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***Interactive comment on “A photochemical model and sensitivity study of the triple-oxygen isotopic ( $\Delta^{17}\text{O}$ ) composition of  $\text{NO}_y$ ,  $\text{HO}_x$ , and  $\text{H}_2\text{O}_2$  in a polluted boundary layer” by G. Dominguez et al.***

**G. Dominguez et al.**

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First of all, as I was offered the privilege (!) of reviewing an earlier version of this manuscript, I have to say I was extremely disappointed that many non-controversial scientific and technical corrections provided in my earlier review have not been taken into account by the authors before submitting a new version to Atmos. Chem. Phys. Discuss. I hope the authors will consider the comments below with more care and attention if they wish to revise their manuscript for potential publication in Atmos. Chem. Phys.

We are puzzled by this comment considering that we actually made substantial revisions  
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sions to an earlier version of this paper specifically to address this reviewer's *technical* comments on the manuscript. We point out, however, that not all of these "corrections" dealt with technical aspects of the manuscript, with some of these bordering on editorial/stylistic suggestions. We certainly noted these and even restructured the paper in response. Other comments, however, we did not adopt since we felt they changed the fundamental focus of a paper that is focused on the atmospheric variable  $\Delta^{17}O$ .

## 1 Reply to General Comments

Dominguez et al. propose an exploration of the factors controlling the isotope anomaly ( $^{17}O$ ) of atmospheric nitrate under polluted condition in the lower atmosphere, by means of computer-based simulation. This goal is useful and very timely since measurement-based studies have accumulated quickly in the recent years, providing the basis (and the need) for a thorough investigation of the causes of variability of this new atmospheric variable.

It's encouraging that we agree on the necessity of sensitivity studies in this area of research.

While the goal of this article is of great relevance to the current development of isotopic atmospheric chemistry, the manuscript in its current form suffers major shortcomings in the presentation of the method employed, the discussion of previous work on the topic, and the discussion of the results reached. The presentation and the discussion of the results is at best superficial, and in many cases totally irrelevant to atmospheric chemistry. Most of the "results" provided by the authors seem to be driven more by

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mathematical curiosity than by the need to address atmospheric chemistry issues.

We fundamentally disagree with the statement regarding relevance made by the reviewer and the reviewer has failed to demonstrate how the sensitivity studies performed are “totally” irrelevant, a phrase he appears to be fond of. Could it be that the reviewer is himself/herself in the process of producing work that is similar in scope? If that is the case, then the reviewer should of considered recusing himself, or at the very least, as Dr. Michalski has appropriately done, identified this potential conflict. As such, given the tone of the comments that accompanied the initial review of this paper and the revised paper, we are not confident that this reviewer has met his obligations to provide a fair and constructive review as specified by ACP.

The stated goal of the paper is to provide an assessment of the sensitivity of  $\Delta^{17}O$  to environmental factors. How is the reviewer confused about this point? The simplest way of addressing the importance of factors is to vary these individually as we have done. Mathematical curiosity is essential for establishing the limits and applicability of isotope based techniques that rely on  $\Delta^{17}O$ .

I strongly suggest that the authors take the time to present and discuss their results more carefully, given the potentially high significance of their work. As it, the manuscript definitely does not meet any single criterium for publication in Atmos. Chem. Phys. The first issue to be addressed is the structure of the manuscript. Many sentences throughout the text are introductory in nature, and should be put together in the introduction. Clearly assessing the goals of the paper in the introduction, as well as the potential relevance of the processes taken into account would help the reader (and quite possibly also the authors) to better understand how isotope measurements (and modeling) can be useful for atmospheric chemistry. Before

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presenting the impact of variations of environmental factors on  $^{17}O$  of nitrate, the authors should stress why this study is useful, i.e. whether such variations in environmental factors can occur in the atmosphere, and why it is expected that it has an impact on the  $NO_x$  chemistry and the isotopic composition of atmospheric nitrate.

We are confused here. The structure of the manuscript is in large part left up to authors and we made a choice regarding how to best present to a general atmospheric chemistry community triple-oxygen isotopic measurements and modeling.

Very unfortunately, temporal and spatial scales are totally mixed-up in this article. In terms of temporal scales, one can spot that, even if the focus seems to be put on "polluted boundary layer" issues, which typically develop over time scales of hours to days maximum, references to the Vostok ice-core are provided to support a totally irrelevant sensitivity study to methane mixing ratios ... Another example of spatial inconsistency is that, although the work appears to be based on "polluted boundary layer" issues, some conclusions drawn are applied to Antarctic snow nitrate isotopic composition. The "latitude" test, performed on January 5 for a range of latitudes makes no sense at all, since the composition of the atmosphere varies latitudinally to a great extent (whether the air masses are marine, continental, close to pollution sources or not etc.).

This reviewer has been completely inconsistent in his critique of this paper. In our original submission, this reviewer complained that not enough discussion was given to measurements and modeling of  $\Delta^{17}O$  in Arctic environments. Now the reviewer is complaining about our use of a paper on Vostok ice-core measurements of methane concentrations that was used purely to ground the range of concentrations studied in the current work? If the reviewer has an issue regarding whether the concentration of

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atmospheric gas in ice cores is really an accurate proxy of global concentrations, that is fine, but to suggest that these measurements are “totally irrelevant” seems provincial. We will further address the reviewer’s sweeping “totally irrelevant” comment later in this reply.

Regarding antarctic snow nitrate, last time we checked, photochemical cycling is an important factor in determining the  $\Delta^{17}O$  composition of nitrate found in Antarctica. Does the reviewer feel that radiative transfer and photochemical reaction rates are completely different in these environments? Clearly some aspects of gas-phase photochemistry are universal, with specific environments providing differing inputs, temperatures, and boundary conditions and fluxes.

We are confused as to why the reviewer states that the latitude test “makes no sense at all”? We clearly state that each of the variables tested was varied individually for the explicit purpose of evaluating the sensitivity of  $\Delta^{17}O$  to this variable alone. Clearly, since all other variables are held fixed, the observed variation is the result of changing actinic flux conditions alone and this factor is easier to appreciate, in our opinion, by treating it as an independent variable. Last time we checked, the Pacific ocean by itself appears to have boundary layer chemistry that covers the range of latitudes we tested in our manuscript.

