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Isotope exchange between CO_2 and O_3 in the stratosphere: atmospheric and laboratory measurements

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Outline

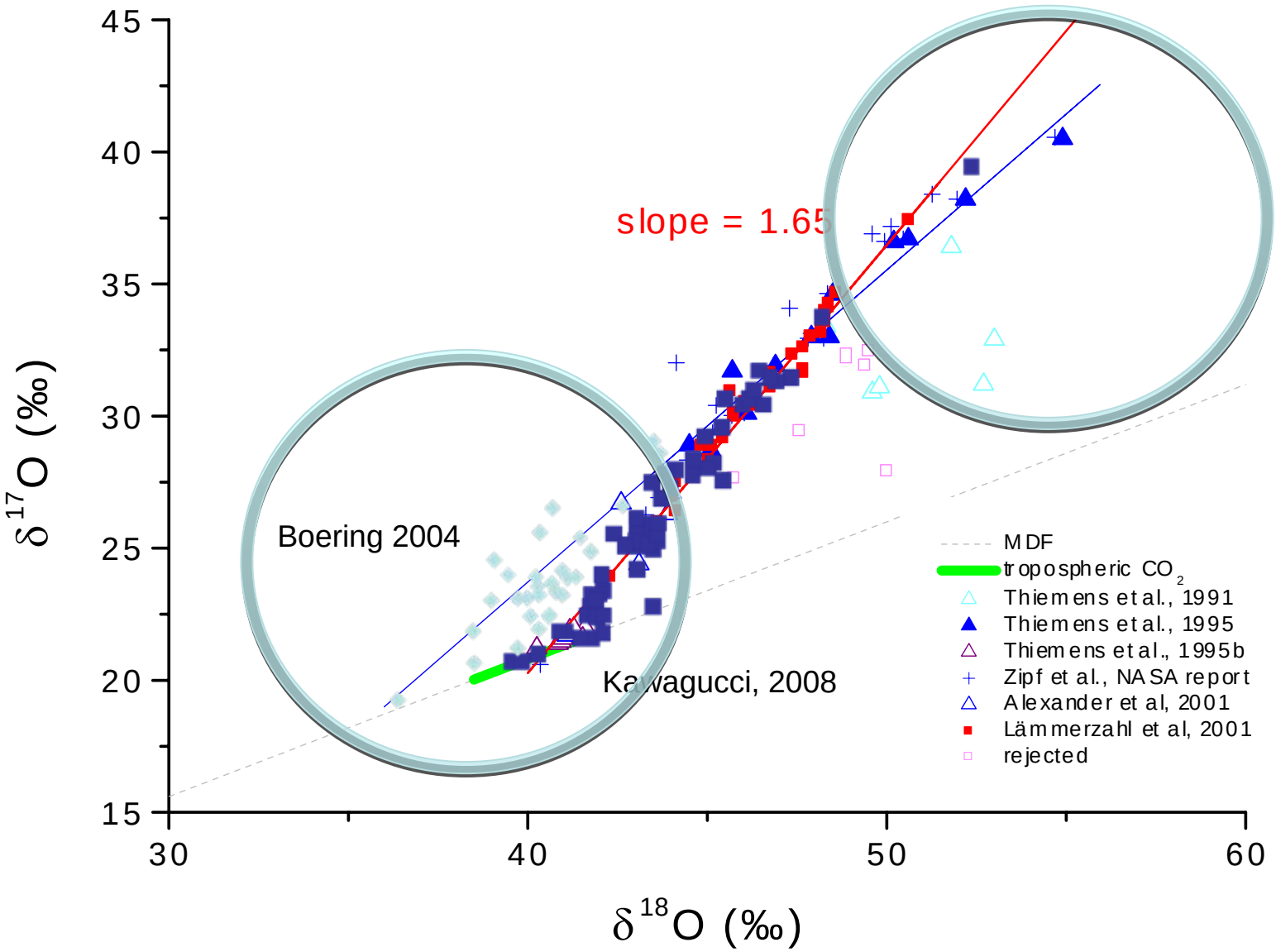
Stratospheric observations

Proposed mechanism

Laboratory experiments

Conclusions and outlook

Stratospheric CO_2 data

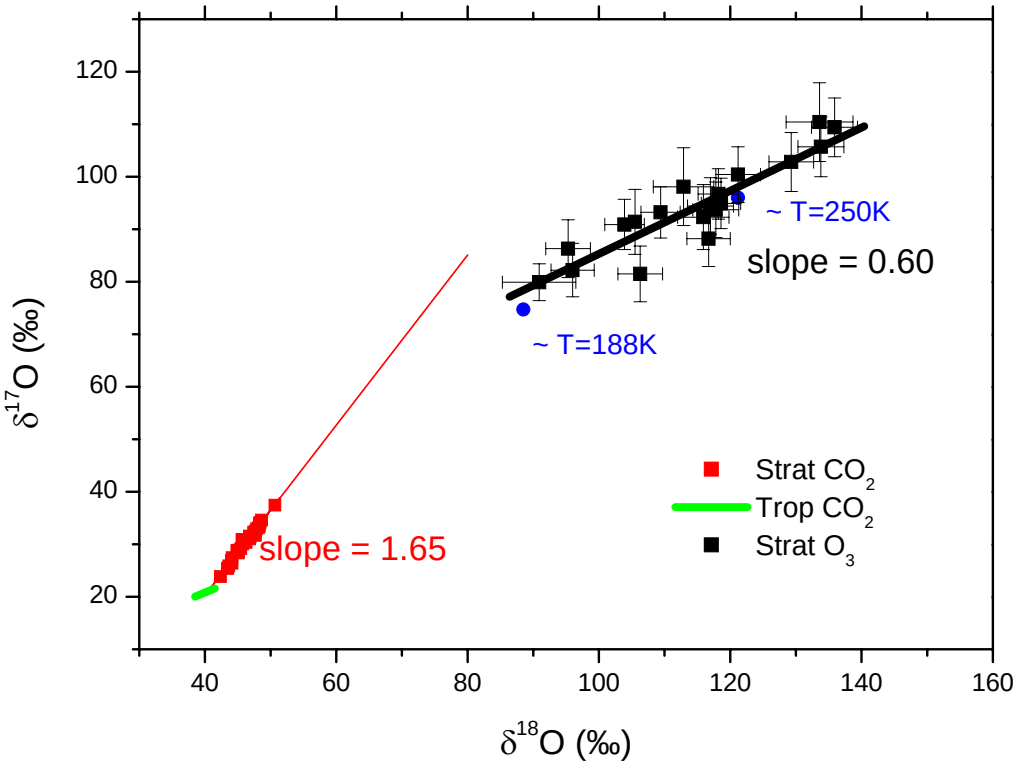


The link to ozone

