Calibration of $\delta^2H_{n\text{-alkane}}$ and $\delta^{18}O_{sugar}$ for paleoclimate reconstructions in South Africa and its first application to peat sediments from Vankervelsvlei

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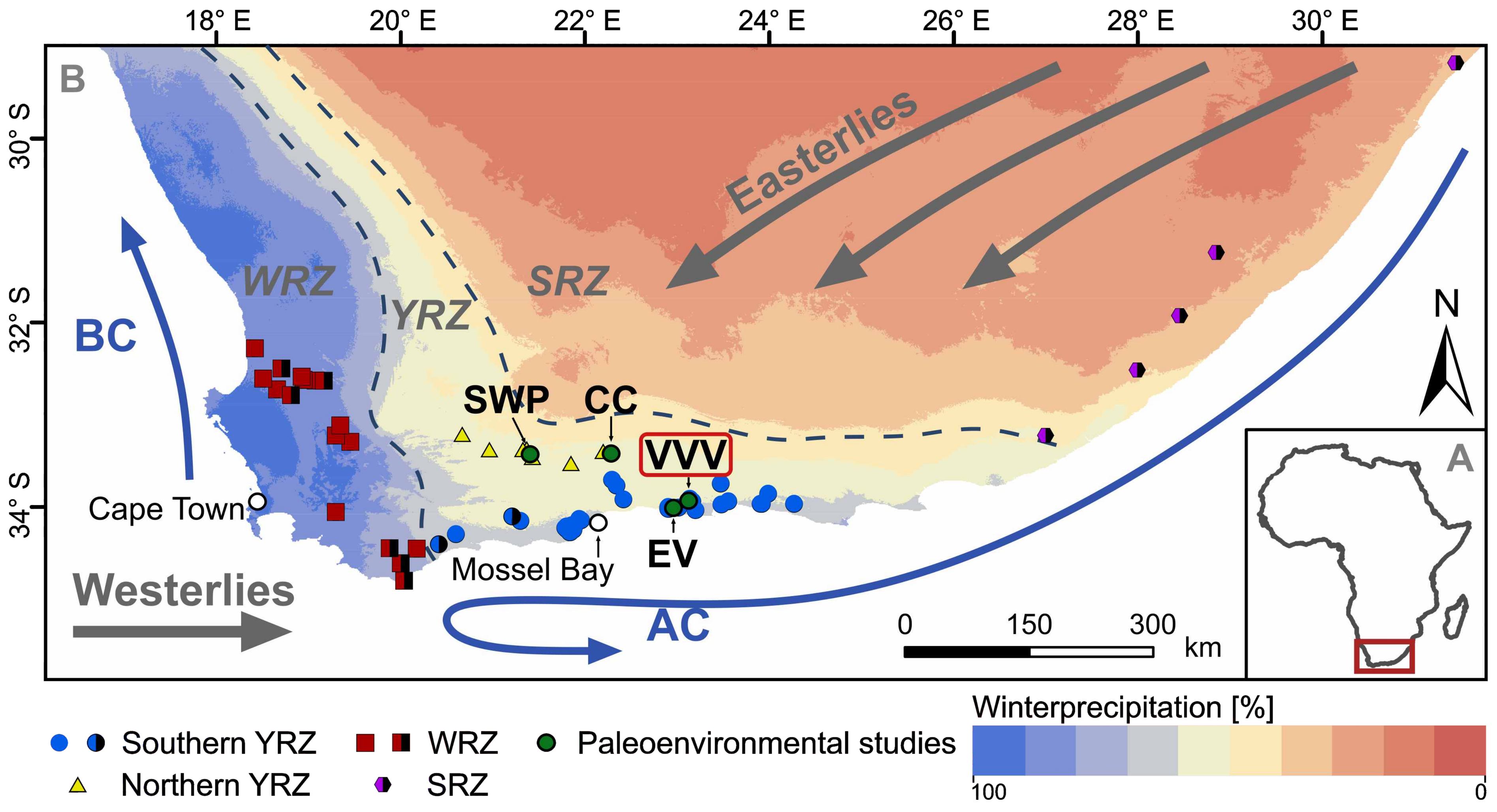
Background and study site



