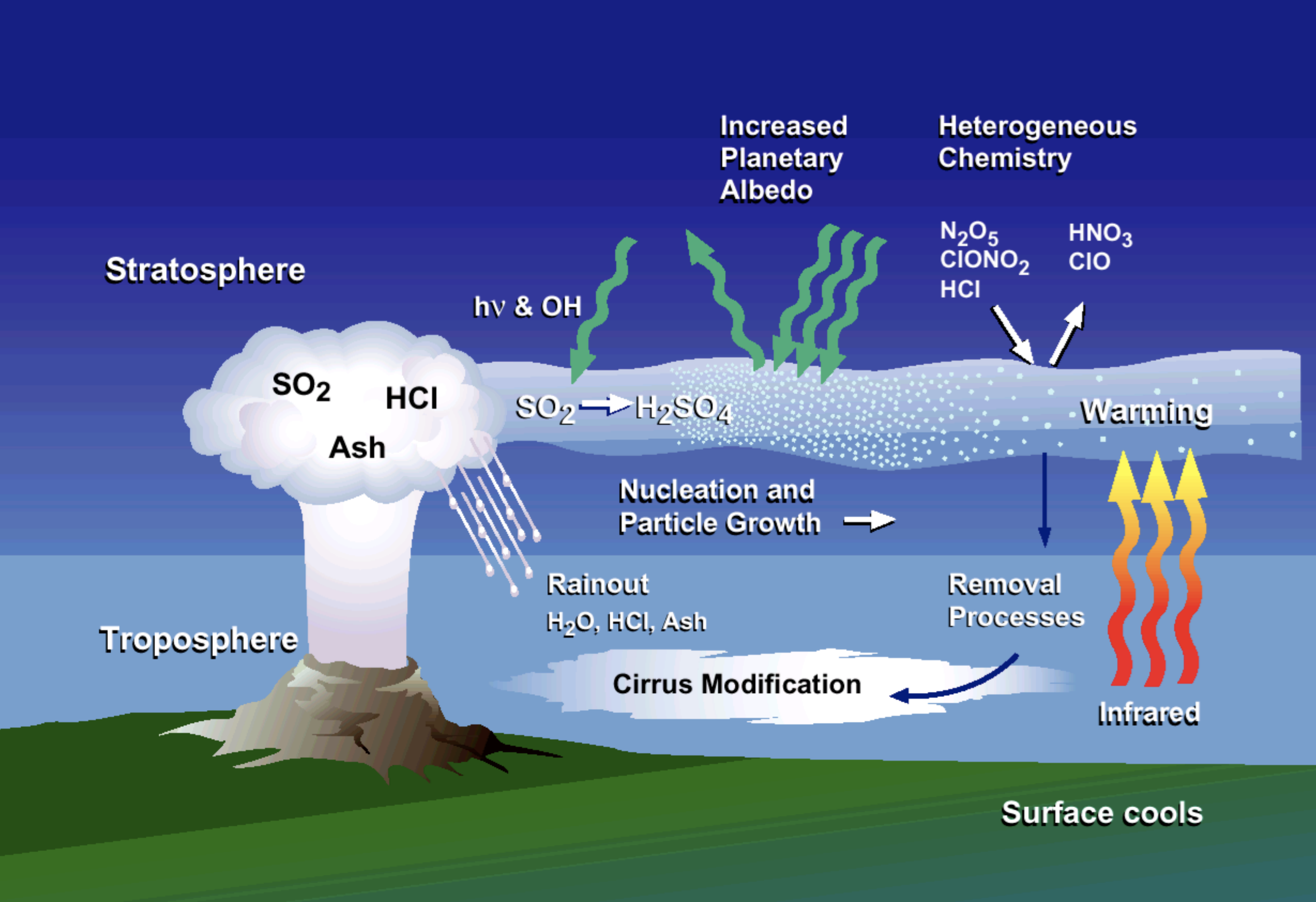
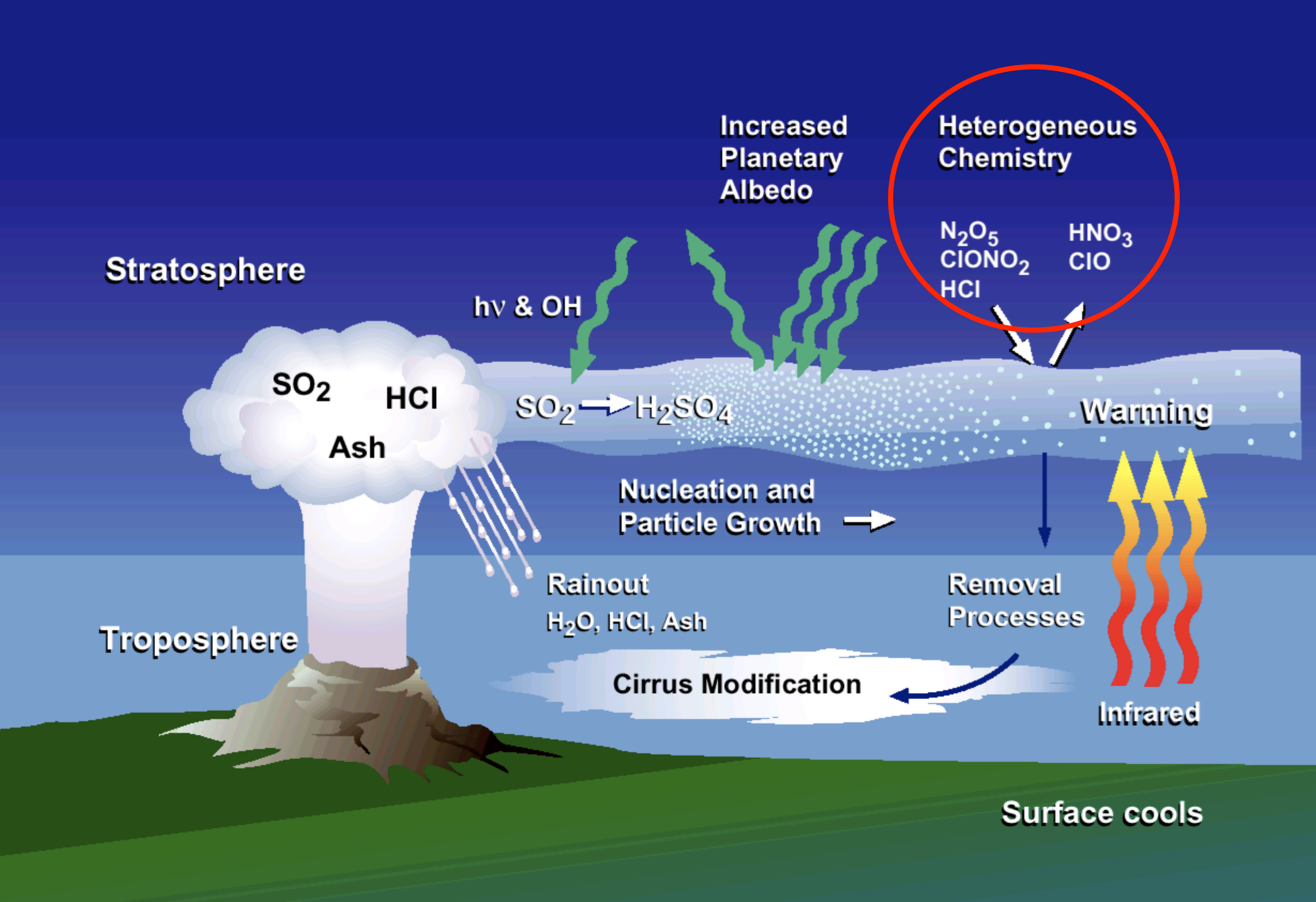
Sulfate Aerosol and Ozone Loss

Mike Mills
NCAR



Courtesy Eric Jensen, as published in McCormick *et al.*, 1995



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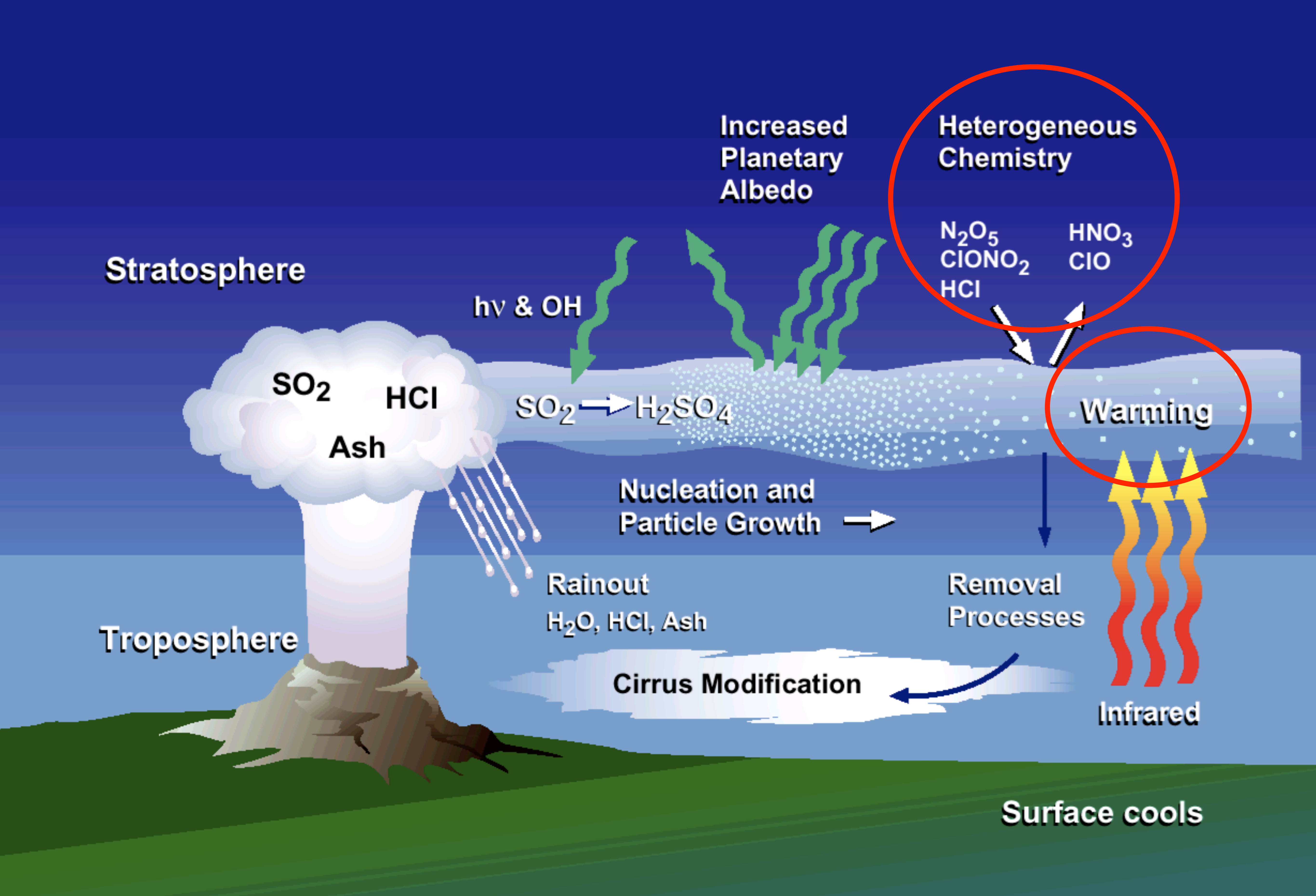
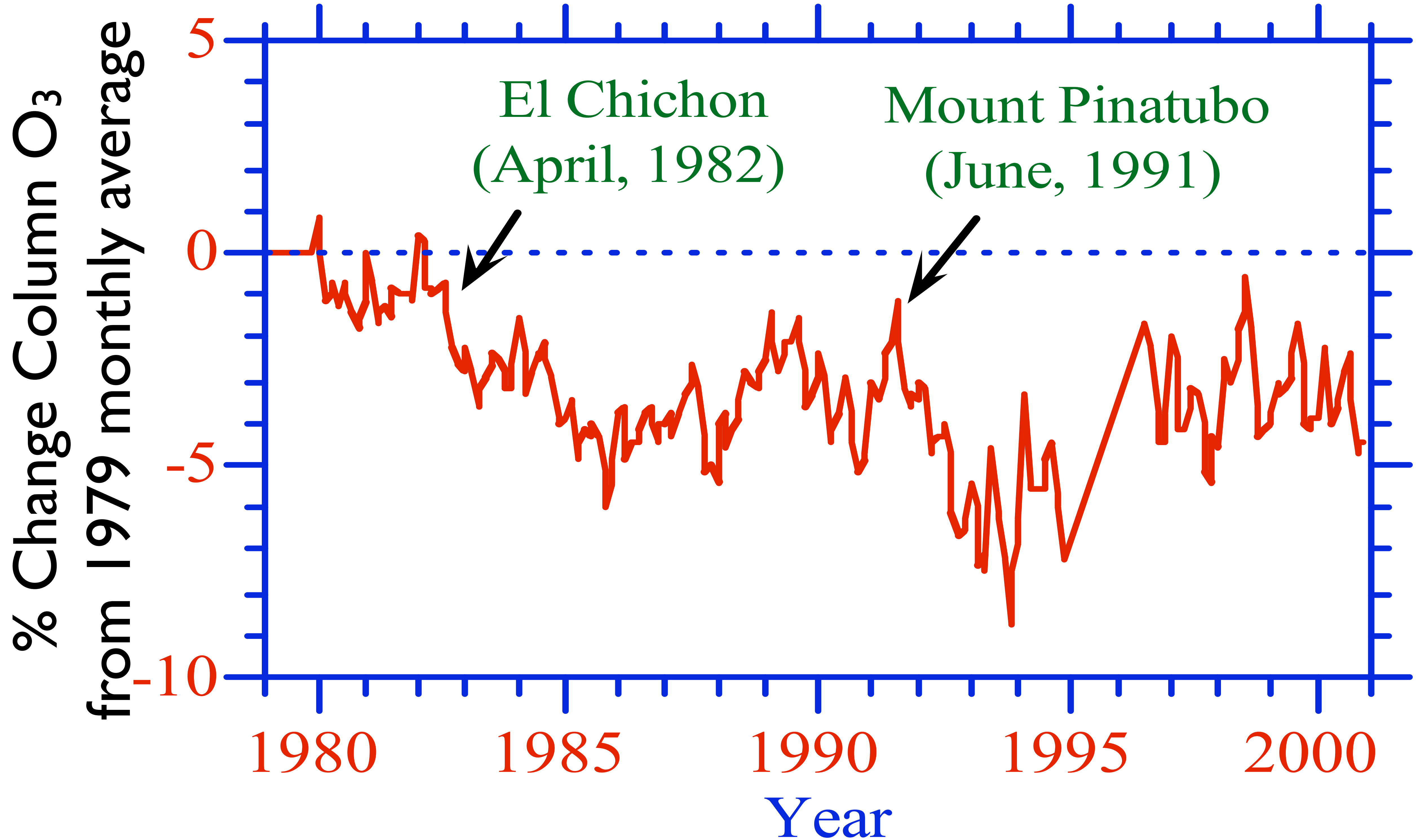


Courtesy Eric Jensen, as published in McCormick *et al.*, 1995

Changes in Monthly-Averaged Global Ozone From 1979-2001



Source: TOMS (NASA) via Mark Jacobson, *Atmospheric Pollution*

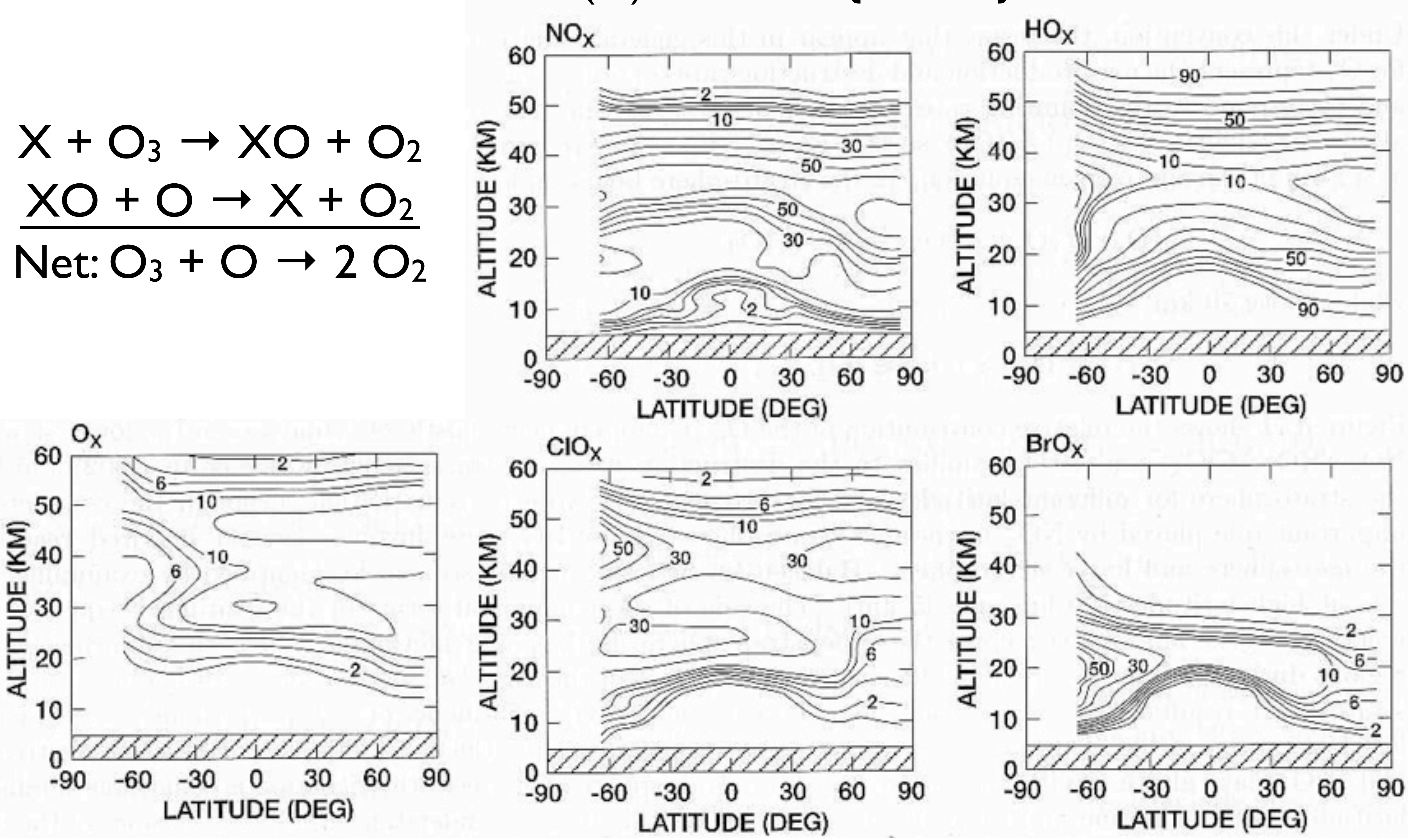
Catalytic Cycles in the Stratosphere

Relative contribution (%) to $O_x = \{O+O_3\}$ destruction

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

$$\underline{XO + O \rightarrow X + O_2}$$

$$\text{Net: } O_3 + O \rightarrow 2\,O_2$$



Based on calculations by the NASA/Goddard 2D model, courtesy C.H. Jackman, as published in Brasseur and Solomon, Aeronomy of the Middle Atmosphere, 2005.

