Impact of recent laboratory measurements of the absorption cross section of ClOOCl on our understanding of polar ozone chemistry

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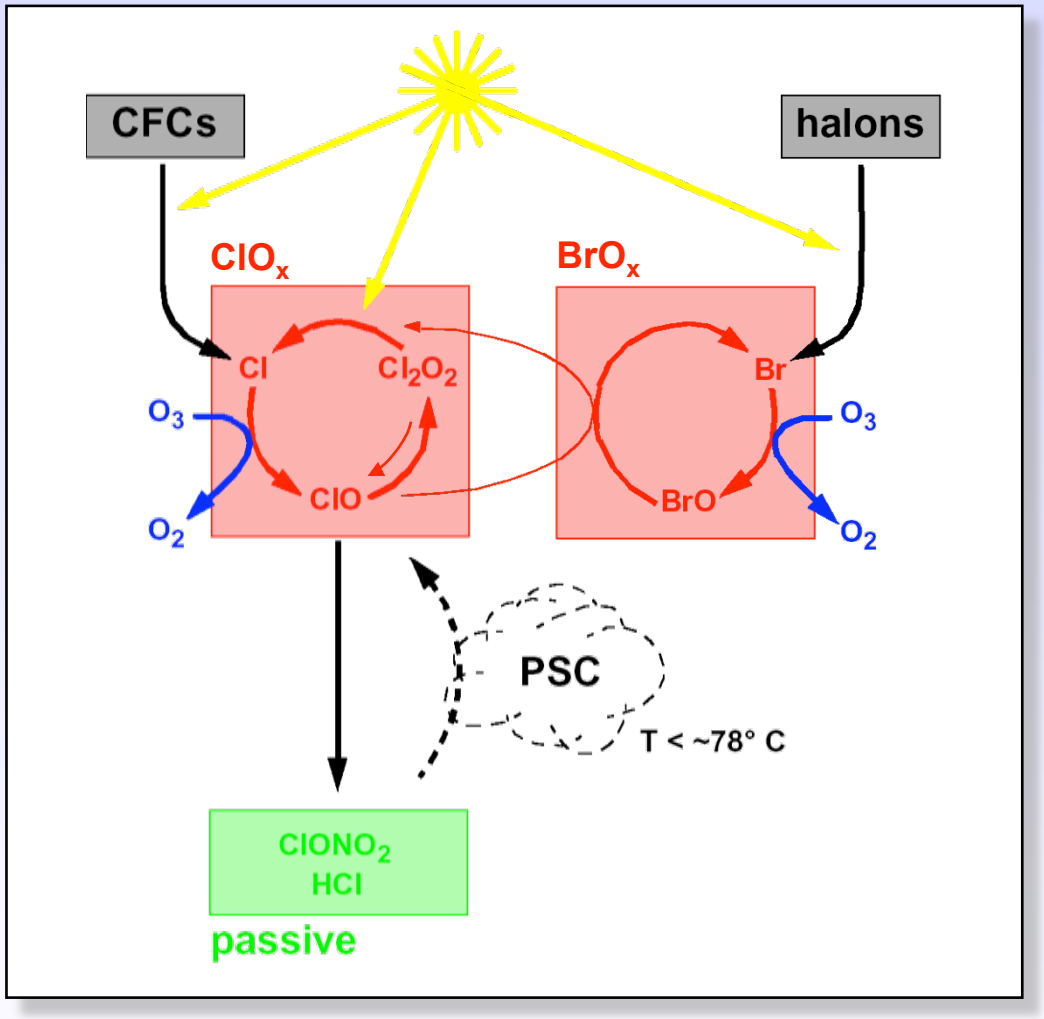
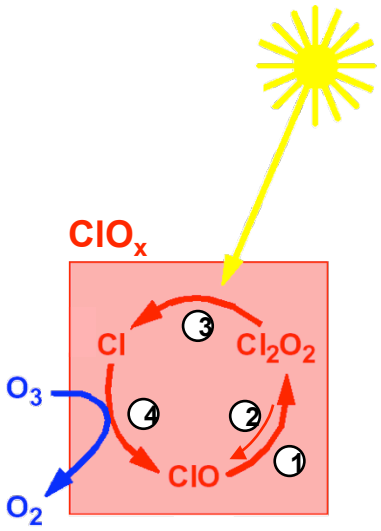
Polar ozone loss process



Kinetics of the dimer cycle

Balance of ClO / ClO_x and ozone loss rate are governed by:



Step (1): „Forward Reaction“

$ClO + ClO \xrightarrow{M} ClOOCl$, Rate = k_f x $[ClO]^2$

Step (2): „Thermal decomposition“

$ClOOCl \xrightarrow{M} ClO + ClO$, Rate: k_b x [ClOOCl]

$k_{eq} = k_f / k_b$

Step (3): „Photolysis“

$ClOOCl + h\nu \rightarrow Cl + ClOO \xrightarrow{M} Cl + Cl + O_2$

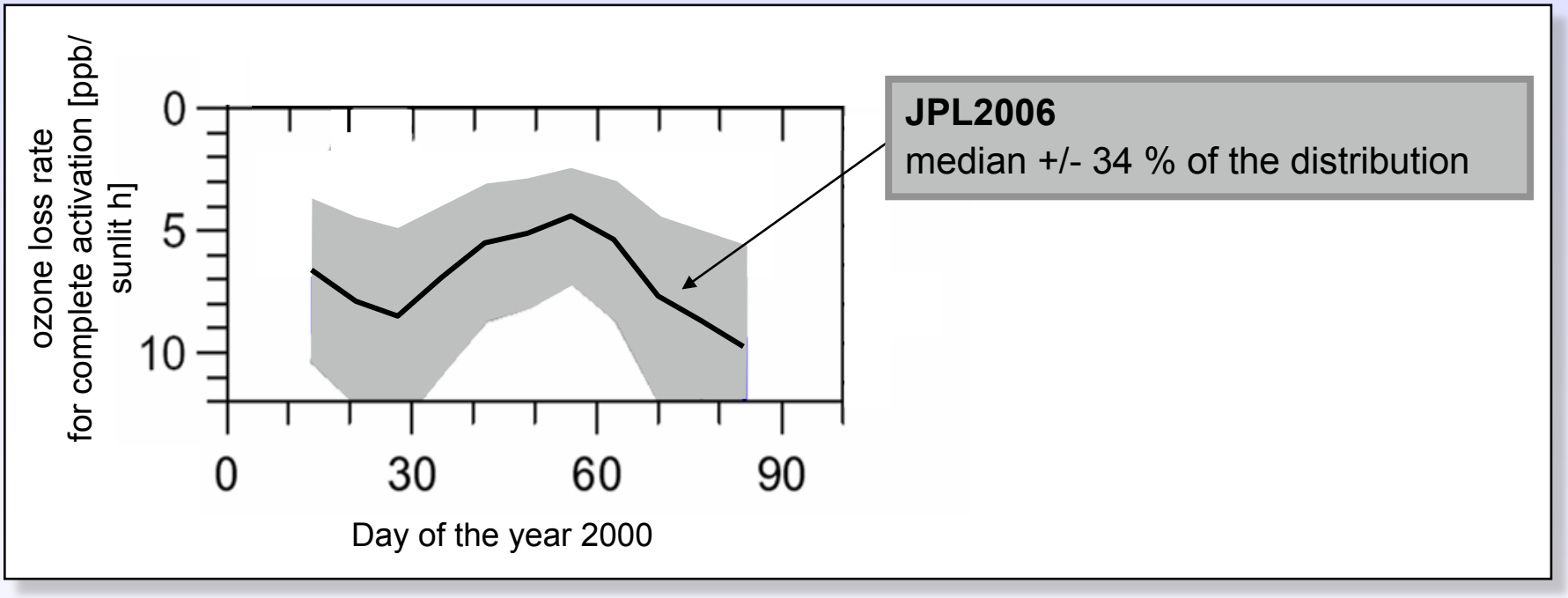
Rate = J_{ClOOCl} x [ClOOCl]

Step (4): $Cl + O_3 \rightarrow ClO + O_2$:

Rapid. ClO/ClO_x and ozone loss rate not sensitive on rate of step (4).

Model uncertainties

Monte Carlo simulations of model uncertainties
hundreds of model runs distributed according to the uncertainties stated in JPL2006

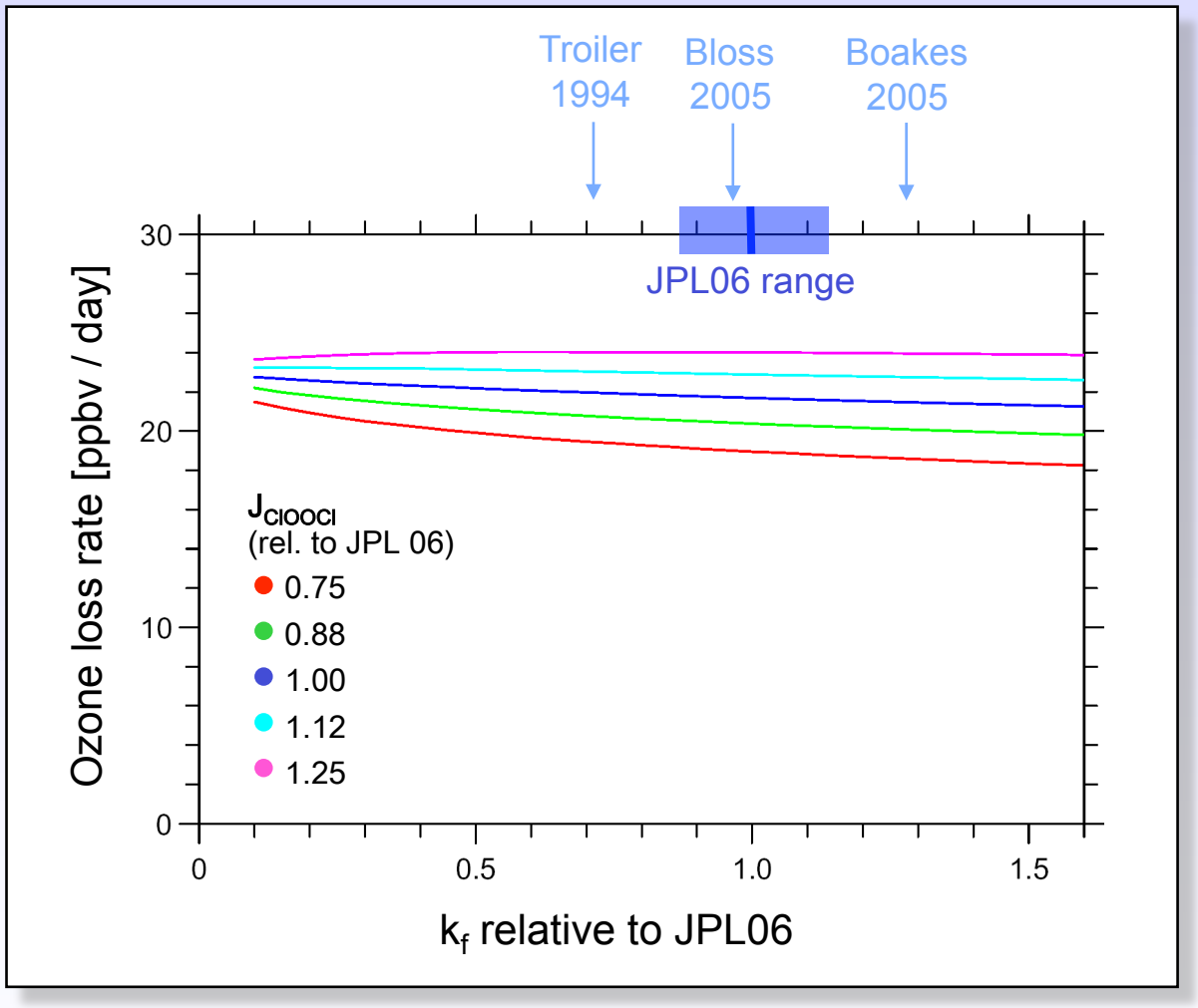


=> up to a factor of 3 uncertainty due to uncertainty in gas phase kinetic data

Frieler et al., PhD work, 2006

24 hour average ozone loss rate versus k_f

195 K, 50 hPa, early February, ClO_x = 2 ppbv, little sensitivity on k_{eq}

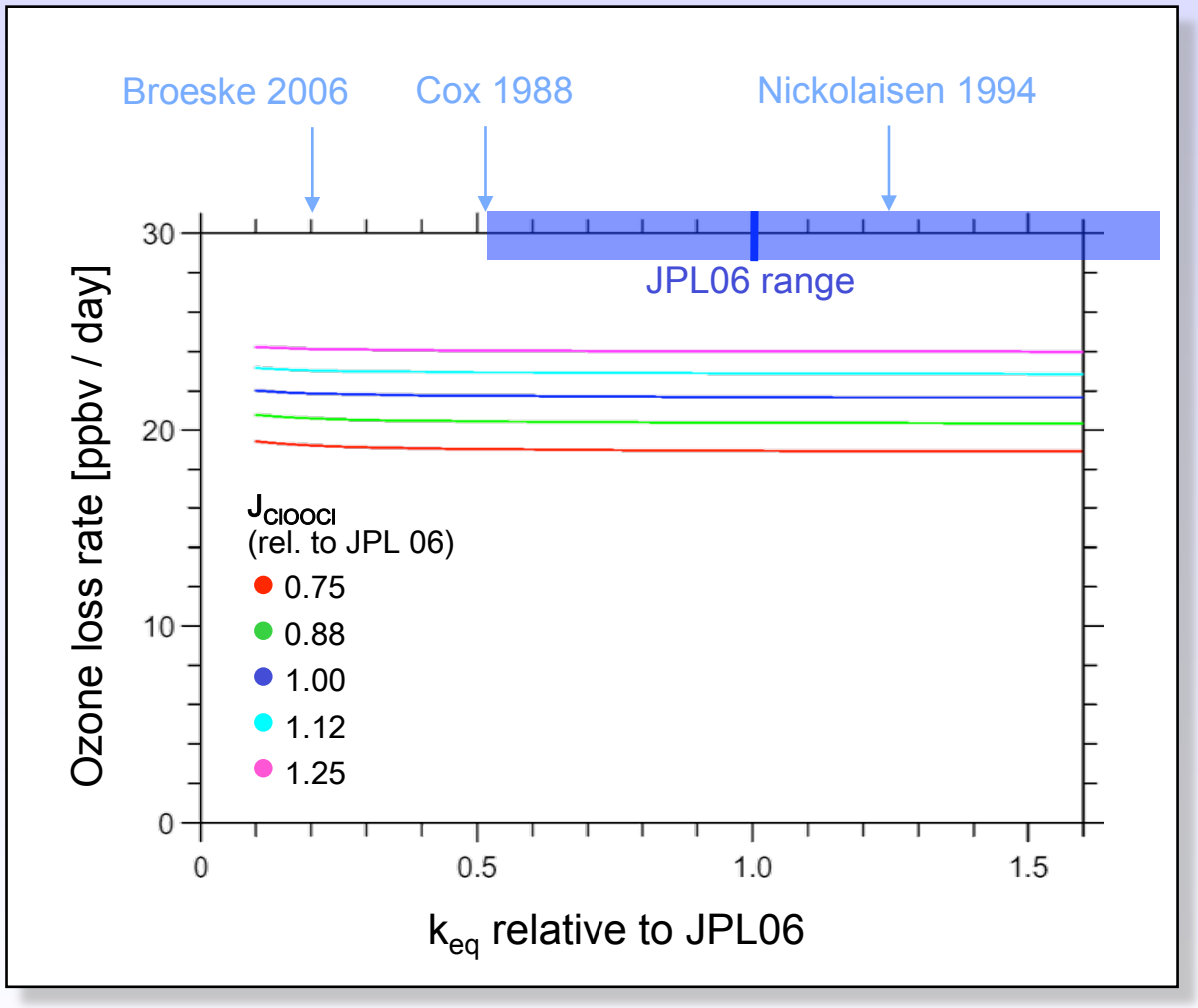


=>

Calculated ozone loss rate is fairly insensitive on uncertainties in k_f

24 hour average ozone loss rate versus k_{eq}

195 K, 50 hPa, early February, ClO_x = 2 ppbv, little sensitivity on k_f



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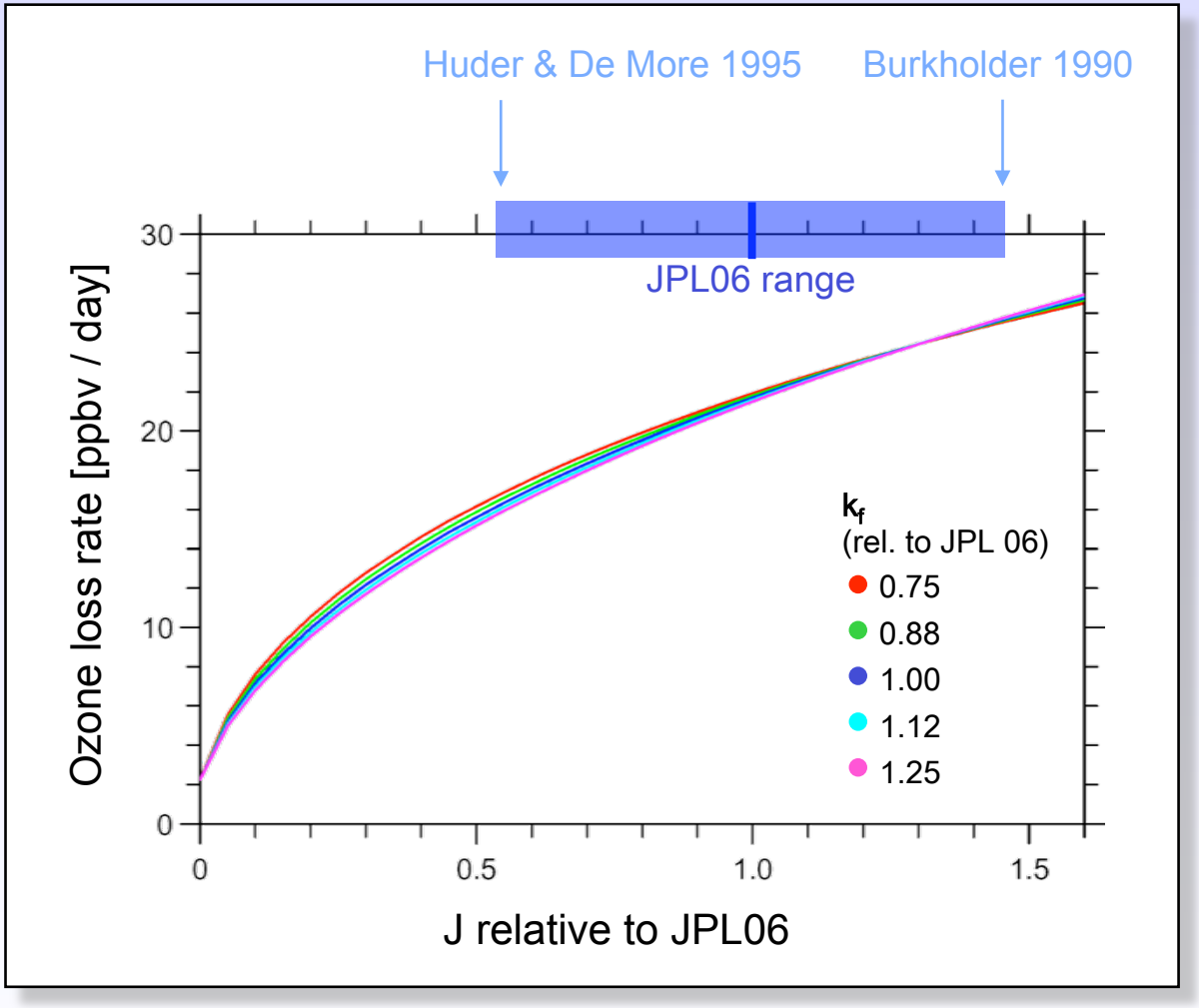
Calculated ozone loss rate is fairly insensitive on uncertainties in k_{eq}

