Sustained surface nitrate recycling on the Antarctic plateau throughout the last climatic cycle : a stable isotopic view

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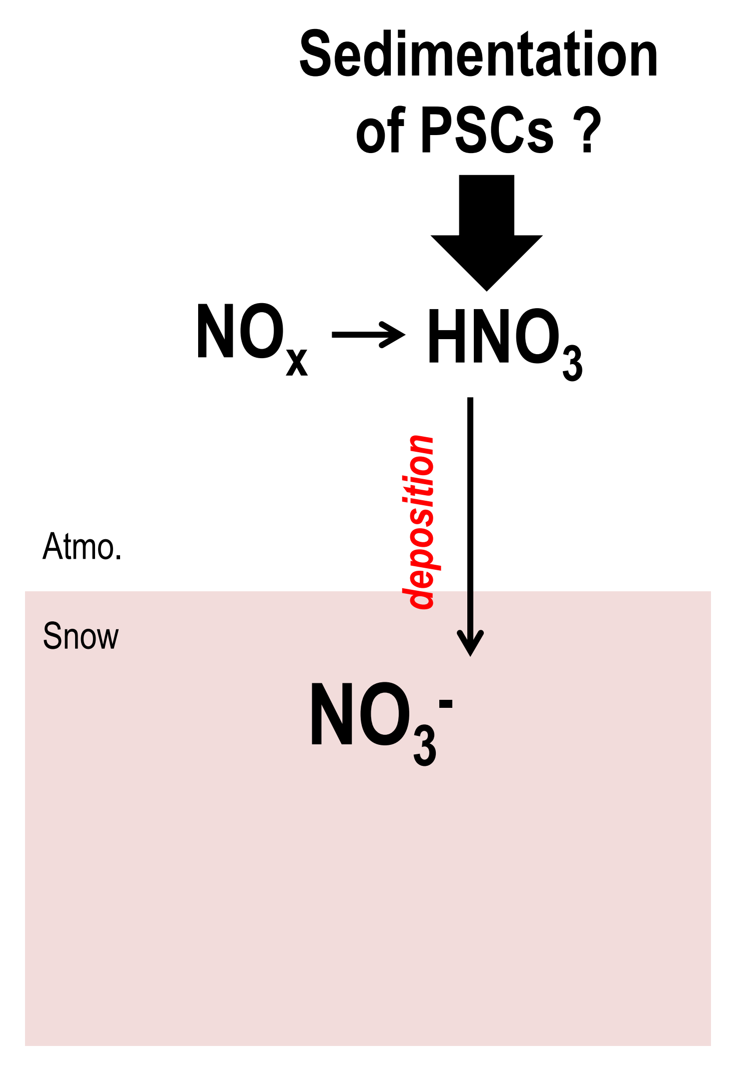
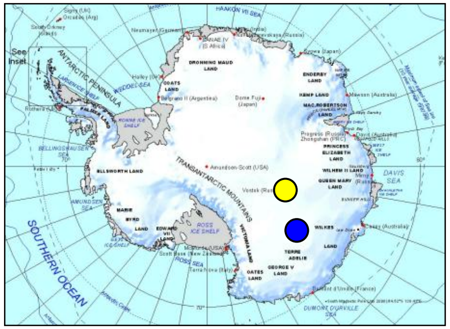
Outline

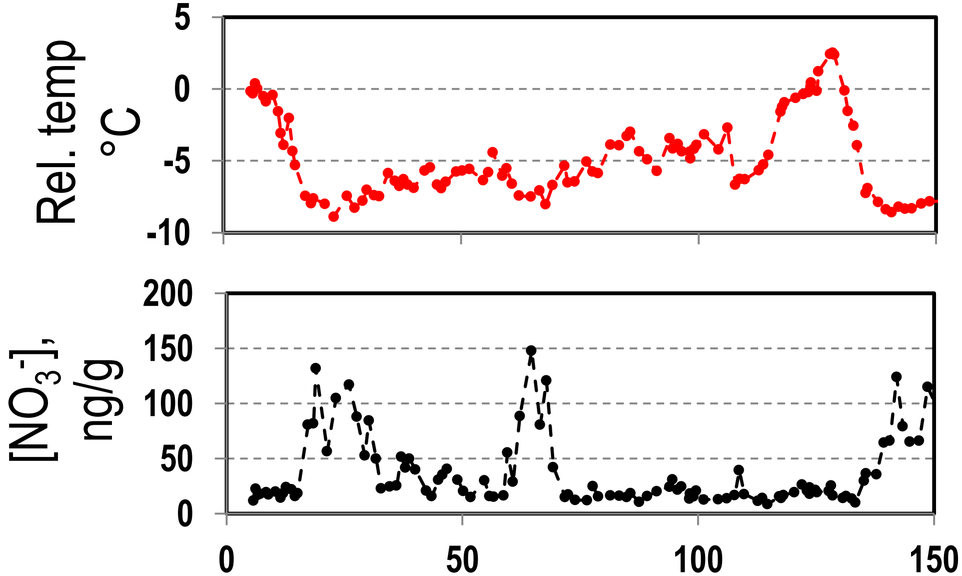
Goal : document the nitrogen cycle over the Antarctic plateau at glacial timescales

