The Carrington event not observed in most ice core nitrate records

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[1] The Carrington Event of 1859 is considered to be among the largest space weather events of the last 150 years. We show that only one out of 14 well-resolved ice core records from Greenland and Antarctica has a nitrate spike dated to 1859. No sharp spikes are observed in the Antarctic cores studied here. In Greenland numerous spikes are observed in the 40 years surrounding 1859, but where other chemistry was measured, all large spikes have the unequivocal signal, including co-located spikes in ammonium, formate, black carbon and vanillic acid, of biomass burning plumes. It seems certain that most spikes in an earlier core, including that claimed for 1859, are also due to biomass burning plumes, and not to solar energetic particle (SEP) events. We conclude that an event as large as the Carrington Event did not leave an observable, widespread imprint in nitrate in polar ice. Nitrate spikes cannot be used to derive the statistics of SEPs. **Citation:** Wolff, E. W., M. Bigler, M. A. J. Curran, J. E. Dibb, M. M. Frey, M. Legrand, and J. R. McConnell (2012), The Carrington event not observed in most ice core nitrate records, *Geophys. Res. Lett.*, *39*, L08503, doi:10.1029/2012GL051603.

1. Introduction

[2] A range of phenomena is associated with sporadic events of energy release in the solar corona, that are observed visibly as solar flares [*Space Studies Board*, 2008]. One consequence is the appearance in Earth's atmosphere of solar energetic particle (SEP) events (also often referred to in the literature cited here as solar proton events (SPE)). These events lead to enhanced ionisation in the middle atmosphere, and are of considerable societal interest because of the impact SEP can have both on spacecraft and on power and communication systems on Earth. In order to assess the risk of serious damage from such events, and therefore the requirement to protect or insure systems against such events, one needs to know the frequency of occurrence for events of different magnitudes. However, the record of routine observation on Earth is very short (just a few solar cycles), and insufficient to assess the frequency of larger events. Observations of other stars may allow an improved sense of the statistics of larger events, but the most relevant extension of the statistics would come from a longer dataset on Earth. One possibility is to examine records of cosmogenic radionuclides deposited on Earth, for example ^{10}Be in ice cores [*Usoskin et al.*, 2006]; however, the relatively small enhancements expected over background over the averaging times of the deposition records mean that only very large events could be identified.

[3] Enhanced ionisation that acts particularly at high latitudes will lead to the production of NO (and subsequently other oxidised nitrogen compounds). In some polar ice cores, sharp spikes of nitrate concentration exceeding the background variability by a large factor are observed. It has been suggested that such spikes are the result of NO_x production in the atmosphere caused by SEPs [e.g., *Zeller et al.*, 1986, 1989], and that the frequency and amplitude of the nitrate events can be used as a way of assessing the frequency of SEP events of different magnitudes [*McCracken et al.*, 2001]. A number of objections to this interpretation of ice core nitrate have been raised [e.g., *Legrand and Delmas*, 1986; *Wolff et al.*, 2008]. The major thrust of the objections has been twofold:

[4] 1. SEPs would not produce a signal in ice that was as sharp, strong or immediate as those that are observed. SEP deposit their energy mainly in the middle stratosphere or at higher elevations. For instance, the well-documented 1972 SPE provided a maximum NO production at 40 km [*Jackman et al.*, 1980]. As discussed previously [*Legrand et al.*, 1989], NO produced at such elevations at high latitudes would (after interconversion to other NO_y components) not only be downward transported but also be horizontally diffused from high to low latitudes where it is transported to high levels again with diabatic circulation. As a result, the NO perturbation should take some 2 years to reach ground level and would be diluted within other sources acting in the lower stratosphere or upper troposphere (N_2O oxidation and galactic cosmic rays).

[5] 2. In contrast, there are other ways in which sharp spikes in nitrate are produced, for example via sporadic scavenging and deposition of nitrate by aerosol [*Wolff et al.*, 2008].