A) Simplified map of Africa and the red box highlights the studied area. B) Location of the topsoil sample sites. Red squares: samples from the Winter Rainfall Zone, (WRZ); blue circles from the southern Year-round Rainfall Zone (YRZ), yellow triangles from the northern YRZ, and pink hexagons from the Summer Rainfall Zone (SRZ; investigated by Hahn et al., 2018). Green circles show sites of paleoenvironmental studies (VVV = Vankervelsvlei, this study, Strobel et al., 2019; CC = Cango Cave, Talma and Vogel, 1992; EV = Eilandvlei, Quick et al., 2018; SWP = Seweweekspoort, Chase et al., 2017). Additionally, the circumpolar Westerlies, the tropical Easterlies, the Agulhas Current (AC) and the Benguela Current (BC) are depicted. (Data source: Rainfall seasonality: Worldclim 2 dataset (Fick and Hijmans, 2017); Circulation systems after Chase and Meadows (2007)).

- the climatic evolution and ecosystem dynamics in South Africa have been highly debated
- three major rainfall zones occur in South Africa today:
  1) Summer Rainfall Zone (SRZ; >66% rainfall during austral summer), isotopically enriched in ^{2}H and ^{18}O
  2) Winter Rainfall Zone (WRZ; >66% rainfall during austral winter), isotopically depleted in ^{2}H and ^{18}O
  3) Year-round Rainfall Zone (YRZ)
- 62 topsoils (0-5 cm) from each rainfall zone were sampled and analysed for their isotopic signature of leaf wax-derived *n*-alkanes ($\delta^2H_{n\text{-alkane}}$) and hemicellulose-derived sugars ($\delta^{18}O_{sugar}$)
- Vankervelsvlei (VVV) is located in the YRZ and ideally suited to reconstruct past environmental and climate variability