24 hour average ozone loss rate versus J

195 K, 50 hPa, early February, ClO_x = 2 ppbv, little sensitivity on k_{eq}



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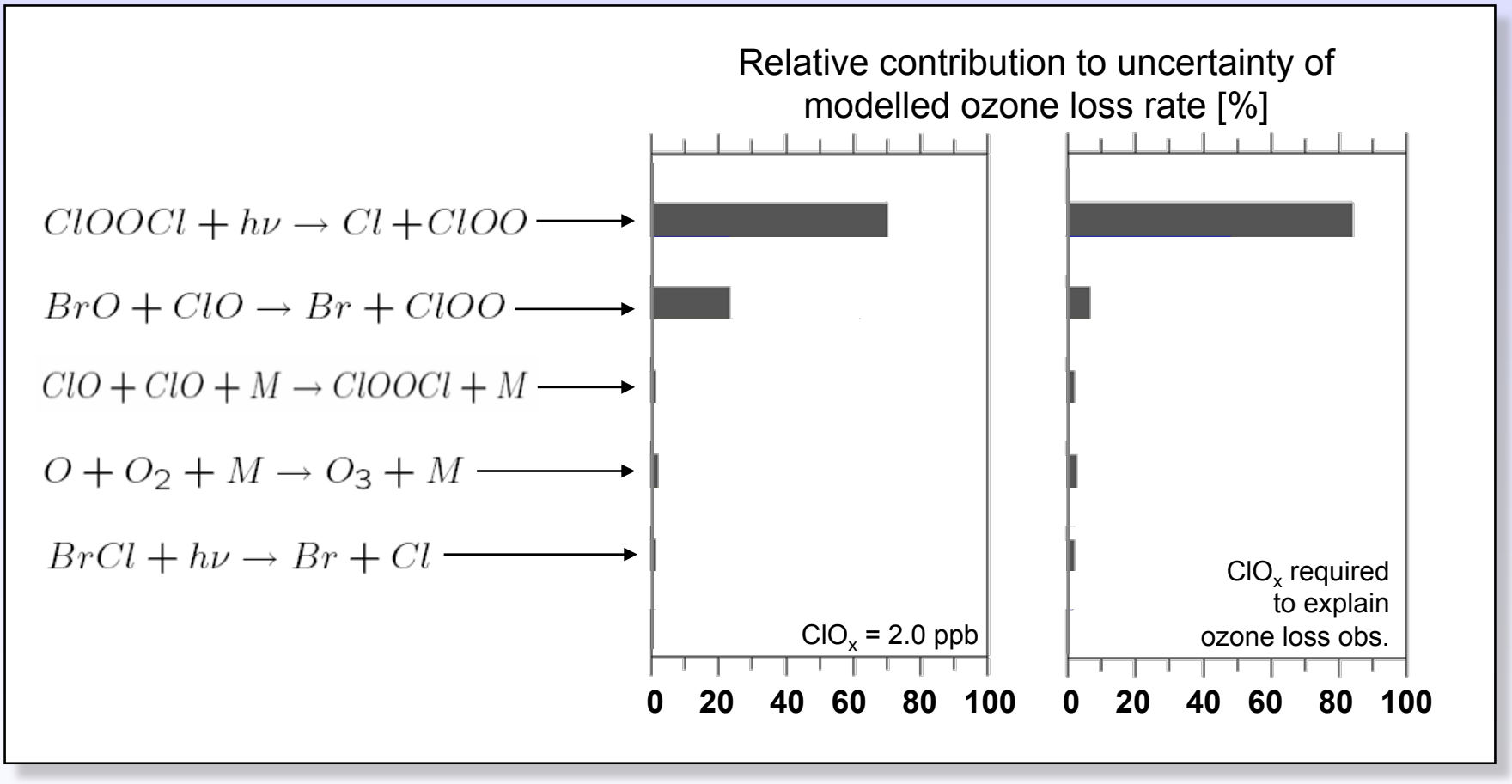
Calculated ozone loss rate is highly sensitive on uncertainties in J

Sources of model uncertainties

from Monte Carlo simulations



Frieler et al., PhD work, 2006

Sources of uncertainty in J

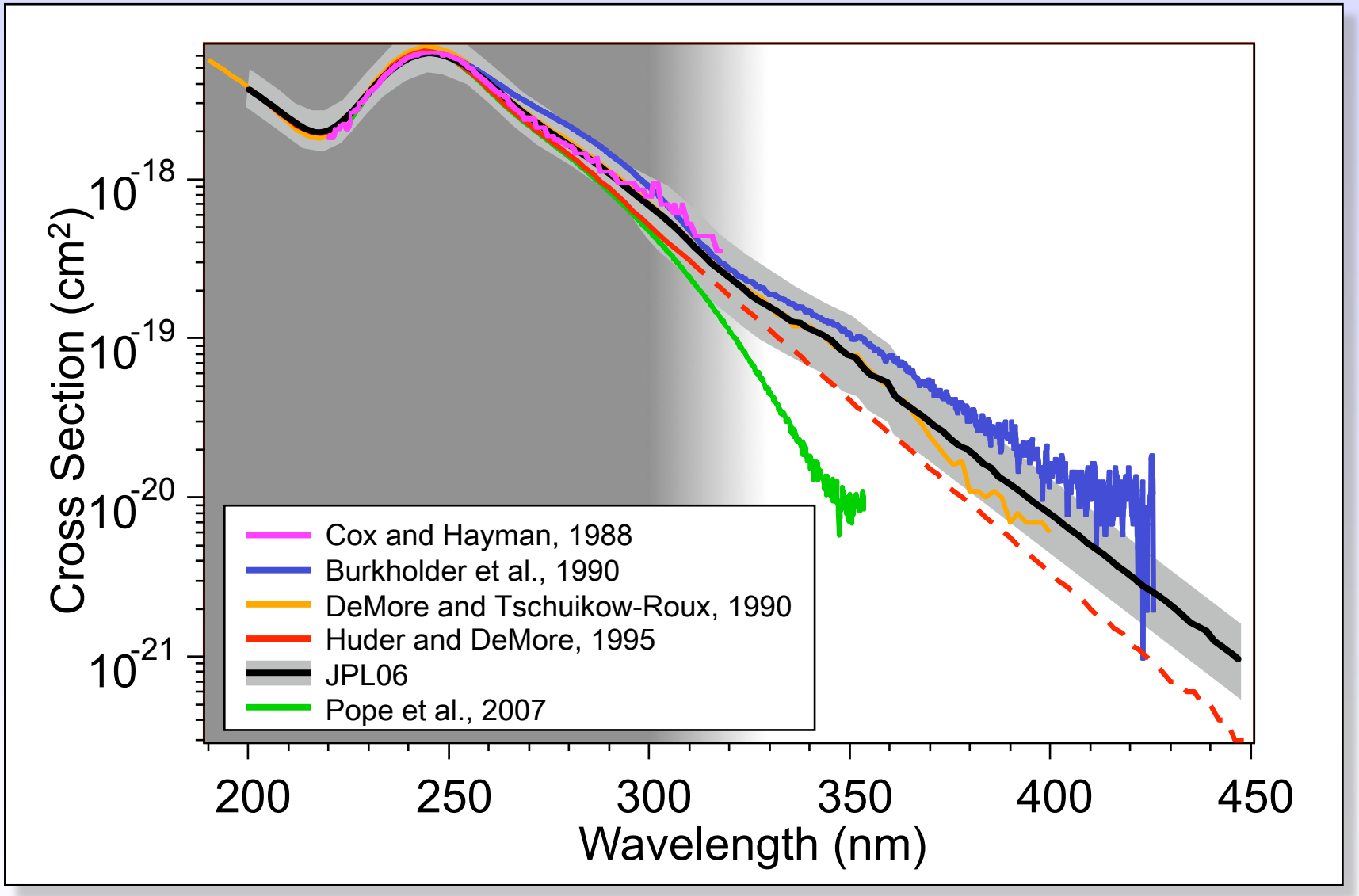
$$J = \int \sigma(\lambda) \cdot \Phi(\lambda) \cdot I(\lambda)\, d\lambda$$

absorption cross sections:
from lab measurements

Quantum yield: 0.9 -1.0

Actinic flux (i.e. photon flux):
calculated with radiation transfer model

Measurements of ClOOCl cross sections



24 hour average ozone loss rate versus J

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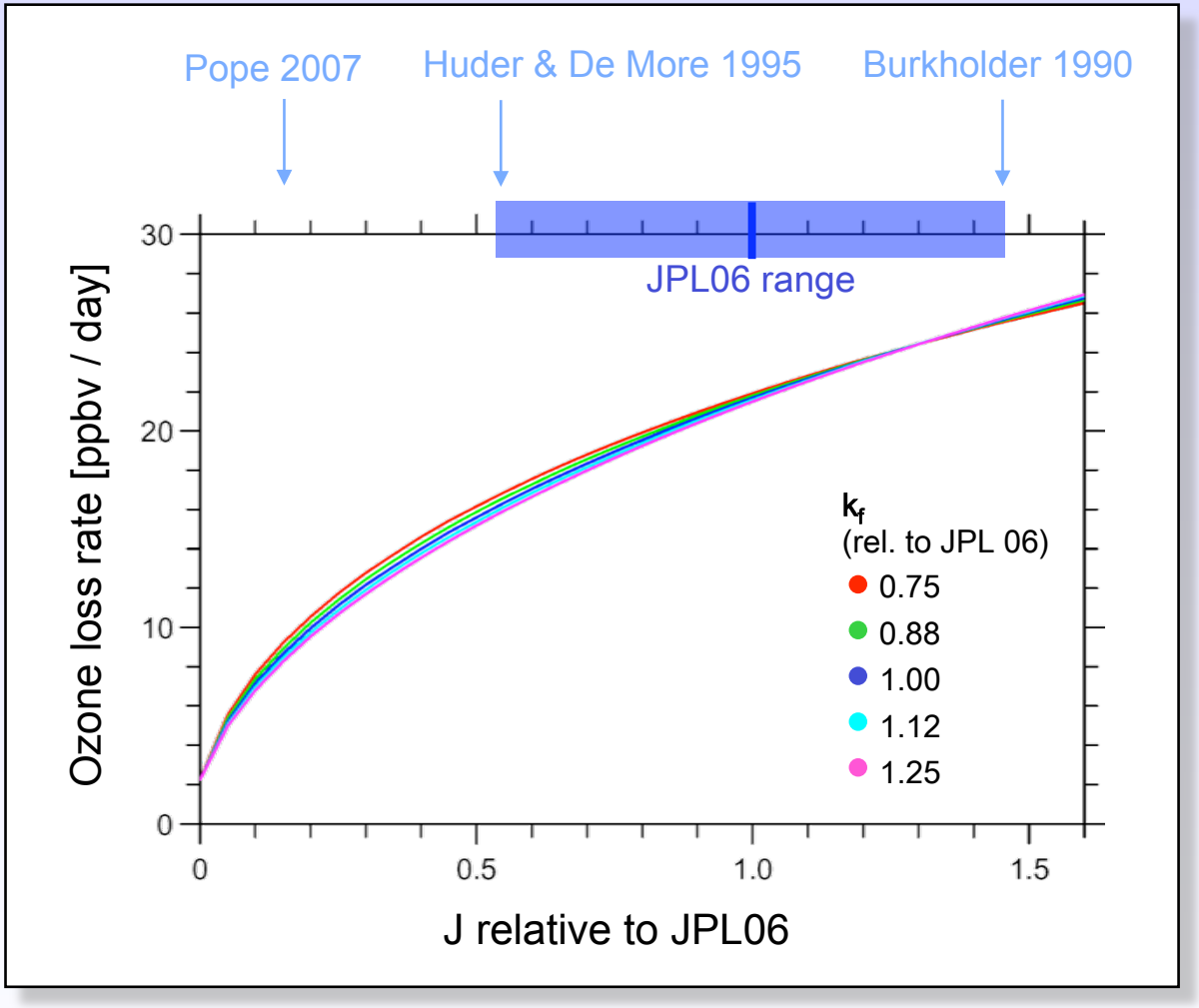

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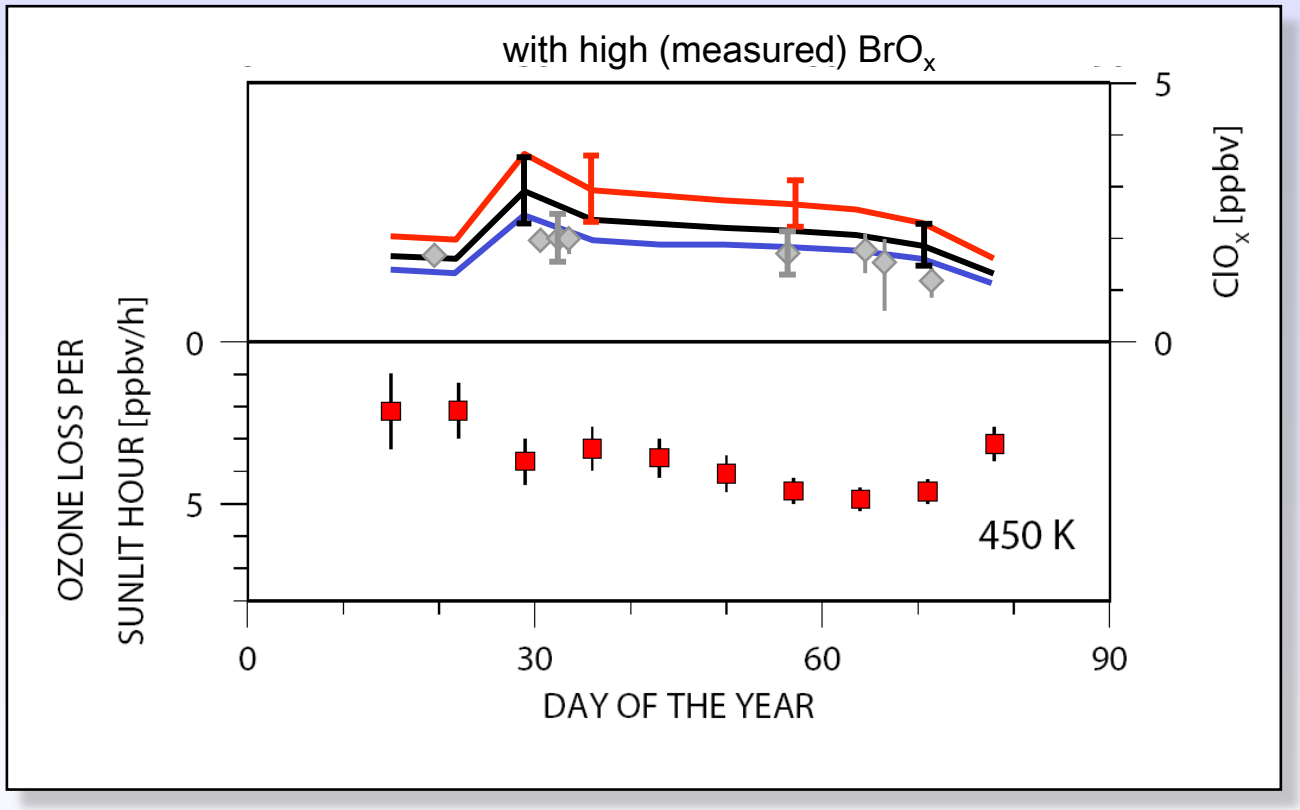
Calculated ozone loss rate drops by more than a factor of two if Pope et al. cross sections are used

