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Key Points:

- There are no coincident nitrate enhancement events in polar ice cores following the largest solar storms known to date
- Nitrate concentrations between robustly synchronized ice cores show a poor agreement but a good agreement with biomass burning plumes in Greenland
- Ice core nitrate cannot be used to document atmospheric ionization by solar energetic particle events

Supporting Information:

- Supporting Information S1
- Data Set S1
- Data Set S2

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No Coincident Nitrate Enhancement Events in Polar Ice Cores Following the Largest Known Solar Storms

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Abstract Knowledge on the occurrence rate of extreme solar storms is strongly limited by the relatively recent advent of satellite monitoring of the Sun. To extend our perspective of solar storms prior to the satellite era and because atmospheric ionization induced by solar energetic particles (SEPs) can lead to the production of odd nitrogen, nitrate spikes in ice cores have been tentatively used to document both the occurrence and intensity of past SEP events. However, the reliability of the use of nitrate in ice records as a proxy for SEP events is strongly debated. This is partly due to equivocal detection of nitrate spikes in single ice cores and possible alternative sources, such as biomass burning plumes. Here we present new continuous high-resolution measurements of nitrate and of the biomass burning species ammonium and black carbon, from several Antarctic and Greenland ice cores. We investigate periods covering the two largest known SEP events of 775 and 994 Common Era as well as the Carrington event and the hard SEP event of February 1956. We report no coincident nitrate spikes associated with any of these benchmark events. We also demonstrate the low reproducibility of the nitrate signal in multiple ice cores and confirm the significant relationship between biomass burning plumes and nitrate spikes in individual ice cores. In the light of these new data, there is no line of evidence that supports the hypothesis that ice cores preserve or document detectable amounts of nitrate produced by SEPs, even for the most extreme events known to date.

1. Introduction

Earth is repeatedly hit by high-energy solar particles, most of which are protons. These particles are accelerated during solar flares or by shock waves driven by coronal mass ejections (CMEs). Solar energetic particles (SEPs) are a challenge for our ever-modernizing society as they can severely damage satellites and technological infrastructures such as transformers, in the case of a CME (Shea & Smart, 2012). They also represent a radiation hazard to spacecraft crews and air travel (Townsend et al., 1991). Yet knowledge on the magnitude and on the occurrence rate of the most extreme SEP events is largely limited by the relatively short period of satellite monitoring of the Sun.

1.1. The SEP Events of 774/5 and 993/4 Common Era

To extend our perspective on solar activity variability beyond the satellite era, we rely on environmental archives. The most commonly used proxies in these archives are cosmogenic radionuclides, such as radiocarbon (^{14}C) in tree rings and beryllium-10 (^{10}Be) as well as chlorine-36 (^{36}Cl) in ice cores. Cosmogenic radionuclides are produced in a nuclear cascade which is triggered when atmospheric constituents are hit by galactic cosmic rays. Analyses of cosmogenic radionuclide concentrations in various archives have resulted in a number of solar activity reconstructions for the past millennia (e.g., Bard et al., 2000; Muscheler et al., 2007, 2016; Solanki et al., 2004; Steinhilber et al., 2012). It is also suggested that radionuclides can embed the signature of extreme SEP events (McCracken & Beer, 2015; Usoskin et al., 2006; Webber et al., 2007). This was recently confirmed by the discovery of sharp increases in the atmospheric ^{14}C content (as expressed in $\Delta^{14}C$ which denotes $^{14}C/^{12}C$ corrected for fractionation and decay, relative to a standard) measured in Japanese cedar trees (Miyake et al., 2012; Miyake et al., 2013) at 774/5 and 993/4 Common Era (CE) which were corroborated with increased ^{10}Be and ^{36}Cl concentration in ice cores for the same periods (Mekhaldi et al., 2015; Miyake et al., 2015; Sigl et al., 2015). These ^{14}C spikes subsequently were attributed to extreme SEP events which were characterized by a very hard energy spectrum (high number of protons >100 MeV) and a fluence >30 MeV (F_{30}) of about 2.5 × 10^{10} and 1.3 × 10^{10} protons/cm^2, respectively (Mekhaldi et al., 2015). These SEP events were an order of magnitude stronger than the one observed on 23 February 1956 (Meyer et al., 1956) which yielded the highest F_{30} directly measured for a hard spectrum event and the largest ground level enhancement (GLE), i.e., when SEPs lead to increased counts in neutron monitors.

1.2. Disputed Interpretation of Ice Core Nitrate

The peak response energy of ^{10}Be to solar protons is at ~100–300 MeV (Webber et al., 2007). Therefore, only extremely intense SEP events with a hard energy spectrum can lead to a considerable enhancement in atmospheric ^{10}Be production rate. Another chemical species found in ice cores, which is tentatively used to document SEP events, is nitrate (NO_3^-) (Kepko et al., 2009; McCracken et al., 2001; Melott et al., 2016; Palmer et al., 2001; Zeller & Dreschhoff, 1995). Nitrate has a peak response energy at ~15 MeV, where solar proton fluxes are highest (Webber et al., 2007). Because solar protons ionize the atmosphere and enhance polar stratospheric odd nitrogen (NO_y) by dissociation of N_2 (Jackman et al., 1980; Legrand et al., 1989), it is hypothesized that SEP events eventually can leave an imprint in the nitrate concentration of polar ice, through downward mixing into the troposphere. However, the representativeness of nitrate from single sites, and the interpretation of concentration spikes, is strongly disputed (e.g., Gfeller et al., 2014; Wolff et al., 2012). As such, different sources can potentially lead to the occurrence of nitrate spikes such as surface sources with biomass burning, dust, and anthropogenic pollution (since about the 1950s) or atmospheric sources with lightning and stratospheric intrusions (Legrand & Delmas, 1986; Legrand & Kirchner, 1990). This is evidenced by their frequent association with other chemical species in ice cores, for instance, sea salts and biomass burning compounds (Wolff et al., 2008, 2012). The Carrington event of 1859 CE (Carrington, 1859) has served as a benchmark for SEP-produced nitrate (McCracken et al., 2001) as it was considered to be the strongest historical solar storm. However, there is now an emerging consensus that events with a harder spectrum, and thus producing ^{10}Be (which the Carrington event did not (Beer et al., 1990; Berggren et al., 2009)) as well as more nitrate in the lower 30 km of the atmosphere, are more suitable for detection in ice cores (Melott et al., 2016). A very hard SEP event occurred in February 1956 (Meyer et al., 1956), and it was suggested that it resulted in a nitrate spike in the GISP2-H ice core (McCracken et al., 2001; Zeller & Dreschhoff, 1995). In recent years, there have been considerable efforts from both empirical (Kepko et al., 2009; Smart et al., 2014; Sukhodolov et al., 2017; Wolff et al., 2012) and modeling (Duderstadt et al., 2016; Melott et al., 2016) sides to assess the robustness of ice core nitrate concentrations to document SEP events, though many differences in the main conclusions remain (Duderstadt et al., 2016; Sinnhuber, 2016; Smart et al., 2016; Wolff et al., 2016), for instance, in terms of how much stratospheric odd nitrogen can be enhanced relative to background and how this signal can be transported down to the troposphere.

