

Dear Dr. Kaiser,

Please find our revised manuscript, "On the origin of the occasional spring nitrate peak in Greenland snow" by Geng et al.

In this revision, we have corrected all the parts pointed by the reviewer. In particular, we deleted the "Tilde" signs in Page 8, 32 and 33, and added the uncertainty for the snow accumulation at Summit in Page 8 ($233 \pm 38 (1\sigma)$ kg/m²/a during 2000-2006). We have replaced the symbol of "yr" with "a" as suggested by the reviewer. In addition, we corrected some typos we find we proofread the manuscript. For example, in Page 24, L16, we deleted the redundant word "nitrate".

In the rest of this file, we attached the "change-tracked" version of the manuscript, and we also upload a new version of the manuscript.

We are grateful to the editor and all the reviewers for the helpful suggestions and comments during the reviewing process.

Sincerely,
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1 **On the origin of the occasional spring nitrate peak in Greenland snow**

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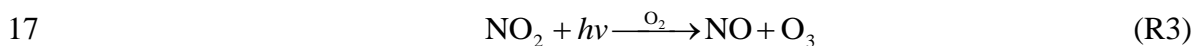
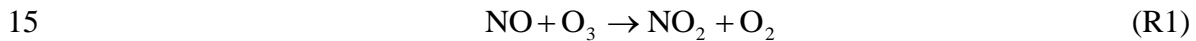
Abstract

1
2 Ice-core nitrate concentrations peak in the summer in both Greenland and
3 Antarctica. Two nitrate concentration peaks in one annual layer have been observed in
4 some years in ice cores in Greenland from samples dating post-1900, with the
5 additional nitrate peak occurring in the spring. The origin of the spring nitrate peak
6 was hypothesized to be pollution transport from the mid-latitudes in the industrial era.
7 We perform a case study on the origin of a spring nitrate peak in 2005 measured from
8 a snowpit at Summit, Greenland covering three years of snow accumulation. The
9 effect of long-range transport of nitrate on this spring peak is excluded by using
10 sulfate as a pollution tracer. The isotopic composition of nitrate ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$)
11 combined with photochemical calculations suggest that the occurrence of this spring
12 peak is linked to a significantly weakened stratospheric ozone (O_3) layer. The
13 weakened O_3 layer resulted in elevated UV-B (Ultraviolet B) radiation on the snow
14 surface, where the production of OH and NO_x from the photolysis of their precursors
15 was enhanced. Elevated NO_x and OH concentrations resulted in enhanced nitrate
16 production mainly through the $\text{NO}_2 + \text{OH}$ formation pathway, as indicated by
17 decreases in $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of nitrate associated with the spring peak. We further
18 examined the nitrate concentration record from a shallow ice core covering the period
19 from 1772 to 2006 and found 19 years with double nitrate peaks after the 1950s. Out
20 of these 19 years, 14 of the secondary nitrate peaks are accompanied by sulfate peaks,
21 suggesting long-range transport of nitrate as their source. In the other five years low
22 springtime O_3 column density is observed, suggesting enhanced local production of
23 nitrate as their source. The results suggest that, in addition to direct transport of nitrate
24 from polluted regions, enhanced local photochemistry can also lead to a spring nitrate

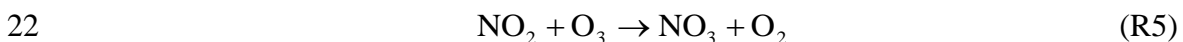
1 peak. The enhanced local photochemistry is probably associated with the interannual
2 variability of O₃ column density in the Arctic which leads to elevated surface UV
3 radiation in some years. In this scenario, enhanced photochemistry causes increased
4 local nitrate production under the condition of elevated local NO_x abundance in the
5 industrial era.

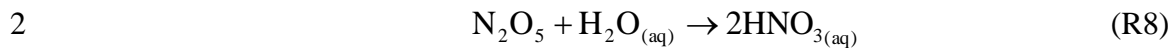
6 **1. Introduction**

7 Knowledge of the abundance and variability of reactive nitrogen oxides (NO_x =
8 NO + NO₂) is valuable because of the critical role that NO_x plays in determining the
9 oxidative capacity of the atmosphere. The oxidative capacity of the atmosphere is
10 determined by the tropospheric abundance of hydrogen oxide radicals (HO_x = OH +
11 HO₂) and O₃ and largely controls the residence times of pollutants (e.g., CO) and
12 greenhouse gases (e.g., CH₄). NO_x is emitted from a variety of sources including
13 fossil fuel combustion, biomass burning, soil emissions, and lightning (Logan, 1983).
14 In the atmosphere, NO_x cycle rapidly between NO and NO₂ according to:



18 The main sink of NO_x is thought to be atmospheric oxidation to nitrate which
19 distributes between the gas- and particulate phases. In general, the formation of nitrate
20 involves reactions of NO_x with OH and O₃:





3 Reactive halogen species (e.g., BrO) may also play a role in NO_x cycling and
4 nitrate formation, especially in the Arctic (Morin et al., 2007). R4 mainly occurs
5 during daytime, as the result of diurnal variations in OH concentrations. The
6 conversion to nitrate via O₃ (R5-R8) is negligible during the day, since the NO₃
7 radical is rapidly photolyzed back to NO_x in sunlight. Globally, oxidation of NO_x by
8 OH (R4) is thought to be the dominant nitrate formation pathway on an annual basis
9 (Alexander et al., 2009). Once formed, nitrate is removed from the atmosphere mainly
10 through wet and dry deposition to the surface. Efforts have been made to use ice core
11 nitrate records to assess information about past changes in the global NO_x
12 environment (Fischer et al., 1998; Mayewski et al., 1990), and potentially about the
13 past variations in the atmospheric oxidation capacity (Alexander et al., 2004).
14 However, nitrate concentration in polar snow is also influenced by variations in snow
15 accumulation rate and by post-depositional processes such as evaporation and
16 photolysis (Röthlisberger et al., 2002) of nitrate in near-surface snow. Post-
17 depositional processing of snowpack nitrate has hampered the interpretation of ice
18 core nitrate records in terms of assessing past atmospheric NO_x variability.

19 Examination of detailed chronological nitrate records in snowpits and ice cores
20 may provide clues on the primary factor(s) controlling nitrate concentration and its
21 temporal variability in snow. For example, a clear seasonal pattern in nitrate
22 concentration may be linked to a source with an annual cycle and/or modulated by
23 seasonally varying atmospheric conditions. Many previous studies of snow samples
24 and ice cores from central Greenland have found that nitrate concentration reaches a

1 maximum in summer snow and a minimum in winter snow (Davidson et al., 1989;
2 Finkel and Langway, 1986; Whitlow et al., 1992). This seasonal variation in nitrate
3 concentration in general is due to the active photochemical reactions during polar
4 summer (Yang et al., 1995), when peroxyacetyl nitrate (PAN), snowpack nitrate and
5 other NO_x reservoir species act as local NO_x sources through recycling reactions
6 (Moxim et al., 1996; Thomas et al., 2012). A few investigators (Burkhart et al., 2006;
7 Yang et al., 1995; Whitlow et al., 1992) noticed that a single nitrate peak appears
8 annually in summer snow/ice layer deposited prior to 1900, whereas two nitrate peaks
9 are seen in some post-1900 annual layers. Although it seems the timing of the
10 additional nitrate peak differs as observed in ice cores from different locations
11 (Burkhart et al., 2006), Yang et al. (1995) stated that at Summit the additional peak
12 occurs in late winter/early spring, which is consistent with the dating in Burkhart et al.
13 (2006).

14 The occurrence of this occasional spring nitrate peak has been hypothesized to be
15 associated with pollution transport from the mid-latitudes (Burkhart et al., 2006; Yang
16 et al., 1995), though this hypothesis and the occasional nature of the spring nitrate
17 peak were not carefully examined. Anthropogenic NO_x emissions from fossil fuel
18 combustion have increased the concentration_s of atmospheric NO_x and other nitrogen
19 species (e.g., HNO₃) in the northern hemisphere since 1900, especially in the last 50
20 years (Galloway et al., 2003). A corresponding increase in nitrate concentrations in
21 Greenland ice cores has been documented (Mayewski et al., 1990). Direct transport of
22 NO_x from the mid-latitudes to the Arctic is unlikely given the short lifetime of NO_x
23 (1-3 days (Levy et al., 1999)). Alternatively, long range transport of nitrate and NO_x
24 precursors (e.g., PAN) from anthropogenic NO_x source regions could lead to increases

1 in Greenland snow nitrate concentrations. However, the relative importance of nitrate
2 and NO_x precursors to Greenland snow nitrate is unclear. An earlier study suggested a
3 significant contribution from PAN (e.g., (Ford et al., 2002)), whereas a recent study
4 (Geng et al., 2014) suggests that transport to Greenland occurs mainly in the form of
5 gaseous HNO₃. In addition to PAN decomposition as a potential local source of NO_x,
6 the photolysis of nitrate in snowpack produces NO_x, which is quickly transported to
7 the overlying atmosphere by diffusion and wind pumping (Zatko et al., 2013). This is
8 consistent with the elevated NO_x concentrations observed in the ice sheets during
9 polar summers (Honrath et al., 1999). In particular, a model study (Thomas et al.,
10 2012) suggested that at Summit, NO_x produced from snow nitrate photolysis in
11 summer can account for all of the observed NO_x concentrations in the overlying
12 atmosphere. In addition, Kramer et al. (2014) implied that, after polar sunrise,
13 atmospheric NO_y (odd nitrogen species other than PAN and NO_x) can release NO_x
14 through photochemistry. In summary, there are two ways that pollution transport can
15 influence the springtime nitrate budget at Summit, 1) direct transport of nitrate, and 2)
16 transport of NO_x precursors. In order to cause a spring nitrate peak, the latter requires
17 local conditions favoring NO_x release from its precursors and its subsequent
18 conversion to nitrate.

