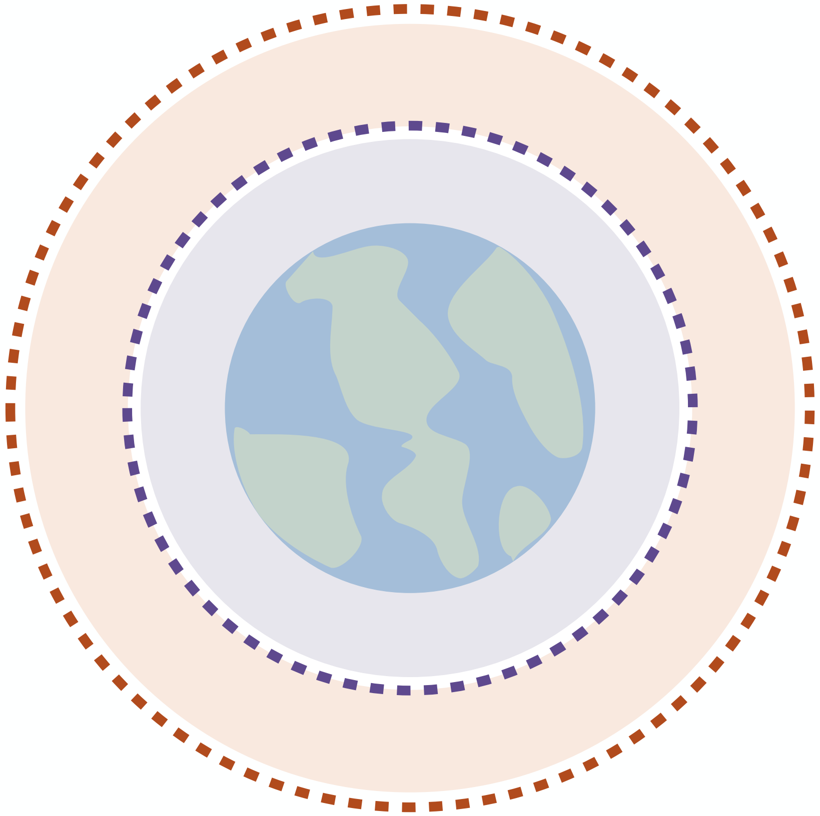
Atmospheric Chemistry:

The Many Roles of Ozone in the Stratosphere and Troposphere



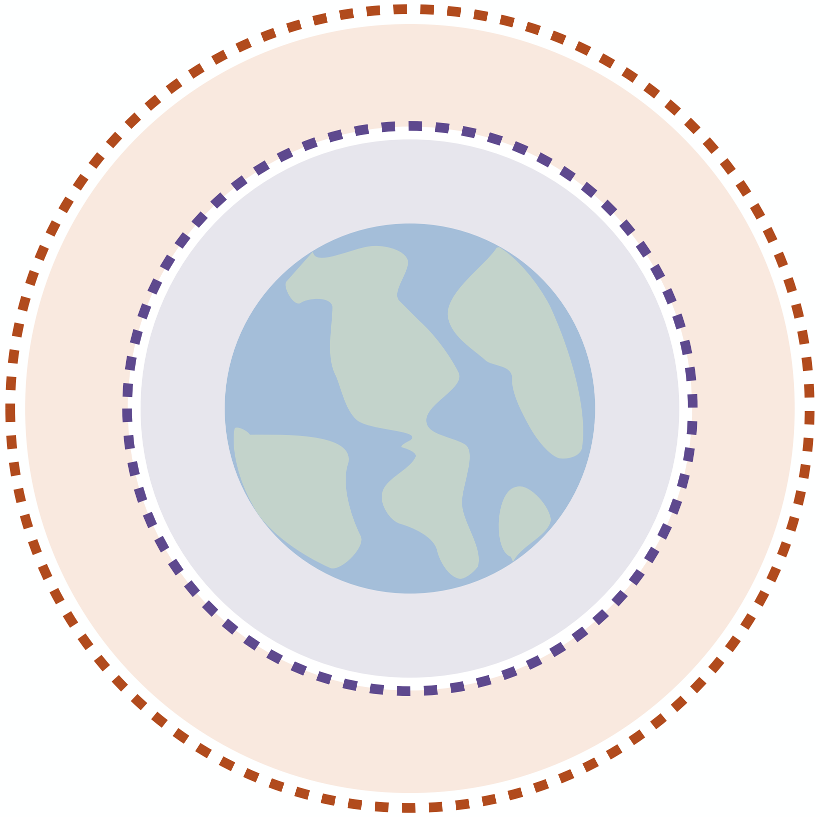
Marissa Lavagnino

MacMillan Group Meeting

4 March 2020

What is the atmosphere?

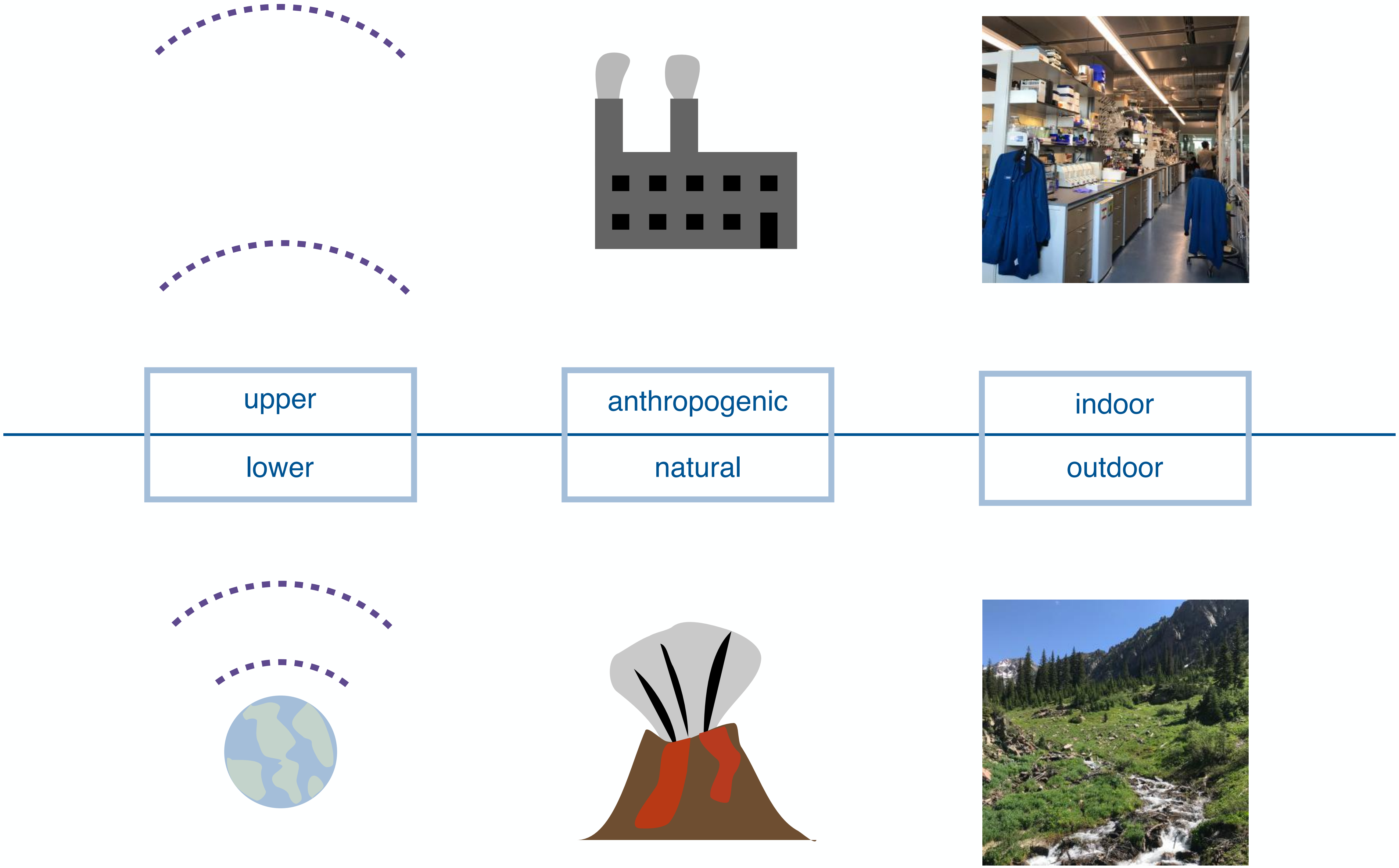
"…the gas and aerosol envelope that extends from the ocean, land and ice-covered surface of a planet outward into space"



Earth's atmosphere: 78.08% $\mathbf{N_2}$ 20.95% $\mathbf{O_2}$ 0.93% **Ar** 0.04% $\mathbf{CO_2}$ + *other minor components*

Atmosphere. *Encyclopædia Britannica* [Online]; Encyclopædia Britannica, Posted February 13, 2020. https://www.britannica.com/science/atmosphere/Troposphere (accessed February 29, 2020).

The broad field of atmospheric chemistry



upper

lower

anthropogenic

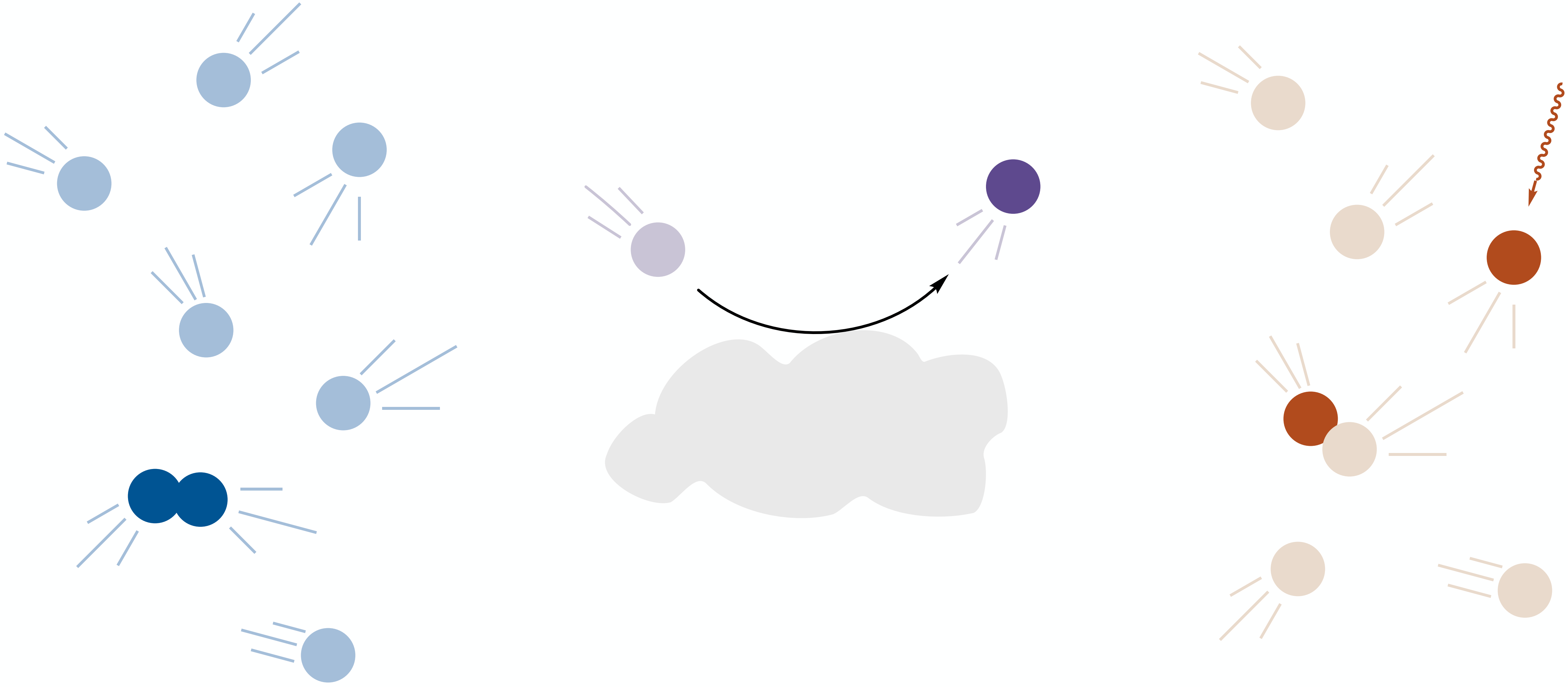
natural

indoor

outdoor

Finlayson-Pitts, B. J. *Proc. Natl. Acad. Sci.* **2010**, *107*, 6566.

The broad field of atmospheric chemistry



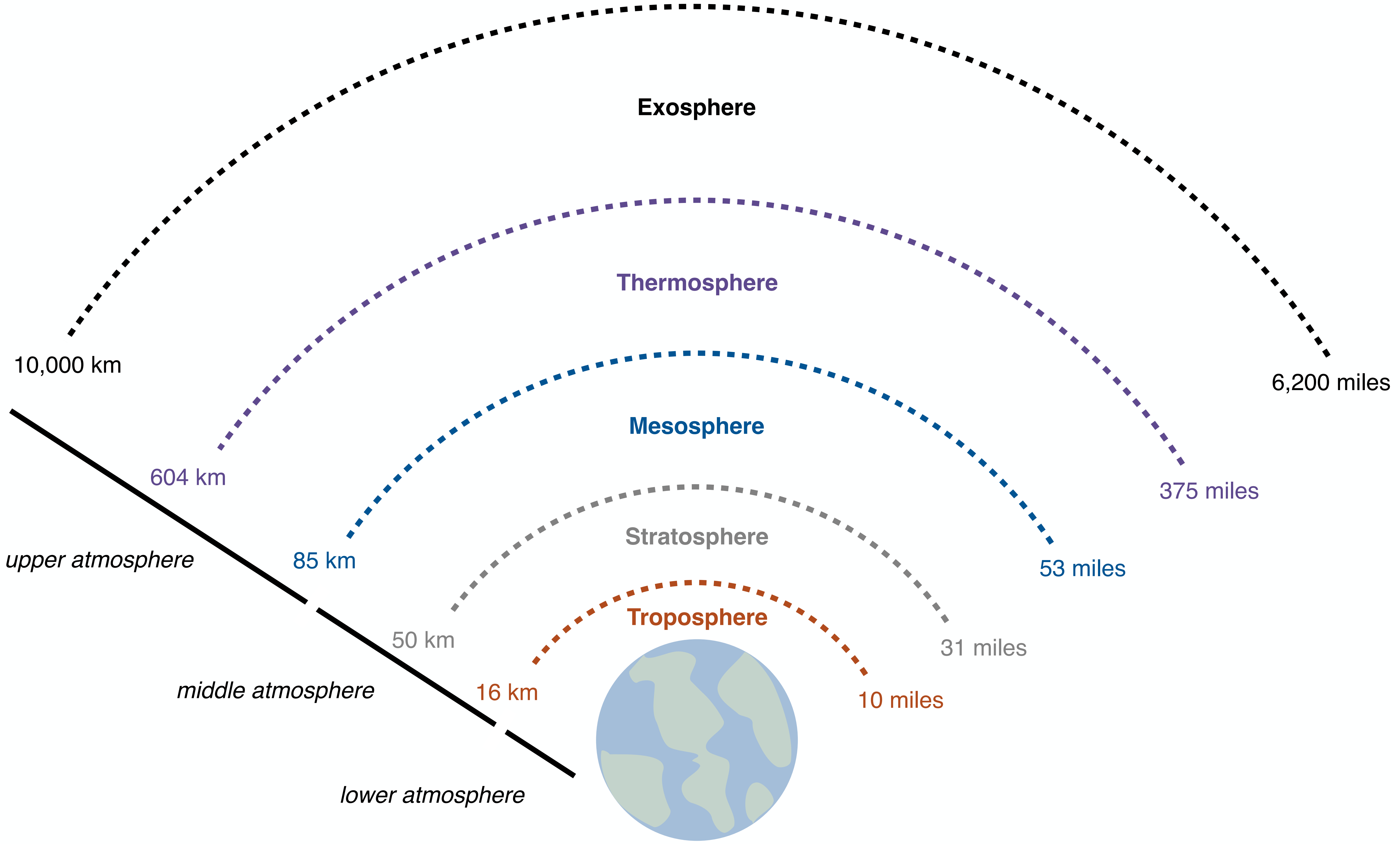
homogeneous

heterogeneous

photochemical

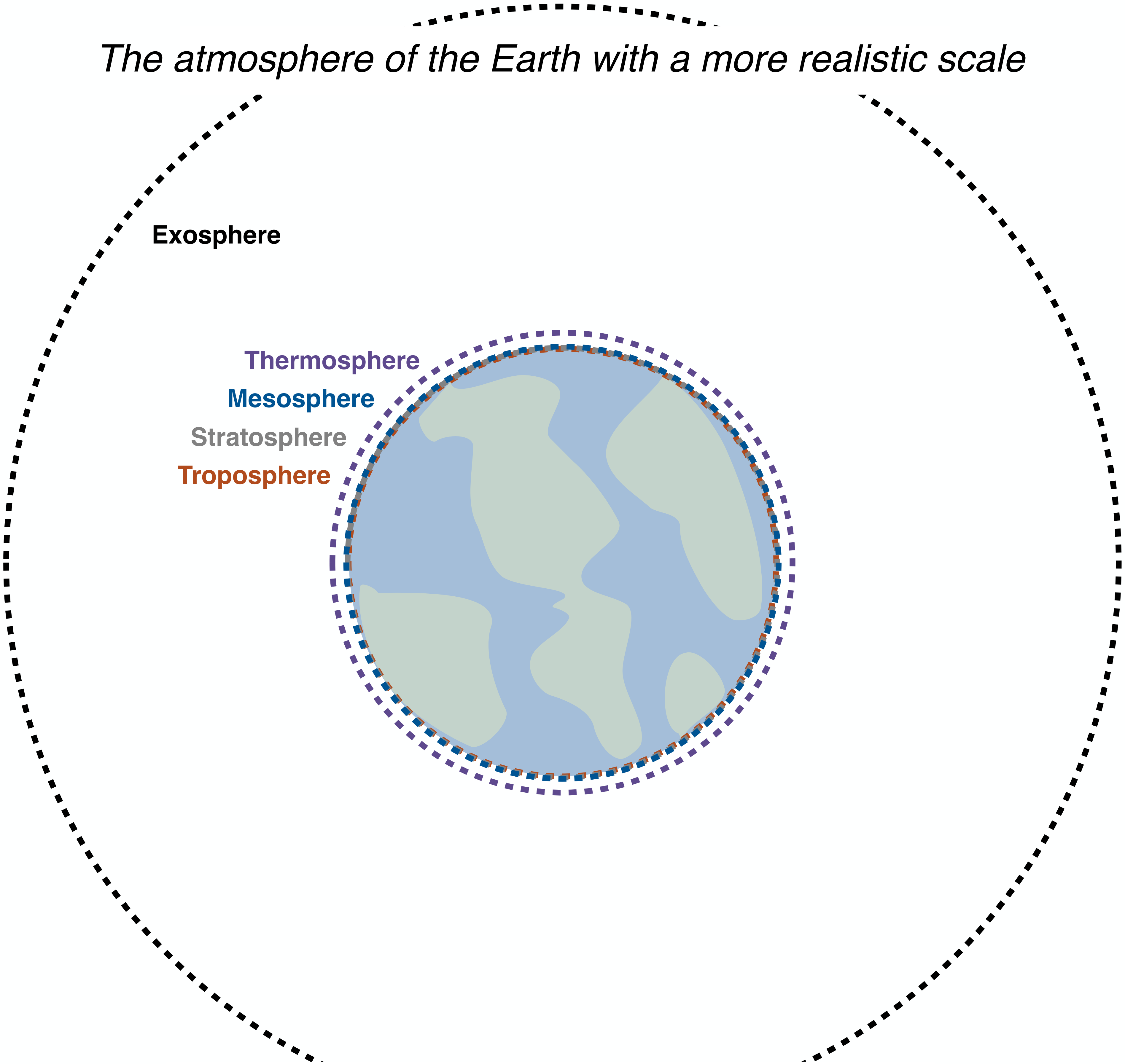
Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Washington, DC, **2009**; 7-15.

The atmosphere of the Earth



Atmosphere. *Encyclopædia Britannica* [Online]; Encyclopædia Britannica, Posted February 13, 2020. https://www.britannica.com/science/atmosphere/Troposphere (accessed February 29, 2020).

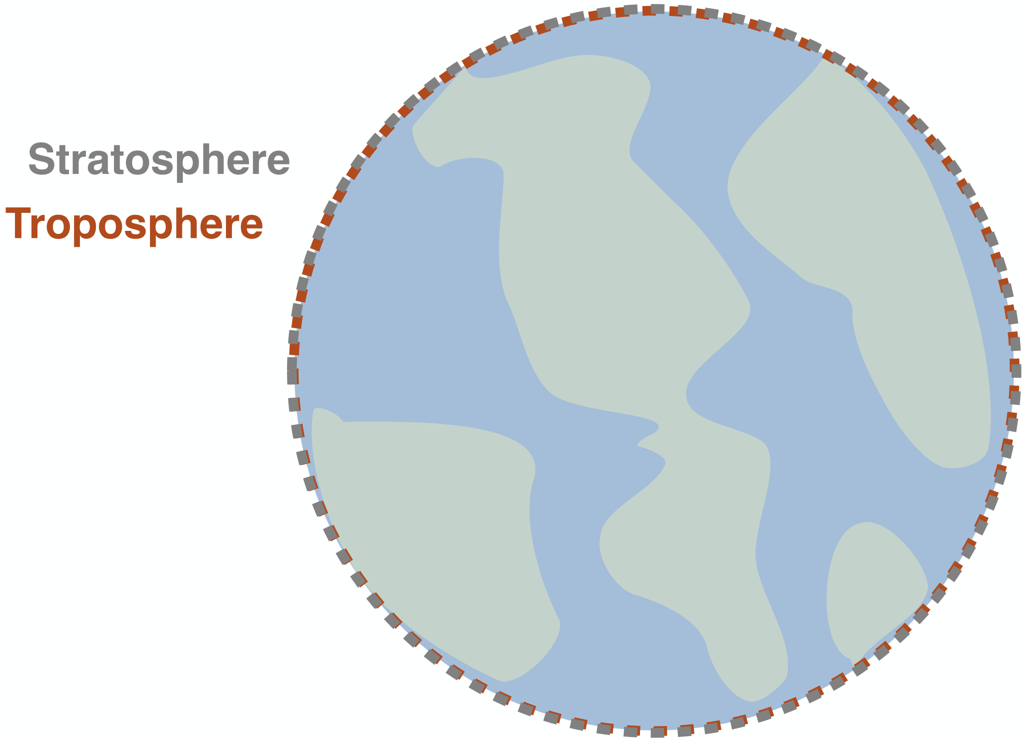
The atmosphere of the Earth with a more realistic scale



Atmosphere. *Encyclopædia Britannica* [Online]; Encyclopædia Britannica, Posted February 13, 2020. https://www.britannica.com/science/atmosphere/Troposphere (accessed February 29, 2020).

The atmosphere of the Earth with a more realistic scale

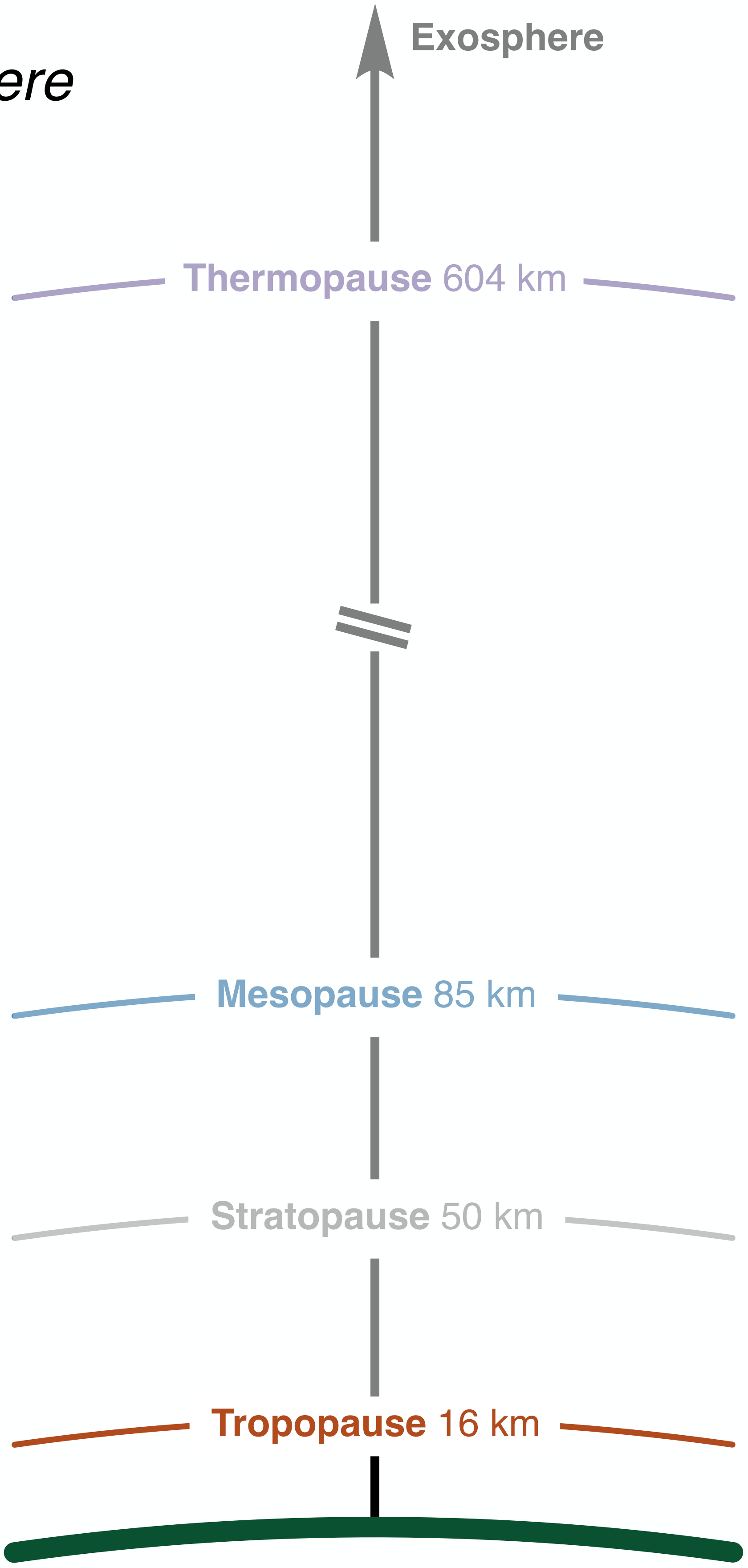
99% of atmospheric mass is contained in the **Stratosphere** and **Troposphere** (50 km)



If the Earth were a basketball, this would be a *1 mm layer*

Back-of-the-Envelope Calculations: The Scale of the Atmosphere. *Teaching Quantitative Skills in the Geosciences,* Carleton College. https://serc.carleton.edu/quantskills/activities/botec_atmosphere.html (accessed February 29, 2020).

The troposphere - lower atmosphere



contains **nearly all water (99%)** and **majority of mass (75%)** in atmosphere

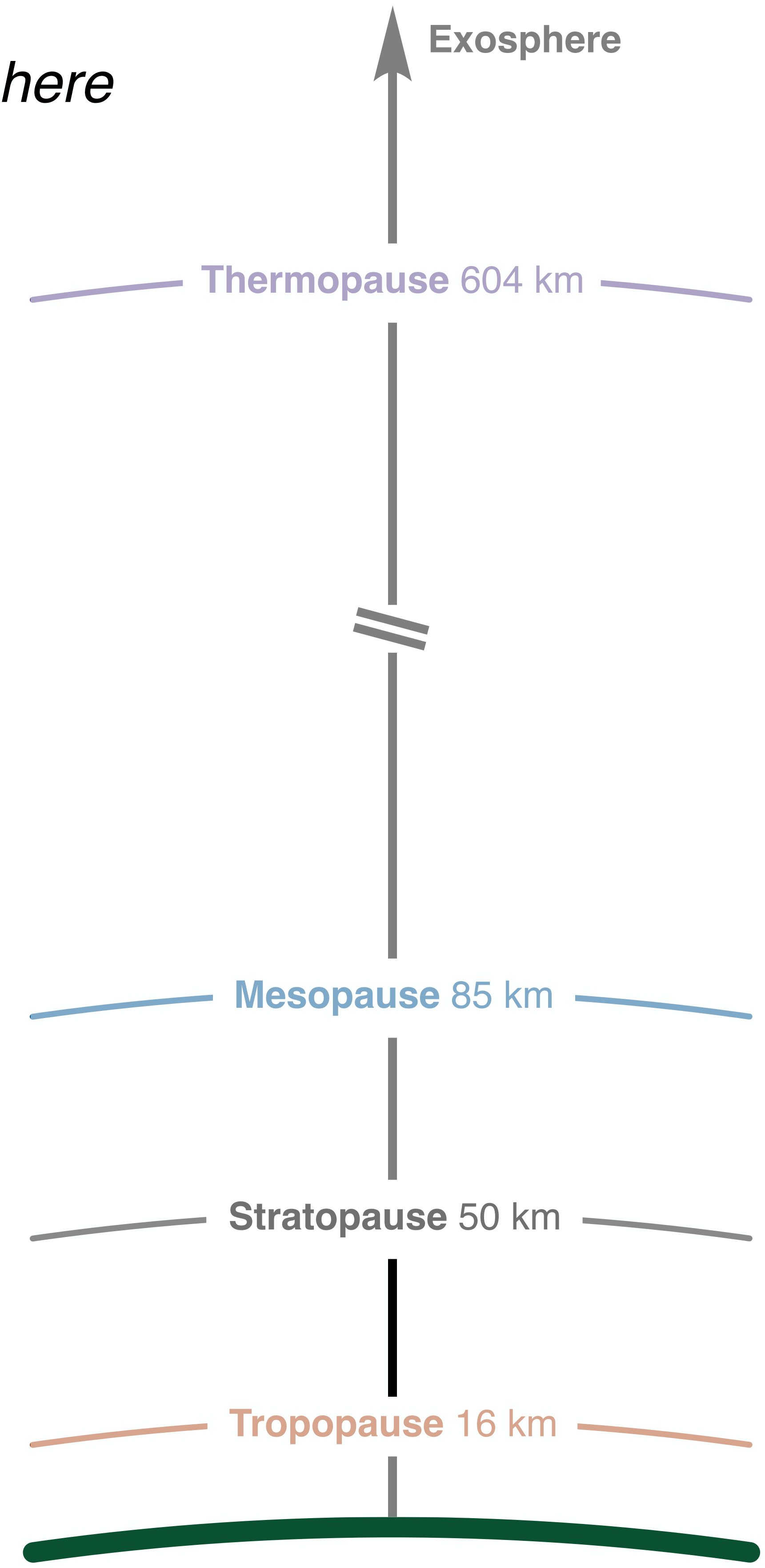
- location of weather and climate (including greenhouse effect and pollution)
- cools at a rate of 6.5 ºC km^{-1} (reaches minimum of –51 ºC)
- highly turbulent, well-mixed due to surface heating by Sun (convection)

Earth's Atmosphere: The Troposphere. Department of Physics, UC Santa Barabra. https://web.physics.ucsb.edu/~lgrace/chem123/troposphere.htm (accessed March 3, 2020).

The stratosphere - middle atmosphere

contains **remaining mass (25%)** and a 10 km wide **ozone layer**

- temperature increases with altitute (–3 °C at the stratopause)
- inverse temperature gradient prevents convection/mixing
- studied via weather balloons (air too thin for planes)

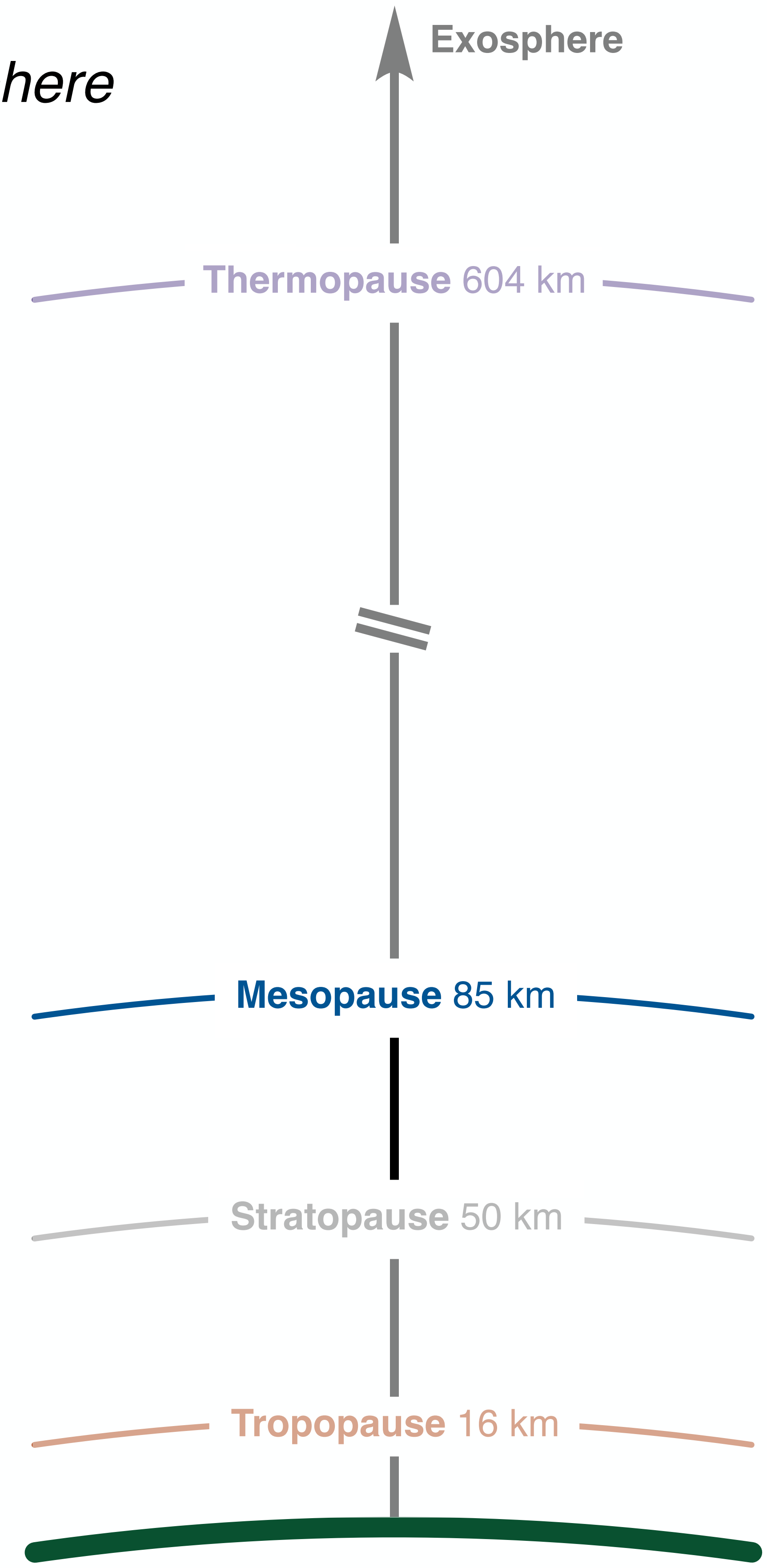


Atmosphere. *Encyclopædia Britannica* [Online]; Encyclopædia Britannica, Posted February 13, 2020. https://www.britannica.com/science/atmosphere/Stratosphere-and-mesosphere (accessed February 29, 2020).

The mesosphere - middle atmosphere

referred to as the **“ignorosphere”** because difficult to study

- too high for planes and balloons, too low for satellites
- probed with sounding rockets (5-20 minute missions)
- temperature decreases to atmospheric minimum (–143 °C)

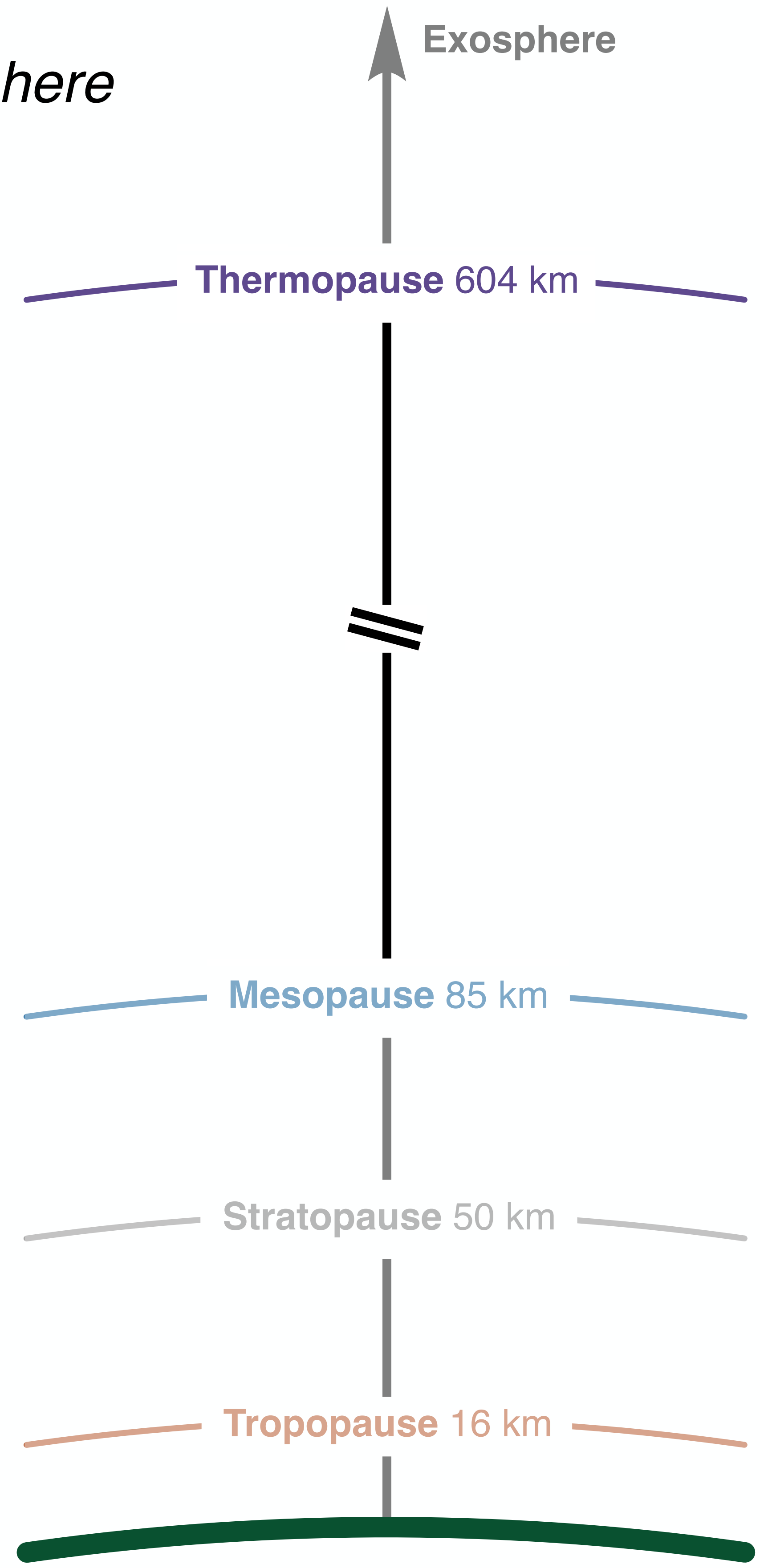


Atmosphere. *Encyclopædia Britannica* [Online]; Encyclopædia Britannica, Posted February 13, 2020. https://www.britannica.com/science/atmosphere/Stratosphere-and-mesosphere (accessed February 29, 2020).

