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Polar Stratospheric Ozone: from the "Hole" to its Recovery

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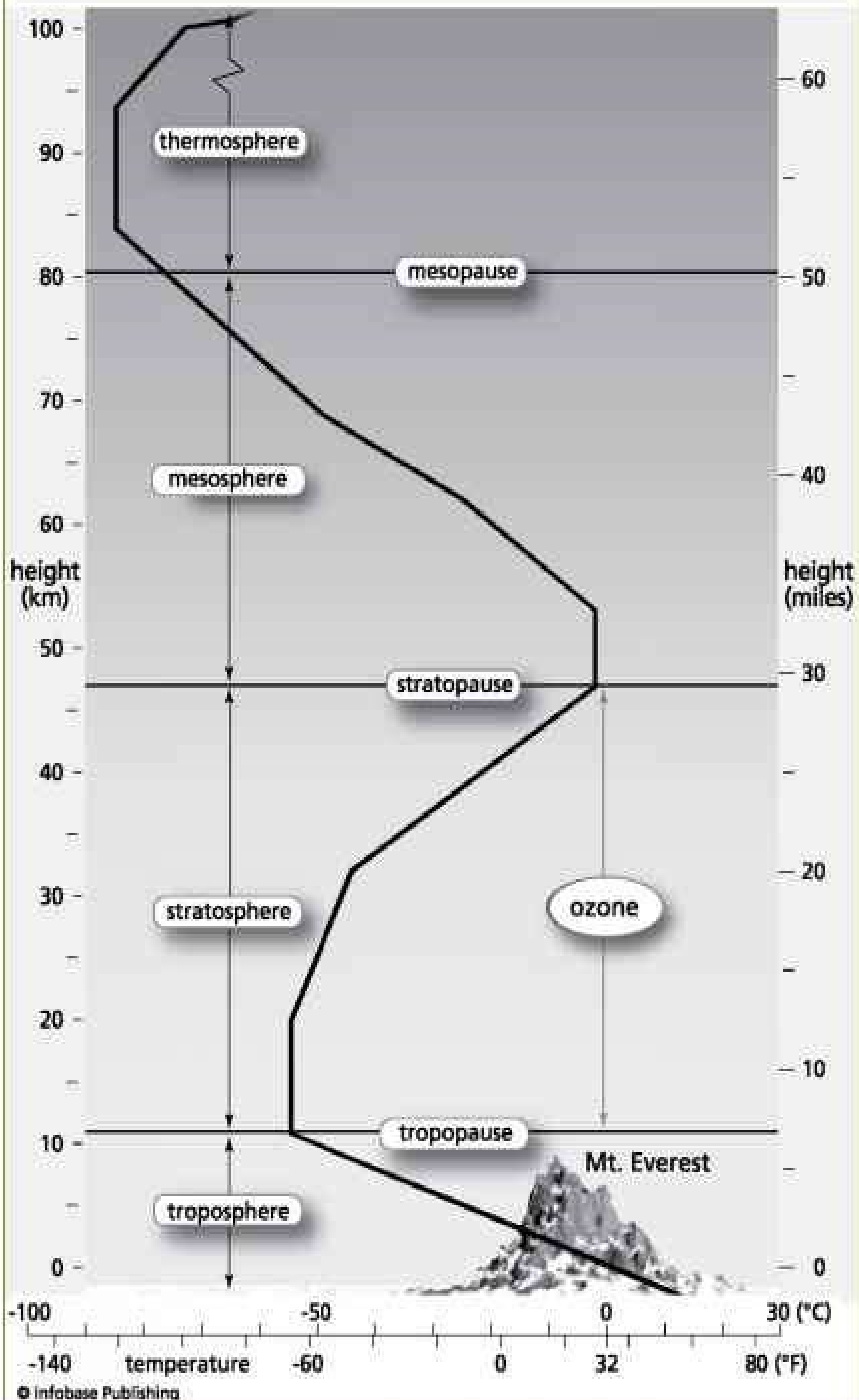
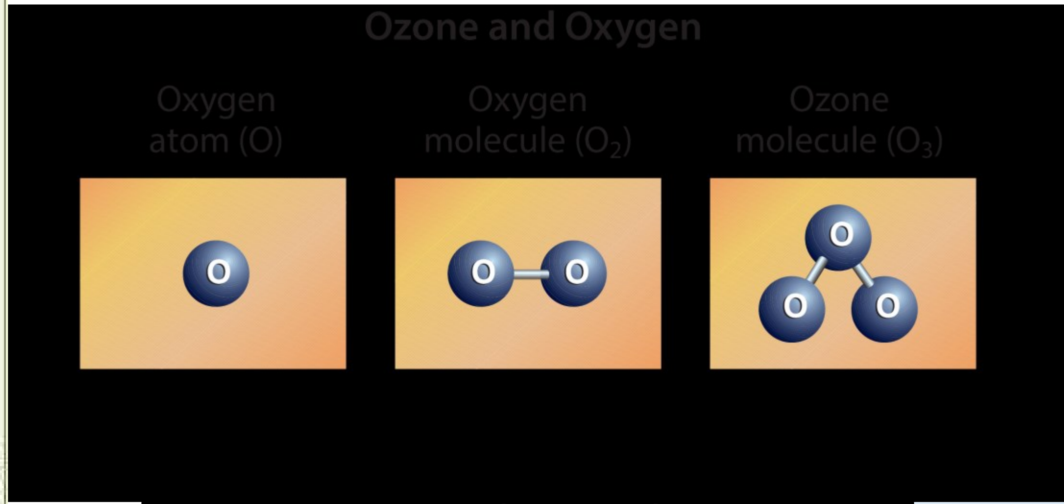
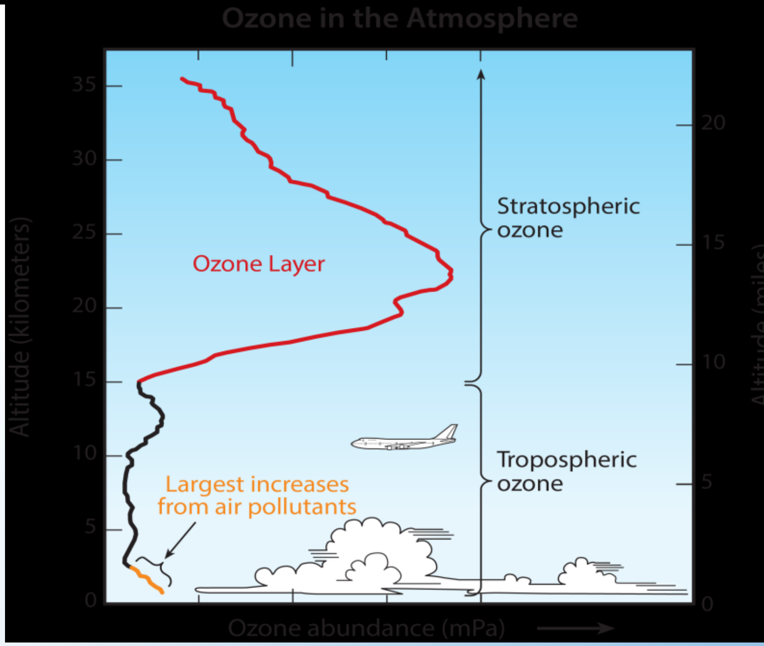
A bit of Stratospheric Chemistry

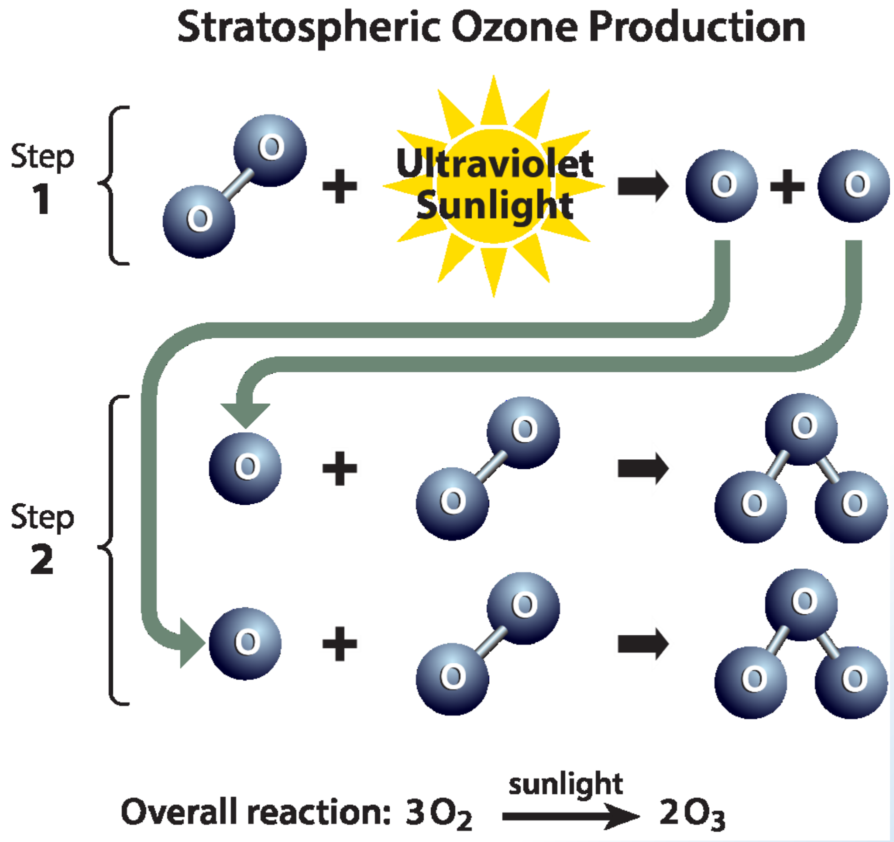
- Chapman Cycle
- Catalytic cycles
- Polar Ozone
- Outlook







Scientific Assessment on Ozone Depletion 2018, WMO



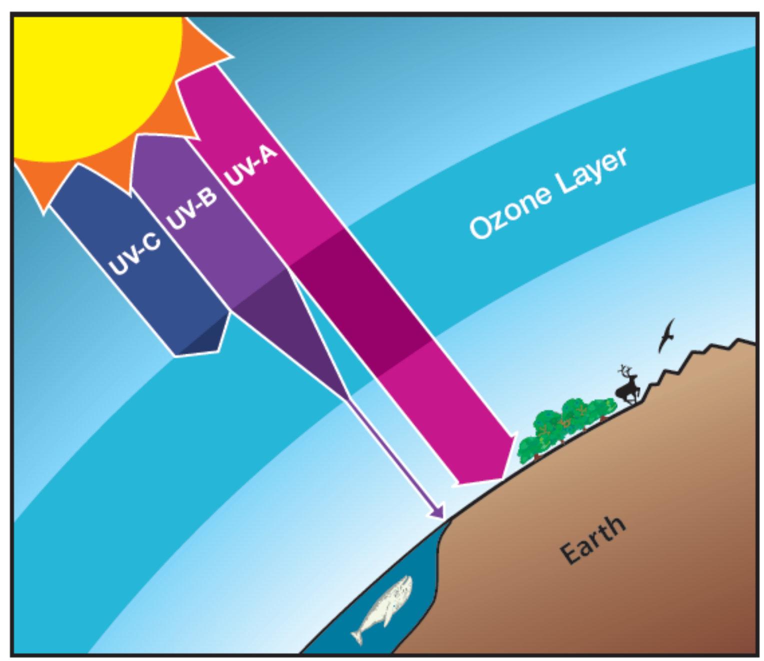
$$O_2 + h\nu\ (<242\,\mathrm{nm}) \xrightarrow{k_1} O + O;\ O_2 + O + M \xrightarrow{k_2} O_3 + M^*\,(\mathrm{excited})$$

$$O_3 + h\nu\,(240 - 320\,\mathrm{nm}) \xrightarrow{k_3} O_2 + O$$

$$O_3 + O \xrightarrow{k_4} 2O_2$$

Das et al., 2022

The ozone layer is located in the **stratosphere** and surrounds the entire Earth. The Sun emits three types of ultraviolet (UV) radiation that reach the top of the ozone layer. **Solar UV-C radiation (wavelength range 100 to 280 nanometer (nm)) is extremely damaging** to humans and other life forms; UV-C radiation is entirely absorbed within the ozone layer. Solar UV-B radiation (280 to 315 nm) is only partially absorbed and, as a result, humans and other life forms are exposed to some UV-B radiation.



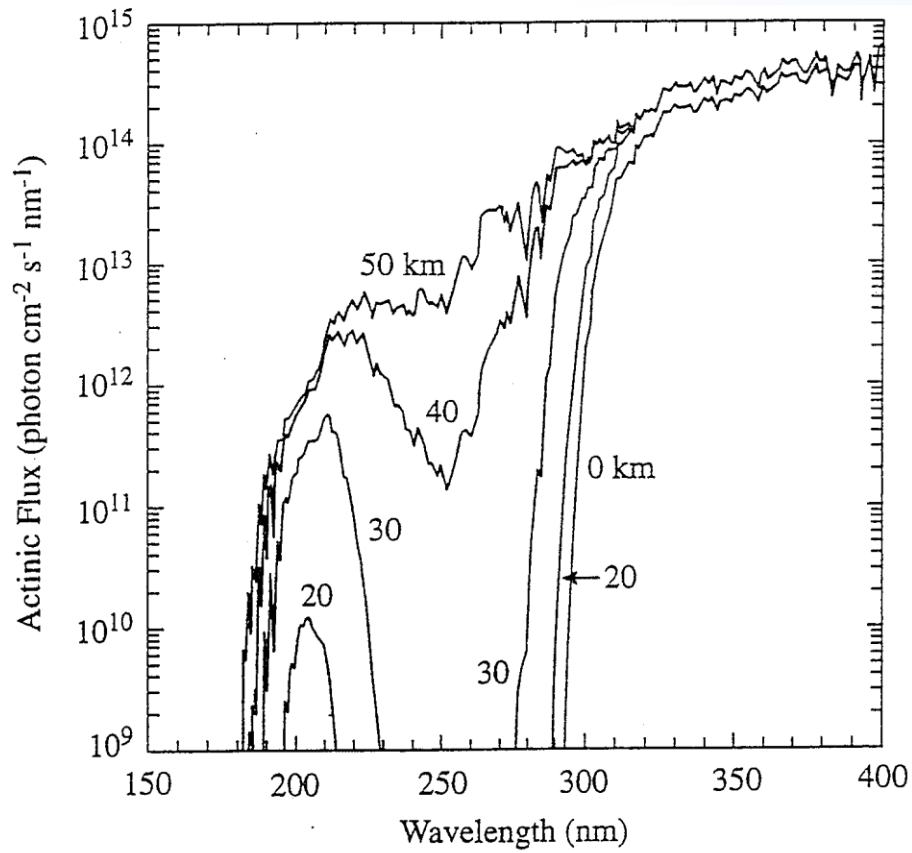
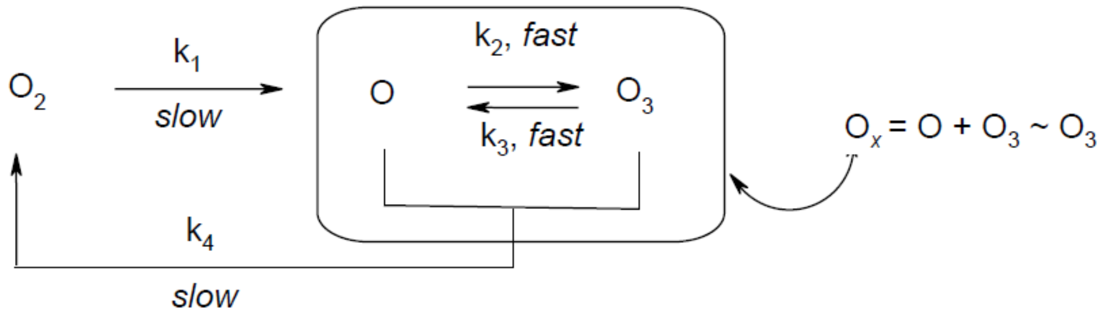


Fig. 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W. B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Publication 97-4. Pasadena, Calif.: Jet Propulsion Lab, 1997.

