# Greenhouse Gases Mitigation $CO_2$ Capture and Utilization

Topic No: 2

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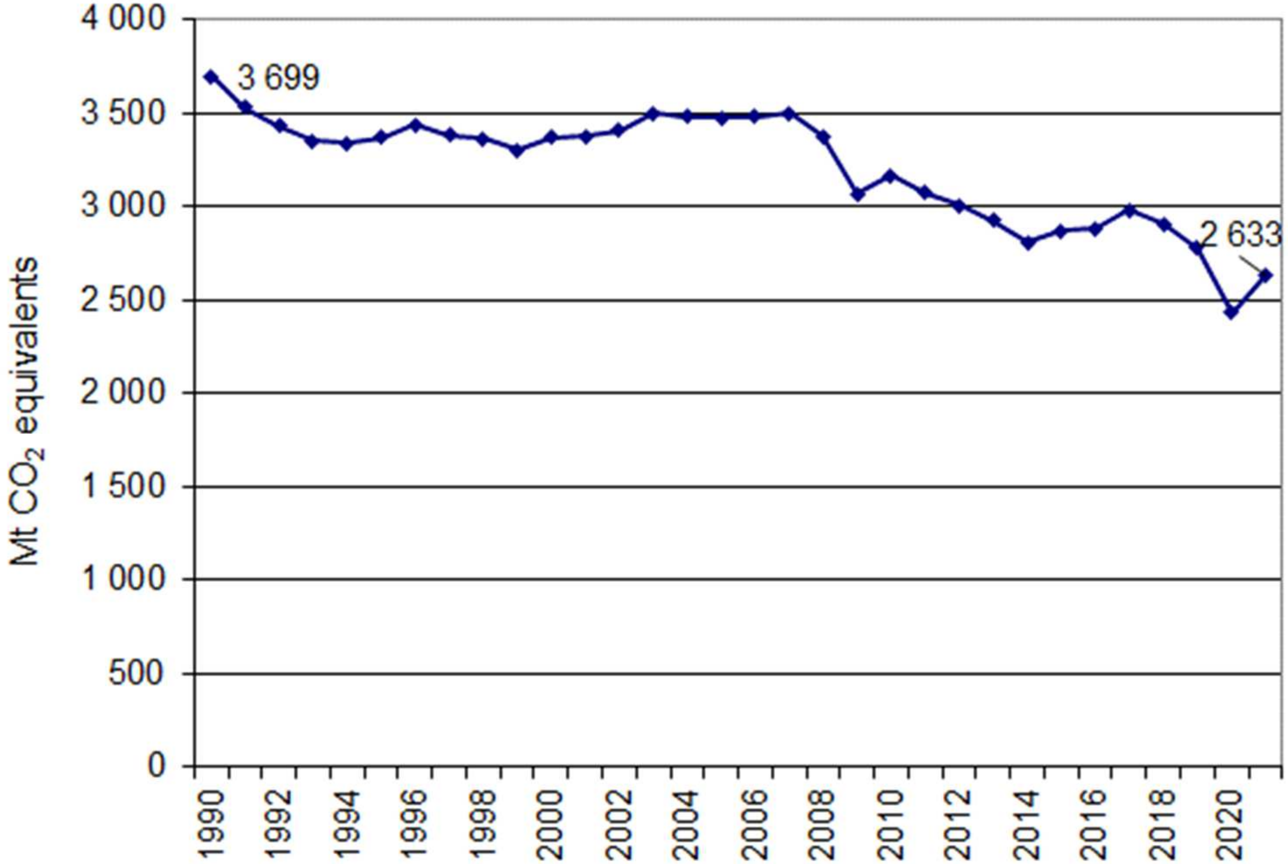
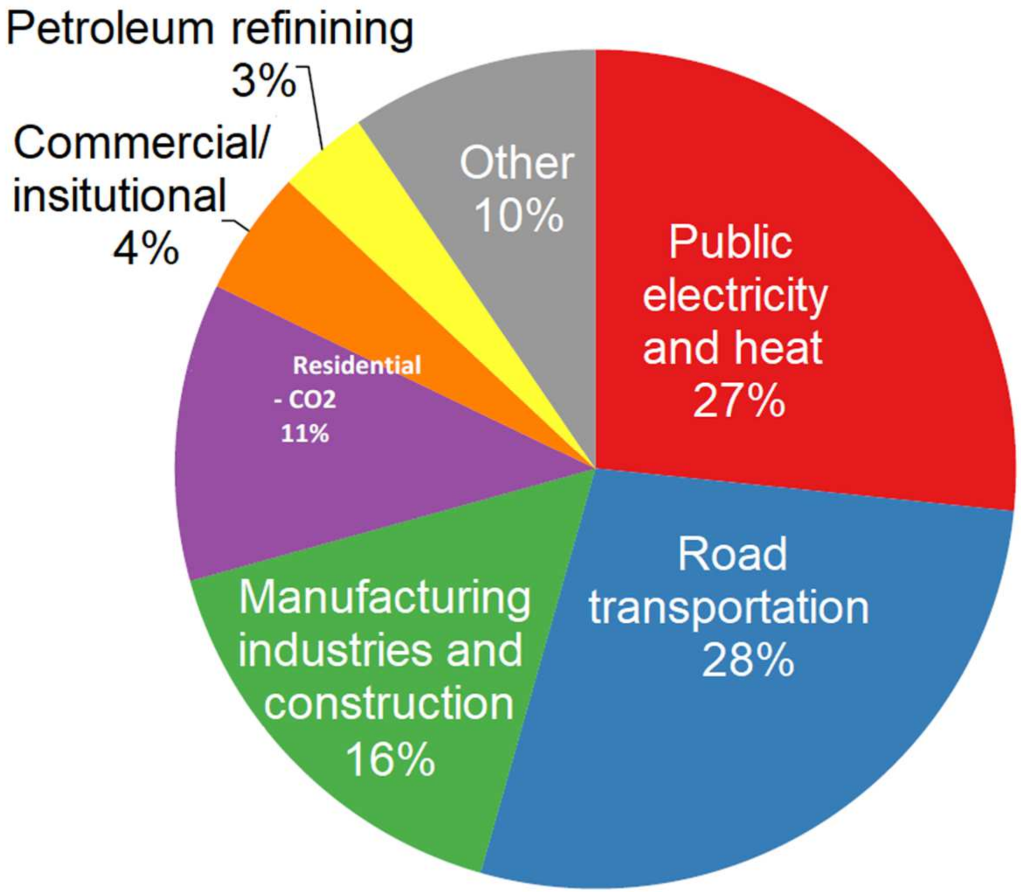
- Based on National Inventory Reports for the last decades
- Example of data available in annual reports
  - ► Summary of $CO_2$ emissions in EU incl. LULUCF and international aviation