The thermosphere - upper atmosphere

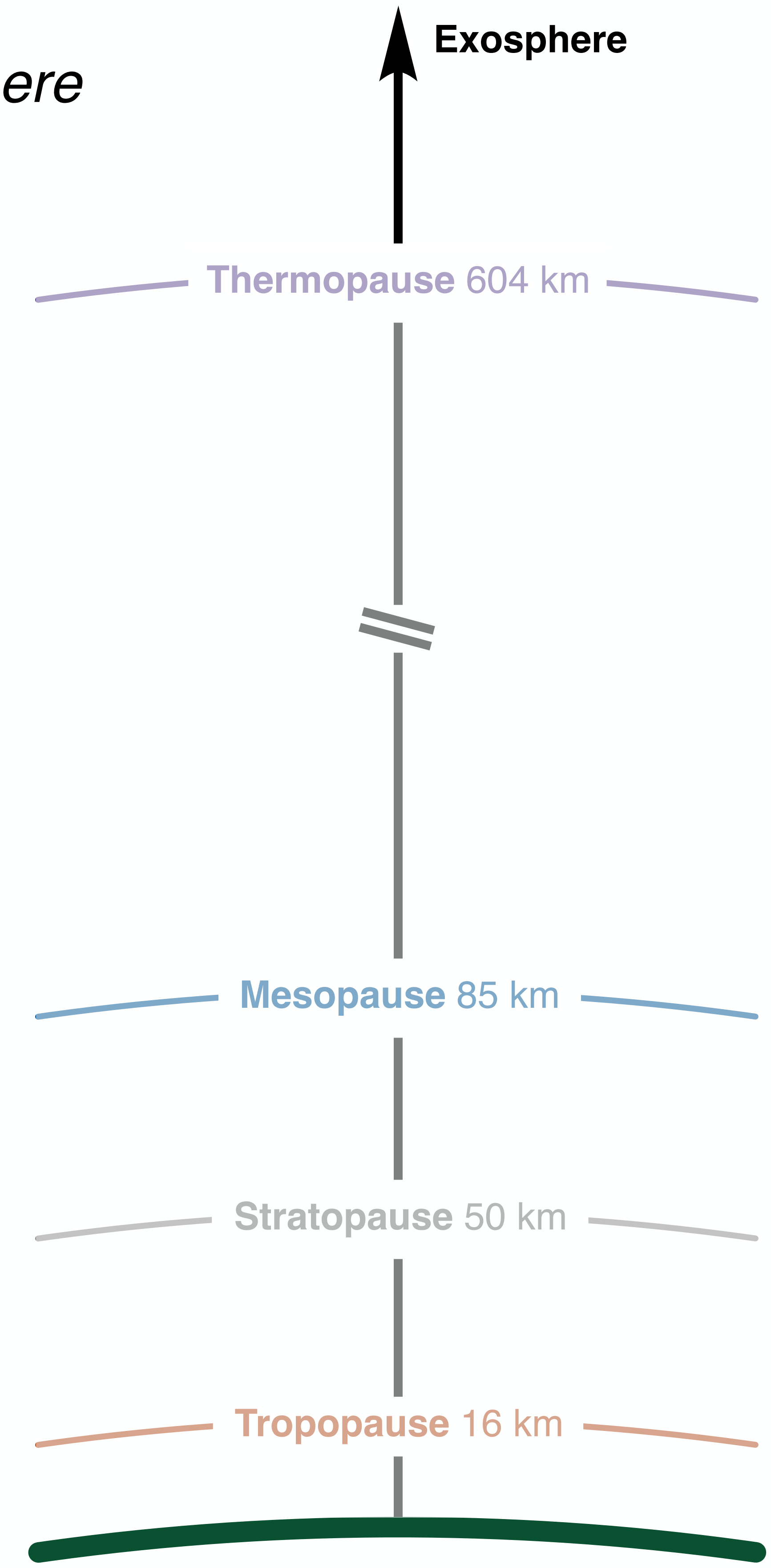
contains **0.002% of mass** and is the realm of **satellites**

- photoionization of N_2 and O_2 blocks UVC and x-rays from Sun
- temperature difficult to define (227–1725 °C depending on sun activity)
- anacoustic zone (no sound) starts at 160 km
- electrically charged, refracts radio waves over horizon



Atmosphere. *Encyclopædia Britannica* [Online]; Encyclopædia Britannica, Posted February 13, 2020. https://www.britannica.com/science/atmosphere/Stratosphere-and-mesosphere#ref261449 (accessed February 29, 2020).

The exosphere - upper atmosphere

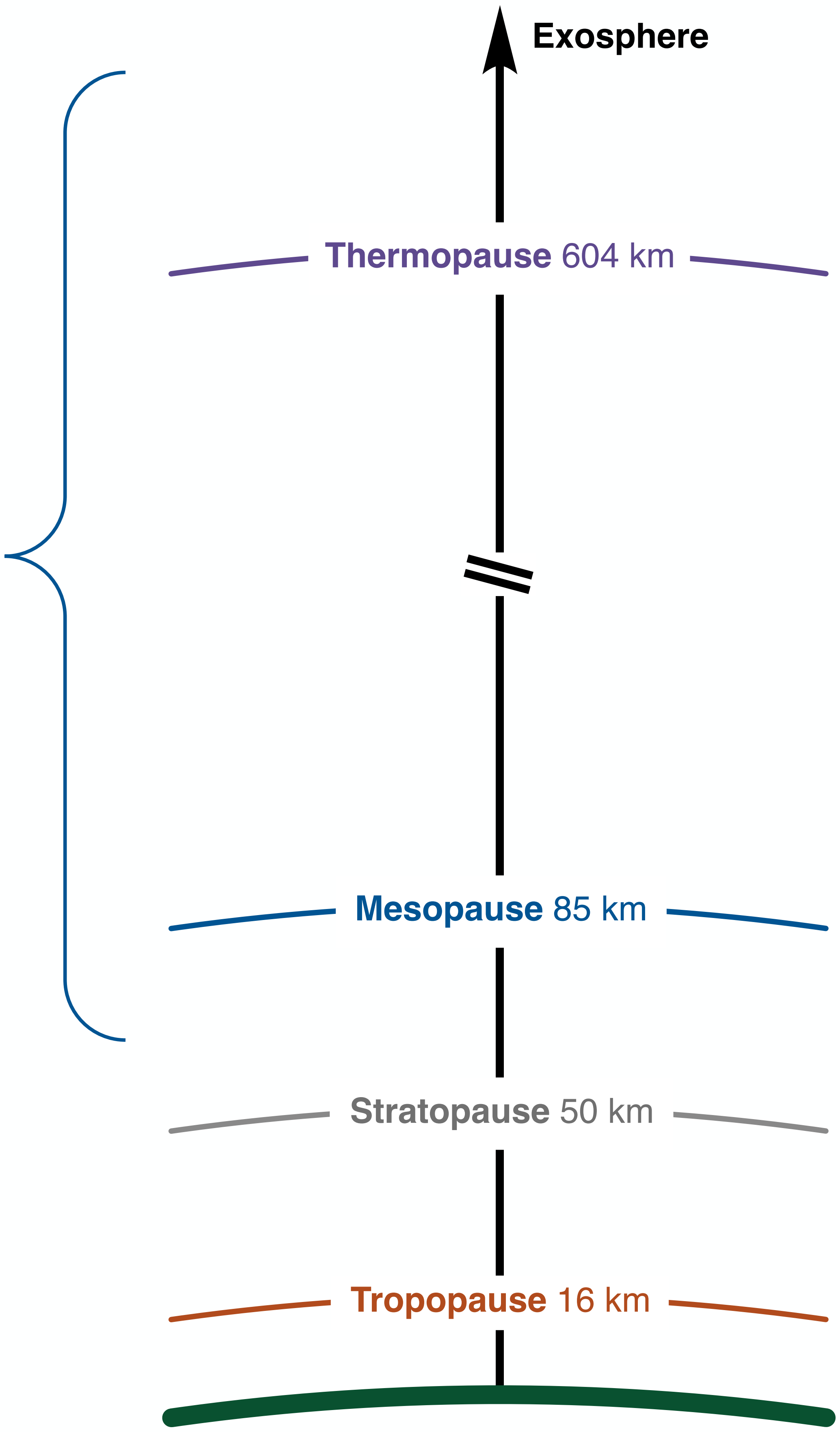


maintains **constant temperature** and composed mainly of **H, He, and O**

- atoms rarely collide, follow ballistic trajectories
- atoms can escape the atmosphere
- extends as far as Earth's gravitaitonal pull

Atmosphere. *Encyclopædia Britannica* [Online]; Encyclopædia Britannica, Posted February 13, 2020. https://www.britannica.com/science/atmosphere/Stratosphere-and-mesosphere#ref261450 (accessed February 29, 2020).

The ionosphere



Exosphere

Thermopause 604 km

Mesopause 85 km

Stratopause 50 km

Tropopause 16 km

region of atmosphere that contains charged species

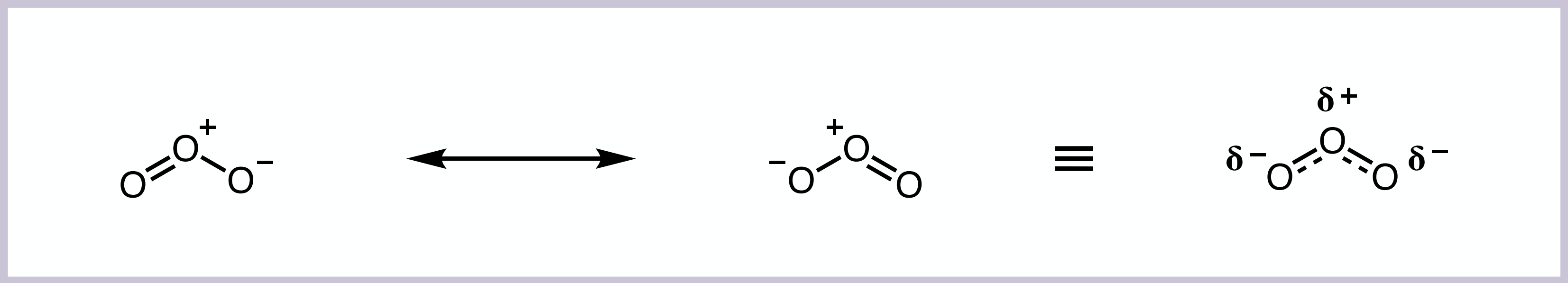
ionization of gas molecules by Sun’s radiation

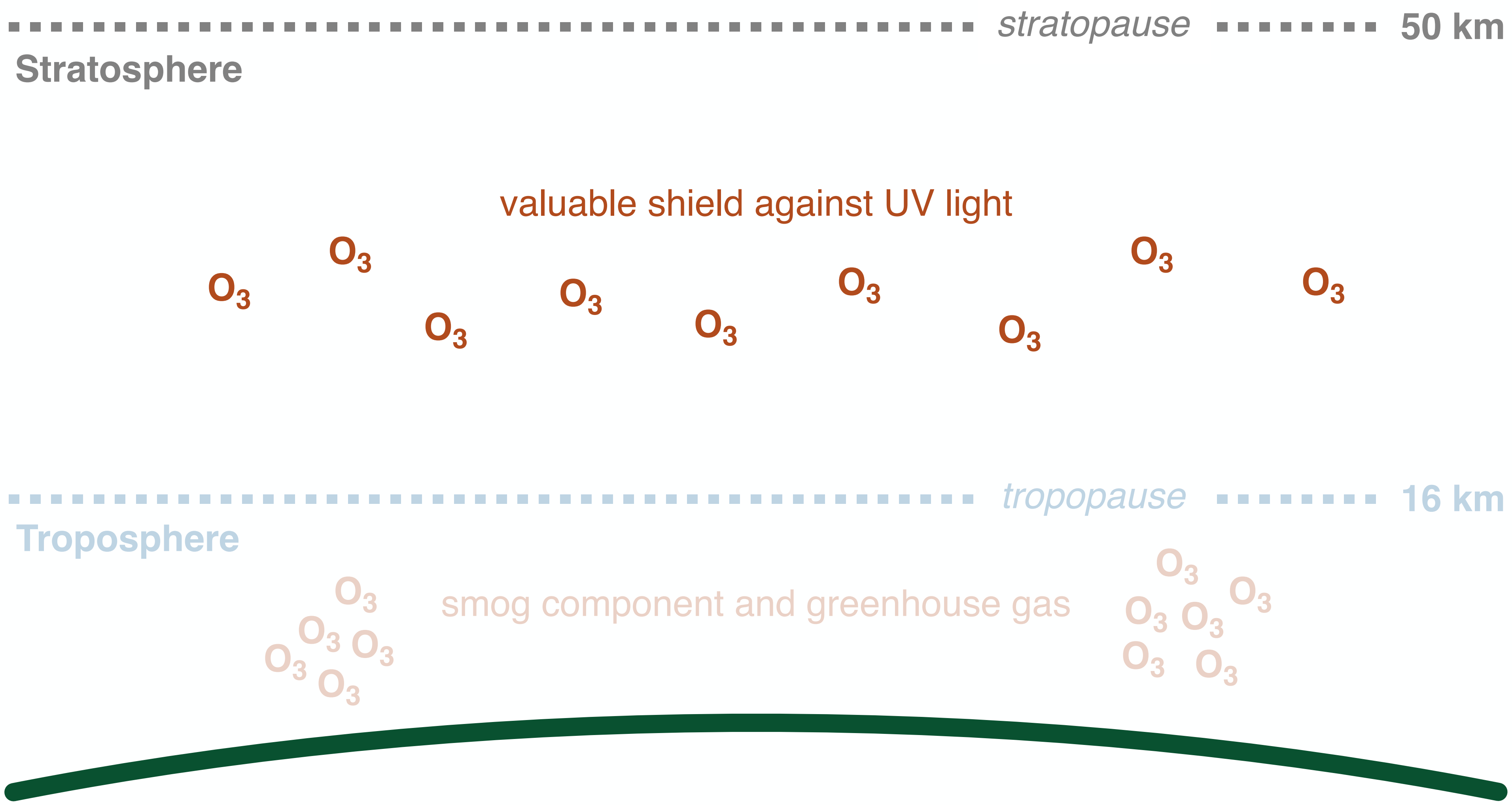
important filter of high energy light

This portion of the atmosphere goes to sleep at night!

Atmosphere. *Encyclopædia Britannica* [Online]; Encyclopædia Britannica, Posted February 13, 2020. https://www.britannica.com/science/atmosphere/Stratosphere-and-mesosphere#ref261450 (accessed February 29, 2020).

Ozone: good up high but bad nearby





stratopause 50 km

Stratosphere

valuable shield against UV light

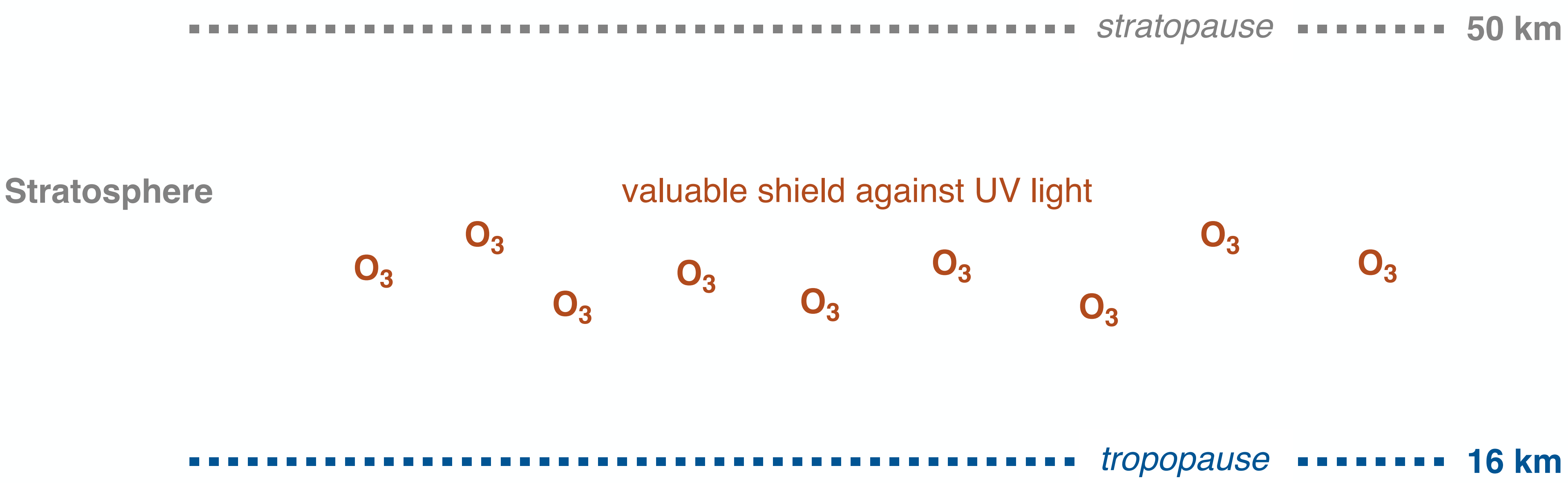
tropopause 16 km

Troposphere

smog component and greenhouse gas

Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Washington, DC, **2009**; 7-15.

The stratospheric ozone layer



stratopause **50 km**

Stratosphere

valuable shield against UV light

O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3

tropopause **16 km**

- Sits in a band 25 to 35 km above the Earth’s surface
- Existed for approximately 700 million years

What are the mechanisms regulating the ozone layer?

Baulch, D. L., *et al. J. Phys. Chem. Ref. Data* **1982**, *11*, 327.

The Chapman mechanism for creation and destruction of ozone

- The Chapman mechanism (1930) was the first *atmospheric cycle* discovered

ozone creation

$$O_2 \xrightarrow{h\nu} O + O \qquad h\nu \leq 242\text{ nm}$$

$$O_2 + O + M \longrightarrow O_3 + M \qquad \textbf{What is M?}$$

ozone destruction

$$O_3 \xrightarrow{h\nu} O_2 + O \qquad h\nu \leq 336\text{ nm}$$

$$O_3 + O \longrightarrow O_2 + O_2$$

Chapman, S. *Mem. Roy. Met. Soc.* **1930**, *3*, 103.
Chapman, S. *Phil. Mag.* **1930**, *10*, 369.
Velasco, R. M.; Uribe, E. J.; Pérez-Chavela, E. *J. Math. Chem.* **2008**, *44*, 529.

Three-body reactions in the gas phase


A **B** $\xrightarrow{\text{collision 1}}$ **AB*** **M** $\xrightarrow{\text{collision 2}}$ **AB** **M***

can fragment

rovibrationally excited

[**M**] dependence

stable product

where **M** = inert molecule (N_2 in atmosphere, Ar in laboratory/computations)

M* *dissipates excess energy as heat*

- Impact of third body on gas phase reaction rate

$$\bullet CH_3 + O_2 \rightleftharpoons CH_3O_2^*$$

$$CH_3O_2^* + M \longrightarrow CH_3O_2 + M^*$$

M = neopentane

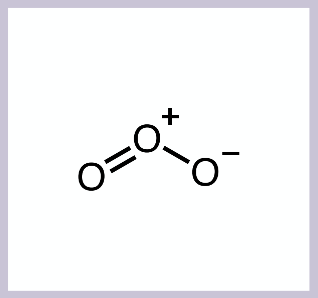
$k_{overall} = 3.6 \times 10^{11}\ M^{-2}\ s^{-1}$

M = N_2

$k_{overall} = 0.94 \times 10^{11}\ M^{-2}\ s^{-1}$

Jacob, D. J. Chemical Kinetics. In *Introduction to Atmospheric Chemsitry*; Princeton University Press: Princeton, **1999**, 155-161.
Basco, N.; James, G. L.; James, F. C. *Int. J. Chem. Kinetics* **1972**, *4*, 129.

The “ozone isotopic anomaly”



$$^{16}O^{16}O^{16}O \quad \underbrace{^{16}O^{16}O^{17}O \quad ^{16}O^{16}O^{18}O \quad \text{etc.}}_{\text{heavy ozone}}$$

Natural Abundance	
99.76%	^{16}O
0.038%	^{17}O
0.205%	^{18}O

Two surprising observations (over a contentious, high impact 18 years):

- 10% heavy ozone observed in the troposphere/stratosphere
- equal ^{17}O and ^{18}O incorporation: **mass-independent fractionation**

Mauersberger *Geophys. Res. Lett.* **1981**, *8*, 935.

Thiemens *Science* **1983**, *219*, 1073.

Mauersberger *Geophys. Res. Lett.* **1987**, *14*, 80.

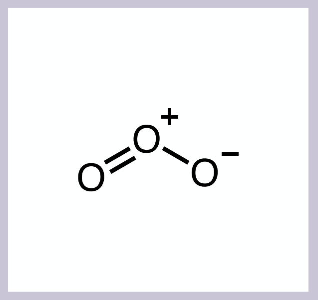
Thiemens *Science* **1999**, *283*, 341.

Mauersberger *Science* **1999**, *283*, 370.

Why are heavy O isotopes overrepresented in atmospheric ozone molecules?

Sur, S.; Quintas-Sánchez, E.; Ndengué, S. A.; Dawes, R. *Phys. Chem. Chem. Phys.* **2019**, *21*, 9168.
Sur, S.; Ndengué, S. A.; Quintas-Sánchez, E.; Bop, C.; Lique, F.; Dawes, R. *Phys. Chem. Chem. Phys.* **2020**, *22*, 1869.

The "ozone isotopic anomaly"



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Natural Abundance

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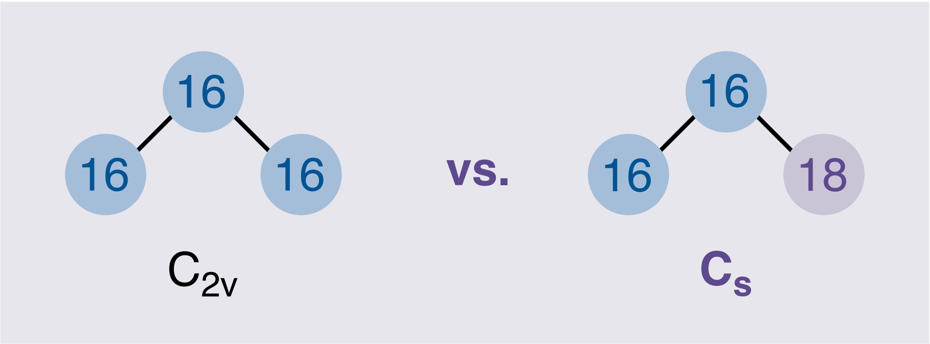
collisional cooling is key isotopic selectivity step:

$$O_3^* + M \xrightarrow{k_{cool}} O_3 + M^*$$



*Breaking C_{2v} symmetry doubles **allowed rovibrational states***

*and **increases probability** of successful collisional cooling with* **M**

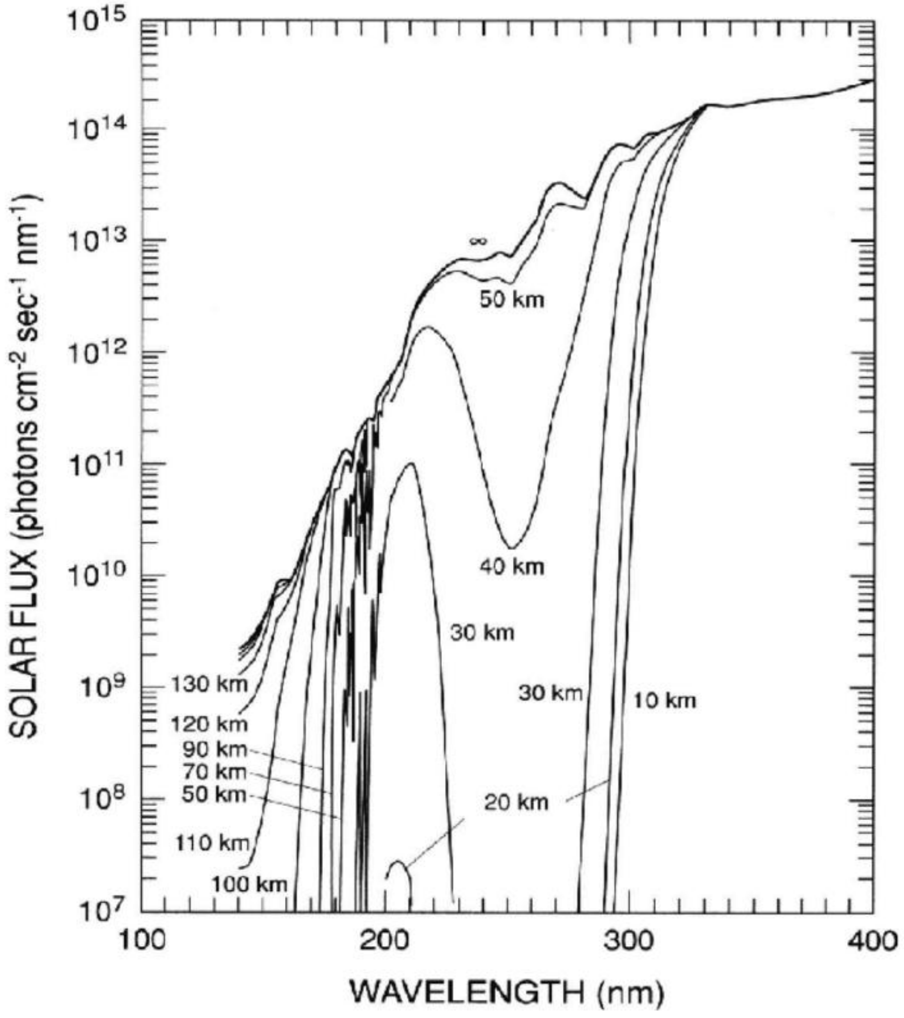
Sur, S.; Ndengué, S. A.; Quintas-Sánchez, E.; Bop, C.; Lique, F.; Dawes, R. *Phys. Chem. Chem. Phys.* **2020**, *22*, 1869.
Quack, M. *Mol. Phys.* **1977**, *34*, 477. (includes specific discussion of the ozone case)

Benefits of stratospheric ozone

Chapman cycle components (O_2 and O_3) absorb UV light

- Allows for life outside of oceans
- Prevents photoinduced DNA damage

UV**A** **315**-400 nm	*not absorbed by O_3 layer*
UV**B** **280**-315 nm	*mostly absorbed by O_3 layer*
UV**C** **100**-280 nm	*entirely absorbed by atmosphere*



Hart, M. H. *Icarus* **1978**, *33*, 23.

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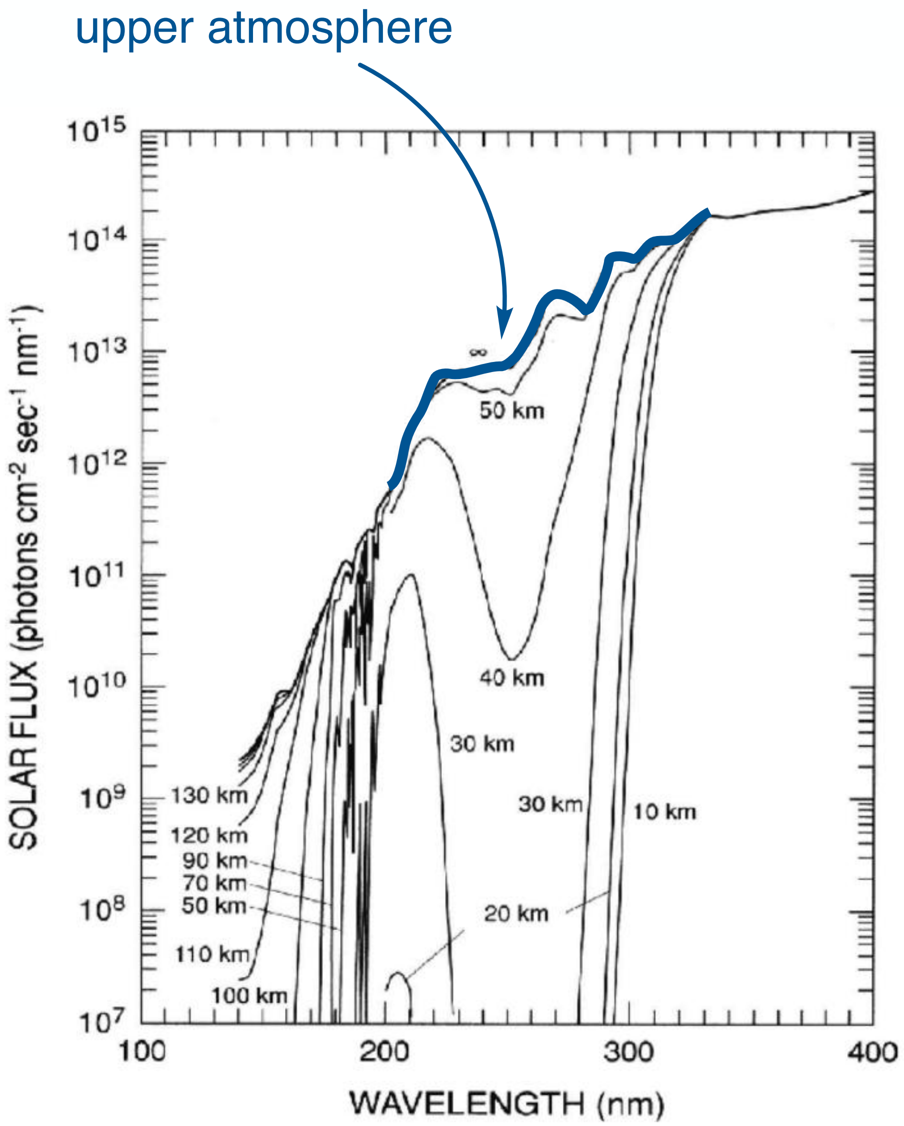
upper atmosphere

Hart, M. H. *Icarus* **1978**, *33*, 23.

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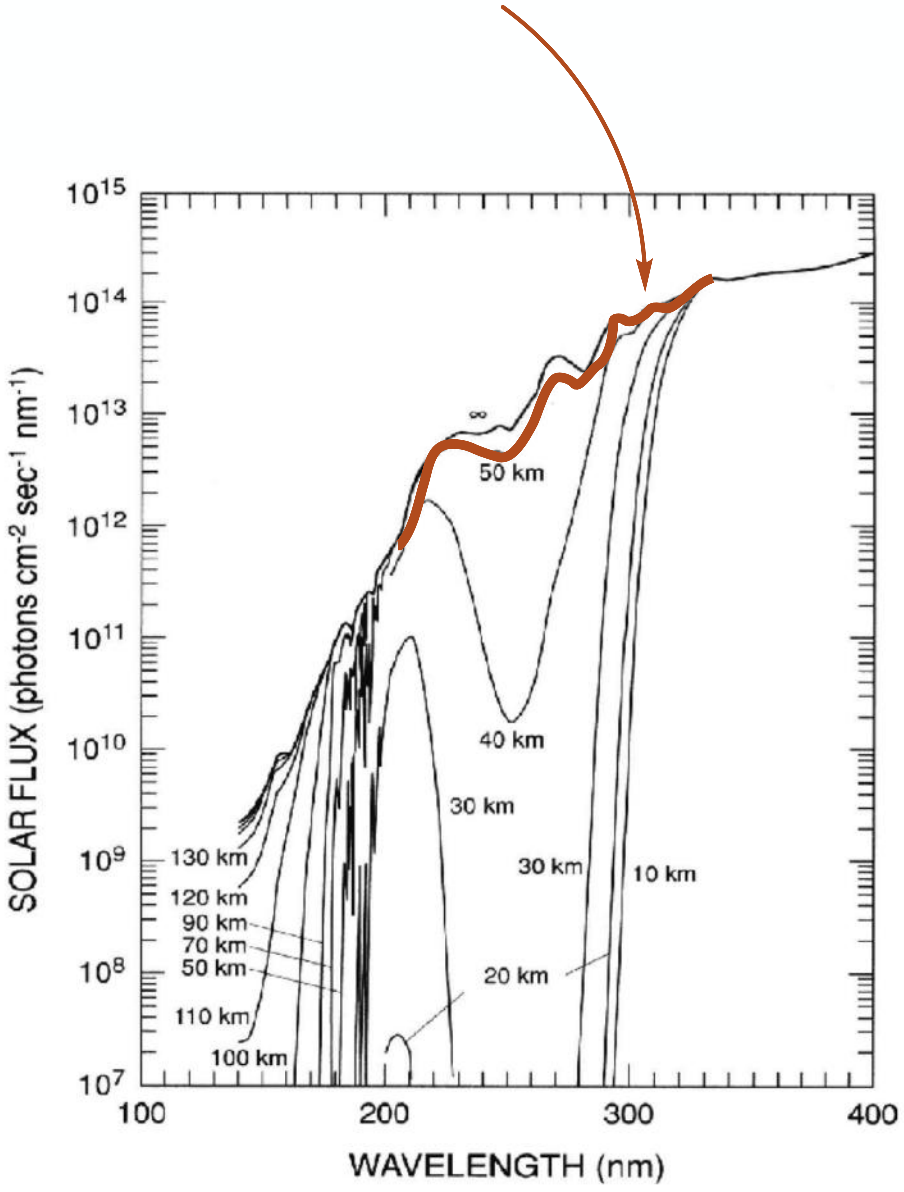
top of stratosphere

Hart, M. H. *Icarus* **1978**, *33*, 23.

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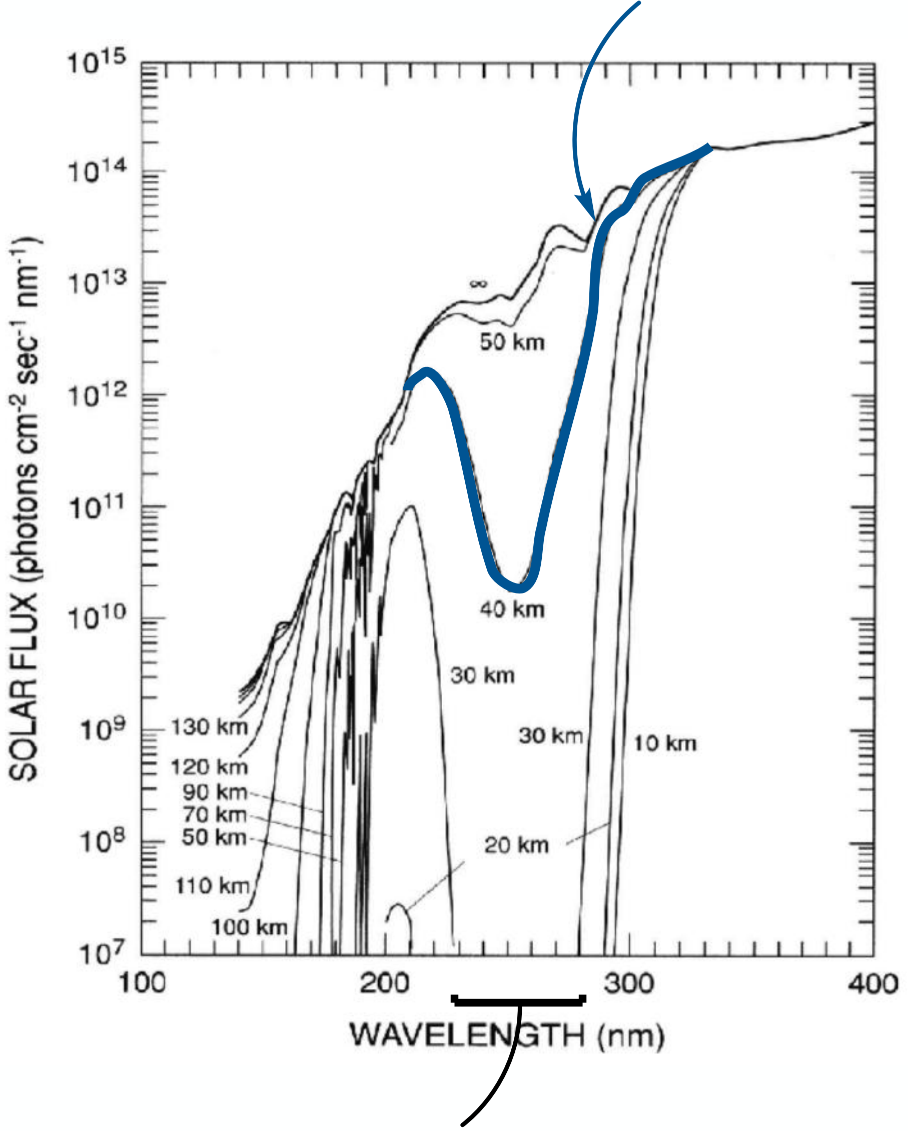

top of ozone layer

O_2 absorbance

Hart, M. H. *Icarus* **1978**, *33*, 23.

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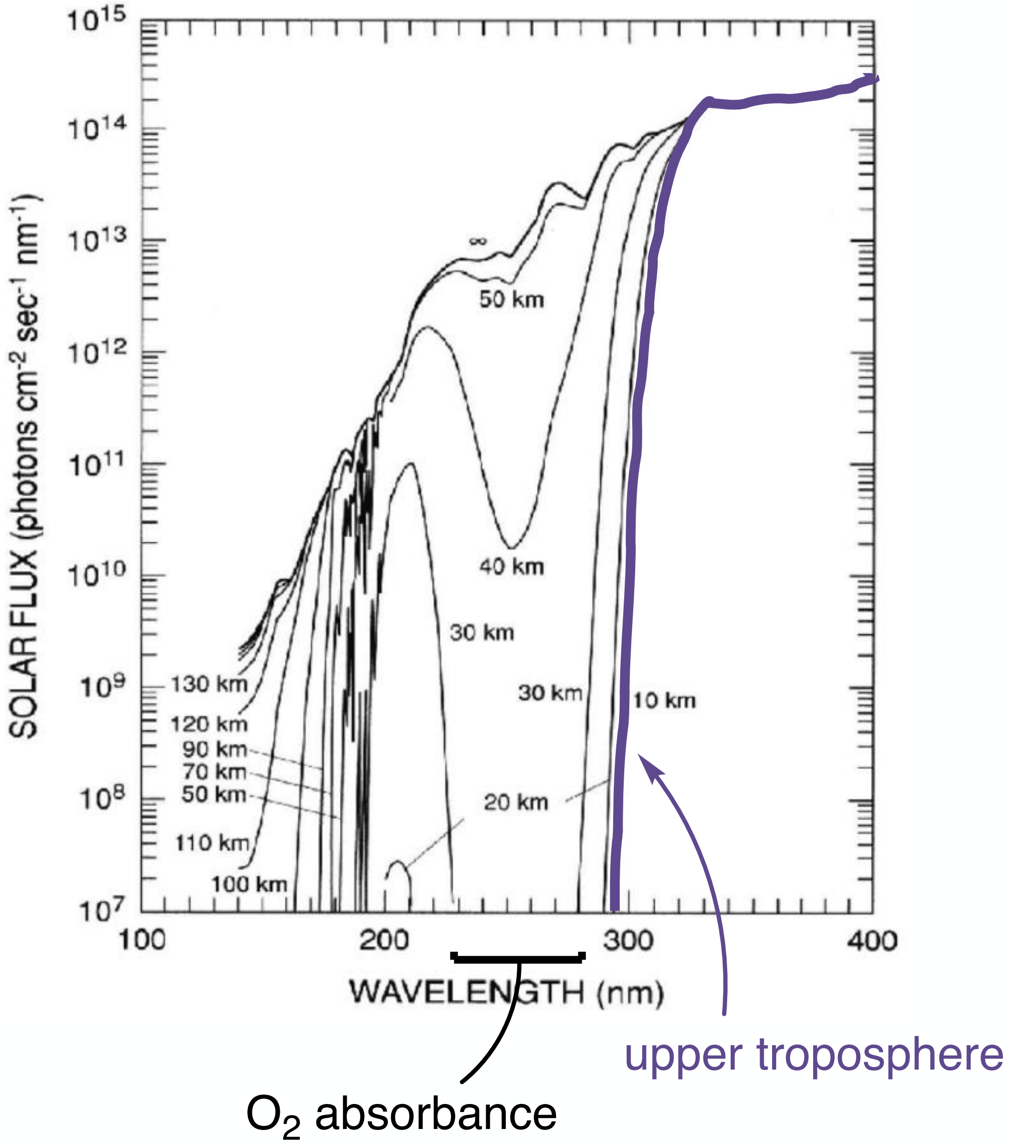

upper troposphere

O_2 absorbance

Hart, M. H. *Icarus* **1978**, *33*, 23.

