

# Insights into anthropogenic nitrogen deposition to the North Atlantic investigated using the isotopic composition of aerosol and rainwater nitrate

Amy R. Gobel,<sup>1</sup> Katye E. Altieri,<sup>1,2</sup> Andrew J. Peters,<sup>3</sup> Meredith G. Hastings,<sup>2</sup> and Daniel M. Sigman<sup>1</sup>

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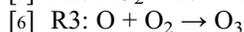
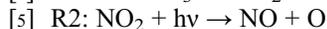
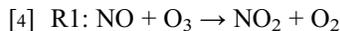
[1] Identifying the dominant sources of atmospheric reactive nitrogen ( $N_r$ ) is critical for determining the influence of anthropogenic emissions on  $N_r$  deposition, especially in marine ecosystems. To test the influence of anthropogenic versus marine air masses, samples were collected in Bermuda, where seasonal atmospheric circulation patterns lead to greater continental transport during the cool season. The  $^{15}\text{N}/^{14}\text{N}$  of aerosol nitrate ( $\text{NO}_3^-$ ) indicates changes in  $N_r$  sources and its  $^{18}\text{O}/^{16}\text{O}$  indicates a seasonal shift in the relative strength of pathways of  $\text{NO}_3^-$  formation. The aerosol  $\delta^{15}\text{N}-\text{NO}_3^-$  was consistently lower than or equal to the rainwater from the same sampling period, the opposite trend of that observed in polluted systems. We propose that this is due to  $\text{HNO}_3(\text{g})$  uptake onto aerosol particles with a kinetic isotope effect, lowering the aerosol  $\delta^{15}\text{N}-\text{NO}_3^-$  relative to residual  $\text{HNO}_3(\text{g})$ . The aerosol  $\delta^{18}\text{O}-\text{NO}_3^-$  was higher than that in rainwater during the cool season, but was not different during the warm season, which we tentatively attribute to the increased importance of heterogeneous halogen chemistry on the formation of  $\text{NO}_3^-$  during the cool season. **Citation:** Gobel, A. R., K. E. Altieri, A. J. Peters, M. G. Hastings, and D. M. Sigman (2013), Insights into anthropogenic nitrogen deposition to the North Atlantic investigated using the isotopic composition of aerosol and rainwater nitrate, *Geophys. Res. Lett.*, 40, 5977–5982, doi:10.1002/2013GL058167.

## 1. Introduction

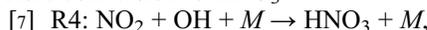
[2] The increasing deposition of anthropogenic reactive nitrogen ( $N_r$ ) to the surface ocean has the potential to alter surface ocean biogeochemistry [Duce *et al.*, 2008; Krishnamurthy *et al.*, 2007]. The Sargasso Sea, in the low-nutrient core of the North Atlantic gyre, may be particularly sensitive to atmospheric inputs of  $N_r$  [Michaels *et al.*, 1993]. Moreover, because it is located downwind of major industrial centers in the eastern

United States, atmospheric deposition models predict that anthropogenic activities have already substantially altered the  $N_r$  deposition to the Sargasso Sea [Duce *et al.*, 2008]. As a result, the region has been the subject of a number of studies of atmospheric deposition of  $N_r$  [e.g., Galloway *et al.*, 1989; Knapp *et al.*, 2010; Prospero *et al.*, 1996], and especially of nitrate ( $\text{NO}_3^-$ ), the primary sink of atmospheric  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) [e.g., Hastings *et al.*, 2003; Jickells *et al.*, 1982; Moody *et al.*, 1989].

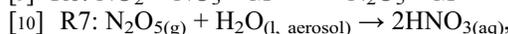
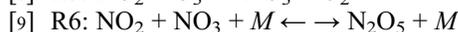
[3] During the daytime, atmospheric  $\text{NO}_x$  undergoes rapid transformations via



before conversion to  $\text{HNO}_3$  via



where  $M$  is an unreactive third body, usually  $\text{N}_2$ . During the nighttime,  $\text{NO}_x$  accumulates as  $\text{NO}_2$ , allowing for both the heterogeneous formation of  $\text{HNO}_3$  via



and the gas-phase reaction with hydrocarbons, especially dimethyl sulfide (DMS), in the marine boundary layer via



[12] Heterogeneous halogen chemistry, discussed in section 3.2, may also contribute to  $\text{NO}_3^-$  formation.

