

In “NO_x cycle and tropospheric ozone isotope anomaly: an experimental investigation” Michalski et al. look at the transfer of the isotope anomaly of ozone to NO_x in the laboratory. Through a system of NO₂ and O₂, both O₃ and atomic O are produced, facilitating oxygen exchange among the species. The degree of oxygen isotope anomaly transfer to NO_x is dependent on the NO₂/O₂ mixing ratio, with lower mixing ratios showing greater enrichment. The experimental results were then compared with model calculations, showing great agreement.

Overall, this study presents clear evidence for terminal oxygen transfer from the O₃ molecule, as well as the effect of NO₂ and O₂ concentrations on $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ in NO₂. There are a few points, however, that seem somewhat oversold based on available data, as well as some conclusions that are overlooked.

First, the NO_x – O-atom exchange is not referenced prominently in the literature about nitrate isotopic composition. If this is in the literature, some references to that should be included. If not, more emphasis should be put on the implications of O-atom exchange and its effects on the isotopic composition of nitrate in natural systems. All the prior literature looks at NO_x cycling and the oxidants involved with NO₂ to NO₃⁻ conversion to determine the oxygen isotopic composition of NO₃⁻.

In general, the implications of these experiments for atmospheric composition of NO_x and O₃ seem overstated. While it is explained why the experiment cannot be run at atmospheric conditions, there are enough differences that it's hard to believe the extrapolation to atmospheric NO_x mixing ratios. This extrapolation seems extreme both because the experimental mixing ratios are so far from the natural and because in the natural system there are additional sources of O atoms beyond photolysis of NO₂, as well as the presence of other oxidants.

In addition, on page 9461, it is explained that the O₃ composition is reset to the tropospheric composition in under one day, so the stratospheric composition can be ignored, however, the lifetime of NO_x is ~1 day, so any O₃ interaction should still have stratospheric character.

The method of measuring the $\delta^{18}\text{O}$ of NO_x is not well explained. The Michalski et al., 2009 reference does not actually mention this Tesla coil method, while the other reference (Bes et al., 1970) seems only to have been published in a journal that is not widely available. Given that there is limited information available, more explanation of the method should be given. (E.g., are there any corrections made to the $\delta^{18}\text{O}$ output? Is any kind of internal or external reference standard used? What kind of error do these measurements have? Is the method 100% efficient at breaking down the NO_x?)

Tables/Figures:

There are too many tables and figures for this length paper. Not all of them are lending a great deal to the discussion in the paper, so some would be better placed in a supplement.

Tables 1 and 2 are mostly contained in figures 2-4. Table 3 could go in a supplement, as it's not adding anything to understanding the paper. Table 5 should also go in a supplement.

Figure 7 is difficult to understand in the context of this study. If you keep this figure in the paper, its importance needs to be better explained.

Technical notes:

The model name is sometimes written as KINTECUS, like it's an acronym, sometimes it's italicized and sometimes it is capitalized as a proper noun. This should be consistent.

p. 9449, line 20- the μmole notation is confusing. Are you trying to define a μmole as 10^{-6} moles?

p. 9451, line 12- number density is not shown on table 3, just number.

p. 9451, line 19- where does the 44% come from? As far as I can tell, that number doesn't make sense with the data in table 3.

p. 9452, line 9- it says here that the $\Delta^{17}\text{O}$ are similar for NO_x and O_3 , but later you explain why they're different. You should be clearer here that you're only referring to similarity in $\delta^{18}\text{O}$.

p. 9456, line 19- the reference should be Finlayson-Pitts

p. 9461, line 23- should be "they are" not "are they."

p.9462, line 8- the lifetime for conversion of NO_2 to HNO_3 by OH should be referenced (or more information on the calculation provided).

p. 9462, line 19- the isotopic values of tropospheric NO_2 should be specified to be for formation at STP.

Table 1- with tank oxygen δ values, you don't specify which is which.

Table 3- are these values from the model or experimental measurement?

Table 4- you have a $d17\text{O}$ that should be $\delta^{17}\text{O}$.

Figure 5b- it's unclear where the data in this figure is coming from.

Figure 6- what is shown in this figure? Is it the selection of coefficients? The caption needs more detail.