L'effet isotopique de l'ozone : observations, études, rôle et applications

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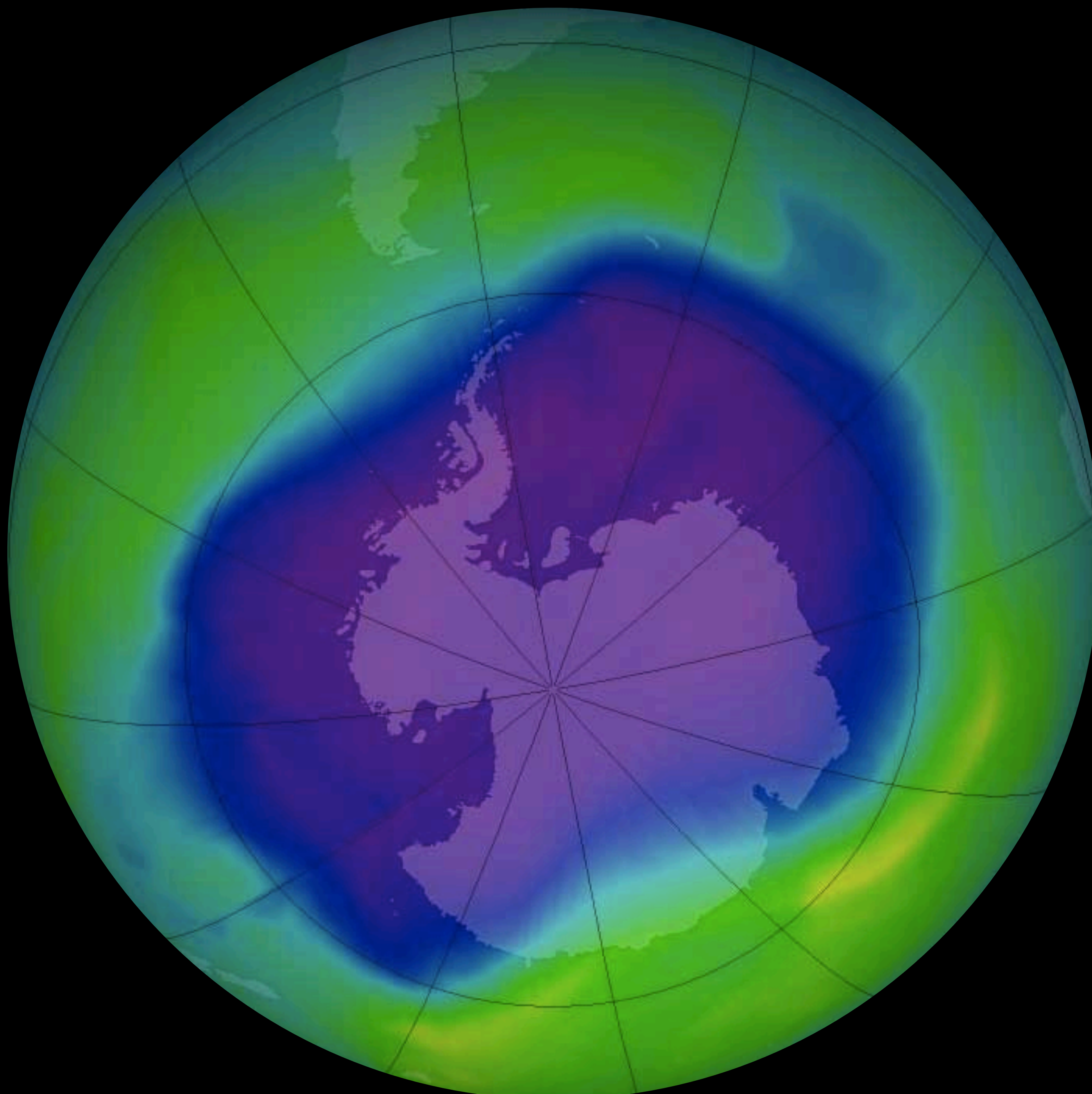
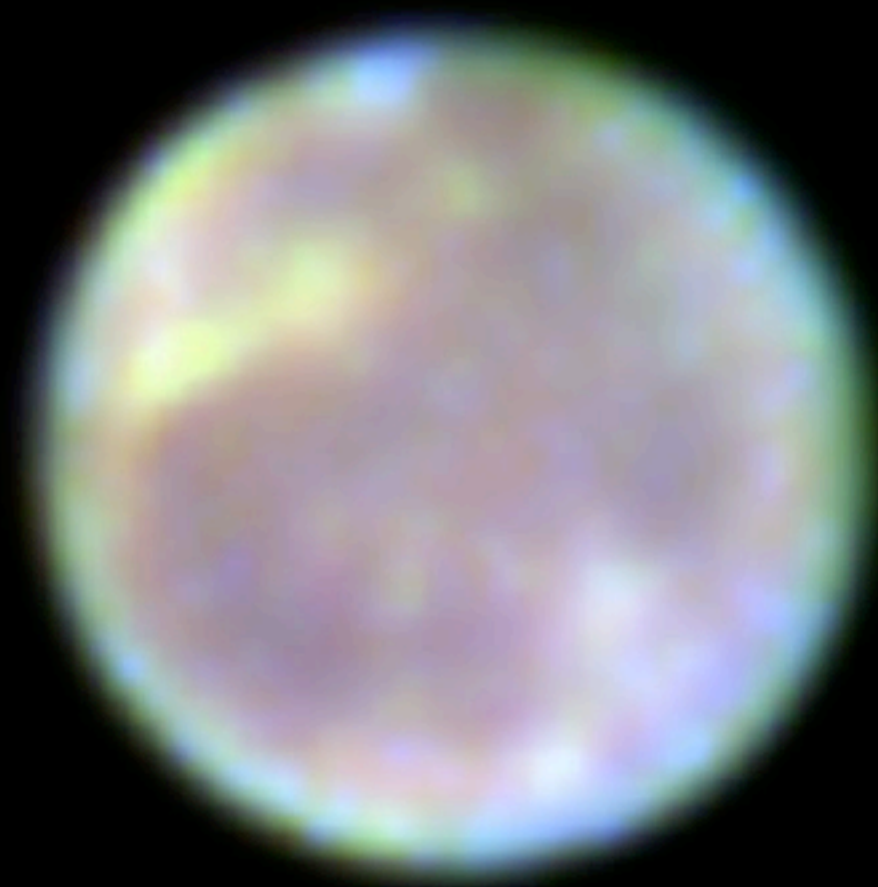
Antarctic Ozone Hole Sep 2006



Ozone on Ganymede



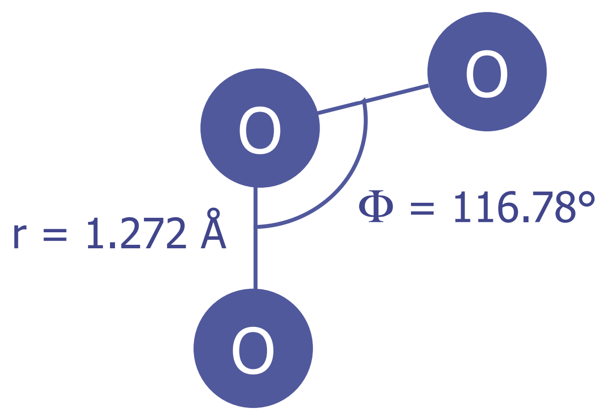
Noll *et al., Science* **273** (1996), Hubble photograph presented at AAS meeting in 1995, courtesy NASA

Overview

- introduction
  - ozone, isotope enrichment, history
  - measurement techniques
- laboratory studies on ozone formation
  - enrichment experiments
  - kinetic studies
- decomposition pathways
  - photolysis
  - other reactions
  - thermal decomposition
- theory and models
- atmospheric observations
  - measurement and sampling
  - stratosphere, troposphere
- isotope transfer processes
  - carbon dioxide
- conclusions & outlook

Ozone

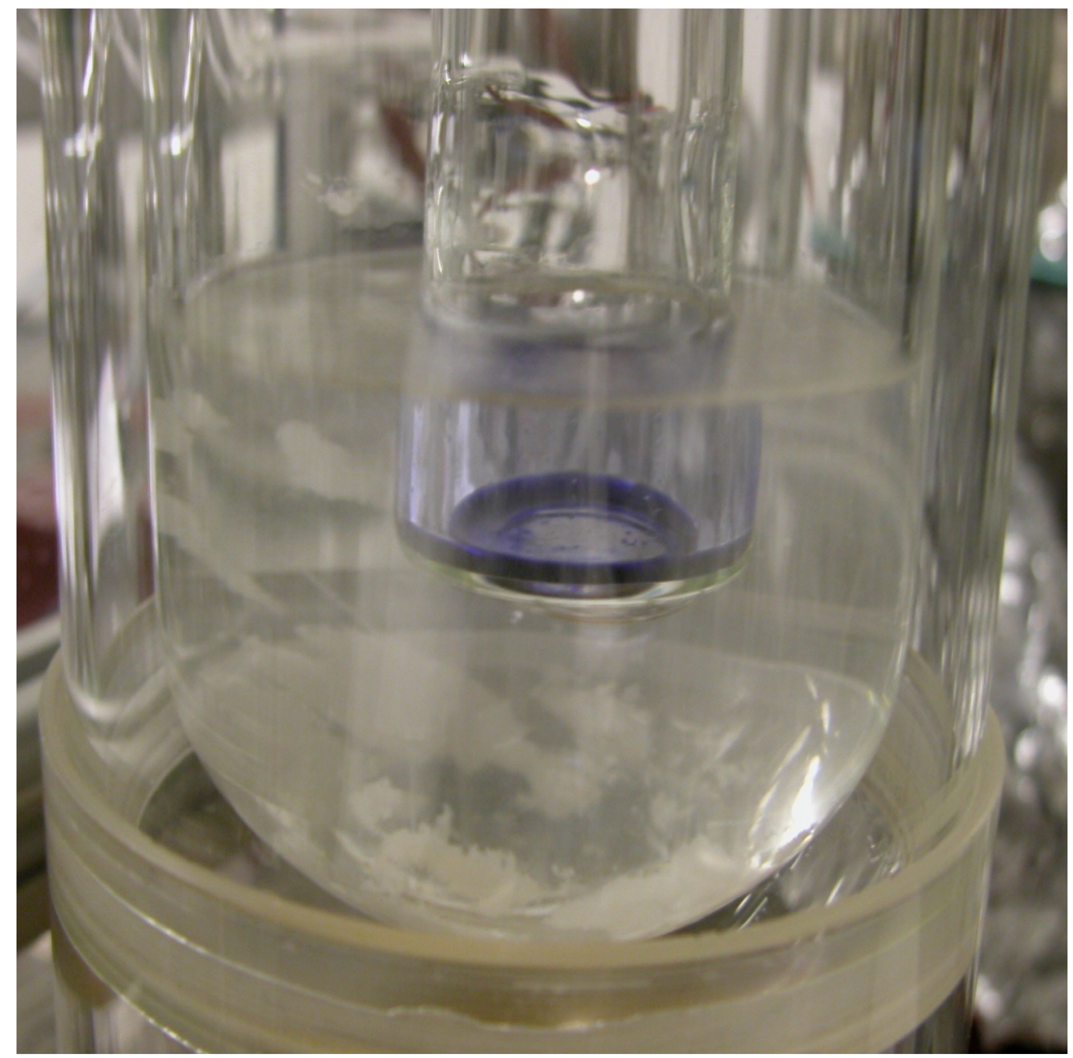
3-atomic allotrope of oxygen



$E_0 =$ 1.05 eV, λ_{diss} < 1180 nm

Oxygen Isotopes:

^{16}O	99,756 %
^{17}O	0,039 %
^{18}O	0,205 %



δ - notation

Standard definition -

The fraction of a heavy isotope in a compound (atom ratio):

$$^{17}R = \frac{^{17}\mathrm{O}}{^{16}\mathrm{O}}, \quad \delta^{17}\mathrm{O} = \frac{^{17}R_{\mathrm{sample}}}{^{17}R_{\mathrm{std}}} - 1, \quad (\text{in \% or ‰})$$

More specific -

Ratios of individual isotopomer ratios (clumped isotopes):

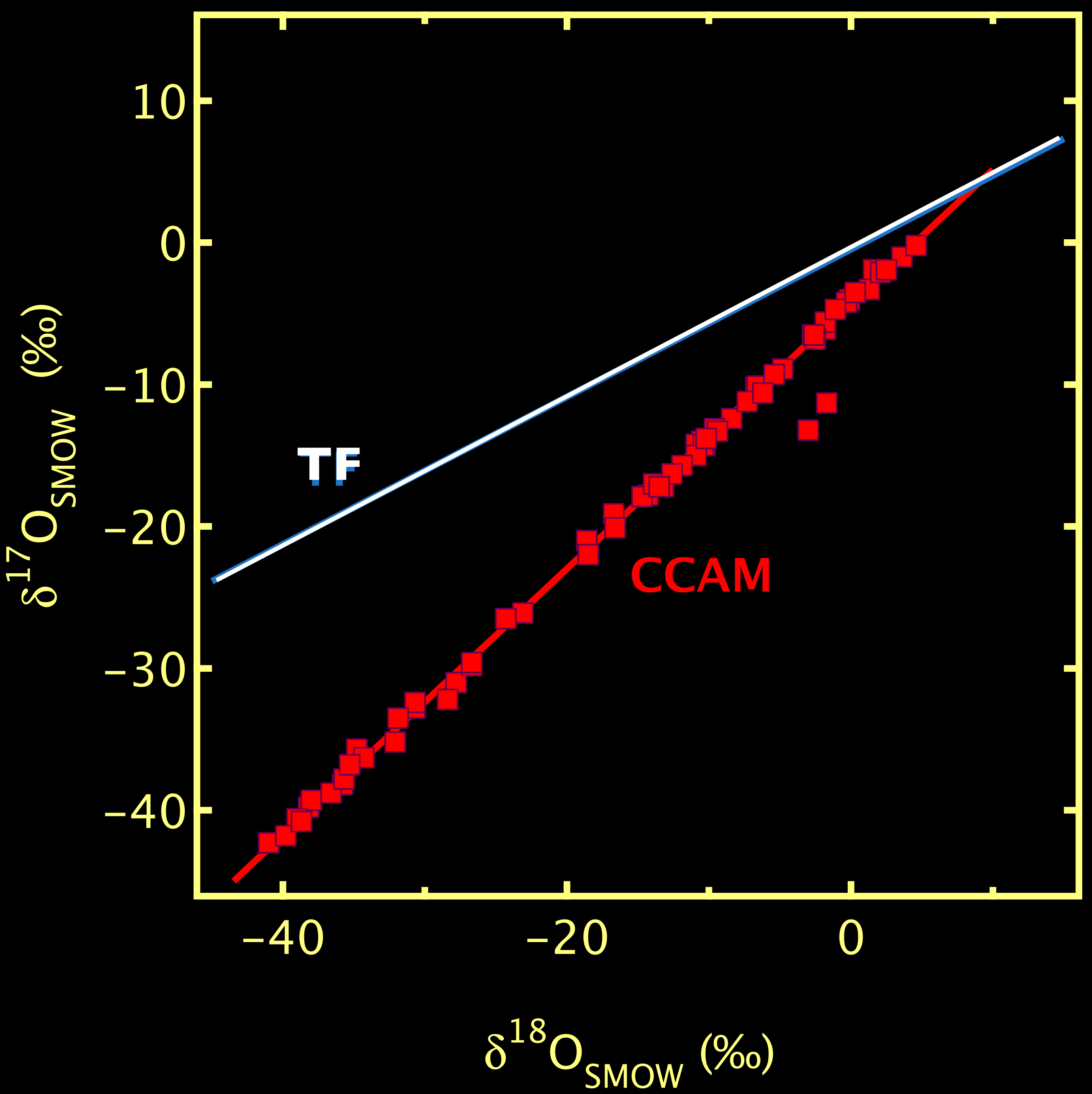
$$E\left(^{16}\mathrm{O}^{16}\mathrm{O}^{17}\mathrm{O}\right) = \frac{\left(\left[^{16}\mathrm{O}^{16}\mathrm{O}^{17}\mathrm{O}\right]/\left[^{16}\mathrm{O}_3\right]\right)_{\mathrm{sample}}}{\left(\left[^{16}\mathrm{O}^{16}\mathrm{O}^{17}\mathrm{O}\right]/\left[^{16}\mathrm{O}_3\right]\right)_{\mathrm{std}}} - 1$$

Standard (std) abundance from molecular oxygen

O–Isotopes in early solar system solids

Allende meteorite (fall 1969):