- Nitrate in Antarctica
- Stable isotopic ratios in nitrate
- Results from the Vostok ice core
- Implications for the nitrogen budget

Nitrate in Antarctica

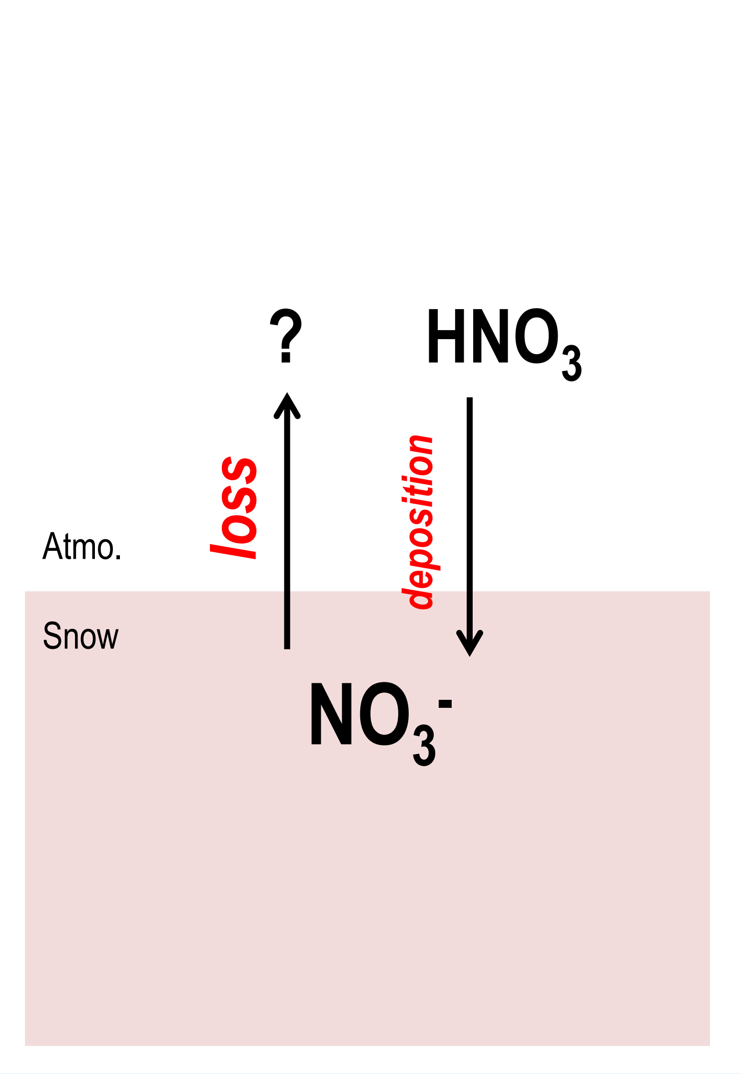


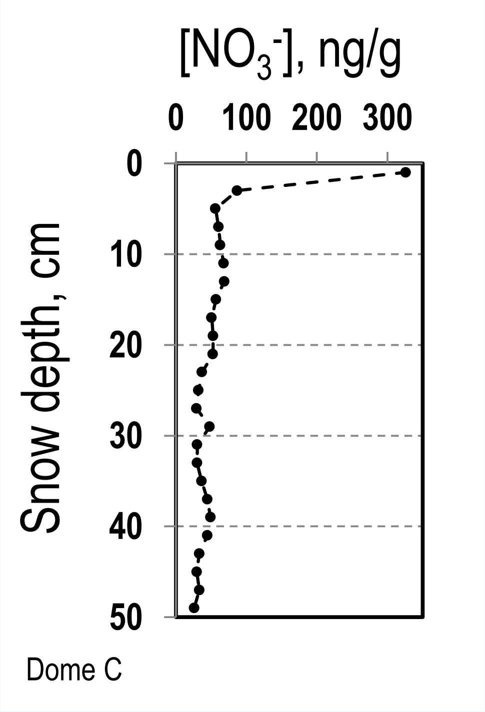




