

Introduction to the Biosphere-Atmosphere system

Lecture Autumn 2023

Part II

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What is the atmosphere?

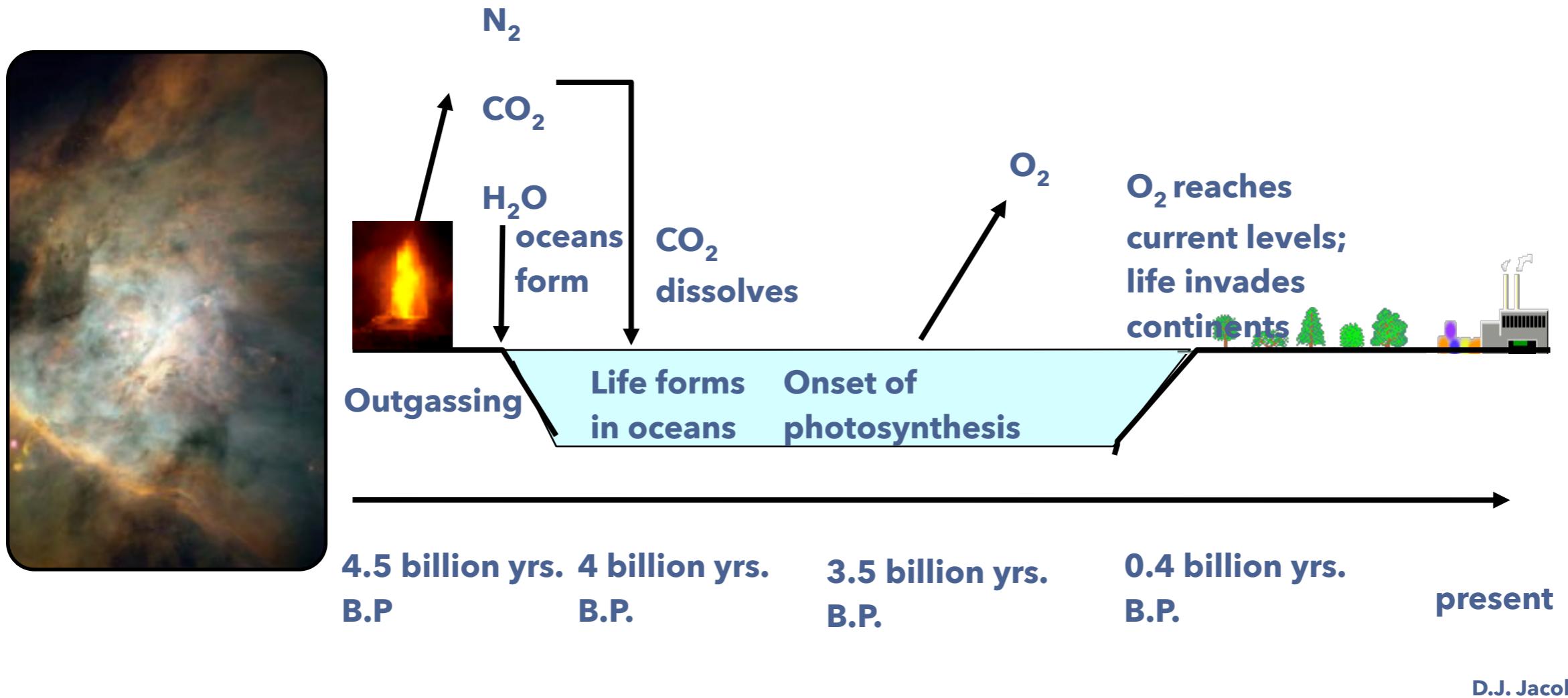
What is the atmosphere?

What do you know about it's components?

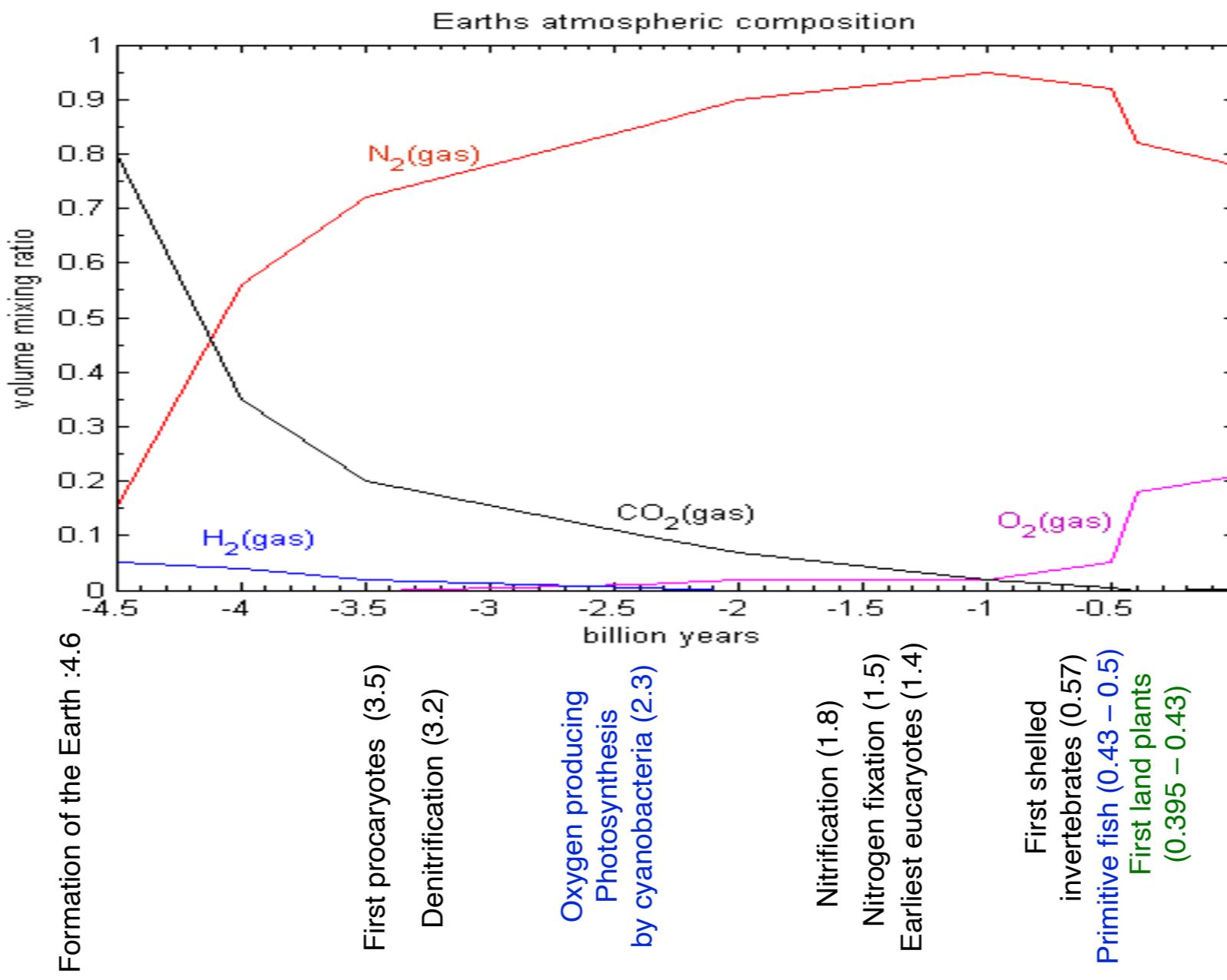
Layers of the atmosphere



Evolution of Earth's atmosphere



History of Earth's atmospheric composition



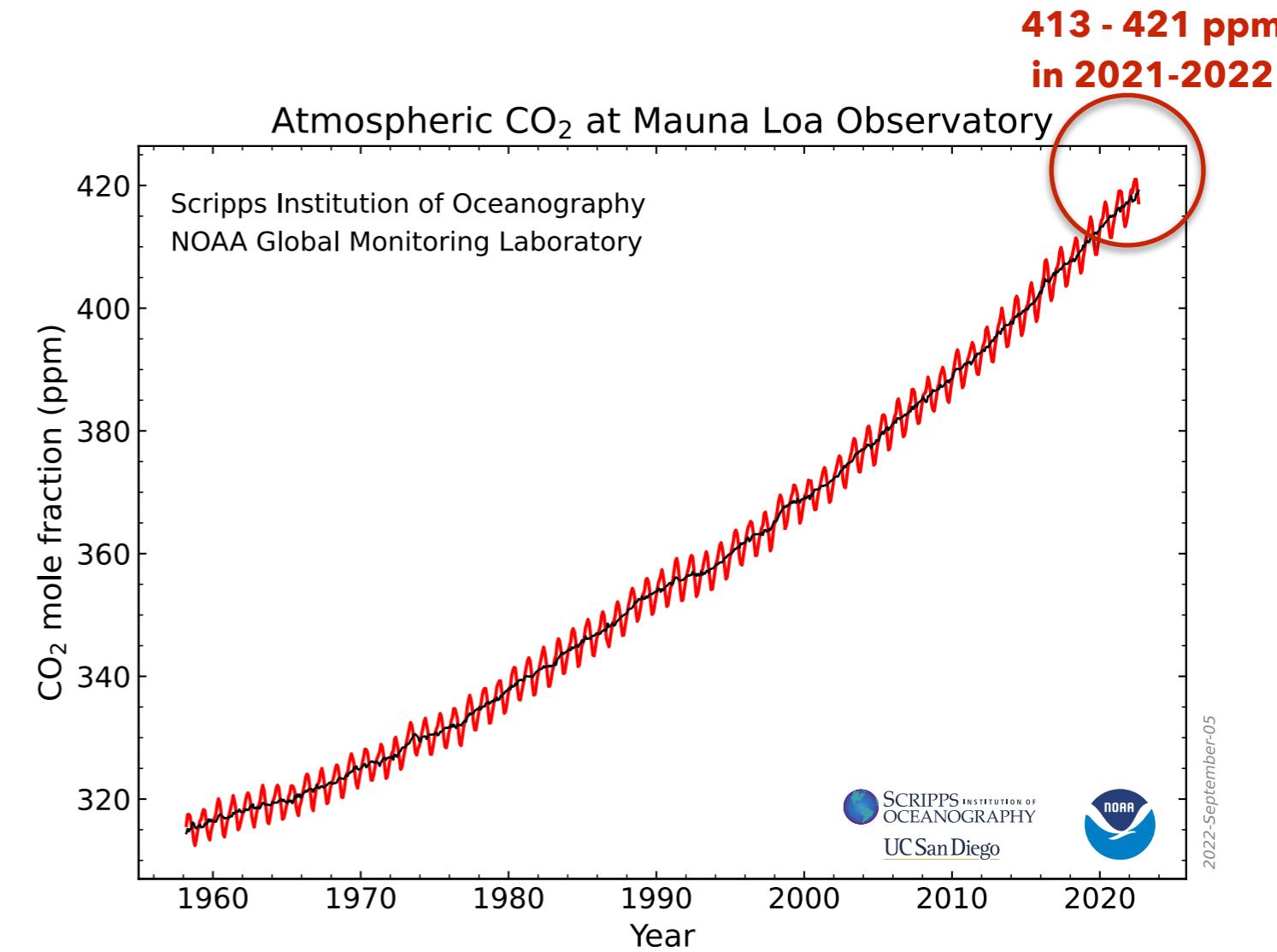
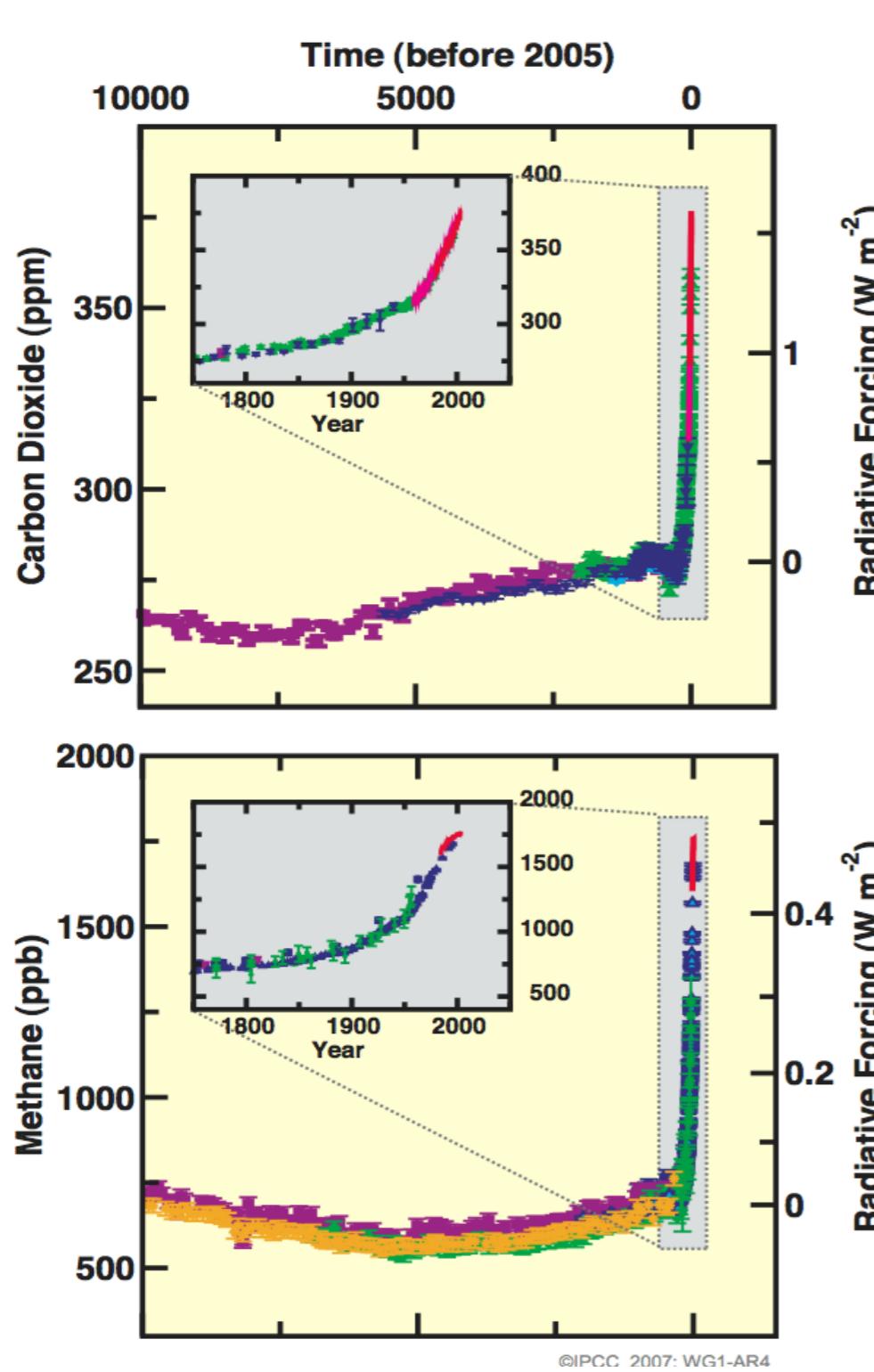
Where all that carbon is now?

