

## RESEARCH ARTICLE

10.1002/2015JD024064

This article is a companion to *Duderstadt et al.* [2016] doi:10.1002/2015JD023805 and *Sinnhuber* [2016] doi:10.1002/2015JD024950.

## Key Points:

- Solar proton events produce nitrate visible in ice cores
- Air shower secondaries must be followed to produce correct results
- Nitrate deposition depends on spectral hardness

## Citation:

Melott, A. L., B. C. Thomas, C. M. Laird, B. Neuenswander, and D. Atri (2016), Atmospheric ionization by high-fluence, hard-spectrum solar proton events and their probable appearance in the ice core archive, *J. Geophys. Res. Atmos.*, 121, 3017–3033, doi:10.1002/2015JD024064.

Received 7 AUG 2015

Accepted 12 FEB 2016

Accepted article online 29 FEB 2016

Published online 18 MAR 2016

## Atmospheric ionization by high-fluence, hard-spectrum solar proton events and their probable appearance in the ice core archive

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**Abstract** Solar energetic particles ionize the atmosphere, leading to production of nitrogen oxides. It has been suggested that some such events are visible as layers of nitrate in ice cores, yielding archives of energetic, high-fluence solar proton events (SPEs). This has been controversial, due to slowness of transport for these species down from the upper stratosphere; past numerical simulations based on an analytic calculation have shown very little ionization below the midstratosphere. These simulations suffer from deficiencies: they consider only soft SPEs and narrow energy ranges; spectral fits are poorly chosen; and with few exceptions secondary particles in air showers are ignored. Using improved simulations that follow development of the proton-induced air shower, we find consistency with recent experiments showing substantial excess ionization down to 5 km. We compute nitrate available from the 23 February 1956 SPE, which had a high-fluence, hard-spectrum, and well-resolved associated nitrate peak in a Greenland ice core. For the first time, we find that this event can account for ice core data with timely (~2 months) transport downward between 46 km and the surface, thus indicating an archive of high-fluence, hard-spectrum SPEs covering the last several millennia. We discuss interpretations of this result, as well as the lack of a clearly defined nitrate spike associated with the soft-spectrum 3–4 August 1972 SPE. We suggest that hard-spectrum SPEs, especially in the 6 months of polar winter, are detectable in ice cores and that more work needs to be done to investigate this.

## 1. Introduction

### 1.1. General Issues

Ionizing events in the Earth's atmosphere result in the formation of a variety of oxides of nitrogen [Crutzen *et al.*, 1975; Heath *et al.*, 1977; Reid and McAfee, 1978; Reagan *et al.*, 1981; Jackman and McPeters, 1985; Jackman *et al.*, 2000, 2001; Thomas *et al.*, 2005, 2007]. Many short-term variations in this ionization are dominated by solar proton events (SPEs), which are of interest for understanding the physics of the Sun and the possible hazards to our terrestrial electromagnetic technology and even to spacecraft systems or crews, particularly on missions outside the Earth's magnetosphere. For this reason, it is valuable to have additional information on their rate of occurrence and intensity over longer time periods than is available from direct cosmic ray monitoring measurements beginning in 1932 [Shea and Smart, 2000].

There has been a controversy over the possibility of using long-term ice deposits, such as those in Greenland or Antarctica, as an archive of solar activity. In particular, the concentration of nitrate as a function of depth in ice cores presents the possibility of identifying times of high ionization, as the main mechanism for removal of the nitrate from the atmosphere is precipitation in snow or rain. There have been competing claims over whether there is or can be a correspondence between ionization events and nitrate concentration in this archive [e.g., Zeller and Parker, 1981; Legrand and Kirchner, 1990; Dreschhoff and Zeller, 1998; Wolff *et al.*, 2012; Smart *et al.*, 2014; Wolff *et al.*, 2016; Smart *et al.*, 2016; Duderstadt *et al.*, 2016]. However, there is growing and now strong evidence for long-term modulation of polar nitrate deposition by solar activity [e.g., Zeller and Parker, 1981; Palmer *et al.*, 2001; de Zafra *et al.*, 2003; Traversi *et al.*, 2012; Poluanov *et al.*, 2014; Traversi *et al.*, 2016].

Nevertheless, the case for short-term nitrate features (spikes) in the polar record from individual SPEs continues to be contentiously disputed. One of the important issues has concerned the argument that

transport from the upper stratosphere and above (where the nitrate has been said to be formed) to the lower stratosphere and troposphere (where it can be precipitated out) is too slow for the events, which typically last a few days, to be detected [e.g., Legrand and Kirchner, 1990; Duderstadt *et al.*, 2014, hereafter D14].

## 1.2. Previous Modeling

Some computations have shown nitrate formation only in the middle stratosphere and up. Seppälä *et al.* [2008] looked at hard-spectrum SPEs. They do not discuss their ionization modeling but list Verronen *et al.* [2005] as the source of their methodology; this paper makes it clear that they use forcing by primary protons up to 2 GeV, but do not consider a full air shower with all the secondary particle types that are generated. As we shall see, this is no doubt why they found little ionization below 35 km. Another example is D14, who selected a relatively soft-spectrum (i.e., no ground level enhancement of neutrons or GLE) SPE on 9 November 2000 and considered only protons in a limited energy range of 10–300 MeV. D14 also used an exponential fit (based on data only up to 100 MeV) to the proton spectrum. However, Atwell *et al.* [2011] have shown that an exponential fit may underestimate the correct ionization at the low-energy end (10 MeV) by a factor of 2–3 and at the high-energy end (300 MeV) by an order of magnitude. Also, importantly, in the air shower modeling, apparently only the primary protons were included, which would not include ionization from secondaries that are responsible for effects in the lower atmosphere. All of the choices of D14 described here would discourage nitrate precipitation due to fewer ionizations and less penetration into the lower atmosphere.

After this paper had been initially submitted we were notified of Duderstadt *et al.* [2016, hereafter D16]. Their method of doing air shower computations has been corrected relative to D14 and now appears to be in basic agreement with the more complete approach we have been using [Atri and Melott, 2011] and advocating [Laird *et al.*, 2014]. D16 use a chemical transport model (Whole Atmosphere Community Climate Model (WACCM)) to calculate nitrates, while we assume that every  $\text{NO}_x$  ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) molecule created through SPE ionization is added to the atmospheric column. Our nitrate values are an upper limit since we assume that all  $\text{NO}_x$  produced is converted to  $\text{HNO}_3$  and then deposited. This is a valid assumption for altitudes below the upper stratosphere [Calisto *et al.*, 2013]; other removal processes, primarily photolysis, are only important above about 40 km and not in polar winter and also of little concern for rapid deposition in snow/ice.

However, there still are areas of concern:

1. D16 do not cite Nicoll and Harrison [2014], an important experimental study whose title we state here for emphasis: “Detection of lower tropospheric responses to solar energetic particles at midlatitudes.” This study shows an ionization peak due to the 11 April 2013 SPE at 18 km and active increased ionization down to 5 km. We are able to closely match the ionization profile, as shown later. None of the events modeled by D16 show these characteristics, indicating, instead, peak ionization near 50 km or above for most events they studied and little to no ionization below 20 km, with the notable exceptions of their “hypothetical” hard and soft events based on the February 1956 and August 1972 SPEs.
2. Despite basic agreement between D16’s method and ours, two differences are important. As mentioned, one is the choice of events. The many simulations shown in D16 do not specifically include the real 1972 or 1956 high-fluence events; instead, they focus on hypothetical events or on those (such as 20 January 2005) which have no observed nitrate spike. The 1956 nitrate spike, which we address later, can be seen in Smart *et al.* [2014].
3. The second and more fundamentally important difference is that we examine the total amount of nitrate expected to be produced in the air column and compare that with ice cores. The purpose of our study is to evaluate the additional amount of nitrate expected to be deposited following an SPE. This approach works very well for 1956, a well-known event.

