

- Know the temperature profile of the atmosphere and the reasons for it.
- Be able to convert units.
- Know the concept of lifetime and what it depends on.
- Know the carbon, sulfur and nitrogen compounds present in the atmosphere.

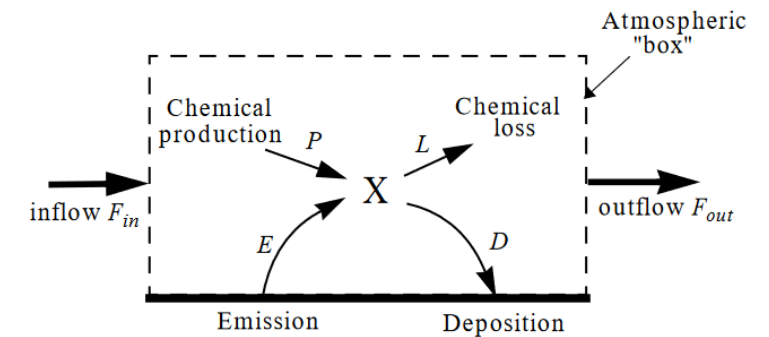
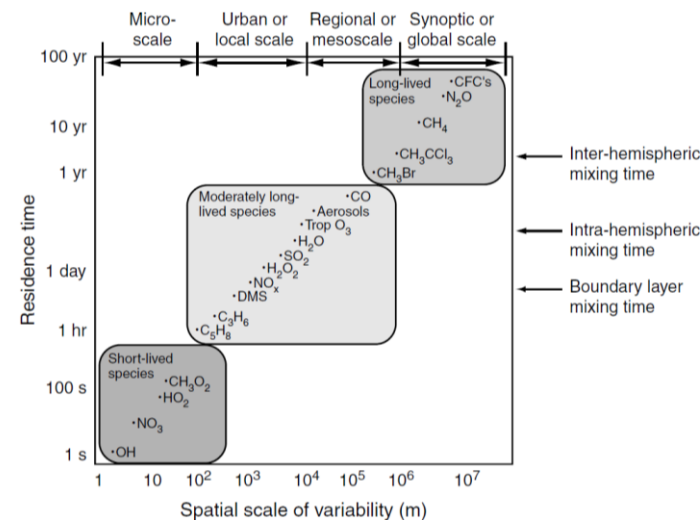
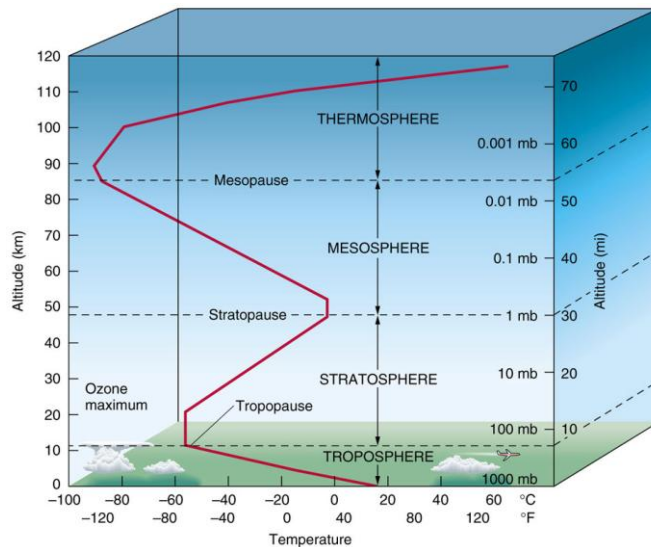


Figure 3-1 One-box model for an atmospheric species X

# Stratospheric Chemistry

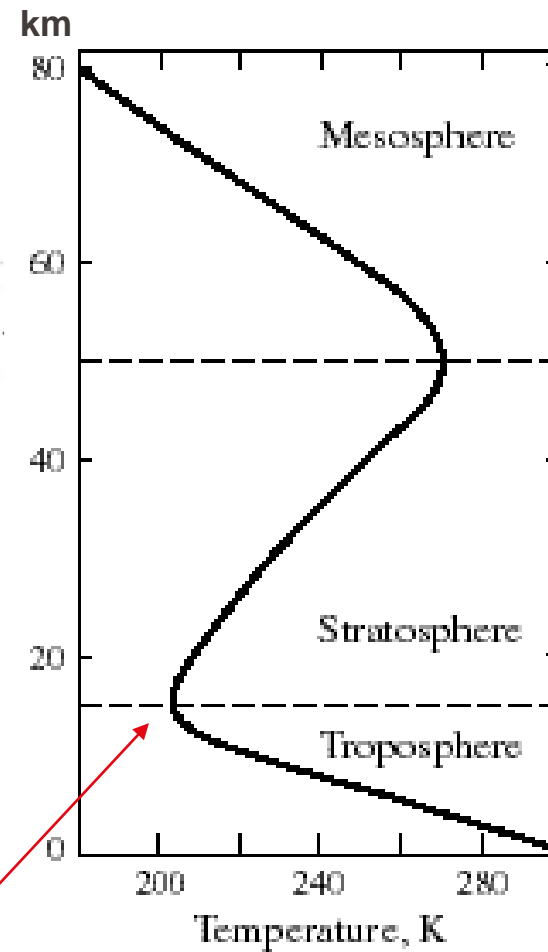
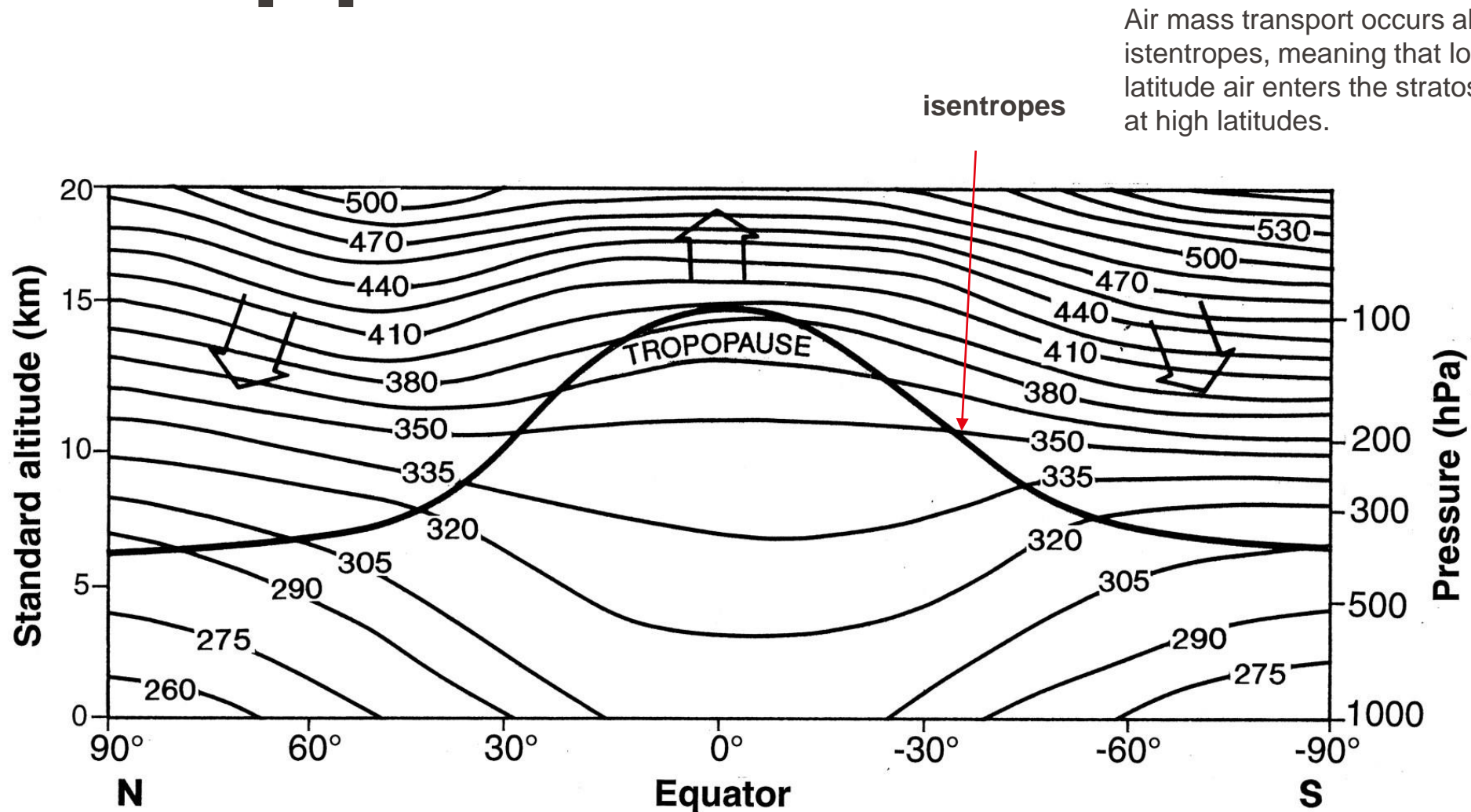
- Stratospheric circulation
- Ozone chemistry
  - Chapman reactions
  - Catalytic cycles
  - Ozone hole
  - Polar stratospheric clouds
- Junge Layer

# «Discovery» of the Stratosphere

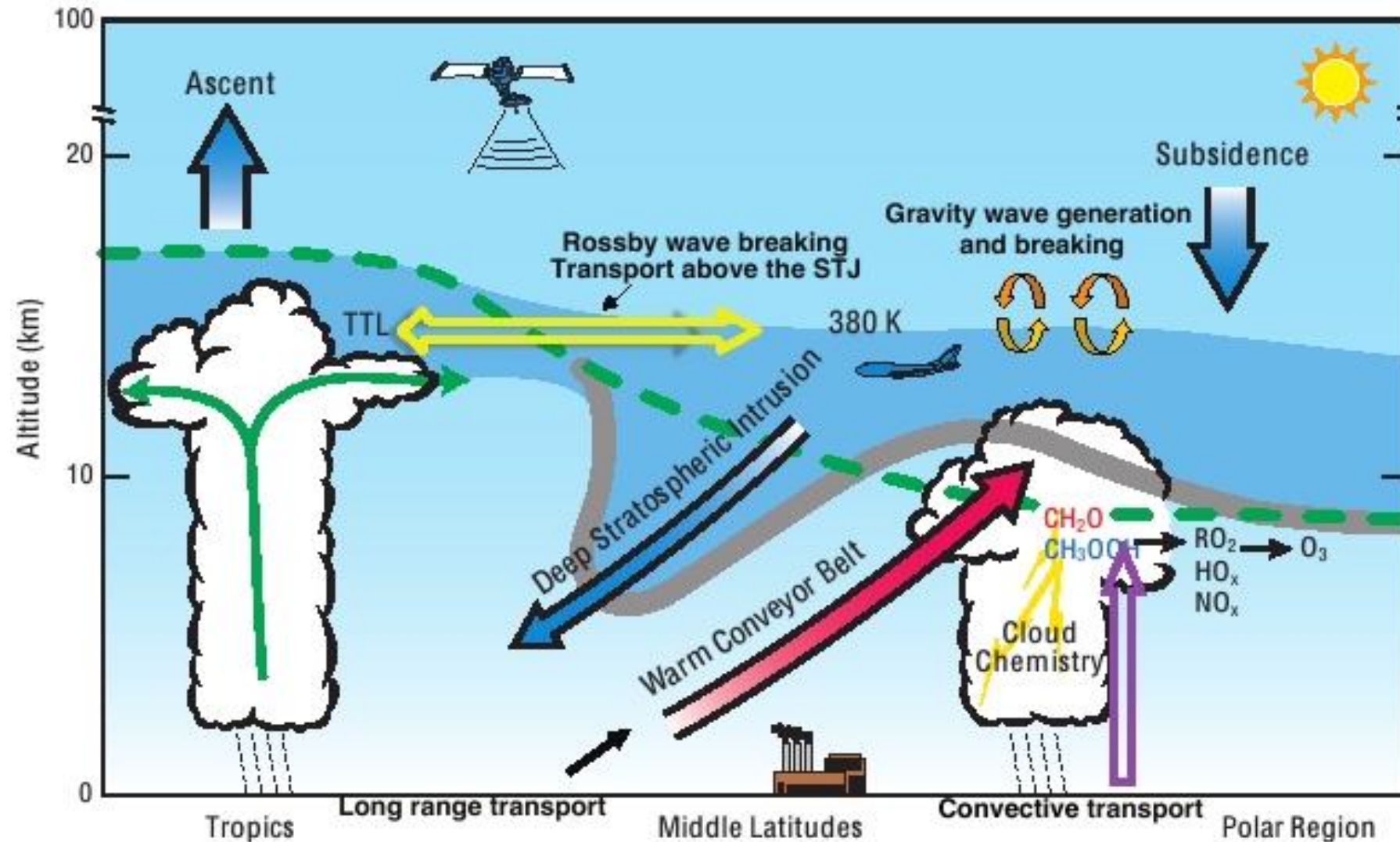


- In 1901, balloon flight to 10.5 km altitude by Reinhard Süring and Arthur Berson of the Prussian Royal Meteorological Institute
- 5400 m<sup>3</sup> hydrogen balloon.
- Objective: temperature measurements. No trust in measurements with balloon soundings.
- tropos (gr.) → «turbulent»  
strato (gr.) → «layered»





# Exchange processes across the tropopause



TTL : tropical transition layer  
STJ: subtropical jet

Water vapor, ozone, aerosols and cirrus cloud in the upper troposphere and lower stratosphere (UTLS) region, controlled by these coupled processes, have important impacts on the Earth's radiation budget.

# Brewer Dobson Circulation

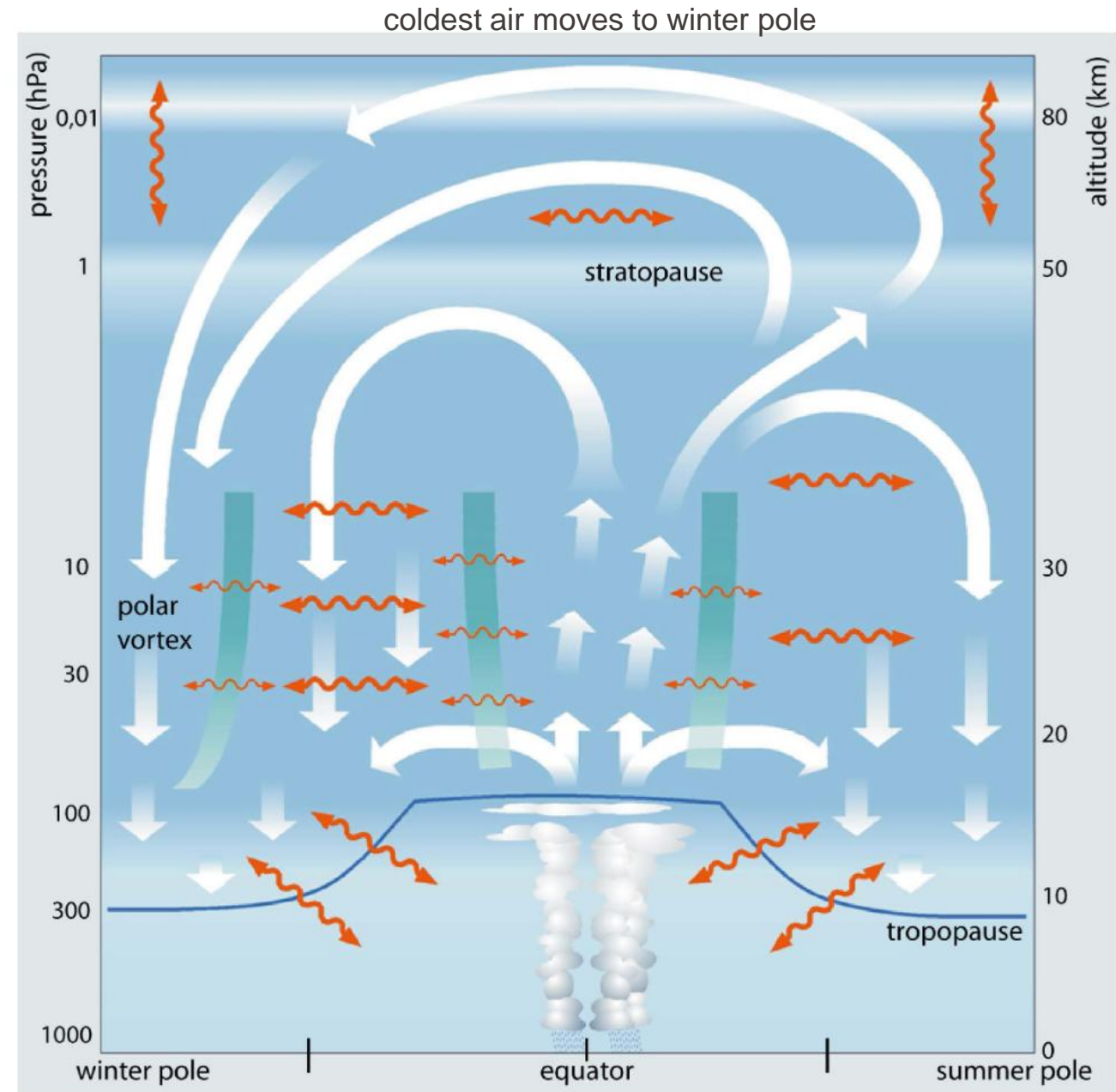
Fig. 1. Schematic of the Brewer Dobson Circulation as the combined effect of residual circulation and mixing in the stratosphere and mesosphere.

