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.

[3] Nitrate (NO₃⁻) is the ultimate sink for atmospheric nitrogen oxides (NOₓ = NO + NO₂), and it is an increasingly significant component of acid rain as effective sulfur dioxide

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 (HNO₃) 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

[1] Emissions of anthropogenic nitrogen (N) to the atmosphere have increased tenfold since preindustrial times [Paerl et al., 2002], 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 δ¹⁵N, and lower average δ¹⁸O (4.4 μM, −1.1‰ versus N₂ in air, and 69.0‰ versus Vienna SMOW, respectively) than those influenced by North American air masses (6.3 μM, −5.4‰, and 75.0‰). The δ¹⁵N decrease and concentration increase from marine to continental air masses are due to a change in NOₓ 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 δ¹⁵N-NO₃⁻ to be deposited near the coast and lower δ¹⁵N-NO₃⁻ to be transported over the open ocean, yielding a low δ¹⁵N for anthropogenic NO₃⁻ deposition. It is possible that this process also contributes to variations in δ¹⁵N-NO₃⁻ from marine air masses. There is a negative linear correlation (r² = 0.58) between δ¹⁵N and δ¹⁸O which is driven by the seasonal change in trajectory influencing both the source NOₓ and the nitrate formation pathways.

regulations lead to decreases in sulfuric acid concentrations. The lifetime of NO\textsubscript{x} is usually hours to days; thus, its conversion to longer lived reservoir species such as HNO\textsubscript{3} or peroxycetyl nitrate (PAN) is needed for reactive N to be transported long distances. The atmospheric cycle of NO\textsubscript{x} and the conversion of NO\textsubscript{x} to NO\textsubscript{3}/CO\textsubscript{3} is complex, with different processes taking place during the day and night (Figure 1a). During the day, cycling between NO and NO\textsubscript{2} is rapid (R1)–(R4).

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (\text{R1})
\]

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \quad (\text{R2})
\]

\[
\text{O} + \text{O}_2 \rightarrow \text{O}_3 \quad (\text{R3})
\]

\[
\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO} \quad (\text{R4})
\]

[4] The oxidation of NO to NO\textsubscript{2} requires ozone (R1), while the breakdown of NO\textsubscript{2} back to NO is photolytic and produces ozone [(R2)–(R3)]. NO can also be oxidized to NO\textsubscript{3} via peroxy radicals (R4), which also ultimately leads to ozone production. At night, (R2) shuts down and (R1) dominates until \([\text{NO}_2] \approx [\text{NO}_3]\). The dominant daytime sink of NO\textsubscript{x} is the oxidation of NO\textsubscript{2} to HNO\textsubscript{3} by the hydroxyl radical (R5).

\[
\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \quad (\text{R5})
\]

[5] During the night, when photolytic production of OH ceases, the concentration of OH decreases and NO\textsubscript{2} reacts preferentially with ozone to form NO\textsubscript{3}, the dominant nighttime oxidant. NO\textsubscript{2} and NO\textsubscript{3} then react further to form...
N₂O₅, and NO₂ and NO₃ remain in thermal equilibrium with N₂O₅ ([R6]–[R7]); M is an unreactive body, usually N₂).

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R6)}
\]

\[
\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad \text{(R7)}
\]

[5] NO₃ 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].

\[
\text{NO}_3 + \text{RH (DMS)} \rightarrow \text{HNO}_3 + \text{products (CH}_3\text{SCH}_2\text{)} \quad \text{(R8)}
\]

[7] The loss of N₂O₅ occurs through heterogeneous hydrolysis on aerosol particles (R9).

\[
\text{N}_2\text{O}_5(g) + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3(aq) \quad \text{(R9)}
\]

[8] Recent studies have shown the potential for halogens to play a significant role in NOx and nitrate chemistry. In the presence of HCl, N₂O₅ can also react heterogeneously on aerosol particles to form both aqueous nitrate and ClNO₂ which partitions to the gas phase (R10) [Thornton et al., 2010].

