



EVROPSKÁ UNIE
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MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Geochemistry on the Earth's surface for analytical geochemists

2b.

Geochemistry of the atmosphere

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

Topics

- Contemporary atmosphere
 - Structure of the atmosphere (temperature-pressure distribution)
 - Composition , mass and energy transfer
 - Photochemical reactions
 - Ozone layer
- Evolution of the atmosphere in the geological past
 - The origin of the atmosphere
 - Oxygenation of the atmosphere
 - The atmosphere in the Phanerozoic



CONTEMPORARY ATMOSPHERE

Atmosphere

- Earth's gravitationally maintained gaseous envelope
- Without a sharp outer boundary – it gradually thins out into outer space
- 120 km – the limit of influence on space flights
- 100 km limit – atmosphere too thin to fly
 - machines at this height must have orbital velocity to maintain – insufficient aerodynamics

Partial pressure

- Expression of component ratios
- Equivalent expression:
 - 21% O₂
 - P_{O₂} = 0.21
 - 210000 ppmv
 - 296 g/m³

The mass of the atmosphere

- 5.2×10^{18} kg
- 50% within 5.6 km from the surface
- 75% within 11 km of the surface
- 99.99997% within 100 km of the surface
- The "thick" part of the atmosphere lies within 30 km
 - Pressure over 0.01 bar

Building atmosphere

- Division based on temperature distribution

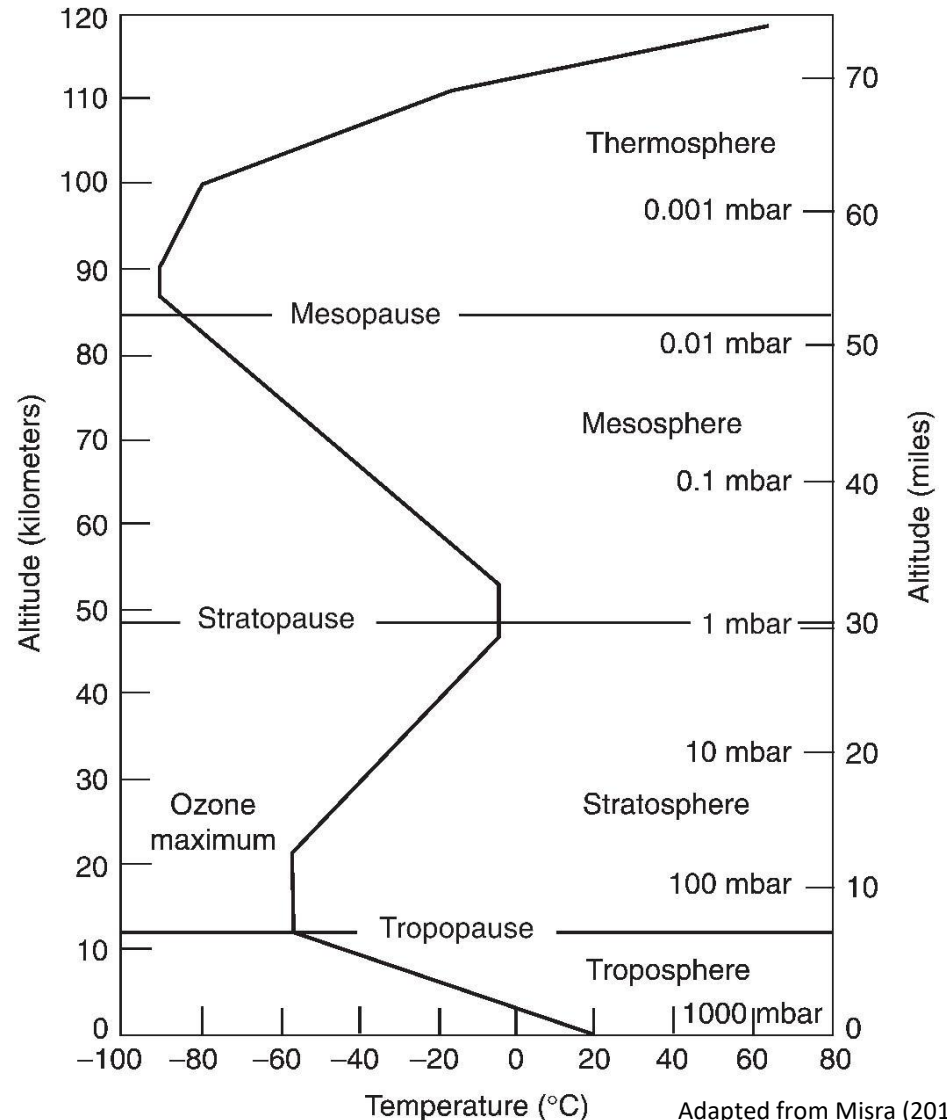
a) *Troposphere*

b) *Stratosphere*

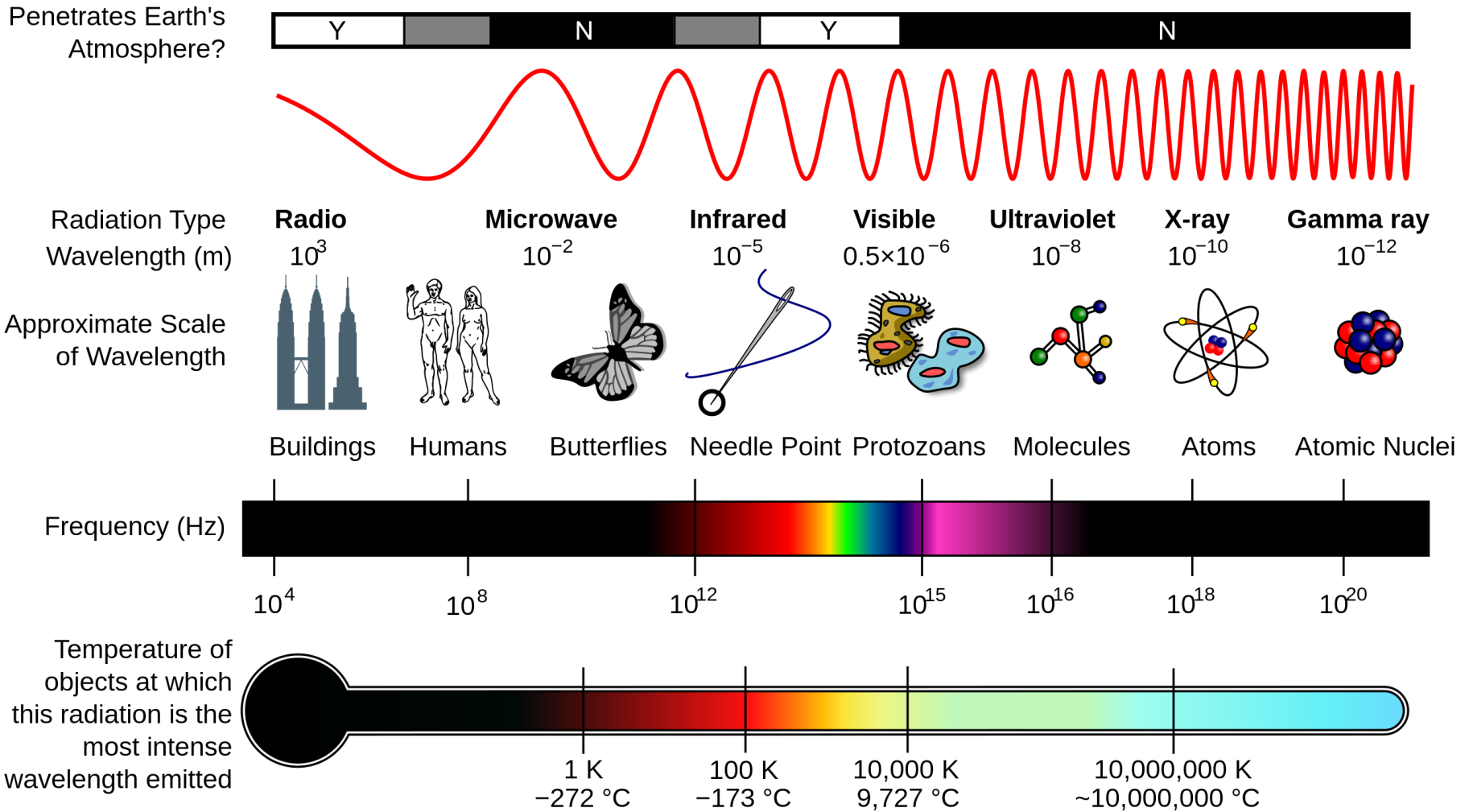
c) *Mesosphere*

d) *Thermosphere*

- Heating from solar radiation
 - Esp. visible and UV radiation
 - Different parts absorb different wavelengths



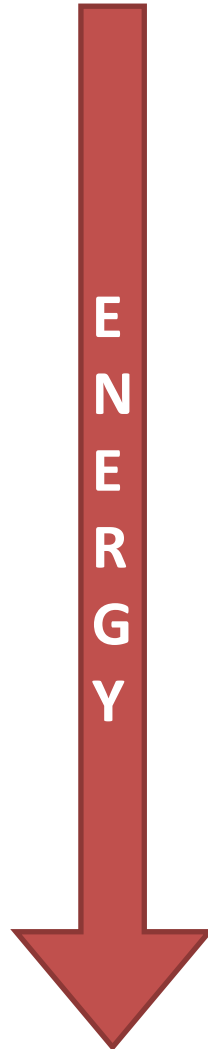
Properties of radiation



Translated from "EM Spectrum Properties edit" by InductivelyElevated, NASA - self-made, information by NASA Based off of File:EM_Spectrum3-new.jpg by NASA The butterflies icon is from the P icon set, P biology.svg the humans are from the Pioneer plaque, Human.svg the buildings are the Petronas towers and the Empire State Buildings, both from Sky scraper/compare.svg. Licensed under CC BY-SA 3.0 via Commons - https://commons.wikimedia.org/wiki/File:EM_Spectrum_Properties_edit.svg#/media/File:EM_Spectrum_Properties_edit.svg

