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Solar cosmic ray events for the period 1561–1994
1. Identification in polar ice, 1561–1950

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Abstract. The geophysical significance of the thin nitrate-rich layers that have been found in both Arctic and Antarctic firn and ice cores, dating from the period 1561–1991, is examined in detail. It is shown that variations of meteorological origin dominate the record until the snow has consolidated to high-density firn some 30 years after deposition. The thin nitrate layers have a characteristic short timescale (<6 weeks) and are highly correlated with periods of major solar-terrestrial disturbance, the probability of chance correlation being less than 10^{-9}. A one-to-one correlation is demonstrated between the seven largest solar proton fluence events that have been observed since continuous recording of the cosmic radiation started in 1936, and the corresponding thin nitrate layers for the event date. The probability of this occurring by chance is $<10^{-6}$. This high degree of statistical correlation, together with the modeling studies of Jackman, Vitt, and coworkers, is interpreted as establishing that the impulsive nitrate events are causally related to the generation of energetic particles by solar activity. The timescale of the nitrate events is too short to be understood in terms of transport mechanisms in the gaseous phase and indicates that the nitrate must be precipitated to the polar caps by the gravitational sedimentation of stratospheric solid particles. A conversion factor is established between the impulsive transient nitrate concentrations and the >30 MeV solar proton fluence. The proton fluences (omnidirectional fluence cm^{-2}) derived from the 70 largest impulsive nitrate events between 1561 and 1950 are tabulated. The proton fluence probability distribution derived from these large impulsive nitrate events are in good agreement with earlier studies of the cumulative probabilities of solar proton events and with the observation of cosmogenic isotopes in moon rocks. The cumulative probability curve derived from the impulsive nitrate events indicates a rapidly decreasing probability of occurrence of >30 MeV solar proton events having an omnidirectional fluence exceeding 6×10^9 cm^{-2}. It is concluded that the impulsive nitrate events are reliable indicators of the occurrence of large fluence solar proton events and that they provide a quantitative measure of these events. It is further concluded that the impulsive nitrate events will permit the study of solar activity for many thousands of years into the past.

1. Introduction

Over the past 15 years there have been a number of publications that have advanced the hypothesis that short-term (approximately 1 month or less) increases in the nitrate component of polar ice are the consequence of solar proton events (SPEs) [e.g., *Dreschhoff and Zeller*, 1990; *Dreschhoff et al.*, 1993; *Shea et al.*, 1993]. The hypothesis has always been a long way removed from one to one, there being many more nitrate anomalies than SPEs and there being some major SPEs for which the nitrate anomaly may have merged with the ambient noise in the record. As a consequence, the hypothesis has been regarded as plausible but unproven without further supporting evidence.

The inability to obtain clear one-to-one correlations be-dated snow.) Further, since 1950 there has been a steady increase in the man-made component of the nitrate signal (the anthropogenic component) in the Greenland ice cores from which the majority of the data in this paper originates [*Legrand and Mayewski*, 1997]. Short-term meteorological influences have modulated the deposition of this steadily increasing nitrate concentration, resulting in a steadily increasing nitrate variability commencing in the vicinity of 1950 and becoming particularly marked about 1970. As a consequence, nitrate events that are many standard deviations above the variability (the noise) in the data from the 19th century might not be distinguishable from the variability of meteorological and anthropogenic origin in the data from 1970 to date.

2. Since high-quality, continuous satellite observations commenced about 1967, the satellite data can only be compared with the nitrate data containing the highest level of noise. Thus errors in these comparisons may be frequent and causal relationships or associations difficult to demonstrate with statistical certainty.

3. There is a ground-based cosmic ray data record from 1936 to the present. The presence of solar proton events in the polar ionosphere was deduced from 1955 through 1962 by analysis of the forward radio scatter data [*Bailey*, 1964] and by riometer data in the Earth's polar caps from 1957 to the present. Some solar proton events in these data correlate well with NO_3 events found in polar ice cores; however, the correlation is weakened by the annual variability in the precipitation of nitrate from the stratosphere to the surface [*Legrand and Mayewski*, 1997]. In addition, there is a distinct seasonal effect in the nitrate transport efficiency, making the detection of solar particle events less probable when the polar vortex is not operating in summer and early autumn. As an example, the well-known high-energy solar cosmic ray event of February 23, 1956 [*Meyer et al.*, 1956], is relatively small in the Greenland nitrate data and difficult to identify in the available Antarctic ice cores. These factors have combined to throw some doubt on the solar proton/nitrate hypothesis in the past.

4. The nitrate record indicates that the relative amplitudes of the impulsive nitrate events above background appear to have been substantially greater in the 19th century than in the 20th century. This, together with the lower noise in the nitrate record noted in factor 1 above, means that there is a much better signal-to-noise ratio for the nitrate events prior to the 20th century.

The possibility that impulsive nitrate events are associated with solar proton events has been assessed from a theoretical point of view. Thus using the solar proton and alpha particle fluxes for the interval 1972–1989 as observed by IMP 8, *Vitt and Jackman* [1996] and *Vitt et al.* [2000] have estimated the annual concentrations of nitrate in the polar stratosphere as a consequence of solar proton events (SPEs), the galactic cosmic radiation, other polar sources, and transport from lower latitudes. Their computations indicate that the major solar proton events in August 1972 and October 1989 resulted in significant (>10%) increases in the total nitrate concentration and that these were the second most important contributions after transport from lower latitudes.

However, *Vitt and Jackman* [1996] and *Vitt et al.* [2000] conclude that their calculated solar proton event effects were too small to explain the very large fluctuations in the high-resolution Greenland nitrate results (2–3 week contiguous samples) between 1972 and 1991. The nitrate record they illustrate [*Vitt et al.*, 2000, Figure 9] contains eight nitrate anomalies that are greater than those that are in time coincidence with the 1972 and 1989 events. This illustrates vividly that the nitrate precipitation events attributed to solar proton events is relatively small (see factor 4 above), while the "meteorological" noise in the data is large (see factor 1). Despite the apparent ambiguity, the modeling results of *Vitt and Jackman* [1996] and *Vitt et al.* [2000] provide a quantitative estimate of the SPE nitrate production, which is an important contribution to the discussion that follows.

This paper seeks to validate the hypothesis that the impulsive nitrate events are associated with solar proton events using several tests in addition to correlation in time. To overcome the noise outlined in factor 1 above, the analysis initially establishes a strong association between the impulsive nitrate events and extreme disturbance of the solar-terrestrial system using the data obtained once the firn has consolidated to high-density firn and ice. We place major weight upon the data from the 19th century and earlier, where the impulsive nitrate events are many standard deviations above the noise in the nitrate data. We then demonstrate a strong association of the nitrate events with SPE since 1942, and we develop a method to estimate the SPE fluence associated with each impulsive nitrate event. The cumulative probability of those fluences is then shown to be in good agreement with the distribution derived from satellite data since 1967, yielding further support to the association of impulsive nitrate anomalies with SPE.

2. Data Procedures and Determination of Time

The nitrate data considered herein were obtained from a 125.6 m ice core drilled at Summit, Greenland (72°N, 38°W, altitude 3210 m) in 1992 and two shorter cores drilled at Windless Bight (78°S, 167°E) on the Ross Ice Shelf, in Antarctica, in 1988/1989 and 1990/1991. The drilling, sampling, and analytical procedures, and the checks for reproducibility have been described previously [*Dreschhoff and Zeller*, 1990; *Zeller and Dreschhoff*, 1995]. The three cores cover the periods 1561–1991 (Greenland) and 1905–1991 (Antarctica). In addition to the nitrate measurements the electrical conductivity of each sample was also obtained. This assists in the estimation of time and in quality control as outlined below and in Appendix A.

The ice cores are sampled for their whole length over contiguous intervals of approximately 15 mm. At both locations the average precipitation yields about 200–300 mm of ice per year after consolidation. Thus the nitrate concentrations (in units of nanograms of nitrate per gram of water) and electrical conductivities (in μS cm^{-1}) are sampled about 20 times per year. Figure 1 displays a typical data record from the Greenland ice core; an annual variation in nitrate is clearly evident. The majority of this nitrate has been transported from lower latitudes in the troposphere with source regions ranging from sea surface release to stratosphere-to-troposphere exchange. The maximum in the summer is affected also by sublimation (thereby concentrating the nitrate). The concentration starts to decline in the vicinity of the autumn equinox accompanied by reduced sublimation. The minimum is reached in late midwinter, and the concentration commences to rise thereafter. This annual behavior is well defined for ~90% of the full length of the Greenland ice core.