Overall, the sensitivity studies presented in this article are in most case totally irrelevant, and their discussion is also flawed to a great extent. It is strongly advised, to help the authors focus their work and anchor it to known atmospheric chemistry issues, to choose a geographical location where the simulations are performed, and to select a time scale for the study undertaken. A suggestion could be to choose the La Jolla site at the seasonal scale, where year-round isotope measurements are already available (Michalski et al., 2003) and direct comparison can be made. Of course, the method can be applied at other locations, but at present the

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presentation of the results (and their relevance to atmospheric chemistry) is so poor that no sense can be made from the present paper. Once a location is fixed, then the authors can investigate the range of variability of the mixing ratio of the species involved (using previous publications, or measurements from local air quality institutions). This will avoid performing sensitivity studies in a range of variation totally inconsistent with basic atmospheric sciences (see details below). On the other hand, relevant sensitivity studies such as testing the value of ( $\text{N}_2\text{O}_5$ ) could be presented in the paper and will be very useful for the community.

We point out that the latitude in the model runs was fixed except for the latitude sensitivity tests. What the reviewer proposes above is a completely different paper than the one presented here. We agree that such a study would be interesting, but that is not the paper that has been submitted.

Last, differences in  $\text{NO}_3$  between submicron and supermicron aerosol nitrate are alluded to in the abstract, and in different places in the manuscript, but never quantitatively assessed, neither in the results or discussion section. This is a pity, as it constitutes one strong appeal to the manuscript, as inferred from the abstract. Published measurements of these differences can not only be found in Patris et al. (2007), but also in Morin et al. (2009).

We are very perplexed by the inaccuracy of this comment. Please see pg. 13380, lines 4-7 in the conclusions section of this paper where we clearly discuss these results.

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## 2 Reply to Specific comments

The numbering of the sections at the beginning of the paper is particularly awkward, see below: 1. Introduction: triple oxygen isotopic composition of atmospheric species 1.1 Recent work on  $^{17}\text{O}$  of tropospheric nitrate and its precursors 2. Motivation for present work 3. Overview of present work 4. The origin of excess  $^{17}\text{O}$  in atmospheric nitrate 4.1 The conservative nature of mass-independent isotopic signatures All of these sections appear to be introductory in nature, so they are treated together; however they seem to be presented to the reader almost in random order. The beginning of the introduction is extremely vague and general. As the focus here is on atmospheric chemistry, and given that the body of literature has grown considerably in recent years for atmospheric applications, there is no need to spend so many words on the history of oxygen isotopes measurements. Instead of focussing on isotope geochemistry (to little appeal to the ACP readership !), the authors could instead try to demonstrate how isotope measurements can help the isotopic chemistry community to solve problems that could not be solved without the help of isotopic measurements, i.e. what is the value of such an approach (not only to expand the number of things that are measured on Planet Earth). I strongly suggest the introduction is totally rewritten and focused on atmospheric chemistry issues, not on isotope geochemistry, that constitutes only the tool, not the focus, of such a study. With this idea in mind, the authors may be able to write up an introduction that identifies the knowledge gaps in atmospheric chemistry problems, where isotopic measurements could be useful. This includes e.g. ...

With this idea in mind, the authors may be able to write up an introduction that identifies the knowledge gaps in atmospheric chemistry problems, where isotopic measurements could be useful. This includes e.g. NO<sub>x</sub>

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processing in the polluted boundary layer, of major relevance to air quality issues (e.g. Brown et al., 2006). An additional issues where isotopic measurements could help is to what extent halogen chemistry in polluted marine regions contributes to air quality deterioration and oxidative chemistry (ozone production or destruction), as recently demonstrated by Osthoff et al. (2008). These are simple examples to illustrate what could be appealing to the broader ACP readership and more useful to the atmospheric chemistry community. Here is a suggestion for streamlining the introduction in a more consistent manner: 1. Introduction 1.1 General atmospheric chemistry of NO<sub>x</sub>, nitrate; impact on air quality; open issues (heterogeneous chemistry ...) 1.2 Isotopic approach (definition of <sup>17</sup>O); why measuring and studying <sup>17</sup>O in atmospheric nitrate; why focus on <sup>17</sup>O and not values (conservativeness of <sup>17</sup>O, "ease" to perform mass-transfer approaches rather than taking into individual fractionation constants associated to each single chemical reaction) 1.3 Overview of previous isotopic assessments of the chemistry of NO<sub>x</sub>; overview of the modeling approaches used so far. 1.4 Precise definition of the "explicit" approach taken by the authors; overview of the content of the study.

One of the modifications made to the original manuscript submitted to ACPD, at the suggestion of this reviewer, was the inclusion of a summary of recent work using  $\Delta^{17}\text{O}$  in atmospheric chemistry including work done in Arctic regions. It seems our choice of structure for the paper is not to this reviewer's liking and the suggested streamlining could improve the paper. This seems like a stylistic point as it doesn't change the findings and conclusions of the paper. That said, the suggested structure is fair and we are open to restructuring the manuscript if the editor also agrees with the suggested structure.

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chemical species ?

Obviously a typo. Addressed.

Page 13356, line 22 : the definition of  $\delta$  should not be relegated to an appendix.

This also seems like a stylistic point. Defining delta within the text, in our opinion, disrupts the flow of the paper and is better served as a footnote or appendix.

Note that the factor 1000 in the definition is extraneous and should be deleted.

We disagree with the reviewer on this point. The factor of 1000 is not extraneous since it provides the context necessary to explain why the quantity is expressed as deviations from the standard in units of parts per thousand (‰).

Page 13357, line 12: if equation (1) gives the definition used by the authors, then the sign "=" should be used.

Addressed.

Page 13357, line 28: too long sentence, to be shortened. Page 13358, line 4: "we briefly previous measurements" : what do the authors mean here ?

Will be changed to "we briefly review previous measurements" in a final paper.

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Section 1.1, Page 13358 : this "review" of recent work is useless since previous results are not confronted to scientific issues, but rather listed in chronological order. This should be shortened to a large extent.

First of all, we strongly disagree with the reviewer's assertion that this section is "useless". In fact, we are confused by the reviewer's comments here, especially in light of his original review that complained about the lack of a comprehensive review. Now he is asking that this review be shortened?