1.3. Study Design

Here we provide new insights to this debate by means of an empirical multiproxy approach. We consider the ancient SEP events of 775 and 994 CE as they represent an ideal and upper limit test case due to their hard spectra and extreme F_{30}. We present highly resolved continuous flow analysis (CFA) measurements of nitrate from eight different polar ice cores—five from the Greenland Ice Sheet and three from the Antarctic Ice Sheet for the period ranging from 700 to 1100 CE. This series also includes all ice cores in which a clear ^{10}Be increase is recorded (Sigl et al., 2015) thus avoiding uncertainties introduced by using ice cores that are not synchronized (e.g., Sukhodolov et al., 2017). In addition, we complement the study with CFA measurements of two biomass burning species—ammonium (NH_4) and black carbon (BC). Finally, we revisit both the Carrington event and the SEP event of February 1956 with CFA measurements of nitrate for the past two centuries from five Greenland and five Antarctic ice cores.

2. Methods

2.1. Ice Core Measurements

Figure 1 shows the location of the different ice cores used in this study. For the period 700–1100 CE, we use five intermediate-depth ice cores from Greenland — the North Greenland Traverse B19 core (B19), North Greenland Eemian Ice Drilling 2011 S1 (NEEM-2011-S1), and two parallel ice cores from the North

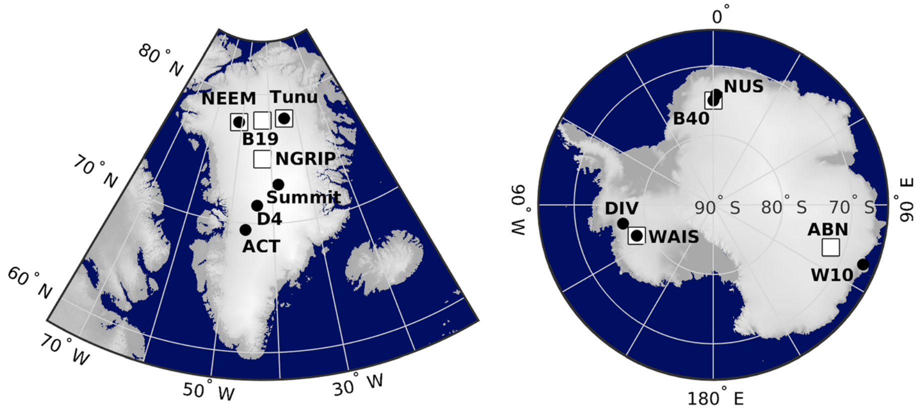

Figure 1. Map of Greenland and Antarctica with the location of the sites of all ice cores used. Squares represent sites with CFA measurements of nitrate for 700–1100 CE as well as NH_4 and BC for 765–785 and 985–1005 CE; dots represent sites with CFA measurements of nitrate for 1800–2000 CE.

Greenland Ice Core Project (NGRIP and NGRIP2) as well as Tunu13. Due to the transport of polar stratospheric nitrate into the troposphere (Legrand & Mayewski, 1997) which occurs most likely during large-scale downwelling of air masses in polar winter (Duderstadt et al., 2016; Melott et al., 2016; Sinnhuber, 2016), it is possible that a nitrate spike produced by a SEP event would be present in only one hemisphere considering the relatively short lifetime of atmospheric nitrate. Hence, we also use three Antarctic ice cores —the intermediate-depth Wilkes Land Aurora Basin North (ABN), Dronning Maud Land B40 (B40), and the upper part of the West Antarctic Divide Ice Core Project 06A (WAIS) core. As mentioned, nitrate in ice cores is often associated with other chemical species linked to biomass burning, particularly in the Arctic. Therefore, we simultaneously investigate chemical species of NH_4 and BC in the same cores and for the depths corresponding to ±10 years of both events. For the period covering the past two centuries (1800–2000 CE), we measured nitrate in 10 polar ice cores. These include five from Greenland—NEEM-2011-S1, Tunu13, Greenland D4 (D4), Arctic Circle Traverse 11D (ACT), and Summit 2010 (Summit10)—and five from Antarctica—B40, WAIS, a Norwegian-U.S. site 8-7 core (NUS) (Pasteris et al., 2014), a traverse core from Dronning Maud Land, DIV2010 (DIV), and W10k from near Law Dome (W10) (Sigl et al., 2014). All chemical species in the ice cores have been measured continuously and simultaneously with the CFA system within the Ultra Trace Chemistry Laboratory (McConnell et al., 2002; Sigl et al., 2016) at the Desert Research Institute. Nitrate was measured using continuous flow methods (Pasteris et al., 2014). Standards that bracketed the sample concentrations were analyzed at the beginning and end of the analysis day. Quality control standards also were analyzed routinely for calibration. Sampling rates typically resulted in more than 40 measurements per year depending on the site-specific snow accumulation rates and the depth in the core. Laminar flow in the continuous analytical system results in smoothing of the signal with depth. For this investigation, measurements were combined to approximate monthly averages (similar to the data used by Wolff et al., 2012, or Sukhodolov et al., 2017) assuming a uniform snow accumulation between annual chemical markers, although missing or badly fractured sections of ice resulted in some years with short gaps (Figures S1 and S2 in the supporting information).

2.2. Chronology

The different ice cores were dated by counting of annual layers using high-resolution measurements of chemical species which have a clear seasonal signal and interpolation between annual markers (e.g., the midwinter minimum in non-sea-salt sulfur [nssS] to sodium [Na] ratio). For consistency, signals from large volcanic eruptions (i.e., spikes in sulfur) subsequently were used to synchronize the different cores to the published NEEM-2011-S1 (NS1-2011 time scale) and WAIS Divide (WD2014 time scale) volcanic records (Sigl et al., 2015) and the annual layer counting for individual cores adjusted accordingly. In addition, we use all ice cores in which a clear ^{10}Be spike was recorded at 775 and 994 CE (Figures 2c–2f) (Sigl et al., 2015). In consequence, timing uncertainties are largely eliminated in the records of NGRIP, NEEM-2011-S1, Tunu13, and WAIS for 775 CE and of NGRIP and NEEM-2011-S1 for 994 CE where nitrate is coregistered with the samples used for detecting the ^{10}Be signal of the two ancient SEP events. This is critical in the light of a previous dating offset of up to 7 years around 775 CE in major ice core chronologies (Baillie & McAneney, 2015; Sigl et al., 2015). For the other records, a relative age uncertainty of ±2 years for nitrate relative to the ^{10}Be signal is supported by the tight volcanic synchronization (Sigl et al., 2015) and by independent comparisons to the IntCal13 time scale (Adolphi & Muscheler, 2016; Sigl et al., 2016).

