Tracing the ozone isotopic anomaly transferred to other atmospheric constituents

J. Savarino

Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS/UJF, France

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
Oxidation capacity:
Radical production
OH, O₃, Cl, HO₂…

Impact the radiative budget: greenhouse, CCN, clouds, albedo

Oxidation capacity:
Radical production
OH, O₃, Cl, HO₂…

Primary species
N₂O, SO₂, NO, CO, CH₄, particulates

Secondary oxidized species
HNO₃, H₂SO₄, CO₂, RCOOH, particulates

Deposition, biosphere interactions

Sources
In the Earth’s atmosphere

Oxidation = transfer of oxygen atoms

Stable oxygen isotopes as tracer of oxidation pathways

What is the best probe to study oxidation reaction?
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: $^{16}\text{O}$, $^{17}\text{O}$, $^{18}\text{O}$

- On Earth and The Moon, the bulk relative abundances are:
  - $^{16}\text{O}$: 99.759 %
  - $^{17}\text{O}$: 0.037 %
  - $^{18}\text{O}$: 0.204 %

- 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:

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

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

in parts per thousand or “per mil” = ‰
The Oxygen Isotopic Anomaly

- 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 \(\rightarrow\) anomaly transferred

17-16 = 1 amu
\(\sim 0.5\)
18-16 = 2 amu
\(\sim 1\)
Transfer of $O_3$ Isotopic Anomaly to Other Constituents

$$O_3-[O(^1D)] + X \rightarrow XO + O_2$$
Nitrogen oxides = NO\textsubscript{x} = NO + NO\textsubscript{2}

\[ \text{PAN} \leftarrow \text{organoics} \quad \text{temp} \quad \text{NOx} \]

\[ \text{NO} \quad \overset{hv}{\longrightarrow} \quad \text{NO}_2 \quad \overset{O_3}{\longrightarrow} \quad \text{O}_3\text{(ozone)} \]

\[ \text{O}_3\text{(dark)} \quad \overset{(\text{hydroxyl radical})}{\longrightarrow} \quad \text{OH} \quad \overset{\text{HNO}_3}{\longrightarrow} \quad \text{(nitric acid, aka nitrate NO}_3^-\text{)} \]

\[ \text{SOURCES} \]

isotopes of NO\textsubscript{3}^- reflect sources and chemistry of NO\textsubscript{x}

Courtesy: M. Hastings
First Measurements and Observations

Aerosol Collected in La Jolla, Ca

Michalski et al., 2003

\[ \Delta^{17}\text{NO}_3 \]

\[ 1000 \times \Delta^{17}\text{O} \]

Dates

Summer \( \Delta \downarrow \)

Winter \( \Delta \uparrow \)
The Nitrate Oxidation Scheme

Precursor Photochemical Equilibrium

Termination reactions

\[ \text{Isotopic transfer sensitive to ratio } \alpha = \frac{O_3}{R'O_2} \]

\[ \text{Isotopic transfer sensitive to night/day chemistry} \]
\[ \alpha = \frac{NO + O_3}{\sum NO oxidations} \]

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

By simple consideration on the origin of the oxygen atom

\[ \Delta^{17}\text{HNO}_3 = \frac{2}{3} \Delta^{17}\text{NO}_2 \]

\[ \Delta^{16}\text{HNO}_3 = \frac{2}{3} \Delta^{17}\text{NO}_2 + \frac{1}{6} \Delta^{17}\text{O}_3 \]

\[ \Delta^{17}\text{HNO}_3 = \frac{2}{3} \Delta^{17}\text{NO}_2 + \frac{1}{3} \Delta^{17}\text{O}_3 \]
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
\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]

To Predict isotopic transfer

Intramolecular distribution of O₃

Atom abstracted by NO
- Ozone made by electrical discharge, by varying P & T \(\rightarrow\) 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
\(\rightarrow\) anomaly transfer
\(\rightarrow\) 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
\[ \Delta^{17}O(NO_2) = \Delta^{17}O(O_3) = 35 \permil \]

Our result using $\Delta^{17}O(O_3) = 25 \permil$
\[ \Delta^{17}O(NO_2) = 36 \permil \]
Microscopic view: Mechanism

\[ \text{ONO} \quad \frac{1}{3} s\delta \]
\[ \text{OO} \quad \frac{2}{3} a\delta \]
\[ \text{OO} \quad \frac{1}{3} (s\delta + a\delta - \epsilon_3) \]
\[ \text{ONO} \quad \frac{1}{3} (a\delta + \epsilon_3) \]
$$\Delta^{17}O(O_{\text{trans}}) = p \ s\Delta^{17}O(sO_3) + (1-p) \ a\Delta^{17}O(aO_3)$$

