

Analysis of $\delta^{18}\text{O}$ in tree rings: Wood-cellulose comparison and method dependent sensitivity

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Abstract. During recent years, new on-line methods in mass spectrometry have been developed for measuring $\delta^{18}\text{O}$ in organic material. They allow a much higher sample throughput than off-line methods with the result that sample preparation becomes the time-limiting factor. Therefore we tested whether analysis of tree ring samples can be made on whole wood instead of pure cellulose, which until now was commonly used in almost all ^{18}O tree ring studies. Measurements with an on-line method based on pyrolysis in an elemental analyzer show that the tree ring $\delta^{18}\text{O}$ time series of wood and cellulose from an oak of the Swiss “Mittelland” are similar ($r^2 = 0.65$). However, there are significant differences, and some climatic information may be lost if bulk wood is analyzed instead of cellulose. This can partly be balanced by an increased sample throughput, resulting in the averaging of more data. Further, we improved an off-line method (pyrolysis in a nickel tube followed by catalytic CO to CO_2 conversion on nickel powder) by adding a CO_2 trap to enhance the CO to CO_2 conversion. The best reproducibility associated with this method is better than 0.1‰. We also found a strong memory effect linked with this method, causing a dampening of the signal of 30–40%. Therefore published climatic interpretation of $\delta^{18}\text{O}$ data measured using similar methods may require revision.

1. Introduction

Stable isotopes in precipitation have already been investigated for a few decades and have been found to strongly reflect climatic conditions, especially temperature [Dansgaard, 1964; Rozanski *et al.*, 1992; Siegenthaler and Oeschger, 1980]. Past variations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in meteoric water are recorded in different materials: for example, in polar ice [Johnsen *et al.*, 1995], in high-altitude glaciers [Thompson *et al.*, 1995; Schotterer *et al.*, 1997], in lake sediments [Eicher, 1995], and in tree rings [Saurer *et al.*, 1997]. The lack of a rapid method for determining the $^{18}\text{O}/^{16}\text{O}$ ratio of organic material resulted in the fact that oxygen isotope measurements in organic material have been much more scarce than carbon isotope measurements until the last few years. Nevertheless, $^{18}\text{O}/^{16}\text{O}$ analysis of tree rings could greatly improve our understanding of the climate system by providing data with high time resolution on continental areas. Since 1996 several on-line methods have been developed [Farquhar *et al.*, 1997; Koziol, 1997; Werner *et al.*, 1996], which allow a much higher sample throughput. However, despite this development the “old” off-line methods are still important, since all these on-line methods require calibrated standards (cellulose, sucrose, etc.) as reference materials. Hence improvements and tests of off-line methods are still useful.

Another obstacle for the production of long series of $\delta^{18}\text{O}$ in tree rings is the need for extracting a pure component (α -cellulose, lignin, etc.) from wood prior to isotope analysis. As determination time has strongly decreased for the on-line methods, sample preparation becomes now the new time-limiting factor. Unlike for $\delta^{13}\text{C}$ time series [Borella *et al.*, 1998; Francey, 1986; Mazany *et al.*, 1980], we are aware of only one comparison study of $\delta^{18}\text{O}$ time series of cellulose and wood on the same core, by Gray and Thompson [1977], who analyzed 16 tree ring samples of *Picea glauca*, with a resolution of 5 years. Yet such comparisons explore the potential of measuring oxygen isotopes in bulk wood to obtain relevant climate information. There is no general agreement to what extent the “original” oxygen isotope signal in photosynthates is preserved during the following synthesis of lignin, sucrose, cellulose, etc. [see, e.g., Farquhar *et al.*, 1998]. In contrast to Cooper and De Niro [1989], who pointed to interpretation problems of fossil cellulose data based on aquatic plant measurements, Sternberg [1989] reported a value of $(27 \pm 3)\text{‰}$ for $\delta^{18}\text{O}$ of cellulose compared to that of the water at the site of synthesis. In a review article, Farquhar *et al.* [1998] summarized the present state of understanding and addressed important gaps of knowledge associated with the origin of oxygen in different organic compounds. They conclude that more studies are required focusing on detailed metabolic effects such as oxygen equilibration between carbonyl groups and water and between oxygen in cellulose and sucrose. However, direct comparison of oxygen between wood and cellulose can serve as an additional constraint for more detailed studies besides its helpfulness for $\delta^{18}\text{O}$ methodology of organic compounds.

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The aims of this paper are (1) to document improvements and problems associated with the Ni tube method (derived from the "Sealed nickel tube pyrolysis" (SNTTP) method from *Brenninkmeijer and Mook* [1981] and *Brenninkmeijer* [1983]) and (2) to address the question of whether cellulose extraction is necessary prior to $\delta^{18}\text{O}$ analysis.

