

The triple oxygen isotopic composition of CO₂ ($\Delta^{17}\text{O}_{\text{CO}_2}$) 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 $\Delta^{17}\text{O}_{\text{CO}_2}$ 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 $\Delta^{17}\text{O}_{\text{CO}_2}$ 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 $\Delta^{17}\text{O}_{\text{CO}_2}$ 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.

General comments

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

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.

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). Appendix should be moved to SM.

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

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.

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

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

As shown in Figure 5, the discrimination of $\Delta^{17}\text{O}$ of CO_2 during photosynthesis varies widely, and controlled by the magnitude of oxygen isotope equilibration at the $\text{CO}_2\text{-H}_2\text{O}$ 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 $\delta^{18}\text{O}$ results. Moreover, In the last paragraph of Discussion, authors mentioned that the main uncertainty is c_m/c_a ratio, which may be same as the main uncertainty of $\delta^{18}\text{O}$. 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 $\Delta^{17}\text{O}$ of CO_2 . What is an advantage to use $\Delta^{17}\text{O}$ instead of $\delta^{18}\text{O}$? Please provide suggestions or implications to general biogeochemists.

Specific comments

L41: “replaced using...” What this means? Be more specific.

L47: “see equation (1)” instead of “see below”

L51: "the latter term" I guess it should be "the former term," which means photosynthetic CO_2 uptake.

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

L56: Delete "the isotopically exchanged"

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.

L63: "mass-dependent fractionation" should be "mass-dependent isotope fractionation" with its definition in detail.

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

L65: Describe a specific value instead using "considerable"

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"

L70-71: This is not sufficient because exchanges with soil and ocean water are also non-enzymatic processes.

L78: "The $\Delta^{17}\text{O}$ of CO_2 " instead of "The ^{17}O -excess of CO_2 ($\Delta^{17}\text{O}$) (equation 4)"

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

L92-106 and Figure 1: The explanation in 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.

L108-109: What is "leaf level"?

L116-117: " $\Delta^{17}\text{O}$ " instead of "triple oxygen isotopic composition"

Equations 1 and 2: Should be merged such as,

$$\delta^n\text{O} = {}^n\text{R}_{\text{sample}}/{}^n\text{R}_{\text{VSMOW}} - 1, \text{ n refers 17 or 18}$$

or simpler,

$$\delta = \text{R}_{\text{sample}}/\text{R}_{\text{VSMOW}} - 1.$$

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

L135-137: Delete "This relation..., respectively."

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

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,"

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

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

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

Equation 5: Use n (18 or 17) or simpler expression as above, then revise or delete L158 and L163.

Equation 12: Move after equation 5 with related sentences.

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

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

L208-213 and Figure 2: Move to SM.

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

L217: Delete “which is a net sink,”

L230: Specify which model is used.

L241-259: Here detail but still insufficient description was made only for δ_m , on the other hand, no description for c_i and δ_i 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.

L262-265: Could it be shorter?

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

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

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

L349: Water was converted to O_2

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

Section 3.6: See related general comment

L403: The last sentence is a refrain.

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

L414-415: Delete this sentence

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

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.

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

Figure 3: Add individual flow direction.

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

Figure 5: Move Panel a to Figure 4 as above

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

improved by blue diamonds?

Typographic errors

Space inserted after semicolon (e.g., L33)

L42: Welp et al. (2011)

L45: The concept of the latter study..

L60: equation 4))

L207: Figure 2

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

L267: Maize

L279, L297: Need grammatical correctness.

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

References: I found typo. in Barbour et al. (2016) and Caemmerer and Farquhar (1981).

There may be more. Confirm all.

L950: “entering and leaving” instead of "leaving and entering"

Equation A1.4: If the referred article (Caemmerer and Farquhar, 1981) was correct, the denominator must be $(g_{ac}^t + E/2)$.