





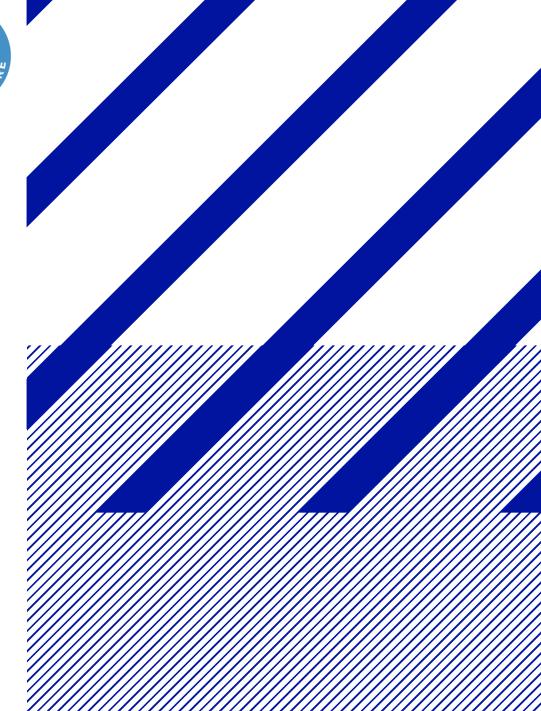
Climate Change & Greenhouse Gases: Causes, Effects, and Solutions

"Lectures for Future L4F"

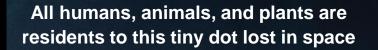
Prof. Dr. Reinhart Job Department of Electrical Engineering Prof. Dr. Thomas Jüstel Department of Chemical Engineering

FH Münster University of Applied Sciences

Status May 2024



What is it about? Our Home Planet!

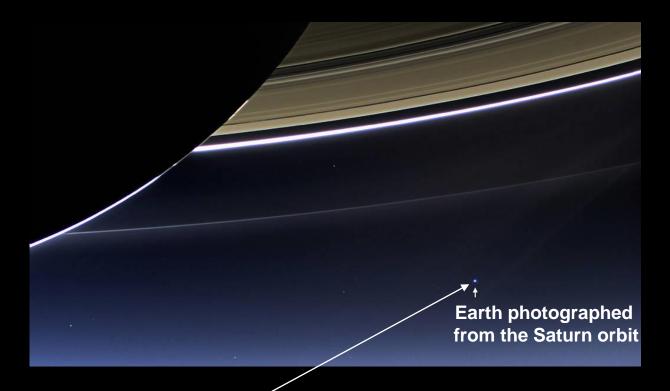


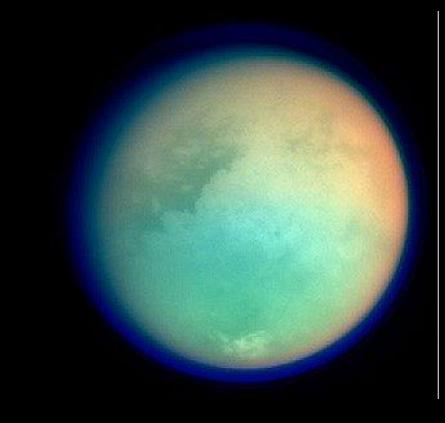
Photographic image of the Earth from 29000 km distance taken by the crew of Apollo 17 on December 7th, 1972: "Blue Marble"

Photographic image of the Earth from 40.5 AU (6.1 bill. km, 1/1500 ly) distance taken by Voyager 1 on February 14th, 1990: "Blue Dot"

What is it about? Impact Factors on Climate!

Titan: Largest Moon of Saturn (d ~ 5150 km)





Earth Distance to sun Ground pressure Greenhouse effect

149.6[.]10⁶ km (1 AU) 1 bar (N₂, O₂, Ar) 255 K → 288 K (13%)

Titan

Distance to sun $1.428 \cdot 10^9$ km (9.546 AU)Ground pressure1.5 bar (N2, O2, Ar?)Greenhouse effect82 K \rightarrow 94 K (15%)

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



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1. Challenges of the 21st century

Emission of climate-active trace gases and climate change

- ▶ CO₂ neutral energy economy: PV, wind \rightarrow H₂, PtG, LNG, battery storage
- > CO₂ capture: $1.0 \cdot 10^{12}$ t CO₂ 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

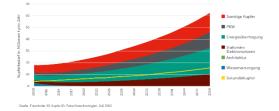
- Threats to food and drinking water security
- Loss of arable land
- Evaporation of inland waters





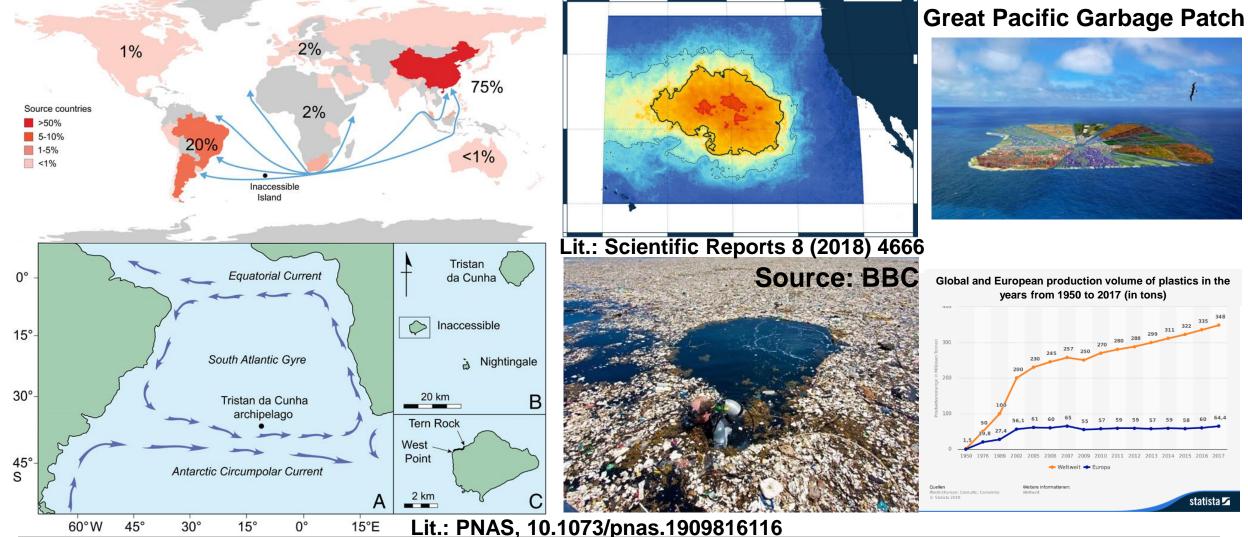
Rising demand for raw materials threatens resources & expansion of renewable energy sources

- 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





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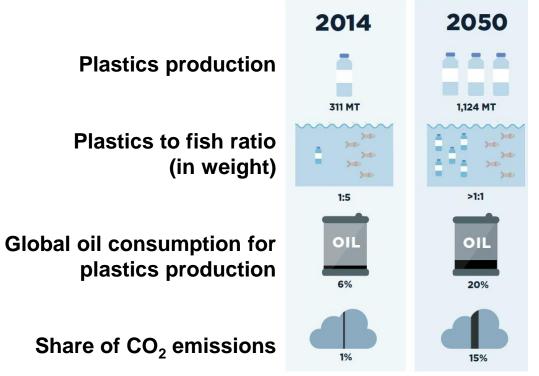


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Trend: Increasing input of plastic into the biosphere

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



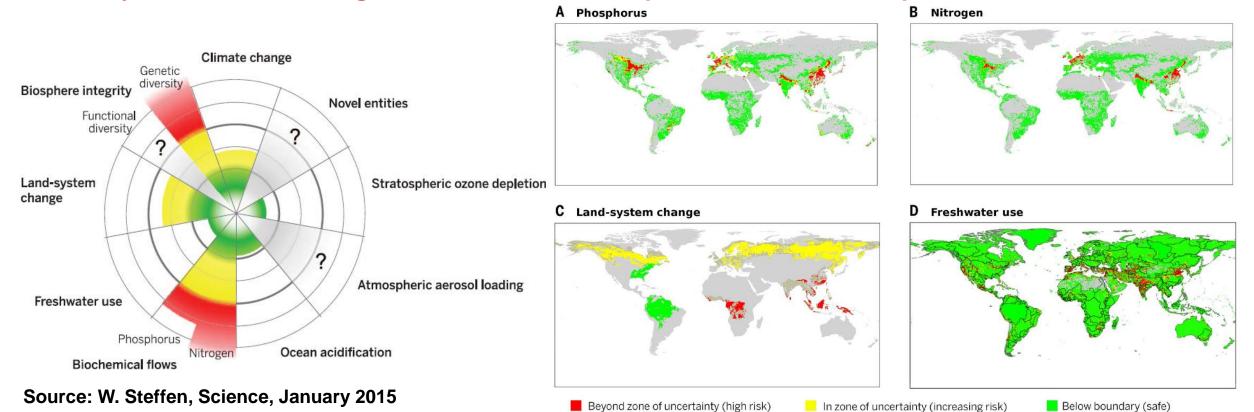
Source: Ellen MacArthur Foundation

- 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

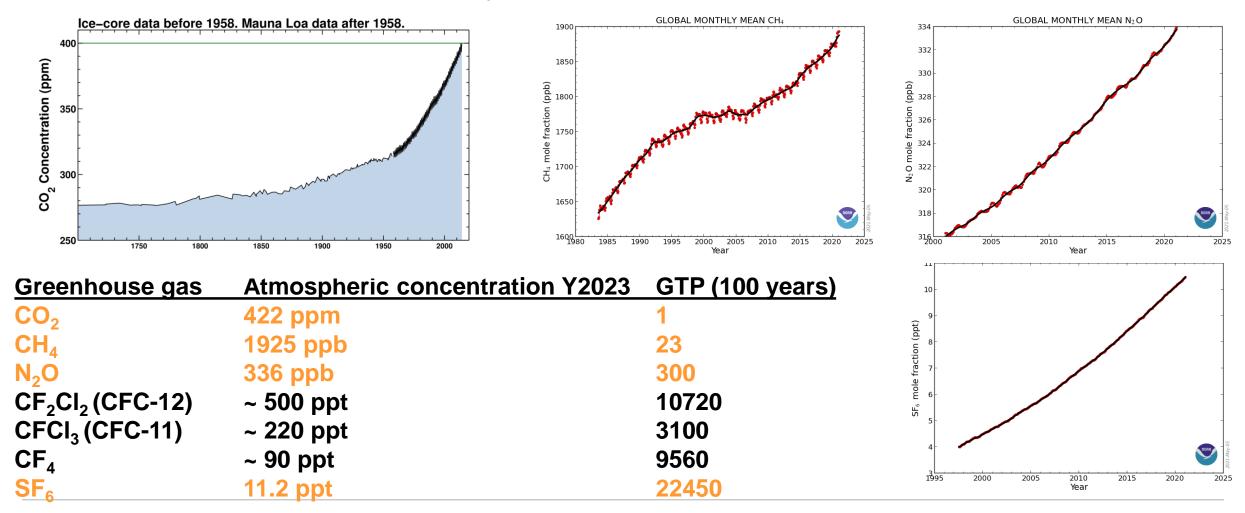
Planetary boundaries as a guide to human development on our home planet



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

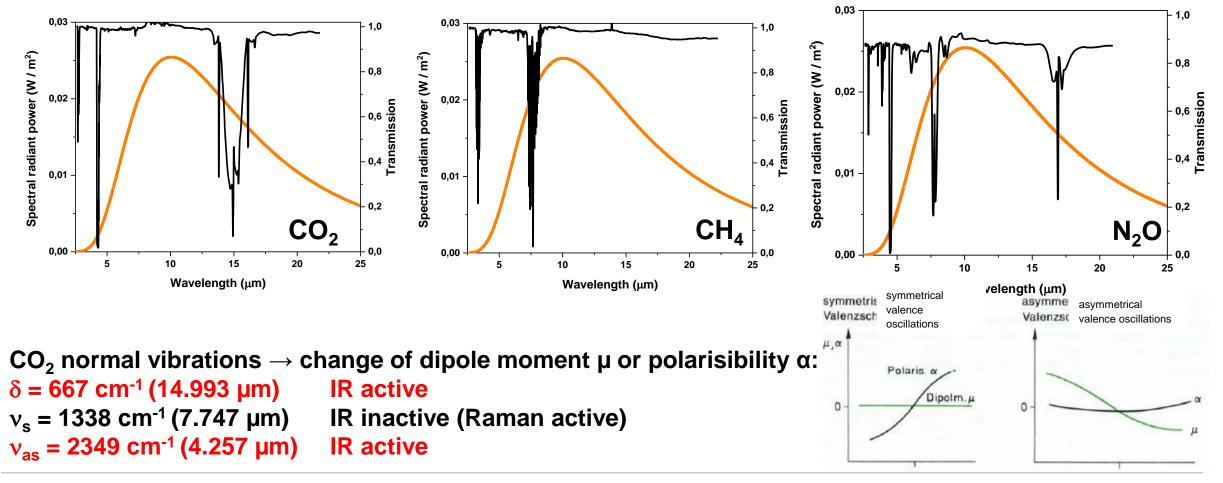


Major trace gases are CO₂, CH₄, N₂O, SF₆ (Source: Mauna Loa, Hawaii, https://gml.noaa.gov/ccgg/trends)



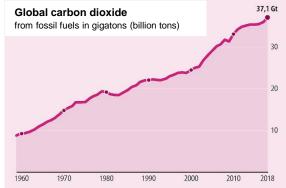


The greenhouse gas potential depends on the absorption spectrum of the trace gases and the average global temperature of the earth's surface ($T_{effective} \sim 288 \text{ K} = 15 \text{ °C} \sim \text{Planck spectrum}$)



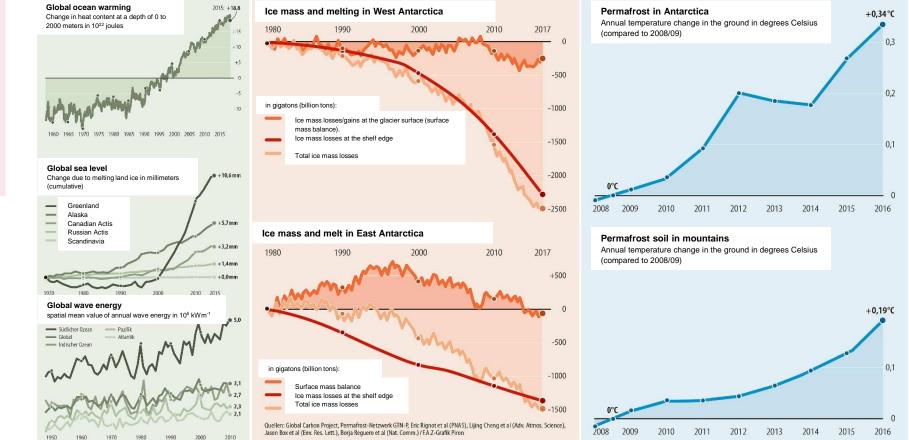


Installed climate protection measures insufficient to limit global temperature rise to 2 K!



Consequences

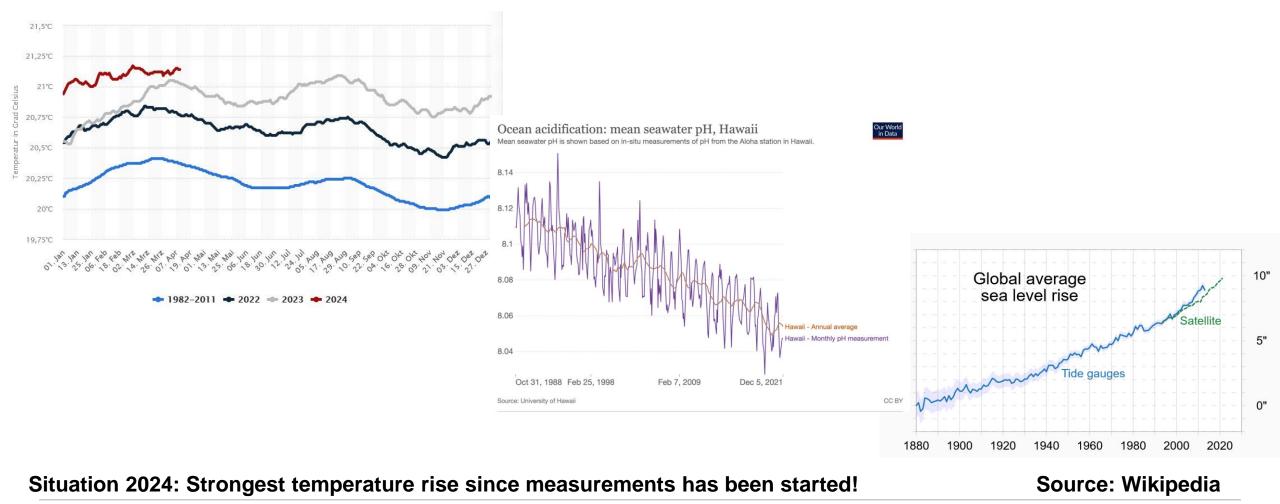
- Melting of ice and glaciers
- Decrease of fresh water
 reservoirs
- Secondary release of CH₄
- Sea level rise
- Change of thermohaline oceanic currents



Situation 2018: Global emission of 37.1 Gt CO₂, Compare Permian-Triassic boundary: 2.6 Gt CO₂ per year (factor 14 less)



Impact on Oceans: Sea level and temperature rise as well as water acidification

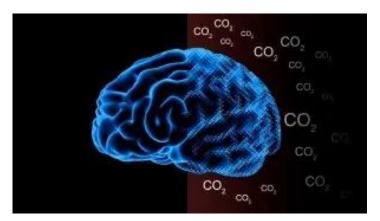




Installed climate protection measures insufficient to avert considerable damage to the biosphere

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

1400 Scripps Institution of Oceanography NOAA Global Monitoring Laboratory 1200 Parts per million (ppm) low air quality 1000 medium air quality 800 high air quality Linear **Extrapolation** 600 SCRIPPS INSTITUTION OF OCEANOGRAPHY NOAR 400 **UC**San Diego 1950 2000 2250 2300 2350 2400 2450 2050 2100 2150 2200 Year

Atmospheric CO₂ at Mauna Loa Observatory



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

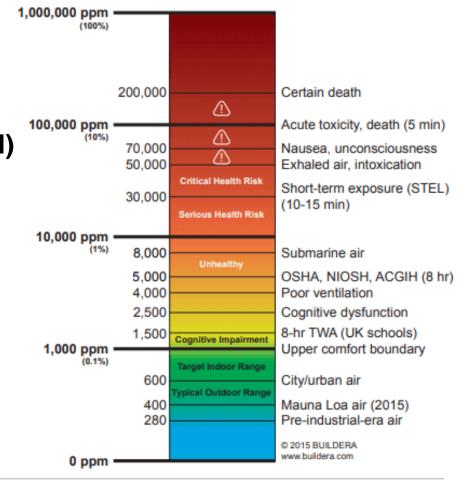
Germany: MAK value CO₂ is 9100 mg/m³ (~ 5000 ppm)

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

Carbon Dioxide (CO₂) Hazard Scale





Origin of anthropogenic emission of trace gases

- Lighting
- Transportation
- Buildings
- Information technology
- Steel production
- Cement production
- Ammonia synthesis
- Chlor-alkali electrolysis

CH₄/N₂O

- Agriculture & livestock
- HNO₃ and nylon production

SF₆/NF₃

Electrical engineering



Fraction

(~ 25%)

(5%)

(6%)

(5%)

(2-3%)

(6-7%)

(1-2%)

(~1%)

Potential counter measures LED technology New drives and fuels Insulation

Server architecture, use of PV H₂ as a reducing agent



Reduction of cement clinker content in concrete N_2 hydrogenation by steam, N_2 photolysis Conversion to membrane process, heat recovery..