The goal of this section was to summarize measurements and modeling that have previously been published. Contrary to the reviewer's assertion, this section is not completely in chronological order, but rather is organized from general to specific. Naturally, since the earliest work established the general framework of using  $\Delta^{17}O$  measurements in atmospheric chemistry, these are represented first. Subsequent work, as stated in this section, has modified the original framework of Michalski to include additional chemical pathways that have observable consequences for the  $\Delta^{17}O$  of nitrate.

Page 13359, line 14: The description of the work of Kunasek et al. (2008) is not correct. Geos-CHEM is not a "box model", and simulation were not performed "over three seasons".

We believe the reviewer is misunderstanding our description of Kunasek et al's work. We are explicit in our statement that Kunasek et al. use a box model to do their  $\Delta^{17}O$  simulations. As described in lines 16-18 of this page, Geo-CHEM was used to provide boundary conditions for the box model.

The reviewer is correct that the simulations were carried out for over three years and not three seasons.

Page 13359, line 16: I would be very interested to know what the authors mean by "modeled the data". To me, a model is a mathematical description

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of physical processes, which is used to perform simulations that are, in turn, confronted by data. "Modeling data" makes no sense.

The intent of the statement is clear given the context of the sentence and paper. If the reviewer prefers to use the term "simulate" data, then he should be upfront and state it. Either way, we agree that this is a frequently used, but awkward way of saying we simulated different environmental conditions to assess the effect of these conditions on the atmospheric observable, the  $\Delta^{17}O$  composition of atmospheric species.

Page 13359, line 27: the description of the modeling work by Morin et al. (2008) is not correct. It is nowhere cited in this publication that "a 0D Lagrangian box model [was used] to track the chemistry along the trajectory followed by air transiting to the sampling site". It is clearly stated in this paper that simulations were performed at 40N and 80N, during summer and winter.

We stand corrected. Lagrangian and the tracking of chemistry along the trajectory will be removed in this description.

Page 13360, line 3: "several simplifying assumptions": please detail what are the simplifying assumptions. In which sense are they assumptions? In which sense are they simplifying? To what extent do the authors deviate from using these assumptions, and how?

The reviewer is correct in pointing out our omission of what these simplifying assumptions are and we had assumed that the rest of the paper had clarified this issue. The major assumptions behind all current semi-analytical calculations of  $\Delta^{17}O$  are that 1)  $\Delta^{17}O(OH)=0$  and 2)  $\Delta^{17}O(HO_2)=0$ . We will gladly be more specific in the final version of this paper.

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Page 13360, line 4: "The authors invoked BrO oxidation of NO to explain their isotopic measurements". First of all, this is only correct for springtime. Second, what explains the high  $^{17}\text{O}$  at this season is the role of BrONO<sub>2</sub> hydrolysis.

We agree that we should rephrase this to accurately indicate when BrO oxidation of NO<sub>2</sub> (followed by hydrolysis to form nitrate) is necessary to explain the high  $^{17}\text{O}$  observed during springtime.

Page 13360, line 17: Brothers et al. is not a published study.

We are not aware of restrictions regarding the citing of unpublished work in ACPD. Indeed, this work was recently cited by (Alexander et al., 2009), which appeared in ACPD.

Dominguez et al. (2008) does not deal with NO<sub>x</sub>-nitrate chemistry.

We are confused about the need to comment on this paper since we don't make any claim that this is a NO<sub>x</sub>-nitrate chemistry paper. It is, however, a paper that uses  $\Delta^{17}\text{O}$  in aerosol sulfate in a polluted marine boundary layer and as I'm sure the reviewer is aware, OH and H<sub>2</sub>O<sub>2</sub> are important precursors to atmospheric sulfate.

In addition, a single paper cannot cover the whole chemistry from tropical rain forest to the polluted (marine) boundary layer. As suggested before, the authors are encouraged to select an atmospheric settings where to perform their sensitivity studies. Addressing global atmospheric chemistry in a single paper clearly is too ambitious at this stage ...

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We are again confused by the reviewer's need to point out the obvious. We are under no illusion that this paper is a comprehensive sensitivity study. It is a box model study that explores what factors affect the  $\Delta^{17}O$  of nitrate yes, but also other oxygen bearing species that are important precursors to other species such as OH, HO<sub>2</sub>, etc. In light of the reviewer's sweeping comments above, does the reviewer feel that the recent work of Alexander et al. (2009) is "too ambitious".

Page 13360, line 23: "explicitly". Please define explicitly what is meant here

...

Addressed in the paragraph that followed.

Page 13361, line 25: Contrary to the claim of the authors, this work may be "significant" but it seems not at all "novel" in nature. Indeed, the authors simply seem to have extended to short (less than 1 hr) lifetime species (HOx, NOx) the mass transfer approach developed before for longer lifetime species (e.g. nitrate) by Michalski et al. (2003) and several following studies. In addition, the authors discuss (often inappropriately) the results of several papers mostly based on new measurements of  $\Delta^{17}O$  of atmospheric nitrate, including the development of modeling approaches to interpret them (Michalski et al., 2003; Morin et al., 2008; Kunasek et al., 2008), but they almost never mention modeling approaches developed in the recent past, dealing with shorter lifetime species: this includes the work of Lyons (2001), Zahn et al. (2006) - although the latter lacks tropospheric chemistry- and Liang and Yung (2007). Such studies have attacked the issue of simulating  $\Delta^{17}O$  of atmospheric HOx and NOx, and it cannot be avoided to compare the authors' results with prior work very similar in scope and nature.

It seems that novel and significant may be in the eye of the beholder. To our knowledge,  
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at the time of the writing of this manuscript and the AGU abstract and poster that preceded it, a mathematical algorithm for explicitly propagating the  $\Delta^{17}O$  of atmospheric species was not available in the literature. We examined Lyons and Zahn and did not find any description of a mass balance or mass transfer algorithm. It is possible that they thought that this was too obvious of a detail to bother mentioning. The reviewer is inaccurate in his assessment of our treatment of Lyons (2001) and Zahn et al. (2006). We do compare our results to those of Lyons and Zahn when appropriate, such as in discussing how our model results compared to theirs. The work of Liang and Yung focused on  $\Delta^{17}O$  of  $N_2O$  and does not specify how the isotopic computations were done either. In contrast to the previous work cited dealing with , we do not make use of chemical partition ratios and thus the  $\Delta^{17}O$  compositions that we calculate are in the same manner for both short and long lived species. Our approach does not require the use of approximations that previous work has relied upon, but at the expense of computational efficiency. That price that we pay however, has allowed us to examine and find the deficiencies of the approximate methods previously used as well as identifying the relevance of additional chemical species in the observable  $\Delta^{17}O$ .

