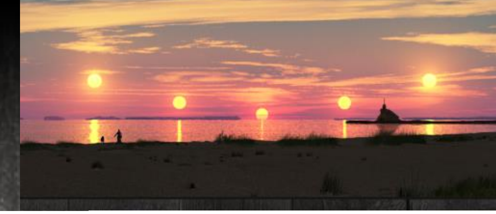
SPACE CLIMATE 5
UNDER THE MIDNIGHT SUN
June 15-19, 2013
Oulu, Finland



A POTENTIAL NEW PROXY OF LONG-TERM SOLAR VARIABILITY: NITRATE IN ANTARCTIC ICE CORES

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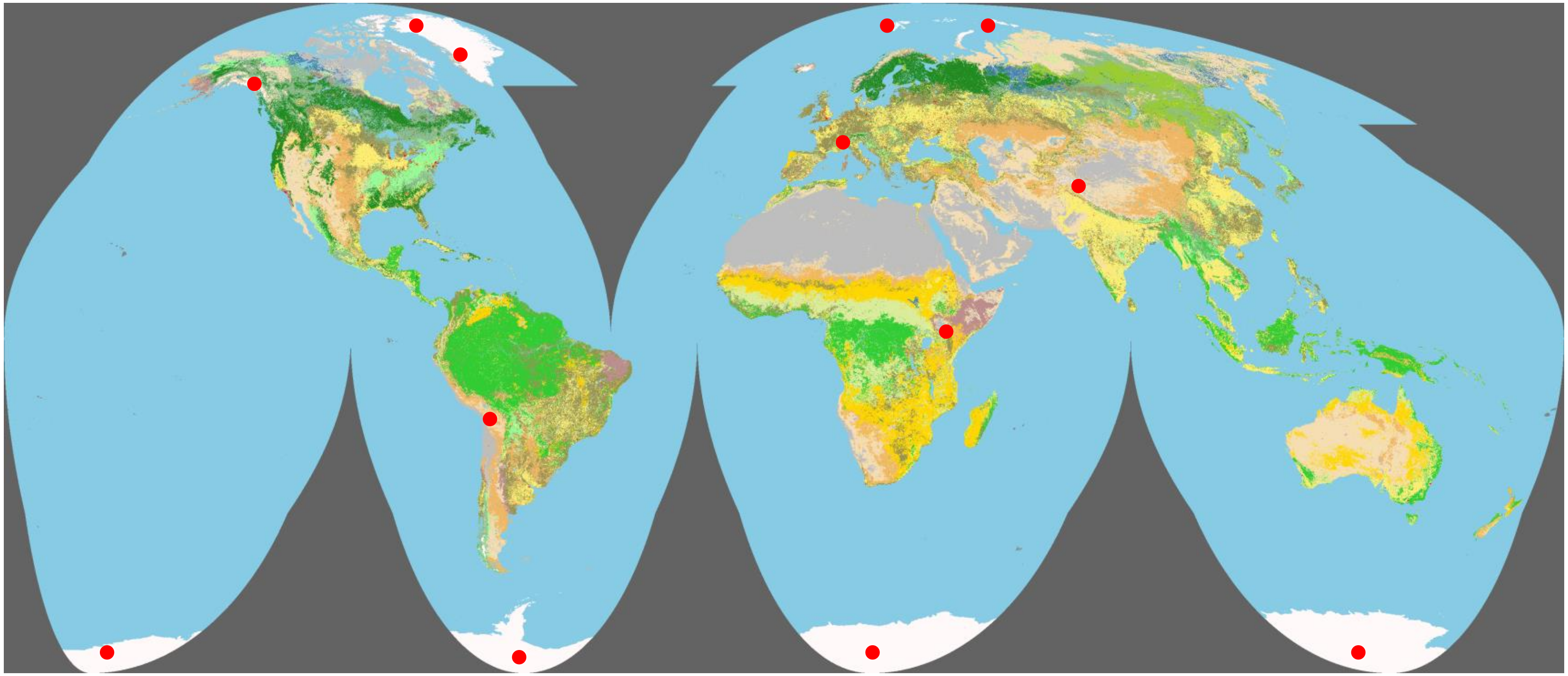
Specificity of ice cores as archives

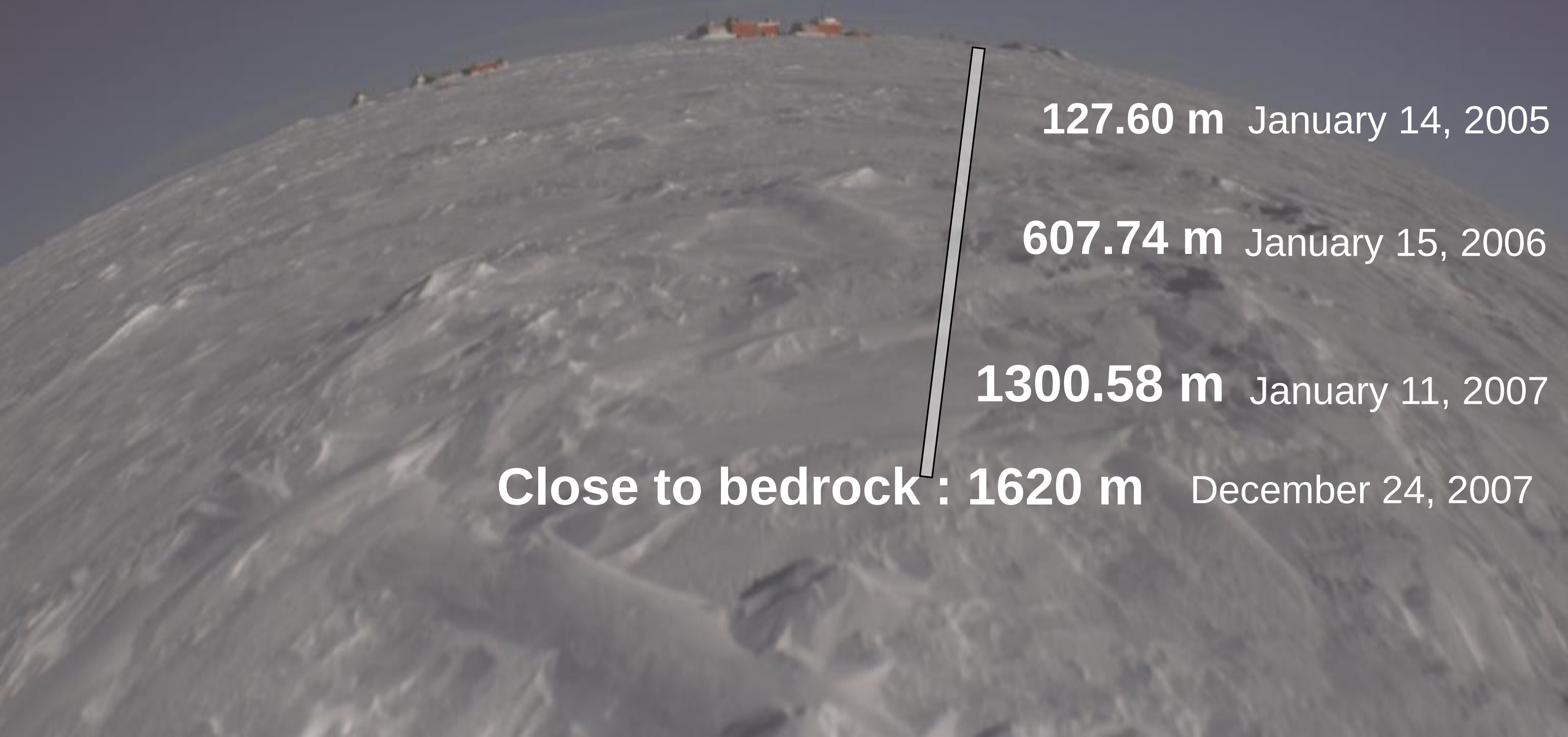


Advantages	Disadvantages
• Temporal resolution • Range of parameters • Regional to global significance • No biology in the transfer function	• Only on poles or mountains • A few 100,000 years coverage (back to 1Myr, so far…) • Physics and chemistry of transfer function not always straightforward

http://www.taldice.org/

Talos Dome
(159° 11’ E   72° 49’ S,   2315 m a.s.l.)

TALDICE drilling: 2005-2007
Ice thickness: 1795 m
Drilled depth: 1620 m; 76 drilling days (21m/day)
Covered time: about 250 kyr



Delivery of materials

Talos Dome site camp

Going to the trench

Inside the drilling trench: casing, drilling, banging the core barrel

Talos Dome camp

Still inside the drilling trench:
Cutting and storing ice core sections

Talos Dome

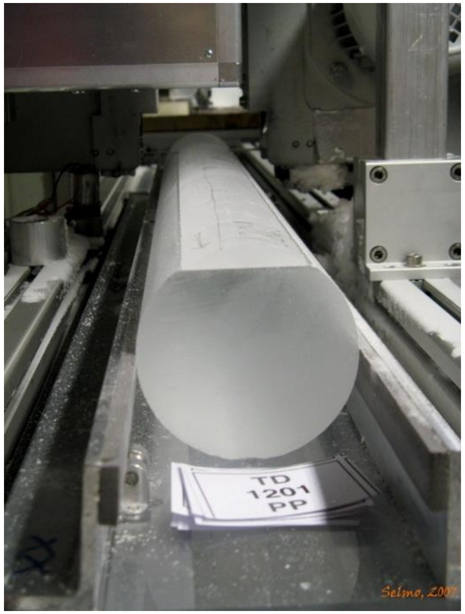
"Coastal-like" site in terms of accumulation rate (80 mm w.e., relatively high)

and

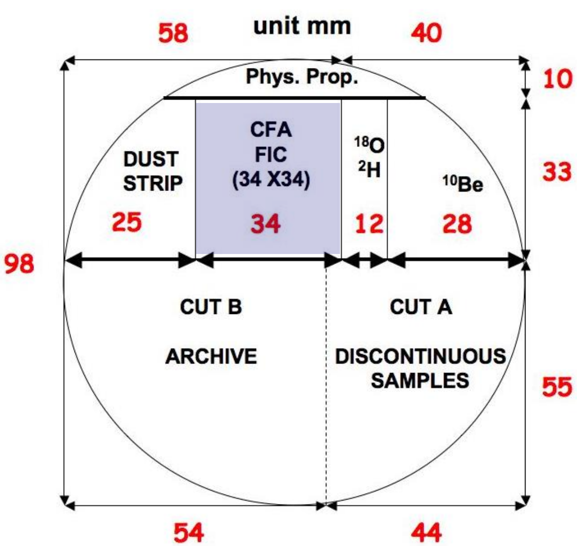
"Plateau-like" site in terms of air masses transport (not local but regional to global climatic signal)

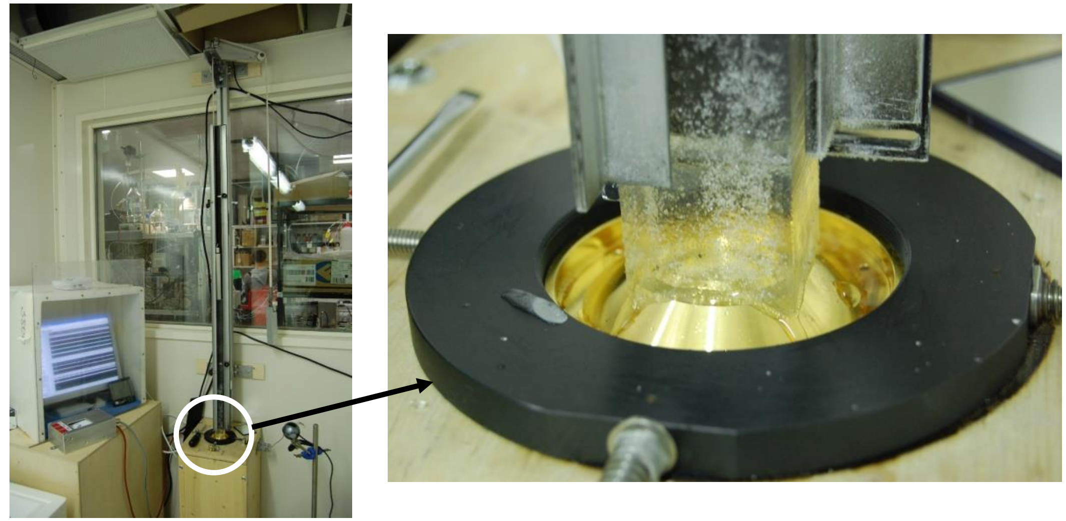
[e.g. Stenni et al., 2011, Nature Geoscience]