Adapted from Legrand et al., 1999

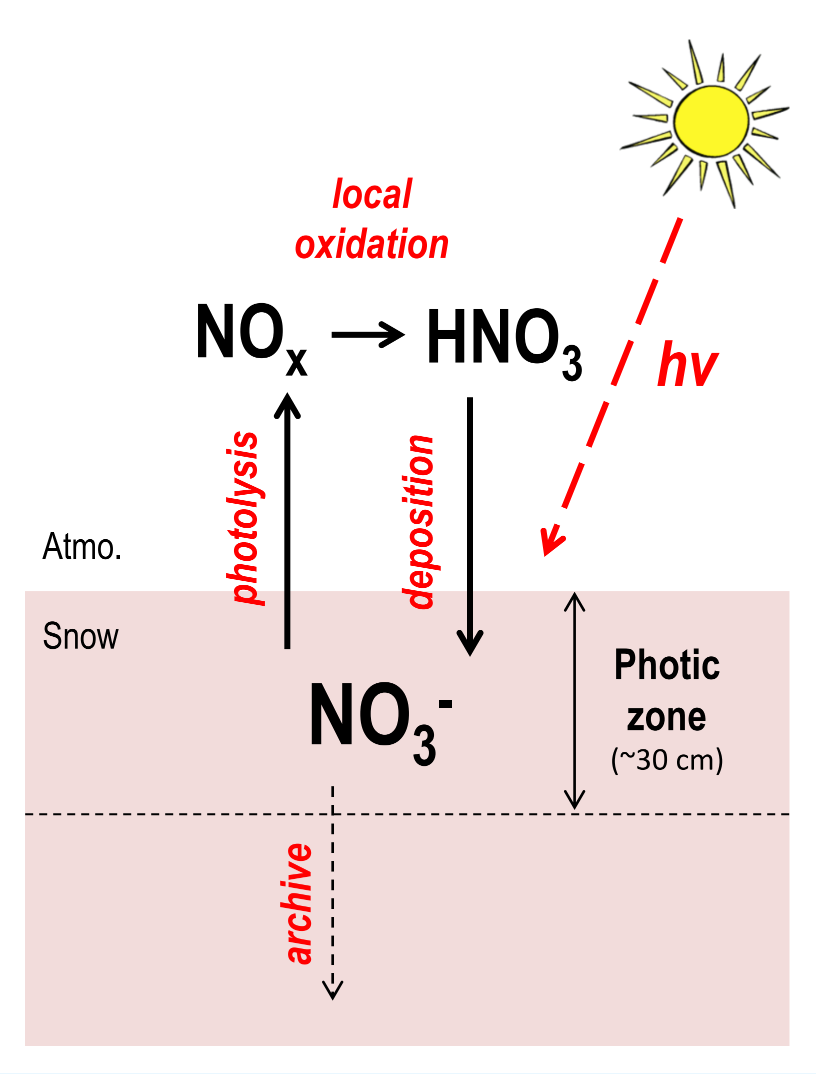
Nitrate in Antarctica





- Strong nitrate mass loss at the surface
- Past nitrate mobility is questioned
  (e.g. Röthlisbgerger et al., 2001)

