Is a major fraction of polar ozone loss due to a currently unknown mechanism ?

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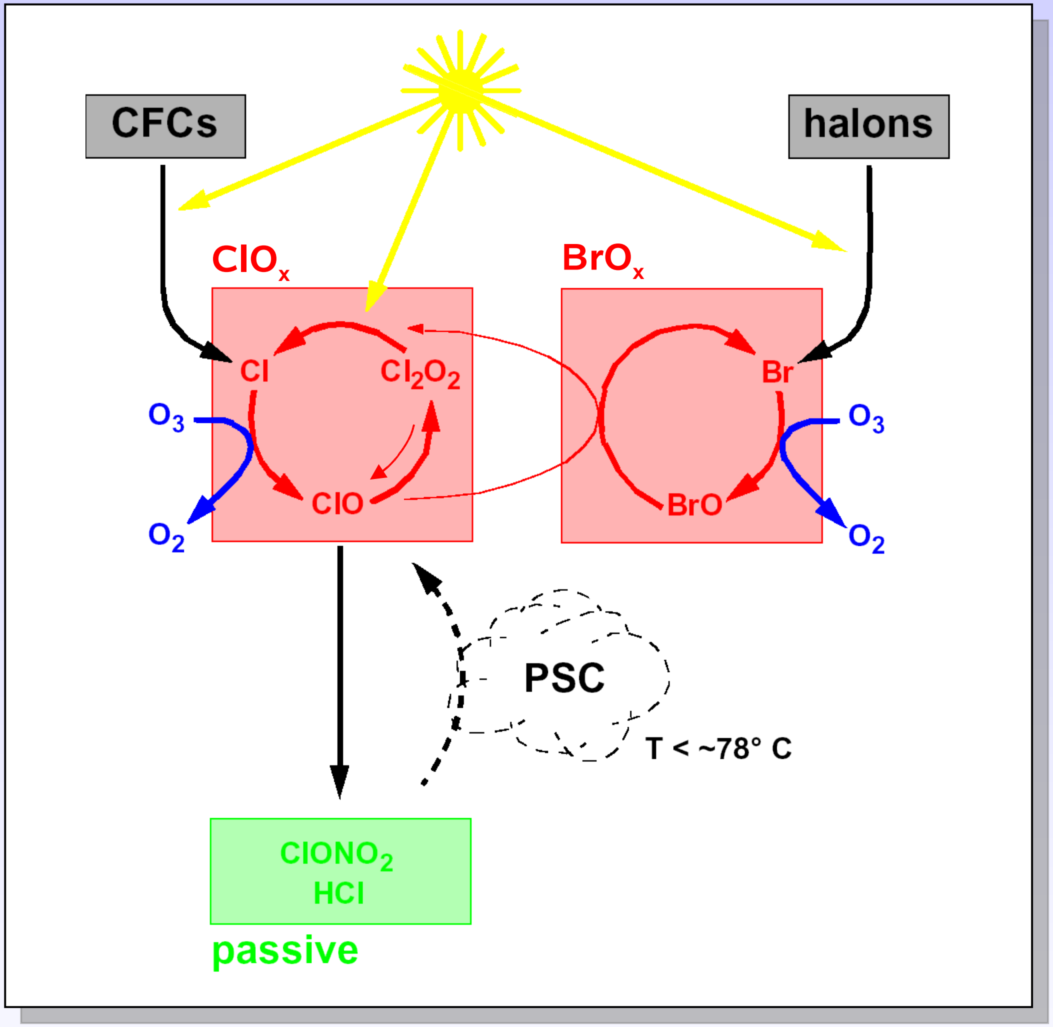
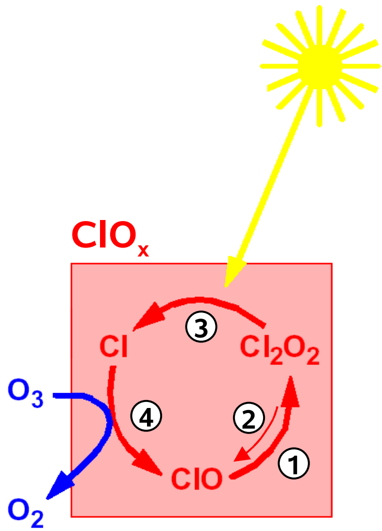
Polar ozone loss process



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 + hν → Cl + ClOO $\xrightarrow{M}$ Cl + Cl + O_2

Rate = J_{ClOOCl} x [ClOOCl]

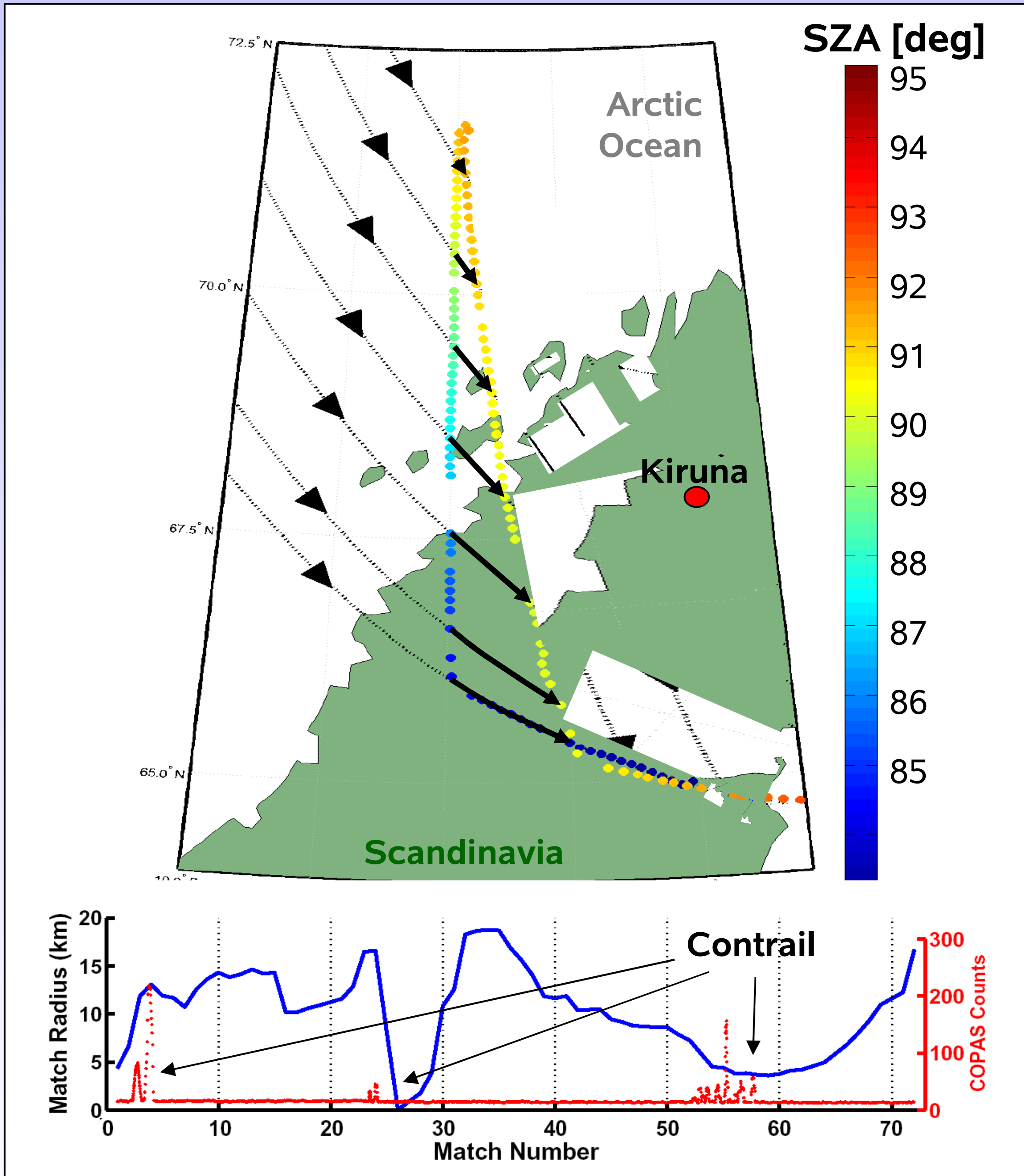
Step (4): Cl + O_3 → ClO + O_2:

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

Kinetics of the dimer cycle

Simultaneous measurements of ClO and ClOOCl are available from:

- SOLVE 2000:
  - Very cold conditions (T~195K)
- EUPLEX during VINTERSOL 2003
  - Unusually warm activated conditions (T~205 K)



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.

