

Recap from last lecture

- 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.

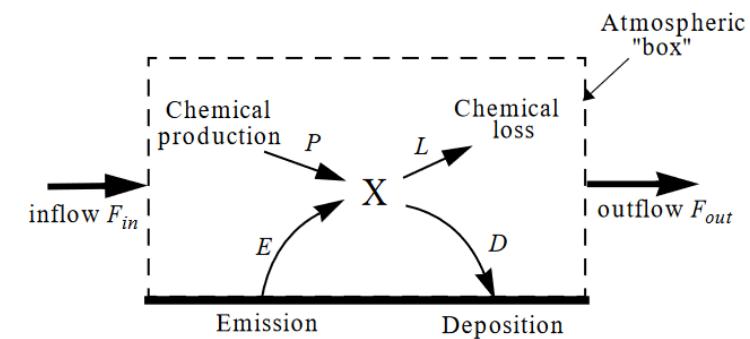
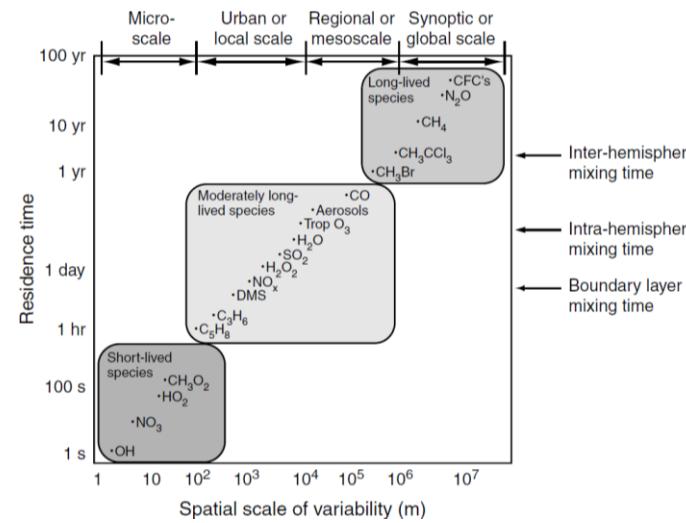
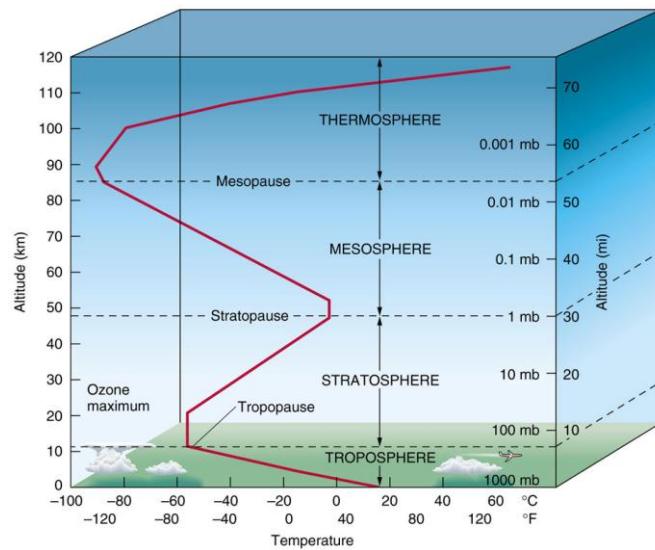
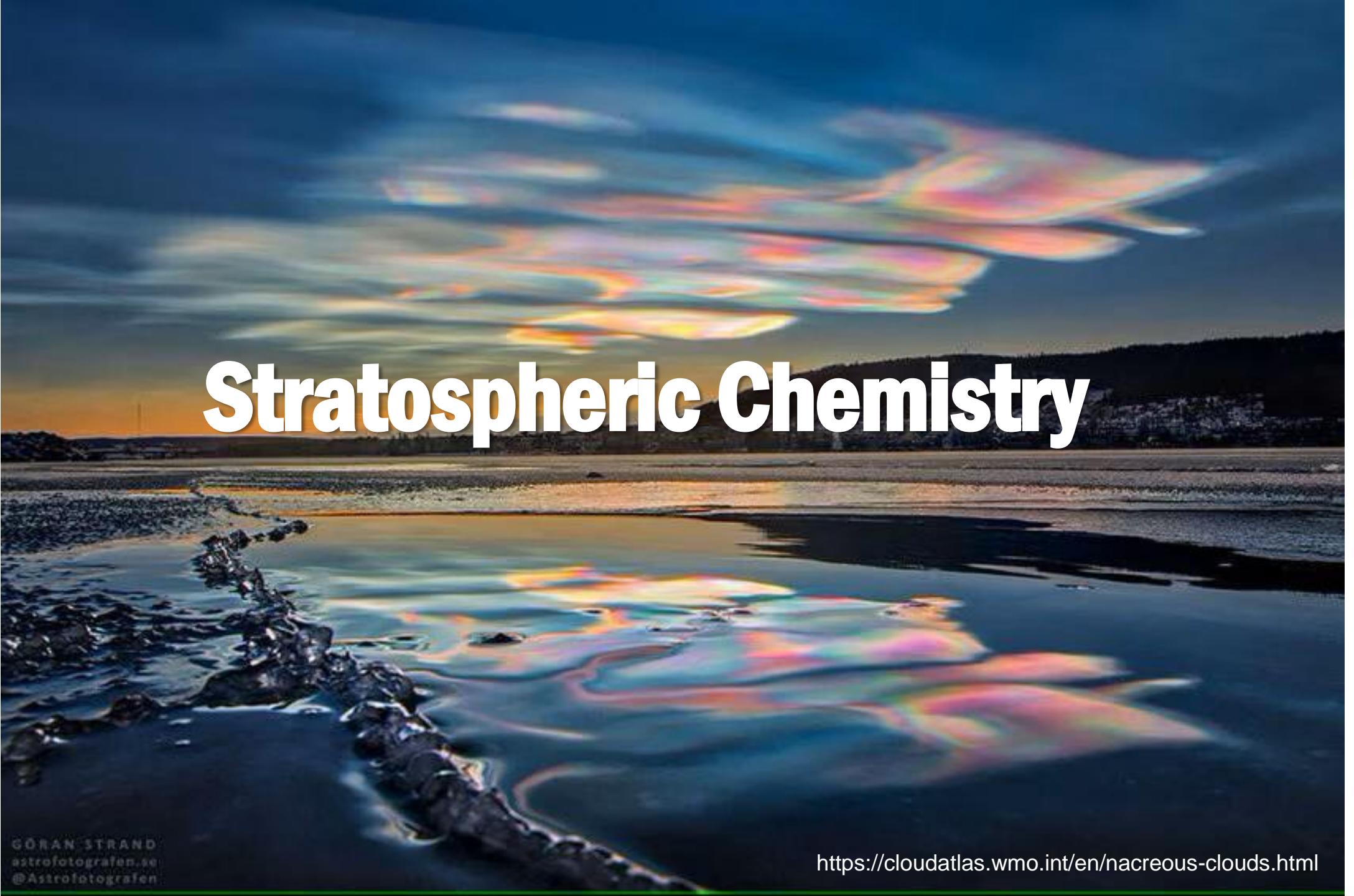


Figure 3-1 One-box model for an atmospheric species X



Stratospheric Chemistry

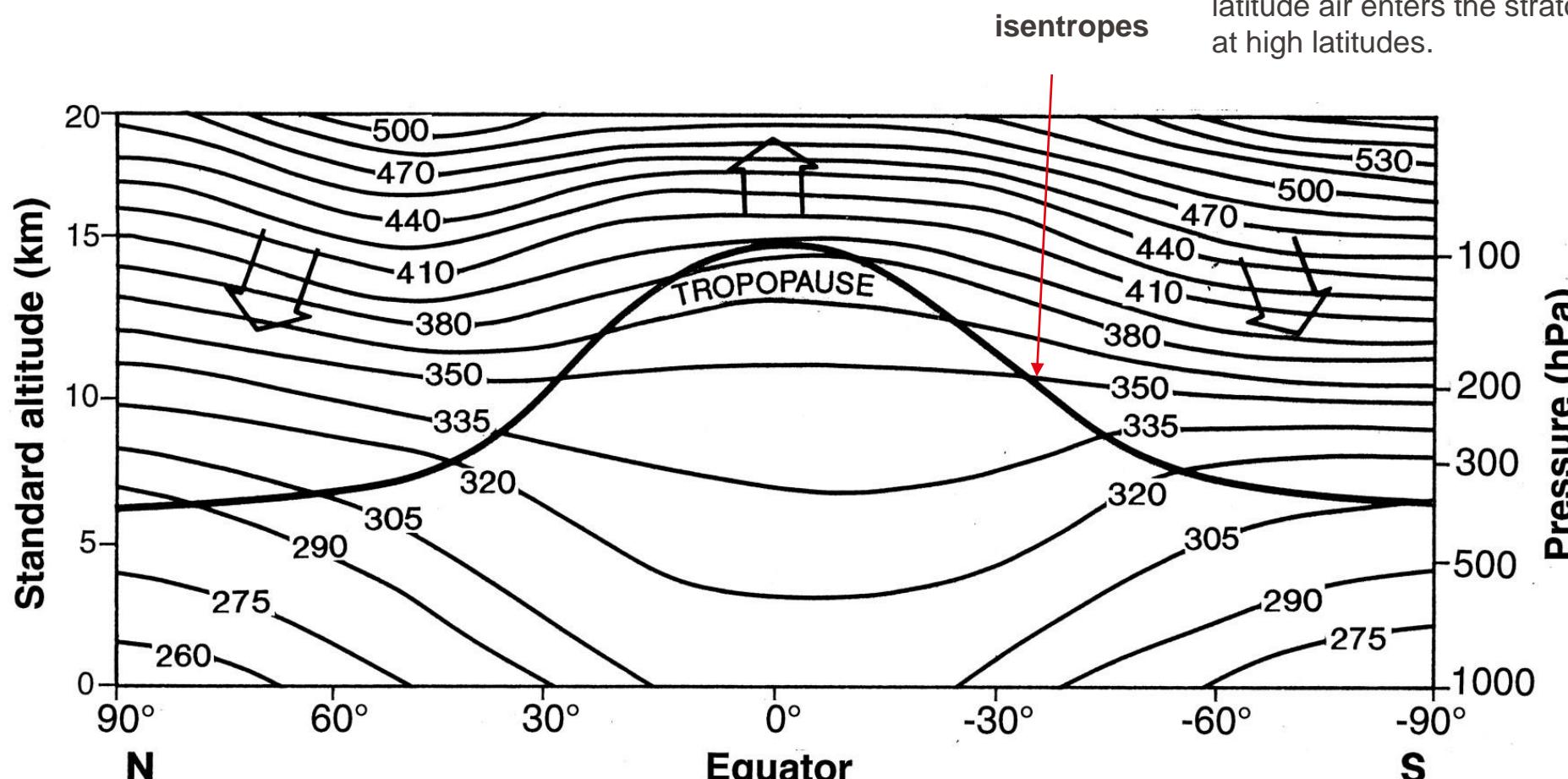
- Stratospheric circulation
- Ozone chemistry
 - Chapman reactions
 - Catalytic cycles
 - Ozone hole
 - Polar stratospheric clouds
- Junge Layer

«Discovery» of the Stratosphere

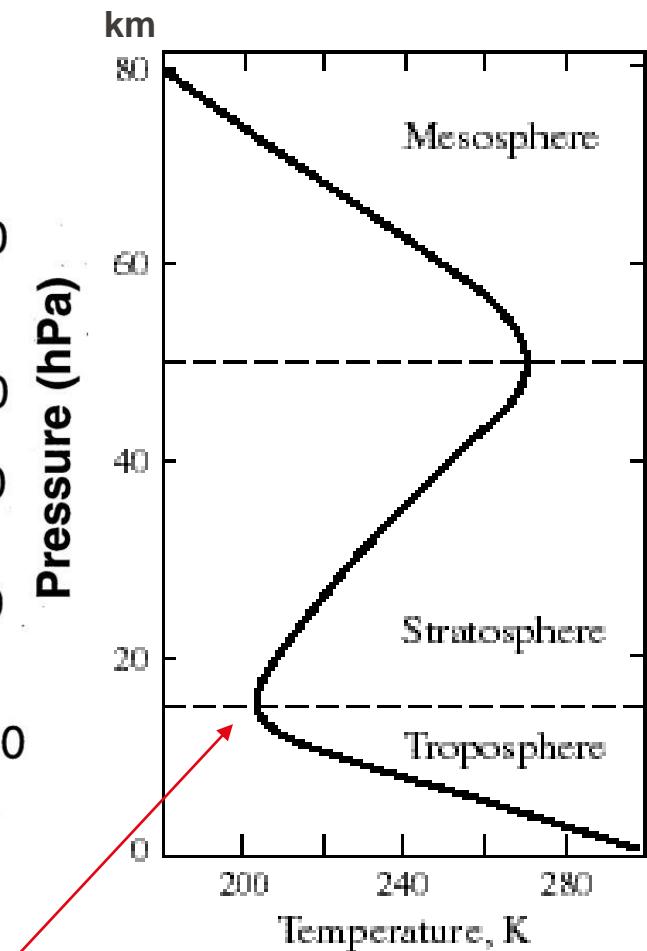


- In 1901, balloon flight to 10.5 km altitude by Reinhard Süring and Arthur Berson of the Prussian Royal Meteorological Institute
- 5400 m³ hydrogen balloon.
- Objective: temperature measurements. No trust in measurements with balloon soundings.
- tropos (gr.) → «turbulent» strato (gr.) → «layered»

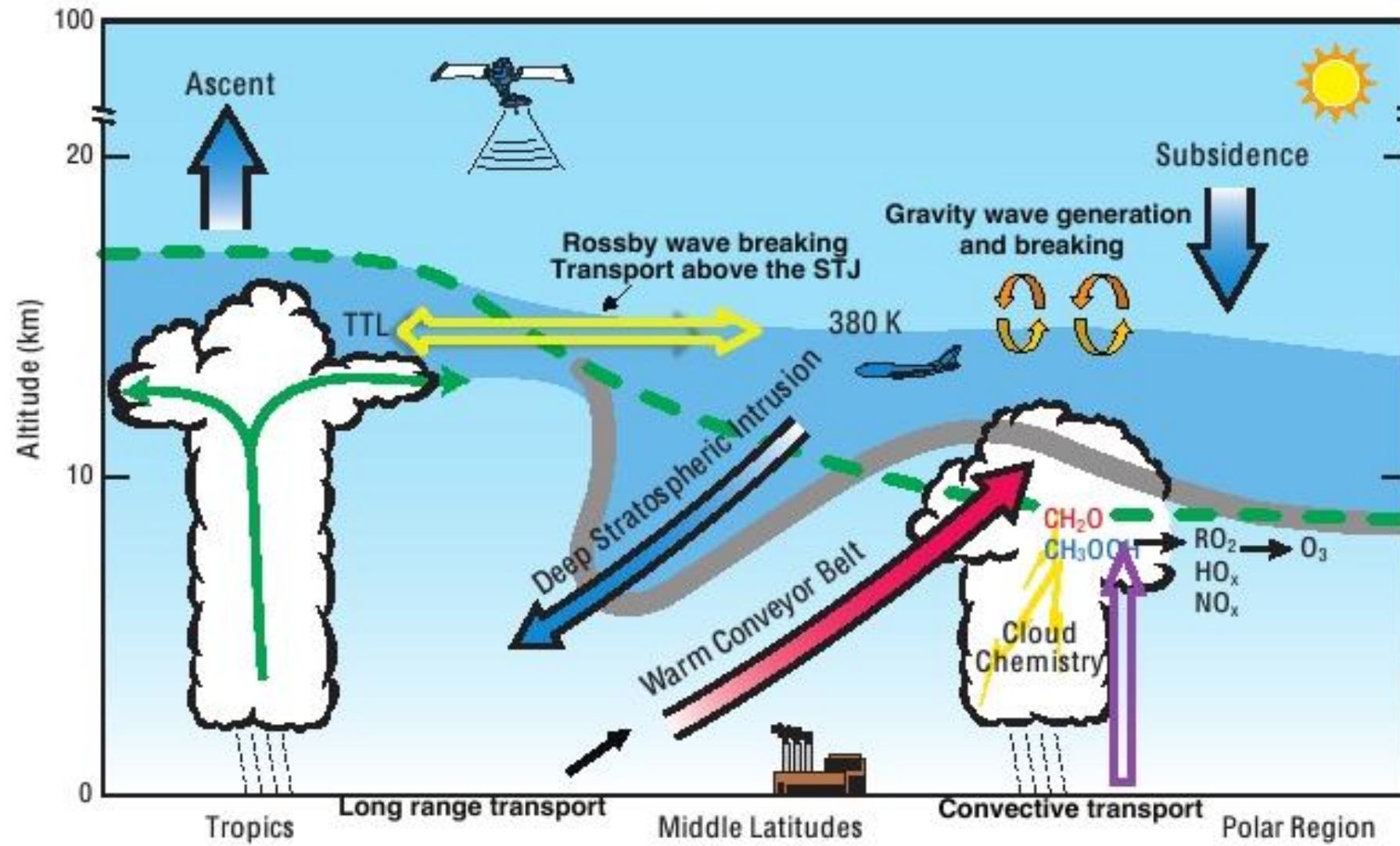
Tropopause



Air mass transport occurs along isentropes, meaning that low-latitude air enters the stratosphere at high latitudes.



