FH MÜNSTER
University of Applied Sciences

Climate Change & Greenhouse Gases: Causes, Effects and Solutions

„Lectures for Future L4F“

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What is it about?

Photographic image of the Earth from 29000 km distance

taken by the crew of Apollo 17 on December 7th, 1972: „Blue Marble“

Outline

1. Challenges of the 21st century
2. The earth's climate and the global energy balance
3. Global energy generation
4. Solar energy generation
5. Water splitting
6. Outlook
7. Literature

1. Challenges of the 21st century

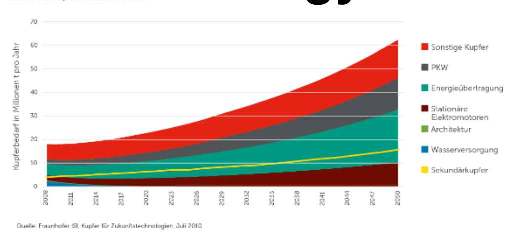



- **Emission of climate-active trace gases and climate change**
  - **CO_2 neutral energy economy: PV, wind → H_2, PtG, LNG, battery storage**
  - **CO_2 capture: 1.10^{12} t CO_2 by 2100 for 2° target (SdW 08/19) → geochemistry?**
  - **New forms of mobility: electric and hybrid drives, artificial fuels**

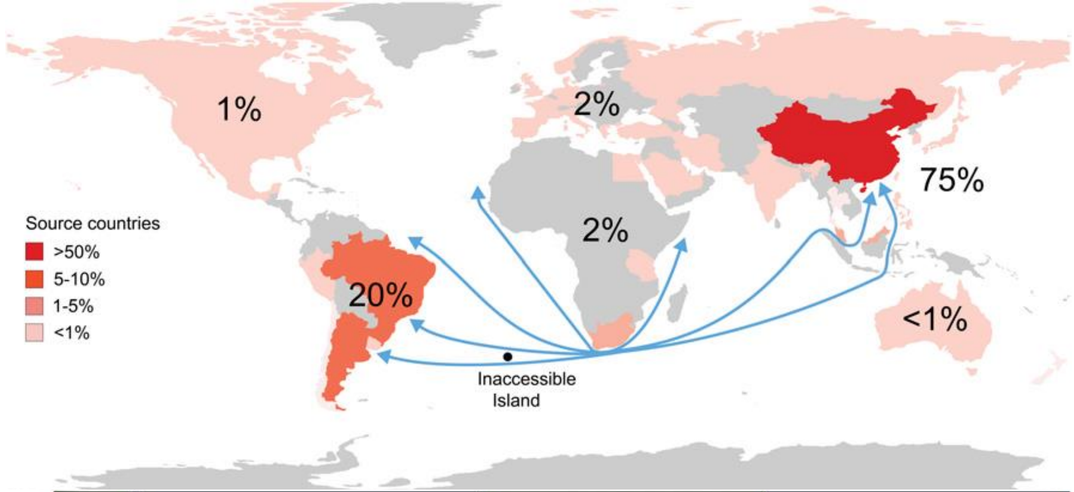
- **(Micro)plastic and nutrient input into the biosphere**
  - **Threats to marine & terrestrial food chains**
  - **Threat to biodiversity (6th mass extinction)**
  - **Expansion of dead zones due to eutrophication**

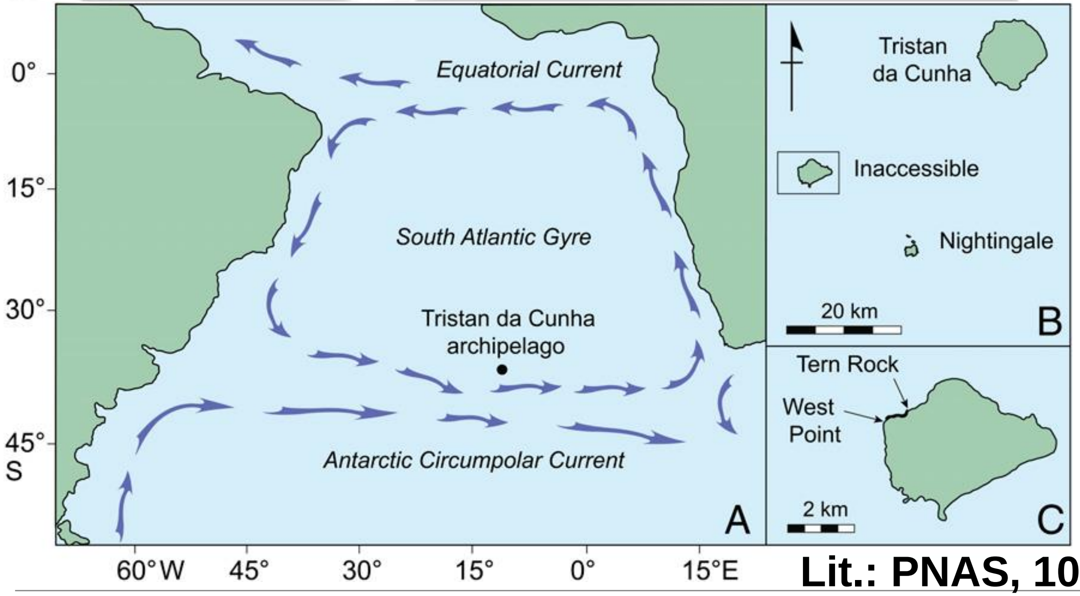
- **Increasing land and water consumption**
  - **Threats to food and drinking water security**
  - **Loss of arable land**
  - **Evaporation of inland waters**

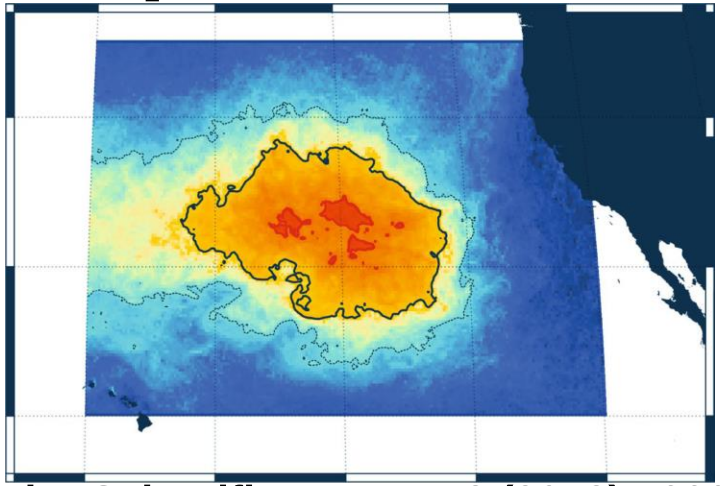
- **Rising demand for raw materials threatens resources & expansion of renewable energy sources**
  - **Strategic metals: Li, Co, Cu, Ga, Ge, In, rare earth metals, W, Ir, Bi, ...**
  - **Plastic crisis: microplastic formation, recycling rate, critical additives and markers**
  - **Quartz crisis: extreme increase in demand for building materials**
  - **Phosphate crisis: mines in North Africa facing exploitation, peak around 2030!**
  - **Iridium crisis: water treatment by electrochlorination increases demand & price strongly**



Trend: Increasing input of plastic into the biosphere



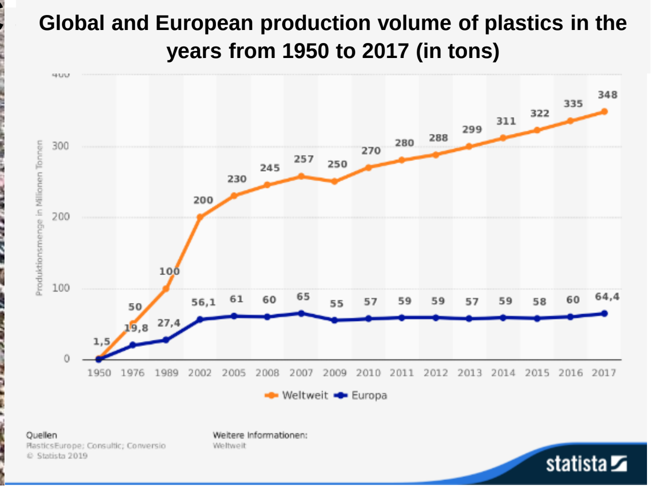




Lit.: Scientific Reports 8 (2018) 4666

Great Pacific Garbage Patch

Source: BBC



Lit.: PNAS, 10.1073/pnas.1909816116

Trend: Increasing input of plastic into the biosphere

Size	Amount
Global cumulative product volume	9 x 1012 kg
Emission rate	3.1 %
Plastic in environment (cumulative, global)	279 x 109 kg
Plastic in the environment per person	37 kg/ cap
of which degradable in 100 years (50%)	18.5 kg /cap
of which degradable in 1000 years (50%)	18.5 kg/cap
Degrations rate (100a)	185 g/(cap a)
Degrations rate (1000a)	18.5 g/cap a)
Plastic degradation rate per year	204 g/ (cap a)
Current plastic input	5400 g/(cap a)
Degradation to maintain current plastic level	Factor 27

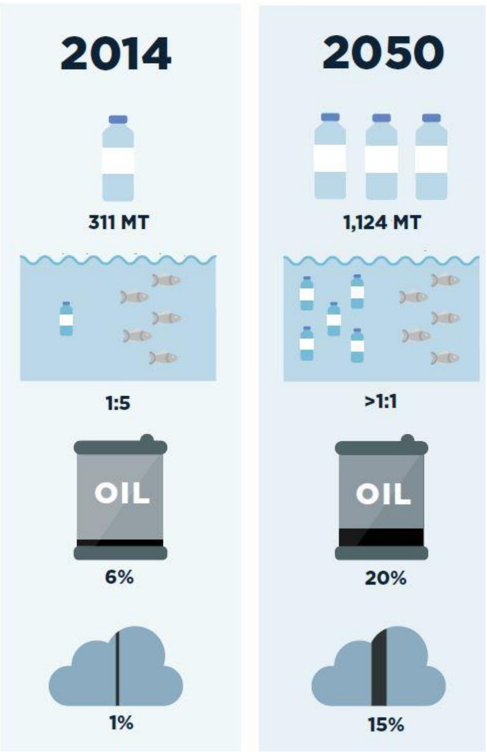
Source: Fraunhofer UMSICHT, Oberhausen, Germany

Plastics production

Plastics to fish ratio (in weight)

Global oil consumption for plastics production

Share of CO_2 emissions



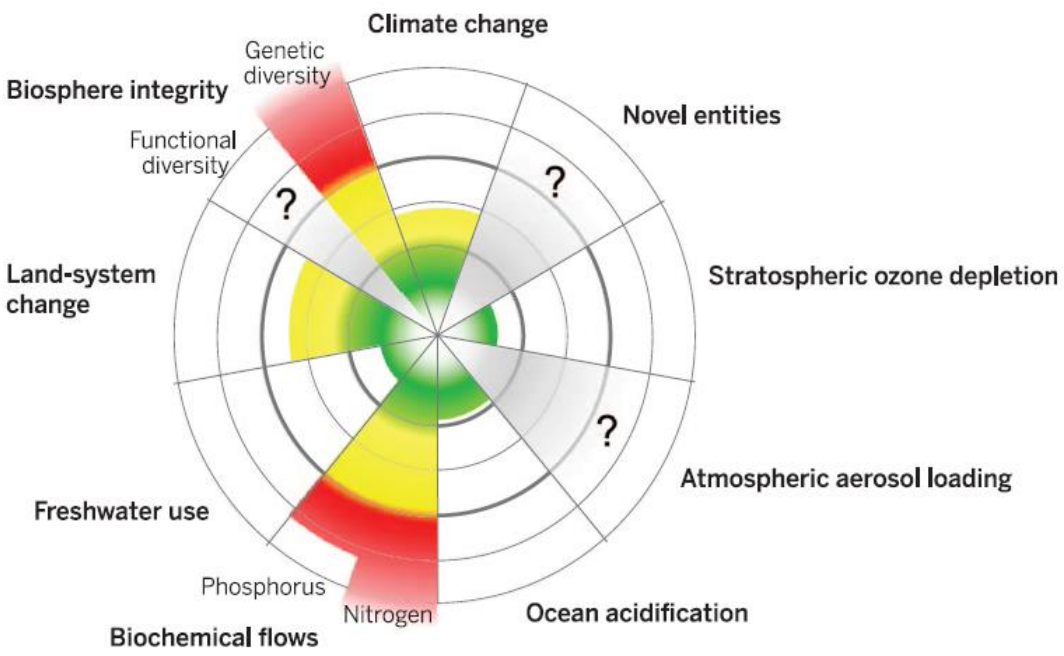
Source: Ellen MacArthur Foundation

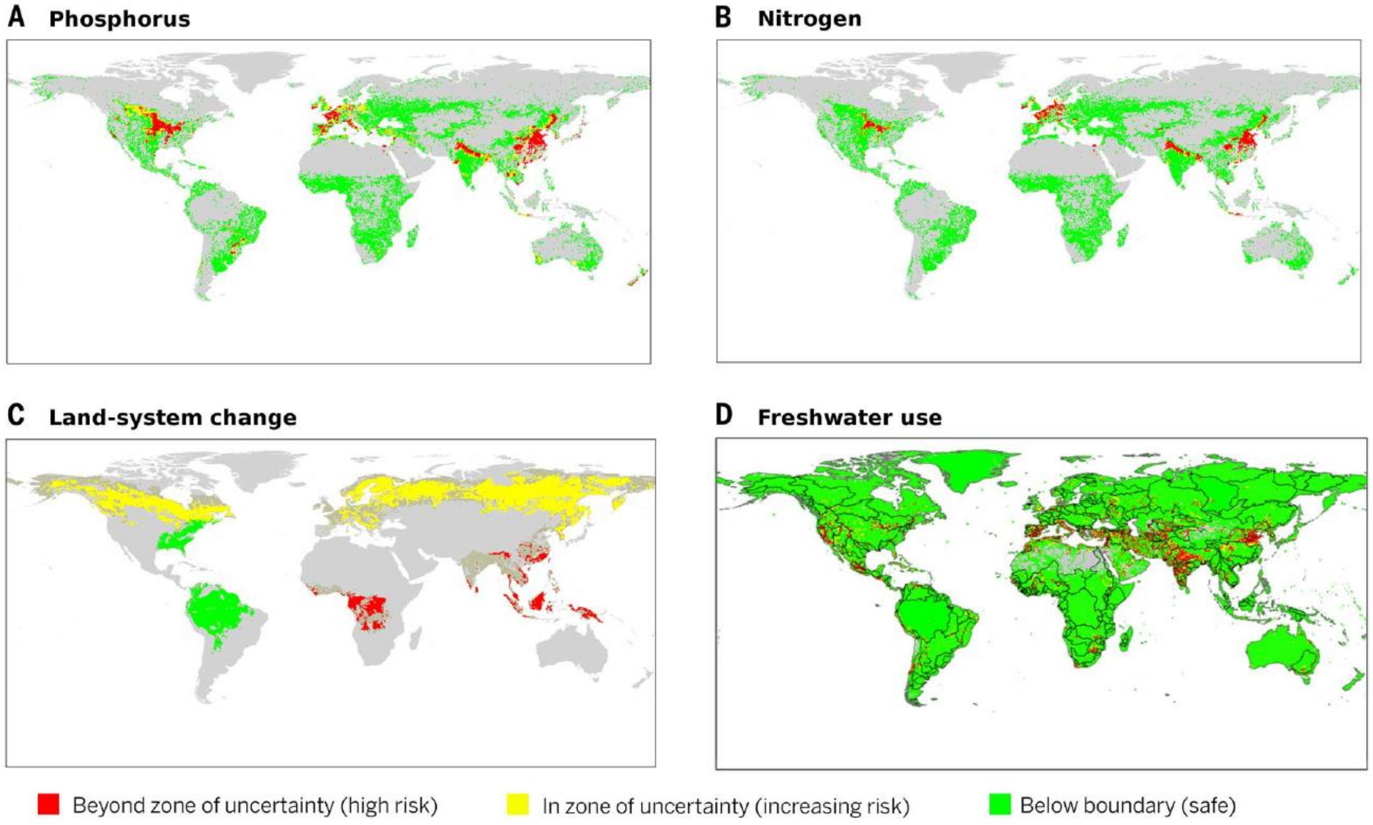
Input of plastic waste into the sea must be reduced 27fold to stabilize current plastic content:

1. Process technology: recycling and prevention of microplastic formation
2. Plastics technology: biopolymers and biodegradable plastics

Trend: Increasing input of phosphate and nitrate

Planetary boundaries as a guide to human development on our home planet



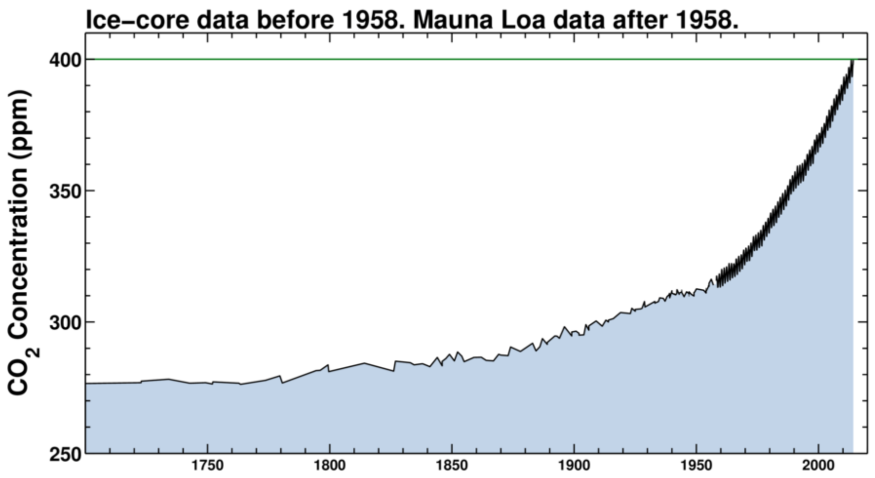


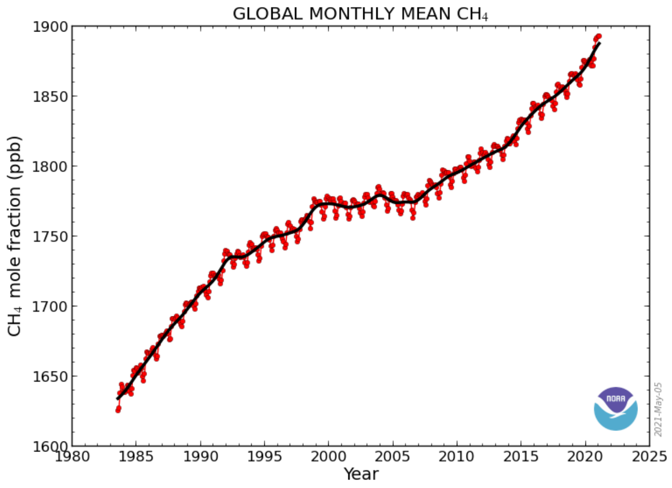
Source: W. Steffen, Science, January 2015

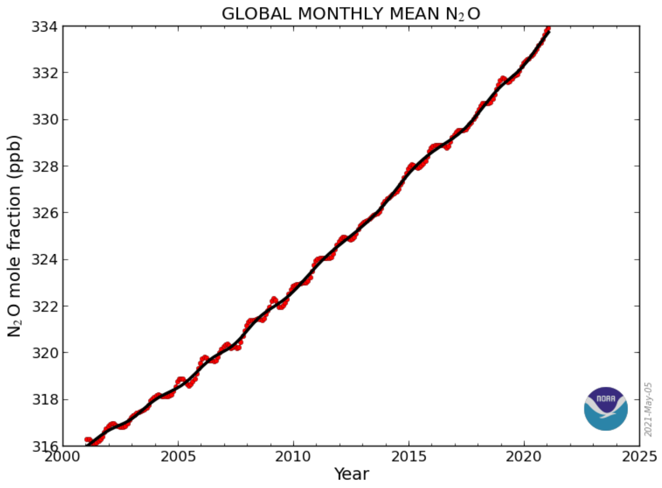
Planetary boundaries are already being breached regionally in phosphate and nitrate inputs and in the decline of genetic diversity → 8 billion people: Excretion ~ 3 million t phosphate per year

Trend: Rising emission of trace gases

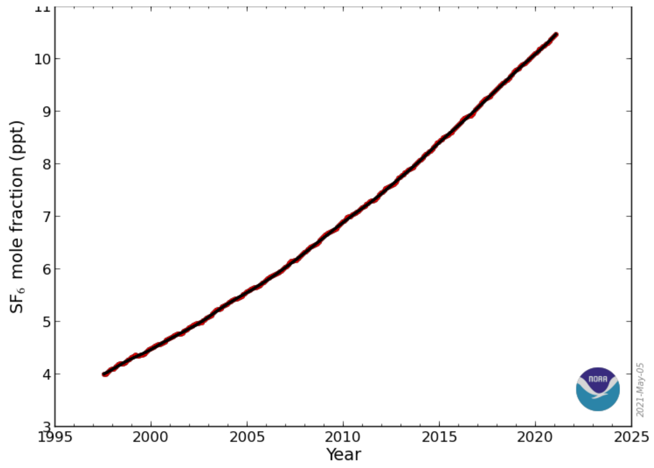
Major trace gases are CO_2, CH_4, N_2O, SF_6 (Source: Mauna Loa, Hawaii, https://gml.noaa.gov/ccgg/trends)





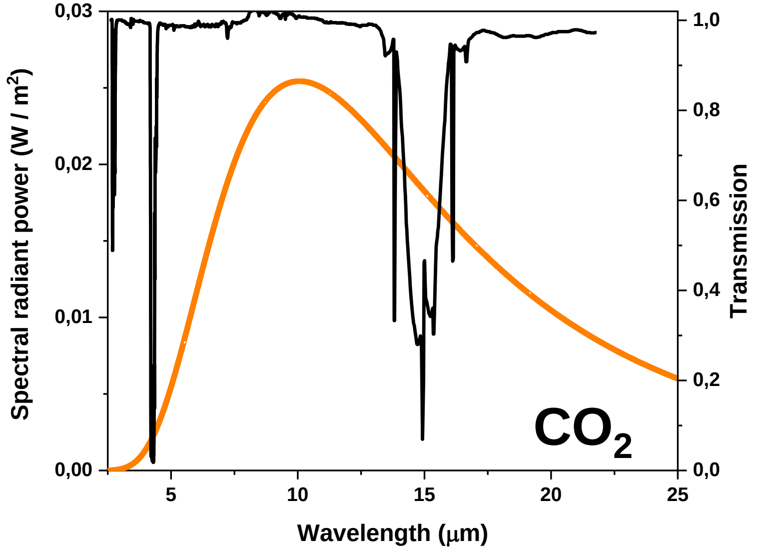


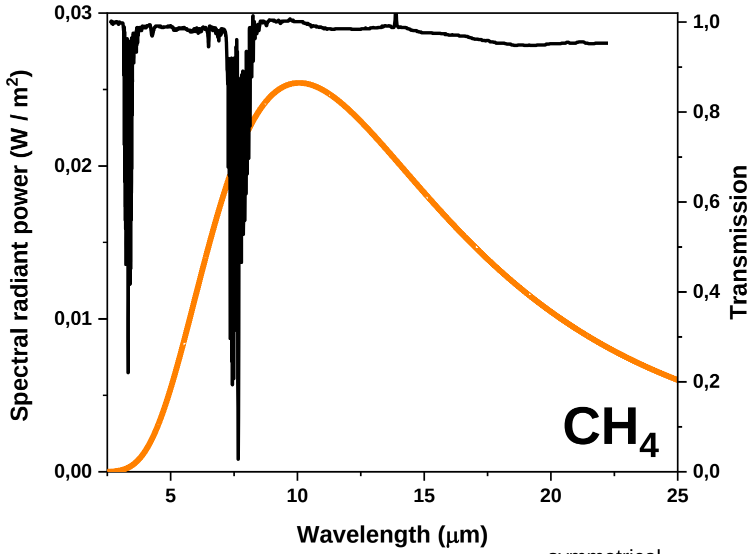
Greenhouse gas	Atmospheric concentration Y2023	GTP (100 years)
CO_2	422 ppm	1
CH_4	1920 ppb	23
N_2O	336 ppb	300
CF_2Cl_2 (CFC-12)	~ 500 ppt	10720
$CFCl_3$ (CFC-11)	~ 220 ppt	3100
CF_4	~ 90 ppt	9560
SF_6	11 ppt	22450

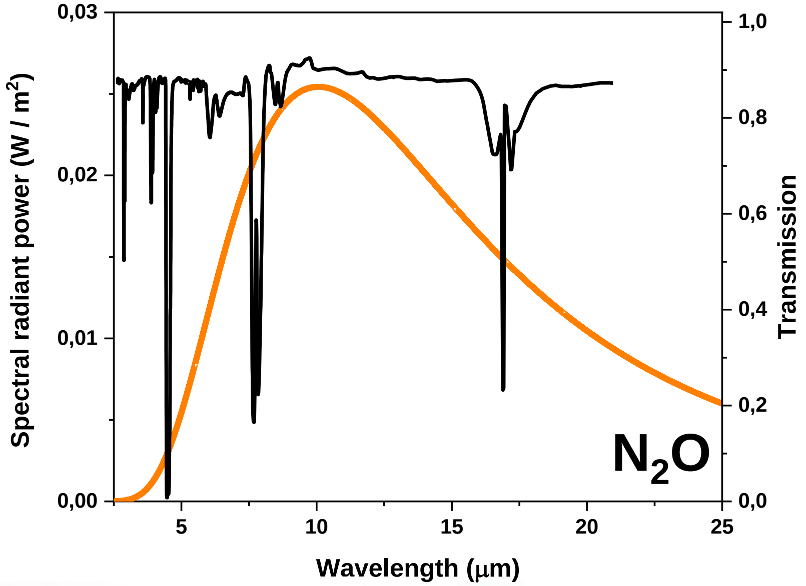


Trend: Rising emission of trace gases

The greenhouse gas potential depends on the absorption spectrum of the trace gases and the average global temperature of the earth's surface ($T_{effective}$ ~ 288 K = 15 °C ~ Planck spectrum)





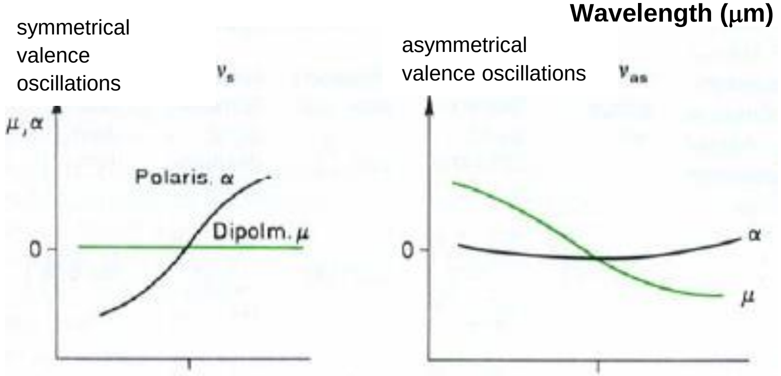


CO_2 Normal vibrations → change of μ and/or α:

δ = 667 cm^{-1} (14.993 µm) IR active

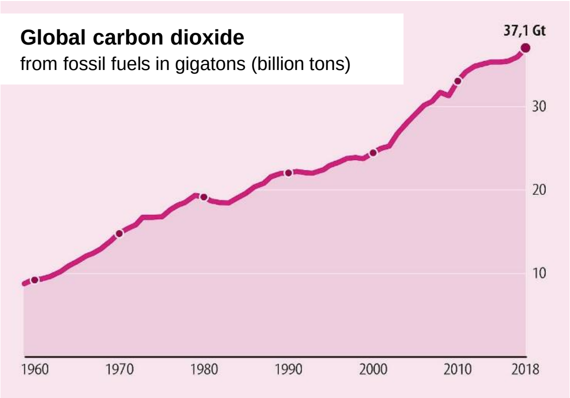
ν_s = 1338 cm^{-1} (7.747 µm) IR inactive

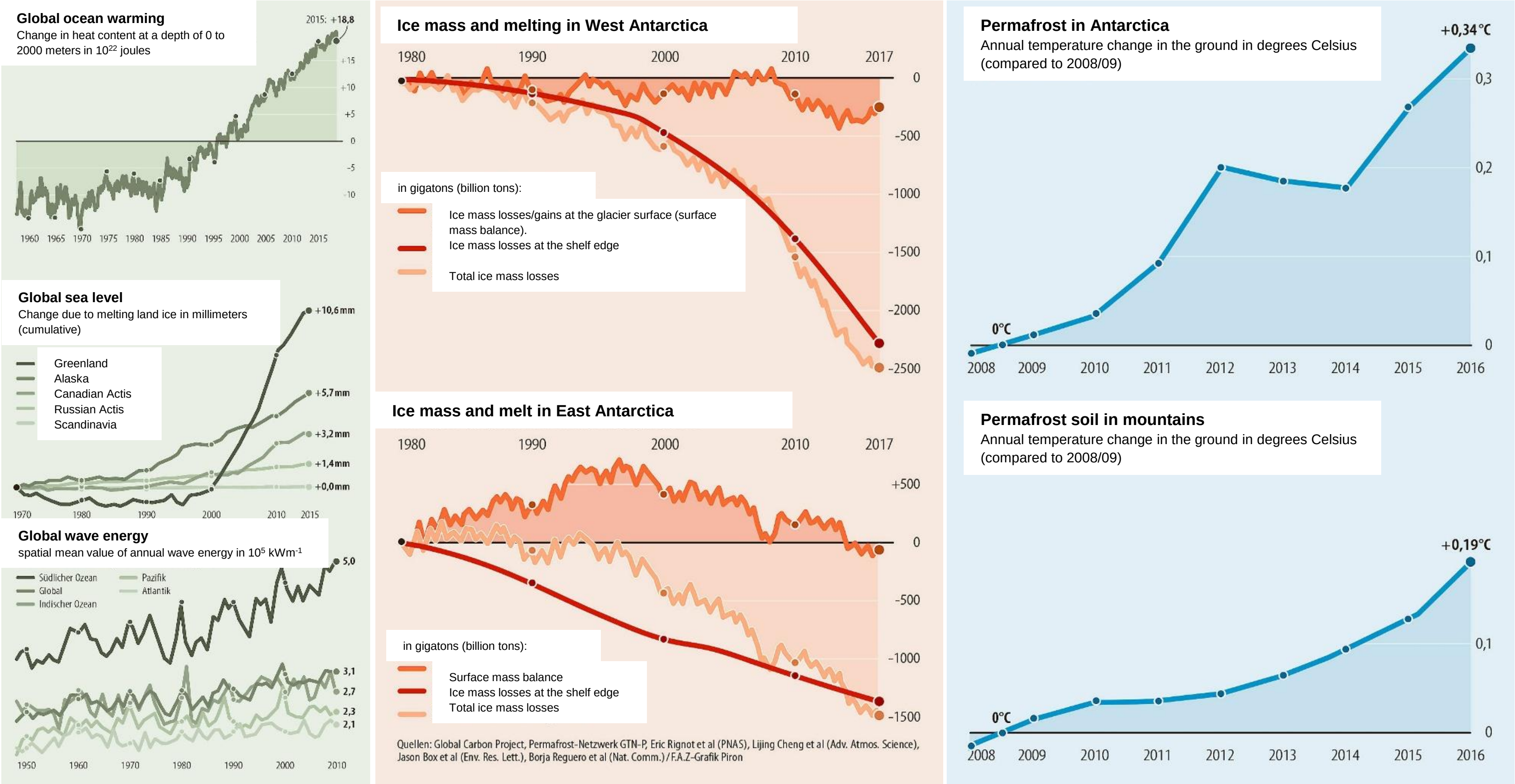
ν_{as} = 2349 cm^{-1} (4.257 µm) IR activ



Trend: Rising emission of trace gases

Installed climate protection measures insufficient to limit global temperature rise to 2 K!





Consequences

- Melting of ice and glaciers
- Decrease of fresh water reservoirs
- Sea level rise
- Secondary release of CH_4
- Change of thermohaline oceanic currents

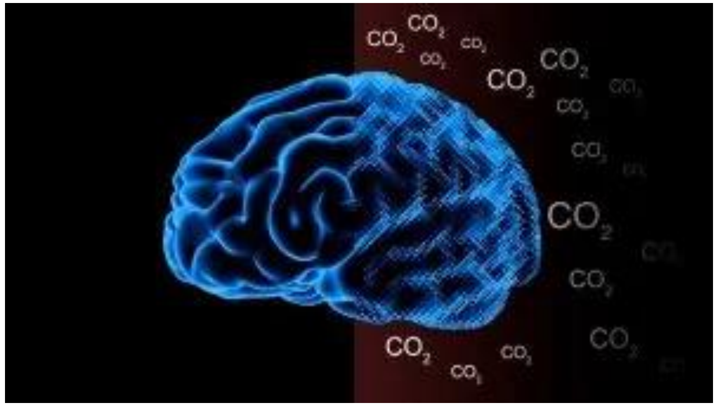
Situation 2018: Global emission of 37.1 Gt CO_2, Compare Permian-Triassic boundary: 2.6 Gt CO_2 per year (factor 14 less)

Trend: Rising emission of trace gases

Installed climate protection measures insufficient to avert considerable damage to the biosphere

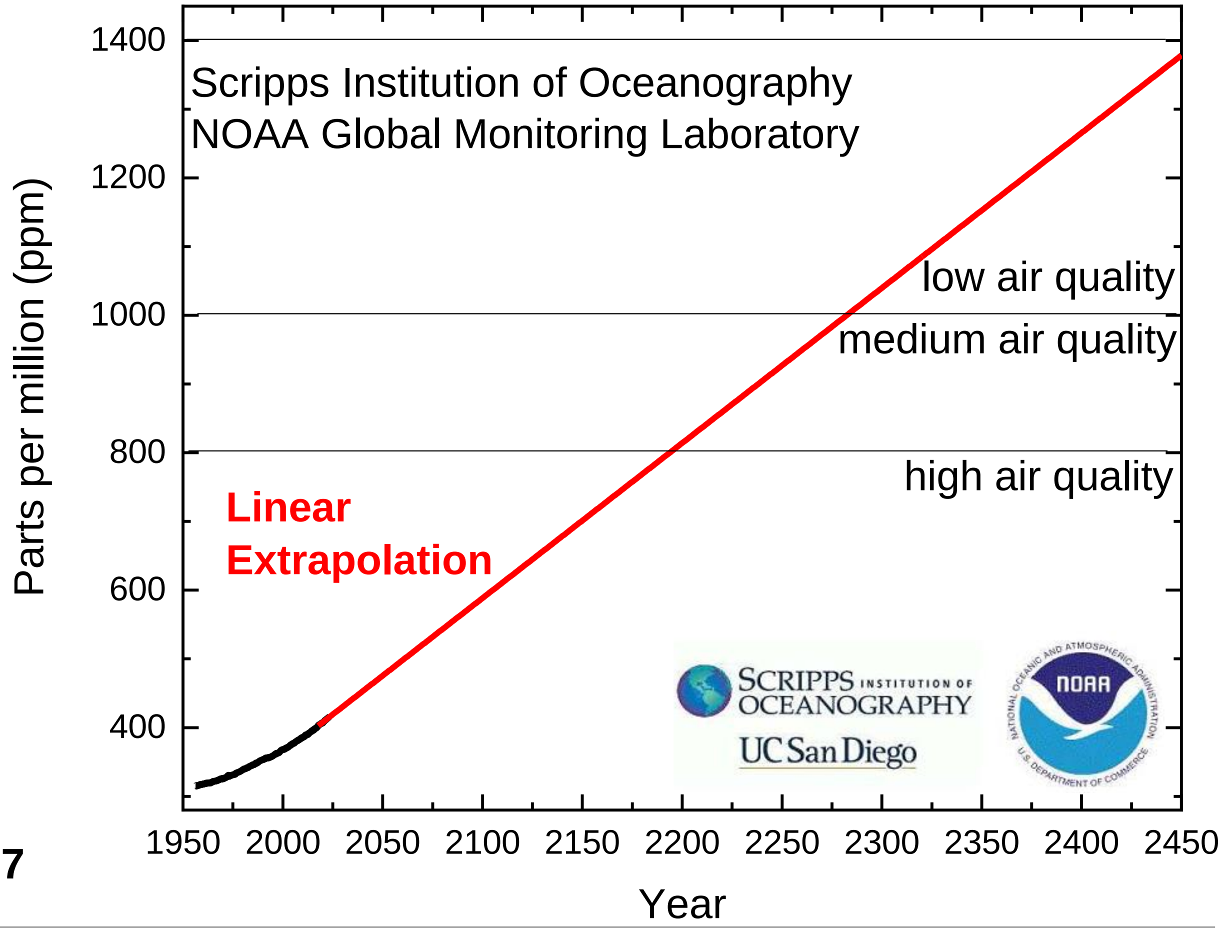
Consequences for the biosphere

- **Extinction of species**
- **Increase in sugar content of crops**
- **pH-value reduction of the oceans**
- **Increase of dead zones in the oceans**
- **Decrease in brain power (~50% at 1400 ppm)**
- **Behavioral changes?**



Lit.: Environmental Health Perspectives 120 (2012) 1671-1677

Atmospheric CO_2 at Mauna Loa Observatory



Trend: Rising emission of trace gases

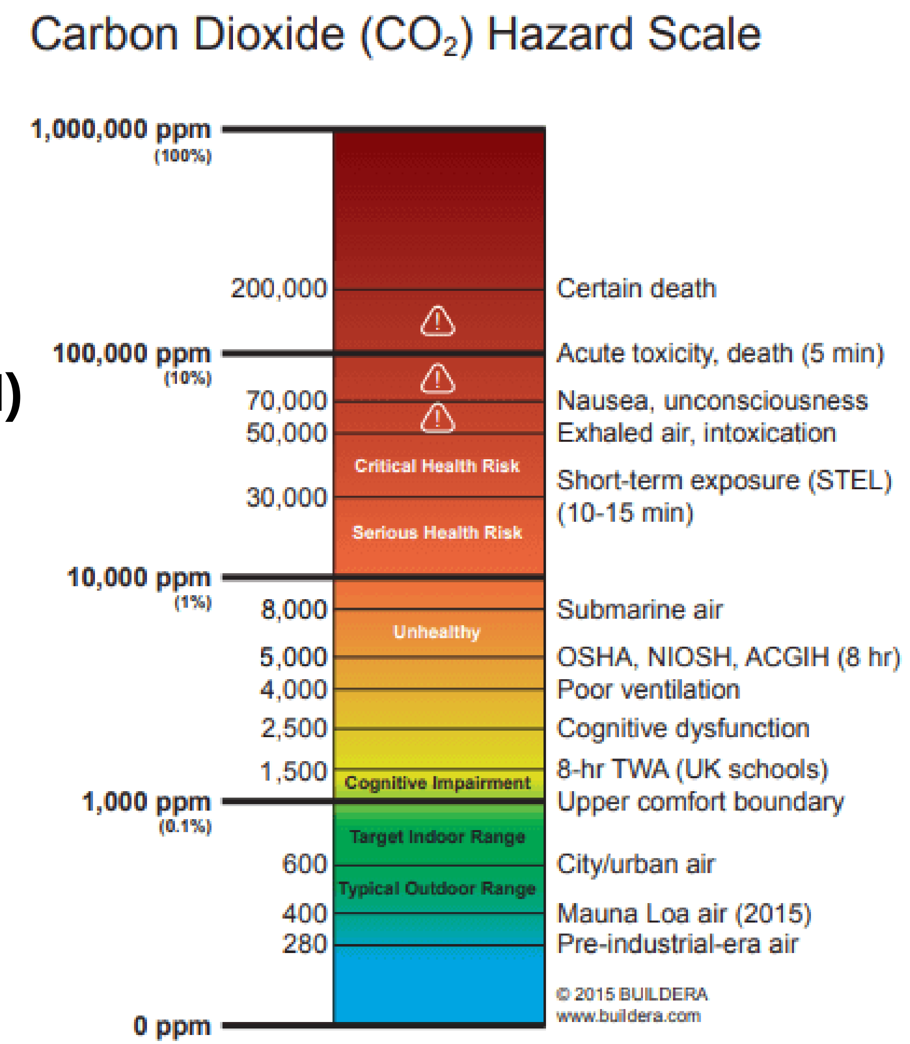
Secondary effect: Increase of indoor or inner-city concentration and thus decrease in human productivity