In addition to the lateral transport of nitrate from midlatitudes, nitrates originate in the polar stratosphere and are then transported downward by the polar vortex [*McElroy*, 1989;

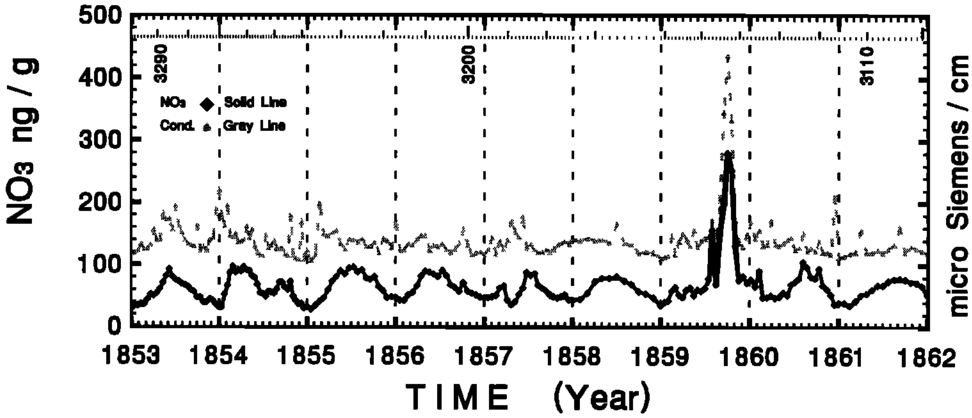


Figure 1. An example of the high-resolution nitrate and electrical conductivity data ($\mu S\ cm^{-1}$) from an ice core after the firn is highly consolidated. The impulsive event at 1859.75 is the largest integrated nitrate deposition in the period 1561–1991 and occurs in close correlation to the September 1, 1859, "white light" flare seen by Carrington. The scale along the top of this and other presentations of the nitrate data gives the sample number in the data deposited with World Data Center A for Glaciology. The nitrate data NO_3 in units of ng g^{-1} are illustrated by the solid line. The electrical conductivity data (Cond.) in units of $\mu S\ cm^{-1}$ are shown as the light gray line.

Iwasaka and Hayashi, 1991]. This transport is most efficient in winter and early spring, especially when there is a well-established polar vortex; however, the extent to which it is effective in the presence of enhanced photoionization in summer is not well known. A portion of this stratospheric source has been explained in terms of ionization by electrons released from the radiation belts in magnetic storms and by ionization by galactic and solar cosmic radiation, as discussed in a later section.

In this paper we examine discrete impulsive nitrate events in the ice core record, such as in the middle of 1859 in Figure 1. It is important that we estimate the time of deposition of each firn/ice sample as precisely as possible, to provide an accurate time base that will allow correlation with other geophysical data. As is common practice in glaciology, we have established the time of deposition relative to a number of well-defined reference horizons in the ice that are due to known geological events in the recent past.

The time assignment procedure is described and illustrated in Appendix A. Briefly, the annual variations in nitrate and conductivity are used to interpolate between the reference horizons to determine the year; the phase of the nitrate variation provides the estimate of time within the year. Wherever possible we have used reference horizons from Icelandic and other nearby volcanoes since these are more sharply defined in time, and the uncertainty due to the transit time of the debris is typically <1 month.

For about 90% of the period 1561–1950 the annual nitrate

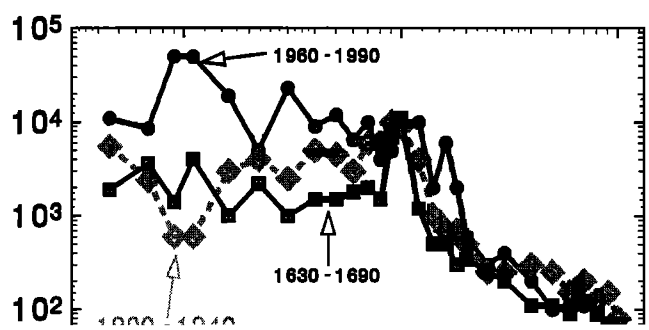
3. Spectral Properties of the Ice Core Data

Before discussing the impulsive nitrate events we examine the time variability of the nitrate data. Figure 2 presents the power spectra of the data for three different periods: (1) 1960–1990, prior to the high consolidation of the firn, and containing a substantial anthropogenic component, (2) 1900–1940, being recently consolidated to high density firn, and (3) 1630–1690, being consolidated ice (and containing the Maunder Minimum).

We note the following features of the power spectral density.

1. The annual variation in nitrate is clearly defined.

2. There is substantial power in the frequency range $0.1 < f < 1$ cycles yr^{-1}. The power in this range is 10 times greater in the contemporary data (1960–1990) than in the consolidated ice (1630–1690). The galactic cosmic radiation only contributes 7% of the nitrate (see section 5), and consequently, the



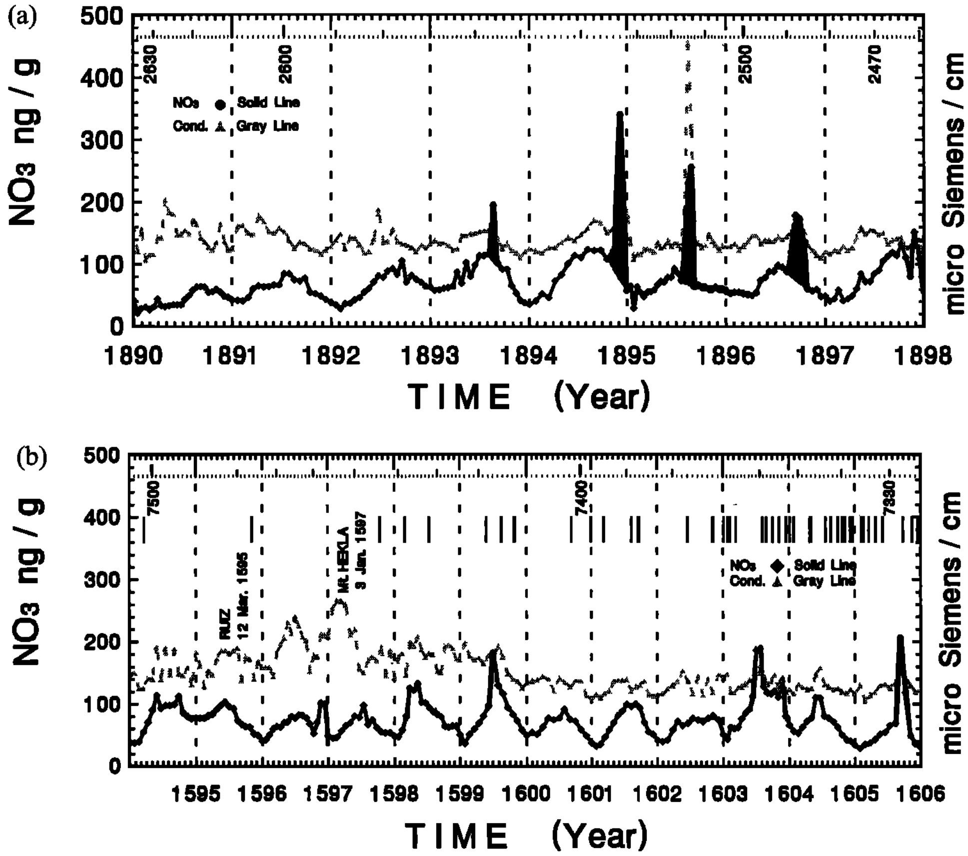


Figure 3. (a) The nitrate data for the interval 1890 to 1898. Four of the large nitrate events in this period have been highlighted for clarity. (b) Illustration of a series of five impulsive nitrate events from the period 1594 to 1606. These five events are listed in Table 1. The dark vertical lines indicate the observation of aurorae in central Europe.

11-year modulation is masked in these data by the nitrate from terrestrial sources.

3. There is a factor of 3 decrease in the high-frequency power ($2 < f < 5$ cycles yr^{-1}) between the latest and earliest data in Figure 2.

4. The higher values of power in the unconsolidated firn containing the most recent nitrate data make it difficult to achieve one-to-one comparisons with other geophysical phenomena. This results in a signal-to-noise ratio for impulsive nitrate events that is 2 to 3 times worse in the most recent nitrate deposits than in those in the consolidated ice pre-1900.

