

## Author response to anonymous referee #2

I thank referee 2 for his/her perceptive and constructive comments and make the following responses:

### General comment

*My one general comment would be that although the approach taken by the author does indeed side-step the concentration dependence arising if one calibrates using a ratio-based approach, IRMS methods arose because of the precision advantage arising when measuring a ratio. It is certainly still the case that the precision with which any of the isotopologue-specific optical instruments can measure the minor isotopologues is limited 0.1 ppm (generously), so this will impact the precision with which one can determine a delta value from these instruments via this otherwise straightforward approach. As such, there remain advantages in working with the ratio even with instruments that 'naturally' lend themselves to this approach. Some acknowledgement of this ought to be made in the text.*

Please see detailed response to the same issue raised by referee 1, I have addressed both together.

### Specific comments

*P 3, line 12: Clumped isotopes are mentioned, but not described, but as I see great value in this manuscript for students, I think it would be helpful to extend the parentheses to something like: (i.e. clumped isotopes, is the term for isotopologues carrying two (or more) of the heavy, rare isotopes.)*

Please see detailed response to referee 1 for the same issue.

*p 9, line11: 2018 should read 2017.*

Corrected.

*p 9. line 25: I think case 7 needs a little more explanation to be clear to readers.*

I have expanded case 7 as follows:

1) is a hypothetical standard with the isotopic composition of VPDB-CO<sub>2</sub>. Examples include typical clean air (case 2), synthetic air synthesised with <sup>13</sup>C-depleted CO<sub>2</sub> with  $\delta^{13}\text{C} = -35\text{‰}$  (case 3), realistic errors of 2‰ in  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  (cases 4,5), and using isotope ratios assumed by Hitran rather than VPDB-CO<sub>2</sub> (case 6). Case 7 simulates the result if only singly-substituted isotopologues are included in the sum and all doubly-substituted minor isotopologues are ignored. Other cases can be assessed