Objectives

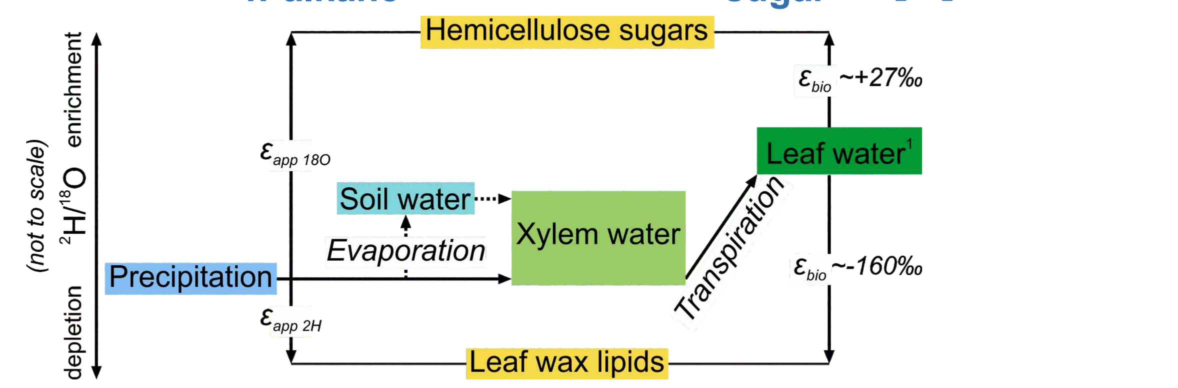
Calibration study

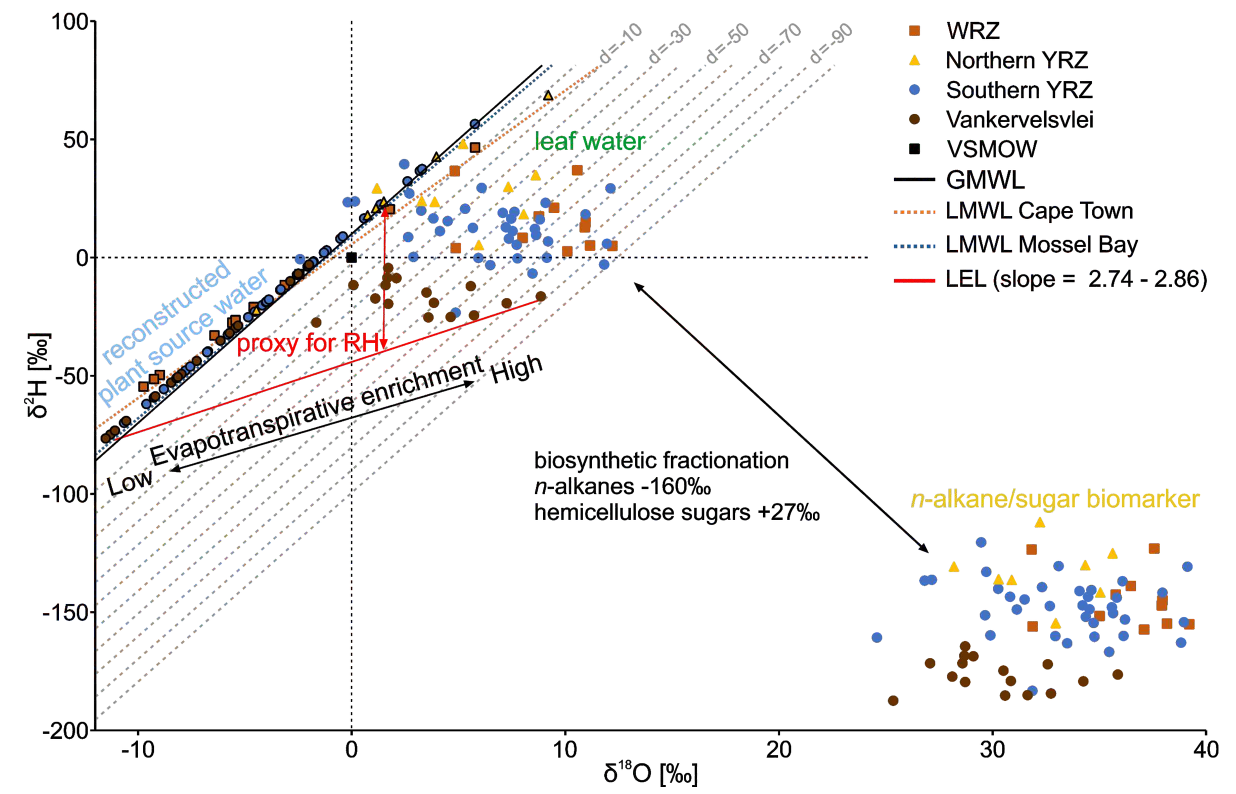
- Are oxygen and hydrogen apparent fractionation (i.e., the difference between $\delta^2H_{n\text{-alkane}}$ and δ^2H_p ($\varepsilon_{app\ 2H}$), and $\delta^{18}O_{sugar}$ and $\delta^{18}O_p$ ($\varepsilon_{app\ 18O}$)) affected by environmental conditions?
- Does the coupling of $\delta^2H_{n\text{-alkane}}$ and $\delta^{18}O_{sugar}$ enable to reconstruct the precipitation and relative humditiy?