$O_3 + h\nu \rightarrow O(^1D) + O_2$

$CO_2 + O(^1D) \rightarrow CO_3^* \rightarrow CO_2 + O(^3P)$ [Yung et al., 1991]

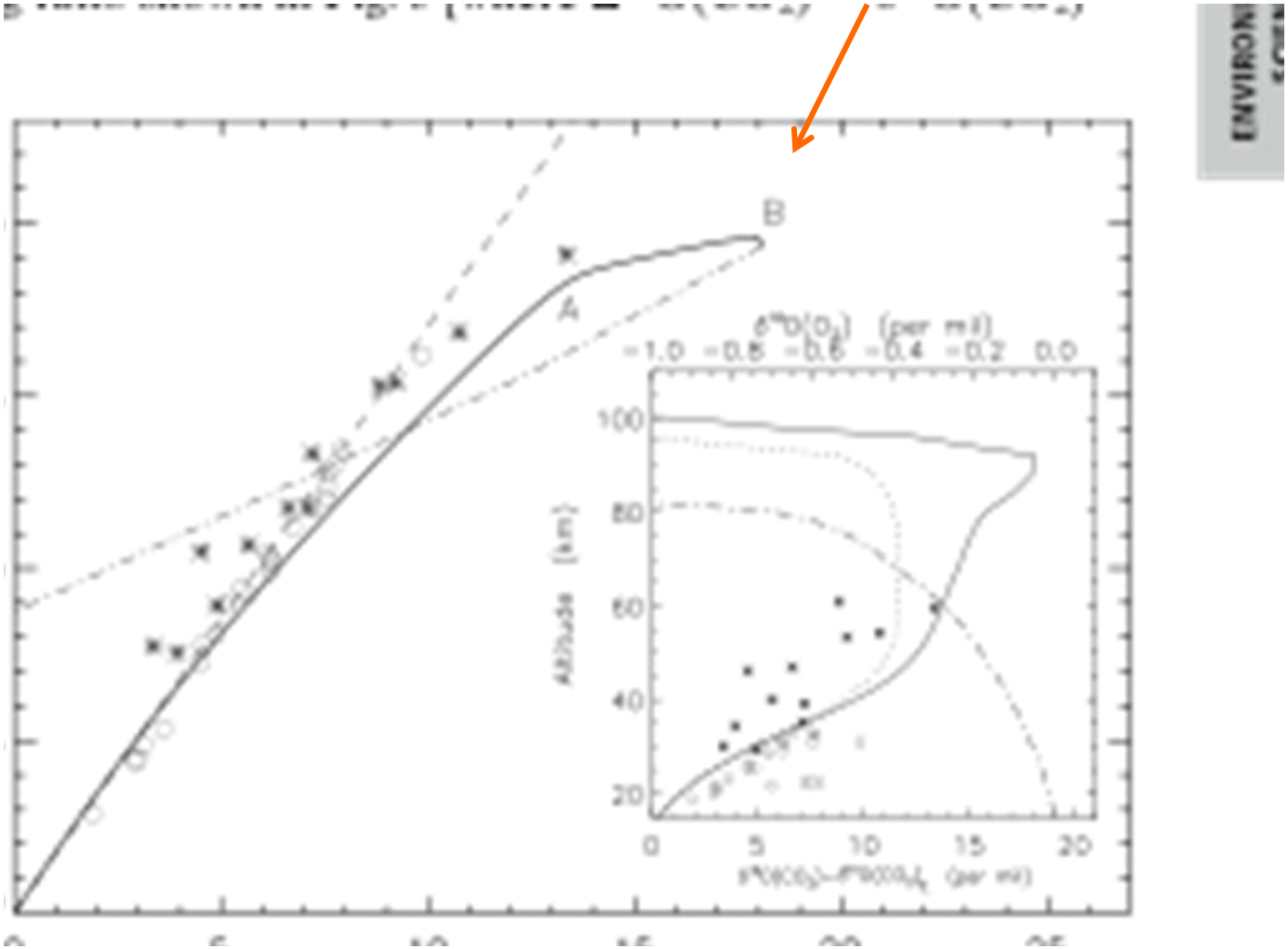
$\rightarrow CO_2 + O(^1D)$ [Perri et al., 2003]



Statistical exchange: Yung et al., 1991, 1997
Mesospheric source: Thiemens et al., 1995, Liang et al., 2007
MIF in CO_3^* complex: Wen&Thiemens, 1993, Johnston et al., 2000
MDF in CO_3^* complex: Barth &Zahn, 1997

