On the origin of the occasional spring nitrate peak in Greenland snow

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Abstract

Ice-core nitrate concentrations peak in the summer in both Greenland and Antarctica. Two nitrate concentration peaks in one annual layer have been observed in some years in ice cores in Greenland from samples dating post-1900, with the additional nitrate peak occurring in the spring. The origin of the spring nitrate peak was hypothesized to be pollution transport from the mid-latitudes in the industrial era. We perform a case study on the origin of a spring nitrate peak in 2005 measured from a snowpit at Summit, Greenland covering three years of snow accumulation. The effect of long-range transport of nitrate on this spring peak is excluded by using sulfate as a pollution tracer. The isotopic composition of nitrate ($\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$) combined with photochemical calculations suggest that the occurrence of this spring peak is linked to a significantly weakened stratospheric ozone (O_3) layer. The weakened O_3 layer resulted in elevated UV-B (Ultraviolet B) radiation on the snow surface, where the production of OH and NO_x from the photolysis of their precursors was enhanced. Elevated NO_x and OH concentrations resulted in enhanced nitrate production mainly through the NO_2 + OH formation pathway, as indicated by decreases in $\delta^{18}O$ and $\Delta^{17}O$ of nitrate associated with the spring peak. We further examined the nitrate concentration record from a shallow ice core covering the period from 1772 to 2006 and found 19 years with double nitrate peaks after the 1950s. Out of these 19 years, 14 of the secondary nitrate peaks are accompanied by sulfate peaks, suggesting long-range transport of nitrate as their source. In the other five years low springtime O_3 column density is observed, suggesting enhanced local production of nitrate as their source. The results suggest that, in addition to direct transport of nitrate from polluted regions, enhanced local photochemistry can also lead to a spring nitrate

peak. The enhanced local photochemistry is probably associated with the interannual variability of O_3 column density in the Arctic which leads to elevated surface UV radiation in some years. In this scenario, enhanced photochemistry causes increased local nitrate production under the condition of elevated local NO_x abundance in the industrial era.

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 plays 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 is 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:

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

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

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

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

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

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

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

$$NO_3 + NO_2 \rightarrow N_2O_5 \qquad (R7)$$

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

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 variations 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 records 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; Whitlow et al., 1992) noticed that a single nitrate peak appears annually in summer snow/ice layer deposited prior to 1900, whereas two nitrate peaks are seen in some post-1900 annual layers. Although it seems the timing of the additional nitrate peak differs as observed in ice cores from different locations (Burkhart et al., 2006), Yang et al. (1995) stated that at Summit the additional peak occurs in late winter/early spring, which is consistent with the dating in Burkhart et al. (2006).

The occurrence of this occasional spring nitrate peak has been hypothesized to be associated with pollution transport from the mid-latitudes (Burkhart et al., 2006; Yang et al., 1995), though this hypothesis and the occasional nature of the spring nitrate peak were not carefully examined. Anthropogenic NO_x emissions from fossil fuel combustion have increased the concentrations of atmospheric NO_x and other nitrogen species (e.g., HNO_3) in the northern hemisphere since 1900, especially in the last 50 years (Galloway et al., 2003). A corresponding increase in nitrate concentrations in Greenland ice cores has been documented (Mayewski et al., 1990). Direct transport of NO_x from the mid-latitudes to the Arctic is unlikely given the short lifetime of NO_x (1-3 days (Levy et al., 1999)). Alternatively, long range transport of nitrate and NO_x precursors (e.g., PAN) from anthropogenic NO_x source regions could lead to increases in Greenland snow nitrate concentrations. However, the relative importance of nitrate and NO_x precursors to Greenland snow nitrate is unclear. An earlier study suggested a significant contribution from PAN (e.g., (Ford et al., 2002)), whereas a recent study (Geng et al., 2014) suggests that transport to Greenland occurs mainly in the form of gaseous HNO_3. In addition to PAN decomposition as a potential local source of NO_x, the photolysis of nitrate in snowpack produces NO_x, which is quickly transported to the overlying atmosphere by diffusion and wind pumping (Zatko et al., 2013). This is consistent with the elevated NO_x concentrations observed in the ice sheets during polar summers (Honrath et al., 1999). In particular, a model study (Thomas et al., 2012) suggested that at Summit, NO_x produced from snow nitrate photolysis in summer can account for all of the observed NO_x concentrations in the overlying atmosphere. In addition, Kramer et al. (2014) implied that, after polar sunrise, atmospheric NO_y (odd nitrogen species other than PAN and NO_x) can release NO_x through photochemistry. In summary, there are two ways that pollution transport can influence the springtime nitrate budget at Summit, 1) direct transport of nitrate, and 2) transport of NO_x precursors. In order to cause a spring nitrate peak, the latter requires local conditions favoring NO_x release from its precursors and its subsequent conversion to nitrate.