ClO_x required to reproduce observed ozone loss rates

based on model with different assumptions for σ_{ClOOCl}



ozone loss rate observations

ClO_x observations

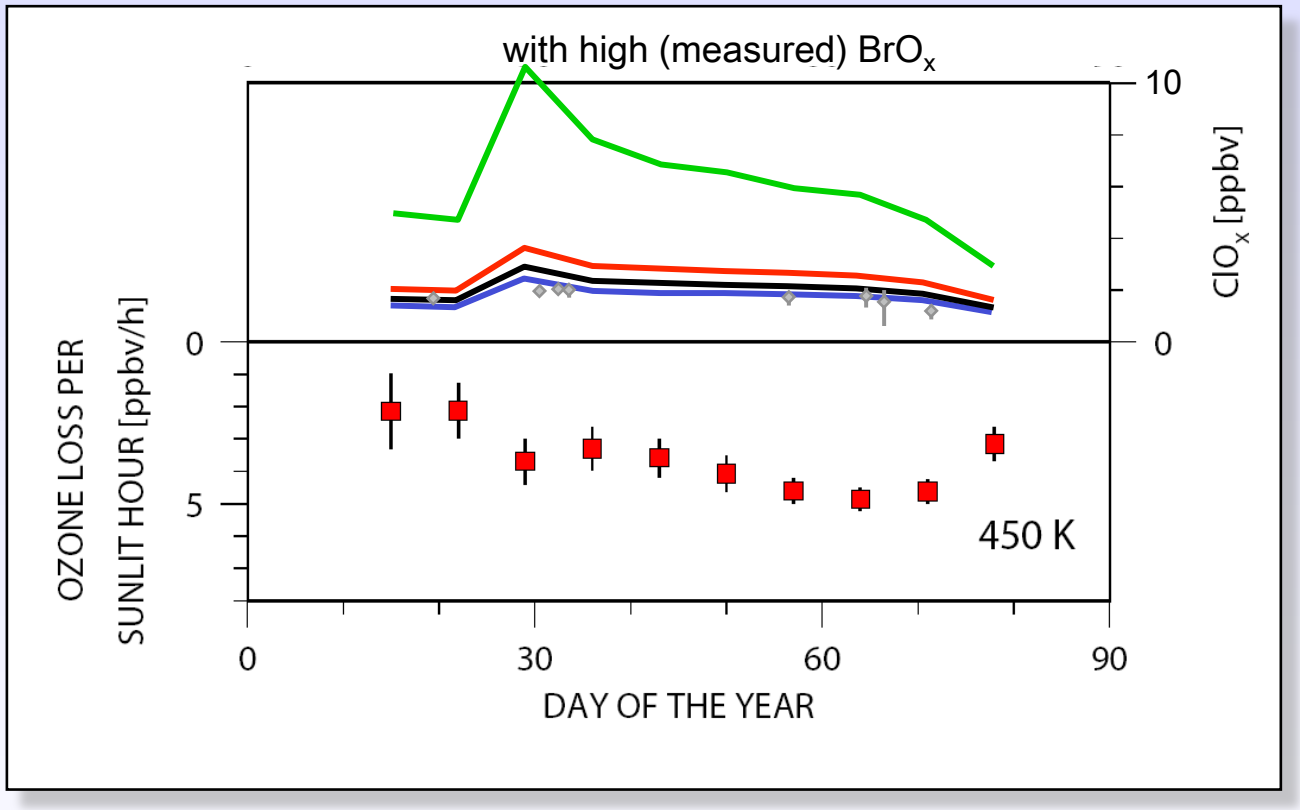
modelled ClO_x with J based on σ from:

- Huder & De Moore
- JPL 06
- Burkholder

based on Frieler et al., 2006; WMO 2006

ClO_x required to reproduce observed ozone loss rates

based on model with different assumptions for σ_{ClOOCl}



ozone loss rate observations

ClO_x observations

modelled ClO_x with J based on σ from:

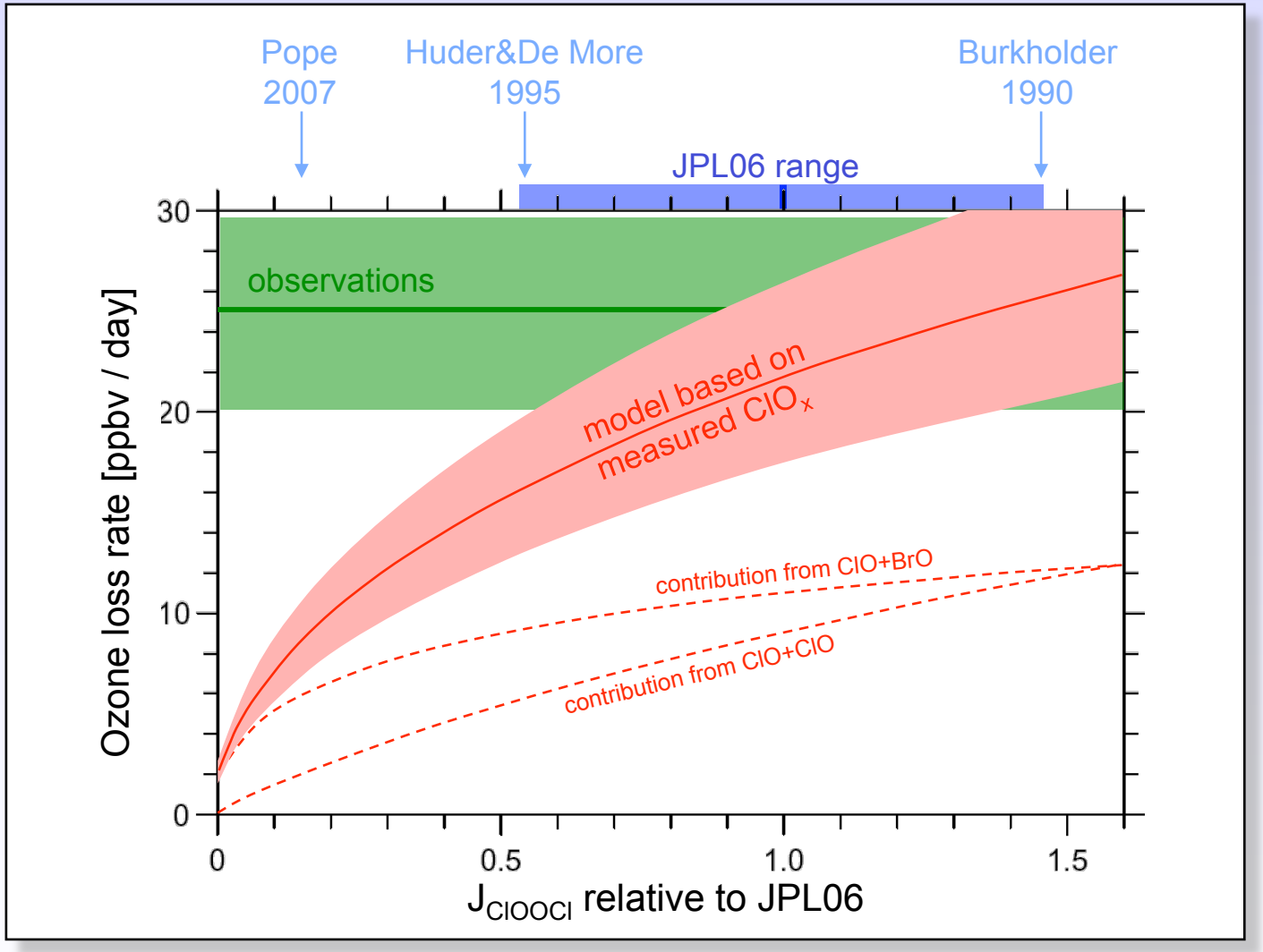
- Pope
- Huder & De Moore
- JPL 06
- Burkholder

update of Frieler et al., 2006; WMO 2006

Overall polar ozone loss rate versus J_{ClOOCl}

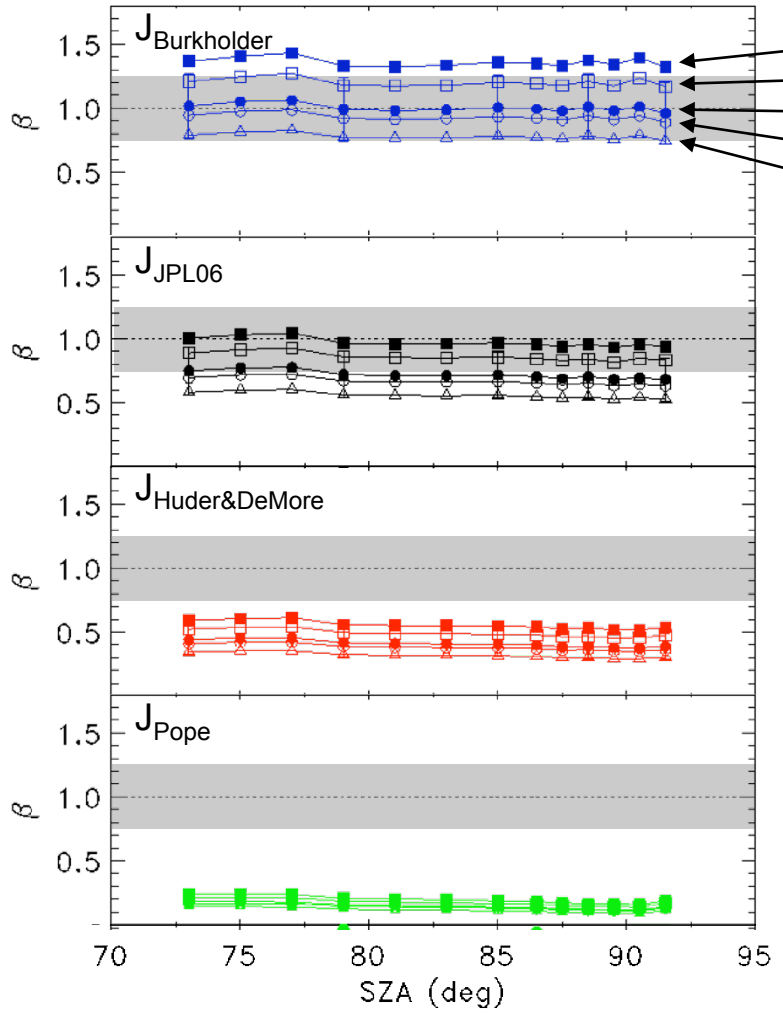
model constraint by measurements during SOLVE flight 000202

ozone loss rates from Match



Diurnal variation of ClO

Data from SOLVE 2000

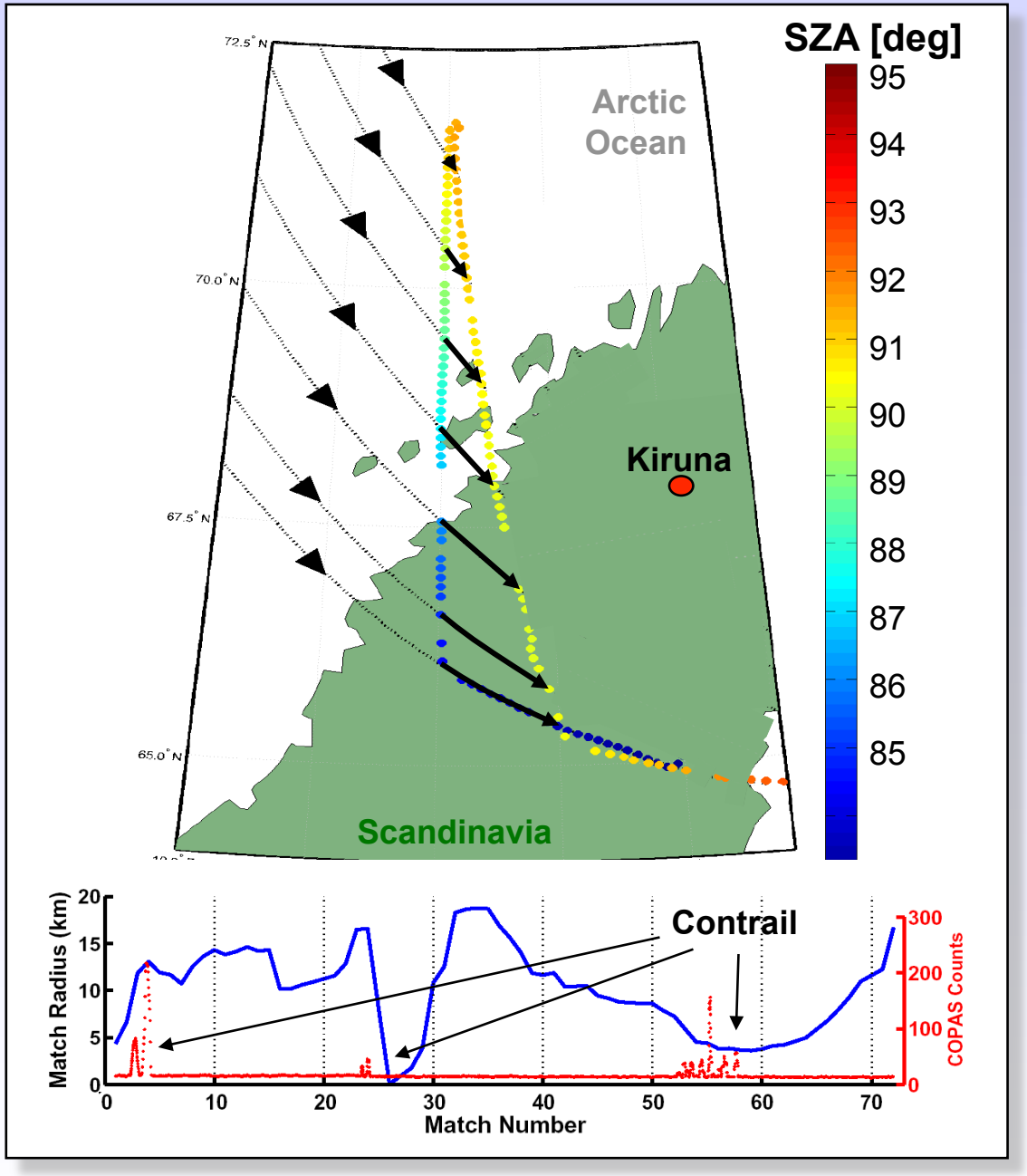


K_f

- Troiler et al. (1990)
- JPL00
- Bloss et al. (2001)
- **JPL06**
- Boakes et al. (2005)

$$\beta = \frac{\alpha^{Obs}}{\alpha^{Model}} = \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Obs} \Big/ \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Model}$$

update of Stimpfle et al., 2004



EUPLEX 2003 Self-Match flight

January 30, 2003

- Individual air masses probed before and after sunset.
- Success of flight planning confirmed by contrail intersections.
- Sensitivity of [ClO] on k_{eq} changes steeply at sunset.

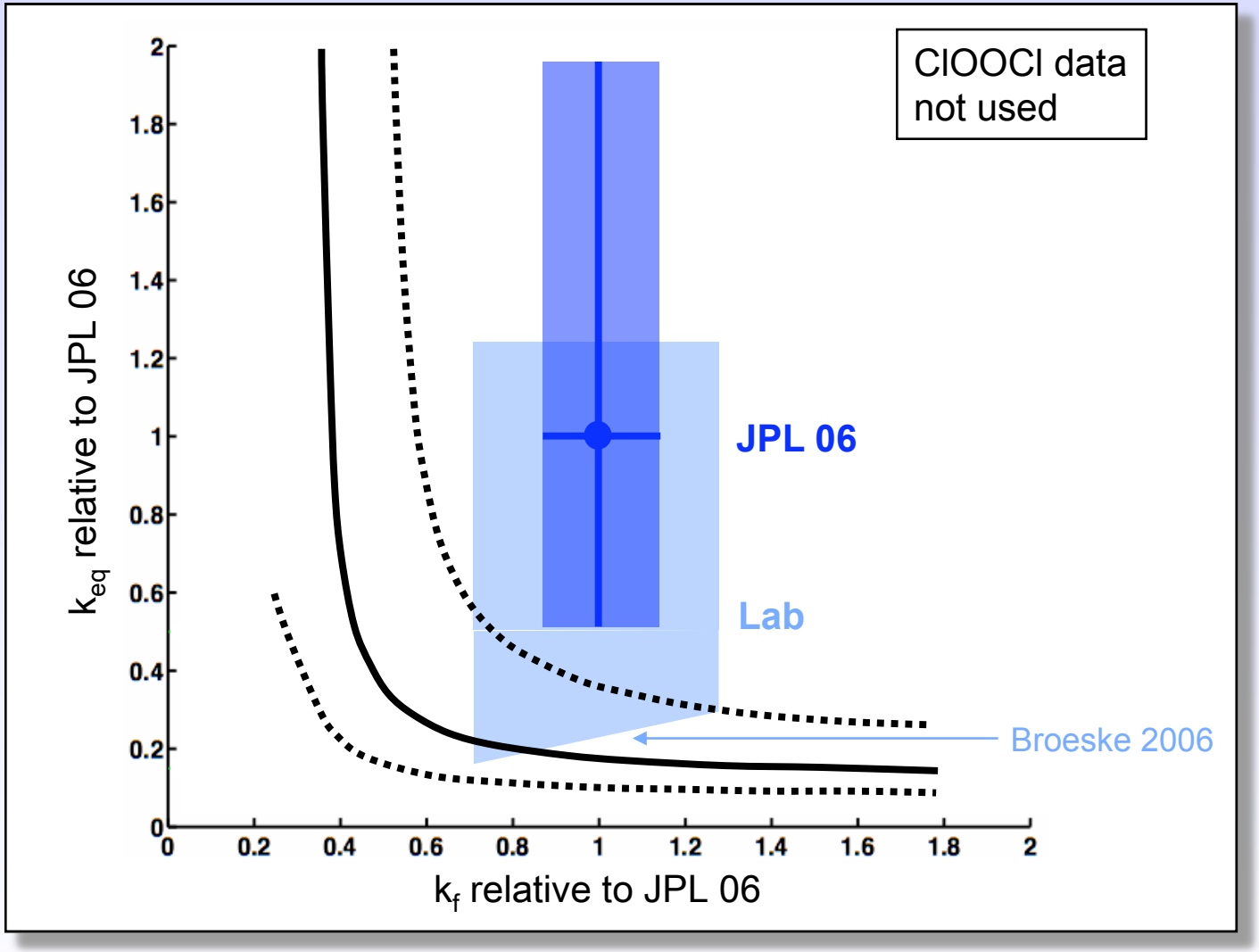
=>

k_{eq} can be derived from measurements of [ClO] alone, without making assumptions on [ClO_x] or [ClOOCl]

