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Materials that enter the stratosphere can remain there for long periods of time, often as stratified layers.

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- **It is involved in many stratospheric chemical reactions.**

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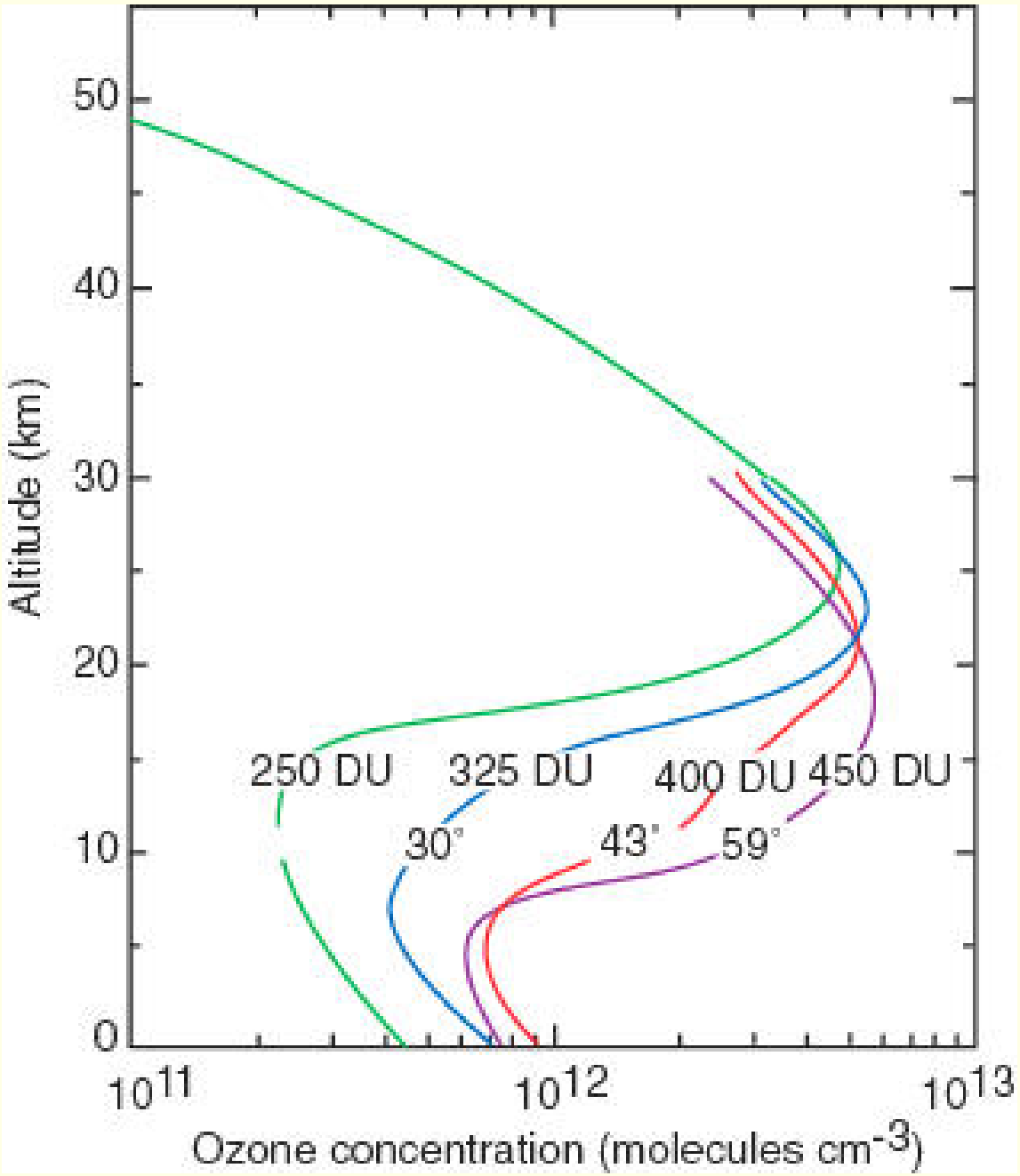
Shown in the figure below are the results of more recent measurements of O_3. The presence of an ozone layer between heights of $\sim$15–30 km is very clear.



Mean vertical distributions of ozone concentrations based on measurements at different latitudes (given in degrees).

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Much of the change in the total column abundance of O_3 is due to differences in the profiles below 20 km.

Techniques for Measuring O_3

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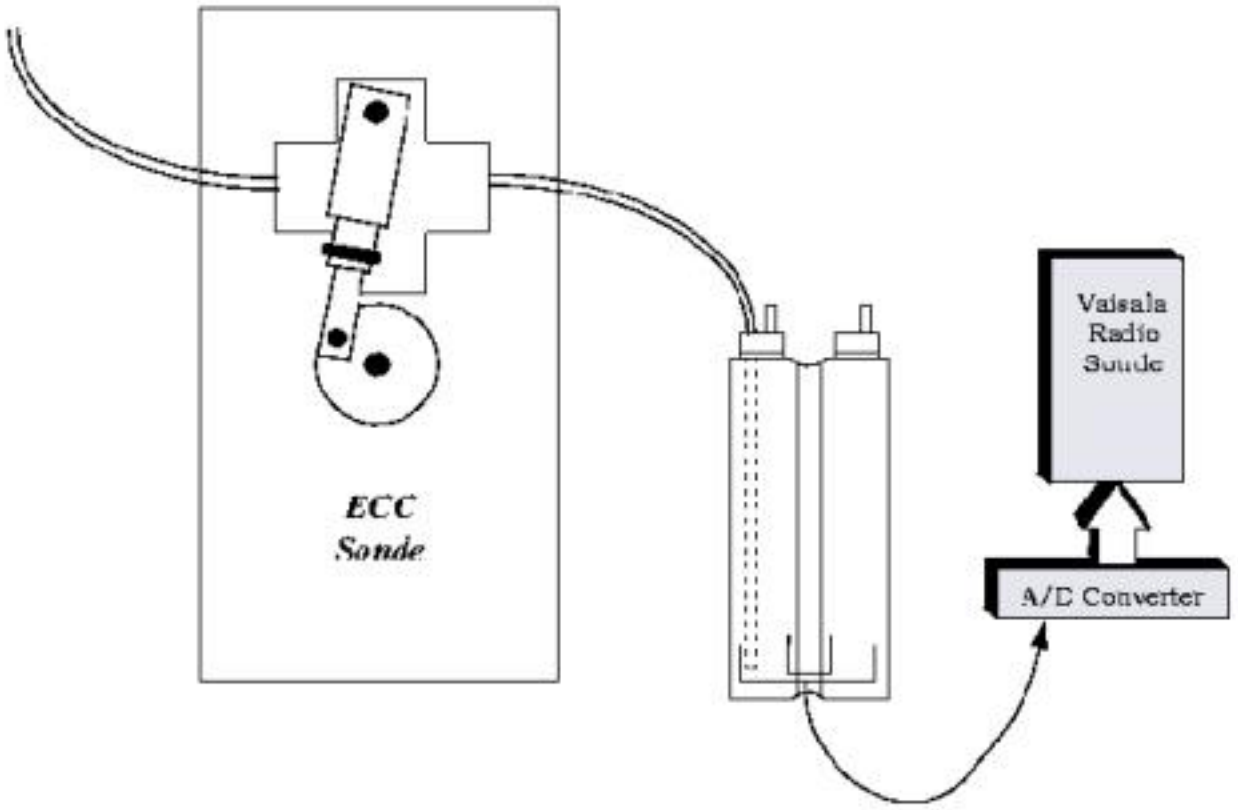
In this way, a vertical profile of O_3 is obtained, the integration of which provides the O_3 column from ground level up to the height of the balloon.