5. The impulse like nitrate events we consider here occupy the frequency region $7 < f < 10$ cycles yr^{-1}. The power in that range is only 16% of the total power in the power spectra for 1630–1690. Thus once the nature of the nitrate events has been established it will be possible to achieve an improvement in the signal-to-noise ratio of the nitrate events through the use of a high-pass filter. This has not been done for any of the analyses reported herein.

As a consequence of the large noise power in the data prior to high consolidation of the firn in the vicinity of 1900, the following analysis commences with study of the nitrate events pre-1900, where the higher signal-to-noise ratio allows the most accurate correlation studies. Having established a clear correlation with major disturbances in the solar-terrestrial system, we will then investigate the causal agent using the more recent data.

4. Impulsive Nitrate Events

Examination of the nitrate record shows that there are many impulsive anomalies, often of amplitude greatly in excess of the annual variation and of duration of 2 months or less. Figures 1, 3, and 4 present some of these, and in the following we describe the correlations that are evident from comparison with the geophysical database. These nitrate anomalies are frequently accompanied by electrical conductivity enhancements showing essentially an identical time profile. This feature, discussed in section 5, is not consistent with a volcanic origin.

In Figure 1 the persistent annual variation in the nitrate signal is interrupted by two impulsive events, the second being the largest such impulsive event in the whole Greenland core nitrate record 1561–1991. Well-known time markers due to the eruptions of Sheveluch in 1854 and Chikurachki-Tatarinov in 1853 provide good definition of the absolute timescale. The time of occurrence of the second nitrate event is estimated with confidence to be 1859.75 ± 0.2. As is well known, *Carrington* [1860] and *Hodgson* [1860] independently observed a white light flare on September 1, 1859, which was accompanied by a large geomagnetic crochet. (A geomagnetic crochet is now recognized as the consequence of a powerful solar EUV and X-ray event. The photons absorbed in the ionosphere create additional ionization in the upper atmosphere resulting in a sudden current flow on the sunward side of the Earth. Thus the continuous recording of the geomagnetic field that started in

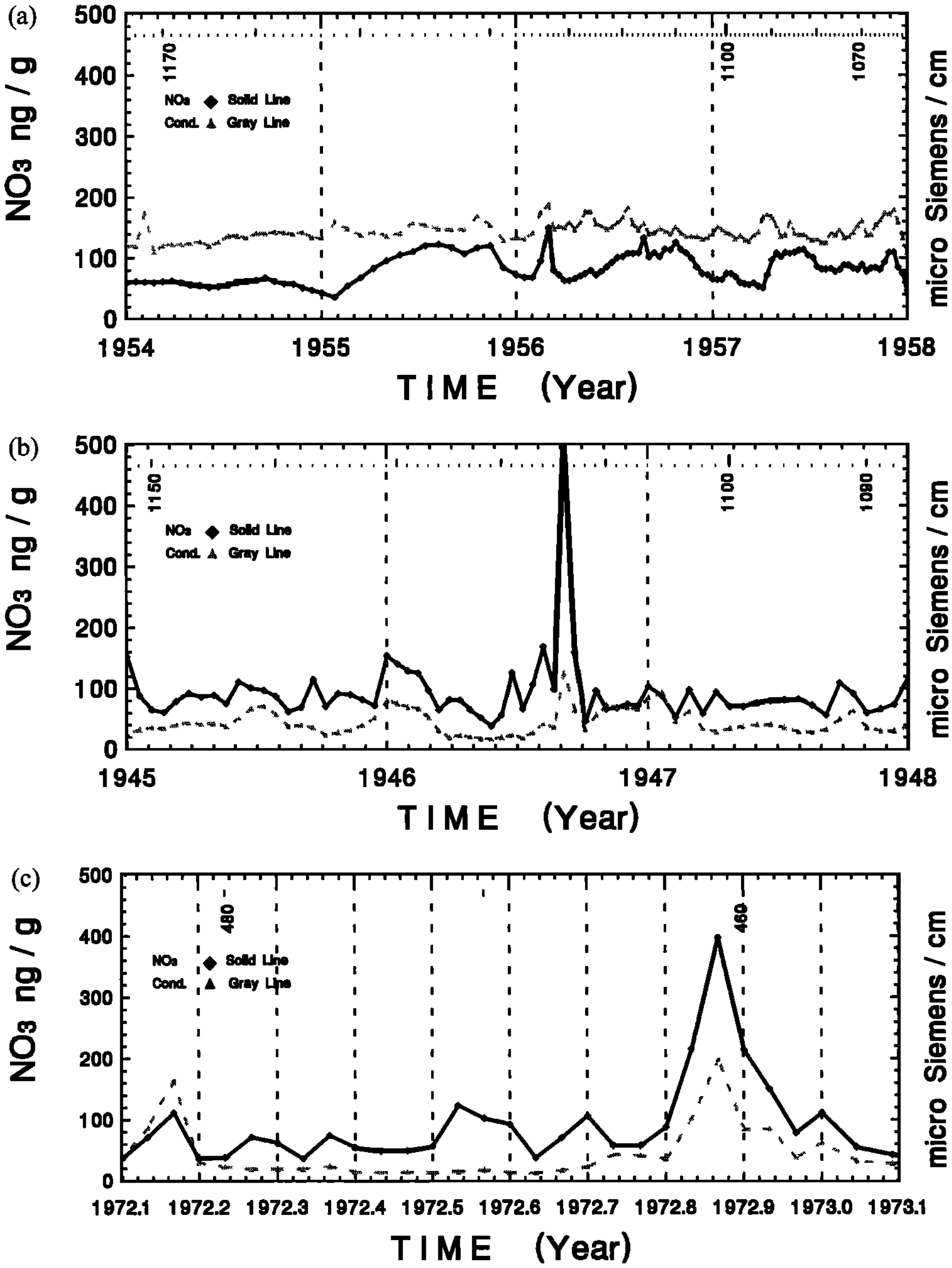


Figure 4. (a) The nitrate data from Greenland showing an impulsive nitrate event at the time of the large ground level cosmic ray increase on February 23, 1956. Note also that the very small impulsive event at about 1956.7 correlates well with the white light flare and ground level event of August 31, 1956. This latter impulsive event is smaller than the lower limit used throughout this paper. (b) The nitrate data from Antarctica showing the impulsive nitrate events at the time of the ground level event of July 25, 1946. (c) The nitrate data from Antarctica showing the large impulsive nitrate event associated with the solar particle events of August 1972.

the mid 19th century provides a proxy for major solar EUV/X-ray events from that date.) The area of the sunspot group was one of the greatest in the geophysical record. It was followed by an exceptionally large geomagnetic storm, which had the very rapid Sun-Earth transit time of 17.1 hours [*Cliver et al.*, 1990a, 1990b]. Thus the largest impulsive event in Figure 1 is closely associated in time with a period of exceptional interplanetary and geomagnetic disturbance.

The probability that the largest impulsive nitrate event in 430 years, and the largest flare seen in white light in 100 years [*McCracken*, 1959], should coincide in time by ±2 months, by chance, is $(1/430) \times (1/3) = 7.8 \times 10^{-4}$. We conclude therefore that there is a very high probability for a direct association between the two events.

Figure 3a presents the nitrate data for the interval 1890 through 1897. This is an exceptional period in the nitrate record with five large impulsive events, there being only one other episode of comparable frequency (circa 1600–1610) in our ~400-year record. The years 1892 (nine great magnetic storms) and 1894 (eight great magnetic storms) contain the highest number of magnetic storms for any year in the Greenwich list of the 112 great magnetic storms that occurred between 1874 and 1952 [see *Royal Greenwich Observatory*, 1955]. Thus the period in the vicinity of 1892 and 1894 were years of exceptional solar, interplanetary, and geomagnetic disturbance. Unfortunately, this period is deficient in sharp volcanic reference horizons (see Appendix A), and the annual variation in nitrate is occasionally indistinct. This leads to a greater uncertainty in the assignment of time, which we estimate to be better than ±1 year. For this reason, and because of the large number of geomagnetic storms, it was impossible to establish a one-to-one correlation of geophysical events with the nitrate anomalies, as done for Figure 1. There are 70 large impulsive events in the period 1561–1950. (See Table 1 for a listing of all nitrate events later computed to correspond to >30 MeV solar proton events with an omnidirectional fluence of $>2.0 \times 10^9$ cm^{-2}.) With 70 large nitrate events in 389 years the probability of one event occurring in a given year is 0.18. Using binomial statistics, we calculate that the probability that five large nitrate events would coincide with this one period of exceptional geomagnetic activity, by chance, is 9.6×10^{-4}.

