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REPLY

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**Correspondence to:**
M. A. Shea,
sssrc@msn.com

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# Reply to comment by E. W. Wolff et al. on "Low time resolution analysis of polar ice cores cannot detect impulsive nitrate events"

**D. F. Smart[1], M. A. Shea[1], A. L. Melott[2], and C. M. Laird[3]**

[1]Retired, Nashua, New Hampshire, USA, [2]Department of Physics and Astronomy, University of Kansas, Lawrence, Kansas, USA, [3]Retired, Lawrence, Kansas, USA

**Abstract** Wolff et al. (2016) comment on Smart et al. (2014) and in doing so concentrate on issues other than the main point. They do not dispute our central assertion, the inadequate resolution of nearly all extant ice cores for detection of impulsive nitrate events (spikes) from any source, including past solar proton events (SPEs). We explain why comparing two short-length cores from other researchers and analyzed by different methods is insufficient for disputing subannual reproducibility, and call for a multiple, fine-resolution, replicate core study to resolve this issue. While acknowledging the creation of nitrate by SPEs and the existence of ice core nitrate spikes detected by others, they present several weak arguments, such as alleged scavenging of nitrate by some unnamed and unmeasured aerosol, and why no enhanced nitrate signal for documenting SPE statistics should be distinguishable in the ice. These are not derived from the main points in our Smart et al. (2014) paper. We address these briefly and show that ionization from the February 1956 SPE was sufficient to produce a winter, likely acidic, nitrate spike at Summit, Greenland. While noting some convergence of interpretation, we show why their claim that nitrate spikes cannot be used for deriving SPE statistics is unproven and why rejection of fine resolution core studies as unreliable is premature.

## 1. Introduction

To understand the complexities regarding the Comment by *Wolff et al.* [2016] and this Reply, some background material is necessary. Table 1 in the *McCracken et al.* [2001] paper is a tabulation of 72 short duration, "impulsive nitrate events" or spikes that those authors proposed as representing very large fluence solar proton events (SPEs) with the solar particles ionizing the atmosphere and forming oxides of nitrogen, leading to enhanced nitrate deposition in polar ice. *Wolff et al.* [2012] chose to concentrate on one event associated with the white light solar flare observed on 1 September 1859 [*Carrington*, 1860] and noted that they were unable to find a corresponding nitrate increase in several "properly dated" ice cores. Based on the analysis of this one event and their assertion that "all large spikes" in their data were "due to biomass burning plumes," they concluded that nitrates in ice cores cannot be used to derive SPE statistics.

*Smart et al.* [2014] noted in the data supplied by Wolff and coworkers that no nitrate spikes corresponding to known high-energy ground level solar cosmic ray events observed by cosmic ray muon detectors could be found. *Smart et al.* [2014] attributed this to insufficient resolution of ice core data primarily acquired to study long-term climatological phenomena. Using standard statistical analysis software, *Smart et al.* [2014] noted a substantial difference between the resolutions reported in Table 1 of *Wolff et al.* [2012] and the statistically significant data resolutions in their Zoe and D4 ice cores (closest in location to the GISP2-H ice core), contradicting their claims of "comparable resolution" to the GISP2-H data, which contained significant nitrate spikes. *Smart et al.* [2014] concluded that only ice cores with statistically significant, fine resolution of less than 2 months are capable of resolving short duration nitrate spikes regardless of their source. This resolution issue has implications regarding inferences drawn previously about a host of short-term phenomena in coarsely resolved ice cores, including the claimed associations between biomass burning, sea salt, and nitrate spikes that cannot be proven with analyses that only delineate broad summer/winter variations. It needs to be addressed.

We are now in the "comment stage." *Wolff et al.* [2016] maintain that the entire nitrate spike concept for deriving SPE statistics is inconsistent with well-regarded standard models for transport through the atmosphere and preservation in ice. These are the key points in the argument *Wolff et al.* [2016] present, but they are not in response to the key point in *Smart et al.* [2014].