# Data on GHG emissions

- Based on National Inventory Reports for the last decades
- Example of data available in annual reports
  - ► Sector Energy: Share of largest key source categories  in the EU in 2021



# Chronostratigraphic history of the Earth

- The age of Earth is ca. 4.54 billion ± 70 mil. years.
- Combination of the three main dating methods:
  - radiometric dating (proportion of radionuclides in minerals)

$$N_t = N_o e^{-\lambda t}$$

$N_t$ … number of atoms of the nuclide in the time t

$N_0$ … initial number of atoms of the nuclide

$\lambda$ … decay rate constant ($s^{-1}$)

  - comparing the mass and luminosity of the Sun with other stars
  - dating of meteorites formed during the formation of the solar system
- Since the formation of the planet, the close connection among:
  - geological processes
  - evolution of organisms
  - properties of the atmosphere.

# Chronostratigraphic history of the Earth

- The geological history of the planet divided into shorter time intervals
- The longest periods of time – eons:
  - Hadean 4,540 – 3,800 mil. years
  - Archean 3,800 – 2,500 mil. years
  - Proterozoic 2,500 – 541 mil. years
  - Phanerozoic 541 mil. years – today
- Complete division (example):
  - **Eon** (e.g. Phanerozoic)
    - **Era** (e.g. Kenozoic 66 mil. years – present)
      - **Period** (e.g. Paleogene 66 – 23.3 mil. years)
        - **Epoch** (e.g. Oligocene 33.9 – 23.3 mil. years)
- The atmosphere changed its: temperature, composition, pressure

