We would like to thank Mr. Wiegel for his polite, insightful and helpful comments as they have helped improve our manuscript and our quest for a better understanding of isotope dynamics during the NOx cycle. In particular his comments regarding the rate of NO oxidation by O_2 after photolysis led to an improvement in the model. We added a dark reaction simulation (discussed in new text) to evaluate the role of O_2 oxidation. In some cases it completes the oxidation of NO into NO_2 (99%) as we previously assumed, while in others there was significant NO remaining in the chamber. Based on this outcome we changed the discussion of the data from it terms of NO_2 to NOx since we likely measuring both NO_2 and NO since both are effectively trapped as N_2O_3. This did not fundamentally change our results however, indeed it improved our model-observation fits since we had been over estimated the influence of O_2, which led to a negative correction in the isotope model values.

"The authors select a J-value for NO2 photolysis that results in model 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."

We have used the lamp specs to calculate a theoretical j coefficient which was higher by a factor of two. Fortunately, the isotope effects are not sensitive to the J value, since to isotope effective is imposed on them. We tested the effect of flux in the model by increasing from 4 to $4*10^{-3}$ but the effect on ozone and NOx δ-values was marginal (this was added to the text). The bulk $\delta^{18}O$ and $\delta^{17}O$ and $\Delta^{17}O$ values change only from 88.9 to 88.3, 91.6 to 91.0 and 45.4 to 45.1 respectively. The delta values of ozone and the NO_2 are not sensitive to the flux value as long as the flux is reasonably close to the real flux in the experiment. It does change the timescale to equilibrium, and was therefore used as the justification for choosing .004 since a higher J would have led to faster equilibrium than what was observed.
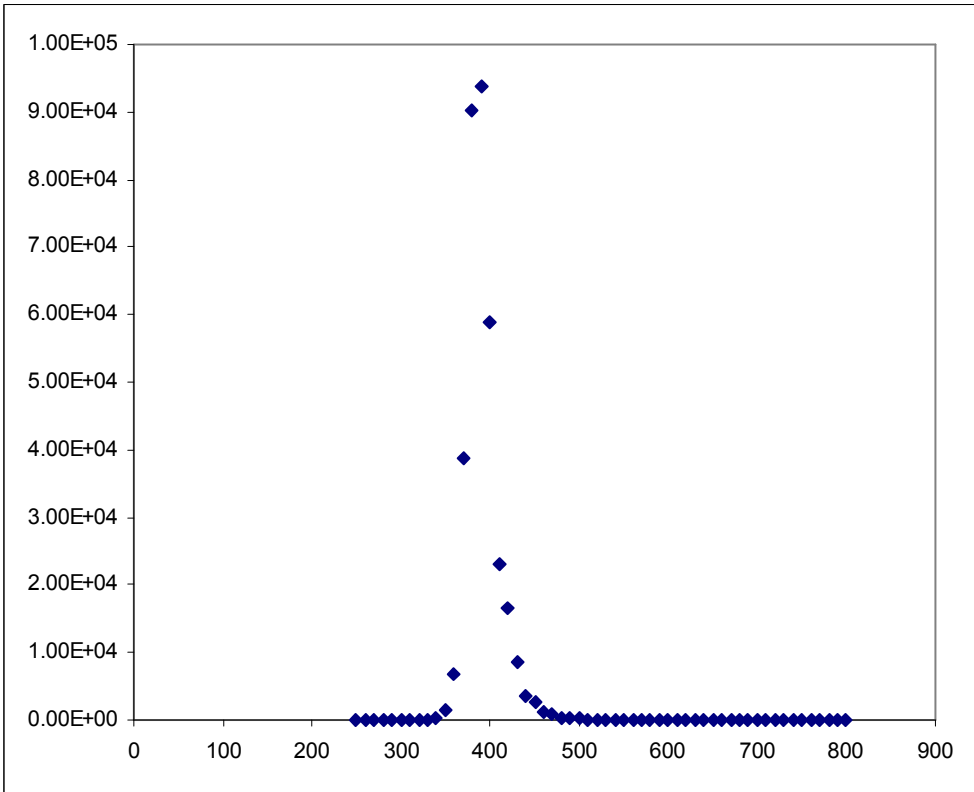
Cross section ratio

The cross section ratio of NO2 to O3 over the range 300 nm to 800 nm varies from 3.2 $*10^{-1}$ at 300 nm to $9.4*10^4$ at 390 nm and again decreasing to 1.7 at 800 nm. There is large change in this ratio. The xenon lamp gives off light from about 250 nm to 900 nm but the major part is from 300 nm. Due to the thick quartz window the UV part is cut off below 300 nm.

