

# Isotopic composition of rainwater nitrate at Bermuda: The influence of air mass source and chemistry in the marine boundary layer

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Received 16 April 2013; revised 1 August 2013; accepted 10 September 2013; published 2 October 2013.

[1] Emissions of anthropogenic nitrogen (N) to the atmosphere have increased tenfold since preindustrial times, resulting in increased N deposition to terrestrial and coastal ecosystems. The current sources of N deposition to the ocean, however, are poorly understood. To investigate the sources of nitrate in rainwater deposited to the ocean, two years of daily rainwater samples were collected on the island of Bermuda in the western North Atlantic. Air mass back trajectories were computed for each sample and two dominant regimes were identified: slow moving events that originate over the ocean and occur all year, and fast moving events that originate over the continental USA and occur primarily during the cool season (October–March). Marine-influenced air masses result in rainwater nitrate with lower concentrations, higher average  $\delta^{15}\text{N}$ , and lower average  $\delta^{18}\text{O}$  (4.4  $\mu\text{M}$ ,  $-1.1\%$  versus  $\text{N}_2$  in air, and 69.0‰ versus Vienna SMOW, respectively) than those influenced by North American air masses (6.3  $\mu\text{M}$ ,  $-5.4\%$ , and 75.0‰). The  $\delta^{15}\text{N}$  decrease and concentration increase from marine to continental air masses are due to a change in  $\text{NO}_x$  source, with increased anthropogenic inputs associated with continental air. We suggest that heterogeneous halogen chemistry in the marine boundary layer leads to isotopic fractionation. This causes higher  $\delta^{15}\text{N}\text{-NO}_3^-$  to be deposited near the coast and lower  $\delta^{15}\text{N}\text{-NO}_x$  to be transported over the open ocean, yielding a low  $\delta^{15}\text{N}$  for anthropogenic  $\text{NO}_3^-$  deposition. It is possible that this process also contributes to variations in  $\delta^{15}\text{N}\text{-NO}_3^-$  from marine air masses. There is a negative linear correlation ( $r^2 = 0.58$ ) between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  which is driven by the seasonal change in trajectory influencing both the source  $\text{NO}_x$  and the nitrate formation pathways.

**Citation:** Altieri, K. E., M. G. Hastings, A. R. Gobel, A. J. Peters, and D. M. Sigman (2013), Isotopic composition of rainwater nitrate at Bermuda: The influence of air mass source and chemistry in the marine boundary layer, *J. Geophys. Res. Atmos.*, 118, 11,304–11,316, doi:10.1002/jgrd.50829.

## 1. Introduction

[2] The emissions of anthropogenic nitrogen (N) to the atmosphere, and its subsequent deposition, have increased tenfold since preindustrial times [Galloway *et al.*, 2004]. The impacts of increased N deposition to terrestrial and coastal systems are well studied [e.g., Elser *et al.*, 2009; Paerl *et al.*, 2002]; however, the implications for open ocean N biogeochemistry remain uncertain [Duce *et al.*, 2008]. Both anthropogenic and natural processes impact the amount and form of N deposition to remote marine environments,

and there have been clear increases in nitrate deposition as a result of increased anthropogenic emissions of N oxides [Elliott *et al.*, 2007; Galloway *et al.*, 2003; Hastings *et al.*, 2009; Kim *et al.*, 2011; Kodama *et al.*, 2011]. The concentration of nitric acid ( $\text{HNO}_3$ ) in seawater is extremely low; therefore, deposition is a one-way process. Identifying the sources of N deposition to the open ocean is critical for understanding the biogeochemical impacts of human activities. If the N deposition is terrestrial in origin, it represents an external input to the open ocean as the reactive N chemistry over the continents is influenced heavily by anthropogenic activities; this input can be expected to change into the future [Duce *et al.*, 2008]. In contrast, if the N originates from natural sources, then it might not be a N input to the ocean as a whole (e.g., if it derives from the upper ocean), and it is in any case less likely to undergo a marked change in the coming decades.

### 1.1. Nitrate in the Marine Atmosphere

[3] Nitrate ( $\text{NO}_3^-$ ) is the ultimate sink for atmospheric nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), and it is an increasingly significant component of acid rain as effective sulfur dioxide

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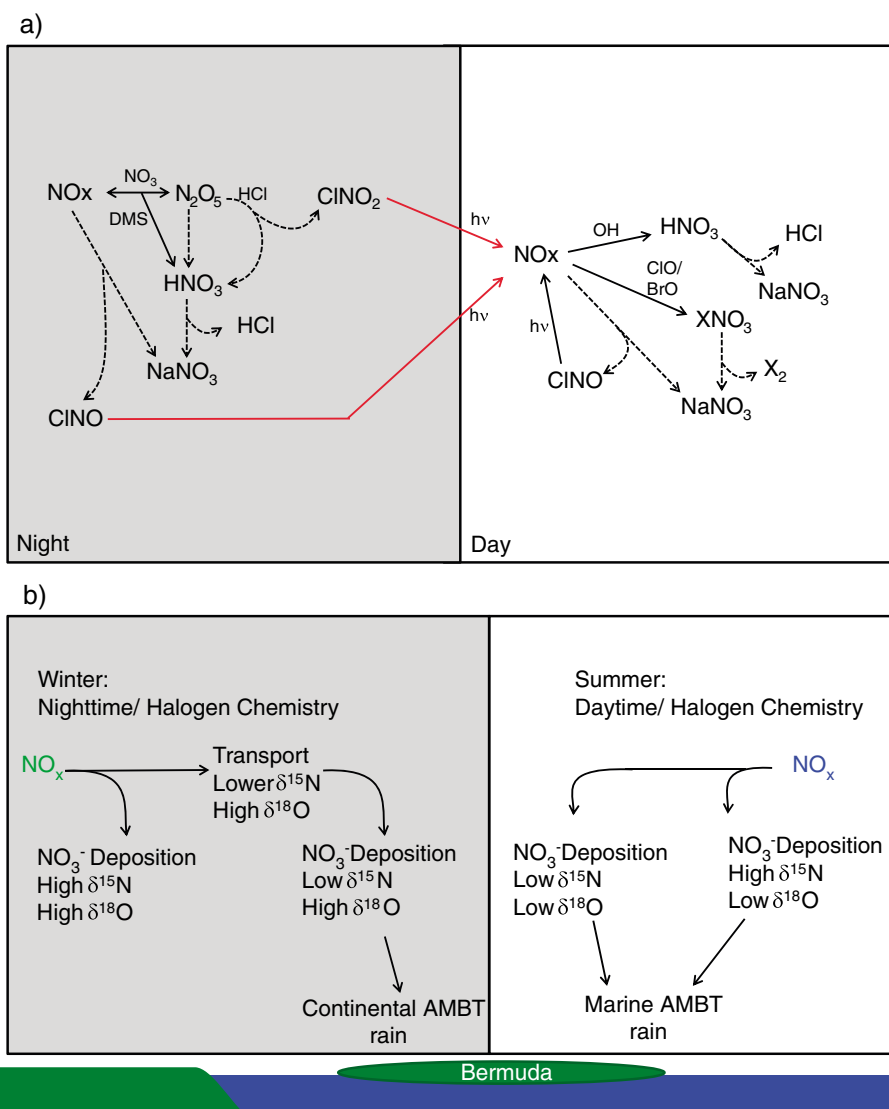
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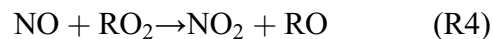
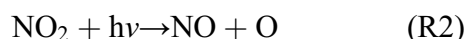
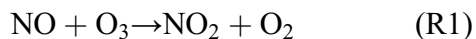
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**Figure 1.** (a) Schematic description of the nighttime and daytime atmospheric chemical processes involving  $\text{NO}_x$  conversion to nitrate. The dashed lines indicate heterogeneous reactions, the solid lines indicate gas phase reactions, and the red solid lines that cross from night to day indicate the nighttime reservoir species that are photolyzed to  $\text{NO}_x$  in the presence of sunlight. (b) The impact of that chemistry on the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of nitrate that reaches Bermuda during continental versus marine AMBT.

regulations lead to decreases in sulfuric acid concentrations. The lifetime of  $\text{NO}_x$  is usually hours to days; thus, its conversion to longer lived reservoir species such as  $\text{HNO}_3$  or peroxyacetyl nitrate (PAN) is needed for reactive N to be transported long distances. The atmospheric cycle of  $\text{NO}_x$  and the conversion of  $\text{NO}_x$  to  $\text{NO}_3^-$  is complex, with different processes taking place during the day and night (Figure 1a). During the day, cycling between  $\text{NO}$  and  $\text{NO}_2$  is rapid (R1)–(R4).

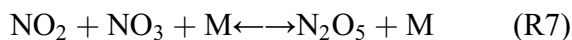
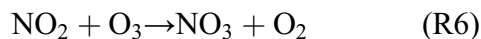


[4] The oxidation of  $\text{NO}$  to  $\text{NO}_2$  requires ozone (R1), while the breakdown of  $\text{NO}_2$  back to  $\text{NO}$  is photolytic and produces ozone [(R2)–(R3)].  $\text{NO}$  can also be oxidized to  $\text{NO}_2$  via peroxy radicals (R4), which also ultimately leads to ozone production. At night, (R2) shuts down and (R1) dominates until  $[\text{NO}_2] \approx [\text{NO}_x]$ . The dominant daytime sink of  $\text{NO}_x$  is the oxidation of  $\text{NO}_2$  to  $\text{HNO}_3$  by the hydroxyl radical (R5).