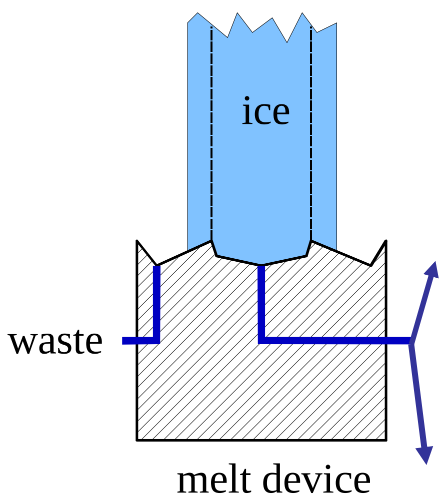
Decontamination and chemical analysis EPICA and TALDICE ice cores



Cutting plan







Discrete sample collection for classical Ion Chrom. bag mean (1 m) and high (7 cm) resolution

(F^-, Cl^-, NO_3^-, SO_4^{2-}, MS^-, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+})

Chemical markers

(Univ. Flo, LGGE, BAS, AWI)

Fast Ion Chromatography

1 cm resol. (Cl^-, NO_3^-, SO_4^{2-})

University of Florence

EPICA Dome C ice core

The longest temporal record currently available from an ice core (850 kyr)

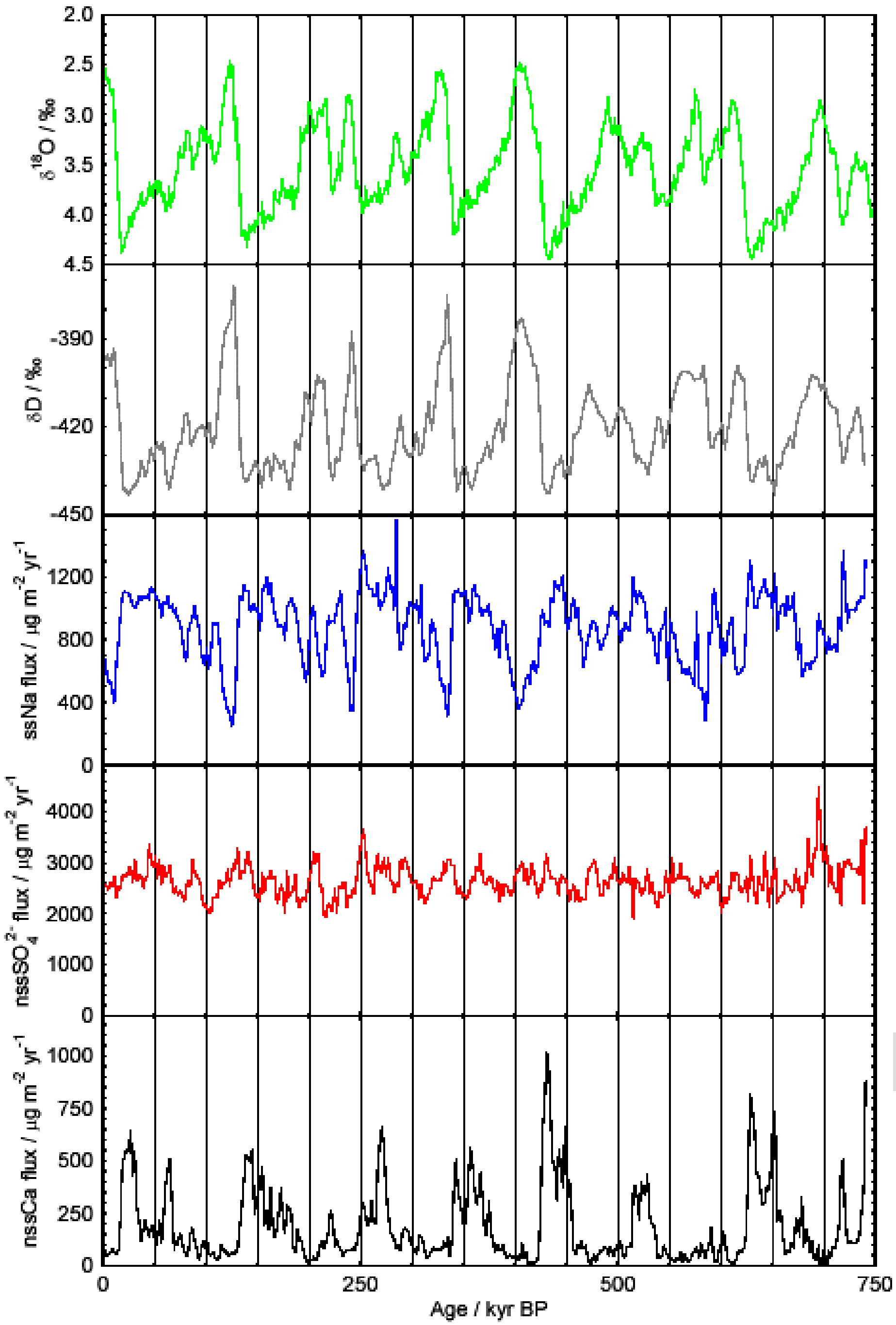
$\delta^{18}O$ sedim

δD (T°)

$ssNa^{+}$ (sea ice and/or atm. turbolence)

$nssSO_4^{2-}$ (biogenic activity)

$nssCa^{2+}$ (mineral dust)



NATURE | VOL 429 | 10 JUNE 2004 | www.nature.com/nature

Eight glacial cycles from an Antarctic ice core

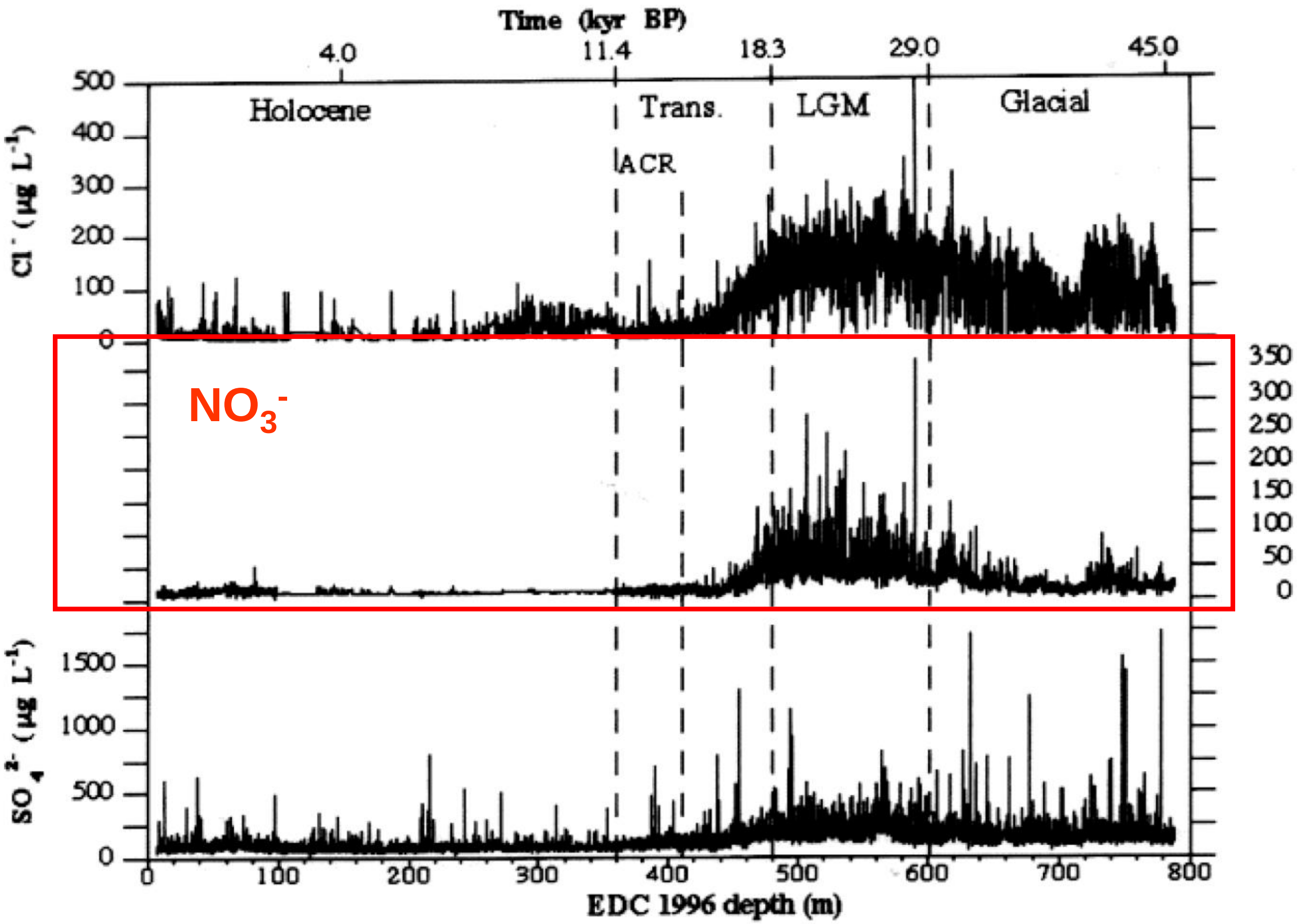
EPICA community members*

Vol 440|23 March 2006|**doi:10.1038/nature04614**

Southern Ocean sea-ice extent, productivity and iron flux over the past eight glacial cycles

E. W. Wolff[1], H. Fischer[2], F. Fundel[2], U. Ruth[2], B. Twarloh[2], G. C. Littot[1], R. Mulvaney[1], R. Röthlisberger[1], M. de Angelis[3], C. F. Boutron[3], M. Hansson[4], U. Jonsell[4], M. A. Hutterli[1,5], F. Lambert[5], P. Kaufmann[5], B. Stauffer[5], T. F. Stocker[5], J. P. Steffensen[6], M. Bigler[5,6], M. L. Siggaard-Andersen[6], R. Udisti[7], S. Becagli[7], E. Castellano[7], M. Severi[7], D. Wagenbach[8], C. Barbante[9,10], P. Gabrielli[10] & V. Gaspari[9]

Nitrate paleoclimatic records from ice cores: a potentiality not yet exploited due to…



EPICA Dome C ice core

High resolution (1 cm) records spanning the last glacial-interglacial cycles

[From: R. Traversi, S. Becagli, E. Castellano, A. Migliori, M. Severi, R. Udisti, Ann. Glaciol., 35, 2002]

…multiple sources of atmospheric nitrate…

Nitrate can be considered the end-product of **NO_x oxidation**.
Deposited as salt in the aerosol and as acid from the gas-phase.
Origin of nitrate in the Antarctic atmosphere not completely understood, likely a combination of inputs

Low-latitude
tropospheric sources

supply of continental NO_x (lighting, biomass burning) and NO_x reservoirs (PAN and alkylNO_3^-) from free troposphere via long-range transport