Let's guess where it might be!



The carbon is still here

Atmospheric CO₂ and CH₄ increase (since ice age)



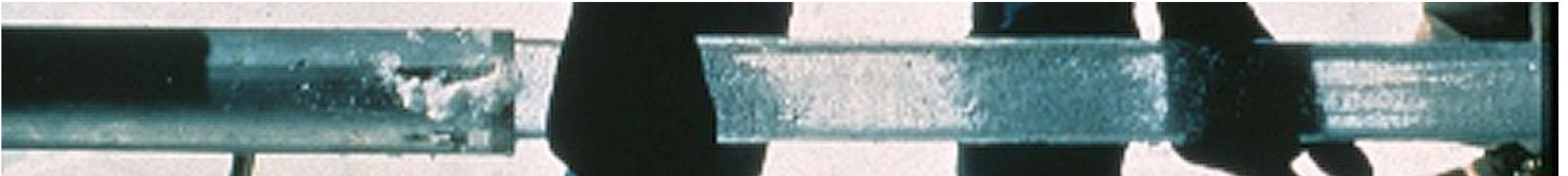
Mixing ratios of gases are not conserved
over the centuries, years or months!

Source: NOAA

How do we know about gas concentration from the past?

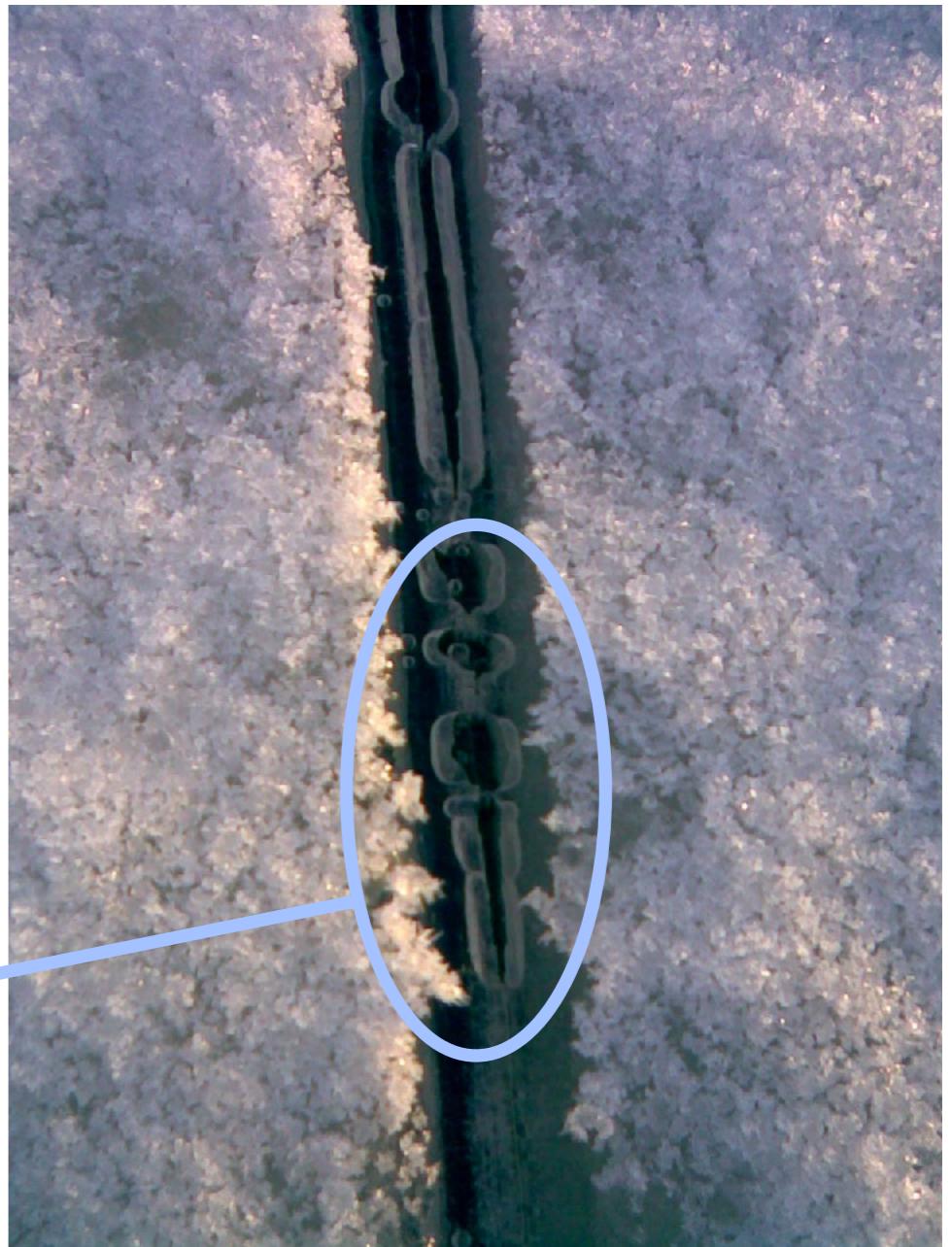
Let's guess where it might be!

How to capture air from the past?



- Ice cores are drilled from arctic and antarctic ice shields and even glaciers.
- Enclosed air bubbles contain air samples from the past.

Enclosed air bubbles found on Elistvere lake, 12/2008



Present atmospheric composition

Composition of **dry air**

trace gases

GAS	Mixing ratio [mol mol ⁻¹]
Nitrogen (N ₂)	0.78
Oxygen (O ₂)	0.21
Argon (Ar)	0.0093
Carbon dioxide (CO ₂)	421×10^{-6}
Neon (Ne)	18×10^{-6}
Ozone (O ₃)	$(0.01-10) \times 10^{-6}$
Helium (He)	5.2×10^{-6}
Methane (CH ₄)	1.8×10^{-6}
Krypton (Kr)	1.1×10^{-6}

Trace gas mixing ratio units

$$\text{percent \%} = 10^{-2} \text{ mol mol}^{-1}$$

$$\text{permille } \text{\textperthousand} = 10^{-3} \text{ mol mol}^{-1}$$

$$\text{ppm}_v = 10^{-6} \text{ mol mol}^{-1} \quad \mu\text{mol mol}^{-1}$$

$$\text{ppb}_v = 10^{-9} \text{ mol mol}^{-1} \quad \text{nmol mol}^{-1}$$

$$\text{ppt}_v = 10^{-12} \text{ mol mol}^{-1} \quad \text{pmol mol}^{-1}$$

Another good reason for the mixing ratio:

It stays constant when air density, pressure or temperature are changing!

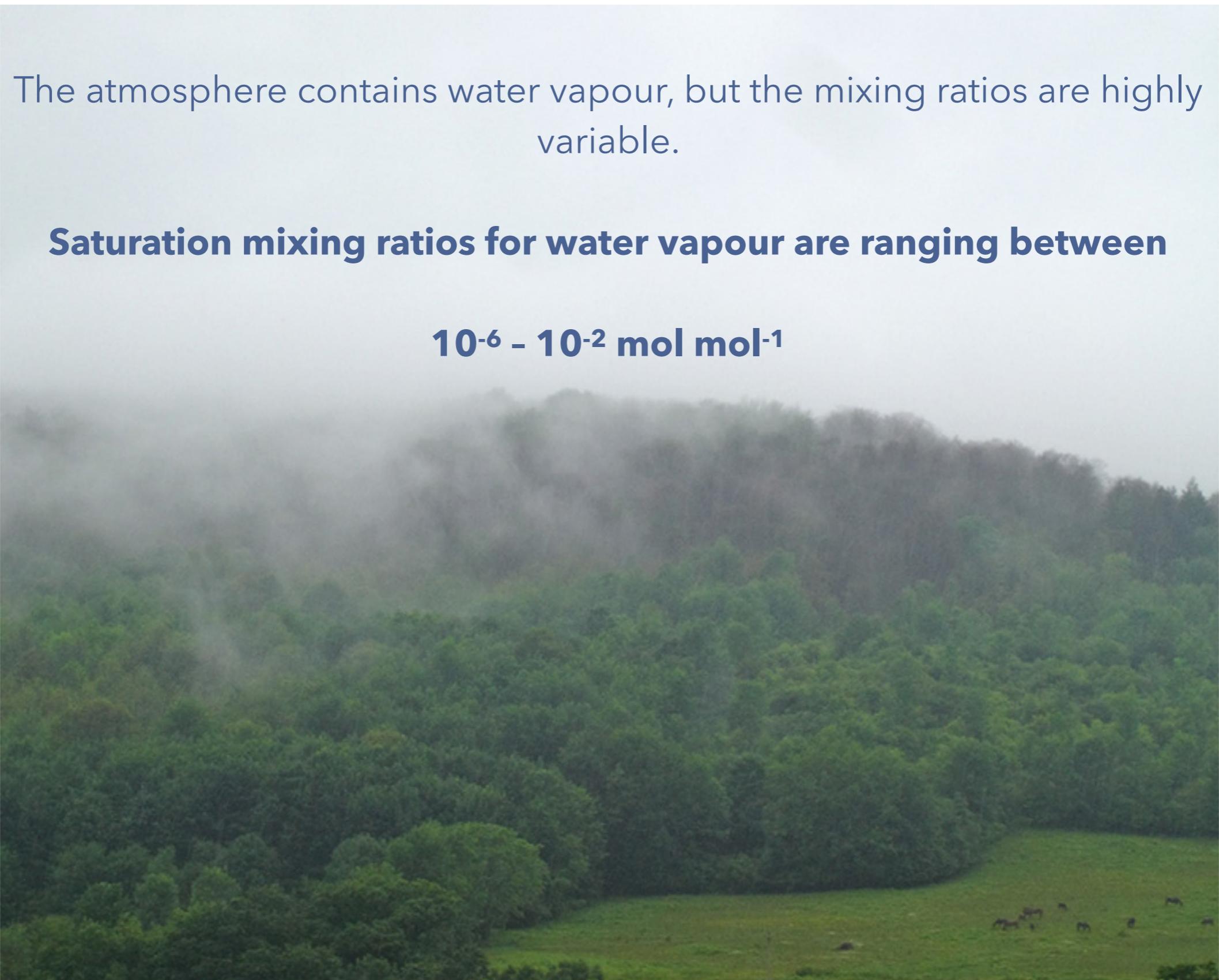
⇒ it's a robust measure of atmospheric composition!

What about wet air?

The atmosphere contains water vapour, but the mixing ratios are highly variable.

Saturation mixing ratios for water vapour are ranging between

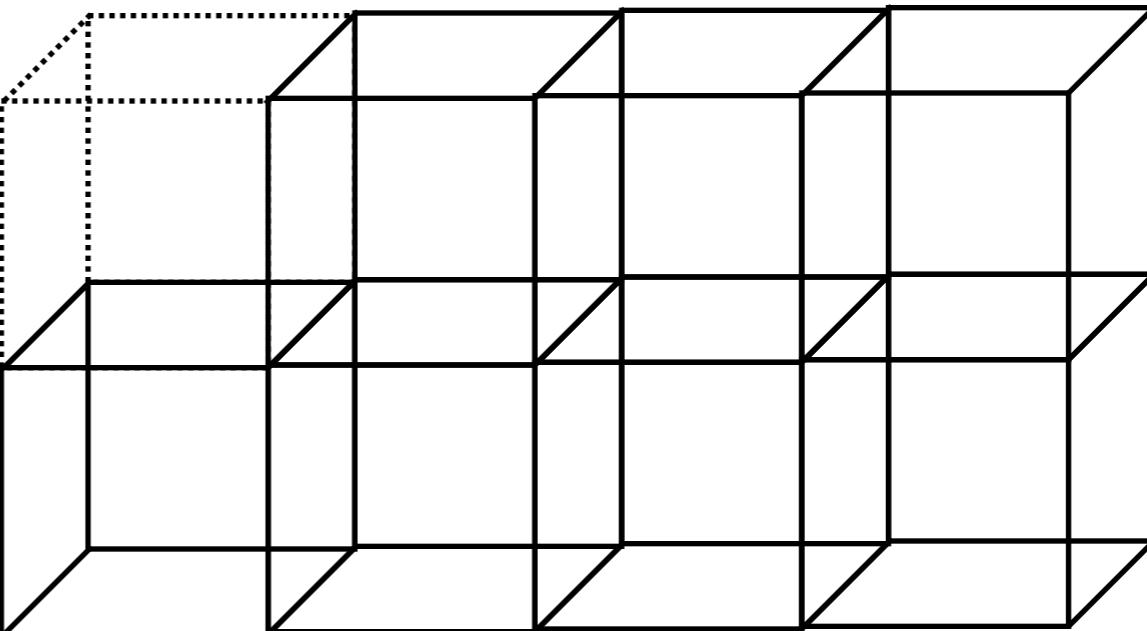
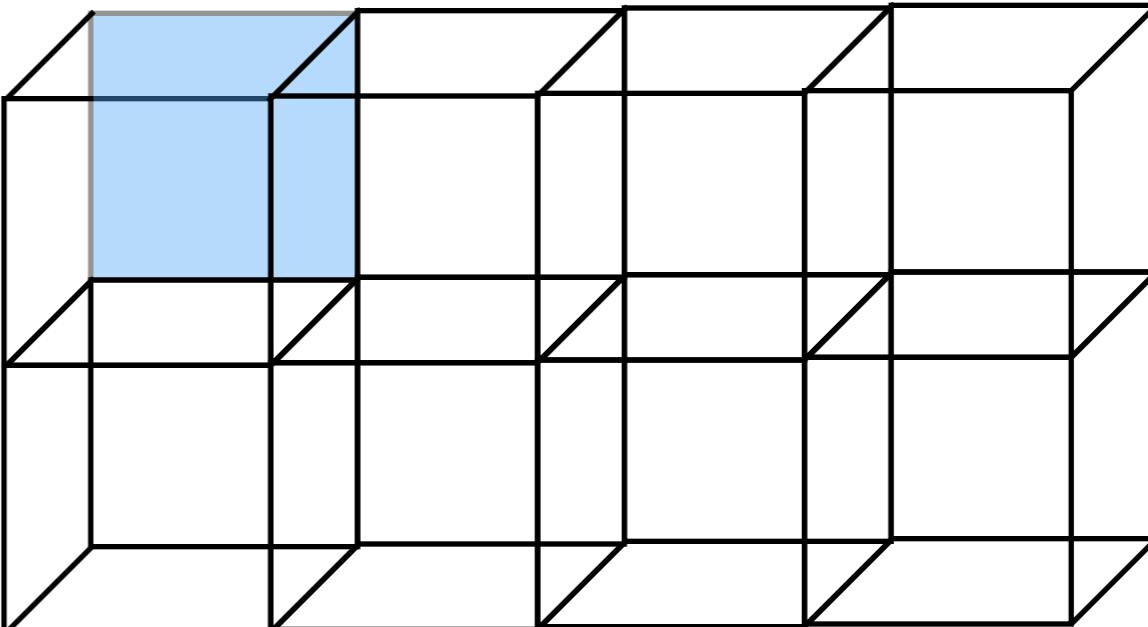
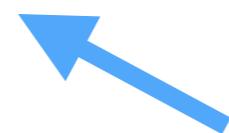
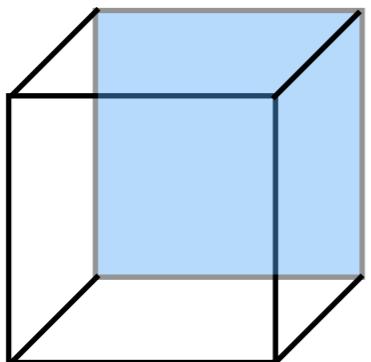
$10^{-6} - 10^{-2}$ mol mol⁻¹



Compensating for wet air in measurements?

