

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

### **Anonymous Referee #1**

Received and published: 30 October 2006

This paper presents original material focused on understanding the atmospheric nitrogen cycle, in the form of air aerosol nitrates in Antarctic, and on the evolution (re-emission) of nitrates from snow. I congratulate the authors for the nicely performed job which brings a new light to this interesting problem. The manuscript is clearly written and well balanced. The reviewer has made several comments as following:

General comments:

1. The authors try to explain the origin of the Antarctic atmospheric nitrates by making a mass-balance for  $\Delta^{17}\text{O}$  values. These estimations are based on the chemical reactions involved and the reactant's isotope signatures as well as on the  $\Delta^{17}\text{O}$  transfer rates. Based on this balance, the authors argue that the range of  $\Delta^{17}\text{O}(\text{HNO}_3)$  mea-

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sured for Antarctic aerosol nitrates cannot be explained by the current knowledge of the reactions, the  $\Delta^{17}\text{O}$  transfer rates and  $\Delta^{17}\text{O}$  assumed for Antarctic ozone. Yes, ozone in the Antarctic should be analysed indeed. However in this chain of reasoning there is a problem as follows: there are some gaps related to measurement uncertainty, scale conversion etc. As a matter of fact, ozone measurements (e.g. Lämmerzahl et al., 2002) have a large uncertainty, about 5 permile for  $\delta^{17}\text{O}(\text{O}_3)$  and 3 permile for  $\delta^{18}\text{O}(\text{O}_3)$  ( $1-\sigma$  values, see Fig. 3 in Lämmerzahl et al., 2002) which gives the uncertainty for  $\Delta^{17}\text{O}(\text{O}_3)$  of 5.8 permile ( $1-\sigma$  value). This factor alone gives an uncertainty of 4 permile (again  $1-\sigma$ ) for  $\Delta^{17}\text{O}(\text{HNO}_3)$ 's estimated limits. Besides, some errors are possibly related to  $\Delta^{17}\text{O}(\text{XO})$  but these are not considered. Thus, the upper value for  $\Delta^{17}\text{O}(\text{HNO}_3)$  (36.3 +/-4 permile) nearly overlaps the range measured on nitrates, values up to 41 permile (Page 8861, Table 1). Next, the uncertainty related to data rescaling from the air- $\text{O}_2$  scale ( $\delta^{17}\text{O}(\text{O}_3)$  and  $\delta^{18}\text{O}(\text{O}_3)$ ) as reported by Lämmerzahl et al., 2002) to the VSMOW scale is also not propagated. (Do the authors use the VSMOW scale for  $\Delta^{17}\text{O}$  values or the air- $\text{O}_2$  scale only?). Uncertainties for the  $\Delta^{17}\text{O}$  transfer rates involved in the reaction chain are also not considered, and the factor 0.8 used in the present work differs from the range 0.9 to 1.0 used by Morin et al (2006). The latter is strange, as these two publications refer to the same unpublished data set of Savarino (2006). All in all, the conclusion that high  $\Delta^{17}\text{O}(\text{HNO}_3)$  cannot be explained by the current knowledge does not stand up.

2. The paper is focused on using  $\Delta^{17}\text{O}$  signals to interpret the nitrate cycle. For this the authors try to make use of the latest publications as well as the accurate formula suggested for  $\Delta^{17}\text{O}$ . However, the reviewer sees here some misinterpretation of definitions and formulas related to the  $\Delta^{17}\text{O}$  reporting. Here are several aspects:

(i) the formula in use was first suggested by Miller (2002). Later Luz and Barkan (2005) demonstrated that the physical meaning of the value after this formula is an ordinate intercept for a given mass-fractionation line on the oxygen three isotope plot. In that case the line should be defined uniquely/specifically by its slope and original isotope com-