Figure 3b presents the nitrate data for the interval 1594–1606. This is a portion of the other period exhibiting a high frequency of large impulsive nitrate anomalies. The 1597 eruption of Mount Hekla in Iceland yielded a clear event in the electrical conductivity data, and the timescale is accurate to within a year. On Figure 3b are superimposed periods of intense auroral activity, extracted from the catalogue of aurorae, 1000–1900 [*Krivsky and Pejml*, 1988]. This catalogue is restricted to aurorae observed south of 55°N and as such provides a proxy for major geomagnetic activity. In the preparation of Figure 3b we have only shown auroral activity which resulted in a number of observations spread over a period of several days, and as such, probably indicative of a series of large geomagnetic storms due to a large sunspot group. As can be seen from the figure, the frequency of impulsive nitrate events, and the frequency of major geomagnetic activity, both increase steadily with time during this interval. The high frequency of impulsive events continues for a decade. The probability that this period of intense auroral activity would occur by chance at the same time as the episode of impulsive nitrate events is 0.116 (binomial statistics).

The three correlations of the nitrate events discussed above

Table 1. Impulsive Nitrate Events (>30 MeV Proton Fluence $>2 \times 10^9$ cm^{-2}) in the Interval 1561–1950

Year	Nitrate Concentration, ng g^{-1}	>30 MeV Proton Fluence,[a] $\times 10^9$ cm^{-2}
1562	80	2.0
1564	94	2.3
1570	194	4.8
1574	99	2.5
1578	86	2.2
1582	119	3.0
1587	92	2.3
1596	118	2.9
1599	118	2.9
1603	209	5.2
1604	90	2.3
1605	284	7.1
1608	136	3.4
1610	187	4.7
1610	116	2.9
1612	108	2.7
1616	159	4.0
1619	319	8.0
1620	83	2.1
1621	89	2.2
1635	113	2.8
1637	246	6.1
1639	170	4.3
1647	208	5.2
1667	164	4.1
1682	112	2.8
1700	234	5.8
1701	111	2.8
1706	129	3.2
1710	188	4.7
1719	298	7.4
1727	252	6.3
1730	102	2.6
1755	216	5.4
1763	156	3.9
1774	180	4.5
1789	118	3.0
1793	219	5.5
1794	146	3.7
1805	141	3.5
1807	118	3.0
1813	255	6.4
1822	131	3.3
1849	101	2.5
1851	373	9.3

See Figure 3a as an example. (In the future it will be appropriate to apply a high-pass filter (>5 cycles yr^{-1}) to the data to overcome this interpolation procedure, but for this analysis we chose not to use signal processing until the nature of the nitrate events was clearly established.)

Examination of all of the nitrate and electrical conductivity data for the interval 1561–1991 led to the following observations.

1. There are short-term fluctuations in the conductivity record (e.g., the period 1853–1854 in Figure 1) during known volcanic episodes that are not accompanied by impulsive events in the nitrate record. This is to be expected as the direct consequence of the fact that volcanic material contains <5% nitrate [see *Legrand and Mayewski*, 1997, Figure 8]. The overwhelming contributor to the conductivity due to volcanic debris is H_2SO_4.

2. Impulsive events in the nitrate record are frequently accompanied by impulsive events in the conductivity record that exhibit essentially identical time dependence. This is the direct consequence of the electrical conductivity of the nitric acid itself, augmented by that of a variable amount of sulfate aerosols scavenged from the stratosphere with the nitrate [*Brasseur et al.*, 1990; *Dreschhoff and Zeller*, 1994].

3. The responses in the conductivity record that are the consequence of Icelandic eruptions are sometimes accompanied by a substantial reduction in the nitrate below the annual variation due to several atmospheric processes associated with OH^- and H_2S in the volcanic ejecta [*Dreschhoff and Zeller*, 1994]. They are occasionally followed immediately by an "overshoot," which is of similar duration to that of an impulsive nitrate event. Three such impulsive nitrate events associated with the volcanic events of Billy Mitchell (in 1567), Hekla (in 1694), and Katla (in 1720) were rejected as being probably of volcanic origin.

It should be noted that it is very uncommon for ice core to be sampled as frequently and as continuously as in this study. Annual means or longer are the norm in glaciology, and as such they constitute a boxcar filter in the time domain rejecting the high-frequency components that are characteristic of the impulsive nitrate events. The conventional sampling procedure has therefore severely discriminated against the impulsive events studied herein. For example, the event of 1859.75, the largest in our record, if sampled by an annual boxcar sample, only increases the annual mean by 24%, which is well within the normal year-to-year variability. Thus this largest event would not be detected by conventional studies of ice cores. The striking characteristic of the nitrate events reported herein is their short timescale, and this implies that they can only be studied effectively if the sampling interval is a month or less.

If we represent the nitrate concentration in the nth sample in the event as C_n, then for a sample length of L centimeters, and ice/firn density of ρ, the NO_3 deposited on the polar surface by a single impulsive event summed over the several time samples in the event is

$$\rho L \Sigma C(n) \text{ ng cm}^{-2}. \quad (1)$$

Throughout this paper we use the sum $\Sigma C(n)$ in units of ng g^{-1} (the quantity ng g^{-1} means nanograms of nitrate per gram of water) to quantify the nitrate events. This measure can be regarded as the nitrate concentration that would have been observed if all the nitrate in that event had been precipitated into a single sample. The density of the firn increases progressively to an asymptote when it becomes consolidated ice, and this has an influence on the conversion of the nitrate data to fluences as discussed in sections 8 and 9.

Based upon the above considerations, we accepted 156 impulsive events in the Greenland core in the interval 1561–1950 each of which had a total integrated nitrate content of >27 ng g^{-1} for the analysis that follows. The 70 impulsive events in the interval 1561–1950 that we later estimate to have had >30 MeV SPE fluences $>2 \times 10^9$ cm^{-2} are tabulated in Table 1.

6. Production of Nitrates by Energetic Particles

In a series of papers, *Jackman et al.* [1980, 1990, 1993], *Vitt et al.* [2000] and *Vitt and Jackman* [1996] have used the NASA Goddard Space Flight Center two-dimensional zonally averaged photochemical transport model to assess the origin of "odd nitrogen" NO_y (comprising N, NO, NO_2, NO_3, $2N_2O_5$, $BrONO_2$, $ClONO_2$, HO_2NO_2, and HNO_3) in the polar stratosphere. Odd nitrogen is the progenitor of nitrate in polar firn and ice. The most recent version of their model is based on the observed ionizing fluxes for the period since 1972 (galactic cosmic rays, solar energetic particle events, and auroral electrons) and on a dynamic model to account for transport of the odd nitrate from lower latitudes to the polar regions. We regard the results to be a useful and instructive indication of the relative importance of many of the complicated time-dependent physical processes involved. Nevertheless, since the calculations do not include the transport processes through the troposphere, they may only serve as a quantitative approximation for the ultra-high-resolution nitrate (i.e., impulsive nitrate events) preserved in the polar ice sheets.

Vitt and Jackman [1996] and *Vitt et al.* [2000] predict that the solar particle events in the period 1972–1995 will have produced 10–20% increases in the total odd nitrogen in the polar stratosphere. For example, for the year 1989, they calculate that the total number of odd nitrogen molecules produced in the northern polar stratosphere from the four largest sources, in ascending order of importance, are

Galactic cosmic radiation	6.90×10^{32}
In situ photochemical production	1.04×10^{33}
SPE of October 1989	1.60×10^{33}
Transport from lower latitudes	9.97×10^{33}

Their calculations imply that the large solar proton events of October 1989 generated an increase in odd nitrogen equivalent to 16% of a full year production from all other sources.

In addition to generation by solar proton events, odd nitrogen is produced in the mesosphere by protons and electrons precipitated from the magnetosphere during magnetic storms, and some of this odd nitrogen descends into the stratosphere over time. For the October 1989 solar proton events, the mesospheric production of odd nitrogen was computed by *Vitt and Jackman* [1996] to be 2.3×10^{33}, while *Jackman et al.* [1980] cite the annual production rate due to relativistic electron precipitation from the magnetosphere to be above 10^{34} in years near solar maximum. It is important to note that model calculations in conjunction with the results from contemporary satellite measurements by *Callis et al.* [1996] and *Callis and Lambeth* [1998] show that a portion of the odd nitrogen formed above 70 km by relativistic electrons can be transported downward at rates of between 0.7 and 1.0 km d^{-1} and that it ultimately contributes to the odd nitrogen in the upper stratosphere.

