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Interactive comment on "Leaf-scale quantification of the effect of photosynthetic gas exchange on $\triangle^{17}$O of atmospheric CO_2" *by* Getachew Agmuas Adnew et al.

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Referee: 1

The answers to the questions/ comments and suggestions are stated below each comment, but please note the added supplement where the responses are given with proper formatting and detailed caption of figure 1.

1) As far as I understand the justification for the great effort required in measuring 17O and its "access" (or anomaly), is the discovery of significant mass independent oxygen isotope effects in the stratosphere that is conserved to some extent in the troposphere

(seems to be true both for atmospheric O2 and CO2). The extent to which this anomaly is conserved in the troposphere depends on the CO2 (or O2) cycling through the biosphere, which erases it by exchange with water. Thus, if the stratospheric production of the anomaly is known and it is relatively constant, the residual signal in the troposphere should reflect the biosphere productivity (GPP). This is exiting application considering the uncertainty around GPP.

This summary by the reviewer is correct. We would like to emphasize that if we reliably want to estimate GPP from Δ17O, we need to know the precise effect of photosynthesis and respiration on Δ17O, in the words of the referee, how does the Δ17O signature actually look after being "erased" by exchange with the biosphere.

2) ALL the processes associated with the Biosphere, including leaf gas exchange studied here, seems to be mass dependent and are FULLY covered by the conventional 18O studies.

The referee is correct that in principle 18O indeed cycles through the same biological system, and undergoes the same (bio)physical processes. However, we would like to nuance the idea that δ18O can help us FULLY understand ALL processes of interest. This is because conventional δ18O studies have a number of distinct disadvantages. Notably, the δ18O signature of all water pools in the system must be known to use δ18O as a carbon cycle tracer. In addition, significant changes in δ18O can occur due to processes that are not of primary interest in understanding GPP, e.g., leaf evaporation, or soil equilibration.

Δ17O variation due to kinetic and equilibrium fractionation effects is much smaller and is better defined. This is because conventional bio-geo-chemical processes that modify δ17O and δ18O follow a well-recognized isotope fractionation slope. In earlier studies, many assumptions had to be made, because the effect on Δ17O had never been quantified precisely. This is now accomplished through our study.

3) The only exception may be the small variations observed in the lambda factor that

define the expected ratio of 18O to 17O mass dependent discrimination (âĹij0.5), which is not studied here.

The reviewer correctly identifies that the small variations in λ values can impact the Δ17O we measure. These effects have been studied previously and the three isotope slopes have been established and are used in our study. We have included an additional figure (reproduced below) in the revised manuscript, which shows conceptually how the three-isotope slopes differ between the various processes and how they affect the observed Δ17O signals. In addition, we also include experiments and model studies that involve artificially 17O labeled CO2 for the first time. We demonstrate how the resulting differences in Δ17O between CO2 and leaf water affect the results, and that experiments with 17O labeled CO2 actually increase the signal to (measurement) noise ratio.

4) And so, while the present paper goes through an impressive exercise of gas exchange and isotopic measurements and calculations, I fail to see the purpose and merit of this exercise, beyond a test that verifies that indeed the 17O measurements are consistent with the 18O studies. The occlusions as much as I can see are already fairly well-known form 18O studies and, in fact, much of the calculations here still depends on the 18O measurements.

We appreciate that the referee acknowledges the considerable analytical effort that was made to produce our results. As mentioned above, we think that δ18O measurements alone are not sufficient to study all aspects related to gas exchange between plants and the atmosphere and to quantify GPP. Thus, we posit that an alternative independent tracer is still very useful, and in fact, Δ17O has been repeatedly suggested and already used as an independent and potentially even superior tracer. We nevertheless realize from the comment that the merit of our study was not communicated well, and we have considerably strengthened the motivation. The key point is that so far, the three-isotope slope of each of the processes that participate in plant-atmosphere gas exchange has been studied individually in an idealized experiment. The overall effect of all processes,

which work together in complex interaction, on Δ17O has never been evaluated in a real plant exchange experiment. This is what is achieved in the research described in this manuscript and it is explicitly stated in the revised version.

Specifically, the results communicated in our manuscript

a) demonstrate that the established theory is applicable to Δ17O(CO2) exchange at leaf-level.

b) experimentally quantify for the first time the effect of photosynthesis on Δ17O of atmospheric CO2

c) quantify of the dependence of this effect on critical parameters

d) provide an independent bottom-up Δ17O-isoflux estimate based on these lab experiments.

Furthermore, we have now demonstrated that such studies are possible with IRMS methods, with considerable effort, but they may actually become more widely accessible thanks to novel laser instrumentation in the near future (McManus et al., 2005).