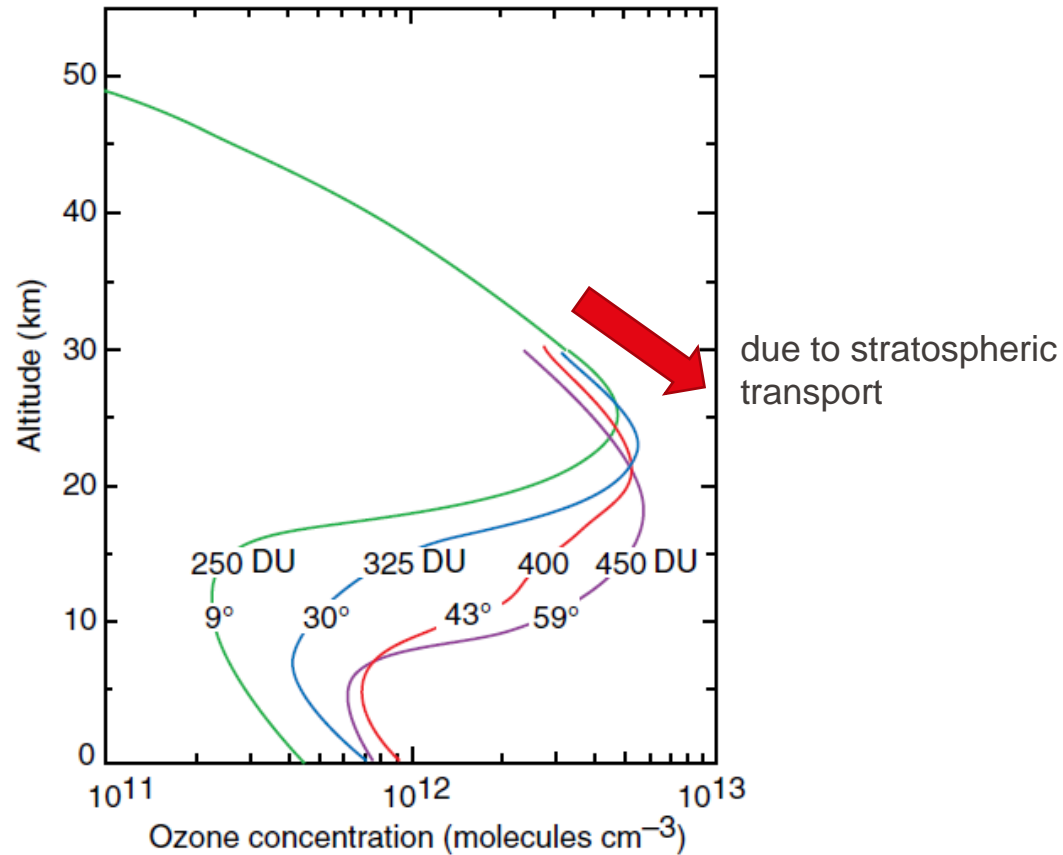
- The thick white arrows depict the general air mass movement as representation of the residual circulation,
- the wavy orange arrows indicate two-way mixing processes.

Both, circulation and mixing are mainly induced by wave activity on different scales (planetary to gravity waves).

- The thick green lines represent stratospheric transport and mixing barriers.

The Figure is by courtesy of Dr. U. Schmidt and it is adapted from a non peer-reviewed research report of our institute.





- It forms a protective shield that reduces the intensity of UV radiation (with wavelengths between 0.23 and 0.32  $\mu\text{m}$ ) from the sun that reaches the Earth's surface.
- Because of the absorption of UV radiation by  $\text{O}_3$ , it determines the vertical profile of temperature in the stratosphere.
- It is involved in many stratospheric chemical reactions.
- 90 % of atmospheric  $\text{O}_3$  is in stratosphere

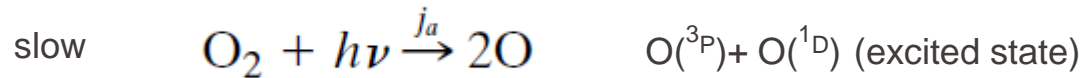


# Chapman reactions

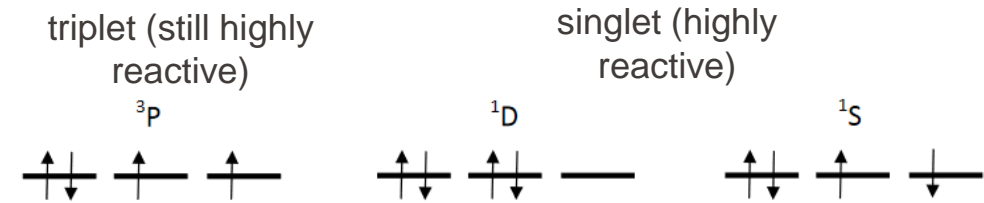
Assumption: oxygen only atmosphere

Note: reaction coefficients depend on temperature

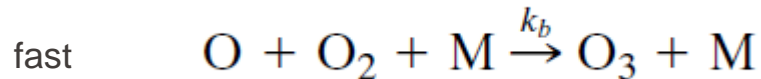
## A. Dissociation of O<sub>2</sub> by UV ( $0.180 \leq \lambda \leq 0.240 \mu\text{m}$ )



4 electrons of the 2p - orbital

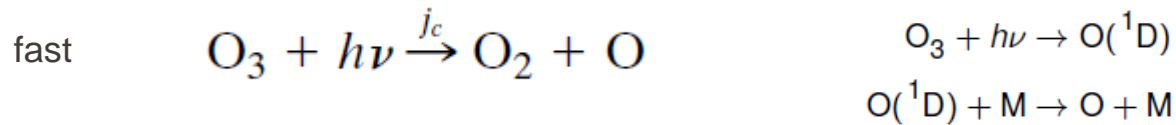


## B. Atomic O and O<sub>2</sub> react to form O<sub>3</sub> (M is N<sub>2</sub> or O<sub>2</sub>) Occurs more rarely than often.

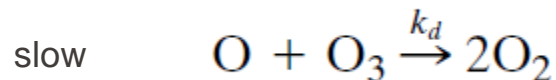


*Needs M to absorb excess energy to form a stable O<sub>3</sub> molecule. Hence time constant increases with altitude, i.e becomes slower.*

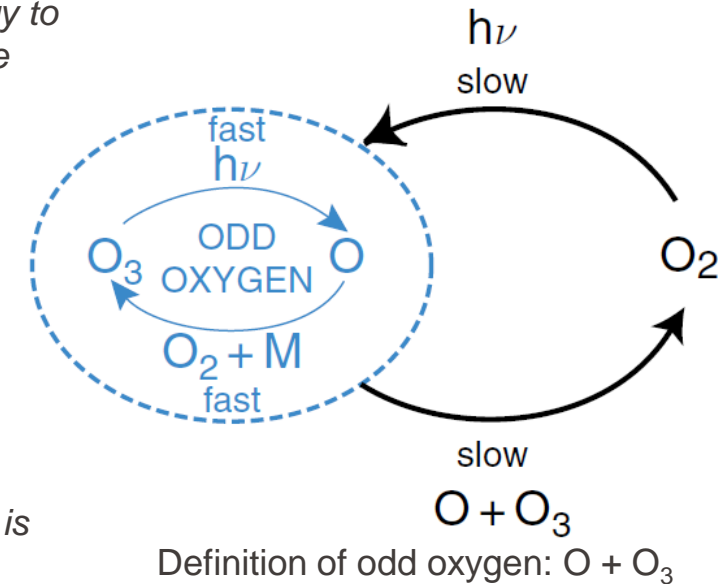
## C. O<sub>3</sub> undergoes photodissociation ( $0.200 \leq \lambda \leq 0.300 \mu\text{m}$ )



## D. Atomic O and O<sub>3</sub> combine to form O<sub>2</sub>



*Reaction becomes faster with higher altitude, because more O is available there.*

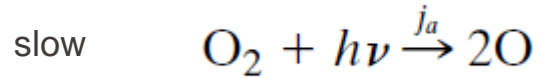


Can be catalytically accelerated by hetero atmos (e.g. Cl, Br).

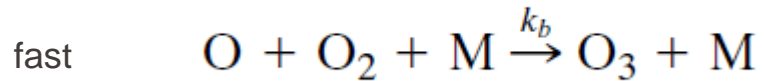
# Is there a diurnal cycle of O<sub>3</sub> in the stratosphere?

- A. No.
- B. Yes.
- C. A small one.

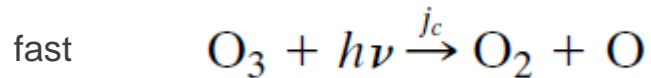
A. Dissociation of O<sub>2</sub> by UV ( $0.180 \leq \lambda \leq 0.240 \mu m$ )



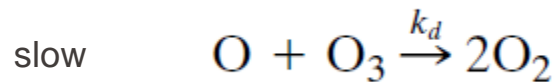
B. Atomic O and O<sub>2</sub> react to form O<sub>3</sub> (M is N<sub>2</sub> or O<sub>2</sub>)  
Occurs more rarely than often.



C. O<sub>3</sub> undergoes photodissociation ( $0.200 \leq \lambda \leq 0.300 \mu m$ )

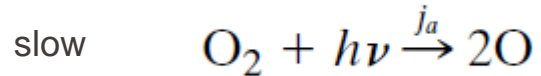


D. Atomic O and O<sub>3</sub> combine to form O<sub>2</sub>

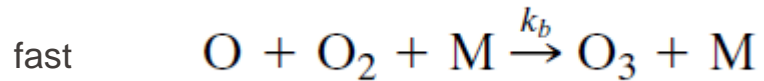


# Is there a diurnal cycle of $O_3$ in the stratosphere?

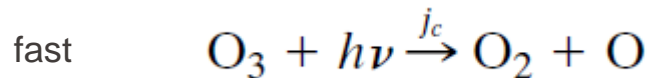
A. Dissociation of  $O_2$  by UV ( $0.180 \leq \lambda \leq 0.240 \mu m$ )



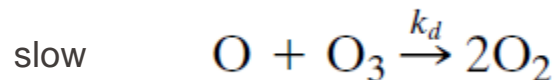
B. Atomic O and  $O_2$  react to form  $O_3$  (M is  $N_2$  or  $O_2$ )  
Occurs more rarely than often.



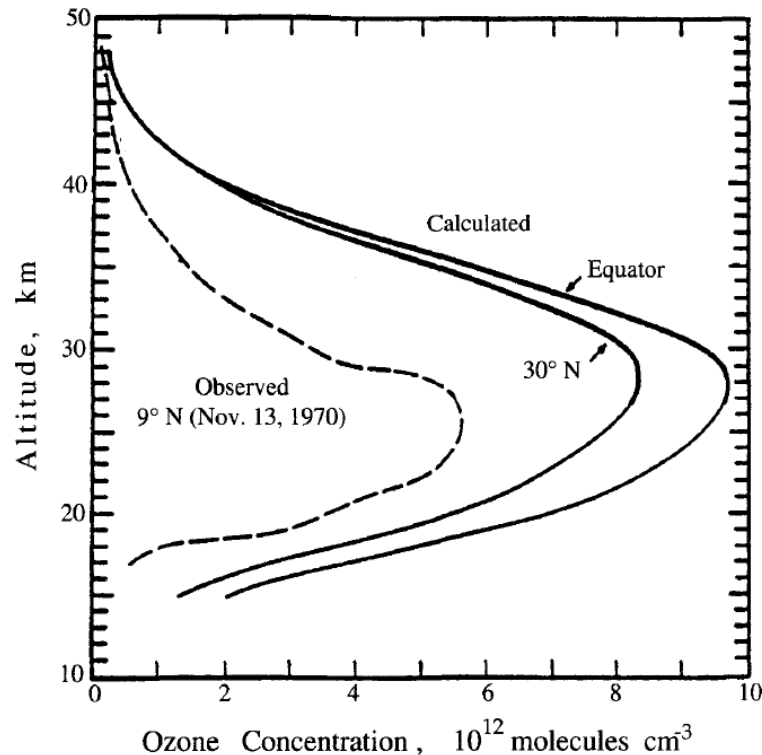
C.  $O_3$  undergoes photodissociation ( $0.200 \leq \lambda \leq 0.300 \mu m$ )



D. Atomic O and  $O_3$  combine to form  $O_2$



- Stratospheric  $O_3$  concentrations exhibit minor diurnal variations with time of day.
- After sunset, both the source (A) and the sink of  $O_3$  (C) are switched off, and the remaining O atoms are then converted to  $O_3$  within a minute or so by (B).
- When the sun rises, some of the  $O_3$  molecules are destroyed by (C) but they are reformed by (A) followed by (B).



**FIGURE 5.5** Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9°N) on November 13, 1970.

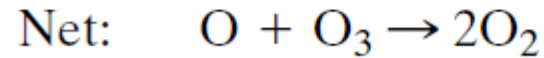
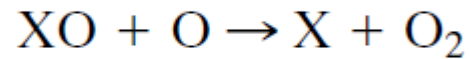
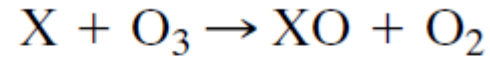
Seinfeld and Pandis, 2006, p. 150

- Chapman reactions predict the shape of the vertical profile correctly.
- They overestimate  $\text{O}_3$  concentration by a factor of two in the tropics and underestimate  $\text{O}_3$  in the higher latitudes.
- The rate of production is too high compared to the actual measured concentration.
- $\text{O}_3$  concentrations are not increasing, hence there must a sink for odd oxygen.



Catalytic cycles of  $\text{O}_3$  depletion involving H, OH, Cl, Br.





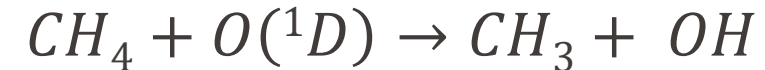
- X catalyst
- XO intermediate product
- Reactions are fast
- Since X is recycled, only a small concentration is sufficient to remove odd oxygen.

