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On the origin of the occasional springtime nitrate concentration maximum in Greenland snow

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Abstract

An occasional spring nitrate concentration maximum was observed in ice cores from Central Greenland but its origin is unknown. This study performs a case study on its origin by measuring concentration and isotopic composition of nitrate (δ^{15}N, δ^{18}O and Δ^{17}O) in a snowpit from Summit, Greenland covering three years of snow accumulation. A nitrate concentration maximum was found in the spring of 2005. Isotopic data of nitrate combined with photochemical calculations suggest that the presence of this spring maximum was linked to a significantly weakened stratospheric ozone (O_3) layer. This weakened O_3 layer resulted in elevated UV-B (Ultraviolet B) radiation on the snow surface, where the productions of OH and NO_x from the photolysis of their precursors were enhanced. A concentration maximum was then observed as the result of enhanced local nitrate production due primarily to the increased OH concentrations, as indicated by decreases in δ^{18}O and Δ^{17}O of nitrate associated with the spring maximum. We further examined the nitrate concentration record from a shallow ice core covering the period from 1772 to 2006 and compared this record to satellite observations of springtime O_3 column density data from 1979 to 2006. We found 19 spring nitrate maxima after the 1950s. After 1979, all spring concentration maxima appeared with O_3 column density near or below the 1979–2006 average. We hypothesize that the presence of the spring nitrate concentration maximum is largely associated with and may be determined by the interannual variability of O_3 column density, under the condition of elevated local NO_x abundance at Summit after the 1950s resulting from enhanced anthropogenic nitrate deposition, though other factor(s) may dominate in some years. Isotopic data covering additional years of low O_3 column density are needed to further examine this hypothesis.

1 Introduction

Knowledge of the abundance and variability of reactive nitrogen oxides ($NO_x = NO + NO_2$) is valuable because of the critical role that NO_x 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 cycles rapidly between NO and NO_2 according to:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R1}$$

$$NO + HO_2(RO_2) \rightarrow NO_2 + OH(RO) \tag{R2}$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \tag{R3}$$

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

$$NO_2 + OH \rightarrow HNO_3 \tag{R4}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{R5}$$

$$NO_3 + DMS/HC \rightarrow HNO_3 + \text{products} \tag{R6}$$

$$NO_3 + NO_2 \rightarrow N_2O_5 \tag{R7}$$

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

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). Reaction (R4) mainly occurs during daytime, as the result of diurnal variation in OH concentrations. The conversion to nitrate via O_3 (Reactions 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 (Reaction R4) is thought to be the dominant nitrate formation pathway on an annual basis

(Alexander et al., 2009). Once formed, nitrate is removed from the atmosphere mainly through wet and dry deposition to the surface. Efforts have been made to use ice core nitrate records to assess information about past changes in the global NO_x environment (Fischer et al., 1998; Mayewski et al., 1990), and potentially about the past variations in the atmospheric oxidation capacity (Alexander et al., 2004). However, nitrate concentration in polar snow is also influenced by variations in snow accumulation rate and by post-depositional processes such as evaporation and photolysis (Röthlisberger et al., 2002) of nitrate in near-surface snow. Post-depositional processing of snowpack nitrate has hampered the interpretation of ice core nitrate record in terms of assessing past atmospheric NO_x variability.

Examination of detailed chronological nitrate records in snowpits and ice cores may provide clues on the primary factor(s) controlling nitrate concentration and its temporal variability in snow. For example, a clear seasonal pattern in nitrate concentration may be linked to a source with an annual cycle and/or modulated by seasonally varying atmospheric conditions. Many previous studies of snow samples and ice cores from central Greenland have found that nitrate concentration reaches a maximum in summer snow and a minimum in winter snow (Davidson et al., 1989; Finkel and Langway, 1986; Whitlow et al., 1992). This seasonal variation in nitrate concentration in general is due to the active photochemical reactions during polar summer (Yang et al., 1995), when peroxyacetyl nitrate (PAN), snowpack nitrate and other NO_x reservoir species act as local NO_x sources through recycling reactions (Moxim et al., 1996; Thomas et al., 2012). A few investigators (Burkhart et al., 2006; Yang et al., 1995) noticed that a single nitrate maximum appears in an annual snow/ice layer deposited prior to the year 1900, whereas two maxima are seen in some post-1900 annual layers. The other annual maximum in the post-1900 period generally appears in the spring but does not occur every year (Yang et al., 1995). The occurrence of this occasional spring nitrate maximum has been proposed to be associated with anthropogenic NO_x emissions at the mid-latitudes (Burkhart et al., 2006; Yang et al., 1995), as a result of fossil fuel combustion. Anthropogenic NO_x emissions from fossil fuel combustion have increased the concentration of atmospheric NO_x since 1900, especially in the last 50 years (Galloway et al., 2003), and the corresponding increase in nitrate concentrations in Greenland snow has been documented (Mayewski et al., 1990). However, the observation that the spring nitrate maximum is only present in some years suggests that other factors, such as atmospheric transport of nitrate or of its precursors and/or atmospheric conditions (e.g., solar radiation, oxidant concentrations), may also be important in determining the appearance of the spring nitrate concentration maximum.

