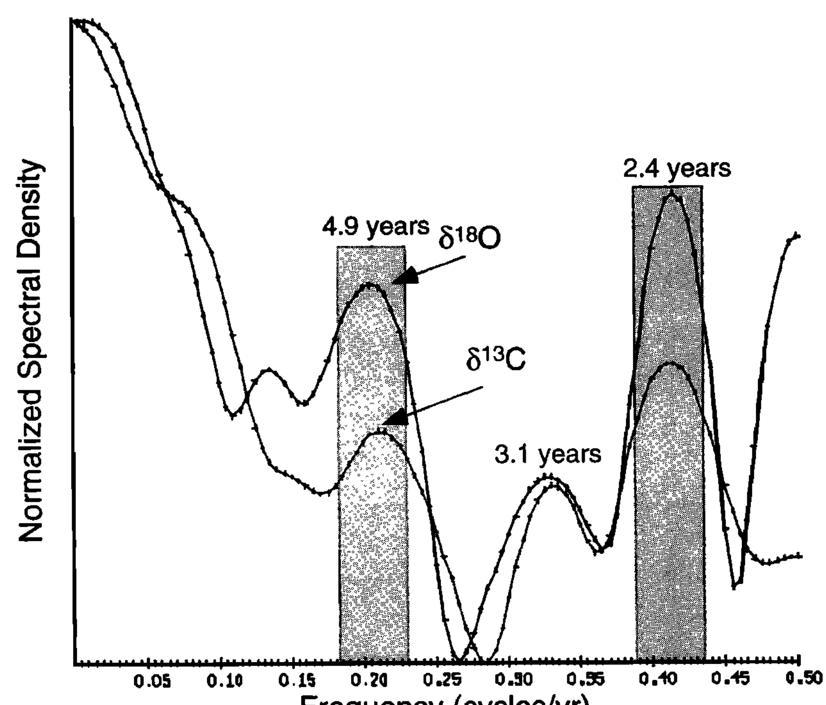

Figure 7. Spectral analysis values for both $^{13}C_{cellulose}$ (1940-1995) and $^{18}O_{cellulose}$ (1913 to 1995), using the Blackman-Tukey method [*Jenkins and Watts*, 1968]. Peaks are significant above the 80% confidence level. Both data sets were prepared with detrending from their respective mean. Band widths for $\delta^{13}C$ and $\delta^{18}O$ data were 0.666×10^{-1} and 0.5333×10^{-1}, respectively. Lags for both $\delta^{13}C$ and $\delta^{18}O$ data were 20 and 25, respectively. Two cycles at 4.9 and 2.4 years, in the grey areas, are above the confidence level, whereas the 3.1 year cycle is below but still distinguishable.

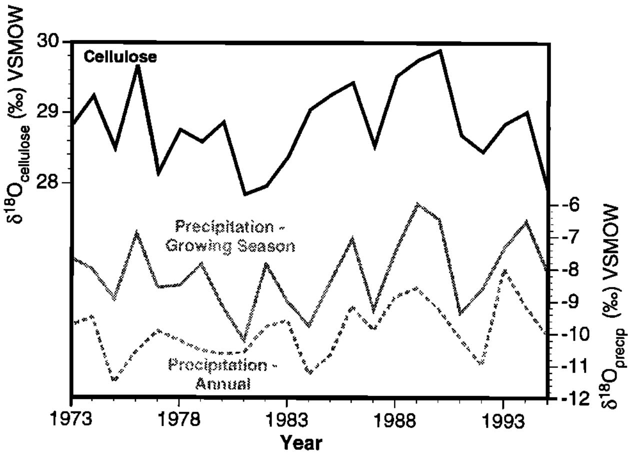

Figure 8. Plots of Eigentobel tree ring $\delta^{18}O_{cellulose}$ values and the weighted Bern GNIP/SNIHC station $\delta^{18}O_{precipitation}$ values for the growing season (solid line) and the annual precipitation (dashed line) for the period from 1973 to 1995. The growing season's $\delta^{18}O$ values have a linear regression correlation with the $\delta^{18}O_{cellulose}$ of $r = 0.64$ (>99% confidence level) and the annual precipitation's $\delta^{18}O$ correlation is $r = 0.36$ (>90% confidence level). The Bern data presented for the growing season was weighted based on a multivariate analysis of the growing season's precipitation (May-September) and the cellulose isotopic data [*Saurer et al.*, 1997b]. The annual Bern data are weighted based upon amount of precipitation in Bern.

$\delta^{18}O_{cellulose}$ value and the $\delta^{18}O$ value of precipitation was calculated with $r = 0.64$ and a slope of 0.34‰/‰ (>99 % confidence interval). Additionally, there is a lesser significant correlation with the annual $\delta^{18}O$ value of precipitation of $r = 0.36$, with a slope of 0.24‰/‰ at the 90% confidence interval. These trees apparently act as a "biologic filter" and dampen the recorded change in the ^{18}O composition of the precipitation by a factor of 2.9.

