Tracing the ozone isotopic anomaly transferred to other atmospheric constituents

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Kaplan workshop, Israel
March 2008

The polar regions: Interests

Arctic

- Ocean surrounded by continent
- Close to pollution sources
- Strong seasonal variations (Temp, light)
- Greenland Ice sheet→ Ice core site

Antarctic

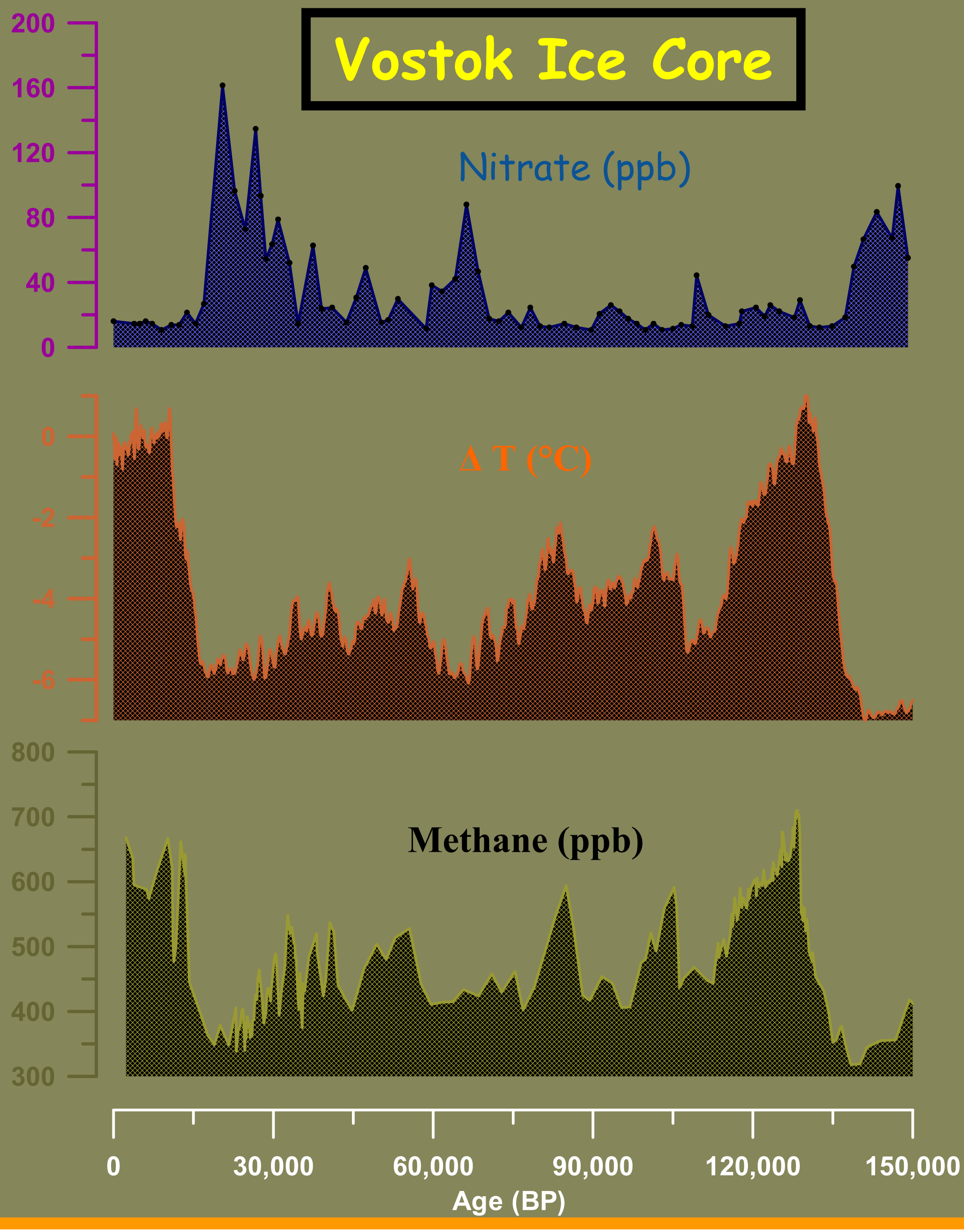
- Continent surrounded by oceans
- Far from pollution sources
- Strong seasonal variations (Temp, light)
- Antarctic Ice sheet→ Ice core site

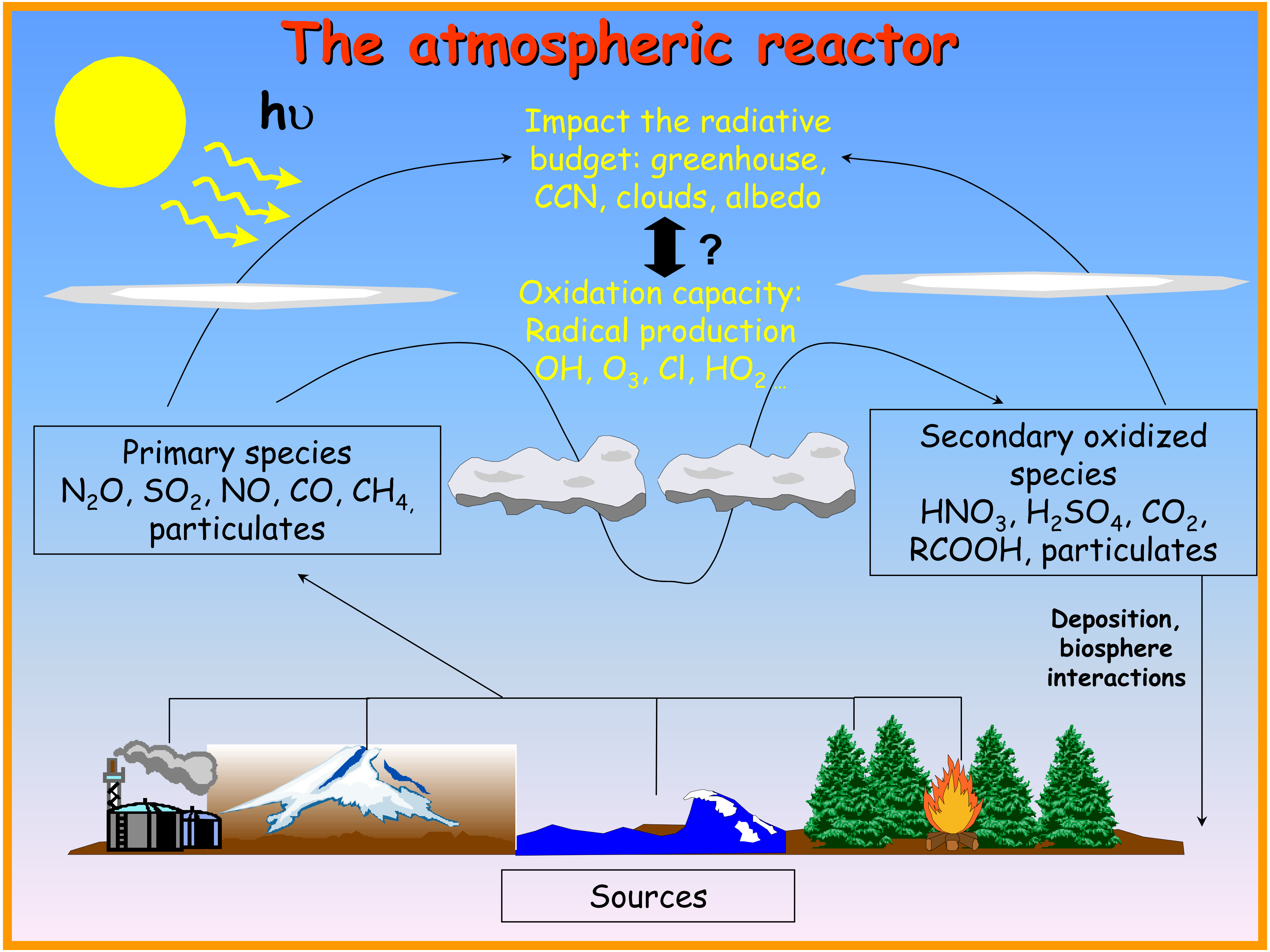
Extreme environment, strong contrast

Unique and exceptional paleoclimatic information from Ice Cores

(Temp., GHGs, Chem.)

… but unable to connect chemistry and climate because radical chemistry missing




The atmospheric reactor
hυ
Impact the radiative budget: greenhouse, CCN, clouds, albedo
?
Oxidation capacity: Radical production OH, O_3, Cl, HO_2…
Primary species N_2O, SO_2, NO, CO, CH_4, particulates
Secondary oxidized species HNO_3, H_2SO_4, CO_2, RCOOH, particulates
Deposition, biosphere interactions
Sources

In the Earth's atmosphere

Oxidation = transfer of oxygen atoms

What is the best probe to study oxidation reaction?

Stable oxygen isotopes as tracer of oxidation pathways

Outlines

- Introduction: Stable isotopes, MDF, MIF
- The NOx/NOy Cycles and First ^{17}O nitrate
- Isotope Anomaly Transfer $O_3 \rightarrow NO_2$
- The Arctic Atmosphere
- The Antarctic Atmosphere

Oxygen Isotope Fractionation

- Three stable isotopes of oxygen: ^{16}O, ^{17}O, ^{18}O

- On Earth and The Moon, the bulk relative abundances are:

^{16}O:	99.759	%
^{17}O:	0.037	%
^{18}O:	0.204	%

→ **2 ratios** $\frac{^{17}O}{^{16}O}$ $\frac{^{18}O}{^{16}O}$

- Diffusion, Phase Changes, Chemical Reactions, etc. act to alter the relative abundances – typically in the decimal places noted in red above: *"Isotope Effects"*

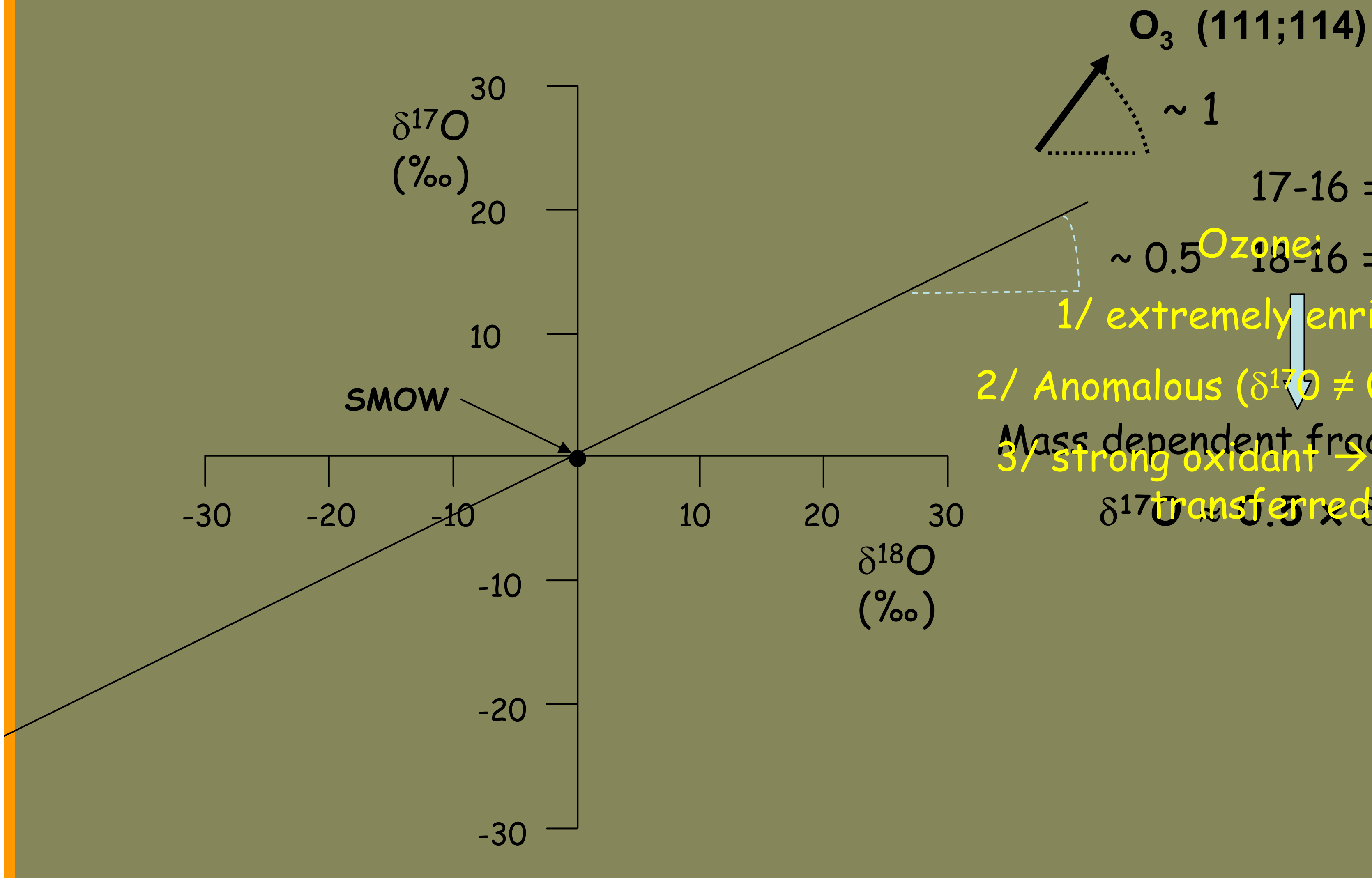
- Such small changes are measured mass spectrometrically:

$$\delta^{17}O = \left[\frac{(^{17}O/^{16}O)_{SAM}}{(^{17}O/^{16}O)_{STD}} - 1\right]$$

in parts per thousand
or "per mil" ≡ ‰

$$\delta^{18}O = \ldots\ldots$$

The Oxygen Isotopic Anomaly



17-16 = 1 amu

18-16 = 2 amu

Mass dependent fractionation

$\delta^{17}O \approx 0.5 \times \delta^{18}O$

Ozone:

