

## Answer to Referee #2

We thank the Referee #2 for his/her comments and respond below:

- **I think a more nuanced discussion about the role and variability of vapor  $^{17}\text{O}$ -excess is warranted. There is very little published vapor  $^{17}\text{O}$ -excess data, so I don't think it is yet quite reasonable (as in line 62) to expect that vapor  $^{17}\text{O}$ -excess will vary little from place to place.**

In agreement with this comment, the sentence describing the  $^{17}\text{O}$ -excess data from water vapor will be specified as follows:

*The very few studies providing information on the variability of  $^{17}\text{O}$ -excess in continental atmospheric vapor at low and middle latitudes (Lin et al., 2013; Surma et al., 2021; Ranjan et al., 2021) show that for a given location, it is in the same order of magnitude as that of rainwater, reflecting continental moisture recycling in addition to the evaporation conditions in the source region.*

- **In thinking about this, it might be useful to draw comparisons between observations of vapor d-excess and expectations of vapor  $^{17}\text{O}$ -excess.**

Indeed, this would be very interesting to do for natural systems, with vapor measurements to back it up. However, this is beyond the scope of the present study. In the present study the isotope composition of the atmospheric water vapor is measured in the growth chambers to feed the Craig and Gordon model used to estimate the isotope composition of the leaf water. The mean values of  $\delta^{18}\text{O}$ ,  $^{17}\text{O}$ -excess and d-excess of the atmospheric water vapor in the growth chambers are now presented in sup. mat. 1.1. The mean values are fairly constant from an experiment to another (average and standard deviation of  $-4.7 \pm 0.5$  ‰,  $9 \pm 8$  per meg and  $12.7 \pm 0.4$  ‰ for  $\delta^{18}\text{O}$ ,  $^{17}\text{O}$ -excess and d-excess) and not statistically different from the mean values of the fogged waters (Student's t-test). This clarification will be added in section 4.1:

*Since the  $^{17}\text{O}$ -excess of the irrigation water is close to that of fogged water the transpiration has little effect on the  $^{17}\text{O}$ -excess of the atmospheric vapor. The mean value of  $^{17}\text{O}$ -excess in atmospheric water vapor (Sup. mat.1.1) is statistically not different from that of the fogged water (Student's t-test)*

- **This study is limited to the tropics, but are there other regions with a limited range of vapor  $^{17}\text{O}$ -excess where a similar paleo-RH proxy might be worth exploring?**

As noted in section 5.1, *sensitivity tests using the bulk leaf water model show that the isotope compositions of the source water (or the irrigation water) and the difference in isotope composition between the source water and the atmospheric water vapor control the starting point from which the isotope composition of the leaf water evolves. When RH decreases, the isotope composition of the source water becomes the overriding factor. Because the  $^{17}\text{O}$ -excess values of the source waters in the current and 2018 experiments are close, this has little effect on the dependency on RH of the  $^{17}\text{O}$ -excess of leaf water.* In natural context, the difference in  $^{17}\text{O}$ -excess between rainwater and atmospheric water should be close to 10 per meg if equilibrium is reached. Source water evaporation and continental vapor recycling may additionally impact this difference, however additional field measurements are required to further assess the magnitude of the involved changes in  $^{17}\text{O}$ -excess of source water and atmospheric water vapor.

This will be nuanced in section 5. 2: *Since the range of  $^{17}\text{O}$ -excess variation in the source waters and the atmospheric water vapor is narrow in the growth chambers and is expected to be narrow at natural sites, both parameters should have little impact on the RH-dependency of the  $^{17}\text{O}$ -excess of phytoliths.* This will additionally be nuanced in section 5.3: *Added to the fact that the  $^{17}\text{O}$ -excess of phytoliths is insensitive to changes in the  $\delta^{18}\text{O}$  of source water,  $T_{\text{air}}$ ,  $p\text{CO}_2$ , or grass physiognomy (Alexandre et al., 2019) and assuming that variations in the  $^{17}\text{O}$ -excess of soil water and atmospheric water vapor are narrow, this consistency between equations supports that in the 40 to 80% range, RH can be reconstructed from (eq. 10).* Note that eq. 10 in the revised version is equivalent to eq. 11 in the version submitted to CPD.