[6] If either of these is true, then it becomes very difficult to use nitrate spikes to discuss the statistics of solar events. Nonetheless, the paradigm that nitrate in ice cores provides a measure of SEP occurrence remains strong in the solar-terrestrial community. This arises largely from an apparent coincidence between large nitrate events in ice and

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Table 1. Characteristics of the Sites and Ice Cores Used in This Paper

Core	Latitude (deg)	Longitude (deg)	Acc Rate/cm H_2O (a^{-1})	Period Available	++[a]	Resolution (a^{-1})	Reference[b]	Shown in Figures?
				Antarctic				
ITASE99-1	80.62 S	122.62 W	14	1707–1999	±1	>10	1	
ITASE00-4	78.08 S	120.08 W	19	1798–2000	±1	>10	1	
ITASE00-5	77.6 S	123.99 W	13	1736–2000	±1	>10	1	Y
ITASE01-3	78.12 S	95.65 W	33	1858–2001	±0	>10	1	
ITASE02-1	82.00 S	110.01 W	23	1790–2002	±1	>10	1	Y
ITASE02-3	85.00 S	105.00 W	17	1848–2002	±1	>10	1	
RIDS-A	78.73 S	116.33 W	22	1503–1995	–[c]	>10	1	
Law Dome	66.78 S	112.82 E	70	1299–1996	±0	∼12	2	Y
				Greenland				
GISP2 H, Summit	72.6 N	38.5 W	25	1561–1991	±0	∼15	3	Y
GISP2 B, Summit	72.6 N	38.5 W	25	818–1987	–[c]	0.5	4	Y
Zoe, Summit	72.6 N	38.3 W	22	1840–1880	±0	∼20	#	Y
GRIP	72.56 N	37.63 W	∼20	1767–1982	±2	∼4	5	Y
(NGT)B20	78.83 N	36.50 W	10	829–1994	±5	∼10	6	Y
NEEM	77.45 N	51.06 W	20	<1840–2011	±1[d]	∼20	7,#	Y
D4	71.4 N	44.0 W	41	1788–2002	±0	∼40	8	Y

[a]++ Quoted uncertainty on age (in years).
[b]References refer either to the previous publication of the data, or to papers giving the accumulation rate and site characteristics. 1 = *Frey et al.* [2006]; 2 = *Morgan et al.* [1997] and *Palmer et al.* [2001]; 3 = *McCracken et al.* [2001]; 4 = *National Snow and Ice Data Center et al.* [1997] and *Whitlow et al.* [1994]; 5 = *Legrand and de Angelis* [1996]; 6 = *Bigler et al.* [2002]; 7 = *Steen-Larsen et al.* [2011]; 8 = *Banta and McConnell* [2007] and *McConnell et al.* [2007]; # =this paper: for Zoe, methods are similar to reference 8, while for NEEM methods are similar to those of reference 6.
[c]Sites where we found no author estimate of the age uncertainty. Uncertainty should be similar to other sites with similar accumulation rates.
[d]The NEEM dating was done by a stratigraphic transfer of the GICC05 age scale from the NGRIP to NEEM core.

known solar events [*McCracken et al.*, 2001]. However, apart from a recent short core extending to the 1930s [*Kepko et al.*, 2009], all the major papers that have claimed to identify or use such events as SEPs have arisen from only two ice cores: one from Windless Bight, Antarctica extending back to ∼1900, and one from Summit in Greenland (GISP2 H core) extending back to the mid-16th century [e.g., *Dreschhoff and Zeller*, 1994; *McCracken et al.*, 2001; *Shea et al.*, 1999, 2006; *Zeller et al.*, 1986, 1989; *Zeller and Dreschhoff*, 1995]. The sharp peaks observed in these studies could be observed because data were collected at a depth resolution that gave a sample frequency of order 10–20/year. While nitrate has been measured in numerous other ice cores, it has until recently been rare for data to be collected at comparable resolution. In one study of a very highly resolved core from Antarctica [*Palmer et al.*, 2001], no spikes comparable to those observed in the previous studies were observed. There was, statistically, a small increase in nitrate concentrations in the year following known solar events, but for most events the nitrate signal was indistinguishable from that of background (no event) years.