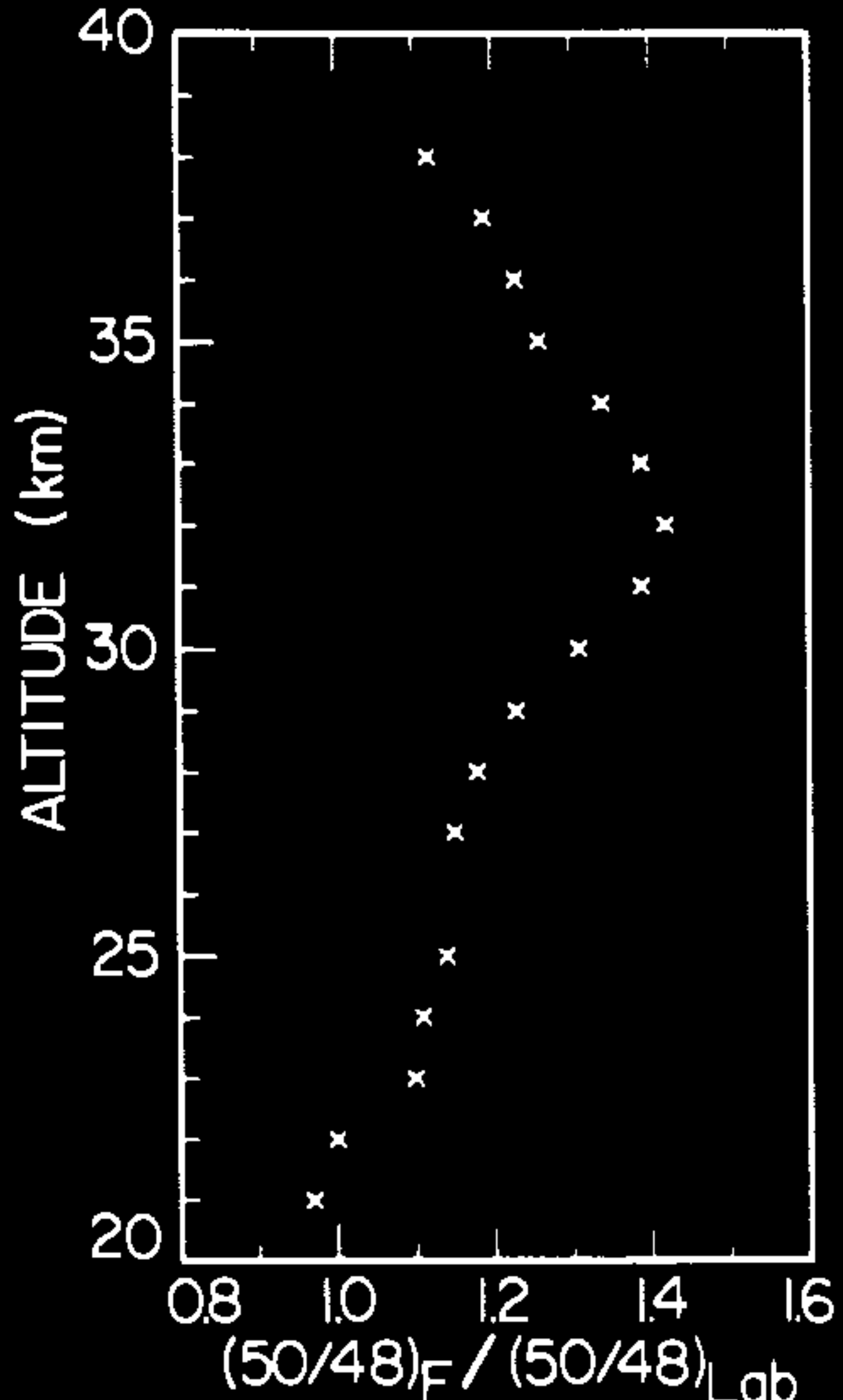
Triple oxygen isotope composition of refractory inclusions (CAI)



Clayton et al., *Science* **182** (1973)

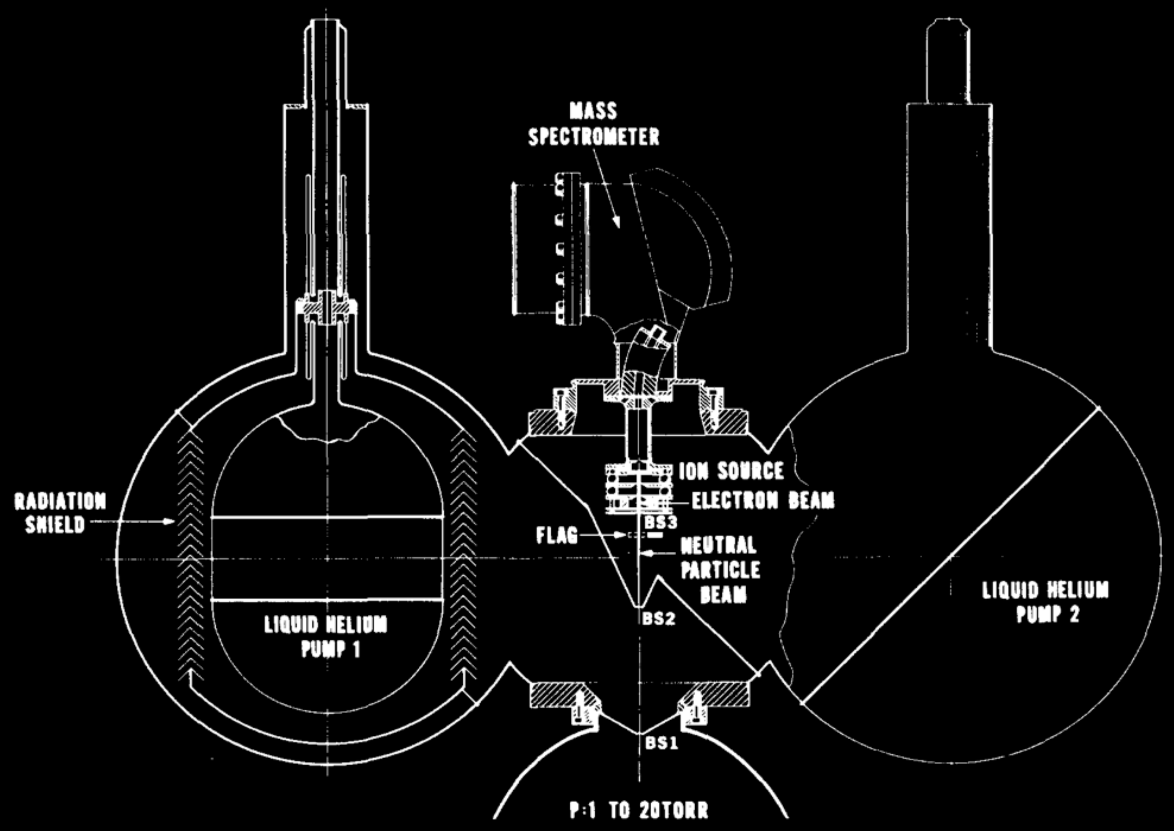
Isotope Fractionation of Stratospheric Ozone

Palestine Texas, Sep 3, 1980



max. ^{18}O enrichment (@ 32 km):

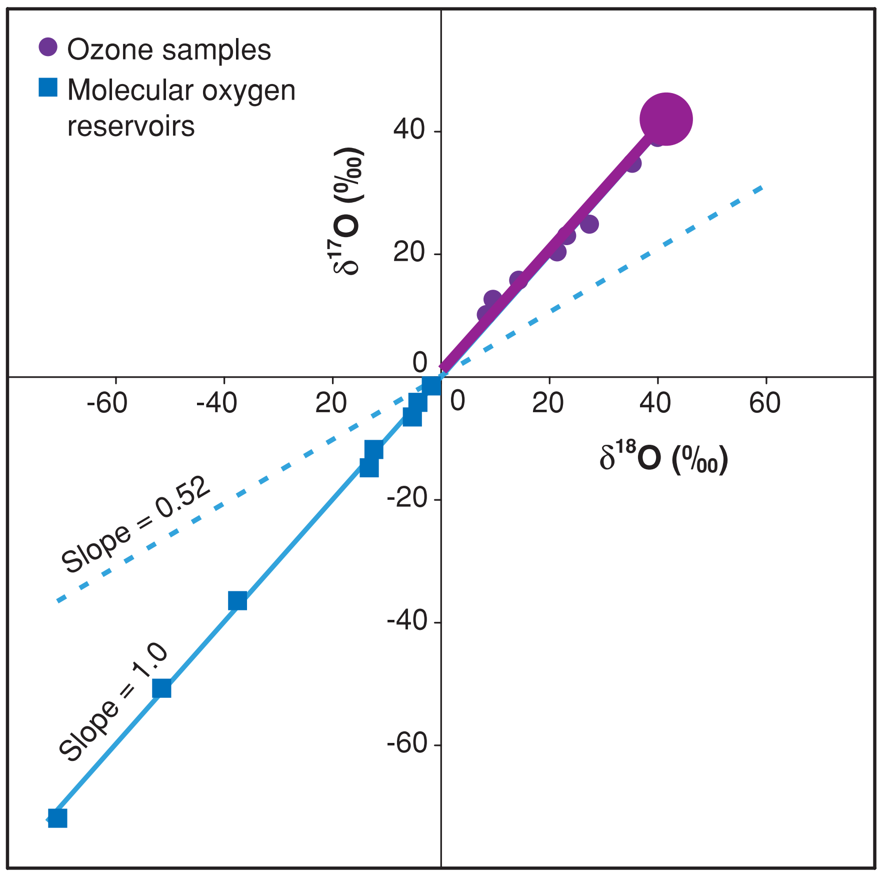
$\boxed{(40 \pm 15)\ \%}$

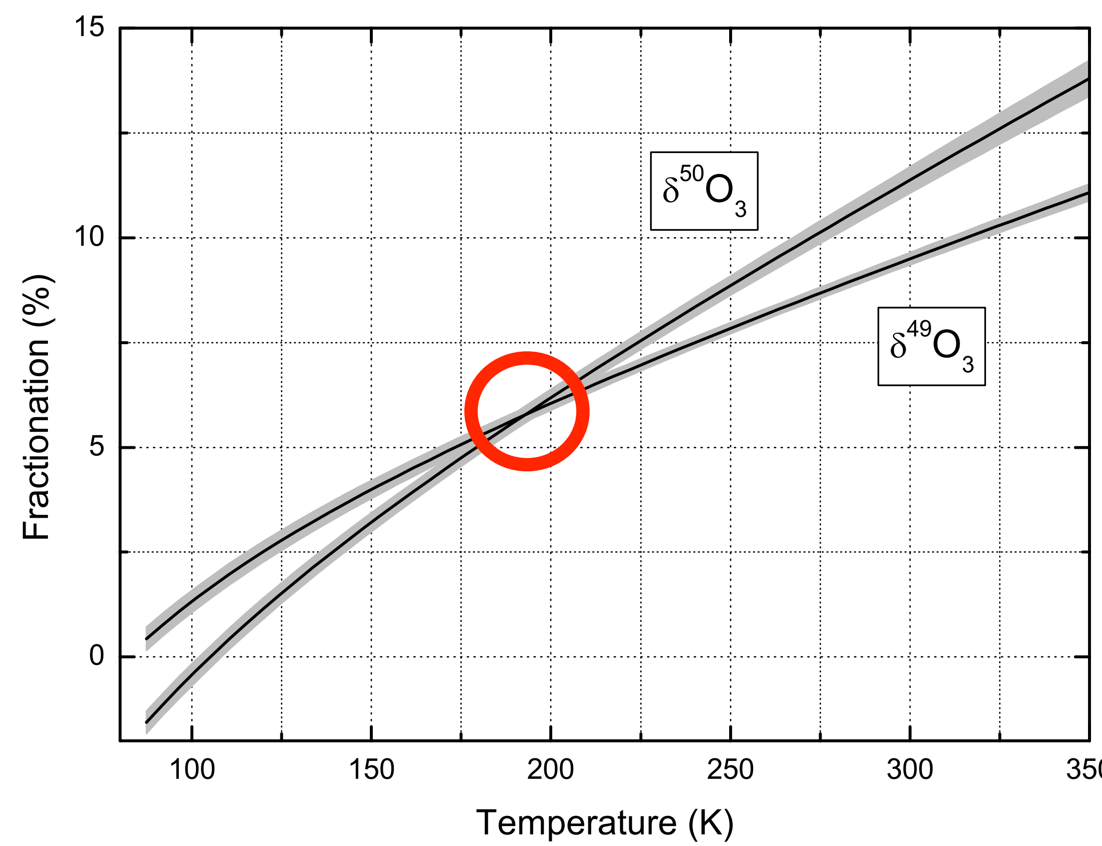


1170 Rev. Sci. Instrum., Vol. 48, No. 9, September 1977 Mass spectrometer beam system

Mauersberger, *GRL* **8** (1981)

Enrichment measurements

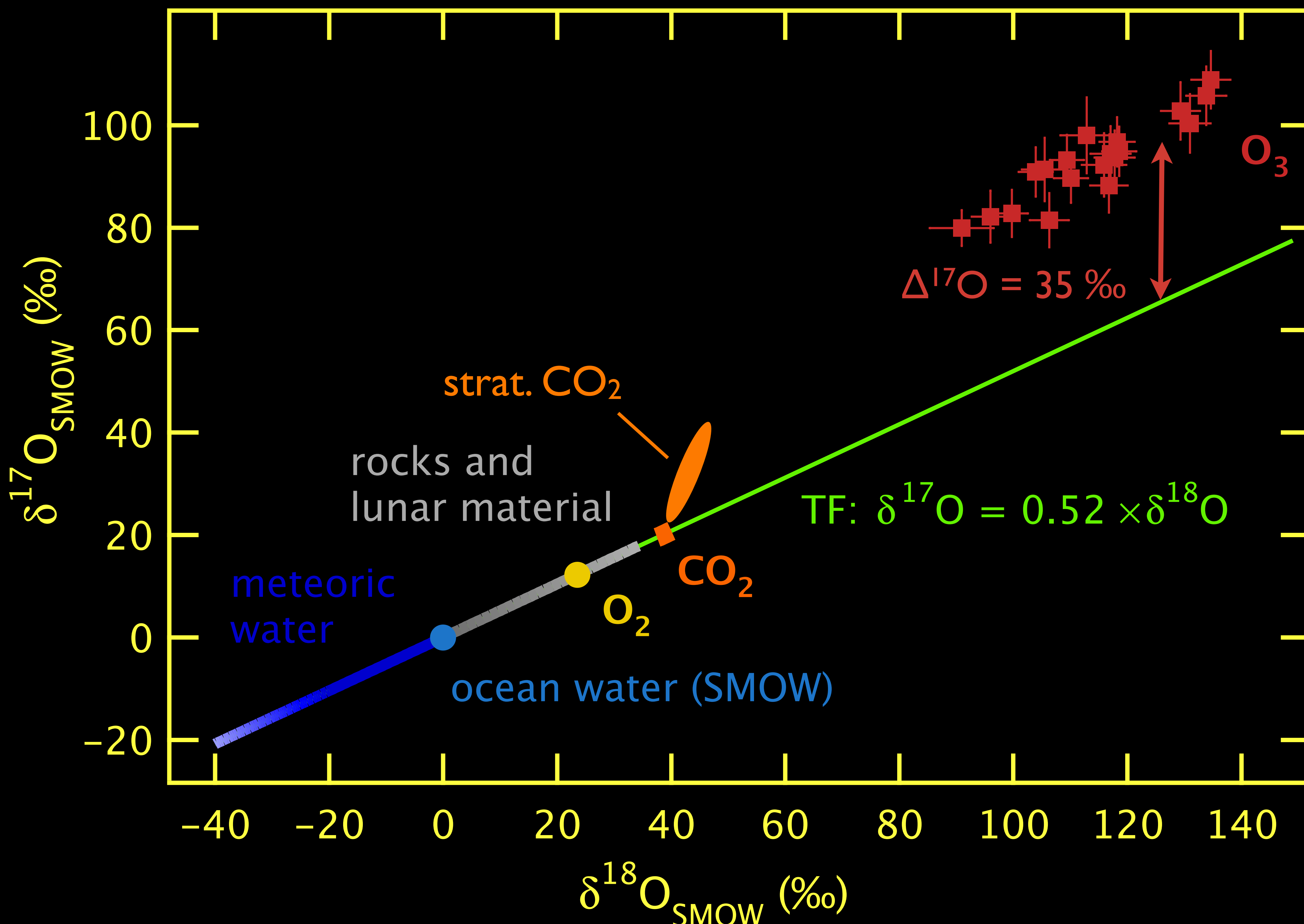




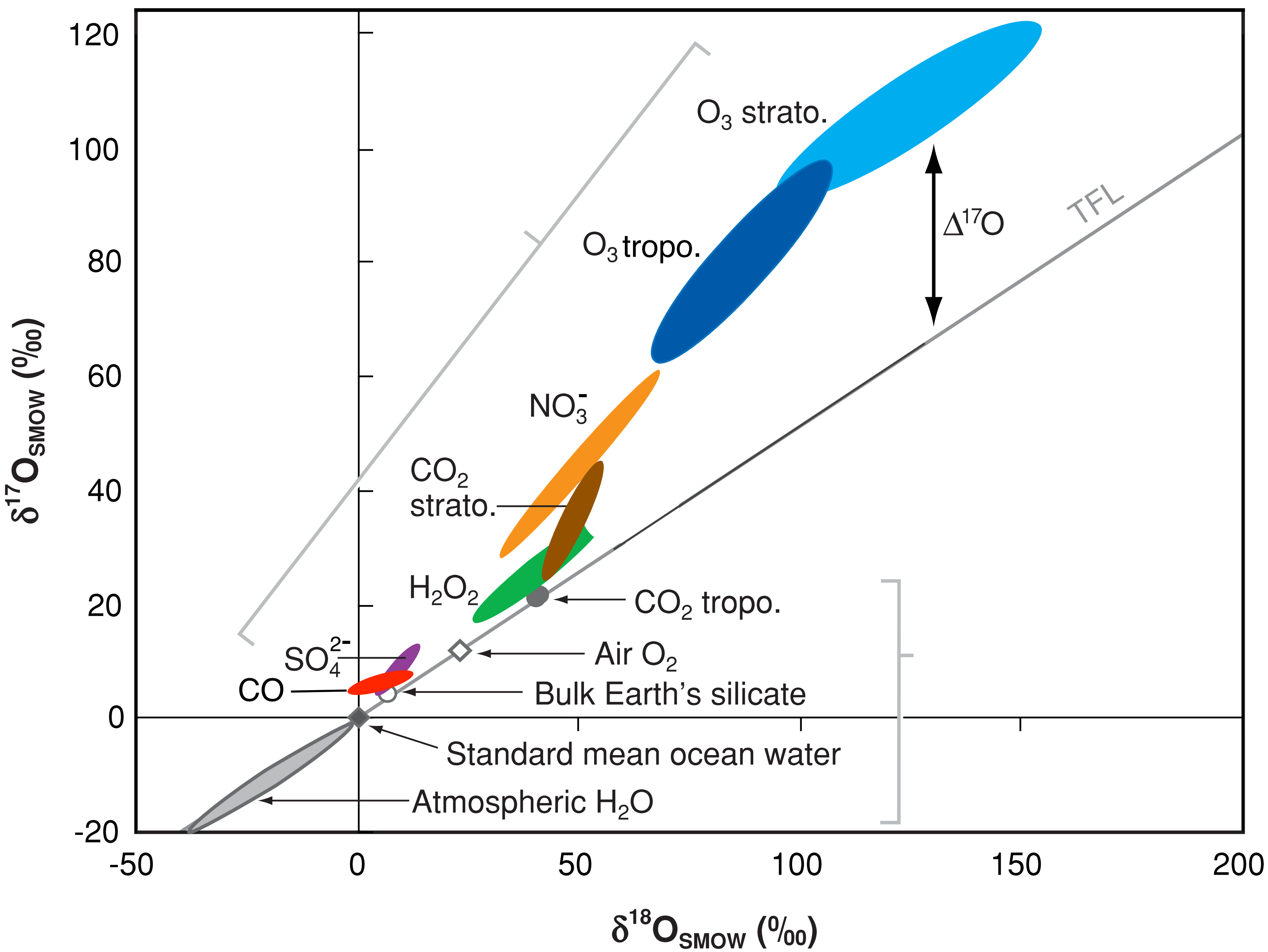
Thiemens & Heidenreich Science (1983)
Figure from Thiemens Ann Rev Earth Planet Sci (2006)