5. Discussion

The presented data show interesting trends indicating that even when the tree ring index does not show significant correlations with climatic variables, the isotopic data do. Yet on a first-order basis the $\delta^{13}C_{cellulose}$ and $\delta^{18}O_{cellulose}$ records do not display a correlation, except during 1940-1952, when both show an overall enrichment. However, the Eigentobel $\delta^{13}C_{cellulose}$ and $\delta^{18}O_{cellulose}$ high-frequency records do display a positive correlation (Figure 6). Additionally, spectral analysis indicates that the same cyclicity exists in both data sets with major cycles at 4.9 and 2.4 years (Figure 7). A similar 2.4 years cycle was observed in both a δD and $\delta^{13}C$ in a spruce tree ring cellulose record from southwest Germany [*Lipp et al.*, 1996]. The positive correlation and the same spectral frequencies indicate that a similar climatic forcing is probably acting on both of these data sets. Annual mean temperature data from other European stations show cycles with similar timing, and, in particular, a site in southern Germany shows similar cycles to the Eigentobel site at 2.63-2.08 and 4.5 years. [*Schoenwiese and Rapp*, 1997].

A decrease in the long-term $\delta^{13}C_{cellulose}$ record is expected from the burning of fossil fuels, which has caused a decrease in atmospheric CO_2 by >1‰ since the beginning of this century [*Friedli et al.*, 1986]. The Eigentobel carbon isotope record clearly does not display the predicted anthropogenic ^{13}C trend. In fact, it displays the opposite trend with a 3‰ enrichment in the last 50 years. Apparently other factors, such as age-related physiological changes and potential local canopy effects, are affecting the long-term carbon record, as similarly observed by *Lipp et al.* [1996] . It is argued that trees in open settings will not have "canopy effects" and should record past changes in the ^{13}C concentration of the atmosphere, such as studies in the American Southwest [*Leavitt*, 1988]. Whereas the Eigentobel trees were selected from a spruce stand, they are clearly affected by canopy effects, such as the observed juvenile trend before 1940. However, the anthropogenic carbon depletion trend has not been observed in other studied areas, including several European locations [*Lipp et al.*, 1996; *Robertson et al.*, 1997a; *Switsur et al.*, 1996] and in Tasmania [*Francey*, 1981]. Additionally, the increase of fossil fuel burning over the last 100 years has increased the atmospheric concentration of CO_2 from 295 to 350 ppm [*Friedli et al.*; 1986, *Keelıng et al*, 1989]. A study by *Bert et al.* [1997] on *Albies alba* in the Jura mountians (northwest from the Eigentobel site; Figure 1) found that carbon isotope discrimination decreases by ~1.5‰ from the 1930s to the 1980s. This decrease corresponds to an increase in $\delta^{13}C$ values, of the same magnitude (~1.5‰), during the same period. They correlated this decrease with an increase in water use efficiency, which is possibly caused by the increase in atmospheric CO_2 during their study period. This result is supported by previous experimental work showing that an increase in CO_2 concentration leads to an increase in carbon assimilation and a decrease stomatal conductance, allowing for elevated levels of water-use efficiency (see review in *Morison*, [1993]). The change in atmospheric CO_2 concentrations could also have a similar effect on the Eigentobel's first-order enrichment trend since 1940. Yet *Bert et al.* [1997] suggest that other controls cannot be ruled out, such as an increase in atmospheric nitrogen fertilization and/or air pollutants (ozone and sulfur), which can have similar effects. In general, correlation between $\delta^{13}C_{cellulose}$ and $\delta^{18}O_{cellulose}$ values are not expected, although both parameters are related to stomatal controls. For example, when carbon is limited due to high photosynthetic rates, an enrichment trend in $\delta^{13}C_{cellulose}$ values would be expected [*Farquhar et al.*, 1998], whereas the $\delta^{18}O_{precipitation}$ value and consequently the $\delta^{18}O_{cellulose}$ value is controlled by atmospheric processes, such as rain-out and temperature [*Dansgaard*, 1964].

The lower-frequency environmental variables are clearly not as well related to the Eigentobel $\delta^{13}C_{cellulose}$ record as the high-frequency data. Yet the time series of the high-frequency data shows that not all parameters display the same relationship. The $\delta^{13}C_{cellulose}$ value of these trees responds in a predicted manner inversely correlating with changes in relative humidity and precipitation, indicating a dominant soil moisture control on the carbon response to these variations. This inverse-relationship between carbon isotope values and the soil moisture controls verifies the high degree of stomatal limitation to photosynthesis (see above section on background theory).

