# On the origin of the occasional springtime nitrate concentration peak in Greenland snow

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# Abstract

An occasional spring nitrate concentration peak was observed in ice cores from Central Greenland but its origin is unknown. This study performs a case study on its origin by measuring concentration and isotopic composition of nitrate ($\delta^{15}$N, $\delta^{18}$O and $\Delta^{17}$O) in a snowpit from Summit, Greenland covering three years of snow accumulation. A nitrate peak was found in the spring of 2005. Isotopic data of nitrate combined with photochemical calculations suggest that the presence of this spring maximum was linked to a significantly weakened stratospheric ozone ($O_3$) layer. This weakened $O_3$ layer resulted in elevated UV-B (Ultraviolet B) radiation on the snow surface, where the productions of OH and $NO_x$ from the photolysis of their precursors were enhanced. A peak was then observed as the result of enhanced local nitrate production due primarily to the increased OH concentrations, as indicated by decreases in $\delta^{18}$O and $\Delta^{17}$O of nitrate associated with the spring maximum. We further examined the nitrate concentration record from a shallow ice core covering the period from 1772 to 2006 and compared this record to satellite observations of springtime $O_3$ column density data from 1979 to 2006. We found19 spring nitrate maxima after the 1950s. After 1979, all spring concentration maxima appeared with $O_3$ column density near or below the 1979-2006 average. We hypothesize that the presence of the spring nitrate peak is largely associated with and may be determined by the interannual variability of $O_3$ column density, under the condition of elevated local $NO_x$ abundance at Summit after the 1950s resulting from enhanced anthropogenic nitrate deposition, though other factor(s) may dominate in some years. Isotopic data covering additional years of low $O_3$ column density are needed to further examine this hypothesis.

## 1. Introduction

Knowledge of the abundance and variability of reactive nitrogen oxides ($NO_x$ = NO + $NO_2$) is valuable because of the critical role that $NO_x$ play in determining the oxidative capacity of the atmosphere. The oxidative capacity of the atmosphere is determined by the tropospheric abundance of hydrogen oxide radicals ($HO_x$ = OH + $HO_2$) and $O_3$ and largely controls the residence times of pollutants (e.g., CO) and greenhouse gases (e.g., $CH_4$). $NO_x$ are emitted from a variety of sources including fossil fuel combustion, biomass burning, soil emissions, and lightning (Logan, 1983). In the atmosphere, $NO_x$ cycle rapidly between NO and $NO_2$ according to:

$$\mathrm{NO + O_3 \rightarrow NO_2 + O_2} \qquad \text{(R1)}$$

$$\mathrm{NO + HO_2(RO_2) \rightarrow NO_2 + OH(RO)} \qquad \text{(R2)}$$

$$\mathrm{NO_2} + hv \xrightarrow{\mathrm{O_2}} \mathrm{NO + O_3} \qquad \text{(R3)}$$

The main sink of $NO_x$ is thought to be atmospheric oxidation to nitrate which distributes between gas- and particulate phases. In general, the formation of nitrate involves reactions of $NO_x$ with OH and $O_3$:

$$\mathrm{NO_2 + OH \rightarrow HNO_3} \qquad \text{(R4)}$$

$$\mathrm{NO_2 + O_3 \rightarrow NO_3 + O_2} \qquad \text{(R5)}$$

$$\mathrm{NO_3 + DMS/HC \rightarrow HNO_3 + products} \qquad \text{(R6)}$$

$$\mathrm{NO_3 + NO_2 \rightarrow N_2O_5} \qquad \text{(R7)}$$

$$\mathrm{N_2O_5 + H_2O_{(aq)} \rightarrow 2HNO_{3(aq)}} \qquad \text{(R8)}$$

Reactive halogen species (e.g., BrO) may also play a role in $NO_x$ cycling and nitrate formation, especially in the Arctic (Morin et al., 2007). R4 mainly occurs during daytime, as the result of diurnal variation in OH concentrations. The conversion to nitrate via $O_3$ (R5-R8) is negligible during the day, since the $NO_3$ radical is rapidly photolyzed back to $NO_x$ in sunlight. Globally, oxidation of $NO_x$ by OH (R4) is thought to be the dominant nitrate formation pathway on an annual basis (Alexander et al., 2009). Once formed, nitrate is removed from the atmosphere mainly through wet and dry deposition to the surface. Efforts have been made to use ice core nitrate records to assess information about past changes in the global $NO_x$ environment (Fischer et al., 1998; Mayewski et al., 1990), and potentially about the past variations in the atmospheric oxidation capacity (Alexander et al., 2004). However, nitrate concentration in polar snow is also influenced by variations in snow accumulation rate and by post-depositional processes such as evaporation and photolysis (Röthlisberger et al., 2002) of nitrate in near-surface snow. Post-depositional processing of snowpack nitrate has hampered the interpretation of ice core nitrate record in terms of assessing past atmospheric $NO_x$ variability.

Examination of detailed chronological nitrate records in snowpits and ice cores may provide clues on the primary factor(s) controlling nitrate concentration and its temporal variability in snow. For example, a clear seasonal pattern in nitrate concentration may be linked to a source with an annual cycle and/or modulated by seasonally varying atmospheric conditions. Many previous studies of snow samples and ice cores from central Greenland have found that nitrate concentration reaches a maximum in summer snow and a minimum in winter snow (Davidson et al., 1989; Finkel and Langway, 1986; Whitlow et al., 1992). This seasonal variation in nitrate concentration in general is due to the active photochemical reactions during polar summer (Yang et al., 1995), when peroxyacetyl nitrate (PAN), snowpack nitrate and other $NO_x$ reservoir species act as local $NO_x$ sources through recycling reactions

(Moxim et al., 1996; Thomas et al., 2012). A few investigators (Burkhart et al., 2006; Yang et al., 1995) noticed that a single nitrate peak appears in an annual snow/ice layer deposited prior to the year 1900, whereas two peaks are seen in some post-1900 annual layers. The other annual peak in the post-1900 period generally appears in the spring but does not occur every year (Yang et al., 1995). The occurrence of this occasional spring nitrate peak has been proposed to be associated with anthropogenic $NO_x$ emissions at the mid-latitudes (Burkhart et al., 2006; Yang et al., 1995), as a result of fossil fuel combustion. Anthropogenic $NO_x$ emissions from fossil fuel combustion have increased the concentration of atmospheric $NO_x$ since 1900, especially in the last 50 years (Galloway et al., 2003), and the corresponding increase in nitrate concentrations in Greenland snow has been documented (Mayewski et al., 1990). However, the observation that the spring nitrate peak is only present in some years suggests that other factors, such as atmospheric transport of nitrate or of its precursors and/or atmospheric conditions (e.g., solar radiation, oxidant concentrations), may also be important in determining the appearance of the spring nitrate peak.

The isotopic composition of nitrate can provide valuable information not available from concentration measurement alone, for example, regarding the pathways of $NO_x$ conversion to nitrate in the atmosphere (Michalski et al., 2003). Stable isotope ratios in nitrate are expressed as $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$, where $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$ and $\delta = R_{sample}/R_{reference} - 1$ with R denoting the $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope ratios. The references are $N_2$-AIR and VSMOW for N and O, respectively. $\delta^{15}N$ and $\Delta^{17}O$ of nitrate (hereafter denoted as $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$, respectively) have been used to investigate the origin and fate of $NO_x$ in the Arctic troposphere (Morin et al., 2008). In particular, $\Delta^{17}O(NO_3^-)$ is related to oxidizing conditions and nitrate formation pathways (R4 vs. R5-R8) in the atmosphere (Alexander et al., 2004; Alexander et al., 2009; Kunasek et al., 2008; Michalski et al., 2003; Morin et al., 2011). For example, Michalski et al. (2003) found that nitrate formed during nighttime (i.e., via R5-R8) has higher $\Delta^{17}O$ than nitrate formed during daytime (via R4) because of the high $\Delta^{17}O$ of the dominant nighttime oxidant $O_3$ (Johnson et al., 2000; Lyons, 2001) which is transferred to nitrate. The $\Delta^{17}O(NO_3^-)$ in Greenland snow also reflects the seasonality of nitrate production, with $O_3$ oxidation (R1, R5) being more important in winter than in summer (Kunasek et al., 2008).

In this study, the concentrations of major ions ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$) in a snowpit and a shallow ice core from central Greenland were measured. In addition, we measured the isotopic composition of nitrate with high temporal resolution from the snowpit. The concentration data were used to establish their temporal patterns and to identify spring nitrate peak(s). The isotopic data were used to assess the chemistry of nitrate in a spring peak identified in the snowpit, and further examinations were conducted to determine the occasional nature of the spring nitrate peak observed in Greenland snow since 1900.

## 2. Methods

### 2.1. Snowpit and ice core sample collection

In July 2007, six snow blocks (dimensions: 0.35 m long × 0.25 m wide × 0.35 m deep) were excavated from the surface down to a depth of 2.10 m at Summit, Greenland (72.5 ºN, 38.5 ºW; elevation: 3200 m). These snow blocks were wrapped with clean polyester film with their dimensions labeled and stored in a hard-shell box to avoid external compaction during delivery. Several ice cores including a 79 meter shallow core were drilled approximately 100 meters from the location of the snow blocks. These snow blocks and the ice cores were shipped frozen to the laboratory at South Dakota State University (SDSU) and stored in a freezer at -20 ºC until analysis. At the same time, a set of snowpit samples were also collected in the field every 5 cm from the surface down to the depth of 2.10 m, at the same location of the collected snow blocks. This set of snowpit samples (referred to as SP-1) were double sealed in clean plastic bags and shipped frozen to Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) for nitrate concentration and isotope analysis. All tools/containers directly touching the snowpit samples and/or the snow blocks were pre-cleaned with 18 MΩ water before use.

The density profile of the snow blocks were also measured in the field. In particular, in the field, a small snow cube was collected every 5 cm from the wall of a snowpit. The weight and the volume of the snow cube were measured and then the density of the snow was calculated. The snow density profile from the surface to the depth of 2.1 m was included as supplemental data.

## 2.2. Chemical and isotope analysis

At SDSU, another set of snow samples (referred to as SP-2) in a vertical sequence was chiseled out from the snow blocks, after the removal of a surface layer of at least 1 cm in thickness, and collected in clean plastic sample containers. All tools and sample containers were pre-cleaned with 18 MΩ water prior to use, and clean disposable plastic gloves were always worn during sample handling. In total, 71 samples with a depth resolution of 3 cm were obtained. These samples were allowed to melt at room temperature and the meltwater samples were then analyzed by ion chromatography for concentrations of major ions in snow ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$). The ion chromatography instrumentation and methodology are similar to that described by Cole-Dai et al. (2006). Ice blanks were made from deionized water, processed and analyzed following the same procedure as that for the snow samples. High blank values of $Ca^{2+}$ (up to 5 μg $L^{-1}$) indicated that the snowpit samples were probably contaminated with $Ca^{2+}$ during sample preparation. No evidence of contamination was found for the other ions. Therefore, the snowpit $Ca^{2+}$ data were not used in interpretation in this study. The 79 meter shallow core was analyzed for the ionic species using the technique of continuous flow analysis with ion chromatography (CFA-IC) detection (Cole-Dai et al., 2006). One advantage of the CFA-IC technique is that it minimizes the potential contamination by eliminating sample preparation. Replicate analysis of blanks with CFA-IC showed no contamination of any of the ions including $Ca^{2+}$.

