

## ***Interactive comment on “Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica” by J. Savarino et al.***

**J. Savarino et al.**

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We thank the referee # 1 for his encouraging review. According to referee # 2, the manuscript was suffering from a lack of organization. Despite the fact that the present referee found it clear and well balanced, we decided to reorganize the manuscript.

No original conclusions were altered by this reorganization. We closely followed the structure given by referee # 2. We have eliminated redundant parts of the text, grouped all technical data at the beginning of the manuscript and now present the discussion section in a more logical way. We first estimate the mass flux of the three anticipated nitrate sources and their likely isotopic composition. We then compare these estimates with our observations before drawing conclusions.

1. Uncertainty of O<sub>3</sub> isotopic composition This issue is still debated in the community

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and we will not be resolved here. The underlying question is: is the ozone variability observed the result of an analytical uncertainty that can be reduced by simply increasing the number of measurements of the same variable or is it the result of a natural variability and in this case not much can be done other than trying to decipher the causes for these variations? Some people argue that T and P variations cannot explain the observed variability, and conclude that it is an analytical variability and divide  $\frac{1}{\sqrt{N}}$ ; by  $\sqrt{N}$  to report a standard error. Other groups consider that other processes may influence the isotopic ozone composition (photolysis, catalytic destruction) and feel that it is a natural variability and report standard deviation. We chose the safest way, the one that gives the larger uncertainty, and use a range instead of a mean + standard deviation. We also emphasize better all issues related to the uncertainty of the anomaly transfer from O<sub>3</sub> to HNO<sub>3</sub>, ozone values been just one of them. We finally agree with the referee that considering all the uncertainties, the high D17O (HNO<sub>3</sub>) can still be explained by the current knowledge. Our entire measurements are reported vs VSMOW and AIR for O and N isotope ratios respectively. Since now we are using the linear approximation for D17O, there is no need to propagate data rescaling uncertainty. The transfer mechanism of the reaction O<sub>3</sub> + NO will be consistent between the two publications by our group (this paper, Morin et al. (2006, ACPD)), as for this latter MS it is also in the review process.

2. As stated before we decided to use the linear approximation in order to be consistent with previous publications on the same topic. This choice is now justified in the text as well as the slope coefficient. The bottom line here is that D17O calculation is only a definition, not a natural law. As long as the same definition is used for all species, comparisons are consistent. We therefore used also the linear definition for ozone and follow the Morin et al's approach in order to facilitate comparison between published studies. Mass balance calculation, based on D17O is now fully justified with the linear definition.

3. The recent paper by Shaheen et al. is a really interesting work and is now refer-

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enced in our MS. This work demonstrates that the isotopic photochemical equilibrium composition of CO<sub>2</sub> in a CO<sub>2</sub>/O<sub>3</sub>/O<sub>2</sub> system is independent of starting composition of CO<sub>2</sub>, when CO<sub>2</sub> represents a small fraction of O budget. Obviously the mixing line connecting starting CO<sub>2</sub> and final CO<sub>2</sub> depends on the starting CO<sub>2</sub>. If the same idea is applied to NO<sub>x</sub>/O<sub>3</sub>/O<sub>2</sub> system NO<sub>2</sub> should also reach an isotopic photochemical equilibrium. The line of figure 3 might then be interpreted as the result of the termination reaction schemes leading to nitrate formation (via N<sub>2</sub>O<sub>3</sub>, XONO<sub>2</sub>, etc). This is now made explicit in the text when figure 3 is discussed.

Technical comments:

-Technical references of Brand/Casciotti et al are now separated

-Morin did not measure d<sup>15</sup>N. To the best of our knowledge, D<sup>17</sup>O and d<sup>15</sup>N have never been presented together.

-A supplemental table is added for comparing d<sup>18</sup>O results from the two different techniques

-D<sup>17</sup>O was calculated using the gold technique for obviously consistency reasons between delta's

-“Gold furnace” and “gold decomposition” changed to Gold tube in an oven and “catalytic decomposition on gold” -As stated in table 2 and text, all data are reported according to the international scale. D<sup>17</sup>O was calibrated using internationally recognized standard, namely usgs34 and 35 and IAEA N-3 (Kaiser et al. Analytical paper is now accepted and in press for publication in Anal Chem. The reader can refer to this work for details).

-Cap17 definition solved, using linear approximation

-Blank values are now given. Clarification is given about blanks. Actually there was only one blank collected during the entire sampling. Reasons are given why.

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-Discrepancies between table 2 and text are solved

-Regarding interpretation of figure 3, answer is given above. We don't think it is necessary to distinguish data plotted as function of periods because they all have well distinct D17O. Highest values are for period 3, lowest for period 1 and intermediate for period 2 and 4. No better alignment is obtained within a given period. Again we want to stress that the goal of this manuscript is to interpret the main tendencies not second order variations. To go in that direction a transport chemistry model will be required.

-As stated above the discrepancy between the two studies is solved. "Why the reader should take that the result for granted?" Well, it is difficult for us to leave aside this experimental result and write like it wasn't in our hand. We had two options : ignoring or mentioning it. We prefer to use the second option at least if people are not convinced, NO<sub>x</sub>/O<sub>3</sub> reaction is a standard reaction in atmospheric simulation chamber that can be performed in many labs. Regarding Zahn et al. paper, the referee makes confusion between the internal isotopic composition of ozone and the NO+O<sub>3</sub> reaction. We agree that Zahn et al. used 80% enrichment for asymmetric ozone but regarding NO+O<sub>3</sub> they are assuming 100% reaction with terminal ozone atom as demonstrated in their fig 1a where D17O NO<sub>2</sub> = D17O asymO<sub>3</sub>)

- Morin et al. reference corrected.

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