IMPULSIVE NITRATE DEPOSITION EVENTS IN POLAR ICE THE RESULT OF SOLAR PROTON EVENTS

D. F. Smart and M. A. Shea

Emeritus at AFRL (RVBXS), Bedford, MA, 01731, USA

SYNOPSIS

The endothermic chemical reaction models in the polar atmosphere that result in NOx are adequate to explain depletion of ozone in the polar atmosphere and the annual and seasonal variation in the nitrates found in polar ice.

Ultra high-resolution analyses (~20 samples per year) of the nitrate concentration in polar ice finds impulsive transient nitrate depositions that have a one-to-one association with each of the very large solar proton events in the last century.

Impulsive nitrate deposition events are found in the polar ice within weeks of the solar cosmic ray event, a result not explained by contemporary transport models.

Contemporary models predict less NOy than is found in these impulsive transient nitrate deposition events.

The seasonal distribution of these impulsive nitrate events is different from the expected classical patterns with more events found in the polar ice during the sunlight season than the polar night season.

Nitrate chemistry in the Polar Atmosphere

Polar summer "daytime" reaction"

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + h\nu \longrightarrow NO + O(^3P)$$

$$O(^3P) + O_2 \xrightarrow{M} O_3$$

$$NO_2 + OH \xrightarrow{M} HNO_3$$

Polar winter "night-time" reaction"

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \xleftrightarrow{M} N_2O_5 \xrightarrow{H_2O} 2HNO_3$$

$$NO_3 + DMS, HC \rightarrow HNO_3 + \text{products}$$

(Javis et al., GRL, 35, L21804, 2008)

The NO_2 dissociation energy is ~10 eV.

In addition to the EUV
there are other energy sources to
drive the endothermic reaction.

Solar Flare X-Rays
Auroral Electrons

(80 km)

Galactic Cosmic Rays
Solar Energetic Particles

All levels of the mesophere

A very large solar proton event
with a >30 MeV fluence (10^9 cm^{-2})
is equivalent to a
11-year solar cycle of
cosmic ray flux

ENERGETIC PARTICLES

(AURORAL ELECTRONS AND SOLAR PROTONS) PROVIDE THE ENERGY TO DRIVE AN ENDOTHERMIC REACTION

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + O \rightarrow NO + O_2$$

Net: $O_3 + O \rightarrow O_2 + O_2$

The result is "odd nitrogen"

(*a complex of nitrate radicals designated by the symbol* NO_X)

Some of the NO_X is transported downward to the troposphere, then it is precipitated to the surface in ~6 weeks.

Nitrate deposition in polar ice are markers of the NO_Y precipitation.

The NOy controversy for nitrate enhancement

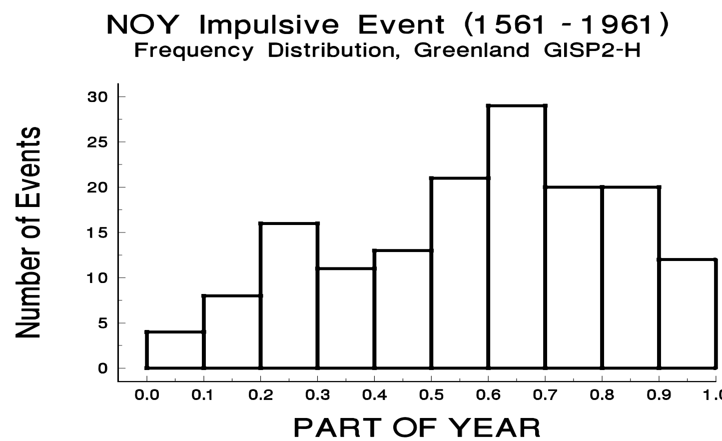
The classical scenario

- Enhanced electrons in the **polar-night mesosphere** produced NO **(it is dissociated by UV if sunlit)**
- The NO-rich air descends via the upper branch of the Brewer-Dobson circulation
- Encountering O_3, it reacts to NO_2
- Descent continues to the stratosphere, and HNO_3 is formed
- PSCs form, taking the HNO_3 to the lowest stratosphere
- The lowest part of the Brewer-Dobson circulation takes this air to mid-latitudes where it enters the troposphere via tropopause folds

The POAM measurements have validated the Brewer-Dobsen circulation

The impulsive nitrate deposition scenario

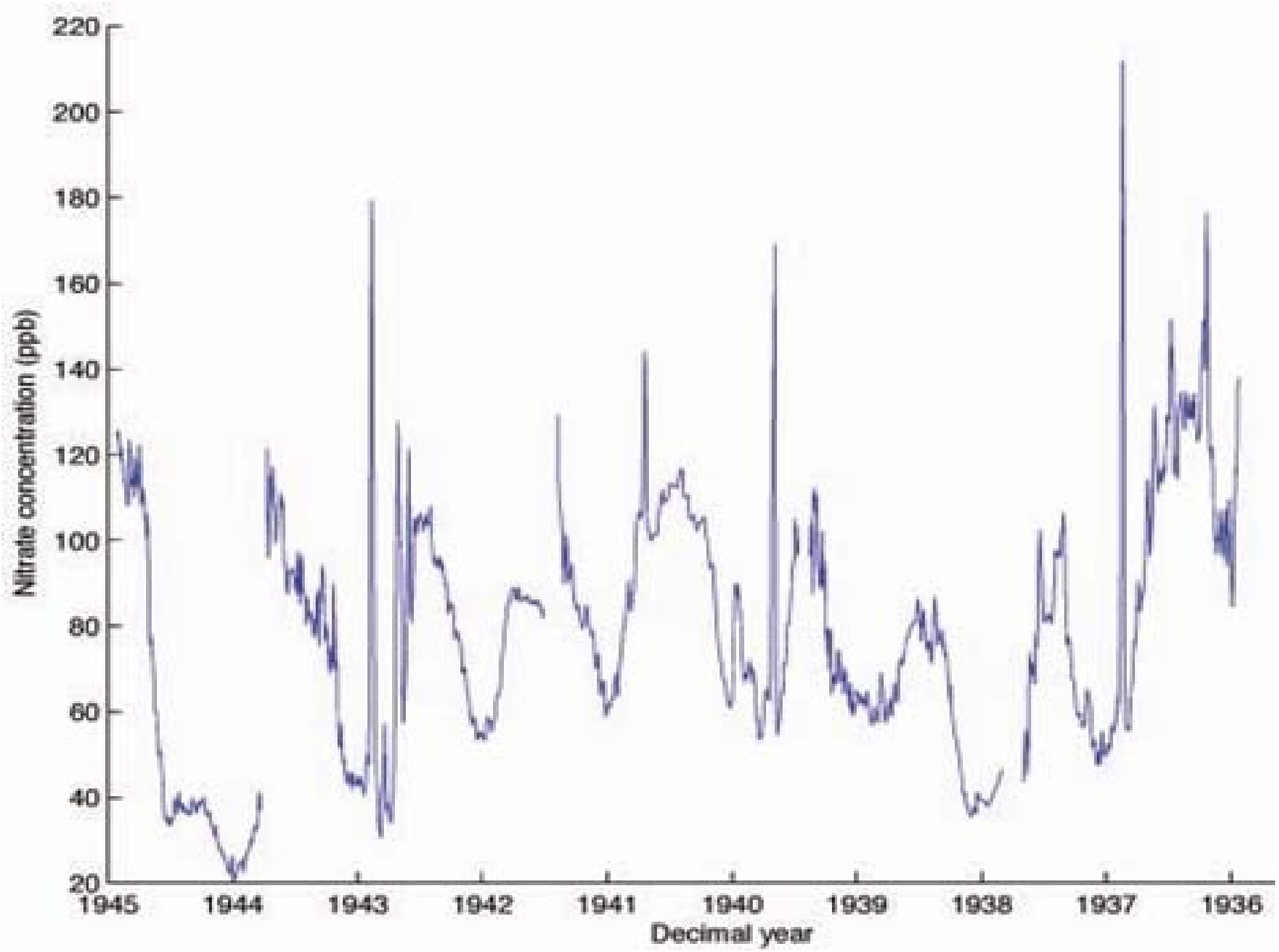
- NOx is generated by solar proton penetration to low altitudes
- *Some is attached to a heavy aerosol*
- *Gravitational sedimentation into the polar ice in 4-6 weeks*
- Many events during polar sunlight
- 1-to-1 correspondence to every 10^9 fluence >30 MeV proton event in the space era



