Atmospheric Chemistry and Physics Discussions

Interactive Comment

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

Anonymous Referee #2

General comments

The present paper reports on the first oxygen triple isotope measurements of Arctic nitrate and a correlation of Δ^{17}O with ozone mixing ratios. The importance of BrNO$_3$ hydrolysis as nitrate source is recognized, an explanatory framework for oxygen isotope anomalies in Arctic nitrate is put forward and potential applications in paleo-atmospheric studies are pointed out. As referee #1 pointed out, these findings merit publication in ACPD. However, I also concur with referee #1's conclusion that the paper in its present form suffers from unnecessarily imprecise statements and a biased presentation of previous δ^{17}O and δ^{18}O measurements of tropospheric O$_3$. Indeed, the

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explanatory framework put forward by the authors can only be brought into agreement with the measurements if a higher than previously measured isotopic anomaly is assumed for tropospheric O_3. Specifically, measurements of Krankowsky et al. (1995) and Johnston & Thiemens (1997) give an average $\Delta^{17}O(O_3)$ value of (25.6±1.0) per mille (n = 89, standard error of the mean), as opposed to the value of 35 per mille used by the authors. A lower $\Delta^{17}O(O_3)$ also implies a lower $\Delta^{17}O(BrO)$ value as BrO acquires its isotopic composition from ozone. Arguments might be found for a higher anomaly than 25.6 per mille, but are lacking at present in the paper. See below for more detailed comments.

The authors of the paper frequently uses qualitative expressions ("greatly", "strongly", "significantly", "mainly", "pronounced", etc.) rather than quantitative arguments. This should be avoided. At other occasions, quantitative arguments are made, but without estimates of uncertainty, e.g., the $\Delta^{17}O(O_3)$ or the Monte-Carlo modeling results for the free parameters of the budget calculations. Calculations are not always fully documented. Notably, it is not explained how "mean back-trajectories" were calculated (see my Specific Comments below).

I would like to emphasize that I agree with almost all points made by Referee #1. In the following, I will comment mainly on additional issues that arose during my review of the paper.

Specific comments

1) Title of the paper:

I suggest deleting the word "pronounced". A variation of 4 standard deviations (stated to be greater than 1 per mille on p. 6260, l. 27) can hardly be described as "pronounced". Also delete "after polar sunrise". This is an unnecessary discriminator, as there are no ODEs before polar sunrise, as far as I know. Replace "on $\Delta^{17}O$ in atmospheric nitrate" by "in $\Delta^{17}O$ values of atmospheric nitrate" or by "in the isotope anomaly

of atmospheric nitrate". Arctic is spelled with capital "A" (needs to be changed everywhere in the paper as it refers to the region, not the temperature). The new title should then be "Signature of Arctic surface ozone depletion events in $\Delta^{17}O$ values of atmospheric nitrate" or Signature of Arctic surface ozone depletion events in the isotope anomaly of atmospheric nitrate".

2) p. 6257, l. 9:

The value of 35 per mille cannot be justified by the experimental evidence in Krankowsky et al. (1995) and Johnston & Thiemens (1997). None of these two reference give $\Delta^{17}O$ values. Using the linear definition with 0.52 as factor for $\delta^{18}O$ one finds (25.1±1.7) per mille ($n = 47$, standard error of the mean) from Krankowsky et al.'s data and (26.4±0.9) per mille for La Jolla, CA, (31.4±1.5) per mille for WSMR, NM and (21.2±0.5) per mille for Pasadena, CA from Johnston & Thiemens' data. The grand average is (25.6±1.0) per mille, far less than 35 per mille. Theoretical arguments used by Lyons (2001) give a value of 35 per mille, but there are problems in his calculations as pointed out by Zahn et al. (ACP, 2006). Calculations of Zahn et al. give $\Delta^{17}O$ values of about 35 per mille in the lower stratosphere, but their validity for the Arctic troposphere needs to be discussed, because stratospheric temperatures and pressures are lower than those in the Arctic troposphere. Zahn et al. also use a different definition of $\Delta^{17}O$. In any case, Zahn et al. (2006) needs to be referenced.