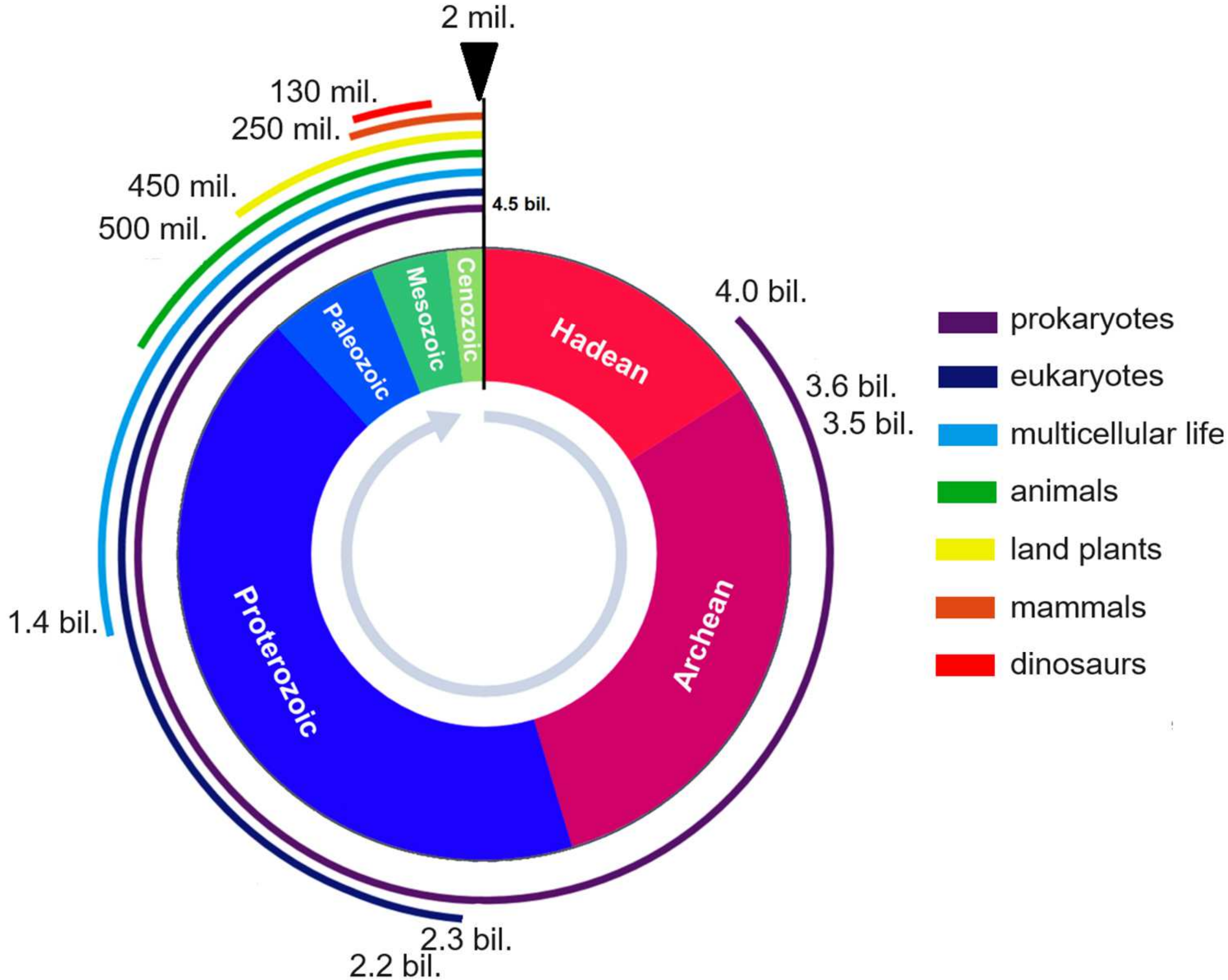
# Chronostratigraphic history of the Earth

- The complete list of eons, eras, periods and epochs:

| Eon | Era | Period | Epoch | Time [mil. years] | | Organisms |
|---|---|---|---|---|---|---|
| Hadean | | | | 4 540 - | 3 800 | |
| Archean | Eoarchean | | | 3 800 - | 3 600 | |
| | Paleoarchean | | | 3 600 - | 3 200 | Genesis of archebacteria |
| | Mesoarchean | | | 3 200 - | 2 800 | |
| | Neoarchean | | | 2 800 - | 2 500 | |
| Proterozoic | Paleoproterozoic | | | 2 500 - | 1 600 | First eucaryotic cells |
| | Mesoproterozoic | | | 1 600 - | 1 000 | |
| | Neoproterozoic | | | 1 000 - | 541 | Genesis of multicellular organisms, worms |
| Phanerozoic | Paleozoic | Cambrian | | 541 - | 485 | Cambrian explosion, genesis of trilobites |
| | | Ordovician | | 485 - | 443 | Growth of invertebrates |
| | | Silurian | | 443 - | 419 | First terrestrial plants |
| | | Devonian | | 419 - | 359 | Genesis of amphibians (salamanders etc.) |
| | | Carboniferous | | 359 - | 299 | Growth of insect, genesis of reptiles |
| | | Permian | | 299 - | 252 | Growth of reptiles |
| | Mesozoic | Triassic | | 252 - | 201 | Genesis of dinosaurs, oviparous mammals |
| | | Jurassic | | 201 - | 145 | Genesis of birds and marsupial mammals |
| | | Cretaceous | | 145 - | 66 | Genesis of placentals, extinction of dinosaurs |
| | Kenozoic | Paleogene | Paleocene | 66 - | 56 | |
| | | | Eocene | 56 - | 33.9 | |
| | | | Oligocene | 33.9 - | 23.3 | |
| | | Neogene | Miocene | 23.3 - | 5.3 | |
| | | | Pliocene | 5.3 - | 2.6 | |
| | | Quaternary | Pleistocene | 2.6 - | 0.01 | Evolution of modern human |
| | | | Holocene | 0.01 - | 0 | |

# Milestones in the Earth‘s history

- Earth‘s history can be projected as a clock face:

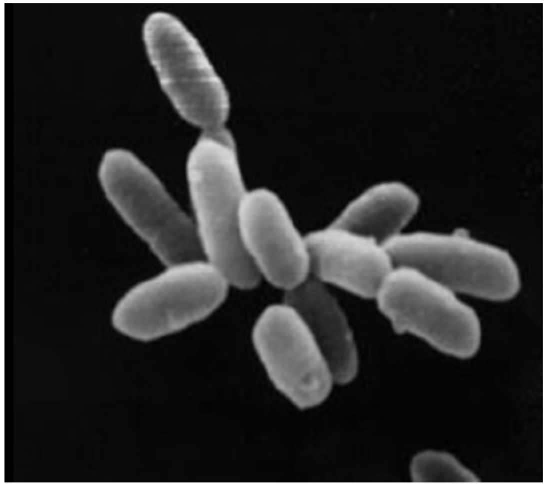



| | |
|---|---|
| 4.0 bil. | primary atmosphere |
| 3.6 bil. | archebacteria |
| 3.5 bil. | photosynthesis starts |
| 2.3 bil. | first oxygen rich atm. |
| 2.2 bil. | eukaryotes |
| 1.4 bil. | multicellular organisms |
| 500 mil. | cambrian life explosion |
| 450 mil. | invertebrates |
| 250 mil. | dinosaurs |
| 130 mil. | placentals |
| 2 mil. | hominids |

# Milestones in the Earth's history

| | |
|---|---|
| 4.0 – 3.8 billion years ago (Hadean eon) | primary atmosphere formed |
| 3.8 – 3.6 billion years ago (Eoarchean era) | secondary atm. formed |
| ca. 3.6 billion years ago (Paleoarchean era) | first archaebacteria |
| ca. 2.2 bil. years ago (Paleoproterozoic era) | first eucaryotes |
| ca. 1.4 bil. years ago (Neoproterozoic era) | first multicellular organisms (Grypania spiralis) |

Secondary atmosphere



Archaebacteria

Fossil worms tracks

# Milestones in the Earth's history

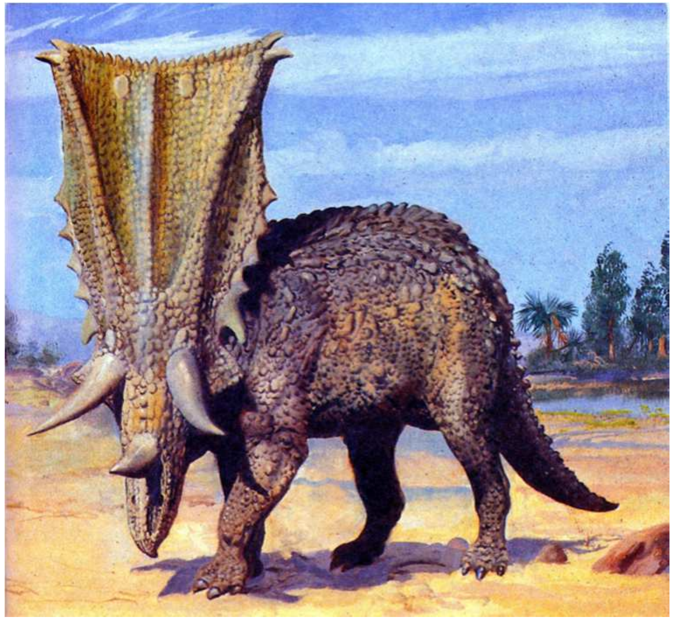
- ca. 500 mil. y. ago (Cambrian period) „cambrian explosion“ of life
- ca. 450 mil. y. ago (Ordovician period) first invertebrates
- ca. 430 mil. y. ago (Silurian period) first terrestrial plants
- ca. 390 mil. y. ago (Devonian period) first amphibians (salamanders etc.)
- ca. 330 mil. y. ago (Carboniferous p.) first insect, first reptiles

Anomalocaris

Silurian flora

Edaphosaurus

- ca. 250 mil. y. ago (Triassic period) first dinosaurs
- ca. 180 mil. y. ago (Jurassic period) first birds and marsupial mammals
- ca. 130 mil. y. ago (Cretaceous period) first placentals
- ca. 2 mil. y. ago (Quaternary period) first hominids (direct ancestors of human)



Chasmosaurus

Phorusrhacos

H. neanderthalensis

# Evolution of Earth's atmosphere

- Three stages of the historical atmosphere
  - primary atmosphere 4.0 – 3.8 billion years ago
  - secondary atmosphere 3.8 – 2.3 billion years ago
  - tertiary atmosphere ($O_2$ rich) 2.3 bil. years ago – present

Primary atm.

(no greenhouse effect)

Secondary atm.

(extreme greenhouse effect)

Tertiary atm.

(moderate greenhouse ef.)