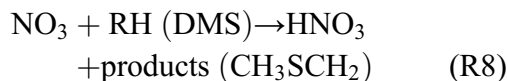


[5] During the night, when photolytic production of  $\text{OH}$  ceases, the concentration of  $\text{OH}$  decreases and  $\text{NO}_2$  reacts preferentially with ozone to form  $\text{NO}_3$ , the dominant nighttime oxidant.  $\text{NO}_2$  and  $\text{NO}_3$  then react further to form

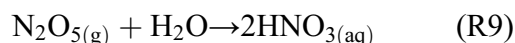
$\text{N}_2\text{O}_5$ , and  $\text{NO}_2$  and  $\text{NO}_3$  remain in thermal equilibrium with  $\text{N}_2\text{O}_5$  [(R6)–(R7)]; M is an unreactive body, usually  $\text{N}_2$ .



[6]  $\text{NO}_3$  can also be lost via gas phase reactions with volatile organic compounds (VOCs), including dimethyl sulfide (DMS) in marine areas (R8) [Stark *et al.*, 2007].



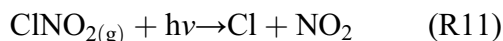
[7] The loss of  $\text{N}_2\text{O}_5$  occurs through heterogeneous hydrolysis on aerosol particles (R9).



[8] Recent studies have shown the potential for halogens to play a significant role in  $\text{NO}_x$  and nitrate chemistry. In the presence of HCl,  $\text{N}_2\text{O}_5$  can also react heterogeneously on aerosol particles to form both aqueous nitrate and  $\text{ClNO}_2$  which partitions to the gas phase (R10) [Thornton *et al.*, 2010].

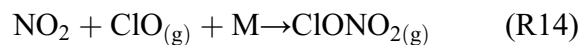
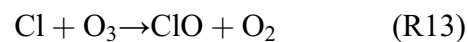


[9] It is hypothesized that the branching ratio between formation of  $\text{HNO}_3(\text{aq})$  in (R9) and  $\text{ClNO}_2(\text{g})$  and  $\text{HNO}_3(\text{aq})$  in (R10) is determined by the relative concentrations of chloride and water in the aerosol particles. In the polluted marine boundary layer where high concentrations of  $\text{NO}_x$  and NaCl particles mix, i.e., in coastal regions,  $\text{ClNO}_2$  is produced in high yields, exceeding previously predicted values by a factor of 2 to 30 [Osthoff *et al.*, 2008]. Maximum production of  $\text{ClNO}_2$  has been found thus far in polluted coastal regions of the North Atlantic, with the largest fluxes occurring in the northern hemisphere winter [Erickson *et al.*, 1999]. The  $\text{ClNO}_2$  acts as a reservoir species, building up in concentration at night and regenerating  $\text{NO}_x$  during the day through photolysis (R11).

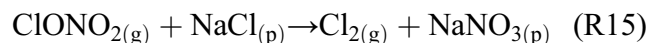


[10] The combination of (R10) and (R11) increases the lifetime of reactive N in the marine atmosphere by regenerating  $\text{NO}_x$ , in contrast to the reaction without halogen chemistry (R9), in which the conversion of  $\text{N}_2\text{O}_5$  to aqueous nitrate aerosol ensures efficient removal of reactive N.

[11] In the presence of halides, another potential mechanism for  $\text{NO}_x$  conversion to  $\text{NO}_3^-$  is through reaction with ClO or BrO during the day to form  $\text{ClONO}_2$  or  $\text{BrONO}_2$  [(R12)–(R14)].



[12] First, acid displacement reactions occur when  $\text{HNO}_3(\text{g})$  in continental outflow reacts with NaCl in the marine boundary layer, releasing HCl and forming  $\text{NaNO}_3(\text{p})$ . The HCl then reacts with OH to produce Cl radicals, which quickly form ClO by reaction with ozone; BrO is formed in an analogous manner. The  $\text{ClONO}_2$  (or  $\text{BrONO}_2$ ) formed can then combine with sea-salt aerosol to form coarse mode aerosol nitrate (R15).



[13] The conversion of  $\text{HNO}_3$  to coarse mode  $\text{NO}_3^-$  should significantly decrease its lifetime as coarse mode particles are deposited preferentially through gravitational settling and precipitation scavenging via inertial impaction.

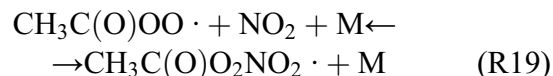
[14]  $\text{NO}_x$  can also react with sea-salt aerosol to form ClNO and  $\text{NaNO}_3$  (R16).



[15] The ClNO produced has two potential fates, photolysis and hydrolysis [(R17)–(R18)].



[16] In polluted environments,  $\text{NO}_x$  can react with peroxyacetyl radicals to form PAN, a long lived  $\text{NO}_x$  reservoir which can be transported long distances at high altitudes. When air masses subside, PAN thermally decomposes to again form  $\text{NO}_2$  (R19) [Fischer *et al.*, 2011, and references therein].



[17] The chemical and physical processing of  $\text{NO}_x$  and nitrate, along with the frequency and amount of precipitation as an air mass travels, controls how much reactive N will be transported to the remote marine atmosphere and the isotopic composition of reactive N.

## 1.2. Previous N Isotope Studies

[18] Inorganic N is the dominant form of N deposition in both polluted [Cornell *et al.*, 2003; Russell *et al.*, 1998] and remote sites [Duce *et al.*, 2008; Galloway *et al.*, 1996; Galloway *et al.*, 1982; Galloway *et al.*, 1989], and nitrate typically represents ~50% of inorganic N deposition. Previous studies have used N and O isotopes of nitrate as a tool for distinguishing nitrate sources and chemical formation pathways in polluted

[Elliott et al., 2007; Freyer, 1978] and open ocean environments [Hastings et al., 2003; Morin et al., 2009]. In the above reactions (section 1.1), as  $\text{NO}_x$  is converted to nitrate, the N atom is conserved. As such, it is generally expected that the  $\delta^{15}\text{N}$  of nitrate will reflect the  $\delta^{15}\text{N}$  of the  $\text{NO}_x$  source. Indeed, previous work suggests that the conversion of  $\text{NO}_x$  to nitrate imparts little isotopic fractionation [Freyer et al., 1993]. In contrast, the O atoms of atmospheric  $\text{NO}_x$  are rapidly exchanged with  $\text{O}_3$  in (R1)–(R4).  $\text{NO}_2$  can be converted to  $\text{NO}_3^-$  through multiple pathways, all resulting in the addition of one oxygen atom. Therefore, the  $\delta^{18}\text{O}$  of nitrate is set by the oxidants that convert  $\text{NO}_x$  to nitrate (e.g., OH versus  $\text{O}_3$ ).

[19] Hastings et al., [2003] showed that nitrate in Bermuda (32.27°N, 64.87°W) rain has higher  $\delta^{15}\text{N}\text{-NO}_3^-$  and lower  $\delta^{18}\text{O}\text{-NO}_3^-$  in the warm season (April to September;  $-2.1\text{‰}$  and  $68.6\text{‰}$ ) as compared to the cool season (October to March;  $-5.9\text{‰}$  and  $76.9\text{‰}$ ; isotope ratios are reported using the delta ( $\delta$ ) notation in “per mil” (‰):  $\delta^{15}\text{N}_{\text{sample}} = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{N}_2 \text{ in air}} - 1] * 1000\text{‰}$  and  $\delta^{18}\text{O}_{\text{sample}} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{18}\text{O}/{}^{16}\text{O})_{\text{VSMOW}} - 1] * 1000\text{‰}$ ). However, the concentration of nitrate was not significantly different from the warm to the cool season (5.0 and 6.4  $\mu\text{M}$ , respectively). They concluded that during the warm season there is substantial nitrate in Bermuda rain that has an isotopic signature distinct from the nitrate coming off North America, implying an alternative nitrate source over the North Atlantic. The rainwater nitrate originating from the south of Bermuda (i.e., marine air) has a  $\delta^{15}\text{N}$  of  $\sim 0\text{‰}$ , which Hastings et al., [2003] attributed to an increased contribution from lightning  $\text{NO}_x$ . Two rain samples collected on research cruises in the Eastern Atlantic Ocean had  $\delta^{15}\text{N}$  values of  $-1.4$  and  $-0.9\text{‰}$  [Baker et al., 2007] consistent with rains at Bermuda.

[20] One interesting and heretofore unresolved result of the Hastings et al. [2003] study is that during the cool season when North America is the air mass source region, the  $\delta^{15}\text{N}\text{-NO}_3^-$  in rain is lower in Bermuda than in the United States. The N and O isotopes of nitrate in weekly rainwater collections were measured in the northeastern USA at National Atmospheric Deposition Program (NADP) sites during the same time frame as the Hastings et al., [2003] study [Elliott et al., 2007; Elliott et al., 2009], and from October to March, the rainwater  $\delta^{15}\text{N}\text{-NO}_3^-$  varied from 0 to 3.5‰. In contrast, the Bermuda cool season average  $\delta^{15}\text{N}$  was  $-5.9 \pm 3.3\text{‰}$  ( $\pm 1\text{SD}$ ).

[21] To investigate the sources and chemistry that influence atmospheric nitrate deposition to the ocean, two years of event-based rainwater samples were collected on the island of Bermuda. Samples were analyzed for major ion concentrations and N and O isotopic ratios of nitrate. NOAA’s Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) was used to determine air mass history for each rainwater sample, and events were classified as originating over the continental USA or as marine in origin.