X =	altitude
*	lower stratosphere
**	below 30 km
OH	below ~40 km
NO	middle stratosphere
Cl	middle and upper stratosphere

\*, \*\* atomic oxygen is scarce

**Hydrogen species as candidate for O destruction: OH, HO<sub>2</sub> (HO<sub>x</sub>)**

Three sources of OH in the stratosphere:

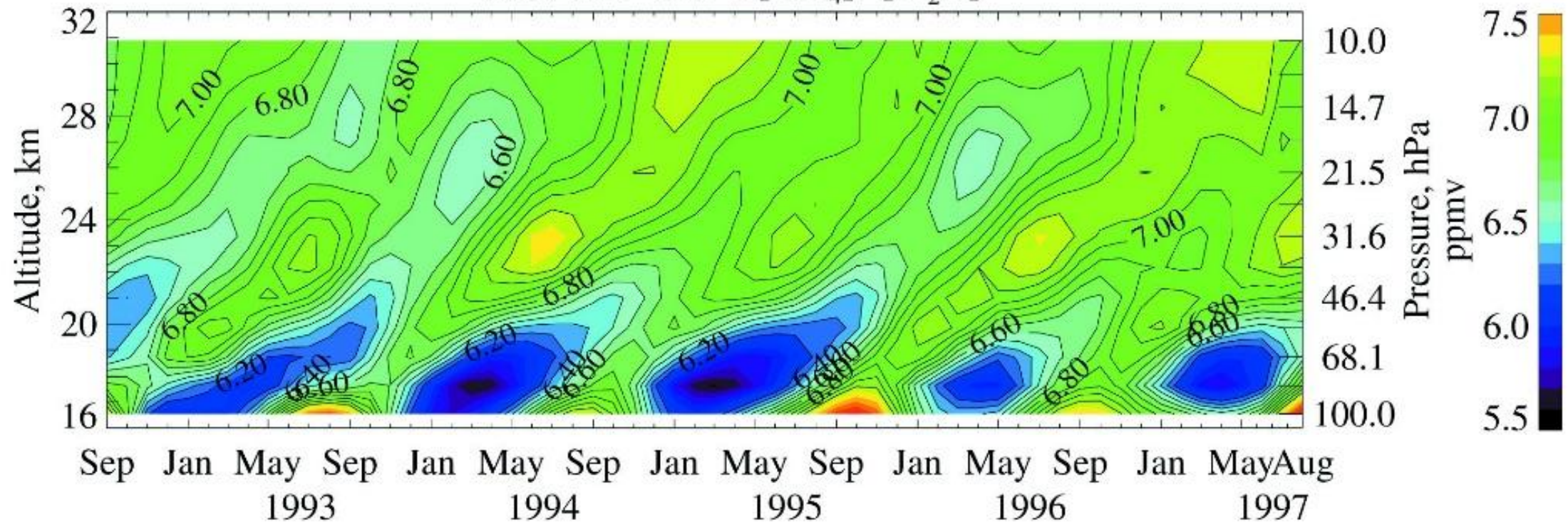


# Stratospheric tape recorder: source of water vapor and methane

Satellite data

Way of describing total hydrogen ( $H_2$ ) in stratosphere

HALOE V18  $2[CH_4] + [H_2O]$

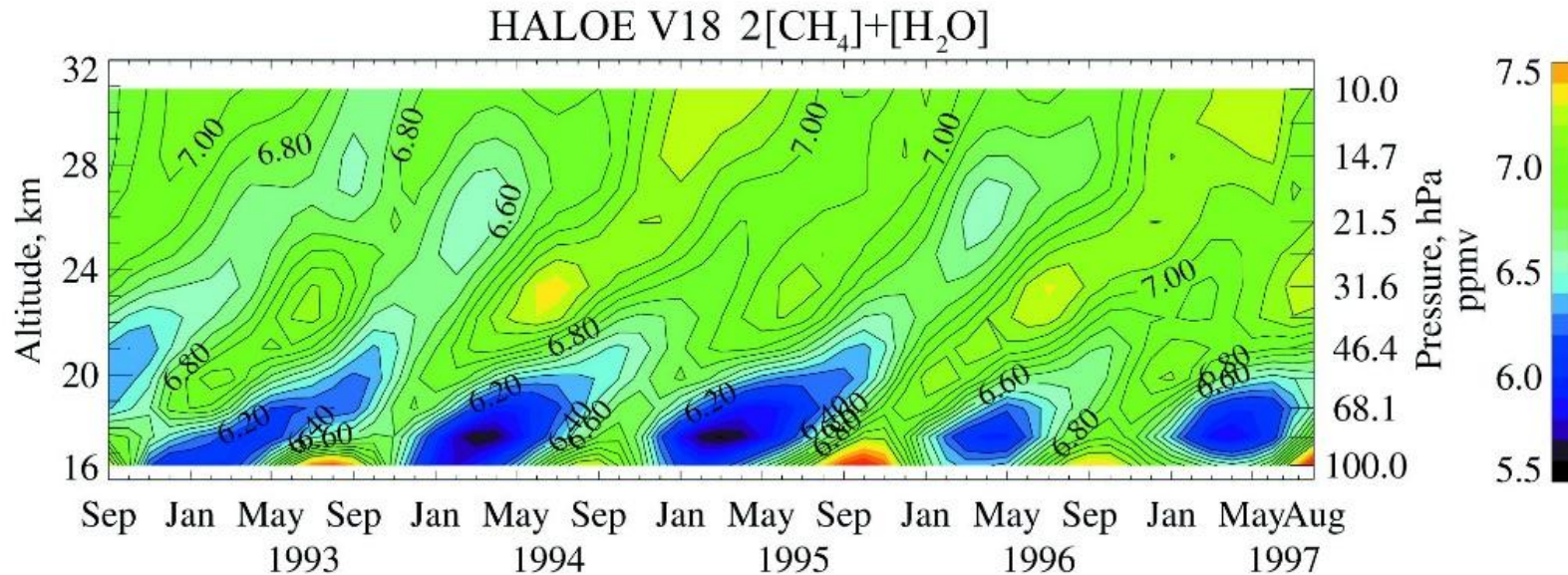


MO, Global Ozone Research and Monitoring Project-Report No. 44

Scientific Assessment of Ozone Depletion: 1998, Chapter 7, page 7.21, Fig 7-07.

# What happens in the annual cycle?

- A. There is less methane in winter because of lower emissions.
- B. There is less water vapor in summer because of more frequent rain.
- C. There is less water vapor in winter because of colder temperatures.
- D. A and C.

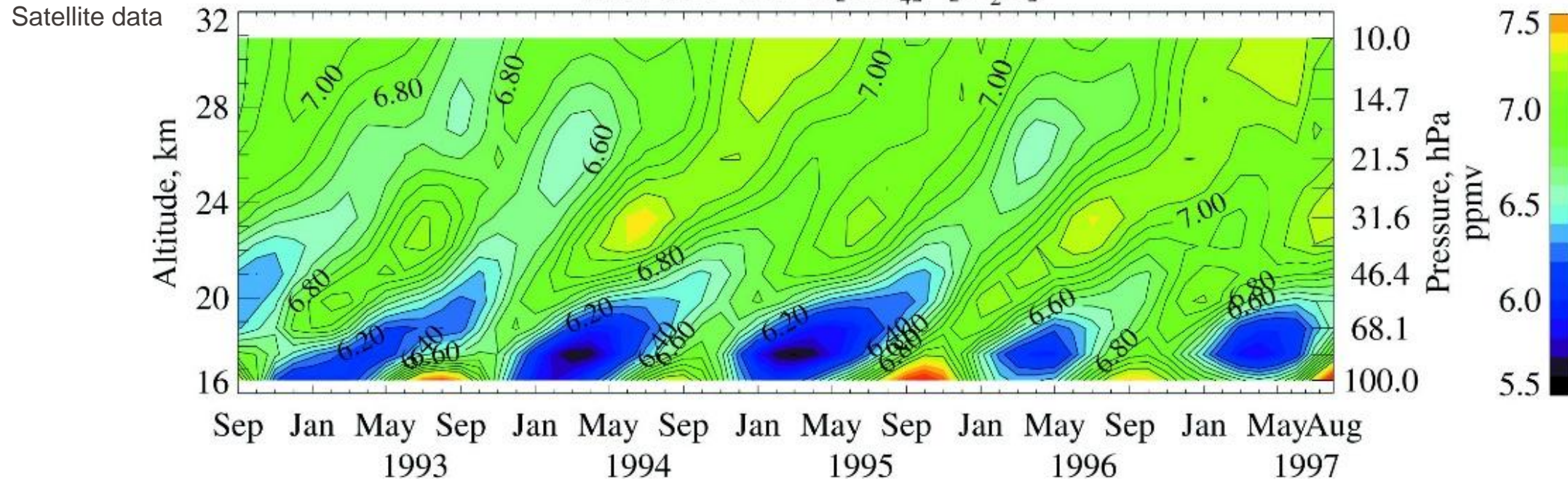




# Stratospheric tape recorder: source of water vapor and methane

Way of describing total hydrogen in stratosphere

HALOE V18  $2[\text{CH}_4] + [\text{H}_2\text{O}]$

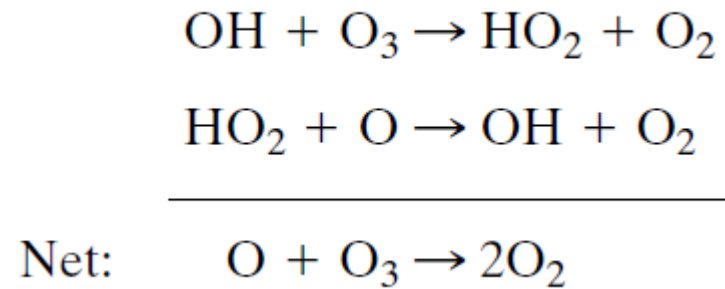


Temperatures at tropical tropopause have a yearly cycle. When they are colder, the water vapor mixing ratio is lower (condensation, ice crystal formation, precipitation). Hence less water vapor is introduced into the stratosphere. Methane is not affected by the temperature.

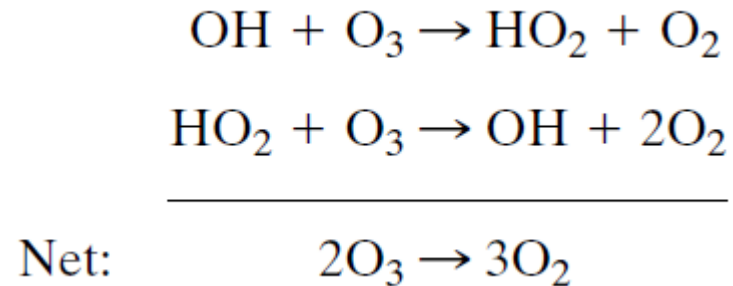
Each air mass which passes the tropopause carries that specific water vapor signature (color code, tape recorder).



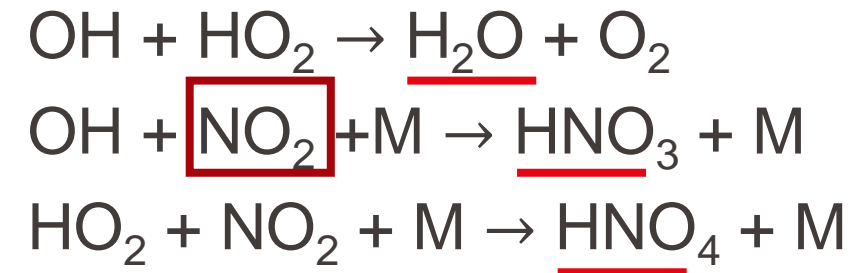
Below ~40 km where atomic oxygen is available:



Below ~30 km, where less atomic oxygen is available:



Cycle disruption by removal of HO<sub>x</sub>:

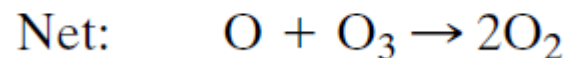
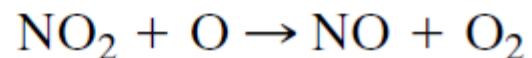
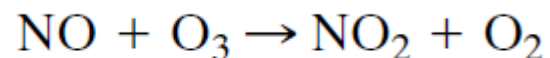


Reservoir species

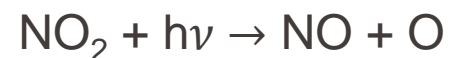
Reservoir species remove HO<sub>x</sub> from fast reaction cycles.

In analogy to HO<sub>x</sub>.

Most important in the middle stratosphere.



Cycling between NO and NO<sub>2</sub>  
(interference cycle):



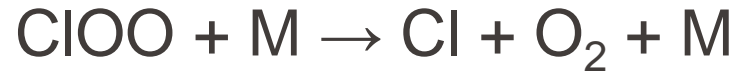
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NET: No change

Removal of NO<sub>x</sub> into **reservoir species**



# $\text{Cl}_x$ and $\text{Br}_x$ catalytic cycles



-----



Natural sources of Br and Cl are

- $\text{CH}_3\text{Br}$
- $\text{CH}_3\text{Cl}$

from oceanic, terrestrial (plants, soils) emissions.  
The methyl compounds are photolyzed by UV radiation.

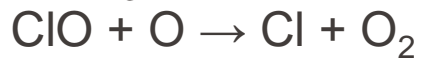
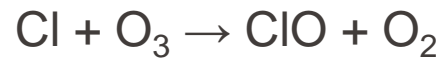
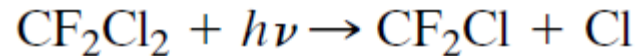
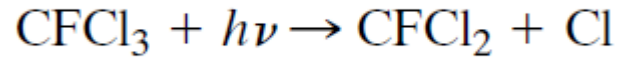


Overall, the many chemical reactions and catalytic cycles constitute a delicate equilibrium that maintains the stratospheric ozone layer.

# Anthropogenic changes to catalytic cycles

Source of  $\text{Cl}_x$  are CFCs, through photolytic generation of Cl (photodissociation)

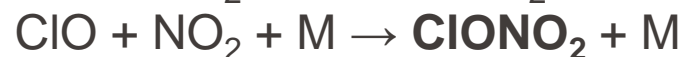
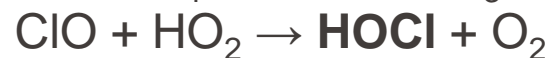
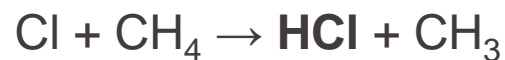
( $0.190 \leq \lambda \leq 0.220 \mu\text{m}$ ).



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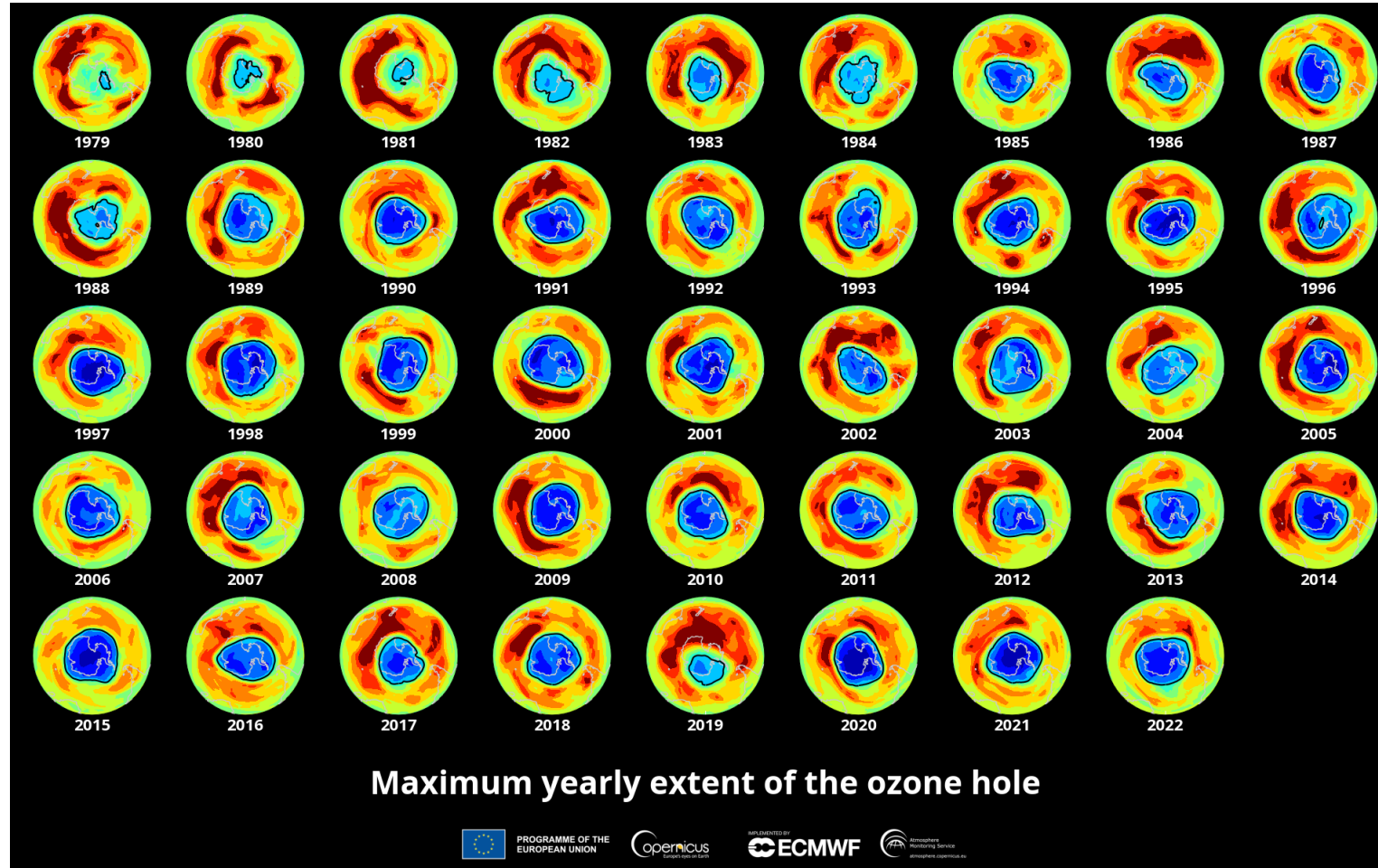


Transformation into **reservoir species**:



- CFCs originate from cooling agents and other applications. They have first been synthesized in 1928.  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$  are the most common (Freon).
- They have a long lifetime (several hundred years) because they are basically inert, only solar radiation in the stratosphere can photolyze them.
- In 1990 85 % of stratospheric chlorine originated from anthropogenic sources.
- CFCs absorb strongly in the infrared and are hence potent greenhouse gases.