- **Is the  $\Delta'$  (or  $\Delta'$ , note the difference between the apostrophe and the prime notation and please be consistent throughout the manuscript) defined in Equation 3 necessary? This may be confusing for beginning readers because some recent triple oxygen isotope studies (e.g., Aron et al., 2021, Sharp et al., 2018, the 2021 RiMG book) have used the  $\Delta'_{\text{O}}$  notation rather than  $^{17}\text{O}$ -excess. If possible, I think it would be good to avoid the  $\Delta'_{\text{O}}$  symbol in this instance to minimize confusion.**

In agreement with this comment the  $\Delta^{17}\text{O}_{\text{A-B}}$  notation will be replaced in the manuscript (text and tables) by  $\delta^{17}\text{O}_{\text{A}}$  -  $\delta^{17}\text{O}_{\text{B}}$ .

- **Section 3.2, paragraph 1: Did the authors account for potential memory effects in the vapor measurements when switching between ports on the manifolds? Were any measurements dropped or ignored just after switching to vapor measurements from a new chamber? Previous vapor isotope studies have shown that memory effects on vapor d18O and d-excess need to be accounted for when a this type of manifold setup is used (e.g., Simonin et al., 2013). I imagine that the sensitivity of 17O-excess to mixing makes this consideration important in this case as well.**

To address all the methodological points raised by the referees #1 and #2, the atmospheric water vapor measurement protocol will be detailed in the method section as follows :

*The humid air of the chambers was analyzed at Ecotron by Wavelength-Scanned Cavity Ring Down Spectroscopy (CRDS) with a Picarro L2140-i spectrometer operated in  $^{17}\text{O}$ -excess mode.*

*For each chamber, the water vapor in the air was measured every second over a 420 min period before switching to the next chamber using a 16-port distribution manifold (Picarro A0311). After discarding the first twenty minutes to account for potential memory effects, the raw data were averaged over 80 minutes, which resulted in 5 averages per vapor measurement period. Before each 420 min vapor measurement period, three working standards of liquid water were analyzed for calibration. This high calibration frequency allows to counteract a potential drift of the instrument. In order to estimate the background noise, the atmospheric water vapor fogged (without fractionation) from a constant water source into the three empty chambers was measured for each climate combination (except for the growth at 300 ppm  $\text{CO}_2$ ) and two types of humidifiers. The precision on the 80 min vapor measurements was 0.04 ‰ for  $\delta^{18}\text{O}_v$  and lower than 10 per meg for  $^{17}\text{O}$ -excess<sub>v</sub> (means of s.d., n=19).*

*The liquid water standards measurements necessary for the calibration of the water vapor measurements consisted of ten injections per vial with the first six being discarded to account for memory effects. The dry air stream used for the liquid measurements was devoid of  $\text{CO}_2$ , contained less than 400 ppm of water vapor and was the same as the one flushed in the growth chamber to reach the required RH (Appendix A). This should limit measurement bias due to differences in the chemical composition of the atmospheric water vapor analyzed and the dry gas used for calibration (Aemisegger et al., 2012). The volumes of water standards vaporized to the spectrometer were adjusted to reach water vapor mixing ratios similar to those of the growth chamber atmospheres (i.e. between 12000 and 30000 ppm which corresponds to temperature/RH conditions of 24°C/40% and 28°C/80%). The precision on the liquid water measurements for this range of mixing ratio was 0.02 ‰ and 12 per meg for  $\delta^{18}\text{O}$  and  $^{17}\text{O}$ -excess, respectively (means of s.d., n = 21). The variation for this range of mixing ratio was 0.04 ‰ and 7 per meg for  $\delta^{18}\text{O}$  and  $^{17}\text{O}$ -excess, respectively (s.d. of the means, n = 21). Thus, no correction for a mixing ratio dependency (e.g. Weng et al., 2020) was applied.*