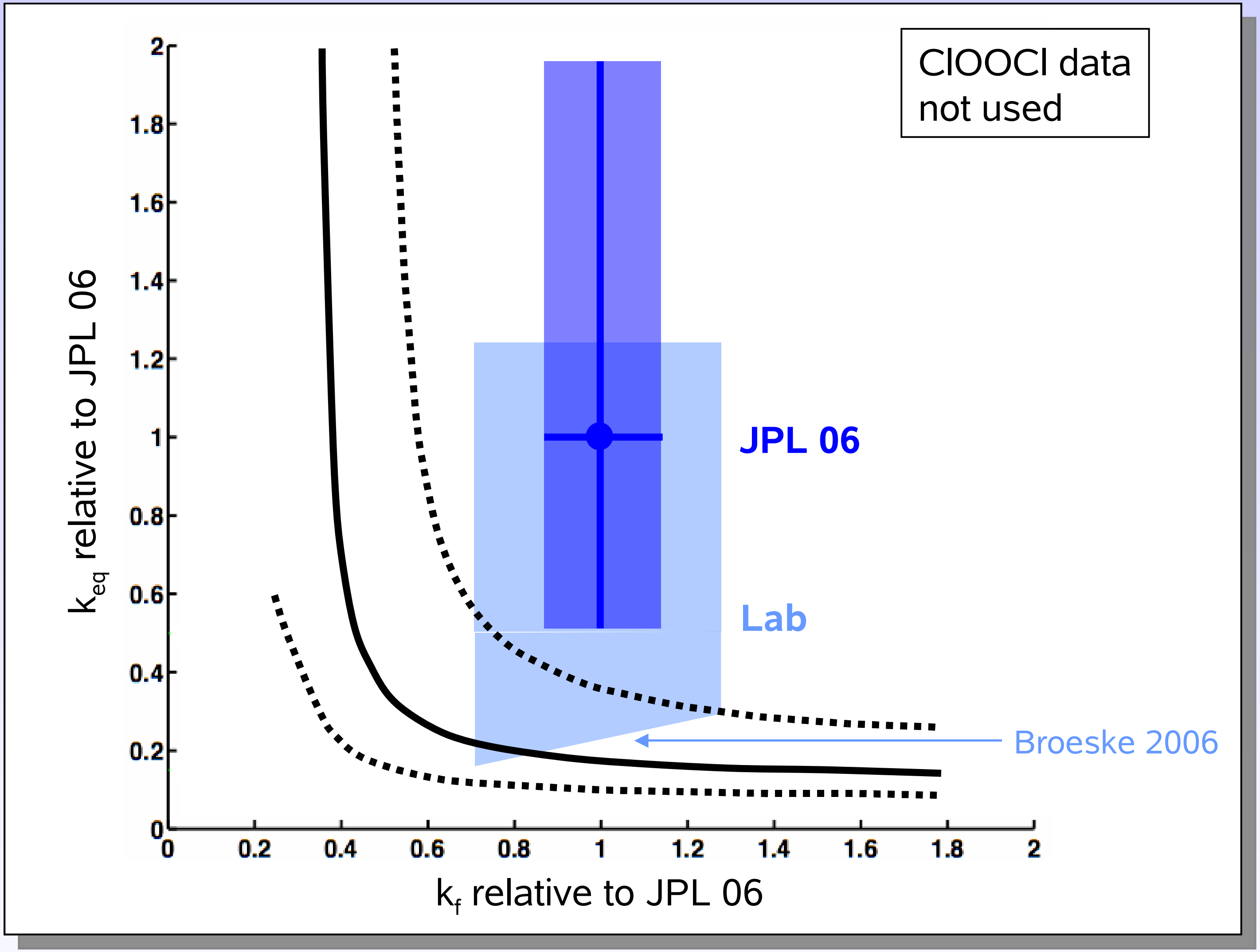
=>

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., submitted

k_{eq} from EUPLEX self-match flight



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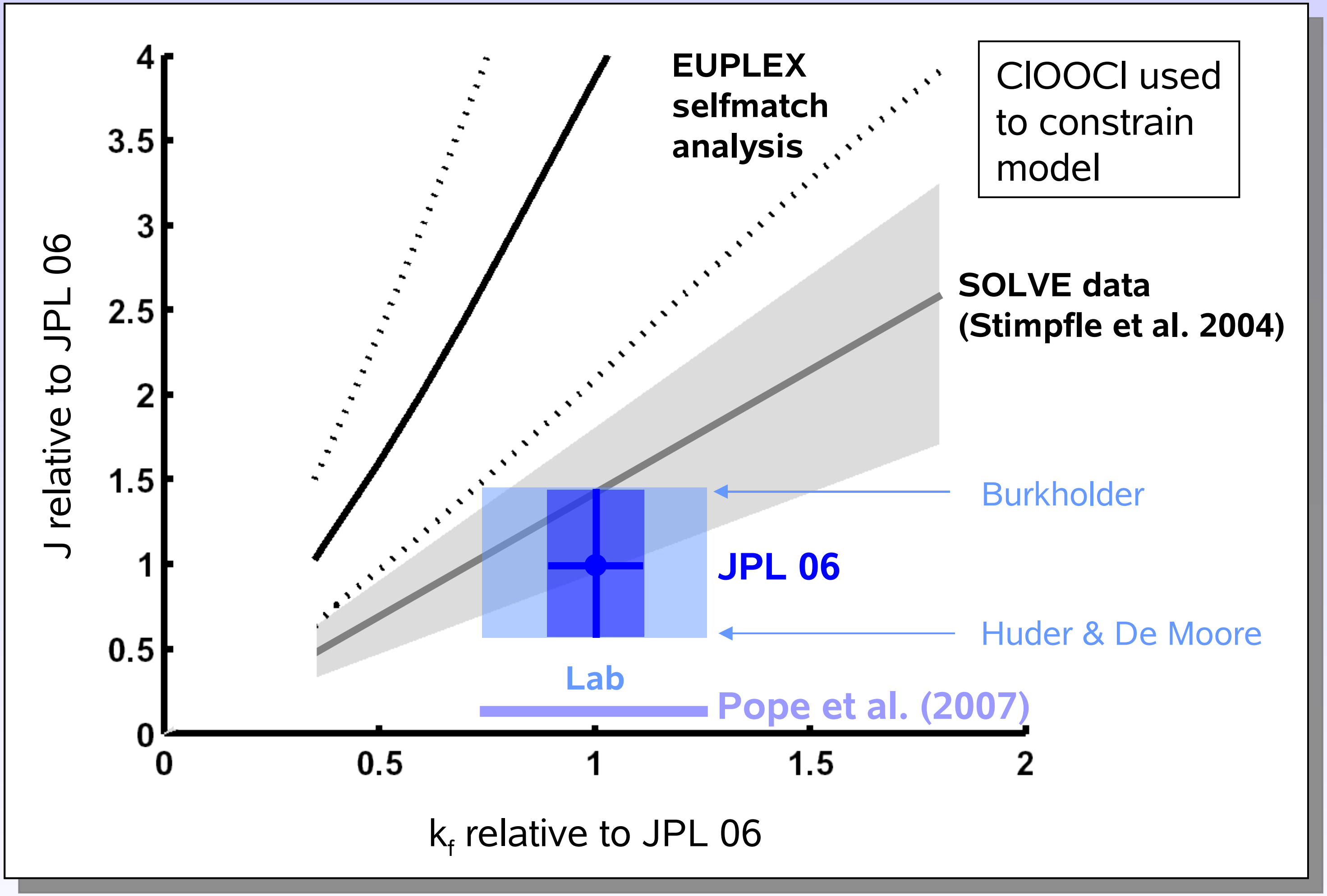
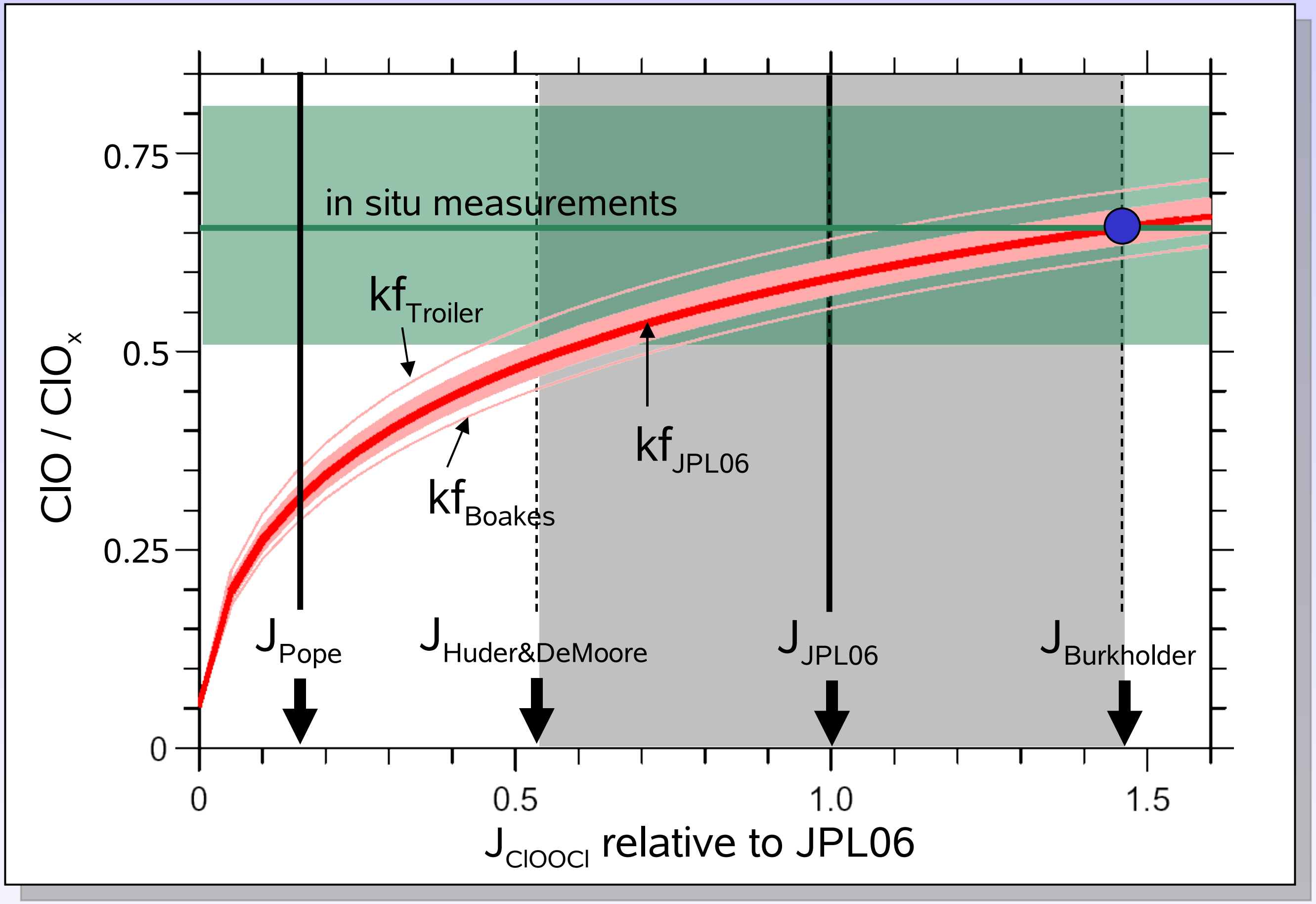


