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# Comment on “Low time resolution analysis of ice cores cannot detect impulsive nitrate events” by D. F. Smart et al.

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# Comment on "Low time resolution analysis of polar ice cores cannot detect impulsive nitrate events" by D.F. Smart et al.

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**Abstract** Smart et al. (2014) suggested that the detection of nitrate spikes in polar ice cores from solar energetic particle (SEP) events could be achieved if an analytical system with sufficiently high resolution was used. Here we show that the spikes they associate with SEP events are not reliably recorded in cores from the same location, even when the resolution is clearly adequate. We explain the processes that limit the effective resolution of ice cores. Liquid conductivity data suggest that the observed spikes are associated with sodium or another nonacidic cation, making it likely that they result from deposition of sea salt or similar aerosol that has scavenged nitrate, rather than from a primary input of nitrate in the troposphere. We consider that there is no evidence at present to support the identification of any spikes in nitrate as representing SEP events. Although such events undoubtedly create nitrate in the atmosphere, we see no plausible route to using nitrate spikes to document the statistics of such events.

## 1. Introduction

Large solar energetic particle (SEP) events have the potential to severely disrupt satellite, communications, and electronic systems. There is therefore strong motivation to establish a proxy that could document the statistics of occurrence of SEP events of different magnitudes and in particular the recurrence frequency of the largest events. There has long been a controversy as to whether spikes in the concentration of nitrate in polar ice cores can be used as such a proxy [*Legrand and Delmas*, 1986; *Zeller et al.*, 1986, 1989; *McCracken et al.*, 2001; *Palmer et al.*, 2001; *Wolff et al.*, 2008]. The perspective of the proponents, coming from the space physics community, has been that SEP events will produce $NO_x$ in the atmosphere, some of which will be deposited in ice. They have then attempted to align measured spikes with known SEP event dates to establish a link. The perspective of the opponents, coming from the atmospheric chemistry and ice core community, has been that any signal would be too small and broad to be detected as a spike, and that there are other causes of such spikes, unrelated to SEPs.

In an attempt to answer the questions posed by the controversy, and to reach both scientific communities, we presented a study [*Wolff et al.*, 2012] in which numerous high-resolution ice core profiles of nitrate from Greenland and Antarctic ice cores were compiled and compared for a 40 year period surrounding the well-known Carrington space weather event of 1859. We showed that a peak corresponding to that event was not present in most cores and that most nitrate peaks in Greenland during the 40 year period were due to the transit of biomass burning plumes over the ice core site (simultaneously depositing ammonium, formate, and to a lesser extent nitrate [*Savarino and Legrand*, 1998], along with specific fire tracers).

Subsequently, a new paper [*Smart et al.*, 2014] has been published, essentially as a critique of our paper [*Wolff et al.*, 2012]. This has three main conclusions:

1. The Carrington Event was a poor choice of test case because it is not clear whether it had the characteristics that the authors would expect to lead to a significant and sharp nitrate enhancement.
2. The resolution typically used to discern nitrate spikes in ice cores is insufficient to discover the kind of events the authors have in mind.

3. Analysis at higher resolution and measuring multiple chemical species may allow nitrate spikes caused by SEPs to be isolated, reinstating the possibility to assess their occurrence using the ice core record.

In this comment we would like to discuss each of these points in turn. Before doing so, we think it would be helpful to summarize two issues on which we think that the authors of the commented paper [*Smart et al*., 2014] and ourselves can now agree, which may not have been so obvious in earlier discussions.

SEPs deposit most of their energy and therefore produce most $NO_x$ in the middle stratosphere or above. A source of $NO_x$ at these altitudes would take months to years to reach ground level, would be broad and diffuse over time, and would be diluted by other sources. The signature of such a source could never be a sharp spike deposited almost immediately after the event. It seems therefore to now be a common ground that only hard spectrum events that can deposit energy into the troposphere could possibly produce the kind of spikes being described, and only nitrate produced at low altitudes should be seen as spikes.

It also is agreed that there are other causes of sharp nitrate spikes in polar ice, and in particular that some nitrate spikes, previously attributed to SEPs, are in fact caused by biomass burning plumes. This is critical because it instantly establishes that inventories of nitrate spikes without additional chemical information cannot be used to establish the statistics of SEP events, and this was actually the main message intended in our earlier paper [*Wolff et al*., 2012].