if [ClO_x] is constrained by measured [ClOOCl], J can be derived

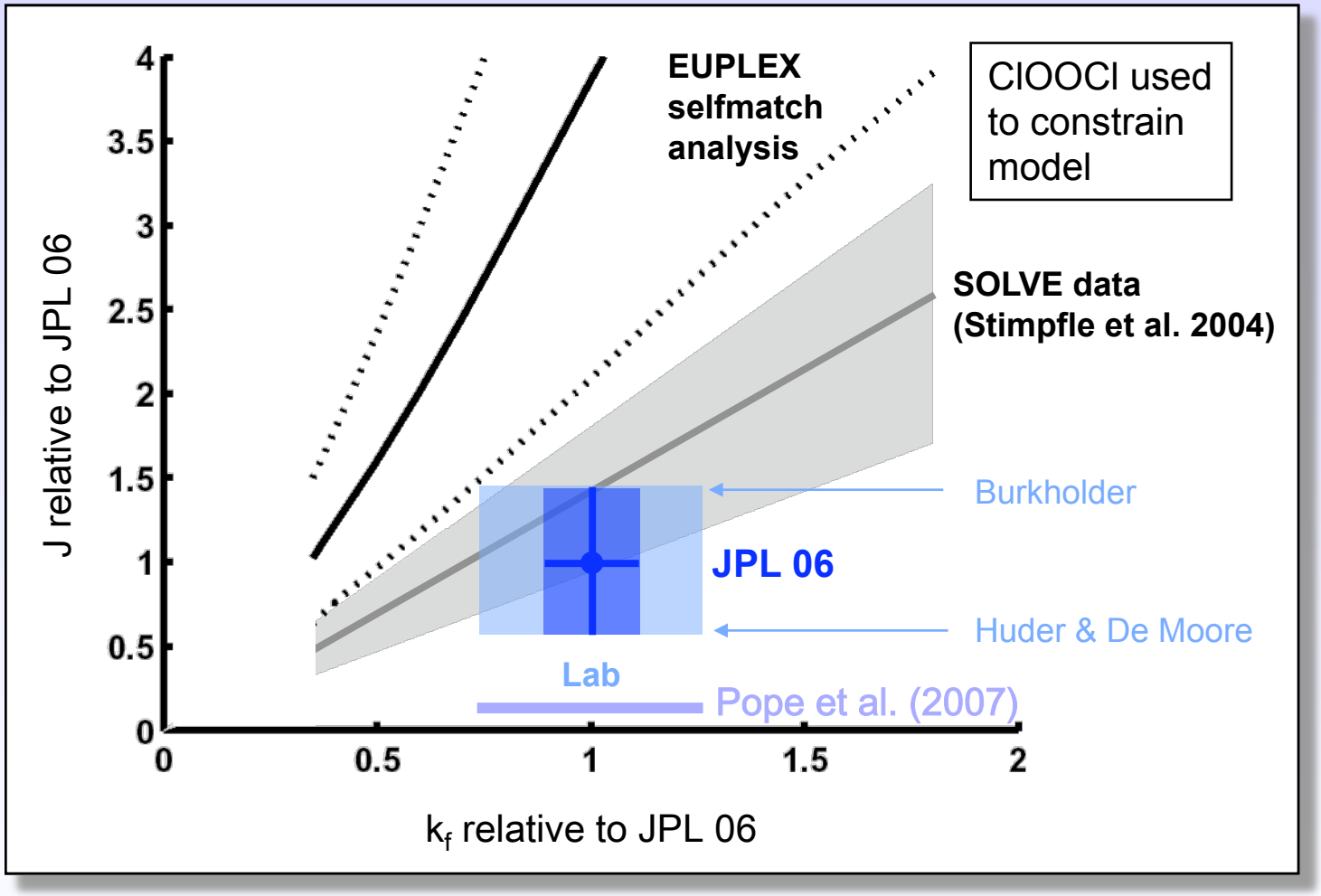
Schofield et al., 2008

k_{eq} from EUPLEX self-match flight



Schofield et al., 2008

J from EUPLEX self-match flight



Schofield et al., 2008

Atmospheric measurements show that:

- Based on standard chemistry observed ozone loss rates

  -agree best with models that are based on $J_{Burkholder}$

  -J_{JPL06} recommendations are within uncertainty

  -marginal agreement for $J_{Huder\&DeMore}$

- If J is anywhere close to J_{Pope}, a large fraction of the observed ozone loss can not be explained by standard chemistry

- If Pope et al. 2007 is correct an unknown mechanism breaks down ClOOCl and is responsible for most of the observed ozone loss

Daytime loss vs. nightime loss

Bivariate regression analysis:

Rate of change during darkness

time in darkness

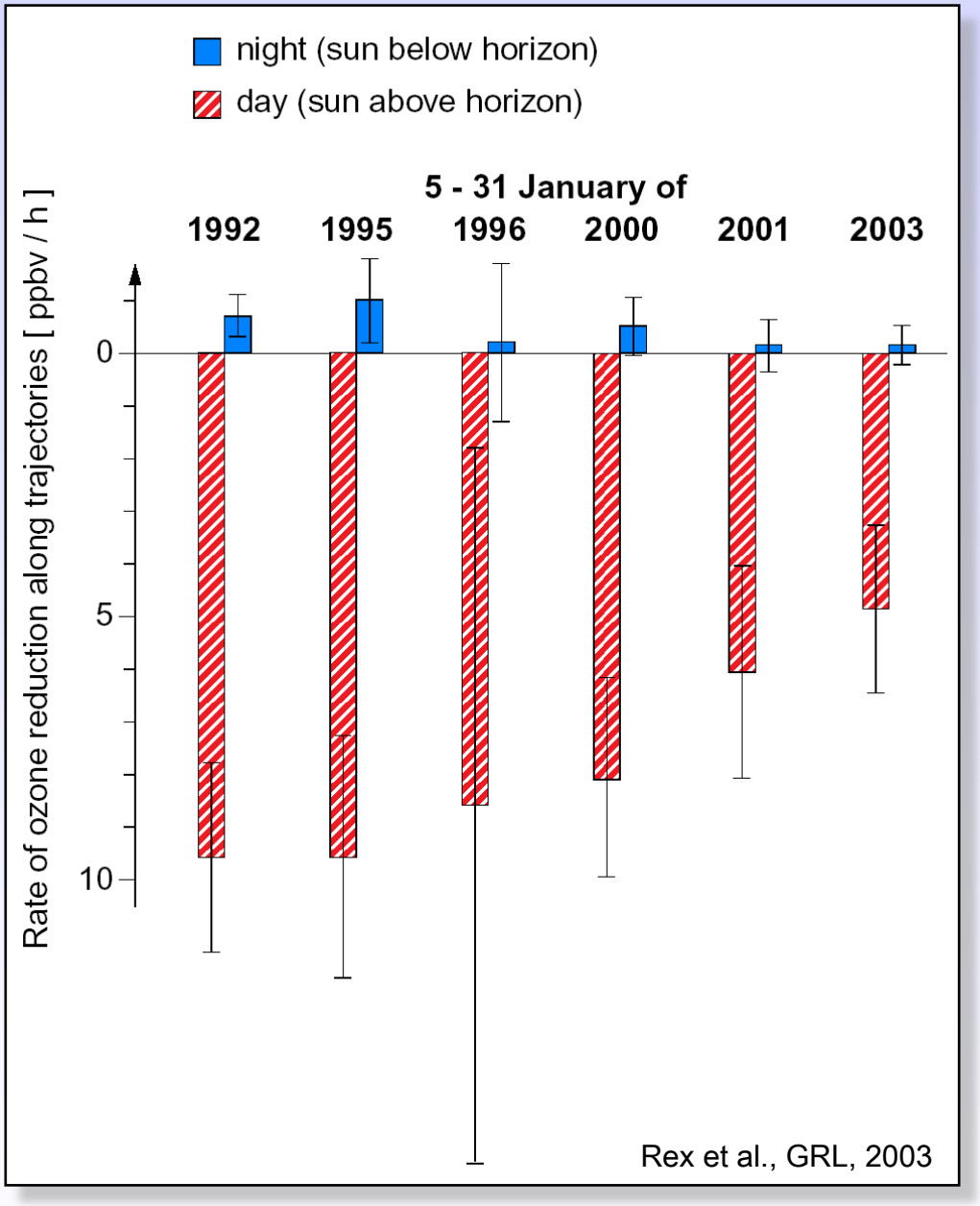
$$\Delta O_3 = L_s \cdot t_s + L_d \cdot t_d$$

Loss rate during sunlit times

sunlit time

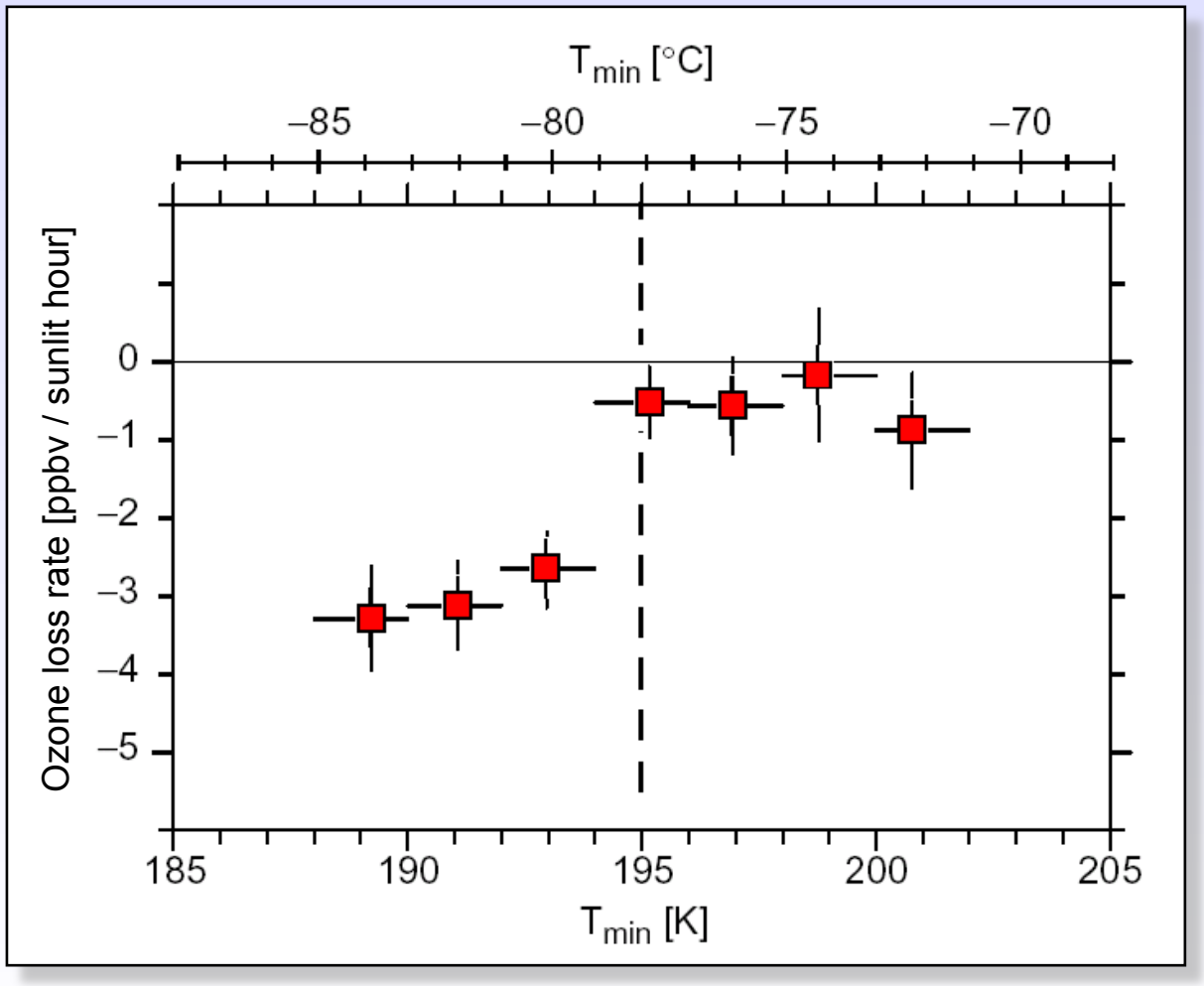
=>

- loss of ozone only in sunlight
- no change in darkness



Relation between ozone loss rate and temperature history

February, data from all years, Θ=450-500K



T_{min} is the minimum temperature encountered during the past ten days (along individual air mass trajectory)

lifetime of ClO_x is in the order of 10 days in February

Ozone loss only in air masses that have been exposed to temperatures below 195K

Schulz, Dissertation, 2000

Constraints for potential mechanisms:

(1) Daytime ClO production needs to mimic „Burkholder photolysis“ (Stimpfle et al., 2004). This applies to both, am and pm conditions !

(2) Nightime source of ClO (based on several observations of ClO during night)

(3) Ozone loss rates are as calculated with a model using „Burkholder photolysis“ (Frieler et al, 2006)

Potential mechanisms

Potential mechanisms fall into two categories:

(1) Direct mechanism:

$ClOOCl + X \rightarrow \ldots \rightarrow Cl + Cl + O_2$ (without photolytic step)

(2) Formation of an unknown nightime reservoir (Cl~)

$ClOOCl + X \rightarrow Cl\sim + \ldots$

$Cl\sim + h\nu \rightarrow \ldots \rightarrow Cl + Cl + O_2$

(1) Direct mechanism

$$ClOOCl + X \rightarrow \ldots \rightarrow Cl + Cl + O_2$$

- k x [X] roughly equals $J_{Burkholder}$ for all sza, for am and pm
- collision rate theory: daytime abundance of X > 10 pptv

=> BrO and ClO are options

- X=ClO is probably not consistent with Bloss et al., 2001
- X=BrO model fails to reproduce diurnal variation of ClO

=> direct mechanism appears to be unlikely

(2) Formation of an unknown nightime reservoir (Cl~)

$ClOOCl + X \rightarrow Cl\sim + \ldots$

$Cl\sim + h\nu \rightarrow \ldots \rightarrow Cl + Cl + O_2$

- „efficient photolysis“ similar to Burkholder photolysis:

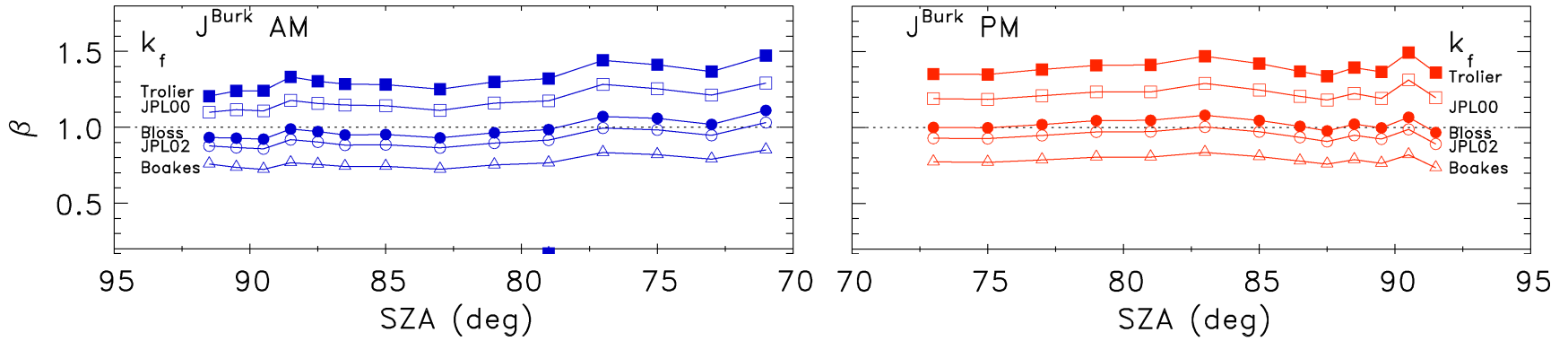
  $J_{ClOOCl_Pope} \times [ClOOCl] + J_{Cl\sim} \times [Cl\sim] = J_{Burkholder} \times [Cl_{Havard}]$

  (Cl_{Havard} = total Cl in all species that are seen as ClOOCl in Harvard type instruments, i.e. all species that decompose into ClO at T~370K, without also producing Cl atoms)

am/pm differences in efficient J ?

measurements during EUROSOLVE/SOLVE 2000
analysis like in Stimpfle et al.(2004), but am/pm separately

$$\beta = \frac{\alpha^{Obs}}{\alpha^{Model}} = \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Obs} \Big/ \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Model}$$



=> ClO production rate similar to $J_{Burkholder}$ x $[Cl_{Havard}]$ for all sza, for both am and pm

=> slow buildup of unknown nighttime reservoir over night can be ruled out

(2) Formation of an unknown nightime reservoir (Cl~)

$ClOOCl + X \rightarrow Cl\sim + \ldots$

$Cl\sim + h\nu \rightarrow \ldots \rightarrow Cl + Cl + O_2$

=> either reaction is rapid and converts all ClOOCl to Cl~

=> or rapid equilibrium between ClOOCl and Cl~

(2) Formation of an unknown nightime reservoir (Cl~)

(2.1) Rapid conversion of ClOOCl into unknown nighttime reservoir Cl~

- ClOOCl does not exist at all; Cl~ is the only nighttime reservoir
  => $J_{Cl\sim} = J_{Burkholder}$ (for all sza)
  => Cl~ is either Cl_2, Cl_2O (or Cl_2O_5)