Reduction of meat and fertilizer consumption Optimization of the Ostwald process

Alternative insulator gases, optimization of processes for production of screens & solar cells



South Korea

Lighting consumes 20% of the electrical energy generated globally (5% of anthropogenic CO₂ emissions, source: NASA)

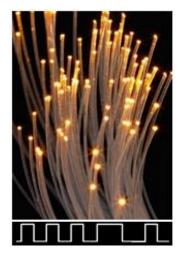
Replacement of all traditional light sources with LEDs ⇒
Potential to shut down about 684 power plants globally (source: US DOE)
1989 Fall of the Berlin Wall "The wind of change"
1993 Blue LED
1996 White LED
2014 White LED with > 300 Im/W & Nobel Prize Shuji Nakamura
2015 25th anniversary of German unity "The light of change
2024 Separation of Korea well visible "Sitting in the dark"



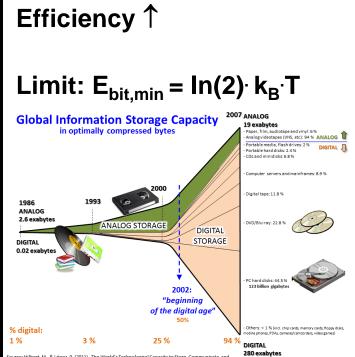
But: Rebound effects ↔ Technology advances

"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 \downarrow



Data volume ↑ ↑

University of Applied Sciences IT \leftrightarrow Energy savings urgently needed

CO₂ emissions from IT services are rising relentlessly and sometimes exponentially....

2018 547 EBs stored in data centers 294 billion e-mails per day Annual electricity demand in terawatt hours (TWh) 6453

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

36 billion t CO₂ in 2019

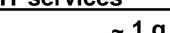


VAE 119

Quelle: Cambridge Bitcoin Electricity Consumption Inde

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<u>CO₂ balance of IT services</u>



- **1** Bitcoin transaction
- $\sim 1 \text{ g CO}_2$ 320,000 t CO₂ per day in 2021 = 117 mill. t CO₂ in 2021 ~ 453,000 credit card transfer 190,000 t CO₂ per day in 2018 = 69 mill. t CO₂ in 2018
- $\sim 0.2 \text{ g CO}_2$
- 1 h video streaming
- For comparison

1 Google query

- 1 km train travel
- 1 km driving a car
- 1 km flying

1 e-mail

- ~ 150 g CO₂ (UHD: 4K resolution)
- $\sim 32 \text{ g CO}_{2}$

~ 147 g CO₂

~ 380 g CO₂ (Retour flight: Germany to Chile ~ 25,000 km ~ 9.5 t CO₂)



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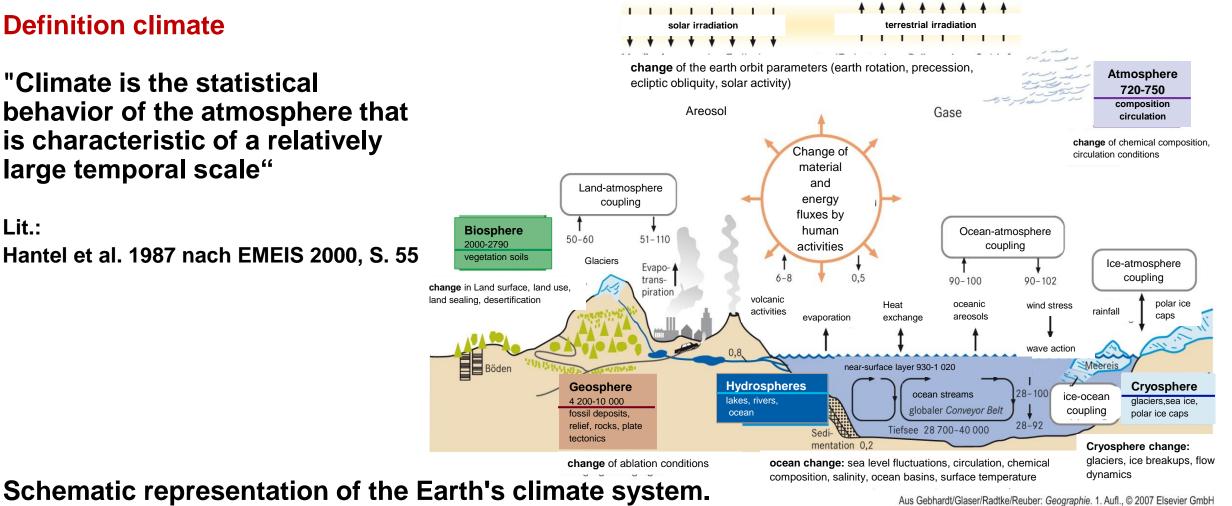
2. The earth's climate and the global energy balance

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

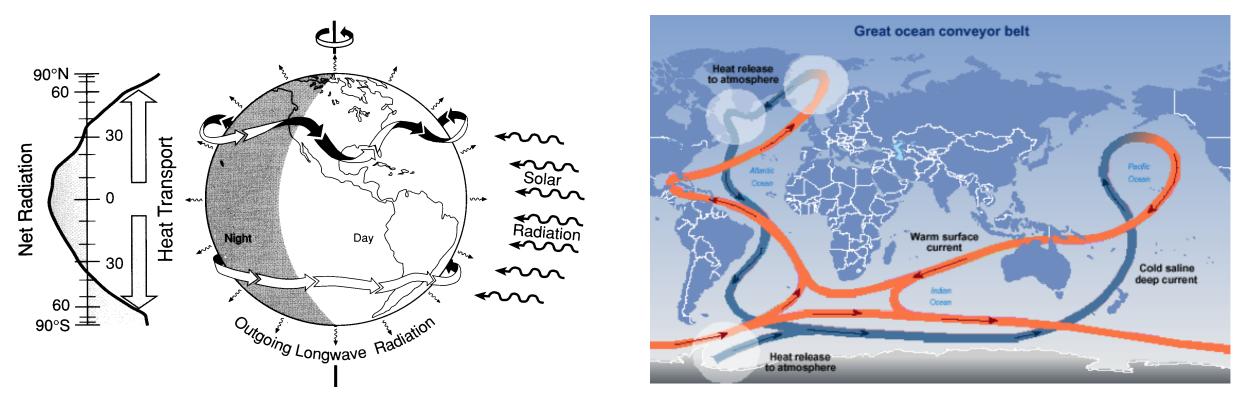


Lit.: Casper 2007 after draft of R. Glaser and H. Saurer, modified after IPCC 2001



Global heat transport ~ from the tropics to the poles

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



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



Composition of the earth's atmosphere

- Atmosphere = Gaseous air envelope of celestial bodies, which is gravitationally bound
- Total mass: 5.13*10¹⁸ kg = 5.13*10¹⁵ t = 5.13 Petatons (Pt)
- 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 (IR active)

- Carbon dioxide CO₂
- Carbon monoxide CO
- Methane CH₄
- Terpenes and isoprenes C_xH_y
- Ammonia NH₃
- Nitrogen oxides NO_x
- Nitrous oxide N₂O
- Sulfur dioxide \overline{SO}_2
- Methyl chloride CH₃CI
- Methyl bromide CH₃Br
- Ozone O_3
- Sulfur hexafluoride SF₆
- Nitrogen trifluoride NF₃
- CFCs: $CCI_mF_{4-m} \& C_2CI_mF_{6-m}$ with m > 0



Structure of the earth's atmosphere

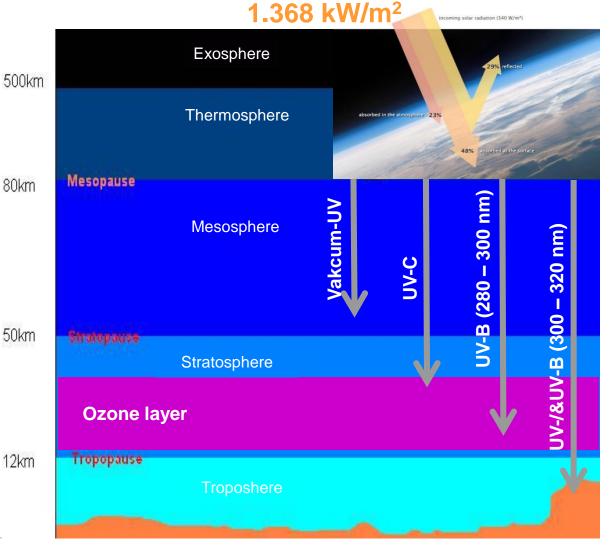
O = 510[·]10¹² m², m = 10.076 kg/m² → p = F/A = 101.325 Pa (N/m²)

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, around ~ 0.1%) Ozone splitting

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

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





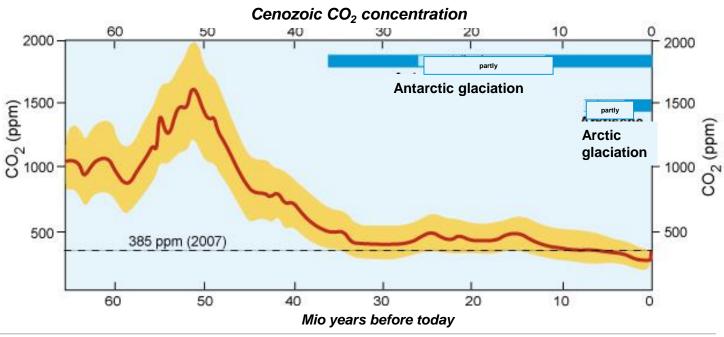
Climate factors, history and reconstruction

"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, p. 246

Climate factors

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



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



Climate factors

- **1. Astrophysical impact**
- a) Sun
- b) Earth's orbital parameters
- c) Tidal effects
- d) Impacts
- e) Supernovae/Gamma-ray flashes
- f) Close encounters with celestial objects



Luminosity

- Temperature

todav

Radius

1.8

1.4

Sonne 50176

heutigen

zur

S

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

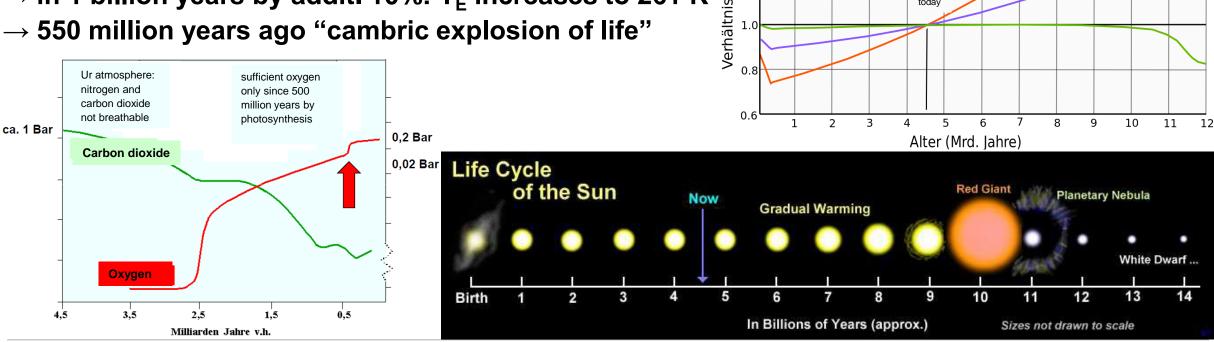
Climate factors

1a) Sun

Continuous increase in luminosity L_o

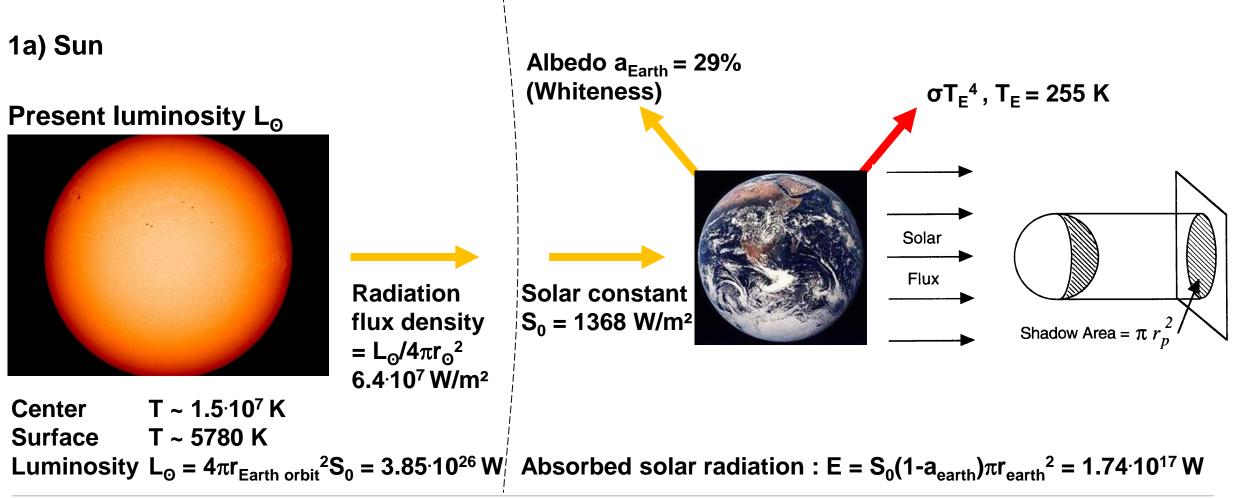
- \rightarrow 25-30% in the past 4.6 billion years
- \rightarrow in 1 billion years by addit. 10%: T_F increases to 261 K

 \rightarrow 550 million years ago "cambric explosion of life"





Climate factors





Climate factors

1a) Sun

Absorbed solar radiation $S_0(1-a_{Earth})\pi r_{Earth}^2$ withAlbedo $a_{Erde} = 0.29$ Longwave radiation $\sigma T_{Erde}^4 4\pi r_{Erde}^2$ with $\sigma = 5.670 \cdot 10^{-8} Wm^{-2}K^{-4}$
(Stefan-Boltzmann constant)

Global energy balance: insolation = radiation

$$S_{0}(1-a_{Earth})\pi r_{Earth}^{2} = \sigma T_{Earth}^{4} 4\pi r_{Earth}^{2}$$

$$S_{0}/4(1-a_{Earth}) = \sigma T_{Earth}^{4}$$

$$T_{Earth} = (S_{0}(1-a_{Earth})/4\sigma)^{1/4} = T_{E} = \sqrt[4]{\frac{(1368 \text{ Wm}^{-2}/4)(1-0.29)}{5.67 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}}} = 255 \text{ K} (-18 \text{ °C})$$



AMO

Climate factors

1a) Sun

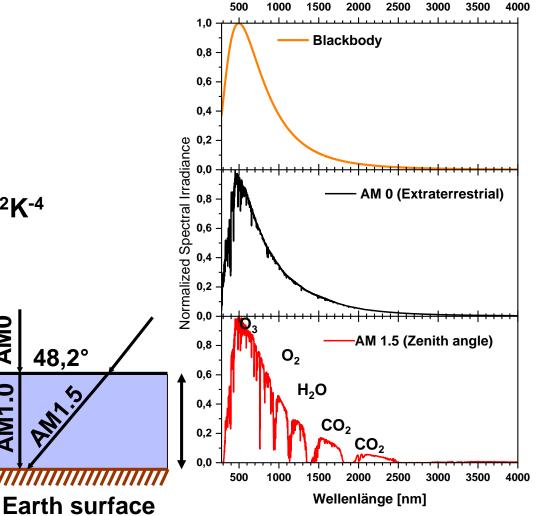
Spectrum ~ Black-Body (BB) or Planck radiation

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

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

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

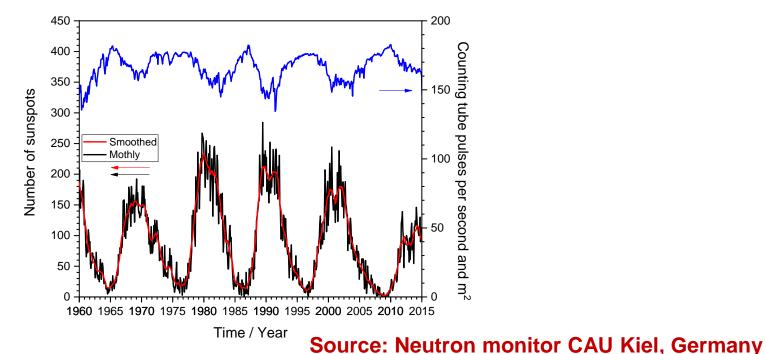
AM1.0 Airmass AM0: Spectrum of the photosphere **BB** spectrum including Fraunhofer absorption lines Airmass AM1.0: Spectrum at sea level



