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## Calibration of $\delta^2\text{H}_n$ -alkane and $\delta^{18}\text{O}_{\text{sugar}}$ for paleoclimate reconstructions in South Africa and its first application to peat sediments from Vankervelsvlei

Paul Strobel<sup>1</sup>, Roland Zech<sup>1</sup>, Marcel Bliedtner<sup>1</sup>, Julian Struck<sup>1</sup>, Bruno Glaser<sup>2</sup>, Michael Zech<sup>3</sup>, Michael E. Meadows<sup>4,5</sup>, and Torsten Haberzettl<sup>6</sup>

<sup>1</sup>Physical Geography, Institute of Geography, Friedrich-Schiller-University Jena, Jena, Germany

<sup>2</sup>Institute of Agronomy and Nutritional Sciences, Soil Biogeochemistry, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany

<sup>3</sup>Physical Geography with focus on paleoenvironmental research, Institute of Geography, Dresden University of Technology, Dresden, Germany

<sup>4</sup>Department of Environmental and Geographical Science, University of Cape Town, Rondebosch, South Africa

<sup>5</sup>School of Geographic Sciences, East China Normal University, Shanghai, China

<sup>6</sup>Physical Geography, Institute of Geography and Geology, University of Greifswald, Germany

Hydrogen isotope analyses of leaf wax n-alkanes ( $\delta^2\text{H}_{\text{wax}}$ ) are widely applied to reconstruct paleoclimate changes. To date, it has proved difficult to disentangle past changes in the isotopic signal of precipitation ( $\delta^2\text{H}_p$ ) and other fractionation factors, e.g. evapo-transpirative enrichment. Oxygen isotopes from hemicellulose sugars ( $\delta^{18}\text{O}_{\text{sugar}}$ ) have been proposed to complement  $\delta^2\text{H}_{\text{wax}}$  and enable more robust paleohydrological reconstructions by coupling both isotopes. However, up to now, there is a lack of studies analysing both water isotopes in South Africa.

Therefore, we analysed  $\delta^2\text{H}_{\text{wax}}$  and  $\delta^{18}\text{O}_{\text{sugar}}$  from topsoils from South Africa to evaluate the coupled isotope approach on modern reference material as an initial step towards more robust paleohydrological reconstructions. The results indicate that  $\delta^2\text{H}_{\text{wax}}$  significantly correlates with  $\delta^2\text{H}_p$  values for growing season precipitation. However, no correlation exists between  $\delta^{18}\text{O}_{\text{sugar}}$  and growing season  $\delta^{18}\text{O}_p$ . While the apparent fractionation  $\epsilon_{\text{app } 2\text{H}}$ , i.e. the difference between  $\delta^2\text{H}_{\text{wax}}$  and  $\delta^2\text{H}_p$ , is relatively constant and not affected by climate,  $\epsilon_{\text{app } 18\text{O}}$  correlates significantly with both potential evapotranspiration and the aridity index, indicating a strong influence of evapo-transpirative enrichment on  $\delta^{18}\text{O}_{\text{sugar}}$ . Coupling  $\delta^{18}\text{O}_{\text{sugar}}$  and  $\delta^2\text{H}_{\text{wax}}$  facilitates the reconstruction of  $\delta^2\text{H}_p$  and  $\delta^{18}\text{O}_p$  in South Africa with a  $1\sigma$  accuracy of  $\pm \sim 27\text{‰}$  and  $\pm \sim 3.7\text{‰}$ , respectively, and relative humidity (RH) with a  $1\sigma$  accuracy of  $\pm \sim 17\%$ .

In a second step, we applied the coupled isotope approach to a 14.6 m long sediment core to complement geochemical and sedimentological analyses. The core is from Vankervelsvlei, a fen near the southern Cape coast located 152 m above mean sea level within the year-round rainfall zone of South Africa. Our results show relatively high values for  $\delta^2\text{H}_{\text{wax}}$  between  $7,020^{+200}/_{-1270}$  and  $4,770^{+280}/_{-1230}$  cal BP. Conventionally, this would be interpreted to indicate more arid conditions (referring to the 'amount effect' or enhanced evapo-transpirative enrichment). However,

corresponding reconstructed RH values are high and point to more humid conditions. Thus, we interpret the higher  $\delta^2\text{H}_{\text{wax}}$  (as well as the isotopically positive reconstructed precipitation) to reflect changing moisture sources, i.e. more summer precipitation related to greater prominence of the Easterlies. Enhanced RH as well as increased wind speed inferred from high wind driven allochthonous input (Al, Sr, Ti), is associated with a maximum in obliquity during that time. Drier and less windy conditions are indicated between 4,770  $^{+280}_{-230}$  and 2,820  $^{+350}_{-330}$  cal BP, as suggested by lower  $\delta^2\text{H}_{\text{wax}}$  and reconstructed precipitation, low RH and reduced wind driven allochthonous input. Moist conditions persisted between 2,820  $^{+350}_{-330}$  and 1,620  $^{+430}_{-280}$  cal BP and are followed by a ~1 kyr dry period. Moisture levels have been increasing since 640  $^{+90}_{-100}$  cal BP.