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

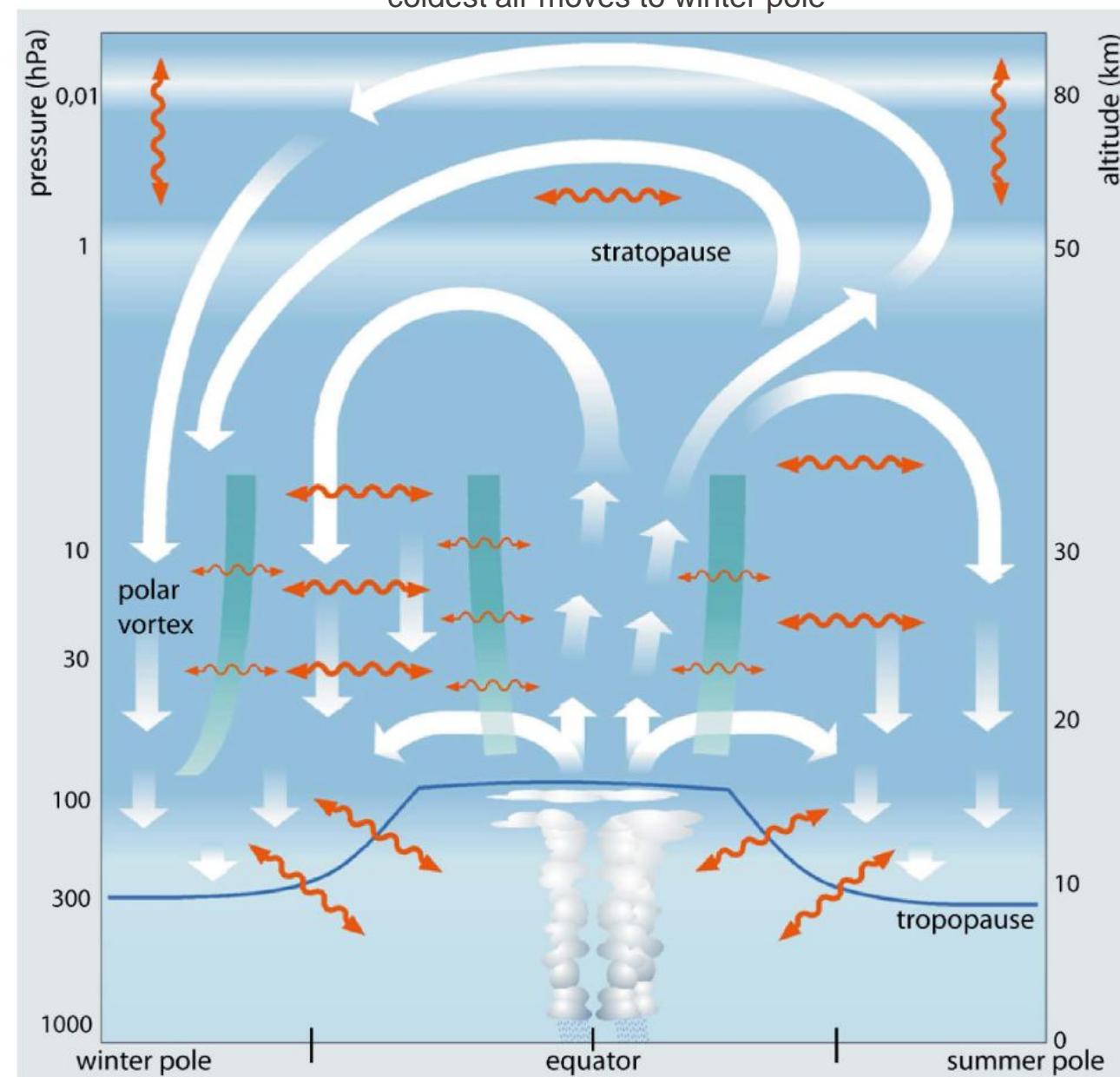
Fig. 1. Schematic of the Brewer Dobson Circulation as the combined effect of residual circulation and mixing in the stratosphere and mesosphere.

- 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.

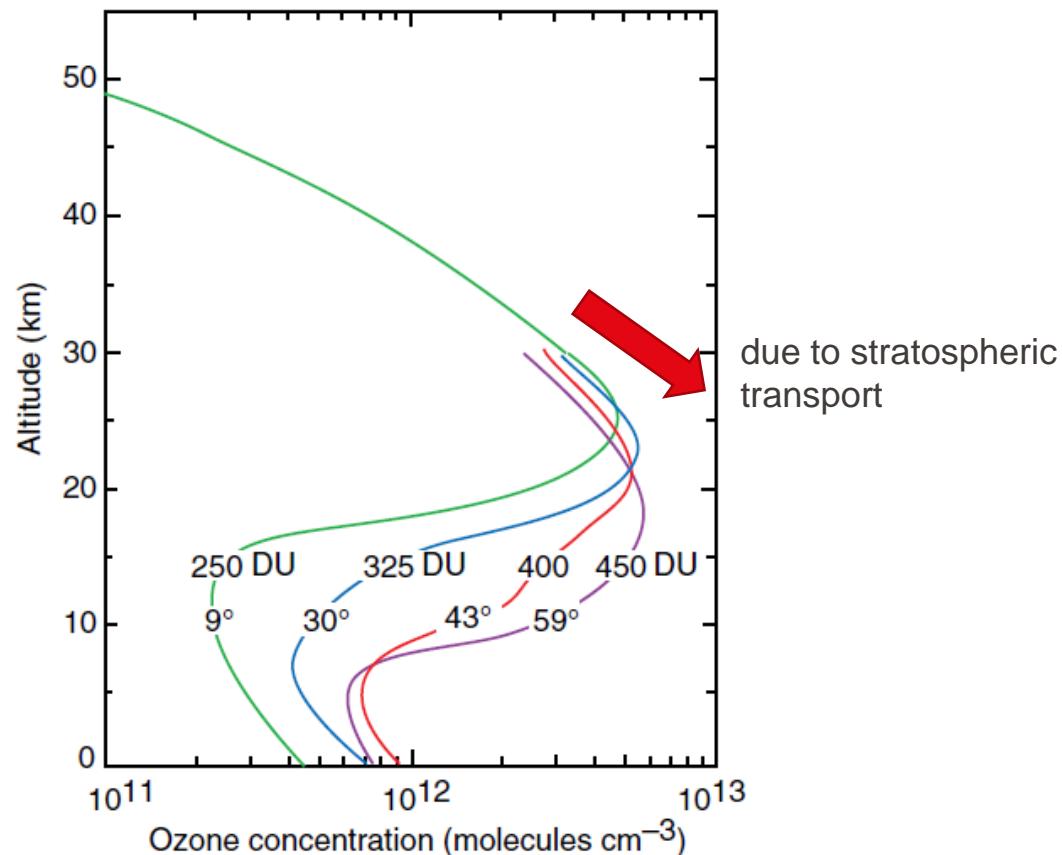
Both, circulation and mixing are mainly induced by wave activity on different scales (planetary to gravity waves).

- 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.



Ozone vertical profiles



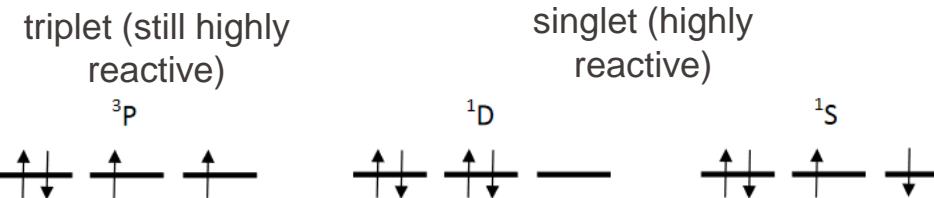
- It forms a protective shield that reduces the intensity of UV radiation (with wavelengths between 0.23 and 0.32 μm) from the sun that reaches the Earth's surface.
- Because of the absorption of UV radiation by O_3 , it determines the vertical profile of temperature in the stratosphere.
- It is involved in many stratospheric chemical reactions.
- 90 % of atmospheric O_3 is in stratosphere

Chapman reactions

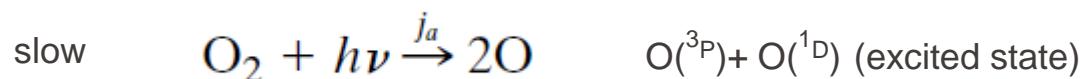
Assumption: oxygen only atmosphere

Note: reaction coefficients depend on temperature

4 electrons of the 2p - orbital

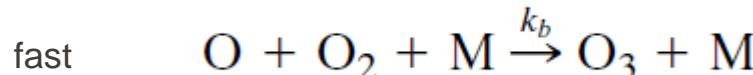


A. Dissociation of O_2 by UV ($0.180 \leq \lambda \leq 0.240 \mu m$)



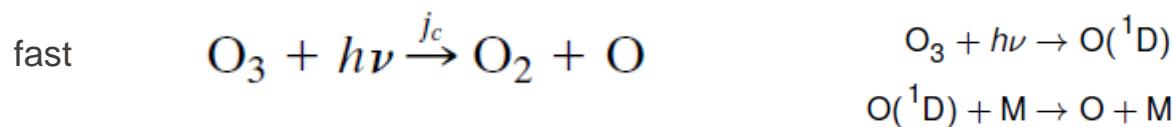
B. Atomic O and O_2 react to form O_3 (M is N_2 or O_2)

Occurs more rarely than often.

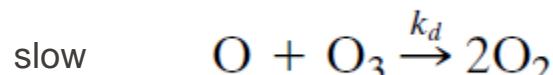


Needs M to absorb excess energy to form a stable O_3 molecule. Hence time constant increases with altitude, i.e becomes slower.

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

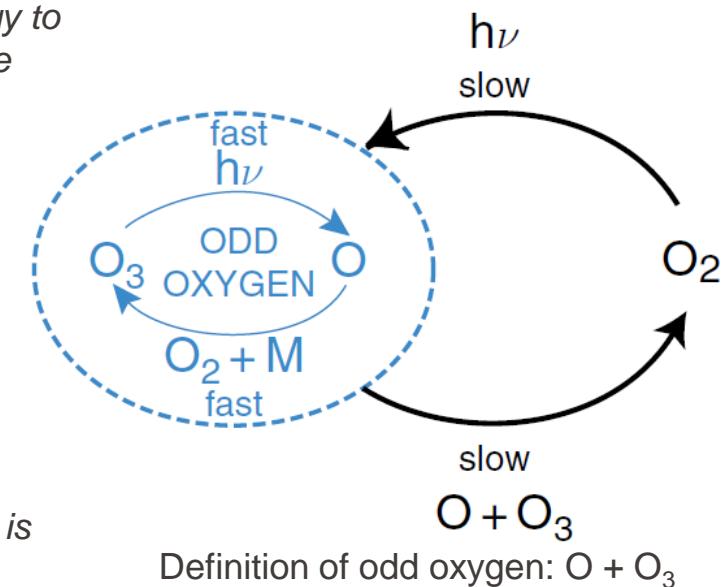


D. Atomic O and O_3 combine to form O_2



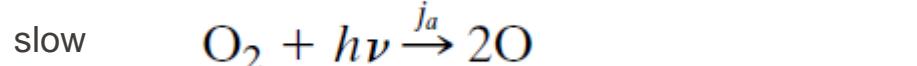
Reaction becomes faster with higher altitude, because more O is available there.

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



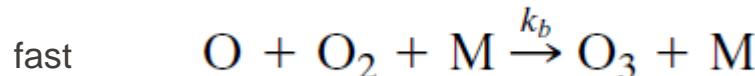
Is there a diurnal cycle of O₃ in the stratosphere?

A. Dissociation of O₂ by UV ($0.180 \leq \lambda \leq 0.240 \mu m$)

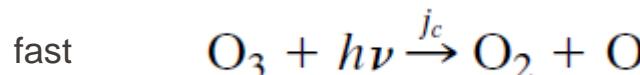


B. Atomic O and O₂ react to form O₃ (M is N₂ or O₂)

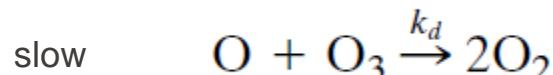
Occurs more rarely than often.



C. O₃ undergoes photodissociation ($0.200 \leq \lambda \leq 0.300 \mu m$)



D. Atomic O and O₃ combine to form O₂

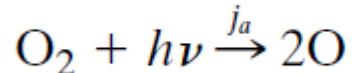


- A. No.
- B. Yes.
- C. A small one.

Is there a diurnal cycle of O₃ in the stratosphere?

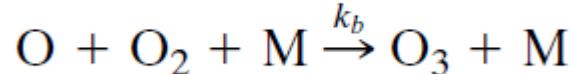
A. Dissociation of O₂ by UV (0.180 $\leq \lambda \leq$ 0.240 μm)

slow



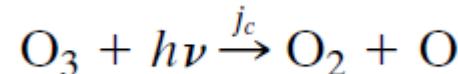
B. Atomic O and O₂ react to form O₃ (M is N₂ or O₂) Occurs more rarely than often.

fast



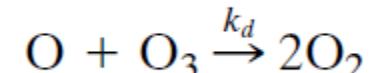
C. O₃ undergoes photodissociation (0.200 $\leq \lambda \leq$ 0.300 μm)

fast



D. Atomic O and O₃ combine to form O₂

slow



- Stratospheric O₃ concentrations exhibit minor diurnal variations with time of day.
- After sunset, both the source (A) and the sink of O₃ (C) are switched off, and the remaining O atoms are then converted to O₃ within a minute or so by (B).
- When the sun rises, some of the O₃ molecules are destroyed by (C) but they are reformed by (A) followed by (B).

