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Atmospheric
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Discussions

Interactive comment on “Pronounced signature of arctic surface ozone depletion events after polar sunrise on Δ^{17}O in atmospheric nitrate” *by* S. Morin et al.

Anonymous Referee #1

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1 General Remarks

The paper describes new observations of the O isotope composition of arctic particulate nitrate in combination with measurements of ambient ozone. An interesting correlation between $\Delta^{17}\mathrm{O} = \delta^{17}\mathrm{O} - 0.52 \times \delta^{18}\mathrm{O}$ and the ozone mixing ratio is found. The comparison with a model scenario supports the assertion that changes in oxidation pathways may well lead to the observed variability in particulate nitrate. This requires that NO_x is oxidized by BrO and that hydrolysis of $BrONO_2$ is an important pathway of nitrate formation during ODE events. The observation itself, the latter conclusions as well as a potential application to the paleo-chemistry of the atmosphere clearly place this manuscript within the scope of ACP.

Very long sentences and not always appropriate terminology make the article sometimes difficult to read. But more importantly, the reasoning and the conclusions don't seem to be stringent at times. In particular, the discussion of the isotope composition of tropospheric ozone appears to use wrong conclusions or ignores existing field measurements (which are in conflict with the assumptions of the paper). Because the ozone anomaly is the (direct and/or indirect) source of what is finally measured in particulate nitrate, proper quantification and discussion of related uncertainties are a "must". At this point, the paper needs major revision. Revision of the paper may also be required, because—contrary to what is stated—equilibration of OH with H_2O may not be fast enough to rule out an anomaly in OH.

The structure of the discussion section (4) is not clear and complicates understanding of the presented achievements. At the end, it remains obscure how results were tested, whether they have been inferred or predicted. Finally, what are the quantitative estimates with respect to the importance of individual oxidation pathways? The results of the Monte-Carlo simulations, that provide such information, lack any error assignment!

2 Specific Comments

1. $\Delta^{17}\mathrm{O}$ of tropospheric ozone, section 4.5.1

   Despite the importance of a correct value of $\Delta^{17}\mathrm{O}(\mathrm{O}_3)$ for quantitative modeling (one goal of the paper), the value of $\Delta^{17}\mathrm{O} = 35‰$ has not been chosen in a convincing and transparent way. Instead, arguments presented in favour of 35‰ are misleading and confusing. They are misleading, because literature data are not always cited correctly and they are confusing, because interpretation of the field data is in conflict with standard reasoning. This situation may partly be due to some inconsistency in the literature. Since one of the purposes of the paper is to establish a quantitative isotopic tool, a thorough reevaluation and balanced account of the literature data is necessary. If discrepancies on tropospheric ozone cannot be resolved, it will be necessary to discuss the implications of the associated uncertainty in ozone (which appears to be quite large $\sim 10‰$) for the interpretation of the data on particulate nitrate.

(a) References to literature values

– "We use the widely accepted tropospheric value for $\Delta^{17}O$ of 35‰ (Thiemens, 1999; Röckmann et al., 2001; Lyons, 2001; Michalski et al., 2003, 2005; McCabe et al., 2006)."

Thiemens (1999) is an inappropriate reference. Neither a value for $\Delta^{17}O(O_3)$ is reported, nor is a value of 35‰ mentioned. There are three-isotope data in a plot (Fig. 2), but they do not refer to an atmospheric situation and give much lower values. In the section on atmospheric ozone, one finds references to the field measurements (Krankowsky et al., 1995, Johnston and Thiemens, 1997), but no values are given.

Instead of what is quoted, Röckmann et al. (2001) use $\Delta^{17}O(O_3) \simeq 40‰$.

– "To the best of our knowledge, only two studies (Johnston and Thiemens, 1997; Krankowsky et al., 1995) attempted to describe this variable in the troposphere based on field measurements."

The work of Krankowsky et al. (1995) is cited, but the corresponding $\Delta^{17}O(O_3)$ value of about 25‰ is not mentioned and does not find consideration. Why? Only the results of the other field study are discussed later. Furthermore, both field measurements are played down ("they attempt to describe") in comparison to the previously mentioned references. These references, however, either refer to the same two field measurements, or to a modeling paper (Lyons 2001), or they make reference to stratospheric measurements (Johnson et al., J. Geophys. Res., 105, 9025–9031, 2000.). The modeling paper, in turn, is based on an *ad hoc* assumption on the isotope effect in ozone containing ^{17}O and it neglects the pressure dependence of the ozone isotope effect and therefore likely overestimates tropospheric values. The stratospheric measurements (Johnson et al. 2000) not only have a very large uncertainty but also cannot be representative of the troposphere.