On the other hand, comparing nitrate production from an SPE to the existing  $\text{NO}_y$  atmospheric background at any given time does not achieve this goal. D16 defines SPE-produced  $\text{NO}_y$  as  $\text{NO}_y = \text{N} + \text{NO} + \text{NO}_2 + \text{NO}_3 + 2\text{N}_2\text{O}_5 + \text{HNO}_3 + \text{HO}_2\text{NO}_2 + \text{ClONO}_2 + \text{BrONO}_2$ , but they then compare the amount of SPE-produced nitrate with the *total*  $\text{NO}_y$  present in their WACCM model atmospheric reservoir that includes many more species than they list in their definition. Calculating a percentage increase relative to this total  $\text{NO}_y$  background to estimate potential nitrate deposition from SPEs is inappropriate for the following reasons:

1. As documented [Ridley *et al.*, 2000, and references therein; Jones *et al.*, 2011], the atmospheric budget of nitrate can be dominated by organic nitrates that have a long residence time. Nitrates in surface ice at the sites studied were found to be more closely correlated with nitric acid, which is expected to be produced by only a few sources, including SPEs, and which is deposited much more rapidly than organic nitrates. D16's total  $\text{NO}_y$  background includes species such as PAN ( $\text{C}_2\text{H}_3\text{NO}_5$ ) and other organic nitrates [e.g., Kelly *et al.*, 1967; Jones *et al.*, 1999; Fahey *et al.*, 1985; Penkett *et al.*, 2009]. In addition, D16 use the WACCM model, normalized for 2004. As documented in Lamarque *et al.* [2013] and tested in Brakebusch *et al.* [2013], this normalized model also includes organic nitrates from anthropogenic sources of  $\text{NO}_y$ . Since organic nitrates typically come out slowly, they are not an appropriate "background" against which to compare SPE-produced nitrates. This background reservoir will be much larger than the  $\text{NO}_y$  that is available to precipitate rapidly.
2. It is well known that polluted air masses, due primarily to anthropogenic  $\text{NO}_x$  emissions, have significantly increased the Arctic  $\text{NO}_y$  background, as evidenced by a doubling in surface nitrate deposition in Greenland since 1950 [Herron, 1982; Mayewski *et al.*, 1986; Fischer *et al.*, 1998]. As the WACCM model adopted by D16 is set to 2004 [Brakebusch *et al.*, 2013; Lamarque *et al.*, 2013], it uses a much larger  $\text{NO}_y$  background or reservoir than actually existed during the early and prehistoric SPEs that are of interest.

D16's choice to include organic and other anthropogenic sources of  $\text{NO}_y$  has consequently both severely inflated the  $\text{NO}_y$  background beyond what should be considered for evaluating past SPE impacts and significantly reduced the apparent relative production of  $\text{NO}_y$  by SPEs. Their analysis makes it appear that any resulting nitrate deposition, even from large, scaled-up events, would be too small to detect above background sources when a more straightforward approach suggests differently. In contrast, our method of directly computing the absolute amount of additional nitrate available for deposition is more closely tied to the ground-truth nitrate measurements in ice cores.

### 1.3. Directly Measured Data on Atmospheric Ionization

As mentioned above, recent, balloon-borne, direct measurements [Nicoll and Harrison, 2014] show substantial ionization from an SPE within the lower stratosphere and troposphere. Considerable full modeling of air showers with proton primaries has been completed, which takes full account of ionization caused by the secondaries in the air shower [Atri *et al.*, 2010; Usoskin and Kovaltsov, 2006; Usoskin *et al.*, 2010, 2011]. This is the basis of our work here. In what follows, we briefly compare these ionization results with older computations [Jackman *et al.*, 1980; D14]. Then, we use our results to estimate the nitrate production as a function of altitude for the major SPEs of 23 February 1956 and 3–4 August 1972 and compare the results with experimental data from ice cores.

## 2. Numerical Modeling

### 2.1. Numerical Procedure Determining Ionization From Primary Cosmic Rays

In this work we use existing results of computations of atmospheric ionization. We employ two data sets, one a result of our own computations, the other provided by I. Usoskin (personal communication, 2015). The calculations provided by I. Usoskin were performed with a hybrid model that uses an analytic approach for proton energies between 10 MeV and 100 MeV, combined with results of full air shower modeling for energies above 100 MeV, to a maximum of 10 GeV. The low-energy calculations follow the approach described in Jackman *et al.* [1980] [see also Verronen *et al.*, 2005; Jackman *et al.*, 2011; Kokorowski *et al.*, 2012]. The energy deposited in altitude bin  $i$  by protons with kinetic energy  $E$  and pitch angle  $\theta$  is given by

$$E_{di}(\theta, E) = E - \left\{ -\frac{\Delta Z_i}{A} \sec\theta + E^B \right\}^{1/B} \text{ MeV}$$

using the range energy relation [Bethe and Ashkin, 1953; Whaling, 1958; Sternheimer, 1959; Green and Peterson, 1968]:

$$R(E) = A \left( \frac{E}{1 \text{ MeV}} \right)^B \text{ gm cm}^{-2}$$

with  $A = 2.71 \times 10^{-3}$  and  $B = 1.72$  for  $1 \leq E \leq 70$  MeV.

For proton energies above 100 MeV, ionization values use results of numerical modeling performed with the CORSIKA package, a widely used Monte Carlo-based simulation tool [Heck *et al.*, 1998]. This combined

approach makes the model more accurate than simple models that use only the Bethe-Bloch equation for Bragg curve calculations. The model is implemented with protons as primary particles incident isotropically from the hemisphere and setting the secondary particle cutoff energies as described below.

CORSIKA is calibrated with state-of-the-art experimental results worldwide. The model is capable of simulating all the electromagnetic and hadronic interactions resulting from a particle-induced cascade in the atmosphere down to the cutoff energy possible with the model. The lower energy cutoffs are as follows: hadrons = 50 MeV, muons = 50 MeV, electrons = 50 keV, and photons = 50 keV. The CORSIKA code allows the use of two hadronic interaction models, one for interactions up to 80 GeV and the other one beyond that. Since all the interactions modeled here are below 80 GeV, the outcome depends only on the low-energy model in CORSIKA. The data provided by I. Usoskin were produced using the FLUKA (v.2006.3b) [Fassò *et al.*, 2001] model in CORSIKA. Full details on that implementation may be found in *Usoskin and Kovaltsov* [2006], *Usoskin et al.* [2010], and *Usoskin et al.* [2011].

Our own calculations were performed for proton energies above 300 MeV, and we used the UrQMD (Ultrarelativistic Quantum Molecular Dynamics) model in CORSIKA [Bass *et al.*, 1998; Bleicher *et al.*, 1999], which is used widely for air shower simulations. We also used this model in our earlier work to compute atmospheric ionization with higher-energy primaries [Atri *et al.*, 2010]. Showers are tracked from the point of first interaction in the upper atmosphere down to the ground level in bins of  $10 \text{ g cm}^{-2}$ . The standard bin size recommended for simulations is  $20 \text{ g cm}^{-2}$  [Heck and Pierog, 2000]; we chose  $10 \text{ g cm}^{-2}$  for higher accuracy but had to use  $10^7$  showers for each energy to achieve satisfactory numerical and statistical accuracy. A link to the lookup table is provided in the paper where these results can be accessed.

## 2.2. Numerical Procedure Computing Ionization and Dissociation From Specific Events

The procedure used to compute ionization for solar protons is described in *Usoskin et al.* [2011], using the ionization tables described in the previous section. The total ionization for the event at altitude  $z$  is given by

$$I(z) = \int_{T_1}^{T_2} S(T) \cdot Y(z, T) dT,$$

where  $S(T)$  gives the number of protons with kinetic energy  $T$ ,  $Y(z, T)$  gives the number of ion pairs produced at altitude  $h$  by a single proton with kinetic energy  $T$ , and  $T_1$  and  $T_2$  give the range of proton kinetic energy values.