The concentration measurements of the SP-2 samples described above were used to estimate the volume of meltwater needed to provide sufficient nitrate mass (500 nmoles, allowing for replicate measurements) for isotopic analysis. Based on that estimate, the snow blocks were carved vertically to yield large samples for isotope measurement. A total of 29 clean snow samples (referred to as SB) were obtained from the depth interval of 0.70 m to 1.75 m of the snow blocks (snow outside this depth interval had been consumed for other purposes). The depth resolution of these samples varies from 2 cm to 6 cm because the concentration of nitrate is different at different depths. These samples were melted at room temperature and concentrated, following the method described by Frey et al. (2009), to 10 mL solutions, collected in HDPE bottles, and stored frozen until isotopic analysis. Measurements of N and O isotope ratios in nitrate of the SB samples were performed in the stable isotope laboratory at University of Washington (UW) using the bacterial denitrifier method (Kaiser et al., 2007). Briefly, nitrate in the samples was first converted into $N_2O$ gas by the bacteria *Pseudomonas aureofaciens*; the $N_2O$ was carried on-line by helium gas into a heated gold tube where it was thermally decomposed to $N_2$ and $O_2$. These were then separated by gas chromatography and the isotopic ratio(s) of each gas ($^{15}N/^{14}N$ for $N_2$, and $^{18}O/^{16}O$ and $^{17}O/^{16}O$ for $O_2$) was measured with an isotope ratio mass spectrometer. The $\delta^{15}N$ values were calculated with respect to $N_2$-Air and calibrated against the two international reference materials IAEA-NO-3 ($\delta^{15}N$ = 4.7 ‰) and USGS34 ($\delta^{15}N$ = -1.8 ‰) (Kaiser et al., 2007). The $\delta^{17}O$ and $\delta^{18}O$ values were calculated with respect to VSMOW and calibrated against the two international reference materials USGS34 ($\delta^{17}O$ = - 14.5 ‰, $\delta^{18}O$ = - 27.9 ‰) and USGS35 ($\delta^{17}O$ = 51.3 ‰, $\delta^{18}O$ = 57.5 ‰) (Kaiser et al., 2007). The $\Delta^{17}O$ values were then calculated by using the linear equation $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$. No replicate samples were possible due to the limited amount of snow available in the snow blocks, and no seasonally resolved isotopic measurements of the ice core samples were preformed because of the limited amount of ice available. The analytical uncertainty of $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ measured at the UW laboratory was estimated to be 0.1 ‰ and 0.5 ‰ (1σ), and that of $\delta^{15}N$ was 1.0 ‰ (1σ), based on repeated measurements of the oxygen and nitrogen isotope ratios in the international reference materials USGS35 and IAEA-NO-3, respectively (Table 1 for details).

The SP-1 samples at LGGE were measured for nitrate concentration and isotopic composition ($\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$). A small portion of each sample was taken for nitrate concentration measurement using the well-established Griess method in continuous flow analysis (Seal Analytical, Method No 1000223-1784-09). The rest of samples were processed following the similar procedure described above and the N and O isotope ratios were determined by the bacterial denitrifier method. Instrumentation details at the LGGE laboratory are similar to that described in Erbland et al. (2013). International reference materials (USGS34, USGS35 and IAEA-NO-3) were used for data reduction. The uncertainties of $\Delta^{17}O(NO_3^-)$, $\delta^{18}O(NO_3^-)$ and $\delta^{15}N(NO_3^-)$ measured at the LGGE laboratory were 0.3 ‰, 2.0 ‰ and 0.3 ‰, respectively, estimated as the reduced standard deviation of the residuals from the linear regression between the measured reference materials and their accepted values.

## 3. Results

### 3.1. Dating and identifying spring nitrate maxima

The concentration data from the SP-1 and SP-2 samples, and the isotopic data from the SP-1 and SB samples , were plotted as a function of depth in Figure 1 (data are available in Supplemental Material). The concentration profiles of nitrate from SP-1 and SP-2 are nearly identical and each displays five peaks approximately at the same depths (labeled 1, 2, 3, 3′ and 4 in Figure 1d). Since the snowpit and snow blocks were excavated in July of 2007, the partial Peak 1 at the surface identifies the summer of 2007. The other peaks could be summer or spring peaks. According to the concentration profile of sodium (Figure 1e) that has an annual winter peak (Whitlow et al., 1992), nitrate Peak 3′ represents the spring of 2005 and Peak 2, 3 and 4 represent the summer of 2006, 2005 and 2004, respectively. This dating by nitrate summer peaks and sodium winter peaks (referred to here as Method A) is consistent with the results of weekly recorded snow accumulation data determined by stake height measurements at Summit (data are available at ftp://ftp.summitcamp.org/pub/data/GEOSummit/Bales_UCM/Bamboo%20Forest/Bamboo%20Forest%20Accumulation%20Log.xls) (referred to here as Method B). The approximate months of snowfall at depths of 0, 0.5, 1.0, 1.5 and 2.0 m identified by Method B were indicated with vertical dashed lines of Figure 1. Both dating methods identify Peak 3′ occurring in the (early) spring of 2005. Some small discrepancies exist between the two dating methods. For example, the month of snowfall at the surface was identified as May of 2007 using Method B instead of July. This discrepancy is due to negligible snowfall (around 2 cm) from May to July 2007. The month of snowfall at the depth of 2 m was identified as March of 2004 using Method B, suggesting that Peak 4 is also a spring peak. However, according to the snow accumulation data, there was only about 3 cm of snow accumulation from March to June of 2004 (Supplemental Figure 1). Negligible snowfall during this time resulted in nitrate produced in summer dry depositing to the prior spring snow layers, making it appear as if the peak occurs in spring using Method B. In addition, the nitrate profiles in SP-1 and SP-2 are slightly different (i.e., nitrate peaks are not exactly at the same depths), which is likely due to the spatial variability of snow accumulation rates in the field due to snow drifting. But the overall temporal patterns of the nitrate profiles in SP-1 and SP-2 are similar, suggesting there was negligible disturbance of the stratigraphy of the snow blocks during delivery and storage.

The record of nitrate concentrations from the shallow ice core is shown in Figure 2 (data are available in Supplemental Material). This core was dated by counting the annual spring peak of calcium (Cole-Dai et al., 2013). Nineteen spring nitrate concentration maxima were found in the period of 1960 to 2006, obtained by subtracting total calcium peaks from total nitrate peaks in this period (Figure 2). The frequency of the spring peak in each decade in this period was listed in Table 2. No such spring peak was seen before 1960, similar to the finding by Finkel and Langway (1986) that the spring nitrate peak started appearing after the 1950s, though others (Burkhart et al., 2006; Yang et al., 1995) stated in general that elevated spring nitrate concentrations are seen in snow layers after around 1900.

### 3.2. $\delta^{18}O(NO_3^-)$, $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ variations

The $\delta^{18}O(NO_3^-)$, $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ data from the SP-1 and SB samples are shown in Figure 1a, 1b and 1c, respectively. The depth range of the SP-1 samples (0 to 2.10 m) corresponds to the period of the 2007 summer to 2004 summer, while the depth range of the SB samples (0.7 to 1.75 m) corresponds to the time period of the 2006 spring/summer to the 2004/2005 winter. Approximate seasons were marked according to Method A. In general, all three isotopic signatures of nitrate display large seasonal variations. $\delta^{18}O(NO_3^-)$ is low in summer and high in winter, while $\delta^{15}N(NO_3^-)$ is high in spring/early summer and low in winter, consistent with previous measurements of Summit snow samples from Hastings et al. (2004). In the spring of 2005 (the time period corresponding to the depths of the spring nitrate peak), the means (± 1σ) of $\delta^{15}N(NO_3^-)$ from the SP-1 and SB samples were (5.3 ± 3.3) ‰ and (6.4 ± 2.1) ‰, respectively, much higher than the winter values which were (-9.2 ± 3.3) ‰ from the SP-1 samples and (-7.4 ± 4.4) ‰ from the SB samples. A local minimum in $\delta^{18}O(NO_3^-)$ was also observed from both the SP-1 and the SB samples at the depths of the 2005 spring nitrate peak (Figure 1a).

The observed seasonality of $\Delta^{17}O(NO_3^-)$ (Figure 1c) was consistent with the expectation of high $\Delta^{17}O(NO_3^-)$ during winter (polar night) due to the dominance of the $O_3$ oxidation pathway of $NO_x$ (R5-R8). The magnitude of the seasonality was also consistent with the observations of $\Delta^{17}O(NO_3^-)$ at Summit by Kunasek et al.(2008). The seasonality of $\Delta^{17}O(NO_3^-)$ is regulated by the shift of the dominant nitrate formation pathway from OH oxidation (R4) in polar summer/day to that via $O_3$ (R5-R8) in polar winter/night (low summer values and high winter values). Modeling by Kunasek et al. (2008) showed that, in early spring, $\Delta^{17}O$ of locally produced nitrate at Summit should be close to that in winter snow, as oxidation by OH (R4) is very limited at this time due to the lack of sunlight. In other words, at Summit $\Delta^{17}O(NO_3^-)$ values in winter and early spring should be similar. However, in the early spring of 2005, the $\Delta^{17}O(NO_3^-)$ values display apparent declines from the prior winter values (Figure 1c). To test whether the declines are significant, we calculate the mean $\Delta^{17}O(NO_3^-)$ value in the early spring of 2005 and compare that to the mean of measured winter $\Delta^{17}O(NO_3^-)$ values. The winter mean $\Delta^{17}O(NO_3^-)$ was calculated from the 2004/2005 to 2006/2007 winters from the SP-1 samples, and from the 2004/2005 to 2005/2006 winters for the SB samples (samples used to calculate the winter and 2005 early spring means are as marked in Figure 1c). The mean winter value was (32.9 ± 1.1) ‰ from the SP-1 samples and (32.4 ± 0.6) ‰ from the SB samples. In contrast, the mean $\Delta^{17}O(NO_3^-)$ value in the early spring of 2005 was (31.1 ± 0.6) ‰ from SP-1 and (30.8 ± 0.8) ‰ from SB, approximately 1.7 ‰ lower than the winter means, which is statistically significant based on one-tailed t-test (for SP-1 samples: $t = 3.434$, DOF = 24, $P = 0.001$; for SB samples: $t = 4.637$, DOF = 17, $P \leq 0.0005$). A previous study measuring $\Delta^{17}O(NO_3^-)$ in Summit snow by Kunasek et al. (2008) also noted significantly low $\Delta^{17}O(NO_3^-)$ values (around 26 ‰) in the spring of 2005, compared to the prior winter of $\Delta^{17}O(NO_3^-)$ around 33 ‰.