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. δ^{15}N and Δ^{17}O of nitrate (hereafter denoted as δ^{15}N(NO_3^-) and Δ^{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, Δ^{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 Δ^{17}O than nitrate formed during daytime (via R4) because of the high Δ^{17}O of the dominant nighttime oxidant O_3 (Johnson et al., 2000; Lyons, 2001) which is transferred to nitrate. The Δ^{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).

After atmospheric nitrate is deposited to the snow, UV photolysis will convert snow nitrate back to NO_x, which is then released to the atmosphere (Honrath et al., 1999; Thomas et al., 2012; Zatko et al., 2013). This snow-sourced NO_x will be re-oxidized in the atmosphere to nitrate, which is subsequently re-deposited to surface snow or transported away. Reformation of nitrate in the condensed phase of snow grains can also occur if the nitrate being photolyzed is trapped inside the snow grain instead of on the surface (Meusinger et al., 2014). This is the so-called post-depositional processing of snow nitrate, which includes the steps of photolysis, recombination of photoproducts in the condensed phase and in the overlying atmosphere (i.e., recycling), and the re-deposition and/or export of snow-sourced nitrate. Post-depositional processing induces isotopic effects (Frey et al., 2009). In general, the photolysis of nitrate will enrich δ^{15}N and δ^{18}O of nitrate remaining in snow, but will not alter $\Delta^{17}O$ as photolysis induces mass-dependent fractionation. If the photolytic products of nitrate are re-oxidized and re-deposited to the snow surface (i.e., no expert/no net loss), no measurable effect on $\delta^{15}N(NO_3^-)$ will be observed assuming negligible nitrogen isotopic fractionation during the re-formation of nitrate. However, changes in $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ are expected even without net loss of nitrate. The reformation of nitrate in the condensed phase of snow grains will cause oxygen isotope exchange with water (Frey et al., 2009), which lowers $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$. In addition, the re-oxidation of the snow-sourced NO_x to nitrate in the overlying atmosphere will occur mainly through the OH formation pathway. This is because active snow nitrate photolysis requires strong radiation, which is also when atmospheric nitrate is mainly formed through the daytime reaction channel(NO_x + OH). Recycling of snow-sourced NO_x in the atmosphere will thus likely lower $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$, particularly if the initially deposited nitrate was formed through the O_3 oxidation pathway (e.g., formed in polar winters when $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ values are the highest (Alexander et al., 2009; Kunasek et al., 2008)). The deposition of this reformed nitrate will then lower the bulk snow $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$. At sites with snow accumulation rates greater than 100 kg/m^2/a, the oxygen isotope exchange in the condensed phase is minimal (Erbland et al., 2013). This is consistent with the discussion in Fibiger et al. (2013) that the condensed phase process can't explain the observed relationship between $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ in surface snow, given the high snow accumulation rate at Summit (233 ± 38 (1σ) kg/m^2/a during 2000-2006 (Cole-Dai et al., 2013)). However, the Fibiger et al. (2013) analysis neglected atmospheric process, i.e., the reformation of nitrate from snow-sourced NO_x in the atmosphere and its subsequent deposition to surface snow. This process alters $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ simultaneously and can explain the relationship between $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ in surface snow observed by Fibiger et al. (2013). In addition, Fibiger et al. (2013) suggested that there is little to no post-depositional loss of nitrate at Summit, which might be true. But post-depositional loss is only one (possible) step of the post-depositional processing. Post-depositional processing of snow nitrate at Summit could be very active while little post-depositional loss occurs, given a fast recycling rate of nitrate in the air-snow interface.

