# First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate

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[1] Atmospheric nitrate is anomalously enriched in both the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotopic ratios, with $\Delta^{17}O = 20–30.8‰$ ($\Delta^{17}O = \delta^{17}O − .52 \times \delta^{18}O$). We have modeled the seasonal variation in $\Delta^{17}O$ by utilizing the transfer of $\Delta^{17}O$ from ozone to $HNO_3$ during $NO_x$ oxidation reactions and by evaluating the relative source strengths of heterogeneous and homogenous $HNO_3$ production. The implications for new insights into the global nitrogen cycle, $N_2O$ production and paleoclimate studies are discussed. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 1040 Geochemistry: Isotopic composition/chemistry; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615). **Citation:** Michalski, G., Z. Scott, M. Kabiling, and M. H. Thiemens, First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate, *Geophys. Res. Lett.*, *30*(16), 1870, doi:10.1029/2003GL017015, 2003.

## 1. Introduction

[2] Stable isotopes have long been used to trace atmospheric chemical reaction pathways and to constrain source and sink budgets in biogeochemical cycles [*Hoefs*, 1973]. Kinetic and equilibrium isotopic fractionations occur because differences in the nuclear mass alter the ratio of partition functions for identical molecules containing different isotopes. For the three isotopes of oxygen this difference results in a mass dependent relationship, which is determined by $\delta^{17}O = .52 \times \delta^{18}O$. Where $\delta$ (‰) = $(R_{sample}/R_{standard} − 1) \times 1000$ and R is the $^{18}O/^{16}O$ or $^{17}O/^{16}O$ ratios in the sample and the standard [*Criss*, 1999]. $\Delta^{17}O$ is a measure of the deviation from this mass dependent relationship and is quantified by $\Delta^{17}O = \delta^{17}O − .52 \times \delta^{18}O$ (termed a mass independent composition). $\Delta^{17}O$ measurements are particularly useful for studies related to atmospheric chemistry because they are only found in photochemical reactions and are increasingly well characterized [*Thiemens*, 1999]. Observations of mass independent fractionations occurring in ozone formation have been thoroughly documented [*Thiemens*, 1999; *Krankowsky et al.*, 2000], as is the transfer of isotopically anomalous oxygen atoms during photolysis and chemical reactions involving ozone [*Savarino et al.*, 2000; *Thiemens*, 1999]. Here the first measurements of $\Delta^{17}O$ in atmospherically produced nitrate are reported. An isotopic/photochemical model interprets the data and we discuss the data's relevance to tropospheric oxidation chemistry, paleoclimate and nitrogen deposition studies.

## 2. Experimental and Observations

[3] We have collected atmospheric nitrate aerosols in coastal La Jolla, Ca. (32.7°N, 117.2°W) for a one-year period beginning in March of 1997. Aerosols were collected for 3 days on pre cleaned glass fiber filters using a high volume aerosol sampler (flow rate = 1200 l min$^{−1}$) equipped with a 4 stage, size-segregating impactor. Nitrate was isolated and converted to $AgNO_3$ by a multiple step purification scheme from *Silva et al.* [2000]. The oxygen isotopic composition of $AgNO_3$ was determined by its partial conversion to $O_2$ and analysis on a Finnigan-Mat 251 isotope ratio mass spectrometer [*Michalski et al.*, 2002]. The complete experimental method has a $\Delta^{17}O$ analytical precision is ±0.2‰ for samples as small as 5 μmol $NO_3^−$, with samples for this study typically exceeding 100 μmol [*Michalski et al.*, 2002].

[4] The $^{\Delta}NO_{3atm}^−$ values and their variability with time are presented in Figure 1 (For brevity, the $\Delta^{17}O$ of molecule X will be denoted $^{\Delta}X$ and should be read as "the capital delta 17 of X"). All $^{\Delta}NO_{3atm}^−$ measurements exhibited large $^{17}O$ excesses ranging from 20 to 30‰, the second largest measured $\Delta^{17}O$ after atmospheric ozone. In addition a strong seasonal trend is observed with maximum value of $^{\Delta}NO_{3atm}^−$ occurring in mid winter. A three-isotope plot of the data also shows that there is also a large isotopic enrichment (50–89‰) in $^{18}O$ relative to SMOW (Figure 1B). Similar enrichments and seasonal trends in $NO_{3atm}^−$ $\delta^{18}O$ values have been previously reported [*Williard et al.*, 2001; *Kendall*, 1998] and our values are similar to these measurements.