Schofield et al., submitted

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

sza = 82.5°, pm, little sensitivity on keq

measurements during SOLVE 2000, flight 000202

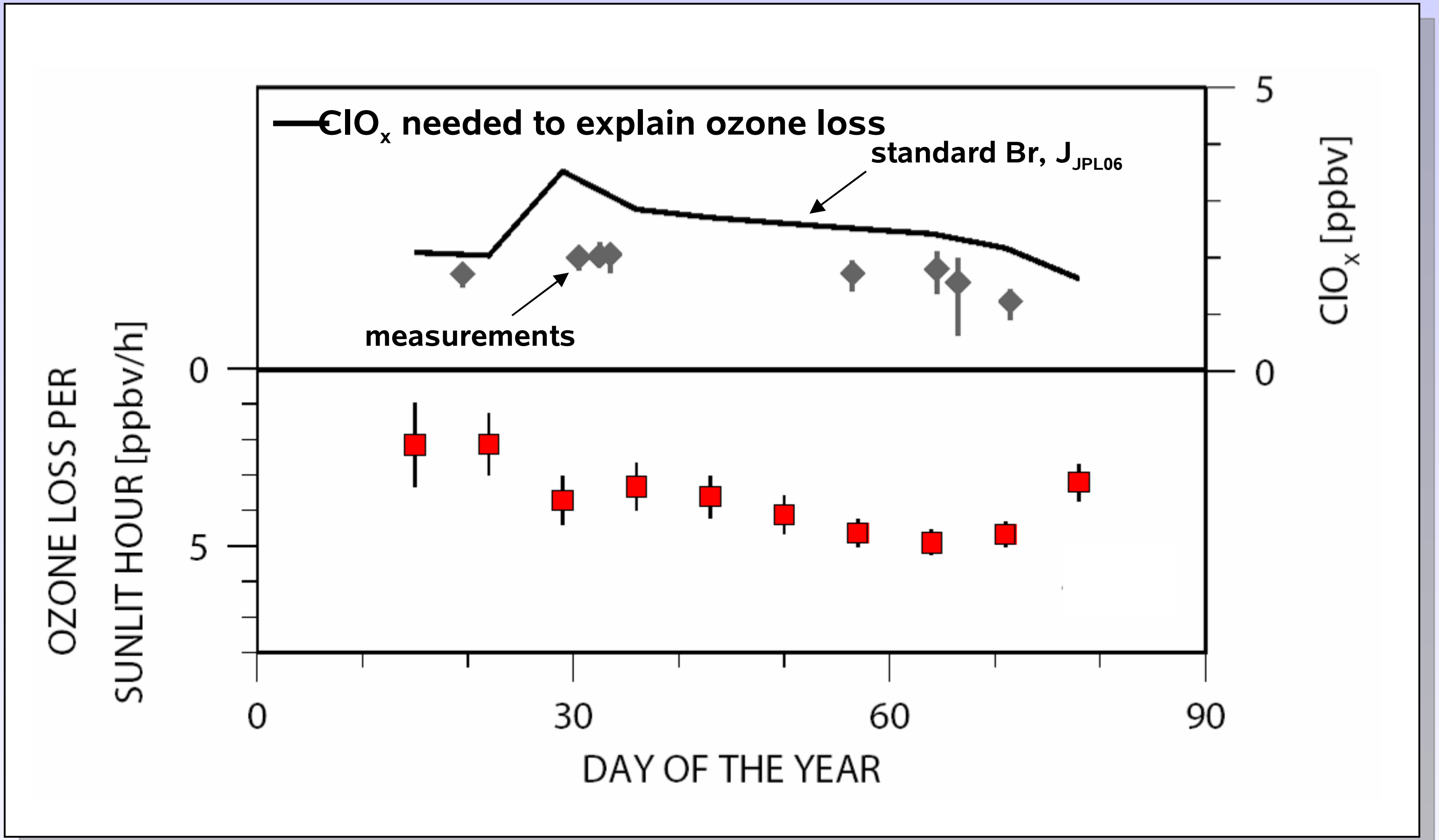


=> $J_{Burkholder}$ results in best fit to data (consistent with Stimpfle et al., 2004)