2. Material and Methods

2.1. Material

For internal and interlaboratory calibrations we used three different cellulose standards: "Merck," "IAEA-C₃," and "WSL." Merck is a commercial cellulose available as powder, mostly used for thin-layer chromatography. It is extremely fine (<0.01 mm) and hence can be regarded as homogeneous compared to our sample sizes (1-10 mg) and our precision (0.1-0.3‰). This standard is used as reference material for the on-line method described in section 2.2.3. On the basis of measurements with the Ni tube method we assign a $\delta^{18}\text{O}$ value of 28.67‰ (VSMOW (Vienna SMOW)) to this cellulose. IAEA-C₃ is a standard cellulose for ¹⁴C determination available from the International Atomic Energy Agency, Vienna (cellulose standard 191). WSL is an α -cellulose extracted in our lab from wood of a 1-year-old birch grown in a controlled chamber. This standard is not as homogeneous as the other two, but $\delta^{13}\text{C}$ measurements [*Borella et al.*, 1998] have shown that any residual heterogeneity does not increase the measurement uncertainty. Furthermore, it better represents our real samples, since it has undergone the same extraction steps. To study the relation between $\delta^{18}\text{O}$ of wood and α -cellulose, we used a 15-year-long tree ring series from an oak of the Swiss "Mittelland."

2.2. Methods

2.2.1. Sample preparation. Prior to cellulose extraction and analysis the wood is milled with a modified, commercially available coffee mill, until a fineness of <0.1 mm is reached (for more details, see *Borella et al.*, 1998). Afterward, α -cellulose is extracted in three successive steps: (1) removal of the extractives with a 1:1 toluene-ethanol mixture, (2) removal of the lignin with a NaClO₂ - acetic acid solution, and (3) removal of the hemicelluloses with NaOH. We separated some subsamples from the extraction line after the first step (labeled hereafter as "wood," which corresponds to the term "TE" used by *Borella et al.* [1998]) in order to test the correlation between wood and cellulose $\delta^{18}\text{O}$ time series.

2.2.2. Ni tube method. Our Ni tube method is based on the Sealed Nickel Tube Pyrolysis (SNTTP) method of *Brenninkmeijer* [1983], with important modifications initiated by *Saurer* [1993]. The principal steps of our method for $\delta^{18}\text{O}$ analysis from tree ring material are (1) pyrolysis (i.e., thermal decomposition under vacuum or in an oxygen-free atmosphere) of the cellulose, (2) removal of the hydrogen by diffusion through the Ni tube walls at high temperature (~1100°C), (3) catalytic reaction of CO to CO₂ on Ni powder, (4) cryogenic extraction of the CO₂ from the possible H₂O, N₂, and CO residuals, and (5) isotope measurement of the CO₂ gas with a mass spectrometer. More details on the method are given by *Saurer et al.* [1997].

Saurer [1993] and *Borella* [1994] found that the most critical step is the conversion of CO to CO₂. Indeed, if less than ~92% of the oxygen is in the form of CO₂ after this step,

the measurement uncertainty is >1‰. Despite many tests with varying temperatures and reaction times it was not possible to reach conversions better than 95-97%. Nevertheless, this permitted a reproducibility of ~0.2-0.3‰. *Brenninkmeijer* [1983] and *Borella* [1994] also found that this conversion method does not work with bulk organic material, as documented by measurements of "visibly impure" cellulose from peat and leaves, respectively. To improve the conversion, we added a liquid N₂ trap during the CO to CO₂ conversion step. This allows us to reduce the CO₂ partial pressure in the Ni tube and hence forces the conversion of CO to CO₂. In this way, we could reach conversion efficiencies above 99%.

We determined the duration required for complete diffusion of the hydrogen through the Ni tubes and found a dependence on the age of the tubes. For approximately 4 year old Ni tubes (70 samples pyrolyzed) we found fluxes (proportional to the square root of hydrogen pressure) which were 2 times lower than *Saurer* [1993] measured for almost new Ni tubes. Furthermore, it was found that the time required for a successful pyrolysis is greater than estimated from direct hydrogen diffusion measurements. This is most probably an effect of a significant slowdown of hydrogen flux through the Ni tubes at low hydrogen pressures. Being aware of the large oxygen isotope fractionation between water (formed from residual hydrogen and sample oxygen) and CO₂ converted from CO, a complete removal of hydrogen is a necessity. Therefore it is helpful to check the remaining water after pyrolysis.