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 $\delta = R_{\mathrm{sample}}/R_{\mathrm{reference}} - 1$ with R denoting the $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope ratios. The references are N_2-AIR and VSMOW for N and O, respectively. $\delta^{15}N$ and $\Delta^{17}O$ of nitrate (hereafter denoted as $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$, respectively) have been used to investigate the origin and fate of NO_x in the Arctic troposphere (Morin et al., 2008). In particular, $\Delta^{17}O(NO_3^-)$ is related to oxidizing conditions and nitrate formation pathways (Reaction R4 vs. Reactions R5–R8) in the atmosphere (Alexander et al., 2004, 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 Reactions R5–R8) has higher $\Delta^{17}O$ than nitrate formed during daytime (via Reaction R4) because of the high $\Delta^{17}O$ of the dominant nighttime oxidant O_3 (Johnson et al., 2000; Lyons, 2001) which is transferred to nitrate. The $\Delta^{17}O(NO_3^-)$ in Greenland snow also reflects the seasonality of nitrate production, with O_3 oxidation (Reactions R1 and R5) being more important in winter than in summer (Kunasek et al., 2008).

In this study, the concentrations of major ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) in a snowpit and a shallow ice core from central Greenland were measured. In additon, we measured the isotopic composition of nitrate with high temporal resolution from the snowpit. The concentration data were used to establish their temporal patterns and to identify spring nitrate concentration maxima. The isotopic data were used to assess the chemistry of nitrate in a spring maximum identified in the snowpit, and further examinations were conducted to determine the occasional nature of the spring nitrate concentration maximum 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). Several ice cores including a 79 m shallow core were drilled approximately 100 m 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 plastic bags and shipped frozen to Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) for nitrate concentration and isotope analysis.

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. 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 m 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 nmol, 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 Air–N_2 and calibrated against the two international reference materials IAEA-NO-3 (δ^{15}N = 4.7 ‰) and USGS34 (δ^{15}N = −1.8 ‰). The δ^{17}O and δ^{18}O values were calculated with respect to V-SMOW and calibrated against the two international reference materials USGS34 (δ^{17}O = −14.5 ‰, δ^{18}O = −27.9 ‰) and USGS35 (δ^{17}O = 51.3 ‰, δ^{18}O = 57.5 ‰). The Δ^{17}O values were then calculated by using the linear equation $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$. 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 $\Delta^{17}\text{O}(\text{NO}_3^-)$ and $\delta^{18}\text{O}(\text{NO}_3^-)$ measured at the UW laboratory was estimated to be 0.1 ‰ and 0.5 ‰ (1σ), and that of δ^{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 (δ^{15}N, δ^{18}O and Δ^{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 followed 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 $\Delta^{17}\text{O}(\text{NO}_3^-)$, $\delta^{18}\text{O}(\text{NO}_3^-)$ and $\delta^{15}\text{N}(\text{NO}_3^-)$ measured at the LGGE laboratory were 0.3 ‰, 2.0 ‰ and 0.3 ‰, respectively, estimated as the reduced standard deviation of the residuals from the linear regression between the measured reference materials and their accepted values.

3 Results

3.1 Dating and identifying spring nitrate maxima

The concentration data from the SP-1 and SP-2 samples, and the isotopic data from the SP-1 and SB samples, were plotted as a function of depth in Fig. 1 (data are available in Supplement). 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 Fig. 1d). Since the snowpit and snow blocks were excavated in July of 2007, the partial Peak 1 at the surface identifies the summer of 2007. The other peaks could be summer or spring peaks. According to the concentration profile of sodium (Fig. 1e) that has an annual winter peak (Whitlow et al., 1992), nitrate Peak 3 represents the spring of 2005 and Peak 2, 3 and 4 represent the summer of 2006, 2005 and 2004, respectively. This dating by nitrate summer peaks and sodium winter peaks (referred to here as Method A) is consistent with the results of weekly recorded snow accumulation data determined by stake height measurements at Summit (data are available at ftp://ftp.summitcamp.org/pub/data/GEOSummit/Bales_UCM/BambooForest/BambooForestAccumulationLog.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 Fig. 1. Both dating methods identify Peak 3 occurring in the (early) spring of 2005. Some small discrepancies exist between the two dating methods. For example, the month of snowfall at the surface was identified as May of 2007 using Method B instead of July. This discrepancy is due to negligible snowfall (around 2 cm) from May to July 2007. The month of snowfall at the depth of 2 m was identified as March of 2004 using Method B, suggesting that Peak 4 is also a spring peak. However, according to the snow accumulation data, there was only about 3 cm of snow accumulation from March to June of 2004. 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.