A large coronal mass ejection (CME) in the central portion of the solar disk can therefore make two distinct contributions

Table 2. Data for Seven Large Solar Cosmic Ray Events in the Nitrate Records in Greenland and Antarctica[a]

Solar Cosmic Ray Event(s)	$P > 30$ MeV Fluence, cm^{-2}	Integrated Nitrate Impulse, %		Geomagnetic Storm[d]	
		Greenland	Antarctica		
Feb. 28 and March 7, 1942		73 ± 15	117 ± 44[b,c]	large	AA* = 168
July 25, 1946		in noise	422 ± 21[b,c]	large	AA* = 200
Nov. 19, 1949		65 ± 29	336 ± 28[b,c]	moderate	AA* = 78
Feb. 23, 1956	1.0×10^9	99 ± 36	117[e] ± 73[b,c]	moderate	AA* = 60
Nov. 12–15, 1960	9.7×10^9	116 ± 52	183 ± 13[b,c]	large	AA* = 372
Aug. 2–9, 1972	5.0×10^9	213 ± 68[e]	696 ± 26[b,c]	large	AA* = 290
Oct. 19–30, 1989	4.2×10^9	318 ± 14[e]	393 ± 26[b,c]	large	AA* = 183

[a] The fluence data are from *Shea and Smart* [1990, 1993].
[b] Average of two different cores.
[c] There is an uncertainty in the background subtraction, as a consequence of the unconsolidated nature of the core.
[d] See *Allen* [1982] for the definition of the geomagnetic index, AA*.
[e] Uncertainty due to presence of sublimation peaks in the unconsolidated snow.

to the odd nitrogen in the stratosphere. The initial contribution occurs immediately, due to in situ ionization by the solar cosmic radiation accelerated by the CME. The CME also generates an interplanetary shock wave that may result in a geomagnetic storm that can result in the precipitation of relativistic electrons to altitudes in the mesosphere above 70 km. Odd nitrogen from that source can therefore appear as a second contribution to the stratospheric odd nitrogen extending over an interval of some 2–3 months.

In addition to the above, *Vitt et al.* [2000] have modeled the evolution of the concentration of odd nitrogen at an altitude of 30 km and concluded that the percentage increase due to SPEs is approximately twice that averaged over the whole stratosphere (tropopause to 50 km) as listed above. Their model concludes that the odd nitrogen from SPEs has a tendency to be concentrated near the lower limit of the stratosphere.

In summary, known physical processes predict that large solar proton events such as occurred in October 1989 will produce an increase in odd nitrogen in the lower stratosphere at the time of the event that approximates 27% of the annual production from all other sources. Furthermore, odd nitrogen may be subsequently transported from the mesosphere to augment the stratospheric source some 1–2 months later.

Vitt et al. [2000] point out that while their model is comprehensive to the point of the assessment of the time variation of the odd nitrogen in the polar lower stratosphere, there is a remaining uncertainty in the physics and transfer function of the odd nitrogen from the lower stratosphere to produce nitrate in the ice sheet. Section 10 of this paper will assist in the clarification and quantification of that process.

7. Comparison With the Cosmic Ray Record

We have shown that impulsive nitrate events are closely associated with large disturbances in the solar-terrestrial environment and have summarized mathematical models that indicate that SPEs and associated phenomena can generate substantial quantities of odd nitrogen in the lower stratosphere. We now compare the historical SPE record with the impulsive nitrate events discussed in section 4 to further explore the origin of the nitrate events. To overcome the effects of the meteorological noise outlined in section 3, we have used data from firn after consolidation to a high-density state where the noise power is reduced by a factor between 3 and 10, and the annual signal is beginning to be clearly defined (i.e., the period of time prior to 1960).

The first continuously operating cosmic ray detectors were the "Carnegie Type C" ionization chambers operated by Scott Forbush. While the first of the network of four instruments (Greenland, United States, Peru, and New Zealand) commenced operating in 1936 [*Shea and Smart*, 2000], the first solar cosmic ray effects were not recorded until 1942 [*Forbush*, 1946]. Other more sensitive solar cosmic ray detectors were developed in the following years. However, for this part of the analysis we choose to use the events seen by the ionization chambers [*Smart and Shea*, 1991] for the following three reasons: (1) they allow us to seek correlations with the cosmic ray record before the increase in variability in the nitrate record in the vicinity of 1950, as noted in the introduction, (2) the relative insensitivity of the ionization chamber means that they are automatically selecting a uniform sample of exceptional solar cosmic ray events having a "hard" spectrum, and (3) the instruments were identical, and no adjustments for relative sensitivity are required. In addition, the following discussion considers two of the largest episodes of solar particle events from the satellite era, August 1972 and October 1989, while acknowledging the higher noise in the nitrate record as noted earlier.

Table 2 lists five "Forbush era" and two "satellite era" large solar proton events with their corresponding nitrate deposition. The nitrate data corresponding to three of these events are presented in Figures 4a, 4b, and 4c, and these impulsive nitrate signals are coincident (±2 months) with these exceptionally large solar proton events. The other events in Table 2 are also consistent with this degree of association in time. The statistical probability that the seven impulsive nitrate events, and the seven solar proton events, would exhibit this close degree of correlation by chance is $<1.0 \times 10^{-6}$.

For some of the events in Table 2 the nitrate peak is well defined and has an estimated accuracy in the vicinity of 20% or better (see Figures 4b and 4c). In other cases there are uncertainties associated with the unconsolidated snow and firn, as indicated in the Table 2 footnotes. The integrated nitrate impulse is given in units of ng g^{-1}. Note that some of the nitrate impulses in this table do not appear in Table 1 because they are smaller than the lower cutoff applied there.

A priori we know that the transport of nitrates from the stratosphere is more efficient during winter than during summer [*Van Allen and Murcray*, 1994; *Wauben et al.*, 1997], and this is evident in Table 2 for the two events occurring in the depth of winter in the Antarctic (July 1946 and August 1972).

We also note that on average the magnitudes of the impulsive nitrate events in the Antarctic ice core are substantially greater than the magnitudes of the events in the Greenland ice core. It appears possible that these differences will allow us to study the details of the nitrate deposition processes in the future.

In summary, the calculations of *Vitt and Jackman* [1996] show that known physical processes predict that spacecraft observed large SPEs will generate high concentrations of nitrates in the lower stratosphere, while the data in Table 2 show that all of the largest observed SPEs that occurred in the time prior to 1960 (in the consolidated, more noise-free ice core) have associated impulsive nitrate anomalies. The extremely low probability of this correlation occurring by chance, in addition to the modeling results of *Vitt et al.* [2000], leads us to conclude that solar cosmic radiation is the causal agent between major solar-terrestrial disturbances and impulsive nitrate events that was established earlier.

Finally, referring to Figure 4a, note the small impulsive event in August 1956. This only has a nitrate concentration of 27 ng g^{-1} and it would be indistinguishable from the noise in the data after 1960. Nevertheless, it appears likely that it is correlated with the small ground level (neutron monitor observed) SPE on August 31, 1956 [*McCracken*, 1959]. The conversion developed in section 1.9 yields a fluence of 5×10^8 cm^{-2} for this nitrate event, and our experience indicates that this is the likely threshold for the detection of SPEs in ice cores after further refinement of the technique.

8. Radiation Fluence of the Nitrate Events

It was shown above that the statistical correlations in the geophysical record, and known physical processes, are consistent with the hypothesis that the impulsive nitrate events in polar ice are produced by solar proton events. In the absence of any other plausible cause for these events we proceed using the working hypothesis that the impulsive nitrate events are a direct and observable consequence of the arrival of solar cosmic rays at Earth.

As noted in our discussion of the "out of phase detection" of nitrate events in the Arctic and Antarctic, the efficiency with which stratospheric nitrates can reach the surface is reduced by photoionization during summer and by enhanced precipitation processes in winter. Using (1), we define the conversion factor between fluence and the nitrate event as $K(t, \lambda)$ in the equation

$$\text{nitrate deposited} = \rho L \Sigma C(n)$$
$$= K(t, \lambda) \times \text{fluence}/(1.0 \times 10^9), \qquad (2)$$

where $K(t, \lambda)$ is an explicit function of time and latitude, to allow for the annual variation in the efficiency of detection, and its phase difference between the north and south polar regions. The sample length L is 1.5 cm for the data in this paper. Knowing the fluence (F) and nitrate deposition at time 0, (2) can be rewritten to give the fluence of the event at the nth sample as

$$F(n) = \frac{\rho(n)}{\rho(o)} \times \frac{\Sigma C(n)}{\Sigma C(o)} \times F(o). \qquad (3)$$

Since the firn/ice density varies from 0.3 at the top to 0.9 at the bottom of the 126 m Greenland core, it is clear from (3) that the fluences derived at various depths in the firn/ice will be systematically underestimated by a monotonic increasing function of time, up to factor of 3, if the density is not taken into account.