MAK value CO_2: 9100 mg/m³ (~ 5000 ppm)

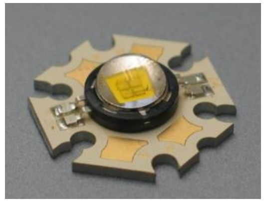
National Institute for Occupational Safety and Health (NIOSH) Recommendation: 40,000 ppm

Occupational Safety and Health Administration (OSHA) Standard is 5000 ppm as an 8-hour time-weighted average (TWA) concentration

Source: https://www.osha.gov/publications/hib19960605

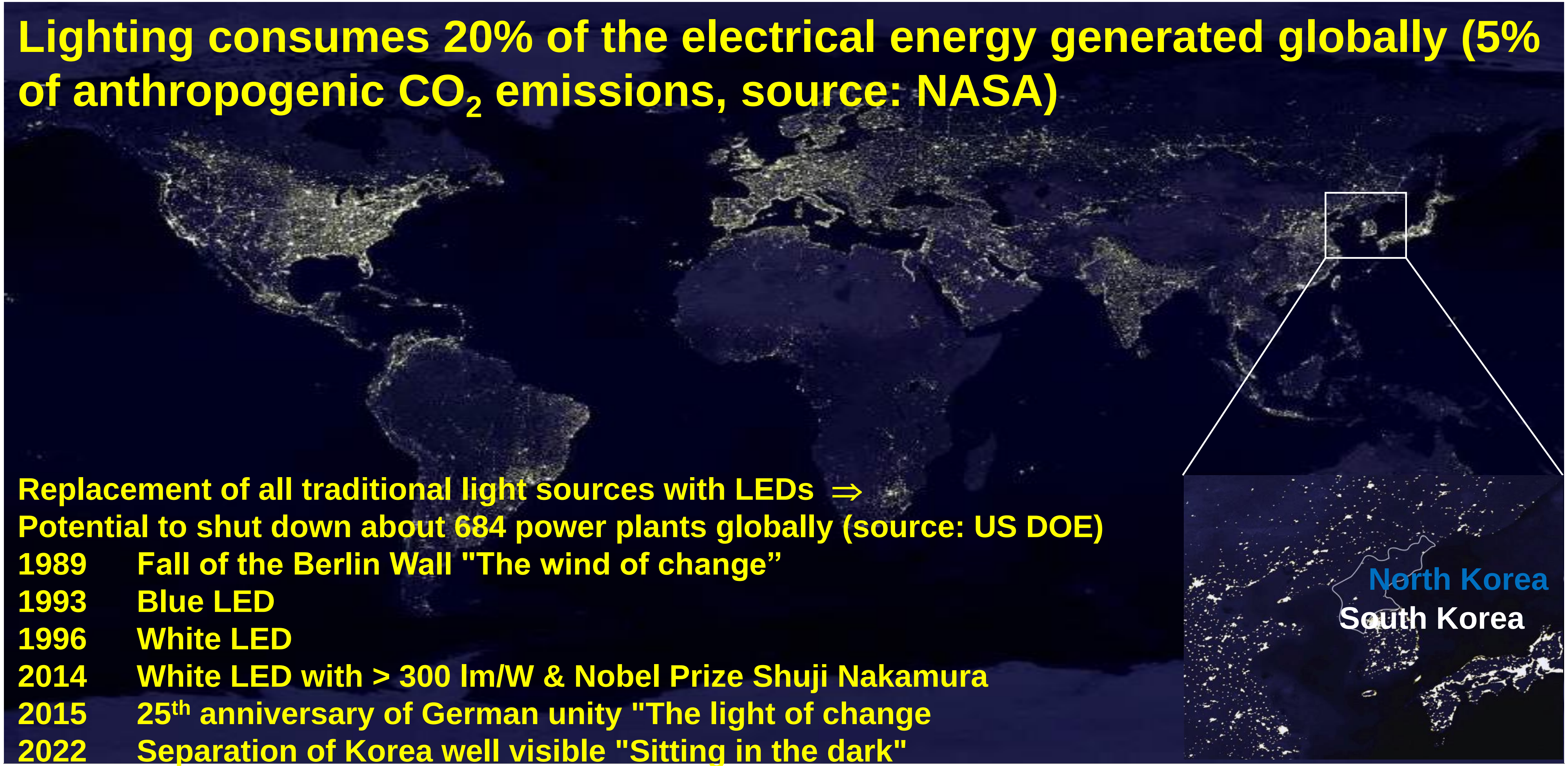


Origin of anthropogenic emission of trace gases



CO_2	Fraction	Potential counter measures
• Lighting	(5%)	LED technology
• Transportation	(~ 25%)	New drives and fuels
• Buildings	(6%)	Insulation
• Information technology	(2-3%)	Server architecture, use of PV
• Steel production	(5%)	H_2 as a reducing agent
• Cement production	(6-7%)	Reduction of cement clinker content in concrete
• Ammonia synthesis	(1-2%)	N_2 hydrogenation by steam, N_2 photolysis
• Chlor-alkali electrolysis	(~1%)	Conversion to membrane process, heat recovery..
CH_4/N_2O		
• Agriculture & livestock		Reduction of meat and fertilizer consumption
• HNO_3 and nylon production		Optimization of the Ostwald process
SF_6/NF_3		
• Electrical engineering		Alternative insulator gases, optimization of proc. for the production of screens & solar cells

Lighting consumes 20% of the electrical energy generated globally (5% of anthropogenic CO_2 emissions, source: NASA)



Replacement of all traditional light sources with LEDs ⇒
Potential to shut down about 684 power plants globally (source: US DOE)

1989 Fall of the Berlin Wall "The wind of change”
1993 Blue LED
1996 White LED
2014 White LED with > 300 lm/W & Nobel Prize Shuji Nakamura
2015 25th anniversary of German unity "The light of change
2022 Separation of Korea well visible "Sitting in the dark"

But: Rebound effects ↔ Technology advances

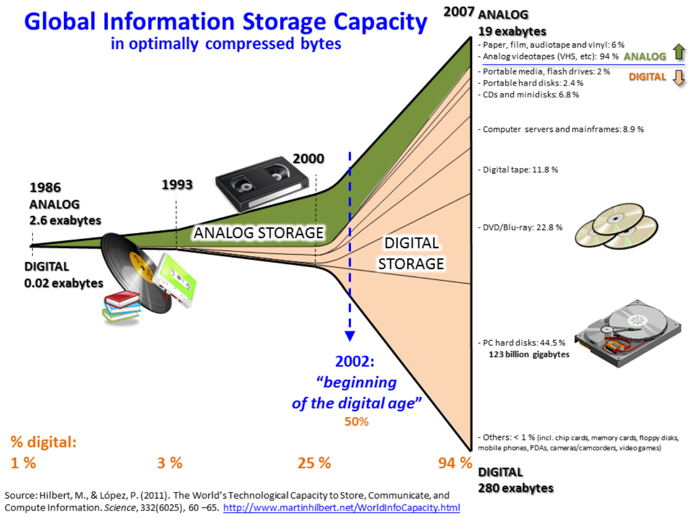
"Rebound effect" (rebound effect) using the example of data storage and transmission

1455 Gutenberg Bible: First book printed with movable Pb types
1815 Fresnel and the wave nature of light
1865 Maxwell and the electromagnetic waves
1915 General relativity - light in space and time
1945 Z4 by Konrad Zuse (2200 relays)
1965 Cosmic Microwave Background (CMB)
& Technology of optical fibers
1989 Birth of the WWW
2002 Beginning of the digital age
2007 ~ 300 exabytes (EB) stored
2010 50 Gbps transmission (through four lasers)
2014 Data transmission rate > 100 Gbps
2015 "International Year of Light" (IYL), > 1 zettabyte (ZB)
2018 4-5 ZB stored, 294 billion mails and 230 million tweets/day
2020 ~ 44 ZB stored
2030 Internet ~ 21% of projected electricity demand (Lit.: Nature 561 (2018) 163)

Energy consumption / bit ↓

Efficiency ↑

Limit: $E_{bit,min} = \ln(2) \cdot k_B \cdot T$



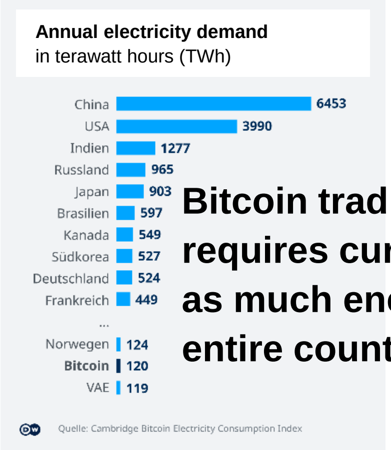
Data volume ↑↑

IT ↔ Energy saving urgently needed

CO_2 emissions from IT services are rising relentlessly and sometimes exponentially….

2018 547 EBs stored in data centers 294 billion e-mails per day

2021 1327 EBs stored in data centers 320 billion e-mails per day



Bitcoin trading currently requires currently about as much energy as the entire country of Norway

<u>CO_2 balance of IT services</u> 36 billion t CO_2 in 2019

1 e-mail ~ 1 g CO_2 320,000 t CO_2 per day in 2021 = 117 mill. t CO_2 in 2021

1 Bitcoin transaction ~ 453,000 credit card transfer 190,000 t CO_2 per day in 2018 = 69 mill. t CO_2 in 2018

1 Google query ~ 0.2 g CO_2

1 h video streaming ~ 150 g CO_2 (4K resolution)

<u>For comparison</u>

1 km train travel ~ 32 g CO_2

1 km driving a car ~ 147 g CO_2

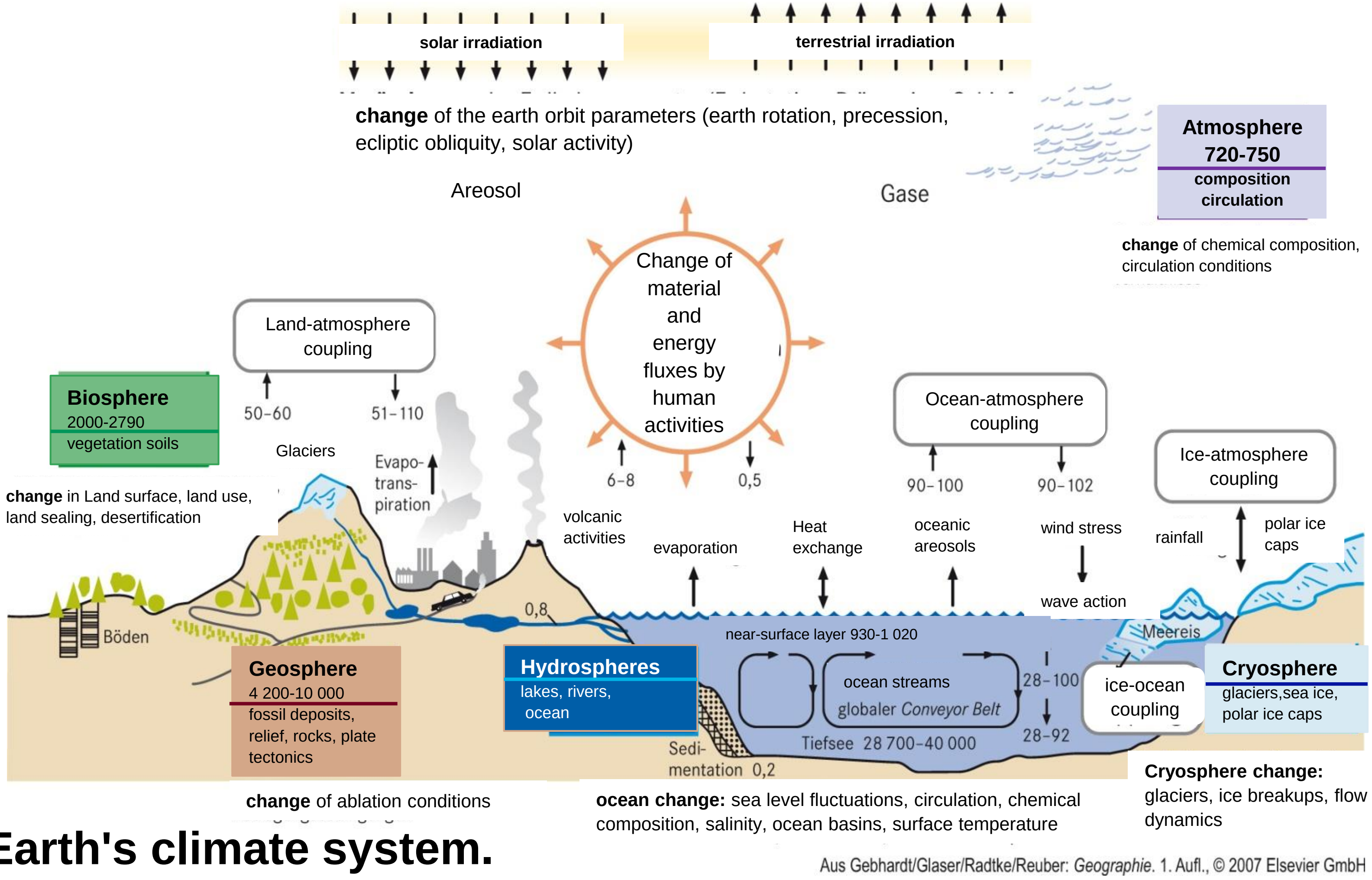
1 km flying ~ 380 g CO_2 (Retour flight: Germany to Chile ~ 25,000 km ~ 9.5 t CO_2)

2. The earth's climate and the global energy balance

Definition climate

"Climate is the statistical behavior of the atmosphere that is characteristic of a relatively large temporal scale“

Lit.:
Hantel et al. 1987 nach EMEIS 2000, S. 55

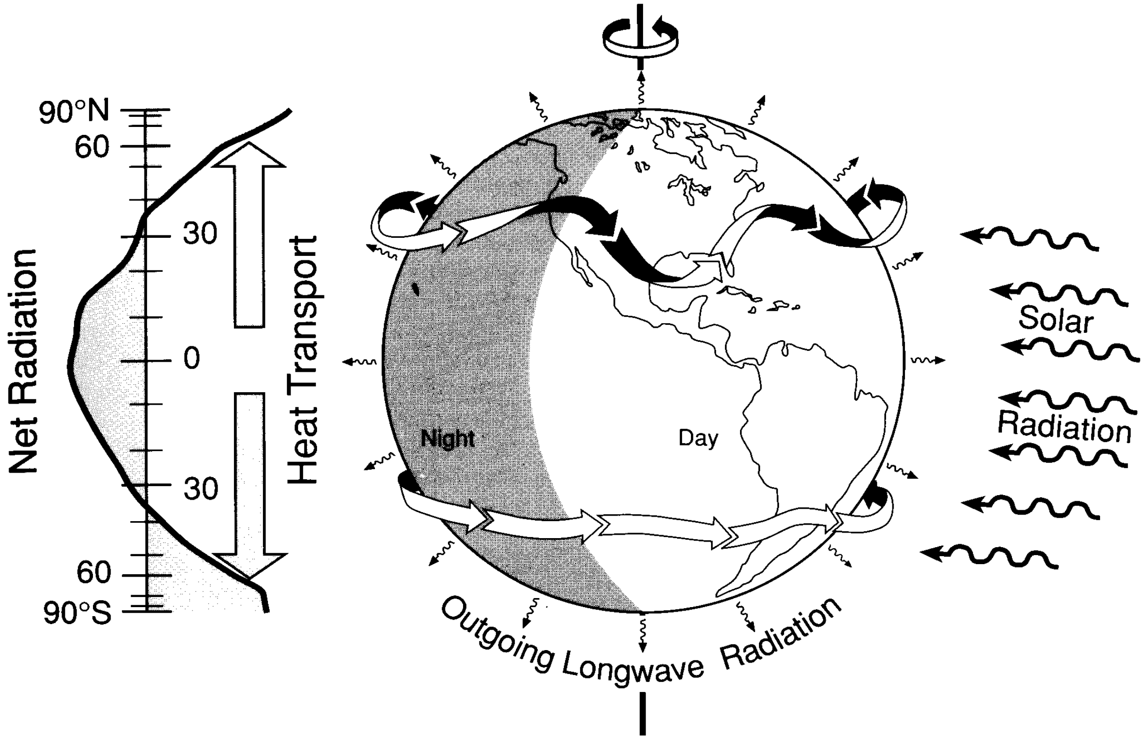


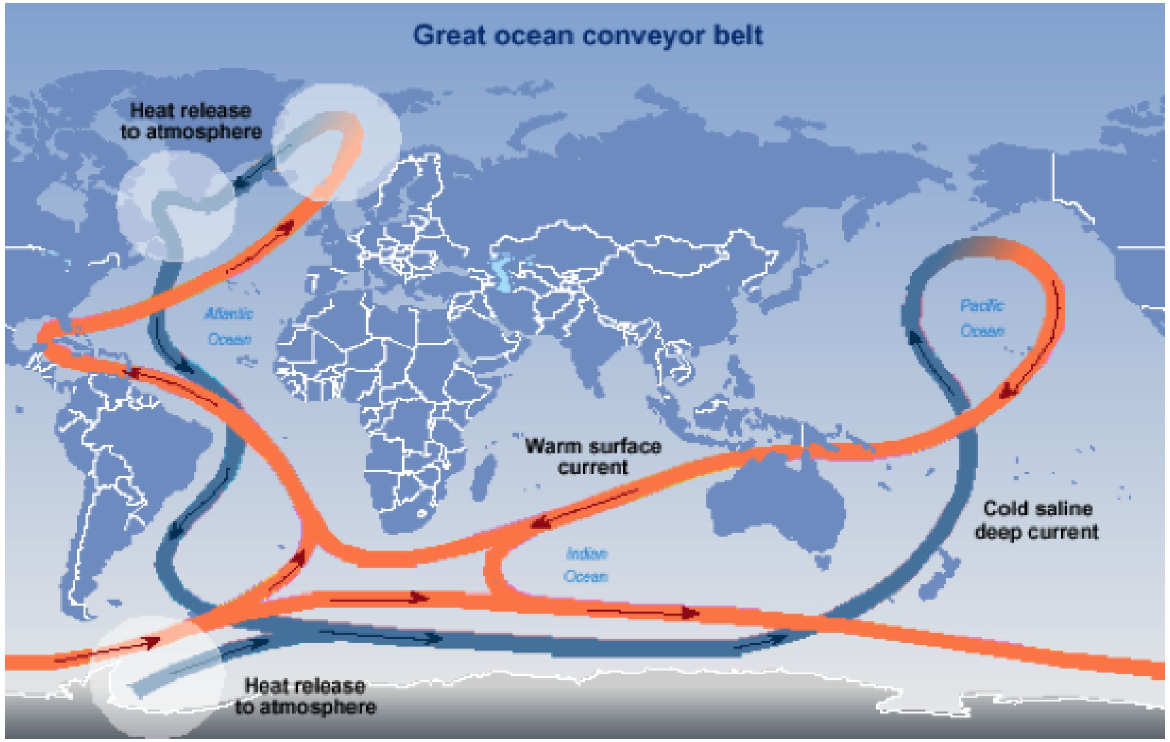
Schematic representation of the Earth's climate system.
Lit.: Casper 2007 after draft of R. Glaser and H. Saurer, modified after IPCC 2001

2. The earth's climate and the global energy balance

Global heat transport ~ from the tropics to the poles

37° N - 37° S: net irradiation (UV-VIS-IR) ↔ > 37° N/S: net irradiation (IR)





Heat transport drivers: Earth rotation, seasons, salinity and temperature differences of seawater

2. The earth's climate and the global energy balance

Composition of the earth's atmosphere

- Atmosphere = Gaseous air envelope of the earth, which is gravitationally bound
- Total mass: 5.13*1018 kg = 5.13*1015 t = 5.13 Pt
- Main constituents

Main constituents	(vol%)	Mass %.
– Nitrogen	78.08	75.52
– Oxygen	20.94	23.14
– Argon	0.93	1.29

- Water vapor (up to 4%!)
- Aerosols, water droplets and ice crystals
- Trace gases

Trace gases

- Carbon dioxide CO_2
- Carbon monoxide CO
- Methane CH_4
- Terpenes and isoprenes C_xH_y
- Ammonia NH_3
- Nitrogen oxides NO_x
- Nitrous oxide N_2O
- Sulfur dioxide SO_2
- Methyl chloride CH_3Cl
- Methyl bromide CH_3Br
- Ozone O_3
- Sulfur hexafluoride SF_6
- Nitrogen trifluoride NF_3
- CFC: $CFCl_3$, CF_2Cl_2 and so on

2. The earth's climate and the global energy balance

Structure of the earth's atmosphere

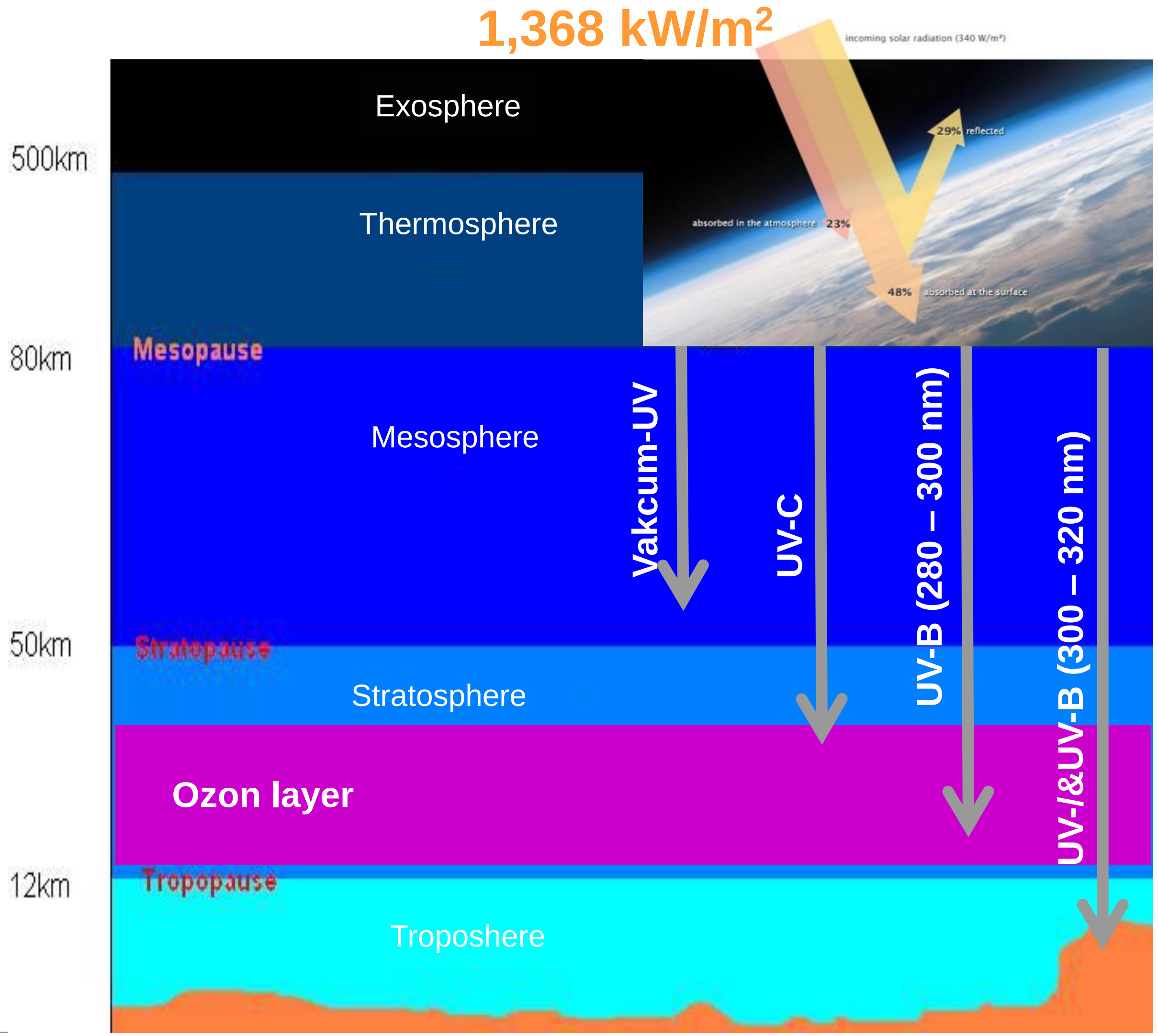
O = $510 \cdot 10^{12}$ m², m = 10.076 kg/m²
→ p = F/A = 101.325 Pa (N/m²)

Vacuum-UV (< 200 nm, Anteil < 0,1%)
Photolysis of water, nitrogen, oxygen, ...
Ozone formation, NO_x formation

UV-C and UV-B (200 – 320 nm, amound ~ 0,1 %)
Ozone splitting

UV-A (320 – 400 nm, amound ~ 5%)
Tropospheric ozone formation (via NO_x)

VIS and NIR (> 400 nm ~ 95%)
Warming of the atmosphere and earth's surface



2. The earth's climate and the global energy balance

Climate factors, history and reconstruction.

„Since the Earth has existed, that is, for about 4.6 billion years, the climate has been changing, and in different ways and for different reasons "

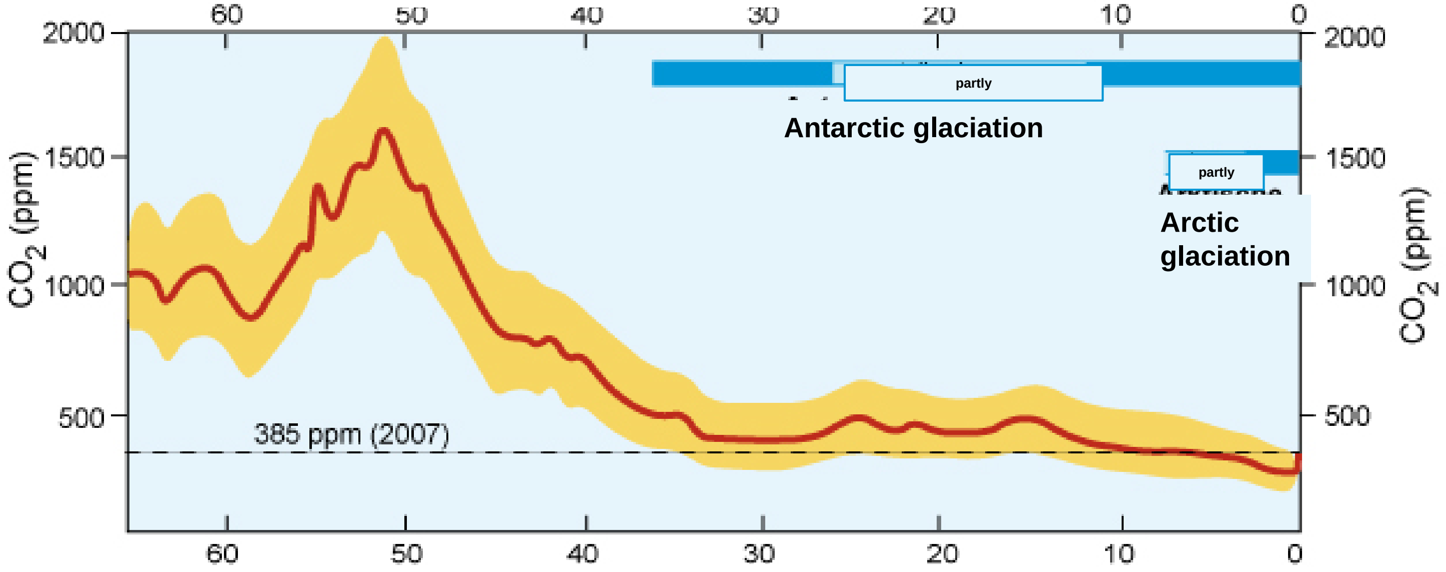
Lit.: C.-D. Schönewiese in Gebhardt et al. 2007, S. 246

The earth is since approximately 35 million years in an ice age

Climate factors

1. Astrophysical
2. Terrestrial (geophysical)
3. Biogenic
4. Anthropogenic

Cenozoic CO_2 concentration



Mio years before today

2. The earth's climate and the global energy balance

Climate factors

1. Astrophysical impact

a) Sun
b) Earth's orbital parameters
c) Tidal effects
d) Impacts
e) Supernovae/Gamma-ray flashes
f) ......

2. The earth's climate and the global energy balance

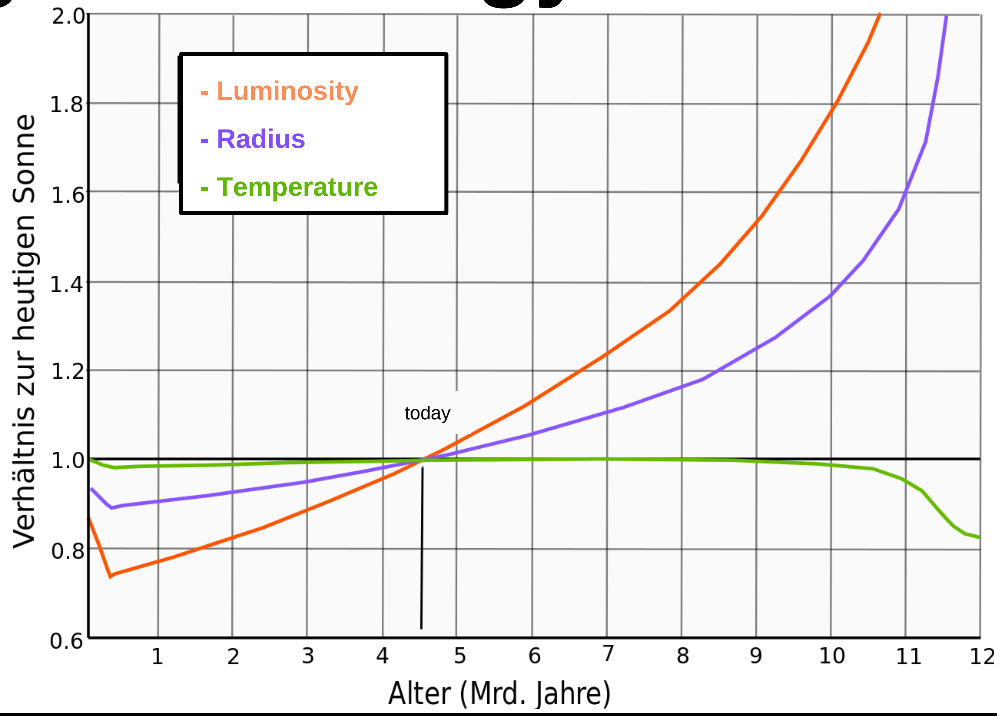
Climate factors

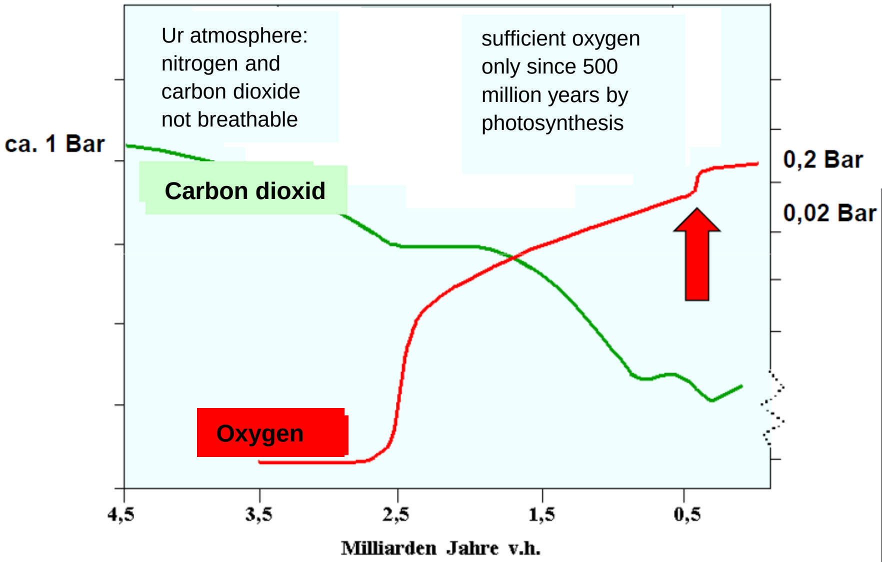
1a) Sun

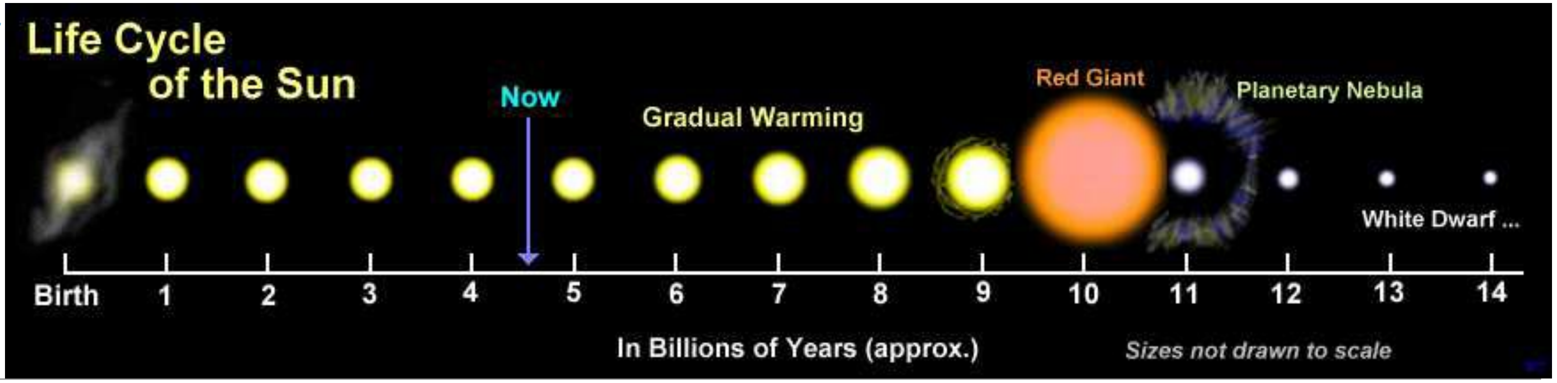
Continuous increase in luminosity $L_{\odot}$

→ 25-30% in the past 4.6 billion years

→ in 1 billion years by another 10%: T_E increases to 261 K





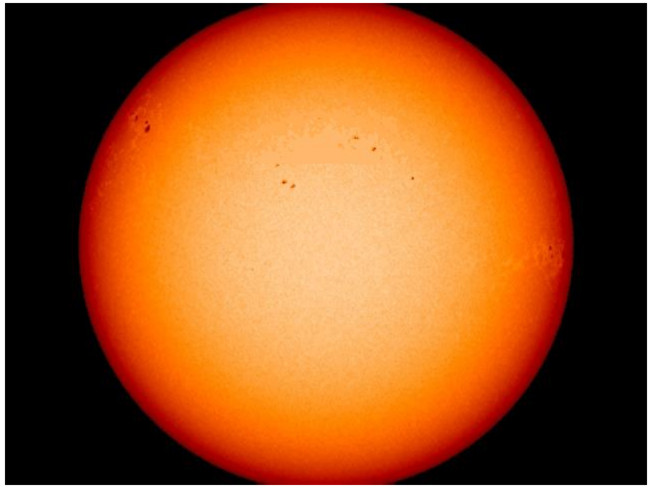


2. The earth's climate and the global energy balance

Climate factors

1a) Sun

Present luminosity $L_\odot$

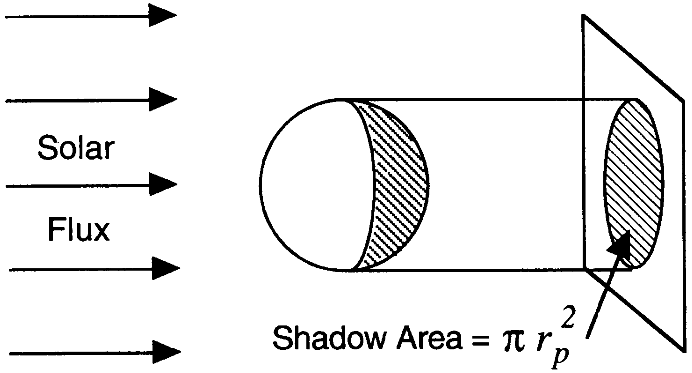


Radiation flux density
$= L_\odot/4\pi r_\odot^2$
$6.4 \cdot 10^7$ W/m²

Albedo a_{Erde} = 29%
(Whiteness)

σT_E^4 , T_E = 255 K

Solar constant
S_0 = 1368 W/m²



Center	**T ~ $1.5 \cdot 10^7$ K**
Surface	**T ~ 5780 K**
Luminosity	**$L_\odot = 4\pi r_{Earth\ orbit}^2 S_0 = 3.85 \cdot 10^{26}$ W**

Absorbed solar radiation : $E = S_0(1-a_{earth})\pi r_{earth}^2 = 1.74 \cdot 10^{17}$ W

2. The earth's climate and the global energy balance

Climate factors

1a) Sun

Absorbed solar radiation $S_0(1-a_{Earth})\pi r_{Earth}^2$ **with** **Albedo** $a_{Erde} = 0.29$

Longwave radiation $\sigma T_{Erde}^4\, 4\pi r_{Erde}^2$ **with** $\sigma = 5.670 \cdot 10^{-8}\ Wm^{-2}K^{-4}$ **(Stefan-Boltzmann-Konstante)**