All gases are in all boxes,
if we know that one box
would be only water
vapour!

and we would take it off,
“dry air”!



There is less volume left for
the rest of the other “dry”
gases!

It means we have “counted”
less molecules!

Their mixing ratio is corrected some few percents up!

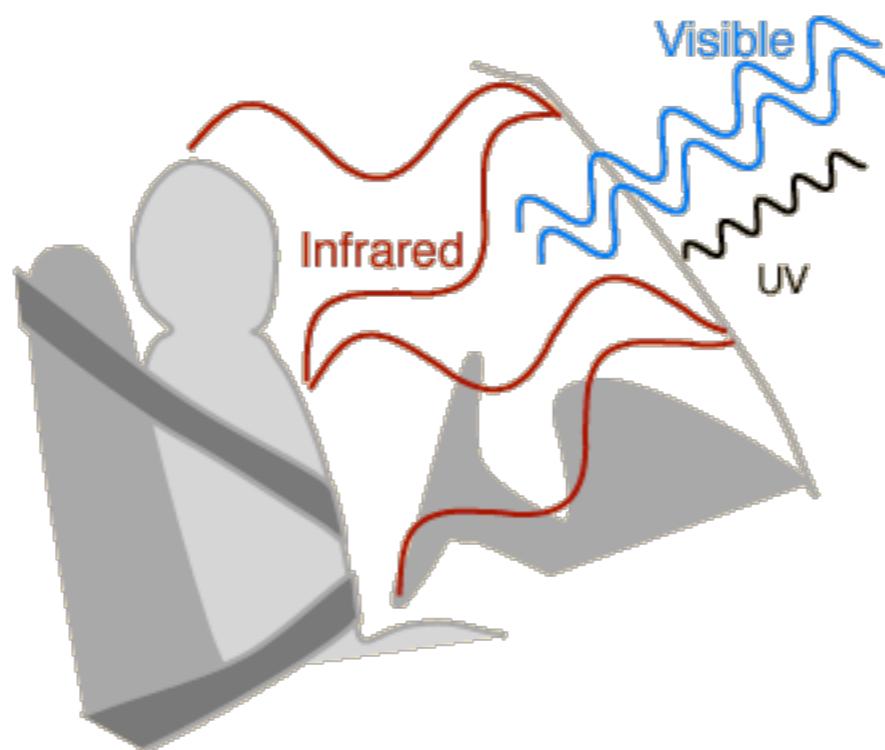
Water vapour contributes strongest to the greenhouse effect

percent contribution to greenhouse effect

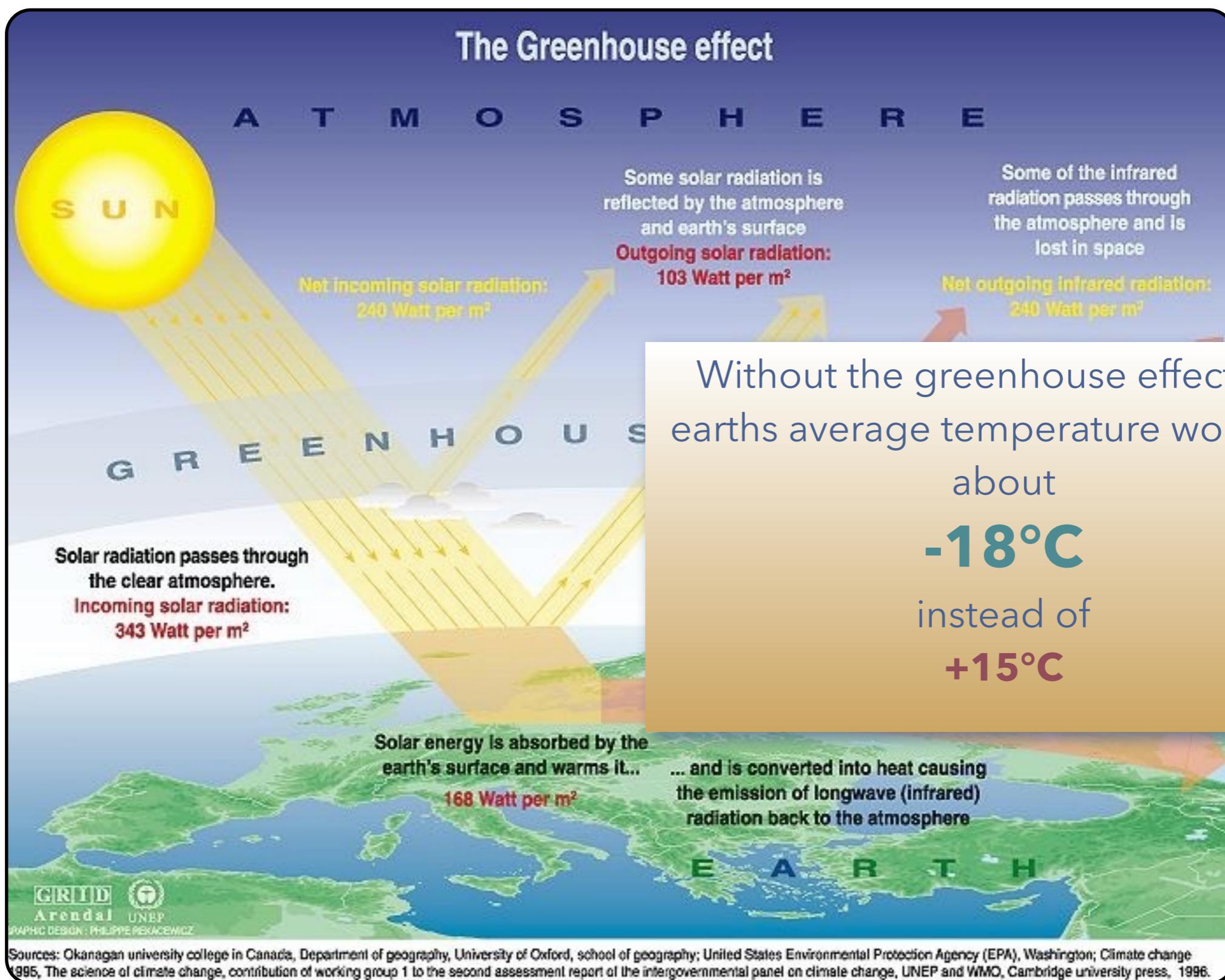
Water vapor	H2O	36-72%
Carbon dioxide	CO2	9-26%
Methane	CH4	4-9%
Ozone	O3	3-7%

The greenhouse effect in one sentence...

Solar energy that is transmitted to earth by radiation is there converted into heat, to balance out this input, earth emits heat back to space, which is partly captured by the “greenhouse gases” and radiated back...

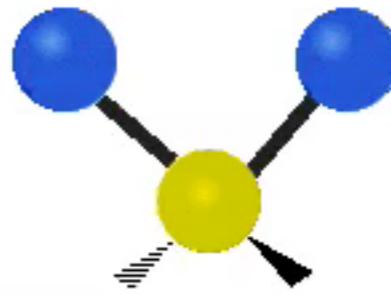
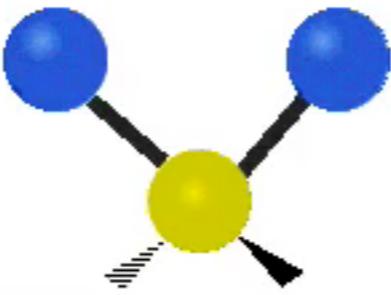
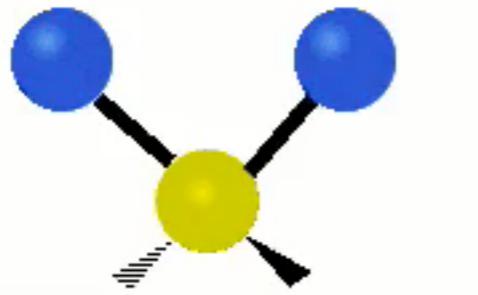


Sun provides the Earth with energy



Energy absorption by gas molecules

Due to absorption, energy is transferred from the beams of the solar radiation to the gas molecules, causing movement.



Movement of molecules is seen as “heat”!

Climate warming was recognised already 200 years ago!



by Eunice Foote

Climate warming was recognised already 200 years ago!

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On the Heat in the Sun's Rays.

ART. XXXI.—*Circumstances affecting the Heat of the Sun's Rays;*
by EUNICE FOOTE.

(Read before the American Association, August 23d, 1856.)

My investigations have had for their object to determine the different circumstances that affect the thermal action of the rays of light that proceed from the sun.

Several results have been obtained.

First. The action increases with the density of the air, and is diminished as it becomes more rarified.

The experiments were made with an air-pump and two cylindrical receivers of the same size, about four inches in diameter and thirty in length. In each were placed two thermometers, and the air was exhausted from one and condensed in the other. After both had acquired the same temperature they were placed in the sun, side by side, and while the action of the sun's rays rose to 110° in the condensed tube, it attained only 88° in the other. I had no means at hand of measuring the degree of condensation or rarefaction.

The observations taken once in two or three minutes, were as follows:

Exhausted Tube		Condensed Tube.	
In shade.	In sun.	In shade.	In sun.
75	80	75	80
76	82	78	95
80	82	80	100
83	86	82	105
84	88	85	110

This circumstance must affect the power of the sun's rays in different places, and contribute to produce their feeble action on the summits of lofty mountains.

Secondly. The action of the sun's rays was found to be greater in moist than in dry air.

In one of the receivers the air was saturated with moisture—in the other it was dried by the use of chlorid of calcium.

Both were placed in the sun as before and the result was as follows:

Dry Air.		Damp Air.	
In shade.	In sun.	In shade.	In sun.
75	75	75	75
78	88	78	90
82	102	82	106
82	104	82	110
82	105	82	114
88	108	92	120

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Marcou's Geological Map of the United States.

The high temperature of moist air has frequently been observed. Who has not experienced the burning heat of the sun that precedes a summer's shower? The isothermal lines will, I think, be found to be much affected by the different degrees of moisture in different places.

Thirdly. The highest effect of the sun's rays I have found to be in carbonic acid gas.

One of the receivers was filled with it, the other with common air, and the result was as follows :

In Common Air.		In Carbonic Acid Gas.	
In shade.	In sun.	In shade.	In sun.
80	90	80	90
81	94	84	100
80	99	84	110
81	100	85	120

The receiver containing the gas became itself much heated—very sensibly more so than the other—and on being removed, it was many times as long in cooling.

An atmosphere of that gas would give to our earth a high temperature; and if as some suppose, at one period of its history the air had mixed with it a larger proportion than at present, an increased temperature from its own action as well as from increased weight must have necessarily resulted.

On comparing the sun's heat in different gases, I found it to be in hydrogen gas, 104°; in common air, 106°; in oxygen gas, 108°; and in carbonic acid gas, 125°.

ART. XXXII.—*Review of a portion of the Geological Map of the United States and British Provinces by Jules Marcou,* by WILLIAM P. BLAKE.*

GEOLOGICAL maps of the United States published in Europe and widely circulated among European geologists, are necessarily regarded by us with no small degree of attention and curiosity. This is more especially true, when such maps embrace regions of which the geography has only recently been made known and the geology has never before been laid down on a map with any approach to accuracy.

The recent geological map and profile by M. J. Marcou, which has appeared in the *Annales des Mines* and in the *Bulletin of*

* *Carte Géologique des Etats-Unis et des Provinces Anglaises de l'Amérique du Nord par Jules Marcou. Annales des Mines, 5^e Série, T. vii, p. 329.* Published also with the following :

Résumé explicatif d'une carte géologique des Etats-Unis et des provinces anglaises de l'Amérique du Nord, avec un profil géologique allant de la vallée du Mississippi aux côtes du Pacifique, et une planche de fossiles, par M. Jules Marcou *Bulletin de la Société Géologique de France*, Mai, 1855, p. 813.