Benefits of stratospheric ozone

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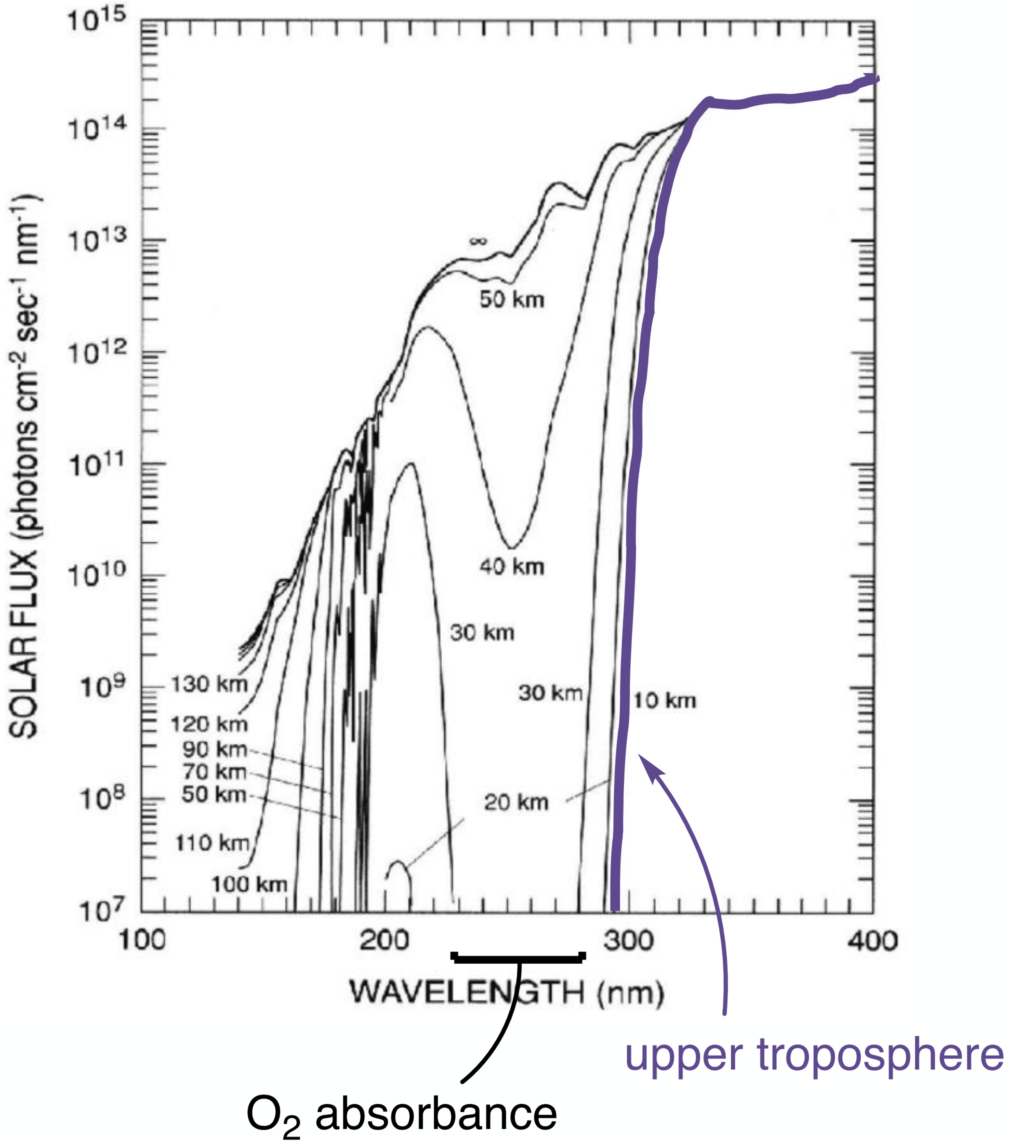
How did Earth develop an atmosphere with such a useful UV light filter?



upper troposphere

O_2 absorbance

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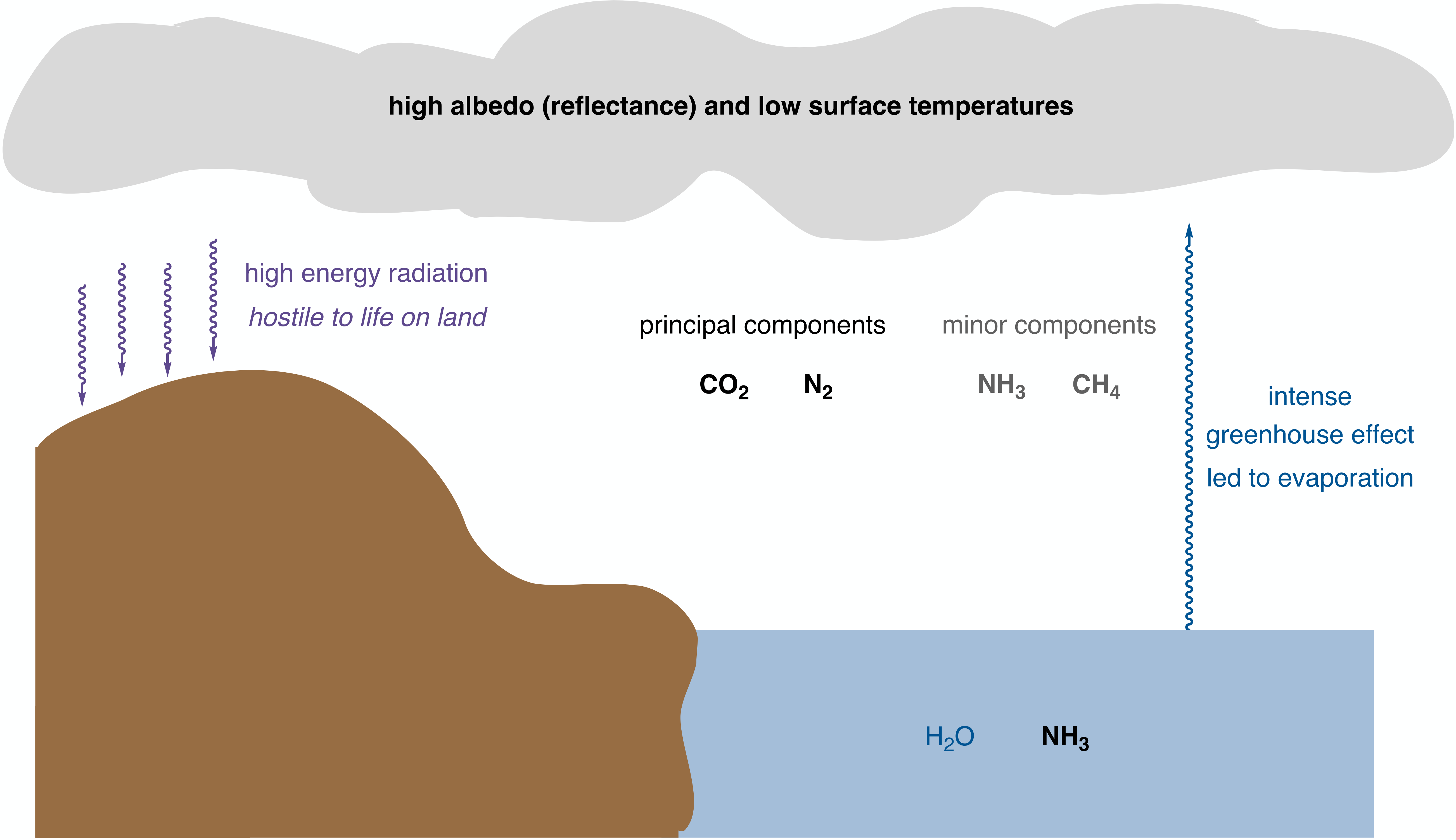
The evolution of Earth's atmosphere

4.5 billion years ago



high albedo (reflectance) and low surface temperatures

high energy radiation

hostile to life on land

principal components

CO_2 **N_2**

minor components

NH_3 **CH_4**

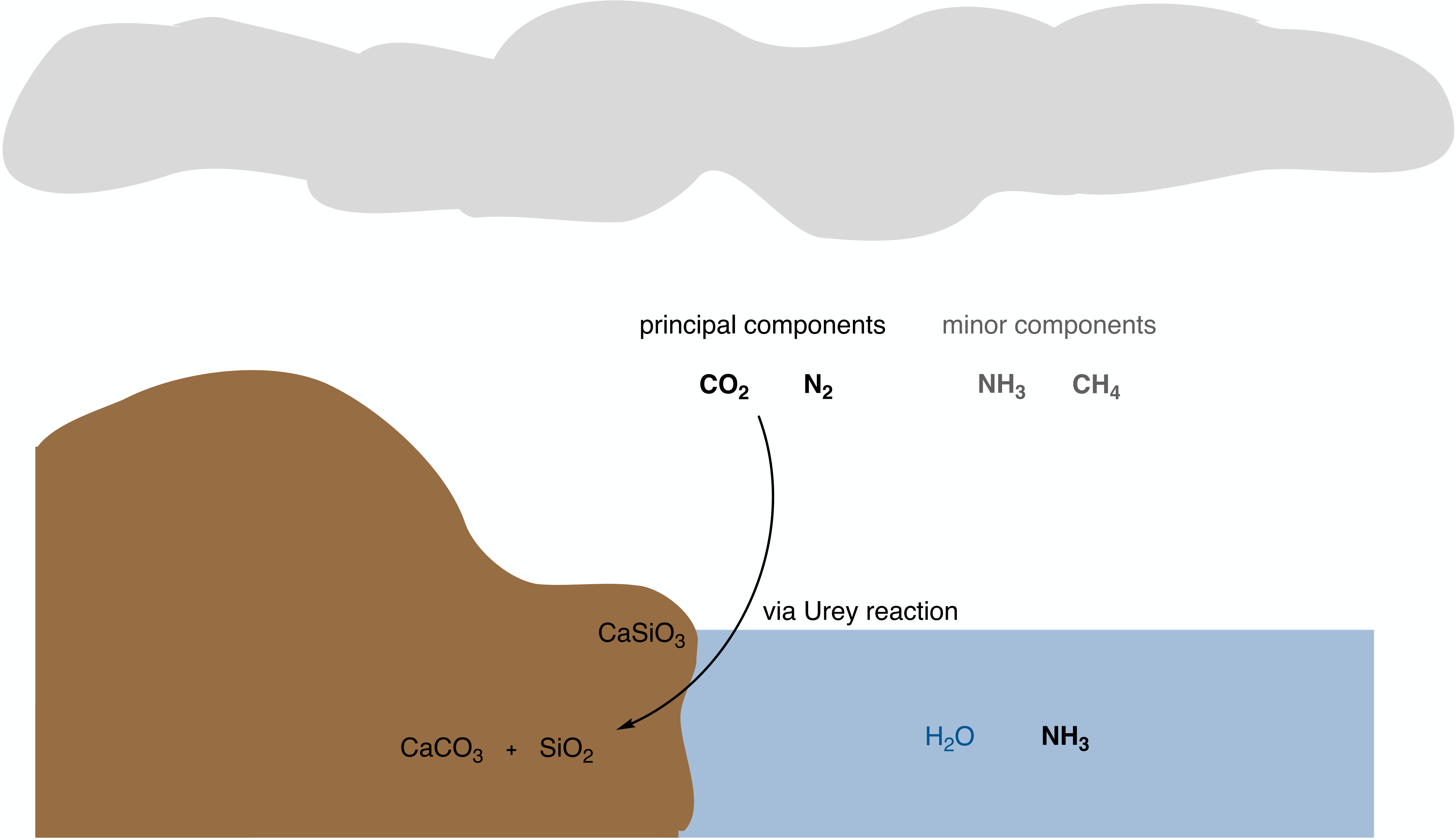
intense greenhouse effect led to evaporation

H_2O **NH_3**

Hart, M. H. *Icarus* **1978**, *33*, 23.

The evolution of Earth's atmosphere

4.5 billion years ago



principal components

CO_2 **N_2**

minor components

NH_3 **CH_4**

via Urey reaction

$CaSiO_3$

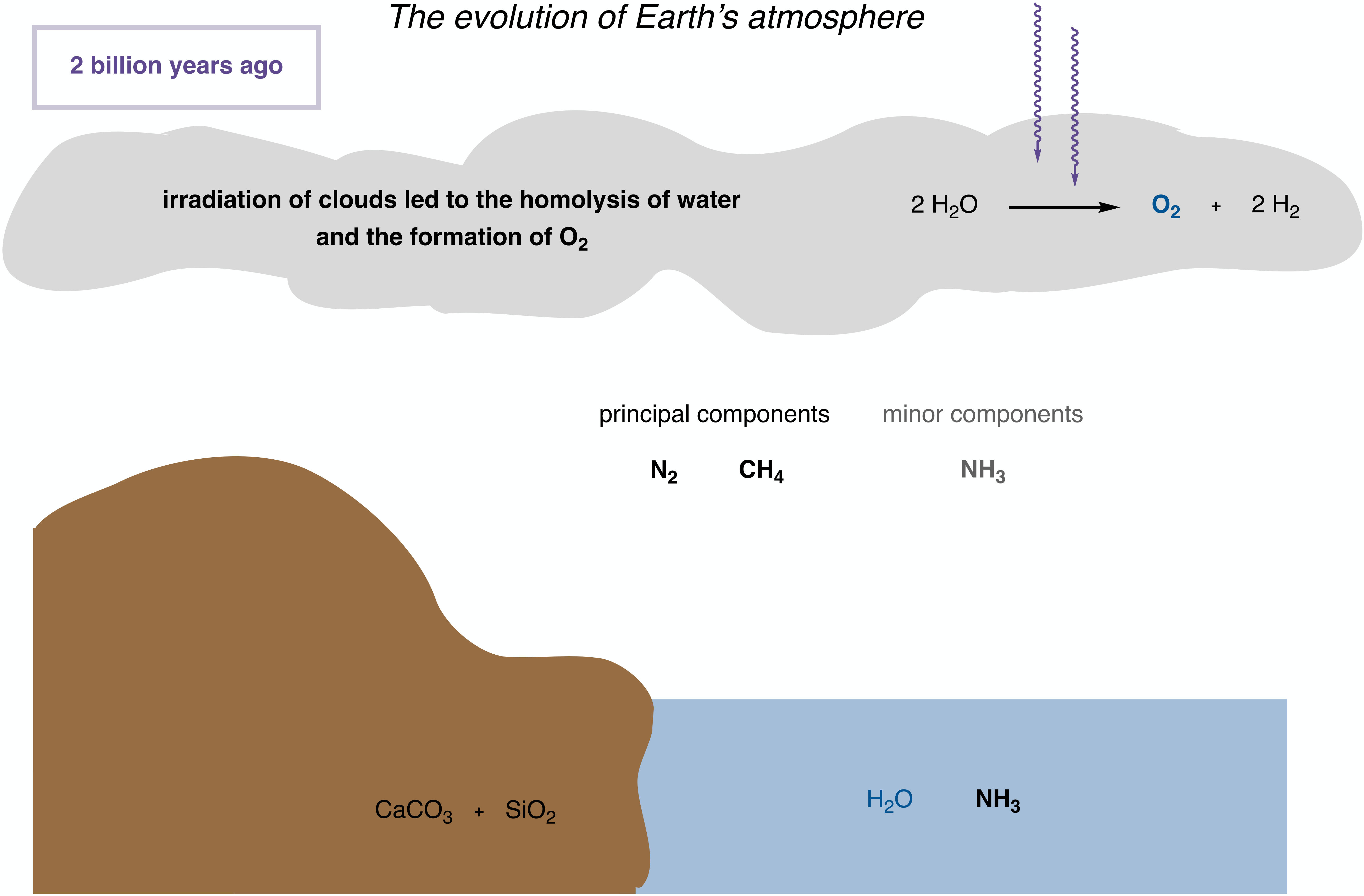
$CaCO_3$ + SiO_2

H_2O **NH_3**

Hart, M. H. *Icarus* **1978**, *33*, 23.

The evolution of Earth’s atmosphere

2 billion years ago



irradiation of clouds led to the homolysis of water and the formation of O_2

$$2\ H_2O \longrightarrow O_2 + 2\ H_2$$

principal components

N_2 **CH_4**

minor components

NH_3

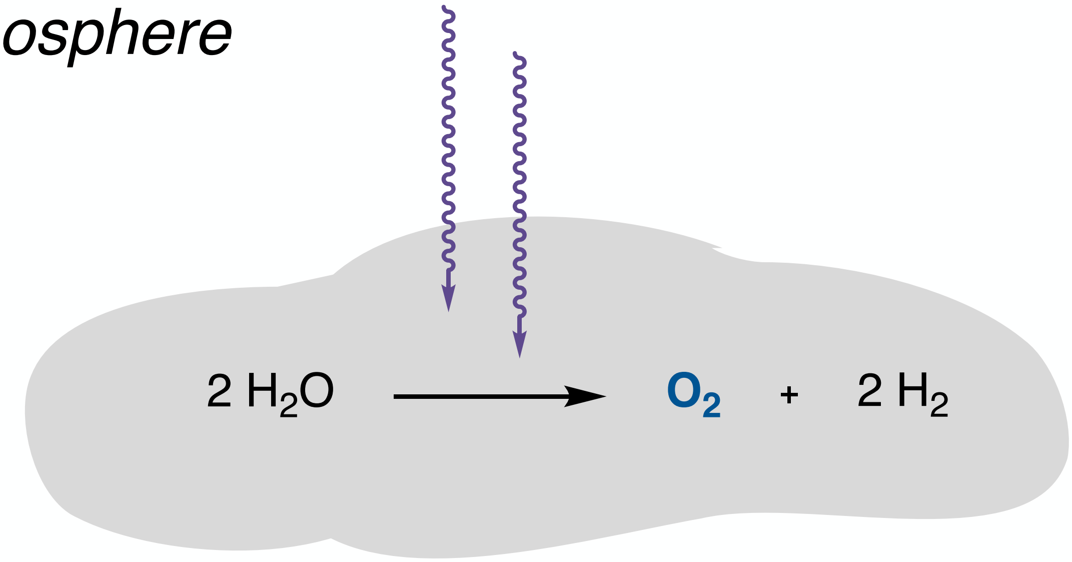
$CaCO_3$ + SiO_2

H_2O **NH_3**

Hart, M. H. *Icarus* **1978**, *33*, 23.

The evolution of Earth's atmosphere

2 billion years ago


$2\,H_2O \longrightarrow O_2 + 2\,H_2$

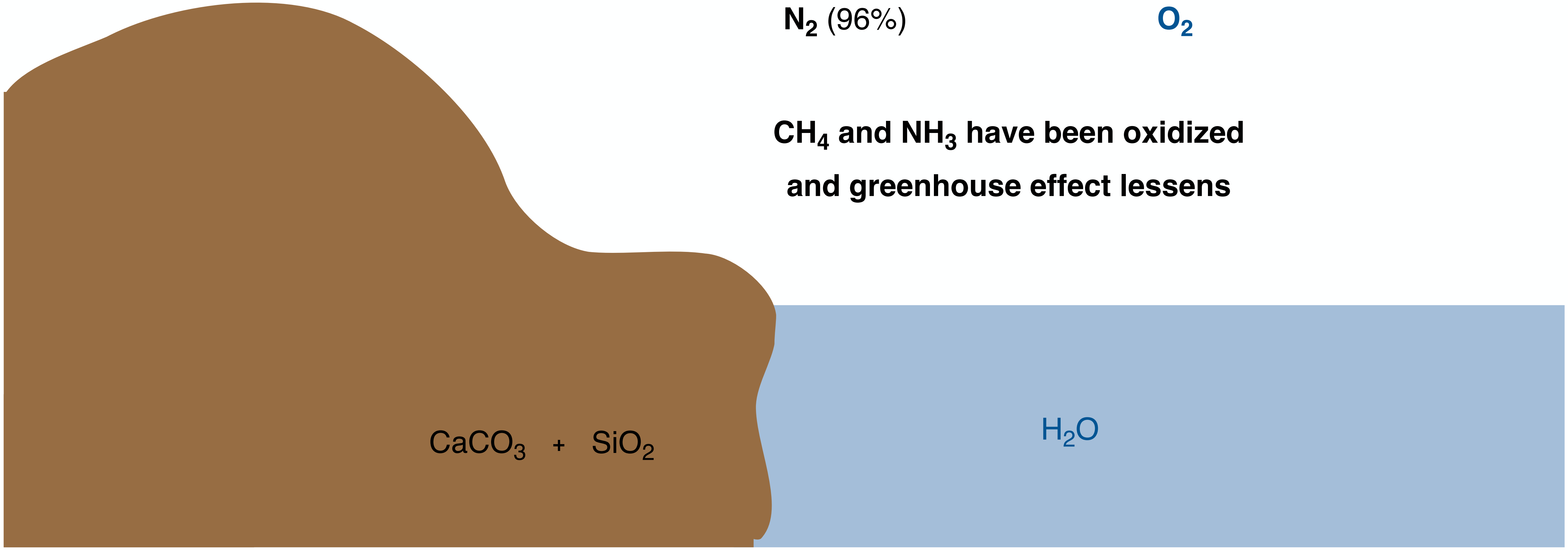
principal components

minor components

N_2 (96%)

O_2

CH_4 and NH_3 have been oxidized and greenhouse effect lessens


$CaCO_3 + SiO_2$

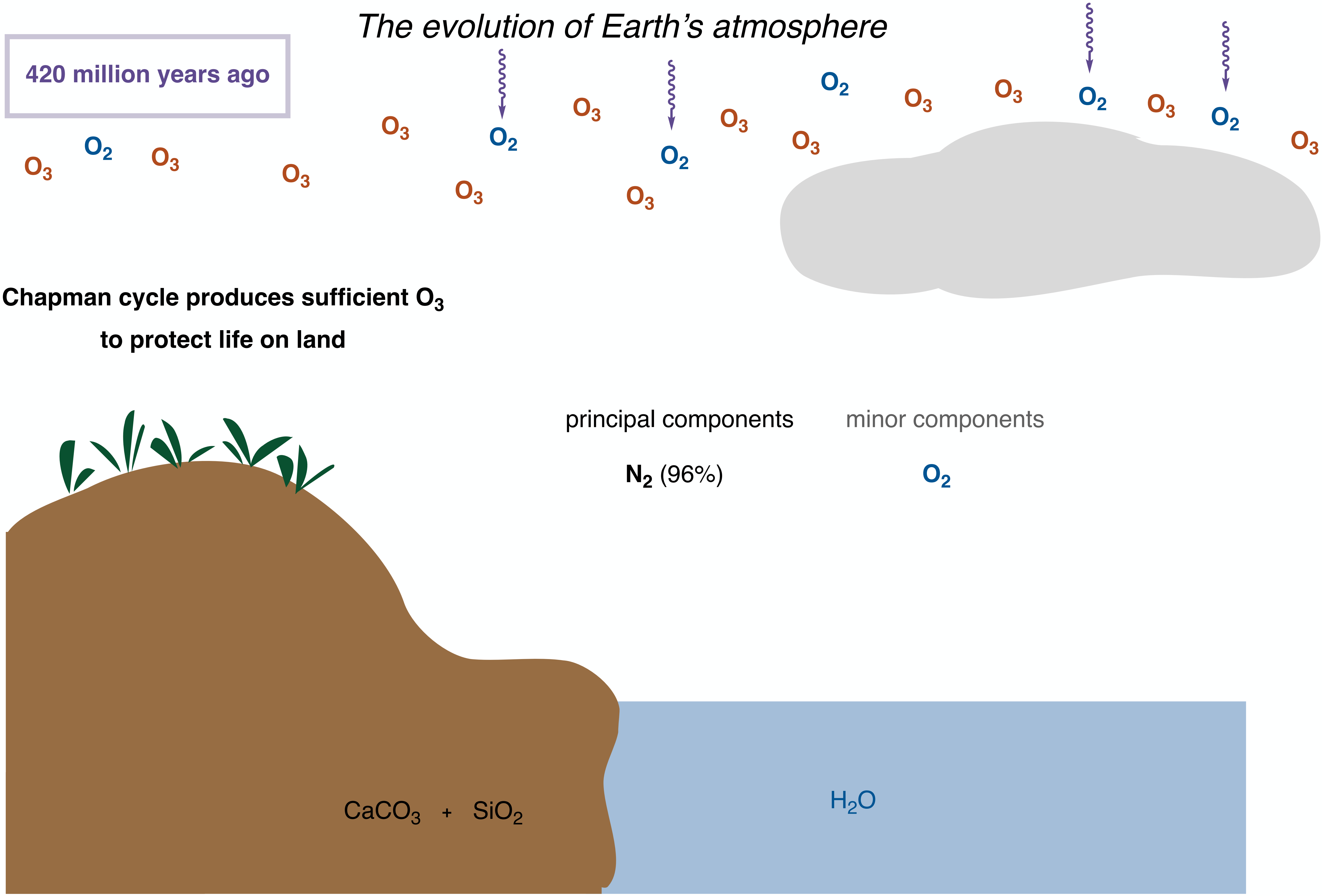
H_2O

Hart, M. H. *Icarus* **1978**, *33*, 23.

The evolution of Earth's atmosphere

420 million years ago

Chapman cycle produces sufficient O_3 to protect life on land



principal components	minor components
N_2 (96%)	O_2

Hart, M. H. *Icarus* **1978**, *33*, 23.

Why is the ozone layer in the stratosphere?

Mesosphere

insufficient gas density for three body reactions

stratopause **50 km**

Stratosphere

correct balance of light penetration and gas density

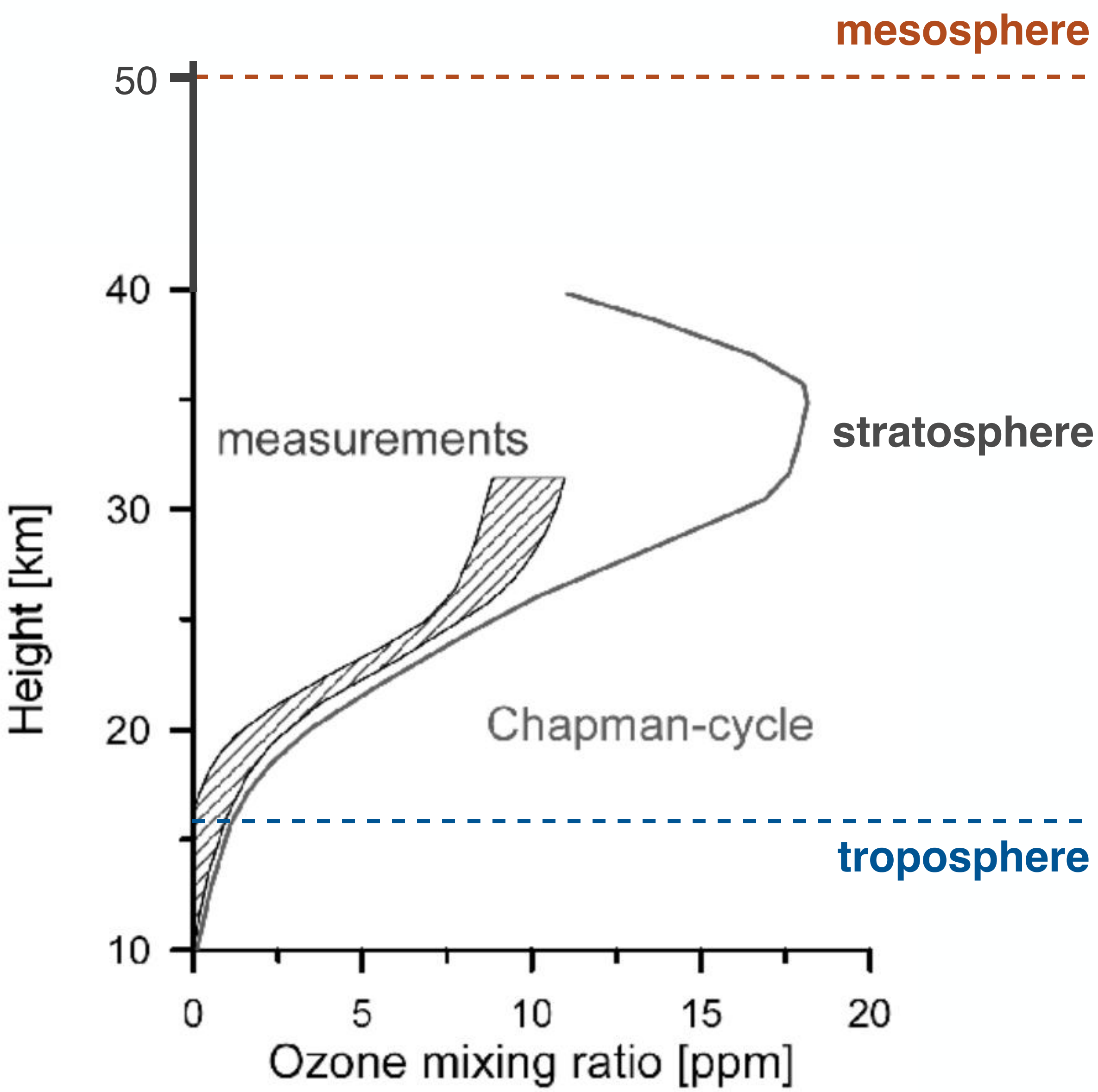
tropopause **16 km**

Troposphere

minimal light penetration at required λ

Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Washington, DC, **2009**, 7-15.

The Chapman mechanism overestimates ozone concentrations



There must be additional mechanisms of ozone destruction

Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Washington, DC, **2009**, 7-15.

Mechanism of stratospheric ozone depletion

- Chapman cycle balances ozone *creation* with ozone *destruction*

$$O_3 \xrightarrow{h\nu} O_2 + O \qquad h\nu \leq 336 \text{ nm}$$

$$O_3 + O \longrightarrow O_2 + O_2$$

What if this step were catalyzed?

General mechanism of catalytic ozone destruction

$$\begin{array}{l} \quad O_3 + Z \longrightarrow ZO + O_2 \\ +\quad ZO + O \longrightarrow Z + O_2 \\ \hline \quad O_3 + O \longrightarrow O_2 + O_2 \end{array}$$

catalysts (**Z**)

HO_x

NO_x

ClO_x

Sur, S.; Quintas-Sánchez, E.; Ndengué, S. A.; Dawes, R. *Phys. Chem. Chem. Phys.* **2019**, *21*, 9168.
Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Weshington, DC, **2009**, 7-15.

The HO_x cycle

- In the HO_x cycle, the OH radical serves as a catalyst

$$\begin{array}{l} \quad O_3 + OH \longrightarrow HO_2 + O_2 \\ \quad HO_2 + O \longrightarrow OH + O_2 \\ + \\ \hline \quad O_3 + O \longrightarrow O_2 + O_2 \end{array}$$

*Major source of OH in the stratosphere is reaction of **atomic oxygen** and **water vapor***

$$O + H_2O \longrightarrow OH + OH$$

*with minor contributions from **hydrogen** and **methane***

$$O + H_2 \longrightarrow OH + H$$

$$O + CH_4 \longrightarrow OH + CH_3$$

Bates, D. R.; Nicolet, M. *J. Geophys. Res.* **1950**, *55*, 301.
Wofsy, S. C.; McElroy, M. B. *Can. J. Chem.* **1974**, *52*, 1582.

The NO_x cycle

- In the NO_x cycle, the NO radical serves as a catalyst

$$\begin{array}{lcccccc} & O_3 & + & NO & \longrightarrow & NO_2 + O_2 \\ + & NO_2 & + & O & \longrightarrow & NO + O_2 \\ \hline & O_3 & + & O & \longrightarrow & O_2 + O_2 \end{array}$$

sources of NO

in upper atmosphere $\quad O_2 + N_2 + h\nu \ (< 220\ \text{nm}) \longrightarrow NO + NO$

in stratopsphere $\quad NO_2$ (fertilizers) $+ h\nu \ (< 398\ \text{nm}) \longrightarrow NO + O$

Crutzen, P. J. *Quart. J. R. Met. Soc.* **1970**, *96*, 320.
Crutzen, P. J. *J. Geophys. Res.* **1971**, *76*, 7311.

The HO_x and NO_x cycles are dependent

interplay of HO_x and NO_x cycles

$$HO_2 + NO + M \longrightarrow \boxed{HNO_3} + M$$

reservoir

mechanism of reactivation:

$$\boxed{HNO_3} + h\nu\ (< 546\ \mathrm{nm}) \longrightarrow OH + NO_2$$

$$NO_2 + h\nu\ (< 398\ \mathrm{nm}) \longrightarrow NO + O$$

anthropogenic HNO_3 also adds to the concentration of HO_x and NO_x catalysts

Crutzen, P. J. *Quart. J. R. Met. Soc.* **1970**, *96*, 320.
Crutzen, P. J. *J. Geophys. Res.* **1971**, *76*, 7311.

The ClO_x cycle

- In the ClO_x cycle, the Cl radical is the catalyst

$$O_3 + Cl \longrightarrow ClO + O_2$$

$$+\quad ClO + O \longrightarrow Cl + O_2$$

$$\overline{O_3 + O \longrightarrow O_2 + O_2}$$

10x faster than
NO_x cycle

1 Cl atom can
destroy 100,000 O_3

- Generation of odd Cl from Cl_2 and HCl

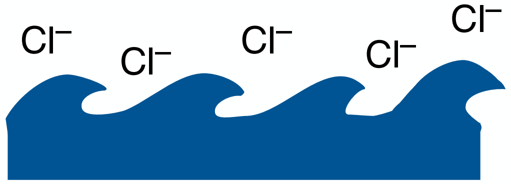
$$Cl_2 + h\nu \longrightarrow Cl + Cl$$

$$HCl + OH \longrightarrow Cl + H_2O$$

Stolarski, R. S.; Cicerone, R. J. *Can. J. Chem.* **1974**, *52*, 1610.
Wofsy, S. C.; McElroy, M. B. *Can. J. Chem.* **1974**, *52*, 1582.
Chlorofluorocarbons (CFCs). Earth System Research Laboratory. NOAA. http://www.esrl.noaa.gov/gmd/hats/publictn/elkins/cfcs.html

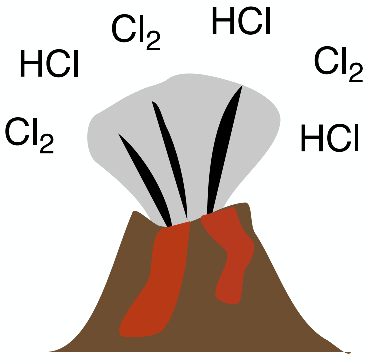
Sources of Cl

natural sources of atmospheric Cl



2×10^8 tons/yr

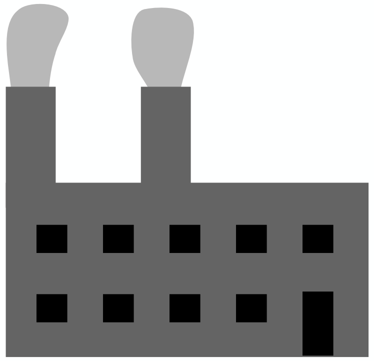
oceans



9×10^6 tons/yr

volcanoes

anthropogenic sources

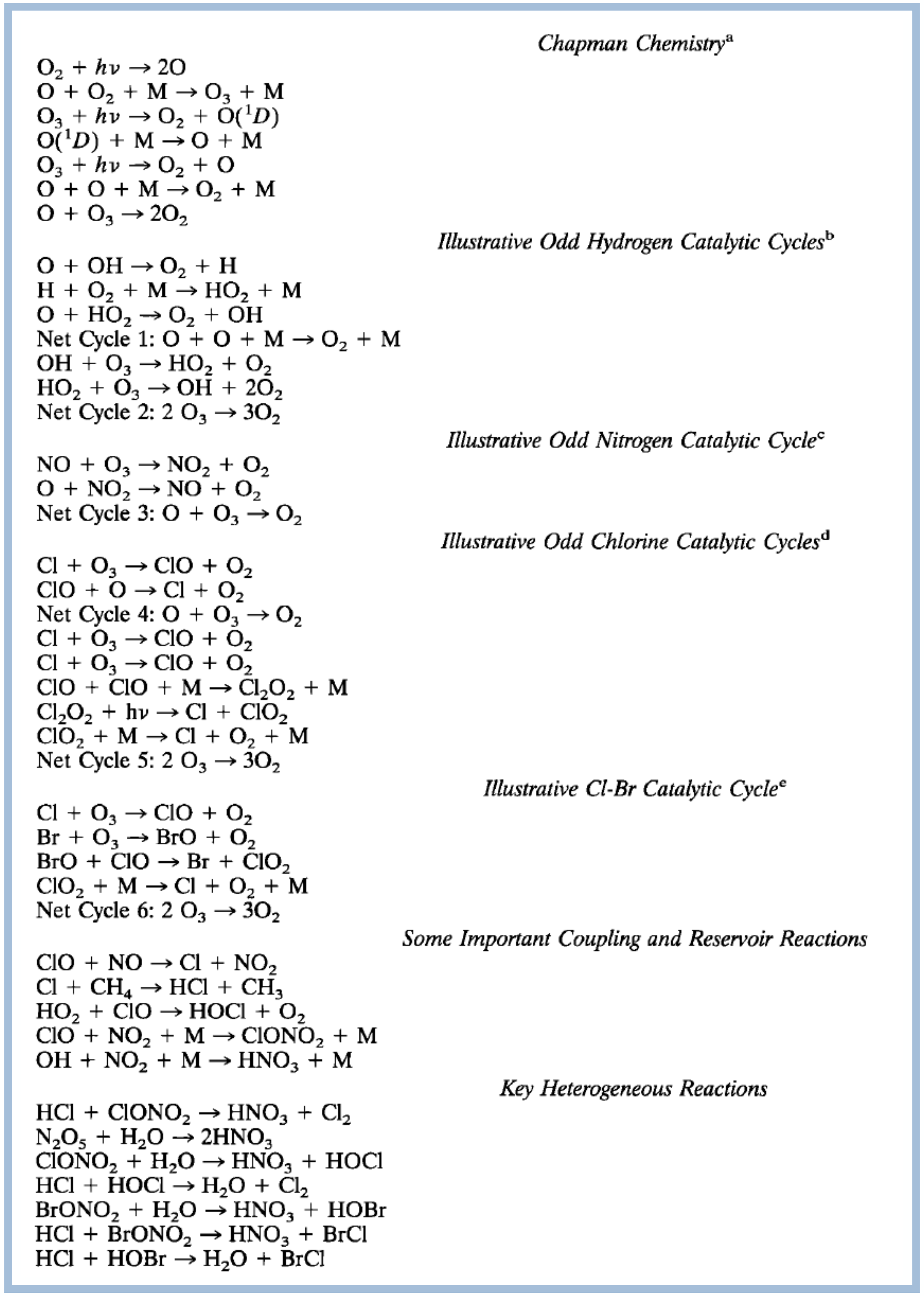


$\sim 1 \times 10^7$ tons/yr

industry (pre-Montreal Protocol)

Stolarski, R. S.; Cicerone, R. J. *Can. J. Chem.* **1974**, *52*, 1610.
Wofsy, S. C.; McElroy, M. B. *Can. J. Chem.* **1974**, *52*, 1582.

