Dear Dr. Kaiser,

Please find our revised manuscript, “On the origin of the occasional springtime nitrate concentration peak in Greenland snow” by Geng et al. We have received comments from two reviewers. In this file, we combine the "ponit-to-point" response to reviewer 1 (**Pages 2-8**) and reviewer 2 (**Pages 9-39)**, followed by a "change-tracked" manuscript (**Pages 40-80)**.

The first reviewer thinks our manuscript is well-written and with solid conclusion, but asked to provide more details on sample collection and to clarify some confusions on the snowpit dating. In the revised manuscript, we have added more information on sampling (e.g., how the snow blocks were handled) in the method part. Regarding the dating on snowpit, it looks like the reviewer was confused mainly by the difference in the snow depth(s) of the 2005 spring nitrate peak in SP-1 and SP-2. We have added an explanation that the difference is because the spatial variability in snow accumulation rates. In addition, we revised Figure 1 so that samples from SP-1, SP-2 and SB are more easily to differentiate. Please refer to our point-to-point response to this reviewer for details.

Reviewer 2 has many comments, but most of them don't make sense at all to us. The two main reasons that this reviewer refused to recommend our paper to publish are 1) our conclusion is "*basically a single data point* ", and 2) we "*does not fully consider the effects of nitrate photolysis in snow*". However, the first one is totally not true. As we have clearly stated that this work is a case study, and based on the snowpit data we made the hypothesis which is supported by previously published data and by the comparison between ice core data and column ozone record. In other words, our conclusion/hypothesis is not based on the snowpit samples alone. In terms of the second one, by reading the relevant comments, it is clear that this reviewer misinterpreted the discussion in the Frey et al. 2009 and Erbland et al. 2013. Please refer to our point-to-point response to this reviewer for details.

In addition to the major comments from this two reviewers, we appreciate their attentions on the grammars and some technical details. We have corrected them all accordingly. Please refer to the "change-tracked" version of the manuscript for details. In addition, we have added the snow density profile, and a figure of weekly cumulative snow accumulation in supplemental materials.

We are grateful to the reviewers and editor for the helpful suggestions and comments, and look forward to hearing from you at your earliest convenience.

Sincerely,
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Point-to-point response to reviewer 1:

We thank this reviewer very much for the positive comments. Below we provide point-to-point response to the reviewer's comments. The comments are in italics, followed by the response in normal font.

Report summary:

Geng et al. present and interesting study on the origin of occasional nitrate concentration maxima detected during springtime at Summit, Greenland snow. By using stable nitrogen and oxygen isotopes of nitrate in the context of photochemical processes, they linked the nitrate maxima with a weakened stratospheric ozone layer during the studied episodes that enhanced photochemical reactions in the snow surface. They further compare nitrate ice core record with satellite ozone measurements during ~20 years.

The manuscript is well written and present solid arguments linking nitrate maxima with low stratospheric ozone periods. However, some issues need to be addressed before the manuscript can be fully accepted for publication, especially regarding snowpit dating.

Major comments:

***Major comment 1**: The collection and storage of the snowblocks must be described in more detail. Where they collected in bags or boxes? Did they suffer compaction during transport and storage? Including density profile of the snowblocks and snowpit would be convenient. It is hard for me to imagine transporting those snowblocks without disturbing their stratigraphy. A description of the sampling methods and tools is also missing. I assume that clean protocols (clean overalls, gloves, etc.) were followed but this should be described in the text.*

Response: We have added more details in the method part regarding sample collection in the field, transport and storage of samples back to the lab. The snow density data have been added in the Supplemental Material. Briefly, SP-1 sample were "collected in the field every ~5 cm from the surface down to the depth of 2.10 m". Each of the SP-1 samples was then stored in a clean (pre-cleaned with 18 MΩ water) plastic bag and shipped frozen back to LGGE. Thus there is no issue of snow mixing after sampling for SP-1 samples. SP-2 samples were collected as snow blocks in the field, i.e., "six snow blocks were excavated from the surface down to a depth of 2.10 m", and then each block was stored in a plastic bag with upper and bottom layer marked. The bag was then put in a white, thermal box (hard shell) and shipped back to SDSU. Compaction or stratigraphy disturbance does not seem to be an issue as the dimensions of the snow blocks were identical before and after shipment. The nitrate concentration and isotopic profiles from SP-1 and SP-2 (SB) are similar (Fig 1 a-d), which further demonstrates that stratigraphy disturbance during shipment of the snow blocks was insignificant. In addition, as we stated in the manuscript, when we collected snow samples from the snow blocks at SDSU, the surface layer of each block (~1 cm) was removed first to avoid contamination during sample processing.

Major comment2 : *In section 3.1 the peaks in figure 1.d were chosen arbitrary. There are two peaks in between 2007 and 2006 that have moreless the same concentration than peak 1 and 3 (second) (black line) but were not considered as candidate peaks. Also peak 3 (and second 3) need to be re-labelled since it is confusing having two peaks "3".*

Response: To answer this question, and to support our picking of peaks in the manuscript, we apply the built-in MatLab function, "PeakFinder" (available at http://www.mathworks.com/matlabcentral/fileexchange/25500-peakfinder/content/peakfinder.m) to the nitrate concentration data in SP-1 and SP-2. This function "finds local maxima (peaks) or minima (valleys) in a noisy signal", and we use the default setup of the function. The result is plotted as a function of sample numbers versus sample values, with peak(s) identified and marked as red dots. As shown in **Figure** S1 below, the peaks identified by the program are consistent with what we identified in the manuscript. In the manuscript, to differentiate 2005 summer and spring peaks, we label the summer peak as Peak 3, and the spring peak as Peak 3'. We agree it is easy to overlook the superscript symbol in Peak 3', we will change it as Peak 3s.

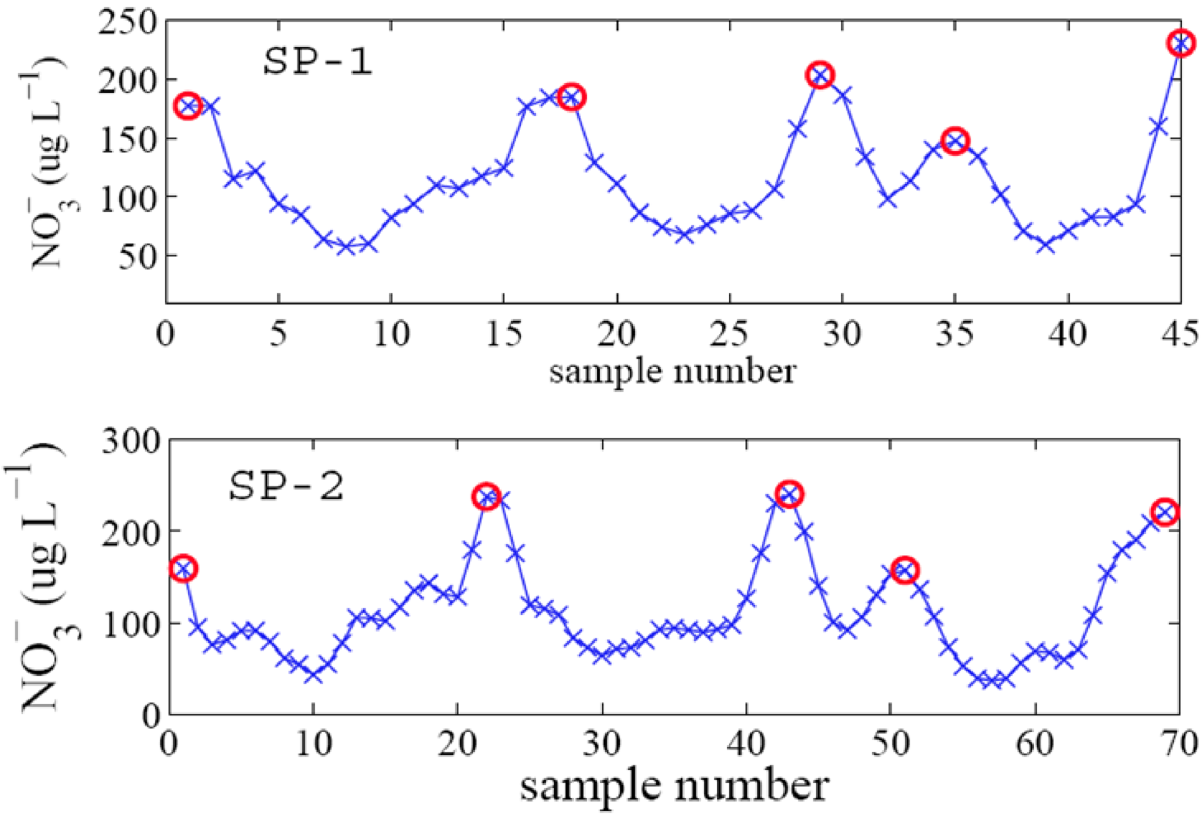

Figure 1S. Nitrate peaks identified in SP-1 (top) and SP-2 (bottom) snowpits using the PeakFinder function of MatLab. Note that in each figure the X-axis is plotted as sample number, this follows the MatLab function and assumes the concentration data is a vector evenly distributed in space (this assumption is true for SP-2 samples but SP-1 samples were not collected evenly in depths). In addition, as we are looking for seasonal peaks, so we use the 3-

point running averages of original data which smooth out short-term variations (endpoints of each data set are also omitted).

Major comment 3*: In page 9, line 19, peak 3 (black line) is located in February (winter) while in the SP-1 record (gray line record) is located even earlier in the winter 2005. What is the dating error of the snowpits?*

Response: The "gray line" and the "black line" represent different snowpits (SP-1 and SP-2, respectively). The depth-age profiles of these two snowpits are slightly different (by ~ 5 cm), which means, for example, the depth of 2005 spring peak in SP-1 is ~5 cm different from that in SP-2. This is shown clearly in Figure 1d. Additionally, not only the depth(s) of the spring peak in SP-1 (gray curve) is different from that in SP-2 (black curve), but also the summer nitrate peaks. This difference is due to the spatial variability of snow accumulation rate, i.e., blowing snow by wind after snowfalls, which is usually referred to as the so-called 'snow drafting' phenomenon (e.g., (Lenaerts et al., 2014)). Snow drifting results in difference in the depth-age profiles of snowpits and ice cores is commonly observed, for example, the depth-age profiles of two ice cores drilled at Summit, Greenland at the same time in 2007 summer are off by ~10 cm on average, although the two cores were drilled only 10 meters away from each other (Geng et al., 2014).

Major comment 4: *When calculating the winter means (fig.1 c), blue dots overlap with two red dots (2004/2005), how were winter and spring delimited then?*

Response: As we responded to the last comment, SP-1 and SP-2 (or SB in terms of isotopic data) are different snowpits (i.e., two different datasets) with slightly different depth-age profiles due to spatial variability in snow accumulation rate. In each dataset, we calculated the spring 2005 mean from samples within the depth range of the spring 2005 peak, the winter mean from samples beyond the depths of summer and/or spring peaks, and compared them within a dataset (e.g., we don't compare the spring mean from SP-1 to the winter mean from SP-2). Because of the spatially variability of snow accumulation rates, the depths of nitrate peaks in SP-1 and SP-2 are slightly different (Fig.1 d, not only the 2005 spring peak, but also the summer peak of 2005 and other summer nitrate peaks), which makes two samples in the depth range of the 2005 spring peak in SP-1 appears to be in the depth range of winter snow in SP-2, i.e., the "overlap". We should have labeled the sample dots in each data set with different colors to avoid confusions, which have been done in the revised manuscript.

Major comment 5: *When using the t-test, samples should come from a normal distribution, is this the case for the isotope samples?*

Response: It is difficult to do a normality test due the small number of samples. However, McDonald (2009) suggests that when the sample size is too small, one can combine the residuals (observations minus the mean of observations) of all datasets and look for the normality of the combined residuals. Follow this strategy, we combined the residuals of all data used to perform the t-test in the manuscript, and plotted the histogram of all residuals. The figure is shown below (**Figure S2**), from which we can see the data is approximately normally distributed.

We note that, usually in the literature when t-test is used, the data is assumed to be normally distributed without a test of normality, e.g., (Schauer et al., 2012; Zaarur et al., 2013).