Discovered by remote sensing of  $O_3$  from Halley base in 1985.

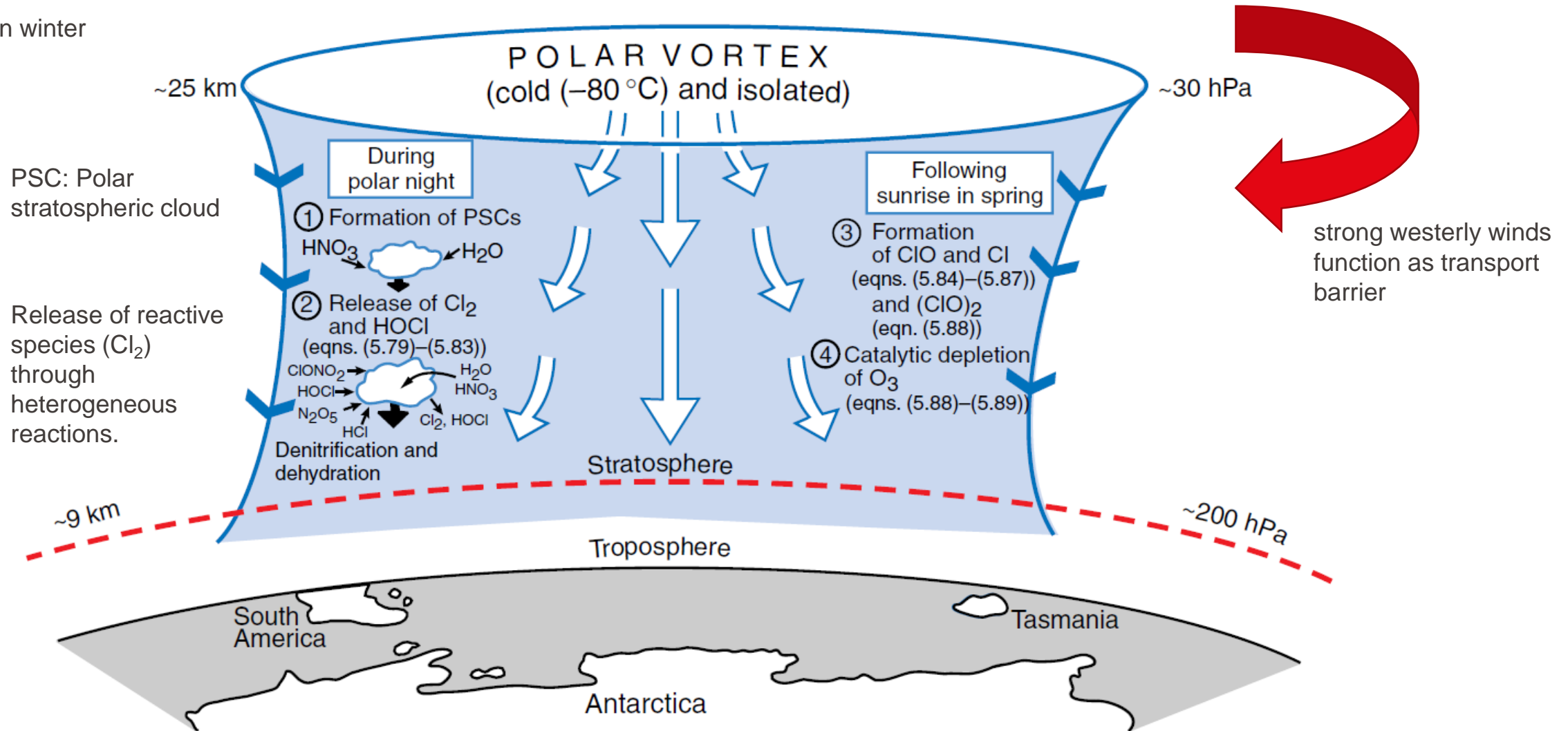


<https://atmosphere.copernicus.eu/three-peculiar-antarctic-ozone-hole-seasons-row-what-we-know>

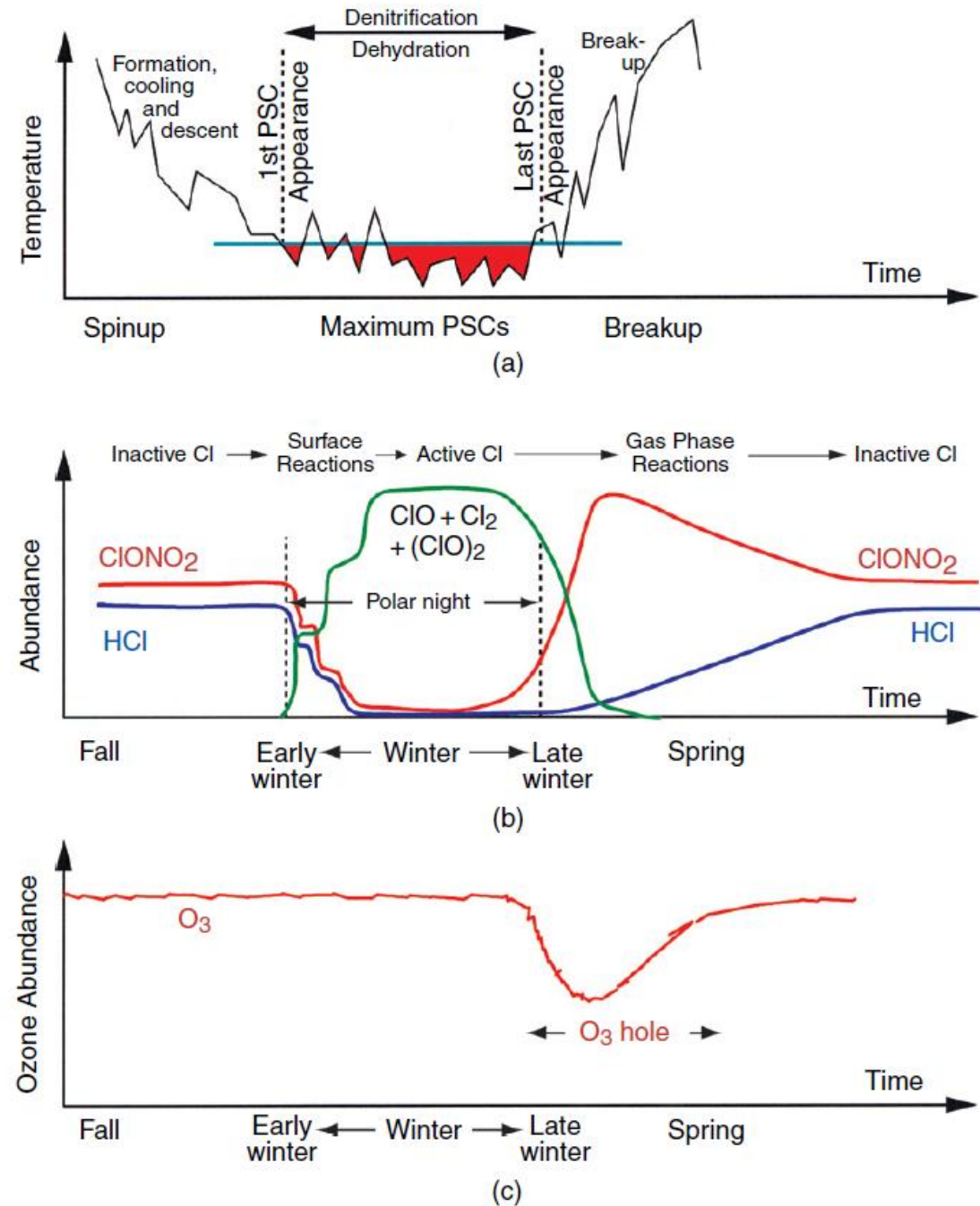
[https://twitter.com/BAS\\_News/status/298753260574097408/photo/1](https://twitter.com/BAS_News/status/298753260574097408/photo/1)

- Why over Antarctica?
- Why during spring?
- Why could models not predict it?

Builds up in winter



# Antarctic ozone destruction





- Three types of PSCs
  - Type I: forms near  $-78^{\circ}\text{C}$ , mixture of nitric acid trihydrate  $\text{HNO}_3(\text{H}_2\text{O})_3$  (NAT), and  $\text{HNO}_3\text{-H}_2\text{O-H}_2\text{SO}_4$ , particle size  $\sim 1\text{ }\mu\text{m}$ , very slow sedimentation
  - Type II: forms near  $-85^{\circ}\text{C}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}$ , sulfuric acid tetrahydrate  $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_4$  (SAT) particles  $> 10\text{ }\mu\text{m}$ , settle quickly
  - Type III: rapid freezing of  $\text{H}_2\text{O}$  due to orographic flow, (mother of pearl clouds, short-lived)

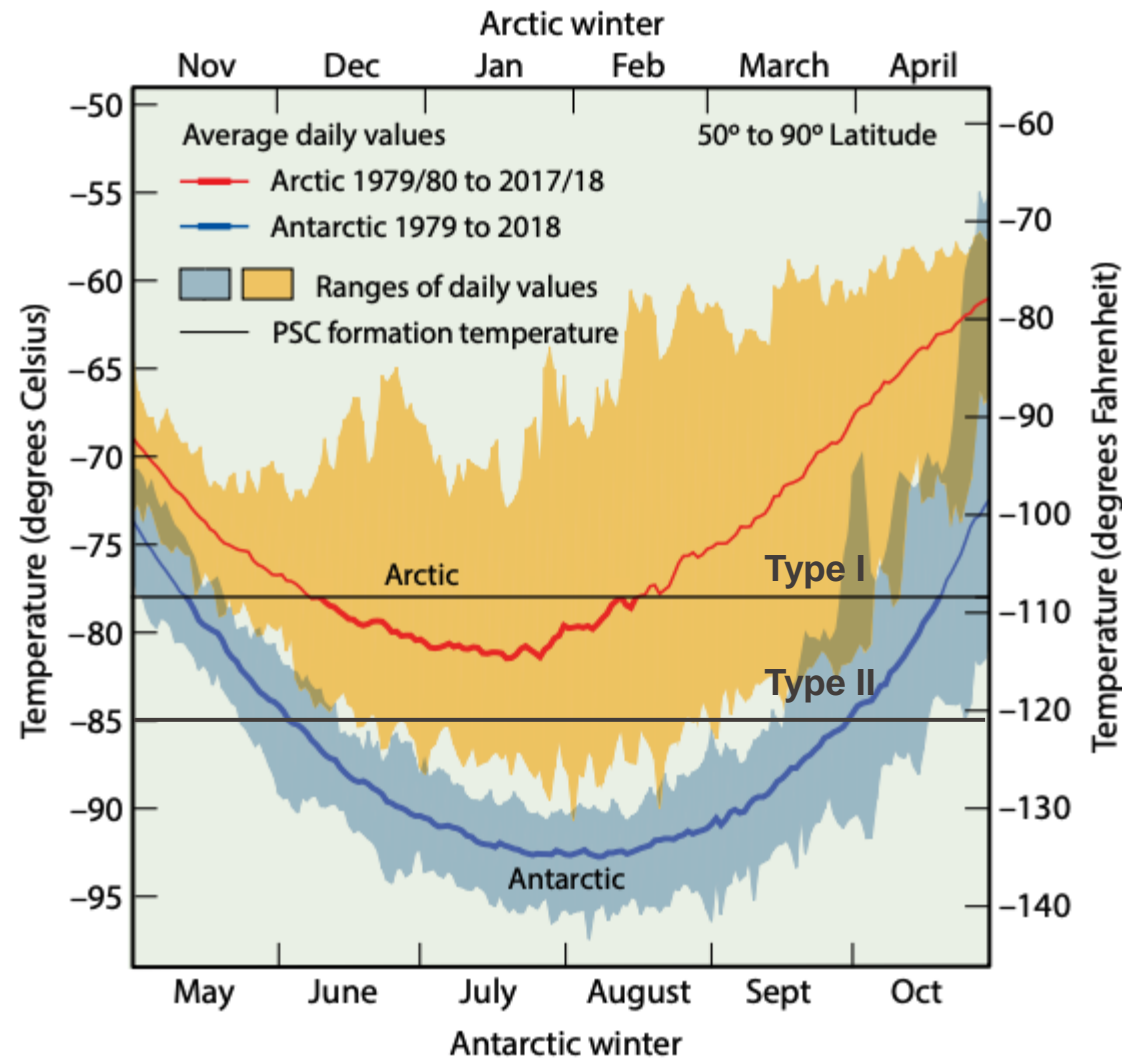


[https://de.wikipedia.org/wiki/Polare\\_Stratosph%C3%A4renwolken#/media/Datei:Arctic\\_stratospheric\\_cloud.jpg](https://de.wikipedia.org/wiki/Polare_Stratosph%C3%A4renwolken#/media/Datei:Arctic_stratospheric_cloud.jpg)



PSCs dehydrate and denitrify the stratosphere.

# Polar Stratospheric Clouds (PSC)



Type I:  
 $\text{HNO}_3(\text{H}_2\text{O})_3$  (NAT),  $\text{HNO}_3\text{-H}_2\text{O-H}_2\text{SO}_4$   
Type II:  
 $\text{HNO}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_4$  (SAT)

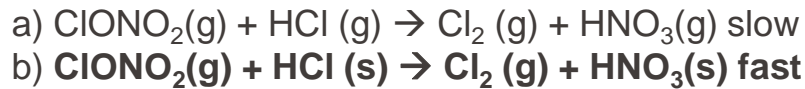
PSCs are responsible for the formation of reactive halogens (e.g.,  $\text{Cl}_2$ ) in the stratosphere that deplete ozone.

# Heterogeneous chemistry: Adsorption mechanisms

Means at least two phases are involved, e.g., gas and solid or liquid

- Physisorption (van der Waals forces)
- Chemisorption (bonds forming)

Key reaction to create reactive  $\text{Cl}_2$  is:



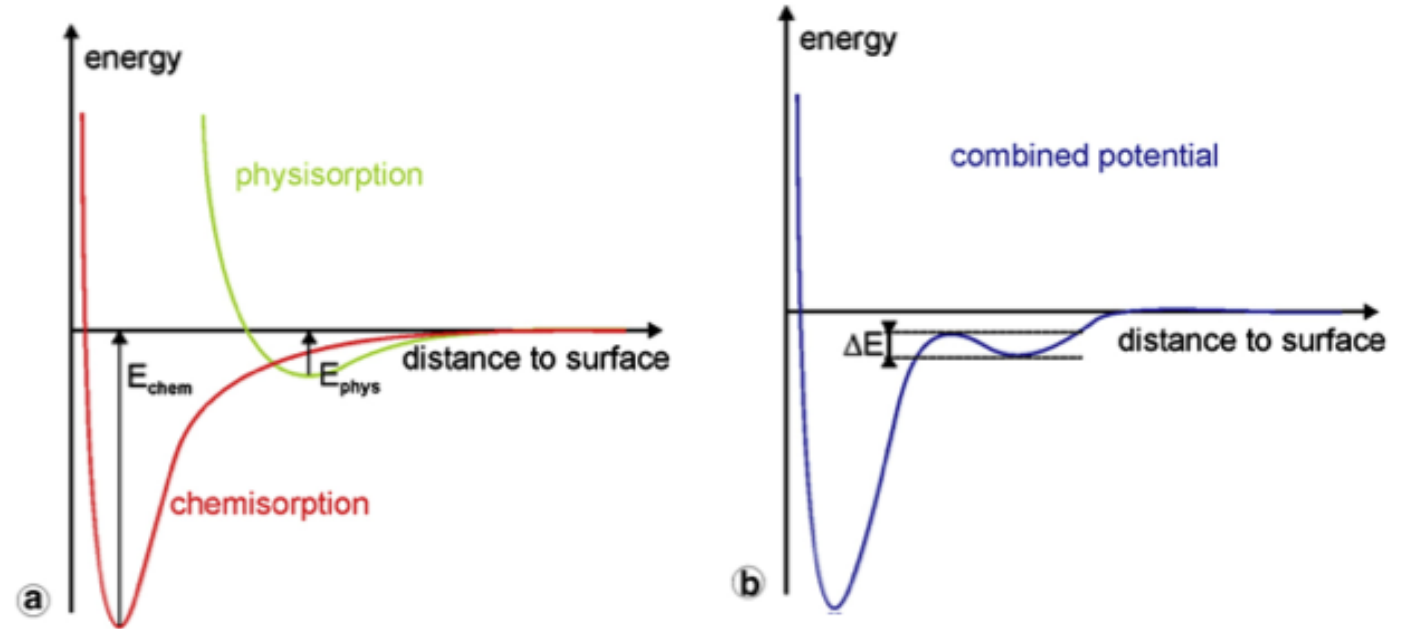
Why is b faster?