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position. Luz and Barkan also noted that this ordinate intercept (offset vs. zero of the scale) characterises the entire line. Assonov and Brenninkmeijer (2005) discussed various aspects of  $\Delta^{17}\text{O}$  reporting and stressed that another, traditional definition which has been used for years, aims to consider how a single data point (e.g. a nitrate sample) deviates from the MDF-line expected. In this case  $\Delta^{17}\text{O}$  is defined/calculated as a deviation of this point from the expected MDF-line and characterises the point vs. the line. And that is the case with nitrates. Thus another formula should be applied, either in the linear approximation form or in the exponential form (Eqns. 12 and 13 in Assonov and Brenninkmeijer, 2005). As a matter of fact, discrepancy of  $\Delta^{17}\text{O}$  values calculated by different formulas increases with increase of  $\delta^{18}\text{O}$  deviation from the scale zero (e.g. Miller, 2002). For the present work this discrepancy may be comparable with the uncertainty of 0.9 permile reported for  $\Delta^{17}\text{O}$ ;

(ii) Use of  $\lambda = 0.528$  is not well justified, a better justification for  $\lambda$  must be given. The reference to (Barkan and Luz, 2005) is not relevant here; it gives the  $\delta^{17}\text{O}$ - $\delta^{18}\text{O}$  relationship for natural waters and thus cannot be simply considered as an expected value for nitrates. A numerical example given by Zahn et al. (2006) - when  $\delta^{18}\text{O}$  is 128 permile (in fact ozone has  $\delta^{18}\text{O}$  100 permile), use of  $\lambda=0.513$  instead of 0.529 (kinetic and equilibrium fractionation, e.g. Young et al, 2002) gives a  $\Delta^{17}\text{O}$  bias of 2 permile which, when the utmost accuracy of  $\Delta^{17}\text{O}$  is suggested, cannot be neglected.

(iii) Morin et al. (2006) is another publication on  $\Delta^{17}\text{O}$  in polar atmospheric nitrates and there J.Savarino is the second author. However here the formula for  $\Delta^{17}\text{O}$  was considered differently. I cite: "Since we focus on nitrate, characterized by large and strongly variable heavy oxygen enrichments and anomalies, the use of this [the exponential] definition is not as crucial as for slightly anomalous species (e.g.  $\text{N}_2\text{O}$ ), for which the historical linear definition (Thiemens, 1999) may be responsible for inaccuracies. In the case of nitrate, the choice of the expression for  $\Delta^{17}\text{O}$  has therefore very little influence on the results." For this reason Morin et al. (2006) used a simple linear approximation for  $\Delta^{17}\text{O}$ , without aiming the utmost accuracy.

(iv) The  $\Delta^{17}\text{O}$  mass-balance. When  $\delta^{18}\text{O}$  significantly deviates from zero (ozone has  $\Delta^{18}\text{O}$  around +100 permile), a simple  $\Delta^{17}\text{O}$  mass balance (Eqn 4) gives an approximation only (e.g. Assonov and Brenninkmeijer, 2005); accurate calculations must include a mass-balance for all isotopes of all species. The deviation is magnified when the exponential formula for  $\Delta^{17}\text{O}$  is in use. Let us consider a numerical example. A compound with very low contents of  $^{17}\text{O}$  and  $^{18}\text{O}$  (say  $\delta^{17}\text{O}=-998$  permile and  $\delta^{18}\text{O}=-999.999$  permile) has  $\Delta^{17}\text{O}=1945$  permile (after Eqn. 4 in the present work, with  $\lambda=0.528$ ) which is a huge effect. In fact, the  $\delta^{17}\text{O}$  excess is of 1.3 permile only when that is calculated after Eqn. 13 in (Assonov Brenninkmeijer, 2005) as a vertical distance/deviation from the MDF line of  $\lambda=0.528$ . When the authors really want to discuss the utmost accuracy of  $\Delta^{17}\text{O}$ , they should consider and clarify all the related aspects. The reviewer concludes that use of the novel formula together with unjustifiably selected exponent of 0.528 is misleading and cannot be recommended. All in all, use of this formula appears to give no advantage in this work.

3. Recently Shalen et al. (ACP-D, 2006) demonstrated some aspects of  $\text{CO}_2$  equilibration with  $\text{O}_3$ , via  $\text{O}(^1\text{D})$  produced by  $\text{O}_3$  photolysis. They also demonstrated that lines on the three isotope plots, when started from original  $\text{CO}_2$  may have different slopes. These observations may in principle help explain/interpret the Figure 3 of the present manuscript.