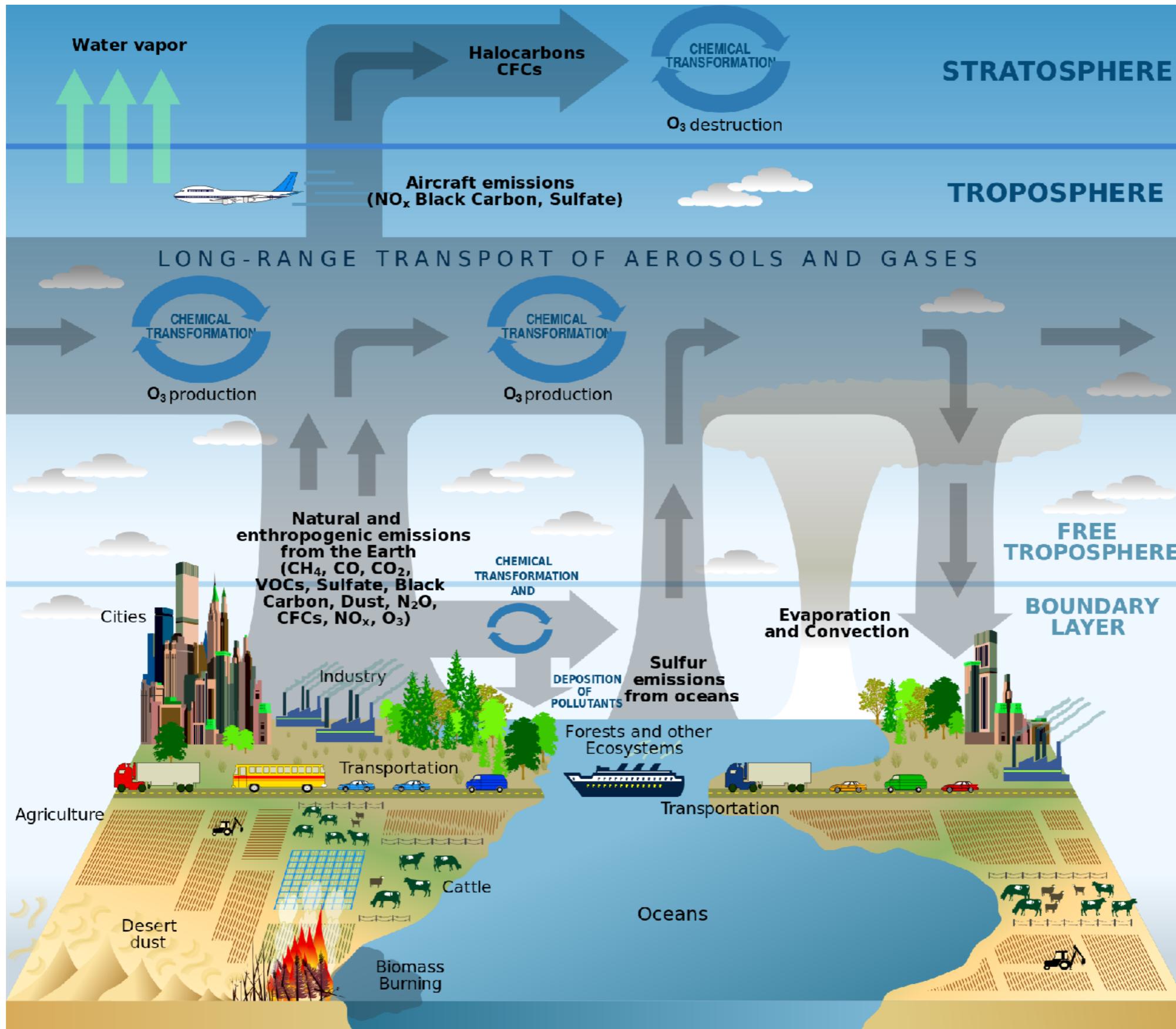
Atmospheric lifetimes

Name	Formula	usual atm. state	avg. lifetime
Methane	CH ₄	gas	10-15 years
Carbon monoxide	CO	gas	30-90 days
Carbon dioxide	CO ₂	gas	30-95 years
Biogenic hydrocarbons VOCs	many (>30 000)	gas	minutes to days
water vapour	H ₂ O	gas	0-9 days

Methane is most abundant hydrocarbon in atmosphere, trend rising. Carbon monoxide originates from industrial processes and oxygenation of hydrocarbons. (Biogenic) hydrocarbons are usually denoted as C_iH_jR_k forms. The rest (R) decides the final organic species (eg. Alkanes, Ketones, organic acid...)

Water vapour is a condensing "gas"!

The atmosphere as chemical reactor



Stratospheric ozone formation

Stratospheric Ozone Production

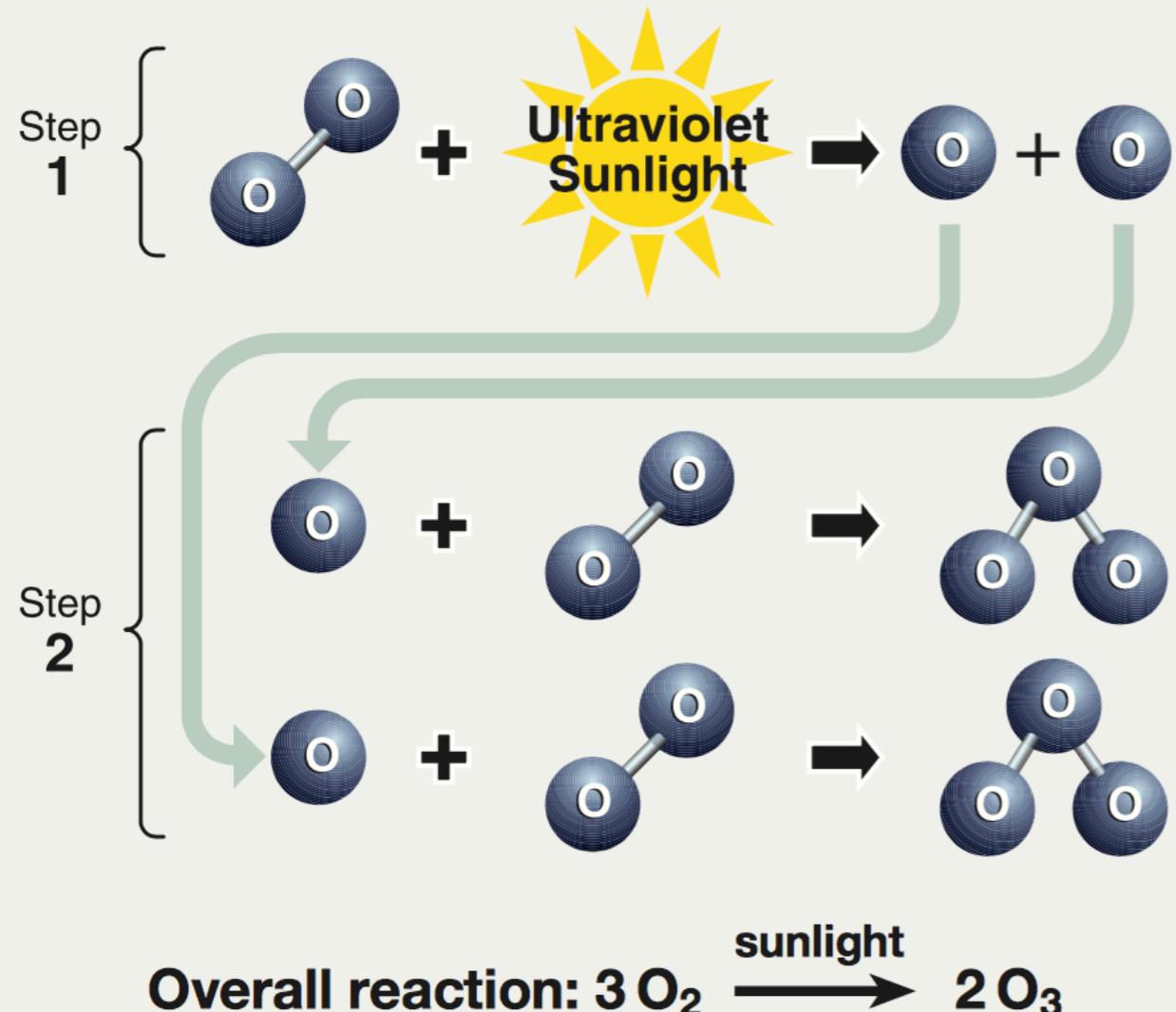
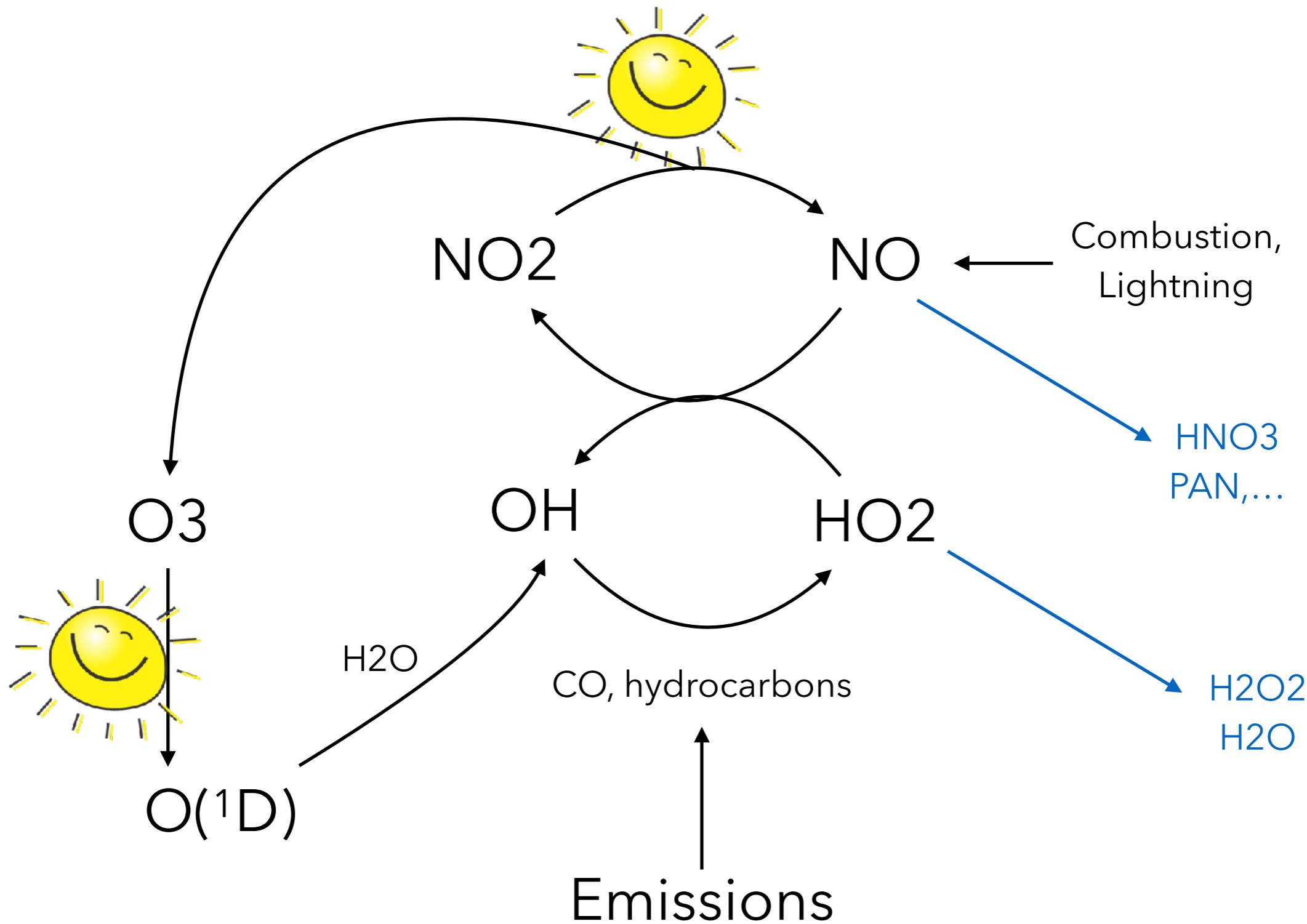


Figure Q2-1. Stratospheric ozone production. Ozone is naturally produced in the stratosphere by a two-step reactive process. In the first step, solar ultraviolet radiation (sunlight) breaks apart an oxygen molecule to form two separate oxygen atoms. In the second step, each atom then undergoes a binding collision with another oxygen molecule to form an ozone molecule. In the overall process, three oxygen molecules plus sunlight react to form two ozone molecules.