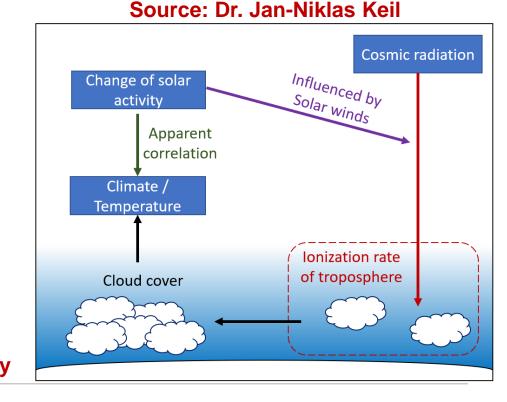


Climate factors

1a) Sun



Solar wind \leftrightarrow Cosmic rays \rightarrow Cloud formation and albedo

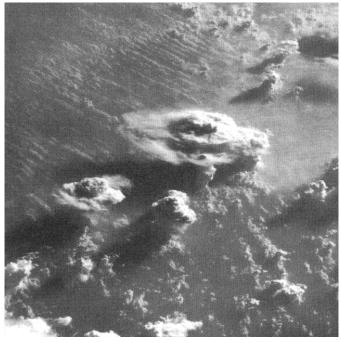


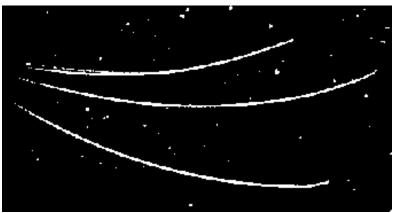


Climate factors

1a) Sun

Solar wind \rightarrow 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



Climate factors

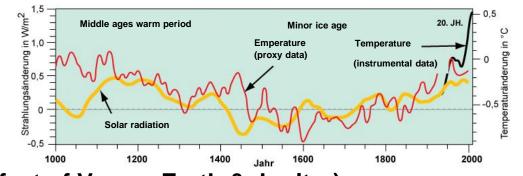
1a) Sun

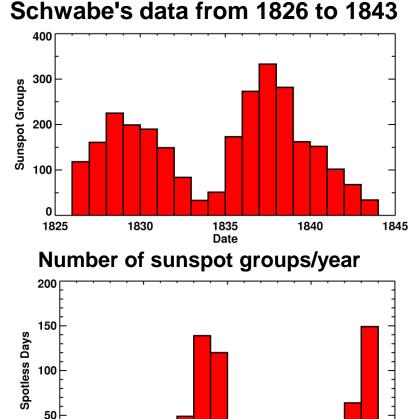
Some sunspot cycles

- 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)





1835

Date

Number of days without spots

1840

1845

1830

1825



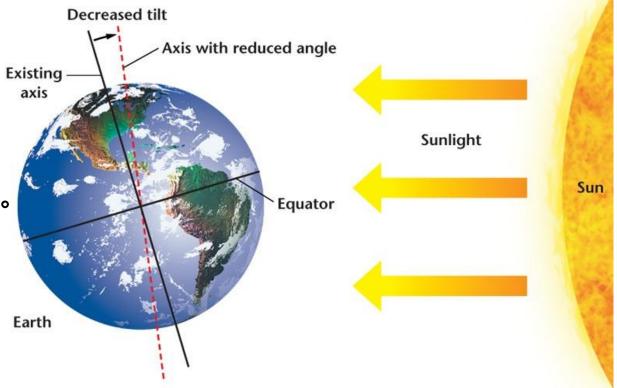
Climate factors

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

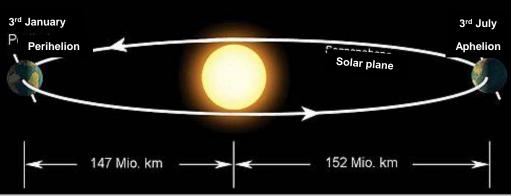


2. The earth's climate and the global energy balance Climate factors

1b) Earth orbit parameters

Eccentricity e (period ~ 100 ka) 1st law of planet motion by Johannes Kepler (1571 - 1630)

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")

Planet	Perihelion and Aphelion Distance in astronomical units (AU)	Solar radiation (solar cons maximum and minimum (M	tant) (1 AU = 149.6 Mio. km) V/m²) Remarks	
Mercury	0.3075 – 0.4667	14,446 – 6,272	Bound rotation	
Venus	0.7184 – 0.7282	2,647 – 2,576	Greenhouse gases CO₂ and H ₂ O determine habitability	
Earth	0.9833 – 1.017	1,413 – 1,321		
Mars	1.382 – 1.666	715 – 492	In ₂ O determine habitability	
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		



North Pole

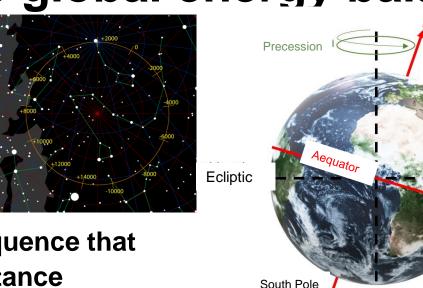
Axis to ecliptic pole

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)



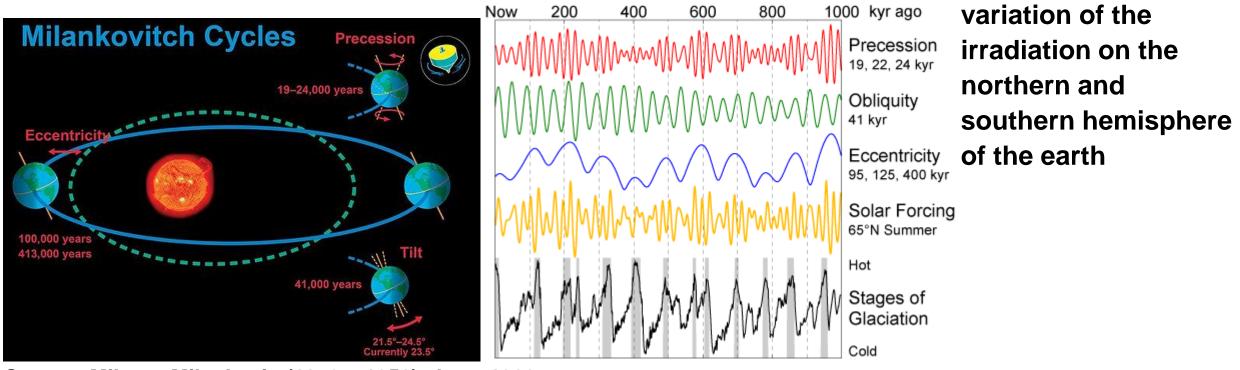
The gyroscopic motion or precession has the consequence that the distance between earth and sun (actual mean distance 149,597,870 km) changes gradually in a certain season.

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

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



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



Source: Milutan Milankovic (1879 – 1958) about 1920



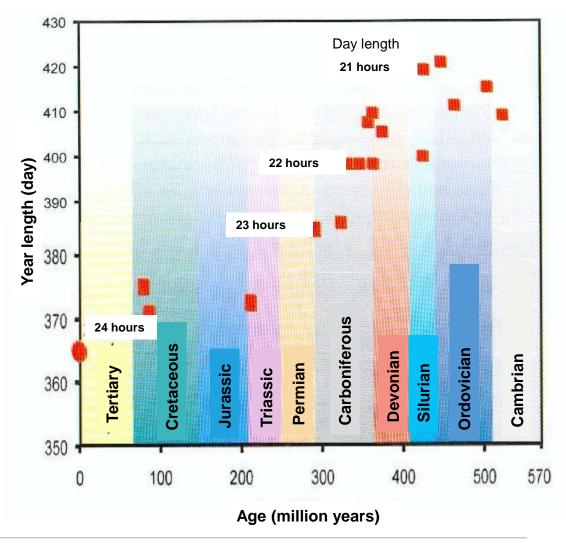
Climate factors

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 = $94 \times 10^{18} \text{ J/a}$ (94 EJ/a)





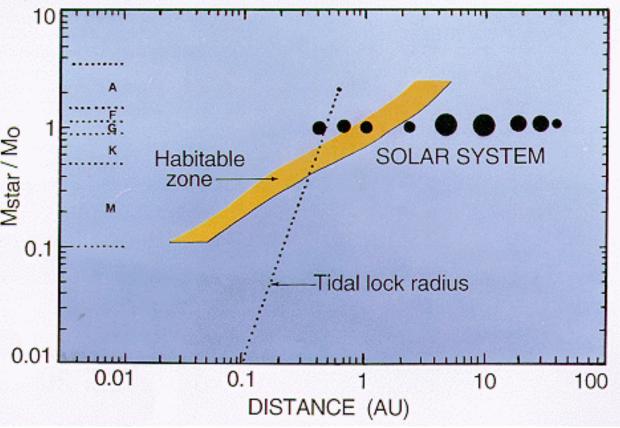
1c) Tidal effects: Causes the presence of a lock radius in any (exo)planetary system

Solar system

- Mercury: Tidal locking \rightarrow 3:2 resonance
- Earth: No tidal locking → moderate rotation

Other systems comprising exoplanets

- Habitable planets around M stars are likely tidal locked
- Unlocked habitable planets solely around stars from spectral class K onwards





of the Yucatan Peninsula

in Mexico. Faintly visible

24 Gt TNT

Chicxulub crater.

Climate factors

1d) Meteor impacts

(Source: Wikipedia) 66,040 Million years ago: K/T boundary Lit.: Science 208 (1980) 1095 > 1000 km³ ejecta (proven by Iridium anomaly) > 100 Gt TNT

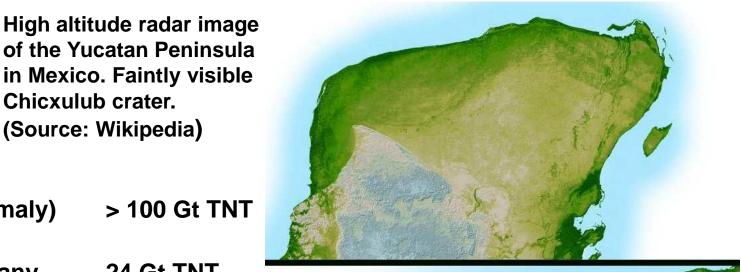
15 Mill. years ago: Nördlinger Ries, Germany

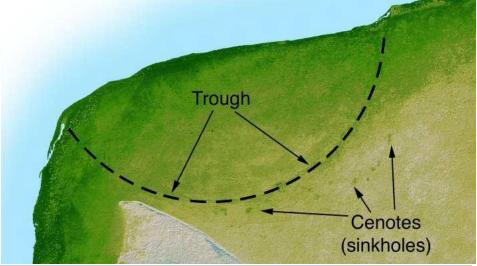
50,000 years ago: Barringer crater, AZ, USA **15 Mt TNT**

1908 4-5 Mt TNT Tunguska-Event, Sibiria

Shoemaker-Levy-9, Jupiter, south. Hemi. 650 Gt TNT 1994

2013 Chelyabinsk explosion, Ural 500 kt TNT







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

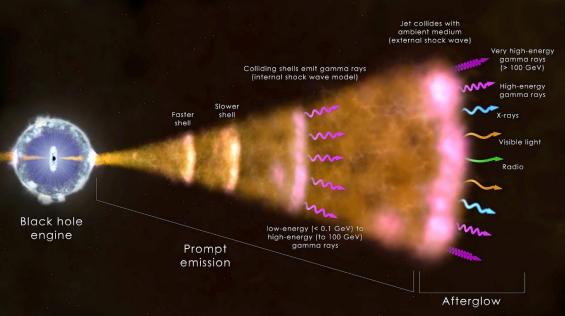
1e) Supernovae (SN) & Gamma Ray Flashes (GRF)

Supernovae \Rightarrow Increase in cosmic rays \Rightarrow Ionization of Earth's atmosphere \Rightarrow increase in cloud formation \Rightarrow 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 Fe₃O₄ as part of sediments at the ground of the Pacific Ocean

Next candidate in our cosmic "vicinity" to may cause GRF Betelgeuse (α Orionis), a 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

1e) Supernovae (SN) & Gamma Ray Bursts (GRBs)

October 09th, 2022: Brightest Of All Time "The BOAT" \rightarrow GRB from a distance of 2.4 billion light-years

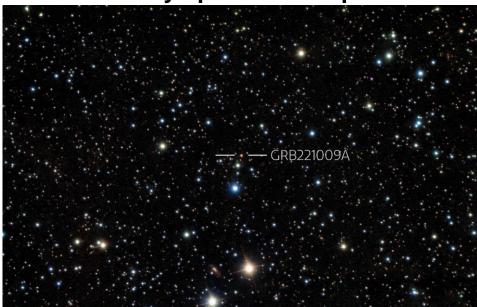
Duration 10 hours after detection by SWIFT observatory and Fermi-Gamma-Ray space telescope

Peak flux: 3.1.10⁻⁹ Wcm⁻²

Peak irradiation Earth: 3.1.10⁻⁹ Wcm⁻² π r² ~ 4 GW

Peak intensity GRB 221009A > 10⁴⁰ W

Photon energy up to 18 TeV





Climate factors

- 2. Terrestric (geophysical) impact
- a) Albedo
- b) Magnetic field
- c) Plate tectonics
- d) Volcanism
- e) Silicate-carbonate cycle



modified after Jacob, Wikipedia

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

Climate facto		1020	Planet	Distance from Sun [km]	Albedo	Effective Temperature [K]	Real Temperature [K]	ΔΤ [K]
2a) Albedo a	24°C	13°C	Mercury*	5.79 x 10 ⁷	0.12	434	~ 440	-
			Venus	1.08 x 10 ⁸	0.75	232	737	500
Earth complet	ely		Earth	1.5 x 10 ⁸	0.30	255	288	33
covered with		and the second se	Mars*	2.28 x 10 ⁸	0.15	217	210-218	-
	32°C	-52°C	Jupiter	7.79 x 10 ⁸	0.73	85	165	80
Forest Deser	1 52 C	14742518	Saturn	1.43 x 10 ⁹	0.34	81	134	53
Water Ice	and the second second		Uranus	2.87 x 10 ⁹	0.30	59	76	17
			Neptune	4.5 x 10 ⁹	0.29	47	72	25
Surface	Albedo a	Absorption (1-a)	Pluto	5.91 x 10 ⁹	0.50	37	44	7
			Moon	1.5 x 10 ⁸	0.11	271	-123 – 380	-

*no Atmosphere

Albedo a	<u>Absorption (1-a)</u>
0.9 – 1.0	0.0 – 0.1
0.57 – 0.65	0.35 – 0.43
0.06 – 0.18	0.82 – 0.94
0.06 - 0.09	0.91 – 0.94
0.06 - 0.08	0.92 – 0.94
	0.9 - 1.0 0.57 - 0.65 0.06 - 0.18 0.06 - 0.09

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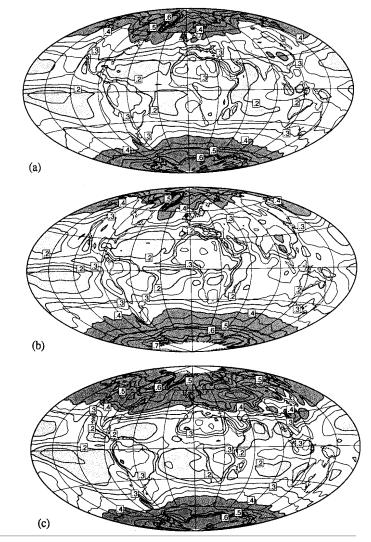
Climate factors

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)





3 480 km

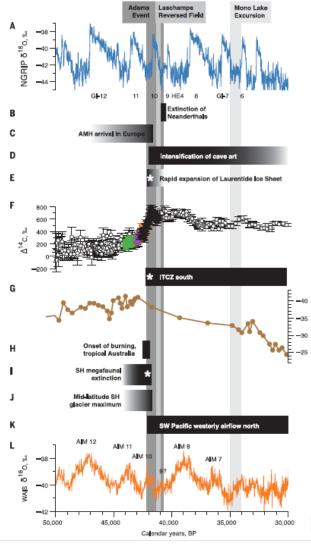
Climate factors

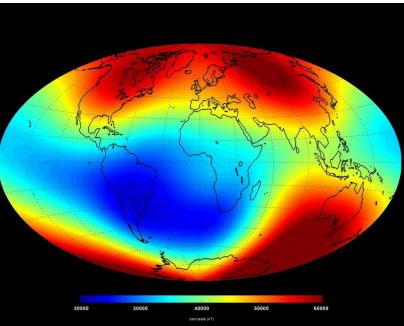
2b) Magnetic field pole jumps

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?