Ozone Sonde Schematics



Air pump (teflon)

Electrochemical Cell

Transmitter

Brewer Spectrophotometer

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By taking the ratio of the two measured values, absorption by O_3 in the total vertical column can be obtained.

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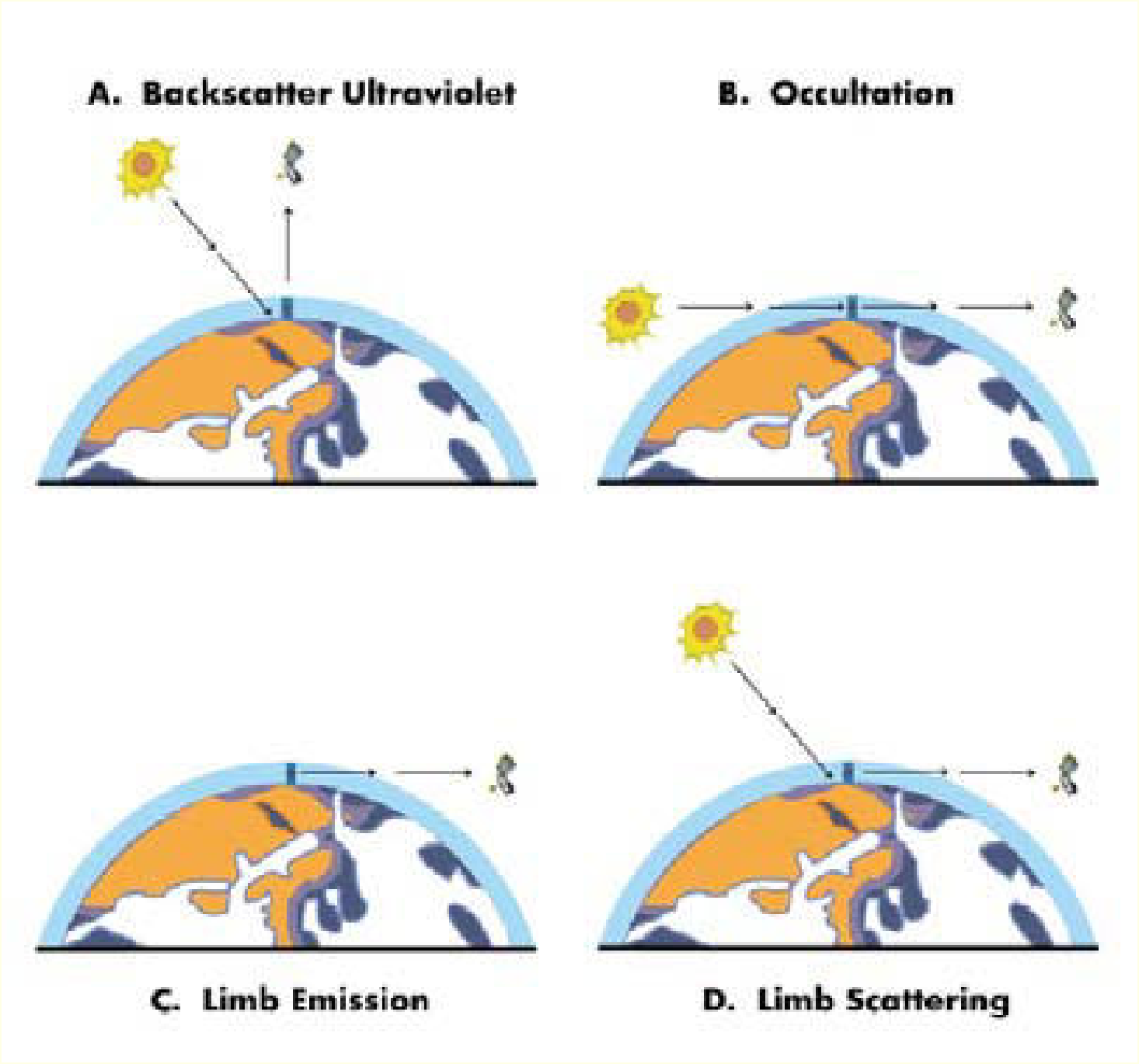
For a description of these methods, see *Wallace & Hobbs*.



Four passive techniques for measuring ozone from satellites.