– "Johnston and Thiemens (1997) show highly variable measurements, with $\Delta^{17}\mathrm{O}(\mathrm{O}_3)$ ranging between 22 and 35‰ depending on the environmental conditions at the sampling site, and especially the $\mathrm{NO_x}$ load of the atmosphere."

Taking mean values from Johnston and Thiemens (1997) for three different sampling sites (Table 4 in their paper) one calculates 21 ± 5, 26 ± 9 and 31 ± 15‰ for $\Delta^{17}\mathrm{O}(\mathrm{O}_3)$ at the different sites (errors of the mean were calculated from individual data points). How has the range of 22 – 35‰ been obtained from the data and why has the highest value of that range been chosen as a representative number?

It seems that tropospheric measurements are more compatible with a value of about 25‰ (see also discussion below) and that the higher value of 35‰ used in the literature is essentially based on *ad hoc* assumptions and simplifications made by Lyons (2001).

(b) Discussion of tropospheric measurements

The use of $\Delta^{17}\mathrm{O} = 35$‰ despite of the observation of much lower $\Delta^{17}\mathrm{O}$ in La Jolla and Pasadena can certainly not be justified by the reasoning given in the manuscript: "Johnston and Thiemens (1997) show highly variable measurements, with $\Delta^{17}\mathrm{O}$ ranging between 22 and 35‰ depending on the environmental conditions at the sampling site, and especially the NO_x load of the atmosphere. According to these authors, 'the greater the degree of photochemistry, the more mass-dependently fractionated the ozone' i.e. the lower the $\Delta^{17}\mathrm{O}$, because it is controlled by the balance between ozone formation (mass-independent) and its decomposition (mass-dependent)."

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> Mass-dependent decomposition may alter the isotopic composition of ozone, but mass-dependent processes don't have *any* effect on $\Delta^{17}\mathrm{O}(\mathrm{O}_3)$ acquired in the process of ozone formation. This is because mass-dependent processes conserve any offset with respect to the terrestrial fractionation line in a three isotope diagram. Variable $\Delta^{17}\mathrm{O}(\mathrm{O}_3)$ therefore may imply i) there is a mass-independent decomposition process for ozone, ii) ozone formation conditions have been different at different sites (variable $\Delta^{17}\mathrm{O}$ in ozone formation) iii) there are measurement artifacts or iv) the observed variation is a combination of effects i) – iii). Given these consequences, there may have been a problem with the high 31‰ data of Johnston and Thiemens (1997) that carries a large uncertainty as compared to the others. Nevertheless, within error limits, the value is still compatible with $\Delta^{17}\mathrm{O}(\mathrm{O}_3) \simeq 25‰$.

There appears to be no obvious reason why the measurements of Krankowsky et al. (1995) and Johnston and Thiemens (1997) should not be trusted. In particular $\Delta^{17}\mathrm{O}$ is usually regarded a robust quantity. Therefore $\Delta^{17}\mathrm{O}(\mathrm{O}_3) \simeq 25‰$ must be used in the analysis or better justification for the use of another value must be presented.

2. Equilibration of OH with H_2O

Lines 13-15 on page 6277 claim "In all meteorological conditions found in the Arctic basin, the equilibration between H_2O and OH is always the fastest process, compared to other sink reactions for OH." Is this really true? At the low temperature limit ($T = -30°$C, see l. 6, page 6262), the rate for exchange with water is 4.1×10^{-17}, whereas reaction with CO proceeds at 2.4×10^{-13}. Assuming about 100% rel. humidity (a mixing ratio of 0.04%) and 100 pbb CO, reaction of OH with CO is about $y = (2.4 \times 10^{-13}\ 10^{-7})/(4.1 \times 10^{-17}\ 4 \times 10^{-4}) \sim 1.5$ times *faster* than exchange. At lower humidity and in the presence of other OH sinks

(CH$_4$,...), isotope equilibration with H_2O will be even more ineffective. Anyway, complete equilibration will require something like $y \leq 0.3$.