[7] If it is possible to use the statistics of nitrate spikes in any single core to assess SEP occurrence, then it follows that most large spikes should appear in most ice cores. In recent years, improved analytical techniques, and in particular the use of continuous flow techniques in which a stick of ice is melted on a hotplate and analysed in a continuous stream [*Röthlisberger et al.*, 2000], have meant that several cores have been analysed (for nitrate and other constituents) at a resolution sufficient to identify the relevant spikes where they exist. The time is therefore now ripe to re-assess whether the spikes observed to date are present in other ice cores, and to consider whether they do indeed represent SEP events. As a first and particularly strong test, we will consider the period surrounding just one event, the Carrington event of 1859. The first reported solar flare in September 1859 was associated with a significant magnetic disturbance. The event is often considered to be one of the largest in the last 150 years [*Cliver and Svalgaard*, 2004]. In the previous statistical study [*McCracken et al.*, 2001] a nitrate signal was observed in the ice dated to late 1859 that caused the authors to consider it the strongest SEP event in the last 400 years.

2. Ice Core Nitrate Data

[8] We have therefore compiled a suite of ice cores from both Greenland and Antarctica: the criteria for including them in the main analysis is that they must reach 1859, they must be well-dated, and analysed at a resolution equivalent to at least 10 samples per year. We later consider two cores with lower resolution (GRIP, GISP2 B) that were drilled near Summit, Greenland, because they allow a further comparison with existing records. The ice cores and their characteristics are presented in Table 1. Figure 1 shows the location of the different ice cores, including the GISP2 H core in which evidence for the Carrington event was originally claimed [*McCracken et al.*, 2001].

[9] In Figures 2 and 3 we present the data for the period 1840 to 1880 for the GISP2 H core, and for a selection of the other cores in our study. The first result is that none of the cores other than the GISP2 H core show a peak in the layer identified as 1859, or within the declared dating uncertainty of the cores. This is true whether we consider East Antarctica, West Antarctica, or Greenland.

[10] None of the Antarctic cores in Table 1 (including the three shown in Figure 2), show any sharp spikes, exceeding the typical seasonal cycle and ranging well above 100 $\mu g\ kg^{-1}$, of the kind that characterised the claimed SEP peaks at both GISP2 (H core) and Windless Bight. It has previously been suggested [*Wolff et al.*, 2008] that spikes at Windless Bight may result from depositional processes, nitrate being scavenged from the atmosphere when there is