19 The isotopic composition of nitrate can provide valuable information not
20 available from concentration measurement alone, for example, regarding the
21 pathways of NO_x conversion to nitrate in the atmosphere (Michalski et al., 2003).
22 Stable isotope ratios in nitrate are expressed as $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, where $\Delta^{17}\text{O} =$
23 $\delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ and $\delta = R_{\text{sample}}/R_{\text{reference}} - 1$ with R denoting the $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$
24 and $^{17}\text{O}/^{16}\text{O}$ isotope ratios. The references are N₂-AIR and VSMOW for N and O,

1 respectively. $\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$ of nitrate (hereafter denoted as $\delta^{15}\text{N}(\text{NO}_3^-)$ and
2 $\Delta^{17}\text{O}(\text{NO}_3^-)$, respectively) have been used to investigate the origin and fate of NO_x in
3 the Arctic troposphere (Morin et al., 2008). In particular, $\Delta^{17}\text{O}(\text{NO}_3^-)$ is related to
4 oxidizing conditions and nitrate formation pathways (R4 vs. R5-R8) in the
5 atmosphere (Alexander et al., 2004; Alexander et al., 2009; Kunasek et al., 2008;
6 Michalski et al., 2003; Morin et al., 2011). For example, Michalski et al. (2003) found
7 that nitrate formed during nighttime (i.e., via R5-R8) has higher $\Delta^{17}\text{O}$ than nitrate
8 formed during daytime (via R4) because of the high $\Delta^{17}\text{O}$ of the dominant nighttime
9 oxidant O_3 (Johnson et al., 2000; Lyons, 2001) which is transferred to nitrate. The
10 $\Delta^{17}\text{O}(\text{NO}_3^-)$ in Greenland snow also reflects the seasonality of nitrate production, with
11 O_3 oxidation (R1, R5) being more important in winter than in summer (Kunasek et al.,
12 2008).

13 After atmospheric nitrate is deposited to the snow, UV photolysis will convert
14 snow nitrate back to NO_x , which is then released to the atmosphere (Honrath et al.,
15 1999; Thomas et al., 2012; Zatko et al., 2013). This snow-sourced NO_x will be re-
16 oxidized in the atmosphere to nitrate, which is subsequently re-deposited to surface
17 snow or transported away. Reformation of nitrate in the condensed phase of snow
18 grains can also occur if the nitrate being photolyzed is trapped inside the snow grain
19 instead of on the surface (Meusinger et al., 2014). This is the so-called post-
20 depositional processing of snow nitrate, which includes the steps of photolysis,
21 recombination of photoproducts in the condensed phase and in the overlying
22 atmosphere (i.e., recycling), and the re-deposition and/or export of snow-sourced
23 nitrate. Post-depositional processing induces isotopic effects (Frey et al., 2009). In
24 general, the photolysis of nitrate will enrich $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate remaining in

1 snow, but will not alter $\Delta^{17}\text{O}$ as photolysis induces mass-dependent fractionation. If
2 the photolytic products of nitrate are re-oxidized and re-deposited to the snow surface
3 (i.e., no export/no net loss), no measurable effect on $\delta^{15}\text{N}(\text{NO}_3^-)$ will be observed
4 assuming negligible nitrogen isotopic fractionation during the re-formation of nitrate.
5 However, changes in $\delta^{18}\text{O}(\text{NO}_3^-)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ are expected even without net loss
6 of nitrate. The reformation of nitrate in the condensed phase of snow grains will cause
7 oxygen isotope exchange with water (Frey et al., 2009), which lowers $\delta^{18}\text{O}(\text{NO}_3^-)$ and
8 $\Delta^{17}\text{O}(\text{NO}_3^-)$. In addition, the re-oxidation of the snow-sourced NO_x to nitrate in the
9 overlying atmosphere will occur mainly through the OH formation pathway. This is
10 because active snow nitrate photolysis requires strong radiation, which is also when
11 atmospheric nitrate is mainly formed through the daytime reaction channel ($\text{NO}_x +$
12 OH). Recycling of snow-sourced NO_x in the atmosphere will thus likely lower
13 $\delta^{18}\text{O}(\text{NO}_3^-)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$, particularly if the initially deposited nitrate was formed
14 through the O_3 oxidation pathway (e.g., formed in polar winters when $\delta^{18}\text{O}(\text{NO}_3^-)$ and
15 $\Delta^{17}\text{O}(\text{NO}_3^-)$ values are the highest (Alexander et al., 2009; Kunasek et al., 2008)). The
16 deposition of this reformed nitrate will then lower the bulk snow $\delta^{18}\text{O}(\text{NO}_3^-)$ and
17 $\Delta^{17}\text{O}(\text{NO}_3^-)$. At sites with snow accumulation rates greater than $100 \text{ kg/m}^2/\text{yfa}$, the
18 oxygen isotope exchange in the condensed phase is minimal (Erbland et al., 2013).
19 This is consistent with the discussion in Fibiger et al. (2013) that the condensed phase
20 process can't explain the observed relationship between $\delta^{18}\text{O}(\text{NO}_3^-)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ in
21 surface snow, given the high snow accumulation rate at Summit (~~$-260233 \pm 38 (1\sigma)$~~
22 $\text{kg/m}^2/\text{yfa}$, during 2000-2006 (Cole-Dai et al., 2013)). However, the Fibiger et al.
23 (2013) analysis neglected atmospheric process, i.e., the reformation of nitrate from
24 snow-sourced NO_x in the atmosphere and its subsequent deposition to surface snow.

1 This process alters $\delta^{18}\text{O}(\text{NO}_3^-)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ simultaneously and can explain the
2 relationship between $\delta^{18}\text{O}(\text{NO}_3^-)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ in surface snow observed by Fibiger
3 et al. (2013). In addition, Fibiger et al. (2013) suggested that there is little to no post-
4 depositional loss of nitrate at Summit, which might be true. But post-depositional loss
5 is only one (possible) step of the post-depositional processing. Post-depositional
6 processing of snow nitrate at Summit could be very active while little post-
7 depositional loss occurs, given a fast recycling rate of nitrate in the air-snow interface.

8 In this study, the concentrations of major ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- ,
9 NO_3^- , and SO_4^{2-}), and the isotopic composition of nitrate in a snowpit from central
10 Greenland were measured. The concentration data were used to establish their
11 temporal patterns and to identify any spring nitrate peak(s). The isotopic data were
12 used to assess the chemistry of nitrate in any identified spring peaks and to discern the
13 origin of the peak. Further examinations were conducted on a shallow ice core to
14 determine whether the mechanism leading to the spring nitrate peak observed in the
15 snowpit is representative of the occasional nature of the spring nitrate peaks observed
16 in Greenland snow since 1900.

17 **2. Methods**

18 **2.1. Snowpit and ice core sample collection**

19 In July 2007, six snow blocks (dimensions: 0.35 m long \times 0.25 m wide \times 0.35 m
20 deep) were excavated from the surface down to a depth of 2.10 m at Summit,
21 Greenland (72.5 °N, 38.5 °W; elevation: 3200 m). These snow blocks were wrapped
22 with clean polyester film with their dimensions labeled and stored in a hard-shell box
23 to avoid external compaction during delivery. Several ice cores including a 79 meter
24 shallow core were drilled approximately 100 meters from the location of the snow

1 blocks. These snow blocks and the ice cores were shipped frozen to the laboratory at
2 South Dakota State University (SDSU) and stored in a freezer at -20 °C until analysis.
3 At the same time, a set of snowpit samples were also collected in the field every 5 cm
4 from the surface down to the depth of 2.10 m, at the same location of the collected
5 snow blocks. This set of snowpit samples (referred to as SP-1) were double sealed in
6 clean plastic bags and shipped frozen to Laboratoire de Glaciologie et Géophysique
7 de l'Environnement (LGGE) for nitrate concentration and isotope analysis. All
8 tools/containers directly touching the snowpit samples and/or the snow blocks were
9 pre-cleaned with 18 MΩ water before use.

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

15 **2.2. Chemical and isotope analysis**

16 At SDSU, another set of snow samples (referred to as SP-2) in a vertical sequence
17 was chiseled out from the snow blocks, after the removal of a surface layer of at least
18 1 cm in thickness, and collected in clean plastic sample containers. All tools and
19 sample containers were pre-cleaned with 18 MΩ water prior to use, and clean
20 disposable plastic gloves were always worn during sample handling. In total, 71
21 samples with a depth resolution of 3 cm were obtained. These samples were allowed
22 to melt at room temperature and the meltwater samples were then analyzed by ion
23 chromatography for concentrations of major ions in snow (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} ,
24 Cl^- , NO_3^- , and SO_4^{2-}). The ion chromatography instrumentation and methodology are

1 similar to that described by Cole-Dai et al. (2006). Ice blanks were made from
2 deionized water, processed and analyzed following the same procedure as that for the
3 snow samples. High blank values of Ca^{2+} (up to $5 \mu\text{g L}^{-1}$) indicated that the snowpit
4 samples were probably contaminated with Ca^{2+} during sample preparation. No
5 evidence of contamination was found for the other ions. Therefore, the snowpit Ca^{2+}
6 data were not used in interpretation in this study. The 79 meter shallow core was
7 analyzed for the ionic species using the technique of continuous flow analysis with
8 ion chromatography (CFA-IC) detection (Cole-Dai et al., 2006). One advantage of the
9 CFA-IC technique is that it minimizes the potential contamination by eliminating
10 sample preparation. Replicate analysis of blanks with CFA-IC showed no
11 contamination of any of the ions including Ca^{2+} .