## 4. Discussion

The low $\Delta^{17}O(NO_3^-)$ values in the spring of 2005 suggest an increase in OH oxidation in the formation of nitrate associated with the peak. This is qualitatively consistent with the observed decrease in $\delta^{18}O(NO_3^-)$, as increases in the relative importance of OH oxidation will also result in decreases in $\delta^{18}O(NO_3^-)$ (Hastings et al., 2004). The extra nitrate deposited during the spring of 2005 was estimated to be 5.7 nmol × $cm^{-2}$, which was obtained by subtracting the flux of nitrate (9.4 nmol × $cm^{-2}$) in the spring of 2006 from the nitrate flux in the spring of 2005 (15.1 nmol × $cm^{-2}$). The 2006 spring was a normal spring without nitrate peak. This suggests a 60 % increase in nitrate deposited in the spring of 2005 compared to the spring of 2006. The additional nitrate in the spring of 2005 could either come from enhanced transport of nitrate produced elsewhere or be produced locally. In the discussion to follow, we consider separately the possibility of enhanced transport and enhanced local production of nitrate in the Arctic being responsible for this spring nitrate peak. We further examine whether the explanation for the case of spring 2005 is representative of the occasional nature of the spring nitrate peak observed in the shallow ice core.

### 4.1. Enhanced transport

### 4.1.1. Stratospheric denitrification

Stratospheric denitrification refers to the sedimentation process of Polar Stratospheric Clouds (PSCs) containing nitric acid trihydrate. Research on nitrate in Antarctic snow (Mulvaney and Wolff, 1993) suggested that stratospheric denitrification associated with the winter polar vortex could result in a late winter/early spring nitrate peak. Although denitrification occurs less frequently and less extensively in the Arctic than in Antarctica due to the warmer winter and the weaker and less persistent Arctic vortex (Waugh and Randel, 1999), significant denitrification has been observed in Arctic for some exceptionally cold winters, including the winter of 2004/2005 (Mann et al., 2003; Jin et al., 2006; Kleinbohl et al., 2005). Could stratospheric denitrification in the winter of 2004/2005 have resulted in the early spring nitrate peak?

Stratospheric nitrate is expected to possess high $\Delta^{17}$O since it is mainly formed via $O_3$ oxidation (McCabe et al., 2007; Savarino et al., 2007) and stratospheric $\Delta^{17}O(O_3)$ is up to 5 ‰ higher than that in the troposphere (Liang et al., 2006; Lyons, 2001; Mauersberger et al., 2001). In addition, stratospheric nitrate can also be formed via ClO oxidation (McCabe et al., 2007). Nitrate formed via ClO oxidation also possesses high $\Delta^{17}$O (McCabe et al., 2007; Savarino et al., 2007) due to the internal non-statistical distribution of isotopes in $O_3$ which transfers its terminal oxygen atoms to ClO (Bhattacharya et al., 2008).

If the additional nitrate in the 2005 spring snow originated from stratospheric denitrification, the $\Delta^{17}O(NO_3^-)$ would be expected to be anomalously high, not low as was observed. It is possible that the $\Delta^{17}$O value of nitrate deposited to the snow surface is reduced by post-depositional processing, for the photolytic recycling of snowpack nitrate (photodenitrification followed by re-formation and redeposition of nitrate) can reduce the $\Delta^{17}$O signature of nitrate finally preserved in snow (Erbland et al., 2013). If all of the nitrate produced in the stratosphere undergoes photolytic recycling, the stratospheric $\Delta^{17}$O signature would be completely erased (i.e., $\Delta^{17}$O of the nitrate would be the same as that of nitrate produced in the tropospheric boundary layer). Given the high snow accumulation rate at Summit (the degree of snowpack photodenitrification decreases with increasing snow accumulation rate (Röthlisberger et al., 2002)), it is unlikely that all additional nitrate underwent photolytic recycling. Consequently, $\Delta^{17}O$ of the preserved nitrate originally produced in the stratosphere should be no lower than that of the tropospheric nitrate deposited in a typical spring. Therefore, the observed $\Delta^{17}O(NO_3^-)$ suggests stratospheric denitrification cannot account for the spring nitrate peak.

### 4.1.2. Transport from mid-latitudes

The model results in Kunasek et al. (2008) suggest significant transport of nitrate from the mid-latitudes to Summit. The $\Delta^{17}O$ of nitrate from mid-latitudes is likely lower than that of nitrate formed in the Arctic troposphere due to the latitudinal gradient in $\Delta^{17}O(NO_3^-)$ resulting from the latitudinal gradient in $O_3/HO_x$ ratio (Alexander et al., 2009). Thus, enhanced long-range transport of mid-latitude nitrate to Greenland during the spring could elevate nitrate concentration in snow with relatively low $\Delta^{17}O(NO_3^-)$ as observed here. Pollution from the Northern mid-latitudes is transported to Arctic by poleward meridional circulation, which is strong when the North Atlantic Oscillation (NAO) is in its positive phase (Eckhardt et al., 2003). However, a weak NAO in the 2004/2005 winter and early spring of 2005 was seen in the NAO index data (Osborn, 2011), suggesting no enhanced transport from the mid-latitudes at this time. In addition, if the additional nitrate in the spring of 2005 was from enhanced transport, elevated concentrations of other species derived from anthropogenic and continental sources, such as $SO_4^{2-}$ and $Mg^{2+}$, would also be expected, especially for $SO_4^{2-}$ because it has a very similar atmospheric lifetime (4 to 6 days) as nitrate (3 to 7 days) (Park et al., 2004; Pye et al., 2009). However, the data from the snowpit show that neither $SO_4^{2-}$ nor $Mg^{2+}$ concentrations were elevated

(Figure 1f and 1g) in the spring of 2005 when the nitrate peak was present. Therefore, it is unlikely that the 2005 spring nitrate peak was caused by enhanced long-range transport of nitrate from the mid-latitudes.

### 4.2. Enhanced local production

#### 4.2.1. PAN decomposition

Previous work has found that peroxyacetyl nitrate (PAN) is the dominant form of reactive nitrogen in the Arctic troposphere during winter/spring (Beine and Krognes, 2000; Bottenheim et al., 1993; Honrath and Jaffe, 1992; Jacobi et al., 1999) and its decomposition yields $NO_x$ that is subsequently converted to nitrate. If the decomposition rate of PAN is enhanced in the spring of 2005, more $NO_x$ would be produced resulting in an increase in local nitrate production. PAN decomposes to $NO_x$ either thermally or via photolysis (Talukdar et al., 1995). At temperatures above 255 K, thermal decomposition dominates, while photolysis becomes more important at lower temperatures (Talukdar et al., 1995). The typical spring (February and March) air temperature at Summit is about 240 K (242 K in 2005 and average of 236 K in the springs of 2006 to 2008; data are from http://www.summitcamp.org/resources/files). At these low temperatures, the $NO_x$ release from PAN is dominated by photolysis at wavelengths between 290-345 nm (Talukdar et al., 1995; Flowers et al., 2005).

The stratospheric $O_3$ layer filters out most of the UV-B ($\lambda$ = 290-320 nm) portion of the solar spectrum. A weakened stratospheric $O_3$ layer will allow more UV-B penetration into the troposphere. In Figure 3, the spring (average of February and March values) $O_3$ column density at Summit for the years of 1979-2006 were shown (data are from NASA Total Ozone Mapping Spectrometer program). The 2005 spring level (290 Dobson Unit (DU)) was significantly lower than the average of spring values from 1979 to 2006 (390 ± 50 ($1\sigma$) DU), suggesting a relatively high UV-B flux to the surface in the spring of 2005.

The photolysis of PAN in the spring of 2005 could have been enhanced due to the elevated UV-B radiation caused by stratospheric $O_3$ loss, leading to increased local $NO_x$ abundance, and subsequently resulting in the unusual spring nitrate peak in snow. The increase in PAN photolysis resulting from the decreased $O_3$ column density (290 DU) can be estimated with the UCAR Tropospheric Ultraviolet & Visible (TUV) radiation model (available at http://cprm.acd.ucar.edu/Models/TUV/). Calculations with the TUV model showed a 24 % increase in the photolysis rate constant of PAN ($j = (9.0 \pm 5.4) \times 10^{-8}$ $s^{-1}$ vs. $(7.3 \pm 4.3) \times 10^{-8}$ $s^{-1}$, both are daytime averages) in the spring of 2005 compared to that in a typical spring (column $O_3$ density of 390 DU). This would lead to an increase of only $1.6 \times 10^5$ $cm^{-3}$ in $NO_x$ number concentration, which is, on average, 0.04 % of the observed springtime $NO_x$ concentration of $(3.9 \pm 3.1) \times 10^8$ $cm^{-3}$ in the Arctic (Stroud et al., 2003). The above calculation assumes steady stead of PAN with number concentration of $(2.3 \pm 0.7) \times 10^9$ $cm^{-3}$ (Stroud et al., 2003) and $[NO_2] = (([PAN] \times j_{PAN}) / k)^{1/2}$, where $[NO_2]$ and $[PAN]$ represent the number concentrations of $NO_2$ and PAN, respectively, and $j_{PAN}$ ($s^{-1}$) is the photolysis rate constant of PAN calculated from the TUV model and $k$ ($cm^3 \times s^{-1}$) is the reaction rate constant of PAN formation at T = 240 K and P = 650 hPa (Summit springtime condition) calculated based on the equation from Atkinson et al. (2006). This is negligible compared to the observed 60 % enhancement in nitrate deposition flux (5.7 nmol × $cm^{-2}$) during the spring of 2005. This is consistent with the model prediction by Stroud et al. (2003) that, during spring, PAN is a net sink of $NO_x$, rather than a source. A similar conclusion was also reached by Singh et al.

(1992) who found that the PAN reservoir is not a significant source of $NO_x$ until summer.

### 4.2.2. Snowpack $NO_x$ emissions

The photolysis of nitrate in the snowpack at snow depths of up to 20 cm or more (Zatko et al., 2013; France et al., 2011; Grannas et al., 2007) emits $NO_x$ to the overlying atmosphere (Frey et al., 2009), serving as a local $NO_x$ source. $NO_x$ originating from the photolysis of nitrate in the snowpack can be re-oxidized to nitrate and re-deposited to the surface. A recent model study (Thomas et al., 2012) suggested that at Summit the photolysis of snowpack nitrate alone can sustain observed NO concentrations in the local atmospheric boundary layer. If the emission of $NO_x$ from snowpack were enhanced, local atmospheric nitrate production was expected to be elevated. The reduction in $O_3$ column density in the spring of 2005 led to more UV radiation at the surface, which in turn may significantly enhance the snowpack photodenitrification. Consequently, the oxidation of $NO_x$ released from the snowpack by enhanced photolysis of snowpack nitrate at depths, and subsequent re-deposition of the nitrate to the surface in spring, would result in elevated nitrate concentration in surface snow during spring.