\[
\text{N}_2\text{O}_5(g) + \text{HCl}(g) \rightarrow \text{ClNO}_2(g) + \text{HNO}_3(aq) \quad \text{(R10)}
\]

[9] It is hypothesized that the branching ratio between formation of HNO₃(aq) in (R9) and ClNO₂(g) and HNO₃(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 NOx and NaCl particles mix, i.e., in coastal regions, ClNO₂ is produced in high yields, exceeding previously predicted values by a factor of 2 to 30 [Osthoff et al., 2008]. Maximum production of ClNO₂ 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 ClNO₂ acts as a reservoir species, building up in concentration at night and regenerating NO₃ during the day through photolysis (R11).

\[
\text{ClNO}_2(g) + \text{hv} \rightarrow \text{Cl} + \text{NO}_2 \quad \text{(R11)}
\]

[10] The combination of (R10) and (R11) increases the lifetime of reactive N in the marine atmosphere by regenerating NO₃ in contrast to the reaction without halogen chemistry (R9), in which the conversion of N₂O₅ to aqueous nitrate aerosol ensures efficient removal of reactive N.

[11] In the presence of halides, another potential mechanism for NO₃ conversion to NO₃⁻ is through reaction with ClO or BrO during the day to form ClONO₂ or BrONO₂ ([R12]–[R14]).

\[
\text{HNO}_3(g) + \text{NaCl}(p) \rightarrow \text{HCl}(g) + \text{NaNO}_3(p) \quad \text{(R12)}
\]

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad \text{(R13)}
\]

\[
\text{NO}_2 + \text{ClO}_2(g) + \text{M} \rightarrow \text{ClONO}_2(g) \quad \text{(R14)}
\]

[12] First, acid displacement reactions occur when HNO₃(g) in continental outflow reacts with NaCl in the marine boundary layer, releasing HCl and forming NaNO₃(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 ClONO₂ (or BrONO₂) formed can then combine with sea-salt aerosol to form coarse mode aerosol nitrate (R15).

\[
\text{ClNO}_2(g) + \text{NaCl}(p) \rightarrow \text{Cl}_2(g) + \text{NaNO}_3(p) \quad \text{(R15)}
\]

[13] The conversion of HNO₃ to coarse mode NO₃⁻ should significantly decrease its lifetime as coarse mode particles are deposited preferentially through gravitational settling and precipitation scavenging via inertial impaction.

[14] NOx can also react with sea-salt aerosol to form ClNO and NaNO₃ (R16).

\[
2\text{NO}_2 + \text{NaCl}(p) \rightarrow \text{ClNO}_2(g) + \text{NaNo}_3(p) \quad \text{(R16)}
\]

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

\[
\text{ClNO}_2(g) + \text{hv} \rightarrow \text{NO} + \text{Cl} \quad \text{(R17)}
\]

\[
\text{ClNO}_2(g) + \text{H}_2\text{O} \rightarrow \text{HONO}_2(g) + \text{HCl}(g) \quad \text{(R18)}
\]

[16] In polluted environments, NO₃ can react with peroxyacetyl radicals to form PAN, a long lived NO₃ reservoir which can be transported long distances at high altitudes. When air masses subside, PAN thermally decomposes to again form NO₂ (R19) [Fischer et al., 2011, and references therein].

\[
\text{CH}_3\text{C(O)OO} \cdot + \text{NO}_2 + \text{M} \rightarrow
\]

\[
\rightarrow \text{CH}_3\text{C(O)O}_2\text{NO}_2 \cdot + \text{M} \quad \text{(R19)}
\]

