# $^{17}O$ Isotopic anomaly in $NO_3$ aerosol at Chebogue Point during ITCT 2k4

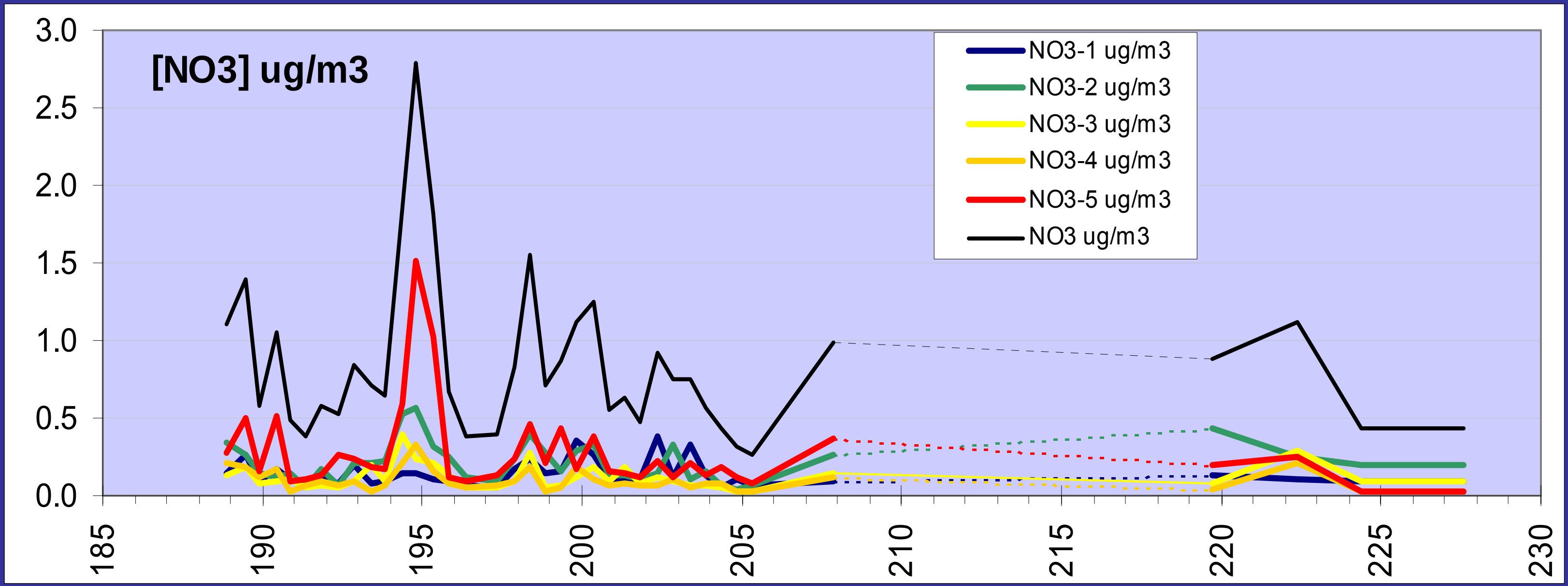
**Nicolas PATRIS, Larry HERNANDEZ, Mark Thiemens**

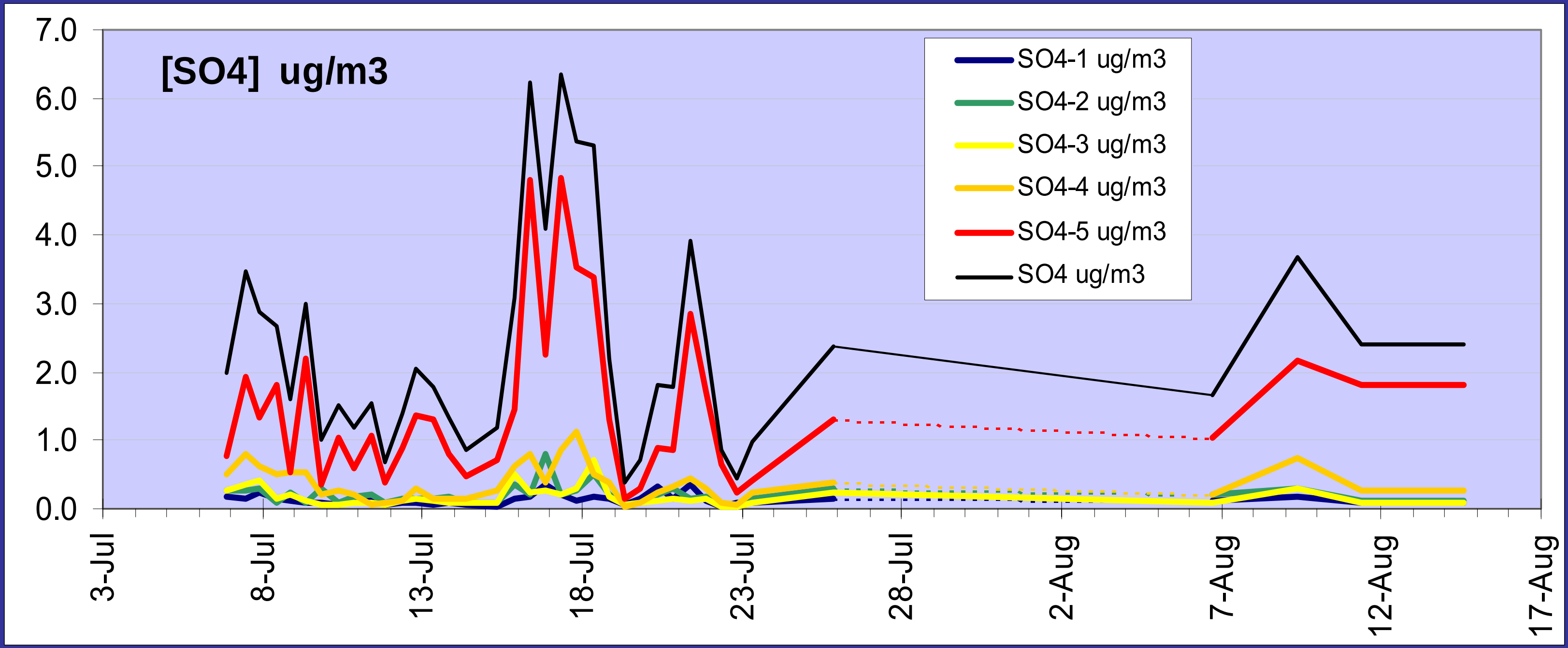
**UCSD, La Jolla CA**

# Sampling & Analysis

- 5-Stage impactors
- 12-hr collections Jul 06 – Jul 23 (33 sets)
- 3-days collections Aug 6 – Aug 14 (4 sets)