Possible influence of mesospheric O(^{1}D)

Mesospheric O_2 source:
Lyman α photolysis



Liang et al. 2007

Internal and external factors in CO_2 + $O(^1D)$ exchange

External:

- O_3enrichment (symmetric / asymmetric ?)
- Fractionation in photolysis ($O_3 \rightarrow O(^1D)$)
- $O(^1D)$ quenching
- Non-quenching exchange

$O(^1D)$ reactant

nternal:

•

ractionation in CO_3* complex (formation/dissociation)

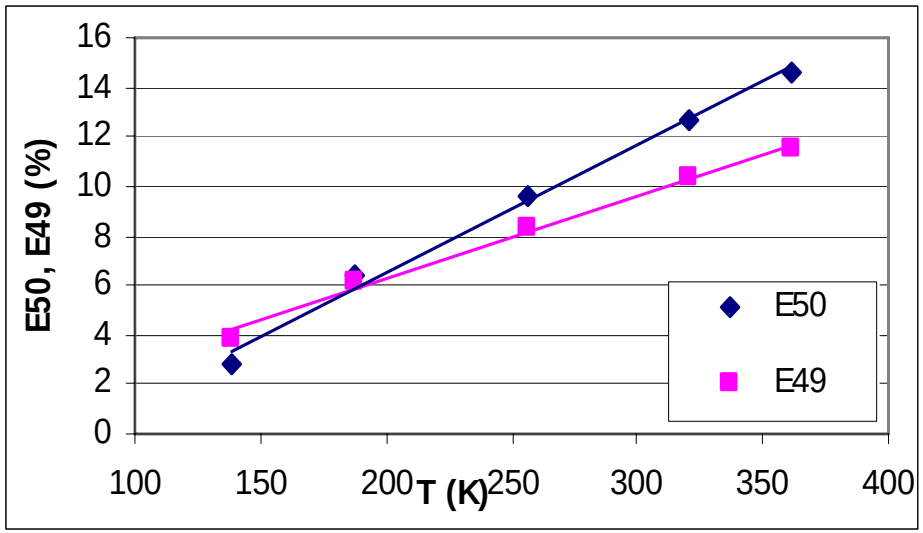
Distribution of oxygen isotopes in O_3

asymmetric symmetric

overall enrichment: 3E = 2A + S

measurements
(Morton et al., JGR, 1990)

calculate
temp. dep.