Page 13362, line 10: Please change the syntax of this sentence. At present, "emissions" are "oxidized" ...

?

Page 13363, line 8: The authors seem to be doubtful that  $NO_x$  and  $O_3$  are photochemically interrelated. Where do these doubts come from ?

The reviewer misinterprets this statement. We can change this to indicate that during daytime conditions, these are linked via the stated photochemical reactions.

Page 13363, line 15: what does "not typically available" mean ?

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We meant the following: Simultaneous measurements of  $\Delta^{17}O$  of  $O_3$  and  $NO_y$  are not usually available.

Page 13364, true line 4 (pb in the numbering of this page): the authors seem to have misunderstood the study by Bhattacharya et al. (2008).

Ozone made in the laboratory can have a very variable  $^{17}O$  (see Thiemens and Heidenreich III, 1983 ...). So it is not correct so state that the  $^{17}O$  of lab-made ozone is 25 %. In contrast, it is true that Bhattacharya et al. (2008) quantified the degree of isotopic asymmetry of ozone in terms of  $^{17}O$ .

Yes this is a fair point and we agree with the reviewer that this is a misstatement. This will be changed in a final version of the paper.

Page 13364, true line 6 : "finding" ! "findings"

Addressed.

Page 13364, true line 8: The link between the 3rd and 4th sentence of this paragraph can only be understood if the authors explain that the photolysis of ozone mostly produces  $O(1D)$  by expulsion of a terminal  $O$  atom. The proportion (on the order of 90 %) has been quantified by Sheppard and Walker (1983), which surprisingly misses from the reference list.

We thank the reviewer for bringing this paper and omission to our attention. The results of this Sheppard and Walker's theoretical studies of ozone photodissociation are obviously relevant and will be cited in a final paper.

2.2 Section 5 - Photochemical modeling ... First of all, note that the syntax of the title of the section is incorrect (missing "of", probably).

We disagree with the point regarding syntax. If one takes out Photochemical modeling, would the inclusion of "of" before  $\Delta^{17}O$  make sense?

The description of the atmospheric chemistry model used is too short, in particular because very few other studies have used the model used by the authors. It is absolutely needed that the authors provide a complete listing of all chemical reactions used in the model, with explicit references to the reaction rates used (both must be provided as an electronic supplement). This is standard practice for publication of atmospheric chemistry box-modeling.

As we stated in the text, we adapted the code of Yvon et. al to do the  $\Delta^{17}O$  calculations. Because of this, we didn't think it was necessary to republish the list of reactions given that this paper is available in the literature and has been used previously. That said, if addressing this point (which was also made by reviewer Dr. Michalski and who also published  $\Delta^{17}O$  results without a complete reproduction of all of the photochemical reactions of the Yvon et. al paper) is seen as "absolutely necessary", then we will of course produce such a table.

Page 13365, line 10: I believe concentrations (or mixing ratios), and not the species themselves (what would this mean ?), are calculated by the model.

This is a minor point. Obviously the time-evolution of the concentration of species is what is meant. Addressable.

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Page 13366, line 5: it is extremely surprising that ozone is an input parameter for a photochemical box model used in the polluted boundary layer. Apparently the authors ignore that the lifetime of ozone in a polluted boundary layer is only a few hours (because it is titrated by NO emissions, before it builds up due to photochemical ozone production). Thus it makes no sense, in a polluted boundary layer, to have ozone mixing ratios as a fixed input for a photochemical model. Here again, if the authors had chosen a specific situation where to apply their model, they could have realized that this approach is not consistent with a polluted boundary layer.

As explained in our reply to G. Michalski, treatment of ozone as an independent parameter allows us to probe the effect of ozone concentration alone without getting into the details of how it is made. For example, the relationship between NO<sub>x</sub>-VOC-O<sub>3</sub> is admitted a highly relevant (and uncertain!) topic in atmospheric chemistry (Stein et al., 2005), but treatment of VOC chemistry was deemed by us to be well beyond the scope of the modeling study we conducted. Therefore, the simplest way to probe the effect of lower versus higher ozone concentrations alone was to treat this as an independent input.

A few lines below, one discovers that a polluted marine boundary layer is dealt with.

We are confused by this comment given that the manuscript's title is "A Photochemical Model and Sensitivity Study of the Triple-Oxygen Isotopic ( $\Delta^{17}O$ ) Composition of NO<sub>y</sub>, HO<sub>x</sub>, and H<sub>2</sub>O<sub>2</sub> in a Polluted Boundary Layer".

What does this change in terms of ozone life time (up to a month in a clean marine boundary layer in the absence of local NO emissions) ? This confusion must be solved before the authors can proceed with a revised article.

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We are not confused. See our previous statement regarding VOC chemistry.

Page 13366, line 15: the equation presented by the authors is problematic for a number of reasons. For of all, it is dimensionally not homogeneous (i.e., the units don't match). On the right hand side of the equation the little "d" ( $d[X]_j$ ) doesn't match with the rest of the equation.

The reviewer is mistaken here regarding the units of the left and right hand side. Just because a quantity is a differential quantity does not mean that the units have somehow changed. For example, if  $N$  is a number, the differential quantity  $dN$  still remains a number. In this case, if  $[X]$  is a concentration with units of number per  $cm^3$ , the a differential quantity,  $d[X]$  also retains these units.

It looks to me that this equation represents the numerical implementation of a general equation, in the "isotopic sub-model". Rather than providing this wrong equation (what is "i", by the way ???), the authors could explain better their approach by providing the general mass-balance equation. Rather than providing this wrong equation (what is "i", by the way ???), the authors could explain better their approach by providing the general mass-balance equation.

