

Interactive comment on “Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica” by J. Savarino et al.

Anonymous Referee #3

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General comments:

This manuscript presents a unique new dataset of measurements of the $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$, $^{17}\text{O}/^{16}\text{O}$ ratios as well as concentrations of atmospheric particulate nitrate at the Dumont d'Urville (DDU) research station over an entire year and an interesting analysis of the observed seasonal cycles. The authors present a number of reasonable but still arguably qualitative estimates for the isotopic compositions of the various possible sources of particulate nitrate and how these may vary in magnitude throughout the year, and, with these constraints, they make some generally compelling arguments about the changing sources throughout the year. While not the first to suggest that the highly depleted $^{15}\text{N}/^{14}\text{N}$ ratios for nitrate when nitrate peaks in late spring likely result from photochemical processing and release of gaseous precursors from snow (and not

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Interactive Discussion

Discussion Paper

from sedimentation of PSCs from the stratosphere as had been previously suggested by others), they are the first to show that this scenario is also likely consistent with the observed oxygen isotope ratios, adding support to this interpretation. The triple oxygen isotope compositions of the collected nitrates also provide for the first time additional constraints on sources at other times of year. Thus, the major strength of this study lies in the measurements of multiple isotopes, which together lead to a more convincing – albeit still qualitative – deconvolution of the various possible sources of nitrate and related species and should thus aid in a better understanding of what drives chemistry in the relatively pristine Antarctic boundary layer. A major weakness is how comfortable the authors appear to be throughout the text in concluding that relatively rough estimates of the isotopic compositions of some of the sources agree or do not agree with their observations. This weakness should be addressed with a more sober analysis with larger error bars/uncertainties on their estimates and more specific discussion and caveats about the limitations of their analysis. In addition, some of this overconfidence can be also addressed by more carefully choosing the language used and by rewriting and changing the emphasis in several sections, as noted below.

Specific comments:

* Abstract: The authors note that size-segregated aerosol samples were collected, and yet the measurements on the size-segregated samples are combined in a weighted average in all the analyses. I recommend removing this description from the abstract as it is misleading for the analyses presented here.

* Abstract: In the abstract as well as in the text, the authors make, in my opinion, an overly flashy claim that the "failure" of their estimate of the isotopic composition of atmospheric particulate nitrate using the "current knowledge of isotopic anomaly transfers during chemical reactions" to match what they measure means that we must not know the isotopic composition of ozone in the Antarctic Ozone Hole. To place this argument in the abstract distracts from their most important (and more easily supportable) conclusion that the stratosphere is most likely the source of an anomaly this large

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(with an emphasis on "most likely"). But this very important conclusion and distinction is lost in their arguments in the text that (1) 41 per mil is a lot larger than 36 per mil (Is it really, given the large number of uncertainties in the many chemical steps governing the transfer of isotope anomalies between ozone and particulate nitrate?) and therefore that (2) this discrepancy means that something unique must be affecting the isotopic composition of ozone in the Antarctic stratosphere. Their analysis and arguments left me thinking that the authors are too confident in their calculation of 36 per mil and its uncertainties to support these conclusions. To reiterate, the more interesting and supportable conclusion is that tropospheric chemistry is unlikely to produce such large anomalies. Of course, measurements of the triple oxygen isotope composition of ozone in the Antarctic vortex and in the aftermath of its breakup could be very interesting, but this is not a main conclusion of the authors' analysis that should go in the abstract or take center stage in their discussion of results.

* Sampling issues (Section 2): It is unclear from the text exactly how blanks were performed and how many. It seems in some parts of the procedural description that one particular blank was associated with one particular sample so that the number of blanks equaled the number of samples. In other places, it seemed as though only one or an occasional blank was performed. This should be clarified throughout Sections 2 and 3 where blanks are discussed.

* Sampling issues (Section 2 and, especially, Section 3.1 "data treatments"): While I on the one hand trust that the authors are not led astray in their analysis by contamination of nitrates or precursors emitted by the local penguin population, parts of the text, especially Section 3.1 in which it states that samples with feathers or in that memorable scientific euphemism "brown ornithological soil," left me wondering just how tainted the summer samples might be in general. For example, it is unclear to me which of the authors' arguments that the local penguin population is not an issue correspond with what other field studies have shown (at other research stations and/or at DDU specifically) and which come directly from this study. I recommend that the authors clarify

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

their arguments as to why direct or indirect (e.g., via elevation of apparent background concentrations in the summer) penguin contamination was not an issue and coordinate the arguments between the different sections (2 and 3) in which this issue is discussed.