## 3. The Origin and Modeling of $\Delta^{17}O$ in $NO_{3atm}^−$

[5] The large positive $\Delta^{17}O$ and $\delta^{18}O$ values found in $NO_{3atm}^−$ and the intimate coupling between $NO_x$ and $O_3$ suggests that the observed $^{\Delta}NO_{3atm}^−$ is the result of reactions involving tropospheric ozone. In order to test this hypothesis and to interpret the seasonal variation observed in $^{\Delta}NO_{3atm}^−$ we have coupled a secondary $\Delta^{17}O$ isotope fractionation model to a photochemical box model for a polluted marine boundary layer (PMBL). Our $\Delta^{17}O$ isotope model is similar to other $\Delta^{17}O$ modeling studies [*Lyons*, 2001; *Rockmann et al.*, 2001], where $\Delta^{17}O$ values are generated only by mass transfer of O atoms from ozone to products during oxidation reactions. $NO_{3atm}^−$ is predominantly formed by the oxidation of $NO_2$ by two homogeneous (R1, R2) and one heterogeneous (R3) reaction:
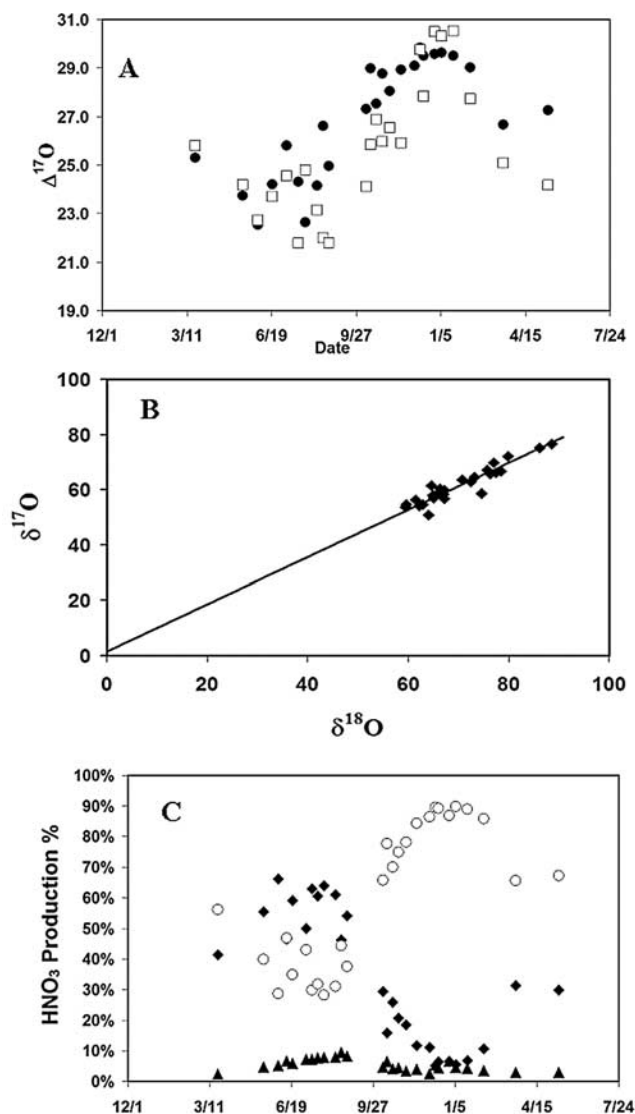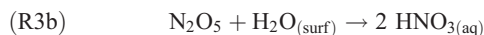
(R1)        $NO_2 + OH + M \rightarrow HNO_3 + M$

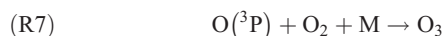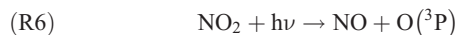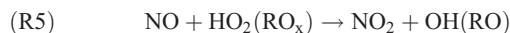(R2)        $NO_2 + O_3 \rightarrow NO_3 + O_2$

**Figure 1.** (a) $\Delta NO_{3atm}^-$ measurements (open squares) from La Jolla Ca., compared to the model predictions (circles). Winter and spring values agree within 1‰ but late summer and fall vary by 2–4‰. (b) Observed $\delta^{18}O$ and $\delta^{17}O$ of $NO_{3atm}^-$ showing a mixing line between the isotopic compositions of tropospheric ozone and $H_2O$ (intercept is at $\delta^{18}O = -5$‰, $\Delta^{17}O = 0$). (c) $HNO_3$ production by $NO_2 +$ OH (diamonds), $NO_3 +$ HC, DMS (triangles) and $N_2O_5$ heterogeneous hydrolysis (open circles). The strong seasonal variation is the result of temperature dependences, $NO_x$ concentrations and hours of sunlight.