[17] The chemical and physical processing of NOx 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
Hastings et al. [2003] showed that nitrate in Bermuda (32.27°N, 64.87°W) rain has higher δ15N-NO3− and lower δ18O-NO3− in the warm season (April to September; −2.1‰ and 68.6‰) as compared to the cool season (October to March; −5.9‰ and 76.9‰); isotope ratios are reported using the delta (δ) notation in “per mil” (‰): δ15Nsample = ([15N/14N]sample/ [15N/14N]N2 in air − 1) * 1000‰ and δ18Osample = ([18O/16O]sample/ [18O/16O]H2O SMOW − 1) * 1000‰. However, the concentration of nitrate was not significantly different from the warm to the cool season (5.0 and 6.4 μM, 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 δ15N of −0‰, which Hastings et al. [2003] attributed to an increased contribution from lightning NOx. Two rain samples collected on research cruises in the Eastern Atlantic Ocean had δ15N values of −1.4 and −0.9‰ [Baker et al., 2007] consistent with rains at Bermuda.

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 δ15N-NO3− 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 rainfall δ15N-NO3− varied from 0 to 3.5‰. In contrast, the Bermuda cool season average δ15N was −5.9 ± 3.3‰ (±1SD).

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

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 NOx, SO2, and particulate matter (A. Peters, TSP, PM10, and PM2.5, 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 (Aerocem 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°C. Freezing at −20°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).

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

The rainwater samples were analyzed by ion chromatography for anions (Cl−, NO3−, NO2−, SO42−) using an ICS-1600 (Thermo Scientific Dionex, Sunnyvale, USA) at BIOS. Anions were analyzed using an IonPac AS14A 5 μm analytical column (3 × 150 mm) with an IonPac AG14A 5 μm guard column (3 × 30 mm). The mobile phase was a solution of 8 mM Na2CO3 and 1 mM NaHCO3. Calibration curves for each analyte were generated using five points over the range of 1 to 1000 μM. 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 μM for NO3−, 0.08 μM for SO42−, and 0.04 μM for 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 μM) in all rainwater samples.

2.3. Nitrate Isotopic Analysis

Measurements of the 15N/14N and 18O/16O ratios of NO3− 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 N2O reductase activity are used to quantitatively convert NO3− to nitrous oxide (N2O). The ion current ratios (m/z 45/44 and 46/44) of the resultant N2O were measured using a modified GasBench II in line to a Thermo DeltaPlus IRMS [Casciotti et al., 2002], allowing the coupled determination of the 15N/14N
and $^{18}$O/$^{16}$O ratios of the N$_2$O analyte. Individual analyses are referenced to injections of N$_2$O from a pure gas cylinder and then standardized through comparison to the international reference materials of IAEA-N3 and USGS34 for $\delta^{15}$N-NO$_3^-$, and IAEA-N3, USGS34, and USGS35 for $\delta^{18}$O-NO$_3^-$ (see Table S1 in the supporting information) [Bohike et al., 2003]. The $^{15}$N/$^{14}$N is corrected for a bacterial culture blank quantified with each run. The $^{15}$N/$^{14}$N of samples is corrected for the contribution of $^{17}$O to the peak at mass 45 using an average $\Delta^{17}$O value for Bermuda rainwater (26‰) [Hastings et al., 2003]. The pooled standard deviation for all measurements of IAEA-N3 and USGS34 for $\delta^{15}$N-NO$_3^-$, and for all measurements of IAEA-N3, USGS34, and USGS35 for $\delta^{18}$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 $\delta^{15}$N-NO$_3^-$ and 0.79‰ for $\delta^{18}$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 NO$_x$. Three-dimensional

![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) $\delta^{15}$N-NO$_3^-$ in the cool season, (b) $\delta^{15}$N-NO$_3^-$ in the warm season, (c) $\delta^{18}$O-NO$_3^-$ in the cool season, and (d) $\delta^{18}$O-NO$_3^-$ in the warm season, respectively.](image-url)
standard deviation is smaller than the size of the marker. Error bars denote the standard deviation of replicate isotopic columns denote the cool season (October to March). denote the warm season (April to September) while the between June 2009 and November 2011. The pink columns with the meteoro-logical observation archive on the Bermuda National Weather by cross-referencing sample collection dates with the meteoro-