The basic thesis of our paper [*Smart et al*., 2014] that the data in *Wolff et al*. [2012] lack the resolution to identify 0.5–2 month duration impulsive nitrate events has not been challenged in a substantive way. Nevertheless, *Wolff et al*. [2016] continue to maintain that their ice core data are "high resolution" and "The resolution typically used to discern nitrate spikes." We strongly dispute these assertions. In their Comment, *Wolff et al*. [2016] focus primarily on side issues to dispute our paper and to repeat previous arguments [e.g., *Legrand and Delmas*, 1986; *Wolff et al*., 2012; *Duderstadt et al*., 2014] against the feasibility of observing very large, hard spectrum SPEs as spikes in the polar nitrate record. For example, they list our side point that the Carrington SPE was not well documented and is not a good test as our first main conclusion. Our conclusion was not an attempt at "reinstating" SPE-produced nitrate spikes because the concept has never been disproved, despite *Wolff et al*.'s [2016] continuing efforts. Although it appears that the two sides in this debate have drawn incrementally closer, as our understanding of the physical and chemical processes involved has improved, there is still considerable disagreement, and we welcome this opportunity to respond to these additional arguments to clarify the issues. *Wolff et al*.'s [2016] assumption, coming from the atmospheric chemistry and ice core community, that both sides agree SPEs deliver most of their energy to the middle stratosphere and above, is only partly correct. Coming from the space physics, cosmic ray, and atmospheric physics communities and with expertise in polar glaciology, we emphatically disagree that this is the only locale for energy deposition to generate nitrate spikes and that this generalization applies to all SPEs. Standard energy deposition models have routinely omitted primary particles with energies above 300 MeV and have neglected air shower cascades that deposit additional energy in the lower stratosphere (from which rapid deposition can occur and which *Wolff et al*. [2016] continue to ignore), as well as the troposphere. We contend it is the high-fluence, high-energy events that can produce an impulsive nitrate enhancement in ice cores. We discuss this issue below.

*Wolff et al*. [2016] now assert that "many" nitrate spikes in Greenland cores are "likely" caused from scavenging by "sea salt, biomass burning, or dust aerosol," but this is very different from their previous claims [i.e., *Wolff et al*., 2012] and has not been proven. First, we find it remarkable that they assert that most nitrate spikes must have this association using ice core analyses that have not resolved a single impulsive nitrate spike. Given their limited 3–5 month resolution, the *Wolff et al*. [2012] data essentially only reflect the annual cycle where nitrates, biomass burning, and a number of additional indicators vary in phase and tend to peak in summer. This summer maximum does not apply to impulsive nitrate enhancements, which are of shorter duration and can occur at any time of year, including in winter when biomass burning interference is minimal. For example, Figure 1 in *Smart et al*. [2014] shows the winter nitrate spike in Greenland associated with the 23 February 1956 SPE. Second, *Wolff et al*. [2008] conducted a coastal study at Halley, Antarctica, which reflects a marine environment with associated high sea-salt and nitrate concentrations in surface snow samples, not ice cores. They specifically state that in central Greenland, which is remote from the oceans, sea salt "…will rarely be at the concentrations that could cause the effects described…" Third, there are exceptions even with the coarse-resolution data. The strong statement in *Wolff et al*.'s [2012] abstract that "in the 40 years surrounding 1859…where other chemistry was measured, *all* large spikes have the unequivocal signal…of biomass burning plumes" is simply wrong. Their supporting Figure 4 selectively covers only 20 of the 40 years in their study. When the full 40 year interval for the D4 core is shown (Figure 1), two of the five highest summer nitrate peaks display no associated biomass burning signal. Similar results also can be observed in the Zoe core. Given these issues, nitrate spike source conclusions must be considered speculative.

We also agree that impulsive nitrate spikes produced by SPEs are difficult to isolate from nitrate produced by other sources without additional chemical information, which is why we support multispecies analyses in our call for fine-resolution, follow-on studies. However, the concluding statement at the end of *Wolff et al*.'s [2012] abstract and *Wolff et al*.'s [2016] main message continues to be "Nitrate spikes cannot be used to derive the statistics of (SPEs)." Given that *Wolff et al*. [2012] did not resolve impulsive nitrate events in any of their ice cores used to dispute an association with SPEs, the subsequent effect of their absolute conclusion on the glaciology and space physics communities compelled us to take issue with their publication.