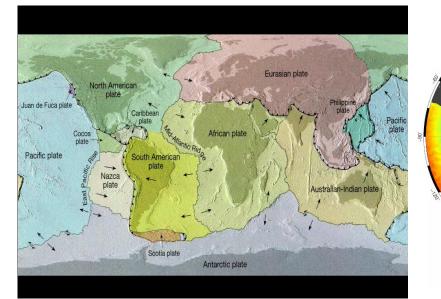
Spatial distribution of magnetic field strength in nT (in blue South Atlantic anomaly)



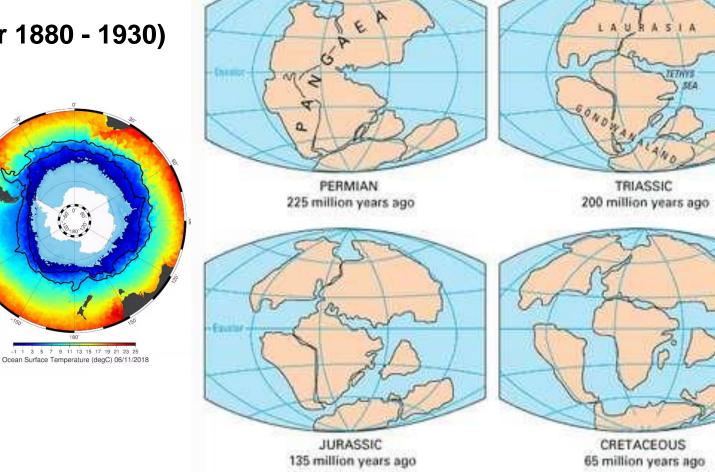


Climate factors

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



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





Climate factors

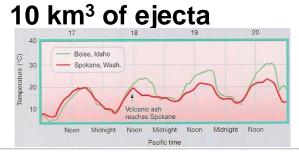
2d) Volcanism

- 1815 Tambora, Indonesia 150 km³ of ejecta 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**



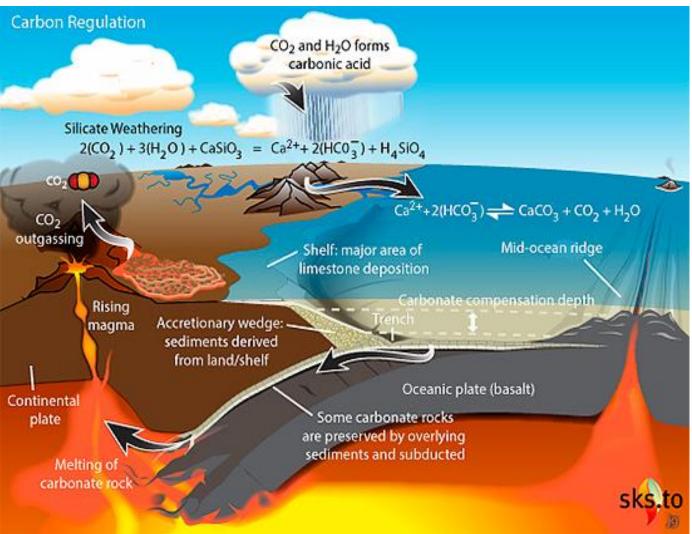




Climate factors

- 2e) Silicate-carbonate cycle: long-term regulation of the atm. CO₂ concentration
- High global temperature High evaporation and erosion $CO_2(aq) + H_2O(I) \rightarrow H_2CO_3(aq)$
- Precipitation : CaSiO₃(s) + 2 H₂CO₃(aq) \rightarrow Ca²⁺ + 2 HCO₃⁻ + H₂O + SiO₂ \downarrow Ca(HCO₃)₂ \rightarrow CaCO₃ \downarrow + H₂O + CO₂
- Subduction of carbonate sediments
- CO₂ emission by volcanoes

Complete CO₂ exchange ~ 500,000 a





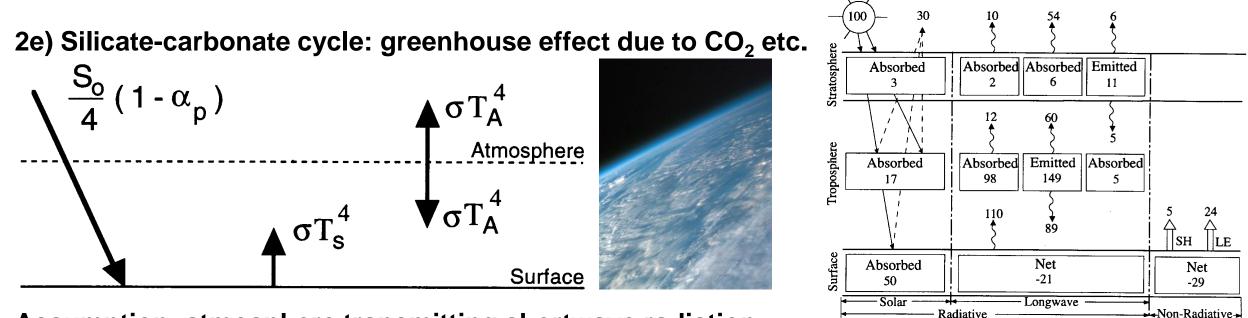
Climate factors

2e) Silicate-carbonate cycle: long-term regulation of the atm. CO₂ concentration (prehistoric)

	<u>CO₂(g) [Vol%]</u>	pH(Rain)	Year / Epo	<u>ch</u>		
٠	0.0280	5.64	ca. 1750		Phanerozoic Carbon Dioxide	
٠	0.0317	5.62	1960	8000-	Measurements Models -30	
٠	0.0339	5.60	1980	7000 -	Royer Compilation GEOCARB III 30 Myr Filter —	ē
٠	0.0370	5.58	2000	(6000 - udd 5000 -	30 Myr Filter — COPSE — ²⁵ Rothman = 20	eraç
٠	0.0400	5.57	2015	 ອ		
٠	0.0420	5.55	2022	Dioxide		ernai
٠	0.2	5.22	Jurassic	G 3000-		luate
٠	0.7	4.94	Cambrian	Que 2000-		
٠	1.0	4.87		1000-		Times
٠	2.0	4.72		0	Cm O S D C P Tr J K Pg N ⁰	
•	5.0	4.52	Archaean	L	500 400 300 200 100 0 Millions of Years Ago	



Climate factors



Assumption: atmosphere transmitting shortwave radiation, $\xrightarrow{\text{Radiative}}$ and $\Delta T = 33 \text{ K}$ but completely absorbs longwave radiation (e = 1) $\rightarrow T_{real} = 288 \text{ K} (+15 \text{ °C}) \rightarrow \Delta T = 33 \text{ K}$

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



Climate factors

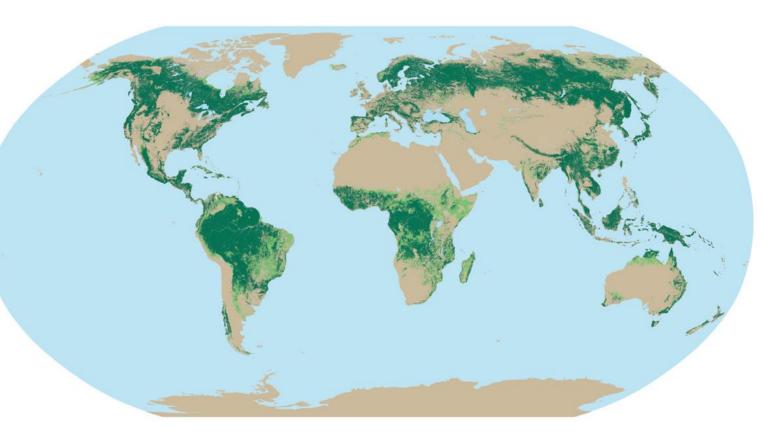
- 3. Biogenic impact
- a) Forestation
- b) Phytoplankton
- c) Peatlands



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 CO₂/a
- Since 1850, about 20% of total anthropogenic CO₂ emissions

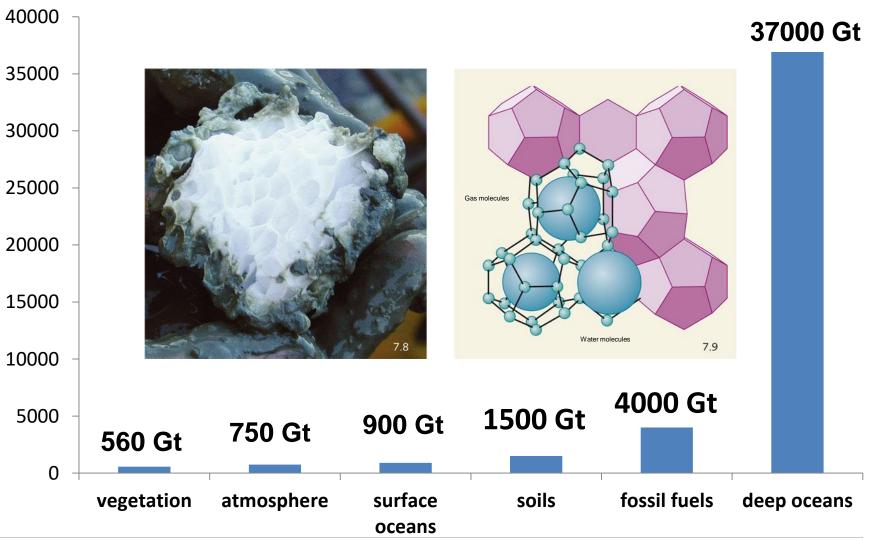


Lit.: Nature 585 (2020) 545



3a) Forestation Vegetation & Forest serve as carbon storage (Pg) 5 But: The majority of all carbon is stored in fossil fuels and bound as methane hydrate on the ocean floor

Climate factors





Climate factors

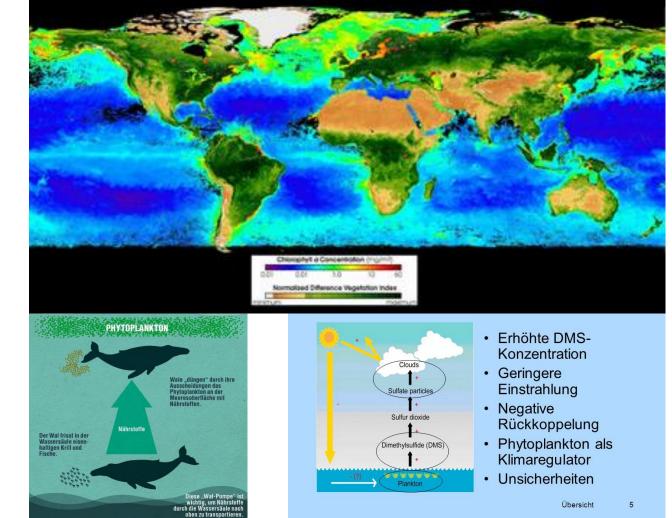
3b) Phytoplankton

High concentration due to

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

Effect of phytoplankton

- CO₂ consumption + O₂ emission
- Aerosols according to Claw hypothesis: Phytoplankton → CH₃-S-CH₃ (Dimethyl sulphide, DMS) → SO₂ → SO₄²⁻ → aerosols → clouds (negative feedback)





Climate factors

3c) Peatlands

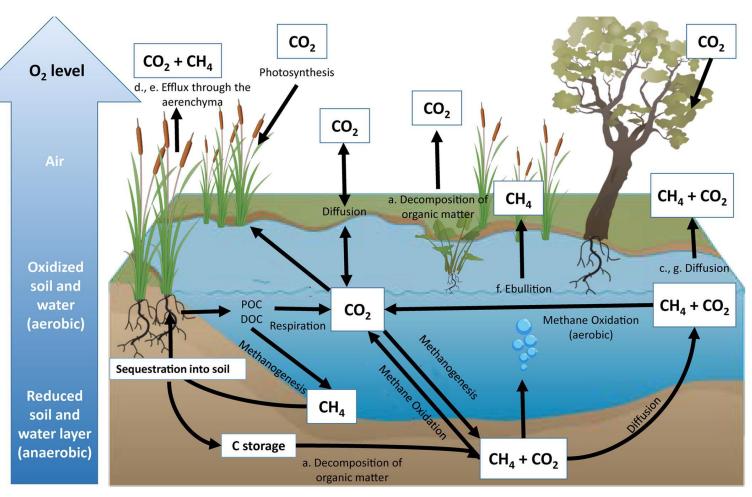
Humid: CO₂ / CH₄ consumer

Dry: CO₂ / CH₄ 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



Climate factors

3c) Peatlands

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

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

	System		Trace emission		Climate effectiveness
	Effectiveness 100 a	CO ₂ -C 1 (Kg C ha ⁻¹ a ⁻¹)	CH₄-C 7,63 (Kg C ha ⁻¹ a ⁻¹)	N ₂ O-N 133 (Kg N ha ⁻¹ a ⁻¹)	CO ₂ -C equivalent (Kg CO ₂ -C equ ha ^{.1} a [.] ¹)
	natural (Rzecin)	-2000	120	0.1	-1070
Low	near-natural (boreal)	-490	120	0.112	442
Lowland Peatland	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
-	near-natural (boreal)	-200	37.5	0	87
Highland	near-natural (Temperate)	710	174	-0.0112	618
	drained forest	1100	20	0.04	1258
Peatland	grassland	2350	2	0.1	2379
land	arable land	4400	0	0	4400
	Peat cutting	1750	17.25	0.4	1935

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

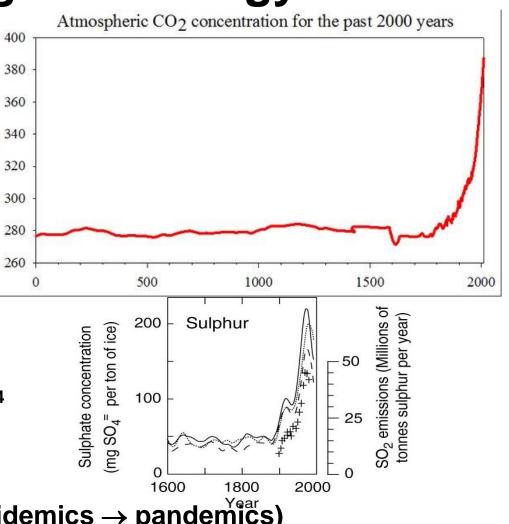
On average 700 tons of CO₂ stored per ha



CO₂ concentration (ppm)

Climate factors

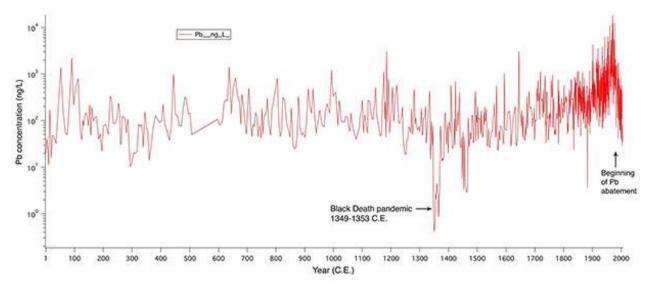
- 4. Anthropogenic impact (since romain empire)
- a) CO_2 emission rate[†] by fossil fuels, deforestation
- b) Sulfate aerosol emission
- c) Black carbon on snow
- d) Tropospheric ozone
- e) CH₄ emission from livestock, rice cultivation, waste dumps, natural gas production (leakages)
- f) N₂O emission from fertilization, deforestation, biomass burning
- g) Emission of fluorine compounds: HFC, SF₆, NF₃, CF₄
- h) Building development and urban climate
- i) Drainage of peatlands
- j) Lead emission: formation of aerosols and clouds
- k) CO_2 emission rate \downarrow by globalisation of diseases (epidemics \rightarrow pandemics)





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

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



Causes of the decrease of Pb concentration in air 1350 Plague epidemic 1460 Further epidemic 1885 World economic crisis **Consequences of increased Pb conc. in air:**

- Increased aerosol formation: Clouds (albedo)
- neurotoxic effects
- hypertonia (today 8-11 ppm Pb in the skeleton)
- 1966: 102[.]10³ t Pb aerosol northern hemisphere 200 ng Pb per kg snow (Greenland)

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



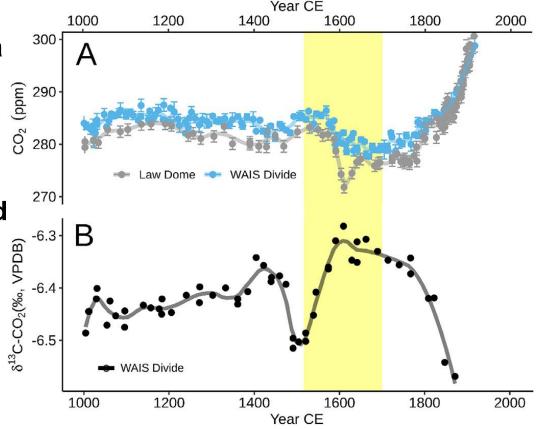
4k) Anthropogenic influences: CO_2 emission rate \downarrow by epidemics due to migration

1492 Arrival of Europeans in Latin America

1500 - 160055 Mill. indigenous people died due
to European epidemics
 \rightarrow Secondary succession of rain
forest on 56 mill. hectares of farmland16107-10 ppm decline in atmospheric
 CO_2 concentration

1650 - 1850 Additional global cooling by 0.15 K "Little ice age" \rightarrow hunger in Europe

Lit.: Quaternary Science Reviews 207 (2019) 13





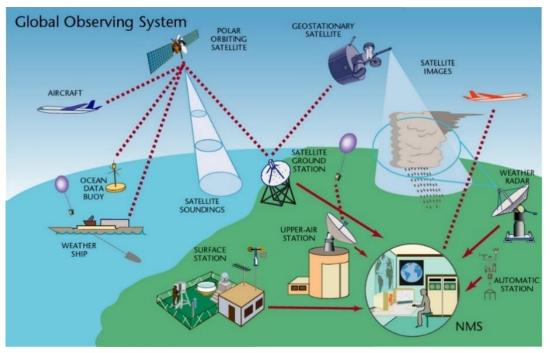
Summary of climate factors

ATMOSPHERE	OCEAN	LAND	
SURFACE	PHYSICS	Above-Ground Biomass	
Precipitation	Ocean Surface Heat Flux	Albedo	
Pressure	Sea Ice	Anthropogenic Greenhouse Gas Fluxes	
Surface Radiation Budget	Sea Level	Anthropogenic Water Use	
Surface Wind Speed and Direction	Sea State	Fire	
Temperature	Sea Surface Salinity	Fraction of Absorbed Photosynthetically Active Radiation	
Water Vapour	Sea Surface Temperature	(FAPAR)	
UPPER-ATMOSPHERE	Subsurface Currents	Glaciers	
Earth Radiation Budget	Subsurface Salinity	Groundwater	
Lightning	Subsurface Temperature	Ice Sheets and Ice Shelves	
Temperature	Surface Currents	Lakes	
Water Vapour	Surface Stress	Land Cover	
Wind Speed and Direction	BIOGEOCHEMISTRY	Land Surface Temperature	
COMPOSITION	Inorganic Carbon	Latent and Sensible Heat Fluxes	
Aerosols Properties	Nitrous Oxide	Leaf Area Index	
Carbon Dioxide, Methane and other Greenhouse Gases	Nutrients	Permafrost	
Carbon Dioxide, Methane and other Greenhouse Gases	Ocean Colour	River Discharge	
Cloud Properties	Oxygen	Snow	
Ozone	Transient Tracers	Soil Carbon	
	BIOLOGY/ECOSYSTEMS		
Precursors	Marine Habitat Properties	Soil Moisture	
	Plankton		