# Evolution of Earth's atmosphere

- Primary atmosphere
  - Formation 4.0 – 3.8 billion years ago
  - Absence of heavier molecules –mostly consisting of $H_2$ + He
  - Big leakage to the outer space
- Secondary atmosphere
  - Formation 3.8 – 2.3 billion years ago
  - Formed due to volcanic processes during cooling of the Earth's Crust
  - Composed of: $CO_2$, $CH_4$, higher $C_xH_y$, $NH_3$, $H_2O$ + small quantity of $N_2$
  - Maximum greenhouse effect reached ca. 3.75 bil. years ago
  - max. t = ca. 44 °C, max p = 1.4 times higher than present
  - Subsequent condensation of water leading to first seas and rivers
  - Absorption of $CO_2$ in $H_2O$ $\Rightarrow$ carbonate sediments $\Rightarrow$ decrease of $CO_2$ $\Rightarrow$ suppression of greenhouse effect.
- Tertiary atmosphere = oxygen rich
  - Conditioned by photosynthesis

# Oxygen rich atmosphere – $O_2$ fluctuations

- First organisms
  - ► Heterotrophic organisms obtained energy by the anaerobic process:

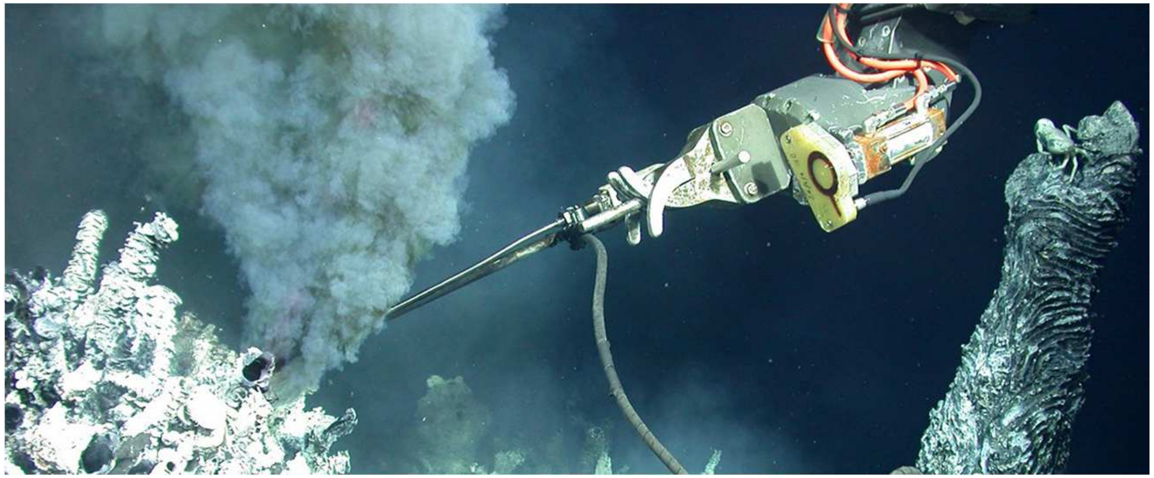
$$NH_4^+ + 2H_2O \rightarrow NO_2^- + 8H^+ + 6e^-$$
$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

or …..

alternative mechanism of cleavage of simple organic molecules

$$CH_3COOH \rightarrow CH_4 + CO_2$$

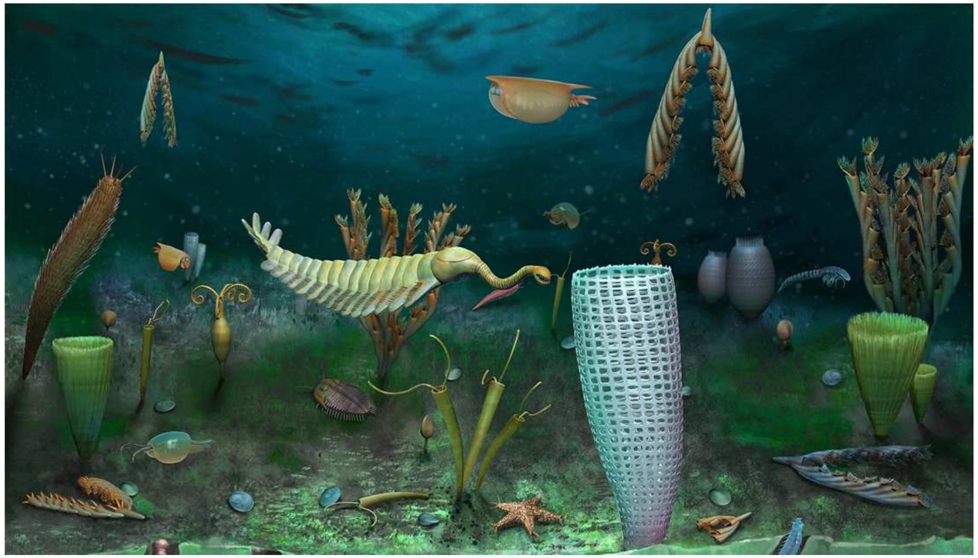
  - ► Heterotrophic metabolism = no oxygen produced
  - ► similar to deep-sea thermophilic microbes



- Beginning of photosynthesis (3.5 bil. years ago)
  - cyanobacteria - the first life form able to synthesize saccharides via photosynthesis (i.e. photoautotrophs)

$$CO_2 + H_2O + h\nu \rightarrow [CH_2O]n + O_2$$

- No oxygen in the air – $O_2$ completely dissolved in water
  - $O_2$ bonded by reactions with $Fe^{2+}$ in ancient oceans
  - after consuming $Fe^{2+}$ ions $O_2$ reacted with pyrite $FeS_2$