Nitrate in Antarctica



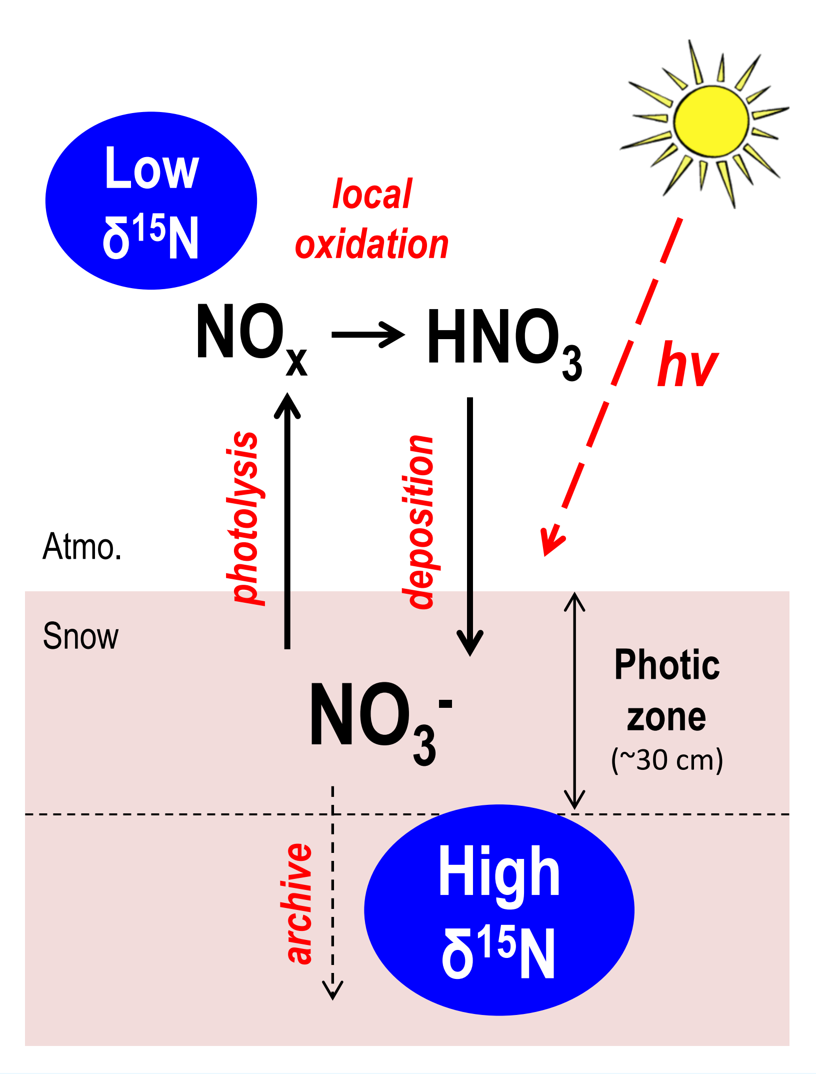
Dominating photolysis at sites low snow accumulation rates :

- Significant NO_x fluxes (e.g. Jones et al., 2001)
- Photolysis can explain 80% of the loss at Dome C (France et al., in prep.)

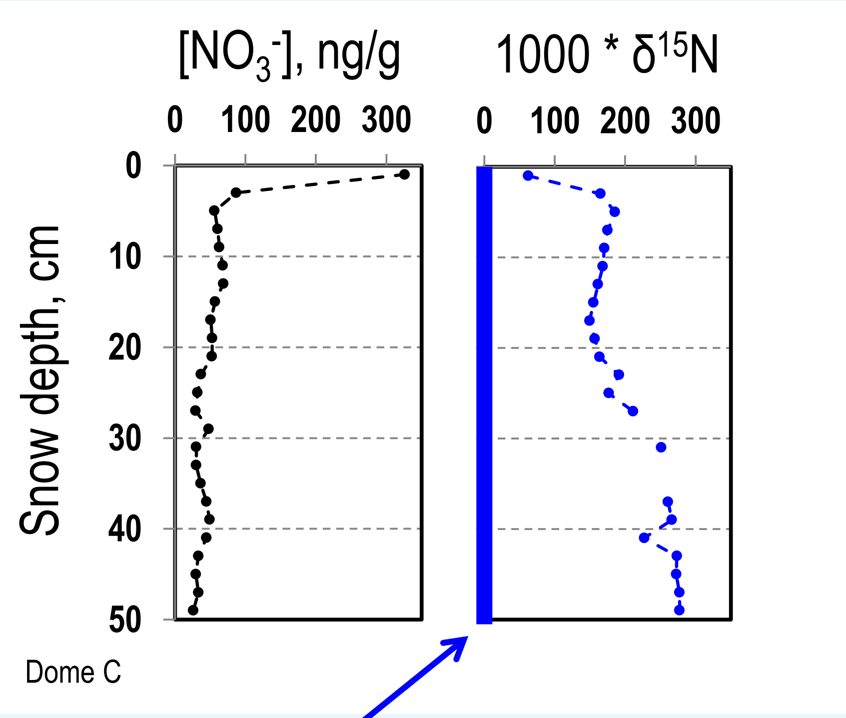
Local NO_x production implies :

