Factors controlling the triple oxygen isotope composition of grass leaf water and phytoliths: insights for paleo-environmental reconstructions

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Rationale

$\Delta'^{17}O$
leaf water

Photosynthesis

Silica polymerization

$\Delta'^{17}O$
atmospheric CO_2
and O_2

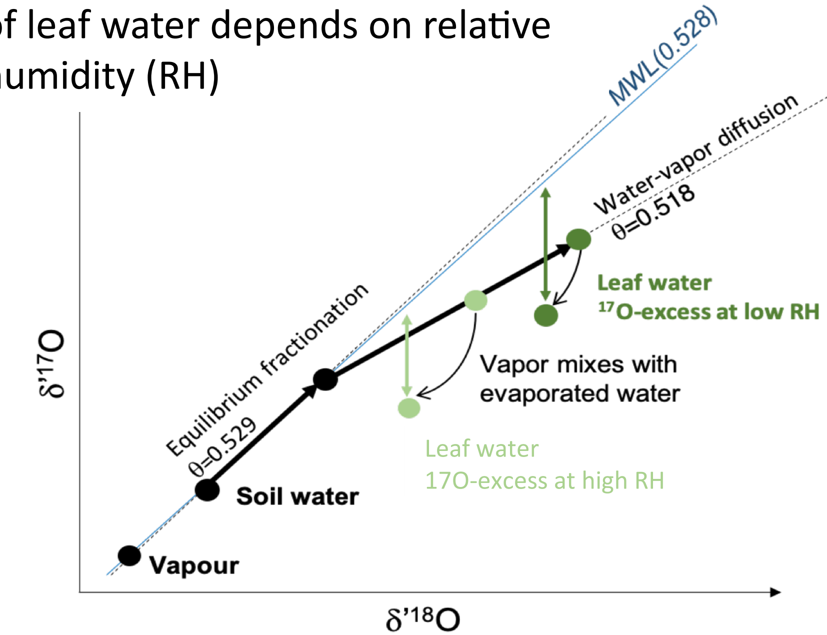
$\Delta'^{17}O$
leaf silica
(phytoliths)

Reconstructions

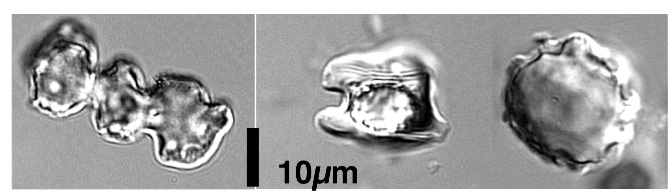
Past changes in gross primary production
?

Past changes in climate parameters
?

^{17}O –excess ($=\delta'^{17}O - 0.528 * \delta'^{18}O$) of leaf water depends on relative humidity (RH)



Phytoliths polymerize from leaf water in leaf cells (isotope equilibrium assumed)



(e.g. Farquhar et al., 1993; Farquhar et al., 1993; Luz et al., 1999; Farquhar and Gan, 2003; Angert et al., 2003; Eisenstadt et al., 2010; Helman et al., 2005; Landais et al., 2007; Alexandre et al., 2018; Koren et al., 2019; Alexandre et al., 2019)

Questions

- What are the key-processes that control grass leaf water and phytoliths $\delta'^{18}O$ and ^{17}O-excess ?
- Is the ^{17}O-excess of phytoliths a proxy for changes in continental atmospheric relative humidity ?
- Can we reconstruct $\Delta'^{17}O$ ($\Delta'^{17}O = \delta'^{17}O - \lambda_{reference} * \delta'^{18}O$) of grass leaf water from phytolith ?