Below is the general mass-balance equation for a given species  $X$  in the atmosphere:

$$\frac{d}{dt}[X] = \sum_j P_j - L \quad (1)$$

where  $P_j$  represents each production flux of the species  $X$ , and  $L$  represents the sum of each loss flux. When isotopes are taken into account, this mass-balance equation now reads:

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$$\frac{d}{dt} ([X] \times \Delta^{17}O(X)) = \sum_j P_j \times \Delta^{17}O(X)_j - L \times \Delta^{17}O(X) \quad (2)$$

In this equation,  $\Delta^{17}O(X)_j$  represents the isotope anomaly inherited by the species X through the production channel j. Note that this equation takes sinks into account, although they do not induce specific isotope anomalies (they are assumed to be mass-dependent). Thus they can be treated together and summed up before applying the equation above (contrary to the source reactions, which induce specific isotope anomalies because the mass-transfer rates are different). The authors are correct to state that individual sinks do not induce isotopic anomalies, but they should be included in the equation anyway, because sinks have a huge impact on the variability of  $^{17}O(X)$  (smoothing effect, discussed later by the authors in terms of nitrate, but this also applies to any other species). In summary, I strongly suggest the authors to include the above paragraph in their article, because it makes the whole concept of mass-transfer much easier to understand. Also, I would like to be sure that the sinks are properly taken into account in the calculations, which seems not to be the case at the moment.

The reviewer is correct in observing that this equation represents a numerical implementation of the algorithm used to calculate the shift in the  $\Delta^{17}O$  of species. The equation as stated is not incorrect, but we admit that it could of been explained more clearly. *i* refers to the iteration in the for loop that steps through the chemistry and photochemistry. The reason why there aren't any sink terms present in the equation stems from how our algorithm was implemented into the 4th order Runge-Kutta integration. At the beginning of each iteration, the change in the isotopic composition of a species X is calculated by adding up all of the sources and their respective isotopic ( $\Delta^{17}O$ ) compositions and recalculating the isotopic composition of species X. Then, the sinks

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for the species X are calculated and these are assumed to be mass dependent, taking away differential amounts of species X with the same  $\Delta^{17}O$ . Because of this, we stated that the sink reactions do not affect the  $\Delta^{17}O$  of a species. Based on this algorithm design, we are confident that the effect of sink reactions, which is to change the reservoir size, was properly implemented. We also ran the code with the sinks preceding the sources and their  $\Delta^{17}O$  contributions and did not find a significant ( $< 1E - 6\%$ ) difference in the  $\Delta^{17}O$  of species we reported. Again, we do admit that this could have been better explained in the paper and will address this in a final version.

We will strongly consider placing the general mass-balance equation and a description of our discrete implementation of this equation in a final paper.

Page 13367, line 10: the formatting of the equations is awkward. Please put them on the same line.

We had some difficulty fitting these equations on the same line. We can address what options are available in LaTeX for making these less “awkward” in a final paper.

Page 13367, line 13: what is Y ???

Y is the uncertainty in the central atom  $\Delta^{17}O$  which we estimated to be 0.9. This will be changed in the final manuscript.

Page 13367, line 19 : a reference clearly misses to support the value of 91 %.

This will again be addressed as before by citing Sheppard and Walker’s work.

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Page 13368, line 8: what is the impact of neglecting mass-independent fractionation on the calculations ? The "explicit" treatment used by the authors should be able to quantify this.

Regarding the  $CO + OH \rightarrow CO_2 + H$  reaction, this effect was ignored since it is a very minor reaction pathway for OH and the  $\Delta^{17}O$  of  $CO_2$  was not tracked in this study since. To do this properly would require its own detailed study.

Regarding the  $H + O_2 + M$  reaction, it is not clear to us what value of  $\Delta^{17}O$  to assign to this reaction based on the information and conditions provided in (Savarino and Thiemens, 1999). Therefore, we set the  $\Delta^{17}O$  of this step as zero as well.

Page 13368, line 10: why is the treatment of so OH specific ? Following the isotopic mass-balance equation above should make it straightforward for each species. Including isotopic exchange reactions should be straightforward. This whole paragraph is very confusing a casts doubts on the whole approach. Or it simply attempts to explain what is the model doing at each time step, which is clearly not helping the reader at all.

Our discussion of exchange reactions focused on OH to illustrate how exchange reactions *in general* were implemented in the computations. Apparently this was not a problem for the other reviewer, but this point could be made more explicit to please the anonymous reviewer.

The discussion on the  $^{17}O$  of OH seems too quick, given that the complete framework (involving OH sinks and sources) was extensively detailed in Morin et al. (2007) and discussed by Kunasek et al. (2008).

If the reviewer feels that the discussion of  $\Delta^{17}O$  of OH was extensively and conclusively done in the works cited above, then we are confused as to why he feels that more

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space should be devoted to discussing this aspect of isotope exchange reactions. In our examination of the treatment given to OH and its  $\Delta^{17}O$ , we felt that our approach handled its isotopic composition without resorting to the approximations given in these papers.

Page 13369, line 3: what supports the lifetimes given here ? References are clearly missing. Such values could be tested during the sensitivity study (variable lifetimes).

We stated in the paper that these lifetimes for fine and coarse aerosols were “rough”. We can obviously place a citation to justify these values in a final paper. Yes, one could vary these values, or the ratio of these two in a sensitivity study. We don’t think that this parameter, of all the other ones tested, will affect the results of the sensitivity tests.

Page 13369, line 7: how much for "your" aerosol nitrate ?

Thank you for pointing this out, although in the future I think the ACPD would prefer that you keep the sarcasm to yourself. We will leave out “our” in the final manuscript.

Page 13369, line 24: the presentation of the values is astoundingly short and does not take into account any of the recent literature on values for  $N_2O_5$  and  $HNO_3$ . The authors are encouraged to go read recent papers on such issues, such as Evans and Jacob (2005), Brown et al. (2006) and more recently by the Thornton group, the Brown group and so on. It is unbelievable that such literature was apparently not read by the authors. This is a crucial issue in atmospheric chemistry at the moment, and the authors have, so far, missed the opportunity to demonstrate (or not) how isotopic approaches could be used to address this issue quantitatively.