A missing sink

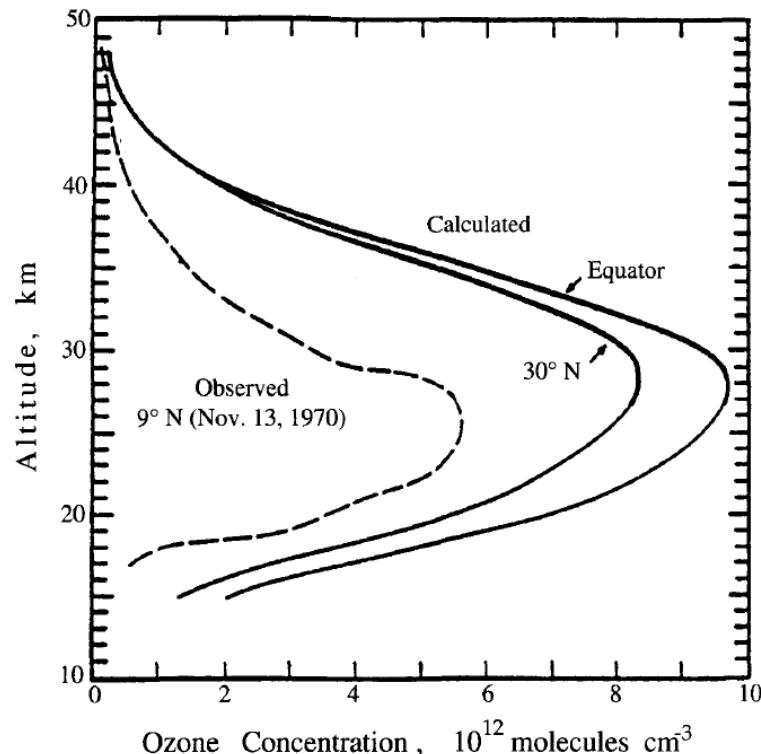


FIGURE 5.5 Comparison of stratospheric ozone concentrations as a function of altitude as predicted by the Chapman mechanism and as observed over Panama (9°N) on November 13, 1970.

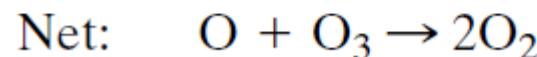
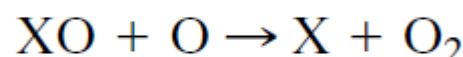
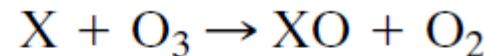
Seinfeld and Pandis, 2006, p. 150

- Chapman reactions predict the shape of the vertical profile correctly.
- They overestimate O_3 concentration by a factor of two in the tropics and underestimate O_3 in the higher latitudes.
- The rate of production is too high compared to the actual measured concentration.
- O_3 concentrations are not increasing, hence there must a sink for odd oxygen.



Catalytic cycles of O_3 depletion involving H , OH , Cl , Br .

Catalytic cycles



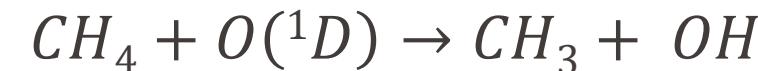
- X catalyst
- XO intermediate product
- Reactions are fast
- Since X is recycled, only a small concentration is sufficient to remove odd oxygen.

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

*, ** atomic oxygen is scarce

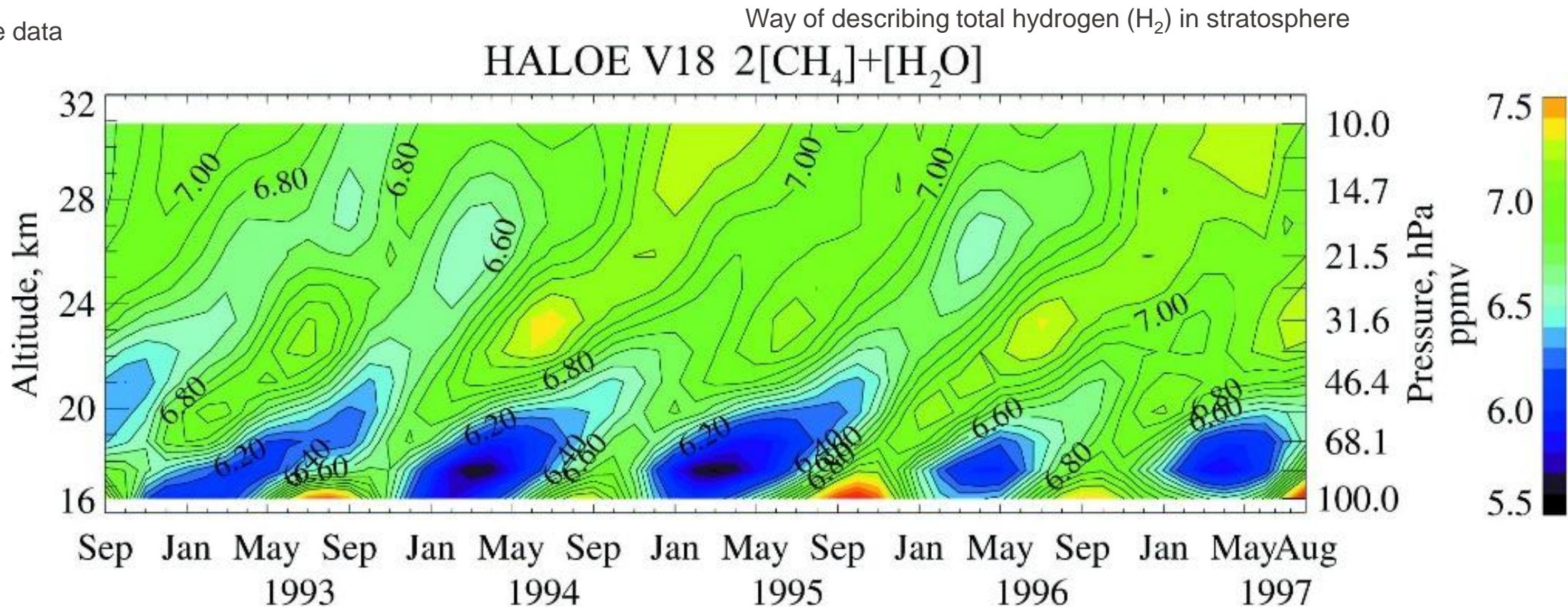
Hydrogen species as candidate for O destruction: OH, HO₂ (HO_x)

Three sources of OH in the stratosphere:



Stratospheric tape recorder: source of water vapor and methane

Satellite data

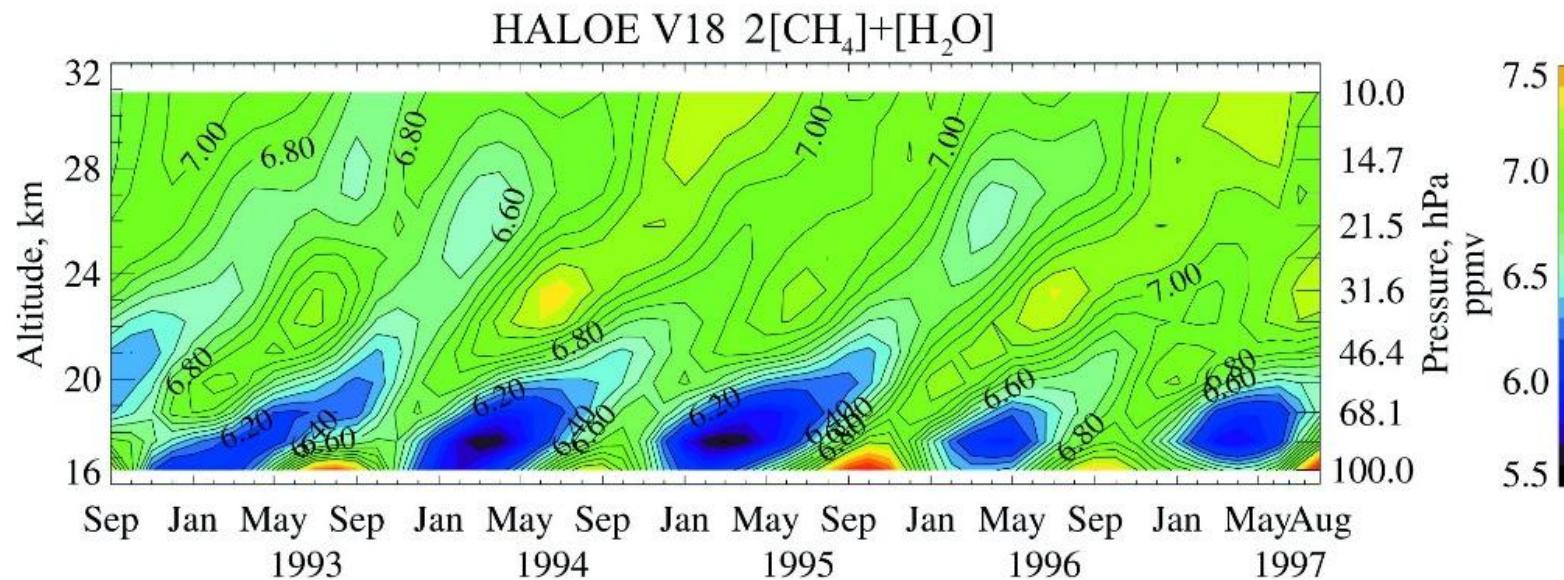


MO, Global Ozone Research and Monitoring Project-Report No. 44

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

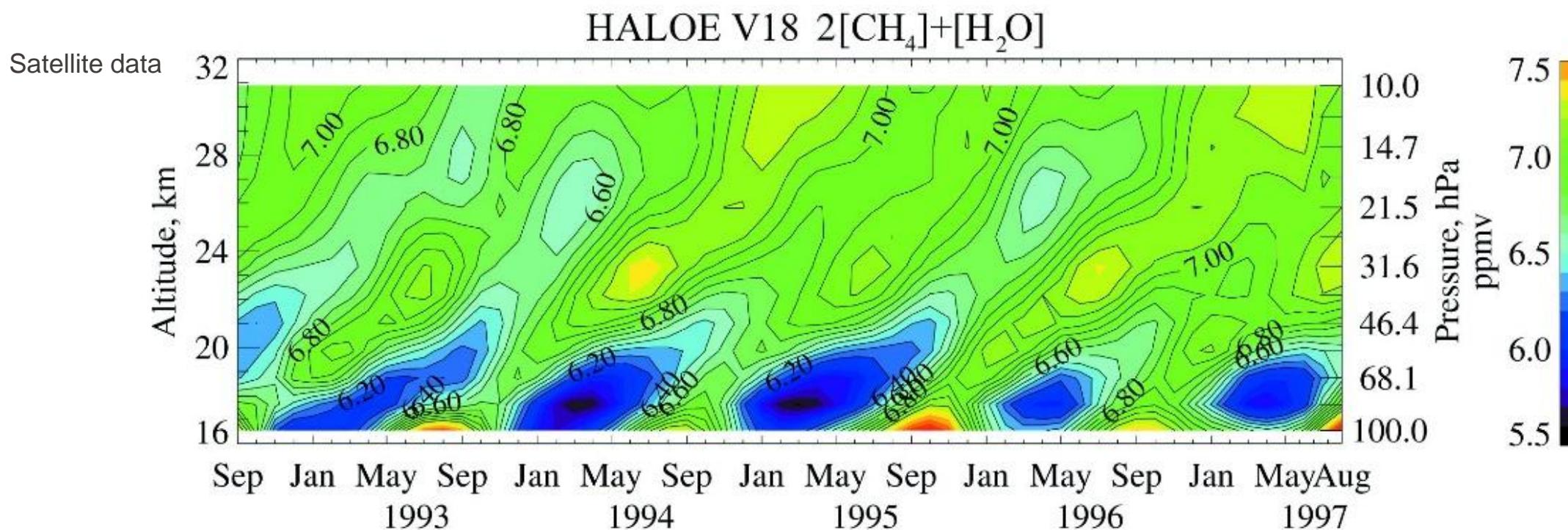
What happens in the annual cycle?

- 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

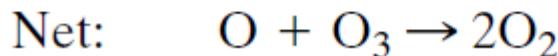
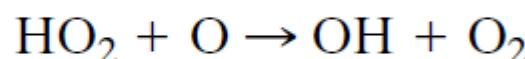
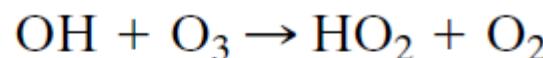


Temperatures at tropical tropopause have a yearly cycle. When they are colder, the water vapor mixing ratio is lower (condensation, ice crystal formation, precipitation). Hence less water vapor is introduced into the stratosphere. Methane is not affected by the temperature.

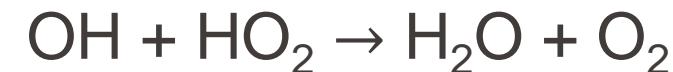
Each air mass which passes the tropopause carries that specific water vapor signature (color code, tape recorder).

HO_x Catalytic cycles

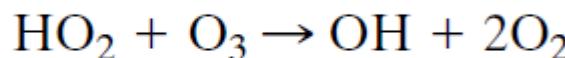
Below ~40 km where atomic oxygen is available:



Cycle disruption by removal of HO_x:



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



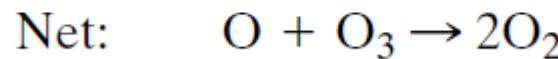
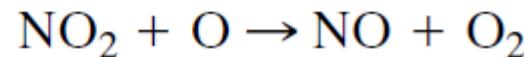
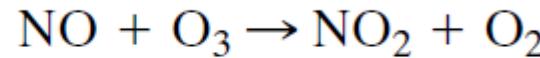
Reservoir species

Reservoir species remove HO_x from fast reaction cycles.

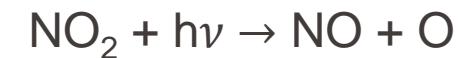
NO_x catalytic cycles

In analogy to HO_x.

Most important in the middle stratosphere.



Cycling between NO and NO₂
(interference cycle):

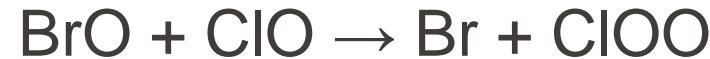


NET: No change

Removal of NO_x into **reservoir species**



Cl_x and Br_x catalytic cycles



Natural sources of Br and Cl are

- CH_3Br
- CH_3Cl

from oceanic, terrestrial (plants, soils) emissions.

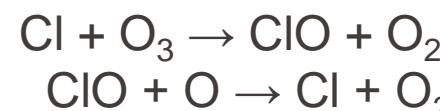
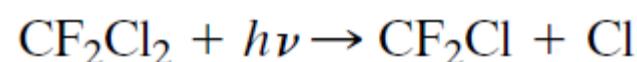
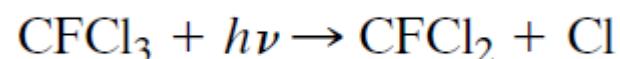
The methyl compounds are photolyzed by UV radiation.



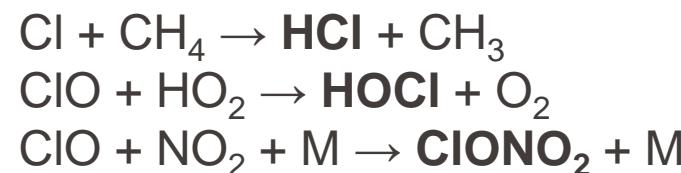
Overall, the many chemical reactions and catalytic cycles constitute a delicate equilibrium that maintains the stratospheric ozone layer.

Anthropogenic changes to catalytic cycles

Source of Cl_x are CFCs, through photolytic generation of Cl (photodissociation) ($0.190 \leq \lambda \leq 0.220 \mu\text{m}$).