Paleoenvironmental study

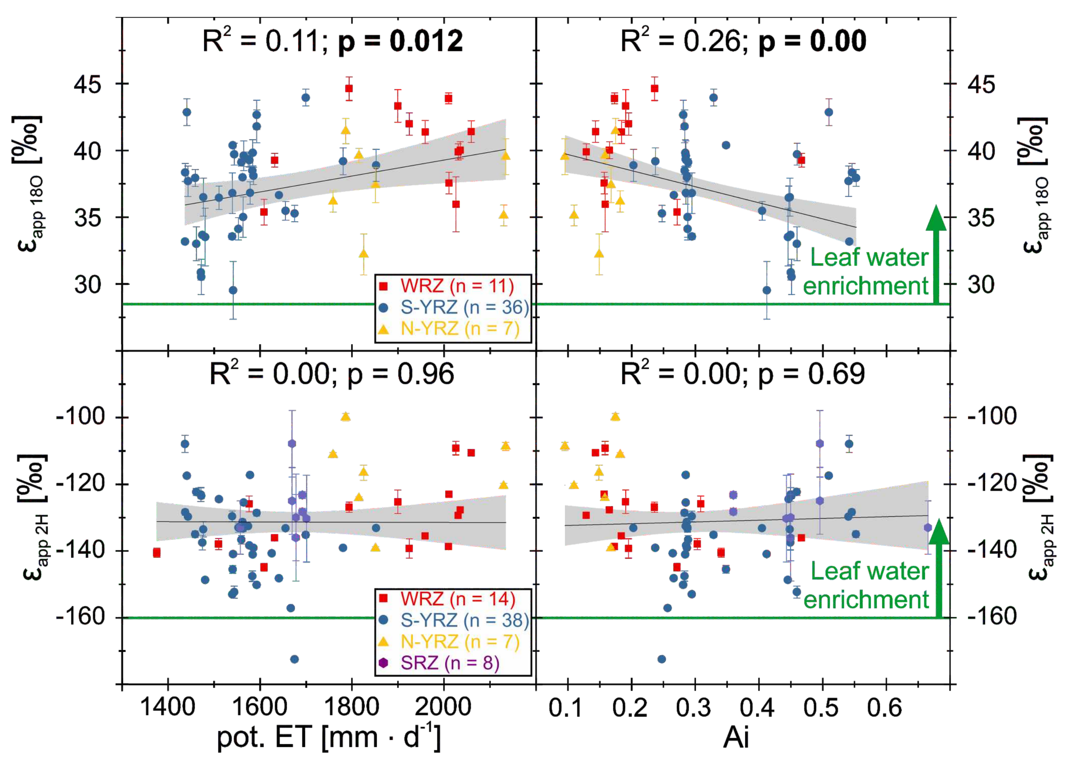
- Which paleoenvironmental changes can be reconstructed in the YRZ during the last 7 ka cal BP?
- Does the application of the coupled $\delta^2H_{n\text{-alkane}}$ - $\delta^{18}O_{sugar}$ approach shows changes in the plants source water and relative humidity (RH) and how do this complement standard (in)organic (bio)geochemical analyses?

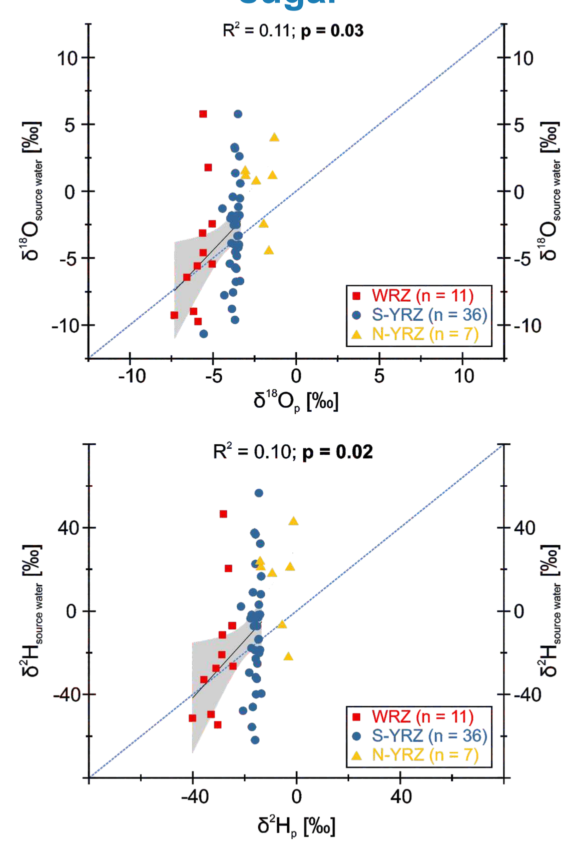
Coupled $\delta^2H_{n\text{-alkane}}$ and $\delta^{18}O_{sugar}$ approach