Climate reconstruction \Rightarrow Measurement techniques

- Earth-orbiting satellites, remote meteorological stations, and ocean buoys are used to monitor present-day weather and climate
- Paleoclimatology data from natural sources like ice cores, tree rings, corals, and ocean and lake sediments
- Isotope analysis of water: H₂¹⁸O enriches in the liquid phase, i.e.¹⁶O/¹⁸O ratio of water is temperature dependent
- \Rightarrow Determination of ¹⁸O in foraminifere, mollusca, and CaCO₃ sediments



Source: WMO: https://public.wmo.int/en/programmes/global-observing-system



Photo credit: Ludovic Brucker



Year

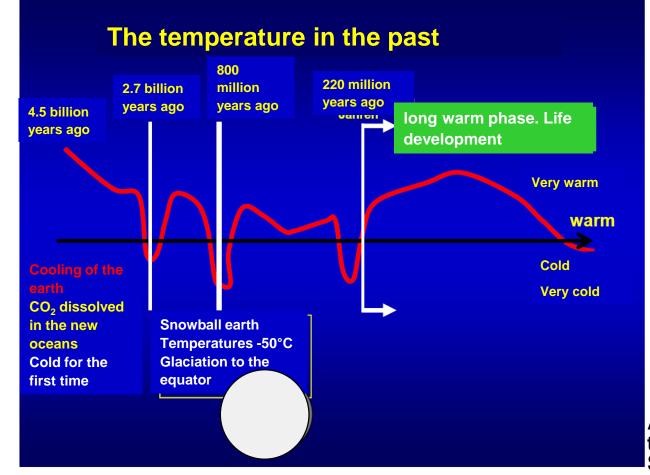
2. The earth's climate and the global energy balance

Climate reconstruction \Rightarrow Time scales

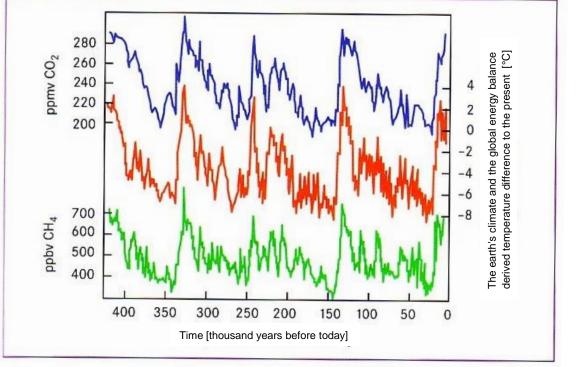
Mechanism	time scale [years]	
Solar radiation		
Fusion power	10 ⁹	
Orbital parameters	10 ⁴ - 10 ⁶ "Baur" temperature	series
Sunspot cycles	10 - 1000 for Central Europe 17	61 - 2010
Albedo of the Earth All	All ^{2,5} Warming is striking —	
Plate tectonics		
Mountain building, continental drift, ocean currents	10⁶ - 10⁸	
Greenhouse effect		
CO ₂ , CH ₄ , H ₂ O, N ₂ O, CF ₄ , NF ₃ , SF ₆ , FCKW, …	Personal and the second	1947 1947 1947 1959 1959 1971 1971 1971 1983 1983 1983 1983 1983 1986 1986 1986 1986 1986 1986 1986 1986
Aerosols		
Volcanoes, air pollution	1 - 10	1
Land use	1 - 100	



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



CO₂, CH₄, and temperature fluctuations over the past 420,000 years (\rightarrow 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)



Earth

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

Venus



2.61 kW/m² Albedo = 0.76 \rightarrow T_E = 232 K 96% CO₂ + 3% N₂ + SO₂ + H₂O + Ar (ppms)



 $\begin{array}{l} 1.37 \ \text{kW/m^2} \\ \text{Albedo} = 0.29 \rightarrow \text{T}_{\text{E}} = 255 \ \text{K} \\ 78\% \ \text{N}_2 + 21\% \ \text{O}_2 + 0.9\% \ \text{Ar} \\ + \ \text{CO}_2 + \text{H}_2\text{O} + \text{CH}_4 \ (\text{ppms}) \end{array}$

Mars



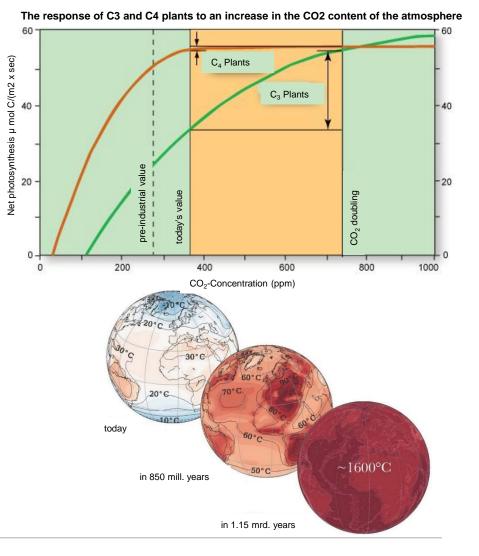
 $\begin{array}{l} 0.59 \ \text{kW/m^2} \\ \text{Albedo} = 0.15 \rightarrow \text{T}_{\text{E}} = 213 \ \text{K} \\ 95\% \ \text{CO}_2 + 3\% \ \text{N}_2 + 1.5\% \ \text{Ar} \\ + \ \text{H}_2 \text{O} \ (\text{ppms}) \end{array}$

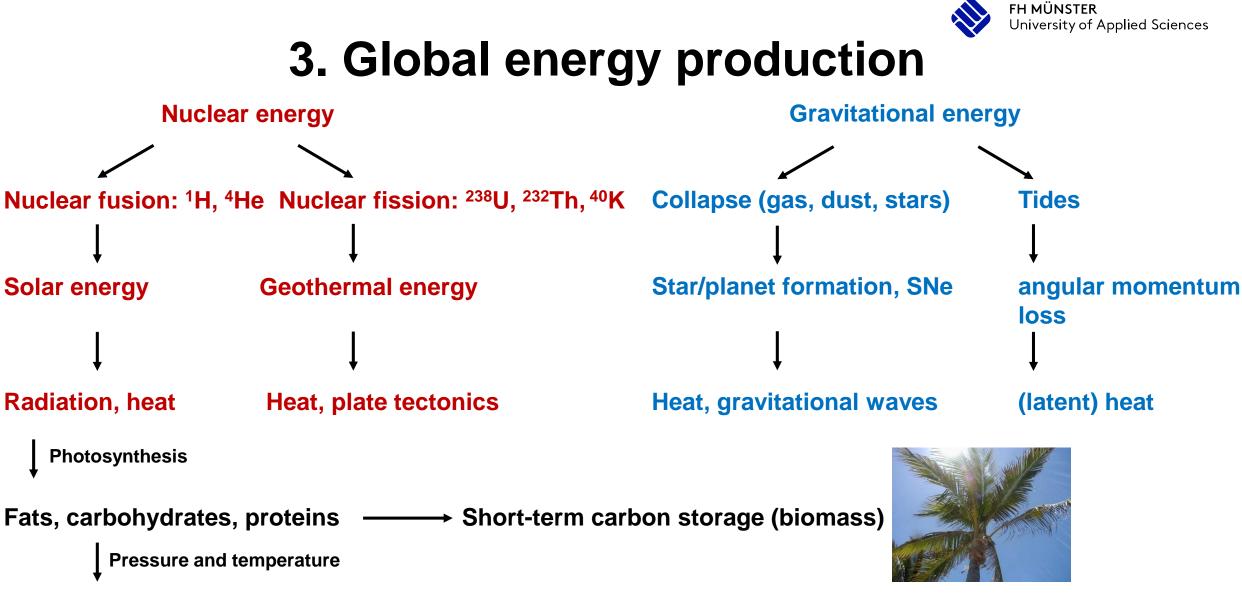
93 bar \rightarrow T_{real} = 740 K1 bar \rightarrow T_{real} = 288 K5.6 mbar \rightarrow T_{real} = 225 K715 Mio. years ago: strong CO2Biology: H2O(I) is solvent and H2 source5.6 mbar \rightarrow T_{real} = 225 Kincrease (earlier: T_{real} ~ 323 K!)H2O \rightarrow 4 H⁺ (ATP) + 4 e⁻ (NADH) + O2[↑]Note: Ar origins from ⁴⁰K decay



Far future (10⁶ - 10⁹ years) of the earth climate

- Development of a CO₂ deficit
 - Biosphere will continue to remove CO₂ from the atmosphere as a reservoir and consumer.
 - Plate tectonics as driver of silicate-carbonate cycle will slow, causing CO₂ consumption to exceed replenishment.
 - Biological limit of photosynthesis at about 25 ppm $CO_2 (\rightarrow C_4 \text{ plants})$
- Further increase of solar radiation intensity
- Loss of the hydrosphere (oceans)
- Fission of carbonate rocks: (Mg,Ca)CO₃ → (Mg,Ca)O + CO₂





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



3. Global energy production

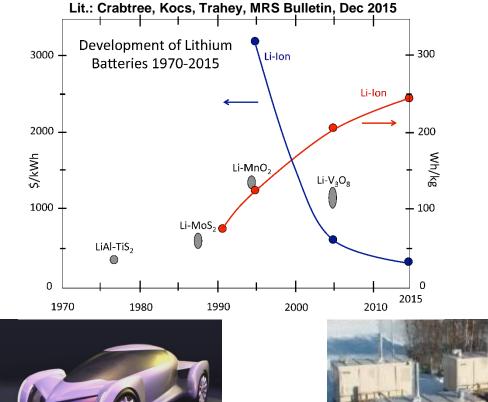
power plants?

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 plan
Antimatter annih.	90 PJ/kg	"Science Fiction"

For comparison: Fossil fuels

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







Decentralized & mobile Decentralized & stationary batteries, NH₃, H₂, EtOH batteries, CH₄, MeOH, EtOH



3. Global energy production

Problem of burning fossil carbon reservoirs

Primordial CO₂ (1.47·10⁹ t) \rightarrow O₂ (sediments: Fe²⁺ 10⁻⁷ mol/l in ocean with 1.332·10²¹ l water)

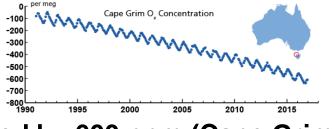
 \rightarrow 4 Fe(OH₃) \downarrow (1.42·10¹⁰ t) + C (4.0·10⁸ t) \Rightarrow negligible!

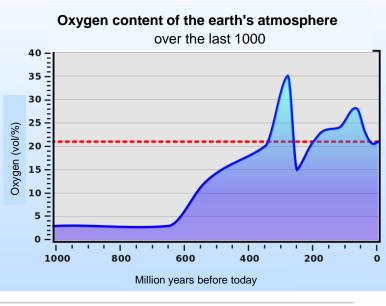
Primordial CO₂ (1.64·10¹⁵ t) \rightarrow O₂ (atmosphere: 1.19·10¹⁵ t) + C (0.45·10¹⁵ t)

CO₂ emission 2021 ~ 36.3 Gt:

- Since 1985 O₂ 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....







Verlag , München, 2009

6. Auflage, Hanser

3. Global energy production

Future options	s (excluding fossil fue	els) for meeting	anthropogenic energ	gy demand.	eme,
	 Solar radiation:UV/Vis and IR Wind 		 Photovoltaics Solar collectors Solar ovens Wind turbines 		nerative Energiesyst
	 Water cycle Ocean currents 		 Wave power plants Hydroelectric 		nera
Sun	• Waves		power plants		Reger
Moon	Biomass		 Biogas plants 		aschning,
	• Tidal range		 Tidal power plants 		Quasch
CLA-M	Geothermal Energy	And the owned to be	Heat pumps	52.53	Volker
		a Mate shawa Stills be a	 Geothermal power plants 		.ce: V
Earth	Geothermal energy (int	ternal heat) = 996	•		Sour

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

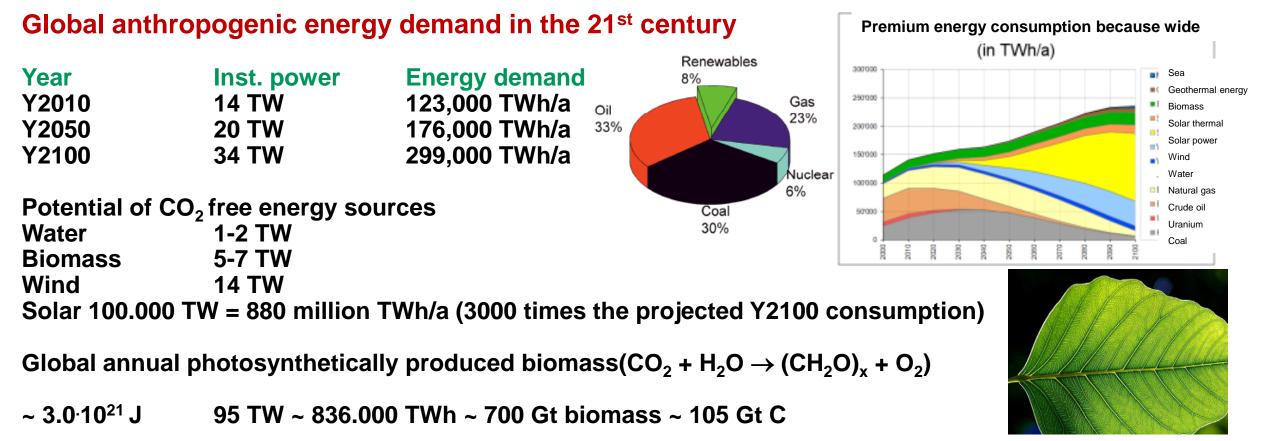
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Photosynthesis based

on [Mn₄Ca] clusters

3. Global energy production



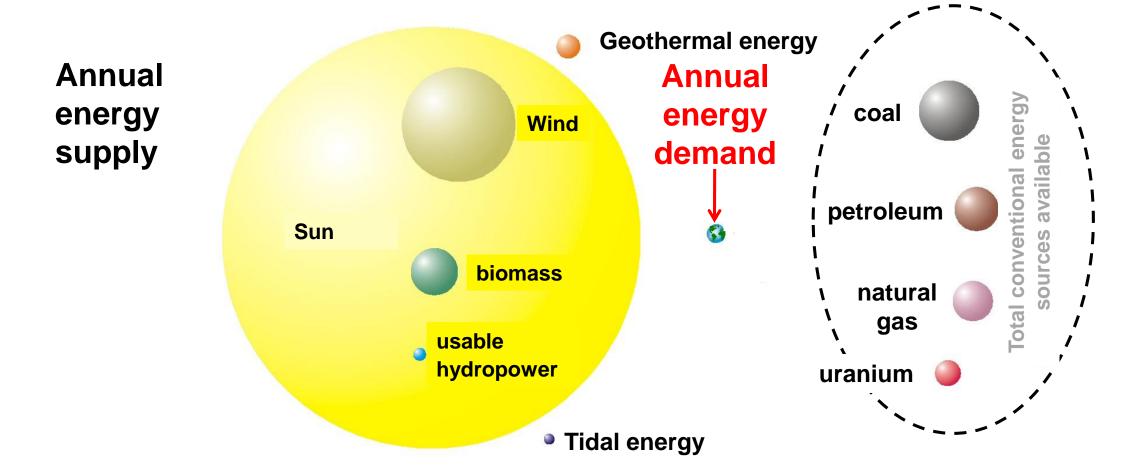
biomass total ~ 560 Gt C/a (Wikipedia)

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

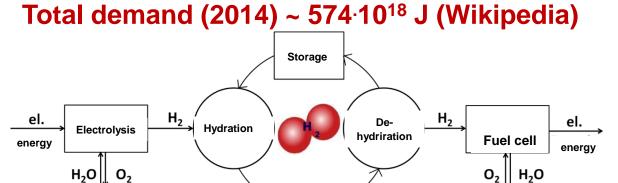


3. Global energy production

Globally generated altern. Energy (2016) 80.5-10¹⁸ J

- Biomass
- Hydroelectric power
- Geothermal
- Photovoltaics (PV)
- Solar thermal power
- Wind power
- Tidal power

56.5.10¹⁸ J 14.6.10¹⁸ J 3.37.10¹⁸ J 1.18.10¹⁸ J 1.41.10¹⁸ J 3.45.10¹⁸ J 0.004.10¹⁸ J



Storage

Functional materials for a green or sustainable energy economy require metallic raw materials

- Magnetics
- PV materials
- Electrocatalysts
- Photocatalysts
- Fuel cells
- Battery materials
- Alternative fuels

 $SrFe_{12}O_{19}$, $SmCo_5$, Sm_2Co_{17} , $Nd_2Fe_{12}B$

- Si, CdTe, GaAs, Cu(In,Ga)S₂, perovskites APbX₃
- Co, Ni, Cu, Pd, Rh, Pt, Ir
 - TiO_2 , $SrTiO_3$, (Na,K)TaO_3:La, (Cd,Zn)S, $K_3Ta_3B_2O_{12}$, GaN:Zn,O
 - ZrO_2 : Y(Ca,Sc), BaZrO₃: Y, CeO₂:Gd, LaGaO₃
 - Li₂CO₃, cobaltates, carbon,
 - H_2^{-} , CH_4^{-} , LPG, MeOH, EtOH, Mg, AI, dibenzyltoluene, N-ethylcarbazole



3. Global energy production

Area required for the consumption of Germany (~ 360,000 km²)