CALIBRATION

Growth chamber water isotope ($\delta'^{18}O$, $\delta'^{17}O$) monitoring for changing relative humidity, air temperature and partial pressure of CO_2 mimicking past climate changes

VERIFICATION

Field datasets

Monitoring

CALIBRATION

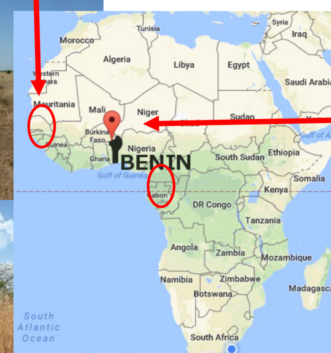
Growth chambers

- Climate variables: relative humidity, air temperature, atmospheric pCO2
- *Festuca arundinacea*: 14 days of growth, 7 experiments, 3 replicates/experiment
- Samples:
  - All water compartments including atmospheric water vapor
  - Phytoliths

VERIFICATION

Humidity and vegetation transect in West Africa

- Climate variable: relative humidity
- 57 samples: Soil phytoliths



VERIFICATION

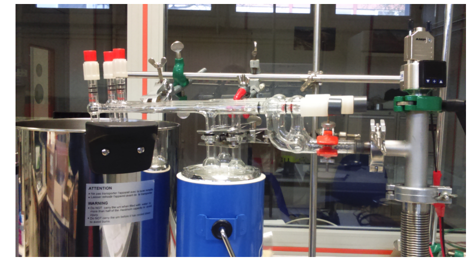
AMMA-CATCH Observatory in Benin (Djougou)

- Climate variable: relative humidity, air temperature, vapor pressure deficit
- 6 samples (2 seasons, 2 sites) :
  - Grass stems water
  - Grass stem phytoliths

Isotope analyses

LSCE
Laboratoire des sciences du climat & de l'environnement

Plant water ^{17}O-excess
Extraction by vacuum distillation
fluorination-IRMS
^{17}O-excess precision= **5 per meg**



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Water and vapor ^{17}O-excess
Laser analyzer
^{17}O-excess precision= **10 per meg**

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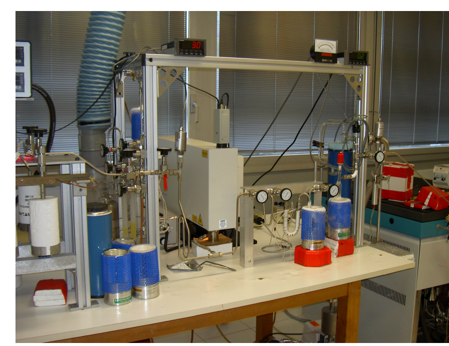
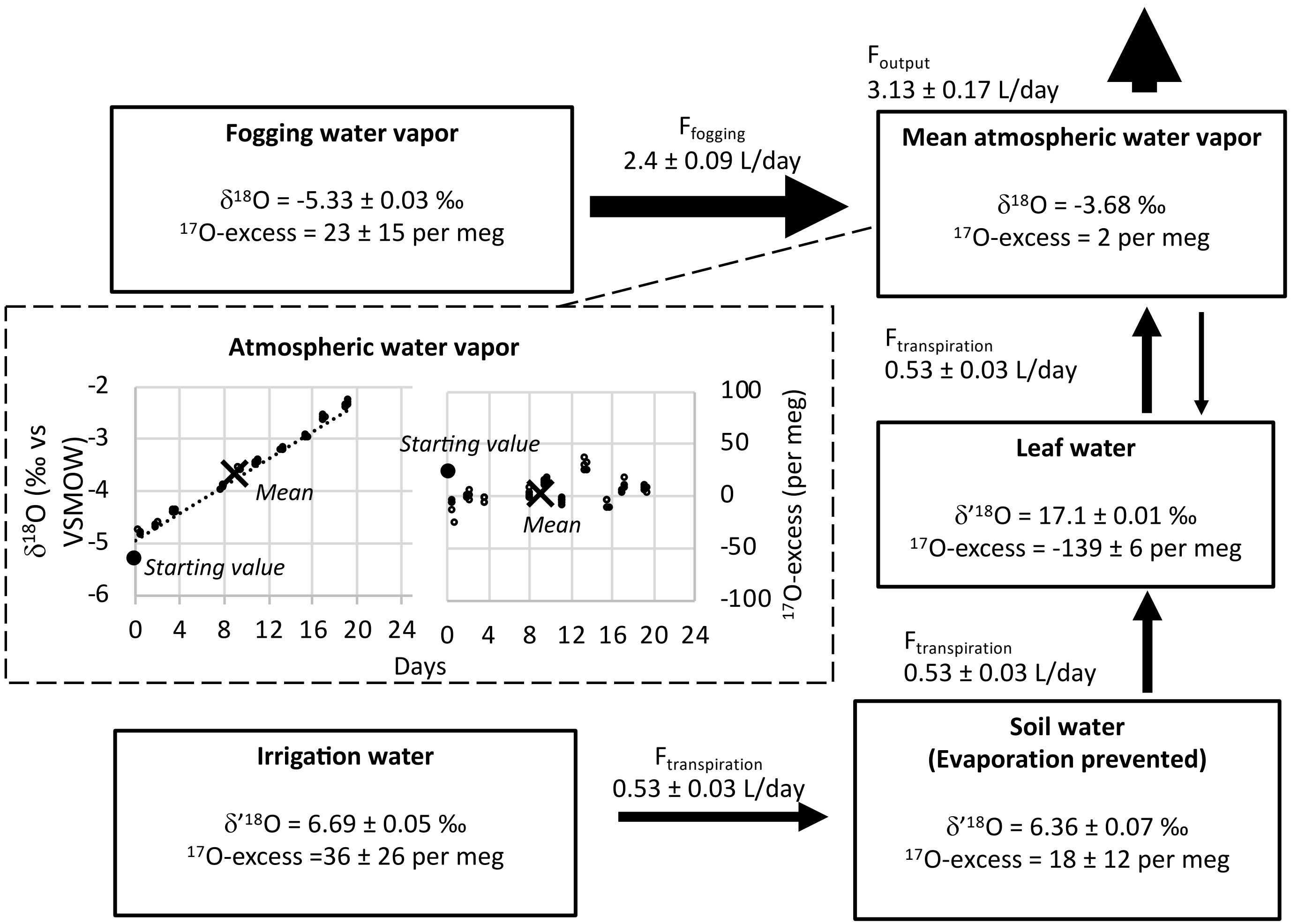
Phytolith ^{17}O-excess
High purity extraction
N_2 flow dehydration
IR-Laser-fluorination-IRMS
^{17}O-excess precision **= 10 per meg**