Atmospheric cycles involve many elementary steps



Chapman Chemistry[a]

$O_2 + h\nu \rightarrow 2O$
$O + O_2 + M \rightarrow O_3 + M$
$O_3 + h\nu \rightarrow O_2 + O(^1D)$
$O(^1D) + M \rightarrow O + M$
$O_3 + h\nu \rightarrow O_2 + O$
$O + O + M \rightarrow O_2 + M$
$O + O_3 \rightarrow 2O_2$

Illustrative Odd Hydrogen Catalytic Cycles[b]

$O + OH \rightarrow O_2 + H$
$H + O_2 + M \rightarrow HO_2 + M$
$O + HO_2 \rightarrow O_2 + OH$
Net Cycle 1: $O + O + M \rightarrow O_2 + M$
$OH + O_3 \rightarrow HO_2 + O_2$
$HO_2 + O_3 \rightarrow OH + 2O_2$
Net Cycle 2: $2\ O_3 \rightarrow 3O_2$

Illustrative Odd Nitrogen Catalytic Cycle[c]

$NO + O_3 \rightarrow NO_2 + O_2$
$O + NO_2 \rightarrow NO + O_2$
Net Cycle 3: $O + O_3 \rightarrow O_2$

Illustrative Odd Chlorine Catalytic Cycles[d]

$Cl + O_3 \rightarrow ClO + O_2$
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$ClO + ClO + M \rightarrow Cl_2O_2 + M$
$Cl_2O_2 + h\nu \rightarrow Cl + ClO_2$
$ClO_2 + M \rightarrow Cl + O_2 + M$
Net Cycle 5: $2\ O_3 \rightarrow 3O_2$

Illustrative Cl-Br Catalytic Cycle[e]

$Cl + O_3 \rightarrow ClO + O_2$
$Br + O_3 \rightarrow BrO + O_2$
$BrO + ClO \rightarrow Br + ClO_2$
$ClO_2 + M \rightarrow Cl + O_2 + M$
Net Cycle 6: $2\ O_3 \rightarrow 3O_2$

Some Important Coupling and Reservoir Reactions

$ClO + NO \rightarrow Cl + NO_2$
$Cl + CH_4 \rightarrow HCl + CH_3$
$HO_2 + ClO \rightarrow HOCl + O_2$
$ClO + NO_2 + M \rightarrow ClONO_2 + M$
$OH + NO_2 + M \rightarrow HNO_3 + M$

Key Heterogeneous Reactions

$HCl + ClONO_2 \rightarrow HNO_3 + Cl_2$
$N_2O_5 + H_2O \rightarrow 2HNO_3$
$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$
$HCl + HOCl \rightarrow H_2O + Cl_2$
$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr$
$HCl + BrONO_2 \rightarrow HNO_3 + BrCl$
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The comprehensive HO_x NO_x and ClO_x cycles involve many more **elementary steps** and **reservoir species**

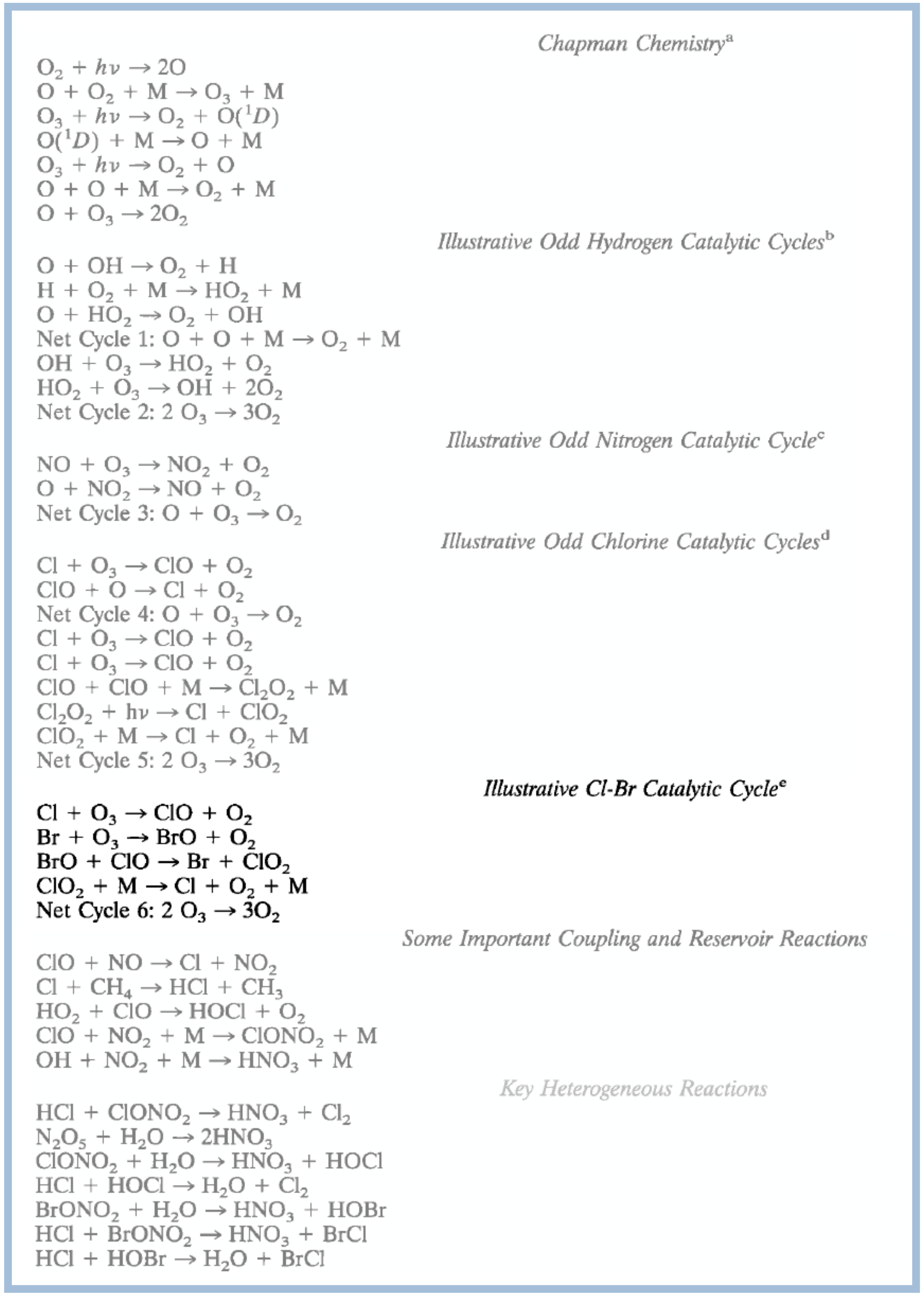
The kinetic relevance of each step depends on the **altitude, latitude, season, etc.**

Also worth noting,

these cycles *go to sleep at night!*

Solomon, S. *Rev. Geophys.* **1999**, *37*, 275.

Atmospheric cycles involve many elementary steps



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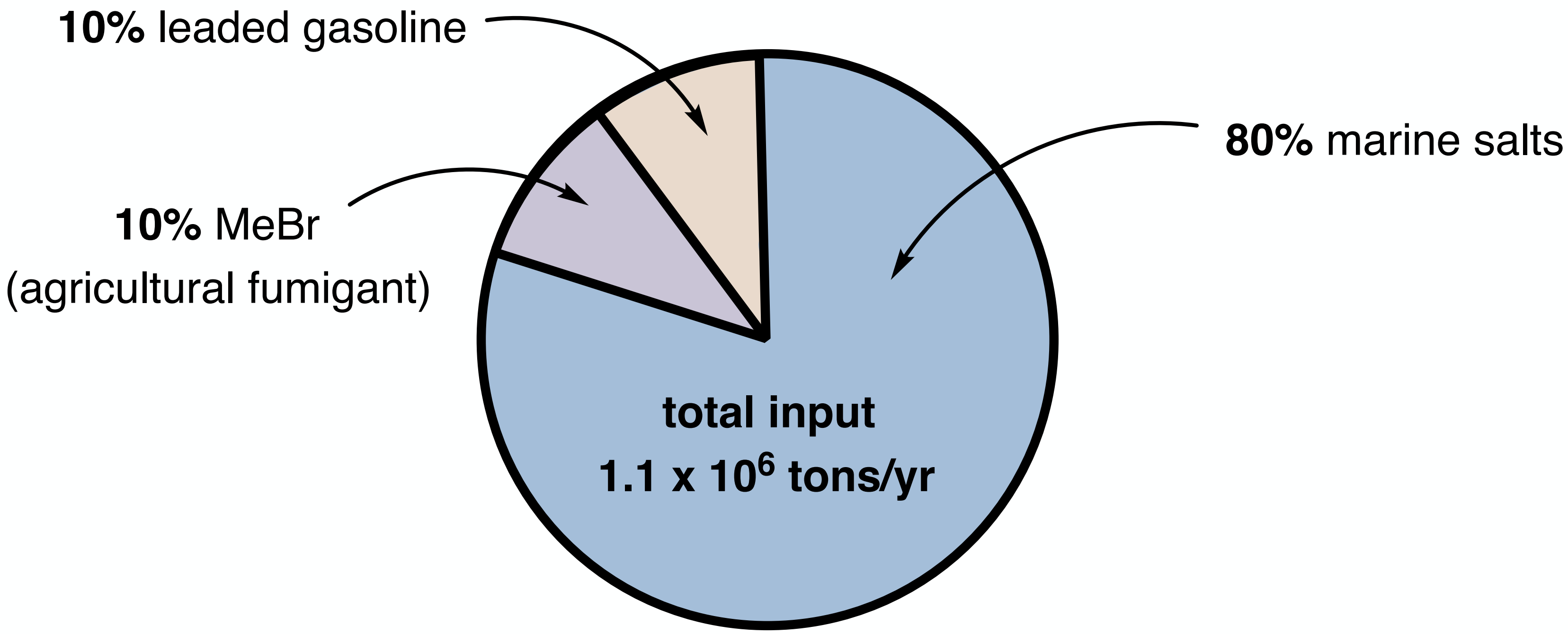
Also worth noting, these cycles *go to sleep at night!*

Solomon, S. *Rev. Geophys.* **1999**, *37*, 275.

Br is an even more potent O_3 depletor

A concentration of **1 in 10^{-11} (v/v) Br** was tied to a **0.3% loss of O_3** in the stratosphere

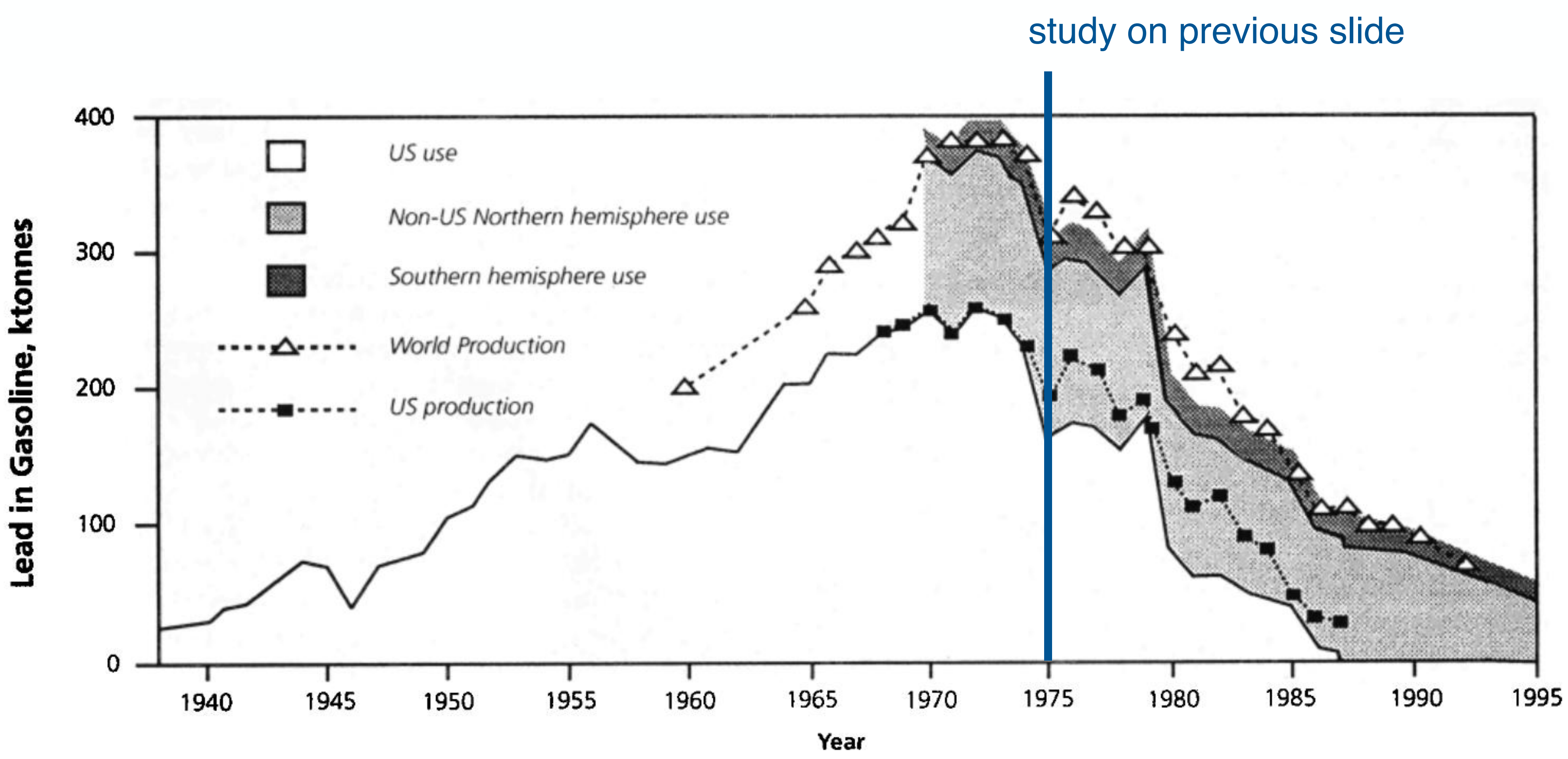
~20% of atmospheric Br could be traced to human activity in 1975



Wofsy, S. C.; McElroy, M. B.; Yung, Y. L. *Geophys. Res. Lett.* **1975**, *2*, 215.

Bromine emissions are brought under control

- From 1970 to 1995 leaded gasoline usage plummets



- MeBr is phased out as a fumigant in the Montreal Protocol (discussed later in detail)

Thomas, V. M.; Bedford, J. A.; Cicerone, R. J. *Geophys. Res. Lett.* **1997**, *24*, 1371.

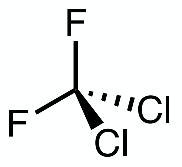
The chlorofluorocarbons (CFCs)

Small organic molecules consisting of **chlorine**, **fluorine**, and **carbon**

characterized by low toxicity and non-flammability

Developed by Thomas Midgley, Jr. and Albert Henne (General Motors) in 1928

- General Motors-Frigidaire-DuPont collaboraiton
- safer refrigerant (vs. ammonia, methyl chloride, sulfur dioxide)



CFC-12

“Freon-12”

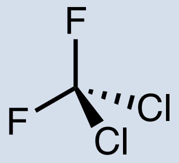
main uses of CFCs are as **refrigerants** and **propellants** (spray foam insulation and rescue inhalers)

Chlorofluorocarbons (CFCs). Earth System Research Laboratory. NOAA. http://www.esrl.noaa.gov/gmd/hats/publictn/elkins/cfcs.html

Midgley Jr., T.; Henne, A. L. *Ind. Eng. Chem.* **1930**, *22*, 542.

Giunta, C. J. *Bull. Hist. Chem.* **2006**, *31*, 66.

CFC Nomenclature



CFC-12

“Freon-12”

“CFC” is a systematic acronym, “Freon” is a proprietary name

- back-calculate composition from number

Step 1: add 90

Step 2: examine three-digit number

CFC-12 Example

12 + 90 = **102**

1 C

0 H

2 F

\- - - - - - - - - -

2 Cl (satisfy octet rule)

Chlorofluorocarbons (CFCs). Earth System Research Laboratory. NOAA. http://www.esrl.noaa.gov/gmd/hats/publictn/elkins/cfcs.html

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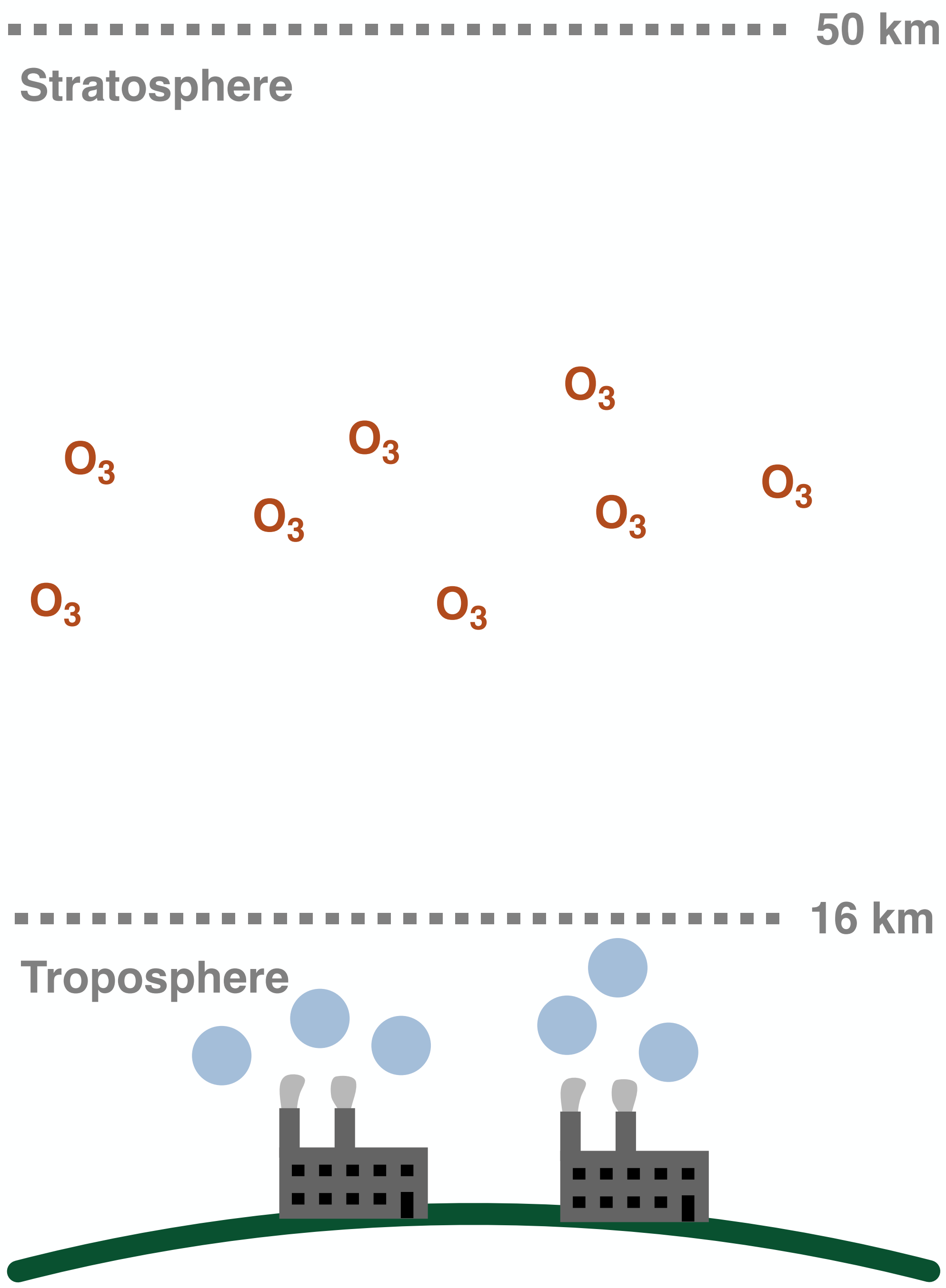
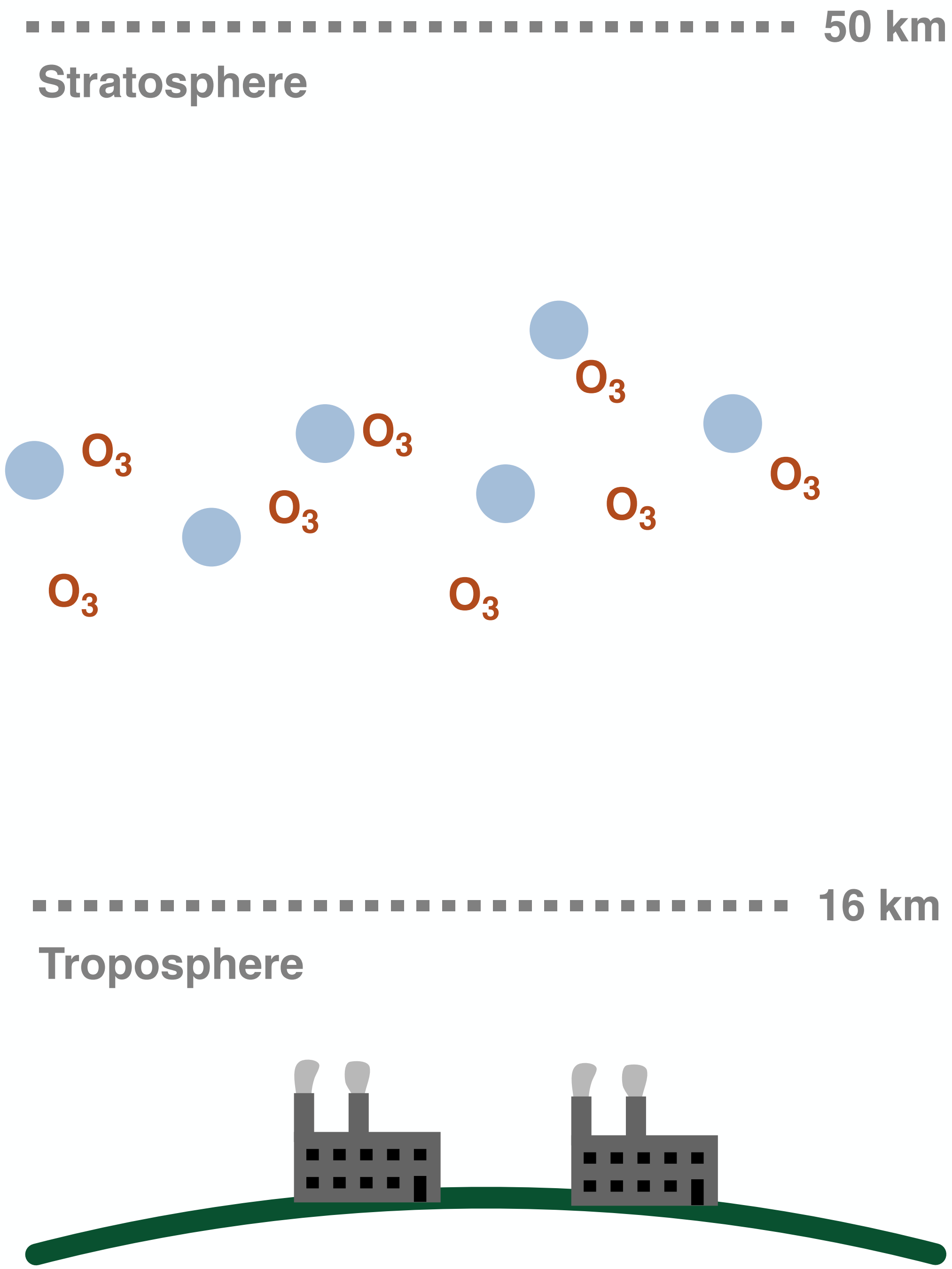
CFCs and the destruction of ozone



CFCs are unreactive in the troposphere and survive into the stratosphere

Molina, M. J., Rowland, F. S. *Nature*, **1974**, *249*, 810.

CFCs and the destruction of ozone



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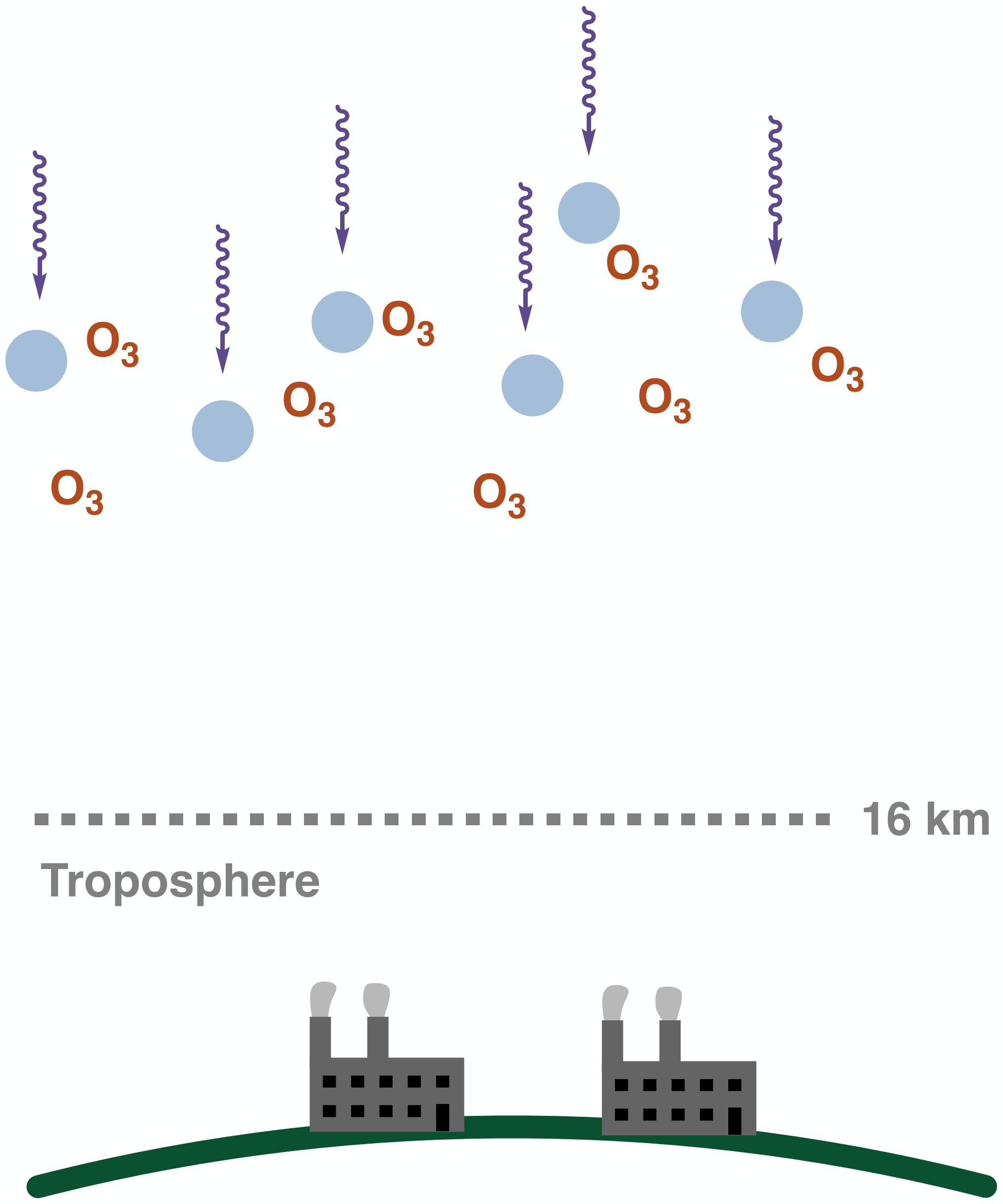

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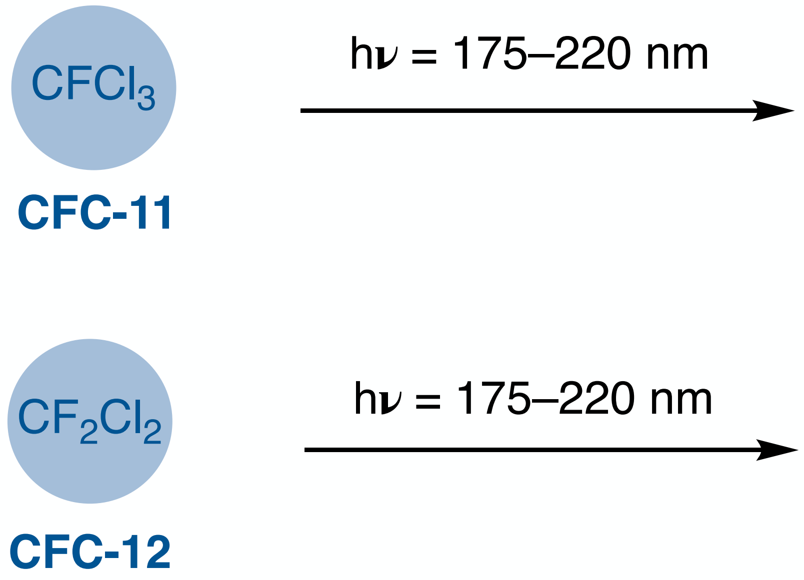


$CFCl_3$ $\xrightarrow{h\nu = 175–220 \text{ nm}}$

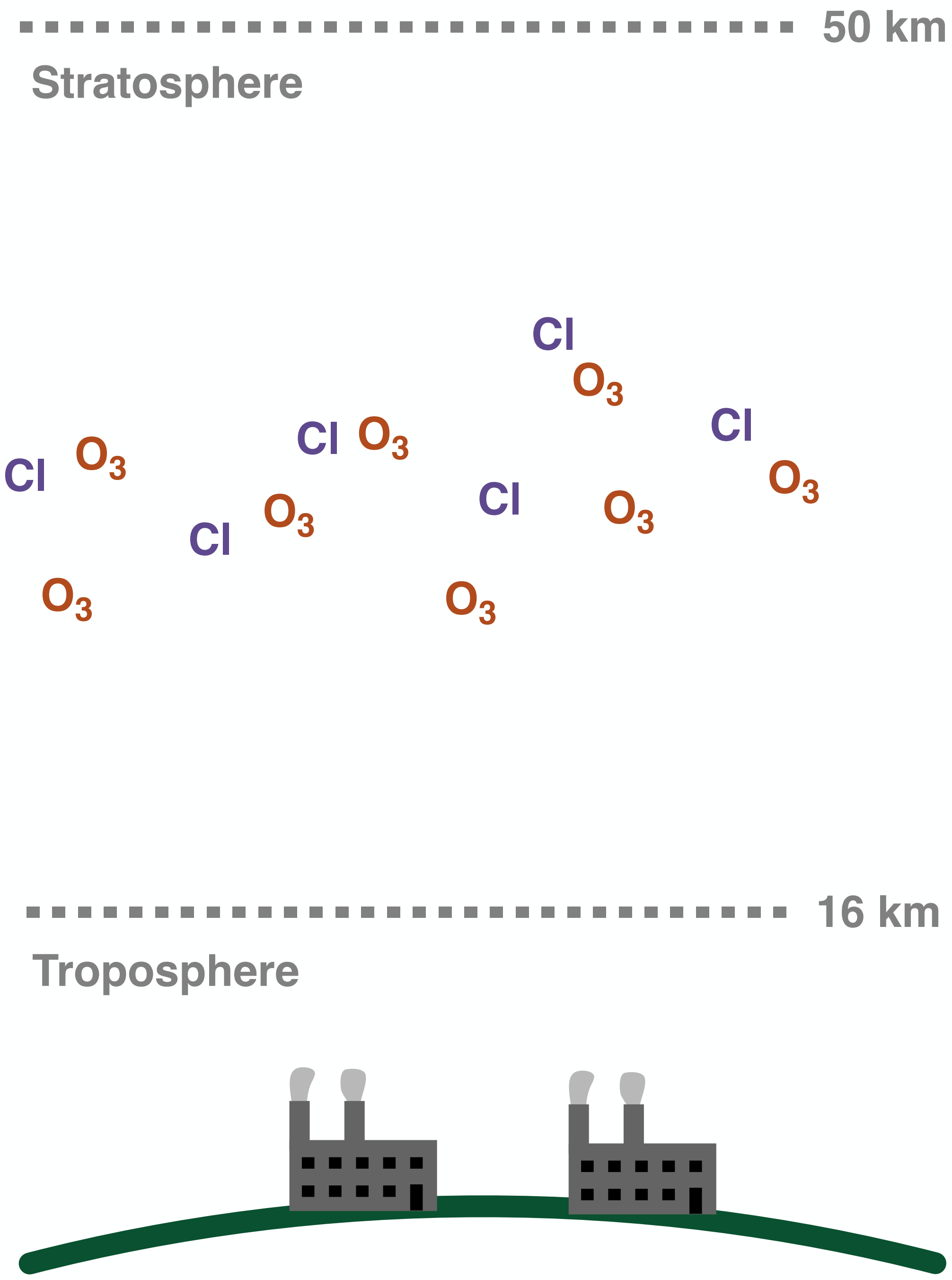
CFC-11

CF_2Cl_2 $\xrightarrow{h\nu = 175–220 \text{ nm}}$

CFC-12

Molina, M. J., Rowland, F. S. *Nature*, **1974**, *249*, 810.

CFCs and the destruction of ozone



CFCs are unreactive in the troposphere and survive into the stratosphere

$$CFCl_3 \xrightarrow{h\nu = 175\text{–}220\ \text{nm}} CFCl_2 + Cl$$

CFC-11

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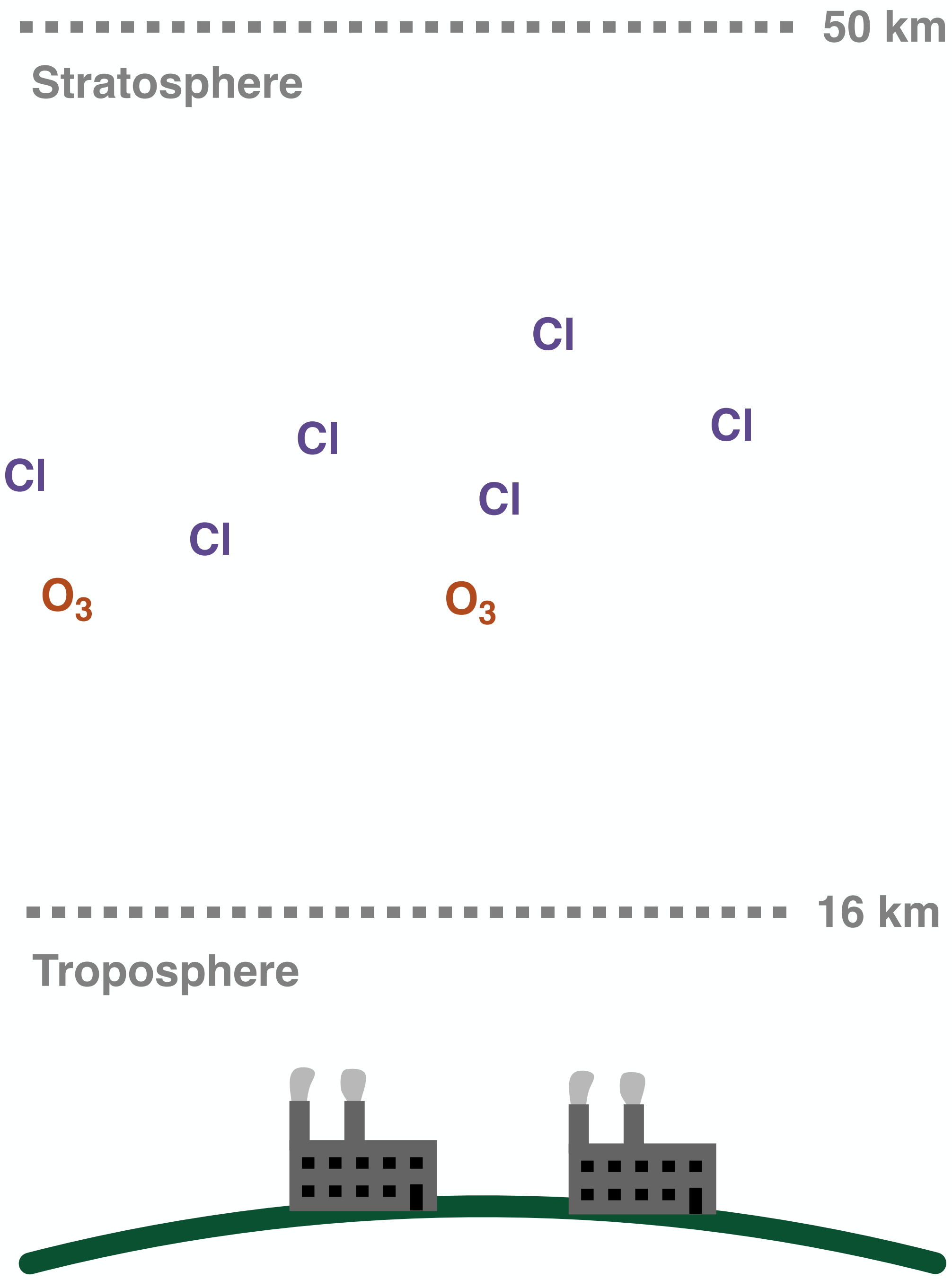

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$$\begin{array}{lcl} O_3 + Cl & \longrightarrow & ClO + O_2 \\ ClO + O & \longrightarrow & Cl + O_2 \\ \hline O_3 + O & \longrightarrow & O_2 + O_2 \end{array}$$

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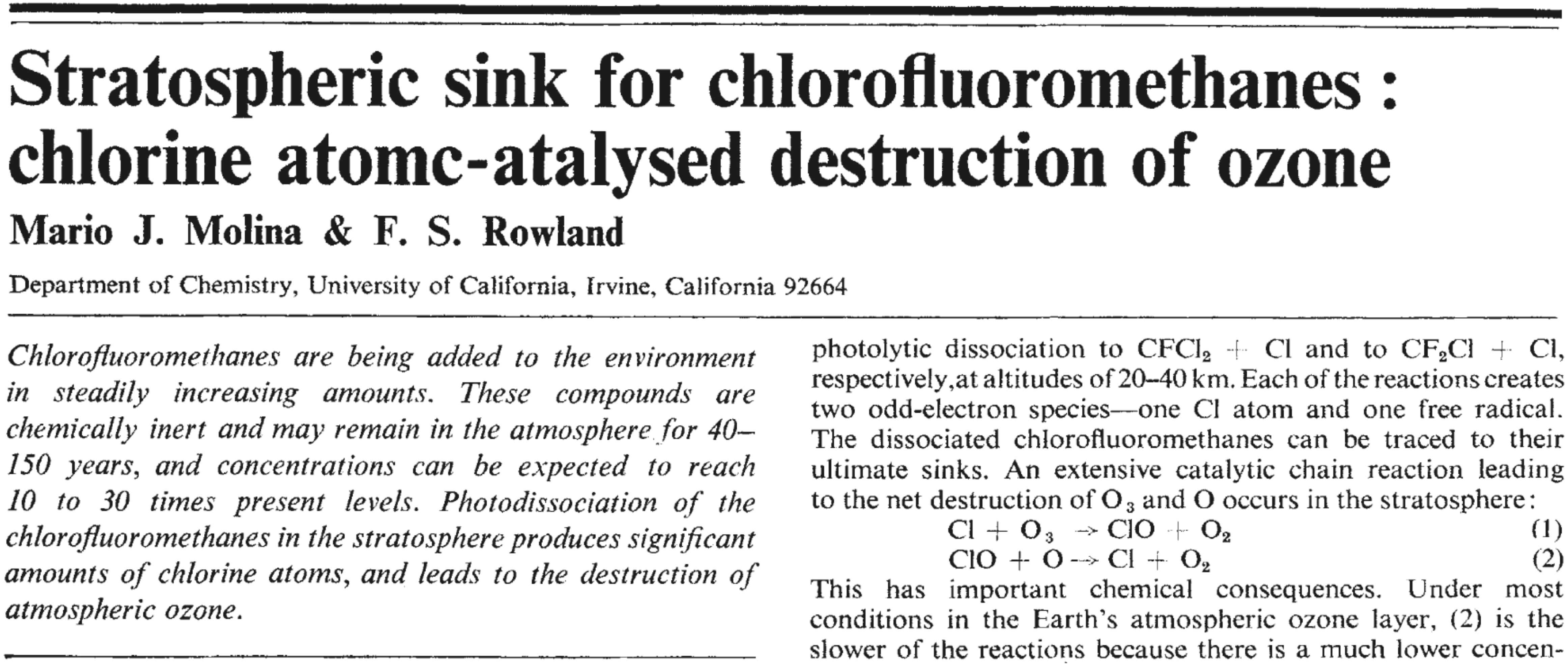


Stratospheric sink for chlorofluoromethanes : chlorine atomc-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

photolytic dissociation to $CFCl_2$ + Cl and to CF_2Cl + Cl, respectively, at altitudes of 20–40 km. Each of the reactions creates two odd-electron species—one Cl atom and one free radical. The dissociated chlorofluoromethanes can be traced to their ultimate sinks. An extensive catalytic chain reaction leading to the net destruction of O_3 and O occurs in the stratosphere:

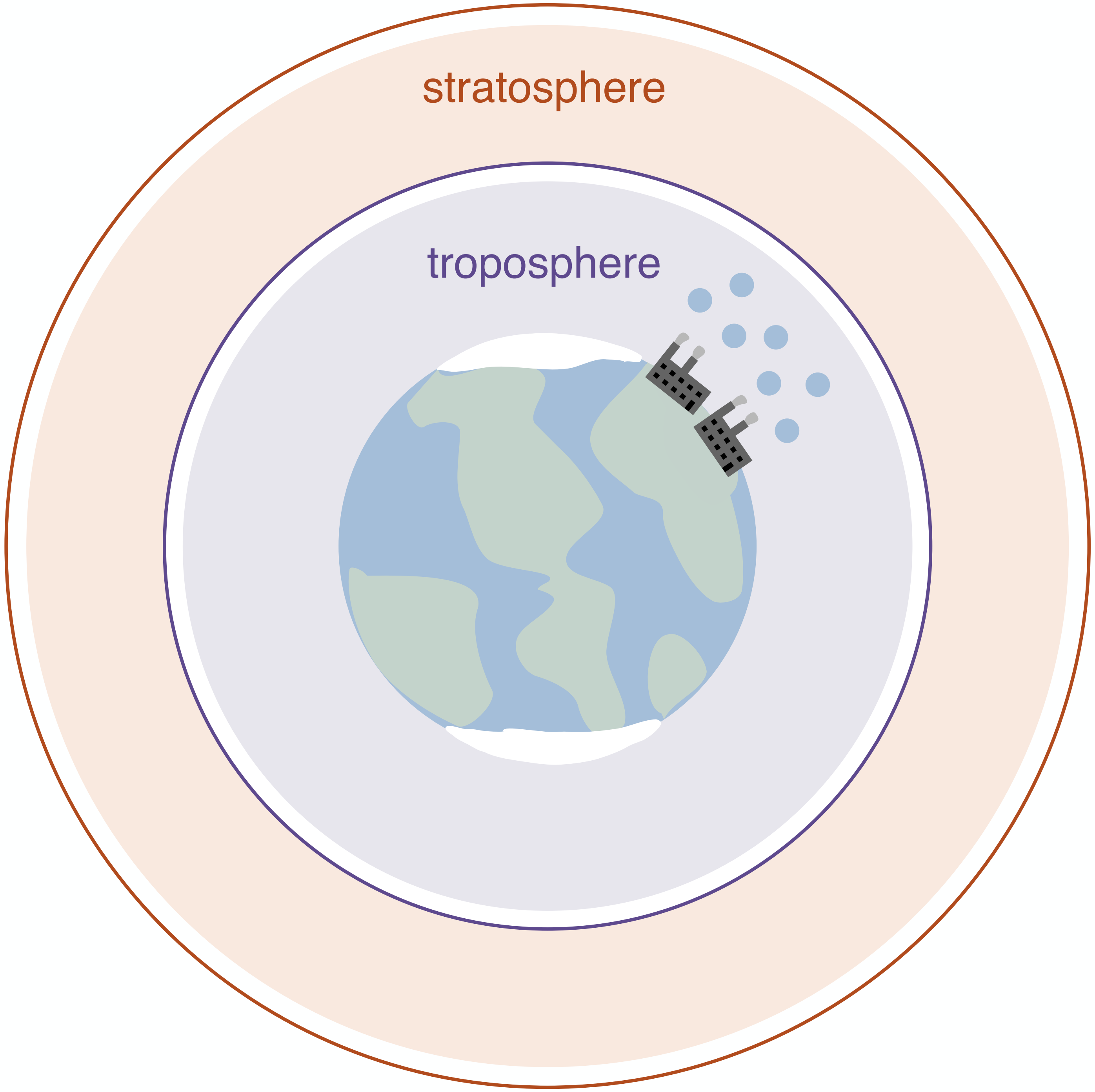
$$Cl + O_3 \rightarrow ClO + O_2 \quad (1)$$

$$ClO + O \rightarrow Cl + O_2 \quad (2)$$

This has important chemical consequences. Under most conditions in the Earth's atmospheric ozone layer, (2) is the slower of the reactions because there is a much lower concen-

Molina, M. J., Rowland, F. S. *Nature*, **1974**, *249*, 810.