Tropospheric ozone formation

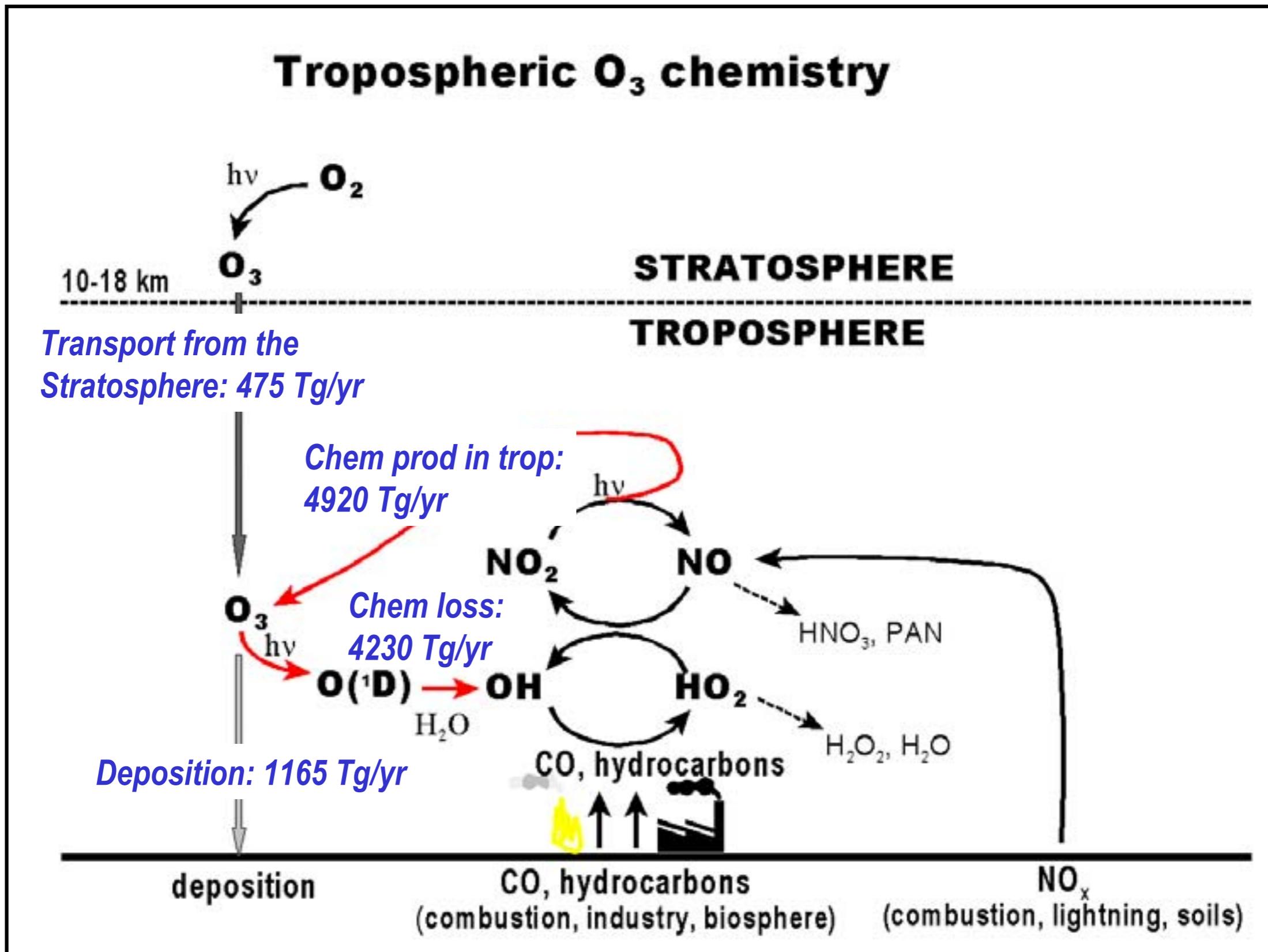


Tropospheric ozone budget

Table 11-4 Present-Day Global Budget of Tropospheric Ozone

	$Tg\ O_3\ yr^{-1}$
Sources	3400–5700
Chemical production	3000–4600
$\text{HO}_2 + \text{NO}$	(70%)
$\text{CH}_3\text{O}_2 + \text{NO}$	(20%)
$\text{RO}_2 + \text{NO}$	(10%)
Transport from stratosphere	400–1100
Sinks	3400–5700
Chemical loss	3000–4200
$\text{O}({}^1D) + \text{H}_2\text{O}$	(40%)
$\text{HO}_2 + \text{O}_3$	(40%)
$\text{OH} + \text{O}_3$	(10%)
others	(10%)
Dry deposition	500–1500

The ozone in the atmosphere

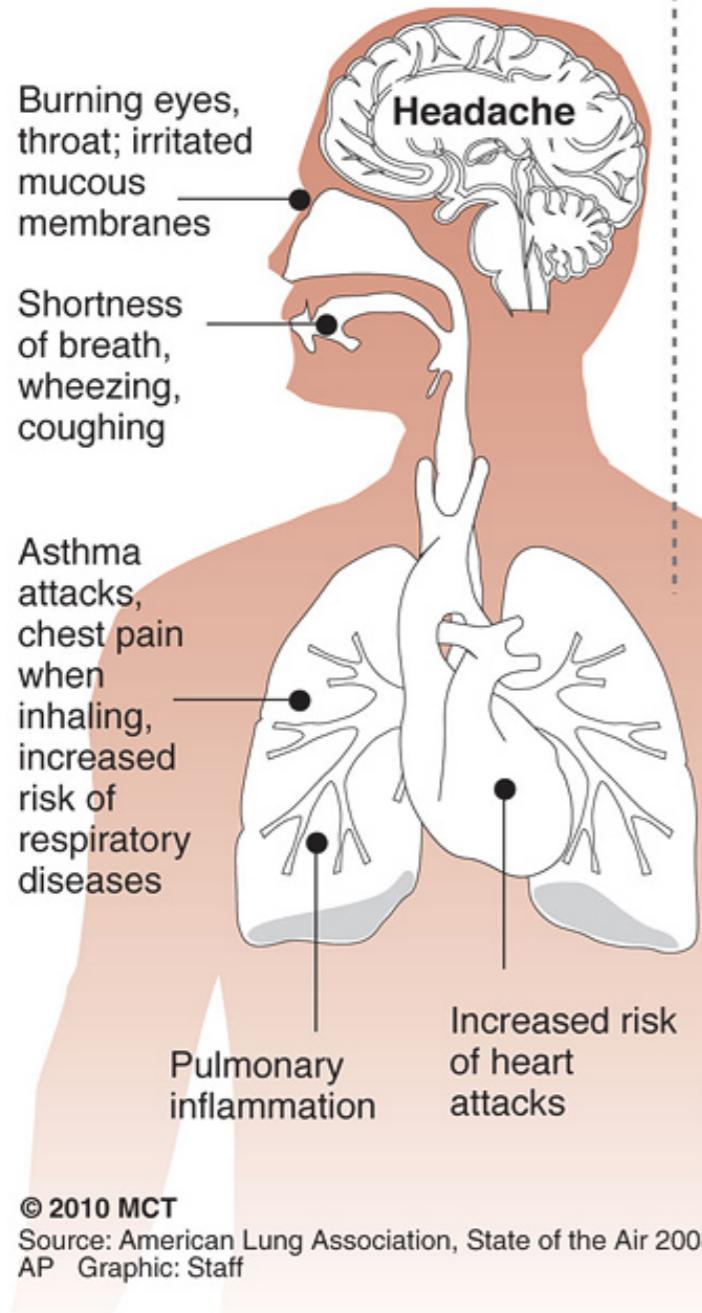


What does ozone do?

Why smog is harmful

Ozone, the main ingredient in smog, is one of the most widespread air pollutants and among the most dangerous.

Effects on health



How ozone forms

1 Oxygen in the atmosphere  O_2

2 Nitric oxide, byproduct of combustion  NO

3 Sunlight breaks up nitric oxide



4 Ozone formed by three oxygen atoms  O_3

U.S. ozone limits

In parts per billion

• 1997-2008 **84**

• 2008-present **75**

• New EPA proposal **60-70**

Negative health effects
Plant damage

This is a cost factor of ongoing pollution and climate change!



Ozone trends

RESEARCH ARTICLE

Multi-decadal surface ozone trends at globally distributed remote locations

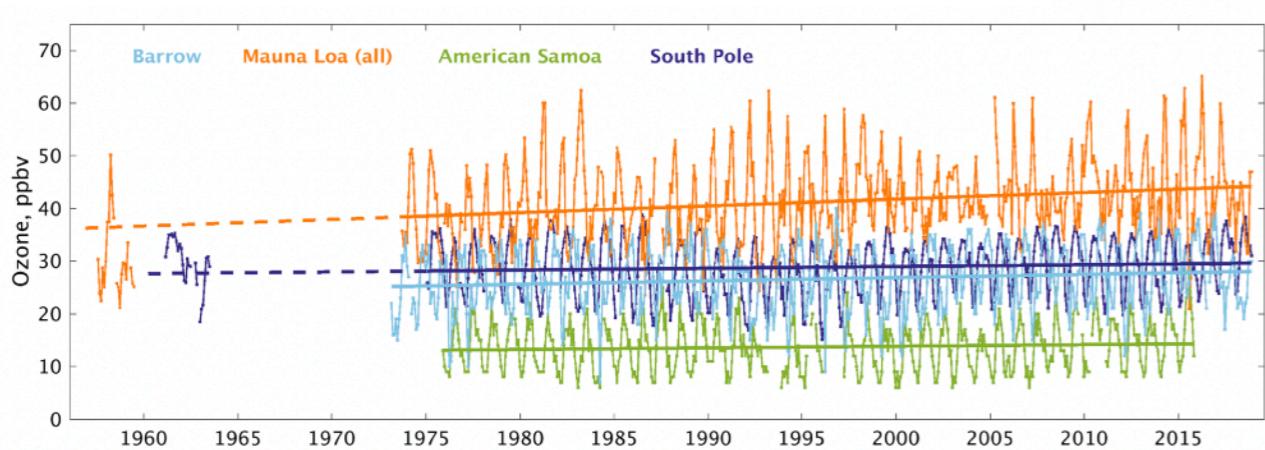


Figure 3: (top) Monthly mean ozone at the four NOAA GML baseline observatories. The top panel shows the full time series from all four sites, while the bottom panel shows monthly mean ozone in the mutually exclusive low humidity (red) and high humidity (blue) air masses at MLO. Solid straight lines represent the simple least-squares linear regression fit through the monthly mean values. Dashed lines represent the MLO and SPO linear regressions extended back in time to the years with historical ozone observations at MLO and SPO; the historical observations do not influence the linear regressions. For trend values, refer to the trends estimated from monthly anomalies in Tables 2 and 3. DOI: <https://doi.org/10.1525/elementa.420.f3>

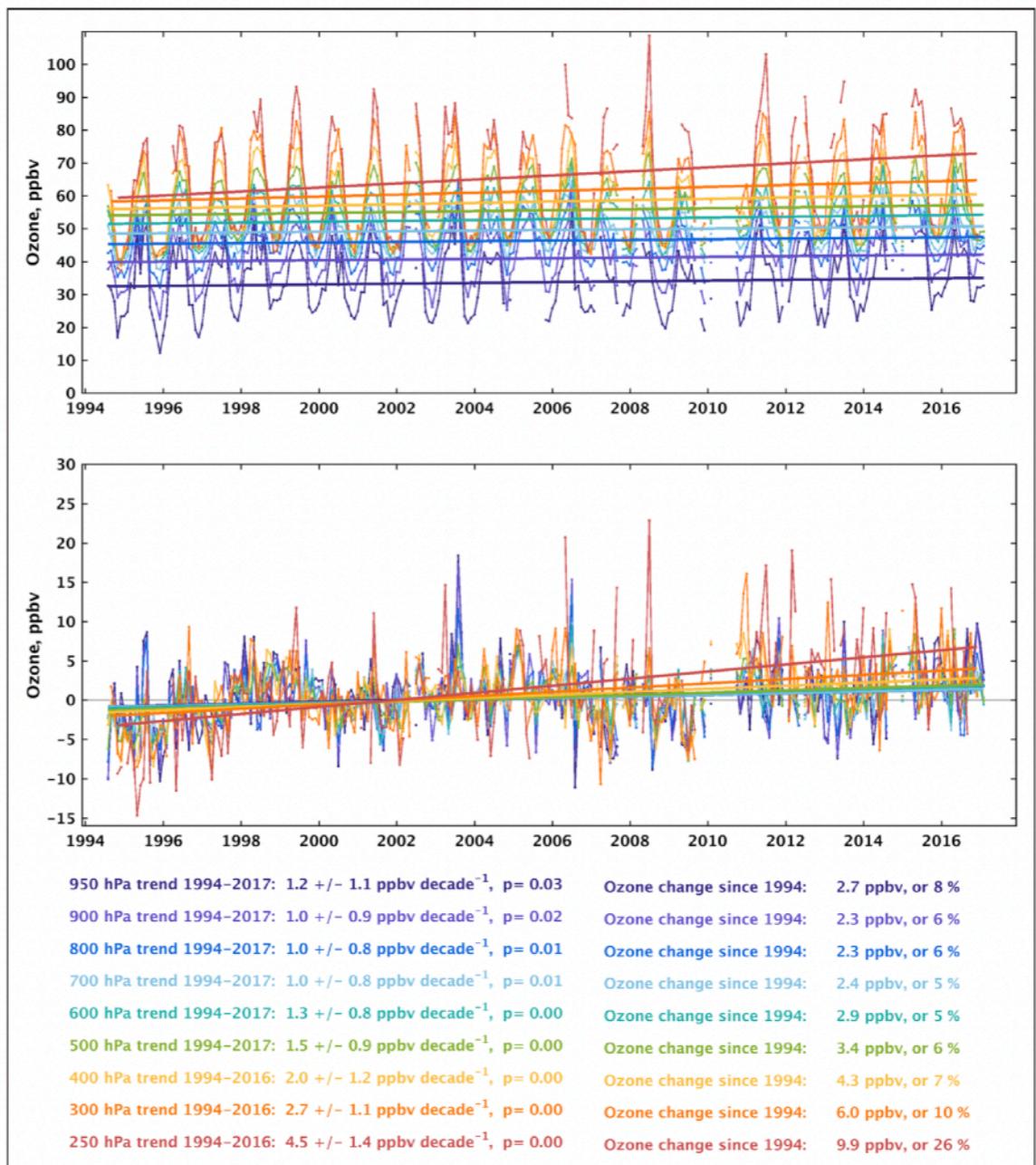
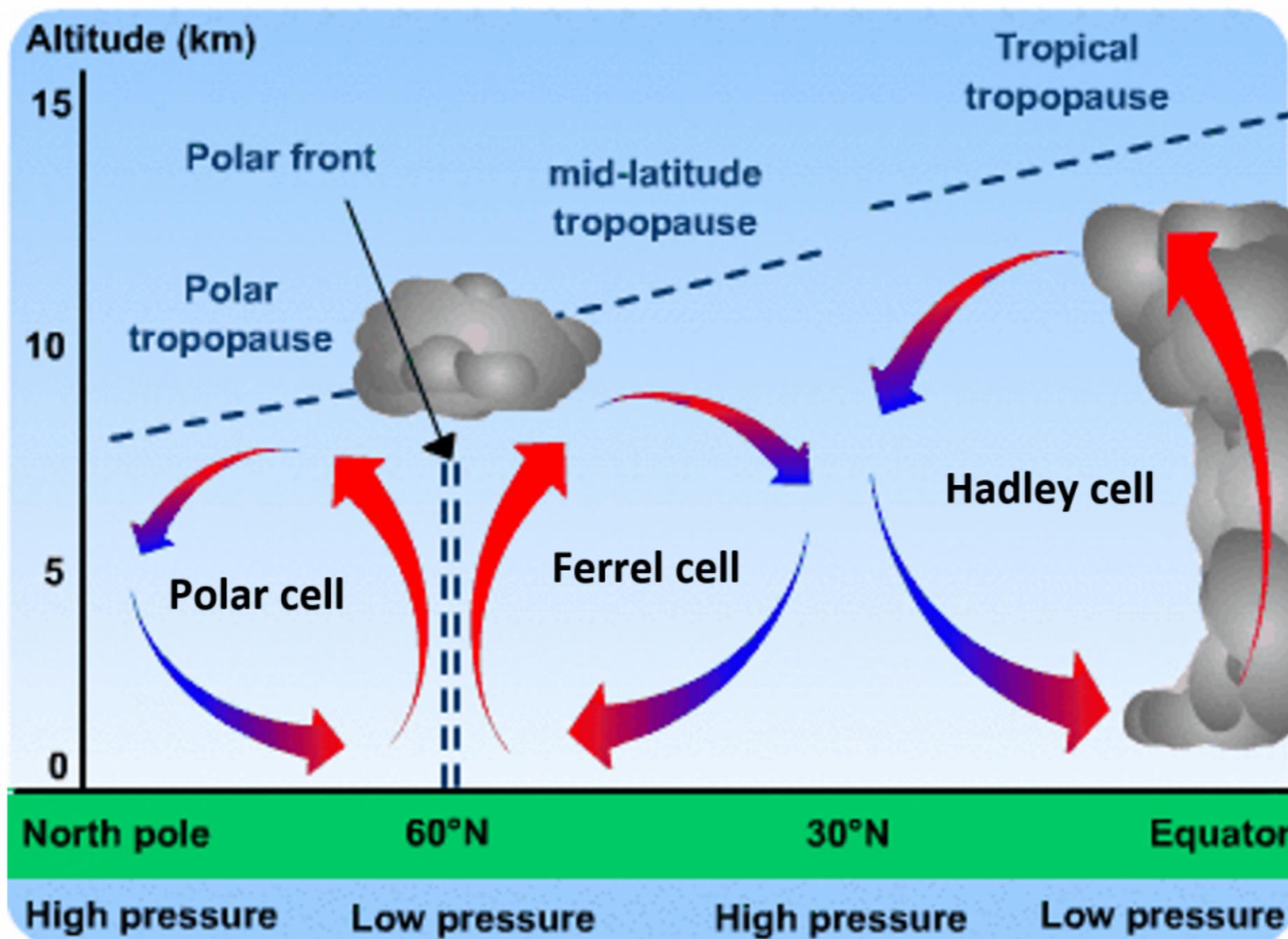
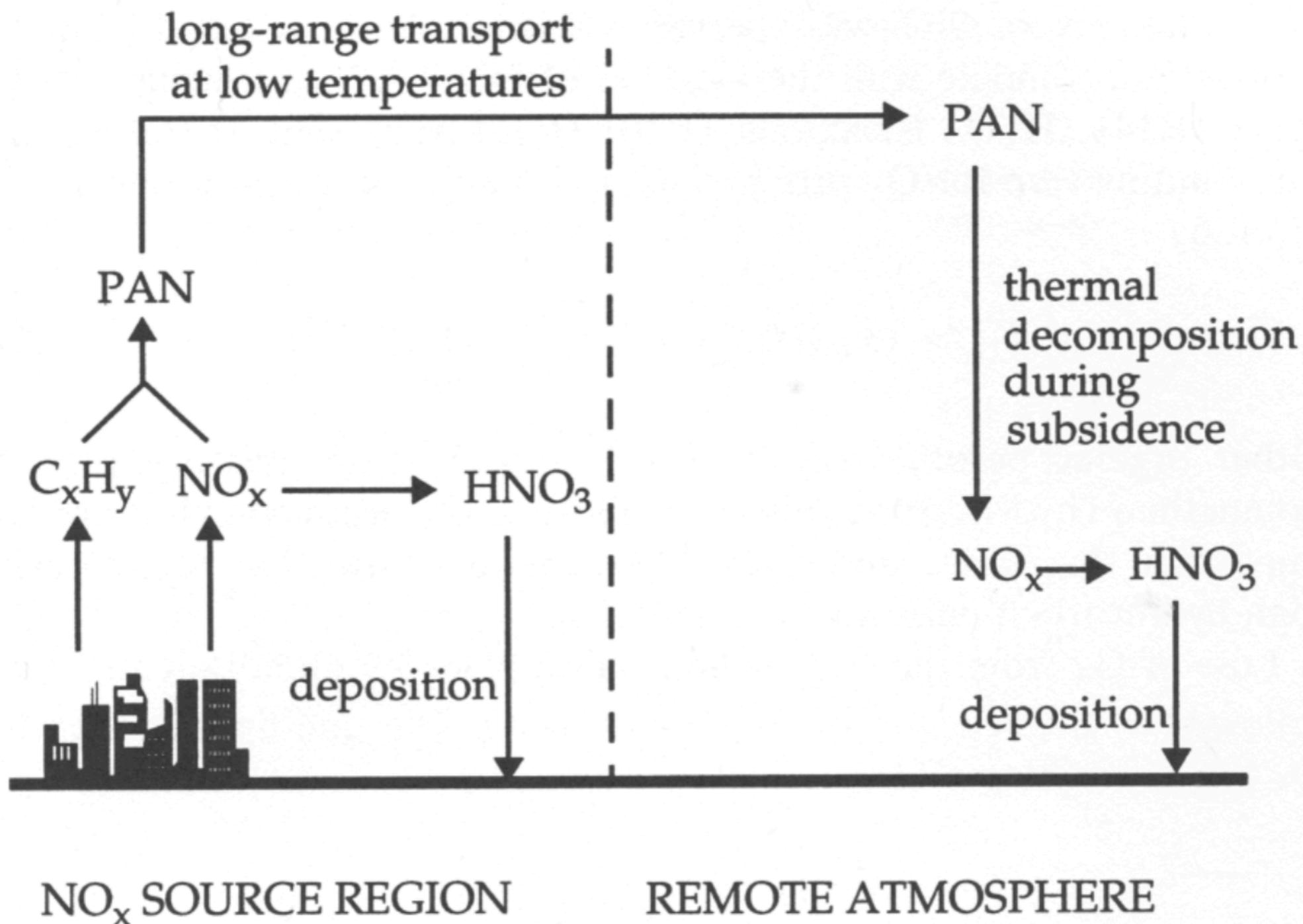