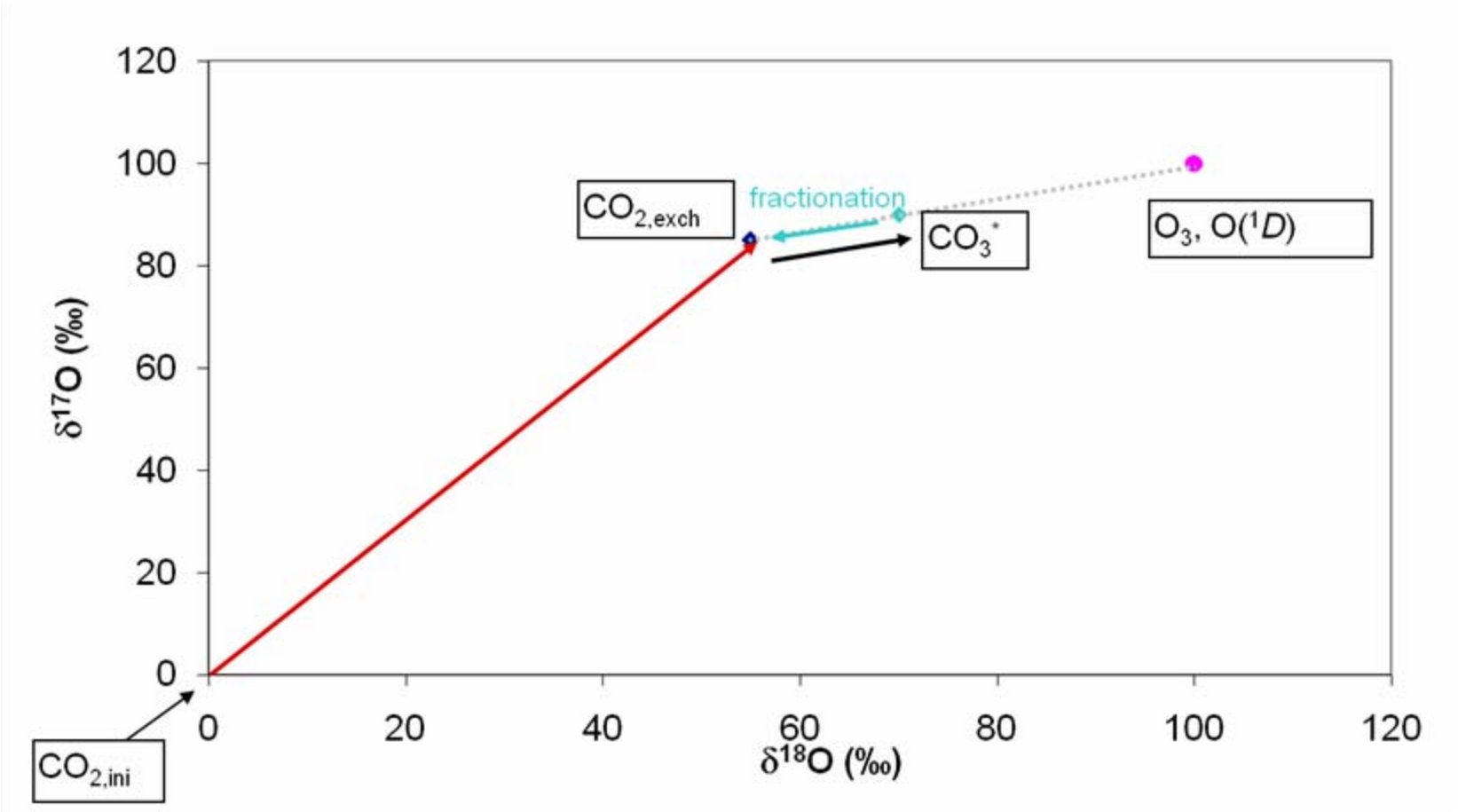


$6 + 86 \rightarrow 686$
$6 + 76 \rightarrow 676$

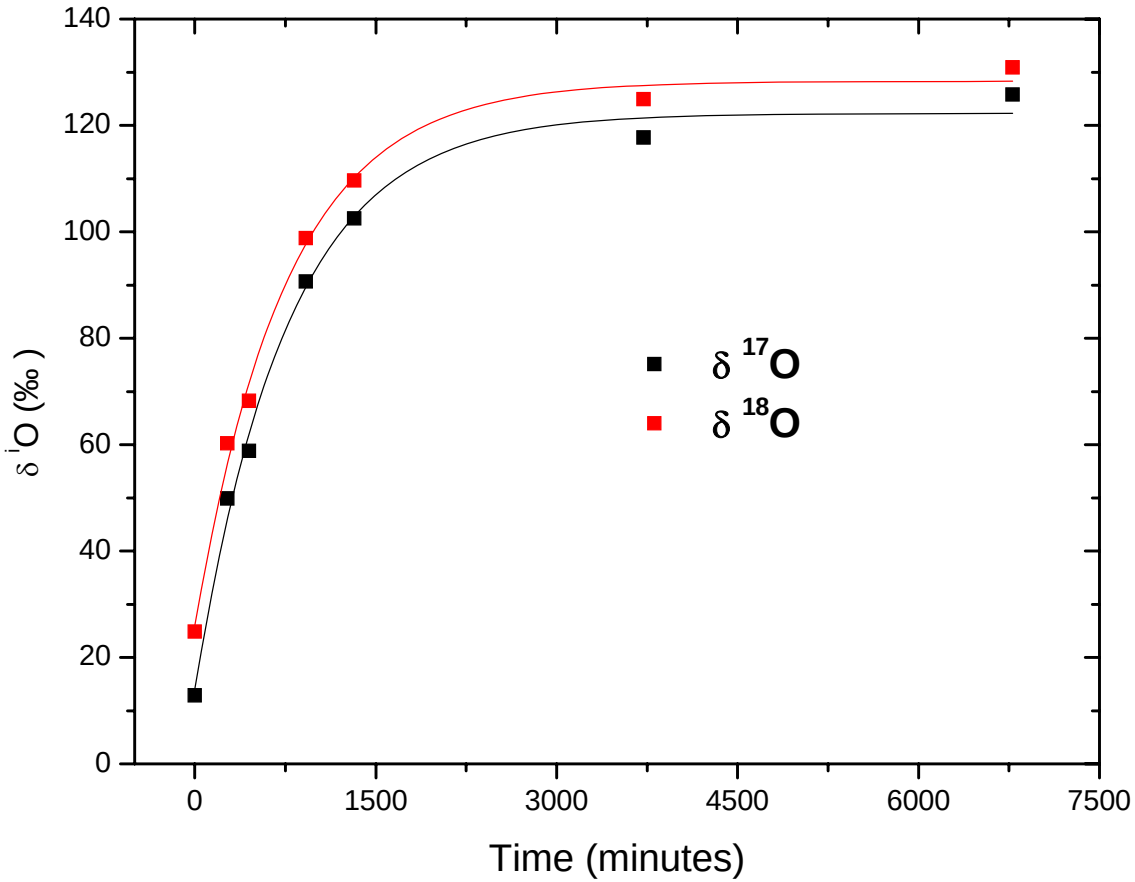
from theory
(Gao & Marcus, 2002)