For protons of rigidity  $R$  in GV and kinetic energy  $T$  in GeV, the event-integrated omnidirectional-integrated fluence (protons  $\text{cm}^{-2}$ ; integrated over the event-specific duration) is given by the Band function

$$J(> R) = J_0 \cdot R^{-\gamma_1} e^{-R/R_0}, \quad \text{for } R \leq (\gamma_2 - \gamma_1)R_0,$$

$$J(> R) = J_0 \cdot A \cdot R^{-\gamma_2}, \quad \text{for } R > (\gamma_2 - \gamma_1)R_0,$$

where

$$A = [(\gamma_2 - \gamma_1)R_0]^{(\gamma_2 - \gamma_1)} e^{(\gamma_1 - \gamma_2)},$$

$$R = \sqrt{T^2 - 2T_0 \cdot T},$$

and  $T_0 = 0.938 \text{ GeV}$  is the rest mass energy of the proton. The numerical method uses the event-integrated differential spectrum in proton kinetic energy (protons  $\text{cm}^{-2} \text{sr}^{-1} \text{GeV}^{-1}$ ):

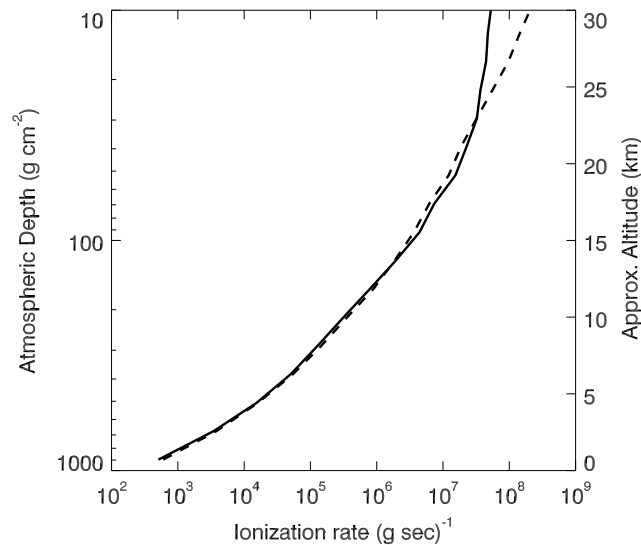
$$S = \frac{1}{4\pi} J_0 \cdot R^{-\gamma_1} e^{-R/R_0} \frac{(\gamma_1 R_0 + R)(T + T_0)}{R^2 R_0}, \quad \text{for } R \leq (\gamma_2 - \gamma_1)R_0,$$

$$S = \frac{1}{4\pi} J_0 \cdot A \cdot \gamma_2 \cdot R^{-\gamma_2} \frac{T + T_0}{R^2}, \quad \text{for } R > (\gamma_2 - \gamma_1)R_0.$$

For the 23 February 1956 event, the spectrum values are  $J_0 = 1.747 \times 10^8$ ,  $R_0 = 0.5661$ ,  $\gamma_1 = 1.758$ , and  $\gamma_2 = 5.04$ . For the 3–4 August 1972 SPE the values are  $J_0 = 6.340 \times 10^6$ ,  $R_0 = 0.2980$ ,  $\gamma_1 = 3.260$ , and  $\gamma_2 = 6.27$ . Data for both events were taken from *Tylka and Dietrich* [2009].

## 2.3. Comparison With Other Work, Data Sources, and Test Cases

*Jackman et al.* [1980] follow only ionization produced by primaries and secondary electrons generated by them. *Jackman et al.* [2011] apparently supplemented this with data inferred from GLEs, usually a burst of



**Figure 1.** Comparison of ionization rate profile generated using our model for primaries of energy greater than 300 MeV (solid line) and that presented in Figure 2B of *Usoskin et al.* [2011] (dashed line) for the 20 January 2005 SPE, assuming 1 day duration. The greatest difference is at the highest altitude (30 km), probably because *Usoskin et al.* [2011] included lower energy primaries.

excess neutrons observed at the ground [*Overholt et al.*, 2013], but did not include muons, which dominate ionization at lower altitudes [*Atri and Melott*, 2011]. A more complete approach [*Bazilevskaya et al.*, 2008; *Atri et al.*, 2010; *Usoskin et al.*, 2011; *Calisto et al.*, 2013] follows the production of all secondaries. *Atri et al.* [2010] published lookup tables so that new simulations do not need to be done for each new spectrum. Ionization tables as a function of altitude for primaries ranging from 70 MeV to 1 PeV are given. An analytical fit (described above) is available for primaries below 70 MeV [*Jackman et al.*, 1980]. Any SPE spectrum can be modeled by convolution with this table.

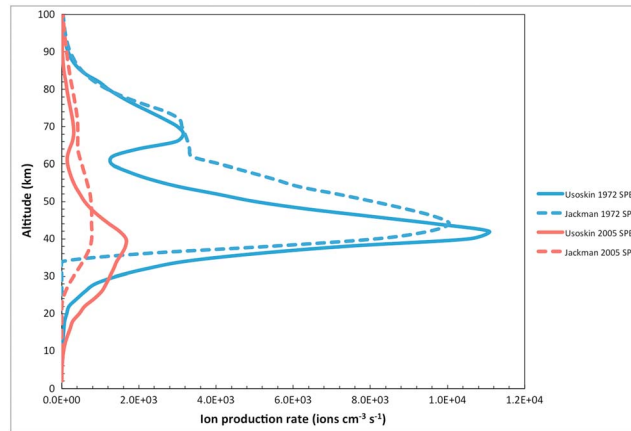
The general characteristics of the table of *Atri et al.* [2010] can be compared with the table of *Usoskin and*

*Kovaltsov* [2006] and *Usoskin et al.* [2010]. The latter includes results for alpha particles, which *Atri and Melott* do not. *Atri and Melott* show 10 entries per decade in primary energy, while *Usoskin and Kovaltsov* [2006] and *Usoskin et al.* [2010] show two. *Atri and Melott* show 46 vertical bins in atmospheric density; *Usoskin and Kovaltsov* [2006] and *Usoskin et al.* [2010] combined show 52. *Usoskin and Kovaltsov* [2006] and *Usoskin et al.* [2010] combined show primary energies from 100 MeV up to 1 TeV; *Atri and Melott* include primary energies from 300 MeV up to 1 PeV (3 orders of magnitude higher than the other tables). One PeV is far beyond the range necessary for SPE events but does assure that the high-energy tail will be included, which is important for hard, major GLE-producing events as well as making possible the modeling of effects of nearby supernovae, gamma ray bursts, or other high-energy astrophysical events [*Melott and Thomas*, 2011; *Piran and Jimenez*, 2014]. As noted earlier, the two tables agree well in their region of overlap.

As a check on our modeling results, we have compared them to an ionization profile for the 20 January 2005 SPE reported in *Usoskin et al.* [2011]. Figure 1 shows results of our model applied to the 20 January 2005 SPE case (assuming a 1 day duration) along with those from Figure 2B of *Usoskin et al.* [2011] (for the same SPE). We note that the agreement is very good below ~23 km. A divergence does begin to appear at the highest altitudes, probably because *Usoskin et al.* [2011] included lower energy primaries, which contribute more ionization at higher altitudes.

Both sets of results include ionization far below 20 km, the cutoff shown in D14. The GLE on 20 January 2005 clearly shows that ionization in the troposphere is possible, even though it is not shown in the simulations of D14, who considered a softer event whose conclusions cannot be generalized to harder spectrum events. However, the production of a significant flux of muons for detection on the ground and ionization in the lower atmosphere requires some primaries about 10 GeV or above [*Atri and Melott*, 2011], while a GLE (detection of a neutron excess on the ground) can be generated by primary particles with energy below 2 GeV [see, e.g., *Overholt et al.*, 2013]. A GLE is therefore a necessary but not sufficient condition for substantial lower atmosphere effects.