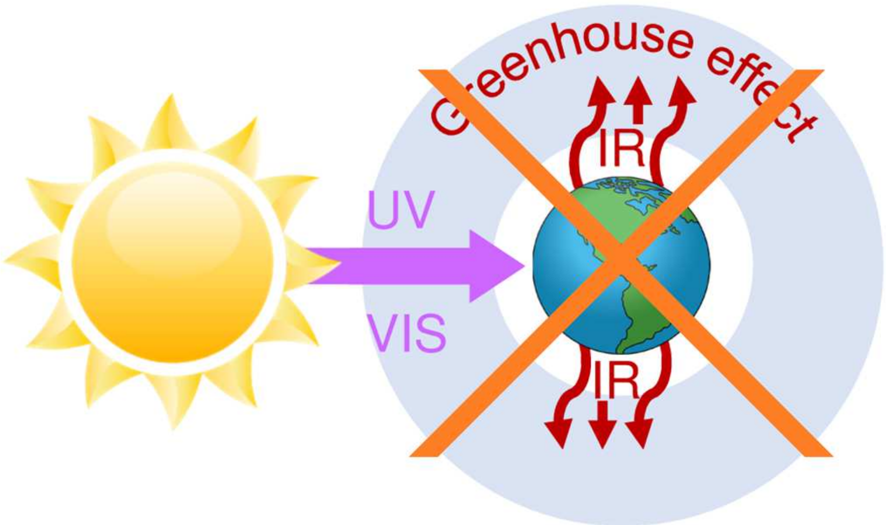
$O_2$ reacts with iron easily!

# Oxygen rich atmosphere – long way

- Oxygen rich atmosphere (since 2.3 bil. years ago)
  - after consuming $Fe^{2+}$ and $FeS_2$ oxygen started to leak into the air
  - but the air contained $CH_4$, $NH_3$ and $C_xH_y$ ….. what happened?
  - 2 billion years ago $O_2$ removed these compounds from the atmosphere
  - greenhouse effect weakened:

$$2CH_4 + 4O_2 \rightarrow 2CO_2 + 4H_2O$$
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

low temperature period began
6 °C, pressure 0.6 of the current value




- Gradual stabilization ca. 400 million years ago

# Stable climate in history? – not by chance!

- $O_2$ concentration has probably not been constant since Palaeozoic up to the present
- $O_2$ concentrations obtained by measurement of ratio of C isotopes in the deep sea rocks (calculation using bio-geochemical models)
- Fluctuation as a result of various factors:
  - changes in photosynthesis intensity along wet/dry periods
  - changes in photosynthesis intensity due to solar activity
  - rate of erosion of rocks and minerals
  - movement of continents (e.g. breaking of Pangea resulting in flat seas with huge concentration of photosynthesizing organisms, algae)
  - biomass putrefaction in large swamps during declination of dry lands
- Temperature fluctuated as well
- Big impact on evolution

# Air composition – climate – evolution of life

- $O_2$ extreme values since Devonian till present
  - 300 – 350 million years ago — Devonian — 35% vol.
  - 205 million years ago — Triassic — 10% vol.
  - 55 million years ago — Eocene — 23% vol.
- Possible consequences:
  - $O_2$ < 13–16% suppression of spontaneous forest fires
  - evolution of large forms of terrestrial arthropods
  - transition of primitive amphibians and amphibious fish to dry land
  - growth of big mammals (indricotherium, mastodon etc.) due to higher $O_2$ concentration in Kenozoic era

# Air composition – climate – evolution of life

- $O_2$ maximum concentration in Devonian (35% vol.) + Carboniferous period
  - gigantic insect species (insects generally do not have lungs)
  - tracheas are less efficient ⇒ functional only in small bodies
  - large species may survive only at higher concentrations of Oxygen

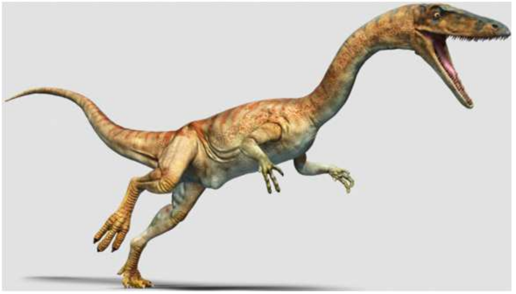
Arachnid: Megarachne servinei (50 cm)

Dragonfly: Meganeura 75 cm)