or experiment
(Janssen et al., 1999) making reasonable assumptions on ^{17}O

Schematic view of fractionation process



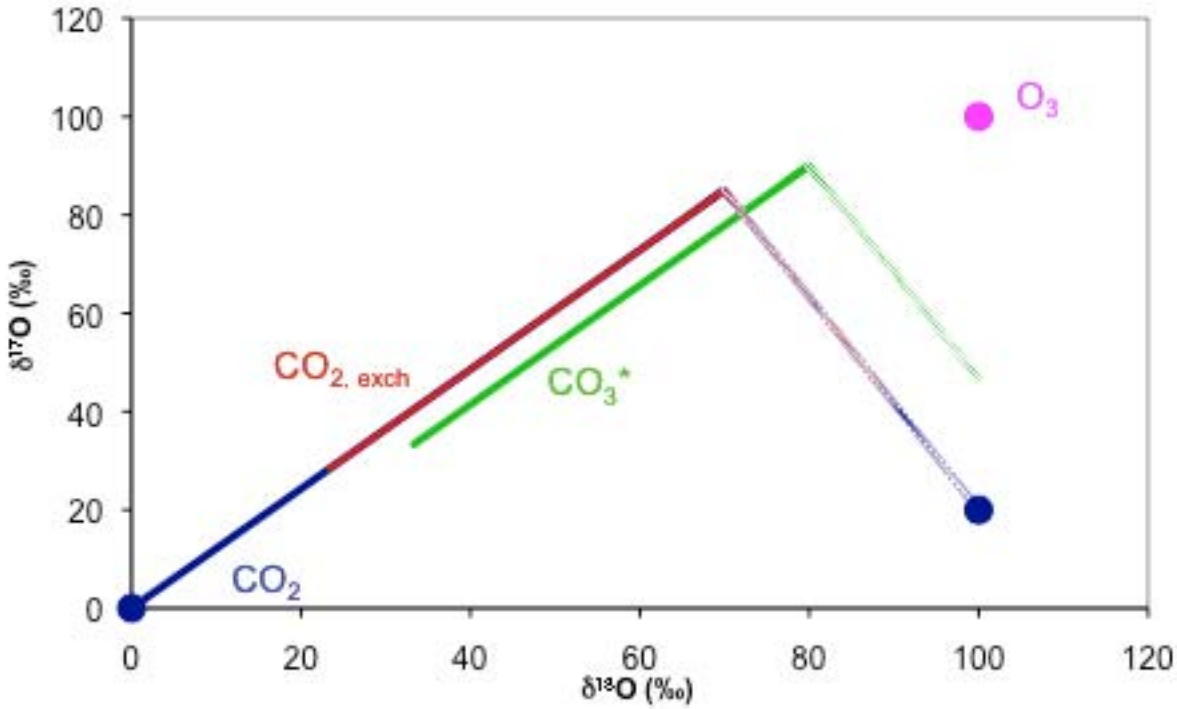
Isotope equilibrium point studies



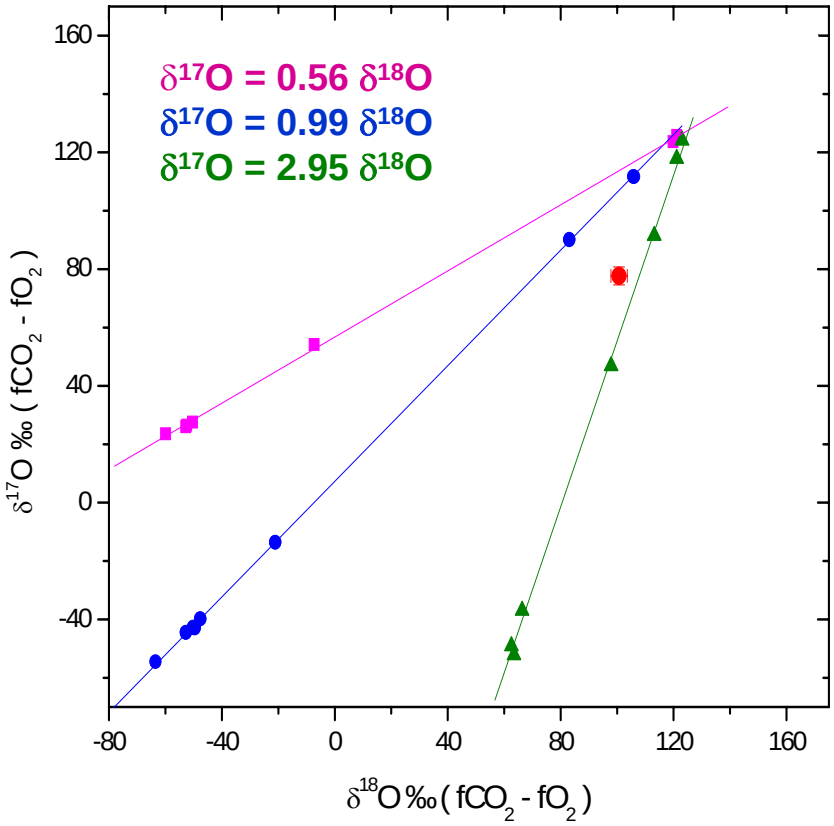
Use δ values of CO_2 versus O_2

Temporal evolution $\delta(t) = \delta_{eq} - (\delta_{eq} - \delta_i) \exp(-t/t_{eq})$