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

Ozone loss rates

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



Frieler et al., GRL 2006; WMO 2006

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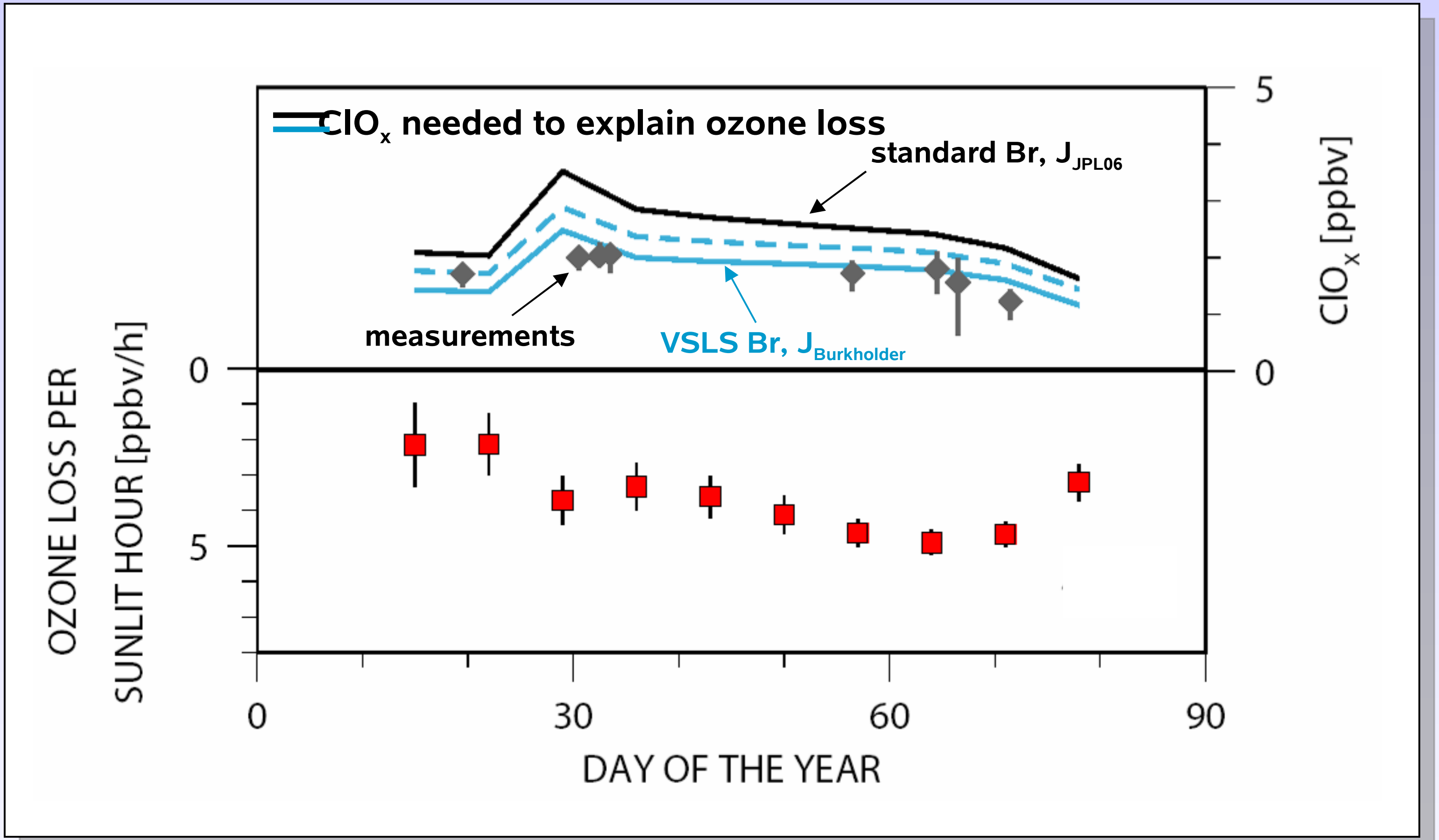
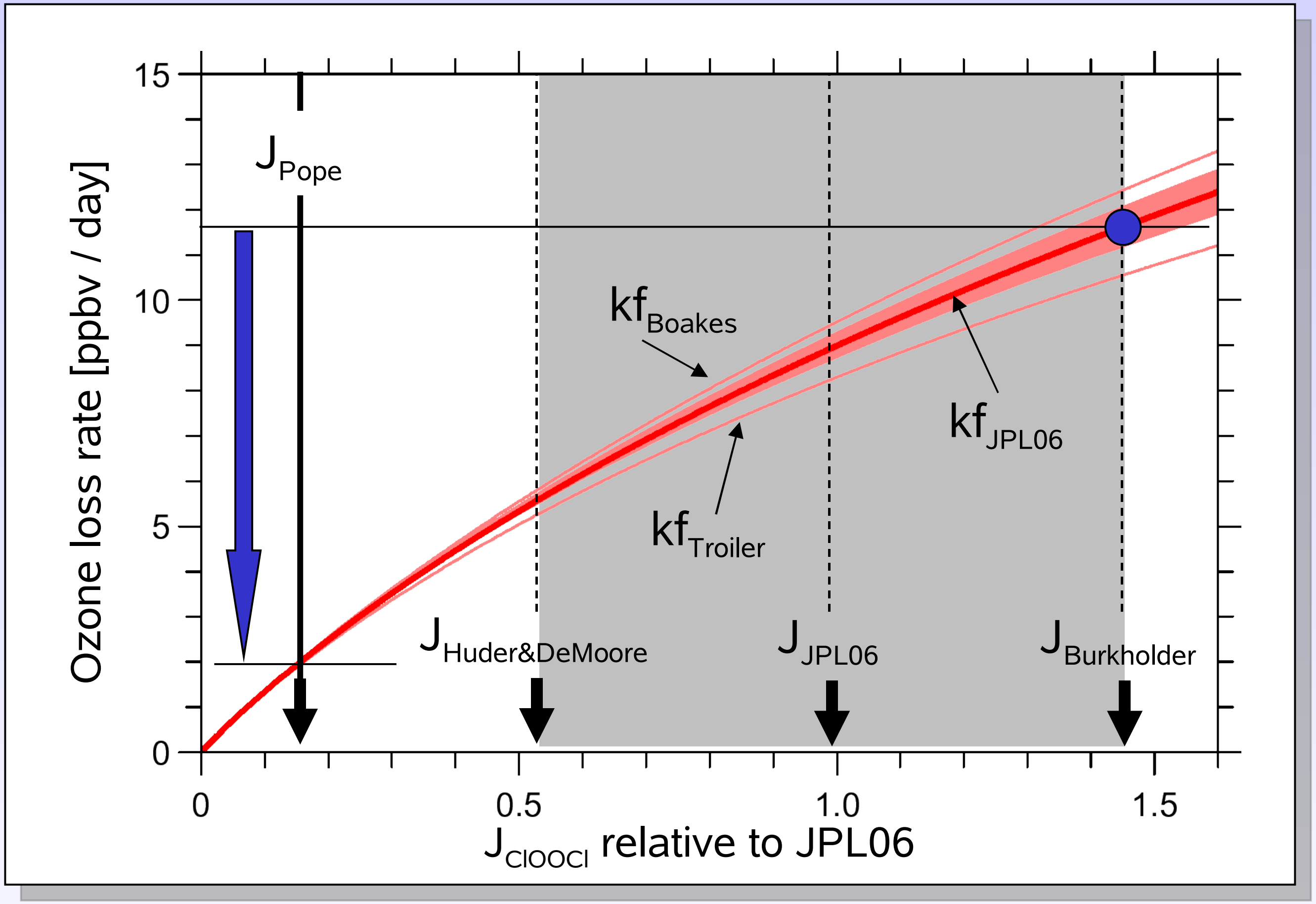