In this study, the concentrations of major ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}), and the isotopic composition of nitrate in a snowpit from central Greenland were measured. The concentration data were used to establish their temporal patterns and to identify any spring nitrate peak(s). The isotopic data were used to assess the chemistry of nitrate in any identified spring peaks and to discern the origin of the peak. Further examinations were conducted on a shallow ice core to determine whether the mechanism leading to the spring nitrate peak observed in the snowpit is representative of the occasional nature of the spring nitrate peaks 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 °N, 38.5 °W; 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 °C 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 peak(s)

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). We used the sodium (Na^+) peak as a winter snow layer indicator and the peak of the Cl^-/Na^+ ratio as a summer snow layer indicator (Whitlow et al., 1992). Sodium concentration in Greenland snow peaks in winter/late winter due to winter Arctic aerosols (with high sea salt content) and/or late winter cyclonic storms, while Cl^-/Na^+ peaks in summer likely due to long range transport of aged sea salt aerosols (Whitlow et al., 1992) which is depleted in Na^+ because of the preferential removal of Na^+ in aerosols relative to gaseous HCl following sea salt-acid displacement (Legrand and Delmas, 1988). Since the snowpit and snow blocks were excavated in July of 2007, the partial peak of Cl^-/Na^+ at the surface identifies the summer of 2007. The other Cl^-/Na^+ peaks represent the summer of 2006, 2005 and 2004, respectively (Figure 1e) The nitrate peaks 1, 2, 3 and 4 are in almost identical layers as the Cl^-/Na^+ peaks, providing independent evidence that they can be considered summer peaks. Nitrate Peak 3' is between a winter Na^+ peak and a summer Cl^-/Na^+ peak, clearly identifying it as a spring peak. This dating by Cl^-/Na^+ and Na^+ 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. According to Method B, snow in the layer of the Peak 3' fell in February of 2005, suggesting it is a early spring peak, consistent with previous studies that the additional annual nitrate peak occurs in late winter/early spring (Burkhart et al., 2006; Yang et al., 1995). 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). The annual layer dating of this core was performed by counting the annual spring peak of calcium (Cole-Dai et al., 2013). From this ice core, we found there are nineteen years with two nitrate peaks in the period of 1960 to 2006, obtained by subtracting total calcium peaks from total nitrate peaks in this period (Figure 2). We don't attempt to specifically identify the seasonality of these peaks due to the lack of a reliable summer layer indicator in the firn core. The Cl^-/Na^+ ratio is influenced by atmospheric acidity (details in Supplemental Material). In the preindustrial period, atmospheric acidity peaks in summer due to high summer production of non-sea-salt sulfate and nitrate (Whitlow et al., 1992). This leads to an enhancement in excess chloride in summer through acid-sea salt displacement (Legrand and Delmas, 1988). Given the summer low Na^+ concentrations, the Cl^-/Na^+ peak falls almost precisely in summer in the preindustrial period, making it a good summer layer indicator. However, in much of the industrial era, the annual Cl^-/Na^+ peak shifts toward the major annual non-sea-salt sulfate peak (usually in winter, Figure S2, top panel) inhibiting its ability to serve as a summer layer indicator. This makes it difficult to unambiguously identify the secondary nitrate peak in the years with double nitrate peaks as occurring in a specific season (e.g., spring), though we note that previous studies have been able to identify the secondary nitrate peak as occurring in the spring by using summer layer indicators (e.g., H_2O_2, and $\delta^{18}O(H_2O)$) independent of major ion concentrations (Burkhart et al., 2006; Whitlow et al., 1992; Yang et al., 1995). We note that, in the snowpit, sulfate concentrations are as low as they were prior to 1900 (Geng et al., 2014), minimizing its impact on the timing of the Cl^-/Na^+ peak. The frequency of years with double nitrate peaks in each decade is listed in Table 2. Prior to 1960, only a single nitrate peak is observed in each annual layer, consistent with 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. 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 depth 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 winter values (-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 depth of the 2005 spring nitrate peak (Figure 1a).

The observed seasonality of $\Delta^{17}O(NO_3^-)$ (Figure 1c) is 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 is 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 it 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 $\delta^{18}O(NO_3^-)$ from a previous study (Hastings et al., 2004), as increases in the relative importance of OH oxidation will also result in decreases in $\delta^{18}O(NO_3^-)$. The extra nitrate deposited during the spring of 2005 was estimated to be 5.7 $\text{nmol} \times \text{cm}^{-2}$, which was calculated by subtracting the flux of nitrate (9.4 $\text{nmol} \times \text{cm}^{-2}$) in the spring of 2006 from the nitrate flux in the spring of 2005 (15.1 $\text{nmol} \times \text{cm}^{-2}$). 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 enhanced local nitrate production involving NO_x precursors. 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 the spring 2005 nitrate peak. We further examine whether the explanation for the case of spring 2005 is representative of the occasional nature of the additional nitrate peaks observed in the firn core.