uncertainty in the timing of the rain event, trajectories were run starting every hour during the rain event, or if there was variability associated with starting time, 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). 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., NO$_3^-$ + 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 NO$_3^-$ concentrations ranged from 0.78 to 33.3 μM (Figure 3a) with a numerical average of 6.8 ± 5.4 μM (±1SD unless otherwise noted). For the different AMBT regimes, the NO$_3^-$ concentrations ranged from 0.78 to 17.6 μM for the marine AMBT (n = 99), 1.8 to 33.3 μM for the continental AMBT (n = 50), and 1.1 to 5.9 μM for the coastal AMBT (n = 6). The volume weighted average NO$_3^-$ concentration for marine AMBT was 4.4 ± 3.1 μM, continental AMBT was 6.3 ± 4.5 μM and for coastal AMBT was 2.1 ± 1.1 μM (Table 1). In Bermuda rainwater measured from 1980 to 1984, the volume weighted average NO$_3^-$ concentration was 4.57 μM in the warm season and 4.33 μM in the cool season [Moody and Galloway, 1988]. In Bermuda rainwater measured from 2000–2001, the volume weighted average NO$_3^-$ concentration was 5.0 μM in the warm season and 6.4 μM in the cool season [Hastings et al., 2003].

Figure 3. (a) Nitrate concentration, (b) δ$^{15}$N-NO$_3^-$, and (c) δ$^{18}$O-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.
[30] The 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 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 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 $\delta^{15}$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 $-2.6\pm3.7\%$ (Table 1). The $\delta^{15}$N-NO$_3^-$ does not correlate with [NO$_3^-$] (Figure S4), [NH$_4^+$], [nss-SO$_4^{2-}$], or rainfall amount (not shown). However, the $\delta^{15}$N-NO$_3^-$ does correlate with $\delta^{18}$O-NO$_3^-$, which is discussed below (Figure 5). The mean $\delta^{15}$N-NO$_3^-$ for the continental AMBT was $-5.4\pm3.2\%$, and for the marine AMBT was $-1.1\pm3.0\%$. The $\delta^{15}$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 $\delta^{15}$N-NO$_3^-$ of $-5.7\pm2.4\%$ is also significantly lower than the marine AMBT mass-weighted average $\delta^{15}$N-NO$_3^-$ of $-1.6\pm2.8\%$.

### Table 1. The Average (± 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)

<table>
<thead>
<tr>
<th></th>
<th>Marine AMBT</th>
<th>Continental AMBT</th>
<th>Coastal AMBT</th>
<th>Average of All Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO$_3^-$]$^{\bullet\bullet}$ (μM)</td>
<td>4.38±3.13 (99)</td>
<td>6.33±4.46 (50)</td>
<td>2.08±1.13 (6)</td>
<td>4.88±3.64 (155)</td>
</tr>
<tr>
<td>$\delta^{15}$N-NO$_3^-$ (%)</td>
<td>$-1.6\pm2.8$</td>
<td>$-5.7\pm2.4$</td>
<td>$-4.5\pm2.2$</td>
<td>$-3.1\pm3.3$</td>
</tr>
<tr>
<td>$\delta^{18}$O-NO$_3^-$ (%)</td>
<td>69.3±5.1</td>
<td>76.5±4.5</td>
<td>69.4±2.6</td>
<td>71.9±6.0</td>
</tr>
<tr>
<td>$\delta^{15}$N-NO$_3^-$ (%)</td>
<td>$-1.1\pm3.0$</td>
<td>$-5.4\pm3.2$</td>
<td>$-5.3\pm2.6$</td>
<td>$-2.6\pm3.7$</td>
</tr>
<tr>
<td>$\delta^{18}$O-NO$_3^-$ (%)</td>
<td>69.0±6.4</td>
<td>75.0±4.8</td>
<td>71.3±4.7</td>
<td>71.1±6.4</td>
</tr>
</tbody>
</table>

*The number of samples measured for nitrate concentrations and isotopes in each category is in parentheses.