Krankowsky et al. *GRL* 112 (2007)

O–Isotopes in the environment



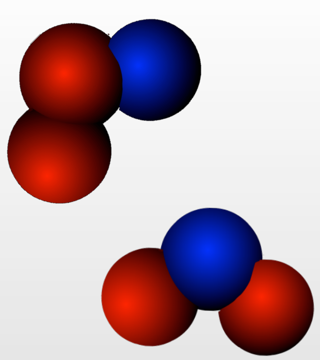
Oxygen isotope anomalies in nature (MIF)

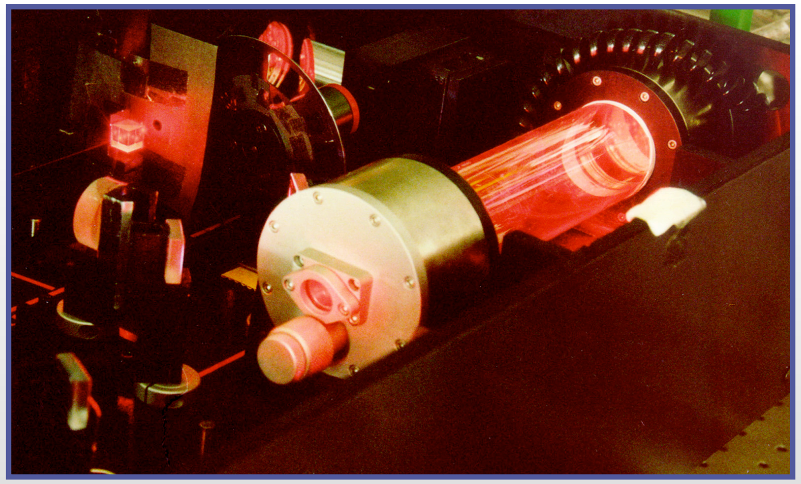


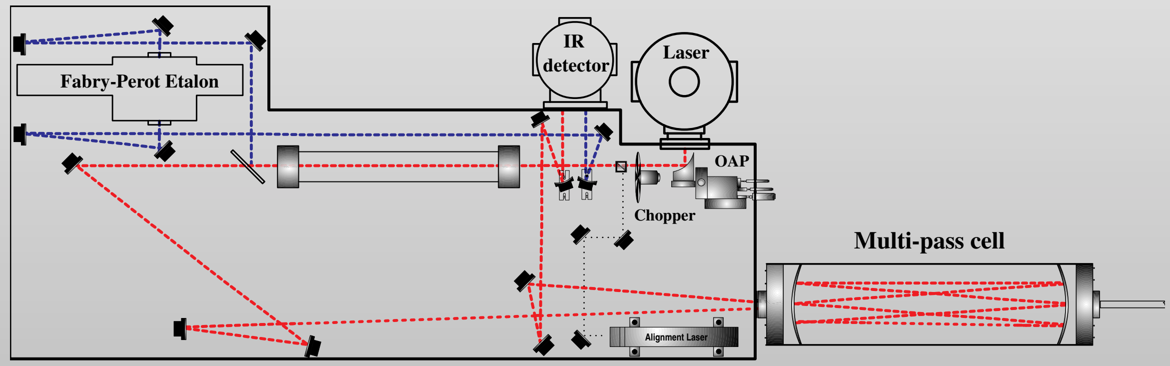
adapted from Thiemens, *Ann Rev Earth Planet Sci* **34** (2006)

Detection Techniques

O_3:
TDLAS @ 1000 cm^{-1}

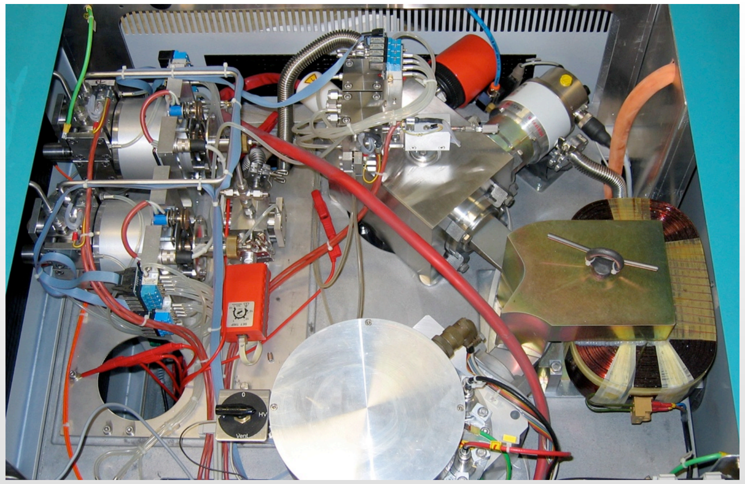


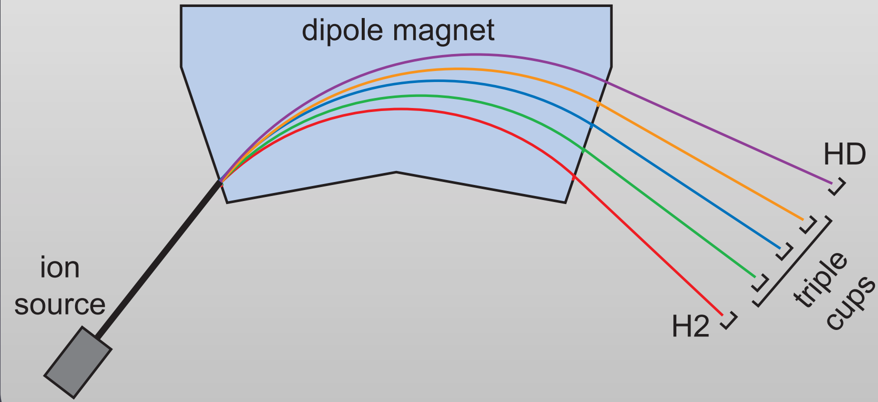




C. Janssen & B. Tuzson, *Appl. Phys. B* **82** (2006)

O_2, CO_2:
IRMS & CeO_2-Exchange





O_2	CO_2
32	44
33	45
34	46

S. Assonov & C. Brenninkmeijer, *RCM* **15** (2001)
ThermoFinnigan, Delta Plus^{XL}

Less Direct Measurement Techniques

- isotope ratio mass spectrometry of O_2 after conversion of O_3 ⇒ total/ isotopologue enrichment

- conversion on reactive surfaces (Ag), measure residual O_2 ⇒ increase importance of central atom

  Bhattacharya et al. *JGR* **113** (2008)

- reaction of $NO_2^- + O_3 \rightarrow NO_3^- + O_2$ ⇒ enrichment in terminal atom (isotopomer specific)

  Michalski and Bhattacharya et al. *PNAS* **14** (2009)

  Vicars et al. *RCMS* **26** (2012)

Ozone generation methods

El. Discharge

$O_2 + e^- \rightarrow O + O^-$

$O + O_2 + M \rightarrow O_3 + M$

$O + O_3 \rightarrow 2\,O_2$

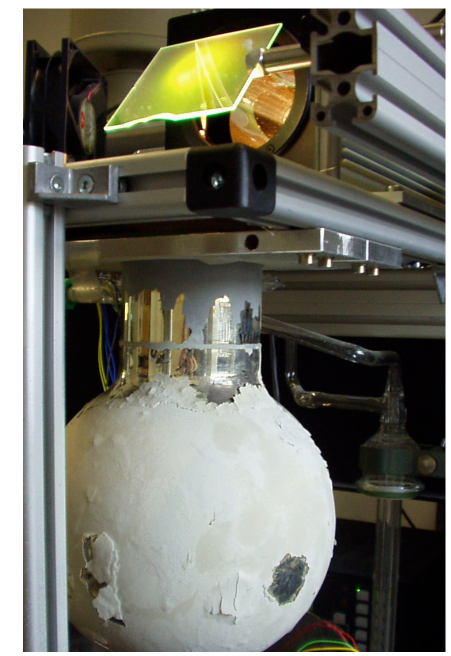
many others

Photolysis

$O_3 + h\nu \rightarrow O_2 + O$

$O + O_2 + M \rightarrow O_3 + M$

$\cancel{O + O_3 \rightarrow 2\,O_2}$



Morton et al. *JGR* **95** (1990)

Water Electrolysis

Anode: $3H_2O \rightarrow O_3 + 6H^+ + 6e^-$

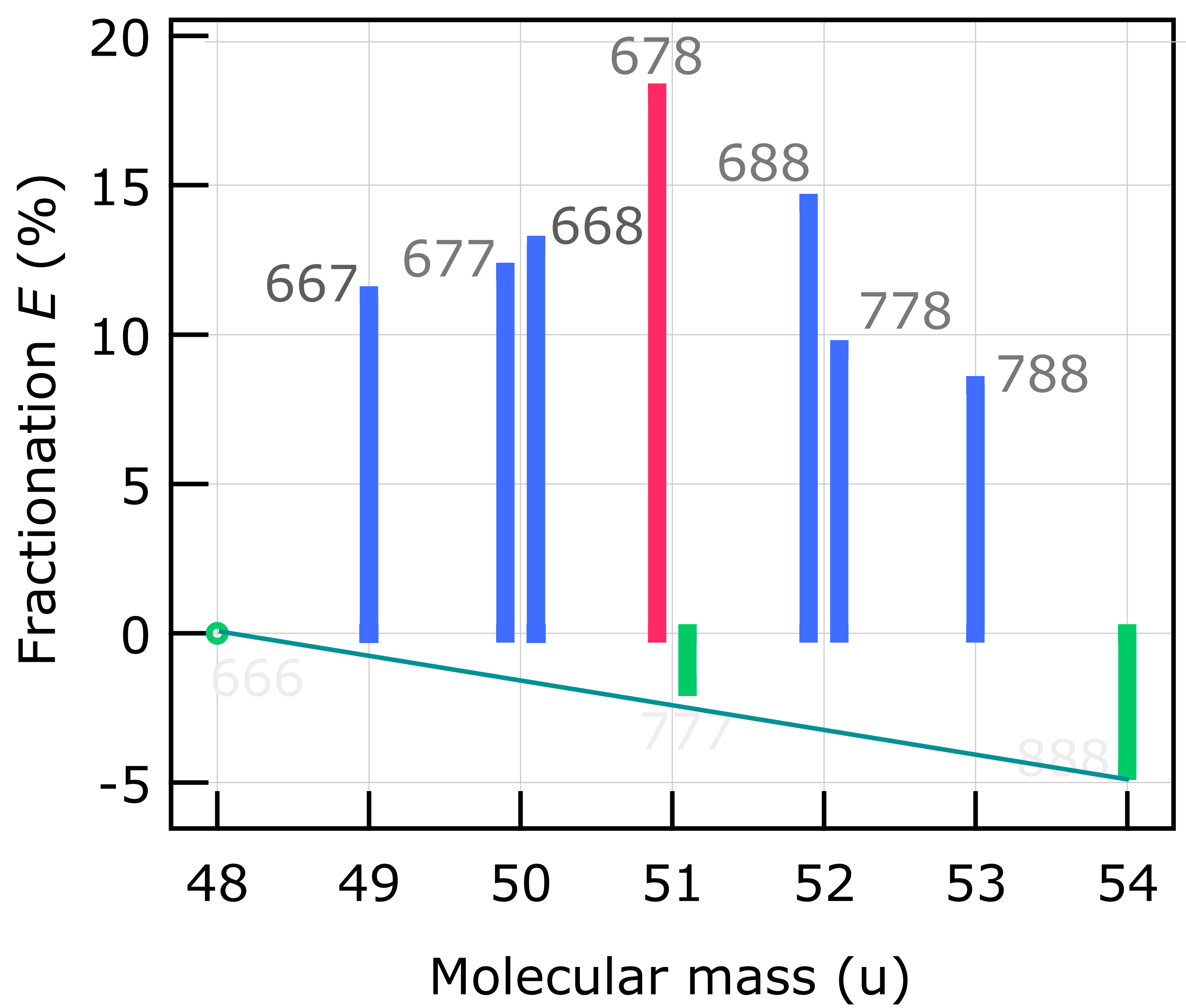
Enrichment measurements

thermodynamic (atom exchange) and **kinetic** fractionation effects

$$\mathrm{O} = {}^{16}\mathrm{O}, \quad \mathrm{Q} = {}^{18}\mathrm{O}$$

$$\mathrm{Q} + \mathrm{O_2} \rightleftharpoons \mathrm{OQ} + \mathrm{O}$$

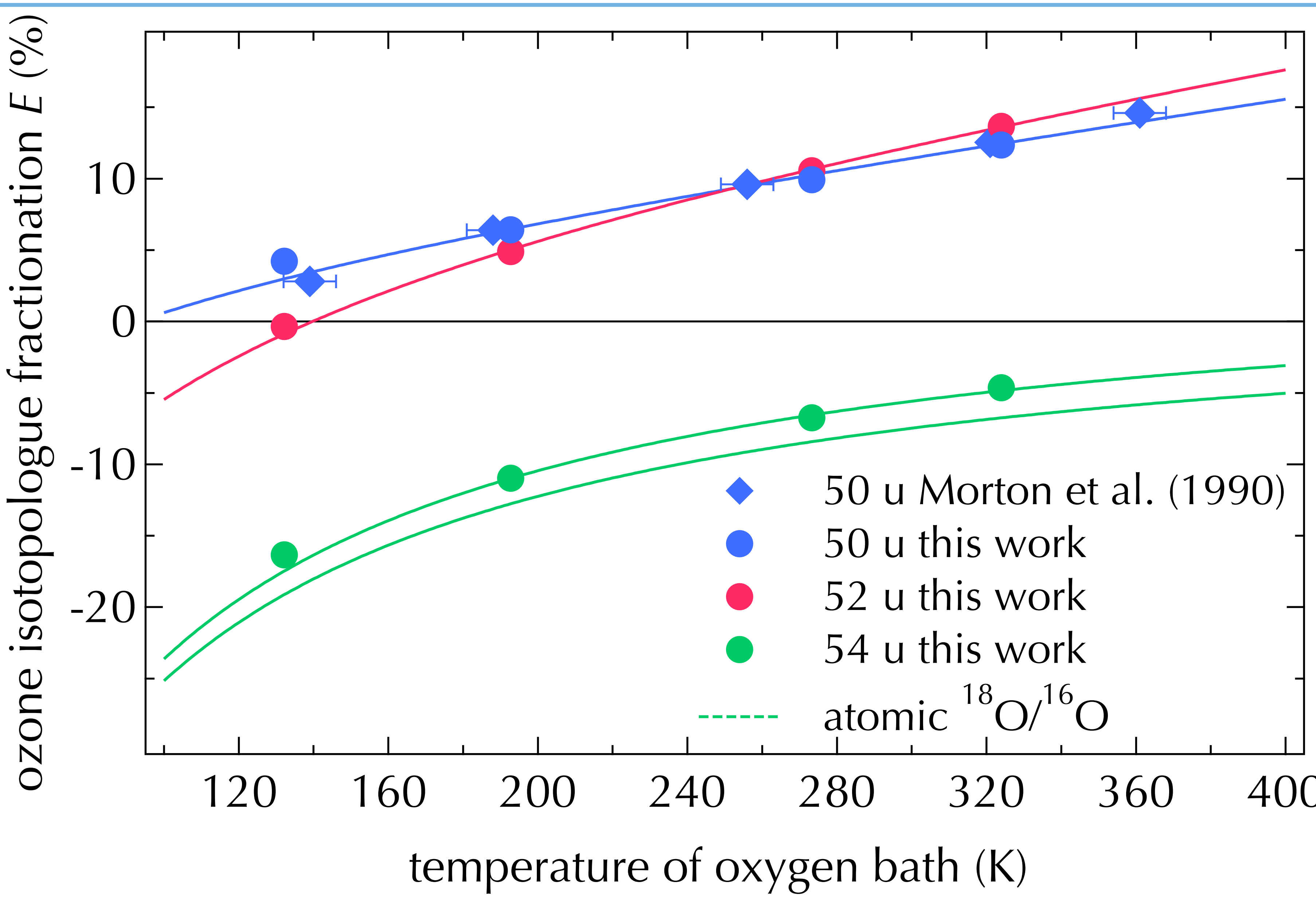
$$\frac{[\mathrm{Q}]}{[\mathrm{O}]} = \frac{1}{K_{eq}(T)} \frac{[\mathrm{OQ}]}{[\mathrm{O_2}]}$$