ICE CORE STATISTICS

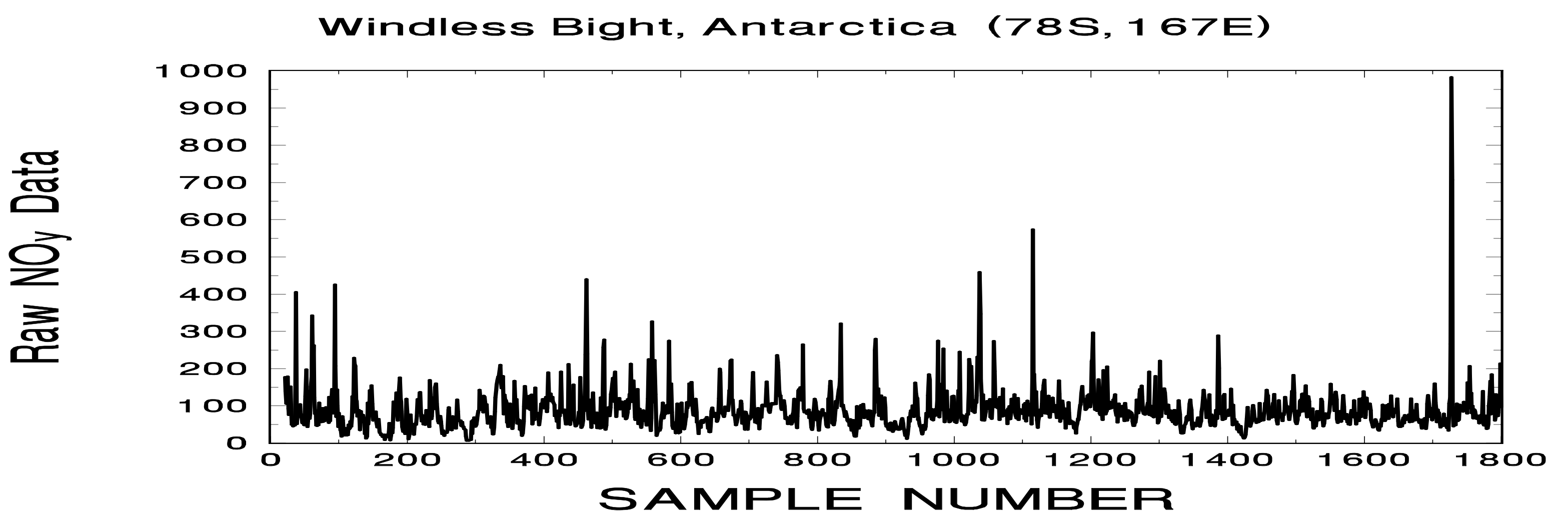
PIT-1	PIT-2	CORE-3	CORE-4
WB Pit-1	WB Pit-2	GISP-H	2004-A
Antarctica (78 S)	Antarctica (78 S)	Greenland (72 N)	Greenland (72 N)
88/89	90/91	1992	2004
27 m	27 m	125.6 m	30 m
15 mm samples	15 mm samples	15 mm samples	Continuous
1800 samples	1800 samples	8002 samples	Continuous
1900-1988	1900-1990	1561-1950	1937-1950
10 Events	**10** Events	**125** Events	**13** Events
~10^9 threshold	~10^9 threshold	~10^9 threshold	~10^8 threshold
Univ. Kansas	Univ. Kansas	Univ. Kansas	Boston Univ.
Zeller & Dreschhoff	Zeller & Dreschhoff	Zeller & Dreschhoff	Spence