Figure 7: Monthly ozone above Western Europe as measured by IAGOS aircraft. Data are reported on 9 pressure levels from the lower troposphere to the upper troposphere, with 99% of aircraft profiles from Frankfurt, Paris, Munich, Brussels, Dusseldorf and Amsterdam. Data were filtered to only include observations below the tropopause. Ozone data are shown as observed monthly means with simple linear regression lines (top) and monthly anomalies with trends and regression lines based on the linear regression model (1) (bottom). DOI: <https://doi.org/10.1525/elementa.420.f7>

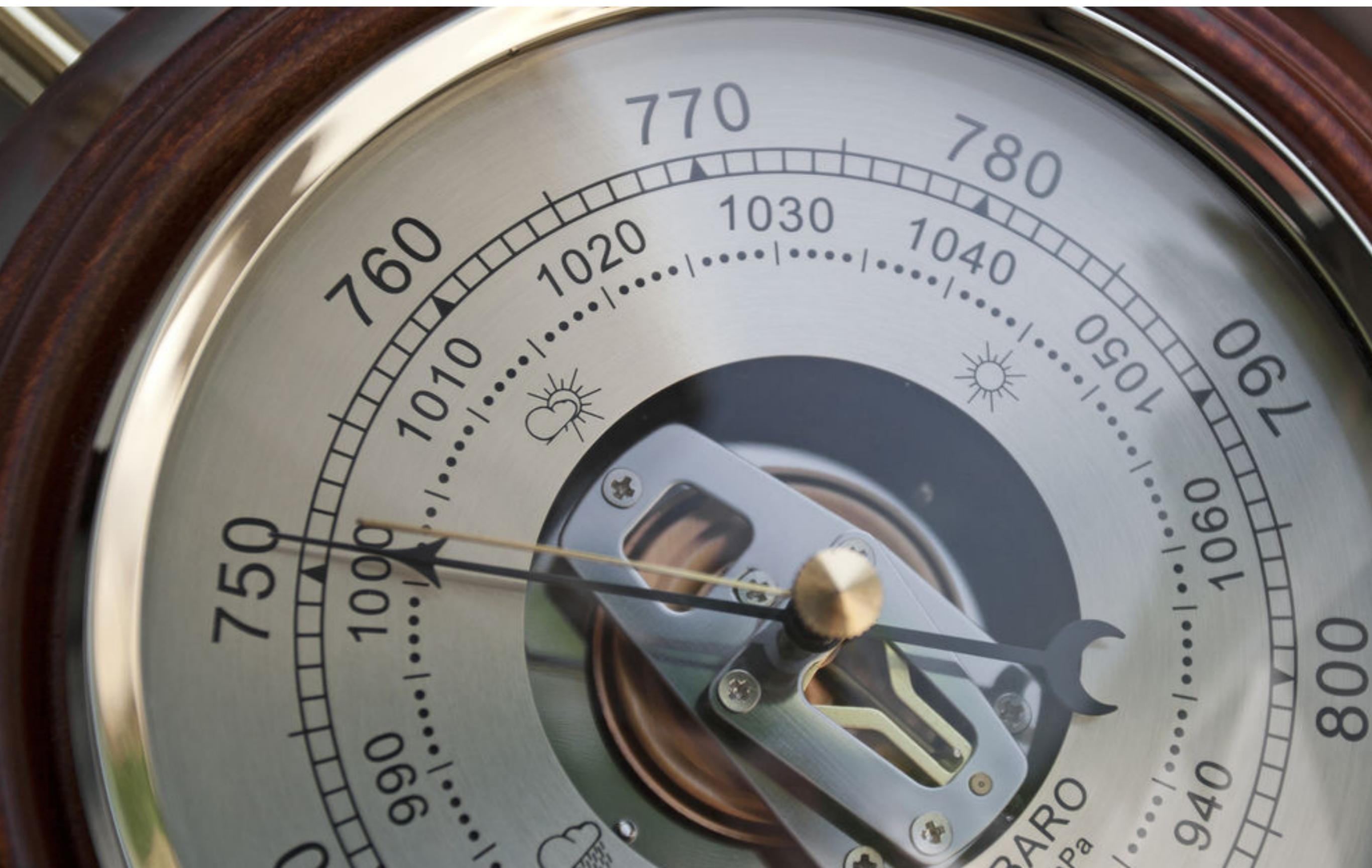
Atmospheric transport



Atmospheric transport



Important atmospheric measures



Measures of gaseous compounds

The SI unit for the **amount** of a substance is the mole (mol). The number of atoms or molecules in 1 mol is given by the **Avogadro's number** N_A .

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

Given the ideal gas law, concentration is expressed as the amount (or mass) of a substance in a given volume divided by that volume.



$$C = \frac{N}{V} = \frac{P}{RT}$$

The **mixing ratio** or **mole fraction** is defined as the ratio of amount (or mass) of the substance in a given volume to the total amount (or mass) of all constituents in that volume.

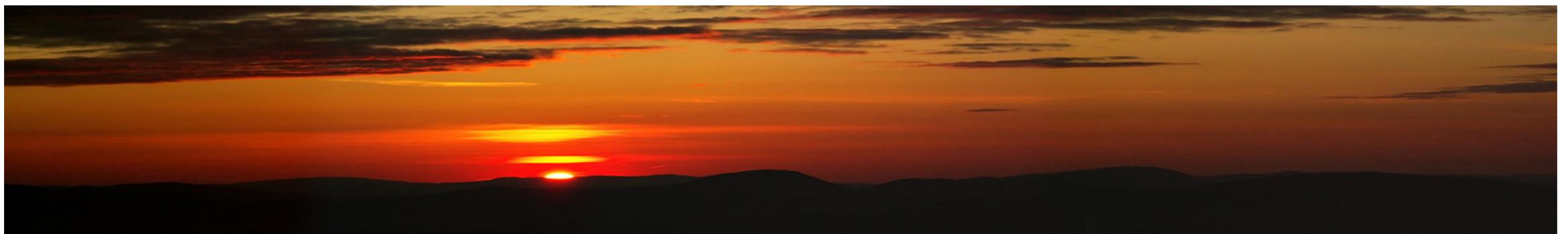
The volume mixing ratio C_i or vmr , assumed an ideal gas

$$C_i = vmr = \frac{V_i}{V_{air}} = \frac{n_i}{n_{air}} = \frac{p_i}{p_{air}}$$

The unit of C_i is $[\text{mol mol}^{-1}]$

Mass mixing ratios

The atmosphere contains beside gaseous compounds also particular matter such as aerosol particles, ice crystals and water droplets (clouds).



To express those, it's sometimes useful to use mass mixing ratios (mmr).

$$mmr = \frac{m_i}{m_{air}} = \frac{n_i M_i}{n_{air} M_{air}} = vmr \frac{M_i}{M_{air}}$$

Molecular weight of dry air:

$$M_{air} = 0.78 \times 28 \text{ g mol}^{-1} + 0.21 \times 32 \text{ g mol}^{-1} + 0.01 \times 40 \text{ g mol}^{-1} = \mathbf{28.96 \text{ g mol}^{-1}}$$

Example CO₂ (44 g mol⁻¹):

$$mmr = vmr \frac{44 \text{ g mol}^{-1}}{28.96 \text{ g mol}^{-1}} = vmr \times 1.52 \quad \approx 407 \times 1.52 \approx 619$$

The concept of partial pressure

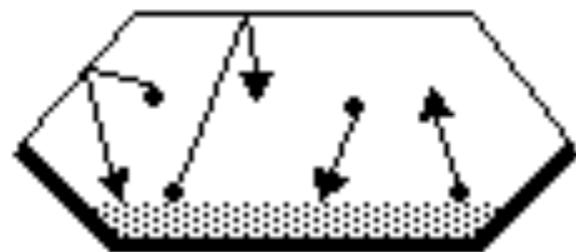
Dalton's law

$$p_i = \text{vmr} \times p = C_i \times p$$

$$p = \sum_i p_i$$

Partial pressure p_x [Pa] is the proper measure for phase changes such as condensation of water vapour to droplets or new particle formation from gases.