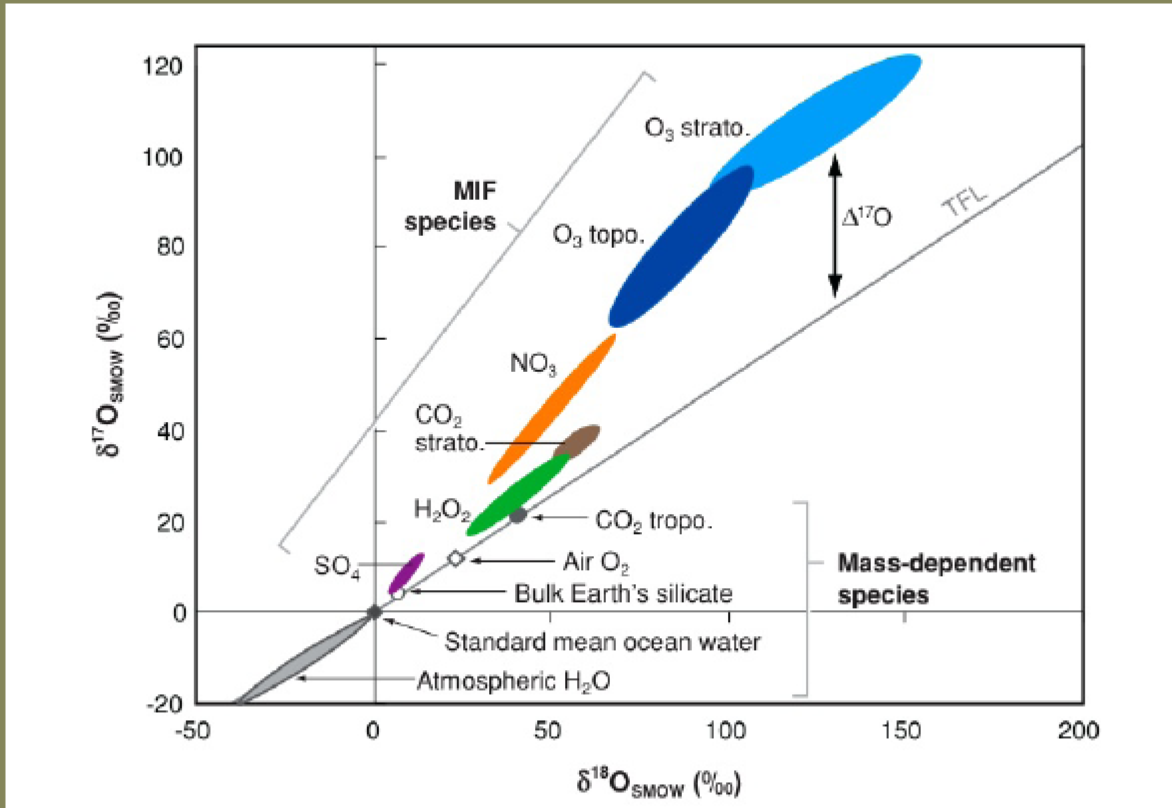
1/ extremely enriched

2/ Anomalous ($\delta^{17}O \neq 0.52\ \delta^{18}O$)