The record of nitrate concentrations from the shallow ice core is shown in Fig. 2 (data are available in Supplement). This core was dated by counting the annual spring peak of calcium (Cole-Dai et al., 2013). Nineteen spring nitrate concentration maxima were found in the period of 1960 to 2006, obtained by subtracting total calcium peaks from total nitrate peaks in this period (Fig. 2). The frequency of the spring maximum in each decade in this period was listed in Table 2. No such spring maximum was seen before 1960, similar to the finding by Finkel and Langway (1986) that the spring nitrate concentration maximum 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 Fig. 1a–c, 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 0.75 m) corresponds to the time period of the 2006 spring/summer to the 2004/2005 winter. Approximate seasons were marked according to Method A. In general, all three isotopic signatures of nitrate display large seasonal variations. $\delta^{18}O(NO_3^-)$ is low in summer and high in winter, while $\delta^{15}N(NO_3^-)$ is high in spring/early summer and low in winter, consistent with previous measurements of Summit snow samples from Hastings et al. (2004). In the spring of 2005 (the time period corresponding to the depths of the spring nitrate maximum), the means ($\pm 1\sigma$) of $\delta^{15}N(NO_3^-)$ from the SP-1 and SB samples were (5.3 ± 3.3) ‰ and (6.4 ± 2.1) ‰, respectively, much higher than the winter values which were (-9.2 ± 3.3) ‰ from the SP-1 samples and (-7.4 ± 4.4) ‰ from the SB samples. A local minimum in $\delta^{18}O(NO_3^-)$ was also observed from both the SP-1 and the SB samples at the depths of the 2005 spring nitrate peak (Fig. 1a).

The observed seasonality of $\Delta^{17}O(NO_3^-)$ (Fig. 1c) was consistent with the expectation of high $\Delta^{17}O(NO_3^-)$ during winter (polar night) due to the dominance of the O_3 oxidation pathway of NO_x (Reactions R5–R8). The magnitude of the seasonality was also consistent with the observations of $\Delta^{17}O(NO_3^-)$ at Summit by Kunasek et al(2008). The seasonality of $\Delta^{17}O(NO_3^-)$ is regulated by the shift of the dominant nitrate formation pathway from OH oxidation (Reaction R4) in polar summer/day to that via O_3 (Reactions 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 (Reaction 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 (Fig. 1c). To test whether the declines are significant, we calculate the mean $\Delta^{17}O(NO_3^-)$ value in the early spring of 2005 and compare that to the mean of measured winter $\Delta^{17}O(NO_3^-)$ values. The winter mean $\Delta^{17}O(NO_3^-)$ was calculated from the 2004/2005 to 2006/2007 winters from the SP-1 samples, and from the 2004/2005 to 2005/2006 winters for the SB samples (samples used to calculate the winter and 2005 early spring means are as marked in Fig. 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 concentration maximum. This is qualitatively consistent with the observed decrease in $\delta^{18}O(NO_3^-)$, as increases in the relative importance of OH oxidation will also result in decreases in $\delta^{18}O(NO_3^-)$ (Hastings et al., 2004). The extra nitrate deposited during the spring of 2005 was estimated to be 5.7 nmol cm^{-2}, which was obtained by subtracting the flux of nitrate (9.4 nmol cm^{-2}) in the spring of 2006 from the nitrate flux in the spring of 2005 (15.1 nmol cm^{-2}). The 2006 spring was a normal spring without nitrate concentration maximum. This suggests a 60 % increase in nitrate deposited in the spring of 2005 compared to the spring of 2006. The additional nitrate in the spring of 2005 could either come from enhanced transport of nitrate produced elsewhere or be produced locally. In the discussion to follow, we consider separately the possibility of enhanced transport and enhanced local production of nitrate in the Arctic being responsible for this spring nitrate concentration maximum. We further examine whether the explanation for the case of spring 2005 is representative of the occasional nature of the spring nitrate concentration maximum observed in the shallow ice core.