## 2. The Role of Large, Hard Spectrum Solar Proton Events

*Wolff et al*. [2016] argue that (1) prior studies show no evidence for measurable SPE influence on nitrate deposition, (2) without a Carrington signature there is no longer any smoking gun in the data, and (3) large events such as the Carrington "cannot be logged through nitrate." We disagree. First, prior studies of possible

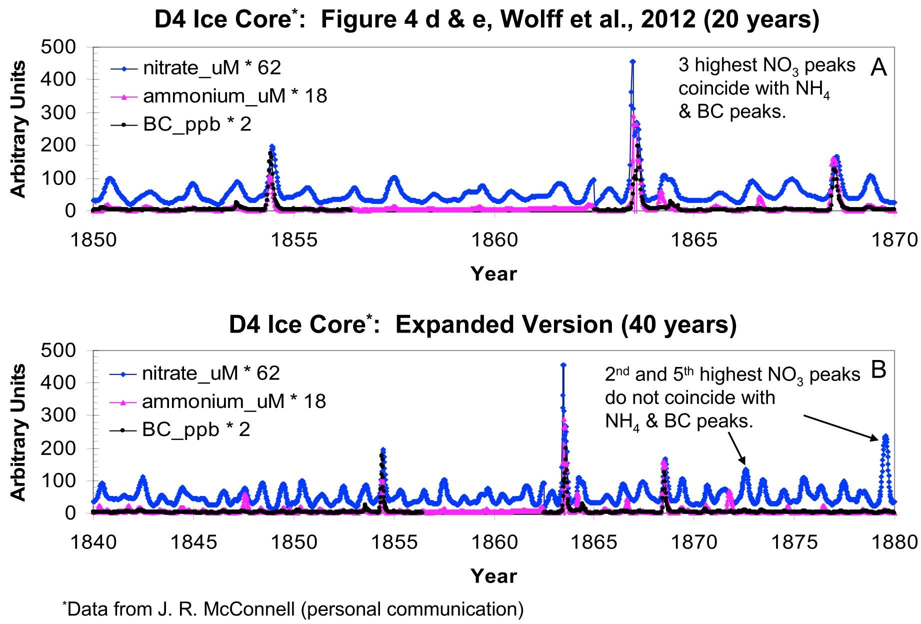


**Figure 1.** (a) D4 ice core data taken from Figure 4 of *Wolff et al.* [2012] supporting their statement that biomass burning plumes were associated with all major nitrate peaks in the 40 years around 1859. (b) When the full 40 year interval for the D4 core is shown, two of the five highest summer nitrate peaks display no anomalous biomass burning association.

SPE impacts have been very incomplete, and second, there are other major SPE/nitrate spike candidates in the ice core sequence that have not been properly studied. We address both issues here.

Most past numerical simulations involving analytic range-energy calculations [e.g., *Duderstadt et al.* [2014], and references therein] used an incomplete model that is more appropriate for soft spectrum SPEs such as the August 1972 and November 2000 events. These calculations use atmospheric inputs covering a limited energy range and ignore elementary particle interaction cascades in the atmosphere. These studies *contradict experimental data*—balloon-measured ionization—which show substantial SPE-induced ionization in the lower stratosphere and troposphere, revealing an SPE ionization peak at about 17 km, the bottom of the stratosphere at midlatitudes [*Nicoll and Harrison*, 2014]. Most studies that have included a more complete air shower simulation [e.g., *Usoskin et al.*, 2011, 2013] have not looked specifically at nitrate deposition. The models and simulations have ignored high-fluence, hard spectrum SPEs that can produce enough ionization in the troposphere and lower stratosphere to be deposited as nitrate spikes in the snow in just weeks to months, particularly if they occur at the right time of year (i.e., winter).