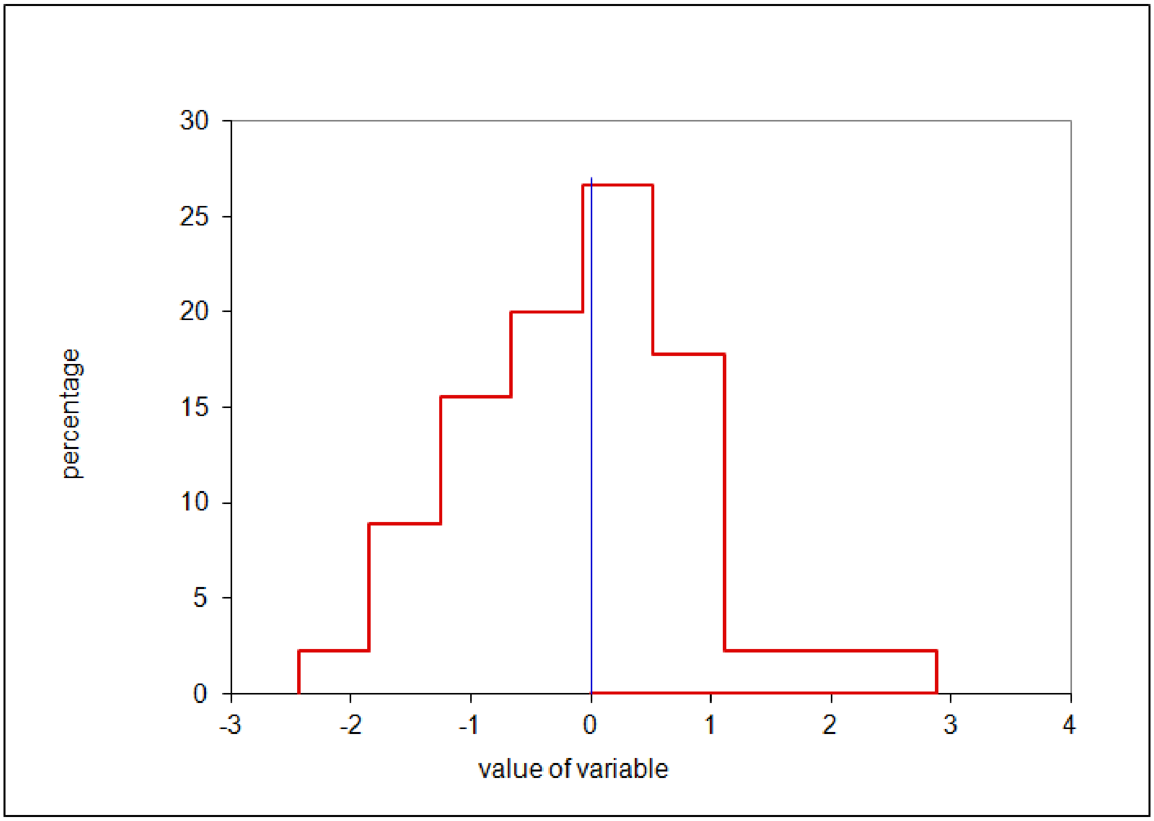

Figure S2: Histogram of the combined residuals of all data used to performed the t-test in the manuscript. Vertical blue indicates the mean of the residuals.

Minor comments:

P.3.L.7: NOx are emitted; P.3.L.9: cycle; P.8.L.17: following; P.14.L.26: NOx that are

Response: We thank the review for pointing these. These have been corrected in the revised manuscript.

P.6.L.14: which kind of plastic bags? Where they pre-cleaned?

Response: The tools and containers have been cleaned in the lab with 18 MΩ water before bringing to the field. These are noted in the revised manuscript.

P.7.L.19: were samples filtered before isotopic analyses?

Response: Polar snow and ice core samples are usually very clean so that no filtration is required before lab analysis. However, in this study, we extracted nitrate from the melt water of snow samples by using ion-exchange resin, and frit filters were placed at the top and bottom of the resin column in order to hold the resin in place.

P.8.L.18: indicate the bacteria strain

Response: The bacteria strain, *Pseudomonas aureofaciens* , is already listed in this section when we describe the analytical procedures in UW IsoLab.

P.13.L.20: state the accumulation rate at Summit during the study period.

Response: We will add the mean weekly snow accumulation rate during the period of 2004 to 2007.

Reference:

Geng, L., Alexander, B., Cole-Dai, J., Steig, E. J., Savarino, J., Sofen, E. D., and Schauer, A. J.: Nitrogen isotopes in ice core nitrate linked to anthropogenic atmospheric acidity change, Proceedings of the National Academy of Sciences, 111, 5808-5812, 10.1073/pnas.1319441111, 2014.
Lenaerts, J. T. M., Smeets, C. J. P. P., Nishimura, K., Eijkelboom, M., Boot, W., van den Broeke, M. R., and van de Berg, W. J.: Drifting snow measurements on the Greenland Ice Sheet and their application for model evaluation, The Cryosphere, 8, 801-814, 10.5194/tc-8-801-2014, 2014.
McDonald, J. H.: Handbook of Biological Statistics 2nd ed., Sparky House Publishing, Baltimore, Maryland, 2009.
Schauer, A. J., Kunasek, S. A., Sofen, E. D., Erbland, J., Savarino, J., Johnson, B. W., Amos, H. M., Shaheen, R., Abaunza, M., Jackson, T. L., Thiemens, M. H., and Alexander, B.: Oxygen isotope exchange with quartz during pyrolysis of silver sulfate and silver nitrate, Rapid Commun. Mass Spectrom., 26, 2151-2157, 10.1002/Rcm.6332, 2012.
Zaarur, S., Affek, H. P., and Brandon, M. T.: A revised calibration of the clumped isotope thermometer, Earth Planet. Sc. Lett., 382, 47-57, http://dx.doi.org/10.1016/j.epsl.2013.07.026, 2013.

Point-to-point response to Reviewer 2:

We thank the reviewer very much for reviewing our manuscript, especially for pointing out the grammatical and technical errors. However, we do not agree with the reviewer on almost all of this reviewer's comments on the scientific parts. Please refer to the detailed discussions we provide below in response to each of the reviewer's comments. The comments are in italics, followed by the response in normal font.

Comment Summary:

Geng et al. offer an explanation for an episodic spring peak in nitrate concentration found in snow at Summit, Greenland. The authors hypothesize that increased UV radiation during these springs, due to lower total column ozone, leads to higher photolytic production of OH from O3 and other precursor molecules, and consequently an increase in nitrate formation and deposition. Much of the spring nitrate may be derived from NOx emitted from the snow by photolysis of nitrate. In support, the authors argue that a spring nitrate peak in a three year snowpit is characterized by lower Δ17O relative to winter values. Since O3 imparts a high positive Δ17O (and δ18O) signature to nitrate, this decrease is taken to reflect a proportional increase in oxidation of NO2 to nitrate by OH, for which Δ17O is effectively zero. Additionally, 19 spring peaks in a nearby ice core are taken to coincide with average or low overhead O3 levels. Such spring nitrate peaks are only observed in Greenland ice cores after ~1900-1960, depending on the record, presumably because nitrate concentrations in the snow were insufficiently high prior to an anthropogenic contribution.

The nature of this work is relevant, the hypothesis is interesting, and the submission is well suited to this journal. The authors' conclusions are substantial, but I believe they are overstated and not soundly supported by the data they present. Their argument stems from what is basically *a single data point (the 2005 spring nitrate peak) in a snowpit that contains more isotopic variability and dating uncertainty than the authors acknowledge. This leads to a discussion that is highly speculative and does not fully consider the effects of nitrate photolysis in snow. I elaborate on these points in the comments below, but without a larger isotopic dataset to build confidence in their arguments I unfortunately cannot recommend this manuscript for publication.*

Response: Overall, this reviewer thought our "*work is relevant, the hypothesis is interesting, and the submission is well suited to this journal"*. However, the reviewer stated that our argument "*stems from what is basically a single data point (the 2005 spring nitrate peak)* ", and thus our discussion is highly speculative. We don't agree with the reviewer on this. As stated in the abstract, we used isotopic data from **two snowpits** as a case study to discern the nature of the 2005 spring nitrate peak. Based on our discussion and calculations, we conclude that the occurrence of this spring nitrate peak is due to enhanced local photochemistry (due to enhanced OH concentration, and also increases in snow-sourced NO_x concentration), as indicated by the relatively low $\Delta^{17}O(NO_3^-)$ values during the 2005 spring peak. We hypothesized that the enhanced photochemistry resulted from a low column ozone abundance during that spring, based on observations of total column ozone abundance. To determine whether or not the interpretation of this case represents the nature of all spring nitrate peak observed in the other years for which we did not measure, we further examined previously reported snowpit isotopic data from Hastings et al. (2004) (see details later), and compared an ice core record of spring nitrate peaks with column ozone abundance records. The Hastings et al. (2004) data shows a spring nitrate peak in 2000 when column ozone abundance was low, and the oxygen isotopic signature $\delta^{18}O(NO_3^-)$ in the 2000 spring is $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ is anomalously low relative to the other springs in that snowpit. In addition, the ice core and column ozone abundance records indicate that in most years (though not all) that the spring nitrate peak coincides with low column ozone abundance. It is based on all of the above arguments that we hypothesize that the occurrence of the spring nitrate peak after ~1960 observed in Greenland ice cores is likely the result of enhanced anthropogenic reactive nitrogen contribution and inter-annual variability of stratospheric ozone abundance. We stated in the manuscript that highly resolved data from more snowpit samples is required to verify this hypothesis, but clearly, our argument/conclusion is not based on "*one single data point* ".

In addition, we want to note that, it is difficult to obtain isotopic data covering specifically the years with a spring nitrate peak, because 1) the appearance of the spring nitrate peak is occasional, for example, in the 2 meter deep snowpit we measured, only one spring nitrate peak was found; 2) For reliable isotopic measurements, more than 200 nmol nitrate is required for each sample. This requires ~ 120 g ice assuming an average snow nitrate concentration of 100 ng/g. This means it is almost impossible to measure high resolution isotopic data (< 3 cm per sample to reveal the seasonal differences of isotopic signal) from polar ice cores (usually a 10 cm diameter ice tube) to reveal clear seasonal signals of nitrate isotopes (but can be obtained from snowpit samples as collecting large snow blocks is relatively easy).

The reviewer highlighted in the comment summary that we "*does not fully consider the effects of nitrate photolysis in snow".* By reading the detailed comment on this point the reviewer elaborated below, we think that the reviewer misinterpreted the discussions on snow nitrate photolysis in Frey et al. (2009) and Erbland et al. (2013). In particular, we think the reviewer ignored one aspect of the snow nitrate photolysis discussed in Frey et al. (2009) and Erbland et al. (2013), which is the recycling of nitrate between surface snow and the above atmosphere (i.e., the so called "**A dynamic equilibrium at the air–snow interface at Dome C in summer"** in

Section 4.2 of Erbland et al. (2013)). It is this process we discussed in our manuscript. There is another process related to snow nitrate processed discussed in Frey et al. (2009) and Erbland et al. (2013), which is the oxygen isotope exchange between nitrate photoproducts and water occurring in the so-called "disordered surface transition region (Domine et al., 2013) " or "disordered interface (Kahan et al., 2014)" of a snow grain surface (previously called as quasi-liquid layer, e.g., in (Frey et al., 2009)). We think the reviewer overstated the importance of this process, because this is a very slow process as indicated by the small isotope fractionation constant of $\Delta^{17}O(NO_3^-)$ (-2 ‰ to 4 ‰ calculated in Erbland et al. (2013)), and it is not important at all at sites with high snow accumulation rate (Figure 8, (Erbland et al., 2013)). The reason is that nitrate photoproducts do not stay in the disordered interface very long before escaping to the interstitial air, minimizing the oxygen isotope exchange. Only in the East Antarctic Plateau, where extremely low snow accumulation rates ensure that snow nitrate stays in the photolytic zone for a sufficiently long duration (> 10 years, with > 90% nitrate loss through photolysis (Erbland et al., 2013)), that the accumulated effect of isotope exchange in the disordered interface results in measurable decreases in $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ of nitrate remaining in snow. While in sites with relatively high snow accumulation rates (e.g., coastal east Antarctic sites reported in Erbland et al. (2013)), this effect is negligible. In particular, in Figure 8 of Erbland et al. (2013), it is clearly illustrated that at sites with annual snow accumulation rates greater than 100 kg/m^2/yr, the effect of isotopic exchange in the disordered interface is non-detectable. Summit, Greenland has a very high snow accumulation rate of ~ 260 kg/m^2/yr (Cole-Dai et al., 2013), thus the process in the disordered interface specified by the reviewer is not expected to be significant at Summit. Please refer to our response to **"Major Comment 4"** below for more details.

Below, we provide our point-to-point response to the reviewer's comments.

Major comments:

Major comment 1: *Is the spring 2005 Δ17O out of the ordinary?*

This paper rests on the Δ17O of nitrate during a spring concentration peak being anomalously low, thereby reflecting an increase in nitrate produced by OH oxidation. To me, a difference in Δ17O of ~1.7 ‰ between the spring of 2005 and the average winter value is not large (page 9411, line 21). The Δ17O differences between winters alone (e.g., the 2005/2006 and 2006/2007 winters) and between the two sets of samples at similar depths (e.g., at ~0.8 m) appear on the order of 1-2 ‰. I just do not see how it can be concluded from this dataset alone that spring nitrate peaks are always characterized by low Δ17O.

The authors do provide a t-test, which is indeed significant based on the data points they have chosen, but the selection of points is not well explained nor do I think justified. Why, first and foremost, were data from all winters included? If early spring Δ17O should normally (i.e., average O3 springs) be similar to the preceding winter Δ17O (page 9411), then a comparison between spring 2005 and all winters is implicitly making the assumption that all winter Δ17O is the same, or in statistical terms, that all winter nitrate is drawn from the exact same sample population. If the Δ17O of an ordinary O3 spring should be similar to the winter immediately preceding it, then it would make much more statistical and logical sense to test, should additional data become available, the paired differences between a winter and its following spring for years with and without a spring nitrate peak.

As it stands, the authors' use of a t-test seems statistically inappropriate and misleading. Also, it is not stated if the t-test took into account the non-equal sample sizes and why data from what is labeled as spring 2006 in Fig. 1 were included in the winter averages?