Distribution of radiation according to wavelengths

optical spectrum	infrared IR, IR 790 nm – 1 mm	far away	25 μm – 1 mm
		medium	2.5 μm – 25 μm _
		close	0.79 μm – 2.5 μm _
	Visible, VID, VIS 390 – 790 nm	red	~ 650 nm
		Orange	~ 600 nm
		yellow	~ 580 nm
		green	~ 525 nm
		blue	~ 450 nm
		purple	~ 400 nm
	ultraviolet region, UV 1 nm – 400 nm	close	200 nm – 400 nm
		distant	1 nm – 200 nm _ _



Troposphere

- Tropos – Greek to rotate, mix
- Closest to the surface
- 7 km (poles) to 17 km (equator)
 - avg. 11 km
- Heated by radiation reflected from the Earth's surface
- Temperature decreases with altitude
- The most extensive vertical movements
 - Most meteorological phenomena
- 80–90% of the mass of the atmosphere
- Most of the water in the atmosphere
- The upper boundary is the tropopause

Thermosphere

Noctiluscent cloud
80 km

Mesosphere

Stratosphere

Troposphere

Nacreous cloud
15–25 km

Cirrus clouds
6–12 km

Contrails
6–12 km

International
Space Station
330–410 km

Auroræ

Kármán line 100 km

Mesopause 80 km

Stratopause 50 km

Ozone layer

Tropopause 12 km

Cumulonimbus
clouds

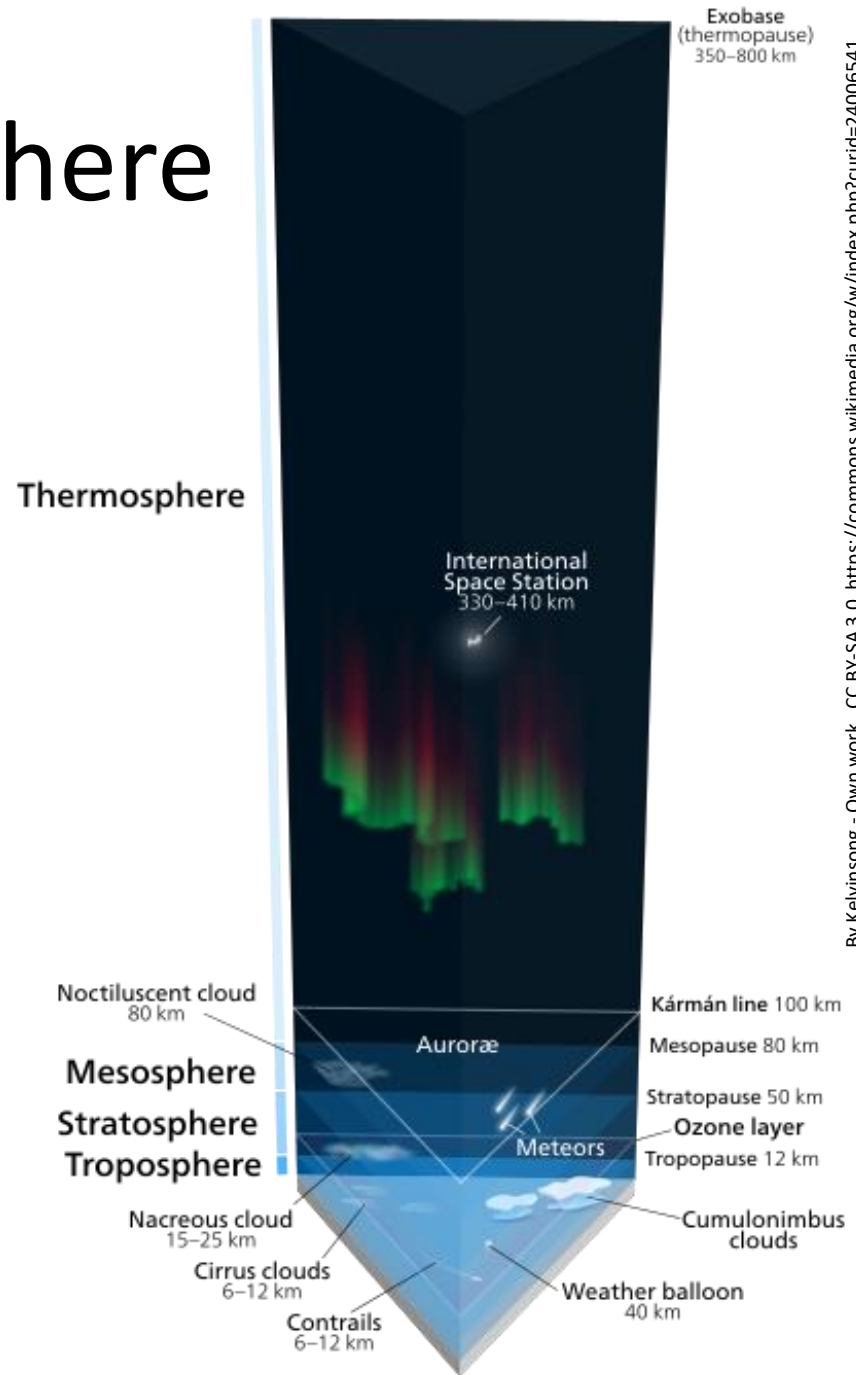
Weather balloon
40 km

Exobase
(thermopause)
350–800 km

OBJECTS WITHIN LAYERS NOT DRAWN TO SCALE

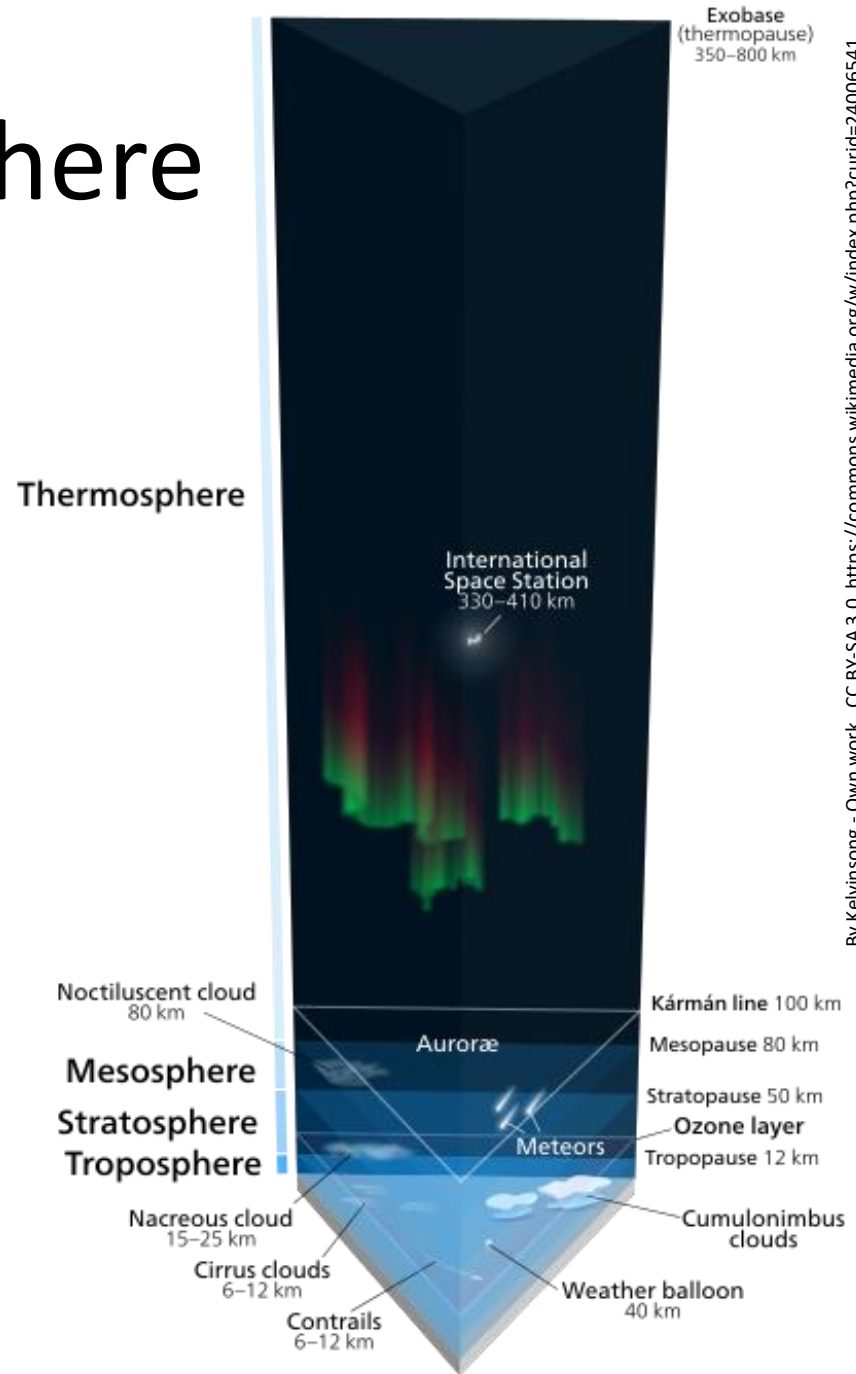
Stratosphere

- Stratos – Greek for layer
- Up to ca. 50 km
- Ozone layer – protection against UV radiation
 - Most at 20–25 km
- Temperature increases with altitude
 - Ozone absorbs UV and emits IR (thermal) radiation
- Pressure at the upper edge (stratopause): 0.001 bar