Stratosphere

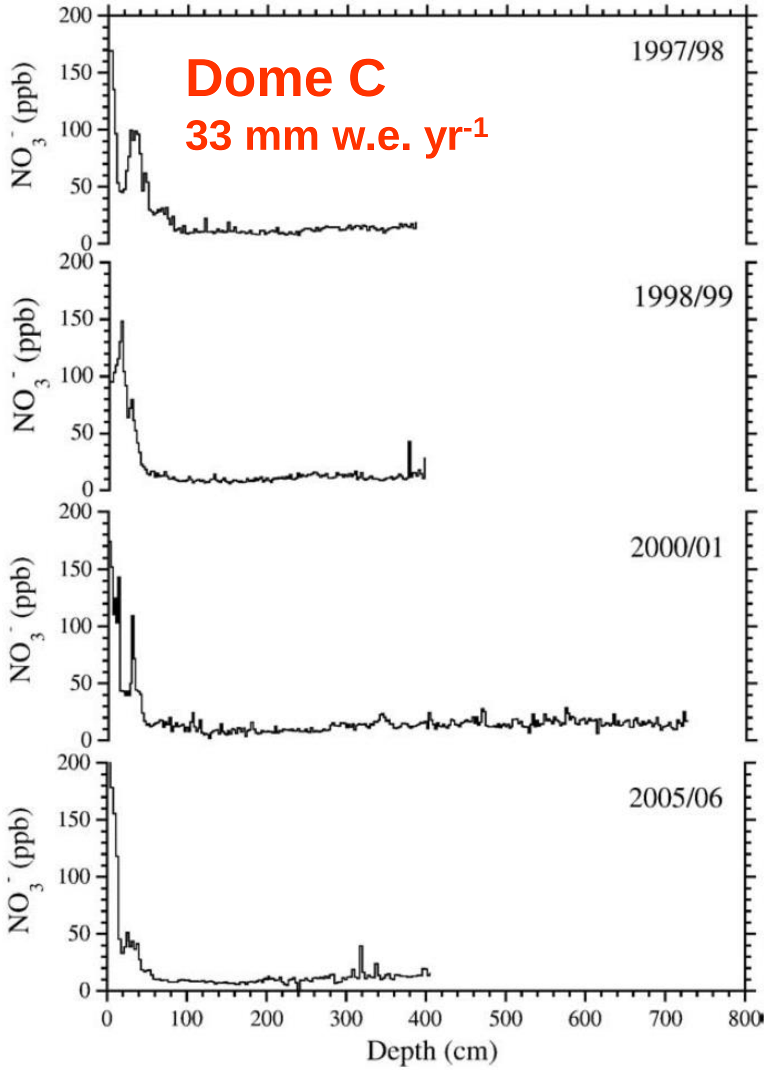
Production of NOx from N_2O oxidation, N_2 photo-ionization and dissociation (from thermosphere to stratosphere) and PSC sedimentation (HNO_3)

Snowpack (source or sink?)

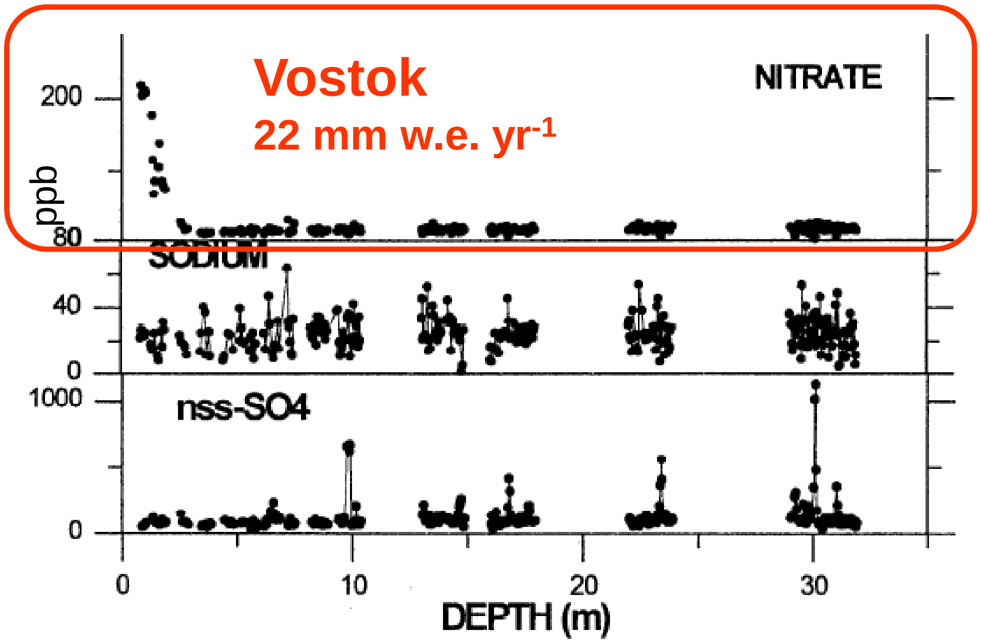
Dynamic nitrate photolysis and production and evaporation/condensation processes from snow layers in low accumulation sites

..and to troublesome nitrate preservation in firn/ice

[From: Traversi et al., 2009 Microchem. J.]



Significant nitrate loss in low accumulation sites (East Ant. Plateau) - implications for paleorecostrunctions from ice core records



[From: Wagnon et al., 1999 J. Geophys. Res.]

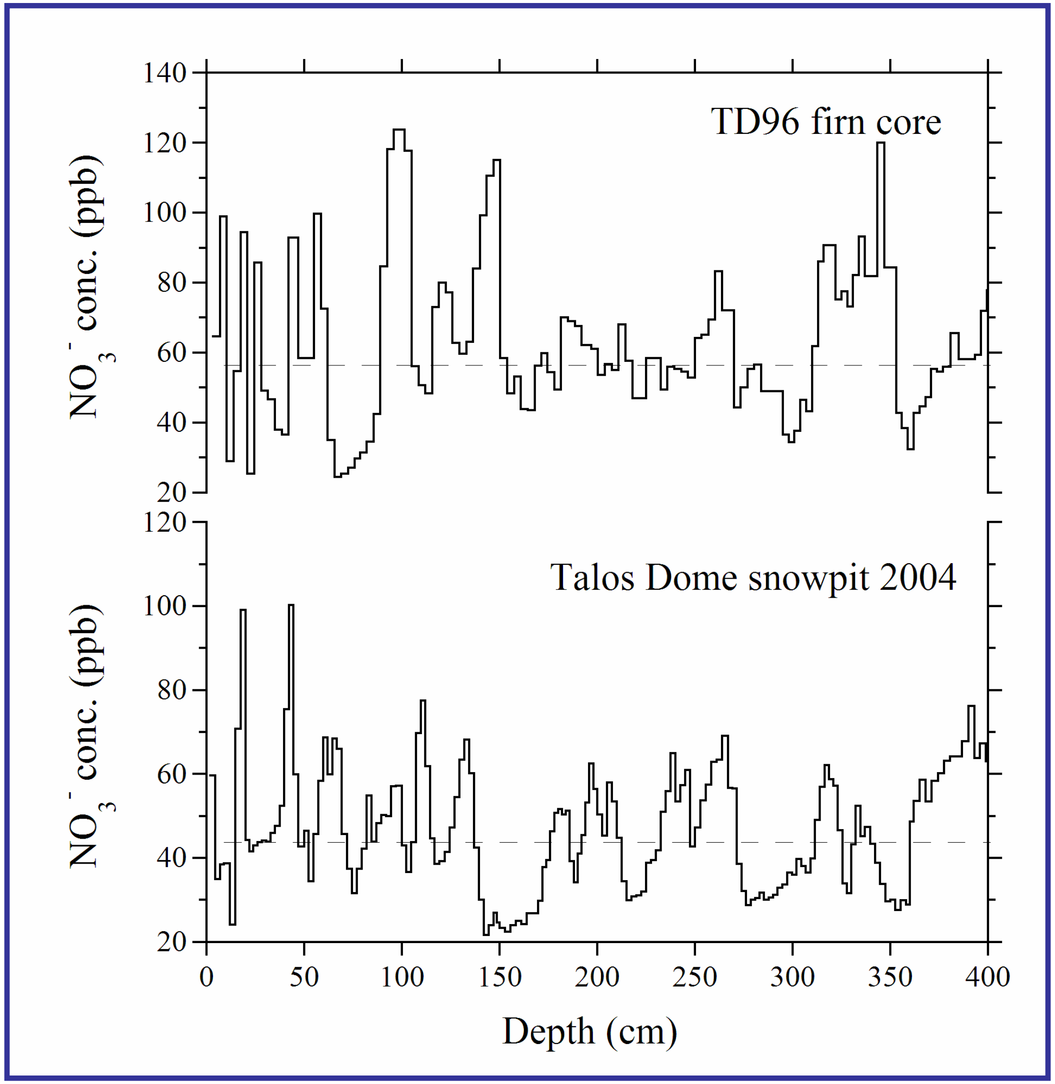
Dome C: loss around 90% in the first 80 cm depth

Vostok: loss around 90% in the first 2.5 m depth

Nitrate preservation in firn/ice - Talos Dome: positive

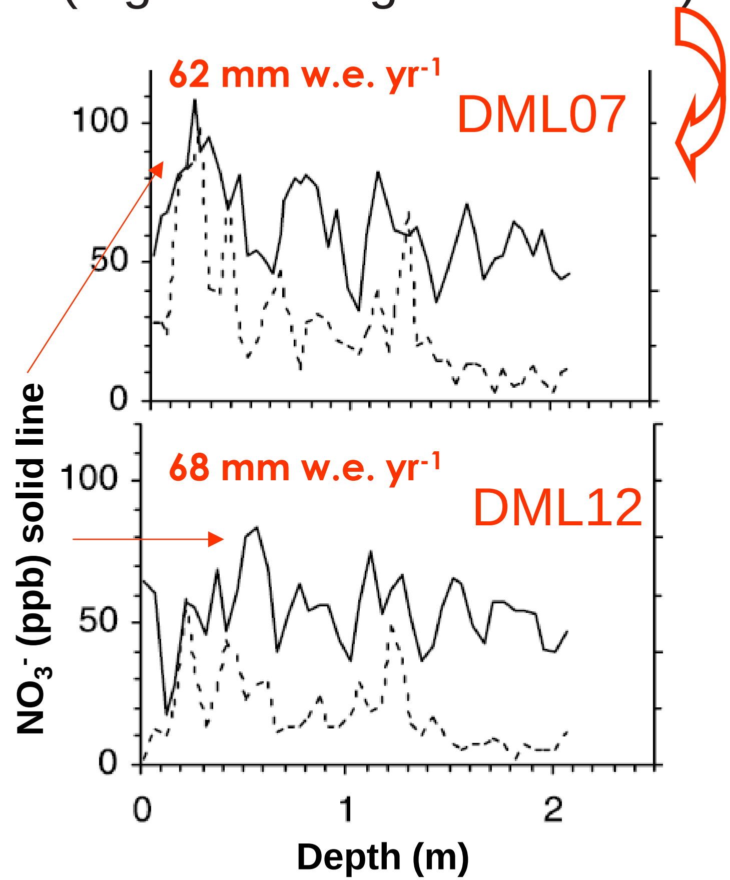
No evidence of significant nitrate loss

acc. rate about 80 mm w.e. yr^{-1}



[From: Traversi et al., 2012, Solar Physics]

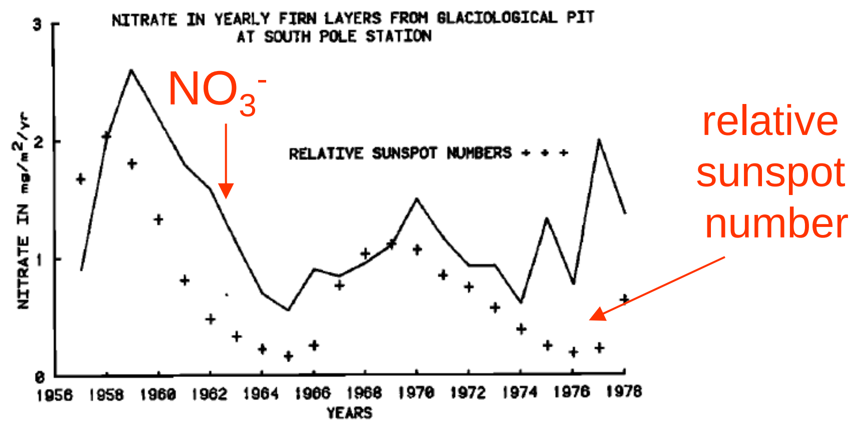
Consistent with results from other sites with comparable acc. rate (e.g. Dronning Maud Land)



[From: Weller et al., 2004 J. Geophys. Res.]