Global energy balance: insolation = radiation

$$S_0(1-a_{Earth})\pi r_{Earth}^2 = \sigma T_{Earth}^4 \cdot 4\pi r_{Earth}^2$$

$$S_0/4(1-a_{Earth}) = \sigma T_{Earth}^4$$

$$T_{Earth} = (S_0(1-a_{Earth})/4\sigma)^{1/4} = T_E = \sqrt[4]{\frac{(1368\ Wm^{-2}/4)(1-0.29)}{5.67\times10^{-8}\ Wm^{-2}K^{-4}}} = 255\ K\ (-18\ °C)$$

2. The earth's climate and the global energy balance

Climate factors

1a) Sun

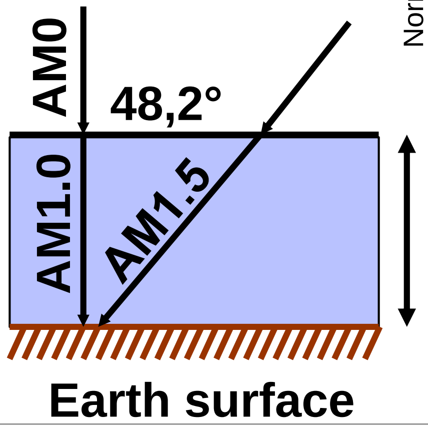
Spectrum ~ Black-Body (BB) or Planck radiation

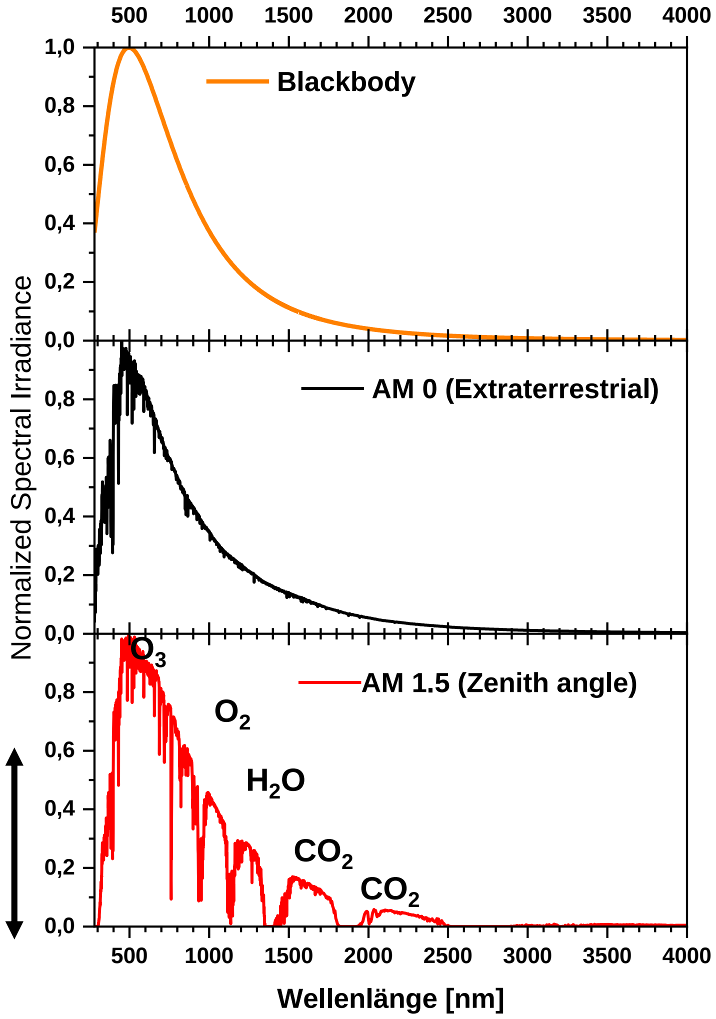
Stefan-Boltzmann law: $E_{BB} = \sigma T^4$ mit $\sigma = 5.67 \cdot 10^{-8}\ Wm^{-2}K^{-4}$

$6.4 \cdot 10^7\ W/m^2 = 5.67 \cdot 10^{-8}\ Wm^{-2}K^{-4} \cdot T_{Photosphere}$

$\Rightarrow T_{Photosphere} = (6.4 \cdot 10^7\ W/m^2 / 5.67 \cdot 10^{-8}\ Wm^{-2}K^{-4})^{1/4} = 5796\ K$

Airmass AM0: Spectrum of the photosphere
BB spectrum with Fraunhofer absorption lines
Airmass AM1.0: Spectrum at sea level



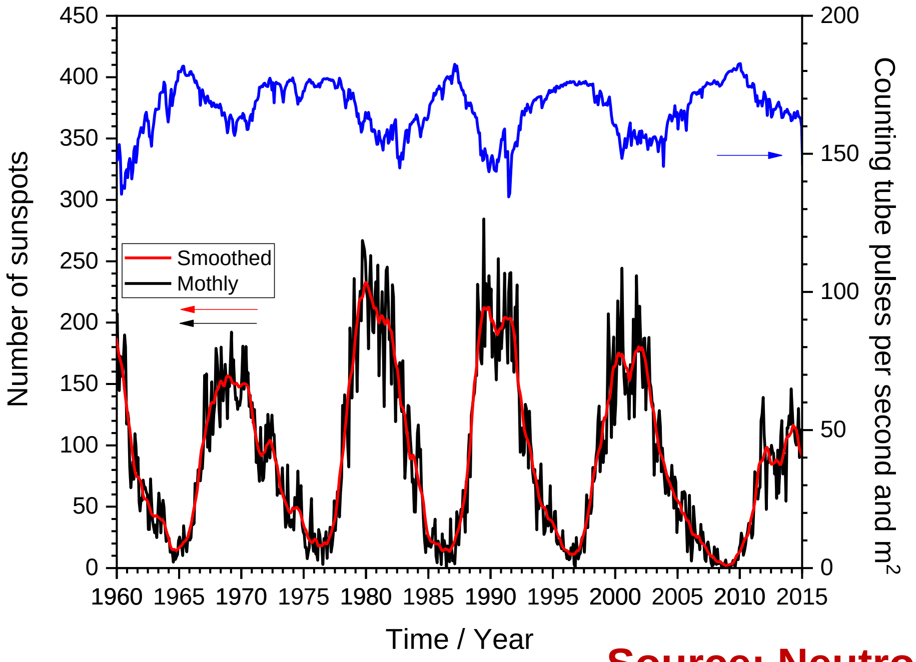


2. The earth's climate and the global energy balance

Climate factors

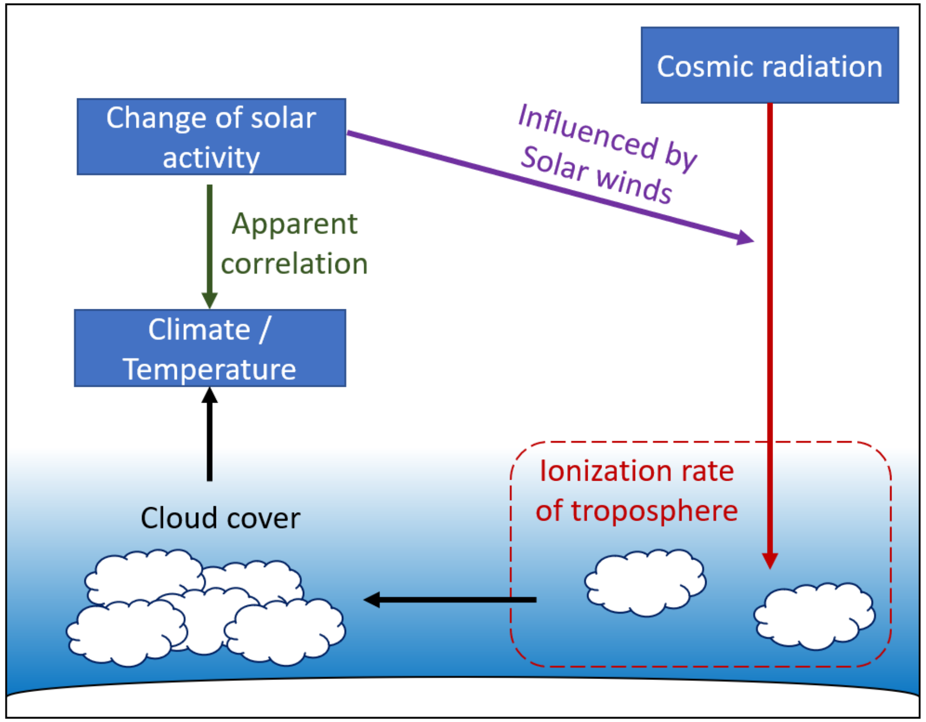
1a) Sun

Solar wind ↔ Cosmic rays → Cloud formation and albedo



Source: Neutron monitor CAU Kiel

Source: Dr. Jan-Niklas Keil

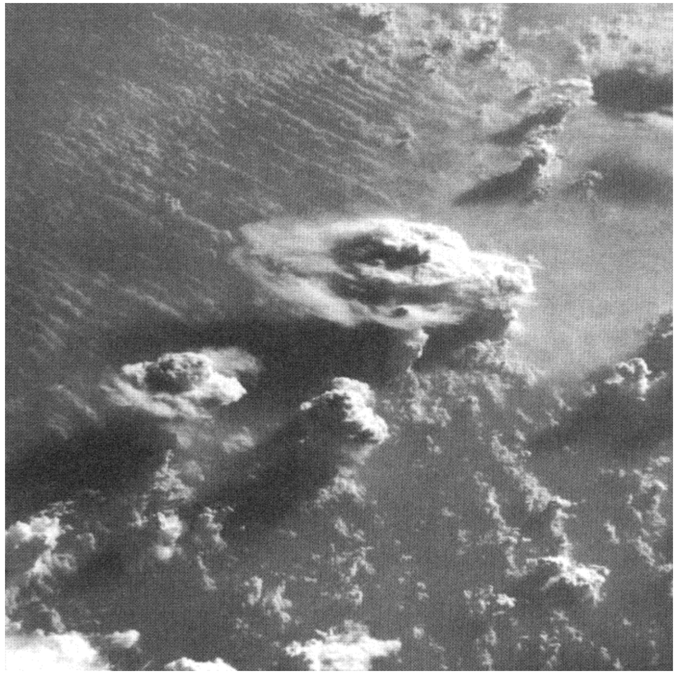


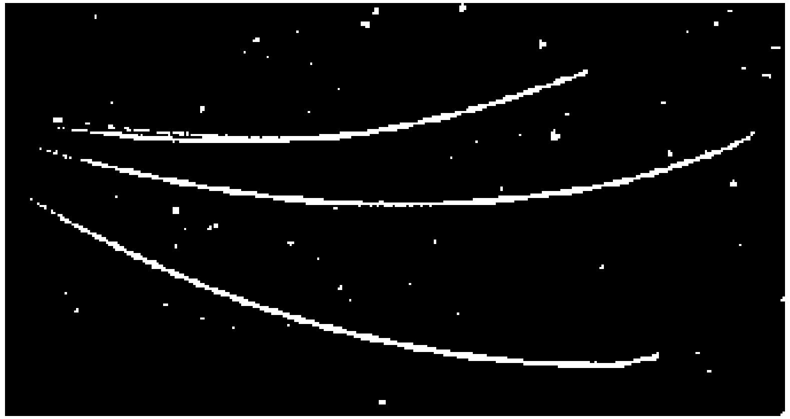
2. The earth's climate and the global energy balance

Climate factors

1a) Sun

Solar wind → Cloud formation: Result of atmospheric convection and cosmic radiation





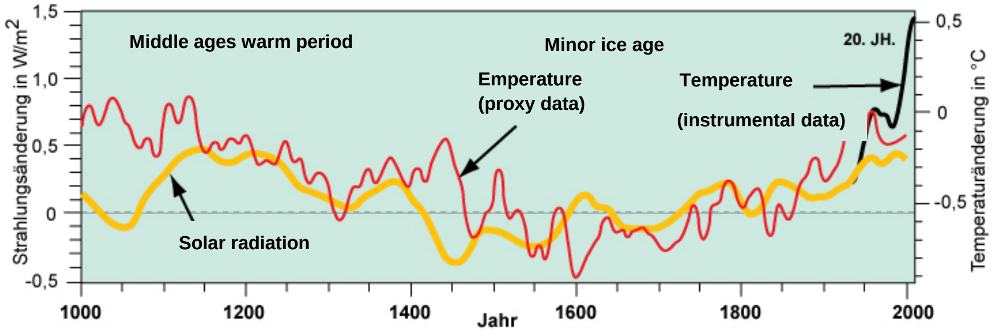
Top: Cloud chamber image showing three particle tracks; Left: Cumulonimbus clouds over Zaire, photographed from the Shuttle of NASA, April 1983
(Picture 1.1 from Hartmann, 1994)

Clouds

- transport heat and moisture vertically (by convection) up to the tropopause
- influence radiation pattern in the atmosphere can balance positive radiation (~100 Wm^{-2}) on the ground
- have complex three-dimensional structure
- cast shadows or increase global albedo

2. The earth's climate and the global energy balance

Climate factors



1a) Sun

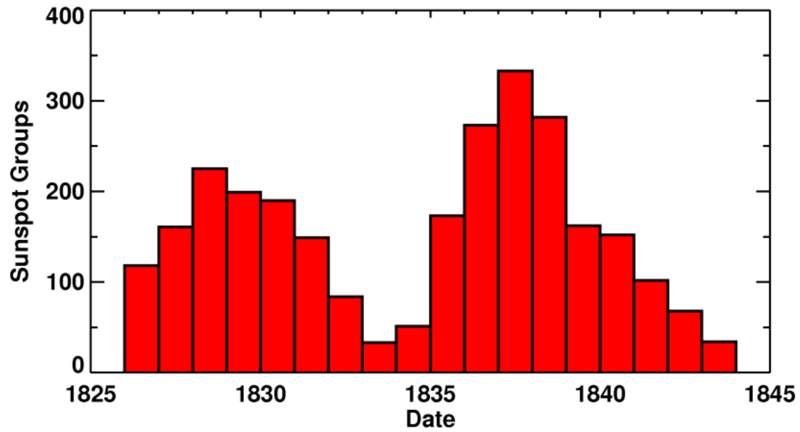
Sunspot cycles

- Schwabe 11 a (tidal effect of Venus, Earth & Jupiter)
- Gleisberg 70 - 100 a
- Eddy 800 - 1200 a
- Bray-Hallstatt 2100 - 2500 a

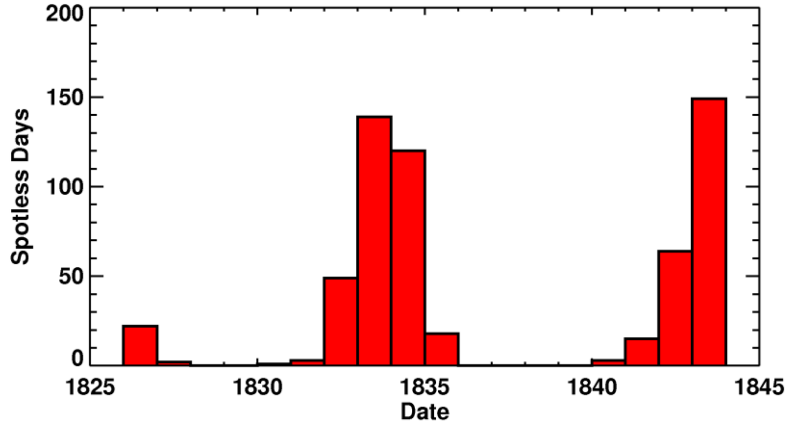
Cause: Planetary modulation of solar activity?

Discovery by Heinrich Schwabe, amateur astronomer
in Dessau in 1844, winter 1979, 1990, 2001, 2012, 2023?
Number of sunspots and sunspot groups and number of days without sunspots follows several cycles
Maunder Minimum, ca. 1645 - 1715 (little ice age)

Schwabe's data from 1826 to 1843



Number of sunspot groups/year



Number of days without spots

2. The earth's climate and the global energy balance

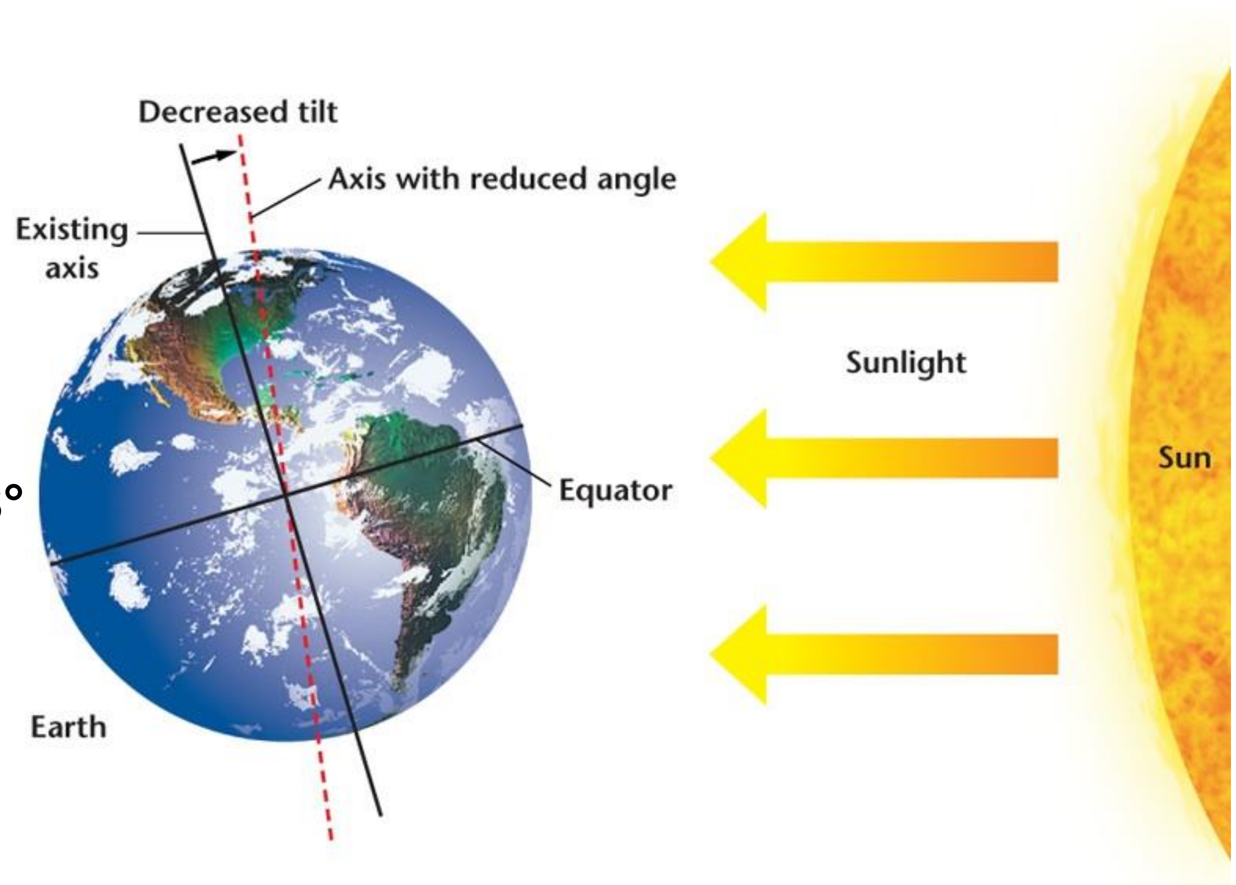
Climate factors

1b) Earth orbit parameters

Obliquity ε (period ~ 41,000 a)

The inclination of the earth axis against the ecliptic varies cyclically between 22.0° and 24.3°

Current inclination of the earth axis: 23.45°
In the year 2200: 23.41°



Cause: Gravitational interaction with the other 7 planets, especially Jupiter

$\varepsilon = (23.4392911111 - 0.0130041667 \cdot T - 0.000000164 \cdot T^2 + 0.0000005036 \cdot T^3)°$ with T = time in Julian centuries since J2000.0

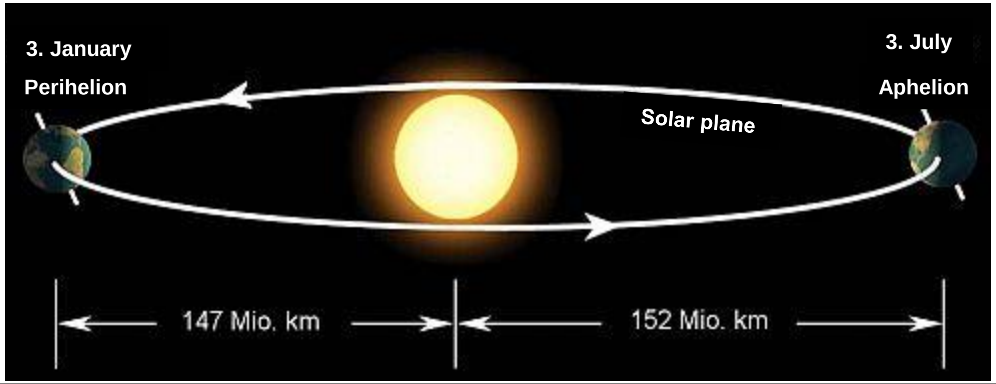
2. The earth's climate and the global energy balance

Climate factors

1b) Earth orbit parameters

Eccentricity e (period ~ 100 ka)

The eccentricity of the Earth's orbit changes over a period of about 100.000 years from a nearly perfect circular orbit to an elliptical orbit and back to a circular orbit. At maximum eccentricity, the distance of the Earth from the Sun varies by 18.5 million kilometers (currently only 4.9 million kilometers)



2. The earth's climate and the global energy balance

Climate factors

1b) Earth orbit parameters

Eccentricity e: Influence on the solar constant S0 of the solar planets (green: "habitable zone")

(1 AE = 149.6 Mio. km)

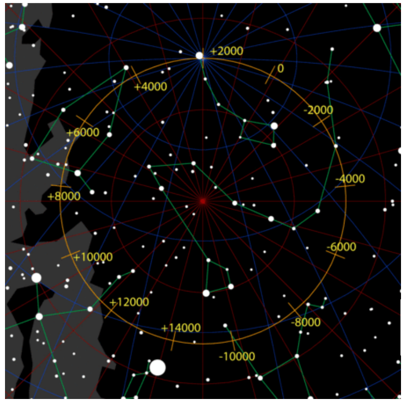
Planet	Perihelion and Aphelion Distance in astronomical units	Solar radiation (solar constant) Maximum and minimum (W/m²)	
Mercury	0.3075 – 0.4667	14,446 – 6,272	bound rotation
Venus	0.7184 – 0.7282	2,647 – 2,576	Greenhouse gases CO_2 and H_2O determine habitability
Earth	0.9833 – 1.017	1,413 – 1,321	
Mars	1.382 – 1.666	715 – 492	
Jupiter	4.950 – 5.458	55.8 – 45.9	Gas giants
Saturn	9.048 – 10.12	16.7 – 13.4	
Uranus	18.38 – 20.08	4.04 – 3.39	Ice giants
Neptune	29.77 – 30.44	1.54 – 1.47	

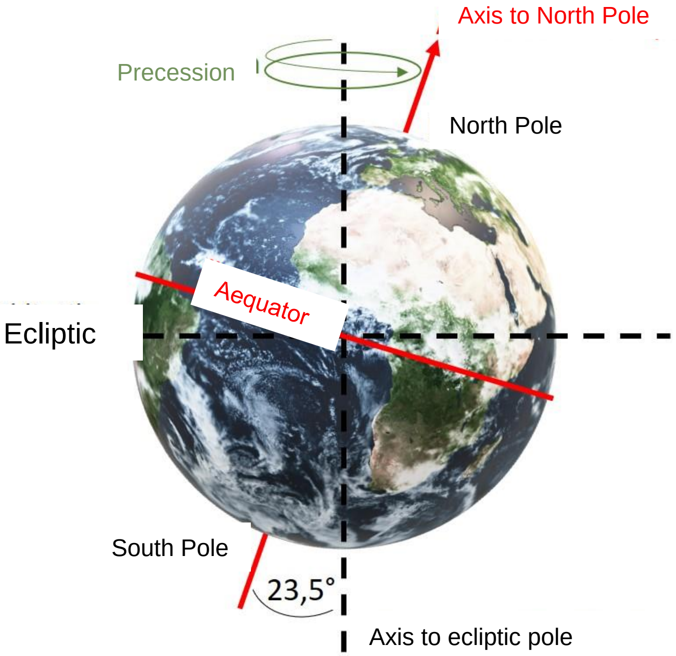
2. The earth's climate and the global energy balance

Climate factors

1b) Earth orbit parameters

Precession (period 25,780 a) + Nutation (18.6 a)





The gyroscopic motion or precession has the consequence that the distance between earth and sun (actual mean distance 149,597,870 km) changes gradually in a certain season.

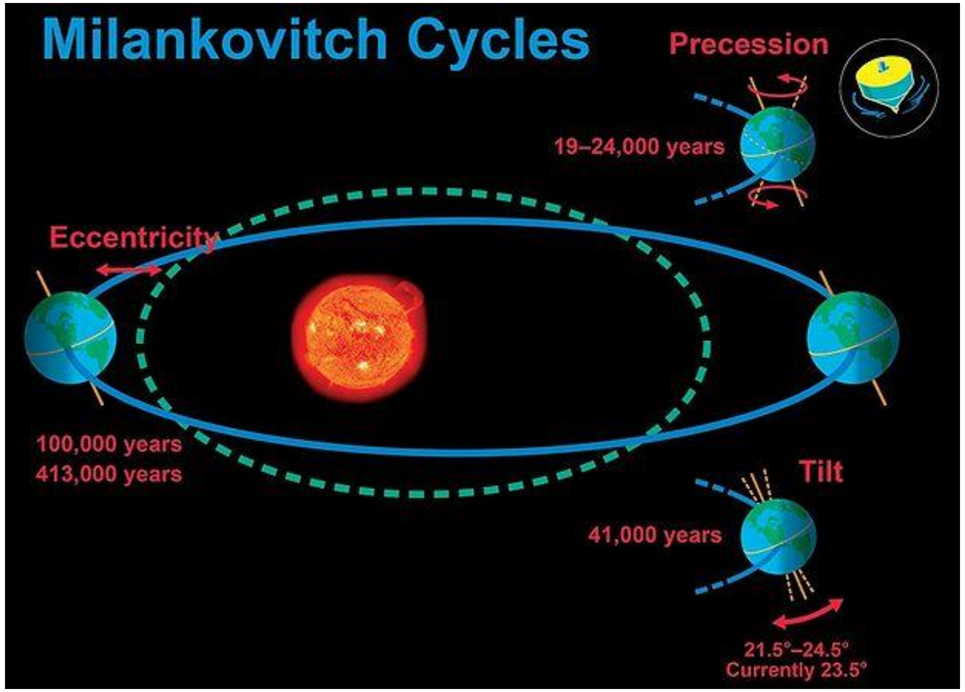
Thus, in the northern hemisphere, the Earth currently reaches its closest point to the Sun in its orbit (the perihelion) in winter (on January 4th with 147,099,600 km near the Sun) and its farthest point from the Sun (the aphelion with 152,096,200 km far from the Sun) on July 04th

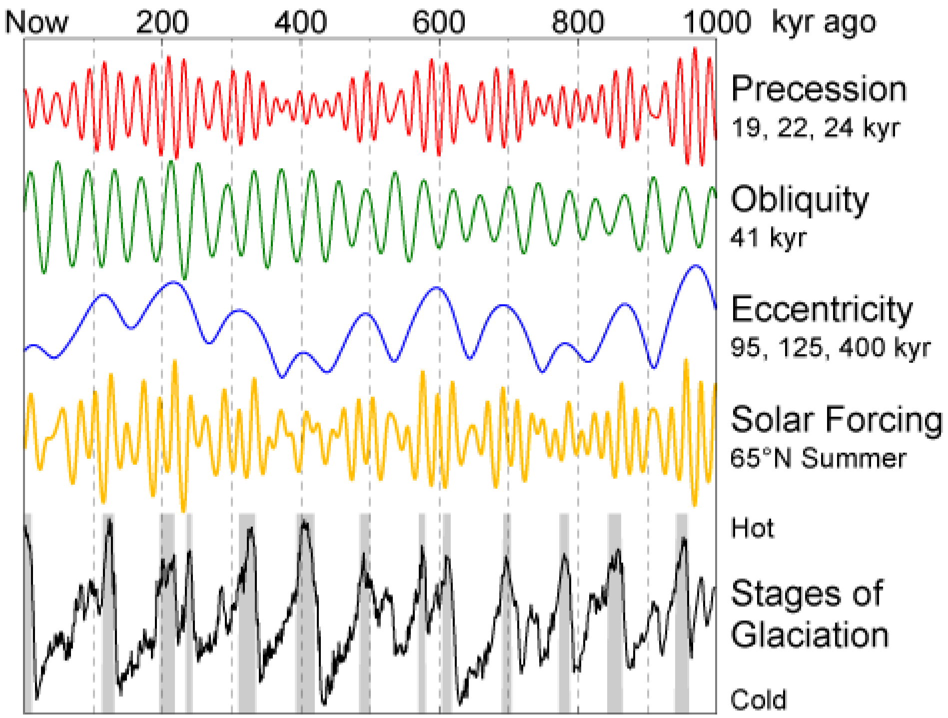
→ Today: Milder and shorter winters and cooler and longer summers in the northern hemisphere

2. The earth's climate and the global energy balance

Climate factors

1b) Earth orbit parameters in the sum, i.e. precession, obliquity and eccentricity as well as perihelion rotation (today: perihelion ~ 147.1 million km, on 04.01 of a year), result in cyclic variation of the irradiation on the northern and southern hemisphere of the earth





Source: Milutan Milankovic (1879 – 1958) about 1920

2. The earth's climate and the global energy balance

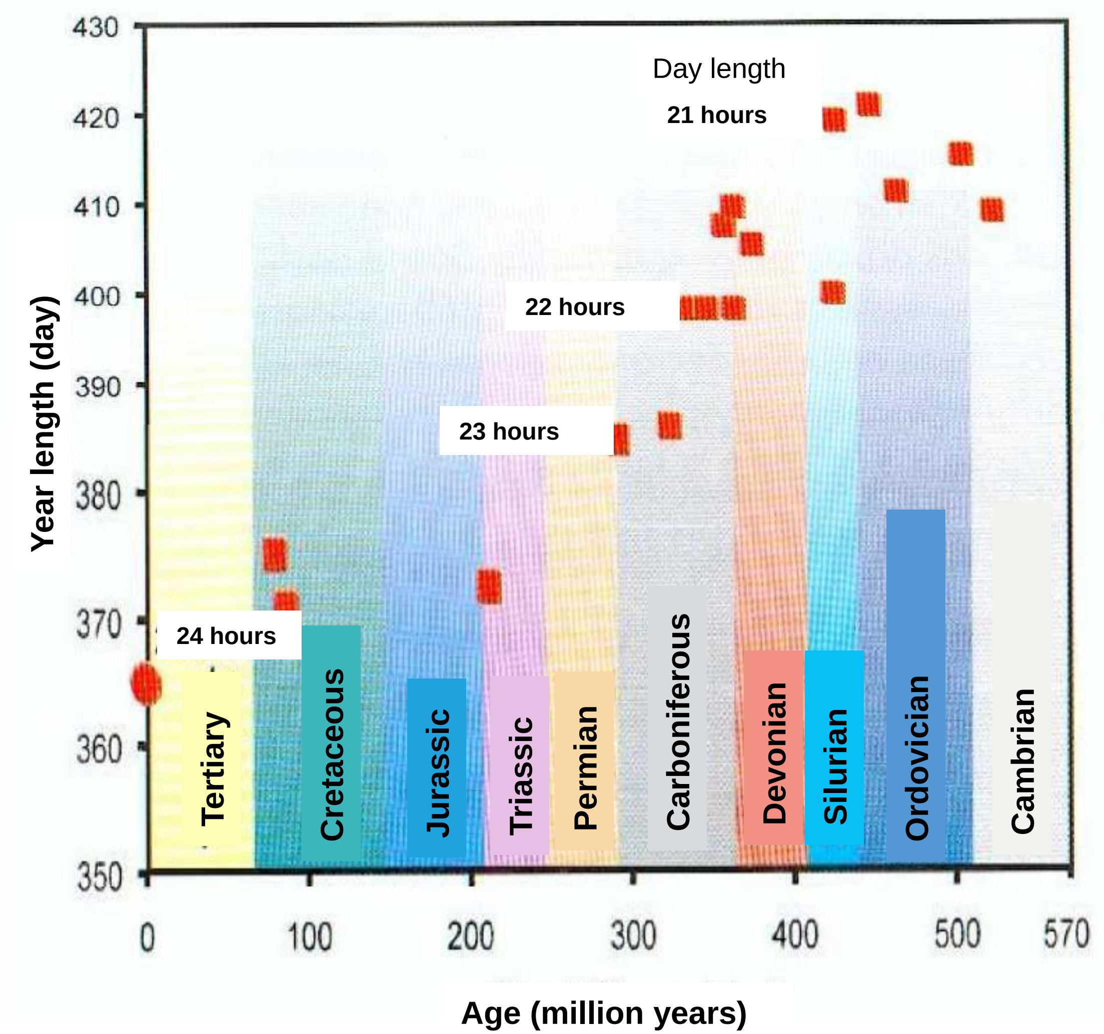
Climate factors

1c) Tidal effects

Cause: Interaction with moon and sun

Consequences
Bound rotation earth-moon
Increase of day length (2 ms/100 a)
Increase of the distance earth-moon (3.8 cm/a)
Increase of distance earth-sun (15 cm/a)
Tidal range (oceans + earth crust!)