Mesosphere

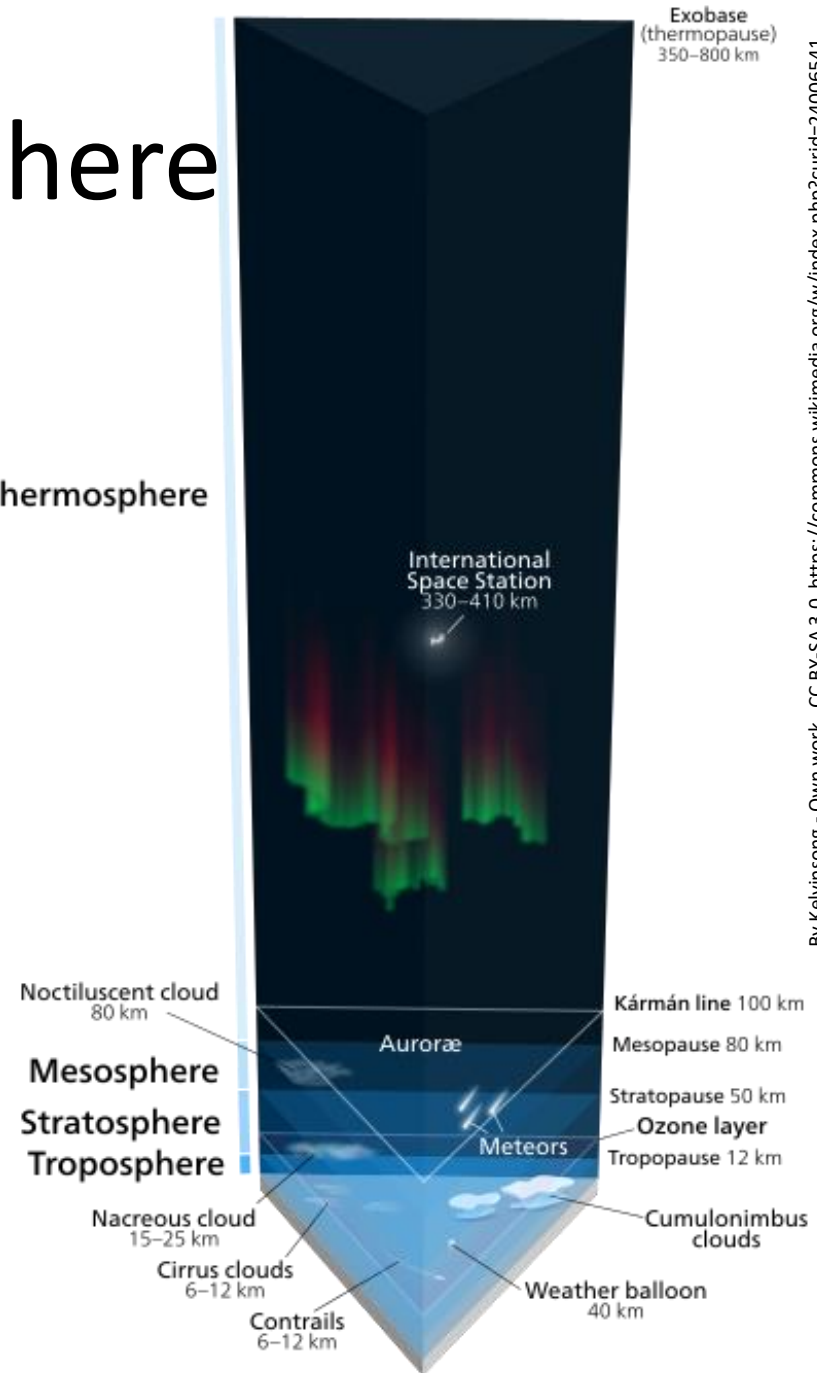
- Mesos – Greek „the middle“
- Up to 80-85 km
- Burning meteorites in the atmosphere
- Without O₃ – temperature decreases with altitude
 - Minimum in the mesopause
 - -100°C
 - The coldest place on earth
- High for aircraft (balloons) and low for satellites – difficult to study



Thermosphere

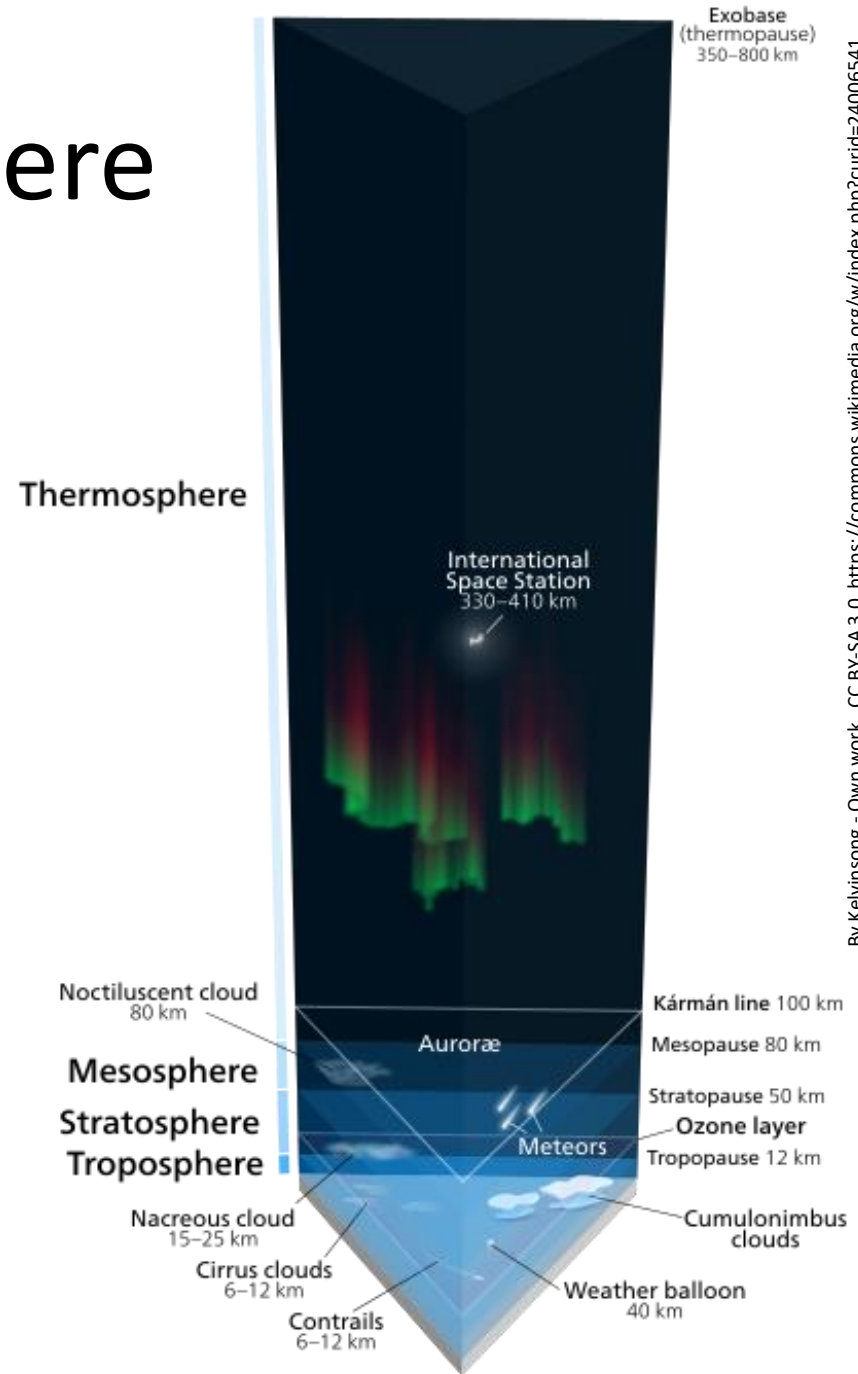
- Variable altitude (up to 800 km)
- Satellites
 - ISS at an altitude of 320–380 km
- The temperature rises up to 1500 °C
 - Absorption of high-energy UV radiation ($\lambda < 0.12 \mu\text{m}$) by oxygen and nitrogen

Thermosphere



Exosphere

- The outermost edge of the atmosphere
 - Variable definitions
- Very diluted – limited molecular collisions
- 500-1000 km to 10,000 km