3. Results

3.1. The Ancient SEP Events of 775 and 994 CE

The CFA measurements in nitrate concentration for the eight different ice cores investigated here for the period 700–1100 CE are displayed in Figure 2. We show that there is no enhancement in the nitrate concentration of any of the eight polar ice cores at 775 CE ±2 years and 994 CE ±2 years. This result contrasts the ^{10}Be (Figures 2c–2f) (Jull et al., 2014; Mekhaldi et al., 2015; Miyake et al., 2015; Sigl et al., 2015), ^{14}C (Güttler et al., 2015; Miyake et al., 2012, 2013), and ^{36}Cl (Mekhaldi et al., 2015; Wagner et al., 2000) increases found for both events. That is, these three cosmogenic radionuclides all document the same global signature of atmospheric reactions induced by solar protons for the two events. Nitrate spikes do occur stochastically throughout the different ice core records although they do not correspond to any known SEP events nor are they repeated in other ice cores. Nitrate concentration for the Greenland ice cores has a mean value of 1.42, 1.63, 1.36, 1.50, and 1.35 μ*M* for B19, NEEM-2011-S1 NGRIP, NGRIP2, and Tunu13, respectively, with an average standard deviation of about 0.4 μ*M* except for NEEM-2011-S1 which exhibits a larger variability of ~0.6 μ*M*. As for the Antarctic ice cores (ABN, B40, and WAIS), they show mean nitrate concentrations of 1.02, 0.82, and 0.51 μ*M*, respectively, with an average standard deviation of ~0.14 μ*M*. The Antarctic ice cores show lower variability, and this is likely due to the typically lower accumulation rates at these Antarctic sites (apart from WAIS) and the greater distance to the main sources that can lead to nitrate spikes, compared to Greenland ice core sites.

3.2. The Carrington Event of 1859 and SEP Event of 1956

The nitrate records from both Greenland and Antarctica for 1800–2000 CE (Figure 3) resemble those described for 700–1100 CE. That is, the records show similar average concentrations and variance as well as stochastic excursions which are not reproduced in multiple ice cores and thus indicating a rather local signal of enhanced scavenging and of higher atmospheric load. One distinguishing feature is the increasing trend in the background level of the five Greenland cores starting at ~1950 CE. This relates to anthropogenic releases (Mayewski et al., 1990) of nitrogen from land use change and fossil fuel burning (Hastings et al., 2009; McConnell et al., 2007). The nitrate concentrations at 1859 ± 2 years and 1956 ± 2 years show no extraordinary and coincident nitrate enhancements, agreeing with Wolff et al. (2012) who have not found nitrate spikes associated with the Carrington event in a series of Greenland and Antarctic ice cores. The only exception is the spike at 1957 in the ACT core (Greenland) and at 1954 in the WAIS Divide core (Antarctica), the time scales of which are very robust. No such nitrate spikes are observed in the eight other ice cores. It is also important to note that there is no evidence for any nitrate enhancement at the Carrington event or the SEP event of February 1956 at Summit10. This highlights the lack of representativeness of previous findings (McCracken et al., 2001; Melott et al., 2016; Shea et al., 2006) which linked a spike in nitrate at ~1859 and ~1956 to both events using another core previously drilled at Summit in Central Greenland (GISP2-H) and which was less robustly dated with the spike likely to represent the year 1863 (Wolff et al., 2012). Finally, we note the corresponding lack of any nitrate spikes at 1859 CE in annually resolved ^{10}Be data from the NGRIP ice core (Berggren et al., 2009) or DYE-3 ice core (Beer et al., 1990).

3.3. Subannual Variability in Nitrate

Our monthly averaged measurements allow further investigation into the subannual variability in nitrate during the time of the two hard-spectrum and high-fluence events of 775 and 994 CE (Figure 4). The monthly variation in nitrate concentration around 1859 and 1956 are also shown for the NEEM-2011-S1 and Tunu13 ice cores in Greenland and for the B40 and WAIS Divide ice cores in Antarctica—the ice cores which cover all four events.

Figure 4 depicts normalized monthly nitrate variation for the 24 months preceding and following the winters (nitrate low) of 774/5, 993/4, 1859/60, and of 1955/6 CE, with the monthly values determined

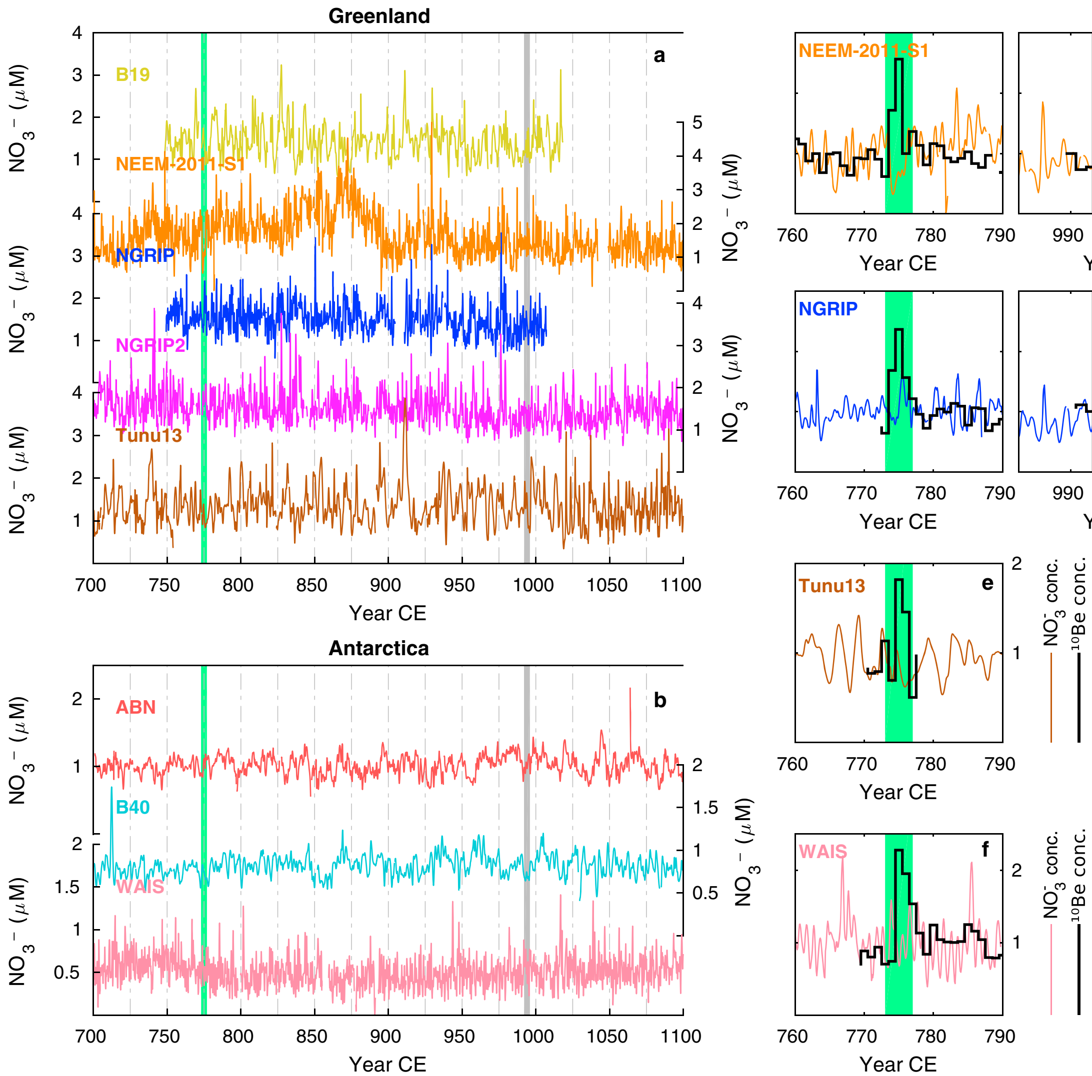

Figure 2. CFA measurements of nitrate concentration for 700–1100 CE in (a) Greenland and (b) Antarctic ice cores. Green and gray bands represent the estimated occurrence of the SEP events of 775 and 994 CE ±2 years, respectively. A comparison of ^{10}Be concentration (Sigl et al., 2015; Mekhaldi et al., 2015) and nitrate concentration (both normalized to their mean) is shown for 775 CE and 994 CE for (c) NEEM-2011-S1 and (d) NGRIP and as for 775 CE for (e) Tunu13 and (f) WAIS.