Response: We don't agree with the reviewer. It is true that $\Delta^{17}O(NO_3^-)$ varies between different winters (e.g., ± 1.1 ‰, 1σ of the SP-1 data). It is because of this variability that we compared $\Delta^{17}O(NO_3^-)$ of the spring peak to the mean winter value over the 3-year period including the variations within a winter and/or between different winters, in order to determine whether or not the $\Delta^{17}O(NO_3^-)$ value of the spring peak is out of ordinary or still within the range of winter $\Delta^{17}O(NO_3^-)$ variability. In particular, the reviewer critiqued " *The Δ17O differences between winters alone (e.g., the 2005/2006 and 2006/2007 winters) and between the two sets of samples at similar depths (e.g., at ~0.8 m) appear on the order of 1-2 ‰".* As we stated earlier, although winter $\Delta^{17}O(NO_3^-)$ values vary (e.g., (32.9 ± 1.1) ‰ of SP-1 data), $\Delta^{17}O(NO_3^-)$ of the spring 2005 peak (e.g., (31.1±0.6) ‰ of SP-1 data) is beyond the low-end of winter variability based on one side t-test. Additionally, the two datasets of $\Delta^{17}O(NO_3^-)$ were measured in different labs (SP-1 measured in LGGE, SB measured in UW IsoLab) and small inter-laboratory discrepancies could exist. Therefore we examined these two dataset independently, i.e., comparing $\Delta^{17}O$ (NO_3^-) of the spring peak with the winter mean in each individual dataset, which gave comparable results.

The reviewer also critiqued " *I just do not see how it can be concluded from this dataset alone that spring nitrate peaks are always characterized by low Δ17O".* **However, we never made this, or any similar conclusions/statements in the manuscript.** As we emphasized in the abstract, this work is a "case study". We learned from the results of the two snowpits that the spring 2005 nitrate peak has a relatively low $\Delta^{17}O(NO_3^-)$ and which is associated with the enhanced local photochemistry resulting from significant stratospheric ozone loss at that time. This ***suggests*** a link between stratospheric ozone loss and the spring nitrate peak. Inspired by this, we examined the results from Hastings et al. (2004) and found a similar link as that in 2000 spring when column ozone abundance was low and a nitrate peak with relatively low $\delta^{18}O(NO_3^-)$ was measured. We further examined an ice core records, and found that most of the years with a spring nitrate peak are also years with low overhead ozone column abundance. It is based on all of these that we hypothesize that the spring nitrate peaks observed in the industrial era are likely due to the combined effect of anthropogenically enhanced NO_x source and the inter-annual variability of stratospheric ozone abundance. We already stated in the manuscript that this hypothesis can be verified by additional isotopic data covering more spring nitrate peaks, although available date in 2005 spring and 2000 spring support it.

In terms of the T-test, as we discussed earlier, it is appropriate to compare with the multi-winter mean, as we have to consider the possible range of variation in winter $\Delta^{17}O$ (NO_3^-). Even if we considered the reviewer's argument to just compare $\Delta^{17}O$ (NO_3^-) of the spring peak and that in the prior winter, it is apparent from Figure 1c that there is a decreasing trend in $\Delta^{17}O(NO_3^-)$ from winter snow layers to the layers of the spring nitrate peak. Qualitatively, this still suggests nitrate in the spring peak is of different (low) $\Delta^{17}O(NO_3^-)$ signature relative to winter nitrate.

The reviewer also stated "*....it is not stated if the t-test took into account the non-equal sample sizes"*. This is a strange statement, as it is known that T-test can be used to compare two datasets with different sample population and different variance, and the method is used frequently in the literature to compare the difference of two data group of lab measurements (e.g., (Schauer et al., 2012; Zaarur et al., 2013)). The calculation of the 't' value accounts for differences in sample size and variance, and the P value is also obtained based on DOF (degree of freedom, a function of sample sizes, and we have given this in the results of our T-test). Thus we don't understand the reviewer's point here.

Finally, indeed when we calculated the winter mean, we included some of spring/early spring values (the springs without a nitrate peak). In springs without a significant stratospheric ozone loss, $\Delta^{17}O(NO_3^-)$ is similar to winter values. This is consistent with the model calculation in Kunasek at al. (2008). The fact that the $\Delta^{17}O(NO_3^-)$ from the other springs is nearly identical to their preceding winter values further suggests that the spring 2005 $\Delta^{17}O(NO_3^-)$ value is anonymously low.

Major comment 2: Justification with additional isotopic data

As additional isotopic evidence, the authors point to δ18O in a snowpit from Hastings et al. (2004) since, like Δ17O, δ18O is also be lowered by OH (page 9421). After looking at this paper, however, I do not see how their justification is valid. First, in referring to the findings of Hastings et al., Geng et al. write that "At the same time, the mean δ18O(NO3-) in the spring of 2000 (69.8 +/- 2.1) ‰ is significantly lower than that in the prior winter (77.5 +/- 2.4) ‰" (page 9421, line 8/9). There is, however, no winter prior to the spring of 2000 in this work. The 77.5 ‰ value is from the winter after (i.e., 2000/2001, see Table 2 in Hastings et al.). Second, the spring of 2000 is at the bottom of the pit and while Hastings et al. do report averages, it should have been acknowledged, in both studies, that the season could easily have been cutoff and not fully sampled. Finally, Hastings et al. explicitly state that the dating was not exact (Section 2.3: "We have not attempted to precisely date the snowpits and our seasonal binning of the isotope data makes the assumption that there has been no migration or re-organization of NO3- within the snowpack. Therefore, our assignments of season and the seasonal averages are susceptible to uncertainties. However, the δ18O of snow, which is highly correlated with seasonal temperatures in Greenland [e.g., Grootes and Stuiver, 1997], qualitatively corroborates the seasonal binning for winter and summer, respectively (see Results section)."

Response: We thank the reviewer for pointing this out. I was a bit enthusiastic when I found that the isotopic data reported by Hastings et al. (2004) is consistent with our hypothesis, so that when I wrote that I mistakenly treated the winter 2001 $\delta^{18}O(NO_3^-)$ value as that of winter 2000. However, we think the data in Hastings et al. (2004) is indeed consistent with our hypothesis. From Table 2 of Hastings et al. (2004), in spring 2000 when column ozone abundance is low (as shown in Figure 3 of this study), $\delta^{18}O(NO_3^-)$ is (69.8 ± 2.1) ‰, compared to (70.5 ± 2.4) ‰ in summer 2000. In contrast, $\delta^{18}O(NO_3^-)$ in winter, spring and summer 2001 are (77.5 ± 2.4) ‰, (77.4 ± 1.9) ‰, and (68.9 ± 2.1) ‰, respectively. This data shows that in 2001, spring $\delta^{18}O(NO_3^-)$ values are similar to the winter values and higher than the summer values over the entire record (covering from 2000 spring to 2001 summer). However, in 2000, the spring $\delta^{18}O(NO_3^-)$ is almost identical to the summer value ((69.8 ± 2.1) ‰ vs. (70.5 ± 2.4) ‰). There is no reason to expect winter $\delta^{18}O(NO_3^-)$ values to be similar or close to that of summer (if so, the seasonality of $\delta^{18}O(NO_3^-)$ should not exist). In addition, $\delta^{18}O(NO_3^-)$ in 2000 spring, when the ozone column abundance is low, is apparently lower than that in 2001 spring ((69.8 ± 2.1) ‰ vs. (77.4 ± 1.9) ‰). Therefore, it seems that the Hastings et al. (2004) data is consistent with our hypothesis, as in addition to the isotopic anomaly in 2000 spring, a nitrate peak (concentration of (2.7 ± 1.1) μmol/L vs. (2.5 ± 1.2) μmol/L and (2.8 ± 1.5) μmol/L in summers) also presents. We have revised this part accordingly in the manuscript.

Regarding the dating precision, Hastings et al. (2004) did state that ***"our assignments of season and the seasonal averages are susceptible to uncertainties"***, but then, Hastings et al. (2004) emphasized that **"However, the $\delta^{18}O$ of snow, which is highly correlated with seasonal temperatures in Greenland [e.g., Grootes and Stuiver, 1997], qualitatively corroborates the seasonal binning for winter and summer, respectively (see Results**

section)”. This indicates that the age (winter, or summer) of snow layers identified by the method of seasonal binning (i.e., combine snow accumulation data and snow profile density) is consistent with that identified by snow water isotopes. In other words, winter or summer snow identified by seasonal binning corresponds to annual minimum or maximum of $\delta^{18}O(H_2O)$. As long as the winter and summer snow layers are identified, we don't see a problem to assign snow layers between the winter and summer layers as spring (or fall for layers between summer and winter).

Major comment 3: Dating

Given the very small differences the authors are trying to resolve, independent and accurate dating is critical. Using nitrate as a summer peak to help date the nitrate peaks does not seem independent. Nitrate may be a fairly reliable summer indicator, but is there ever a split summer peak or a spring peak without a summer peak? The two dating methods disagree on whether the latter is true for peak 4 in Fig. 1. The authors claim this discrepancy is due to minimal snowfall and accumulation of dry deposition, but what is the support for this? I was under the impression that wet deposition of nitrate was much more important than dry deposition at Summit. What was the basis for identifying “early” spring samples, since this is what is stated to be similar to the winter values, or for distinguishing the spring/winter boundaries for your averages? This is particularly critical for peak 3’. It looks like a matter of centimetres could separate the assignment of early/late or spring/winter. However, nitrate and sodium concentrations (which were ultimately chosen to date the pit as Method A) were not measured on the same UW samples run for $\Delta 17O$ (SB) and this introduces error in comparing samples with different depths and depth ranges. Also, it does not appear that ions other than nitrate were measured on the LGGE samples, so the dating of nitrate in SP-1 seems to depend on itself and comparison with UW *samples that, again, are not necessarily from the same depths. This would not be such a problem if there were more than one spring nitrate peak to look at.*

The dating of nitrate in the ice core is also not clearly explained. The division of years was based on the spring calcium peak, but it is not clear if identifying individual spring nitrate peaks required that they coincide with the calcium peak since it is written that the 19 spring peaks since 1960 were obtained by subtracting total calcium peaks from total nitrate peaks in this period (page 9410, line 3-5). This gets back to the question of whether there could be split summer peaks or a spring peak without a summer peak or something else? Looking at Fig. 2, spring peaks 1, 3 and 4 (if counting left to right) look as if they actually come before the winter sodium peak in panel c.

Response: We agree that it is impossible to precisely date each data point. Indeed, this is almost impossible in ice core research. However, we disagree with the reviewer that it is necessary to precisely date each data point in this work. Our goal in this study is to identify a spring nitrate peak out of the regular summer peaks from the snowpit samples we measured. The combination of the two dating methods, which generally agree with one another, clearly identifies the 2005 spring nitrate peak. In other words, we are confident about the seasonality of the dating methods, on which our subsequent analysis rests.

Although any dating method of course has uncertainties, as stated in Hastings et al. (2004), the seasonal information of snow layers identified by the seasonal binning method is consistent with the seasonality of water isotopes. Similarly, in this study, the two methods we used, method A of using nitrate and sodium seasonal peaks, and Method B of using seasonal binning, produced good agreements on the seasonality of snow layers, except for the age of snow at the depth of 2 m (approximately in 2004 spring to summer). The reason as we explained in the manuscript is due to minimal snowfall at this time and the accumulation of dry deposition of nitrate. The following figure (**Figure** 1S) illustrates there was little snowfall from March to July of 2004:

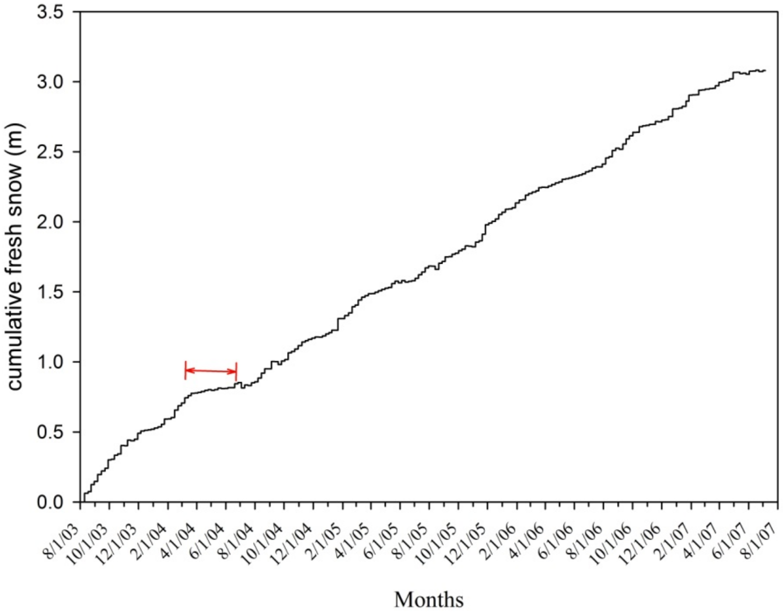

Figure 1S. Fresh snow accumulation at Summit from 2003 to 2007. The red arrow indicates the period from late spring of 2004 to summer of 2004, when only very little snow was accumulated. We think this little snow accumulation under the period labeled by the red arrow is because of lack of snowfalls, instead of wind drifting after snowfall. Since the snow accumulation data are weekly resolved, if there were significantly gain and loss of snow, the curve will display up and down features instead of nearly flat as observed.