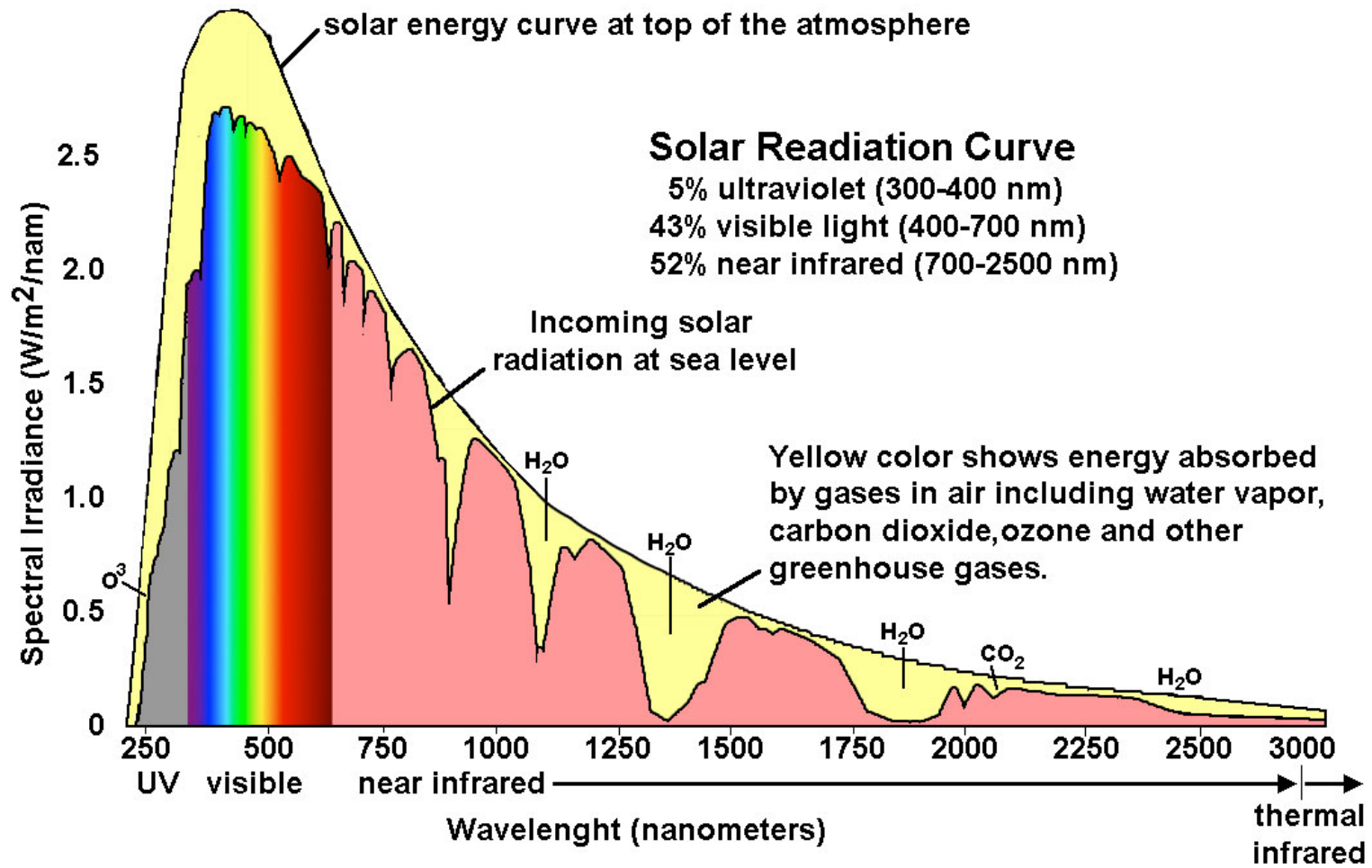


Other parts of the atmosphere

- Defined by other properties
- **Ionosphere** – ionized region important for the propagation of radio waves
 - Overlap with mesosphere and thermosphere

Absorption of radiation in the atmosphere

Solar Energy Distribution



Absorption of radiation in the atmosphere

- Thermosphere (UV with $\lambda < 0.12 \mu m$)
 - $O_2 + \text{UV photon} \Rightarrow O_2^+ + e^-$
 - $O_2^+ + e^- \Rightarrow O + O + \text{heat}$
- Mesosphere and stratosphere (UV with $\lambda = 0.12\text{--}0.3 \mu m$)
 - Absorbed by O_2 , O_3
- UV with $\lambda > 0.3 \mu m$ penetrates into the troposphere
- IR radiation is significantly absorbed by water

Photochemical reactions

- Reaction of a photon with a molecule
- Photolysis – breakdown of molecules by photochemical reaction
- Formation of free radicals – an unpaired electron in the valence layer
 - Very reactive
 - E.g. hydroxyl **radical** $\text{OH}\cdot$

Ozone layer

- Steady-state amount of O_3 in the stratosphere
 - A series of reactions with balanced production and consumption of O_3
- **Production:**
 - $$3O_2 + \text{UV photon} \Rightarrow 2O_3$$
 - A catalyst molecule (receives energy) and a photon of $\lambda = 0.185\text{-}0.22 \mu\text{m}$ are needed
 - All UV consumed within 20 km above the surface
- **Consumption:**
 - $$2O_3 + \text{UV photon} \Rightarrow 3O_2$$
 - A photon of $\lambda = 0.23\text{-}0.32 \mu\text{m}$
 - It goes all the way to the earth's surface

Ozone layer

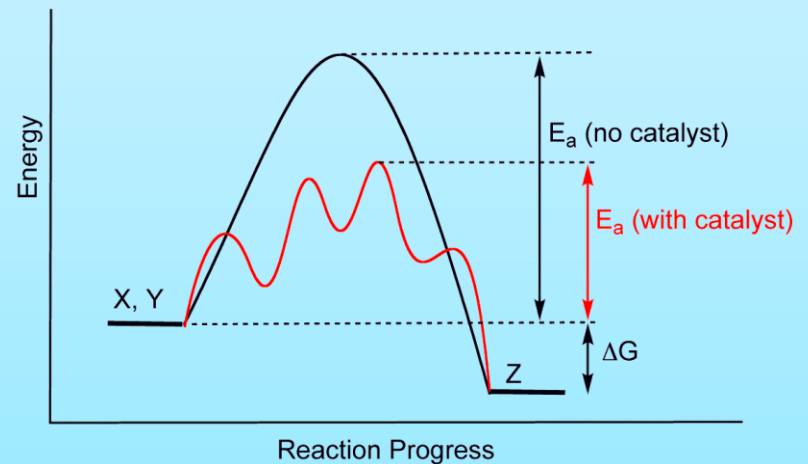
- Total concentration is a combination of:
 - Amount of UV radiation (decreasing towards the surface)
 - Atmospheric density (decreasing from the surface)
- Optimum between 15 and 35 km (equator)
- Ozone layer – 90% of O₃ on Earth
 - About 10 ppmv (100x more than on the surface)

Destruction of O₃

- Expected O₃ concentrations do not correspond with observation
- Catalyzing substances decompose O₃ in the atmosphere
- Especially free radicals
 - HO_x
 - NO_x
 - ClO_x
- In the upper atmosphere, a molecule of NO_x decomposes ~10⁵ molecules of O₃ before it naturally decomposes (below it is about 10)
- Anthropogenic damage

Catalyst

- A substance entering a reaction that is not consumed by the reaction and remains unchanged after
- A small amount of the substance is enough
- Lowers energy barriers, helps with particle orientation for easier interaction...



Exercises

- Look around, think and try to describe:
- 3 ways in which some substances enter the atmosphere
- 3 ways in which some substances get out of the atmosphere
- What effect do they have on air quality?

The composition of the atmosphere

Table 13.2 Average composition of the Earth's unpolluted lower atmosphere (up to an altitude of 25 km).

Gas	Volume%	Source	Estimated residence time
N ₂	78.084	Biologic	10 ⁶ –10 ⁷ yr
O ₂	20.946	Biologic	3000–10,000 yr
Ar	0.934	Radiogenic	Forever
CO ₂	0.0383	Biologic, geologic, anthropogenic	2–10 yr
Ne	0.00182	Earth's interior	Forever
He	0.000524	Radiogenic	~10 ⁶ yr
CH ₄	0.00017	Biologic, geologic, anthropogenic	2–10 yr
Kr	0.000114	Radiogenic	Forever
H ₂	0.000055	Biologic, chemical	4–8 yr
N ₂ O	0.00003	Biologic, anthropogenic	5–200 yr
Xe	0.000009	Radiogenic	Forever
NO ₂	0.0000002	Biologic, anthropogenic	0.5–2 days
O ₃	0 to 0.000007	Chemical	100 days

Water vapor (H₂O) is ~0.40% by volume for the whole atmosphere, typically 1 to 4% near the surface. Other species present in the atmosphere at parts per trillion level concentrations include: NO, SO₂, CO, NH₃, H₂S, CS₂, (carbonyl sulfide), CH₃SCH₃ (dimethyl sulfide), methyl chloride (CH₃Cl), methyl bromide (CH₃Br), methyl iodide (CH₃I), hydrogen chloride, CCl₃F (CFC-11 Freon), CCl₂F₂ (CFC-12 Freon), and carbon tetrachloride (CCl₄).