Kaye & Strobel, *JGR* **88** (1983)

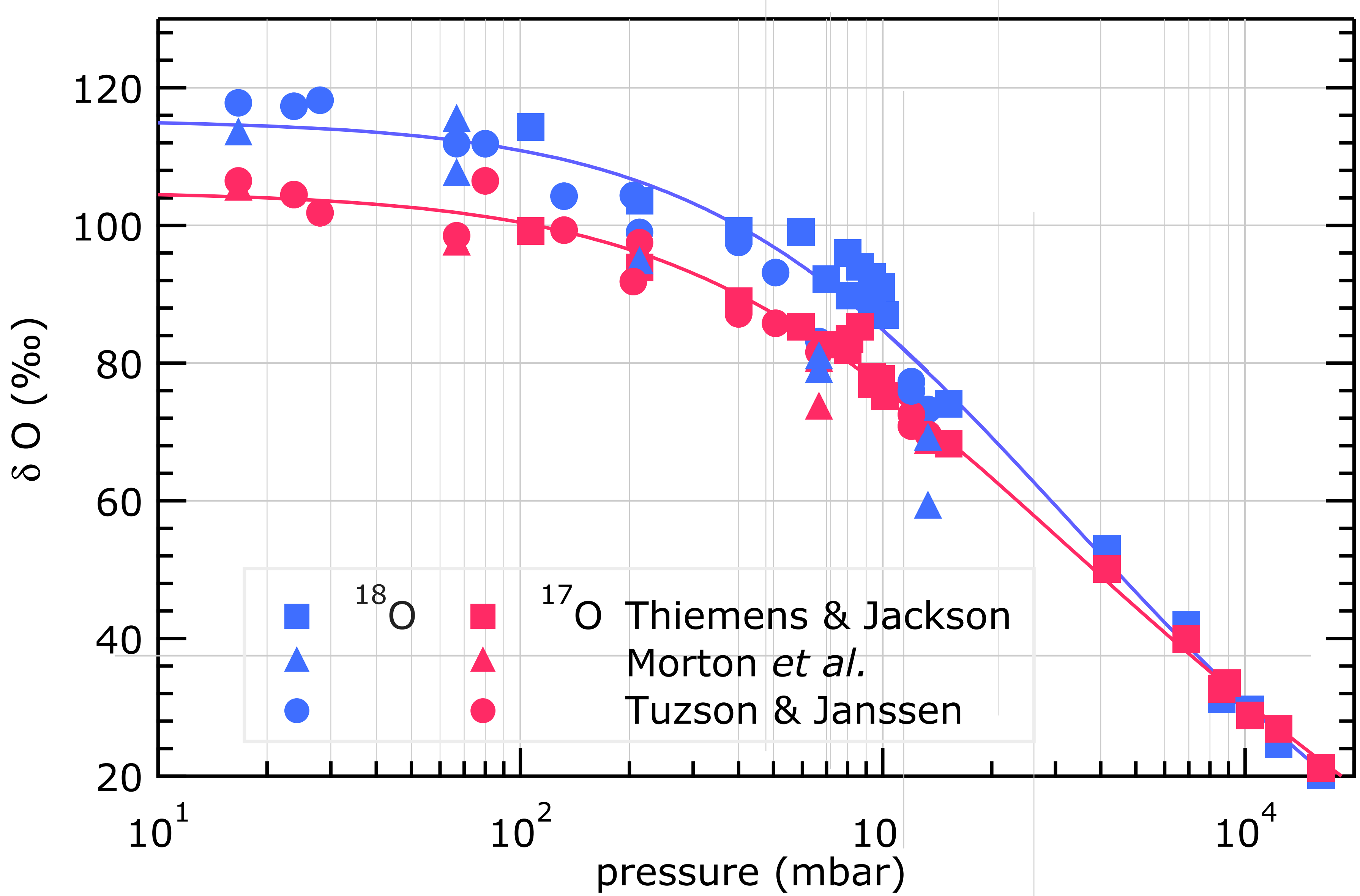
Mauersberger *et al.*, *GRL* **20** (1993)

Temperature Dependence



Janssen et al. *CPL* **367** (2003)

Pressure dependence



Heterogeneous ozone formation

$$O + O_2 + \text{wall} \rightarrow O_3 + \text{wall} : \; k \simeq \frac{2R}{\gamma v}$$

T = 350 K

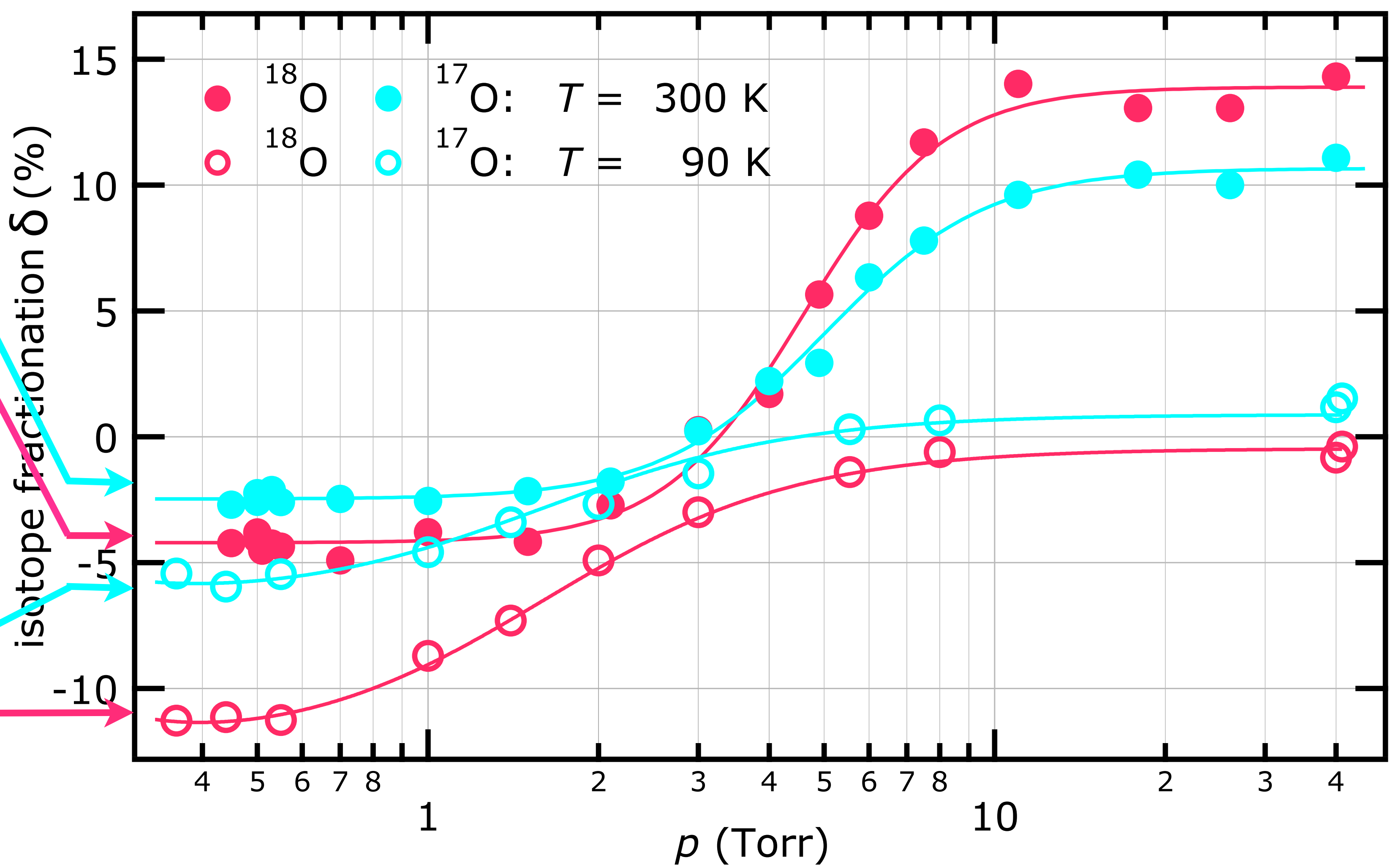
- 2.1 %

- 3.8 %

T = 90 K

- 6.1 %

- 10.6 %



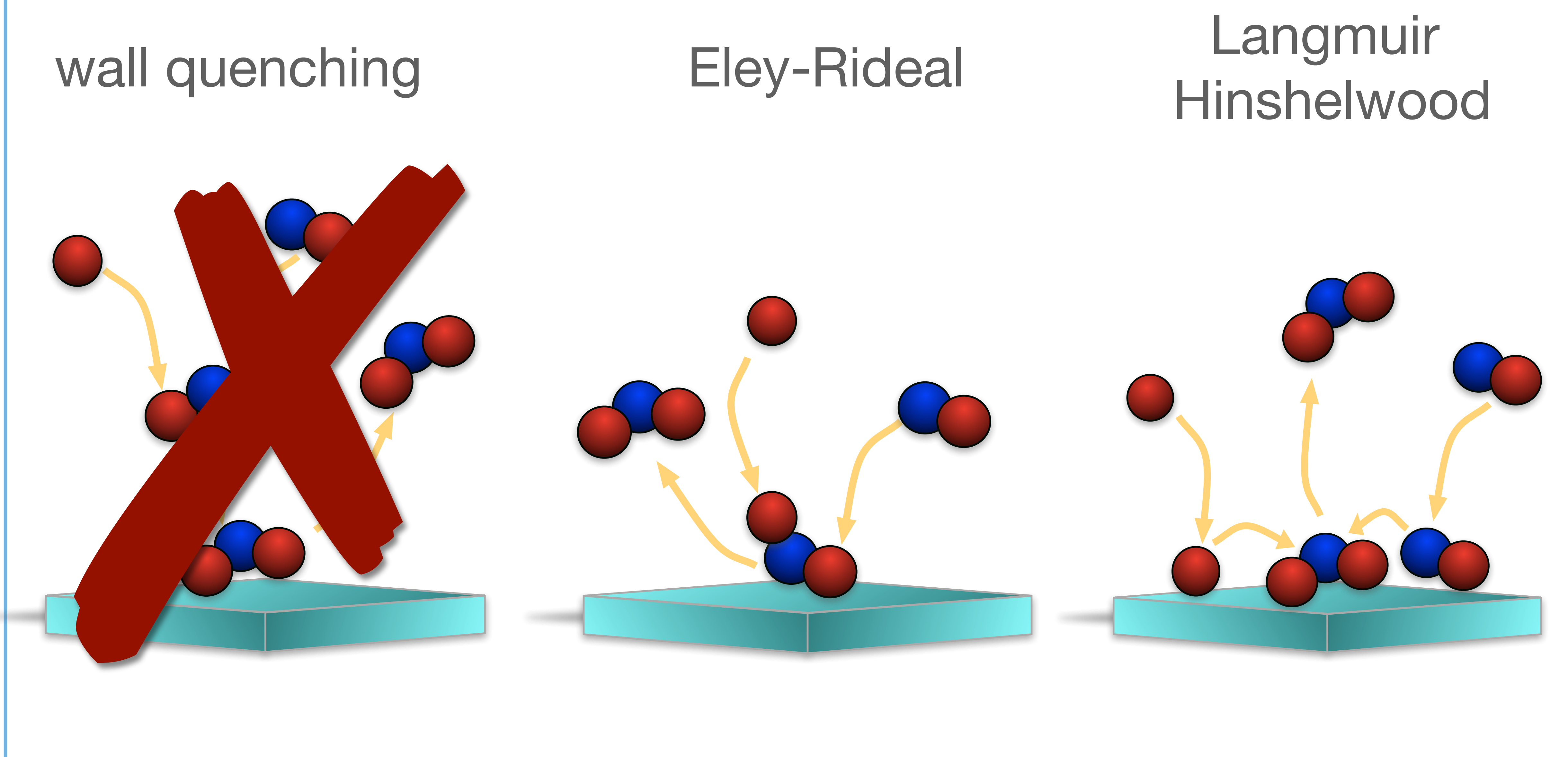
Explain low *p*

- *diffusion*
- *exchange*
- *small IE in wall reaction*
- *determine γ*

$\boxed{\gamma = 4\ 10^{-3}}$

Janssen & Tuzson, *JCPA* (2010)

Heterogeneous ozone formation

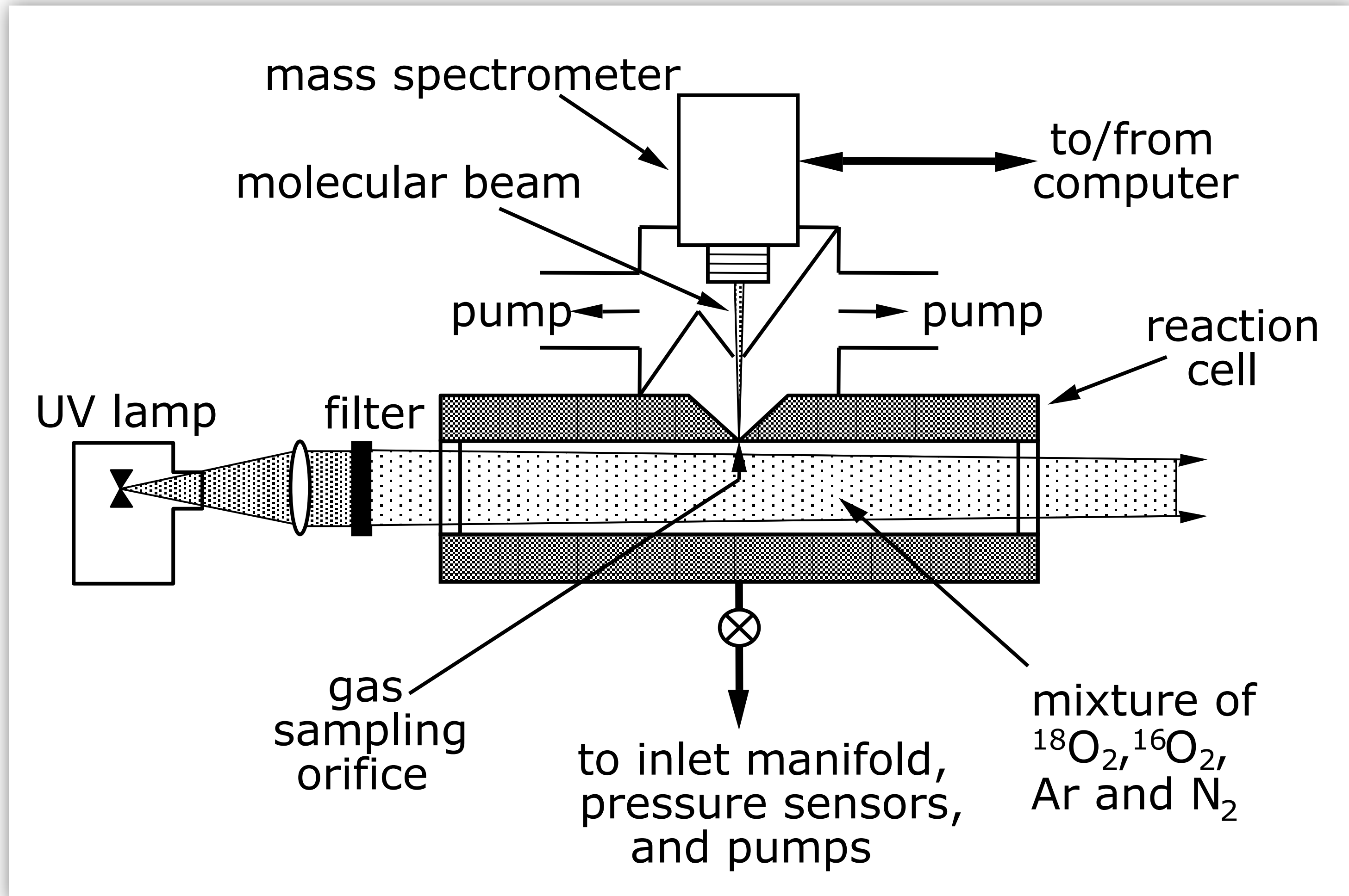


Janssen & Tuzson, *JCPA* (2010)

