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Oxygen isotope ratios ($^{18}O/^{16}O$) of hemicellulose-derived sugar biomarkers in plants, soils and sediments as paleoclimate proxy II: Insight from a climate transect study

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Abstract

The oxygen isotopic composition of precipitation ($\delta^{18}O_{prec}$) is well known to be a valuable (paleo-)climate proxy. Paleosols and sediments and hemicelluloses therein have the potential to serve as archives recording the isotopic composition of paleo-precipitation. In a companion paper (Zech et al., 2014) we investigated $\delta^{18}O_{hemicellulose}$ values of plants grown under different climatic conditions in a climate chamber experiment. Here we present results of compound-specific $\delta^{18}O$ analyses of arabinose, fucose and xylose extracted from modern topsoils ($n = 56$) along a large humid-arid climate transect in Argentina in order to answer the question whether hemicellulose biomarkers in soils reflect $\delta^{18}O_{prec}$.

The results from the field replications indicate that the homogeneity of topsoils with regard to $\delta^{18}O_{hemicellulose}$ is very high for most of the 20 sampling sites. Standard deviations for the field replications are 1.5‰, 2.2‰ and 1.7‰, for arabinose, fucose and xylose, respectively. Furthermore, all three hemicellulose biomarkers reveal systematic and similar trends along the climate gradient. However, the $\delta^{18}O_{hemicellulose}$ values (mean of the three sugars) do not correlate positively with $\delta^{18}O_{prec}$ ($r = -0.54$, $p < 0.014$, $n = 20$). By using a Péclet-modified Craig-Gordon (PMCG) model it can be shown that the $\delta^{18}O_{hemicellulose}$ values correlate highly significantly with modeled $\delta^{18}O_{leaf\ water}$ values ($r = 0.81$, $p < 0.001$, $n = 20$). This finding suggests that hemicellulose biomarkers in (paleo-)soils do not simply reflect $\delta^{18}O_{prec}$ but rather $\delta^{18}O_{prec}$ altered by evaporative ^{18}O enrichment of leaf water due to evapotranspiration. According to the modeling results, evaporative ^{18}O enrichment of leaf water is relatively low (~10‰) in the humid northern part of the Argentinian transect and much higher (up to 19‰) in the arid middle and southern part of the transect. Model sensitivity tests corroborate that changes in relative air humidity exert a dominant control on evaporative ^{18}O enrichment of leaf water and thus $\delta^{18}O_{hemicellulose}$, whereas the effect of temperature changes is of minor importance. While oxygen exchange and degradation effects seem to be negligible, further factors needing consideration when interpreting $\delta^{18}O_{hemicellulose}$ values obtained from (paleo-)soils are evaporative ^{18}O enrichment of soil water, seasonality effects, wind effects and in case of abundant stem/root-derived organic matter input a partial loss of the evaporative ^{18}O enrichment of leaf water.

Overall, our results prove that compound-specific $\delta^{18}O$ analyses of hemicellulose biomarkers in soils and sediments are a promising tool for paleoclimate research. However, disentangling the two major factors influencing $\delta^{18}O_{hemicellulose}$, namely

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$\delta^{18}O_{prec}$ and relative air humidity controlled evaporative ^{18}O enrichment of leaf water, is challenging based on $\delta^{18}O$ analyses alone.

1. INTRODUCTION

Stable oxygen isotope ($^{18}O/^{16}O$) analysis has become one of the most important tools in hydrology and paleoclimate research. This is based on the observation that the isotopic composition of precipitation ($\delta^{18}O_{prec}$ and $\delta^{2}H_{prec}$) is mainly controlled by climatic factors (Dansgaard, 1964; Araguas-Araguas et al., 2000). Various kinds of archives are studied in order to reconstruct the isotopic composition of precipitation and thus to reconstruct paleoclimate; for instance speleothems (Cruz et al., 2005; McDermott et al., 2011), ice-cores (Dansgaard et al., 1993; Thompson et al., 2005), lake sediments (Sauer et al., 2001; Wissel et al., 2008) and plant cellulose (Danis et al., 2006; Loader et al., 2008; Li et al., 2011). Recently, Zech and Glaser (2009) and Zech et al. (2013) developed and applied a method based on gas chromatography-pyrolysis-isotope ratio mass spectrometry (GC-Py-IRMS), which allows compound-specific $\delta^{18}O$ analyses of plant-derived hemicellulose sugar biomarkers extracted from soils and sediments. Given that Zech et al. (2012) report absence of isotope fractionation during decomposition as well as absence of oxygen exchange reactions affecting the $\delta^{18}O$ signature of sugar molecules based on experimental findings and on theoretical biochemical mechanistic considerations, this method has potential to be applied to soil/sedimentary climate archives for paleoclimate research.

Oxygen atoms of plant-biosynthesized sugars originate from water (Schmidt et al., 2001). Therefore, like cellulose, hemicelluloses can be expected to reflect the isotopic composition of precipitation (Gray and Thompson, 1976, 1977; Libby et al., 1976; Burk and Stuiver, 1981). However, it is well acknowledged that $\delta^{18}O_{cellulose}$ is additionally strongly influenced by evaporative ^{18}O enrichment of leaf water due to transpiration (Dongmann et al., 1974; Flanagan et al., 1991; Roden et al., 2000; Barbour et al., 2004; Pendall et al., 2005). The degree of evaporative ^{18}O enrichment of leaf water depends on plant physiological and climatic conditions, such as relative air humidity, temperature and transpiration rate. In a companion paper (Zech et al., 2014) we report the results of an experimental study based on climate chamber experiments that investigate the effect of the above mentioned plant physiological and climate conditions on $\delta^{18}O_{hemicellulose}$.