Volume weighted average.

Numerical average.

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

### Table 2. The Average (± 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)

<table>
<thead>
<tr>
<th></th>
<th>Continental AMBT</th>
<th>Continental AMBT</th>
<th>Marine AMBT</th>
<th>Marine AMBT</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO$_3^-$]$^{\bullet\bullet}$ (μM)</td>
<td>6.23±3.58 (44)</td>
<td>7.02±9.13 (6)</td>
<td>3.82±2.92 (39)</td>
<td>4.85±3.26 (60)</td>
</tr>
<tr>
<td>$\delta^{18}$N-NO$_3^-$ (%)</td>
<td>$-6.0\pm2.3$</td>
<td>$-3.5\pm1.7$</td>
<td>$-2.2\pm2.2$</td>
<td>$-1.2\pm3.2$</td>
</tr>
<tr>
<td>$\delta^{18}$O-NO$_3^-$ (%)</td>
<td>77.2±4.3</td>
<td>72.2±3.7</td>
<td>71.7±5.2</td>
<td>67.7±4.3</td>
</tr>
<tr>
<td>$\delta^{15}$N-NO$_3^-$ (%)</td>
<td>$-5.8\pm3.2$</td>
<td>$-3.0\pm2.1$</td>
<td>$-1.4\pm3.1$</td>
<td>$-0.8\pm3.0$</td>
</tr>
<tr>
<td>$\delta^{18}$O-NO$_3^-$ (%)</td>
<td>75.6±4.7</td>
<td>71.3±4.4</td>
<td>70.3±7.8</td>
<td>68.2±5.1</td>
</tr>
</tbody>
</table>

*The number of samples measured for nitrate concentrations and isotopes in each category is in parentheses.

Volume weighted average.

Mass weighted average.

Numerical average.
and rainwater collected at 17 National Trend Network sites in the USA (~ 60-90‰; [Elliot et al., 2009]). The four samples with low δ^{18}O are also the samples with the highest δ^{15}N-NO₃⁻ (5.8 to 9.8‰), and they all have marine AMBT origins though only two are from the warm season.

In previous work, as with the δ^{15}N-NO₃⁻, the δ^{18}O-NO₃⁻ was binned by cool and warm season instead of marine and continental AMBT and the averages were 76.9 ± 6.3‰ and 68.6 ± 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 δ^{18}O-NO₃⁻ were 73.1 ± 6.7‰ (n = 87) and 68.6 ± 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 δ^{18}O-NO₃⁻ were 74.5 ± 4.6‰ and 68.2 ± 4.5‰. As with the δ^{15}N-NO₃⁻, the statistical significance (i.e., the p values) of the δ^{18}O-NO₃⁻ 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 δ^{18}O-NO₃⁻ than on the mass weighted cool season average was slightly lower than the warm season average (~ 2.2 ± 2.2‰ and ~1.2 ± 3.2‰, respectively; not statistically significant).

### 3.4. O Isotopes of Nitrate

The measurements of δ^{18}O-NO₃⁻ 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 ± 6.4‰ (Table 1). Similar to the δ^{15}N-NO₃⁻, the δ^{18}O-NO₃⁻ does not correlate with [NO₃⁻], [NH₄⁺], [nss-SO₄²⁻], or rainfall amount (not shown), but it does correlate with δ^{15}N-NO₃⁻ (Figure 5). The mean δ^{18}O-NO₃⁻ is significantly different (independent t test, 95%, p < 10⁻⁹) for the different AMBTs, with the continental AMBT averaging 75.0 ± 4.8‰ and the marine AMBT averaging 69.0 ± 6.4‰. The mass-weighted continental AMBT average δ^{18}O-NO₃⁻ of 76.5 ± 4.5‰ was also higher than the marine AMBT mass-weighted average δ^{18}O-NO₃⁻ of 69.3 ± 5.1‰.