Chapman (1930)



rate of O_3 formation = rate of O_3 depletion,

$$\tau_{Ox} = \frac{[O_x]}{2\,k_4\,[O][O_3]} \approx \frac{1}{2\,k_4\,[O]}$$

$$[O_3] = \sqrt{\frac{k_1\,k_2\,\chi_{O2}^2 n_{air}^3}{k_3 k_4}} = \left(\frac{k_1\,k_2}{k_3\,k_4}\right)^{1/2} \chi_{O2}\; n_{air}^{3/2}$$

Jacobs, 1998

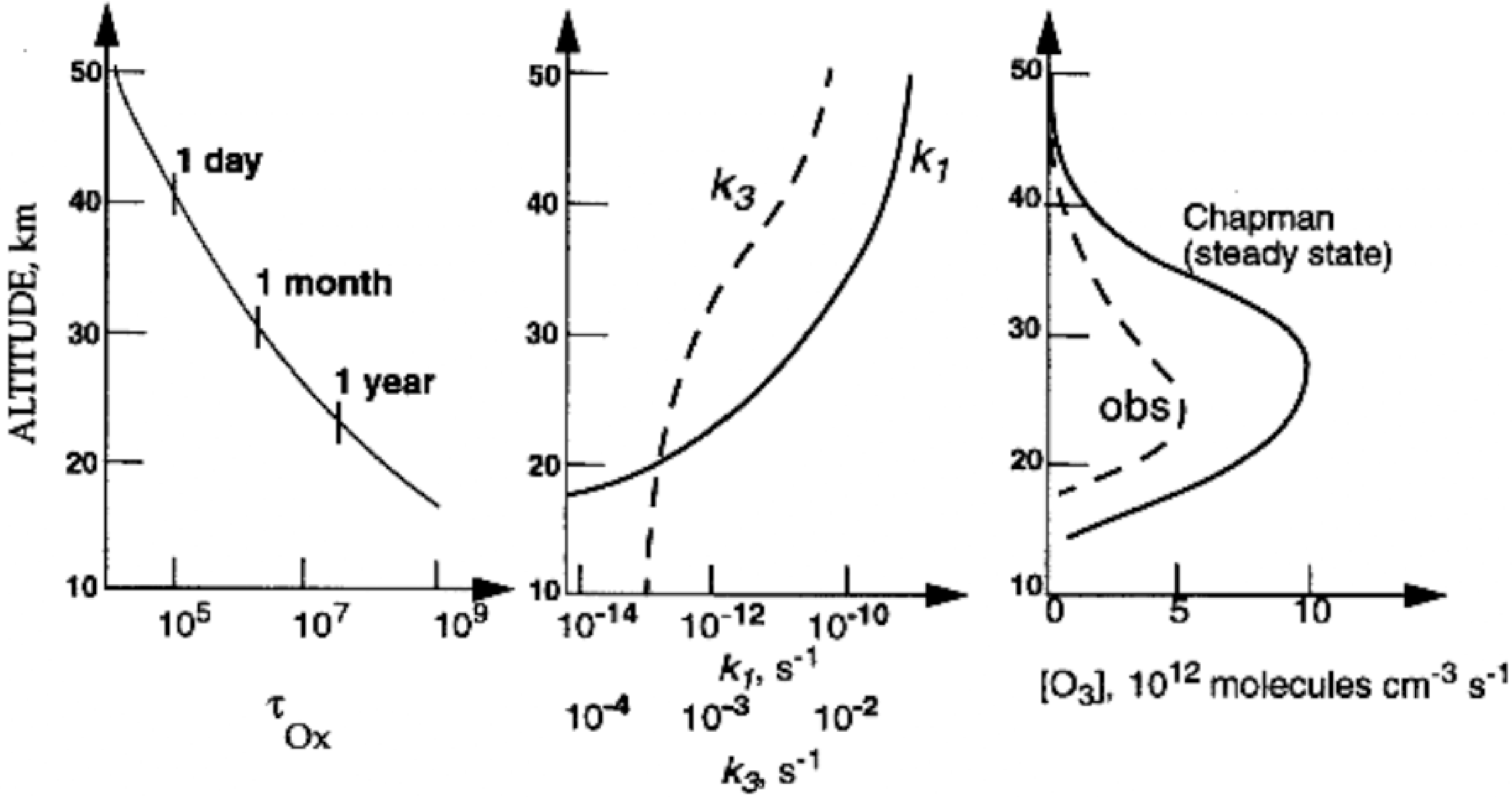


Fig. 10-5 Chapman mechanism at low latitudes. Left panel: Lifetime of O_x. Center panel: O_2 and O_3 photolysis rate constants. Right panel: calculated and observed vertical profiles of O_3 concentrations.

From: *Introduction to Atmospheric Chemistry*, D. J. Jacobs, Princeton Univ. Press, NJ, 1998.

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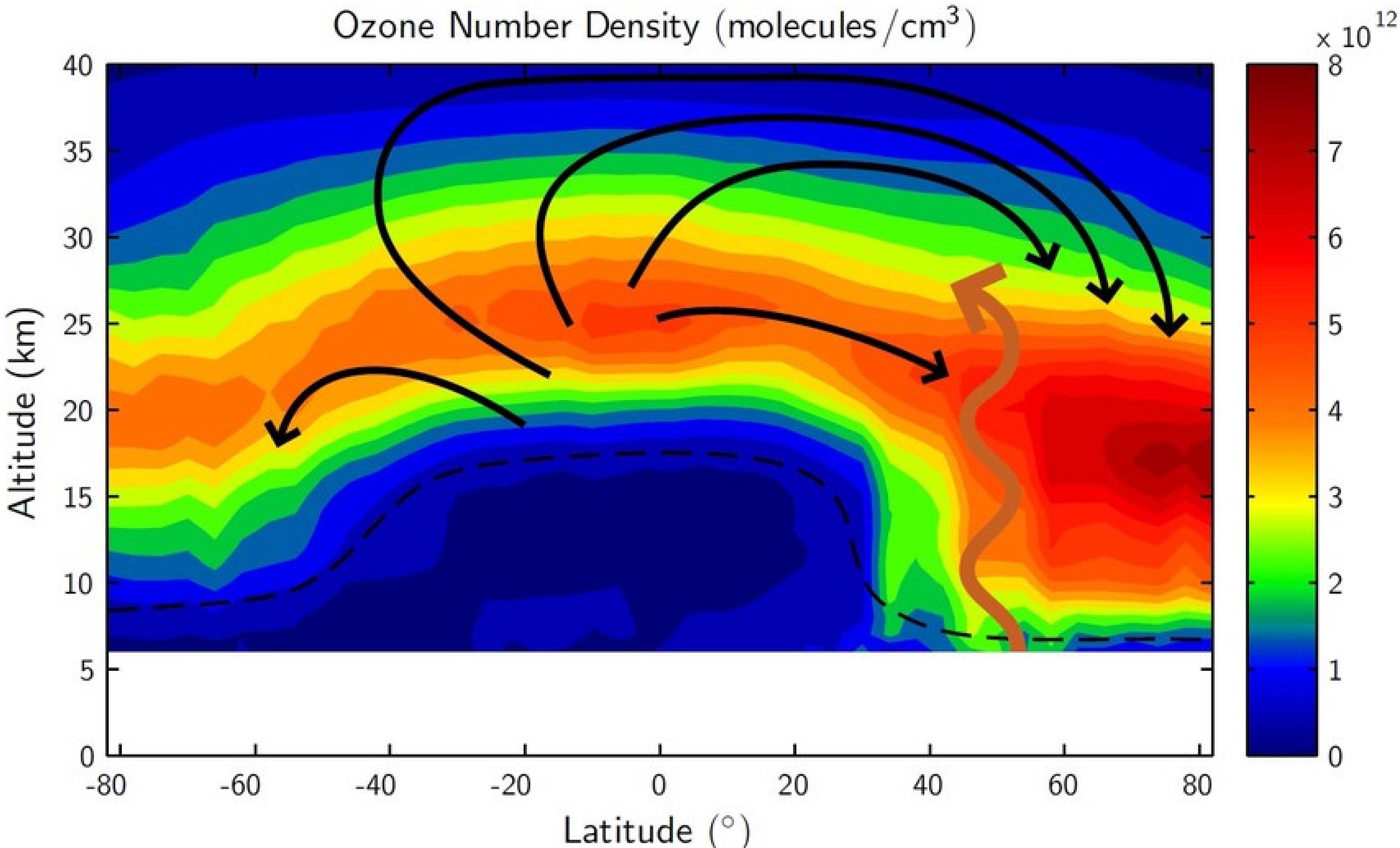
ozone distribution (or its number density in molecules per cm^3 versus latitude and altitude) for March 2004



Shaw and Shepherd, 2008

Some more chemistry to add to the Chapman Cycle:

Catalytic cycles

$$X + O_3 \longrightarrow XO + O_2$$
$$XO + O \longrightarrow X + O_2$$

$$\text{Net: } O_3 + O \longrightarrow O_2 + O_2$$

HO_x cycle (Bateman and Nicolet, 1950)

1) $H + O_3 \longrightarrow OH + O_2$
   $OH + O \longrightarrow H + O_2$

2) $OH + O_3 \longrightarrow HO_2 + O_2$
   $HO_2 + O \longrightarrow OH + O_2$

3) $OH + O \longrightarrow H + O_2$
   $H + O_2 + M \longrightarrow HO_2 + M$

4) $OH + O_3 \longrightarrow HO_2 + O_2$
   $HO_2 + O_3 \longrightarrow OH + O_2 + O_2$

NO_x cycle (Crutzen; 1970 and Johnson; 1971)

1) $NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

2) $NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_3 + hv \rightarrow NO + O_2$

ClO cycle (Stolarski and Cicerone, 1974; Molina and Rowland, 1974; Rowland and Molina, 1975)

1) $Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

The cycles are interrupted when the reactive species, OH, NO_2, Cl and ClO, bind to form more or less stable compounds

$$Cl + CH_4 \longrightarrow HCl + CH_3$$

$$OH + NO_2 + M \longrightarrow HNO_3 + M$$

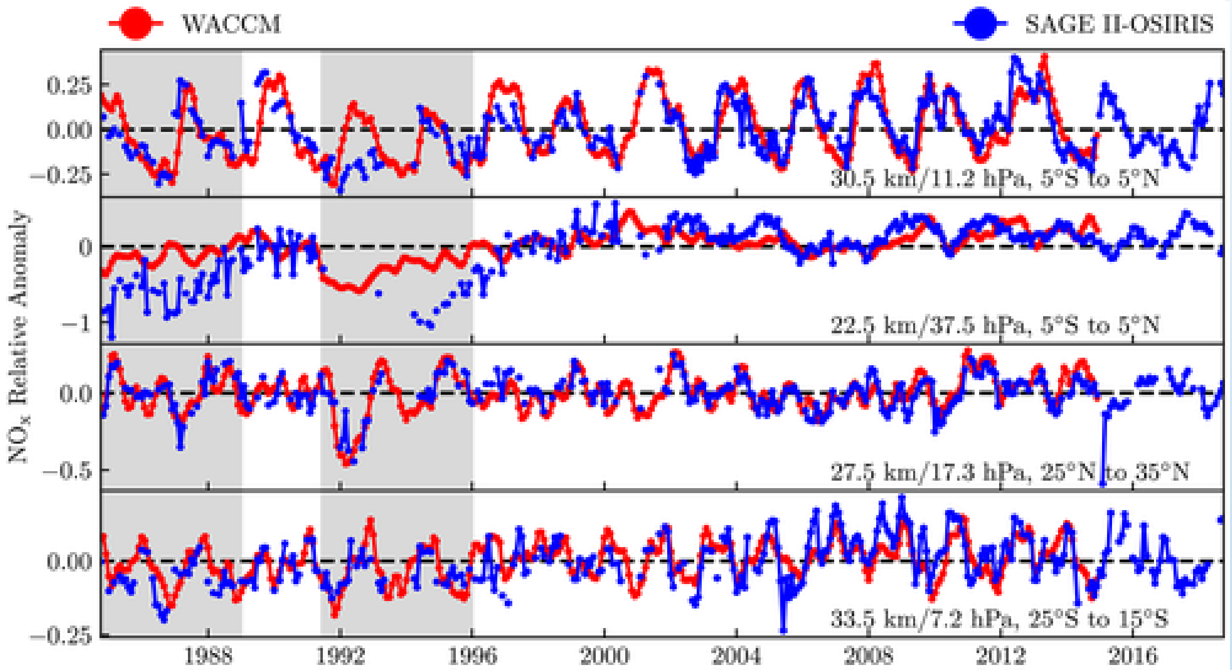
$$ClO + NO_2 + M \longrightarrow ClONO_2 + M$$

$$ClO + HO_2 \longrightarrow HOCl + O_2$$

The first human perturbation to the ozone layer was noted by H. Johnson (1971). Supersonic aircraft would have been able to release nitrogen oxides in the ozone layer at 20 km

