

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

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Referee 2

Thank you for your constructive comments. We carefully went through all the comments and suggestions and have adjusted the manuscript according to the comments made. The answers to the questions/ comments and suggestions are stated below each comment.

Please note the added supplement where the responses are given with proper formatting and detailed caption of figure 1 is provided.

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The triple oxygen isotopic composition of CO₂ ($\Delta^{17}\text{OCO}_2$) had been regarded as spatiotemporally constant in the troposphere because of its short residence time (e.g., Luz et al., 2000). Recently, significant seasonal and temporal variations of $\Delta^{17}\text{OCO}_2$ were first revealed in the atmosphere near the surface by Hofmann et al. (2017) and Liang et al. (2017), respectively, both of which were mainly controlled by the interaction of CO₂ between the atmosphere and biosphere. These studies were then followed by the three dimensional simulation study with an atmospheric physico-chemical model (Koren et al., 2019), to quantify the global CO₂ budget. The next step, therefore, must be the process study involving oxygen isotope fractionations in association with individual CO₂ fluxes.

This study by Adnew, Pons, Koren, Peters, Röckmann, aims to quantify the $\Delta^{17}\text{OCO}_2$ change during photosynthetic CO₂ removal from the atmosphere, caused by tiny difference of ¹⁷O-¹⁸O relationship between kinetic and equilibrium isotope fractionations inside the leaf.

To my knowledge, this is the first experimental study for $\Delta^{17}\text{OCO}_2$ at the leaf-scale; thus, their results provided must be important. However, I am frustrated and feel difficult to plough through the manuscript because 1) the structure of the manuscript (context) seems scattered, 2) experimental results (raw data) were not shown although values in all graphs were processed, 3) there appears a lot of faults in equations or figure number in the main text, and 4) it's a mixture of lengthy and in-short explanations. I strongly recommend the authors to revise the manuscript more simply and concisely.

We thank the referee for acknowledging the relevance of our study. We realize that the manuscript is quite difficult. We, therefore, thank the referee for the concrete suggestions below (including the suggesting for shortening), which helped us to improve the general storyline and readability.

General comments

1) # It spent 11 of 18 pages (until conclusion) from the Introduction to “Materials and

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methods (M&M).” It seems too dominant; in other words, Results and Discussion seem too short. There appears a lengthy description in M&M, and the description for experimental results is too short.

In the revised manuscript, we reduced the description of the materials and methods section. The introduction, from line 91 to 106 was shortened and combined with the previous paragraph We shortened the materials and methods section and moved part of it to the supplementary material Section 2.1 was shortened based on the recommendation of the referee We shortened the theory part, line 170 to 201 in section 2.2 was moved to supplementary material. Section 2.3 was moved to the discussion section Section 2.4 was moved to the supplementary material We have also extended the results section following the concrete suggestions as described below.

2) # L84-90: This block appears the center of your motivation; however, there is no specific description of what the problem or limitation exists currently. Until this block (and perhaps in previous studies), you mentioned the $\Delta^{17}\text{O}$ is free from any terrestrial MDF processes and made readers believe that $\Delta^{17}\text{O}$ be a more robust tracer for estimating GPP. You must describe what actual problems lying among previous studies such as inconsistency, uncertainty, speculation, assumption and so on. Without this explanation, readers could not have motivations to read the next pages. I strongly recommend adding descriptions for the different slopes of three-isotope plots due to the different MDF processes.

Thank you very much for your suggestion. Indeed, different MDF processes with different three-isotope slopes are involved, and in the revised manuscript we incorporated the following schematic figure (Figure 1) to illustrate this point and to illustrate the objective of our study.

Furthermore, we have reformulated our 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

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of all processes, which work together in complex interaction, on $\Delta^{17}\text{O}$ 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.

3) # I strongly recommend the authors to revise the Theory part completely. The structure is scattered and forces readers to jump frequently between the main text, Appendix, and Supplementary Materials (SM).

We revised the theory part of the manuscript and incorporated your suggestions into the modified manuscript.

4) # Appendix should be moved to SM.

In the revised manuscript, the appendix is moved to the supplementary material.

5) # The term “fractionation” should be replaced to “isotope fractionation” for all.

We use isotope fractionation instead of fractionation alone throughout the revised manuscript.

6) # My major concern is the relation between dots of “Farquhar model” and curves in Figs 4 and 5a) and related description in Section 3.6. If I were not misunderstanding, both are results calculated from the “Farquhar model.” Dots were obtained by giving several observed results and curves were simulated by giving similar boundary conditions to the experimental setting. Is the former necessary? This is very confusing.