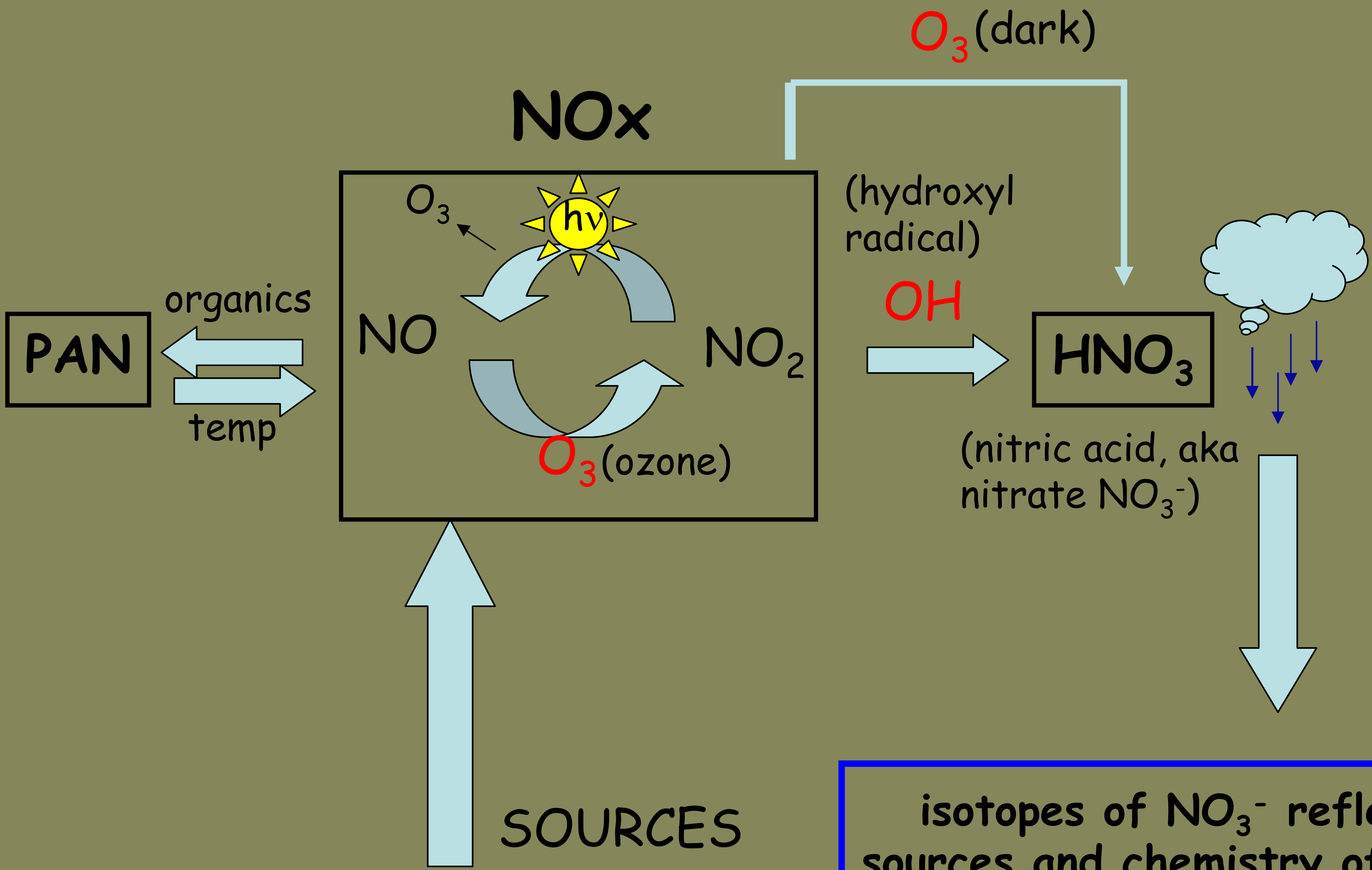
3/ strong oxidant → anomaly transferred

Transfer of O_3 Isotopic Anomaly to Other Constituents

$$O_3\text{-}[O(^1D)] + X \rightarrow XO + O_2$$



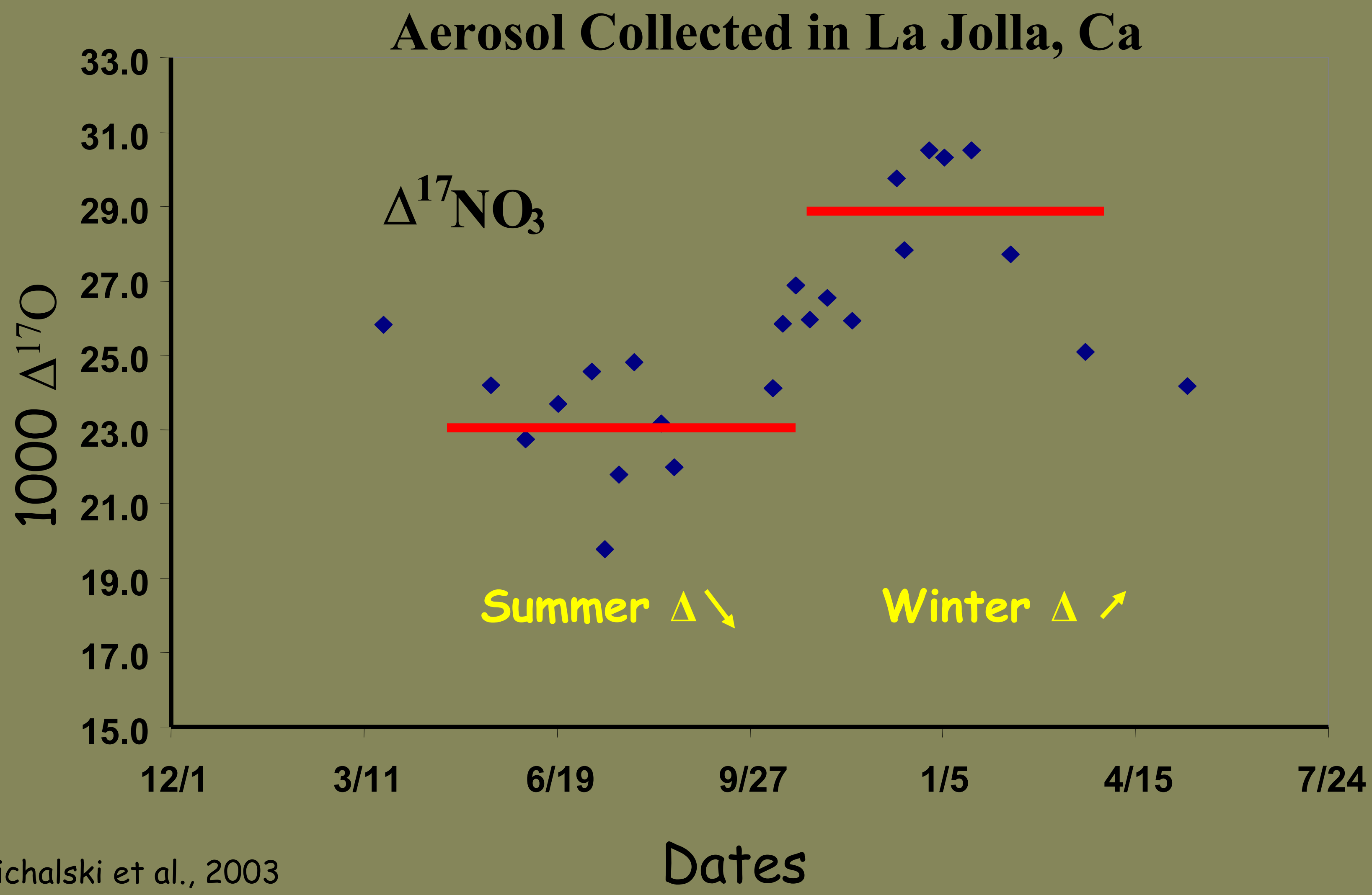
Nitrogen oxides = NOx = $NO+NO_2$



isotopes of NO_3^- reflect sources and chemistry of NO_x

Courtesy: M. Hastings

First Measurements and Observations

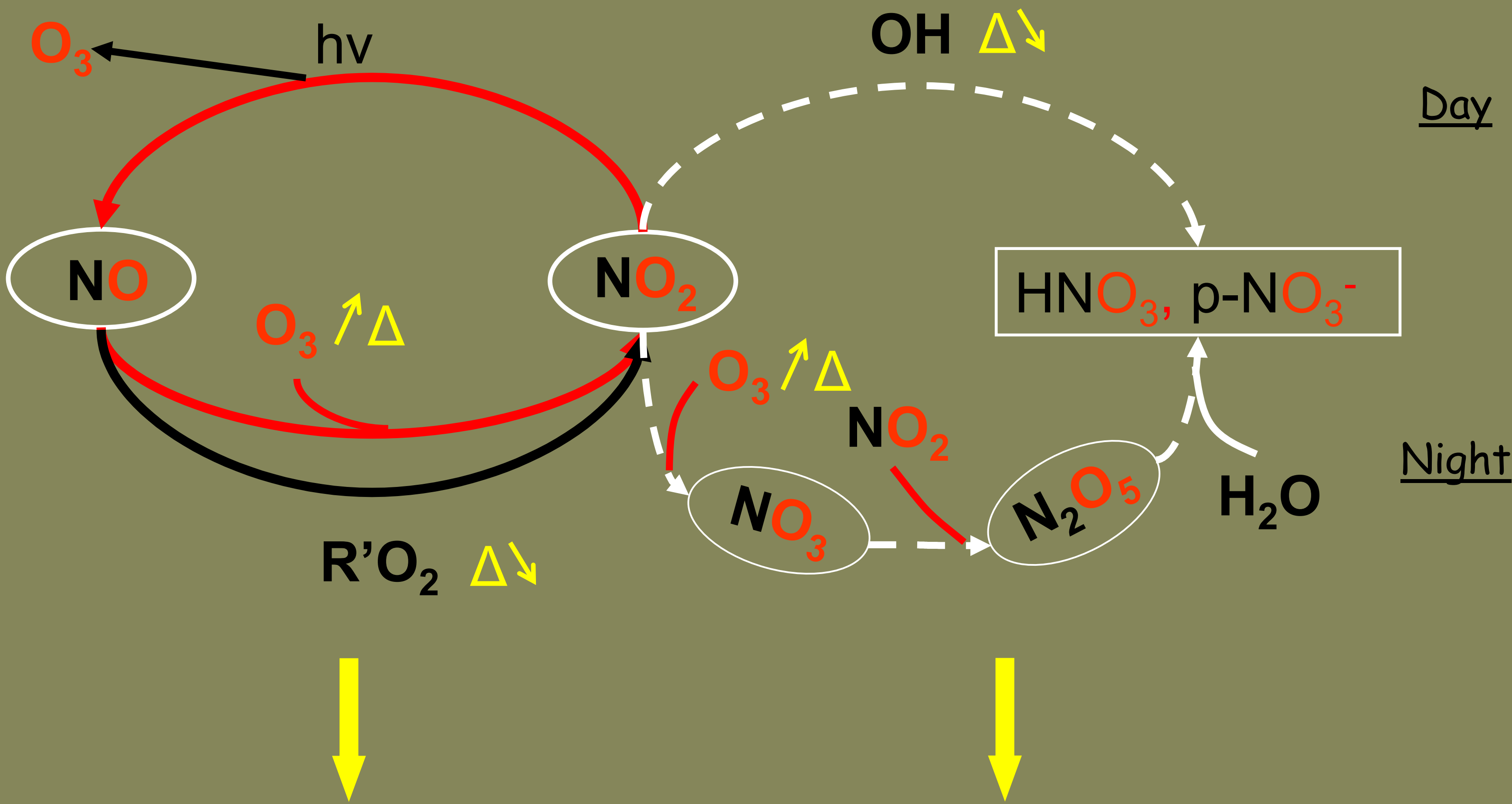


Michalski et al., 2003

The Nitrate Oxidation Scheme

Precursor Photochemical Equilibrium

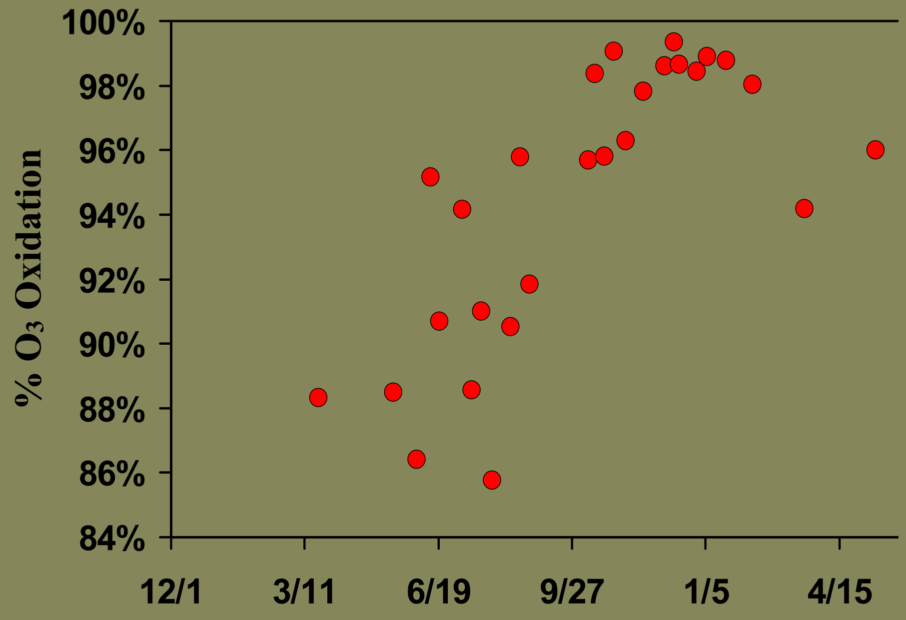
Termination reactions



Isotopic transfer sensitive to ratio α = O_3/R'O_2

Isotopic transfer sensitive to night/day chemistry

$NO_x/O_3/HO_x$ Interactions



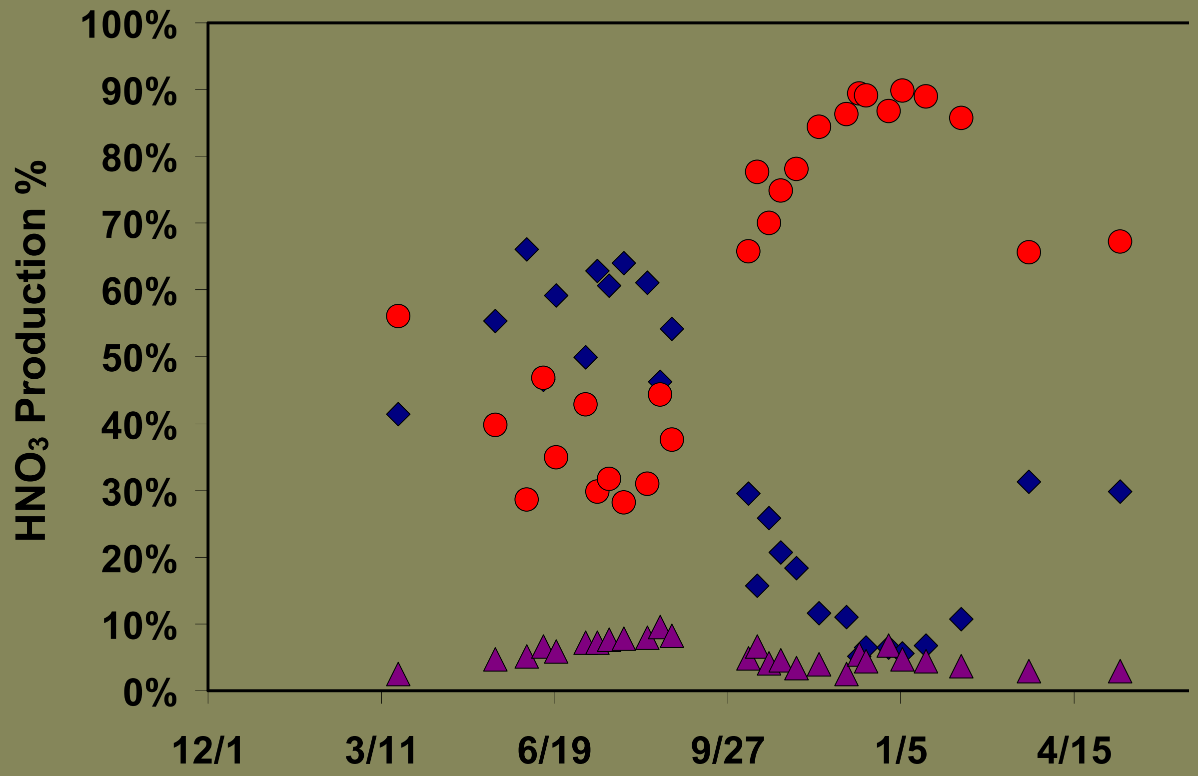
MBL model gives

$$\alpha = \frac{NO + O_3}{\sum NOoxidation}$$

Hypothesis

$NO + O_3 \rightarrow NO_2$	$NO + RO_2 \rightarrow NO_2$
$\Delta^{17}O(NO_2) = \Delta^{17}O_3$	$\Delta^{17}O(NO_2) = \Delta^{17}O(RO_2) = 0$

Termination Reactions



◆ $NO_2 + OH \rightarrow HNO_3$ ● $NO_2 \rightarrow N_2O_5 \rightarrow HNO_3$ ▲ $NO_3 + RH \rightarrow HNO_3$

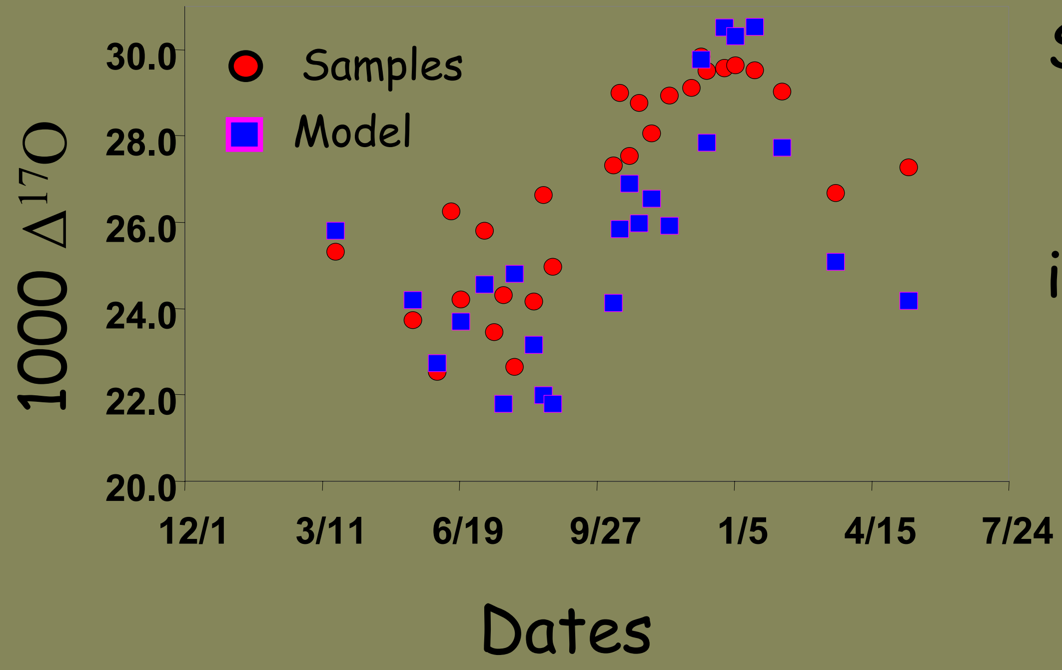
By simple consideration on the origin of the oxygen atom

$\Delta^{17}HNO_3 = \frac{2}{3}\,\Delta^{17}NO_2$

$\Delta^{17}HNO_3 = \frac{2}{3}\,\Delta^{17}NO_2 + 1/6\,\Delta^{17}O_3$

$\Delta^{17}HNO_3 = \frac{2}{3}\,\Delta^{17}NO_2 + \frac{1}{3}\,\Delta^{17}O_3$

Model Results based on Polluted MBL:



Samples well modeled but using a ozone anomaly of 35 ‰ while is only 25‰ in the troposphere and on unverified assumptions notably the anomaly transfer

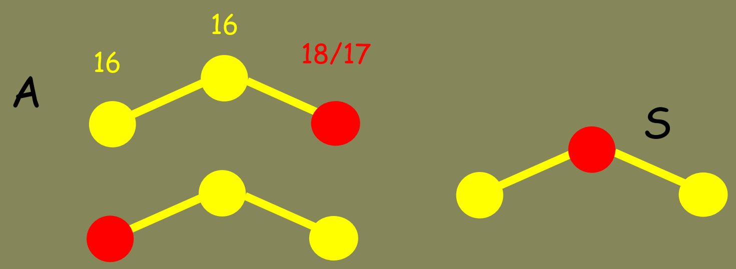
$\Delta^{17}O(NO_2) = \Delta^{17}O(O_3)$

We have studied the NO + O_3 isotope transfer in laboratory

$NO + O_3 \rightarrow NO_2 + O_2$

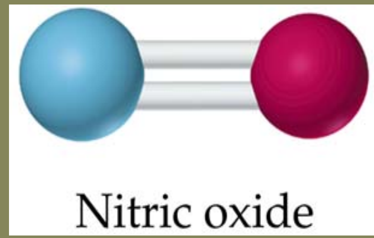
To Predict isotopic transfer

Intramolecular distribution of O_3



Atom abstracted by NO

Lab Set Up



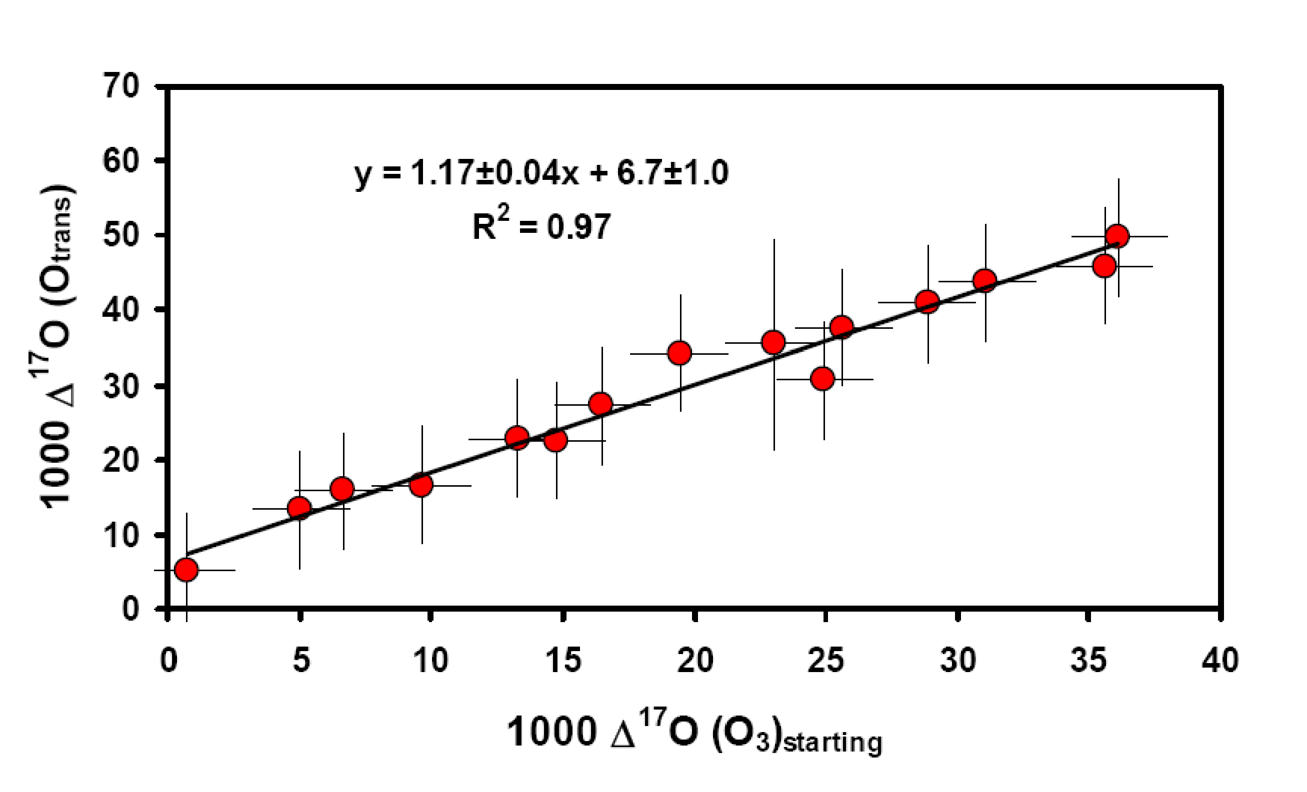
- Ozone made by electrical discharge, by varying P & T → control isotopic anomaly
- NO of known isotope composition is mixed with O_3 in a 10 l dark cell at stoichiometry quantity
- Products NO_2 and O_2 are collected & analyzed for O isotopes