Chapman's Theory

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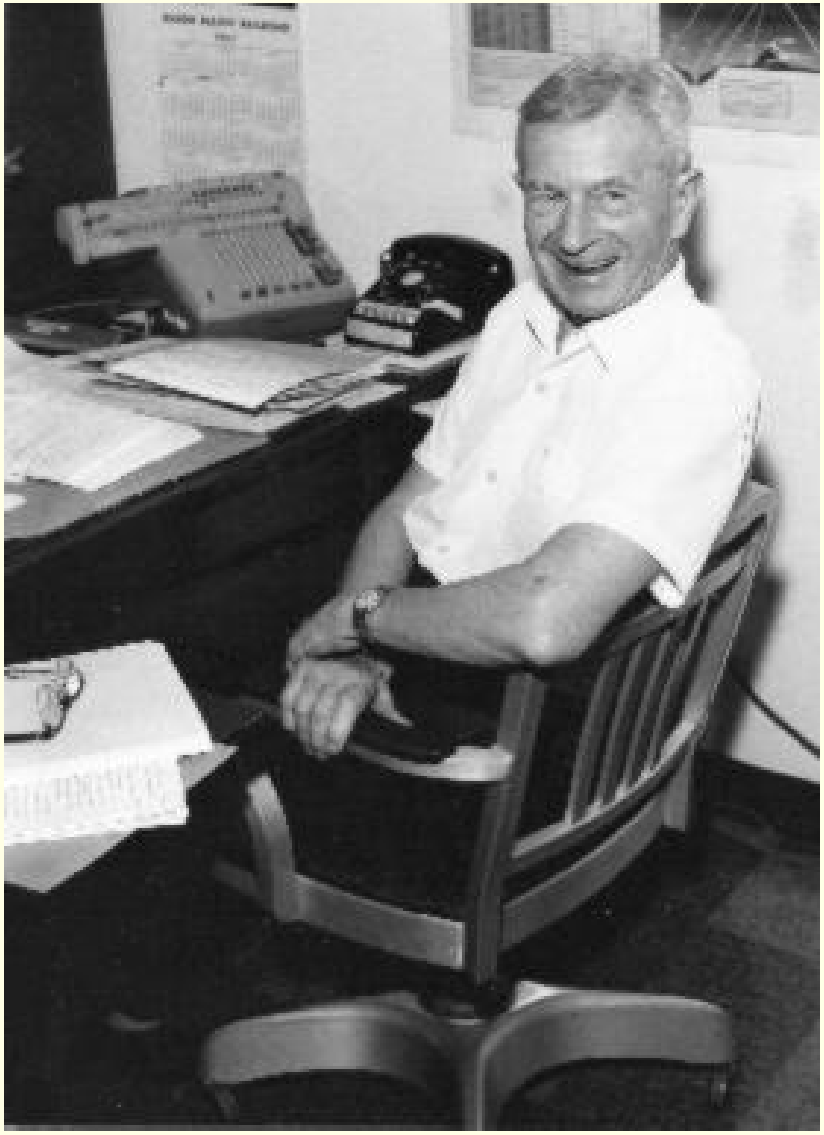

In 1930 Sydney Chapman proposed a simple chemical scheme for maintaining steady state concentrations of O_3 in an "oxygen-only" stratosphere.

These reactions are called the Chapman reactions.

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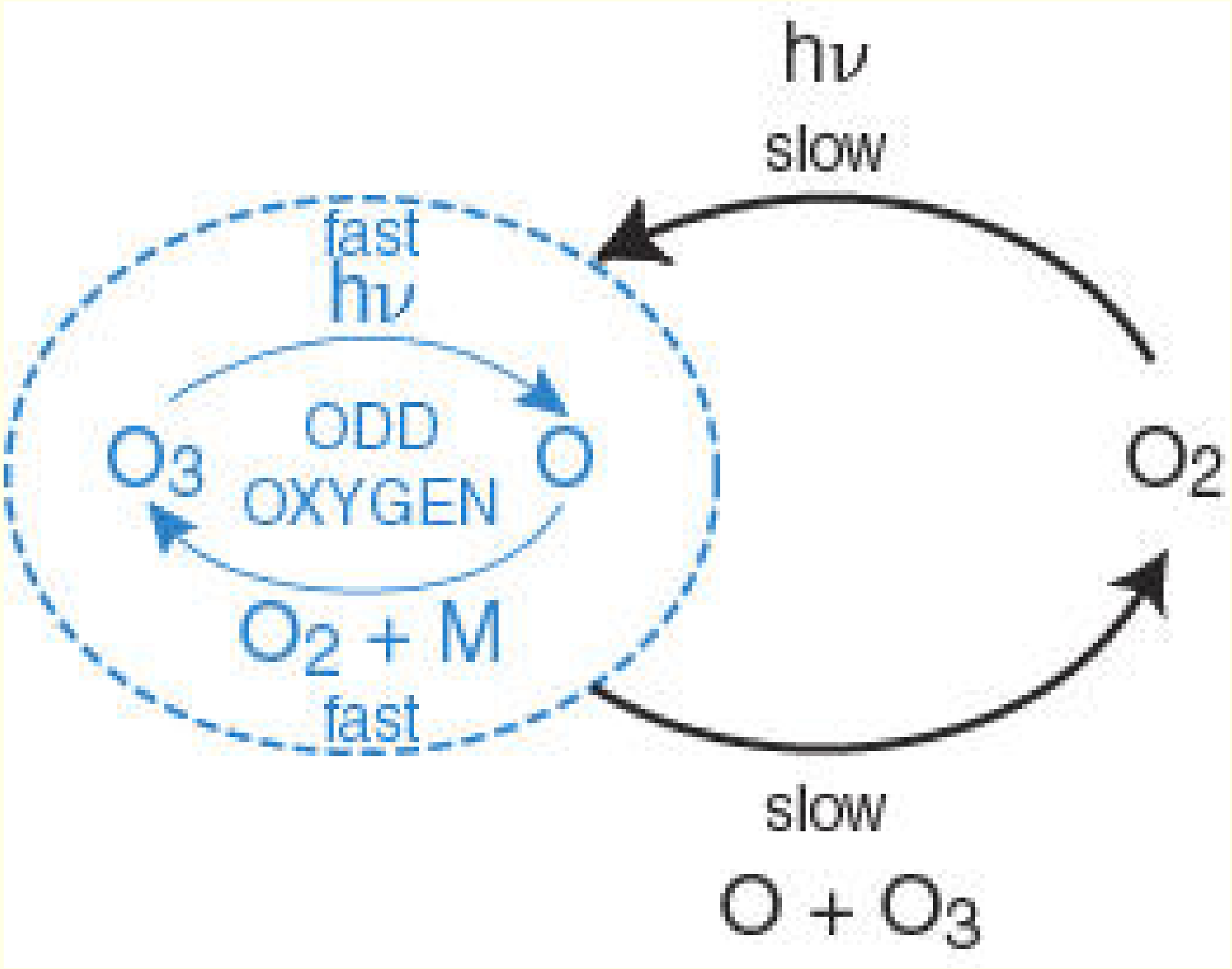
Since the concentration of M decreases with increasing altitude, the time constant for converting O atoms and O_2 molecules to O_3 increases with altitude (e.g., from a few seconds at 40 km to $\sim$100 s at 50 km).