Raw data from the 2004 Greenland core

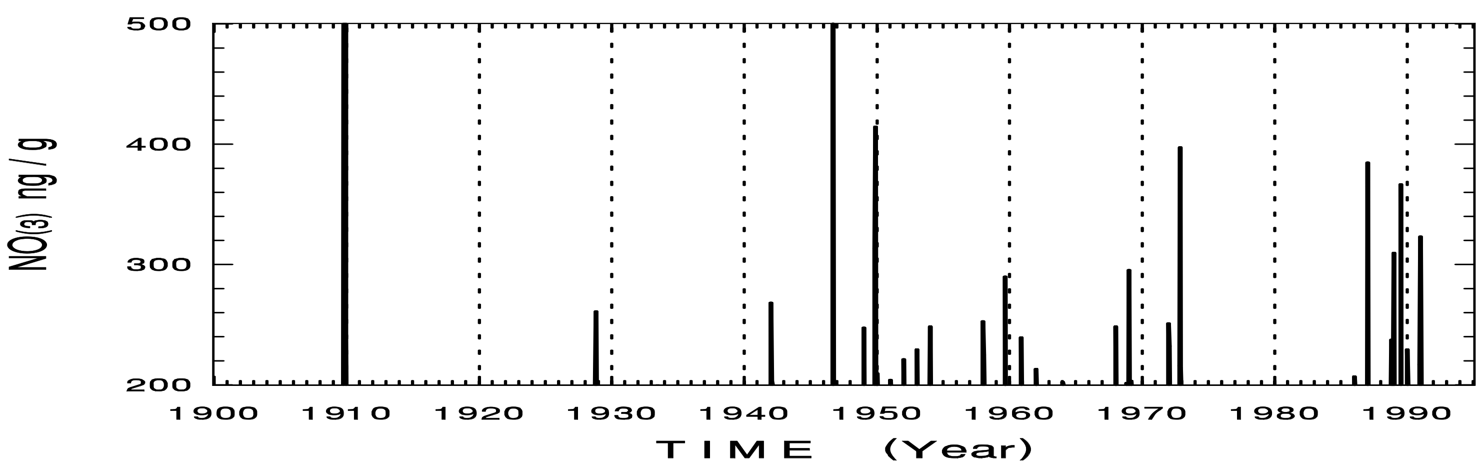


Raw data from continuous flow analysis of melted ice core

Raw Data



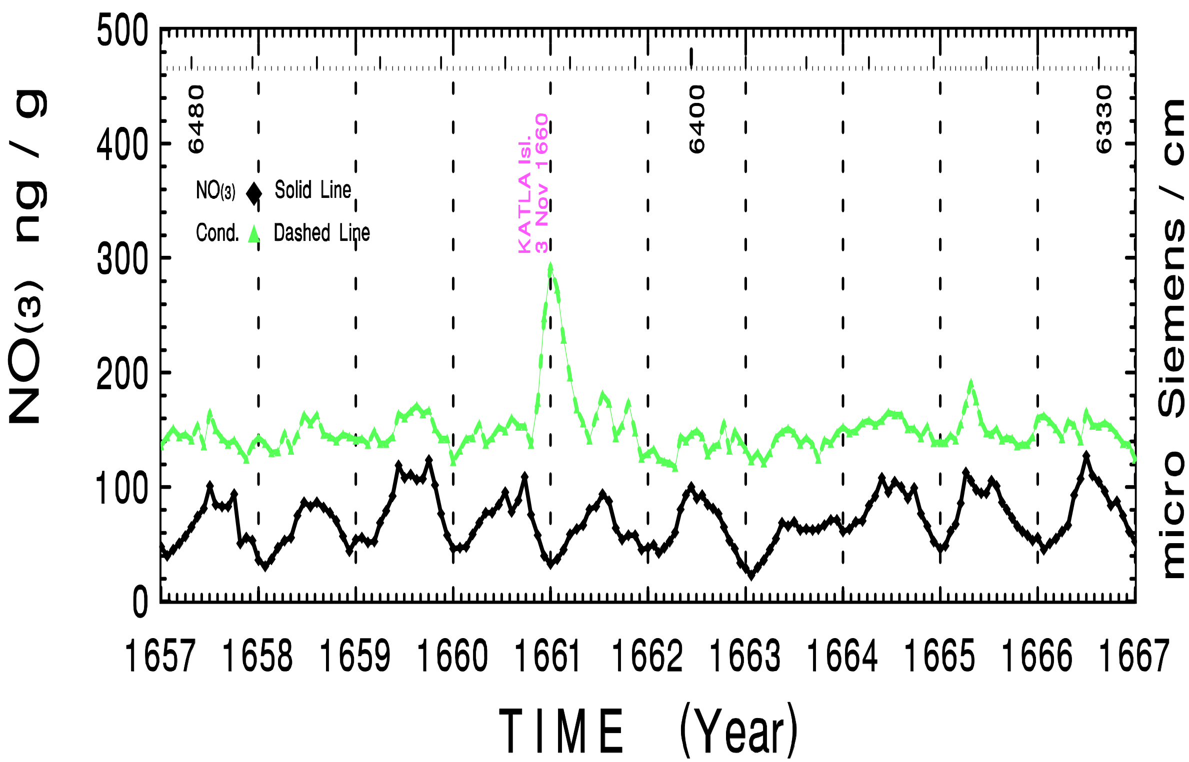
Calibrated and time-marked data



DATING ICE CORES

Seasonal Variation
(Summer Hi - Winter Low)

Volcanic Eruptions



Average
Depth-time
profile

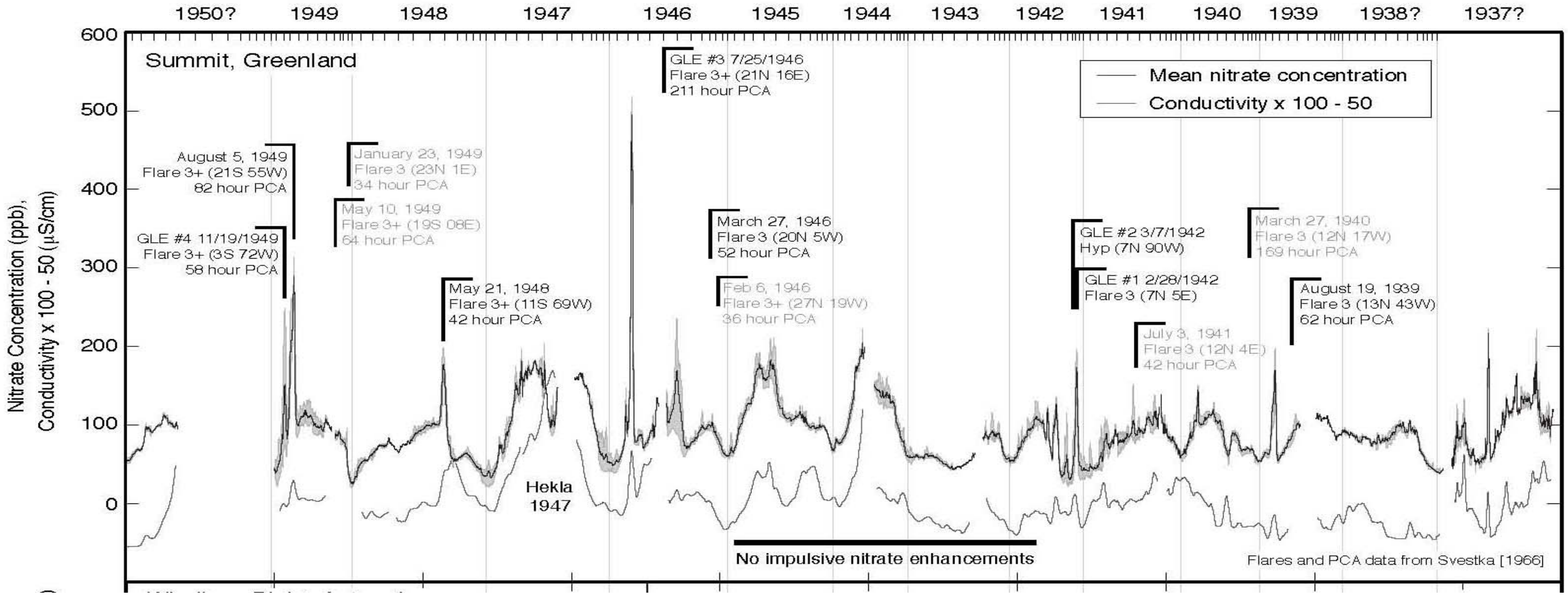
There is a consensus snow-depth-time profile derived from the composite of all the ices cores drilled at Summit, Greenland, using known volcanic sulfate dust time markers as absolute year calibrations.

We have dated the 2004 core using the standard snow depth – time profile derived from the previous GISP ice core records.

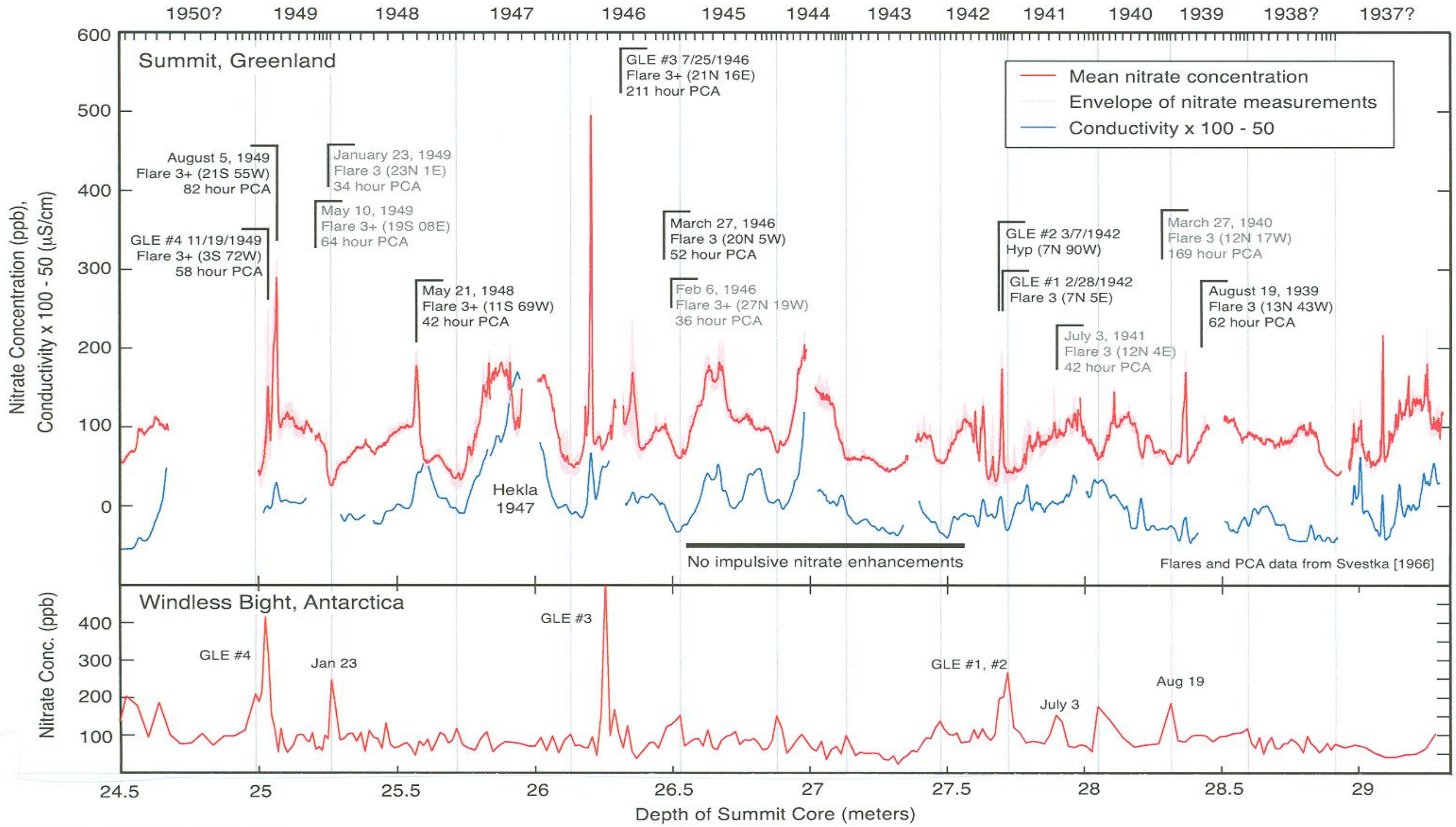
An unambiguous time marker is the eruption of the Hekla, Iceland volcano in 1947.