Table 3. Evaluation of $K(t, \lambda)$

Event	Ice Density	Greenland $K(t, \lambda)$	Antarctica $K(t, \lambda)$
Feb. 23, 1956	0.53	113	93
Nov. 12–15, 1960	0.52	9	15
Aug. 2–9, 1972	0.45	29	94
Oct. 19–30, 1989	0.33	37	46
Average, all four		47	62
Average, last two		33	70

Table 3 lists our estimates of the conversion factor $K(t, \lambda)$ computed using (2) and the data in Table 2. The firn densities listed are from the Greenland drilling site, and the densities in Antarctica are assumed to vary in a similar manner with time.

Referring to Table 3, we note the following features:

1. There is a wide variation in the computed conversion factors for individual events. The more extreme values are for the two earlier events for which the fluences are based on riometer measurements, which saturate at high flux levels, and ground level solar cosmic ray data, and are therefore liable to errors that could be a factor of 2 or more.

2. While the fluences for the events of 1972 and 1989 are based on direct satellite measurements, the nitrate feature is subject to noise as discussed in section 3.

3. Using the last two events in Table 3, the average value of $K(t, \lambda)$ for the Greenland core is 33.0 with a spread of $\pm 25\%$.

4. The computations of *Vitt et al.* [2000] are in broad agreement with this determination of $K(t, \lambda)$. Thus as discussed in section 6, their computations for the October 1989 solar proton events yield an increase in odd nitrogen of 27% at 30 km when compared to the annual input of odd nitrogen from all natural sources. The integral under the annual nitrate curve for Greenland in the vicinity of 1989 is approximately 2500 ng g^{-1}, and allowing for a 50% contribution from the anthropogenic component [*Legrand and Mayewski*, 1997, Figure 10], this implies a 337 ng g^{-1} nitrate enhancement due to the SPEs. The known >30 MeV proton fluence of 4.2×10^9 cm^{-2} yields $K(t, \lambda) = 39.6$ to be compared with the range 29–37 in Table 3.

5. In view of the errors that must remain in any of these estimates and computations, we take the upper limit of these estimates (40) to be the conversion factor for the nitrates in the Greenland core in this analysis. In making this choice we are being conservative and probably underestimating the fluence prior to 1950. *McCracken et al.* [this issue] consider the implications of a value of $K(t, \lambda)$ of 20, as suggested by Table 3, when applied to the event of September 1, 1859.

6. The average value of the conversion factor for the last two events in Table 3 are 2 times larger in the Antarctic than in the Arctic. The computations of *Vitt et al.* [2000] have shown a similar north/south difference.

7. There is some suggestion of the expected annual variation in the conversion factor (e.g., August 1972 compared to October 1989); however, the errors discussed above are too large to allow accurate determination of this feature at this time.

Note that $K(t, \lambda)$ should be a function of the solar proton spectrum. For the same fluence a hard spectrum will ionize preferentially at lower altitudes, resulting in a more intense precipitation event. The August 1972 proton event sequence

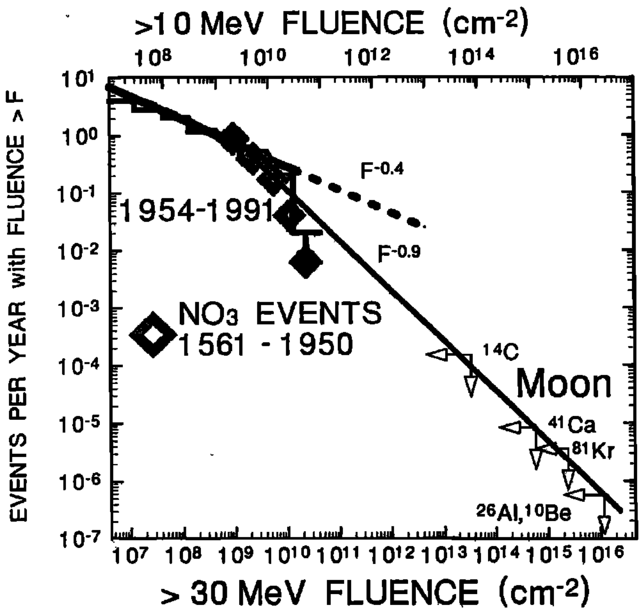


Figure 5. A comparison of the cumulative normalized probabilities of large solar proton events as derived from the impulsive nitrate events with the normalized probabilities of SPE as derived from terrestrial data and moon rocks [*Reedy*, 1996]. The >10 MeV Earth-sensed fluence data from Reedy (top scale) are indicated by the three lines. The solid heavy line is an extrapolation from the analysis of cosmogenic isotopes in lunar samples. The diamond-shaped symbols indicate the cumulative normalized probabilities of >30 MeV proton event fluence (bottom scale) derived from the impulsive nitrate events, 1561–1950.

was a relatively "soft" spectrum while the October 1989 proton event sequence had a relatively "hard" spectrum. Thus some of the differences in Table 3 may be due to spectral differences between the very small sample of events that is available to us.

9. Estimates of the Fluence of Large Solar Proton Events, 1561–1950

Taking the average annual conversion factor $K(t, \lambda)$ for Greenland as 40, we have used (2) to convert all of the integral nitrate anomalies >27 ng g^{-1} into estimates of fluence. Thus the impulsive nitrate event in Figure 1 dated 1859.75, which we associate with the Carrington white light flare, is computed to have had an omnidirectional fluence (>30 MeV) of 18.8 × 10^9 cm^{-2}. The 70 events calculated to have fluences in excess of 2 × 10^9 cm^{-2} are listed in Table 1. There were a further 55 events with fluences between 1 and 2 × 10^9 cm^{-2}, and these are used in the second paper [*McCracken et al.*, this issue] in addition to those in Table 1.

We have used the fluence data for the 125 impulsive nitrate events with fluences >1 × 10^9 cm^{-2} as computed above to derive cumulative normalized probabilities for the occurrence of SPE with fluences >30 MeV. We compare this distribution with the cumulative probability curve for >10 MeV fluence published by *Reedy* [1996]. This comparison is displayed in Figure 5, which makes allowance for the average dependence of SPE fluence upon energy between 10 and 30 MeV (see upper and lower proton fluence scales). It can be seen that the probability distribution function based upon the nitrate data is in good agreement with the distribution derived from a combination of direct spacecraft measurements and analysis of cosmogenic isotopes in moon rocks by Reedy. This provides further confirmation that the impulsive nitrate events provide a quantitative measurement of the SPE fluence, as observed for the whole period 1561–1950.

The slope of the distribution becomes much steeper for >30 MeV fluences larger than 6 × 10^9 cm^{-2}, and this distribution is consistent with the upper limits set by the cosmogenic isotopes in lunar samples. Our two highest fluence bins exhibit a rapidly decreasing probability, and since they contain a total of eight solar proton events, the rapid decrease in probability in Figure 5 is statistically significant. We conclude that in addition to confirming the consistency of the nitrate data with the known properties of SPE, Figure 5 indicates that the probability of occurrence of SPE decreases rapidly at >30 MeV fluences above ~6 × 10^9 cm^{-2}. Section 8 in *McCracken et al.* [this issue] shows that this feature is consistent with the effects of the ion-wave interactions that give rise to the streaming limited fluxes observed by satellite instruments in large solar proton events [*Reames*, 1999].

10. Timescale of the Impulsive Nitrate Events

As noted previously, the impulsive events in the nitrate record are all short lived. This is clear for the events in Figures 1, 3, and 4 and is universally true for the events in Table 1. In general, many have a time constant as short as 2 weeks, while none has one greater than 6 weeks. This observation sets considerable constraints upon the precise source of the nitrate that is observed in the ice core record.