Nitrate - solar activity relationship: a controversial issue
Previous positive results (1) - Short-term scale

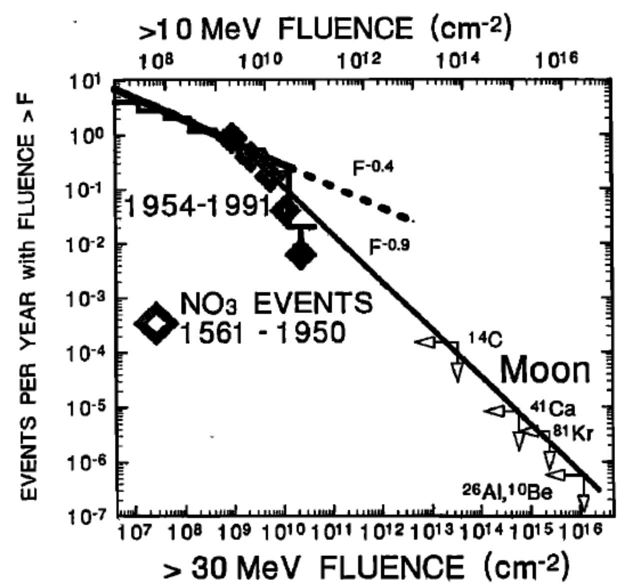
- Evidence of 11-yr solar cycle periods in nitrate records from East Antarctic plateau (South Pole Station)



[From: Zeller and Parker, 1981, Geophys. Res. Lett.]

- One-to-one relations between large fluence SPEs and corresponding nitrate peaks (e.g. McCracken et al., 2001, J. Geophys. Res.).

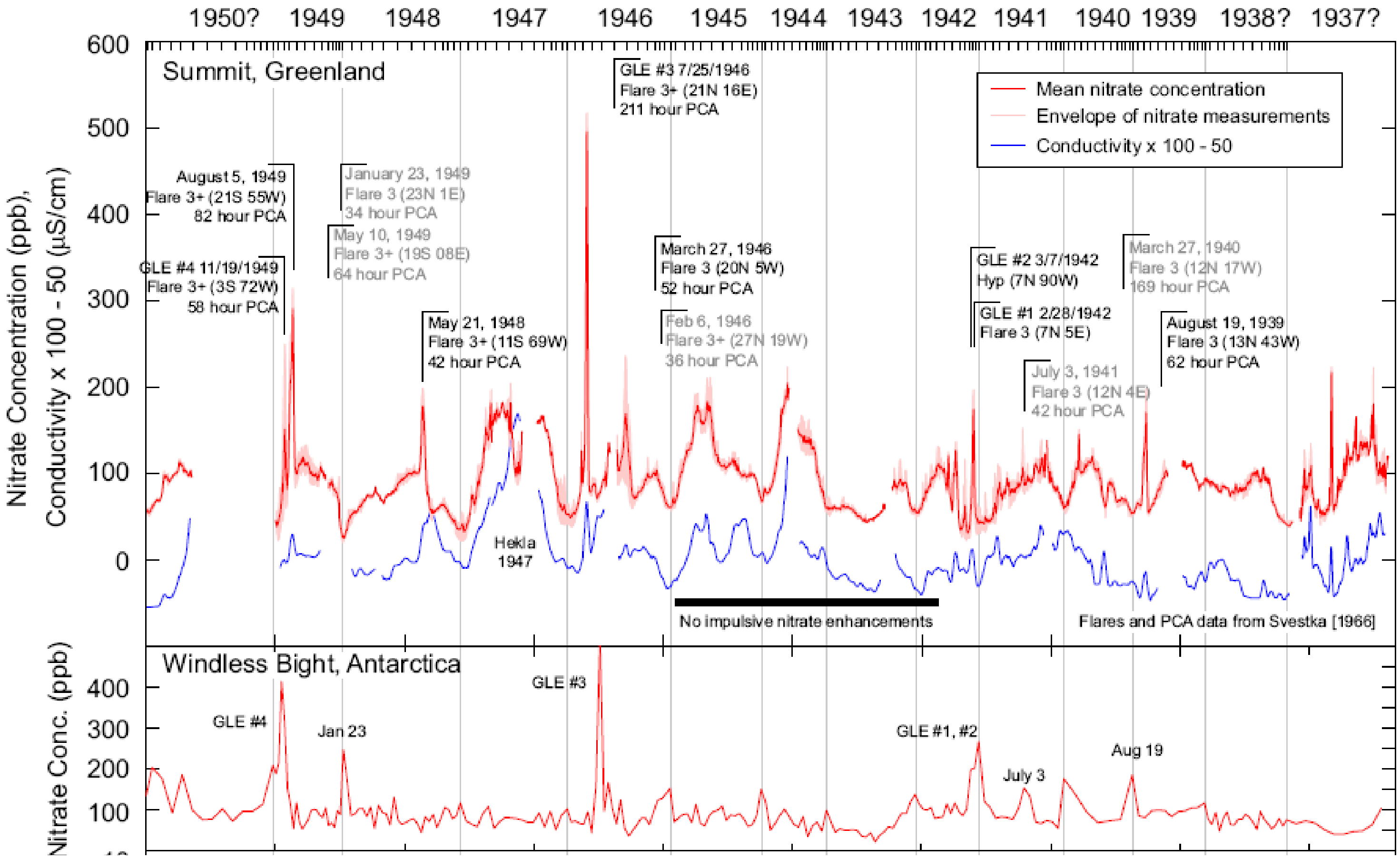
- Probability distribution of proton fluence derived from the largest impulsive nitrate events (1561-1950 AD) was found in agreement with studies of SPE cumulative probabilities and with observations of cosmogenic isotopes in moon rocks



[From: McCracken et al., 2001, J. Geophys. Res.]

Nitrate - solar activity relationship: a controversial issue
Previous positive results (2) - Short-term scale

➢ Observations of impulsive nitrate enhancements in an Antarctic and a Greenland ice core shortly after a large fluence SPEs

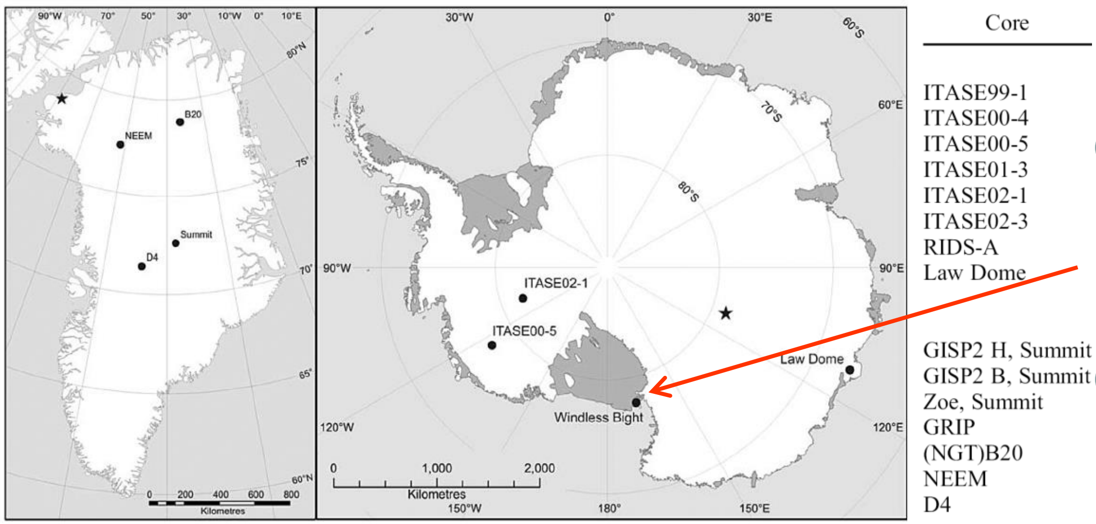


[From: Kepko et al., 2009, J. Atm. Sol. Terr. Phys.]

causal connection between solar activity and nitrate levels in polar ice including both production and (fast) transport

Nitrate - solar activity relationship: a controversial issue … and negative results (3) - Short-term scale

Carrington (1859) - the most intense space weather event in the last 150 yr



[From: Wolff et al., 2012, Geophys. Res. Lett., 39, L08503]

14 high res. ice core records:

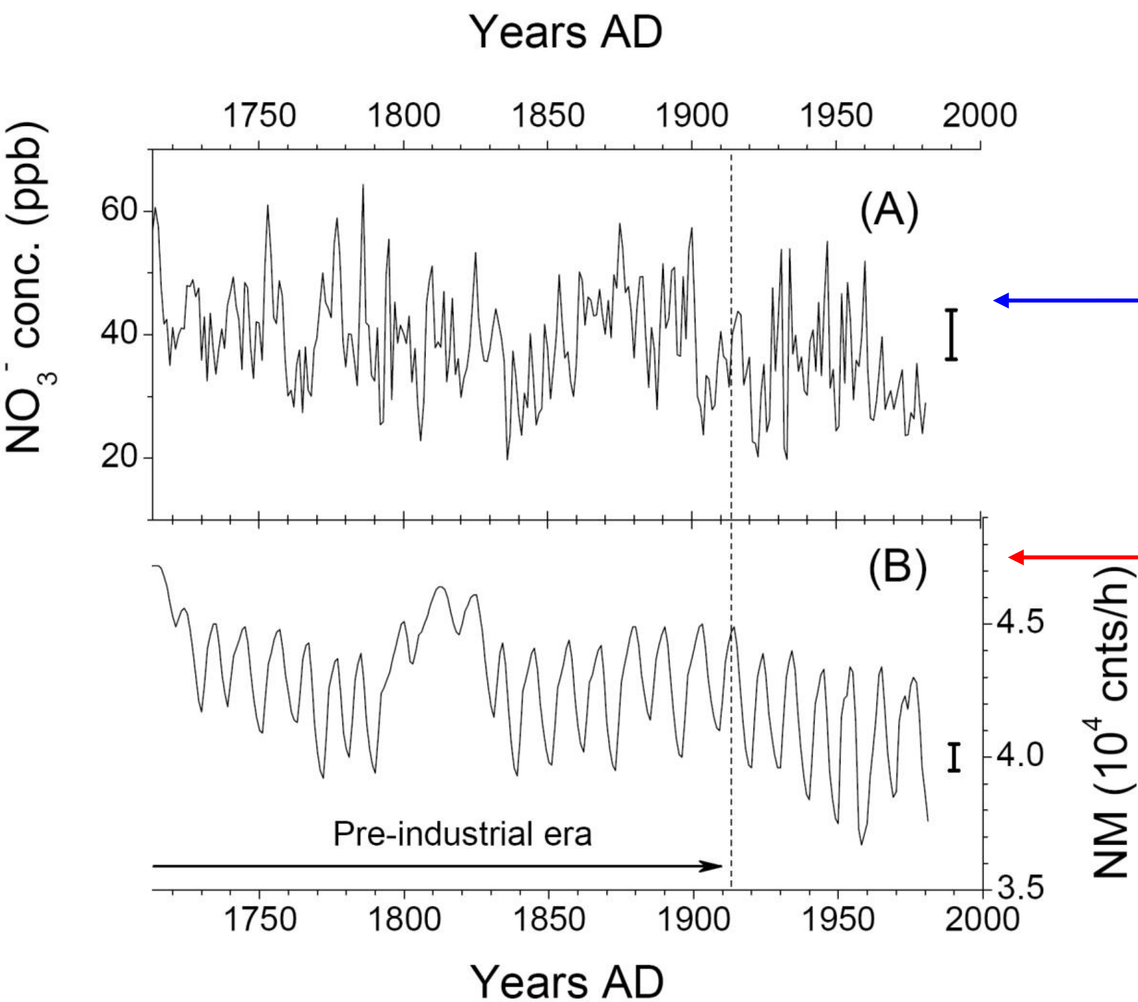
- Antarctica: only one site exhibits a nitrate spike dated 1859. No sharp spikes in the other cores.
- Greenland: many evident spikes around 1859 but most likely due to biomass burnings rather than SEP events (as shown by other chemical markers).