3) p. 6259, l. 20:

Explain why isotopic measurements are not sensitive to aerosol collection efficiencies. This does not appear to be counter-intuitive. There might be size- or surface-reactivity related isotope effects, which would be expressed in case of ineffective collection rates.

4) p. 6260, l. 5 & p. 6296, caption Fig. 5:

Reactions at the gas-particle boundary might not necessarily be mass-dependent as recent work on refractory oxides by the Thiemens group has shown

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5) p. 6260, l. 27:

The origin of this 1.0 per mille uncertainty is not clear. 0.14 μmol of O_2 correspond to 7-14% of the sample size (by the way, it is also unclear whether all samples were between 1 and 2 μmol in size). The difference in $\Delta^{17}O$ between O_2 and nitrate is (29$\pm$2) per mille. The blank stated here implies that is invariant from sample to sample and its relative contribution can then be inferred without significant error from the nitrate sample size, such that the necessary correction is (2.9$\pm$0.2) per mille for a relative contribution of 10% of atmospheric O_2. Even the remaining uncertainty of 0.2 per mille is an overestimate, since the isotopic composition of the (O_2-blank affected) sample is known. Please explain the origin of this large uncertainty attributed to the blank correction.

6) p. 6261, l. 1:

"[...] sources are inversely related to the size". Even this is not entirely true. It is true for the blank correction, but the mass-spectrometric error is governed by Poisson counting statistics and therefore more likely to be correlated to the inverse square root of the sample size.

7) p. 6261:

Thiemens (1999) does not mention nitrates. Delete reference from l. 7 and l. 9. Also, only Michalski and co-workers use the linear definition. Böhlke et al. (2003) and Coplen et al. (2004) use the definition given in Eq. 1. Therefore, the statement that "most articles dealing with nitrate" use the linear definition is biased towards one group of authors. Also, note that Miller (2002) does not endorse a specific lambda as implied by Eq. 1. The value of 0.525 was only adopted in Böhlke et al. (2003). Moreover, the qualification of Eq. 1 as "unambiguously" in l. 13 is misleading, as there is a multitude of possible definitions of $\Delta^{17}O$, none less unambiguous than the other (after all, a

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definition is just that). The only ambiguities arise when it is not clearly stated which $\Delta^{17}O$ definition has been used in a publication. Finally, the main advantage of the linear $\Delta^{17}O$ definition is that it simplifies (linear) mass-balance calculations, as pointed out by Kaiser et al. (2004). This also appears to be the main appealing factor in the present case, as the Discussion section of the paper delves deeply into mass-balance calculations, which would appear slightly more complicated had the definition given by Eq. 1 been adopted.

8) p. 6261, l. 21-23:

I calculate a value of (0.90±0.07) per mille from the values given in Table 1. Please check. Given a possible miscalculation of the measurement uncertainty (see above), this might well be outside the uncertainty of the measurements. Moreover, other than l. 23 implies, this does imply a systematic bias of the results, even though it might not matter for the correlation between $\Delta^{17}O$ values and O_3 mixing ratios.

9) p. 6263, section 3.4 - back-trajectory calculations:

It is not clear how the authors have calculated "mean back-trajectories". How is a "mean back-trajectory" defined? It appears to be highly ambiguous to me. As an extreme cases, consider two trajectories starting at 70°N 90°W and 70°N 90°E and ending at the North Pole. Where does the "mean back-trajectory" originate? At 70°N 0°? At 70°N 180°? At the North Pole? Or, take another example: Two trajectories originating at 70°N 60°W and 70°N 60°E and ending at the North Pole. Do you take the mean in polar co-ordinates, which would correspond to an origin at 70°N 0°? Or do you take the mean in Cartesian co-ordinates, which would come to lie north of the 70°N parallel? How do you calculate the mean in the general case of N back-trajectories?