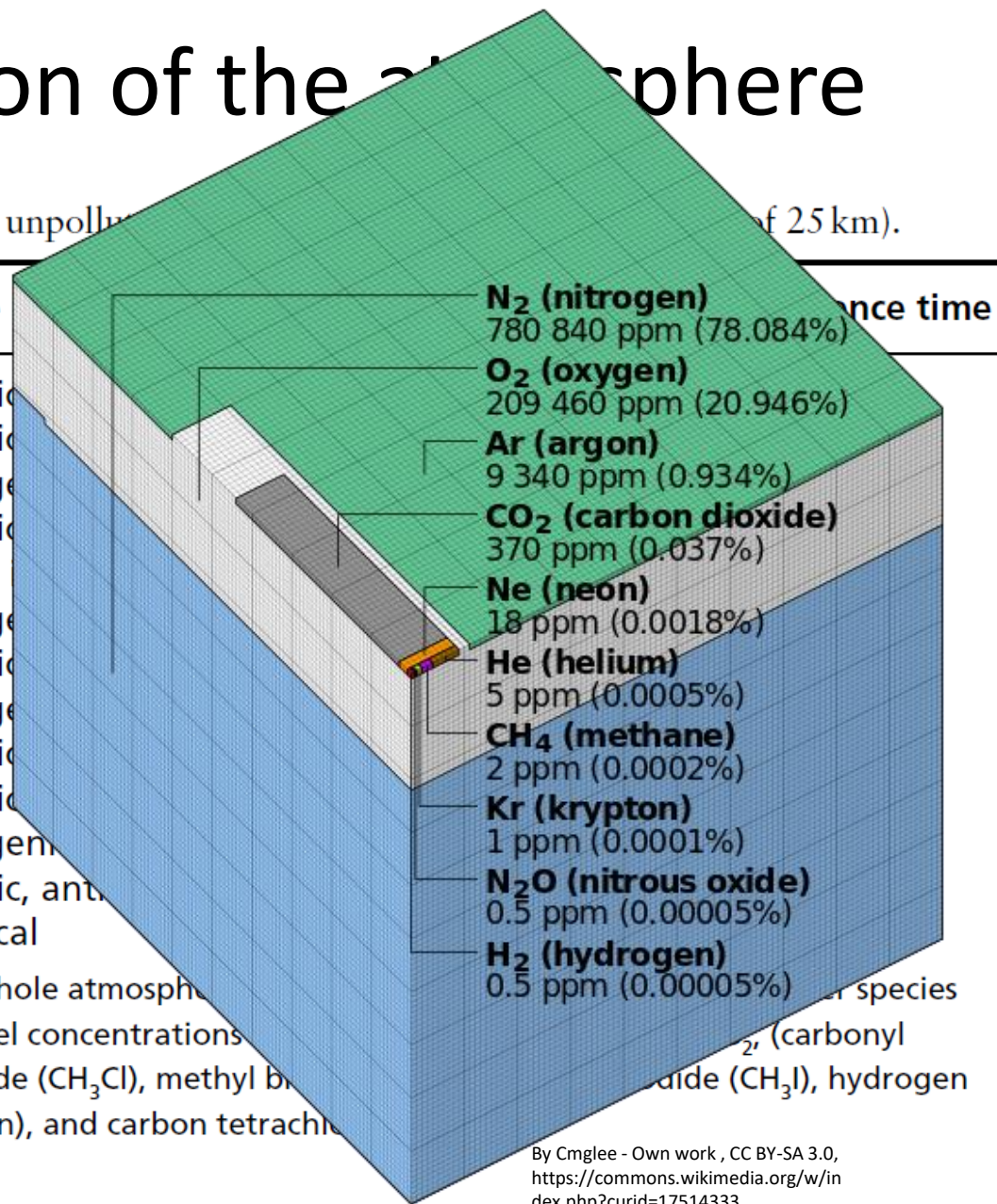
Sources of data: Hobbs (2000); Railsback (2006).

The composition of the atmosphere

Table 13.2 Average composition of the Earth's unpolluted atmosphere (at sea level, up to an altitude of 25 km).

Gas	Volume%	Source	Residence time
N ₂	78.084	Biogenic	
O ₂	20.946	Biogenic	
Ar	0.934	Radiogenic	
CO ₂	0.0383	Biogenic	
Ne	0.00182	Earth's	
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Xe	0.000009	Radiogenic	
NO ₂	0.0000002	Biogenic, anthropogenic	
O ₃	0 to 0.000007	Chemical	

99%



Water vapor (H₂O) is ~0.40% by volume for the whole atmosphere. Other trace gases present in the atmosphere at parts per trillion level concentrations include: carbonyl sulfide, CH₃SCH₃ (dimethyl sulfide), methyl chloride (CH₃Cl), methyl bromide (CH₃Br), hydrogen sulfide (CH₃I), hydrogen chloride, CCl₃F (CFC-11 Freon), CCl₂F₂ (CFC-12 Freon), and carbon tetrachloride (CCl₄).

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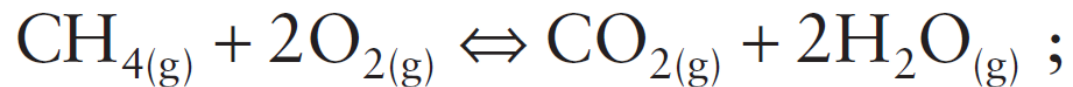
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The composition of the atmosphere

- The composition is very homogeneous
- It differs from other planets mainly in the presence of abundant O₂
- Rock environment: reducing conditions vs. atmosphere: oxidizing conditions
- The composition reflects the balance between volcanic, biological and sedimentary processes
 - Thermodynamic equilibrium?

Thermodynamic equilibrium of the atmosphere

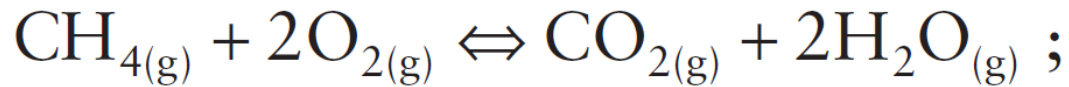
- Can be judged from substance concentrations – do they correspond to equilibrium concentrations in terms of TD?
- E.g. methane oxidation



$$K_{\text{eq}} = \frac{P_{\text{CO}_2} (P_{\text{H}_2\text{O}})^2}{P_{\text{CH}_4} (P_{\text{O}_2})^2}$$

- The value of $K_{\text{eq}} = 10^{140}$
- *What should dominate in equilibrium?*

Thermodynamic equilibrium of the atmosphere



$$K_{\text{eq}} = \frac{P_{\text{CO}_2} (P_{\text{H}_2\text{O}})^2}{P_{\text{CH}_4} (P_{\text{O}_2})^2}$$

- The value of $K_{\text{eq}} = 10^{140}$
- Eq. partial pressure of $\text{CH}_4 = 3.5 \times 10^{-148}$ atm
- Real value 1.7×10^{-6} atm
- The constituents of the atmosphere are in a steady state with residence times ranging from days to millions of years

Residence times

Table 13.2 Average composition of the Earth's unpolluted lower atmosphere (up to an altitude of 25 km).

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Sources of data: Hobbs (2000); Railsback (2006).

EVOLUTION OF THE ATMOSPHERE IN THE GEOLOGICAL PAST

The evolution of the atmosphere

- A difficult topic
 - We do not know all mechanisms
 - Reconstruction of a series of assumed successive equilibrium states
 - Are they even possible? Even today there is no equilibrium...

NASA photo



Primal atmosphere

- First tens of millions of years after formation
- Gas composition of the original nebula
- Similar to gas giants
 - H, He, H₂O, CH₄, NH₃
- Blown away with the demise of the nebula
 - The influence of the solar wind



Secondary atmosphere

- Formed by outgassing of the mantle
 - Mantle-like representation of volatiles
 - Metals have not yet separated into the core
 - More reductive than today
 - It is gradually approaching the current volcanism (also thanks to the decrease in temperature)
- Material from meteorites
 - Water contained in hydrated silicates or adsorbed on dust grains



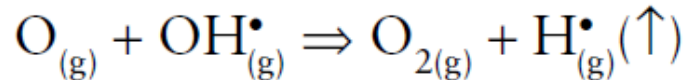
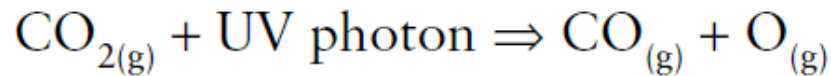
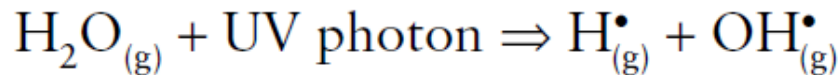
Secondary atmosphere

- Especially nitrogen and carbon
 - Based on preserved weathering products
- Almost no free oxygen
- Increased concentrations of greenhouse gases (CO₂ and CH₄)
 - E.g. from the absence of glacial sediments (the Sun had a lower luminosity than today)
 - The oldest glacial 2.5 Ga
 - P_{CO2} drop from 1-10 bar to 0.3-0.03 bar
 - Information from marine sediments, banded Fe ores
 - Methane could be released by living organisms (reduction of CO₂)

Oxygenation of the atmosphere

- The oxic/anoxic nature of the environment indicates the balance of oxygen input/output from the system

- **Abiotically:**



- Free H escapes into space – it does not react back into H₂O
- Released O₂ consumed by weathering, oxidation of volcanic gases and Fe in seawater
- Little overall input!
- Without oxygen there is no ozone layer
 - Life underground or in the sea, chemotrophic

Phototrophic organisms

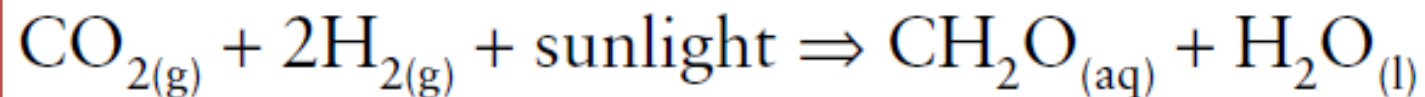
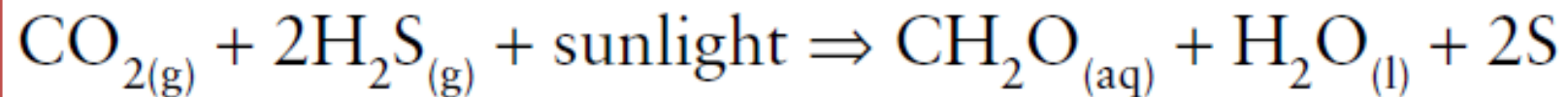
Anoxygenic photosynthesis

- Sunlight and reducing agents (H_2 , H_2S) as a source of energy for synthesis of organic matter from CO_2
- The by product is oxidized sulfur or water – not oxygen!

By daveyn from United States - Morning Glory Pool, Yellowstone National Park, CC BY 2.0, <https://commons.wikimedia.org/w/index.php?curid=29855827>



Today, chemotrophic bacteria inhabit extreme environments – for example, geysers.