In order to estimate the impact of the reduced overhead $O_3$ column density in the spring of 2005 on local $NO_x$ concentration via the photolysis of snowpack nitrate, we used the TUV model to calculate the surface actinic flux at Summit in the spring of 2005 (290 DU) versus normal springtime with average $O_3$ column density (390 DU, which was close to the value (380 DU) in the spring of 2006). The parameterization from Zatko et al. (2013) was then used to calculate the photolysis frequency ($s^{-1}$) of snowpack nitrate at wavelengths from 298 to 345 nm (peak wavelength for nitrate photolysis is around 320 nm (Chu and Anastasio, 2003)). This calculation suggested a 30 % enhancement of the snowpack nitrate photolysis frequency in the spring of 2005 relative to 2006, and thus a similar enhancement of the $NO_x$ emission from the snowpack, due to the reduced overhead $O_3$ column density alone. This likely contributed to the enhanced local nitrate production in the spring of 2005. However, the relative importance of snowpack photodetrification to local $NO_x$ abundance in springtime is unknown, making it difficult to quantitatively assess the contribution from snowpack emissions to the observed spring nitrate peak. If snowpack photodenitrification is the dominant source of boundary layer $NO_x$ at Summit as suggested by Thomas et al. (2012), then this could account for up to half of the additional nitrate in the observed 2005 spring nitrate peak.

The high $\delta^{15}N(NO_3^-)$ in the spring of 2005 (SP-1: (5.3 ± 3.3) ‰; SP-2 (6.4 ± 2.1) ‰)  also suggests that strong post-depositional recycling of snowpack nitrate (dominated by photolysis (Frey et al., 2009)) occurred in the spring of 2005, as post-depositional recycling tends to increase $\delta^{15}N(NO_3^-)$ in snow (Frey et al., 2009; Morin et al., 2008). In particular, Jarvis et al. (2009) calculated that the recycling can cause 1.9 ‰ to 9.4 ‰ increase in snow $\delta^{15}N(NO_3^-)$ at Summit; and in surface snow, daytime $\delta^{15}N(NO_3^-)$ is significantly higher than nighttime $\delta^{15}N(NO_3^-)$ due to daytime photolytic recycling (Hastings et al., 2004). However, other factors such as variations in $NO_x$ sources (Hastings et al., 2004) and atmospheric processing (Freyer et al., 1993) may also influence the observed seasonality in $\delta^{15}N(NO_3^-)$, making quantitative interpretation of $\delta^{15}N(NO_3^-)$ difficult in terms of the degree of the photolytic recycling of snow nitrate .

### 4.2.3. Enhanced conversion of $NO_x$ to nitrate

The number concentration of $NO_x$ in the Arctic mid-troposphere (58-85 °N, 3-6 km) during spring of 2002 has been reported to be $(3.9 \pm 3.1) \times 10^8$ $cm^{-3}$ (Stroud et al., 2003), which is similar to the summer $NO_x$ level at Summit (Jacobi et al., 2004). Under this scenario with sufficient $NO_x$, an increase in nitrate concentration would be expected if the oxidation rate of $NO_x$ to $HNO_3$ is enhanced, even in the absence of increased springtime $NO_x$ concentrations. The oxidation rate can be enhanced by increased oxidant ($O_3$, OH, BrO) levels. Both $O_3$ and BrO have high $\Delta^{17}O$ values (Lyons, 2001; Morin et al., 2007), thus an increase in either $O_3$ or BrO concentrations would result in additional nitrate with high $\Delta^{17}O$. The relatively low $\Delta^{17}O(NO_3^-)$ in the spring 2005 snow (Figure 1c) suggests that increased tropospheric $O_3$ and/or BrO concentrations are unlikely to be the direct cause of enhanced nitrate production.

On the other hand, increased oxidation of $NO_x$ by OH would produce additional nitrate with low values of $\Delta^{17}O$ as was observed. In general, the concentration of tropospheric OH is dependent on concentrations of tropospheric $O_3$ and water vapor and the available UV-B radiation through following reactions:

$$O_3 + hv \rightarrow O_2 + O(^1D) \qquad (290\text{ nm} < \lambda < 320\text{ nm}) \qquad \text{(R9)}$$

$$O(^1D) + H_2O \rightarrow 2OH \qquad \text{(R10)}$$

Either a substantial increase in UV-B in the troposphere or an increase in the water vapor content at elevated atmospheric temperatures can increase OH production and therefore enhance the conversion of $NO_x$ to $HNO_3$ via OH oxidation (R4). In addition, two other important oxidants involved in NO-$NO_2$ cycling (R2), $HO_2$ and $RO_2$, are formed by reactions of carbon monoxide (CO) and hydrocarbons (RH) with OH:

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2 \qquad \text{(R11)}$$

$$RH + OH \xrightarrow{O_2} H_2O + RO_2 \quad (R12)$$

Increased OH will enhance NO-$NO_2$ cycling via $HO_2$ and $RO_2$ and reduce the relative importance of $O_3$ in $NO_x$ cycling, which also leads to lowered $\Delta^{17}O$ in nitrate.

The temperature and relative humidity data at Summit is available from Greenland Climate Network Data (GCND, http://cires.colorado.edu/science/groups/steffen/gcnet/order/admin/station.php). Using these data, the spring (February and March average) atmospheric water vapor mixing ratio in 2005 was calculated to be 40 % higher than that in 2006 due to high temperatures in the 2005 spring (-30 ºC) relative to the 2006 spring (-34 ºC). Assuming this high water vapor in spring 2005 will result in a  maximum increase in OH production of 40 %, the increase in water vapor is not enough to account for the 60 % enhancement in the nitrate deposition flux in the spring of 2005. In fact, as discussed later, OH must be increased by 200 % to explain the spring nitrate maximum. Although the relatively high temperature in the spring of 2005 may have contributed around 20 % (40 % increase versus the required 200 % increase) to the enhanced local nitrate production, it was likely not the dominant factor producing the spring nitrate peak in 2005.

To determine the effect of reduced column $O_3$ density on OH production at the surface, we used the TUV model to estimate the OH production rate (R9 and R10) at Summit due to enhanced photolysis of boundary layer $O_3$. Our calculation showed that the OH production rate due to this mechanism alone was increased by 90 % in the spring of 2005 resulting from the decrease of $O_3$ column density from 390 to 290 DU. Assuming that the production of $HNO_3$ via OH oxidation was increased by the same factor, enhanced local OH production could easily account for the 60 % enhancement of nitrate flux in the spring of 2005, if all nitrate was formed via OH oxidation (R4). During a typical Arctic spring, $O_3$ is expected to be the major oxidant in the oxidation of $NO_x$ to $HNO_3$ (Kunasek et al., 2008), so it is unlikely that R4 is solely responsible for the local oxidation of $NO_x$ to $HNO_3$. Using a global chemical transport model (GEOS-Chem), Alexander et al. (2009) estimated that about 30 % of total nitrate in a normal spring (average in February and March) is produced via OH oxidation at Summit. With this more realistic value, a 200 % increase in the local OH production rate was needed to account for the additional nitrate flux in the spring of 2005. Therefore, the enhanced local production rate of OH due to solely the enhanced photolysis of tropospheric $O_3$ in the spring of 2005 can explain about 50 % of the observed spring nitrate peak.

In addition to production via $O_3$ photolysis (R9 and R10), OH can be formed by the photolysis of snowpack emitted $CH_2O$, $H_2O_2$, and HONO (Dassau et al., 2002; Hutterli et al., 2001; Zhou et al., 2001; Sjostedt et al., 2007). Model studies suggested that photolysis of $CH_2O$, $H_2O_2$ and HONO contributes a similar amount to local OH production as that from $O_3$ photolysis (Hutterli et al., 2001; Yang et al., 2002). A recent model study (Thomas et al., 2012) suggested that at Summit snow sourced $NO_x$ by photolysis also contributes to the local OH concentration (20-50 %) via shifting the local OH/$HO_2$ ratio in favor of OH. The production of OH via $CH_2O$, HONO and $H_2O_2$ photolysis is also strongly influenced by UV-B radiation (Hutterli et al., 2001; Molina et al., 2002; Zhou et al., 2001; Hullar and Anastasio, 2013). Therefore, it is conceivable that under the condition of reduced $O_3$ column density in the spring of 2005, the OH production rate could be increased by 200 % from the combined contribution of OH precursors from the snowpack and enhanced tropospheric $O_3$

photolysis, even without considering the effect of elevated water vapor mixing ratio due to the temperature increase (around 3 ºC).

Thus, we propose that the elevated tropospheric UV-B level due to a weakened stratospheric ozone layer in the spring of 2005 likely led to additional local nitrate production in sufficient quantities to account for the spring nitrate peak. The additional nitrate was generated primarily through increased tropospheric OH production from the enhanced photolysis of tropospheric $O_3$ and $CH_2O$, $H_2O_2$ and HONO emitted from the snowpack, and also possibly from enhanced $NO_x$ emission from the photolysis of snowpack nitrate. The enhanced snowpack $NO_x$ emission, contributed to the spring nitrate peak by enhancing the local $NO_x$ source and by increasing OH production rate.