It therefore appears that equilibration with H_2O is not guaranteed under *all* conditions and will depend on the concentration of CO, CH$_4$ and others. It is not clear whether this has really been taken into consideration, but—quite interestingly—equilibration of OH with H_2O may be too slow to assure $\Delta^{17}\mathrm{O(OH)} \simeq 0$‰ under extreme arctic and antarctic low temperature conditions (perhaps at temperatures as high as $T \simeq -20°$C). This would be due to the strong T-dependence of the exchange reaction and the reduced water content at low T. Nevertheless, it is recommended to give a number for the upper limit of the rate ratio y that was obtained under the measurement conditions.

3. Discussion, section 4.

The discussion section is about 17 pages long which has to be compared to roughly 12 pages that make up the remaining text. This (spatial) emphasis on the discussion all the more requires a good structure and that the layout of the section is reflected in the corresponding summary and section headings. Unfortunately, this is not always the case.

The structure of the whole section is described as follows: "In this section, we first review the current knowledge regarding the origin of the isotopic anomaly in atmospheric nitrate and adapt it to the conditions experienced in the arctic springtime. Based on this analysis, we then derive from known chemical mechanisms a relationship between $\Delta^{17}\mathrm{O}$ in inorganic nitrate and the relative magnitude of the processes involved in its formation. We test this relationship using measured or estimated variables during the course of the measurement campaign, using a simple Monte-Carlo approach."

First, I think it is impossible to understand the meaning of the last sentence of the summary. Then, the above summary seems to correspond only marginally to the layout of the section, which is given by

4.1 Overview of the present theory about the origin of $\Delta^{17}\mathrm{O}$ to atmospheric nitrate
4.2 Bromine oxides and ozone depletion events
4.3 Oxidation of NO in the Arctic
4.4 Nitrate formation
4.5 Estimation of variables of Eq. (18) and implications

It is not at all evident where isotopes come into play (other than in the overview section 4.1). Heading 4.5 does not tell anything (without actually looking up and understanding the equation). And the above mentioned Monte-Carlo method, that according to the short summary is used to check one of the papers main derivations, is "hidden" in the section entitled "4.5.3 $[\mathrm{BrO}]^\dagger$".

In similar veins, the content of section 4.3. is summarised as "We now examine the competition between the three major NO oxidants identified in the arctic troposphere in springtime (O_3, RO_2 and BrO), in terms of kinetics and the subsequent influence on the isotopic composition of oxygen in NO_2.". Nevertheless, after the discussion of the NO + O_3 and the NO + RO_2 reaction in two separate subsections, suddenly a subsection on the evaluation of $\Delta^{17}\mathrm{O(BrO)}$ follows—even though one would logically expect that paragraph only *after* the discussion of the general kinetics of BrO + NO.

Since one goal of the section is to demonstrate the use of $\Delta^{17}\mathrm{O}(\mathrm{NO}_3^-)$ as a tool for identifying oxidation pathways, the following streamlining is suggested: 4.1. general (i.e. not specific to isotopes) chemistry, with subsections on the different aspects (BrO, ODE) and identification of oxidation pathways. 4.2. isotopic signatures of sources and products of the oxidation pathways (with all the details and open questions). 4.3. quantification of different oxidation pathways based on the measurements and the derived relation, comparison with existing knowledge. The advantage over the present organisation is that the streamlined version could avoid some redundancies, namely those topics in section 4.1 that are later repeated and discussed again. It would also allow to nicely separate between already known facts (on the subject of arctic chemistry) and new insights provided by the authors (who critically discuss, evaluate and apply isotope chemistry).

As a final remark, the Monte-Carlo results are presented without error estimates. If the simulation is to serve as a test, then the pressing question is, how sensitive to assumptions are the derived variables and how significant are they?

3 Minor Comments

1. p. 6256, l. 16-20 "In addition, the isotopic finger print of the activity of ozone in a relatively stable compound appears somewhat promising in the perspective of using the isotopic composition of nitrate embedded in polar ice-cores as a paleo-indicator of the atmospheric ozone level that may yield an indirect proxy for the oxidative power of past atmospheres." How does this agree with or contradict the following statement made in the conclusion section? "This extended theoretical framework predicts that, [. . .] Indeed, we found evidence for such a situation in samples collected at Barrow, Alaska in March 2005 (Morin et al., 2006), where the linear correlation between $\Delta^{17}\mathrm{O}(\mathrm{NO}_3^-)$ and the ozone mixing ratio reversed for low ozone mixing ratios."