- Recycling
- Incorporation of local oxygen atoms

δ15N in nitrate



Photolysis imprint in δ15N in nitrate
(Frey et al., 2009)



Any primary source signature in δ15N (range -10 to 10‰, Morin et al., 2009) is erased

$\Delta^{17}O$ in nitrate

- $\Delta^{17}O$ mostly originates from ozone
- Transfer of $\Delta^{17}O$ during the formation of atmospheric nitrate
- $\Delta^{17}O$ traces the activity of ozone
- Current $\Delta^{17}O$ archived in snow : around 28‰
- Stratospheric winter time signature : 42‰
  (Savarino et al., 2007, Frey et al., 2009)

Isotopic measurements

- 64 selected ice core samples (~30 years), down to 2100 meters

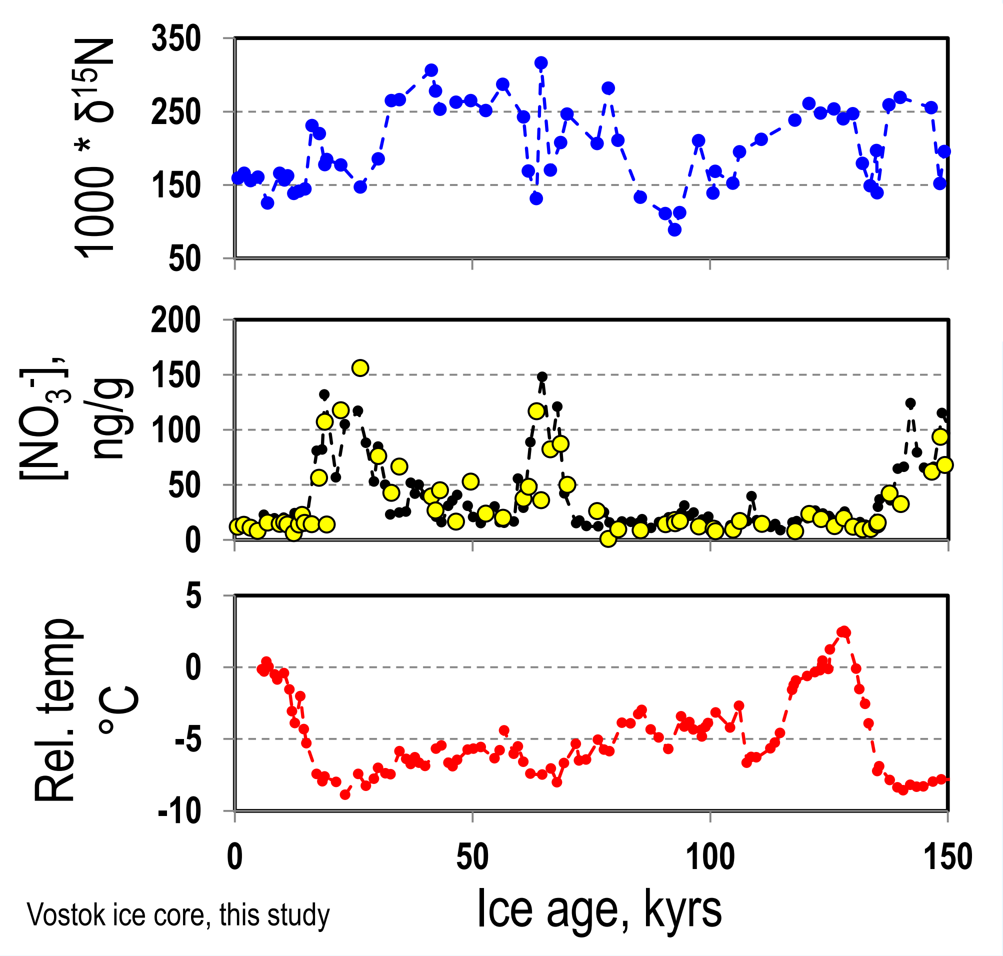
- Over the last 150,000 years (1 ½ climatic cycle)