*Calisto et al.* [2013] modeled a scaled-up, Carrington-like, February 1956 SPE at the end of August and predicted up to a 50% increase in total nitric acid deposition for the next month over the South Pole. In asserting that once the Carrington Event is removed from consideration, "…the idea that any nitrate spikes above background are due to (SPEs) reverts to speculation." *Wolff et al.* [2016] ignore the 23 Feb 1956 SPE, which also has a well-resolved, associated nitrate peak in a Greenland ice core [*Smart et al.* 2014, Figure 1]. The 1956 SPE is the largest amplitude (a 46-fold increase in 15 min data) and the largest fluence (above 200 MeV) ground level event (GLE) in the cosmic ray monitoring history [*Kovaltsov et al.*, 2014], and it had a hard spectrum [*Pfotzer*, 1958; *Smart and Shea*, 1990; *Belov et al.*, 2005]. This event was worldwide in character, observed at the geomagnetic equator, and had estimated maximum proton energies >50 GeV [*Sarabhai et al.*, 1956]. In contrast, even though low-latitude aurorae coincident with an extreme geomagnetic storm were associated with it, there is no spectral information on the Carrington event. Using greatly improved simulations that follow the development of the proton-induced air shower and its ionizing effect on the atmosphere, we found consistency with the recent experiments showing substantial excess ionization down to 10 km and demonstrate sufficient nitrate deposition from the 1956 SPE. We discuss our results in section 4.

SPE candidates deserving consideration in addition to the February 1956 event include the impulsive nitrate spikes observed in the fine resolution Boston University (BU) core that correspond to the very hard spectrum solar cosmic ray ground level events observed by muon detectors in 1942, 1946, and 1949. Other candidates include the probable medieval SPEs of 775 A.D. and 994 A.D. [*Miyake et al*., 2012, 2013; *Melott and Thomas*, 2012; *Thomas et al*., 2013; *Ding et al*., 2015]. *Wolff et al*. [2016] assert that the 1937–1951 nitrate spikes in the BU core are not reliably reproduced in the GISP2-H core. In section 3.3 we show why their claim cannot be substantiated without fine-resolution, replicate core studies. The 775 A.D. event may have been 25–50 times stronger than the February 1956 SPE [*Usoskin et al*., 2013; *Thomas et al*., 2013] and should be detectable at Summit if it occurred in winter. There is also evidence suggesting that the 775 A.D. probable SPE may have been several somewhat smaller events occurring in Northern Hemisphere summer 776 A.D. [*Ding et al*., 2015], which would not be detectable at Summit or in Antarctic ice cores with resolutions corresponding to fewer than 10 samples per year. The problem is that almost no replicate ice core nitrate profiles exist with the fine temporal/depth resolution required to detect such events. This is why the inadequate resolution of the ice cores presented by *Wolff et al*. [2012] is a major issue in the SPE/nitrate deposition debate and why we are calling for a dedicated campaign of replicate, fine resolution, ice core analyses.

## 3. Ice Core Resolution—The Central Issue

### 3.1. General Comments

We do not dispute *Wolff et al*.'s [2016] general method of applying a rapid concentration change at the melter for characterizing smoothing in their system or that this method can be used to derive a resolution that is attainable, in principle, by an ideal Continuous Flow Analysis (CFA) system. However, this method is valid "only for systems with negligibly small dispersion" [*Breton et al*., 2012], and it is indisputable that there was a huge loss of resolution, whatever the cause, somewhere between the value *Wolff et al*. [2012] derived by this method (and reported in their Table 1) and the final statistical resolution that they actually obtained from the Zoe and D4 cores.