Oxygen isotope data also display similar trends associated with the carbon isotope data, but, with the $\delta^{18}O_{cellulose}$ record, both the low- and the high-frequency climatic variables display relationships. Additionally, the isotopic composition of precipitation is know to correlate well with temperature and inversely correlate with the amount of precipitation [*Rozanski et al.*, 1993]. During the growing season of the trees (May-September), the relationship between the $\delta^{18}O$ of precipitation at the Bern GNIP/SNIHC station (1973-1995) with average monthly temperature and the monthly amount of precipitation is 0.50 ‰/°C (r=0.67) and –0.15 ‰/cm (r=-0.42), respectively.

These relationships explain the observed correlations between $\delta^{18}O_{cellulose}$ values and both temperature (Figure 5) and the amount of precipitation (Table 1). Also, the relative humidity is expected to influence the $\delta^{18}O_{cellulose}$ value (see (1) and (2)). If f is assumed to be zero in (1), all leaf water is subject to evaporation, and a slope of -0.36‰/% is predicted. The relationship between both the high- and low-resolution Eigentobel $\delta^{18}O_{cellulose}$ records and relative humidity display slopes of -0.1 to -0.07‰/%, indicating that the influence of humidity is strongly dampened by over 3 times in the tree ring cellulose record. However, the correlation coefficients are higher for the $\delta^{13}C_{cellulose}$ record than the $\delta^{18}O_{cellulose}$ record.

Presently, there are few annual resolution, tree ring cellulose oxygen isotopic records from Europe to compare with our data set, except for the study by *Switsur et al.* [1996] on oak in England. *Saurer et al.* [1997b] conducted a study near Bern at two sites with beech, and the longest of the two records had a 3-year sample resolution. The Eigentobel spruce data display a correlation of 0.77 with *Saurer et al.*'s [1997b] beech record, which is based on averaging three consecutive years of the spruce record to accommodate for the sampling of the beech record. Our new oxygen isotopic record exhibits a general correlation after 1940 with the first-order trends of *Switsur et al.* [1996], for example, a depletion greater than 2‰ occurs in both data sets between 1950 and 1960. The cellulose record of *Saurer et al.* [1997b] also displays a similar depletion, but with a lesser order of magnitude. Additionally, there is correlation of 0.71 between their shorter yearly resolution beech $\delta^{18}O_{cellulose}$ record and the Eigentobel spruce record of 0.71 between 1971 and 1992.

The correlation of the Eigentobel $\delta^{18}O_{cellulose}$ record with the GNIP/SNIHC isotopic record at Bern (Figure 8) indicates that the site is sensitive to changes in precipitation, and that soil water is being utilized instead of a homogenized groundwater. This observation is consistent with the fact that spruce trees have shallow root systems. With this in mind, a test of (1) and (2) may be made. A few assumptions are made: (1) we use the average daily temperature (15.8°C) of the growing season for the entire study period; (2) water vapor is in equilibrium with soil water (δ_{atm} = -18.13‰), which is usually the case in Switzerland [*Saurer et al.*, 1997b]; (3) isotopic composition of soil water is that of the average precipitation for the growing season May-September (δ_{sw} = -8.14‰); and 4) ε_k = 28‰, as estimated by *Allison et al.* [1985]. To further test (1) and (2), we input the two average values for humidity data available during the study period, the average and the average midday value (which represents the lowest extreme), 75.6% and 54.6%, respectively. The higher estimate of relative humidity resulted in an under-estimated $\delta^{18}O_{cellulose}$ calculated value of 26.4‰, whereas the true average value from the Eigentobel record is 28.9‰. In addition, the lower estimate (the more extreme) over estimates the isotopic value at 32.8‰. These estimates with (1) and (2) show how a tree would behave with the assumed conditions, when f=0.2, and actual measured values do fall within their range. When f is increased to 0.4, (1) and (2) generate values of 24.5‰ to 29.3‰ for the high and low averages of relative humidity, respectively. Apparently, a higher f value more precisely predicts the observed Eigentobel $\delta^{18}O_{cellulose}$ spruce record. Clearly, the isotopic signature of precipitation is stored in the rings but with a dampened nature. Recently, it has been theoretically estimated that 45% of the oxygen atoms are exchanged with stem water during sucrose transfer to sites of cellulose synthesis [*Farquhar et al.*, 1998]. This estimation of exchange is also indirectly supported by several studies both experimental and in the field [*Hill et al.*, 1995; *Saurer et al.*, 1997a,b; *Sternberg et al.*, 1986]. It is interesting to note that the trees show a 2.9 factor of reduction between the $\delta^{18}O_{cellulose}$ values and the $\delta^{18}O_{precipitation}$ values from Bern station, compared to the 2.2 reduction estimated to be possible through the exchange with stem water (soil water of that growing season). The observed 2.9 reduction in the Eigentobel trees indicates that a dampening between the precipitation and the tree is occurring, which may be explained by a combination postphotosynthetic exchange and evapotranspiration. It should be noted that, if at any time the trees had access to a mixed groundwater (perhaps caused by a change in hydrology) and not soil water, this would also have a homogenizing effect dampening the trees' stable oxygen isotope record.