[13] The  $^{15}\text{N}/^{14}\text{N}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios of  $\text{NO}_3^-$  have been used to distinguish  $\text{NO}_3^-$  sources and chemical formation pathways in both polluted [Elliott *et al.*, 2007, 2009; Mara *et al.*, 2009; Wankel *et al.*, 2009] and remote environments [Altieri *et al.*, 2013; Baker *et al.*, 2007; Hastings *et al.*, 2003, 2004; Morin *et al.*, 2009]. The N atom is conserved during conversion from  $\text{NO}_x$  to  $\text{NO}_3^-$  (R1–R8), so the  $\delta^{15}\text{N}$  ( $\delta^{15}\text{N} = [(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{reference}} - 1] * 1000$ , where the reference is  $\text{N}_2$  in air) of the final  $\text{NO}_3^-$  is taken to indicate the  $\delta^{15}\text{N}$  of the  $\text{NO}_x$  source [Altieri *et al.*, 2013; Elliott *et al.*, 2007, 2009; Hastings *et al.*, 2003; Wankel *et al.*, 2009], although isotopic fractionation during formation may also influence the  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  [Freyer, 1991; Vicars *et al.*, 2013]. In contrast, the oxygen (O) atoms are exchanged with ozone ( $\text{O}_3$ ) in the nighttime pathways (R5–R8) and with both  $\text{O}_3$  and the hydroxyl radical (OH) in the daytime pathway (R1–R4). Because  $\text{O}_3$  has a much higher  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O} = [(^{18}\text{O}/^{16}\text{O})_{\text{sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{reference}} - 1] * 1000$ , where the reference is Vienna Standard Mean Ocean Water) than that expected for OH (+90 to +122‰ and –6 to +2‰, i.e.,  $\text{H}_2\text{O}(\text{v})$ , respectively), the  $\delta^{18}\text{O}-\text{NO}_3^-$  can be used to distinguish among  $\text{NO}_3^-$  formed via the daytime (R4) and nighttime

Additional supporting information may be found in the online version of this article.

<sup>1</sup>Department of Geosciences, Princeton University, Princeton, New Jersey, USA.

<sup>2</sup>Department of Geological Sciences and Environmental Change Initiative, Brown University, Providence, Rhode Island, USA.

<sup>3</sup>Bermuda Institute of Ocean Sciences, St. George's, Bermuda.

Corresponding author: M. G. Hastings, Department of Geological Sciences and Environmental Change Initiative, Brown University, 324 Brook St., Box 1846, Providence, RI 02912, USA. (Meredith\_Hastings@brown.edu)

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(R7–R8) pathways [Altieri et al., 2013; Elliott et al., 2009; Hastings et al., 2003; Wankel et al., 2009].

[14] The  $\delta^{15}\text{N-NO}_3^-$  in rainwater ( $\delta^{15}\text{N-NO}_3^-(aq)$ ) at Bermuda is significantly lower during the cool season, from October to March ( $-5.9 \pm 3.3\%$ ;  $\pm 1$  SD unless otherwise noted), than during the warm season, from April to September ( $-2.1 \pm 1.5\%$ ), corresponding to two distinct atmospheric transport regimes [Hastings et al., 2003]. In the cool season, fast-moving fronts transport relatively polluted air masses from North America to Bermuda [Jickells et al., 1982; Miller and Harris, 1985] associated with tracers for anthropogenic activity (e.g., non-sea-salt sulfate, antimony, and selenium) and high concentrations of sea-salt aerosols (e.g., coarse-mode sodium, chlorine, and calcium) due to increased wind speeds [Arimoto et al., 1992; Huang et al., 1999; Wolff et al., 1986]. In the warm season, the Azores high pressure system develops over Bermuda, blocking most transport from North America [Jickells et al., 1982] and carrying dust plumes from the Sahara over the North Atlantic [Prospero et al., 1996] associated with increased mineral components (e.g., silica, aluminum, and non-sea-salt calcium) [Arimoto et al. 1992; Huang et al., 1999; Wolff et al., 1986]. Interestingly, for concurrent sampling campaigns conducted in 2000, the cool season  $\delta^{15}\text{N-NO}_3^-(aq)$  in Bermuda ( $-5.9\%$ ) [Hastings et al., 2003] was much lower than that measured in the eastern United States ( $+0.1\%$ ) [Elliott et al., 2007], the presumed source region, which could indicate an additional  $\text{NO}_x$  source over the ocean or some isotopic transformation during transport from the U.S. to Bermuda.