In the study presented here, we take advantage of an Argentinian climate transect in order to answer the question "do hemicellulose biomarkers in soils reflect the $^{18}O/^{16}O$ isotopic composition of precipitation?". Furthermore, we use a Péclet-modified Craig-Gordon (PMCG) model to model the isotopic composition of leaf water ($\delta^{18}O_{leaf\ water}$) and leaf cellulose ($\delta^{18}O_{leaf\ cellulose}$) and to test if additional environmental variables influence $\delta^{18}O$ values of hemicellulose biomarkers. By combining empirical data analyses with the mechanistic model simulations we aim to detect and evaluate the dominant climate variables influencing $\delta^{18}O_{hemicellulose}$ along the investigated transect and to draw implications for paleoclimate studies applying the $\delta^{18}O_{hemicellulose}$ method.

2. MATERIAL AND METHODS

2.1. Study area and topsoil samples

The investigated Argentinian transect comprises 20 sampling localities (Fig. 1 and Table 1). It ranges from ~32° to 47° southern latitude and covers a large climate gradient with warm humid subtropical conditions in the north (Zárate, Buenos Aires Province), pronounced arid conditions in the middle part of the transect and cool temperate conditions in the south (Bajo Caracoles, Santa Cruz Province). Mean annual temperature and mean annual precipitation at the sampling sites range from 11.4 to 18.0 °C and from 185 to 1100 mm $year^{-1}$, respectively (Fig. 2B) (GeoINTA, 2012). Fig. 1A depicts that according to the interpolated $\delta^{18}O$ estimates retrieved from Bowen (2012), $\delta^{18}O_{prec}$ along the investigated transect is characterized by a systematic trend towards more negative values in the south.

The large range of different climatic conditions is reflected in the vegetation zones of the study area (Fig. 1B). The northernmost sampling sites are located in the Humid Pampa (grasslands featuring a humid-subhumid climate with incipient water excess). Further south, the Dry Pampa under subhumid-arid climate forms the transition to the Espinal vegetation zone that prevails under semi-arid climate (Burgos and Vidal, 1951). The Low Monte vegetation zone prevails in the most arid region of Argentina (total annual precipitation of 100–350 mm) (Fernández and Busso, 1997) and the Patagonian Steppe in the southernmost part of the transect under cool-temperate, arid climate (Le Houérou, 1996; Paruelo et al., 1998).

During a field campaign in March and April 2010, a total of 56 mixed topsoil (A horizon) samples from maximum 51 cm depth were taken from the 20 sampling localities. Sampling in triplicates (duplicates for locations No. 1 and 18–20) at a distance of ~100 m was conducted in order to investigate possible topsoil heterogeneities at each sampling locality. The soil samples were air-dried in the field and later dried in an oven at 50 °C.

2.2. Compound-specific $\delta^{18}O$ analyses of the hemicellulose sugar biomarkers

Extraction and purification of the hemicellulose sugars from grinded soil samples was performed according to the method described by Amelung et al. (1996) and Zech and Glaser (2009). Accordingly, 4 M trifluoroacetic acid (TFA) was used at 105 °C for 4 h in order to liberate the monosaccharides from hemicelluloses and other non-cellulose