4.1. Enhanced transport of nitrate

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 (nitrate photolysis followed by re-formation and re-deposition 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 nitrate photolysis 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

Previous studies (Burkhart et al., 2006; Yang et al., 1995) hypothesized that the spring nitrate peak results from pollution transport in the industrial era, though the occasional nature of the peak was not explicitly discussed. In case of strong meridional transport of nitrate, a spring nitrate peak may be expected. In addition, the $\Delta^{17}O$ of nitrate formed in the 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 concentrations in snow with relatively low $\Delta^{17}O(NO_3^-)$, consistent with the observations. Direct transport of nitrate from the mid-latitudes to Summit is also consistent the conclusions in Kunasek et al. (2008) and Geng et al. (2014).

Pollution from the Northern mid-latitudes is transported to the Arctic by poleward meridional circulation, which is strong when the North Atlantic Oscillation (NAO) is in its positive phase (Eckhardt et al., 2003). However, the NAO index data in the 2004/2005 winter and early spring of 2005 is not strong compared with other years during the period of 1997 to 2009 (Osborn, 2011), suggesting that meridional transport is not particularly strong in the spring of 2005 compared to other springs. However, frequent pollution transport events occur even in years with a negative NAO phase (Kramer et al., 2014). To examine the possibility of pollution transport as the direct cause of the 2005 spring nitrate peak, we examine the profiles of SO_4^{2-} and Mg^{2+} from the snowpit. Enhanced transport from the mid-latitudes will also elevate concentrations of other species derived from anthropogenic and continental sources, such as SO_4^{2-} and Mg^{2+}, especially 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 during that time period.

In addition to pollution from industrial areas, biomass burning (e.g., wild fire) plumes from Boreal North America could also potentially increase snow nitrate concentrations in Greenland. However, the global fire emission data (Giglio et al., 2013) suggests that fire emissions in Boreal North America (nor in Temperate North America and Europe) are not strong in the spring of 2005 compared to other years during the period from 1997 to 2011. In addition, chemical species transported from fire events will likely cause episodic, sharp spikes, such as the NH_4^+ spikes frequently observed in Greenland ice cores (Savarino and Legrand, 1998). The duration (> 1 month) of the 2005 spring nitrate peak argues against an episodic biomass-burning source.

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 and 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. The possibility of PAN decomposition in spring leading to the spring nitrate peak has been mentioned in Yang et al. (1995), but not explicitly examined. Here we provide a detailed examination of the possible role of PAN decomposition in the spring 2005 nitrate peak.

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 (λ = 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 are 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 (1σ) 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) is 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 1.6×10^5 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 state 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). The additional production of NO_x from enhanced PAN photolysis 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 (Honrath et al., 1999; 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 in the atmosphere 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 would also 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 photolysis of snow nitrate. 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 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 nitrate photolysis 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 nitrate photolysis nitrate photolysis 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 relatively high $\delta^{15}N(NO_3^-)$ values in the spring of 2005 (SP-1: (5.3 ± 3.3) ‰; SP-2 (6.4 ± 2.1) ‰) indicate some post-depositional loss of snowpack nitrate at that time. Since post-depositional loss is driven by photolysis (Berhanu et al., 2014; Frey et al., 2009), the observed high $\delta^{15}N(NO_3^-)$ values suggest active snow nitrate photolysis during spring 2005. This is qualitatively consistent with the observations at Summit by Hastings et al. (2004) that $\delta^{15}N(NO_3^-)$ in surface snow is significantly higher in daytime when snow nitrate photolysis is active compared to during the nighttime.