- observations of high ClO during warm nights => nighttime source of ClO
- „ClOOCl“ measurements of Havard type instruments
  => Cl~ needs to decompose thermally
  => rules out Cl_2

=> Cl~ is Cl_2O (or Cl_2O_5)
=> reaction partner X is an odd oxygen species with VMR >> 10pptv
  => X could be O_3 (or N_2O, HNO_3)

- gas phase reaction with O_3 is too slow (DeMoore and Tschuikow-Roux, 1990)

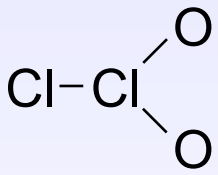
=> heterogenous mechanism (EUPLEX: on sulfate !) ?
  - surface area densities needed (collision rate theory): $10 \mu m^2 cm^{-3}$
  - available: $\sim 1 \mu m^2 cm^{-3}$

(2) Formation of an unknown nightime reservoir (Cl~)

(2.2) Back reaction also exist, ClOOCl and Cl~ coexist close to equilibrium

=> $J_{Cl\sim} >> J_{Burkholder}$; shape of $J_{Cl\sim}(sza) \sim J_{Burkholder}(sza)$

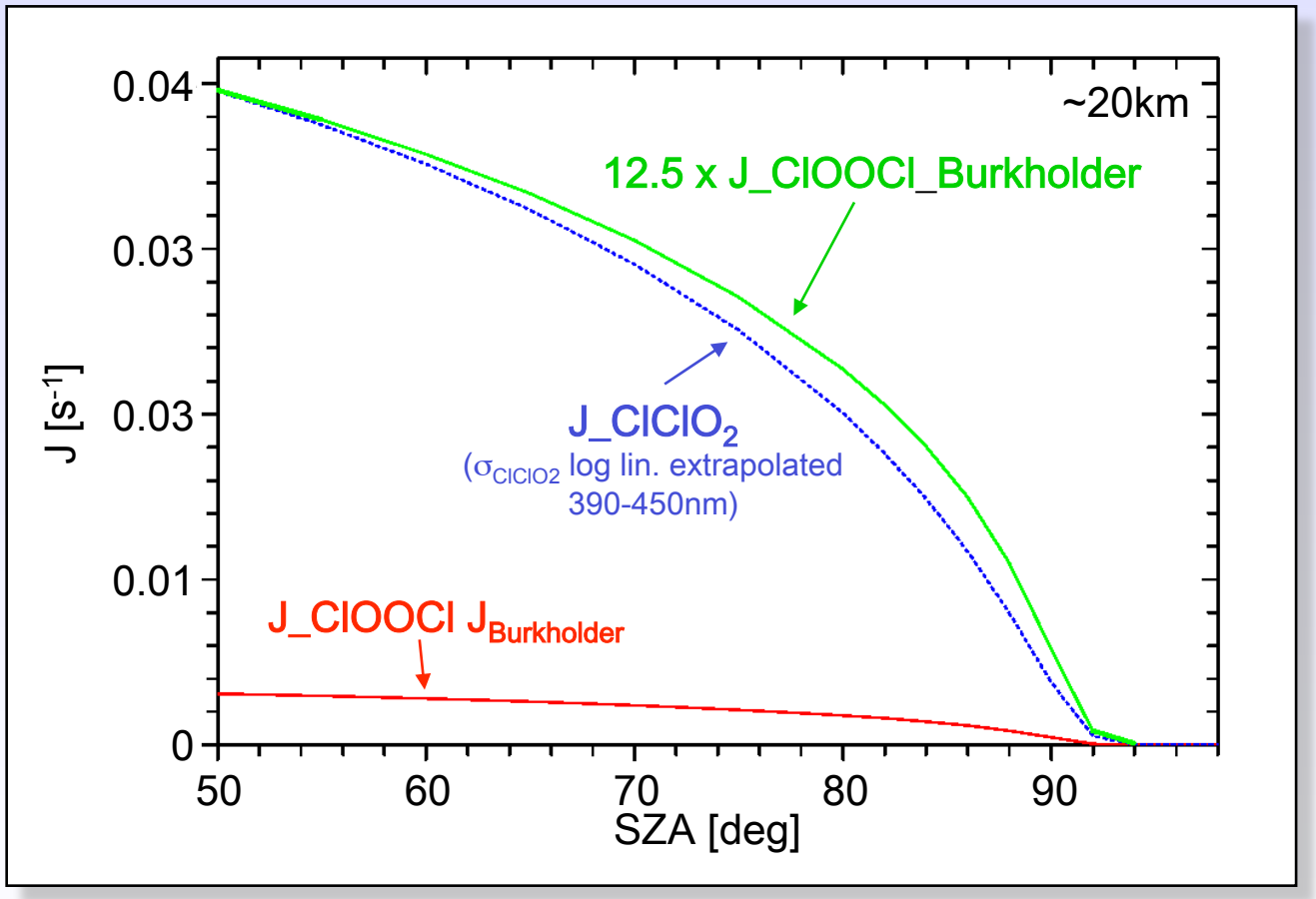
=> Cl~ = $ClClO_2$!?



Rapid equilibrium between ClOOCl and $ClClO_2$ (Cl – Cl(O)O)?

$ClOOCl \Leftrightarrow ClClO_2$ barrier too high

e.g. by: $ClOOCl + ClO \rightarrow ClClO_2 + ClO$
$ClClO_2 + ClO \rightarrow ClOOCl + ClO$



=>

~10% of Cl_2O_2 in the form of $ClClO_2$ leads to „Burkholder like“ photolysis of the mixture

Temperature dependend equilibrium could explain SOLVE / EUPLEX differences in efficient J and k_{eq}

ClO and ClOOCl observations

Model that

- is based on J_{ClOOCl} from Pope et al.
- and includes the „$ClClO_2$-mechanism“

reproduces all available observations of ClO and ClOOCl. It even reproduces the SOLVE / EUPLEX differences, that are hard to resolve with a model based on standard chemistry

But !

- To explain observed ozone loss photolysis of $ClClO_2$ would have to restore the O-O bond !

- New upper limits for the abundance of $ClClO_2$ in the atmosphere are an order of magnitude to low (Jucks et al. in preparation, limit derived from Stimpfle et al., 2004)

Conclusions

- Uncertainties in J_{ClOOCl} limit our ability to model polar ozone loss quantitatively
  - Based on JPL06 uncertainties (i.e. even without considering Pope et al., 2007), modeled ozone loss rates have up to a factor of three uncertainty.
- If Pope et al. (2007) is correct:
  - An unknown breakdown mechanism for ClOOCl exists
  - Most of the observed ozone loss is due to this unknown mechanism
- It is extremely hard to reconcile Pope et al. (2007) with atmospheric measurements
  - Mechanism has to mimic photolysis according to Burkholder et al. cross sections.
  - Most potential mechanisms are not consistent with in-situ data of ClO, observed ozone loss rates or lab studies.
- New lab measurements of the ClOOCl cross section needed to resolve this issue (several under way)
- SPARC initiative on chlorine chemistry (led by M. Kurylo and B.-M. Sinnhuber). Info: https://sparchpo.icg.kfa-juelich.de/SPARCHPO

END

Conclusions

- **Uncertainties in J_{ClOOCl} limit our ability to model polar ozone loss quantitatively**

  Based on JPL06 uncertainties (i.e. even without considering Pope et al., 2007), modeled ozone loss rates have up to a factor of three uncertainty.

- **Based on standard chemistry observed ozone loss rates:**

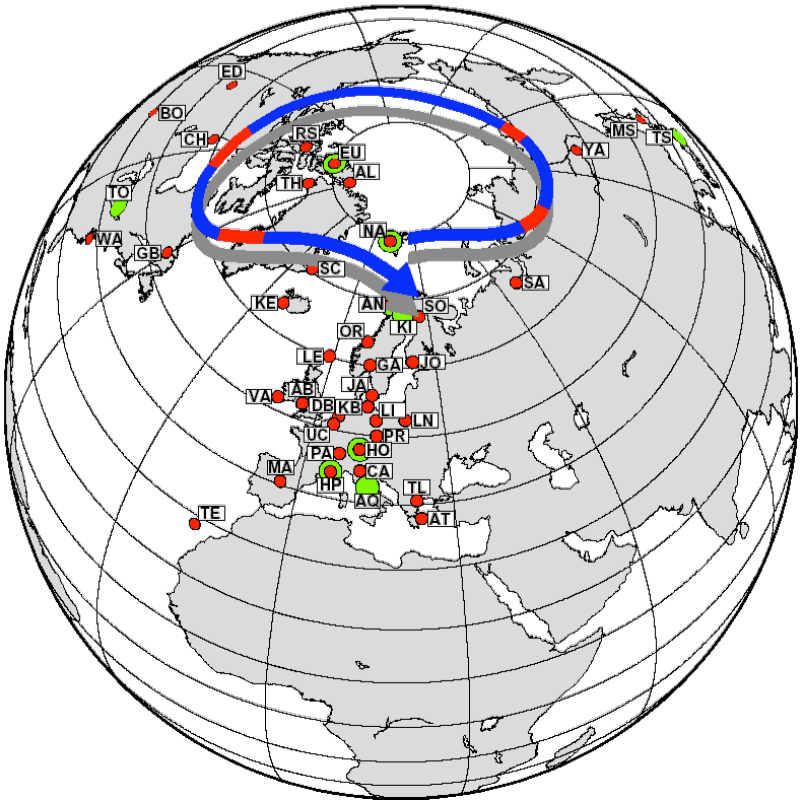
  - agree best with models that are based on $J_{Burkholder}$
  - J_{JPL06} recommendations are within uncertainty
  - $J_{Huder\&De\ Moore}$ would require to push all uncertainties to the limits

- **If J is anywhere close to J_{Pope}, a large fraction of the observed ozone loss can not be explained by standard chemistry**

- **Ozone loss occurs only in sunlight**

- **Ozone loss occurs only in air masses that have been exposed to temperatures below 195K**

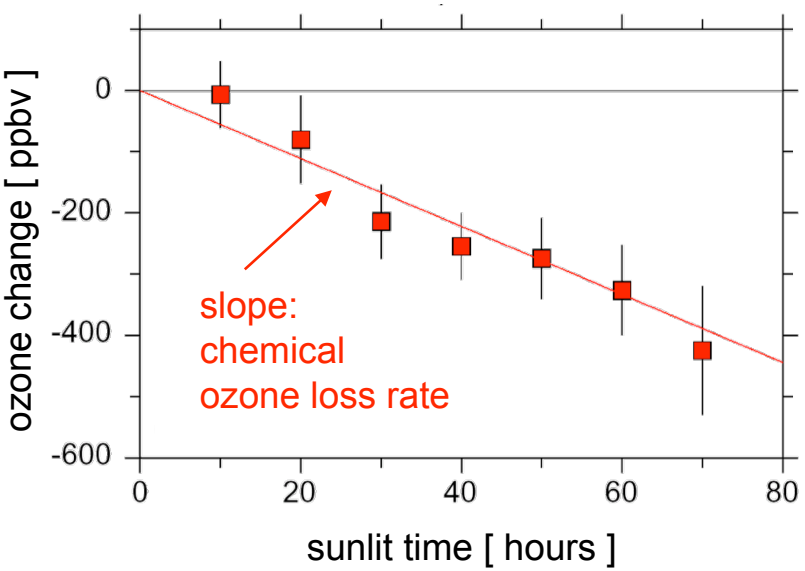
The Match Project



ozone sonde station Lidar station

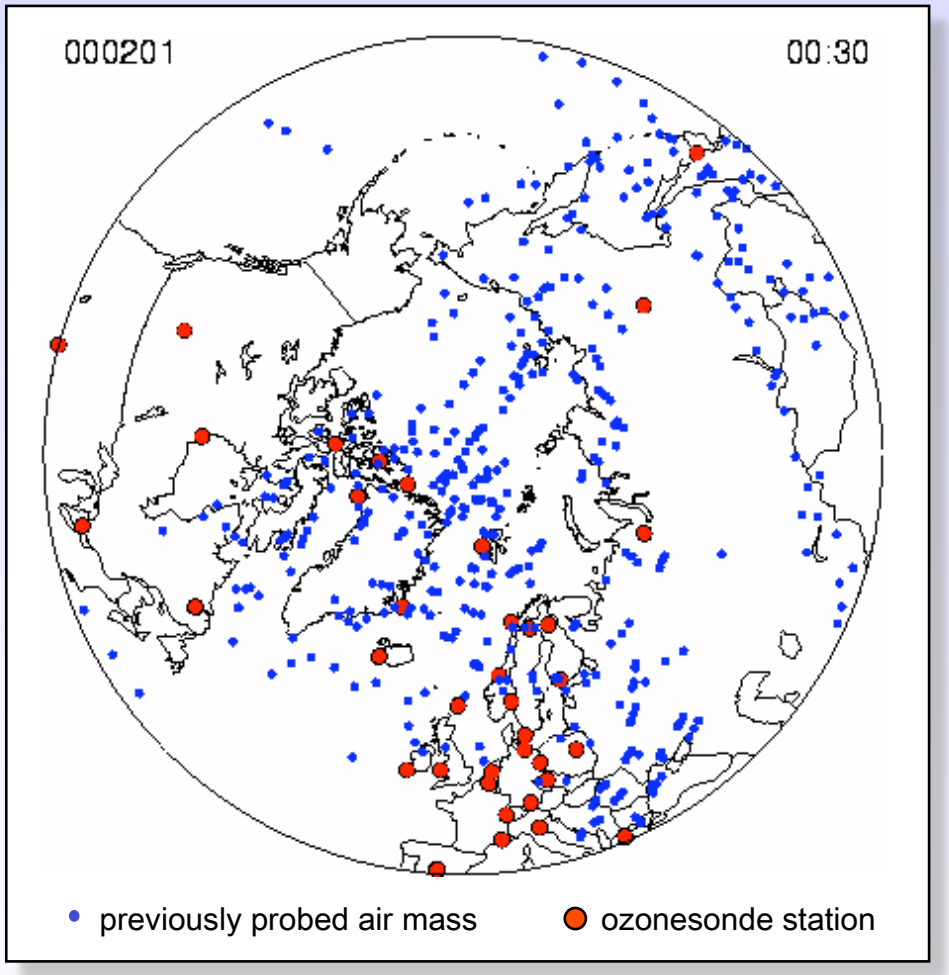
air mass trajectory (day/night)

Separation of chemistry and transport
=> chemical ozone loss rate

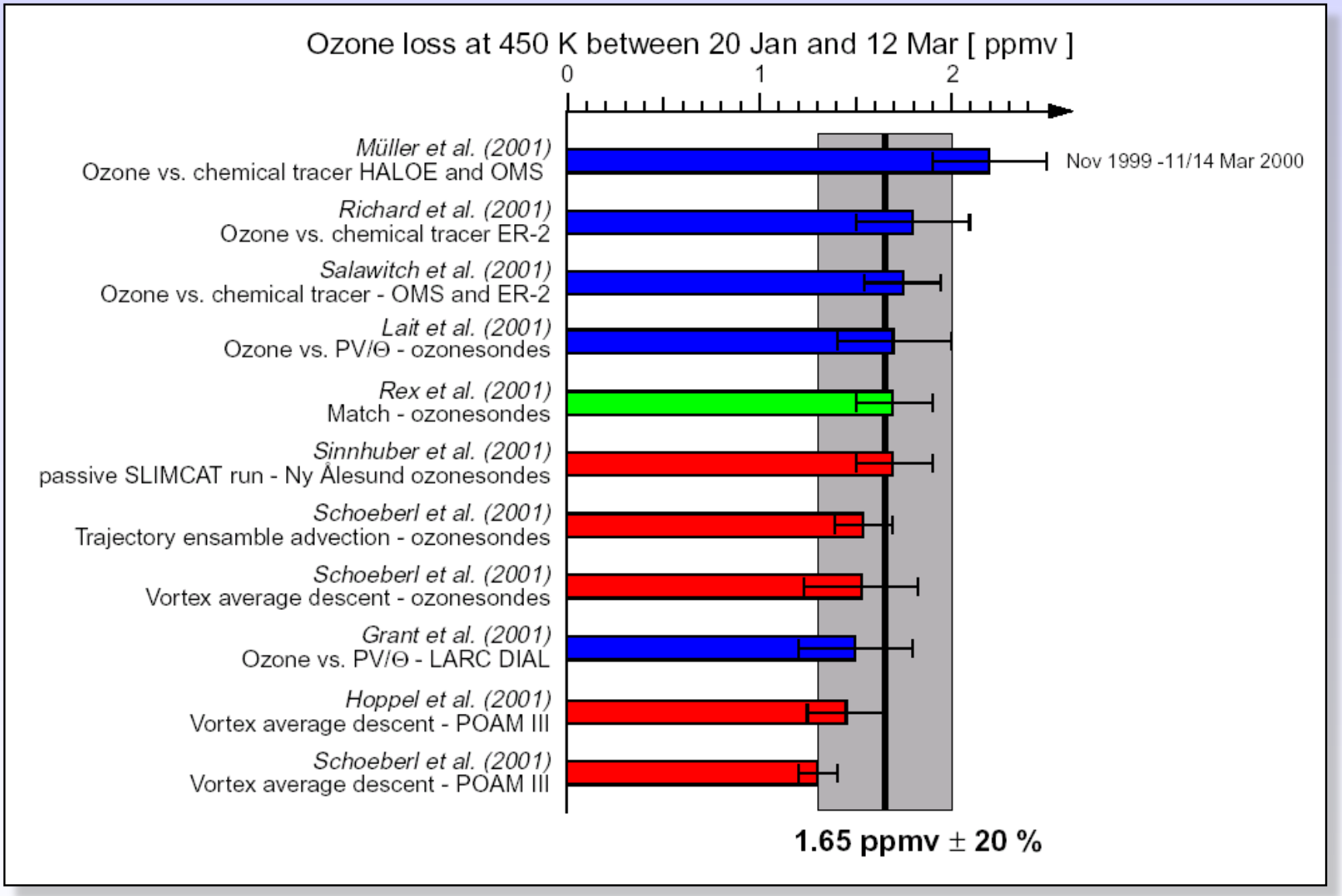


e.g. Rex, 1993; von der Gathen et al., Nature, 1995; Rex et al., Nature, 1997

Match campaigns



- 35 stations
- ~500-1200 ozonesondes per winter
- >1000 match events per winter
- 11 Arctic and 2 Antarctic campaigns since the early 90ies (EU + natl. funding)



based on Newman et al., JGR, 2002

Results from measurements of ClO / ClOOCl

all values relative to JPL-06
estimates are based on known chemistry

- **k_{eq}**
  - SOLVE: k_{eq} = 50% best fit
  - EUPLEX self-match: k_{eq} = 20% best fit; $k_{eq} \leq 40\%$
- **J**
  - SOLVE: J = 150% best fit; J ≥ 75%
  - EUPLEX self match: J >> 200% best fit
  - Pope et al.: J = 16% (~ 9 times smaller than in-situ suggests)