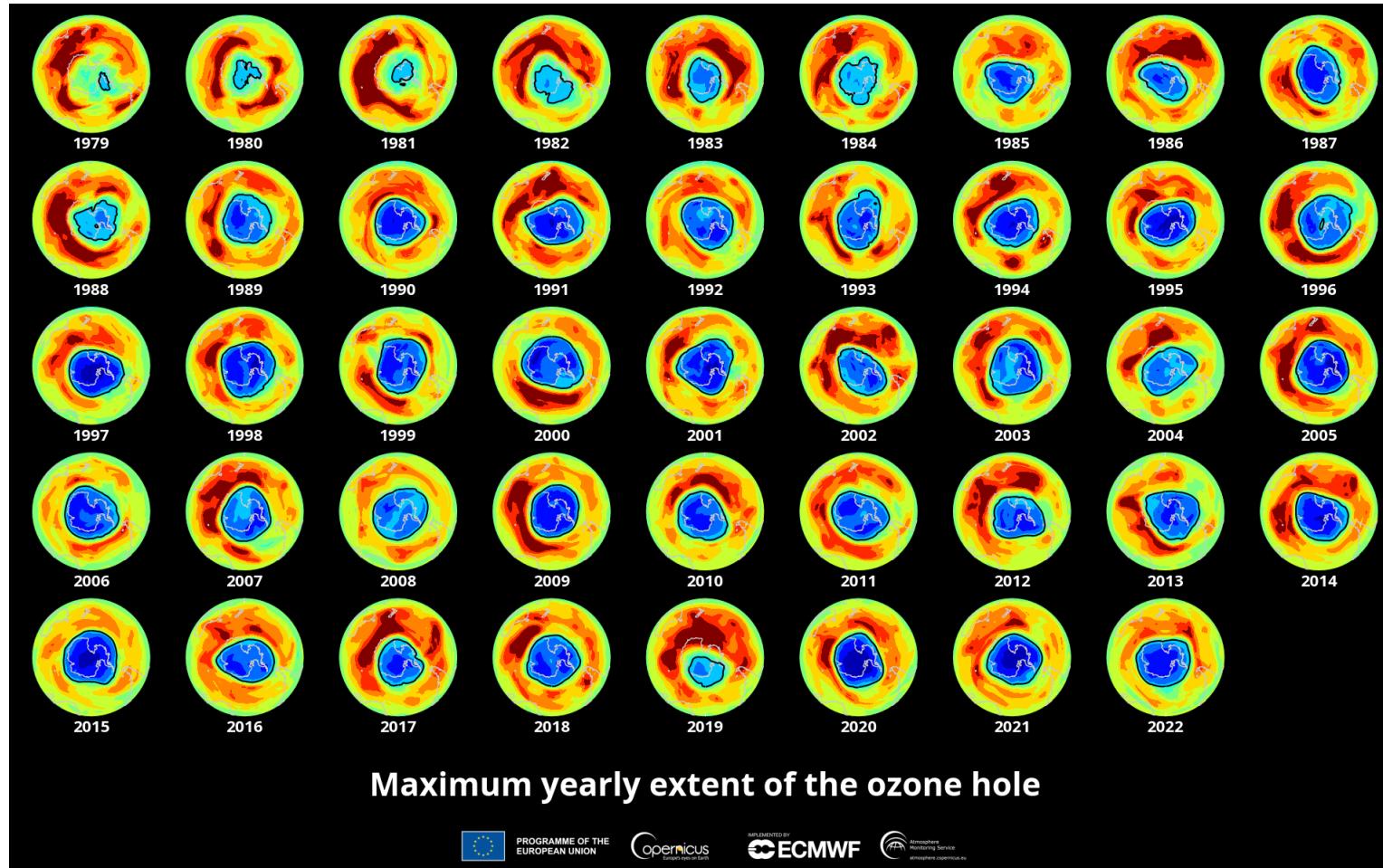


Transformation into **reservoir species**:



- CFCs originate from cooling agents and other applications. They have first been synthesized in 1928. CFCl_3 and CF_2Cl_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.

Antarctic Ozone hole



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



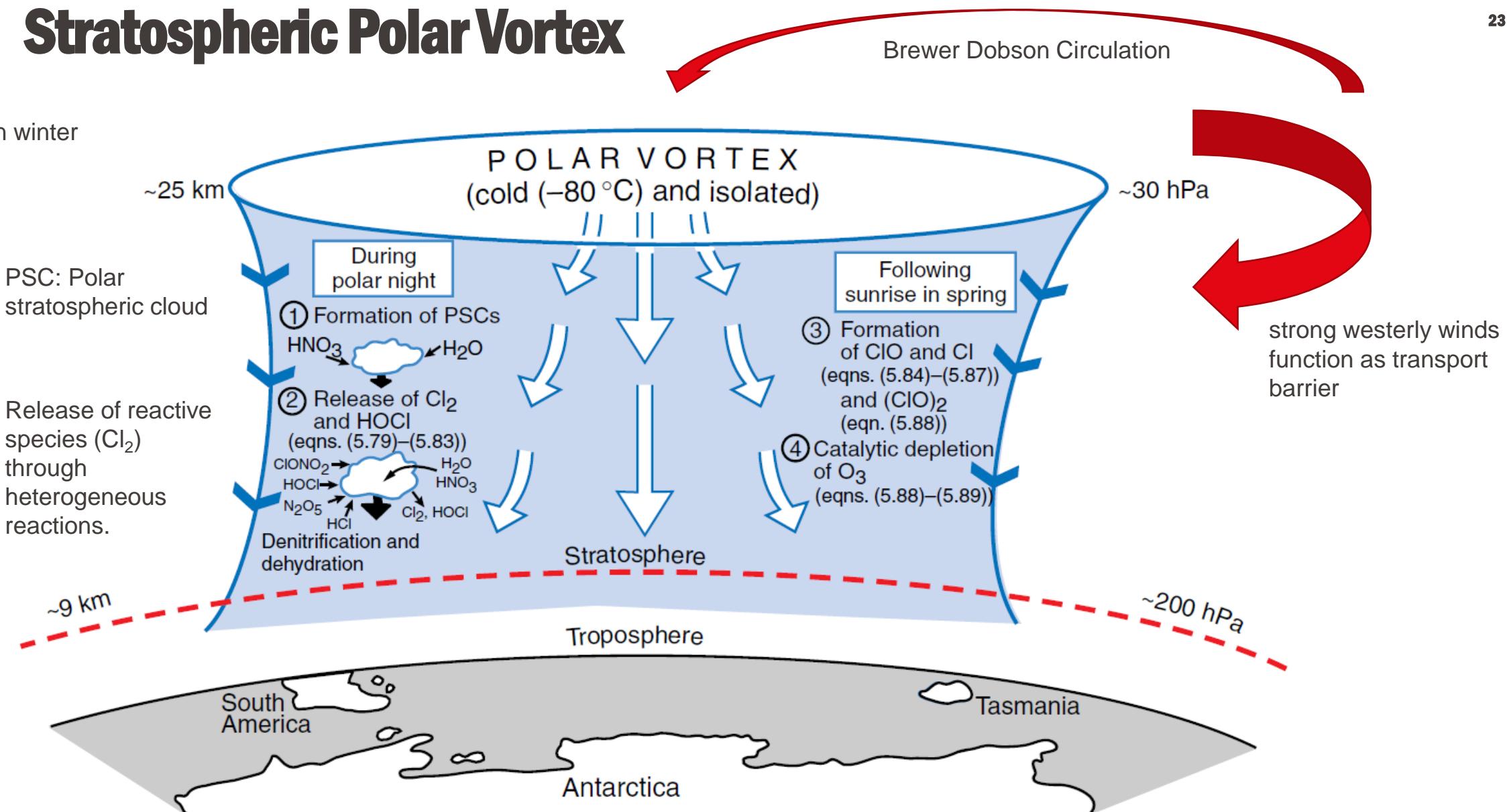
<https://atmosphere.copernicus.eu/three-peculiar-antarctic-ozone-hole-seasons-row-what-we-know>

https://twitter.com/BAS_News/status/298753260574097408/photo/1

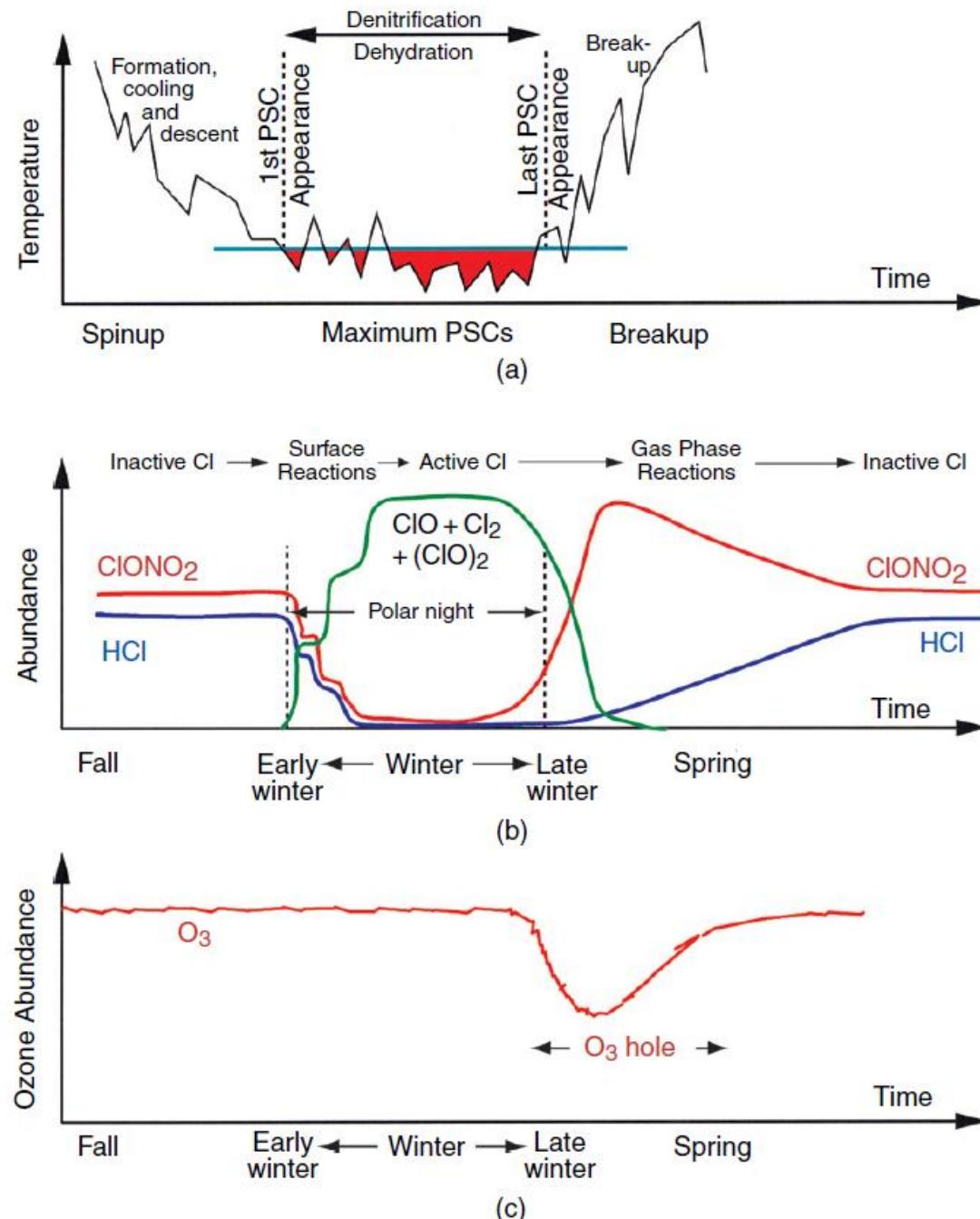
- Why over Antarctica?
- Why during spring?
- Why could models not predict it?

Stratospheric Polar Vortex

Builds up in winter



Antarctic ozone destruction



Wallace and Hobbs, 2006, Fig. 5.22

- Three types of PSCs

- Type I: forms near -78°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 $\sim 1 \mu\text{m}$, very slow sedimentation
- Type II: forms near -85°C , HNO_3 , H_2O , sulfuric acid tetrahydrate $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_4$ (SAT) particles $> 10 \mu\text{m}$, settle quickly
- Type III: rapid freezing of H_2O due to orographic flow, (mother of pearl clouds, short-lived)

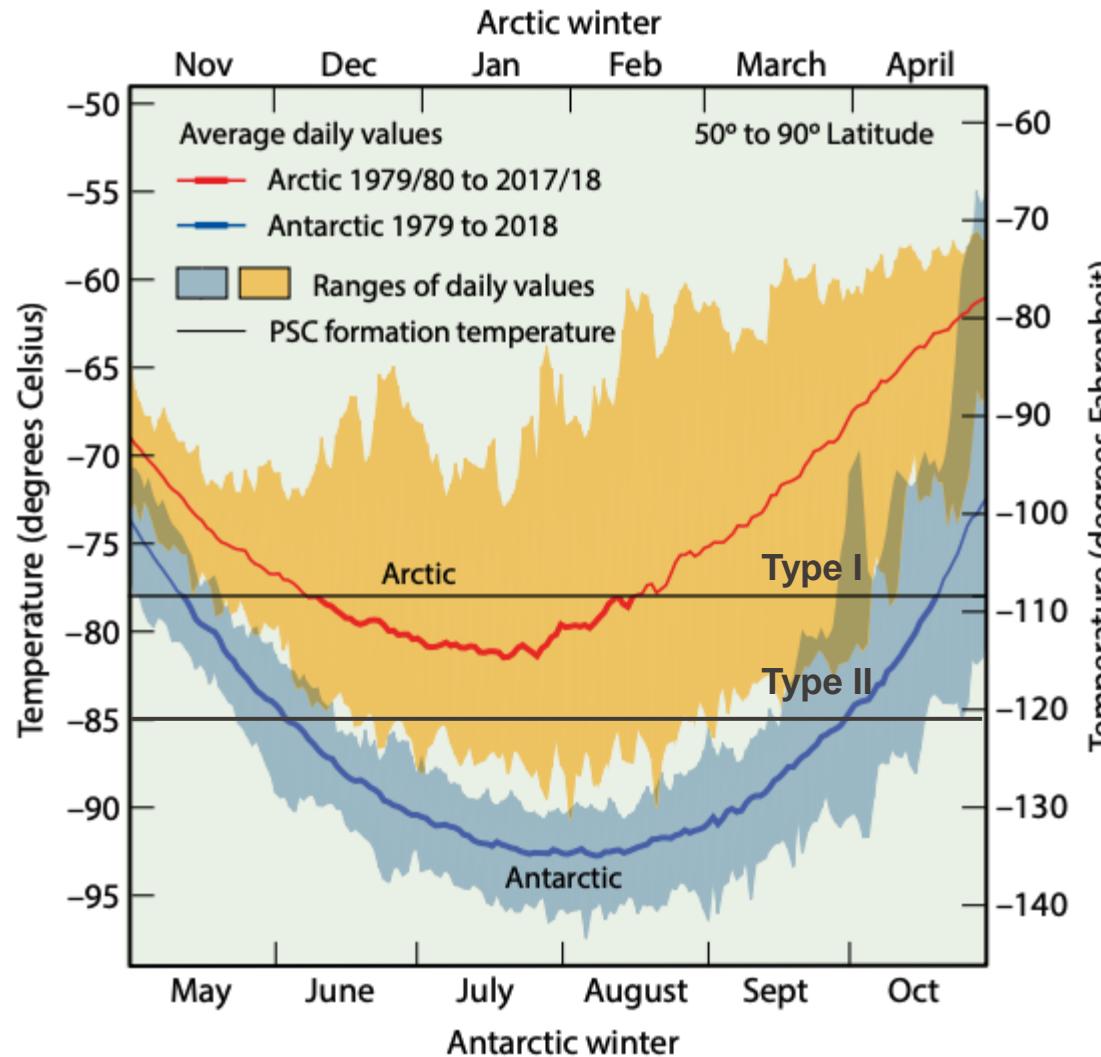


https://de.wikipedia.org/wiki/Polare_Stratosph%C3%A4renwolken#/media/Datei:Arctic_stratospheric_cloud.jpg



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:
 HNO_3 , H_2O , $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_4$ (SAT)

PSCs are responsible for the formation of reactive halogens (e.g., Cl_2) in the stratosphere that deplete ozone.