4.2.3. Enhanced conversion of NO_x to nitrate

Field observations suggest that in present day, there is probably sufficient NO_x at Summit to ensure local nitrate production even in the spring. 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). In addition, Kramer et al. (2014) reported that February NO_x concentration at Summit is $(1.6 \pm 3.2) \times 10^8$ cm^{-3} which overlaps with summer values due to the large uncertainty. Kramer et al. (2014) also suggested that pollution transport during polar winters leads to accumulation of NO_y as well as NO_x in the Arctic, and implied that part of the NO_y will be converted to NO_x after polar sunrise through photolysis. Under sufficient local NO_y and NO_x abundances in the industrial era, an increase in nitrate concentration would be expected if the oxidation rate of NO_x to HNO_3 is also enhanced. The NO_x 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_2 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:

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

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

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:

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

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

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.

Using temperature and relative humidity data at Summit from the Greenland Climate Network Data (GCND, http://cires.colorado.edu/science/groups/steffen/gcnet/order/admin/station.php), we estimate that the spring (February and March average) atmospheric water vapor mixing ratio in 2005 was 40 % higher than that in 2006 due to high temperatures in the 2005 spring (-30 ℃) relative to the 2006 spring (-34 ℃). 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 full magnitude of 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 in 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 of the additional 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 (Alexander et al., 2009), 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). Some model studies suggested that at Summit photolysis of snow-sourced CH_2O, H_2O_2 and HONO contributes to OH 2-3 times more than that from O_3 photolysis [e.g.,(Yang et al., 2002)] while the others seem to have different results [e.g., (Chen et al., 2007)]. Although the photolysis of these species are more sensitive to UV-A radiation (Grannas et al., 2007), the production/emission of HONO and CH_2O from the snowpack are influenced by snow nitrate photolysis (Thomas et al., 2012) which is sensitive to UV-B radiation. In addition, a recent model study by Thomas et al. (2012) suggested that at Summit, snow-sourced NO_x lead to as much OH production as that from ozone photolysis via shifting the local OH/HO_2 ratio in favor of OH, with additional 10-18% contribution from snowpack bromine chemistry. These processes are also sensitive to UV-B radiation. These model studies suggested that snow photochemistry is more important than ozone photolysis for OH production at Summit (Thomas et al., 2012; Yang et al., 2002). It is thus 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 enhanced snow photochemistry and tropospheric O_3 photolysis, even without considering the effect of elevated water vapor mixing ratio due to the temperature increase (around 3 ℃, but this will enhance the emissions of H_2O_2, CH_2O from snow (Grannas et al., 2007)).

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 snowpack photochemistry involving NO_x, halogens, HONO, CH_2O, and H_2O_2. Increased NO_x abundance from the photolysis of snowpack nitrate and/or other NO_x precursors that accumulated during the polar winter also contributes (Kramer et al., 2014).

4.3. Further examination with additional snow and ice core data

Hastings et al. (2004) reported seasonal variations in concentrations, δ^{18}O and δ^{15}N of snow nitrate at Summit covering the years of 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) ‰). 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, each suggesting enhanced local photochemistry as a contributor to the observed spring nitrate peaks. 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 in 2000 is caused by a weakened stratospheric ozone layer, consistent with the observations in the spring of 2005.

We further examined the 19 years with double nitrate peaks found in the firn core. In order to assess the effect of long-range transport of nitrate on the occurrence of the double nitrate peaks, we compared the nitrate and sulfate records. This comparison indicates that in most (14 out of 19) years, the secondary (earlier and smaller) peak is accompanied by a sulfate peak. This suggests that direct transport of nitrate from polluted regions is likely responsible for the occurrence of the double nitrate peaks in these years. However, there are five years, including 2000 and 2005, in which the secondary peak does not appear with a rise in sulfate concentration. To determine if enhanced local photochemistry could be responsible for the occurrence of the double nitrate peaks in these years, we examined 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., (Holton et al., 1995; 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 40-80 °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, there are 12 years with double nitrate peaks and five of them are years with O_3 column density well below the average for that period. In other years, one of the double peaks is accompanied by a sulfate peak. The results from the firn core, combined with that from the snowpit, thus suggest that there are two mechanisms leading to occurrence of double nitrate peaks, 1) direct transport of nitrate from polluted regions, and 2) enhanced local photochemical production of nitrate. The second mechanism requires local sources of NO_x. Possible local NO_x sources at Summit include PAN decomposition and the photolysis of snowpack nitrate, as well as photolysis of other winter accumulated NO_y species in the atmosphere (Kramer et al., 2014). For example, a model study (Stroud et al., 2003) 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. These NO_x precursors accumulate in the polar winter through a combination of pollution transport from the mid-latitudes and lack of sunlight, and contribute to springtime NO_x abundance through photochemical decomposition after polar sunrise (Kramer et al., 2014). This is consistent with the observation that there are no double nitrate peaks observed prior to the 1950s as dramatic increases in anthropogenic emissions of NO_x did not occur until 1950 (Lamarque et al., 2010).