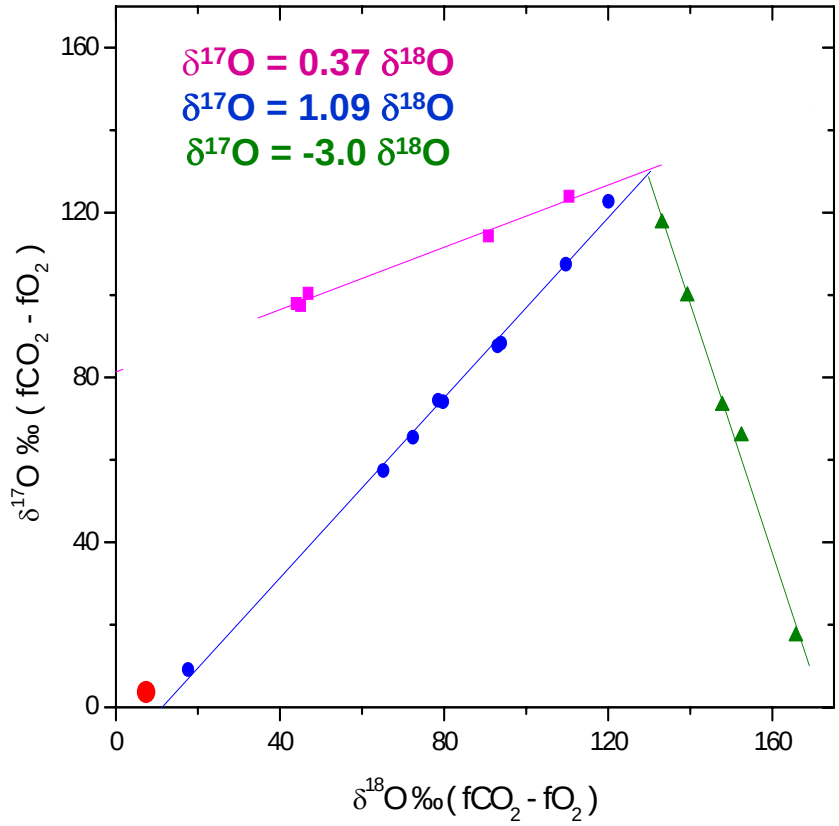
Triangulation approach



Triangulation results



CO_2-O_3 mixture

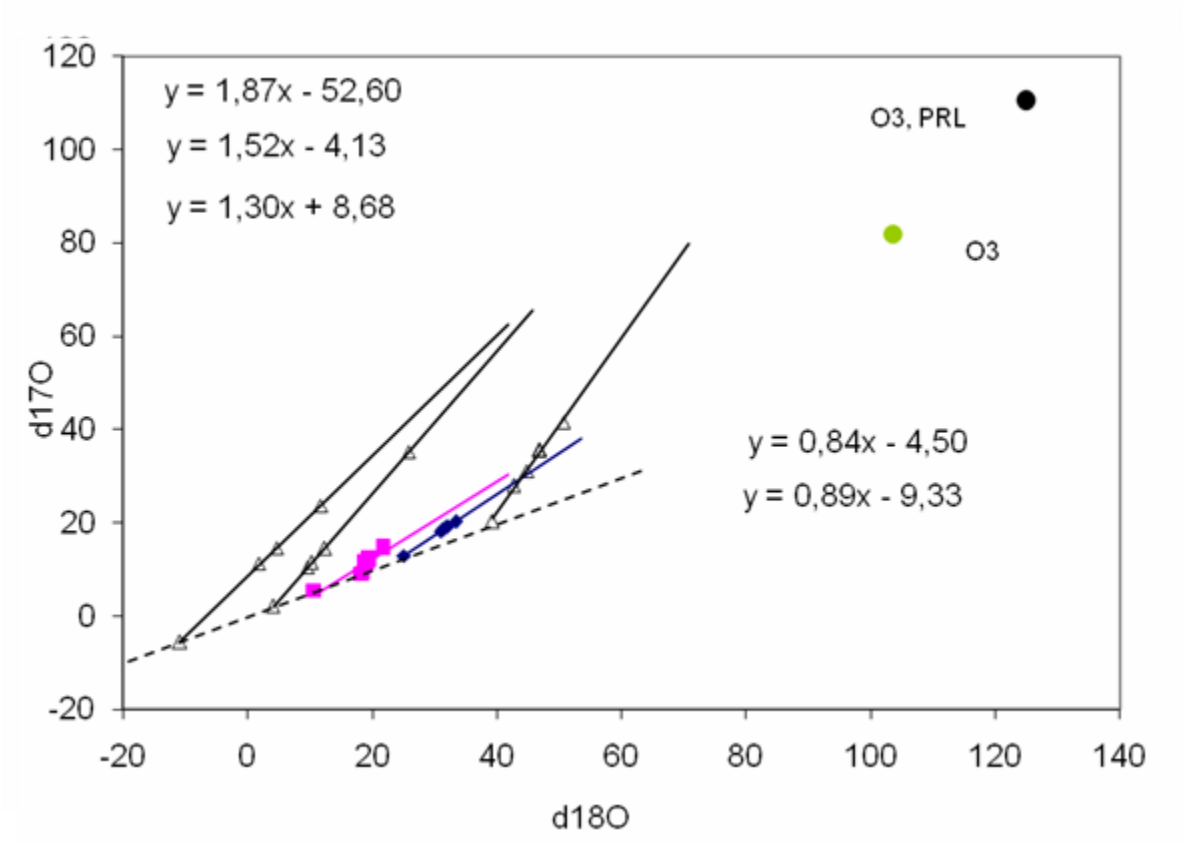


CO_2-O_2 mixture

Isotope equilibrium well-defined

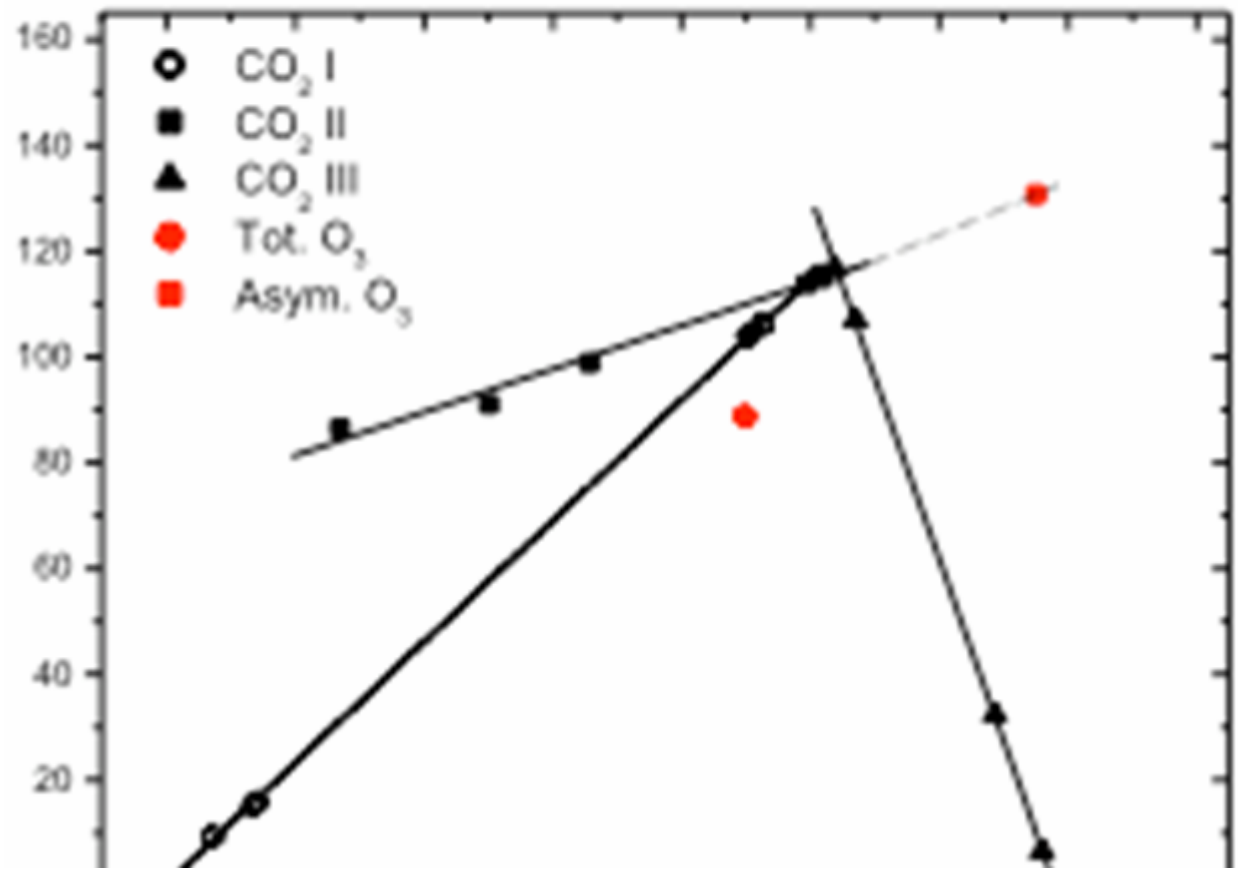