Frieler et al., GRL 2006; WMO 2006

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

ClO_x = 2 ppbv

little sensitivity on k_{eq}



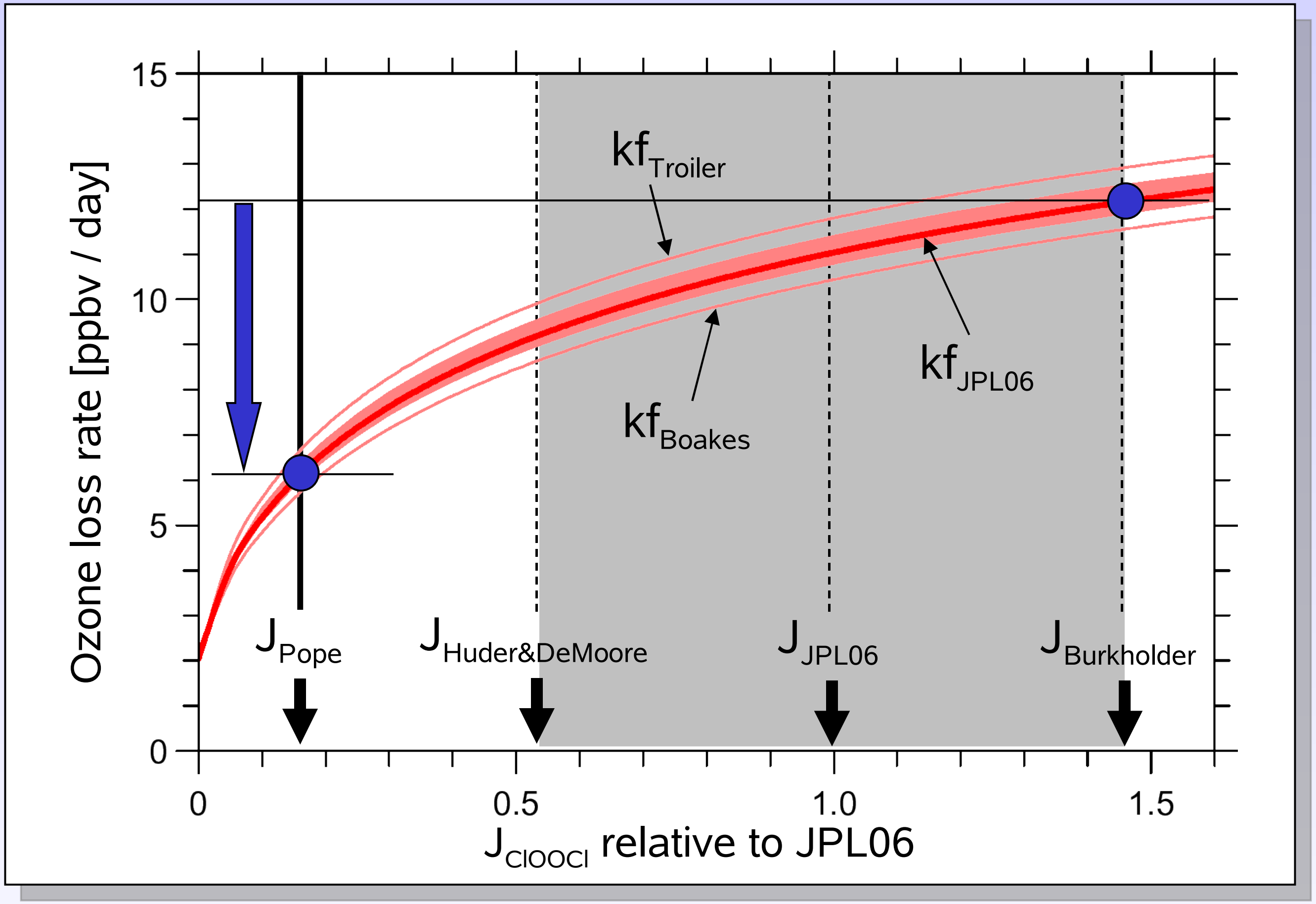
=> J_{Pope} leads to reduction by more than 80%

=> 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}

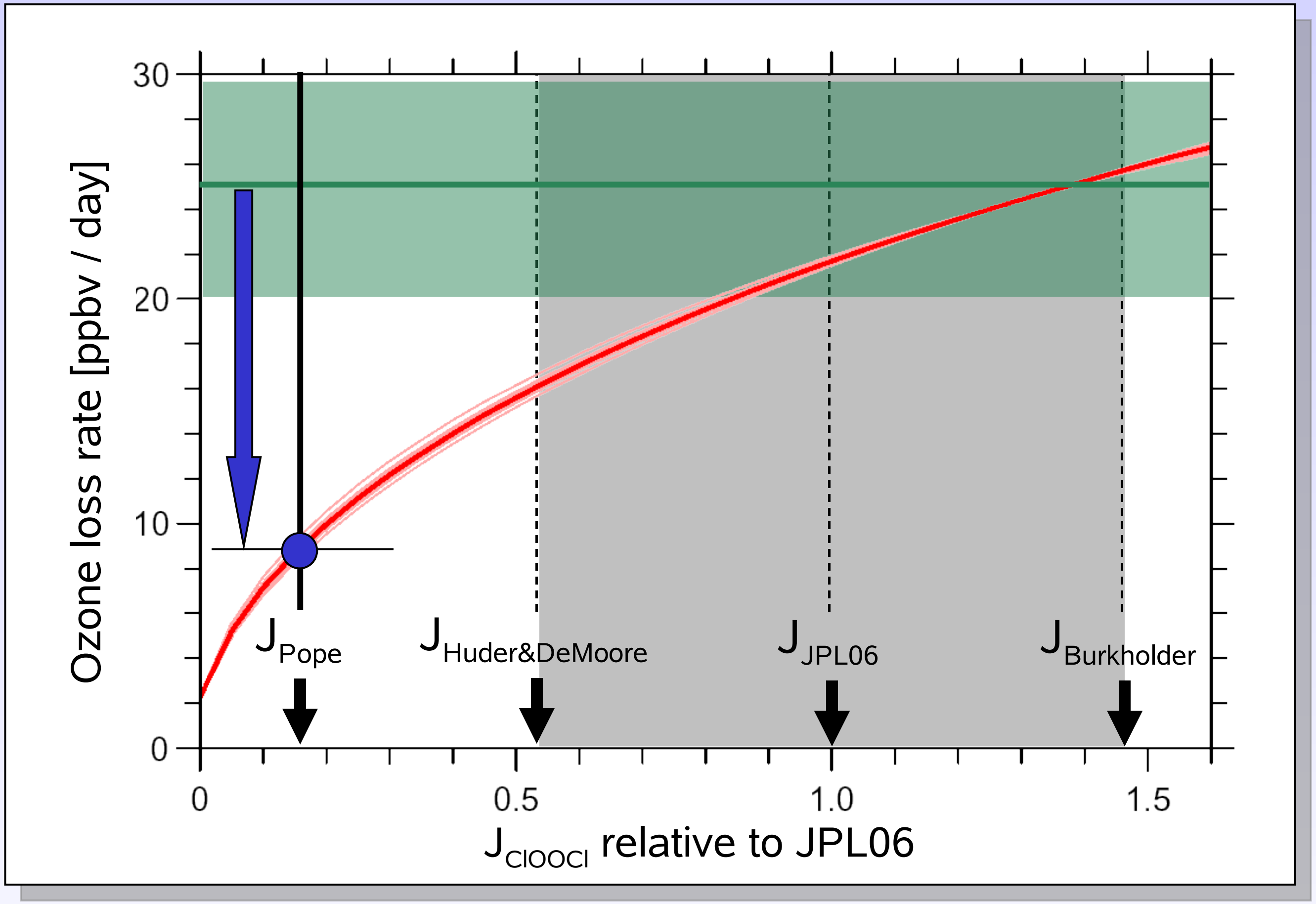


=> J_{Pope} leads to reduction by ~50%

Overall polar ozone loss rate versus J_{ClOOCl}

ClO_x = 2 ppbv

little sensitivity on k_{eq} and k_f



=> J_{Pope} leads to reduction by 60%

=> major fraction of the observed ozone loss due to unknown process ?