If **nitrate** records from polar ice do not show a widespread signature of an event as large as the Carrington, can nitrate spikes be used to reconstruct **SEP** occurrence? …

NO, according to Wolff et al., 2012 (GRL) and Schrijver et al., 2012 (JGR)

What about being related to solar activity on a different time scale?

Insights from TALDICE firn/ice core: decadal to centennial variability in the 1713 -1981 AD period



Nitrate concentration from TALDICE superficial part (firn, 6-73 m depth, subannual resolution, 3.5 cm depth)

Cosmic Ray intensity reconstructed from sunspot numbers after the MM and from values actually measured after 1951.

[From: Traversi et al., 2012, Solar Physics]

Integral coherence between annual TALDICE nitrate and CR reconstructions in the last two centuries

	Frequency band of Schwabe cycle	Frequency band of Gleissberg cycle (55-100 yr)
Time interval	7 – 15 yr	55 – 100 yr
1713 – 1913	**0.31** (0.01)	**0.6** (0.01)
1713 – 1981	*0.24* (0.03)	*0.49* (0.02)
	Coh *(p)*	Coh *(p)*

7-10% common variab.

25% common variab.

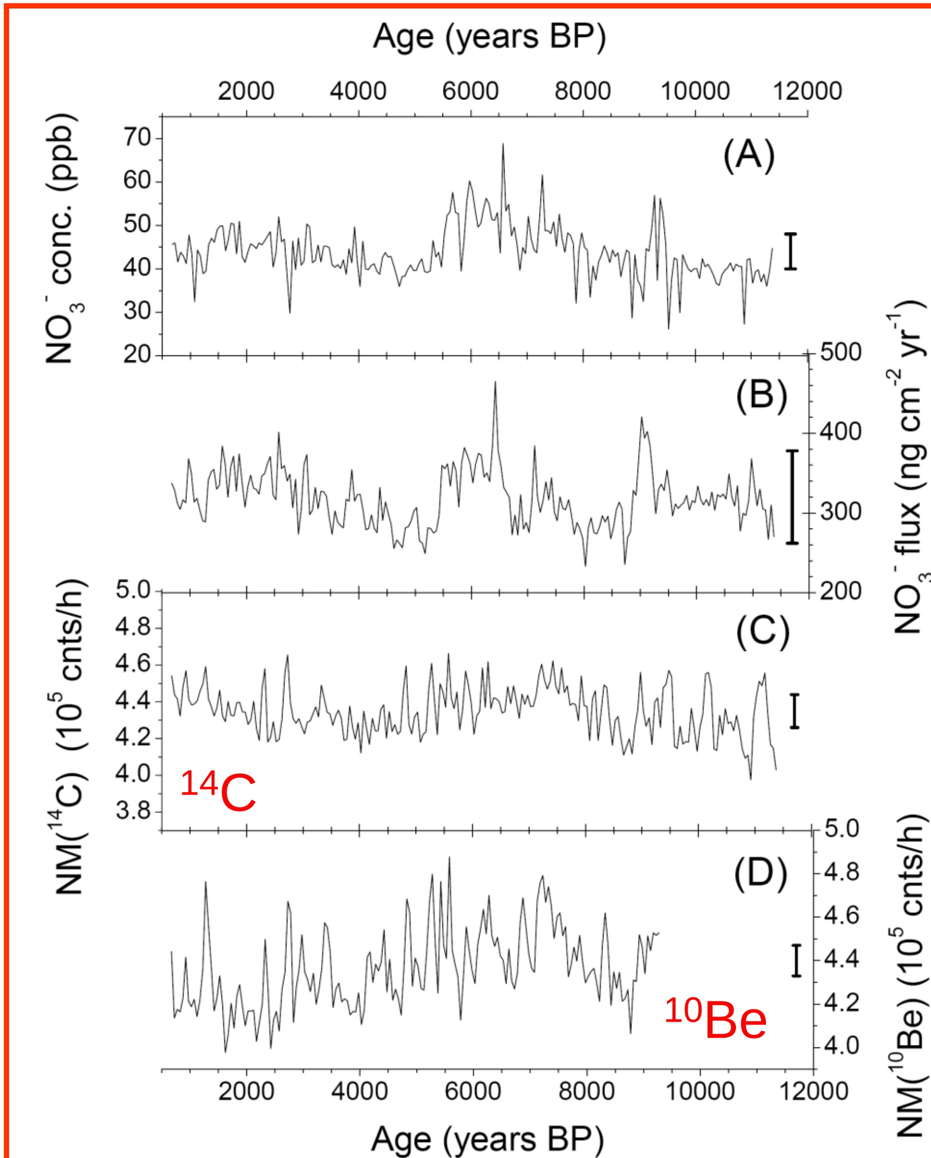
Statistically significant and in-phase (within 1 yr) relation between nitrate in TALDICE firn core and GCR variability at the time scale including the solar 11-yr and Gleissberg cycles.

Less significant agreement when the temporal frame is enlarged to 1981, likely due to anthropogenic inputs to nitrate budget

Bivariate correlation nitrate - GCR is low (R=0.17) and scarcely significant (p=0.06), comparable with ^{10}Be - GCR (R=0.14) [Beer et al., 1990, Nature]

Insights from TALDICE ice core

Long-term scale



[From: Traversi et al., 2012, Solar Physics]

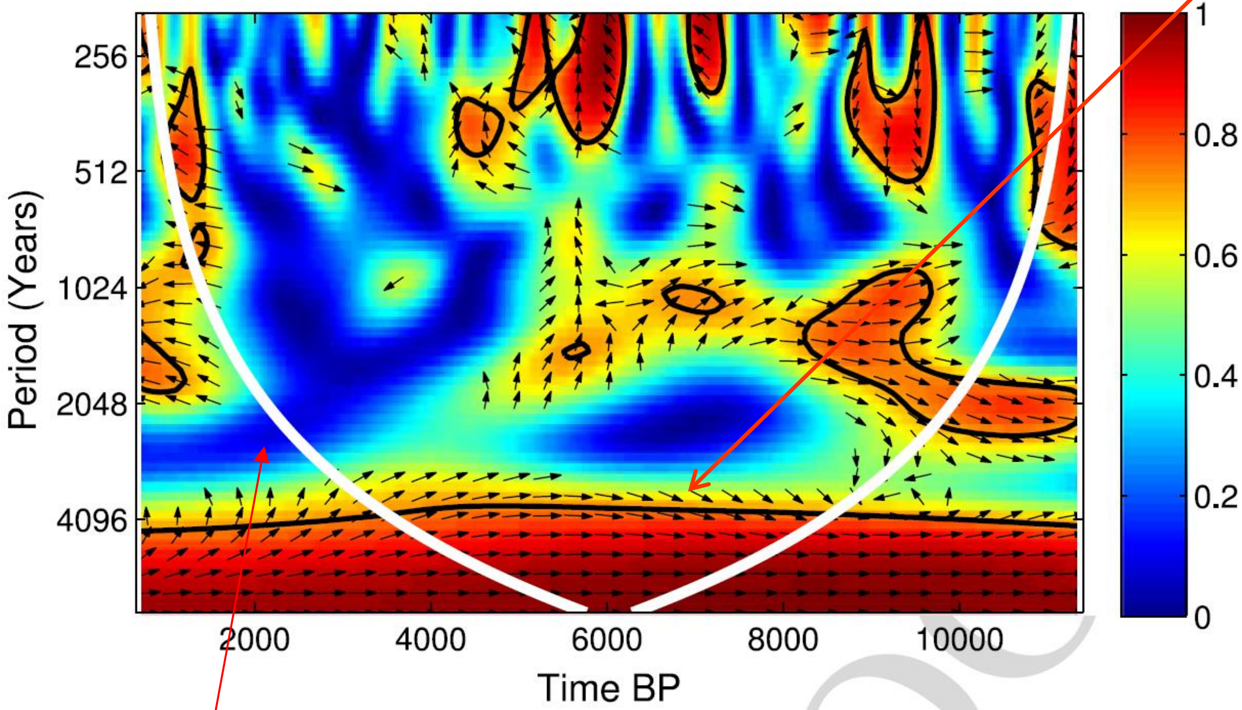
Temporal frame: the Holocene
(73-600 m depth)

Resolution: 10 to 30 yr
(1 m depth res.)
All data averaged over 50 yr

Nitrate record
(concentr. and flux) compared
with

Cosmic Ray intensity
(quantified in count rates of a standard polar neutron monitor) reconstructed from **^{14}C** and **^{10}Be** cosmogenic isotope records
(commonly used proxy of SA)

Wavelet coherence between nitrate concentration and CR (^{14}C) over the Holocene



Multi-millennial time scale: stable, **highly significant**, perfectly **in-phase** coherence

Millennial scale during the early and mid-Holocene (orange to red areas at the 1 – 2 kyr time scale): **intermittent significance** of coherence, fluctuating phase

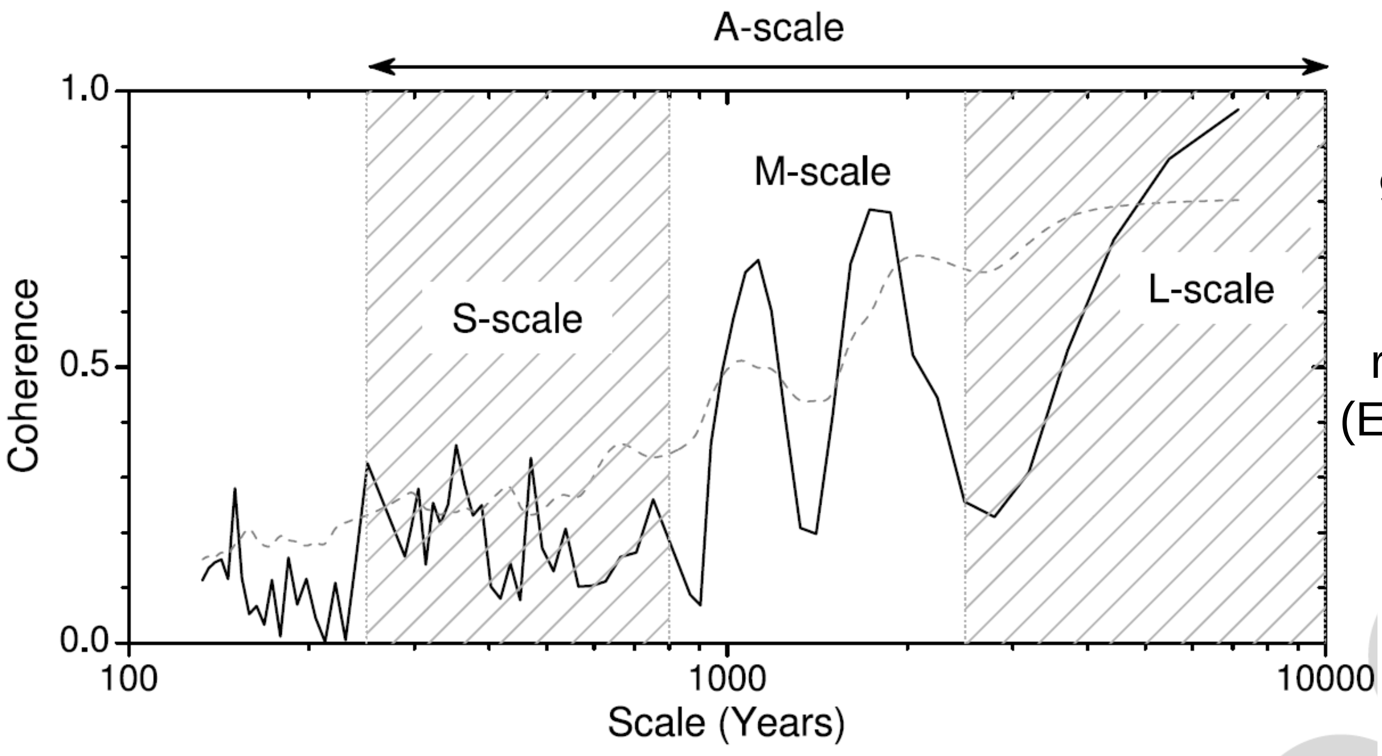
Multi-centennial scale: intermittent coherence, **unclear** stability and phase

Contours bound areas with significant (95 %) coherence.