We subdivided each year into months using an interpolation based upon the average monthly precipitation observed in central Greenland.

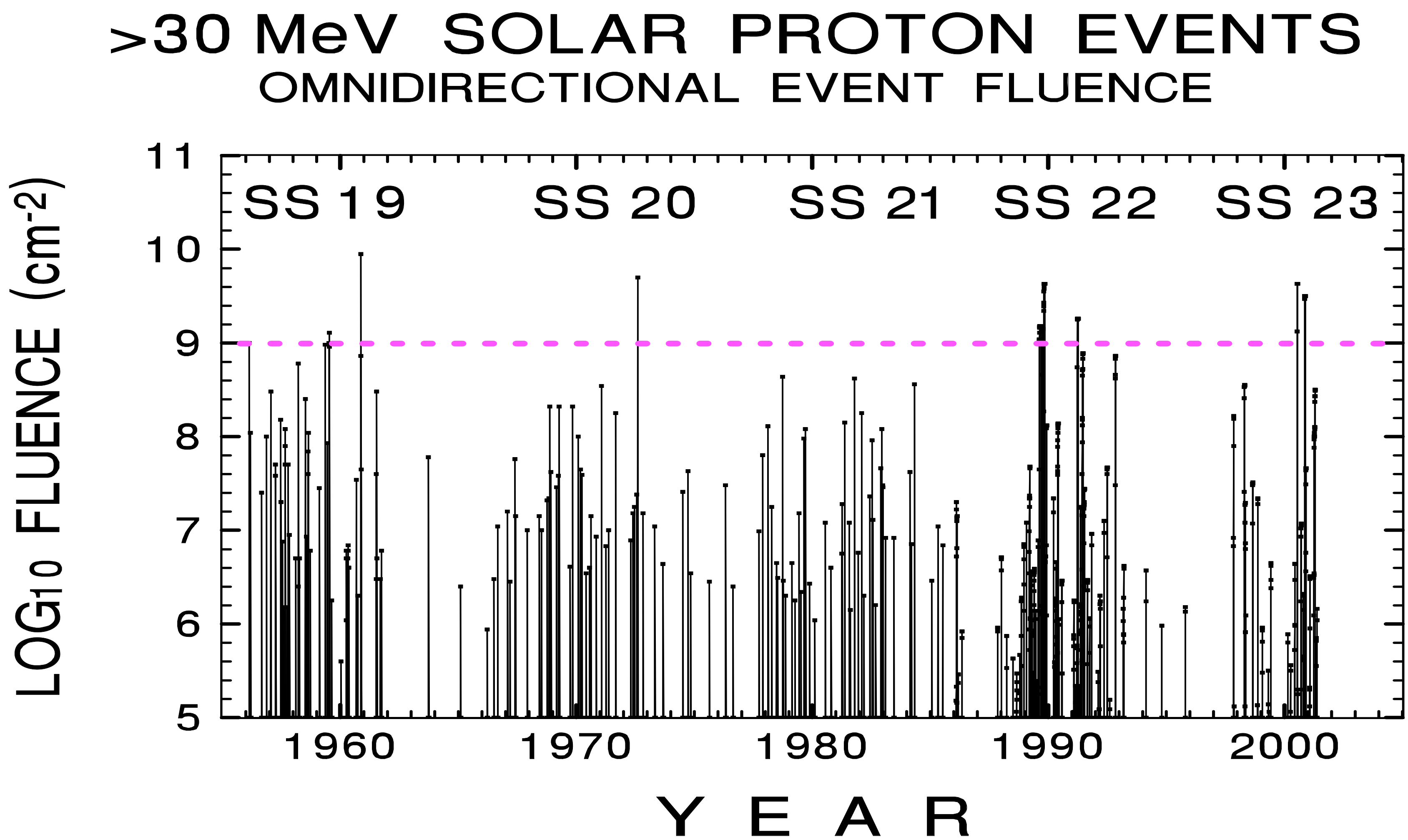
At this Greenland location more precipitation during summer; nearly a factor of 2 larger than winter months.



Both Greenland cores and the Antarctic cores see the same large events where they overlap in time



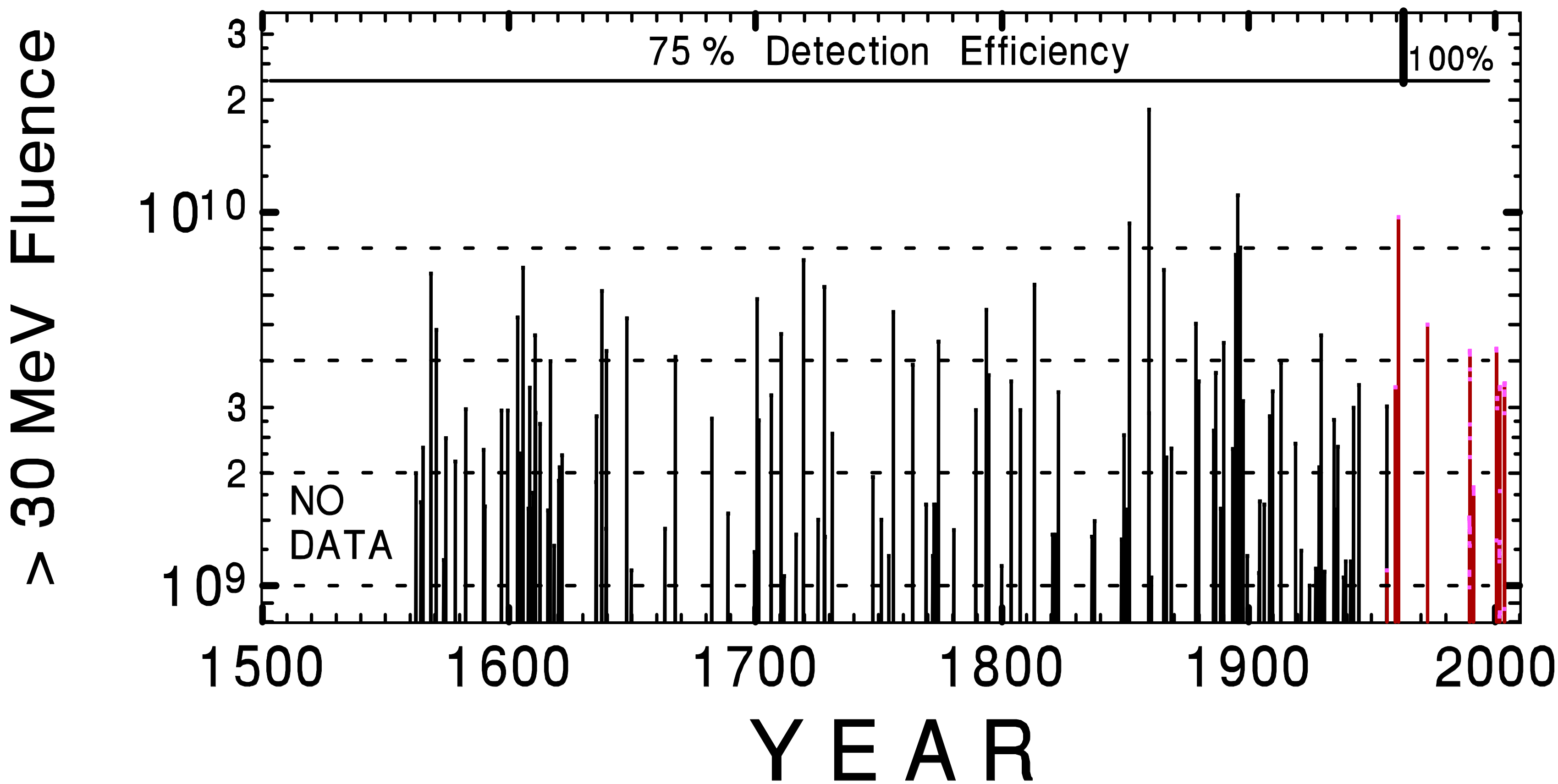
Top: Nitrate data from the 2004 Greenland core with annotated solar events. (High resolution)
Bottom: Nitrate deposition data from 1988-1989 Antarctica ice cores. (1.5 cm resolution)



