

Interactive comment on “NO_x cycle and tropospheric ozone isotope anomaly: an experimental investigation” by G. Michalski et al.

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The authors here wish to explore the chemistry of isotope exchange between O₃ and NO_x using photochemical experiments and kinetics modeling. Experiments and kinetics of this type are indeed needed to develop a more quantitative picture of the ¹⁷O isotope anomaly in NO_x. They are able to obtain great agreement between the experimental and model results. However, the interpretation of both the experiments and modeling relies on assumptions that have not been adequately justified with evidence from the experiments, the model, or other sources. Without properly validating these

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assumptions, this work contains artifacts in both the experimental results and modeling. Therefore, the agreement between the experiments and model is likely fortuitous.

1 Photochemical J-values and associated isotope effects

The authors select a J-value for NO₂ photolysis that results in model δ values closest to their experiments. However, selecting a J-value this way is dependent on the reactions and isotope effects assumed in the model, and thus the chosen J-value might not be realistic. As the authors note, the competition between O atom exchange and reaction with O₃ is important for determining the final ¹⁷O anomaly in NO₂, so having accurate J-values for both NO₂ and O₃ is crucial to modeling the system well. As such, the authors should verify the J-value through independent means. In that regard, two different methods would be useful to help quantify the flux of the xenon lamp into the reaction chamber. One method would be to estimate the J-value from the known output and emission spectrum of the lamp, the transmission coefficient of quartz, the geometry of the reaction chamber, and the absorption cross sections of NO₂ at each possible wavelength. Another method would be to do a chemical actinometry experiment in the reaction chamber using the xenon lamp. Both of these methods would help constrain the J-value to ensure that the chemistry in the model is as accurate as possible. In addition to an additional calculation or experiment, the following description (line 25, page 9457) of how the J-value for O₃ photolysis was obtained is unclear: “the rate for the main ozone isotopologue ¹⁶O¹⁶O¹⁶O ... was fixed by taking the cross section ratio of NO₂ and O₃ at the wave-length range used for the experiment.” A more detailed and clear description of the calculation would be helpful.

In addition, the length of the reaction chamber may also be introducing experimental artifacts in photolysis. The long path length (122 cm) in the reaction chamber may allow for self-shielding of the rare isotopes by the common isotope, leading to non-

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mass-dependent isotope effects. A Beer's law calculation with an estimated flux could show that self-shielding is not present in these experiments.

Another concern is the isotope effects for ozone photolysis used in the model. The isotope effects that the authors use were originally derived in Wen and Thiemens (1991) from photolysis at 532nm rather than a broadband light source such as the one used in this experiment. Because isotope effects in any photolysis reaction can be quite different at a single wavelength compared with those integrated over the entire spectrum of the light source (Miller et. al., 2005), the derived isotope effects from Wen and Thiemens (1991) are likely not valid for these experiments. The relative rate coefficients for the ^{17}O and ^{18}O isotope effects in ozone photolysis that the authors use (0.988 and 0.972, respectively) are also non-mass-dependent as demonstrated by the following calculation:

$$\frac{\ln(0.988)}{\ln(0.972)} = 0.425$$

The O_3 photolysis isotope effects used are therefore not mass-dependent (≈ 0.5 to 0.53) as claimed in the text of the manuscript on line 26 of page 9457. The non-mass-dependent isotope effect could have introduced an artificial negative ^{17}O isotope anomaly into the model calculation, thus affecting everything from the relative rates chosen for O_3 formation to the final results for NO_2 .

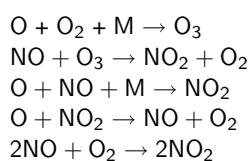
2 Reaction of NO with O_2

The experimental work presented here seems to rely heavily on the assumption that the reaction of NO with O_2 goes to completion. However, this reaction is very slow, with a three-body rate coefficient of only $2 \times 10^{-38} \text{ cm}^6\text{s}^{-1}$. Initially, the authors generate NO_2 by reacting NO with excess O_2 . However, no detail is given about the amounts used, the time of reaction, or the cryogenic separation process. Depending on the

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concentrations and time of reaction, significant NO may remain in the reaction vessel. If the authors used liquid nitrogen in the cryogenic separation process, the remaining NO would condense with NO_2 so that the gas would not be pure NO_2 as assumed. This could have potentially unintended consequences for the experiments and modeling since incomplete reactions tend to produce somewhat larger isotopic fractionations. The model is also initialized assuming that NO is not present, and the partially reacted NO may have a much different isotopic composition than the NO produced from NO_2 photolysis. As such, the conditions for the reaction and cryogenic separation of the initial NO_2 should be stated more explicitly so that the assumption that all of the NO reacts can be justified with an argument from kinetics and the experimental conditions. If it cannot be justified, the model is not an accurate representation of the initial experimental conditions.