by assuming uniform accumulation rates between annual chemical markers. These 48 months encompass the time frames at which the largest ancient SEP events (Mekhaldi et al., 2015), the largest historical solar storm (Carrington, 1859), and the strongest measured hard SEP event have occurred, within time scale uncertainties. For reference, the mean nitrate annual cycle for each ice core and for the pre-industrial period 750–1000 CE is shown. The mean monthly curves show a discernible seasonality in nitrate for ice cores with a high accumulation rate (NEEM-2011-S1, NGRIP, NGRIP2, and WAIS). Figure 4 also shows no large nitrate increases and also that nitrate mainly varied within 1σ of the respective average seasonal cycles during the four events. Only for NGRIP at 775 CE, B40 at 1857 CE, and at 1859/60 CE, and for WAIS Divide at 1954 CE, did nitrate increase slightly above the 1σ envelope, which is not significant. Thus, there is never a nitrate increase above 1σ which is observed in more than one ice core following the two largest known SEP events (775 and 994 CE). Furthermore, there is a visually poor inter–ice core agreement at subannual resolution with distinct differences, even for cores where there is no timing uncertainty relative to the SEP events (NEEM-2011-S1, NGRIP, Tunu13, and WAIS; see Figures 2c–2f). This result highlights the limitations in the interpretation of nitrate data as a proxy of a global source signature unless it is corroborated in multiple cores and is further discussed in the following section.

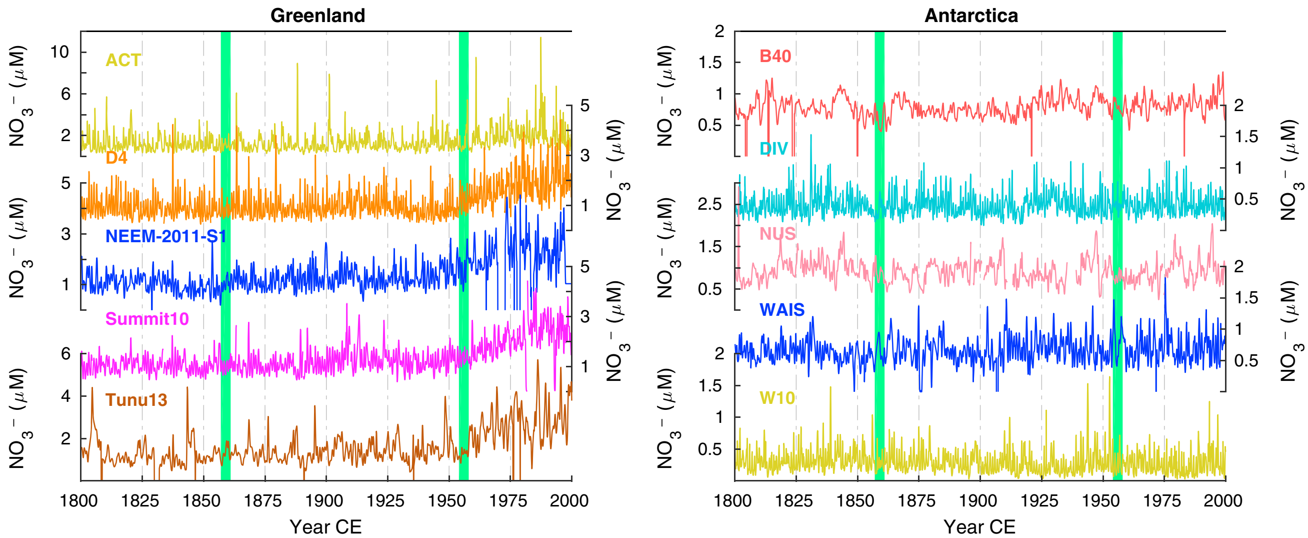

Figure 3. CFA measurements of nitrate concentration for 1800–2000 CE. Green bands indicate the time of occurrence of the Carrington event (1859 CE) and of the SEP event/GLE of February 1956 ± 2 years.

In summary, our high-resolution nitrate measurements show that there is no coincident nitrate enhancement in the eight ice cores studied here from Greenland and Antarctica during the exceptional 775 and 994 CE SEP events, including the four ice cores in which a clear ^{10}Be spike was measured (Figure 2). A similar result of no coincident nitrate enhancement is observed in 10 ice cores during the timing of the Carrington event of 1859 and the high-fluence hard-spectrum SEP event of 1956. These results also suggest that the nitrate spikes in GISP2-H around 1859 CE and 1956, and which have been proposed to be related to atmospheric ionization, cannot be unequivocally associated to the Carrington event, as pointed out by Wolff et al. (2012), or to the SEP event of February 1956.

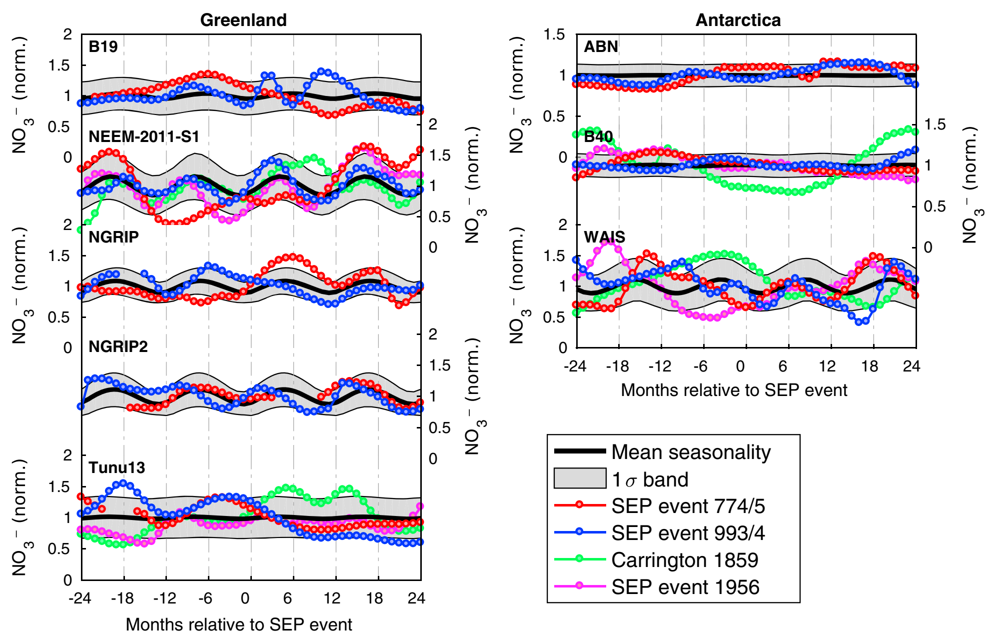

Figure 4. Subannual variability of nitrate concentration, and normalized by its mean, 24 months prior to and following the winters of 774/5, 993/4, 1859/1860, and 1955/1956. The black curves depict the mean annual cycle in nitrate concentration for each ice core and for 750–1000 CE with a 1σ envelope.