=>

- **No overlap between uncertainties from in-situ estimates of J and Pope et al.**
- **Discrepancies appear to be larger for warmer conditions**

Potential solutions:
(1) Direct mechanism

Breakdown of ClOOCl directly recycles Cl:

$ClOOCl + X \rightarrow ... \rightarrow Cl + Cl + O_2 + Y$

↓

Collision rate theory and diurnal variation: X = BrO

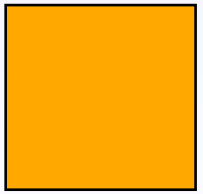
Thermodynamically only
ClOOCl + BrO -> ClOO + BrOCl
can occur

Thermal decomposition of BrOCl has to be rapid to prevent loss of bromine to BrOCl

↓

Model that includes this mechanism does not reproduce diurnal variation of ClO

Not likely



Potential solutions: (2) Indirect mechanism

ClOOCl + X -> Cl~ + Y

=> J_ClOOCl x [ClOOCl] + J_Cl~ x [Cl~] similar to "Burkholder rate"

Cl~ could be: ~~OClO~~, Cl_2, Cl_2O, ClOClO, $ClClO_2$, ~~Cl_2O_3~~, ~~Cl_2O_4~~, Cl_2O_5, ~~Cl_2O_6~~, ~~Cl_2O_7~~

(2.1)
reaction is slow [1]
=> Cl~ and ClOOCl coexist
=> ratio Cl~/ClOOCl goes up over night
=> am/pm differences in $J_{Cl^- + ClOOCl}$(sza)

in contrast to in-situ data

(2.2)
Reaction is fast[2]
=> Cl~ is the only reservoir
=>
(1) J_{Cl^-} similar to $J_{ClOOCl_Burkholder}$
=> *Cl~: Cl_2, Cl_2O, (ClOClO, Cl_2O_5)*

(2) Cl~ decomposes thermally
=> *Cl~: Cl_2O, (ClOClO, Cl_2O_5)*

(2.3)
reaction
Cl~ + Y -> ClOOCl + X
also exists, i.e.
Cl~ and ClOOCl
coexist in equilibrium
=>
J_{Cl^-} much larger than
$J_{ClOOCl_Burkholder}$
=> *Cl~:$ClClO_2$,*
(ClOClO, Cl_2O_5)

(2.2.1)
Cl~ isn't odd oxygen
Cl~: ClOClO

J_{ClOClO} similar to $J_{ClOOCl_Burkholder}$?
unlikely

(2.2.2)
Cl~ is odd oxygen
Cl~: Cl_2O or Cl_2O_5
=> X is odd oxygen
=> X is O_3
=> $k \geq 10^{-15}$

(2.2.2.1)
gas phase reaction

too slow (DeMoore and Tschuikow-Roux, 1990)

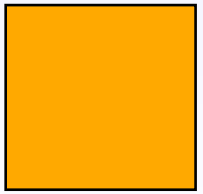
(2.2.2.2)
heterogenous reaction
=> must occur on sulfate

surface area dens. not sufficient

(2.3.1)
Cl~ is $ClClO_2$
(or ClOClO)
=>
X,Y are any M,
ClO or ClOOCl

possible,
but photolysis
would need to restore
the O-O bond

(2.3.1)
Cl~ is Cl_2O_5
=> X is O_3
=> see 2.2.2



Potential solutions (2)

(2.1) ClOOCl does not exist at all; Cl~ is the only nighttime reservoir

=> $J_{Cl\sim} = J_{Burkholder}$

=> Cl~ = Cl_2O (or Cl_2O_5), X = O_3

=> gas phase reaction too slow (DeMoore and Tschuikow-Roux, 1990)

heterogenous mechanism (EUPLEX: on sulfate !) ?

=> surface area densities needed (collision rate theory): $10 \mu m^2 cm^{-3}$

=> available: ~$1 \mu m^2 cm^{-3}$

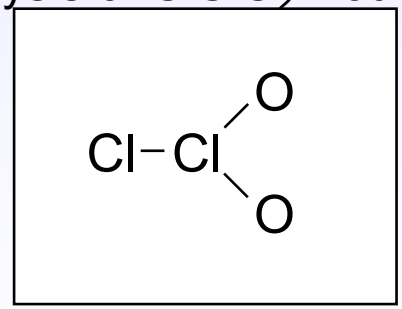
(2.2) Back reaction also exist, ClOOCl and Cl~ coexist close to equilibrium

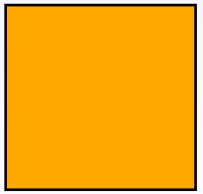
=> $J_{Cl\sim} > J_{Burkholder}$; $J_{Cl\sim}(sza) \sim J_{Burkholder}(sza)$

=> Cl~ = $ClClO_2$!?

Formation e.g. by reaction ClOOCl + ClO or ClOOCl + ClOOCl

=> to explain observed ozone loss photolysis of $ClClO_2$ would have to restore the O-O bond !





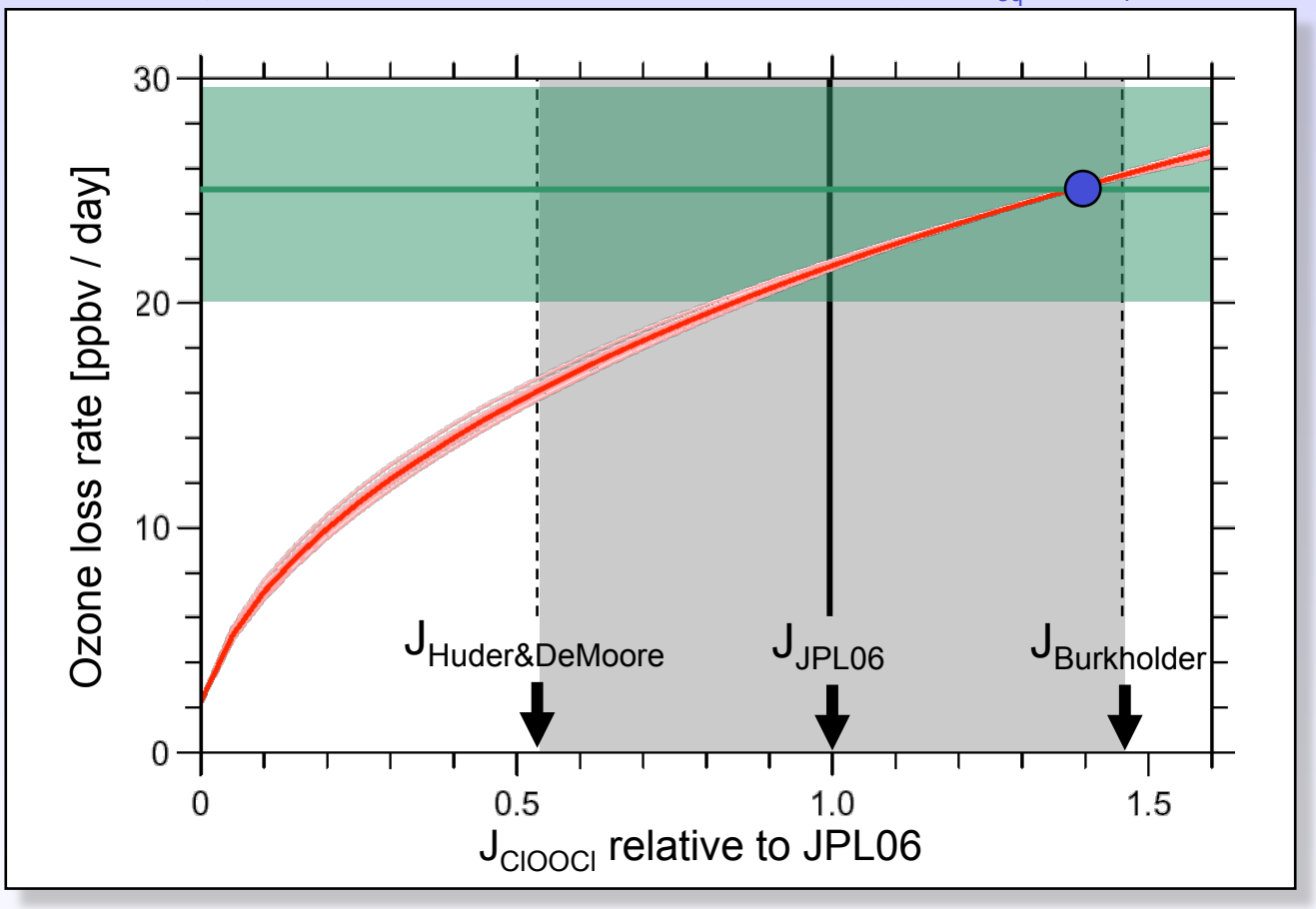
Research needs

- Verify Pope et al. (2007) results in the lab
- Measure ClOOCl cross sections in O_2 atmosphere
- Identify photolysis products of $ClClO_2$, ClOClO (lab and ab initio calculations)
- Measure IR/microwave spectra of $ClClO_2$ and ClOClO and look for features of these species in existing IR/microwave data sets.
- Study dynamics of ClO/ClOOCl system in-situ, preferably with match flight patterns extending from local noon to late night and including am and pm measurements.

Overall polar ozone loss rate versus J_{ClOOCl}

measurements during EUROSOLVE/SOLVE 2000

flight 000202, sza = 82.5°, pm, little sensitivity on k_{eq} and k_f

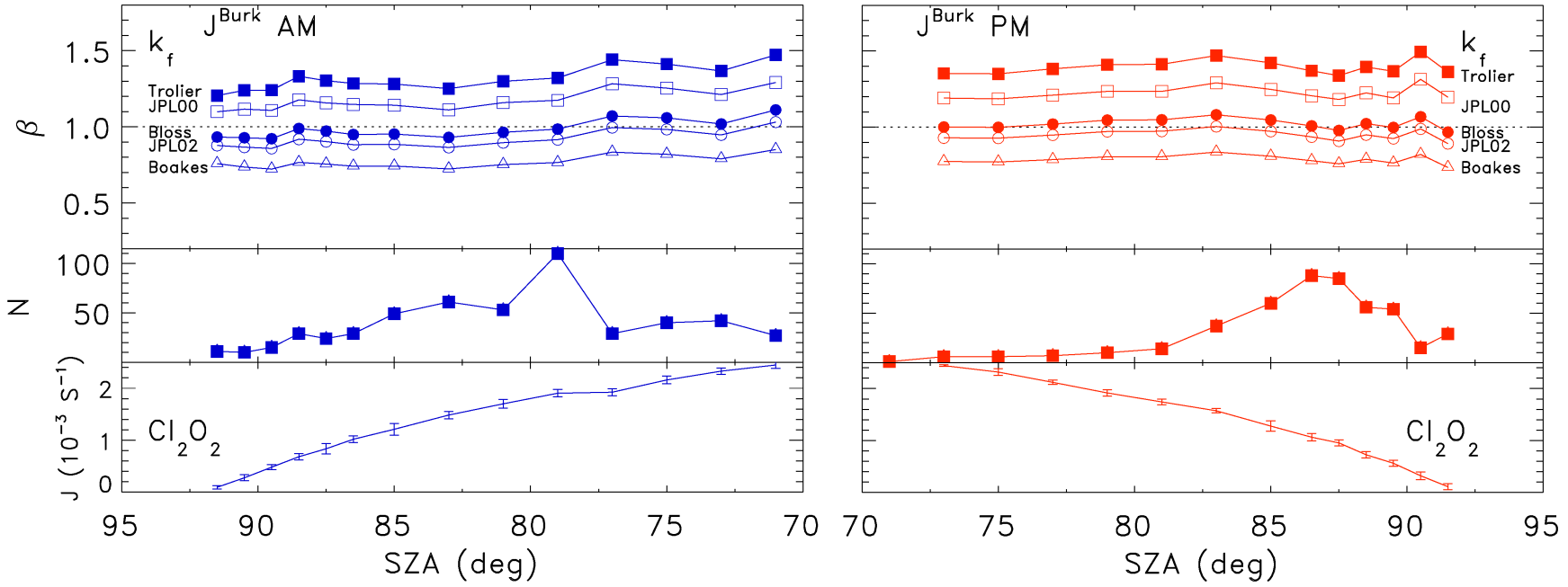


=> model based on $J_{Burkholder}$ reproduces observed loss rate

am/pm differences in efficient J ?

measurements during EUROSOLVE/SOLVE 2000

$$\beta = \frac{\alpha^{Obs}}{\alpha^{Model}} = \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Obs} \Big/ \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Model}$$