We are sorry for the confusion, but the two are not the same. The curves are based on the leaf cuvette model which we implemented for this study and the blue diamonds were the results for the individual experiments using the Farquhar model. In the revised manuscript, we excluded the blue diamond points because this is not really necessary for our line of argumentation.

7) # I strongly recommend the authors to provide “List of symbols.” for all parameters used and defined.

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In the revised manuscript, the list of symbols for all parameters used in this study are provided

8) # The parameter cm seems one of the most important numbers in this study. For obtaining this, only $\delta^{18}O$ and α^{18} values were used concerning isotope ratio, though. Is it possible to use $\Delta^{17}O$ and λ values to evaluate cm instead? At least does it make sense to test its feasibility?

Yes, it is possible to calculate the mole fraction of CO_2 at the CO_2 - H_2O exchange site (cm) using the $\Delta^{17}O$ and λ values. Since this requires the development of yet another complicated set of equations and detailed discussion of the process of assimilation from a plant physiology point of view, it would make our paper even more complex and less focused. A companion manuscript with detailed description and derivation of the cm using $\Delta^{17}O$ and λ values is under preparation.

9) # As shown in Figure 5, the discrimination of $\Delta^{17}O$ of CO_2 during photosynthesis varies widely, and controlled by the magnitude of oxygen isotope equilibration at the CO_2 - H_2O site, that is to say, the relative contribution of kinetic (diffusion) and equilibrium isotope fractionation. This conclusion is almost identical to the knowledge using conventional $\delta^{18}O$ results. Moreover, In the last paragraph of Discussion, authors mentioned that the main uncertainty is cm/ca ratio, which may be same as the main uncertainty of $\delta^{18}O$. My impression after reading this manuscript is that the intra-MDF variation dominate that of MIF signature on tropospheric CO_2 , which weakens the merit to study $\Delta^{17}O$ of CO_2 . What is an advantage to use $\Delta^{17}O$ instead of $\delta^{18}O$? Please provide suggestions or implications to general biogeochemists.

The referee is correct that the processes that affect $\delta^{18}O$ are the same that affect $\Delta^{17}O$. Nevertheless, the quantitative evaluation of $\Delta^{17}O$ is largely independent of $\delta^{18}O$. The limitation of using $\delta^{18}O$ of atmospheric CO_2 as a tracer is its dependency on the $\delta^{18}O$ value of different water reservoirs and fractionation processes in the hydrological cycle, water isotopic inhomogeneity, and dynamics, which are difficult to

ascertain (Hoag et al., 2005). Unlike $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$ variation is much smaller and is better defined (Miller, 2018). This is because conventional bio-geo-chemical processes that modify $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ follow well-defined three-isotope fractionation slope. Consequently, the formulation of the CO_2 budget using $\Delta^{17}\text{O}$ is a lot simplified, compared to using $\delta^{18}\text{O}$. Furthermore, unlike δ 's, λ is insensitive to temperature (Cao and Liu, 2011; Bao et al., 2016; Hofmann et al., 2012; Dauphas and Schauble, 2016; Miller, 2018).

Specific comments

10) L41: "replaced using..." What this means? Be more specific.

In the revised manuscript it is replaced with "replicated based on cross-consistency checks with atmospheric inversions, sun-induced fluorescence (SIF) and dynamic global vegetation models"

11) L47: "see equation (1)" instead of "see below"

In the revised manuscript we used "see equation (1)"

12) L51: "the latter term" I guess it should be "the former term," which means photo-synthetic CO_2 uptake.

Thank you, in the revised manuscript corrected it to "the former term"

13) L53: "variable $\delta^{18}\text{O}$ gradient" I think "significant $\delta^{18}\text{O}$ variation" is more appropriate.

In the revised manuscript we used significant $\delta^{18}\text{O}$ variation

14) L56: Delete "the isotopically exchanged"

Deleted

15) L45-57: In this block, you should use the term "isotope fractionation" with its definition for the subsequent block. More desirably, the term "mass-dependent isotope fractionation (MDF)" with its definition.

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In the revised manuscript, we included “These physico-chemical processes change $^{17}\text{O}/^{16}\text{O}$ by approximately half the corresponding change in $^{18}\text{O}/^{16}\text{O}$, a process called mass-dependent isotope fractionation (see equation 2). This is because the mass difference between ^{17}O and ^{16}O (1.0042 amu) is approximately half as large as the mass difference between ^{18}O and ^{16}O (2.0042 amu).” at the end of the paragraph.

16) L63: “mass-dependent fractionation” should be “mass-dependent isotope fractionation” with its definition in detail.