(R2b)    $NO_3 + HC, DMS \rightarrow HNO_3 + products$

(R3)    $NO_2 + NO_3 \leftrightarrow N_2O_5$

(R3b)    $N_2O_5 + H_2O_{(surf)} \rightarrow 2\ HNO_{3(aq)}$

$HNO_{3(gas)}$ produced in the R1 and R2 subsequently reacts on aerosol surfaces to yield particulate nitrate. The common reactant for each $HNO_3$ production channel is $NO_2$, which is generated by the oxidation of NO by either ozone, $HO_2$ or peroxy radicals ($RO_x$). $NO_2$ is also readily photolyzed by uv/vis light to regenerate NO and $O_3$

(R4)    $NO + O_3 \rightarrow NO_2 + O_2$

(R5)    $NO + HO_2(RO_x) \rightarrow NO_2 + OH(RO)$

(R6)    $NO_2 + h\nu \rightarrow NO + O(^3P)$

(R7)    $O(^3P) + O_2 + M \rightarrow O_3$

[6] The $NO_x$ photo-stationary state (R4–R7) achieves steady state 3 orders of magnitude faster than the sink reactions (R1–R3) [*Atkinson et al.*, 1997] and the oxygen atoms in $NO_2$ achieve isotopic equilibrium with $O_3$ and $HO_2$ ($RO_x$). Empirical evidence [*Savarino and Thiemens*, 1999] and modeling studies [*Lyons*, 2001] have suggested a small $\Delta HO_2 \sim 1$‰. For simplicity we have taken the $\Delta HO_2$ (and $RO_x$) to be zero [*Rockmann et al.*, 2001] and subsequent sensitivity analyses demonstrated that this assumption affects $\Delta^{17}O$ values by <1‰, which is smaller than our analytical uncertainty. This simplification results in $\Delta NO_2 = \alpha \Delta O_3$, where $\alpha$ is the proportion of NO oxidation by $O_3$ relative to $HO_2$ and $RO_x$.

[7] No isotopic measurements of ozone were conducted during the sampling period. However the $\Delta^{17}O$ of tropospheric $O_3$ (35‰) has been previously calculated [*Johnson et al.*, 2000; *Lyons*, 2001] using the experimental isotopomer reaction rates and branching ratios for the measured temperature and pressure ranges [*Morton et al.*, 1990]. Ozone's terminal O atoms are isotopically enriched relative to the central atom [*Anderson et al.*, 1989] suggesting the dynamics of the NO + $O_3$ reaction may play an important role in determining the $\Delta^{17}O$ value of $NO_2$. Molecular beam studies have shown that the reaction has two transition states, one where the central atom is extracted and a second where the terminal atom is transferred to the newly formed $NO_2$ [*Vandenende et al.*, 1982; *Redpath et al.*, 1978; *Vandenende and Stolte*, 1984]. In addition, chemiluminescence data indicates that the three oxygen atoms in $O_3$ have an approximately statistical probability of transferring during R4 [*Vandenende and Stolte*, 1984]. Therefore the evaluation of the isotopic enrichment found in the terminal atoms need not be considered when applying mass balance to R4 [*Lyons*, 2001].

[8] The final O atom in R2 also derives from $O_3$ but no experimental data exists on the dynamics of this reaction. Therefore both a total ozone, and a terminal atom only, transfer mechanism were used to assess the impact of R2 on $\Delta NO_{3atm}^-$. The final O atom in R3b is from tropospheric water ($\Delta^{17}O = 0$) by inspection and we neglect the possibility of isotopic exchange between $N_2O_5$ and water during the hydrolysis reaction (discussed below). The isotopic exchange between the OH radical (R1) and gas phase $H_2O$ [*Dubey et al.*, 1997] is rapid under tropospheric conditions and eliminates any $\Delta^{17}O$ arising from photochemistry [*Lyons*, 2001].