## 2. Methods

### 2.1. Sample Collection

[22] Rainwater samples were collected on the island of Bermuda (32.27°N, 64.87°W) from 1 July 2009 to 16 September 2011 ( $n=155$ ) at an active ambient air quality monitoring site (station Prospect). All sample data including

concentrations and N and O isotopic composition of nitrate have been made publicly available at the SOLAS Project Integration Aerosol and Rain Composition and Deposition Database. Ambient air quality at this location is characterized by low levels of  $\text{NO}_x$ ,  $\text{SO}_2$ , and particulate matter (A. Peters, TSP,  $\text{PM}_{10}$ , and  $\text{PM}_{2.5}$ , unpublished data). The site is located atop a water catchment 65 m above sea level. It is unobstructed in all directions and is the second highest point on the island. Rainwater samples were collected in acid-washed polyethylene buckets using an automatic rain collector (Aerochem Metrics model 301). Samples were collected on an event basis and retrieved daily to limit microbial degradation of organic matter and consumption of inorganic nutrients. For all samples, the pH, rain volume, and conductivity were measured before being stored at  $-20^\circ\text{C}$ . Freezing at  $-20^\circ\text{C}$  is sufficient to preserve the concentration and isotopic composition of nitrate in rainwater [Hastings et al., 2003]. Field blanks were collected by placing 200 mL of deionized water into the rainwater collector overnight and then collecting the water in the same way as a rainwater sample. The full suite of chemical analyses was also performed on the field blanks to assess possible contamination from the collector or from sample handling. The concentration of nitrate in the field blanks was below the method detection limit (section 2.2).

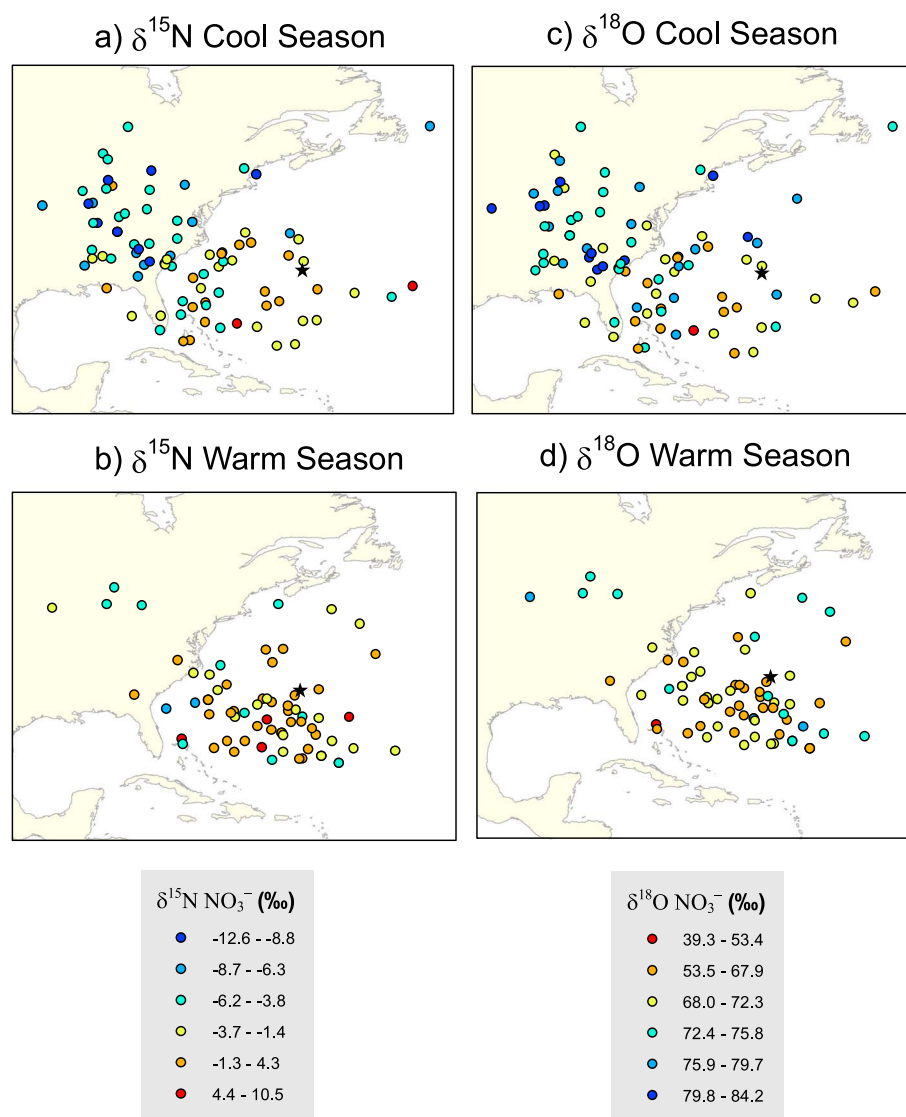
[23] An additional 11 rainwater samples were collected on an event basis at the Bermuda Institute of Ocean Sciences from 2 July 2010 to 13 August 2010, and four rainwater samples were collected at the Tudor Hill Marine-Atmospheric Sampling Observatory tower located 23 m above sea level in March of 2010. These samples are treated in the same manner as those collected at station Prospect.

### 2.2. Anion Concentrations

[24] The rainwater samples were analyzed by ion chromatography for anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ) using an ICS-1600 (Thermo Scientific Dionex, Sunnyvale, USA) at BIOS. Anions were analyzed using an IonPac AS14A 5  $\mu\text{m}$  analytical column ( $3 \times 150 \text{ mm}$ ) with an IonPac AG14A 5  $\mu\text{m}$  guard column ( $3 \times 30 \text{ mm}$ ). The mobile phase was a solution of 8 mM  $\text{Na}_2\text{CO}_3$  and 1 mM  $\text{NaHCO}_3$ . Calibration curves for each analyte were generated using five points over the range of 1 to 1000  $\mu\text{M}$ . The instrument detection limits (defined as the concentration calculated to produce a peak height three times that of a Milli-Q water blank) were: 0.17  $\mu\text{M}$  for  $\text{NO}_3^-$ , 0.08  $\mu\text{M}$  for  $\text{SO}_4^{2-}$ , and 0.04  $\mu\text{M}$  for  $\text{Cl}^-$ . Nitrate concentrations were also determined for a subset of samples by reduction of nitrate and nitrite to nitric oxide followed by chemiluminescence detection of nitric oxide [Braman and Hendrix, 1989]. Nitrite was below detection limit (0.15  $\mu\text{M}$ ) in all rainwater samples.

### 2.3. Nitrate Isotopic Analysis

[25] Measurements of the  ${}^{15}\text{N}/{}^{14}\text{N}$  and  ${}^{18}\text{O}/{}^{16}\text{O}$  ratios of  $\text{NO}_3^-$  were made using the denitrifier method at Princeton University [Casciotti et al., 2002; Sigman et al., 2001]. Natural strains of denitrifying bacteria, in this case *Pseudomonas aureofaciens*, that lack  $\text{N}_2\text{O}$  reductase activity are used to quantitatively convert  $\text{NO}_3^-$  to nitrous oxide ( $\text{N}_2\text{O}$ ). The ion current ratios ( $m/z$  45/44 and 46/44) of the resultant  $\text{N}_2\text{O}$  were measured using a modified GasBench II in line to a Thermo DeltaVPlus IRMS [Casciotti et al., 2002], allowing the coupled determination of the  ${}^{15}\text{N}/{}^{14}\text{N}$



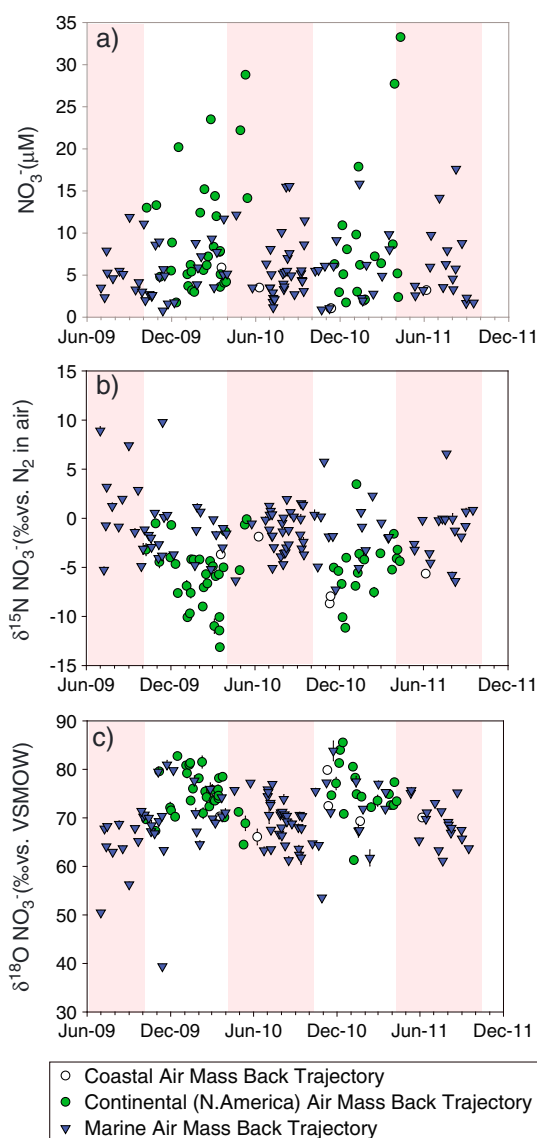
**Figure 2.** Geographic distribution of samples at 36 h before reaching Bermuda (shown as star), based on NOAA HYSPLIT model air mass back trajectories. Colors demark ranges in (a)  $\delta^{15}\text{N-NO}_3^-$  in the cool season, (b)  $\delta^{15}\text{N-NO}_3^-$  in the warm season, (c)  $\delta^{18}\text{O-NO}_3^-$  in the cool season, and (d)  $\delta^{18}\text{O-NO}_3^-$  in the warm season, respectively.