[15] Aerosol  $\text{NO}_3^-$  ( $\text{NO}_3^-(p)$ ) can contribute 20–65% of total  $\text{NO}_3^-$  deposition in marine environments [Baker et al., 2007] and to our knowledge has not been investigated in the marine atmosphere downwind of North America, a region of high anthropogenic  $\text{NO}_x$  emissions. In addition, rainwater efficiently scavenges both particles and gases from the atmosphere. Therefore, the  $\delta^{15}\text{N-NO}_3^-(p)$  will both influence the  $\delta^{15}\text{N-NO}_3^-(aq)$  and illuminate the source and formation pathways of the  $\text{NO}_3^-(p)$  itself. This study determined the N and O isotopic composition of  $\text{NO}_3^-(p)$  to investigate the importance of anthropogenic contributions to  $\text{NO}_3^-(p)$  and to provide insight into the formation pathways of  $\text{NO}_3^-(p)$  in comparison to  $\text{NO}_3^-(aq)$ .

## 2. Methods

[16] Aerosol samples were collected in March 2010 and from June to August 2010 on the island of Bermuda at the Tudor Hill Marine-Atmospheric Sampling Observatory (32.27°N, 64.87°W) using cassette-based samplers fitted with Whatman 41 cellulose substrates. The filters were frozen until extraction into aqueous solution following the methods of Chen et al. [2006] and Wankel et al. [2009]. The extracts were subsequently analyzed for  $[\text{NO}_3^-]$ , using reduction to NO followed by chemiluminescent detection of NO [Braman and Hendrix, 1989], and for  $^{15}\text{N}/^{14}\text{N}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios, using the denitrifier method [Casciotti et al., 2002; Sigman et al., 2001]. Rainwater samples collected on an event basis from July 2009 through June 2011, including the dates of the aerosol sampling campaign, were analyzed using the same methods. NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model was used to calculate air mass back trajectories (AMBTs) for each

aerosol sample in order to confirm that specific trajectories conformed to expected seasonal atmospheric circulation patterns (Figure S2). Further detail on methods is presented in the supporting information.

## 3. Results and Discussion

[17] HYSPLIT AMBTs support the assumption that the seasonal designations are effective proxies for air mass source, with cool season samples originating over North America and warm season samples originating over the subtropical North Atlantic (Figures S1 and S2), consistent with the longer time series reported by Hastings et al. [2003] and Altieri et al. [2013]. Therefore, the aerosol results are considered representative of seasonal trends. Comparisons below were calculated by season, following the methods of Hastings et al. [2003], and using a two-tailed  $t$  test for populations of unequal variance, where  $p < 0.05$  indicates a statistically significant difference between populations.

[18] Previous studies [Arimoto et al., 1992; Huang et al., 1999; Wolff et al., 1986] and recent collections (Peters et al., unpublished data collected January 2007–June 2008) show that sea salt dominates the composition of Bermuda aerosols compared to mineral dust by over an order of magnitude year round. Infrequent strong dust events, usually during the summer, may cause mineral dust to reach levels comparable to sea salt concentrations [Arimoto et al., 1992; Huang et al., 1999; Peters et al., 2008, unpublished data]. For the samples in this study, however, AMBTs suggest little to no transport from North Africa, the main dust source to Bermuda. While we did not directly address bulk ionic composition of aerosols in this study, an (occasional) important contribution of mineral dust should not significantly affect the trends observed.

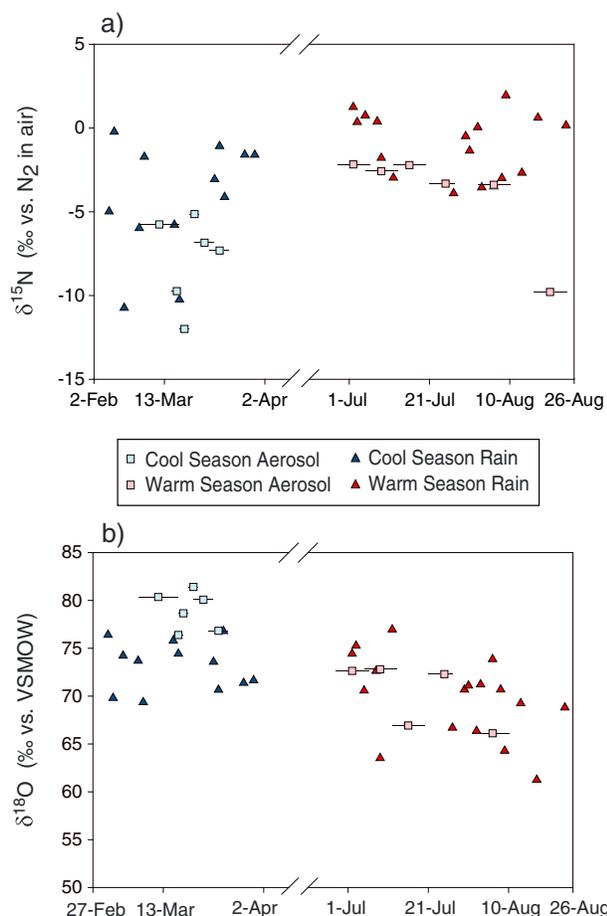
### 3.1. Aerosol and Rainwater $\delta^{15}\text{N-NO}_3^-$