CFCs are a global problem



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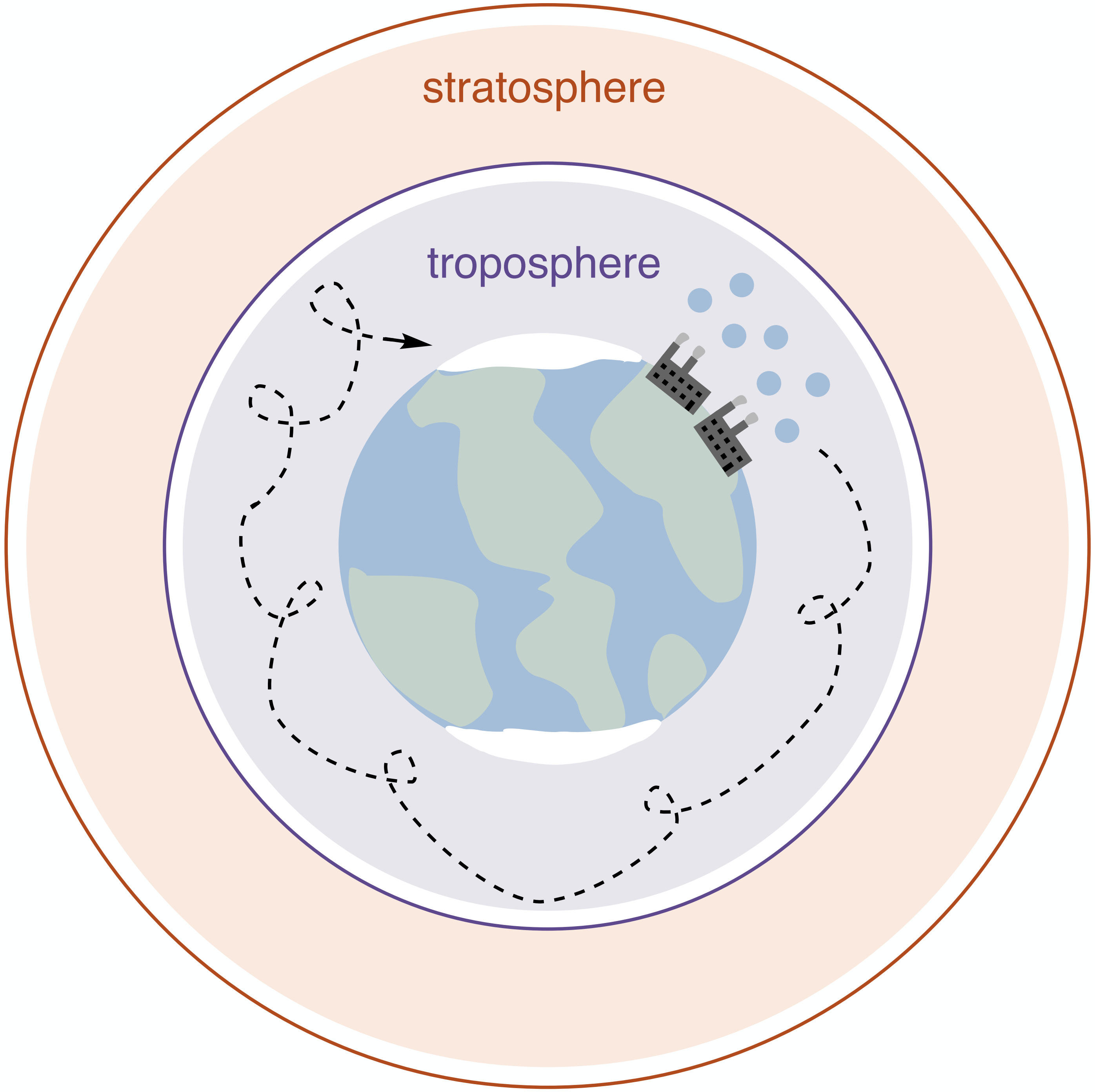

troposphere is turbulent and well-mixed

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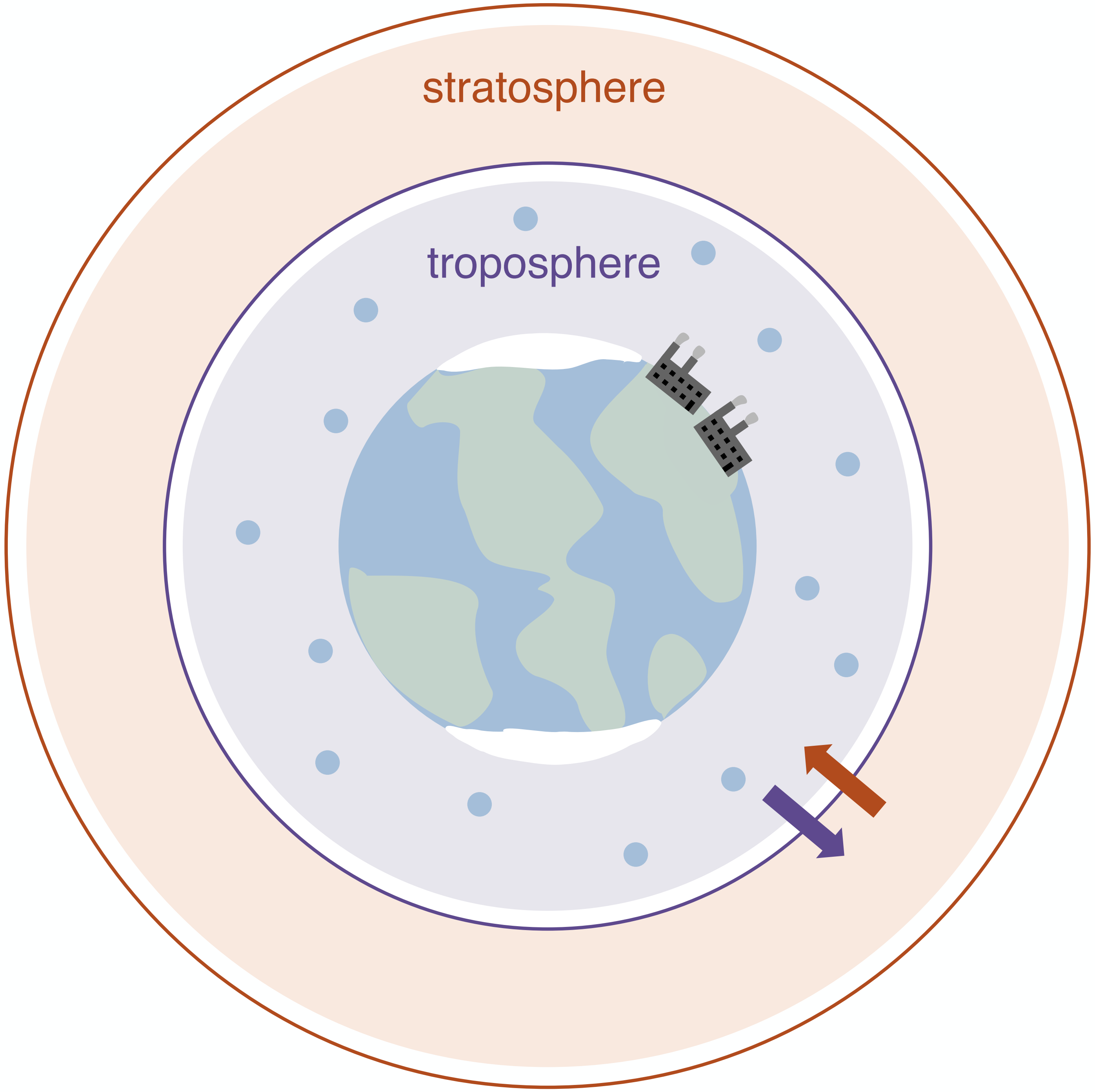

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exchange with stratosphere is slow

(10% of the troposphere mixes every 5 years)

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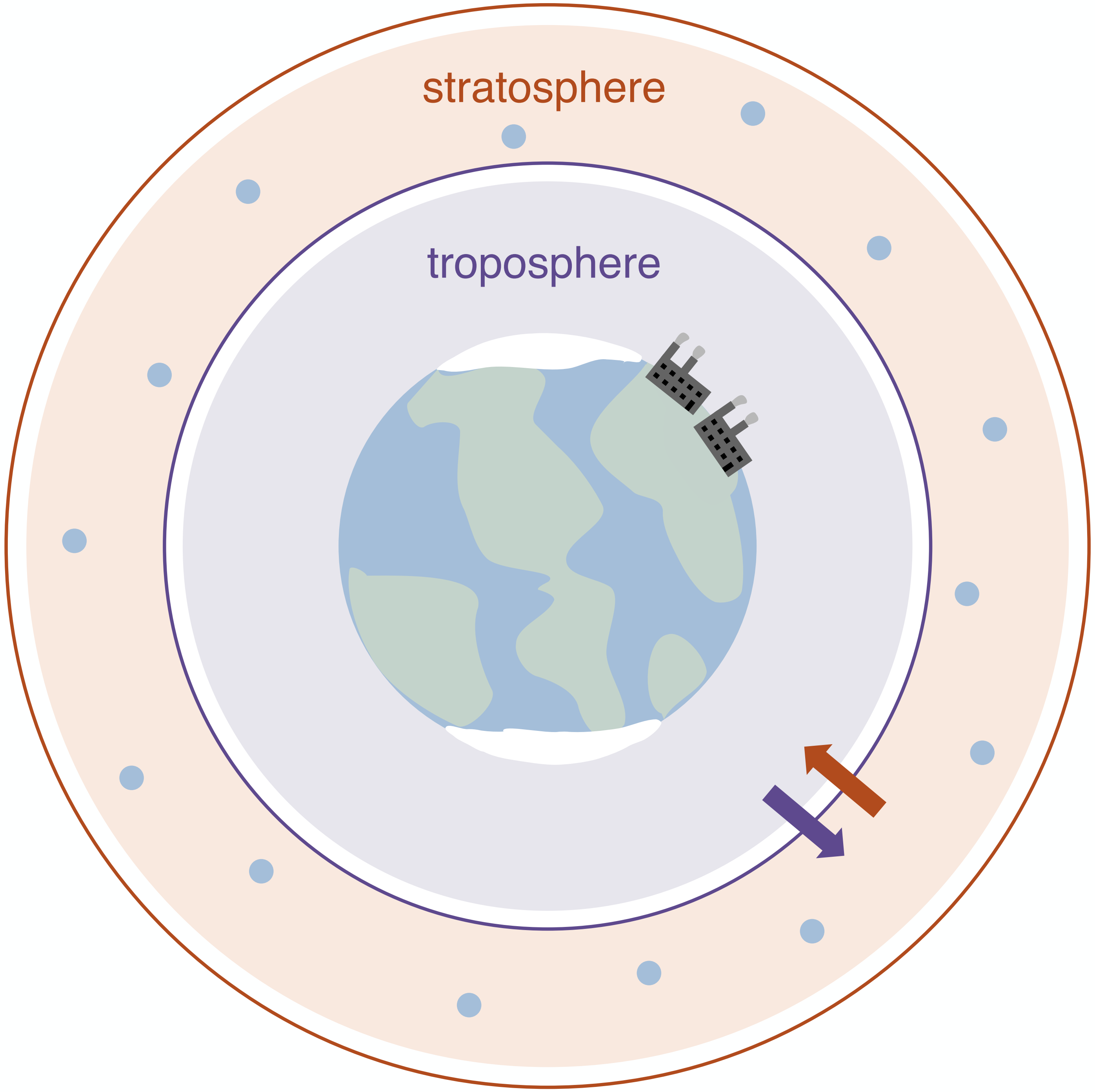

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uniform distribution of CFCs in stratosphere,
regardless of source

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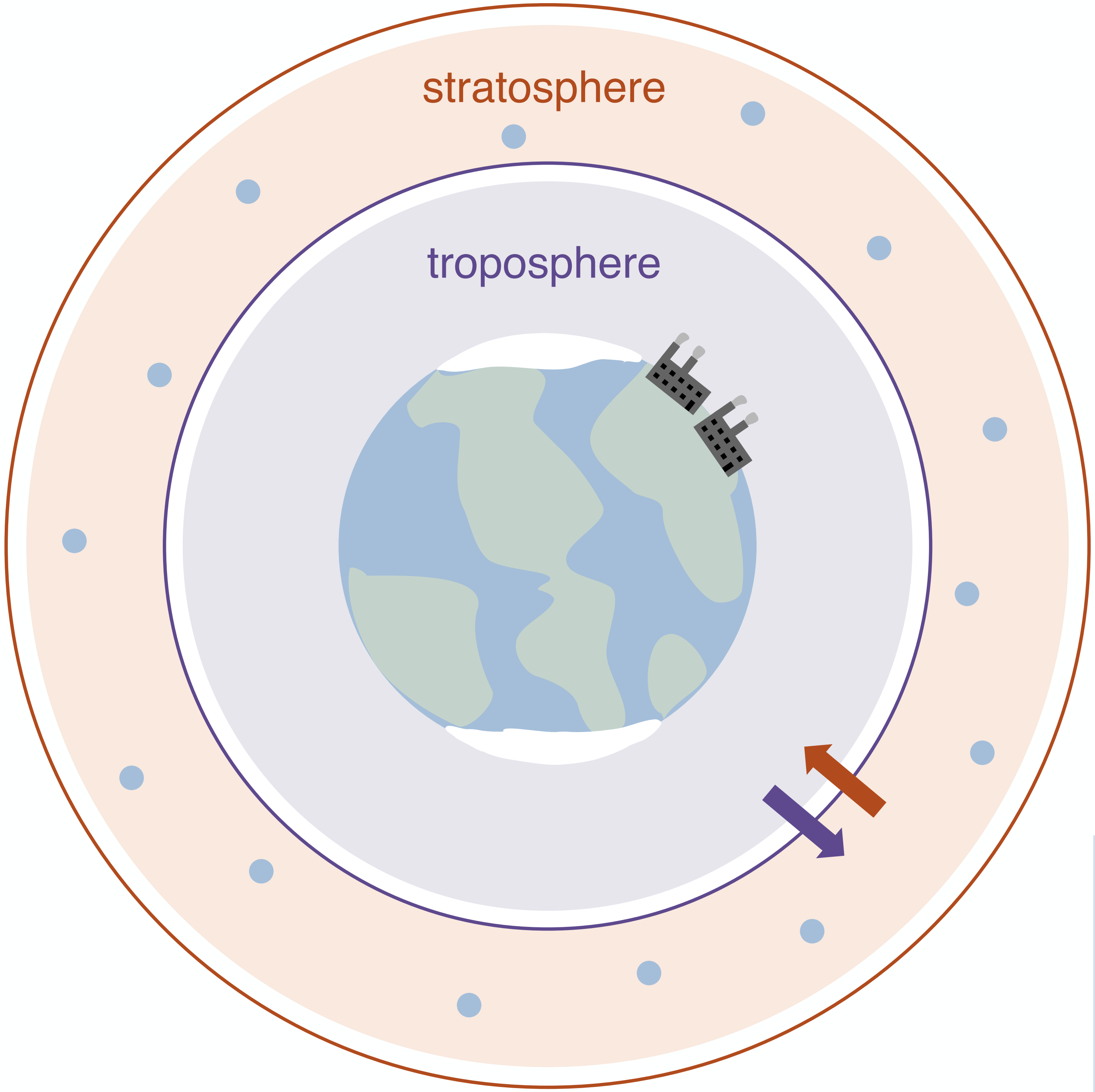

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long stratospheric lifetimes

50-100's of years

rained out as HCl in troposphere

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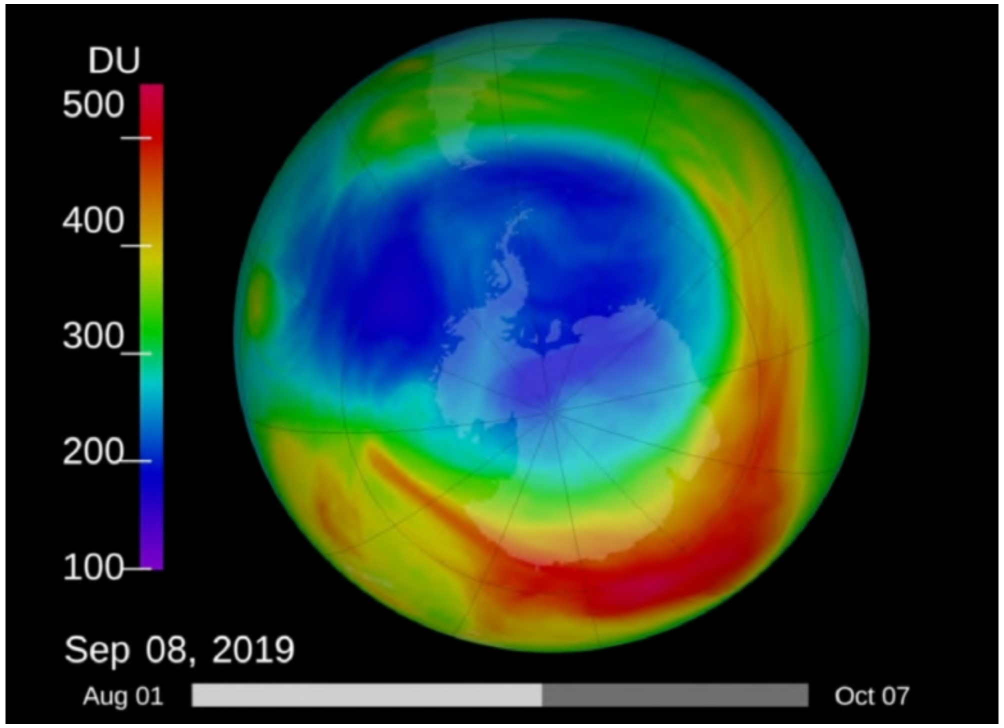
Two kinds of ozone depletion

I. Continual loss of ozone throughout the atmosphere and around the globe

II. Formation every winter/spring of an "ozone hole" over Antartica



2019 ozone hole smallest on record. NOAA Research News. https://research.noaa.gov/article/ArtMID/587/ArticleID/2566/

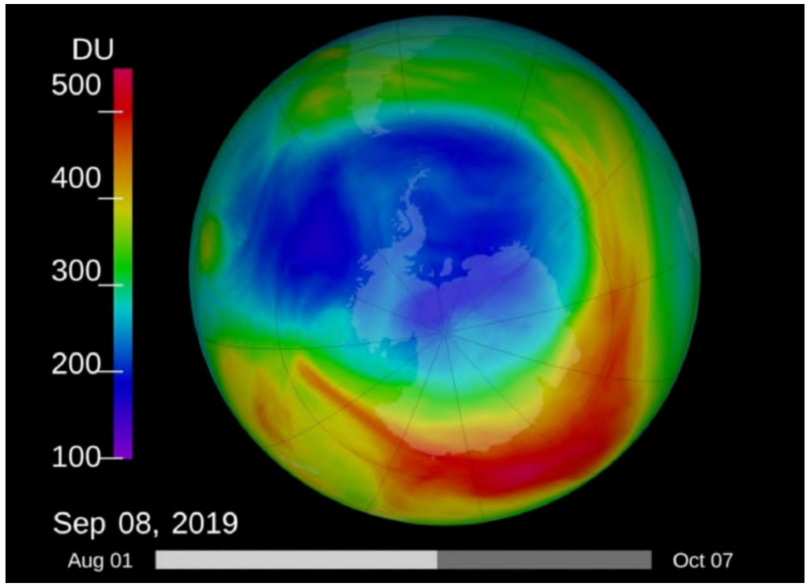
Questions about the Antarctic ozone hole

1. Why over Antarctica?

extended cold periods (–78 ºC) and isolated stratosphere (polar vortex)

2. How big is it?

typically 8 million mi^2 (16.4 million km^2)



Fahey, D. W.; Hegglin, M. I. World Meteorological Organization Global Ozone Research and Monitoring Project - Report No. 52.
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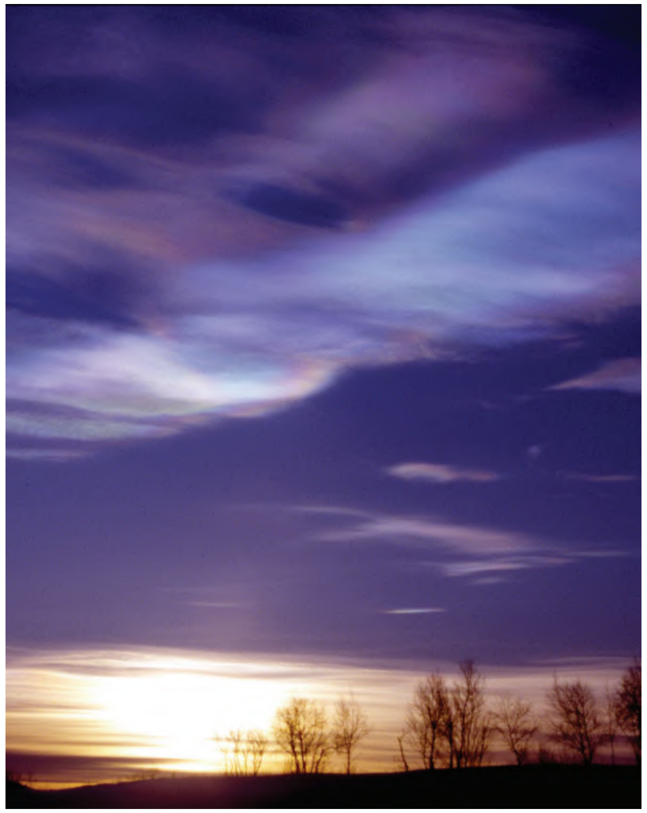

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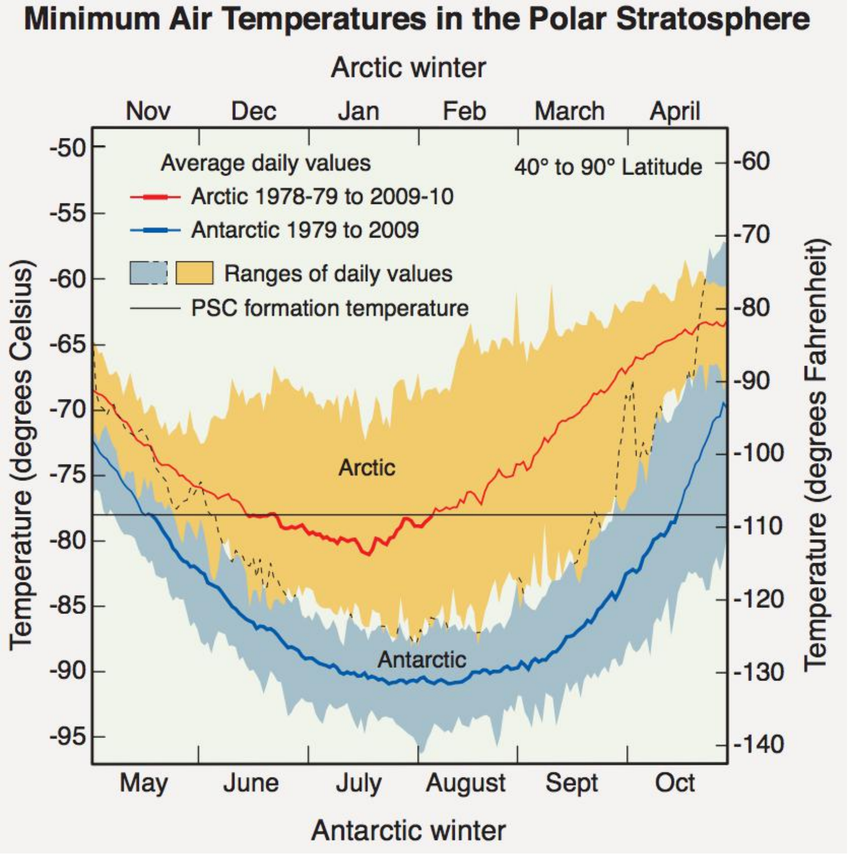
4. Why not the Arctic?

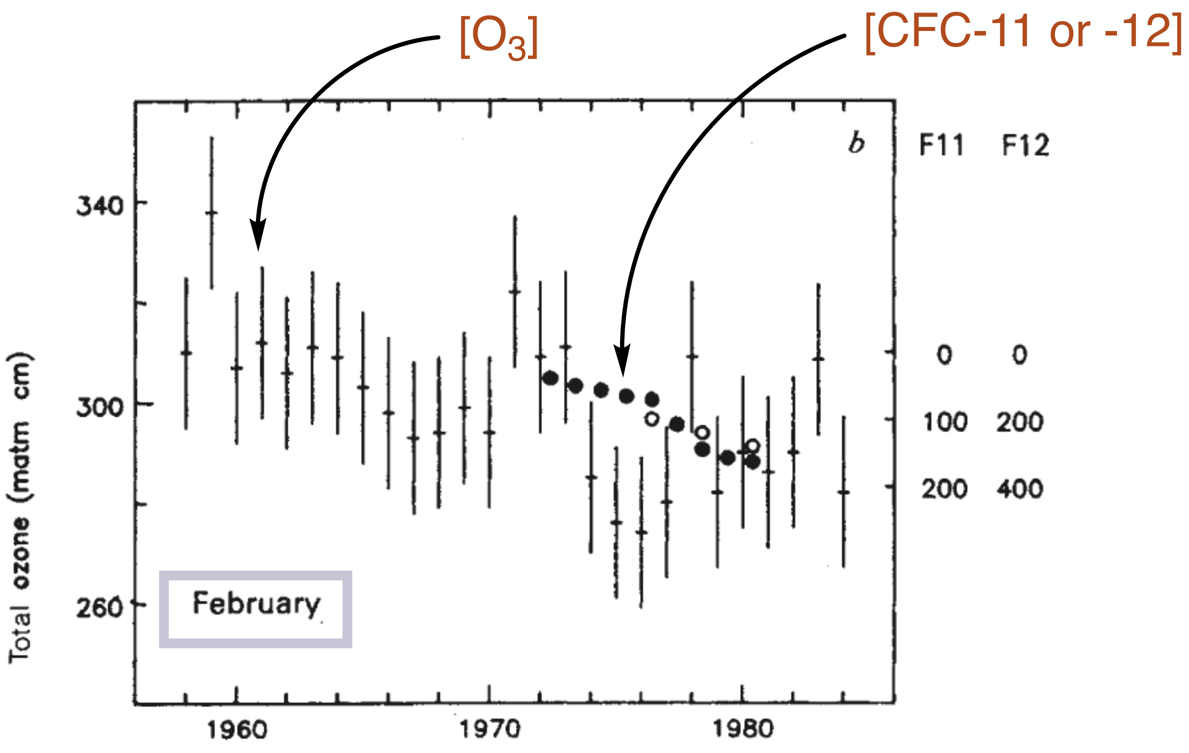
higher temperatures, only form PSCs for 10-60 days (*5 months in Antarctica*)

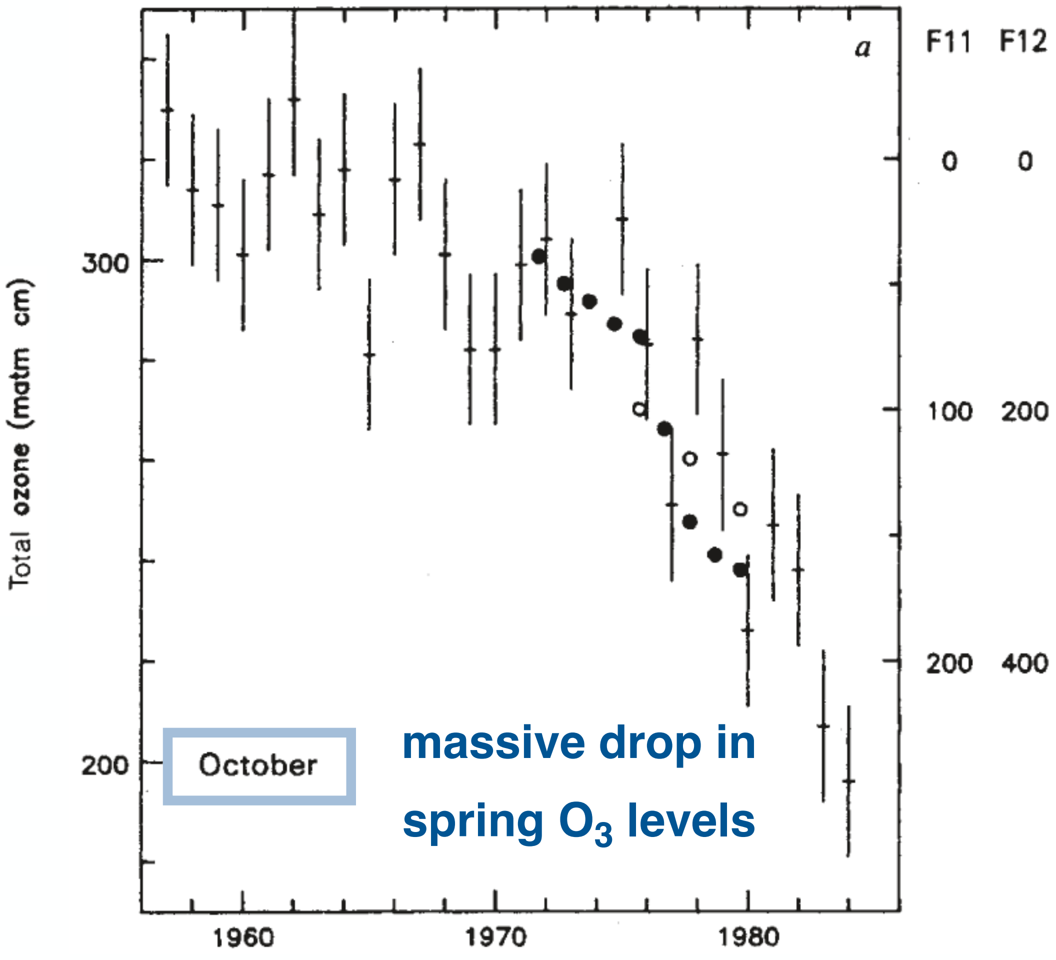


Fahey, D. W.; Hegglin, M. I. World Meteorological Organization Global Ozone Research and Monitoring Project - Report No. 52.
http://acd-ext.gsfc.nasa.gov/Documents/O3_Assessments/Docs/WMO_2010/Q2_QA.pdf

The discovery of the Antarctic ozone hole

- First reported in 1985, data from **Halley Bay (Antarctica)** revealed a *seasonal pattern of ozone depletion*





massive drop in spring O_3 levels

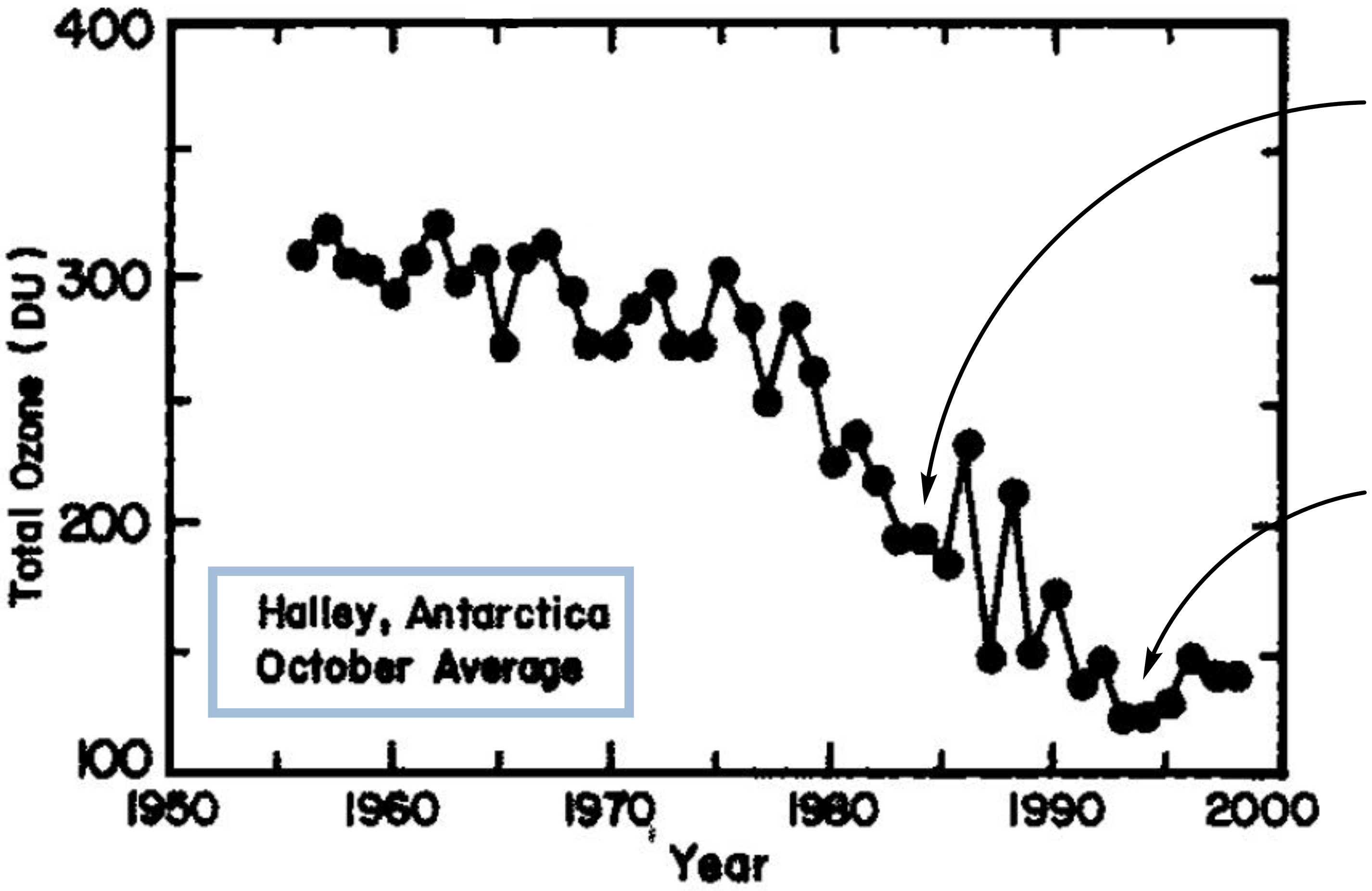
decline in both [CFC] and [O_3] suggests

transformation of CFCs into O_3-destroying species

Farman, J. C.; Gardiner, B. G.; Shanklin, J. D. *Nature* **1985**, *315*, 207.

The growth of the Antarctic ozone hole

- The ozone hole increased in severity until reaching a minimum in 1994

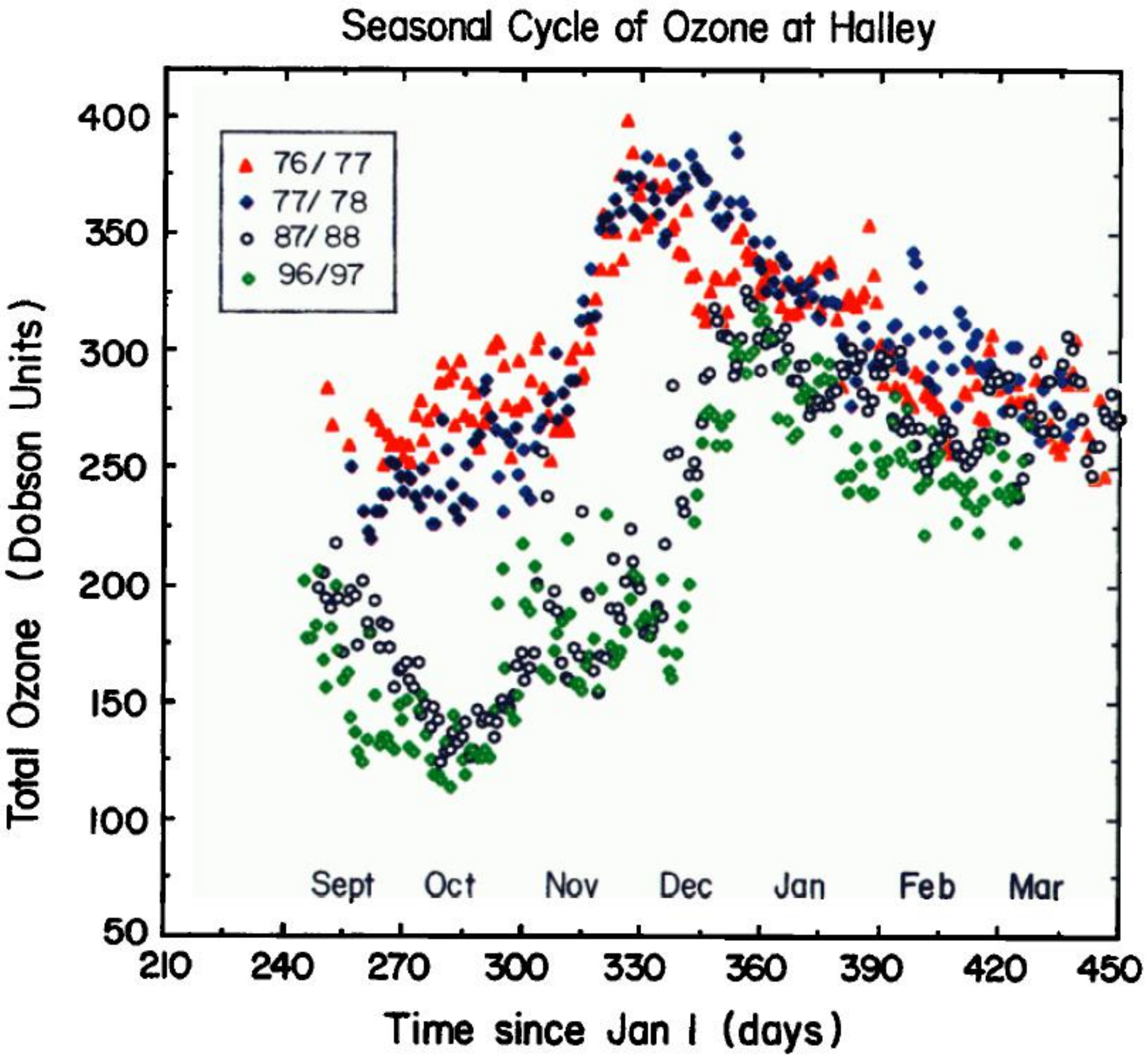


first report of O_3 hole

lowest years on record

Solomon, S. *Rev. Geophys.* **1999**, *37*, 275.