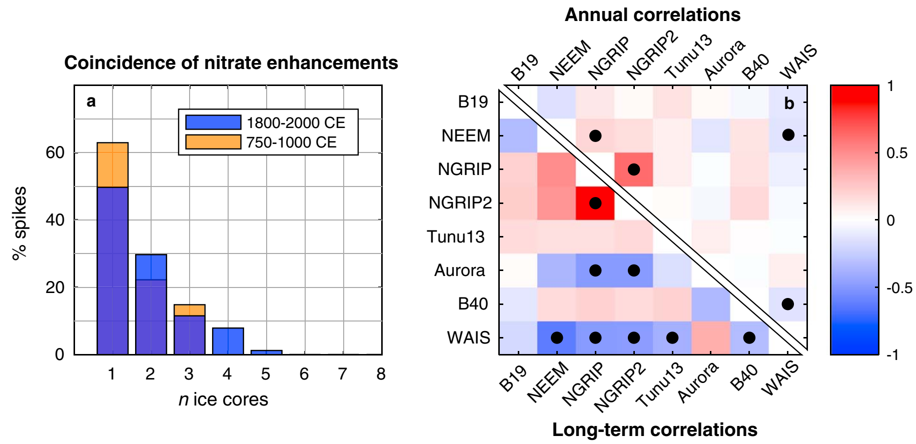

Figure 5. The overall agreement between the different nitrate records. (a) Percentage of nitrate enhancements (3σ above background) coincidentally observed (within ±2 and ±1 years for 750–1000 CE and 1800–2000 CE, respectively) in *n* ice cores. (b) Color-coded matrix showing Pearson correlation coefficients (color bar) between the different nitrate records for the period 750–1000 CE, shown in Figure 2, for annual averages (upper right triangle) and long-term changes (lower left triangle, low-pass filter with cutoff frequency of 1/30 years^{-1}). Dots represent significant correlations ($p < 0.01$).

4. Discussion

4.1. Low Inter–Ice Core Agreement

Although several nitrate spikes are observed throughout the different ice core records, only insignificantly few of them correspond to a period within the intervals of the SEP events of 775 CE, 994 CE, and 1956 or of the Carrington event (Figures 2–4). In addition, very few of the nitrate outliers falling outside of these time ranges are observable in multiple ice cores. Figure 5a shows the percentage of nitrate enhancements occurring simultaneously in multiple ice cores (within ±2 years for 750–1000 CE and within ±1 year for 1800–2000 CE). The nitrate enhancements were defined as measurements rising above 3σ of a background estimated as the low-pass-filtered signal of each nitrate record (first-order Butterworth filter and cutoff frequency 1/30 years^{-1}). For the period 750–1000 CE which is covered by eight ice cores (Figures 2a and 2b), most nitrate enhancements (63%) are observed in only one ice core, while 22% and 15% nitrate enhancements are coincident in two and three ice cores, respectively. For the recent period 1800–2000 CE which is covered by 10 ice cores (Figure 3), only 30%, 12%, and 8% of the nitrate enhancements are observed in two, three, and four ice cores, respectively. This result shows that the spikes in nitrate concentration that are measured in the different ice cores are not representative of a global source event because they are not observable at multiple locations. Rather and most likely, they originate from different source locations, local effects such as postdepositional processes (Legrand & Mayewski, 1997; Rothlisberger et al., 2002), or from different sources (e.g., biomass burning (Wolff et al., 2012)), as is discussed in section 4.4. The poor agreement also confirms the findings of a recent study (Gfeller et al., 2014) which has shown the low interannual representativeness of certain ionic aerosol proxies, including nitrate, for several parallel ice cores within a single site (NEEM).

Another means to illustrate the low inter–ice core agreement in nitrate content is given by the color-coded correlation matrix (Figure 5b). In the upper right triangle, Pearson correlation coefficients for annually averaged nitrate time series (750–1000 CE) are shown, with the degree of shading showing the strength of the correlation (red) or anticorrelation (blue) and the dots representing statistically significant relationships, based on a random-phase test using 10,000 iterations and accounting for autocorrelation (see Ebisuzaki, 1997). The lower left triangle corresponds to correlation coefficients of low-pass-filtered nitrate time series (first-order Butterworth filter and cutoff frequency of 1/30 years^{-1}). The figure shows that most nitrate records are not significantly ($p < 0.01$) correlated to one another even when considering long-term variability (lower left triangle). Of the 28 possible ice core pairs and when considering annual variability (upper right triangle), the only exceptions to this result are NGRIP-NEEM and NGRIP-NGRIP2. The latter pair, which represents a single site, shows a correlation of 0.65

consistent with findings from Gfeller et al. (2014) at the NEEM site. We note, however, that time scale uncertainties and local glaciological processes could account to some extent for the poor annual correlations.

The poor agreement between the different nitrate records agrees with previous studies showing that nitrate concentrations from a single core are not well representative of a global source signal. Instead, it is an expression of local deposition (Wolff et al., 2008), a more local source, and, to a lower extent, postdepositional effects, for instance, reevaporation of nitric acid (Mulvaney et al., 1998) and wind scouring of the snowpack (Gfeller et al., 2014). It was also proposed that nitrate can be used as a proxy for solar variability based on suggested spectral similarities between ^{10}Be/^{14}C and single-core nitrate from Talos Dome, at subcentennial and millennial scale (Traversi et al., 2012). However, the correlation matrix (Figure 5b) distinctly points to a poor agreement in long-term variability of nitrate with only a few ice core pairs showing positive correlations above 0.5 (NEEM-NGRIP, NEEM-NGRIP2, and NGRIP-NGRIP2), with only the latter pair showing a very significant ($p < 0.01$) result, as opposed to ^{10}Be records which agree well in long-term changes (Muscheler et al., 2016). Therefore, our analysis casts doubts on the potential of nitrate spikes and annual to subcentennial nitrate variability for a single site to represent a global source signature such as enhanced atmospheric production of NO_y by solar energetic particles or galactic cosmic rays, supporting the arguments of Legrand and Delmas (1986) and Legrand et al. (1989). Finally, we note the strong anticorrelation between WAIS and Greenland ice core data which is mathematically significant but does not necessarily indicate a physical link.