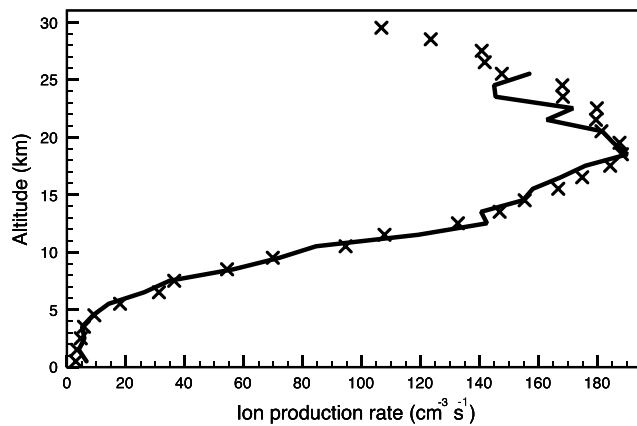
In Figure 2 we compare ionization rates computed using a full air shower treatment (provided by I. Usoskin) versus ionization rates computed using only the low-energy analytic method described in section 2.1 (data provided by C. Jackman, downloaded from <http://solarisheppa.geomar.de/solarprotonfluxes>). We show ionization rates for two SPEs; 3–4 August 1972, which had a soft spectrum (but high fluence), and 20 January 2005, which had a hard spectrum (but lower fluence). As can easily be seen, the analytic-only method significantly underestimates the ionization in the middle to low atmosphere, even for the soft-spectrum



**Figure 2.** Comparison of ionization rate profiles for the 3–4 August 1972 SPE and the 20 January 2005 SPE, computed using two different methods: a low-energy analytic-only method, data from C. Jackman (dashed lines); and a full air shower treatment, data from I. Usoskin (solid lines). Note that the analytic-only SPE profiles significantly underestimate ionization rates in the middle to lower stratosphere. The disagreement is even more pronounced for the hard-spectrum (but lower fluence) 2005 event.

found that by implementing a low-flux, power law index spectrum of  $dN/dE = 0.91 \times E^{-2.4}$  protons ( $\text{cm}^{-2} \text{sr}^{-1} \text{GeV}^{-1} \text{s}^{-1}$ ); consistent with these data we reproduce the ionization plotted in NH. (Due to the geomagnetic cutoff rigidity  $47.5^\circ\text{N}$  in the vicinity of the UK [Smart et al., 2006], the lower end of the spectrum is irrelevant here.) The GOES proton data are on the NOAA database <http://satdat.ngdc.noaa.gov/sem/goes/data/>

As we discuss later, winter conditions are generally much better than summer for the preservation of ice core nitrate signals. Since fine-resolution winter ice core data from Greenland are not available for 2005 or 2013, we cannot do a direct comparison with nitrate production for either event. We therefore now focus on the

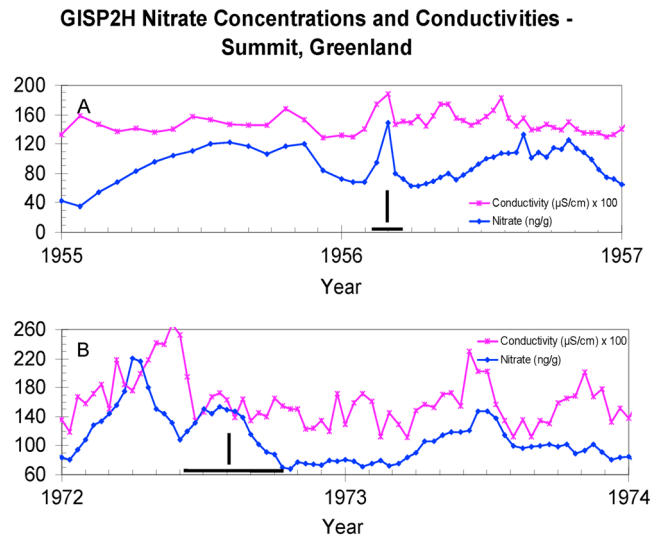


**Figure 3.** Results of a balloon experiment described in Nicoll and Harrison [2014] which was launched on 11 April 2013 from Reading, UK, compared with results of our air shower computations. A proton spectrum with  $-2.4$  spectral index was applied and added to the ambient ionization rate (assuming the rigidity for  $47.5 \text{ N}$  at Reading, UK) measured by the balloon experiments. The data were provided to us by Keri Nicoll. The measured ionization profile during the event is shown as a solid line and compared against our calculated values (cross marks). The maximum percentage difference between the two is 16% at 24 km. We note that in the Nicoll and Harrison [2014] Figure 2 (right), the excess ionization due to the SPE peaks at 18 km and reaches down to 5 km.

case (1972). In fact, the low-energy analytic-only method yields zero ionization below the stratosphere in both cases, while the air shower method shows significant ionization in the troposphere.

We supplemented the above test with comparison against the balloon data of Nicoll and Harrison [2014], hereafter NH, which directly measured ionization from the 11 April 2013 SPE over a range of altitudes from 1 to 30 km. This comparison is shown in Figure 3. We note that in this experiment the SPE-induced ionization, as shown by NH, peaked at about 18 km and is clearly nonzero down to 5 km. The GOES high-energy proton and alpha data provide the flux and spectral information on this event for energies in excess of 433 MeV/nucleon, and we

SPE of 23 February 1956, which is the largest GLE in amplitude (a 46-fold increase in 15 min data) and fluence above 200 MeV in the cosmic ray monitoring history [Kovaltsov et al., 2014], and had a hard spectrum [Pfozter, 1958; Smart and Shea, 1990; Belov et al., 2005]. This event was worldwide in character and observed at the geomagnetic equator by [Sarabhai et al., 1956], who estimated the maximum energy of solar protons to be  $>50 \text{ GeV}$ . More importantly, since our goal is to compare atmospheric computations with ice core data, there is an observed impulsive nitrate event in the ice core from Summit, Greenland [Smart et al., 2014, 2016]. In this case quantitative comparison is possible proceeding from the measured spectrum to the amount of nitrate produced in the atmosphere and the amount found in the ice (see Figure 4a). We use data provided by I. Usoskin (personal communication, 2015), which was produced following the procedure



**Figure 4.** The nitrate and conductivity records for two time periods in the GISP2H ice core, as discussed in the text. (a) The nitrate and conductivity peaks in early 1956 (indicated by horizontal bar, which runs between the adjacent nitrate minima) coincide with a hard-spectrum SPE and coincident GLE event on 23 February (time indicated approximately by the vertical bar). The area under the nitrate peak (composed of four data points) and minus the local background (the average of the two adjacent end points and local minima) corresponds to a deposition of  $116 \text{ ng NO}_3 \text{ cm}^{-2}$  (see text). (b) The soft-spectrum SPE on 3–4 August 1972 (vertical bar) does not produce a nitrate peak clearly distinguishable above background here, though the secondary peak (indicated by horizontal bar) is a possible candidate.

observed. The nitrate deposition above background for the winter 1956 GISP2H peak identified by *McCracken et al.* [2001] that is superimposed on the annual cycle was determined by computing the average concentration of the four data points that comprise the peak and subtracting from it the local background represented by the average of the two adjacent local minima. The resulting average nitrate concentration ( $33.9 \text{ ng g}^{-1}$ ) above background was then multiplied by the thickness of all four samples (6.0 cm) and by the average density of the ice at that depth ( $0.568 \text{ g cm}^{-3}$ ), yielding a deposition of  $116 \text{ ng NO}_3 \text{ cm}^{-2}$ . In sections 4 and 5 we will specifically investigate whether the SPE of 23 February 1956 can provide this amount of  $\text{NO}_3$ .

It is difficult to put an error estimate on this number because there are many potential sources of error related to deposition that are external or environmental. The calculated nitrate deposition was derived from the best available data. The nitrate concentration instrument error is less than a few percent, and the density measurement error is roughly a few percent. Additional cores and measurements will be required to better estimate errors resulting from other environmental factors.

The Figure 4 horizontal axes were constructed under the assumption of linearity between time and deposition within a given year (i.e., equally spaced samples). This time approximation is not strictly true at the subannual scale. *Dibb and Fahnstock* [2004] conducted a 2 year snow stake study of accumulation rates at Summit. They concluded that most of the accumulation occurs in summer (warm) months. Using their monthly averages for those 2 years to refine our approximation starting on 1 March, we estimate that it took roughly 2–4 months for the winter 1956 nitrate peak to be deposited. Increased photochemistry during the summer and absence of the polar vortex may make it more difficult to see an SPE-produced nitrate peak then. So events like this SPE may need to be large and have a bias toward winter occurrence in order to be observed in nitrates.

#### 4. Results

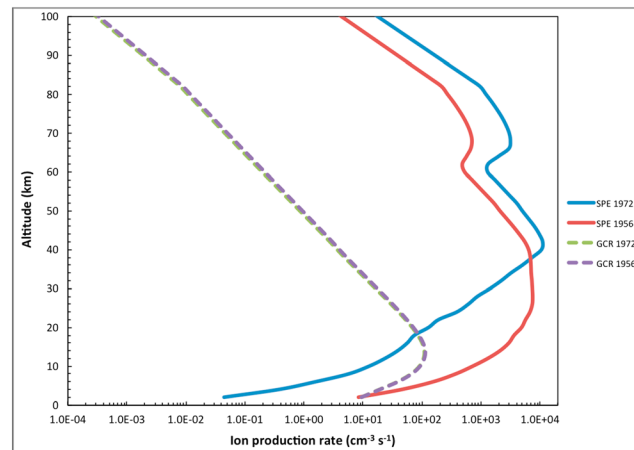
In Figure 5 we show a summary of the atmospheric ionization results for 23 February 1956 and 3–4 August 1972, obtained from I. Usoskin (personal communication, 2015), generated using the procedure detailed in section 2. The dashed lines show the background ionization due to galactic cosmic rays (GCRs) in

described in sections 2.1 and 2.2, using the derived high-energy-fluence spectrum specified for 1956 in the previous section of this paper [*Tylka and Dietrich, 2009*] over the range 10 MeV to 10 GeV, although there were higher energy primaries present; so our conclusions are conservative in that they will underestimate the amount of ionization and its penetration into the troposphere.