Another problem associated with oxygen isotope measurements is contamination with atmospheric oxygen. To minimize this effect, *Saurer* [1993] stored the hydrogen-reduced Ni catalyst in a nitrogen atmosphere. To further improve the precision, we investigated the possibility to reduce the Ni tube with H₂ at 400°C during 1 hour prior to each pyrolysis. Unlike the first modification (adding a liquid N₂ trap), this change in the procedure proved not to be useful. Indeed, the overall oxygen yield decreased below 85%, and the $\delta^{18}\text{O}$ values were enriched by more than 1‰, with large scatter (>1‰), although the CO to CO₂ conversion was optimal. Therefore a preconditioning of the Ni tubes is necessary (i.e., the Ni walls must be saturated with oxygen). This also means that a strong memory effect could occur. This is in fact the case and will be discussed in detail in section 2.2.4. We would like to mention here that to our knowledge, no memory effect has been mentioned yet by any author using this method [see *Thompson and Gray*, 1977; *Brenninkmeijer and Mook*, 1981; *Edwards et al.*, 1994] but that *Brenninkmeijer and Mook* [1981] found a marked decrease of the overall oxygen yield when pyrolysis duration is extended to more than 14 min.

2.2.3. On-line method. *Saurer et al.* [1998] modified the on-line method of *Werner et al.* [1996] for $\delta^{18}\text{O}$ determination in organic material. The basics of this method are (1) pyrolysis of the samples (~1.5mg) at 1080°C in presence of glassy carbon in an elemental analyzer, (2) separation of the different gases (CO, CO₂, H₂O) through chemical traps and a gas chromatographic (GC) column, and (3) on-line analysis of the 30/28 ratio of CO in a mass spectrometer. Since we mainly analyze cellulose samples, which principally contain no nitrogen, we do not separate N₂ from CO. For other organic compounds containing even small amounts of nitrogen such a separation is required, or otherwise a strong underestimation

of the $\delta^{18}\text{O}$ values occurs (approximately $-10\text{‰}/\text{‰N}_2$, according to Borella [1998]). However, we did not separate CO from N_2 , even for our wood samples, since we calibrate all our measurements with a cellulose of known isotopic values and hence measured both materials in the same series. For more technical details on this method, see Saurer *et al.* [1998]. The results obtained with this method for a number of cellulose and tree ring samples have been shown to compare well with measurements by the Ni tube and the mercury (II) chloride methods. The standard deviation for repeated analysis of cellulose is $\sim 0.2\text{‰}$. Saurer *et al.* [1998] investigated a possible memory effect by using this method and concluded that no such significant effect can be detected for analysis of subsequent samples which differed by no more than approximately 4‰. On the basis of our results presented in section 3.1 and of the comparison results between the on-line and the Ni tube methods presented by Saurer *et al.* [1998] it seems probable that the on-line technique is indeed also affected by a slight memory effect that cannot be quantified yet.

2.2.4. Description of the memory effect. As presented in section 2.2.2, tests with the Ni tube method led us to the expectation that there could be a memory effect for this $\delta^{18}\text{O}$ measurement method (i.e., sample values influenced by previously measured samples). Here we present how we correct for this effect, on the basis of theoretical assumptions and on autocorrelation calculations. The following assumptions are made:

Prior to pyrolysis the Ni tube contains the cellulose sample and oxygen, which is chemically or physically fixed to the tube walls. At the end of pyrolysis and catalysis, CO_2 gas is present in the tube, and oxygen is fixed to the tube walls. When equilibrium between sample and the Ni tube has been reached (i.e., after three to four successive equally large sub-samples of the same cellulose in the same tube), the oxygen yield in CO_2 gas is 100% (relative to cellulose oxygen). Further, we assume constant values (1) for the fractionation ϵ between CO_2 gas in the Ni tube and oxygen fixed to the tube walls and (2) for the ratio of oxygen in CO_2 in the tube to total oxygen in the tube (g):

$$\delta_{\text{wall}} = \delta_{\text{gas}} + \epsilon \quad (1)$$

Conservation of oxygen and ^{18}O leads to

$$\begin{aligned} g\delta_i^m + (1-g)(\delta_i^m + \epsilon) &= g\delta_i + (1-g)(\delta_{i-1}^m + \epsilon) \\ \Leftrightarrow \delta_i^m &= g\delta_i + (1-g)\delta_{i-1}^m \end{aligned} \quad (2)$$

where δ_i is the $\delta^{18}\text{O}$ of sample number i (equal to the “real” $\delta^{18}\text{O}$ of the cellulose), δ_i^m corresponds to $\delta^{18}\text{O}$ as measured for CO_2 from sample i , and g is the ratio of oxygen in CO_2 form in the tube to total oxygen in the tube. Index $i-1$ denotes the sample that has been processed previously.