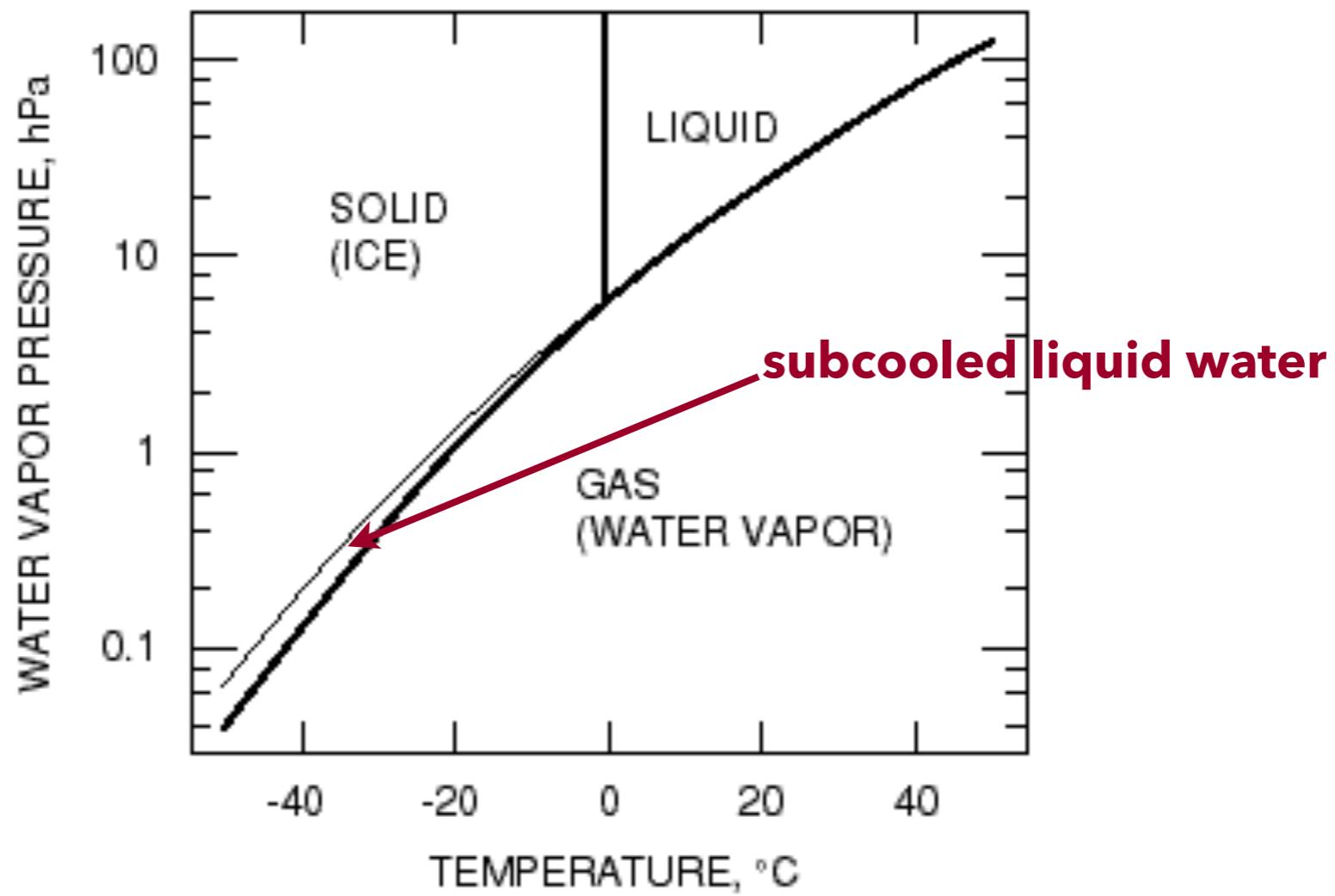
no lid - water molecules escape from the pan - evaporation!



add lid -

- water molecules collide with lid and return to surface
- if flux escaping = flux returning : saturation ($p_{\text{H}_2\text{O},\text{SAT}}$)
- increasing temperature increases $p_{\text{H}_2\text{O},\text{SAT}}$
- eg. cloud formation needs $p_{\text{H}_2\text{O}} > p_{\text{H}_2\text{O},\text{SAT}}$

The phase diagram of water



$$\text{Relative humidity (\%)} = 100 \times p_{\text{H}_2\text{O}} / p_{\text{H}_2\text{O},\text{SAT}}$$

Dew point: temperature T_d such that $p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O},\text{SAT}}(T_d)$

Number density or concentration

$[C_i] = \frac{\text{number of molecules}}{\text{unit volume of air}}$

$$[C_i] = \frac{n_i N_A}{V}$$

Proper measure for the
- calculation of reaction rates
- optical properties of the
atmosphere

$[C_i]$ is related to vmr by the ideal gas law

$$pV = NRT = nN_A RT$$

$$[C_i] = \frac{n_i N_A p}{R T n} = \frac{N_A p}{R T} vmr \approx 2.5 \times 10^{19} \frac{\text{molecules}}{\text{cm}^3} vmr$$

n_i : mole number [mole] of compound I per volume V [cm^{-3}]

N_A : Avogadro's number (6.022×10^{23} molecules mole^{-1})

p : total pressure [Pa]

R : ideal gas constant ($8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$)

T : temperature [K]

Some examples...

Ozone concentrations at surface and at the tropopause

$O_3 = 100 \text{ ppbv}$ ($T = 25^\circ\text{C}$, $p = 1000 \text{ hPa}$, surface)

$$\Rightarrow [O_3] = 2.4 \times 10^{12} \text{ molecules cm}^{-3}$$

$O_3 = 100 \text{ ppbv}$ ($T = -40^\circ\text{C}$, $p = 150 \text{ hPa}$, $\sim 10 \text{ km}$ height, tropopause)

$$\Rightarrow [O_3] = 4.7 \times 10^{11} \text{ molecules cm}^{-3}$$

Note: **the concentration is changing with height and temperature**

$CO_2 = 380 \text{ ppmv}$ ($T = 0^\circ\text{C}$, $p = 500 \text{ hPa}$, free troposphere)

$$\Rightarrow [CO_2] = 5.0 \times 10^{15} \text{ molecules cm}^{-3}$$

Mass concentration

$$\rho_i = \frac{\text{mass of } i}{\text{unit volume of air}} = \frac{M_i[C_i]}{N_A} \times 10^6$$

Used for aerosol sampling on filters for example. Typical units are then g m⁻³ or liter

M_i : molar mass in g mol⁻¹

[C_i]: number concentration in molecules cm⁻³

N_A : Avogadro's number (6.022x10²³ molecules mol⁻¹)

Some examples...

$$[\text{O}_3] = 2.4 \times 10^{12} \text{ molecules cm}^{-3}, M_{\text{O}_3} = 48 \text{ g mol}^{-1}$$

$$\Rightarrow \rho(\text{O}_3) = 1.9 \times 10^{-4} \text{ g m}^{-3} = 190 \text{ } \mu\text{g m}^{-3}$$

$$[\text{H}_2\text{O}] = 4.7 \times 10^{16} \text{ molecules cm}^{-3}, M_{\text{H}_2\text{O}} = 18 \text{ g mol}^{-1}$$

$$\Rightarrow \rho(\text{H}_2\text{O}) = 1.4 \text{ g m}^{-3}$$

$$[\text{CO}_2] = 5.0 \times 10^{15} \text{ molecules cm}^{-3}, M_{\text{CO}_2} = 44 \text{ g mol}^{-1}$$

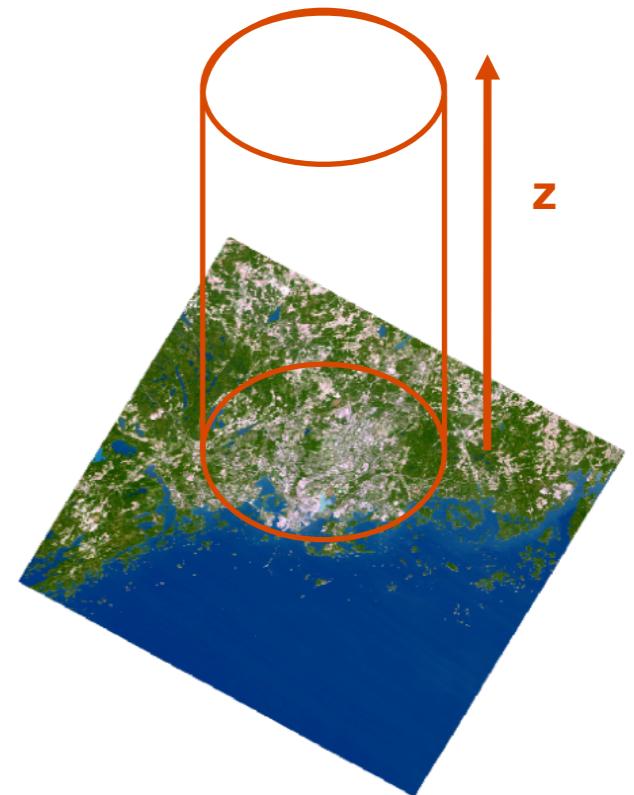
$$\Rightarrow \rho(\text{CO}_2) = 1.5 \times 10^{-1} \text{ g m}^{-3} = 150 \text{ mg m}^{-3}$$

Column density or concentration

$$\bar{n} = \text{Column concentration} = \int_0^{\infty} n(z) dz$$

The unit of the column concentration is
molecules cm⁻²

measured in Dobson units - **DU**

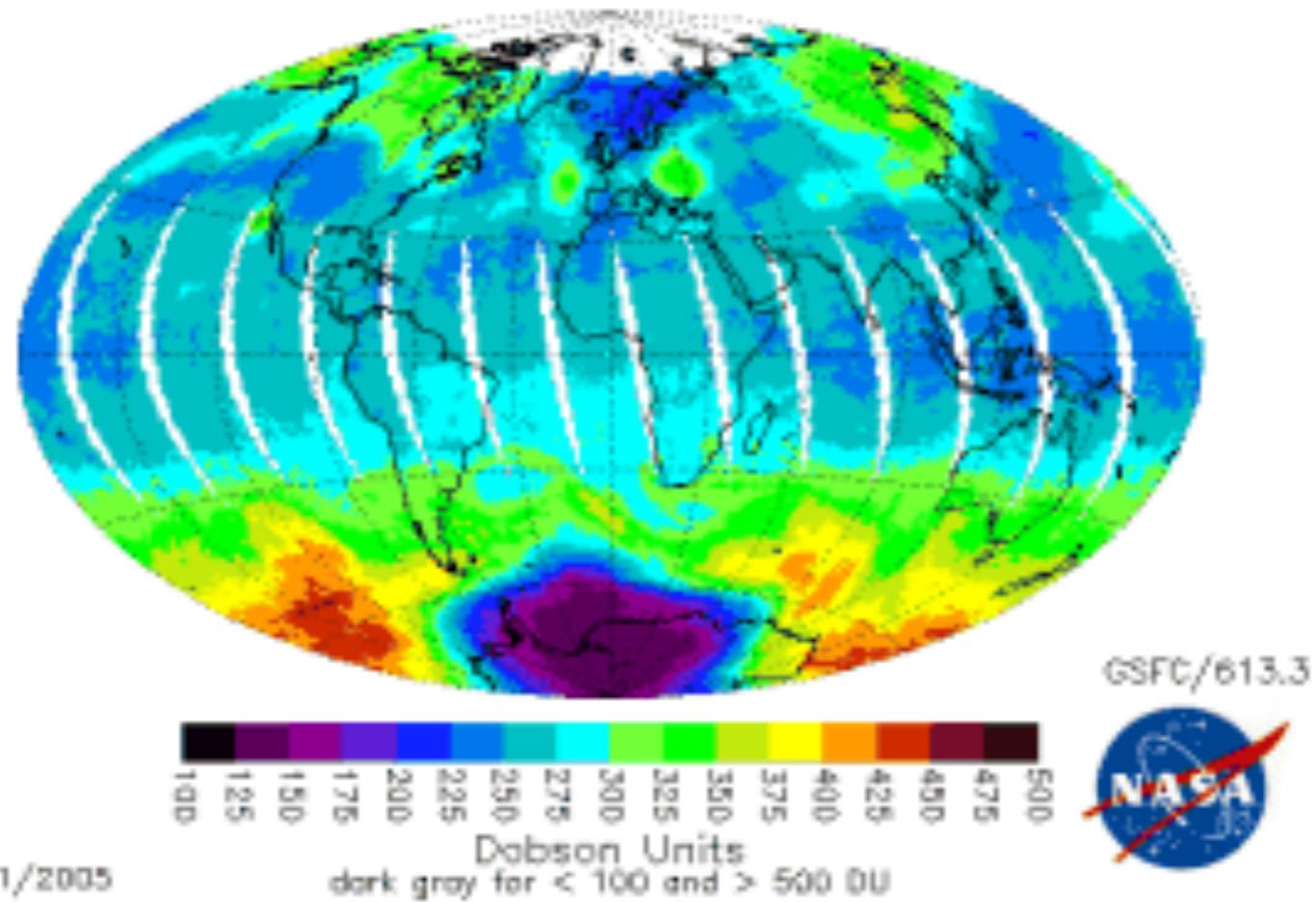


Imagine all ozone in a vertical column is concentrated into a single layer on earth surface, the thickness of that layer, measured in 1DU = 10 µm, is the abundance of ozone in the whole column!

The Dobson unit is used in remote sensing, satellite measurements, solar spectrometers etc. to assess light scattering, aerosol load, atmospherical optical depth (AOT) for instance.

Example: stratospheric ozone

EP/TOMS Total Ozone Oct 17, 2005



1 "Dobson Unit (DU)" = 0.01 mm ozone at STP = 2.69×10^{16} molecules cm^{-2}
⇒ Usually there is a layer of about 3 mm of ozone above your head.