and  $^{18}\text{O}/^{16}\text{O}$  ratios of the  $\text{N}_2\text{O}$  analyte. Individual analyses are referenced to injections of  $\text{N}_2\text{O}$  from a pure gas cylinder and then standardized through comparison to the international reference materials of IAEA-N3 and USGS34 for  $\delta^{15}\text{N-NO}_3^-$ , and IAEA-N3, USGS34, and USGS35 for  $\delta^{18}\text{O-NO}_3^-$  (see Table S1 in the supporting information for standard values) [Bohlke *et al.*, 2003]. The  $^{15}\text{N}/^{14}\text{N}$  is corrected for a bacterial culture blank quantified with each run. The  $^{15}\text{N}/^{14}\text{N}$  of samples is corrected for the contribution of  $^{17}\text{O}$  to the peak at mass 45 using an average  $\Delta^{17}\text{O}$  value for Bermuda rainwater (26‰) [Hastings *et al.*, 2003]. The pooled standard deviation for all measurements of IAEA-N3 and USGS34 for  $\delta^{15}\text{N-NO}_3^-$ , and for all measurements of IAEA-N3, USGS34, and USGS35 for  $\delta^{18}\text{O-NO}_3^-$  can be found in Table S1. All samples were measured at least in duplicate, with 50% being analyzed in triplicate or more. The pooled standard deviation from all replicate analyses

of the samples is 0.24‰ for  $\delta^{15}\text{N-NO}_3^-$  and 0.79‰ for  $\delta^{18}\text{O-NO}_3^-$ .

#### 2.4. Air Mass Back Trajectory Analysis

[26] To determine the source regions for each rainwater event, air mass back trajectories were computed for all sample days using NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT v 4) with NCEP Global Data Assimilation System (GDAS) output. It is accessed via the NOAA ARL READY website at <http://www.arl.noaa.gov/ready/hysplit4.html> (NOAA Air Resources Laboratory, Silver Spring, Maryland). HYSPLIT is used to compute the trajectory of a suspended particle backward in time from a specified point, in this case the island of Bermuda, using a simple particle dispersion simulation and meteorological data. The 36 h back trajectories were chosen to represent the lifetime of  $\text{NO}_x$ . Three-dimensional



**Figure 3.** (a) Nitrate concentration, (b)  $\delta^{15}\text{N}\text{-NO}_3^-$ , and (c)  $\delta^{18}\text{O}\text{-NO}_3^-$  in rain samples collected on Bermuda between June 2009 and November 2011. The pink columns denote the warm season (April to September) while the white columns denote the cool season (October to March). Error bars denote the standard deviation of replicate isotopic measurements. Where error bars are not visible, the standard deviation is smaller than the size of the marker.

trajectories were determined at three altitudes: 100 m, 2000 m, and 5000 m. Sensitivity tests to changes in initial conditions indicated that the main sources of uncertainty in the final trajectory were the starting time and the altitude, hence the use of multiple altitudes for each back trajectory. To deal with the variability associated with starting time, trajectories were run starting every hour during the rain event, or if there was uncertainty in the timing of the rain event, trajectories were run starting every hour that the sample bucket was deployed (i.e., all 24 h). The duration of the rain event was determined by cross-referencing sample collection dates with the meteorological observation archive on the Bermuda National Weather Service Web site ([www.weather.bm](http://www.weather.bm)). Five mean trajectories

were extracted from the multiple trajectories associated with a single rain event through HYSPLIT's clustering algorithm, which calculates the mean trajectory by averaging over all of the input trajectories at every hour.

### 3. Results

#### 3.1. Air Mass Back Trajectory

[27] The computed and clustered back trajectories from the NOAA HYSPLIT model for the duration of each rain event show the geographic distribution of air masses 36 h prior to the collection of a rain event in Bermuda (Figures 2, S1, and S2). During the warm season, (April to September), when the Bermuda Azores high pressure system sets in, almost all events originate over the ocean with a mixture of events coming primarily from the south, but from both east and west of the island (i.e., southeast and southwest; Figures 2b, 2d). During the cool season, (October to March), the Bermuda Azores high breaks down, and there are an almost equal number of events originating over the ocean as there are over the continental USA ( $n=39$  versus  $n=44$ , respectively; Figures 2a, 2c). The events with air mass back trajectories that originate over the continental USA tend to travel much faster and therefore much farther than events that originate over the ocean (Figures S1 and S2). Previous work at Bermuda classified events according to their season (cool versus warm); however, due to the variability in air mass source region during the cool season, season is an inadequate metric of air mass origin. Thus, the data are analyzed in terms of both the season of collection and the air mass source, which will be denoted as marine air mass back trajectory (AMBT) for the air masses that originate over the ocean, and continental AMBT for air masses that originate from the continental USA 36 h prior to arriving at Bermuda. Those few samples that had AMBT origins on the coast of the USA are classified as coastal AMBT to avoid bias in assigning them to either marine or continental AMBT categories.

#### 3.2. Nitrate Concentrations

[28] Nitrate constituted 13–78% of total N (i.e.,  $\text{NO}_3^- + \text{NH}_4^+ +$  organic N) in Bermuda rainwater, with an average of 54 % across all rain samples. There were 155 rainwater samples collected between 1 July 2009 and 16 September 2011 that were analyzed for nitrate concentrations and isotopes (discussed below). The  $\text{NO}_3^-$  concentrations ranged from 0.78 to 33.3  $\mu\text{M}$  (Figure 3a) with a numerical average of  $6.8 \pm 5.4 \mu\text{M}$  ( $\pm 1\text{SD}$  unless otherwise noted). For the different AMBT regimes, the  $\text{NO}_3^-$  concentrations ranged from 0.78 to 17.6  $\mu\text{M}$  for the marine AMBT ( $n=99$ ), 1.8 to 33.3  $\mu\text{M}$  for the continental AMBT ( $n=50$ ), and 1.1 to 5.9  $\mu\text{M}$  for the coastal AMBT ( $n=6$ ). The volume weighted average  $\text{NO}_3^-$  concentration for marine AMBT was  $4.4 \pm 3.1 \mu\text{M}$ , continental AMBT was  $6.3 \pm 4.5 \mu\text{M}$  and for coastal AMBT was  $2.1 \pm 1.1 \mu\text{M}$  (Table 1). In Bermuda rainwater measured from 1980 to 1984, the volume weighted average  $\text{NO}_3^-$  concentration was 4.57  $\mu\text{M}$  in the warm season and 4.33  $\mu\text{M}$  in the cool season [Moody and Galloway, 1988]. In Bermuda rainwater measured from 2000–2001, the volume weighted average  $\text{NO}_3^-$  concentration was 5.0  $\mu\text{M}$  in the warm season and 6.4  $\mu\text{M}$  in the cool season [Hastings et al., 2003].

**Table 1.** The Average ( $\pm 1$  SD) Concentrations and Isotopic Ratios of N and O in Rainwater Nitrate Binned by the Source Region of the Event Air Mass Back Trajectory (AMBT)<sup>a</sup>

	Marine	Continental	Coastal	Average of All Data
	AMBT	AMBT	AMBT	
$[\text{NO}_3^-]^{\text{b}}$ ( $\mu\text{M}$ )	4.38 $\pm$ 3.13 (99)	6.33 $\pm$ 4.46 (50)	2.08 $\pm$ 1.13 (6)	4.88 $\pm$ 3.64 (155)
$\delta^{15}\text{N NO}_3^-^{\text{c}}$ (‰)	-1.6 $\pm$ 2.8	-5.7 $\pm$ 2.4	-4.5 $\pm$ 2.2	-3.1 $\pm$ 3.3
$\delta^{18}\text{O NO}_3^-^{\text{c}}$ (‰)	69.3 $\pm$ 5.1	76.5 $\pm$ 4.5	69.4 $\pm$ 2.6	71.9 $\pm$ 6.0
$\delta^{15}\text{N NO}_3^-^{\text{d}}$ (‰)	-1.1 $\pm$ 3.0	-5.4 $\pm$ 3.2	-5.3 $\pm$ 2.6	-2.6 $\pm$ 3.7
$\delta^{18}\text{O NO}_3^-^{\text{d}}$ (‰)	69.0 $\pm$ 6.4	75.0 $\pm$ 4.8	71.3 $\pm$ 4.7	71.1 $\pm$ 6.4

<sup>a</sup>The number of samples measured for nitrate concentrations and isotopes in each category is in parentheses.

<sup>b</sup>Volume weighted average.

<sup>c</sup>Mass weighted average.

<sup>d</sup>Numerical average.

\*Statistically different means at the 0.0025 level  $H=9.1$ , Kruskal-Wallis test for nonparametric data.

\*\*Statistically different means at 95% confidence interval, independent  $t$  test assuming unequal variance.

\*\*\* $p < 0.0001$ .

\*\*\*\* $p < 10^{-9}$ .

[29] The  $\text{NO}_3^-$  concentrations measured in the continental and marine AMBT are statistically different (Table 1, Figure S3) (Kruskal-Wallis test for nonparametric data,  $H=9.1$ ,  $p=0.002$ ). Previous studies that binned rainwater by cool and warm season, and not by event-based trajectory, typically report that  $\text{NO}_3^-$  concentrations are not statistically different from the cool to the warm season in Bermuda [Galloway *et al.*, 1982; Hastings *et al.*, 2003; Moody and Galloway, 1988] and this is true in our data set as well: if the  $\text{NO}_3^-$  concentrations are binned by cool and warm season, they are not statistically different (Kruskal-Wallis test  $H=0.75$ ,  $p=0.387$ ). This highlights the importance of using event-based AMBT analysis, as during the cool season, the AMBT are quite variable and include a large number of marine AMBT which dilute the anthropogenic signals inherent in the continental AMBT (Figures 2, 3).