We do not have the emission spectrum of the lamp as it enters the chamber and propagates. Therefore, the flux ratio is not known. One can only consider the effective flux ratio to be in the range of a few 100's. We took the ratio as 400 which reproduces the ozone enrichment obtained by Guenther et al. This flux ratio number should be determined by more detailed experiment which is not possible in the present set up. Moreover, this ratio is not important as the ozone dissociation effect does not change the model results significantly as most of the ozone reacts with NO2. The dissociation was considered for completeness. This is explained below.
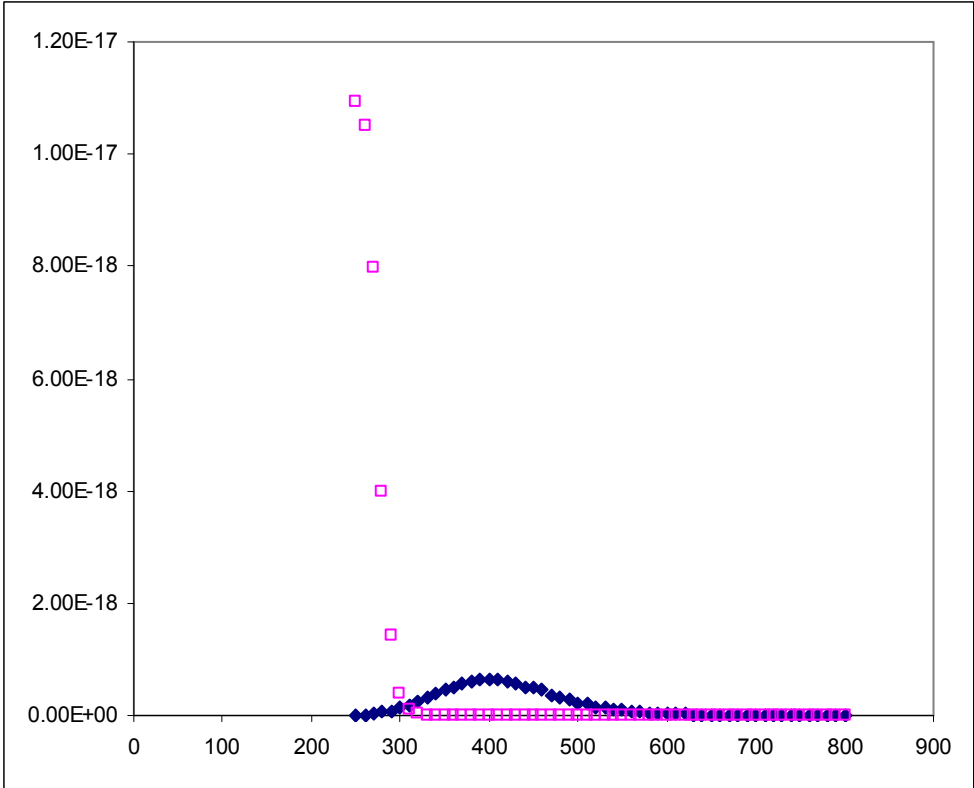
Cross section of ozone and NO2 (pink: ozone, blue: NO2)

Cross section ratio of NO2 to Ozone
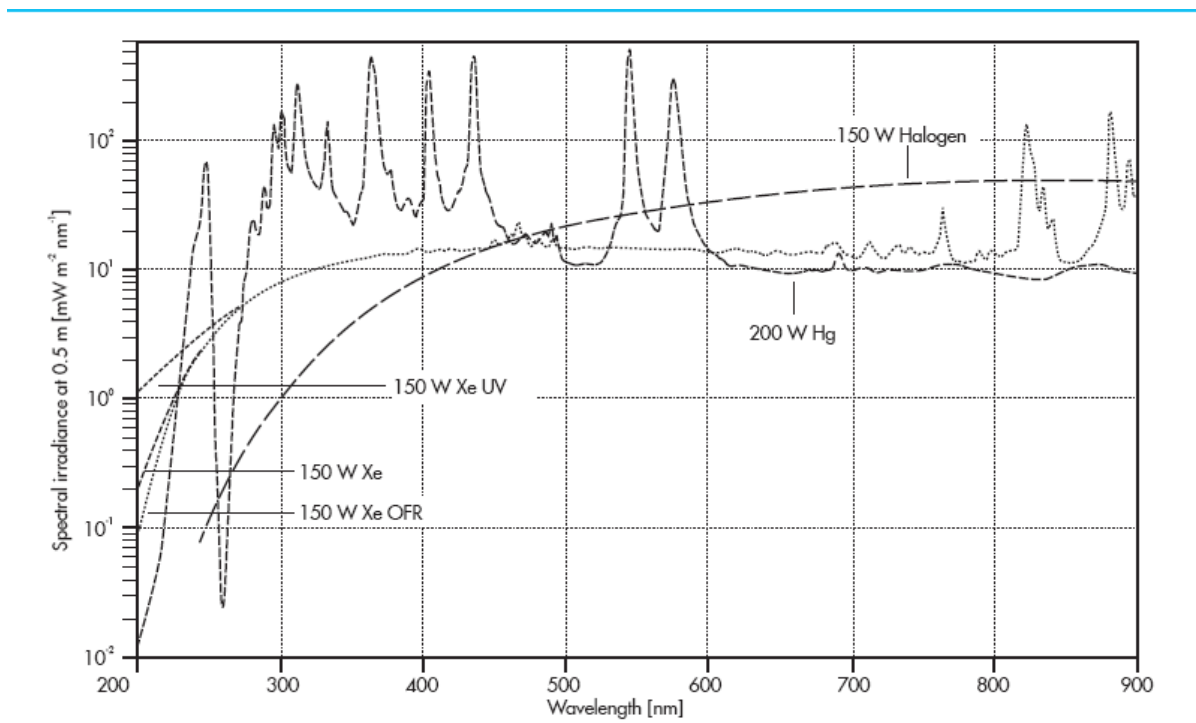
Ozone photolysis isotope dependence