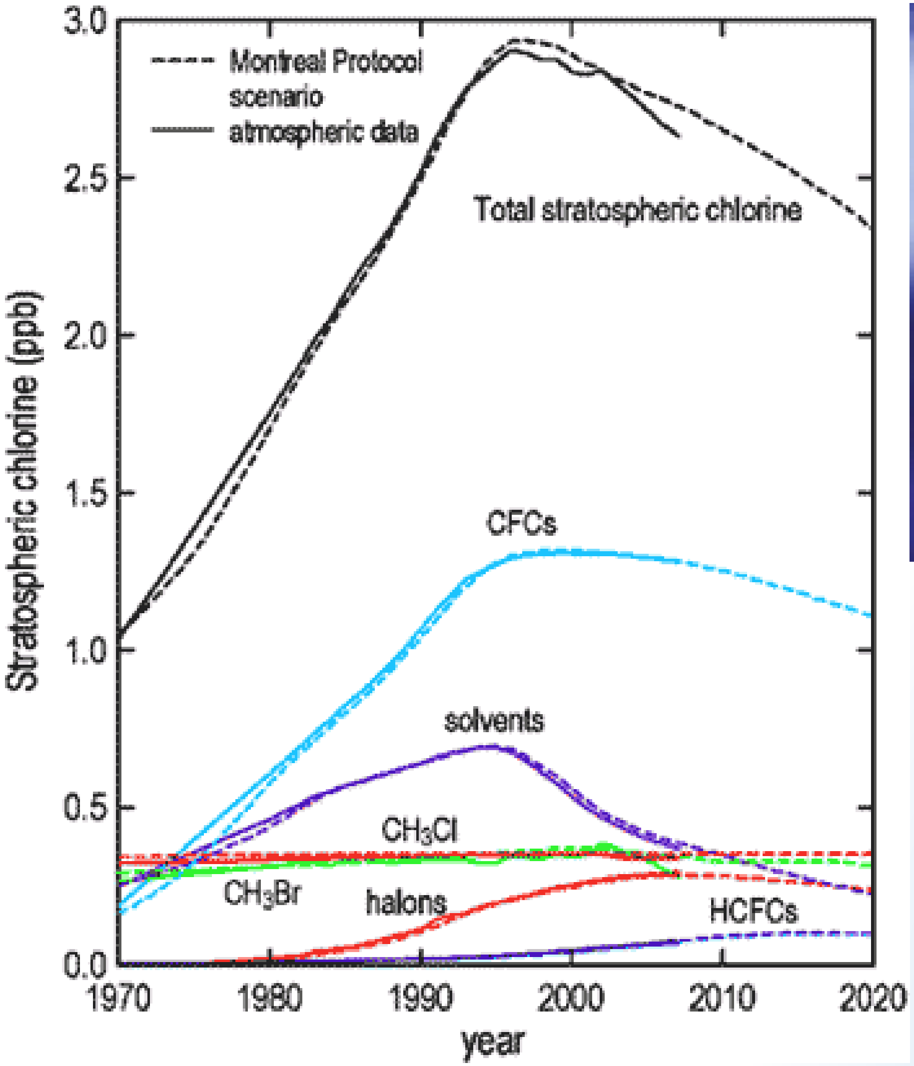
$$N_2 + O_2 \rightarrow 2NO, \text{(in jet engine)}$$

$$NO + O_3 \rightarrow NO_2 + O_2; NO_2 + O \rightarrow NO + O_2$$



Dubè et al. 2020

In 1974 F. S. Rowland and Mario J. Molina claimed that CFCs could deplete the ozone layer, CFCs were widely used as refrigerant gases and as propellants in aerosol sprays.



$$CFCl_3 + h\nu \longrightarrow CFCl_2 + Cl$$

$$CF_2Cl_2 + O \longrightarrow CF_2Cl_2 + ClO$$

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"In the decade following the publication of our Nature paper, field observations corroborated many of the predictions based on model calculations and on laboratory measurements of reaction rates. However, the effects on ozone were unclear, because the natural ozone levels have relatively large fluctuations. "

(M. J. Molina, Nobel Lecture in Chemistry, 1995)

What happens at the Poles?

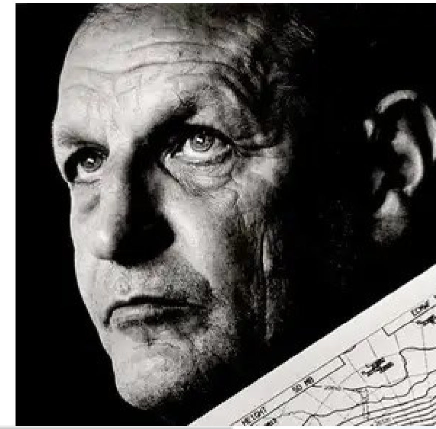
“There had been concern at the time that exhaust gases from Concorde (the supersonic passenger aircraft), or chlorofluorocarbons (CFCs) from spray cans, might damage the ozone layer.

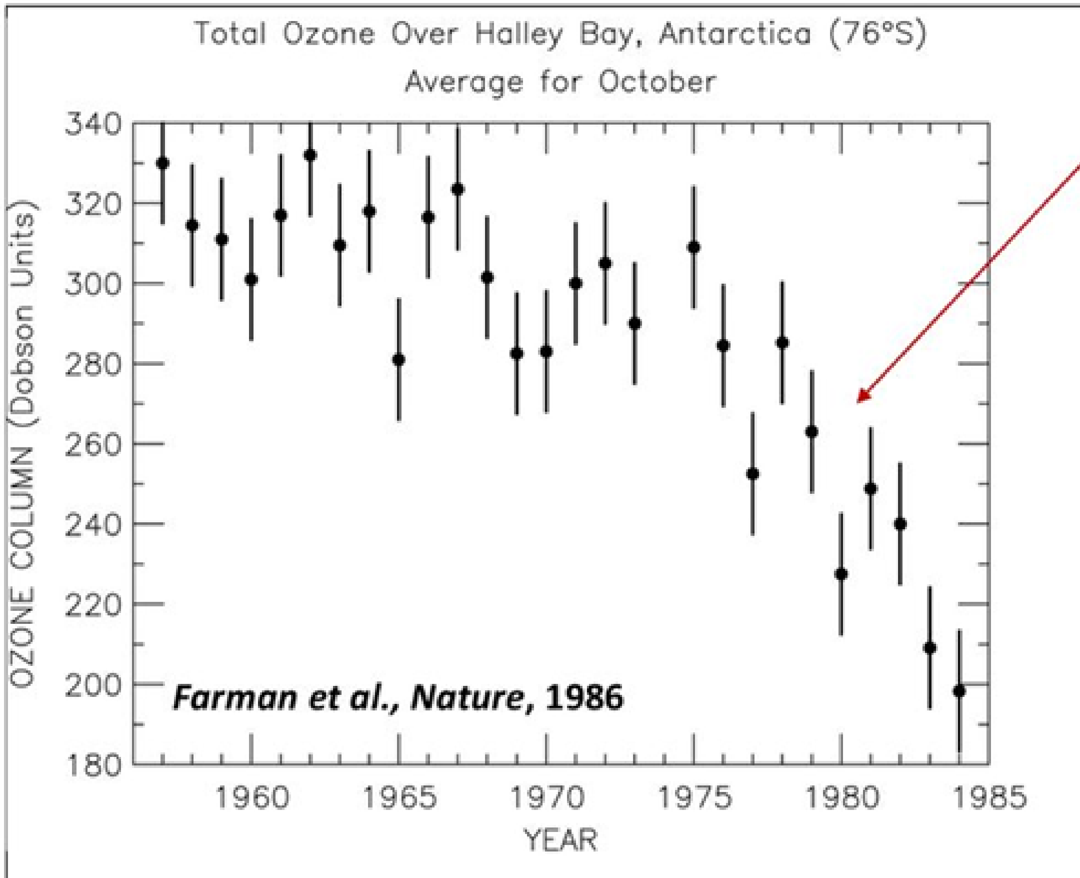
Being an ignorant physicist, I thought this unlikely, so decided to present that year’s data and compare it with values my boss (Joe Farman, editor’s note), had computed from a decade earlier. I expected them to be the same, so Concorde would be able to keep flying and the public could keep using their spray cans. “

(24-year-old Jonathan Shank, British Antarctic Survey)

They weren’t the same.

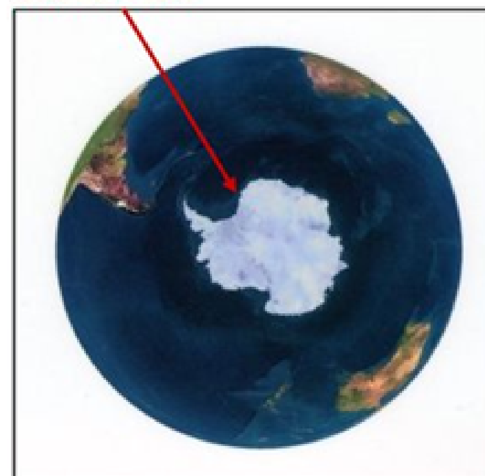
1986 – Discovery Of the Antarctic Ozone Hole



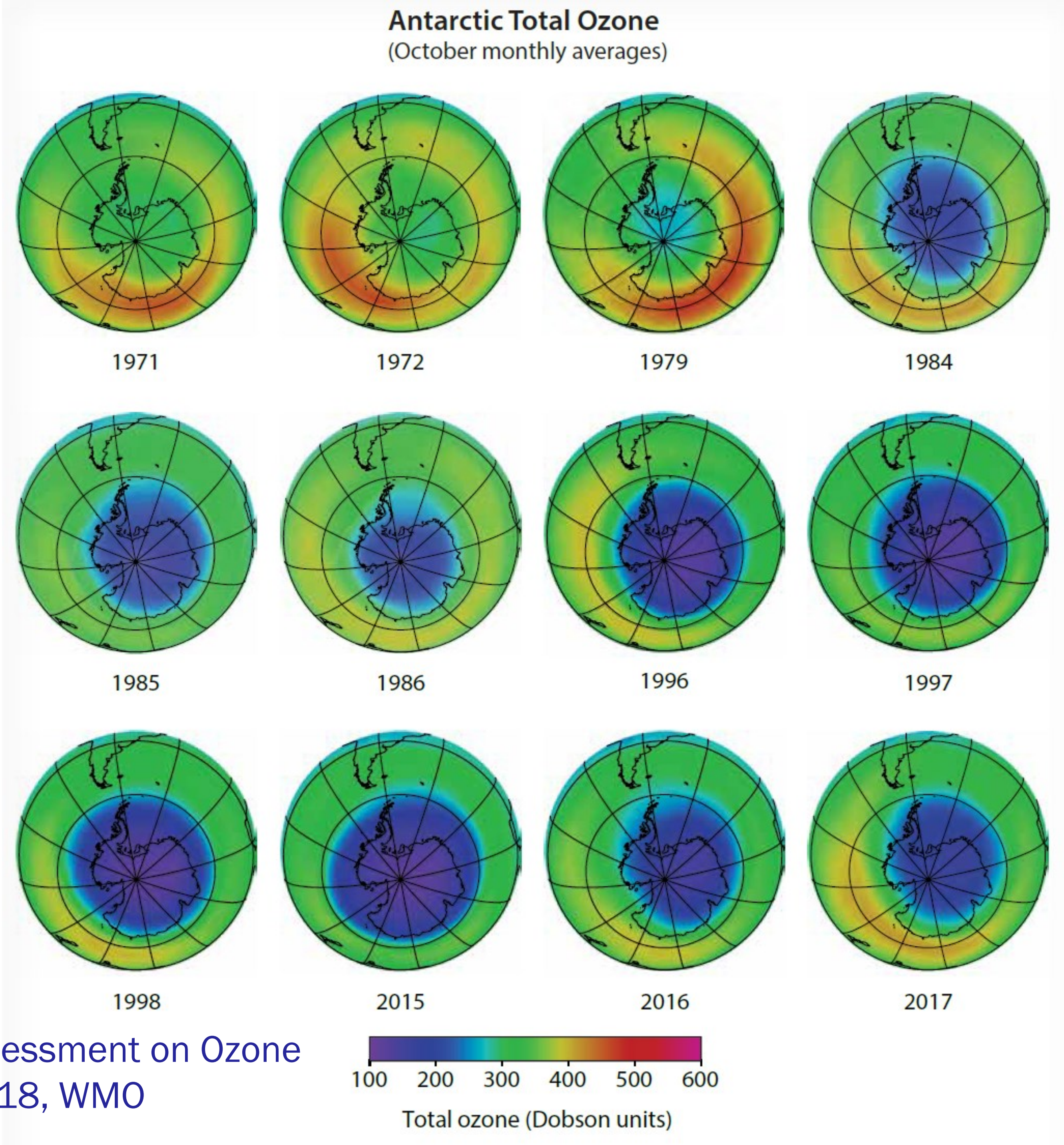


Column ozone decreases sharply each October since 1975

HALLEY BAY



Southern Hemisphere



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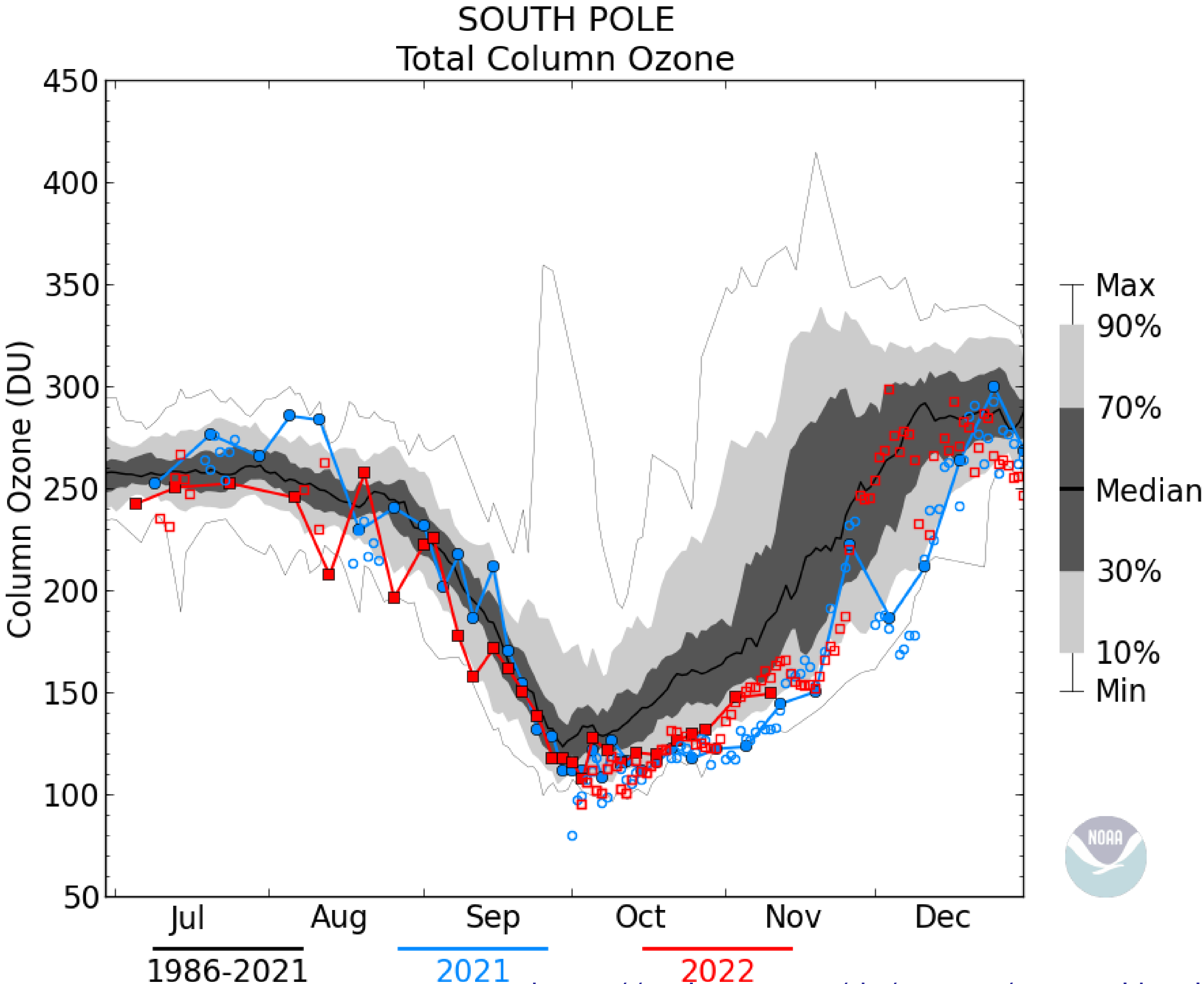