Absorbed tidal energy = 94 x 10^{18} J/a (94 EJ/a)

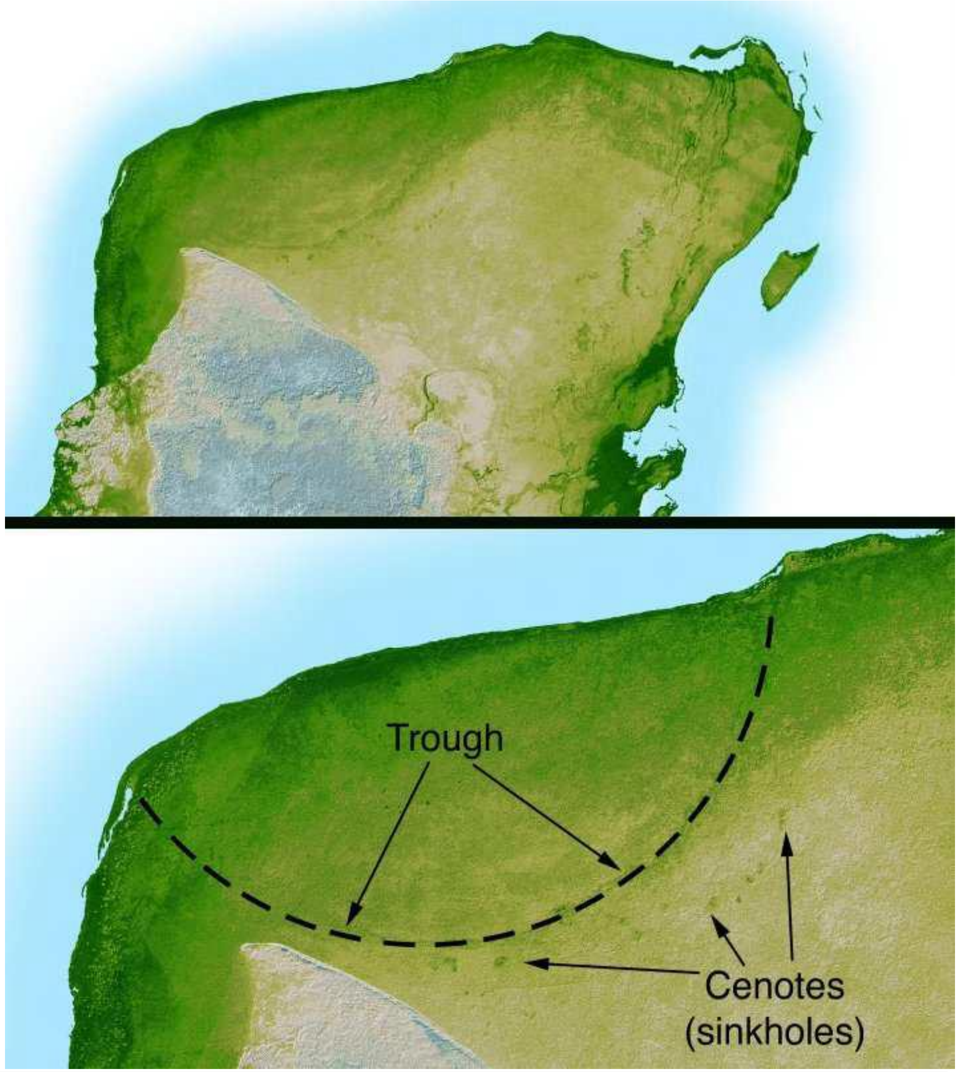


2. The earth's climate and the global energy balance

Climate factors

1d) Meteor impacts

High altitude radar image of the Yucatan Peninsula in Mexico. Faintly visible Chicxulub crater.
(Source: Wikipedia)



66,040 Million years ago: K/T boundary Lit.: Science 208 (1980) 1095 > 1000 km^3 ejecta (proven by Ir anomaly)		>100 Gt TNT
15 Mill. years ago: Nördlinger Ries, Germany		24 Gt TNT
50000 years ago: Barringer crater, AZ, USA		15 Mt TNT
1908	Tunguska-Event, Sibiria	4-5 Mt TNT
1994	Shoemaker-Levy-9, Jupiter, south. Hemi.	650 Gt TNT
2013	Chelyabinsk Explosion, Ural	500 kt TNT

2. The earth's climate and the global energy balance

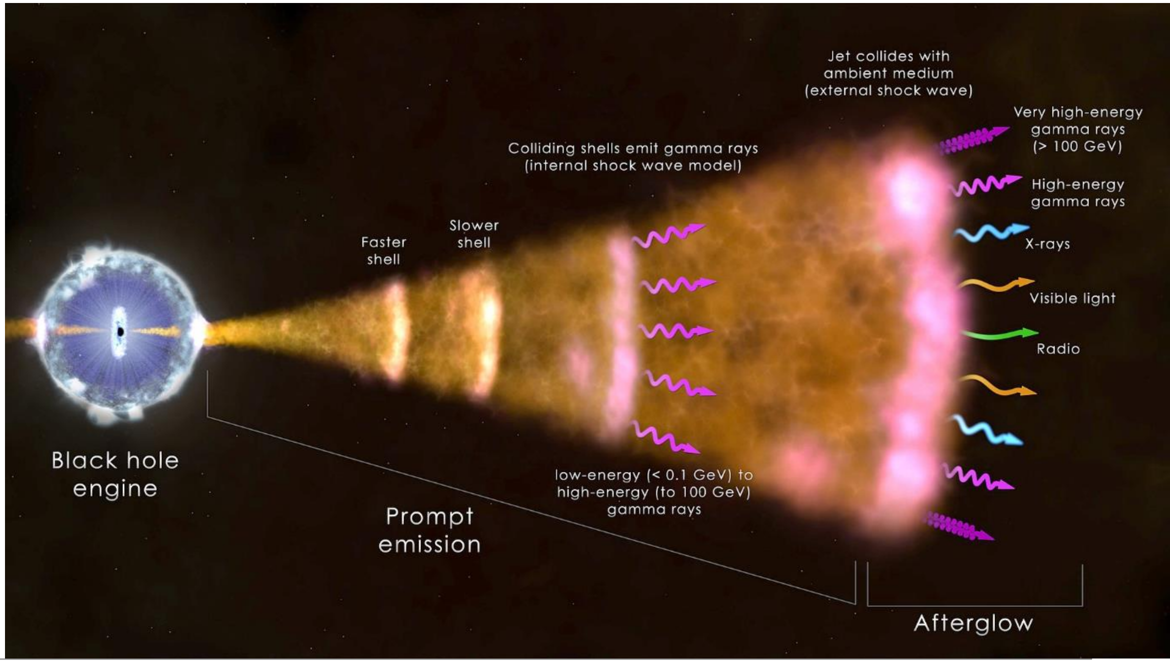
Climate factors

1e) Supernovae & Gamma Ray Flashes

Supernovae (SN) ⇒ Increase in cosmic rays ⇒ Ionization of Earth's atmosphere ⇒ ncrease in cloud formation ⇒ Increase in albedo a and cooling

2.2 million years ago:
SN in the "vicinity" of the earth led to the formation of ^{60}Fe, found in Fe_3O_4 as part of sediments of the Pacific Ocean

Next candidate in our cosmic "vicinity"
Betelgeuse (α Orionis), red supergiant star
Distance: 500 - 700 light years
Radius: 617 million km (~ almost radius of Jupiter's orbit)



2. The earth's climate and the global energy balance

Climate factors

2. Terrestric (geophysical) impact

a) Albedo
b) Magnetic field
c) Plate tectonics
d) Volcanism
e) Silicate-carbonate cycle

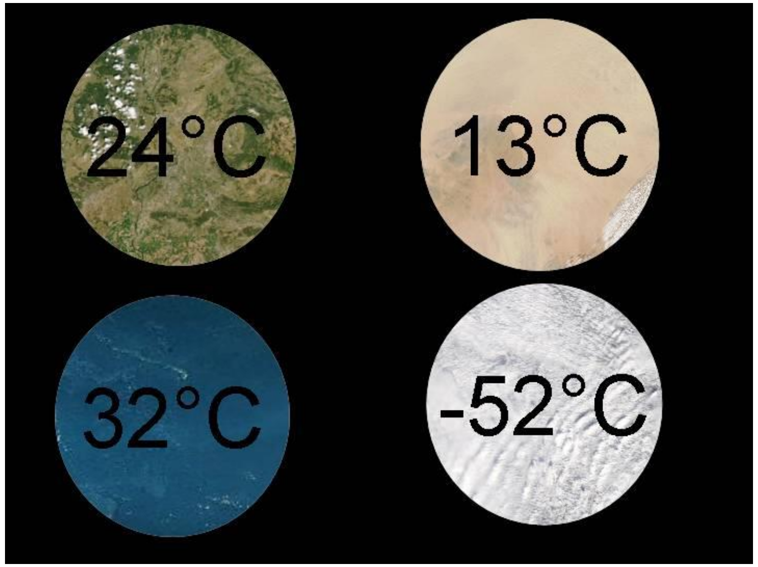
2. The earth's climate and the global energy balance

Climate factors

2a) Albedo a

Earth completely covered with

Forest Desert
Water Ice



Surface	Albedo a	Absorption (1-a)
Snow	0.9 – 1.0	0.0 – 0.1
Salt surface	0.57 – 0.65	0.35 – 0.43
Forest	0.06 – 0.18	0.82 – 0.94
Desert	0.06 – 0.09	0.91 – 0.94
Ocean	0.06 – 0.08	0.92 – 0.94

Planet	Distance from Sun [km]	Albedo	Effective Temperature [K]	Real Temperature [K]	ΔT [K]
Mercury*	5.79×10^7	0.12	434	~ 440	-
Venus	1.08×10^8	0.75	232	737	500
Earth	1.5×10^8	0.30	255	288	33
Mars*	2.28×10^8	0.15	217	210-218	-
Jupiter	7.79×10^8	0.73	85	165	80
Saturn	1.43×10^9	0.34	81	134	53
Uranus	2.87×10^9	0.30	59	76	17
Neptune	4.5×10^9	0.29	47	72	25
Pluto	5.91×10^9	0.50	37	44	7
Moon	1.5×10^8	0.11	271	-123 – 380	-

*no Atmosphere

modified after Jacob, Wikipedia

2. The earth's climate and the global energy balance

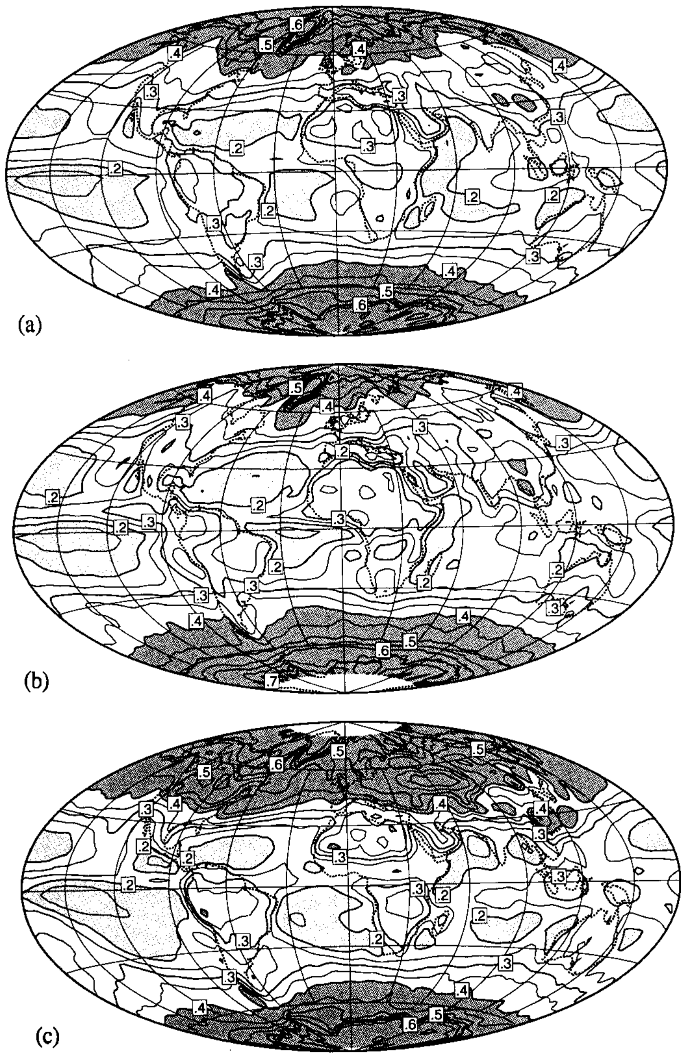
Climate factors

2a) Albedo: Spatial and temporal dependence

World maps of planetary albedo in the areal hammer projection in the

(a) annual mean
(b) northern summer (June - July - August)
(c) northern winter (December - January - February)

The isoline distance is 0.05
Values greater than 0.4 are dark shaded
Values smaller than 0.2 are light shaded
(Figure 2.9 from Hartmann, 1994)

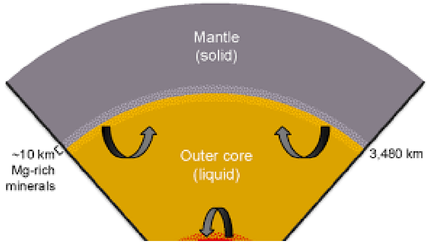


2. The earth's climate and the global energy balance

Climate factors

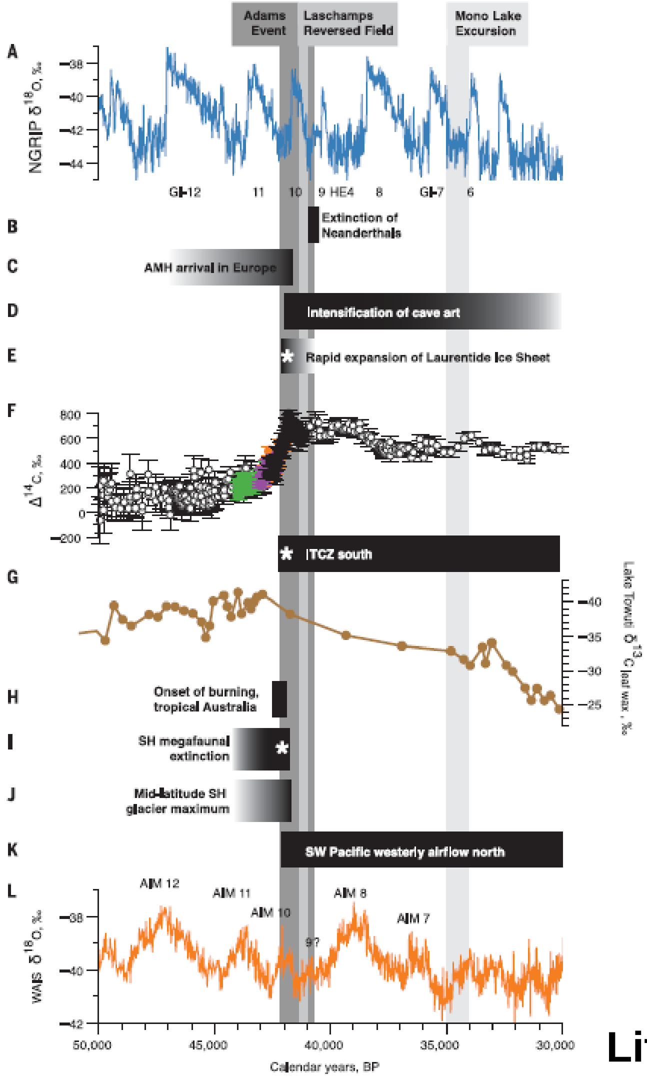
2b) Magnetic field pole jumps

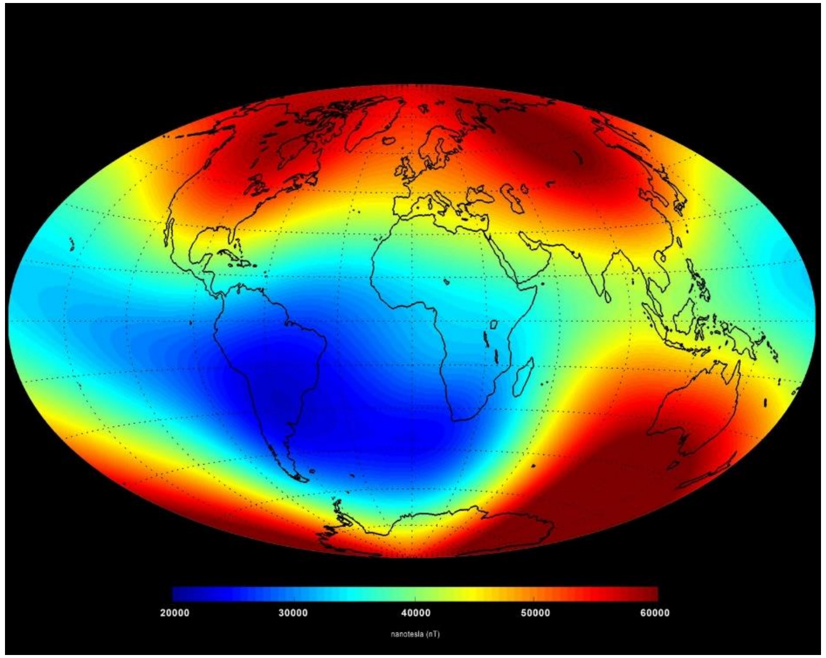
Last pole jump
about 42.000 years ago



Decrease of the magnetic field strength of to about 28% of the original value

Consequences
Mass extinction in Australia
Increase of glaciation in North America
Increase of UV radiation
Invention of cave painting?





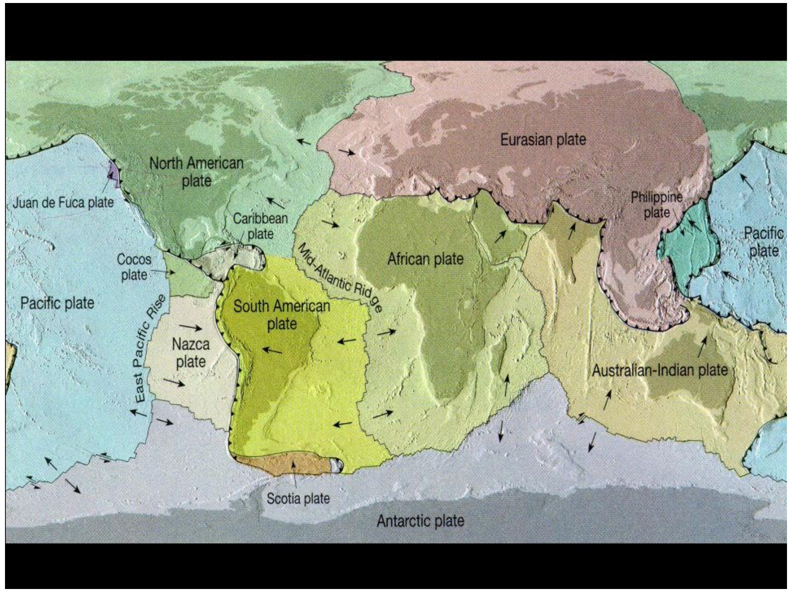
Spatial distribution of magnetic field strength in nT (in blue South Atlantic anomaly)

Lit: Cooper et al., Science 371 (2021) 811

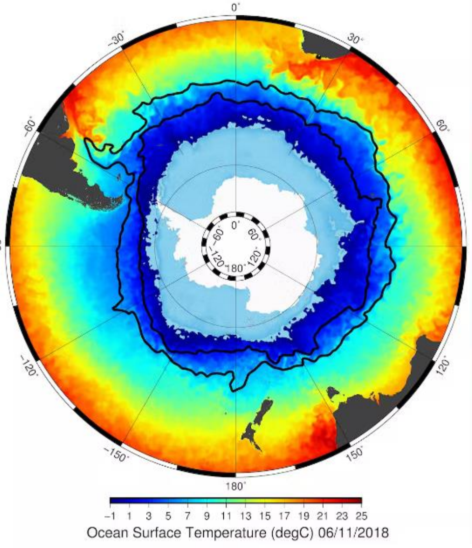
2. The earth's climate and the global energy balance

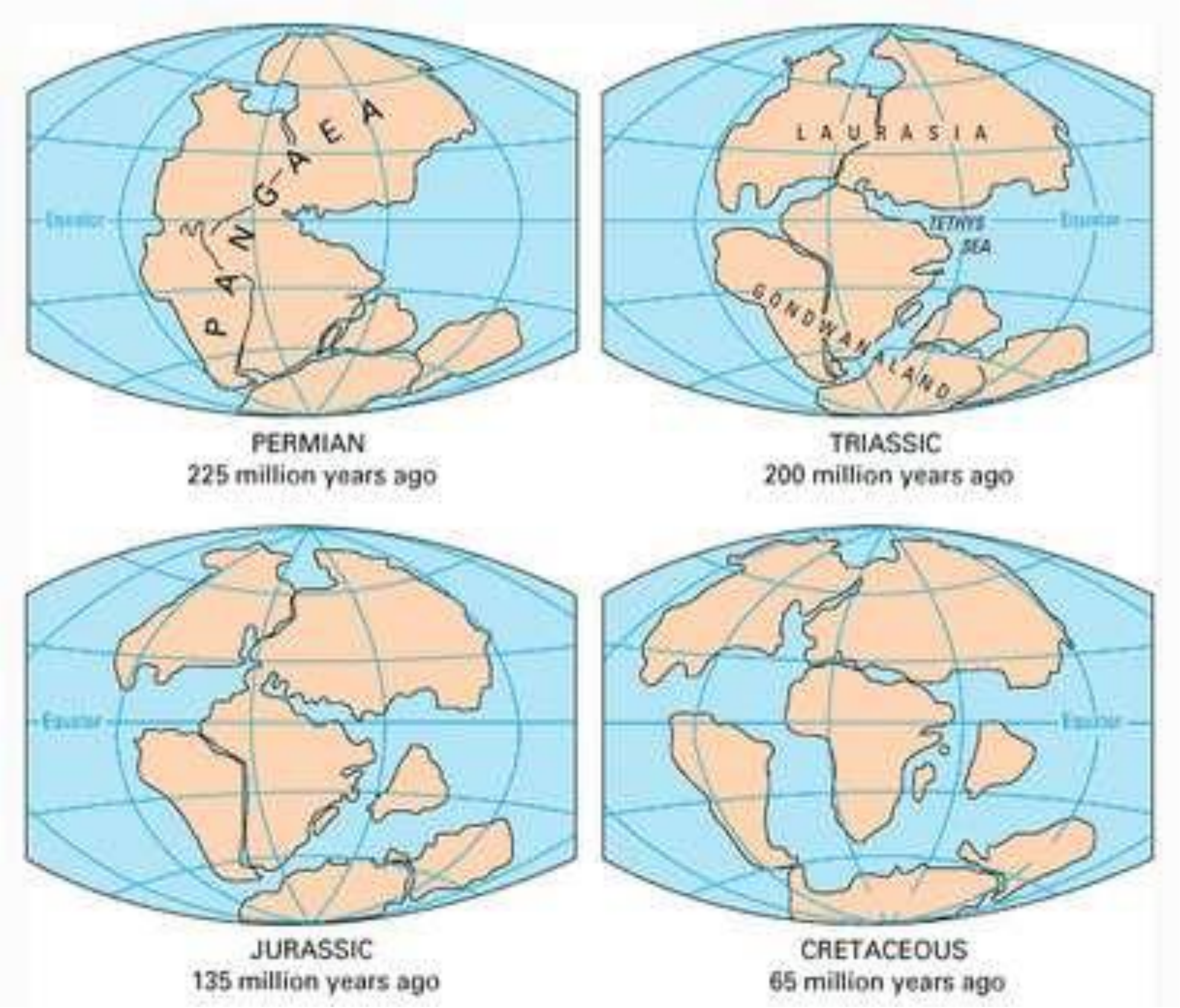
Climate factors

2c) Plate tectonics (Alfred Wegener 1880-1930)



Glaciation of the Antarctic as a re the formation of the circumpolar current about 5 million years ago





2. The earth's climate and the global energy balance

Climate factors

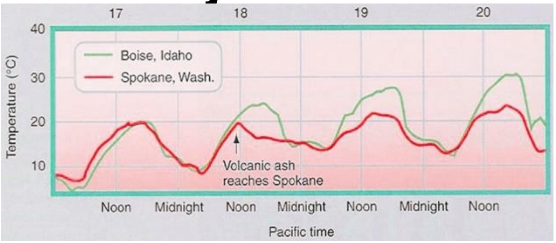
2d) Volcanism

1815 Tambora, Indonesia — 150 km³ ejection
The year without summer 1816 frosts in Europe & NA

1883 Krakatoa, Indonesia — 20 km³ of ejecta

1980 Mt. St. Helens, WA, USA — < 1 km³ of ejecta

1991 Pinatubo, Philippines — 10 km³ ejection



2. The earth's climate and the global energy balance

Climate factors

2e) Silicate-carbonate cycle: long-term Regulation of the atm. CO_2 concentration

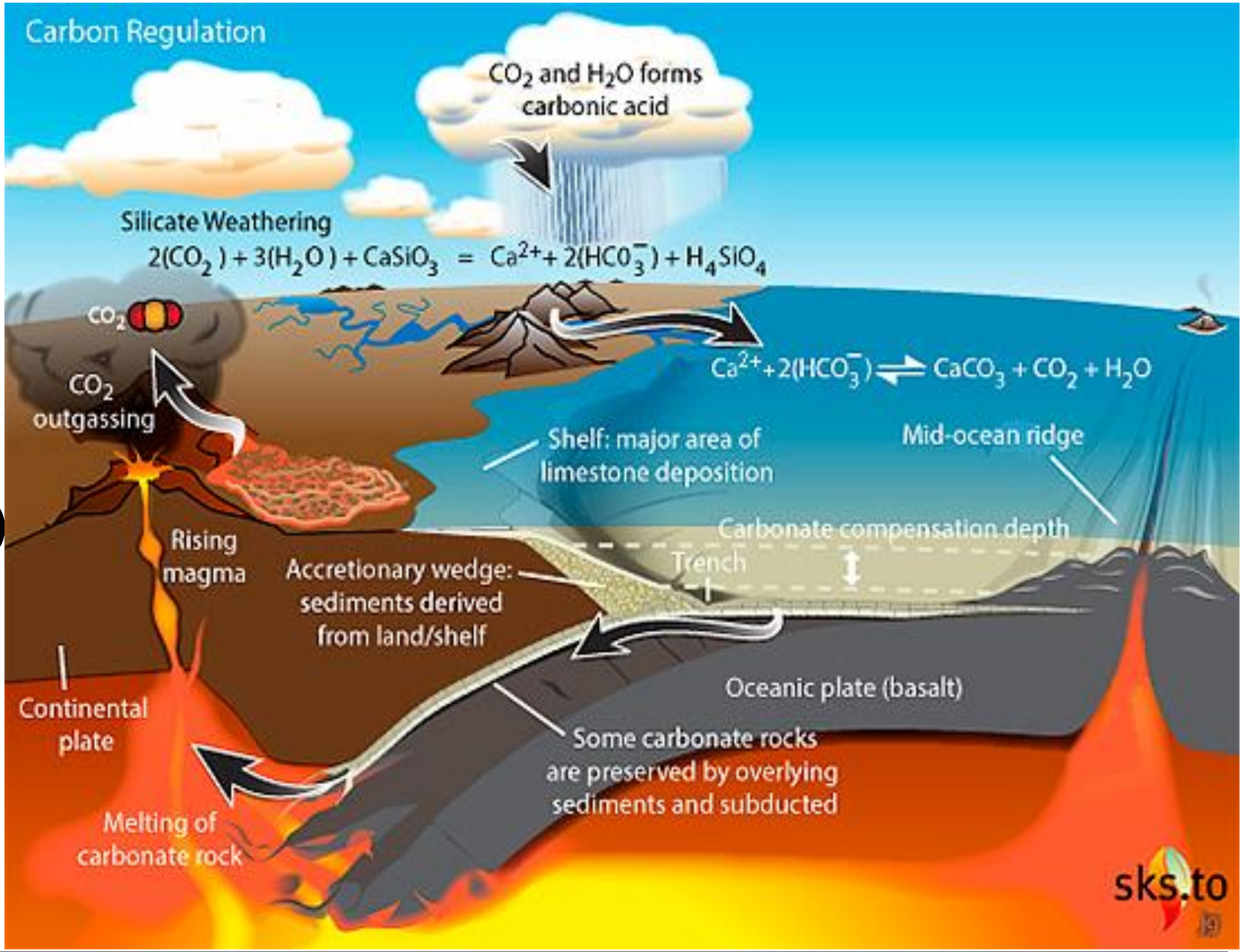
<u>High global temperature</u>

High evaporation and erosion

$CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq)$

- **Precipitation : $CaSiO_3(s) + 2\ H_2CO_3(aq)$**
  $\rightarrow Ca^{2+} + 2\ HCO_3^- + H_2O + SiO_2\downarrow$
  $Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2$
- **Subduction of carbonate sediments**
- **CO_2 emission by volcanoes**

Complete CO_2 exchange ~ 500,000 a

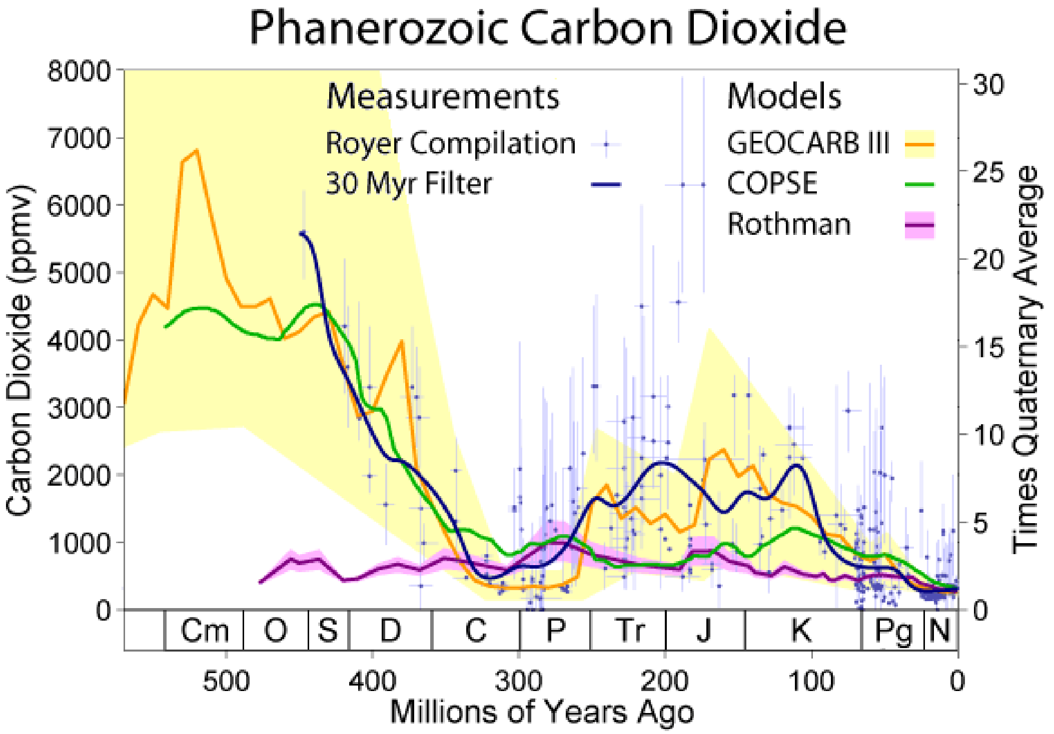


2. The earth's climate and the global energy balance

Climate factors

2e) Silicate-carbonate cycle: long-term regulation of the atm. CO_2 concentration (prehistoric)

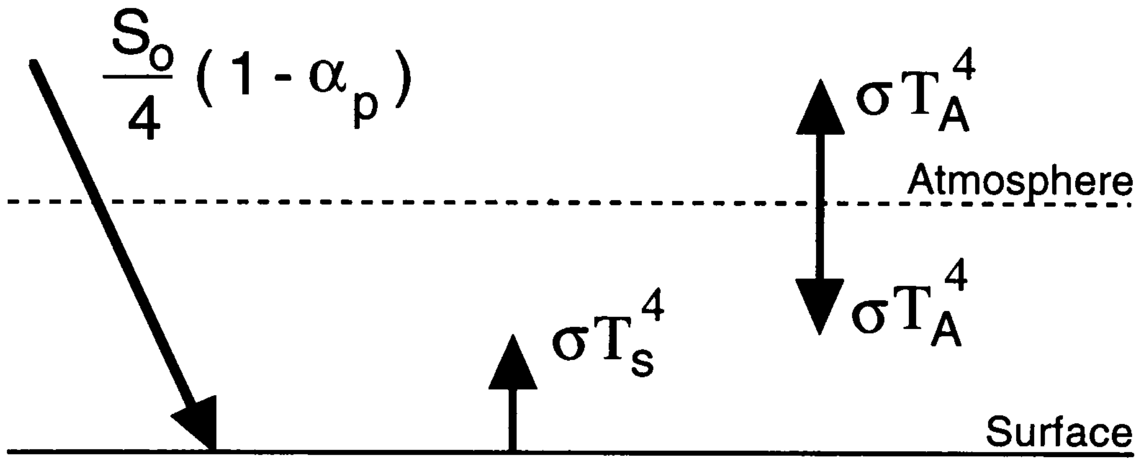
CO_2(g) [Vol.-%]	pH(Rain)	Year / Epoch
• 0.0280	5.64	ca. 1750
• 0.0317	5.62	1960
• 0.0339	5.60	1980
• 0.0370	5.58	2000
• 0.0400	5.57	2015
• 0.0420	5.55	2022
• 0.2	5.22	Jurassic
• 0.7	4.94	Cambrian
• 1.0	4.87	
• 2.0	4.72	
• 5.0	4.52	Archean

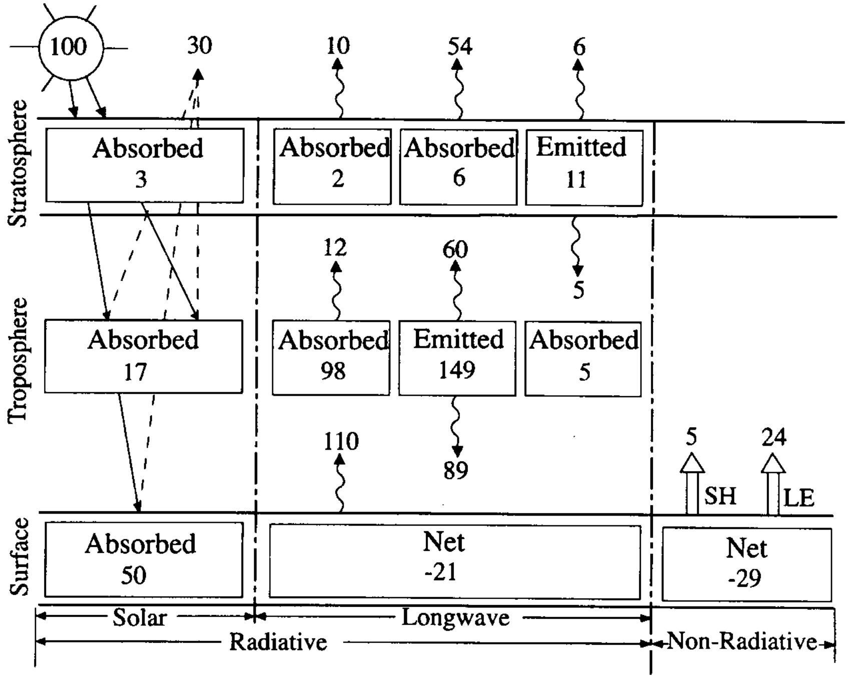


2. The earth's climate and the global energy balance

Climate factors

2e) Silicate-carbonate cycle: greenhouse effect due to CO_2 etc.





Assumption: atmosphere transmitting shortwave radiation, but completely absorbs longwave radiation (e = 1) → T_{real} = 288 K (+15 °C) → ΔT = 33 K

$S_0/4(1-a_{Earth}) = \sigma T_A^4 = \sigma T_E^4$ mit T_A = atmospheric temperature and TE = surface temperature.
Energy balance for the Earth's surface: $S_0/4(1-a_{Earth}) + \sigma T_A^4 = \sigma T_S^4 \Rightarrow \sigma T_S^4 = 2\sigma T_E^4$

2. The earth's climate and the global energy balance

Climate factors

3. Biogenic impact

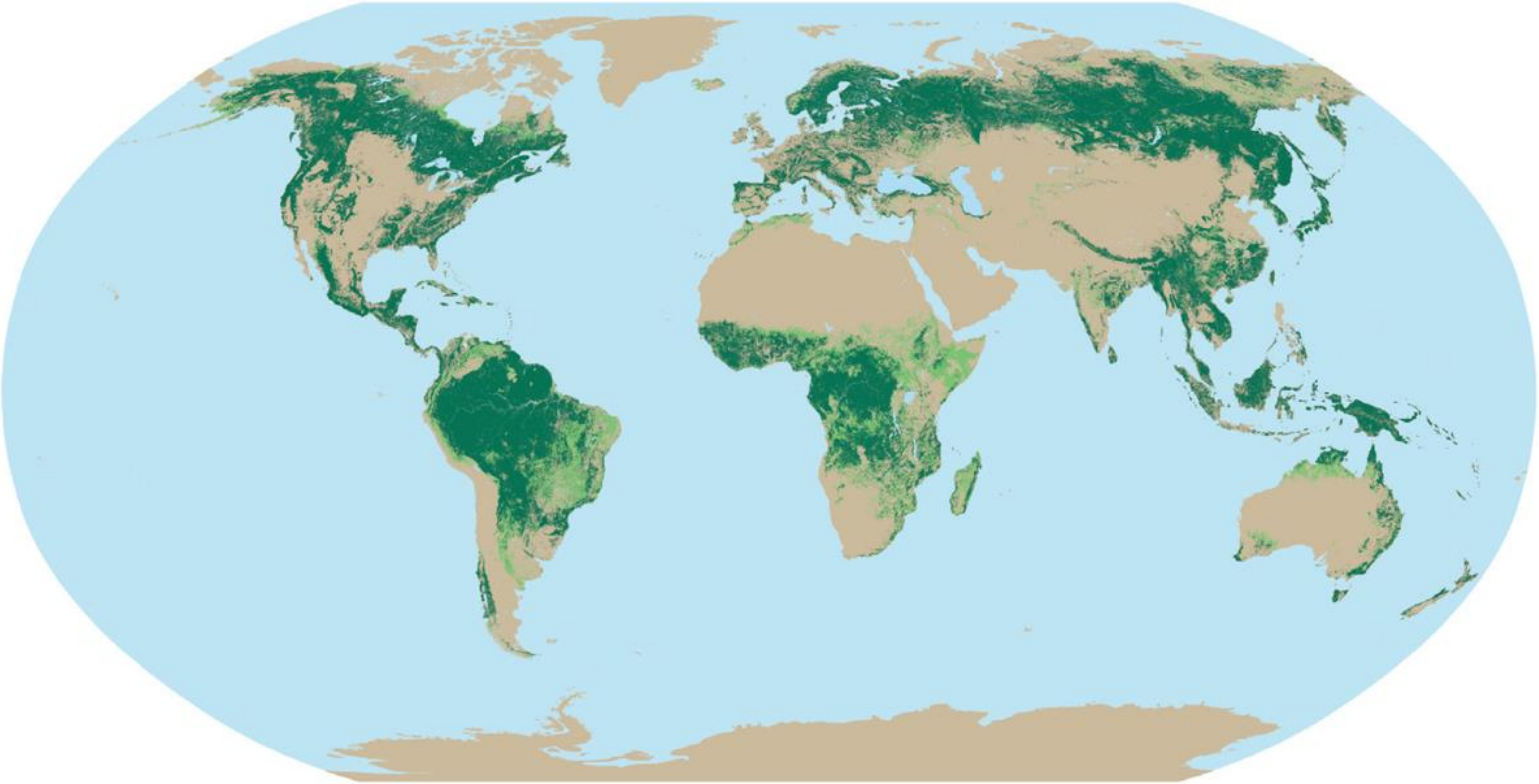
a) Forestation
b) Phytoplankton
c) Peatlands

2. The earth's climate and the global energy balance

Climate factors

3a) Forestation

- Today: 40 million km² almost 25% of the land area (168 million km²)
- In the past 8000 years, about 50% of the forests have been cleared
- Deforestation currently releases 1.6 Gt C/a or 5.9 Gt CO_2/a
- Since 1850, about 20% of total anthropogenic CO_2 emissions



Lit.: Nature 585 (2020) 545

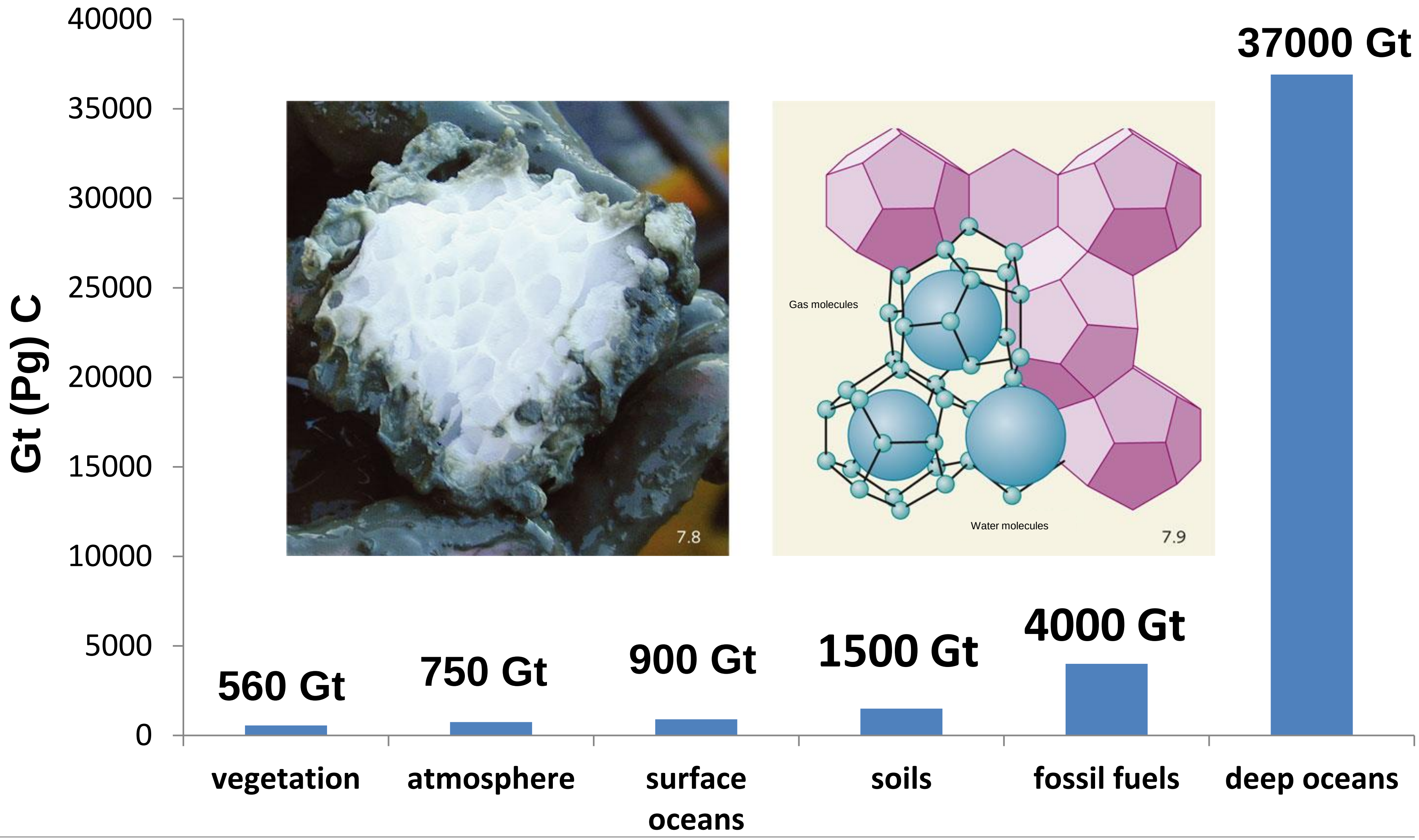
2. The earth's climate and the global energy balance