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 al., 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

Supported by:

- the non-Arrhenius behavior of the kinetic rate reaction $\rightarrow$ two step mechanisms

- Molecular beam reactions showing two preferential scattering angles for products
Molecular Beam Scattering Experiment
(van den Ende et al., 1982)

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 !!!!!
Total inorganic nitrate aerosols collected on glass fiber filter

Sampling Sites
Analytical procedure

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

100 nmol of nitrate + 10 ml of denitrifying bacteria solution

Flushed with He to Au catalyst

Produce N$_2$O

Produce N$_2$ + O$_2$

To MS: $\delta^{15}$N, $\delta^{17}$O, $\delta^{18}$O

Not quantitative $\rightarrow$ calibration
Ozone Depletion Events (ODEs)

High Arctic, at polar sunrise → destruction of surface ozone
Bromine source
\[ \text{BrO} + \text{HO}_2 \rightarrow \text{HOBr}_g + \text{O}_2 \]
\[ \text{HOBr}_g \rightarrow \text{HOBr}_{aq} \]
\[ \text{HOBr}_{aq} + \text{Br}^- + \text{H}^+ \rightarrow \text{Br}_{2aq} + \text{H}_2\text{O} \]
\[ \text{Br}_{2aq} \rightarrow \text{Br}_{2g} \]

Catalytic destruction
\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} \]
\[ \text{BrO} + \text{BrO} \rightarrow 2\text{Br} + \text{O}_2 \]

Richter et al., 2001

VC BrO [molec cm\(^{-3}\)]

\[ > 8.0 \times 10^{13} \]
\[ 7.5 \times 10^{13} \]
\[ 7.0 \times 10^{13} \]
\[ 6.5 \times 10^{13} \]
\[ 6.0 \times 10^{13} \]
\[ 5.5 \times 10^{13} \]
\[ 5.0 \times 10^{13} \]
\[ 4.5 \times 10^{13} \]
\[ 4.0 \times 10^{13} \]
\[ < \]
BrO/O$_3$ Relationship

Ozone and BrO cannot coexist both at high concentration

Two regimes

O$_3$ low
BrO high

O$_3$ high
BrO low

Hönninger and Platt, 2002
Sea salt chemistry

\[ O_3 + Br \rightarrow BrO + O_2 \]
\[ BrO + BrO \rightarrow 2Br + O_2 \] \( \Delta \)

Effect 1: Destroy \( O_3 \), \( \Delta \)

But ....

\[ BrO + NO \rightarrow Br + NO_2 \] \( \Delta \)
\[ BrO + NO_2 \rightarrow HNO_3 + \ldots \] \( \Delta \)

Effect 2: Transfer \( \Delta \)

Bromine: 2 opposing effects
\[ \Delta^{17}O_{NO_3^{-}} = \frac{2 \Delta^{17}O_{NO-O_3} k_{NO+O_3}[O_3]}{3 k_{NO+O_3}[O_3] + k_{NO+HO_2}[HO_2]} + cst \]
Indicates a change in the way nitrate is formed.
\[
\Delta^{17}O_{NO_3^-} = \frac{2}{3} \frac{\Delta^{17}O_{NO-O_3} k_{NO+O_3} [O_3] + \Delta^{17}O_{NO-BrO} k_{NO+BrO} [BrO]}{k_{NO+O_3} [O_3] + k_{NO+HO_2} [HO_2] + k_{NO+BrO} [BrO]} + \text{cst}
\]
Strong ODE chemistry

- $\text{O}_3 \xrightarrow{hv} \text{NO}$
- $\text{NO} \xrightleftharpoons{\Delta} \text{NO}_2$
- $\text{NO}_2 \xrightarrow{\Delta} \text{BrO}$
- $\text{BrO} \xrightarrow{\Delta} \text{BrNO}_3$
- $\text{BrNO}_3 \xrightarrow{} \text{HNO}_3, p-\text{NO}_3^-$
- $\text{H}_2\text{O}$

BrO replaces $O_3$ in oxidizing NO

BrNO$_3$ branch 100 times faster than OH branch
Box model ODE
The Antarctic Environment
Strong post depositional effects

- 95% of $\text{NO}_3^-$ lost
- $^{15}\text{N}$ jumps for 0 to 200 %

Blunier et al., 2005
$^{15}$N DDU-DC Traverse
$^{15}\text{N}$ of nitrate aerosol at DDU
Nitrogen budget schematic and the recycling of reactive nitrogen on the Antarctic plateau

Davis et al., 2004
Oxygen isotopic anomalies (excess $^{17}O$) are very sensitive to oxidation processes.

Not only sensitive to the isotopic composition but also to radical concentrations.

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 ...