5. Conclusion

Spring nitrate peaks have been observed in Greenland ice core records beginning 1900 and was hypothesized to originate from pollution transport from the mid-latitudes in the industrial era (Burkhart et al., 2006; Whitlow et al., 1992; Yang et al., 1995). But the specific mechanism leading to the additional peak is unclear as it could be from direct transport of nitrate or transport of NO_x precursors followed by enhanced local photochemistry. Here we report observations of nitrate concentrations and isotopes in a snowpit from Summit, Greenland. After identifying a spring nitrate peak in the year of 2005, we performed a case study regarding its origin. The isotopic composition of nitrate in the snowpit, combined with photochemical calculations, suggests the presence of the 2005 spring nitrate peak was caused by enhanced local nitrate production, instead of long range pollution transport. 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. Elevated UV-B radiation at the surface was the result of a significant reduction of the stratospheric ozone layer in the Arctic in spring 2005. Increased local NO_x concentrations 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 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.

Further examination on a firn core indicates that in most years direct transport of nitrate from polluted regions is likely responsible for the additional nitrate peak. This, combined with the snowpit results, suggests that there are two mechanisms for the occurrence of the additional annual nitrate peak in the industrial era, 1) direct transport of nitrate from polluted regions, and 2) enhanced local photochemical production of nitrate. We note that both of these mechanisms are related to pollution transport, as the additional nitrate from either direct transport or enhanced local photochemistry requires enhanced nitrogen sources from anthropogenic emissions.

6. Acknowledgments

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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 years with double nitrate peaks 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). 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 (40-80 °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 ± 50 (1σ) 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 and green indicate years with double nitrate peaks, while the green symbols indicate one of the double nitrate peaks is accompanied with a sulfate peak.

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.

		δ^{15}N (‰)	δ^{17}O (‰)	δ^{18}O (‰)	Δ^{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 (1σ);
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 ± 1σ (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 years with double nitrate peaks 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