In addition, we examine the large SPE of 3–4 August 1972, which had a high fluence but a very soft spectrum. The purpose of this is primarily to demonstrate the ionization changes due to a soft spectrum.

#### 3. Comparison With Ice Core Data for 1956

In the following, we compare the results of our computations with the GISP2H ice core data [*Dreschhoff and Zeller, 1998*], which show a nitrate spike coincident with the SPE and its accompanying GLE (Figure 4a). The annual cycle of summer high-winter low can be



**Figure 5.** Ionization rate profiles (provided by I. Usoskin). Note the logarithmic x axis in contrast to the linear scale of Figure 2. The dashed lines are the background ionization rates (nearly identical) in the atmosphere due to Galactic Cosmic Rays in February 1956 and August 1972. The solid lines are ionization rates assuming a 1 day event duration. The red solid line shows ionization due to the 23 February 1956 SPE. Note that there is considerable ionization below 20 km, which is not shown or included in many computations. The blue solid line shows ionization due to the 3–4 August 1972 SPE, which does not produce a sharp peak clearly distinguishable above the background. This had a larger fluence of protons with energy above 30 MeV but a softer spectrum than the 1956 event. Consequently, there is more ionization at high altitudes than in 1956 but much less at lower altitudes.

value may range from 15% to 95% [Funke *et al.*, 2011; Sinnhuber *et al.*, 2012]. Here we use 55%, which in any case is about the middle of that range. In order to get an estimate for the total  $\text{NO}_3$  deposited, we first convert the total ionization for the entire event at each altitude bin in the model to  $\text{NO}_x$  produced by multiplying by  $1.25 \times 0.55$ . In the stratosphere, the  $\text{NO}_x$  produced is subsequently converted to  $\text{HNO}_3$  over a few weeks' time [Funke *et al.*, 2011]. Therefore, we take the  $\text{NO}_x$  value computed at each altitude, assume it is all converted to  $\text{HNO}_3$ , and then sum over a given altitude range to give a total event-integrated deposited value in  $\text{ng NO}_3 \text{ cm}^{-2}$ . It is important to emphasize that our ionization results used to compute nitrate deposition represent the total ionization for the event considered, that is, integrated over the entire event duration. This time integration is implicit in the proton spectrum parameters used in this work, so that when we apply the spectrum in our ionization model we have computed ionization for the event as a whole, rather than an ionization rate, which then leads to a total nitrate deposition value.

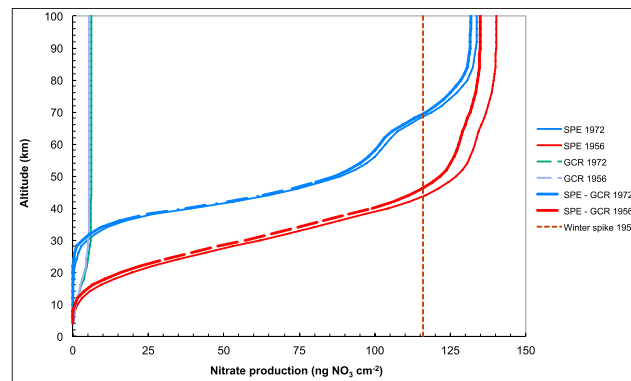
In Figure 6 we present results of these calculations for the 23 February 1956 and 3–4 August 1972 events, along with the corresponding results due to GCR ionization at these two dates. GCR ionization produces nitrate in the same way SPEs do and so represents a background source with the same properties (as opposed to other background sources such as  $\text{NO}_y$  that is transported from lower latitudes). Nitrate values (in  $\text{ng NO}_3 \text{ cm}^{-2}$ ) summed from the ground to the altitude indicated are given, computed from modeled ionization as described above. We also show the difference between the SPE and GCR values for both cases. We are interested here in the enhancement due to SPEs above the background GCR ionization. Therefore, assuming a normal GCR background, the enhancement of nitrate for deposition is given by the SPE-GCR values. On the other hand, GLEs are often associated with a reduction in GCR flux known as a Forbush decrease. In the case of a complete elimination of GCR background (an extreme example), the enhancement is given by the SPE values alone. This allows us to define a maximum (SPE values only) and minimum (SPE-GCR) enhancement.

We find that summing from the surface (3.2 km at Summit) to an altitude of 44–46 km, we reach approximately the  $116 \text{ ng NO}_3 \text{ cm}^{-2}$  found in the ice core peak (see Figures 4a and 6), both with and without the GCR background (and hence the presence/absence of a Forbush decrease does not make a significant difference for our results). We also note that half the needed production occurs below 30 km. So there is

February 1956 and August 1972 and the solid lines the ionization rate produced by the SPEs. The proton spectrum used is event integrated, but here we present ionization rate, assuming a 1 day duration for the SPEs, in order to allow for comparison with GCR ionization rates acquired from <http://cosmicrays.oulu.fi/CR11/CR11.html> [Usoskin and Kovaltsov, 2006; Usoskin *et al.*, 2010].

The ionization values are mapped into nitrate production as follows. Ionization and dissociation of  $\text{N}_2$  and  $\text{O}_2$  by solar protons leads to production of about 1.25 N atoms per ion pair [Porter *et al.*, 1976; Jackman *et al.*, 2005]. These N atoms are distributed between the electronic ground state  $\text{N}(^4\text{S})$  and the excited state  $\text{N}(^2\text{D})$ . The excited state  $\text{N}(^2\text{D})$  production determines the net production of  $\text{NO}_x$ . It is usually assumed that 55% of the N atoms are in the excited state [Rusch *et al.*, 1981; Jackman *et al.*, 2005]; however, the actual





**Figure 6.** Integral nitrate production, i.e., summed from the surface (at 3.2 km elevation appropriate for Summit, Greenland) to the altitude indicated, computed from modeled ionization as described in section 4. The profiles for 1972 and 1956 presented here are results of modeling using the 3–4 August 1972 and 23 February 1956 SPE spectra, the GCR ionization appropriate for those times (see section 4), and the difference of the SPE and GCR contributions. The SPE-GCR values (dashed blue and red curves) give the enhancement over GCR background assuming a normal GCR flux (dashed green and purple curves). The SPE-only values (solid blue and red curves) give the enhancement in the case of no GCR background (i.e., a complete Forbush decrease). The intersection of the February 1956 SPE and SPE-GCR nitrate production curves with the dashed vertical line ( $116 \text{ ng NO}_3 \text{ cm}^{-2}$ ) at 44–46 km corresponds to the GISP2H ice core winter nitrate spike deposition above background and shows that nitrate production from 3.2–45 km by the 23 February 1956 SPE and subsequent deposition over 2–4 months is sufficient to explain the spike. Note that half of the nitrate is produced below 30 km, where deposition times are on the order of 1 month. As can be seen, the assumption of a Forbush decrease does not make a significant difference in sum values at the altitudes discussed in the text.

up to 100 km (Figure 6), but the distribution was very different, emphasizing ionization at higher altitudes. In contrast to 1956, one would have to go to 68 km to account for an ice core spike like 1956 from the 1972 results.

Our results constitute the first comparison of ionization and nitrate production by high-fluence SPEs with nitrate deposits in ice cores, which are candidate signals of these events. We find that at least for a major hard-spectrum event, there is good agreement between the computed results and the amount measured in the ice core.

