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.
The NO$_2$ dissociation energy is $\sim$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 mesosphere

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

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2
\end{align*}
\]

Net: \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \)

The result is “odd nitrogen”
(a complex of nitrate radicals designated by the symbol \( \text{NO}_X \))

Some of the \( \text{NO}_X \) is transported downward to the troposphere,
then it is precipitated to the surface in \( \sim 6 \) weeks.

Nitrate deposition in polar ice are markers of the \( \text{NO}_Y \) 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 O₃, it reacts to NO₂
- Descent continues to the stratosphere, and HNO₃ is formed
- PSCs form, taking the HNO₃ 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-Dobson 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 10⁹ fluence >30 MeV proton event in the space era
## ICE CORE STATISTICS

<table>
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<th>PIT-1</th>
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<th>CORE-4</th>
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<td>Location</td>
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<td>Zeller &amp; Dreschhoff</td>
<td>Zeller &amp; Dreschhoff</td>
<td>Spence</td>
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Raw data from the 2004 Greenland core

Raw data from continuous flow analysis of melted ice core
Raw Data

Windless Blight, Antarctica (78S, 167E)

Raw NO$_y$ Data

Calibrated and time-marked data

NO$_y$ ng/g

TIME (Year)
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

>30 MeV SOLAR PROTON EVENTS
OMNIDIRECTIONAL EVENT FLUENCE

LOG$_{10}$ FLUENCE (cm$^{-2}$)

SS 19  SS 20  SS 21  SS 22  SS 23

YEAR

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.)
All proton data summed over each solar cycle
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 $F^{-0.4}$.

![Graph showing cumulative probabilities of large solar proton events with event fluence and year range. The graph demonstrates a different distribution for very large events compared to common events.]
NOY AURORA (NOY Max - 90d)
NE AURORA (Conn, Mass, RI)

TOP (RED) - NOY EVENT
BOTTOM (BLUE) - ASSOCIATED AURORA

YEAR

TOP (RED) - NOY EVENT
BOTTOM (BLUE) - KOREA AURORA

YEAR
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.