

We thank the 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 an 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 presents 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 will add more details regarding sample collection in the field, transport and storage of samples back to the lab. The snow density data will be added in the Supplemental

Material. Briefly, SP-1 samples 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 M Ω 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.

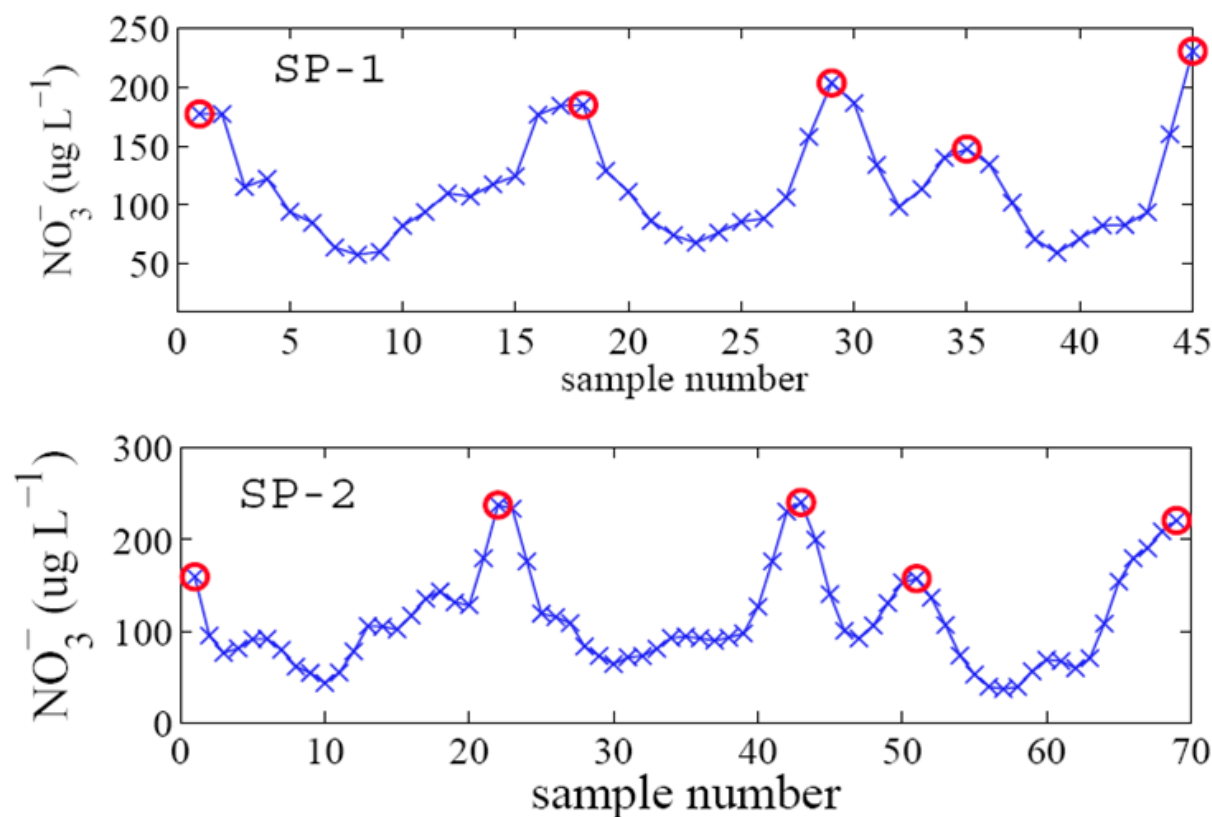


Figure 1S. Nitrate peaks identified in SP-1 (top) and SP-2 (bottom) snowpits using the PeakFinder function of MatLab. Note that in each figure the X-axis is plotted as sample number, this follows the MatLab function and assumes the concentration data is a vector evenly distributed in space (this assumption 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 will be 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).

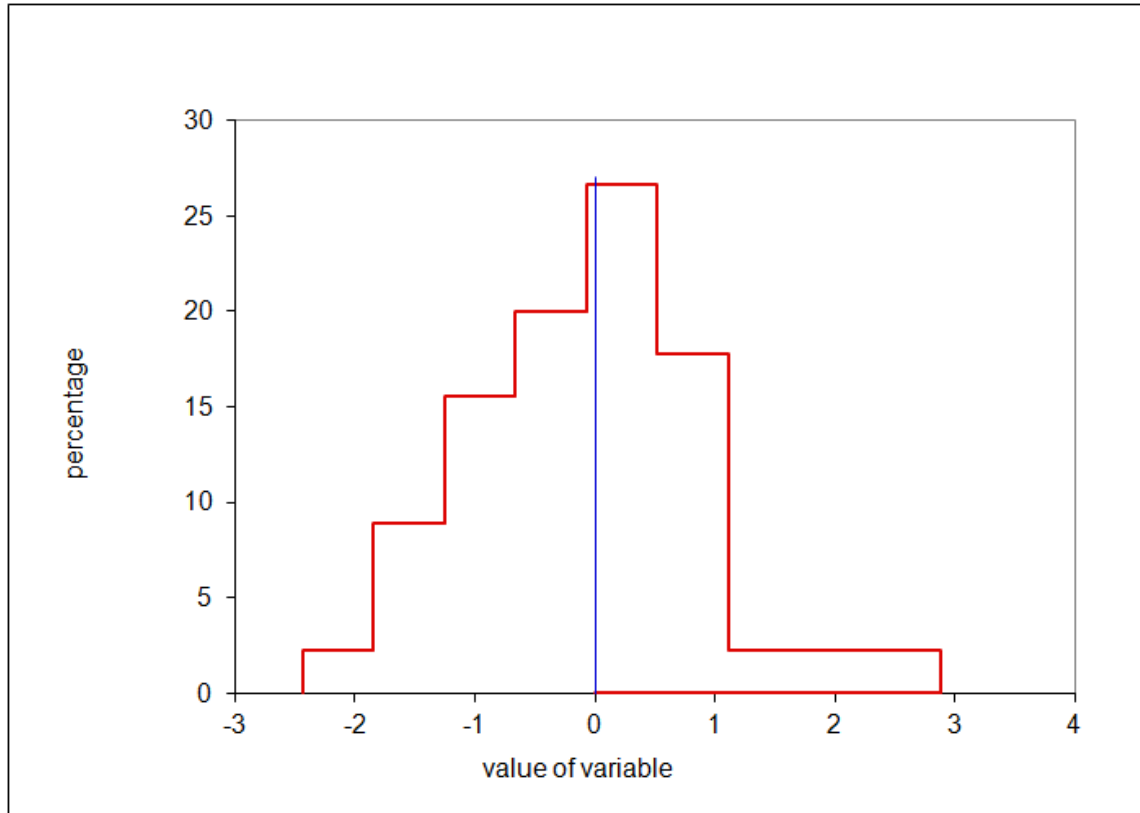


Figure S2: Histogram of the combined residuals of all data used to performed the t-test in the manuscript. Vertical blue indicates the mean of the residuals.

Minor comments:

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

Response: We thank the review for pointing these. We will correct them.

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. This will be noted in the 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.

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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.

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