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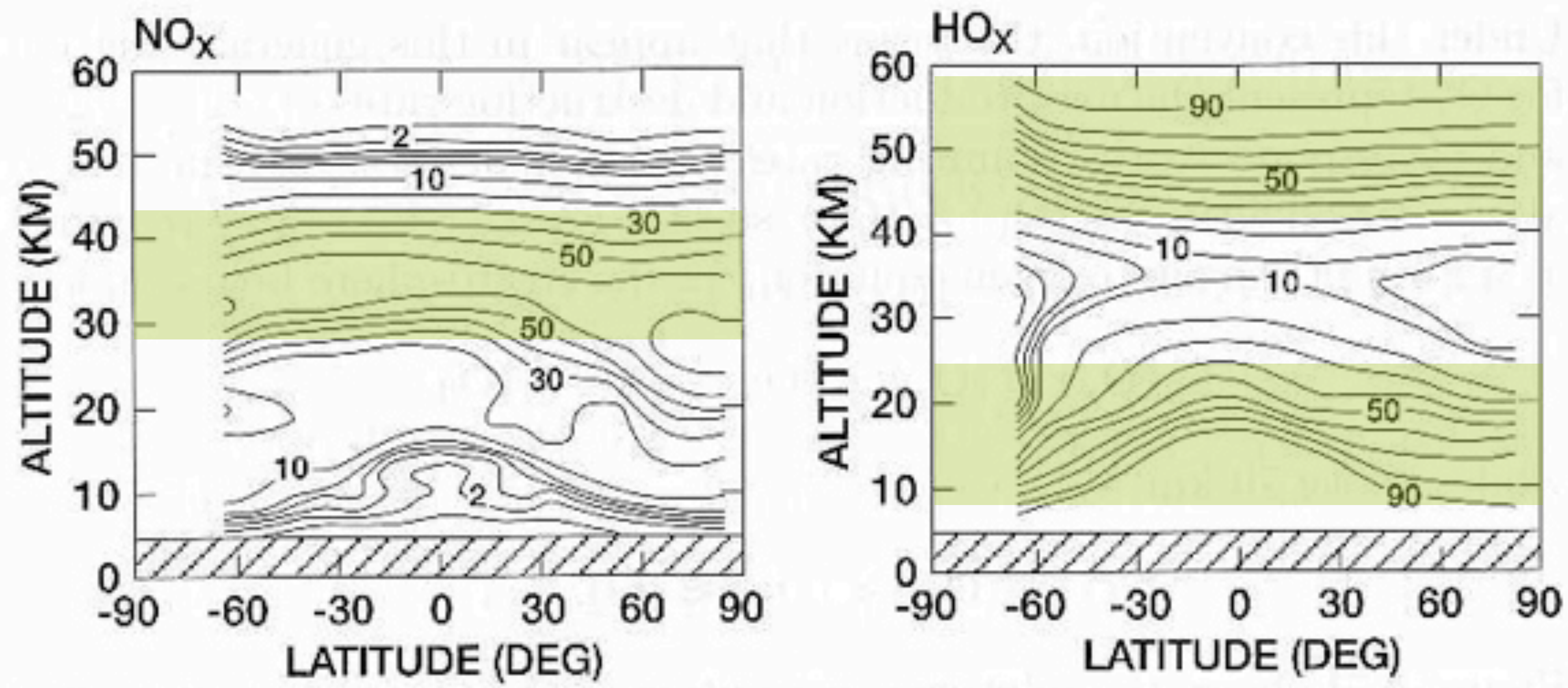

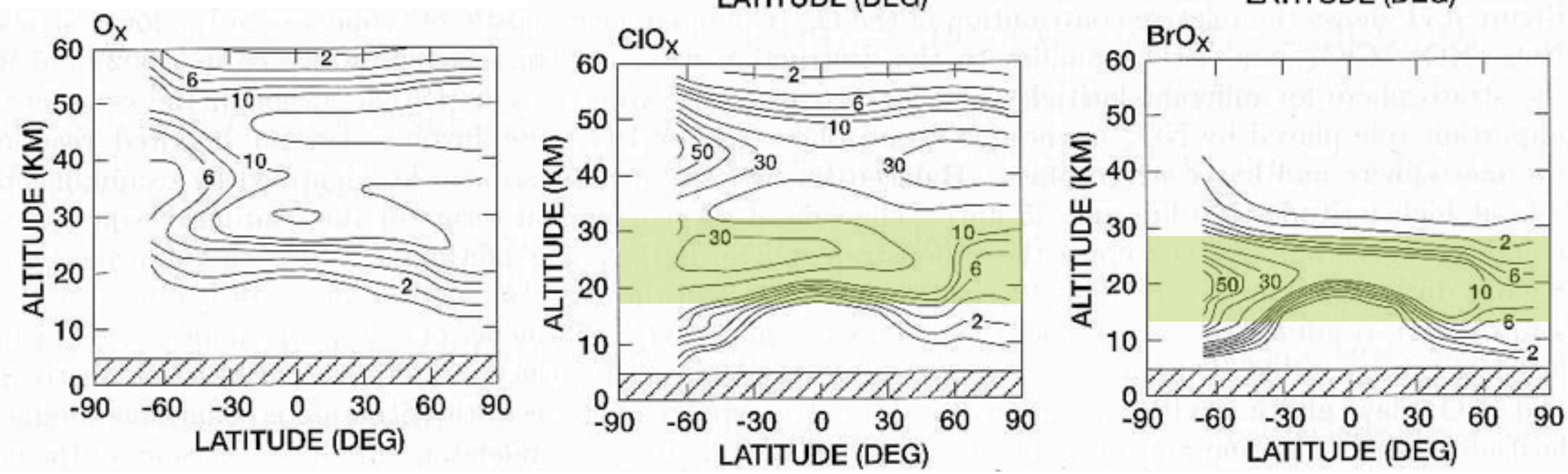

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Stratospheric Chlorine Chemistry:

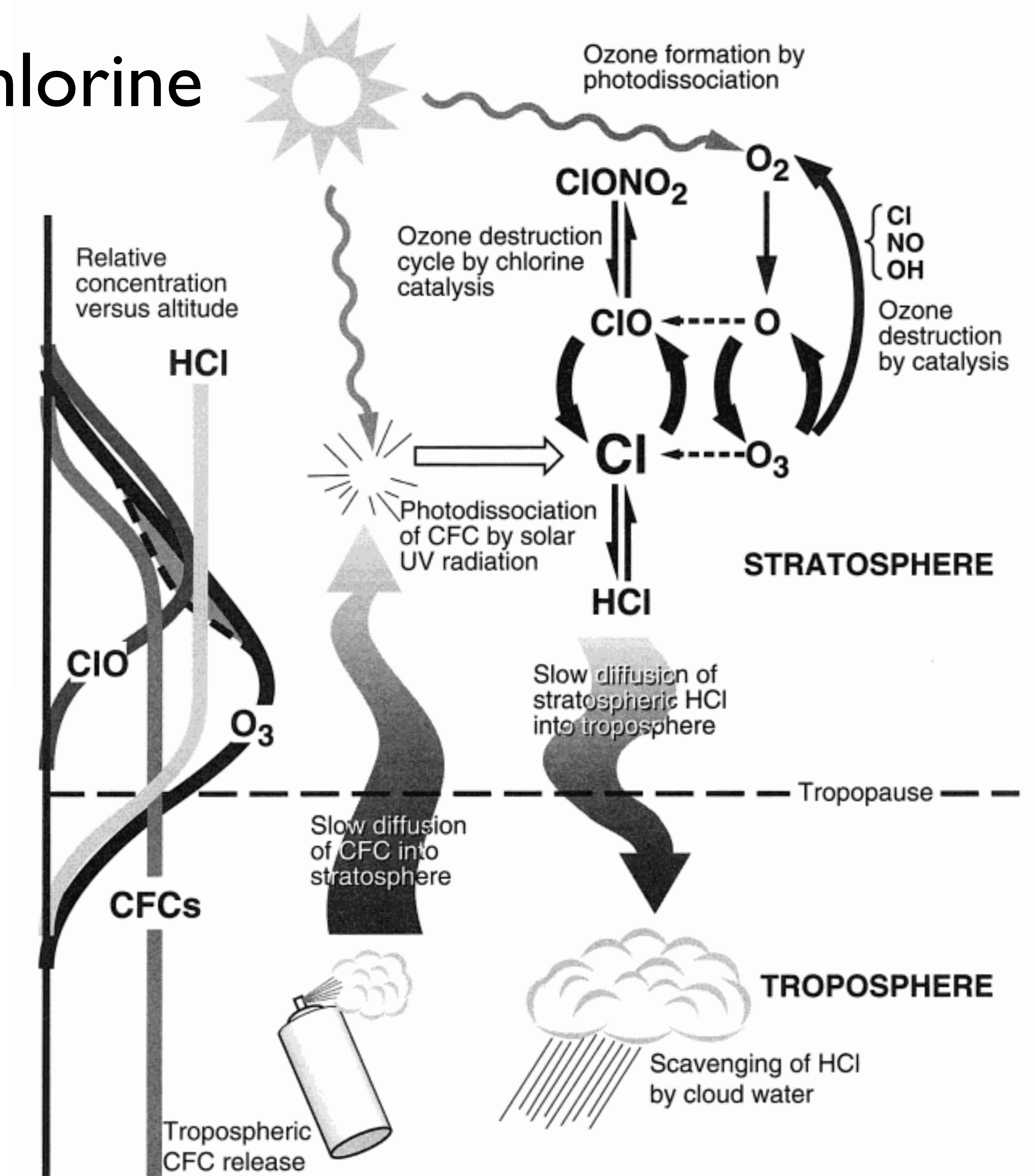
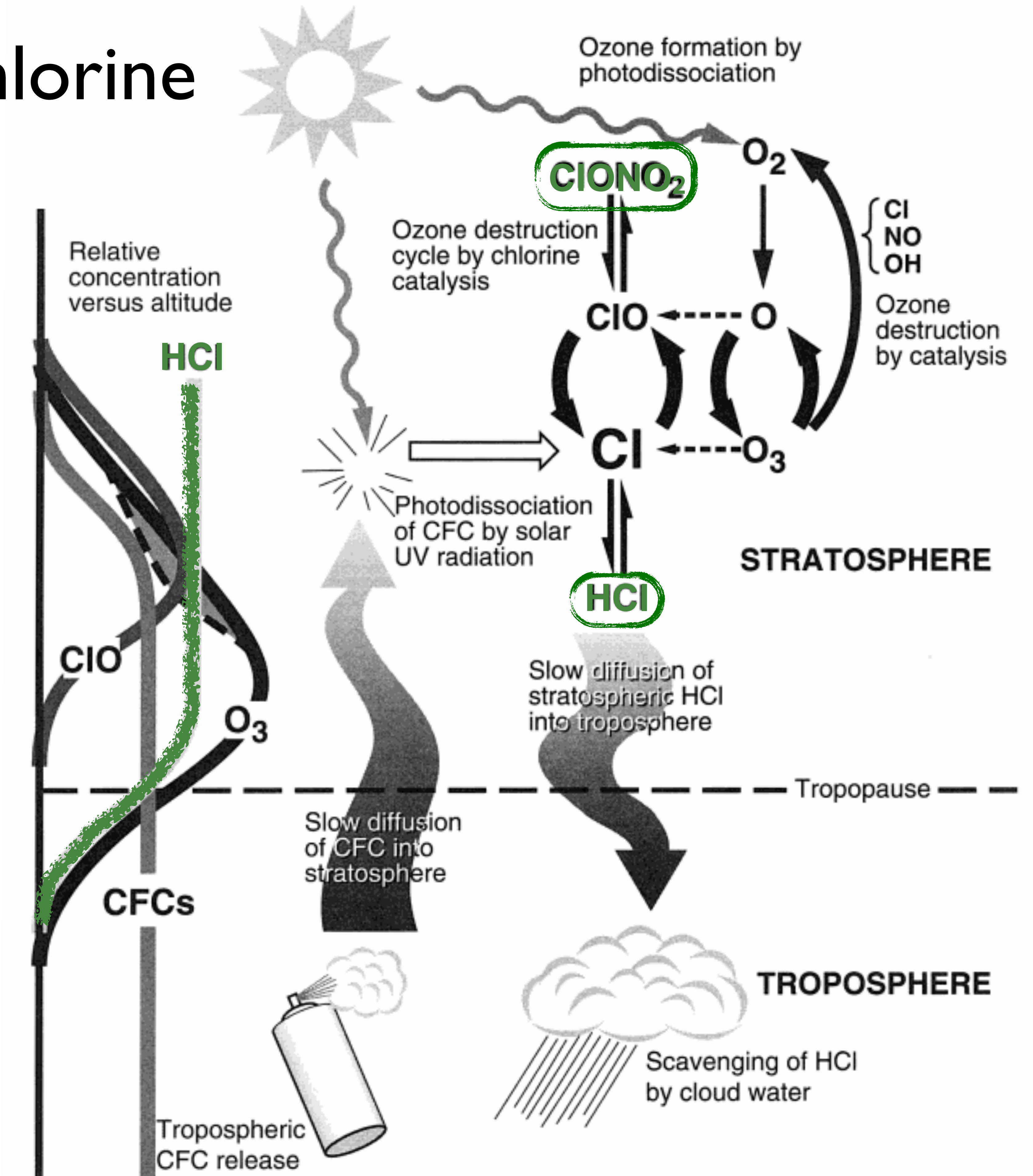


Figure from *Earth Under Siege: From Air Pollution to Global Change*, by Richard Turco, 2002

Stratospheric Chlorine Chemistry:

- Most of the chlorine is in the forms **HCl** and **$ClONO_2$**, which are **inert "reservoirs"** that don't affect ozone.



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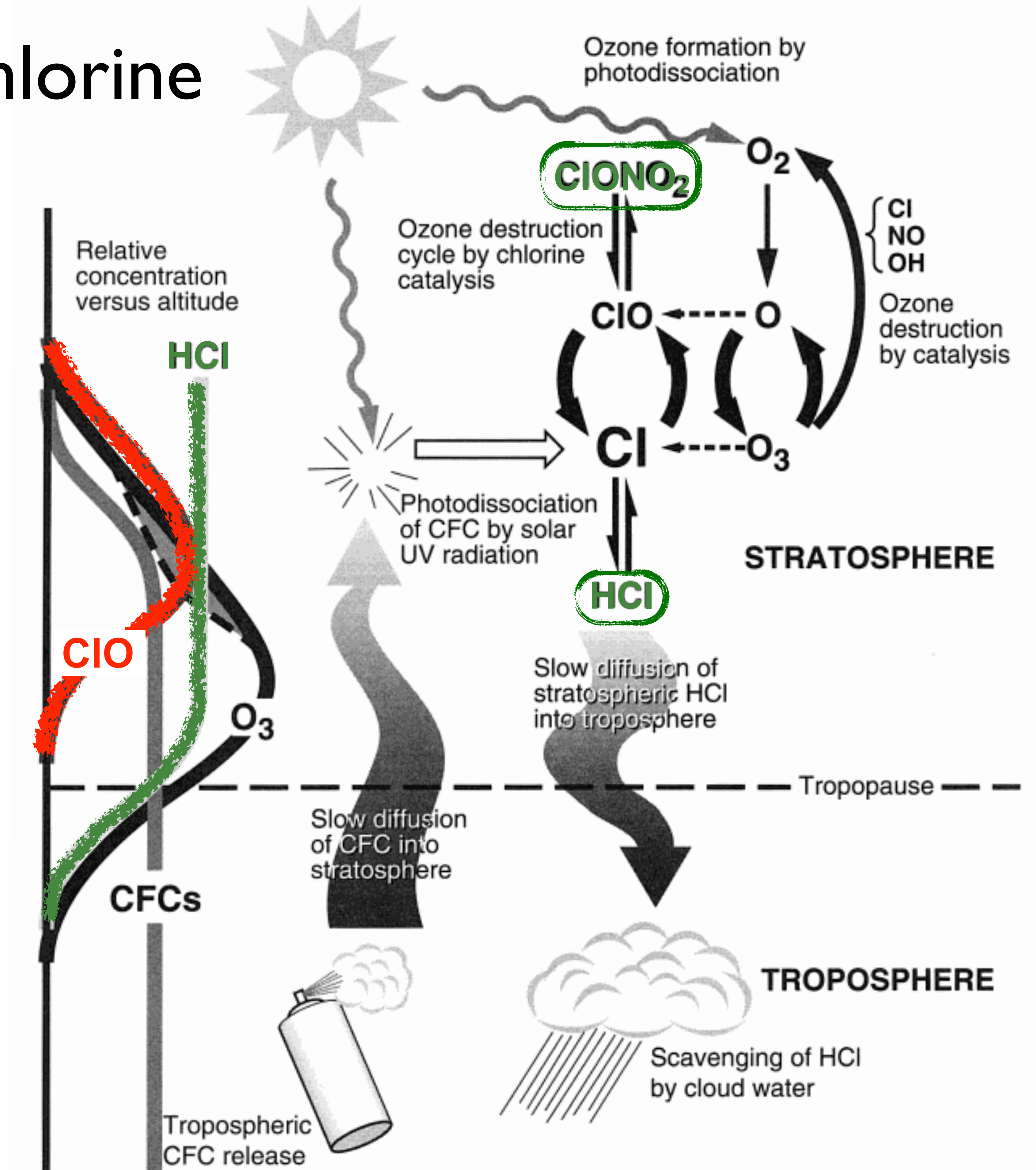
Stratospheric Chlorine Chemistry:

- Most of the chlorine is in the forms **HCl** and **$ClONO_2$**, which are **inert "reservoirs"** that don't affect ozone.
- In the lower stratosphere, only a small percentage (about 1-5%) is in the form of **ClO**, which catalyzes ozone loss.



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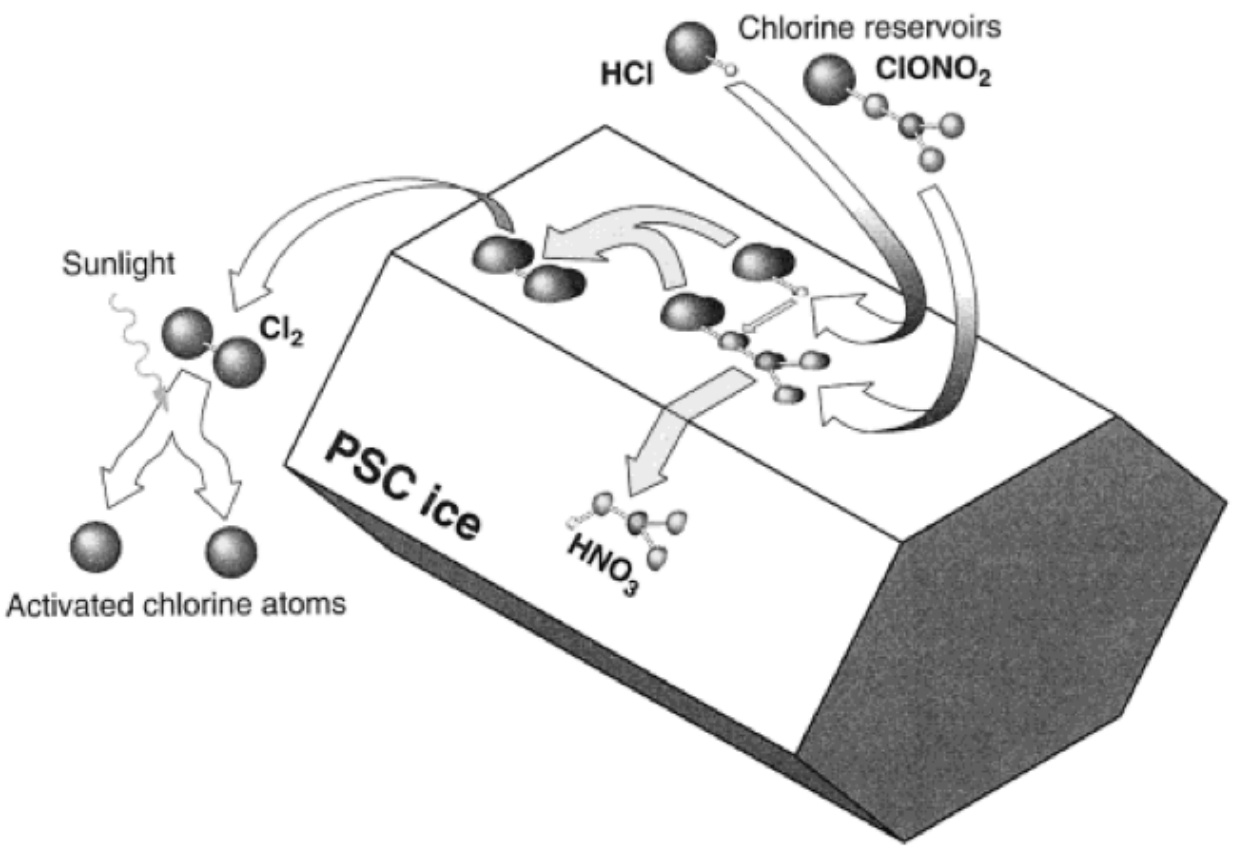
Aerosols and Stratospheric Ozone Depletion

Heterogeneous reactions on polar stratospheric clouds directly convert HCl and $ClONO_2$ reservoirs into active forms in the polar winter.