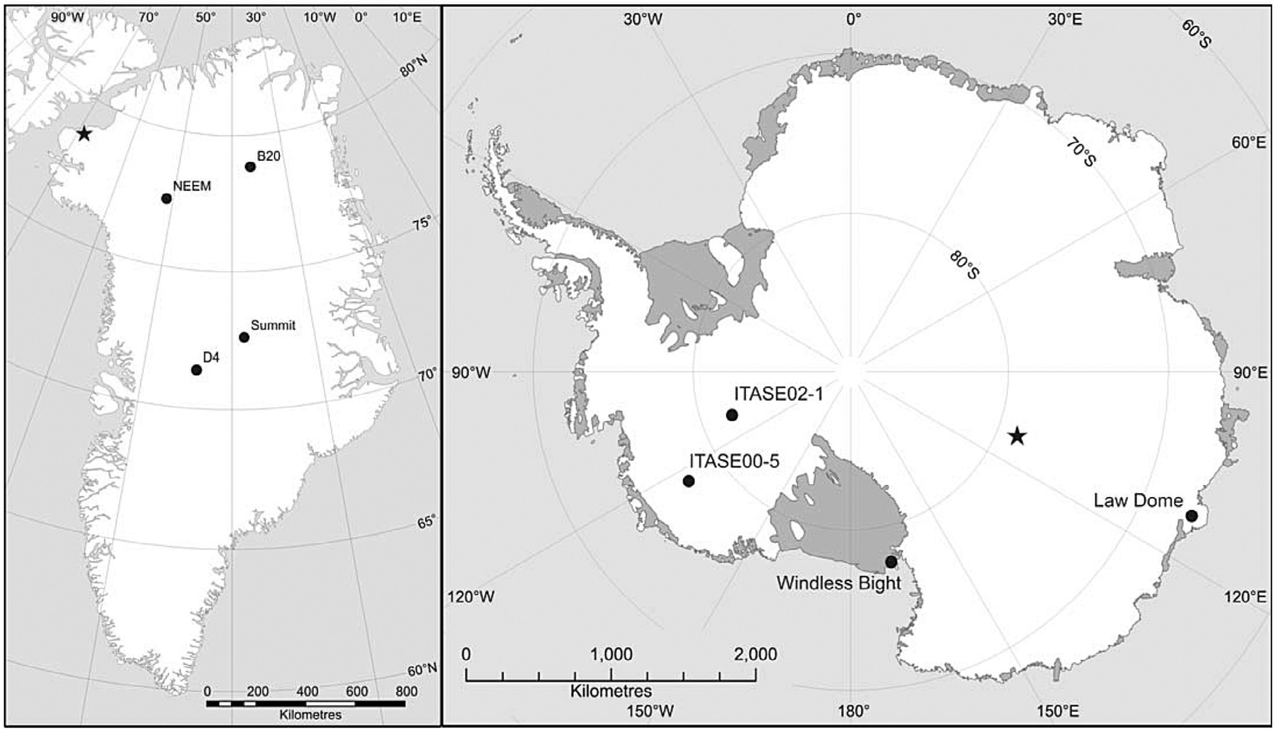

Figure 1. Maps of Greenland and Antarctica showing locations of the sites presented in the later figures. Summit is the location of the GISP2 H, GISP 2 B and Zoe cores, while GRIP is 30 km distant. The stars show the estimated location of the geomagnetic poles in the year 1900.

a strong spike of sea salt. We do not have data to confirm this speculation, but the absence of spikes at sites with lower sea salt concentrations seems consistent with this interpretation.

[11] Spikes in nitrate of the nature observed in the GISP H core are observed at all the Greenland sites (Figure 3), although not in 1859. The pattern of spikes seen at Zoe (very close to GISP2-H) and D4 (230 km away) appears similar to that in the GISP-H core with 3 peaks at 1854 (1851), 1863 (1859) and 1868 (1864) in Zoe/D4 (H core). If these are in fact the same peaks, then the dating of GISP2-H is 4 years different to the other cores at this period, and the peak identified as 1859 is found in 1863 in the later cores. D4 and Zoe were dated using annual cycles in a range of elements and chemical species linked to sea salts, continental dust, marine biogenic emissions, atmospheric photochemistry, biomass burning, and industrial pollution. Given this multi-parameter annual layer counting used to date the later cores, it is unlikely that GISP2-H (dated with nitrate cycles alone) has the more reliable dating. A different pattern of peaks is seen in the more northerly B20 and NEEM cores, but again with no spike in 1859.

2.1. Biomass Burning Components

[12] Whether or not the peaks are the same in the different cores, we can fingerprint their origin by looking at other chemical components. Every major nitrate spike in each core shown in Figure 3 is accompanied by a spike in ammonium (which was not measured in the GISP2 H core). Previously it has been asserted that sharp ammonium spikes in Greenland cores arise from the transport of biomass burning plumes, primarily from North America [*Fuhrer and Legrand*, 1997; *Legrand et al.*, 1992, 1995; *Whitlow et al.*, 1994]. The association of nitrate with these ammonium spikes was noted previously [*Savarino and Legrand*, 1998; *Whitlow et al.*, 1994], and may result both from nitrate being another component of such plumes, and from nitrate being scavenged by

