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.

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 Δ17O (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:

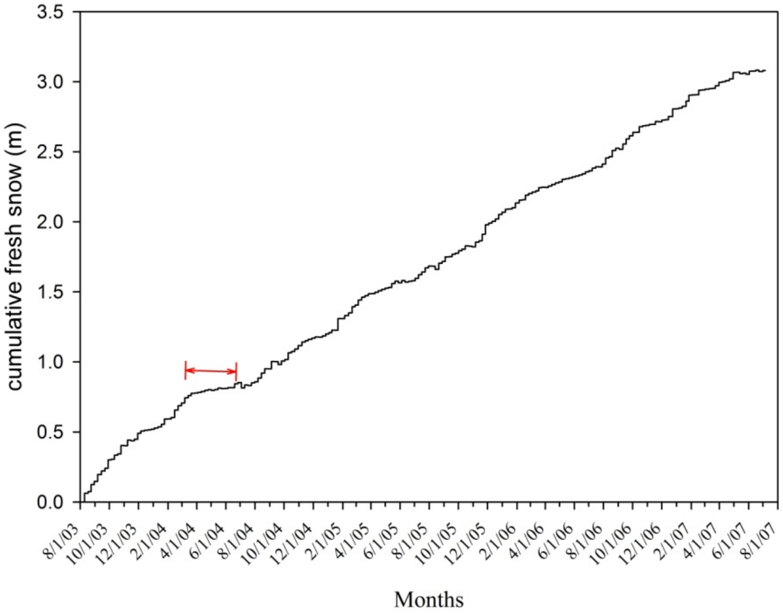

Figure 1S. Fresh snow accumulation at Summit from 2003 to 2007. The red arrow indicates the period from late spring of 2004 to summer of 2004, when only very little snow was accumulated. We think this little snow accumulation under the period labeled by the red arrow is because of lack of snowfalls, 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 $\delta^{15}N$**." 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 $\Delta^{17}O$ 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 Δ^{17}O) to stay at surface for enough time to allow for sufficient recycling to erase the high stratospheric Δ^{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).

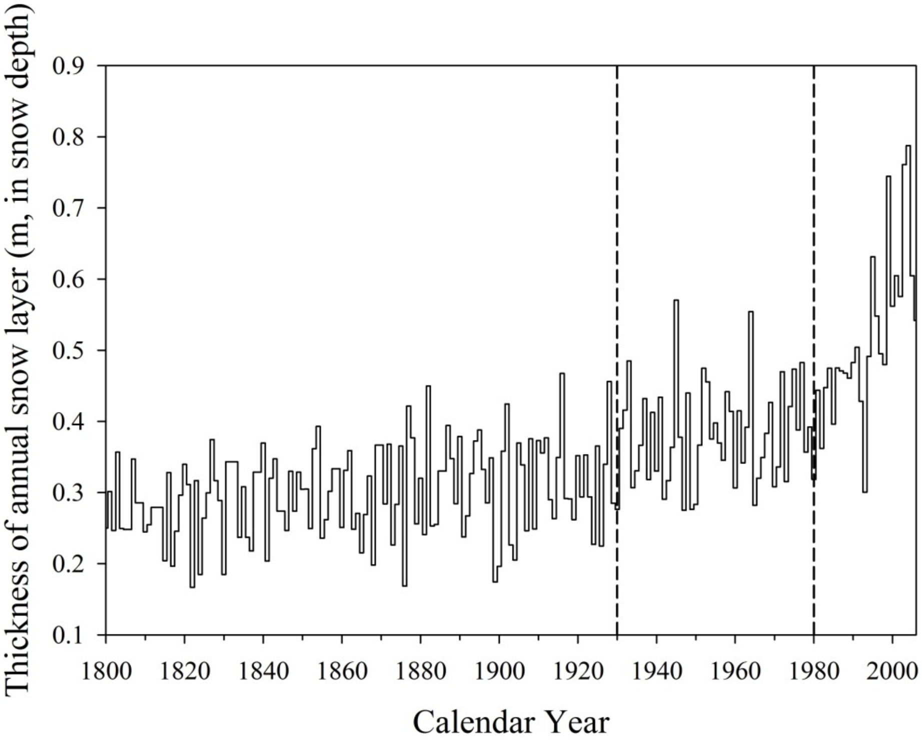

Figure S2. Annual snow layer thickness in the Greenland ice core we used.

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. We will revise this in the 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 will re-label the SB and SP-2 data.

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 will make the correction.

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. We will add that reference.

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

Response: We thank the reviewer for pointing this out, we will add 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 thank the reviewer for pointing this out. We will proofread the manuscript and make them consistent.

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 will correct this.

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 will fix this.

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 will make the correction.

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 will make the corrections.

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 will make the corrections.

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: We thank the reviewer for pointing this out. We make the corrections.

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 will make them look different in the revised figure.

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 will replace "concentration maximum" with "peak".

Reference:

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