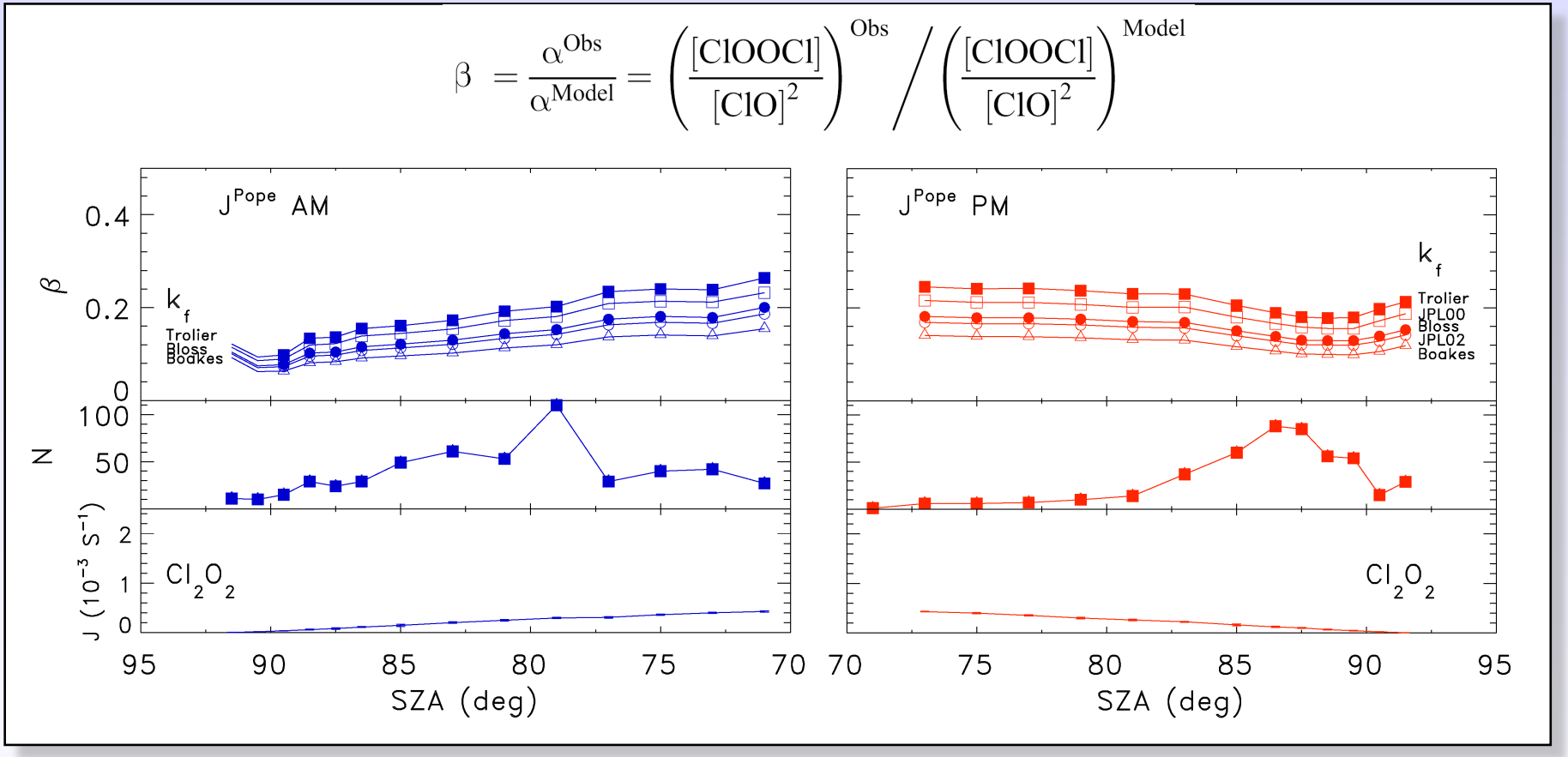


=> no significant am/pm difference in efficient J

J_{Pope} and SOLVE data

measurements during EUROSOLVE/SOLVE 2000

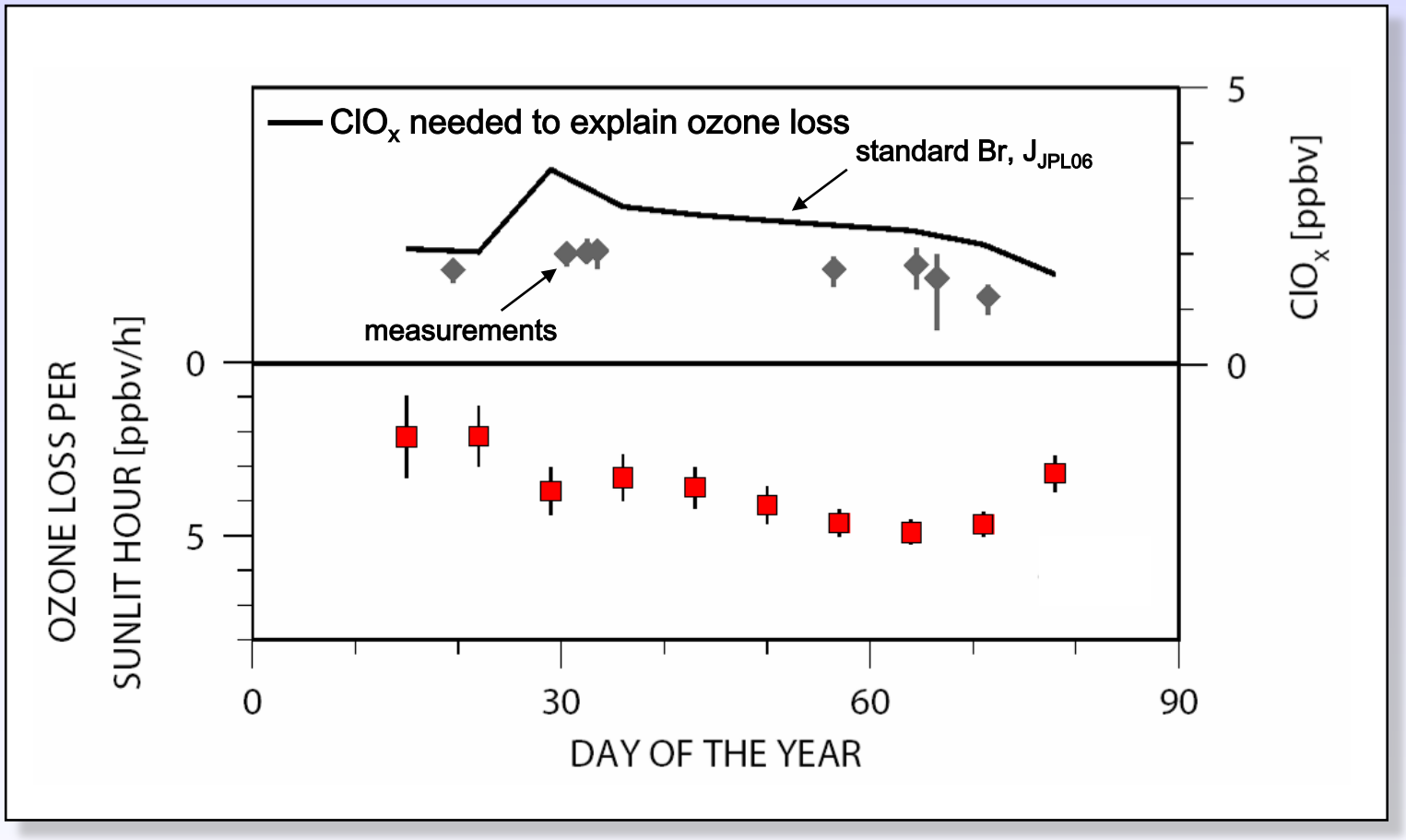
$$\beta = \frac{\alpha^{Obs}}{\alpha^{Model}} = \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Obs} \Big/ \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Model}$$



=> J_{Pope} is not consistent with data and known chemistry

Theoretical understanding of loss process

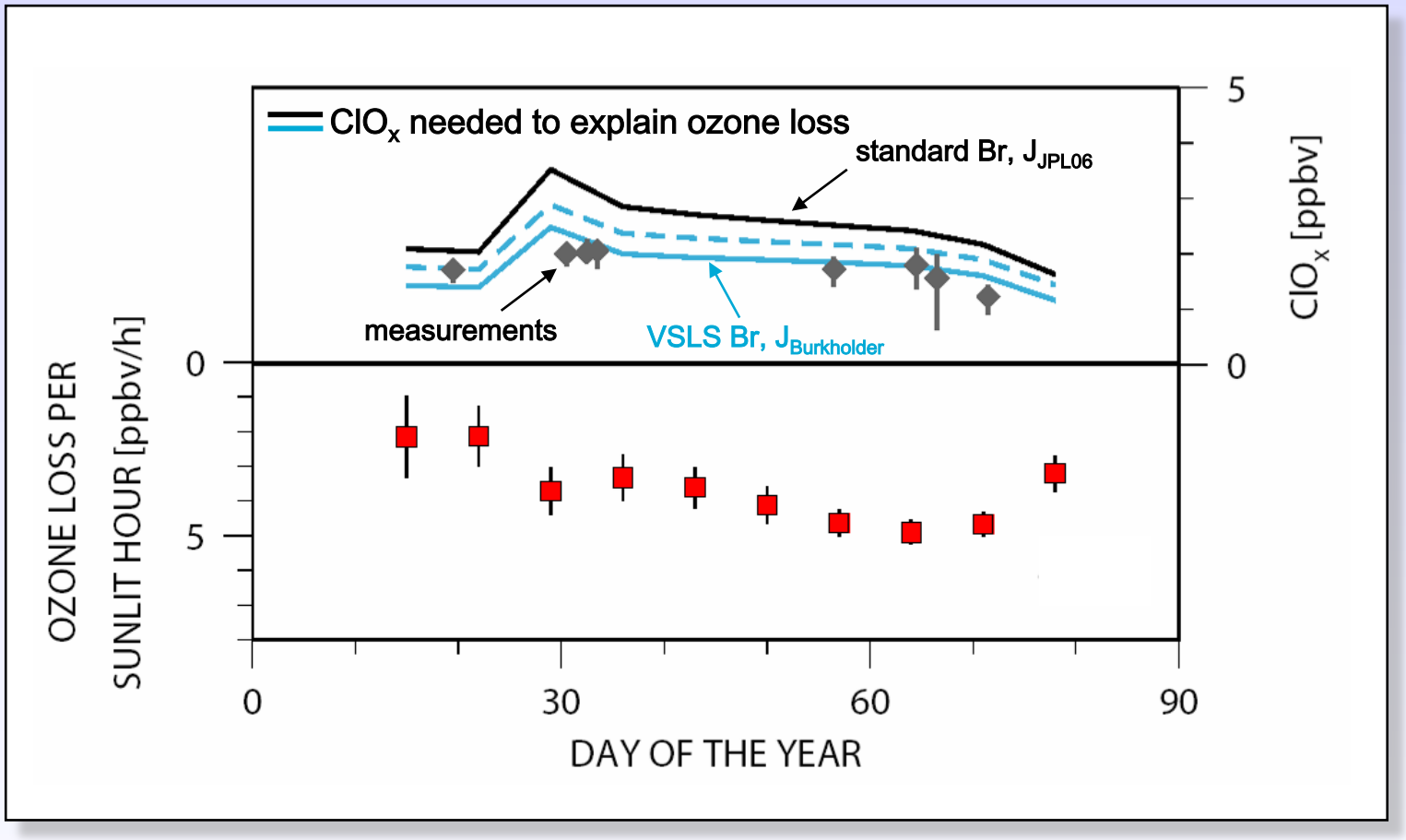
measurements of ClO_x ($ClO + 2Cl_2O_2$) during EUROSOLVE/SOLVE 2000



Frieler et al., GRL 2006; WMO 2006

Theoretical understanding of loss process

measurements of ClO_x ($ClO + 2Cl_2O_2$) during EUROSOLVE/SOLVE 2000

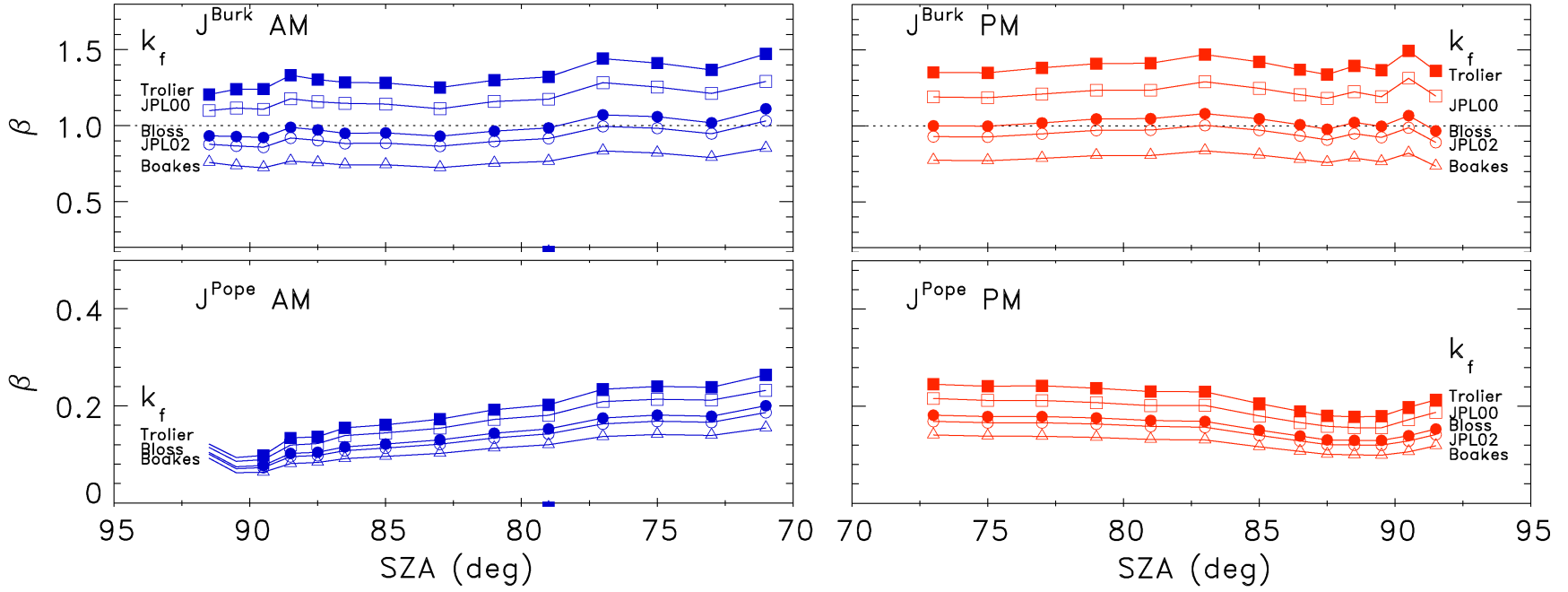


Frieler et al., GRL 2006; WMO 2006

am/pm differences in efficient J ?

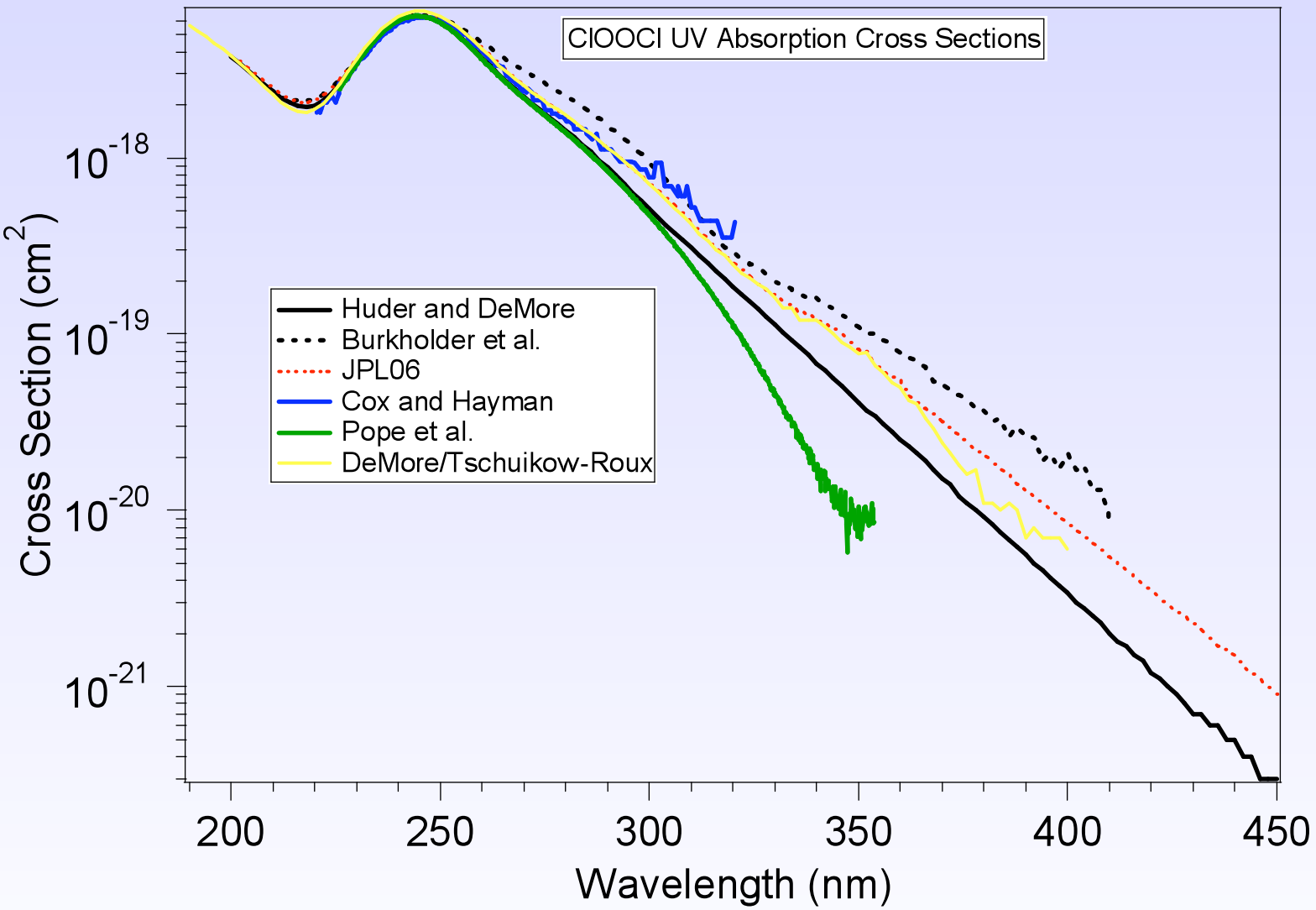
measurements during EUROSOLVE/SOLVE 2000
analysis like in Stimpfle et al.(2004), but am/pm separately

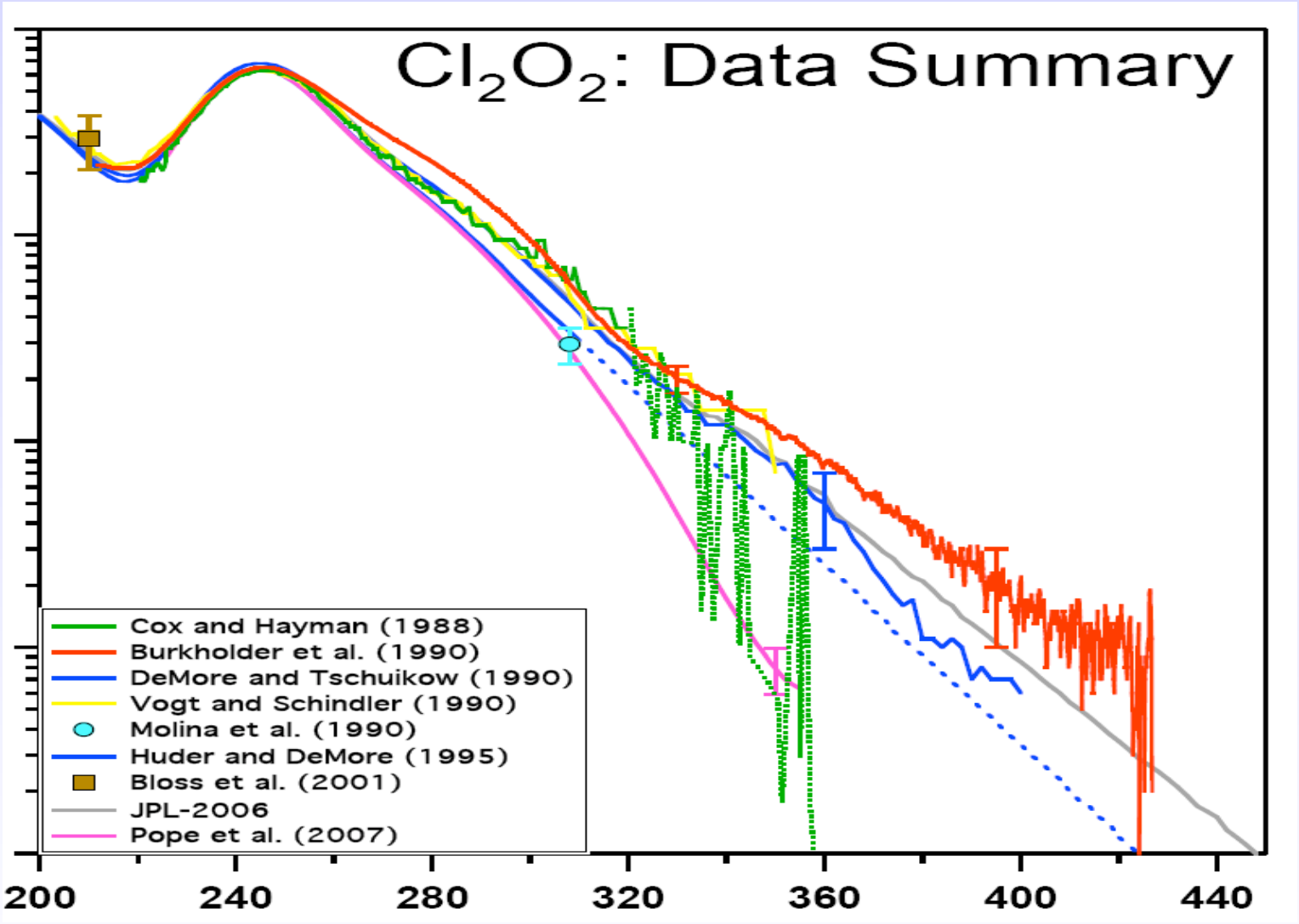
$$\beta = \frac{\alpha^{Obs}}{\alpha^{Model}} = \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Obs} \Big/ \left(\frac{[ClOOCl]}{[ClO]^2}\right)^{Model}$$