Knowing isotope composition of reactants and products

→ anomaly transfer

→ mechanism of reaction

Macroscopic view: Anomaly Transfer from O_3 to NO_2



$\Delta^{17}O(NO_2) = 1.17\ \Delta^{17}O(O_3) + 6.7$

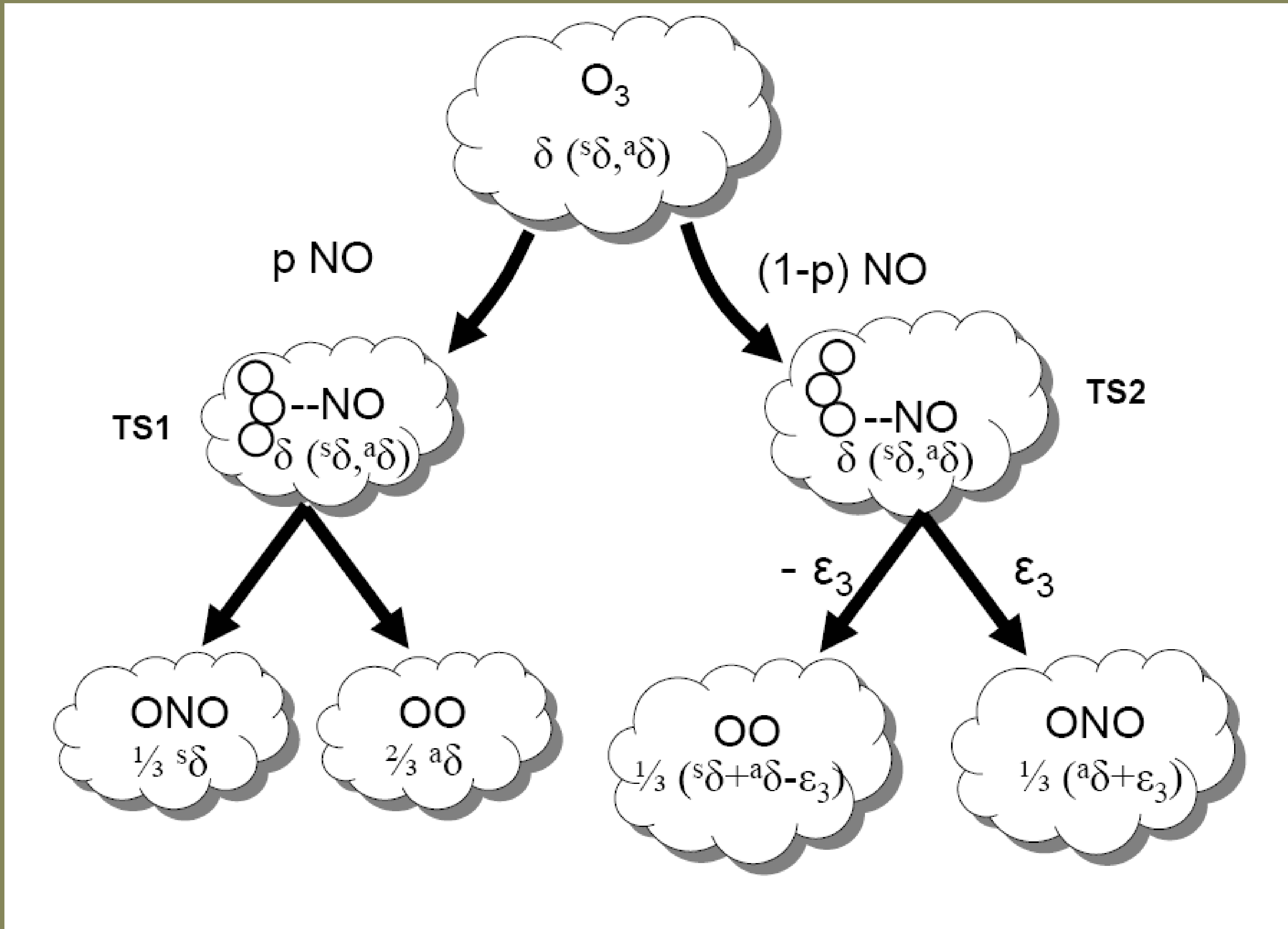
Michalski

$\Delta^{17}O(NO_2) = \Delta^{17}O(O_3) = 35$ ‰

Our result using $\Delta^{17}O(O_3) = 25$ ‰

$\Delta^{17}O(NO_2) = 36$ ‰

Microscopic view: Mechanism

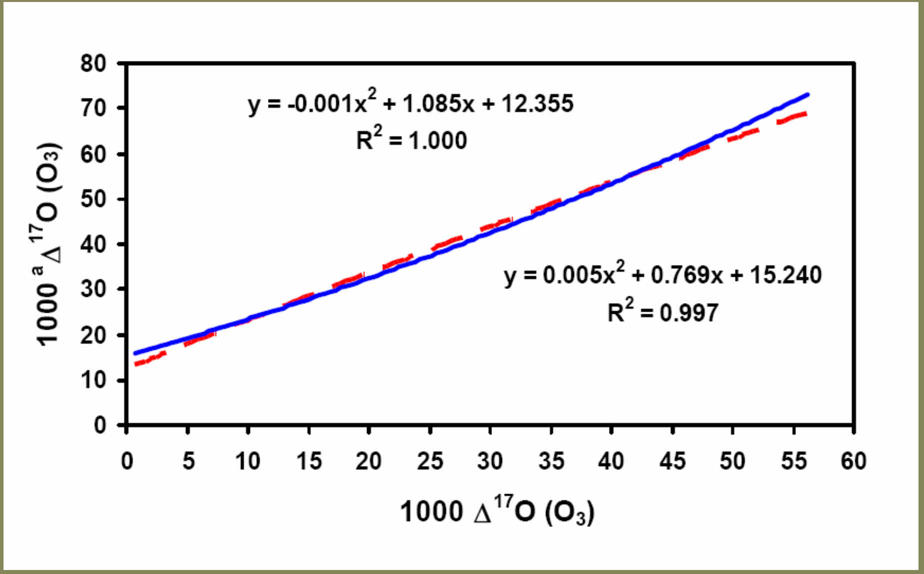


$$\Delta^{17}O(O_{trans}) = p\ s\Delta^{17}O(sO_3) + (1\text{-}p)\ a\Delta^{17}O(aO_3)$$

With p: probability to react with central atom

Three unknowns but only two are independents:

p, $(s\Delta^{17}O, a\Delta^{17}O)$

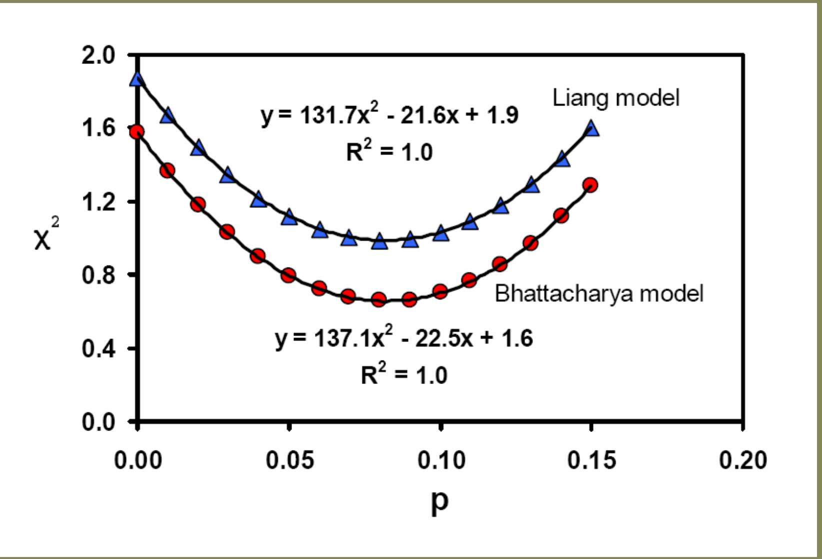


Models of internal ozone isotope distribution

(Bhattacharya et , 2008, Liang et al, 2006)

Connect bulk $\Delta^{17}O$ with $a\Delta^{17}O$ & $s\Delta^{17}O$

Statistical treatment



$p = 8 \pm 5$ %

Central atom takes part in the reaction !!!

<u>Supported by</u>:

- the non-Arrhenius behavior of the kinetic rate reaction → two step mechanisms
- Molecular beam reactions showing two preferential scattering angles for products

Molecular Beam Scattering Experiment

(van den Ende et al., 1982)

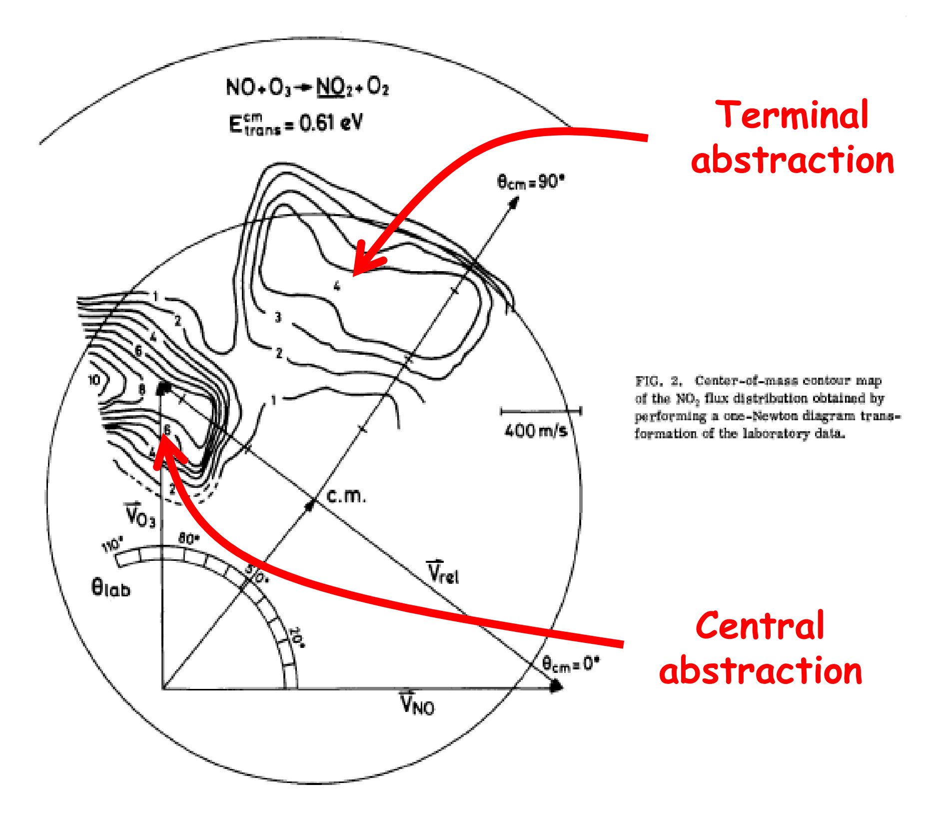


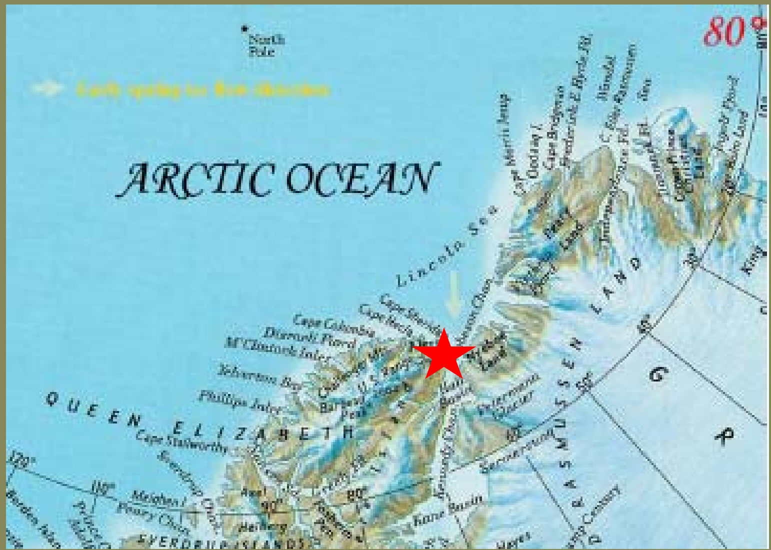
FIG. 2. Center-of-mass contour map of the NO_2 flux distribution obtained by performing a one-Newton diagram transformation of the laboratory data.

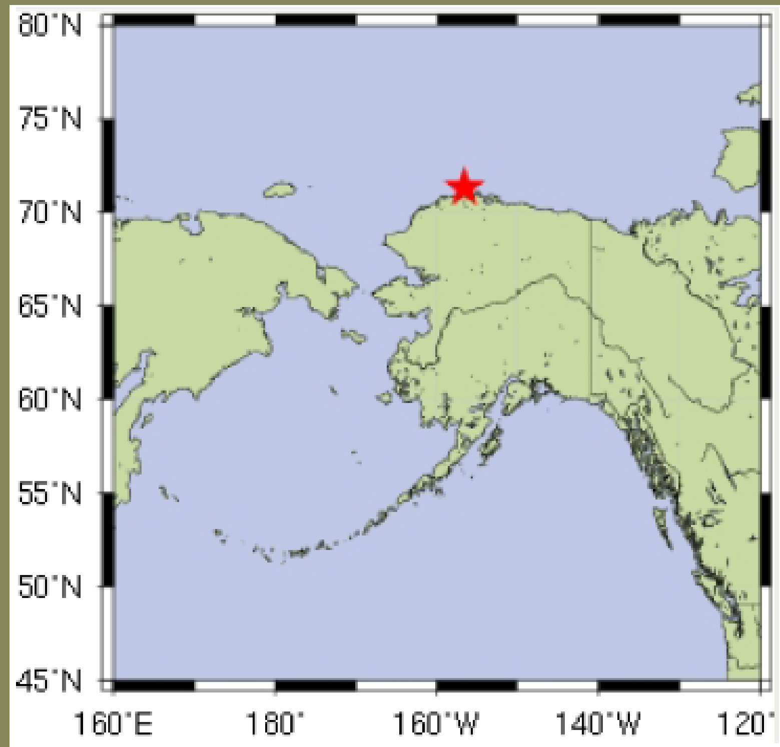
Quote "… the NO molecule with "head" orientation strikes in a central collision (…) abstracts the central O atom to form NO_2 and recoils backwards.