Regarding the occurrence of nitrate dry deposition at Summit, indeed wet deposition dominates at Summit, but dry deposition does also occur. *Bergin et al.* (1995) concluded that less than 10% of snow nitrate at Summit is through dry deposition, but the conclusion was based on one summer's observations and only considered dry deposition of particulate nitrate (gas phase HNO_3 is the dominant form of atmospheric nitrate at Summit). In addition, *Dibb et al.* (1998) observed a significant increase in surface snow nitrate concentration in 6 days without snowfall or ice fog, which is due at least in part to the dry deposition of nitrate, though *Dibb et al.* suggested the atmospheric concentration of HNO_3 is not high enough to account for their observed increase in surface snow nitrate concentration.

The reviewer critiqued "*Using nitrate as a summer peak to help date the nitrate peaks does not seem independent"*. We used nitrate summer peak as a summer layer indicator, and sodium winter peak as a winter layer indicator. These are independent, and dating by seasonal peaks is not the only dating method we used in the manuscript. We note that sodium usually is not used to date Greenland ice cores because 1) oceanic storms could result in episodic sodium peaks due to the close location of Greenland to the marine sea salt source, 2) calcium is a better indicator. However, as seen in Figure 2 of this study, in general, one sodium peak corresponds to one calcium peak in the depth range of a year. This suggests that at Summit, sodium is also a good dating proxy. By using sodium and nitrate peaks in the snowpit samples, and the seasonal binning method, we think the winter and summer snow layers are clearly identified.

Knowledge of which season a particular species peaks is obtained by measuring samples from surface snow (where annual layers are still very thick to ensure high resolution, because the effect of gravitational compression is not significant near the surface), and comparing with the variations in the strength of the relevant source of that species (e.g., (Whitlow et al., 1992)). For ice core samples, the annual peak of a certain ion can be still detected, but it is difficult to observe the phenomenon that, for example, a winter sodium peak is strictly before a spring calcium peak, and the spring calcium peak is strictly before a summer nitrate peak. At depth, due to the compression of snow gravity, all peaks of species in a single year usually appear at a similar depth range and it is difficult to discern which one proceeds the other. This is illustrated in Figure 2 of this study that in the shallow ice core, the winter sodium peaks and spring calcium peaks always appear at similar depths. In order to examine how frequently the spring nitrate peak appeared in the past, the best we can do in ice cores is to count the number of years in a depth range (indicated by the number calcium peaks) and compare this to the total number of nitrate peaks in the same depth range. The number of times that total nitrate peaks exceeds the total of calcium peaks indicates the number of spring nitrate peaks in that depth (and time) range. In other words, the existence of two nitrate peaks between two calcium (or sodium) peaks is indicative of a year with a spring nitrate peak.

The reviewer also asked "*whether there could be split summer peaks or a spring peak without a summer peak or something else?"* We can't say that this is impossible, but it would be inconsistent with what we know about the chemistry of nitrate production in the polar regions, and inconsistent with previous observations. Nitrate production from its precursors is enhanced in polar summer by photochemistry, that is why a predominant summer nitrate peak is observed in numerous Greenland ice core records (e.g., (Burkhart et al., 2006; Whitlow et al., 1992; Yang et al., 1995)). In the industrial era, a bimodal distribution of nitrate concentration throughout some years is observed, the additional peak of nitrate is recognized as late winter/early spring peak (e.g., (Burkhart et al., 2006; Whitlow et al., 1992; Yang et al., 1995).

Major comment 4: Nitrate photolysis and snow-sourced NOx

Page 13, lines 14-27: It is true that nitrate photolysis may lower Δ17O in the snow, but the mechanism from the Erbland et al., 2013 paper you cite (which follows the Frey et al., 2009 work cited and McCabe et al., 2005, JGR, 110, D15310) is not consistent with the expected effects you describe here. These papers suggest that the apparent lowering of Δ17O and δ18O in East Antarctica is due to the products of nitrate photolysis (e.g., NO2) being re-oxidized to nitrate by OH/H2O in the liquid like layer (LLL). This aqueous phase chemistry is not the gas phase re-oxidation you describe on this page and argue should not lead to nitrate preserved with a Δ17O lower than tropospheric nitrate in a typical spring (page 9413, lines 24/25). The latter may be true for the gas phase NOx which escapes the LLL and is oxidized back to nitrate in the *firn or above the surface, but the remaining nitrate should now be lower in Δ17O (and presumable higher in δ15N).*

Response: We don't agree with the reviewer. We have briefly discussed this point at the beginning where we responded to the "Comment Summary". Here we explain in more details that why we think the reviewer ignored one aspect of snow nitrate photolysis and overstated the other.

In Frey et al. (2009) and Erbland et al. (2013), they actually discussed two regions of snow layers with different isotopic exchange/fractionation processes related to snow nitrate photolysis. In Frey et al. (2009), the last sentence of second paragraph in Section 4.3 states: " **We therefore suggest the existence of two regions, a skin layer with isotope ratios close to atmospheric equilibrium and high NO_3^- concentrations and the snowpack underneath strongly depleted in NO_3^- and therefore enriched in δ^{15}N**." Frey et al. (2009) then described the equilibrium between surface snow and the overlaying atmosphere as photo-chemically released NO_x and HONO diffusing to the atmosphere above snow, "**where eventually all reduced species are oxidized again to NO_3^- and re-deposited to snow**". In Erbland et al. (2013), Section 4.2, this air-snow equilibrium process was further interpreted as "**A dynamic equilibrium at the air–snow interface at Dome C in summer"**. In this same section, Erbland et al. (2013) described that in spring, UV radiation starts to cause NO_x emissions form snowpack, and then the re-oxidized NO_3^- (referred to as snow-sourced nitrate) in the atmosphere with low Δ^{17}O values results in a lower atmospheric $\Delta^{17}O(NO_3^-)$ than $\Delta^{17}O(NO_3^-)$ in the snow skin layer (Figure 6, (Erbland et al., 2013)). Since the skin layer nitrate reservoir is on average 100 times larger than the atmospheric nitrate reservoir (Erbland et al., 2013), lower $\Delta^{17}O(NO_3^-)$ in the skin layer caused by the re-deposition of snow-sourced nitrate is delayed compared to that in the atmosphere (the difference gets smaller as summer approaches when the snow-sourced nitrate increases as the result of increasing UV radiation).

It is this process that will potentially erase any stratospheric nitrate $\Delta^{17}O$ signature, if this process is significant at Summit.

In terms of the process occurring in the disordered interface of snow grain surface, i.e., **"the oxygen isotope exchange between the nitrate photoproducts and water molecules from the surrounding ice**" (Erbland et al., 2013), which is used to explain the decrease of $\Delta^{17}O(NO_3^-)$ (as well as $\delta^{18}O$) from the snow skin layer (or the top ~2 cm snow layer) to snow layers at depth (~50 cm), and is observed only in the East Antarctic Plateau. Frey et al. (2009) and Erbland et al. (2013) found that in the plateau, $\Delta^{17}O(NO_3^-)$ (and also $\delta^{18}O(NO_3^-)$) decreases from surface snow to a depth of ~ 50 cm, where $\Delta^{17}O(NO_3^-)$ becomes stable which they defined as "asymptotic $\Delta^{17}O(NO_3^-)$" (Erbland et al., 2013). This decrease in oxygen isotopic signals of nitrate remaining in snow was interpreted as the oxygen isotope exchange between nitrate photoproducts and water in the disordered interface, before the photoproducts escape from that interface. However, the oxygen isotopic effect associated with this process in the disordered interface is very small, as reflected by the small fractionation constant of $\Delta^{17}O(NO_3^-)$ calculated by Frey et al. (2009) and Erbland et al. (2013): varying from -2 ‰ to 4 ‰. The reason, although not specified in Frey et al. (2009) and Erbland et al. (2013), is likely because the photoproducts of nitrate readily escape to the interstitial air. This means the duration of nitrate photoproducts in the disordered interface is very short, which limits the effectiveness of oxygen isotope exchange with water. Only when snow nitrate stays in the photolytic ozone for sufficiently long (e.g., > 10 years in the East Antarctic Plateau, with > 90% net loss of nitrate via photolysis), the accumulated effect of isotope exchange with water will lead to a measurable decrease in snow $\Delta^{17}O(NO_3^-)$ and

$\delta^{18}O(NO_3^-)$. The duration that snow nitrate stays in the photolytic zone is determined by snow accumulation rate (Zatko et al., 2013), thus only in the East Antarctic Plateau where the snow accumulation rate is extremely low that an apparent decrease in $\Delta^{17}O(NO_3^-)$ from surface snow to asymptotic $\Delta^{17}O(NO_3^-)$ is observed, as illustrated in Figure 8 in Erbland et al. (2013). In particular, in locations with snow accumulation rates greater than 100 kg/m^2/yr in East Antarctica (Figure 8, (Erbland et al., 2013)), the oxygen isotope exchange in the disordered interface is negligible. At Summit, the annual snow accumulation rate is 26 cm/yr in water equivalent size (260 kg/m^2/yr) (Cole-Dai et al., 2013), thus the effect of oxygen isotope exchange between nitrate photoproducts and water in the disordered interface is not expected, as the observations from this study.

We note that although the isotopic effect in the disordered interface for nitrate is negligible at Summit, the post-depositional processing of nitrate is not. As shown in Figure 8 in Erbland et al. (2013), it is apparent that in coastal Antarctica with relatively high snow accumulation rates, asymptotic $\delta^{15}N(NO_3^-)$ (similar to the definition of asymptotic $\Delta^{17}O(NO_3^-)$) is significantly enriched compared to $\delta^{15}N(NO_3^-)$ in surface snow, indicating the existence of active post-depositional processing. But asymptotic $\Delta^{17}O(NO_3^-)$ is indistinguishable from $\Delta^{17}O(NO_3^-)$ in surface snow, indicating a negligible oxygen isotopic effect from processes in the disordered interface.

Comments: *This leads into the problems I have with the suggestion that much of the extra nitrate in a low-O3 spring could be snow-sourced. First, I am not sure how more photolysis of nitrate in the snow, i.e., more nitrate loss, leads to more nitrate gain? If what you are trying to describe is accumulation of re-oxidized nitrate at the surface from deeper in the snowpack, which may explain the very high surface (top few mm) concentrations in East Antarctica but which is not* *preserved with burial due to photolysis, then you should see decreases in Δ17O in the snow below. This is problematic since it means that if photolysis is occurring, and is occurring to such a degree that it is providing a significant amount of NOx to the overlying atmosphere, then you should have alteration overprinting your Δ17O record via the condensed phase chemistry suggested by Erbland, Frey and McCabe. Following from this, if there is significant photolysis occurring in early spring – when, going off the solar zenith angles calculated in the TUV model, the sun is only above the horizon for about 6 hours a day in mid-Feb and 12 hours a day in mid-March – then in summer there should be much larger loss and lowering of Δ17O in the snow below (i.e., affecting the spring snow) as photolysis rates are orders of magnitude higher at this time. Following from this, it seems that either nitrate photolysis is relatively insignificant, or you must seriously consider the possibility that alteration has overprinted your record.*

Response: We don't agree with the reviewer on this. In this part of manuscript (i.e., Page 13, lines 14-27), we are discussing the possibility of stratospheric nitrate inputs causing the spring nitrate peak. We excluded this possibility because stratospheric nitrate has very high $\Delta^{17}O(NO_3^-)$, and $\Delta^{17}O(NO_3^-)$ should be well preserved at Summit given the high snow accumulation rate. Indeed, in the East Antarctic Plateau, recycling of snow nitrate will lead to an equilibrium between surface snow and the atmosphere which lowers the oxygen isotope ratios of nitrate in surface snow (Erbland et al., 2013), given the fact that a given layer of snow stays at surface for a long time (e.g., ~ 2 cm/yr snow accumulation rate at Vostok). However, at Summit, the relatively high snow accumulation rate will limit the degree of post-depositional photolysis of snow nitrate (weekly snow accumulation rate is (1.7 ± 1.2) cm snow at Summit in the period of 2005 Feb. to May) compared to East Antarctica. Therefore, it is unlikely for the snow layers with stratospheric nitrate (of high $\Delta^{17}O$) to stay at surface for enough time to allow for sufficient recycling to erase the high stratospheric $\Delta^{17}O$ signal.

The reviewer's suggestion here is based on the assumption that oxygen isotope exchange in the disordered interface of snow grain surface occurs effectively at Summit. However, as we discussed earlier, a measureable effect of this process in the disordered interface, or the so-called " *the condensed phase chemistry suggested by Erbland, Frey and McCabe"* by the reviewer, is only observed in East Antarctic Plateau where snow accumulation rate is extremely low (Figure 8, (Erbland et al., 2013)). At sites with high snow accumulation rates, the oxygen isotope exchange in the disordered interface is negligible so that post-depositional processing of nitrate will affect $\delta^{15}N(NO_3^-)$ only, but not $\Delta^{17}O(NO_3^-)$ and $\delta^{18}O(NO_3^-)$ in remaining snow (Figure 8, (Erbland et al., 2013)). Again, this is because nitrate photoproducts escape readily from the disordered interface to the surrounding air, and are transferred effectively to the overlaying atmosphere via diffusion and wind pumping (Zatko et al., 2013). Only when snow nitrate stays in photolytic zone sufficiently long (e.g., > 10 years in East Antarctic Plateau), the accumulated effect of oxygen isotope exchange in the disordered interface becomes measurable.