### 4.3. Justification with additional snow/ice core data

Hastings et al. (2004) reported seasonal variations in concentrations, $\delta^{18}O$ and $\delta^{15}N$ of snow nitrate at Summit covering 2000 and 2001. Qualitatively, $\delta^{18}O(NO_3^-)$ is similar to $\Delta^{17}O(NO_3^-)$, because the $\delta^{18}O(NO_3^-)$ value is also determined by the relative importance of $O_3$ versus OH oxidation (higher $\delta^{18}O(NO_3^-)$ values are associated with increased $O_3$ oxidation and lower $\delta^{18}O(NO_3^-)$ values indicate increased $HO_x$ oxidation) (Hastings et al., 2004). Consequently, $\delta^{18}O(NO_3^-)$ is high in winter snow and low in summer snow (as shown in Figure 1a, and also in Hastings et al. (2004)). The data shown in Hastings et al. (2004) indicated a spring nitrate peak in 2000. The spring nitrate concentration peak in 2000 in Hastings et al. (2004) had $\delta^{18}O(NO_3^-)$ values ((69.8 ± 2.1) ‰) similar to those during the summer of 2000 ((70.5 ± 2.4) ‰). Although the winter of 1999/2000 (i.e., the winter prior to the spring of 2000) was not covered in Hastings et al. (2004), $\delta^{18}O(NO_3^-)$ values in this winter should be higher than those in the 2000 summer according to the seasonality of $\delta^{18}O(NO_3^-)$. Therefore, in the 2000 spring, the $\delta^{18}O(NO_3^-)$ values are lower than those in the previous winter. In contrast, in the 2001 spring when no nitrate concentration peak was observed, $\delta^{18}O(NO_3^-)$ was (77.5 ± 2.4) ‰, which is similar to the $\delta^{18}O(NO_3^-)$ values observed during the prior winter ((77.4 ± 1.9) ‰), and higher than those observed during the subsequent summer ((68.9 ± 2.1) ‰). In addition, the mean $\delta^{15}N(NO_3^-)$ in the spring of 2000 ((5.9 ± 6.2) ‰) from Hastings et al. (2004) is similar to that observed in the spring of 2005 (6.4 ± 2.1) ‰, and is higher than that observed in Hastings et al. (2004) during the spring of 2001((-1.4 ± 3.0) ‰). In summary, the isotopic features of nitrate associated with the spring peaks observed in 2000 (Hastings et al., 2004) and in 2005 are similar to each other, each suggesting enhanced local photochemistry. This is consistent with the low $O_3$ column density in the spring of 2000 (337 DU, Figure 3) and 2005 (294 DU, Figure 3). Therefore, the results of Hastings et al. (2004) support the explanation that the appearance of the spring nitrate peak is caused by a weakened stratospheric ozone layer.

To further determine whether the above explanation is representative of the occasional nature of the spring nitrate peak observed in modern snow in Central Greenland, we compared the nitrate concentration record from the shallow core with $O_3$ column density data from 1979 to 2006, the time period when global $O_3$ data are available from satellite observations. The year-to-year variability of polar stratospheric $O_3$ is largely controlled by the Brewer-Dobson circulation (BDC) through direct transport and indirect coupling between dynamics and chemistry [e.g., (Randel et al., 2002; Shepherd, 2008; Weber et al., 2011)]. Halogen-catalyzed chemical destruction leads to a decreasing trend in column $O_3$ density since 1980

(WMO, 2007) and causes sudden drops in $O_3$ column density in years when the winter temperatures are anomalously low [e.g., the winter of 2004/2005 (Jin et al., 2006; Kleinbohl et al., 2005)]. The strength of the BDC is related to the wave force, which is represented by extratropical poleward eddy heat flux in the lower stratosphere (Fusco and Salby, 1999; Weber et al., 2011). From the NCEP/NCAR reanalysis data (http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.pressure.html), we retrieved the average eddy heat flux in the lower stratosphere at 40-80º N in January and February (due to the transport lag, January and February eddy heat flux determines the February and March polar stratospheric $O_3$ abundance) from 1979 to 2006 (Figure 3). Reanalysis data before 1979 are also available, but less reliable due to lack of constraints by satellite observations. Therefore in this study, we only use the data after 1979.

As shown in Figure 3, in the period from 1979 to 2006, the spring nitrate peak only appears when $O_3$ column density is near or below the average for that period. We note that although spring nitrate concentration peaks are observed in all years with especially low (lower than the average) $O_3$ column density, there are a few years (3 out of 12) with a spring nitrate peak when $O_3$ column density is near the 1979-2006 average. In addition, there are other years with similarly average $O_3$ column density when no spring nitrate peak is observed. We suggest that this is because the presence of the spring nitrate peak also requires other conditions (e.g., sufficient local $NO_x$ abundance), and that this is especially true when $O_3$ column density is near the 1979-2006 average. Additional factors may also be important, such as stratospheric input of nitrate and/or long range transport of nitrate, as discussed previously. With isotopic data and other relevant information available, we were able to exclude many possible sources of nitrate to the spring peak in 2005; however, it is difficult to explicitly assess the dominant source(s) of nitrate contributing to the spring peak in each individual year observed in the shallow ice core, mainly due to the lack of isotopic data. It is possible that episodic events bring sufficient nitrate so that a spring peak is detected, when local photochemistry is not significantly enhanced.

Possible local $NO_x$ sources at Summit include PAN decomposition and snowpack photodenitrification. A model study (Stroud et al., 2003) also suggested that $HNO_4$ is a source of $NO_x$ in remote regions through recycling reactions, but its importance is unclear due to a lack of field observations. In spring, PAN acts as a sink of $NO_x$, which leaves the snowpack photodenitrification as the most likely local source of $NO_x$. As shown in Figure 2a, snow nitrate concentrations at Summit began to increase around 1950 due to increasing anthropogenic $NO_x$ emissions in the mid-latitudes (Fischer et al., 1998), and reached and maintained the highest level from 1970 to the present. Since snow nitrate can be photolyzed, releasing $NO_x$ to the boundary layer, the increase in snow nitrate concentrations represents an increase in a potentially important $NO_x$ reservoir in Greenland. Anthropogenic $NO_x$ emissions also increase other reservoir species that may contribute to springtime $NO_x$ abundance at Summit. Prior to the 1950s, when local $NO_x$ abundance was not sufficiently high, no spring nitrate concentration peaks were detected.

## 5. Conclusion

We report observations of spring nitrate concentration peaks in a snowpit and a shallow ice core from Summit, Greenland. A case study regarding the origin of the spring nitrate peak was conducted by measuring the isotopic signature of nitrate in the spring of 2005 when a peak was observed. The isotopic composition of snow nitrate in this spring, combined with photochemical calculations, suggests the presence of the 2005 spring nitrate peak was caused by enhanced local nitrate production. An analysis of the possible causes suggests that this enhancement was primarily due to increased OH concentration mainly resulting from enhanced photolysis of OH precursors ($O_3$, HONO, $H_2O_2$, etc.) in the troposphere caused by elevated UV-B radiation at the surface, which was the result of a significant reduction of stratospheric ozone layer in Arctic at the same time. Increased local $NO_x$ concentration due to enhanced snowpack nitrate photolysis may also contribute to up to half of the additional nitrate in the spring peak, if snowpack nitrate photolysis is the dominant local $NO_x$ source. Either the increase in OH concentration or the increase in local $NO_x$ concentration relies on the enhanced photochemical reactions initiated by the reduced $O_3$ column density. This mechanism is supported by the appearance of a spring nitrate peak in 2000 (Hastings et al., 2004), when a reduced $O_3$ column density also occurred. For the spring peaks observed in the shallow ice core, most of them appear in springs with significantly low $O_3$ column density, though there are exceptions likely because $O_3$ column density is not the only factor influencing local nitrate production. Nevertheless, the evidence available together suggests that the occasional nature of the spring nitrate peak observed in Greenland snow is largely associated with the interannual variability of $O_3$ column density. The interannual variability of $O_3$ column density is mainly controlled by the Brewer-Dobson circulation, while chemical destruction may also play a role beginning around 1980 (WMO, 2007). The presence of the spring nitrate maximum, however, also requires sufficient amount of local $NO_x$, which is likely to exist only after the 1950s when dramatic increases in anthropogenic

$NO_x$ emissions started to lead to the buildup of $NO_x$ reservoir species at Summit and thereby increase the local abundance of $NO_x$. Seasonal resolved isotopic data ($\Delta^{17}O(NO_3^-)$ and $\delta^{15}N(NO_3^-)$) covering additional years with spring nitrate concentration peaks are needed to further examine how robust the connection is between the spring nitrate peak and $O_3$ column density. Although it is difficult to conduct such efforts with ice core measurements because of the large sample requirements (> 50 g ice), measurements of snowpit samples can be performed. Snow samples from Summit covering the years of 2010 to 2012 may be ideal for this purpose because there is unprecedented $O_3$ loss in the spring of 2011 in Arctic (Manney et al., 2011).

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## References

Alexander, B., Savarino, J., Kreutz, K. J., and Thiemens, M. H.: Impact of preindustrial biomass-burning emissions on the oxidation pathways of tropospheric sulfur and nitrogen, J. Geophys. Res., 109, D08303, 10.1029/2003jd004218, 2004.

Alexander, B., Hastings, M. G., Allman, D. J., Dachs, J., Thornton, J. A., and Kunasek, S. A.: Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ($\Delta^{17}$O) of atmospheric nitrate, Atmos. Chem. Phys., 9, 5043-5056, 10.5194/acp-9-5043-2009, 2009.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, 10.5194/acp-6-3625-2006, 2006.

Beine, H. J., and Krognes, T.: The seasonal cycle of peroxyacetyl nitrate (PAN) in the European Arctic, Atmos. Environ., 34, 933-940, 10.1016/S1352-2310(99)00288-5, 2000.

Bhattacharya, S. K., Pandey, A., and Savarino, J.: Determination of intramolecular isotope distribution of ozone by oxidation reaction with silver metal, J. Geophys. Res., 113, D03303, 10.1029/2006jd008309, 2008.

Bottenheim, J. W., Barrie, L. A., and Atlas, E.: The Partitioning of Nitrogen-Oxides in the Lower Arctic Troposphere during Spring 1988, J. Atmos. Chem., 17, 15-27, 10.1007/BF00699111, 1993.

Burkhart, J. F., Bales, R. C., McConnell, J. R., and Hutterli, M. A.: Influence of North Atlantic Oscillation on anthropogenic transport recorded in northwest Greenland ice cores, J. Geophys. Res., 111, D22309, 10.1029/2005jd006771, 2006.

Chu, L., and Anastasio, C.: Quantum yields of hydroxyl radical and nitrogen dioxide from the photolysis of nitrate on ice, J. Phys. Chem. A, 107, 9594-9602, 10.1021/Jp0349132, 2003.

Cole-Dai, J., Budner, D. M., and Ferris, D. G.: High speed, high resolution, and continuous chemical analysis of ice cores using a melter and ion chromatography, Environ. Sci. Technol., 40, 6764-6769, 10.1021/Es061188a, 2006.

Cole-Dai, J., Ferris, D. G., Lanciki, A. L., Savarino, J., Thiemens, M. H., and McConnell, J. R.: Two likely stratospheric volcanic eruptions in the 1450s C.E. found in a bipolar, subannually dated 800 year ice core record, J. Geophys. Res., 118, 7459-7466, 10.1002/jgrd.50587, 2013.

Dassau, T. M., Sumner, A. L., Koeniger, S. L., Shepson, P. B., Yang, J., Honrath, R. E., Cullen, N. J., Steffen, K., Jacobi, H. W., Frey, M., and Bales, R. C.: Investigation of the role of the snowpack on atmospheric formaldehyde chemistry at Summit, Greenland, J. Geophys. Res., 107, 4394, 10.1029/2002jd002182, 2002.