The range of δ^{18}O-NO₃⁻ in the Bermuda rainwater (61.1 to 85.5‰), excluding the four samples with δ^{18}O less than 60.0‰, is consistent with rainwater nitrate measured previously in Bermuda (60.3 to 86.5‰; [Hastings et al., 2003]),
\[
\delta^{15}N-NO_3^- \text{ (Table 2 and Figure 4). The continental AMBT had the highest } \delta^{18}O-NO_3^- \text{ values overall, but within all of the continental AMBT data, the cool season mass-weighted average was higher than the warm season average (77.2 ± 4.3‰ and 72.2 ± 3.7‰, respectively; independent } t \text{ test, 95%, } p < 0.02). \text{ Likewise, the marine AMBT were lower in } \delta^{18}O-NO_3^-, \text{ but within all of the marine AMBT data, the cool season mass weighted average was higher than the warm season mass weighted average (71.7 ± 5.2‰ and 67.7 ± 4.3‰, respectively; independent } t \text{ test, 95%, } p < 0.0001). \]

3.5. Relationship Between N and O Isotopes of Nitrate

[35] Across the entire rainwater sample set, there was a negative correlation \((r^2 = 0.58, y = -0.44x + 28.52, p < 10^{-3})\) between the \(\delta^{15}N\) and \(\delta^{18}O\) of 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 cool season marine AMBT (highest \(\delta^{15}N\) and lowest \(\delta^{18}O\)) and the cool season continental AMBT (lowest \(\delta^{15}N\) and highest \(\delta^{18}O\)) 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 \(\delta^{15}N\)

[36] The \(\delta^{15}N\) of nitrate should reflect the \(\delta^{15}N\) of the NO\(_3^−\) source, overprinted by any fractionation associated with the chemical pathway that converts NO\(_x\) to nitrate. Rain events with continental AMBT origins occur primarily during the cool season (October to March) and are consistently lower in \(\delta^{15}N\)-NO\(_3^−\) and higher in NO\(_3^−\) concentration than rain events from marine AMBT, which occur all year (Figure 3b). North American NO\(_x\) emissions are dominated by anthropogenic sources with \(87\%\) coming from fossil fuel burning of automobiles, power plants, and industry [Zhang et al., 2003]. Therefore, the lower \(\delta^{15}N\) and higher concentrations during rain events with continental AMBT suggests that when air masses come from the continental USA, they bring NO\(_3^−\) with a different, and likely anthropogenic, NO\(_3^−\) source (Figure 1b). This interpretation is consistent with previous work on rainwater \(\delta^{15}N\)-NO\(_3^−\) in this region [Hastings et al., 2003], which interpreted the \(\delta^{15}N\)-NO\(_3^−\) changes from the cool to the warm season as a change in NO\(_3^−\) 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 \(\delta^{15}N\)-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 NO\(_3^−\) source.

[37] In the few continental AMBT rain events that occurred during the warm season, the \(\delta^{15}N\)-NO\(_3^−\) was significantly higher than for those that occurred during the cool season, likely as a result of mixing with the high \(\delta^{15}N\)-NO\(_3^−\) present in the warm season atmosphere near Bermuda (Figures 3b and 4a). We do not believe that this increase in \(\delta^{15}N\) is due to changes in North American \(\delta^{15}N\)-NO\(_3^−\) or \(\delta^{15}N\)-NO\(_x\) as the summer months are when North American rainwater \(\delta^{15}N\)-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 \(\delta^{15}N\)-NO\(_3^−\) during the cool season from North American transport and higher \(\delta^{15}N\)-NO\(_3^−\) during the warm season from the marine atmosphere. Thus, an anomalous trajectory for that season brings with it the \(\delta^{15}N\) source signature of the NO\(_3^−\), 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 \(\delta^{15}N\) 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 \(\delta^{15}N\)-NO\(_3^−\) varied from −0.5 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 \(\delta^{15}N\)-NO\(_3^−\) in Bermuda rain were at their minimum (−5.4 ± 3.2‰; Table 1). This is also true in previously published data on \(\delta^{15}N\)-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 ± 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 μM, with an average of 16.5 ± 16.9 μM (data accessible online at www.nadp.sws.uiuc.edu [NADP, 2007]), compared to an average nitrate concentration in Bermuda rain from continental AMBT of 6.3 ± 4.5 μM. The difference in \(\delta^{15}N\) and concentration of nitrate from the continental USA to Bermuda suggests that there must be loss of nitrate, or NO\(_x\), as polluted continental air masses move off of the continent, and that this loss has a preference for \(\delta^{15}N\) (Figure 1b). Below we outline three potential mechanisms to explain the \(\delta^{15}N\)-NO\(_3^−\) difference between North American rainwater and rainwater collected at Bermuda from North American transport, involving (1) equilibrium fractionation between NO and NO\(_2\) over the continents, (2) heterogeneous reaction of N\(_2\)O\(_5\) with HCl (R10), and (3) reaction of NO\(_2\) with NaCl particles (R16).