Other comments:

Comment 1: *On page 12, the authors calculate a 60 % increase in deposited nitrate during the spring of 2005 (15.1 nmol cm-2) compared to the spring of 2006 (9.4 nmol cm-2). This "extra" nitrate, they say, should be derived from oxidation of NOx by OH (Section 4.2.3). I'll leave the calculations to the authors, but does such a small observed difference in Δ17O fit with what would be expected from mass balance for a 60 % increase in the OH pathway?*

Response: We did not say that the additional nitrate is purely (100%) produced from OH oxidation, but that the total fraction of OH oxidation is enhanced compared to typical springs, resulting in lower $\Delta^{17}O(NO_3^-)$. As we stated in the manuscript, the enhanced local nitrate production is **in large part** due to increased OH concentration, as evident in the $\Delta^{17}O(NO_3^-)$ observations. In addition, as discussed in the manuscript, up to 50% of the additional nitrate could be due to enhanced NO_x concentration from snow nitrate photolysis, if snowpack photodenitrification is the dominant source of boundary layer NO_x at Summit as implied by Thomas et al. (2012). This snow-sourced NO_x could be oxidized to nitrate through other pathways than just OH oxidation, as the lifetime of NO_x at polar snow surface is around one day in spring and summer at Summit (Munger et al., 1999).

In Section 4.2.3., we estimated that if the additional nitrate (60% enhancement) is all from OH oxidation, a 200% increase in OH concentration is required to explain the production of additional nitrate. This is an upper limit estimate for the required increase in OH concentrations because it is unlikely that all of the nitrate is produced through the OH pathway. In section 4.2.3., we discussed that in the condition of a severe stratospheric ozone loss in 2005 spring, OH production from enhanced O_3 photolysis alone is enhanced by 90%. Additional increases in OH may also occur due to enhanced production from the photolysis of snow species (e.g., HONO, CH_2O, H_2O_2), which can easily account for the required degree of OH concentration increase.

Here we provide a quick estimate to assess the value of $\Delta^{17}O(NO_3)$ in the spring of 2005, in the case that the additional nitrate is dominated by production via OH oxidation of NO_2. The calculation is shown below:

$$\Delta^{17}O(NO_3^-)_{spring} = \Delta^{17}O(NO_3^-)_{winter} * (1-f) + \Delta^{17}O(NO_3^-)_{OH} * f \qquad (1)$$

$$f = (F_{2005} - F_{base})/F_{2005} \qquad (2)$$

In equation (1) above, $\Delta^{17}O(NO_3^-)_{winter}$ is the winter mean $\Delta^{17}O(NO_3^-)$ from the SB samples over the winters of 2004/2005 and 2005/2006 (= 32.4 ‰). $\Delta^{17}O(NO_3^-)_{winter}$ represents normal spring $\Delta^{17}O(NO_3^-)$ values in the case of no stratospheric ozone loss (winter and spring $\Delta^{17}O(NO_3^-)$ are similar according to the model of Kunasek et al. (2008) and in the snowpit samples without a nitrate production, and is estimated by the lowest measured summer $\Delta^{17}O(NO_3^-)$ (= 26.8 ‰ in 2005 summer from SB, assuming nitrate is mainly locally produced). We note this may result in an underestimate of $\Delta^{17}O(NO_3)_{spring}$ as the relative importance of HO_2/RO_2 in the NO_x cycle is higher in polar summers than that in springs/winters (Alexander et al., 2009), so that $\Delta^{17}O(NO_3^-)_{OH}$ in polar summers is lower than that in polar springs.

In equation (2) above, F_{2005} is the total flux of nitrate in 2005 spring (15.1 nmol/cm^2), and is estimated by multiplying the mean nitrate concentration in the spring 2005 peak (2.15 nmol/ml) by the depth of snow that contains that peak (7.04 cm water equivalent). F_{base} is the total flux of nitrate in a normal spring (9.4 nmol/cm^2), and is estimated by multiplying the mean nitrate concentration in a normal spring (here we use the spring of 2006 when mean nitrate concentration is 1.34 nmol/ml) by the same depth of snow that contains the 2005 spring peak (7.04 cm water equivalent). Alternatively, F_{base} can be estimated by multiplying the mean nitrate concentration from samples immediately above and below the 2005 spring nitrate peak (1.32 nmol/ml) and the water equivalent depths, which gives similar results (F_{base} = 9.3 nmol/cm^2). The difference between F_{2005} and F_{base} gives the amount of additional nitrate flux in 2005 spring relative to a normal spring (2006), and $f = (F_{2005} - F_{base})/F_{2005}$ gives the fraction of this additional nitrate flux relative to the total nitrate flux in 2005 spring. We note that "f" is different from the "enhancement of nitrate" reported in the manuscript, as the enhancement refers to how much more nitrate is deposited in 2005 spring relative to that in a normal spring and is calculated as (F_{2005} - F_{base})/$\mathbf{F}_{base}$ ≈ 60 %.

Substituting relative values to the above equation 1 and 2, we get **f ≈ 38% and $\Delta^{17}O(NO_3^-)_{spring}$ ≈ 30. 3 ‰, which is similar to the measured values of (30.8 ± 0.8) ‰**. Here we made another assumption that in the spring of 2005, despite increased UV radiation, the recycling of nitrate between air and surface snow is still not able to effectively lower snow $\Delta^{17}O(NO_3^-)$, consistent with the interpretation of high snow accumulation rate regions in Erbland et al. (2013).

Comment: *The analytical uncertainties from the LGGE measurements should be included in Table 1. If anything, these numbers are more important since these samples are the bulk of your isotopic dataset.*

Response: The analytical uncertainties are specifically stated in the method section of SP-1 sample analysis. In Table 1 we just listed analytical uncertainties of the UW IsoLab as we observed something unusual only in UW IsoLab, and thus the editor asked us to add a table to illustrate the details of our results in UW IsoLab.

Comment: *What is the approximate annual layer thickness at the depths where you start to no longer observe spring nitrate peaks in the ice core? And what is the sampling resolution compared to this thickness? The absence of such peaks is not simply a matter of not being able to resolve them, correct?*

Response: The reviewer seems to suggest that the occasional feature of the spring nitrate peak could be simply because the sample resolution is not enough to resolve them in some years. To answer the reviewer's question, we provide the following figure (**Figure** S2). In this figure, we plotted the annual snow layer thickness (m) at Summit from 1800 to 2006. It can be seen that the annual snow layer thickness is relatively constant from 1930 to 1980 (our resolution of ice core samples is approximately 3 cm per sample as stated in the manuscript). This indicates if the reviewer was correct, we should have observed spring nitrate peaks in the period of 1930 to 1960 as frequently as from 1960 to 1980. However, this is not the case (i.e., we don't observe spring nitrate peaks before 1960). In addition, we don't observe significantly more spring nitrate peaks after 1980 than before 1980 (Table 2 of the manuscript).

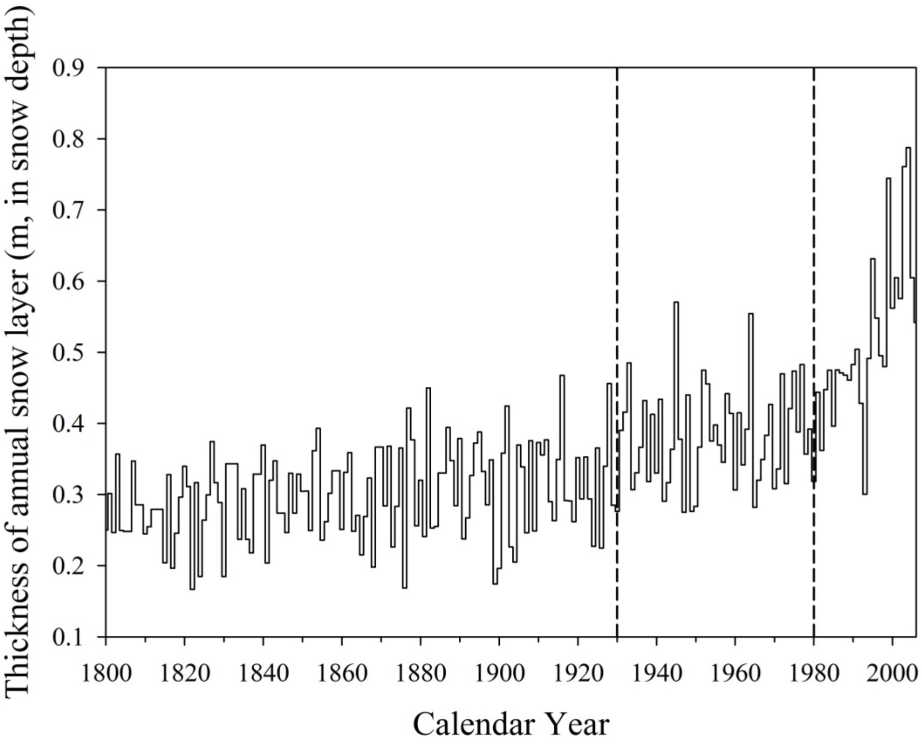

Figure S2. Annual snow layer thickness in the Greenland ice core we used.

Comment: *The spring nitrate peak in the snowpit is preceded by a single winter sodium peak, while the other years show double sodium peaks (I'm not sure if this is a split winter peak or a winter and a spring peak). Is a double sodium peak a common feature in Greenland?*

Response: As we discussed earlier, due to the close location of Greenland to the marine sea salt source, sometimes a single oceanic storm could cause an episodic sodium peak in Greenland snow. This is likely the case for the double peaks observed in the shallower part of the snowpit. But the ice core data of this study reveal almost perfectly one sodium peak and one calcium peak every year. In other words, "a double sodium peak" is not a common feature in central Greenland.

Comment: *Does there seem to be any correspondence between single or double sodium peaks with the spring nitrate peaks you identify in the ice core?*

Response: No, we don't observe this. As shown in Figure 2, there is always one sodium peak with one calcium peak. While during the same depth range, occasional double nitrate peaks exist.

Comment: *Page 08: It is stated that the LGGE samples were processed similarly to the UW samples. Does this mean that the concentration and isotope measurements were not made on the same aliquot of sample? If so, the isotopic samples should be re-named along the lines of the SB samples.*

Response: We have stated in the sampling part of the manuscript, that the SP-1 samples were "**collected in the field every 5 cm from the surface down to the depth of 2.10 m**", while SB samples were obtained from the snow blocks which are "**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**". So there are not the same aliquot of sample.

But we don't understand what the reviewer meant by "*the isotopic samples should be re-named along the lines of the SB sample".* The isotopic samples are already named differently, i.e., samples measured in LGGE are named SP-1, and samples measured in UW IsoLab are named SB (please refer to method part, and Figure 1 of the manuscript).

Comment: *Page 12, line 5-10: Are these calculations made from the raw data or the 3-pt means? It would not be appropriate to use the running averages.*

Response: They are made from the raw data, and what we reported in the Supporting information are also raw data, not 3-point running averages. In Figure 1, we plotted the 3-point running averages because we were looking for the seasonality of snow nitrate concentrations and isotopes and using 3-point running average was to smooth out short-term fluctuations of the data.

Comment: *Page 17, lines 5-6: 302 nm is the peak in the spectral absorption cross section for nitrate (from Chu and Anastasio at 298 K), not nitrate photolysis. The peak wavelength for nitrate photolysis, in a strict sense, is taken in terms of the spectral photolysis rate coefficient (units of s-1 nm-1) since this is a convolution of the absorption cross section, the spectral actinic flux and the quantum yield. See Fig. 5b in the Frey et al., 2009 reference for an example. Additionally, this doesn't reflect "all" nitrate photolysis since the quantum yield is reaction-specific; the Chu and Anastasio yields are for the aqueous phase reaction NO3 - + H+ + hv --> NO2 + OH pathway. Finally, the Chu and Anastasio cross section spans 280-360 nm, so why was the calculation made only for 298-345 nm?*

Response: 302 nm is indeed the absorption cross section for nitrate, and the peak wavelength of nitrate photolysis should be around 320 nm at earth surface (Frey et al., 2009) as the actinic flux reaches the highest level at ~340 nm. This has been corrected in the revised manuscript.

$NO_3^- + H^+ + hv \rightarrow NO_2 + OH$ is indeed only one pathway of the snow nitrate photolysis, but it is the dominant one (see (Frey et al., 2009) and reference therein). The absorption cross section for nitrate is from 280 to 360 nm in Chu and Anastasio (2003), but for wavelength greater than ~340 nm there is only minimum absorption (molar absorptivity of nitrate is almost zero (Chu and Anastasio, 2003)). In addition, since the peak wavelength of nitrate photolysis is ~320 nm, calculation from the range of 298 to 345 nm should represent the great majority of the production.