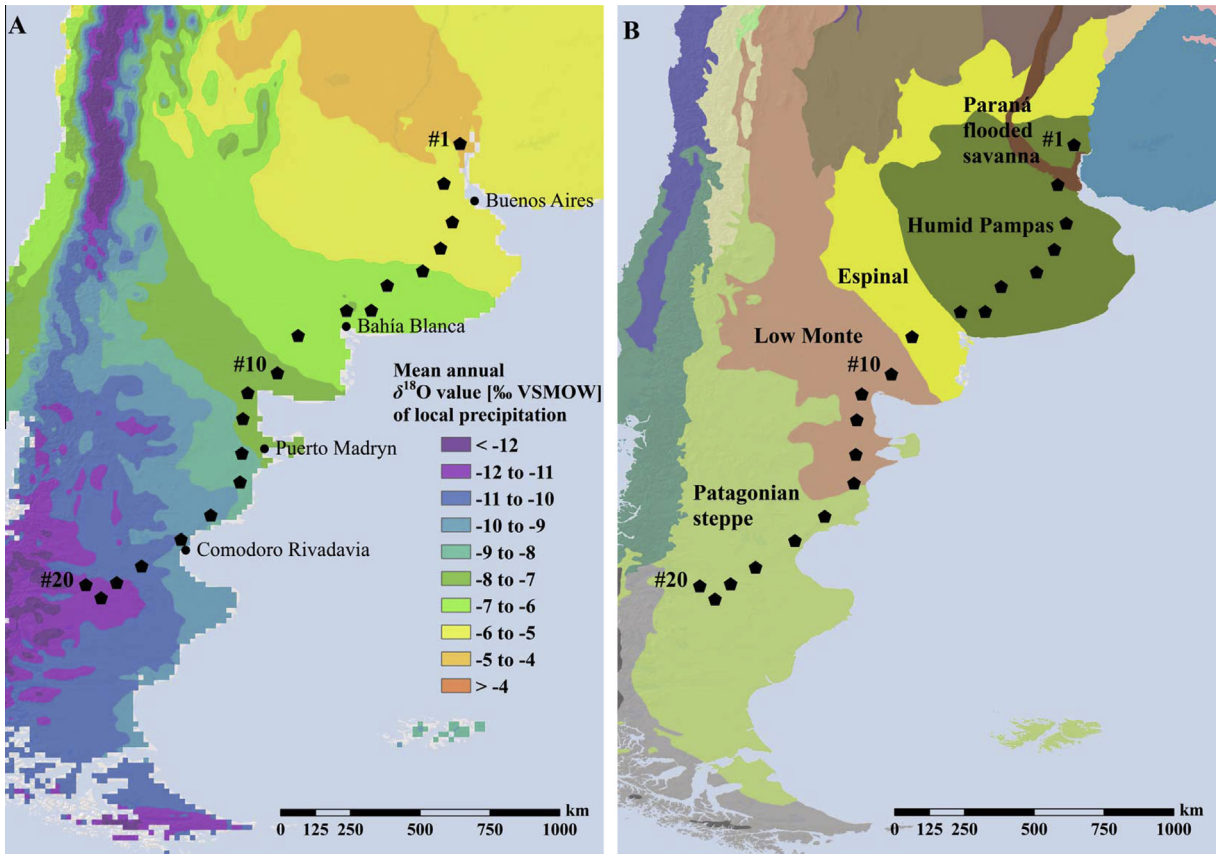

Fig. 1. (A) Sampling localities along the investigated Argentinian climate transect and interpolated $\delta^{18}O$ estimates of annual precipitation (from Bowen, 2012). (B) Vegetational zonation in the study area (from Olson et al., 2001).

Table 1
Geographical description of the 20 sampling localities, mean ($n = 3$) total organic carbon (TOC) contents of the investigated topsoil samples and soil type classification.

Sampling locality	Latitude	Longitude	Altitude (m)	TOC (%)	Soil type*
1	32°46′19″S	58°38′11″W	26	1.7	Vertisol
2	34°03′39″S	59°09′30″W	22	1.8	Phaeozem
3	35°18′10″S	58°53′02″W	29	1.8	Planosol
4	36°08′50″S	59°16′04″W	42	2.2	Phaeozem
5	36°52′43″S	59°50′23″W	154	3.9	Chernozem
6	37°20′55″S	60°58′42″W	198	2.1	Kastanozem
7	38°08′57″S	61°29′45″W	314	2.7	Kastanozem
8	38°09′34″S	62°17′15″W	257	1.0	Chernozem
9	38°57′51″S	63°51′12″W	100	1.3	Kastanozem
10	40°10′19″S	64°31′05″W	102	0.9	Solonetz
11	40°48′47″S	65°28′14″W	165	0.6	Solonetz
12	41°38′44″S	65°37′51″W	348	1.0	Leptosol
13	42°44′45″S	65°39′43″W	119	0.9	Calcisol
14	43°40′46″S	65°43′21″W	250	0.6	Calcisol
15	44°44′29″S	66°39′56″W	453	1.0	Solonetz
16	45°31′33″S	67°37′28″W	625	1.1	Solonetz
17	46°23′19″S	68°53′41″W	632	1.4	Luvisol
18	46°55′10″S	69°41′43″W	501	0.8	Luvisol
19	46°59′15″S	70°41′29″W	736	1.5	Vertisol
20	47°24′35″S	70°11′57″W	962	2.2	Planosol

* WRB Classification.

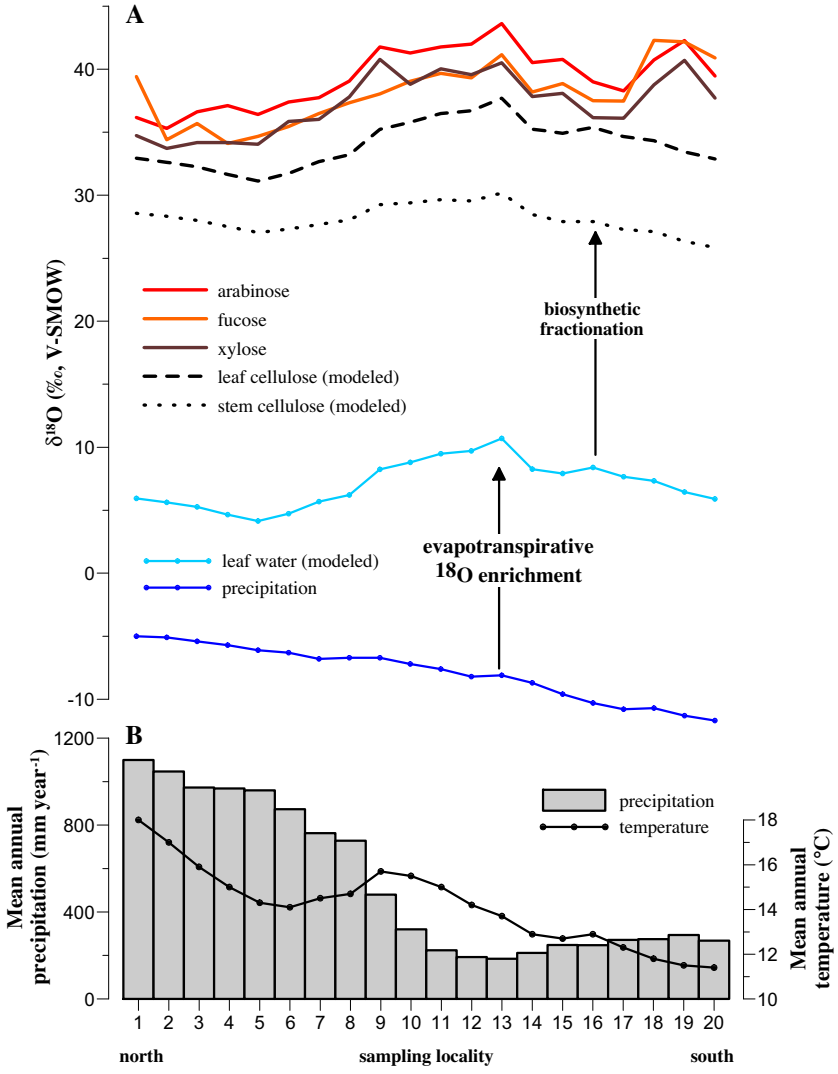

Fig. 2. (A) Comparison of measured $\delta^{18}O_{hemicellulose}$ values of arabinose, fucose and xylose extracted from topsoils along the Argentinian climate transect with modeled $\delta^{18}O_{prec}$, $\delta^{18}O_{leaf\ water}$, $\delta^{18}O_{stem\ cellulose}$ and $\delta^{18}O_{leaf\ cellulose}$. (B) Mean annual precipitation and temperature characterizing the investigated sampling sites.