Moreover, many of the statements about the origin of air masses lack statistical support. For example, the caption to Figure 4 or the last paragraph of section 3.4 are vague ("most air masses", "rather motionless"). It would be better if these statements were quantitative (e.g., 3 out 4 samples, 11 out of 14 samples, etc., with the significance in

parentheses, where appropriate).

10) p. 6269:

It is not clear why the rate of transfer of $\Delta^{17}O$ from O_3 to NO_2 (τ) is one of the most critical parameters of the analysis. The isotopic composition of O_3 and BrO as well as the relative contribution of $BrNO_3$ hydrolysis to inorganic nitrate formation seem to be just as critical.

It is not true that Röckmann et al. (2001) assume that the terminal O atoms in O_3 react with NO. Please correct.

The statement in l. 21-24 is not in "in addition". It is in fact crucial to what is implied in the previous sentence, namely that the central O atom also reacts with NO_2. If the intramolecular isotope distribution in O_3 was statistical, the NO-O_3 reaction mechanisms would not matter at all.

Again, reference to Zahn et al. (2006) should be made here (see my comments in bullet point 1 above).

11) p. 6271, l. 13:

Such a high terminal O atom anomaly is unlikely as discussed in Zahn et al. (2006). It would require a large negative anomaly of the central O atom. A recent thesis (Tuzson, 2006) reports on new intramolecular ^{17}O isotope measurements in O_3 and should be referenced here.

12) p. 6278:

The relationship given by "Eq. 18" is non-linear in O_3 mixing ratios. This needs to be pointed out. Moreover, it is strongly temperature dependent ($\Delta^{17}O$ changes by about 1 per mille per 10 K temperature change.). In light of this temperature dependence, more accurate temperature estimates than given in the present Table 1 should be given (they are only given in 5 K increments at present). This temperature depen-

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dence explains some of the variability in the $\Delta^{17}O$ values. I recommend an additional figure to illustrate the temperature-dependence and the non-linearity of the predicted $\Delta^{17}O(NO_3^-)$ vs. O_3 mixing ratio relationship, with a range of relevant temperatures.

13) p. 6282:

The discussion of the parameters derived from the Monte Carlo model needs to be improved significantly. Which parameters are derived, which are assumed, what are the uncertainties of the assumed and the derived parameters? The explanatory framework fails if the O_3 isotope anomaly is only 25 per mille or would require unrealistic value for $\Delta^{17}O(BrO)$ or *r*. The value of *r* = 0.9 is at odds with other estimates of r given on p. 6277 and p. 6278. This needs to be discussed. p. 6282, l. 14: This cannot be construed as a "confirmation" as there are no measurements of the isotopic anomaly of BrO.

14) p. 6283, l. 22-25:

This sentence needs to be rephrased. What does "did not happen significantly" mean? Moreover, the predicted relationship between O_3 mixing ratios and $\Delta^{17}O$ (Eq. 18, which is not numbered in the text, but can be identified with l. 6 on p. 6278), is non-linear and curves strongly towards the origin. This is in addition to changes of the BrO mixing ratio.

15) p. 6291, Table 1:

The average residual difference between measured and calculated Delta $^{17}O(NO_3\text{-})$ is non-zero. This indicates an incomplete optimization. A better solution exists, which needs to be computed. Give the arrange of possible parameters to solve the isotopic budget calculations. Please also give the average fitting error (average absolute deviation of calculated from measured value). The missing values in Table 1 should be indicated by "n. a." (not analyzed).

16) p. 6297, Fig. 6:

Fig. 6 is not necessary and can be combined with Fig. 3.