12 The concentration measurements of the SP-2 samples described above were used
13 to estimate the volume of meltwater needed to provide sufficient nitrate mass (500
14 nmoles, allowing for replicate measurements) for isotopic analysis. Based on that
15 estimate, the snow blocks were carved vertically to yield large samples for isotope
16 measurement. A total of 29 clean snow samples (referred to as SB) were obtained
17 from the depth interval of 0.70 m to 1.75 m of the snow blocks (snow outside this
18 depth interval had been consumed for other purposes). The depth resolution of these
19 samples varies from 2 cm to 6 cm because the concentration of nitrate is different at
20 different depths. These samples were melted at room temperature and concentrated,
21 following the method described by Frey et al. (2009), to 10 mL solutions, collected in
22 HDPE bottles, and stored frozen until isotopic analysis. Measurements of N and O
23 isotope ratios in nitrate of the SB samples were performed in the stable isotope
24 laboratory at University of Washington (UW) using the bacterial denitrifier method

1 (Kaiser et al., 2007). Briefly, nitrate in the samples was first converted into N₂O gas
2 by the bacteria *Pseudomonas aureofaciens*; the N₂O was carried on-line by helium
3 gas into a heated gold tube where it was thermally decomposed to N₂ and O₂. These
4 were then separated by gas chromatography and the isotopic ratio(s) of each gas
5 (¹⁵N/¹⁴N for N₂, and ¹⁸O/¹⁶O and ¹⁷O/¹⁶O for O₂) was measured with an isotope ratio
6 mass spectrometer. The δ¹⁵N values were calculated with respect to N₂-Air and
7 calibrated against the two international reference materials IAEA-NO-3 (δ¹⁵N = 4.7
8 ‰) and USGS34 (δ¹⁵N = -1.8 ‰) (Kaiser et al., 2007). The δ¹⁷O and δ¹⁸O values
9 were calculated with respect to VSMOW and calibrated against the two international
10 reference materials USGS34 (δ¹⁷O = -14.5 ‰, δ¹⁸O = -27.9 ‰) and USGS35 (δ¹⁷O
11 = 51.3 ‰, δ¹⁸O = 57.5 ‰) (Kaiser et al., 2007). The Δ¹⁷O values were then calculated
12 by using the linear equation Δ¹⁷O = δ¹⁷O - 0.52 × δ¹⁸O. No replicate samples were
13 possible due to the limited amount of snow available in the snow blocks, and no
14 seasonally resolved isotopic measurements of the ice core samples were performed
15 because of the limited amount of ice available. The analytical uncertainty of
16 Δ¹⁷O(NO₃⁻) and δ¹⁸O(NO₃⁻) measured at the UW laboratory was estimated to be 0.1
17 ‰ and 0.5 ‰ (1σ), and that of δ¹⁵N was 1.0 ‰ (1σ), based on repeated measurements
18 of the oxygen and nitrogen isotope ratios in the international reference materials
19 USGS35 and IAEA-NO-3, respectively (Table 1 for details).

20 The SP-1 samples at LGGE were measured for nitrate concentration and
21 isotopic composition (δ¹⁵N, δ¹⁸O and Δ¹⁷O). A small portion of each sample was
22 taken for nitrate concentration measurement using the well-established Griess method
23 in continuous flow analysis (Seal Analytical, Method No 1000223-1784-09). The rest
24 of samples were processed following the similar procedure described above and the N

1 and O isotope ratios were determined by the bacterial denitrifier method.
2 Instrumentation details at the LGGE laboratory are similar to that described in
3 Erbland et al. (2013). International reference materials (USGS34, USGS35 and
4 IAEA-NO-3) were used for data reduction. The uncertainties of $\Delta^{17}\text{O}(\text{NO}_3^-)$,
5 $\delta^{18}\text{O}(\text{NO}_3^-)$ and $\delta^{15}\text{N}(\text{NO}_3^-)$ measured at the LGGE laboratory were 0.3 ‰, 2.0 ‰ and
6 0.3 ‰, respectively, estimated as the reduced standard deviation of the residuals from
7 the linear regression between the measured reference materials and their accepted
8 values.

9 **3. Results**

10 **3.1. Dating and identifying spring nitrate peak(s)**

11 The concentration data from the SP-1 and SP-2 samples, and the isotopic data
12 from the SP-1 and SB samples, were plotted as a function of depth in Figure 1 (data
13 are available in Supplemental Material). The concentration profiles of nitrate from
14 SP-1 and SP-2 are nearly identical and each displays five peaks approximately at the
15 same depths (labeled 1, 2, 3, 3' and 4 in Figure 1d). We used the sodium (Na^+) peak
16 as a winter snow layer indicator and the peak of the Cl^-/Na^+ ratio as a summer snow
17 layer indicator (Whitlow et al., 1992). Sodium concentration in Greenland snow peaks
18 in winter/late winter due to winter Arctic aerosols (with high sea salt content) and/or
19 late winter cyclonic storms, while Cl^-/Na^+ peaks in summer likely due to long range
20 transport of aged sea salt aerosols (Whitlow et al., 1992) which is depleted in Na^+
21 because of the preferential removal of Na^+ in aerosols relative to gaseous HCl
22 following sea salt-acid displacement (Legrand and Delmas, 1988). Since the snowpit
23 and snow blocks were excavated in July of 2007, the partial peak of Cl^-/Na^+ at the
24 surface identifies the summer of 2007. The other Cl^-/Na^+ peaks represent the summer

1 of 2006, 2005 and 2004, respectively (Figure 1e) The nitrate peaks 1, 2, 3 and 4 are in
2 almost identical layers as the Cl^-/Na^+ peaks, providing independent evidence that they
3 can be considered summer peaks. Nitrate Peak 3' is between a winter Na^+ peak and a
4 summer Cl^-/Na^+ peak, clearly identifying it as a spring peak. This dating by Cl^-/Na^+
5 and Na^+ peaks (referred to here as Method A) is consistent with the results of weekly
6 recorded snow accumulation data determined by stake height measurements at
7 Summit (data are available at
8 ftp://ftp.summitcamp.org/pub/data/GEOSummit/Bales_UCM/Bamboo%20Forest/Bamboo%20Forest%20Accumulation%20Log.xls) (referred to here as Method B). The
9 approximate months of snowfall at depths of 0, 0.5, 1.0, 1.5 and 2.0 m identified by
10 Method B were indicated with vertical dashed lines of Figure 1. According to Method
11 B, snow in the layer of the Peak 3' fell in February of 2005, suggesting it is a early
12 spring peak, consistent with previous studies that the additional annual nitrate peak
13 occurs in late winter/early spring (Burkhart et al., 2006; Yang et al., 1995). Some
14 small discrepancies exist between the two dating methods. For example, the month of
15 snowfall at the surface was identified as May of 2007 using Method B instead of July.
16 This discrepancy is due to negligible snowfall (around 2 cm) from May to July 2007.
17 The month of snowfall at the depth of 2 m was identified as March of 2004 using
18 Method B, suggesting that Peak 4 is also a spring peak. However, according to the
19 snow accumulation data, there was only about 3 cm of snow accumulation from
20 March to June of 2004 (Supplemental Figure 1). Negligible snowfall during this time
21 resulted in nitrate produced in summer dry depositing to the prior spring snow layers,
22 making it appear as if the peak occurs in spring using Method B. In addition, the
23 nitrate profiles in SP-1 and SP-2 are slightly different (i.e., nitrate peaks are not
24

1 exactly at the same depths), which is likely due to the spatial variability of snow
2 accumulation rates in the field due to snow drifting. But the overall temporal patterns
3 of the nitrate profiles in SP-1 and SP-2 are similar, suggesting there was negligible
4 disturbance of the stratigraphy of the snow blocks during delivery and storage.

5 The record of nitrate concentrations from the shallow ice core is shown in Figure
6 2 (data are available in Supplemental Material). The annual layer dating of this core
7 was performed by counting the annual spring peak of calcium (Cole-Dai et al., 2013).
8 From this ice core, we found there are nineteen years with two nitrate peaks in the
9 period of 1960 to 2006, obtained by subtracting total calcium peaks from total nitrate
10 peaks in this period (Figure 2). We don't attempt to specifically identify the
11 seasonality of these peaks due to the lack of a reliable summer layer indicator in the
12 firn core. The Cl^-/Na^+ ratio is influenced by atmospheric acidity (details in
13 Supplemental Material). In the preindustrial period, atmospheric acidity peaks in
14 summer due to high summer production of non-sea-salt sulfate and nitrate (Whitlow
15 et al., 1992). This leads to an enhancement in excess chloride in summer through
16 acid-sea salt displacement (Legrand and Delmas, 1988). Given the summer low Na^+
17 concentrations, the Cl^-/Na^+ peak falls almost precisely in summer in the preindustrial
18 period, making it a good summer layer indicator. However, in much of the industrial
19 era, the annual Cl^-/Na^+ peak shifts toward the major annual non-sea-salt sulfate peak
20 (usually in winter, Figure S2, top panel) inhibiting its ability to serve as a summer
21 layer indicator. This makes it difficult to unambiguously identify the secondary nitrate
22 peak in the years with double nitrate peaks as occurring in a specific season (e.g.,
23 spring), though we note that previous studies have been able to identify the secondary
24 nitrate peak as occurring in the spring by using summer layer indicators (e.g., H_2O_2 ,

1 and $\delta^{18}\text{O}(\text{H}_2\text{O})$) independent of major ion concentrations (Burkhart et al., 2006;
2 Whitlow et al., 1992; Yang et al., 1995). We note that, in the snowpit, sulfate
3 concentrations are as low as they were prior to 1900 (Geng et al., 2014), minimizing
4 its impact on the timing of the Cl^-/Na^+ peak. The frequency of years with double
5 nitrate peaks in each decade is listed in Table 2. Prior to 1960, only a single nitrate
6 peak is observed in each annual layer, consistent with the finding by Finkel and
7 Langway (1986) that the spring nitrate peak started appearing after the 1950s, though
8 others (Burkhart et al., 2006; Yang et al., 1995) stated in general that elevated spring
9 nitrate concentrations are seen in snow layers after around 1900.