HCl is ionized at the ice surface. That means  $\text{Cl}^-$  ions are available for the reaction with  $\text{ClONO}_2$ . This reaction involving ions is faster.

HCl (s) exists because at the cold temperatures HCl is efficiently absorbed by PSC particles that contain water.

(g) Gas phase

(s) Solid phase, i.e. on ice



Physisorption takes place at larger distances from the surface ( $d > 0.3 \text{ nm}$ ). Chemisorption originates from strong covalent or ionic bonds at shorter distances. Combining the two effects, a barrier  $\Delta E$  might exist which needs to be overcome for chemisorption to occur.

# Uptake of a gas molecule into a particle

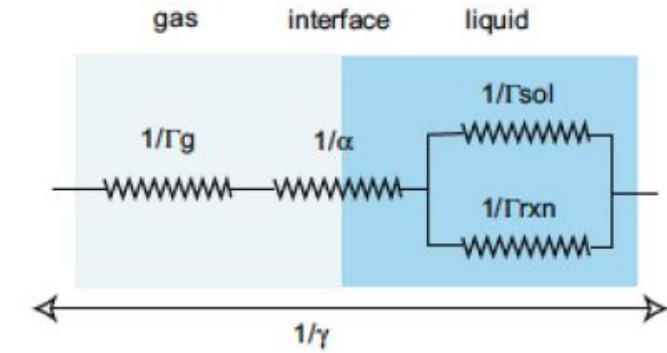
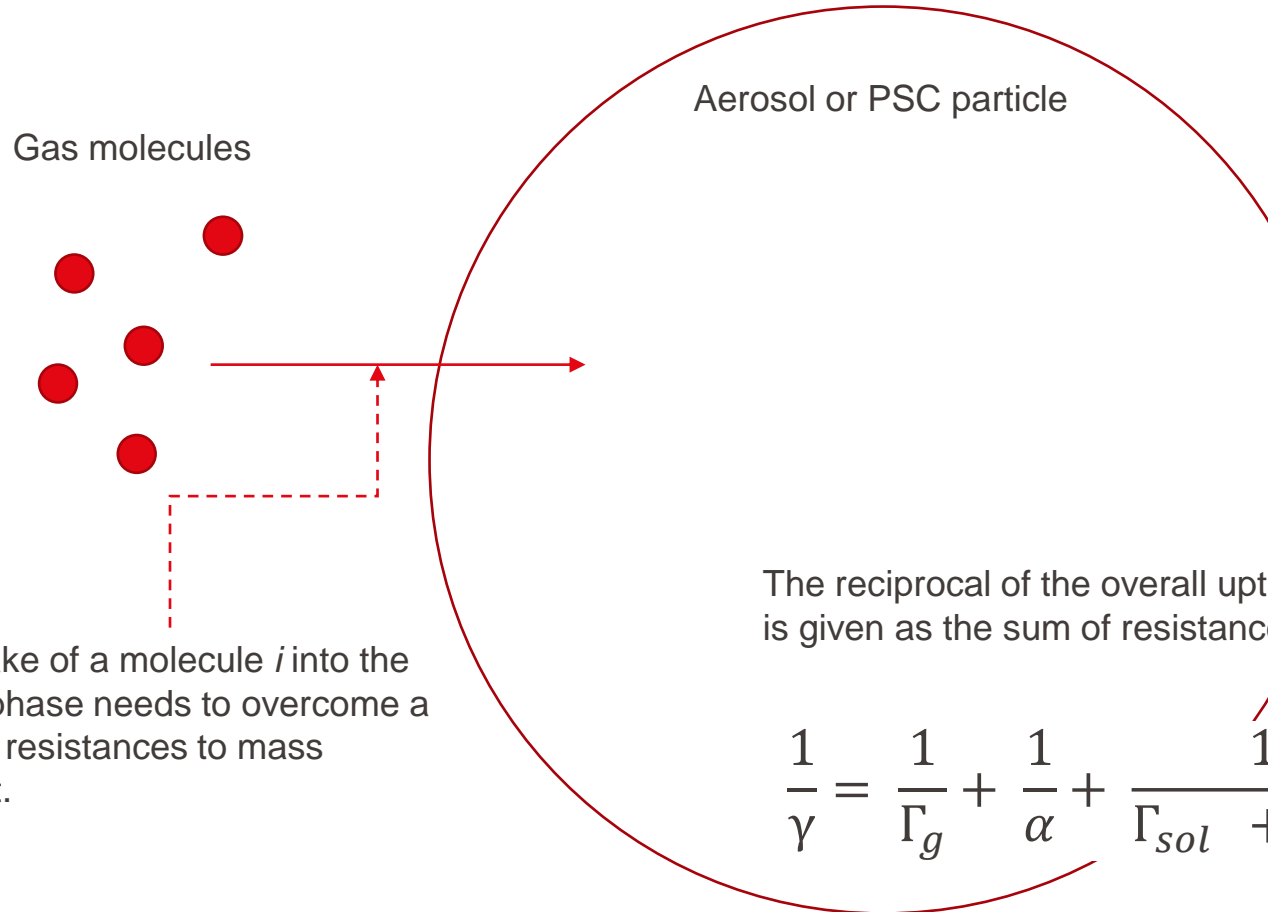


Fig. 1. Schematic of the resistance model for the uptake process.

Morita and Garrett, 2008

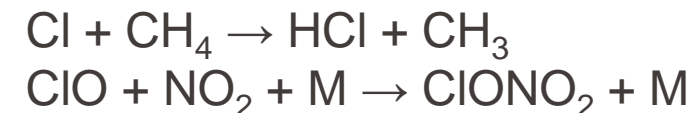
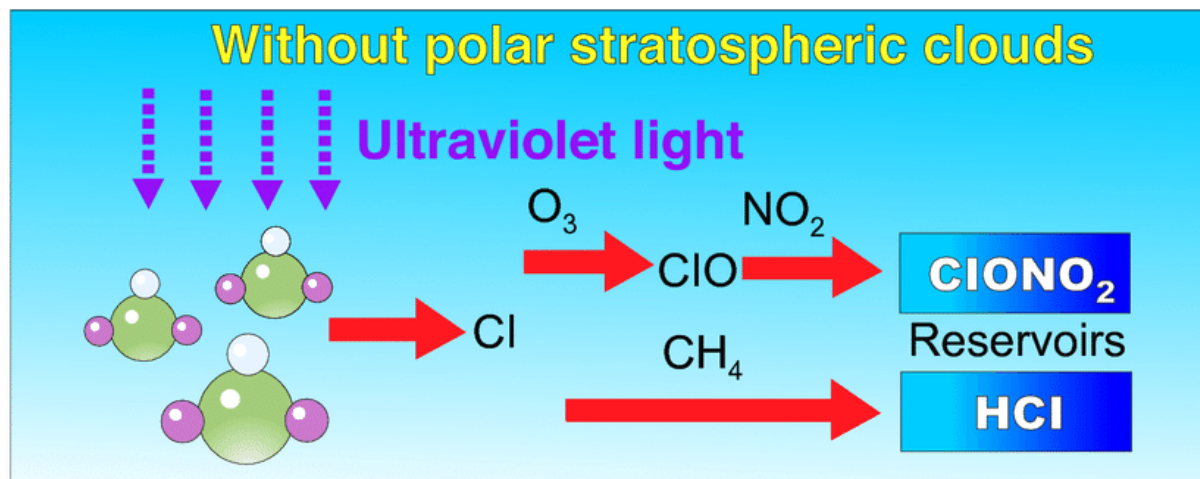
The reciprocal of the overall uptake of molecule  $i$  is given as the sum of resistances:

$$\frac{1}{\gamma} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sol} + \Gamma_{rxn}}$$

g	gasphase diffusion
α	mass accommodation coefficient (i.e. «sticking probability» of a molecule at the interface)
sol	dissolution
rxn	reaction

Important because they convert the benign Cl-reservoir species into reactive species, and they remove  $\text{HNO}_3$  (denitrification) leaving more reactive ClO (because  $\text{NO}_x$  is produced from  $\text{HNO}_3$ , and  $\text{NO}_x$  produces the reservoir substance  $\text{ClONO}_2$ ).

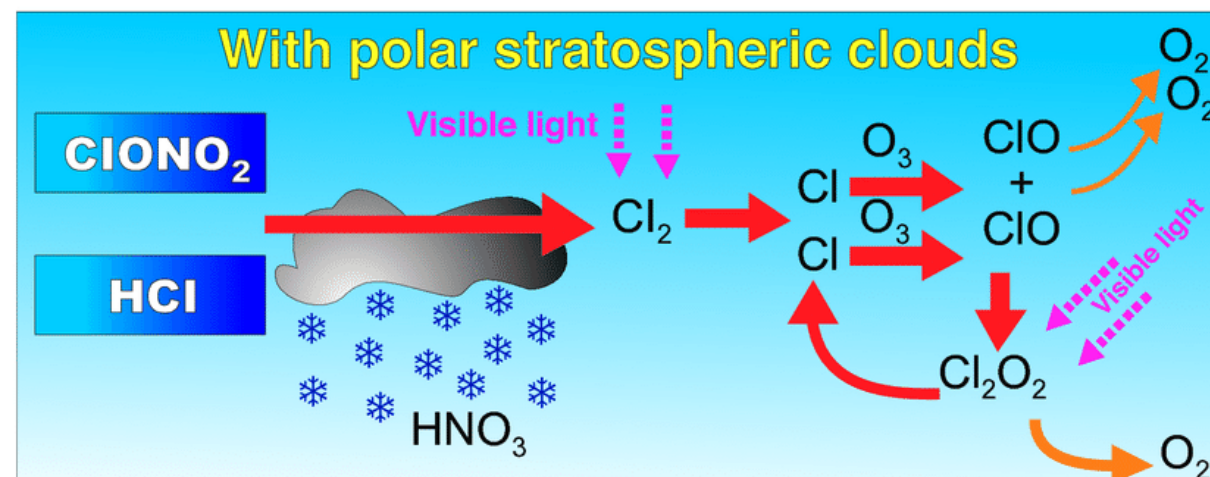
homogeneous  
chemistry  
(gas-phase  
only)



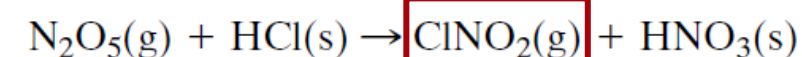
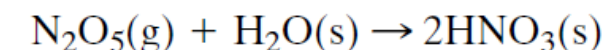
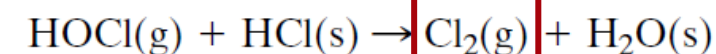
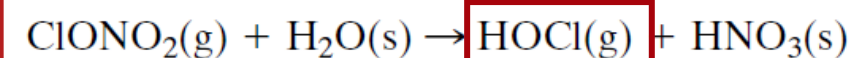
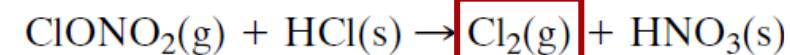
(g) Gas phase

(s) Solid phase, i.e. on ice

heterogeneous  
chemistry (gas  
and particle  
phases)



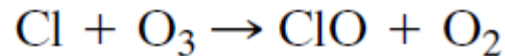
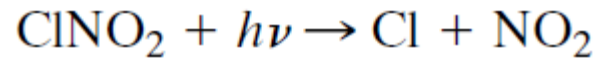
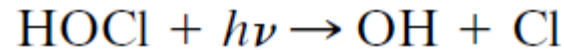
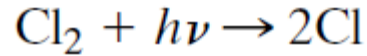
Reservoir → reactive species



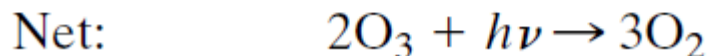
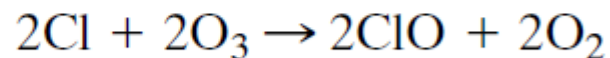
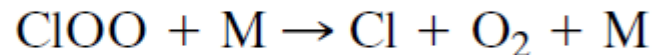
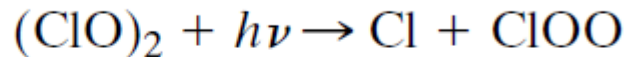
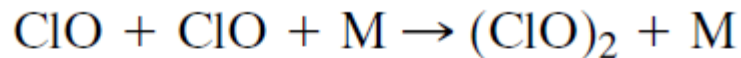