Technical corrections

p. 6256, l. 8 & caption Fig. 4 & p. 6266, l. 3 & p. 6284, l.4: Give uncertainties of slope and y-axis intercept.

p. 6256, l. 9: Delete "to quantitatively interpret this relationship". It's unnecessary and disrupts the flow of argument. Rearrange sentence to read "We derive mass-balance equations from mechanisms in the Arctic boundary layer, which describe $\Delta^{17}O(NO_3-)$ as a function of the concentrations of reactive species and their isotopic characteristics." It is not the equations that depend on the concentrations, but $\Delta^{17}O$ described by the equations.

p. 6256, l. 13: "[...] the large isotopic anomalies of O_3 and BrO are the driving force for the variability in [...]"

p. 6256, l. 16: Replace "activity" by "concentration" and add " (NO_3-)" after "relatively stable compound".

p. 6256, l. 13: l. 6: Not clear what is meant here. Maybe "The necessary correction of the atmospheric concentrations was estimated by dividing the amount [...]".

p. 6256, l. 22: Replace "for a long time" with "since the 1930s" (first works appeared on the hydrological cycle).

p. 6256, l.24: Delete "kinetics" - O_3 formation or CO + OH are counter-examples.

p. 6256, l. 26: Replace "standard reference" with "reference material".

p. 6257, l. 2: Replace Thiemens, 1999 with an appropriate reference for SMOW, e.g., Baertschi (1976) ($^{18}O/^{16}O$) and Li et al. (1988) ($^{17}O/^{16}O$).

p. 6257, l. 4: The discovery by Thiemens and Heidenreich (1983) refers to electrochemically produced O_3, not photochemically produced atmospheric O_3. Rephrase or

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replace by an appropriate reference.

p. 6257, l. 6: Define "several authors". Who?

p. 6257, l. 17: Delete "time" in "springtime".

p. 6257, l. 27: "in the coastal Arctic"

p. 6258, l. 1: Replace "theories about" by "explanations of".

p. 6258, l. 14: "Measurements with this instrument were terminated on 4 May 2004."

p. 6258, l. 15: "between 4 and 18 May 2004"

p. 6259, l. 4: "available for isotopic analysis."

p. 6260, l. 14: "using an ion"

p. 6260, l. 16: Delete "." in "mmol.l-1".

p. 6260, l. 17: "on an isotope ratio"

p. 6260, l. 20: These values are not consistent with the linear $\Delta^{17}O$ definition adopted in the present paper. Rather, one finds $\Delta^{17}O$(USGS-34) = -0.1 per mille and $\Delta^{17}O$(USGS-35) = 21.6 per mille.

p. 6260, l. 22: Again, using the $\Delta^{17}O$ definition adopted here and the isotopic composition of air-O_2 vs. SMOW measured recently by Barkan & Luz (2005), one finds a different value, namely $\Delta^{17}O(O_2)$ = -0.3 per mille.

p. 6260, l. 27: "of the oxygen blank effect"

p. 6262, l. 3: "They consist of meteorological observations (temperature and precipitation), ozone mixing ratios, [...]"

p. 6262, l. 15: "[...] (ODEs), which are ubiquitously [...]"

p. 6263, l. 10 & p. 6264, l. 9 & p. 6282, l. 17: "in line with"

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p. 6264, l. 27: "a molar Na^+:SO_4^{2-} ratio in sea salt of 0.0603"

p. 6266, l. 9: "insight into the budget"

p. 6267 (R8) & p. 6269 (R10): Wrong symbol for equilibrium arrows. Chemical equilibrium is indicated by a "
rightleftharpoon" (LaTeX code) arrow.

p. 6268, l. 19: "In these conditions, elevated levels of BrO ..."

p. 6269, l. 16: "parameters"

p. 6270, l. 2: "these two sources of uncertainty"

p. 6271, (R12) & (R13): Split reaction over two lines. It is against convention in chemistry to "subtract" reaction products in consecutive reactions.

p. 6271, l. 5: Rearrange sentence to "[...] catalytic cycle, a steady state isotopic equilibrium between BrO and O_3 is expected to be reached within minutes".

p. 6273: Equations 3 and 5 are not needed and should be removed. Moreover, their use would actually lead to errors, as double-substituted isotopic species are involved (product of [NQ] and [O_2Q] etc.).

p. 6293, Fig. 2: The projection chosen for the back-trajectory map (Fig. 2) is awkward (the ratio of latitude in the vertical plot direction to latitude in the horizontal plot direction is about 1:1.14). It would be easier to judge distances if this ratio was adjusted to 1:1. Also, "Siberian" is spelled with a capital "S".

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