Linear autoregression analysis (i.e., comparison of two successive measurements of the same sample in the same Ni tube) of the measured δ values yields two numbers a and b :

$$\delta_i^m = a\delta_{i-1}^m + b \quad (3)$$

Comparison of equations (2) and (3) results in

$$a = 1 - g \quad (4)$$

Hence the measured $\delta^{18}\text{O}$ values can be corrected for the memory effect as follows:

$$\delta_i = \frac{1}{g}\delta_i^m - \frac{(1-g)}{g}\delta_{i-1}^m = \frac{1}{(1-a)}\delta_i^m - \frac{a}{(1-a)}\delta_{i-1}^m \quad (5)$$

As $g < 1$, the variations of the measured δ_i^m are less than the actual variations of δ_i (see equation (2)). Hence when comparing the δ_i^m measured with our method with δ_i^{m*} measured with another method, for which no memory effect is present, the linear regression coefficient a^* is expected to be < 1 :

$$\delta_i^m = a^*\delta_i^{m*} + b^* \quad (6)$$

with

$$a^* = g = 1 - a \quad (7)$$

according to equations (2) and (4).

These considerations are used to explain the memory effect found for our data. The good agreement between data and theory (see section 3.1) justifies the above assumptions.

3. Results and Discussion

3.1. Ni Tube Method

As mentioned in section 2.2, tests with reduced Ni tubes pointed our attention to a possible memory effect, i.e. Ni tubes being saturated with oxygen of the preceding sample. To test this hypothesis, we reexamined results from Saurer [1993] by correlating the values obtained for a cellulose stan-

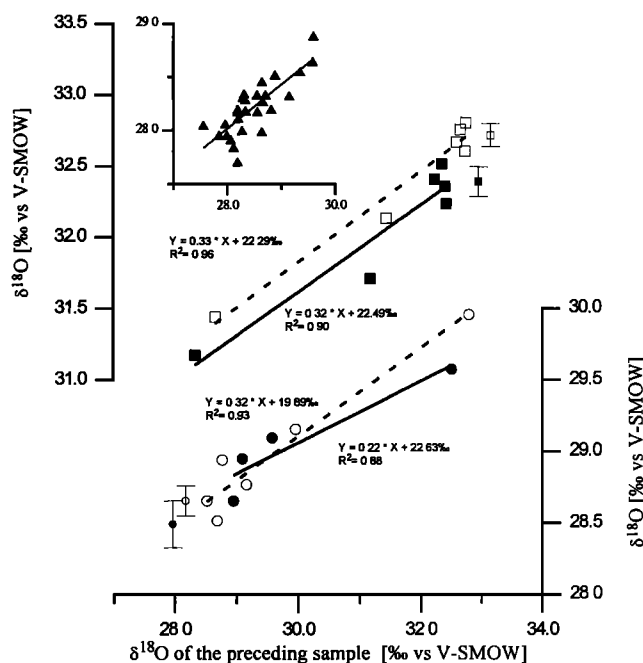


Figure 1. The $\delta^{18}\text{O}$ dependence of a sample on the preceding sample. Circles, commercial standard cellulose “Merck”; and squares, standard cellulose C₃ number 191 from the International Atomic Energy Agency. Two different Ni tubes were used (solid symbols, tube 4; and open symbols, tube 5). The slopes are not significantly different (see Table 1). The symbols in the upper right and bottom left corners represent mean values at equilibrium and their standard deviations, as given in Table 1. In the inset, $\delta^{18}\text{O}$ of the “WSL” standard cellulose as a function of the preceding $\delta^{18}\text{O}$ measurement is shown. (Data are from Saurer [1993].) The solid line is the linear regression ($y = 0.41 \cdot x + 16.56\text{‰}$; $r^2 = 0.64$). VSMOW, Vienna SMOW.

dard (WSL, see section 2.1) with the $\delta^{18}\text{O}$ values of the previously measured cellulose (which were tree ring samples). Figure 1 shows that the measured $\delta^{18}\text{O}$ value of the WSL-standard indeed clearly depends on the $\delta^{18}\text{O}$ value of the preceding sample. The slope of the regression is 0.41‰/‰. According to equation (4) this means that ~59% of the oxygen in the Ni tube after a pyrolysis is present in the form of CO_2 , the remaining part being fixed to the tube walls (see section 2.2). In order to test whether the slope found from the measurements of Saurer [1993] still applies to the modified method, as discussed in section 2.2.2, we pyrolyzed two series of one standard cellulose (Merck, approximately 28.7‰ versus VSMOW) which were separated by a series of another standard cellulose with a very different $\delta^{18}\text{O}$ value (IAEA-C3, approximately 32.5‰ versus VSMOW). The results presented in Figure 1 demonstrate clearly that the memory effect is still observed, although slightly lower than for measurements with relatively new tubes (Saurer's data). The slope of the linear regression between $\delta^{18}\text{O}$ of the present sample and of the preceding sample varies between 0.22‰/‰ and 0.32‰/‰, for the different Ni tubes and standards. The differences are not statistically significant. Table 1 summarizes the results of the different regression analyses. The strength of the memory effect does not depend on the Ni tube or on the cellulose analyzed. The mean memory effect of the modified method is $(0.29 \pm 0.05)\%$. The associated uncertainty corresponds to the standard deviation of the four slopes given by the four different Ni tubes and cellulose combinations.