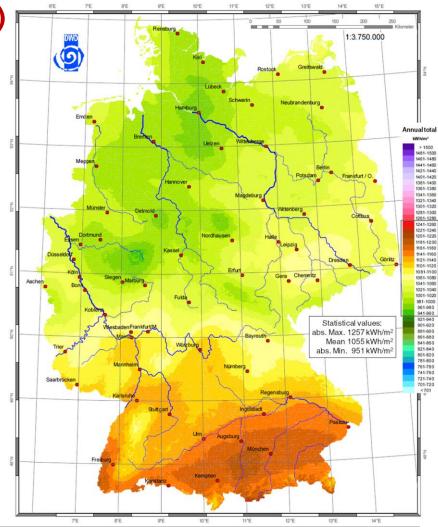
Biogas	45000 km ²	~ 12.5%			
Wind energy	•	~ 2% veen masts can be agriculture or similar)			
BI 4 I 4 I		• • •			

Photovoltaic $1800 \text{ km}^2 \sim 0.5\%$

Total area of streets $15800 \text{ km}^2 \sim 4.4\%$

Consequently:

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





3. Global energy production

Photosynthesis in green plants



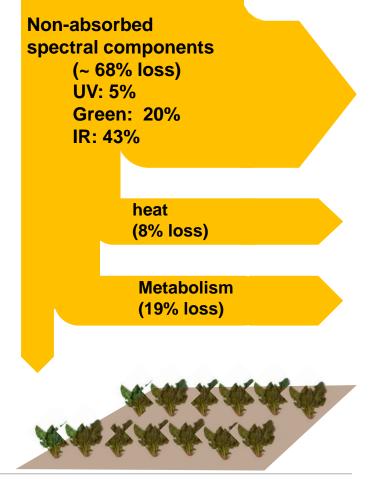
Light energy ~ 1 kW/m²

- → Chemical energy $6 \text{ CO}_2 + 6 \text{ H}_2\text{O} \rightarrow \text{ C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2$ $\Delta \text{G}^0 = 2872 \text{ kJ/mol}$
 - η = 100%: 1.25 mol or 225 g biomass/m²h
 - η = 5%: 0.063 mol oder 11.3 g biomass/m²h

Cultivated cropland

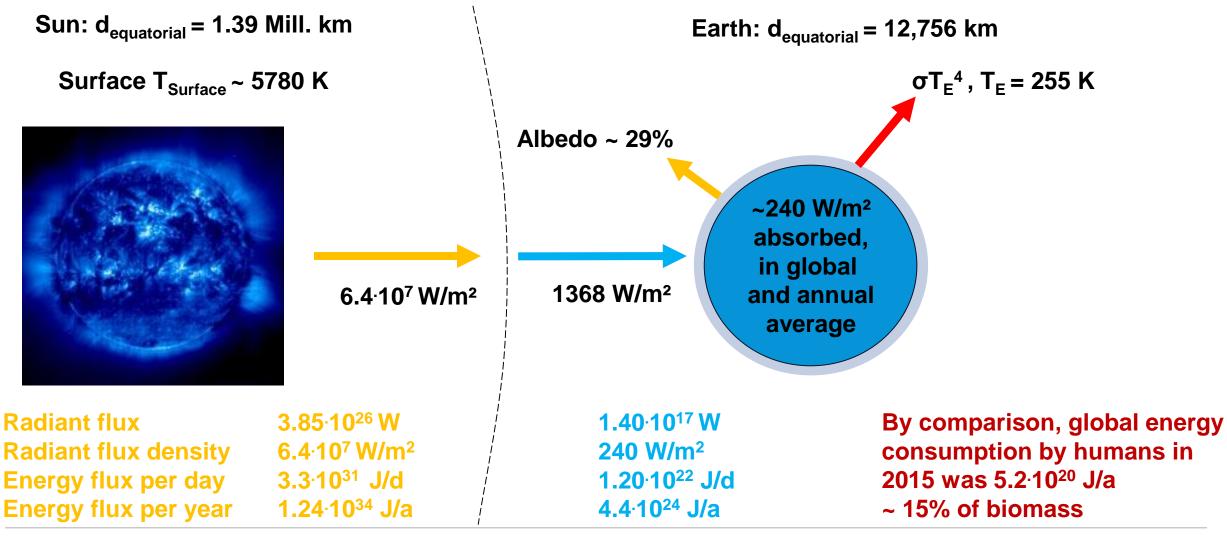
- \rightarrow ~ 650 g biomass/m²a (Wikipedia)
- \rightarrow 0.074 g biomass/m²h
- \rightarrow 0.020 mg biomass/m²s
- \rightarrow $\eta \sim 0.03\%$ (Biomass energy production)

Solar energy (100%)





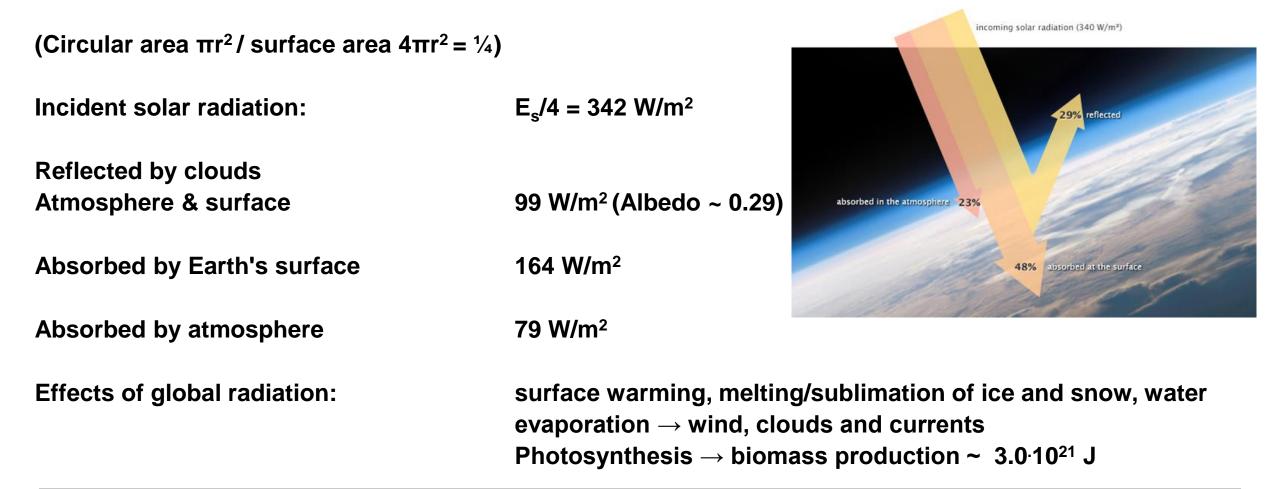
4. Solar power generation

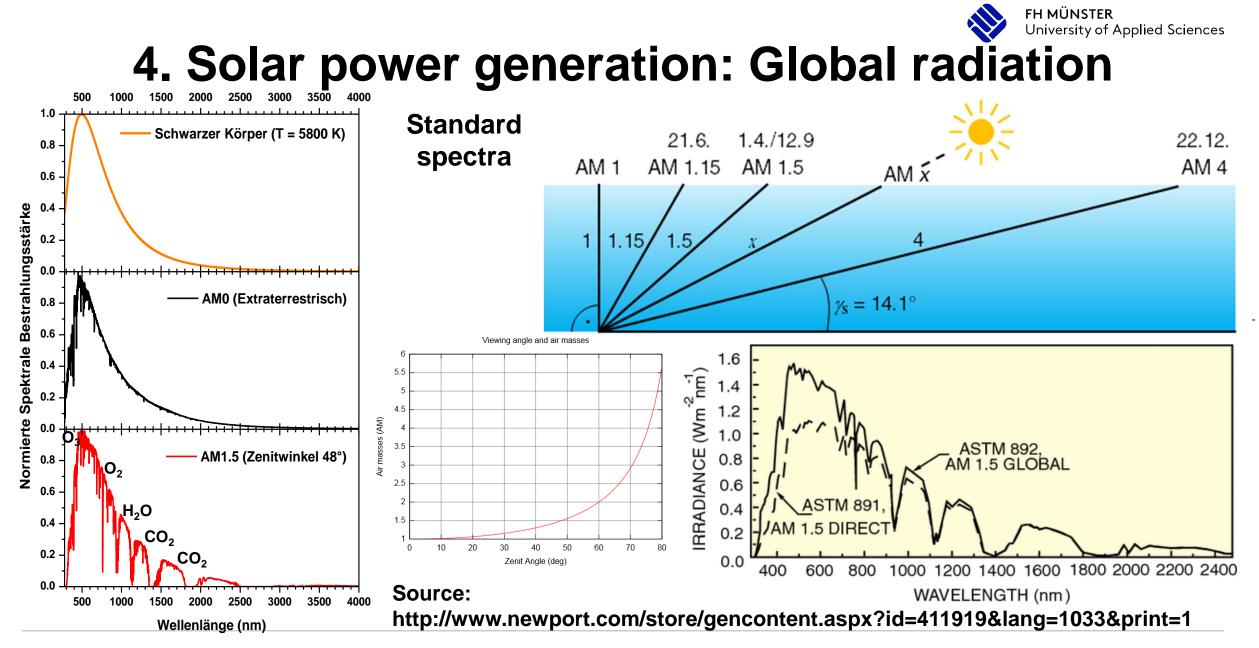




4. Solar power generation: Global radiation

Extraterrestrial solar constant $E_s \sim 1368 \text{ W/m}^2$







4. Solar power generation: Global radiation

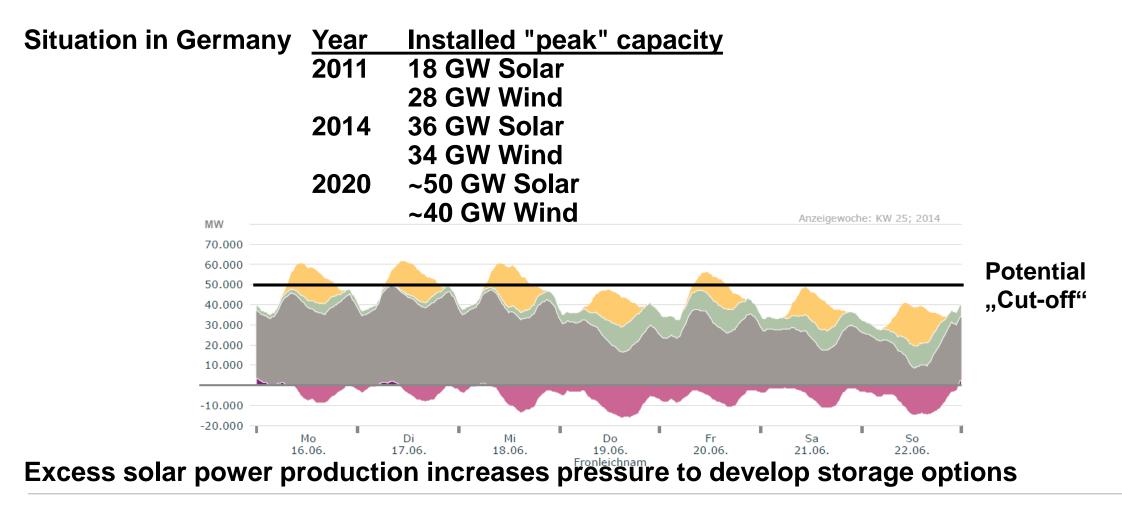
Standard spectra in numbers

Irradiation situation		Standard		Irradiance (Wm ⁻²)				
				Total	25	0 - 2500 nm	250 -	1100 nm (~ Si PV)
		WMO Spectrum		1368				
AM 0		ASTM E 490		1353		1302.6		1006.9
AM 1	CIE Publication 85, Table 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 n	m	400 – 500 nm	5	600 – 600 nm		600 - 700	nm	> 700 nm
37.8 W/r	n²	130.4 W/m ²		144.6 W/m ²		134.0 W/r	n²	26.2 W/m ²
5.3%		18.2%		20.2%		18.7%		37.6%



4. Solar power generation: Global radiation

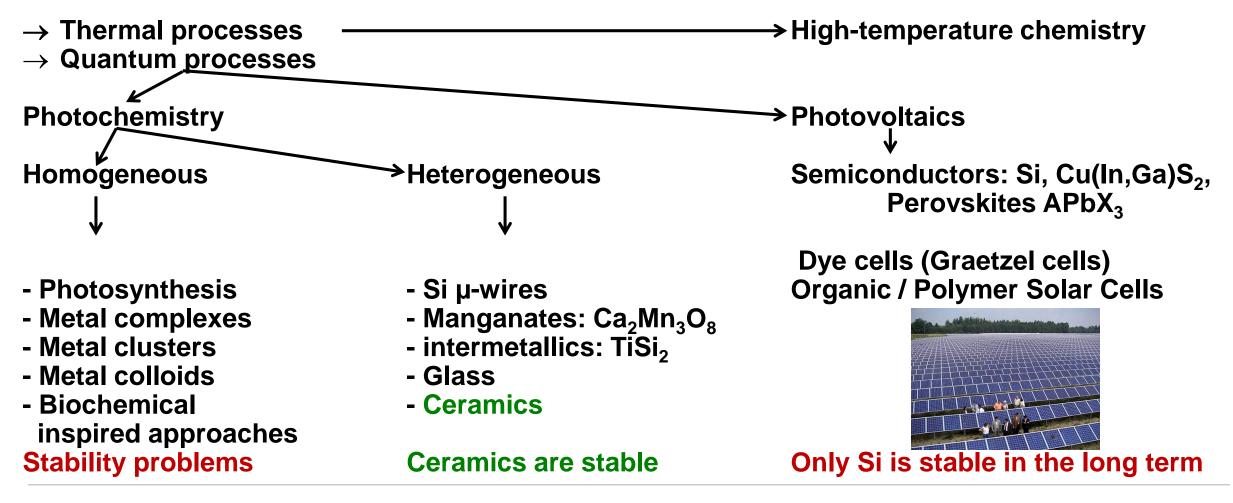
Solar and wind energy production in Germany and worldwide is growing continuously





4. Solar power generation: Options

For conversion





4. Solar power generation: Established solutions

Solar cells

ATP

NADPH

- Solar thermal Light \rightarrow thermal energy Solar collectors
- Photovoltaics (PV) Light → electrical energy
- Photosynthesis Light \rightarrow chemical energy Plants Light reaction: Homogeneous photolysis of water $2 H_2 O \rightarrow O_2^{\uparrow} + 4 H^+ + 4 e^-$

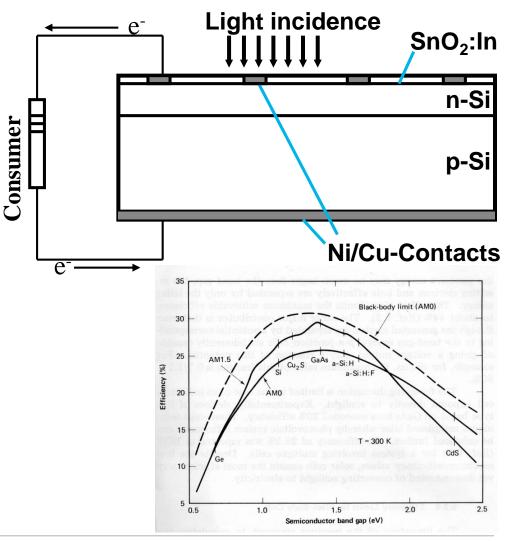
Dark reaction: Synthesis of carbohydrates: $CO_2 + 2 H^+ + 2 NADPH \rightarrow (CH_2O)_x + H_2O + 2 NADP^+$

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 ₂ S	1.2		
• c-Sī	1.107		
• 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%.

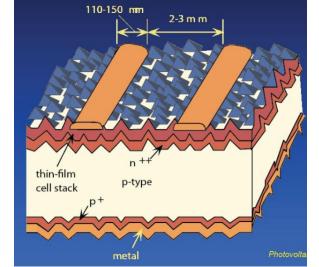


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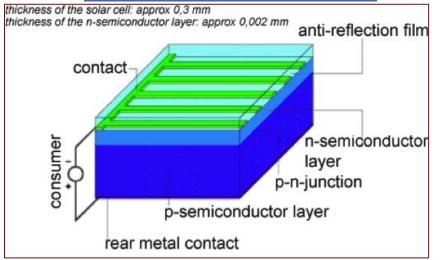
Solar cells from 1954 to today....