https://gml.noaa.gov/dv/spo_oz/spototal.html

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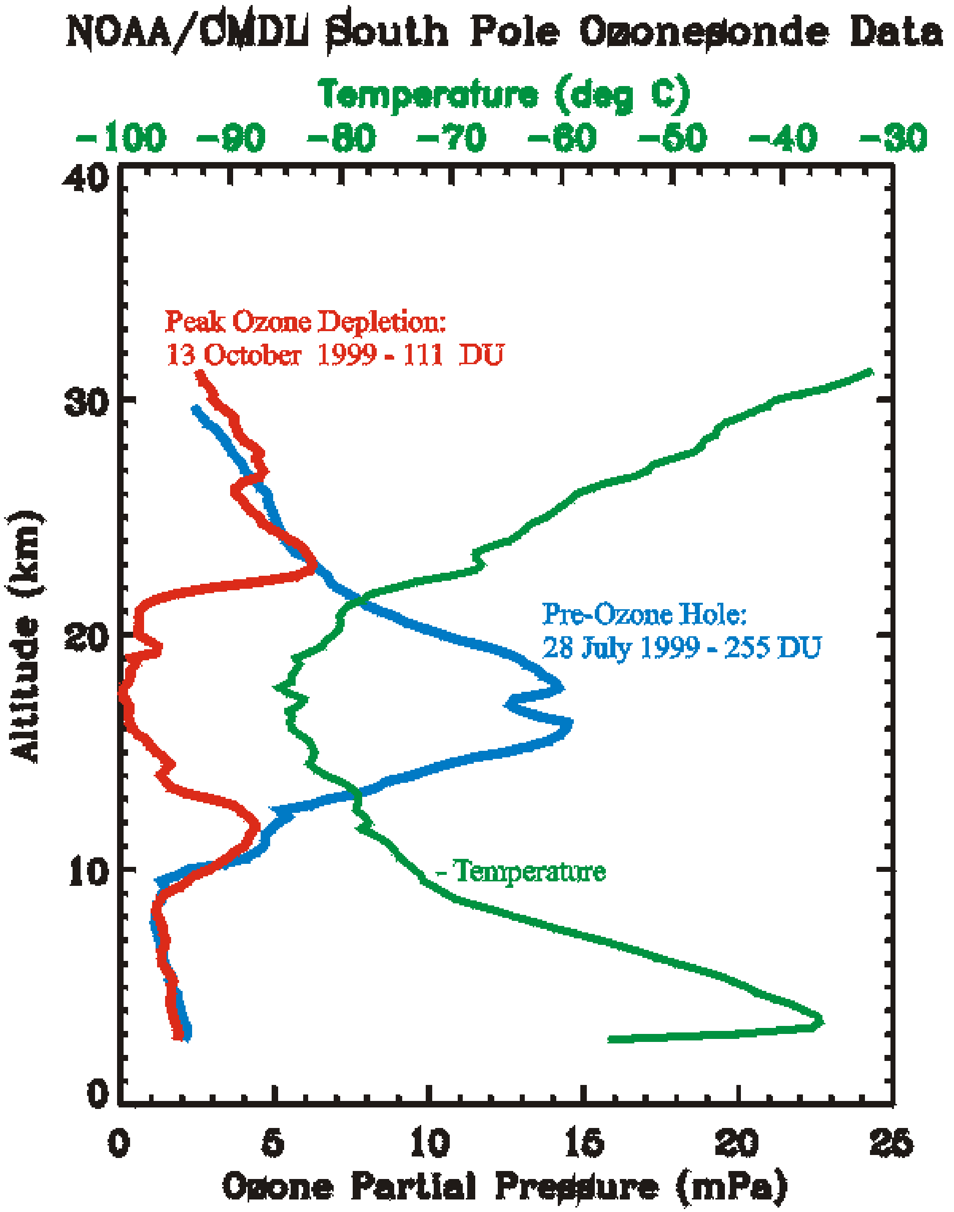


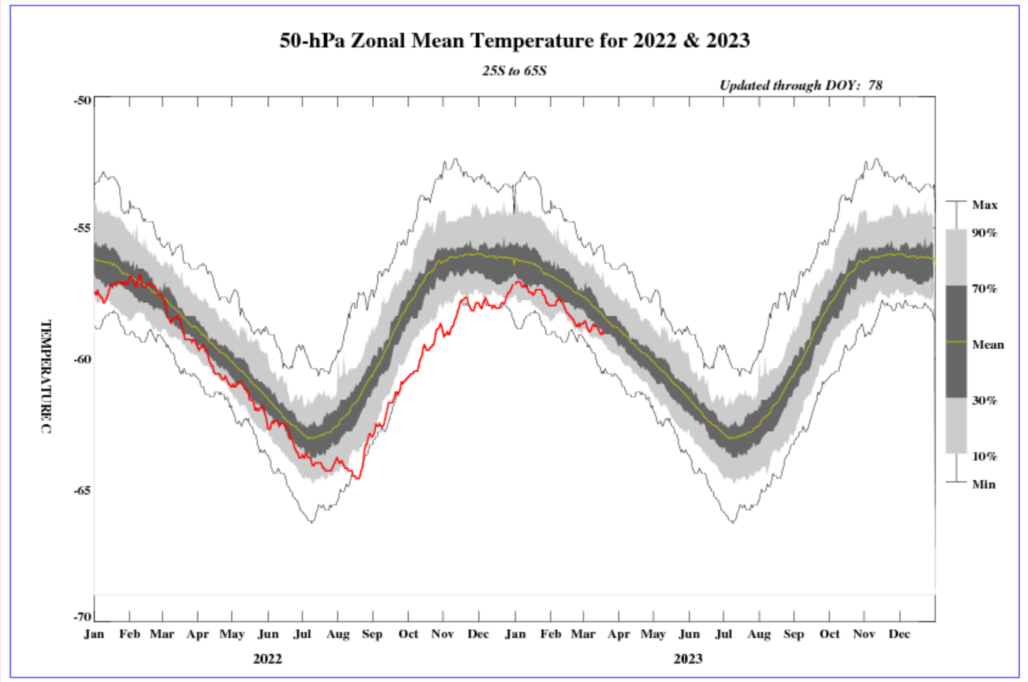
https://www.cpc.ncep.noaa.gov/products/stratosphere/polar/polar.shtml

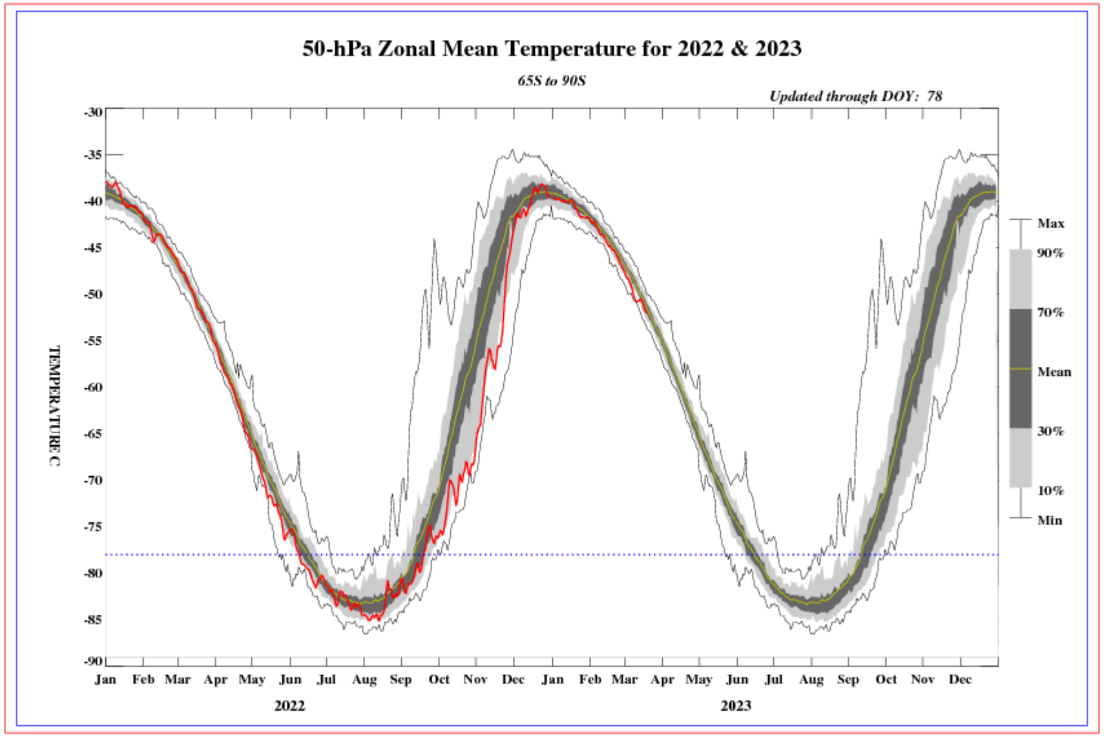
Vertical profile of ozone over the South Pole when the "ozone hole" becomes well established. Nearly complete ozone depletion occurs between 13 km and 23 km.

Above and below these heights ozone amounts remain virtually unchanged.

what is special about the Antarctic stratosphere?

- It is very cold in winter

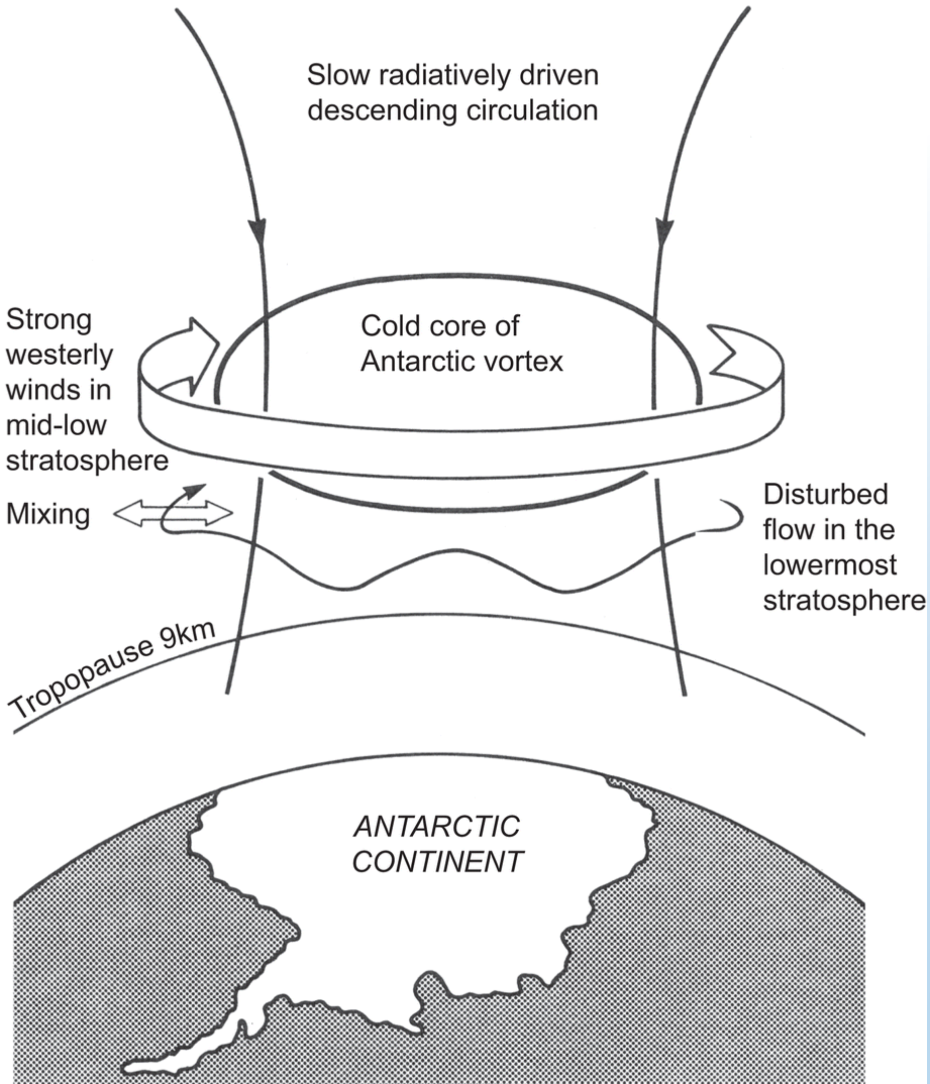




US National Weather Service
Climate Prediction Center

what is special about the Antarctic stratosphere?

- It is isolated from midlatitudes



United Kingdom Stratospheric Ozone Review Group Stratospheric Ozone 1988

what is special about the Antarctic stratosphere?