## 5. Discussion

### 5.1. Was Sufficient Nitrate Available From the 23 February 1956 SPE for Prompt Transport?

As can be seen (Figure 6), although sufficient nitrate is produced in the stratosphere and below, tropospheric nitrate (which could be deposited very rapidly) by itself is insufficient to account for the nitrate peak in the ice core data for 1956. The data appear to require inclusion from the midstratosphere downward, still very different from past assertions that nitrates are made from the midstratosphere upward [e.g., Wolff *et al.*, 2012; D14]. We see three possibilities: (1) Association of the peak with the SPE is simply incorrect. (2) The SPE has a much harder spectrum than assumed, somehow turning back up at higher energies. A harder spectrum would deposit more energy in the troposphere. (3) Transport downward in the midstratosphere can happen rapidly enough to account for this peak—and even narrower peaks identified with GLEs in the 1940s [Smart *et al.*, 2014, 2016]. We discuss each of these possibilities for resolving the question.

### 5.2. Possible Misinterpretation of Coincidence Between 23 February 1956 Event and Nitrate Peak

A number of studies beginning with Wilson and House [1965] have attempted to demonstrate and refine the association between solar activity and nitrate variability in polar ice cores [e.g., Zeller and Parker, 1981;

sufficient nitrate produced in the atmospheric column to account for this ice core peak contemporaneous with the long-duration, high-energy, hard-spectrum SPE, provided timely transport downward from as high as 46 km is feasible.

As noted above, there is uncertainty in the fraction of N atoms in the excited state following ionization, which determines the net production of  $\text{NO}_3$  that is eventually precipitated. If we take the extreme maximum fraction (95%), summing to 32 km gives approximately the ice core value. On the other hand, if we take the extreme minimum fraction (15%), there is not enough  $\text{NO}_3$  produced over the entire atmospheric column to explain the ice core peak. As discussed above, we take 55% as the best estimate, but note here that the deposited nitrate will depend strongly on the exact conversion fraction used.

We contrast this with the results from the 3–4 August 1972 SPE, which are shown in Figure 5. It produced only slightly less nitrate when summed

Laird et al., 1982; Dreschhoff and Zeller, 1994, 1998; McCracken et al., 2001; Smart et al., 2014, 2016]. These studies have invoked statistical correlations between some of the impulsive nitrate peaks that appear to be contemporaneous with known large SPEs. However, spurious correlations could occur in about four ways:

1. The apparent coincidence in timing could be spurious. Ice core dating in historical times is based on identifying major, absolutely dated volcanic eruptions in the sulfate and conductivity (determined primarily by sulfate for the anions) records and interpolating between these tie points using impurity records that display annual cycles. The greater the distance between volcanic tie points, the less certain the dating at the annual scale. The GISP2H conductivity record used the Hekla (1947) and Askja (1961) Iceland eruptions as absolutely dated tie points, together with counting and interpolation of annual nitrate cycles in between, to determine 1956 as the most probable year for the spike in question. However, this peak possibly could be misdated still by as much as 1 or, less likely, 2 years.
2. Postdepositional processing at the surface including physical mixing by winds, sublimation, condensation, and chemical processes involving firn-air interface exchange [e.g., Laird et al., 1986; Zeller et al., 1986; Laird et al., 1987; Dibb and Jaffrezo, 1997; D14] tend to reduce the highest nitrate concentrations found at the surface as they are incorporated into the ice column. Still, it appears feasible for high summer surface nitrate levels unrelated to SPEs to be incorporated in toto on occasion as isolated spikes at random points across the ice sheet and at least partly preserved at depth [e.g., Laird, 1986; Laird et al., 1987; Dibb et al., 2007]. Without additional fine-resolution nitrate studies of ice cores there is no way to verify whether this effect is responsible for the 1956 spike in the GISP2H core or whether the spike persists across the ice sheet (which seems more likely, given its apparent occurrence during winter).
3. Downward transport from the stratosphere (due to subsidence in the winter polar vortex) in lieu of an SPE is a likely background source of nitrate in ice cores. However, as with the anthropogenic background source in the troposphere (discussed below), this process is generally considered to be too slow and steady [e.g., Legrand and Kirchner, 1990; D14] to produce the sharp nitrate spikes observed in the GISP2H core. The 1956 spike was only a 4% enhancement above the integrated background for the entire year, so slow, steady deposition of this excess nitrate would be very difficult to identify.
4. Nitrate peaks have been associated with other, intermittent sources including air plumes with (i) anthropogenic pollution [Herron, 1982; Mayewski et al., 1990], (ii) biomass burning [Whitlow et al., 1994], and (iii) sea salt and possibly dust particulate [Dibb and Jaffrezo, 1997; Wolff et al., 2008]. These potential sources of interference with nitrate have been invoked most recently to argue against a possible SPE source [e.g., Wolff et al., 2012 and D14].

Anthropogenic sources, due to the combustion of fossil fuels and production and application of fertilizer, are observed in the nitrate record increasingly since 1950 as a general upward trend over the last 60–70 years and may contribute to the annual cycle background but are unlikely to produce an impulsive winter nitrate spike of 2–4 month duration. Biomass burning, primarily from large forest fires, which can produce ammonium nitrate but is primarily a summer phenomenon is also unlikely to be the source of the 1956 GISP2H winter nitrate peak. Summit cores such as GISP2 (P. A. Mayewski, personal communication, 2015) and Zoe (J. R. McConnell, personal communication, 2012) have been analyzed for a suite of chemical species, but they either show no interference from biomass burning in the winter of 1956 or lack the resolution required for comparison with GISP2H [Smart et al., 2014, 2016]. Similarly, nitrate salt from marine influences is unlikely to exert much influence at the remote, high-elevation, Summit location [Wolff et al., 2008].

Of course, the winter argument alone does not disprove interference by these nitrate sources in the form of aerosols such as from biomass burning, fertilizer, and sea salts. There is, however, additional information in the GISP2H data set that can be used to get a handle on the potential source of the nitrate spike in question, namely, the conductivity measurements. To do this analysis, we assumed a constant background from the only other major anion, sulfate. This seems reasonable given that no significant volcanic activity is reported during this time period. Standard molar conductivity tables for dilute solutions [Haynes, 2015] predict a rise in the conductivity level associated with the four-point, averaged, 1956 nitrate spike (Figure 4a) of about  $0.230 \mu\text{S cm}^{-1}$  if the nitrate is acidic, as expected if precipitated from polar stratospheric clouds (PCs), and  $0.066\text{--}0.079 \mu\text{S cm}^{-1}$  if the peak is due to an aerosol of nitrate salt (i.e., ammonium, sodium, magnesium, or calcium nitrate), as expected if from biomass burning or marine sources. The actual rise above background of the integrated, colocated, four-point, 1956 GISP2 H conductivity is  $0.205 \mu\text{S cm}^{-1}$ . This is only 11% less than predicted for a nitric acid source but 159%–212% more than is predicted if the spike was formed by a nitrate

salt. In principle, the 1956 peak could result from a combination of nitrate salts instead of nitric acid, but this is increasingly improbable as it requires multiple winter sources and ignores the most straightforward explanation. In lieu of further data, this result lends strong additional support for the conclusion that the 1956 winter nitrate spike is mostly acidic and therefore what would be expected from the February 1956 SPE.

### 5.3. Was the Event Spectrum Harder?

Muons are important to understanding ionization in the troposphere. We must allow that SPEs might have much more complicated spectra with a very strong hard component that has not been well measured. On the other hand, such an energetic component is contradicted by other studies [Swinson and Shea, 1990], which still indicate primaries up to 25 GeV and higher [Sarabhai *et al.*, 1956]. There are recent studies that could be explained by a possible anomalous hard component reaching the ground [Overholt and Melott, 2015]. However, we stress that this is a speculative idea.