We excluded this paragraph, L62-64 in the revised manuscript since it does not add additional information to the paragraph mentioned above.

17) L62-64: Need revision because the latter paragraph is just a refrain of the former.

We excluded this paragraph, L62-64 in the revised manuscript since it does not add additional information.

18) L65: Describe a specific value instead using “considerable”

In the revised manuscript, instead of “considerable $\Delta^{17}\text{O}$ ” we used “the $\delta^{17}\text{O}$ of CO_2 is 1.7 to 2.2 times $\delta^{18}\text{O}$ of CO_2 (Wiegel et al., 2013)”

19) L60-71: In this block, you should use the term “mass-independent isotope fractionation (MIF)” with its definition, and associate it with “photochemical isotope exchange”

In the revised manuscript, we included the following paragraph “In nature, it was believed all process that modifies the oxygen isotope distribution is mass-dependent isotope fractionation until the discovery of the deviation from the assigned mass-dependent three-isotope fractionation line in meteorites (Clayton et al., 1973; Clayton et al., 1976) and ozone formation (Thiemens, 1983; Heidenreich and Thiemens, 1983, 1986), called mass-independent isotope fractionation (see equation 3). The $\Delta^{17}\text{O}$ of ozone can be transferred to other oxygen-bearing molecules via a direct chemical reaction with ozone or via $\text{O}(^1\text{D})$.”

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and rearranged the whole paragraph

20) L70-71: This is not sufficient because exchanges with soil and ocean water are also nonenzymatic processes.

The isotope exchange in the atmosphere is negligible due to lower liquid water content, lower residence time and the absence of carbonic anhydrase (Mills and Urey, 1940;Johnson, 1982;Miller et al., 1971;Silverman, 1982). We incorporated this sentence in the updated section.

It is true that CO₂-H₂O exchange with ocean water is a non-enzymatic process, but CO₂-H₂O exchange with soil water is controlled by carbonic anhydrase (Wingate et al., 2009), similar to the exchange with leaf water.

21) L78: "The $\Delta^{17}\text{O}$ of CO₂" instead of "The ^{17}O -excess of CO₂ ($\Delta^{17}\text{O}$) (equation 4)"

In the revised manuscript, we only used $\Delta^{17}\text{O}$

22) L80: Clarify "well-known three-isotope slope." "Non three-isotope person" cannot understand what this means.

In the revised manuscript, we included the three-isotope fractionation slope of 0.5229, and the figure above.

23) L92-106 and Figure 1: The explanation is this block is too general, should reduce to a few sentences. Detail description may be required if you would like to discuss the difference of results due to the different types in the Discussion. As for Figure 1, not this scheme but simpler scheme in Figure S6 was actually used in this study. Therefore, it seems more appropriate to delete Figure 1 and insert S6 here.

In the revised manuscript, we merged the necessary information with the other paragraphs and we agree that Figure 1 is not necessary, so it is left out. We excluded the general description of plant types. We only kept the following three sentences

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“The mole fraction of CO₂ at the CO₂-H₂O exchange site (cm) is an important parameter to determine the effect of photosynthesis on the triple oxygen isotope composition of atmospheric CO₂. In C₃ plants, CA is found in the chloroplast, cytosol, mitochondria and plasma membrane (Fabre et al., 2007; DiMario et al., 2016) and the CO₂-H₂O exchange can occur anywhere between the plasma membrane and the chloroplast. For C₄ plants, CA is mainly found in the cytosol, the CO₂-H₂O exchange occurs in the cytosol (Badger and Price, 1994).”

24) L108-109: What is "leaf level"?

In the revised manuscript we changed it from leaf level to leaf scale

25) L116-117: "Δ¹⁷O" instead of "triple oxygen isotopic composition"

Changed accordingly

26) Equations 1 and 2: Should be merged such as, $\delta_n O = n R_{\text{sample}} / n R_{\text{VSMOW}} - 1$, n refers 17 or 18 or simpler, $\delta = R_{\text{sample}} / R_{\text{VSMOW}} - 1$.

Thank you, in the revised manuscript we used the first suggestion.

27) L134: I recommend "The MDF factor" instead of "The factor"

Changed accordingly

28) L135-137: Delete “This relation. . . , respectively.

In the revised manuscript we excluded the sentence, based on the suggestion above, we already defined mass-dependent isotope fractionation.

29) L137: "variations" instead of "values." "Small delta value" is meaningless.