- In spring it is in sunlight

Polar stratosphere is so cold to allow formation of clouds in the stratosphere: Polar Stratospheric Clouds

Wikipedia

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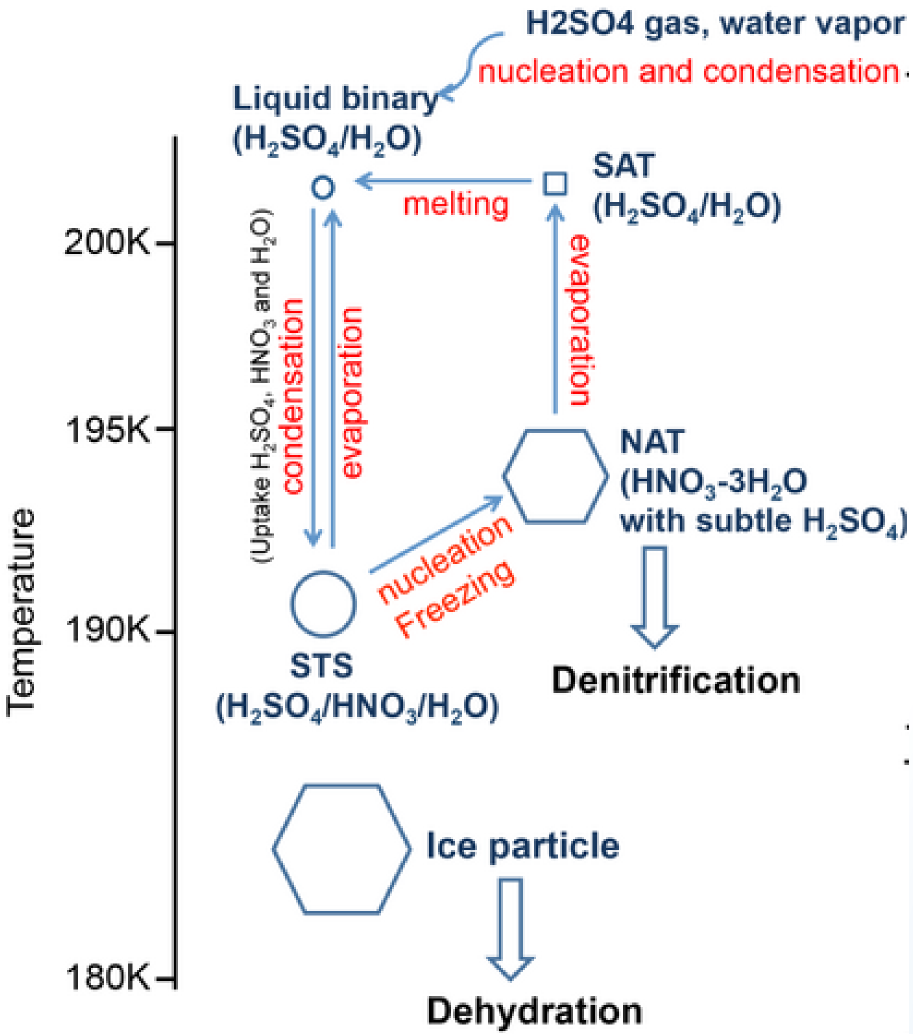

Type I Clouds

They contain water, nitric acid, and/or sulfuric acid. When temperatures fall to -78°C or lower, they form.

Type Ia clouds are made up of large, aspherical particles made up of nitric acid trihydrate (NAT).

Type Ib clouds contain small, non-depolarizing spherical particles of a liquid supercooled ternary solution (STS) of sulphuric acid, nitric acid, and water.

Type II Clouds

They are made up entirely of water ice. They can only form at temperatures of -83°C or lower.

Zhu et al., 2015

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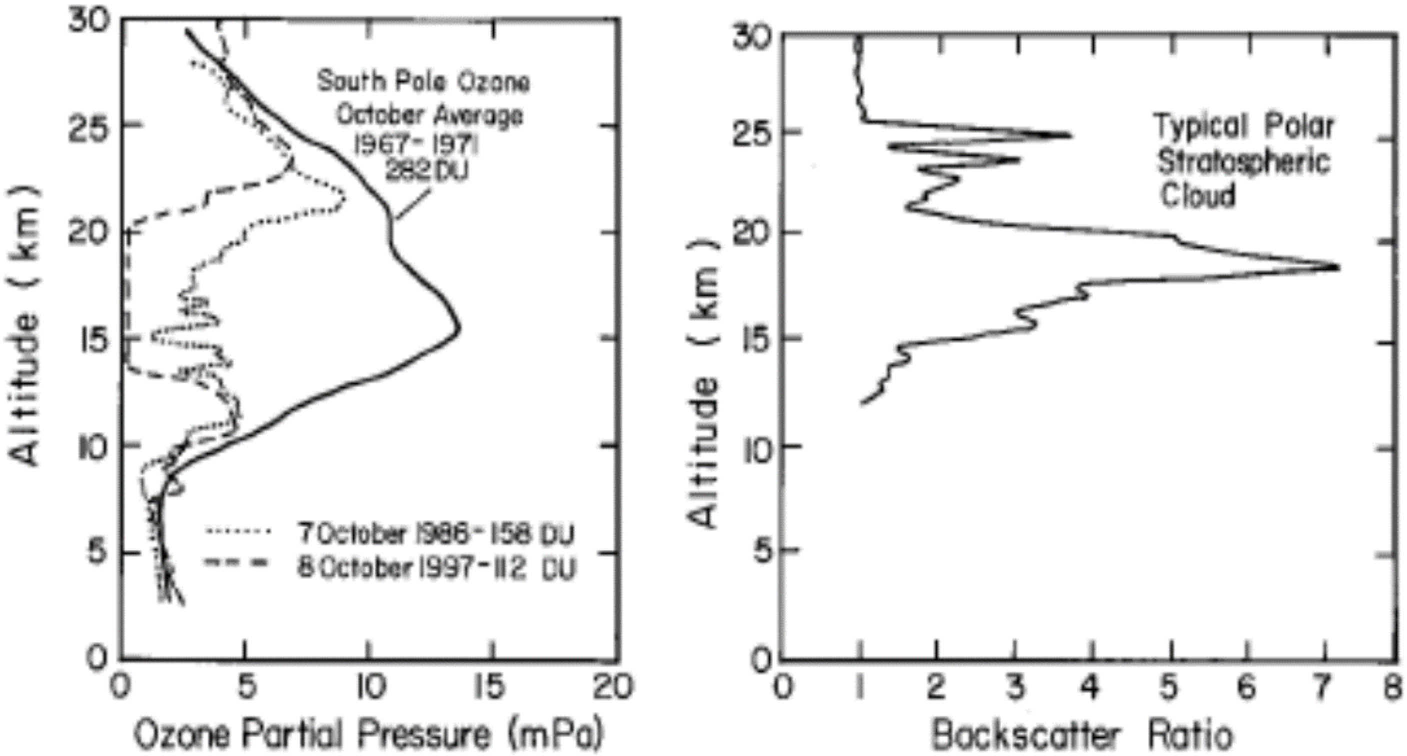

Solomon, 1988

PSC make available surfaces for conversion of Cl reservoir species into active forms via heterogeneous reactions.

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

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

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

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

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

HOCl and CL2 and ClNO2 are short-lived species.

Moreover PSC trap NOX into HNO3, which is removed from the stratosphere via gravitational settling.

Cl can not reform reservoir species!

When the light come, it finds an **isolated stratosphere depleted of NO_x and HNO_3 (denoxified and denitrified) and rich of relatively unstable Cl species.**

$$Cl_2\,(g) + h\nu \rightarrow 2Cl$$

$$ClNO_2\,(g) + h\nu \rightarrow Cl + NO_2$$

$$HOCl + h\nu \rightarrow Cl + OH$$

The destruction of O_3 can proceed efficiently without atomic O due to the relative stability of the dimer Cl_2O_2 in the cold.

Molina and Molina, 1987:

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$

$$Cl_2O_2 + h\nu \rightarrow Cl + Cl + O_2$$

$$2\,[Cl + O_3 \rightarrow ClO + O_2\,]$$

~~Cl_2O_2 + M → 2ClO + M~~

Too cold!

net : $$2\,O_3 + h\nu \rightarrow 3\,O_2$$

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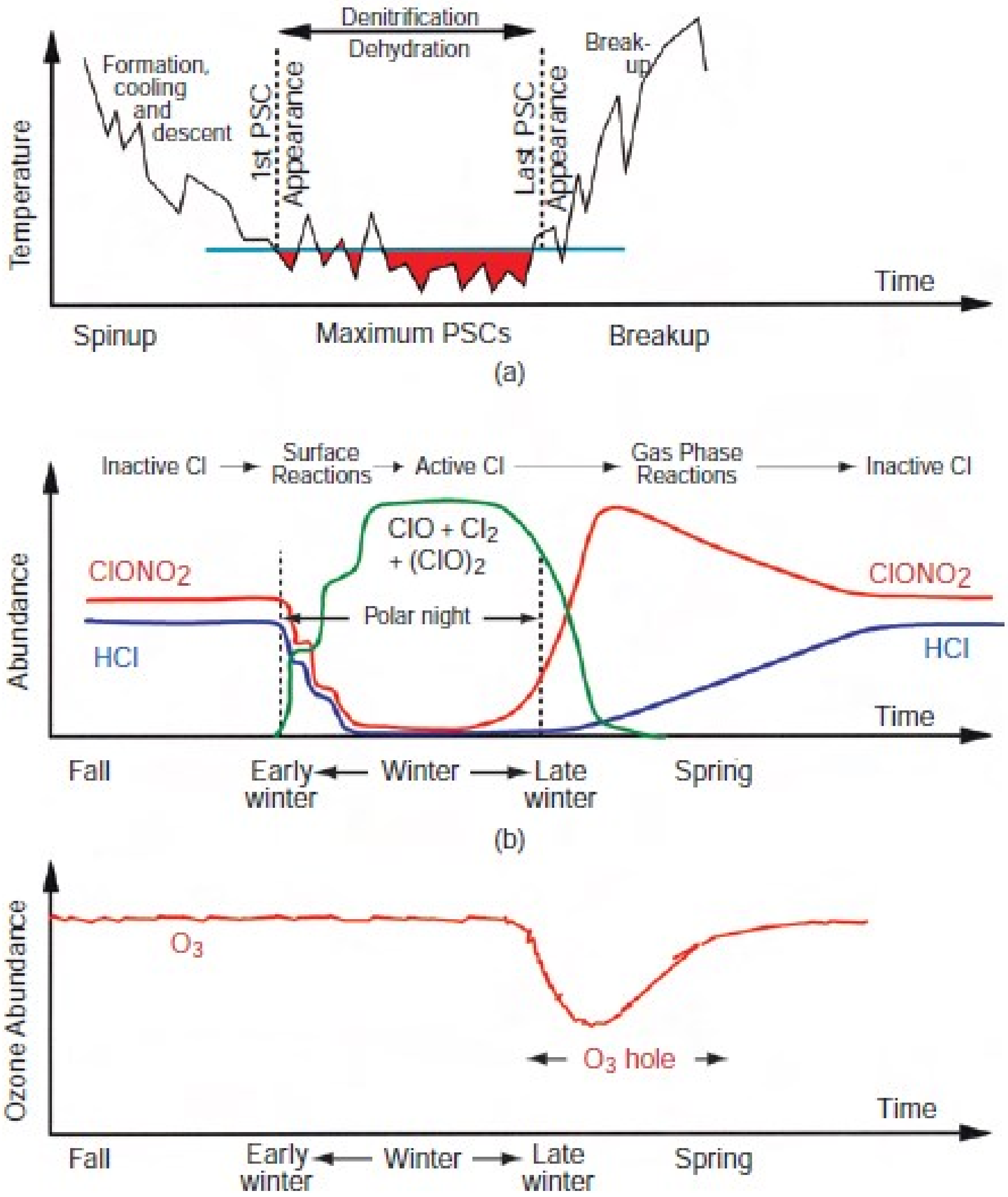
resumee

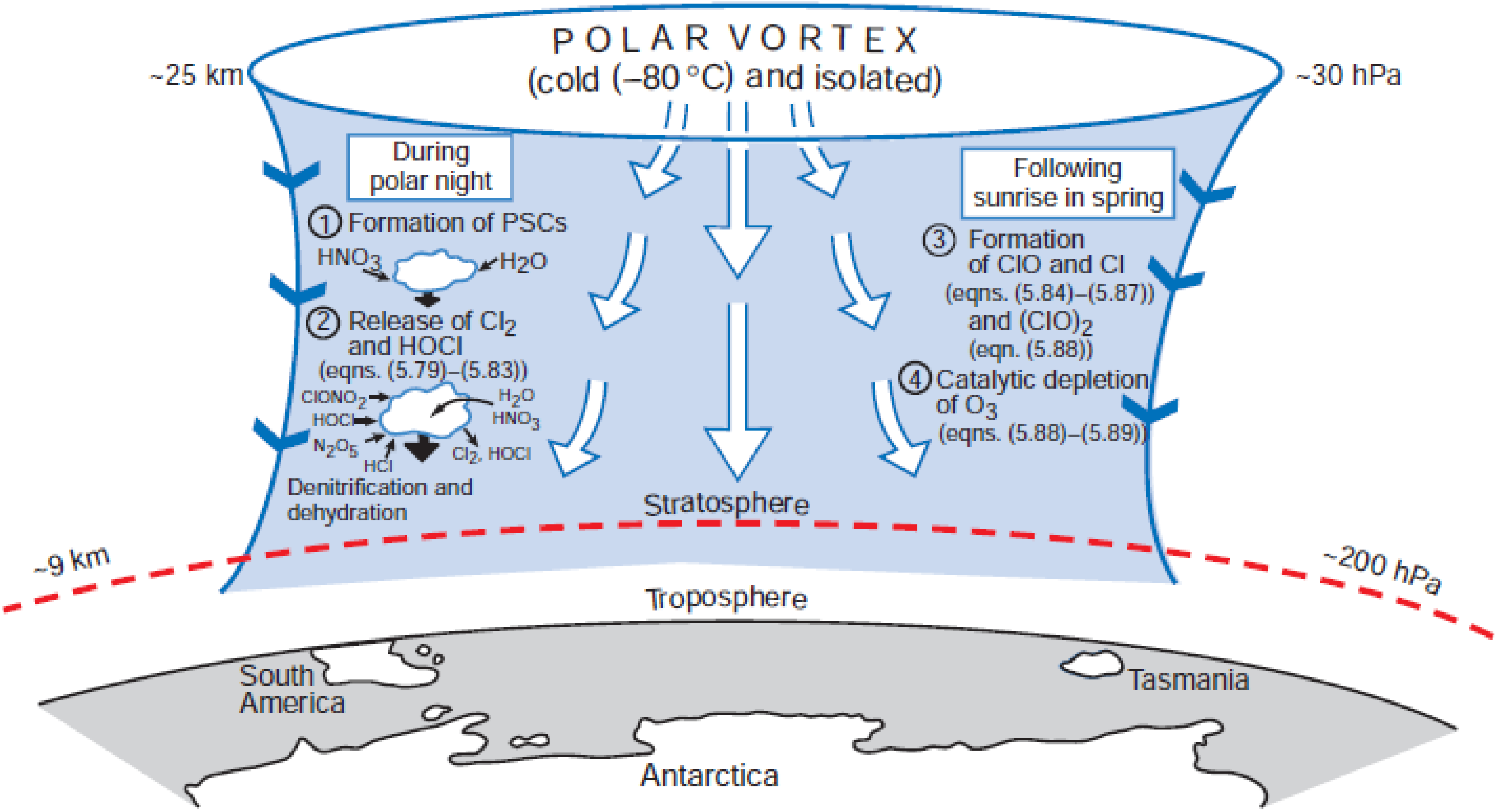
Reservoir species $ClONO_2$ and N_2O_5 react in heterogeneous phase on PSCs on which HCl has been adsorbed to produce Cl_2, HOCl and $ClNO_2$ in the gaseous phase.