The resolution of any time series is generally characterized as the ability to distinguish between two adjacent peaks and, in the case of discrete sampling of an ice core, is only limited by the sample size, sampling rate, and postdepositional processes, whereas what *Wolff et al*. [2012, 2016] are calling resolution corresponds much more closely with their sampling rate, which is already twice the best attainable (Nyquist frequency) resolution in discretely sampled data. With CFA, resolution is additionally limited by mixing issues on the melthead and significant dispersion effects in the meltwater stream, due to nonuniform velocity profiles of a nonideal (real) fluid, causing smoothing of the resulting signal [*Breton et al*., 2012]. In the case of the ice cores listed in Table 1 of *Wolff et al*. [2012], it is clear that significant dispersion effects combined with multispecies analysis and other issues inherent with all CFA logging systems [*Rasmussen et al*., 2005] considerably limited their final, effective resolution. Using the data provided by Wolff and McConnell (personal communication, 2012), we determined their time resolution [*Smart et al*., 2014] and demonstrated that there *is no significant signal* in Zoe and D4 for periods smaller than about 4 months. Our determination of the time resolution, using both power spectral analysis and examination of the full width at half maximum of peaks in each of the four data sets, showed the Zoe and D4 resolutions are far more coarse (by factors of at least ~7–13) than those reported in Table 1 of *Wolff et al*. [2012]. Summer peaks, which are sharp in other data (i.e., GISP2-H and BU), are spread out over months in Zoe and D4 [*Smart et al*., 2014, Figures 4 and 5], and nitrate spikes are completely indiscernible. Asserting in Table 1 of *Wolff et al*. [2012] resolutions of ~0.05 years (0.6 months) for Zoe and ~0.025 years (0.3 months) for D4, both sampled by CFA, versus 0.067 years (0.8 months) for the discretely sampled GISP2-H core without any additional qualification, thereby implying that their ice core resolutions were finer, is misleading, regardless of whether "all the sources of dispersion" have been accounted for or how these numbers were derived. These results show that either the "empirical and direct way" *Wolff et al*. [2012] used to characterize their resolutions in Table 1 and elsewhere needs substantial revision or the term "sampling rate" and the corresponding numbers should be stated instead.

*Wolff et al*. [2016] claim that we ignore the inherent limits on resolution, but the fact is that this issue has not been investigated with fine-resolution, multispecies ice core studies, as our analysis demonstrated. We agree that it is difficult to attach precise calendar dates at subannual resolution because of snowfall variability. Nevertheless, precise dating is not required for deriving useful SPE statistics, and subannual dating estimates can be improved by applying what we know about the distribution of other species and snowfall within a year (e.g., more snow accumulation in summer than winter at Summit, Greenland [*Dibb and Fahnestock*, 2004]). *Wolff et al*. [2016] acknowledge that a resolution of order 1 month (significantly finer than the ~4 months in their data) is probably attainable after controlling for postdepositional processing, and we assert that this should be sufficient for deriving the statistics of large high-energy, hard spectrum SPEs.

### 3.2. Rebinning and Model Resolution

*Wolff et al*. [2016] attempt to compare the BU and GISP2-H cores by rebinning the BU data to mimic the coarser resolution of GISP2-H—and note that they do not exactly correspond. Their choice of 1.5 cm samples or 0.03 year sections is not appropriate. The correct rebinning should be closer to 0.04 years. We do agree that natural variability occurring at the time of deposition and afterward makes matching of fine-resolution nitrate spikes deposited over ~0.5–3.5 months challenging but, we assert, not impossible as discussed below.

### 3.3. Data Reproducibility

The issue of reproducibility of ice cores has long been a legitimate concern. This was a major reason for the duplicate drilling programs of GISP2 (American) and Greenland Ice Core Project-GRIP (European) at Summit, which showed similarities and differences in two parallel ice cores 28 km apart over long time intervals. Significant variability between pits and cores only a few meters apart at annual, as well as sub-annual, time scales (e.g. [*Laird*, 1987] and others) that is primarily related to post-depositional processes is well known. It is possible that some of the misdating scenarios detailed by *Wolff et al*. [2016], occurred with the GISP2-H core during this interval and simple seasonal adjustments would improve peak matching between cores. The comparison is also complicated by the fact that the BU core had a number of breaks and missing data in this time interval.