The > 30 MeV solar proton events since solar sunspot cycle 19

The RED line indicates the NO_y detection threshold

Nitrate enhancements in polar ice; proxy of solar proton events

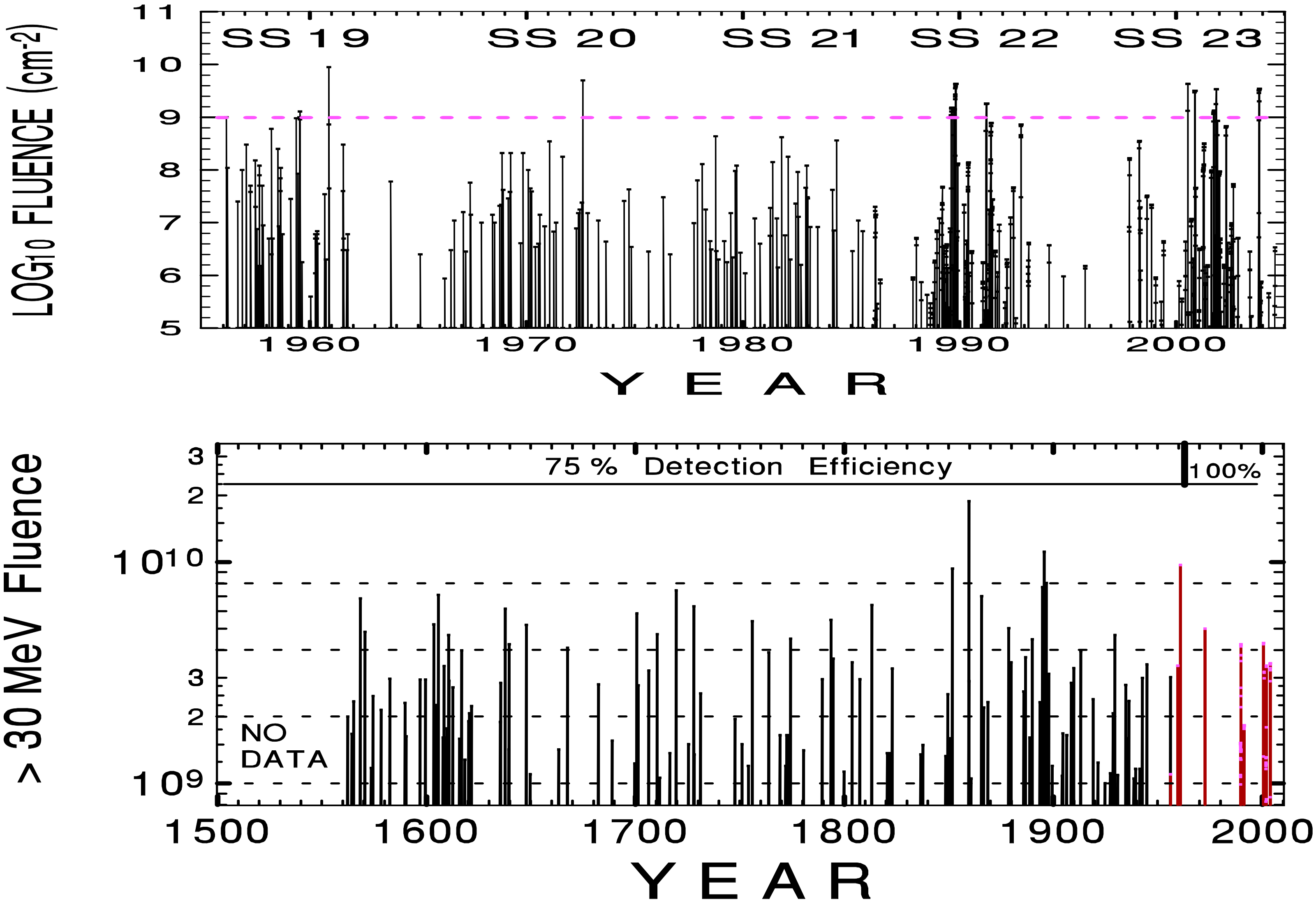


The ~450-year record of >30 MeV solar proton fluence events.

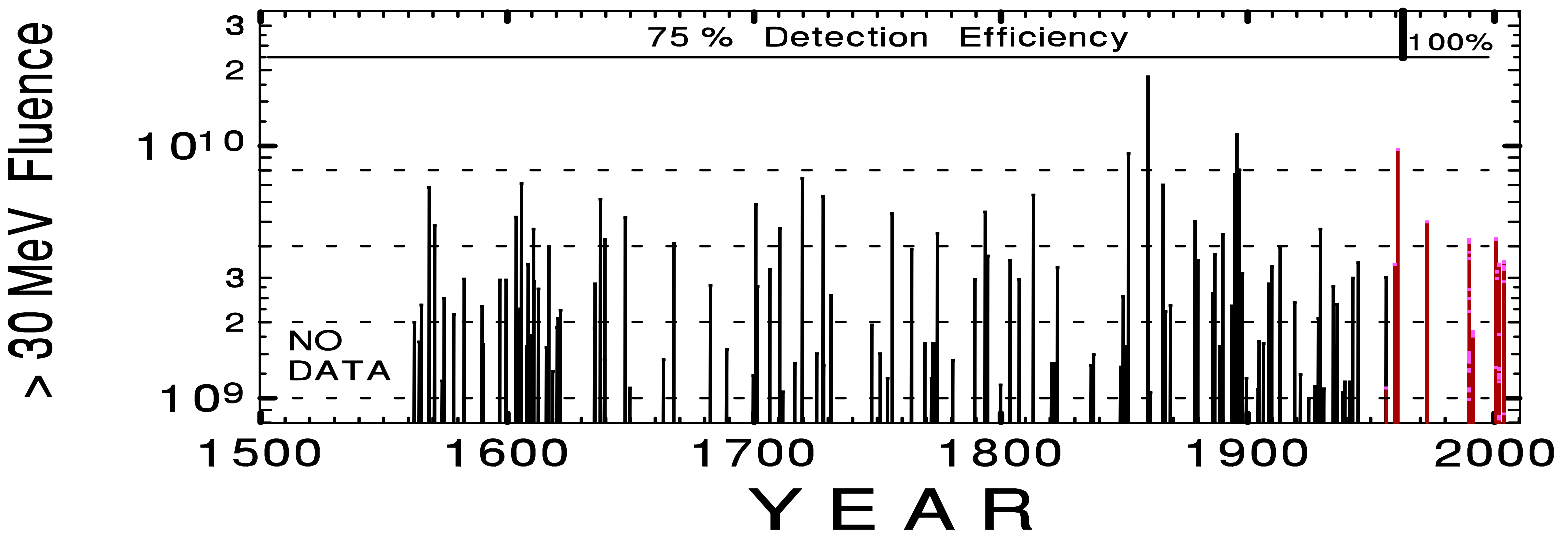
The black lines are NOy events; red lines are SPEs 1965-2000.