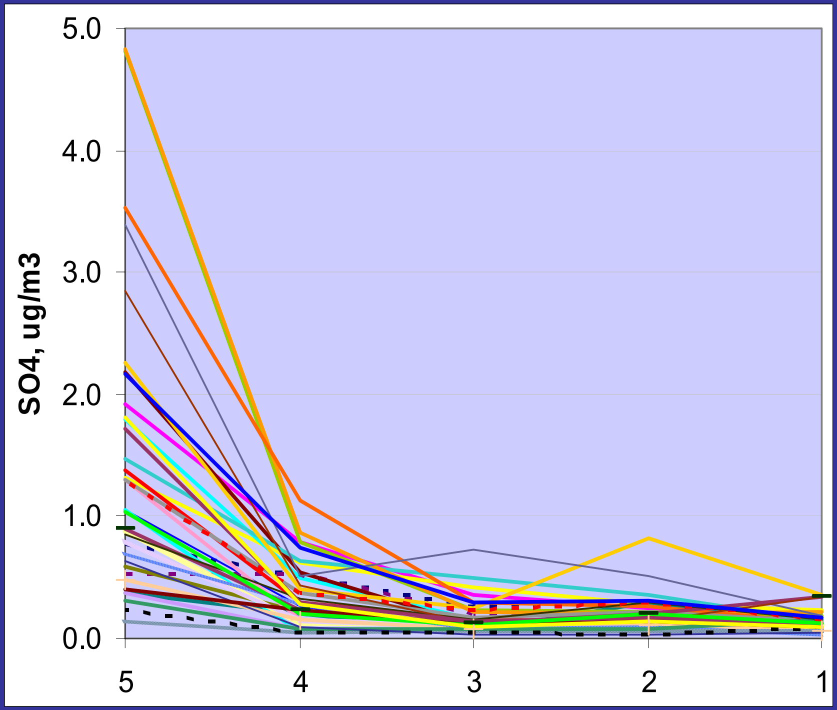
- Extraction in water
- I.C. Purification of $NO_3$, $SO_4$
- Conversion to $AgNO_3$, $Ag_2SO_4$
- Pyrolysis to form $O_2$
- Mass Spec analysis on $O_2$


[NO3] ug/m3
NO3-1 ug/m3
NO3-2 ug/m3
NO3-3 ug/m3
NO3-4 ug/m3
NO3-5 ug/m3
NO3 ug/m3
3.0
2.5
2.0
1.5
1.0
0.5
0.0
185
190
195
200
205
210
215
220
225
230

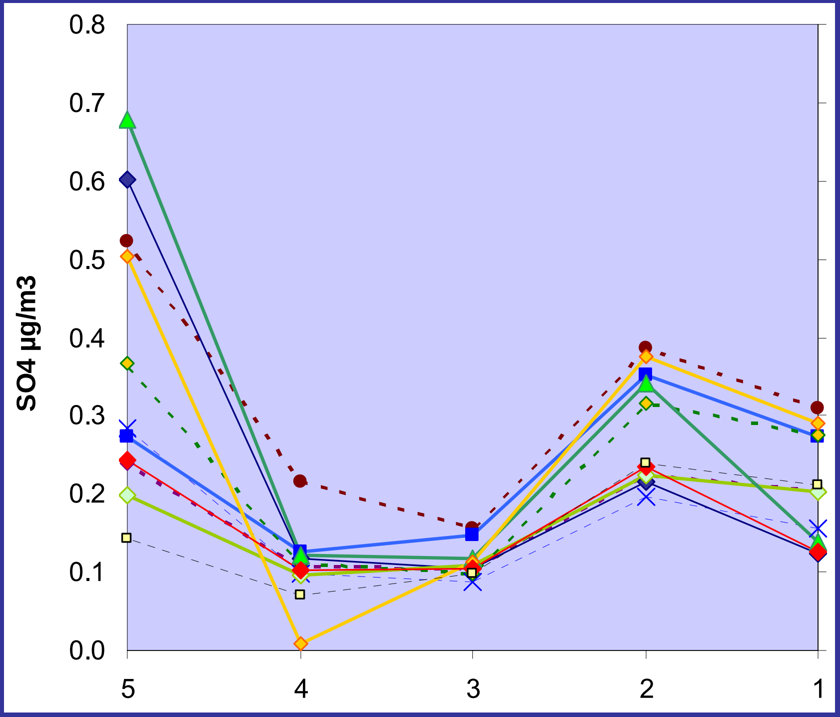

[SO4] ug/m3
SO4-1 ug/m3
SO4-2 ug/m3
SO4-3 ug/m3
SO4-4 ug/m3
SO4-5 ug/m3
SO4 ug/m3
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3-Jul
8-Jul
13-Jul
18-Jul
23-Jul
28-Jul
2-Aug
7-Aug
12-Aug
17-Aug