Similarly, after the NO_2 photolysis reaction, the chamber is left in the dark for 60 minutes to convert the remaining NO to NO_2 . However, the assumption that all of the NO reacts with O_3 and O_2 to form NO_2 is not justified. Using the concentrations given in Table 3 as initial conditions, I constructed the following model in Kintecus without isotopes to simulate the reactions after the lamp is turned off:



Each reaction had the same rate coefficient as used in the model in the manuscript. For the first set of model concentrations given in Table 3, after 60 minutes in the dark much more NO is present than NO_2 , with $[\text{NO}] = 4.88 \times 10^{14} \text{ cm}^{-3}$ and $[\text{NO}_2] = 8.58 \times 10^{13} \text{ cm}^{-3}$. Similarly, using the last two sets of concentrations in Table 3 as initial conditions, the concentration of remaining NO is also still quite high after 60 minutes in the dark, with $[\text{NO}] = 9.63 \times 10^{13} \text{ cm}^{-3}$ and $[\text{NO}_2] = 4.76 \times 10^{14} \text{ cm}^{-3}$ for the 20 μmole NO_2 experiment and

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$[\text{NO}] = 2.5 \times 10^{14} \text{ cm}^{-3}$ and $[\text{NO}_2] = 6.82 \times 10^{15} \text{ cm}^{-3}$ for the 236 $\mu\text{mole NO}_2$ experiment. Only in the last case in Table 3 is the modeled concentration of $[\text{NO}]$ after 60 minutes in the dark somewhat low, but it still makes up about 4% of the total product NO_x .

Given that significant concentrations of NO remain in most of their experiments even after 60 minutes, the authors are not measuring the product NO_x entirely as NO_2 as assumed. While the remaining NO may form N_2 and O_2 in the discharge just like NO_2 , the model output for NO_2 is not comparable to the experimentally derived values for NO_2 as a result. In particular, eqn. 1 is only valid if all of the NO reacts with O_2 , but as I showed above, this is not the case for the model concentrations for the experimental conditions given in Table 3. Because the NO only partially reacts, the addition of the step of reacting NO with O_2 in the dark for 60 minutes introduces more uncertainty into the experimental results. For example, the reaction with O_2 dilutes the $\Delta^{17}\text{O}$ signal in NO_x , so an incomplete reaction with NO would cause the values calculated in eqn. 1 to be systematically too low.

3 Definition issues

To initialize their model, the authors use two different definitions for the isotope ratios for O_2 and O_3 and for NO and NO_2 , but only the definition for NO and NO_2 is correct. Use of two different definitions leads to artificial changes in the isotopic compositions predicted by the model. For example, $\delta^{17}\text{O}$ for O_2 calculated using this definition is too low by 5%. The initial concentration of each isotopologue is more properly defined as:

$$[\text{OO}] = \frac{[\text{O}_2]_{total}}{1 + \frac{[\text{OP}]}{[\text{OO}]} + \frac{[\text{OQ}]}{[\text{OO}]}}$$

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where $\frac{[\text{OP}]}{[\text{OO}]}$ is defined from the $\delta^{17}\text{O}$ value as follows:

$$\frac{[\text{OP}]}{[\text{OO}]} = 2 \times 10^{17} R_{VSMOW} (1 + \delta^{17}\text{O})$$

The initial concentration of OP is then just:

$$[\text{OP}] = [\text{OO}] \times \frac{[\text{OP}]}{[\text{OO}]}$$

The calculation is similar for the concentration of OQ.

In addition, because the definition used for $\Delta^{17}\text{O}$ is a linear approximation for $\Delta^{17}\text{O}$, it is not accurate for the large $\Delta^{17}\text{O}$ values in these experiments and modeling. One of many more proper definitions is the following:

$$\Delta^{17}\text{O} = \ln(1 + \delta^{17}\text{O}) - \lambda \times \ln(1 + \delta^{18}\text{O})$$

These definitions come from Kaiser and Röckmann (2009).

4 Miscellaneous

Finally, I note the following issues:

The authors reference papers in several places where the referenced work did not originally perform the measurement or derivation of the used value. This is fine if the referenced work is a review such as the JPL Data Evaluation, but proper credit should be given otherwise. The way some papers are currently referenced implies that the authors originally measured or derived the isotope effects they used in other papers. Here are some examples in this manuscript:

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- Oxygen isotope exchange: This rate coefficient was measured by Fleurat-Lessard et. al. (2003) for the forward rate constant.
- Ozone dissociation: The isotope effects used by the authors here come from Wen and Thiemens (1991), as noted above.
- NO₂ exchange with NO: These rate coefficients were originally measured by Klein et. al. (1963).

The authors need to conduct a more thorough error analysis of their experimental results. For example, what was the systematic error introduced into the measurements of NO₂ from the experimental procedure? How reproducible are the results for a single set of experiments? Given that in most cases the authors only conducted one experiment for a given set of conditions, the uncertainty in their results may be quite large.

In the model, why was an isotopic equilibrium constant included in oxygen atom exchange with NO and NO₂ but not included for isotope exchange between NO and NO₂?

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