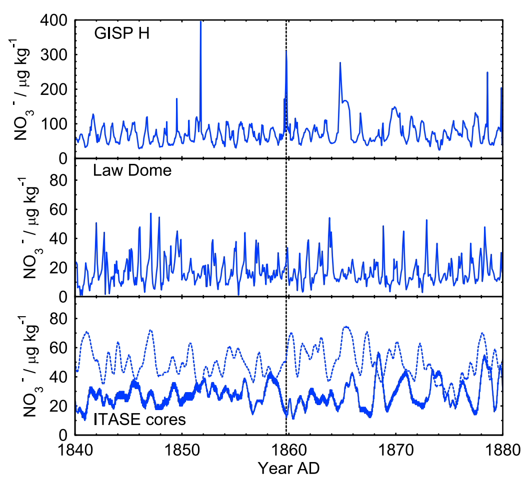

Figure 2. Nitrate concentration in the Greenland GISP2 H core and in three Antarctic cores for the period 1840–1880. Note the different scales on the y-axis for Greenland and Antarctic cores. In the bottom panel, the dashed curve is ITASE 00-5, the solid curve is ITASE 02-1. The dashed vertical line marks the expected date of the proposed Carrington signal. Note that although only a few sites are illustrated, no 1859 event is seen in any of the cores in Table 1.

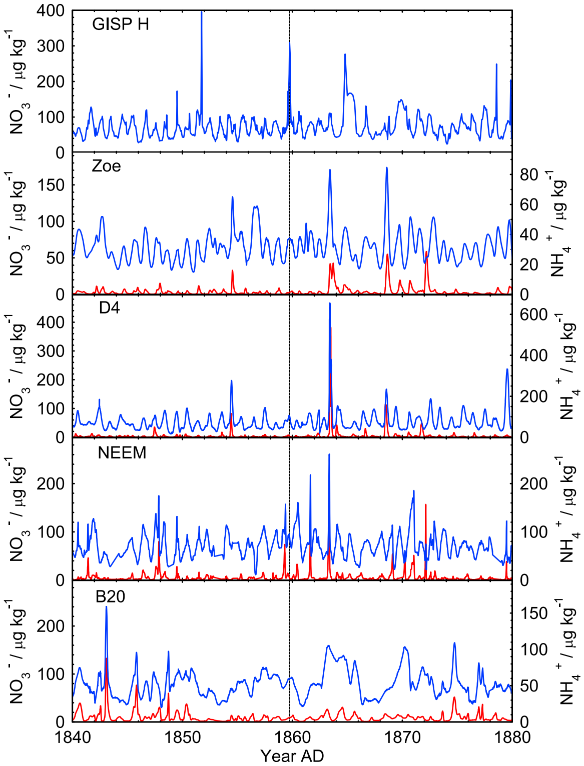

Figure 3. Nitrate and ammonium concentrations in a range of Greenland ice cores for the period 1840–1880. Nitrate is in blue (left axis), ammonium in red (right axis). Note the different scales on the y-axis for each record. The dashed vertical line marks the expected date of the proposed Carrington signal.

the ammonium in the plume. In any case such events appear to be diagnostic of a coincidence of a major biomass burning event, favourable transport, and efficient deposition (probably a snowfall event) at the ice core site. For this reason, we would expect to see a similar pattern of peaks in cores located close to each other, but different patterns at greater distance.

[13] To confirm the nature of the peaks, we show further chemical components for the cores at Summit and D4 (Figure 4). Even at the much lower resolution available, both the GISP2 B core [*Whitlow et al.*, 1994] and the GRIP core (30 km distant) [*Legrand and de Angelis*, 1996] also show a peak in both nitrate and ammonium, in both cases centred on 1862-3. For GRIP, a number of carboxylic acids, diagnostic of biomass burning plumes, also spike above a very low background (including formate, shown in the figure). At Zoe and D4, all three major spikes show an increase in black carbon (BC) concentration, indicating the presence of combustion emissions, and finally D4 shows large spikes in vanillic acid (VA) at each peak. VA is considered as a specific marker for biomass burning emissions [*McConnell et al.*, 2007].