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Heterogeneous Reactions

$ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(a)$

Chlorine nitrate + Water-ice → Hypochlorous acid + Adsorbed nitric acid

$ClONO_2(g) + HCl(a) \rightarrow Cl_2(g) + HNO_3(a)$

Chlorine nitrate + Adsorbed hydrochloric acid → Molecular chlorine + Adsorbed nitric acid

$N_2O_5(g) + HCl(a) \rightarrow ClNO_2(g) + HNO_3(a)$

Dinitrogen pentoxide + Adsorbed hydrochloric acid → Chlorine nitrite + Adsorbed nitric acid

$HOCl(g) + HCl(a) \rightarrow Cl_2(g) + H_2O(s)$

Hypochlorous acid + Adsorbed hydrochloric acid → Molecular chlorine + Water-ice

$N_2O_5(g) + H_2O(s) \rightarrow 2HNO_3(a)$

Dinitrogen pentoxide + Water-ice → Adsorbed nitric acid

Reactions from *Atmospheric Pollution: History, Science, and Regulation, by* Mark Jacobson, 2002

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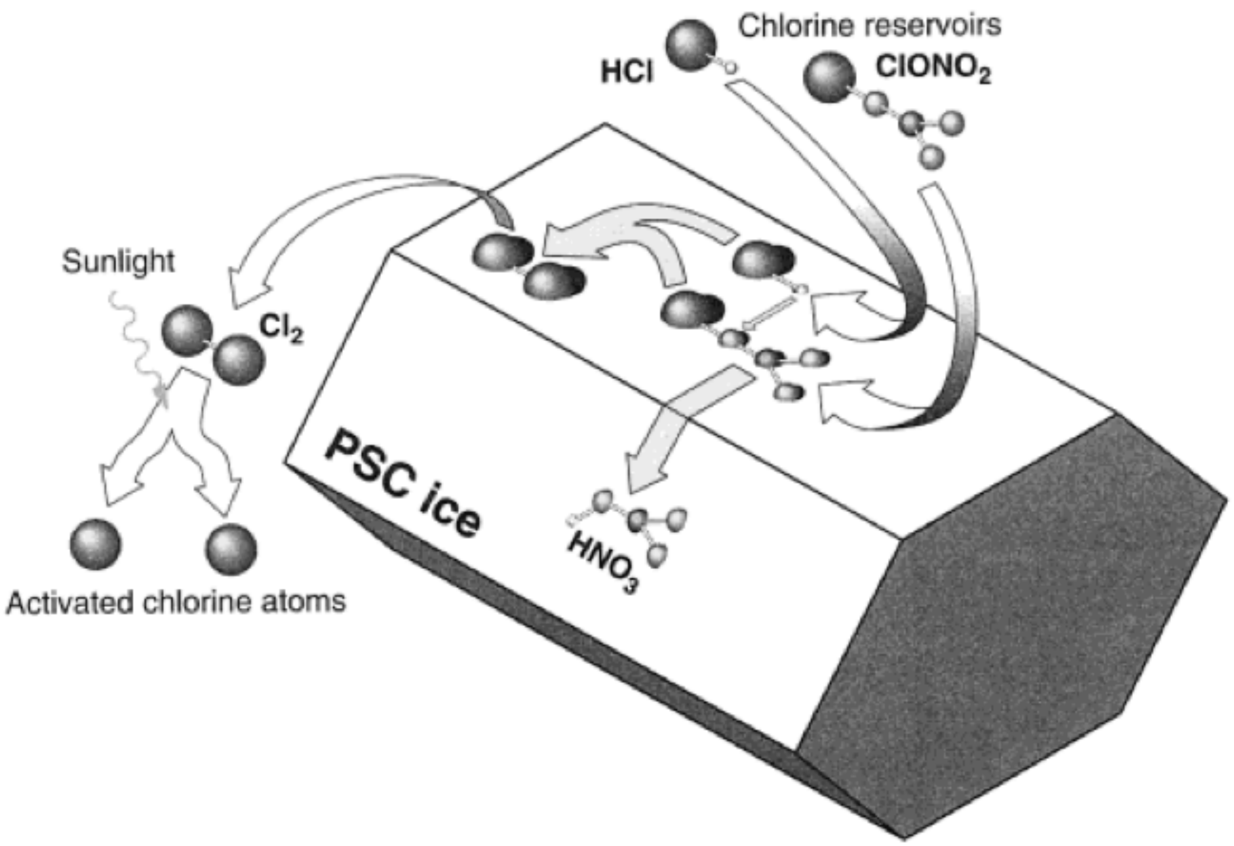

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Chlorine nitrate	Adsorbed hydrochloric acid		Molecular chlorine	Adsorbed nitric acid
$N_2O_5(g)$ +	$HCl(a)$	→	$ClNO_2(g)$ +	$HNO_3(a)$
Dinitrogen pentoxide	Adsorbed hydrochloric acid		Chlorine nitrite	Adsorbed nitric acid
$HOCl(g)$ +	$HCl(a)$	→	$Cl_2(g)$ +	$H_2O(s)$
Hypochlorous acid	Adsorbed hydrochloric acid		Molecular chlorine	Water-ice

COLD POLAR TEMPERATURES

$N_2O_5(g)$ +	$H_2O(s)$	→	$2HNO_3(a)$
Dinitrogen pentoxide	Water-ice		Adsorbed nitric acid

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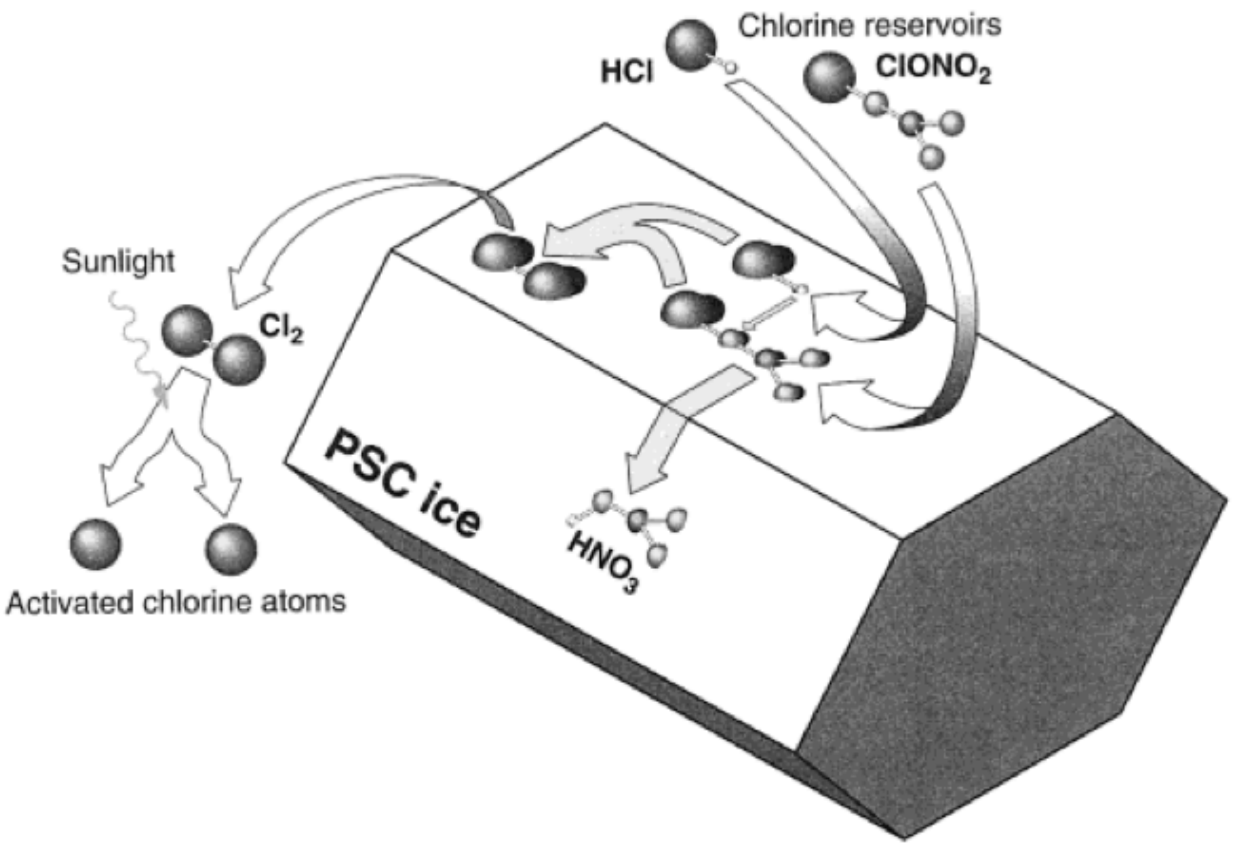

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Remains important on sulfate aerosol at higher temperatures, lower latitudes

Heterogeneous Reactions

COLD POLAR TEMPERATURES

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$HOCl(g)$ +	$HCl(a)$	→	$Cl_2(g)$ +	$H_2O(s)$
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TEMPERATURE-INDEPENDENT

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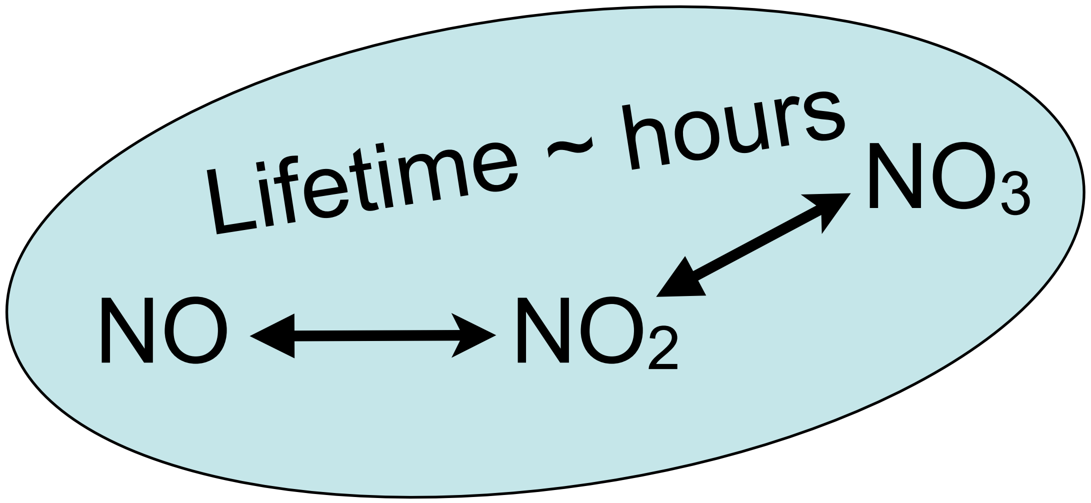
Heterogenous hydrolysis of N_2O_5



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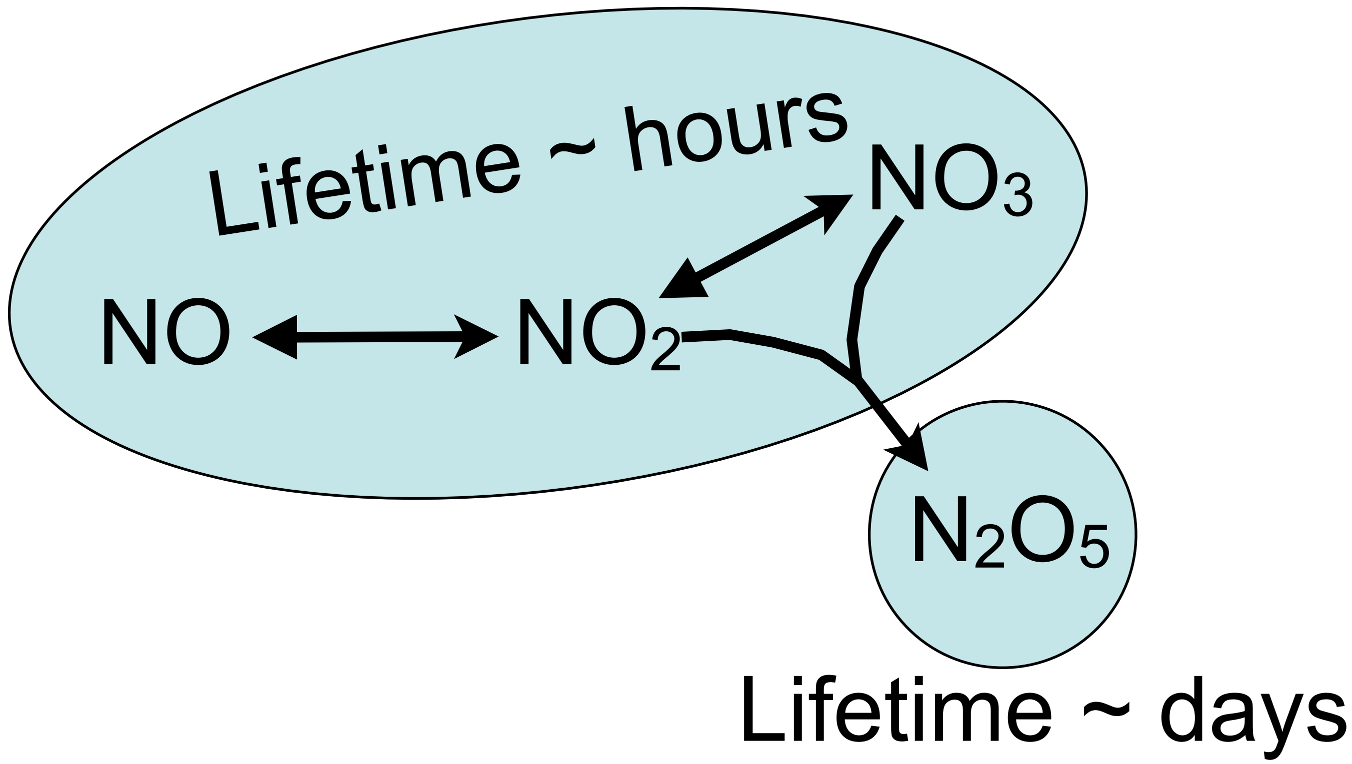

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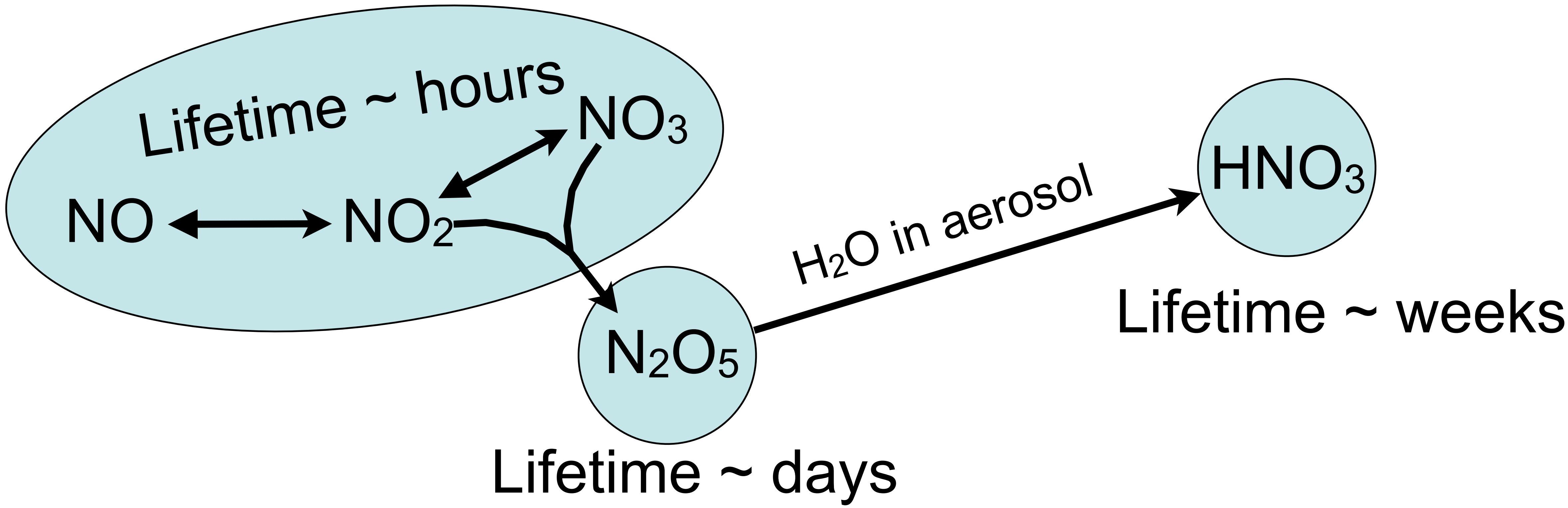

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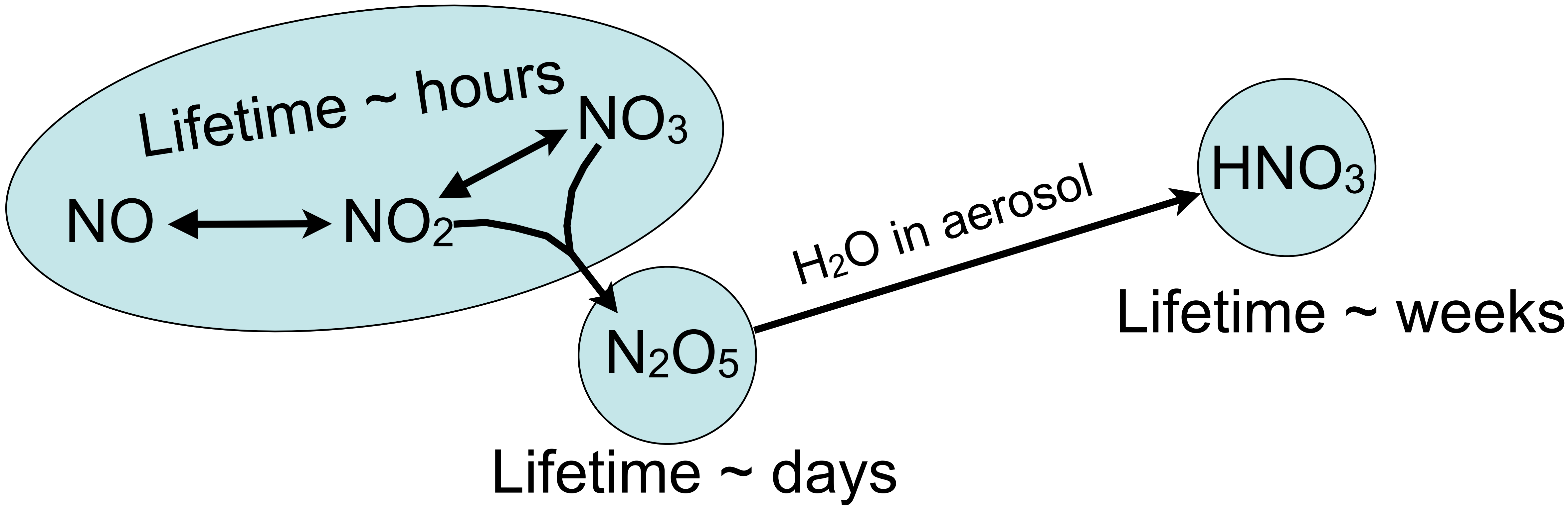

Higher aerosol → lower NO_x

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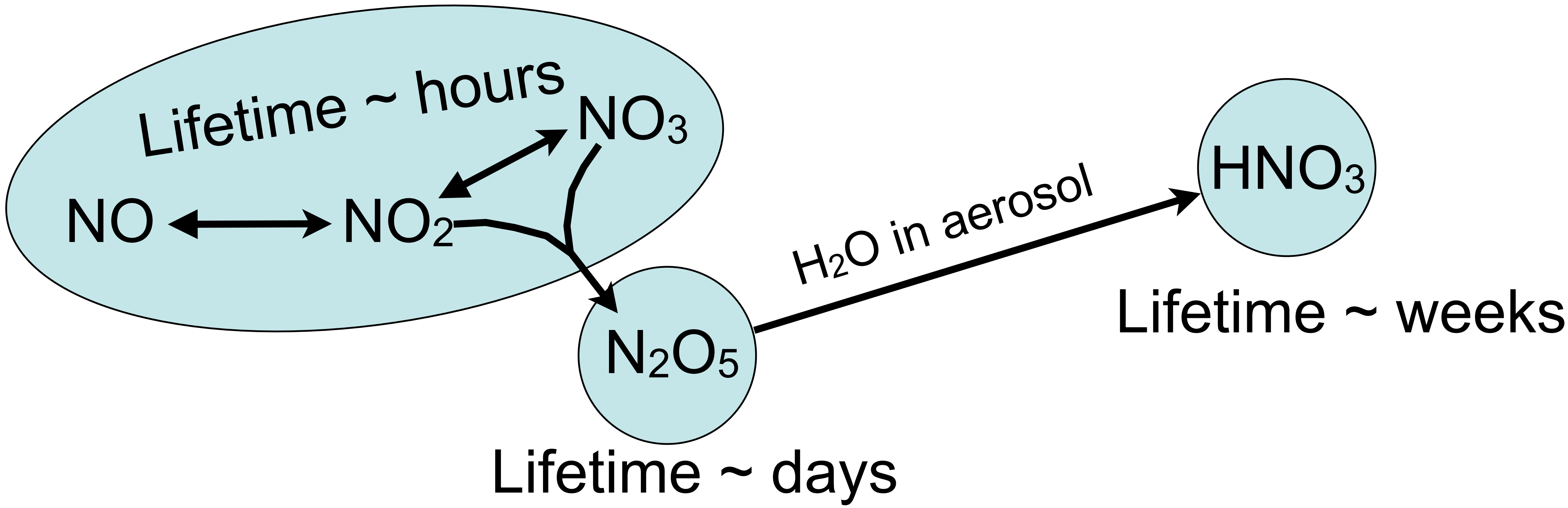