Davidson, C. I., Harrington, J. R., Stephenson, M. J., Small, M. J., Boscoe, F. P., and Gandley, R. E.: Seasonal variations in sulfate, nitrate and chloride in the Greenland ice sheet: relation to atmospheric concentrations, Atmos. Environ., 23, 2483-2493, 10.1016/0004-6981(89)90259-X, 1989.

Eckhardt, S., Stohl, A., Beirle, S., Spichtinger, N., James, P., Forster, C., Junker, C., Wagner, T., Platt, U., and Jennings, S. G.: The North Atlantic Oscillation controls air pollution transport to the Arctic, Atmos. Chem. Phys., 3, 1769-1778, 10.5194/acp-3-1769-2003, 2003.

Erbland, J., Vicars, W. C., Savarino, J., Morin, S., Frey, M. M., Frosini, D., Vince, E., and Martins, J. M. F.: Air-snow transfer of nitrate on the East Antarctic Plateau - Part 1: Isotopic evidence for a photolytically driven dynamic equilibrium, Atmos. Chem. Phys., 13, 6403-6419, 10.5194/acp-13-6403-2013, 2013.

Finkel, R. C., and Langway, C. C.: Changes in Precipitation chemistry at Dye 3, Greenland, J. Geophys. Res., 91, 9849-9855, 10.1029/JD091iD09p09849, 1986.

Fischer, H., Wagenbach, D., and Kipfstuhl, J.: Sulfate and nitrate firn concentrations on the Greenland ice sheet 2. Temporal anthropogenic deposition changes, J. Geophys. Res., 103, 21935-21942, 10.1029/98JD01886, 1998.

Flowers, B. A., Angerhofer, M. E., Simpson, W. R., Nakayama, T., and Matsumi, Y.: Nitrate radical quantum yield from peroxyacetyl nitrate photolysis, J. Phys. Chem. A, 109, 2552-2558, 10.1021/Jp045529n, 2005.

France, J. L., King, M. D., Frey, M. M., Erbland, J., Picard, G., Preunkert, S., MacArthur, A., and Savarino, J.: Snow optical properties at Dome C (Concordia), Antarctica; implications for snow emissions and snow chemistry of reactive nitrogen, Atmos. Chem. Phys., 11, 9787-9801, 10.5194/acp-11-9787-2011, 2011.

Frey, M. M., Savarino, J., Morin, S., Erbland, J., and Martins, J. M. F.: Photolysis imprint in the nitrate stable isotope signal in snow and atmosphere of East Antarctica and implications for reactive nitrogen cycling, Atmos. Chem. Phys., 9, 8681-8696, 10.5194/acp-9-8681-2009, 2009.

Freyer, H. D., Kley, D., Volzthomas, A., and Kobel, K.: On the Interaction of Isotopic Exchange Processes with Photochemical-Reactions in Atmospheric Oxides of Nitrogen, J. Geophys. Res., 98, 14791-14796, 1993.

Fusco, A. C., and Salby, M. L.: Interannual variations of total ozone and their relationship to variations of planetary wave activity, J Climate, 12, 1619-1629, 10.1175/1520-0442, 1999.

Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., and Cosby, B. J.: The nitrogen cascade, Bioscience, 53, 341-356, 2003.

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Domine, F., Frey, M. M., Guzman, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Klan, P., Lefer, B., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J. R., von Glasow, R., Weller, R., Wolff, E. W., and Zhu, T.: An overview of snow photochemistry: evidence, mechanisms and impacts, Atmos. Chem. Phys., 7, 4329-4373, 10.5194/acp-7-4329-2007, 2007.

Hastings, M. G., Steig, E. J., and Sigman, D. M.: Seasonal variations in N and O isotopes of nitrate in snow at Summit, Greenland: Implications for the study of nitrate in snow and ice cores, J. Geophys. Res., 109, D20306, 10.1029/2004jd004991, 2004.

Honrath, R. E., and Jaffe, D. A.: The Seasonal Cycle of Nitrogen-Oxides in the Arctic Troposphere at Barrow, Alaska, J. Geophys. Res., 97, 20615-20630, 1992.

Hullar, T., and Anastasio, C.: Modeling the influence of photochemistry on hydrogen peroxide concentrations in an Arctic snowpack, Geophys. Res. Lett., 40, 2694-2698, 10.1002/Grl.50589, 2013.

Hutterli, M. A., McConnell, J. R., Stewart, R. W., Jacobi, H. W., and Bales, R. C.: Impact of temperature-driven cycling of hydrogen peroxide ($H_2O_2$) between air and snow on the planetary boundary layer, J. Geophys. Res., 106, 15395-15404, 10.1029/2001JD900102, 2001.

Jacobi, H. W., Weller, R., Bluszcz, T., and Schrems, O.: Latitudinal distribution of peroxyacetyl nitrate (PAN) over the Atlantic Ocean, J. Geophys. Res., 104, 26901-26912, 10.1029/1999JD900462, 1999.

Jacobi, H. W., Bales, R. C., Honrath, R. E., Peterson, M. C., Dibb, J. E., Swanson, A. L., and Albert, M. R.: Reactive trace gases measured in the interstitial air of surface snow at Summit, Greenland, Atmos. Environ., 38, 1687-1697, 10.1016/j.atmosenv.2004.01.004, 2004.

Jarvis, J. C., Hastings, M. G., Steig, E. J., and Kunasek, S. A.: Isotopic ratios in gas-phase $HNO_3$ and snow nitrate at Summit, Greenland, J. Geophys. Res., 114, 10.1029/2009jd012134, 2009.

Jin, J. J., Semeniuk, K., Manney, G. L., Jonsson, A. I., Beagley, S. R., McConnell, J. C., Rinsland, C. P., Boone, C. D., Walker, K. A., and Bernath, P. F.: Denitrification in the Arctic winter 2004/2005: Observations from ACE-FTS, Geophys. Res. Lett., 33, L19814, 10.1029/2006gl027687, 2006.

Johnson, D. G., Jucks, K. W., Traub, W. A., and Chance, K. V.: Isotopic composition of stratospheric ozone, J. Geophys. Res., 105, 9025-9031, 10.1029/1999JD901167, 2000.

Kaiser, J., Hastings, M. G., Houlton, B. Z., Rockmann, T., and Sigman, D. M.: Triple oxygen isotope analysis of nitrate using the denitrifier method and thermal decomposition of $N_2O$, Anal. Chem., 79, 599-607, 10.1021/Ac061022s, 2007.

Kleinbohl, A., Bremer, H., Kullmann, H., Kuttippurath, J., Browell, E. V., Canty, T., Salawitch, R. J., Toon, G. C., and Notholt, J.: Denitrification in the Arctic mid-winter 2004/2005 observed by airborne submillimeter radiometry, Geophys. Res. Lett., 32, L19811, 10.1029/2005gl023408, 2005.

Kunasek, S. A., Alexander, B., Steig, E. J., Hastings, M. G., Gleason, D. J., and Jarvis, J. C.: Measurements and modeling of $\Delta^{17}O$ of nitrate in snowpits from Summit, Greenland, J. Geophys. Res., 113, D24302, 10.1029/2008jd010103, 2008.

Liang, M. C., Irion, F. W., Weibel, J. D., Miller, C. E., Blake, G. A., and Yung, Y. L.: Isotopic composition of stratospheric ozone, J. Geophys. Res., 111, D02302, 10.1029/2005jd006342, 2006.

Logan, J. A.: Nitrogen oxides in the troposphere: Global and regional budgets, J. Geophys. Res., 88, 10785-10807, 10.1029/JC088iC15p10785, 1983.

Lyons, J. R.: Transfer of mass-independent fractionation in ozone to other oxygen-containing radicals in the atmosphere, Geophys. Res. Lett., 28, 3231-3234, 10.1029/2000GL012791, 2001.

Mann, G. W., Davies, S., Carslaw, K. S., and Chipperfield, M. P.: Factors controlling Arctic denitrification in cold winters of the 1990s, Atmos. Chem. Phys., 3, 403-416, 10.5194/acp-3-403-2003, 2003.

Manney, G. L., Santee, M. L., Rex, M., Livesey, N. J., Pitts, M. C., Veefkind, P., Nash, E. R., Wohltmann, I., Lehmann, R., Froidevaux, L., Poole, L. R., Schoeberl, M. R., Haffner, D. P., Davies, J., Dorokhov, V., Gernandt, H., Johnson, B., Kivi, R., Kyro, E., Larsen, N., Levelt, P. F., Makshtas, A., McElroy, C. T., Nakajima, H., Parrondo, M. C., Tarasick, D. W., von der Gathen, P., Walker, K. A., and Zinoviev, N. S.: Unprecedented Arctic ozone loss in 2011, Nature, 478, 469-U465, Doi 10.1038/Nature10556, 2011.

Mauersberger, K., Lammerzahl, P., and Krankowsky, D.: Stratospheric ozone isotope enrichments-revisited, Geophys. Res. Lett., 28, 3155-3158, 10.1029/2001GL013439, 2001.

Mayewski, P. A., Lyons, W. B., Spencer, M. J., Twickler, M. S., Buck, C. F., and Whitlow, S.: An ice-core record of atmospheric response to anthropogenic sulphate and nitrate, Nature, 346, 554 - 556, 10.1038/346554a0, 1990.

McCabe, J. R., Thiemens, M. H., and Savarino, J.: A record of ozone variability in South Pole Antarctic snow: Role of nitrate oxygen isotopes, J. Geophys. Res., 112, D12303, 10.1029/2006jd007822, 2007.

Michalski, G., Scott, Z., Kabiling, M., and Thiemens, M. H.: First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate, Geophys. Res. Lett., 30, 1870, 10.1029/2003gl017015, 2003.

Molina, M. J., Smith, G. D., and Molina, L. T.: Measurement of radical quantum yields from formaldehyde photolysis between 269 and 339 nm, J. Phys. Chem. A, 106, 1233-1240, 10.1021/Jp013180n, 2002.

Morin, S., Savarino, J., Bekki, S., Gong, S., and Bottenheim, J. W.: Signature of Arctic surface ozone depletion events in the isotope anomaly ($\Delta^{17}O$) of atmospheric nitrate, Atmos. Chem. Phys., 7, 1451-1469, 10.5194/acp-7-1451-2007, 2007.

Morin, S., Savarino, J., Frey, M. M., Yan, N., Bekki, S., Bottenheim, J. W., and Martins, J. M. F.: Tracing the Origin and Fate of $NO_x$ in the Arctic Atmosphere Using Stable Isotopes in Nitrate, Science, 322, 730-732, 10.1126/science.1161910, 2008.

Morin, S., Sander, R., and Savarino, J.: Simulation of the diurnal variations of the oxygen isotope anomaly (Δ17O) of reactive atmospheric species, Atmos. Chem. Phys., 11, 3653-3671, 10.5194/acp-11-3653-2011, 2011.