4.1 Enhanced transport

4.1.1 Stratospheric denitrification

Stratospheric denitrification refers to the sedimentation process of Polar Stratospheric Clouds (PSCs) containing nitric acid trihydrate. Research on nitrate in Antarctic snow (Mulvaney and Wolff, 1993) suggested that stratospheric denitrification associated with the winter polar vortex could result in a late winter/early spring nitrate concentration maximum. Although denitrification occurs less frequently and less extensively in 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 concentration maximum?

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

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

4.1.2 Transport from mid-latitudes

The model results in Kunasek et al. (2008) suggest significant transport of nitrate from the mid-latitudes to Summit. The Δ^{17}O of nitrate from mid-latitudes is likely lower than that of nitrate formed in the Arctic troposphere due to the latitudinal gradient in $\Delta^{17}O(NO_3^-)$ resulting from the latitudinal gradient in O_3/HO_x ratio (Alexander et al., 2009). Thus, enhanced long-range transport of mid-latitude nitrate to Greenland during the spring could elevate nitrate concentration in snow with relatively low $\Delta^{17}O(NO_3^-)$ as observed here. Pollution from the Northern mid-latitudes is transported to Arctic by poleward meridional circulation, which is strong when the North Atlantic Oscillation (NAO) is in its positive phase (Eckhardt et al., 2003). However, a weak NAO in the 2004/2005 winter and early spring of 2005 was seen in the NAO index data (Osborn, 2011), suggesting no enhanced transport from the mid-latitudes at this time. In addition, if the additional nitrate in the spring of 2005 was from enhanced transport, elevated concentrations of other species derived from anthropogenic and continental sources, such as SO_4^{2-} and Mg^{2+}, would also be expected, especially for SO_4^{2-} because it has a very similar atmospheric lifetime (4 to 6 days) as nitrate (3 to 7 days) (Park et al., 2004; Pye et al., 2009). However, the data from the snowpit show that neither SO_4^{2-} nor Mg^{2+} concentrations were elevated (Fig. 1f and g) in the spring of 2005 when the nitrate maximum was present. Therefore, it is unlikely that the 2005 spring nitrate maximum was caused by enhanced long-range transport of nitrate from the mid-latitudes.

4.2 Enhanced local production

4.2.1 PAN decomposition

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

The stratospheric O_3 layer filters out most of the UV-B (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 Fig. 3, the spring (average of February and March values) O_3 column density at Summit for the years of 1979–2006 were shown (data are from NASA Total Ozone Mapping Spectrometer program). The 2005 spring level (290 Dobson Unit (DU)) was significantly lower than the average of spring values from 1979 to 2006 (390 ± 50 (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 concentration maximum in snow. The increase in PAN photolysis resulting from the decreased O_3 column density (290 DU) can be estimated with the UCAR Tropospheric Ultraviolet and 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 of PAN ($j = (9.0 \pm 5.4) \times 10^{-8}\,s^{-1}$ vs. $(7.3 \pm 4.3) \times 10^{-8}\,s^{-1}$, both are daytime averages) in the spring of 2005 compared to that in a typical spring (column O_3 density of 390 DU). This would lead to an increase of only $1.6 \times 10^5\,cm^{-3}$ in NO_x number concentration, which is, on average, 0.04 % of the observed springtime NO_x concentration of $(3.9 \pm 3.1) \times 10^8\,cm^{-3}$ in the Arctic (Stroud et al., 2003). The above calculation assumes steady stead of PAN with number concentration of $(2.3 \pm 0.7) \times 10^9\,\mathrm{cm^{-3}}$ (Stroud et al., 2003) and $[\mathrm{NO_2}] = (([\mathrm{PAN}] \times j_{\mathrm{PAN}})/k)^{1/2}$, where $[\mathrm{NO_2}]$ and [PAN] represent the number concentrations of NO_2 and PAN, respectively, and j_{PAN} ($\mathrm{s^{-1}}$) is the photolysis rate of PAN calculated from the TUV model and k ($\mathrm{cm^3\,s^{-1}}$) is the reaction rate constant of PAN formation at $T = 240\,\mathrm{K}$ and $P = 650\,\mathrm{hPa}$ (Summit springtime condition) calculated based on the equation from Atkinson et al. (2006). This is negligible compared to the observed 60 % enhancement in nitrate deposition flux ($5.7\,\mathrm{nmol\,cm^{-2}}$) during the spring of 2005. This is consistent with the model prediction by Stroud et al. (2003) that, during spring, PAN is a net sink of NO_x, rather than a source. A similar conclusion was also reached by Singh et al. (1992) who found that the PAN reservoir is not a significant source of NO_x until summer.