# SO4 size distribution

## Chebogue Pt. 2k4

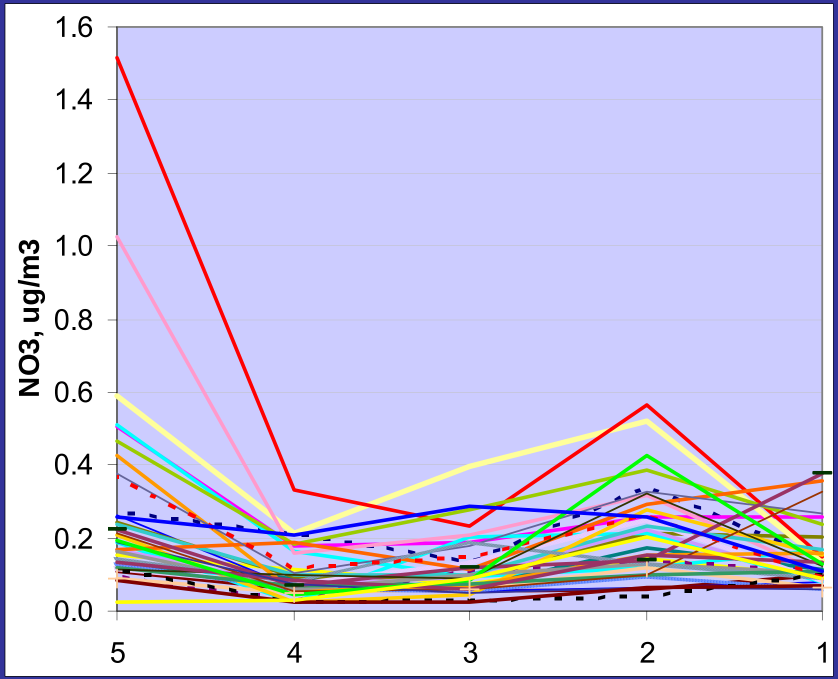



## Trinidad Head 2k2

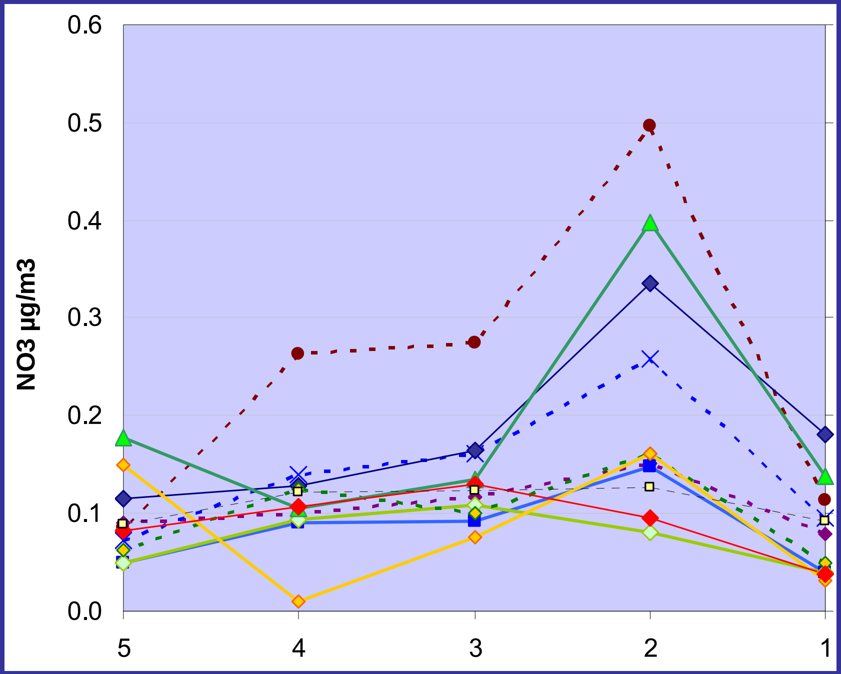


# NO3 size distribution

Chebogue Pt. 2k4




Trinidad Head 2k2



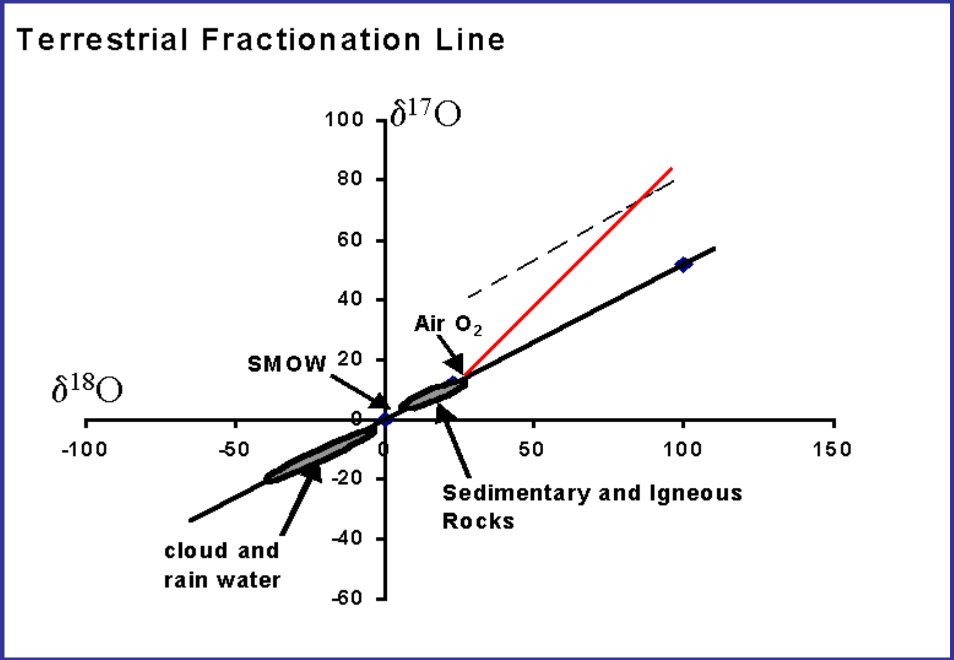
# Single isotope ratio

- Used as tracers of sources or biogeochemical processes ($\delta^{34}S$, $\delta^{18}O$, $\delta^{15}N$)

$$\delta^{18}O = \left[ \frac{\left( {}^{18}O / {}^{16}O \right)_{sample}}{\left( {}^{18}O / {}^{16}O \right)_{std}} - 1 \right] \times 1000$$

- More or less efficient as conservative tracers
- Overlaps in $\delta$ ranges limit applications