Comment: *Page 18, lines 2-7: Is a NOx concentration, for the mid-troposphere, averaged over a latitudinal range from 85 N to as far south as Scotland, really comparable to what you would expect for the boundary layer at the centre of Greenland?*

Response: We think it is comparable. We don't know how/why the reviewer got the sense that " *as far south as Scotland"*. The average NO_x concentration from the TOPSE campaign (Stroud et al., 2003) is the only observational data set covering February and March in the Arctic that we can find, and the sampling campaign does include Greenland, as stated in Stroud et. al. (2003):" the TOPSE campaign was composed of a series of seven round-trip deployments between 4 February 2002 and 23 May 2002 with missions generally sampling the mid-to-high latitude troposphere over North America in the corridor originating in Colorado, traversing over Manitoba and Hudson Bay **before ending north of Greenland** and returning back to Colorado". In particular, the data we used is from the tables (Table 1 and 2) in Stroud et. al. (2003), as listed in Tables, **the latitude range for February and March data in general spans from 60N to 80N**, while the latitude of Summit is 72.5 N.

Comment: *Fig. 1: The SP-2 and SB data should not be plotted using the same color and symbol. This gives the appearance that the ion and isotope data are from the same samples. This distinction is important.*

Response: We agree, we have re-labeled the SB and SP-2 data in Figure 1 in the revised manuscript.

Minor comments:

On page 05, the delta notation references are given as N2-AIR and VSMOW. On pages 9407 and 9408, they are written as Air-N2 and V-SMOW. Please be consistent.

Response: We thank the reviewer for pointing this out, we have made the corrections.

Page 9407, line 20: The Silva et al. (2000) reference in Frey et al. (2009) should also be cited since this is where the concentration method ultimately comes from.

Response: We thank the reviewer for pointing this out. But here we are not trying to descript the method in details, and our samples were actually processed and measured in the same lab as in Frey et al. (2009), so we think it is suitable to cited Frey et al. (2009), anybody interested in the method could find the Silva et al (2000) paper easily from reading Frey et al. (2009).

Page 9408: Citations for the international reference standard values should be provided.

Response: We thank the reviewer for pointing this out, we have added the references.

Page 9408: There seems to be inconsistency in the use of δ15N, δ18O and Δ17O compared to δ15N(NO3-), δ18O(NO3-) and Δ17O(NO3-).

Response: We think we used the terminology without problems. We need to switch between $\delta^{15}N$ and $\delta^{15}N(NO_3^-)$ accordingly. For example, when we state " the $\delta^{15}N$ of nitrate from mid-latitudes...", which is different from the statement of "the $\delta^{15}N(NO_3^-)$ from mid-latitudes....".

Page 9408, lines 16/17: grammar: "The rest of samples were processed followed" needs to be fixed.

Response: We thank the reviewer for pointing this out. We have corrected this in the revision.

Page 9410, line 15: The depth range of the SB samples is listed as 0.7-0.75 m, but it looks like 0.7-1.75 m in Fig. 1.

Response: We thank the reviewer for pointing this out, we have this fixed in the revision.

The units for a flux include time-1. See page 9412, lines 6-9.

Response: When we stated "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})" in this part, we meant the total flux in the spring. The unit time is per spring and is involved in the statement.

Page 9412, lines 24-26: grammar: "in the Arctic" not "in Arctic"

Response: We thank the reviewer for pointing this out. We have corrected this in the revision.

The authors sometimes incorrectly refer to reaction rate coefficients/constants (e.g., s-1) as reaction rates (e.g., molecules cm-3 s-1). See 9415, line 25 and 9416, line 3 for instance.

Response: We thank the reviewer for pointing this out. We have fixed these in the revision.

Number concentrations should be in units of molecules cm-3, not simply cm-3. See pages 9415 and 9416. Hopefully this does not reflect calculation errors where the units were not conserved.

Response: Number concentrations are typically reported as cm^{-3}, and we have double checked our calculations before submission.

Page 9419, lines 28/29: grammar: in (a) normal spring; (a) 200 % increase.

Response: We thank the reviewer for pointing this out. We have corrected these.

Table 1: The equivalent information for USGS34 should be included in this table as well.

Response: We think the results of USGS 35 gives the best information about the analytical uncertainties. USGS34 is a zero standard of $\Delta^{17}O(NO_3^-)$ and it varies closely around zero.

Table 1: Use "refers to" not "refer to" in the footnotes.

Response: These have been corrected in the revision.

Fig. 1: The use of only red and blue for winter and spring data for both SP-1 and SB makes it difficult to tell which samples came from which dataset.

Response: We have labeled the winter and spring data in SP-1 and SB in Figure 1 with different symbols and colors in the revision.

Fig. 2d: Calcium is labeled on the y-axis but the caption says the plot is of magnesium. The use of the word "maximum" to describe the spring peak can be a bit confusing since it is often used to refer to the highest concentration in a given year when describing major ion concentrations in *ice cores. This was how I interpreted the title when I first read it. A consistent use of "peak" may be preferable.*

Response: We thank the reviewer for pointing out the error. To avoid confusion, we have replaced "concentration maximum" with "peak" in the revision, and the error in Figure 2 has also been corrected.

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

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Abstract

An occasional spring nitrate concentration ~~maximum~~peak was observed in ice cores from Central Greenland but its origin is unknown. This study performs a case study on its origin by measuring concentration and isotopic composition of nitrate (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~~peak was found in the spring of 2005. Isotopic data of nitrate combined with photochemical calculations suggest that the presence of this spring maximum was linked to a significantly weakened stratospheric ozone (O_3) layer. This weakened O_3 layer resulted in elevated UV-B (Ultraviolet B) radiation on the snow surface, where the productions of OH and NO_x from the photolysis of their precursors were enhanced. A ~~concentration maximum~~peak 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 found19 spring nitrate maxima after the 1950s. After 1979, all spring concentration maxima appeared with O_3 column density near or below the 1979-2006 average. We hypothesize that the presence of the spring nitrate ~~concentration maximum~~peak is largely associated with and may be determined by the interannual variability of O_3 column density, under the condition of elevated local NO_x abundance at Summit after the 1950s resulting from enhanced anthropogenic nitrate deposition, though other factor(s) may dominate in some years. Isotopic data

covering additional years of low O_3 column density are needed to further examine this hypothesis.

1. Introduction

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

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

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

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

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

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

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

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

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

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

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

Examination of detailed chronological nitrate records in snowpits and ice cores may provide clues on the primary factor(s) controlling nitrate concentration and its temporal variability in snow. For example, a clear seasonal pattern in nitrate concentration may be linked to a source with an annual cycle and/or modulated by seasonally varying atmospheric conditions. Many previous studies of snow samples and ice cores from central Greenland have found that nitrate concentration reaches a maximum in summer snow and a minimum in winter snow (Davidson et al., 1989; Finkel and Langway, 1986; Whitlow et al., 1992). This seasonal variation in nitrate concentration in general is due to the active photochemical reactions during polar summer (Yang et al., 1995), when peroxyacetyl nitrate (PAN), snowpack nitrate and other NO_x reservoir species act as local NO_x sources through recycling reactions (Moxim et al., 1996; Thomas et al., 2012). A few investigators (Burkhart et al., 2006; Yang et al., 1995) noticed that a single nitrate peak ~~maximum~~ appears in an annual snow/ice layer deposited prior to the year 1900, whereas two peaks ~~maxima~~ are seen in some post-1900 annual layers. The other annual peak ~~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 peak ~~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 peak ~~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~~peak.

The isotopic composition of nitrate can provide valuable information not available from concentration measurement alone, for example, regarding the pathways of NO_x conversion to nitrate in the atmosphere (Michalski et al., 2003). Stable isotope ratios in nitrate are expressed as $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$, where $\Delta^{17}O$ =

$\delta^{17}O - 0.52 \times \delta^{18}O$ and $\delta = R_{sample}/R_{reference} - 1$ with R denoting the $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotope ratios. The references are N_2-AIR and VSMOW for N and O, respectively. $\delta^{15}N$ and $\Delta^{17}O$ of nitrate (hereafter denoted as $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$, respectively) have been used to investigate the origin and fate of NO_x in the Arctic troposphere (Morin et al., 2008). In particular, $\Delta^{17}O(NO_3^-)$ is related to oxidizing conditions and nitrate formation pathways (R4 vs. R5-R8) in the atmosphere (Alexander et al., 2004; Alexander et al., 2009; Kunasek et al., 2008; Michalski et al., 2003; Morin et al., 2011). For example, Michalski et al. (2003) found that nitrate formed during nighttime (i.e., via R5-R8) has higher $\Delta^{17}O$ than nitrate formed during daytime (via R4) because of the high $\Delta^{17}O$ of the dominant nighttime oxidant O_3 (Johnson et al., 2000; Lyons, 2001) which is transferred to nitrate. The $\Delta^{17}O(NO_3^-)$ in Greenland snow also reflects the seasonality of nitrate production, with O_3 oxidation (R1, R5) being more important in winter than in summer (Kunasek et al., 2008).

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

2. Methods

2.1. Snowpit and ice core sample collection

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

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

2.2. Chemical and isotope analysis

At SDSU, another set of snow samples (referred to as SP-2) in a vertical sequence was chiseled out from the snow blocks, after the removal of a surface layer of at least

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

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

The SP-1 samples at LGGE were measured for nitrate concentration and isotopic composition (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 following~~ed~~ the similar procedure described above and the N and O isotope ratios were determined by the bacterial denitrifier method. Instrumentation details at the LGGE laboratory are similar to that described in Erbland et al. (2013). International reference materials (USGS34, USGS35 and IAEA-NO-3) were used for data reduction. The uncertainties of $\Delta^{17}O(NO_3^-)$, $\delta^{18}O(NO_3^-)$ and $\delta^{15}N(NO_3^-)$ measured at the LGGE laboratory were 0.3 ‰, 2.0 ‰ and 0.3 ‰, respectively, estimated as the reduced standard deviation of the residuals from the linear regression between the measured reference materials and their accepted values.

3. Results

3.1. Dating and identifying spring nitrate maxima

The concentration data from the SP-1 and SP-2 samples, and the isotopic data from the SP-1 and SB samples , were plotted as a function of depth in Figure 1 (data are available in Supplemental Material). The concentration profiles of nitrate from SP-1 and SP-2 are nearly identical and each displays five peaks approximately at the same depths (labeled 1, 2, 3, 3′ and 4 in Figure 1d). Since the snowpit and snow blocks were excavated in July of 2007, the partial Peak 1 at the surface identifies the summer of 2007. The other peaks could be summer or spring peaks. According to the concentration profile of sodium (Figure 1e) that has an annual winter peak (Whitlow et al., 1992), nitrate Peak 3′ represents the spring of 2005 and Peak 2, 3 and 4 represent the summer of 2006, 2005 and 2004, respectively. This dating by nitrate summer peaks and sodium winter peaks (referred to here as Method A) is consistent with the results of weekly recorded snow accumulation data determined by stake height measurements at Summit (data are available at ftp://ftp.summitcamp.org/pub/data/GEOSummit/Bales_UCM/Bamboo%20Forest/Bamboo%20Forest%20Accumulation%20Log.xls) (referred to here as Method B). The approximate months of snowfall at depths of 0, 0.5, 1.0, 1.5 and 2.0 m identified by Method B were indicated with vertical dashed lines of Figure 1. Both dating methods identify Peak 3′ occurring in the (early) spring of 2005. Some small discrepancies exist between the two dating methods. For example, the month of snowfall at the surface was identified as May of 2007 using Method B instead of July. This discrepancy is due to negligible snowfall (around 2 cm) from May to July 2007. The month of snowfall at the depth of 2 m was identified as March of 2004 using Method B, suggesting that Peak 4 is also a spring peak. However, according to the snow accumulation data, there was only about 3 cm of snow accumulation from March to June of 2004 (Figure S1 in supplemental materials). Negligible snowfall during this time resulted in nitrate produced in summer dry depositing to the prior spring snow layers, making it appear as if the peak occurs in spring using Method B. In addition, the nitrate profiles in SP-1 and SP-2 are slightly different (i.e., nitrate peaks are not exactly at the same depths), which is likely due to the spatial variability of snow accumulation rates in the field due to snow drifting. But the overall temporal patterns of the nitrate profiles in SP-1 and SP-2 are similar, suggesting there was negligible disturbance of the stratigraphy of the snow blocks during delivery and storage.

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

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

The $\delta^{18}O(NO_3^-)$, $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ data from the SP-1 and SB samples are shown in Figure 1a, 1b and 1c, respectively. The depth range of the SP-1 samples (0 to 2.10 m) corresponds to the period of the 2007 summer to 2004 summer, while the depth range of the SB samples (0.7 to 1~~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 peak~~maximum~~), the means (± 1σ) of $\delta^{15}N(NO_3^-)$ from the SP-1 and SB samples were (5.3 ± 3.3) ‰ and (6.4 ± 2.1) ‰, respectively, much higher than the winter values which were (-9.2 ± 3.3) ‰ from the SP-1 samples and (-7.4 ± 4.4) ‰ from the SB samples. A local minimum in $\delta^{18}O(NO_3^-)$ was also observed from both the SP-1 and the SB samples at the depths of the 2005 spring nitrate peak (Figure 1a).

