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 O_3 and other precursor molecules, and consequently an increase in nitrate formation and deposition. Much of the spring nitrate may be derived from NO_x 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 $\Delta^{17}O$ relative to winter values. Since O_3 imparts a high positive $\Delta^{17}O$ (and $\delta^{18}O$) signature to nitrate, this decrease is taken to reflect a proportional increase in oxidation of NO_2 to nitrate by OH, for which $\Delta^{17}O$ is effectively zero. Additionally, 19 spring peaks in a nearby ice core are taken to coincide with average or low overhead O_3 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.

Major comments:

Is the spring 2005 $\Delta^{17}O$ out of the ordinary?

This paper rests on the $\Delta^{17}O$ 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 $\Delta^{17}O$ of ~1.7 ‰ between the spring of 2005 and the average winter value is not large (page 9411, line 21). The $\Delta^{17}O$ 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 $\Delta^{17}O$.

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 $\Delta^{17}O$ should normally (i.e., average O_3 springs) be similar to the preceding winter $\Delta^{17}O$ (page 9411), then a comparison between spring 2005 and all winters is implicitly making the assumption that all winter $\Delta^{17}O$ is the same, or in statistical terms, that all winter nitrate is drawn from the exact same sample population. If the $\Delta^{17}O$ of an ordinary O_3 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?

Justification with additional isotopic data

As additional isotopic evidence, the authors point to $\delta^{18}O$ in a snowpit from Hastings et al. (2004) since, like $\Delta^{17}O$, $\delta^{18}O$ 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 $\delta^{18}O(NO_3^-)$ in the spring of 2000 (69.8 +/- 2.1) ‰ is significantly lower than that in the prior winter (77.5 +/- 2.4) ‰" (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 NO_3^- within the snowpack. Therefore, our assignments of season and the seasonal averages are susceptible to uncertainties. 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)."

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 $\Delta^{17}O$ (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.

Nitrate photolysis and snow-sourced NO_x

Page 9413, lines 14-27: It is true that nitrate photolysis may lower $\Delta^{17}O$ 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 $\Delta^{17}O$ and $\delta^{18}O$ in East Antarctica is due to the products of nitrate photolysis (e.g., NO_2) being re-oxidized to nitrate by OH/H_2O 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 $\Delta^{17}O$ lower than tropospheric nitrate in a typical spring (page 9413, lines 24/25). The latter may be true for the gas phase NO_x 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 $\Delta^{17}O$ (and presumable higher in $\delta^{15}N$).

This leads into the problems I have with the suggestion that much of the extra nitrate in a low-O_3 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 $\Delta^{17}O$ 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 NO_x to the overlying atmosphere, then you should have alteration overprinting your $\Delta^{17}O$ 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 $\Delta^{17}O$ 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.

Other comments:

On page 9412, 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 NO_x by OH (Section 4.2.3). I'll leave the calculations to the authors, but does such a small observed difference in $\Delta^{17}O$ fit with what would be expected from mass balance for a 60 % increase in the OH pathway?

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.

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?

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

Page 9408: 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.

Page 9412, 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.

Page 9417, 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 $NO_3^- + H^+ + hv \rightarrow NO_2 + OH$ pathway. Finally, the Chu and Anastasio cross section spans 280-360 nm, so why was the calculation made only for 298-345 nm?

Page 9418, lines 2-7: Is a NO_x 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?

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.

Minor comments:

On page 9405, the delta notation references are given as N_2-AIR and VSMOW. On pages 9407 and 9408, they are written as Air-N_2 and V-SMOW. Please be consistent.

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.

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

Page 9408: There seems to be inconsistency in the use of $\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$ compared to $\delta^{15}N(NO_3^-)$, $\delta^{18}O(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$.

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

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.

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

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

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.

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.

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

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

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

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.

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.