10 **3.2. $\delta^{18}\text{O}(\text{NO}_3^-)$, $\delta^{15}\text{N}(\text{NO}_3^-)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ variations**

11 The $\delta^{18}\text{O}(\text{NO}_3^-)$, $\delta^{15}\text{N}(\text{NO}_3^-)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ data from the SP-1 and SB samples
12 are shown in Figure 1a, 1b and 1c, respectively. The depth range of the SP-1 samples
13 (0 to 2.10 m) corresponds to the period of the 2007 summer to 2004 summer, while
14 the depth range of the SB samples (0.7 to 1.75 m) corresponds to the time period of
15 the 2006 spring/summer to the 2004/2005 winter. In general, all three isotopic
16 signatures of nitrate display large seasonal variations. $\delta^{18}\text{O}(\text{NO}_3^-)$ is low in summer
17 and high in winter, while $\delta^{15}\text{N}(\text{NO}_3^-)$ is high in spring/early summer and low in
18 winter, consistent with previous measurements of Summit snow samples from
19 Hastings et al. (2004). In the spring of 2005 (the time period corresponding to the
20 depth of the spring nitrate peak), the means ($\pm 1\sigma$) of $\delta^{15}\text{N}(\text{NO}_3^-)$ from the SP-1 and
21 SB samples were $(5.3 \pm 3.3) \text{‰}$ and $(6.4 \pm 2.1) \text{‰}$, respectively, much higher than
22 winter values $(-9.2 \pm 3.3) \text{‰}$ from the SP-1 samples and $(-7.4 \pm 4.4) \text{‰}$ from the SB
23 samples. A local minimum in $\delta^{18}\text{O}(\text{NO}_3^-)$ was also observed from both the SP-1 and
24 the SB samples at the depth of the 2005 spring nitrate peak (Figure 1a).

1 The observed seasonality of $\Delta^{17}\text{O}(\text{NO}_3^-)$ (Figure 1c) is consistent with the
2 expectation of high $\Delta^{17}\text{O}(\text{NO}_3^-)$ during winter (polar night) due to the dominance of
3 the O_3 oxidation pathway of NO_x (R5-R8). The magnitude of the seasonality is also
4 consistent with the observations of $\Delta^{17}\text{O}(\text{NO}_3^-)$ at Summit by Kunasek et al.(2008).
5 The seasonality of $\Delta^{17}\text{O}(\text{NO}_3^-)$ is regulated by the shift of the dominant nitrate
6 formation pathway from OH oxidation (R4) in polar summer/day to that via O_3 (R5-
7 R8) in polar winter/night (low summer values and high winter values). Modeling by
8 Kunasek et al. (2008) showed that, in early spring, $\Delta^{17}\text{O}$ of locally produced nitrate at
9 Summit should be close to that in winter snow, as oxidation by OH (R4) is very
10 limited at this time due to the lack of sunlight. In other words, at Summit $\Delta^{17}\text{O}(\text{NO}_3^-)$
11 values in winter and early spring should be similar. However, in the early spring of
12 2005, the $\Delta^{17}\text{O}(\text{NO}_3^-)$ values display apparent declines from the prior winter values
13 (Figure 1c). To test whether the declines are significant, we calculate the mean
14 $\Delta^{17}\text{O}(\text{NO}_3^-)$ value in the early spring of 2005 and compare it to the mean of measured
15 winter $\Delta^{17}\text{O}(\text{NO}_3^-)$ values. The winter mean $\Delta^{17}\text{O}(\text{NO}_3^-)$ was calculated from the
16 2004/2005 to 2006/2007 winters from the SP-1 samples, and from the 2004/2005 to
17 2005/2006 winters for the SB samples (samples used to calculate the winter and 2005
18 early spring means are as marked in Figure 1c). The mean winter value was $(32.9 \pm$
19 $1.1) \text{‰}$ from the SP-1 samples and $(32.4 \pm 0.6) \text{‰}$ from the SB samples. In contrast,
20 the mean $\Delta^{17}\text{O}(\text{NO}_3^-)$ value in the early spring of 2005 was $(31.1 \pm 0.6) \text{‰}$ from SP-1
21 and $(30.8 \pm 0.8) \text{‰}$ from SB, approximately 1.7 ‰ lower than the winter means,
22 which is statistically significant based on one-tailed t-test (for SP-1 samples: $t =$
23 3.434 , $\text{DOF} = 24$, $P = 0.001$; for SB samples: $t = 4.637$, $\text{DOF} = 17$, $P \leq 0.0005$). A
24 previous study measuring $\Delta^{17}\text{O}(\text{NO}_3^-)$ in Summit snow by Kunasek et al. (2008) also

1 noted significantly low $\Delta^{17}\text{O}(\text{NO}_3^-)$ values (around 26 ‰) in the spring of 2005,
2 compared to the prior winter of $\Delta^{17}\text{O}(\text{NO}_3^-)$ around 33 ‰.

3 **4. Discussion**

4 The low $\Delta^{17}\text{O}(\text{NO}_3^-)$ values in the spring of 2005 suggest an increase in OH
5 oxidation in the formation of nitrate associated with the peak. This is qualitatively
6 consistent with the observed decrease in $\delta^{18}\text{O}(\text{NO}_3^-)$ from a previous study (Hastings
7 et al., 2004), as increases in the relative importance of OH oxidation will also result in
8 decreases in $\delta^{18}\text{O}(\text{NO}_3^-)$. The extra nitrate deposited during the spring of 2005 was
9 estimated to be $5.7 \text{ nmol} \times \text{cm}^{-2}$, which was calculated by subtracting the flux of
10 nitrate ($9.4 \text{ nmol} \times \text{cm}^{-2}$) in the spring of 2006 from the nitrate flux in the spring of
11 2005 ($15.1 \text{ nmol} \times \text{cm}^{-2}$). The 2006 spring was a normal spring without nitrate peak.
12 This suggests a 60 % increase in nitrate deposited in the spring of 2005 compared to
13 the spring of 2006. The additional nitrate in the spring of 2005 could either come from
14 enhanced transport of nitrate produced elsewhere or enhanced local nitrate production
15 involving NO_x precursors. In the discussion to follow, we consider separately the
16 possibility of enhanced transport and enhanced local production of nitrate in the
17 Arctic being responsible for the spring 2005 nitrate peak. We further examine whether
18 the explanation for the case of spring 2005 is representative of the occasional nature
19 of the additional nitrate peaks observed in the firn core.

20 **4.1. Enhanced transport of nitrate**

21 **4.1.1. Stratospheric denitrification**

22 Stratospheric denitrification refers to the sedimentation process of Polar
23 Stratospheric Clouds (PSCs) containing nitric acid trihydrate. Research on nitrate in
24 Antarctic snow (Mulvaney and Wolff, 1993) suggested that stratospheric

1 denitrification associated with the winter polar vortex could result in a late
2 winter/early spring nitrate peak. Although denitrification occurs less frequently and
3 less extensively in the Arctic than in Antarctica due to the warmer winter and the
4 weaker and less persistent Arctic vortex (Waugh and Randel, 1999), significant
5 denitrification has been observed in Arctic for some exceptionally cold winters,
6 including the winter of 2004/2005 (Mann et al., 2003; Jin et al., 2006; Kleinbohl et
7 al., 2005). Could stratospheric denitrification in the winter of 2004/2005 have resulted
8 in the early spring nitrate peak?

9 Stratospheric nitrate is expected to possess high $\Delta^{17}\text{O}$ since it is mainly formed
10 via O_3 oxidation (McCabe et al., 2007; Savarino et al., 2007) and stratospheric
11 $\Delta^{17}\text{O}(\text{O}_3)$ is up to 5 ‰ higher than that in the troposphere (Liang et al., 2006; Lyons,
12 2001; Mauersberger et al., 2001). In addition, stratospheric nitrate can also be formed
13 via ClO oxidation (McCabe et al., 2007). Nitrate formed via ClO oxidation also
14 possesses high $\Delta^{17}\text{O}$ (McCabe et al., 2007; Savarino et al., 2007) due to the internal
15 non-statistical distribution of isotopes in O_3 which transfers its terminal oxygen atoms
16 to ClO (Bhattacharya et al., 2008).

17 If the additional nitrate in the 2005 spring snow originated from stratospheric
18 denitrification, the $\Delta^{17}\text{O}(\text{NO}_3^-)$ would be expected to be anomalously high, not low as
19 was observed. It is possible that the $\Delta^{17}\text{O}$ value of nitrate deposited to the snow
20 surface is reduced by post-depositional processing, for the photolytic recycling of
21 snowpack nitrate (nitrate photolysis followed by re-formation and re-deposition of
22 nitrate) can reduce the $\Delta^{17}\text{O}$ signature of nitrate finally preserved in snow (Erbland et
23 al., 2013). If all of the nitrate produced in the stratosphere undergoes photolytic
24 recycling, the stratospheric $\Delta^{17}\text{O}$ signature would be completely erased (i.e., $\Delta^{17}\text{O}$ of

1 the nitrate would be the same as that of nitrate produced in the tropospheric boundary
2 layer). Given the high snow accumulation rate at Summit (the degree of snowpack
3 nitrate photolysis decreases with increasing snow accumulation rate (Röthlisberger et
4 al., 2002)), it is unlikely that all additional nitrate underwent photolytic recycling.
5 Consequently, $\Delta^{17}\text{O}$ of the preserved nitrate originally produced in the stratosphere
6 should be no lower than that of the tropospheric nitrate deposited in a typical spring.
7 Therefore, the observed $\Delta^{17}\text{O}(\text{NO}_3^-)$ suggests stratospheric denitrification cannot
8 account for the spring nitrate peak.