Schematic illustration of the Chapman reactions.

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There is an equator-to-pole circulation in the stratosphere, known as the Brewer-Dobson Circulation, which transports O_3 from its primary source in the tropical stratosphere to higher latitudes.

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The destruction of stratospheric O_3 by the various chemical mechanisms discussed above, and many other possible mechanisms not discussed here, are not simply additive because the species in one cycle can react with those in another.

Therefore, *advanced numerical models* that consider all the known suspects must be used to unravel the relative importance of the various mechanisms for destroying O_3 in the stratosphere.

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Most of the catalytic reactions that have been proposed for the removal of stratospheric odd oxygen are of the form

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If the concentration of catalyst X is increased significantly by anthropogenic activities, the balance between the sources and sinks of atmospheric O_3 will be disturbed and stratospheric O_3 concentrations can be expected to decrease.

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Of much greater concern, with documented impacts, is the catalytic action of chlorine, from industrially manufactured *chlorofluorocarbons* (CFCs), in depleting stratospheric ozone.

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HFCs and HCFCs are considered to be more "environmentally friendly" than CFCs because they are partially destroyed by OH in the troposphere.

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$$\mathbf{CFCl_3} + h\nu \rightarrow \mathbf{CFCl_2} + \mathbf{Cl}$$

and

$$\mathbf{CF_2Cl_2} + h\nu \rightarrow \mathbf{CF_2Cl} + \mathbf{Cl}$$

The chlorine atom released by these reactions can serve as the catalyst X and destroy odd oxygen in the cycle

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In 1990, ∼85% of the chlorine in the stratosphere originated from anthropogenic sources. Because CFCs absorb strongly in the infrared, they are also significant greenhouse gases.

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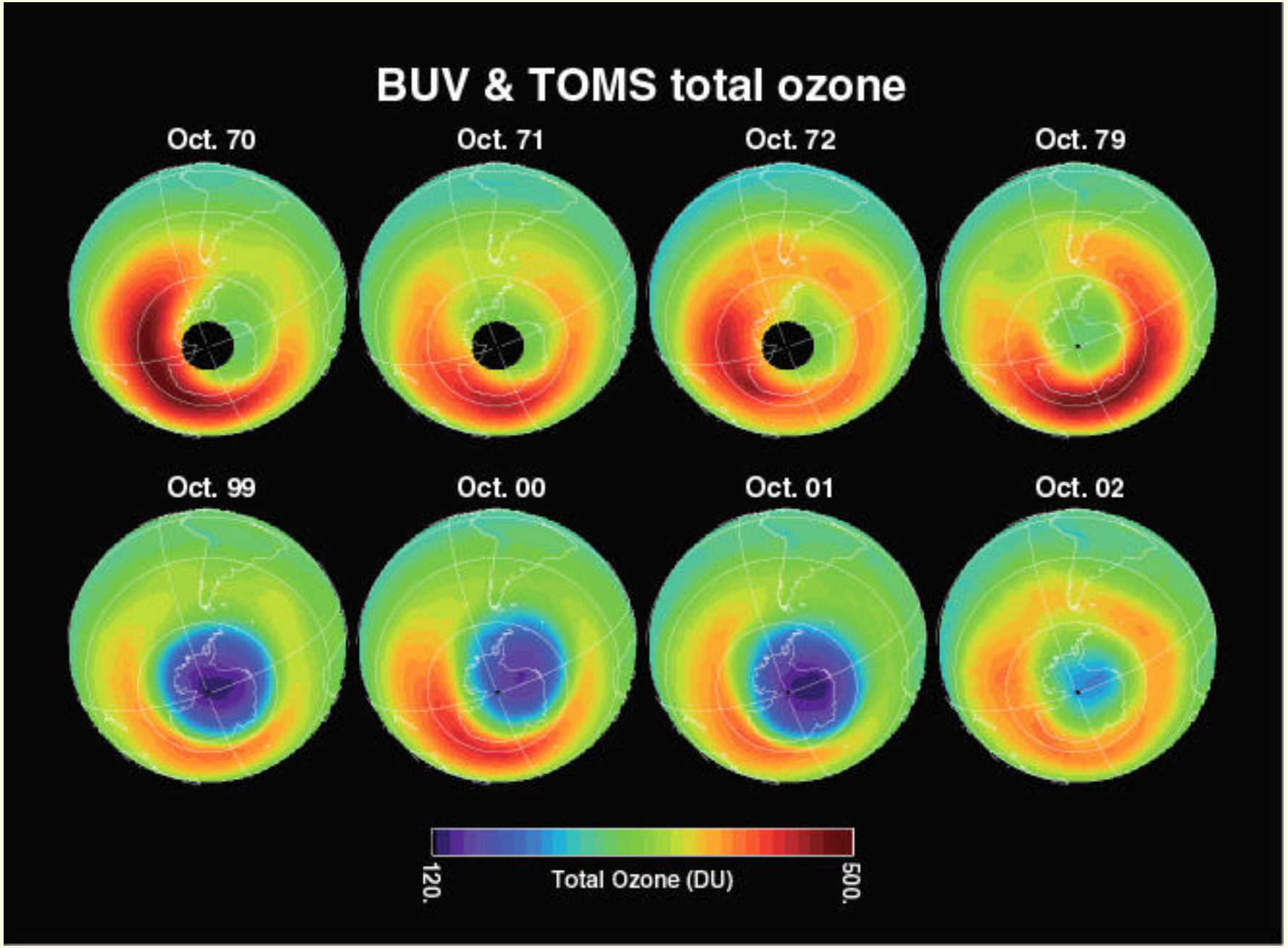
Shown in the next Figure are a series of satellite measurements of the total O_3 column in the southern hemisphere.