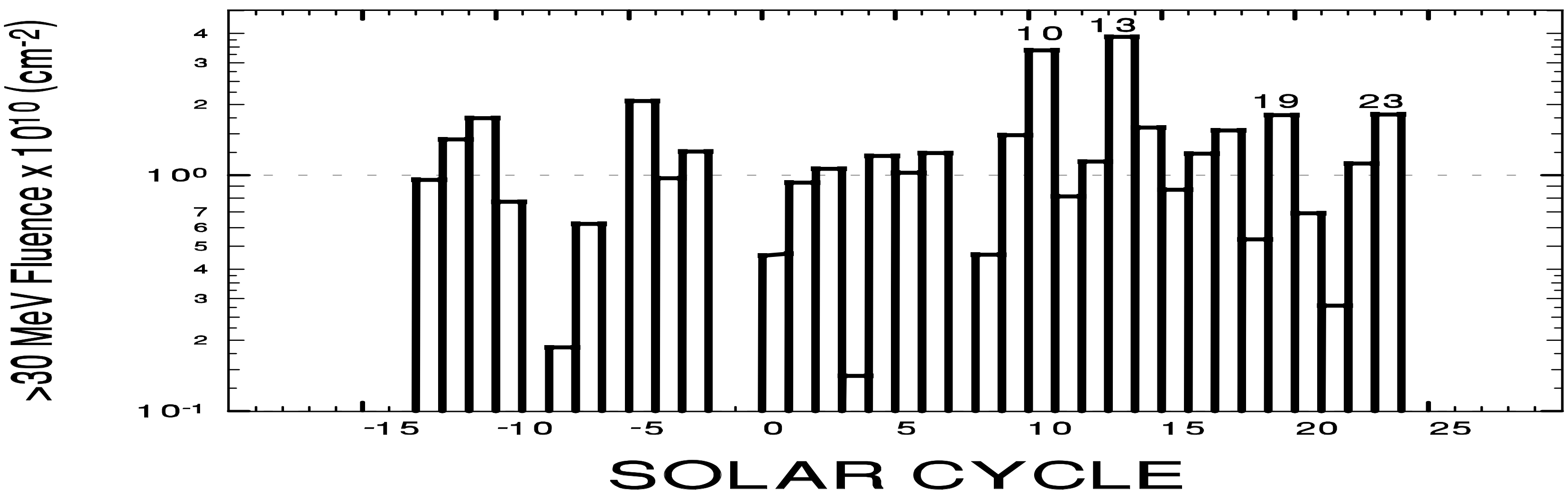
(From McCracken et al., 2001.)

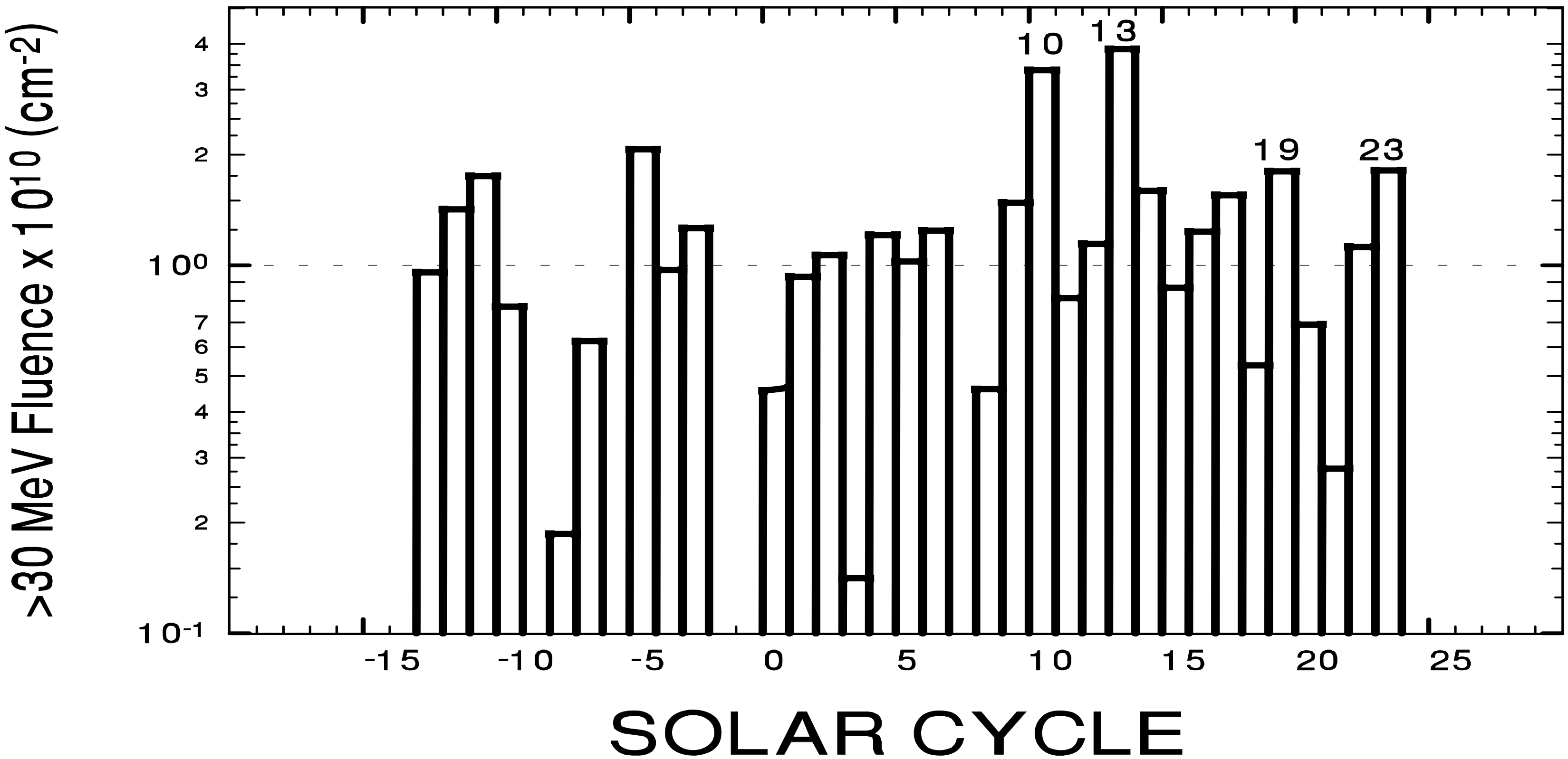
>30 MeV SOLAR PROTON EVENTS
OMNIDIRECTIONAL EVENT FLUENCE