We now discuss the three main issues we have identified from the paper on which we are commenting [*Smart et al*., 2014].

## 2. The Role of the Carrington Event

We acknowledge that this event may not have deposited energy at low altitudes and that a nitrate spike of the kind the authors now propose would therefore not be expected. We emphasize that our earlier paper [*Wolff et al*., 2012] used the 40 years around the Carrington Event as an example period, in which we demonstrated that most peaks previously claimed to be SEP-related actually have a different origin. Our conclusion about the use of nitrate to identify SEP events did not rely on the Event itself or alone. However, the apparent coincidence of timing of the largest integrated nitrate peak in a 400 year period, and the Carrington Event, had previously been used as a major statistical underpinning of the hypothesis that nitrate spikes were indeed caused by SEPs [*McCracken et al*., 2001]. Once that coincidence is removed (because the spike has the signature of a biomass burning event), so that there is no evidence for any spike associated with the Carrington Event, the idea that any nitrate spikes above background are due to SEPs reverts to being speculation.

We agree that it is worthwhile to assess whether other events, known to have a hard spectrum, might show a signature, but the idea cannot be considered to have any prior support. In the reply to this comment [*Smart et al*., 2016], it is claimed that there is a nitrate peak in the GISP2-H core associated with the February 1956 SEP event. However, given the rapidly changing snow accumulation rate deduced in this part of the core [*Smart et al*., 2014, Figure 1] (14 samples in 1955 but 35 in 1956), the dating of the nitrate peak must be considered uncertain within several months, and the evidence that the nitrate peak is related to the SEP is very weak. As an additional point, our earlier work does establish that events such as the Carrington, which was associated with a huge geomagnetic storm, cannot be logged through nitrate.

## 3. Ice Core Resolution

*Smart et al*. [2014] carried out power spectral analysis to assess the resolution of different ice core records, and on this basis they suggest that many of them were inadequate to detect the kind of signals that SEPs might cause. First, we comment that the resolution of most of the analytical systems in use has been characterized directly by applying a rapid change in concentration at the melter and observing the character of the signal at the detector. This is an empirical and direct way to discover what kind of smoothing is caused by mixing of water on the melt head, in the tubes leading to the detector, and in the detector itself. It therefore includes all the sources of dispersion that would occur for a real sample. The resolutions quoted in Table 1 of our earlier paper [*Wolff et al*., 2012] were generally derived in this way. It is certainly likely that the system used on the Boston University (BU) core, analyzing only one component, has a higher resolution than the multi-component systems used at Zoe and D4. However, this analysis ignores many issues concerning the way in which signals are recorded in ice cores, which inherently limit the resolution that is useful and reliable.

Chemicals can be deposited either by wet or dry deposition. If they are dry deposited, they may give a very thin layer between snowfalls. If they are deposited by wet deposition, then they may give a signal that is initially the width of a snowfall (typically millimeters to centimeters). While there are numerous snowfall events each year at Summit (84 events were recorded in 2001), they are far from uniformly distributed through the year [*Dibb and Fahnestock*, 2004]. This has two consequences: first, it is impossible to accurately attach a calendar date to a layer in an ice core, because the snowfall quantity varies strongly from month to month. Based on *Dibb and Fahnestock* [2004], linear interpolation of the quantity of new snow with time within a year would lead to an error of up to about 2 months at some parts of the year. Second, there are months when there are only one or two snowfall events, so that the effective resolution, even in the deposited fresh snow, is 1–2/month. With no a priori way of knowing which months this applies to, the reliable resolution (if one is going to assess event frequencies) in the deposited snow in central Greenland is of order 1 month.

However, after snowfall, snow is redistributed through wind, leading to mixing of different snowfall layers, and to inhomogeneous deposition across sastrugi, where some parts of the surface may contain a thick layer, and the layer may be completely lost from other parts of the surface. Recent model studies suggest that drifting snow occurs on 50 or more days per year in central Greenland [*Lenaerts et al.*, 2012, Figure 8].

Finally, nitrate that is deposited as nitric acid is known to be mobile in the snow pack, so that even sharp peaks become smoothed through vapor redistribution. Nitrate that is deposited as aerosol will not be subject to this process but suffers from the issue that the deposition rate may be controlled by atmospheric concentrations of the countercation [*Wolff et al.*, 2008; *Duderstadt et al.*, 2014] rather than by concentrations of nitrate itself. For example, an influx of marine air containing high concentrations of sea salt will scavenge acidic nitrate from the atmosphere, leading to deposition of a nitrate spike even in the absence of any primary input of nitrate.