Rate coefficients

$O = {}^{16}O$, $Q = {}^{18}O$

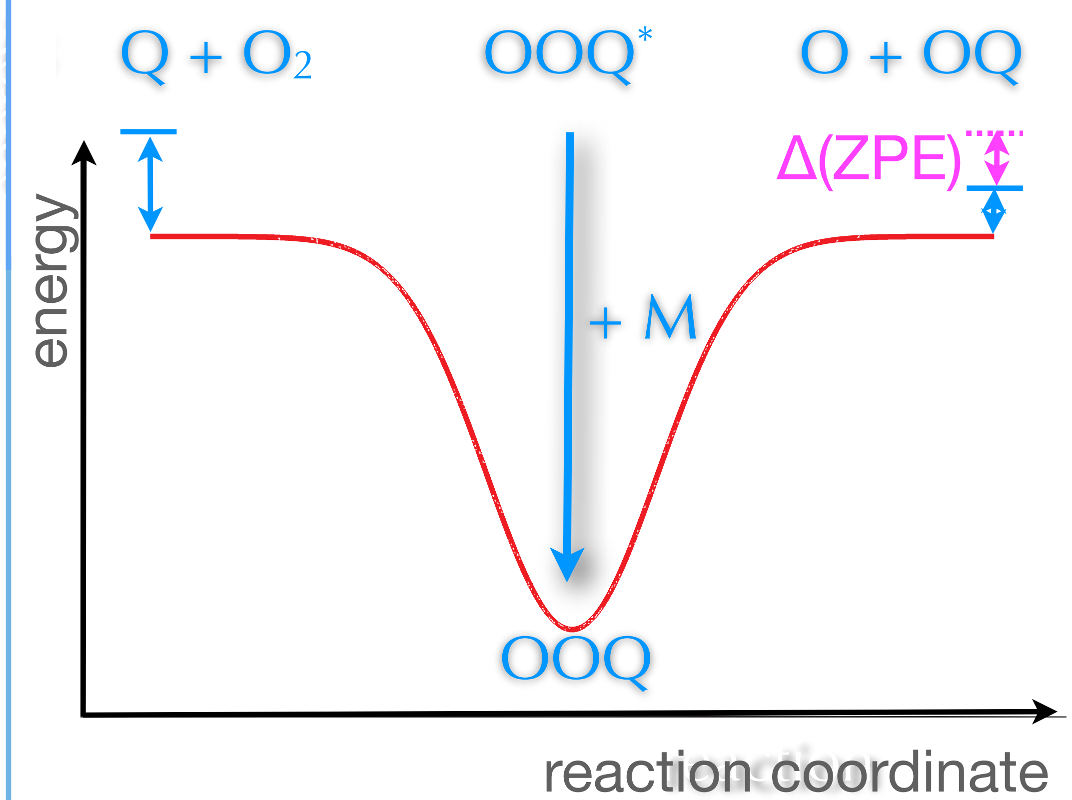
$O + O_2 \rightarrow O_3$	1
$Q + O_2 \rightarrow QO_2$	1.06
$O + Q_2 \rightarrow OQ_2$	1.46
$Q + Q_2 \rightarrow Q_3$	1.03

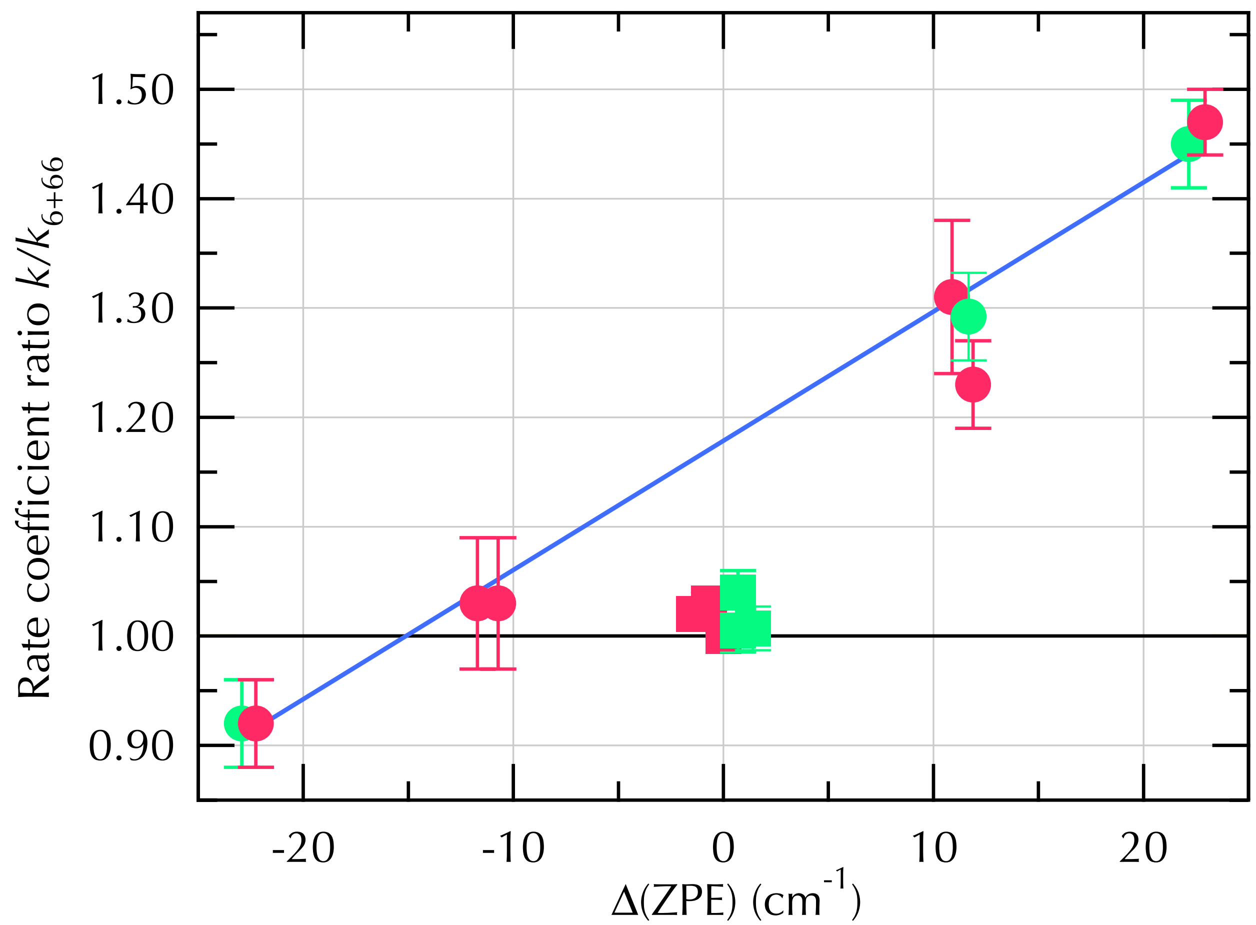


Anderson et al., *JCP* **107** (1997)

Janssen et al., *CPL* **367** (2003)

Rate coefficients

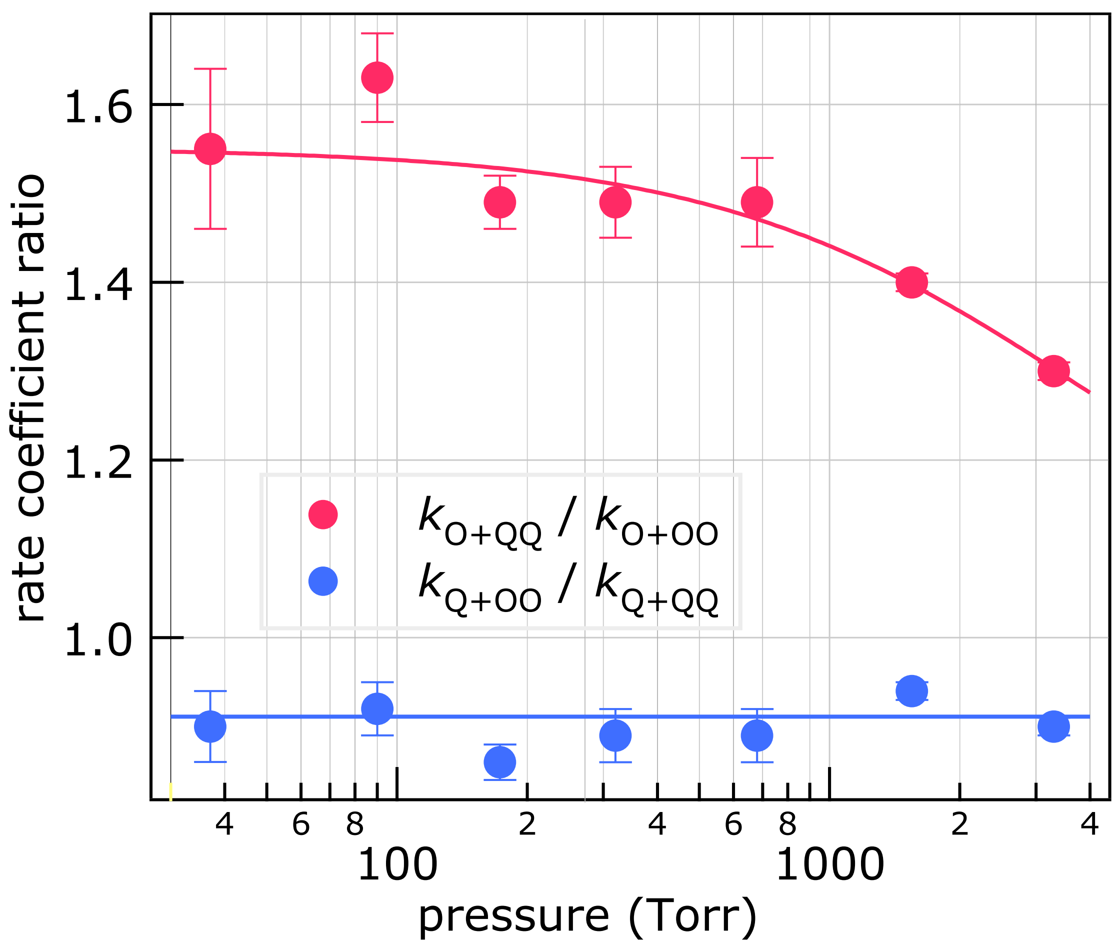




Janssen et al., *PCCP* **3**, 2001

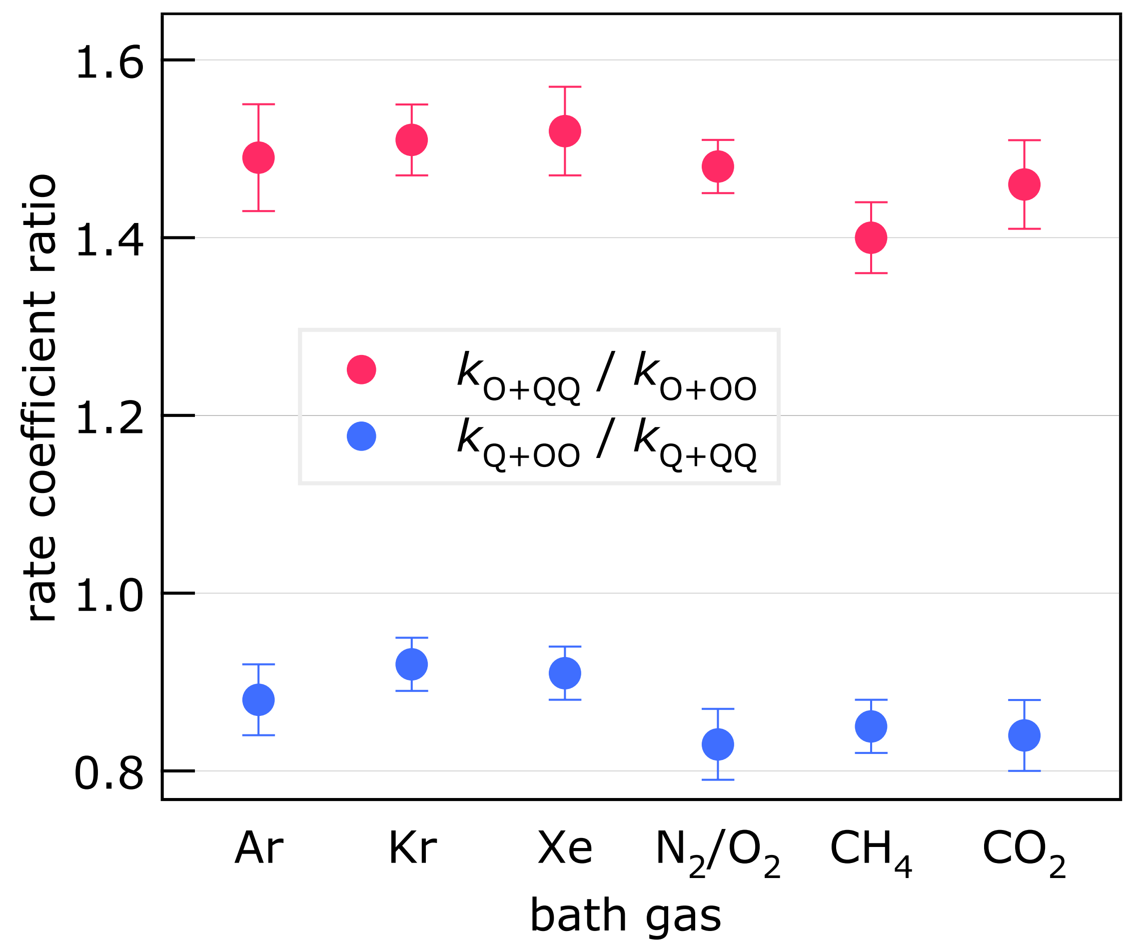
Pressure & bath gas dependence of rates

bath gas N_2 @ 200 Torr



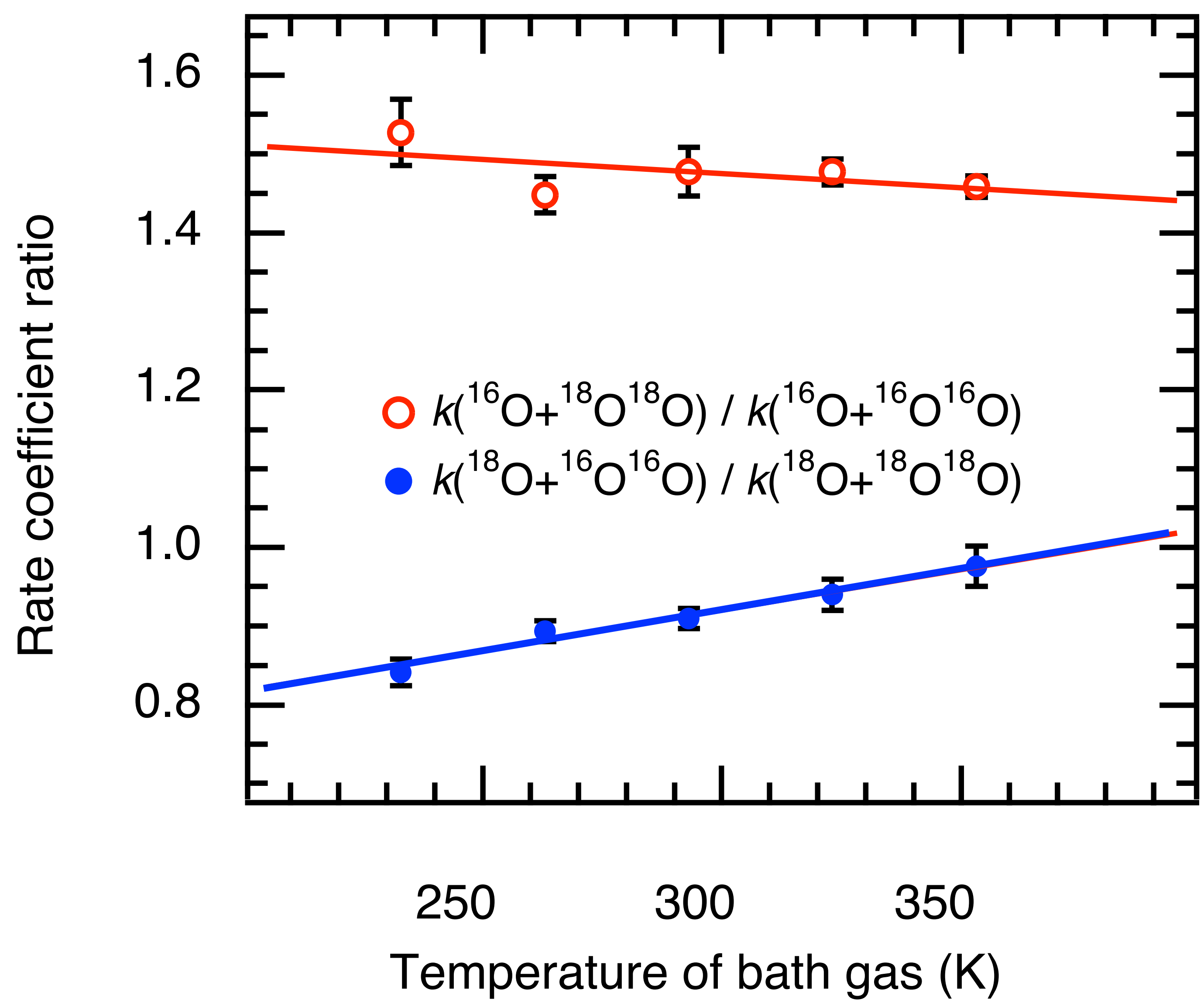
Guenther et al., *CPL* **306** (1999)