4.2.2 Snowpack NO_x emissions

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

In order to estimate the impact of the reduced overhead O_3 column density in the spring of 2005 on local NO_x concentration via the photolysis of snowpack nitrate, we used the TUV model to calculate the surface actinic flux at Summit in the spring of 2005 (290 DU) vs. 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 302 nm (Chu and Anastasio, 2003)). This calculation suggested a 30 % enhancement of the snowpack nitrate photolysis frequency in the spring of 2005 relative to 2006, and thus a similar enhancement of the NO_x emission from the snowpack, due to the reduced overhead O_3 column density alone. This likely contributed to the enhanced local nitrate production in the spring of 2005. However, the relative importance of snowpack photodetrification to local NO_x abundance in springtime is unknown, making it difficult to quantitatively assess the contribution from snowpack emissions to the observed spring nitrate concentration maximum. If snowpack photodenitrification is the dominant source of boundary layer NO_x at Summit as suggested by Thomas et al. (2012), then this could account for up to half of the additional nitrate in the observed 2005 spring nitrate concentration maximum.

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

4.2.3 Enhanced conversion of NO_x to nitrate

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

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

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \quad (290\,nm < \lambda < 320\,nm) \tag{R9}$$

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

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 (Reaction R4). In addition, two other important oxidants involved in NO-NO_2 cycling (Reaction R2), HO_2 and RO_2, are formed by reactions of carbon monoxide (CO) and hydrocarbons (RH) with OH:

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2 \tag{R11}$$

$$RH + OH \xrightarrow{O_2} H_2O + RO_2 \tag{R12}$$

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

The temperature and relative humidity data at Summit is available from Greenland Climate Network Data (GCND, http://cires.colorado.edu/science/groups/steffen/gcnet/order/admin/station.php). Using these data, the spring (February and March average) atmospheric water vapor mixing ratio in 2005 was calculated to be 40 % higher than that in 2006 due to high temperatures in the 2005 spring (−30 °C) relative to the 2006 spring (−34 °C). Assuming this high water vapor in spring 2005 will result in a maximum increase in OH production of 40 %, the increase in water vapor is not enough to account for the 60 % enhancement in the nitrate deposition flux in the spring of 2005. In fact, as discussed later, OH must be increased by 200 % to explain the spring nitrate maximum. Although the relatively high temperature in the spring of 2005 may have contributed around 20 % (40 % increase vs. the required 200 % increase) to the enhanced local nitrate production, it was likely not the dominant factor producing the spring nitrate maximum 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 (Reactions R9 and R10) at Summit due to enhanced photolysis of boundary layer O_3. Our calculation showed that the OH production rate due to this mechanism alone was increased by 90 % in the spring of 2005 resulting from the decrease of O_3 column density from 390 to 290 DU. Assuming that the production of HNO_3 via OH oxidation was increased by the same factor, enhanced local OH production could easily account for the 60 % enhancement of nitrate flux in the spring of 2005, if all nitrate was formed via OH oxidation (Reaction R4). During a typical Arctic spring, O_3 is expected to be the major oxidant in the oxidation of NO_x to HNO_3 (Kunasek et al., 2008), so it is unlikely that Reaction (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 normal spring (average in February and March) is produced via OH oxidation at Summit. With this more realistic value, 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 maximum.

In addition to production via O_3 photolysis (Reactions R9 and R10), OH can be formed by the photolysis of snowpack emitted CH_2O, H_2O_2, and HONO (Dassau et al., 2002; Hutterli et al., 2001; Zhou et al., 2001; Sjostedt et al., 2007). Model studies suggested that photolysis of CH_2O, H_2O_2 and HONO contributes a similar amount to local OH production as that from O_3 photolysis (Hutterli et al., 2001; Yang et al., 2002). A recent model study (Thomas et al., 2012) suggested that at Summit snow sourced NO_x by photolysis also contributes to the local OH concentration (20–50 %) via shifting the local OH/HO_2 ratio in favor of OH. The production of OH via CH_2O, HONO and H_2O_2 photolysis is also strongly influenced by UV-B radiation (Hutterli et al., 2001; Molina et al., 2002; Zhou et al., 2001; Hullar and Anastasio, 2013). Therefore, it is conceivable that under the condition of reduced O_3 column density in the spring of 2005, the OH production rate could be increased by 200 % from the combined contribution of OH precursors from the snowpack and enhanced tropospheric O_3 photolysis, even without considering the effect of elevated water vapor mixing ratio due to the temperature increase (around 3 °C).

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 concentration maximum. The additional nitrate was generated primarily through increased tropospheric OH production from the enhanced photolysis of tropospheric O_3 and CH_2O, H_2O_2 and HONO emitted from the snowpack, and also possibly from enhanced NO_x emission from the photolysis of snowpack nitrate. The enhanced snowpack NO_x emission, contributed to the spring nitrate maximum by enhancing the local NO_x source and by increasing OH production rate.