Once the memory effect has been purged by multiple successive pyrolyses of the same cellulose (i.e., after three to four pyrolyses of the same cellulose and equal sample weight), the modified method permits a reproducibility better than 0.1‰. The equilibrium fractionation ϵ and the ratio g may depend on temperature, temperature gradients, the duration of the different steps, cooling regime, etc. It is therefore very important to

follow exactly the same protocol. Furthermore, there is a "tube effect," different Ni tubes giving different equilibrium $\delta^{18}\text{O}$ values for the same cellulose, as can be seen from Table 1. An analogous tube effect has already been pointed out by Saurer [1993].

Saurer *et al.* [1998] performed an interlaboratory comparison between the on-line method, the mercury (II) chloride method, and the Ni tube method. For these tests they analyzed four different commercial cellulose standards (of which Merck and IAEA-C₃ were also measured in Bern) and three cellulose samples extracted from tree rings (among which was a tree ring series that was also analyzed with the older Ni tube method from Bern). By linear regression between the data obtained with the Ni tube method and those obtained with the mercury (II) chloride method they found a slope of 0.59 ± 0.06 ($r^2 = 0.93$), the values obtained with the Ni tube method being dampened by 41%. This estimate is in perfect agreement with our result from Figure 1 and confirms our interpretation of the process leading to the memory effect. Figure 2 shows that the slope between the mercury (II) chloride values and the Ni tube values becomes, indeed, approximately 1, when the latter are corrected for the memory effect as suggested from Figure 1. These findings have important implications for the interpretation of $\delta^{18}\text{O}$ values obtained using different methods. The derived dependencies of $\delta^{18}\text{O}$ on humidity and temperature given by Saurer *et al.* [1997] need revision; this will be discussed in detail in a forthcoming paper.

3.2. Comparison of α -Cellulose and Wood $\delta^{18}\text{O}$ Analysis

The recent progress in gas chromatography-mass spectrometry (GC-MS) methodology shifted the bottleneck in sample throughput from the actual analysis procedure to the sample preparation, in particular to the cellulose extraction. Borella *et al.* [1998] have shown that $\delta^{13}\text{C}$ measurements in wood and cellulose yield the same information, at least for

Table 1. Memory Effect of the Nickel Tube Method for the Determination of $\delta^{18}\text{O}$ in Cellulose: Autocorrelations, Corrections, and Comparisons, for Two Different Standard Celluloses and Two Different Ni Tubes

Cellulose (Tube Number)	Slope, ‰/‰	r^2	n	$\langle\delta\rangle_{\text{eq}}$, ‰ Versus VSMOW	n	$\langle\delta\rangle_{\text{mem-corr}}$, * ‰ Versus VSMOW	n
WSL (4)	0.32 ± 0.08	0.54	15	$28.22 \pm 0.17\ddagger$	15	28.07 ± 0.21	15
WSL (5)	0.49 ± 0.10	0.71	13	$28.21 \pm 0.34\ddagger$	13	28.00 ± 0.31	13
IAEA-C3 (4)	0.32 ± 0.05	0.90	6	32.39 ± 0.10	5	32.38 ± 0.27	6
IAEA-C3 (5)	0.33 ± 0.03	0.96	6	32.72 ± 0.08	5	32.74 ± 0.25	7
Merck (4)	0.22 ± 0.06	0.88	4	28.49 ± 0.16	3	28.64 ± 0.30	4
Merck (5)	0.32 ± 0.04	0.93	6	28.66 ± 0.10	4	28.69 ± 0.14	5

Column 2, slope of the linear regression between $\delta^{18}\text{O}$ of the current sample and $\delta^{18}\text{O}$ of the previous sample; column 3, correlation coefficient r^2 of the linear regression between $\delta^{18}\text{O}$ and $\delta^{18}\text{O}$ of the previous sample; column 4, number of values used in column 3; column 5, mean $\delta^{18}\text{O}$ after equilibrium is reached (see text); column 6, number of values used in column 5; column 7, mean $\delta^{18}\text{O}$ after memory effect correction (the standard deviations after memory effect correction are larger than those given in column 5, because also samples with high memory effect influence are used here); column 8, number of values used in column 7. These standard celluloses were initially measured versus Vienna Pee Dee Belemnite (VPDB). The formula used for the conversion between both scales is $\delta_{\text{VSMOW}} = 1.0415 \delta_{\text{VPDB}} + 41.5\%$.