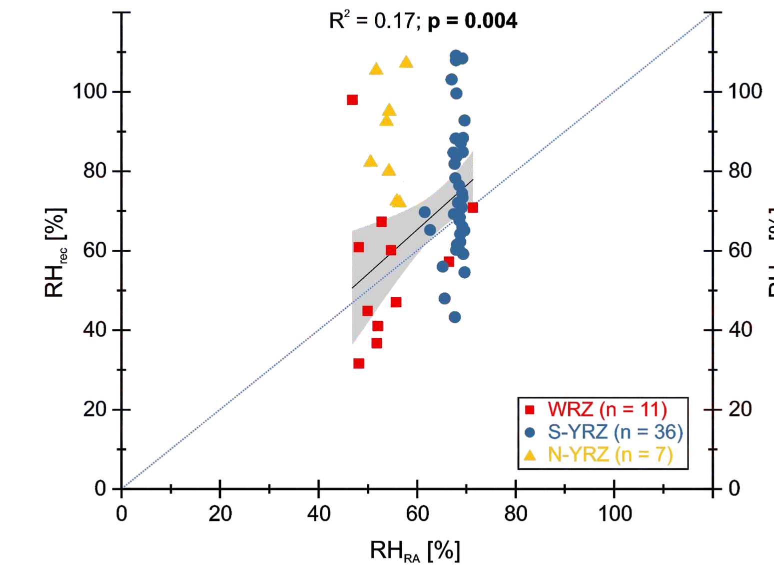




Calibration of $\delta^2H_{n\text{-alkane}}$ and $\delta^{18}O_{sugar}$

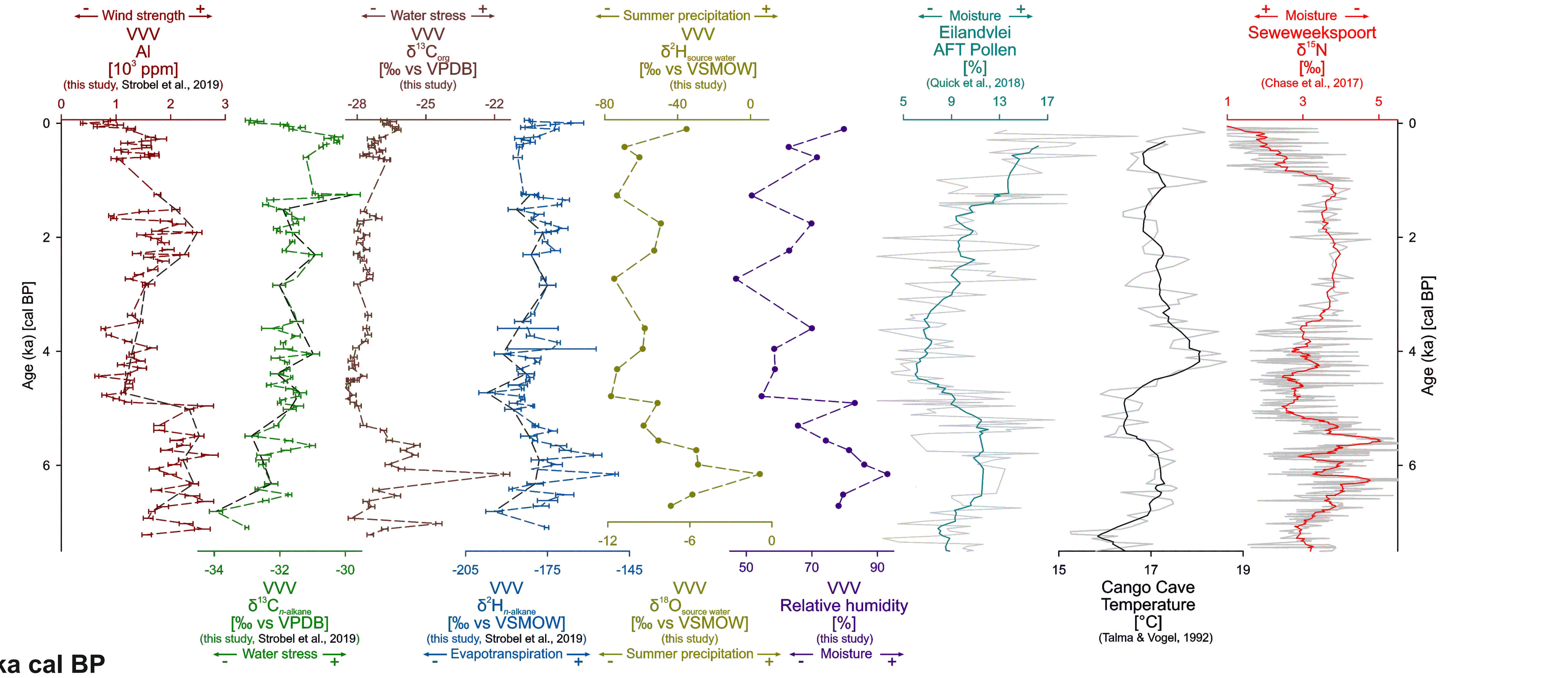






- **$\varepsilon_{app\ 18O}$ is strongly influenced by evapotranspiration**
- **$\varepsilon_{app\ 2H}$ is not climate dependent**
- **plant source water δ^{18}O enables to reconstruct $\delta^{18}O_p$ with an offset of $\Delta^{18}O = 0.8 \pm 3.7$‰**
- **plant source water δ^2H represents δ^2H_p with with an offset of $\Delta^2H = 6 \pm 27$‰**
- **relative humidity (RH) can be reconstructed with an offset of $\Delta RH = 6 \pm 17$%**

Paleoclimate reconstruction at Vankervelsvlei



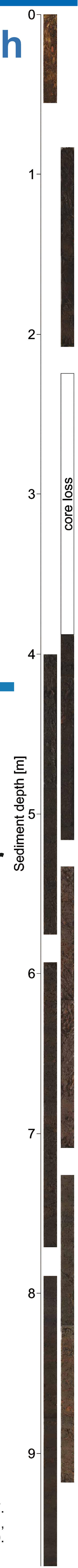
7.0 - 4.7 ka cal BP
- windy (high Al conc.), high evapotranspiration (enriched $\delta^2H_{n\text{-alkane}}$ values), moist conditions (high RH) accompanied by high summer rainfall contribution (plant source water δ^2H and δ^{18}O)
- high temperatures at CC and high Afrotemperate forest pollen percentages at EV are in line with our results, but decreased moisture at SWP is in contradiction

4.7 - 2.0 ka cal BP
- less windy (low Al conc.), less evapotranspiration (depleted $\delta^2H_{n\text{-alkane}}$ values), less summer rainfall contribution (plant source water δ^2H and δ^{18}O) lead to overall dry conditions (low RH)