* Equation 2: A sentence or phrase stating why the authors chose to use the value of 0.528 from Barkan and Luz for λ (for water isotopes) should be included. For example, was this chosen to be near the maximum theoretically possible value (so as to provide lower limits for values for the anomaly since a smaller and perhaps more likely value(s) for the stratosphere is likely to be smaller than this, leading to a difference of up to ~ 2 per mil for the 41 per mil data point)? And/or is there a tropospheric link to water that should dominate for tropospheric nitrate? Is this a reasonable assumption for the stratosphere or, if not, why should we not care at the level of precision or accuracy needed for this analysis?

* Estimating the ^{15}N isotopic composition of a stratospheric "nitrate" source (Line 5 and 6 of 8832): Taking a simple average of the Toyoda et al Antarctic fractionation constants (enrichment factors) is very simplistic. The authors should consider inserting a phrase near this that reassures the reader that using such a simple number is sufficient for their purposes here and does not affect the interpretation of the seasonal cycles under study.

* Laboratory experiment (manuscript in preparation) on macroscopic transfer of the anomaly from ozone to NO_2 (Line 5, 8833): With no details given here with which to evaluate these experiments, a number of caveats about the applicability of these experiments to the atmosphere come to mind: temperature, absolute pressure, chemical interferences in the lab not relevant for the atmosphere, wavelength of light used, and so on. While I think it could be acceptable to mention these results – namely, that about 80% of the D_17O present in ozone in these experiments winds up in NO_2 – and to use them for estimation purposes here, the fact that the authors then go on to conclude (Lines 3-10, 8834) that a value of 36 per mil for HNO_3 derived from stratospheric ozone is NOT in agreement with their observation of 41 per mil and that therefore we don't

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know the isotopic composition of stratospheric ozone in the Antarctic Ozone Hole is an unreasonable stretch. Indeed, the uncertainties from this one experiment alone (for which the reviewers have given no information) is one of many factors to consider that make this overall approach of the authors an ESTIMATE and not a particularly reliable "derivation," "development," "evaluation" or other words the authors use throughout the text to describe this process of coming up with a rough estimate for the oxygen isotope anomaly in nitrate derived from the stratosphere. Rather, the authors should really focus on the "bottom line" they give (Line 10-11, 8834) that "stratospheric chemistry is the only clear candidate to explain such high D17O(NO₃-)," if indeed such a strong conclusion can be supported once the authors also review the large uncertainties in their estimates. Once that argument is made, a few other sources of a POSSIBLE discrepancy could be discussed (with the caveat, I argue, that the uncertainties are large enough that it is difficult to convincingly argue that there IS a discrepancy!). To conclude anything else before this statement is an unnecessary distraction to their most important argument that the stratosphere is likely the only source of such anomalous nitrate and/or nitrate precursors.

* Line 1, 8835: Is it true that the 2 species (HTO and the stratospheric nitrate) must be injected into the troposphere as gases? While this is not likely to have a large impact on the rest of the authors' reasoning, I think this is not necessarily correct under all conditions. The important point is that there are several atmospheric tracers of denitrification/dehydration/ and some combination, perhaps, of strat-trop exchange and sedimentation for the authors to compare their results with.

* Line 13, 8844: This is an estimate and not an "evaluation" (see above for why this is not just an English language usage but a scientific issue). Similarly, in the authors' summary in Section 4.4 of the discussion leading up to this point, they refer to their *estimates* of the isotopic compositions of nitrate derived from stratospheric PSCs and from snow-emitted nitrate as "observations," misusing this term as usually used in atmospheric science. These are calculations and estimates, not observations.

Interactive
Comment

* Line 21, 8844: "Our new scenario. . . reconciles the observed simultaneity between tritium and nitrate." Is this correct? I thought the authors point was that the primary nitrate concentration peak (from nitrate photolysis in the snow) did NOT coincide with the tritium peak from the stratosphere. Furthermore, the authors say this "confirms the potentially higher isotope anomaly of the stratosphere over the troposphere." I think the analysis presented here "suggests" that this is the case, rather than confirming it. And lastly in this paragraph: "ONLY measurements of the stratospheric ozone isotopic composition inside the polar vortex will DEFINITELY permit accurate quantification" Again, I argue that there are many other variables that are just as likely to affect the nitrate (or precursor) isotope anomaly to the degree indicated by the authors' estimates here, so "ONLY" is not appropriate. If the authors disagree, then they need to make better arguments throughout. Finally, "definitely" is much too definite.