We do not accept *Wolff et al*.'s [2016] assertion that such an effort "cannot be successful," and we take strong issue with the comparison of GISP2-H data and binned BU data to show a lack of correlation and to support their asserted futility of finding repeatable SPE nitrate spikes. Just as two deep ice cores 28 km apart could be synchronized over periods in excess of 30,000 years, with careful analysis, it should be possible to extract information at the subannual scale from 4 to 5, relatively shallow ice cores a few meters apart covering a few thousand years. While a casual observer with little or no glaciological experience (with nitrate in particular) might be inclined to agree that there appears to be no matching nitrate spikes between the two cores presented in the figure of *Wolff et al*. [2016], careful, informed analysis suggests otherwise.

We note that the two cores were dated using different methodologies. In the case of GISP2-H, after selecting the yearly fiducial marks based on volcanic tie points and winter nitrate minima (supplemented with annual accumulation information), samples were linearly interpolated to assign subannual dates. The BU dating included an additional step where an annual accumulation cycle (based on surface measurements) was assumed (more snow in summer and less in winter) and dating was interpolated nonlinearly between yearly fiducial marks. This different approach introduced more apparent sample offset between the two cores than would exist had they been analyzed by the same method and is partially responsible for the misalignment of nitrate spikes.

Working backward through the *Wolff et al*. [2016] figure and analyzing their alleged lack of matches, we find approximately six major BU and/or GISP2-H spikes:

First, the BU spike near the end of summer 1949 could correspond to the smaller spike on the right side of the GISP2H 1949 summer nitrate maximum with their different magnitudes resulting from post depositional processes. Natural variability complicates the business of matching peaks, but these issues can be potentially resolved.

Second, the lack of a match between the winter nitrate peak identified as late 1946 in the BU core alleged by *Wolff et al*. [2016] is predicated on "Assuming that the dating of both cores is correct…" We assert that in fact the dating around this time, interval of at least one of the cores is incorrect, and this is the same peak as that dated to early 1947 in GISP2-H. Both peaks clearly occurred in winter, and the year breaks were chosen, in part, on the basis of the minimum nitrate values in those intervals, which are essentially the same on both sides of the GISP2H peak. Another set of analyses might determine that the actual year fiducial mark lies on the right side, at which point the two peaks would line up and match.

Third, the GISP2-H spike on the right side of the summer 1944 nitrate maximum (which *Wolff et al*. [2016] claim occurs in a year when BU has no spike) could correspond to the right side of the slightly offset BU 1944 summer high, which has a break just to the left of this peak. The missing data between the summer maxima and this peak preclude a proper interpretation.

Fourth to sixth, the BU spikes in 1937, 1939, and 1942 all have potential matches with GISP2-H spikes that may be more subdued, due to post depositional processes, or possibly offset (in the case of 1939). Again, these potential matches may not be substantiated but neither are they dismissible without additional analysis.

Despite assertions that our peak matching exercise is too flexible (possibly allowing spurious correlations of spikes), our point is that two cores analyzed with different methodologies are not enough for disputing or resolving such ambiguities. Similarly, arguments that subseasonal resolution at depth in Summit ice cores is inherently unachievable, based on surface studies alone, are also speculative until this issue has been addressed with dedicated, follow-on efforts involving statistical analysis of more than two replicate cores. The actual useful resolution (probably in the 0.5 to 2 month range) in ice cores at Summit, Greenland, has not been determined, thus reinforcing our call for a study involving multiple ice cores. Fine-resolution, multispecies analysis of 4 to 5 overlapping cores from the same site should be sufficient to characterize the subannual variance and reproducibility of each impurity (such as nitrate) and would establish limits on inherent depth and time resolutions. Wolff et al.'s resistance to this is puzzling.

For example, if the winter nitrate spike in the GISP2-H core is from the 23 February 1956 SPE, it should appear in several (though possibly not all) replicate cores, and methods of superposed epoch analysis, used routinely in such studies, would allow for a more complete characterization of such spikes, including their dating. A feasibility study covering a reasonable initial test time interval could be accomplished before funding a dedicated campaign to analyze the last several kyr.