polysaccharides. The extracted monosaccharides were filtered through glass fibre filters and purified using XAD columns to remove dissolved humic substances and Dowex cation exchange columns to remove cations like iron and also amino sugars. After freeze drying, the samples were dissolved in pyridine and derivatised with methylboronic acid (MBA) (Knapp, 1979). The originally included second derivatization step with bis(trimethylsilyl)trifluoroacetamide (BSTFA), which is necessary for derivatising the remaining hydroxyl groups of hexoses, was skipped because no reproducible derivatization results were found in previous studies (Zech and Glaser, 2009). For the investigated pentoses arabinose and xylose, as well as for the deoxyhexose fucose, the MBA derivatization ensures that no foreign oxygen is additionally introduced and that each sugar yields only one peak in the chromatograms. Rhamnose was present in too low concentrations in most samples and could therefore not be evaluated.

The compound-specific $\delta^{18}O$ measurements were performed on a GC-Py-IRMS system for which a Trace GC 2000 gas chromatograph (Thermo Fisher Scientific, Bremen, Germany) was coupled to a Delta plus isotope ratio mass spectrometer (Thermo Fisher Scientific) via a pyrolysis reactor and a GC/TC III interface (Thermo Fisher Scientific). Oxygen from the analytes was converted 'online' into carbon monoxide (CO) in the pyrolysis reactor (Thermo Fisher Scientific) which was preconditioned with iso-octane in order to ensure C surplus in the reactor and full conversion of oxygen in CO. $\delta^{18}O$ measurements were carried out on CO by monitoring the ion currents at m/z 28, 29 and 30. For further details on the principle of compound-specific $\delta^{18}O$ analyses, the reader is referred to Zech et al. (2011). The Argentinian sample batches were measured at least in quadruplicate replication with batches of external sugars standard concentration series being measured in-between. This procedure ensures compliance with the

principle of "Identical Treatment" (PIT) of samples and standards (Werner and Brand, 2001) and allows checking and correcting if necessary for an amount dependence of the $\delta^{18}O$ measurements. The hydrolytically introduced oxygen atoms in C1 position of the sugars are mathematically corrected as described in Zech and Glaser (2009).

All $\delta^{18}O$ results presented in the following are expressed in the δ notation as per mil (‰) deviation from the internationally accepted standard according to the equation (Eq. (1)):

$$\delta = (R_{sample} - R_{standard})/R_{standard} \quad (1)$$

where R_{sample} and $R_{standard}$ are the isotope ratio ($^{18}O/^{16}O$) in the sample and the Vienna Standard Mean Ocean water (V-SMOW), respectively. Mean standard errors for all $\delta^{18}O$ measurements (56 samples done in quadruplicate to fivefold replication) of arabinose, fucose and xylose were 0.57‰, 0.71‰ and 0.41‰, respectively. Rhamnose was excluded from data evaluation because the respective peaks in the chromatograms were either too low to be evaluated reliably or not detected at all.

2.3. Péclet-modified Craig-Gordon model simulations

As mentioned above, leaf water is typically enriched in ^{18}O compared to the source water of plants due to evapotranspiration. This process is primarily driven by the water vapor pressure of the atmosphere (e_a), air temperature (T_{air}), the isotopic composition of atmospheric water vapor ($\delta^{18}O_{prec}$) (Kahmen et al., 2011) and in addition by different plant physiological variables (e.g. leaf temperature and transpiration) (Barbour, 2007; Farquhar et al., 2007). The ^{18}O enrichment of leaf water through evapotranspiration can be predicted by using a mechanistic model originally developed for fractionation processes of water surfaces by Craig and Gordon (1965) and adapted for plants by Dongmann et al. (1974) and subsequently Farquhar and Lloyd (1993).

The model allows estimating $\delta^{18}O_{leaf\ water}$ according to Eq. (2)

$$\delta^{18}O_{leaf\ water} = \Delta^{18}O_{leaf\ water} + \delta^{18}O_{SW} \quad (2)$$

where $\Delta^{18}O_{leaf\ water}$ is the bulk leaf water evaporative enrichment and $\delta^{18}O_{SW}$ is the oxygen isotope composition source or xylem water. $\Delta^{18}O_{leaf\ water}$ can be calculated as follows:

$$\Delta^{18}O_{leaf\ water} = \frac{\Delta^{18}O_e(1 - e^{-\wp})}{\wp} \quad (3)$$