[14] Taken together, these results make an unequivocal case that the three nitrate spikes in Figure 4 are the result of biomass burning plumes passing over the ice core sites, and are not the product of SEPs. Comparison of nitrate, ammonium and, where available, BC, VA , or carboxylic acids, throughout the Greenland cores in Table 1, shows that all significant nitrate spikes have the fingerprint of biomass burning. Because of its great distance from sources we would not expect any sharp biomass burning plumes in Antarctica. We note that the identification of sharp events as arising from short-lived tropospheric plumes removes the need to find an explanation for sharp and fast deposition of nitrate from the middle atmosphere.

3. Discussion on Statistics of SEPs

[15] Undoubtedly, SEPs do produce an enhancement of NO, at least in the stratosphere, and this should be reflected in a small and broad enhancement of nitrate deposition, perhaps of the limited nature reported in Antarctica [*Palmer et al.*, 2001]. Unfortunately such a small enhancement cannot be used to identify individual SEP events, let alone to quantify them. Ongoing atmospheric monitoring of atmospheric nitrate at coastal Antarctica [*Weller et al.*, 2011] could ultimately provide long-term data allowing evaluation of the sensitivity of the lower troposphere to SEPs.

[16] In summary, the nitrate event identified as 1859 in the GISP2 H core [*McCracken et al.*, 2001] is most likely the same event that more recent Greenland cores identify at 1863. The parallel event in other cores, as well as all other significant nitrate spikes in those cores, has an unequivocal fingerprint of a biomass burning plume. Although we cannot prove that this is true for the 1859 event in the GISP2 H-core, it seems overwhelmingly likely. In any case, the GISP2 H core is the only one of the 8 Antarctic and 6 Greenland cores

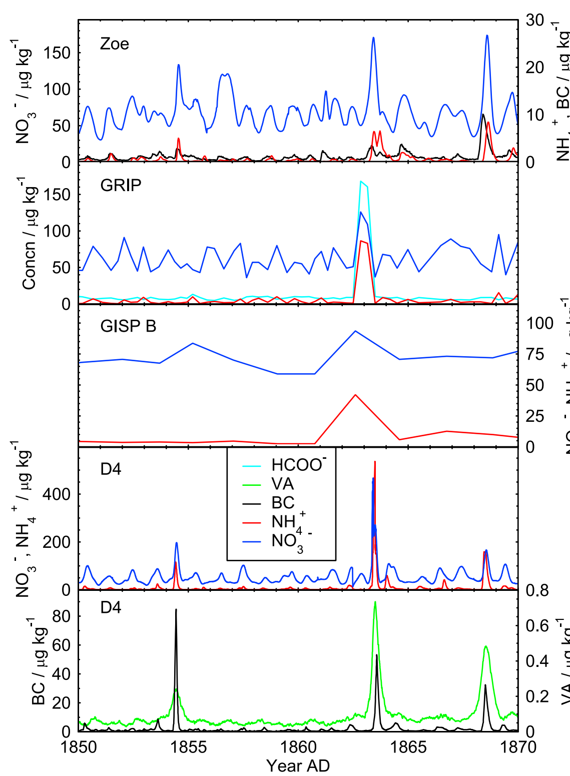

Figure 4. Chemical records for Greenland ice cores for the period 1850–1870. In each case nitrate is in blue, ammonium in red, black carbon (BC) in black, vanillic acid (VA) in green, formate in turquoise. Note the different scales on the y-axis for each record.

with high resolution discussed here (Table 1) that claims a spike in 1859. Taking the data from all the cores discussed here, we can say clearly that an episode of the size of the Carrington Event has not left an observable imprint in nitrate in ice. Existing estimates of the statistics of SEPs using nitrate in Greenland ice must unfortunately be dismissed – they actually describe the co-mingled statistics of biomass burning in North America (and to a lesser extent, Eurasia), with plume transport and deposition events over central Greenland.

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