Now examine dependency on reaction parameters

Chakraborty et al., 2003



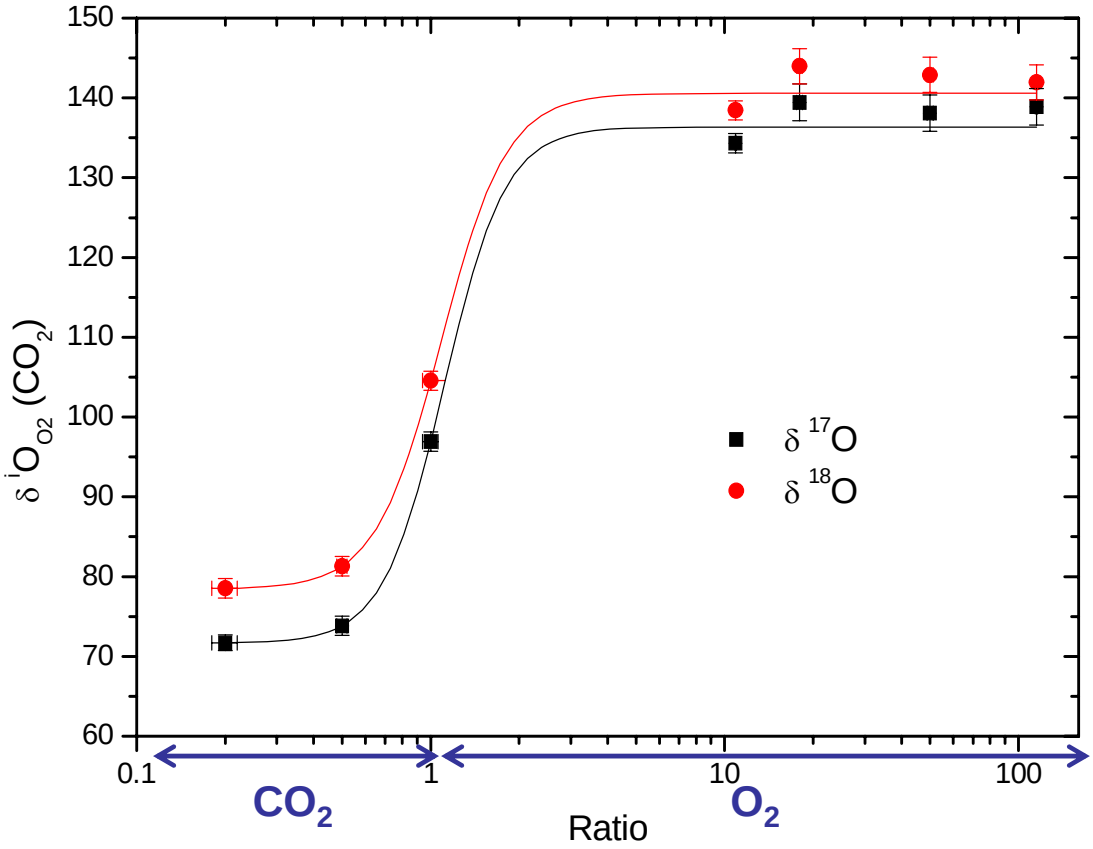
Link to asymmetric O_3

hotochemical equilibrium.



Result: mass dependent fractionation between asymmetric O_3 and $CO_{2,eq}$
Only 1 measurement, low T (280K?)