Satellite observations of the total ozone column (DU) in the southern hemisphere during October for eight years from 1970-2002.

The high O_3 values (red and orange colours) that encircle the Antarctic continent and the lower O_3 values (green) over the continent itself in the 1970s (upper four images) are considered to be close to natural.

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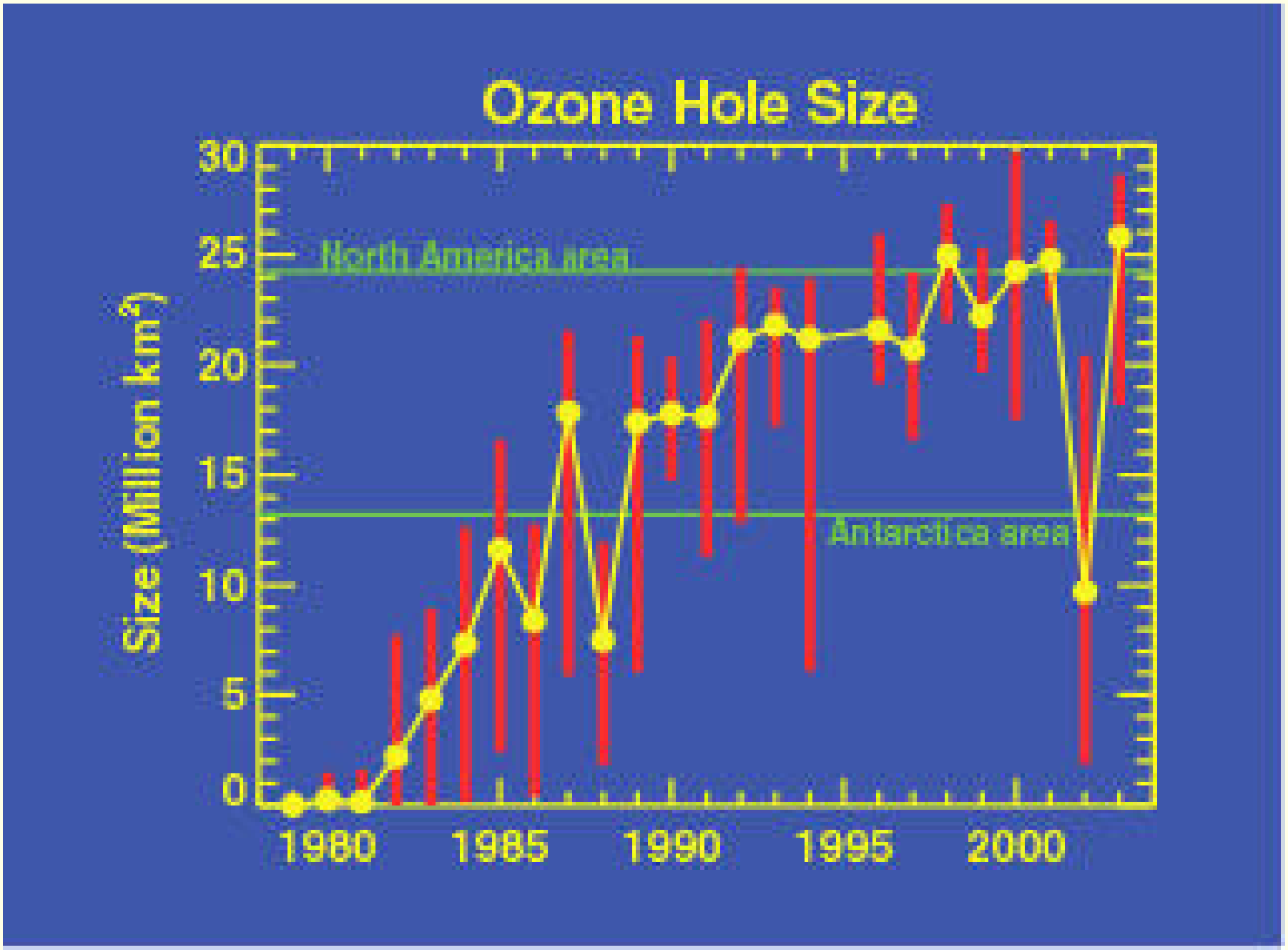
The areal extent of the Antarctic ozone hole, derived from satellite measurements for the period September 7 to October 13 1979-2002 are shown next.

From 1979 to 2001 the ozone hole grew progressively until it occupied an area ($\sim$25 million km^2) similar to that of North America.



Average areal extent of the ozone hole (<220 DU) from September 7-October 13, 1979-2003.

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Paul Crutzen, Mario Molina, and Sherwood Rowland were awarded the Nobel Prize in Chemistry in 1995 for their explanation of stratospheric O_3 loss by CFCs and nitrogen-containing gases.

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In the austral spring, as temperatures rise, the winds around the vortex weaken, and by November the vortex disappears.

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These decreases are due, respectively, to the formation of nitric acid (HNO_3), and to the condensation of water at the very low temperatures inside the vortex.