[19] The  $\delta^{15}\text{N-NO}_3^-(p)$  was generally lower than the  $\delta^{15}\text{N-NO}_3^-(aq)$  for rain events concurrent with the aerosol sampling period. The difference ( $\Delta\delta^{15}\text{N} = \delta^{15}\text{N-NO}_3^-(aq) - \delta^{15}\text{N-NO}_3^-(p)$ ) ranged from  $-2.9\%$  to  $6.0\%$  and averaged  $1.5\%$  over the sampling period, although the populations were only significantly different during the warm season (Figure 1a). The isotopic difference between the  $\delta^{15}\text{N-NO}_3^-(p)$  and the  $\delta^{15}\text{N-NO}_3^-(aq)$  agrees with one other observation from the tropical North Atlantic [Baker et al., 2006] but contrasts with the trend reported in polluted regions, where the  $\delta^{15}\text{N-NO}_3^-(p)$  is consistently higher than the  $\delta^{15}\text{N-NO}_3^-(aq)$  [Elliott et al., 2009; Freyer, 1991; Mara et al., 2009]. This difference in  $\delta^{15}\text{N}$  between aerosol and rain  $\text{NO}_3^-$  is present during both the cool and warm seasons (Figure 1a). Thus, the observed difference is likely independent of the chemistry that converts  $\text{NO}_x$  to  $\text{NO}_3^-$ , which has a strong seasonal dependence, as evidenced by the seasonal distribution in  $\delta^{18}\text{O-NO}_3^-$  (Figure 1b) and previous work on  $\delta^{18}\text{O-NO}_3^-$  [Hastings et al., 2003; Elliott et al., 2009; Wankel et al., 2009]. It also does not depend on AMBT, again suggesting little sensitivity to the bulk composition of the aerosol.

[20] In polluted regions,  $\text{NO}_3^-(p)$  occurs predominantly in the fine mode as  $\text{NH}_4\text{NO}_3$  [Putaud et al., 2004], formed through the following reaction:



[22] Freyer [1991] suggested that  $^{15}\text{N}$  is favored in the more stable solid phase, driving the  $\delta^{15}\text{N-NO}_3^-(p)$  higher than the  $\delta^{15}\text{N-HNO}_3(g)$ . The rainwater  $\text{NO}_3^-$ , comprising both the



**Figure 1.** (a) The  $\delta^{15}\text{N-NO}_3^-(p)$  and  $\delta^{15}\text{N-NO}_3^-(aq)$  were lower, and (b) the  $\delta^{18}\text{O-NO}_3^-(p)$  and  $\delta^{18}\text{O-NO}_3^-(aq)$  were higher in the cool season than in the warm season. For rain samples that occurred during the aerosol sampling campaign, the  $\delta^{15}\text{N-NO}_3^-(aq)$  was generally greater than or equal to the  $\delta^{15}\text{N-NO}_3^-(p)$ ; and the  $\delta^{18}\text{O-NO}_3^-(aq)$  was lower than the  $\delta^{18}\text{O-NO}_3^-(p)$  during the cool season but was not statistically different from the  $\delta^{18}\text{O-NO}_3^-(p)$  during the warm season. Horizontal lines through the aerosol symbols indicate the time during which the filter was deployed. In all cases, error bars for isotopic measurements for multiple filter sections were smaller than the symbol size.

higher  $\delta^{15}\text{N-NO}_3^-(p)$  and the lower  $\delta^{15}\text{N-HNO}_3(g)$ , will therefore consistently have a lower  $\delta^{15}\text{N}$  than the aerosol  $\text{NO}_3^-$ , as is observed in polluted regions. This mechanism becomes insignificant, however, when aerosols are transported into the marine atmosphere and shift from fine mode  $\text{NH}_4\text{NO}_3$  to coarse mode through an association between  $\text{HNO}_3(g)$  and sea salt or mineral dust particles [Mara *et al.*, 2009, and references therein]:

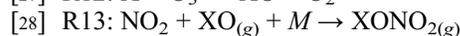
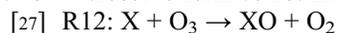


[25] Indeed, about 90% of aerosol  $\text{NO}_3^-$  is in the coarse mode in the North Atlantic marine atmosphere [Baker *et al.*, 2006]. Conversion from fine mode to coarse mode tends to be a unidirectional process; therefore, coarse mode aerosols, unlike fine mode aerosols, are not in equilibrium with  $\text{HNO}_3(g)$  [Keene and Savoie, 1998]. Instead, kinetic fractionation should preferentially form  $^{14}\text{NO}_3^-(p)$ , leaving a  $^{15}\text{N}$ -enriched pool of  $\text{HNO}_3(g)$ . The rainwater  $\text{NO}_3^-$ , integrating the lower

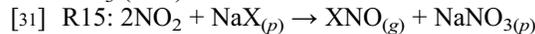
$\delta^{15}\text{N-NO}_3^-(p)$  and the higher  $\delta^{15}\text{N-HNO}_3(g)$ , would yield a  $\delta^{15}\text{N}$  higher than that of the aerosol  $\text{NO}_3^-$ , as observed in the data presented here and by Baker *et al.* [2006].

### 3.2. Aerosol and Rainwater $\delta^{18}\text{O-NO}_3^-$

[26] The  $\delta^{18}\text{O-NO}_3^-(p)$  was significantly higher than the  $\delta^{18}\text{O-NO}_3^-(aq)$  during the cool season but was not significantly different during the warm season (Figure 1b). Recent studies have shown the potential for halogens to play a significant role in  $\text{NO}_x$  and  $\text{NO}_3^-$  chemistry, especially in the polluted marine boundary layer near the continents [Altieri *et al.*, 2013; Osthoff *et al.*, 2008; Thornton *et al.*, 2010; Vicars *et al.*, 2013]. There,  $\text{NO}_x$  may be converted to  $\text{NO}_3^-$  through reaction with  $\text{XO}$  ( $\text{X}=\text{Cl}$  or  $\text{Br}$ ) during the day to form  $\text{XONO}_2$  (R12–R14). First,  $\text{HNO}_3(g)$  in polluted plumes reacts with  $\text{NaCl}$  in the marine boundary layer, releasing  $\text{HCl}$  and  $\text{NaNO}_3(p)$  (R10) or the analogous reaction with  $\text{NaBr}$  to form  $\text{HBr}$ . The  $\text{HX}$  then reacts with  $\text{OH}$  to produce  $\text{Cl}$  or  $\text{Br}$  radicals, which quickly form  $\text{XO}$  by reacting with ozone. The  $\text{XONO}_2$  subsequently formed (R13) can then combine with sea-salt aerosol to form coarse mode  $\text{NO}_3^-(p)$  (R14).



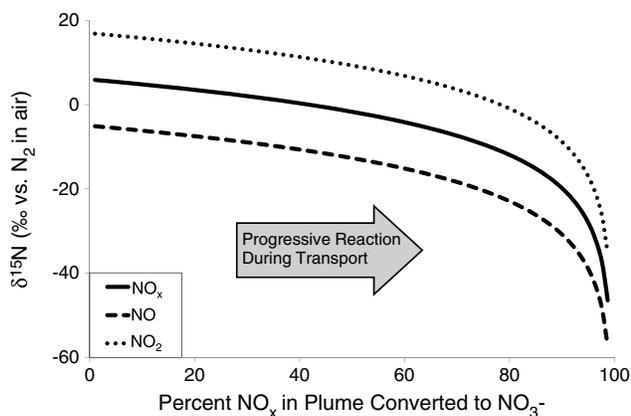
[30]  $\text{NO}_x$  can also react with sea-salt aerosol to form  $\text{XNO}$  and  $\text{NaNO}_3$  (R15).