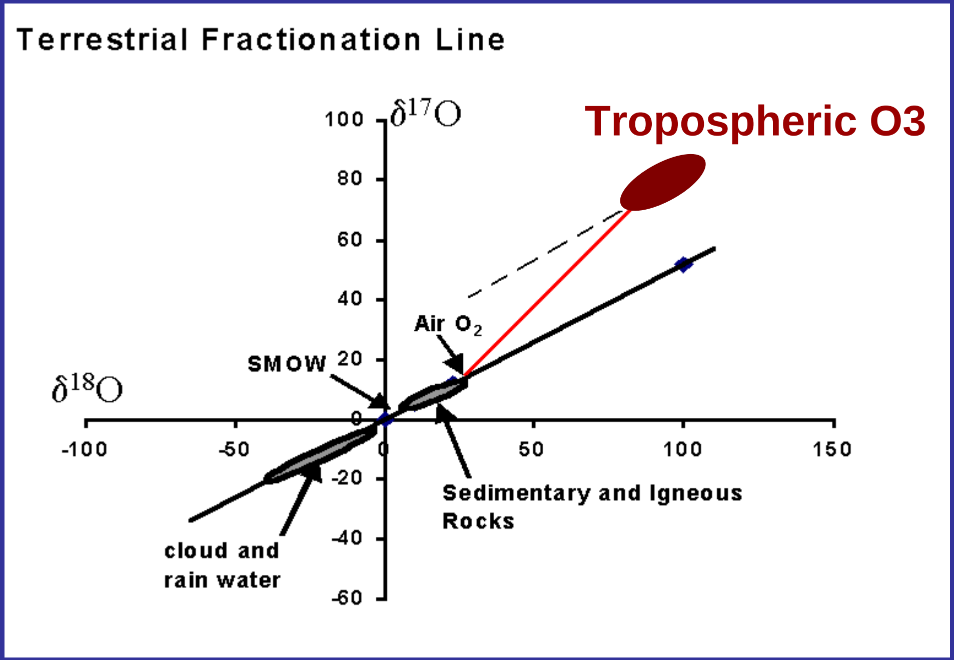
# Multiple isotope ratios




$$\delta^{17}O = 0.52 \times \delta^{18}O$$

Terrestrial Fractionation Line

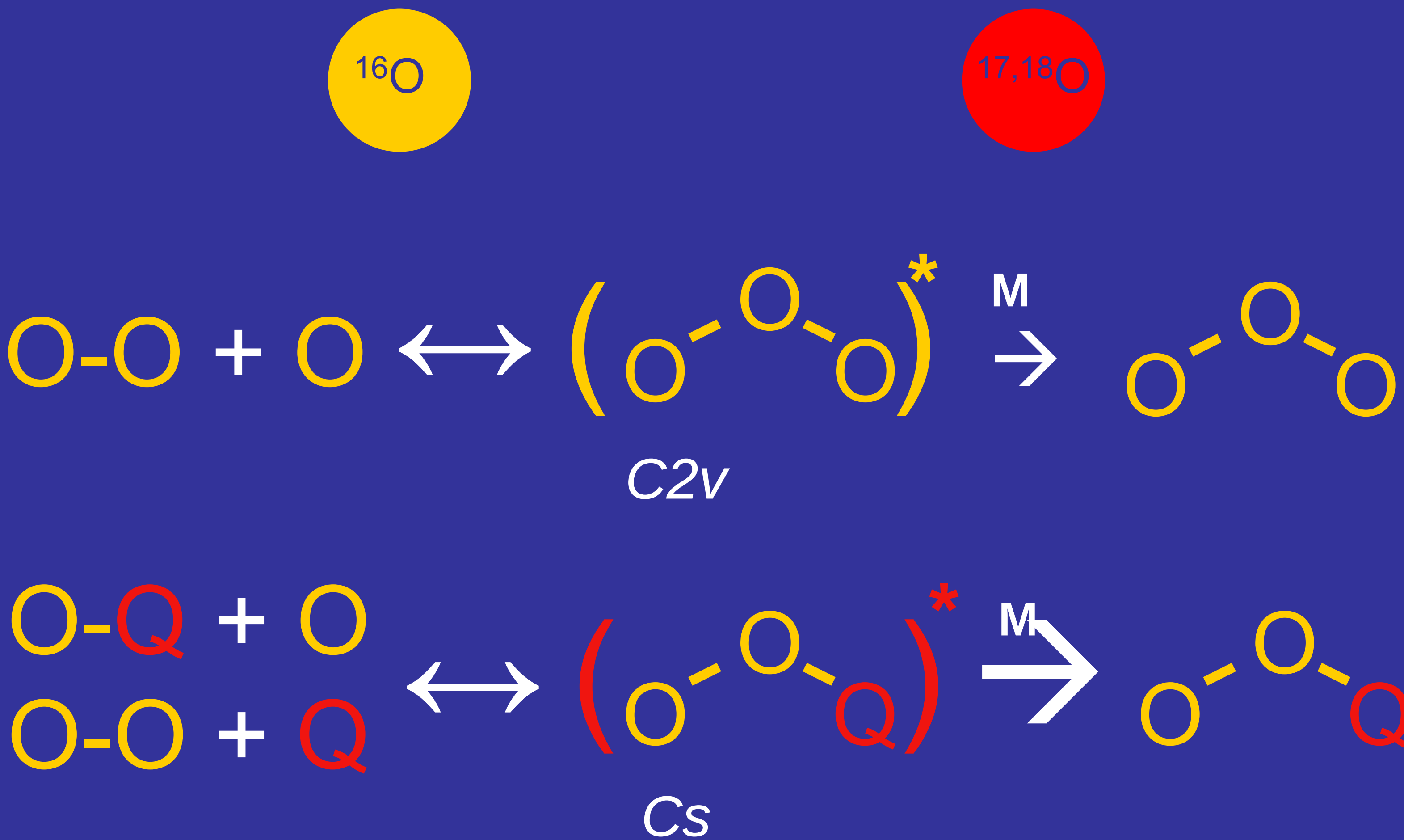
# Multiple isotope ratios




$$\delta^{17}O = 0.52 \times \delta^{18}O$$

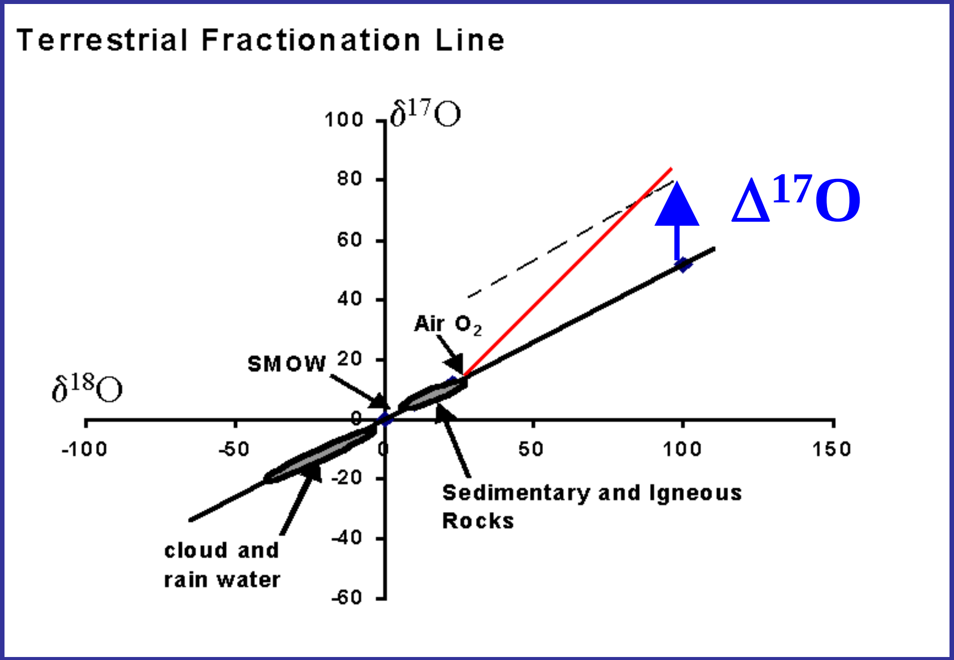
Terrestrial Fractionation Line

# Source of 17-O anomaly
# Ozone formation: symmetry effect



# Multiple isotope ratios

- O and S systems: resp. 3 and 4 stable isotopes



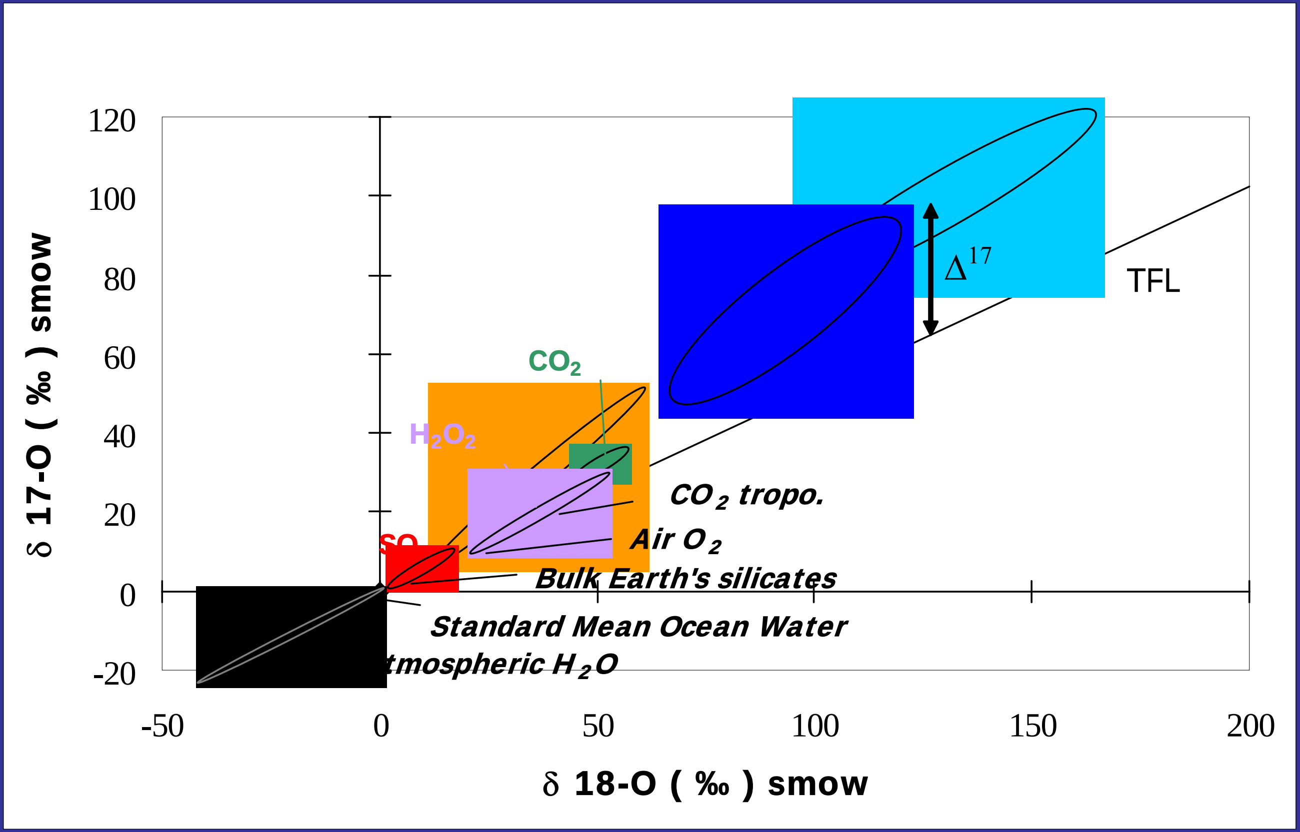

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$$

- Isotopic anomaly highly specific to atmospheric processes (initiated by photochemistry)
- Conservative tracer, can be transferred from reactant to product

# Anomalous "Mass-independent" isotopic compositions

## Main source of $\Delta^{17}O$ : Ozone formation

- Transfer of anomaly from reactants to products
- Very efficient (accurate and conservative) tracer
- Only dilution can modify it



# Anomalous $^{17}O$ composition: Tracer of atmospheric chemistry

- $SO2 + OH \longrightarrow SO_4\ (\Delta^{17}=0)$
- $SO2_{aq} + {}^{\Delta}O_3 \longrightarrow {}^{\Delta}SO_4$
- $SO2_{aq} + {}^{\Delta}H_2O_2 \longrightarrow {}^{\Delta}SO_4$

Tracer of $SO_4$ aqueous phase formation

Tracer of NOx oxidative pathways:

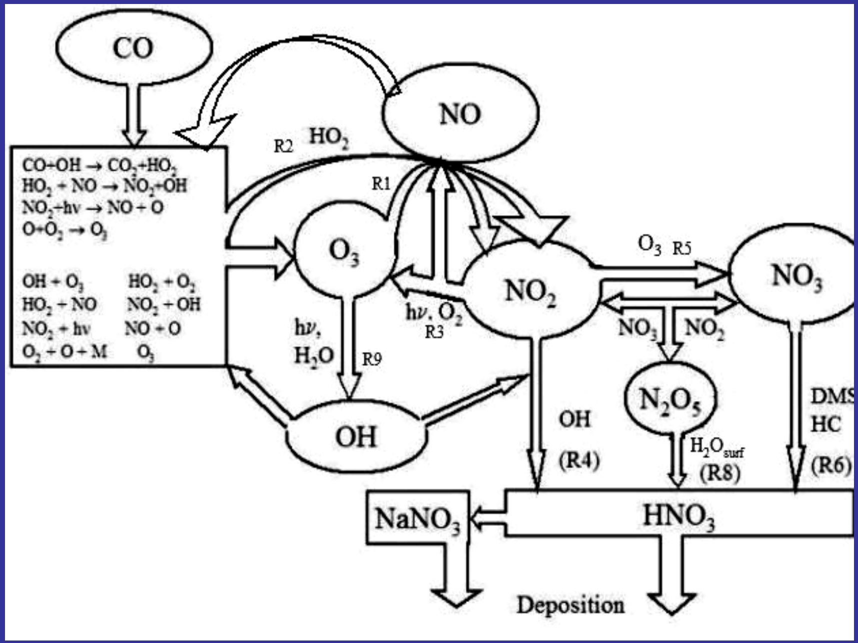
$^{\Delta}NO2 + OH\ (RH)$ ~ 23.3 ‰

$^{\Delta}NO3 + DMS, HC$ ~ 35 ‰

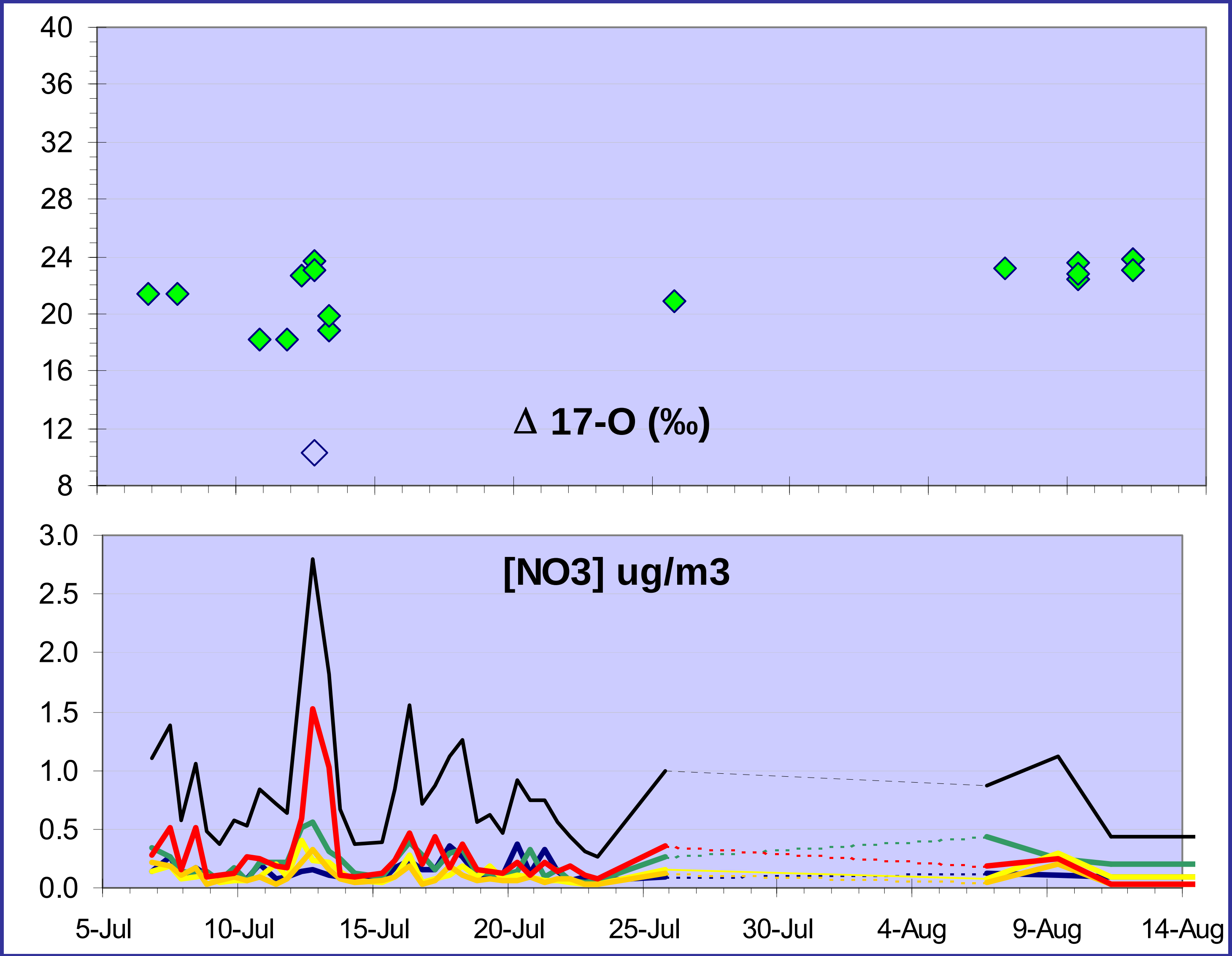
$^{\Delta}N2O5 + H2O$ ~ 29.2 ‰

***Taking*** *: $\Delta^{17}O_3$ ~35 ‰*

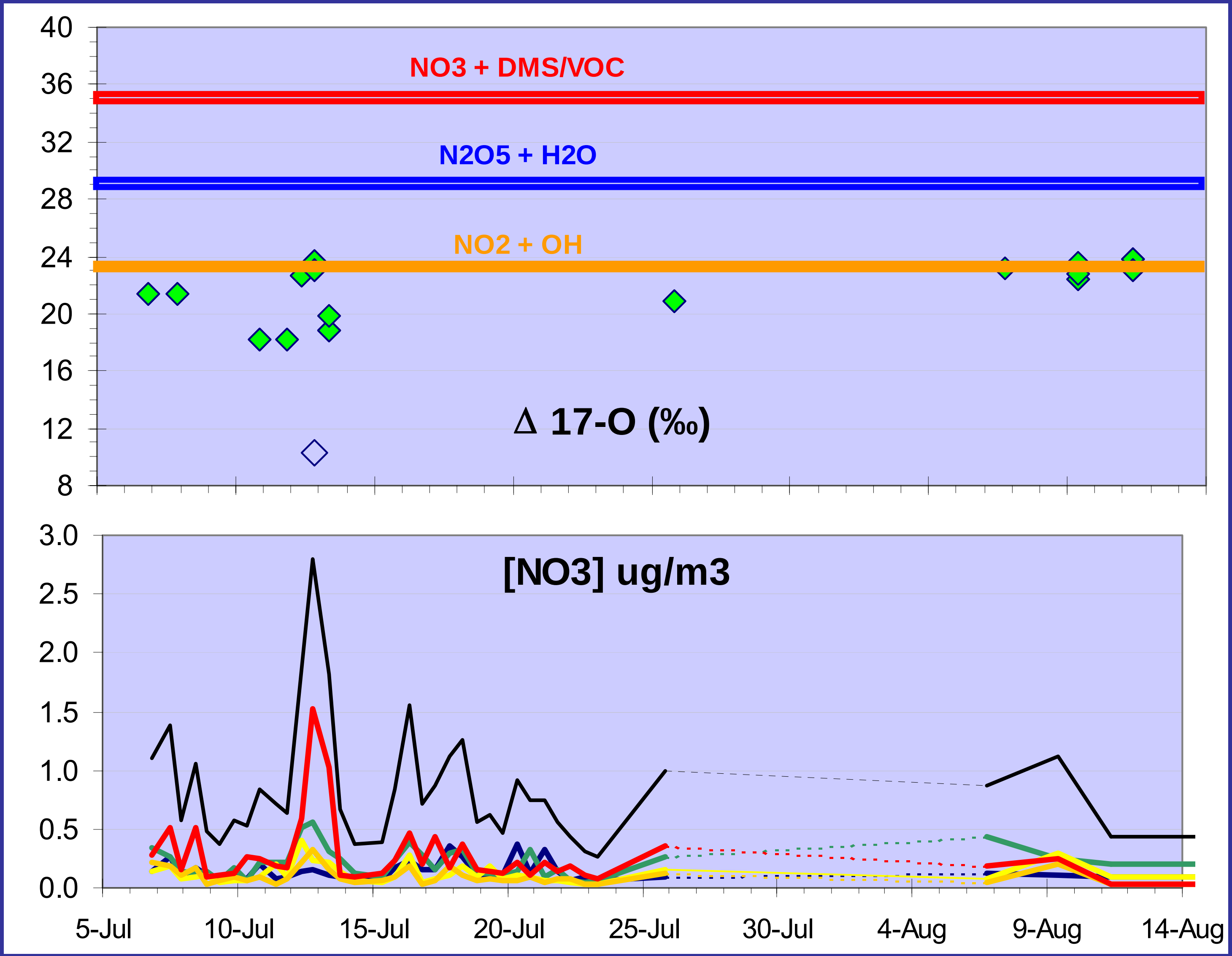
***AND*** *NO -> NO2 oxidation 100% due to O3*