4.3 Justification with additional snow/ice core data

Hastings et al. (2004) reported seasonal variations in concentrations, δ^{18}O and δ^{15}N of snow nitrate at Summit covering 2000 and 2001. Qualitatively, $\delta^{18}O(NO_3^-)$ is similar to $\Delta^{17}O(NO_3^-)$, because the $\delta^{18}O(NO_3^-)$ value is also determined by the relative importance of O_3 vs. 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). The data shown in Hastings et al. (2004) indicated a spring nitrate concentration maximum in 2000. At the same time, the mean $\delta^{18}O(NO_3^-)$ in the spring of 2000 (69.8 ± 2.1) ‰ is significantly lower than that in the prior winter (77.5 ± 2.4) ‰, and is also lower than that in the spring of 2001 (75.4 ± 1.9) ‰. The mean $\delta^{15}N(NO_3^-)$ in the spring of 2000 (5.9 ± 6.2) ‰, similar to that in the spring of 2005 (6.4 ± 2.1) ‰, is higher than that in the spring of 2001 (−1.4 ± 3.0) ‰. The isotopic features of nitrate associated with this spring maximum also suggest enhanced local photochemistry. This is consistent with the low O_3 column density (337 DU, Fig. 3) in the spring of 2000. Therefore, the results of Hastings et al. (2004) support the explanation that the appearance of the spring nitrate maximun is caused by a weakened stratospheric ozone layer.

To further determine whether the above explanation is representative of the occasional nature of the spring nitrate concentration maximum observed in modern snow in Central Greenland, we compared the nitrate concentration record from the shallow core with O_3 column density data from 1979 to 2006, the time period when global O_3 data are available from satellite observations. The year-to-year variability of polar stratospheric O_3 is largely controlled by the Brewer–Dobson circulation (BDC) through direct transport and indirect coupling between dynamics and chemistry (e.g., Randel et al., 2002; Shepherd, 2008; Weber et al., 2011). Halogen-catalyzed chemical destruction leads to a decreasing trend in column O_3 density since 1980 (WMO, 2007) and causes sudden drops in O_3 column density in years when the winter temperatures are anomalously low (e.g., the winter of 2004/2005, Jin et al., 2006; Kleinbohl et al., 2005). The strength of the BDC is related to the wave force, which is represented by extratropical poleward eddy heat flux in the lower stratosphere (Fusco and Salby, 1999; Weber et al., 2011). From the NCEP/NCAR reanalysis data (http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.pressure.html), we retrieved the average eddy heat flux in the lower stratosphere at 40–80° 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 (Fig. 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 Fig. 3, in the period from 1979 to 2006, the spring nitrate maximum only appears when O_3 column density is near or below the average for that period. We note that although spring nitrate concentration maxima are observed in all years with especially low (lower than the average) O_3 column density, there are a few years (3 out of 12) with a spring nitrate maximum when O_3 column density is near the 1979–2006 average. In addition, there are other years with similarly average O_3 column density when no spring nitrate peak is observed. We suggest that this is because the presence of the spring nitrate concentration maximum also requires other conditions (e.g., sufficient local NO_x abundance), and that this is especially true when O_3 column density is near the 1979–2006 average. Additional factors may also be important, such as stratospheric input of nitrate and/or long range transport of nitrate, as discussed previously. With isotopic data and other relevant information available, we were able to exclude many possible sources of nitrate to the spring maximum in 2005; however, it is difficult to explicitly assess the dominant source(s) of nitrate contributing to the spring maximum in each individual year observed in the shallow ice core, mainly due to the lack of isotopic data. It is possible that episodic events bring sufficient nitrate so that a spring maximum is detected, when local photochemistry is not significantly enhanced.