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





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Solar cell generations by material

Si-cells, amorphous, polycrystalline, monocrystalline 1st generation solar cells 8%, 15 - 22%

Lit.:

Thin film) CdTe, GaAs, Cu(In,Ga)(S,Se)₂

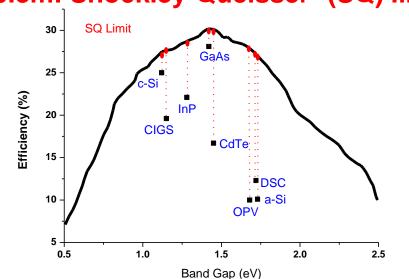
Dye cells, organic and perovskite cells

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



M.B. Prince, JAP 26 (1955) 534

- J. Loferski, JAP 27 (1956) 777
- *W. Shockley, H.J. Queisser, JAP 32 (1961) 510



2nd generation solar cells 12 - 25%

3rd generation solar cells 2 - 3%

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Efficiency η

Solar cells (Grätzel cells) **Incident** light **e**⁻ Glass substrate with SnO_2 :F (0.5 µm) TiO₂-nanoparticle membrane (5 - 10 μm) R +`e∓ Load **Electrolyte solution with redox mediator** R + e Glass substrate with SnO_2 :F (0.5 µm) & Pt coating (2 µm) **e**⁻

TiO₂ is the ideal catalyst for charge separation, but absorbs only UV radiation

→ Sensitization required

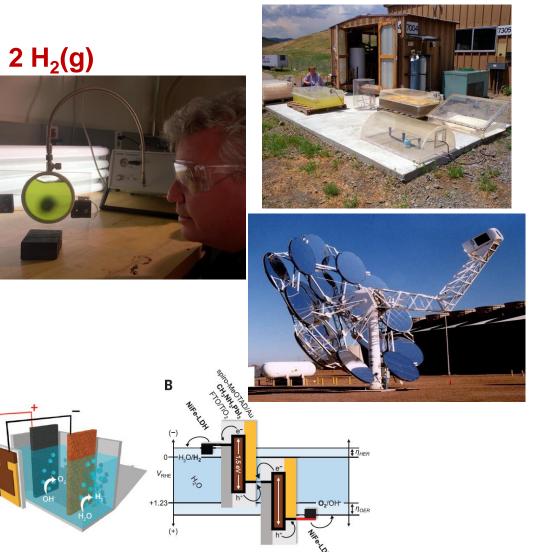
Ways to split water according to $2 H_2O(g) \rightarrow O_2(g) + 2 H_2(g)$

Α

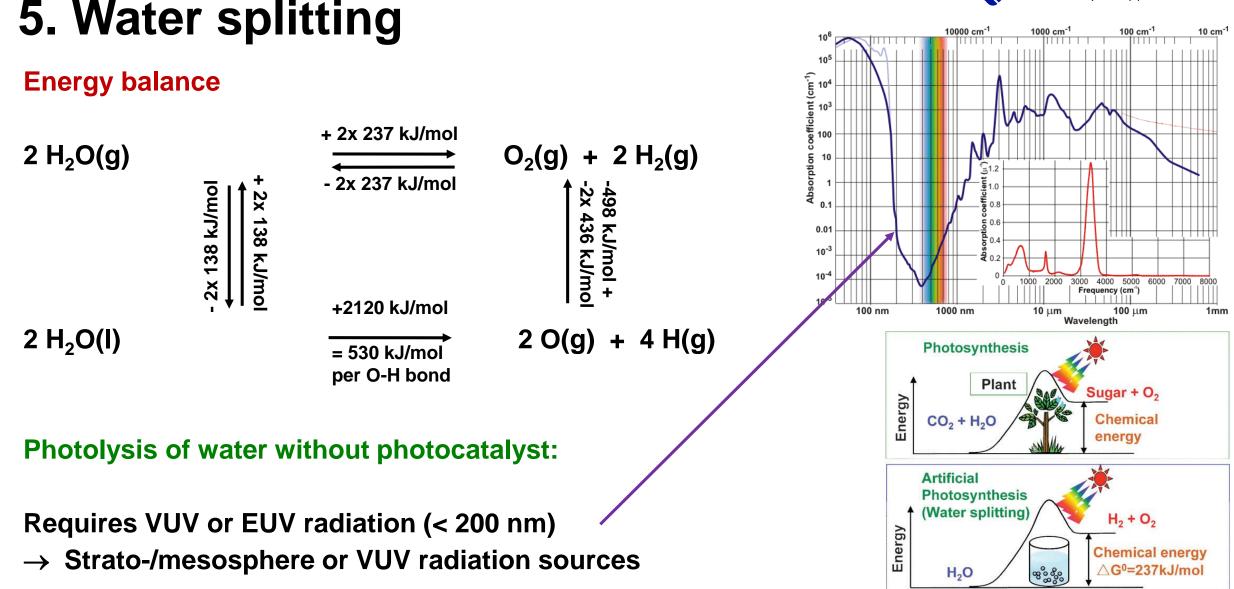
- Photosynthesis
 - Plants (fast growing)
 - (micro)algae
- Electrolysis
- Thermolysis
- Plasmalysis
- Sonolysis
- Photolysis
- Photocatalysis



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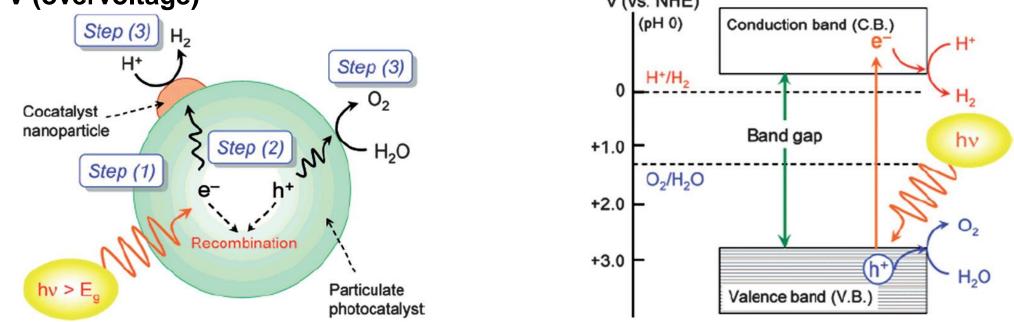
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By photocatalysis with semiconductors

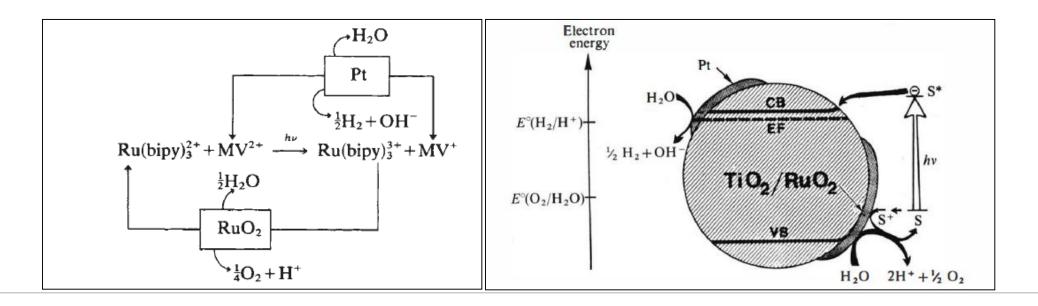
- First system by A. Fujishima und K. Honda (Nature 238 (1972) 38)
 → TiO₂ with Pt as co-catalyst
- Water splitting possible from about 1000 nm (1.23 eV), but in real systems the voltage is higher > ~1.8 V (overvoltage)





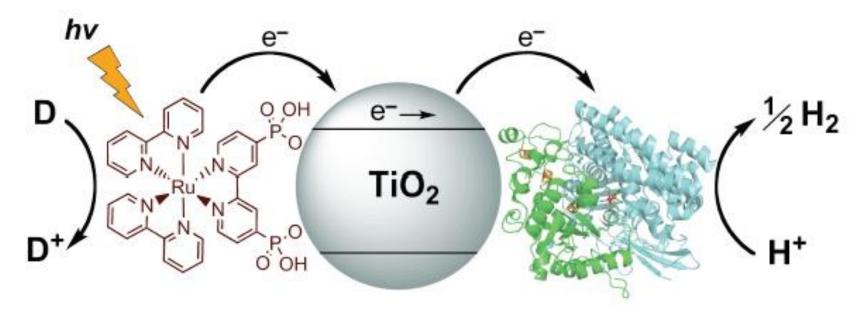
By photocatalysis with semiconductor and a sensitizer

- First system with a sensitizer by Michael Graetzel (Nature 289 (1981) 158)
 - \rightarrow TiO₂ with Pt and RuO₂ as co-catalysts and [Ru(bpy)₃]²⁺ and methyl viologen as sensitizers (antennas)
- Synthesis of Pt nanoparticles starting from H₂PtCl₆ and citrate





By photocatalysis with complexes and enzymes



Schematic of light-induced H₂ production with D [NiFeSe]-H bound to TiO₂ nanoparticles sensitized with a Ru²⁺ complex in the presence of an electron donor D as a "sacrificial cathode"

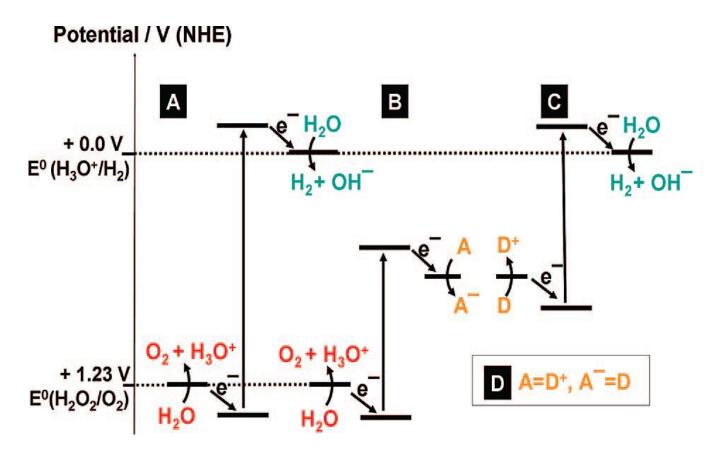
Absorption of light ($\lambda > 420$ nm) excites the photosensitizer [Ru(bipy)₃]²⁺ which injects electrons intoTiO₂

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



Photocatalytic processes with semiconductors - options

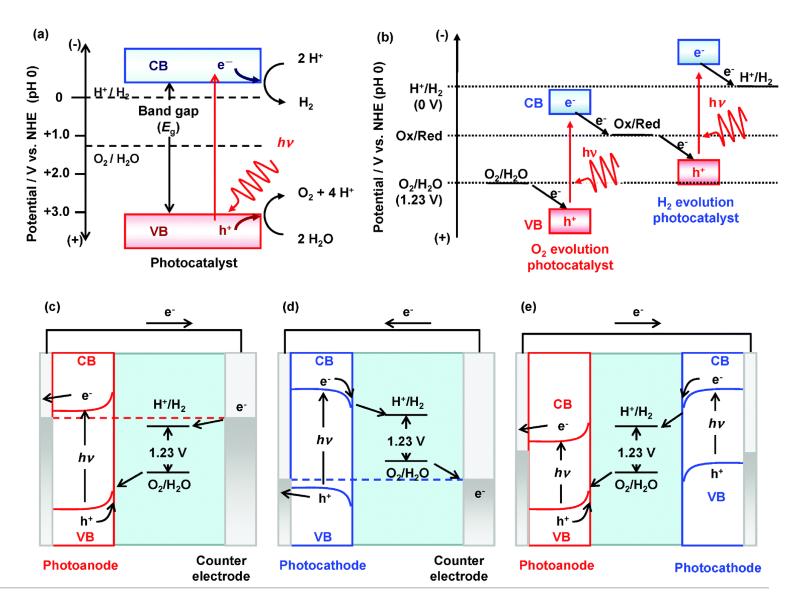
- A: Simple semiconductor
- B: Simple semiconductor with an electron acceptor→ O₂
- C: Simple semiconductor with one electrondonor \rightarrow H₂
- D: Combination of B and C (tandem cell)



Problem: Powder in solution \rightarrow Oxyhydrogen formation (explosive gas)



Photocatalytic processes with semiconductors - options





5. Water splitting: Materials

Requirements for a suitable 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 (~3.0 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)

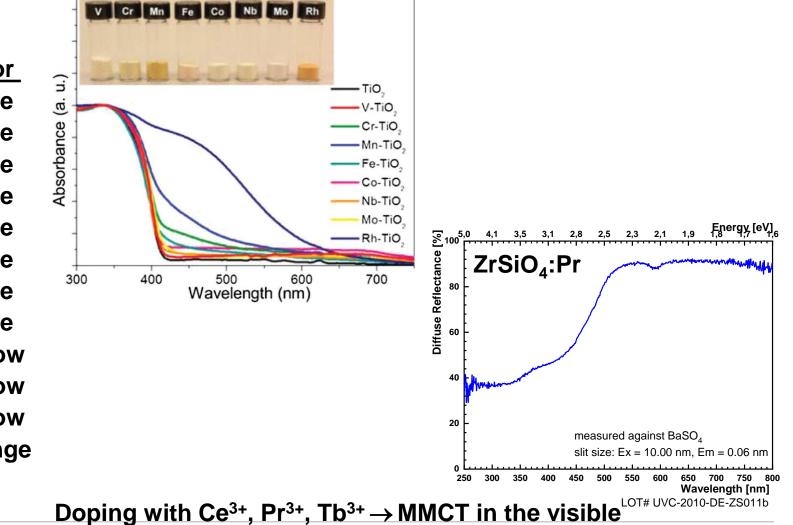
In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energy levels where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of 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

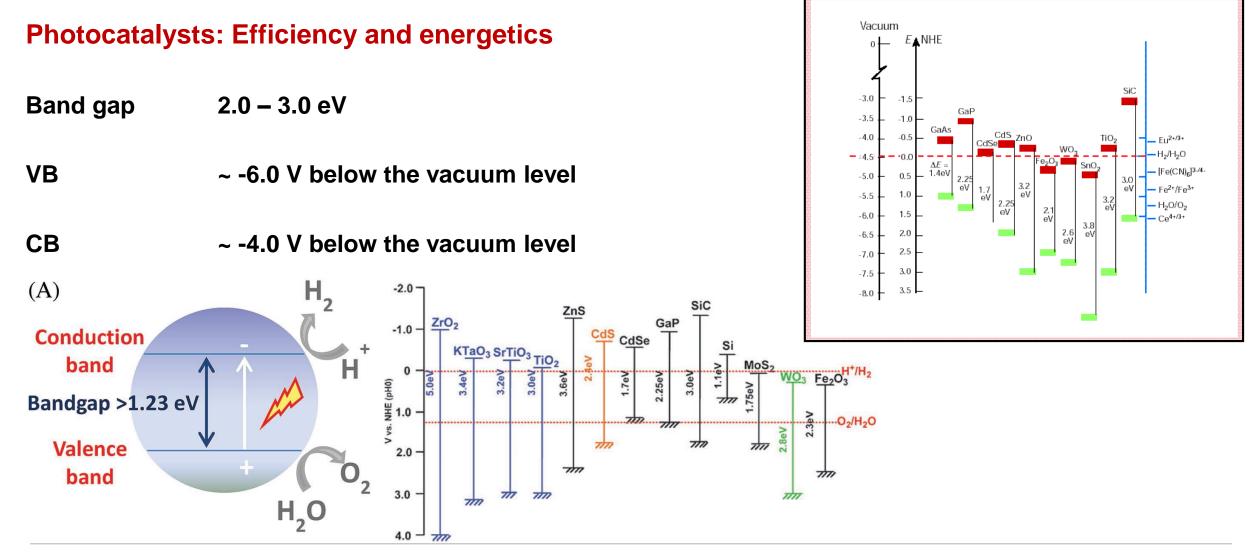
Photocatalysts with high stability?

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
SrTiO₃	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 ₂ O ₃	2.0	red
InN	1.9	red





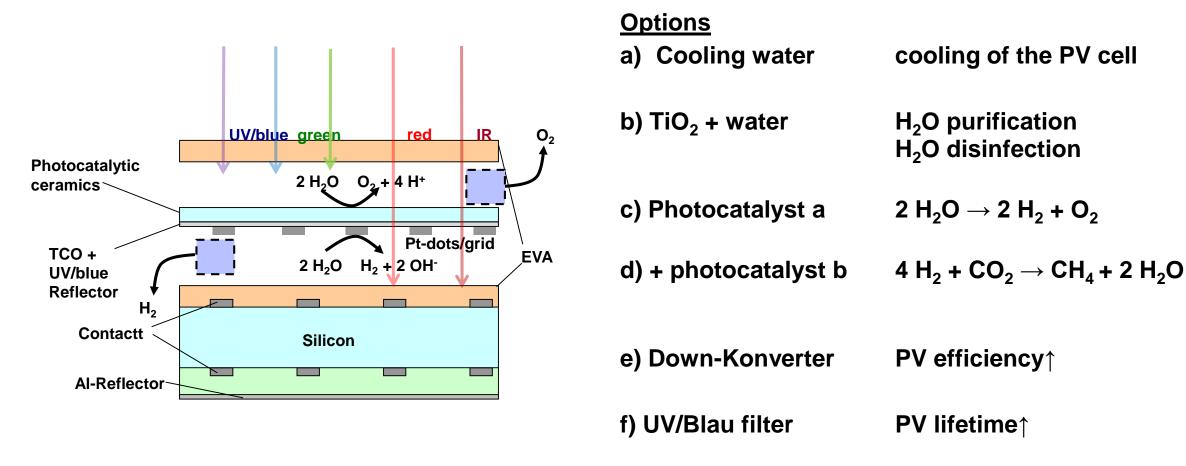
5. Water splitting: Materials





5. Water splitting: Vision

Development of a tandem cell combining PV and other options!

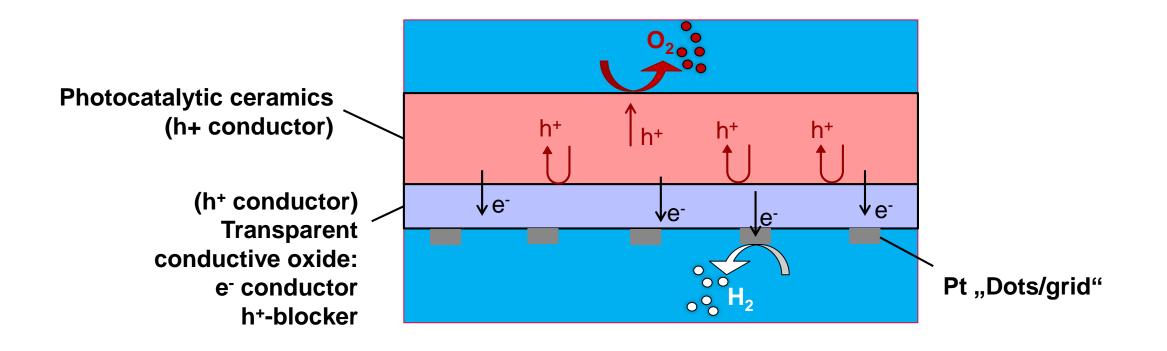


Lit.: T. Jüstel et al., German Patent Application, Energy Conversion System, DE102014107268



5. Water splitting: Vision

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

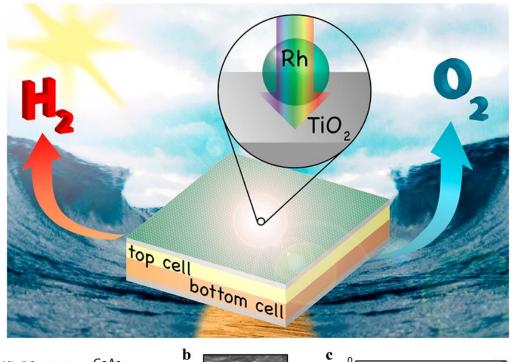


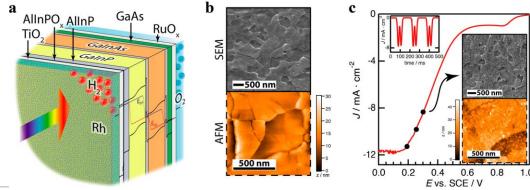


5. Water splitting: State of the art

Recent success

- Charge separation and e⁻ / h⁺ conduction by epitaxially deposited AllnP, AllnPO layers
- Rh on TiO₂ 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, CO₂ 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.

