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Interactive comment on “Investigations of the photochemical isotope equilibrium between O₂, CO₂ and O₃” by R. Shaheen et al.

R. Shaheen et al.

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Comment to referee report by Martin Miller:

We thank Martin Miller for the positive review and the useful suggestions to the manuscript. Here are our comments:

The general comment relates to our approach of reporting the isotopic composition of CO₂ relative to O₂. As pointed out by the referee, this is indeed an uncommon use of δ notation, but it allows to generalize the results from our experiments and to visualize the concept of the photochemical equilibrium point. This use of the notation is crucial in our evaluation, and we have clarified it in the revised manuscript. Following the suggestion of the referee, in the revised version we also give the data on the SMOW

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scale in an additional table. The uncommon use of the delta notation allows us to make the most general and important interpretation of our dataset. The underlying message is actually straightforward and is at the very basis of the concept of isotope equilibrium: In any isotope exchange equilibrium situation the final reactants always have a fixed isotopic relation *relative to each other*, not relative to an international scale. We explained again in the revised version that we use the definition of δ to quantify the relative isotope difference between two compounds, but that in the modified δ units of CO₂ *versus* O₂ what would usually be regarded as a fixed standard is now changing itself during the experiment.

Technical corrections

(i). Stratospheric CO₂ $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of 45 per mil and 54.9 per mil are stated, for the highest altitude (60 km) measurements made so far. It would be helpful to quote the reference, as $\delta^{17}\text{O} < \delta^{18}\text{O}$ in this case and those results are not at all in accord with the 1.7 fractionation line reported by Lämmerzahl et al. (2002). The maximum altitude sampled in the latter work was 33 km.

We have clarified this point. The numbers given are versus the reference material atmospheric O₂, not tropospheric CO₂. On this scale, tropospheric CO₂ itself is has $\delta^{18}\text{O} \sim 41$ per mil and $\delta^{17}\text{O} \sim 21$ per mil enriched. And the slope of 1.7 usually reported is of course the line that connects stratospheric and this tropospheric CO₂.

(ii). Lämmerzahl et al. (2002) reported stratospheric CO₂ $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values relative to tropospheric CO₂, not to air O₂ (as stated by Shaheen et al.).

This has been clarified, see also comment to (i)

(iii). It would be helpful if a definition was provided of the parameter γ , as used in the expression for the branching ratio $\gamma/(1 - \gamma)$.

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A definition has been provided.

(iv). In the final paragraph of this section, the second sentence states that ‘The iso-electronic isotope exchange reaction (R4) could possibly influence the isotopic composition of O(1D).’ But R4 is not an isotope exchange reaction; it is the decomposition pathway of the CO₃ entity. Furthermore, there seems to be no reason to use the term ‘iso-electronic’ in this context.

This has been rewritten in the revised version. Iso-electronic is used to characterize isotope exchange without change in the electronic configuration of the reaction partners.

Section 2.2, Preparation of enriched CO₂:

(v). In the final paragraph of this Section, it is stated that: ‘The accuracy of the δ values for the starting CO₂ material is 0.2 and 0.1 per mil for ^{17}O and ^{18}O , respectively. But there is no mention of how those values were measured to this level of accuracy. If the ^{17}O data were obtained using the Assonov and Brenninkmeijer (2001) method, then (as stated in Section 2.3) the analytical error is no better than 0.6 per mil.

In the original manuscript we had quoted the error from multiple measurements of the starting gases with the mass spectrometer, not the error from the total analytical procedure. We agree that it is better to quote the total error and have changed this in the revised manuscript.

Section 2.4, Blank experiments:

(vi). Similar to the previous comment, it is seen in the final paragraph of this Section that ‘a small fractionation for CO₂ ($\delta^{17}O=0.4$ per mil) is stated. Again, if the $\delta^{17}O$

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data were obtained using the Assonov and Brenninkmeijer (2001) method, then the 2σ analytical error is no better than 0.6 per mil.

This number comes from 3 different measurements, where we indeed had somewhat lower scatter than normal. However, we note that this is of the order of the measurement error, and therefore not a significant number anyway. To avoid confusion, we have written in the revised version that the shift was smaller than the analytical precision.

Section 3, Results:

(vii). Was there a particular reason for choosing the composition of the reactant mixture to be (64 ± 1) μmol CO₂ and (800 ± 10) μmol O₂? It would also be helpful to have mentioned the total pressure in the reactor, although admittedly that can be obtained from the information given. A simple calculation indicated that the pressure was about 80 hPa.

We were aiming at a ratio of roughly 1:10, since at lower CO₂ content the CO₂ isotope determination becomes increasingly more difficult and fractionation effects during extraction and measurement procedures become more important. This information has been added in section 2.1.

(viii). It would be helpful to define what is meant by the 'e-folding time of the equilibration

process'. The same terminology is also used in the caption to Table 1.

Has been explained.

Section 3.1, Photochemical Isotope Equilibrium:

(ix). Commencement of the second paragraph: it should be stated whether the small or large reactor was used and hence what the corresponding pressure was. Similarly,

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with regard to the second set of experiments (as mentioned at the beginning of the third paragraph).

The information has been added.

(x). With regard to the decision to report the isotopic composition of the CO₂ with reference to that of the coexisting O₂, please refer to my comment ('substantive point') given above.

See our comment above.

Section 3.2, Dependence on [O₂]/[CO₂]:

(xi). Referring to equation (2): nowhere in the manuscript could I find the definition of the parameter ρ_0 . It is important that this omission is rectified.

Has been clarified

Section 4.1, Dependence on [O₂]/[CO₂]:

(xii). First sentence: 'Our experiments with varying the O₂/CO₂ ratio at constant pressure

show that the equilibrium enrichments in CO₂ decrease when the CO₂ content exceeds 5%.' I think that what the authors meant to say is that the ¹⁷O and ¹⁸O equilibrium enrichments in CO₂ decrease when the CO₂ content exceeds 5%.

Corrected

Fig. 1 caption:

(xiii). There are no isotope *enrichments* in O₂ indicated by the Figure, only *depletions*

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of ^{17}O and ^{18}O . The caption should perhaps read ‘Oxygen isotope changes in O₂ (squares) and CO₂ (circles)...’

Corrected

Typographic errors noted in the manuscript:

(xiv). Section 1, line 22: ‘45 per mil and 54.9 per mil’

(xv). Page 2, second column, second paragraph: ‘UV-irradited’

(xvi). Page 7, first column, line 15: ‘CO₂ .’

(xvii). Final sentence of the acknowledgements section: ‘... who enabled *her* to complete

this work.’

All typos corrected

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