Climate factors

3a) Forestation

Vegetation & Forest serve as carbon storage

But: The majority of all carbon is stored in fossil fuels and bound as methane hydrate on the ocean floor



2. The earth's climate and the global energy balance

Climate factors

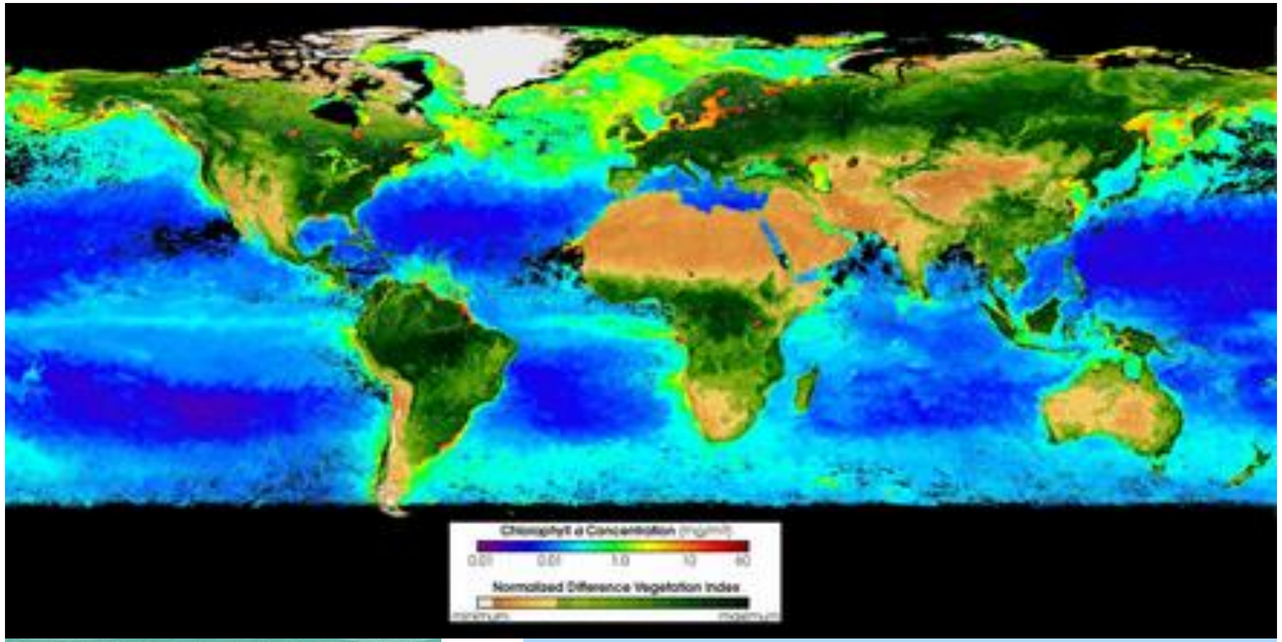
3b) Phytoplankton

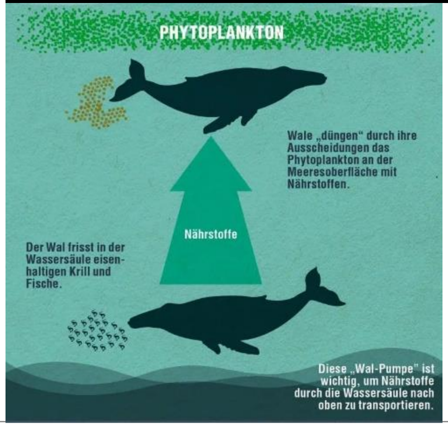
High concentration due to

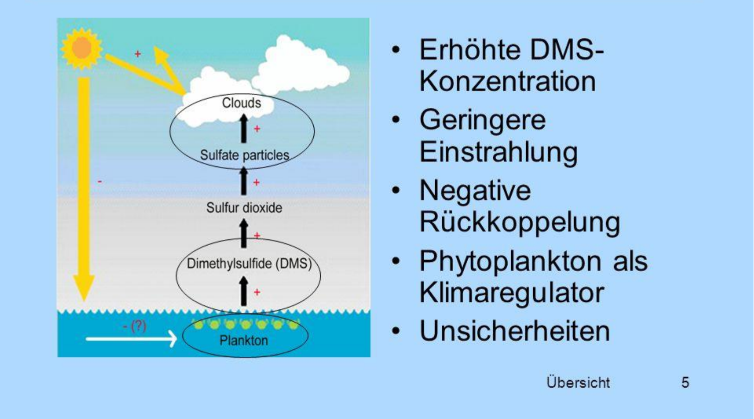
- Cold currents: Polar regions
- Fe^{2+} → "whale pump" and river deltas

Effect of phytoplankton

- CO_2 consumption + O_2 emission
- Aerosols according to Claw hypothesis: Phytoplankton → CH_3-S-CH_3 (Dimethyl sulphide, DMS) → SO_2 → SO_4^{2-} → aerosols → clouds (negative feedback)







2. The earth's climate and the global energy balance

Climate factors

3c) Peatlands

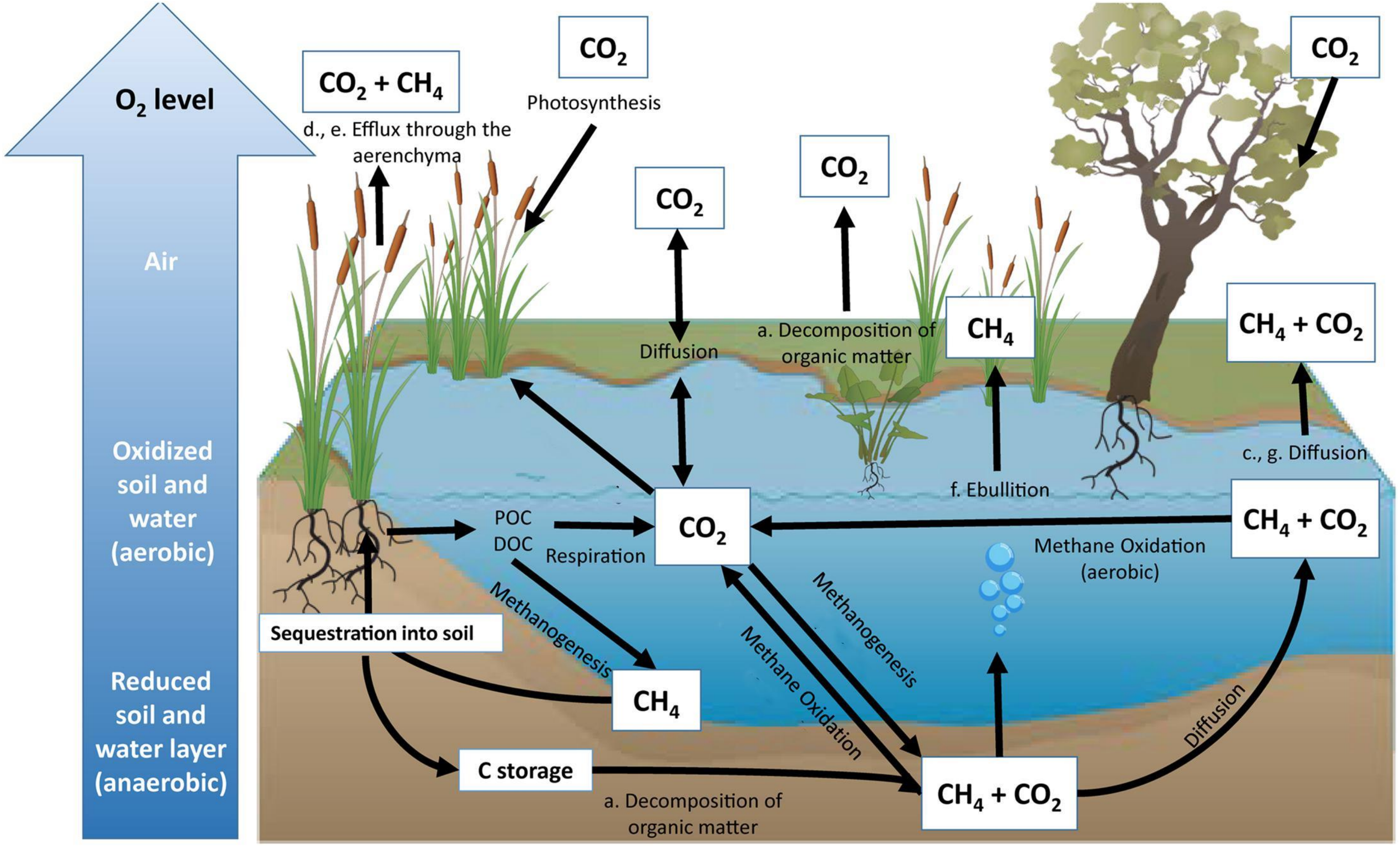
Humid: CO_2 / CH_4 consumer

Dry: CO_2 / CH_4 emitter

Extent: ~ 3% Earth surface

Storage capacity:
~ 30% of the earth's Carbon

Risk: Drought!



Lit.: K.E. Limpert et al., Frontiers in Env. Sci. 8 (2020) 8

2. The earth's climate and the global energy balance

Climate factors

3c) Peatlands

**For Germany
The peatlands store as much
as much carbon as in the forest
Stored**

	System	Trace emission			Climate effectiveness
	Effectiveness 100 a	CO_2-C 1 (Kg C ha^{-1} a^{-1})	CH_4-C 7,63 (Kg C ha^{-1} a^{-1})	N_2O-N 133 (Kg N ha^{-1} a^{-1})	CO_2-C equivalent (Kg CO_2-C equ ha^{-1} a^{-1})
Lowland Peatland	natural (Rzecin)	-2000	120	0.1	-1070
	near-natural (boreal)	-490	120	0.112	442
	near-natural (Temperate)	-400	142		685
	drained forest	400	1	1.05	547
	grassland	4120	0.4	5.05	4795
	arable land	4090	-0.2	11.61	5633
Highland Peatland	near-natural (boreal)	-200	37.5	0	87
	near-natural (Temperate)	710	174	-0.0112	618
	drained forest	1100	20	0.04	1258
	grassland	2350	2	0.1	2379
	arable land	4400	0	0	4400
	Peat cutting	1750	17.25	0.4	1935

**Global 2015
Intact peatlands: -0.36 Gt C
Non-intact peatlands: +1.5 Gt C**

Source: https://www.lubw.baden-wuerttemberg.de/klimawandel-und-anpassung/moorboeden

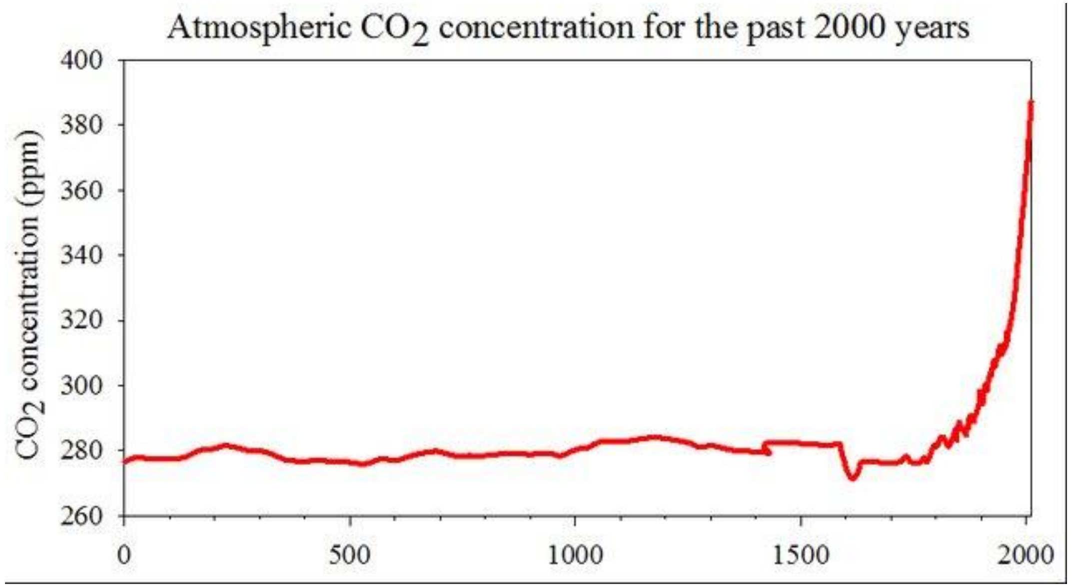
On average 700 tons of CO_2 stored per ha

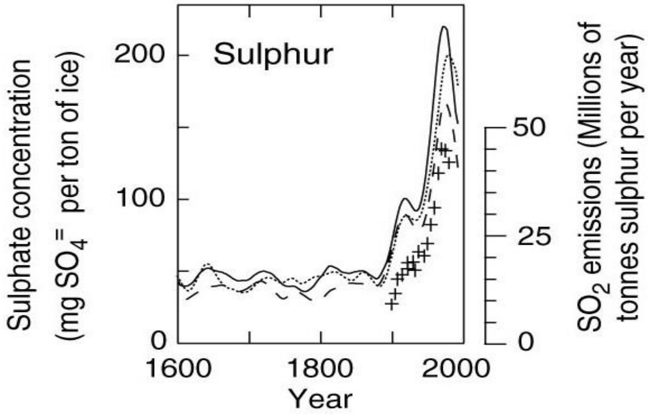
2. The earth's climate and the global energy balance

Climate factors

4. Anthropogenic impact (relevant since about 1750)

a) CO_2 emission: fossil fuels, deforestation
b) Sulfate aerosol emission
c) "Black carbon on snow
d) Tropospheric ozone
e) CH_4 emission from livestock, rice cultivation, waste dumps, natural gas production (leakages)
f) N_2O emission from fertilization, deforestation, biomass burning
g) Emission of fluorine compounds: HFC, SF_6, NF_3, and so on
h) Building development and urban climate
i) Drainage of peatlands
j) Lead emission: formation of aerosols and clouds

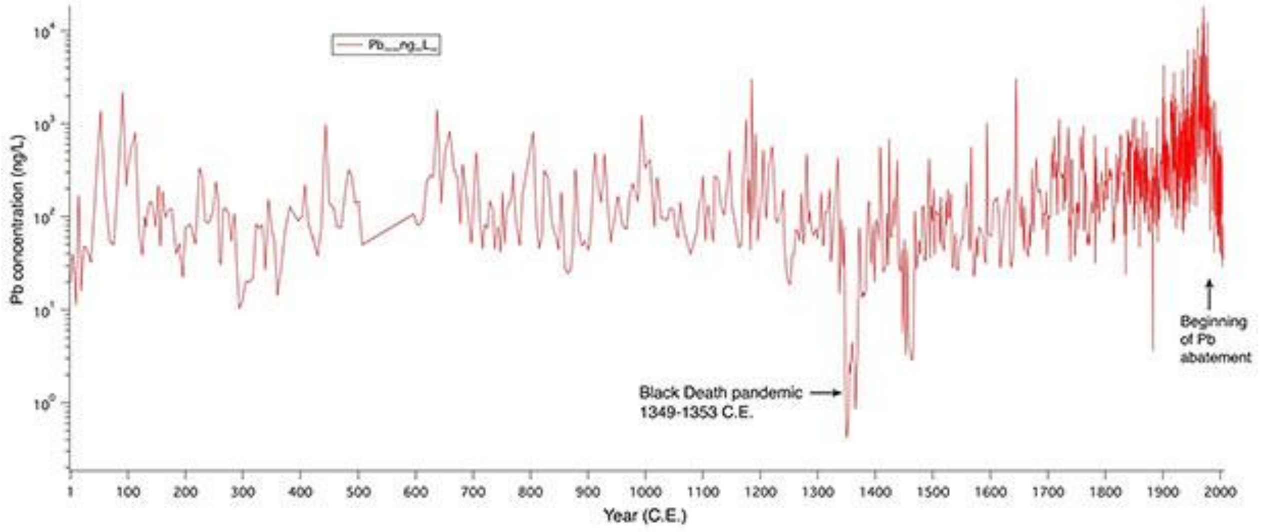




2. The earth's climate and the global energy balance

Climate factors

4. Anthropogenic influences: Effect of lead emissions on concentrations in breathable air



Consequences of increased Pb conc. in air:
- Increased aerosol formation: Clouds (albedo)
- neurotoxic effects
- hypertonia (today 8-11 ppm Pb in the skeleton)

Causes of the decrease of Pb-conc. in air
1350 Plague epidemic
1460 Further epidemic
1885 World economic crisis

1966: $102 \cdot 10^3$ t Pb aerosol northern hemisphere
200 ng Pb per kg snow (Greenland)

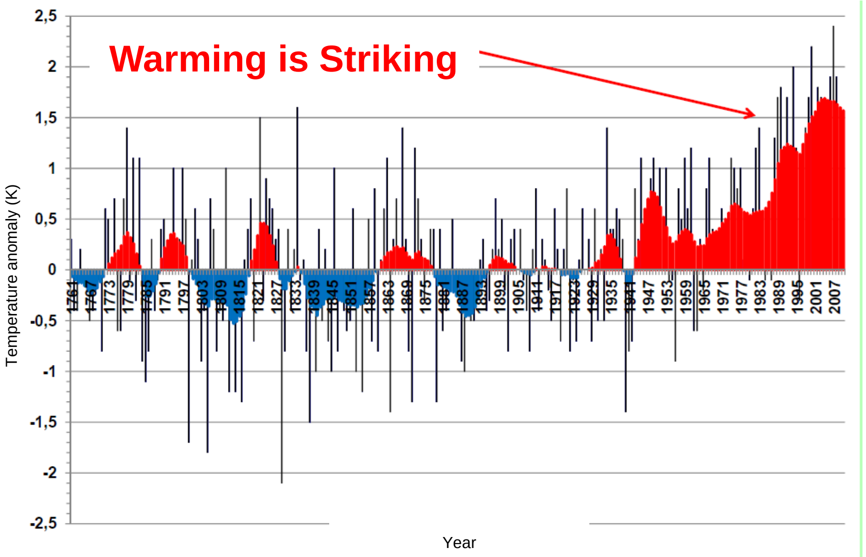
Lit.: Geochim. Cosmochim. Acta 33 (1969) 1247

2. The earth's climate and the global energy balance

Climate reconstruction ⇒ Time scales

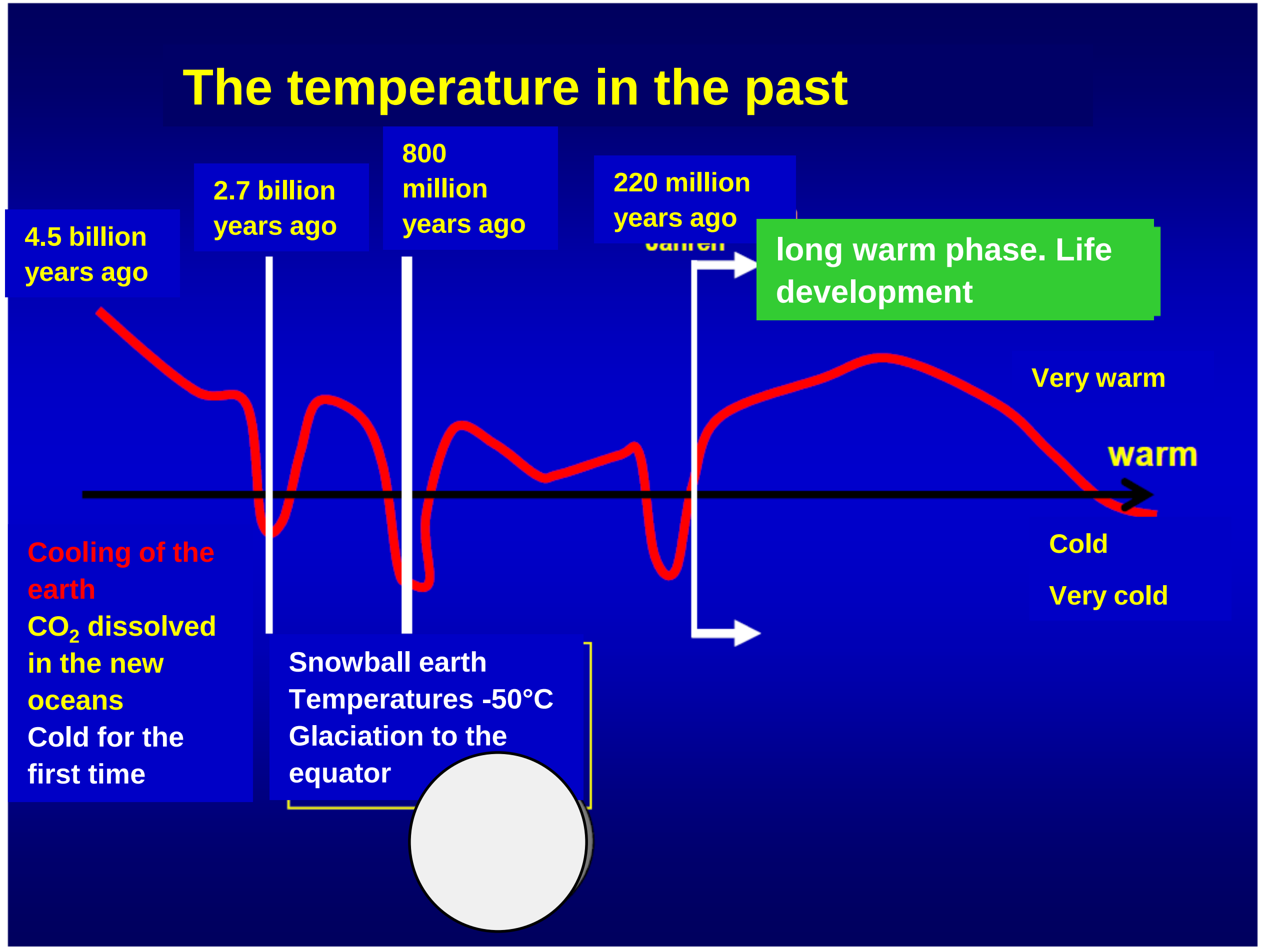
Mechanism	time scale [years]
• **Solar radiation**	
Fusion power	10^9
Orbital parameters	10^4 - 10^6
Sunspot cycles	10 - 1000
• **Albedo of the Earth All**	All
• **Plate tectonics**	
Mountain building, continental drift, ocean currents	10^6 - 10^8
• **Greenhouse effect**	All
CO_2, CH_4, H_2O, N_2O, CF_4, NF_3, SF_6, FCKW, …	
• **Aerosols**	
Volcanoes, air pollution	1 - 10
• **Land use**	1 - 100

„Baur“ temperature series
for Central Europe 1761 - 2010

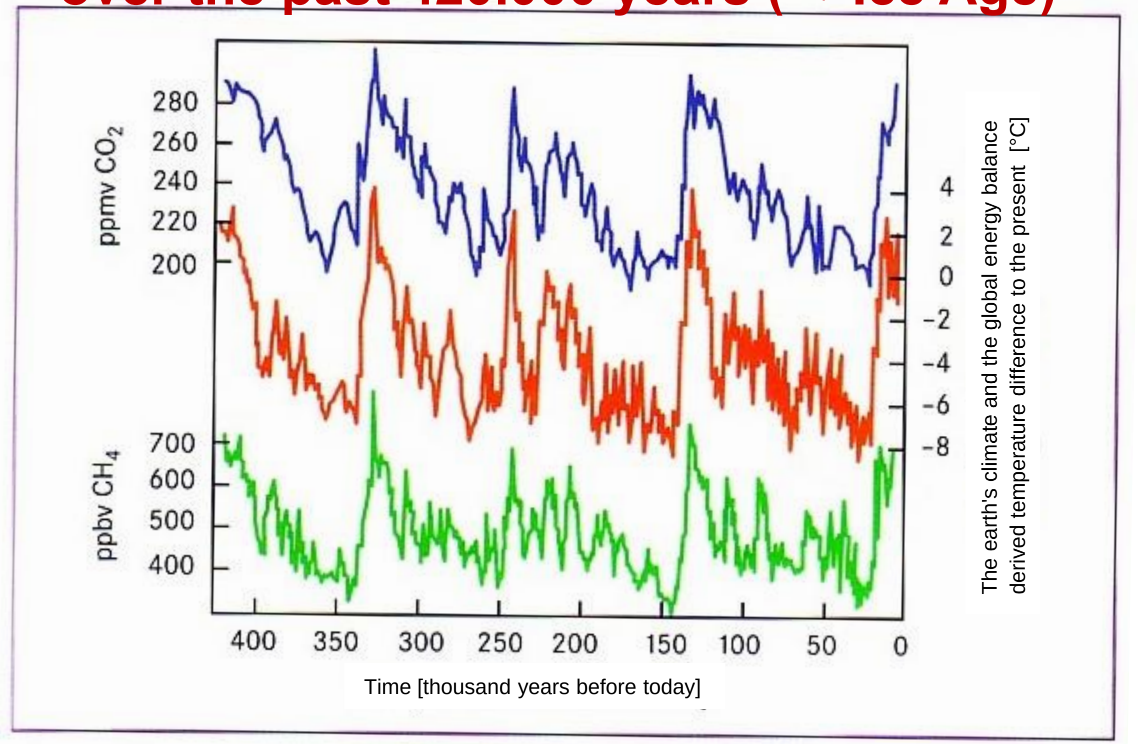


2. The earth's climate and the global energy balance

Climate reconstruction: long and short term.....



CO_2, CH_4, and temperature fluctuations over the past 420.000 years (→ Ice Age)

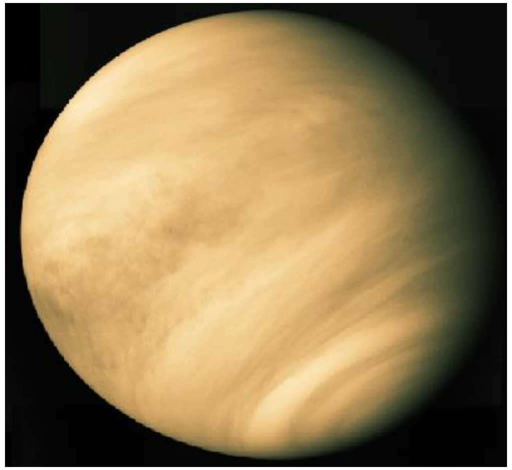


Atmospheric composition reconstructed from ice cores of the Antarctic spherical composition of the last 420.000 years Source: Mauser 2007 in Gebhardt et al., S. 969)

2. The earth's climate and the global energy balance

Comparison of the terrestrial solar planets in the "habitable" zone

Venus



2.61 kW/m²
Albedo = 0.76 → T_E = 232 K
96% CO_2 + 3% N_2 + SO_2 + H_2O + Ar (ppms)

93 bar → T_{real} = 740 K
715 Mio. years ago: strong CO_2 increase (earlier: T_{real} ~ 323 K!)

Earth

1.37 kW/m²
Albedo = 0.29 → T_E = 255 K
78% N_2 + 21% O_2 + 0.9% Ar + CO_2 + H_2O + CH_4 (ppms)

1 bar → T_{real} = 288 K
Biology: $H_2O(l)$ is solvent and H_2 source
$H_2O \rightarrow 4\,H^+$ (ATP) + $4\,e^-$ (NADH) + $O_2\uparrow$

Mars

0.59 kW/m²
Albedo = 0.15 → T_E = 213 K
95% CO_2 + 3% N_2 + 1.5% Ar + H_2O (ppms)

5.6 mbar → T_{real} = 225 K

Note: Ar stems from ^{40}K decay

2. The earth's climate and the global energy balance

Far future (10^6 - 10^9 years) of the earth climate

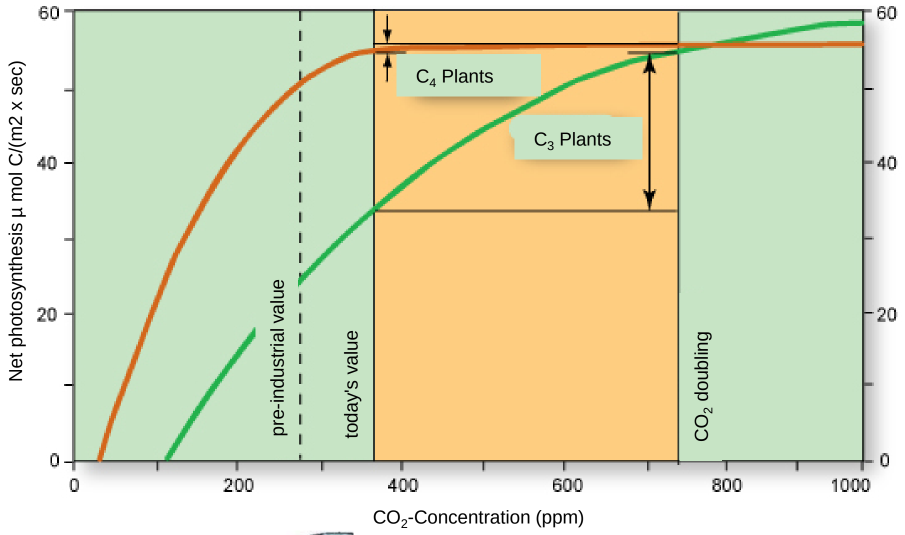
- Development of a CO_2 deficit
  - Biosphere will continue to remove CO_2 from the atmosphere as a reservoir and consumer.
  - Plate tectonics as driver of silicate-carbonate cycle will slow, causing CO_2 consumption to exceed replenishment.
  - Biological limit of photosynthesis at about 25 ppm CO_2 ($\rightarrow C_4$ plants)

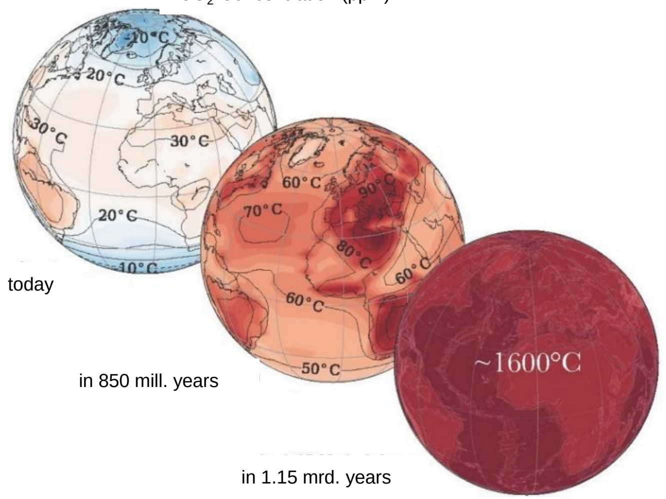
- Further increase of solar radiation intensity

- Loss of the hydrosphere (oceans)

- Fission of carbonate rocks:
  $(Mg,Ca)CO_3 \rightarrow (Mg,Ca)O + CO_2$

The response of C3 and C4 plants to an increase in the CO2 content of the atmosphere





3. Global energy production

Nuclear energy → **Nuclear fusion: ^{1}H, ^{4}He** → **Solar energy** → **Radiation, heat**

Nuclear energy → **Nuclear fission: ^{238}U, ^{232}Th, ^{40}K** → **Geothermal energy** → **Heat, plate tectonics**

Gravitational energy → **Collapse (gas, dust, stars)** → **Star/planet formation, SNe** → **Heat, gravitational waves**

Gravitational energy → **Tides** → **angular momentum loss** → **(latent) heat**

Radiation, heat ↓ Photosynthesis

Fats, carbohydrates, proteins → **Short-term storage (biomass)**

↓ Pressure and temperature

Coal, oil, gas, methane hydrate → **long-term carbon storage (fossil fuels)**

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3. Global energy production

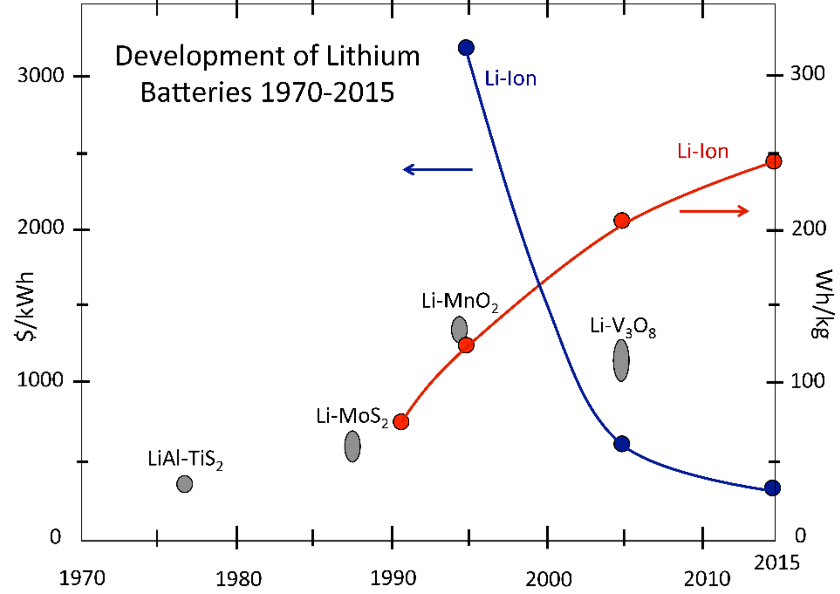
Technical energy storage options

(Li-) batteries	~1 MJ/kg	vehicles
Ammonia	23 MJ/kg	marine
Ethanol	27 MJ/kg	vehicles
H_2 fuel cell	60 MJ/kg	vehicles
H_2 oxyhydrogen	120 MJ/kg	space travel
H_2 nuclear fusion	72 TJ/kg	fusion power plants?
Antimatter annih.	90 PJ/kg	“Science Fiction”

For comparison: Fossil fuels

Hard coal	34 MJ/kg	Coal-fired power plants
Gasoline	40-42 MJ/kg	Vehicles
Diesel	42-43 MJ/kg	vehicles/railways
Kerosene	43 MJ/kg	Aviation

Lit.: Crabtree, Kocs, Trahey, MRS Bulletin, Dec 2015



Decentralized & mobile batteries, NH_3, H_2, EtOH

Decentralized & stationary batteries, CH_4, MeOH, EtOH

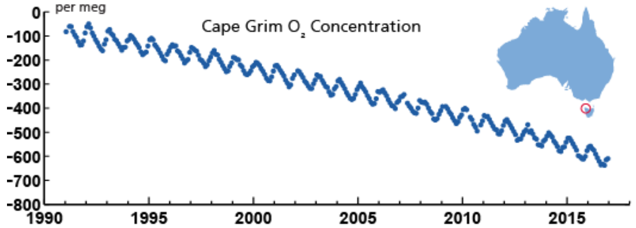
3. Global energy production

Problem of burning fossil carbon reservoirs

Primordial CO_2 (1.47·10^9 t) → O_2 (sediments:Fe^{2+} 10^{-7} mol/l in ocean with 1.332·10^{21} l water)

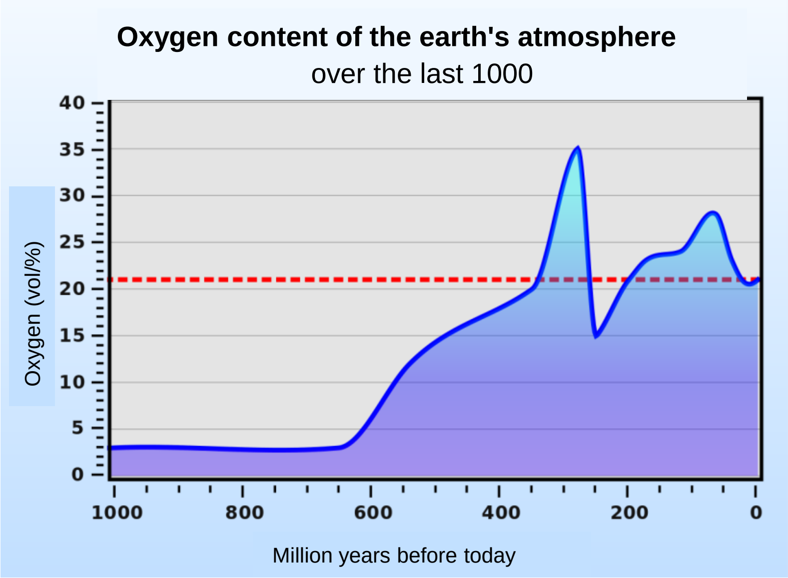
→ 4 $Fe(OH_3)$↓ (1.42·10^{10} t) + C (4.0·10^8 t) ⇒ negligible!

Primordial CO_2 (1.64·10^{15} t)→ O_2 (atmosphere: 1.19·10^{15} t) + C (0.45·10^{15} t)



CO_2 emission 2021 ~ 36.3 Gt:

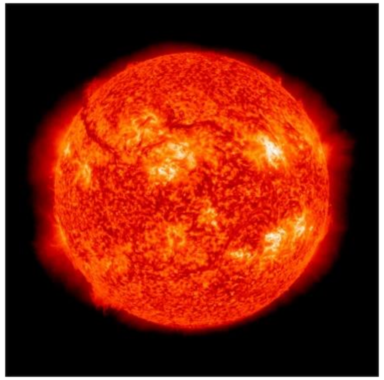
- **Since 1985 O_2 concentration decreased by 600 ppm (Cape Grim)**
- **Continue like this?: In about 45.000 years all atmospheric oxygen would be consumed**
- **Consequence: Reductive atmosphere + oceans with pH << 7!**



End of the biosphere as we know it....

3. Global energy production

Future options (excluding fossil fuels) for meeting anthropogenic energy demand.



