

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

### **Anonymous Referee #2**

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**General comments** Isotopic analyses of the type presented here have the potential to significantly improve our understanding of the sources, sinks, and cycling of nitrogen oxides in polar regions. The dataset presented here is a valuable addition to the very limited prior measurements. However, disentangling the effects of the multiple processes that might affect nitrate isotope ratios is quite difficult and, on top of that, the effect on  $\delta$  values of each individual process is poorly constrained. As a result, it is a difficult task to extract as much as is possible from this dataset without overextending the analysis or losing track of what is truly known, what is suspected, what is merely possible, and what is impossible. This (overextension or losing track) occurs in multiple places in this work, as indicated by the specific comments listed below. Some of these refer to significant issues that may affect the paper's conclusions.

As a suggestion, this work might benefit significantly from a reorganization along the following lines.

- Present the measurement data.
- List the mechanisms that are considered possible sources of nitrate at the DDU site.
- Identify the mechanisms that are rejected as significant sources. For each, identify the reason for rejection.
- Identify the mechanisms remaining as potential causes. For each, first present the supporting data, then identify each inconsistency. (For example, deposition from the stratosphere is identified as a likely important source in spring, but an inconsistency—the fact that the observed  $\Delta^{17}\text{O}$  value is higher than can be explained—is identified.) Finally, suggest further work that could be conducted to support or reject the proposed cause.

## Specific comments

### Discussion

1. P. 8830, lines 8–16. The calculation of steady-state concentration resulting from stratospheric deposition is incorrect. One cannot simply divide by physical volume, because air density is not constant through the troposphere. (The result is that compression will lead to higher concentrations at lower altitudes.) In addition, the steady-state concentration and lifetime are not related by

$$C = (\text{flux}) \cdot (\text{lifetime})$$

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- as used here. Chemical lifetimes are e-folding lifetimes (or perhaps half-lives), and can be interpreted as the reciprocals of rate constants. One way to do this calculation would be to write a simple mass balance equation at steady state for an equivalent STP volume, with input from the stratosphere and loss due to  $1/\tau C$ .
2. P. 8830, lines 16–29. The point being made here is not clear. It reads as though the authors are suggesting that PSC deposition is a likely cause of the late winter concentration increase. But the paragraph ends with a statement that this is implausible. (And later in the paper, isn't it suggested that PSC deposition *is* the cause?) If it is implausible, then what was the point of the attempt to calculate the enhancement that would result if PSCs *were* the cause?
  3. Sec. 4.1.2. This section and the appendix provide an extended derivation that concludes with a result “already suggested by Heaton et al. based on a similar reasoning.” It is not clear what, if anything, is significant, new or different here (relative to the Heaton paper). Please clarify what is new, or replace this section (and perhaps the prior two paragraphs) with a reference to the Heaton work and a brief description of how the present results support or extend their conclusions.  
The last sentence (p. 8832, lines 15–17) states that the  $\delta^{15}\text{N}$  expectation excludes the stratosphere as a source in “late spring.” It would help the reader to discuss all seasons here. What are the conclusions (and the bases for those conclusions) regarding other seasons?
  4. Section 4.1.3. This discussion estimates  $\Delta^{17}\text{O}$  in nitrate produced in the stratosphere, and concludes that best estimates are 20–31, 17–26, or 23–36 (depending on the production mechanism). It is then noted that none of these mechanisms can explain the highest seasonal mean value. This reasoning makes sense. But the authors then conclude (p. 8834, lines 10–11): “The bottom line, however, is that stratospheric chemistry is the only clear candidate to explain such high  $\Delta^{17}\text{O}$ .” No support is provided for this statement. It seems to be an

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- article of faith. To paraphrase Sherlock Holmes, once you have eliminated the probable, whatever remains (however improbable) should be reevaluated. In this case, the way the text is written implies that the observation is inconsistent with the expectation. If so, then either the stratosphere is not the source, or the observations are wrong, or the expectation is wrong. Which of these is the case, or at least might be the case?
5. Section 4.1.4. This section seems to argue against the conclusion at the end of section 4.1.3 (i.e., argues that stratospheric deposition as the main nitrate source cannot be reconciled with the tritium data).
  6. Section 4.3.2. The interpretation of the Blunier paper seems contrary to Blunier et al.'s conclusions. They measured the nitrogen isotope effect from photolysis and concluded that it was too small to explain the much larger isotope variation in the snowpack nitrate.
  7. Section 4.3.3. The Wolff et al. 2002 paper is cited as demonstrating that photolysis and evaporation “are quantitatively equivalent.” That paper makes no such claim. It is then stated that “It can be deduced . . . that flux emission of NO<sub>y</sub> . . . will be . . . NO<sub>x</sub> and HNO<sub>3</sub> in equal proportion.” The evidence does not support such a deduction—this is an assumption.
  8. Page 8840, lines 1–2. Why does the re-emitted nitric acid have the annual average  $\Delta^{17}\text{O}$ , rather than the  $\Delta^{17}\text{O}$  of the seasonally deposited total nitrate (the portion nearest the sunlit surface)?
  9. Page 8839, line 25. Why is the tropospheric nitrate  $\Delta^{17}\text{O}$  value for summer cited here different from the one cited on page 8836, line 12?
  10. Section 4.4. The summary here is very helpful. However, based on the concerns noted above, I feel that some of the conclusions listed here are inadequately supported.

