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

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[1] Atmospheric nitrate is anomalously enriched in both the $^{16}O/^{18}O$ and $^{17}O/^{18}O$ isotopic ratios, with $\Delta^{17}O = 20–30.8$% $\left(\Delta^{17}O = \delta^{17}O = 52 \times 10^{-6} \delta^{18}O\right)$. 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$_2$O production and paleoclimate and model interprets the data and we discuss the data’s rele-

2. Experimental and Observations

[3] We have collected atmospheric nitrate aerosols in coastal La Jolla, Ca. (32.7$^\circ$N, 117.2$^\circ$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$_{3_{atm}}$ 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$_{3_{atm}}$ 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$_{3_{atm}}$ 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$_3_{atm}$$^{18}O$ values have been previously reported [Willard et al., 2001; Kendall, 1998] and our values are similar to these measurements.

3. The Origin and Modeling of $\Delta^{17}O$ in NO$_3$$_{atm}$

[5] The large positive $\Delta^{17}O$ and $\delta^{18}O$ values found in NO$_3_{atm}$ and the intimate coupling between NO$_2$ and O$_3$ suggests that the observed $\Delta$NO$_{3_{atm}}$ is the result of reactions involving tropospheric ozone. In order to test this hypothesis and to interpret the seasonal variation observed in $\Delta$NO$_{3_{atm}}$ 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$_3_{atm}$ is predominantly formed by the oxidation of NO$_2$ by two homogeneous (R1, R2) and one heterogeneous (R3) reaction:

$$\text{(R1)} \quad \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$$

$$\text{(R2)} \quad \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$$
reactant for each HNO₃ production channel is NO₂, which is generated by the oxidation of NO by either ozone, HO₂ or peroxy radicals (ROₓ). NO₂ is also readily photolyzed by UV/vis light to regenerate NO and O₃.

\[(\text{R4})\] \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \)

\[(\text{R5})\] \( \text{NO} + \text{HO}_2(\text{RO}) \rightarrow \text{NO}_2 + \text{OH}(\text{RO}) \)

\[(\text{R6})\] \( \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}^\text{(I)} \text{P} \)

\[(\text{R7})\] \( \text{O}^\text{(I)} \text{P} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 \)

[6] The NOₓ 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 NO₂ achieve isotopic equilibrium with O₃ and HO₂ (ROₓ). Empirical evidence [Savarino and Thiemens, 1999] and modeling studies [Lyons, 2001] have suggested a small \( ^{17}\text{O} \text{HO}_2 \) and \( ^{17}\text{O} \text{RO} \) (and ROₓ) to be zero [Rockmann et al., 2001] and subsequent sensitivity analyses demonstrated that this assumption affects \( ^{17}\text{O} \text{NO}_2 \) values by <1‰, which is smaller than our analytical uncertainty. This simplification results in \( ^{17}\text{O} \text{NO}_2 = \alpha^{17}\text{O}_3 \), where \( \alpha \) is the proportion of NO oxidation by O₃ relative to HO₂ and ROₓ.