Sun

Moon

Earth

- Solar radiation:UV/Vis and IR
- Wind
- Water cycle
- Ocean currents
- Waves
- Biomass

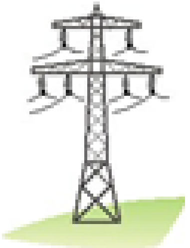
- Tidal range

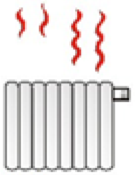
- Geothermal Energy

- Photovoltaics
- Solar collectors
- Solar ovens
- Wind turbines
- Wave power plants
- Hydroelectric power plants
- Biogas plants

- Tidal power plants

- Heat pumps
- Geothermal power plants





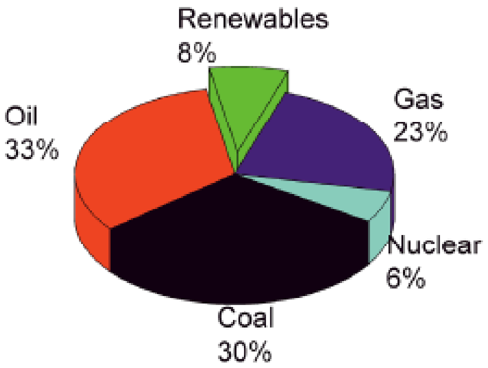
Geothermal energy (internal heat) = $996 \cdot 10^{18}$ J/a = 996 EJ/a

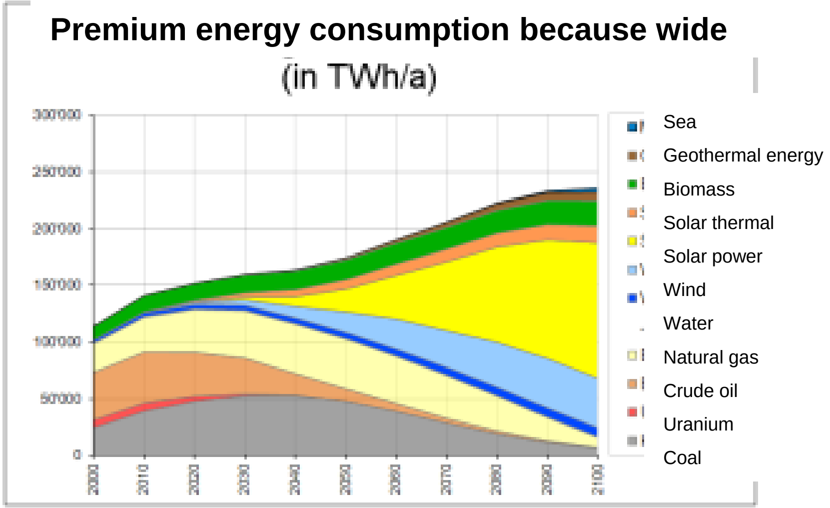
Source: Volker Quaschning, Regenerative Energiesysteme, 6. Auflage, Hanser Verlag , München, 2009

3. Global energy production

Global anthropogenic energy demand in the 21st century

Year	Inst. power	Energy demand
Y2010	14 TW	123,000 TWh/a
Y2050	20 TW	176,000 TWh/a
Y2100	34 TW	299,000 TWh/a





Potential of CO_2 free energy sources

Water	1-2 TW
Biomass	5-7 TW
Wind	14 TW

Solar 100.000 TW = 880 million TWh/a (3000 times the proj. Y2100 consumption)

Global annual photosynthetically produced biomass($CO_2 + H_2O \rightarrow (CH_2O)_x + O_2$)

~ $3.0 \cdot 10^{21}$ J   95 TW ~ 836.000 TWh ~ 700 Gt biomass ~ 105 Gt C

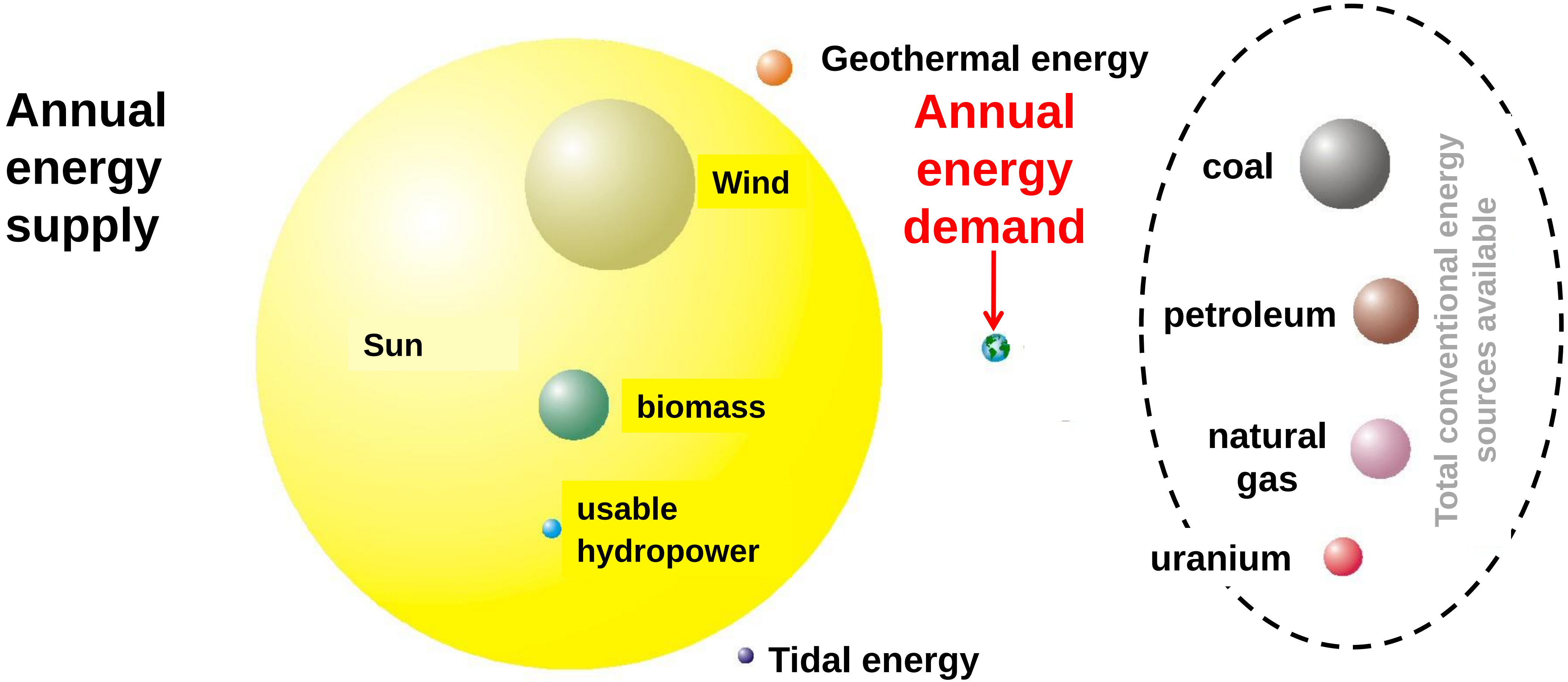
biomass total   ~ 560 Gt C/a (Wikipedia)

Photosynthesis based on [Mn_4Ca] clusters

Ergo: The global energy consumption can be covered in the long term only by solar energy (PV, PS)

3. Global energy production

Global anthropogenic energy demand in the 21st century



Lit.: Volker Quaschning, Regenerative Energiesysteme, 6. Auflage, S. 36, Hanser Verlag, München, 2009

3. Globale Energieerzeugung

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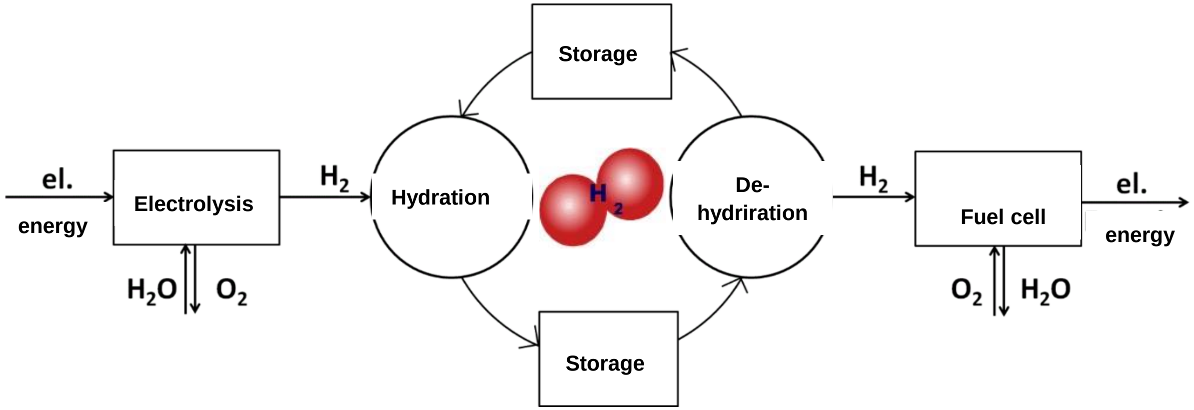
Globally generated altern. Energy (2016)80.5·10^18 J

Total demand (2014) ~ 574·10^18 J (Wikipedia)

- Biomass — $56.5 \cdot 10^{18}$ J
- Hydroelectric power — $14.6 \cdot 10^{18}$ J
- Geothermal — $3.37 \cdot 10^{18}$ J
- Photovoltaics (PV) — $1.18 \cdot 10^{18}$ J
- Solar thermal power — $1.41 \cdot 10^{18}$ J
- Wind power — $3.45 \cdot 10^{18}$ J
- Tidal power — $0.004 \cdot 10^{18}$ J



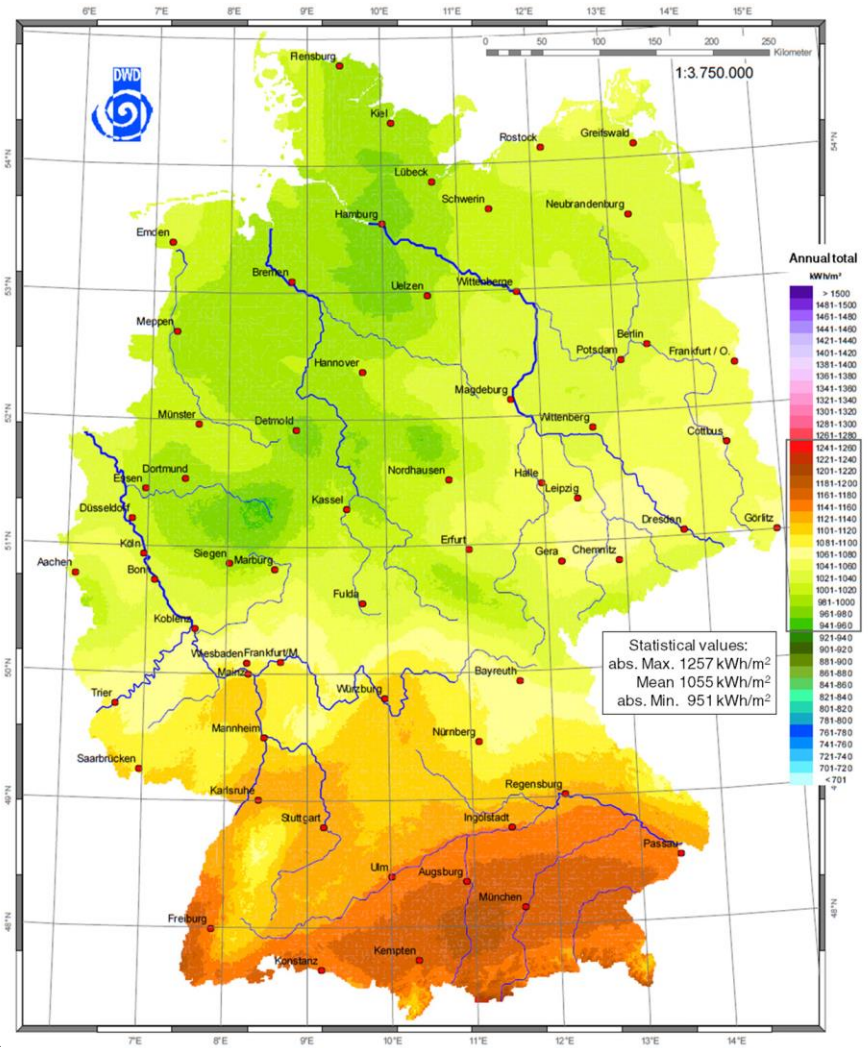
unctional materials for a green or sustainable energy economy Metallic raw materials

- Magnetics — $SrFe_{12}O_{19}$, $SmCo_5$, Sm_2Co_{17}, $Nd_2Fe_{12}B$
- PV materials — Si, CdTe, GaAs, Cu(In,Ga)S_2, perowskites $APbX_3$
- Electrocatalysts — Co, Ni, Cu, Pd, Rh, Pt, Ir
- Photocatalysts — TiO_2, $SrTiO_3$, (Na,K)TaO_3:La, (Cd,Zn)S, $K_3Ta_3B_2O_{12}$, GaN:Zn,O
- Fuel cells — ZrO_2:Y(Ca,Sc), $BaZrO_3$:Y, CeO_2:Gd, $LaGaO_3$
- Battery materials — Li_2CO_3, cobaltates, carbon, …..
- Alternative fuels — H_2, CH_4, LPG, MeOH, EtOH, Mg, Al, dibenzyltoluene, N-ethylcarbazole

3. Global energy production

Area required for the (~ 360,000 km^2)

Biogas	**45000 km^2**	**~ 12.5%**
Wind energy	**7200 km^2** **(area between masts can be used for agriculture or similar)**	**~ 2%**
Photovoltaic	**1800 km^2**	**~ 0.5%**



Consequently:

Solely PV can cover the energy demand of whole Germany as well as of the whole world without creating major conflicts for land

3. Global energy production

Photosynthesis in green plants

Light energy → **Chemical energy**

~1 kW/m²

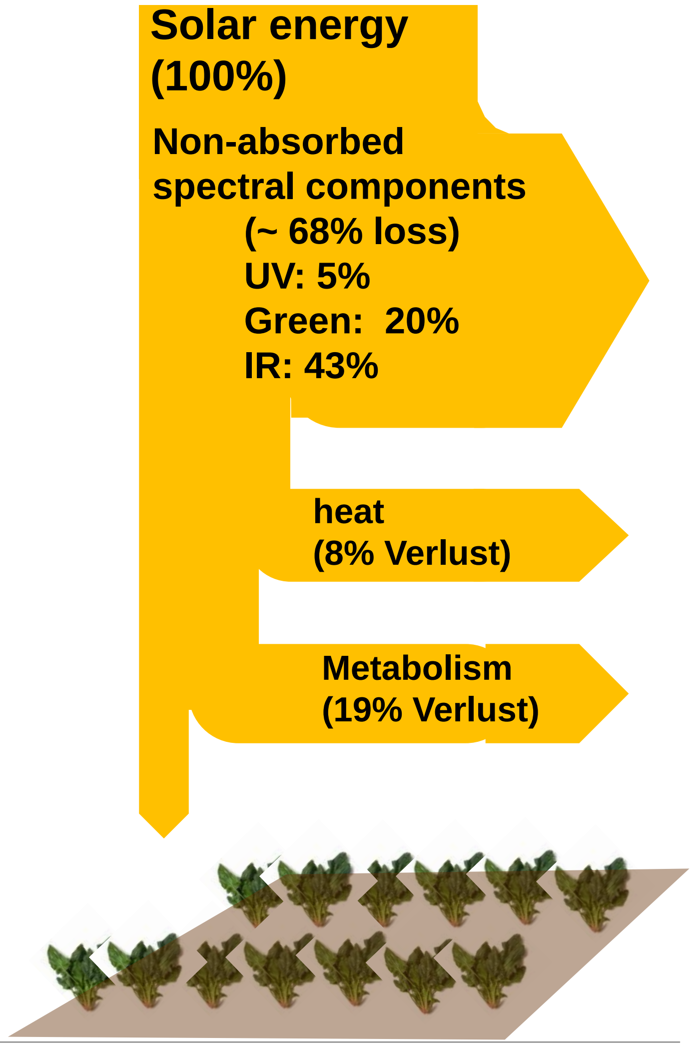
$$6\,CO_2 + 6\,H_2O \rightarrow C_6H_{12}O_6 + 6\,O_2$$

$$\Delta G^0 = 2872\ \text{kJ/mol}$$

η = 100%: 1.25 mol or 225 g biomass/m²h

η = 5%: 0.063 mol oder 11.3 g biomass/m²h

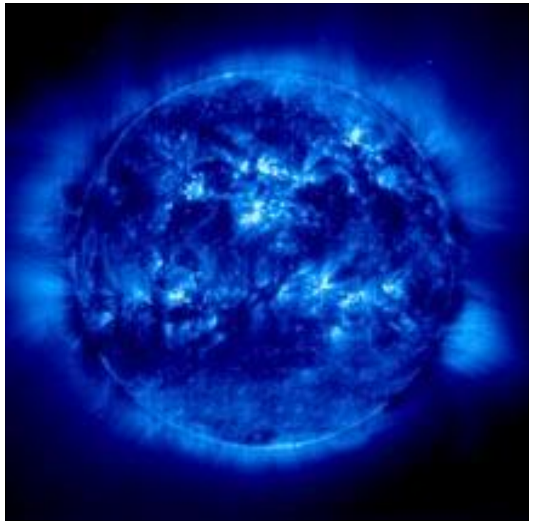
Cultivated cropland
→ ~ 650 g biomass/m²a (Wikipedia)
→ 0.074 g biomass/m²h
→ 0.020 mg biomass/m²s
→ η ~ 0.03% (Biomass energy production)



4. Solar power generation

Sun: $d_{equatorial}$ = 1.39 Mill. km

Surface $T_{Surface}$ ~ 5780 K



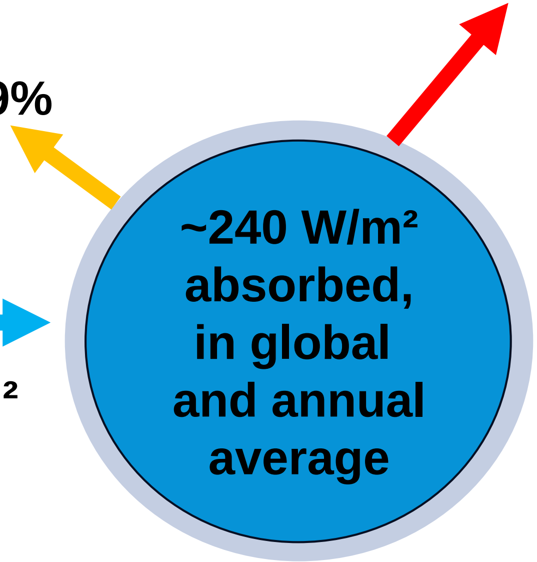
$6.4 \cdot 10^7$ W/m²

Earth: $d_{equatorial}$ = 12,756 km

σT_E^4, T_E = 255 K

Albedo ~ 29%

1368 W/m²



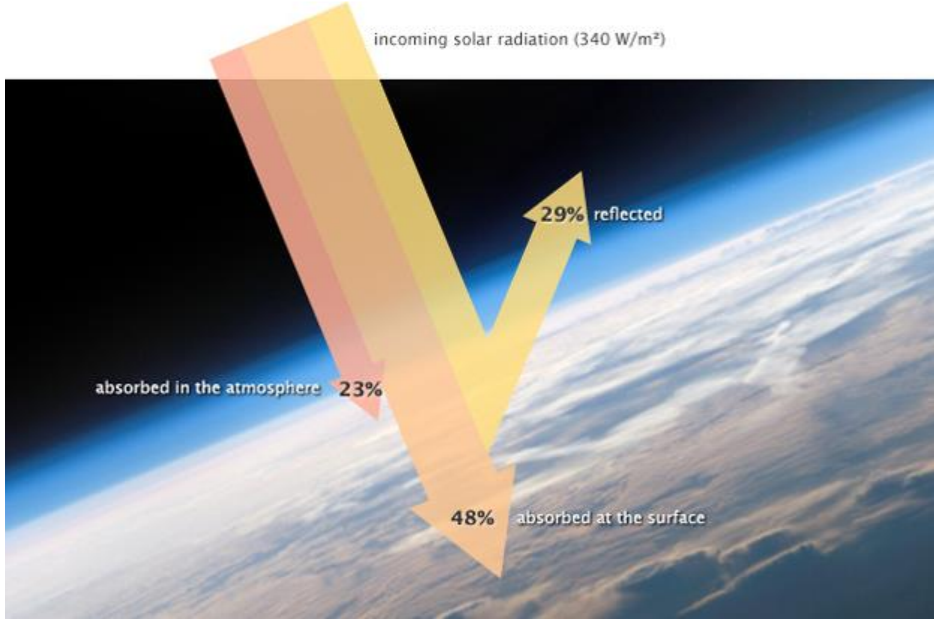
Radiant flux	$3.85 \cdot 10^{26}$ W	$1.40 \cdot 10^{17}$ W
Radiant flux density	$6.4 \cdot 10^{7}$ W/m²	240 W/m²
Energy flux per day	$3.3 \cdot 10^{31}$ J/d	$1.20 \cdot 10^{22}$ J/d
Energy flux per year	$1.24 \cdot 10^{34}$ J/a	$4.4 \cdot 10^{24}$ J/a

By comparison, global energy consumption in 2015 was $5.2 \cdot 10^{20}$ J/a ~ 15% of biomass

4. Solar power generation: Global radiation

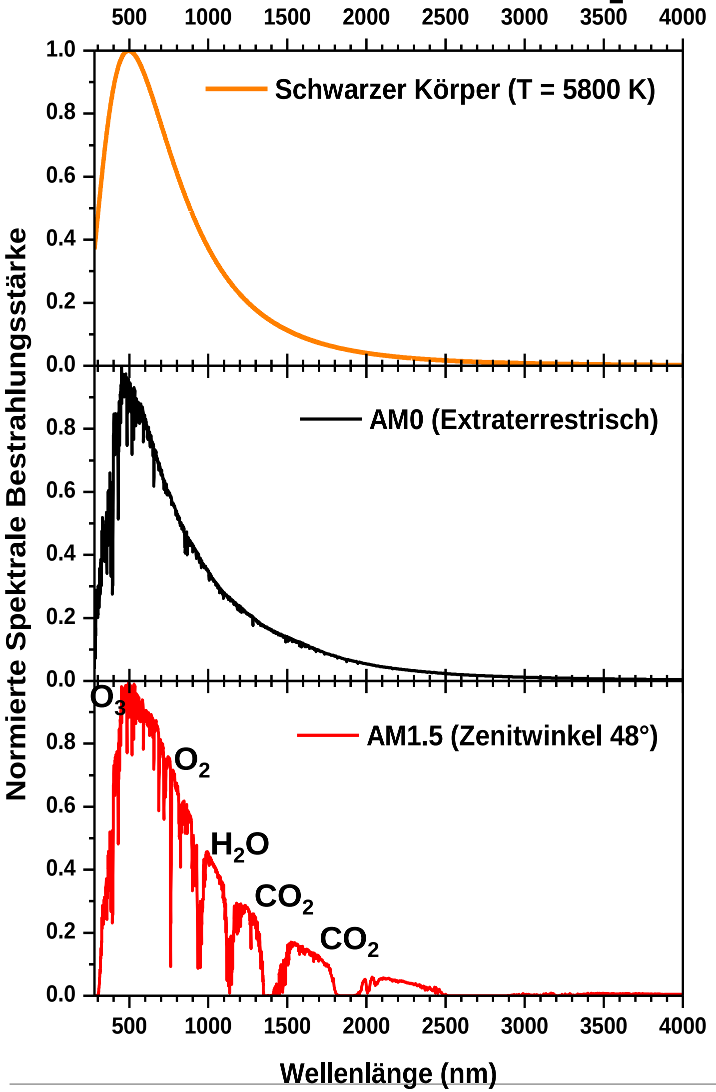
Extraterrestrial solar constant E_s ~ 1368 W/m²

(Circular area πr^2 / surface area $4\pi r^2$ = ¼)

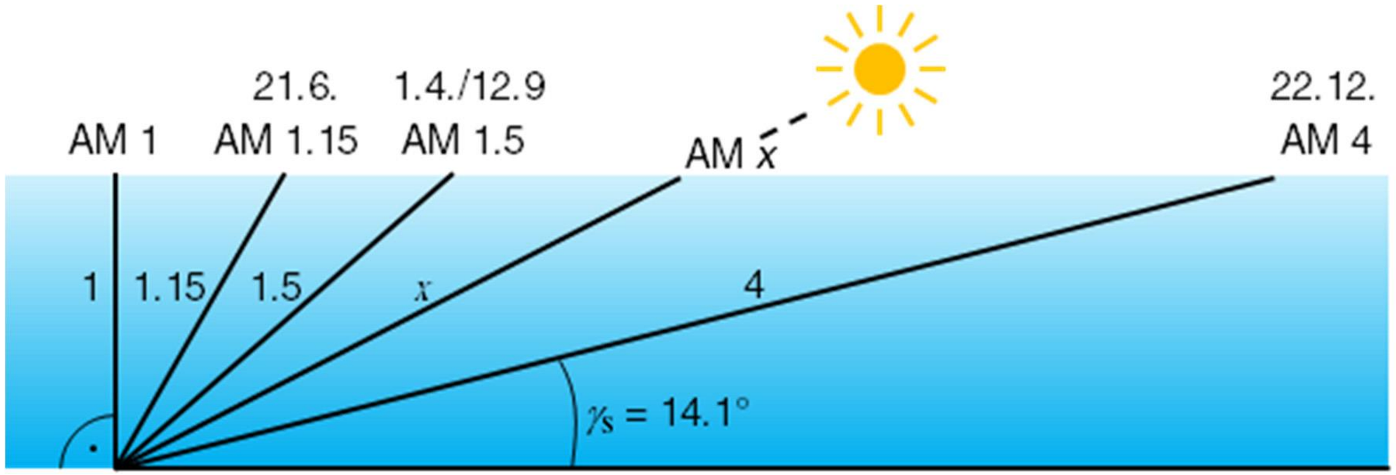


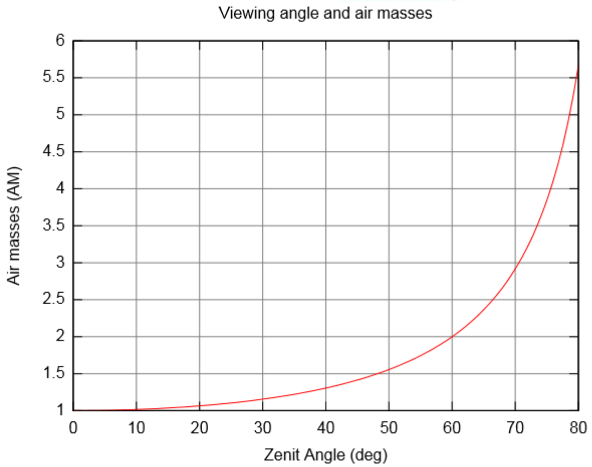
Incident solar radiation:	$E_s/4$ = 342 W/m²
Reflected by clouds Atmosphere & surface	99 W/m² (Albedo ~ 0.29)
Absorbed by Earth's surface	164 W/m²
Absorbed by atmosphere	79 W/m²
Effects of global radiation:	surface warming, melting/sublimation of ice and snow, water evaporation → wind, clouds and currents Photosynthesis → biomass production ~ $3.0 \cdot 10^{21}$ J

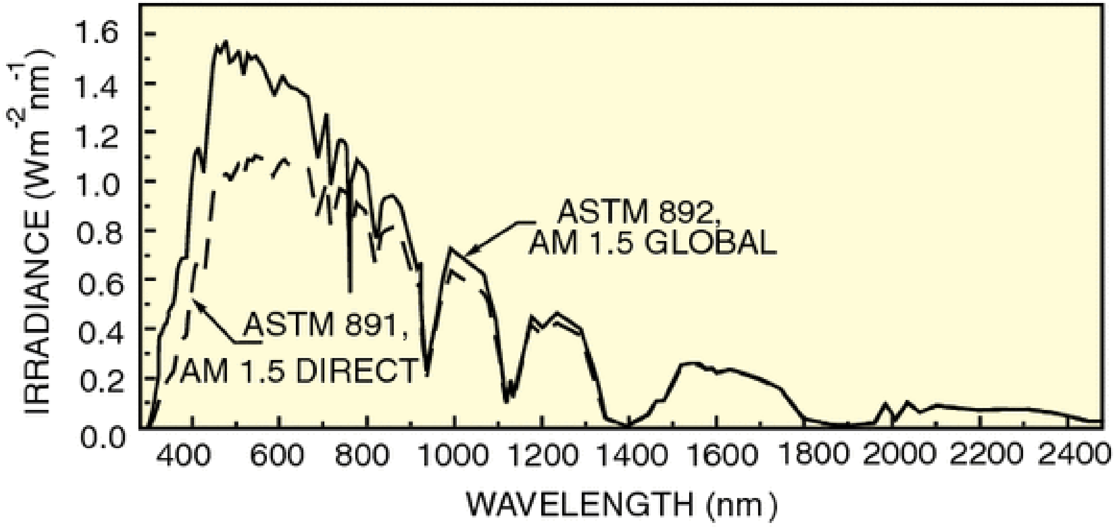
4. Solar power generation: Global radiation



Standard spectra







Source:
http://www.newport.com/store/gencontent.aspx?id=411919&lang=1033&print=1

4. Solar power generation: Global radiation

Standard spectra in numbers

Irradiation situation	Standard	Irradiance (Wm^{-2})		
		Total	250 - 2500 nm	250 - 1100 nm (~ PV)
	WMO Spectrum	1368		
AM 0	ASTM E 490	1353	1302.6	1006.9
AM 1	CIE Publication 85, Tab. 2		969.7	779.4
AM 1,5 D	ASTM E 891	768.3	756.5	584.7
AM 1,5 G	ASTM E 892	963.8	951.5	768.6
AM 1,5 G	CEI/IEC* 904-3	1000	987.2	797.5

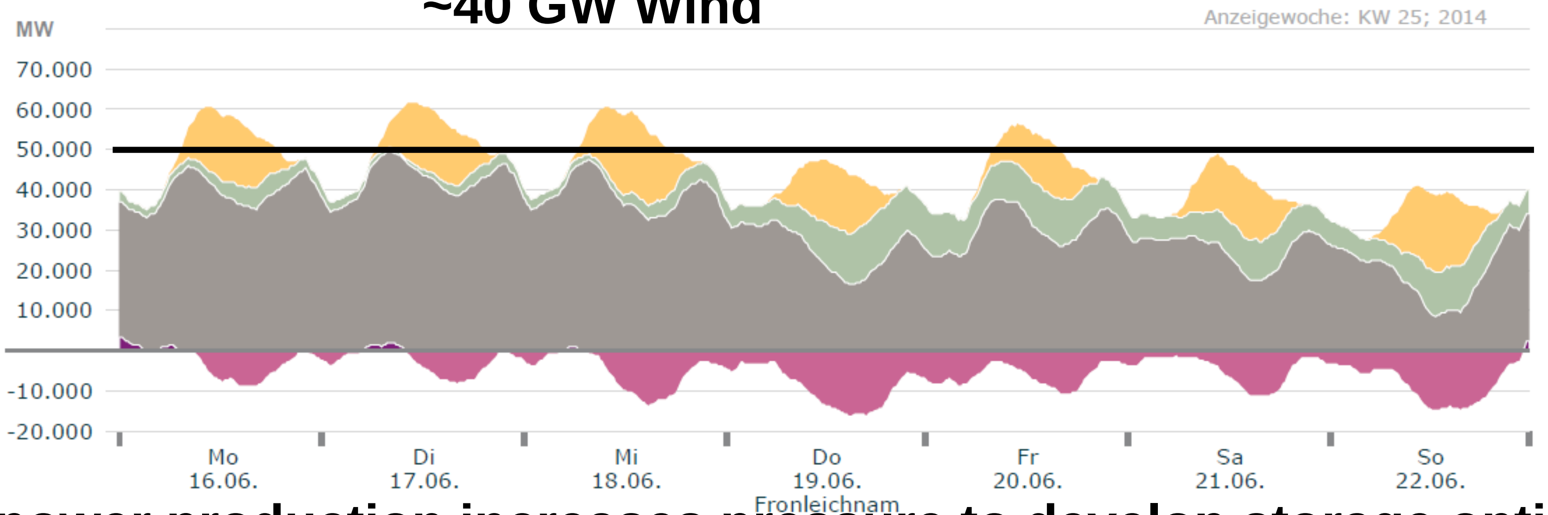
< 400	400 - 500	500 - 600	600 - 700	> 700
37.8 W/m^2	130.4 W/m^2	144.6 W/m^2	134.0 W/m^2	26.2 W/m^2
5.3%	18.2%	20.2%	18.7%	37.6%

4. Solar power generation: Global radiation

Solar and wind energy production in the FRG and worldwide is growing continuously

Situation in the BRD

Year	Installed "peak" capacity
2011	18 GW Solar
	28 GW Wind
2014	36 GW Solar
	34 GW Wind
2020	~50 GW Solar
	~40 GW Wind



Potential „Cut-off“

Excess solar power production increases pressure to develop storage options

4. Solar power generation: Options

For conversion

→ Thermal processes → High-temperature chemistry

→ Quantum processes → Photochemistry, Photovoltaics

Photochemistry

- Homogeneous
  - Photosynthesis
  - Metal complexes
  - Metal clusters
  - Metal colloids
  - Biochemical inspired approaches

  Stability problems

- Heterogeneous
  - Si µ-wires
  - Manganates: $Ca_2Mn_3O_8$
  - intermetallics: $TiSi_2$
  - Glass
  - Ceramics

  Ceramics are stable

Photovoltaics

↓

Semiconductors: Si, $CuInS_2$, Perovskites, …

Dye cells (Graetzel cells)
Organic / Polymer Solar Cells

Only Si is stable in the long term

4. Solar power generation: Established solutions

For conversion

- **Solar thermal** — **Light $\rightarrow$ hermal energy** — **Collectors**
- **Photovoltaics (PV)** — **Light $\rightarrow$ electrical energy** — **Solar cells**
- **Photosynthesis** — **Light $\rightarrow$ chemical energy** — **Plants**

Light reaction:

Homogeneous photolysis of water $2\,H_2O \rightarrow O_2\uparrow + 4\,H^+ + 4\,e^-$

$H^+ \rightarrow$ **ATP**, $e^- \rightarrow$ **NADPH**

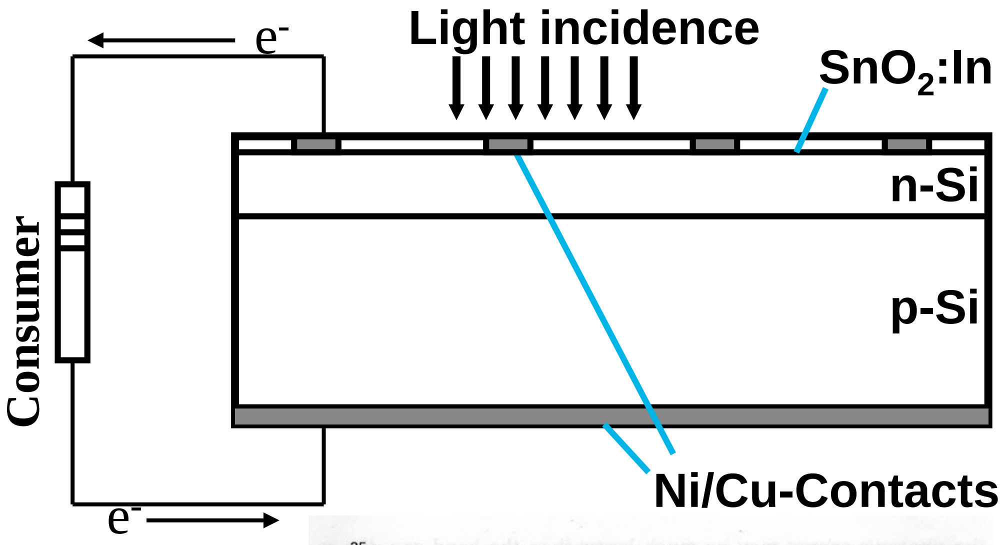
Dark reaction:

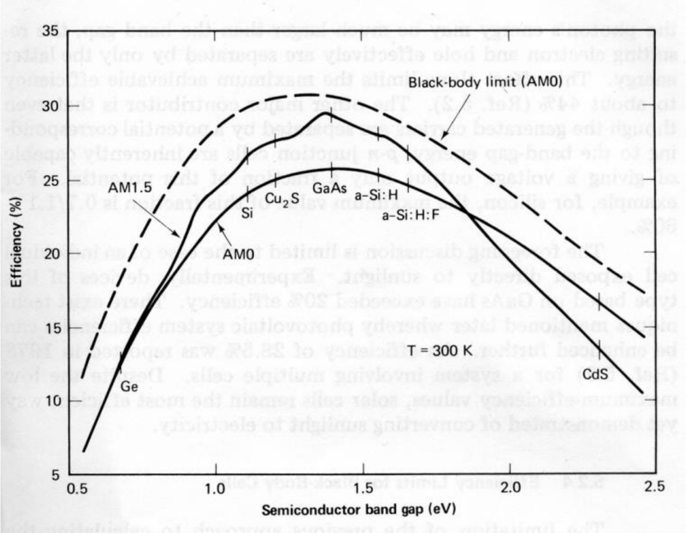
Synthesis of carbohydrates: $CO_2 + 2\,H^+ + 2\,NADPH \rightarrow (CH_2O)_x + H_2O + 2\,NADP^+$

4. Solar power generation: Photovoltaics

Design and efficiency of semiconductor solar cells

Semiconductor material	Band gap [eV]
• CdS	2.2
• a-Si:H,F	1.7
• a-Si:H	1.6
• $CuInS_2$	1.5
• GaAs	1.4
• Cu_2S	1.2
• c-Si	1.1
• Ge	0.6





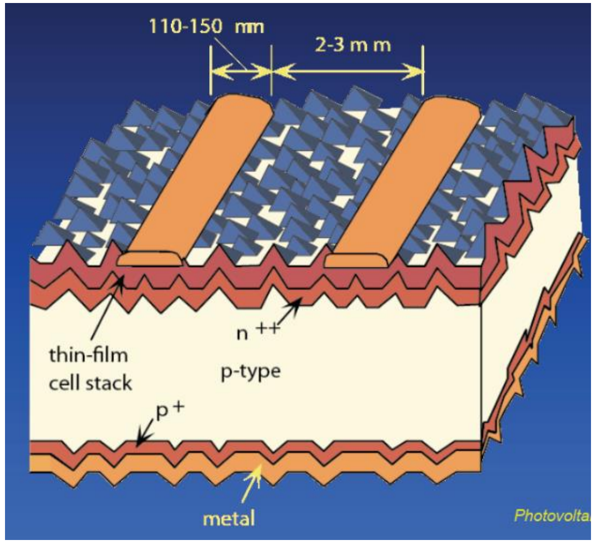
Optimal materials have a band gap of 1.0 to 1.5 eV (800 - 1250 nm): GaAs, a- or c-Si

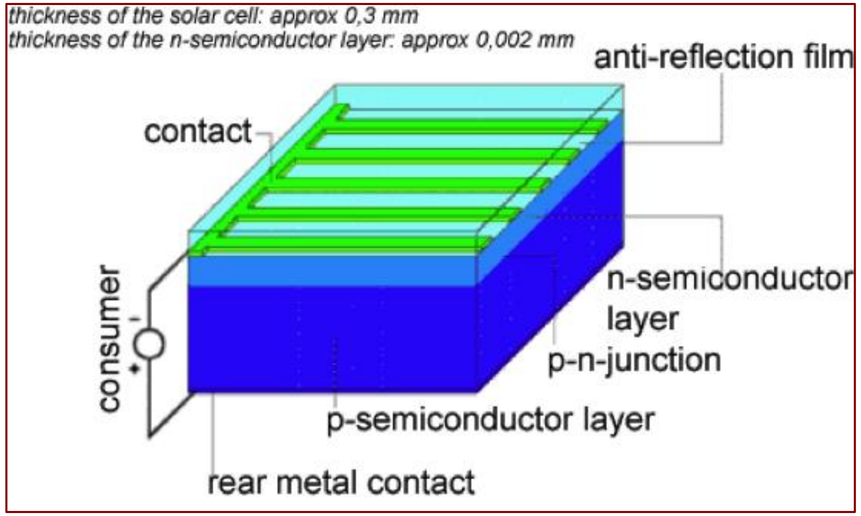
Shockley-Queisser efficiency limit for solar cells ~ 30%.