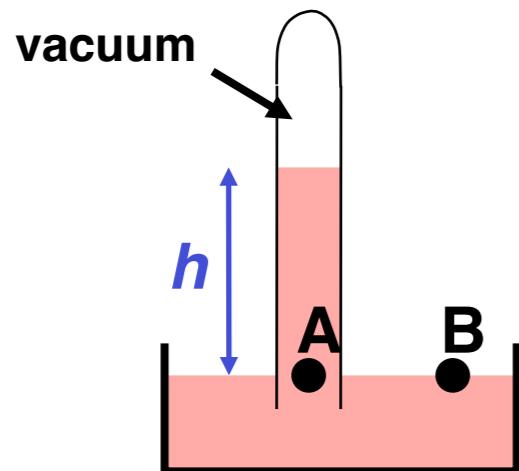
In ozone 'hole' conditions: reduction to ca. 1 mm

The mercury barometer

A pressure is defined as a force per unit area!

$$p = \frac{\text{force}}{\text{area}} = \frac{F}{A} = \left[\frac{N}{m^2} \right] = Pa$$

Principle of measure with the barometer



$$\begin{aligned}\text{Atmospheric pressure} &= P_B = P_A = \rho_{\text{Hg}}gh \\ &= 1.013 \times 10^5 \text{ Pa} = 1013 \text{ hPa} \\ &= 1013 \text{ mb} \\ &= 1 \text{ atm} \\ &= 760 \text{ mm Hg (torr)}\end{aligned}$$

bar: origin in the Greek word βάρος (baros), meaning 'weight'

Torr: derived from E. Torricelli (Italian physicist, 1608-1647)

Pa: derived from B. Pascal (French mathematician and physicist, 1623-1662)

after D.J. Jacob

Atmospheric pressure as water column

$$\text{force} = F = mg = pA$$

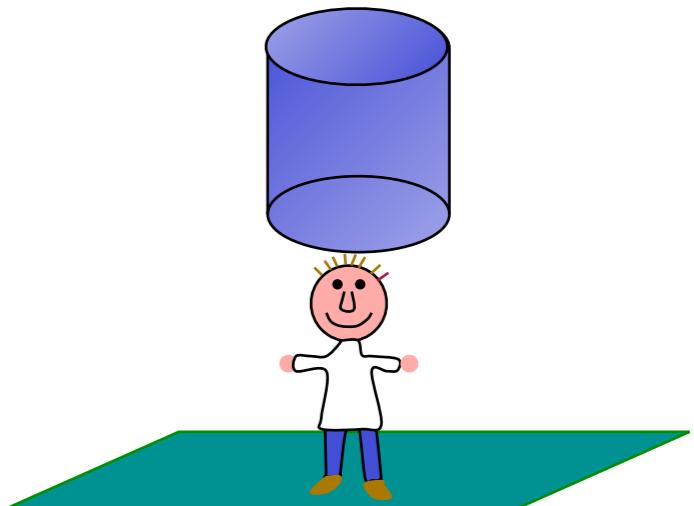
$$m = \frac{pA}{g} = \rho V h$$

$$h = \frac{p}{g\rho_{H2O}} = \frac{1.01325 \times 10^5 \frac{kg}{ms^2}}{9.81 \frac{m}{s^2} \times 10^3 \frac{kg}{m^3}}$$

height = 10.3 meter !

Do you feel that ?

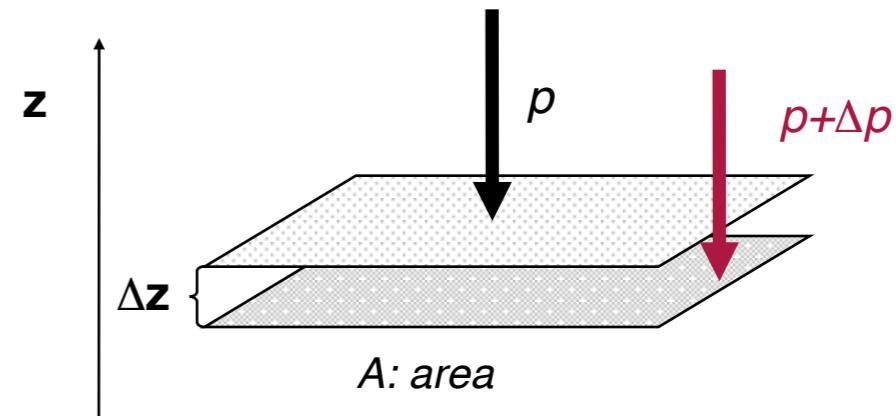
g: acceleration of gravity (9.806 m s⁻²)
m: mass [kg]
A: area [m²]
V: volume [m³]
 ρ : density [kg m⁻³]



Hydrostatic equation - pressure varies with height

$$p = \frac{mg}{A} = \frac{V\rho g}{A}$$

Pressure equals a force per unit area



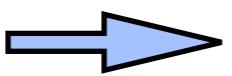
$$(p - \Delta p) = \frac{-(V + \Delta V)\rho g}{A} + \frac{V\rho g}{A}$$

$$\Delta p = \frac{-\Delta V \rho g}{A} = -\rho g \Delta z$$

$$\boxed{\frac{dp}{dz} = -\rho g}$$

→ hydrostatic, because static conditions are assumed
(e.g. no vertical wind)

hydrostatic equation



Problem: ρg is not constant with height z !

Deducing the barometric law

From ideal gas law $\rho_{air} = \frac{pM_{air}}{RT}$ replace ρ and rearrange $\rightarrow \frac{dp_{air}}{p_{air}} = -\frac{M_{air}}{RT}gdz$

assuming T to be constant and integrate for height z

$$\int_0^z \frac{dp_{air}}{p_{air}} = -\frac{M_{air}g}{RT} \int_0^z dz$$

$$\ln p(z) - \ln p(0) = -\frac{M_{air}g}{RT}z$$

yields to a function

$$p(z) = p(0)e^{-z/H}$$

with $H := \frac{RT}{M_{air}g}$

that links the pressure to height!

Implications of the barometric law

$$p(z) = p(0)e^{-z/H}$$

$H := \frac{RT}{M_{air}g}$ is called the **scale height** and is dependent on temperature and a measure for the **thickness of** atmosphere

given the a surface temperature of $T_s = 288K$ and a tropopause temperature $T_t = 217K$, we can use a mean tropospheric temperature of 253K and obtain a **mean scale height of 7.4 km**

$$p(z + H) = \frac{p(z)}{e} \quad \text{thumb rule} \quad p(z + 5\text{km}) \approx \frac{p(z)}{2}$$

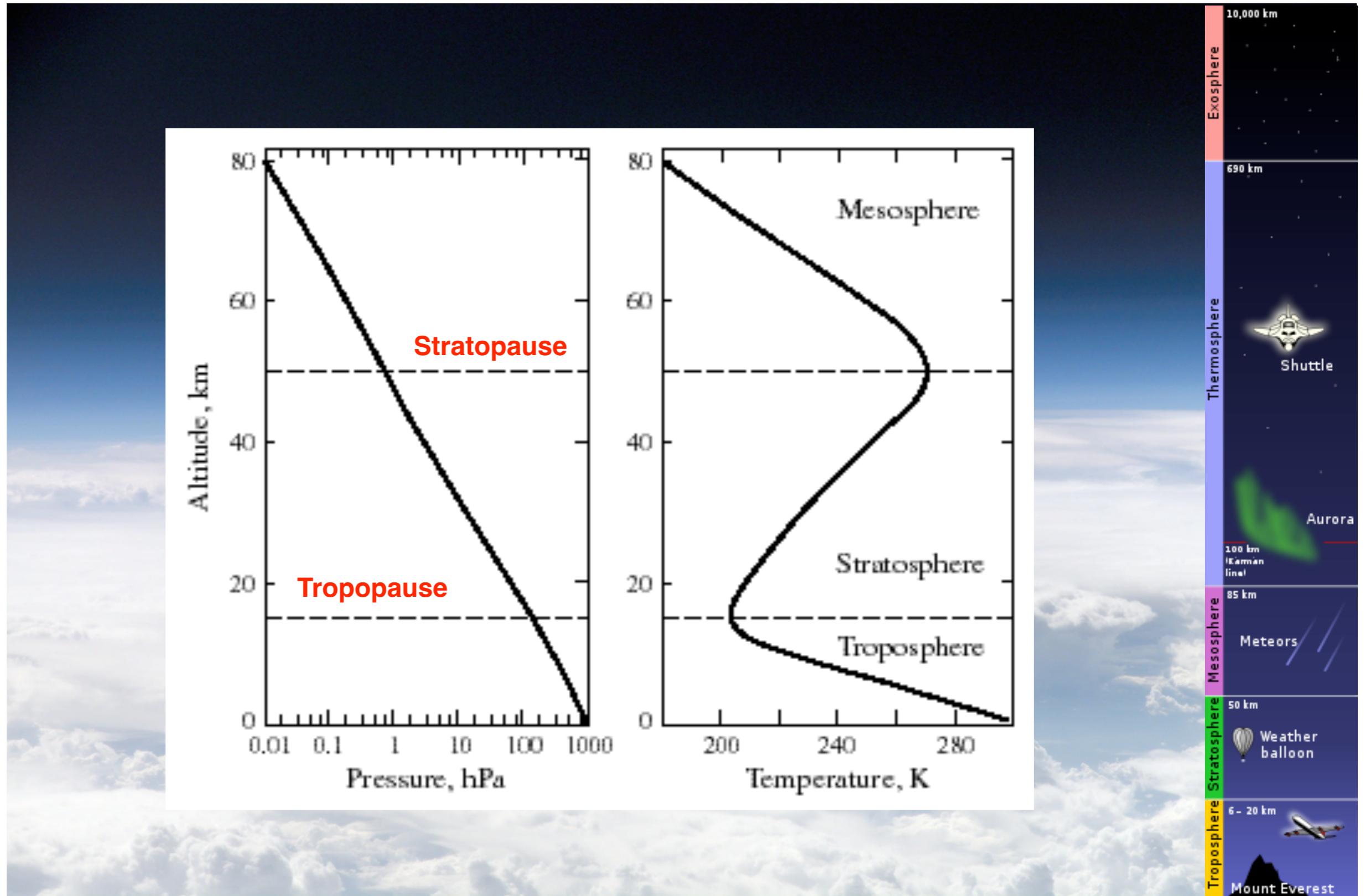
we can also link this concept to the amount of air via the ideal gas law!

$$p \sim n$$

$$n(z) \approx n(0)e^{-z/H}$$

we can also relate to concentrations by multiplication with N_A .

Vertical pressure and temperature profiles



Effects of vertical p and T distributions

The effects of the vertical distribution of p and T on atmospheric composition measures

volume mixing ratio:

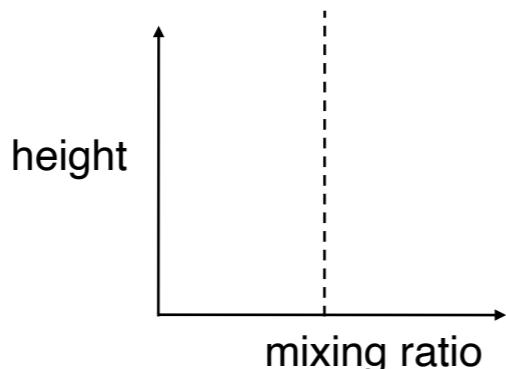
$$vmr = \frac{n_i}{n_{air}} = \frac{p_i}{p}$$

no effect of height

mass mixing ratio:

$$mmr = \frac{m_i}{m_{air}} \propto \frac{p_i}{p}$$

no effect of height as long
as the atmosphere is
well mixed



without specific source and sinks!

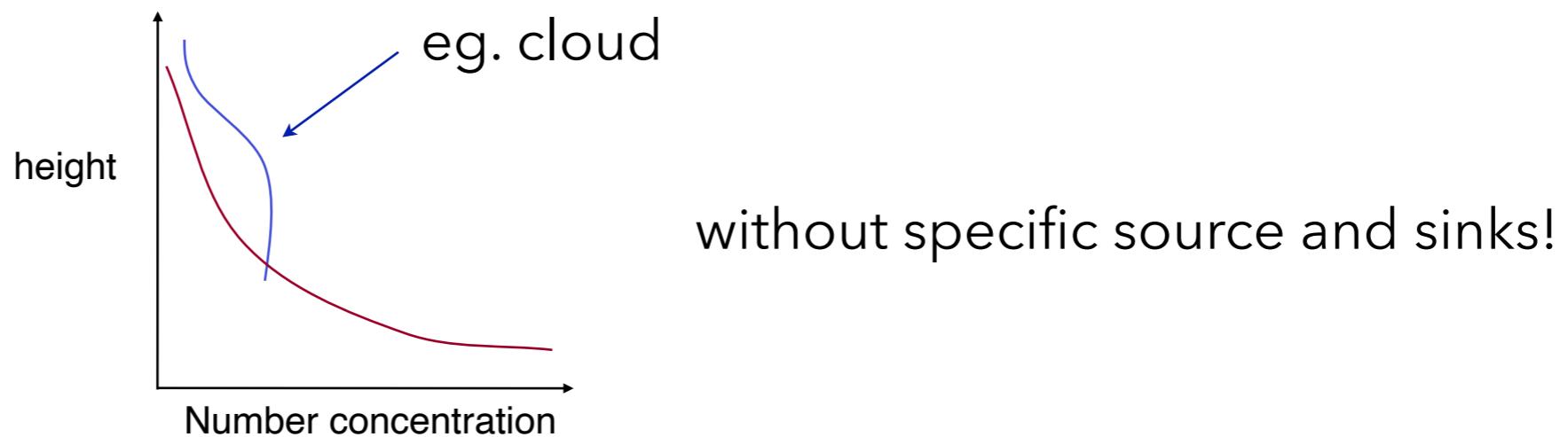
Effects of vertical p and T distributions

The effects of the vertical distribution of p and T on atmospheric composition measures

number concentration:

$$\frac{N_i}{V} = \frac{p}{RT} \propto \frac{p}{T}$$

remarkably changing with height



Vertical temperature gradient (lapse rate)

If air rises adiabatically without water vapour condensing (latent heat release) the temperature decrease per km altitude (dry lapse rate) is:

$$\frac{dT}{dz} = -9.8 \frac{\text{K}}{\text{km}}$$

dry

If water vapour condenses the temperature decrease (moist lapse rate) can be as low as:

$$\frac{dT}{dz} = -3.0 \frac{\text{K}}{\text{km}}$$

moist

Within the troposphere the temperature decrease with altitude in the troposphere (nearly all the water vapour and thus cloud formation) varies between both extremes with its mean of:

$$\frac{dT}{dz} = -6.5 \frac{\text{K}}{\text{km}}$$

mean

humidity affects remarkably the vertical temperature and transport !

Effects of convection

If air is warmer than the surrounding air masses, e.g. It flows over a warmer surface, it is lighter and will start to rise. If its cooler it will sink down



Fundamental quantities in the atmosphere

Total atmospheric mass

Radius of Earth:
6378 km

Mean surface pressure:
984 hPa

$$m_{air} = \frac{4\pi R^2 p_{surface}}{g} = 5.2 \times 10^{18} \text{ kg}$$

Total number of moles of air in atmosphere:

(remember: $M_{air} = 28.96 \text{ g mole}^{-1} = 0.02896 \text{ kg mole}^{-1}$)

$$n_{air} = \frac{m_{air}}{M_{air}} = 1.8 \times 10^{20} \text{ moles}$$

Total number of molecules in the atmosphere:

(remember: $N_A = 6 \times 10^{23} \text{ molecules mole}^{-1}$)

$$N_{air} = n_{air} \times N_A = 1.08 \times 10^{44} \text{ molecules}$$



Lecture