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We are very familiar with the work of Evans and Jacob contrary to what the reviewer would like to assert. The reviewer makes it sound like we have committed an atrocity against nature, when this issue is really a minor one. One of the issues that we were interested in pursuing in this study was a better understanding of the role that N<sub>2</sub>O<sub>5</sub> uptake onto coarse sea-salt dominated particles alone may have in producing significant differences in the  $\Delta^{17}O$  of aerosol nitrate found in fine and coarse aerosols in a polluted marine boundary layer, as had been seen by previous workers in the field and in our own unpublished observations of nitrate in a polluted boundary layer. The uptake coefficient for N<sub>2</sub>O<sub>5</sub> we chose (0.05) is not very different from the value cited in Evans and Jacob for sea-salt of 0.03 for RH $\geq$ 62%.

It was not the goal of this study to demonstrate how isotopic approaches could be used to resolve the issue of uptake coefficients, despite what the reviewer may feel should be the focus of this work. This goal is a worthy goal and well motivated. It is conceivable that this could be addressed someday, although based on the results of the sensitivity study we present here, this task may be very challenging requiring that field studies keep track of RH, cloud albedo, back-trajectory conditions such as NO<sub>x</sub> and ozone concentrations. Other factors that could influence the interpretation of  $\Delta^{17}O$  measurements in the field are pointed out in this manuscript and that is one of our central motivations for the sensitivity studies. If the triple-oxygen isotopic techniques are to be used in addressing “crucial” issues in atmospheric chemistry, then sensitivity studies are needed to assess the likelihood that environmental variable X may affect the  $\Delta^{17}O$  measurements and their interpretation.

2.3 Section 6, Sensitivity study ... The first paragraph is introductory in nature and has nothing to do here. In addition, in general sensitivity studies are only presented after a baseline case has been described in detail. This is clearly missing here. In addition, the “baseline” run provided in Figure 1 is done with a totally unrealistic mixing ratio for ozone (1 ppmv ...). It even does not correspond with the “baseline” conditions presented in Table

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2 (where the ozone mixing ratio was set to 9.3 ppbv, which is also very surprising for a polluted boundary layer ...).

This seems to be a difference in style and not substance. By describing the baseline case, we aimed to illustrate how the  $\Delta^{17}O$  of a species, in this case HNO<sub>3</sub>, is coupled photochemically to OH. The 1 ppmv value for ozone, we agree, is not the baseline value. What we intended to say is that all other variables were set to their baseline values, while O<sub>3</sub> was set a 1 ppmv. We will gladly substitute this with a model output that corresponds to “baseline” conditions for all variables including ozone, to avoid confusing the reader.

This whole section on the sensitivity study is extremely disappointing on a scientific point of view. The relevant tests to be performed have not been presented. Instead, the reader is confronted with meaningless tests. Because of this, the review below is very short, and mostly identifies the most blatantly inconsistent “findings”.

We disagree with the reviewers assessment and will address the specific comments below.

2.3.1 Sensitivity to RH First of all, as noted by Greg Michalski (Reviewer comment), (N<sub>2</sub>O<sub>5</sub>) depends on RH. So changing only one variable makes little sense in atmospheric chemistry.

We agree that RH changes the uptake coefficient. At lower relative humidities (below 62%), it drops substantially to 0.005. That’s a valid point and would likely mean that the differences in  $\Delta^{17}O$  produced by our model for submicron and supermicron aerosol nitrate constitute upper limits for RH less than 62%. A note to this effect can be made in a final version of this manuscript.



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Regarding the effect of changing one variable making sense, we have to disagree with the reviewer's opinion. Yes, many variables change in atmospheric chemistry. Some of these are argueably independent of each other, such as NO<sub>x</sub> flux and cloud albedo, while others like temperature and relative humidity can be strongly coupled, leading to correlated effects. We can worry about how all of these affect one another but at the end of the day, we still have to come back to the question of which variables are most likely to be important and then go from there. We have shown, for example, that temperature by itself, does not have as significant an affect on the chemistry as say NO<sub>x</sub> flux or relative humidity. But, this effect would not be clear if temperature and relative humidity were not treated separately.

In addition, a quick internet search revealed to me that the annual range of RH at La Jolla is 60–83 %. Page 13371, line 21, the authors indicate that the diurnal range of RH can be mild or extreme. Such statements should be replaced by quantitative assessments (NUMBERS !)

An internet search? We are confused by the reviewer's inconsistency regarding rigor. The experience of living in Southern California more than suggests that the relative humidity at noon can be quite different than the relative humidity in the evening when the coastal fogs frequently roll in and change the RH quite drastically (from 40% to 100%). For other days, the RH can be quite stable over several days. Over the course of a couple of days of aerosol sampling, the contrast between the RH at the beginning and end of a sampling period ( 2-3 days) can be quite large. All this said, we will be more than happy to provide more quantitative assessments such as mean and standard deviations when describing diurnal ranges of RH in a final paper, but again the reviewer seems to make much ado about nothing. Or, perhaps the reviewer is confusing monthly averages binned for afternoons and evenings with range. This is impossible to assess given that the reviewer doesn't really specify the source of his RH data for La Jolla.

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In short, it is hard to find a place where tropospheric RH is lower than 30%. So any discussion on model results below this value is irrelevant to atmospheric chemistry. In short, it is hard to find a place where tropospheric RH is lower than 30 %. So any discussion on model results below this value is irrelevant to atmospheric chemistry.

We are surprised by this statement given the reviewer's obvious familiarity with Arctic and Antarctic meteorological conditions. Even in Southern California, during so-called "Santa Ana" conditions, the RH in this coastal polluted boundary layer can fall below 20%. Again, perhaps the reviewer is confusing average values, which are easily found with internet searches, to actual meteorological fluctuations in RH.

In addition, what matters really is the specific humidity of the air, not is relative humidity, because results based on RH are only valid at one given temperature. Thus the authors are strongly advised to think deeply about the implications of changing RH, and how such changes translate in changes in for heterogeneous reactions and so on.