All proton data summed over each solar cycle





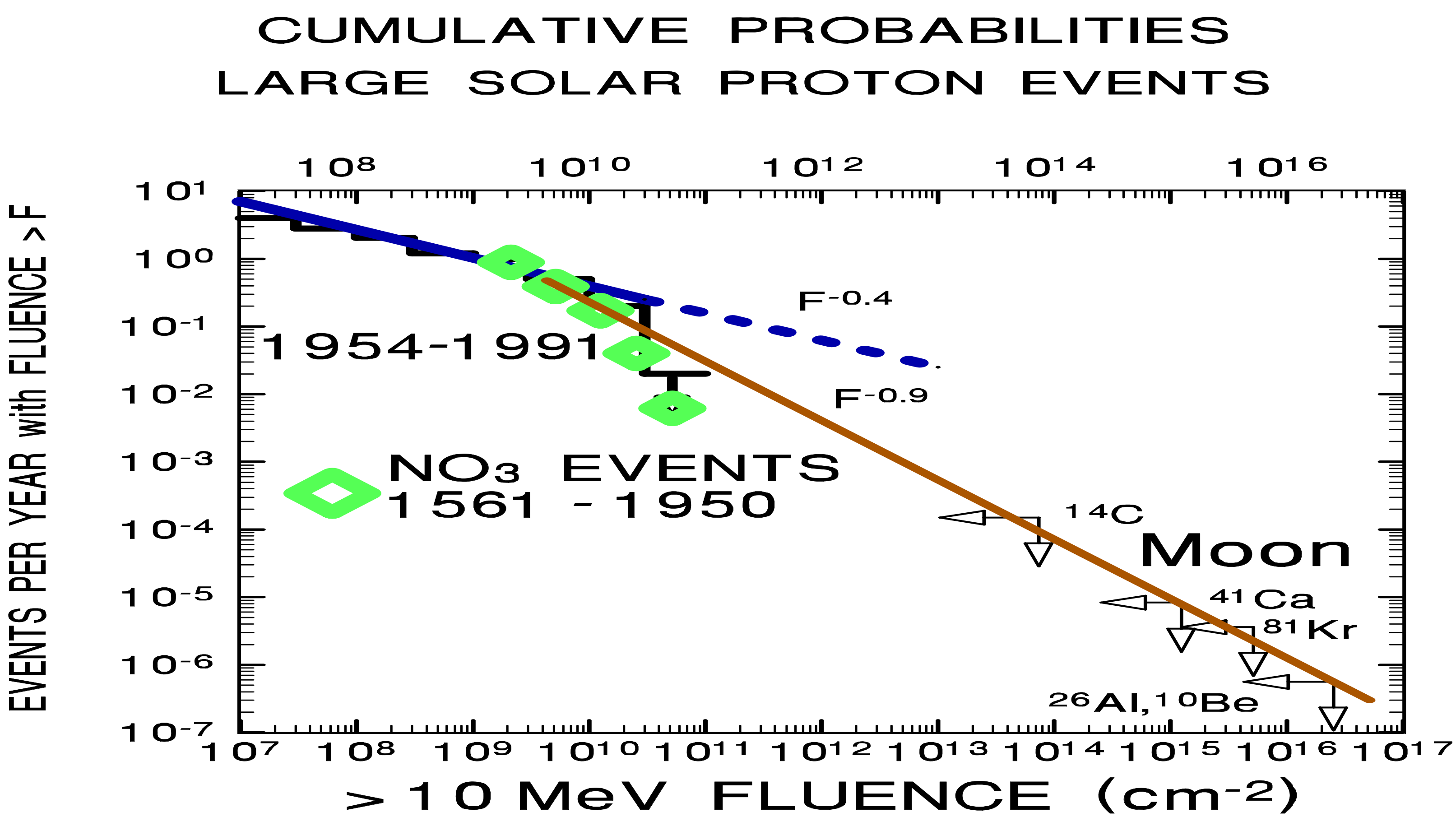


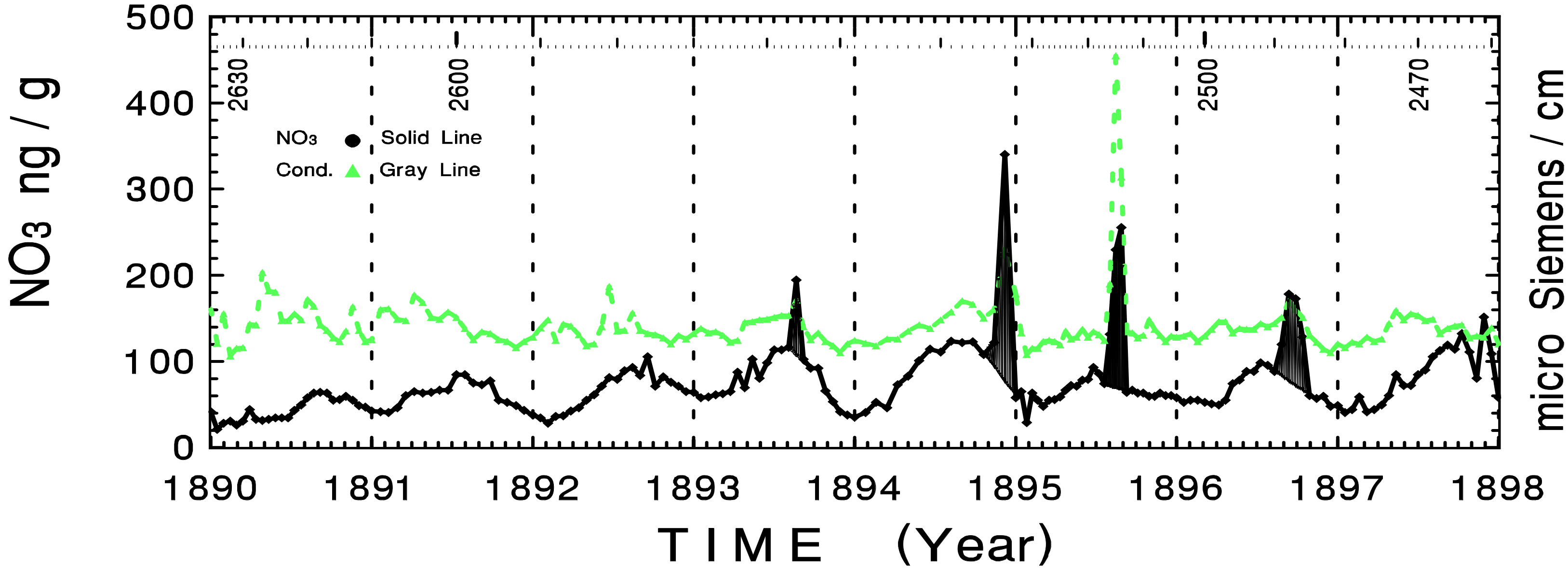
The > 30 MeV omnidirectional proton fluence for 36 solar cycles.