[39] The first hypothesis is dependent on the relative concentrations of NO\(_x\) and ozone in North America and Bermuda. When NO\(_x\) concentrations are higher than ozone concentrations, equilibrium fractionation between NO and NO\(_2\) (R1–R4) results in \(\delta^{15}N\)-enriched NO\(_2\) [Freyer et al., 1993]. When ozone concentrations are higher than NO\(_x\) concentrations, most of the NO\(_x\) is oxidized to NO\(_2\) such that the \(\delta^{15}N\)-NO\(_2\) is equivalent to the \(\delta^{15}N\)-NO\(_3^−\). In Bermuda, ozone concentrations always exceed NO\(_x\) concentrations [Oltmans et al., 1996; Prados et al., 1999], and as a result fractionation between NO and NO\(_2\) has previously been considered to be unimportant [Hastings et al., 2003]. In the atmospheric boundary layer over North America, however, 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 NO2 to be relevant in air masses that are subsequently transported to Bermuda. If 15N enriched NO2 is converted to HNO3, the higher δ15N-HNO3 would be deposited closer to the coast, leaving behind lower δ15N-NOx to be exported to the marine atmosphere.

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 NOx is through formation of N2O5 via reaction of NO2 with NO3 radicals (Figure 1a). The potential for halides to interact with N2O5 is discussed 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 N2O5 reacts with HCl, forming aqueous HNO3 and releasing ClNO2(g) (R10). This ClNO2 acts as a reservoir species until the day, when it is quickly photolyzed to Cl and NO2, recycling the original NO2 and as such the higher fractionation during this process as heavier isotopes are stored as N2O5 (R11). There is the potential for isotopic fractionation of deposition downwind of the continents. We propose two mechanisms for marine AMBT (Figures 3b and 5a), as discussed immediately below, in section 4.2.

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 NOx 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 NOx 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 NOx (R19, [Fischer et al., 2011; Kotchenruther et al., 2001]). In the South Atlantic boundary layer, PAN alone can account for almost all of the NOx 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 δ15N, as it forms in polluted atmospheres close to emissions of 15N enriched NOx, such as coal fired power plants, which produce high δ15N-NOx, both with and without emission control technologies (δ15N-NOx = 10‰, and 15–20‰, respectively) [Felix et al., 2012]. If PAN represents a significant NOx source during the warm season in the North Atlantic, then anthropogenic NOx 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 NOx in the North Atlantic marine atmosphere and the utility of stable isotopes of N in NOx and nitrate to trace that contribution.
2003; Michalski et al., 2003]. Briefly, unlike δ15N-NO3, δ18O-NO3 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 δ18O from ozone is diluted by that of OH, which should have a δ18O close to water vapor in the troposphere (δ18O-H2O(g) = −9 to −17‰ near Bermuda); (H.C. Steen-Larsen, personal communication, 2013). Thus, the variation in δ18O-NO3 is usually interpreted as reflecting seasonal shifts in the atmospheric chemistry that converts NO3 to nitrate. During the summer, longer days and warmer temperatures lead to increased OH concentrations and lower δ18O-NO3. During the winter, shorter days and lower temperatures lead to a greater contribution from the N2O5 hydrolysis pathway [(R6)–(R7), (R9)], resulting in higher δ18O-NO3 as 5/6 of the O atoms in the 2HNO3 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 δ18O-NO3 in the winter. The important influence of season on the δ18O 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 δ18O 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].