2. p. 6257, l. 3-4: "Due to a mass-independent formation process experimentally discovered by Thiemens and Heidenreich (1983), the oxygen isotopic composition in atmospheric O_3 . . . "

   This statement is imprecise. One immediately asks, what is this mass-independent formation process? How is it related to atmospheric ozone? Perhaps: "Due to ozone formation $O + O_2 + M \rightarrow O_3 + M$ being a mass-independent process, …". Also, "composition in" → "composition of"

3. p. 6261, l. 10-15: Definition of $\Delta^{17}O$
The non-linearised eq. (1) is introduced as the "best" definition describing deviations from a standard mass-dependent behaviour, which is also claimed to be an "unambiguous" definition. Eq. (1) is not completely unambiguous in the sense that λ' is not well defined in an atmospheric environment. For the bulk Earth, i.e. for terrestrial silicates $\lambda' = 0.525$. Other specific physico-chemical systems (like meteoric water which has $\lambda' = 0.528$, see Li and Meijer (1998)) have different constants. As cited by Miller (2002): "Matsuhisa et al. (1978), who calculated the logarithmic reduced partition function ratios $\ln(Q_{17}/Q_{16})/\ln(Q_{18}/Q_{16})$, equivalent to the isotopic fractionation factor ratios, for a number of oxygen compounds and exchange reactions. A range of 0.520 to 0.528 was reported for equilibrium conditions, whereas calculations for diffusion processes indicated greater variation, from 0.500 to 0.523." There exist even more pathological cases (e. g. Weston, J. Nucl. Sci. Tech., 4, 295–299, 2006.). In particular ozone equilibrated with molecular oxygen should have $\lambda' > 0.53$ (Weston, 2006). Therefore, the words "best" and "unambiguous" should be used only cautiously, at least in the context of atmospheric nitrate, which appears to obtain its isotope composition through multiple processes. Part ($> 50\,\%$) of the observed difference (0.74‰) between the use of the linearised definition and the one in eq. (1) may be due to the fact that in one case the constant 0.520 was used and in the other case it was 0.525!

4. p. 6257, l. 17-18 A reference to Thiemens (1999) for the linear definition is somewhat unfortunate, because molecular masses instead of atomic masses were used to calculate the fractionation constant λ in Thiemens' paper. Weston (Chem. Rev., 99, 2115–2136, 1999.) gives the correct expression and may therefore be a better reference.

5. p. 6262, l. 7-11: Please add information on pressure.

6. p. 6274, l. 1-2: "The conversion of molecular fractions into atomic ratios is performed using the following equations (Janssen, 2005)": Janssen (2005) did not consider NO_2, RO_2, BrO and there are no such equations given except for the case of ozone. Therefore, it is not a suitable reference.

7. p. 6274, l. 10-15: The result presented in lines 12-15 takes a lot of space. Since it is well explained what needs to be done to obtain the result on the following page (and it is simple algebra anyway) this step should be omitted. It is suggested to modify lines 10-11 according to: "Finally, combining this equation with the linear definition of $\Delta^{17}\mathrm{O}$ (eq. ()) and using $\Delta^{17}\mathrm{O}(\mathrm{RO_2}) \simeq 0$ gives:"

8. p. 6275, l. 10-12: "Additionally, as discussed above, $\Delta^{17}\mathrm{O}(\mathrm{RO_2}) \simeq 0$. We therefore rewrite an approximated form for this equation:" The equation has already been used to derive the equation in line 2 of the same page. The first sentence should be removed completely.

9. p. 6277, l. 9-15: "Dubey et al. (1997) have measured the kinetic rate for the isotopic exchange of $^{18}\mathrm{O}$ between OH and gaseous H_2O at various temperatures. Such an equilibrium is mass-dependent, therefore one expects the exchange rate of $^{17}\mathrm{O}$, and hence the equilibration of $\Delta^{17}\mathrm{O}$ between these two oxygen-bearing species to follow the same temperature dependency. In all meteorological conditions found in the Arctic basin, the equilibration between H_2O and OH is always the fastest process, compared to other sink reactions for OH."