[32] Mineral dust is assumed to play a negligible role in these reactions for two reasons: the aerosol halogens participating in these reactions can reasonably be assumed to come from sea salt, and these reactions would occur predominantly in polluted, off-shore transport from North America, when mineral dust contributions to Bermuda would be minimal. Because the coarse mode  $\text{NO}_3^-(p)$  formed through these heterogeneous pathways derives all its O atoms from  $\text{O}_3$ , it should have a higher  $\delta^{18}\text{O}$  than  $\text{HNO}_3(aq)$  formed from  $\text{N}_2\text{O}_5$  hydrolysis (R7). The  $\delta^{18}\text{O-NO}_3^-(aq)$  should reflect both the high  $\delta^{18}\text{O-NaNO}_3(p)$  and the lower  $\delta^{18}\text{O-HNO}_3(aq)$  formed from  $\text{N}_2\text{O}_5$  hydrolysis and other  $\text{NO}_3^-$  formation pathways (R4–R7). During the warm season, however, the  $\text{OH}$  pathway (R4) dominates  $\text{NO}_3^-$  formation and should set the  $\delta^{18}\text{O}$  of both aerosols and rainwater. Thus, the direct formation of high  $\delta^{18}\text{O-NO}_3^-(p)$  in the polluted marine boundary layer could lead to the isotopic difference between cool season rain and aerosol  $\text{NO}_3^-$ .

### 3.3. Seasonal characteristics of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$

[33] The range of concentrations for both  $\text{NO}_3^-(p)$  (8.1 to 42  $\text{nmol m}^{-3}$ ;  $n=12$ , Table S2) and  $\text{NO}_3^-(aq)$  (0.8 to 33.3  $\mu\text{M}$ ;  $n=126$ , Table S3) was consistent with other analyses in the North Atlantic [Baker *et al.*, 2006, 2007; Hastings *et al.*, 2003]. On average, dry deposition was 30% of total N (wet + dry) deposition (following the calculations of Baker *et al.* [2007] and assuming all  $\text{NO}_3^-$  was in the coarse mode). The concentrations of rainwater and aerosol  $\text{NO}_3^-$  did not vary significantly by season. However, the concentration-weighted average cool season  $\delta^{15}\text{N-NO}_3^-(p)$  was significantly lower ( $p < 0.01$ ) than the warm season  $\delta^{15}\text{N-NO}_3^-(p)$  ( $-6.2 \pm 2.0\text{‰}$  and  $-2.6 \pm 0.6\text{‰}$ , respectively). Consistent with the findings of Hastings *et al.* [2003], the  $\delta^{15}\text{N-NO}_3^-(aq)$  was also significantly lower in the cool season than in the warm season ( $-4.3 \pm 3.0\text{‰}$  and  $-1.4 \pm 3.1\text{‰}$ , respectively,  $p < 10^{-4}$ ). The concentration-weighted averages for cool



**Figure 2.** This model calculates the expected drop in  $\delta^{15}\text{N}$  for both NO and  $\text{NO}_2$  resulting from the conversion of  $^{15}\text{N}$ -enriched  $\text{NO}_2$  to  $\text{HNO}_3$ . During the winter, 65% of  $\text{NO}_x$  is removed, which could result in a decrease of  $^{15}\text{N}$ -enriched  $\text{NO}_2$  from +6.0‰ to -5.6‰. The  $\text{HNO}_3$  formed is assumed to have the same  $\delta^{15}\text{N}$  as its source  $\text{NO}_2$ . This may explain the difference between the  $\delta^{15}\text{N}$ - $\text{NO}_3^-$  in the United States and that in Bermuda. The figure illustrates the  $\delta^{15}\text{N}$ - $\text{NO}_x$  as a function of the percentage of the  $\text{NO}_x$  in the plume that has been removed from the system through deposition as  $\text{NO}_3^-$ .

season  $\delta^{18}\text{O}$ - $\text{NO}_3^-(p)$  and  $\delta^{18}\text{O}$ - $\text{NO}_3^-(aq)$  ( $+79.1 \pm 1.7\text{‰}$  and  $+74.7 \pm 5.5\text{‰}$ , respectively) were significantly higher ( $p < 0.01$  and  $p < 10^{-4}$ , respectively) than those of the warm season ( $+69.7 \pm 3.4\text{‰}$  and  $+67.1 \pm 4.6\text{‰}$ , respectively).

[34] The isotopic data together with the AMBT patterns suggest a seasonal variation in  $\text{NO}_x$  source such that during the cool season, continental (and thus anthropogenic)  $\text{NO}_x$  is the primary contributor to  $\text{NO}_3^-(p)$  deposition. However, during the cool season, both the  $\delta^{15}\text{N}$ - $\text{NO}_3^-(aq)$  ( $-4.3\text{‰}$ ) and the  $\delta^{15}\text{N}$ - $\text{NO}_3^-(p)$  ( $-6.2\text{‰}$ ) are distinctly lower in Bermuda than in the United States, the source region ( $+0.1 \pm 0.2\text{‰}$ , winter average  $\delta^{15}\text{N}$ - $\text{NO}_3^-(aq)$  [Elliott et al., 2007]; and  $-1.5\text{‰}$ , annual mean  $\delta^{15}\text{N}$ - $\text{NO}_3^-(p)$ , with winter values significantly higher than summer values, although they were not reported separately [Elliott et al., 2009]). The isotopic difference between  $\text{NO}_3^-$  deposition in the U.S. and Bermuda is unlikely to be driven by a significant source difference. AMBTs suggest that the air masses transported to Bermuda are representative of the regions sampled by Elliott et al. [2009]. Moreover, the difference was observed in the concurrent sampling events of Elliott et al. [2007] and Hastings et al. [2003], and the  $\delta^{15}\text{N}$ - $\text{NO}_3^-(aq)$  observations of the latter study are comparable to those of this study.