In a second configuration, …, the NO molecule strikes in a broad side tail orientation, …, abstracts an end-O-atom and recoil sideways …..

No branching ratio given !!!!!

Sampling Sites





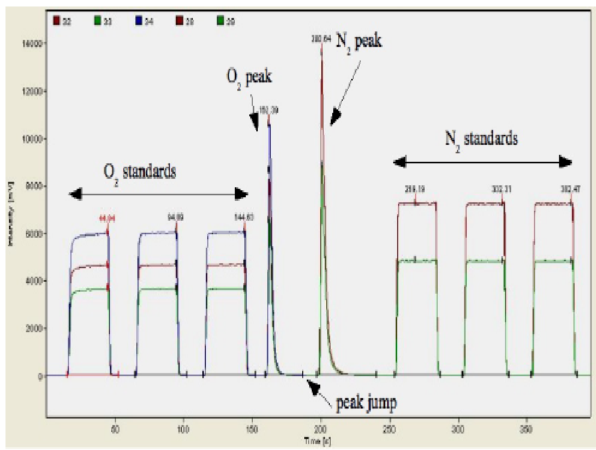
Total inorganic nitrate aerosols collected on glass fiber filter

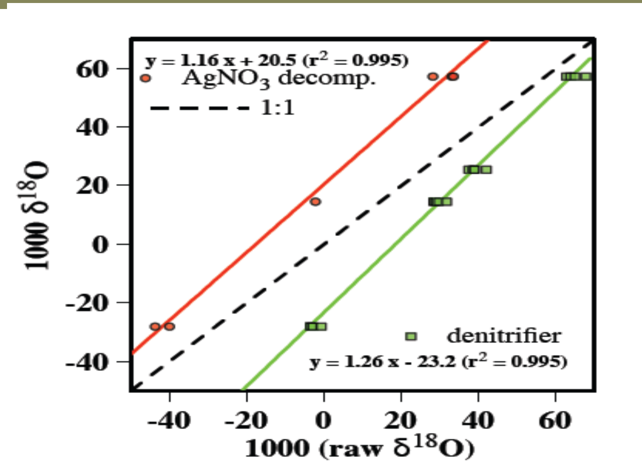
Analytical procedure

Based on the denitrifier method (Sigman, Caciotti, Kaiser)

100 nmol of nitrate + 10 ml of denitrifying bacteria solution → Produce N_2O → Flushed with He to Au catalyst → Produce $N_2 + O_2$ → To MS: $\delta^{15}N$, $\delta^{17}O$, $\delta^{18}O$

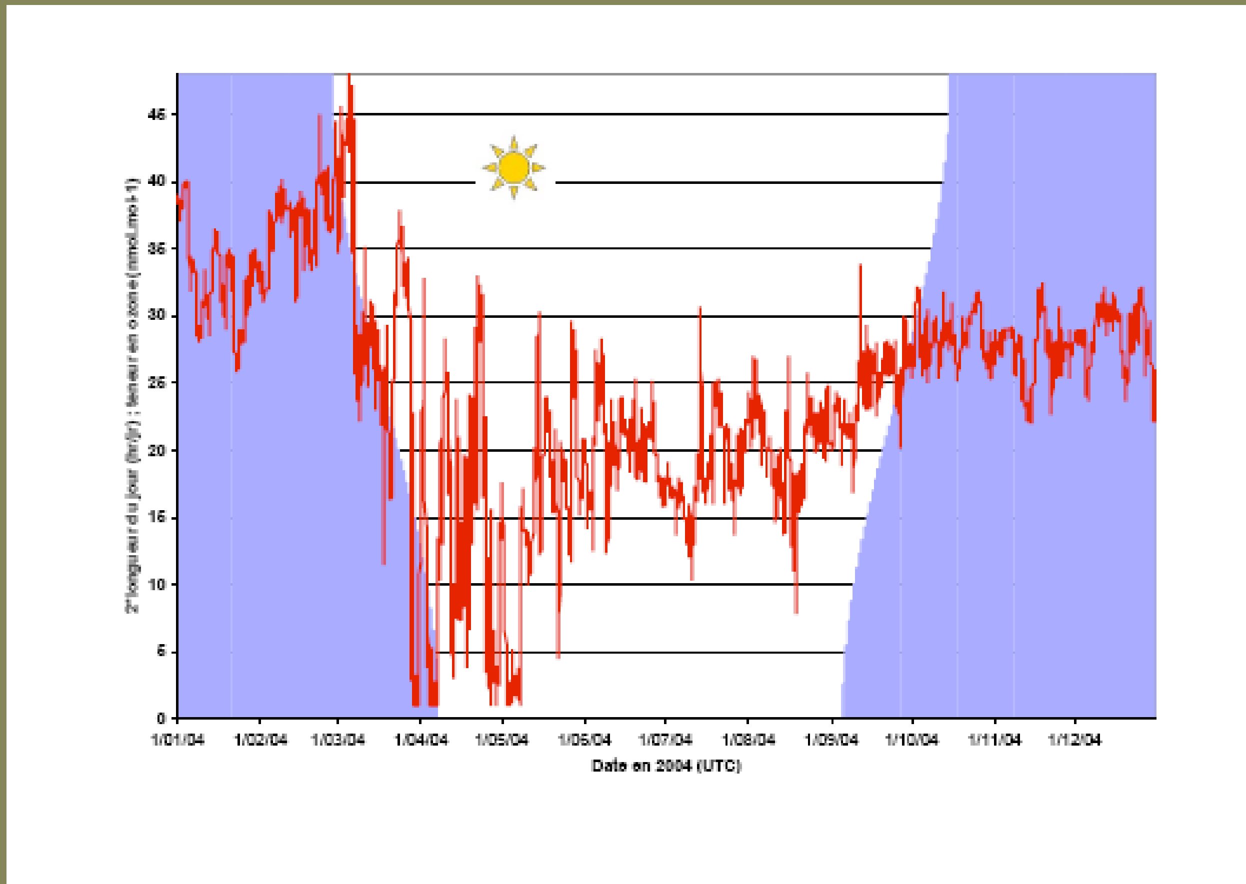
Not quantitative → calibration





Ozone Depletion Events (ODEs)

High Arctic, at polar sunrise → destruction of surface ozone



"Bromine explosion"

Bromine source

$BrO + HO_2 \rightarrow HOBr_g + O_2$

$HOBr_g \rightarrow HOBr_{aq}$

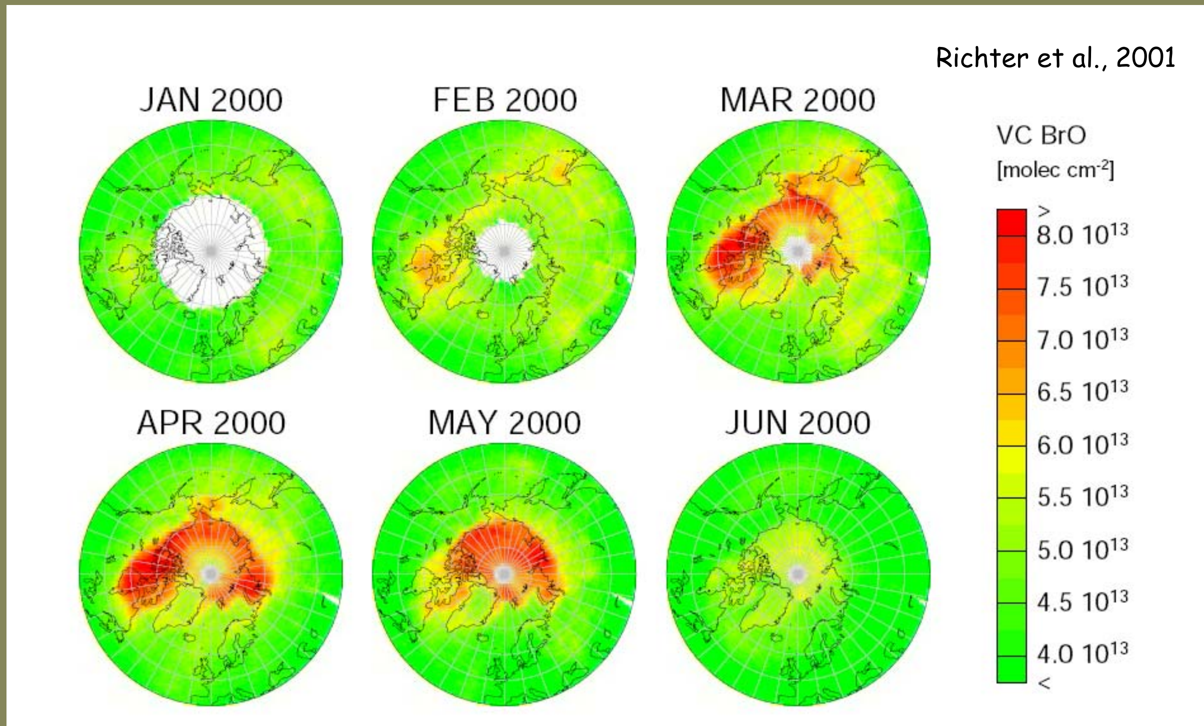
$HOBr_{aq} + Br^- + H^+ \rightarrow Br_{2aq} + H_2O$

$Br_{2aq} \rightarrow Br_{2g}$

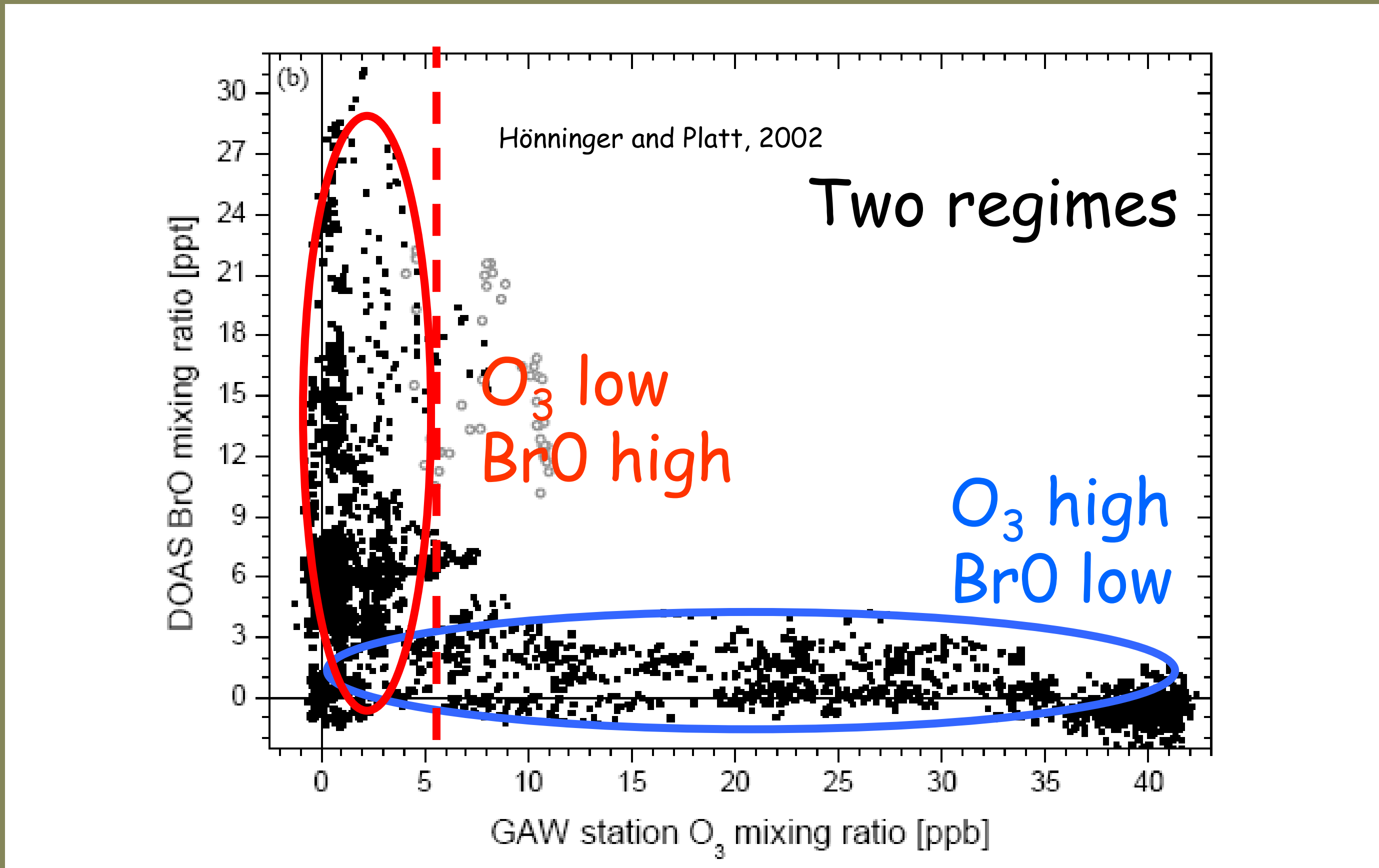
Catalytic destruction

$Br + O_3 \rightarrow BrO$

$BrO + BrO \rightarrow 2Br + O_2$



BrO/O_3 Relationship



Ozone and BrO cannot coexist both at high concentration

Sea salt chemistry

↓

$O_3 + Br \rightarrow BrO + O_2$

$BrO + BrO \rightarrow 2Br + O_2$

} Effect 1: Destroy O_3, Δ ↘

But ....