* For the correction of the memory effect we used a mean slope a : $a = 0.409$ for both WSL standards and $a = 0.310$ for the others.

† The values for WSL are not values at equilibrium; that is, other samples were measured between two WSL standards, explaining the higher standard deviation associated with them.

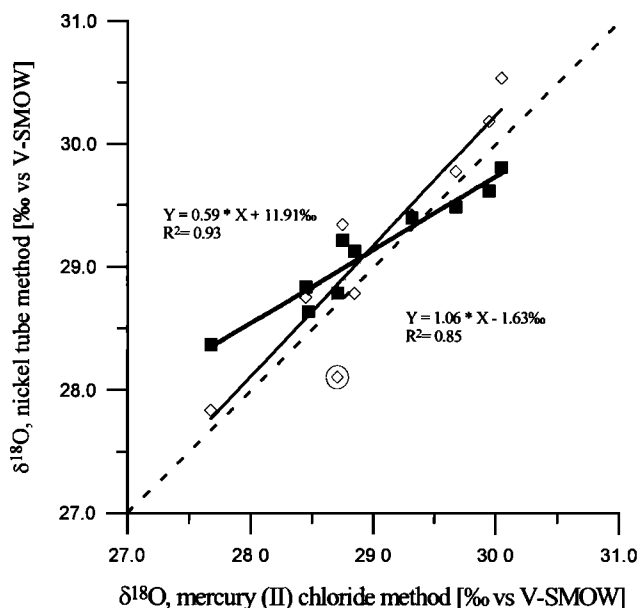


Figure 2. Interlaboratory comparison. The $\delta^{18}\text{O}$ values measured with the Ni tube method (Bern) exhibit a 41% dampening of real signals compared with those measured with the mercury (II) chloride method (Cambridge) (data are from Saurer *et al.* [1998]), as documented by the slope of the correlation ($0.59\text{‰}/\text{‰}$, solid squares and broad line). After correction for the memory effect (as determined from Figure 1), the slope of the correlation between the values measured for both methods is approximately 1 (open diamonds and thin solid line). The dashed line gives the 1:1 relation for comparison. The worse correlation for the corrected data is mainly due to the circled point, for which we have no explanation. Without this point, the correlation coefficient between the mercury (II) chloride method and the corrected Ni tube data is $r^2 = 0.94$ (slope: $1.02\text{‰}/\text{‰}$).

beech and oak trees. It is therefore worthwhile to check whether cellulose extraction is necessary to obtain reliable $\delta^{18}\text{O}$ results. For this investigation we splitted 15 milled tree ring samples in half after removal of the extractives (i.e., first step of the cellulose extraction, as briefly described in section 2.2.1). One half was rinsed with deionized water and dried at 100°C (termed wood samples in the following), and the other half underwent the whole α -cellulose extraction process. The 30 samples were then measured for their $\delta^{18}\text{O}$ using the on-line method.

Both $\delta^{18}\text{O}$ curves show the same general pattern, as can be seen in Figure 3, whereby, on average, the $\delta^{18}\text{O}$ values from wood are $(4.25 \pm 0.55)\text{‰}$ lower than those of α -cellulose. Yet the absolute value of this difference remains uncertain, since up to now, no calibration of the on-line method for wood was undertaken. (The presence of nitrogen, for example, can have a strong influence of up to -3‰ on the measured $\delta^{18}\text{O}$ value of CO, as recently estimated by Borella [1998].) Nevertheless, the difference is similar to the $(5.0 \pm 0.6)\text{‰}$ and 4.5‰ enrichment of cellulose compared to whole wood mentioned by Gray and Thompson [1977] and Farquhar *et al.* [1998], respectively. Furthermore, the $\delta^{18}\text{O}$ variations of wood are larger than those of α -cellulose (standard deviation of 0.92‰ and 0.68‰ , respectively). This could a priori be caused by (1) a loss of sensitivity due to the α -cellulose extraction or (2) an

additional source of noise when analyzing wood. (The influence of nitrogen on the $\delta^{18}\text{O}$ measurement of CO may increase the uncertainty of the $\delta^{18}\text{O}$ values measured for whole wood, since nitrogen content will not be constant between different wood samples, as already suggested by Borella [1998].) In order to better distinguish between these two possibilities, we performed a linear correlation analysis. We obtained a correlation coefficient $r^2 = 0.65$ and a slope of $(1.09 \pm 0.22)\text{‰}/\text{‰}$ (see Figure 3). The slope is not significantly different from unity, which indicates that there is probably no loss of sensitivity during the α -cellulose extraction. A Monte Carlo analysis was performed to test whether the correlation coefficient being lower than 1 could be caused by the measurement uncertainties. We created two data sets x , and y , that are identical except for small variations, i.e., measurement uncertainties, and for a constant shift according to the mean difference between the $\delta^{18}\text{O}$ of cellulose and that of wood:

$$x_i = \delta^{18}\text{O}_{C_i} + f_i \quad (8)$$

$$y_i = \delta^{18}\text{O}_{C_i} + K + g_i \quad (9)$$

where $\delta^{18}\text{O}_{C_i}$ is the actually measured $\delta^{18}\text{O}$ of cellulose sample number i , K is a constant value corresponding to the mean $\delta^{18}\text{O}$ difference between wood and α -cellulose, and f_i is a random variable, Gaussian distributed with $\mu = 0$ and $\sigma = s_{x_i}$, i.e., the square of the standard deviation due to measurement uncertainty (0.16‰ for $\delta^{18}\text{O}$ of α -cellulose measured with the on-line method). The variable g_i is defined like f_i , but

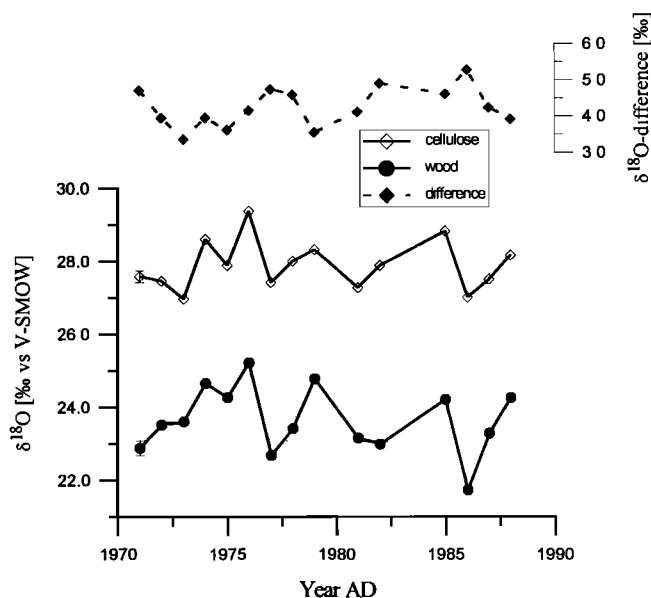


Figure 3. The $\delta^{18}\text{O}$ of cellulose and toluene-ethanol extracted wood (open diamonds and solid circles, respectively), from an oak of the Swiss "Mittelland," and differences between them (solid diamonds). The differences are not correlated with the $\delta^{18}\text{O}$ values either of wood or of cellulose. (This study is mainly restricted to the time period 1971 to 1994 due to the availability of $\delta^{18}\text{O}$ from precipitation for this period. A more detailed climatic interpretation of the tree ring $\delta^{18}\text{O}$ data used in this paper will be the subject of another paper still in preparation.)

the standard deviation of the distribution corresponds to measurement of wood $\delta^{18}\text{O}$ (0.20‰ for $\delta^{18}\text{O}$ of wood ($\delta^{18}\text{O}_w$) measured with the on-line method).

We calculated the square of the correlation coefficient r^2 between x and y , for 10,000 sets of random variables f and g , to allow a statistical interpretation regarding the r^2 distribution. The r^2 distribution that we obtained with the parameters corresponding to our experimental work is given in Figure 4. The correlation coefficient, $r^2 = 0.65$, obtained for our real data is clearly out of the expected range. This means that the discrepancies between $\delta^{18}\text{O}_w$ and $\delta^{18}\text{O}_c$ cannot solely be explained by the measurement uncertainties. Nevertheless, the correlation between both parameters is highly significant ($p < 0.001$, according to t test). An analogous Monte Carlo simulation was performed to test the slope. If the $\delta^{18}\text{O}$ of TE-extracted wood and of cellulose were perfectly correlated with only discrepancies due to measurement uncertainties, the slope of the linear correlation would be between 0.92‰/‰ and 1.00‰/‰ in more than 35% of the cases and would be larger than 1.09‰/‰ in only 7.7% of the cases. This means that the experimentally determined slope is not significantly different from the slope of perfectly correlated $\delta^{18}\text{O}$ of wood and cellulose. However, the large uncertainty of the slope we obtained from our measurements does not permit a final conclusion.