In the revised manuscript we changed values to variations. And at the end of the paragraph, we introduced “Equation 4 can be linearized to $\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda \times \delta^{18}\text{O}$ (Miller, 2002), but this approximation causes an error that increases with $\delta^{18}\text{O}$.” for more clarity.

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30) L139-140: I recommend "Note that $\Delta^{17}\text{O}$ changes not only by MIF processes, but also MDF processes with a different λ value from the definition,"

Changed accordingly

31) L145-146: "which was obtained by the observation of" instead of "the value associated with"

Changed accordingly

32) L147-148: Delete "Note that ... $\delta^{18}\text{O}$."

Changed accordingly

33) L150-258 (Section 2.2-2.4): Revise completely.

In the revised manuscript, we moved most of section 2.2 to the supplementary material we moved section 2.3 to the discussion we moved section 2.4 to the supplementary material

34) Equation 5: Use n (18 or 17) or simpler expression as above, then revise or delete

In the revised manuscript, we implemented the suggestion expression

35) L158 and L163. Equation 12: Move after equation 5 with related sentences.

Changed accordingly

36) L163-168: Delete "We note that...itself."

The sentence is excluded from the revised manuscript.

37) L170-200 and Section 2.4: Integrate and locate in new section such like "Extension of Farquhar-Lloyd model to oxygen triple isotopes. Eqs. 6 and 11 are almost identical so that they should be merged. Equation 15: Use n (18 or 17) or simpler expression, then revise or delete

This section is moved to the supplementary material and revised in the new version of

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the manuscript

38) L208-213 and Figure 2: Move to SM.

Changed accordingly

39) Section 2.3: I recommend moving this section to the Discussion.

Changed accordingly

40) L217: Delete “which is a net sink,”

This section is moved to the discussion part, and “which is a net sink,” is removed in the revised manuscript.

41) L230: Specify which model is used.

In the revised manuscript this section is moved to the discussion section and revised entirely.

42) L241-259: Here detail but still insufficient description was made only for δm , on the other hand, no description for c_i and δi which were driven away to Appendix. This seems out of balance and forces readers to jump here and there. I recommend moving this block to SM.

In the revised manuscript, we moved this part to the supplementary material

43) L256-257 and related sentences in Appendix A3. No definition of c_i .

In the revised manuscript, the definition for all parameters is included as a table in the appendix

44) L262-265: Could it be shorter?

In the revised manuscript we shortened this part by excluding the sentence from line 263 to line 265, “The dwarf type sunflowers were grown until the first leaf pair that was used for the experiments reached the final size, which is about 4 weeks.” We did the

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same for line 267 to 268, i.e. “After at least 6 weeks in the growth chamber, leaves that had developed and matured there were used for the experiment” is excluded in the revised manuscript.

45) L268-269: “The 4th or higher. . .” Is this sentence an explanation for maize or all species?

In the revised manuscript, we write “For maize, the 4th or higher “

46) Section 3.2: Need the model and the manufacturer for halogen lamp, neutral filters, dewpoint meter (the model).

The models and manufacturers are included in the revised manuscript

47) Section 3.3: Could this section be shorter to several sentences? The description for δD and obtaining optimum setting seem appropriate in SM.

In the revised manuscript this section has been considerably shortened and part of it is moved to the supplementary material.

48) L349: Water was converted to O₂

In the revised manuscript L349 - L 354 has been deleted to make the manuscript more concise.

49) Section 3.5: In previous section, unit of $\Delta^{17}O$ is ‰. Here ppm is used. Use a uniform manner.

In the revised manuscript, all numbers are given in ‰.

50) Section 3.6: See related general comment

The leaf cuvette model is described here for the first time, as a result we cannot make it shorter than this.

51) L403: The last sentence is a refrain.

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In the revised manuscript, we excluded the sentence.

52) Results: Show experimental results (raw data) such as c , δ , Δ , w , for entering and leaving from the cuvette, etc. Show a table of them and describe them.

In the revised manuscript, we provided the raw data for the gas exchange parameters at the beginning of the results section

53) L414-415: Delete this sentence

Changed accordingly

54) Section 4.2: Avoid using “ ^{17}O -excess” in the title and L433 for uniformity

Changed accordingly

55) L477-493: I could not understand this block. If the authors applied different lambda values to individual results, the vertical axis in Figure 8 would be meaningless, and one could not evaluate the graph and related description at all.

In the revised manuscript we incorporated the reference triple oxygen isotope fractionation slope (λ), also in the caption. Sorry for the confusion we did not mention it clearly. When we described $\Delta^{17}\text{O}$ in the theory section, we clearly mentioned which lambda value we used ($\lambda=0.528$).