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

5 Conclusion

We report observations of spring nitrate concentration maxima in a snowpit and a shallow ice core from Summit, Greenland. A case study regarding the origin of the spring nitrate maximum was conducted by measuring the isotopic signature of nitrate in the spring of 2005 when a concentration maximum was observed. The isotopic composition of snow nitrate in this spring, combined with photochemical calculations, suggests the presence of the 2005 spring nitrate maximum was caused by enhanced local nitrate production. An analysis of the possible causes suggests that this enhancement was primarily due to increased OH concentration mainly resulting from enhanced photolysis of OH precursors (O_3, HONO, H_2O_2, etc.) in the troposphere caused by elevated UV-B radiation at the surface, which was the result of a significant reduction of stratospheric ozone layer in Arctic at the same time. Increased local NO_x concentration due to enhanced snowpack nitrate photolysis may also contribute to up to half of the additional nitrate in the spring concentration maximum, if snowpack nitrate photolysis is the dominant local NO_x source. Either the increase in OH concentration or the increase in local NO_x concentration relies on the enhanced photochemical reactions initiated by the reduced O_3 column density. This mechanism is supported by the appearance of a spring nitrate concentration maximum in 2000 (Hastings et al., 2004), when a reduced O_3 column density also occurred. For the spring maxima observed in the shallow ice core, most of them appear in springs with significantly low O_3 column density, though there are exceptions likely because O_3 column density is not the only factor influencing local nitrate production. Nevertheless, the evidence available together suggests that the occasional nature of the spring nitrate concentration maximum observed in Greenland snow is largely associated with the interannual variability of O_3 column density. The interannual variability of O_3 column density is mainly controlled by the Brewer–Dobson circulation, while chemical destruction may also play a role beginning around 1980 (WMO, 2007). The presence of the spring nitrate maximum, however, also requires sufficient amount of local NO_x, which is likely to exist only after the 1950s when dramatic increases in anthropogenic NO_x emissions started to lead to the buildup of NO_x reservoir species at Summit and thereby increase the local abundance of NO_x. Seasonal resolved isotopic data ($\Delta^{17}O(NO_3^-)$ and $\delta^{15}N(NO_3^-)$) covering additional years with spring nitrate concentration maxima are needed to further examine how robust the connection is between the spring nitrate maximum and O_3 column density. Although it is difficult to conduct such efforts with ice core measurements because of the large sample requirements (> 50 g ice), measurements of snowpit samples can be performed. Snow samples from Summit covering the years of 2010 to 2012 may be ideal for this purpose because there is unprecedented O_3 loss in the spring of 2011 in Arctic (Manney et al., 2011).

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/14/9401/2014/ acpd-14-9401-2014-supplement.zip.

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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.

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

[a] Continuous flow measurements of reference gases (O_2 and N_2) relative to themselves; values are one standard deviations (1σ).

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

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

[d] Refer to the time period (two days) when samples in this study were measured.

[e] Refer to the period of instrument running since October, 2009 to present.

Table 2. Frequency (number of years per decade) of the spring nitrate maximum 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

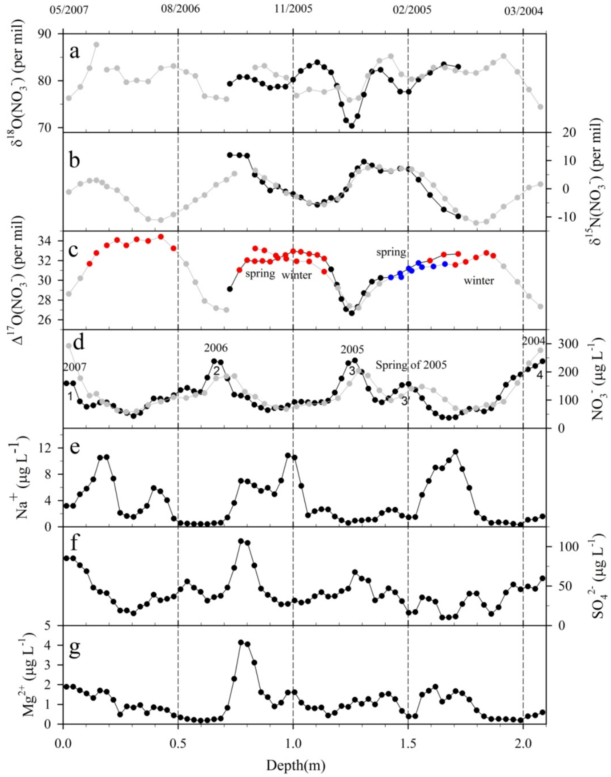

Fig. 1. $\delta^{18}O(NO_3^-)$ **(a)**, $\delta^{15}N(NO_3^-)$ **(b)**, $\Delta^{17}O(NO_3^-)$ **(c)** and concentrations of NO_3^- **(d)**, Na^+ **(e)**, SO_4^{2-} **(f)** and Mg^{2+} **(g)** in the snow samples (data are 3-point running averages). SP-1 data were plotted as gray curves; SP-2 and SB data were plotted as black curves. Red dots represent the data used to calculate winter mean $\Delta^{17}O(NO_3^-)$, while blue dots represent those used to calculate the mean $\Delta^{17}O(NO_3^-)$ in the early spring of 2005. 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.