We agree that the specific humidity of the air what matters. We note, again, that our *simulations were done at a fixed temperature(!)* so that RH in these cases is directly proportional to specific humidity. We would be more than happy to clarify this point in a final paper. We propose that RH and specific humidity (or water vapor concentration) be simultaneously indicated to eliminate any confusion. In any case, the effect of changing water vapor (or RH at a fixed temperature) is clearly shown and a relevant consideration for atmospheric chemistry in a variety of locations and conditions.

Regarding the effect on heterogeneous chemistry, the issue of sticking coefficients and RH has been addressed.

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2.3.2 Sensitivity to the ozone mixing ratio As outlined above, it makes no sense to fix a constant value for the mixing ratio of ozone in a polluted environment.

We addressed this question in our response to G. Michalski. If one is to consider VOC as an independent variable, then treating ozone concentration seems appropriate.

In addition, the range chosen by the authors ( 0-5 ppbv for clean air, to 20 ppbv for polluted air), should simply have prevented this paper from appearing in ACPD. It simply is a pity to find such egregious numbers in a paper dealing with atmospheric photochemistry ...

We are confused by the reviewer's extreme and unconstructive remarks here. Does he feel that these values are too high? Too low? The reviewer is misrepresenting our paper here since we never state that 20 ppbv is a representative value for polluted air. We actually tested a wider range of values for ozone concentrations (See Figure 1 for example) but found that even by 20 ppbv, the enhancement in  $\Delta^{17}O$  saturates (See Figure 4). What is clear is that there is a large difference to be expected in the  $\Delta^{17}O$  of  $NO_y$  species that originate in environments with relatively low ozone concentrations (<5 ppbv) and those in relatively more polluted conditions but that this dependence is not a linear function.

Given the above confusion, we will be more than happy to specify the range of ozone concentrations explicitly with appropriate citations in a final paper.

2.3.3 Sensitivity to NO<sub>x</sub> fluxes What is the chemical impact of such NO<sub>x</sub> fluxes ? Before assessing the isotopic implications, it is expected that the authors demonstrate whether this makes any sense chemically.

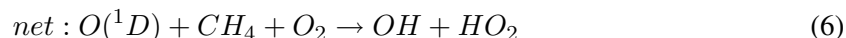
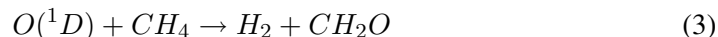
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Aside from affecting ozone, which we addressed previously in relation to VOCs and their role in ozone production, the chemical impact of increased NO<sub>x</sub> fluxes are dealt with in the chemical reaction network that the photochemical model calculates. That is after all the point of doing a sensitivity study.

#### 2.3.4 Sensitivity to methane Simply irrelevant to tropospheric photochemistry at hours to days timescales.

It appears that the reviewer may be confusing issues of time-scales and absolute rates of change on key atmospheric species such as OH and HO<sub>2</sub> as we describe below. Clearly methane concentrations are not irrelevant as shown in Figure 8.

Based on the observed decreases in  $\Delta^{17}O$  of HO<sub>2</sub> (Figure 9.), it seems that effect of methane on the  $\Delta^{17}O$  of NO<sub>y</sub> species may come from the following reaction network:



Both OH and HO<sub>2</sub> concentrations increase as a result of having larger quantities of CH<sub>4</sub> present. The description above illustrates why sensitivity studies, even those partially driven by “mathematical curiosity”, are important.

How can the authors think they can address such issues using a box model with fixed boundary conditions ? Latitudinal changes can only be approached using large scale chemistry/transport model (like GEOS-CHEM, Alexander et al., 2009), because boundary conditions vary very much from place to place.

We are confused here by the reviewer's consistency. Is the reviewer suggesting that only GEOS-CHEM is capable of producing believable  $\Delta^{17}O$  values for atmospheric species at different latitudes? Recent work, including Morin 2008, used box model outputs at two different locations to model  $\Delta^{17}O$  observations. Perhaps the reviewer should consider the broader implications of his assertion.

Even at its core, individual cells within GEOS-CHEM are treated as box models, so the effect of latitude (or equivalently shifts in the actinic flux), in the absence of transport, is built in. Our study, which treats latitude as an independent variable isolates the effect of zenith angle on the production of  $\Delta^{17}O$ . While we don't mention this in this paper and are not interested in "publishing" new data as a comment to ACPD, we have already found that the insights provided by isolating the zenith angle in sensitivity studies to be quite useful for our current work.

Also, what is the relevance of choosing a single date in the year (January 5), when photochemistry is at its winter minimum ??

Winter minimum for the Northern Hemisphere, yes. Is the reviewer forgetting that there is a Southern Hemisphere?!

2.3.6 Sensitivity to cloud albedo It is not clear how cloud albedo is defined. Does this include cloud fraction ? Overall, this whole section makes no sense.

Again, we are confused by the anonymous reviewer's lack of understanding. We clearly specify the range for cloud albedo ranged from 0-1. If the reviewer feels that an explicit definition of cloud albedo and its effect on incoming actinic flux is needed, that is a reasonable suggestion. But, to say that this whole section does not make any sense is to push the limits of credibility. Clearly these tests show that cloud albedo needs to be

taken into account in situations where up to 1/2 of the incoming flux is being reflected by clouds.

Of course Julian Day has a measurable effect. This has been documents from Michalski et al. (2003) onwards. This is called seasonal change in the intensity of photochemistry.

It is insulting, to say the least, that this anonymous reviewer has chosen to take a condescending tone throughout this review. We remind the reviewer that one of the co-authors of this manuscript was a co-author (and PI) of the work described in Michalski et al. (2003). That said, in Michalski et al. (2003), the seasonal shift was attributed to the combination of intensity shift, temperature and RH humidity shifts, and heterogeneous chemistry, but the relative importance of each of these could not be determined. Only a sensitivity study can give you such insight.

3 Section 7, Comparison with ... The authors have "discovered" that  $^{17}\text{O}$  of  $\text{HO}_2$  can be high during the night. However, what is the concentrations at this time of the day ??? What effect can be expected on  $^{17}\text{O}$  of other species? The discussion lacks a clear assessment of the real impact of the findings, which are, in part, driven by the concentration levels.

