

## Answer to Referee #1

We thank the Referee #1 for his/her comments and respond below:

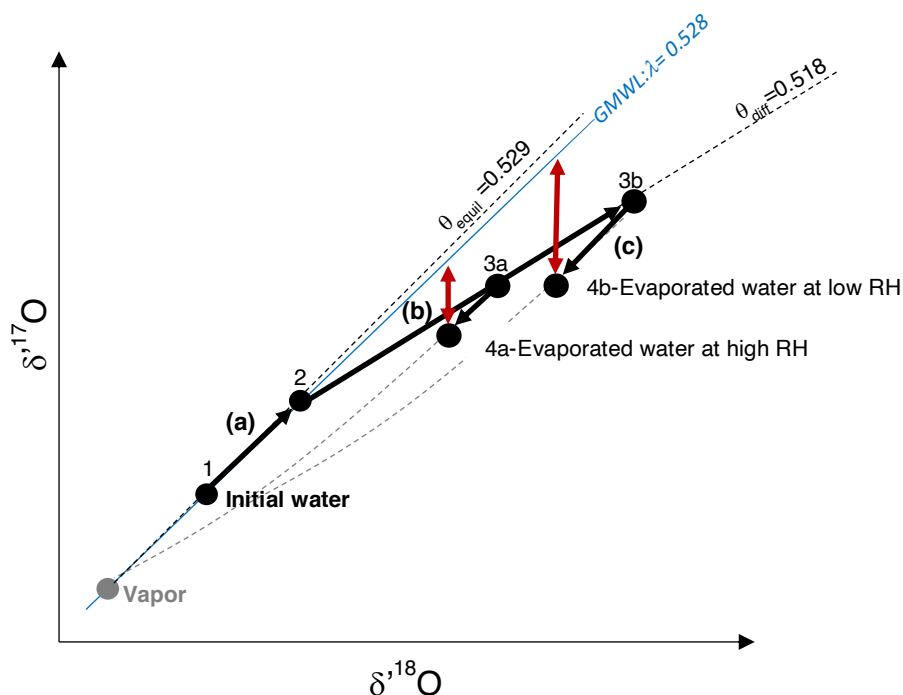
- **Lines 75 to 80.** The authors should cite here recent studies that used triple oxygen and hydrogen isotopes in hydration water of minerals as a quantitative proxy for paleohumidity reconstructions, including Evans et al., 2018 and Gázquez et al., 2018. These studies are totally related to the final goals of this manuscript and should be cited as an example of quantitative RH proxy based on triple oxygen isotopes.

In agreement with this comment the introduction of the manuscript will be modified as follows:

*Model-data comparisons for the pre-instrumental period are necessary for models' improvement but face the lack of truly quantitative proxies of past RH. A promising proxy is the  $\delta D$  of plant biomarkers (Garcin et al., 2012; Sachse et al., 2012; Rach et al., 2017; Schwab et al., 2015; Tuthorn et al., 2015) recovered from buried soils and sediments. However, in addition to RH, the  $\delta D$  of plant biomarkers is dependent on other variables such as the  $\delta D$  in rainwater, the plant functional type and selective degradation of the biomarkers. The  $^{17}O$ -excess of gypsum hydration that records the amplitude of surface water evaporation is also a new promising proxy of RH (Evans et al., 2018; Gázquez et al., 2018; Herwartz et al., 2017) but is limited to conditions favorable to gypsum formation. The  $^{17}O$ -excess of phytoliths may hold the potential to complement the toolbox of proxies for RH reconstructions.*

- **In lines 108 to 114.** I wonder if the author could translate this paragraph into a conceptual figure, explaining the sensitivity the isotope ratios to these parameters. Otherwise, it may be difficult to follow for non-specialized readers.

In agreement with this comment, the following figure will be included in the manuscript:



**Figure 1:** Representation of the three fractionating processes that interplay in the leaf boundary layer during evaporation, as conceptualized by the Craig and Gordon model: (a) from 1 to 2: equilibrium fractionation between initial water and atmospheric vapor; (b) from 2 to 3a or 3b: fractionation due to vapor diffusion in humid (3a) or dry air (3b); (c) from 3a to 4a and 3b to 4b: fractionation due to exchange between evaporated water and atmospheric water vapor at high (3a to 4a) and low (3b to 4b) relative humidity. Red arrows: magnitude of the resulting  $^{17}O$ -excess describing the departure of  $\delta^{17}O$  from a reference line with a slope  $\lambda$  of 0.528, equivalent to the slope of the Global Meteoric Water Line (GMWL).  $\theta_{equil}$ : slope of the equilibrium line;  $\theta_{diff}$ : slope of the diffusion line.

- **Sections 3.1 and 3.2.** Did the air inlet to the chamber atmosphere come from the same cylinder as for the analyzer when doing the calibration with liquid waters? Did the instrument use Air Zero (dry synthetic air)?

Did you replace the air in the chambers with the same carrier? I am asking this because, in my personal experience, the use of different carrier gases (i.e. dry atmospheric air vs dry synthetic air) for calibration and for online measurements of water vapor can produce an offset in  $^{17}\text{O}$  excess. This needs to be clarified in this section.

- In section 3.2. Please, can you give the typical H<sub>2</sub>O concentrations measured with the CRDS analyzer from the chamber atmosphere? Did you consider/apply any linearity correction for the isotopic values? Did you take any measurement to monitor the drift of the instrument between calibrations?

The atmospheric water vapor measurement protocol will be detailed to address these points 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, resulting in 5 averages per vapor measurement period. Prior to 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 CO<sub>2</sub>) and two types of humidifiers. The precision on the means of 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 standard 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 CO<sub>2</sub>, contained less than 400 ppm of water vapor. The same dry air was used for flushing the growth chambers to limit measurement bias due to differences in the chemical composition of the analyzed growth chamber atmosphere and the dry gas used for calibration (Aemisegger et al., 2012; Brady and Hodell, 2021). 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%). Thus, no correction for a mixing ratio dependency (e.g. Weng et al., 2020) was applied. The mean precision on the liquid water measurements for this mixing ratio range 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).*

## References

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