UWG2:
^{17}O-excess $_{UWG-2}$ = -68 ± 27 per meg (n = 5)
San Carlos olivine:
^{17}O-excess$_{SC}$ = -49 ± 24 per meg (n = 3).

Effectiveness of the growth chamber controlled water cycle

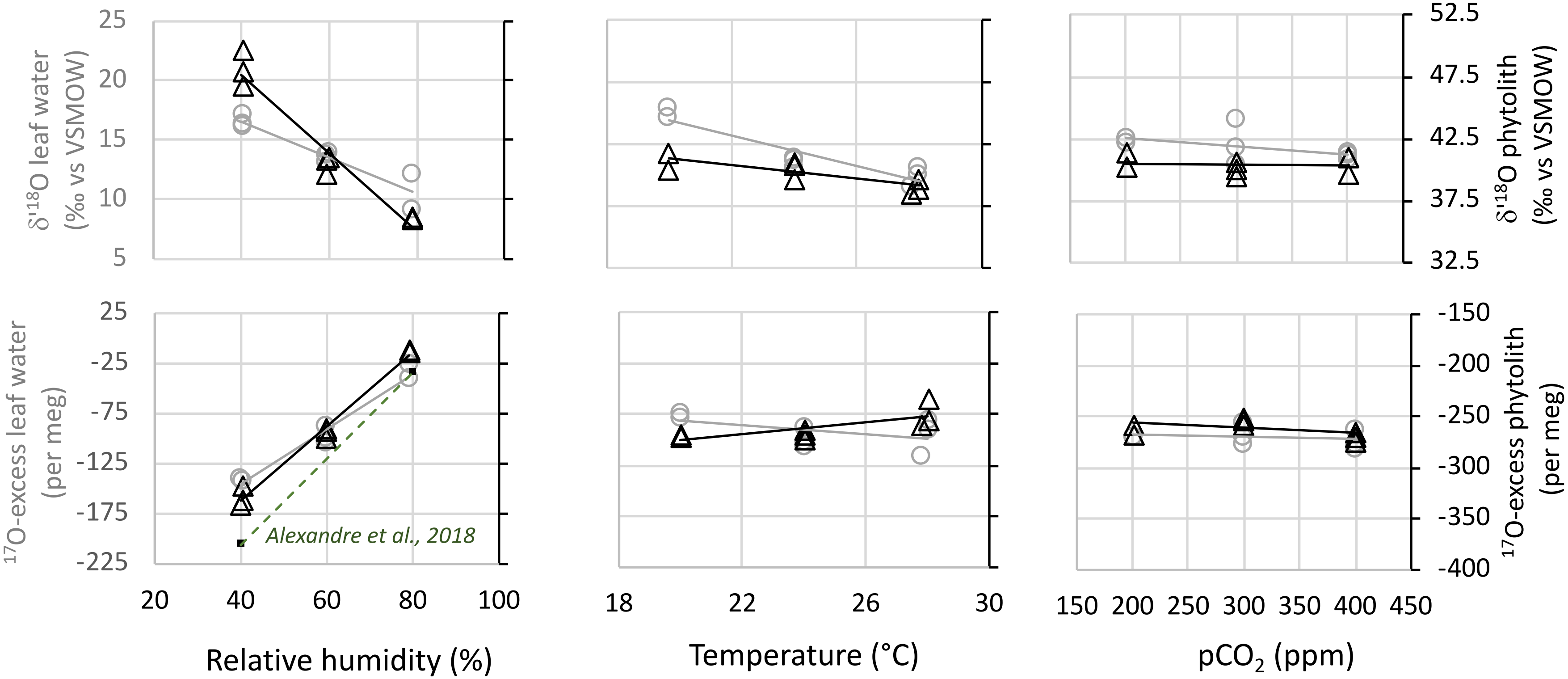
$\delta'^{18}O_{vapor}$ increases linearly in response to the increasing contribution to the atmosphere of transpired water, unfractionated relatively to ^{18}O-enriched irrigation water