The Law Dome ice core [*Palmer et al*., 2001] cited by *Wolff et al*. [2016] as a discretely sampled, very fine resolution core to dispute identification of nitrate spikes from SPEs is a poor example because this core (with at best 2 month resolution for 1840–1880) (like Halley) was drilled at a coastal site and reflects primarily a maritime climate. *Palmer et al*. [2001] and *Roberts et al*. [2015] both stated this caveat clearly in their papers. The fact that statistical evidence for SPEs was found in this core with these resolution and location limitations is remarkable.

## 4. SPE Event Signatures

*Wolff et al*.'s [2016] comments concerning the BU core and the lack of acidic nitrate spikes in the 1940s, especially the two GLEs in 1942 may have some validity, if confirmed with additional fine-resolution studies. However, the 1946 GLE they use as their example occurred in July (Northern Hemisphere summer) and thus may not be a good candidate for observing in the Greenland ice core record for the reasons stated above, though, it may be observable as a winter peak in Antarctica at some suitable site. There is also ambiguity in the interpretation of the 1949 results, and the possibility that the GISP2-H conductivity is more compatible with a nitric acid source for the nitrate spike associated with the November 1949 GLE.

*Wolff et al*. [2016] still neglect conductivity associated with the GISP2-H 1956 winter nitrate spike in Figure 1 of *Smart et al*. [2014]. Applying their same conductivity methodology to the 1956 nitrate peak suggests opposite results. The integrated 1956 peak averages a nitrate concentration of 33.9 ppb ($\mu$g/l) or 0.547 $\mu$equiv/l above the local background. Assuming no significant change in sulfate (i.e., no significant volcanic activity was reported during this period), and using standard molar conductivity tables [*Haynes*, 2015], the conductivity rise is expected to be about 0.23 $\mu$S/cm if the nitrate peak is acidic and 0.066–0.079 $\mu$S/cm if it is due to a nitrate salt.

The conductivity values colocated with nitrates in Figure 1 in *Smart et al*. [2014] were unfortunately mislabeled and are high by a factor of 100. The increase above background of the GISP2-H 1956 conductivity peak is actually 0.21 $\mu$S/cm. This is only 11% less than predicted for nitric acid, but a very large 159% to 212% more than predicted if the 1956 spike was formed by a nitrate salt intrusion, which *Wolff et al*. [2008] state is rare at Summit. In principle, the 1956 peak could result from some combination of sea salt, biomass burning, or dust aerosol scavenged nitrates, as invoked by *Wolff et al*. [2016], but this is increasingly improbable as it requires multiple strong winter sources and ignores the most straight forward explanation, i.e., nitric acid. This is strong circumstantial evidence against *Wolff et al.*'s [2016] thesis that nitrate spikes can only be caused by salts or other aerosol.

*Wolff et al.*'s [2016] mention that they await more detailed modeling studies, which are in progress. Such a study of the 23 February 1956 SPE has recently been conducted where the amount of nitrate available from this SPE has been computed using full spectrum modeling involving high-energy showers [*Melott et al.*, 2016]. These results indicate that nitrate production in the stratosphere is roughly 2–10 times greater than estimated by past limited energy range, analytic models. Summing the February 1956 SPE ionization from the surface to approximately 45 km at Summit produces the nitrate deposition found in the integrated winter 1956 GISP2-H peak. Therefore, this event can account for the measured nitrate with timely (~2 months) transport downward to the surface via mechanisms involving the polar vortex, denitrification, and polar stratospheric cloud assisted nitric acid deposition. These results lend strong support to the conclusion that the 1956 winter nitrate spike in GISP2-H data is mostly acidic and likely due to the February 1956 SPE.