=> ClO production rate similar to $J_{Burkholder}$ x $[Cl_{Havard}]$ for all sza, for both am and pm)
Cl_{Havard} = total Cl in all species that decompose at T~370 K

=> J_{Pope} is not consistent with data and known chemistry

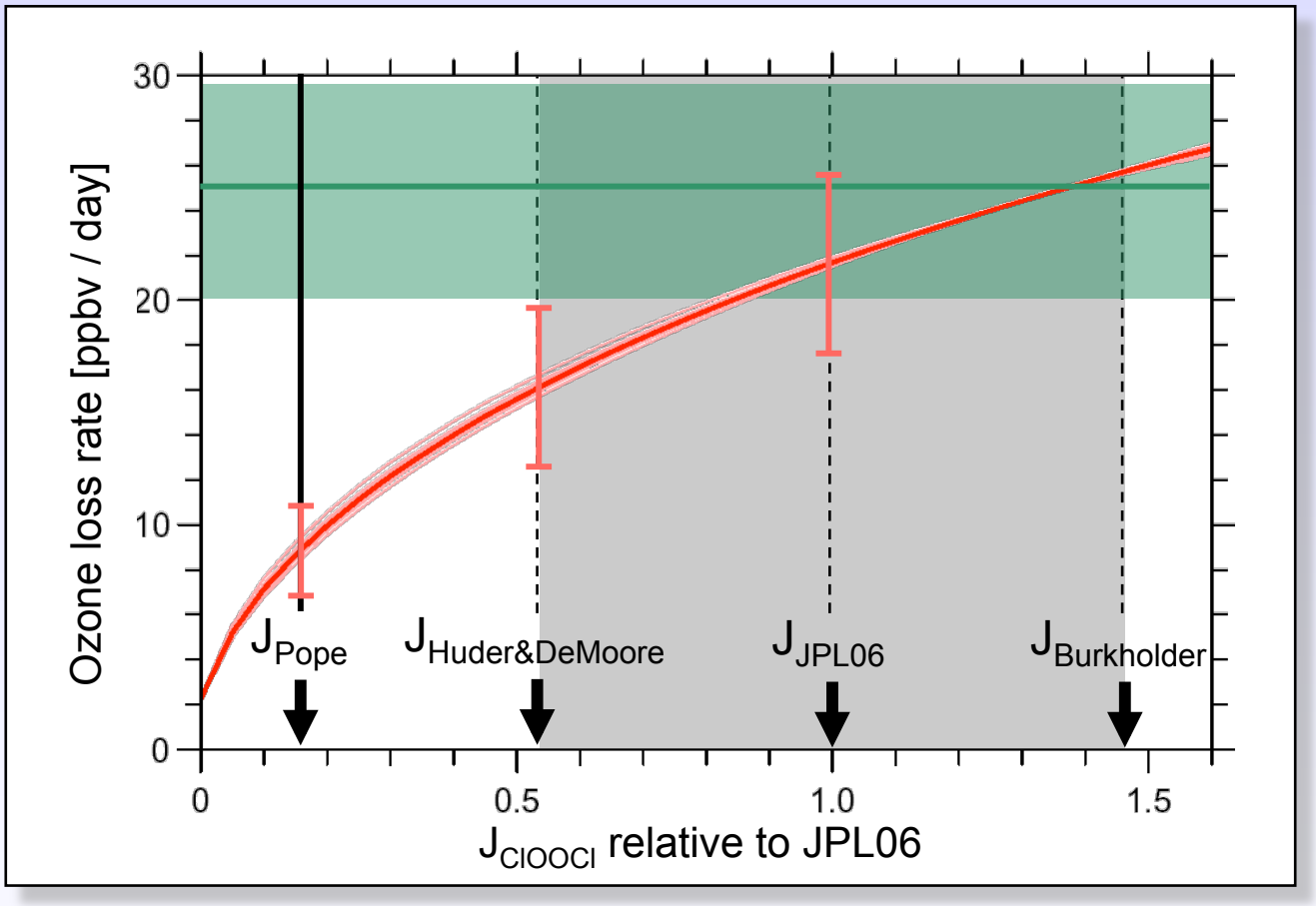

ClOOCl UV Absorption Cross Sections
Huder and DeMore
Burkholder et al.
JPL06
Cox and Hayman
Pope et al.
DeMore/Tschuikow-Roux
Cross Section (cm2)
10-18
10-19
10-20
10-21
200
250
300
350
400
450
Wavelength (nm)


Cl_2O_2: Data Summary
Cox and Hayman (1988)
Burkholder et al. (1990)
DeMore and Tschuikow (1990)
Vogt and Schindler (1990)
Molina et al. (1990)
Huder and DeMore (1995)
Bloss et al. (2001)
JPL-2006
Pope et al. (2007)
200
240
280
320
360
400
440

Overall polar ozone loss rate versus J_{ClOOCl}

model constraint by measurements during SOLVE flight 000202

ozone loss rates from Match

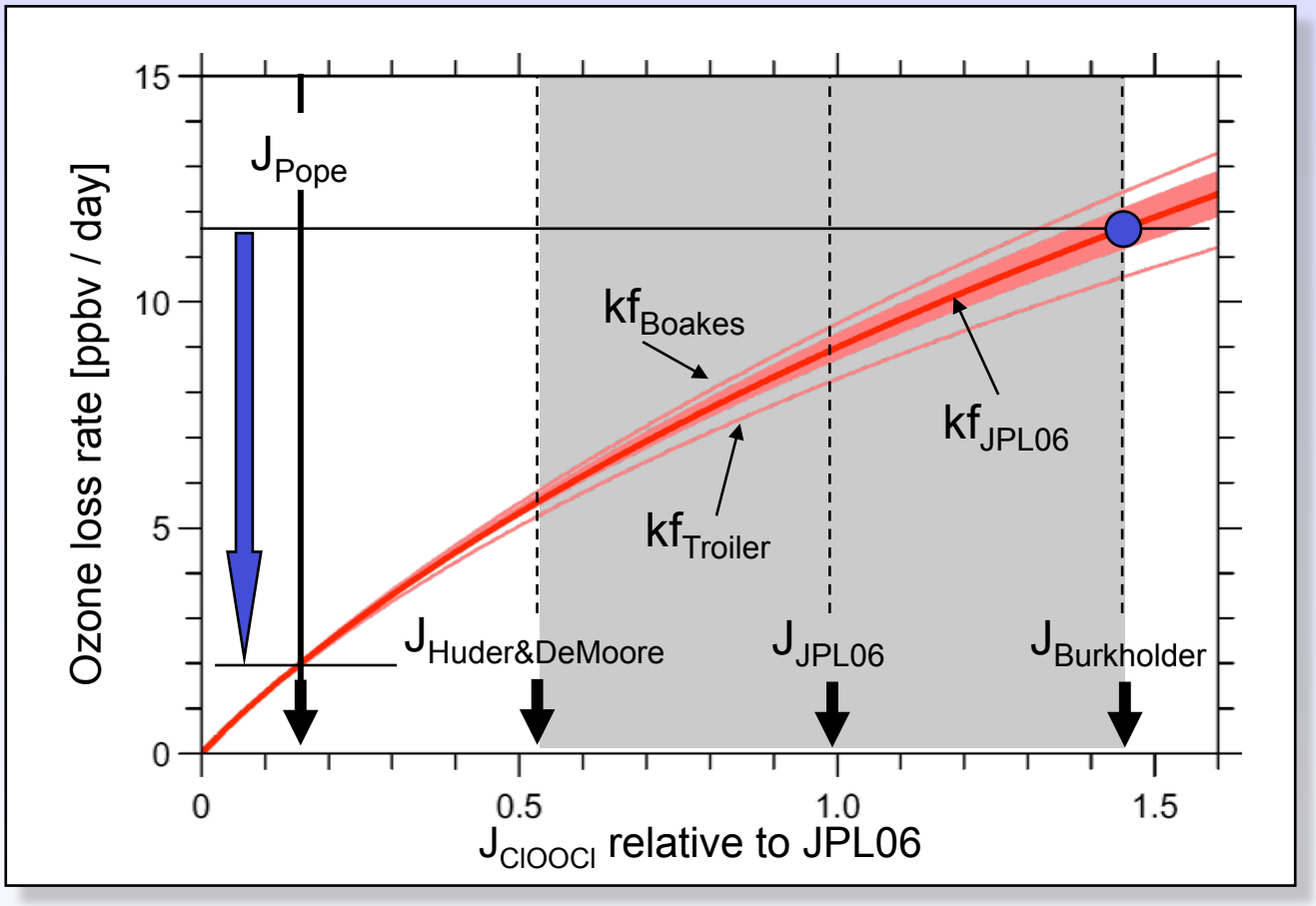


=> Best fit for $J_{Burkholder}$, J_{JPL06} within uncertainties

=> no overlap of uncertainties for $J < J_{Huder\&DeMore}$

ozone loss rate by ClO+ClO versus J_{ClOOCl}

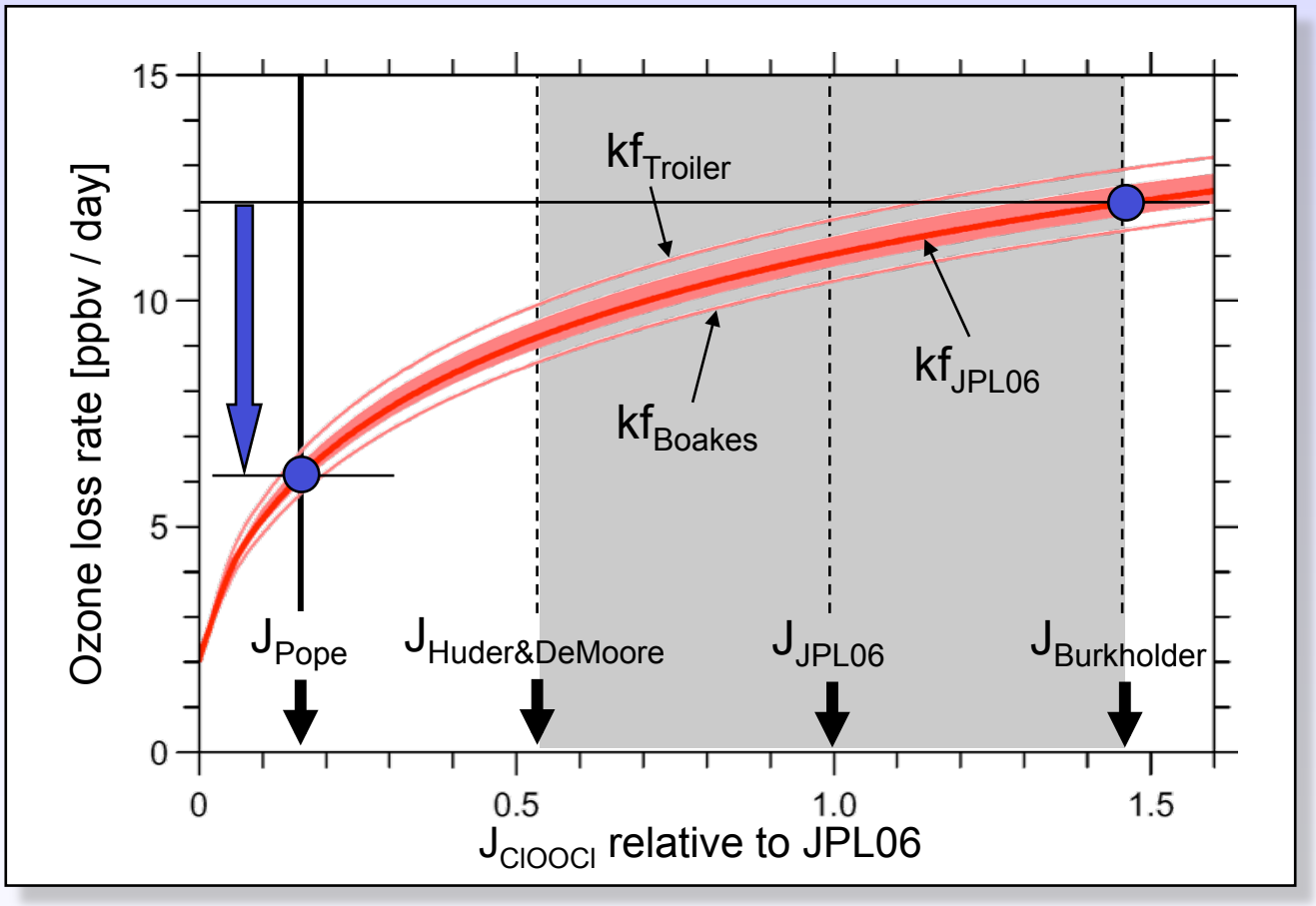
ClO_x = 2 ppbv
little sensitivity on k_{eq}



=> J_{Pope} leads to reduction by more than 80%
=> ClO dimer cycle is no longer a major loss cycle

ozone loss rate by ClO+BrO versus J_{ClOOCl}

ClO_x = 2 ppbv
little sensitivity on k_{eq}

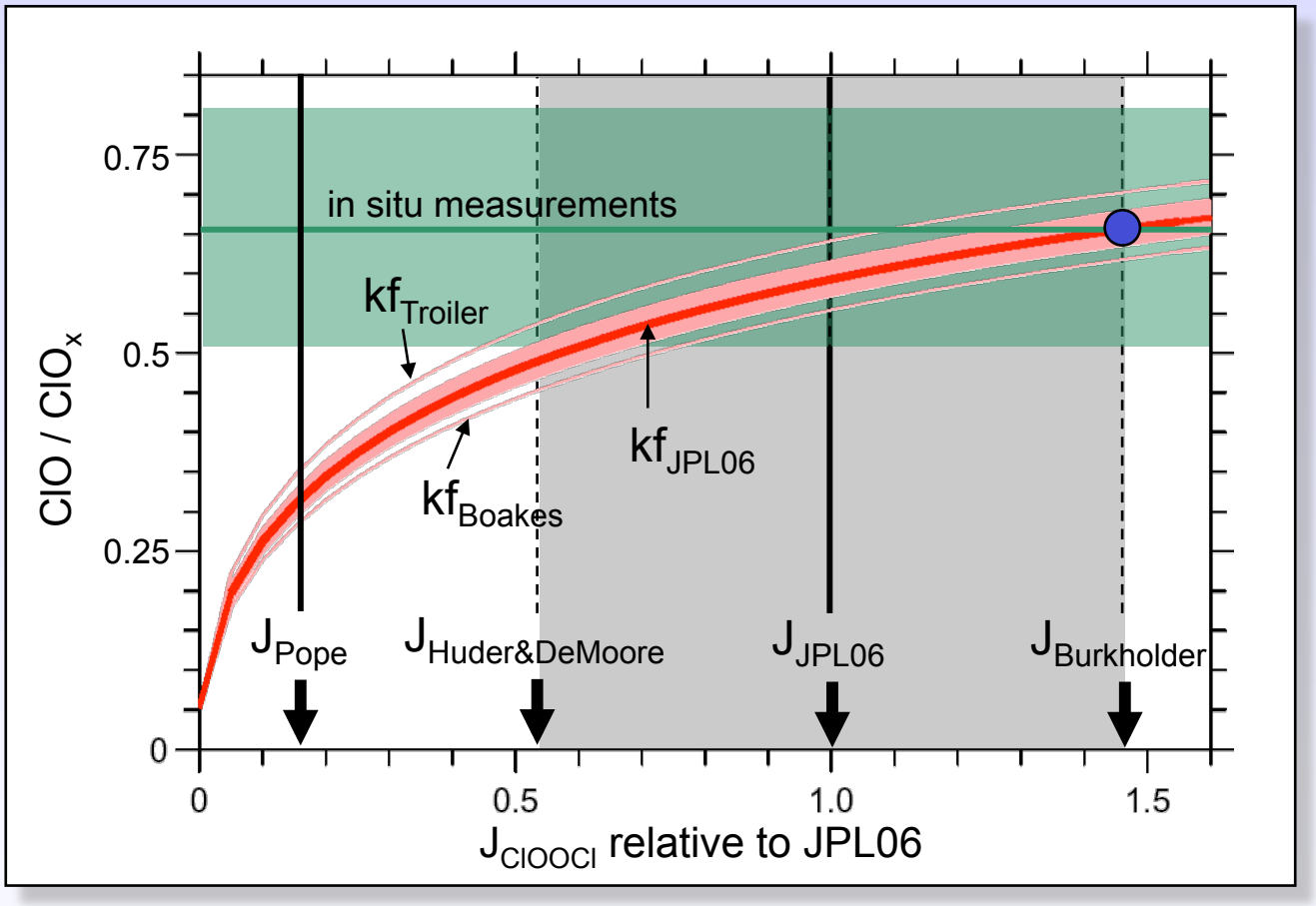


=> J_{Pope} leads to reduction by ~50%

ClO / (ClO + 2ClOOCl) versus J_{ClOOCl}

sza = 82.5°, pm, little sensitivity on keq

measurements during SOLVE 2000, flight 000202



=> $J_{Burkholder}$ results in best fit to data (consistent with Stimpfle et al., 2004)

=> J_{Pope} is not consistent with in situ data => if correct: unknown chemistry