Results from the growth chamber monitoring

δ'^{18}O and ^{17}O-excess of leaf water (circle) and phytoliths (triangles) after 14 days of growth at different relative humidity, air temperature and pCO_2.

3 replicates/experiment



- **Key-control of RH on ^{17}O-excess$_{\text{leaf water}}$ and ^{17}O-excess$_{\text{phytolith}}$**
- **No significant impacts of T_{air} and pCO_2 on ^{17}O-excess$_{\text{leaf water}}$ and ^{17}O-excess$_{\text{phytolith}}$**

Growth chamber data are compared to estimates

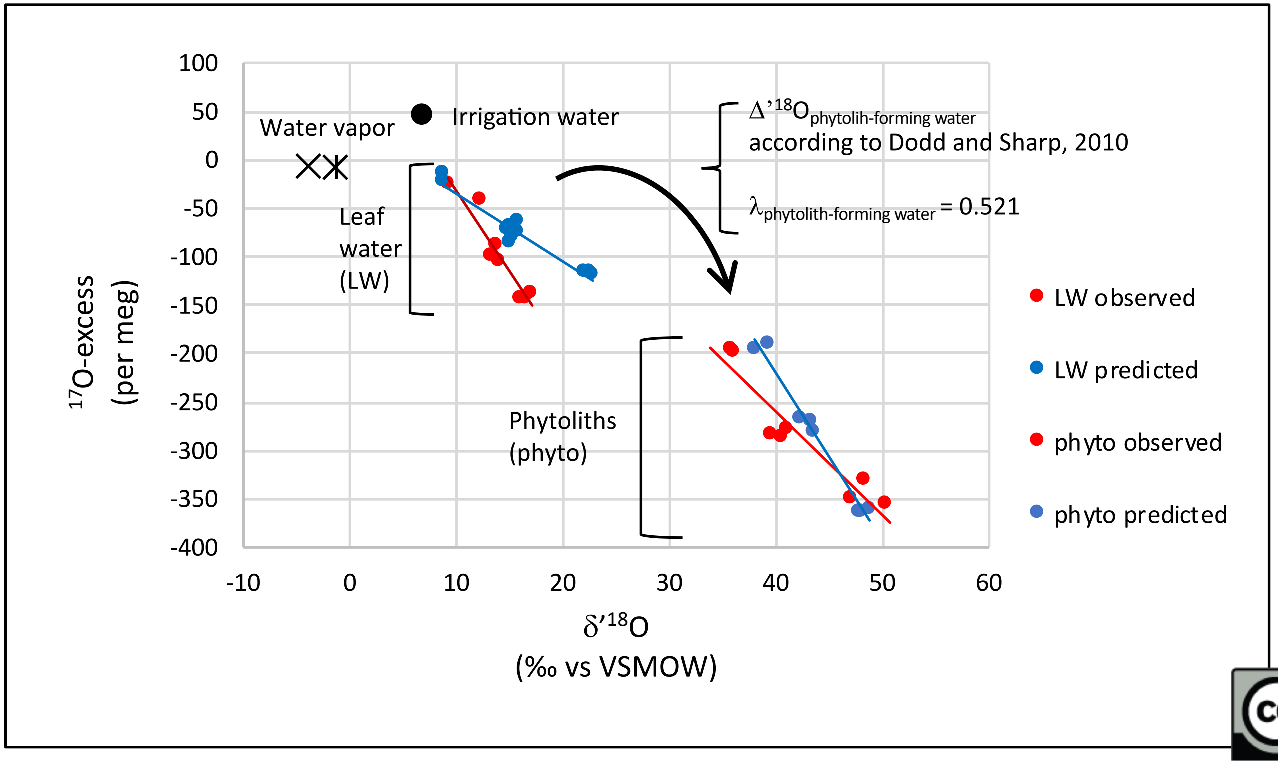
Estimations

- **From irrigation to leaf water**: Craig & Gordon model (Farquhar and Lloyd., 1993)+ two pool model
- **From leaf water (observed) to phytoliths:** equilibrium fractionation + different pattern of silicification

$\Delta^{18}O_{phytolith\text{-}forming\ water}$ according to Dodd and Sharp (2010)

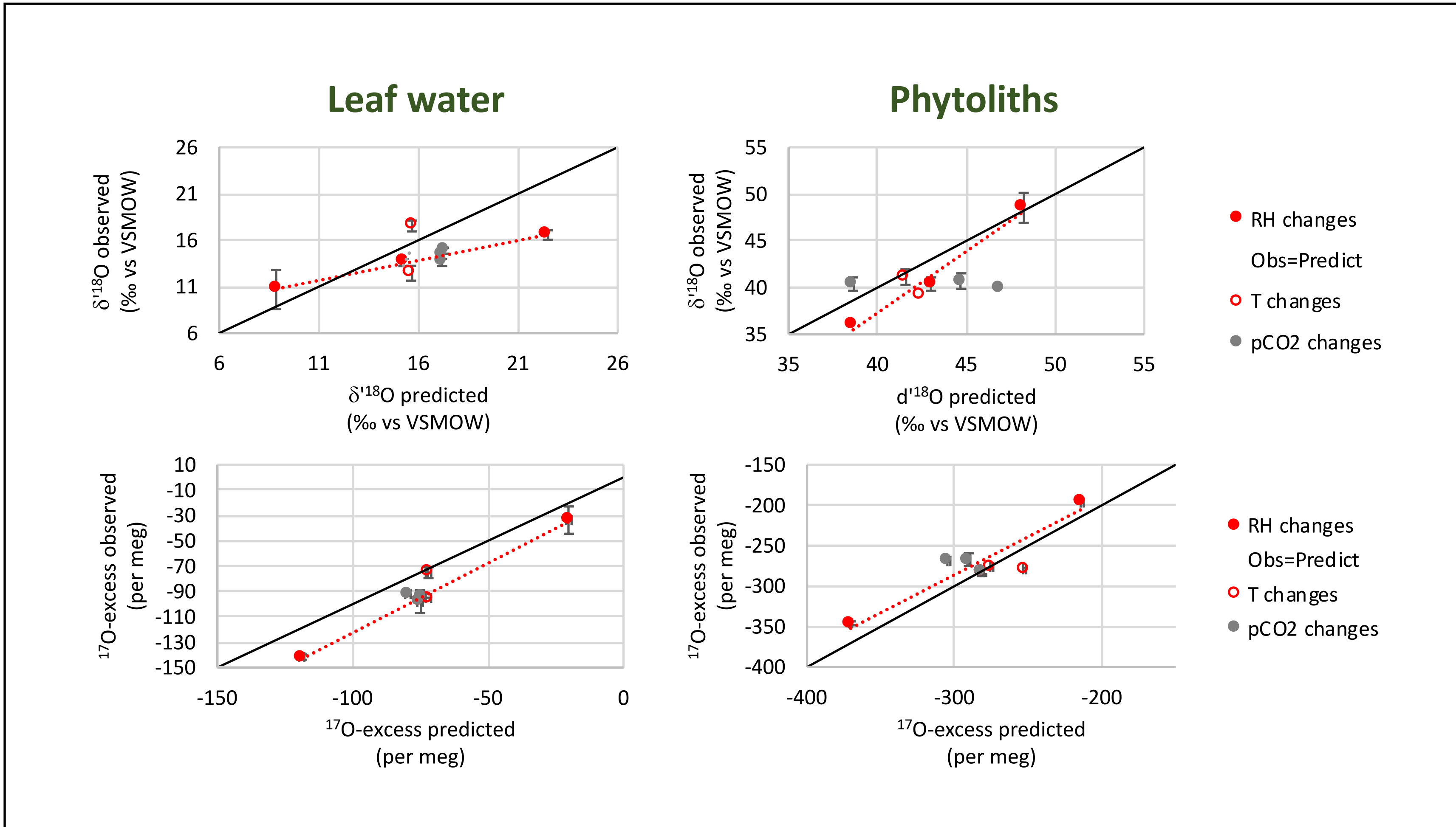
$\lambda_{phytolith\text{-}leaf\ water}$ of 0.521 (Alexandre et al., 2019)