Heterogeneous chemistry: Adsorption mechanisms

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

Key reaction to create reactive Cl_2 is:

a) $\text{ClONO}_2(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{Cl}_2(\text{g}) + \text{HNO}_3(\text{g})$ slow
 b) $\text{ClONO}_2(\text{g}) + \text{HCl}(\text{s}) \rightarrow \text{Cl}_2(\text{g}) + \text{HNO}_3(\text{s})$ fast

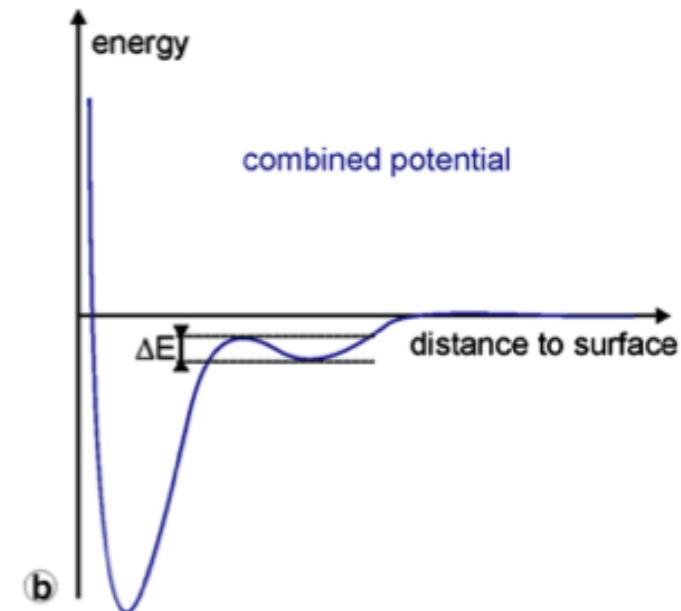
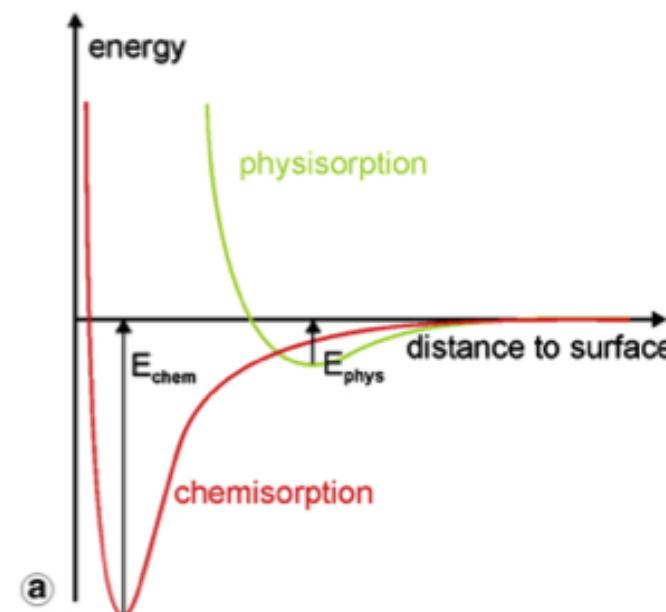
Why is b faster?

HCl is ionized at the ice surface. That means Cl^- ions are available for the reaction with 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.

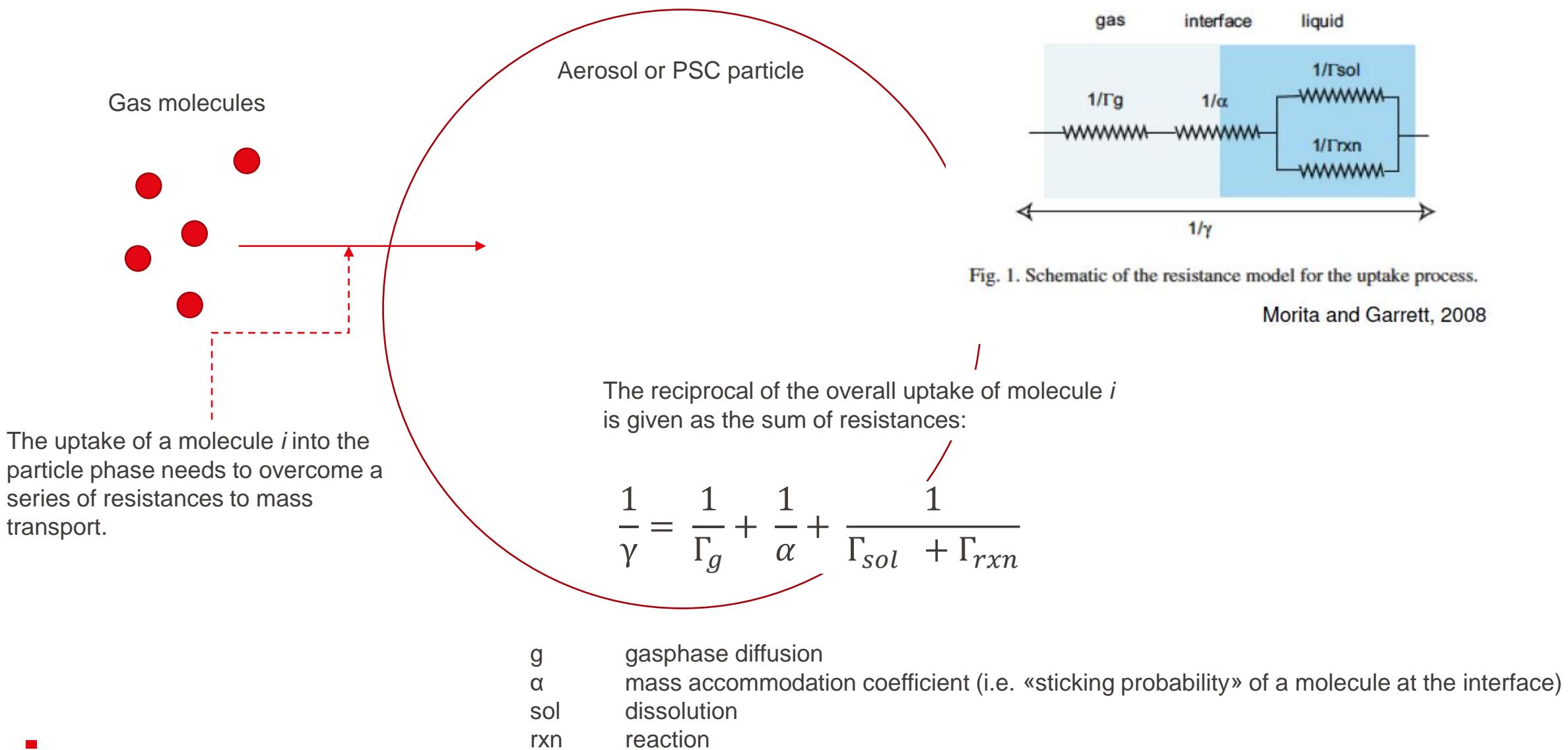
(g) Gas phase
 (s) Solid phase, i.e. on ice

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



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 ΔE might exist which needs to be overcome for chemisorption to occur.

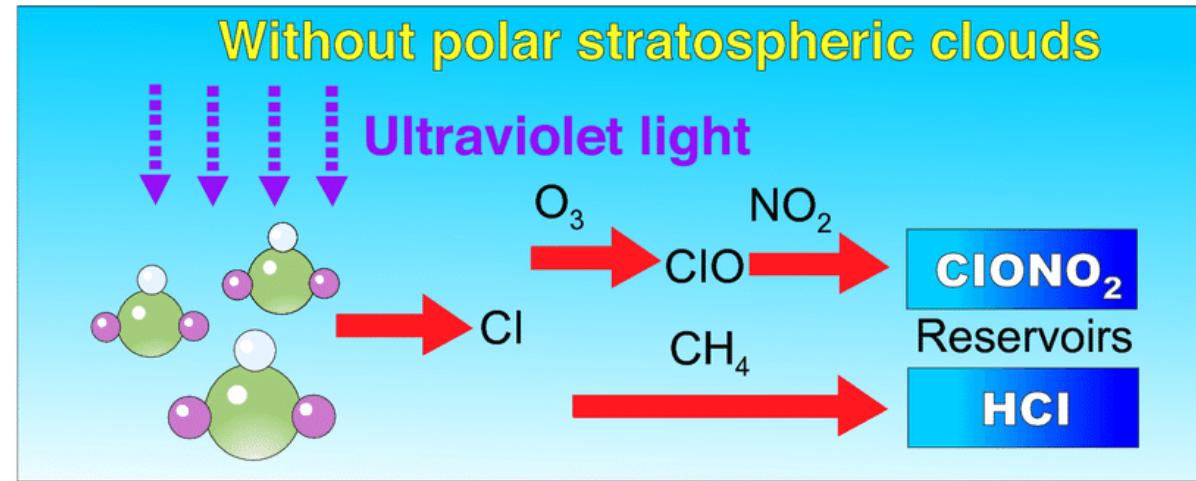
Uptake of a gas molecule into a particle



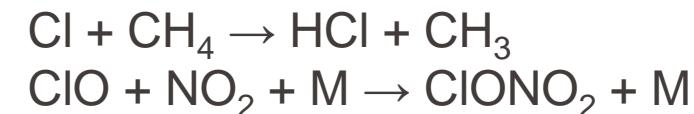
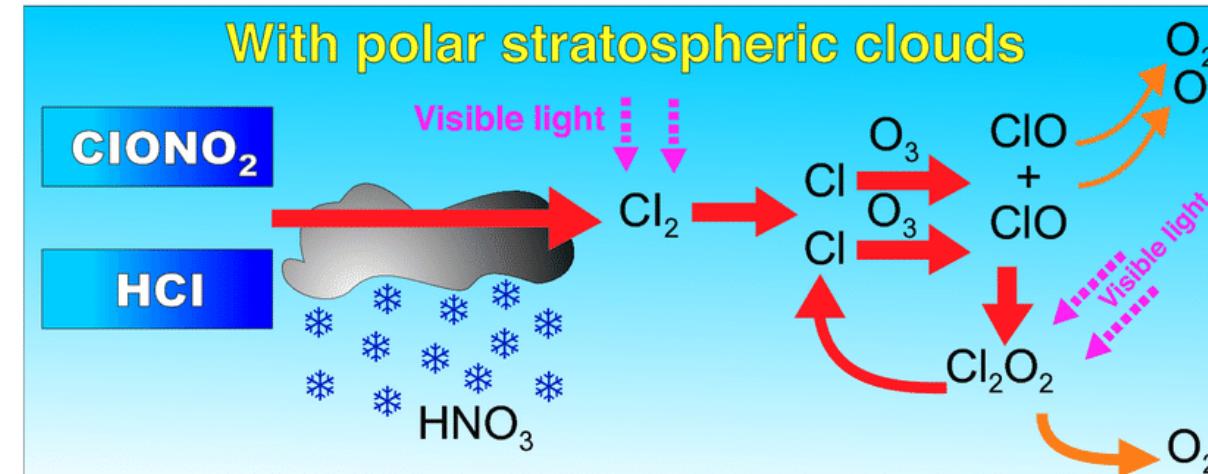
Heterogeneous chemistry on PSC

Important because they convert the benign Cl-reservoir species into reactive species, and they remove HNO_3 (denitrification) leaving more reactive ClO (because NO_x is produced from HNO_3 , and NO_x produces the reservoir substance ClONO_2).

homogeneous chemistry
(gas-phase only)

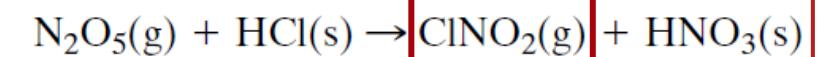
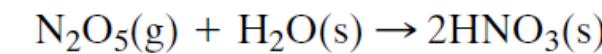
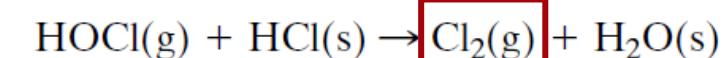
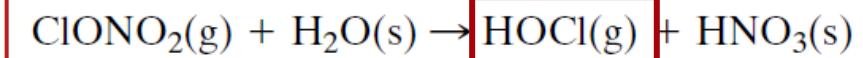
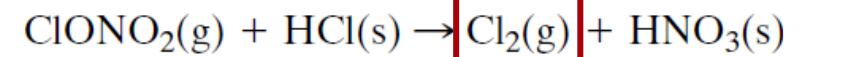


heterogeneous chemistry (gas and particle phases)



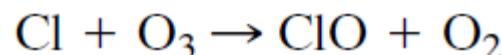
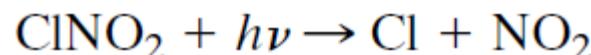
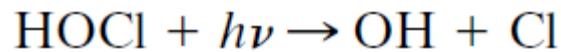
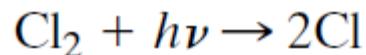
(g) Gas phase
(s) Solid phase, i.e. on ice

Reservoir \rightarrow reactive species

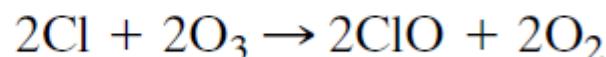
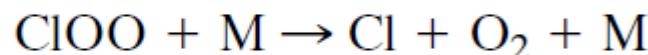
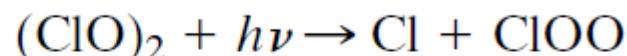


Photolysis during spring and ozone destruction

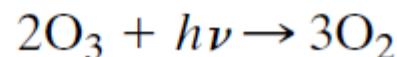
Photolysis



Ozone destruction

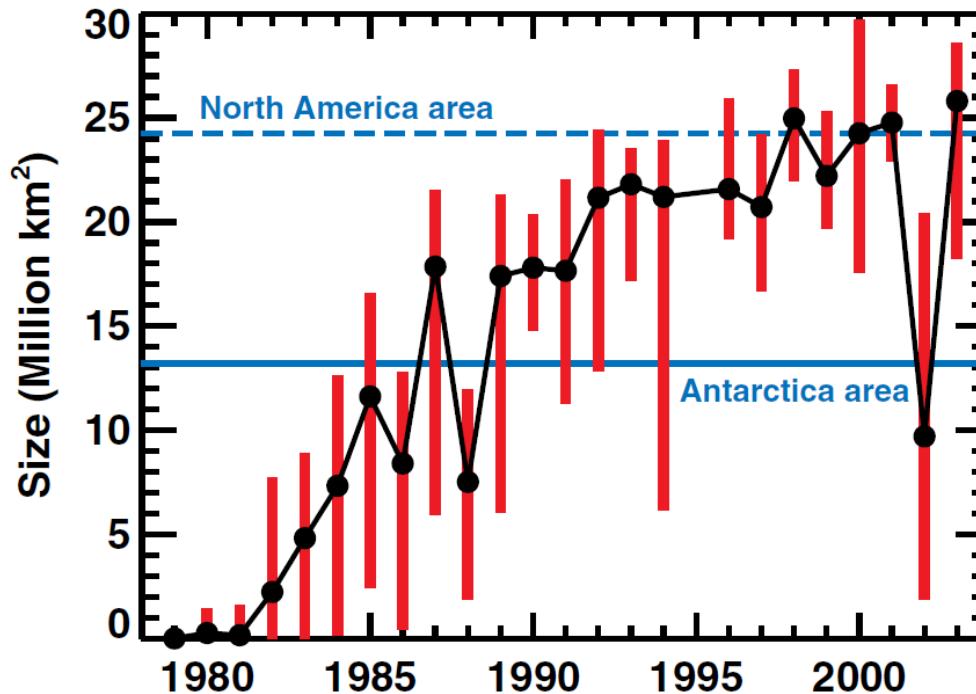


Net:



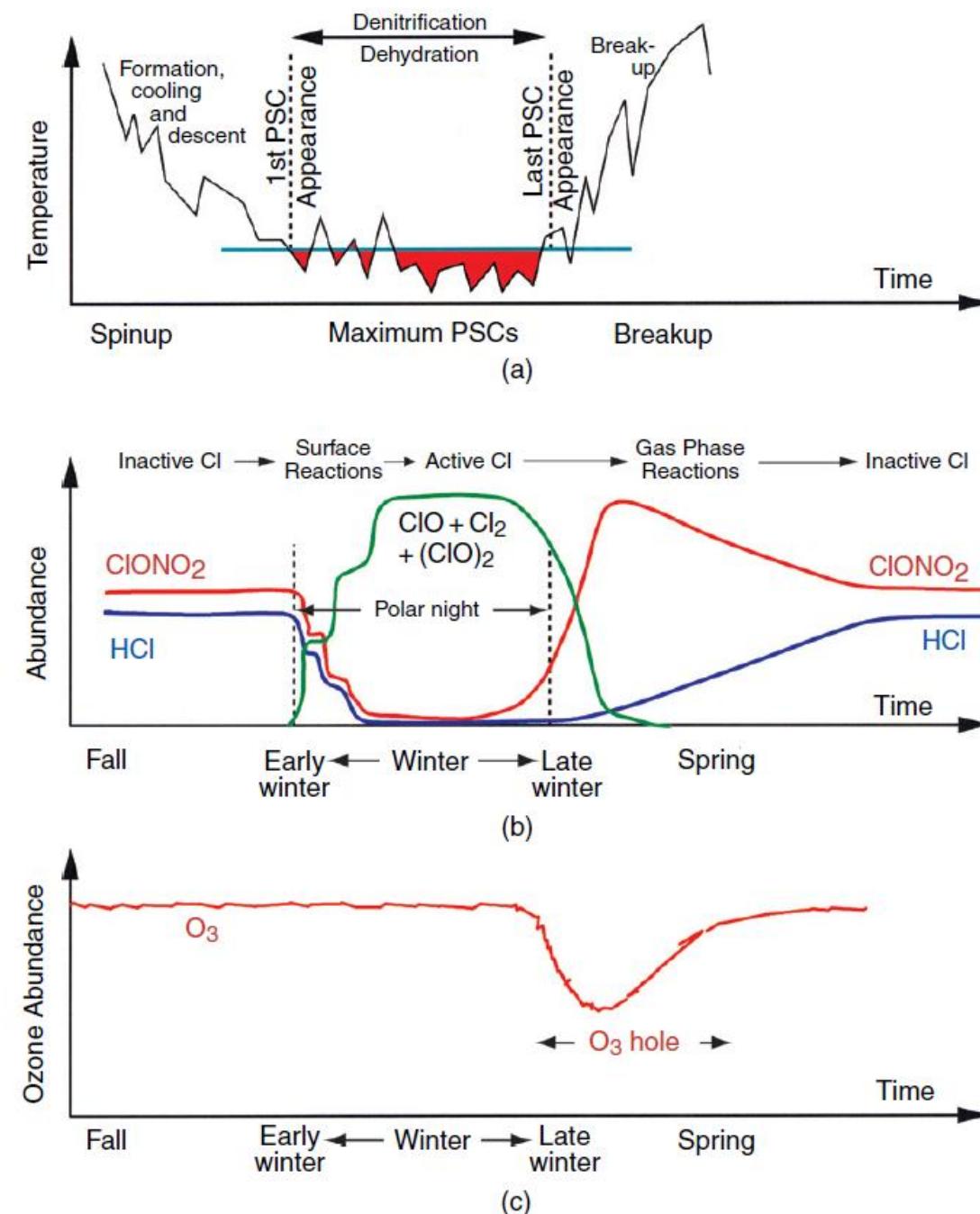
- ClO is the catalyst.
- No dependence on atomic oxygen (low abundance at that altitude)
- Cl comes from CFCs, but is normally tied up in reservoir species (HCl, ClONO₂)
- In the presence of PSCs, Cl₂, HOCl, and ClONO₂ are released and, as soon as the solar radiation reaches sufficient intensity in early spring, Cl and ClO are released, which lead to the rapid depletion of O₃
- The dimer (ClO)₂ 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 O₃.

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

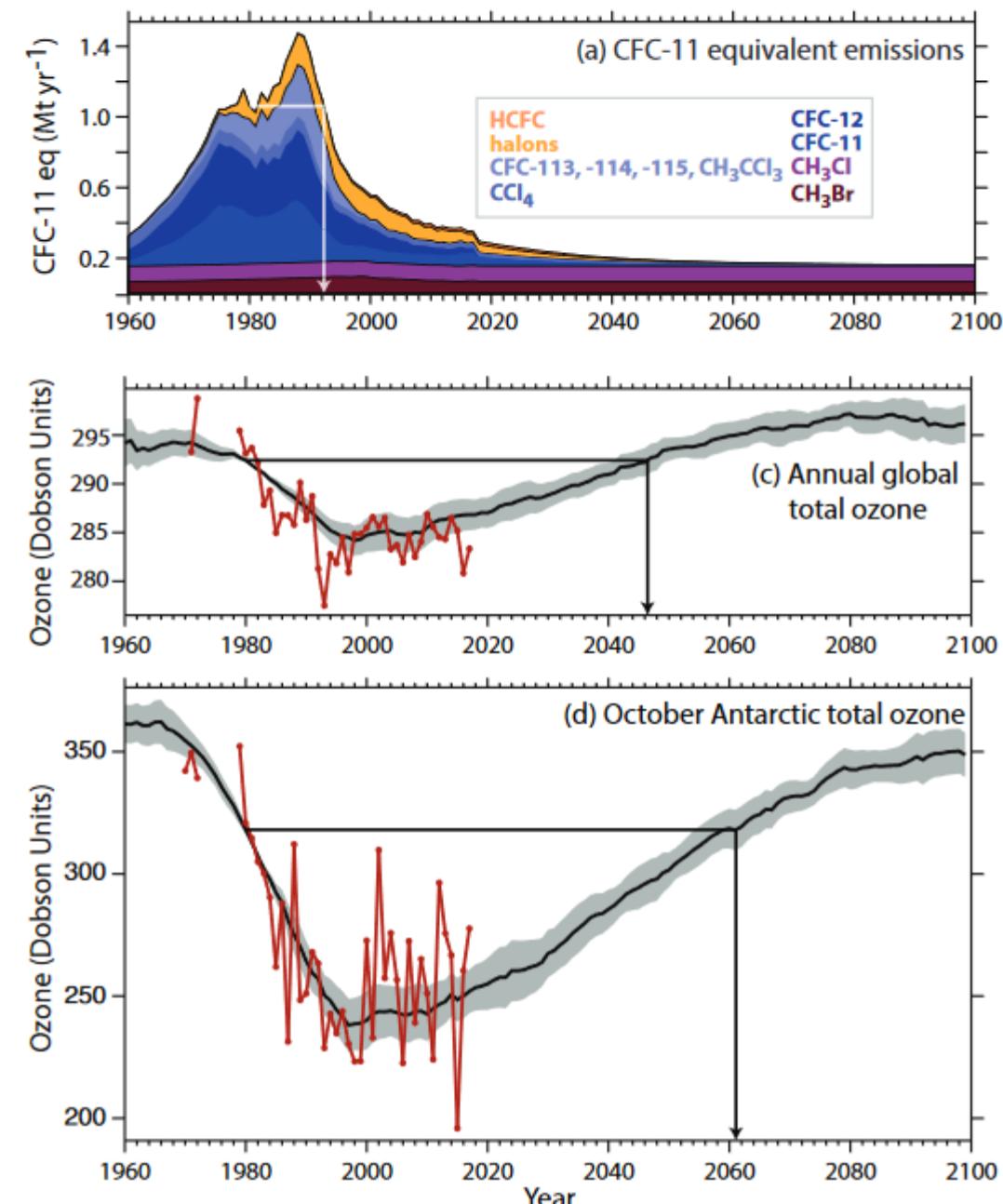


Why was there only a small ozone hole in 2002?

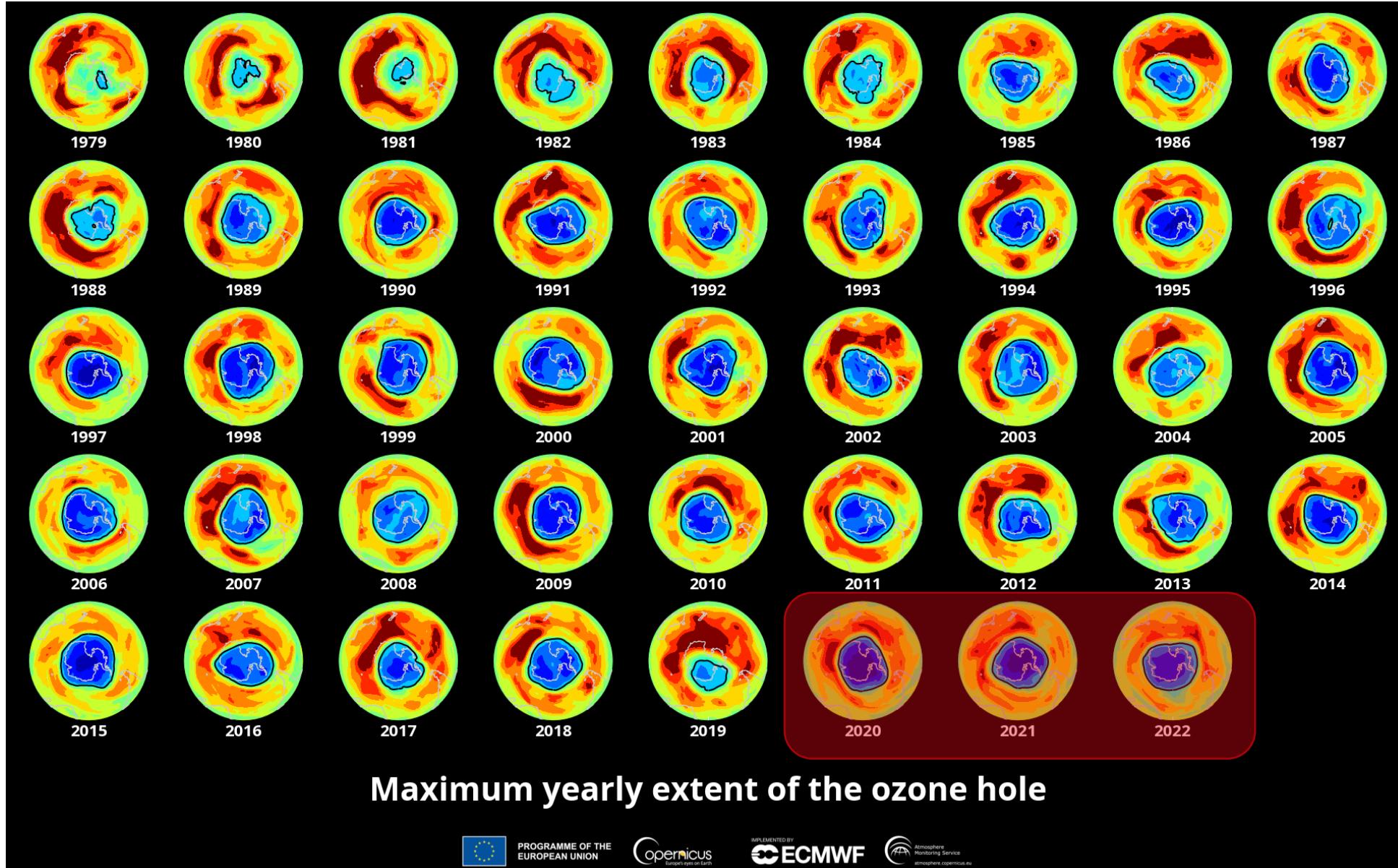
- A. The Brewer Dobson Circulation was disturbed by a volcanic eruption.
- B. No reservoir species were formed that year, because of a volcanic eruption.
- C. There was probably less HCl in the stratosphere.
- D. The winter was warm.
- E. B and D.

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



Antarctic Ozone hole



PROGRAMME OF THE
EUROPEAN UNION



IMPLEMENTED BY
ECMWF



Atmosphere Monitoring Service
atmosphere.copernicus.eu

Arctic ozone hole?

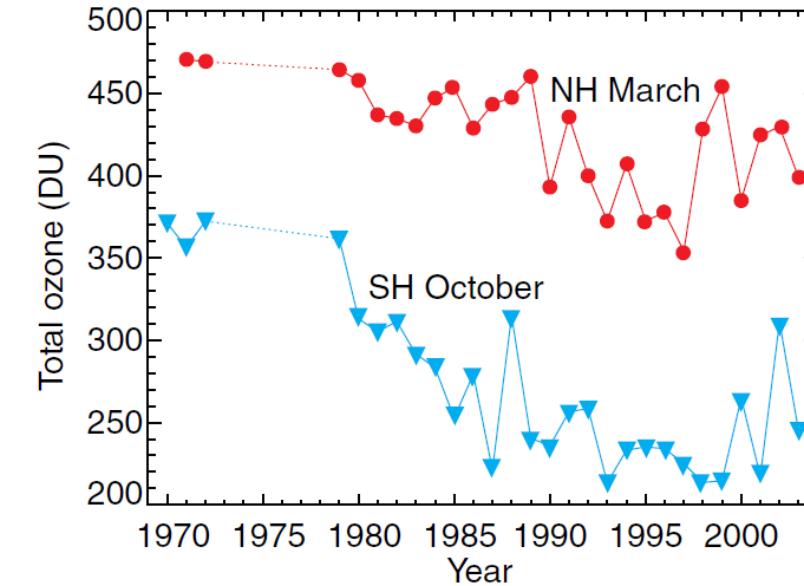
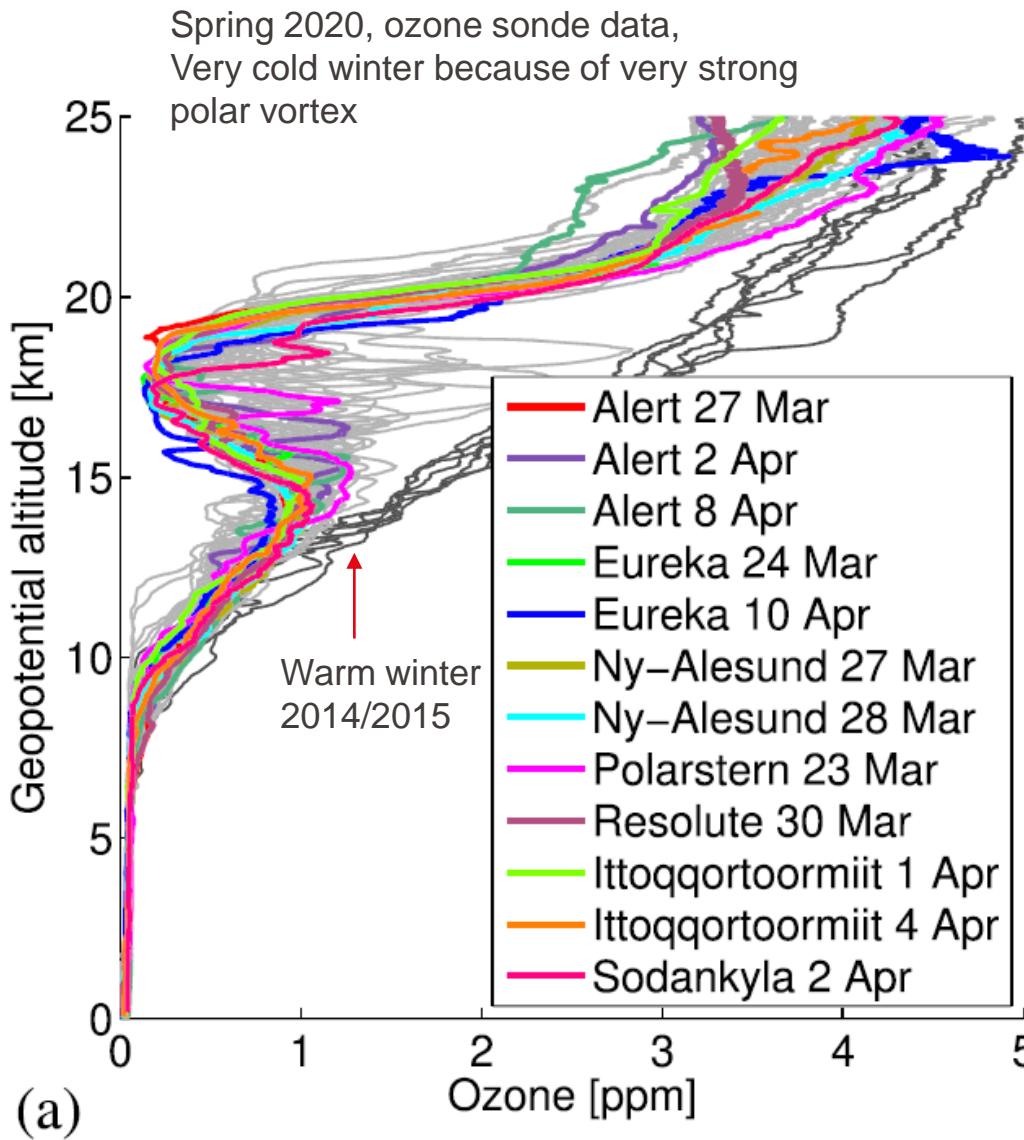


Fig. 5.23 Average ozone columns between latitudes 63° – 90° for the northern hemisphere in March (red line and symbols) and the southern hemisphere in October (blue line and symbols). [Adapted with courtesy of P. Newman, NASA Goddard Space Flight Center.]