Arrows denote the relative phasing.

The cone of influence (COI), where the spectrum may be distorted (thick white lines)

Time-integrated wavelet coherence spectrum for nitrate concentration and CR (^{14}C) as function of time scale/period (excluding COI)

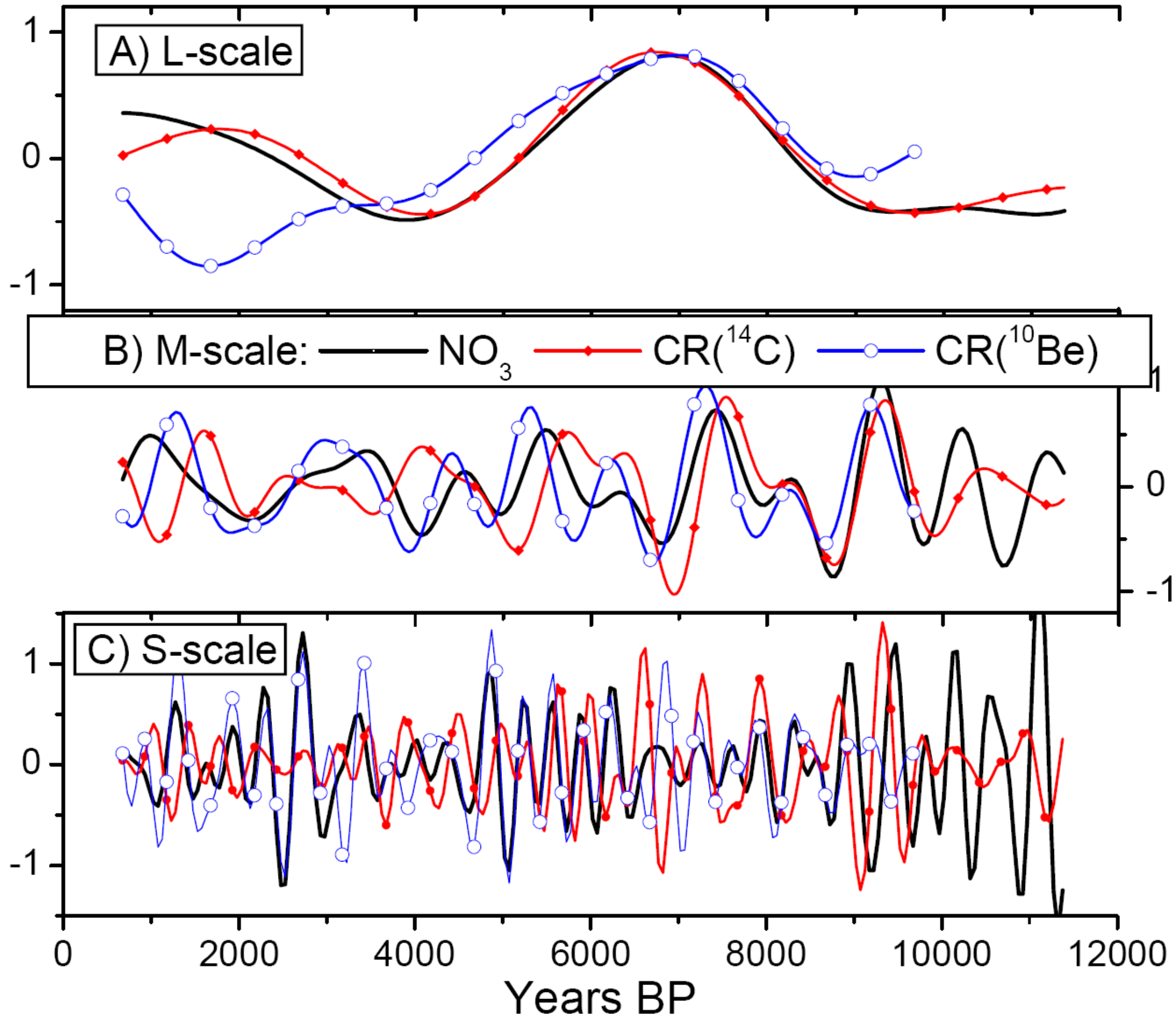


Grey dotted line:
95 % confidence level
calculated using the
non-parametric
random-phase method
(Ebisuzaki 1997, J. Clim.)

The whole Holocene time scale was divided into sub-scales:

short (S) scale: sub-millennial time scale of 250 - 800 yr
millennial (M) time scale: 800 - 2500 yr
long (L) scale: multimillennial scale longer than 2500 yr

Data filtered using wavelet digital filters, in selected time scales



	Coh	(p)
> 2500 yr scale		
NO_3^- vs. CR(^{14}C)	**0.53**	($<10^{-3}$)
NO_3^- vs. CR(^{10}Be)	*0.36*	(0.02)
CR(^{14}C) vs. CR(^{10}Be)	*0.32*	(0.03)
800-2500 yr scale		
NO_3^- vs. CR(^{14}C)	**0.28**	(0.003)
NO_3^- vs. CR(^{10}Be)	**0.36**	(10^{-3})
CR(^{14}C) vs. CR(^{10}Be)	**0.33**	(0.01)
250-800 yr scale		
NO_3^- vs. CR(^{14}C)	*0.20*	(0.02)
NO_3^- vs. CR(^{10}Be)	*0.24*	(0.02)
CR(^{14}C) vs. CR(^{10}Be)	**0.43**	($<10^{-3}$)

Conclusions (1)

TALDICE nitrate record vs. Cosmic Ray flux reconstructions :

- Last centuries: Statistically significant and in-phase relation at the time scale of the solar 11-yr and Gleissberg cycles.

- Holocene: highly significant agreement at the millennial and especially at multi-millennial time scales; less significant agreement at centennial time scales (dating uncertainties: 250-300 yr)

The two proxy records have different production and transport patterns:

^{14}C produced globally, mixed in the geosphere, mostly affected by ocean circulation, nitrate in the Antarctic polar region is produced mostly locally and can be affected by regional Antarctic air masses transport

⇩

Solar activity as common origin of their long-term variability

Conclusions (2)

Nitrate in TALDICE ice core: a new proxy of solar activity on the centennial and longer time scales

- Possible help in resolving some of the discrepancy between ^{14}C and ^{10}Be records (at millennial scale).
- Chance of extending back to the last glacial cycles the reconstruction of solar activity (TALDICE covers the last 250 kyr)
- Nitrate as a potential proxy of solar activity possibly also from other records retrieved in “favourable” sites (allowing both nitrate preservation and recording a regional signal)

Future perspectives (1)

To use effectively nitrate record in reconstructing solar activity in the past

Complete production and transport/deposition model of nitrate in polar atmosphere
in order to understand the mechanism linking nitrate to GCR and to assess the extent of such a relationship
(work on hold now…)

Currently available independent simulations:

- SOCOL model
  (Calisto et al., 2011, ACP; Rozanov et al., 2012, Surv. Geophys.)
- CMAM model (Semeniuk et al., 2011, ACP)

Influence of GCR estimated in 20 - 30 % on-off effect on HNO_3 and NOy (nitrate precursors) in near-ground air in Antarctica

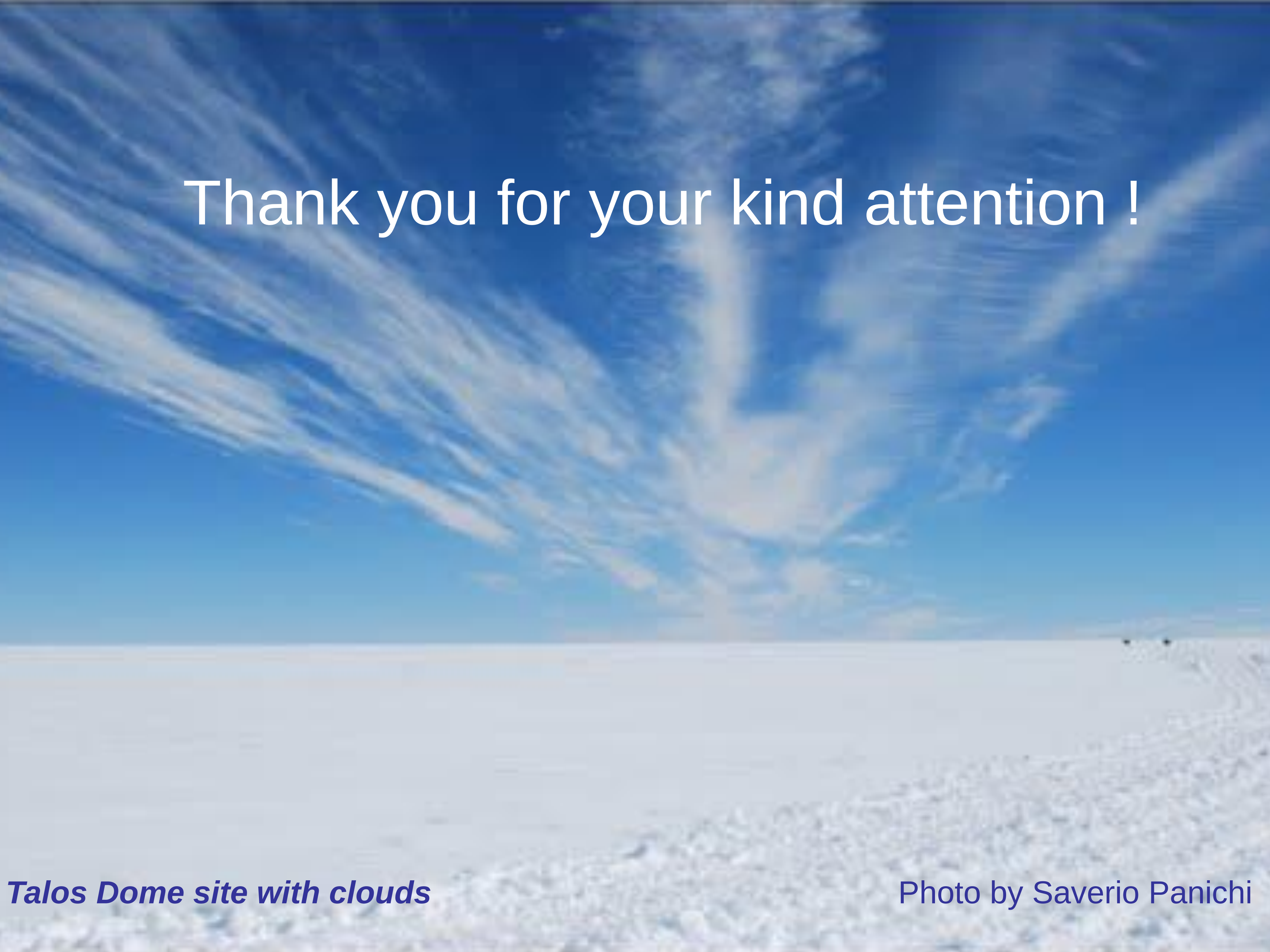
Future perspectives (2)

- New and more accurate (uncertainty reduced to about 100 yr over the Holocene) dating for TALDICE soon to be available: check robustness of the presented results