4.2. Dispersion Effect of CFA

One recent matter of discussion revolves around the method of choice for the detection of nitrate enhancements in ice cores (e.g., discussion between Smart et al., 2014, 2016, and Wolff et al., 2016). More specifically, it is argued by Smart et al. (2014, 2016) that CFA systems are affected by dispersion and mixing leading to a smoothing of the signal which results in a lower effective resolution than the apparent resolution (Breton et al., 2012; Smart et al., 2016). This would thus translate into a loss of the highest frequencies, as opposed to discrete sampling. Before discussing this issue in this section, we point out that Wolff et al. (2016) commented on ice core data and the natural limit to their achievable resolution. As such, even though it is possible to reach an analytical resolution of a few days, the effective resolution of ice core data will be limited by the amount and distribution of snowfall events throughout a year, the mixing of snowfall layers by the wind, the summer melting, and, in the case of nitrate, back diffusion through evaporation of nitric acid (Wolff et al., 2016). Considering these different variables, obtaining an effective resolution of ~10 days as proposed by Smart et al. (2014) is unreasonable, regardless of the method used. In the following, we discuss that in spite of these natural and analytical smoothing factors, a large spike in atmospheric nitrate caused by an extreme surge of solar protons to Earth as in 774/5 CE would still be observable in ice cores, should ice core nitrate be a proxy for SEP events.

4.2.1. Estimating the Effective Resolution

First, we investigate the power spectral density (PSD) of the eight nitrate records analyzed for the SEP events of 775 and 994 CE (750–1000 CE). The PSD of each nitrate record (Figures 6a and 6b) is characterized by a flat white noise spectrum for frequencies <1 year^{-1} as illustrated by the gray line (constant at 1 in power). At frequencies >1 year^{-1}, the spectra become more red, as they decrease in power with increasing autocorrelation at higher frequencies. It is interesting to note that most ice cores are characterized by a peak in power at 1 year corresponding to the seasonal dominance in the variability of nitrate (summer high and winter low (Gfeller et al., 2014; Oyabu et al., 2016; Wolff et al., 2008)). This shows that the effective resolution of most nitrate records is of, at least, 3–4 months which would be necessary to resolve an annual cycle. This is supported by the fact that the different spectra only start significantly deviating from a white noise spectrum (the gray line) at frequencies >1 year^{-1}. More specifically, the breaking point (when the spectrum shifts from white to red) observed in each spectrum can be used to estimate the effective resolution. To illustrate this, we have smoothed a series of 10,000 white noise signals of the same length and sampling rate than our nitrate records with a moving average filter ranging from 2 to 12 months and computed their mean PSDs (Figure 7). This shows that a moving average filter of 2–4 months induces the spectra to start deviating from white noise (the gray line) at about 1–3 years^{-1} as observed in the nitrate records from ice core sites with high accumulation rates (Figure 6c).

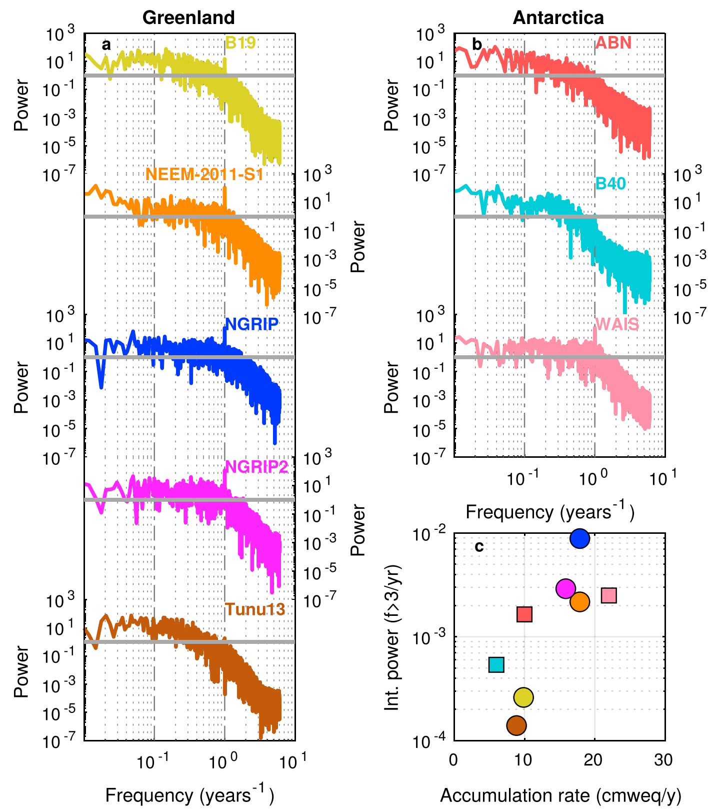

Figure 6. Power spectral density (PSD) of the nitrate records from (a) Greenland and (b) Antarctica, shown in Figure 2. The gray line represents white noise with a constant power of 1. (c) The integral PSD >3 years^{-1} as a function of the accumulation rate of each record. Circles represent Greenland ice cores and squares represent Antarctic ice cores.

Smart et al. (2014) used a similar approach but stipulating that CFA cannot resolve short-lived spikes because of the lack of significant powers at high frequencies in the PSD of the nitrate records they used in their study. We note, however, that confidence levels reflect spectral significance and that nitrate enhancement events would not show as significant as there is, a priori, no high-frequency periodicity in their occurrence. Furthermore, Figure 6c shows that the integral PSD for high frequencies ($f > 3$ years^{-1}) is logically bound to the accumulation rate of each ice core site. Hence, resolving the highest frequencies is a function not only of the sampling method but also of the accumulation rate of each specific site, although a constant smoothing of CFA (in cmweq) would affect low accumulation sites more. From the figure, the records which show the best fit to a 3–4 months smoothing are NEEM-2011-S1, NGRIP, NGRIP2, and WAIS—the four records with the largest accumulation rates, with the other records agreeing more with a smoothing of $>$5 months (Figure 7). Finally, we point out that these effective resolution estimates are coarser than estimates from previous studies (e.g., Kepko et al., 2009; Smart et al., 2014; Wolff et al., 2012) as they take into consideration both the analytical smoothing from CFA and the environmental smoothing occurring to different degree depending on the ice core site (Figure 6c), instead of relating to the sampling rate only.

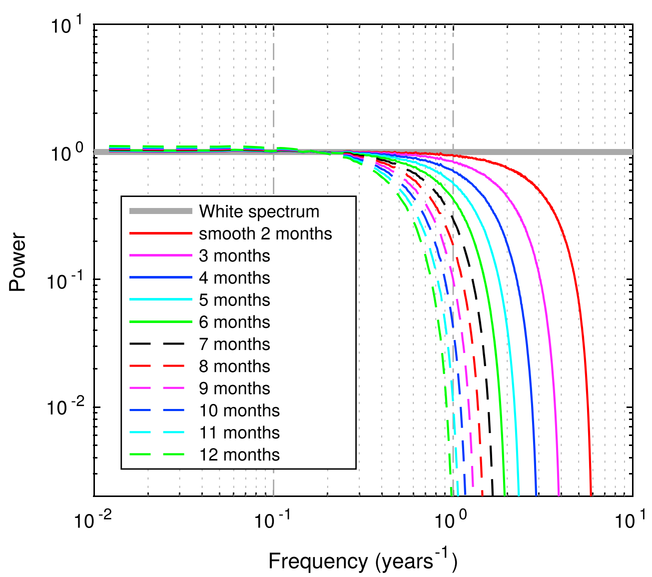

Figure 7. White noise spectrum (gray line) and mean PSDs of a series of 10,000 random white noise signals smoothed with a moving average filter ranging from 2 to 12 months.