Impact of NO_x on other O_x-destroying families:

$NO_2 + ClO \rightarrow ClONO_2$

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$NO_2 + OH \rightarrow HNO_3$

Higher aerosol → lower NO_x

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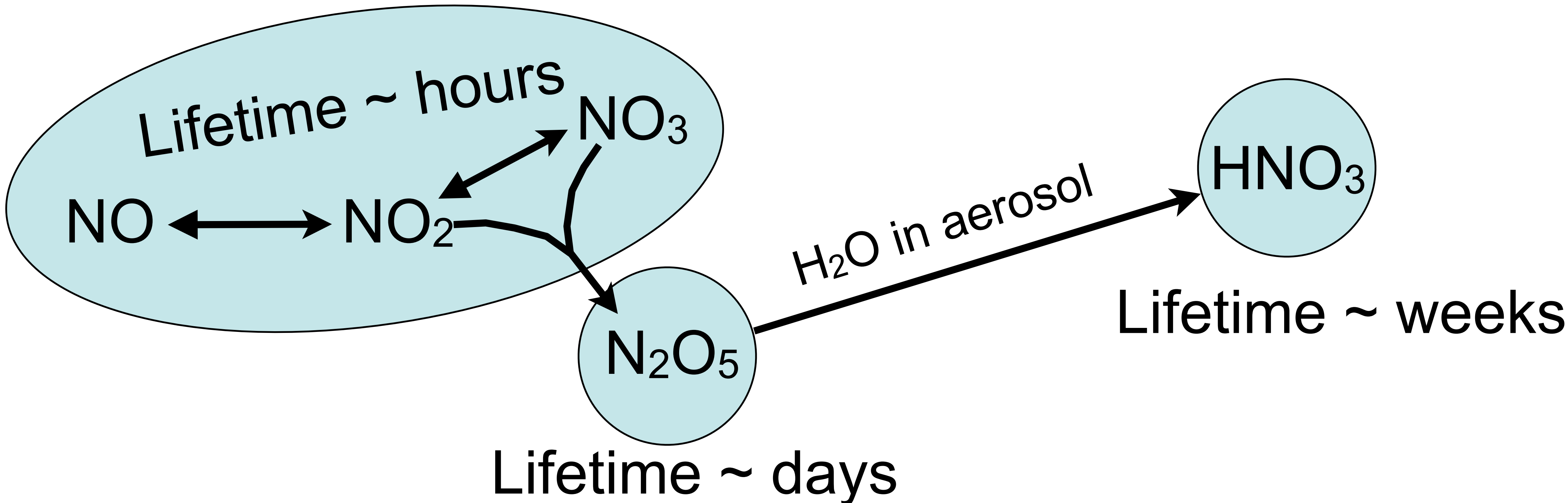

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Active species → Reservoirs

Higher aerosol → lower NO_x

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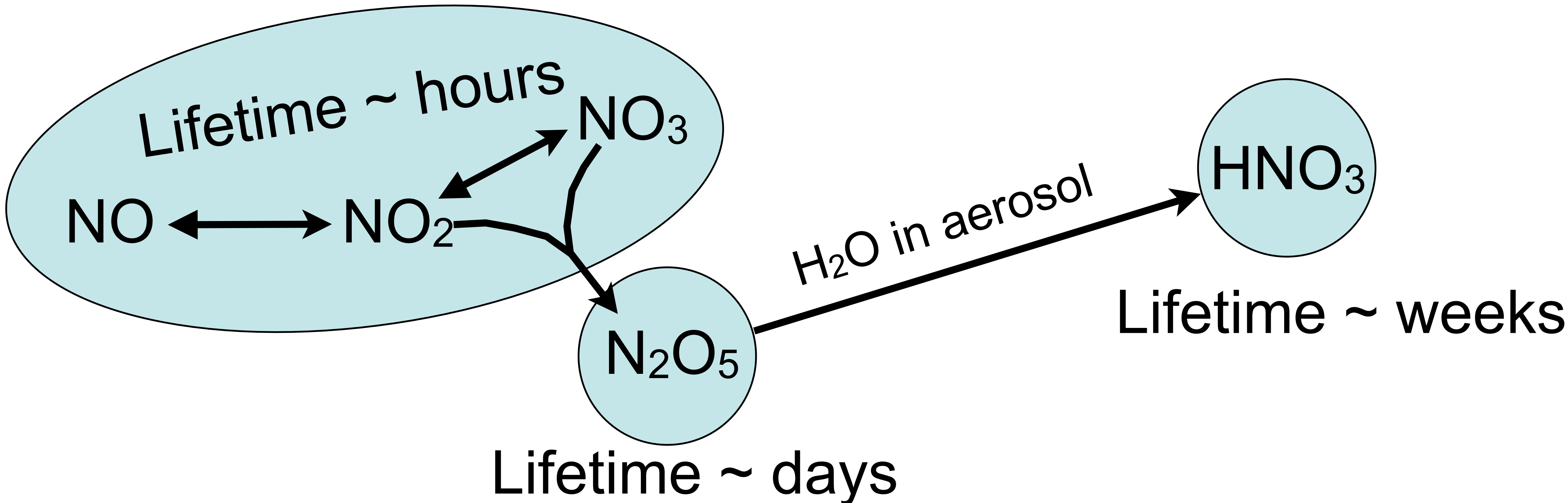

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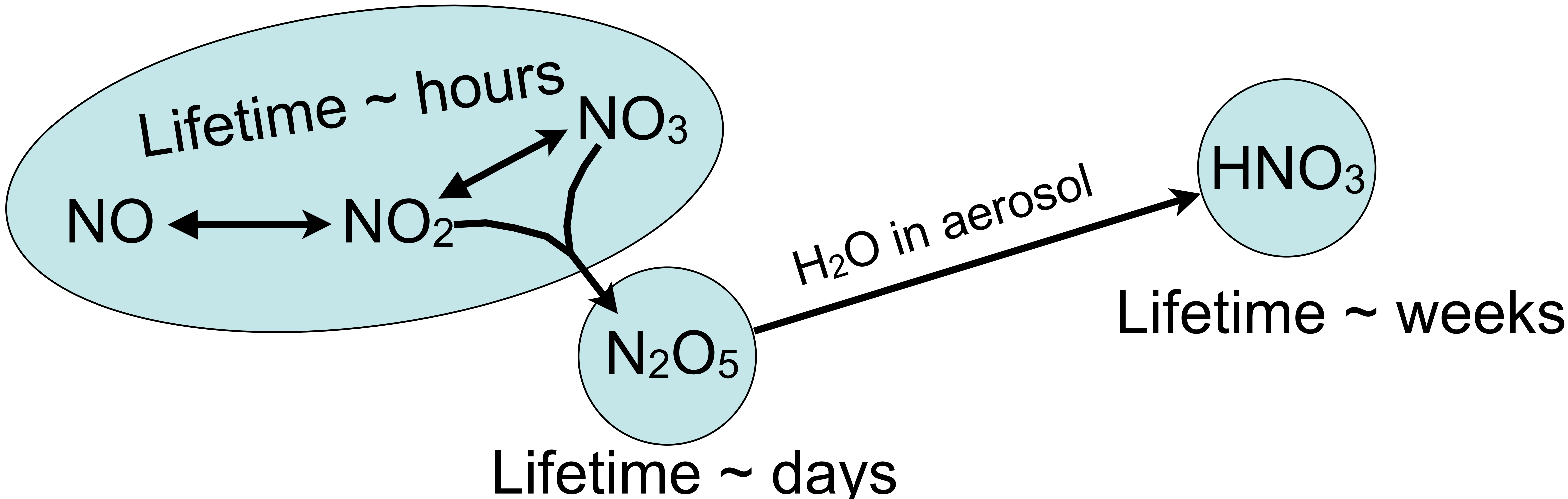

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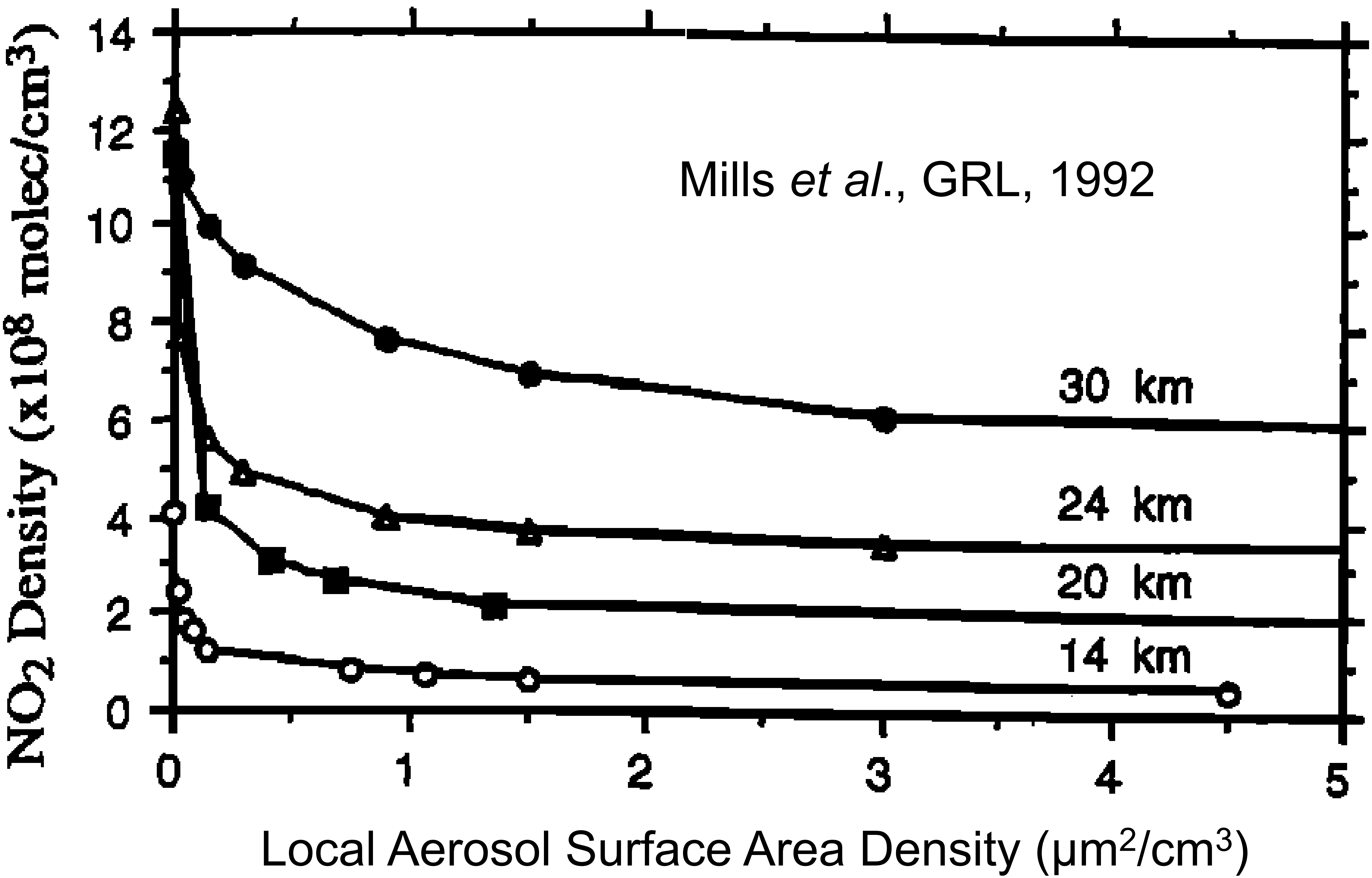
Higher aerosol → lower NO_x → higher ClO_x, BrO_x, HO_x

But this effect "saturates" at high aerosol levels, when N_2O_5 formation becomes rate-limiting.

N_2O_5 Saturation by Sulfate Aerosols



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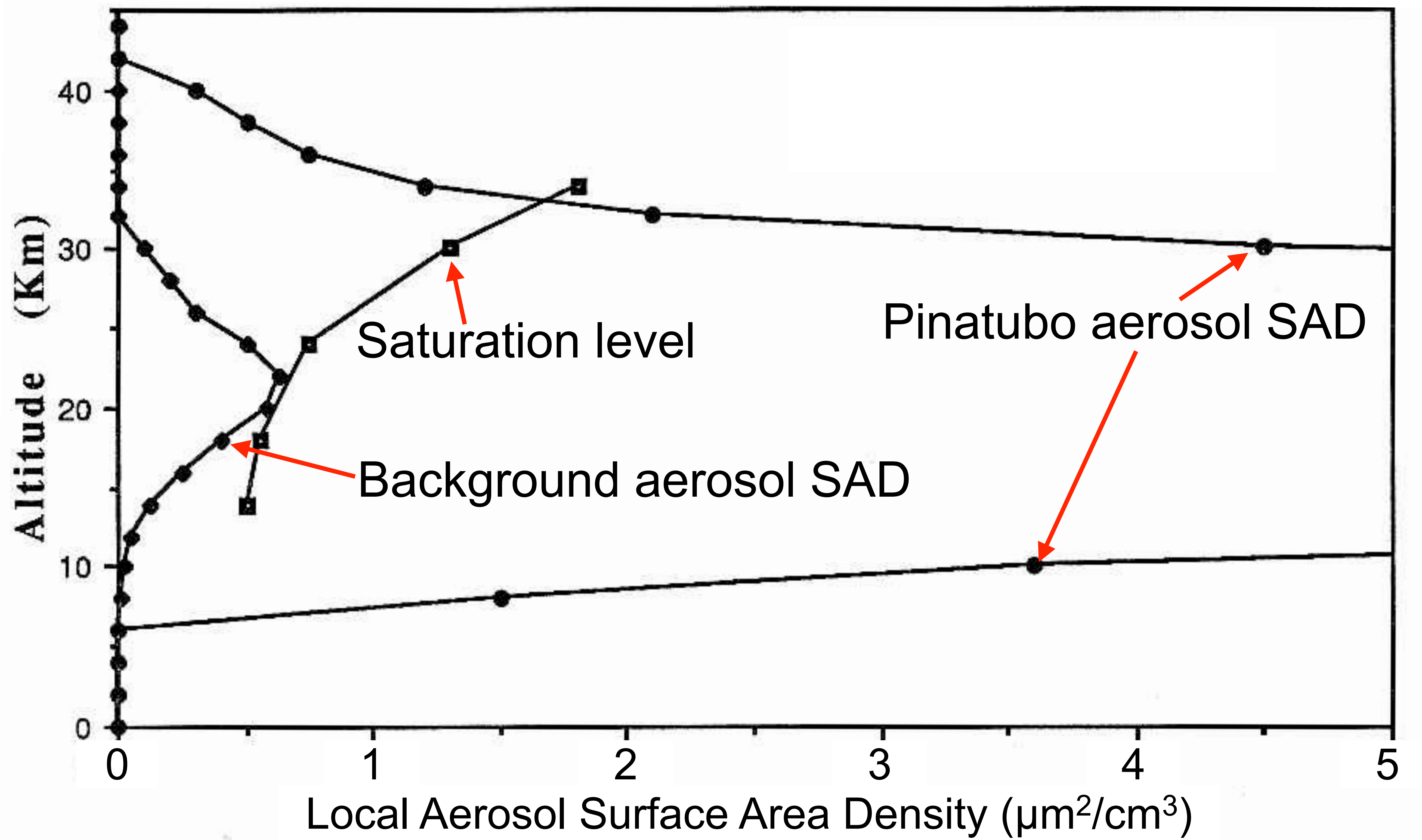
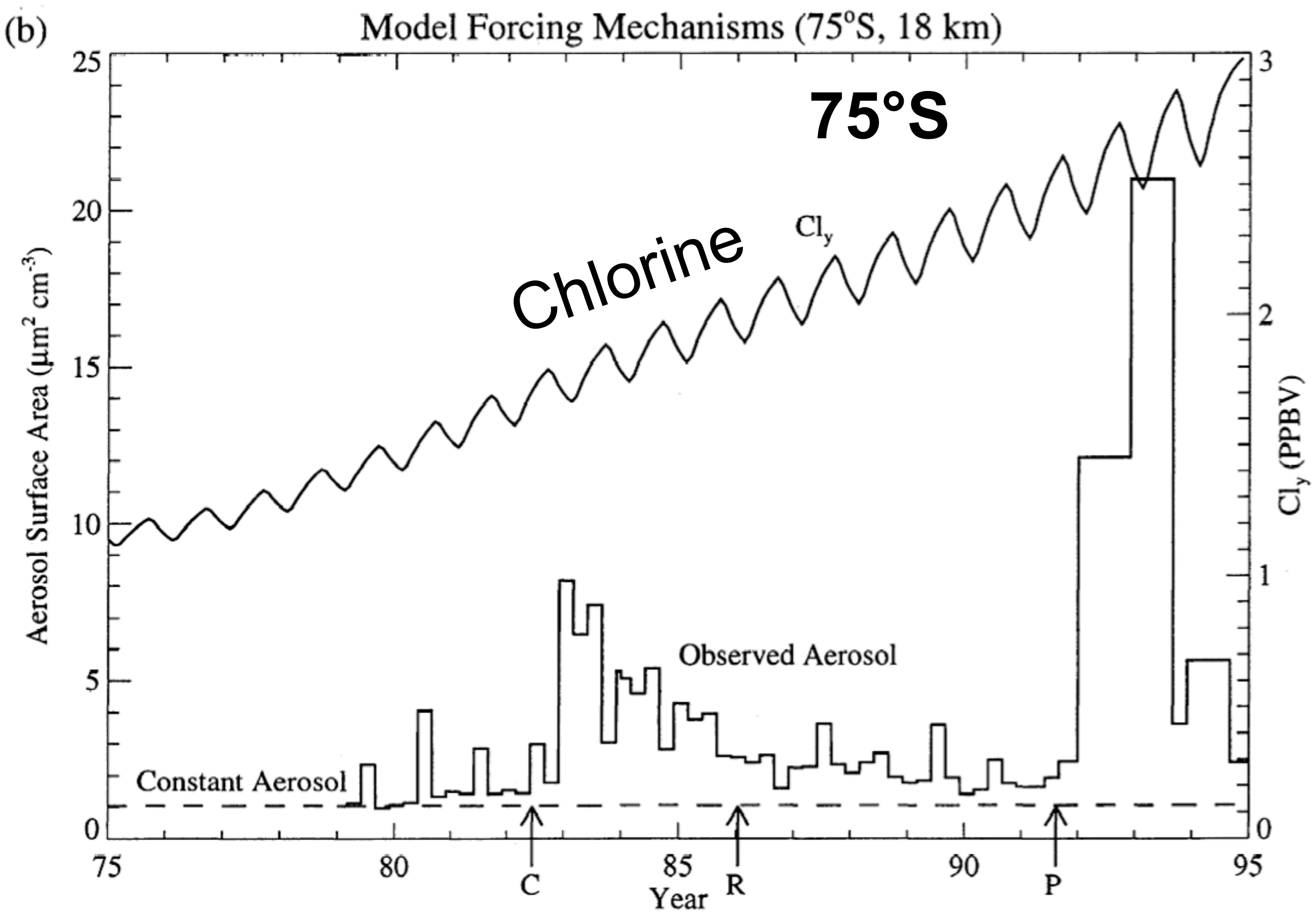
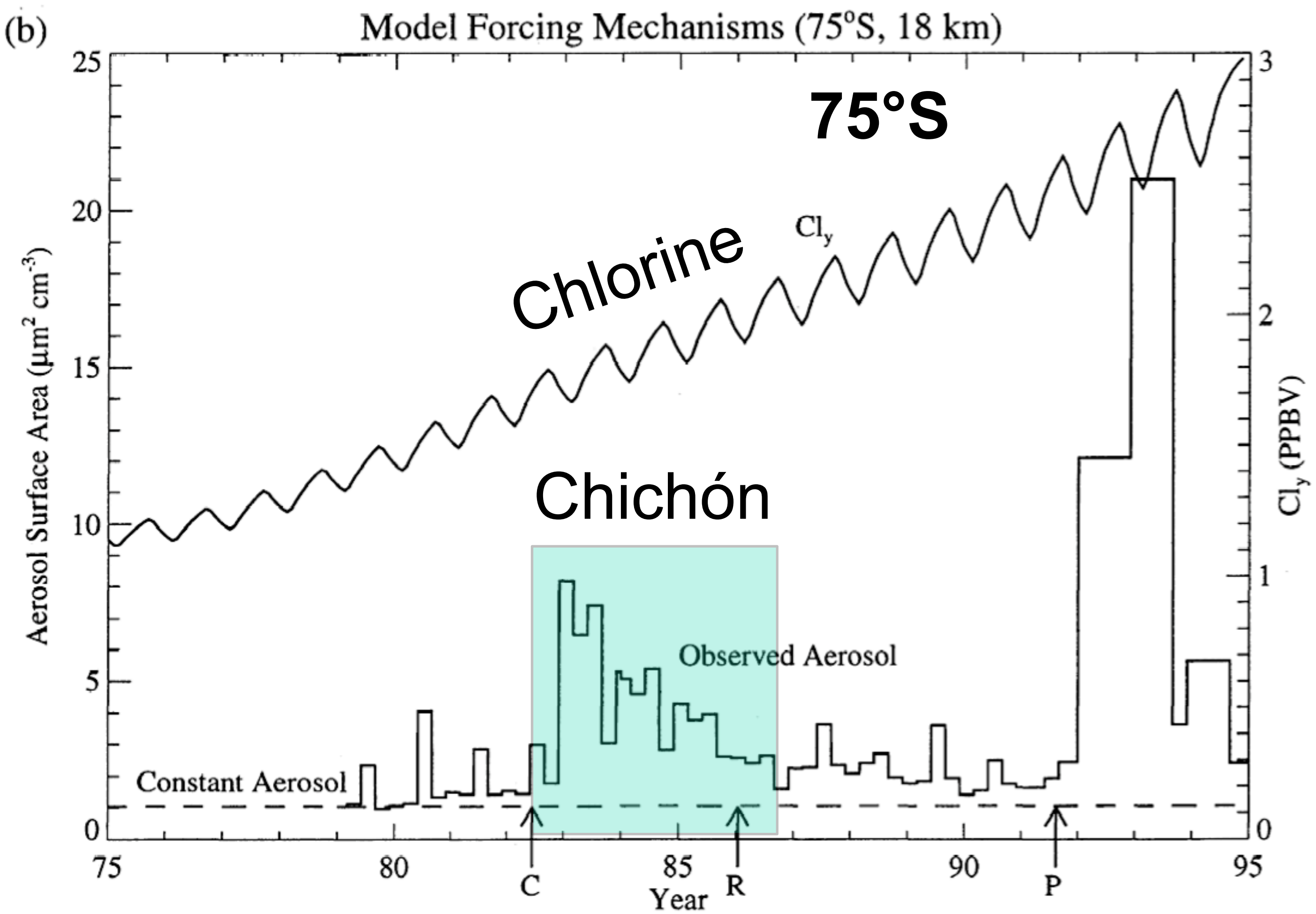


Impacts on stratospheric chemistry are greatest for small aerosol increases, well below those due to Pinatubo.