9 **4.1.2. Transport from mid-latitudes**

10 Previous studies (Burkhart et al., 2006; Yang et al., 1995) hypothesized that the
11 spring nitrate peak results from pollution transport in the industrial era, though the
12 occasional nature of the peak was not explicitly discussed. In case of strong
13 meridional transport of nitrate, a spring nitrate peak may be expected. In addition, the
14 $\Delta^{17}\text{O}$ of nitrate formed in the mid-latitudes is likely lower than that of nitrate formed
15 in the Arctic troposphere due to the latitudinal gradient in $\Delta^{17}\text{O}(\text{NO}_3^-)$ resulting from
16 the latitudinal gradient in O_3/HO_x ratio (Alexander et al., 2009). Thus, enhanced long-
17 range transport of mid-latitude nitrate to Greenland during the spring could elevate
18 nitrate concentrations in snow with relatively low $\Delta^{17}\text{O}(\text{NO}_3^-)$, consistent with the
19 observations. Direct transport of nitrate from the mid-latitudes to Summit is also
20 consistent the conclusions in Kunasek et al. (2008) and Geng et al. (2014).

21 Pollution from the Northern mid-latitudes is transported to the Arctic by
22 poleward meridional circulation, which is strong when the North Atlantic Oscillation
23 (NAO) is in its positive phase (Eckhardt et al., 2003). However, the NAO index data
24 in the 2004/2005 winter and early spring of 2005 is not strong compared with other

1 years during the period of 1997 to 2009 (Osborn, 2011), suggesting that meridional
2 transport is not particularly strong in the spring of 2005 compared to other springs.
3 However, frequent pollution transport events occur even in years with a negative
4 NAO phase (Kramer et al., 2014). To examine the possibility of pollution transport as
5 the direct cause of the 2005 spring nitrate peak, we examine the profiles of SO_4^{2-} and
6 Mg^{2+} from the snowpit. Enhanced transport from the mid-latitudes will also elevate
7 concentrations of other species derived from anthropogenic and continental sources,
8 such as SO_4^{2-} and Mg^{2+} , especially SO_4^{2-} because it has a very similar atmospheric
9 lifetime (4 to 6 days) as nitrate (3 to 7 days) (Park et al., 2004; Pye et al., 2009).
10 However, the data from the snowpit show that neither SO_4^{2-} nor Mg^{2+} concentrations
11 were elevated (Figure 1f and 1g) in the spring of 2005 when the nitrate peak was
12 present. Therefore, it is unlikely that the 2005 spring nitrate peak was caused by
13 enhanced long-range transport of nitrate from the mid-latitudes during that time
14 period.

15 In addition to pollution from industrial areas, biomass burning (e.g., wild fire)
16 plumes from Boreal North America could also potentially increase snow nitrate
17 concentrations in Greenland. However, the global fire emission data (Giglio et al.,
18 2013) suggests that fire emissions in Boreal North America (nor in Temperate North
19 America and Europe) are not strong in the spring of 2005 compared to other years
20 during the period from 1997 to 2011. In addition, chemical species transported from
21 fire events will likely cause episodic, sharp spikes, such as the NH_4^+ spikes frequently
22 observed in Greenland ice cores (Savarino and Legrand, 1998). The duration (> 1
23 month) of the 2005 spring nitrate peak argues against an episodic biomass-burning
24 source.

1 **4.2. Enhanced local production**

2 **4.2.1. PAN decomposition**

3 Previous work has found that peroxyacetyl nitrate (PAN) is the dominant form
4 of reactive nitrogen in the Arctic troposphere during winter and spring (Beine and
5 Krognes, 2000; Bottenheim et al., 1993; Honrath and Jaffe, 1992; Jacobi et al., 1999)
6 and its decomposition yields NO_x that is subsequently converted to nitrate. If the
7 decomposition rate of PAN is enhanced in the spring of 2005, more NO_x would be
8 produced resulting in an increase in local nitrate production. The possibility of PAN
9 decomposition in spring leading to the spring nitrate peak has been mentioned in
10 Yang et al. (1995), but not explicitly examined. Here we provide a detailed
11 examination of the possible role of PAN decomposition in the spring 2005 nitrate
12 peak.

13 PAN decomposes to NO_x either thermally or via photolysis (Talukdar et al.,
14 1995). At temperatures above 255 K, thermal decomposition dominates, while
15 photolysis becomes more important at lower temperatures (Talukdar et al., 1995). The
16 typical spring (February and March) air temperature at Summit is about 240 K (242 K
17 in 2005 and average of 236 K in the springs of 2006 to 2008; data are from
18 <http://www.summitcamp.org/resources/files>). At these low temperatures, the NO_x
19 release from PAN is dominated by photolysis at wavelengths between 290-345 nm
20 (Talukdar et al., 1995; Flowers et al., 2005).

21 The stratospheric O₃ layer filters out most of the UV-B ($\lambda = 290-320$ nm)
22 portion of the solar spectrum. A weakened stratospheric O₃ layer will allow more UV-
23 B penetration into the troposphere. In Figure 3, the spring (average of February and
24 March values) O₃ column density at Summit for the years of 1979-2006 are shown

1 (data are from NASA Total Ozone Mapping Spectrometer program). The 2005 spring
2 level (290 Dobson Unit (DU)) was significantly lower than the average of spring
3 values from 1979 to 2006 (390 ± 50 (1σ) DU), suggesting a relatively high UV-B flux
4 to the surface in the spring of 2005.

5 The photolysis of PAN in the spring of 2005 could have been enhanced due to
6 the elevated UV-B radiation caused by stratospheric O₃ loss, leading to increased
7 local NO_x abundance, and subsequently resulting in the unusual spring nitrate peak in
8 snow. The increase in PAN photolysis resulting from the decreased O₃ column
9 density (290 DU) is estimated with the UCAR Tropospheric Ultraviolet & Visible
10 (TUV) radiation model (available at <http://cprm.acd.ucar.edu/Models/TUV/>).
11 Calculations with the TUV model showed a 24 % increase in the photolysis rate
12 constant of PAN ($j = (9.0 \pm 5.4) \times 10^{-8} \text{ s}^{-1}$ vs. $(7.3 \pm 4.3) \times 10^{-8} \text{ s}^{-1}$, both are daytime
13 averages) in the spring of 2005 compared to that in a typical spring (column O₃
14 density of 390 DU). This would lead to an increase of only $1.6 \times 10^5 \text{ cm}^{-3}$ in NO_x
15 number concentration, which is, on average, 0.04 % of the observed springtime NO_x
16 concentration of $(3.9 \pm 3.1) \times 10^8 \text{ cm}^{-3}$ in the Arctic (Stroud et al., 2003). The above
17 calculation assumes steady state of PAN with number concentration of $(2.3 \pm 0.7) \times$
18 10^9 cm^{-3} (Stroud et al., 2003) and $[\text{NO}_2] = (([\text{PAN}] \times j_{\text{PAN}}) / k)^{1/2}$, where [NO₂] and
19 [PAN] represent the number concentrations of NO₂ and PAN, respectively, and j_{PAN}
20 (s^{-1}) is the photolysis rate constant of PAN calculated from the TUV model and k (cm^3
21 $\times \text{s}^{-1}$) is the reaction rate constant of PAN formation at T = 240 K and P = 650 hPa
22 (Summit springtime condition) calculated based on the equation from Atkinson et al.
23 (2006). The additional production of NO_x from enhanced PAN photolysis is
24 negligible compared to the observed 60 % enhancement in nitrate deposition flux (5.7

1 nmol \times cm⁻²) during the spring of 2005. This is consistent with the model prediction
2 by Stroud et al. (2003) that, during spring, PAN is a net sink of NO_x, rather than a
3 source. A similar conclusion was also reached by Singh et al. (1992) who found that
4 the PAN reservoir is not a significant source of NO_x until summer.

5 **4.2.2. Snowpack NO_x emissions**

6 The photolysis of nitrate in the snowpack at snow depths of up to 20 cm or
7 more (Zatko et al., 2013; France et al., 2011; Grannas et al., 2007) emits NO_x to the
8 overlying atmosphere (Honrath et al., 1999; Frey et al., 2009), serving as a local NO_x
9 source. NO_x originating from the photolysis of nitrate in the snowpack can be re-
10 oxidized in the atmosphere to nitrate and re-deposited to the surface. A recent model
11 study (Thomas et al., 2012) suggested that at Summit, the photolysis of snowpack
12 nitrate alone can sustain observed NO concentrations in the local atmospheric
13 boundary layer. If the emission of NO_x from snowpack were enhanced, local
14 atmospheric nitrate production would also be expected to be elevated. The reduction in
15 O₃ column density in the spring of 2005 led to more UV radiation at the surface,
16 which in turn may significantly enhance the photolysis of snow nitrate
17 ~~nitrate~~ **photolysis**. Consequently, the oxidation of NO_x released from the snowpack by
18 enhanced photolysis of snowpack nitrate at depths, and subsequent re-deposition of
19 the nitrate to the surface in spring, would result in elevated nitrate concentration in
20 surface snow during spring.

21 In order to estimate the impact of the reduced overhead O₃ column density in the
22 spring of 2005 on local NO_x concentration via the photolysis of snowpack nitrate, we
23 used the TUV model to calculate the surface actinic flux at Summit in the spring of
24 2005 (290 DU) versus normal springtime with average O₃ column density (390 DU,

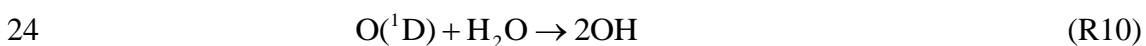
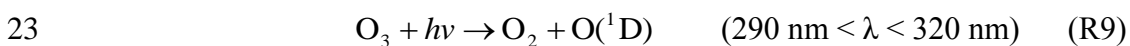
1 which was close to the value (380 DU) in the spring of 2006). The parameterization
2 from Zatko et al. (2013) was then used to calculate the photolysis frequency (s^{-1}) of
3 snowpack nitrate at wavelengths from 298 to 345 nm (peak wavelength for nitrate
4 photolysis is around 320 nm (Chu and Anastasio, 2003)). This calculation suggested a
5 30 % enhancement of the snowpack nitrate photolysis frequency in the spring of 2005
6 relative to 2006, and thus a similar enhancement of NO_x emission from the snowpack,
7 due to the reduced overhead O_3 column density alone. This likely contributed to the
8 enhanced local nitrate production in the spring of 2005. However, the relative
9 importance of snowpack nitrate photolysis to local NO_x abundance in springtime is
10 unknown, making it difficult to quantitatively assess the contribution from snowpack
11 emissions to the observed spring nitrate peak. If snowpack nitrate photolysis nitrate
12 photolysis is the dominant source of boundary layer NO_x at Summit as suggested by
13 Thomas et al. (2012), then this could account for up to half of the additional nitrate in
14 the observed 2005 spring nitrate peak.