$\Delta^{18}O_e$ is the evaporative enrichment of leaf water above the plant's source water in ^{18}O at the sites of evaporation and is calculated as follows:

$$\Delta^{18}O_e = \varepsilon^+ + \varepsilon_k + (\Delta^{18}O_{wv} - \varepsilon_k)\frac{e_a}{e_i} \quad (4)$$

where ε^+ is the equilibrium fractionation between liquid water and vapor at the air–water interface (Bottinga and Craig, 1969), ε_k is the kinetic fractionation, $\Delta^{18}O_{wv}$ is the isotope composition of water vapor and e_a/e_i is the ratio of ambient to intercellular vapor pressures (Craig and Gordon, 1965). The Péclet effect accounts for flux of source water entering the leaf through the transpiration flow opposed by backward diffusion of isotopically enriched water (Farquhar and Lloyd, 1993). The Péclet number was determined as follows:

$$\wp = EL/CD \quad (5)$$

where E is the transpiration rate, L is effective path length, C is the molar concentration of water and D is the diffusivity of $H_2{}^{18}O$. Transpiration rate was calculated using relative humidity, air temperature and atmospheric pressure at each sampling site and mean stomatal conductance of 0.15 mol/m^2/s. For L we used an average value of 20 mm that we kept constant across the transect. A L-value of 20 mm reflects an average value based on reports for a large number of species in the literature (Kahmen et al., 2008, 2009; Song et al., 2013).

Under field conditions, e_a, T_{air} and $\delta^{18}O_{prec}$ are primary climatic drivers of the model with additional influences of secondary variables (O-isotope composition of source water, O-isotope composition of water vapor, leaf temperature, rates of stomatal conductance to water vapor loss and transpiration) (Craig and Gordon, 1965; Dongmann et al., 1974; Farquhar and Cernusak, 2005; Cuntz et al., 2007; Kahmen et al., 2008, 2011). Functional relationships between primary and secondary variables were analyzed and optimized by Kahmen et al. (2011), which reduces the necessary model input data to the primary variables. An isotopic equilibrium between precipitation and water vapor was assumed in order to calculate $\delta^{18}O_{WV}$ (included in Eqn. 4) and subsequently leaf water evapotranspirative enrichment. For our simulations, the primary drivers (e_a, T_{air} and $\delta^{18}O_{prec}$) for the 20 sites were obtained from Bowen (2012) or GeoINTA (2012).

3. RESULTS AND DISCUSSION

3.1. Compound-specific $\delta^{18}O$ values of the hemicellulose biomarkers

The $\delta^{18}O$ values obtained for arabinose, fucose and xylose range from 35.3‰ to 43.6‰, 34.1‰ to 42.3‰ and 33.7‰ to 40.8‰, respectively, and reveal systematic trends over the investigated transect (Table 2 and Fig. 2A). The northern sampling sites are characterized by the lowest $\delta^{18}O_{hemicellulose}$ values whereas $\delta^{18}O_{hemicellulose}$ maxima characterize the middle and southernmost part of the transect. Standard deviations for the field replications are 1.5‰, 2.2‰ and 1.7‰, for arabinose, fucose and xylose, respectively. This finding suggests that the overall homogeneity of topsoils with regard to $\delta^{18}O_{hemicellulose}$ is high. As an exception, the mean standard deviation for fucose at the sampling site 18 and the mean standard errors for all three hemicelluloses at the sampling sites 19 and 20 are higher with up to 6.4‰, indicating lower homogeneity of the topsoil replications.

The $\delta^{18}O$ values (in the following we refer to the means of the field replications) of all three hemicellulose sugar biomarkers are highly significantly correlated with each other, especially arabinose and xylose ($r = 0.96$, $p < 0.001$,

Table 2
Compound-specific $\delta^{18}O$ results for the hemicellulose biomarkers arabinose, fucose and xylose. Standard deviations are given for the field replications. $\delta^{18}O$ values of annual precipitation were retrieved from The Online Isotopes in Precipitation Calculator (Bowen, 2012).

Sampling locality	$\delta^{18}O$ Arabinose (‰, V-SMOW)	Standard deviation Arabinose	$\delta^{18}O$ Fucose (‰, V-SMOW)	Standard deviation Fucose	$\delta^{18}O$ Xylose (‰, V-SMOW)	Standard deviation Xylose	$\delta^{18}O$ Precipitation (‰, V-SMOW)	Coincidence intervals (95%) precipitation
1	36.2	1.5	39.4	4.5	34.7	1.0	−5	0.3
2	35.3	0.6	34.4	1.7	33.7	1.1	−5.1	0.3
3	36.6	0.6	35.7	1.1	34.2	2.4	−5.4	0.3
4	37.1	0.4	34.1	2.2	34.2	0.3	−5.7	0.2
5	36.4	0.4	34.7	1.3	34.1	0.3	−6.1	0.2
6	37.4	0.8	35.5	1.7	35.9	0.9	−6.3	0.2
7	37.7	1.6	36.5	0.7	36.0	2.5	−6.8	0.2
8	39.1	1.6	37.3	2.0	37.8	1.3	−6.7	0.2
9	41.8	2.3	38.0	0.7	40.8	3.9	−6.7	0.2
10	41.3	1.1	39.1	0.3	38.8	1.2	−7.2	0.3
11	41.8	0.6	39.7	1.6	40.0	1.0	−7.6	0.3
12	42.0	0.6	39.3	1.6	39.6	1.1	−8.2	0.4
13	43.6	1.3	41.2	0.6	40.5	0.4	−8.1	0.4
14	40.5	1.9	38.2	1.3	37.8	0.9	−8.7	0.4
15	40.8	1.9	38.9	2.8	38.1	2.5	−9.6	0.6
16	39.0	1.1	37.5	1.5	36.2	1.5	−10.3	0.8
17	38.3	1.7	37.5	2.5	36.1	1.8	−10.8	1.2
18	40.7	0.6	42.3	6.4	38.8	1.1	−10.7	1.2
19	42.3	5.7	42.2	4.9	40.7	6.2	−11.3	1.2
20	39.5	3.5	40.9	4.2	37.7	3.2	−11.7	1.2

$n = 20$). Slightly but systematically more positive $\delta^{18}O$ values of arabinose (Table 2 and Fig. 2A) compared to xylose were also reported in our companion paper (Zech et al., 2014) but not by Zech and Glaser (2009) and Zech et al. (2013, 2012). Both pentoses (arabinose and xylose) are biosynthesized in plants by the decarboxylation of the C6 carbon atoms from glucose (Altermatt and Neish, 1956; Harper and Bar-Peled, 2002; Burget et al., 2003). Given that arabinose is an epimerase product of xylose, more positive $\delta^{18}O$ values of arabinose could reflect a biosynthetic fractionation.