Moxim, W. J., Levy, H., and Kasibhatla, P. S.: Simulated global tropospheric PAN: Its transport and impact on $NO_x$, J. Geophys. Res., 101, 12621-12638, 10.1029/96JD00338, 1996.

Mulvaney, R., and Wolff, E. W.: Evidence for Winter Spring Denitrification of the Stratosphere in the Nitrate Record of Antarctic Firn Cores, J. Geophys. Res., 98, 5213-5220, 10.1029/92JD02966, 1993.

Osborn, T. J.: Winter 2009/2010 temperatures and a record-breaking North Atlantic Oscillation index, Weather, 66, 19-21, 10.1002/Wea.660, 2011.

Park, R. J., Jacob, D. J., Field, B. D., Yantosca, R. M., and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, J. Geophys. Res., 109, 10.1029/2003jd004473, 2004.

Pye, H. O. T., Liao, H., Wu, S., Mickley, L. J., Jacob, D. J., Henze, D. K., and Seinfeld, J. H.: Effect of changes in climate and emissions on future sulfate-nitrate-ammonium aerosol levels in the United States, J. Geophys. Res., 114, 10.1029/2008jd010701, 2009.

Randel, W. J., Wu, F., and Stolarski, R.: Changes in column ozone correlated with the stratospheric EP flux, J Meteorol Soc Jpn, 80, 849-862, 10.2151/Jmsj.80.849, 2002.

Röthlisberger, R., Hutterli, M. A., Wolff, E. W., Mulvaney, R., Fischer, H., Bigler, M., Goto-Azuma, K., Hansson, M. E., Ruth, U., Siggaard-Andersen, M. L., and Steffensen, J. P.: Nitrate in Greenland and Antarctic ice cores: a detailed description of post-depositional processes, Ann. Glaciol., 35, 209-216, 10.3189/172756402781817220, 2002.

Savarino, J., Kaiser, J., Morin, S., Sigman, D. M., and Thiemens, M. H.: Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, Atmos. Chem. Phys., 7, 1925-1945, 10.5194/acpd-6-8817-2006, 2007.

Shepherd, T. G.: Dynamics, stratospheric ozone, and climate change, Atmos Ocean, 46, 117-138, 10.3137/Ao.460106, 2008.

Singh, H. B., Ohara, D., Herlth, D., Bradshaw, J. D., Sandholm, S. T., Gregory, G. L., Sachse, G. W., Blake, D. R., Crutzen, P. J., and Kanakidou, M. A.: Atmospheric Measurements of Peroxyacetyl Nitrate and Other Organic Nitrates at High-Latitudes: Possible Sources and Sinks, J. Geophys. Res., 97, 16511-16522, 1992.

Sjostedt, S. J., Huey, L. G., Tanner, D. J., Peischl, J., Chen, G., Dibb, J. E., Lefer, B., Hutterli, M. A., Beyersdorf, A. J., Blake, N. J., Blake, D. R., Sueper, D., Ryerson, T., Burkhart, J., and Stohl, A.: Observations of hydroxyl and the sum of peroxy radicals at Summit, Greenland during summer 2003, Atmos. Environ., 41, 5122-5137, 10.1016/j.atmosenv.2006.06.065, 2007.

Stroud, C., Madronich, S., Atlas, E., Ridley, B., Flocke, F., Weinheimer, A., Talbot, B., Fried, A., Wert, B., Shetter, R., Lefer, B., Coffey, M., Heikes, B., and Blake, D.: Photochemistry in the arctic free troposphere: $NO_x$ budget and the role of odd nitrogen reservoir recycling, Atmos. Environ., 37, 3351-3364, 10.1016/S1352-2310(03)00353-4, 2003.

Talukdar, R. K., Burkholder, J. B., Schmoltner, A. M., Roberts, J. M., Wilson, R. R., and Ravishankara, A. R.: Investigation of the Loss Processes for Peroxyacetyl Nitrate in the Atmosphere - UV Photolysis and Reaction with OH, J. Geophys. Res., 100, 14163-14173, 10.1029/95JD00545, 1995.

Thomas, J. L., Dibb, J. E., Huey, L. G., Liao, J., Tanner, D., Lefer, B., von Glasow, R., and Stutz, J.: Modeling chemistry in and above snow at Summit, Greenland - Part 2: Impact of snowpack chemistry on the oxidation capacity of the boundary layer, Atmos. Chem. Phys., 12, 6537-6554, 10.5194/acp-12-6537-2012, 2012.

Waugh, D. W., and Randel, W. J.: Climatology of arctic and antarctic polar vortices using elliptical diagnostics, J. Atmos. Sci., 56, 1594-1613, 1999.

Weber, M., Dikty, S., Burrows, J. P., Garny, H., Dameris, M., Kubin, A., Abalichin, J., and Langematz, U.: The Brewer-Dobson circulation and total ozone from seasonal to decadal time scales, Atmos. Chem. Phys., 11, 11221-11235, 10.5194/acp-11-11221-2011, 2011.

Whitlow, S., Mayewski, P. A., and Dibb, J. E.: A Comparison of Major Chemical-Species Seasonal Concentration and Accumulation at the South-Pole and Summit, Greenland, Atmos. Environ., 26, 2045-2054, 10.1016/0960-1686(92)90089-4, 1992.

WMO: Scientific assessment of ozone depletion: 2006, Geneva50, 572, 2007.

Yang, J., Honrath, R. E., Peterson, M. C., Dibb, J. E., Sumner, A. L., Shepson, P. B., Frey, M., Jacobi, H. W., Swanson, A., and Blake, N.: Impacts of snowpack emissions on deduced levels of OH and peroxy radicals at Summit, Greenland, Atmos. Environ., 36, 2523-2534, 10.1016/S1352-2310(02)00128-0, 2002.

Yang, Q. Z., Mayewski, P. A., Whitlow, S., Twickler, M., Morrison, M., Talbot, R., Dibb, J., and Linder, E.: Global Perspective of Nitrate Flux in Ice Cores, J. Geophys. Res., 100, 5113-5121, 10.1029/94JD03115, 1995.

Zatko, M. C., Grenfell, T. C., Alexander, B., Doherty, S. J., Thomas, J. L., and Yang, X.: The influence of snow grain size and impurities on the vertical profiles of actinic flux and associated NOx emissions on the Antarctic and Greenland ice sheets, Atmos. Chem. Phys., 13, 3547-3567, 10.5194/acp-13-3547-2013, 2013.

Zhou, X. L., Beine, H. J., Honrath, R. E., Fuentes, J. D., Simpson, W., Shepson, P. B., and Bottenheim, J. W.: Snowpack photochemical production of HONO: a major source of OH in the Arctic boundary layer in springtime, Geophys. Res. Lett., 28, 4087-4090, 10.1029/2001GL013531, 2001.

**Table 1.** Uncertainties of replicate measurements of reference gases and standards using the bacterial denitrifier method (Kaiser et al., 2007) at the University of Washington IsoLab.

**Table 2.** Frequency (number of years per decade) of the spring nitrate peak in each decade from 1960 to 2006 in the shallow ice core.

**Figure 1.** $\delta^{18}O(NO_3^-)$ (a), $\delta^{15}N(NO_3^-)$ (b), $\Delta^{17}O(NO_3^-)$ (c) and concentrations of $NO_3^-$ (d), $Na^+$ (e), $SO_4^{2-}$ (f) and $Mg^{2+}$ (g) in the snow samples (data are 3-point running averages). SP-1 data were plotted in gray with plus signs; SP-2 and SB data were plotted in black with circle and star signs, respectively. The pink and green stars represent samples in SB used to calculate the winter and 2005 spring mean $\Delta^{17}O(NO_3^-)$, respectively; while the red and blue plus signs represent samples in SP-1 used to calculate the winter and 2005 spring mean $\Delta^{17}O(NO_3^-)$, respectively. The vertical dashed line indicates the approximate months of snowfall at depths of 0, 0.5, 1.0, 1.5 and 2.0 m by Method B as described in the text.

**Figure 2.** (a) Nitrate concentration record from the shallow ice core; (b), (c), (d) show seasonal peaks of $NO_3^-$, $Na^+$ and $Ca^{2+}$, respectively in two sections of the ice core (data shown in b, c and d are 3-point running averages). The arrows in (b) indicate spring nitrate peaks which are only observed after 1960 in this core. Vertical dashed lines in (a) indicate the years of snowfall at relevant depths.

**Figure 3.** Summit springtime $O_3$ column density (February and March averages) and poleward eddy heat flux in the lower stratosphere (40-80º N, January and February averages) from 1979 to 2006. The solid blue line is the average of springtime $O_3$ column density from 1979 to 2006 ($390 \pm 50$ ($1\sigma$) DU), and the dashed blue line is the linear least-squared regression of the $O_3$ column density from 1979 to 2006. The symbols marked as red indicate the years with a spring nitrate peak observed in the shallow ice core.

**Table 1.** Uncertainties of replicate measurements of reference gases and standards using the bacterial denitrifier method (Kaiser et al., 2007) at the University of Washington IsoLab.

| | | $\delta^{15}$N (‰) | $\delta^{17}$O (‰) | $\delta^{18}$O (‰) | $\Delta^{17}$O (‰) |
|---|---|---|---|---|---|
| Zero Enrichment[a] (N = 30) | | 0.02 | 0.10 | 0.01 | 0.10 |
| IAEA-NO-3 (vs. reference gas)[b] | Short term[d] (N = 6) | 5.1 ± 1.0 | 28.9 ± 0.4 | 56.1 ± 0.6 | -0.3 ± 0.1 |
| USGS35 (vs. reference gas)[b] | Short term (N = 6) | 1.4 ± 1.6 | 63.6 ± 0.2 | 85.2 ± 0.4 | 19.3 ± 0.1 |
| IAEA-NO-3 (normalized)[c] | Long term[e] (N > 100) | 4.7 ± 0.8 | 12.9 ± 0.8 | 25.3 ± 1.3 | -0.6 ± 0.4 |
| | Short term (N = 6) | 4.7 ± 1.0 | 12.9 ± 0.6 | 25.2 ± 0.8 | -0.6 ± 0.3 |
| USGS35 (normalized)[c] | Long term (N > 100) | 2.5 ± 0.9 | 51.2 ± 0.9 | 57.1 ± 1.4 | 21.6 ± 0.4 |
| | Short term (N = 6) | 1.9 ± 2.1 | 51.1 ± 0.3 | 56.8 ± 0.5 | 21.6 ± 0.1 |

a. Continuous flow measurements of reference gases ($O_2$ and $N_2$) relative to themselves; values are one standard deviations ($1\sigma$);

b. Refers to raw values not corrected for any isotopic effects during the analytical procedure; reported values are means ± RMSD (root-mean-square deviation);