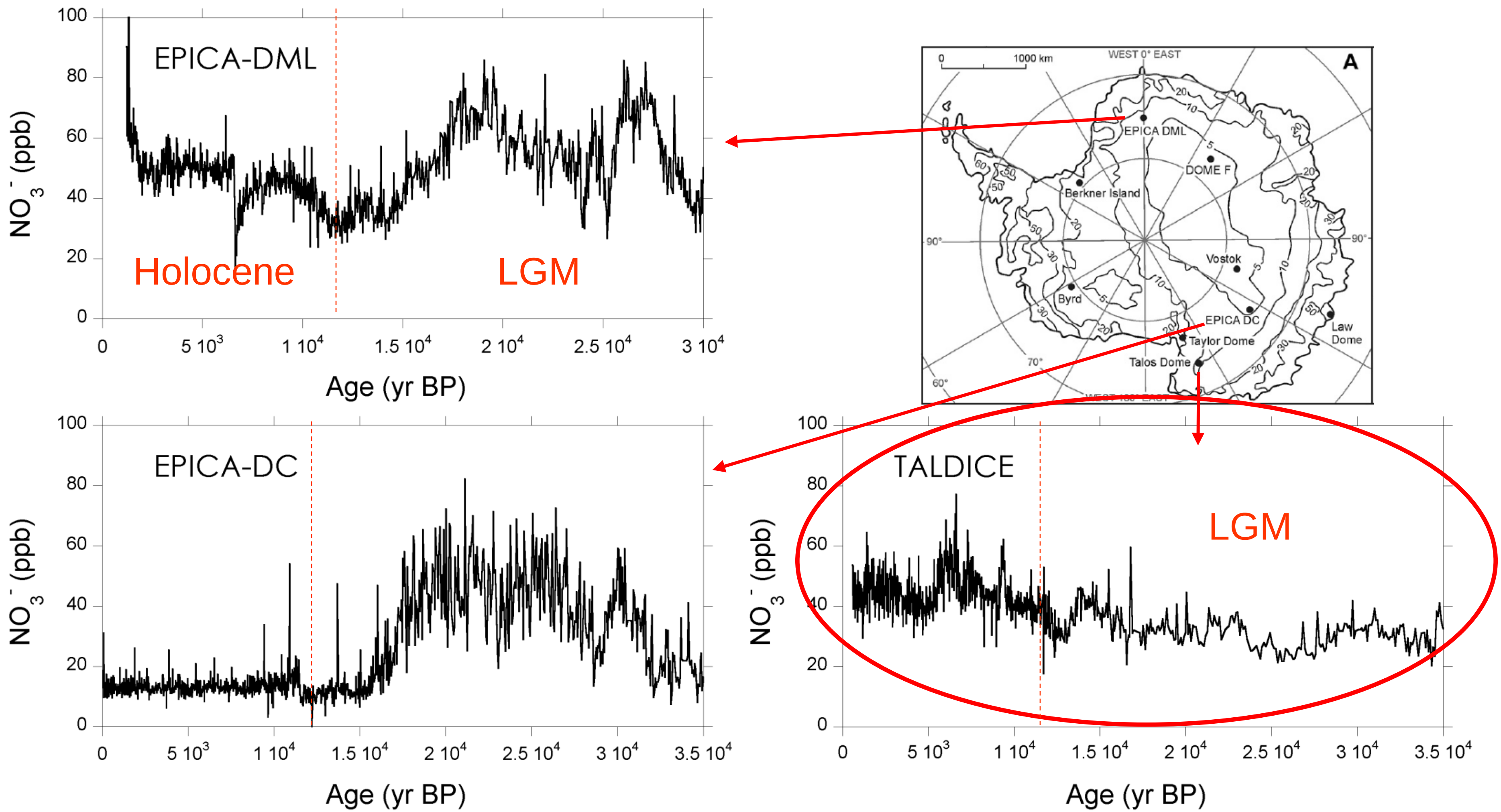
- Possible new record covering the last 2000 yr from a "favourable" site (high accumulation, 237 mm w.e. in the last 150 yr):

GV7 (70° 41' S; 158° 52' E; 1947 m, -31.8° C)

Drilling planned for next field season (Italy PNRA -Korea KOPRI joint project, within "IPICS 2ky Array - a network of ice core climate forcing records for the last two millennia")


Thank you for your kind attention !
Talos Dome site with clouds
Photo by Saverio Panichi

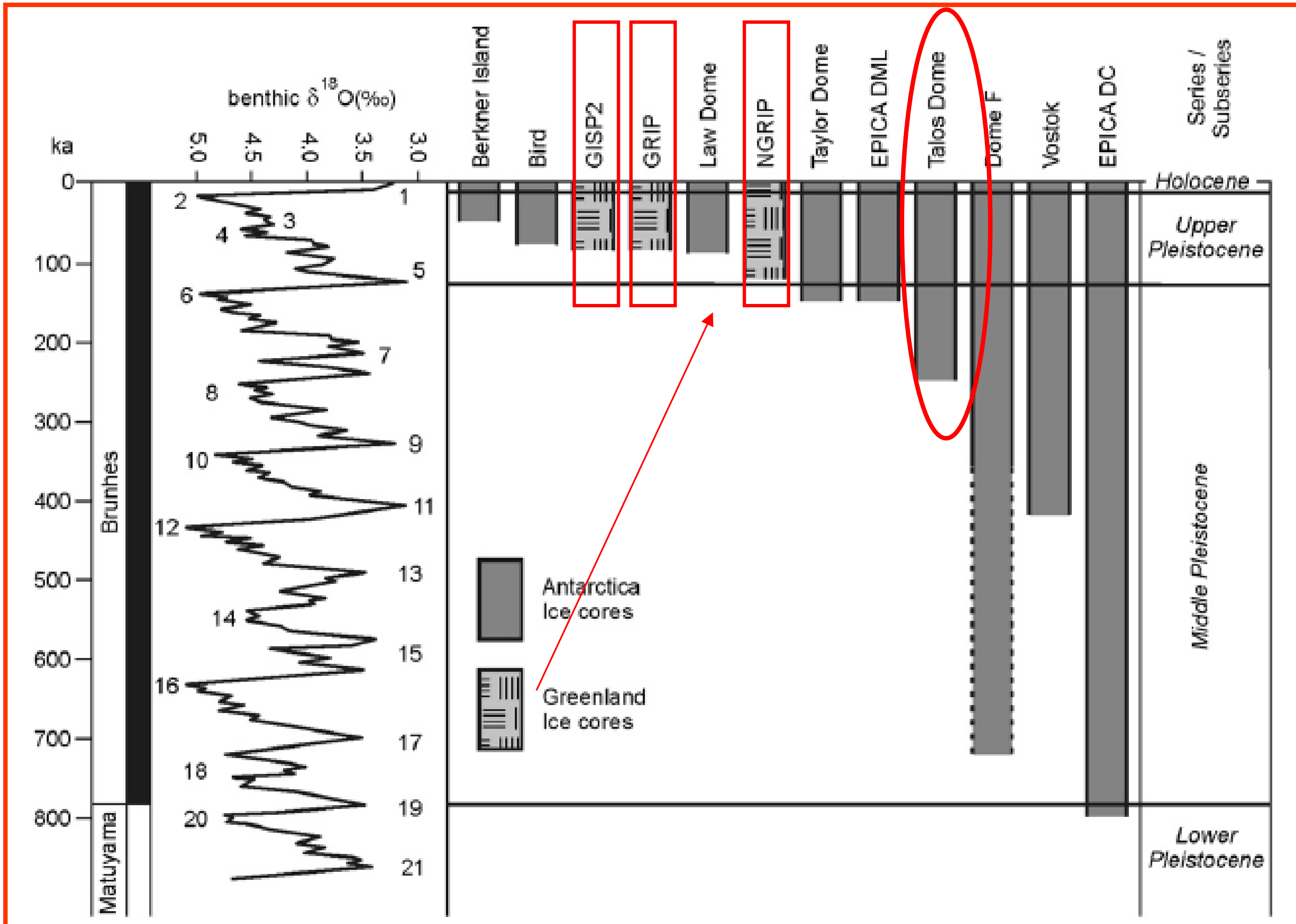
TALDICE ice core (Talos Dome)



NO_3^- concentration vs. age: different glacial-to-interglacial pattern in TALDICE with respect to other deep drilling sites, different information?

The stratigraphic extent reached by the deepest Greenland and Antarctic ice cores

Stacked record of benthic $\delta^{18}O$ from Lisiecki and Raymo (2005)



[From: Orombelli et al., 2009 QSR]

- Greenland ice cores cover Holocene and Upper Pleistocene
- EPICA Dome C (Antarctica) goes back to the Lower Pleistocene

POSITIVE MATRIX FACTORISATION

$$x_{ij} \approx \sum_{k=1}^{p} f_{ik} \cdot g_{kj}$$

x_{ij} = concentration of element “i” in sample “j”

f_{ik} = source profile: fraction of element “i” in source “k”

g_{kj} = source weight: concentration of source “k” in sample “j”

Commonly used for source apportionment in aerosol studies

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} f_{ik} \cdot g_{kj}$$

$$Q(E) = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{s_{ij}} \right)^2$$

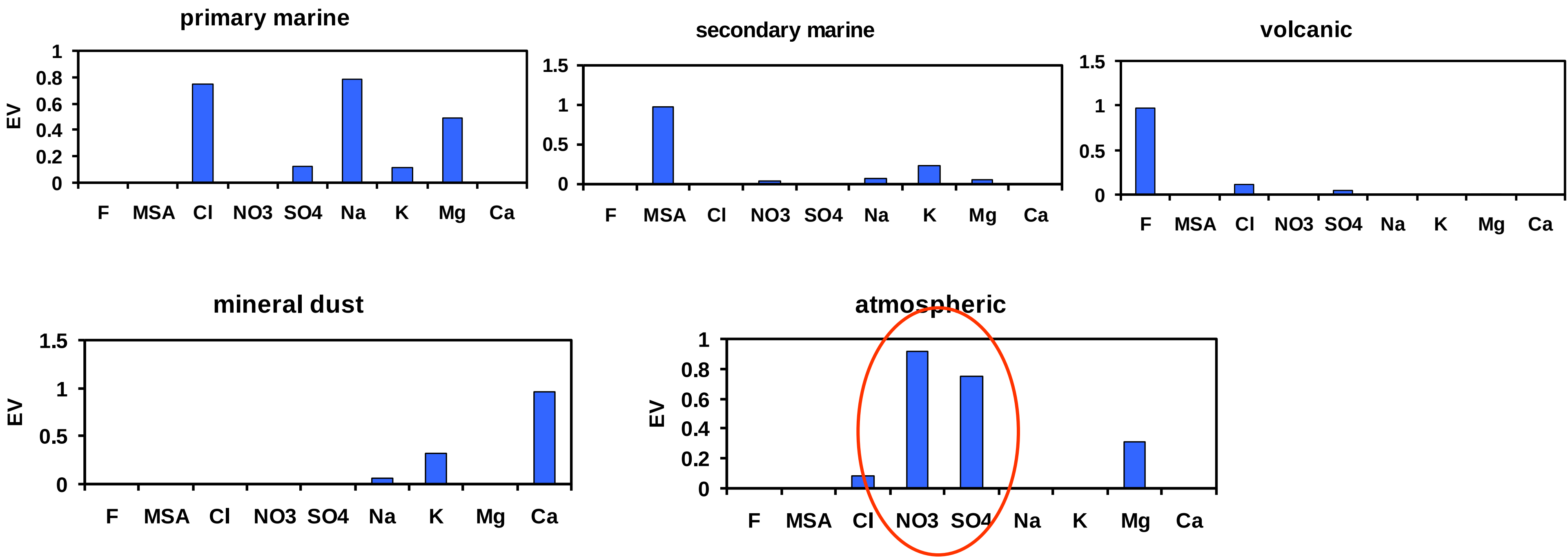
Minimize Q(E) with respect to *G* and *F*
with the constraint that each of the elements of *G* and *F* is **non-negative**

(Paatero & Tapper, Environmetrix 5, 94)

- PMF2 by Paatero (robust mode)
- input data prepared using the Polissar procedure (JGR 98)
- results explored for multiple number of factors and FPEAK values

PMF applied to TALDICE data from Holocene

Chosen solution: 5 factors (rotation +0.4) => 5 main aerosol sources to TD
Consistent with acquired knowledge
but also showing something new and TD-specific