4.2.2. Simulating the Effect of Dispersion for 775 CE

We can now simulate the dispersion effect of the CFA system on the theoretically expected peak that the SEP event of 775 CE could have yielded and assess whether this can account for the lack of nitrate

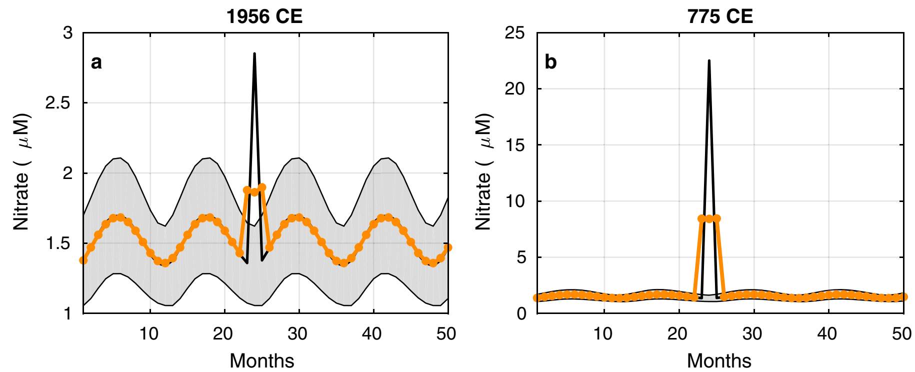

Figure 8. (a) Mean nitrate annual cycle in NGRIP (black curve with a 1σ envelope) with a 99% spike integrated over 1 month and its 3.5 months moving average filtered signal (orange). (b) Same as Figure 8a but with a fourteenfold spike simulating the nitrate increase expected for 775 CE relative to 1956.

enhancements in our measurements. We use the SEP event of February 1956 as an analogue for a high-fluence hard-spectrum event. According to nitrate measurements (Dreschhoff & Zeller, 1994) from the GISP2-H ice core, McCracken et al. (2001) attributed a nitrate increase of about 99% integrated over 1 month to the SEP event of February 1956, although the source of the said increase is disputed (Duderstadt et al., 2016; Wolff et al., 2016). Nevertheless, we (i) use the mean annual cycle in NGRIP2 and for the period 750–1000 CE as a background. Then we (ii) add a peak of 99% above the mean background and lasting 1 month at the seasonal minimum to simulate the winter nitrate deposition enhancement measured in GISP2-H around 1956 and (iii) disperse the composite series with a moving average filter of 3.5 months. Finally, we (iv) repeat the simulation but scaling the peak by a factor of 14 to produce the expected nitrate increase that the SEP event of 775 CE would have had yielded in comparison to the SEP event of 1956 (Melott et al., 2016), as they were both characterized by a hard energy spectrum. The chosen factor of 14 is based on the estimated F_{30} of ~1.8×10^9 and of ~2.6×10^{10} protons/cm^2 for the SEP events of 1956 and of 775 CE, respectively (Mekhaldi et al., 2015).

From these considerations (Figure 8) we can infer that an increase similar to the one observed in GISP2-H, and suggested to be associated to the SEP event of February 1956, would appear as a ~2σ increase spread over 4 months. This means that such an increase could be detectable, especially if repeated in multiple ice cores, albeit not straightforwardly. Yet we observe a similar increase in only two of the 10 ice cores—WAIS Divide (Figures 3 and 4) and ACT (Figure 3). As for a fourteenfold increase of 1956, as would be expected for 775 CE, the nitrate enhancement would rise exceptionally high above seasonal variability and noise and stand out significantly (Figure 8). Yet again, we find no such significant nitrate event in any of the ice cores investigated (Figures 2 and 4). In consequence, although we do not dispute that laborious, high-depth-resolution discrete sampling can theoretically resolve shorter-term variability than CFA systems, we disagree with the statement that the latter have resolution limitations which hinder the detection of any impulsive nitrate event (Smart et al., 2014). This holds particularly true when considering the natural limits of the resolution of ice core data as well as extreme events such as those of 775 and 994 CE which would have left a clear imprint in ice cores should nitrate be a robust tool to document atmospheric ionization by SEP events.

4.3. Comparison to ^{10}Be

The fluence spectra of the SEP events of both 775 and 994 CE were so exceptional that both events produced large and detectable amounts of ^{14}C in tree rings and a ~300% increase in ^{10}Be in ice cores (for 775 CE) despite measurements at "only" an annual resolution (Mekhaldi et al., 2015; Sigl et al., 2015). In comparison, it was computed that the SEP event of February 1956 only induced a ^{10}Be atmospheric production rate increase of ~12% (Webber et al., 2007). More strikingly, the events were also detected in ^{36}Cl (~600% for ^{36}Cl at 775 CE) from the GRIP ice core despite a poor resolution of 5 years. Given the peak response energy for the production of nitrate by solar protons being at ~10 MeV compared to ~15–25 MeV and ~100–200 MeV for ^{36}Cl and ^{10}Be, respectively (Webber et al., 2007), it could be expected that the atmospheric production of nitrate by impinging protons is relatively more enhanced compared to the atmospheric background

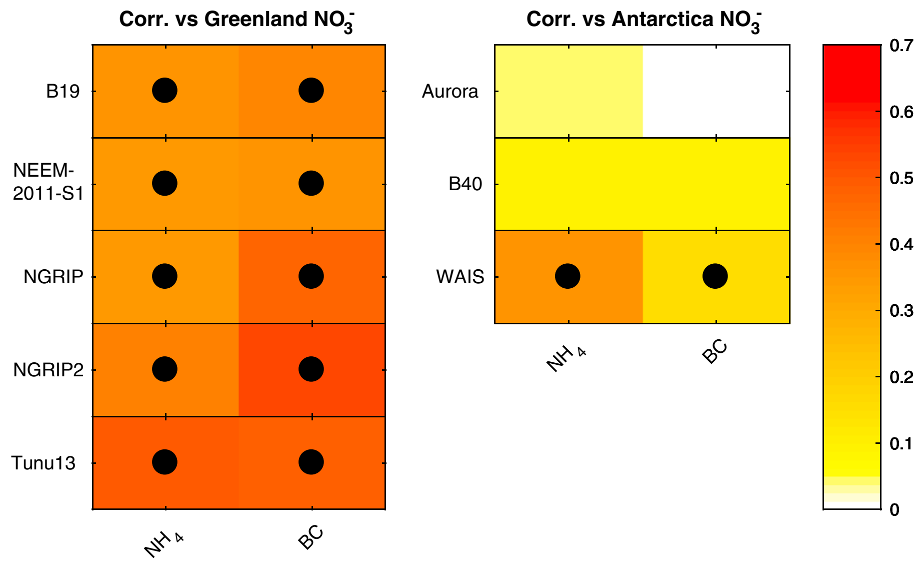

Figure 9. Color-coded matrix showing the Pearson correlation coefficients between the nitrate (Figures 2a and 2b) and the biomass burning records NH_4 and BC (Figures S3 and S4) for 765–785 CE and 985–1005 CE. Dots denote significant correlations ($p < 0.05$).