Polar Stratospheric Clouds

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Type I PSCs. **These probably consist of a mixture of liquid and solid particles of nitric acid trihydrate [$HNO_3(H_2O)_3$ – NAT for short], water and sulfuric acid, which condense at about -78°C. These particles are $\sim 1\,\mu$m in diameter, so they sediment very slowly (~ 10 m per day).**

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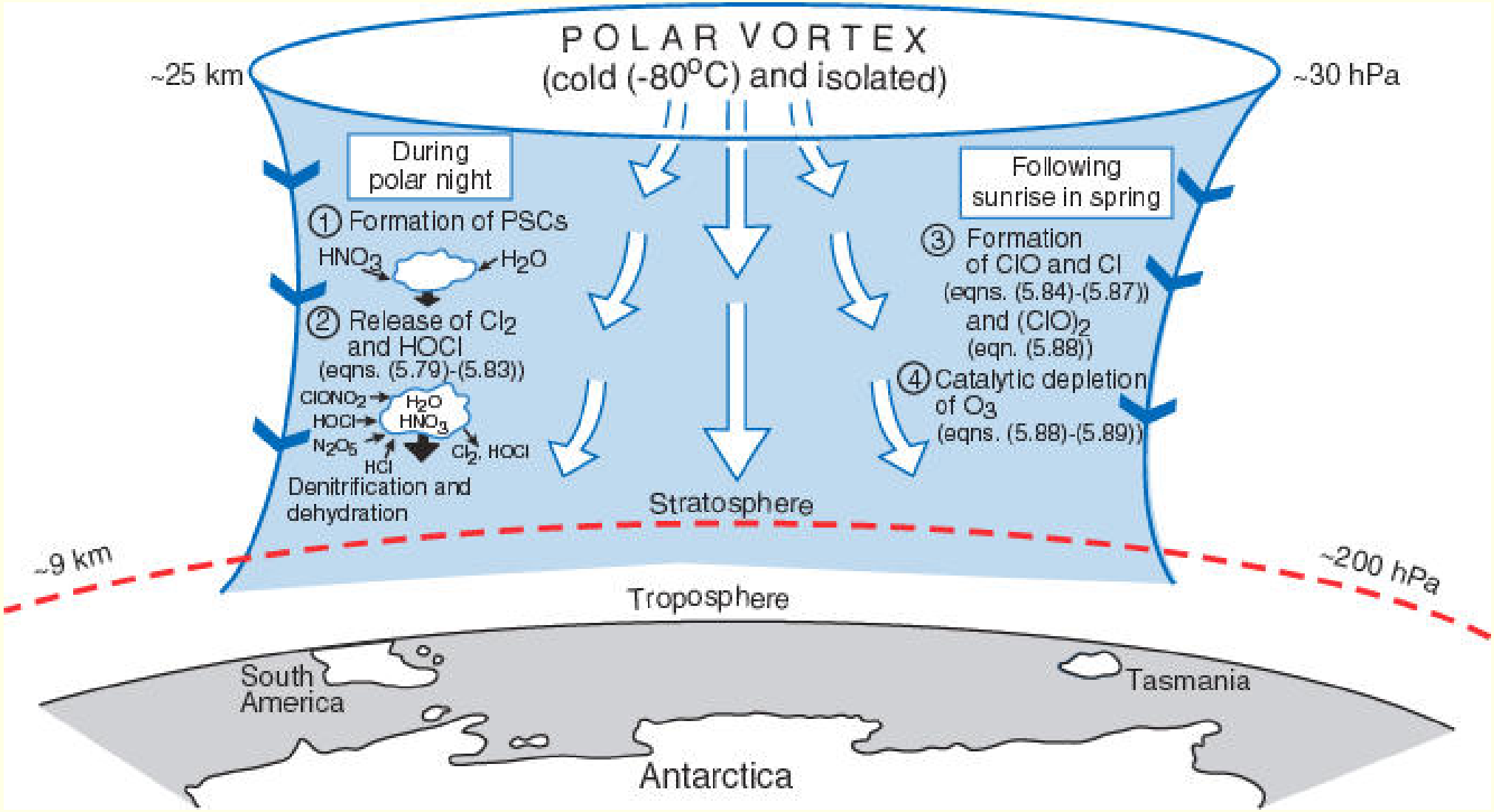
Type III PSCs. These "mother-of-pearl" clouds are produced by the rapid freezing of condensed water in air flow over topography. However, they are of limited extent and duration and do not form over the South Pole.



Schematic of the polar vortex (blue) over Antarctica.

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$$\begin{aligned}
ClONO_2(g) + HCl(s) &\rightarrow Cl_2(g) + HNO_3(s) \\
ClONO_2(g) + H_2O(s) &\rightarrow HOCl(g) + HNO_3(s) \\
HOCl(g) + HCl(s) &\rightarrow Cl_2(g) + H_2O(s) \\
N_2O_5(g) + H_2O(s) &\rightarrow 2HNO_3(s) \\
N_2O_5(g) + HCl(s) &\rightarrow ClNO_2(g) + HNO_3(s)
\end{aligned}$$

[(s) indicates those compounds that are on (or in) ice particles, and (g) indicates species that are released as gases.]

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When the Sun rises in the Antarctic spring, these three species are photolyzed rapidly to produce Cl and ClO

$$\mathbf{Cl_2} + h\nu \rightarrow \mathbf{2Cl}$$
$$\mathbf{HOCl} + h\nu \rightarrow \mathbf{OH} + \mathbf{Cl}$$
$$\mathbf{ClNO_2} + h\nu \rightarrow \mathbf{Cl} + \mathbf{NO_2}$$