EV	F	MSA	Cl	NO3	SO4	Na	K	Mg	Ca
primary marine	0.001	0.001	**0.752**	0	0.124	**0.793**	0.122	**0.497**	0.001
secondary marine	0.001	**0.985**	0	0.052	0	0.087	0.237	0.062	0
mineral dust	0.001	0	0	0.001	0.001	0.07	0.323	0	0.969
volcanic	**0.979**	0.001	0.126	0	0.054	0	0	0.007	0.001
atmospheric	0.001	0.001	0.087	**0.920**	**0.755**	0	0	0.313	0.001
not explained	*0.018*	*0.012*	*0.034*	*0.026*	*0.066*	*0.049*	*0.318*	*0.121*	*0.027*

Factors Influencing nitrate Concentration in Antarctic Snow

Nitrate removed from the atmosphere by adsoprtion processes (gas-phase HNO_3) and wet/dry deposition (particulate NO_3^-)

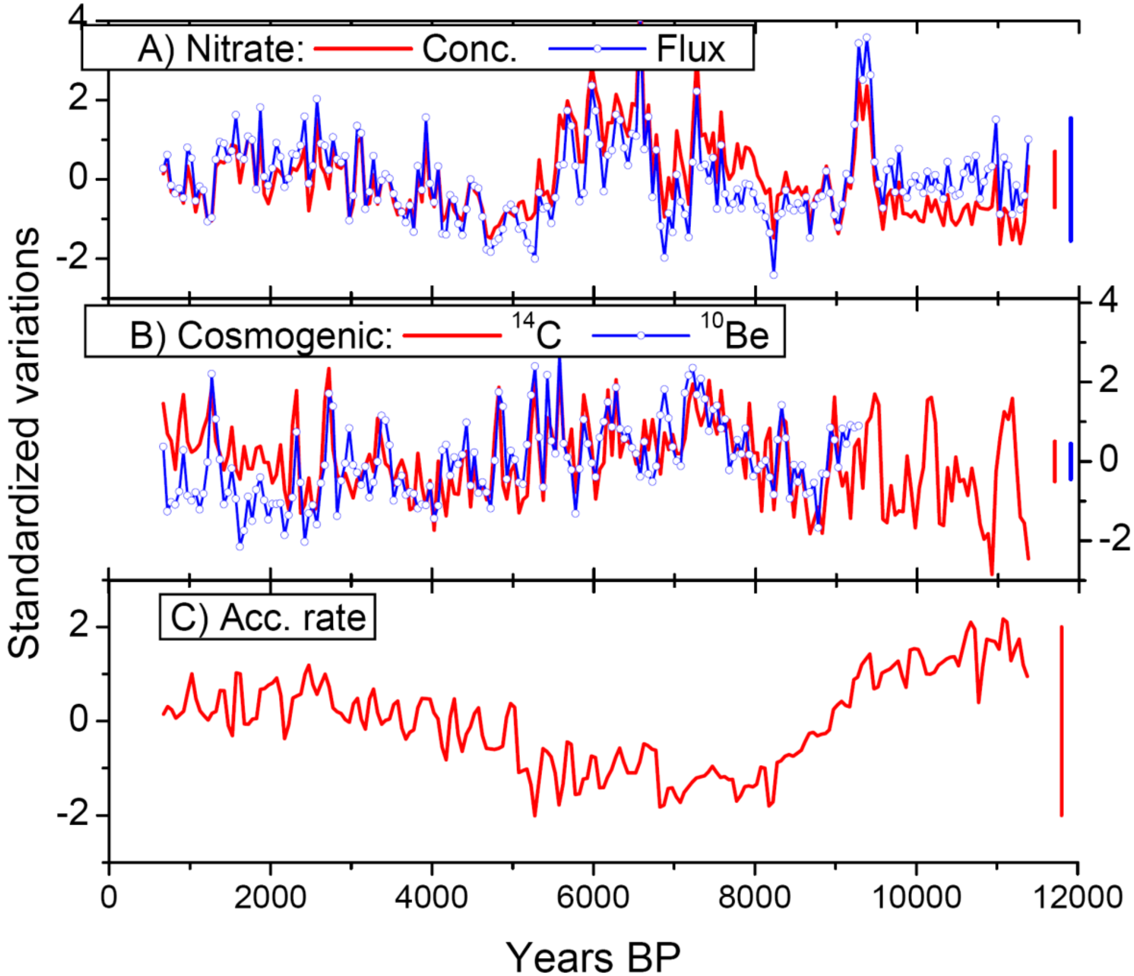
(1) near-surface air concentration (rather than cloud composition).
The surface snow NO_3^- is in equilibrium with atm. HNO_3 , with both uptake and loss taking place at the surface.

(2) accumulation rate, with more nitrate incorporated into snow layers more rapidly buried.

(3) air temperature – ice sheet elevation
Nitrate conc. in surface snow tends to be higher with altitude and lower air T (higher uptake + decreased atm-snow HNO_3 exchange)

(4) total ionic composition (e.g. free acidity, dust content)

Time profiles of standardized data series for the Holocene



Concentration vs. depos. flux (product of conc. by acc. rate)

Uncertainty of snow accumulation rate (estimated as the 15 %, red vertical bar), covers the entire range of variability, making it not distinguishable from a constant rate.

Concentration record is preferred to flux record for statistical analysis

[From: Traversi et al., 2012, Solar Physics]

Chemical markers in ice cores

- Mineral dust: non sea salt Ca^{2+} - nssCa^{2+}
  (nssNa^+, especially during glacials)
  Long-range atmospheric transport – Aridity and position of dust source areas

- Sea Spray: sea salt Na^+ (and, partially, Cl^- e Mg^{2+})
  Zonal wind intensity/pathway and/or sea ice extent

- Marine biogenic activity: MS^- (nssSO_4^{2-} and NH_4^+)
  Negative feedback on climate

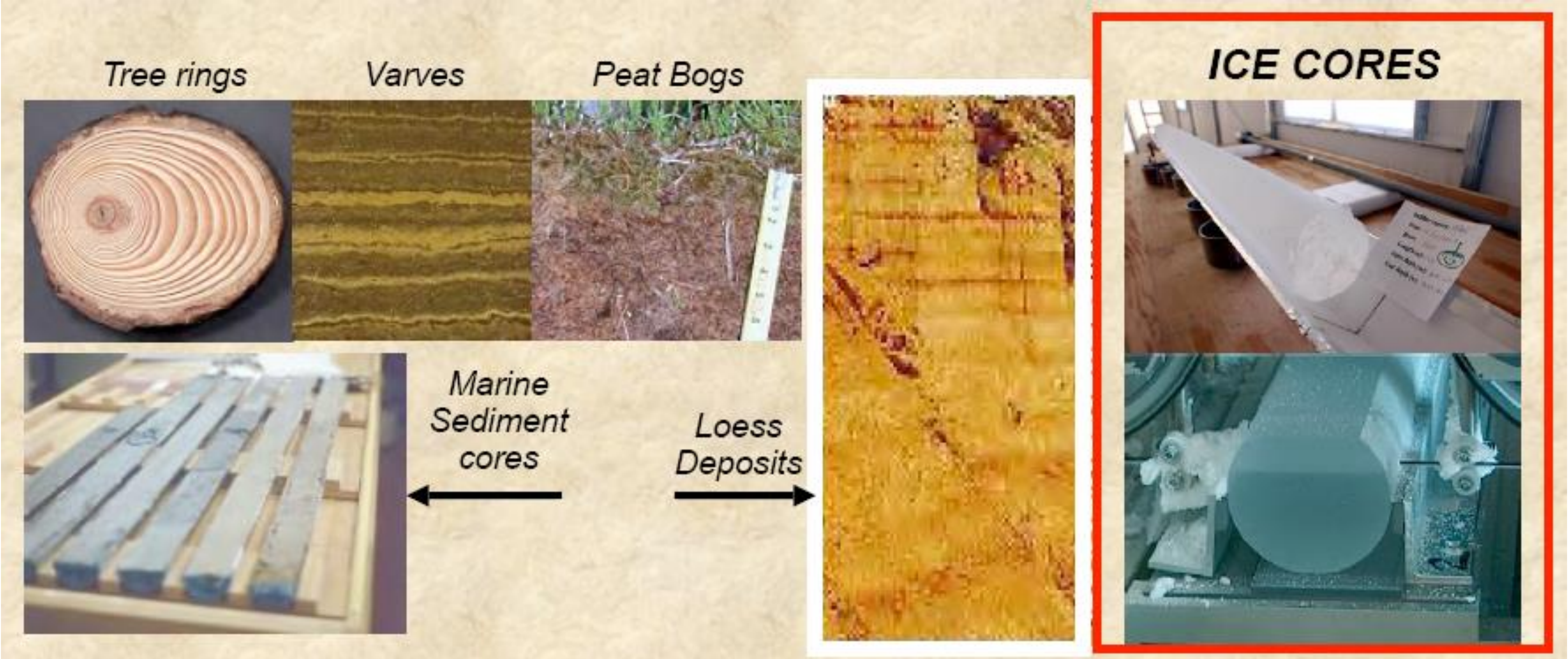
- Volcanic activity: non sea salt SO_4^{2-} (not biogenic), HF, HCl
  Climatic forcing – Tropospheric transport

- NO_x and atmosphere oxidising capacity: NO_3^-
  Solar activity - Stratosphere-troposphere exchange

Reconstructing pattern and timing of Quaternary climatic variations

understand the current “climate change” and to foresee its future developments

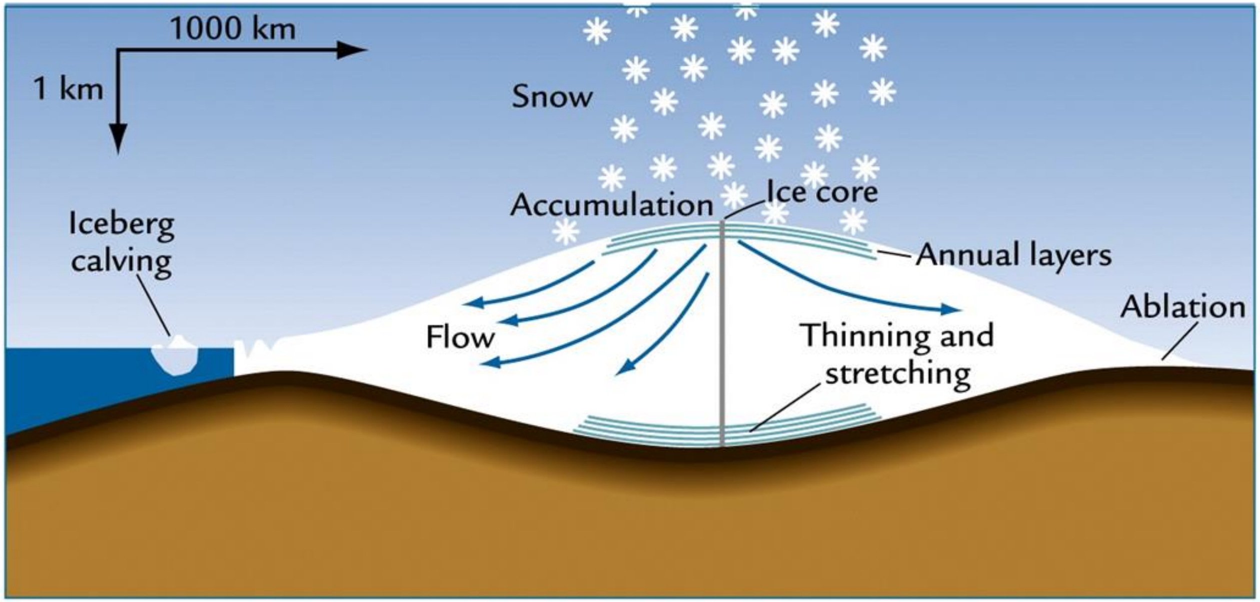
The Earth’s paleoclimatic history is recorded in natural matrices responding to climatic and environmental conditions



Ice as an archive of climatic history

Snow forms by water vapor deposition or by freezing of supercooled droplets.

During formation and precipitation, it incorporates gaseous and particulate compounds



B Continental ice sheets

Ice, progressively accumulated over time,
records the climatic conditions at the time of snow deposition
and preserves samples of past atmosphere