- Approx. 2 kg of ice per sample

- Modified denitrifier method :
  (Sigman et al., 2001, Kaiser et al., 2007, Morin et al., 2009)

$$NO_3^- \xrightarrow{\textit{Pseudomonas Aureofaciens}} N_2O \xrightarrow{\text{Gold, 900°C + GC}} O_2 + N_2 \xrightarrow{\text{IRMS}} \left| \begin{array}{l} \delta^{15}N \\ \delta^{18}O \\ \Delta^{17}O \end{array} \right.$$

Results & discussion

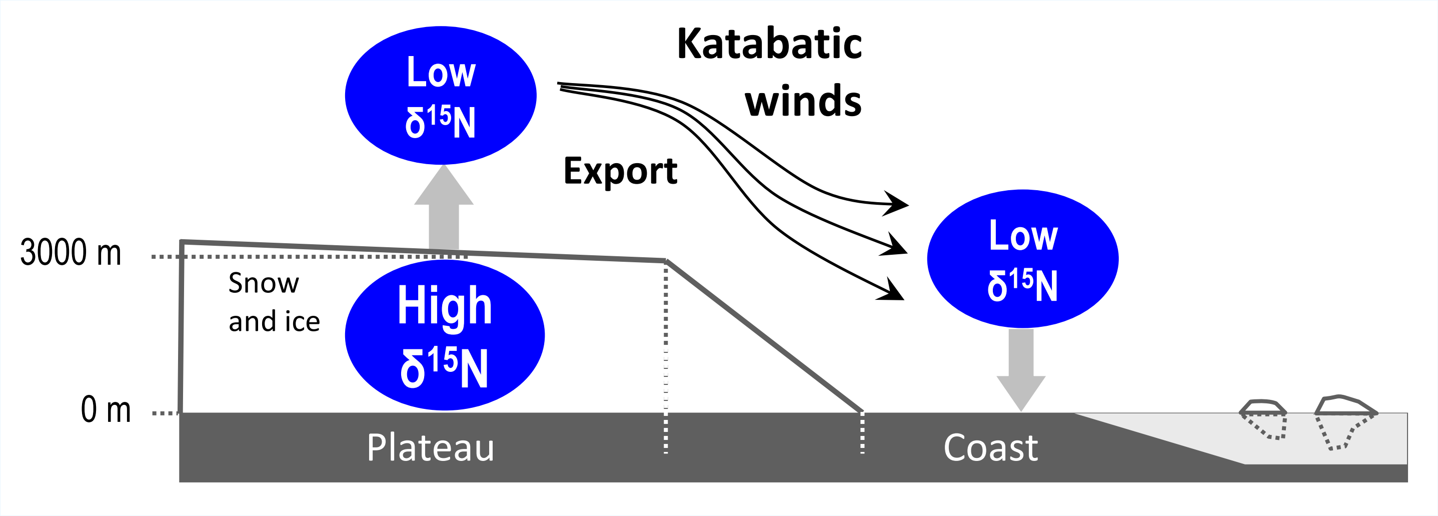


- $\delta^{15}N$ ranges 89 to 316‰ Consistent with the pioneering study of Freyer et al., 1996
- Nitrate loss from snow has not ceased over the last 150,000 years
- Sustained nitrate recycling over this timescale