[35] If the ultimate source of the  $\text{NO}_3^-$  deposited in Bermuda during the cool season is the same as that of the  $\text{NO}_3^-$  deposited in the U.S. as predicted by AMBTs, then the pool of  $\text{NO}_x$  and its oxidation products must preferentially lose  $^{15}\text{N}$  between the U.S. and Bermuda. When  $\text{NO}_x$  concentrations are high relative to  $\text{O}_3$ , equilibrium fractionation between NO and  $\text{NO}_2$  results in  $^{15}\text{N}$ -enriched  $\text{NO}_2$  and  $^{15}\text{N}$ -depleted NO [Freyer et al., 1993]. By contrast, when  $\text{O}_3$  concentrations are greater than  $\text{NO}_x$  concentrations,  $\text{NO}_x$  tends toward  $\text{NO}_2$ , such that the  $\delta^{15}\text{N}$ - $\text{NO}_2$  is expected to equal  $\delta^{15}\text{N}$ - $\text{NO}_x$ . In Bermuda,  $\text{O}_3$  concentrations always exceed  $\text{NO}_x$  concentrations [Prados et al., 1999 and references therein]; therefore, fractionation between NO and  $\text{NO}_2$  has not previously been considered important [Hastings et al., 2003].

In the atmospheric boundary layer over North America, however,  $\text{NO}_x$  concentrations are comparable to  $\text{O}_3$  in many areas and exceed  $\text{O}_3$  in heavily industrialized zones [Liang et al., 1998]. Fractionation between NO and  $\text{NO}_2$  may therefore be important because 65% of  $\text{NO}_x$  emitted in the U.S. is deposited over the continent in the winter [Liang et al., 1998], potentially altering the isotopic composition of the  $\text{NO}_x$  exported from the continent. A simple numerical model described in the supporting information that assumes 65% loss of anthropogenic  $\text{NO}_x$  with a starting  $\delta^{15}\text{N}$  of +6‰ and Rayleigh fractionation with an isotope effect of 1.022 [Freyer et al., 1993] results in a  $\delta^{15}\text{N}$ - $\text{NO}_x$  pool of -5.6‰, consistent with  $\text{NO}_3^-$  deposition at Bermuda (Figure 2; the supporting information also includes a discussion of the model's sensitivity to the assumed isotope effect). This mechanism could be tested by following a coherent plume of  $\text{NO}_x$  and  $\text{NO}_3^-$ , as performed by Neuman et al. [2006] and measuring the time-dependent evolution of both the concentrations and isotopic compositions of  $\text{NO}_3^-$  and  $\text{NO}_x$  as  $\text{NO}_3^-$  is deposited during transport from the U.S. to Bermuda.

[36] Seasonal trends in the  $\delta^{18}\text{O}$ - $\text{NO}_3^-$  similar to the results of this study have been observed in both aerosol [Elliott et al., 2009; Wankel et al., 2009] and rainwater [Elliott et al., 2009; Hastings et al., 2003] and are generally taken to indicate a change in the formation pathway, with the daytime reaction (R4) gaining importance during the warm season and heterogeneous nighttime reaction (R7) gaining importance during the cool season. This interpretation is consistent with the isotopic results of this study, the AMBTs, and modeled predictions of the importance of  $\text{NO}_3^-$  formation pathways [Alexander et al., 2009; Dentener and Crutzen, 1993]. Because of the uncertainty in the absolute values, seasonal trends, and spatial variability of the  $\delta^{18}\text{O}$ - $\text{O}_3$  and  $\delta^{18}\text{O}$ -OH, the  $\delta^{18}\text{O}$ - $\text{NO}_3^-$  alone gives us limited capacity to quantify the contributions of these pathways; nevertheless, a discussion of trends remains possible.