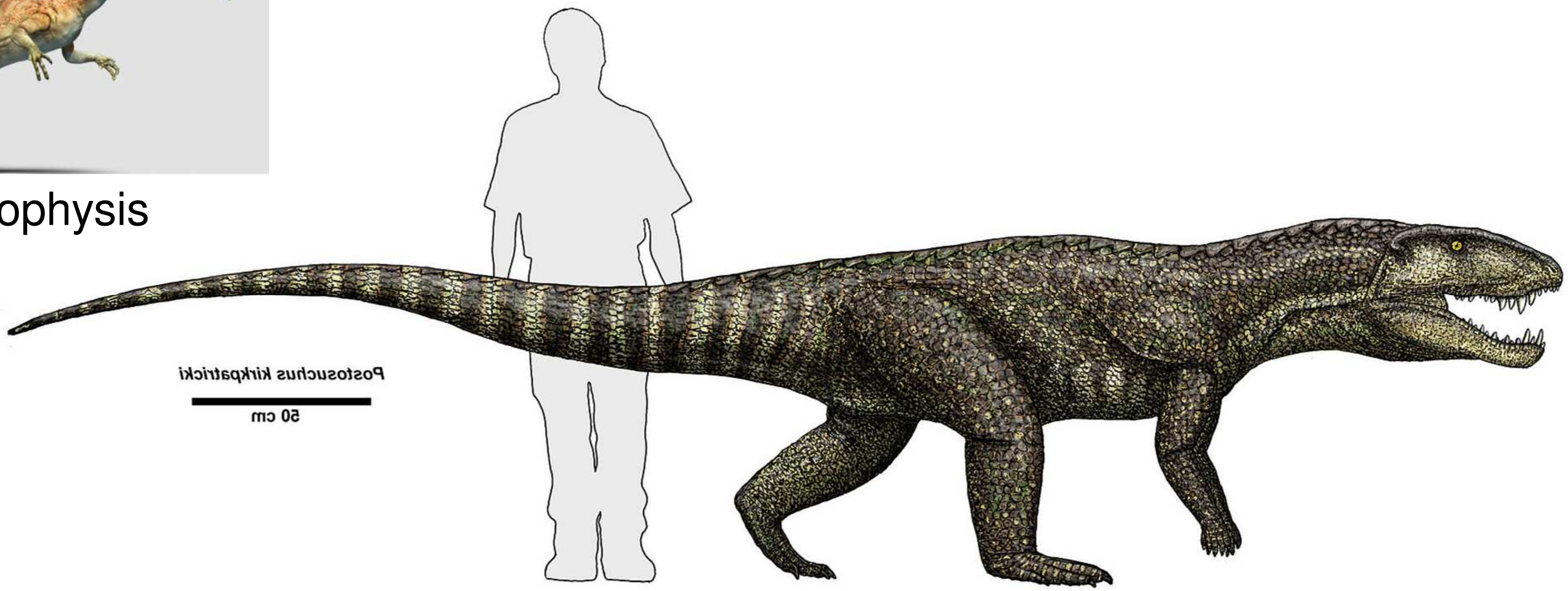
Arthropleura (200 cm) –biggest millipede ever

# Air composition – climate – evolution of life

- $O_2$ minimum concentration in Triassic period (10% vol.)
  - ► extinction of large amphibians
  - ► growth of reptiles in colder, dry period (good lungs, lower food intake, cold-blooded metabolism)



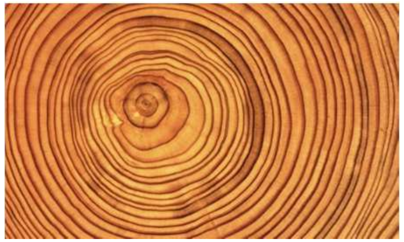
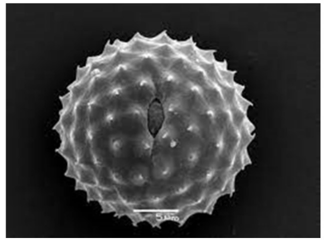
Coelophysis




Postosuchus

# Evolution of global temperatures

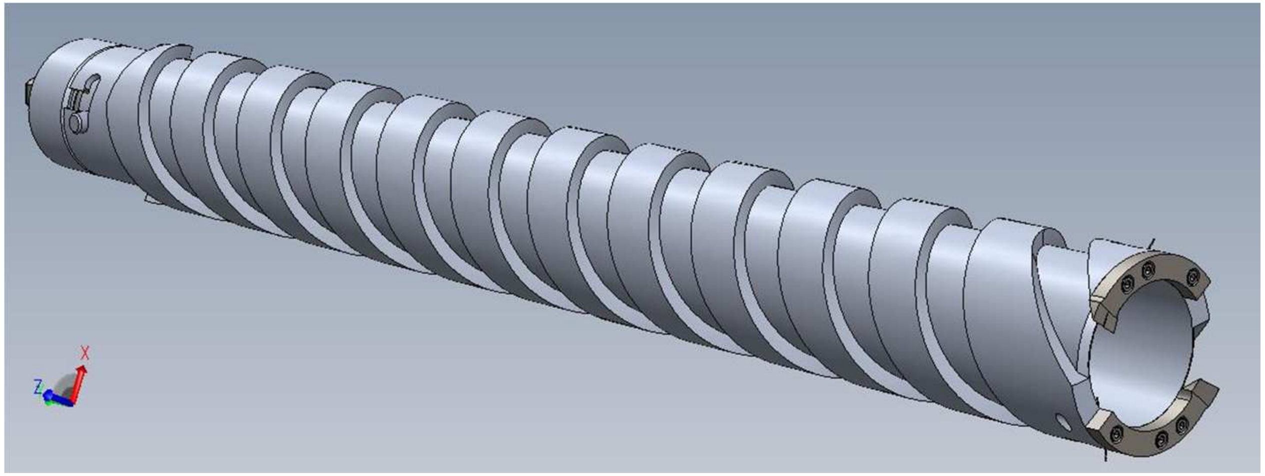
- Several models elaborated
  - ► direct temperature measurement impossible
  - ► combination of indirect paleoclimatological methods
- Paleoclimatological approaches for temperature estimation
  - ► paleobotanical methods
    - tree rings
    - plant microfossils
    - pollen and spore analysis