3.2. Comparison of $\delta^{18}O_{hemicellulose}$ results with $\delta^{18}O_{prec}$

The $\delta^{18}O$ values of annual precipitation retrieved from The Online Isotopes in Precipitation Calculator (Bowen, 2012), calculated from a global data set according to an algorithm published by Bowen and Revenaugh (2003), reveal a systematic trend ranging from −5‰ in the north to −11.7‰ in the south (Table 2 and Fig. 2A). This trend most likely reflects the "temperature effect" on $\delta^{18}O_{prec}$ (Dansgaard, 1964). Since oxygen in hemicelluloses, like in cellulose, originates from plant water (e.g. Schmidt et al., 2001) and thus ultimately from precipitation, $\delta^{18}O_{prec}$ values represent without doubt an important variable influencing $\delta^{18}O_{hemicellulose}$ values. One might thus expect hemicellulose biomarkers in soils to reflect $\delta^{18}O_{prec}$. However, in our study the weighted mean $\delta^{18}O$ values of arabinose, fucose and xylose are negatively correlated with $\delta^{18}O_{prec}$ ($r = -0.54$, $p < 0.014$, $n = 20$) and do not reflect $\delta^{18}O_{prec}$ along the transect.

3.3. Relative air humidity as important controlling factor on $\delta^{18}O_{leaf\ water}$ and $\delta^{18}O_{hemicellulose}$ along the investigated Argentinian transect

The above finding highlights that in addition to $\delta^{18}O_{prec}$ another variable exerts an important control on $\delta^{18}O_{hemicellulose}$. Indeed, amongst plant physiologists it is well known that evapotranspiration results in an ^{18}O enrichment of leaf water and that this signal is incorporated in newly assimilated sugars and in leaf- and stem cellulose (Flanagan et al., 1991; Roden et al., 2000; Barbour, 2007; Farquhar et al., 2007; Kahmen et al., 2011). As well, our experimental investigations presented in the companion paper (Zech et al., 2014) report that $\delta^{18}O_{hemicellulose}$ reflect slightly dampened the climatically controlled evapotranspirative ^{18}O enrichment of leaf water. Several climatic and plant physiological variables such as relative air humidity, temperature and transpiration rate influence the degree of evaporative ^{18}O enrichment of leaf water.

In order to evaluate the effect of air temperature and relative air humidity on $\delta^{18}O_{hemicellulose}$, a Péclet-modified Craig-Gordon Model was used to model $\delta^{18}O_{leaf\ water}$ along the investigated Argentinian transect and to conduct sensitivity tests. Modeled results for $\delta^{18}O_{leaf\ water}$ with e_a, T_{air} and $\delta^{18}O_{prec}$ values from GeoINTA (2012) and Bowen (2012) are shown in Fig. 2A. Accordingly, the general $\delta^{18}O_{prec}$ trend towards more negative values from north to south is not reflected in modeled $\delta^{18}O_{leaf\ water}$. Rather, the modeled $\delta^{18}O_{leaf\ water}$ values correlate highly significantly with the measured $\delta^{18}O_{hemicellulose}$ values ($r = 0.81$, $p < 0.001$, $n = 20$), corroborating that our hemicellulose