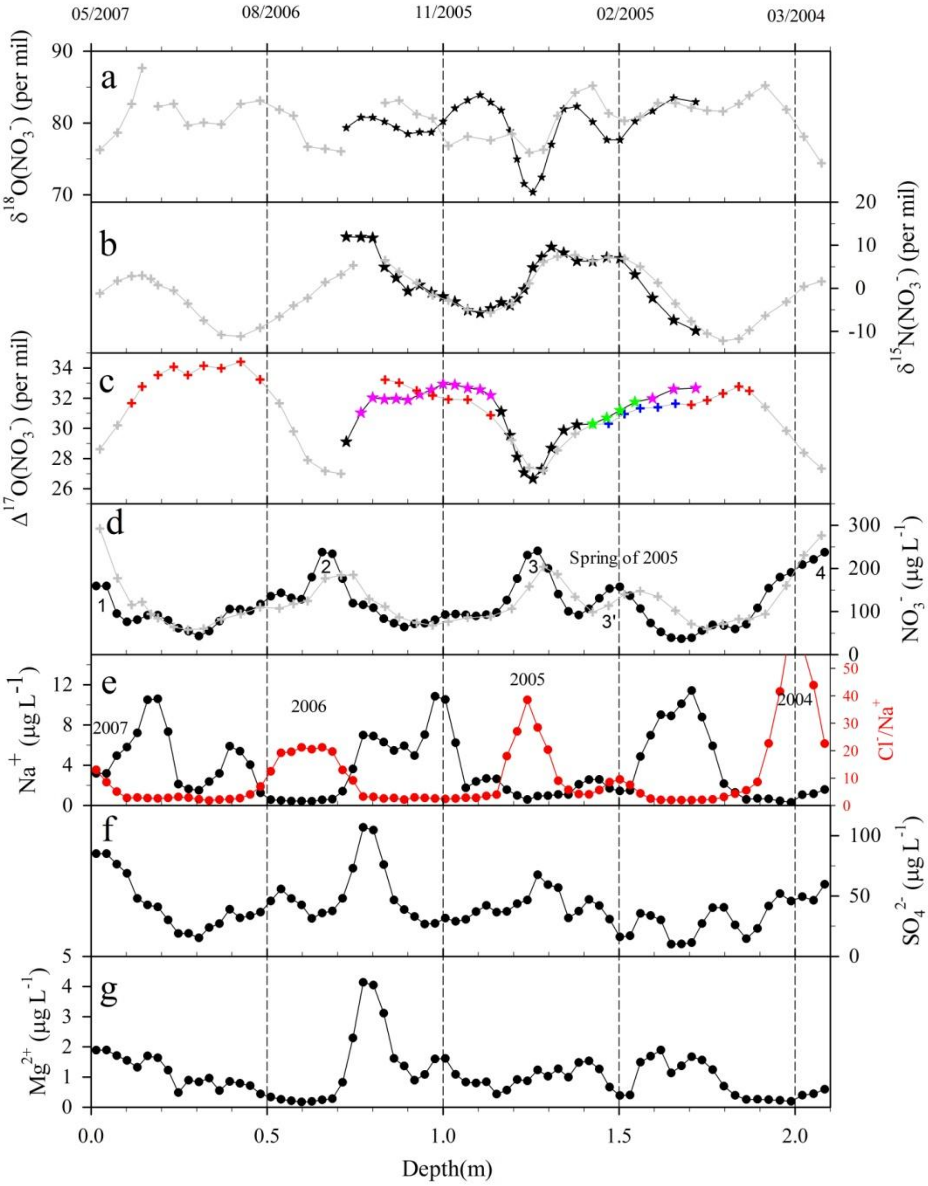

Figure 1. $\delta^{18}O(NO_3^-)$ (a), $\delta^{15}N(NO_3^-)$ (b), $\Delta^{17}O(NO_3^-)$ (c) and concentrations of NO_3^- (d), Na^+ (e), SO_4^{2-} (f) and Mg^{2+} (g) in the snow samples (data are 3-point running averages). SP-1 data were plotted in gray with plus signs; SP-2 and SB data were plotted 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.