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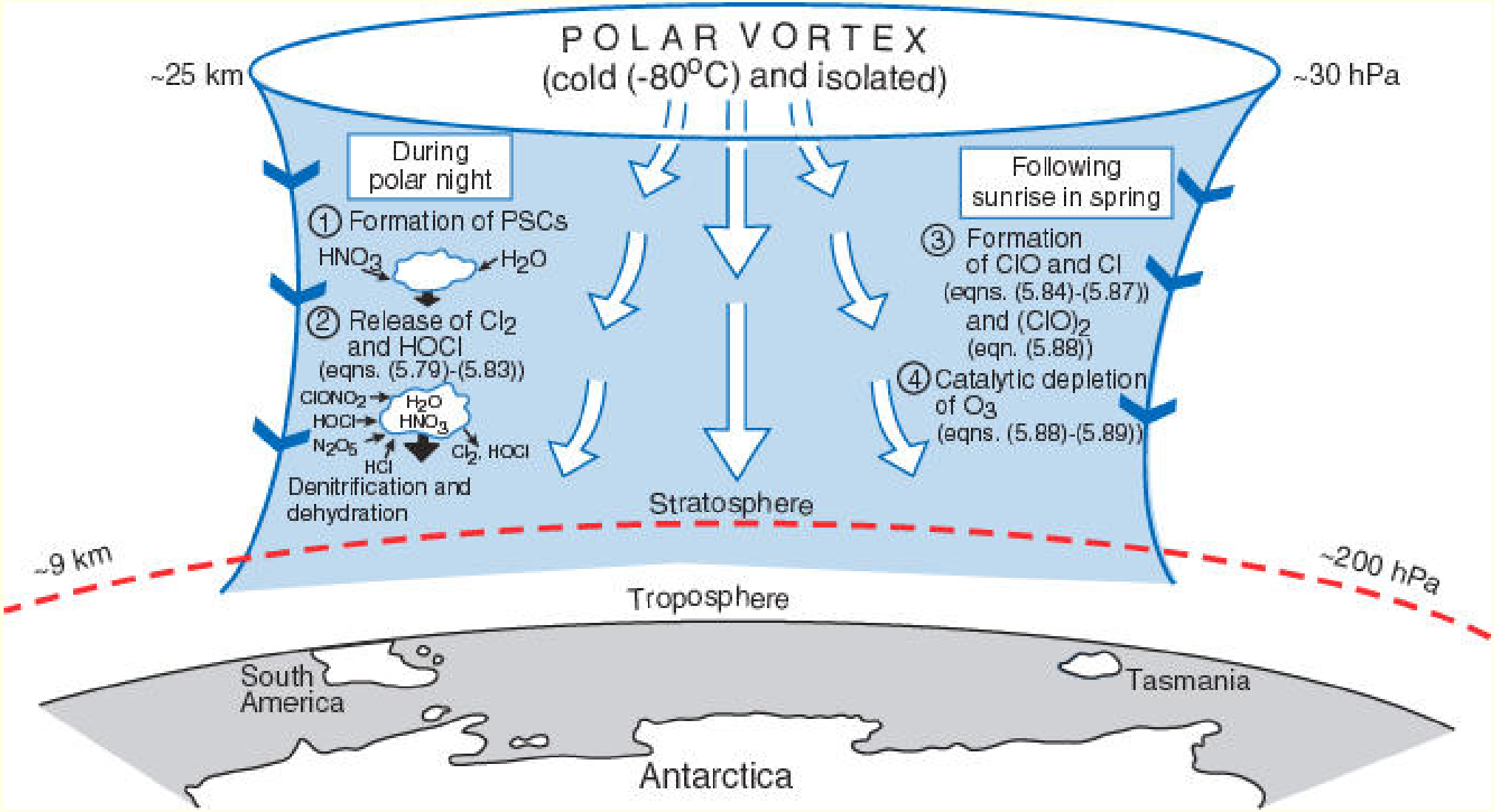
and

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

Ozone is then destroyed efficiently by

$$\begin{aligned} ClO + ClO + M &\rightarrow (ClO)_2 + M \\ (ClO)_2 + h\nu &\rightarrow Cl + ClOO \\ ClOO + M &\rightarrow Cl + O_2 + M \\ 2Cl + 2O_3 &\rightarrow 2ClO + 2O_2 \end{aligned}$$

$$\text{Net:} \quad 2O_3 + h\nu \rightarrow 3O_2$$



Schematic of the polar vortex (blue) over Antarctica.

Again!

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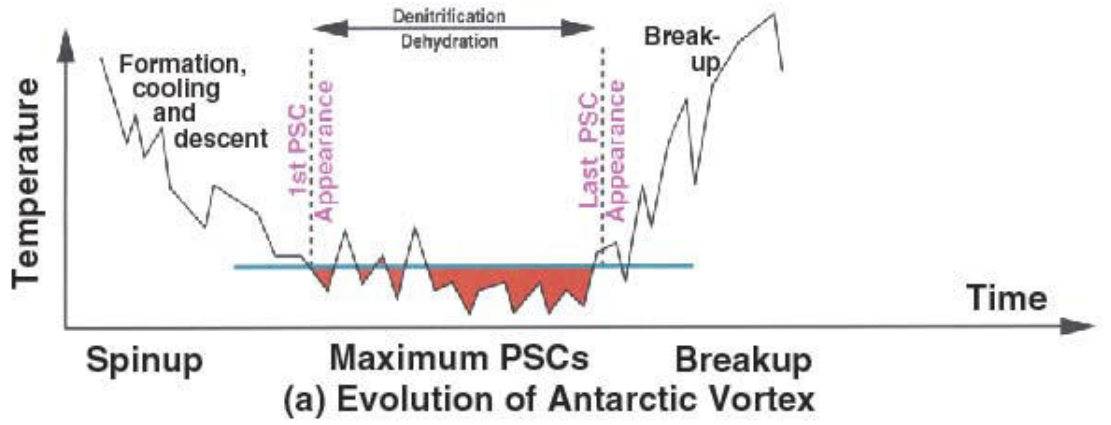
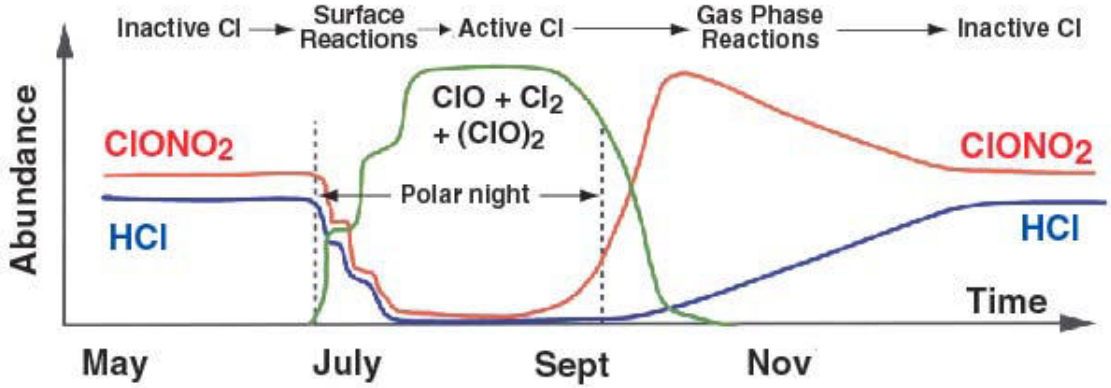
- The dimer $(ClO)_2$ is formed only at low temperatures. Low enough temperatures are present in the Antarctic stratosphere before the Spring.