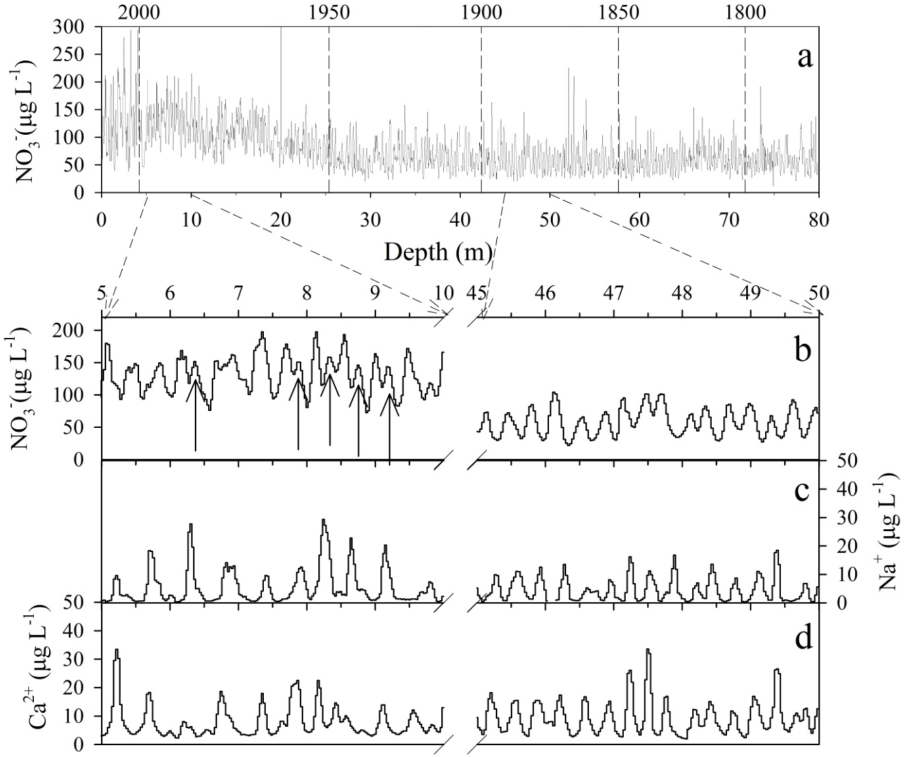

Fig. 2. (a) Nitrate concentration record from the shallow ice core; **(b–d)** show seasonal peaks of NO_3^-, Na^+ and Mg^{2+}, respectively in two sections of the ice core (data shown in **b–d** are 3-point running averages). The arrows in **(b)** indicate spring nitrate maxima which are only observed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

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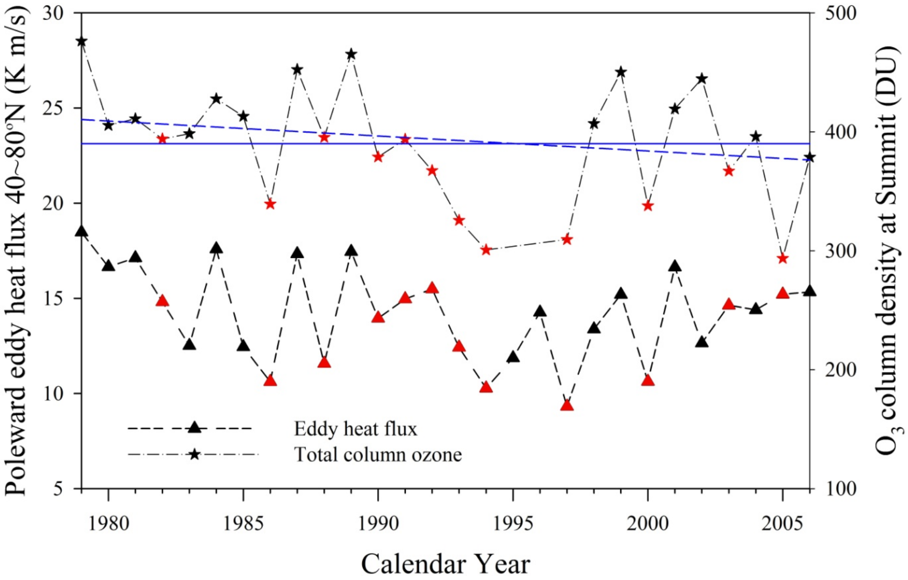

Fig. 3. Summit springtime O_3 column density (February and March averages) and poleward eddy heat flux in the lower stratosphere (40–80° N, January and February averages) from 1979 to 2006. The solid blue line is the average of springtime O_3 column density from 1979 to 2006 (390 ± 50 (1σ) DU), and the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