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

4. Discussion

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

4.1. Enhanced transport

4.1.1. Stratospheric denitrification

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

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

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

4.1.2. Transport from mid-latitudes

The model results in Kunasek et al. (2008) suggest significant transport of nitrate from the mid-latitudes to Summit. The $\Delta^{17}O$ of nitrate from mid-latitudes is likely lower than that of nitrate formed in the Arctic troposphere due to the latitudinal gradient in $\Delta^{17}O(NO_3^-)$ resulting from the latitudinal gradient in O_3/HO_x ratio (Alexander et al., 2009). Thus, enhanced long-range transport of mid-latitude nitrate to Greenland during the spring could elevate nitrate concentration in snow with relatively low $\Delta^{17}O(NO_3^-)$ as observed here. Pollution from the Northern mid-latitudes is transported to Arctic by poleward meridional circulation, which is strong when the North Atlantic Oscillation (NAO) is in its positive phase (Eckhardt et al., 2003). However, a weak NAO in the 2004/2005 winter and early spring of 2005 was seen in the NAO index data (Osborn, 2011), suggesting no enhanced transport from the mid-latitudes at this time. In addition, if the additional nitrate in the spring of 2005 was from enhanced transport, elevated concentrations of other species derived from anthropogenic and continental sources, such as SO_4^{2-} and Mg^{2+}, would also be expected, especially for SO_4^{2-} because it has a very similar atmospheric lifetime (4 to 6 days) as nitrate (3 to 7 days) (Park et al., 2004; Pye et al., 2009). However, the data from the snowpit show that neither SO_4^{2-} nor Mg^{2+} concentrations were elevated (Figure 1f and 1g) in the spring of 2005 when the nitrate peak ~~maximum~~ was present. Therefore, it is unlikely that the 2005 spring nitrate peak ~~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 Figure 3, the spring (average of February and March values) O_3 column density at Summit for the years of 1979-2006 were shown (data are from NASA Total Ozone Mapping Spectrometer program). The 2005 spring level (290 Dobson Unit (DU)) was significantly lower than the average of spring values from 1979 to 2006 (390 ± 50 (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~~peak in snow. The increase in PAN photolysis resulting from the decreased O_3 column density (290 DU) can be estimated with the UCAR Tropospheric Ultraviolet & Visible (TUV) radiation model (available at http://cprm.acd.ucar.edu/Models/TUV/). Calculations with the TUV model showed a 24 % increase in the photolysis rate constant of PAN ($j = (9.0 \pm 5.4) \times 10^{-8}\ s^{-1}$ vs. $(7.3 \pm 4.3) \times 10^{-8}\ s^{-1}$, both are daytime averages) in the spring of 2005 compared to that in a typical spring (column O_3 density of 390 DU). This would lead to an increase of only $1.6 \times 10^{5}\ cm^{-3}$ in NO_x number concentration, which is, on average, 0.04 % of the observed springtime NO_x concentration of $(3.9 \pm 3.1) \times 10^{8}\ cm^{-3}$ in the Arctic

(Stroud et al., 2003). The above calculation assumes steady stead of PAN with number concentration of (2.3 ± 0.7) × 10^9 cm^{-3} (Stroud et al., 2003) and $[NO_2] = (([PAN] \times j_{PAN}) / k)^{1/2}$, where $[NO_2]$ and [PAN] represent the number concentrations of NO_2 and PAN, respectively, and j_{PAN} (s^{-1}) is the photolysis rate constant of PAN calculated from the TUV model and k ($cm^3 \times s^{-1}$) is the reaction rate constant of PAN formation at T = 240 K and P = 650 hPa (Summit springtime condition) calculated based on the equation from Atkinson et al. (2006). This is negligible compared to the observed 60 % enhancement in nitrate deposition flux (5.7 nmol × cm^{-2}) during the spring of 2005. This is consistent with the model prediction by Stroud et al. (2003) that, during spring, PAN is a net sink of NO_x, rather than a source. A similar conclusion was also reached by Singh et al. (1992) who found that the PAN reservoir is not a significant source of NO_x until summer.

4.2.2. Snowpack NO_x emissions

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

In order to estimate the impact of the reduced overhead O_3 column density in the spring of 2005 on local NO_x concentration via the photolysis of snowpack nitrate, we used the TUV model to calculate the surface actinic flux at Summit in the spring of 2005 (290 DU) versus normal springtime with average O_3 column density (390 DU, which was close to the value (380 DU) in the spring of 2006). The parameterization from Zatko et al. (2013) was then used to calculate the photolysis frequency (s^{-1}) of snowpack nitrate at wavelengths from 298 to 345 nm (peak wavelength for nitrate photolysis is around 320~~02~~ 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~~peak. If snowpack photodenitrification is the dominant source of boundary layer NO_x at Summit as suggested by Thomas et al. (2012), then this could account for up to half of the additional nitrate in the observed 2005 spring nitrate ~~concentration maximum~~peak.

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

4.2.3. Enhanced conversion of NO_x to nitrate

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

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

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

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

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

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

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

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

The temperature and relative humidity data at Summit is available from Greenland Climate Network Data (GCND, http://cires.colorado.edu/science/groups/steffen/gcnet/order/admin/station.php). Using these data, the spring (February and March average) atmospheric water vapor mixing ratio in 2005 was calculated to be 40 % higher than that in 2006 due to high temperatures in the 2005 spring (-30 ºC) relative to the 2006 spring (-34 ºC). Assuming this high water vapor in spring 2005 will result in a maximum increase in OH production of 40 %, the increase in water vapor is not enough to account for the 60 % enhancement in the nitrate deposition flux in the spring of 2005. In fact, as discussed later, OH must be increased by 200 % to explain the spring nitrate maximum. Although the relatively high temperature in the spring of 2005 may have contributed around 20 % (40 % increase versus the required 200 % increase) to the enhanced local nitrate production, it was likely not the dominant factor producing the spring nitrate peak ~~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 (R9 and R10) at Summit due to enhanced photolysis of boundary layer O_3. Our calculation showed that the OH production rate due to this mechanism alone was increased by 90 % in the spring of 2005 resulting from the decrease of O_3 column density from 390 to 290 DU. Assuming that the production of HNO_3 via OH oxidation was increased by the same factor, enhanced local OH production could easily account for the 60 % enhancement of nitrate flux in the spring of 2005, if all nitrate was formed via OH oxidation (R4). During a typical Arctic spring, O_3 is expected to be the major oxidant in the oxidation of NO_x to HNO_3 (Kunasek et al., 2008), so it is unlikely that R4 is solely responsible for the local oxidation of NO_x to HNO_3. Using a global chemical transport model (GEOS-Chem), Alexander et al. (2009) estimated that about 30 % of total nitrate in a normal spring (average in February and March) is produced via OH oxidation at Summit. With this more realistic value, a 200 % increase in the local OH production rate was needed to account for the additional nitrate flux in the spring of 2005. Therefore, the enhanced local production rate of OH due to solely the enhanced photolysis of tropospheric O_3 in the spring of 2005 can explain about 50 % of the observed spring nitrate ~~maximum~~peak.

In addition to production via O_3 photolysis (R9 and R10), OH can be formed by the photolysis of snowpack emitted CH_2O, H_2O_2, and HONO (Dassau et al., 2002;

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

Thus, we propose that the elevated tropospheric UV-B level due to a weakened stratospheric ozone layer in the spring of 2005 likely led to additional local nitrate production in sufficient quantities to account for the spring nitrate ~~concentration maximum~~peak. The additional nitrate was generated primarily through increased tropospheric OH production from the enhanced photolysis of tropospheric O_3 and CH_2O, H_2O_2 and HONO emitted from the snowpack, and also possibly from enhanced NO_x emission from the photolysis of snowpack nitrate. The enhanced snowpack NO_x emission, contributed to the spring nitrate peak ~~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, $\delta^{18}O$ and $\delta^{15}N$ of snow nitrate at Summit covering 2000 and 2001. Qualitatively, $\delta^{18}O(NO_3^-)$ is similar to $\Delta^{17}O(NO_3^-)$, because the $\delta^{18}O(NO_3^-)$ value is also determined by the relative importance of O_3 versus OH oxidation (higher $\delta^{18}O(NO_3^-)$ values are associated with increased O_3 oxidation and lower $\delta^{18}O(NO_3^-)$ values indicate increased HO_x oxidation) (Hastings et al., 2004). Consequently, $\delta^{18}O(NO_3^-)$ is high in winter snow and low in summer snow (as shown in Figure 1a, and also in Hastings et al. (2004)). The data shown in Hastings et al. (2004) indicated a spring nitrate peak in 2000. The spring nitrate concentration peak in 2000 in Hastings et al. (2004) had $\delta^{18}O(NO_3^-)$ values ((69.8 ± 2.1) ‰) similar to those during the summer of 2000 ((70.5 ± 2.4) ‰). Although the winter of 1999/2000 (i.e., the winter prior to the spring of 2000) was not covered in Hastings et al. (2004), $\delta^{18}O(NO_3^-)$ values in this winter should be higher than those in the 2000 summer according to the seasonality of $\delta^{18}O(NO_3^-)$. Therefore, in the 2000 spring, the $\delta^{18}O(NO_3^-)$ values are lower than those in the previous winter. In contrast, in the 2001 spring when no nitrate concentration peak was observed, $\delta^{18}O(NO_3^-)$ was (77.5 ± 2.4) ‰, which is similar to the $\delta^{18}O(NO_3^-)$ values observed during the prior winter ((77.4 ± 1.9) ‰), and higher than those observed during the subsequent summer ((68.9 ± 2.1) ‰). In addition, the mean $\delta^{15}N(NO_3^-)$ in the spring of 2000 ((5.9 ± 6.2) ‰) from Hastings et al. (2004) is similar to that observed in the spring of 2005 (6.4 ± 2.1) ‰, and is higher than that observed in Hastings et al. (2004) during the spring of 2001((-1.4 ± 3.0) ‰). In summary, the isotopic features of nitrate associated with the spring peaks observed in 2000 (Hastings et al., 2004) and in 2005 are similar to each other, each suggesting enhanced local photochemistry. This is consistent with the low O_3 column density in the spring of 2000 (337 DU,

Figure 3) and 2005 (294 DU, Figure 3). Therefore, the results of Hastings et al. (2004) support the explanation that the appearance of the spring nitrate peak ~~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~~peak observed in modern snow in Central Greenland, we compared the nitrate concentration record from the shallow core with O_3 column density data from 1979 to 2006, the time period when global O_3 data are available from satellite observations. The year-to-year variability of polar stratospheric O_3 is largely controlled by the Brewer-Dobson circulation (BDC) through direct transport and indirect coupling between dynamics and chemistry [e.g., (Randel et al., 2002; Shepherd, 2008; Weber et al., 2011)]. Halogen-catalyzed chemical destruction leads to a decreasing trend in column O_3 density since 1980 (WMO, 2007) and causes sudden drops in O_3 column density in years when the winter temperatures are anomalously low [e.g., the winter of 2004/2005 (Jin et al., 2006; Kleinbohl et al., 2005)]. The strength of the BDC is related to the wave force, which is represented by extratropical poleward eddy heat flux in the lower stratosphere (Fusco and Salby, 1999; Weber et al., 2011). From the NCEP/NCAR reanalysis data (http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.pressure.html), we retrieved the average eddy heat flux in the lower stratosphere at 40-80º N in January and February (due to the transport lag, January and February eddy heat flux determines the February and March polar stratospheric O_3 abundance) from 1979 to 2006 (Figure 3). Reanalysis data before 1979 are also available, but less reliable due to lack of constraints by satellite observations. Therefore in this study, we only use the data after 1979.

As shown in Figure 3, in the period from 1979 to 2006, the spring nitrate peak~~maximum~~ only appears when O_3 column density is near or below the average for that period. We note that although spring nitrate concentration peaks ~~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 peak ~~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~~peak also requires other conditions (e.g., sufficient local NO_x abundance), and that this is especially true when O_3 column density is near the 1979-2006 average. Additional factors may also be important, such as stratospheric input of nitrate and/or long range transport of nitrate, as discussed previously. With isotopic data and other relevant information available, we were able to exclude many possible sources of nitrate to the spring ~~maximum~~ peak in 2005; however, it is difficult to explicitly assess the dominant source(s) of nitrate contributing to the spring peak~~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 peak~~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 Figure 2a, snow nitrate concentrations at Summit began to increase around 1950 due to increasing anthropogenic NO_x emissions in the mid-latitudes (Fischer et al., 1998), and reached and maintained the highest level from 1970 to the present. Since snow nitrate can be photolyzed, releasing NO_x to the boundary layer, the increase in snow nitrate concentrations represents an increase in a potentially important NO_x reservoir in Greenland. Anthropogenic NO_x emissions also increase other reservoir species that may contribute to springtime NO_x abundance at Summit. Prior to the 1950s, when local NO_x abundance was not sufficiently high, no spring nitrate concentration peaks ~~maxima~~ were detected.

5. Conclusion

We report observations of spring nitrate concentration peaks ~~maxima~~ in a snowpit and a shallow ice core from Summit, Greenland. A case study regarding the origin of the spring nitrate peak~~maximum~~ was conducted by measuring the isotopic signature of nitrate in the spring of 2005 when a ~~concentration maximum~~peak was observed. The isotopic composition of snow nitrate in this spring, combined with photochemical calculations, suggests the presence of the 2005 spring nitrate peak~~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~~peak, if snowpack nitrate photolysis is the dominant local NO_x source. Either the increase in OH concentration or the increase in local NO_x concentration relies on the enhanced photochemical reactions initiated by the reduced O_3 column density. This mechanism is supported by the appearance of a spring nitrate ~~concentration maximum~~peak in 2000 (Hastings et al., 2004), when a reduced O_3 column density also occurred. For the spring peaks ~~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~~peak observed in Greenland snow is largely associated with the interannual variability of O_3 column density. The interannual variability of O_3 column density is mainly controlled by the Brewer-Dobson circulation, while chemical destruction may also play a role beginning around 1980 (WMO, 2007). The presence of the spring nitrate maximum, however, also requires sufficient amount of local NO_x, which is likely to exist only after the 1950s when dramatic increases in anthropogenic NO_x emissions started to lead to the buildup of NO_x reservoir species at Summit and thereby increase the local abundance of NO_x. Seasonal resolved isotopic data ($\Delta^{17}O(NO_3^-)$ and $\delta^{15}N(NO_3^-)$) covering additional years with spring nitrate concentration peaks ~~maxima~~ are needed to further examine how robust the connection is between the spring nitrate peak~~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).