- maximum temperature at ~4.5 ka cal BP (CC), less moisture at EV but a trend to moister conditions, SWP shows opposed picture with a trend from moist to dry conditions

since 2.0 ka cal BP
- less windy (Al), variing evapotranspiration ($\delta^2H_{n\text{-alkane}}$), high summer rainfall contribution (plant source water δ^2H and δ^{18}O) lead to an overall trend of increasing moisture (low RH)
- incrasing moisture is also reconstructed at EV and SWP

Conclusions

- **coupling $\delta^2H_{n\text{-alkane}}$ and $\delta^{18}O_{sugar}$ allows to reconstruct δ^2H_p, $\delta^{18}O_p$ and relative humidity**
- terrestrial dust (Al concentration) as **wind indicator**
- $\delta^2H_{n\text{-alkane}}$ influenced by **evaporation** and **source effect**
- summer and winter precipitation contribution **is** reflected by **plant source water** δ^2H and δ^{18}O
- **VVV = evapotranspiration controlled system**
- three major climatic phases:
  1) moist phase with high summer precipitation contribution and strong wind between 7,0 to 4,7 ka cal BP
  2) drier phase accompanied by less summer precipitation contribution and less wind intensity (4.7 - 2 ka cal BP)
  3) since 2 ka cal BP moisture have been increased with high summer precipitation contribution but decreasing wind intensity



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