(a) Evolution of Antarctic Vortex



(b) Chlorine Reservoirs in Antarctic Vortex

(c) Ozone in Antarctic Vortex

Schematic to illustrate the time evolution of the main processes associated with the development of the Antarctic ozone hole.
(a) The polar vortex.
(b) Chlorine species.
(c) Ozone.

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In 2003, which was a cold year, the ozone hole returned to its earlier extent of $\sim$25 million square kilometers.

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However, prior to the winter of 1995–96 there was not a stratospheric ozone hole in the Arctic comparable to that in the Antarctic.

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In the winter of 1999–2000 the average total ozone column in March poleward of 63°N was lower by $\sim$75 DU than the average climatological value, and these low values continued through 2003.

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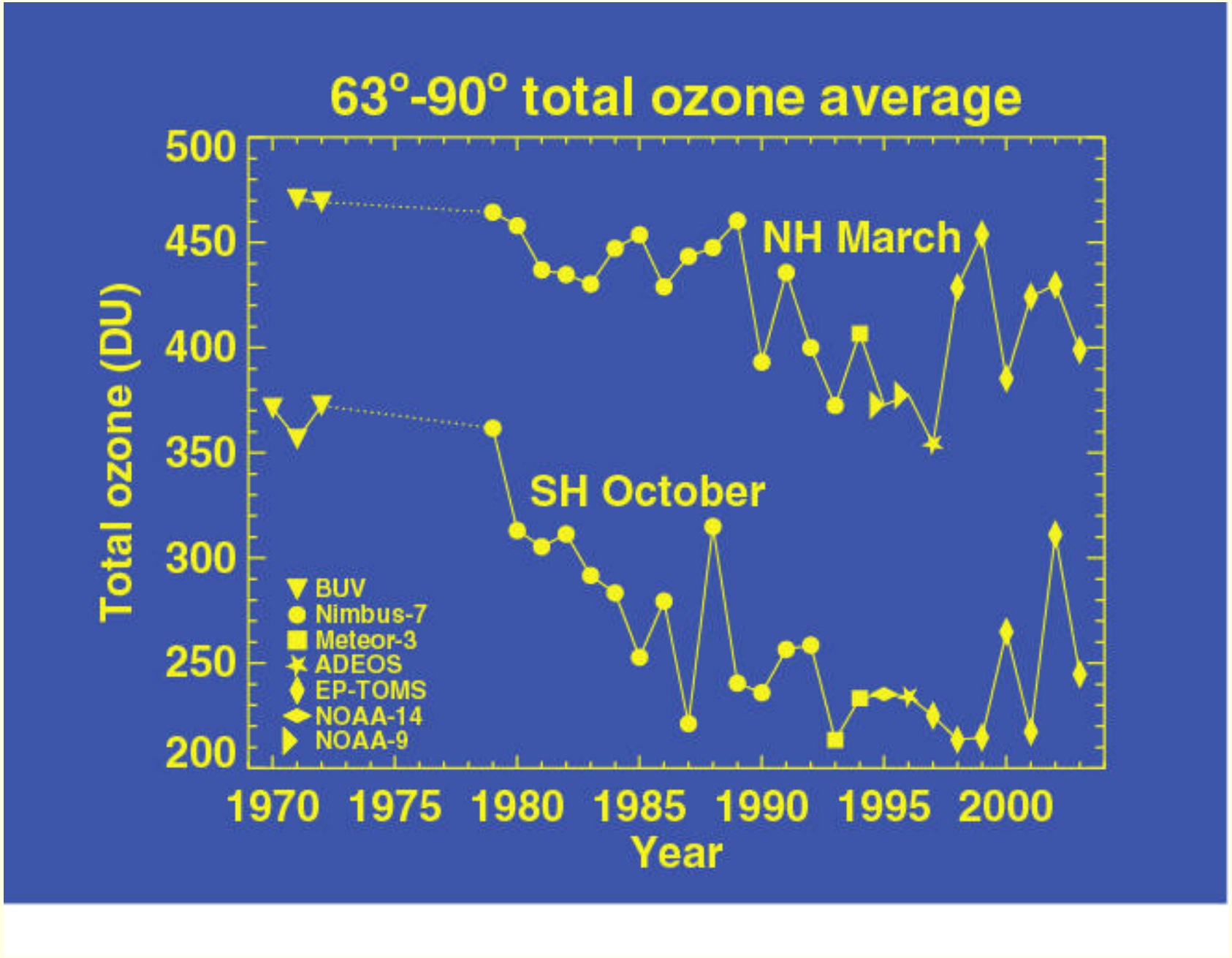
No trends in total column ozone were observed in the tropics (25°N–25°S) during the period 1980–2000.



Average ozone columns between latitudes $63° - 90°$ for the northern hemisphere in March and the southern hemisphere in October.

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Therefore, it is predicted that the O_3 layer will not completely recover until about the middle of the 21^{st} century.

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The *Copenhagen Amendment* (1992) called for the complete elimination of CFCs by 1996, and the *Vienna Amendment* (1995) called for the complete elimination of HCFCs by 2020.

An Interesting Historical Review

For an interesting review of the emergence of evidence on the ozone hole in the Antarctic, see the article:

Data Collection and the Ozone Hole:
Too much of a Good Thing?
Maureen Christie, *Proc. ICHM*, 1.1 (2004).
On course website.