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## Publication

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

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The oxygen isotopic composition of precipitation ( $\delta^{18}\text{O}_{\text{prec}}$ ) 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 paleoprecipitation. In a companion paper (Zech et al., 2014) we investigated  $\delta^{18}\text{O}_{\text{hemicellulose}}$  values of plants grown under different climatic conditions in a climate chamber experiment. Here we present results of compound-specific  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}_{\text{prec}}$ . The results from the field replications indicate that the homogeneity of topsoils with regard to  $\delta^{18}\text{O}_{\text{hemicellulose}}$  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  $\delta^{18}\text{O}_{\text{hemicellulose}}$  values (mean of the three sugars) do not correlate positively with  $\delta^{18}\text{O}_{\text{prec}}$  ( $r = -0.54$ ,  $p > 0.014$ ,  $n = 20$ ). By using a Péclet-modified Craig-Gordon (PMCG) model it can be shown that the  $\delta^{18}\text{O}_{\text{hemicellulose}}$  values correlate highly significantly with modeled  $\delta^{18}\text{O}_{\text{leaf water}}$  values ( $r = 0.81$ ,  $p < 0.001$ ,  $n = 20$ ). This finding suggests that hemicellulose biomarkers in (paleo-)soils do not simply reflect  $\delta^{18}\text{O}_{\text{prec}}$  but rather  $\delta^{18}\text{O}_{\text{prec}}$  altered by evaporative  $^{18}\text{O}$  enrichment of leaf water due to evapotranspiration. According to the modeling results, evaporative  $^{18}\text{O}$  enrichment of leaf water is relatively low ( $\sim 10\%$ ) 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  $^{18}\text{O}$  enrichment of leaf water and thus  $\delta^{18}\text{O}_{\text{hemicellulose}}$ , 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  $\delta^{18}\text{O}_{\text{hemicellulose}}$  values obtained from (paleo-)soils are evaporative  $^{18}\text{O}$  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  $^{18}\text{O}$  enrichment of leaf water. Overall, our results prove that compound-specific  $\delta^{18}\text{O}$  analyses of hemicellulose biomarkers in soils and sediments are a promising tool for paleoclimate research. However, disentangling the two major factors influencing  $\delta^{18}\text{O}_{\text{hemicellulose}}$ , namely  $\delta^{18}\text{O}_{\text{prec}}$  and relative air humidity controlled evaporative  $^{18}\text{O}$  enrichment of leaf water, is challenging based on  $\delta^{18}\text{O}$  analyses alone.

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