What is going on ???

- Either: Pope et al. 2007 is not correct
- Or: An unknown mechanism breaks down ClOOCl and causes most of the observed ozone loss.

Constraints for potential mechanisms

- Daytime ClO production needs to mimic „Burkholder photolysis“ (for am AND pm) !
- Nightime source of ClO
- Ozone loss rates as calculated using „Burkholder photolysis“

What is going on ???

Potential mechanisms fall into two categories:

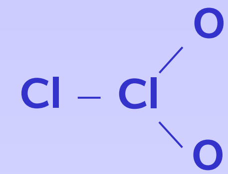
(1) Direct mechanism:

ClOOCl + X ⟶ … ⟶ Cl + Cl + O2 (without photolytic step)

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

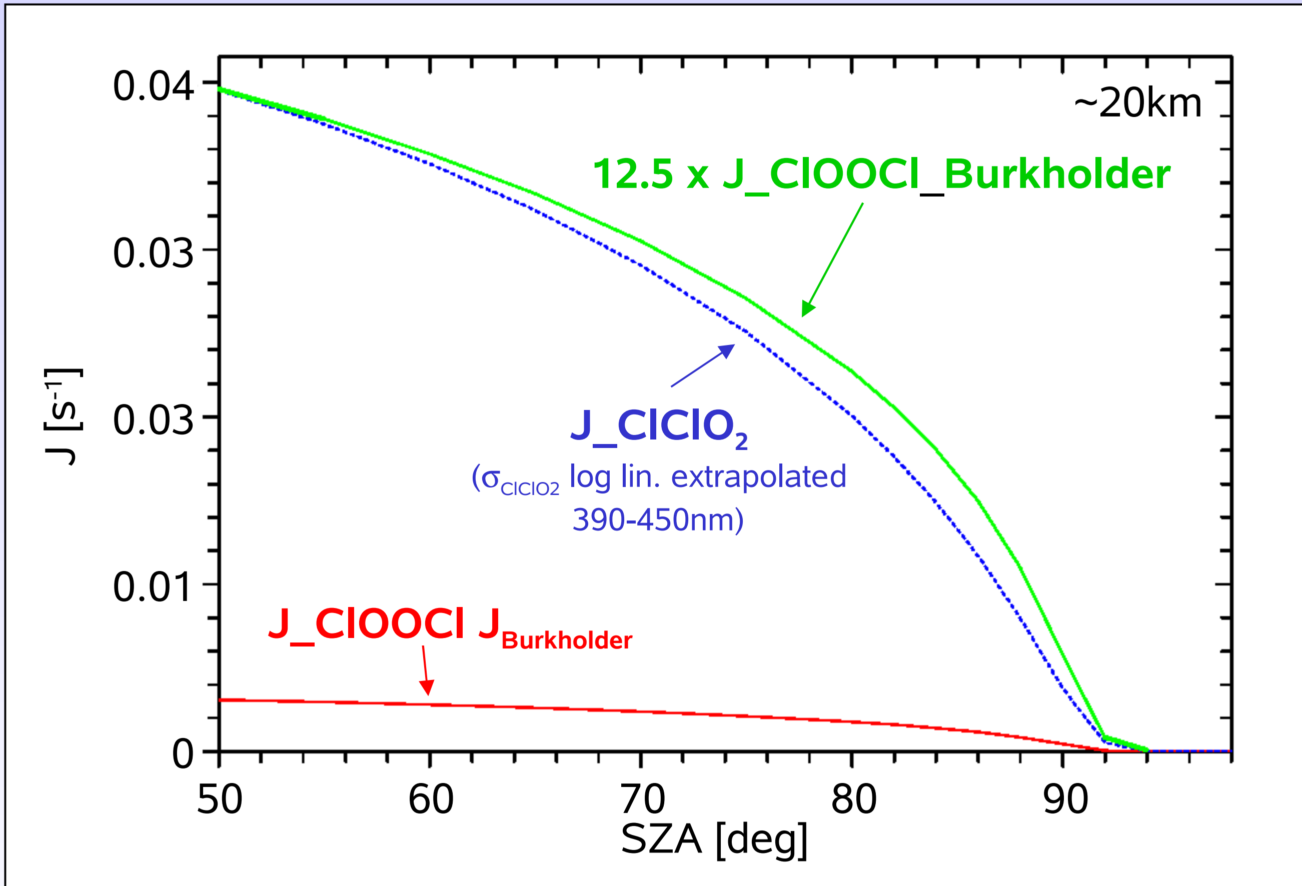
ClOOCl + X ⟶ Cl~ + …

Cl~ + hν ⟶ … ⟶ Cl + Cl + O_2

Rapid equilibrium between ClOOCl and $ClClO_2$ ()?

e.g. by: ClOOCl + ClO → $ClClO_2$ + ClO

$ClClO_2$ + ClO → 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}

Conclusions

- **It is hard to reconcile Pope et al. (2007) with atmospheric measurements**
- **If Pope et al. (2007) is correct:**
  - **More than 60% of observed polar ozone loss is due to a currently unknown mechanism.**
  - An unknown breakdown mechanism for ClOOCl has to exist, that mimics photolysis according to Burkholder et al. cross sections.
  - The formation of a fairly rapid equilibrium between ClOOCl and $ClClO_2$ (ratio ~90:10 at 195K and ~80:20 at 205K) would explain all available ClO and Cl_2O_2 observations.
    - This would also explain observed ozone losses if the photolysis of $ClClO_2$ restores the O-O bond (e.g. products Cl + ClOO).
  - Formation of ClOOCl / O_2 clusters makes absorption of ClOOCl more „Burkholder like“ ?
  - Most other potential mechanisms are not consistent with in-situ data of ClO, observed ozone loss rates or lab studies.

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.

Pope et al, The Ultraviolet Spectrum of Chlorine Peroxide, ClOOCl, J. Phys. Chem., in press

END

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 = 390% best fit; J ≥ 200%
  - 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) Breakdown of ClOOCl directly recycles Cl:

ClOOCl + X -> … -> 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

(2) Breakdown of ClOOCl results in the formation of a nightime reservoir (Cl~)

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 $J_{Cl\sim+ClOOCl}$(sza)

↓

in contrast to in-situ data

(2.2)

Reaction is fast[(2)]

=> Cl~ is the only reservoir

=>

(1) $J_{Cl\sim}$ 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)*

(2.2.1)

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)

reaction

Cl~ + Y -> ClOOCl + X

also exists, i.e.

Cl~ and ClOOCl

coexist in equilibrium

=>

$J_{Cl\sim}$ much larger than $J_{ClOOCl\_Burkholder}$

=> *Cl~: $ClClO_2$, (ClOClO, Cl_2O_5)*

(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 (1)

(1) Direct mechanism:

ClOOCl + X → … → Cl + Cl + O2 (without photolytic step)

- [X] (sza) ~ $J_{Burkholder}$(sza) !
- collision rate theory: daytime abundance of X > 10 pptv

=> X is none of the known species

Potential solutions (2)

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

ClOOCl + X → Cl~ + ...

Cl~ + hν → ... → Cl + Cl + O_2

- „efficient photolysis" similar to Burkholder photolysis:
  J_{ClOOCl_Pope} x [ClOOCl] + $J_{Cl\sim}$ x [Cl~] = $J_{Burkholder}$ x [Cl_{Havard}]

  (Cl_{Havard} = total Cl in all species that decompose at T~370 K)

- analysis of SOLVE data: no am/pm difference in photolysis
  - ratio [Cl~]/[ClOOCl] is the same for pm and am
    → either reaction converts all ClOOCl to Cl~
    → or rapid equilibrium between ClOOCl and Cl~

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: $\sim 1 \mu m^2 cm^{-3}$

(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 !