### 3.3. N Isotopes of Nitrate

[30] The measurements of  $\delta^{15}\text{N-NO}_3^-$  in Bermuda rain ranged from -13.1 to 9.8‰ from 1 July 2009 to 16 September 2011 (Figure 3b) with a numerical average of -2.6 $\pm$ 3.7‰ (Table 1). The  $\delta^{15}\text{N-NO}_3^-$  does not correlate with  $[\text{NO}_3^-]$  (Figure S4),  $[\text{NH}_4^+]$ ,  $[\text{nss-SO}_4^{2-}]$ , or rainfall amount (not shown). However, the  $\delta^{15}\text{N-NO}_3^-$  does correlate with  $\delta^{18}\text{O-NO}_3^-$ , which is discussed below (Figure 5). The mean  $\delta^{15}\text{N-NO}_3^-$  for the continental AMBT was -5.4 $\pm$ 3.2‰, and for the marine AMBT was -1.1 $\pm$ 3.0‰. The  $\delta^{15}\text{N-NO}_3^-$  for the different AMBT regimes is significantly different (independent  $t$  test, 95%,  $p < 10^{-13}$ ). If the

continental AMBT average is weighted using the nitrate concentration and rain volume of each event, the mass-weighted average  $\delta^{15}\text{N-NO}_3^-$  of -5.7 $\pm$ 2.4‰ is also significantly lower than the marine AMBT mass-weighted average  $\delta^{15}\text{N-NO}_3^-$  of -1.6 $\pm$ 2.8‰.

[31] In previous work, the  $\delta^{15}\text{N-NO}_3^-$  was binned by cool and warm season instead of marine and continental AMBT, and averages of -5.9 $\pm$ 3.3‰ and -2.1 $\pm$ 1.5‰ were found in the cool and warm seasons, respectively ( $n=65$ , [Hastings *et al.*, 2003]). For comparison, the season based  $\delta^{15}\text{N-NO}_3^-$  averages for this data set were -3.9 $\pm$ 3.8‰ ( $n=87$ ) and -1.2 $\pm$ 3.0‰ ( $n=68$ ) in the cool and warm seasons, respectively, which are statistically different (independent  $t$  test, 95%,  $p < 10^{-6}$ ). The mass-weighted average cool season  $\delta^{15}\text{N-NO}_3^-$  was -4.3 $\pm$ 2.5‰ and warm season was -1.4 $\pm$ 3.1‰. However, the statistical significance (i.e., the  $p$  values) of the  $\delta^{15}\text{N-NO}_3^-$  comparison is much stronger when the values are compared by AMBT (Table 1) as the cool season back trajectories can be quite variable. Interestingly, if the data are compared by both AMBT and season, it appears that the season does have an influence on the measured  $\delta^{15}\text{N-NO}_3^-$  value (Table 2 and Figure 4a). The continental AMBT had the lowest  $\delta^{15}\text{N-NO}_3^-$  values, but within all of the continental AMBT data, the mass weighted cool season average was lower than the warm season average (-6.0 $\pm$ 2.3‰ and -3.5 $\pm$ 1.7‰, respectively; independent  $t$  test, 95%,  $p=0.02$ ). The marine AMBT were higher in  $\delta^{15}\text{N-NO}_3^-$ , but within all of the marine AMBT data, the

**Table 2.** The Average ( $\pm 1$  SD) Concentrations and Isotopic Ratios of N and O in Rainwater Nitrate Binned by Both the Season (Cool and Warm) and the Source Region of the Events AMBT (Marine, Continental, Or Coastal)<sup>a</sup>

	Continental AMBT	Continental AMBT	Marine AMBT	Marine AMBT
	Cool Season	Warm Season	Cool Season	Warm Season
$[\text{NO}_3^-]^{\text{b}}$ ( $\mu\text{M}$ )	6.23 $\pm$ 3.58 (44)	7.02 $\pm$ 9.13 (6)	3.82 $\pm$ 2.92 (39)	4.85 $\pm$ 3.26 (60)
$\delta^{15}\text{N NO}_3^-^{\text{c}}$ (‰)	-6.0 $\pm$ 2.3	-3.5 $\pm$ 1.7	-2.2 $\pm$ 2.2	-1.2 $\pm$ 3.2
$\delta^{18}\text{O NO}_3^-^{\text{c}}$ (‰)	77.2 $\pm$ 4.3	72.2 $\pm$ 3.7	71.7 $\pm$ 5.2	67.7 $\pm$ 4.3
$\delta^{15}\text{N NO}_3^-^{\text{d}}$ (‰)	-5.8 $\pm$ 3.2	-3.0 $\pm$ 2.1	-1.4 $\pm$ 3.1	-0.8 $\pm$ 3.0
$\delta^{18}\text{O NO}_3^-^{\text{d}}$ (‰)	75.6 $\pm$ 4.7	71.3 $\pm$ 4.4	70.3 $\pm$ 7.8	68.2 $\pm$ 5.1

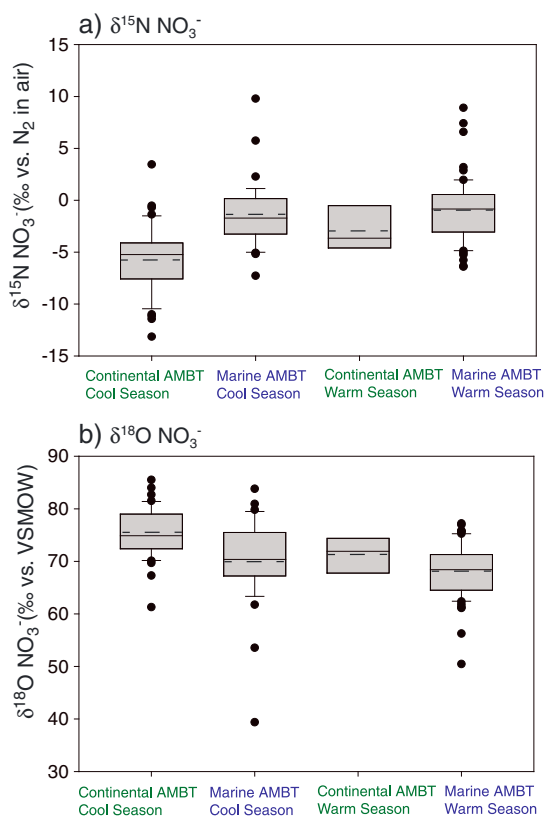
<sup>a</sup>The number of samples measured for nitrate concentrations and isotopes in each category is in parentheses.

<sup>b</sup>Volume weighted average.

<sup>c</sup>Mass weighted average.

<sup>d</sup>Numerical average.





**Figure 4.** Box and whisker plot of (a) rainwater  $\delta^{15}\text{N-NO}_3^-$  and (b)  $\delta^{18}\text{O-NO}_3^-$ . The solid line is the median; the dashed line is the numerical average. The whisker lines above and below the box indicate the 90th and 10th percentiles. The  $\delta^{15}\text{N-NO}_3^-$  of continental AMBT cool season is statistically different than the  $\delta^{15}\text{N-NO}_3^-$  of the continental AMBT warm season. The  $\delta^{18}\text{O-NO}_3^-$  of continental AMBT is statistically different from the cool to the warm season, and the  $\delta^{18}\text{O-NO}_3^-$  of marine AMBT is also statistically different from the cool to the warm season.

mass weighted cool season average was slightly lower than the warm season average ( $-2.2 \pm 2.2\%$  and  $-1.2 \pm 3.2\%$ , respectively; not statistically significant).

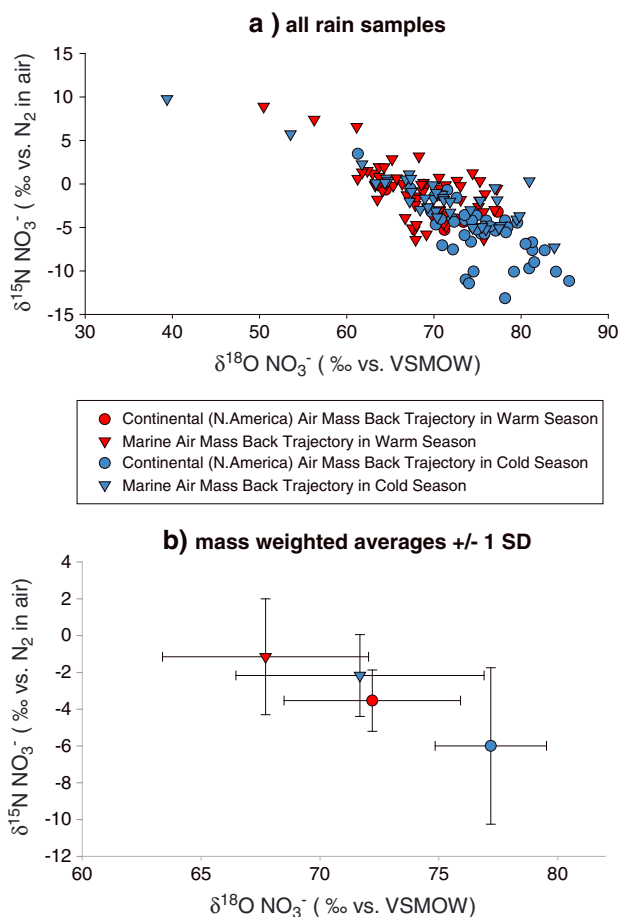
### 3.4. O Isotopes of Nitrate

[32] The measurements of  $\delta^{18}\text{O-NO}_3^-$  in Bermuda rain ranged from 39.4 to 85.5‰ from 1 July 2009 to 16 September 2011 (Figure 3c) with a numerical average of  $71.1 \pm 6.4\%$  (Table 1). Similar to the  $\delta^{15}\text{N-NO}_3^-$ , the  $\delta^{18}\text{O-NO}_3^-$  does not correlate with  $[\text{NO}_3^-]$ ,  $[\text{NH}_4^+]$ ,  $[\text{nss-SO}_4^{2-}]$ , or rainfall amount (not shown), but it does correlate with  $\delta^{15}\text{N-NO}_3^-$  (Figure 5). The mean  $\delta^{18}\text{O-NO}_3^-$  is significantly different (independent  $t$  test, 95%,  $p < 10^{-9}$ ) for the different AMBTs, with the continental AMBT averaging  $75.0 \pm 4.8\%$  and the marine AMBT averaging  $69.0 \pm 6.4\%$ . The mass-weighted continental AMBT average  $\delta^{18}\text{O-NO}_3^-$  of  $76.5 \pm 4.5\%$  was also higher than the marine AMBT mass-weighted average  $\delta^{18}\text{O-NO}_3^-$  of  $69.3 \pm 5.1\%$ .