4. Solar power generation: Photovoltaics

Solar Cells from 1954 to Today....

First practicable photovoltaic cell:
Chapin, Fuller and Pearson demonstrate a Si cell with an efficiency of about 6% at Bell Laboratories in 1954

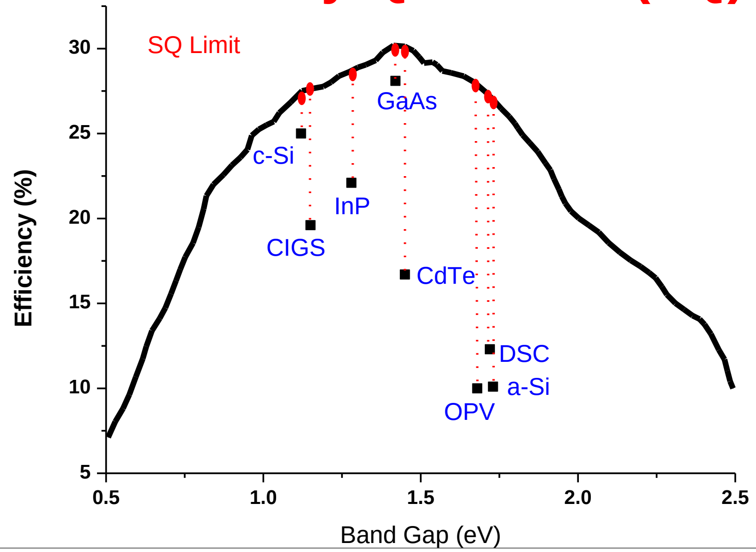




4. Solar power generation: Photovoltaics

Solar cell generations by material		Efficiency η
Si-cells, amorphous, polycrystalline, monocrystalline	1st generation solar cells	8%, 15 - 22%
Thin film) CdTe, GaAs, $Cu(In,Ga)(S,Se)_2$	2nd generation solar cells	12 -25%
Dye cells, organic and perovskite cells	3rd generation solar cells	2 - 3%

Main problem: Shockley-Queisser* (SQ) limit → PV efficiency < 30% !



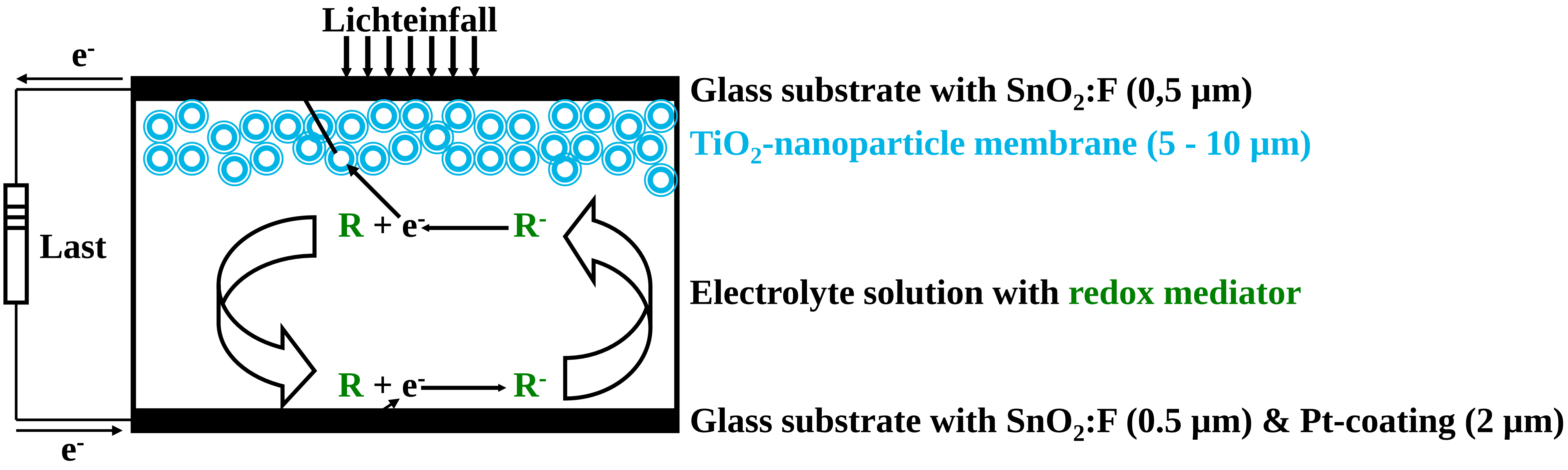
Optimal band gap : 1.34 eV ~ GaAs η ~ 25%

Lit.:

- M.B. Prince, JAP 26 (1955) 534
- J. Loferski, JAP 27 (1956) 777
- *W. Shockley, H.J. Queisser, JAP 32 (1961) 510

4. Solar power generation: Photovoltaics

Solar cells (Grätzel cells)



TiO_2 is the ideal catalyst for charge separation, but absorbs only UV radiation

→ Sensitization required

5. Water splitting

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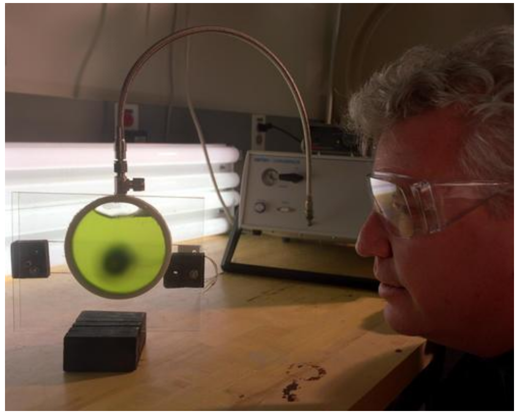
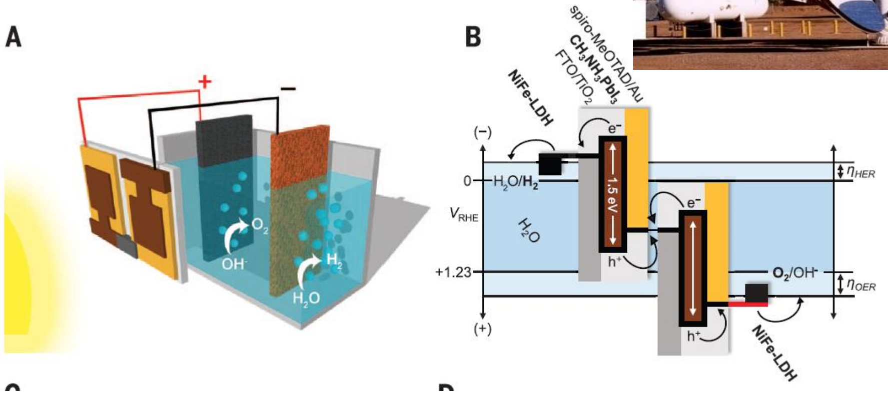
Ways to split water according to 2 $H_2O(g) \rightarrow O_2(g) + 2\ H_2(g)$

- Photosynthesis
  - Plants (fast growing)
  - (micro)algae
- Electrolysis
- Thermolysis
- Plasmalysis
- Sonolysis
- Photolysis
- Photocatalysis





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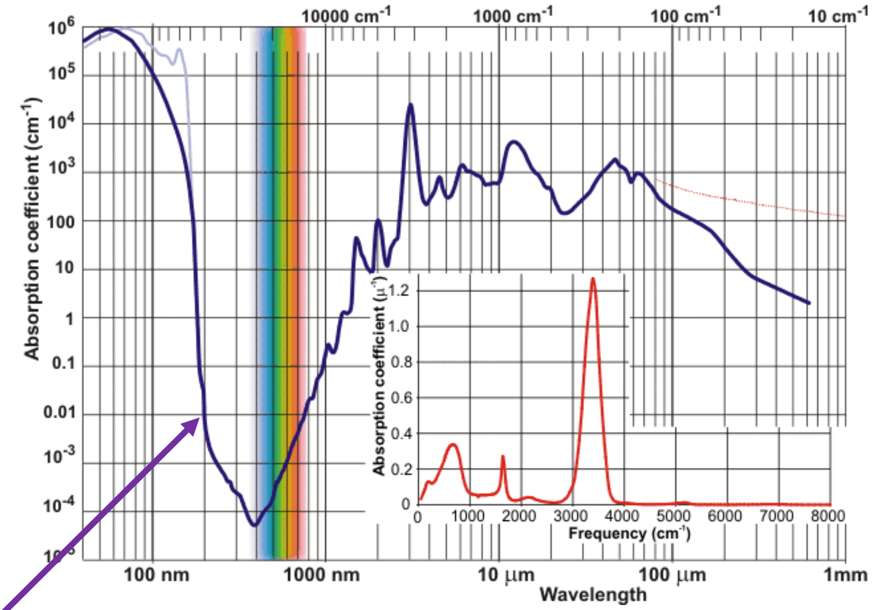
Energy balance

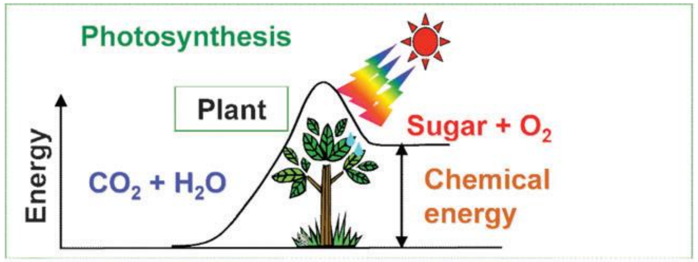
$2\ H_2O(g)$ → (+ 2x 237 kJ/mol) / ← (- 2x 237 kJ/mol) $O_2(g) + 2\ H_2(g)$

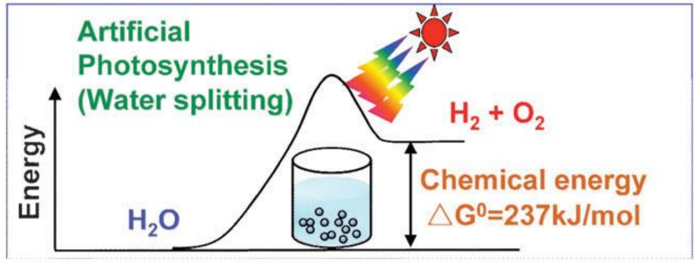
$2\ H_2O(l)$ ↑ (+ 2x 138 kJ/mol) / ↓ (- 2x 138 kJ/mol) $2\ H_2O(g)$

$2\ O(g) + 4\ H(g)$ ↑ (-498 kJ/mol + -2x 436 kJ/mol) $O_2(g) + 2\ H_2(g)$

$2\ H_2O(l)$ → (+2120 kJ/mol = 530 kJ/mol per O-H bond) $2\ O(g) + 4\ H(g)$







Photolysis of water without photocatalyst:

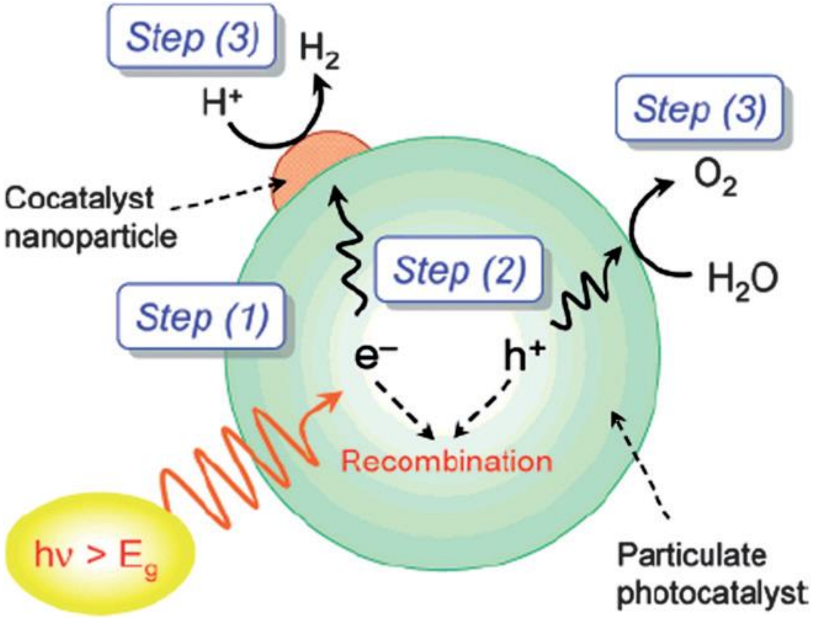
Requires VUV or EUV radiation (< 200 nm)

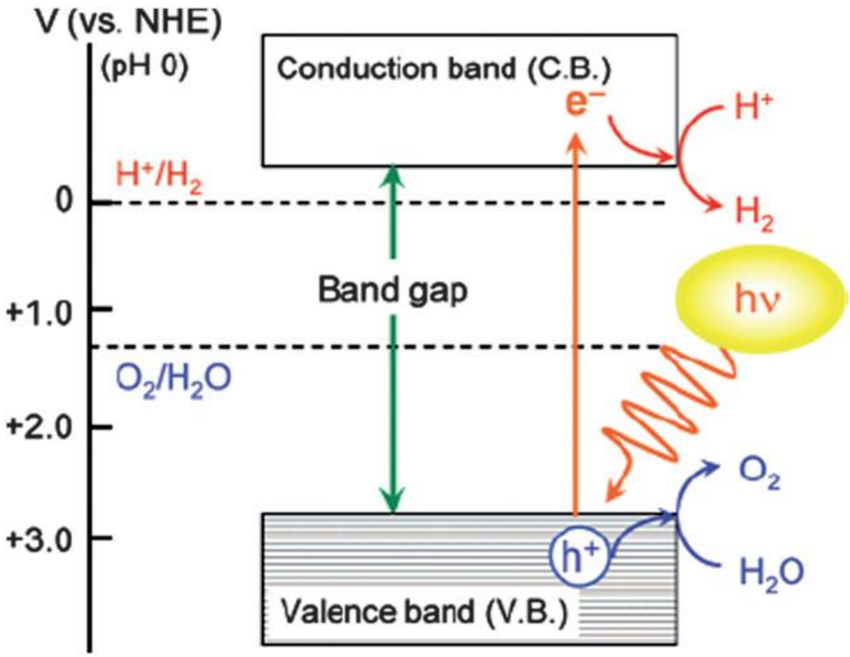
→ Strato-/mesosphere or VUV radiation sources

5. Water splitting

By photocatalysis with semiconductors

- First system by A. Fujishima und K. Honda (Nature 238 (1972) 38)
  → TiO_2 with Pt as co-catalyst
- Water splitting possible from about 1000 nm (1.23 eV), but in real systems the voltage is higher > ~1.8 V (overvoltage)

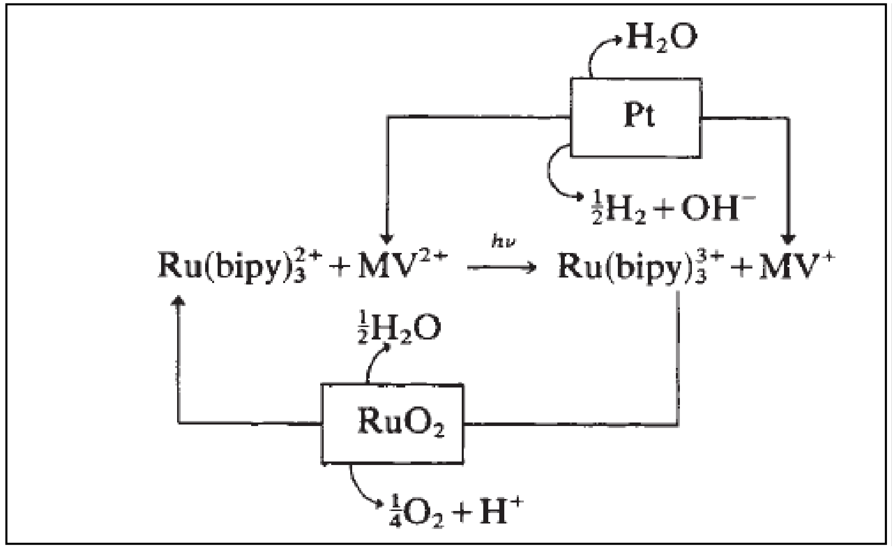


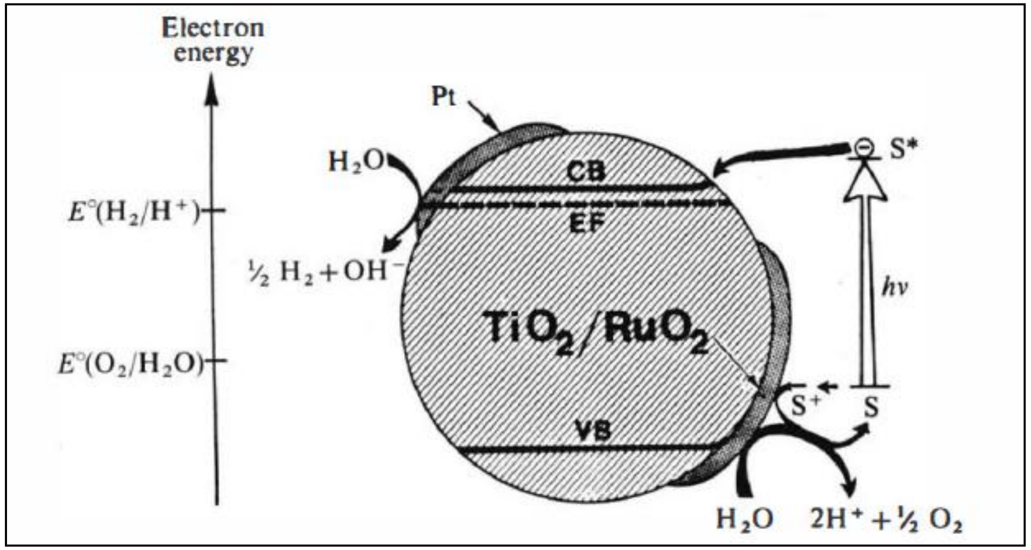


5. Water splitting

By photocatalysis with semiconductor and a sensitizer

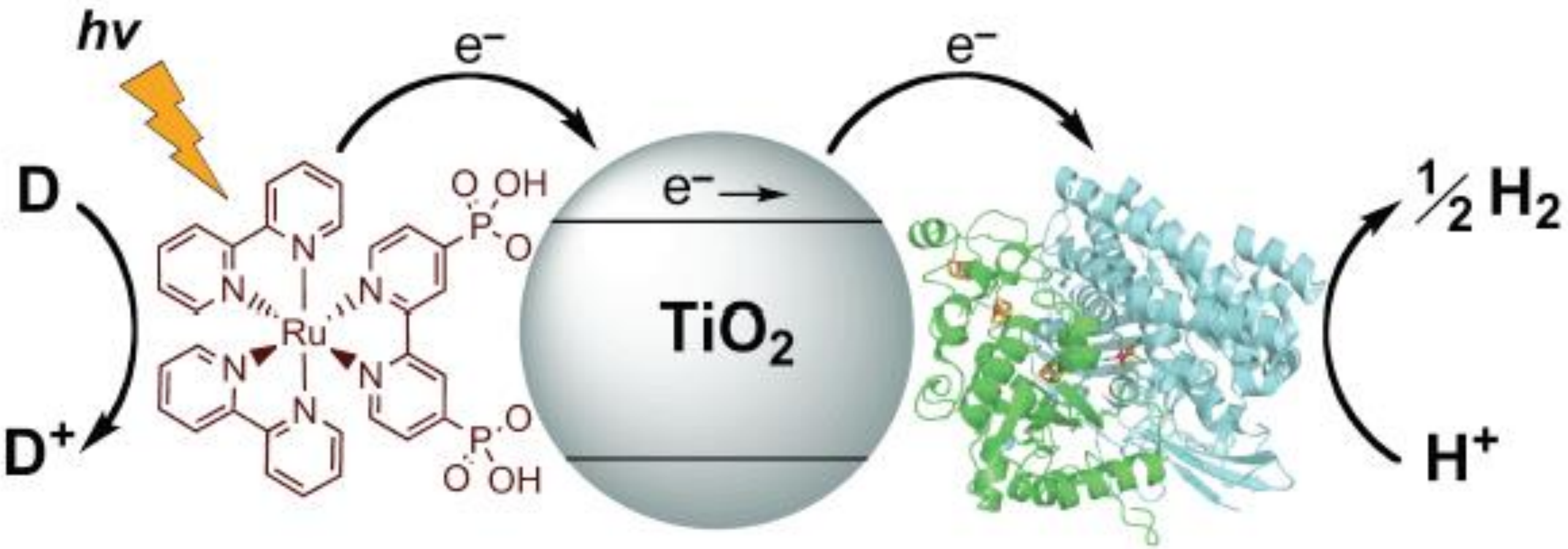
- **First system with a sensitizer by Michael Graetzel (Nature 289 (1981) 158)**
  → TiO_2 with Pt and RuO_2 as co-catalysts and $[Ru(bpy)_3]^{2+}$ and methyl viologen as sensitizers (antennas)
- **Synthesis of Pt nanoparticles starting from H_2PtCl_6 and citrate**





5. Water splitting

By photocatalysis with complexes and enzymes



Schematic of light-induced H_2 production with D [NiFeSe]-H bound to TiO_2 nanoparticles sensitized with a Ru^{2+} complex in the presence of an electron donor D as a "sacrificial cathode".

Absorption of light (λ > 420 nm) excites the photosensitizer. $[Ru(bipy)_3]^{2+}$ which injects electrons intoTiO_2

Lit.: F.A. Armstrong, E. Reisner et al., Chemical Society Reviews 108 (2008) 2439

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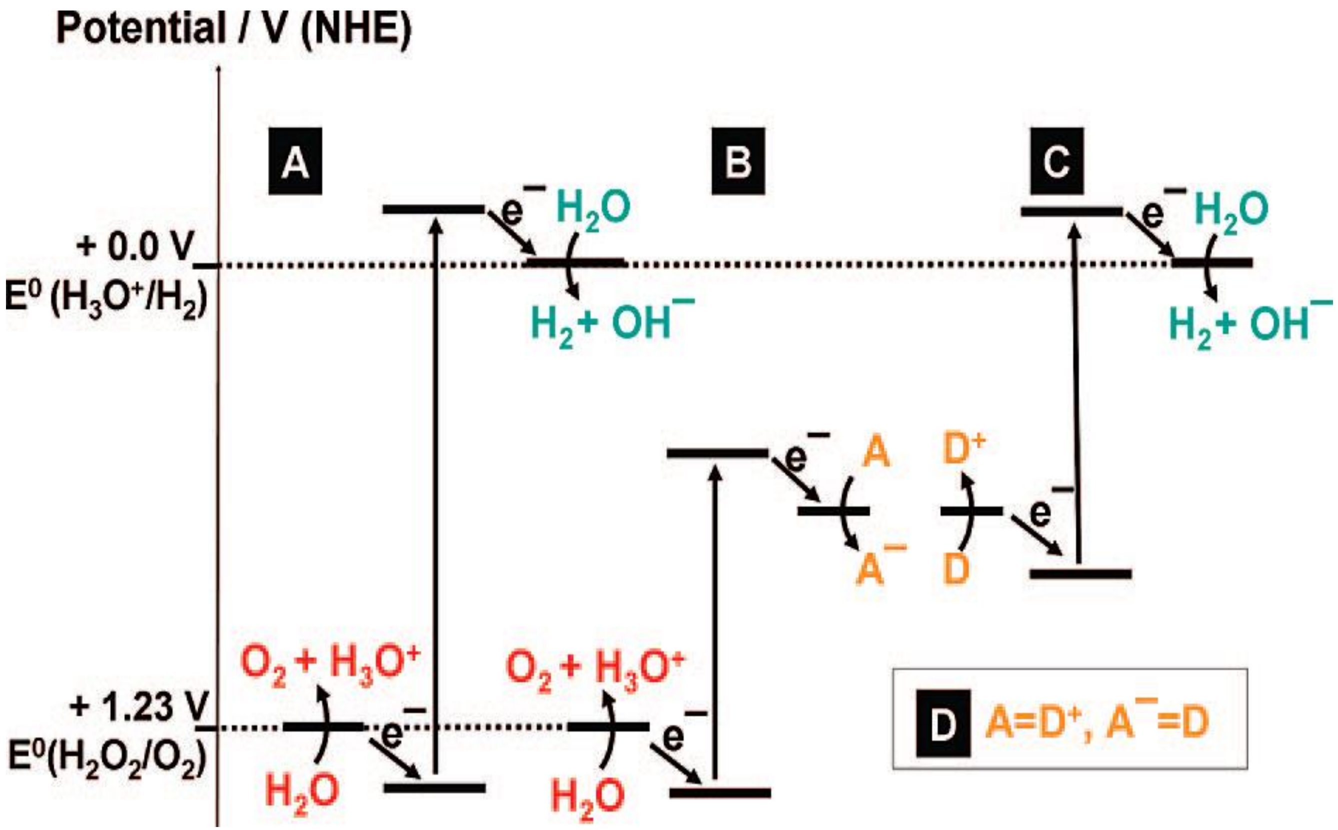
Photocatalytic processes with semiconductors - options

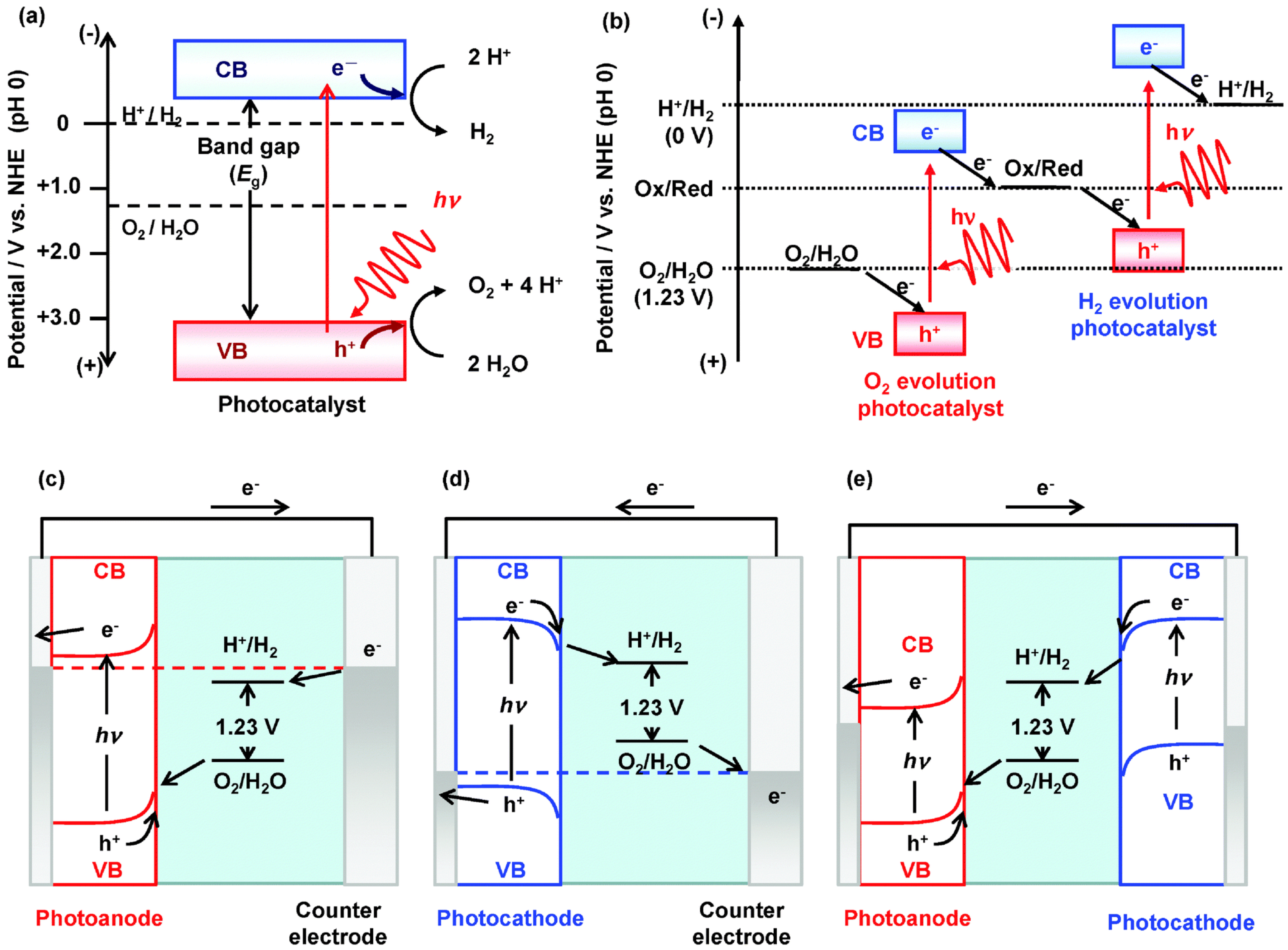
- A: Simple semiconductor
- B: Simple semiconductor
  with an electron acceptor → O_2
- C: Simple semiconductor
  with one electrondonor → H_2
- D: Combination of B and C (tandem cell)



Problem: Powder in solution → Oxyhydrogen formation (explosive gas)

5. Water splitting

Photocatalytic processes with semiconductors - options



5. Water splitting: Materials

Requirements for a good photocatalyst

- **Stability (lifetime)**
  The most photochemically stable semiconductors in aqueous solution are oxides, but their band gaps are either too large for efficient light absorption (~3 eV), or their semiconductor characteristics are poor.

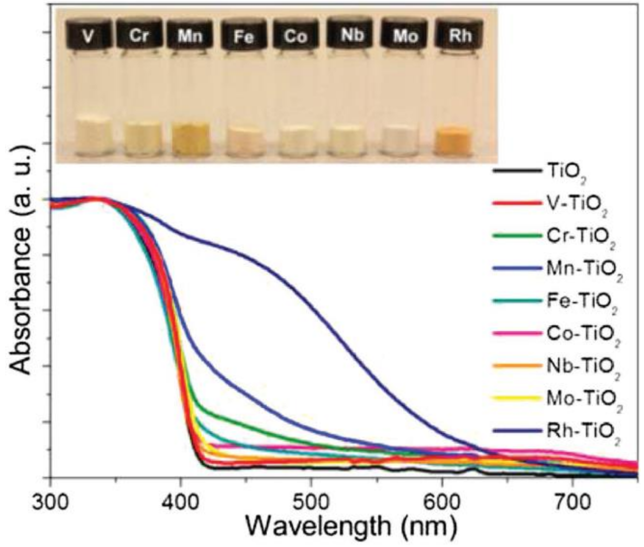
- **Efficiency (band gap)**
  For reasonable solar efficiencies, the band gap must be less than 2.2 eV, unfortunately, most useful semiconductors with band gaps in this range are photochemically unstable in water.

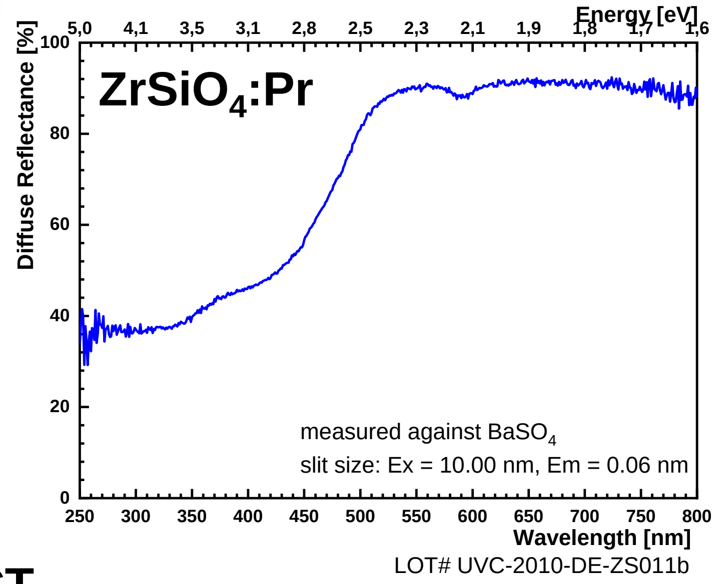
- **Energetics (redox potentials)**
  In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energy levels where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous water splitting, the oxygen and hydrogen reactions must lie between the valence and conduction band edges, and this is almost never the case.

5. Water splitting: Materials

Photocatalysts with high stability?

Material	Band gap [eV]	Color
$ZrSiO_4$	6.5	white
ZrO_2	5.0	white
$CaWO_4$	4.1	white
ZnS	3.8	white
$KTaO_3$	3.4	white
ZnO	3.3	white
$SrTiO_3$	3.2	white
TiO_2	3.0	white
CeO_2	2.8	yellow
WO_3	2.7	yellow
$BiVO_4$	2.4-2.5	yellow
CdS	2.3	orange
Fe_2O_3	2.0	red
InN	1.9	red



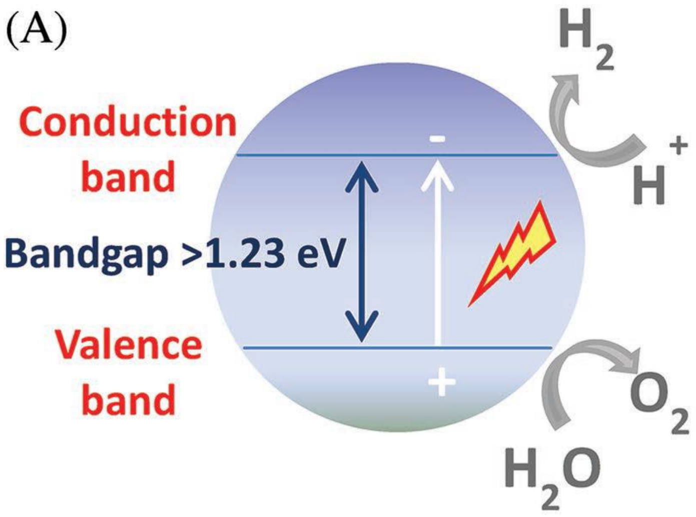


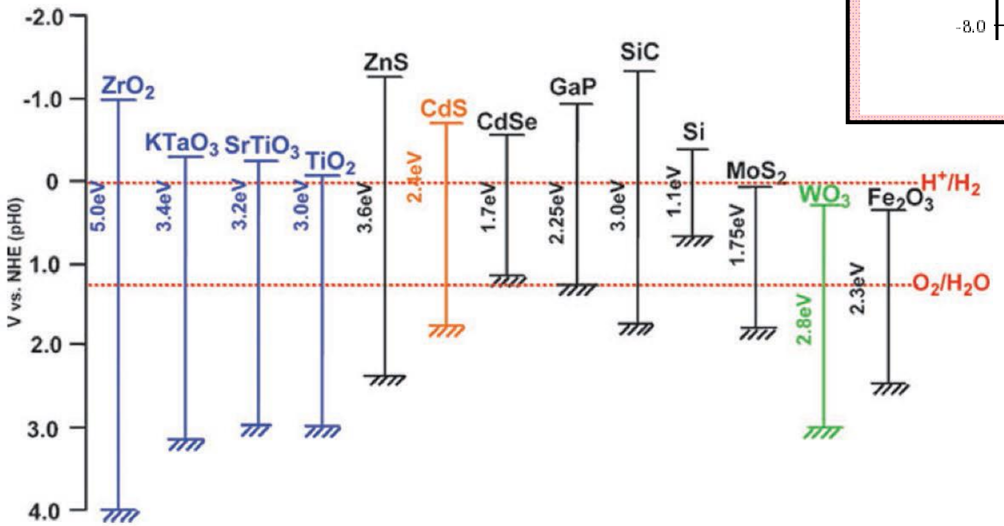
Doping with Ce^{3+}, Pr^{3+}, Tb^{3+} MMCT

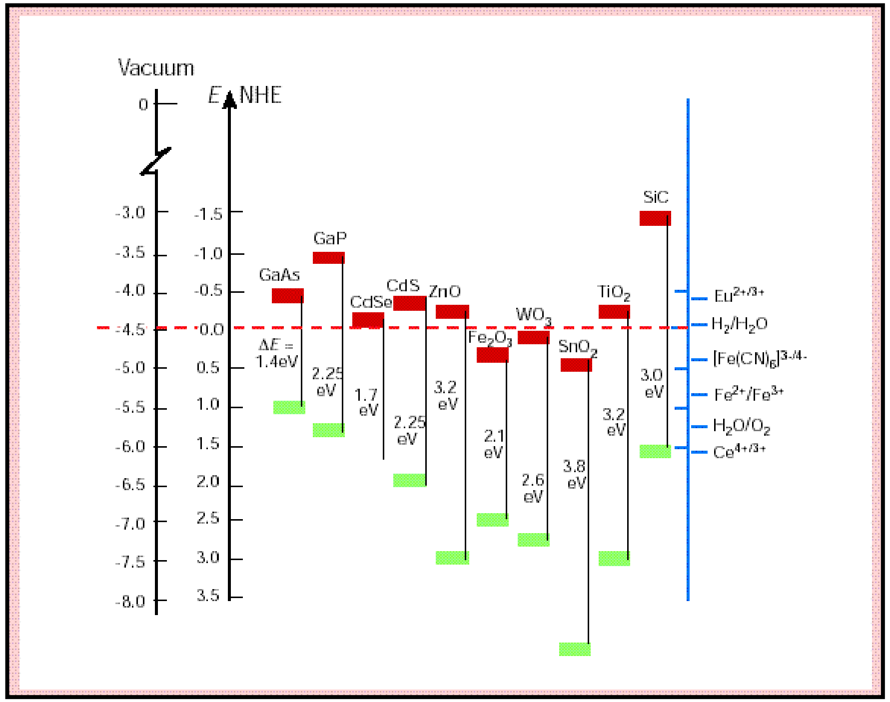
5. Water splitting: Materials

Photocatalysts: Efficiency and energetics

Band gap	**2.0 – 3.0 eV**
VB	**~ -6.0 V below the vacuum level**
LB	**~ -4.0 V below the vacuum level**







5. Water splitting: Vision

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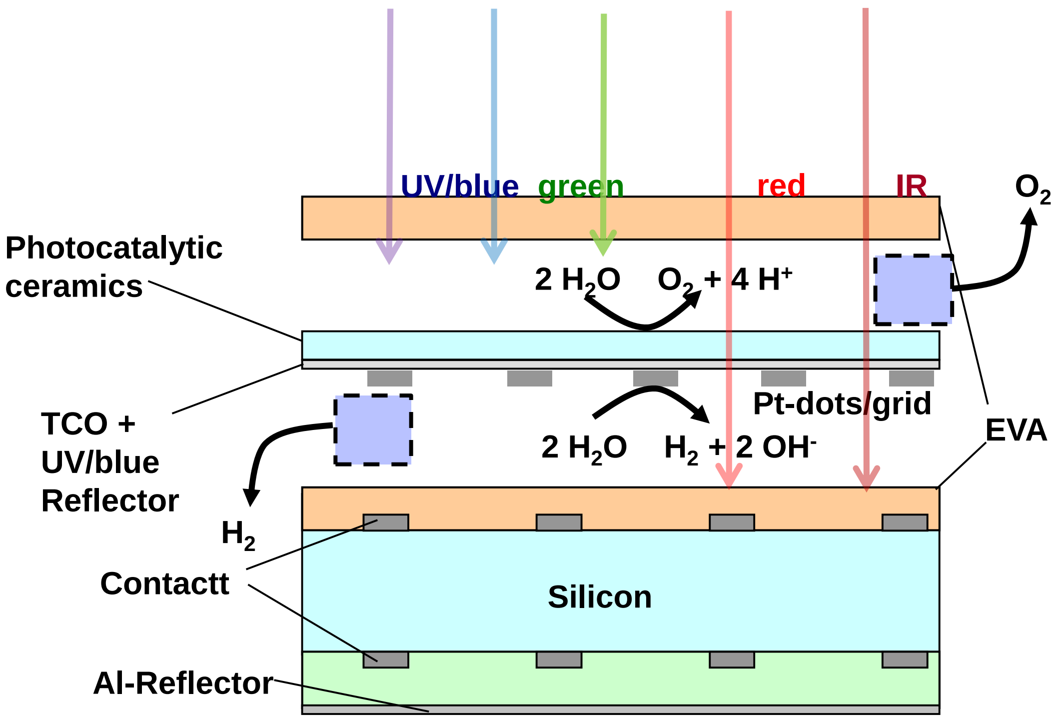
Development of a tandem cell combining PV and other options!