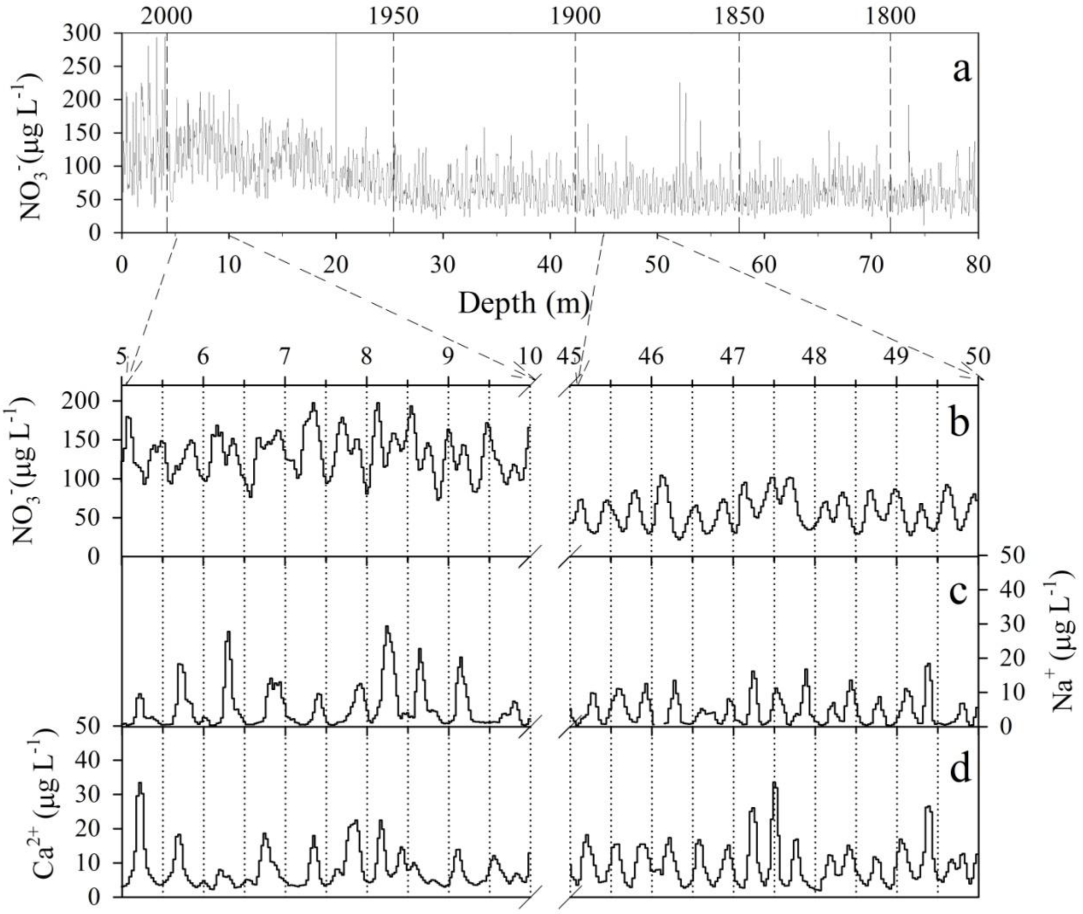

Figure 2. (a) Nitrate concentration record from the shallow ice core; (b), (c), (d) show seasonal peaks of NO_3^- , Na^+ and Ca^{2+}, respectively in two sections of the ice core (data shown in b, c and d are 3-point running averages). Vertical dashed lines in (a) indicate the years of snowfall at relevant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

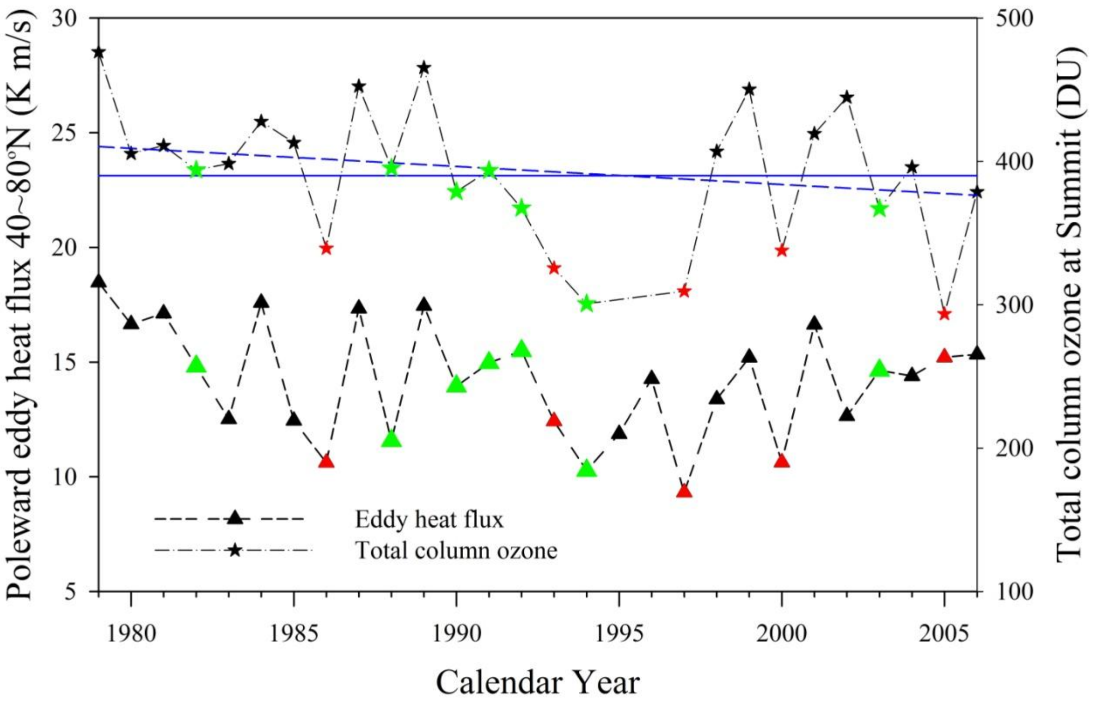

Figure 3. Summit springtime O_3 column density (February and March averages) and poleward eddy heat flux in the lower stratosphere (40-80 °N, January and February averages) from 1979 to 2006. The solid blue line is the average of springtime O_3 column density from 1979 to 2006 (390 ± 50 (1σ) DU), and 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 and green indicate years with double nitrate peaks, while the green symbols indicate one of the double nitrate peaks is accompanied with a sulfate peak.