Wallace and Hobbs, 2006

Can fires contribute to the ozone hole formation?

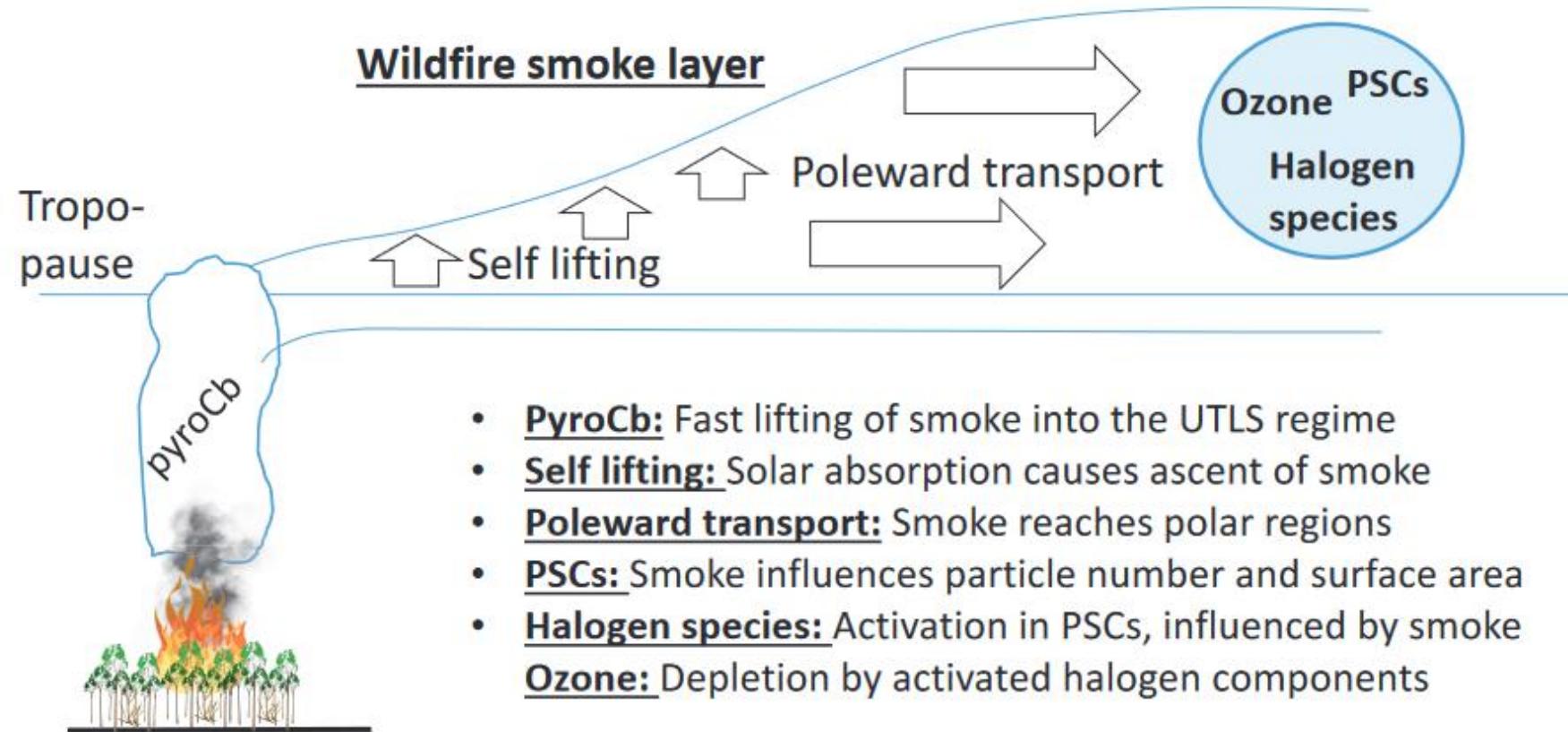
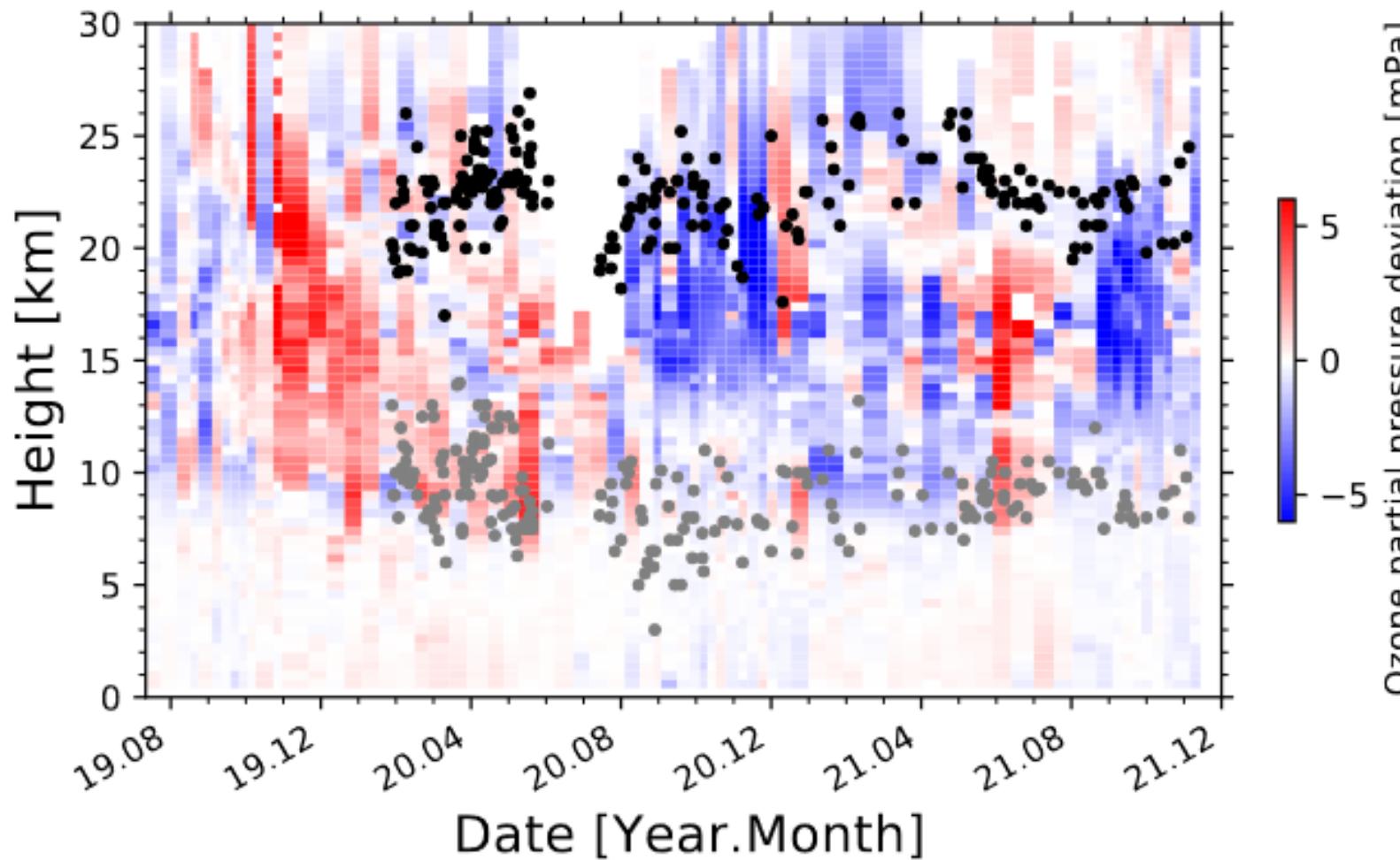


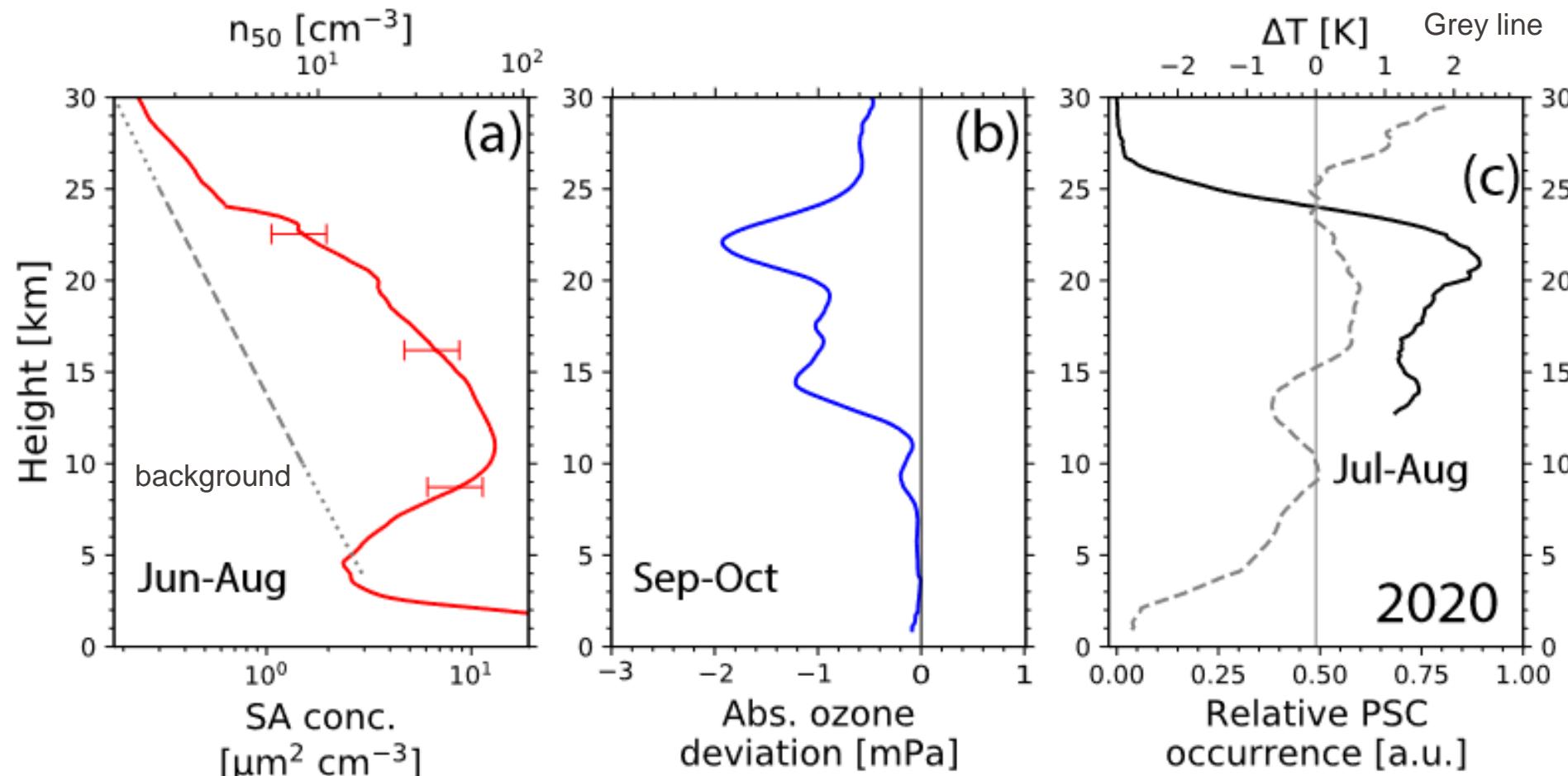
Figure 3. Key processes of the vertical and meridional transport of wildfire smoke from the emission sources to the polar regions.

Fires and Antarctic ozone whole



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.

Fires and Antarctic ozone whole



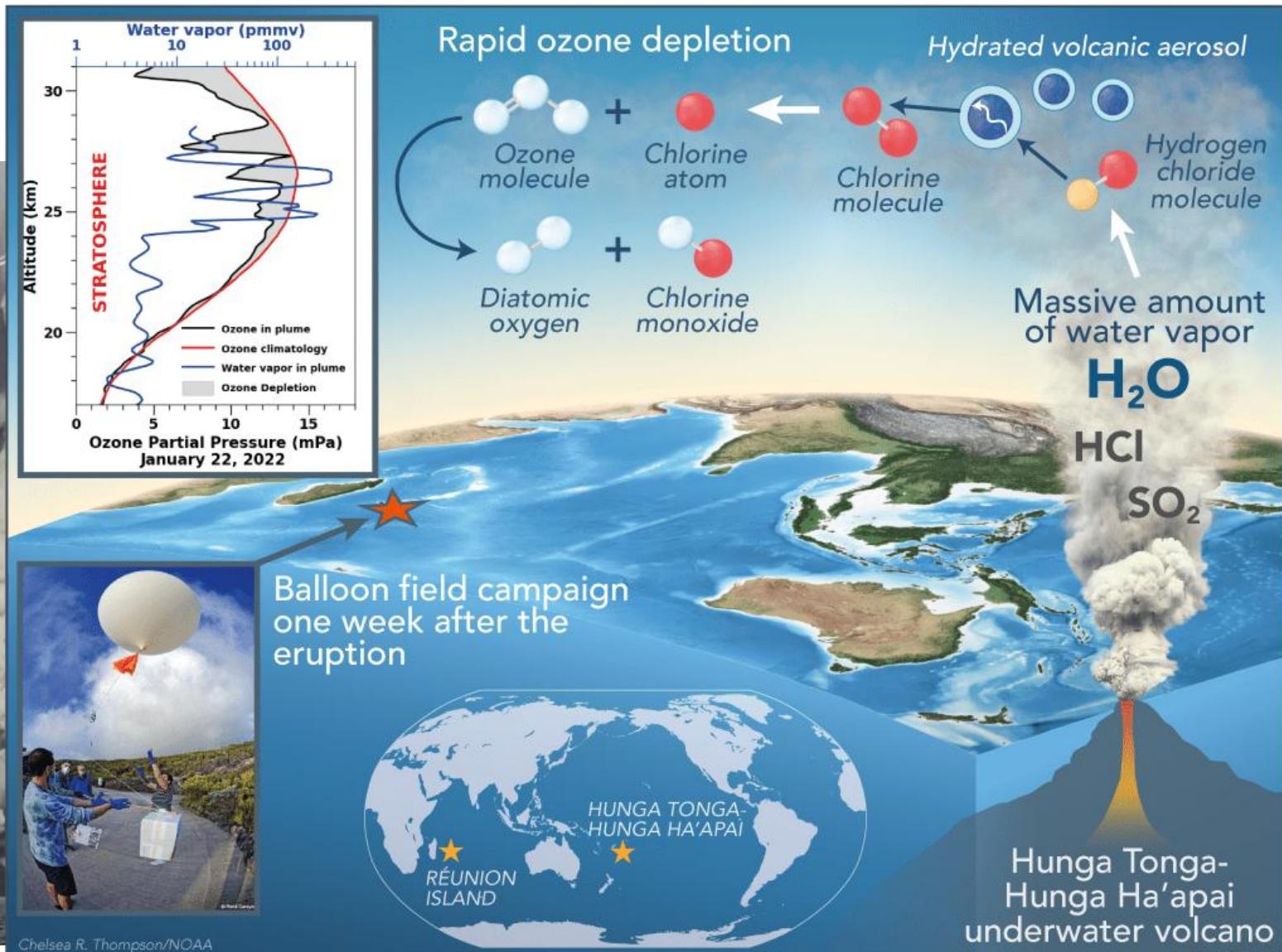
n50 (particles with radius >50 nm)