At sunrise the latter are photolysed and release Cl which reacts with O_3, forming ClO and O_2. After the accumulation of ClO, the reaction (Molina and Molina) also starts.

Since much of the NO_x is in the form of HNO_3 and removed from the gaseous phase, it lacks its moderating effect, through the formation of reservoir $ClONO_2$



Webster et al., 1993



Wallace and Hobbs, 2006

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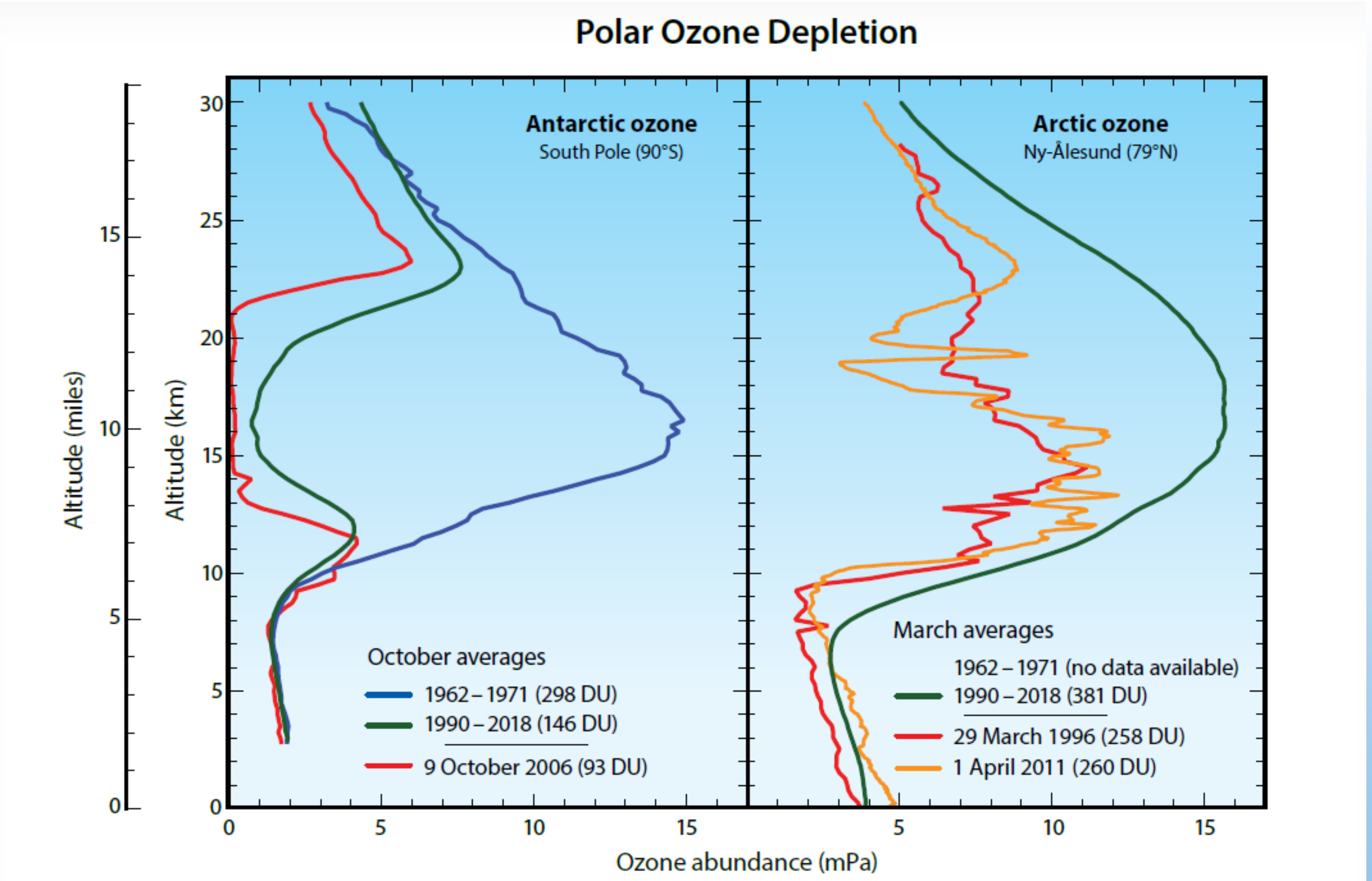
What happens in the Arctic?



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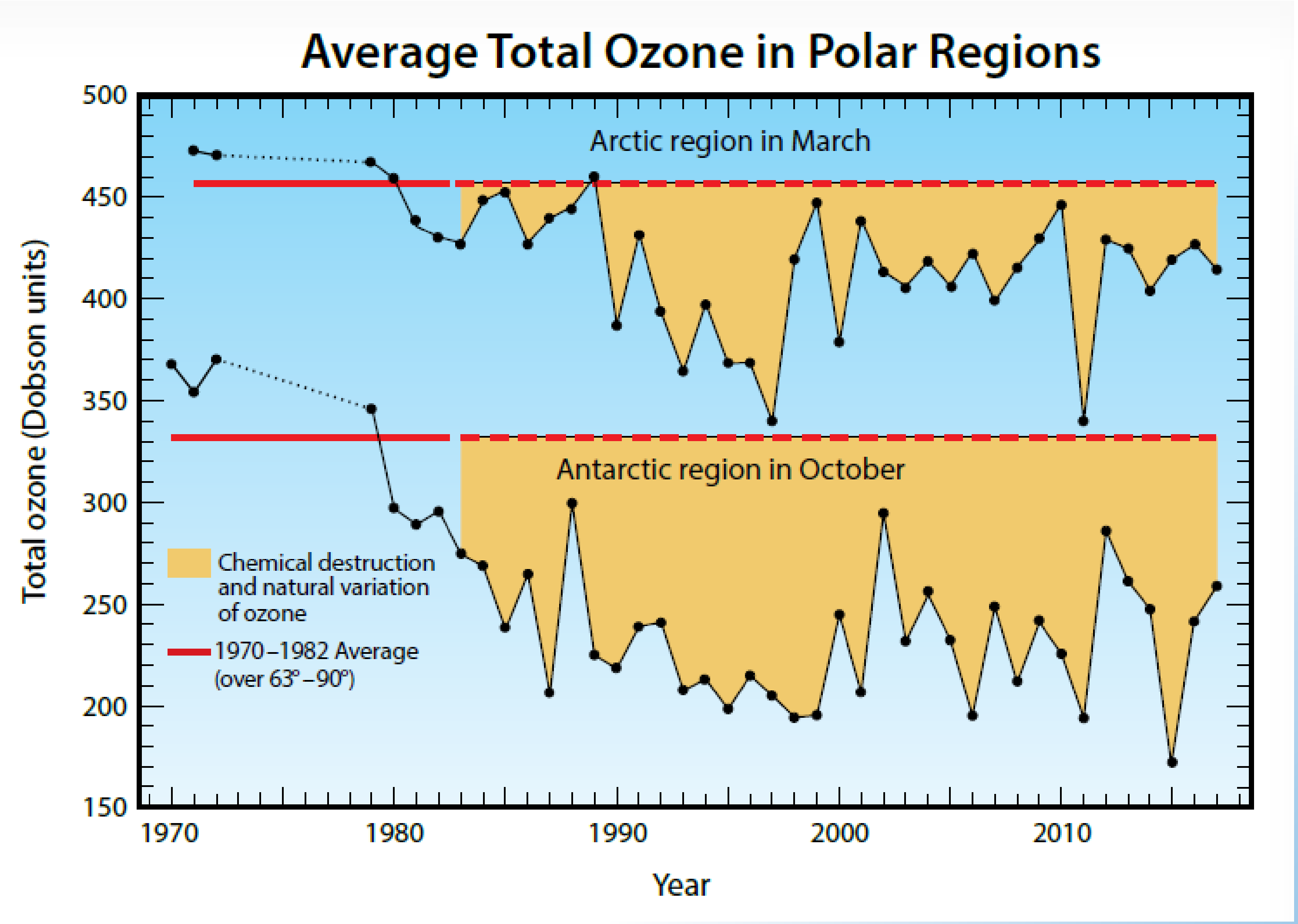

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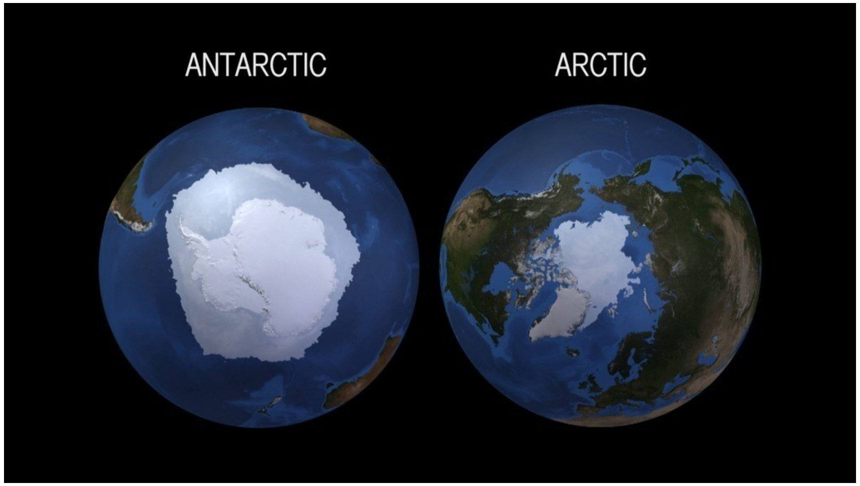
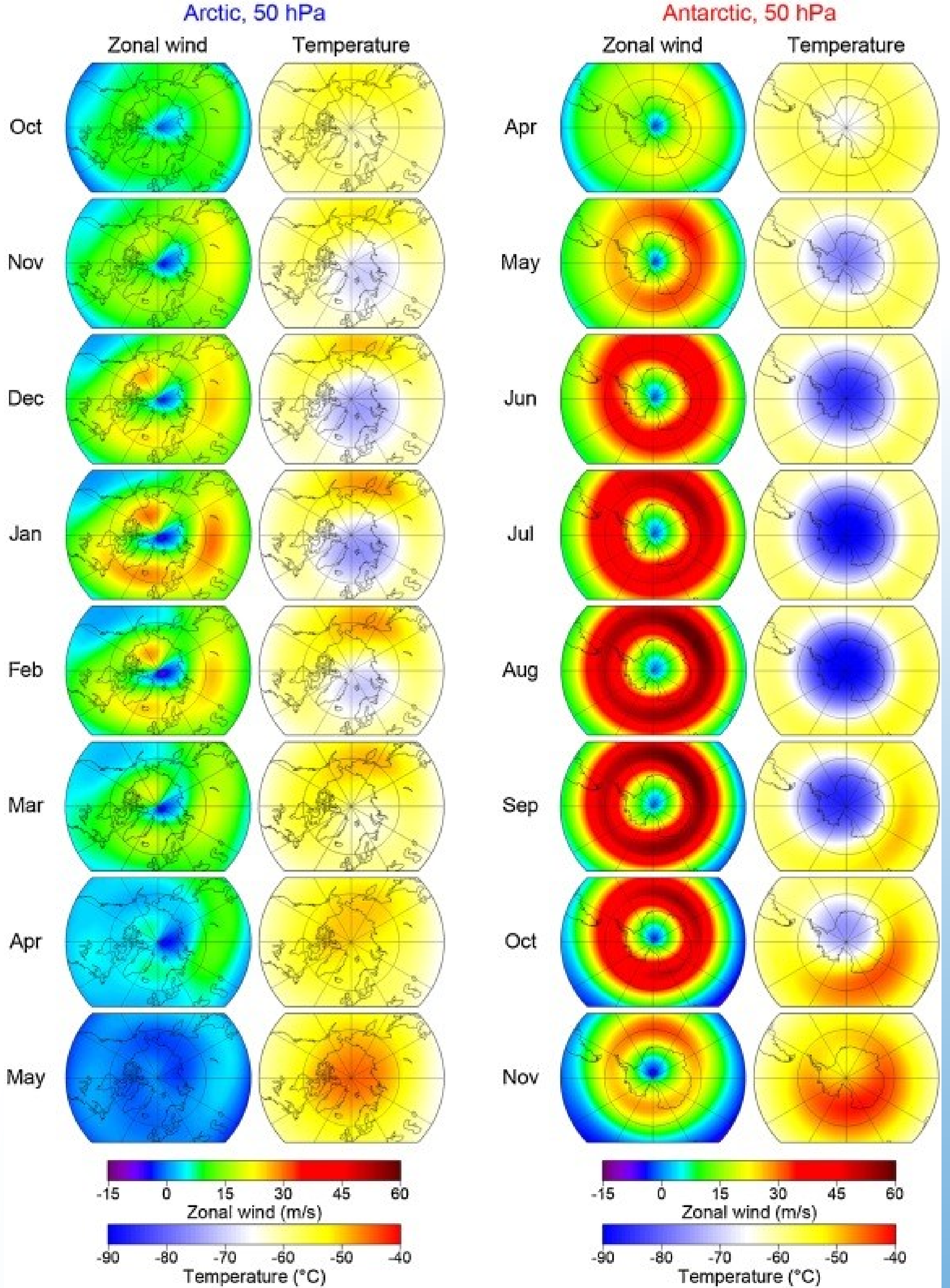
The 1979–2016 monthly climatological means of zonal wind and temperature at the 50 hPa pressure level over the Arctic from October to May and over the Antarctic from April to November.