[7] No isotopic measurements of ozone were conducted during the sampling period. However the \( ^{17}\text{O} \text{O}_3 \) (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 + O₃ reaction may play an important role in determining the \( ^{17}\text{O} \text{NO}_2 \) value. Molecular beam studies have shown that the reaction has two transition states, one where the terminal atom is extracted and a second where the terminal atom is transferred to the newly formed NO₃ [Vandenende et al., 1982; Redpath et al., 1978; Vandenende and Stolte, 1984]. In addition, chemiluminescence data indicates that the three oxygen atoms in O₃ 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 O₃ 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 \( ^{17}\text{O} \text{NO}_3 \text{atm} \). The final O atom in R3b is from tropospheric water (\( ^{17}\text{O} = 0 \)) and we neglect the possibility of isotopic exchange between N₂O₅ and water during the hydrolysis reaction (discussed below). The isotopic exchange between the OH radical (R1) and gas phase H₂O [Dubey et al., 1997] is rapid under tropospheric conditions and eliminates any \( ^{17}\text{O} \) arising from photochemistry [Lyons, 2001].
[9] Using R1–R3 and the above considerations, we write
\[ \Delta \text{HNO}_3 \text{ in terms of ozone and } \alpha \text{ only:} \]
\[ \Delta \text{HNO}_3(\text{R1}) = \frac{\beta}{\alpha} \Delta \text{O}_3 \]
\[ \Delta \text{HNO}_3(\text{R2}) = \frac{\beta}{\alpha} \Delta \text{O}_3 + \frac{\chi}{\alpha} \Delta \text{O}_3 \]
\[ \Delta \text{HNO}_3(\text{R3}) = \frac{\beta}{\alpha} \Delta \text{O}_3 + \frac{\chi}{\alpha} \Delta \text{O}_3 + \frac{\varepsilon}{\alpha} \Delta \text{O}_3 \]  

The predicted \( \Delta \text{NO}_3_{\text{atm}} \) is then \( \beta(\text{EQ1}) + \chi(\text{EQ2}) + \varepsilon(\text{EQ3}) \) where \( \beta, \chi, \varepsilon \) are the relative proportions of HNO₃ production by each reaction channel (R1–R3). The three-isotope plot of \( \text{NO}_3_{\text{atm}} \) (Figure 1b) supports the assumption that the O atoms found in \( \text{NO}_3_{\text{atm}} \) are ultimately derived from either O₂ or H₂O.

[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 online1) 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} \text{molec. cm}^{-2} \text{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 NOₓ emissions for this region relatively constant throughout the year. The model was run for 4 days to achieve stability, after which the fraction of O₃ oxidation of NO (\( \alpha \)) and the three HNO₃ production channels (\( \beta, \chi, \varepsilon \)) were explicitly tracked for days 5 through 8. The modeled HO₂ concentrations were doubled to account for the observed underestimation of HO₂ (by a factor of two) by photochemical models in high NOₓ conditions [Jaegle et al., 2000]. Equations 1–3 were then used to calculate the \( \Delta \text{HNO}_3 \) values, which are shown in Figure 1a.

4. Results and Discussion

[11] There is excellent agreement between the modeled and measured \( \Delta \text{NO}_3_{\text{atm}} \) values in the spring and winter (\( \leq 1\% \)), however the late summer and fall values are over estimated by 2–4\%. This discrepancy is likely due to the model’s inadequate account of transport. The model overestimates \( \Delta \text{NO}_3_{\text{atm}} \) 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 \( \Delta ^{17} \text{O} \) variation is the seasonal shift from ~50\% 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 HNO₃ production models [Dentener and Crutzen, 1993; Russell et al., 1985], and is the first isotopic evidence supporting such chemical NOₓ models. The dominance of N₂O₅ hydrolysis in

5. Implications

[14] The application of \( \Delta \text{NO}_3_{\text{atm}} \) 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 ($\pm 38\%$) 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$_{3}$am deposition for $\delta^{18}$O values as low as $-2\%$ and have observed $\sim 20\%$ NO$_{3}$am loading with $\delta^{18}$O values of only 10%. [Michalski et al., in preparation]. $\Delta$NO$_{3}$am may also be an alternate source of the $\Delta^{17}$O measured in tropospheric and stratospheric N$_2$O [Cliff and Thiemens, 1997]. Denitrification of NO$_{3}$am 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$_2$O $\sim 25\%$. Measurements of $\Delta$N$_2$O in the atmosphere may then represent the percentage of N$_2$O produced by NO$_{3}$am denitrification. Finally, the ability to trace NO$_x$ oxidation paths using $\Delta$NO$_{3}$am offers new possibilities for extracting paleoclimate NO$_x$ concentrations from ice core nitrate isotopes, where no such proxy currently exists.

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References


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