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 continuously produced NO3. As discussed in section 1.1, in the presence of NaCl particles, N2O3 can form aqueous HNO3 and ClNO2(g) (R10). NO2 can react with ClO(g) to form ClONO2, or it can react with sea-salt particles to form NaNO3(p) [(R14), (R15)]. This chemistry should increase the influence of high δ18O-NO3 in the formation of nitrate. For example, the aqueous HNO3 formed from N2O3 and HCl (R10) should be higher in δ18O than HNO3 from N2O3 hydrolysis (R9) as it is not diluted with O atoms from water. Likewise, ClO is formed from Cl and ozone (R13), therefore, the NaN3 formed from ClNO2 should also be higher in δ18O. The same is true as 2NO2 molecules react with sea-salt particles to form NaNO3(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 NO3− formed should be higher in δ18O (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 δ18O-NO3− as the N2O3 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 ClNO2 are highest in the winter when sea salt and ozone concentrations peak, and they correlate strongly with N2O3 [Osthoff et al., 2008], suggesting that the influence of heterogeneous halogen chemistry on δ18O-NO3− should be limited to the cool season. In summary, in contrast to the situation with δ15N-NO3−, the halogen chemistry simply adds to the list of causes for the elevation of δ18O-NO3− in the winter, and the task for future work is to parse the observed δ18O-NO3− variations between the halogen-related and nonhalogen-related mechanisms.

4.3. Relationship of N and O Isotopes of Nitrate

There is a negative linear correlation (r² = 0.58) between δ15N and δ18O of NO3− 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 δ15N and δ18O 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 δ15N from preferential removal of 15N into the particle phase which deposits near the coast, leaving lower δ15N NO3 or nitrate for transport to the remote marine atmosphere (Figure 1b and section 4.1). This low δ15N-NO3 is associated with high δ18O-NO3− 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 H2O in the nitrate formation pathways, resulting in an overall lower δ18O-NO3−. This, in combination with an increased contribution from lightning NO3 and potentially PAN, results in higher δ15N and lower δ18O nitrate deposited at Bermuda associated with marine AMBT. In summary, the negative correlation of nitrate δ15N and δ18O, thus far unique to nitrate in marine rainwater, is driven largely by the seasonal change in trajectory influencing both the source NO3 and the chemical formation pathways of nitrate.

5. Conclusions

The changes in concentration and δ15N 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 NO3 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 δ15N particles due to isotopic fractionation during heterogeneous halogen chemistry in the coastal marine boundary layer. This then leads to the transport of low δ15N-NO3 over the North Atlantic that is subsequently deposited to Bermuda as nitrate. Our data suggest that while lightning NO3 likely plays an important role in the formation of nitrate in the marine atmosphere, a number of high δ15N-NO3− values with marine AMBT (reaching 9.8‰) are especially hard to account for with a lightning NO3 source alone. Instead, these data are explained by the rain out of high δ15N particles formed from halogen chemistry, or an additional higher δ15N-NO3 source, potentially PAN. There is a seasonal predictability to the chemical pathways that form nitrate from NO3, with greater contributions from ozone leading to higher δ18O during the cool season and from continental AMBT, and with a greater role for OH leading to lower δ18O during the warm
season and marine AMBT. The strong negative correlation of nitrate $^{15}$N and $^{18}$O, thus far unique to nitrate in remote ecosystems, is driven by the seasonal change in trajectory influencing both the source NO$_3$ 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/integration_products/group1/aerosol_rain/).

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