Portmann *et al*., JGR, 1996



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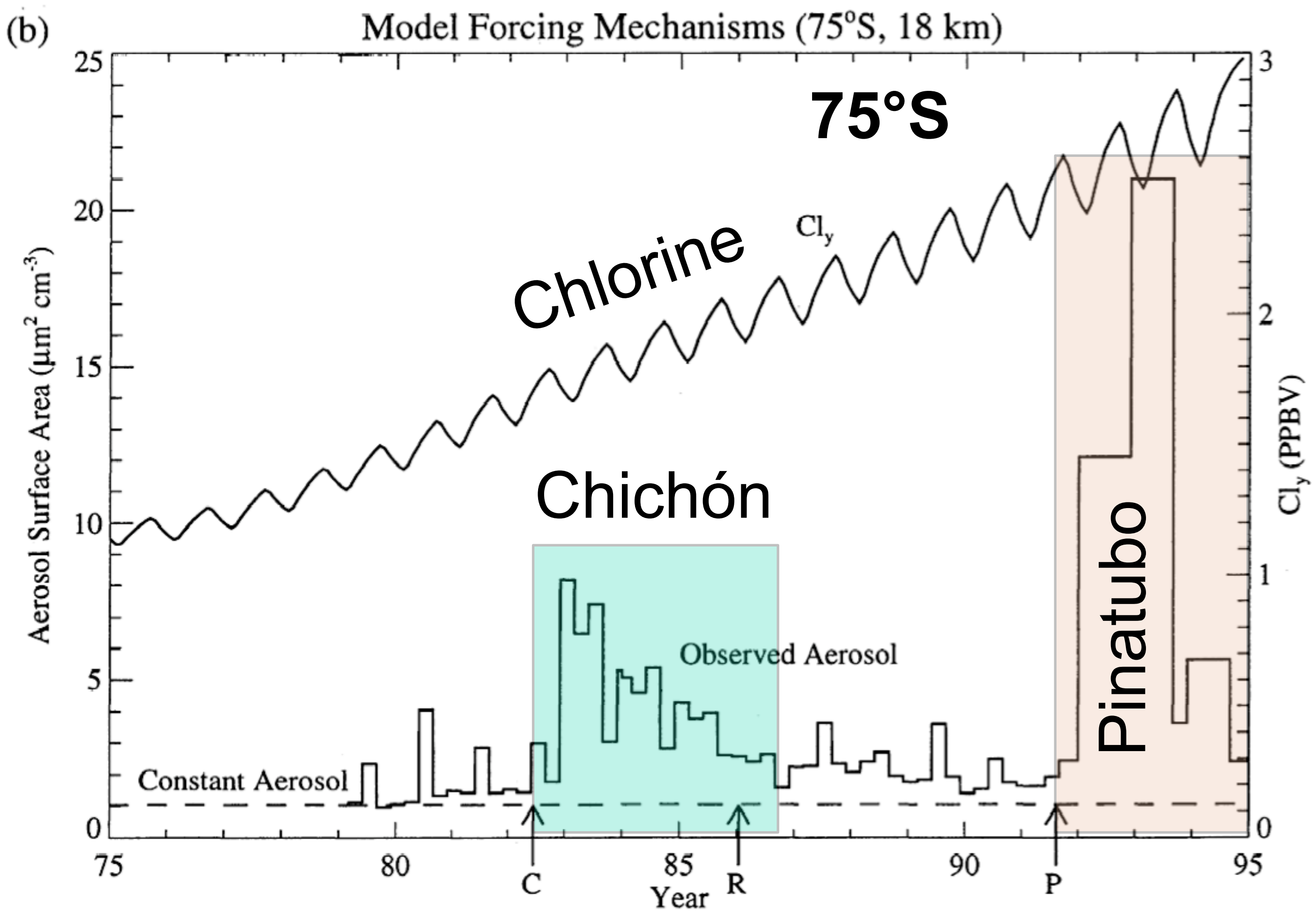

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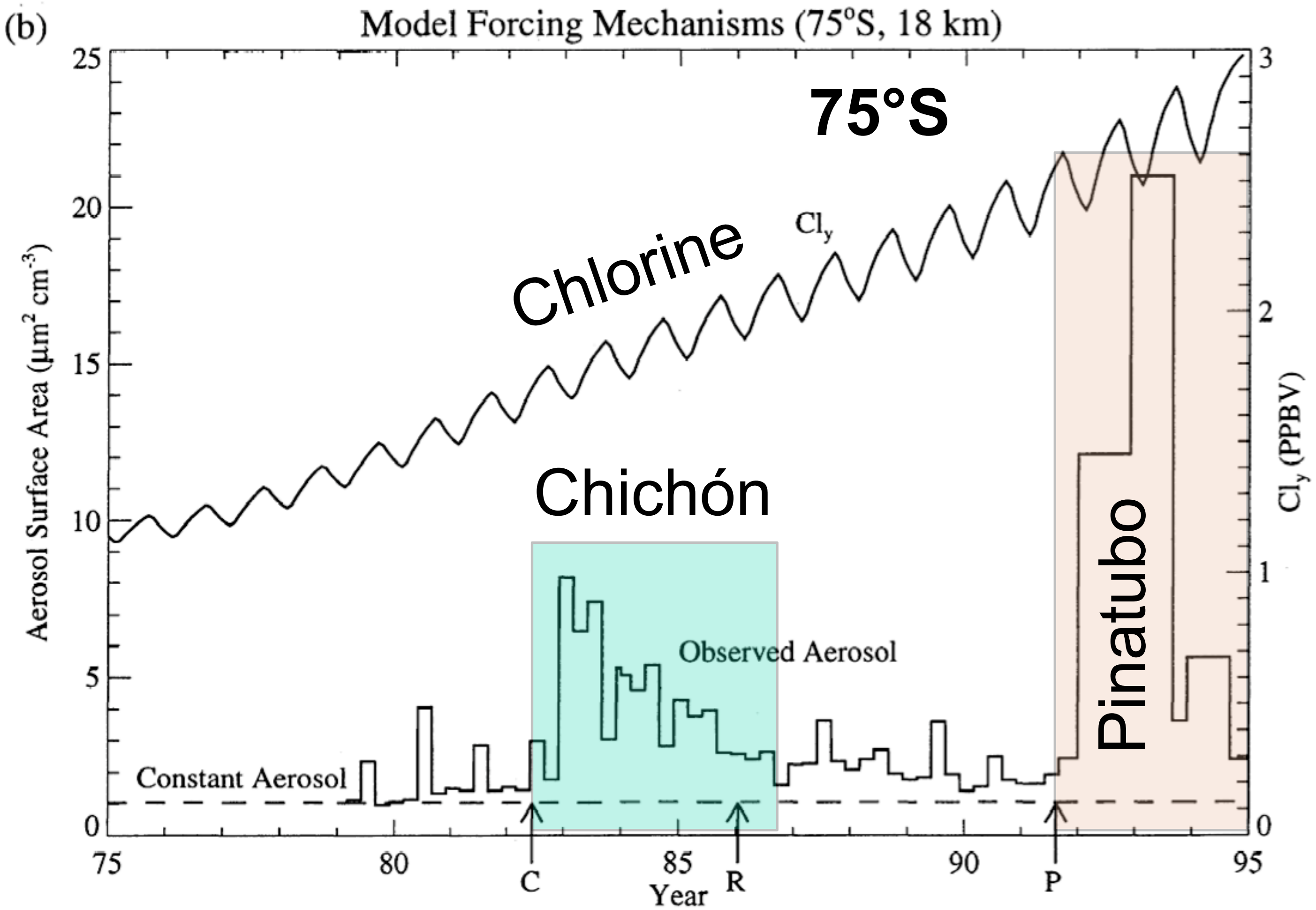

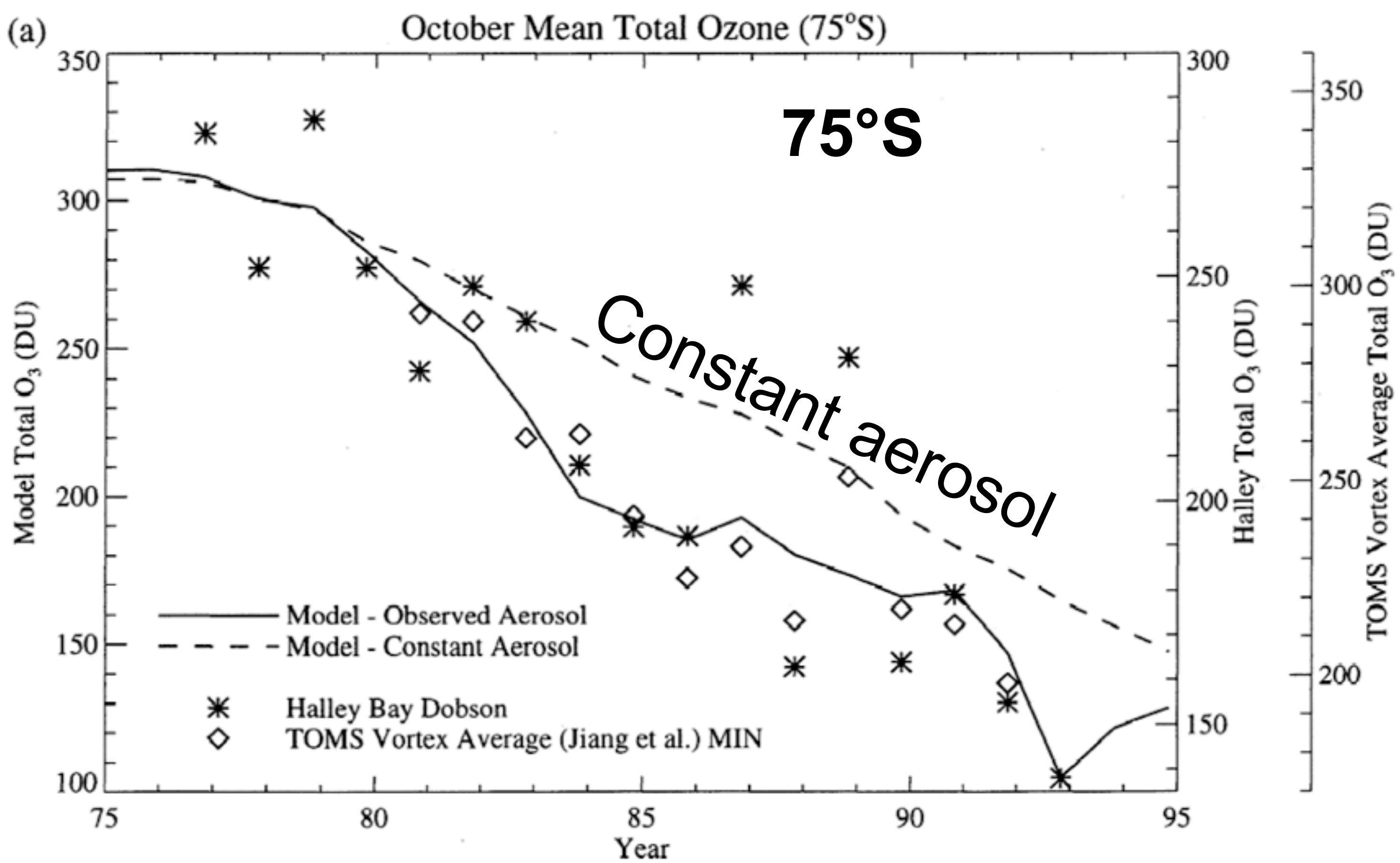

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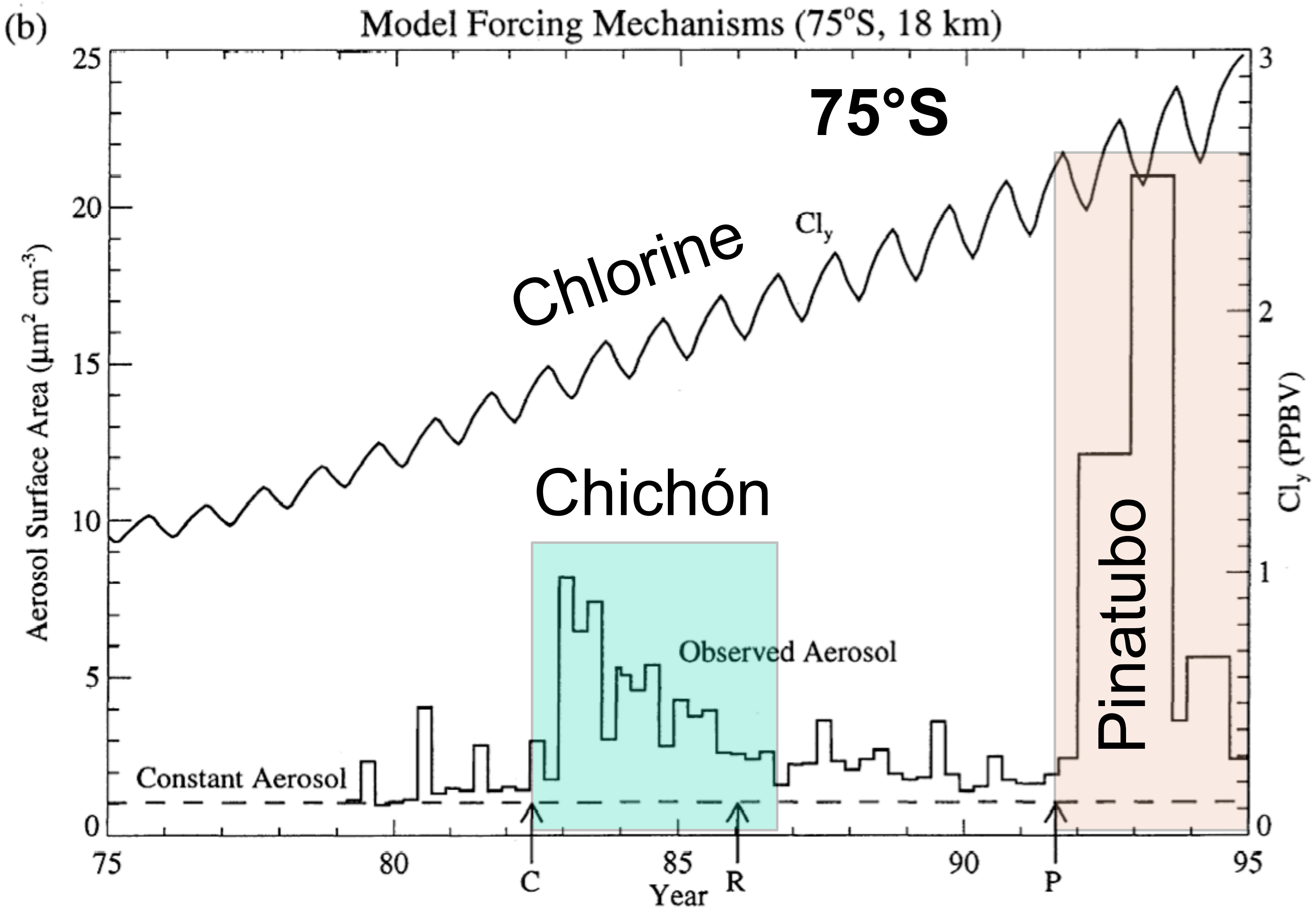