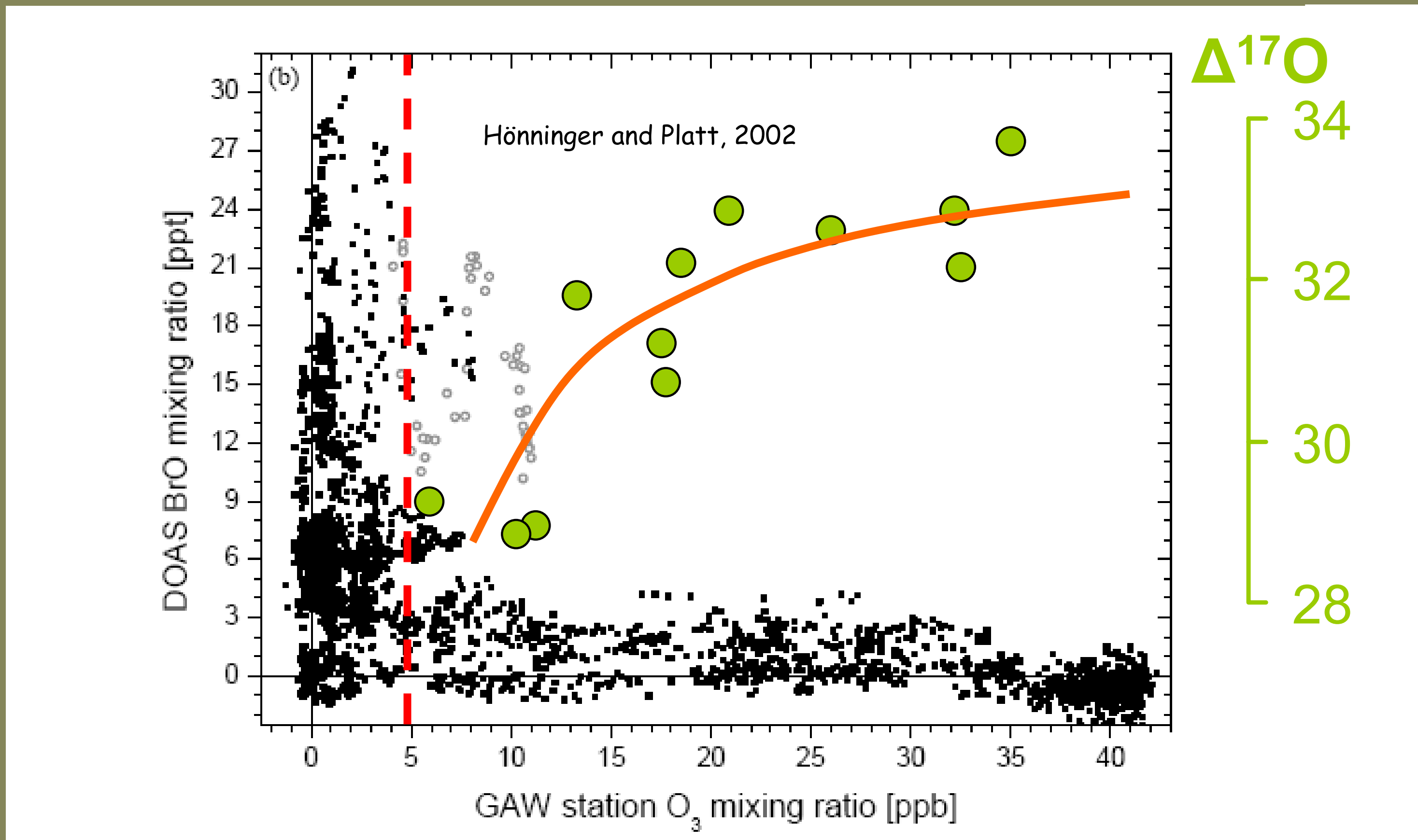
$BrO + NO \rightarrow Br + NO_2$

$BrO + NO_2 \rightarrow HNO_3 + ...$

} Effect 2: Transfer Δ ↗

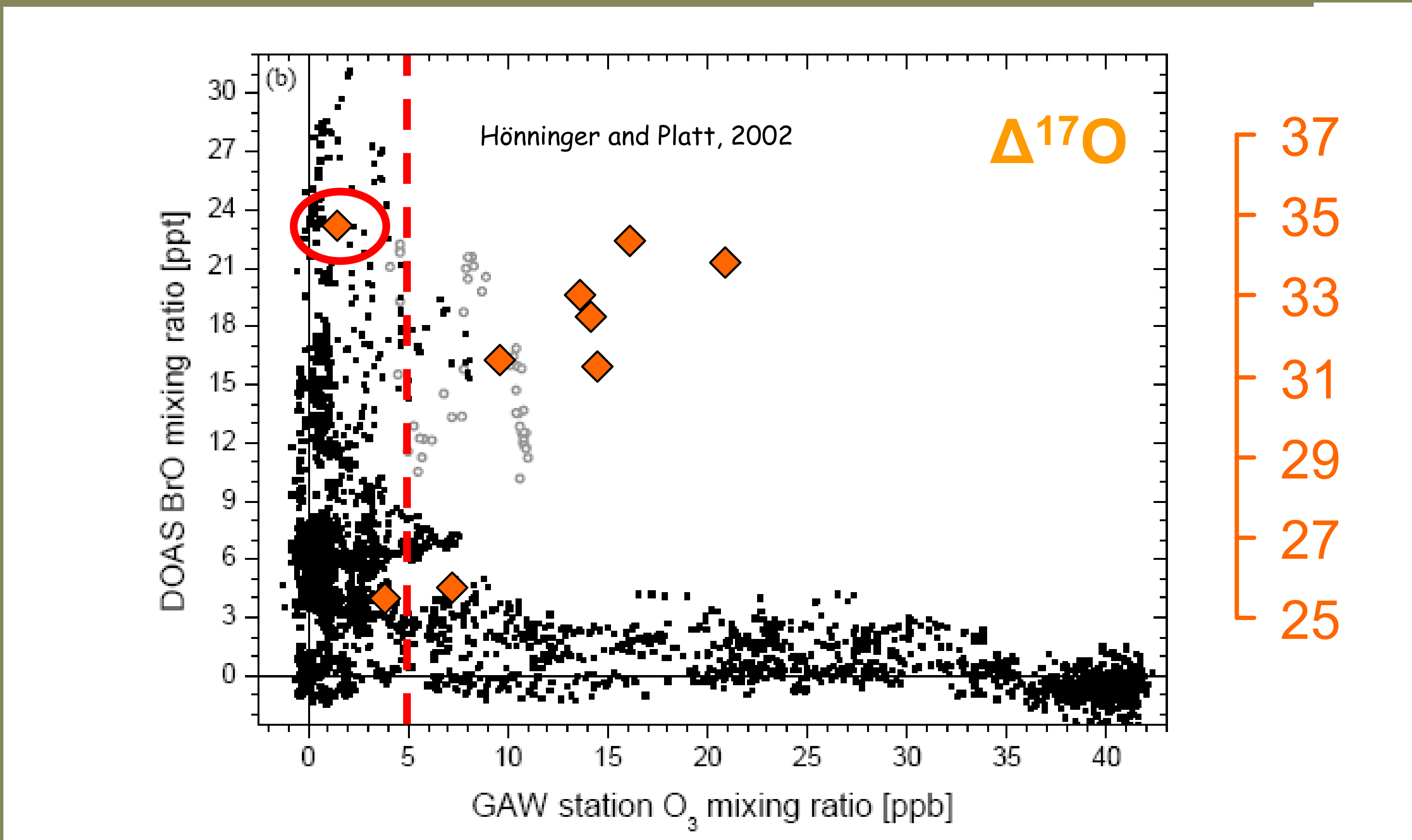
⇨ Bromine : 2 opposing effects

OOTI 2004 - Alert, Canada



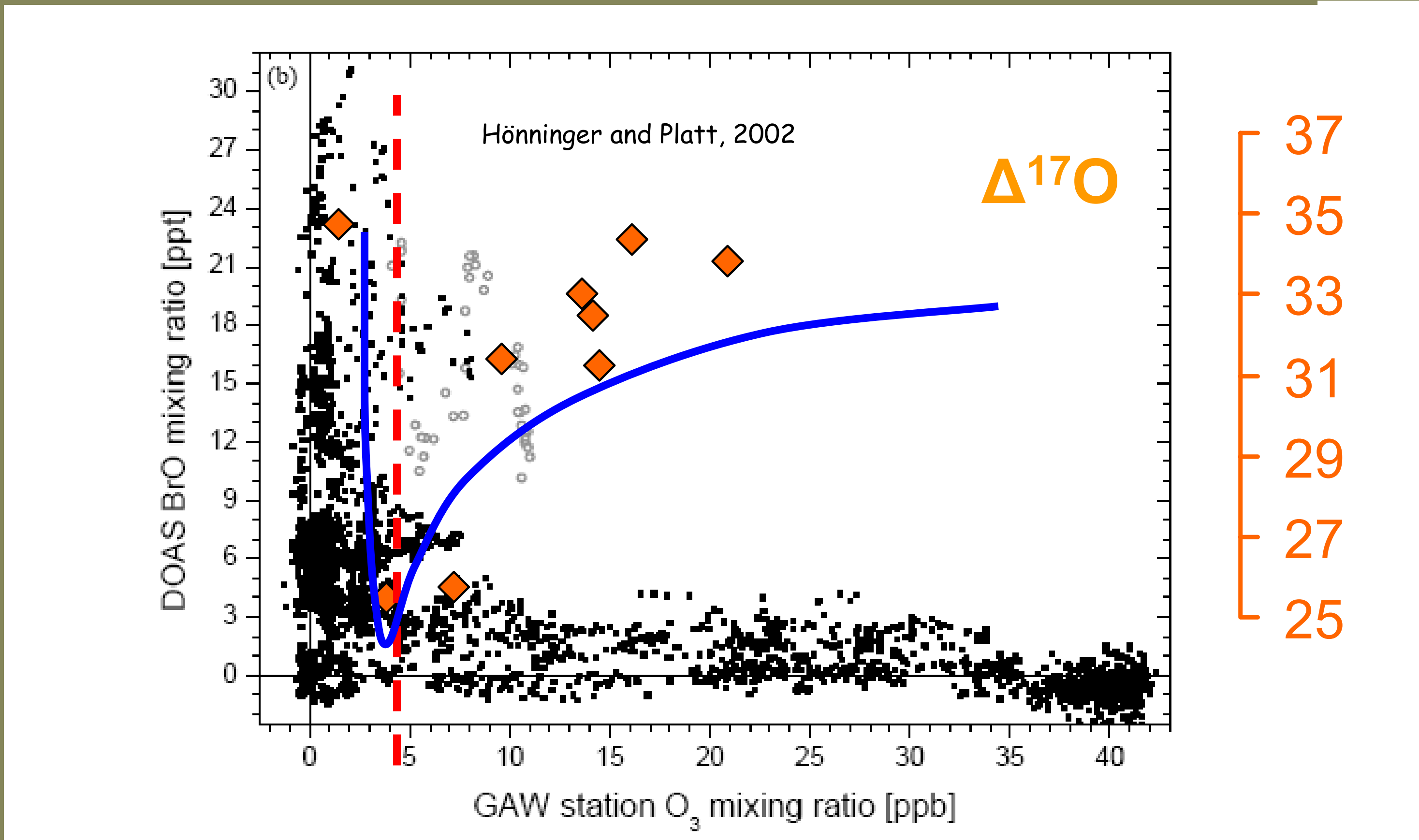
$$\Delta^{17}O_{NO_3^-} = \frac{2}{3}\frac{\Delta^{17}O_{NO-O_3}k_{NO+O_3}[O_3]}{k_{NO+O_3}[O_3]+k_{NO+HO_2}[HO_2]} + cst$$

IOANA 2005 – Barrow, Alaska



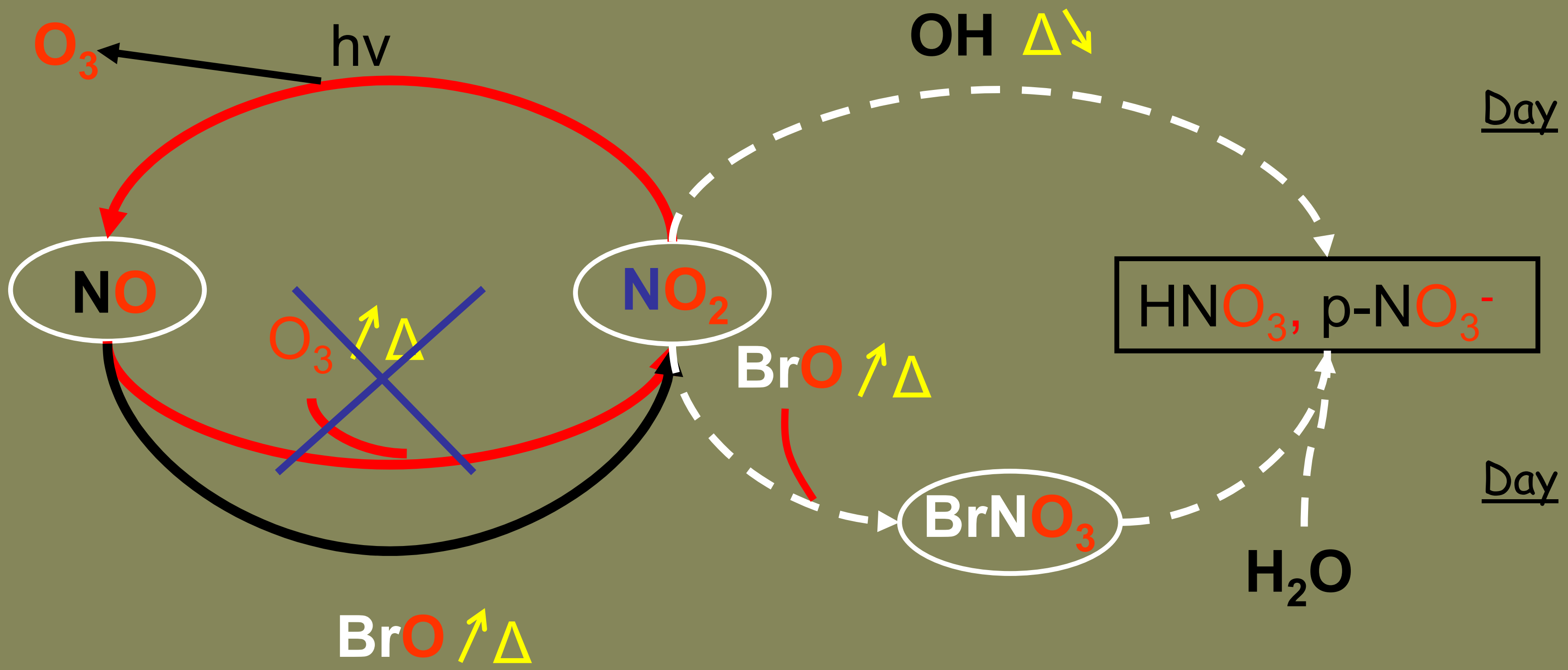
Indicates a change in the way nitrate is formed