[9] Using R1–R3 and the above considerations, we write $^{\Delta}HNO_3$ in terms of ozone and $\alpha$ only:

$$^{\Delta}HNO_3(R1) = \tfrac{2}{3}\alpha\,^{\Delta}O_3 \qquad (1)$$

$$^{\Delta}HNO_3(R2) = \tfrac{2}{3}\alpha\,^{\Delta}O_3 + \tfrac{1}{3}\,^{\Delta}O_3 \qquad (2)$$

$$^{\Delta}HNO_3(R3) = \tfrac{1}{3}\alpha\,^{\Delta}O_3 + \tfrac{1}{2}\left(\tfrac{2}{3}\alpha\,^{\Delta}O_3 + \tfrac{1}{3}\,^{\Delta}O_3\right) \qquad (3)$$

The predicted $^{\Delta}NO_{3atm}$ is then $\beta(EQ1) + \chi(EQ2) + \varepsilon(EQ3)$ where $\beta$, $\chi$, $\varepsilon$ are the relative proportions of $HNO_3$ production by each reaction channel (R1–R3). The three-isotope plot of $NO_{3atm}^-$ (Figure 1b) supports the assumption that the O atoms found in $NO_{3atm}^-$ are ultimately derived from either $O_3$ or $H_2O$.

[10] To evaluate $\alpha$, $\beta$, $\chi$, $\varepsilon$ we have utilized a zero dimensional, time dependent, photochemical box model for a PMBL from Yvon et al. [*Yvon et al.*, 1996]. The input parameters were taken from 3-day averages of trace gas measurements and meteorological data (supplemental data tables are available at online[1]) from the APCDSD and a total ozone column that was obtained from TOMS archives. A DMS flux was determined by using the seasonal variation in DMS concentrations in California coastal surface waters [*Bates et al.*, 1987] and a piston velocity that was calculated using average daily wind speeds and sea surface temperatures [*Saltzman et al.*, 1993]. A constant NO flux of $7 \times 10^{11}$ molec. $cm^{-3}s^{-1}$ was taken from the APCDSD annual emission inventory for the San Diego basin. The absence of heavy industry and yearlong mild climate keeps $NO_x$ emissions for this region relatively constant throughout the year. The model was run for 4 days to achieve stability, after which the fraction of $O_3$ oxidation of NO ($\alpha$) and the three $HNO_3$ production channels ($\beta$, $\chi$, $\varepsilon$) were explicitly tracked for days 5 through 8. The modeled $HO_2$ concentrations were doubled to account for the observed underestimation of $HO_2$ (by a factor of two) by photochemical models in high $NO_x$ conditions [*Jaegle et al.*, 2000]. Equations 1–3 were then used to calculate the $^{\Delta}HNO_3$ values, which are shown in Figure 1a.

## 4. Results and Discussion

[11] There is excellent agreement between the modeled and measured $^{\Delta}NO_{3atm}^-$ values in the spring and winter ($\pm<1‰$), however the late summer and fall values are overestimated by 2–4‰. This discrepancy is likely due to the model's inadequate account of transport. The model overestimates $^{\Delta}NO_{3atm}^-$ by 5–7‰ for the entire year if terminal atom transfer mechanism is used in R2 indicating the oxidation mechanism of R2 is similar to R4. However this conclusion should be investigated experimentally. The main factor impacting the $\Delta^{17}O$ variation is the seasonal shift from $\sim50\%$ homogeneous reactions (R1 + R2) in the spring to more than 90% heterogeneous (R3) in the winter (Figure 1c). This shift is in agreement with both regional and global $HNO_3$ production models [*Dentener and Crutzen*, 1993; *Russell et al.*, 1985], and is the first isotopic evidence supporting such chemical $NO_x$ models. The dominance of $N_2O_5$ hydrolysis in
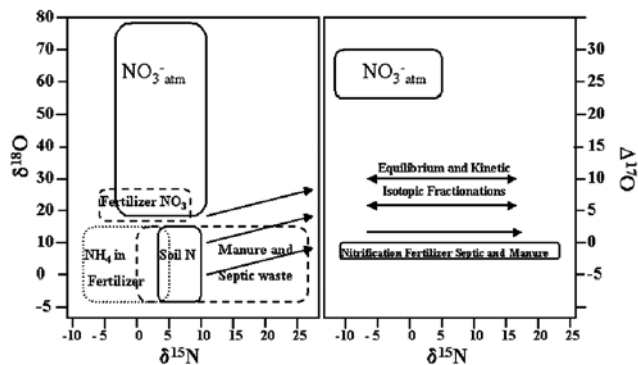
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[1] Auxiliary material is available at ftp://ftp.agu.org/apend/gl/ 2003GL017015.