Phototrophic organisms

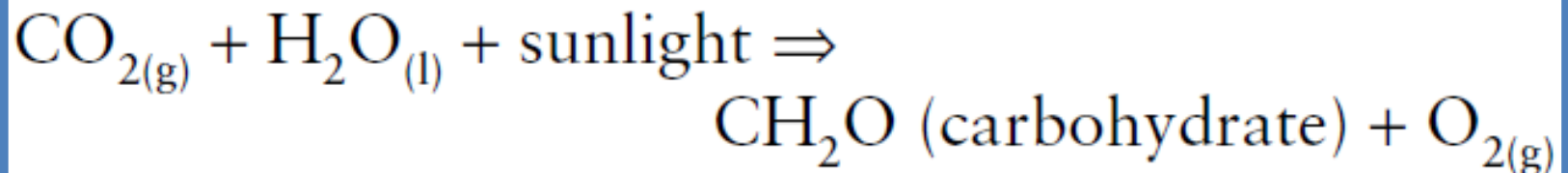
By Christian Fischer, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=33920504>



Today, cyanobacteria can cause serious environmental problems in eutrophicated waters, where they consume oxygen and produce toxins.

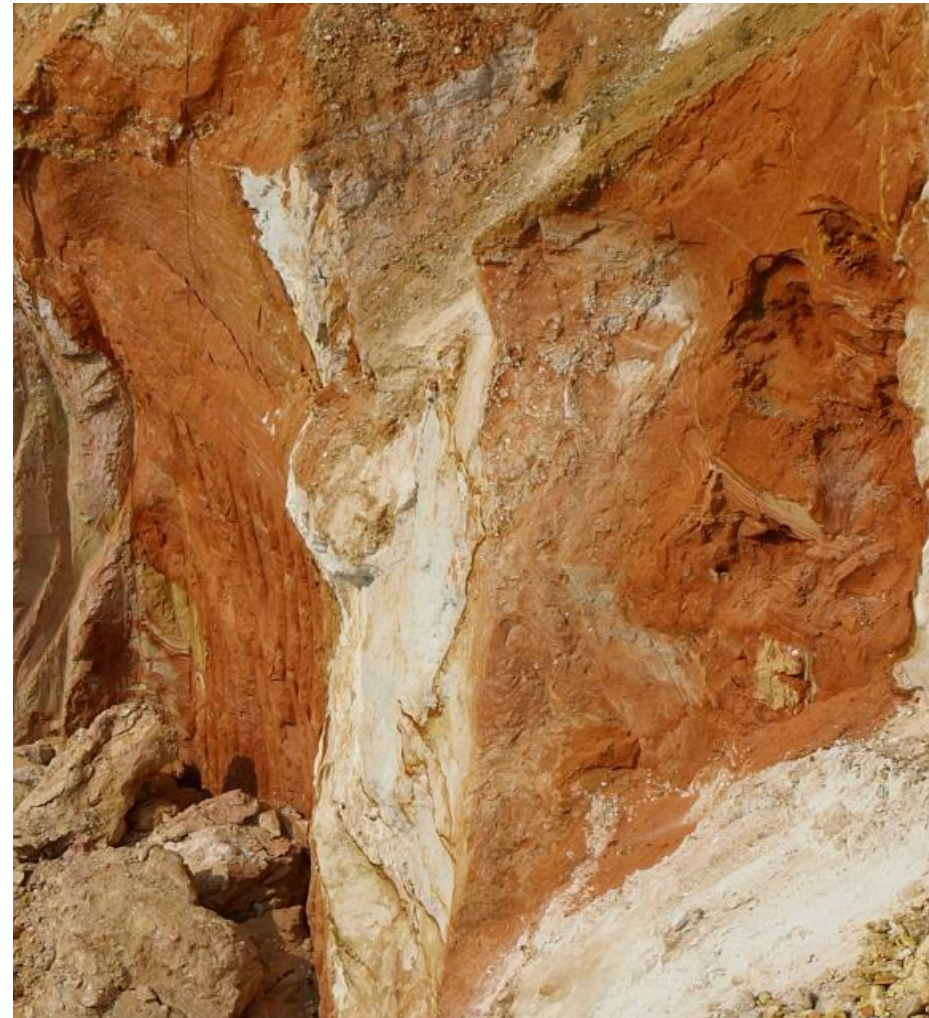
Oxygenic photosynthesis

- Cyanobacteria
- Synthesis of organic matter from solar energy, water and CO₂
- O₂ is a waste product



Oxygenation of the atmosphere

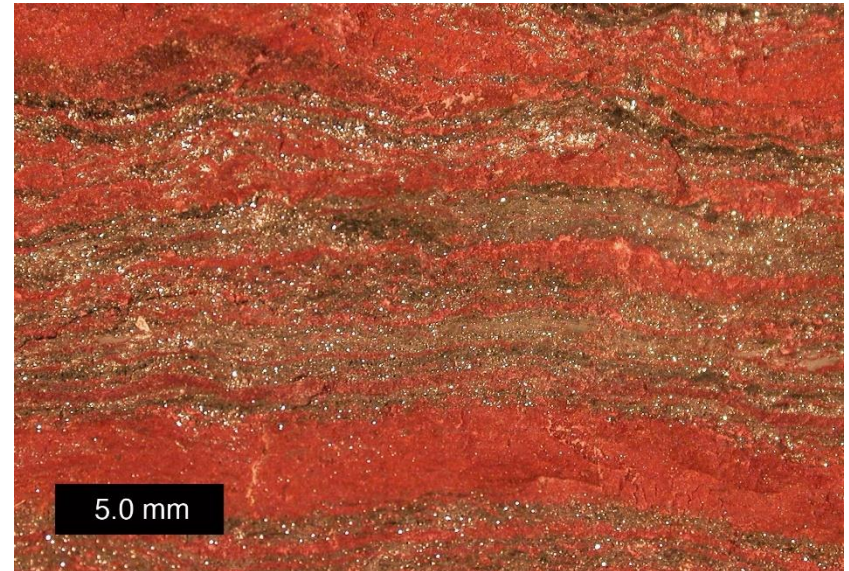
- Increase in O_2 in the atmosphere given by the absorption of O_2
 - Reoxidation of organic matter
 - Oxidative reactions in the environment (weathering, oxidation of volcanic gases)
 - Oxidation products re-reduced by bacteria
- Today approx. 99% of O_2 recaptured (respiration and decomposition of organic matter)
- 0.1% Organic matter retained in sediments



Iron oxides in sand.

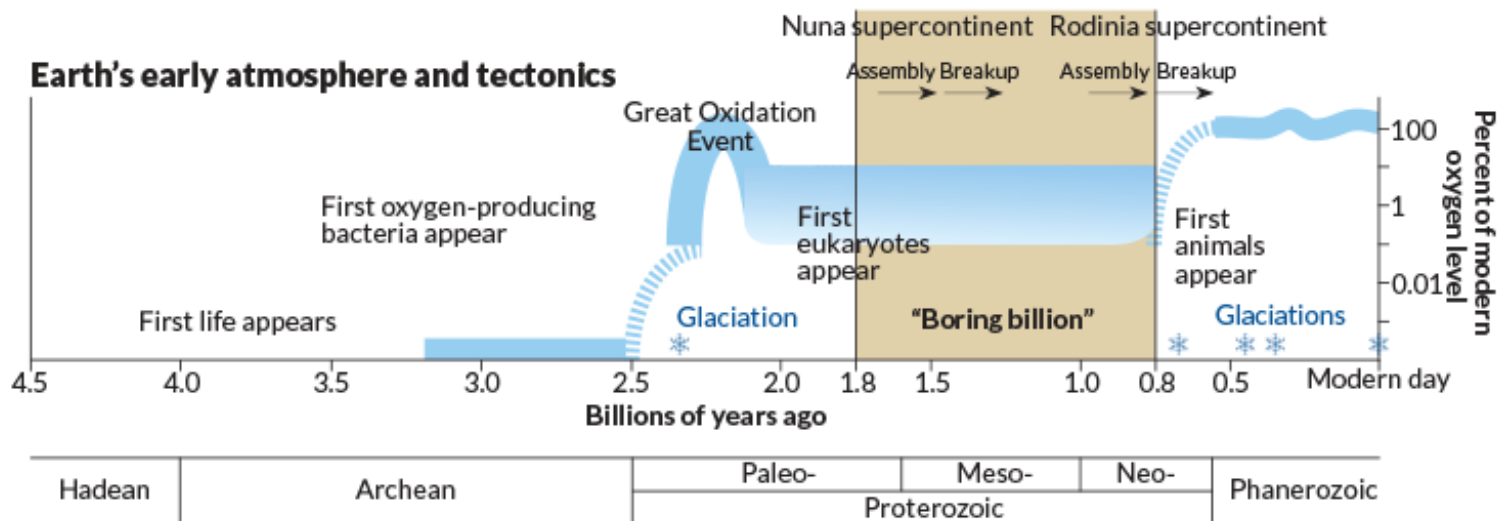
Oxygenation of the atmosphere

- Expected sharp increase in the O₂ content in the atmosphere in the period of 2.4–2.2 Ga
- Older paleo-soils have lost most of their iron (Fe²⁺ leaching)
- Continental red sediments appear by 2.2 Ga
- Banded iron ores (BIF) – abundant before 2.4 Ga, Fe²⁺ must have been abundant in water to form
- Isotopic traces
 - Sulfur isotopes
 - Carbon isotopes



Causes of the increase

- Cyanobacteria documented 2.7 Ga – 400 mil. year gap to increase
- Increased O₂ input
 - More intensive burial of organic matter (shelf development?)
- Decreased O₂ output
 - Reduction of volcanic activity (decrease in gas oxidation)
 - Gradual change in the oxidation conditions of the upper mantle and the composition of volcanic gases
- The great unknown...