[33] The range of  $\delta^{18}\text{O-NO}_3^-$  in the Bermuda rainwater (61.1 to 85.5‰), excluding the four samples with  $\delta^{18}\text{O}$  less than 60.0‰, is consistent with rainwater nitrate measured previously in Bermuda (60.3 to 86.5‰; [Hastings et al., 2003]),

and rainwater collected at 17 National Trend Network sites in the USA ( $\sim 60$ – $90\%$ ; [Elliott et al., 2009]). The four samples with low  $\delta^{18}\text{O}$  are also the samples with the highest  $\delta^{15}\text{N-NO}_3^-$  (5.8 to 9.8‰), and they all have marine AMBT origins though only two are from the warm season.

[34] In previous work, as with the  $\delta^{15}\text{N-NO}_3^-$ , the  $\delta^{18}\text{O-NO}_3^-$  was binned by cool and warm season instead of marine and continental AMBT and the averages were  $76.9 \pm 6.3\%$  and  $68.6 \pm 3.6\%$  for the cool and warm seasons, respectively ( $n = 65$  [Hastings et al., 2003]). For this data set, the cool and warm season average  $\delta^{18}\text{O-NO}_3^-$  were  $73.1 \pm 6.7\%$  ( $n = 87$ ) and  $68.6 \pm 5.0\%$  ( $n = 68$ ), respectively, and they are statistically different (independent  $t$  test, 95%,  $p < 10^{-6}$ ). The mass weighted average cool and warm season  $\delta^{18}\text{O-NO}_3^-$  were  $74.5 \pm 4.6\%$  and  $68.2 \pm 4.5\%$ . As with the  $\delta^{15}\text{N-NO}_3^-$ , the statistical significance (i.e., the  $p$  values) of the  $\delta^{18}\text{O-NO}_3^-$  comparison is much stronger when the values are compared by back trajectory. However, if the data are compared by both AMBT and season, it appears that season has even more of an influence on the measured  $\delta^{18}\text{O-NO}_3^-$  than on the



**Figure 5.** The relationship of  $\delta^{15}\text{N-NO}_3^-$  as a function of  $\delta^{18}\text{O-NO}_3^-$  for (a) all rain samples ( $r^2 = 0.58$ ,  $y = -0.44x + 28.52$ ,  $p < 10^{-30}$ ) and (b) the mass weighted averages with the error bars denoting one mass-weighted standard deviation of the mean. Symbols denote the source region based on the 36 h air mass back trajectory and the color indicates the warm versus cool seasons, respectively. Note the change in scale for the x and y axes from Figures 5a to 5b.



$\delta^{15}\text{N-NO}_3^-$  (Table 2 and Figure 4). The continental AMBT had the highest  $\delta^{18}\text{O-NO}_3^-$  values overall, but within all of the continental AMBT data, the cool season mass-weighted average was higher than the warm season average ( $77.2 \pm 4.3\%$  and  $72.2 \pm 3.7\%$ , respectively; independent  $t$  test, 95%,  $p < 0.02$ ). Likewise, the marine AMBT were lower in  $\delta^{18}\text{O-NO}_3^-$ , but within all of the marine AMBT data, the cool season mass weighted average was higher than the warm season mass weighted average ( $71.7 \pm 5.2\%$  and  $67.7 \pm 4.3\%$ , respectively; independent  $t$  test, 95%,  $p < 0.0001$ ).

### 3.5. Relationship Between N and O Isotopes of Nitrate

[35] Across the entire rainwater sample set, there was a negative correlation ( $r^2 = 0.58$ ,  $y = -0.44x + 28.52$ ,  $p < 10^{-30}$ ) between the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  (Figure 5a), consistent with the previous study of rainwater N and O isotopes in Bermuda [Hastings *et al.*, 2003]. The samples cluster according to both their season (cool versus warm) and air mass history (continental versus marine) characteristics (Figure 5b). The warm season marine AMBT (highest  $\delta^{15}\text{N}$  and lowest  $\delta^{18}\text{O}$ ) and the cool season continental AMBT (lowest  $\delta^{15}\text{N}$  and highest  $\delta^{18}\text{O}$ ) are the end members, while the samples with anomalous trajectories for their season (e.g., a warm season sample with continental AMBT) fall in the middle.

## 4. Discussion

### 4.1. Rainwater Nitrate $\delta^{15}\text{N}$

[36] The  $\delta^{15}\text{N}$  of nitrate should reflect the  $\delta^{15}\text{N}$  of the  $\text{NO}_x$  source, overprinted by any fractionation associated with the chemical pathway that converts  $\text{NO}_x$  to nitrate. Rain events with continental AMBT origins occur primarily during the cool season (October to March) and are consistently lower in  $\delta^{15}\text{N-NO}_3^-$  and higher in  $\text{NO}_3^-$  concentration than rain events from marine AMBT, which occur all year (Figure 3b). North American  $\text{NO}_x$  emissions are dominated by anthropogenic sources with  $\sim 87\%$  coming from fossil fuel burning of automobiles, power plants, and industry [Zhang *et al.*, 2003]. Therefore, the lower  $\delta^{15}\text{N}$  and higher concentrations during rain events with continental AMBT suggests that when air masses come from the continental USA, they bring  $\text{NO}_3^-$  with a different, and likely anthropogenic,  $\text{NO}_x$  source (Figure 1b). This interpretation is consistent with previous work on rainwater  $\delta^{15}\text{N-NO}_3^-$  in this region [Hastings *et al.*, 2003], which interpreted the  $\delta^{15}\text{N-NO}_3^-$  changes from the cool to the warm season as a change in  $\text{NO}_x$  source despite a lack of concurrent change in nitrate concentration in their data set. Classification by AMBT makes a stronger argument in favor of this interpretation since the  $\delta^{15}\text{N-NO}_3^-$  has an even greater statistical difference, and the nitrate concentration is also found to be significantly higher with continental AMBTs than marine AMBT, although nitrate concentrations are not significantly different from cool to warm season. Therefore, we also conclude that nitrate deposition at Bermuda associated with continental AMBT from North America has a continental and thus anthropogenic  $\text{NO}_x$  source.

[37] In the few continental AMBT rain events that occurred during the warm season, the  $\delta^{15}\text{N-NO}_3^-$  was significantly higher than for those that occurred during the cool season, likely as a result of mixing with the high  $\delta^{15}\text{N-NO}_3^-$  present

in the warm season atmosphere near Bermuda (Figures 3b and 4a). We do not believe that this increase in  $\delta^{15}\text{N}$  is due to changes in North American  $\delta^{15}\text{N-NO}_3^-$  or  $\delta^{15}\text{N-NO}_x$  as the summer months are when North American rainwater  $\delta^{15}\text{N-NO}_3^-$  is lowest [Elliott *et al.*, 2009]. This suggests that during the cool and warm seasons, the dominant transport pathways lead to a background nitrate isotopic composition that is consistent with the default transport pattern in that season, i.e., low  $\delta^{15}\text{N-NO}_3^-$  during the cool season from North American transport and higher  $\delta^{15}\text{N-NO}_3^-$  during the warm season from the marine atmosphere. Thus, an anomalous trajectory for that season brings with it the  $\delta^{15}\text{N}$  source signature of the  $\text{NO}_x$ , which is then mixed with the nitrate from that particular season's dominant transport pathway, diminishing the originating source signal.

[38] Interestingly, the nitrate concentration and  $\delta^{15}\text{N}$  of rainwater collected in Bermuda during continental AMBT are typically lower than those of rainwater collected in the USA, the source region. The N and O isotopes of nitrate in weekly rainwater collections were measured in the northeastern USA at NADP sites [Elliott *et al.*, 2007; Elliott *et al.*, 2009]. From October to March, the rainwater  $\delta^{15}\text{N-NO}_3^-$  varied from  $\sim 0$  to  $3.5\%$  at those sites. In Bermuda rainwater during the cool season of October to March, when AMBTs almost exclusively originate over the continental USA, the  $\delta^{15}\text{N-NO}_3^-$  in Bermuda rain were at their minimum ( $-5.4 \pm 3.2\%$ ; Table 1). This is also true in previously published data on  $\delta^{15}\text{N-NO}_3^-$  in Bermuda rain [Hastings *et al.*, 2003] which were collected during the same time frame as the Elliott *et al.* [2007, 2009] studies and were in the same range as those reported here ( $-5.9 \pm 3.3\%$ ). The nitrate concentration in NADP weekly rainwater collections in the eastern USA from October to March, 2009–2011 ranged from 0.7 to 147  $\mu\text{M}$ , with an average of  $16.5 \pm 16.9 \mu\text{M}$  (data accessible online at [www.nadp.sws.uiuc.edu](http://www.nadp.sws.uiuc.edu) [NADP, 2007]), compared to an average nitrate concentration in Bermuda rain from continental AMBT of  $6.3 \pm 4.5 \mu\text{M}$ . The difference in  $\delta^{15}\text{N}$  and concentration of nitrate from the continental USA to Bermuda suggests that there must be loss of nitrate, or  $\text{NO}_x$ , as polluted continental air masses move off of the continent, and that this loss has a preference for  $^{15}\text{N}$  (Figure 1b). Below we outline three potential mechanisms to explain the  $\delta^{15}\text{N-NO}_3^-$  difference between North American rainwater and rainwater collected at Bermuda from North American transport, involving (1) equilibrium fractionation between  $\text{NO}$  and  $\text{NO}_2$  over the continents, (2) heterogeneous reaction of  $\text{N}_2\text{O}_5$  with  $\text{HCl}$  (R10), and (3) reaction of  $\text{NO}_2$  with  $\text{NaCl}$  particles (R16).