- A mechanism, not considered in the model and likely linked to water phase change at the leaf evaporative sites, influences $\delta'^{18}O_{leaf\ water}$. However, this does not impact $^{17}O\text{-excess}_{leaf\ water}$.
- The relative humidity-dependency of $^{17}O\text{-excess}_{leaf\ water}$ is transmitted to phytoliths whatever is T_{air} (and T_{leaf}). This is because although T_{leaf} determines the equilibrium fractionation $\Delta'^{18}O_{phytolith\text{-}forming\ water}$, its impact on $^{17}O\text{-excess}_{phytolith\text{-}forming\ water}$ is weak.



Growth chamber data are compared to estimates

Another way of comparison



Precising the new proxy of atmospheric relative humidity

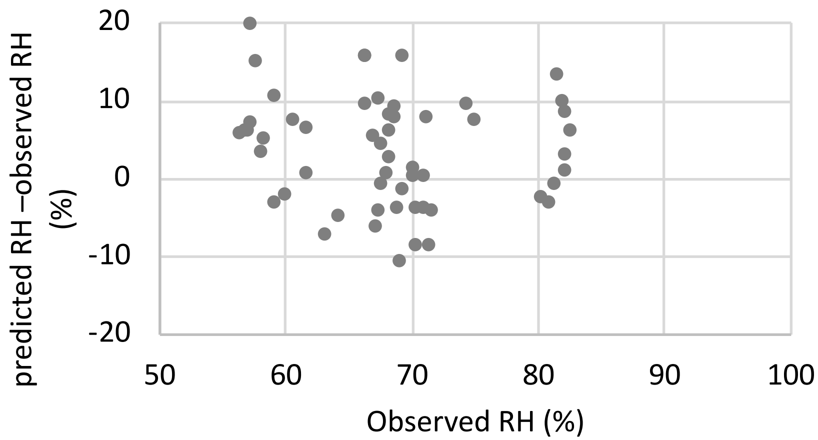
Atmospheric relative humidity (RH) can be estimated from the following equation:

$$\mathrm{RH}\ (\%) = 0.26 \pm 0.02\ (\mathrm{S.E.}) * {}^{17}\mathrm{O\text{-}excess}_{phytolith} + 130 \pm 5\ (\mathrm{S.E.})$$

The precision (S.E.) on the predicted RH is ± 2.7%.

The equation is close to the one previously proposed by Alexandre et al., (2018)

Verification on the West African dataset:
Reconstructed RH is overestimated by 3.5 ± 7 % (average, s.d.).