Results & discussion

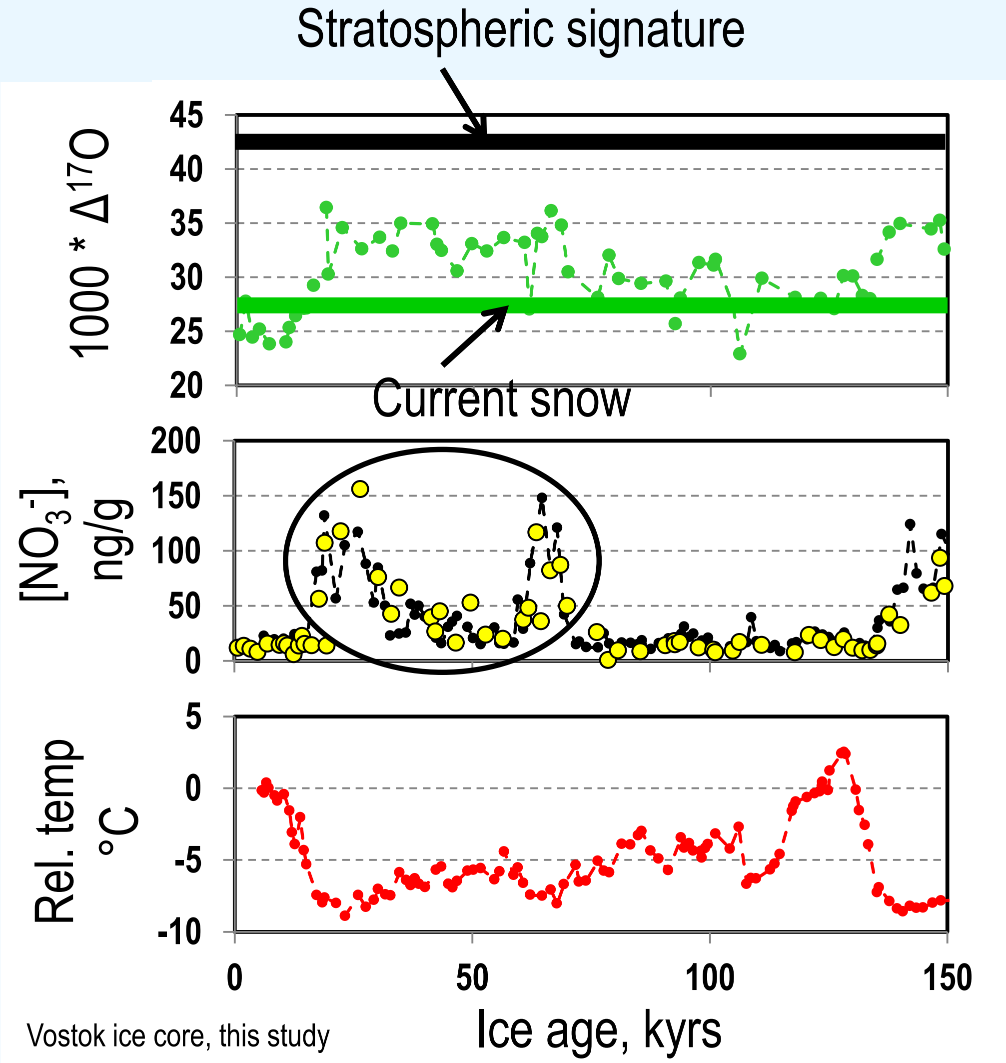
Relevance to the nitrogen cycle in coastal Antarctica :

- Possible greater nitrogen export
- Export features low (negative) $\delta^{15}N$

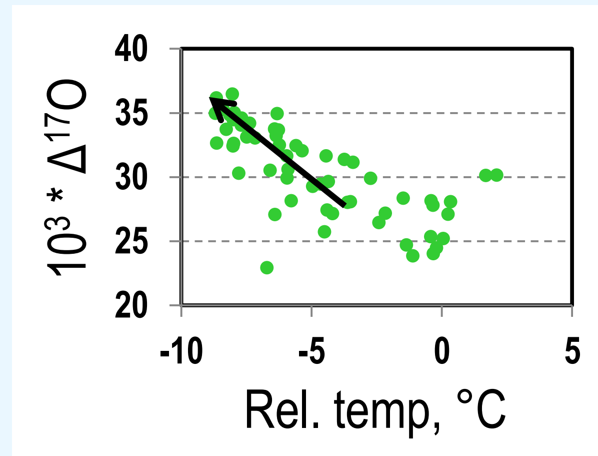


- This source may fuel coastal ecosystems
- Can this explain the extraordinary low $\delta^{15}N$ values observed in coastal soils? (e.g. in the dry valleys, Wada et al., 1981 and Michalski et al., 2005)

Results & discussion



- $\Delta^{17}O$ ranges 23 to 36‰
- Higher values found at lower local temperatures



- Better preservation of the stratospheric signal in cold conditions:
  - Higher stratospheric input
  - Greater local oxidation by stratospheric ozone

Conclusions & perspectives

In the last 150,000 years,

- $\delta^{15}N$ in nitrate reveals sustained surface mass loss
- Subsequent recycling has some relevance to the nitrogen cycle in coastal Antarctica

- High $\Delta^{17}O$ found in cold conditions shows a better preservation of the stratospheric signature
    - Greater primary input ?
    - Direct oxidation by stratospheric ozone

In the coming months…
- Derive the air/snow transfer function

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