*Wolff et al.* [2016] assert that our SPE/nitrate spike evidence is "very weak" by questioning the GISP2-H dating based on a sample number ratio of 2.5 between 1956 and 1955. However, our conclusion is also based on the likely acidic composition of this spike, and the new results mentioned above show that 1956 class SPEs can quantitatively explain spikes of this size and does not rely on dating alone. Additionally, snow accumulation can vary significantly from one year to the next at any given point on the ice sheet. Sample numbers from the nearby Zoe core dated as 1939 and 1941 differ from 1940 by factors of 2.2 and 2.3, respectively. The GISP2-H core section was dated using the Hekla (1947), and Askja (1961), Iceland volcanic eruptions as tie points, together with counting and interpolating annual nitrate cycles to determine 1956 as the most probable year for the spike in question. *Wolff et al.* [2016] consider the dating "uncertain within several months," but it is difficult to justify shifting the well-defined, midwinter, nitrate low (where the spike is found) from February by more than about 1 month.

Finally, *Wolff et al.* [2016] cite model studies by *Duderstadt et al.* [2015] as evidence opposing nitrate spikes produced by large SPEs. Duderstadt et al. now use essentially the same full air shower approach that we have been advocating for some time [e.g., *Melott et al.*, 2010]. They calculated percentage increases in SPE-produced nitrate relative to all $NO_y$ species in the atmospheric reservoir and concluded that they were too small to account for Greenland nitrate spikes. This approach is still incorrect for comparing with surface nitrate concentrations, which correlate more with nitric acid at Halley, Antarctica, because the atmospheric reservoir consists largely of organic nitrates [*Jones et al.*, 2011], which have a long residence time compared to $HNO_3$ [*Ridley et al.*, 2000]. Using a percentage enhancement dilutes the expected effect. Instead, calculations of the absolute amount of additional, SPE-produced, inorganic, nitric acid available for prompt deposition are consistent with the observed nitrate increase [*Melott et al.*, 2016].

## 5. Conclusions

We agree that the *McCracken et al.* [2001] calibration must be revised before nitrate spikes in ice cores can be used for identifying extremely large SPEs. This is very different from *Wolff et al.*'s assertion that it cannot be done.

As our understanding of the physics and chemistry by which SPEs can deposit nitrate in the snow has evolved, it has become apparent that most events do not have the spectral hardness and/or sufficient fluence to produce an observable spike, and we agree with the opponents on this point. Nevertheless, the standard atmospheric production model used by *Duderstadt et al.* [2014] and others has been clearly inadequate. It totally ignored the particle cascade in the atmosphere that results in energy deposition in the lower atmosphere. Consequently, we emphatically dispute the extrapolations by *Wolff et al.* [2012, 2016], *Duderstadt et al.* [2014], *Duderstadt et al.* [2015], and others that no SPEs can be found in polar ice core nitrates and that these records cannot be used to obtain statistics of past, very large SPEs. On the contrary, recent work, showing direct experimental and model evidence of substantial lower stratosphere/troposphere ionization from SPEs (e.g., *Usoskin et al.* [2011, 2013], *Nicoll and Harrison* [2014], and *Melott et al.* [2016]) indicates exactly the opposite may be the case. Thus, the SPE/polar ice nitrate hypothesis is still very much alive.

*Wolff et al*. [2016] advocate the alternate use of cosmogenic isotopes such as $^{10}$Be to study past SPEs. We agree that these provide useful information. However, they omit recently published work [*McCracken and Beer*, 2015] that has identified *all of the same events* in the 1940–1956 time interval previously identified as impulsive nitrate events in Figures 1 and 7 of *Smart et al*. [2014]. The $^{10}$Be and $^{14}$C records are annual; the $^{10}$Be increases appear 12–15 months after the high-energy SPEs. Including fine-resolution nitrate signatures together with the $^{10}$Be and $^{14}$C records would enhance the overall database of historic high-energy SPEs and might refine the dating and enable estimates of the spectral shape and fluence of past events.

In dismissing nitrates, while acknowledging their production by SPEs in the middle atmosphere and troposphere, *Wolff et al*.'s [2016] conclusion that "…we cannot see a plausible route to identifying and using their deposition in snow to diagnose past (SPEs)" is unproven, and their call for excluding nitrates from $^{14}$C and $^{10}$Be studies, based on inadequate analyses and incomplete models, is premature. We reiterate and stand by our main point: "Low time resolution analysis of polar ice cores cannot detect impulsive nitrate events."

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