- (a) P. 8840, lines 19–20. The  $\Delta^{17}\text{O}$  range cited for PSCs is that presented in section 4.1.3 for XONO<sub>2</sub>-derived nitrate. Please add to section 4.1.3 information on why only that source is expected to be important.
- (b) P. 8840, lines 21–23. The fact that the potential role of BrO reactions has been neglected should be noted here.
- (c) P. 8840, line 25. The uncertainty for the  $\delta^{15}\text{N}$  value should be increased. The quoted uncertainty would be appropriate only if the assumed value of 30% nitrate loss were known precisely. In fact, that value is poorly constrained.
11. Section 4.4.1. The conclusion that winter nitrate is locally generated from NO<sub>x</sub> is not supported, and I am skeptical that it is correct. What is the rate of NO<sub>x</sub> production expected from any level of organic nitrates that would be compatible with wintertime Antarctic NO<sub>y</sub> levels, under dark, low-temperature conditions? How is long-range transport of background nitrate excluded?
12. Section 4.4.2, paragraph 1. The upper limit of  $\Delta^{17}\text{O}$  referred to is still too low to explain the observed values. This should be reworded to clarify what is consistent and what is not, and to explicitly indicate that one of (specify a list of) items must be wrong or misunderstood. As I understand it, the authors reasoning is that the observed maximum  $\Delta^{17}\text{O}$  is not consistent with any of the expected values for the sources considered, but it is *closest to* (though still not consistent with) the PSC value. (But is it really so far from the tropospheric value as to be impossible?)

### Methods.

13. Page 8821, line 20: “analyses have shown only sporadic nitrate contamination by station activities.” Please briefly describe what analyses are referred to and, more importantly, how the sporadic contamination that resulted was eliminated from the analysis (or specify its magnitude and demonstrate that it is not significant).

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14. P. 8823, lines 7–8: size cutoffs are referred to as “representing  $\dots < 1 \mu\text{m}$ ” and  $> 1 \mu\text{m}$ . The term “representing” is overly vague. What was the aerodynamic diameter cutoff calculated for the impactor as used?
15. The text in the results section (p. 8827, lines 7–9) explains why the results may apply to total nitrate, rather than just particulate nitrate. This information belongs in the methods section. In addition, p. 8825, lines 17–19 notes that prior work implies that even the particulate nitrate at DDU probably includes a significant contribution from local uptake of nitric acid vapor (some of which may be the result of high ammonia levels due to the penguin colony). Thus, the particulate measurement at DDU may not refer to particulate nitrate levels in the regional atmosphere. For both these reasons, the authors should refer to their measurements as total nitrate rather than particulate nitrate. (The last sentences of section 2.2 seem a little extreme. Some of the compounds identified as possibly contributing to the particulate nitrate signal can be eliminated from this list with a high degree of certainty.
16. The information on the sampling time uncertainty and the pressure and temperature correction currently located in the first paragraph of section 3.2 would better fit in the Methods section.
17. P. 8826, lines 10–16: The justification for presenting data that may have errors in sample volume is acceptable since the volume is unknown. (Though it might make sense to use a best estimate rather than a maximum estimate of the volume.) However, the same reasoning does not apply to the omission of temperature and pressure corrections. The temperature correction in particular should be easy to apply and may be significant in terms of the seasonal cycle.

## Technical corrections

1. P. 8820, Line 2. As written, this reference implies that Neubauer and Heumann (1988) proposed or recognized nitrate photolysis as a potential cause of nitrate lost from snow. Similarly, the reference lists on lines 5–6 and 8–10 include references from work before snow nitrate photolysis was recognized in 1999. This can be corrected by using separate sets of citations in support of nitrate *loss* and in support of nitrate *photolysis*.
2. p. 8829, lines 4–5. “The only real effort to interpret the seasonal pattern . . .” This sounds like the authors are suggesting that there have been other efforts also, which were not “real.” “Real” should be removed, and any additional citations should be added.
3. P. 8842, line 19: Where does the value 30 come from?
4. Figure 4. The caption here includes a discussion of the processes that would fit better into the text.

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

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