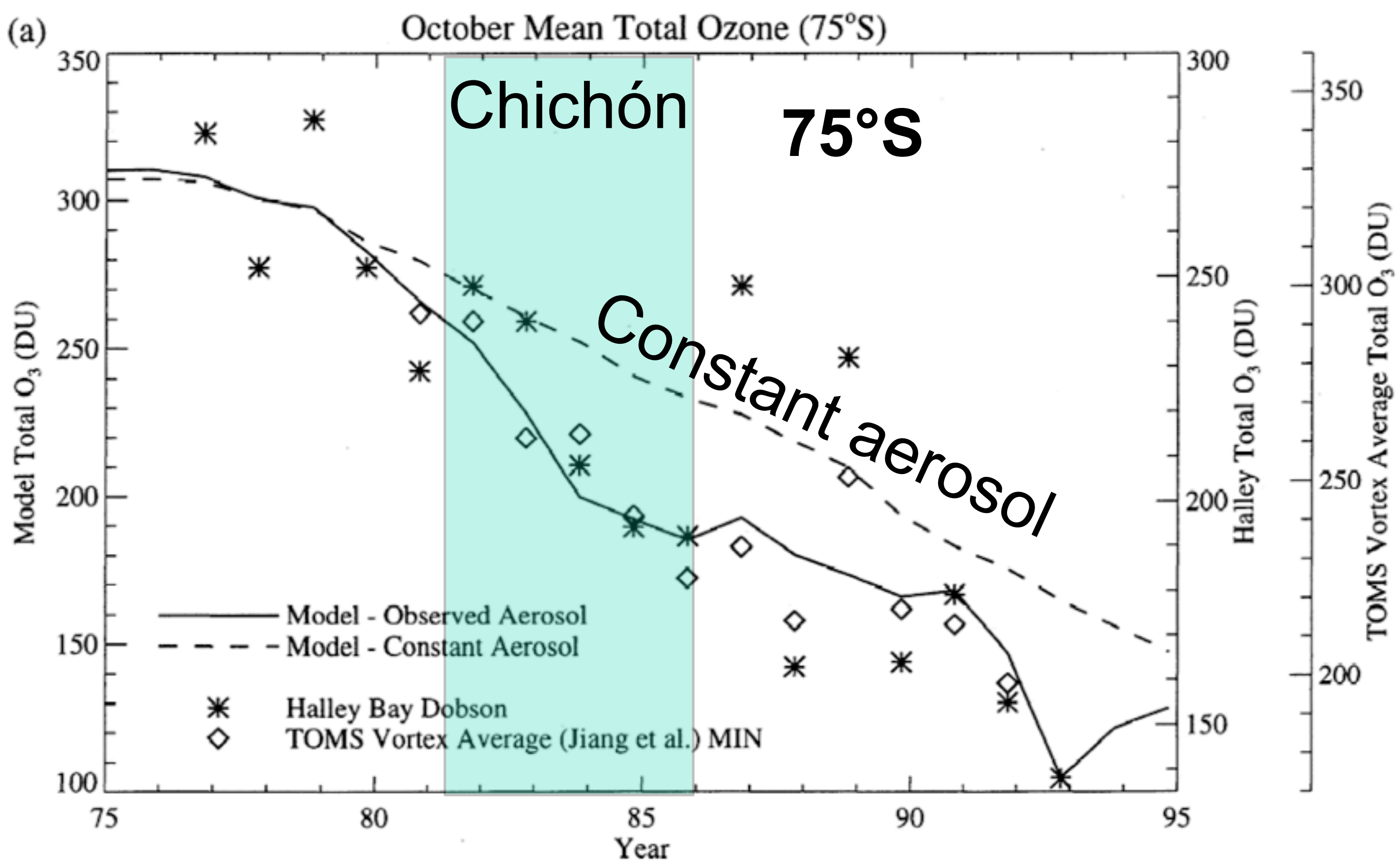

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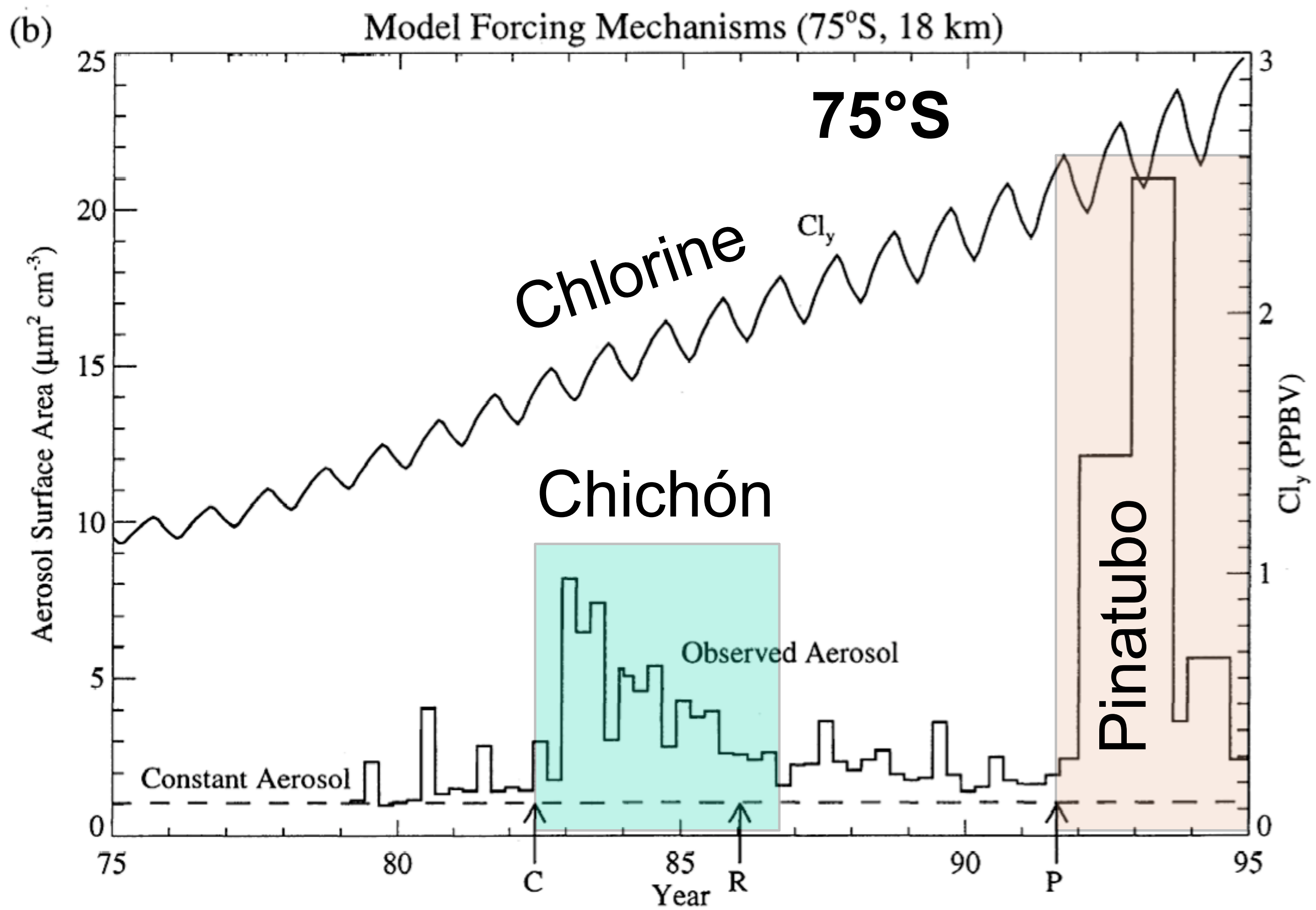

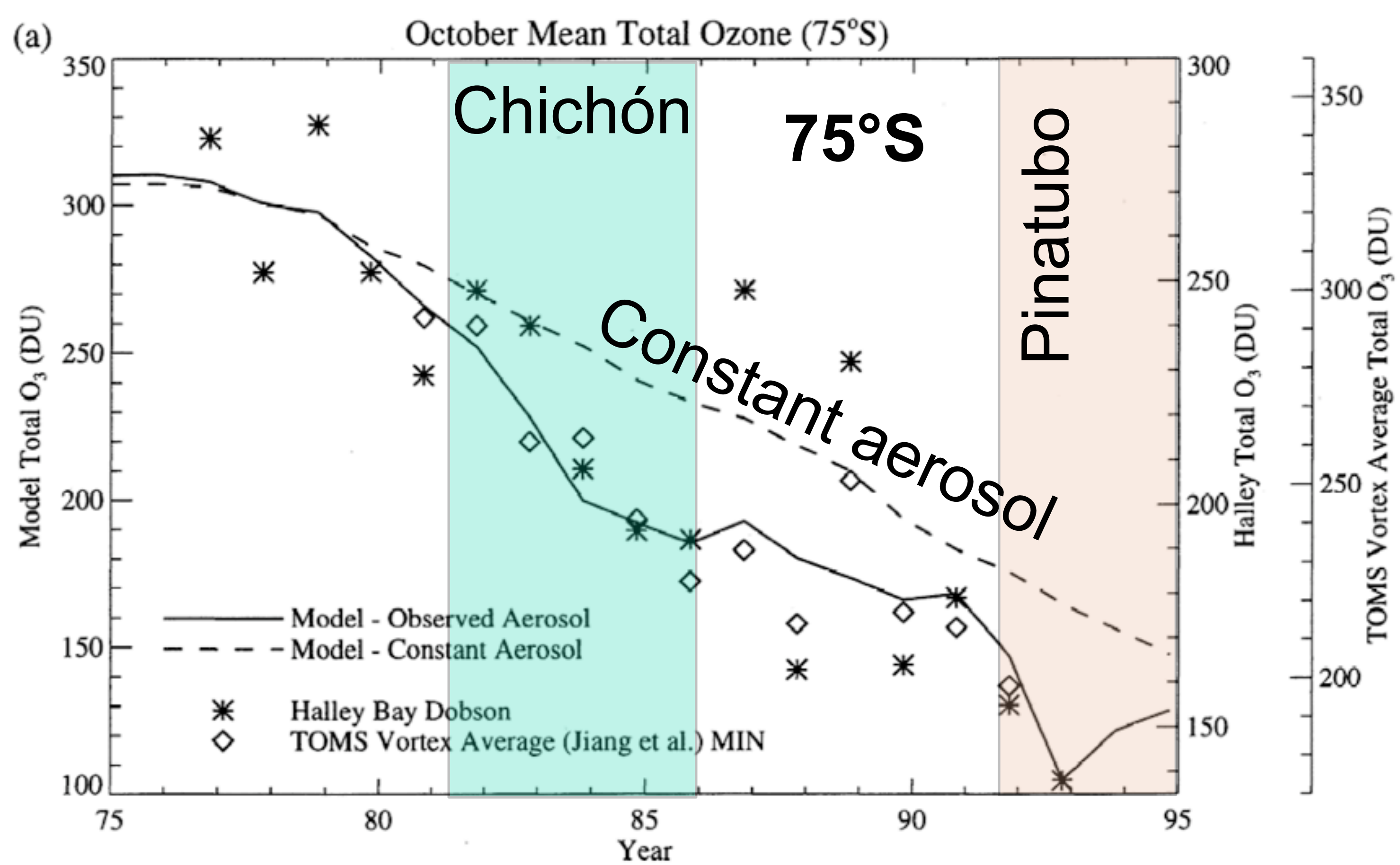

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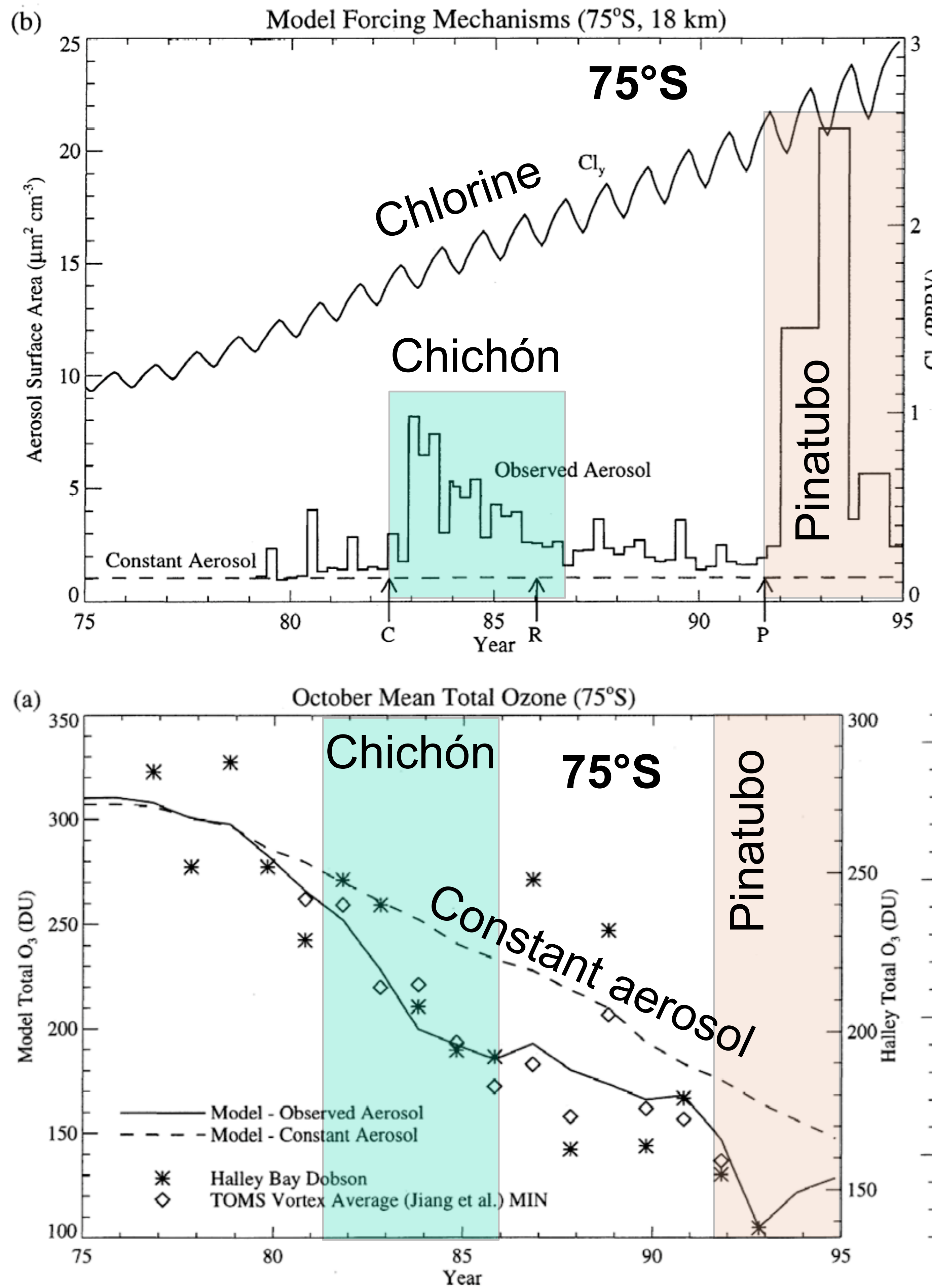

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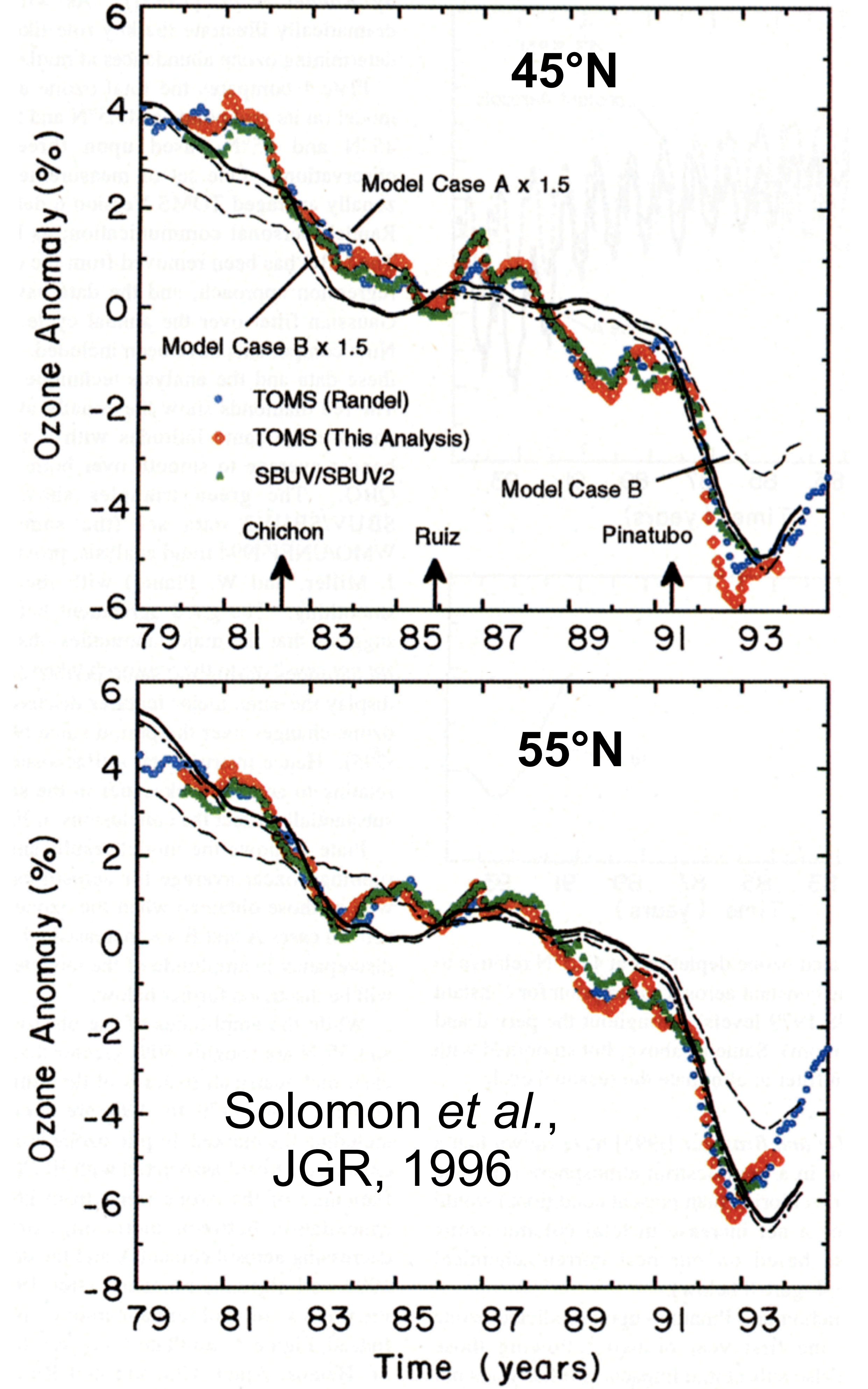
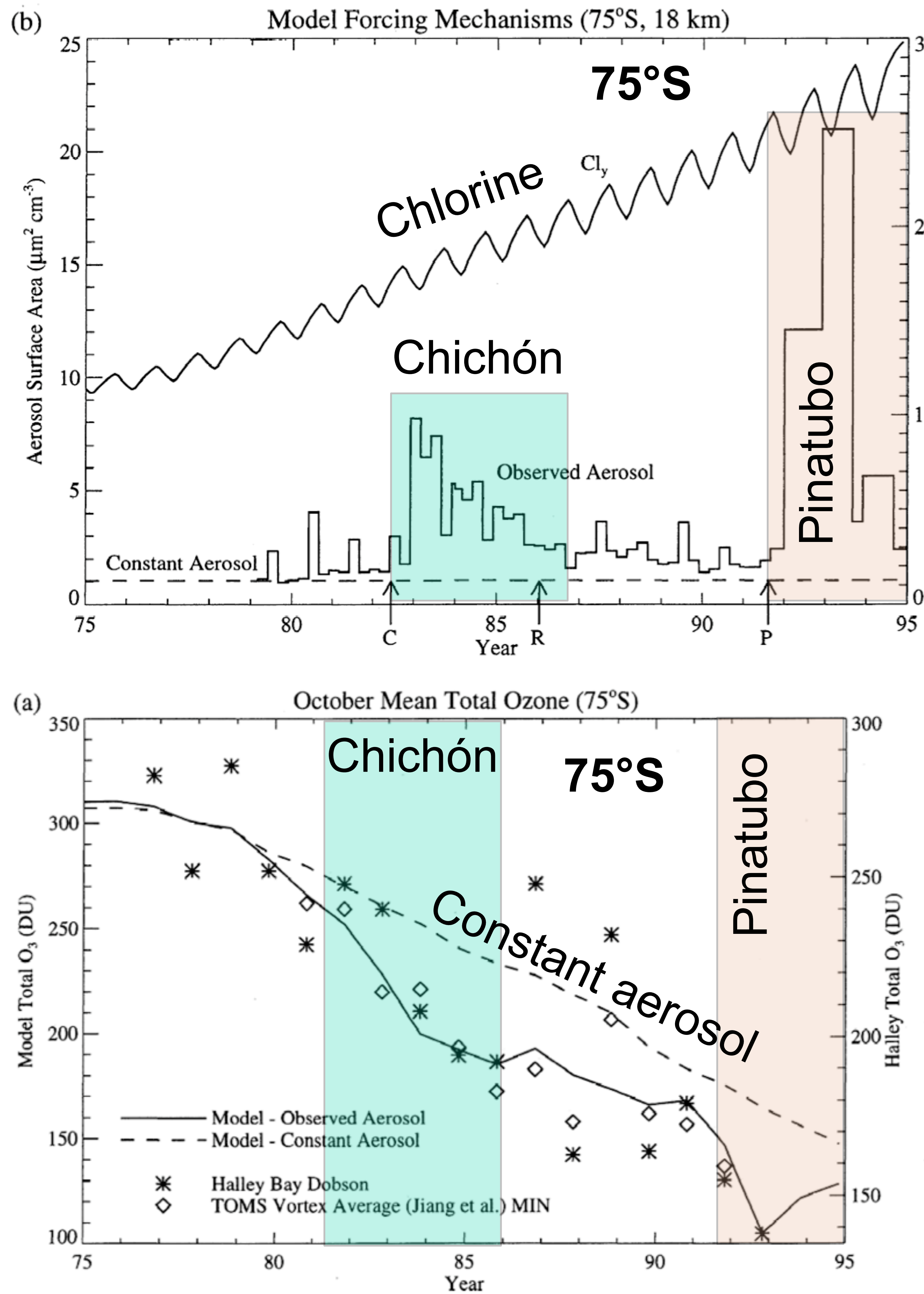