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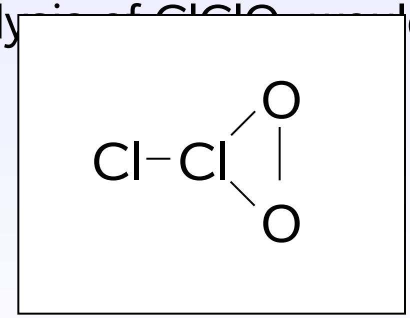
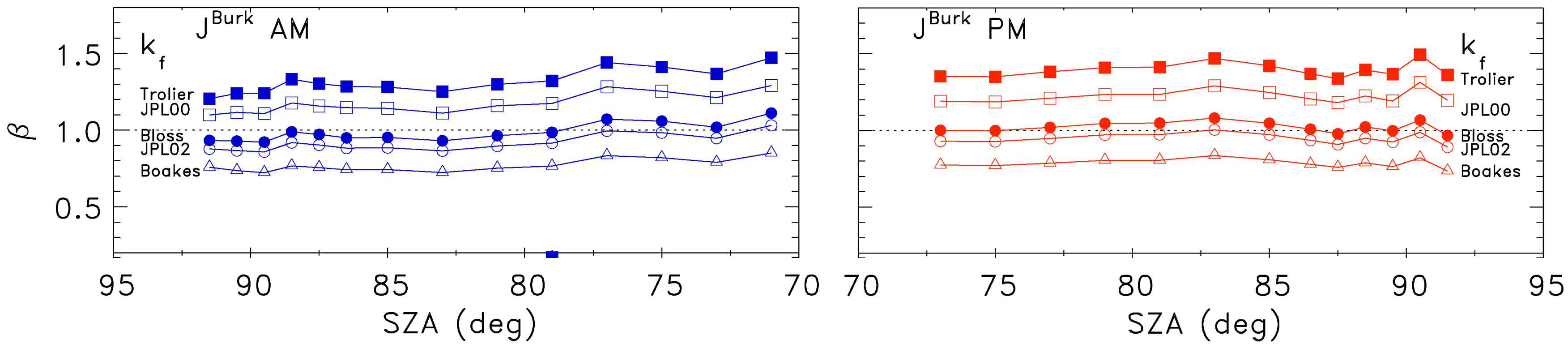


am/pm differences ?

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

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



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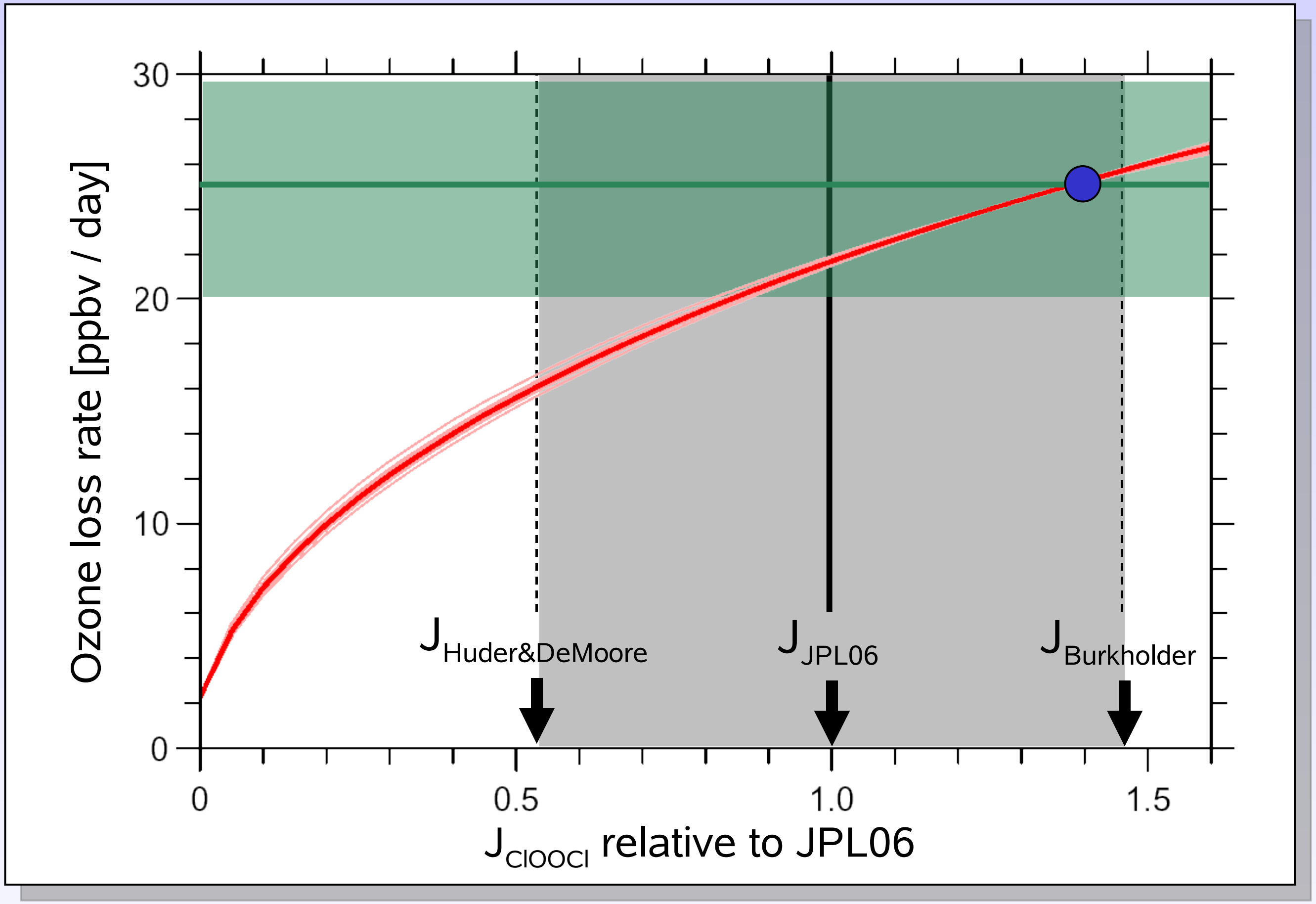

=> model based on $J_{Burkholder}$ reproduces observed loss rate

am/pm differences in efficient J ?

measurements during EUROSOLVE/SOLVE 2000

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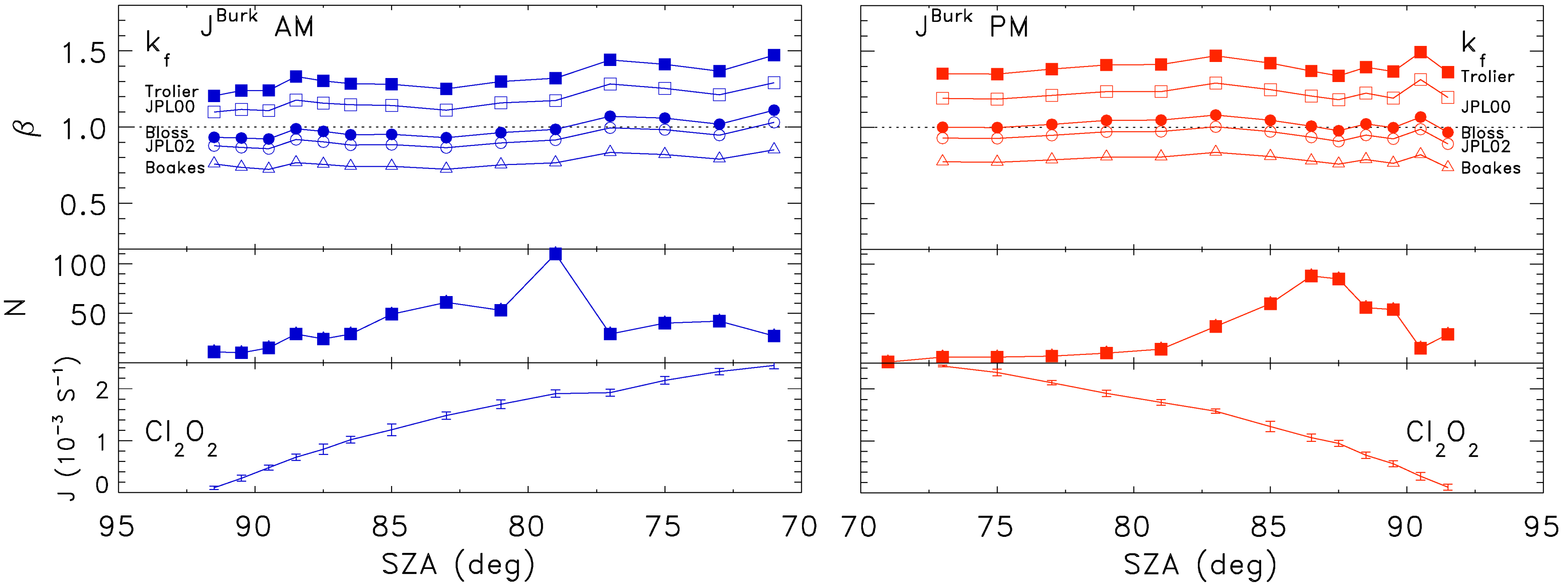