### 5.4. Transport From 45 km Is Possible and Sufficient for the Data

In order to account for the 1956 impulsive ice core peak, the total odd nitrogen (i.e., nitrate and its precursors) found in the atmospheric column from the surface up to 44–46 km would have to be deposited over a period of roughly 2–4 months. The short timing of this deposition is an issue and has not been supported by previous modeling. However, since these altitudes are much lower than were previously thought, the mechanism of vertical subsidence due to the polar vortex [Traub *et al.*, 1995; Vogel *et al.*, 2008; D14] coupled with denitrification by PSCs [Crutzen and Arnold, 1986; Fahey *et al.*, 1990; Hamill and Toon, 1991; Northway *et al.*, 2002a; Solomon, 1999; Toon *et al.*, 1986] and followed by rapid deposition to the surface becomes viable. Since half the nitrate required for the 1956 winter peak is produced below 30 km, it will be subject to the denitrification process and removal in PSCs within about 1 month, as described below

Within the winter polar vortex, subsidence rates and their estimates vary. For example, an average descent rate of roughly  $0.19 \text{ km d}^{-1}$  for 32–49 km altitude can be inferred from Figure 1a in the Vogel *et al.* [2008] CLaMS model. A previous study by Traub *et al.* [1995] measured an average of  $0.43 \text{ km d}^{-1}$  at 18 km altitude during the winter months of 1992. The D14 WACCM model propagated  $\text{NO}_x$  at a rate of  $\sim 0.33 \text{ km d}^{-1}$  from the upper to middle stratosphere during the months of November–December. Using the intermediate rate from D14, a parcel of air between 30 and 46 km, containing the upper half of the  $\text{NO}_y$  column that is required to produce the spike, would travel down to an altitude of PSC formation (28 km) within 8 weeks, and from 34 km (assuming 95% conversion efficiency from  $\text{N}^{(2)\text{D}}$  to  $\text{NO}_x$ ) in less than 2 weeks. Normal downward transport with a speed of 200–300 m/day would also transport  $\text{NO}_y$  from 34–46 km down to 14 km within 8–23 weeks (2–5 months).

Although more variable and generally less intense than in the Antarctic, denitrification of the Arctic middle to low stratosphere can be significant [Hamill and Toon, 1991; Mann *et al.*, 2003; Popp *et al.*, 2001]. Denitrification occurs due to gravitational settling of PSCs (type I), which form at sufficiently low temperatures and consist of nitric acid trihydrate (NAT) particles, generally between altitudes of 15 and 25 km [Voigt *et al.*, 2000], although altitudes from 10 to 28 km are possible [Hamill and Toon, 1991]. While the altitude of PSC formation is generally lower than 28 km, the presence of a PSC is evidence that denitrification has already occurred at significantly higher altitudes since it takes time for NAT particles to grow, during which they have fallen vertically as far as  $\sim 6 \text{ km}$  over a period of 6 days [Fahey *et al.*, 2001]. The altitude for denitrification, therefore, encompasses the 15–31 km range. The speed of downward vertical transport for NATs is a function of the particle size; large particles (10–20  $\mu\text{m}$ ) are subject to downward gravitational transport at a rate of 1–2 km/day which is sufficient to transport to the troposphere within 1–2 weeks, provided temperatures remain low enough that the particles do not evaporate [Fahey *et al.*, 2001; Hamill and Toon, 1991; Northway *et al.*, 2002a]. Smaller particles move downward more slowly. Aircraft have measured NAT particles of this size in the Arctic [Fahey *et al.*, 2001; Northway *et al.*, 2002b].

Once nitric acid crosses the tropopause, it is subject to the relatively short residence time of particles in the troposphere (3–10 days) [Papastefanou, 2006; Poet *et al.*, 1972; Rodhe and Grandell, 1972; Warneck, 2000; Winkler *et al.*, 1998] where it will be largely removed in a couple of snowstorms [Schwikowski *et al.*, 1998]. Although widespread PSC formation has been seen in the Arctic during winters with a strong polar vortex, it is more common for PSCs to be localized [Engel *et al.*, 2013; Fahey *et al.*, 2001; Pawson *et al.*, 1995]. Unfortunately, temperature data for the stratosphere above Summit is not available for 1956 and troposphere

temperatures may not correlate very well with those of the stratosphere [Liu and Schuurmans, 1990]. We note, however, that the Arctic vortex has been weakening due to climate change and would have been stronger in the past.

The involvement of PSCs in nitrate deposition of the winter 1956 ice core peak is also supported by the conductivity analysis in section 5.2, which indicates an acid source. Therefore, subsidence and denitrification by PSCs can qualitatively account for the ~2–4 month time scale consistent with the 1956 GISP2H winter ice core peak; however, more realistic modeling is necessary to establish this quantitatively. Proper modeling of PSC development is lacking (e.g., D16) and is complicated by an incomplete understanding of NAT nucleation and evolution, including evidence suggesting that strong SPEs can enhance the formation of large NAT particles [Engel et al., 2013; Mironova et al., 2008; Popp et al., 2006; Yu, 2004].

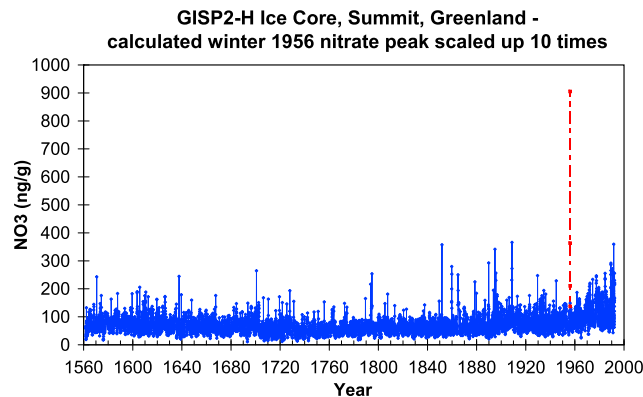
### 5.5. Computation Results for the 3–4 August 1972 SPE

We found total nitrate production from the ground to 100 km for the 3–4 August 1972 SPE to be similar to that for 1956 (shown in Figures 5 and 6). However, there were considerably smaller contributions at lower altitudes due to the softer spectrum.

There are conflicting claims for the observation of this event in the ice core records [e.g., Laird et al., 1982; Zeller et al., 1986; Legrand and Kirchner, 1990; Wolff et al., 2012], which could be more problematic, given that it was not a winter event in the Northern Hemisphere and would be subject to photolysis in the atmosphere and at the surface and other deposition issues, as well as an absent polar vortex. Observations in Antarctica could also be hampered by the fact that high-deposition areas, such as occur at Summit, are generally absent on the high south polar plateau or are along the coast, where they are subject to marine interferences. We show this time period from the GISP2H ice core in Figure 4b. The event does not show up clearly as either a nitrate or conductivity spike above background fluctuations, but, interestingly, there is a second subdued nitrate peak, which occurs after the prominent summer maximum that might partly represent deposition from this softer SPE over a 4–6 month interval. If so, it would require  $\text{NO}_y$  inputs from above 65 km, which seems to be problematic. Also, the corresponding conductivity local background is higher than the values associated with the nitrate peak making any assessment of source more difficult. We regard these ambiguous findings as due to a combination of the soft spectrum and the less than optimal conditions described above.

## 6. Conclusions

1. The results of full air shower simulation, including effects of secondary particles, are necessary to properly model atmospheric ionization by SPEs; otherwise, lower atmosphere ionization is underestimated. It is now possible to bypass redoing the full air shower simulation step for each new event by using the tables published by Atri et al. [2010] or alternately by Usoskin and Kovaltsov [2006] and Usoskin et al. [2010]. See the comparison of the two approaches in section 2.3. Our estimates are conservative, in that they do not include alpha particles, which will increase ionization by about 10% [Jackman, 2013]. Primary electrons are unimportant except at very high altitudes.
2. Computations based on air showers with low fluence or a soft spectrum (e.g., D14) are not generalizable to high-fluence showers or those with hard primary energy spectra. In order to be done correctly at mid-stratospheric down to tropospheric levels, atmospheric ionization must include the effects of secondaries and must include the high-energy primaries, which penetrate to lower altitudes and produce effects there. It may be that only showers with fairly hard energy spectra and high fluence are traceable as elevated nitrate levels in the ice cores. The results of Nicoll and Harrison [2014] are perfectly reasonable on the basis of theory for a hard-spectrum, moderate-fluence event, showing excess ionization down to 5 km. As research into the potential impact of SPEs on nitrate deposition in polar snow and ice has evolved, it has become increasingly evident that major events are required to produce the needed ionization. As discussed in section 1, D16 have improved on the methods used in D14 and indeed produce more ionization at lower altitude (attributable to having adopted the more correct air shower ionization calculations that we have been advocating and use in this work), though they still do not address or cite the observed tropospheric ionization reported in Nicoll and Harrison [2014], which we reproduce here. While not irrelevant to our work, the D16 results are given in terms of percentage increase in  $\text{NO}_y$  against the normal atmospheric background [see also Calisto et al., 2013]. This addresses a different question than we seek to answer here—that is, can SPEs produce enough nitrate (in absolute terms) available for rapid deposition to explain spikes observed in ice cores? As we have shown, the answer is yes in at least one case.