Solomon *et al.*, JGR, 1996



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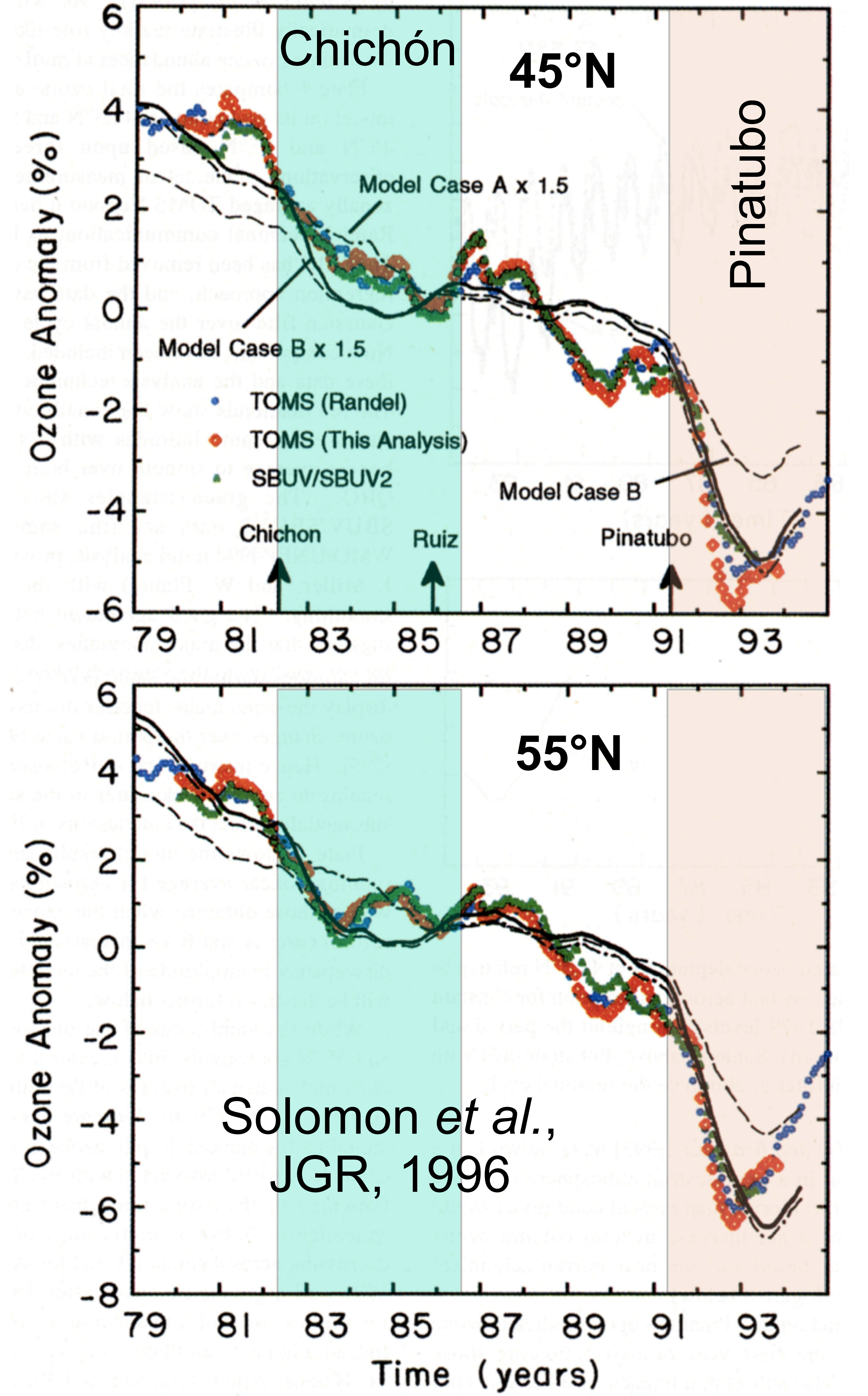

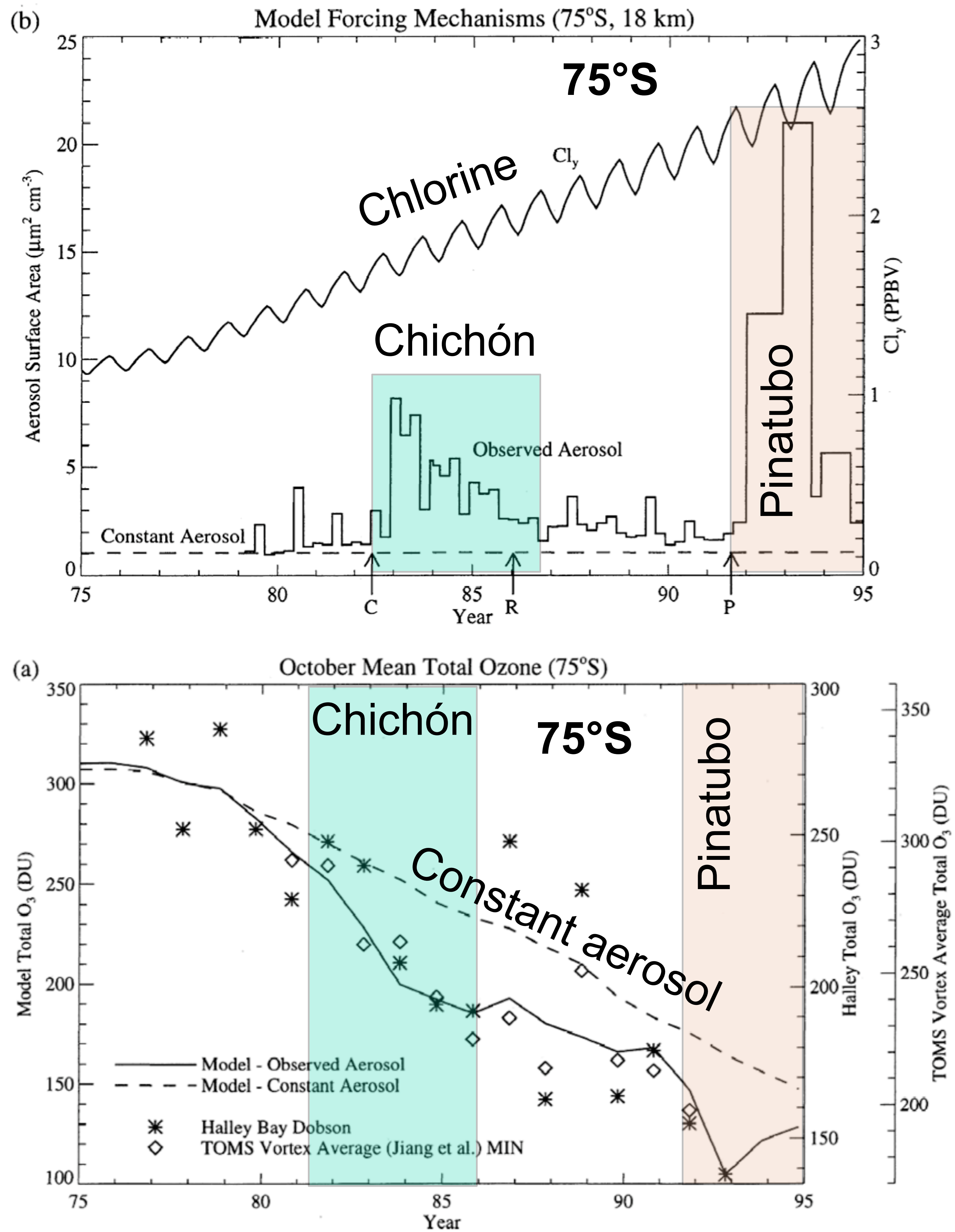

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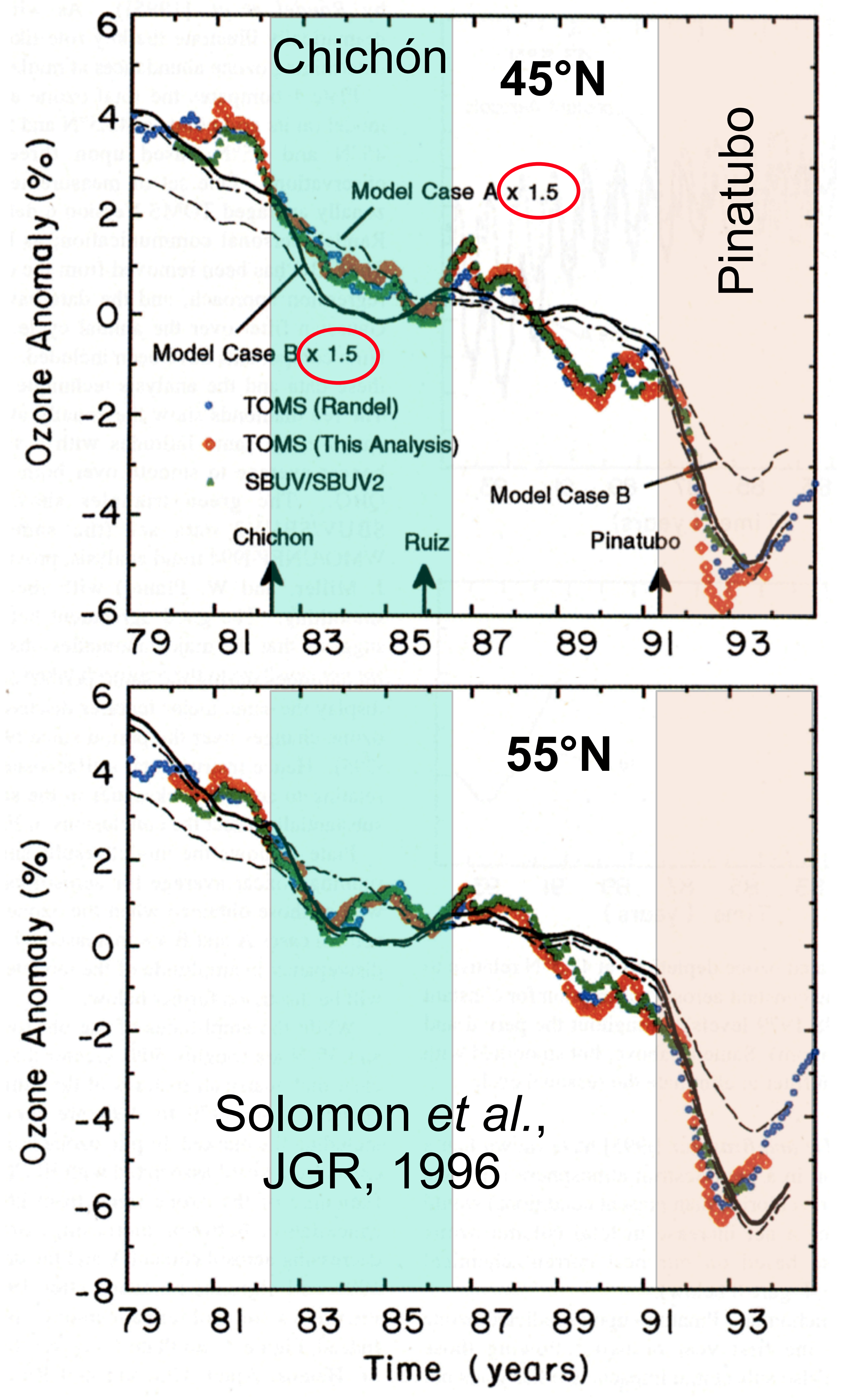


JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 101, NO. D3, PAGES 6713–6727, MARCH 20, 1996

The role of aerosol variations in anthropogenic ozone depletion at northern midlatitudes

S. Solomon,[1] R. W. Portmann,[1,2] R. R. Garcia,[3] L. W. Thomason,[4] L. R. Poole,[4] and M. P. McCormick[4]

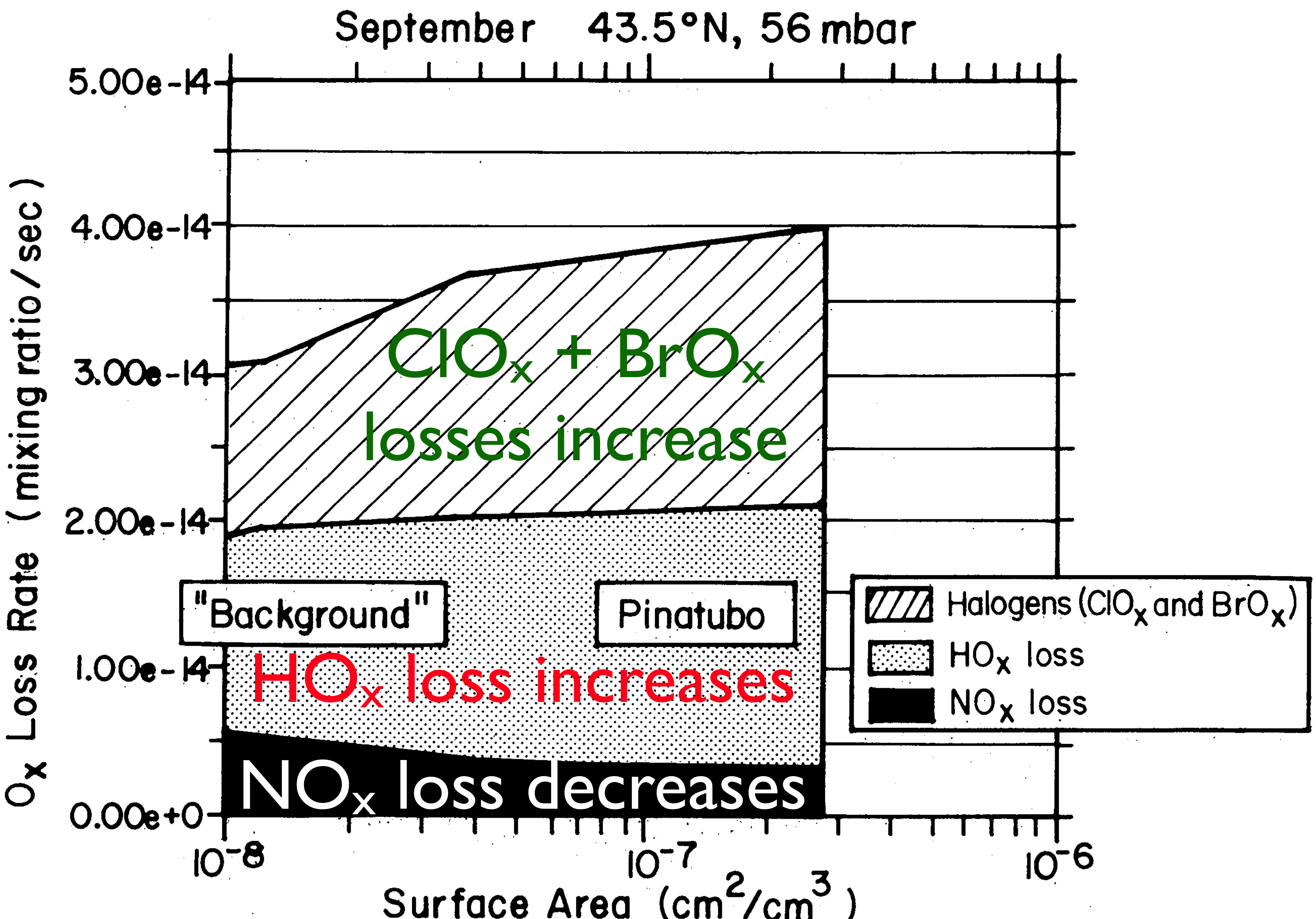
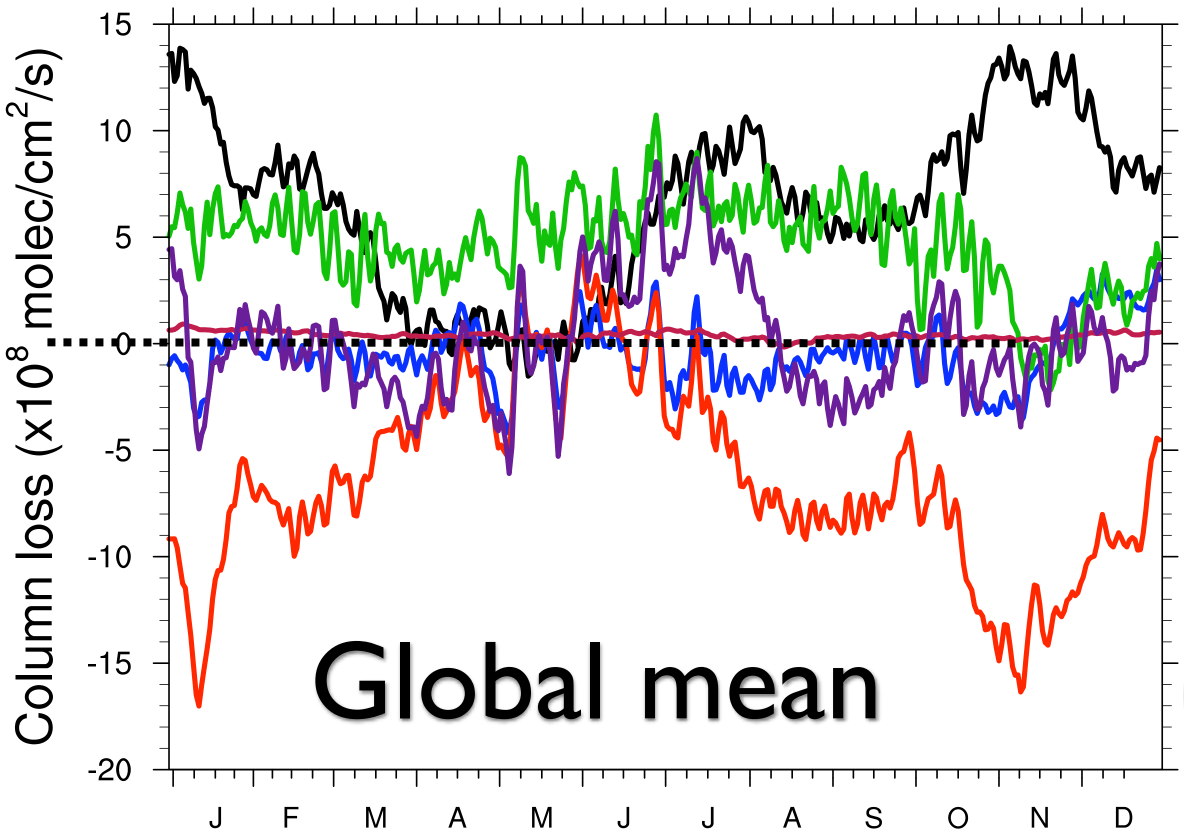


Figure 7. Calculated odd oxygen loss rates versus surface area at 43.5°N near 20 km (56 mbar) for 1990 levels of total chlorine and bromine, for NO_x, HO_x, and halogen chemistry.