On conventional thinking, the storage time for the stratosphere (including time for transport to the troposphere) is considerably longer than 1 month. It has been estimated [*Dunkerton*, 1978] that the downward transport of HNO_3 in the gaseous phase would take at least 3–6 months. However, rapid removal from the stratosphere by gravitational sedimentation and transport into the troposphere is a function not only of the winter polar vortex with extension into the end of spring but also of the size of particles formed in the cold stratosphere. Larger ice particles, which would help to remove nitric acid from the gas phase, may have settling speeds of the order of kilometers per day [*Jones*, 1990], and some estimates are in the range of 1 week for the fallout to reach the surface [*Iwasaka and Hayashi*, 1991]. Satellite (Stratospheric Aerosol and Gas Experiment II) observations have led to the conclusion that there is a preferential loss of larger aerosols in the polar vortex. These serve as polar stratospheric cloud nuclei and are irreversibly transported by sedimentation through the tropopause to lower altitudes in the form of large cloud particles [*Thomason and Poole*, 1993]. Our observation of time constants in the range 2–6 weeks for the impulsive nitrate events is consistent with these gravitational mechanisms and gives support to the hypothesis of accelerated precipitation of NO_3 following irradiation of the stratosphere by ionizing nuclei such as are present in solar proton events.

Although polar stratospheric clouds form in the cold polar winter atmosphere every year, the process is expected to be enhanced during and after major ionization events. Large fluence SPEs were shown to introduce local cooling within the proton stopping region in the lower stratosphere [*Kodama et al.*, 1992]. It seems that these findings from Antarctica correlate with the detection of large increases of stratospheric aerosols in the Arctic (~17 km altitude) after the occurrence of SPEs [*Shumilov et al.*, 1996].

In section 6 we discussed the possibility that the impulsive nitrate event would consist of two components, the first "prompt" component due to the SPE ionization in the lower stratosphere, and the second component extending some 2–3 months later due to the downward transport to the stratosphere of odd nitrogen generated by the precipitation of relativistic electrons in a magnetic storm. The latitude of the electron precipitation is likely to be equatorward of the polar vortex during these large magnetic storms. (See *Gussenhoven et al.* [1983] for the relationship between the latitude of auroral electron precipitation and magnetic activity.) While the relative importance of these two components will not be investigated here in detail, we note that the nitrate event of July 1946 (Figure 4b) was one of the shortest in the data record, being completely over within 1 month. This known high-energy multi-GeV hard spectrum solar proton event was accompanied by one of largest of the "great magnetic storms" in the interval 1874–1954 [*Royal Greenwich Observatory*, 1955]. For the nitrate event in July 1946, we estimate that any "second component" from the mesosphere was <5% of the amplitude of the first component due to ionization by the solar protons in the lower stratosphere. Nevertheless, the possibility of a small contribution to the impulsive nitrate event from processes initiated by a magnetic storm remains open.

Finally, we note that the nature and duration of the nitrate events will be a function of the altitudes in the stratosphere at which the solar protons deposit their energy by ionization. This implies that solar proton events with a hard spectrum result in substantial ionization at low altitudes (e.g., 25 km), which would then precipitate quickly. In addition, very hard spectrum ground level solar cosmic ray events will initiate pair production, which will increase the ionization density in the stratosphere. Alternatively, a SPE with a soft spectrum would result in the majority of the ionization occurring at higher altitudes (e.g., >40 km) and the timescale of the precipitation would be longer. Thus a solar particle event that is the result of solar activity near the western limb of the Sun (harder spectrum) would produce a short duration nitrate event, while a solar particle event that is the result of solar activity near the solar central meridian (often a softer spectrum) would be more prolonged.

11. Conclusions

This paper has demonstrated that the impulsive nitrate events in the polar ice record are highly correlated with periods of extreme disturbance in the solar terrestrial environment. The statistics of occurrence indicate that the nitrate events are the consequence of ionization of the upper atmosphere by solar cosmic radiation. We argue that the probability that the observed associations with disturbances in the solar-terrestrial environment, and with solar proton events in the cosmic ray record, should occur by chance is less than 1×10^{-6}. This is supported by one-to-one correlations between seven large SPEs and impulsive nitrate events.

The presence of meteorological "noise" in unconsolidated firn largely obscures the solar proton events subsequent to 1960. The optimum sensitivity for detection of SPEs is only attained once the consolidated ice stage is reached, some tens of years after deposition. Comparison with the historic cosmic ray record 1936–1999 indicates that the impulsive nitrate deposition to the surface is approximately 2 times larger in Antarctica than in Greenland. We have derived a hemisphere-dependent calibration factor to convert impulsive nitrate deposition in polar ice (after compensation for the ice density) to incident >30 MeV proton event fluence. The SPE fluence cumulative probability distribution resulting from this analysis is consistent with that derived from contemporary spacecraft and moon rock data. The large fluence solar proton event distribution derived from the impulsive nitrate data exhibits a substantial steepening of slope in the vicinity of a >30 MeV fluence of 6×10^9 cm^{-2}.

We find that the timescale of the impulsive nitrate events is too short to be consistent with gas phase transport of the nitrate from the point of production to the polar caps. We conclude that the short timescales (<6 weeks) support the hypothesis of a gravitational precipitation process involving water droplets or ice crystals. The timescale suggests that there is condensation on the intense ionization tracks at the end of the ionizing range of solar protons, with a possible association with polar stratospheric clouds as well. The short timescale implies that the impulsive nitrate events will only be seen if ice core is sampled at an interval that corresponds to a deposition time of 1 month or less. The impulsive nitrate events will be difficult to detect using the annual or longer samples used in conventional glaciology.

We have shown that the impulsive nitrate events in polar ice provide a good record of solar proton events that have occurred in the recent past. The nitrate is securely trapped in the crystals of consolidated ice, and there are no known decay mechanisms [*Legrand and Mayewski*, 1997]. On this basis we conclude that the impulsive nitrate events in polar ice are terrestrial records of the occurrence of solar proton events in the past and that they can be used as proxies of solar activity patterns as is done by *McCracken et al.* [this issue]. Drill holes extending into 40,000-year-old ice are common. There are two drill holes that extended to ice deposited >200,000 years before present [*Legrand and Mayewski*, 1997]. Consequently, we suggest that it is feasible to consider the identification of solar proton events extending many thousands of years into the past. This could provide the ability to investigate long-term changes in the temporal characteristics of the dynamo processes that generate the variable solar magnetic fields and to investigate any links that may exist between solar activity and climatic change during recent geological time.

Appendix A: Time Assignment Procedure

To estimate the time of deposition of each of the 8000 core samples from the period 1561–1991, a timescale was established relative to 33 reference horizons in the ice that are associated with well-known geological events. We have used reference horizons from Icelandic and other nearby volcanoes wherever possible, since the transit time of the debris to Greenland can be less than a week [*Laj et al.*, 1993]. Figures A1a through A1c illustrate several of these reference horizons, well known in ice deposits in Greenland from volcanic eruptions in nearby Iceland, and some (e.g., Figure A1c) that are well known worldwide. Volcanic material contains a high percentage of sulfates, which yields a very characteristic signature in the conductivity record (see discussion in section 5) and not in the nitrate record. Further, as is illustrated by the conductivity response from Katla in Figure A1a, the conductivity signature is often short lived (<6 months), because the debris