p = 200 Torr, $p(O_2)$ = 40 Torr



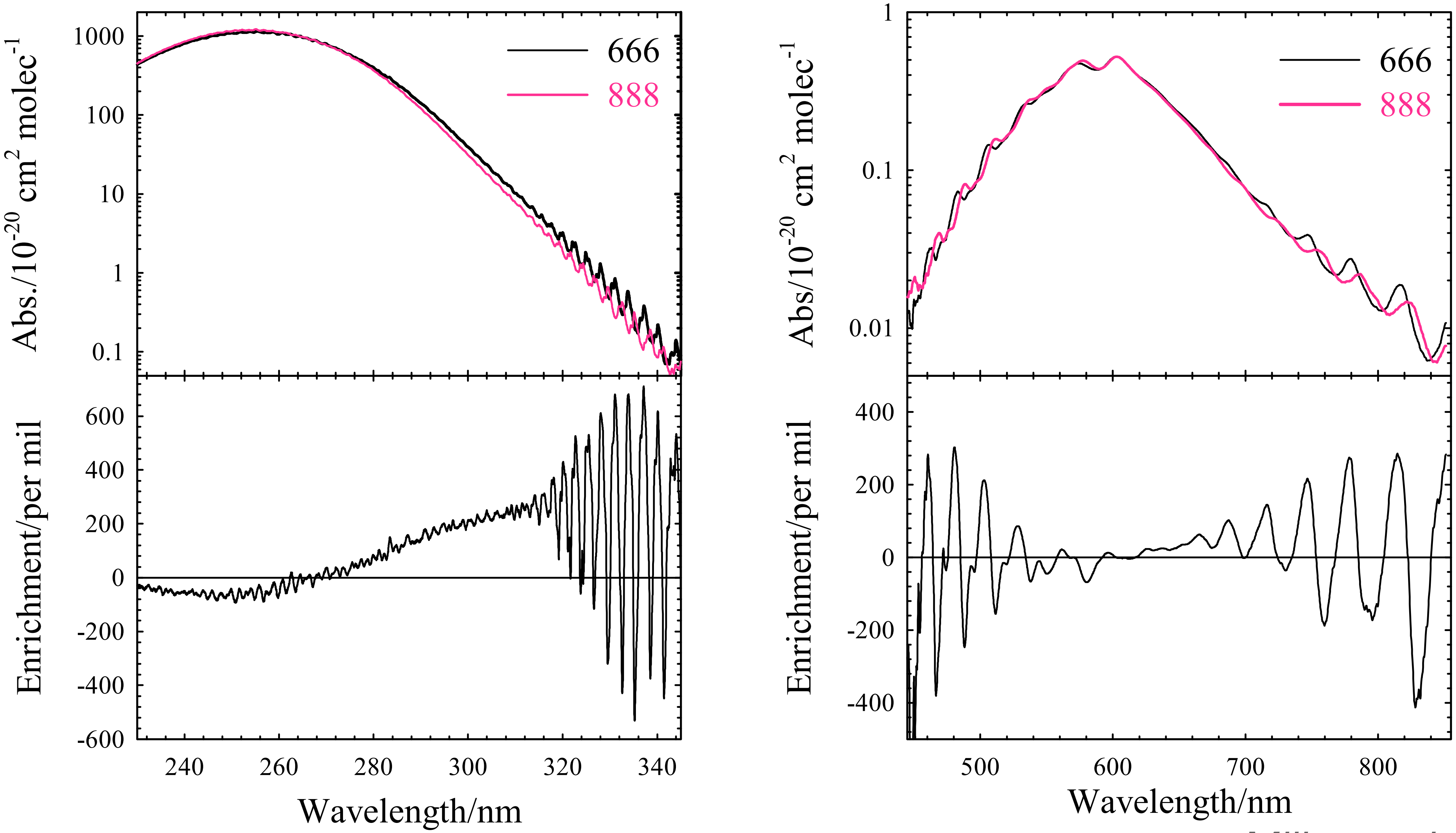
Guenther et al., *CPL* **324** (2000)

Temperature dependence of rates



Janssen et al., CPL 367 (2000)

Modeling of O_3 photolysis



*Miller et al. GRL **32** (2005)*

Photolysis measurements

Remark:

Cross section measurements exist only for $^{16}O_3$ and $^{18}O_3$

Photodecomposition measurements suffer from side reaction:

$$O_3 + h\nu \rightarrow O + O_2$$

$$O + O_3 \rightarrow 2O_2$$

Light source	α_{18}	Reference
MW-Hg lamp	1.019	Bhattacharya & Thiemens *GRL 15* (1988)
Nd-Yag @ 532 nm	1.017	Wen & Thiemens *CPL* **172** (1990)
Hg lamp	1.016	Wen & Thiemens *CPL* 172 (1990)
Hg lamp	1.017	Chakraborty & Bhattacharya *JCP* **118** (2003)
630, 520 nm	1.015	Chakraborty & Bhattacharya *JCP* **118** (2003)

Thermal reactions

$$O_3 + XO \rightarrow O_2 + XO_2$$

$$O_3 + X \rightarrow O_2 + XO$$

$$X = NO, NO_2, Br, Cl, OH$$

are important reactions that determine the concentration and isotope balance of ozone.

Have not been measured yet.

Thermal decomposition

Formation

$O + O_2 + M \rightarrow O_3 + M$, $k = 6.0 \cdot 10^{-34} (300/T)^{2.5}$ cm^6 molec.$^{-2}$ s^{-1}

- strong isotope fractionation (> 10%, T > 50°C)
- symmetry plays important role

Decomposition

$O_3 + M \rightarrow O + O_2 + M$, $k = 1.65 \cdot 10^{-9} \exp(-11435/T)$ cm^3 molec.$^{-1}$ s^{-1}

$$\boxed{\tau(150\ °C,\ p = 100\ \text{Torr}) = 167\ \text{s}}$$

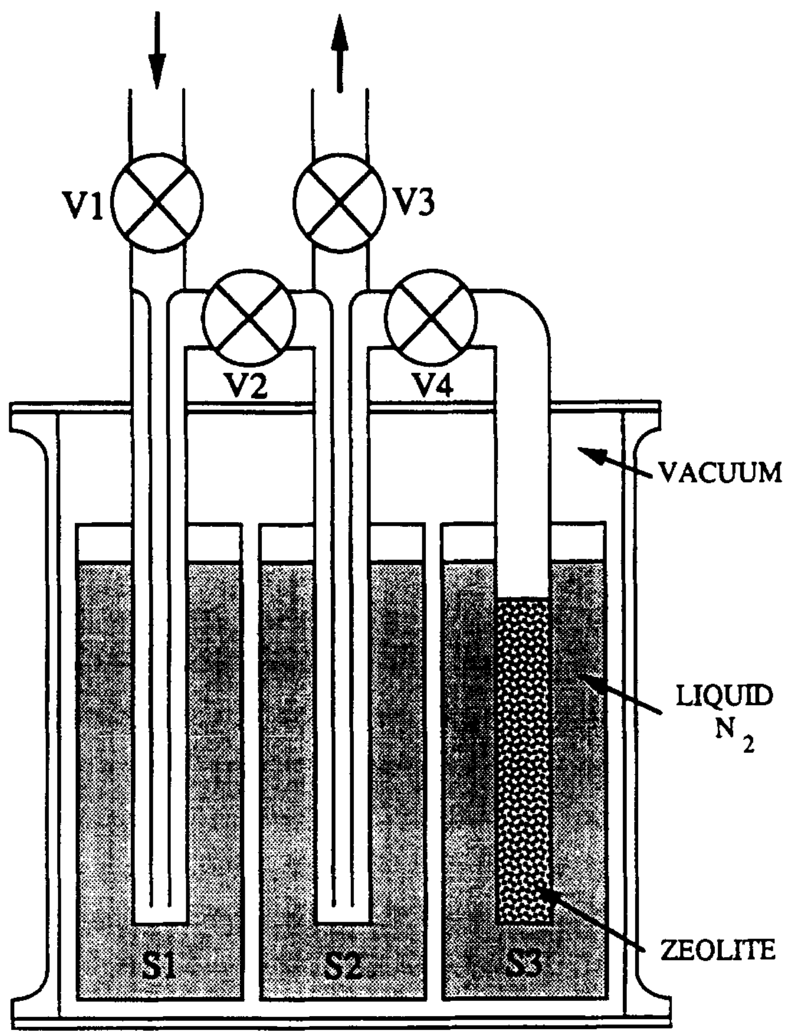
- 2 measurement attempts : small isotope fractionation (< 2.2%, T ~ 100°C)
- systematic errors (wall decomposition, side reaction $O + O_3 \rightarrow 2O_2$)
- studies are not symmetry resolved

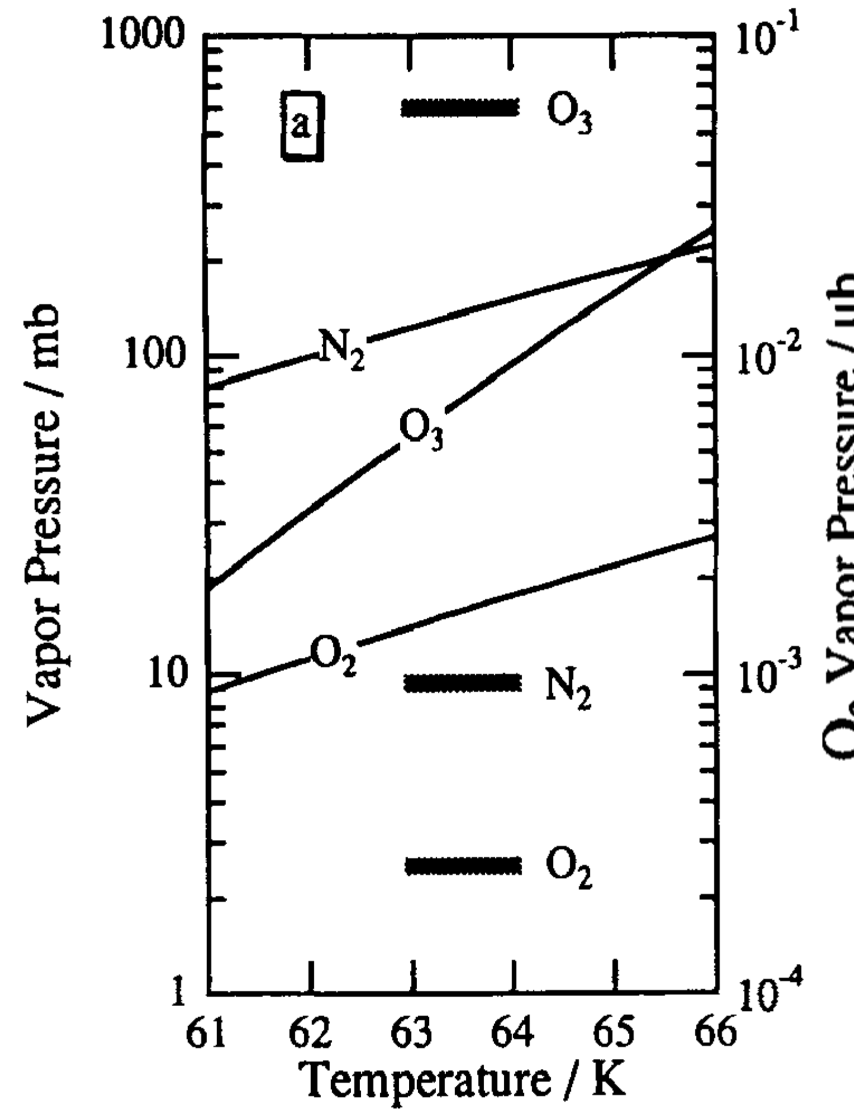
Model comparison

Model	Reference	Parameters	Features
Angular Scattering Model	Robert & Camy-Peyret, Ann. Geophys. (2001)	5	p, T = 300 K
Classical Trajectories	Schinke et al. Ann Rev Phys Chem. (2006)	2	highly accurate ab-initio PES
Modified RRKM	Gao & Marcus, JCP (2002)	2 for each T, ET & non RRKM factor	p, T
Vibrational Excitation Model	Miklavc & Peyerimhoff, CPL (2002)	1	low p, T = 300 K, no exchange
QM scattering VCC-IOS	Charlo & Clary, JCP (2004)	0	low p, T, fixed geometry
QM scattering approach	Babikov et al., JCP (2003)	0	low p, J = 0

Cryogenic samplers

Stratosphere

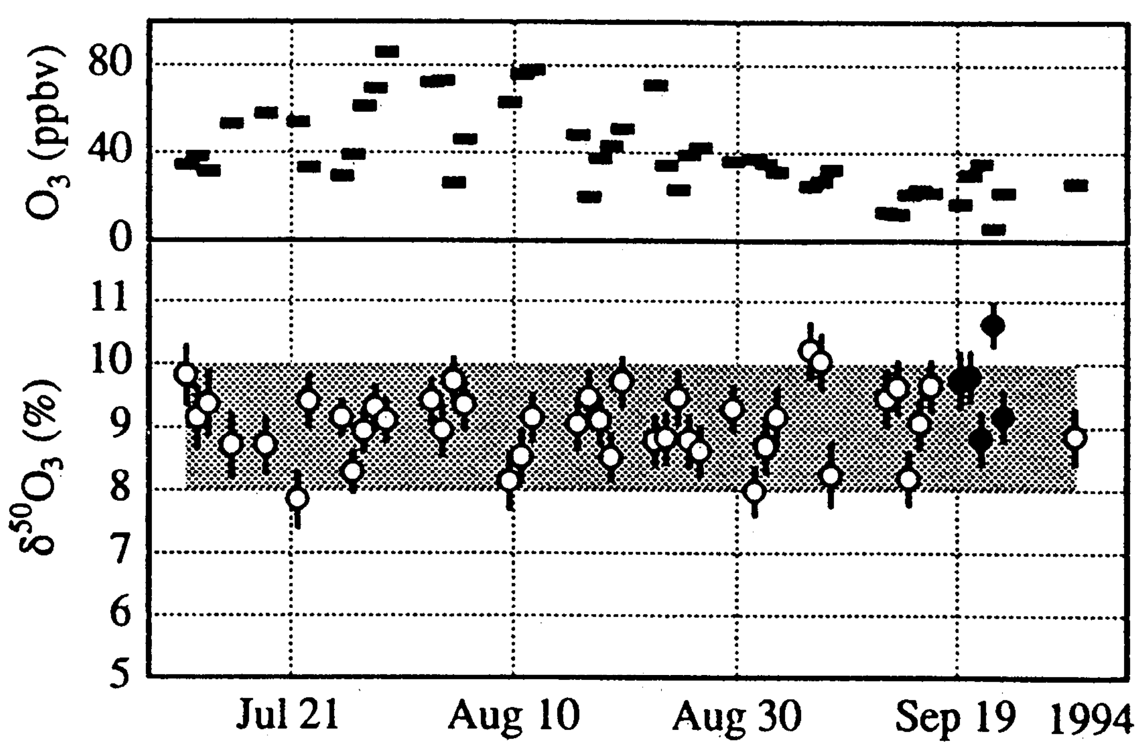


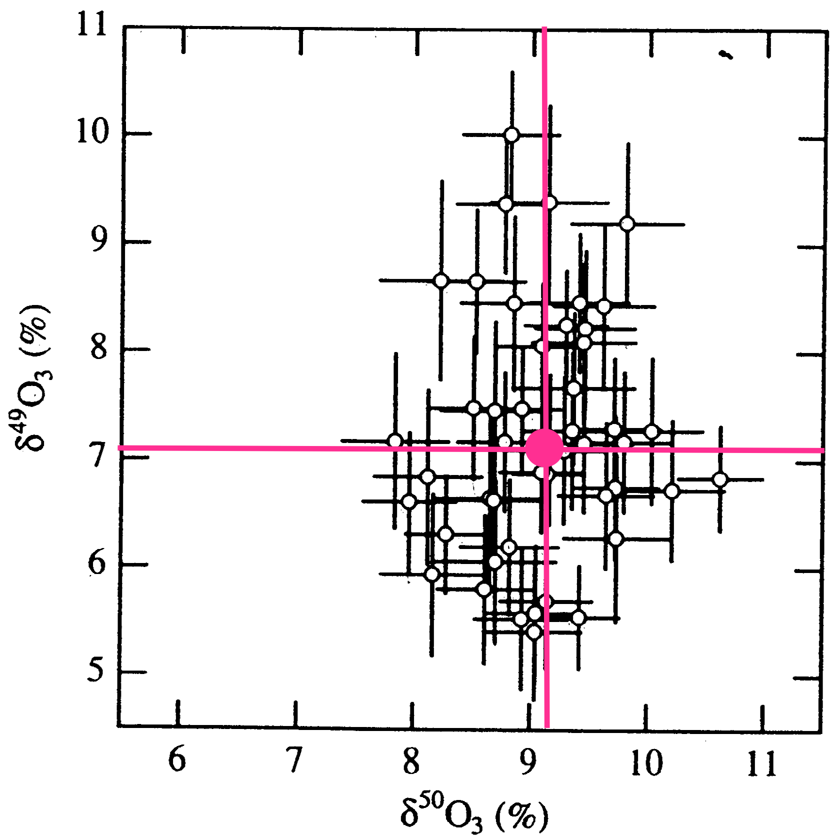


Stehr et al. *JAC* **24** (1996)

Tropospheric data

Outskirts of Heidelberg, Germany 49.4°N (n = 49)