[39] The first hypothesis is dependent on the relative concentrations of  $\text{NO}_x$  and ozone in North America and Bermuda. When  $\text{NO}_x$  concentrations are higher than ozone concentrations, equilibrium fractionation between  $\text{NO}$  and  $\text{NO}_2$  (R1–R4) results in  $^{15}\text{N}$ -enriched  $\text{NO}_2$  [Freyer *et al.*, 1993]. When ozone concentrations are higher than  $\text{NO}_x$  concentrations, most of the  $\text{NO}_x$  is oxidized to  $\text{NO}_2$  such that the  $\delta^{15}\text{N-NO}_2$  is equivalent to the  $\delta^{15}\text{N-NO}_x$ . In Bermuda, ozone concentrations always exceed  $\text{NO}_x$  concentrations [Oltmans *et al.*, 1996; Prados *et al.*, 1999], and as a result fractionation between  $\text{NO}$  and  $\text{NO}_2$  has previously been considered to be unimportant [Hastings *et al.*, 2003]. In the atmospheric boundary layer over North America, however,  $\text{NO}_x$  concentrations are comparable to ozone in many areas

and exceed ozone in heavy industrial zones [Liang *et al.*, 1998], causing the equilibrium fractionation between NO and NO<sub>2</sub> to be relevant in air masses that are subsequently transported to Bermuda. If <sup>15</sup>N enriched NO<sub>2</sub> is converted to HNO<sub>3</sub>, the higher δ<sup>15</sup>N-HNO<sub>3</sub> would be deposited closer to the coast, leaving behind lower δ<sup>15</sup>N-NO<sub>x</sub> to be exported to the marine atmosphere.

[40] The second and third hypotheses are related in that both rely on fractionation between the gas and particle phases due to heterogeneous halogen chemistry. At night and in the winter, the dominant loss mechanism for NO<sub>x</sub> is through formation of N<sub>2</sub>O<sub>5</sub> via reaction of NO<sub>2</sub> with NO<sub>3</sub> radicals (Figure 1a). The potential for halides to interact with N<sub>2</sub>O<sub>5</sub> forming ClNO<sub>2</sub> has been documented in numerous laboratory studies [Behnke *et al.*, 1997; Finlayson-Pitts, 2003], with recent direct measurements suggesting that this process is significant in the coastal marine atmosphere [Osthoff *et al.*, 2008; Pechtl and von Glasow, 2007] (see section 1.1). In the presence of NaCl particles, the N<sub>2</sub>O<sub>5</sub> reacts with HCl, forming aqueous HNO<sub>3</sub> and releasing ClNO<sub>2(g)</sub> (R10). This ClNO<sub>2</sub> acts as a reservoir species until the day, when it is quickly photolyzed to Cl and NO<sub>2</sub>, recycling the original NO<sub>x</sub> stored as N<sub>2</sub>O<sub>5</sub> (R11). There is the potential for isotopic fractionation during this process as heavier isotopes are preferentially incorporated into the more stable phase: during the heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> on the aerosol particle, the <sup>14</sup>N should be preferentially incorporated into the gas phase ClNO<sub>2</sub>, leaving <sup>15</sup>N behind in the more stable particle phase. Similarly, one might speculate based on the preference of heavier isotopes to prefer the more stable phase, that when NO<sub>2</sub> reacts with sea-salt aerosol to form NaNO<sub>3(p)</sub> and ClNO<sub>(g)</sub>, the <sup>15</sup>N should be preferentially incorporated into the NaNO<sub>3(p)</sub> and the <sup>14</sup>N should be preferentially incorporated into the gas phase ClNO<sub>(g)</sub>. The lifetime of a particle with respect to deposition is much shorter than the lifetime of NO<sub>2</sub> and as such the higher δ<sup>15</sup>N particle-associated nitrate should be deposited fairly rapidly while the lower δ<sup>15</sup>N-NO<sub>x</sub> (from (R11) and (R17)) will persist in the atmosphere to again form nitrate, potentially contributing to a decrease in the δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> of deposition downwind of the continents (Figure 1b). This chemistry may also explain the smaller number of very high δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> (>0‰) events associated with marine AMBT (Figures 3b and 5a), as discussed immediately below. Partially because of this apparent confluence, we favor the above halogen chemistry as the explanation for the δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> decrease from North America to Bermuda. The impact of these processes on the δ<sup>18</sup>O-NO<sub>3</sub><sup>-</sup> is also discussed below, in section 4.2.

[41] The previous work at Bermuda measured a δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> range of -4.7 to 1.4‰ in the warm season N isotopes, and this relatively high δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> was tentatively attributed to an increased contribution from lightning NO<sub>x</sub> (with a δ<sup>15</sup>N of 0‰) during the warm season [Hastings *et al.*, 2003]. Indeed, improved satellite estimates of the contribution of lightning NO<sub>x</sub> confirm an enhancement over the tropical Atlantic Ocean due to upper tropospheric transport that is not present over the Pacific Ocean. However, a lightning NO<sub>x</sub> source at 0‰ cannot explain the regular occurrence of δ<sup>15</sup>N values above 0‰ (20% of samples > 0‰), with values up to 9.8‰ for marine AMBT. We propose two mechanisms to explain these high δ<sup>15</sup>N events, (1) the halogen chemistry described above, producing high δ<sup>15</sup>N particles in air with

a marine AMBT or (2) a higher δ<sup>15</sup>N-NO<sub>x</sub> source, such as PAN.

[42] The halogen chemistry described above leads to the formation of aerosol nitrate with a high δ<sup>15</sup>N relative to the original NO<sub>x</sub> load in a given air parcel. While our focus above was on the occurrence of this process in continentally derived air, it could also occur in the marine atmosphere, due to the high concentrations of sea-salt particles, and will depend on the concentrations of NO<sub>2</sub> and NO<sub>3</sub> which control the formation of N<sub>2</sub>O<sub>5</sub> at night through thermal equilibrium. Unlike continental air masses, where much of the original NO<sub>x</sub> is deposited before transport to the open ocean, resulting in consistent depletion of <sup>15</sup>N prior to deposition, marine air masses may deposit NO<sub>3</sub><sup>-</sup> at any stage of the atmospheric processing of NO<sub>x</sub>. On average, this fractionation should have no net effect for marine AMBT nitrate wet deposited at Bermuda: rain would scavenge both the high δ<sup>15</sup>N aerosol formed initially in some events and the lower δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup> from the regenerated NO<sub>x</sub> in other events. However, the process should lead to variability in δ<sup>15</sup>N-NO<sub>3</sub><sup>-</sup>. We propose that the small number of very high δ<sup>15</sup>N marine AMBT events (Figures 3b and 5a) result from the presence of NO<sub>3</sub><sup>-</sup> formed in the initial stages of high δ<sup>15</sup>N aerosol formation (Figure 1b).

[43] While there are certainly other possibilities that cannot be ruled out, the most plausible alternative is the continental export of PAN, a potential source of NO<sub>x</sub> to the remote marine troposphere during the warm season. Briefly, PAN forms in urban environments where OH and aldehydes form peroxyacetyl radicals, which react with NO<sub>x</sub> to form PAN. PAN is transported on a hemispheric scale at high altitudes due to its stability at cold temperatures. When air masses subside into the boundary layer, the lifetime of PAN decreases to ~1 h and thermal decomposition results in the release of the stored NO<sub>x</sub> (R19, [Fischer *et al.*, 2011; Kotchenruther *et al.*, 2001]). In the South Atlantic boundary layer, PAN alone can account for almost all of the NO<sub>x</sub> present [Heikes *et al.*, 1996]. PAN production is much higher in the Northern Hemisphere than in the Southern Hemisphere, suggesting that it could be a major contributor; however, there are few studies of PAN in the North Atlantic, making it hard to estimate its contribution to this system. While there are no measurements of the isotopic composition of PAN to date, it could have a high δ<sup>15</sup>N, as it forms in polluted atmospheres close to emissions of <sup>15</sup>N enriched NO<sub>x</sub>, such as coal fired power plants, which produce high δ<sup>15</sup>N-NO<sub>x</sub> both with and without emission control technologies (δ<sup>15</sup>N-NO<sub>x</sub> = 10‰, and 15–20‰, respectively) [Felix *et al.*, 2012]. If PAN represents a significant NO<sub>x</sub> source during the warm season in the North Atlantic, then anthropogenic NO<sub>x</sub> is contributing to deposition even when AMBT have not recently been over the continents. This would have significant implications and future work is necessary to assess the potential for PAN to contribute to NO<sub>x</sub> in the North Atlantic marine atmosphere and the utility of stable isotopes of N in NO<sub>x</sub> and nitrate to trace that contribution.