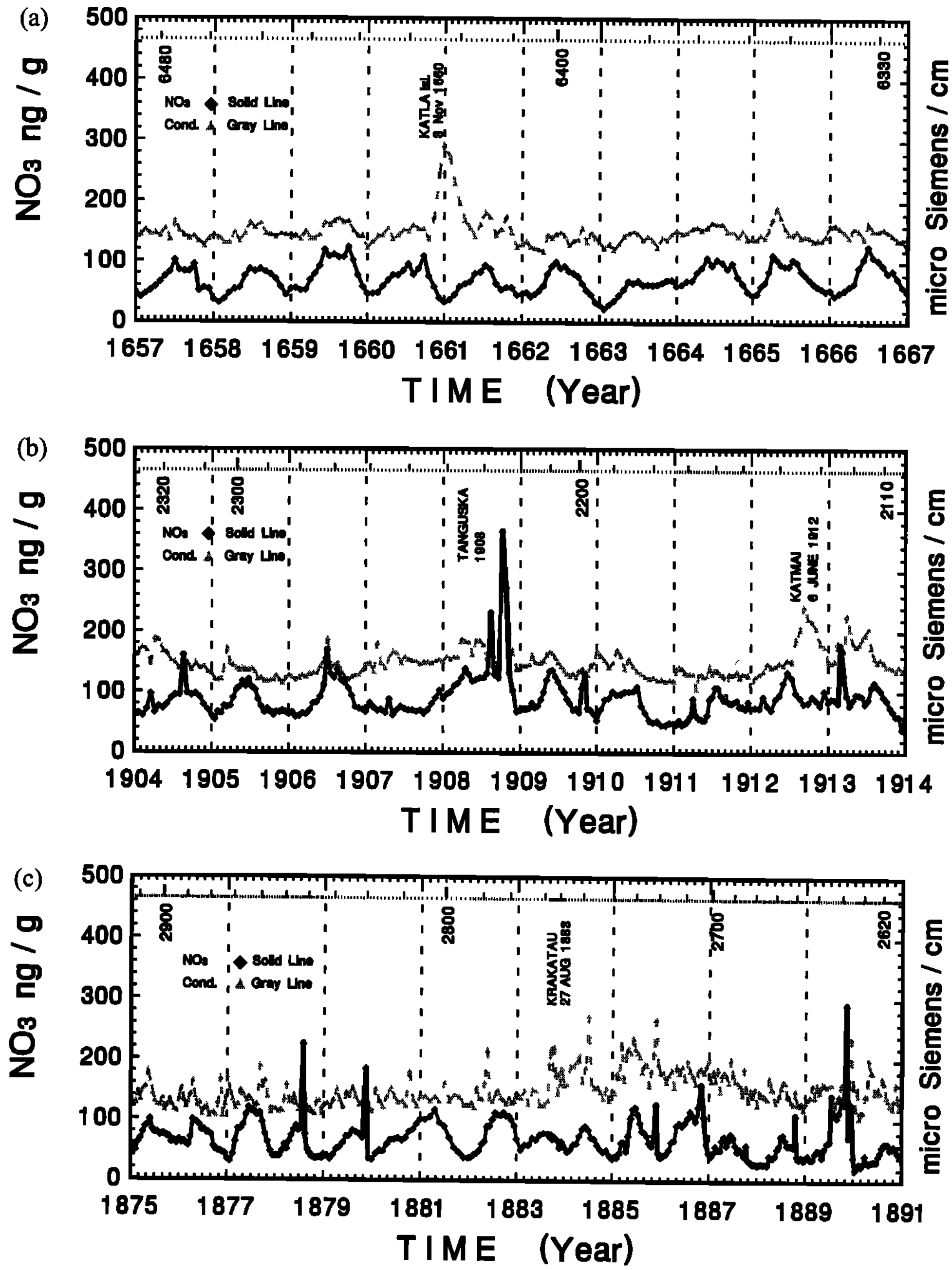


Figure A1. (a) An example of the data from a period in the Maunder Minimum. This illustrates our two-time assignment techniques, the use of the electrical conductivity events due to the precipitation of volcanic debris, and through counting the annual wave in the nitrate data. Note the absence of impulsive nitrate events. (b) A further example of the time assignment procedure. This illustrates the fact that for some 10% of the record the annual wave is poorly defined, and this can lead to errors of ±1 year if there are few good volcanic markers. A number of impulsive nitrate events are evident in these data. (c) Illustrating a rare difficulty in time assignment, when the volcanic event is poorly defined in time, and the inferred time therefore may be as much as a year in error. A number of impulsive nitrate events are evident in these data.

from Icelandic volcanoes seldom penetrates into the stratosphere. The impulsive events we attribute to a solar proton cause appear in the nitrate record, and because NO_3 ion is also a conductor, usually in the conductivity record as well. The annual precipitation varies with time, and therefore the number of ice samples per year varies. A precise mathematical relationship between sample number and time is not possible. We have also used the annual nitrate and conductivity variation to interpolate between marker horizons and to estimate time within each year.

There are 33 known reference horizons in the electrical conductivity record from Greenland in the period 1561–1991. Those that we have used as primary volcanic time markers are listed in Table A1. In about 90% of the record the phase of the annual variation is well defined (e.g., Figures 1 and A1) and allows the year to be identified with confidence. However, the

Table A1. Major Volcanic Eruptions Used as Primary Time Markers for the Greenland Ice Core[a]

Volcano	Occurrence	Location	Transit Time
Agua de Pau	June 28, 1563	Azores	<1 year
Billy Mitchell	1567? (1580 ± 20)	6°S, 155°E	1 year
San Salvador	1575	14°N, 89°W	<1 year
Colima Complex	Jan. 10, 1585	Mexico	<1 year
Kelut	1586	Java (8°S, 122°E)	1 year
Ruiz	March 12, 1595	Columbia (5°N, 75°W)	<1 year
Hekla	Jan. 3, 1597	Iceland	<months
Katla	Sept. 2, 1625	Iceland	<months
Furnas	Sept. 3, 1630	Azores (37°N, 25°W)	<1 year
Katla	Nov. 3, 1660	Iceland	<months
Tarumai	Aug. 6 or Sept. 23, 1667	Japan	<1 year
Hekla	Feb. 13, 1693	Iceland	<months
Katla	May 11, 1721	Iceland	<months
Myvaten Fire	1724	Iceland	<months
Oraefajokull	Aug. 3, 1727	Iceland	<months
Krafla	Dec. 18, 1728	Iceland	<months
Tarumai	Aug. 19, 1739	Japan	<1 year
Laki	June 8, 1783	Iceland	<months
Unknown	1810		
Tambora	Apr. 10, 1815	8°S, 118°E	1 year
Babuyan Claro	1831	19°N, 122°E	<1 year
Cosiguina	Jan. 12 or June 20, 1835	13°N, 87°W	<1 year
Chikurachki-Tatarinov	December 1853	Kuril Island (50°N, 155°E)	<1 year
Sheveluch	Feb. 18, 1854	Kamchatka (56°N, 161°E)	<1 year
Krakatau	Aug. 27, 1883	Indonesia (6°S, 105°E)	1 year
Augustine	Oct. 6, 1883	Alaska	<1 year
Katmai	June 6, 1912	Alaska (58°N, 155°W)	<1 year
Katla	Oct. 12, 1918	Iceland	<months
Raikoke	Feb. 15, 1924	Kuril Island (48°N, 153°E)	<1 year
Hekla	March 29, 1947	Iceland	<months
Askja	Oct. 26, 1961	Iceland	1 week
Hekla	May 5, 1970	Iceland	<months

[a]After *Newhall and Self* [1982], *Bardarson* [1973], *Volcanological Society of Sacramento* (*VSSAC*) [1994, 1995], and T. Simkin and L. Siebert (Chronology of large Holocene eruptions, a data file, Smithsonian Institution, personal communication, 1993).

time within the year is more problematical, since the snow precipitation rate varies throughout the year, introducing a nonlinearity into the conversion from sample number to time. For the present study we have used a linear interpolation of time. We estimate that intrayear time is accurate to ±0.2 year.

The time allocation procedures are illustrated in Figures A1a through A1c. The conductivity peak in Figure A1a is the result of the Katla, Iceland, volcanic explosion on November 3, 1660, and the electrical conductivity provides a clear indication of the commencement of the eruption. This gives the absolute time of that sample, after making an allowance for the transit time of the debris to Greenland. The annual wave in the nitrate data is then used to determine the time of deposition of nearby samples, where the minimum of the nitrate annual wave is taken to be in the middle of winter. Using this procedure, and the volcanic eruptions of Hekla (in 1597 and 1660), Katla (in 1625) and Furnas (in 1630), together with a well-defined annual wave, provides us with a time accuracy that is estimated to be ±2 months for the period of the Maunder Minimum, and for a period of frequent occurrence of nitrate events in the period 1570–1620.

The large nitrate and conductivity anomaly in Figure A1b is attributed to the Tunguska meteorite impact in Siberia on June 30, 1908. Another well-known time marker is the Katmai, Alaska, volcano that erupted June 6, 1912, and is assumed to have deposited volcanic material shortly after the explosion [*Laj et al.*, 1993].

Figure A1c displays the effects of the Krakatau eruption in Indonesia (6°S, 105°E). This eruption continued for several months and contained several major explosions before the cataclysmic explosion on August 27, 1883. The electrical conductivity again is the best indicator of the arrival of the volcanic debris, and this illustrates a difficulty that is only rarely encountered in this analysis. The arrival of the debris is so protracted (several years), and there are so many major peaks in the conductivity record, that there is some uncertainty about the assignment of time. We associate the "first arrival" with the known date of the eruption (with allowance for transit time) and the fact that "brilliant sunsets" were observed in England in the autumn of 1883. It is the late 19th century where we have difficulty in time assignments due to the absence of nearby volcanic activity between 1854 and 1908. Any impact of this uncertainty is noted in the detailed analyses.

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