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

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

Figure 1. $\delta^{18}O(NO_3^-)$ (a), $\delta^{15}N(NO_3^-)$ (b), $\Delta^{17}O(NO_3^-)$ (c) and concentrations of NO_3^- (d), Na^+ (e), SO_4^{2-} (f) and Mg^{2+} (g) in the snow samples (data are 3-point running averages). SP-1 data were plotted in gray with plus signs; SP-2 and SB data were plotted in black with circle and star signs, respectively. The pink and green stars represent samples in SB used to calculate the winter and 2005 spring -mean

$\Delta^{17}O(NO_3^-)$, respectively; while the red and blue plus signs represent samples in SP-1 used to calculate the winter and 2005 spring mean $\Delta^{17}O(NO_3^-)$, respectively. The vertical dashed line indicates the approximate months of snowfall at depths of 0, 0.5, 1.0, 1.5 and 2.0 m by Method B as described in the text.

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

Figure 3. Summit springtime O_3 column density (February and March averages) and poleward eddy heat flux in the lower stratosphere (40-80° 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~~peak observed in the shallow ice core.

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

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

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

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

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

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

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

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

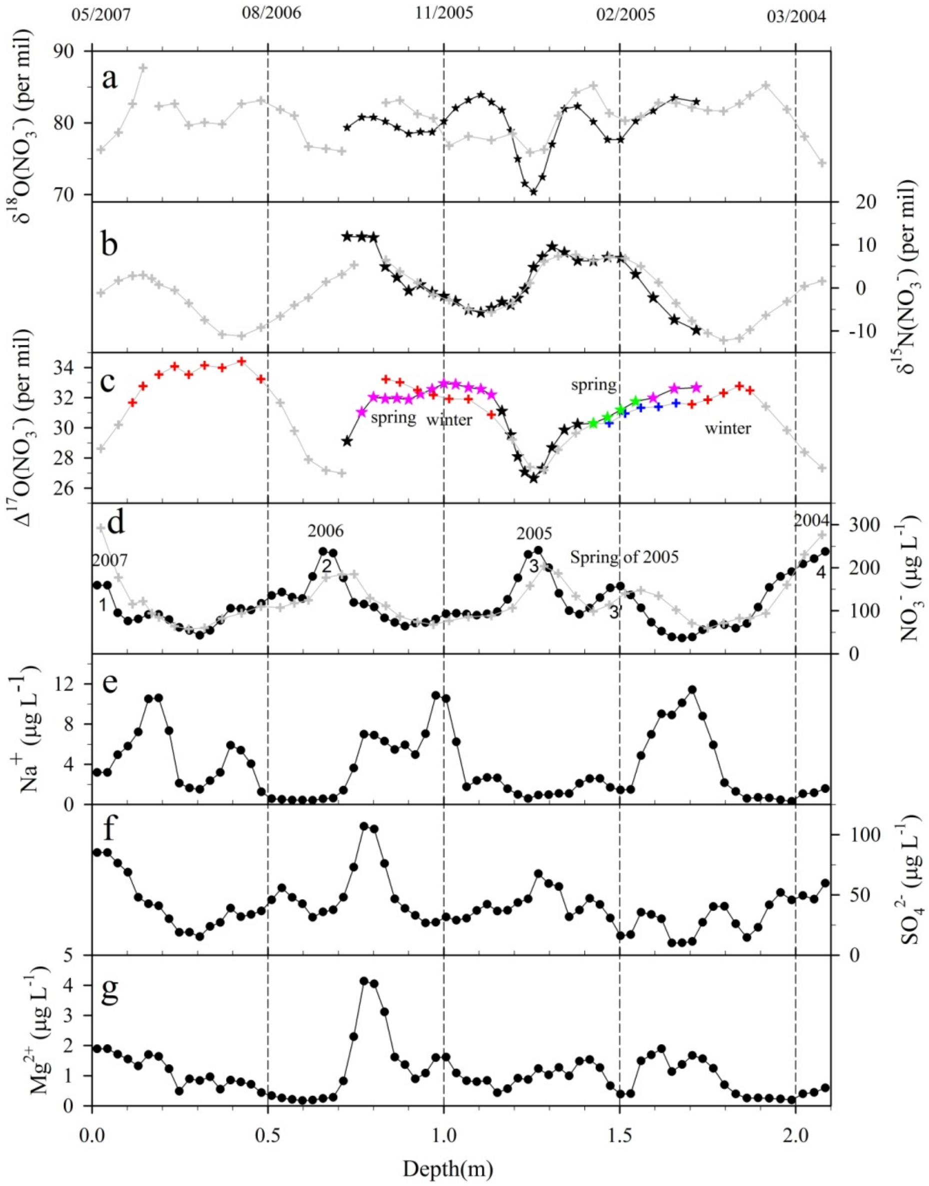

Figure 1. $\delta^{18}O(NO_3^-)$ (a), $\delta^{15}N(NO_3^-)$ (b), $\Delta^{17}O(NO_3^-)$ (c) and concentrations of NO_3^- (d), Na^+ (e), SO_4^{2-} (f) and Mg^{2+} (g) in the snow samples (data are 3-point running averages). SP-1 data were plotted in gray with plus signs; SP-2 and SB data were plotted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

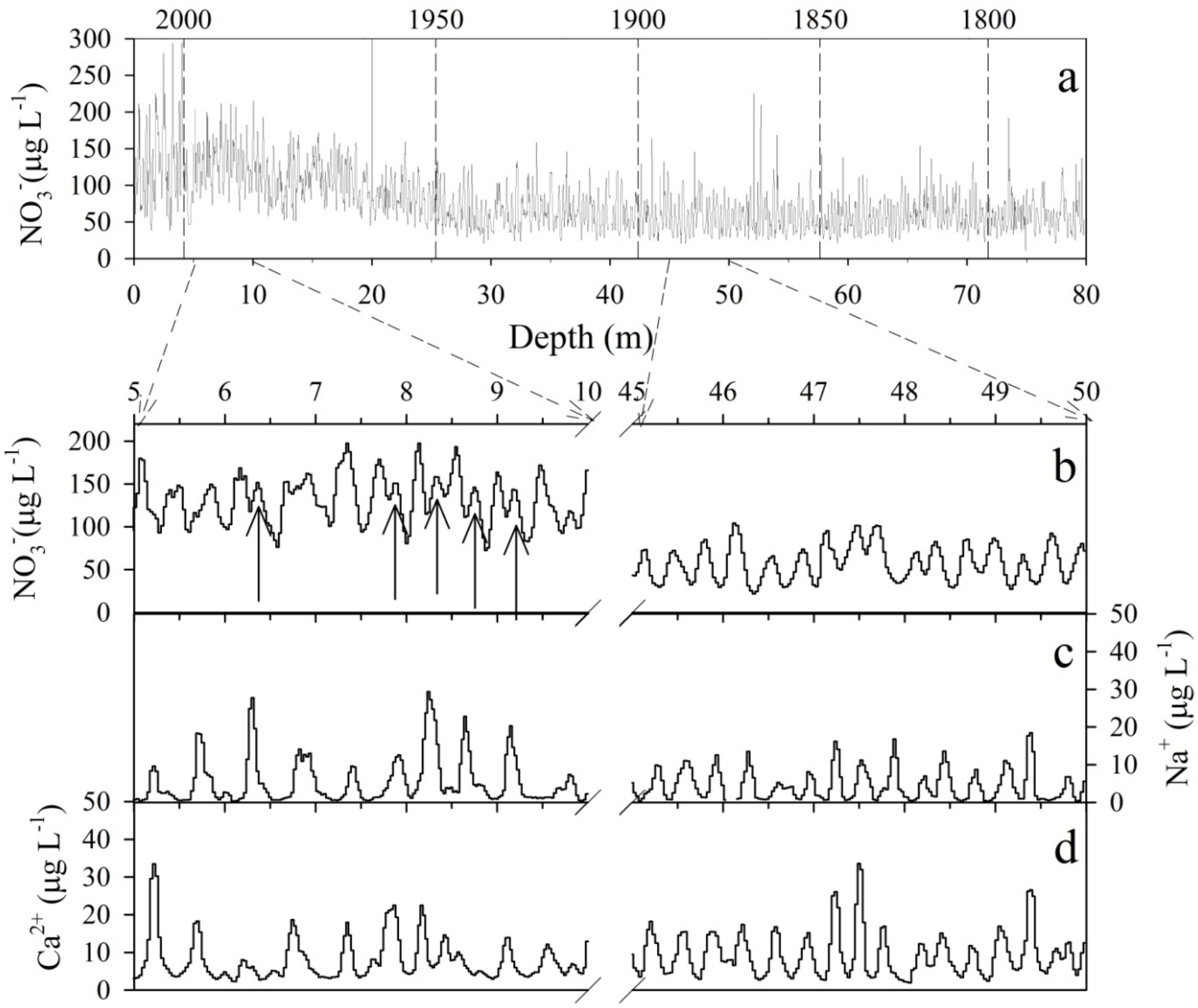

Figure 2. (a) Nitrate concentration record from the shallow ice core; (b), (c), (d) show seasonal peaks of NO_3^- , Na^+ and Ca~~Mg~~$^{2+}$, respectively in two sections of the ice core (data shown in b, c and d are 3-point running averages). The arrows in (b) indicate spring nitrate peaks~~maxima~~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

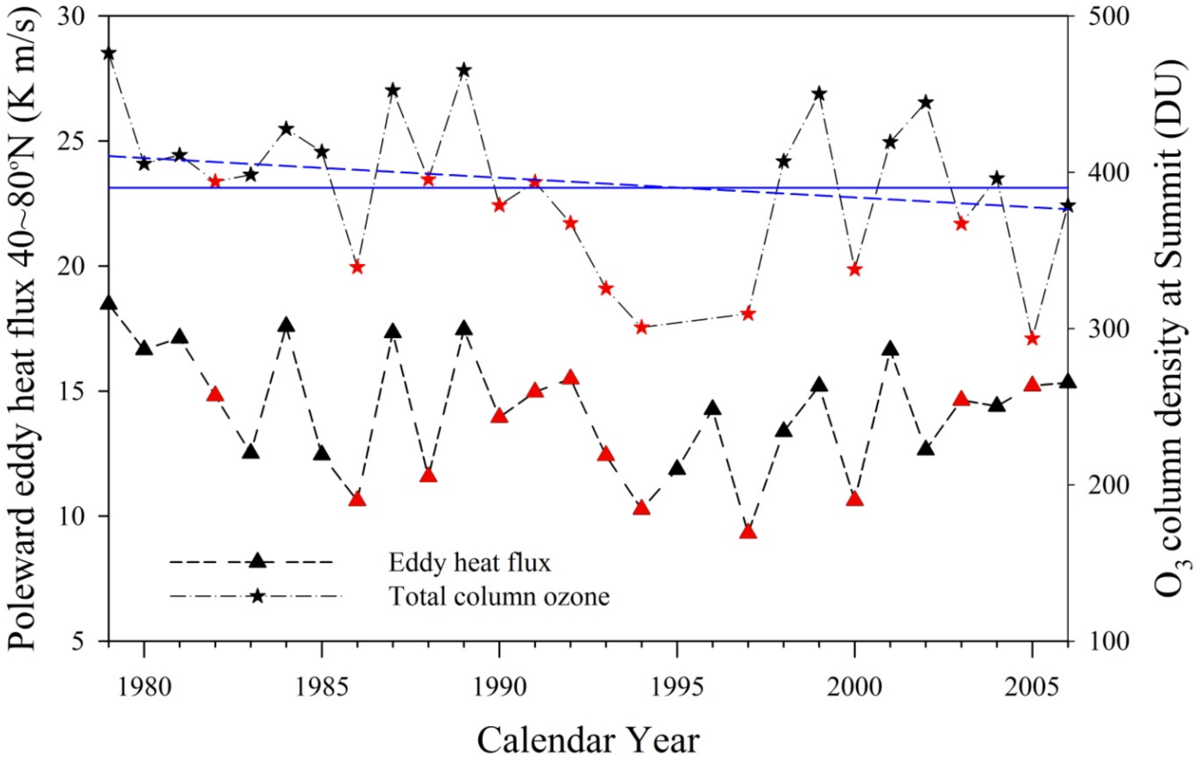

Figure 3. Summit springtime O_3 column density (February and March averages) and poleward eddy heat flux in the lower stratosphere (40-80º N, January and February averages) from 1979 to 2006. The solid blue line is the average of springtime O_3 column density from 1979 to 2006 (390 ± 50 (1σ) DU), and 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~~peak observed in the shallow ice core.