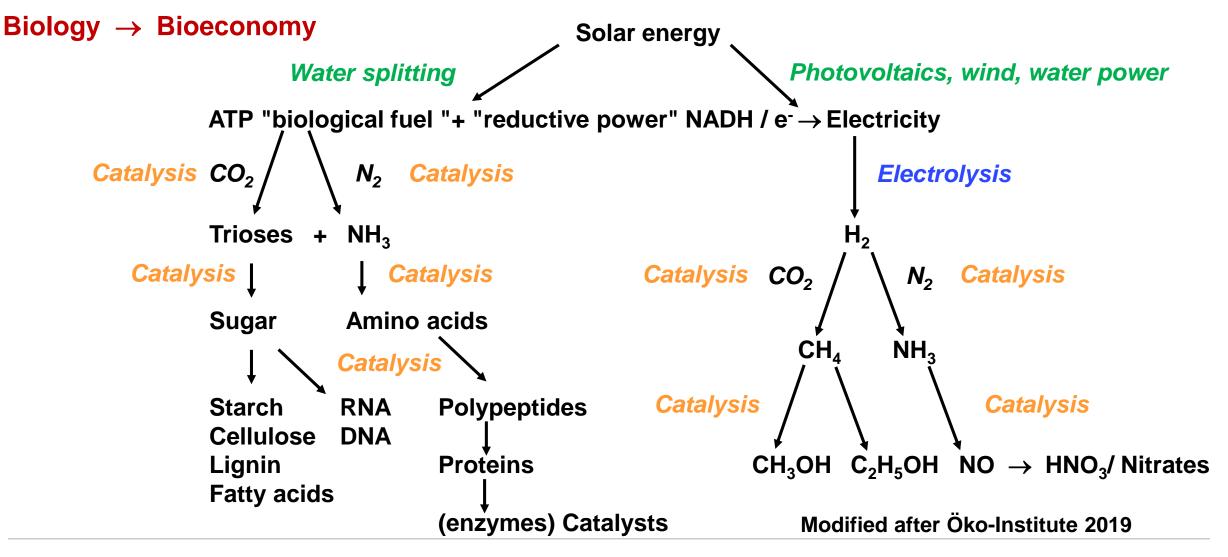
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- Compared to the hydrogen heating value, about one third of the electrical energy is lost in this process.
- Favorites for hydrogen storage are LOHCs (Liquid Organic Hydrogen Carriers), primarily dibenzyl toluene (DBT).

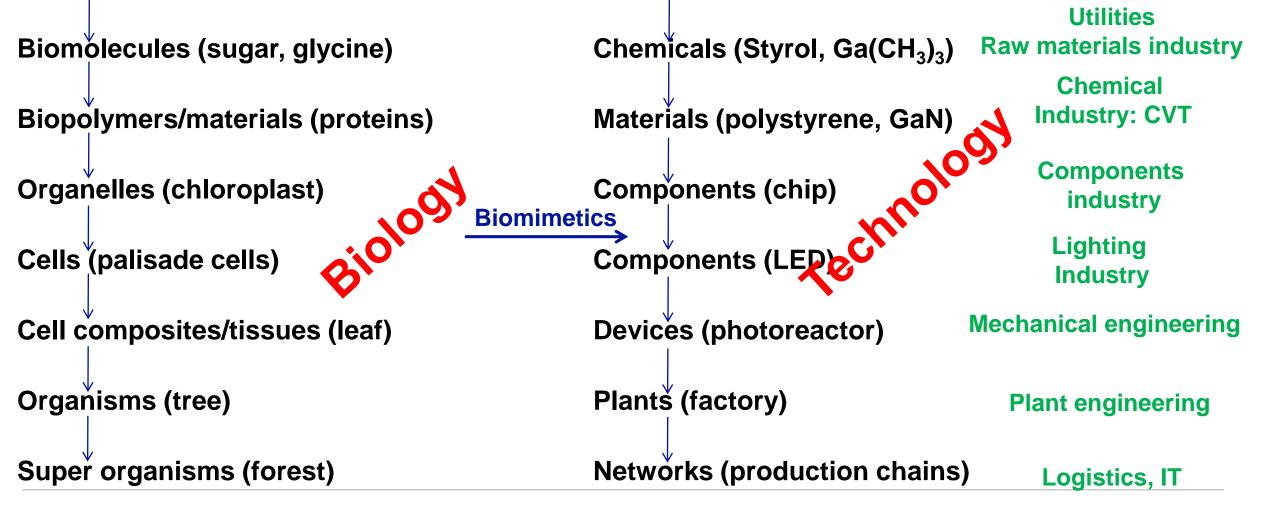
Source: Prof. Jochen Fricke, Cluster Energietechnik, October 2018







Energy (light, fossile fuels) + resources (H₂O, CO₂, N₂, methan, minerals, ores)





6. Outlook: New fuels

- Globally, shipping is responsible for emitting about 1 billion tons of CO₂ per year, which is almost 3% of total man-made CO₂ 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 \rightarrow 2026 Car ferries \rightarrow 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 H₂ (700-1000 bar, 20 °C)
- Heating value of ammonia is 5.2 kWh/kg
 (~ 50% of gasoline, diesel,....)
- ✓ Heating value of NH₃ 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

Pathways to ammonia NH₃

- Haber-Bosch (α-Fe)
- V-nitrogenases (Feⁿ⁺⁾
- Mo-nitrogenases (Feⁿ⁺) 2 N₂
- Heterogeneous photocatalysis up-conversion induced photoionization using doped semiconductor materials such as LaOF $e^{-} + N_2 \rightarrow (N_2)^{-}$ $(N_2)^{-} + H_2O \rightarrow OH^{-} + N_2H$

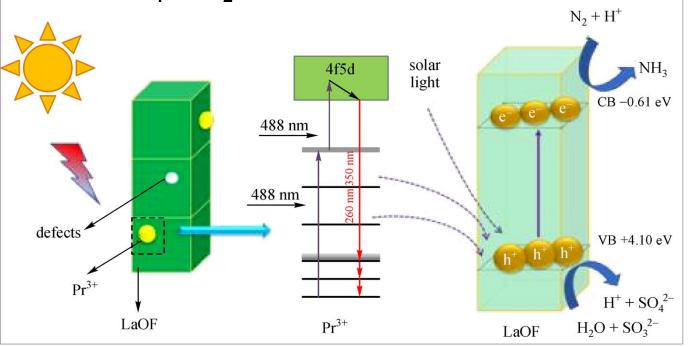
$$2 N_2 H \rightarrow N_2 H_2 + N_2$$
$$2 N_2 H_2 \rightarrow N_2 H_4 + N_2$$

 $3 N_2 H_4 \rightarrow 4 N H_3 + N_2$

 $N_2 + 3 H_2 \leftrightarrows 2 NH_3$ 2 N₂ + 14 H⁺ + 12 e⁻ \(\Gamma 2 NH_4^+ + 3 H_2)

 $2 \text{ N}_2 + 10 \text{ H}^+ + \underline{8 \text{ e}^-} \Rightarrow 2 \text{ NH}_4^+ + \text{H}_2$

450 - 550 °C, 250 - 350 bar RT, 1 bar RT, 1 bar

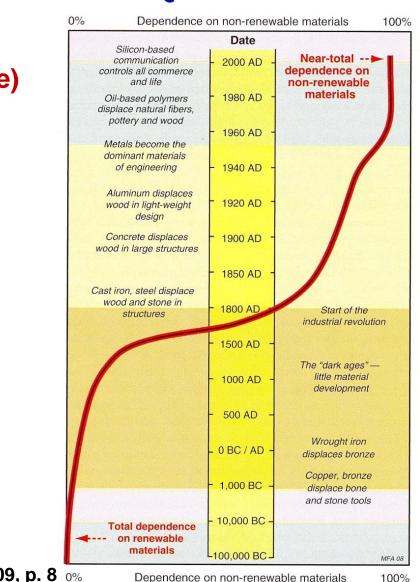


Lit.: LaOF:Pr Microwave hydrothermal synthesis for photocatalytic N fixation, Frontier Mater. Science 14 (2020) 43

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 nonregenerable materials recycling rate < 10%</p>

Source: M.F. Ashby, Materials and the Environment, Elsevier (Butterworth-Heinemann), 2009, p. 8 0%



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



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

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Recycling: Pressure to act

Pollution of the atmosphere

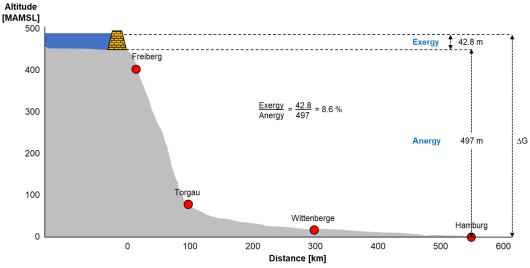
- Climate-active greenhouse gases: CO₂, CH₄, N₂O, SF₆, NF₃, FKW, and so on
- Aerosols and dust ("metals", e.g. Pb or Hg)
- Acid rain: NO_x, SO₂, HCI
- Pollution of the hydrosphere
 - Micro- and nanoplastics
 - Metals (Cu, Cd, Hg, Sn,), nitrate and phosphate
 - Micropollutants: Hormones, drugs, cosmetics, radioactive substances,
- Pollution of the pedosphere
 - "Organic" waste
 - Micro- and nanoplastics
 - Metals: Cr, Ni, Zn, As, Cd, Hg, Tl, Pb,



Recycling: Challenges

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

- a) Energy source \rightarrow utilization \rightarrow heat
- b) Deposit(fuels/ore) \rightarrow utilization \rightarrow 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 \rightarrow natural gas (CH₄: 75% C) \rightarrow CO₂/N₂/Ar-exhaust (5% C) \rightarrow CO₂ in air (420 ppm CO₂ ~ 115 ppm C) \Rightarrow Dilution by a factor of 7000!

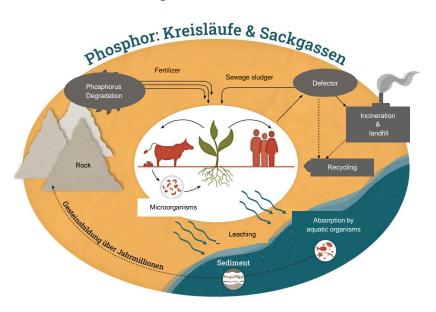
Lit.: M. Bertau, T. Jüstel, R. Pöttgen, C.A. Strassert, Chemical products: Gradients, energy balances, entropy in Appl. Inorg. Chem., De Gruyter (2022)

Recycling: The Phosphorus/Phosphate Challenge

Options for sewage sludge treatment

Crystallization or precipitation from (sewage) sludge water with

- with Mg²⁺ / NH₄⁺ \rightarrow (NH₄)MgPO₄·6H₂O \downarrow (Struvit)
- with Ca²⁺ \rightarrow CaHPO₄ \downarrow
- Thermochemical digestion
 - Incineration → Phosphate-containing slag (Ca-Si mixed phosphate)
 - Incineration \rightarrow 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 \rightarrow CaHPO₄, P₄ or H₃PO₄







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

Humans shape the environment: Green Evolution or Bioeconomy (BMBF: National strategy) Selected topics

- 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 (indoor) farming in the vertical: PV, LED, and robotics
- Current less long-term data storage DNA in glass ceramics
- Energy generation
- Recyclable fibers
- Microplastic "Challenge"
- Functional textiles without fluorine (PFAS) chemistry
- CO_2 sink
- Post-Antibiotic Age
- (Quantum) sensor technology

Artificial photosynthesis (see above) Spider silk from bioprocess engineering Microbial enzymes, e.g. PETases

Bird feather instead of fluorine, "gecko" coatings Whale protection \rightarrow "whale pump" \rightarrow c(Fe²⁺)_{surface} $\uparrow \rightarrow CO_2 \downarrow$ Skin- and eye-safe "deep UV-C" emitters or up-converters Coleoptera as smoke detectors (black pine fruit beetle), NV diamond

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Today's crisis is not a CO₂ 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

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- 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,

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 (H₂S consumed by archaea)

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- Evolutionary way out: invention of CO₂ using species → first algae & then plants transformed sunlight + CO₂ 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 CO₂ 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:

•
$$x CO_2 + y H_2O \xrightarrow{\text{Light}} x O_2\uparrow + C_x(H_2O)_y$$
 (Energy source) \rightarrow Carbon deposits + y H_2O↑
Photocatalyst
 $[CaMn_4]^{n+}$ \rightarrow Entropy export from the Earth's
envelope/biosphere by IR radiation

6. Outlook: Its Time to Act

Urgent need for the reduction of atmospheric concentration of CO₂ and other greenhouse gases

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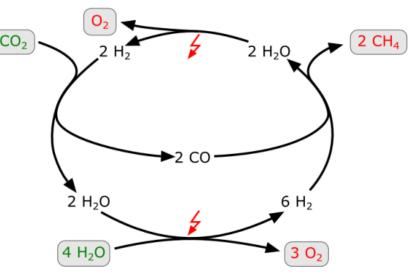
Light reaction	Dark reaction to generate storable fuels
$2 H_2 O \rightarrow 4 H^+ + 4 e^- + O_2^{\uparrow}$	x ATP + 12 NADPH + 6 CO_2 + 12 H ⁺ \rightarrow x ADP + 12 NADP ⁺ + $C_6H_{12}O_6$ + 6 H_2O_6
electrolysis of water \rightarrow H ₂ photolysis of water \rightarrow H ₂ Atmospheric CO ₂ at Mauna Loa Observatory	$H_2 + CO_2 \rightarrow HCOOH (methanol)$ 3 $H_2 + N_2 \rightarrow 2 NH_3 (ammonia)$
20 Scripps Institution of Oceanography NOAA Global Monitoring Laboratory	
)m	
UC San Diero	Keeling curve today $ ightarrow$ annual growth rate \uparrow
	$2 H_2 O \rightarrow 4 H^+ + 4 e^- + O_2 \uparrow$ $electrolysis of water \rightarrow H_2$ $photolysis of water \rightarrow H_2$ $photolysis of water \rightarrow H_3$ $D_1 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2 O_2$

6. Outlook: Its Time to Act



Establish bioeconomy to enable long-term survival of humanity on planet Earth

- Increase of power density & yield of alternative energy sources (geothermal, solar, wind and water)
- Hydrogen technology: Storage & distribution systems, fuel cells, electrical engines
- Power to gas: Conversion of electrical energy to H_2 and then methane, ethane, propane, butane
- Photochemistry, in particular photocatalytic H₂O cleavage or CO₂ sequestration and towards high value organic compounds ^{2 CO₂}
- Biodegradable and bioactive materials, especially polymers
- Materials for photocatalytic purification processes
- Technologies for safe food, pharmaceuticals & water
- Anticounter feiting to enhance product safety
- Antimicrobial materials for the post antibiotics age
- Reduction of energy consumption of data storage
- Green mining: Phago-, phyto-, proteino-, or bacteriomining
- Green chemistry: Chemistry in bioreactors with microorganisms, photochemistry including solar chemistry, sustainable chemical processes without toxic solvents
- Green farming: (Vertical) urban indoor farming to save water and without herbicides and insecticides
- Green mobility: Renewable fuels from CO₂ for automotive and aircrafts





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Thank you very much for your attention!

Questions?

<u>Web pages</u> Prof. Dr. Reinhart Job Prof. Dr. Thomas Jüstel

https://www.fh-muenster.de/eti/personal/professoren/job/index.php https://www.fh-muenster.de/ciw/personal/professoren/juestel/index.php







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

"Lectures for Future L4F"

Prof. Dr. Reinhart Job Department of Electrical Engineering Prof. Dr. Thomas Jüstel Department of Chemical Engineering

FH Münster University of Applied Sciences

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Appendix



Causes of Extinction of a Species

- habitat fragmentation
- global change (climate, atmosphere composition, dust, radioactive background)
- natural disasters (impacts, eruptions, earthquakes, wildfire, hurricanes, floods)
- overexploitation of resources (especially sweet water, phosphate)
- evolutionary changes in their members
 - genetic inbreeding
 - poor reproduction (not valid for humans)
 - decline in population numbers (not yet valid for humans)

Appendix



Some Physical Units and Constants

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1 pc = parsec = 206,265 AU = 3.086 \times 10^{12} km = 3.26156 ly
1 \text{ AU} = 149.6 \times 10^{6} \text{ km}
M_{\odot} = solar mass = 1.98855×10<sup>30</sup> kg = 1048 Jupiter masses = 332950 Earth masses
L_{\odot} = solar luminosity = 3.90×10<sup>33</sup> erg s<sup>-1</sup> = 3.846×10<sup>26</sup> W
1 \text{ eV} = 1.6022 \times 10^{-12} \text{ erg} = 1.6022 \times 10^{-19} \text{ J}
1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m} = 100 \text{ pm}
1 \text{ Jansky} = 10^{-23} \text{ erg s}^{-1} \text{ cm}^{-2} \text{ Hz}^{-1}
1 Rayleigh = 10^6 photons s<sup>-1</sup> cm<sup>-2</sup> (4\pi sr)<sup>-1</sup>
1 Debye = 10^{-18} esu cm
1 \text{ esu} = 3.33564 \times 10^{-10} \text{ C}
1 kcal/mol = 4.184 kJ/mol = = 6.947 \times 10^{-14} erg atom<sup>-1</sup>
Hubble constant H_0 = 70.1 \text{ km s}^{-1} \text{ Mpc}^{-1}
Planck constant h = 6.626075 \times 10^{-34} Js = 4.135669 \times 10^{-15} eVs
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Appendix



The Periodic Table of Elements for Biochemistry