IOANA 2005 - Barrow, Alaska



$$\Delta^{17}O_{NO_3^-} = \frac{2}{3}\frac{\Delta^{17}O_{NO-O_3}k_{NO+O_3}[O_3]+\Delta^{17}O_{NO-BrO}k_{NO+BrO}[BrO]}{k_{NO+O_3}[O_3]+k_{NO+HO_2}[HO_2]+k_{NO+BrO}[BrO]}+cst$$

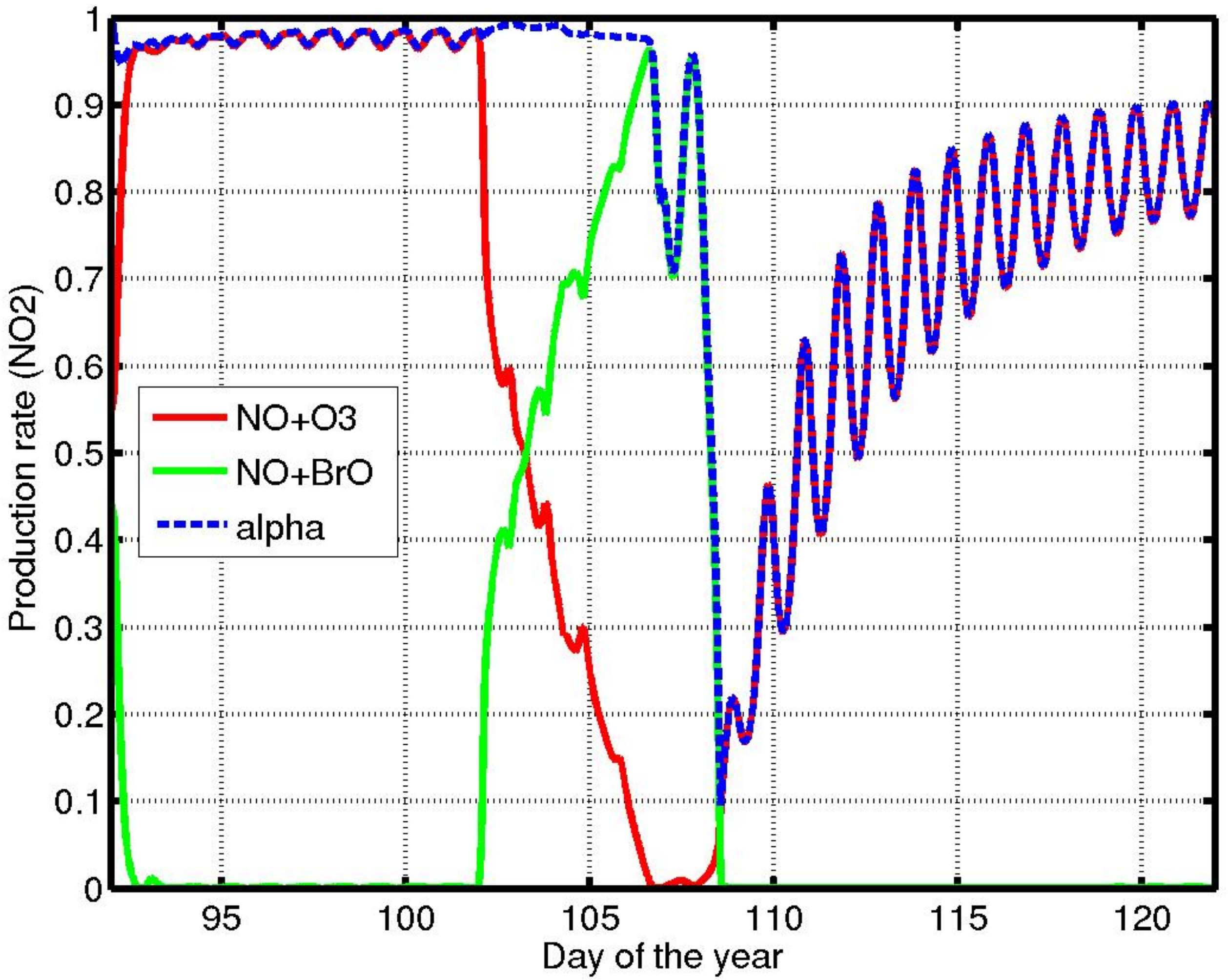
Strong ODE chemistry

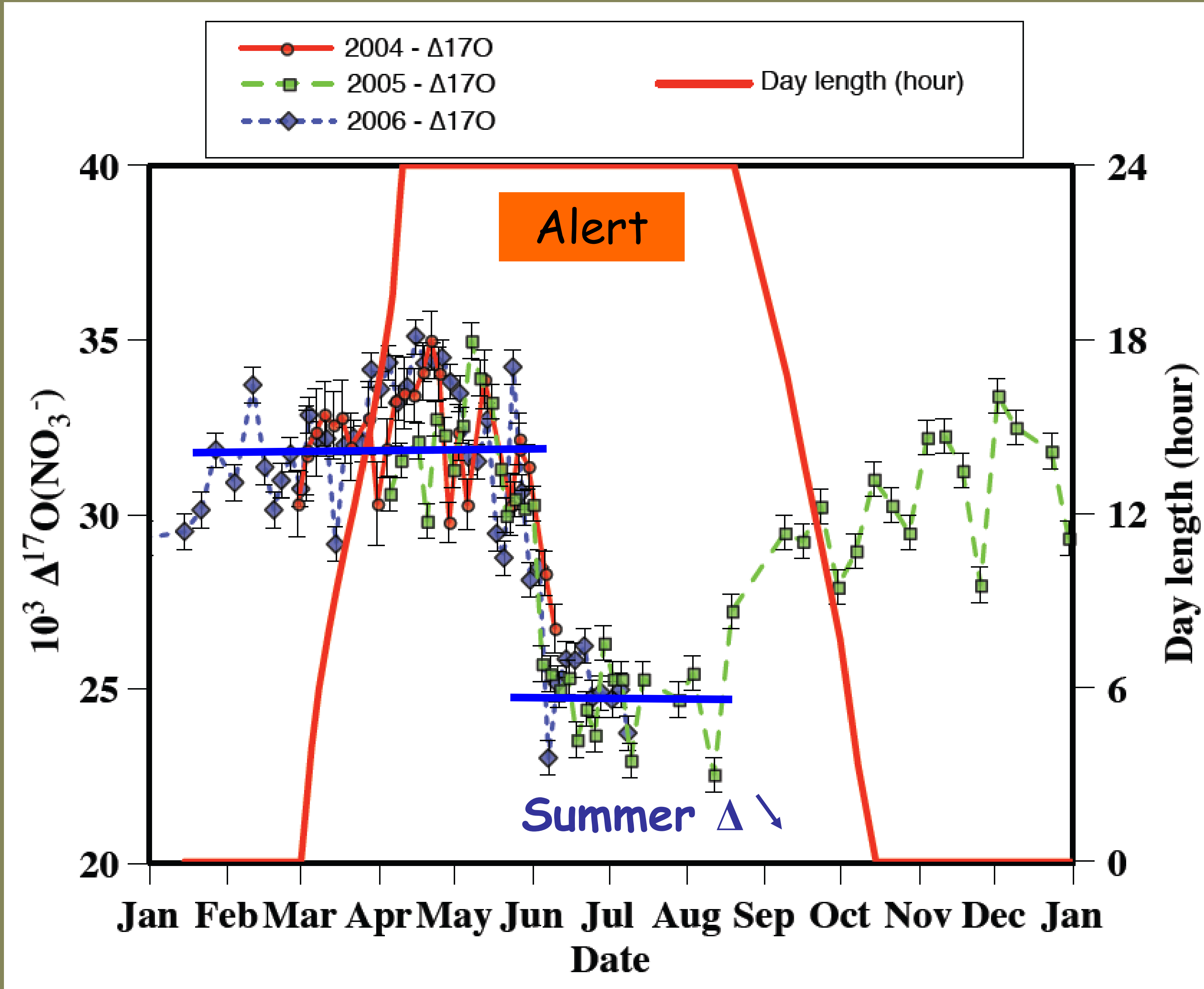


BrO replaces O_3 in oxidizing NO

$BrNO_3$ branch 100 times faster than OH branch

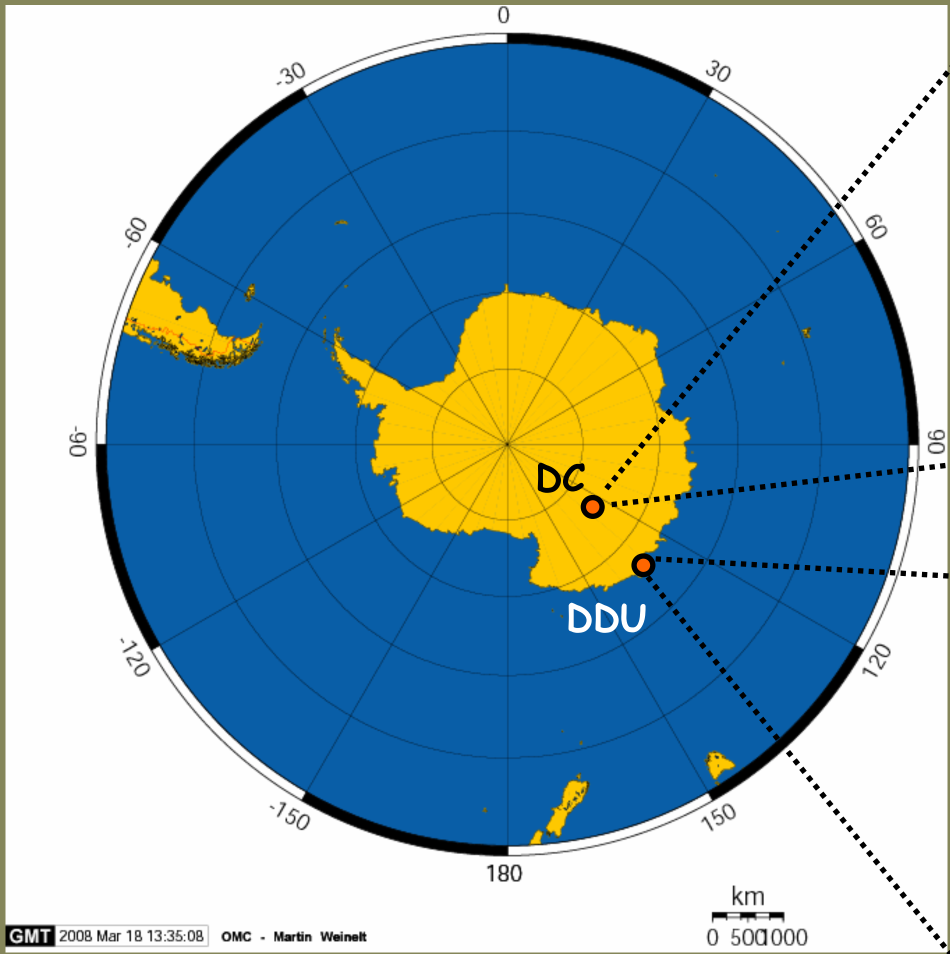
Box model ODE



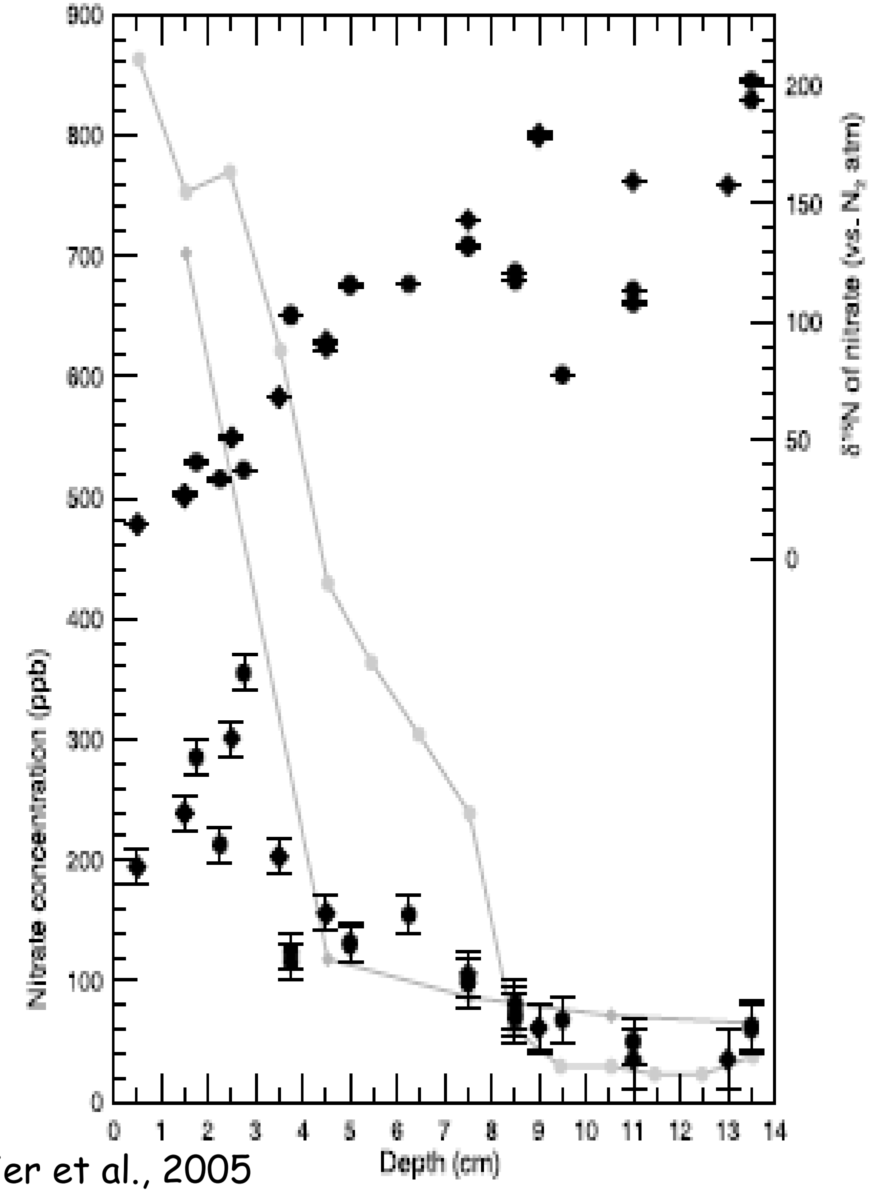


2004 - Δ17O
2005 - Δ17O
2006 - Δ17O
Day length (hour)
Alert
Summer Δ ↘
40
35
30
25
20
24
18
12
6
0
10³ Δ¹⁷O(NO₃⁻)
Day length (hour)
Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec Jan
Date

The Antarctic Environment



^{15}N Snow surface DC

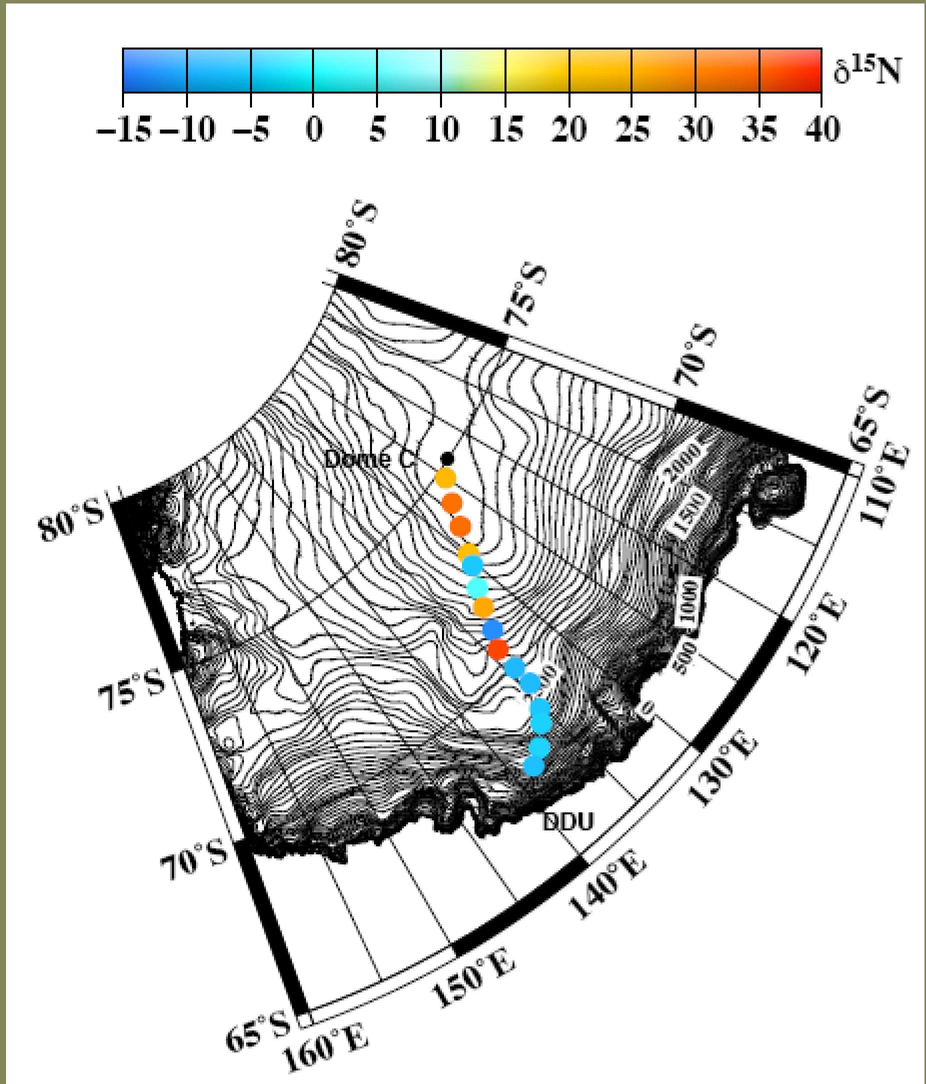