A recent analysis of regional Swiss climatological data reveals that over the last century, minimum temperatures have increased 2°C, surpassing the global warming trend of 0.5°C [*Beniston et al.*, 1994]. The factors reflected in this enhanced warming can only be understood from an evaluation of the complex interaction between the different weather systems converging over Switzerland (Mediterranean, continental, Atlantic, and polar regimes). Thus each site selected for study will have not only particular site conditions (wet vs. dry), but also particular climatological conditions as well. High-resolution proxy records, such as tree ring studies, need climatic data to validate and calibrate their chronologies. The analysis by *Beniston et al.* [1994] shows that the unique geographic position of the Swiss plateau between two mountain belts allows for high pressure atmospheric blocking situations to occur, which are correlated with larger-scale teleconnection patterns, specifically the North Atlantic Oscillation (NAO) Index [*Hurrell*, 1995]. Yet the Eigentobel trees do not respond to the NAO index, which is a winter (December through February) phenomenon, as might be expected because the trees are recording climatic information during the growing season (May through September).

However, the Eigentobel isotopic record does have a 2.4 year cycle, which falls into the 2-3 year range of the Quasi-biennial Oscillation (QBO) a larger-scale atmospheric phenomena [*Brázdil and Zolotokrylin*, 1995]. The QBO is the 2-3 year oscillation of the temperature and zonal wind in the tropical stratosphere in eastern and western modes, which in turn affects the Northern and Southern Hemispheres' stratospheres [*Wallace*, 1973; *Wanner et al*, 1997]. The effect of the temperature oscillation can even cause a breakdown in the polar vortex [*Wanner et al.*, 1997]. These stratospheric zonal wind direction changes affect the troposphere in a delayed mode with a variation dependent upon the season [*Schove*, 1987]. This oscillation has a direct correlation with European temperatures [*Lamb*, 1985; *Schoenwiese and Rapp*, 1997] and increased September-October rainfall during the eastern mode [*Brázdil and Zolotokrylin*, 1995]. In the QBO eastern mode the westerlies are weakened allowing northern air mass advection (and thus northern sourced precipitation) into central Europe resulting in a 50% increase in monthly rainfall [*Brázdil and Zolotokrylin*, 1995; *Wanner et al.*, 1997].

6. Conclusions

The Eigentobel isotopic record indicates that trees from temperate zones, and not growing at their ecological limits, record important climatic information. The similar cyclicity and correlation of the high-frequency $\delta^{13}C$ and $\delta^{18}O$ values in tree ring cellulose indicate a similar forcing is acting upon both isotopic proxies. The observed 2.4 year cycle in both data sets has been previously linked to the solar cycle and the QBO [*Schove*, 1987]. The first-order trend of $\delta^{13}C$ values does not show an anthropogenic depletion trend, as predicted. The high-frequency changes are, however, sensitive to the climatic changes, whereas the low-frequency ones were not well represented. The lack of correlation with the low-frequency $\delta^{13}C$ values is possibly caused by biological influences, such as aging trends. The $\delta^{18}O$ values correlate with both low- and high-frequency data but do not correlate as well as the $\delta^{13}C$ values does with the high-frequency data. The high-frequency times series comparisons between the climatic variables and both $\delta^{13}C$ and $\delta^{18}O$ values indicate that they do not necessarily respond to perturbations simultaneously or with the same magnitude. This fact will be important for future model development for paleoclimate reconstructions. Most importantly, the $\delta^{18}O$ value correlates with the isotopic composition of precipitation, although the signal appears to be dampened by a factor of 3. With an increase in the spatial distribution of tree ring data sets from properly chosen sites, the nature of these variations can be examined.

The mapping of spatial and temporal changes in the oxygen isotopic composition of precipitation using the proxy data from trees is the ultimate aim of this work. We propose that isotopic and climate data presented here are controlled by atmospheric temperature and potential precipitation source area changes, which in turn are controlled by changes in the geometry and position of the westerly jet stream. Clearly, the oxygen isotopic composition of the precipitation falling during the growing season is transferred to the trees. With an increase in the number of isotopic tree ring records from more sites throughout Europe, our preliminary correlation with England and the other Swiss sites may be further verified. Eventually, with an increased spatial and temporal resolution of proxy records for the isotopic composition of precipitation, it will be possible to map out changes throughout the Holocene. In conclusion, we propose that changes in atmospheric climate system, such as the QBO, are stored in the $\delta^{18}O$ value of soil water and are transferred to the tree cellulose during the growing season. This hypothesis requires future testing.

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