Detailed comments are as followed:

Page 8820, lines 20-21, I cite: "With the recent advances of online mass spectrometry techniques (Brand, 1996; Casciotti et al., 2002; Sigman et al., 2001)..." This combination of references is not fortunate. While the first ref. considers continuous-flow method in general, the next two works consider use of bacterially produced  $\text{N}_2\text{O}$  to determine nitrate isotope ratios.

Page 8821, lines 1-2, I cite: "This study represents the first comprehensive picture of nitrate isotopes that combines the three isotopic ratios  $^{15}\text{N}/^{14}\text{N}$ ,  $^{17}\text{O}/^{16}\text{O}$  and

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18O/16O." Have Morin et al. (2006) not analysed nitrates for  $\delta^{15}\text{N}$ ?, that seems to be much easier than the methods for  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  they used.

Pages 8823, 8828. Obviously, the novel on-line conversion on a gold catalyst gives a result  $\Delta^{17}\text{O}$  as well as  $\delta^{18}\text{O}$  values. Can the authors demonstrate (in a tabulated form) how these  $\delta^{18}\text{O}$  values correspond to the  $\delta^{18}\text{O}$  values obtained by the denitrifier method in use? Figure 1c demonstrates the discrepancy from 2 to 6 permile. How does this discrepancy correspond to the standard deviation of 0.2 permile listed (page 8827)? Which values were used for  $\Delta^{17}\text{O}$  and what bias might that cause? (The reviewer also notes that use of the terms "a gold furnace", page 8823, and "gold decomposition", page 8828, is jargon).

Page 8824: It looks like all the  $\Delta^{17}\text{O}$  values are reported on the VSMOW scale (is that correct?) How was the calibration of  $\Delta^{17}\text{O}$  values performed?

Page 8824: The statement that the formula for  $\Delta^{17}\text{O}$  is non-approximated and accurate is misleading; see the general comments above. Stating that this formula is reference-independent is erroneous. Imagine that another scale is shifted by  $\delta^{17}\text{O}=100$  permile vs. the scale in use, then all  $\Delta^{17}\text{O}$  values will be also shifted. Angert et al. (2005) stressed that use of this very formula (e.g. in the logarithmic form) facilitates rescaling  $\Delta^{17}\text{O}$  values from one scale to another.

Page 8825, lines 14-15: Can the authors give the isotope composition of blanks? How variable are blank values?

Page 8827, lines 23 and 24 as well as the heading of Table 2: In the text standard deviations are given as 0.2, 0.5 and 0.9 permile ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  respectively), but in the table heading as 0.2, 0.9 and 0.5 permile for ( $\delta^{15}\text{N}$ , ( $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ ). Values for  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  are different; which is correct?

Page 8828, lines 23 to 26 and Figure 3: the authors claim that "...fractionations during these transfers are of only marginal importance." Figure 3 does not demonstrate a

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straight array which one might have expected in this case if the enrichment is due to reaction with O(1D) or ozone is the only process. Several questions may arise:

(i) Do the authors imply mass-dependent fractionations?

(ii) The plot may indicate some kind of mixing between two end-members (extremely enriched nitrate being in equilibrium with O<sub>3</sub> and a normal nitrate processing  $\Delta^{17}\text{O}=0$ ) and/or decrease of high  $\Delta^{17}\text{O}$  due to nitrate photolysis (e.g. McCabe et al., 2005). Also the authors may try to use the new data on O<sub>2</sub>-O<sub>3</sub>-CO<sub>2</sub> system (Shalen et al., ACP-D 6, 7869, 2006) discussing reaching an equilibrium point.

(iii) The authors may discuss how samples from different periods deviate from or agree with each other. Maybe plotting symbols in different colours?

Page 8833, lines 3 to 11. I cite: "In a set of laboratory experiments (manuscript in preparation), we have observed the macroscopic anomaly transfer of  $\Delta^{17}\text{O}(\text{NO}_2)=0.8*\Delta^{17}\text{O}(\text{O}_3)$ ." Morin et al. (2006) gives 0.9 to 1.0 and refers to the same manuscript in preparation. Why should the reader take that statement for granted, without reading all experimental details etc. The fact that terminal O-atom of ozone bears about 80 percent of <sup>17</sup>O enrichment has been mentioned by Zahn et al. (2006), see references therein.

References: Reference to Morin et al. (2006) is erroneous - the work has been published in ACP-Discussions, not in ACP.

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

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