A change in the seasonal cycle of ozone depletion



Antarctic ozone levels **decrease overall**

and **decrease sharply** into a **lower spring minimum**

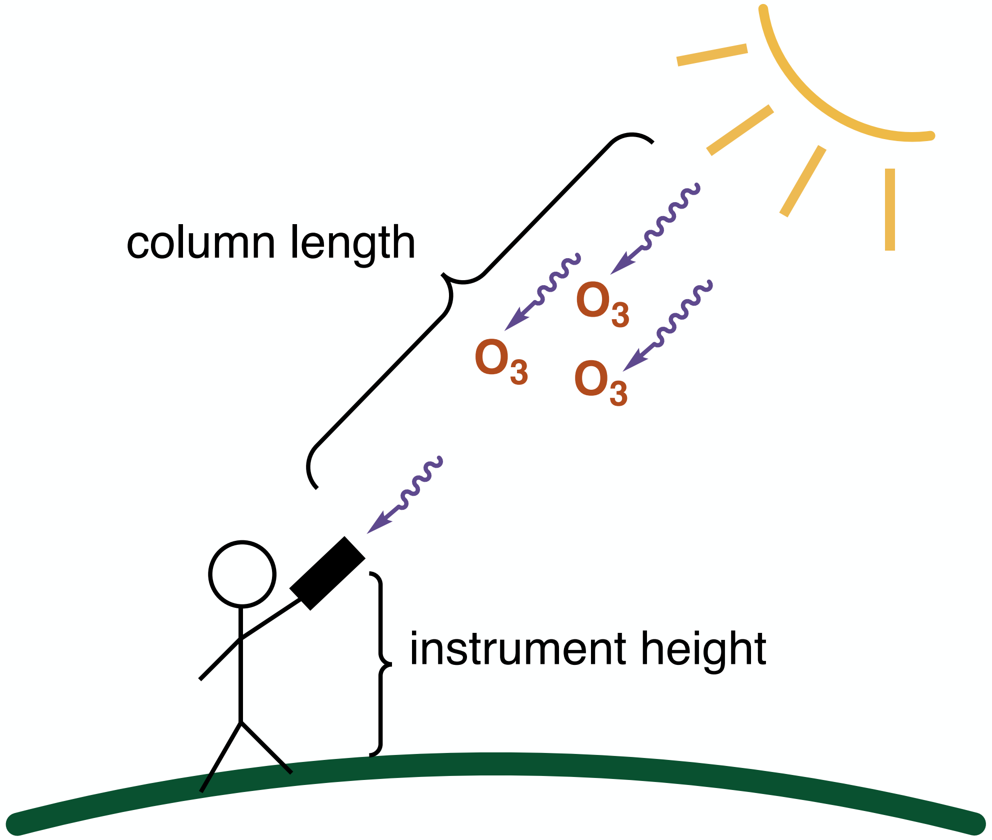
Cold season **persists longer** because

stratospheric warmth provided by **O_3 UV absorption**

Solomon, S. *Rev. Geophys.* **1999**, *37*, 275.

Measuring ozone concentrations

Ozone is measured as a "total" or "column" amount between instrument and Sun



Common Undergraduate Experiment

1. measure absorbance at multiple characteristic λ

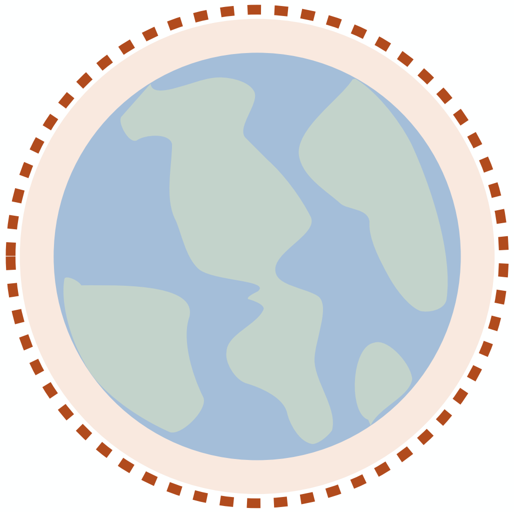
2. apply modified Beer-Lambert Law (no I_o)

$$\frac{I}{I_o} = e^{-\varepsilon \ell [\text{ozone}]}$$

3. account for scattering by air (Mie) and aerosols (Rayleigh)

Solomon, S. *Rev. Geophys.* **1999**, *37*, 275.
Boering, K. A. *Lab 2: Ground- and Space-Based Ozone Column Measurements.* CHEM C182 Laboratory Notebook. UC Berkeley, Spring 2017.

Dobson units (DU)



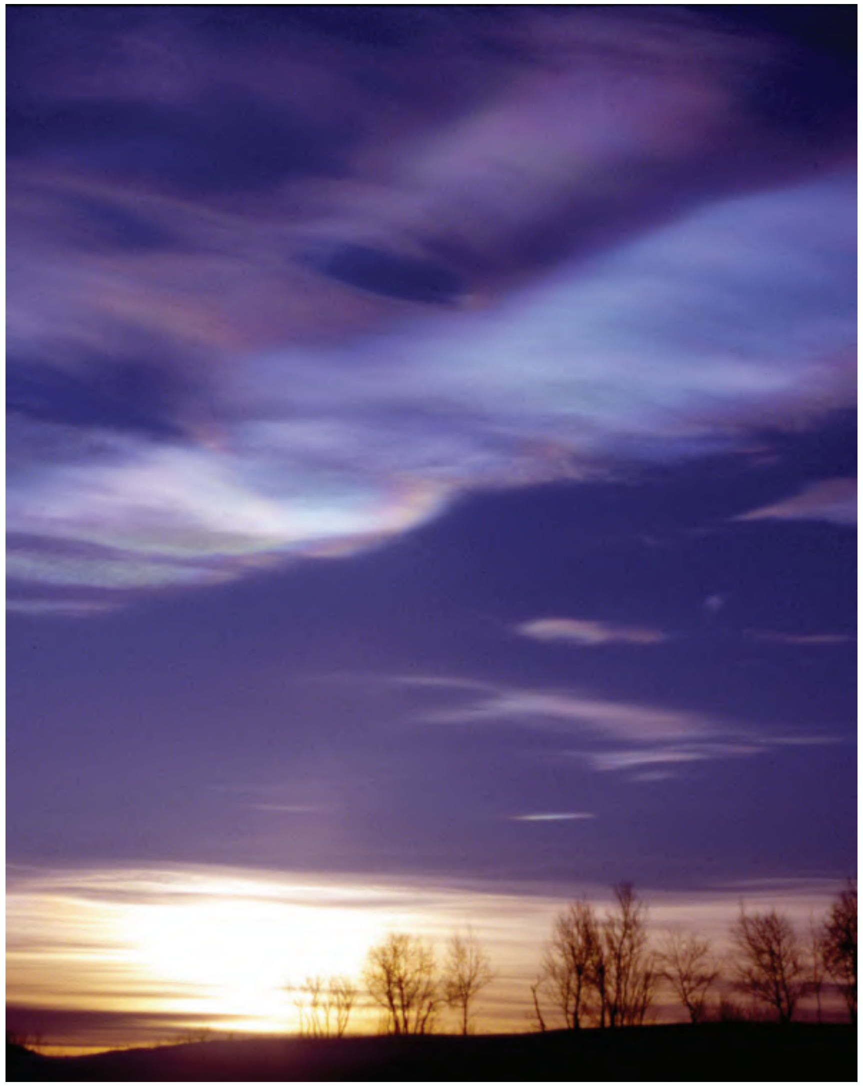
the thickness of the layer of pure ozone that would over the Earth (in units of 10 µm) at STP

example: **300 DU** would correspond to a **3 mm layer** of ozone on the Earth surface

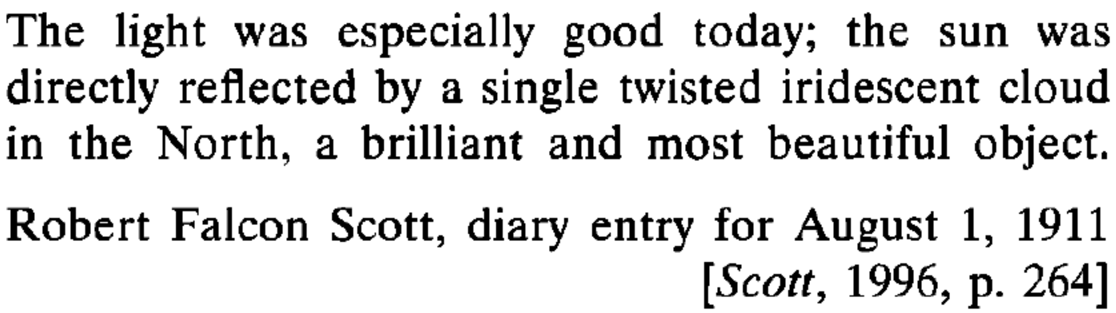
Solomon, S. *Rev. Geophys.* **1999**, *37*, 275.
Boering, K. A. *Lab 2: Ground- and Space-Based Ozone Column Measurements.* CHEM C182 Laboratory Notebook. UC Berkeley, Spring 2017.

Ozone-destroying clouds?

- Polar Stratospheric clouds (PSCs) have long been a feature of the Antarctic sky



http://acd-ext.gsfc.nasa.gov/Documents/
O3_Assessments/Docs/WMO_2010/Q2_QA.pdf



> The light was especially good today; the sun was directly reflected by a single twisted iridescent cloud in the North, a brilliant and most beautiful object.
>
> Robert Falcon Scott, diary entry for August 1, 1911
> [*Scott*, 1996, p. 264]

Type 1 PSCs

clouds of nitric acid and water crystallizing below -78 °C

key component is **nitric acid trihydrate (NAT)**

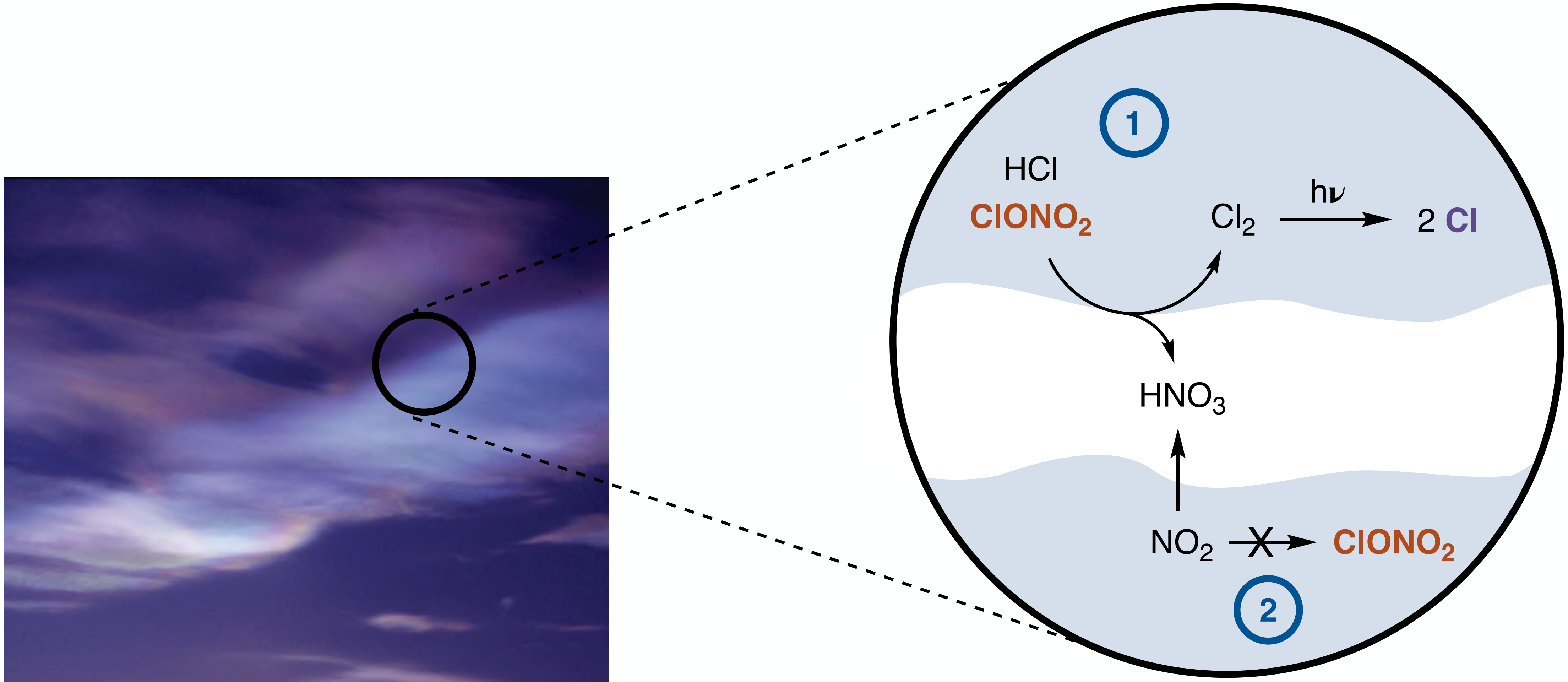
catalytically active in ozone depletion

Type 2 PSCs

brightly-colored clouds composed mainly of water

Solomon, S. *Rev. Geophys.* **1999**, *37*, 275.

Ozone-destroying clouds?



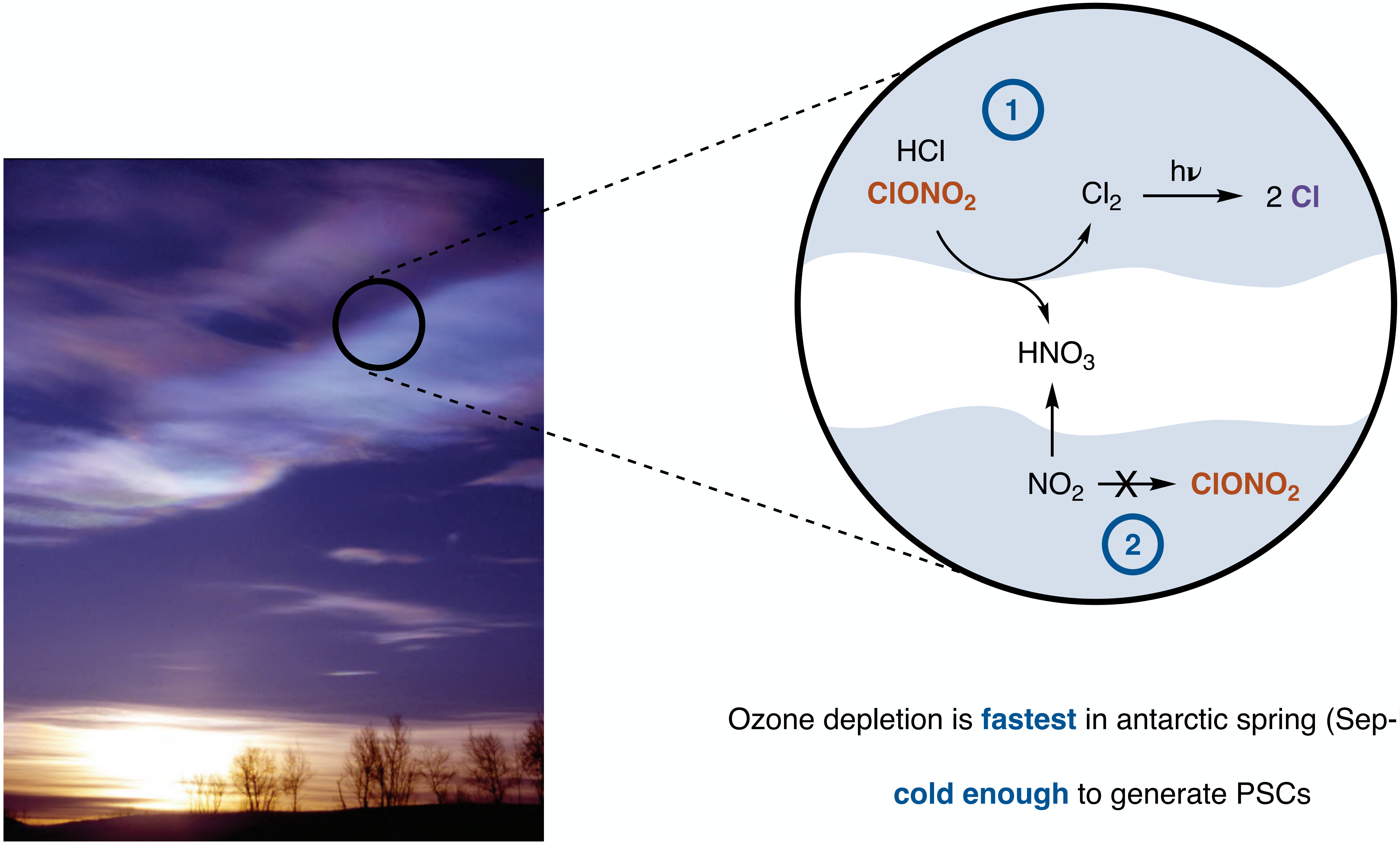
http://acd-ext.gsfc.nasa.gov/Documents/
O3_Assessments/Docs/WMO_2010/Q2_QA.pdf

① PSCs catalyze activation of **Cl** from inert precursors

② PSCs sequester NO_2 (key **Cl**-deactivating species)

Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *321*, 755.
Molina, M. J.; Tso, T.-L.; Molina, L. T.; Wang, F. C.-Y. *Science* **1987**, *238*, 1253.
Molina, M. J.; Zhang, R.; Wooldridge, P. J.; McMahon, J. R.; Kim, J. E.; Chang, H. Y.; Beyer, K. D. *Science* **1993**, *261*, 1418.

Ozone-destroying clouds?



http://acd-ext.gsfc.nasa.gov/Documents/
O3_Assessments/Docs/WMO_2010/Q2_QA.pdf

Ozone depletion is **fastest** in antarctic spring (Sep-Dec):

cold enough to generate PSCs

sufficient sunlight to initiate photochemical reactions

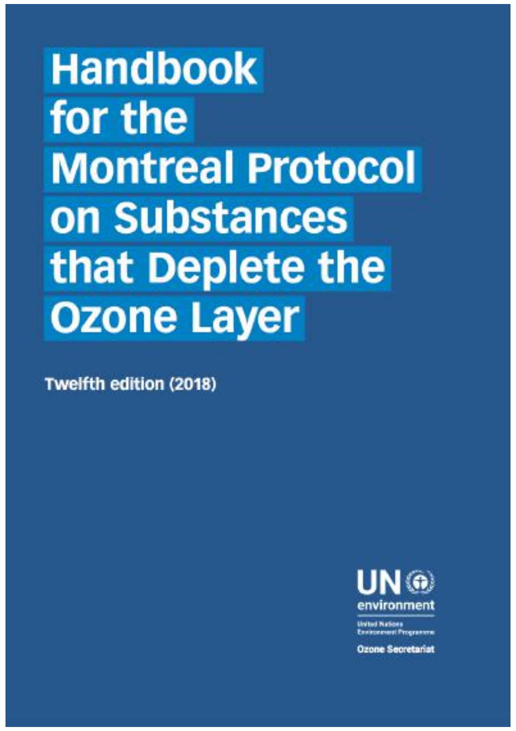
Solomon, S.; Garcia, R. R.; Rowland, F. S.; Wuebbles, D. J. *Nature* **1986**, *321*, 755.
Molina, M. J.; Tso, T.-L.; Molina, L. T.; Wang, F. C.-Y. *Science* **1987**, *238*, 1253.
Molina, M. J.; Zhang, R.; Wooldridge, P. J.; McMahon, J. R.; Kim, J. E.; Chang, H. Y.; Beyer, K. D. *Science* **1993**, *261*, 1418.

The Montreal Protocol (1987)

> “The Parties to this protocol [are]…determined to protect the ozone layer by…control[ling] equitably
> total global emissions of substances that deplete it, with the ultimate objective
> of their elimination ***on the basis of developments in scientific knowledge***…”

from the ***Preamble***

- deadlines for **stop in production and consumption** of ODS
- established scientific committees to **evaluate progress** and **modify protocol**
- **delegated funds** to assist developing countries in meeting standards



Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer

Twelfth edition (2018)

UN environment

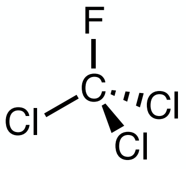
Ozone Secretariat

The only United Nations environmental aggreement ratified by *every country in the world* (as of 2009)

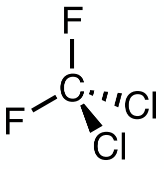
Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer, Thirteenth Edition (2009). UNEP Ozone Secretariat.

Ozone depleting substances and timelines for phaseout

Article A, Group I: **CFCs**



CFC-11



CFC-12

1.0	1.0

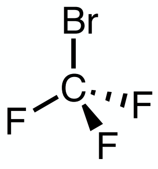
ozone depleting potential (ODP)

100% reduction for

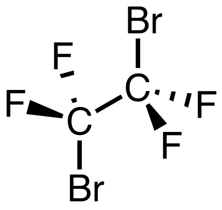
developed countries 1996

developing countries 2010

Article A Group II: **Halons**



Halon-1301



Halon-2402

10.0	6.0

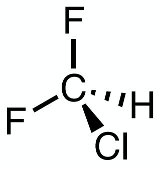
ozone depleting potential (ODP)

100% reduction for

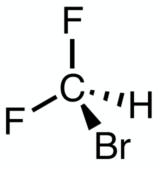
developed countries 1994

developing countries 2010

Article C Group I/II: **HCFCs/HBFCs**



HCFC-22



HBFC-22B1

0.055	0.74

ozone depleting potential (ODP)

100% reduction for

developed countries 2020

developing countries 2030

Handbook for the Montreal Protocol on Substances that Deplete the Ozone Layer, Thirteenth Edition (2009). UNEP Ozone Secretariat.

The Ozone Secretariat

An **administrative body** within the United Nations Environment Programme (UNEP) that **implements the Montreal Protocol**

- founded in 1991 in Nairobi, Kenya
- collects reporting data from governement agencies
- supervises the **Assessment Panels**

Scientific Assessment Panel (**SAP**)

assesses status of ozone layer depletion and current atmospheric science

Technology and Economic Assistance Panel (**TEAP**)

investigates new alternative technologies

Environmental Effects Assessment Panel (**EEAP**)

assesses effects of ozone depletion and remediation efforts

International Treaties and Cooperation about the Protection of the Stratospheric Ozone Layer. EPA. https://https://www.epa.gov/ozone-layer-protection/international-treaties-and-cooperation-about-protection-stratospheric-ozone

Amendments to the Montreal Protocol

London (1990) accelerated CFCs/halons/CCl_4 phaseout (**2000**), extended to CCl_3CH_3

Copenhagen (1992) accelerated CFCs/halons/CCl_4 phaseout (**1996**), extended to hydrochlorofluorocarbons (HCFC)

Montreal (1997) established phaseout of MeBr to **2005** (developed)/ **2015** (developing countries)

Beijing (1999) restricted trade/production of HCFCs, extended to $BrClCH_2$ (**2004**)

Kigali (2016) extended to hydrofluorocarbons (HFC, weak ODS, strong greenhouse gas)

Parties to the Montreal Protocol to meet in Rome, Italy from 4-8 November 2019. UN environment programme ozone secretariat. http://ozone.unep.org.
Amendments to the Montreal Protocol. International Treaties and Cooperation about the Protection of the Stratospheric Ozone Layer. http://EPA.gov

Annual meeting of the parties (MOP)

London (1990) accelerated CFCs/halons/CCl_4 phaseout (**2000**), extended to CCl_3CH_3

Copenhagen (1992) accelerated CFCs/halons/CCl_4 phaseout (**19** C)

Annual meetings involve documenting **compliance**,

reevaluating the state of the ozone layer,

and **proposing** amendments

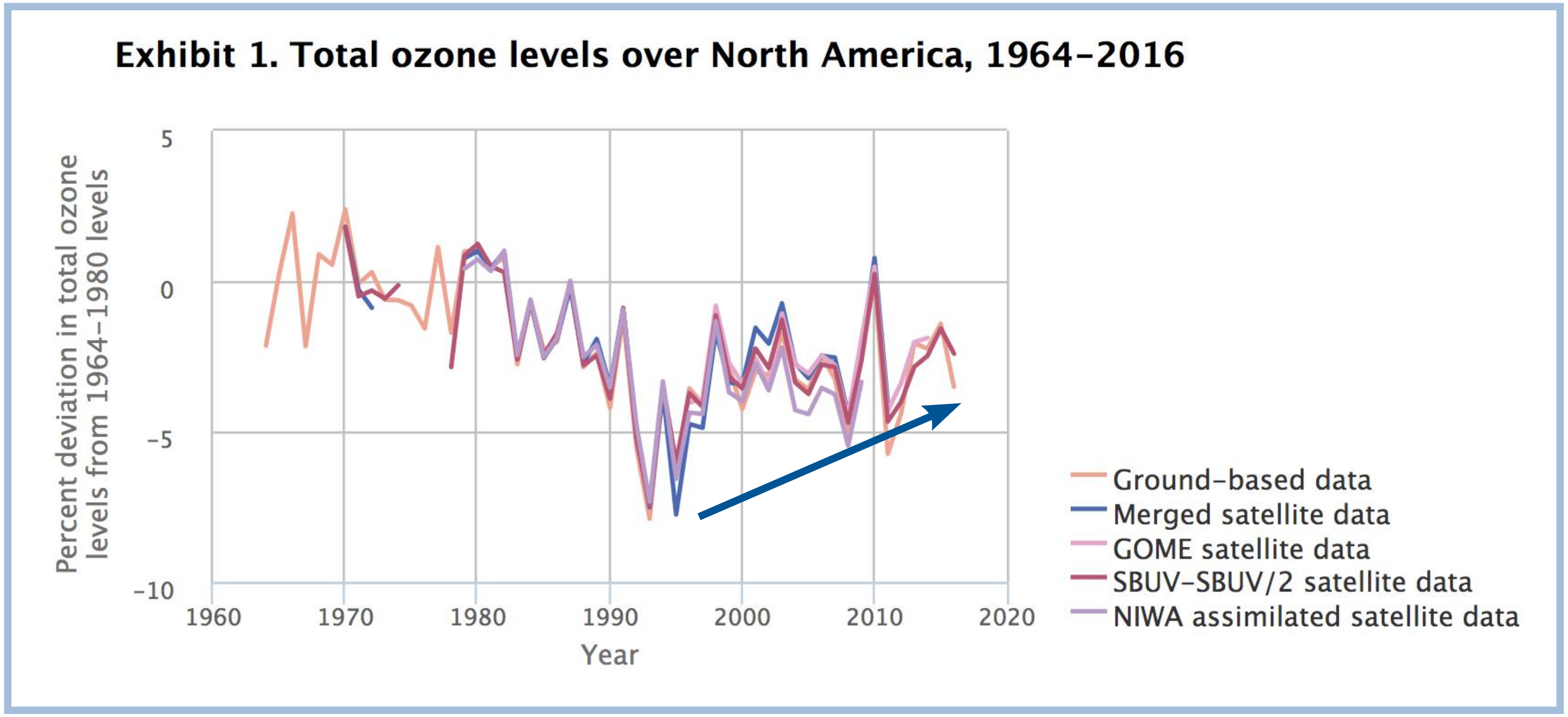
2005 (

Beijing (1999) restricted trade/production of HCF

Kigali (2016) extended to hydrofluorocarbons (HFC, weak ODS, strong greenhouse gas)

Parties to the Montreal Protocol to meet in Rome, Italy from 4-8 November 2019. UN environment programme ozone secretariat. http://ozone.unep.org.
Amendments to the Montreal Protocol. International Treaties and Cooperation about the Protection of the Stratospheric Ozone Layer. http://EPA.gov

Has the Montreal Protocol proven effective?



The ozone layer is recovering!

Full recovery expected by 2050

(Antarctic ozone hole expected to recover by 2060)

"Thirty years on, what is the Montreal Protocol doing to protect the ozone?" UN environment programme. 15 Nov. 2019. http://www.unenvironment.org/
Stratospheric Ozone Levels Over North America. United States Environmental Protection Agency (EPA). http://cfpub.EPA.gov/roe/indicator.cfm?i=18.

Compliance through the mid-2010's appears promising

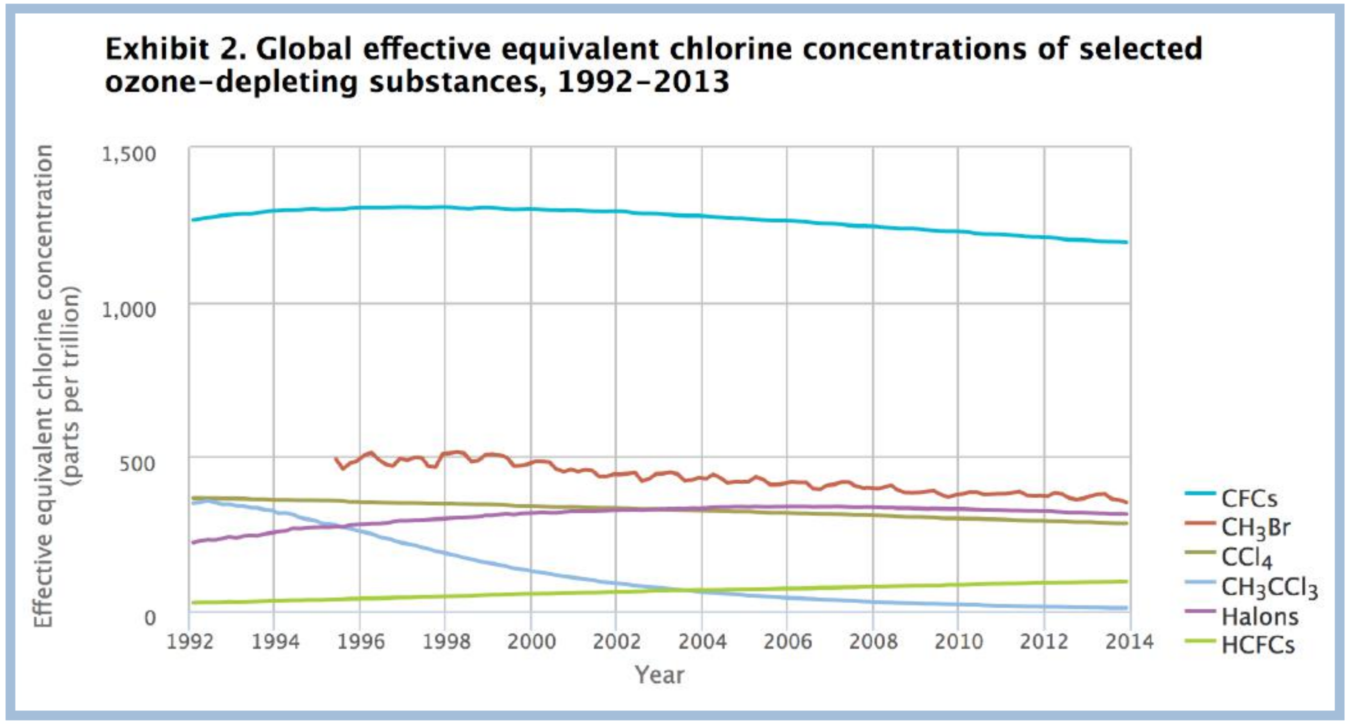


Exhibit 2. Global effective equivalent chlorine concentrations of selected ozone-depleting substances, 1992–2013

ODS levels in the atmosphere have

decreased or leveled off

in accordance with Montreal Protocol

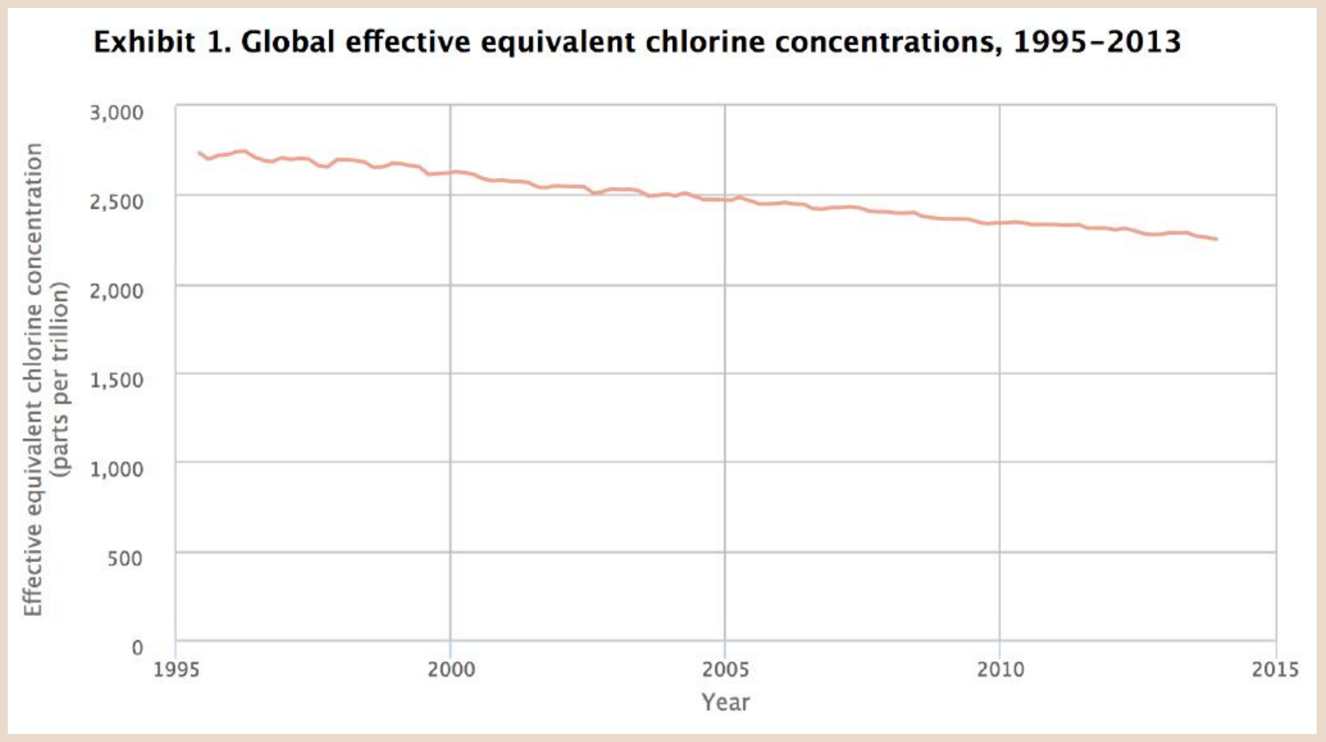


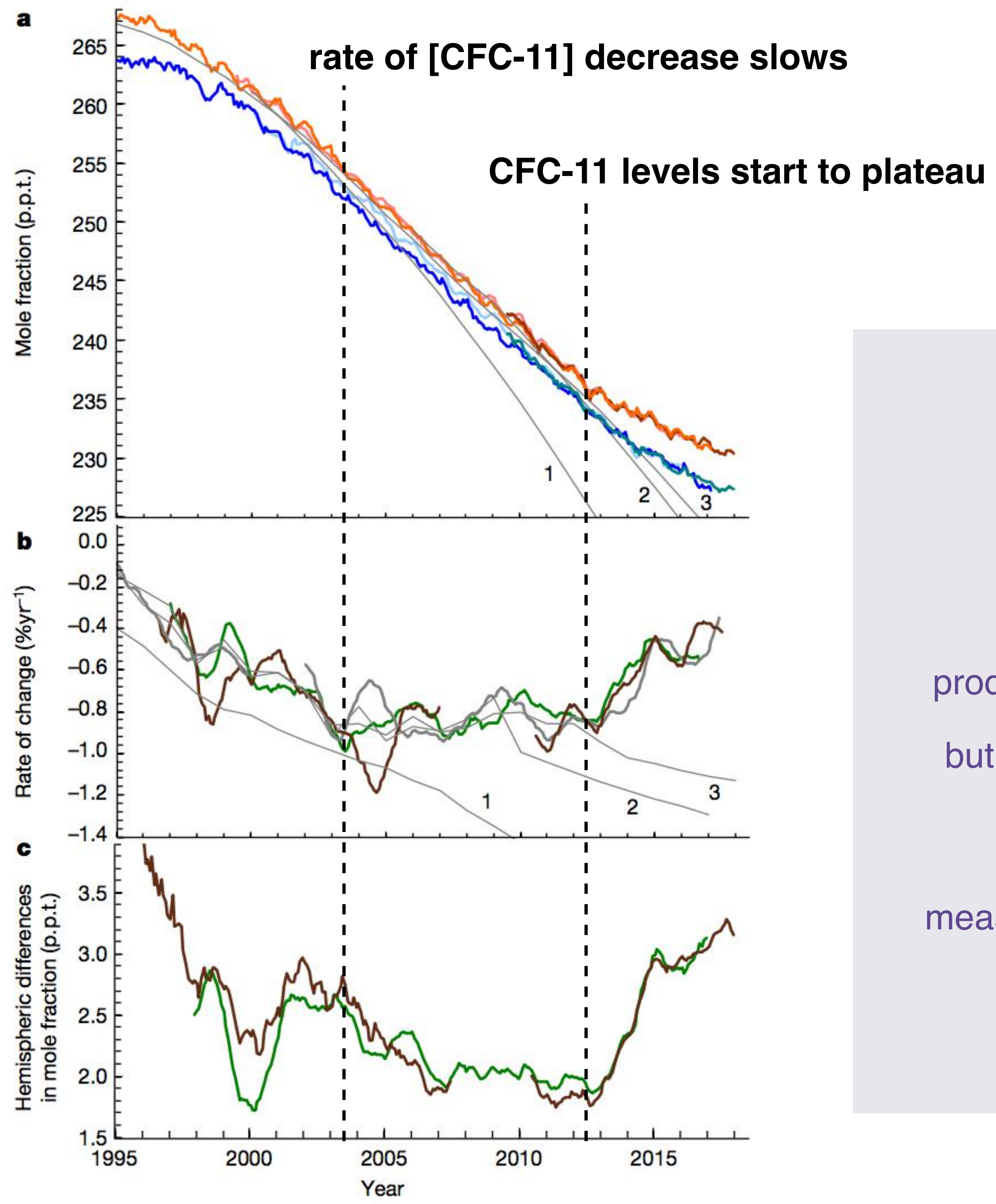
Exhibit 1. Global effective equivalent chlorine concentrations, 1995–2013

Total amount of global atmospheric chlorine

is **decreasing steadily**

Concentrations of Ozone-Depleting Substances. Exhibits 1 and 2. United States EPA. https://cfpub.epa.gov/roe/indicator.cfm?i=11#1

An unexpected rise in CFC-11 emissions



rate of [CFC-11] decrease slows

CFC-11 levels start to plateau

Fig. 1 | Observations of atmospheric CFC-11 over time.

promising CFC-11 reduction trends

are **threatening to reverse**

production **reported as nearly zero** since 2006,

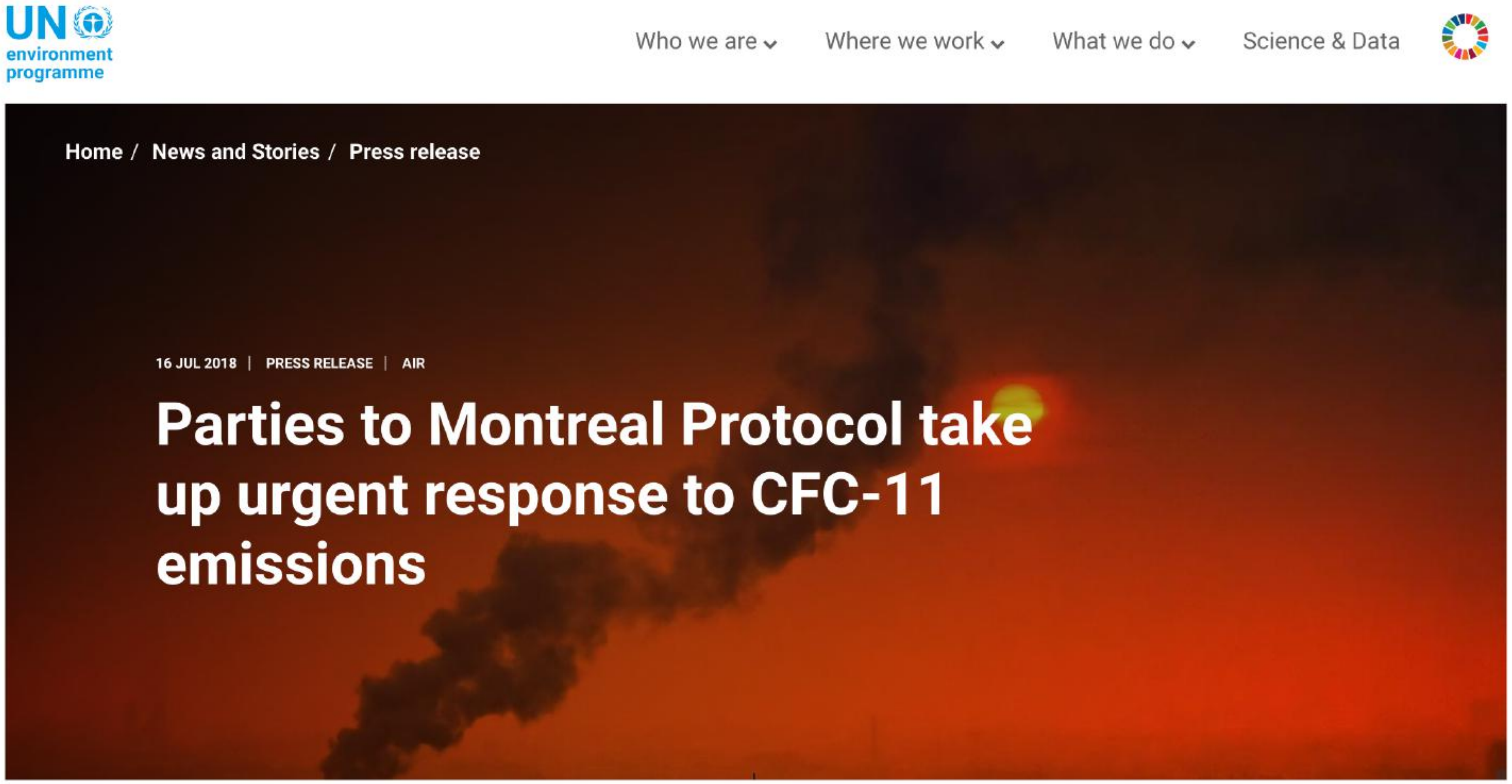
but emissions consistent with **new production**

measurements **confirmed in both hemispheres**

(not an artifact of measurement devices)

Montzka, S. A. *et al. Nature* **2018**, *557*, 413.