5) For example, the key results indicated in the Abstract are: “Our results demonstrate that two key factors determine the effect of gas exchange on the Δ17O of atmospheric CO2. The relative difference between Δ17O of the CO2 entering the leaf and the CO2 in equilibrium with leaf water, and the back-diffusion flux of CO2 from the leaf to the atmosphere, which can be quantified by the Cm/Ca ratio”. Isn’t it that these ‘basic principles’ of leaf gas exchange are already fairly well known from previous CO2 and the 18O studies?

We clearly acknowledge in our paper that the processes affecting δ18O and Δ17O are indeed the same, and in fact, we use the established conceptual models, with appropriate references. Nevertheless, this is the first experimental leaf-scale study where the applicability of these theoretical concepts to Δ17O is actually demonstrated.

6) It seems also that the notion of "discrimination against Δ17O of atmospheric CO2" is not clear. If this is confused with D in leaf photosynthesis as for D18, then again 17O is predictable and has no clear additional information (other than perhaps the reflection of the possible variations in the lambda factor). The final estimate of global 17O discrimination anomaly is back of the envelope calculation based on these known principles and literature values. I am not sure what new insights are provided.

We realize from this comment that we have not explained clearly enough the difference of measuring δ17O and Δ17O. What the referee calls "ΔA in leaf photosynthesis as for ΔA18O" would be ΔA17O. This was also shown in our original paper for consistency but does indeed not provide additional information. Only the combination of ΔA18O and ΔA17O to ΔAΔ17O provides independent information. In the revised manuscript, we only present the results for ΔA18O and ΔAΔ17O. Some of the confusion may have to do with the notation because the plant communities and atmospheric communities have used the symbol Δ for different quantities that are both used here. Our final estimate of GPP is not dependent on the individual áž§17O and áž§18O values, but only on ΔAΔ17O. It is indeed a box model calculation, but to incorporate more variability, the entire mechanism would need to be incorporated into a global model. We are considering implementing this in the future, but for the box model presentations in this paper, we have used a global estimate of Δ17O of CO2 and leaf water from a recent 3D global Δ17O study (Koren et al., 2019).

7) And so, while the experimental setup, measurements, and going through the isotopic theory are impressive and seems to be well done on first look, I think the authors have to re-think the presentation and provide a better justification of what in these measurements takes advantage of any mass-independent effects (as declared), and in what ways this goes beyond a sophisticated confirmatory report. We realized already in the preparation of the manuscript that the presentation was difficult, and the referee comment confirms this. Nevertheless, we still think that the four conclusions identified above (copied below) make this a valuable study, whereas the referee sees only point

1 as significant merit.

a) demonstrate that the established theory is applicable to Δ17O(CO2) exchange at leaf-level

b) experimentally quantify for the first time the effect of photosynthesis on Δ17O of atmospheric CO2

c) study of the dependence of this effect on critical parameters

d) provide an independent bottom-up Δ17O-isoflux estimate based on these lab experiments.

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Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2020-91/bg-2020-91-AC1-supplement.pdf

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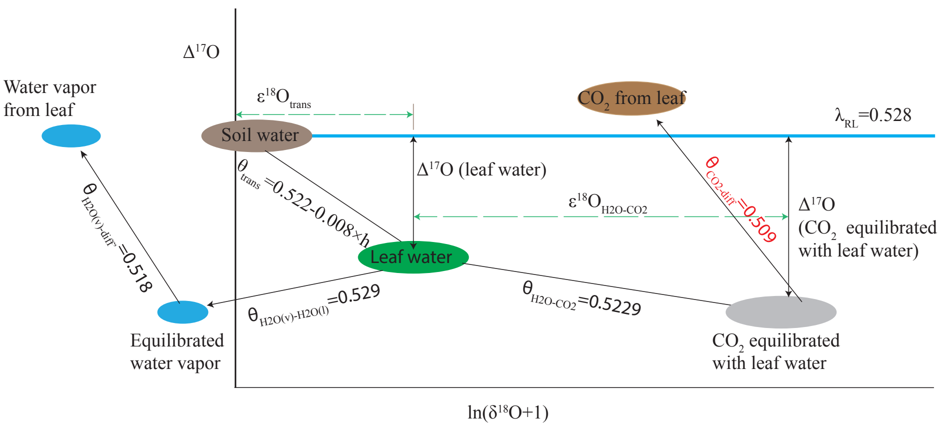

Fig. 1. Schematic representation of the processes that affect the Δ17O of CO2 and H2O during photosynthetic gas exchange (not to scale)