[37] The  $\text{NO}_2 + \text{OH}$  pathway (R4) becomes relatively more important during the warm season: increased radiation from longer days and a decreased angle of solar incidence result in greater production of OH; and decreased atmospheric transport from the U.S. results in less competition with  $\text{O}_3$  in polluted air. The  $\text{NO}_3 + \text{DMS}$  pathway (R8) should also contribute the most in absolute terms during the warm season, when the flux of DMS to the marine atmosphere peaks [Bates et al., 1992]. This pathway would tend to increase the  $\delta^{18}\text{O}$ - $\text{NO}_3^-$  because  $\text{NO}_3$ , the precursor, derives all its O atoms from  $\text{O}_3$ . Since the average  $\delta^{18}\text{O}$ - $\text{NO}_3^-$  decreases during the summer, we can infer that despite the likely increase in total  $\text{NO}_3^-$  formed by the  $\text{NO}_3 + \text{DMS}$  pathway compared to the cool season, the relative strengthening of the  $\text{NO}_2 + \text{OH}$  pathway drives the isotopic composition during the warm season.

[38] The  $\text{N}_2\text{O}_5$  pathway (R7) becomes important under the opposite conditions that lead to increased importance of the  $\text{NO}_2 + \text{OH}$  pathway: longer nights, increased angle of solar incidence, and increased pollution, all occurring during the cool season, lead to the increased relative contribution of  $\text{O}_3$ . The heterogeneous halogen reactions (R12–R15) also become more important during the cool season because of the transport of halogens in polluted air and the increased salt load in the marine atmosphere due to higher wind speeds. Both halogen reactions and the  $\text{N}_2\text{O}_5$  pathway would increase  $\delta^{18}\text{O}$ - $\text{NO}_3^-$ , and thus both may contribute to the

observed trend. Future studies should pursue the quantification of these pathways through simultaneous gas, aerosol, and rainwater sampling, and combined  $^{18}\text{O}$  and  $^{17}\text{O}$  measurements [Morin et al., 2009; Vicars et al., 2013].

#### 4. Conclusion

[39] The N and O isotopic composition of  $\text{NO}_3^-$  at Bermuda follows the same seasonal trends as  $\text{NO}_3^-$ : lower  $\delta^{15}\text{N}$  and higher  $\delta^{18}\text{O}$  during the cool season than during the warm season. The seasonal change in  $\delta^{15}\text{N}-\text{NO}_3^-$  is best interpreted as a seasonal change in  $\text{NO}_x$  source associated with the shift in dominant transport patterns. The cool season  $\delta^{15}\text{N}-\text{NO}_3^-$  observed is much lower than that of  $\text{NO}_3^-$  observed in the presumed source region in North America, a difference best explained by the loss of  $^{15}\text{N}$ -enriched aerosols during transport of anthropogenic  $\text{NO}_x$  from North America to Bermuda, although the mechanism of this loss requires further investigation. The seasonal change in  $\delta^{18}\text{O}-\text{NO}_3^-$  is consistent with a cool-to-warm season shift in the relative importance of the  $\text{O}_3$ -driven nighttime and halogen chemistry versus OH-driven daytime chemistry, respectively.

[40] Aerosol  $\delta^{15}\text{N}-\text{NO}_3^-$  is generally lower than or equal to rainwater  $\delta^{15}\text{N}-\text{NO}_3^-$  collected concurrently. A study in the marine atmosphere showed the same trend [Baker et al., 2007], while studies over continents showed the opposite trend [Elliott et al., 2007, 2009; Freyer, 1991; Mara et al., 2009]. We propose that this isotopic difference is driven by kinetic fractionation during the formation of coarse mode aerosol  $\text{NO}_3^-$  from  $\text{HNO}_3(\text{g})$  due to acid displacement when  $\text{HNO}_3(\text{g})$  reacts with sea-salt and mineral dust particles. This mechanism explains the difference in  $\delta^{15}\text{N}$  between  $\text{NO}_3^-$  and  $\text{NO}_3^-$  during both the cool and warm seasons, and why the offset over the continents is in the opposite direction. The difference between aerosol and rainwater  $\delta^{18}\text{O}-\text{NO}_3^-$  unique to the cool season could be driven by heterogeneous halogen chemistry in the polluted marine boundary layer leading to the formation of high  $\delta^{18}\text{O}-\text{NO}_3^-$ . This work demonstrates the utility of isotopes as a tracer of seasonal changes in  $\text{NO}_x$  source and  $\text{NO}_3^-$  formation pathways, as well as differences in atmospheric chemistry between polluted and marine regions.

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