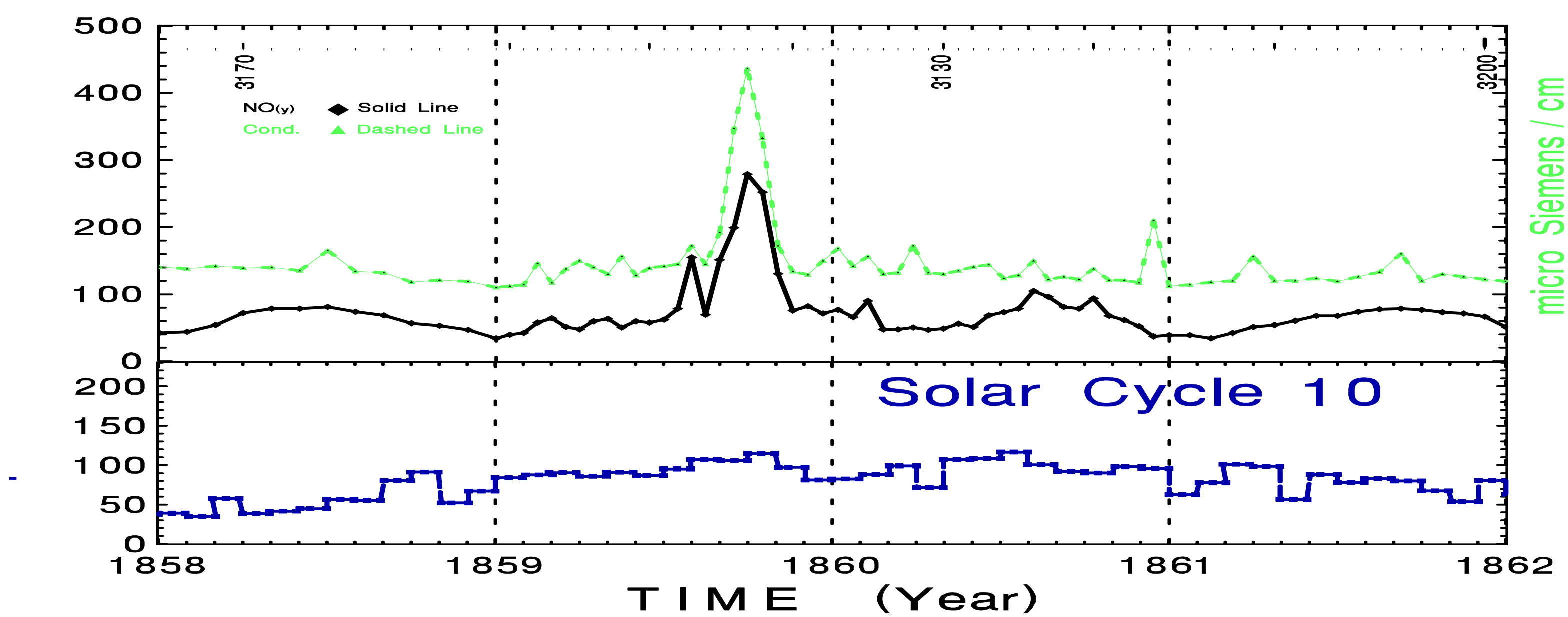
cycle 10 was dominated by one major event (the Carrington event in 1859)
cycle 13 had 7 major events contributing to the total fluence.

The total fluence for most cycles is within a factor of 2 of the maximum fluence per cycle measured by spacecraft since 1965.

Very large proton events have
a different distribution $F^{-0.9}$
than the most common events $F^{-0.4}$




NO3 ng / g
micro Siemens / cm
NO3 Solid Line
Cond. Gray Line
2630
2600
2500
2470
1890
1891
1892
1893
1894
1895
1896
1897
1898
TIME (Year)

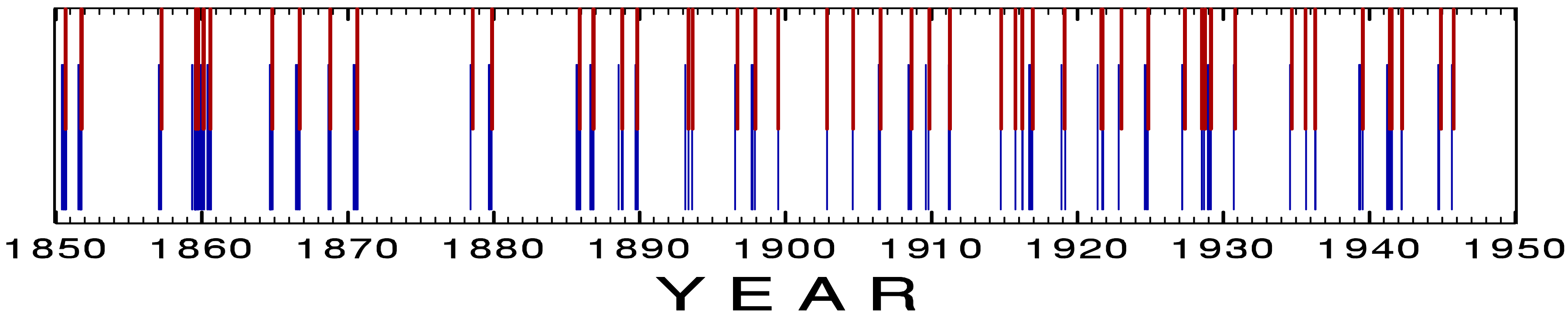

NO(y) Solid Line
Cond. Dashed Line
3170
3130
3200
micro Siemens / cm
Solar Cycle 10
1858
1859
1860
1861
1862
TIME (Year)

NOY AURORA (NOY Max - 90d)

NE AURORA (Conn, Mass, RI)

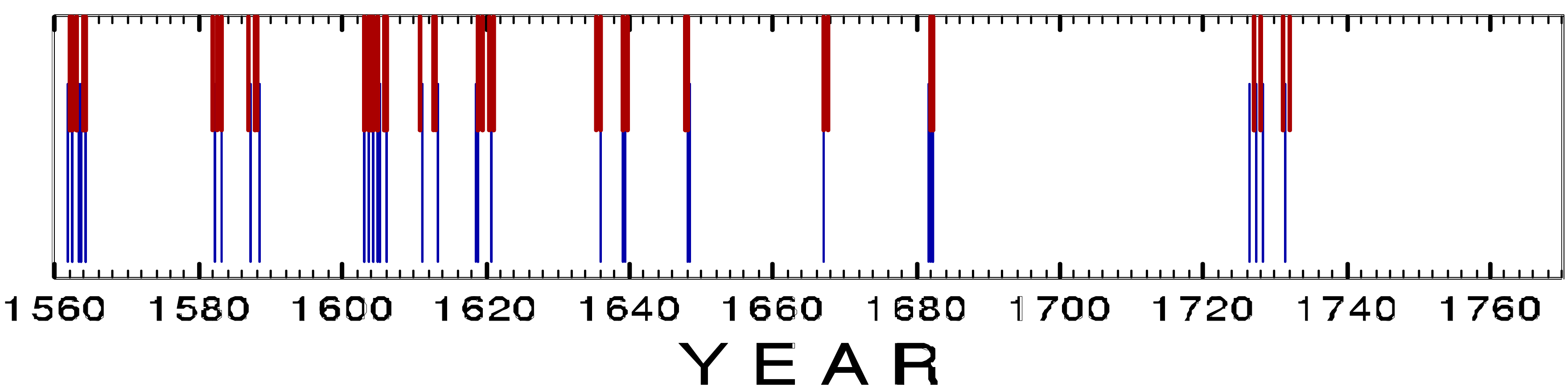
TOP (RED) - NOY EVENT

BOTTOM (BLUE) - ASSOCIATED AURORA



TOP (RED) - NOY EVENT

BOTTOM (BLUE) - KOREA AURORA



SUMMARY

Ultra high-resolution analyses (~20 samples per year) of the nitrate concentration in polar ice finds impulsive transient nitrate depositions that have a one-to-one association with each of the very large solar proton events in the last century.

Impulsive nitrate deposition events are found in the polar ice within weeks of the solar cosmic ray event, a result not explained by contemporary transport models.

The seasonal distribution of these impulsive nitrate events is different from the expected classical patterns with more events found in the polar ice during the sunlight season than the polar night season.

The impulsive nitrate deposition events provide a record of solar activity for the past 450 years. This provides a record for 36 solar cycles.

The total fluence for most cycles is within a factor of 2 of the maximum fluence per cycle measured by spacecraft since 1965.