* Other specific suggestion for easier flow of arguments throughout: I found the authors' use of "late winter", "late spring", "spring", "winter," and so on, at best difficult to follow and at worst quite confusing. For example, the definition of what is winter and what is spring is never given and it is not clear whether they mean colloquial usages with regard to seasons and temperatures or with respect to the annual solar cycle (e.g., solstices, equinoxes) or sometimes one and sometimes another (see below). In addition, their putting several or partial seasons together in their 4 different periods (with different time lengths) adds some confusion, as does referring to other studies which have different definitions of such time periods (e.g., Wagenbach 1998). I recommend one or more of the following steps to make their arguments more convincing and easier to follow: (1) coming up with a consistent definition of "winter," "late winter," etc., (2) simply using months and/or a range of months (e.g., July, July-Sep) to describe what is intended throughout, and/or (3) defining winter, late winter, etc. in text in Figure 2 along with the delineation of Periods 1-4 given there. Such clarifications might also help with several details that appear to be incorrect in terms of timing – e.g., that temperatures don't drop below the PSC thresholds until "the end of winter" (Line 26, 8829). The "end of winter" to me implies August or even September, while

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temperatures are this low, climatologically speaking at least, by late June (see, e.g., http://www.ccpo.edu/SEES/ozone/class/Chap_11/11_Js/11-45.jpg) and a number of other instances (too numerous to list) exist in which the precision of the argument is lost due to the imprecision of these terms.

* I recommend, if permission is obtained, putting the tritium time series (as in Wagenbach et al 1998) into Figure 1. The Wagenbach d15N data are already shown in this figure, and it would make the arguments in this paper easier to follow.

Figure 5: Which color and symbol go with which month/date? It was very time consuming to have to pick this out from the small legend and to grasp the significance of the plot quickly. Furthermore, the timing implied by this plot for the most stratospheric intrusions into the troposphere is not necessarily that implied by hemispheric-scale mass fluxes out of the stratosphere, which maximize (weakly) in the SH in June and July (e.g., Appenzeller, Holton, and Rosenlof, JGR 1996). The authors should add a sentence or two and several references (since they are using Figure 5 as a supporting argument) putting these single temperature profiles into a climatological perspective and why or why not hemispheric-scale STE vs stratospheric intrusions regionally are similar or different.

Supplemental materials, Figure S1: Only the size-segregated d15N measurements are shown and compared here. Since this is supplemental material, not taking up space in the journal pages, why are the oxygen isotope data also not shown (or "no [sic] represented" as stated in the caption)? One inference that might be made from the fact they're not shown is that the authors' arguments for averaging the size-segregated results together is weakened if the actual data were shown. This seems like an unnecessary hazard that could easily be avoided if the oxygen isotope data are also included.

Technical corrections:

* An additional reading for correct English grammar, missing words, subject-verb agree-

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ment, and other issues is still needed. I list a few more interesting and/or important ones here:

Line 26, 8843: "even if some significant disparities exist punctually." First, I have no idea what existing punctually actually means. Second, use of the word "differences" instead of "disparities" would have a more exact scientific meaning, if the authors believe the differences are real, as disparities has a nuance of being used in English most often as not just a difference but a fundamental and incomparable difference. Furthermore, because it is unusual to refer to such a difference as a "disparity" in English, I wondered next if the authors meant "discrepancy" instead; however, I take it the authors think that the differences measured between the size fractions may be real and not, as discrepancy might connote, the result of artifacts. Simply using the word "differences" would solve these issues if this is what the authors intended.

Figure 6 caption: I recommend changing "with a little concurrent concentration increase" to "with a small concurrent concentration increase." The problem with it as written is that, given the other English usage issues in this manuscript (albeit relatively minor but also not infrequent), a reader is likely to read (as I did) "with little concurrent concentration increase" which the authors definitely do not mean. Using "small" instead removes this ambiguity.

Table 2 caption: The standard deviation for d18O of nitrate for the Kaiser method is listed as 0.9 per mil here, while that for the Kaiser method in the text is given as 0.3 per mil. Which is it?

Figure 4: The colors on colors in this figure of the chemical mechanisms are very difficult to see in a printed version (and perhaps online as well although I did not check that).

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 8817, 2006.

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