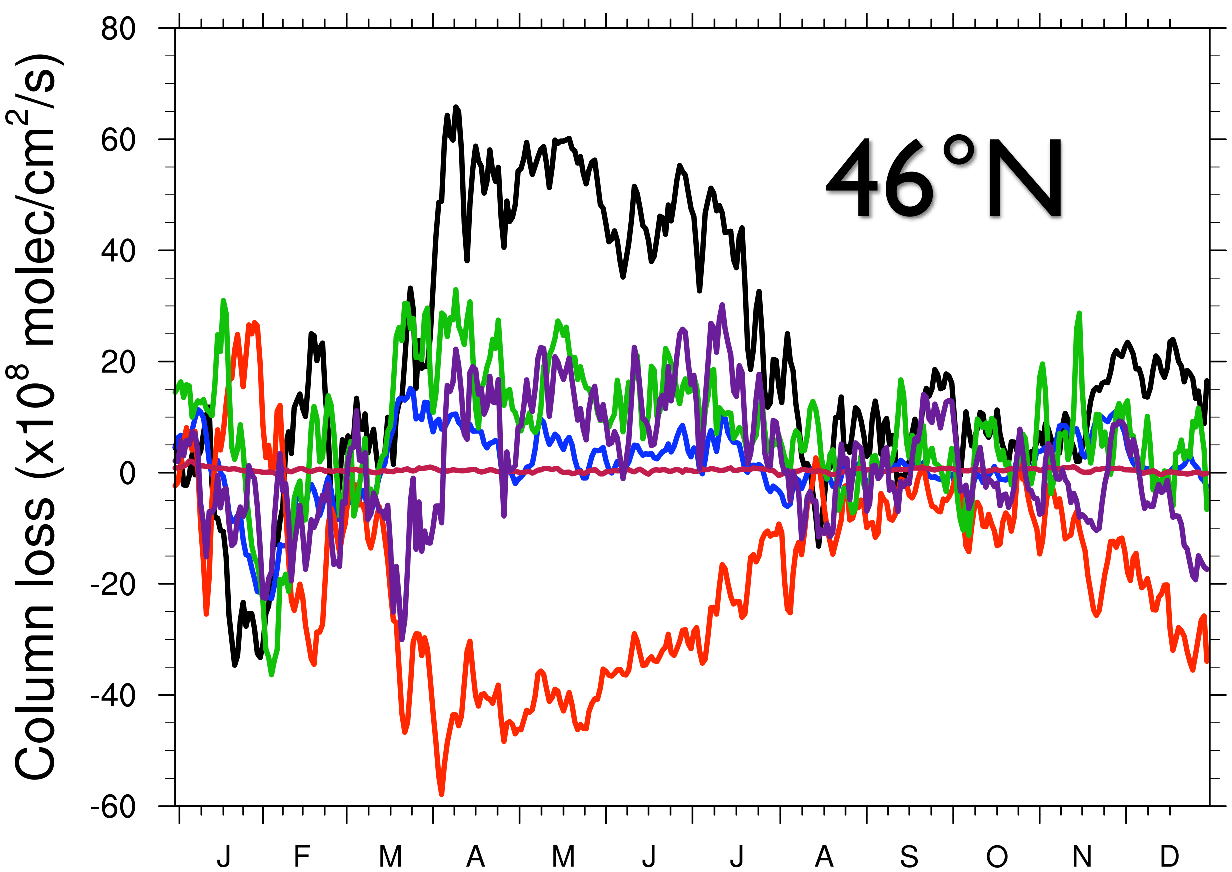
WACCM3/CARMA with 50x OCS

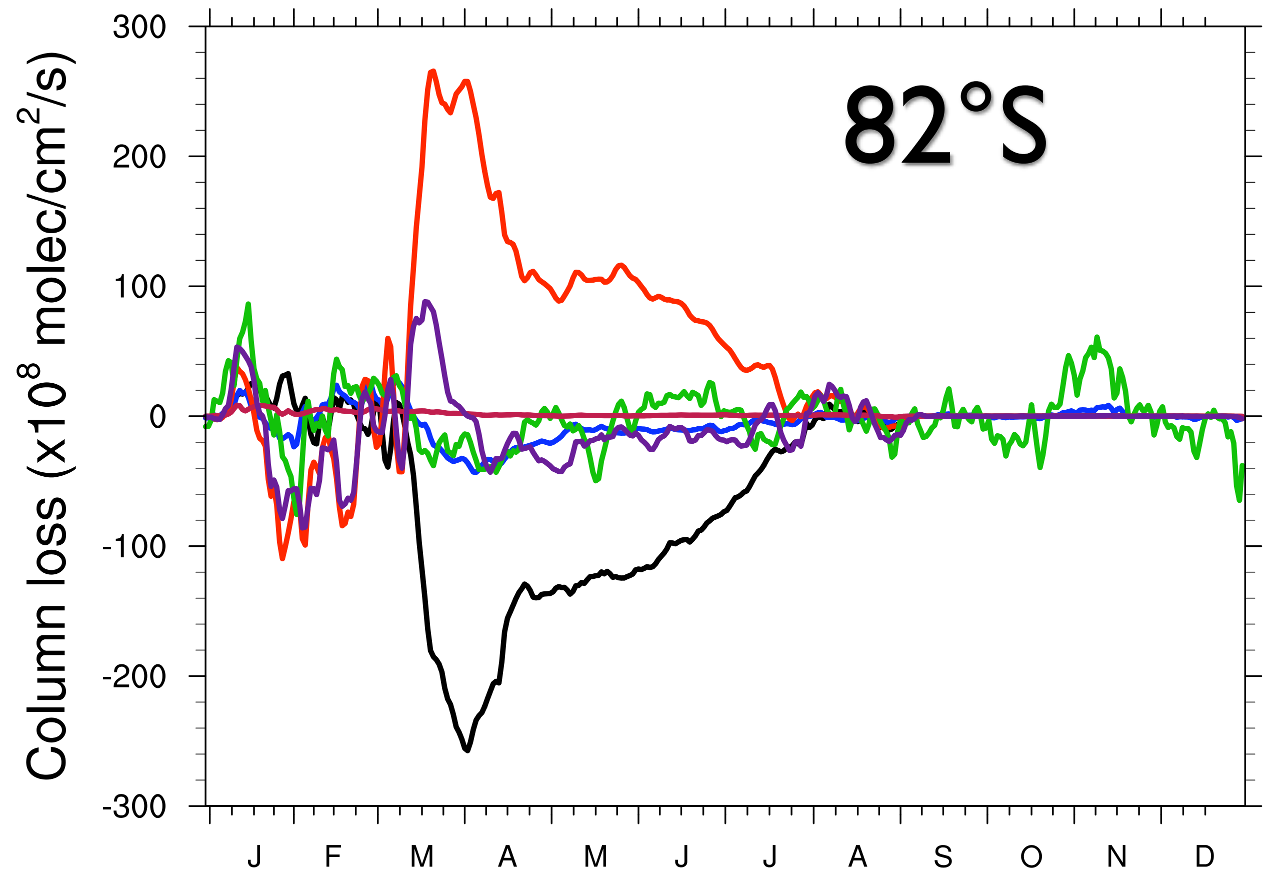
Changes to O_x Column Loss Rates for 1995 conditions



ClOx
HOx
BrO_x
O_x
NO_x
ClO_x+NO_x

ClO_x increases offset by NO_x decreases. HO_x increases produce global loss.





Impacts on stratospheric H_2O?

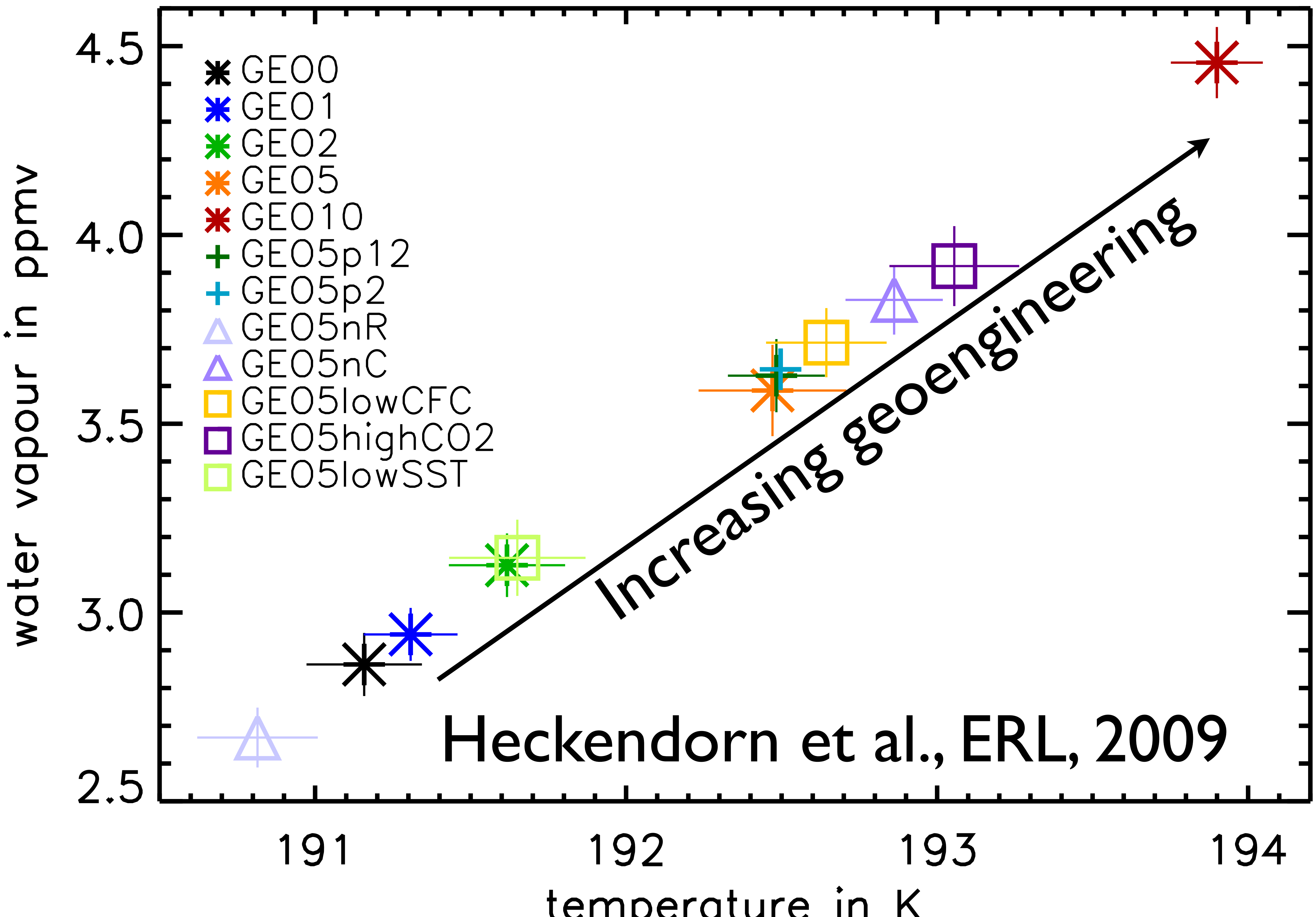


Figure 9. Annual mean water vapour in relation to annual mean temperature, both at 90 hPa at the equator, i.e. close to the tropical tropopause. The slope of this relationship is in good agreement with the Clausius–Clapeyron equation of water vapour pressure over ice.

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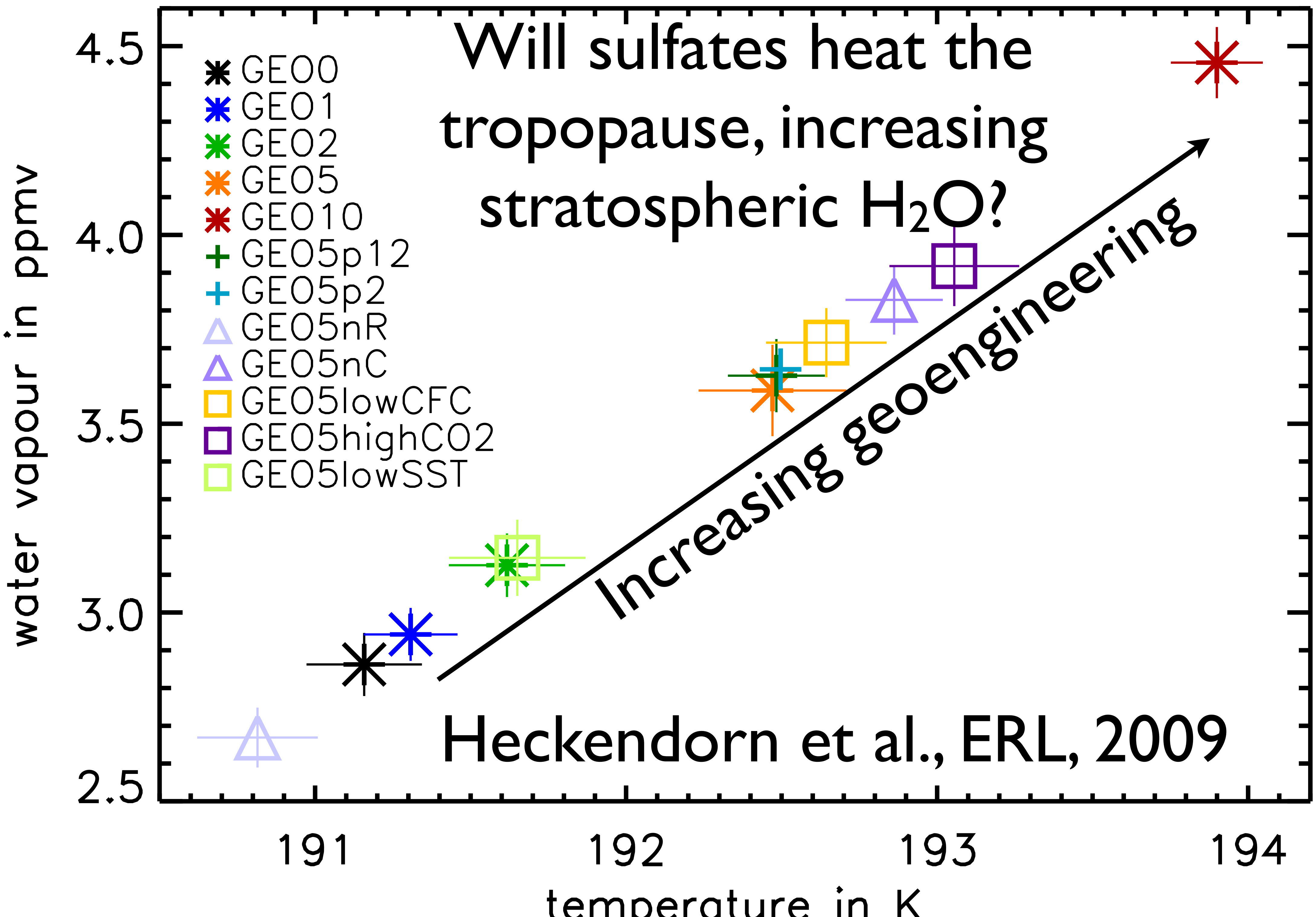

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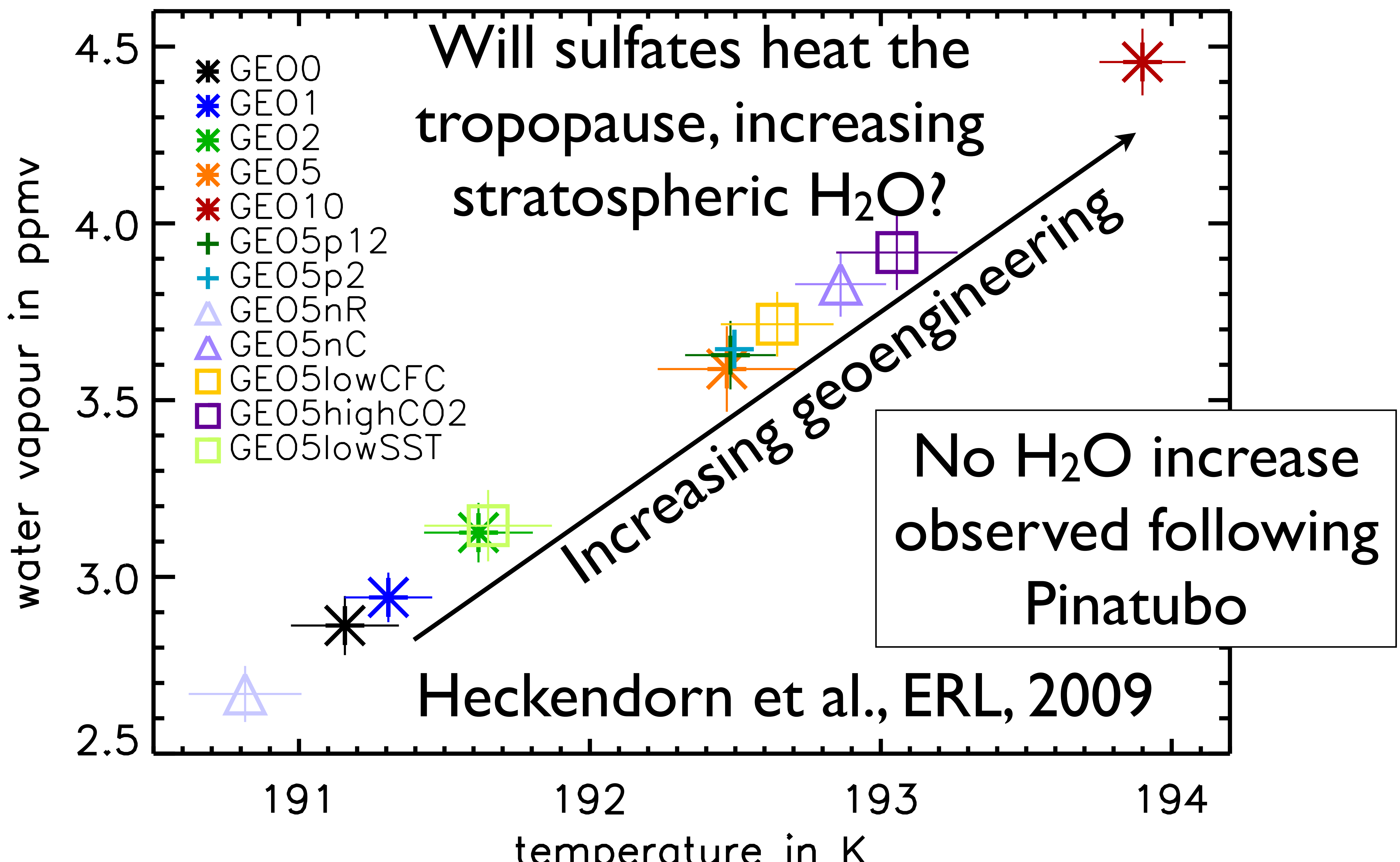

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Summary

- Stratospheric aerosol impacts ozone chemistry differently with latitude:
  - Polar regions: directly activates ClO_x & BrO_x
  - Mid-latitudes: reduces NO_x, which releases active ClO_x, BrO_x, & HO_x
    - Saturation: impact greatest for increases at low aerosol levels
- Present-day conditions: ClO_x, BrO_x, & HO_x increases more than offset NO_x decreases, producing a net O_3 loss
- Future low halogen conditions: O_3 may increase due to reduces NO_x loss
- Impacts on stratospheric water vapor uncertain

Extra Slides

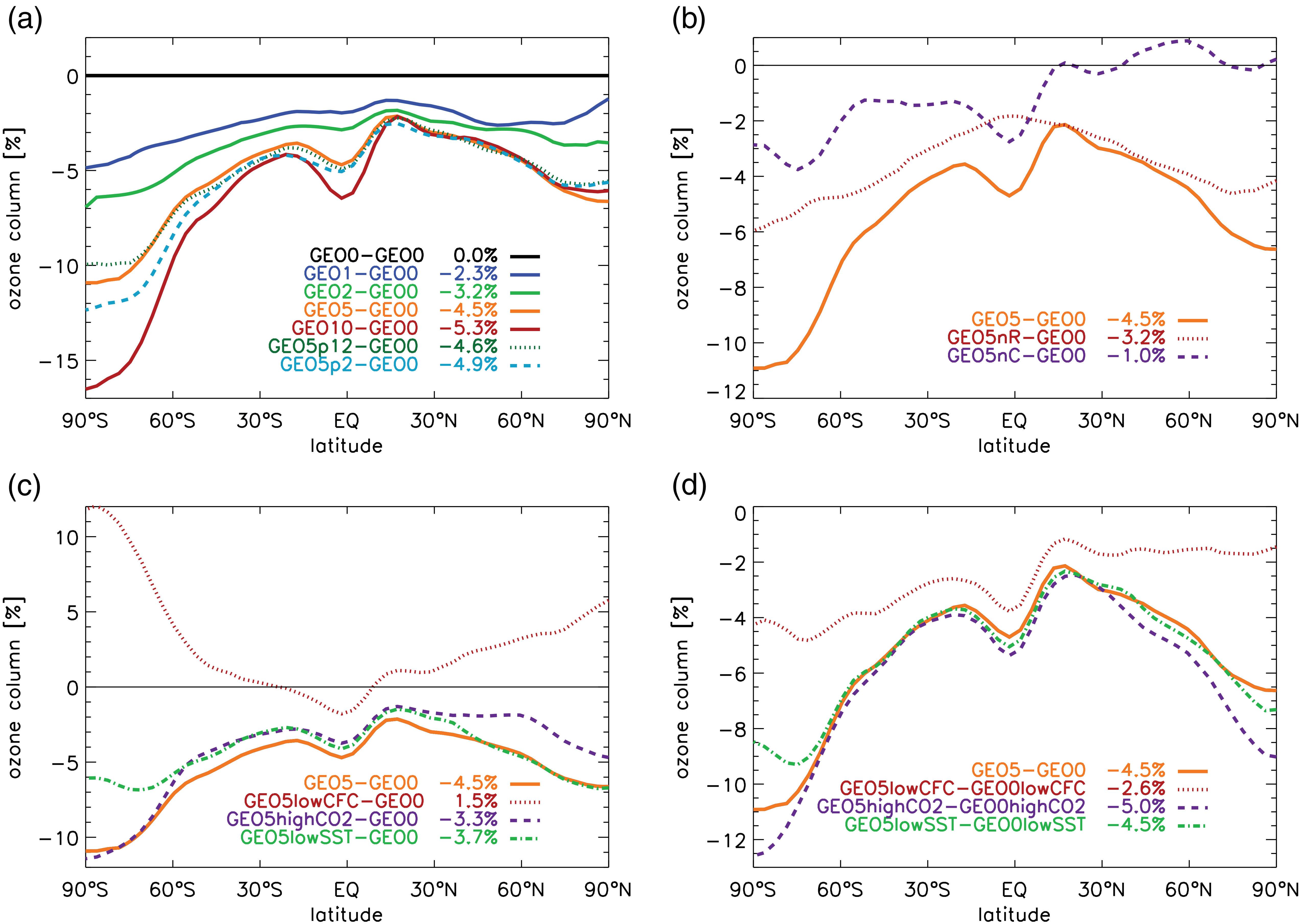
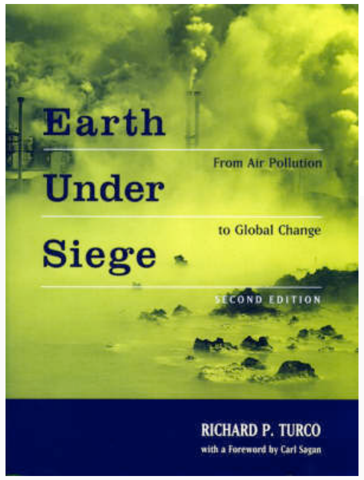


Figure 6. Predicted geoengineering-induced changes in annual mean zonal mean total ozone column. Listed values show annual global mean values. (a) Standard scenarios (solid curves) and pulsed scenarios (dotted: monthly; dashed: semiannually) relative to GEO0. (b) Scenarios with no surface enhancement (nC) and no radiative enhancement (nR) relative to GEO0. (c) Special scenarios with low CFC, high CO_2 or low SST relative to GEO0. (d) Same as in (c), but relative to special scenarios without geoengineering. The orange GEO5–GEO0 curve is shown in all panels for clarity.



Cheap Sulfate Geoengineering with **OCS**

(Richard Turco, *Earth Under Siege*, 1997)