# Photolysis during spring and ozone destruction

## Photolysis

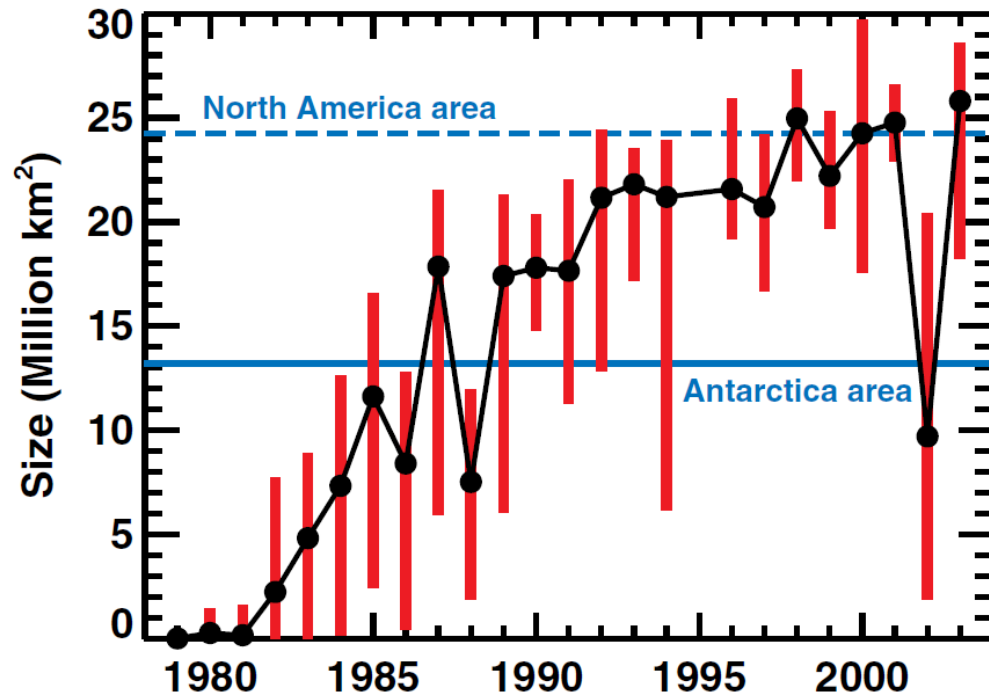


## Ozone destruction



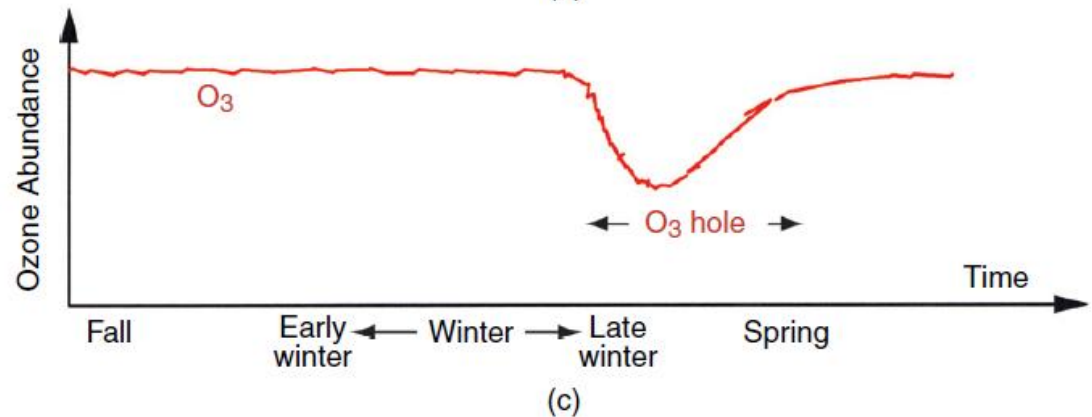
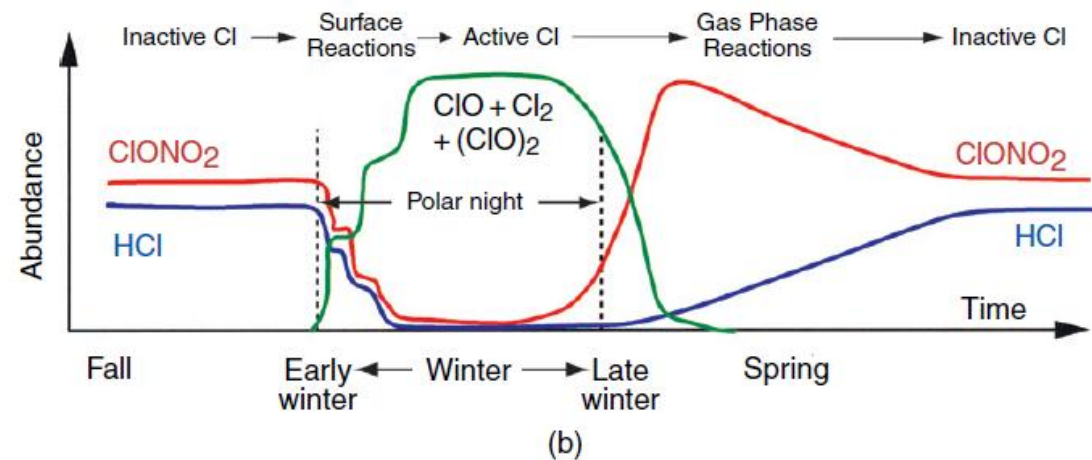
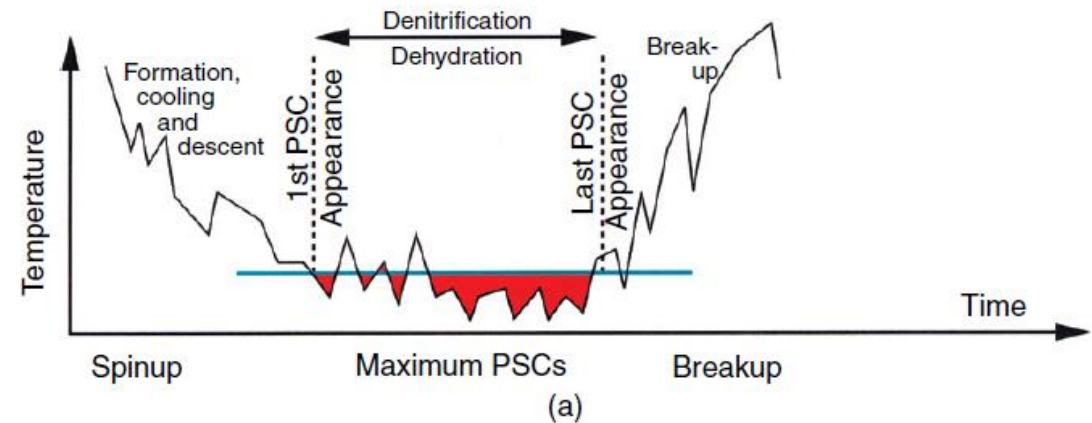
- ClO is the catalyst.
- No dependence on atomic oxygen (low abundance at that altitude)
- Cl comes from CFCs, but is normally tied up in reservoir species (HCl, ClONO<sub>2</sub>)
- In the presence of PSCs, Cl<sub>2</sub>, HOCl, and ClONO<sub>2</sub> are released and, as soon as the solar radiation reaches sufficient intensity in early spring, Cl and ClO are released, which lead to the rapid depletion of O<sub>3</sub>
- The dimer (ClO)<sub>2</sub> is formed only at low temperatures. Low enough temperatures are present in the Antarctic stratosphere, where there are also large concentrations of ClO.
- Therefore, the Antarctic stratosphere in spring is a region in which the reaction cycle can destroy large quantities of O<sub>3</sub>.

# Antarctic ozone destruction



Cold temperatures and sunlight are key features that need to be met to produce the ozone hole.

Wallace and Hobbs, 2006, Fig. 5.22

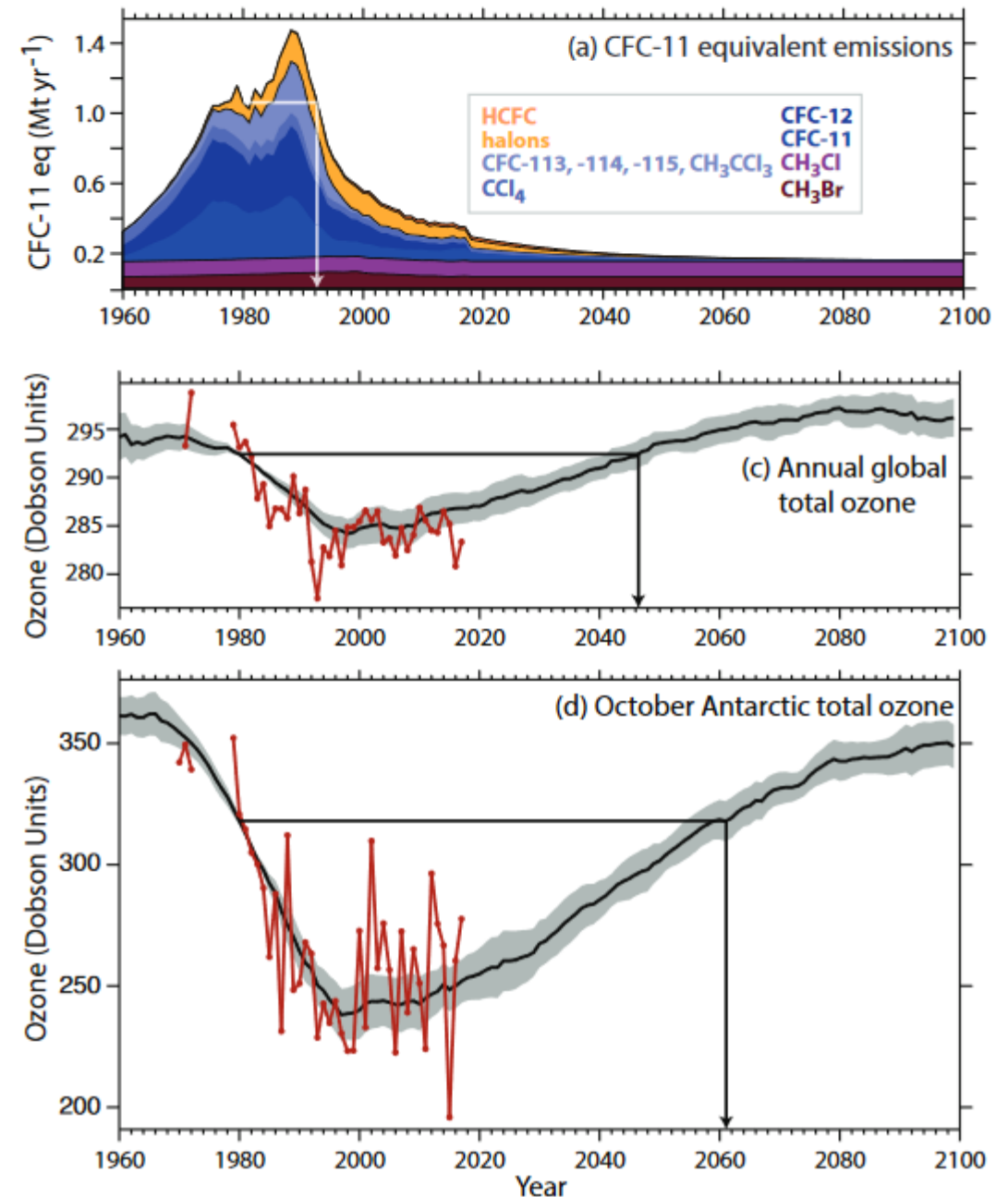


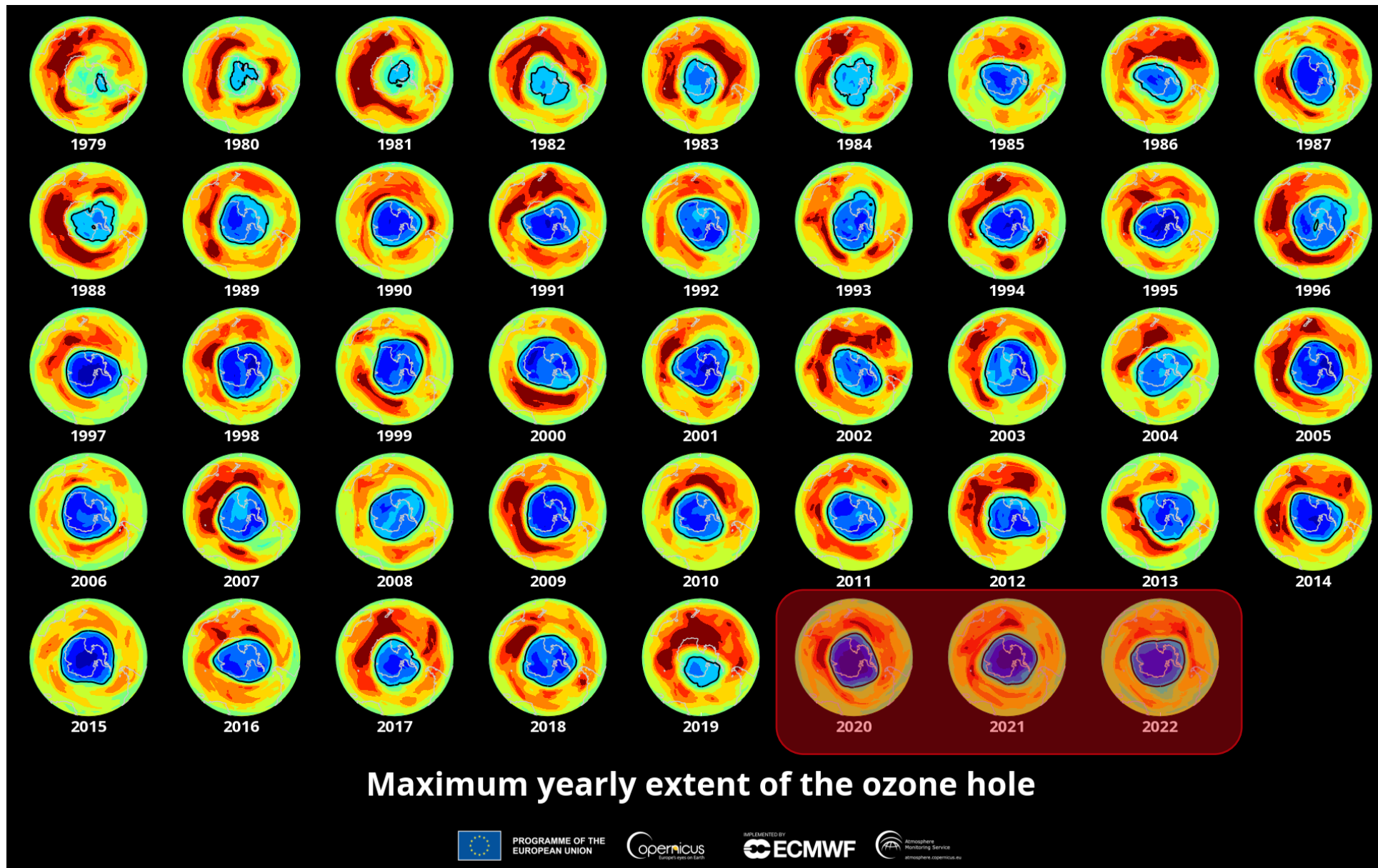
# Why was there only a small ozone hole in 2002?

- A. The Brewer Dobson Circulation was disturbed by a volcanic eruption.
- B. No reservoir species were formed that year, because of a volcanic eruption.
- C. There was probably less HCl in the stratosphere.
- D. The winter was warm.
- E. B and D.

# Montreal protocol

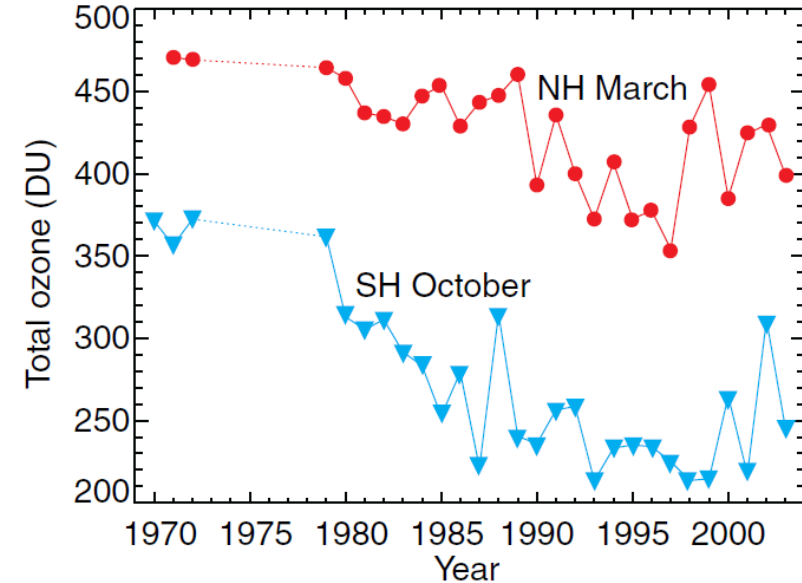
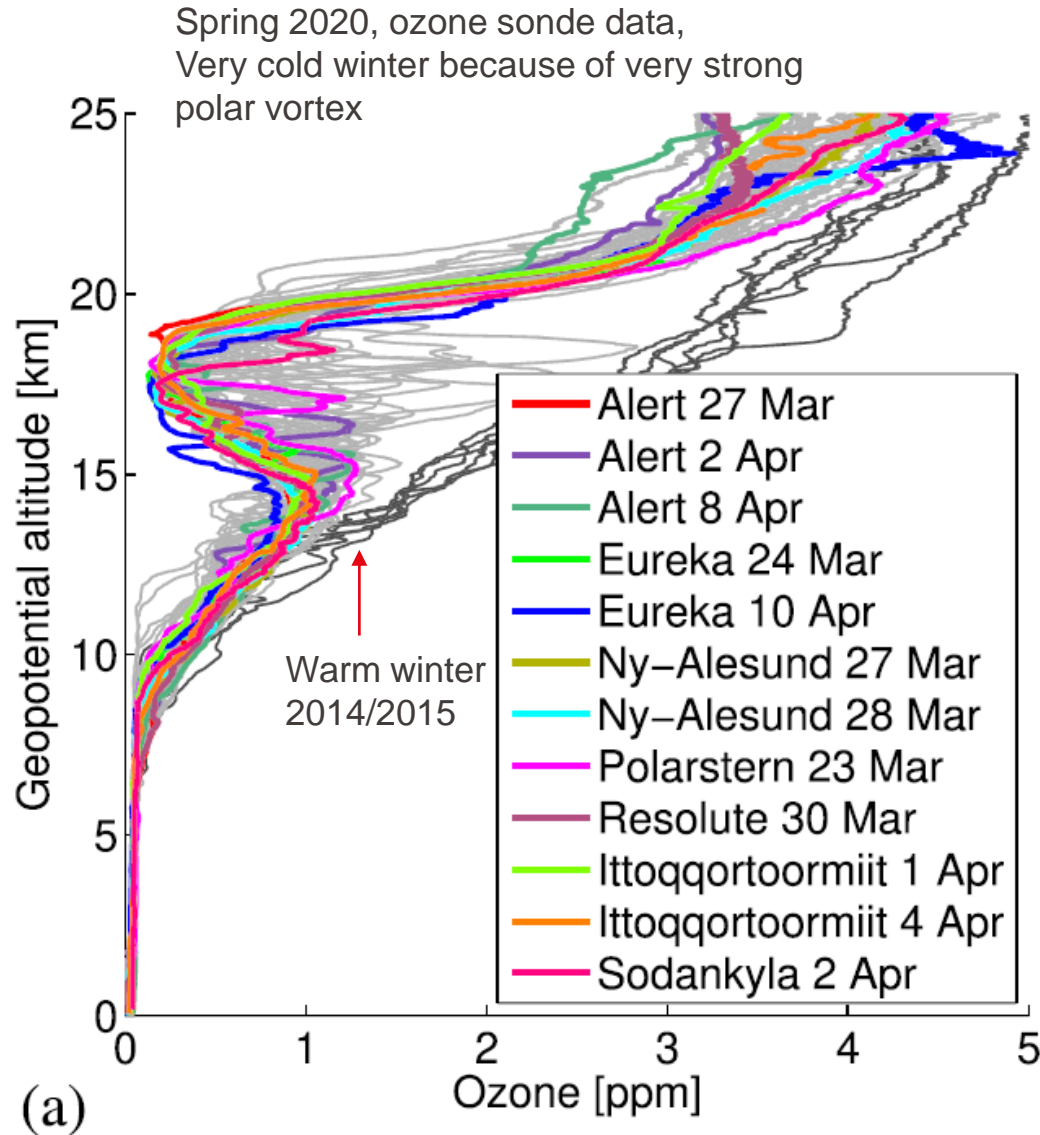
- The Montreal Protocol is the first and only treaty ever to have been ratified by every nation on Earth.
- In 1974 first paper on ozone destruction by CFCs.
- 1985 first paper showing the ozone hole.
- 1985 Vienna convention for the protection of the ozone layer.
- 1987 Montreal protocol to reduce CFCs.
  - Reduction by > 98 % between 1986 and 2016
  - CFCs replaced by HFCs (potent greenhouse gases)
- 1995 Nobel prize (Paul Crutzen, Mario Molina, Sherwood Rowland)
- 2016 Kigali Amendment: reduce HFCs by 85 % in the medium term