- **Figure 1 provides a very useful schematic to understand the experimental setup. However, I have a few questions about the isotopic values reported. First, if evaporation is prevented from the soil, why are the soil d18O and soil 17O-excess values not identical (within analytical precision) to those of the irrigation water? Second, why is the 17O-excess of the final vapor (-6 per meg) so low? Is this a product of vapor mixing within the chamber? I encourage the authors to add d-excess data when possible (I assume this is accessible from the Picarro measurements) to explore the hydrologic processes that are going on in the chambers.**

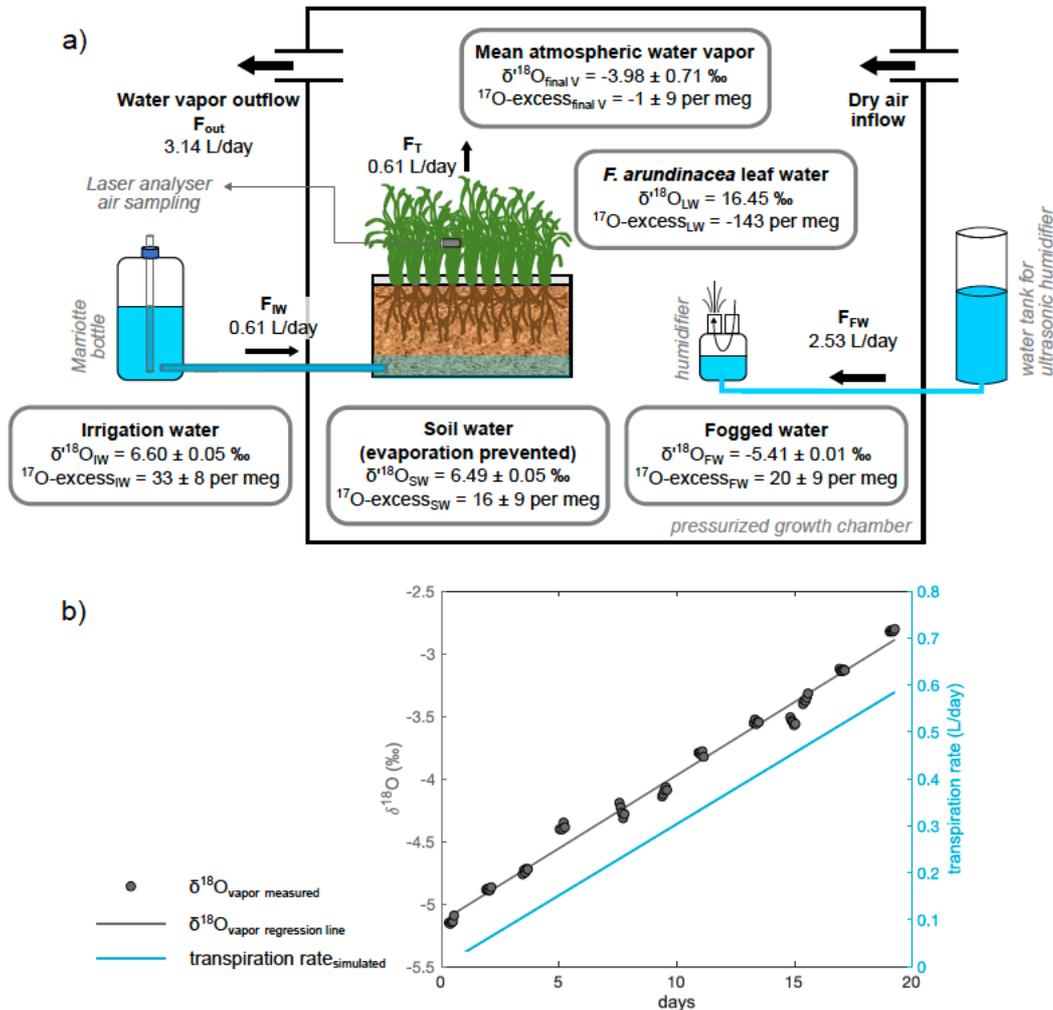
The purpose of this study was to monitor the isotope composition of atmospheric water vapor in order to better constrain the Craig and Gordon model for estimating the isotope composition of leaf water. Therefore, the  $^{17}\text{O}$ -excess of the irrigation and fogged water were set close, which prevents to examine variations in  $^{17}\text{O}$ -excess in atmospheric water vapor in relation to transpiration and mixing processes.