These results are not sufficient to decide whether measuring $\delta^{18}\text{O}$ of wood instead of cellulose means a significant loss of climatic information. To further investigate this question, we compare both $\delta^{18}\text{O}$ data sets with climatic parameters and $\delta^{18}\text{O}$ values of precipitation water. Regression analysis between $\delta^{18}\text{O}_c$ and $\delta^{18}\text{O}$ of the June precipitation in Bern (~15 km east from the oak site analyzed) gives a correlation coefficient, $r^2 = 0.47$, which is significant at $p < 0.01$ (according to t test). The same analysis with $\delta^{18}\text{O}_w$ gives a correlation coefficient, $r^2 = 0.19$, which is not significant at the 5% level. Tak-

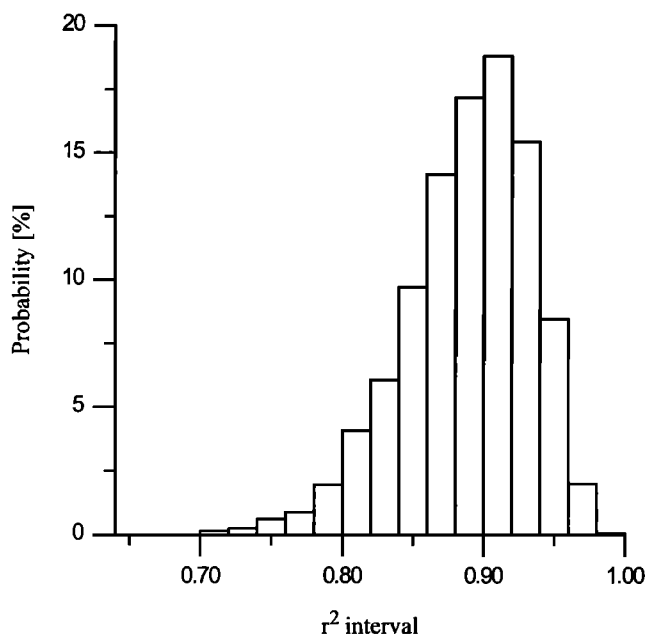


Figure 4. The r^2 distribution from the Monte Carlo simulation of correlations between $\delta^{18}\text{O}$ of cellulose and $\delta^{18}\text{O}$ of wood. (See text for details.)

ing the first differences of the data, the difference between the correlation coefficients for α -cellulose and wood is slightly smaller ($r^2 = 0.66$ and 0.43 , respectively). Both correlations are significant ($p < 0.001$ and $p < 0.05$, for cellulose and wood, respectively). The difference between both correlation coefficients (with $\delta^{18}\text{O}_c$ and with $\delta^{18}\text{O}_w$) is significant to $p < 0.01$ in both cases (original data and first differences). Further, we made analogous comparisons with temperature data and also found better correlations for $\delta^{18}\text{O}_c$ than for $\delta^{18}\text{O}_w$. The differences between both correlation coefficients with temperature are only significant when working with original (not first differences) data. Nevertheless, neither of the correlations between tree ring $\delta^{18}\text{O}$ and temperature are significant. Analogous calculation also shows that relative humidity of June better correlates with $\delta^{18}\text{O}_c$ than with $\delta^{18}\text{O}_w$ ($r^2 = 0.38$ and 0.21 , respectively). However, when using a mean relative humidity of the months April to August the difference between both correlations are no more significant ($r^2 = 0.31$ and 0.30 , for cellulose and wood, respectively). This could reflect the fact that different wood components are produced at different times [see, e.g., *Wilson and Grinstead, 1977*].

On the basis of these results it is clear that information is lost if $\delta^{18}\text{O}$ of tree rings of oak is measured in bulk wood, as already found for white spruce by *Gray and Thompson [1977]*. This loss may possibly be compensated by an increased sample throughput, which allows averaging of data from more trees and sites.

4. Conclusion

A reproducibility of $\sim 0.1\%$ can be reached with the Ni tube pyrolysis method for measuring $\delta^{18}\text{O}$ in cellulose. Nevertheless, a memory effect, which varies depending on the details of the procedure, dampens the signal variations up to 40%. The strength of this memory effect has to be determined separately by each laboratory using this technique. In order to reach an acceptable correction one has to follow a given measurement methodology which prevents additional sources of error.

The $\delta^{18}\text{O}$ values of α -cellulose and wood from tree rings of an oak are well correlated ($r^2 = 0.65$). Despite this good agreement there is a significant discrepancy between both parameters. This is clearly shown by a Monte Carlo simulation of correlations between two artificial data sets, taking only the difference due to measurement uncertainties into account. As our results on the comparison between $\delta^{18}\text{O}$ of α -cellulose and of wood concern only one oak tree, no definitive conclusion can be made yet, whether cellulose extraction is a necessity for reliable $\delta^{18}\text{O}$ measurements of tree rings. The variations of oxygen isotope measurements significantly increase if wood is analyzed. This additional "noise" can partly be compensated by multiple measurements using fast on-line techniques.

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