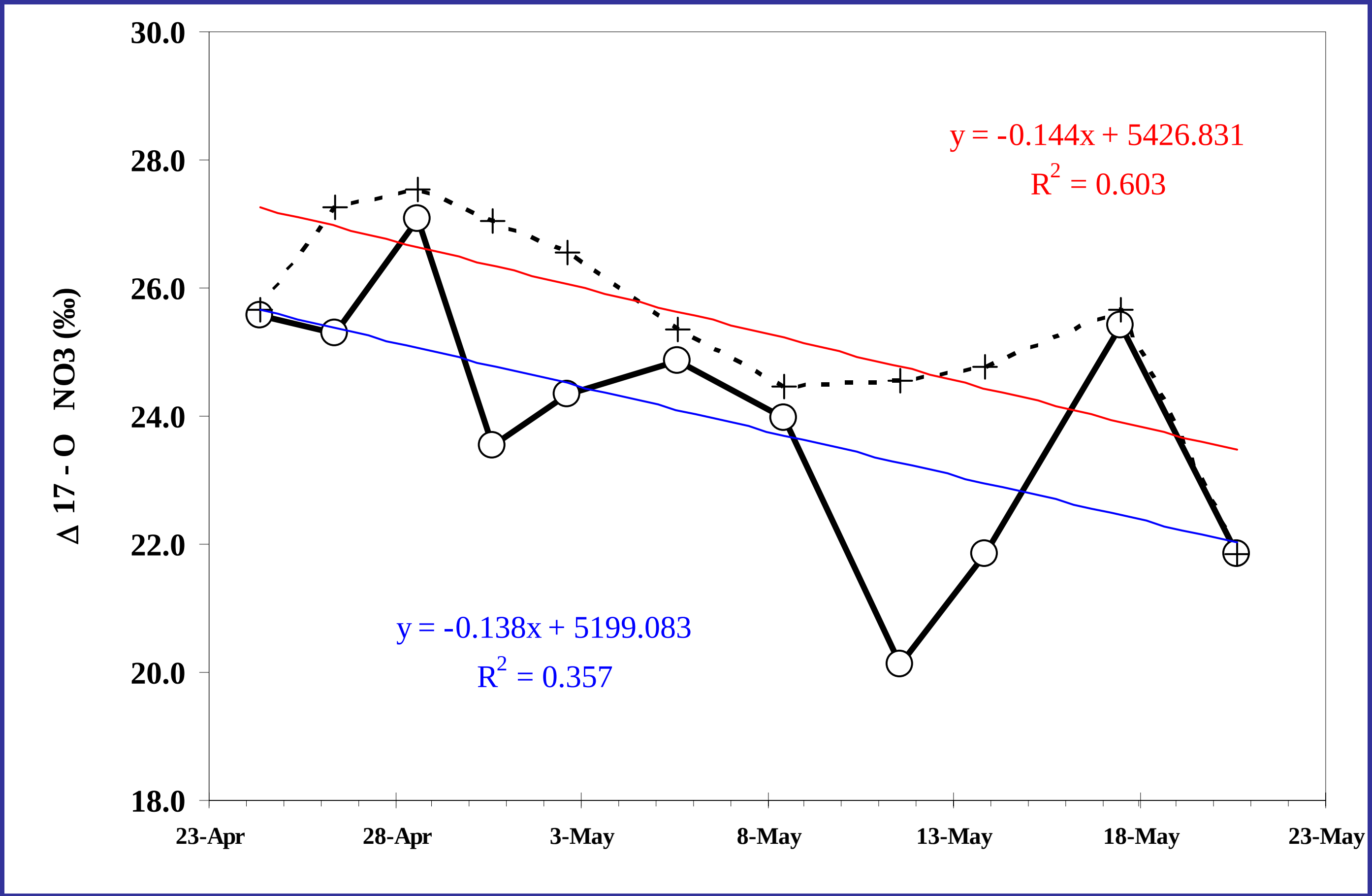
# Nitrate $\Delta^{17}O$ at Chebogue Pt.