For a given climate combination, there is no detectable trend regarding the  $^{17}\text{O}$ -excess in atmospheric water vapor. It is thus more appropriate to present the mean values of  $\delta^{18}\text{O}_{\text{mean v}}$  and  $^{17}\text{O}$ -excess<sub>mean v</sub> in figure 1 (presented below).  $\delta^{18}\text{O}_{\text{mean v}}$  and  $^{17}\text{O}$ -excess<sub>mean v</sub> values will be added in sup. mat. 1.1 for all the climate combinations.

The differences in mean isotopic composition between irrigation water and soil water and between fogged water and atmospheric water vapor are due to methodological variability. When taking into account the totality of the climate combinations (sup. mat. 1.1),  $\delta^{18}\text{O}$  and  $^{17}\text{O}$ -excess averages obtained for soil water ( $6.28 \pm 0.16$  ‰ and  $15 \pm 10$  per meg, respectively) and irrigation water ( $6.50 \pm 0.06$  ‰ and  $24 \pm 9$  per meg, respectively) are not significantly different

(Student's t-tests), confirming that no fractionation occurred during the vaporization. In the same way,  $^{17}\text{O}$ -excess averages obtained for fogged water ( $17 \pm 6$  per meg, respectively) and mean atmospheric water vapor ( $9 \pm 8$  per meg, respectively) are not significantly different (Student's t-tests). This will be added in caption of Figure 1.

The d-excess data were available for irrigation, soil water and atmospheric vapor, but not for leaf water (analyzed by IRMS), therefore, d-excess data for irrigation and soil waters are not presented since they don't add significant information. The average d-excess of the atmospheric vapor during the experiment remained very stable (d-excess =  $12.5 \pm 0.4$  ‰) and similar to that of the fogged water (d-excess =  $11.4 \pm 0.5$  ‰). The data will be presented in Sup.mat. 1.1.



**Revised Figure 1 (which will be figure 2 in the revised manuscript):** Scheme of the growth chamber setup for the isotope monitoring of the water compartments in the soil-plant-atmosphere continuum. (a) Isotope data are given for the final state of the P2-40-120717 regrowth as an example (data from Sup. mat. 1.1). The vapor outflux in humid air ( $F_{\text{out}}$ ) is equal to the sum of the fogged water influx ( $F_{\text{fog W}}$ ) and the irrigation water influx ( $F_{\text{IW}}$ ) equivalent to the transpired water flux ( $T$ ).  $F_{\text{fog W}}$  is adjusted to keep a constant the relative humidity (RH). (b) Linear correlation with the number of growing days of the atmospheric vapor  $d^{18}\text{O}$  ( $d^{18}\text{O}_v$ ) in the growth chamber.  $d^{18}\text{O}$  values of the initial and final water vapor ( $d^{18}\text{O}_{\text{initial V}}$  and  $d^{18}\text{O}_{\text{final V}}$  in Sup. mat. 1.1) were extrapolated from this correlation. The transpiration rate can be calculated on a daily basis using  $d^{18}\text{O}_v$  and an isotope mass balance as detailed in Sup. mat 1.1.

The differences in mean isotopic composition between irrigation water and soil water and between fogged water and atmospheric water vapor are due to methodological variability. When taking into account the totality of the climate combinations (sup. mat. 1.1),  $d^{18}\text{O}$  and  $^{17}\text{O}$ -excess averages obtained for soil water ( $6.28 \pm 0.16$  ‰ and  $15 \pm 10$  per meg, respectively) and irrigation water ( $6.50 \pm 0.06$  ‰ and  $24 \pm 90$  per meg, respectively) or  $^{17}\text{O}$ -excess averages obtained for fogged water ( $17 \pm 6$  per meg, respectively) and mean atmospheric water vapor ( $9 \pm 8$  per meg, respectively) are not significantly different (Student's t-tests).

## References

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