Our response to Savarino. We encourage him to consider adopting a more congenial tone while critiquing papers, there is a difference between being "wrong" and failing to explain or detail aspects of the data sufficiently. We address his concerns below.

Savarino comments that "Not taking into account the treatment of the HOx/RO2 and their interaction with NOx prevents the model to predict any atmospheric observations, thus the conclusion that their model can predict atmospheric isotopic composition is an overstatement."

We agree, which is why our article states "Oxidation of NO by HO_2 and RO_2 should also follow mass dependent isotope rules; so NO_2 produced during peroxy radical oxidation should have a $\Delta^{17}O$ value of zero. Therefore, peroxy radical may alter the final $\Delta^{17}O$ value based on the proportion of peroxy radical oxidation relative to O_3 oxidation (Michalski et al., 2003; Morin et al, 2004)".

We are not sure how we can make the statement any clearer.

Our objective is not to predict the $\delta^{18}O$ or $\Delta^{17}O$ of NO_2 in the troposphere but to predict these values in **tropospheric NO_2 produced by O_3-NOx only chemistry** as implied by the experimental data and modeling (95% of the paper). We realize now this may have been unclear by not distinguishing between the NOx-O_3 and actual tropospheric NOx. We have clarified this by using the "O_3-NOx equilibrium" term more liberally. This value is critical for current models that use isotope balance models to predict nitrate $\Delta^{17}O$ values, the only observable (to date) of the NOx system. These models, Mr. Savarino's included, use an a priori assumption of $\Delta^{17}O$ values in NOx-O_3 equilibrium, this value is then reduced by the fraction of peroxy radical oxidation (as stated in our text), the rates of which are calculated by the photochemical scheme of choice (carbon bond series, RACM, RADM etc). Our paper experimentally shows what the NO_2 $\delta^{18}O$ and $\Delta^{17}O$ values are under the NOx-O_3 equilibrium, required for the initial step of the model, rather than using the assumption.

Mr. Savarino's assertion that isotopic equilibrium occurs at the same rate as chemical equilibrium is also flawed. It is well known that isotope mass balance and scale length are important limitations when comparing the two. For example, CO_2 - ocean chemical equilibrium is rapid (year) but isotopic equilibrium is slow (1,000 years) because of the scale length of ocean mixing. In our case scale length effects should be minimal because of rapid mixing of gases, but mass balance is important. For example, after 1 oxidation reaction between NO and O_3, only ½ the $\Delta^{17}O$ anomaly is transferred as shown by Savarino himself. At two 2 reactions it is 75%, following an exponential decay series and it thus requires 8-10 oxidation-photolysis reactions to achieve isotopic equilibrium, at least 10 times longer that chemical equilibrium. This can be shown in our model, where NOx-O_3 chemical equilibrium occurs in less than 5 minutes, but isotopic equilibrium required 45 minutes, in agreement with the isotope mass balance argument.

"This state is again wrong. As recognized by the authors few lines below"

We do not disagree that NOx-O_3 equilibrium would occur on short time scales under most circumstance. This was shown in the experimental data and modeling results. This is why we state the non equilibrium situation would be “unlikely”. And by unlikely we meant not likely to occur. We have altered the text to say ”highly unlikely” to emphasize that point. However, while Mr. Savarino presumes to know the minimum ozone (30ppbv) and NOx concentrations across the globe, past and present, we do not. For example Pacific and Atlantic ocean summer O_3 mixing ratios are typically below 10 ppbv, and can even drop below 5 ppbv (Figure 15 from Hu et al. 2011). 5ppb levels were also observed by Morin and Savarino, ACP 2007. When initializing our model using that papers Alert Canada values of 10ppb O_3, assuming 20pptNOx, isotopic equilibrium requires 15 (March 29 noon Jcoeff (1.7E-3)) to 20 hours (March 29 6pm Jcoeff (5.6E-4)). Even these lower O_3 mixing values are high relative the natural world because global O_3 has been elevated as a consequence of human emission of ozone precursor gases. A comparison of the latest global chemical transport models, validated by modern O_3 mixing ratios, suggest the remote ocean areas would have 2-15 ppb less O_3 (Figure 11 from Young et al 2013 ACP), suggesting surface mixing ratios could be as low as 300 pptv, two orders of magnitude lower than 30 ppbv assumed by Savarino. At these low O_3 levels, even at mid-latitudes (40 N), the model does not come into isotopic equilibrium until after 18 hours, even using the noon jcoff (.007) and ignoring nights. If one is interested in paleo-chemistry using ice core data, such low O_3 mixing ratios may limit equilibrium over the timescale of NO_2 oxidation into HNO_3 and exchange should be included in models rather than assuming equilibrium. Even here we agree that exchange by O atom only would likely be too slow relative to oxidation, however our model simulations also take into account the NO-NO_2 exchange which orders of magnitude faster than the O + NOx exchange because of the higher NOx mixing ratios and are therefore more important to the equilibrium the O + NOx exchange

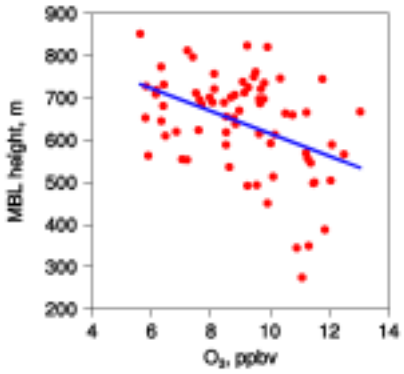

Fig. 15 Correlation between observed MBL height and O_3 during the summer of 1999. The correlation coefficient is −0.43. The blue line represents the linear regression of all data points

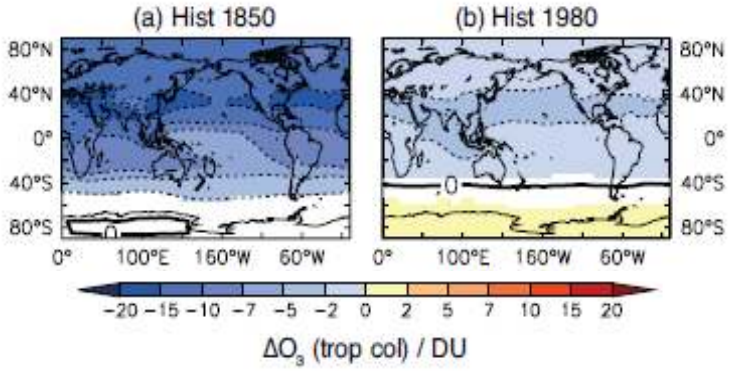

Fig. 11. As Fig. 9, but for the absolute change in surface ozone (ppbv).

Also the assumption of using an average j coefficient to show NOx-O3 equilibrium everywhere and at all times is flawed, and this is clearly relevant with respect to the mass balance issue discussed above. We point out that at high latitudes in winter and at night, the J coefficient approaches zero. When j is zero, only a single oxidation will occur therefore isotopic equilibrium can not be achieved. Clearly NOx emitted at high

latitudes and oxidized to HNO_3 in the polar winter may not reach isotopic equilibrium; a similar situation exists at night. Such an effect may appear in high temporally resolved (day vs night) NO_3^- isotope measurements. This shows that using the simple ratio of rates approach does not represent the isotopic system because it only considers instantaneous reaction rates and not the time evolution of isotope material balance as our model does. Indeed we expected rapid equilibrium and were surprised when the model required significant time to achieve isotopic equilibrium, albeit under extreme circumstances.

We have expanded and refined the final section of the paper to address the miscommunication of our results in our earlier draft and give specific examples of equilibrium times under modern, ambient conditions.