Zuev et al., 2019

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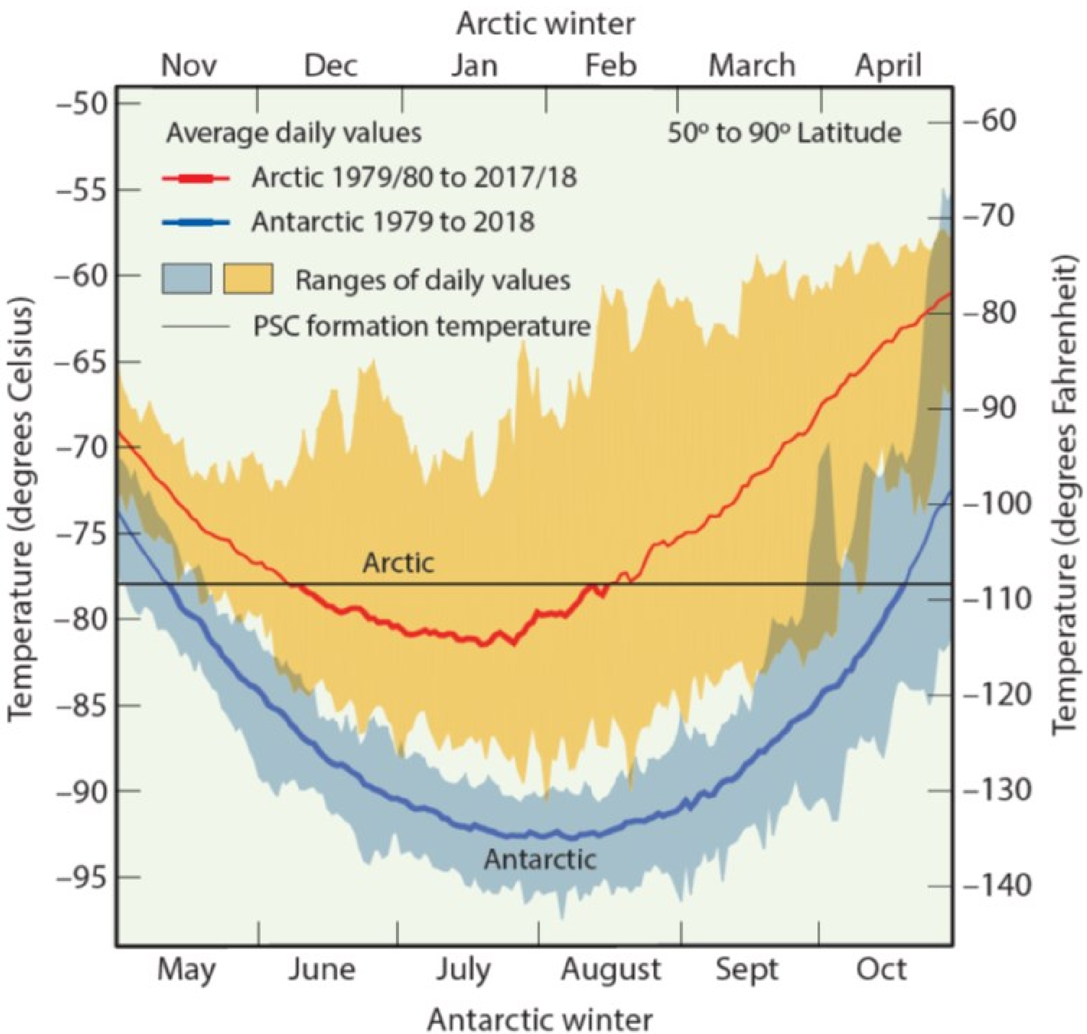
Minimum Air Temperatures in the Polar Stratosphere



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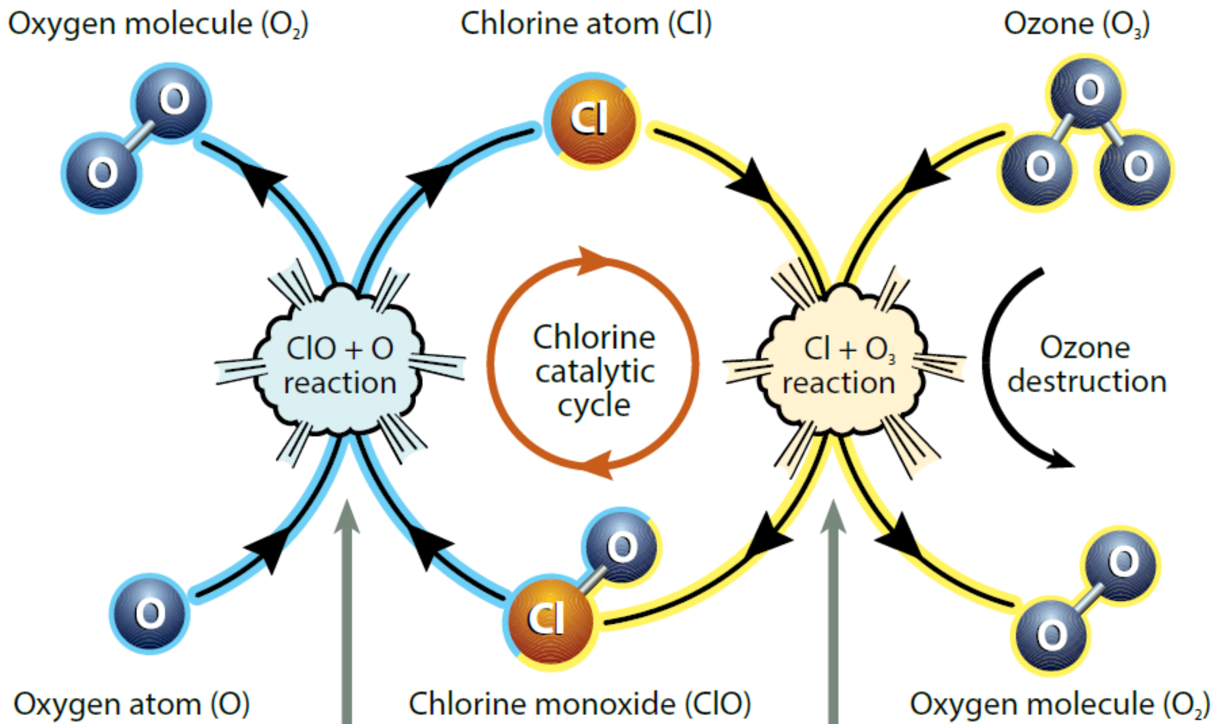
Ozone Destruction Cycle 1



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

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Ozone Destruction Cycles in Polar Regions

Cycle 2

Molina and Molina, J. Phys. Chem., 1987

$$ClO + ClO \rightarrow (ClO)_2$$
$$(ClO)_2 + \text{sunlight} \rightarrow ClOO + Cl$$
$$ClOO \rightarrow Cl + O_2$$
$$2(Cl + O_3 \rightarrow ClO + O_2)$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

Cycle 3

McElroy et al., 1986

$$ClO + BrO \rightarrow Cl + Br + O_2$$

or

$$\left(\begin{array}{r} ClO + BrO \rightarrow BrCl + O_2 \\ BrCl + \text{sunlight} \rightarrow Cl + Br \end{array} \right)$$

$$Cl + O_3 \rightarrow ClO + O_2$$
$$Br + O_3 \rightarrow BrO + O_2$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

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The Nobel Prize in Chemistry 1995

Paul J. Crutzen
Mario J. Molina
F. Sherwood Rowland

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The Nobel Prize in Chemistry 1995

Photo from the Nobel Foundation archive.

Paul J. Crutzen

Prize share: 1/3

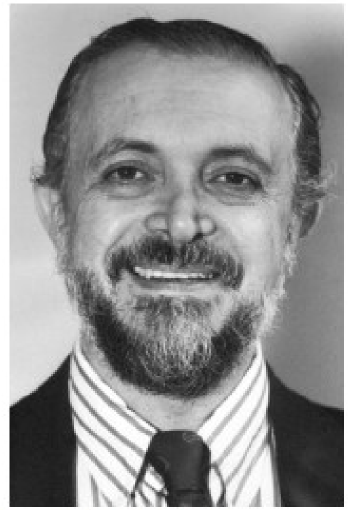


Photo from the Nobel Foundation archive.

Mario J. Molina

Prize share: 1/3

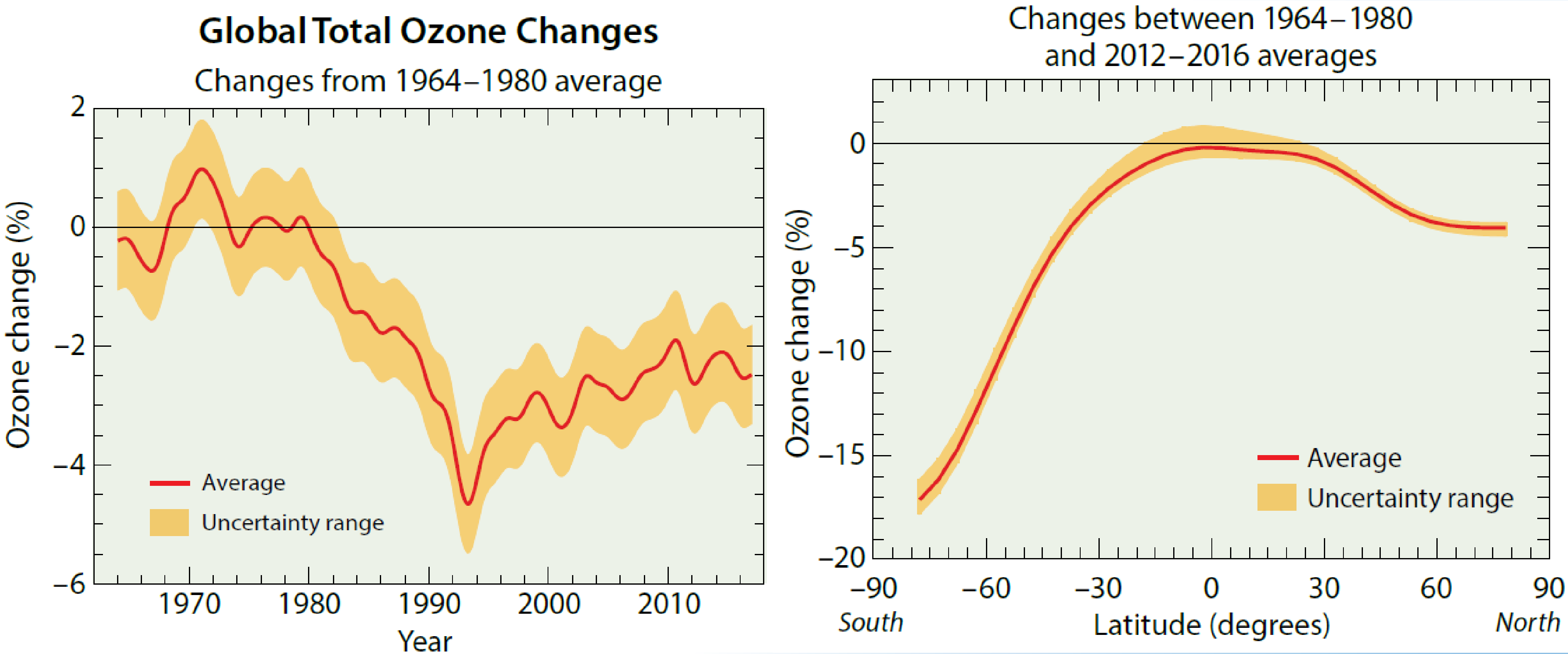
Photo from the Nobel Foundation archive.

F. Sherwood Rowland

Prize share: 1/3

The Nobel Prize in Chemistry 1995 was awarded jointly to Paul J. Crutzen, Mario J. Molina and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"

There is a much smaller ozone loss in midlatitudes, also linked to the increase in atmospheric chlorine and bromine through human activities, though the activation of chlorine occurs on sulfate aerosols rather than PSCs. These aerosols are enhanced following large volcanic eruptions which reach the stratosphere.



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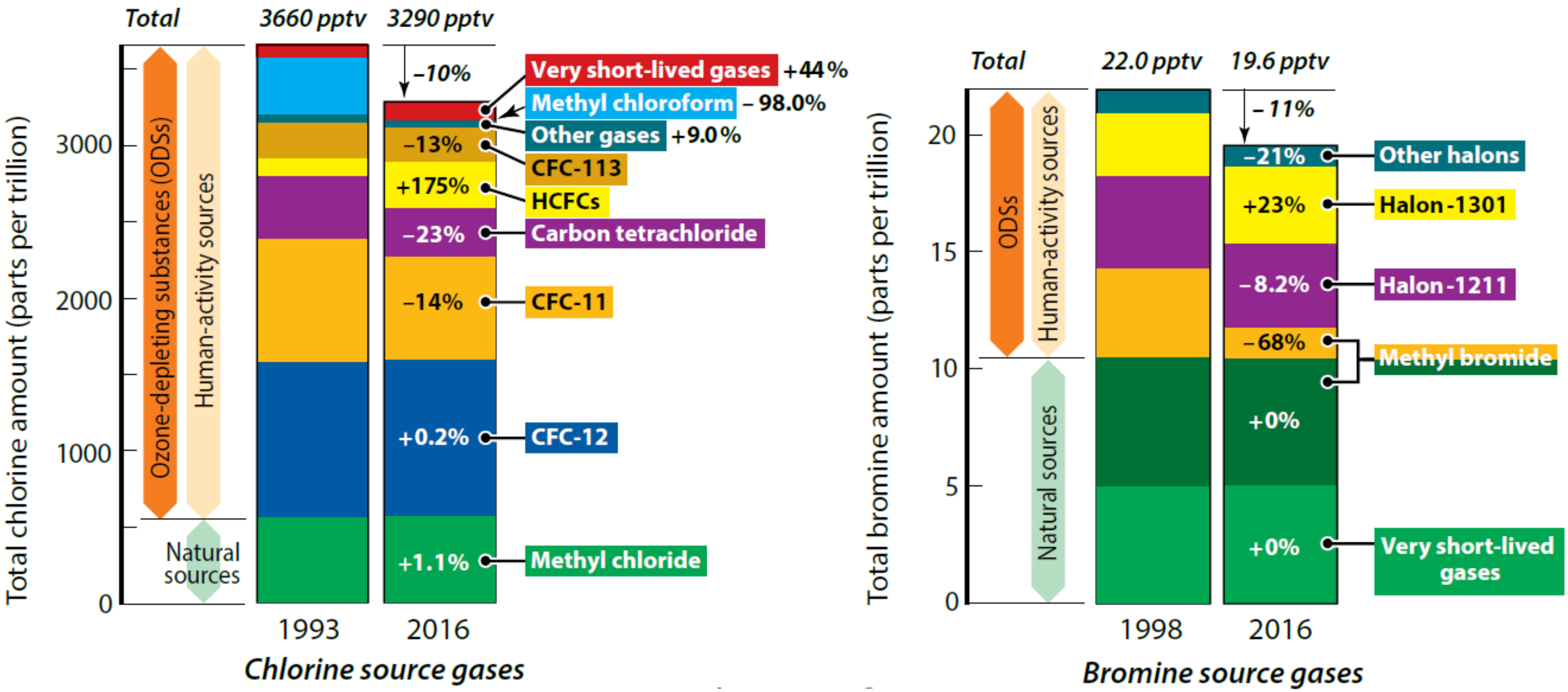
Halogen Source Gases Entering the Stratosphere