15 The relatively high $\delta^{15}N(NO_3^-)$ values in the spring of 2005 (SP-1: (5.3 ± 3.3)
16 ‰; SP-2 (6.4 ± 2.1) ‰) indicate some post-depositional loss of snowpack nitrate at
17 that time. Since post-depositional loss is driven by photolysis (Berhanu et al., 2014;
18 Frey et al., 2009), the observed high $\delta^{15}N(NO_3^-)$ values suggest active snow nitrate
19 photolysis during spring 2005. This is qualitatively consistent with the observations at
20 Summit by Hastings et al. (2004) that $\delta^{15}N(NO_3^-)$ in surface snow is significantly
21 higher in daytime when snow nitrate photolysis is active compared to during the
22 nighttime.

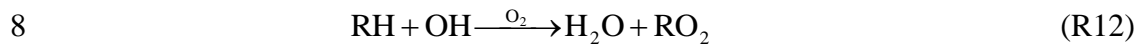
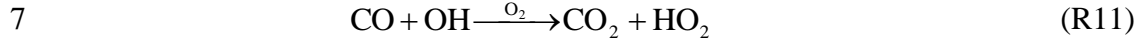
23 **4.2.3. Enhanced conversion of NO_x to nitrate**

1 Field observations suggest that in present day, there is probably sufficient NO_x
2 at Summit to ensure local nitrate production even in the spring. The number
3 concentration of NO_x in the Arctic mid-troposphere (58-85° N, 3-6 km) during spring
4 of 2002 has been reported to be $(3.9 \pm 3.1) \times 10^8 \text{ cm}^{-3}$ (Stroud et al., 2003), which is
5 similar to the summer NO_x level at Summit (Jacobi et al., 2004). In addition, Kramer
6 et al. (2014) reported that February NO_x concentration at Summit is $(1.6 \pm 3.2) \times 10^8$
7 cm^{-3} which overlaps with summer values due to the large uncertainty. Kramer et al.
8 (2014) also suggested that pollution transport during polar winters leads to
9 accumulation of NO_y as well as NO_x in the Arctic, and implied that part of the NO_y
10 will be converted to NO_x after polar sunrise through photolysis. Under sufficient local
11 NO_y and NO_x abundances in the industrial era, an increase in nitrate concentration
12 would be expected if the oxidation rate of NO_x to HNO₃ is also enhanced. The NO_x
13 oxidation rate can be enhanced by increased oxidant (O₃, OH, BrO) levels. Both O₃
14 and BrO have high $\Delta^{17}\text{O}$ values (Lyons, 2001; Morin et al., 2007), thus an increase in
15 either O₃ or BrO concentrations would result in additional nitrate with high $\Delta^{17}\text{O}$. The
16 relatively low $\Delta^{17}\text{O}(\text{NO}_3^-)$ in the spring 2005 snow (Figure 1c) suggests that increased
17 tropospheric O₃ and/or BrO concentrations are unlikely to be the direct cause of
18 enhanced nitrate production.

19 On the other hand, increased oxidation of NO₂ by OH would produce additional
20 nitrate with low values of $\Delta^{17}\text{O}$ as was observed. In general, the concentration of
21 tropospheric OH is dependent on concentrations of tropospheric O₃ and water vapor
22 and the available UV-B radiation through following reactions:



1 Either a substantial increase in UV-B in the troposphere or an increase in the
2 water vapor content at elevated atmospheric temperatures can increase OH production
3 and therefore enhance the conversion of NO_x to HNO₃ via OH oxidation (R4). In
4 addition, two other important oxidants involved in NO-NO₂ cycling (R2), HO₂ and
5 RO₂, are formed by reactions of carbon monoxide (CO) and hydrocarbons (RH) with
6 OH:



9 Increased OH will enhance NO-NO₂ cycling via HO₂ and RO₂ and reduce the relative
10 importance of O₃ in NO_x cycling, which also leads to lowered $\Delta^{17}\text{O}$ in nitrate.

11 Using temperature and relative humidity data at Summit from the Greenland
12 Climate Network Data (GCND,
13 <http://cires.colorado.edu/science/groups/steffen/gcnet/order/admin/station.php>), we
14 estimate that the spring (February and March average) atmospheric water vapor
15 mixing ratio in 2005 was 40 % higher than that in 2006 due to high temperatures in
16 the 2005 spring (-30 °C) relative to the 2006 spring (-34 °C). Assuming this high
17 water vapor in spring 2005 will result in a maximum increase in OH production of 40
18 %, the increase in water vapor is not enough to account for the 60 % enhancement in
19 the nitrate deposition flux in the spring of 2005. In fact, as discussed later, OH must
20 be increased by 200 % to explain the full magnitude of the spring nitrate maximum.
21 Although the relatively high temperature in the spring of 2005 may have contributed
22 around 20 % (40 % increase versus the required 200 % increase) to the enhanced local
23 nitrate production, it was likely not the dominant factor producing the spring nitrate
24 peak in 2005.

1 To determine the effect of reduced column O₃ density on OH production at the
2 surface, we used the TUV model to estimate the OH production rate (R9 and R10) at
3 Summit due to enhanced photolysis of boundary layer O₃. Our calculation showed
4 that the OH production rate due to this mechanism alone was increased by 90 % in the
5 spring of 2005 resulting from the decrease in O₃ column density from 390 to 290 DU.
6 Assuming that the production of HNO₃ via OH oxidation was increased by the same
7 factor, enhanced local OH production could easily account for the 60 % enhancement
8 of nitrate flux in the spring of 2005, if all of the additional nitrate was formed via OH
9 oxidation (R4). During a typical Arctic spring, O₃ is expected to be the major oxidant
10 in the oxidation of NO_x to HNO₃ (Alexander et al., 2009), so it is unlikely that R4 is
11 solely responsible for the local oxidation of NO_x to HNO₃. Using a global chemical
12 transport model (GEOS-Chem), Alexander et al. (2009) estimated that about 30 % of
13 total nitrate in a normal spring (average in February and March) is produced via OH
14 oxidation at Summit. With this more realistic value, a 200 % increase in the local OH
15 production rate was needed to account for the additional nitrate flux in the spring of
16 2005. Therefore, the enhanced local production rate of OH due to solely the enhanced
17 photolysis of tropospheric O₃ in the spring of 2005 can explain about 50 % of the
18 observed spring nitrate peak.

19 In addition to production via O₃ photolysis (R9 and R10), OH can be formed by
20 the photolysis of snowpack emitted CH₂O, H₂O₂, and HONO (Dassau et al., 2002;
21 Hutterli et al., 2001; Zhou et al., 2001; Sjostedt et al., 2007). Some model studies
22 suggested that at Summit photolysis of snow-sourced CH₂O, H₂O₂ and HONO
23 contributes to OH 2-3 times more than that from O₃ photolysis [e.g.,(Yang et al.,
24 2002)] while the others seem to have different results [e.g., (Chen et al., 2007)].

1 Although the photolysis of these species are more sensitive to UV-A radiation
2 (Grannas et al., 2007), the production/emission of HONO and CH₂O from the
3 snowpack are influenced by snow nitrate photolysis (Thomas et al., 2012) which is
4 sensitive to UV-B radiation. In addition, a recent model study by Thomas et al. (2012)
5 suggested that at Summit, snow-sourced NO_x lead to as much OH production as that
6 from ozone photolysis via shifting the local OH/HO₂ ratio in favor of OH, with
7 additional 10-18% contribution from snowpack bromine chemistry. These processes
8 are also sensitive to UV-B radiation. These model studies suggested that snow
9 photochemistry is more important than ozone photolysis for OH production at
10 Summit (Thomas et al., 2012; Yang et al., 2002). It is thus conceivable that under the
11 condition of reduced O₃ column density in the spring of 2005, the OH production rate
12 could be increased by 200 % from the combined contribution of enhanced snow
13 photochemistry and tropospheric O₃ photolysis, even without considering the effect of
14 elevated water vapor mixing ratio due to the temperature increase (around 3 °C, but
15 this will enhance the emissions of H₂O₂, CH₂O from snow (Grannas et al., 2007)).

16 Thus, we propose that the elevated tropospheric UV-B level due to a weakened
17 stratospheric ozone layer in the spring of 2005 likely led to additional local nitrate
18 production in sufficient quantities to account for the spring nitrate peak. The
19 additional nitrate was generated primarily through increased tropospheric OH
20 production from the enhanced photolysis of tropospheric O₃ and snowpack
21 photochemistry involving NO_x, halogens, HONO, CH₂O, and H₂O₂. Increased NO_x
22 abundance from the photolysis of snowpack nitrate and/or other NO_x precursors that
23 accumulated during the polar winter also contributes (Kramer et al., 2014).