SA (surface area)

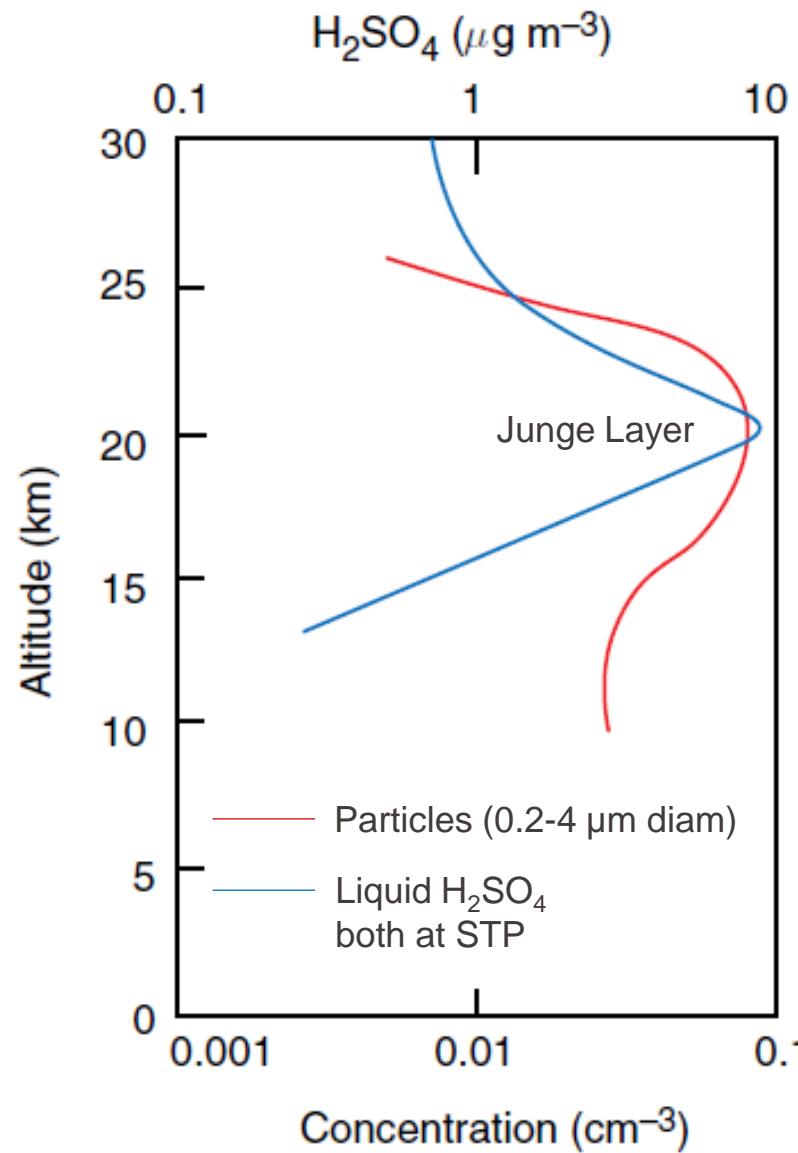
a.u. (arbitrary units)

Hunga-Tonga eruption

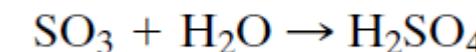
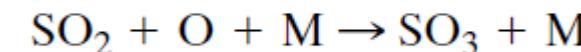
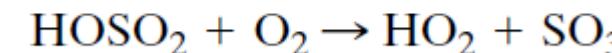
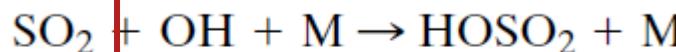
15 Jan 2022



Stratospheric sulfur (aerosols)



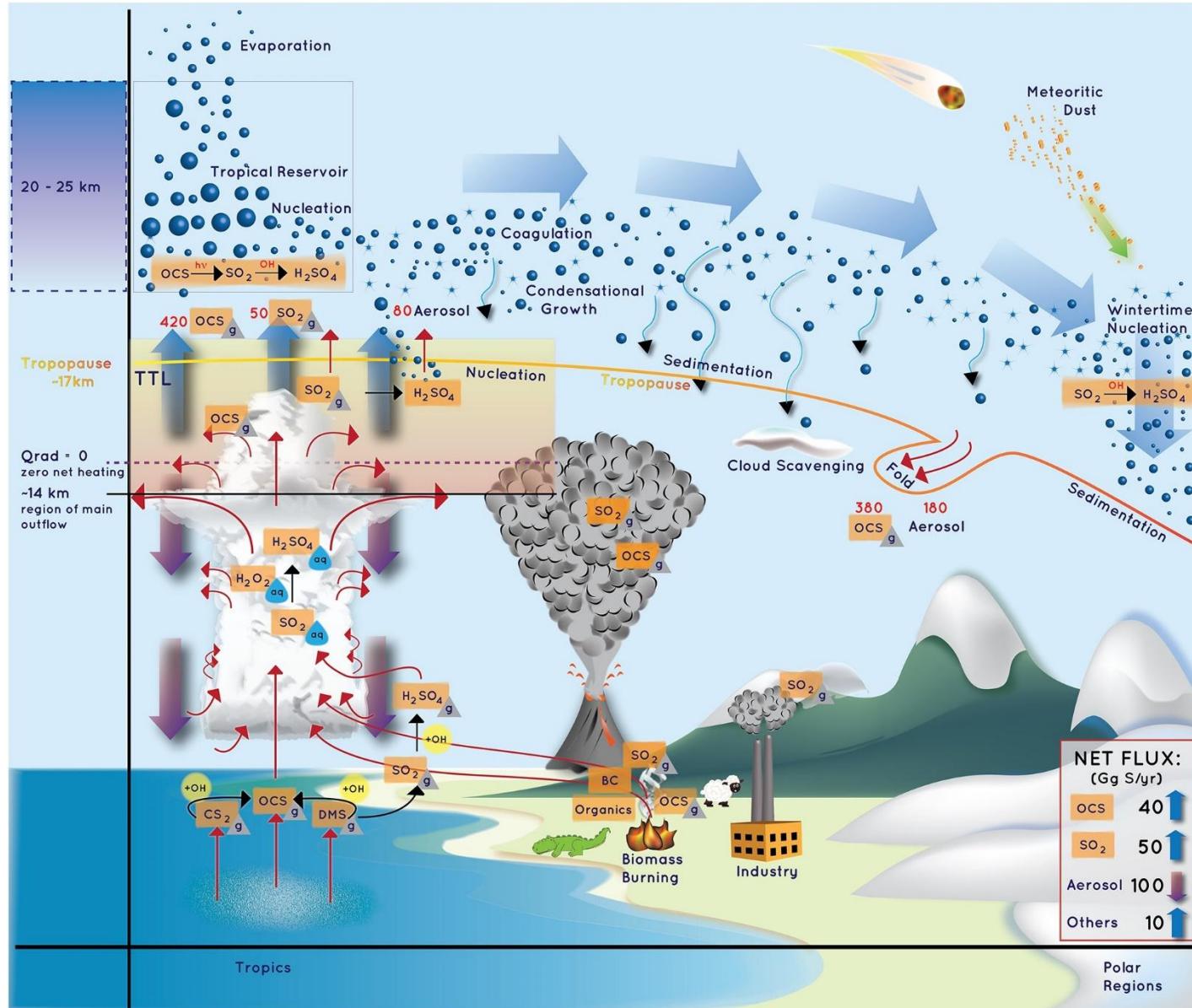
Formation of gaseous H_2SO_4



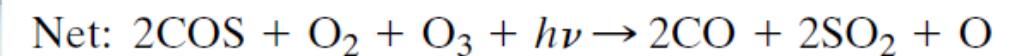
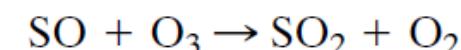
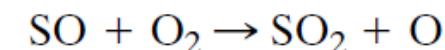
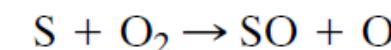
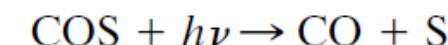
Particle formation:

- The combination of molecules of H_2SO_4 and H_2O (i.e., ***homogeneous, bimolecular nucleation***) and or the combination of H_2SO_4 , H_2O , and HNO_3 to form new (primarily sulfuric acid) droplets (i.e., ***homogeneous, heteromolecular nucleation***).
- Vapor condensation of H_2SO_4 , H_2O , and HNO_3 onto the surfaces of preexisting particles with radius 0.15 μm (i.e., ***heterogeneous, heteromolecular nucleation***).

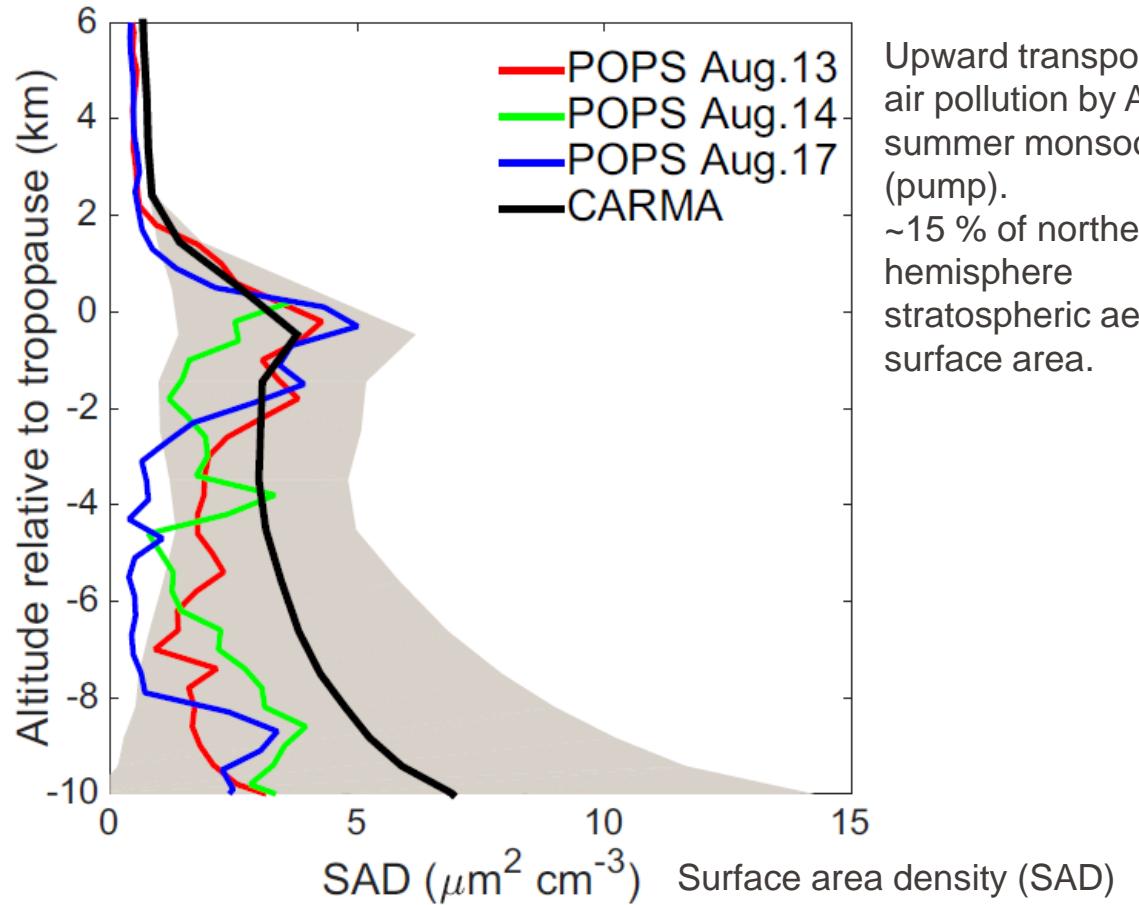
Sources of stratospheric aerosols



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

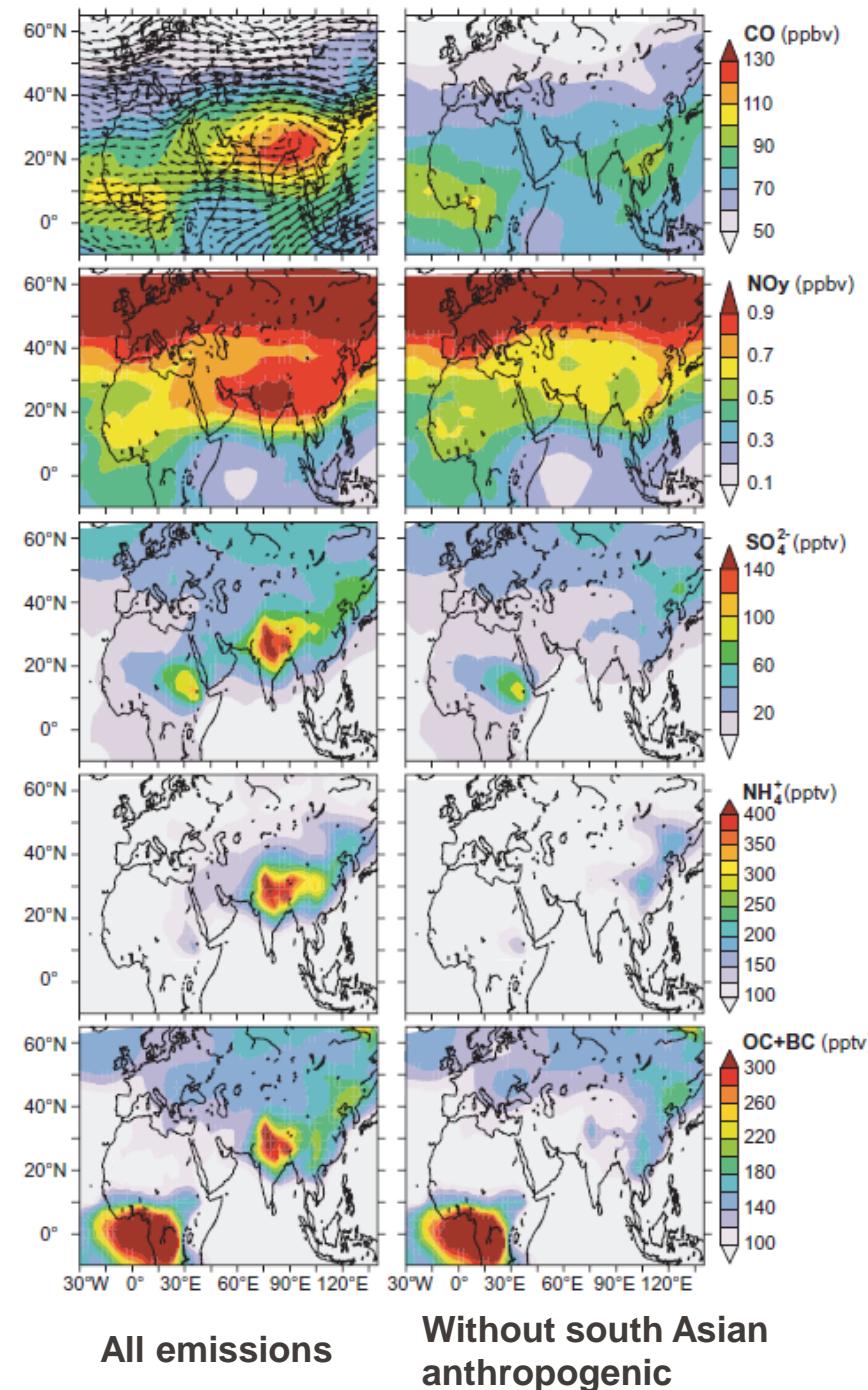


Contribution of Asian Emissions



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, NO_y (NO_x and all other oxidized nitrogen species except N₂O), 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.