The rate constants used in the model are from experimental numbers as available in previous studies. They have a very small effect in the final delta values as well as in the $\Delta^{17}O$ anomaly of NO_2 predicted by the model. We compare this prediction with experimental numbers. It is true that they would introduce small extra mass independence in the ozone at steady state. But this is not artificial and is quite expected. Photolysis of ozone in case of atmosphere does introduce an extra anomaly (whose magnitude is small) as shown by Liang et al (2006). Moreover, the dissociation rate of ozone is orders of magnitude smaller than ozone lost by reaction with NO and it was considered only for completeness. It does not have any significant effect on the final d-values of NO_2.

Beer's law

We included this calculation in the text as an argument against self shielding and photolysis in a new paragraph on page 14. The Beer-Lampert calculation actually argues against self shielding as the highest $\Delta^{17}O$ had the lowest I/Io (0.97) while the lowest $\Delta^{17}O$ had the mist light attenuation (0.68). The spectrum from the Xe lamp is reasonably flat over the Gaussian cross section shape of the NO2 dissociation (shown above). Also the NO_2 spectrum is convoluted and has chaotic state mixing near the dissociation limit which would likely limit any zero point energy effect during photolysis, because of an

embedded electronic state. Therefore, one does not expect any significant effect due to zero point energy induced isotope dependence in its dissociation. We consider that the rates of dissociation of all isotopologues are the same.

Definition of deltas

The issue of definition of delta in this work depends on what is to be calculated. We take oxygen molecules as composed of three species OO, OQ and OP. This is of course not true in real case but only assumed for the model calculations as have been done by many others. The Q/O ratio under this assumption is obviously given by

Q/O= Total Q atoms/ Total O atoms= [OQ]/{2*[OO]+[OQ]+[OP]

And similarly for P/O ratio. With this composition we compute the d18O of this special O2 gas as:
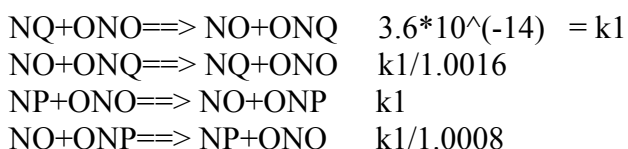
d18O= [{Q/O}/{Q/O}smow-1]*1000

This is just a model delta and obviously cannot be same as the experimentally measured delta. However, it does not matter. In the kintecus model we have to finally compute only enrichment relative to this model delta and that enrichment is not sensitive to this assumption as long as same definition is used for gases before and after the model run. The model evaluation would give correct numbers without inconsistency as long as we use only enrichment. In Table 4 we give the usual delta values just as a guide which cannot be (and should not be) the same as calculated from the relative numbers given. We compute the model d-values as : -8.06 and -13.17 in contrast to the real values: -5.69 and -10.84 (See Table 4). This is quite expected as heavy species of QQ, PP and QP are neglected.

We have checked that the predictions are the same even for very different delta values when enrichments are only considered. The definition given by the reviewer is to be used only if we want to calculate real delta values which include all species. This is expressed by him as [O2]total.

Moreover, there is no inconsistency between NO2 definition and O2 definition as in both cases we are concerned with only relative enrichments.

Exchange equilibrium

The expressions for exchange between NO and NO2 are:

NQ+ONO==> NO+ONQ   3.6*10^(-14) = k1
NO+ONQ==> NQ+ONO   k1/1.0016
NP+ONO==> NO+ONP   k1
NO+ONP==> NP+ONO   k1/1.0008

We used the beta factors of Richet et al at 20 C :

NO===>   1.1017 for Q and 1.0536 for P exchange
ONO===> 1.0923 for Q and 1.0545 for P exchange

So for exchange between NO and NO2 we can take the ratio 1.1035/1.1017= 1.0016 for Q and 1.0545/1.0536=1.0008 for P. The reactions favor heavy isotope transfer to NO2 over NO as expected. We note that the equilibrium constant is nearly equal to 1.00. This has been adopted in our model.

However, for O+QNO or O+NQ exchanges the equilibrium constants are much larger and taken from Richet et al. as noted by the reviewer correctly.

Ultimately, it is difficult to evaluate the NO_x exchange reactions because it is a challenge to try and separate NO and NO_2 and analyze them separately. Since the equilibriums are take as mass dependent it does not change the $\Delta^{17}O$ but may impact the $\delta^{18}O$. We noted in the text that this may be the cause of the model/observed difference in $\delta^{18}O$. For the atmospheric condition simulations this is largely unimportant because exchange is small compared to oxidation.

We have also added several paragraphs discussing the sensitivity of NOx isotope exchange reactions under different conditions and discuss which are important and why.