We agree with the reviewer that, given its potential significance, a lengthier discussion of the concentration and  $\Delta^{17}\text{O}$  of  $\text{HO}_2$  is warranted. We have had similar questions from other experts in the field as well. The most obvious species to be affected by this discovery is  $\text{H}_2\text{O}_2$  and this was clearly discussed in the manuscript. Even the issue of time vs. concentration averaged  $\Delta^{17}\text{O}$  was addressed briefly, although this discussion can certainly be expanded to avoid any confusion.

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Also, the authors find that the thermal dissociation of HNO<sub>4</sub> (pernitric acid, PNA) can yield a significant <sup>17</sup>O in HO<sub>2</sub>. However, to support such a statement it must be demonstrated that there is an isotopic scrambling within HNO<sub>4</sub> before the dissociation. It appears from its structure that O atoms surrounding the central N atom are not equivalent (<http://www.chemindustry.com/chemicals/1230672.html>). Thus the thermal dissociation of HNO<sub>4</sub> does not necessarily lead to HO<sub>2</sub> with a different <sup>17</sup>O than before HNO<sub>4</sub> is formed. Clearly this requires more investigation.

When coding for the isotopic transfer of this reaction, we had to make a choice. How would the potential importance of this reaction be assessed without mathematical curiosity? We agree that this requires more investigation.

The discussion of <sup>17</sup>O of NO<sub>2</sub> could have been interesting, as it was recently shown that the photochemical steady-state does not hold throughout the night, so that the "classical" formula for <sup>17</sup>O of NO<sub>2</sub> does not always hold (see the recent interactive discussion on Alexander et al., 2009).

As the reviewer is well aware, this manuscript was originally submitted before the appearance of Alexander et al. 2009 and the interactive discussion that followed. Are we to assume that the reviewer would like us to cite a discussion that followed the original writing of this paper?

It appears here that the authors want to include HO<sub>2</sub> as a species bearing a positive <sup>17</sup>O in this equation, which could be interesting. However, it seems that HO<sub>2</sub> is not treated explicitly (see Page 13378, line 13).

The reviewer is misunderstanding our work. In the sentences before line 13, we clearly note that in order to compare the  $\Delta^{17}O$  outputs of our model to those of the "classical" partitioning approach taken by previous work, we had to calculate what values of

$\Delta^{17}O$  would be produced by the “classical” partitioning approach. Our model, just as Kunasek et al. (2008) does not calculate the rate of oxidation of NO by  $RO_2$ . That is why line 13 appears in this discussion.

Also, it is not clear how the difference ( $\epsilon$ ) can be negative, and not positive for the baseline case. Maybe a confusion?

This was actually discussed in the paper.

Last, the choice of  $\epsilon$  is very poor, as this generally refers to isotopic fractionation.

The audience is a general atmospheric chemistry audience. We don't think this choice is poor or confusing and neither did the other reviewer. Would the reviewer like to make a suggestion for this variable that is not redundant with any other definition used in some other field?

Why is this plotted vs. total ozone column ? Here again, this has no relevance to polluted boundary layer issues.

Total ozone column affects the spectral actinic flux that reaches the troposphere. The relevance of total ozone column densities was clearly recognized by Michalski et al. (2003), so we are confused as to why the reviewer asserts that this has no relevance. It clearly is relevant.

There are again many problems in the typesetting here: Page 13378, equation 8 : check the parentheses Page 13378, line 17: what does "ref-sec:isotopesubmodel" mean ?

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These are typos and LaTeX cross-references and can be fixed in a final paper.

3.1 Conclusions In the conclusion, the link with atmospheric processes in polar areas is not supported by solid evidence. In addition, the authors seem to ignore that atmospheric chemistry under polar conditions proceeds under very different conditions and that reactivity of nitrate after deposition on the snow has a major impact on the overlying NO<sub>x</sub> budget (Davis et al., 2008). Thus drawing conclusions from the present study into the results presented by McCabe et al. (2007) is at least purely speculative, on the basis of the results presented here. Same with the reference to the work of Alexander et al. (2004). Both should simply be removed, or the authors should undertake a specific study, dealing with polar regions.

The increase in  $\Delta^{17}O$  observed by Alexander et al's (2004) paper was attributed to increased NO<sub>x</sub> flux in *North America*, which is not a polar region. If the reviewer would like to quibble with that interpretation, he should talk to Alexander et al. We are merely pointing out that the box model sensitivity tests are consistent with that interpretation.

The effect of total ozone column density on the  $\Delta^{17}O$  of nitrate that is produced as a result of photochemical cycling is not speculative. Is the reviewer suggesting that total ozone column somehow ceases to be important in polar regions? He has not given a citation showing this and thus we are confused by the statement.

We agree that a statement on the importance of the photochemistry of nitrate found in the snow would clarify that the issue of  $\Delta^{17}O$  variability is complex, with post-depositional photochemistry being important, but to say that total ozone column and its likely relevance for polar regions is not true, is very hard to understand.

4 Plots Almost all plots refer to an unknown chemical species (NO<sub>3</sub><sup>-1</sup>) ...They all are very poor in design, not informative; the captions are useless. All of them should be redrawn, following up the entire revamping of

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the paper, with a much more focussed approach and the identification of atmospheric chemistry issues to be solved using stable isotope approaches.

We are confused, given that  $\text{NO}_3^{-1}(C)$  and  $\text{NO}_3^{-1}(F)$  were defined repeatedly in the text of the paper. If the reviewer is suggesting that it would be more helpful to the reader if these quantities were defined in the captions, for each and every figure, then the above comments could be classified as being constructive.

5 References Many missing references (some indicated in the text above). In contrast, too many references from isotopic geochemistry; at least half of them should be eliminated from the reference list. This distracts the reader's attention and brings nothing to the discussion on atmospheric chemistry.

We are confused. The reviewer took great offense that we did not cite Sheppard and Walker's work previously and now he thinks we have too many geochemical references? At least half of them should be eliminated? Which ones? How are references a distraction? Shouldn't the need to cite references be driven by the need to support claims made in a paper?

Many errors in authors names (e.g. Rockmann ! Ršckmann etc.), chemical formulae, wrong formatting. eg. Page 13382, line 10: Please fix the extraneous "?". Page 13383, line 2: fix the missing exponents In addition, why is Morin et al. (2007) listed twice ?

These obviously can be addressed and are errors in the bibliographic database.

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## References

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 13355, 2009.

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