Of course, despite these issues, an event lasting only a few days can be detected if it is large enough. Indeed, the numerous biomass burning events that have been detected on the basis of markers such as ammonium, formate [e.g., *Whitlow et al.*, 1994; *Legrand and de Angelis*, 1996], and vanillic acid clearly derive from events that would only have passed over the ice core site for days, but many give clear nitrate signals [*Wolff et al.*, 2012]. However, a method that would rely on very narrow signals being reliably present in an ice core at such high resolution cannot be successful.

This is illustrated in *Smart et al.*'s [2014] own paper. The BU core shows perhaps five peaks that could be identified as sharp nitrate spikes in the period 1937–1951. These spikes appear to be 1–2 cm across and therefore should clearly show up in the GISP2-H core (which has a resolution of 1.5 cm from discretely cut samples, which equates to about 0.03 years at this age). We have (Figure 1) binned the data from the BU core into 0.03 year sections to mimic what the H core should show if the same peaks were recorded. We bin rather than smooth [*Smart et al.*, 2016], because discrete samples are indeed bins of the ice section. Some years have more than 30 samples in the H core; however, changing our bins to 0.04 or even 0.05 years does not affect the result. Assuming the dating of both cores is correct, it is immediately obvious that the largest peak in BU (in late 1946), which should show a peak of 250–340 ppb after binning (depending on the position of the bin boundaries), is not seen in the H core. Other significant sharp spikes in BU are also not seen at the expected depth in the H core; although one can find peaks in the H core at ages near to those in BU in some cases (e.g., at the end of 1949), they actually occur in the wrong part of the seasonal nitrate curve. The attempts to find plausible peak matches [*Smart et al.*, 2016, section 3.3] require such a flexible attitude to dating, seasonality and peak size and shape that it is hard to imagine a situation in which an apparent match would not be found. In fact, the GISP2-H core also shows one very clear spike, but it is in a year when BU shows no spike. Even if these spikes could be attributed to SEPs, they are not reliably recorded in adjacent cores.

We note that the very high resolution Law Dome (Antarctica) ice core was sampled discretely at about 12–20 samples/year (decreasing with depth) and also showed no significant nitrate enhancement, let alone a sharp spike, after individual SEP events [*Palmer et al.*, 2001], although a small, broad, enhancement of nitrate concentrations was found between 3 and 15 months after the SEP date, when averaged over the event population. We note also that we see no clear nitrate signal in the Law Dome DSS core around the $^{10}$Be peak associated with an event in 775 A.D. [*Miyake et al.*, 2012], recently identified as most likely a hard spectrum event 25–50 times as strong as the February 1956 event [*Usoskin et al.*, 2013].

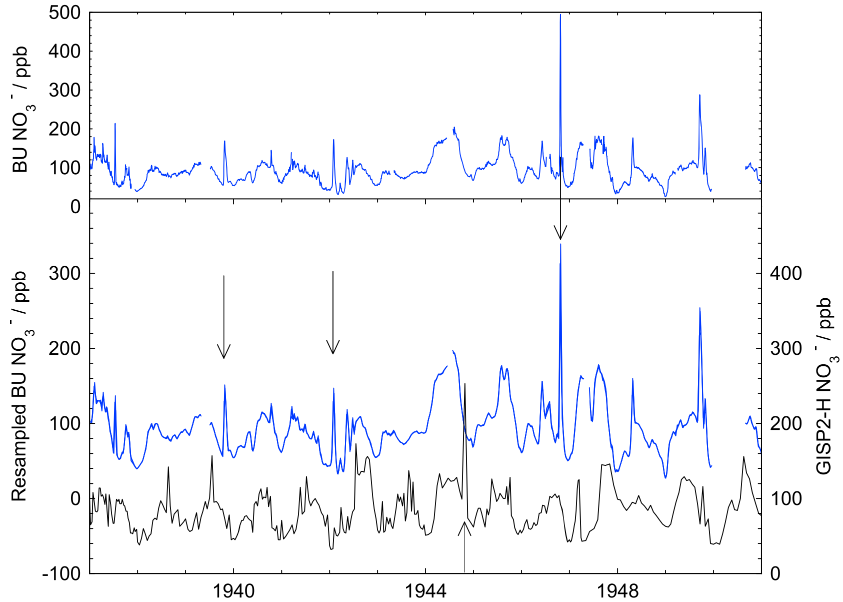


**Figure 1.** Nitrate in ice cores from the Greenland Summit region. (top) BU core data at its original resolution. (bottom) In black on the right axis, H core data. In blue offset by 100 ppb (left axis), BU core binned into sections with the same resolution (0.03 years) as the H core at this age. This was done with a range of starting points, so that the width of the blue line represents the variability caused by binning with different boundaries. Down arrows are at the position of prominent BU peaks; the up arrow marks the most prominent H core peak.