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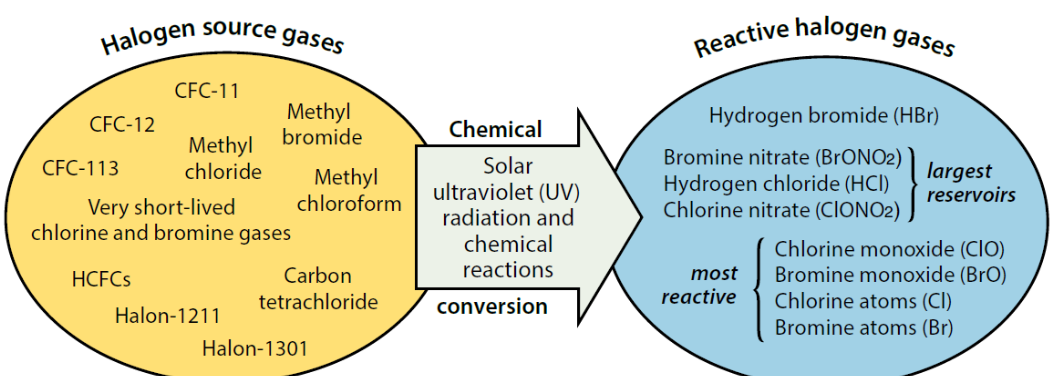

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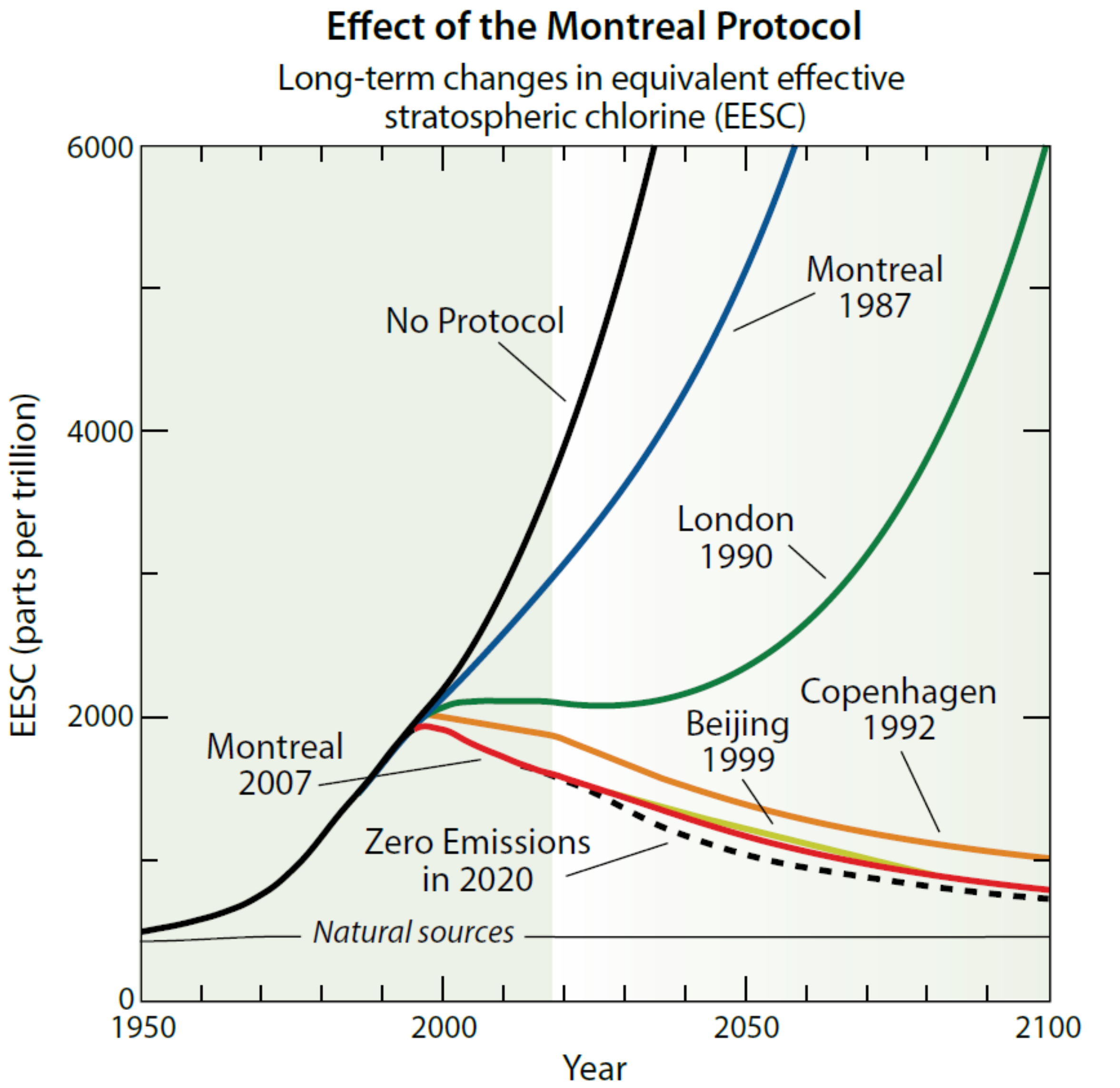

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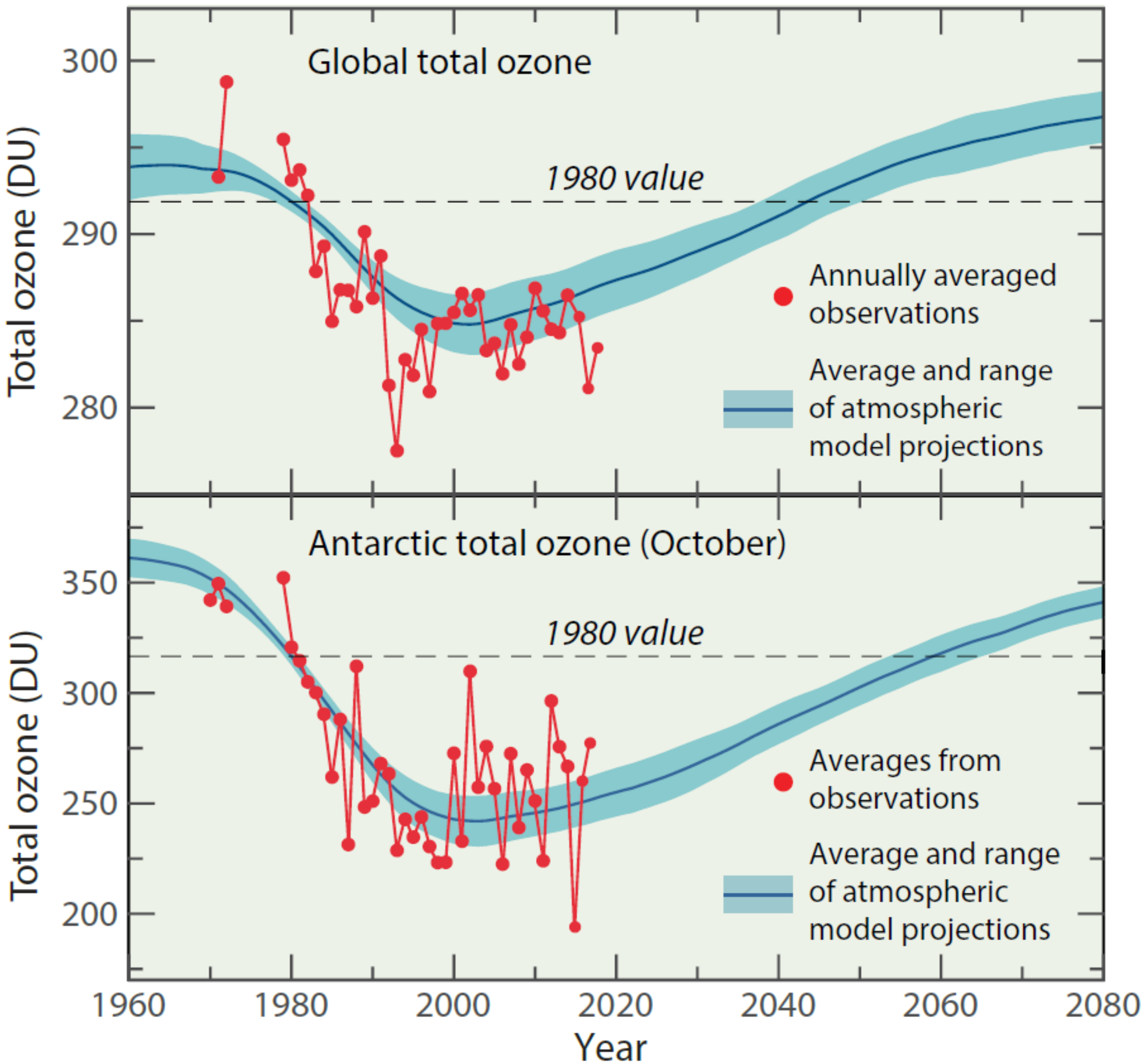
Changes in Global and Antarctic Ozone

Observations and model projections



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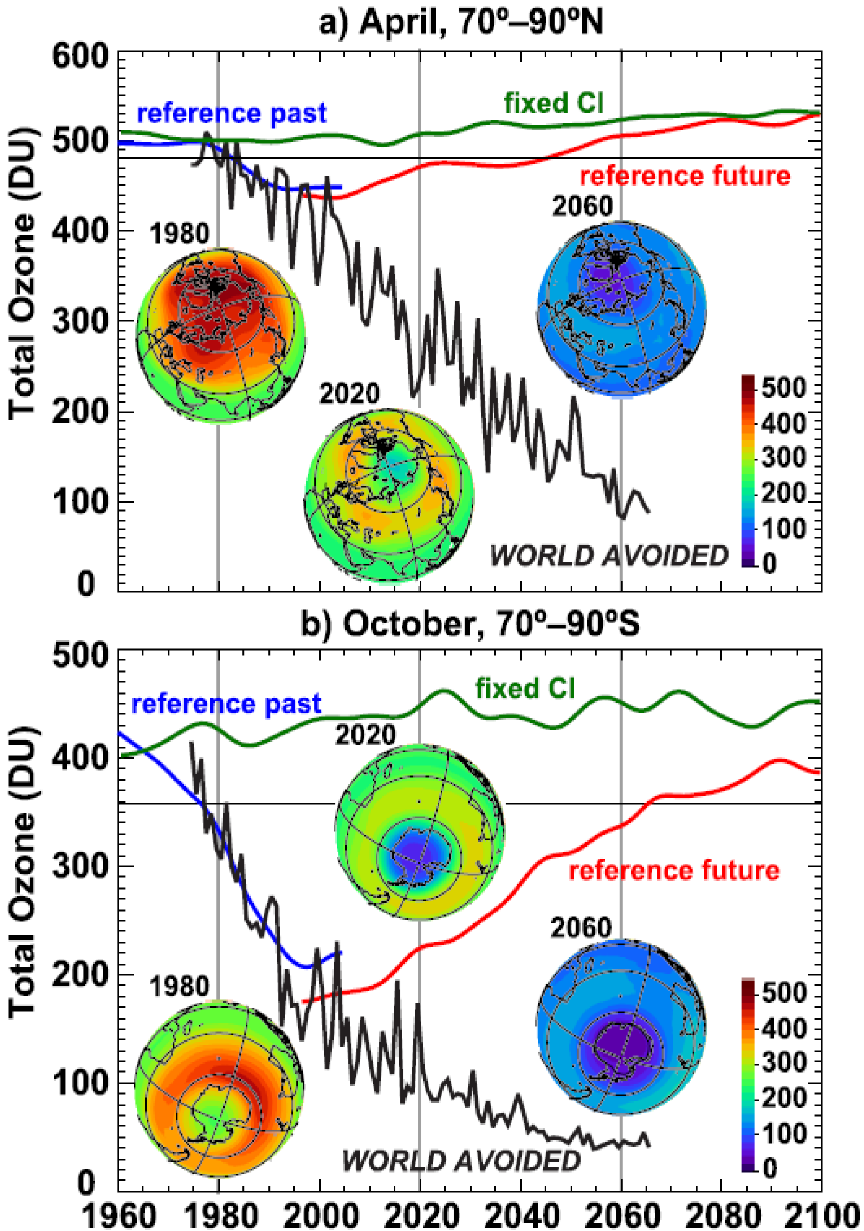
The World Avoided



Newman et al., 2009

Simulation	Year range	ODS scenario	Prescribed SSTs
Reference past	1950–2004	Ab[a]	Observations: HadISST1[b]
Reference future	1996–2099	Ab[a]	A: HadGEM1[c]
	2000–2099		B: NCAR CCSM3 SRESA1B
Fixed chlorine	1960–2100	Ab[a], fixed to 1960	1960–2000: Observations: HadISST1[b]
			2001–2100: NCAR CCSM3 PCMDI
WORLD AVOIDED	1974–2065	+3% per year	1974–2049: NCAR CCSM2 SRESA1B
			2050–2065: NCAR CCSM3 SRESA1B

"The year is 2065. Nearly two-thirds of Earth's ozone is gone—not just over the poles, but everywhere. The infamous ozone hole over Antarctica, first discovered in the 1980s, is a year-round fixture, with a twin over the North Pole. The ultraviolet (UV) radiation falling on mid-latitude cities like Washington, D.C., is strong enough to cause sunburn in just five minutes. DNA-mutating UV radiation is up more than 500 percent, with likely harmful effects on plants, animals, and human skin cancer rates." (https://www.earthobservatory.nasa.gov/features/WorldWithoutOzone)

Bibliography

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- F. S. Rowland Nobel Lecture in Chemistry, 1995
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