56) Section 5.2: Avoid using “ ^{17}O -excess” for uniformity Changed accordingly

57) Figure 3: Add individual flow direction. Changed accordingly

58) Figure 4: Panel b seems unnecessary. Delete and insert Figure 5a here.

Changed accordingly

59) Figure 5: Move Panel a to Figure 4 as above

Changed accordingly

60) Figure 6: Is it important to plot both of blue diamonds and curve. Should the curve

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be improved by blue diamonds?

The curves are based on the leaf cuvette model which we implemented for this study. The blue diamonds were the results for the individual experiments using the Farquhar model. In the revised manuscript, we excluded the blue diamond points.

Typographic errors

61) Space inserted after semicolon (e.g., L33) corrected 62) L42: Welp et al. (2011) Corrected

63) L45: The concept of the latter study.. Corrected

64) L60: equation 4)) Corrected, now it is “see equation 2”

65) L207: Figure 2 Now Figure S1

66) L237: “Following (Farquhar.)” Need grammatical correctness

Corrected to: “The CO₂ mole fraction at the site of CO₂-H₂O exchange is calculated as shown in equation S10 following (Farquhar and Cernusak, 2012;Barbour et al., 2016;Osborn et al., 2017). “ This section has also been moved to the supplementary material.

67) L267: Maize In the revised manuscript, “Mays” is corrected to “Maize”

68) L279, L297: Need grammatical correctness. Line 279

In the revised manuscript “of” is replaced by “for”, now it reads as follow: A schematic for the gas exchange experimental setup is shown in Figure 2

L297 In the revised manuscript, we deleted the phrase “as described in detail in” since it does not change the meaning of the sentence. Now it reads as:

“The isotopically enriched CO₂ was prepared by photochemical isotope exchange between CO₂ and O₂ under UV irradiation (Adnew et al., 2019). “

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69) Section 3.2: “Figure 3” instead of “Figure 2” (If Figure 2 were moved to SM, they are accidentally correct, though)

Thank you, this is corrected in the revised manuscript

70) References: I found typo. in Barbour et al. (2016) and Caemmerer and Farquhar (1981). There may be more. Confirm all.

Thank you very much. In the revised manuscript we corrected all of them. All of them related to the name von Caemmerer.

73) L950: “entering and leaving” instead of “leaving and entering” In the revised manuscript, we re-ordered it chronologically. The appendix has also been moved to the supplementary material.

74) Equation A1.4: If the referred article (Caemmerer and Farquhar, 1981) was correct, the denominator must be $(g_a + E/2)$.

Corrected Thank you very much, all the Typographic errors are corrected in the revised manuscript.

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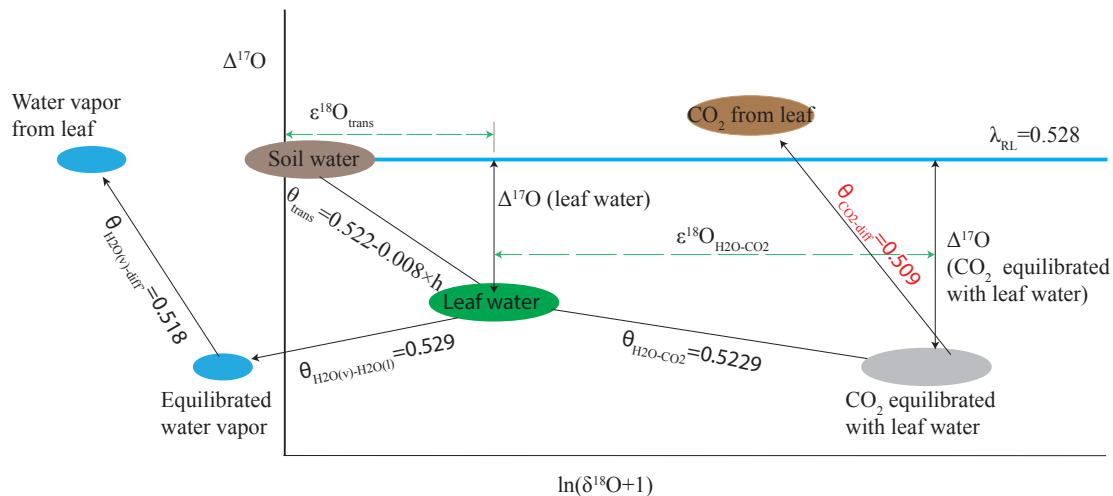


Fig. 1. Schematic of the process that affect the $\Delta^{17}\text{O}$ of CO_2 and H_2O during photosynthetic gas exchange (not to scale)

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