24 **4.3. Further examination with additional snow and ice core data**

1 Hastings et al. (2004) reported seasonal variations in concentrations, $\delta^{18}\text{O}$ and
2 $\delta^{15}\text{N}$ of snow nitrate at Summit covering the years of 2000 and 2001. Qualitatively,
3 $\delta^{18}\text{O}(\text{NO}_3^-)$ is similar to $\delta^{17}\text{O}(\text{NO}_3^-)$, because the $\delta^{18}\text{O}(\text{NO}_3^-)$ value is also determined
4 by the relative importance of O_3 versus OH oxidation (higher $\delta^{18}\text{O}(\text{NO}_3^-)$ values are
5 associated with increased O_3 oxidation and lower $\delta^{18}\text{O}(\text{NO}_3^-)$ values indicate
6 increased HO_x oxidation) (Hastings et al., 2004). Consequently, $\delta^{18}\text{O}(\text{NO}_3^-)$ is high in
7 winter snow and low in summer snow (as shown in Figure 1a, and also in Hastings et
8 al. (2004)). The data shown in Hastings et al. (2004) indicated a spring nitrate peak in
9 2000. The spring nitrate concentration peak in 2000 in Hastings et al. (2004) had
10 $\delta^{18}\text{O}(\text{NO}_3^-)$ values ($(69.8 \pm 2.1) \text{‰}$) similar to those during the summer of 2000 ($(70.5$
11 $\pm 2.4) \text{‰}$). In contrast, in the 2001 spring when no nitrate concentration peak was
12 observed, $\delta^{18}\text{O}(\text{NO}_3^-)$ was $(77.5 \pm 2.4) \text{‰}$, which is similar to the $\delta^{18}\text{O}(\text{NO}_3^-)$ values
13 observed during the prior winter ($(77.4 \pm 1.9) \text{‰}$), and higher than those observed
14 during the subsequent summer ($(68.9 \pm 2.1) \text{‰}$). In addition, the mean $\delta^{15}\text{N}(\text{NO}_3^-)$ in
15 the spring of 2000 ($(5.9 \pm 6.2) \text{‰}$) from Hastings et al. (2004) is similar to that
16 observed in the spring of 2005 ($6.4 \pm 2.1) \text{‰}$, and is higher than that observed in
17 Hastings et al. (2004) during the spring of 2001 ($(-1.4 \pm 3.0) \text{‰}$). In summary, the
18 isotopic features of nitrate associated with the spring peaks observed in 2000
19 (Hastings et al., 2004) and in 2005 are similar, each suggesting enhanced local
20 photochemistry as a contributor to the observed spring nitrate peaks. This is consistent
21 with the low O_3 column density in the spring of 2000 (337 DU, Figure 3) and 2005
22 (294 DU, Figure 3). Therefore, the results of Hastings et al. (2004) support the
23 explanation that the appearance of the spring nitrate peak in 2000 is caused by a

1 weakened stratospheric ozone layer, consistent with the observations in the spring of
2 2005.

3 We further examined the 19 years with double nitrate peaks found in the firn
4 core. In order to assess the effect of long-range transport of nitrate on the occurrence
5 of the double nitrate peaks, we compared the nitrate and sulfate records. This
6 comparison indicates that in most (14 out of 19) years, the secondary (earlier and
7 smaller) peak is accompanied by a sulfate peak. This suggests that direct transport of
8 nitrate from polluted regions is likely responsible for the occurrence of the double
9 nitrate peaks in these years. However, there are five years, including 2000 and 2005,
10 in which the secondary peak does not appear with a rise in sulfate concentration. To
11 determine if enhanced local photochemistry could be responsible for the occurrence
12 of the double nitrate peaks in these years, we examined O₃ column density data from
13 1979 to 2006, the time period when global O₃ data are available from satellite
14 observations. The year-to-year variability of polar stratospheric O₃ is largely
15 controlled by the Brewer-Dobson circulation (BDC) through direct transport and
16 indirect coupling between dynamics and chemistry [e.g., (Holton et al., 1995; Randel
17 et al., 2002; Shepherd, 2008; Weber et al., 2011)]. Halogen-catalyzed chemical
18 destruction leads to a decreasing trend in column O₃ density since 1980 (WMO, 2007)
19 and causes sudden drops in O₃ column density in years when the winter temperatures
20 are anomalously low [e.g., the winter of 2004/2005 (Jin et al., 2006; Kleinbohl et al.,
21 2005)]. The strength of the BDC is related to the wave force, which is represented by
22 extratropical poleward eddy heat flux in the lower stratosphere (Fusco and Salby,
23 1999; Weber et al., 2011). From the NCEP/NCAR reanalysis data
24 (<http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.pressure.html>), we

1 retrieved the average eddy heat flux in the lower stratosphere at 40-80 °N in January
2 and February (due to the transport lag, January and February eddy heat flux
3 determines the February and March polar stratospheric O₃ abundance) from 1979 to
4 2006 (Figure 3). Reanalysis data before 1979 are also available, but less reliable due
5 to lack of constraints by satellite observations. Therefore in this study, we only use the
6 data after 1979.

7 As shown in Figure 3, in the period from 1979 to 2006, there are 12 years with
8 double nitrate peaks and five of them are years with O₃ column density well below the
9 average for that period. In other years, one of the double peaks is accompanied by a
10 sulfate peak. The results from the firn core, combined with that from the snowpit, thus
11 suggest that there are two mechanisms leading to occurrence of double nitrate peaks,
12 1) direct transport of nitrate from polluted regions, and 2) enhanced local
13 photochemical production of nitrate. The second mechanism requires local sources of
14 NO_x. Possible local NO_x sources at Summit include PAN decomposition and the
15 photolysis of snowpack nitrate, as well as photolysis of other winter accumulated NO_y
16 species in the atmosphere (Kramer et al., 2014). For example, a model study (Stroud
17 et al., 2003) suggested that HNO₄ is a source of NO_x in remote regions through
18 recycling reactions, but its importance is unclear due to a lack of field observations.
19 These NO_x precursors accumulate in the polar winter through a combination of
20 pollution transport from the mid-latitudes and lack of sunlight, and contribute to
21 springtime NO_x abundance through photochemical decomposition after polar sunrise
22 (Kramer et al., 2014). This is consistent with the observation that there are no double
23 nitrate peaks observed prior to the 1950s as dramatic increases in anthropogenic
24 emissions of NO_x did not occur until ~1950 (Lamarque et al., 2010).

1 **5. Conclusion**

2 Spring nitrate peaks have been observed in Greenland ice core records beginning
3 ~1900 and was hypothesized to originate from pollution transport from the mid-
4 latitudes in the industrial era (Burkhart et al., 2006; Whitlow et al., 1992; Yang et al.,
5 1995). But the specific mechanism leading to the additional peak is unclear as it could
6 be from direct transport of nitrate or transport of NO_x precursors followed by
7 enhanced local photochemistry. Here we report observations of nitrate concentrations
8 and isotopes in a snowpit from Summit, Greenland. After identifying a spring nitrate
9 peak in the year of 2005, we performed a case study regarding its origin. The isotopic
10 composition of nitrate in the snowpit, combined with photochemical calculations,
11 suggests the presence of the 2005 spring nitrate peak was caused by enhanced local
12 nitrate production, instead of long range pollution transport. An analysis of the
13 possible causes suggests that this enhancement was primarily due to increased OH
14 concentration mainly resulting from enhanced photolysis of OH precursors (O₃,
15 HONO, H₂O₂, etc.) in the troposphere caused by elevated UV-B radiation at the
16 surface. Elevated UV-B radiation at the surface was the result of a significant
17 reduction of the stratospheric ozone layer in the Arctic in spring 2005. Increased local
18 NO_x concentrations due to enhanced snowpack nitrate photolysis may also contribute
19 to up to half of the additional nitrate in the spring peak, if snowpack nitrate photolysis
20 is the dominant local NO_x source. Either the increase in OH concentration or the
21 increase in local NO_x concentration relies on enhanced photochemical reactions
22 initiated by the reduced O₃ column density. This mechanism is supported by the
23 appearance of a spring nitrate peak in 2000 (Hastings et al., 2004), when a reduced O₃
24 column density also occurred.

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

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24

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1 **Table 1.** Uncertainties of replicate measurements of reference gases and standards
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5 **Table 2.** Frequency (number of years per decade) of years with double nitrate peaks
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1 **Figure 1.** $\delta^{18}\text{O}(\text{NO}_3^-)$ (a), $\delta^{15}\text{N}(\text{NO}_3^-)$ (b), $\Delta^{17}\text{O}(\text{NO}_3^-)$ (c) and concentrations of NO_3^-
2 (d), Na^+ (e), SO_4^{2-} (f) and Mg^{2+} (g) in the snow samples (data are 3-point running
3 averages). SP-1 data were plotted in gray with plus signs; SP-2 and SB data were
4 plotted in black with circle and star signs, respectively. The pink and green stars
5 represent samples in SB used to calculate the winter and 2005 spring mean $\Delta^{17}\text{O}(\text{NO}_3^-)$
6), respectively; while the red and blue plus signs represent samples in SP-1 used to
7 calculate the winter and 2005 spring mean $\Delta^{17}\text{O}(\text{NO}_3^-)$, respectively. The vertical
8 dashed line indicates the approximate months of snowfall at depths of 0, 0.5, 1.0, 1.5
9 and 2.0 m by Method B as described in the text.