Large ozone holes  
in 2020-2022



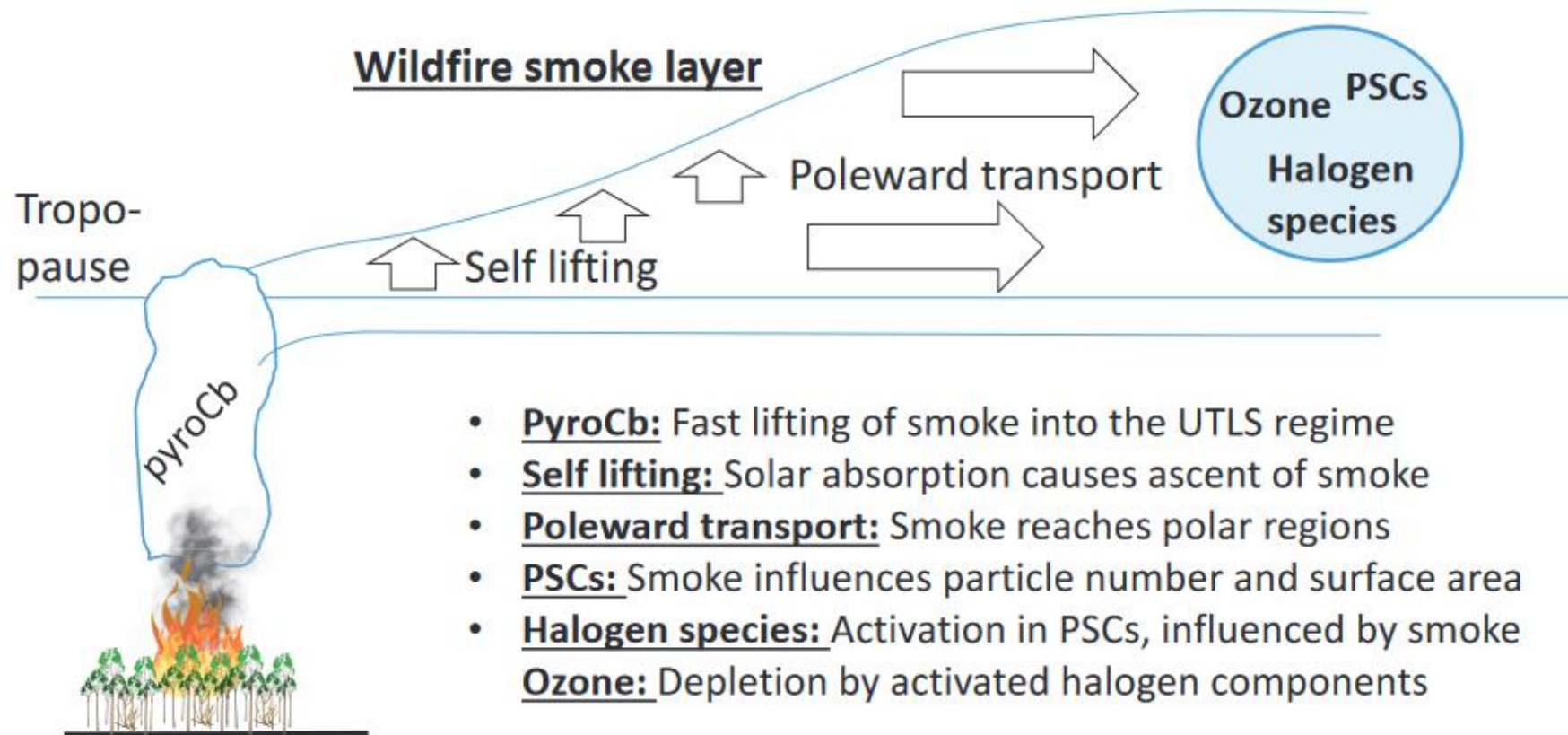


**Fig. 5.23** Average ozone columns between latitudes  $63^{\circ}$ – $90^{\circ}$  for the northern hemisphere in March (red line and symbols) and the southern hemisphere in October (blue line and symbols). [Adapted with courtesy of P. Newman, NASA Goddard Space Flight Center.]

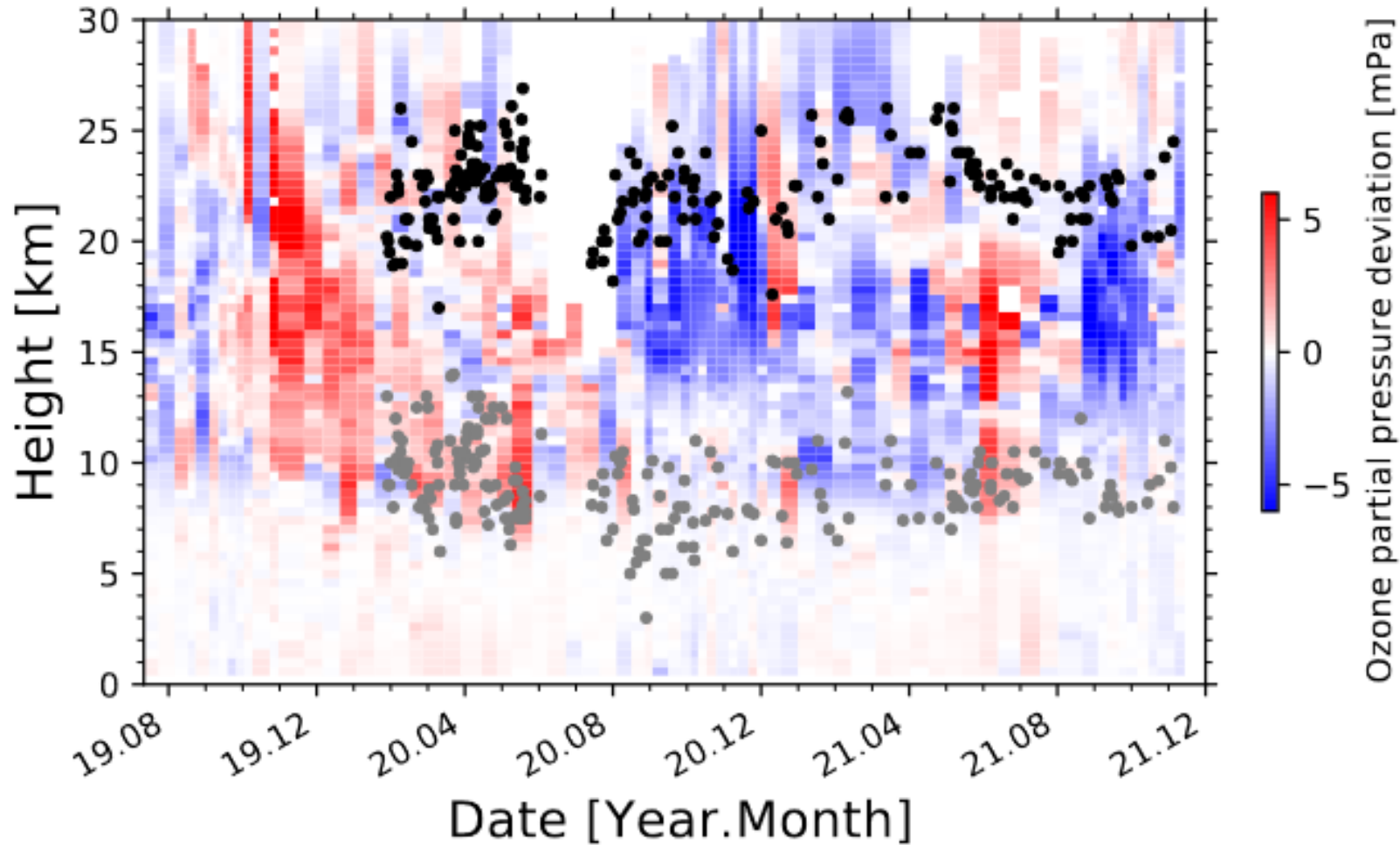
Wallace and Hobbs, 2006



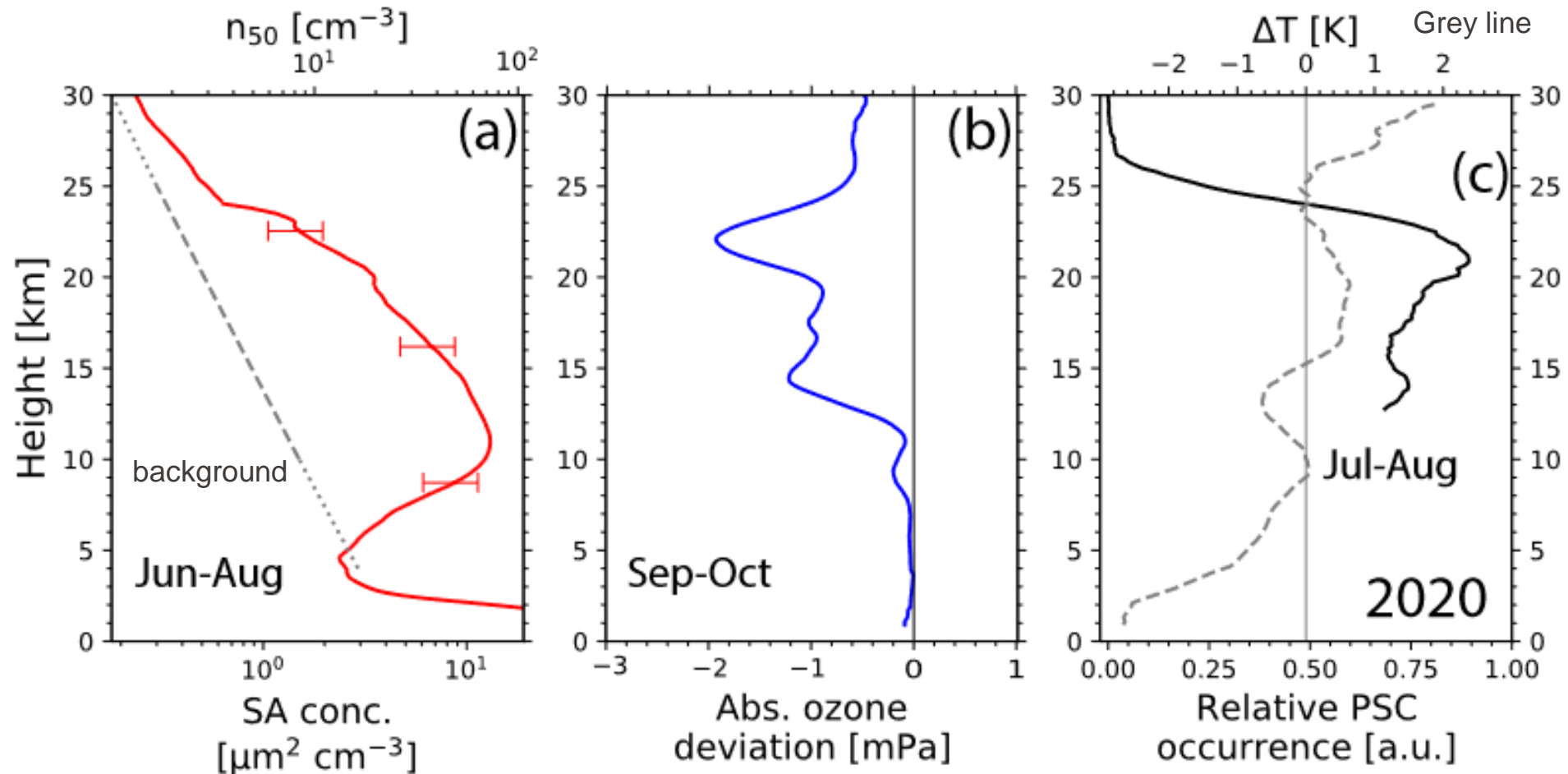
# Can fires contribute to the ozone whole formation?



**Figure 3.** Key processes of the vertical and meridional transport of wildfire smoke from the emission sources to the polar regions.



Deviation of individual ozone profiles from the long-term monthly mean (2010-2019) at Neumayer station (70.6°S). Grey and black dots show the aerosol smoke layer from the Australian fires in 2019.



$n_{50}$  (particles with radius  $>50$  nm)

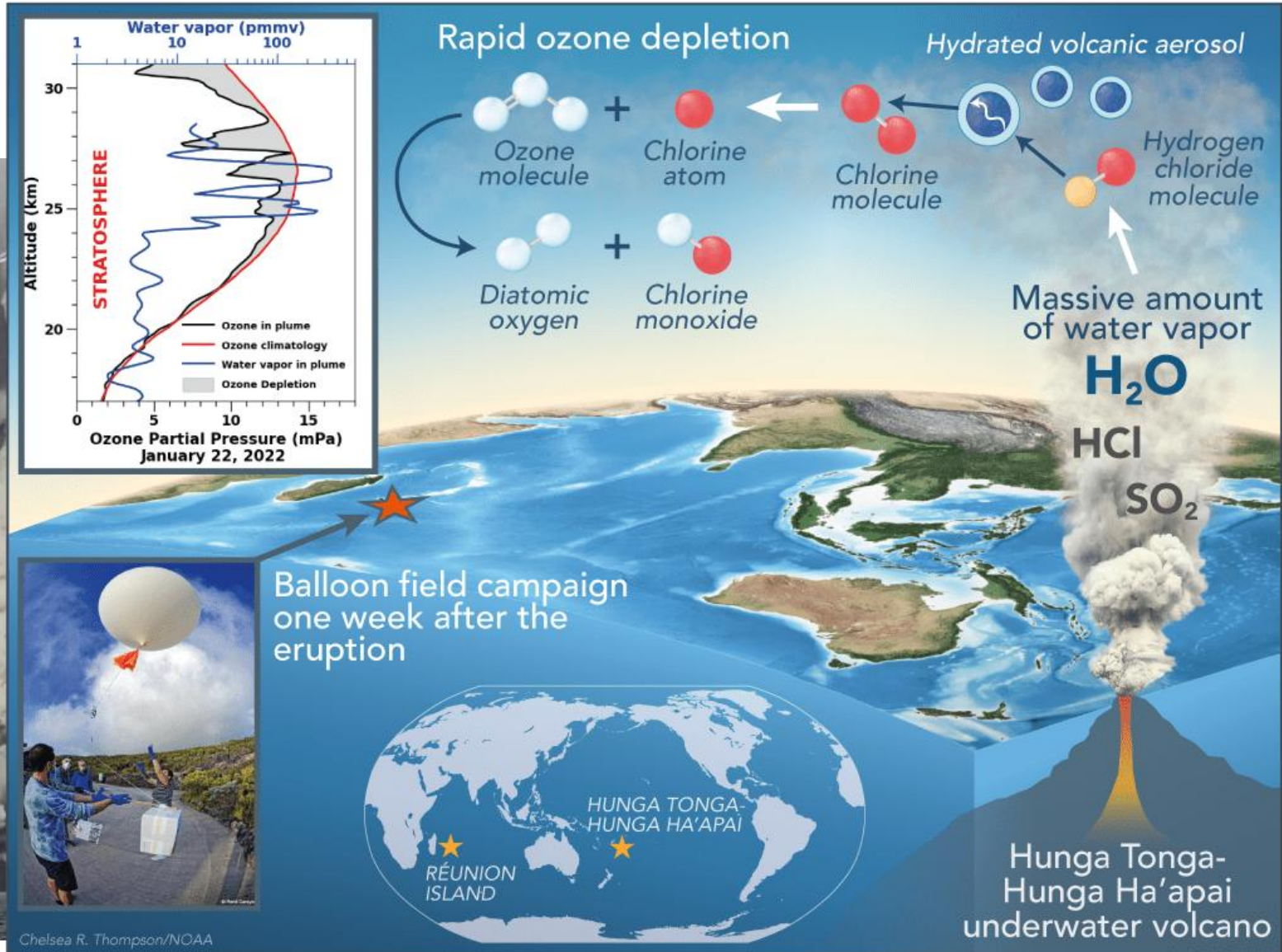
SA (surface area)

a.u. (arbitrary units)