## 4. A Signature of SEP Events

It has been suggested that replicate sampling of several cores, with multiple chemical species, and at very high resolution, will allow SEP signals to be isolated [*Smart et al.*, 2014]. In principle, deposition of acidic nitrate might, at least in the preindustrial era, be indicative of SEP or other events of atmospheric origin, distinguishable from biomass burning events (with associated ammonium) or deposition of nitrate as a consequence of scavenging by sea salt or dust. This criterion (of nitrate peaks with no measured countercation) was used to isolate candidate peaks in surface snow in a recent paper [*Duderstadt et al.*, 2014]. However, if an additional requirement is that the peak preserved in ice at depth must be very narrow, such as those discussed [*Smart et al.*, 2014], then we would predict that they must have been deposited as aerosol and will therefore not have an acidic signature that might be a fingerprint of an SEP event. No cation information exists for the BU or GISP2-H core data. However, we can infer the nature of the cation from the liquid conductivity, which was also presented [*Kepko et al.*, 2009; *Smart et al.*, 2014]. The largest nitrate peak in the BU core, in 1946, rises about 400 ppb (6.5 $\mu$eq $L^{-1}$) above the background. Using well-documented ionic conductances, we would expect such a peak to be accompanied by a liquid conductivity increase of almost 3 $\mu$S $cm^{-1}$ if the nitrate was present as acid ($HNO_3$). The actual measured increase was about 0.8 $\mu$S $cm^{-1}$, exactly what would be expected in the case where $Na^+$ is the countercation (and similar for ammonium or calcium). A similar calculation confirms that none of the sharp peaks shown in the BU core between 1937 and 1951 are acidic.

Finally, we need to consider whether it is plausible that the events discussed [*Smart et al.*, 2014] could arise from a hard SEP event acting in the lower atmosphere. Modeling studies are needed to assess this. Newly accepted work [*Duderstadt et al.*, 2015] using the Whole Atmosphere Community Climate Model found that very large hypothetical SEP events, 2–3 orders of magnitude larger than those observed in recent decades, produced, as expected, $NO_y$ enhancements above the troposphere but insufficient $NO_x$ in the lowest 15 km of the atmosphere to produce spikes in Greenland ice cores. Earlier work [*Calisto et al.*, 2013] would also not support the kind of enhancements in nitrate deposition flux that would be needed to observe spikes for events such as those in the 1940s and 1950s. We understand that other modeling studies are in progress, and we await their results with interest, emphasizing that to be relevant to the production of very sharp spikes, such models will need to focus on production in the troposphere or lowest stratosphere.

## 5. Conclusion

*Smart et al*. [2014] showed that very sharp nitrate peaks may be detected in a system with very high resolution. However, there is no evidence that these arise from SEPs. Liquid conductivity data confirm that many sharp peaks are not acidic, making it likely that they are a by-product of influx of sea salt, biomass burning, or dust aerosol, rather than a consequence of a significant influx of nitrate. There seems no a priori way to distinguish SEP signals from other causes of nitrate enhancement, and we again emphasize that the evidence that was used previously, regarding the coincidence in date of SEP events and nitrate spikes, is no longer valid. In any case, we have shown clearly that such spikes are not reliably deposited in adjacent cores, for reasons we have discussed, which makes the use of such sharp features to log the power and frequency of SEP events impractical. We do not doubt that the largest SEPs will cause an enhancement of nitrate in the middle atmosphere and in extreme cases the troposphere. As ice core scientists, we would very much like to be able to use a proxy such as that envisaged, but we cannot see a plausible route for identifying and using nitrate deposition in snow to diagnose past SEPs. The use of $^{10}$Be [e.g., *Usoskin et al*., 2013], although at much lower time resolution, seems a much more promising path.

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