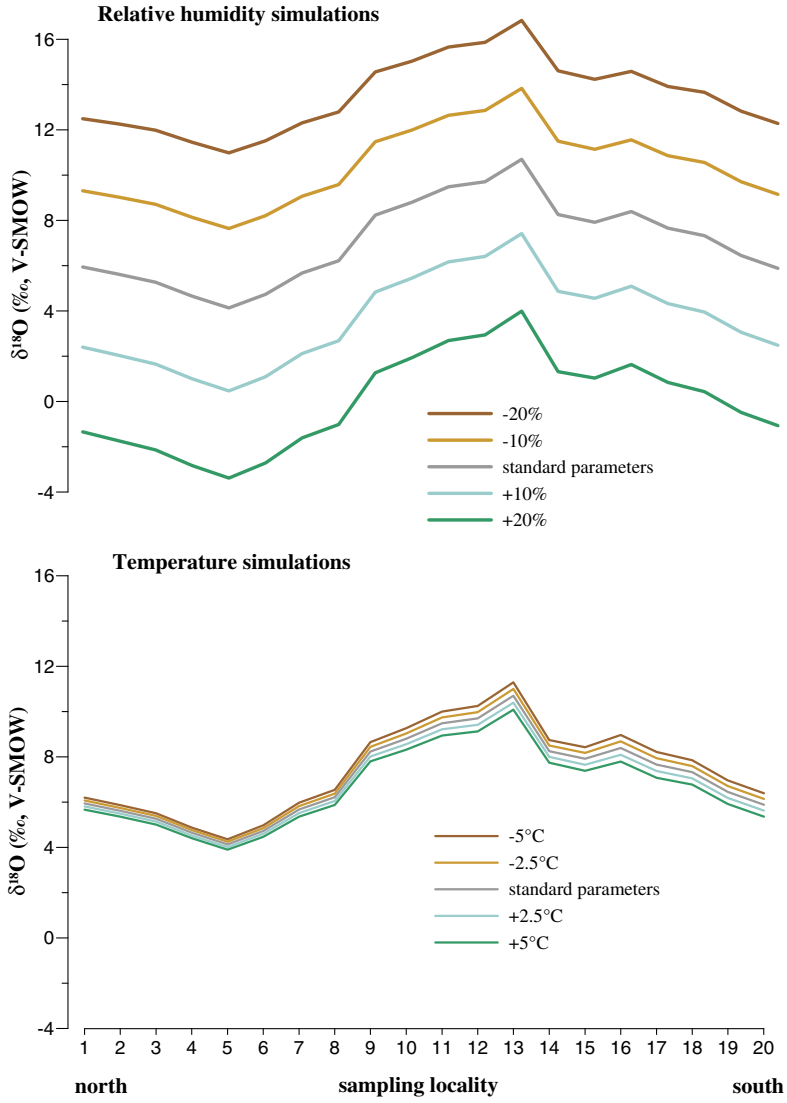

Fig. 3. Model sensitivity tests based on a Péclet-modified Craig-Gordon model (Kahmen et al., 2011) showing the dependency of $\delta^{18}O_{leaf\ water}$ on relative air humidity and temperature changes.

biomarker results reflect $\delta^{18}O_{leaf\ water}$, i.e. $\delta^{18}O_{prec}$ altered by evaporative ^{18}O enrichment during transpiration rather than $\delta^{18}O_{prec}$ alone.

Leaf water $\delta^{18}O$ is driven in model simulations by three primary variables; temperature, relative humidity and $\delta^{18}O_{prec}$. To test if leaf water is more sensitive to relative humidity or temperature, we performed a sensitivity analysis with the model where mean annual humidity and mean annual T_{air} were varied by 10% and 20% and by 2.5 and 5.0 °C (Fig. 3). These model sensitivity tests demonstrate that reasonable changes in relative humidity strongly influence $\delta^{18}O_{leaf\ water}$ resulting in shifts of 12.8–14.0‰ depending on the sampling site, whereas changes in T_{air} have only a marginal effect in the range of 0.5–1.2‰ on $\delta^{18}O_{leaf\ water}$. The same was observed in a previous study for alpha cellulose (Kahmen et al., 2011) and in our chamber experiments presented in the companion paper for hemi celluloses (Zech et al., 2014). Given the large relative air humidity gradient prevailing along the investigated Argentinian transect (ranging from 48.0% to 73.2%), this finding helps to explain why $\delta^{18}O_{hemicellulose}$ values do not reflect $\delta^{18}O_{prec}$ values. Evaporative ^{18}O enrichment of leaf water is relatively low (~10‰) in the humid northern part of the transect and high (up to ~19‰) in the arid middle and southern part of the transect (Fig. 2A).

3.4. Comparison between measured $\delta^{18}O_{hemicellulose}$ and modeled $\delta^{18}O_{cellulose}$ values

Based on the notion that $\delta^{18}O$ values of primary assimilates (glucose and ultimately sucrose) are approximately 27‰ more enriched compared to leaf water (Sternberg et al., 1986; Yakir and DeNiro, 1990), the PMCG model also allows calculating values for $\delta^{18}O_{leaf\ cellulose}$ and $\delta^{18}O_{stem\ cellulose}$ by accounting for 40% of exchangeable oxygen atoms during cellulose formation with leaf water (for leaf cellulose) and xylem water (for stem cellulose) (Roden et al., 2000). Calculated values represent the

maximum possible difference between leaf and stem cellulose. The modelling results range from 31.14‰ to 37.70‰ and 25.85‰ to 30.18‰ for $\delta^{18}O_{leaf\ cellulose}$ and $\delta^{18}O_{stem\ cellulose}$, respectively, and show weaker ^{18}O enrichment than the measured $\delta^{18}O_{hemicellulose}$ values (Fig. 2A). We acknowledge that the measured $\delta^{18}O_{hemicellulose}$ values reflect a mixture of leaf and stem/root organic matter. Stem/root (hemi)celluloses are depleted in ^{18}O compared to leaf (hemi)celluloses because approximately 40% of the O atoms during stem cellulose synthesis are exchanging with not enriched stem water (Sternberg et al., 1986). Hence, it can be expected that varying input of leaf vs. stem/root (hemi)celluloses results in varying $\delta^{18}O$ (hemi)cellulose values in soils. In fact, modeled stem cellulose is depleted in ^{18}O by approximately 7‰ compared to modeled leaf cellulose (Fig. 2A). While it is difficult to address the question leaf- versus stem-derived qualitatively at the current state of research, based on the model simulations we would consider that leaf input in soil organic matter along here investigated transect is greater compared to stem/root input.

The observed systematic offset between modeled cellulose and measured hemicellulose values might be attributed to inaccurate model input variables. Neither relative air humidity, nor temperature nor the isotopic composition of atmospheric water vapor ($\delta^{18}O_{prec}$) are actually measured values but interpolated values from GeoINTA (2012) and from Bowen (2012). For the interpolated $\delta^{18}O_{prec}$ values used in the PMCG model, Bowen and Revenaugh (2003) show a confidence intervals (95%) ranging from 0.2‰ to 1.2‰. Furthermore, evaporative ^{18}O enrichment of soil water is not considered in the model results and can potentially cause a considerable positive offset of the actual $\delta^{18}O_{hemicellulose}$ values.