produced by galactic cosmic rays than that of radionuclides, considering the higher fluxes of solar protons at lower kinetic energies. Instead, we observe no such increases in ice cores from both Greenland and Antarctica. Furthermore, the ^{10}Be peaks at 775 CE have been measured in the NEEM-2011-S1, NGRIP, Tunu13, and WAIS ice cores (Sigl et al., 2015). Hence, we can, in contrast to other studies (Sukhodolov et al., 2017), precisely compare nitrate with ^{10}Be from the same cores with no chronological uncertainties (Figures 2c–2f). Doing so, it is evident that nitrate deposition for 775 CE and 994 CE is not comparable to that of ^{10}Be, the atmospheric production of which is yet less sensitive to solar protons than nitrate. This is likely due to a large atmospheric reservoir of nitrate relative to the additional nitrate produced by SEPs, as opposed to radionuclides. This is especially true when considering tropospheric production which is the fraction which could have a direct influence on ice core concentrations, as the larger stratospheric fraction would be spread over months (Duderstadt et al., 2016; Sukhodolov et al., 2017).

4.4. Nitrate and Biomass Burning Plumes

Another line of argument advocating against the use of ice core nitrate to document past SEP events is that nitrate deposition does not necessarily represent a global source signal. For instance, nitrate concentration in ice was shown to be influenced by sea salt possibly due to a partitioning of gas-phase nitrate to aerosol or a trapping of nitrate in snow (Jourdain, 2002; Wolff et al., 2008). In addition, it was observed that nitrate is often associated to biomass burning species such as spikes in ammonium, possibly due to a then more efficient scavenging of the former (Savarino & Legrand, 1998) or to locally enhanced nitrate input in the atmosphere. This effect results in ice layers enriched in nitrate content that do not relate to an increase in polar atmospheric input (Wagenbach et al., 1998; Wolff et al., 2012).

We investigate the latter possibility by comparing our nitrate data to the biomass burning species ammonium (NH_4) and black carbon (BC) around both 775 and 994 CE (Figures S3 and S4). Figure 9 displays Pearson correlation coefficients between nitrate and NH_4 as well as BC for each ice core with a color-coded correlation matrix. Similar to the findings of Wolff et al. (2012), we report a strong and significant relationship between nitrate and biomass burning species for Greenland ice core sites which are closer to potential terrestrial sources of biomass burning plumes in comparison to Antarctica. It is interesting to note, though, that the WAIS Divide ice core does have high and significant correlations ($p < 0.05$) between nitrate and NH_4 as well as BC. The only core which exhibits no relationship at all between nitrate and biomass burning is from ABN which is located more inland than EDML (B40) and WAIS sites. As a result, it could be argued that this site is best suited to investigate the possibility of ice layers enriched in SEP-produced nitrate as it is less

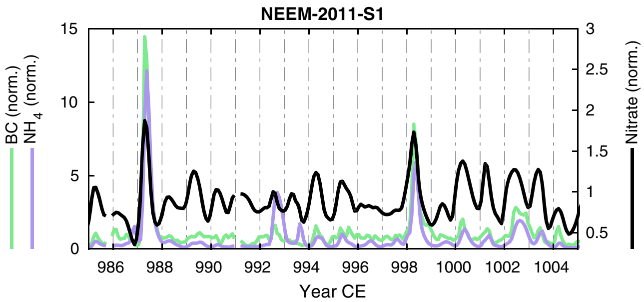

Figure 10. Normalized nitrate, ammonium (NH4), and black carbon (BC) concentration in NEEM-2011-S1 for 985–1005 CE.

biased by biomass burning. However, such East Antarctic sites typically experience less precipitation making them less adequate to resolve short-lived excursions (Figure 6c). We can also precisely compare excursions in nitrate to the two biomass burning species in depth/time owing to CFA (Figures S3 and S4). Our CFA data show that many nitrate spikes in most Greenland ice cores and in the WAIS ice core are coeval with spikes in NH_4 and/or BC. A good example is shown in Figure 10 which displays nitrate as well as NH_4 and BC in the NEEM-2011-S1 ice core for the period 985–1005 CE. It shows that the two large nitrate enhancement events occurring in the spring/summer of 987 and 998 CE are synchronous with large increases in both NH_4 and BC, most likely related to biomass burning. This provides further evidence that enhanced nitrate precipitation is influenced in part by biomass burning plumes. We note, however, that the strong correlations could be attributed to some extent to the common transport processes of nitrate, NH_4, and BC for arctic ice core sites.

We showed in section 4.1 that nitrate has a poor global representativeness for sporadic spikes and for annual and decadal-to-centennial time scales. In addition, there is strong evidence that enhanced precipitation of nitrate to arctic ice shows strong covariability with other chemical impurities in the ice, either through common source strength variations, that are not solar, or through transport and deposition processes. In consequence, previous nitrate spikes which have been attributed to SEP events but that are from single cores and lacking measurements of biomass burning species, such as GISP2-H, cannot reliably be used to document such events and derive their occurrence rate. Therefore, we see no line of evidence to support that ice cores can hold detectable amounts of SEP-produced nitrate, even for the most extreme events known to date.

5. Conclusions

1. We report no nitrate enhancement events following the extreme solar energetic particle (SEP) events of 775 and 994 CE, based on CFA measurements from five Greenland and three Antarctic ice cores. In contrast to previous work (Sukhodolov et al., 2017), this series includes all ice cores in which a clear ^{10}Be spike was reported in annually resolved measurements (Sigl et al., 2015) allowing us to rule out dating uncertainties in four of the eight records.
2. We also report the lack of coincident nitrate enhancement events for the past two centuries in five Greenland and five Antarctic ice cores. This period covers both the Carrington event and the hard-spectrum high-fluence SEP event of February 1956. Hence, none of the largest ancient, historical, and measured solar events was accompanied by a global increase in nitrate concentration in polar ice records. This result supports the model-based suggestion that nitrate spikes observed in ice cores should not be used as a proxy for SEP events (Duderstadt et al., 2016).
3. We have taken in consideration the affirmation that CFA systems lead to a lower effective resolution than high-resolution discrete sampling (Smart et al., 2014). However, we show that CFA in addition to environmental processes occurring at ice core sites leads to a smoothing of, at most, ~3–4 months in our data. This would not hinder the detection of large nitrate increases such as what would be expected for the extreme events of 775 and 994 CE compared to 1956.
4. We confirm the poor representativeness of nitrate spikes and of annual to subcentennial variability in nitrate concentration to global-scale processes such as solar activity. This suggests that polar ice does not hold detectable concentrations of nitrate ions produced by either solar or galactic cosmic rays.
5. We also confirm the strong and significant association of nitrate enhancement events with biomass burning species in Greenland ice cores (Wolff et al., 2008, 2012), as well as WAIS.
6. Using the ideal test cases that are the SEP events of 775 and 994 CE, we show strong evidence that ice core nitrate cannot be used to document the occurrence rate of extreme SEP events as these events did not yield any coincident nitrate enhancements in polar ice core records.

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