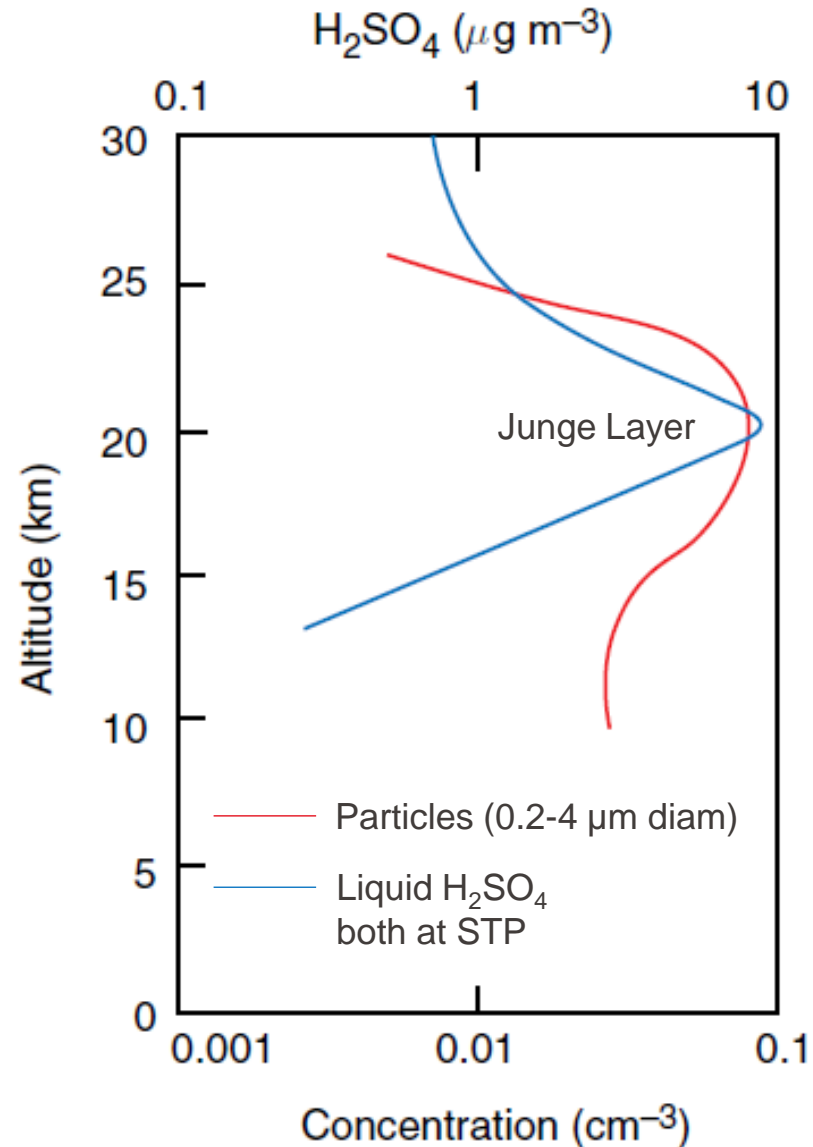


# Hunga-Tonga eruption

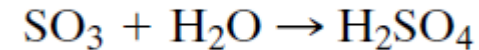
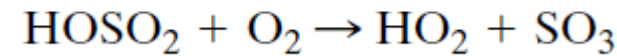
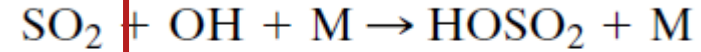
## 15 Jan 2022



# Stratospheric sulfur (aerosols)



## Formation of gaseous $\text{H}_2\text{SO}_4$

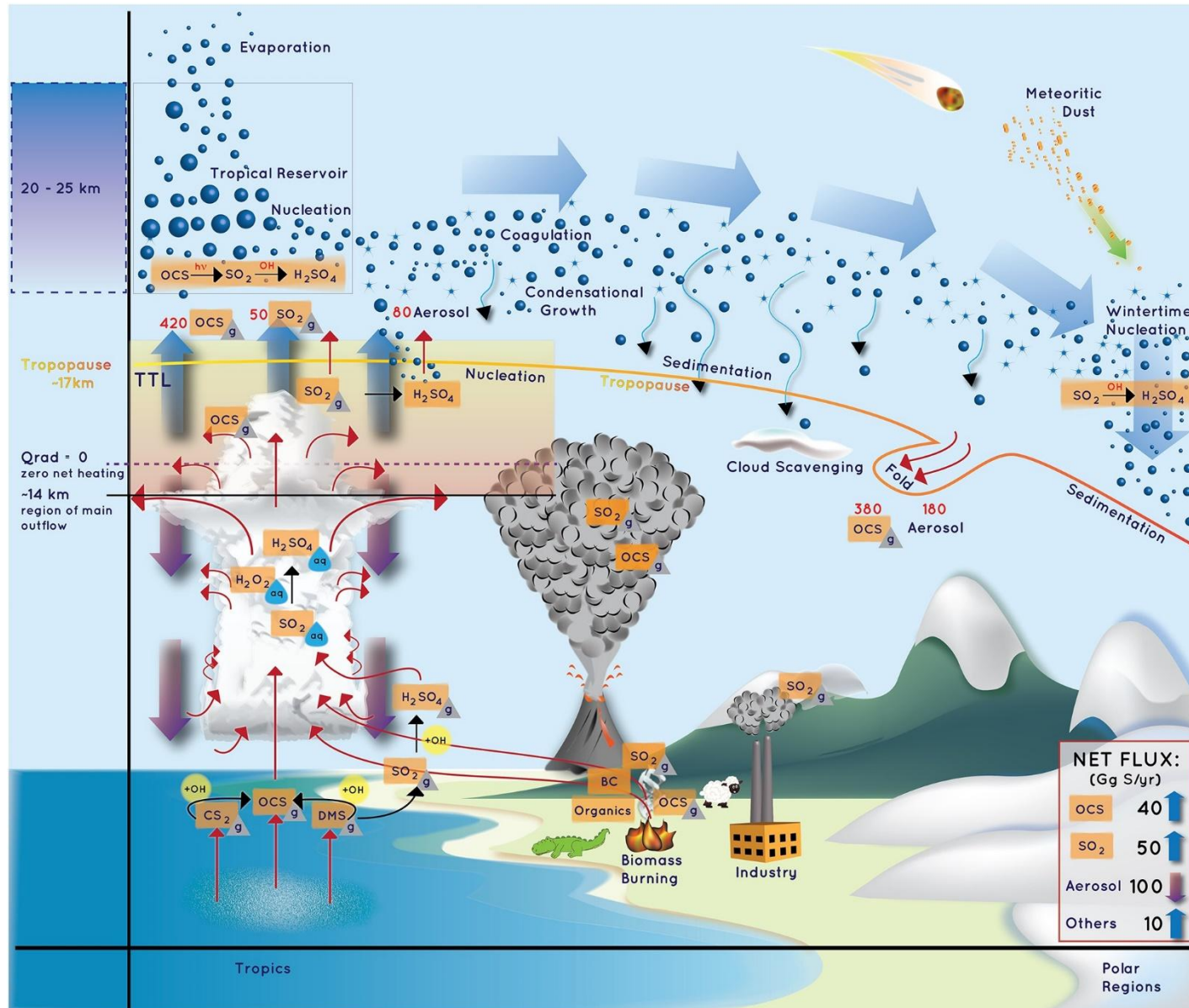


## Particle formation:

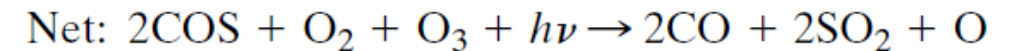
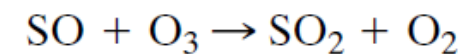
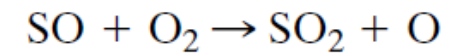
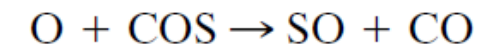
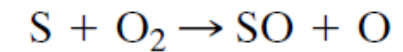
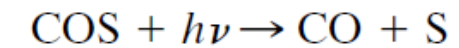
- The combination of molecules of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  (i.e., **homogeneous, bimolecular nucleation**) and or the combination of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{HNO}_3$  to form new (primarily sulfuric acid) droplets (i.e., **homogeneous, heteromolecular nucleation**).
- Vapor condensation of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{HNO}_3$  onto the surfaces of preexisting particles with radius 0.15  $\mu\text{m}$  (i.e., **heterogeneous, heteromolecular nucleation**).



# Sources of stratospheric aerosols

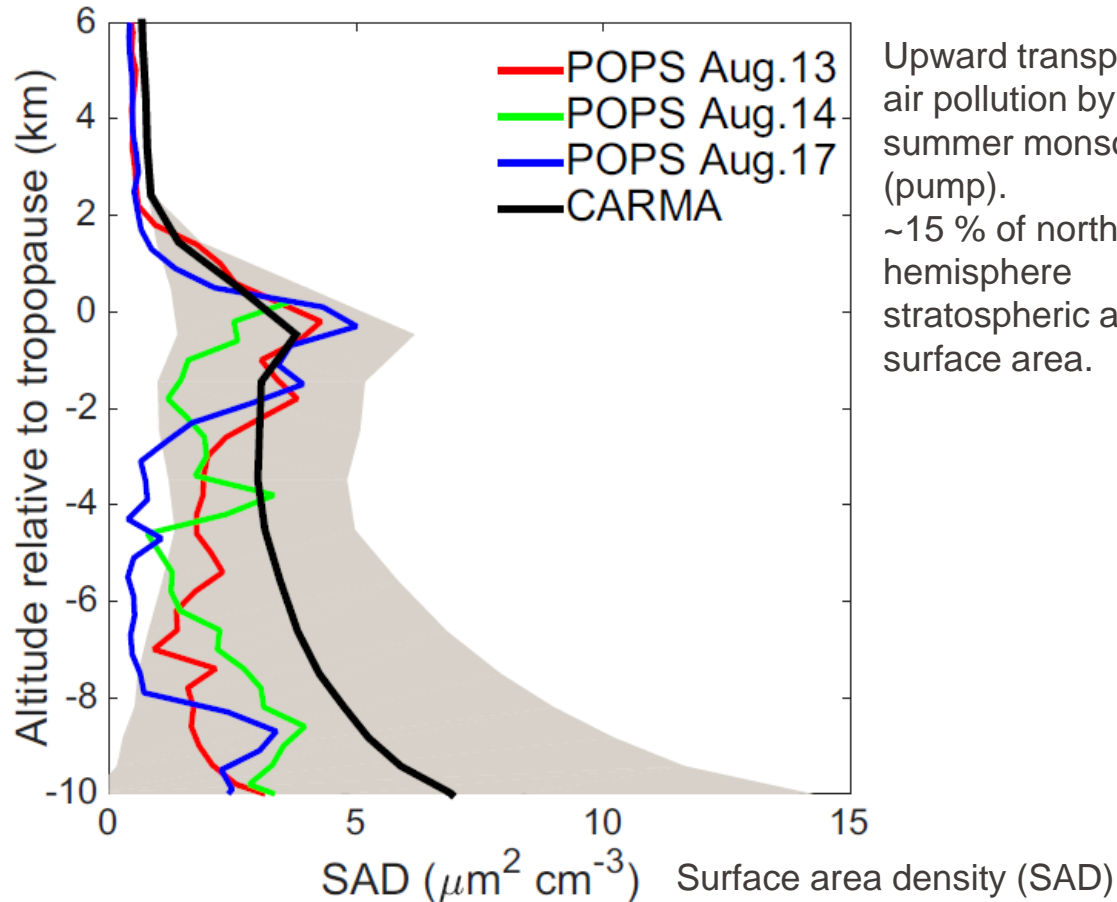


In absence of volcanic eruptions COS is the most important supply of S in the stratosphere:



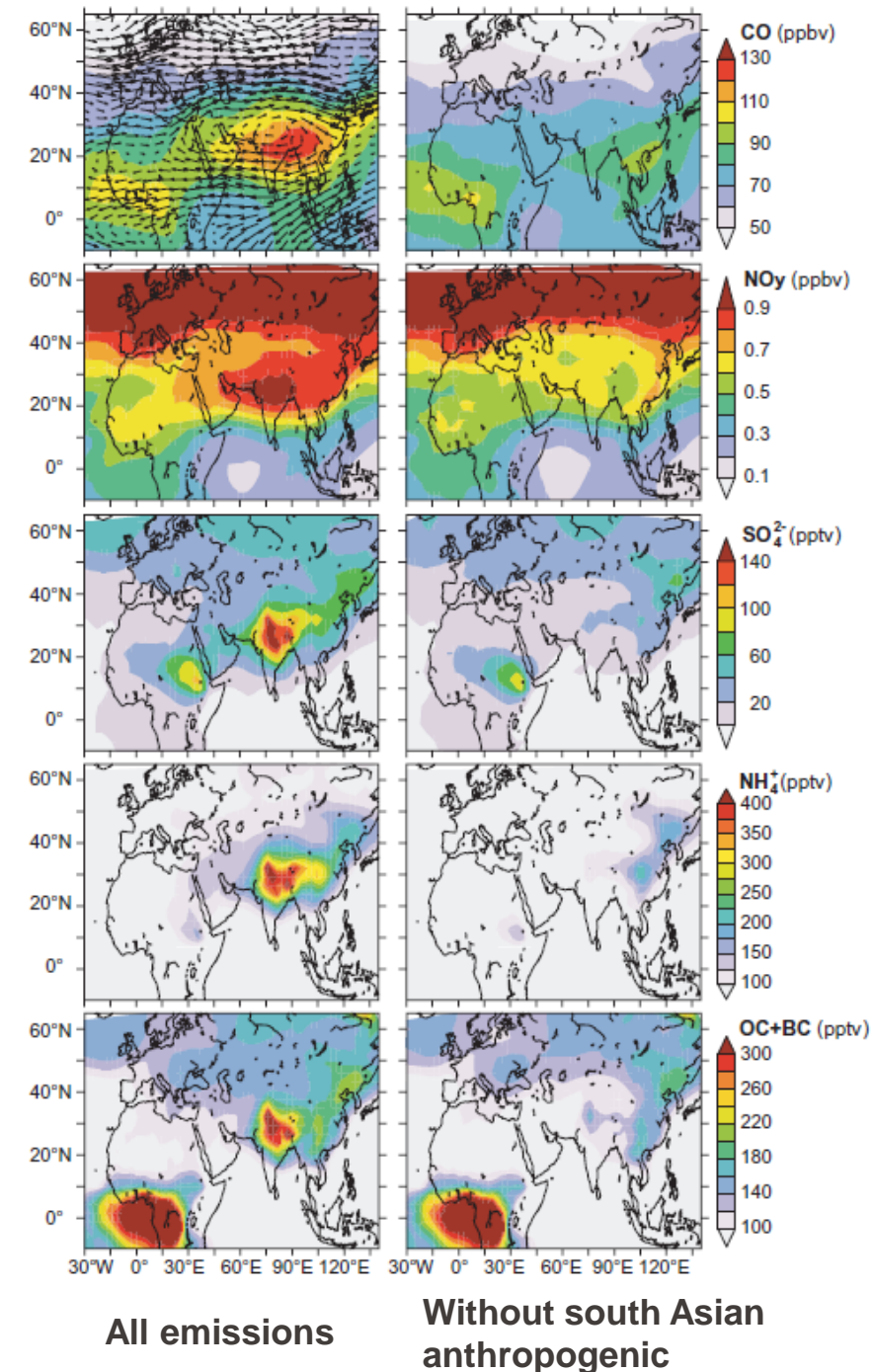
Kremser et al., 2016,  
[10.1002/2015RG000511](https://doi.org/10.1002/2015RG000511)

# Contribution of Asian Emissions



Upward transport of air pollution by Asian summer monsoon (pump). ~15 % of northern hemisphere stratospheric aerosol surface area.

**Fig. 2. Influence of South Asian emissions.** Model-calculated mean CO, plus wind field,  $\text{NO}_y$  ( $\text{NO}_x$  and all other oxidized nitrogen species except  $\text{N}_2\text{O}$ ), sulfate, ammonium, and carbonaceous (OC and BC) aerosol at 200 hPa (~12 km altitude) during summer. Results with all emissions (left) and without South Asian anthropogenic emissions (right) are shown. For additional results, also at 100 hPa (~16 km altitude), see figs. S6 to S12.



- Know stratosphere-troposphere exchange mechanisms.
- The stratospheric ozone layer protects us from UV radiation.
- Chapman reactions and the missing sink.
- CFCs contribute to ozone destruction at the poles.
  - Cold temperatures and polar stratospheric clouds are needed.
- Also forest fires can contribute to PSC formation.
- There is a natural sulfate aerosol layer in the stratosphere.
- Anthropogenic emissions contribute to aerosol in the stratosphere.