A call to action



Home / News and Stories / Press release

16 JUL 2018 | PRESS RELEASE | AIR

Parties to Montreal Protocol take up urgent response to CFC-11 emissions

40th Open-Ended Working Group of the Montreal Protocol (OEWP) **reviewed scientific data**

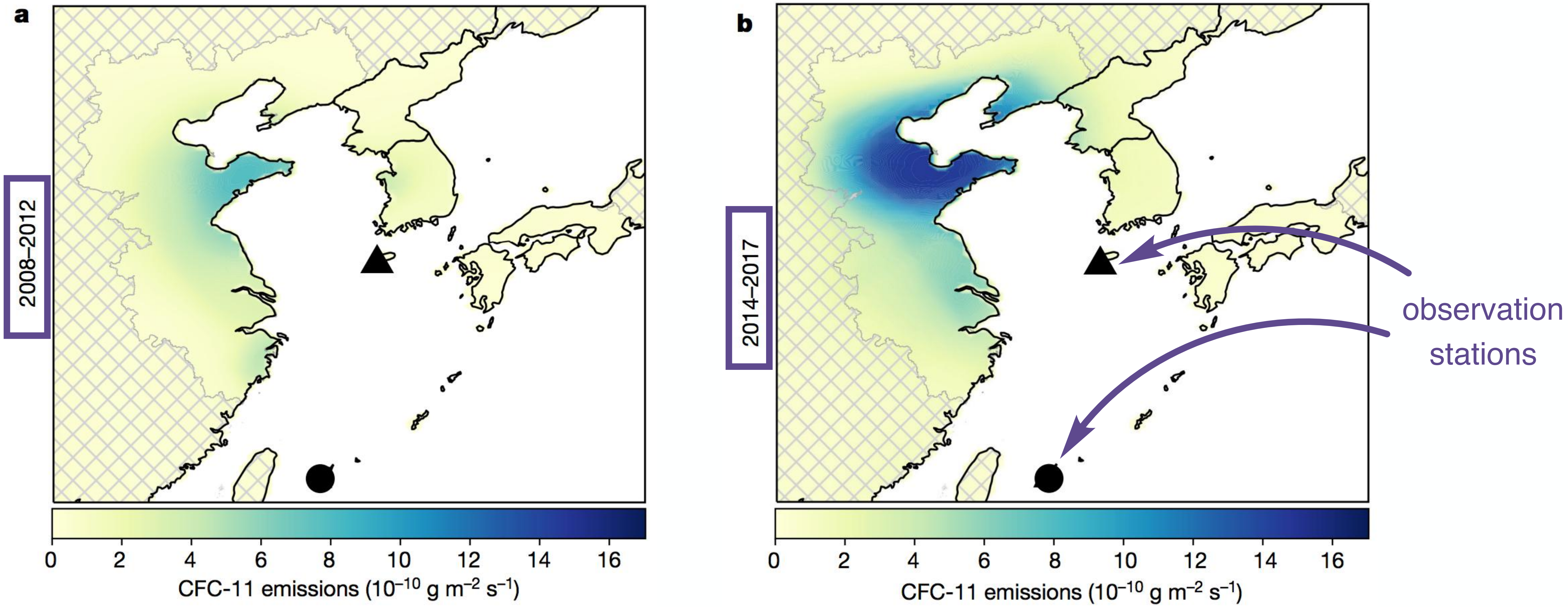
and **provided recommendation** to 30th Annual Meeting of the Parties (MOP)

to call for **thorough investigation of new CFC-11 production sources**

Ozone Secretariat Press Release. UN Environment Programme. https://www.unenvironment.org/news-and-stories/press-release/parties-montreal-protocol-take-urgent-response-cfc-11-emissions (accessed Feb 29, 2020).

Multinational research collaboration locates CFC-11 emission source

Chinese provinces of Shandong and Hebei identified as two sites of emission



observation stations

- at least 40-60% of observed increase in CFC-11 emissions
- emissions are observed at **site of use (e.g., spray foam insulation)** ***not production***

Rigby, M. *et al. Nature* **2019**, *569*, 546.

The world responded quickly to the ozone crisis

early 1970's

Crutzen and others describe mechanisms of ClO_x cycle

1974

Molina and Rowland propose CFCs as source of Cl

1985

Shanklin reports formation of the Antarctic ozone hole

1985

Vienna Convention signed

1987

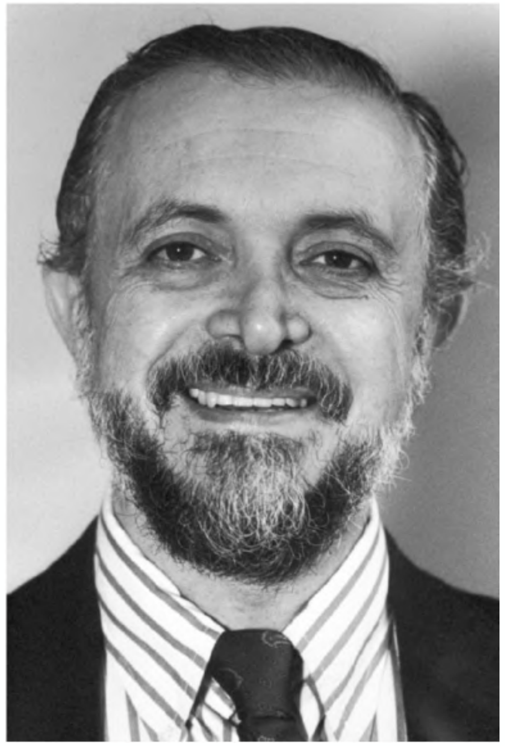
Montreal Protocol signed

1995

Nobel Prize awarded

The 1995 Nobel Prize in Chemistry

Paul J. Crutzen



Mario J. Molina

F. Sherwood Rowland

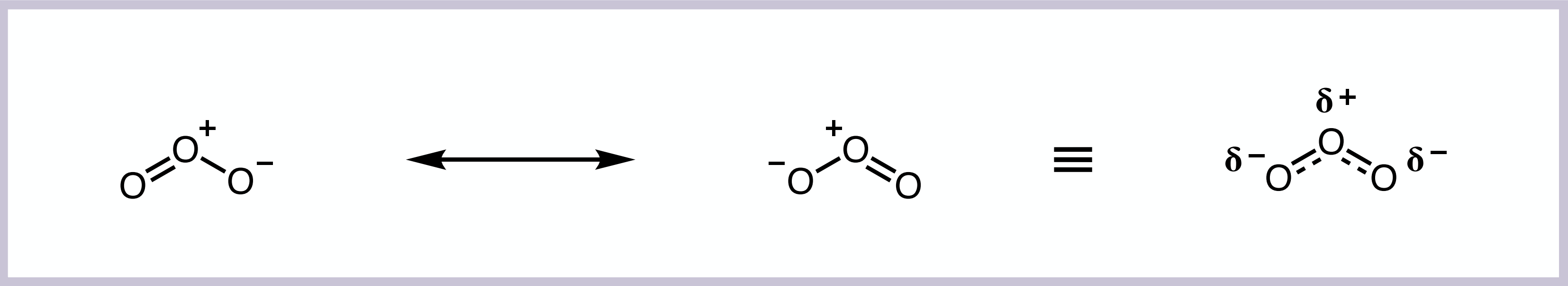
The Nobel Prize in Chemistry 1995 was awarded jointly to

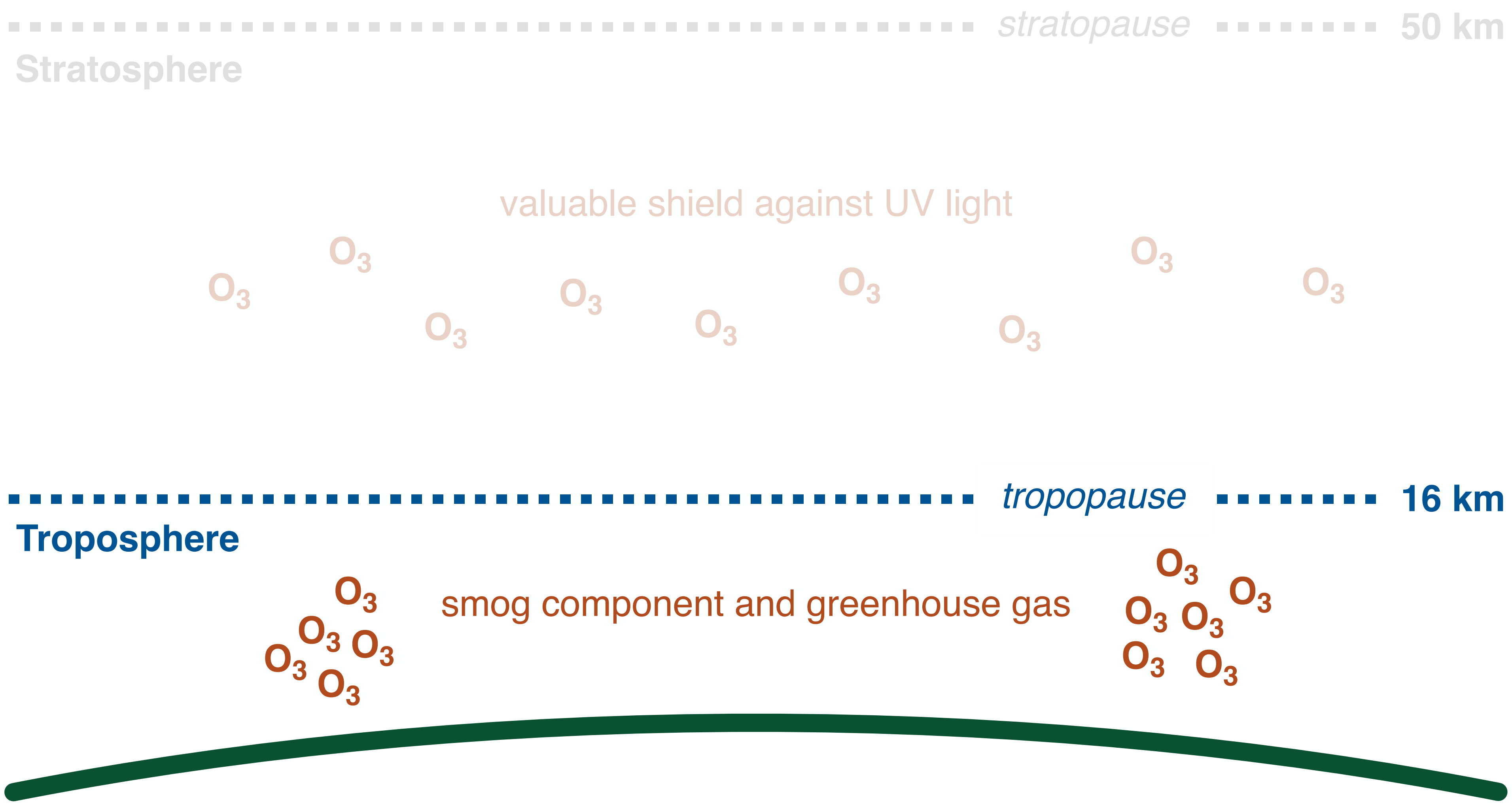
Paul J. Crutzen, Mario J. Molina and F. Sherwood Rowland

"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."

The Nobel Prize in Chemistry 1995. The Nobel Prize. http://www.nobelprize.org/prizes/chemistry/1995/summary/ (accessed Feb 15, 2020).

Ozone: good up high but bad nearby





stratopause 50 km

Stratosphere

valuable shield against UV light

O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3

tropopause **16 km**

Troposphere

smog component and greenhouse gas

O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3 O_3

Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Washington, DC, **2009**; 7-15.

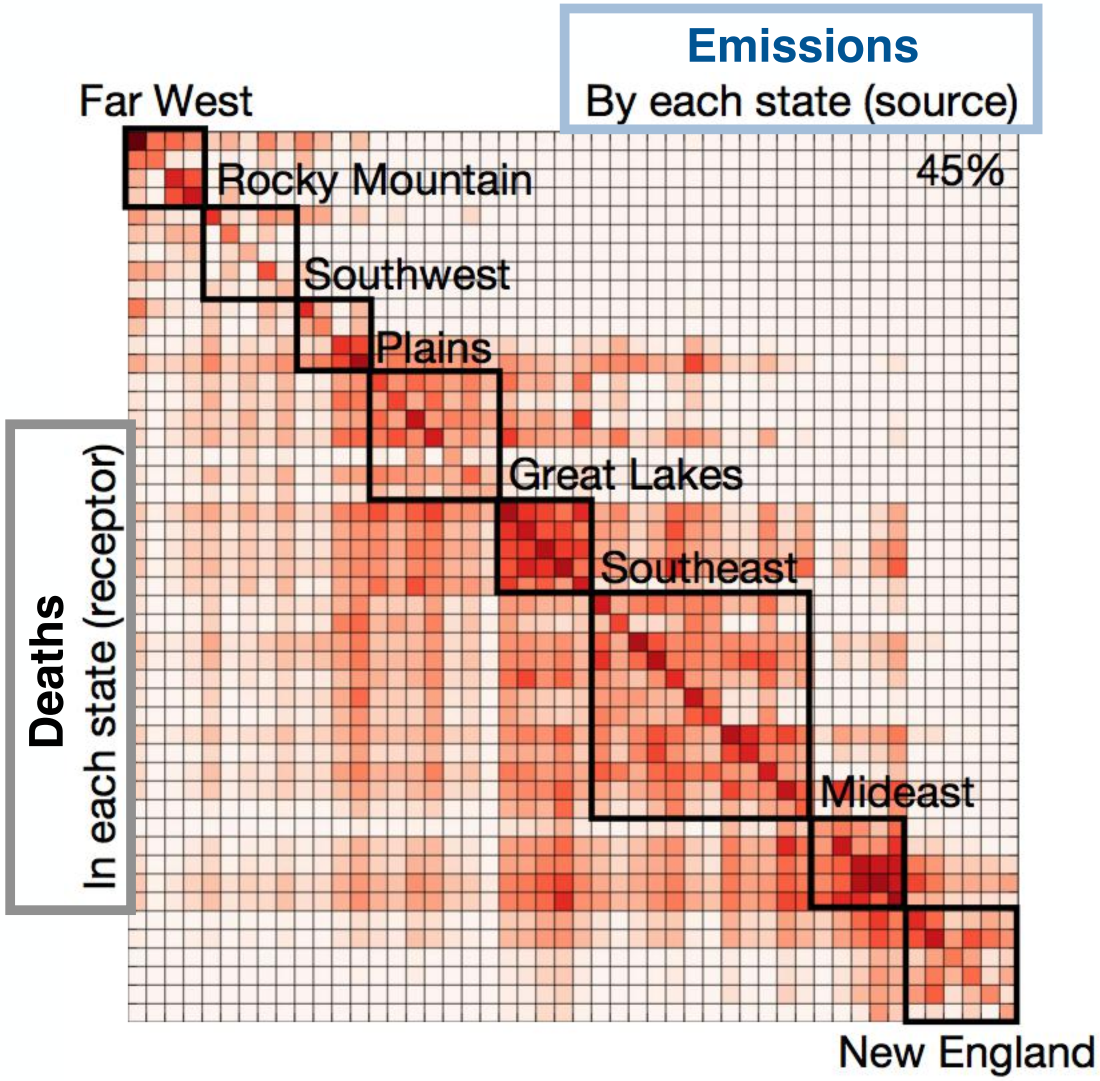
The cross-state effects of tropospheric ozone pollution

Smog

“smoke” + “fog”

ozone and **fine pariculate matter** are deadliest components

responsible for 90% of total air pollution-related mortality



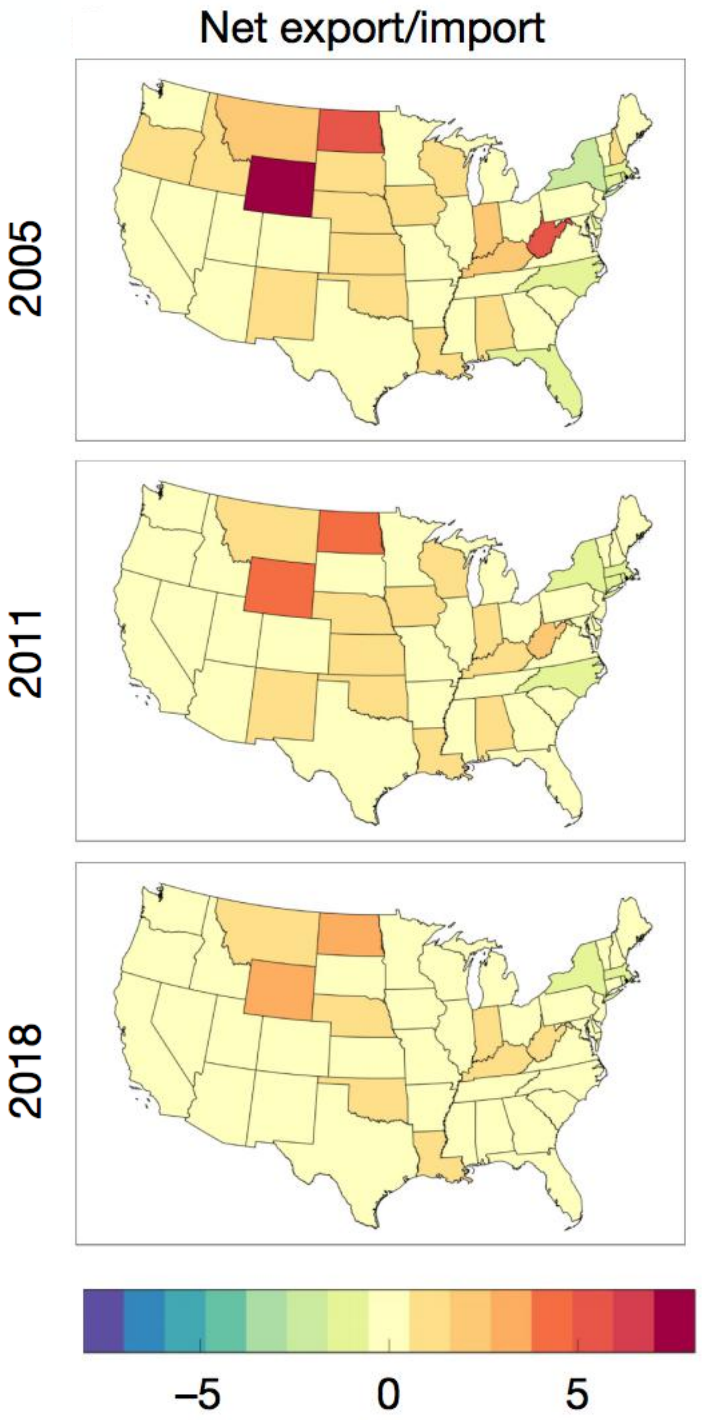
Lack of symmetry about the diagonal indicates

that some state are **“exporters of early death”** and

some are **“importers of early death”**

Dedoussi, I. C.; Eastham, S. D.; Monier, E.; Barrett, S. R. H. *Nature*, **2020**, *578*, 261.

The cross-state effects of tropospheric ozone pollution



Biggest exporters: Wyoming, North Dakota, West Virgina

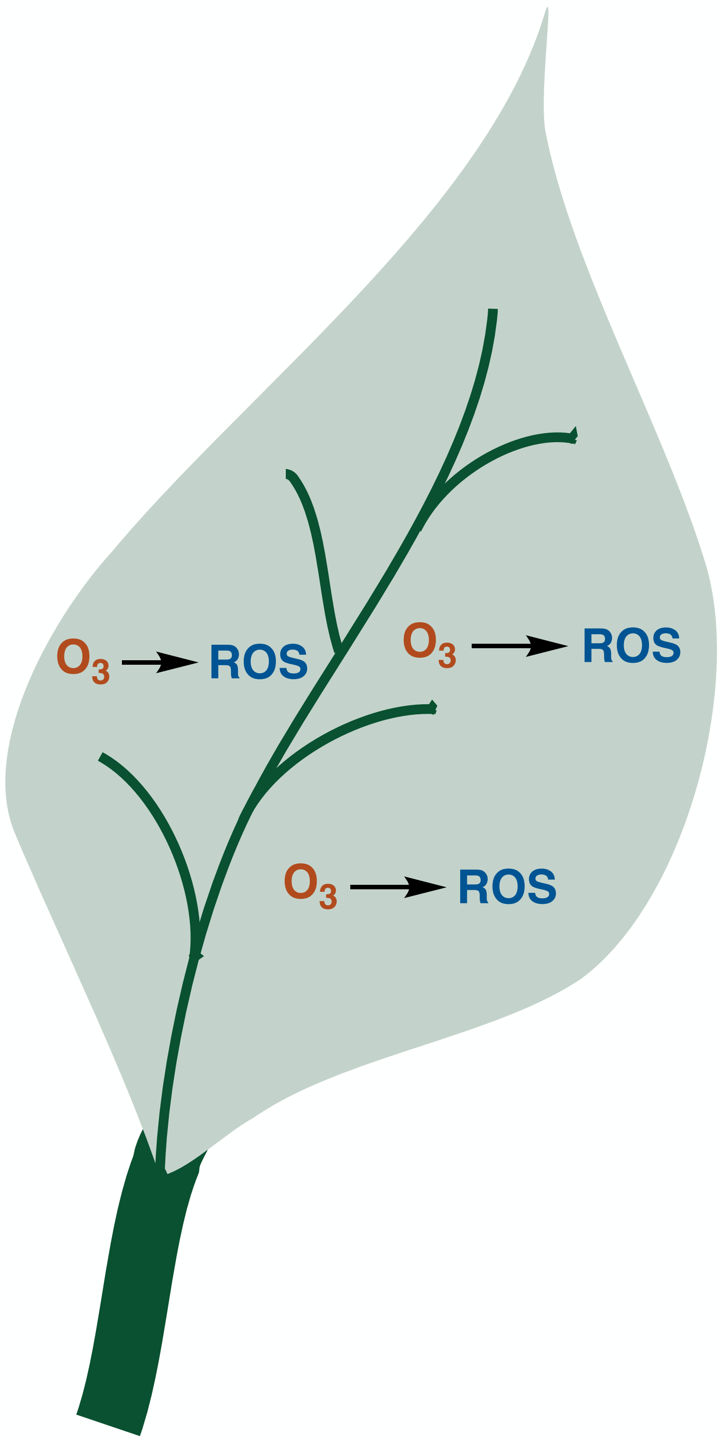
Biggest importers: New York and Massachusetts

fine particulate matter 8x more deadly, ozone travels farther

40% of combustion-emission-related early deaths cross state lines

Dedoussi, I. C.; Eastham, S. D.; Monier, E.; Barrett, S. R. H. *Nature*, **2020**, *578*, 261.

Tropospheric ozone decreases crop yields



- reactive oxygen species (**ROS**) trigger antioxidant defense system
- resultant decrease in CO_2 consumption **lowers biomass production**

calculated economic loss of $6.3-12.0 billion globally in 2000

wheat, rice, maize, soybean

bulk of losses occurred in India (22%) and China (21%)

Booker, F., *et al. J. Integr. Plant Biol.* **2009**, *51*, 337.
McCrady, J. K.; Anderson, C. P. *Environ. Pollut.* **2000**, *107*, 465.
Van Dingenen, R., *et al. Atmos. Environ*. **2009**, *43*, 604.
for a review of the effects on India's agricultural industry, see: Singh, A. A.; Agrawal, S. B. *Environ. Sci. Pollut. Res.* **2017**, *24*, 4367.

Tropospheric ozone cycles

Topospheric ozone is *not* from the stratosphere (slow mixing, hence the long lifetimes of CFCs)

tropospheric ozone creation

$$NO_2 \xrightarrow{h\nu} NO + O \qquad h\nu \leq 420\text{ nm}$$

$$O + O_2 + M \longrightarrow O_3 + M$$

fossil fuel combustion is a major source of NO_x compounds

tropospheric ozone destruction

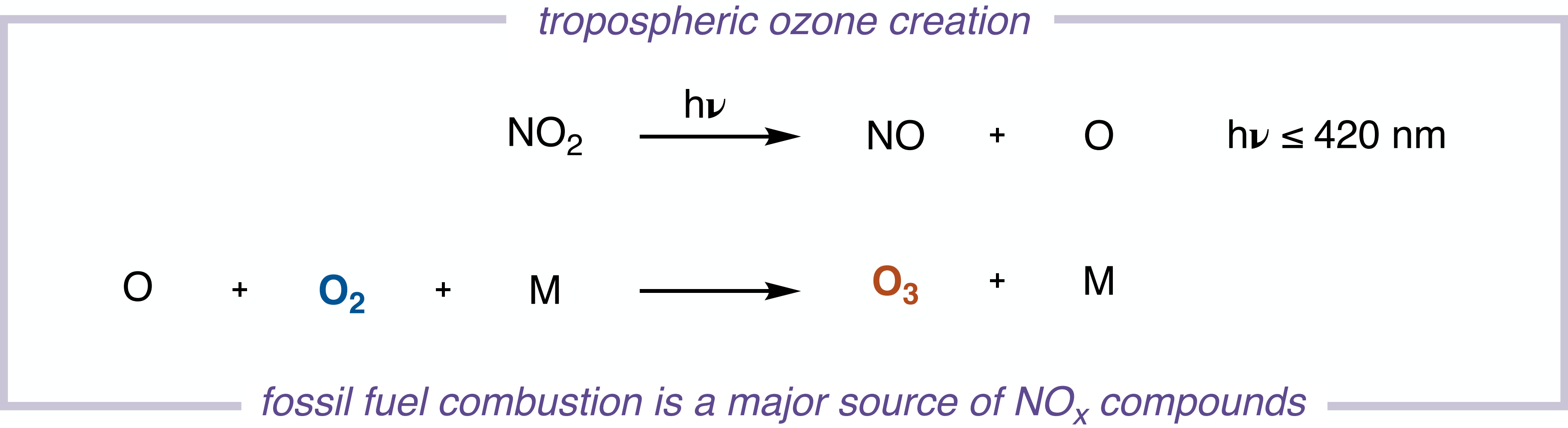
$$O_3 + NO \longrightarrow O_2 + NO_2$$

This cycle does not lead to the buildup of ozone, so what does?

Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Washington, DC, **2009**, 7-15.

Tropospheric ozone cycles

Topospheric ozone is *not* from the stratosphere (slow mixing, hence the long lifetimes of CFCs)

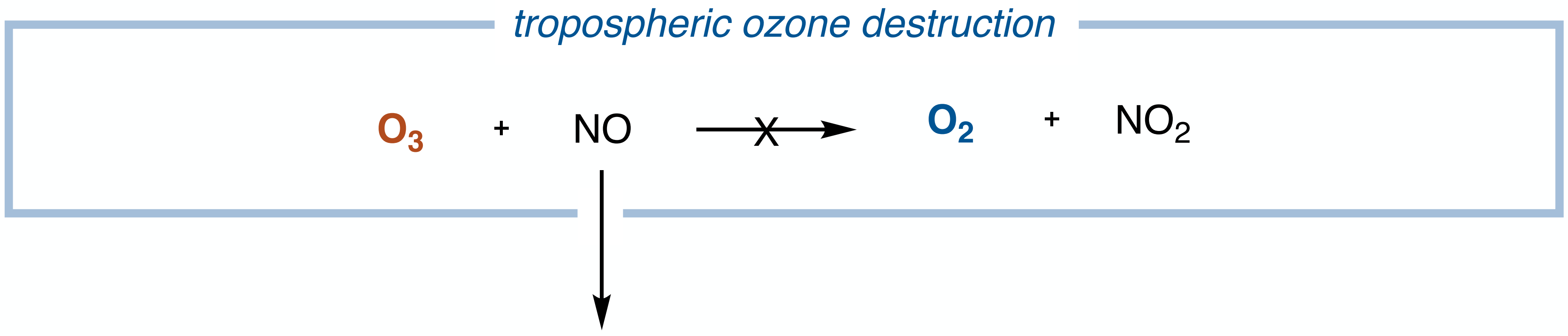


tropospheric ozone creation

$$NO_2 \xrightarrow{h\nu} NO + O \qquad h\nu \leq 420\ \text{nm}$$

$$O + O_2 + M \longrightarrow O_3 + M$$

fossil fuel combustion is a major source of NO_x compounds



tropospheric ozone destruction

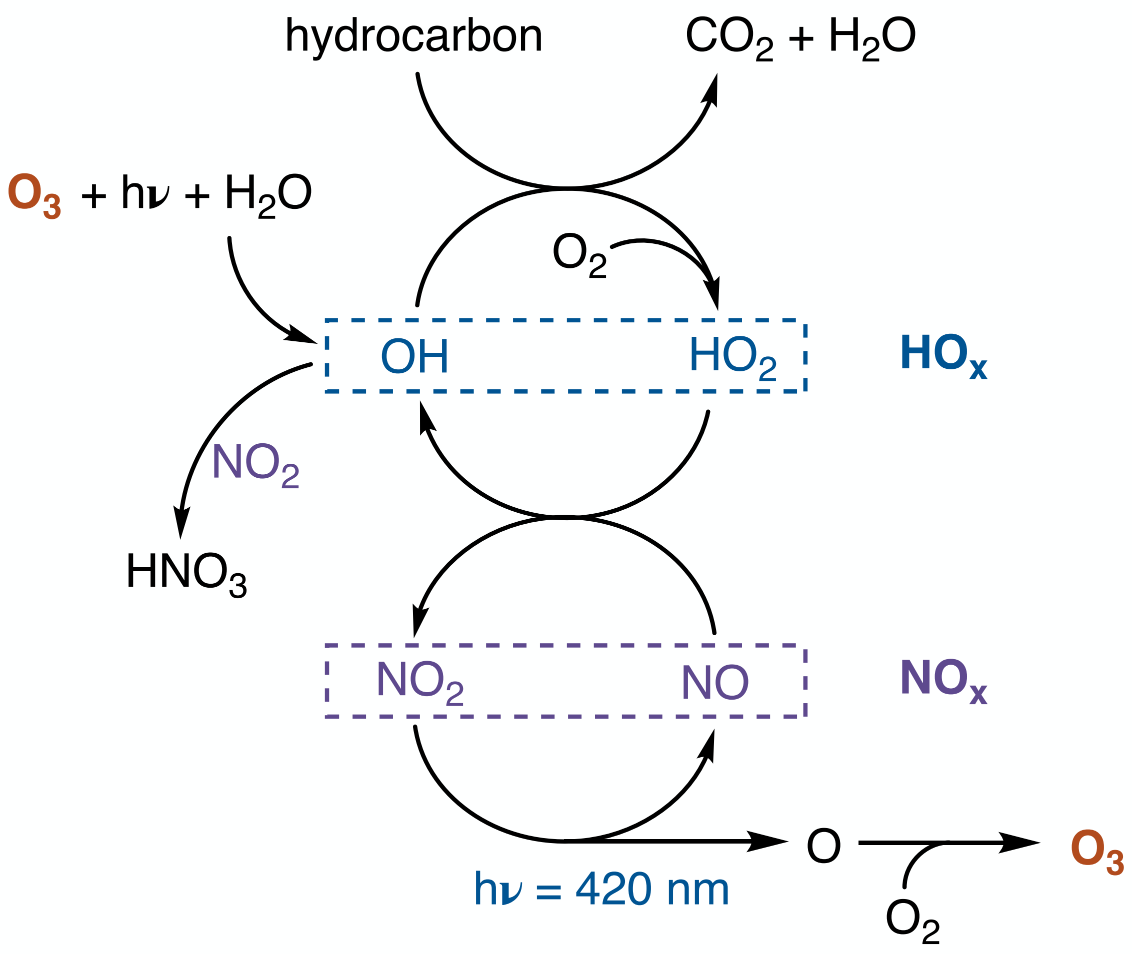
$$O_3 + NO \xrightarrow{\times} O_2 + NO_2$$

NO_2 *via alternative pathways*

Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Washington, DC, **2009**, 7-15.

HO_x and NO_x cycles are also relevant in the troposphere

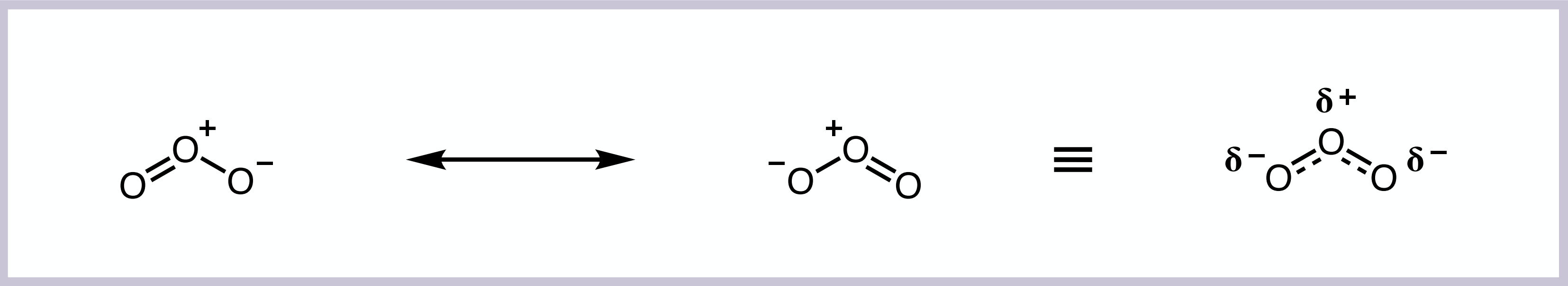
HO_x, NO_x, and volatile organic compound (VOC) pollution create positive feedback loop

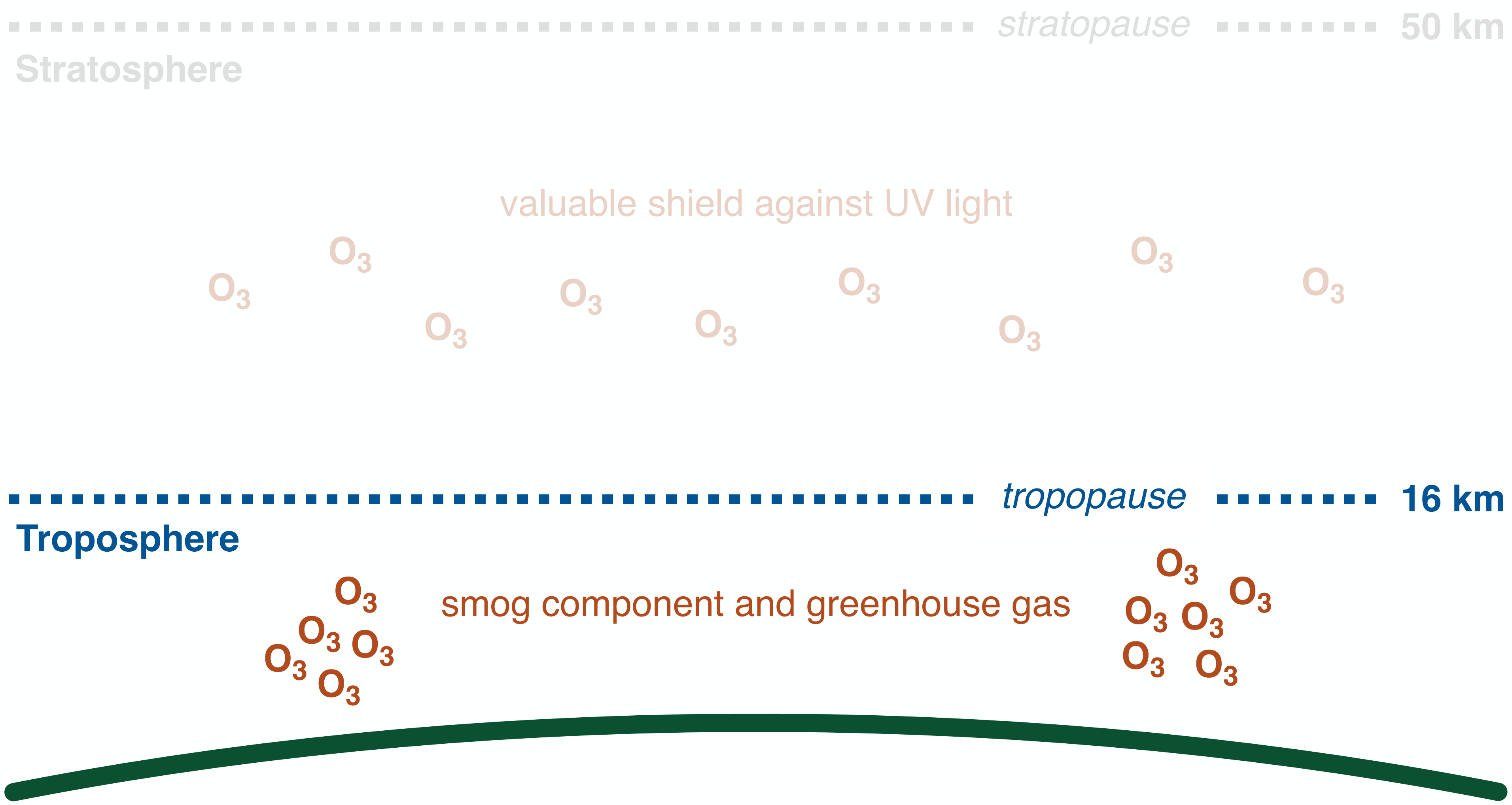


for net O_3 destruction, need to lower [NO] to 10 ppt (atmosphere of 30 ppb O_3)

Platt, U. Atmospheric Gas Phase Reactions. In *Surface Ocean-Lower Atmosphere Processes*; Le Quéré, C., Saltzman, E. S. Eds.; Geophysical Monograph Series 187; American Geophyscial Union: Washington, DC, **2009**, 7-15.