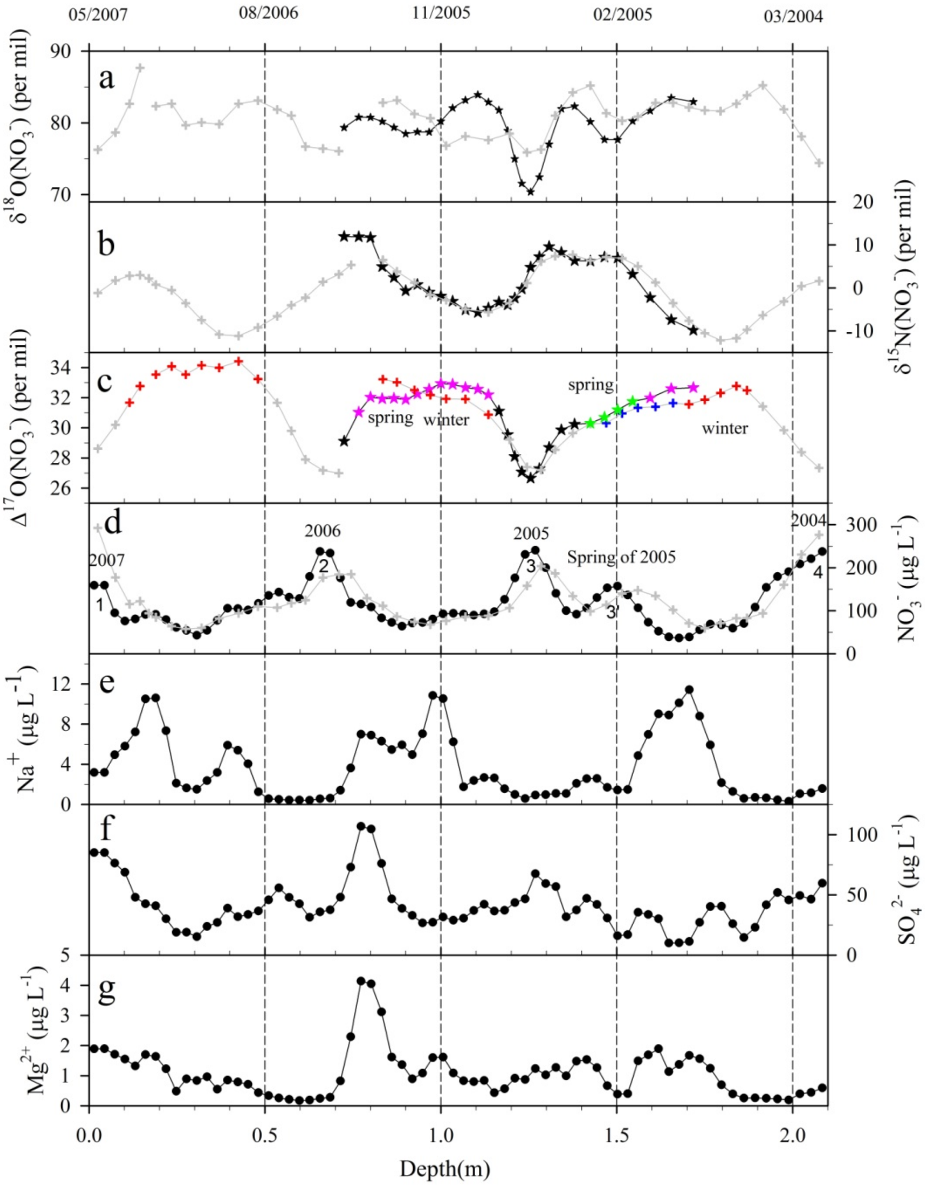
c. Refers to corrected values using the least squares linear regression curve between the measured and accepted values of reference materials; reported values are means ± $1\sigma$ (standard deviation);

d. Refers to the time period (two days) when samples in this study were measured;

e. Refers to the period of instrument running since October, 2009 to present.

**Table 2.** Frequency (number of years per decade) of the spring nitrate peak in each decade from 1960 to 2006 in the shallow ice core.

| Decade | 1960s | 1970s | 1980s | 1990s | 2000-2006 |
|---|---|---|---|---|---|
| Frequency | 2 | 5 | 3 | 6 | 3 |



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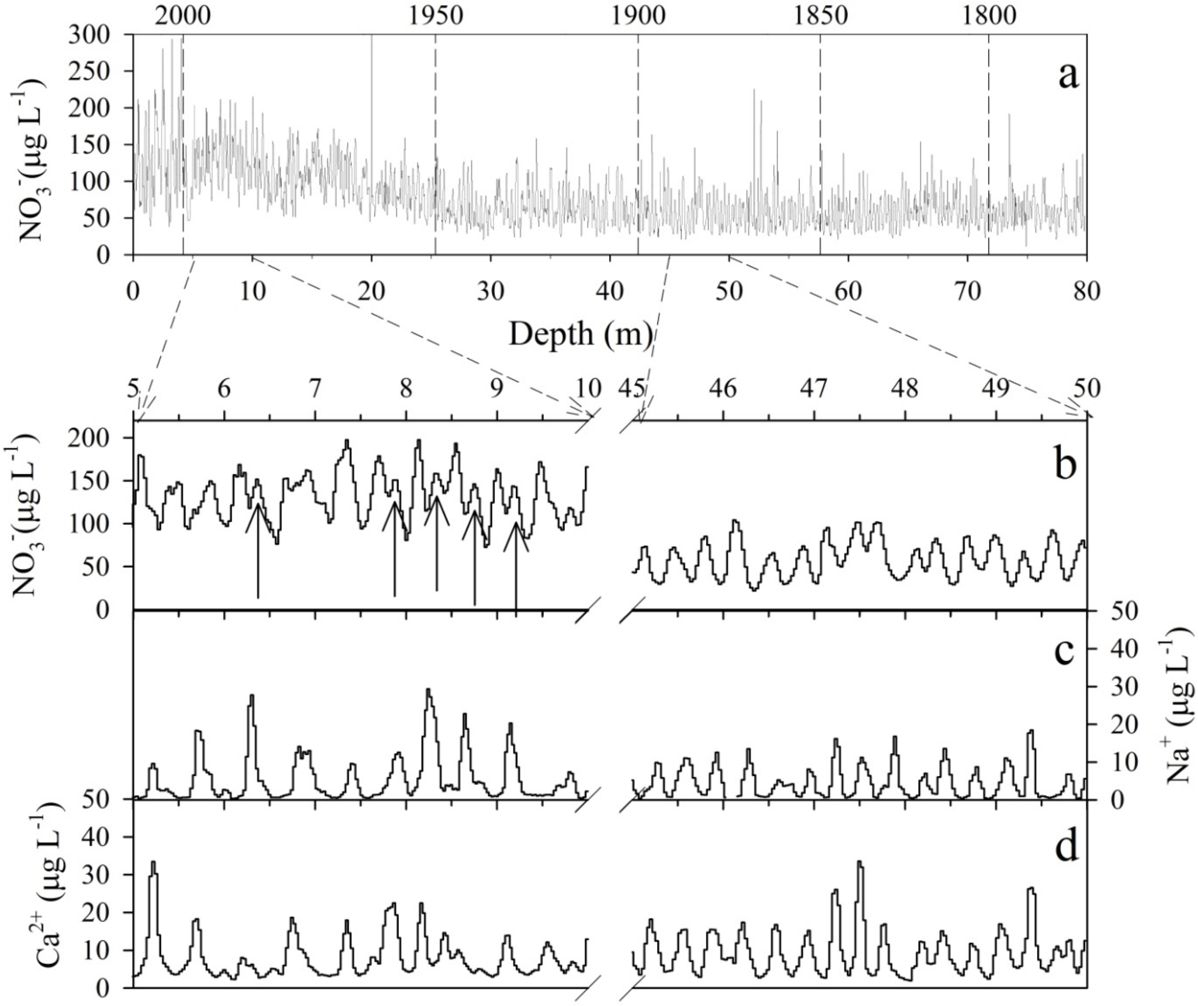

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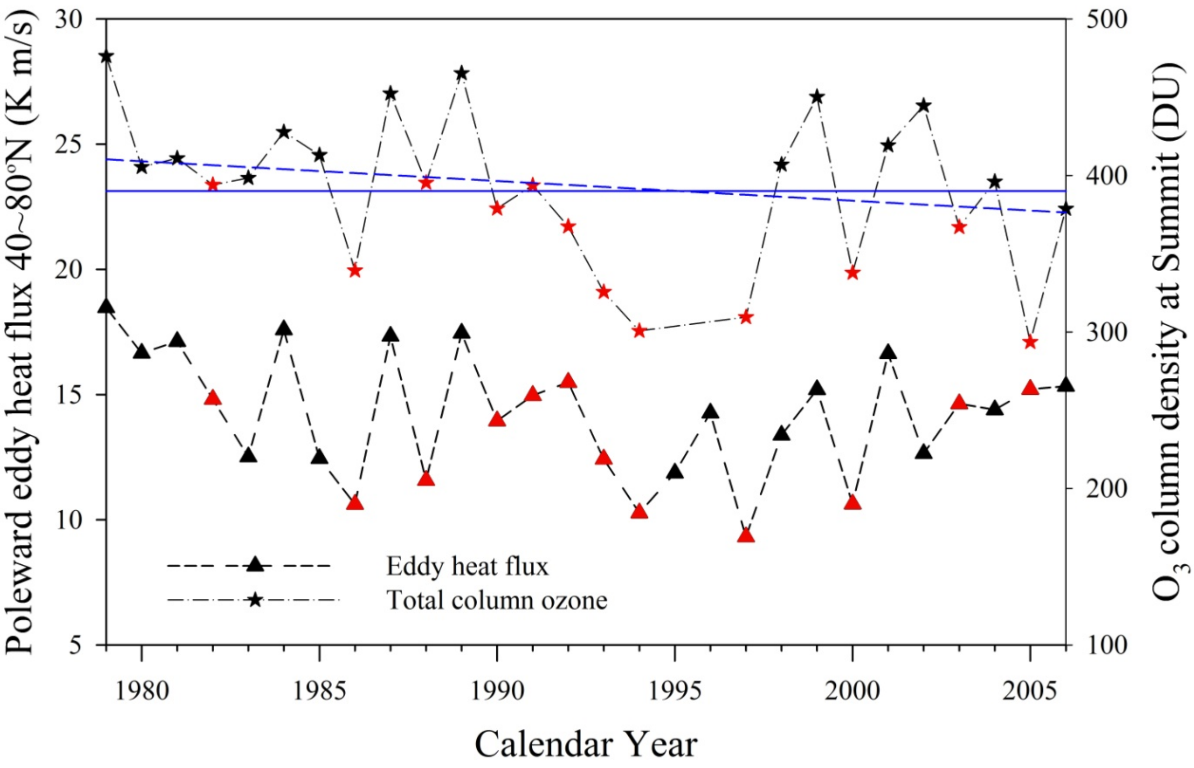

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