Blunier et al., 2005

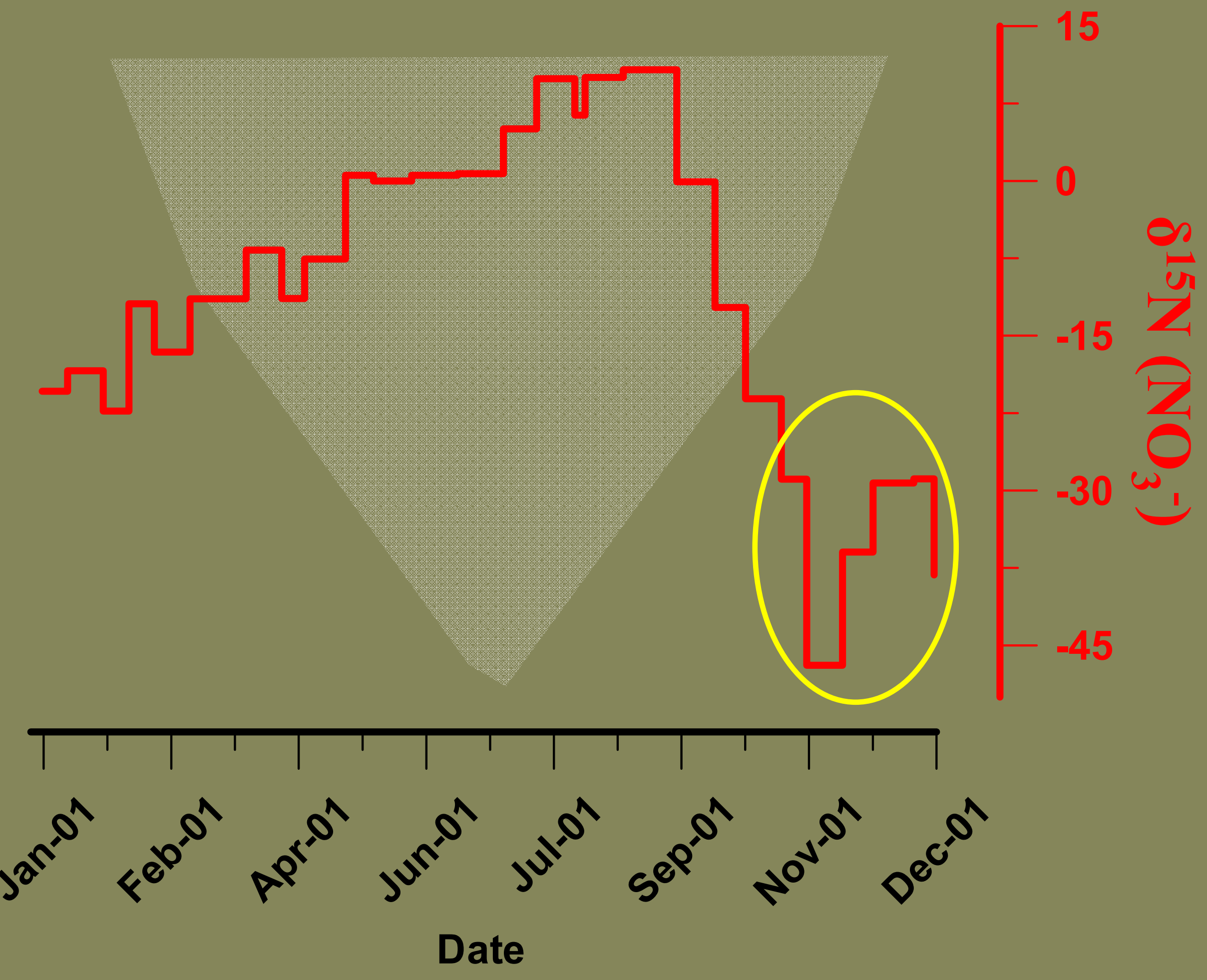
Strong post depositional effects

- 95% of NO_3^- lost
- ^{15}N jumps for 0 to 200 ‰

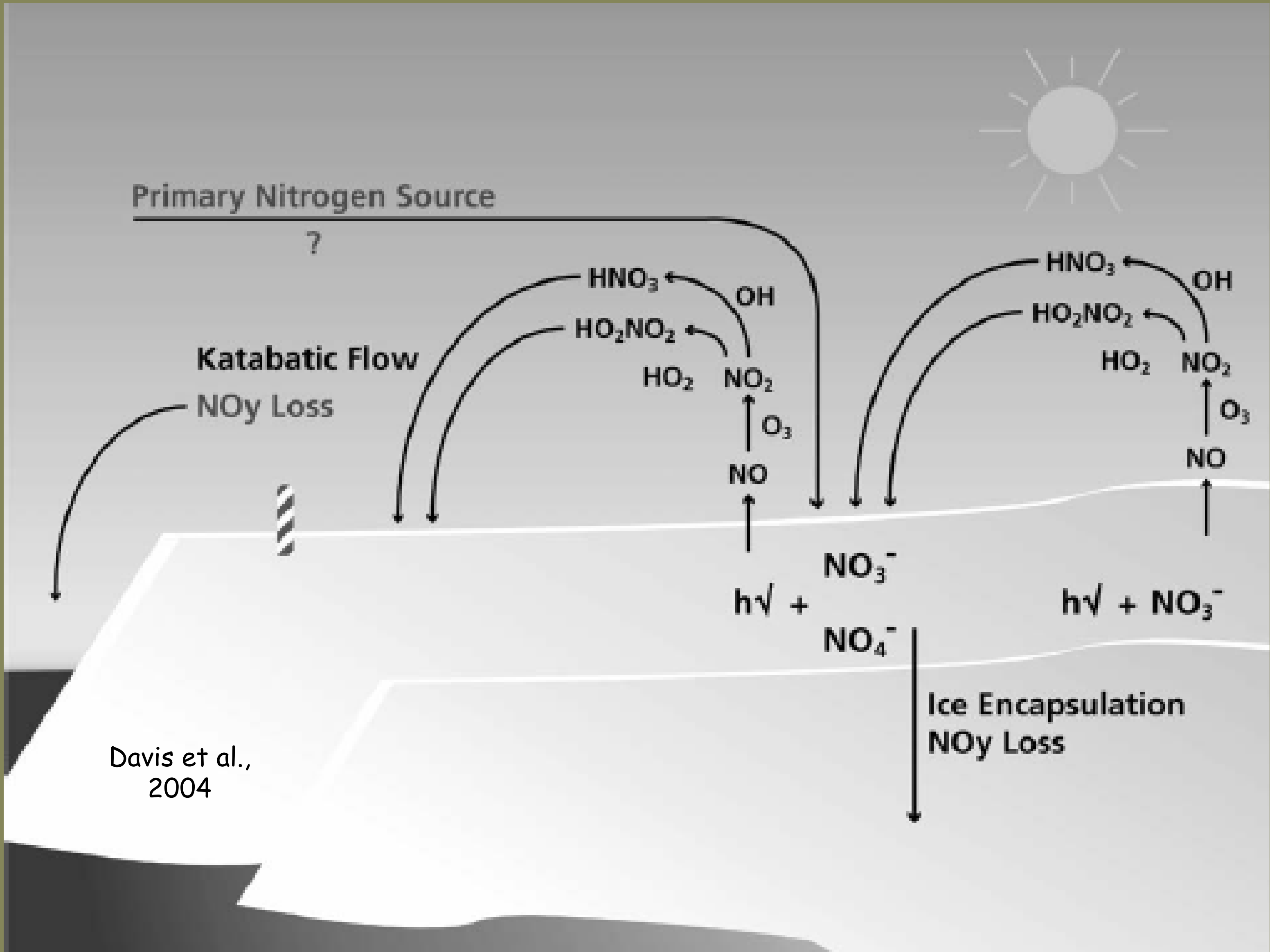
^{15}N DDU-DC Traverse



^{15}N of nitrate aerosol at DDU



Nitrogen budget schematic and the recycling of reactive nitrogen on the Antarctic plateau



Davis et al., 2004

Conclusions

- Oxygen isotopic anomalies (excess ^{17}O) are very sensitive to oxidation processes
- Not only sensitive to the isotopic composition but also to <u>radical concentrations</u>
- May be used in the future as a marker of the OCA of paleo atmospheres

Acknowledgements

Funding agencies

Collaborators

M. Thiemens

S. Morin

M. Frey

J. McCabe

J. Kaiser

S. Battacharya

J-F Doussin

Thank you for your attention …