This supports the applicability of the proxy equation for reconstructing from phytoliths atmospheric relative humidity prevailing during the growth season of plants

Next steps

Reconstructing past atmospheric relative humidity

This calibration offers a basis for reconstructing past variations of relative humidity from fossil phytolith assemblages produced by grasslands (in progress)**.**

Advantages of the proxy over d-excess

- Little ^{17}O-excess variations in water during its course from the ocean source to rainfall (Uemura et al., 2010; Uechi and Uemura, 2019). After rainfall reaches the soil, limited ^{17}O-excess variations due to evaporation is expected, given the sheer size of soil water and water vapor pools (ongoing assessment).
- Weak sensitivity of $^{17}O\text{-excess}_{\text{leaf water}}$ and $^{17}O\text{-excess}_{\text{phyto-forming water}}$ to T_{leaf} (this study).

Calibrating $\theta_{\text{silica-water}}$ at low temperature

For the studied temperature range (18-26°C), $\lambda_{\text{phytolith-forming water}}$ (0.521) is lower than $\theta_{\text{silica-water}}$ calculated after Sharp et al., 2016 (0.524).

Systematic kinetic fractionation occurring during phytolith formation is unlikely.

There is a need for a proper VSMOW-SLAP scale normalization to enhance the accuracy of the phytolith data (Miller et al., 2020; Pack et al., 2016). However, a normalization bias is insufficient to explain that a $\theta_{\text{silica-water}}$ value of 0.524 does not fit with the $\lambda_{\text{phytolith-forming water}}$ observed values.

This argues for $\theta_{\text{silica-water}}$ being overestimated at low temperature. Further $\theta_{\text{silica-water}}$ calibration is needed for the low temperature domain, using appropriated silica-water couples.

Tracks for reconstructing $\Delta'^{17}O$ of leaf water from phytoliths

- if T_{leaf} can be approximated
- If the forming water is the bulk leaf water
- If the equilibrium fractionation $\Delta'^{18}O_{Phytolith\text{-}forming\ water}$ is known

Here isotope compositions are in ‰

$$^{17}O\text{-excess}_{phytolith\text{-}forming\ water} = (\lambda_{phytolith\text{-}forming\ water} - 0.528) * \Delta'^{18}O_{phytolith\text{-}forming\ water}$$

$$\delta'^{18}O_{leaf\ water} = \delta'^{18}O_{phytolith} - \Delta'^{18}O_{phytolith\text{-}forming\ water}$$

$$\delta'^{17}O_{leaf\ water} = {}^{17}O\text{-excess}_{phytolith\text{-}forming\ water} + 0.528 * \delta'^{18}O_{phytolith}$$

$$\Delta'^{17}O_{leaf\ water} = \delta'^{17}O_{leaf\ water} - \lambda_{reference} * \delta'^{18}O_{leaf\ water}$$

Verification on the AMMA-CATCH grass stem dataset

- Measured $\Delta'^{18}O_{phytolith\text{-}forming\ water}$ (32.7 ± 1.7 ‰) is higher than estimated $\Delta'^{18}O_{phytolith\text{-}forming\ water}$ average (28.8 ± 0.4 ‰).
- Despite of this difference, measured $^{17}O\text{-excess}_{phytolith\text{-}stem\ water}$ (-191 ± 16 per meg) is between the $^{17}O\text{-excess}_{phytolith\text{-}forming\ water}$ values predicted with $\lambda_{phytolith\text{-}forming\ water}$ of 0.521 (-202 ± 3 per meg) and and 0.522 (-173 ± 2 per meg).

Next steps

Reconstructing $\Delta'^{17}O_{leaf\ water}$

- The inaccuracy of $\Delta'^{18}O_{phytolith\text{-}forming\ water}$ weakly impact the ^{17}O-excess$_{phytolith\text{-}forming\ water}$ estimates.
- However, the absence of an accurate thermo-dependent equation for determining $\Delta'^{18}O_{phytolith\text{-}forming\ water}$ prevents the use of phytoliths for reconstructing $\Delta'^{17}O_{leaf\ water}$ defined with $\lambda_{reference}$ different from 0.528.

Further calibration of $\Delta'^{18}O_{phytolith\text{-}forming\ water}$ is required. This is worthwhile as it would give us an alternative to estimate the plant transpiration imprint on the triple oxygen isotope compositions of atmospheric CO_2 and O_2 for the present and the past.