The companion experimental study by Zech et al. (2014) has also reported more positive $\delta^{18}O_{hemicellulose}$ compared to $\delta^{18}O_{cellulose}$ values. This feature can possibly be attributed to position-specific $\delta^{18}O$ differences of oxygen atoms in glucose molecules forming (hemi-) cellulose. Sternberg et al. (2006) reported that the fractionation factor for the oxygen atoms in C2 position is 19.6‰, while for the oxygen atoms associated with the carbon atoms C3–C6 it is on average 28.8‰. Since pentoses are biosynthesized by the decarboxylation of the C6 carbon atoms from glucose (Altermatt and Neish, 1956; Harper and Bar-Peled, 2002; Burget et al., 2003), more positive $\delta^{18}O_{hemicellulose}$ values would indicate that the oxygen atoms in C6 position of glucose building up cellulose are isotopically depleted compared to the average of the oxygen atoms in position C2–C5. This is in agreement with recent study by Waterhouse et al. (2013) indicating that oxygen atoms at C6 position undergo around 80% exchange with medium water during heterotrophic cellulose synthesis.

Finally, two additional factors may help explaining the increased offset between measured $\delta^{18}O_{hemicellulose}$ and modeled $\delta^{18}O_{cellulose}$ values characterizing the three southernmost sampling sites (18–20). First, while modeling is carried out with mean annual climate values, the growing season (when biosynthesis of hemicelluloses actually occurs) for these sites does not coincide with the months when precipitation falls, i.e. during the winter months (Jobbágy et al., 2002). Taking this seasonality effect into account, the PMCG model yields by 1–2‰ more positive $\delta^{18}O_{cellulose}$ values. Second, Patagonia is characterized by dry westerly winds (foehn) (Beltrán, 1997), which presumably additionally contribute to higher evaporative ^{18}O enrichment of leaf water.

4. CONCLUSIONS AND IMPLICATIONS FOR PALEOCLIMATE STUDIES

Investigating the compound-specific $\delta^{18}O$ values of hemicellulose sugar biomarkers of modern topsoils along a climate transect in Argentina allows drawing conclusions, which have implications for the interpretation of $\delta^{18}O$

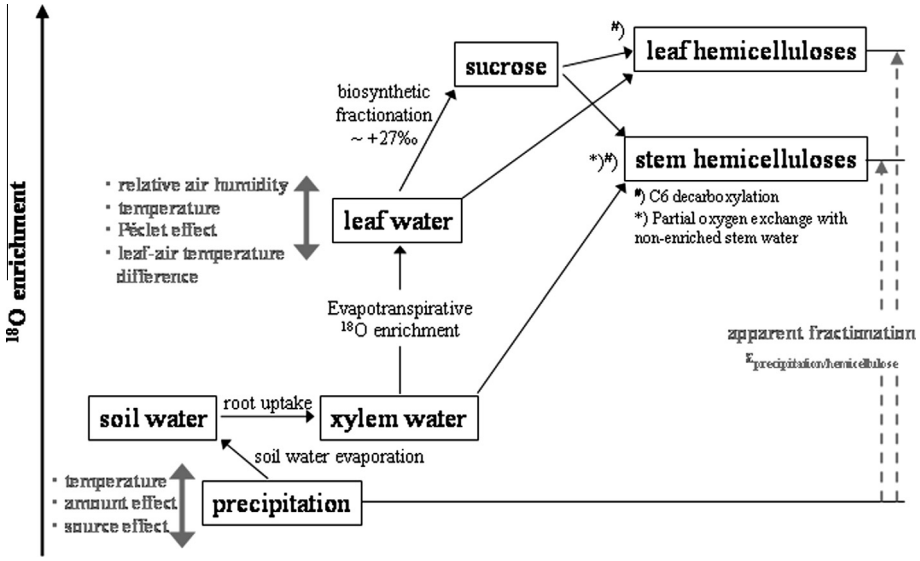

Fig. 4. Conceptual diagram illustrating the major factors influencing the oxygen isotopic composition of hemicellulose sugar biomarkers (from Zech et al., 2014).

values of hemicellulose sugars derived from paleosols for the reconstruction of climate history.

- Although oxygen in hemicelluloses derives from water and thus ultimately from precipitation, the hemicellulose biomarkers arabinose, fucose and xylose do not simply reflect $\delta^{18}O_{prec}$ but rather $\delta^{18}O_{leaf\ water}$. The correlation between measured $\delta^{18}O_{hemicellulose}$ and modeled $\delta^{18}O_{leaf\ water}$ is highly significant ($r = 0.81$, $p < 0.001$, $n = 20$).
- This finding can be attributed to the evaporative ^{18}O enrichment of leaf water during transpiration. Model sensitivity tests using a Péclet-modified Craig-Gordon (PMCG) model corroborate that relative air humidity is a very rigorous climate parameter influencing $\delta^{18}O_{leaf\ water}$, whereas temperature is of minor importance.
- While oxygen exchange and degradation effects on $\delta^{18}O$ values of hemicelluloses sugar biomarkers seem to be negligible (Zech et al., 2012), further effects that need to be considered when interpreting $\delta^{18}O_{hemicellulose}$ values obtained from (paleo-)soils are evaporative ^{18}O enrichment of soil water, seasonality effects, wind effects and in case of abundant stem/root-derived organic matter input a partial loss of the evaporative ^{18}O enrichment of leaf water.
- Overall, our Argentinian climate transect study is in agreement with an experimental study conducted on plant material from a climate chamber experiment presented in the companion paper (Zech et al., 2014). Our results corroborate the conceptual model proposed by Zech et al. (2014) for interpreting $\delta^{18}O_{hemicellulose}$ results in paleoclimate studies (Fig. 4).

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