Ratio of reactants: O_2/CO_2



$\delta_h(^{18}O) = 146 \pm 4‰$
$\delta_h(^{17}O) = 142 \pm 4‰$

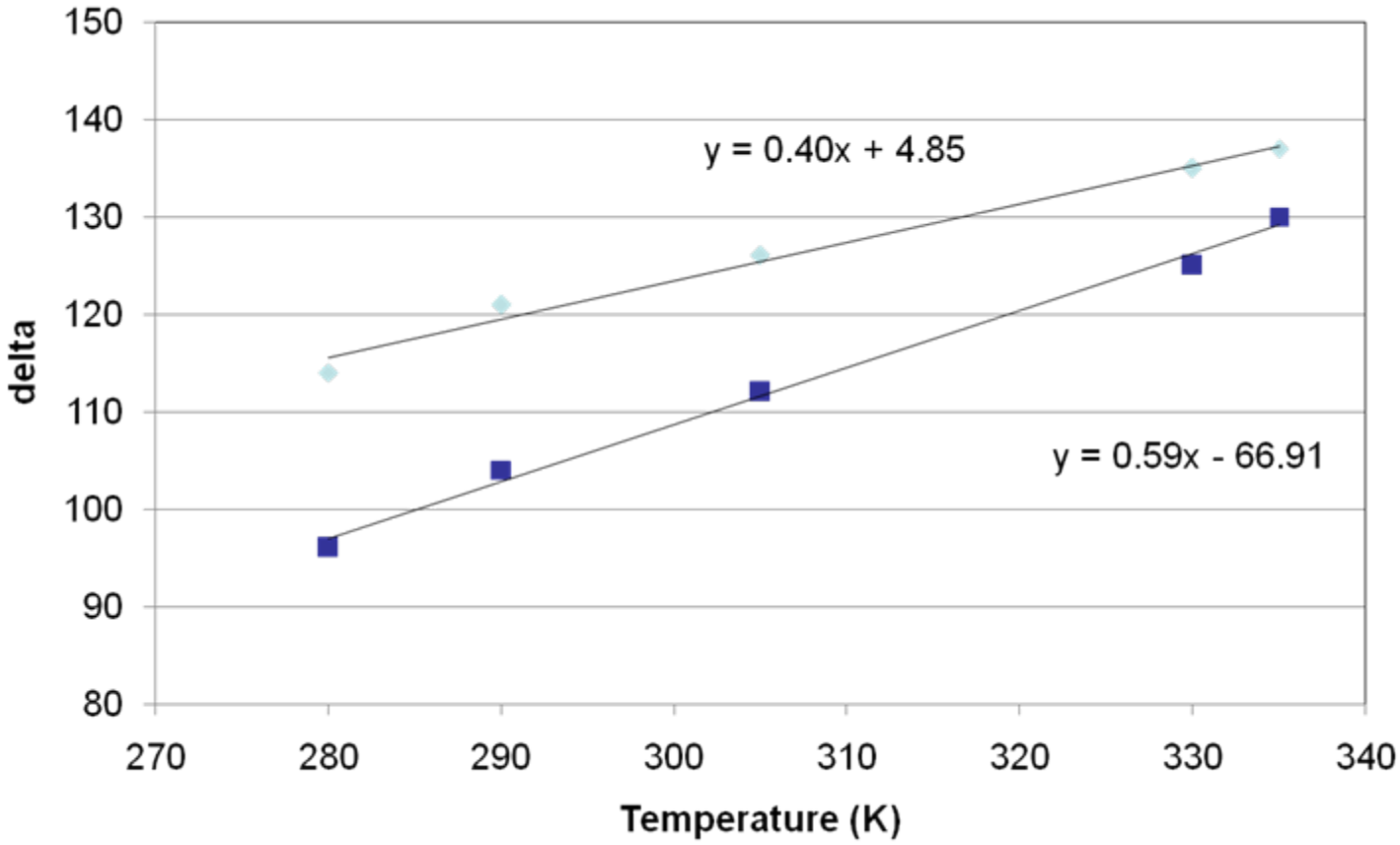
$\delta_l(^{18}O) = 64 \pm 11‰$
$\delta_l(^{17}O) = 58 \pm 11‰$

External effect:
CO_2 affects O_3 isotopic composition (better quencher)
Non-quenching exchange?

Internal effect: 1:1 change -> MIF in $CO_3^{\#}$ complex?

T-dependence of Isotope Equilibrium

Asymmetric O_3,
T dependence:
d17O: ~0.4‰/K
d18O: ~0.7‰/K



But: large corrections (errors) on T measurement
Repeat with better T control
Also pressure dependency!

Conclusions/outlook

- Stratospheric CO_2 possesses the highest oxygen-3-isotope-slope in nature
  - Affects tropospheric reservoir
  - Tracer for "photochemical age"
  - Origin of the O_2 isotope anomaly

- What is the exact slope in the stratosphere?
  - Variability close to tropopause?
  - Decrease of slope at high altitudes?

  - Dynamics of the exchange process
  - Origin of slope 1.7?
  - Mass (in)dependent effect in CO_3 complex?
  - External processes – relation to O_3?

INTRAMIF

INitialTRAining in Mass Independent Fractionation

A Marie Curie Initial Training Network

13 PhD projects

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University of East Anglia
University of Copenhagen
University Pierre et Marie Curie, Paris,
CEA-LSCE, Paris
University Joseph Fourier, Grenoble
University of Bern

http://www.phys.uu.nl/~intramif/

Yeung et al.: Δ_{47} measurements

Additional process:
Mesospheric photochemistry?
Heterogeneous chemistry?

vortex

mid-lat

CO_2 + O(^1D) exchange:
Towards random distrib.