#### 4.2. Rainwater Nitrate δ<sup>18</sup>O

[44] The high δ<sup>18</sup>O of atmospheric nitrate reflects the influence of ozone (δ<sup>18</sup>O-O<sub>3</sub> = 90 to 122‰ versus Vienna SMOW (VSMOW); [Johnston and Thiemens, 1997]) on the reactions that produce nitrate from NO<sub>x</sub> [Hastings *et al.*,

2003; Michalski *et al.*, 2003]. Briefly, unlike  $\delta^{15}\text{N-NO}_x$ ,  $\delta^{18}\text{O-NO}_x$  is not conserved and is instead reset by rapid exchange with ozone during [(R1)–(R4)]. When nitrate is formed through the OH pathway favored during the summer and during the day (R5), the high  $\delta^{18}\text{O}$  from ozone is diluted by that of OH, which should have a  $\delta^{18}\text{O}$  close to water vapor in the troposphere ( $\delta^{18}\text{O-H}_2\text{O}_{(\text{g})} = -9$  to  $-17\%$  near Bermuda); (H.C. Steen-Larsen, personal communication, 2013). Thus, the variation in  $\delta^{18}\text{O-NO}_3^-$  is usually interpreted as reflecting seasonal shifts in the atmospheric chemistry that converts  $\text{NO}_x$  to nitrate. During the summer, longer days and warmer temperatures lead to increased OH concentrations and lower  $\delta^{18}\text{O-NO}_3^-$ . During the winter, shorter days and lower temperatures lead to a greater contribution from the  $\text{N}_2\text{O}_5$  hydrolysis pathway [(R6)–(R7), (R9)], resulting in higher  $\delta^{18}\text{O-NO}_3^-$  as 5/6 of the O atoms in the  $2\text{HNO}_3$  formed will be from ozone. In addition, wintertime transport imports air from over North America and higher latitudes, while summertime transport tends to import air from the South: these transport changes reinforce the locally driven seasonal cycle at Bermuda to produce higher  $\delta^{18}\text{O-NO}_3^-$  in the winter. The important influence of season on the  $\delta^{18}\text{O}$  is also demonstrated by the increased significance of the seasonal comparison within AMBT regimes: within both the marine and continental AMBT events, the cool season rains are significantly higher in  $\delta^{18}\text{O}$  than warm season rains (Figure 4b). This winter/summer and high latitude/low latitude distinction has been the focus of interpretations to date [Elliott *et al.*, 2007; Hastings *et al.*, 2003; Morin *et al.*, 2009; Wankel *et al.*, 2010].

[45] As with the nitrate N isotopes, the presence of halogens in the marine atmosphere may have an important role in the nitrate O isotopes, especially in the case of continentally produced  $\text{NO}_x$ . As discussed in section 1.1, in the presence of NaCl particles,  $\text{N}_2\text{O}_5$  can form aqueous  $\text{HNO}_3$  and  $\text{ClONO}_{2(\text{g})}$  (R10).  $\text{NO}_2$  can react with  $\text{ClO}_{(\text{g})}$  to form  $\text{ClONO}_2$ , or it can react with sea-salt particles to form  $\text{NaNO}_{3(\text{p})}$  [(R14), (R15)]. This chemistry should increase the influence of high  $\delta^{18}\text{O-O}_3$  in the formation of nitrate. For example, the aqueous  $\text{HNO}_3$  formed from  $\text{N}_2\text{O}_5$  and HCl (R10) should be higher in  $\delta^{18}\text{O}$  than  $\text{HNO}_3$  from  $\text{N}_2\text{O}_5$  hydrolysis (R9) as it is not diluted with O atoms from water. Likewise, ClO is formed from Cl and ozone (R13), therefore, the  $\text{NaNO}_{3(\text{p})}$  formed from  $\text{ClONO}_2$  should also be higher in  $\delta^{18}\text{O}$ . The same is true as  $2\text{NO}_2$  molecules react with sea-salt particles to form  $\text{NaNO}_{3(\text{p})}$  (R16). As a result, when polluted continental air masses move into the marine environment with high concentrations of ozone, sea-salt particles, and halogens, the  $\text{NO}_3^-$  formed should be high in  $\delta^{18}\text{O}$  (Figure 1a), which is consistent with what we observe in Bermuda rainwater from continental AMBT during the cool season (Figure 3c). This chemistry further reinforces the previous interpretations of  $\delta^{18}\text{O-NO}_3^-$  as the  $\text{N}_2\text{O}_5$  pathway will be most prevalent in winter, with its lower temperatures and longer nights. Though the heterogeneous halogen chemistry is also likely to occur during marine AMBT as discussed above, the yields of  $\text{ClONO}_2$  are highest in the winter when sea salt and ozone concentrations peak, and they correlate strongly with  $\text{N}_2\text{O}_5$  [Osthoff *et al.*, 2008], suggesting that the influence of heterogeneous halogen chemistry on  $\delta^{18}\text{O-NO}_3^-$  should be limited to the cool season. In summary, in contrast to the situation with  $\delta^{15}\text{N-NO}_3^-$ , the halogen chemistry simply

adds to the list of causes for the elevation of  $\delta^{18}\text{O-NO}_3^-$  in the winter, and the task for future work is to parse the observed  $\delta^{18}\text{O-NO}_3^-$  variations between the halogen-related and nonhalogen-related mechanisms.

### 4.3. Relationship of N and O Isotopes of Nitrate

[46] There is a negative linear correlation ( $r^2 = 0.58$ ) between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  in the rainwater samples (Figure 5a), consistent with the previous study of rainwater N and O isotopes in Bermuda [Hastings *et al.*, 2003]. Correlations are rarely observed between the  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of atmospheric nitrate, and if any relationship is present, it is typically positive [Elliott *et al.*, 2009]. The presence of halogens and sea-salt aerosols influences the chemistry of nitrate formation in the coastal marine boundary layer. As discussed above, this chemistry can lead to a decrease in  $\delta^{15}\text{N}$  from preferential removal of  $^{15}\text{N}$  into the particle phase which deposits near the coast, leaving lower  $\delta^{15}\text{N}$   $\text{NO}_x$  or nitrate for transport to the remote marine atmosphere (Figure 1b and section 4.1). This low  $\delta^{15}\text{N-NO}_3^-$  is associated with high  $\delta^{18}\text{O-NO}_3^-$  due to the increased role of ozone in its formation, both because of high concentrations of ozone in the North American source region and because the continental AMBT occur almost exclusively during the cool season with lower temperatures and longer nights. During the slow and stagnant marine AMBT, the ozone signal is diluted by an increased role of OH and  $\text{H}_2\text{O}$  in the nitrate formation pathways, resulting in an overall lower  $\delta^{18}\text{O-NO}_3^-$ . This, in combination with an increased contribution from lightning  $\text{NO}_x$  and potentially PAN, results in higher  $\delta^{15}\text{N}$  and lower  $\delta^{18}\text{O}$  nitrate deposited at Bermuda associated with marine AMBT. In summary, the negative correlation of nitrate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , thus far unique to nitrate in marine rainwater, is driven largely by the seasonal change in trajectory influencing both the source  $\text{NO}_x$  and the chemical formation pathways of nitrate.

## 5. Conclusions

[47] The changes in concentration and  $\delta^{15}\text{N}$  of nitrate with AMBT suggest that while continental air contributes anthropogenic nitrate from North America to the subtropical surface ocean, nitrate associated with marine AMBTs comes from different  $\text{NO}_x$  sources. We hypothesize that the differences in nitrate isotopic composition between the USA and Bermuda are due to the formation and subsequent deposition of high  $\delta^{15}\text{N}$  particles due to isotopic fractionation during heterogeneous halogen chemistry in the coastal marine boundary layer. This then leads to the transport of low  $\delta^{15}\text{N-NO}_x$  over the North Atlantic that is subsequently deposited to Bermuda as nitrate. Our data suggest that while lightning  $\text{NO}_x$  likely plays an important role in the formation of nitrate in the marine atmosphere, a number of high  $\delta^{15}\text{N-NO}_3^-$  values with marine AMBT (reaching 9.8‰) are especially hard to account for with a lightning  $\text{NO}_x$  source alone. Instead, these data are explained by the rain out of high  $\delta^{15}\text{N}$  particles formed from halogen chemistry, or an additional higher  $\delta^{15}\text{N-NO}_x$  source, potentially PAN. There is a seasonal predictability to the chemical pathways that form nitrate from  $\text{NO}_x$ , with greater contributions from ozone leading to higher  $\delta^{18}\text{O}$  during the cool season and from continental AMBT, and with a greater role for OH leading to lower  $\delta^{18}\text{O}$  during the warm

season and marine AMBT. The strong negative correlation of nitrate  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ , thus far unique to nitrate in remote ecosystems, is driven by the seasonal change in trajectory influencing both the source  $\text{NO}_x$  and the pathway of nitrate formation.

[48] **Acknowledgments.** This work was supported by NSF ATM-1044997. Postdoctoral research support for K.E.A. was also provided by the NOAA Climate and Global Change Fellowship. We thank A. Marks and J. Rosset for sample collection assistance, R. Lauck and J. Garcia for analytical support, and A. Buffen for helpful discussions on statistics. All sample data including concentrations and N and O isotopic composition of nitrate have been made publicly available at the SOLAS Project Integration Aerosol and Rain Composition and Deposition Database ([http://www.bodc.ac.uk/solas\\_integration/implementation\\_products/group1/aerosol\\_rain/](http://www.bodc.ac.uk/solas_integration/implementation_products/group1/aerosol_rain/)).

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