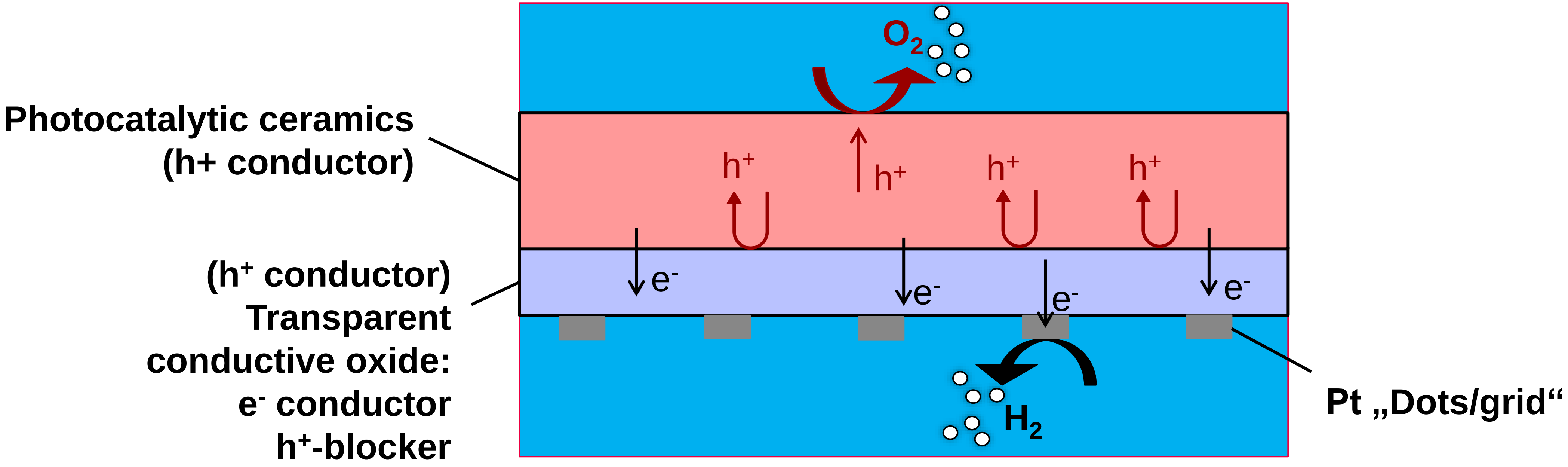
Options

a) Cooling water	cooling of the PV cell
b) TiO_2 + water	H_2O purification H_2O disinfection
c) Photocatalyst a	$2\ H_2O \rightarrow 2\ H_2 + O_2$
d) + photocatalyst b	$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$
e) Down-Konverter	PV efficiency↑
f) UV/Blau filter	PV lifetime↑

Lit.: T. Jüstel et al., German Patent Application, Energy Conversion System, DE102014107268

5. Water splitting: Vision

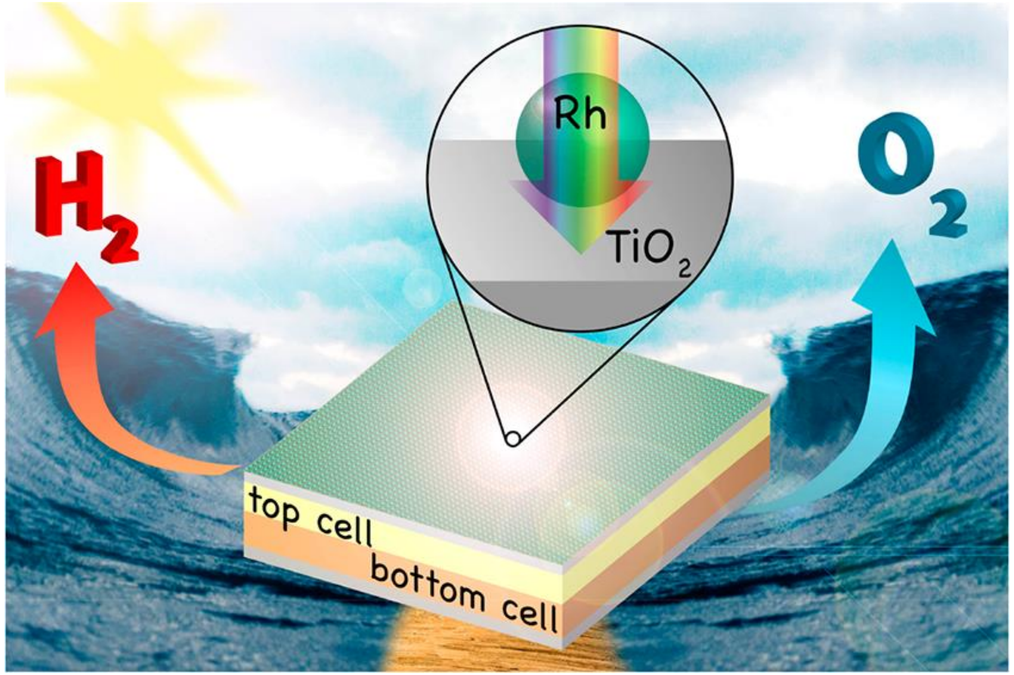
Development of a photocatalytic cell with electron and hole conductors for H_2/O_2 separation.

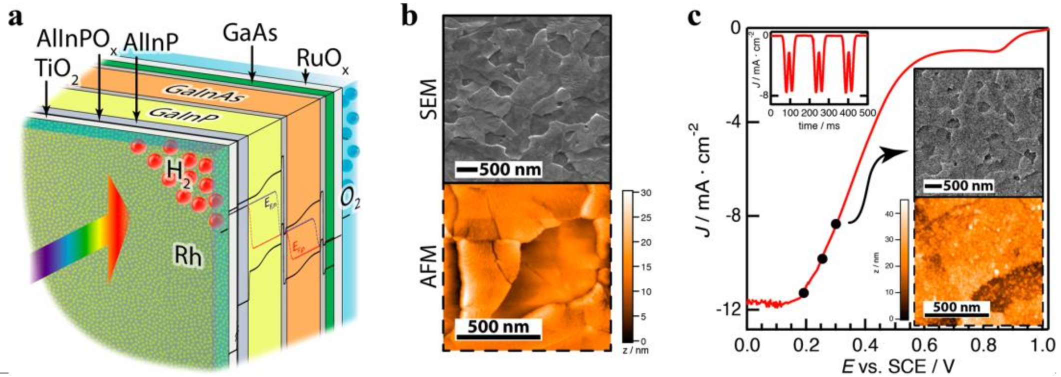


5. Water splitting: State of the art

Recent success

- **Charge separation and e^- / h^+ conduction by epitaxially deposited AlInP, AlInPO layers**
- **Rh on TiO_2 as photocathode**
- **RuO_x on GaAs as photoanode**
- **Problem: Formation of a pH gradient**

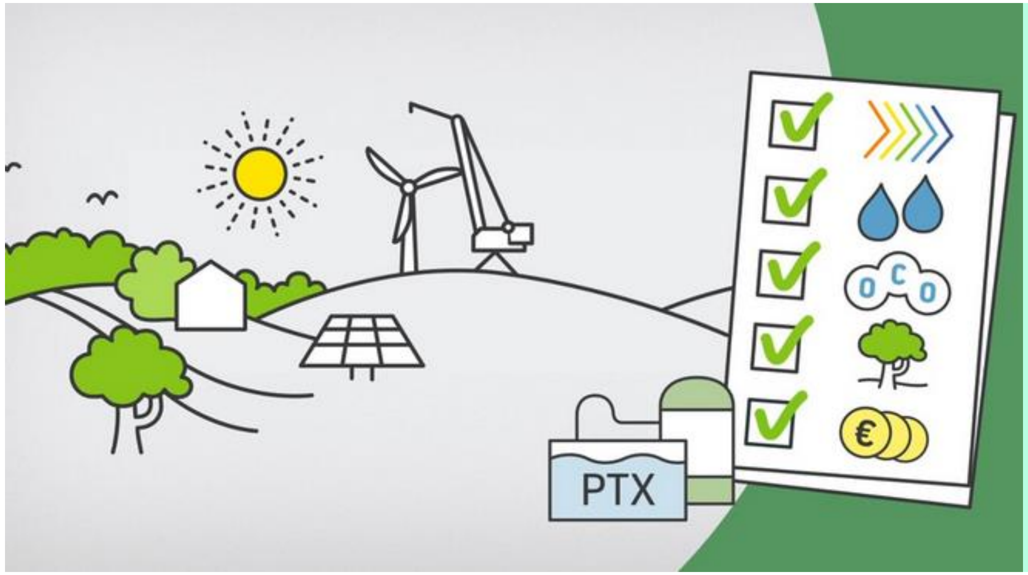




Lit.: ACS Energy Lett. 3 (2018) 1795-1800

5. Water splitting: Significance?

- **Hydrogen has the highest mass-specific energy density (calorific value) of all fuels at 33.3 kWh/kg, 700 billion m³ of hydrogen are now produced worldwide annually via steam reforming from methane**
- **Engineering science is working on Power-to-X (PTX) with hydrogen as reactant**
- **Important!: Electricity from new green power plants, no water shortage at the site, CO_2 from biomass Renewable raw materials (NAWARO), ecological land use and local value creation**

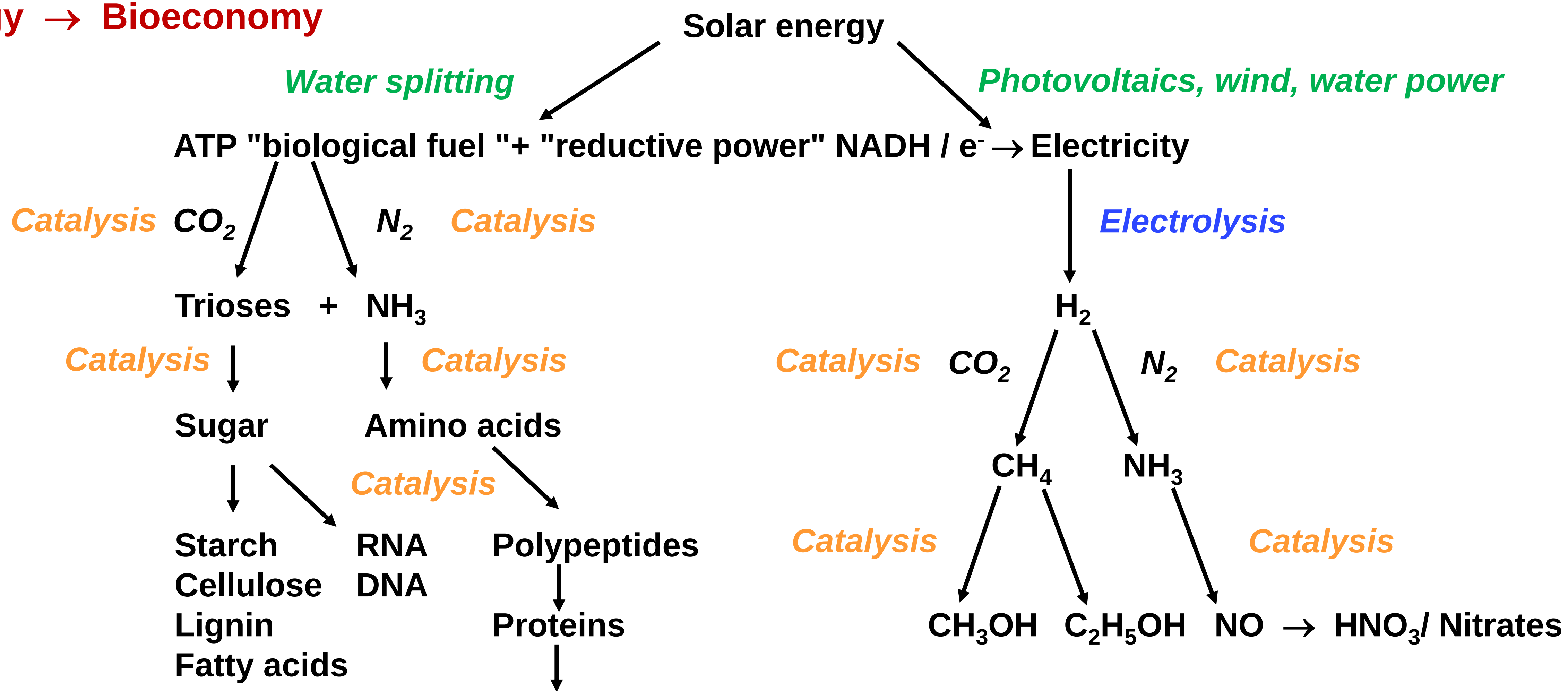


- ✓ **1 m³ hydrogen at normal pressure requires electrical energy of 4.3 - 4.9 kWh.**
- ✓ **Compared to the hydrogen heating value, about one third of the electrical energy is lost in this process.**
- ✓ **Favorites for hydrogen storage are LOHCs (Liquid Organic Hydrogen Carriers), primarily dibenzyl toluene (DBT).**

Source: Prof. Jochen Fricke, Cluster Energietechnik, October 2018

6. Outlook

Biology → Bioeconomy



Modified after Öko-Institute 2019

6. Outlook

Energy (light, foss. fuels) + resources (H_2O, CO_2, N_2, methan, minerals, …)

Biology	Technology	
Biomolecules (sugar, glycine)	Chemicals (Styrol, $Ga(CH_3)_3$)	Utilities Raw materials industry
Biopolymers/materials (proteins)	Materials (polystyrene, GaN)	Chemical Industry: CVT
Organelles (chloroplast)	Components (chip)	Components industry
Cells (palisade cells)	Components (LED)	Lighting Industry
Cell composites/tissues (leaf)	Devices (photoreactor)	Mechanical engineering
Organisms (tree)	Plants (factory)	Plant engineering
Super organisms (forest)	Networks (production chains)	logistics, IT

Biomimetics →

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6. Outlook: New fuels

- **Globally, shipping is responsible for emitting about 1 billion tons of CO_2 per year, which is almost 3% of total man-made CO_2 emissions**
- **Shipping also causes about 15% of global nitrogen oxide emissions and 13% of sulfur dioxide emissions, and the trend continues to rise**
- **Greta Thunberg 2019 sailed a sailing yacht across the Atlantic to the climate summit**
- **Engineering scientists working with ammonia (NH_3) as fuel, global NH_3 production 2021 ~ 150 million t**

© DRONE PLANET / GETTY IMAGES / ISTOCK (AUSSCHNITT)

Time horizon
2022 Sport yachts → 2026 Car ferries
→ 2030 1st AIDA cruise ship

- ✓ **NH_3: Chemically bound hydrogen, burns without CO_2 emission to N_2 and H_2O**
- ✓ **Much lower pressure at RT (9 bar, 20 °C) than H_2 (700-1000 bar, 20 °C)**
- ✓ **Heating value of ammonia is 5.2 kWh/kg (~ 50% of gasoline, diesel,....)**
- ✓ **Heating value of NH_3 is 2.6 times higher than that of Liquid Organic Hydro Carbons (e.g. DBT)**

Source: Prof. Dr. Jochen Fricke, Cluster Energietechnik (Status: October 2018)

https://de.euronews.com/2022/11/07/welche-rolle-spielt-ammoniak-in-einem-saubereren-energiemix

6. Outlook: Ammonia synthesis

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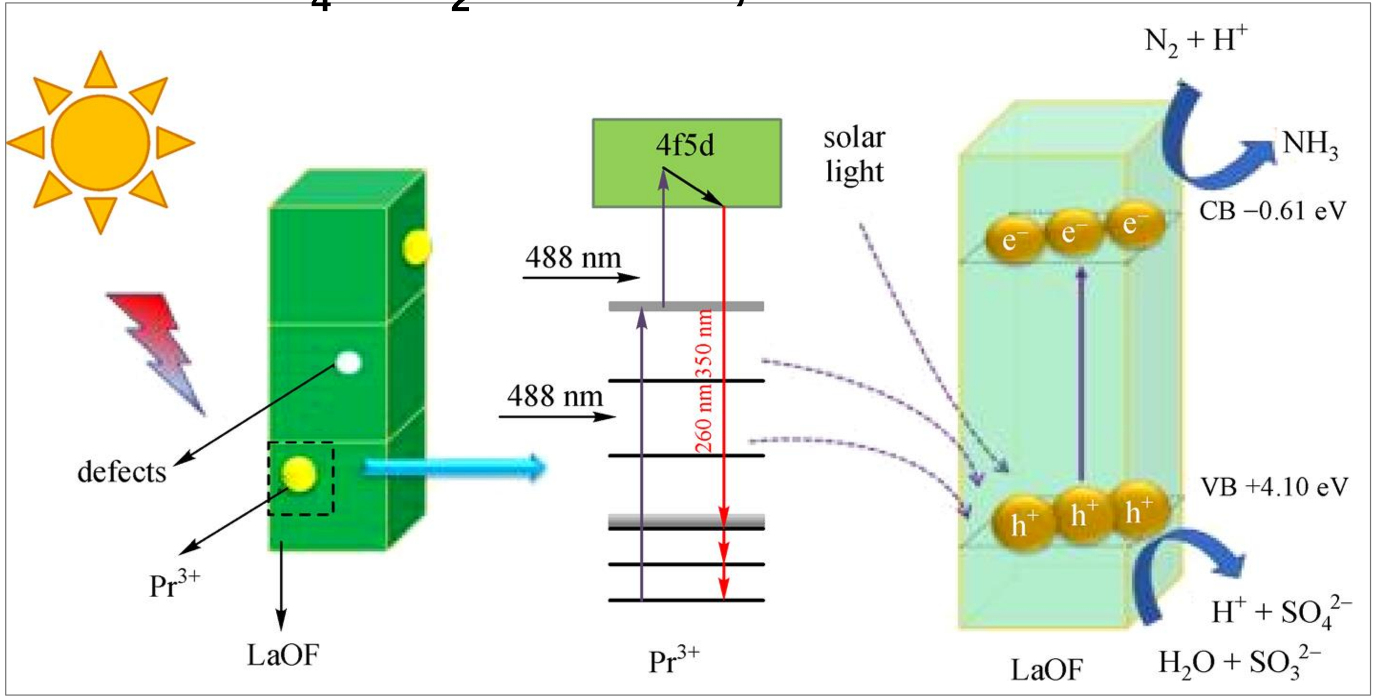
Pathways to ammonia NH_3

- Haber-Bosch (α-Fe) — $N_2 + 3\,H_2 \leftrightarrows 2\,NH_3$ — 450 - 550 °C, 250 - 350 bar
- V-nitrogenases (Fe^{n+}) — $2\,N_2 + 14\,H^+ + 12\,e^- \leftrightarrows 2\,NH_4^+ + 3\,H_2$ — RT, 1 bar
- Mo-nitrogenases (Fe^{n+}) — $2\,N_2 + 10\,H^+ + 8\,e^- \leftrightarrows 2\,NH_4^+ + H_2$ — RT, 1 bar

- Heterogeneous photocatalysis
  up-conversion induced photoionization
  using doped semiconductor materials
  such as LaOF

$$e^- + N_2 \longrightarrow (N_2)^-$$
$$(N_2)^- + H_2O \longrightarrow OH^- + N_2H$$
$$2\,N_2H \longrightarrow N_2H_2 + N_2$$
$$2\,N_2H_2 \longrightarrow N_2H_4 + N_2$$
$$3\,N_2H_4 \longrightarrow 4\,NH_3 + N_2$$

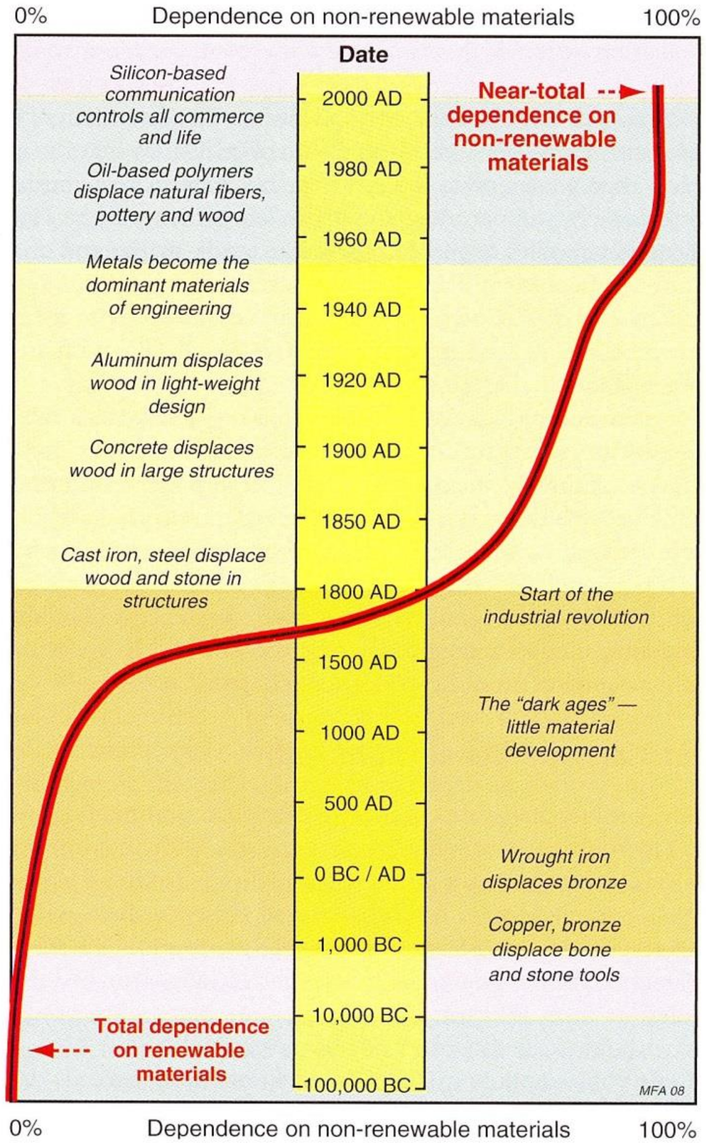


Lit.: LaOF:Pr Microwave hydrothermal synthesis for photocatalytic N fixation, Frontier Mater. Science 14 (2020) 43

6. Outlook

Recycling: Global dependence on raw materials (non-renewable)

- Until about the year 1000 BCE
  → only regenerative materials
  used Recycling rate almost 100%
- 1000 BCE - 1000 CE
  → weak increase in the use of
  non-regenerative materials
- after 1000 (especially after 1500)
  → strong increase in the use of
  non-regenerative materials
- since about 1960
  → de facto 100% dependence on non-
  regenerable materials recycling rate < 10%



Source: M.F. Ashby, Materials and the Environment, Elsevier (Butterworth-Heinemann), 2009, p. 8

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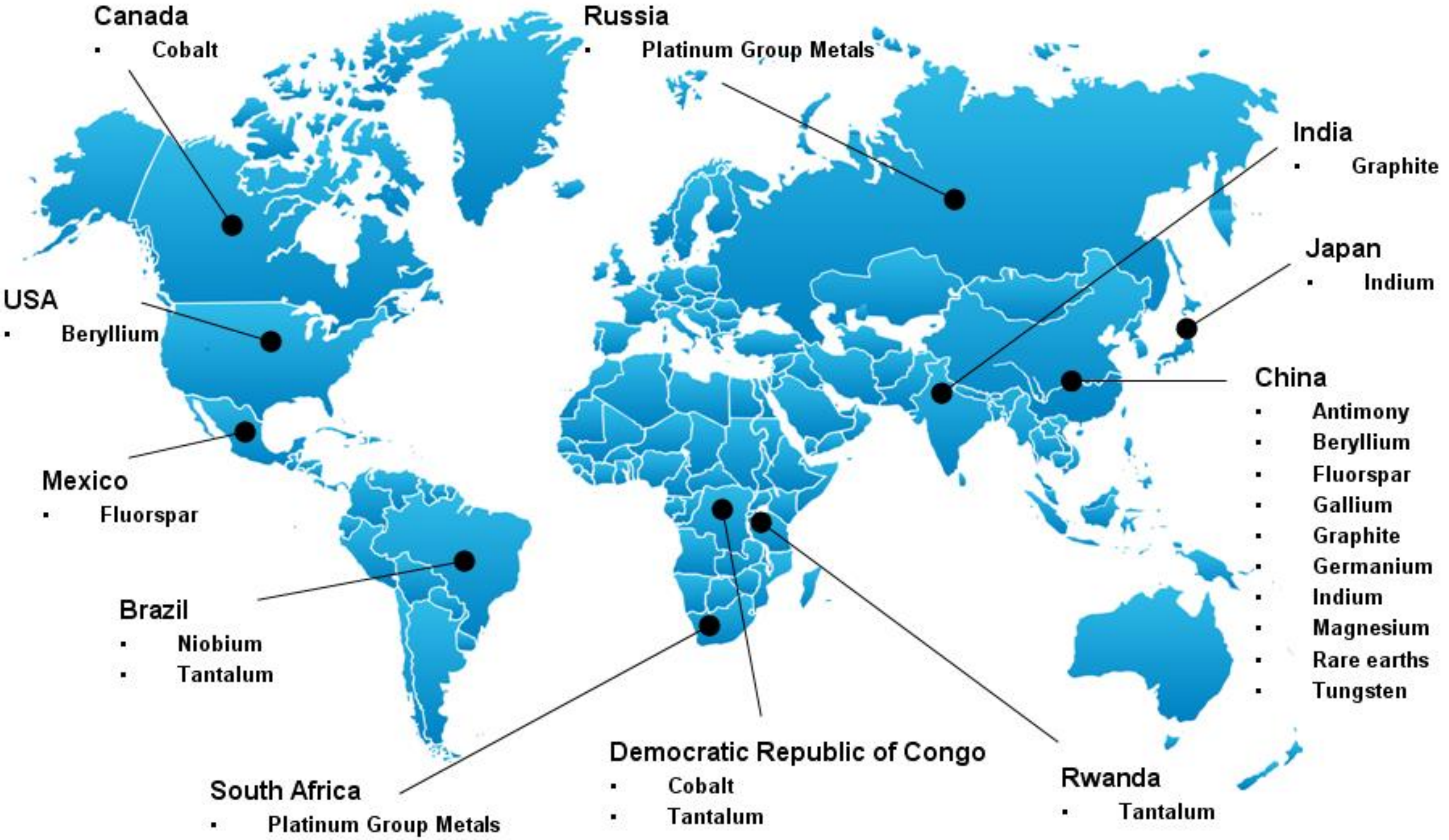
6. Outlook

Recycling: Global dependence on raw materials (non-renewable)



Source: http://europa.eu/rapid/press-release_IP-10-752_de.htm

6. Outlook

Recycling: Pressure to act

Pollution of the atmosphere

- **Climate-active greenhouse gases: CO_2, CH_4, N_2O, SF_6, NF_3, FKW, and so on**
- **Aerosols and dust (“metals”, e.g. Pb)**
- **Acid rain: NO_x, SO_2**

- **Pollution of the hydrosphere**
  - **Micro- and nanoplastics**
  - **Metals (Cu, Cd, Hg, Sn, ...), nitrate and phosphate**
  - **Micropollutants: Hormones, drugs, cosmetics, radioactive substances, ...**

- **Pollution of the pedosphere**
  - **"Organic" waste**
  - **Micro- and nanoplastics**
  - **Metals: Cr, Ni, Zn, As, Cd, Hg, Tl, Pb, ...**

6. Outlook

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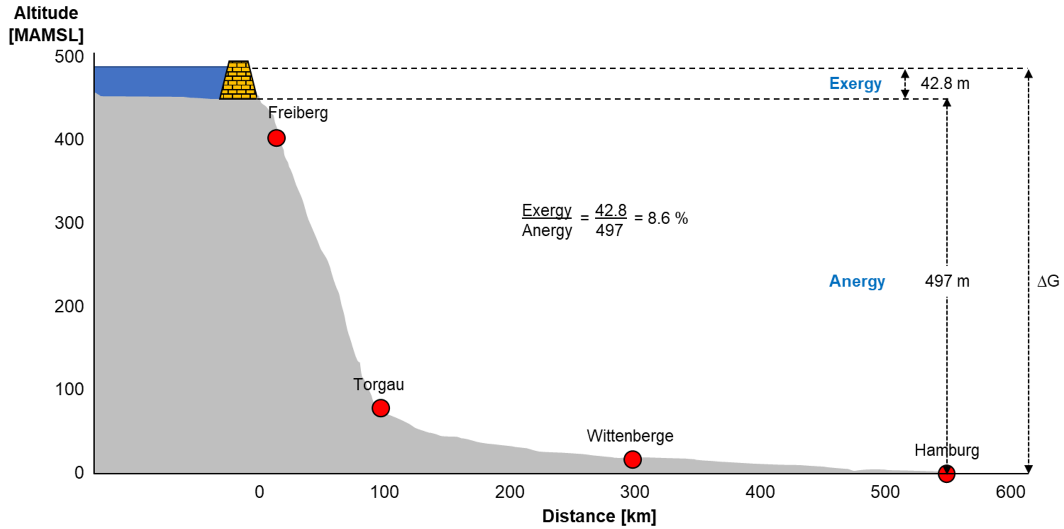
Recycling: Challenges



Use of energy or raw materials (exergy / anergy):

a) Energy source → utilization → heat
b) Deposit(fuels/ore) → utilization → dissipation

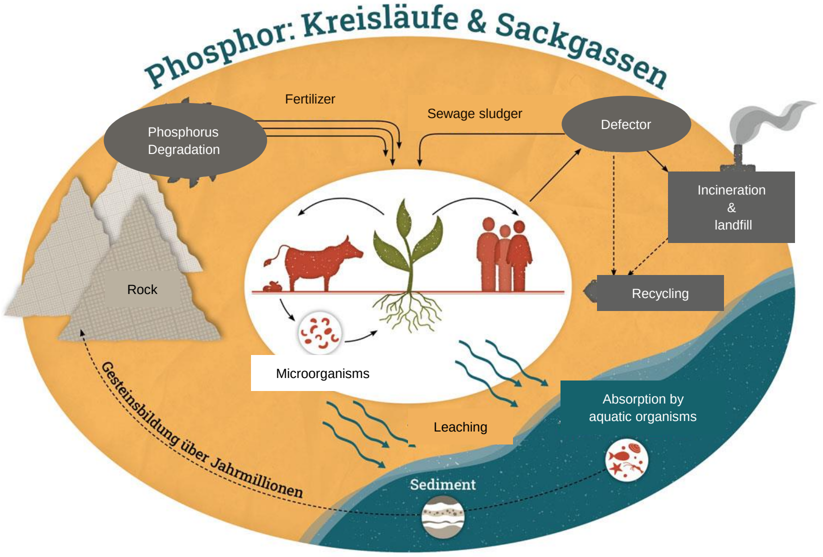
Ergo: strong increase of entropy due to dissipation of Concentration gradients or dilution in the atmosphere, biosphere, hydrosphere, lithosphere or pedosphere.

Example: natural gas reservoir → natural gas (75% C) → CO_2/N_2/Ar-exhaust (5% C) → CO_2 in air (420 ppm CO_2 ~ 115 ppm C) ⇒ Dilution by a factor of 7000!

Lit.: M. Bertau, T. Jüstel, R. Pöttgen, C.A. Strassert, Chemical products: Gradients, energy balances, entropy in Appl. Inorg. Chem., De Gruyter (2022)

6. Outlook

Recycling: The Phosphorus/Phosphate Challenge



Options for sewage sludge treatment

Crystallization or precipitation from (sewage) sludge water with

- with Mg^{2+} / $NH_4^+ \rightarrow (NH_4)MgPO_4 \cdot 6H_2O$ (Struvit)
- with $Ca^{2+} \rightarrow CaHPO_4$

- Thermochemical digestion
  - Incineration → Phosphate-containing slag (Ca-Si mixed phosphate)
  - Incineration → Phosphate-containing biochar (Ca-Si mixed phosphate)
  - Acid digestion of sewage sludge ash
  - $\rightarrow H_3PO_4$
- Thermochemical digestion of sewage sludge ash
  - with alkali salt → $CaHPO_4$, P_4 or H_3PO_4

6. Outlook: The Anthropocene

Observations

- **Climate change (see above)**
- **Species decline**
- **Land consumption**
- **Resource depletion**
- **Micro pollutants in drinking water**
- **Micro pollutants in food**
- **"Rebound" effects**

Source: https://www.swr.de/swraktuell/rheinland-pfalz/daten-wald-rheinland-pfalz-100.html

6. Outlook: The Anthropocene

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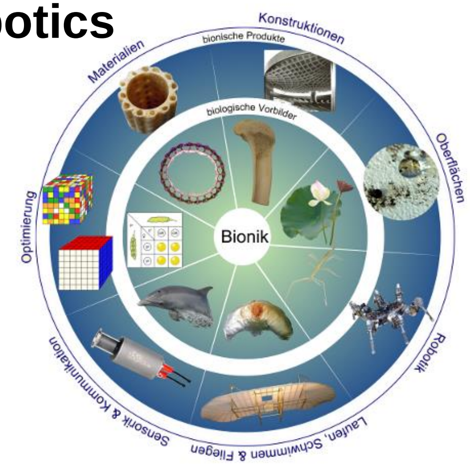
Humans shape the environment: Evolution 2.0 or bioeconomy

• Metal recycling by biochemistry	Bacterio-, phyto- and proteinomining of the about 50 metals in use
• Antifouling coatings without copper	Echinodermata as a model, but spines made of minerals!
• Reduction of land consumption	Urban farming in the vertical: PV, LED and robotics
• Currentless long-term data storage	DNA in glass ceramics
• Energy generation	Artificial photosynthesis (see above)
• Recyclable fibers	Spider silk from bioprocess engineering
• Microplastic "Challenge"	Microbial enzymes, e.g. PETases
• Post-Antibiotic Age	Skin- and eye-safe "Deep UV-C" emitters
• CO_2 sink	Ocean species protection: see "whale pump" $\rightarrow$ Fe^{2+}
• Functional textiles without F-chemistry	Feather instead of fluorine!
• Sensor technology	Coleoptera as smoke detectors, e.g. black pine fruit beetle



6. Outlook: The Anthropocene

Today's crisis is not a CO_2 or temperature crisis but more an entropy crisis

We are creating too much entropy globally by exploiting resources or deposits of fossil fuels and ores, today especially rare earths and other non-ferrous metals like Li, Co, Ni, Cu, Ga, Ge, In, Sn, and W, and dissipating the waste products in soils, waters and the atmosphere

- **From the entropy point of view: it is not a global solution to cover the earth with asphalt, concrete slabs and towers, because they are expensive, represent a high manufacturing cost and a poor entropy balance, much worse than trees or wooden buildings**

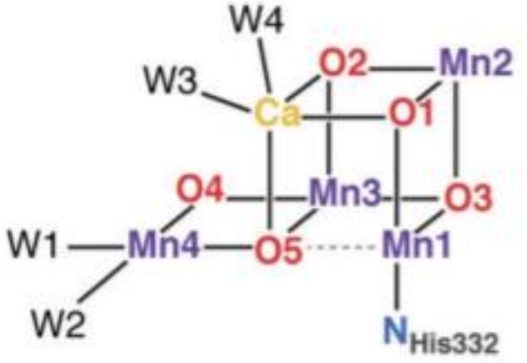
- **Because of the entropy balance and for economical as well as aesthetical reasons, there are some recommendations. Reasons some recommendations result:**
  - **Development of artificial photosynthesis and use of hydrogen as an energy carrier.**
  - **Stop the clearing of forests & primeval forests**
  - **Introduction of an innovative forestry, land and sea economy**
  - **Development of real green technologies based on closed cycles**

Solutions: Technical water splitting, reforestation and use of algae fields, wood architecture, ...

6. Outlook: The Anthropocene

Today's crisis is not the first CO_2 and temperature crisis, because about 2 - 3 billion years ago planet Earth was already in a similar environmental crisis (H_2S consumed by archaea)

- **Evolutionary way out: invention of CO_2 using species → first algae & then plants transformed sunlight + CO_2 by photosynthesis into solid usable materials (biomass), which after use were converted by pressure and temperature to natural gas, coal, petroleum and methane hydrate → decrease of atmospheric CO_2 concentration incl. cooling.**



- **Ergo: Photosynthesis has already proven once that one can produce cheap & environmentally friendly energy and at the same time reduce entropy by building up carbon deposits:**

- $x\,CO_2 + y\,H_2O \xrightarrow[\text{Photocatalyst } [CaMn_4]^{n+}]{\text{Light}} x\,O_2\uparrow + C_x(H_2O)_y$ **(Energy source) → Carbon deposits +** $y\,H_2O\uparrow$
  → Entropy export from the Earth's envelope/biosphere

7. Literature: Peer-Reviewed Papers

- **Influence of Carbonic Acid upon Temperature of the Ground (Phil. Mag. J. Science 41 (1896) 237) !**
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Thank you very much for your attention!

Questions?

Web pages

Prof. Dr. Reinhart Job https://www.fh-muenster.de/eti/personal/professoren/job/index.php

Prof. Dr. Thomas Jüstel https://www.fh-muenster.de/ciw/personal/professoren/juestel/index.php

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Climate Change & Greenhouse Gases: Causes, Effects, and Solutions

„Lectures for Future L4F“

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Prof. Dr. Thomas Jüstel
Department of Chemical Engineering

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Status February 2023

Planet Earth:
“I have Homo Sapiens”

Planet Venus: “Do not worry this will pass by”