   The second sentence interrupts the flow of arguments between the first and the last one. It should be moved to the end. Moreover, the second sentence is misleading and should also be reconsidered. It is completely irrelevant here whether a reaction is mass-dependent or not. The gross temperature dependence of isotopic rate coefficients is about equal. Finally, one should probably talk about equilibration of OH with H_2O, because, H_2O being of much higher abundance does not adjust to OH—essentially, it is the other way round.

10. p. 6283, l. 20-22 "This complements the widely accepted crucial role of this process in recycling BrO and acting to destroy ozone in the arctic boundary layer in springtime (Fan and Jacob, 1992)." The meaning of this sentence is not clear. Did you mean" This complements existing knowledge about the crucial role . . . "?

11. p. 6283, l. 22-25 "We also showed that, in the conditions experienced during our measurement campaign, the expected increase in BrO mixing ratio during strong depletion events did not happen significantly, since the correlation between $\Delta^{17}\mathrm{O}(\mathrm{NO}_3^-)$ and the mixing ratio of ozone during the sampling interval was not changed at low ozone mixing ratio." This is hard to read. Perhaps: "We have also shown that the BrO mixing ratio did not increase significantly during our measurement campaign. This result may have been unexpected, but it is indicated by the correlation between $\Delta^{17}\mathrm{O}(\mathrm{NO}_3^-)$ and the ozone mixing ratio persisting even at low ozone levels." However, the arguments are not quite clear here. Are you referring to ozone mixing ratios below 10 ppb? Fig. 4 indicates that the three points with the lowest ozone mixing ratio actually define the correlation. Without these points, no significant correlation would exist at all, questioning the validity of the argument. Moreover, where does the expectation of increased BrO levels come from? According to sec. 4.5.3, increased BrO is only to be expected for $O_3 < 5$ ppb (Hönninger and Platt, 2002), which, taking average concentrations, does not apply to your measurements (see Fig. 3).

12. p. 6283, l. 26: "This extended theoretical framework predicts that, . . . " Do you mean "Our modeling (calculations) predicts (predict) . . . "? I tend to follow the convention that connotation to a theory or, similarly, mentioning a theoretical framework should be reserved for hypotheses or models that have a *broad* range of applications and consequences (e.g. continental drift, atomic theory of gases,

. . .).

13. p. 6284, l. 14-16: "during ODEs, the ozone mole fraction drops are associated with a strong decrease in the oxidative power of the atmosphere, as O_3 is a prominent oxidant of the atmosphere and chemically linked to HO_x chemistry." Is this an evident argument or just an assertion? Can't halogen compounds make up for the loss of ozone with respect to the overall oxidation capacity?
14. p. 6297, caption Fig. 6: "The calculated isotopic anomalies are based on the analysis summarized in Eq. (18) and variables measured or estimated (see text for details)." It is always a little bit annoying to jump between figures and text. If reference to the text needs to be made, it helps to refer to the relevant section. Where is Eq. (18), by the way?
15. p. 6296, caption Fig. 5: Do you mean "Simplified processes for the release and the cycling of BrO are included in this figure", or "Processes for the release and the cycling of BrO have been simplified."? "in this figure" seems to be redundant information.
16. p. 6296, caption Fig. 5: "This has no implication on the isotopic budget presented here since gas-to-particle conversions obey mass-dependent relationships." I am not sure about the validity of this statement. Recently, heterogeneous condensation/oxidation of refractory monoxides (by O atoms or H_2O molecules) has been suggested to be a mass-independent process causing mass-independent oxygen isotopic compositions in some meteorites (Marcus, J. Chem. Phys. 121, 8201–8211, 2004.).

4 Technical & Spelling

1. p. 6256, l. 14 "high variability"—what is high? "variability" is better, more precise.