**Figure 2.** (a). The published range of $\delta^{15}N$ and $\delta^{18}O$ values for known nitrate sources within a given watershed adapted from Kendall [*Kendall*, 1998]. Note the large $\delta^{18}O$ ranges and source overlaps. Kinetic and equilibrium mass dependent isotopic fractionations that enrich (or deplete) $\delta^{15}N$ and $\delta^{18}O$ in a $\sim$2:1 ratio over time are shown by the arrows. (b) The $\Delta^{17}O$ of the same nitrate sources and arrows depicting the effects of mass dependent fractionations. Nitrification and synthetic production of nitrate derive their oxygen from either air $O_2$ or water and have a $\Delta^{17}O = 0$ (these values were confirmed by measurements). The clear separation and narrow range of $\Delta^{17}O$ make mass balance calculations simple and accurate and allow for the use $\delta^{15}N$ to further constrain nitrate sources.

the winter and the corresponding maximum in $\Delta^{17}O$ also rules out possible isotopic exchange during the hydrolysis reaction (R3), for complete isotopic exchange would eliminate the $\Delta^{17}O$ signal. This is not surprising since the hydrolysis intermediate, $NO_2^+$, has a lifetime of only $\sim10^{-9}$s [*Mentel et al.*, 1999] before it is converted to $HNO_3$. $HNO_3$ in turn does not undergo isotopic exchange for conditions typical of the troposphere [*Bunton et al.*, 1952].

[12] Although the nitrate radical is an important nighttime sink for NMHC and DMS in the PMBL, its contribution to $HNO_3$ production is shown to be small with a maximum of 10%. This maximum corresponds to our calculated summer DMS emission maximum, yet even this relatively small $HNO_3$ source can still contribute up to $\sim3.5‰$ to $^{\Delta}NO_{3atm}^-$.

[13] The seasonal variation cannot be due to $^{\Delta}O_3$ pressure and temperature effects [*Morton et al.*, 1990]. For our sampling conditions these enrichments would only amount to 1–2‰ variations in $\Delta^{17}O$ and the dominating temperature effect (where $\Delta^{17}O$ scales with T) is in the opposite direction of our data and may even be dampening the seasonal cycle. The larger spread $NO_{3atm}^-$ $\delta^{18}O$ in other studies [*Kendall*, 1998] is probably due to the difference in $\delta^{18}O$ values of tropospheric water vapor and the temperature dependence of kinetic fractionation factors in R1–R6, both of which vary with season and location. We conclude that $\Delta^{17}O$ and $\delta^{18}O$ variability is not strictly due to differing point sources as has been suggested [*Kendall*, 1998]. Rather, it is due to differences in oxidative pathways that depend on the source conditions (e.g., plume versus dispersed).

## 5. Implications

[14] The application of $^{\Delta}NO_{3atm}^-$ for detecting and quantifying atmospheric deposition in watershed and ecosystem

studies is unambiguous Figure 2. This is a 3–16 fold improvement in the quantification of compared with current $\delta^{18}O$ methods, which has a maximum quantification error (±38%) at $\delta^{18}O \sim 15$–20‰, a value typical of watershed and soil studies [*Mayer et al.*, 2002]. Using $\Delta^{17}O$ we have detected $NO_{3atm}^-$ deposition for $\delta^{18}O$ values as low as $-2$‰ and have observed $\sim 20\%$ $NO_{3atm}^-$ loading with $\delta^{18}O$ values of only 10‰ [*Michalski et al.*, in preparation]. $^{\Delta}NO_{3atm}^-$ may also be an alternate source of the $\Delta^{17}O$ measured in tropospheric and stratospheric $N_2O$ [*Cliff and Thiemens*, 1997]. Denitrification of $NO_{3atm}^-$ that occurs with little or no isotopic exchange between the $NO_3^-$ oxygen atoms and surrounding cellular water [*Casciotti et al.*, 2002] would produce $^{\Delta}N_2O \sim 25$‰. Measurements of $^{\Delta}N_2O$ in the atmosphere may then represent the percentage of $N_2O$ produced by $NO_{3atm}^-$ denitrification. Finally, the ability to trace $NO_x$ oxidation paths using $^{\Delta}NO_{3atm}^-$ offers new possibilities for extracting paleoclimate $NO_x$ concentrations from ice core nitrate isotopes, where no such proxy currently exists.

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