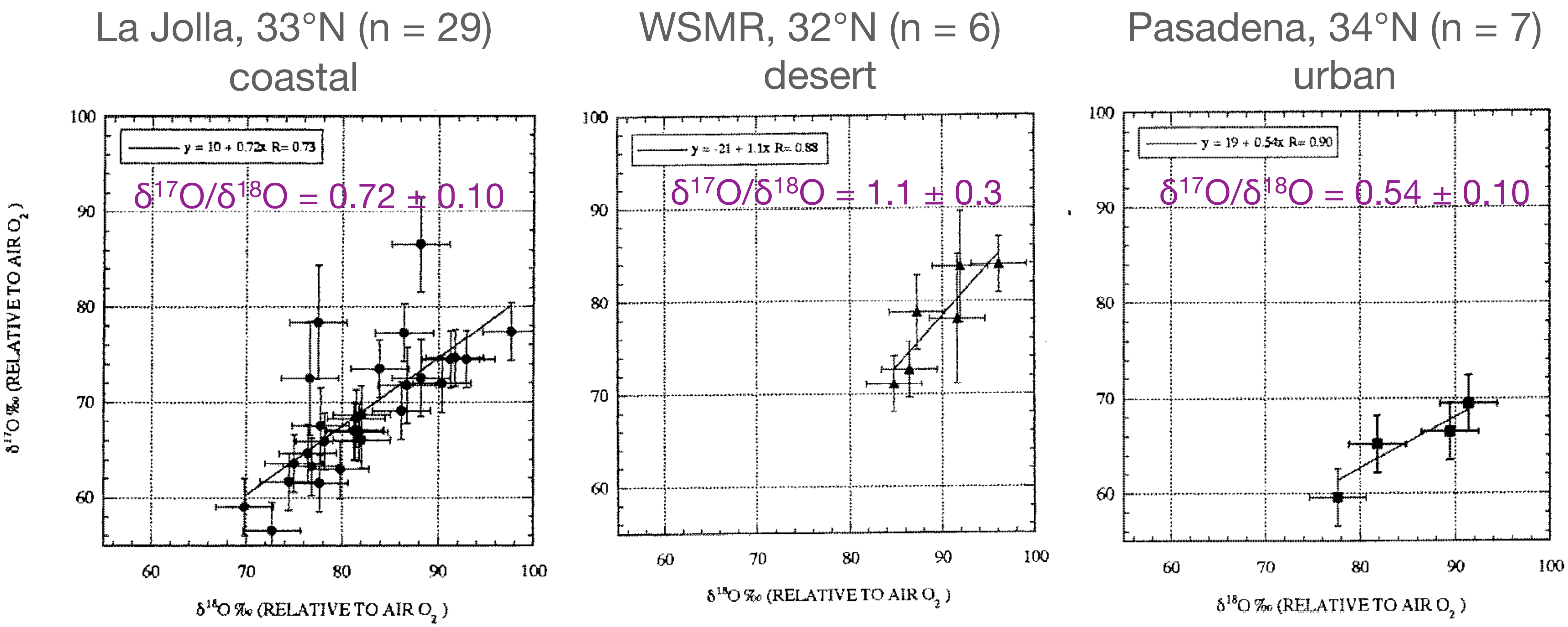




Krankowsky et al, *GRL* **22** (1995)

Tropospheric Data

Three locations US



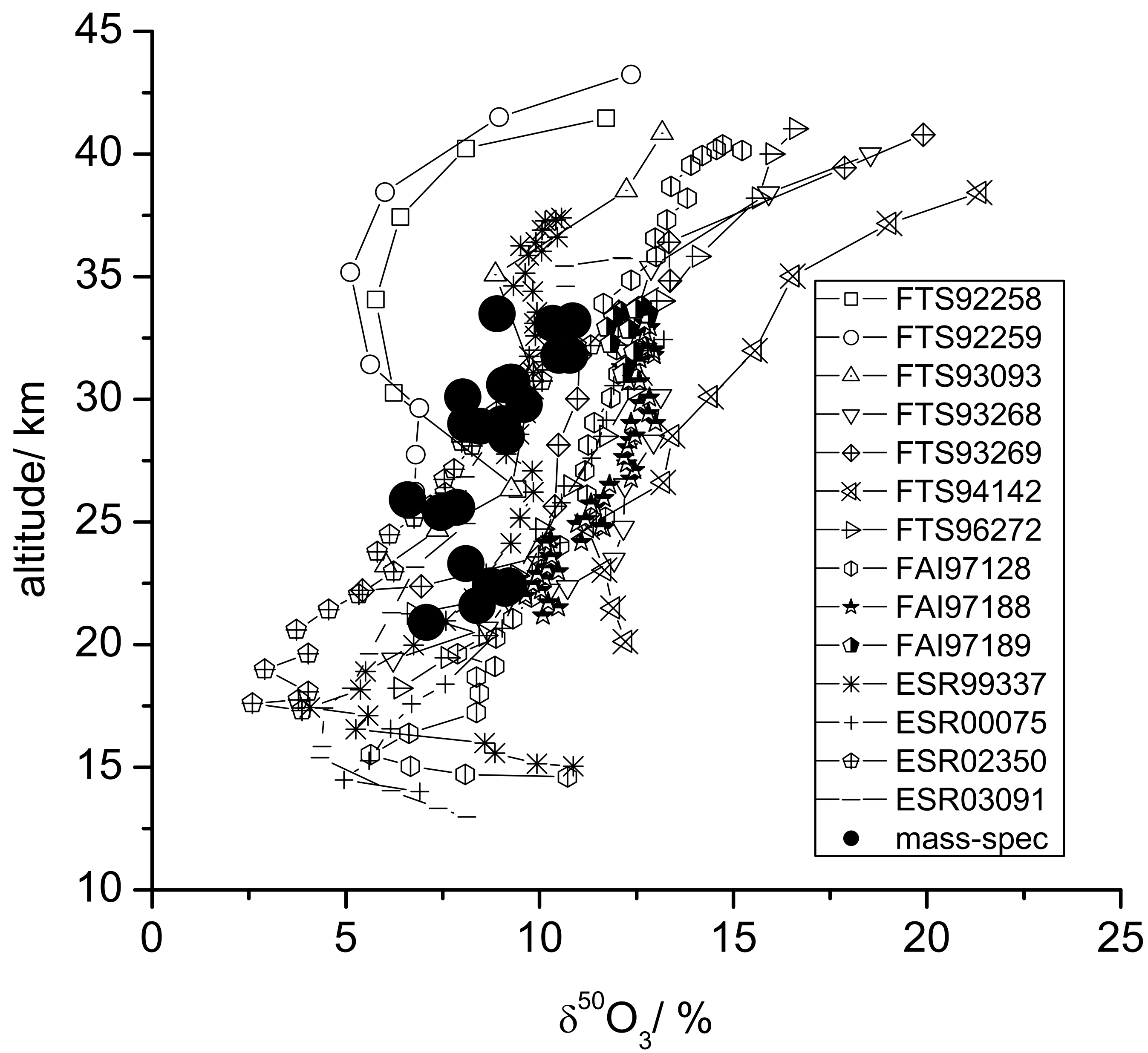
Johnston and Thiemens, *JGR* **102** (1997)

Summary tropospheric data

location	period	n	p (hPa)	T (K)	δ^{17}O (%)	δ^{18}O (%)
Heidelberg	7/94-9/94	47	975	298	7.1 ± 0.3	9.1 ± 0.2
La Jolla	1/95-4/96	29	1015	292	6.9 ± 0.2	8.2 ± 0.2
WSMR	3/95	6	874	290	7.8 ± 0.3	9.0 ± 0.3
Pasadena	9/95	7		301	6.6 ± 0.2	8.6 ± 0.4

Brenninkmeijer et al., *CR* **103** (2003)

Stratospheric ozone



Polar latitudes (67.9°N, 65°N):

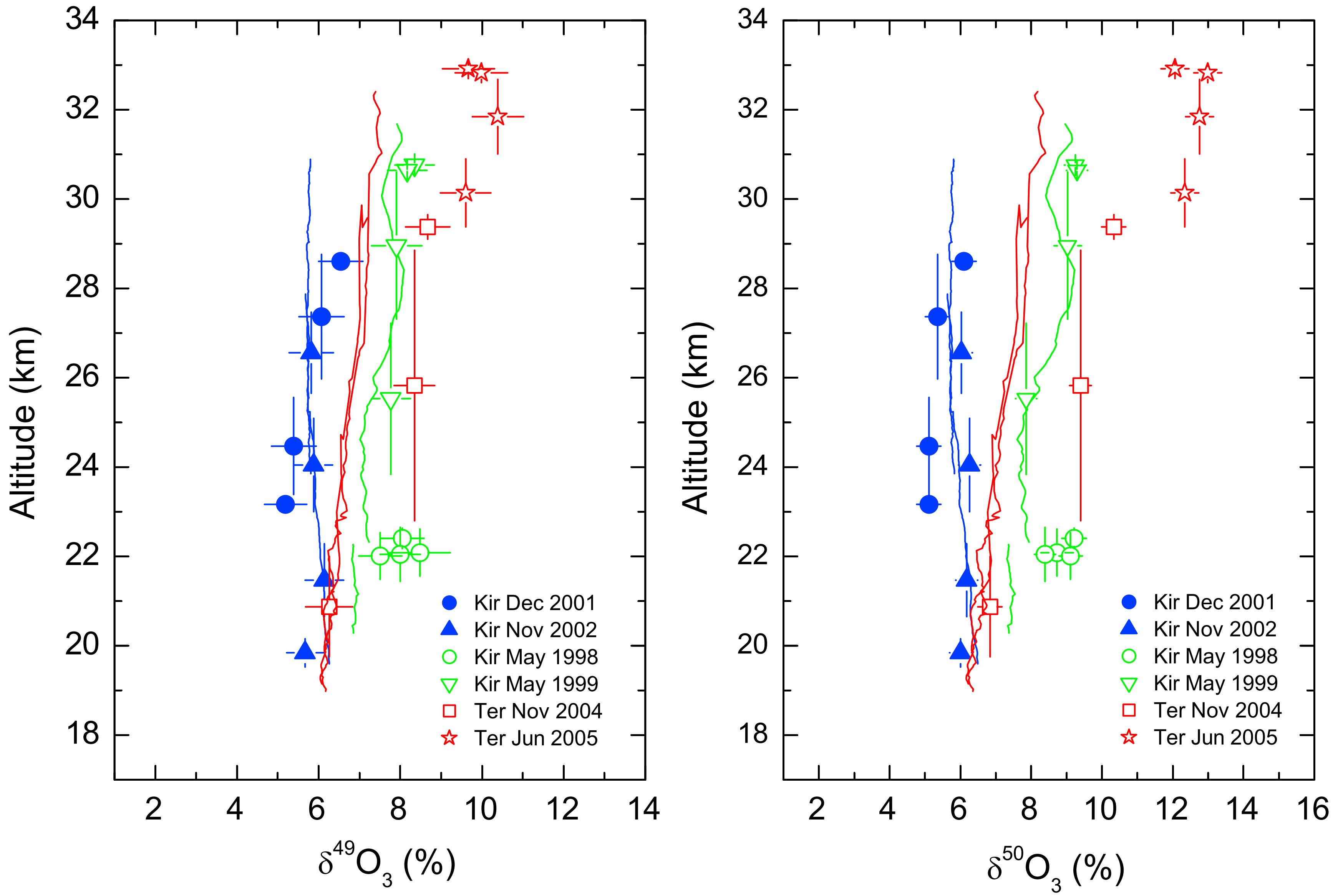
Kiruna, SUE &
Fairbanks, Al (5.1°S):

Mid nortern (34°N),

Fort Sumners, NM

*Haverd et al. GRL **32** (2005)*

Stratospheric ozone



Polar latitudes (67.9°N):

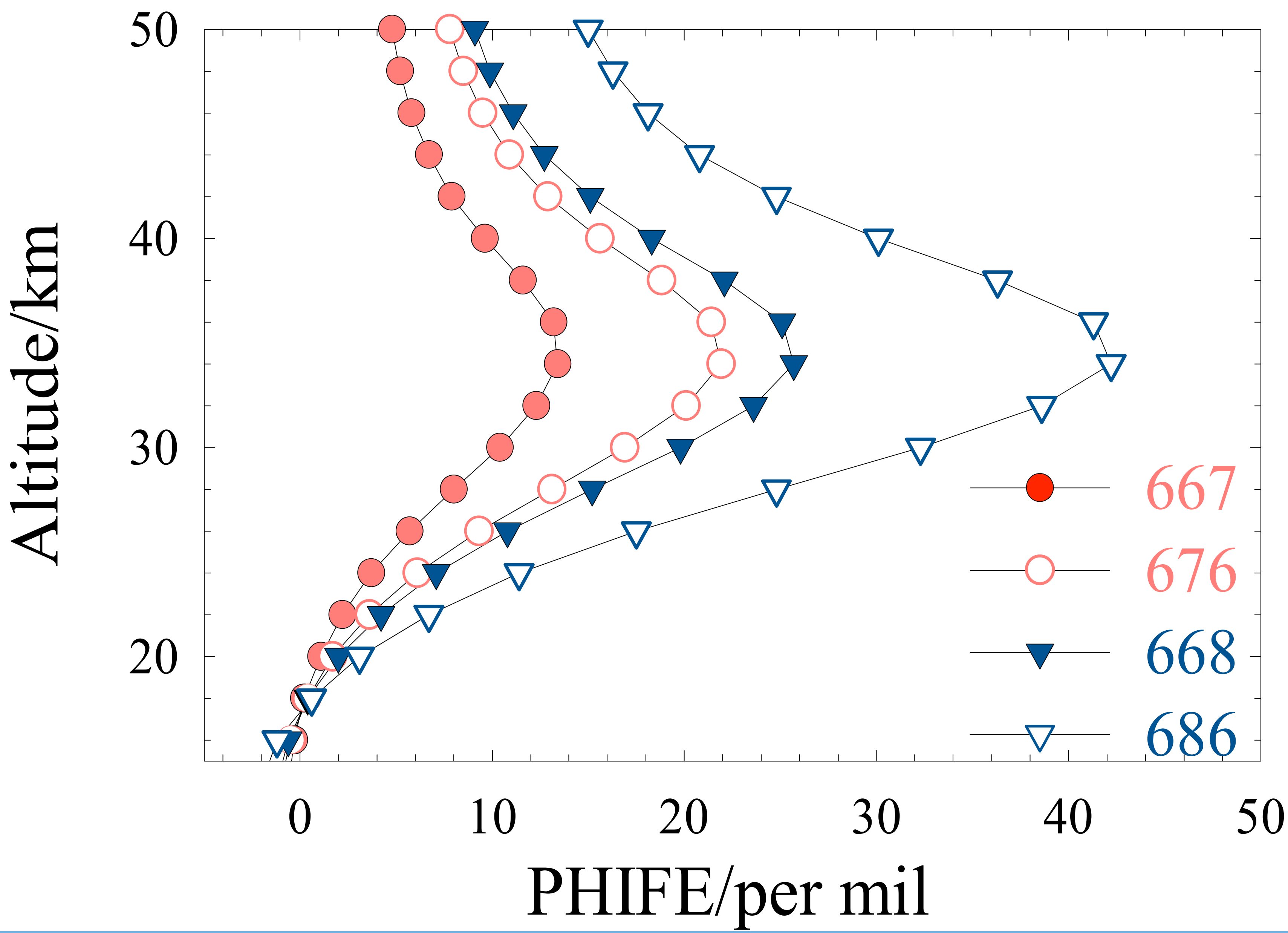
Kiruna, SUE &

Equatorial (5.1°S):