2. p. 6257, l. 9 The lin. definition of $\Delta^{17}\mathrm{O}$ should appear as a numbered equation, because this definition is central to the paper.
3. p. 6257, l. 13-14 "Michalski et al. (2003) showed that atmospheric models could reproduce the temporal evolution of the anomaly measured in particulate nitrate oxygen in a polluted marine boundary layer." The term "atmospheric model" nowadays refers to something more complex than 0D kinetic box modeling and in the reference cited, only one model is described. "anomaly measured in particulate nitrate oxygen" → "oxygen isotope anomaly measured in particulate nitrate"
4. p. 6257, l. 27 "enhances" → "enhance"
5. p. 6258, l. 1 "existing theories" → "existing models or hypotheses" in order to avoid overuse of the word "theory", see no. 12 in 'Minor Comments'
6. p. 6261, l. 12: hardly readable outer parentheses in eq. (1) are superfluous and should be omitted.
7. p. 6264, l. 21: Did you mean "isotopic composition of TIN"?
8. p. 6266, l. 15: "to" → "in"
9. p. 6266, l. 15 & 21: "Theory" is a grande word for what seems to be more of a hypothesis, see also remark no. 12 in 'Minor Comments'.
10. p. 6266, l. 25: "...role an interacts greatly": "and" has lost its "d" and a better word for "greatly" is "strongly"
11. p. 6267, l. 5 & 16: Finlayson-Pitts and Pitts (2000) is not an original reference but a textbook. If it needs to be cited, it is better to use (e.g. Finlayson-Pitts and Pitts 2000)
12. p. 6267, l. 17 & 20, (R5, R8): M missing on top of reaction arrow.

13. p. 6269, l. 4-7: "Since it may be difficult to separate these two effects (even in controlled experiments), we introduce an integrated $\Delta^{17}\mathrm{O}$ transfer coefficient (τ) for this reaction, such that at photochemical steady-state, when only considering Reaction (R3) and the subsequent photolysis of NO:" is hard to read. May be one can split it in two separate sentences, the second one being: "When we only consider Reaction 3 with the subsequent photolysis of NO and further assume a steady state equilibrium, we obtain:"

14. p. 6269, l. 11, p. 6270, l. 23, p. 6272, l. 4: Notation: $\mathrm{k}_{\mathrm{O_3+NO}}$, $\mathrm{k}_{\mathrm{RO_2+NO}}$, and $\mathrm{k}_{\mathrm{BrO+NO}}$ have been previously defined as $\mathrm{k}_{\mathrm{NO+O_3}}$, etc.

15. p. 6270, l. 2: To be consistent with previous notation, equilibrium arrow in (R10) should have M on top.

16. p. 6274, l. 8-9: outer parentheses should be increased in size.

17. p. 6275, l. 19 "Denoting"?

18. p. 6276, l. 6: "any processes" → "any process"

19. p. 6278, l. 6: This appears to be the important equation (18) which is referred to several times. The equation number is missing, however.

20. p. 6282, l. 2: "if" → "into".

21. p. 6282, l. 3: There is one opening bracket and two closing brackets in the line.

22. p. 6282, l. 6-7: Two consecutive sentences starting with "From these data"

23. p. 6283, l. 11-17: "Using present knowledge regarding the transmission of the ozone oxygen isotopic anomaly to particulate nitrate through photochemical reactions between $\mathrm{NO_x}$ and ozone, and the mechanisms responsible for the conversion of $\mathrm{NO_2}$ to inorganic nitrate in the polar atmosphere after polar sunrise, we

demonstrated in this paper that its isotopic composition records a footprint of the tropospheric ozone depletion events, which occur in this environment, based on atmospheric inorganic nitrate samples collected at Alert during 7 weeks in spring 2004." – This sentence is very long and hard to read. Perhaps, one should make a first statement on the measurements and then state that TIN records an isotopic footprint of ODE?

24. p. 6289, l. 1: "Mauersberger" is misspelled
25. p. 6291, caption of Table 1: ". . . so the end of sampling correspond to the beginning of the next sample." third person singular "s" is missing.
26. p. 6295, caption Fig. 4: "horizontal error bars refer to the standard deviation." → "horizontal error bars refer to one standard deviation."
27. p. 6296, Fig. 5: In my opinion, the diagram is easier to read (less crowded) when arrows not pointing towards a reaction product are omitted (e.g. the lines from NO and O_3 to NO_2 would just join without an extra arrow on the line originating from O_3).
28. p. 6296, caption Fig. 5: I recommend to omit "regarding the theoretical framework about $\Delta^{17}\mathrm{O}(\mathrm{NO}_3^-)$"
29. p. 6297, Fig. 6 and caption: irritating legend; only two out of three curves are displayed. "plain line" → "solid line", "Errors bars" → "Error bars".