# Nitrate $\Delta^{17}O$ at Chebogue Pt.



# Trinidad Head NO3 17-O anomaly:

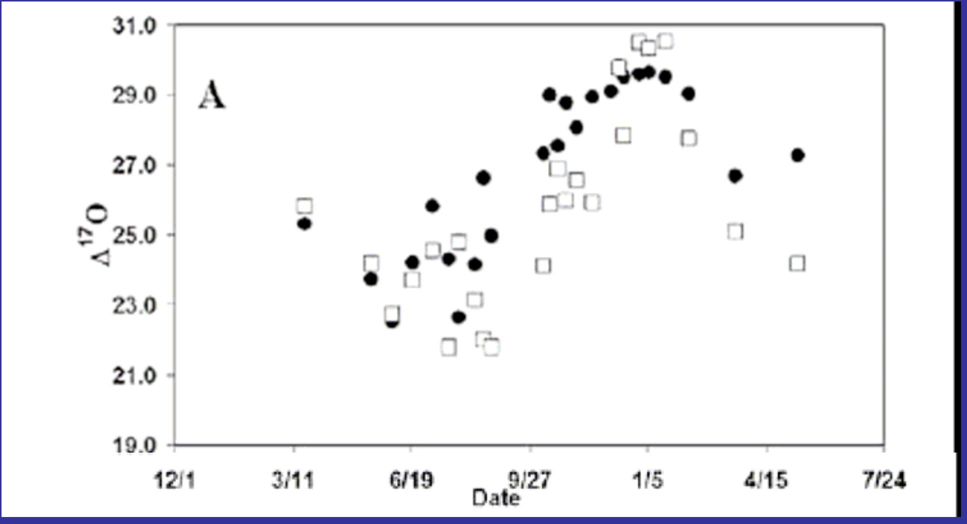


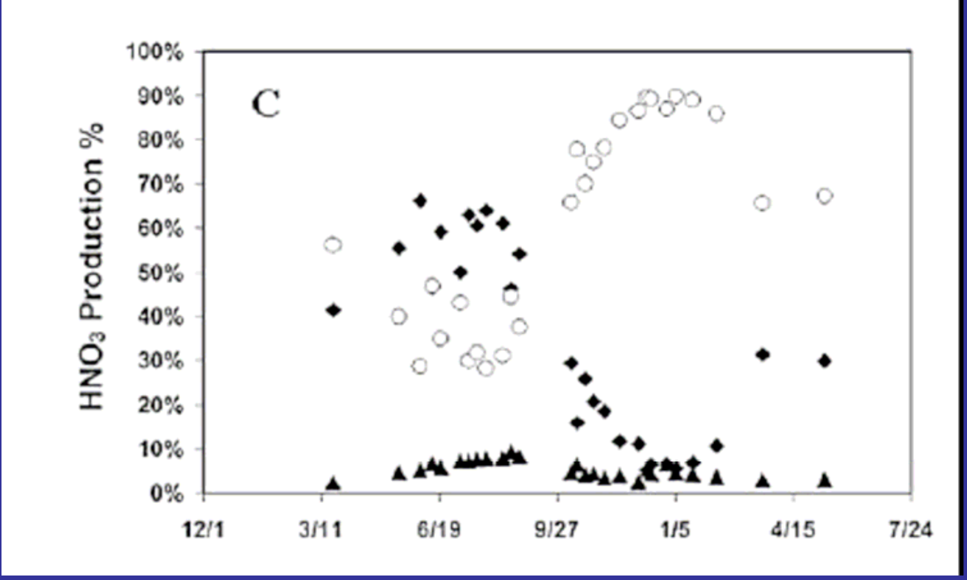

- Differential NO3 formation pathway budgets with respect to particle size in a given air mass
- Seasonal trend ?

GEOPHYSICAL RESEARCH LETTERS, VOL. 30, NO. 16, 1870, doi:10.1029/2003GL017015, 2003

# First measurements and modeling of $\Delta^{17}O$ in atmospheric nitrate

Greg Michalski, Zack Scott, Melanie Kabiling, and Mark H. Thiemens
University of California, San Diego Department of Chemistry and Biochemistry, USA



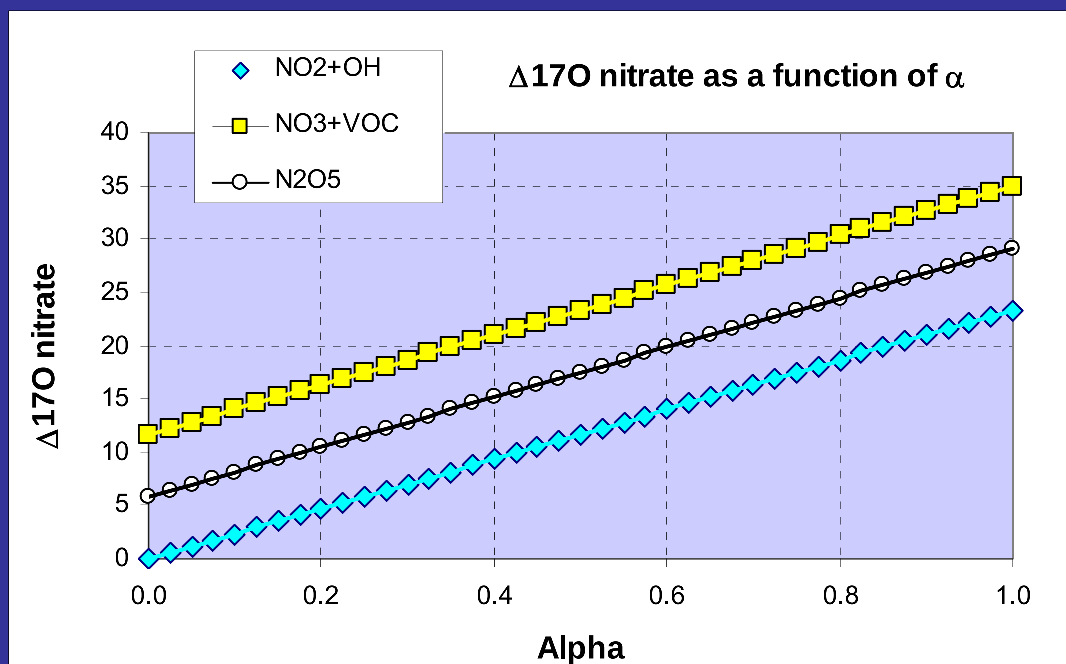
# Effects on Δ$^{17}$O-NO3 of NO oxidation by HO2 or peroxy radicals

$$^{\Delta}HNO_3(R1) = \tfrac{2}{3}\alpha\,^{\Delta}O_3$$

$$^{\Delta}HNO_3(R2) = \tfrac{2}{3}\alpha\,^{\Delta}O_3 + \tfrac{1}{3}\,^{\Delta}O_3$$

$$^{\Delta}HNO_3(R3) = \tfrac{1}{3}\alpha\,^{\Delta}O_3 + \tfrac{1}{2}\left(\tfrac{2}{3}\alpha\,^{\Delta}O_3 + \tfrac{1}{3}\,^{\Delta}O_3\right)$$

| | |
|---|---|
| (R1) | $NO_2 + OH + M \rightarrow HNO_3 + M$ |
| (R2) | $NO_2 + O_3 \rightarrow NO_3 + O_2$ |
| (R2b) | $NO_3 + HC, DMS \rightarrow HNO_3 + \text{products}$ |
| (R3) | $NO_2 + NO_3 \leftrightarrow N_2O_5$ |
| (R3b) | $N_2O_5 + H_2O_{(surf)} \rightarrow 2\ HNO_{3(aq)}$ |



# Preliminary conclusions, future work

- Preliminary dataset strongly suggests NO2 + OH as the dominant formation pathway of NO3-
- Coupling of the isotope data with chemistry/transport modeling and observations will help determine the role of NO oxidation in low $\Delta$17O of nitrate

➢ Achieve completion of > 30 supplemental NO3 isotopic measurements

➢ Achieve completion of > 100 sulfate 17-O measurements

➢ Perform multi-sulfur isotope analysis on a chosen sub-sampling of interest

➢ Integrate isotope tracers in modeling to constrain formation/transformation mechanisms during transport