Terezina, BRA

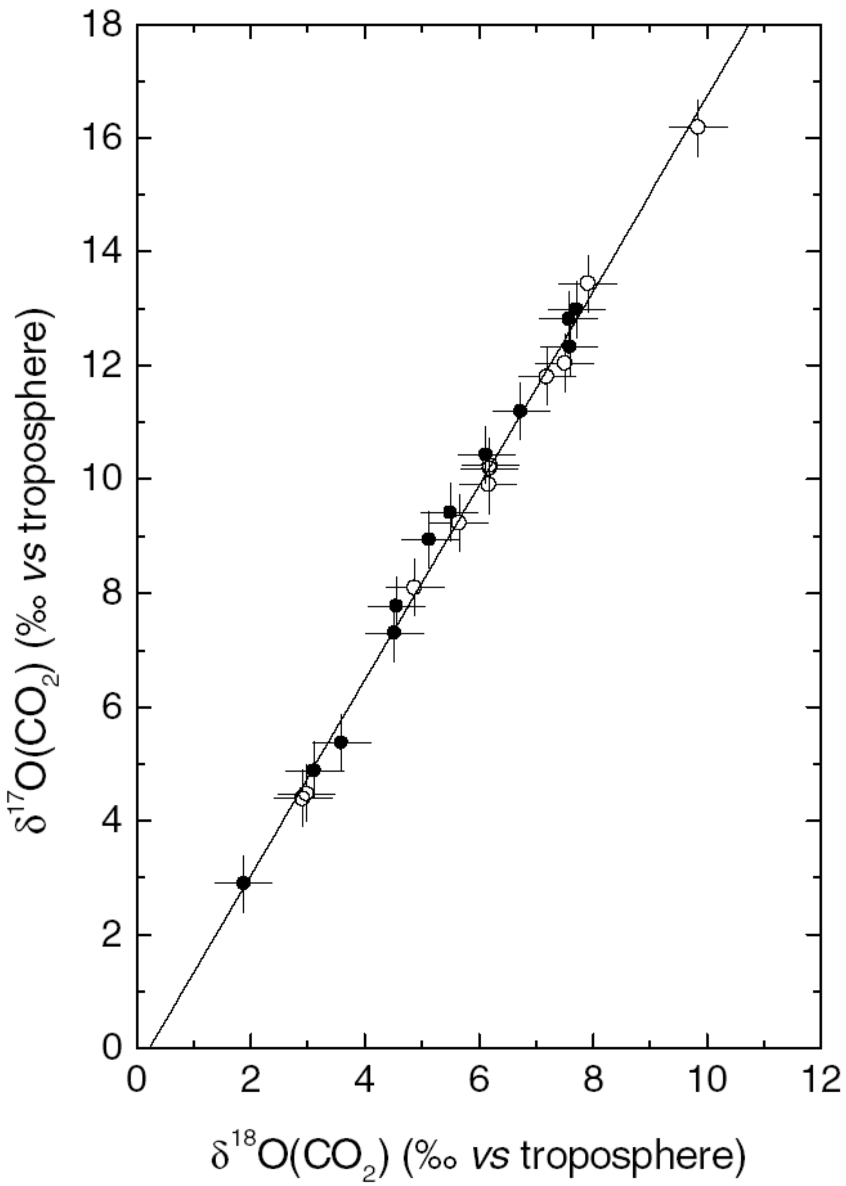
*Krankowsky et al. JGR **112** (2007)*

Modeling of O_3 photolysis



*Miller et al. GRL **32** (2005)*

Isotope transfer into CO_2



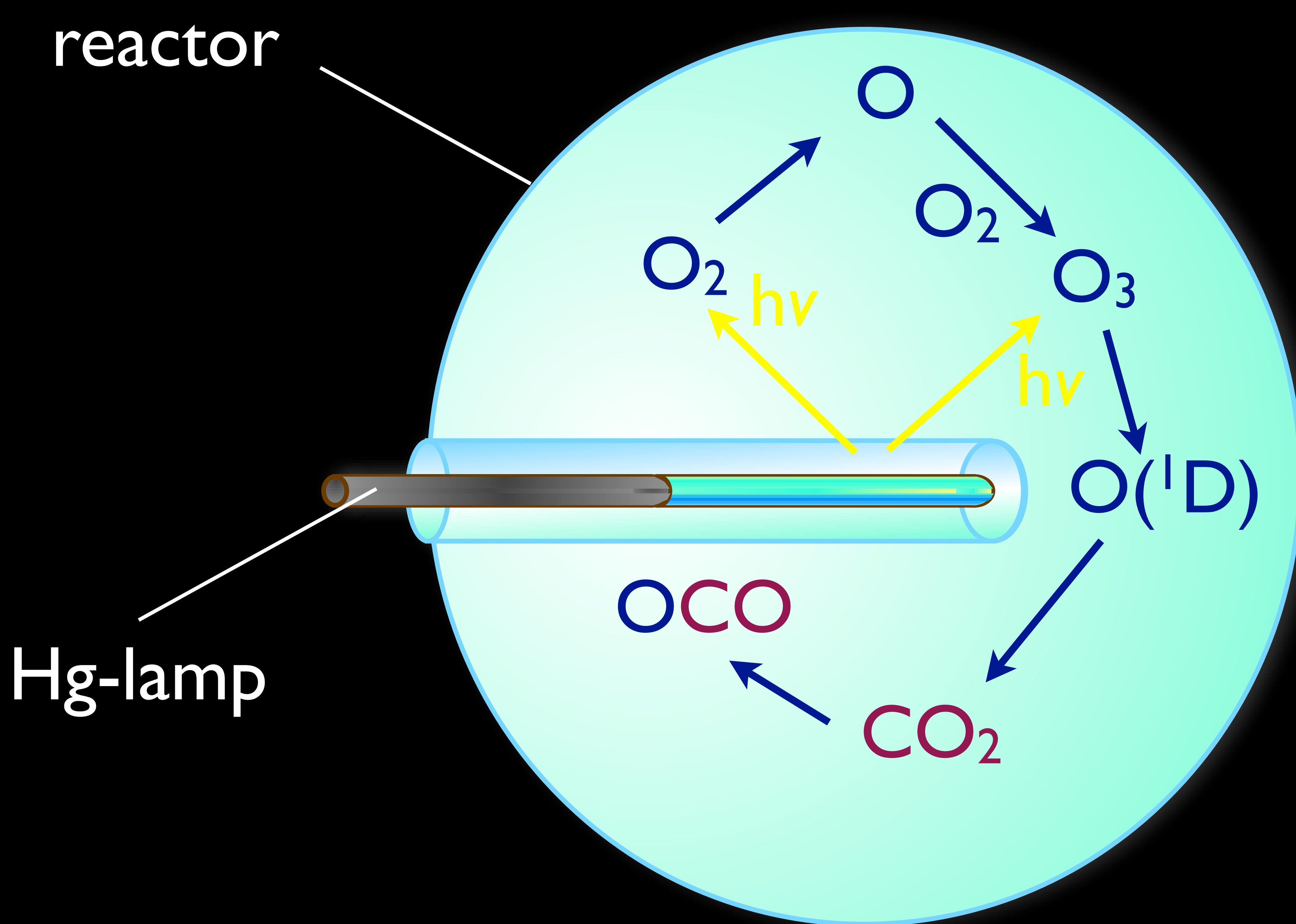
$\delta^{17}O/\delta^{18}O = 1.7$

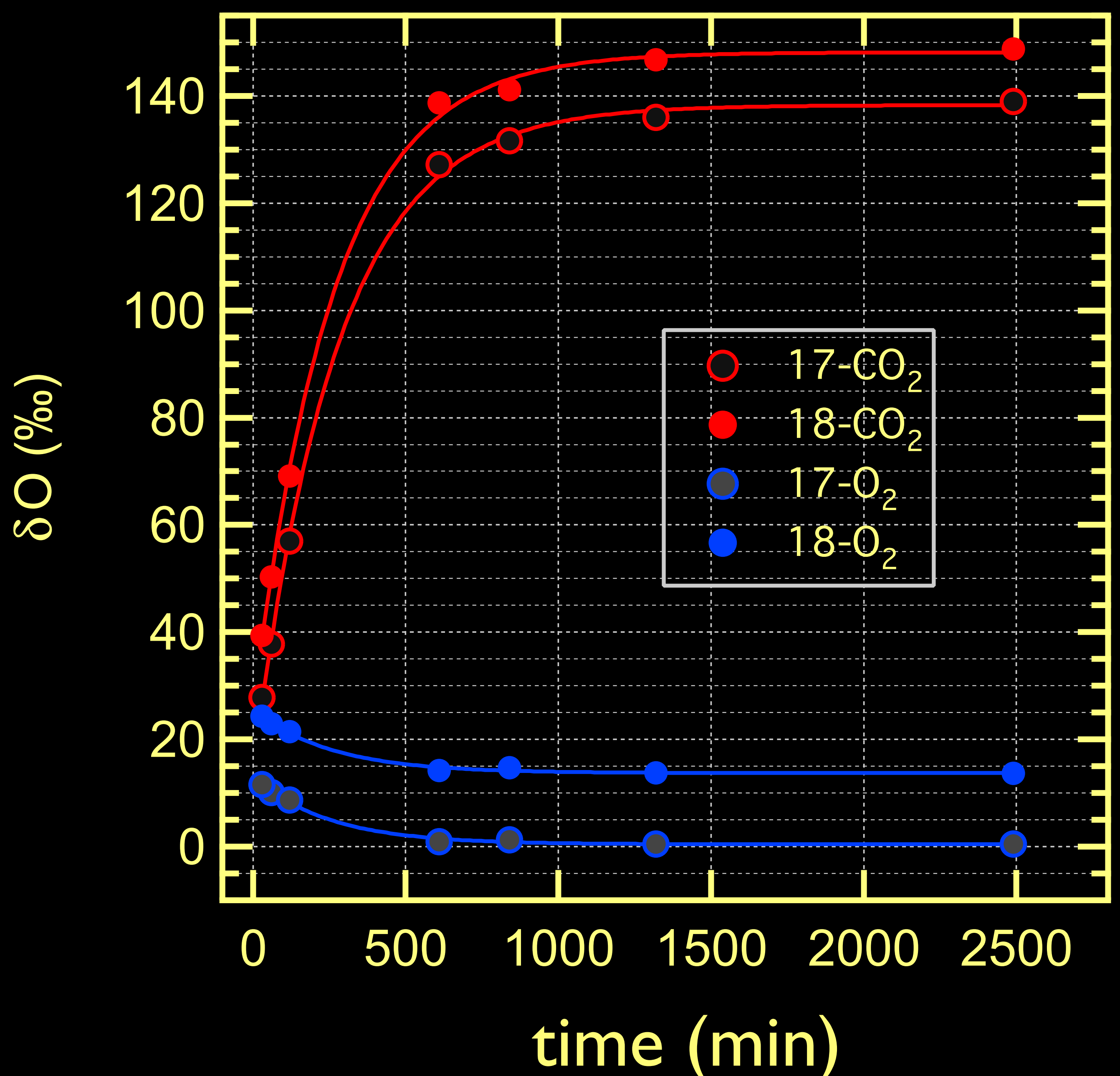
Mechanism (Yung et al. *JGR* **102** (1991)), complemented by Perri et al. *JCPA* **108** (2004)

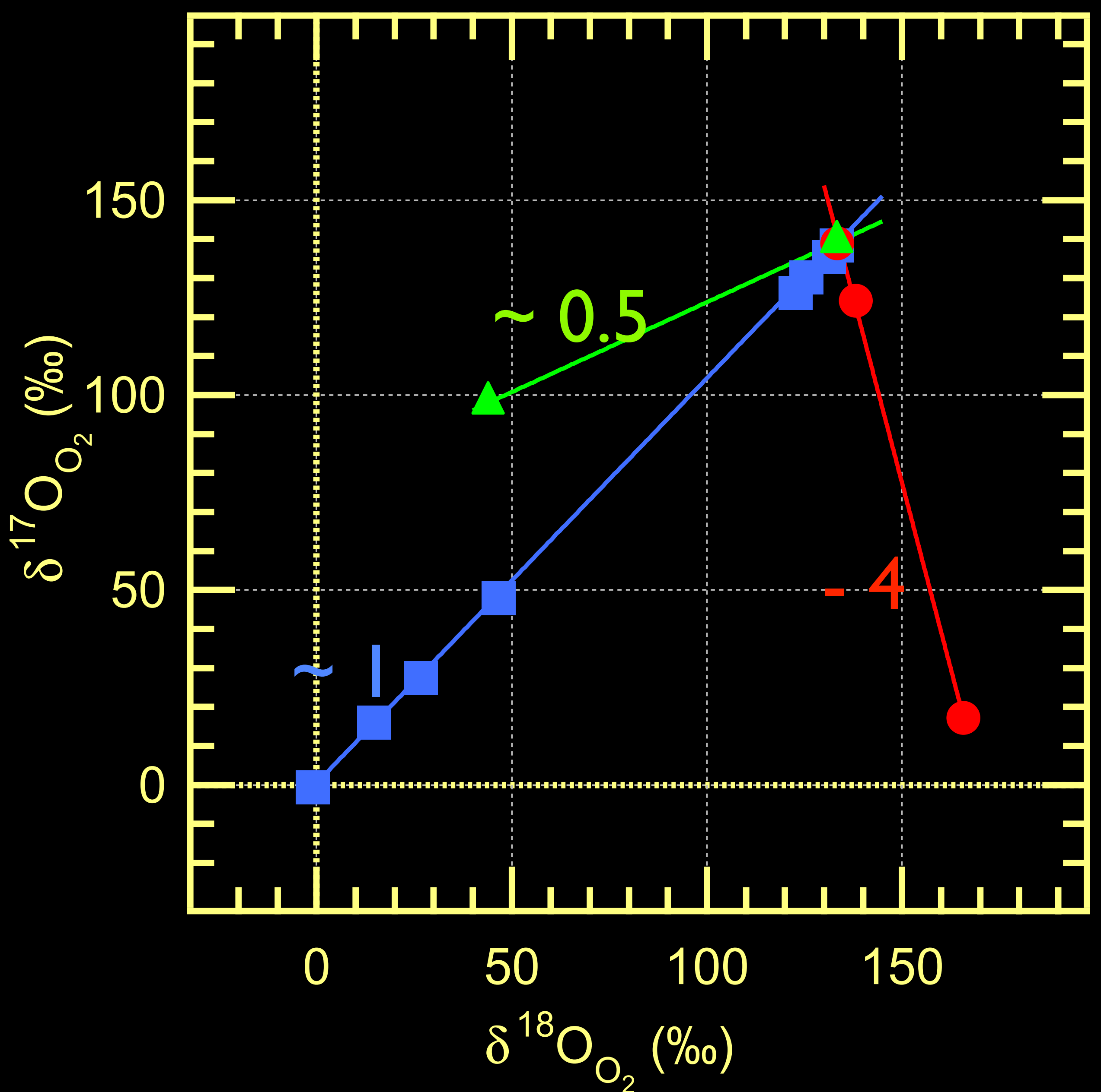
$$
\begin{aligned}
O_3 + h\nu &\rightarrow O(1D) + O_2 \\
O'\left({}^1D\right) + CO_2 &\rightarrow O\left({}^3P, {}^1D\right) + COO'
\end{aligned}
$$

other data show variable or different $\delta^{17}O/\delta^{18}O$

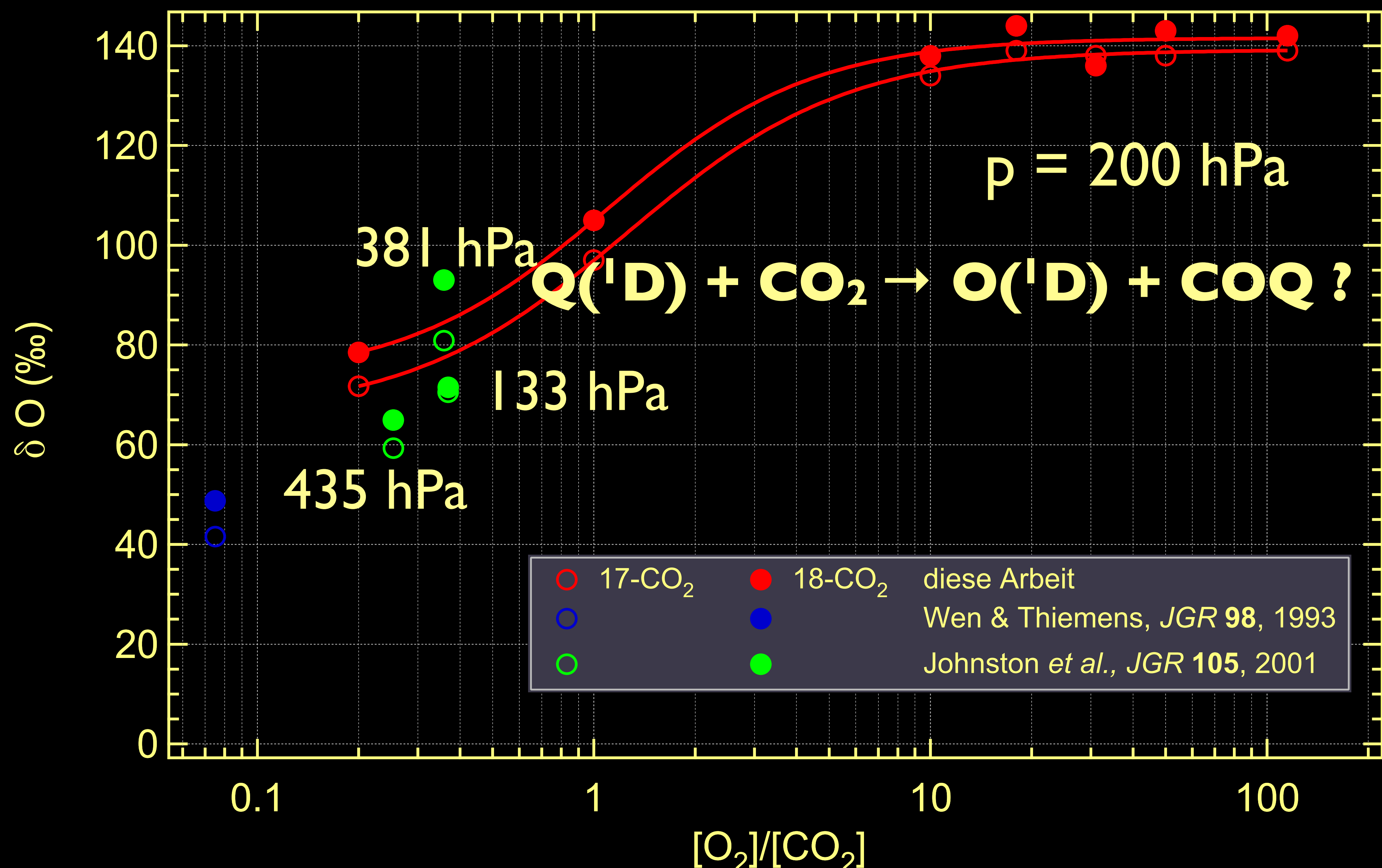
Lämmerzahl et al. *GRL* **29** (2002)


reactor
O
O2
O2
O3
hv
hv
O(1D)
OCO
CO2
Hg-lamp





Shaheen et al. *ACP* **7** (2007)



Shaheen et al. *ACP* **7** (2007)

Current Projects on Thermal Decomposition

ANR - IDEO (no ANR-09-BLAN-0022-03)

Isotope and Dynamic fffects in Excited Ozone

ITN FP7 - INTRAMIF (no 237890)

International Teching Network on Mass Independent isotope Fractionation

Conclusion and Outlook

- Anomaly has kinetic origin
- Are there other molecules ?
- Can we predict isotope anomalies ?
- Studies on ozone decomposition are missing
- Agreement between lab and atmosphere ?
- Role of ozone decomposition processes
- Isotope transfer: What do we miss in $O(^1D) + CO_2$?