ENVIRONMENTAL ASPECTS

Atmospheric pollution

- Can be divided into three types:
 - Inorganic gases
 - Nitrogen oxides (N_2O , NO , NO_2)
 - Sulfur oxides (SO_2 , SO_3)
 - Carbon oxides (CO , CO_2)
 - O_3 , NH_3 , H_2S , HF , HCl , Cl_2 , Rn
 - Volatile organic substances
 - Methane, freon...
 - Particulate matter (PM 10)

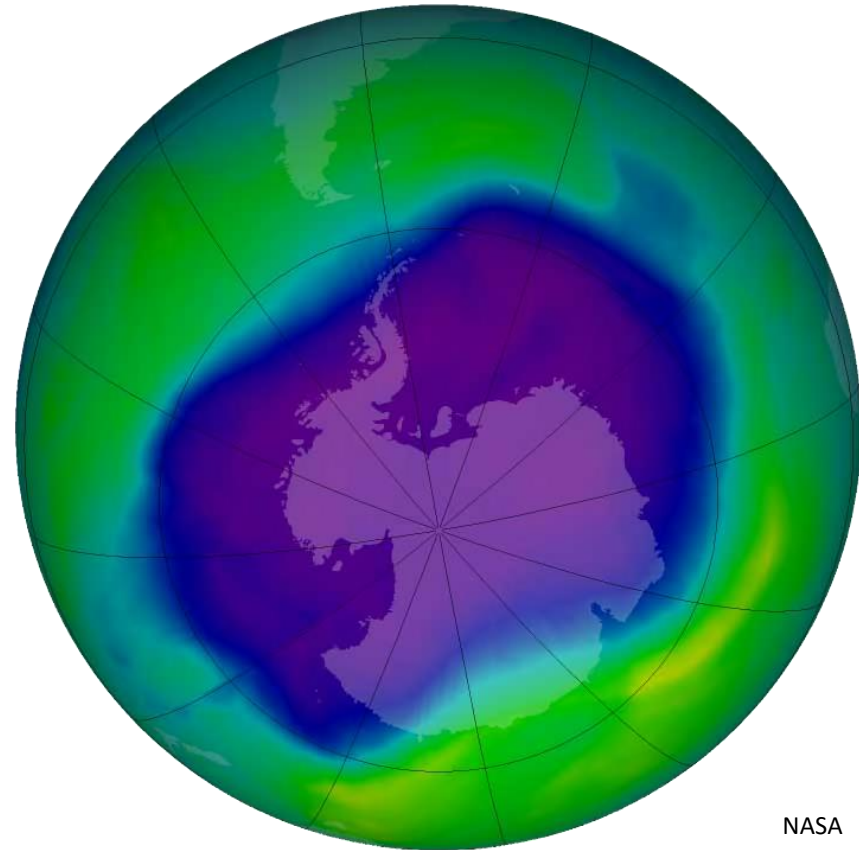
Air pollution as a tragedy of the commons



- <https://www.youtube.com/watch?v=0b2Tl0x-niw>
- <https://youtu.be/CxC161GvMPc>

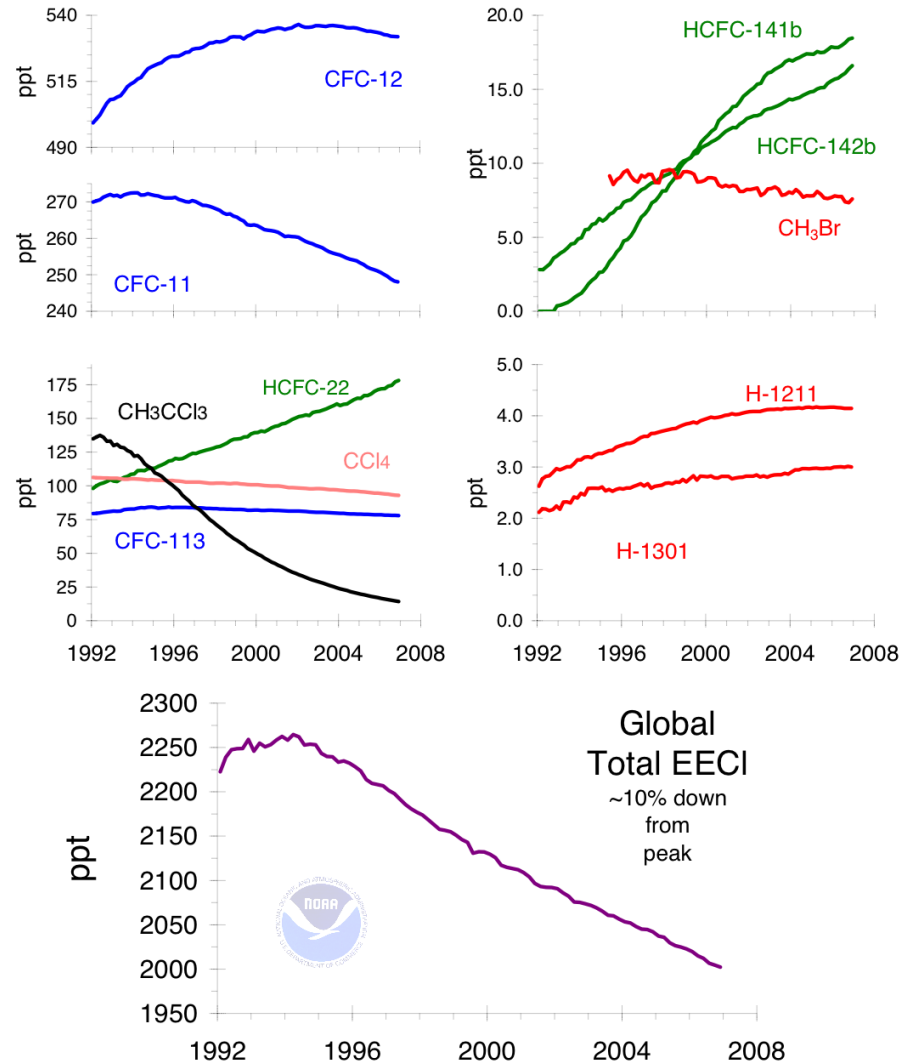
The ozone hole

- Ozone in the upper parts of the atmosphere, necessary for the existence of life
- Most at the equator, decreasing towards the poles
- In the 1970s and 1980s, a significant decrease was observed over Antarctica
- Seasonal phenomenon (mostly in spring)
- Decomposition by free radicals and halogens



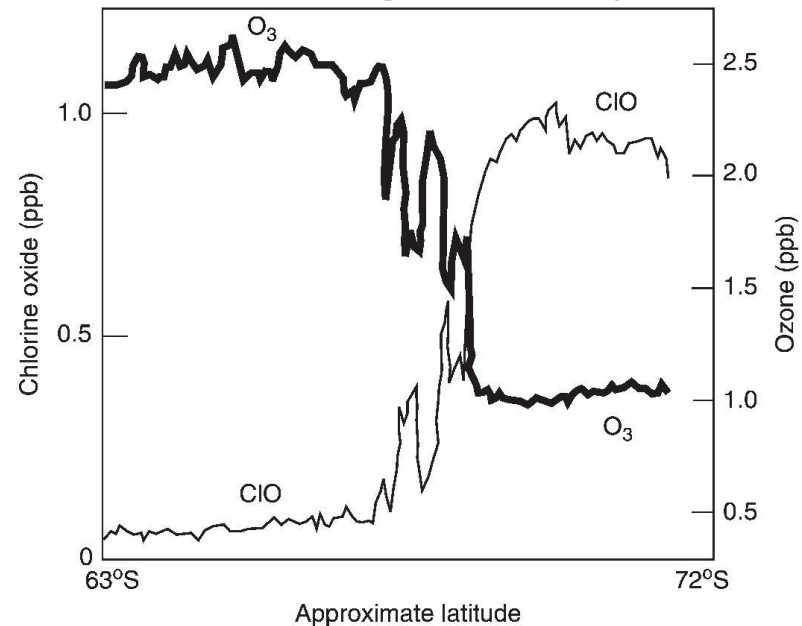
The ozone hole

NOAA, Public Domain, <https://commons.wikimedia.org/w/index.php?curid=515657>



Development of concentrations of ozone-depleting

- Halogenated hydrocarbons
- End of production by Montreal Protocol (1987)
- Gradual restoration in the following century



Adapted from Misra (2012)

Fig. 13.11 Inverse correlation between chlorine oxide (ClO) and ozone concentrations in the atmosphere over the Antarctic polar region on September 16, 1987. Note that in the high latitudes of Antarctica, the very low ozone concentrations are matched by the relatively high concentrations of ClO produced by the reaction of ozone with Cl. The curves have been smoothed for simplicity. (After Anderson *et al.*, 1991.)

The ozone hole

- Still, there are other complications – just look at the headlines from the Guardian :
- [Ozone layer not recovering over populated areas, scientists warn \(February 2018\)](#)
- [Mysterious rise in banned ozone-destroying chemical shocks scientists \(May 2018, someone in East Asia is producing CFCs\)](#)
- [Mysterious source of illegal ozone-killing emissions revealed, say investigators \(July 2018, 18 out of 21 companies in China use banned substances in production\)](#)
 - "We confirmed companies use CFC, while acknowledging the illegality and being very blase about its use (...) These companies, again and again, told us everybody else does this."
 - "Despite efforts to get rid of this activity, it continues."
 - "The profit margins were very high, the demand was high and the risks were very low."
- [Beijing is playing its part in cracking down on the use of banned ozone-depleting CFC-1 \(August 2018\)](#)
- [Record-size hole opens in ozone layer above the Arctic \(April 2020, though it was allegedly more of a natural geophysical curiosity\)](#)

Smog

- Smoke + fog
- Smoke – an aerosol created by burning, a mixture of solids, gas and liquid
- Fog – is formed by the condensation of water vapor on aerosol particles (condensation nuclei)
- Dispersed particles (0.2-2 μm) cause reduced visibility (haze)
- They may contain substances harmful to health

By Bobak - Own work, CC BY-SA 2.5, <https://commons.wikimedia.org/w/index.php?curid=2190112>

Beijing after the rain.