=> no significant am/pm difference in efficient J

J_{Pope} and SOLVE data

measurements during EUROSOLVE/SOLVE 2000

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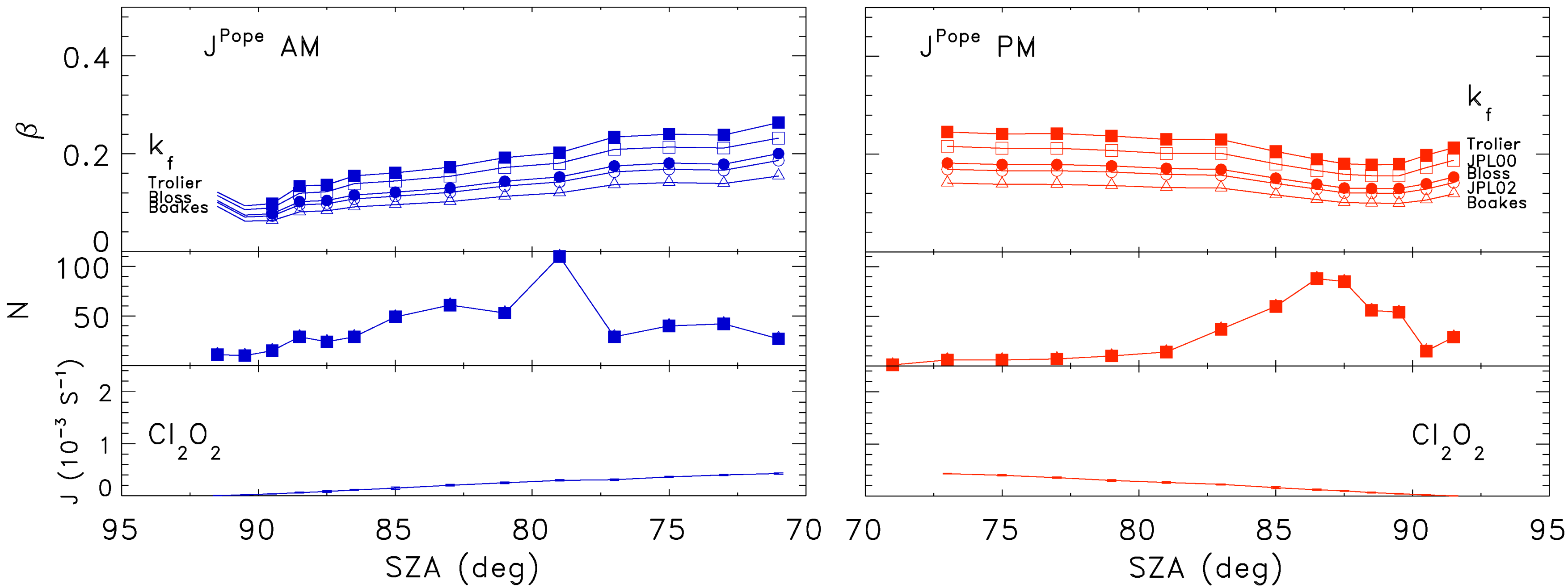

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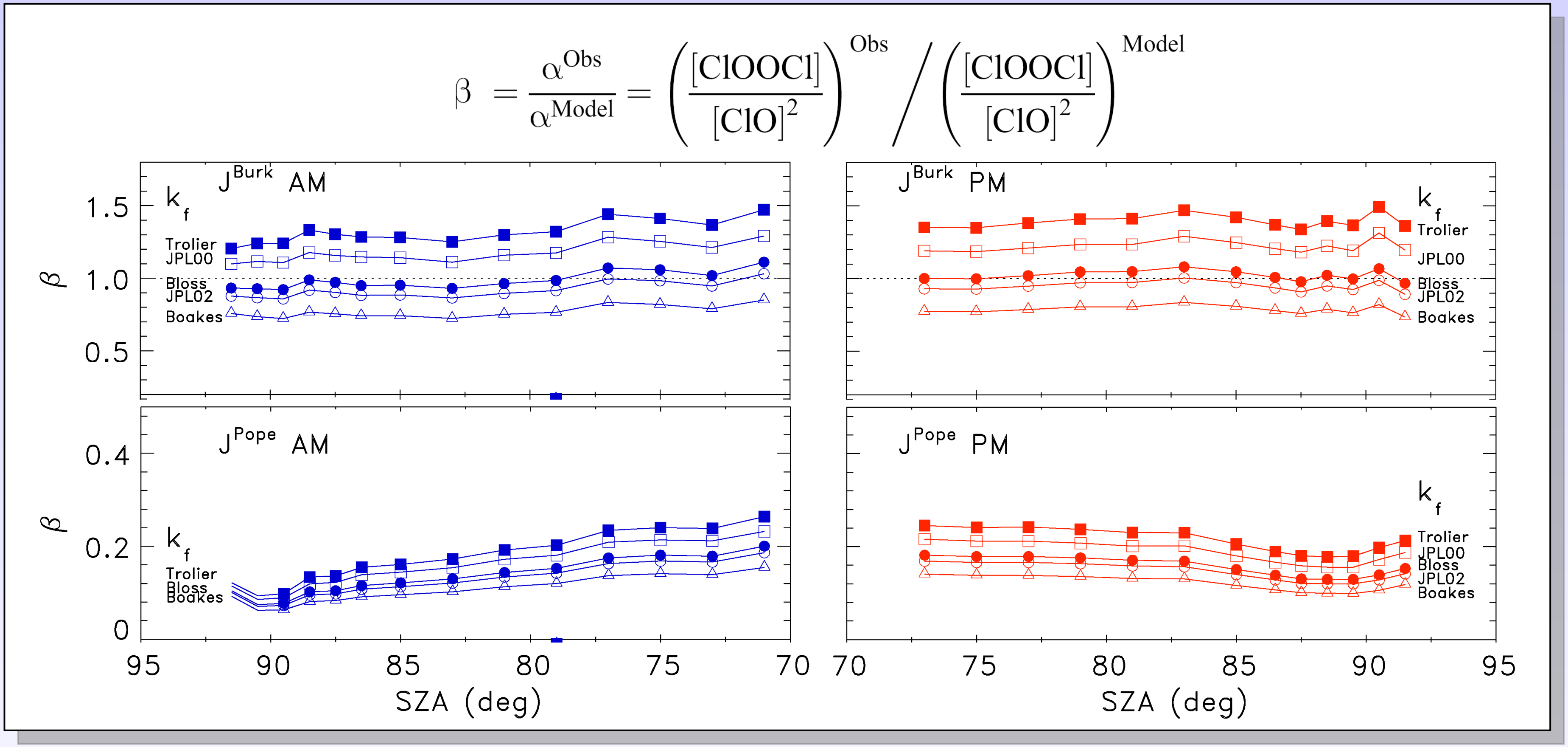

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