**Figure 7.** The GISP2H ice core data [Dreschhoff and Zeller, 1998] but with the nitrate enhancement of the 1956 SPE (dashed portion of curve) scaled up by a factor of 10. It is intended as an example of the kind of information that may exist for events such as those in 775 and 993 A.D., which were already found in  $^{14}\text{C}$  records from tree rings and corals but have not yet been sought systematically (i.e., at fine resolution) in the nitrate record in ice cores. It should be noted that evidence suggesting several smaller events in 775 A.D. may have occurred (instead of one large one) and in Northern Hemisphere summer [Ding *et al.*, 2015] would greatly reduce the size of any resulting nitrate spikes at Summit accordingly. It also suggests that Antarctica would be the place to look for nitrates associated with this event. Comparing nitrate,  $^{14}\text{C}$ , and  $^{10}\text{Be}$  may enable estimates of the spectral shape of such events.

3. There may be a bias away from visibility of summer events due to increased photochemistry and absence of the polar vortex, but more needs to be done here. A higher fluence may be required in order to be visible in summer ice deposits. *Smart et al.* [2014] noted one summer event in an ice core associated with a hard-spectrum GLE in the 1940s. This deficiency could be surmounted by data from both polar regions. Polar winters are about 6 months, which helps.
4. Events with hard-spectrum GLEs are more likely to appear as a layer of elevated nitric acid in the ice that is associated with higher conductivities and precipitation from PSCs. A strong GLE indicates deep penetration into the atmosphere, suggesting a hard primary spectrum and the possibility of rapid deposition as indicated in *Smart et al.* [2014, 2016].
5. There are no direct data for the SPE spectrum or presence of a GLE associated with the Carrington Event, which occurred at the beginning of September 1859 [Clauer and Siscoe, 2006]. It is therefore unclear whether or not its effects are expected to appear in ice core data. *Wolff et al.* [2012] found no evidence for SPE-produced nitrates in ice cores, but *Smart et al.* [2014, 2016] showed that the resolution of the data used by Wolff *et al.* was too poor to detect nitrate spikes.
6. The alternate use of cosmogenic isotopes such as  $^{10}\text{Be}$  to study past SPEs, advocated by many, is currently being accomplished by other researchers [McCracken and Beer, 2015], and they have identified four of the five same events in the 1940–1956 time interval as the impulsive nitrate events identified in Figures 1 and 7 of *Smart et al.* [2014]. Only the GLE of 25 July 1946 was not captured in the  $^{10}\text{Be}$  data. This is a strong vindication of the *Smart et al.* [2014] identification of these events in the ice core data.
7. High-fluence, hard-spectrum, winter events such as the 23 February 1956 SPE produce enough nitrate in mid-stratosphere down through the troposphere to account for ice core nitrate spikes and suggest that polar ice cores may be useful archives of such events covering the last several millennia. To our knowledge, this is the first study to obtain this result. All previous simulations have concluded that nitrate deposition values in Greenland and Antarctica from SPEs were far too low to appear above the background.

As there is current  $^{14}\text{C}$  data which may be produced by extremely high fluence past SPEs [Miyake *et al.*, 2013 and references therein; Melott and Thomas, 2012; Usoskin *et al.*, 2013; Thomas *et al.*, 2013], combining cosmogenic isotope-based estimates [Beer *et al.*, 2011; Kovaltsov *et al.*, 2014] with nitrate data may give some insight into the spectrum of hard events (which pose the greatest risk to aircraft and spacecraft) in the pretechnological past and provide useful statistics on such events for the future. As an example, the nondetection of cosmogenic isotopes for the Carrington Event [Usoskin and Kovaltsov, 2012; McCracken and Beer, 2015] tells us that if nitrate spikes were to be found in future studies, the combination of this with the isotope data would constrain this event to be very high fluence, e.g., much greater than 1972 and sufficient to penetrate to the lower atmosphere, with a rather soft spectrum.

The probable medieval SPEs of 775 A.D. and 994 A.D. [Miyake *et al.*, 2013; Melott and Thomas, 2012; Usoskin *et al.*, 2013; Ding *et al.*, 2015; Mekhaldi *et al.*, 2015] are of concern. The 775 A.D. event may have been 25–50 times stronger than that of 23 February 1956 [Usoskin *et al.*, 2013] and could pose a threat to our technological civilization if it occurred today. There is considerable uncertainty in the spectrum and fluence of this event,

but evidence to date suggests that it was likely very hard and high fluence [Thomas *et al.*, 2013; Mekhaldi *et al.*, 2015]. As an example, we consider that the 775 A.D. event might resemble that of 1956 scaled up conservatively by a factor of 10. As an exercise in what might be found in high-resolution data, we show in Figure 7 the GISP2H ice core data [Dreschhoff and Zeller, 1998] using these assumptions. If they were as strong as suggested, both 775 A.D. and 994 A.D. should be clearly detectable as large nitrate spikes above background in the ice cores. We note, however, that a recent study [Ding *et al.*, 2015] indicates that there may have been three smaller events that occurred in the Northern Hemisphere summer 775–776 A.D. If so, it suggests that conditions would be more favorable for detecting this event in Antarctica than at Summit and that three smaller nitrate spikes would be less prominent.

Smart *et al.* [2014, 2016] showed that fine resolution is needed to see such events, yet nitrate analyses at sufficient resolution for these periods are currently lacking. Tree ring and coral  $^{14}\text{C}$  analyses have provided other stunning examples of the value in analysis at increased temporal resolution. We argue that additional fine-resolution ice core nitrate studies coupled with conductivity and multispecies analysis for determining interferences from non-SPE sources in both polar regions, covering the last two millennia, could shed important light on these events and should be undertaken. We urge consideration of such examination of ice cores from that period.

#### Acknowledgments

We are grateful for helpful comments from M. Shea and D. Smart. We thank the referees, whose comments improved the manuscript. I. Usoskin provided SPE ionization data, and A. Tylka provided spectral information on SPE events. A.L.M. and B.C.T. were supported by NASA grant NNX14AK22G. Initial creation of the tables of Atri *et al.* [2010] which were used was supported in part by the National Science Foundation through TeraGrid resources provided by the National Center for Supercomputing Applications. Additional computation time was provided by the High Performance Computing Environment (HiPACE) at Washburn University; thanks to Steve Black for assistance. We also acknowledge G.A.M. Dreschhoff for providing the detailed GISP2-H core data used in Figures 4 and 7. We thank Keri Nicoll for sharing the balloon measurement data. The original GISP2-H data are available at <http://nsidc.org/data/arcs026.html> and in graphic form by sample number in Dreschhoff and Zeller [2015]. The primary ionization tables used for the air shower computations which were published in Atri *et al.* [2010] can be downloaded at <ftp://kusmos.phsx.ku.edu/data/melott/crtables/atmoionization/>. Data used in Figures 5 and 6 were acquired from I. Usoskin (SPEs) and downloaded from <http://cosmicrays.oulu.fi/CRII/CRII.html> (GCRs). The GOES data cited in section 5 can be downloaded at <http://satdat.ngdc.noaa.gov/sem/goes/data/>. The data files are [http://satdat.ngdc.noaa.gov/sem/goes/data/new\\_avg/2013/04/goes13/csv/g13\\_epead\\_cp\\_flux\\_5m\\_20130401\\_20130430.csv](http://satdat.ngdc.noaa.gov/sem/goes/data/new_avg/2013/04/goes13/csv/g13_epead_cp_flux_5m_20130401_20130430.csv) and [http://satdat.ngdc.noaa.gov/sem/goes/data/new\\_avg/2013/04/goes13/csv/g13\\_epead\\_p17ew\\_5m\\_20130401\\_20130430.csv](http://satdat.ngdc.noaa.gov/sem/goes/data/new_avg/2013/04/goes13/csv/g13_epead_p17ew_5m_20130401_20130430.csv). The Galactic Cosmic Ray ionization data used were downloaded from <http://cosmicrays.oulu.fi/CRII/CRII.html>. Solar Proton Event ionization profiles by C. Jackman were downloaded from <http://solarisheppa.geomar.de/solarprotonfluxes>.

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