A typical day in Beijing.



London smog

- Sulphurous, winter, reducing...
- Burning fossil fuels
- CO production
- Sulfur oxides – coal 0.2-7% sulphur
- SO₂ forms an acid on contact with water
- Today on the decline – developing countries



By NT Stobbs , CC BY-SA 2.0, <https://commons.wikimedia.org/w/index.php?curid=4094275>

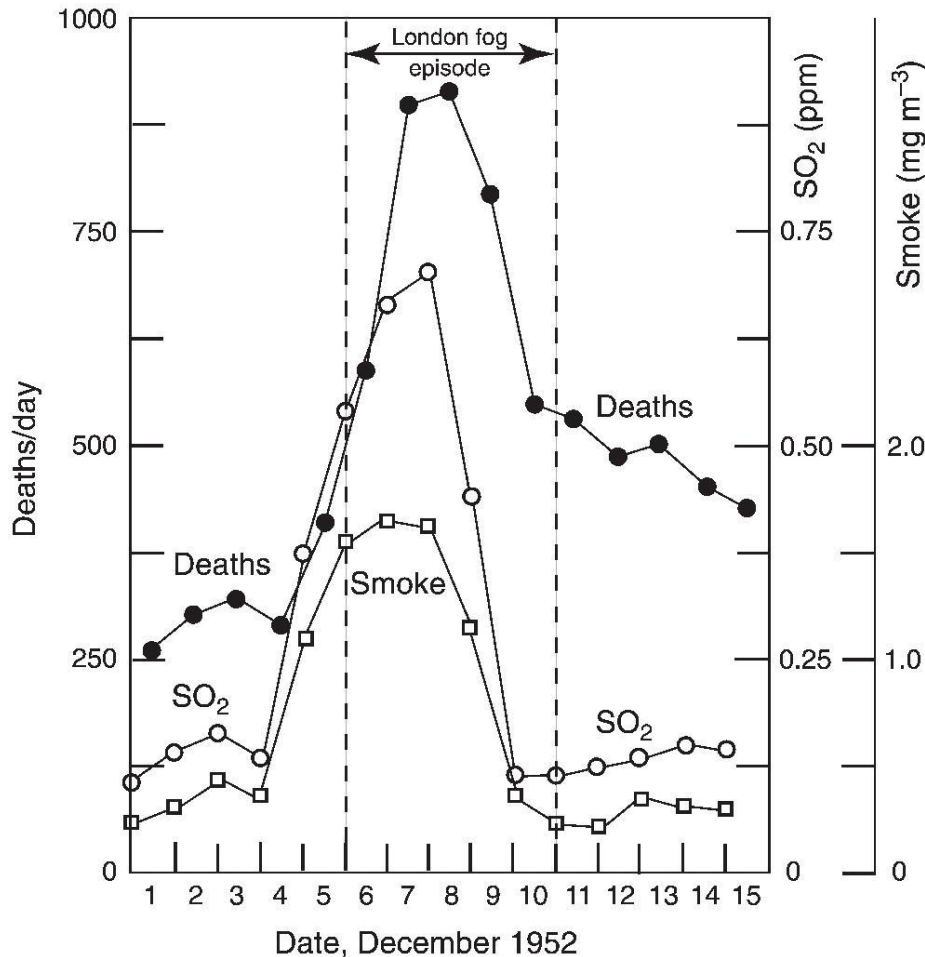
Great Smog of London



© Getty Images



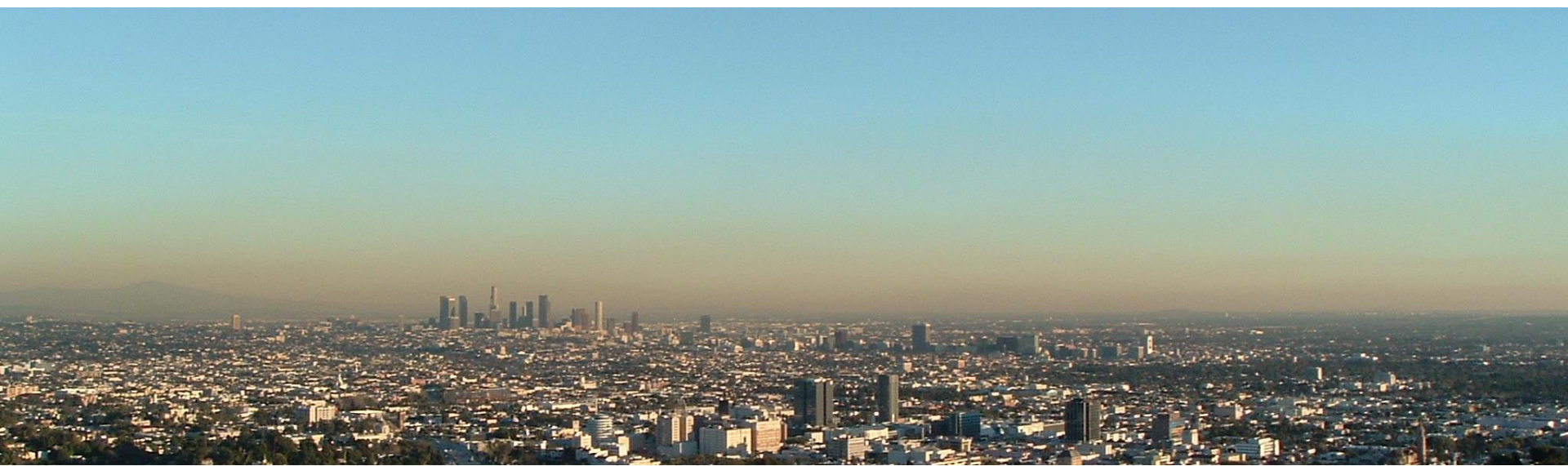
Great Smog of London



- December 1952
- Cloudiness over the city caused cooling and formation of mist
- Further cooling led to thickening of smog by heating exhalations
- A combination of circumstances leading to 4,000 deaths and 100,000 illnesses

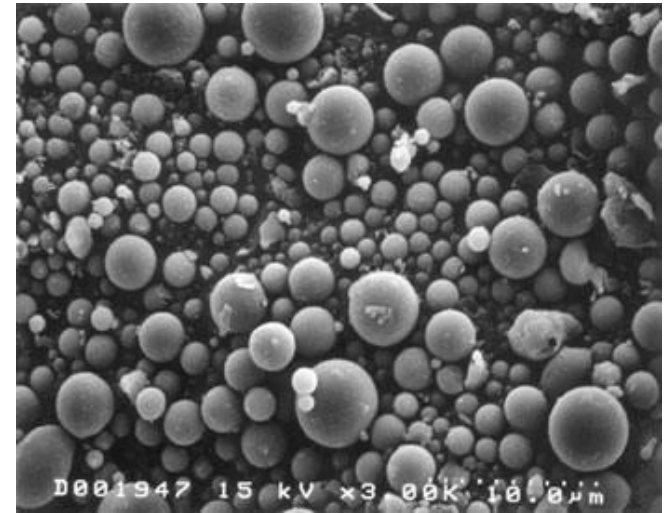
Photochemical smog

- Los Angeles, Californian, oxidative...
- No smoke, no fog
- Varied composition: dust particles, NO_x , O_3 , CO, hydrocarbons...
- It is created by photochemical reactions – daily cycles, mostly at noon
- The primary sources are exhalation of NO_x and hydrocarbons from industry and transport
- Due to sunlight interaction, other harmful substances are produced
- Damage to plants, human health (esp. respiratory)



Particulate matter

- A mixture of solid particles and droplets – defined by size, not composition
- The smaller the particles, the more dangerous
 - PM10 (10 μm)
 - PM2.5 (2.5 μm) – get deep into the lungs and irritate (the smallest particles even in the bloodstream)
- Internal combustion engines, coal burning, fires, road/tyre abrasion, dust from operations, windblown dust...



Fly ash from coal power plants.

Acid rains

- Acid rain is created by the interaction of gases, aerosol particles and rain
- Sulfuric acid, nitric acid and hydrochloric acid
- Volcanic activity, biological processes, human activity
- It damages the water environment, soils, vegetation, buildings, but also human health.

Acid rains

- On the example of H_2SO_4
- In the gas phase:
 1. Oxidation of gaseous SO_2 to H_2SO_4
 2. Condensation of gaseous H_2SO_4 and water to solution (aerosols or clouds)
 3. Dissociation of H_2SO_4 to SO_4^{2-} and H^+
- In the liquid phase:
 1. Dissolving gaseous SO_2 into solution
 2. Conversion to H_2SO_3 and dissociation
 3. Conversion of sulfites to sulfates
- The result is acidification of precipitation – H^+ increase

Greenhouse gases

- They maintain the average temperature of the planet at today's level (+15 °C)
 - Without an atmosphere, the temperature is -18 °C
- Visible sunlight (radiation) passes to the Earth's surface
- Reflected IR radiation (thermal radiation) absorbed by greenhouse gases
- Especially. CO₂, CH₄, N₂O and H₂O
- Anthropogenic supply of greenhouse gases
 - Increase in avg. temperatures during the 20th century by 0.7 °C



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