Ozone: good up high but bad nearby





stratopause 50 km

Stratosphere

valuable shield against UV light

tropopause **16 km**

Troposphere

smog component and greenhouse gas

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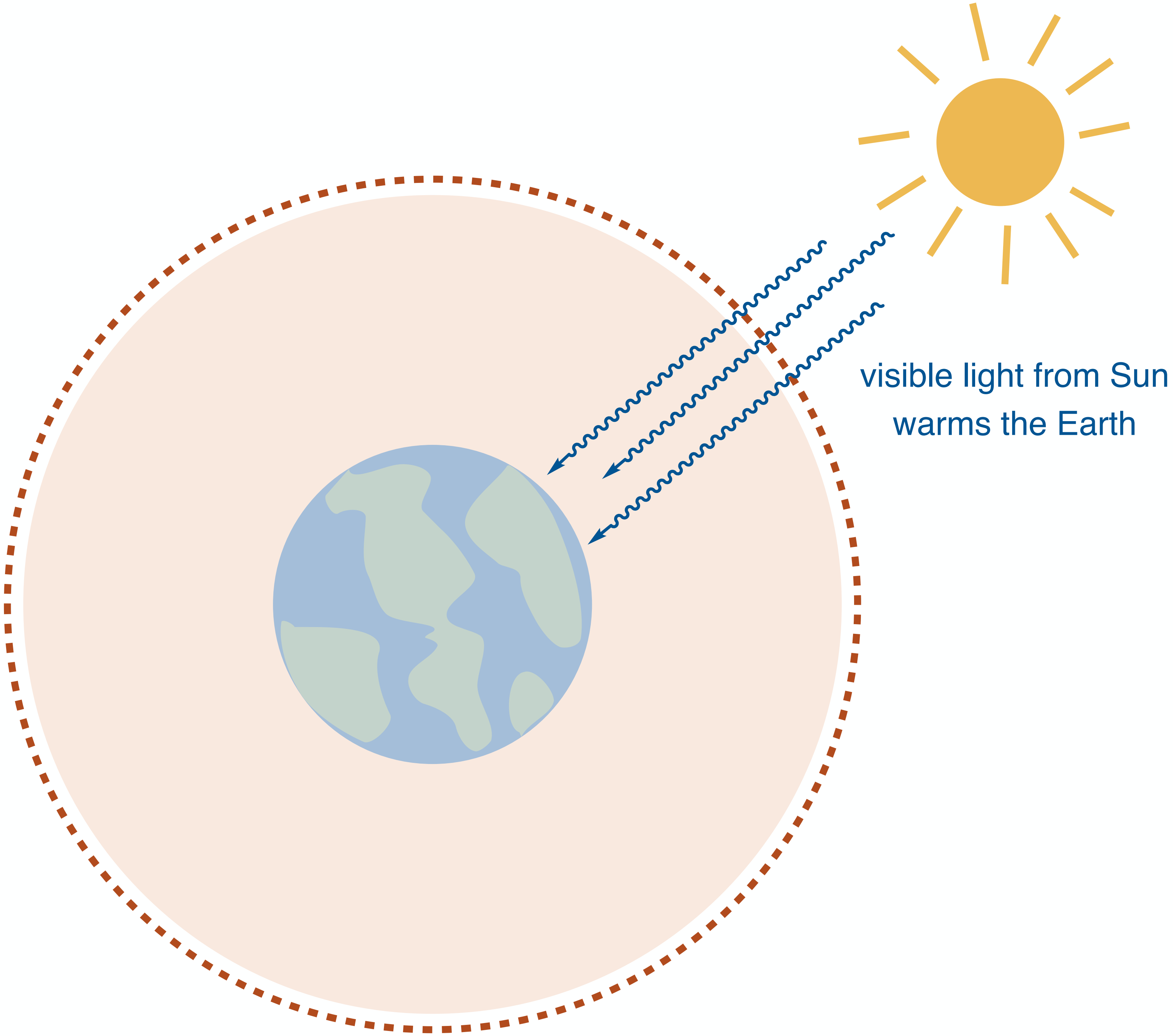

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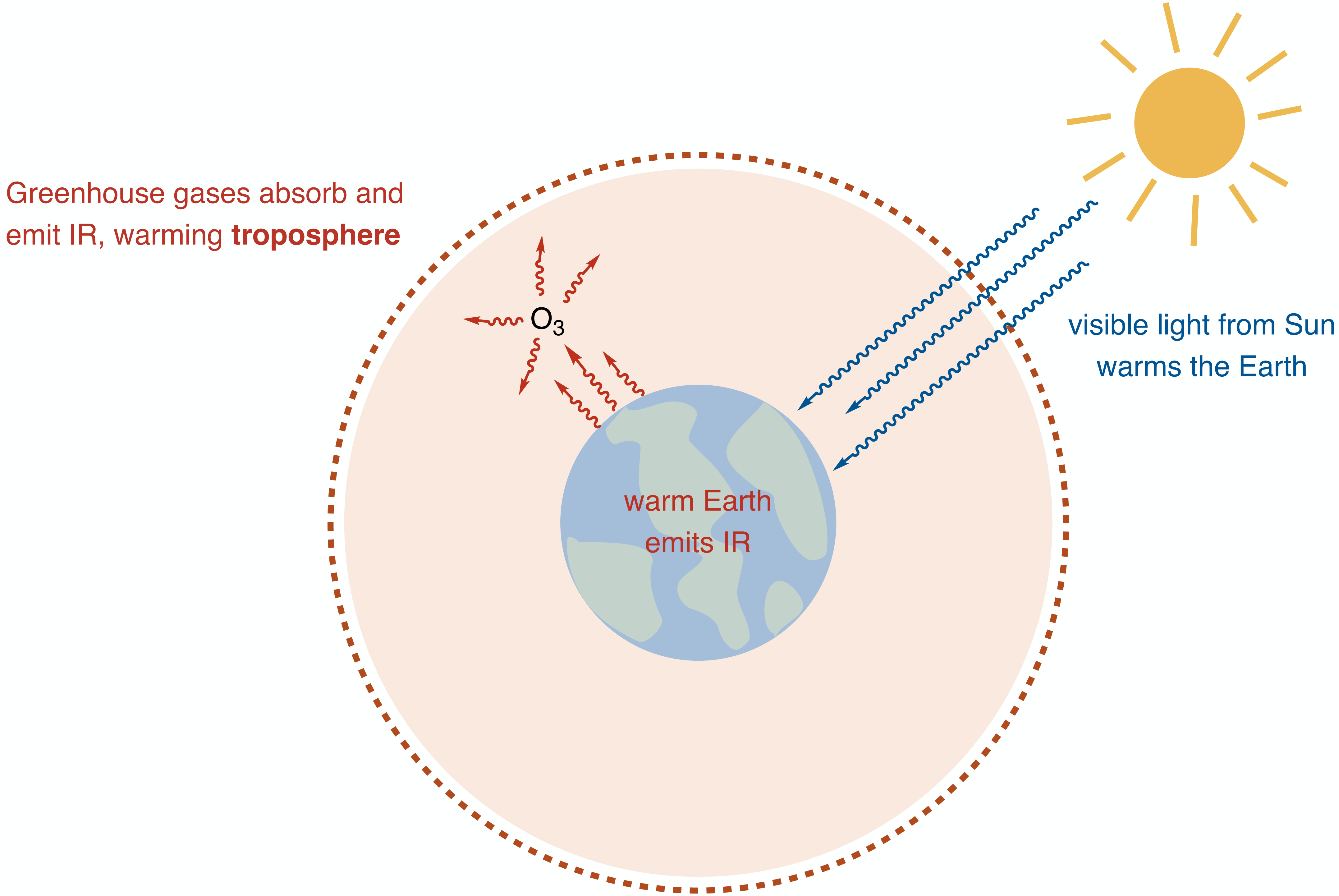

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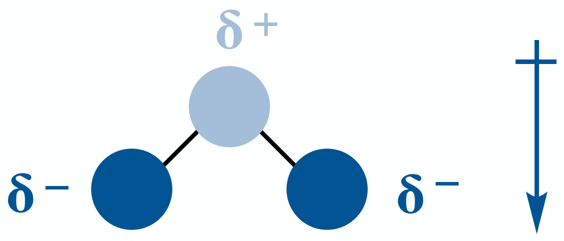
What makes a molecule a greenhouse gas?

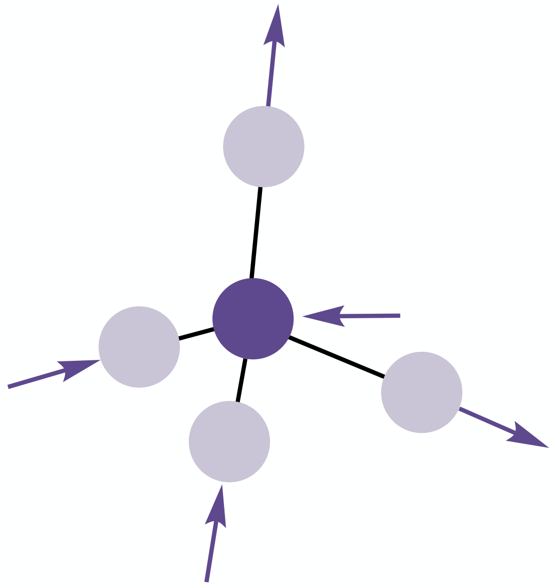
Greenhouse gases must absorb and emit infrared radiation

- need IR-active vibrational modes
- permanent or transient dipoles

ozone has a permanent dipole



CH_4 has a transient dipoles



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Factors determining the strength of a greenhouse gas

1. Global Warming Potential (GWP)

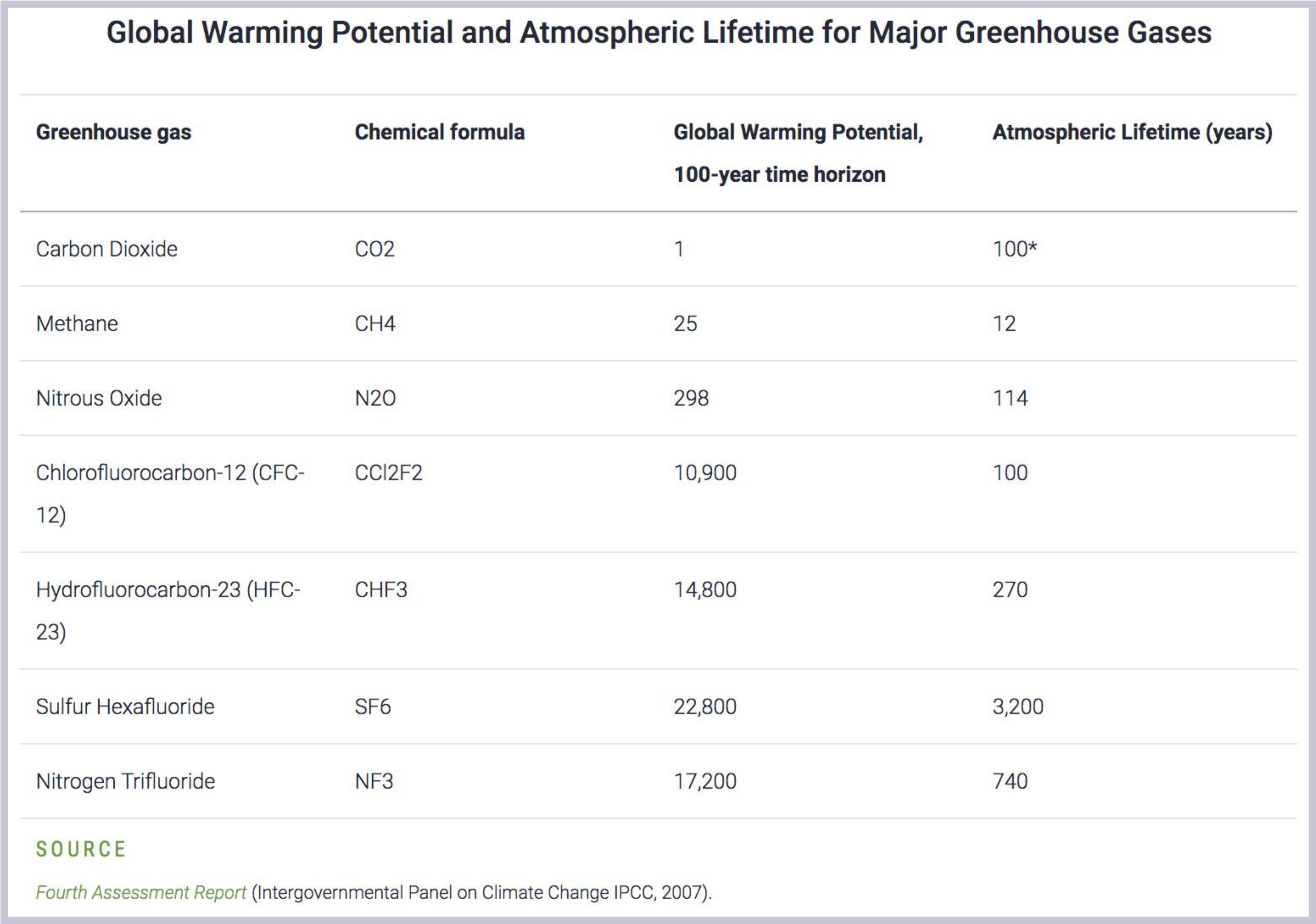
radiative effect of a unit of gas over a specified time, defined relative to CO_2

2. Atmospheric Lifetime

how long a gas survives in the troposphere (tie-breaker between equal GWP substances)

Main Greenhouse Gases. *Center for Climate and Energy Solutions*. https://www.c2es.org/content/main-greenhouse-gases/ (accessed March 3, 2020).

Is ozone the greenhouse gas we are worried about?



Global Warming Potential and Atmospheric Lifetime for Major Greenhouse Gases

Greenhouse gas	**Chemical formula**	**Global Warming Potential, 100-year time horizon**	**Atmospheric Lifetime (years)**
Carbon Dioxide	CO2	1	100*
Methane	CH4	25	12
Nitrous Oxide	N2O	298	114
Chlorofluorocarbon-12 (CFC-12)	CCl2F2	10,900	100
Hydrofluorocarbon-23 (HFC-23)	CHF3	14,800	270
Sulfur Hexafluoride	SF6	22,800	3,200
Nitrogen Trifluoride	NF3	17,200	740

SOURCE

Fourth Assessment Report (Intergovernmental Panel on Climate Change IPCC, 2007).

No, although the GWP is high (~1000), the short lifetime of *22 days* mitigates the concern

Energy Education: Greenhouse Gas. University of Calgary. https://energyeducation.ca/encyclopedia/Greenhouse_gas (accessed March 3, 2020).
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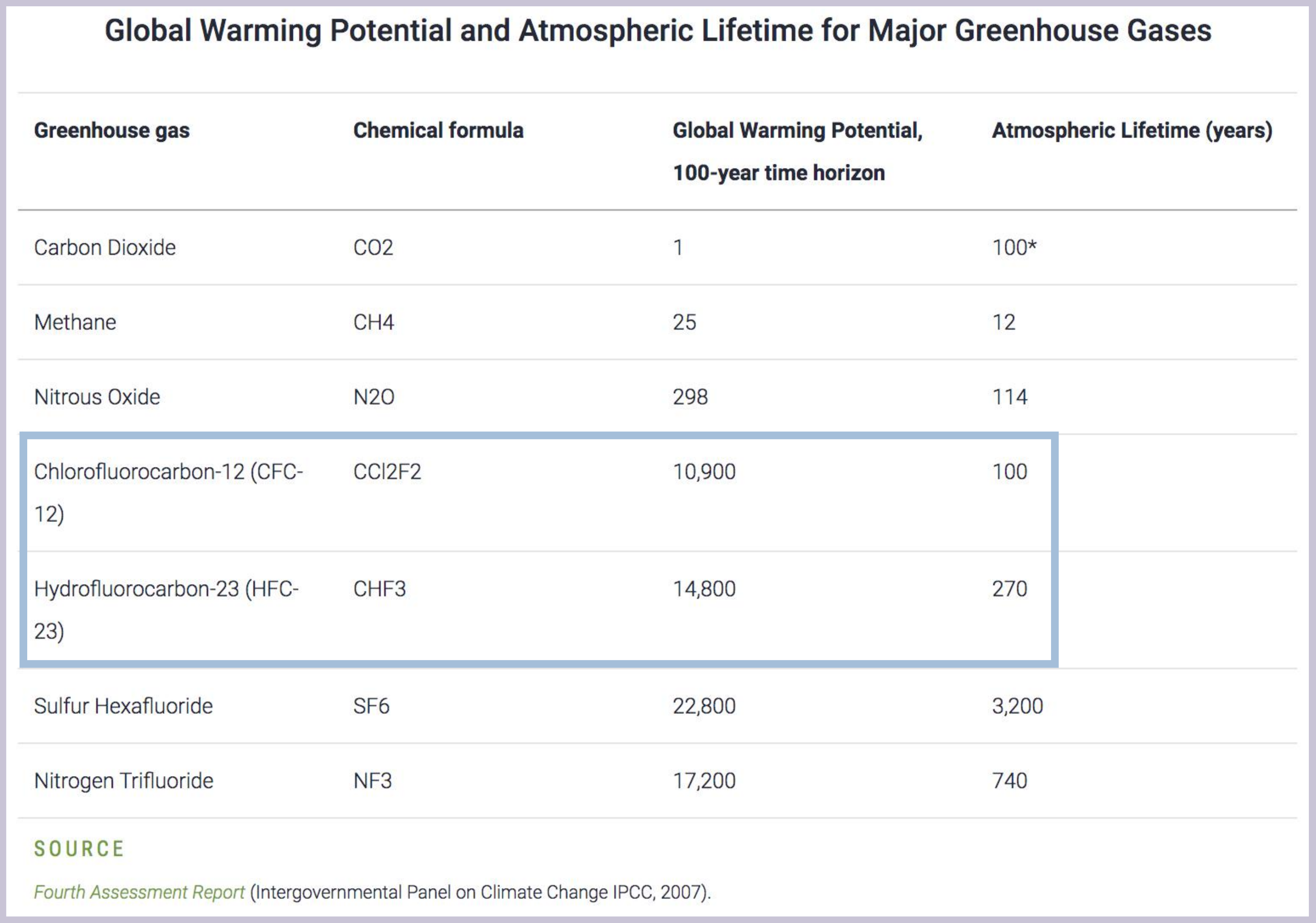

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ODS are much more worrisome greenhouse gases

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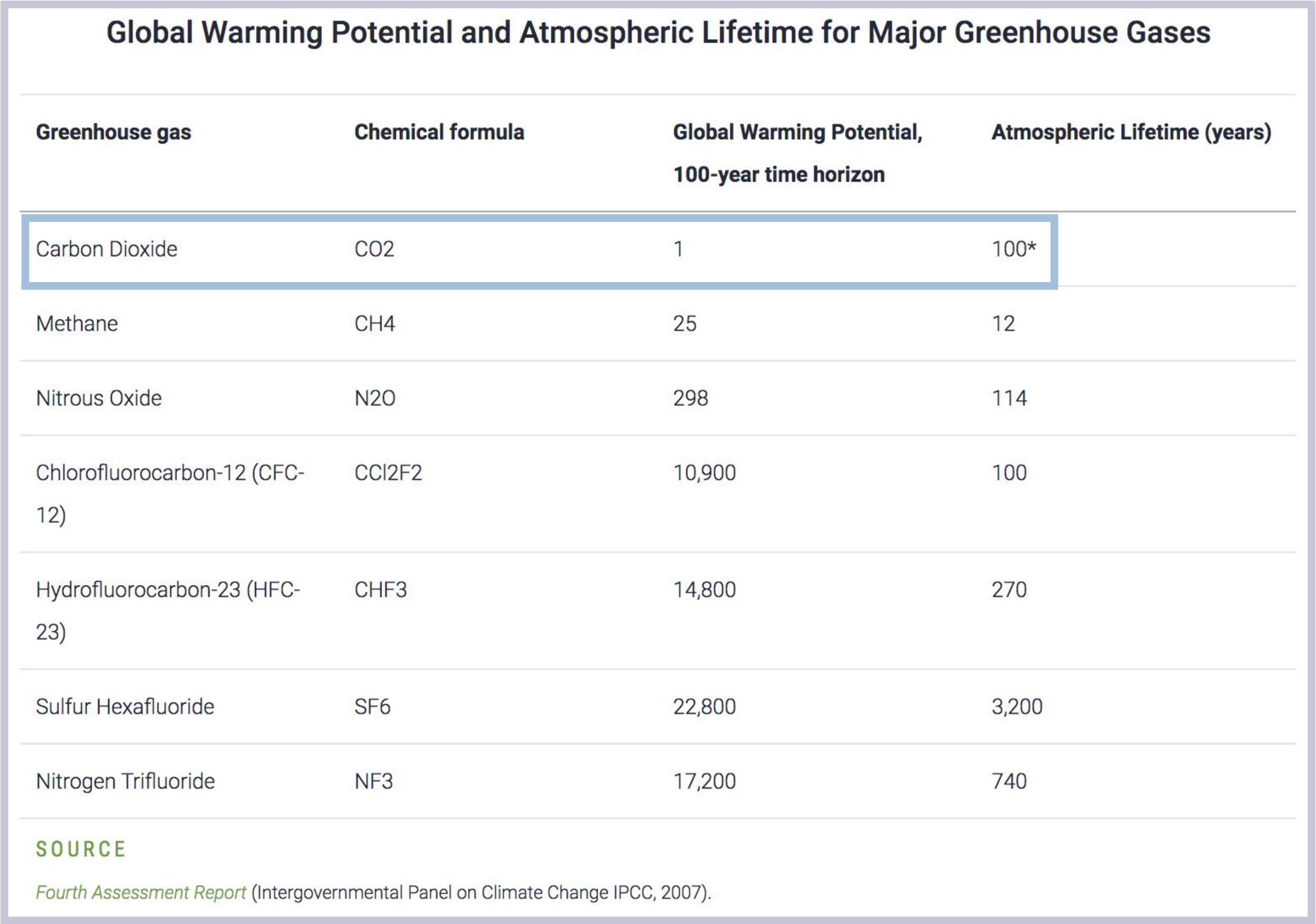

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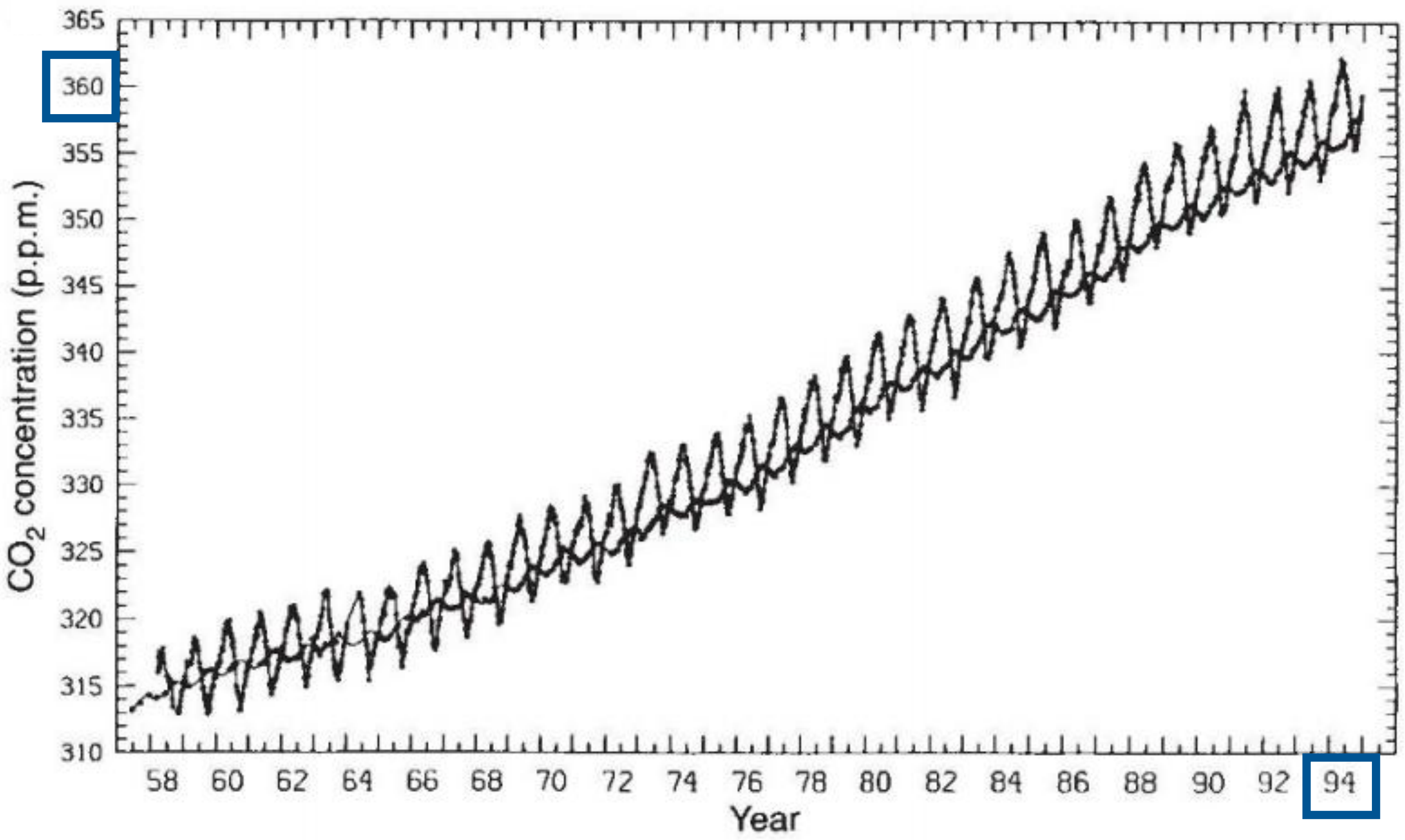
An atmospheric crisis in the troposphere



The world was told 25 years ago that CO_2 levels are rising anomalously…

Keeling, C. D.; Worf, T. P.; Wahlen, M.; van der Plicht, J. *Nature* **1995**, *375*, 666.

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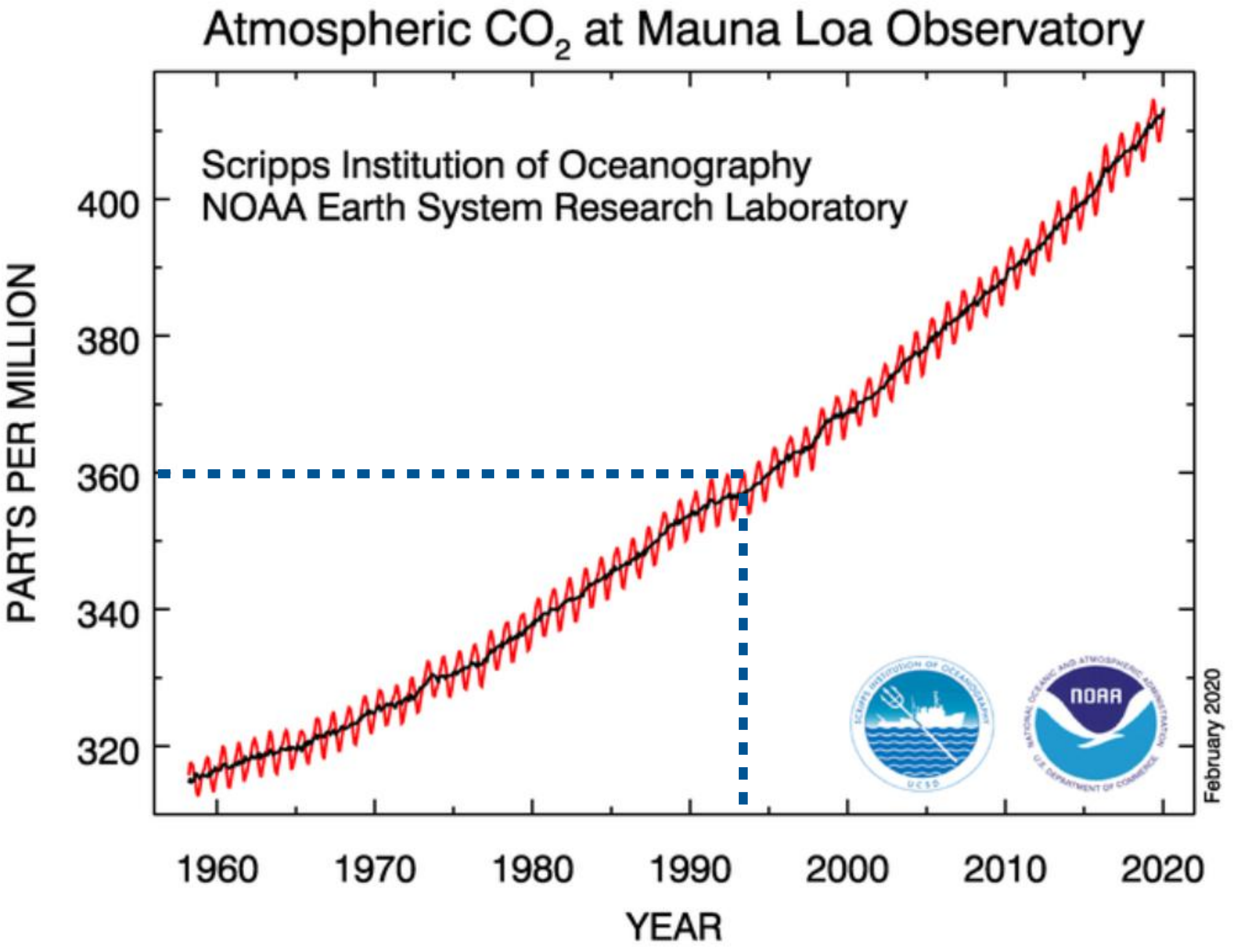

…and CO_2 levels have been allowed to rise essentially unchecked

Trends in Atmospheric Carbon Dioxide. *NOAA Global Monitoring Division*. https://www.esrl.noaa.gov/gmd/ccgg/trends/mlo.html (accessed Mar 3, 2020).

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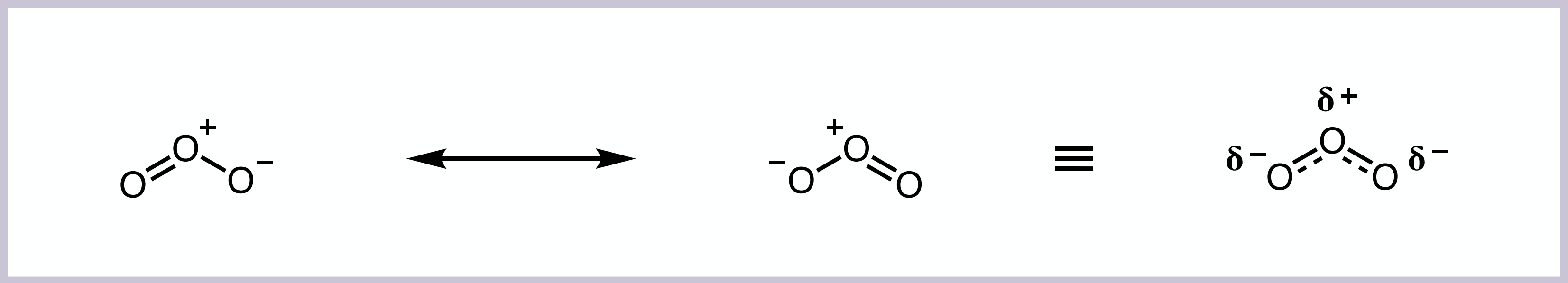

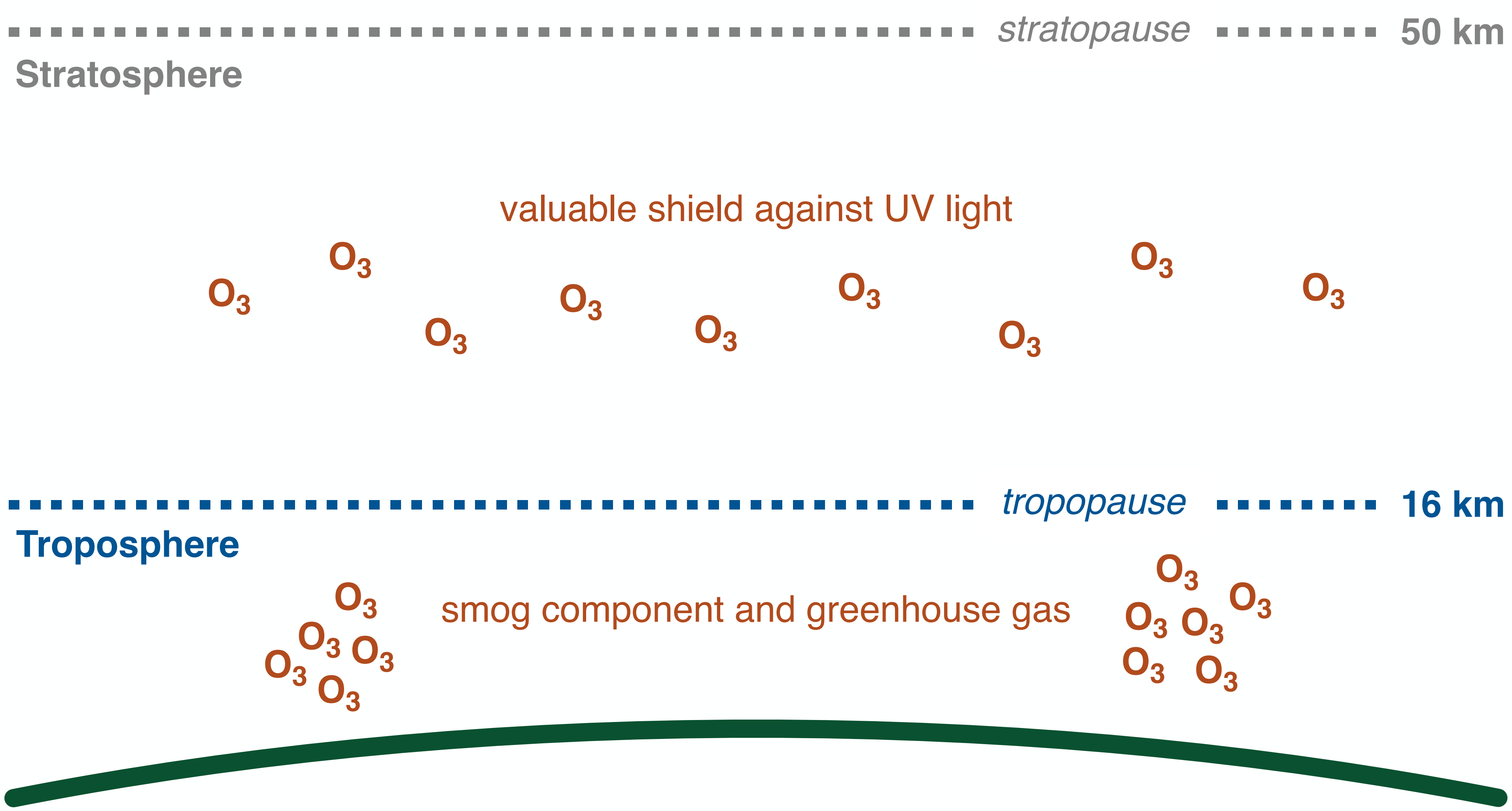

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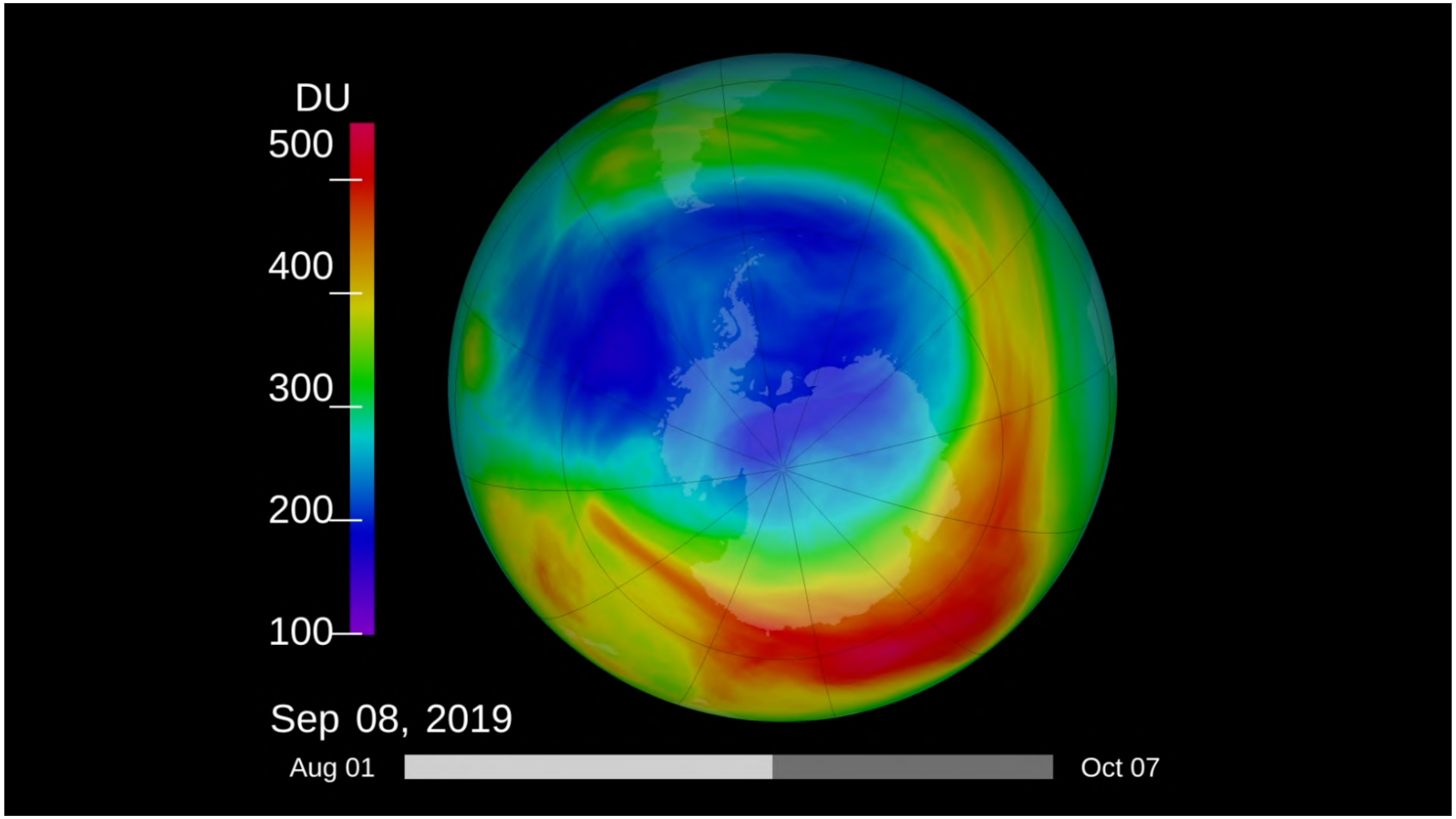
The interconnected cycles of atmospheric chemistry

2019 Antarctic ozone hole was the smallest recorded since 1982

An unusually warm Antarctic winter limited polar stratospheric cloud formation



2019 Antarctic ozone hole smallest on record. *UN Ozone Secretariat*. Published October 22, 2019. https://ozone.unep.org/2019-antarctic-ozone-hole-smallest-record (accessed March 3, 2020).

Questions?