10

11 **Figure 2.** (a) Nitrate concentration record from the shallow ice core; (b), (c), (d) show
12 seasonal peaks of NO_3^- , Na^+ and Ca^{2+} , respectively in two sections of the ice core
13 (data shown in b, c and d are 3-point running averages). Vertical dashed lines in (a)
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16 **Figure 3.** Summit springtime O_3 column density (February and March averages) and
17 poleward eddy heat flux in the lower stratosphere (40-80 °N, January and February
18 averages) from 1979 to 2006. The solid blue line is the average of springtime O_3
19 column density from 1979 to 2006 (390 ± 50 (1σ) DU), and the dashed blue line is the
20 linear least-squared regression of the O_3 column density from 1979 to 2006. The
21 symbols marked as red and green indicate years with double nitrate peaks, while the
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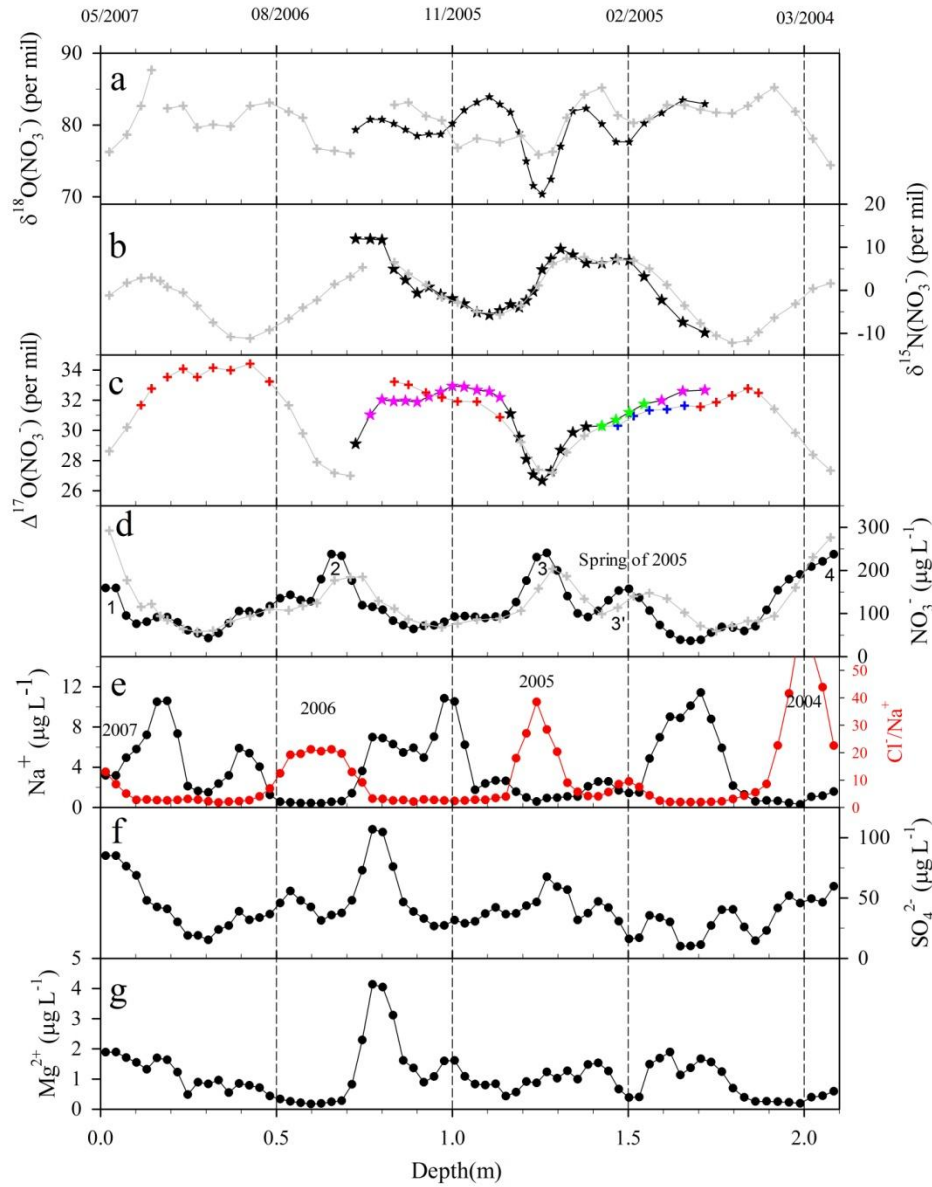
		$\delta^{15}\text{N}$ (‰)	$\delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
Zero Enrichment ^a (N = 30)		0.02	0.10	0.01	0.10
IAEA-NO-3 (vs. reference gas) ^b	Short term ^d (N = 6)	5.1 ± 1.0	28.9 ± 0.4	56.1 ± 0.6	-0.3 ± 0.1
USGS35 (vs. reference gas) ^b	Short term (N = 6)	1.4 ± 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

4 a. Continuous flow measurements of reference gases (O₂ and N₂) relative to
 5 themselves; values are one standard deviations (1σ);
 6 b. Refers to raw values not corrected for any isotopic effects during the analytical
 7 procedure; reported values are means ± RMSD (root-mean-square deviation);
 8 c. Refers to corrected values using the least squares linear regression curve between
 9 the measured and accepted values of reference materials; reported values are means
 10 ± 1σ (standard deviation);
 11 d. Refers to the time period (two days) when samples in this study were measured;
 12 e. Refers to the period of instrument running since October, 2009 to present.

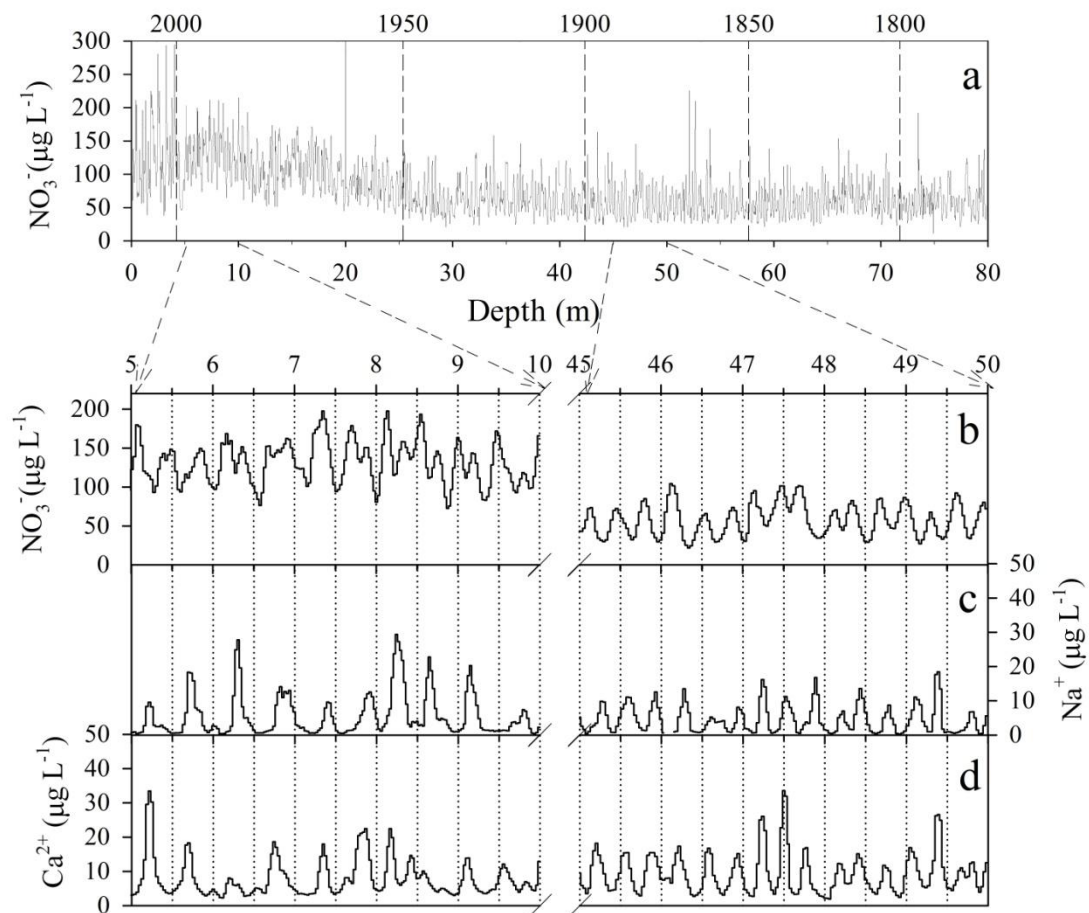
22 **Table 2.** Frequency (number of years per decade) of years with double nitrate peaks
 23 in each decade from 1960 to 2006 in the shallow ice core.

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

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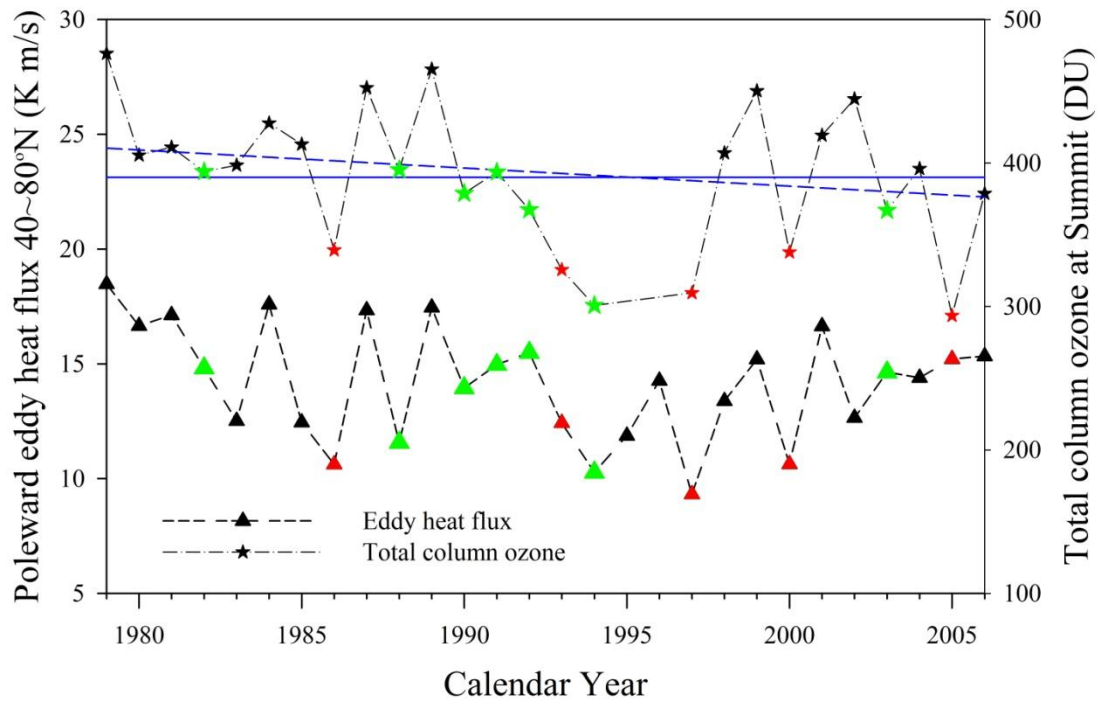


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