

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

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The article of J. Savarino and coauthors presents new results on the triple oxygen isotope composition of Antarctic particulate nitrate, that may tell a very interesting story about the chemical history of atmospheric nitrogen oxides. As pointed out in some of the referee comments, however, interpretation of the isotope data is not straightforward and there are several uncertainties present in the analysis. To a considerable extent, this is due to the current lack of knowledge regarding the triple isotope composition of the molecules that are involved in the O atom transfer from ozone into nitrate. Likewise, fractionation factors and the O atom transfer mechanisms of the reactions that lead to the isotope transfer are not very well constrained either.

At this point, I feel obliged to make the cautionary remark that the mechanism of the

$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ reaction and the extent of the transfer of the isotope anomaly into NO_2 , for example, is not as clear as it might be inferred from the article (which is cited here for reasons of convenience):

"Recently, Zahn et al. (2006) improved and updated the isotopic anomaly transfer scheme between O_3 and NO_x . However, in both models, the authors assume that NO reacts only with the terminal atom of O_3 , a hypothesis contradicted by experimental observations (van den Ende et al., 1982; Viswanathan and Raff, 1983) and recently discussed in Morin et al. (2006) for its isotopic implications. In a set of laboratory experiments (manuscript in preparation), we have observed the macroscopic anomaly transfer of $\Delta^{17}\text{O}(\text{NO}_2) \approx 0.8\Delta^{17}\text{O}(\text{O}_3)$."

It thus appears as if the results of van den Ende et al. (1982) and Viswanathan and Raff (1983) were a) agreeing with each other, b) presenting experimentally based evidence, and c) demonstrating that the $\text{NO} + \text{O}_3$ reaction does not dominantly proceed by end atom abstraction. Unfortunately, this is an incorrect summary of the two cited papers because of several reasons.

Firstly, the experiments of van den Ende et al. (1982) have been performed at translational energies of 0.7 eV (Nijmegen experiment) and 0.61 eV (Los Alamos experiment, see Fig. 2) in the CMS frame. These high kinetic energies are representative for temperatures well above 7000 K, which obviously does not allow for direct conclusions on the reaction mechanism at thermal energies of 300 K and below. It must further be noted that the experiments themselves do not provide direct evidence for a particular transfer mechanism. Thus it appears highly speculative to interpret them as a clear indication for O atom transfer not dominantly proceeding by end atom abstraction under atmospheric conditions – even though this might actually be the case. Secondly, Viswanathan and Raff (1983) have written a purely theoretical and not an experimental paper which is already implied by the title of their article "Theoretical investigations of the reaction dynamics of polyatomic gas-phase systems: The $\text{NO} + \text{O}_3$ reaction". The only experiments of relevance for the transfer mechanism, that

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are cited by Viswanathan and Raff (1983), actually are those experiments of van den Ende et al. (1982). Consequently there appears to be only this single study that can provide evidence based on experimental observations – however these observations have to be interpreted. Thirdly, while van den Ende et al. (1982) see the results of their crossed molecular beam study as evidence for both, a center and an end atom abstraction pathway, the quasiclassical trajectory study of Viswanathan and Raff (1983) on several simplified model potential energy surfaces seems to indicate that center atom abstraction is not important. The two publications are clearly at odds with each other in this regard.

In summary, the apparent systematic uncertainties and contradictions in the cited experimental and theoretical work indicate that the exact mechanism of the isotope transfer in the $\text{NO} + \text{O}_3$ reaction is not known, in particular not on a quantitative level and not under atmospheric conditions. Experiments to directly study the isotope transfer, such as that announced by the authors, are therefore urgently needed to remove the yet existing uncertainties in O isotope modeling of atmospheric nitrogen oxides. Without the results of such dedicated experiments the systematic error in nitrogen dioxide could be well on the order of 10 permil, assuming $\Delta^{17}\text{O}(\text{O}_3) \approx 30$ permil and that all of $\Delta^{17}\text{O}(\text{O}_3)$ resides in asymmetric ozone.

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