  - ► chemistry of sediments (oxygen ($^{18}O/^{16}O$), carbon ($^{13}C/^{12}C$), hydrogen ($^{2}H/^{1}H$) and nitrogen isotope ratios
    - ice core analysis
    - lake sediments
    - speleosystems
    - sea sediments

# Ice coring in Antarctica

- EPICA model = European Project for Ice Coring in Antarctica
- Core drilling in the Dome C area in East Antarctica since 1996
  - realized on the iceberg with the thickness of 3,270 m
- Due to EPICA climatological data for 8 glacials (ice ages) known
  - calculated temperatures (0.8 mil years ago)
  - measured $CO_2$ concentration (0.65 mil. years ago)
  - measured $CH_4$ concentration (0.65 mil. years ago)

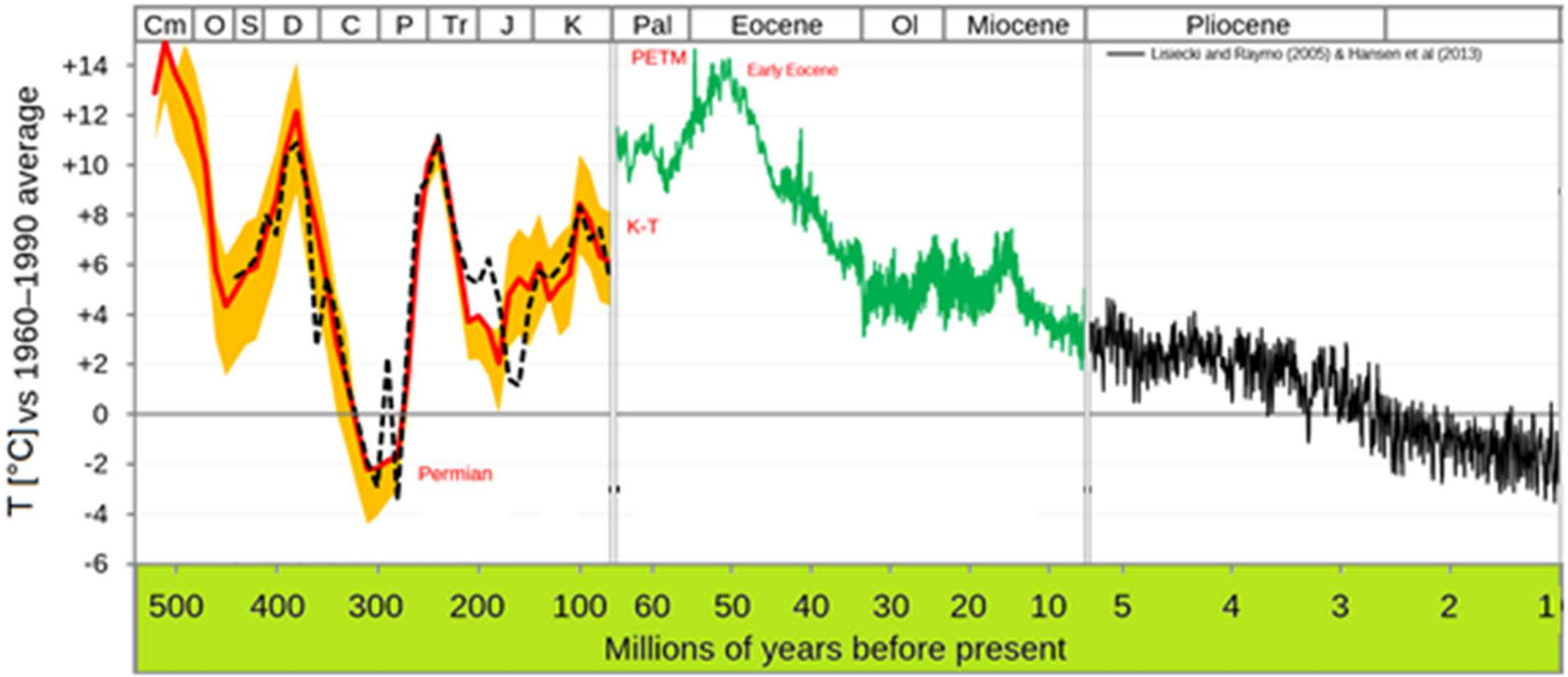


Core drill


Ice sample

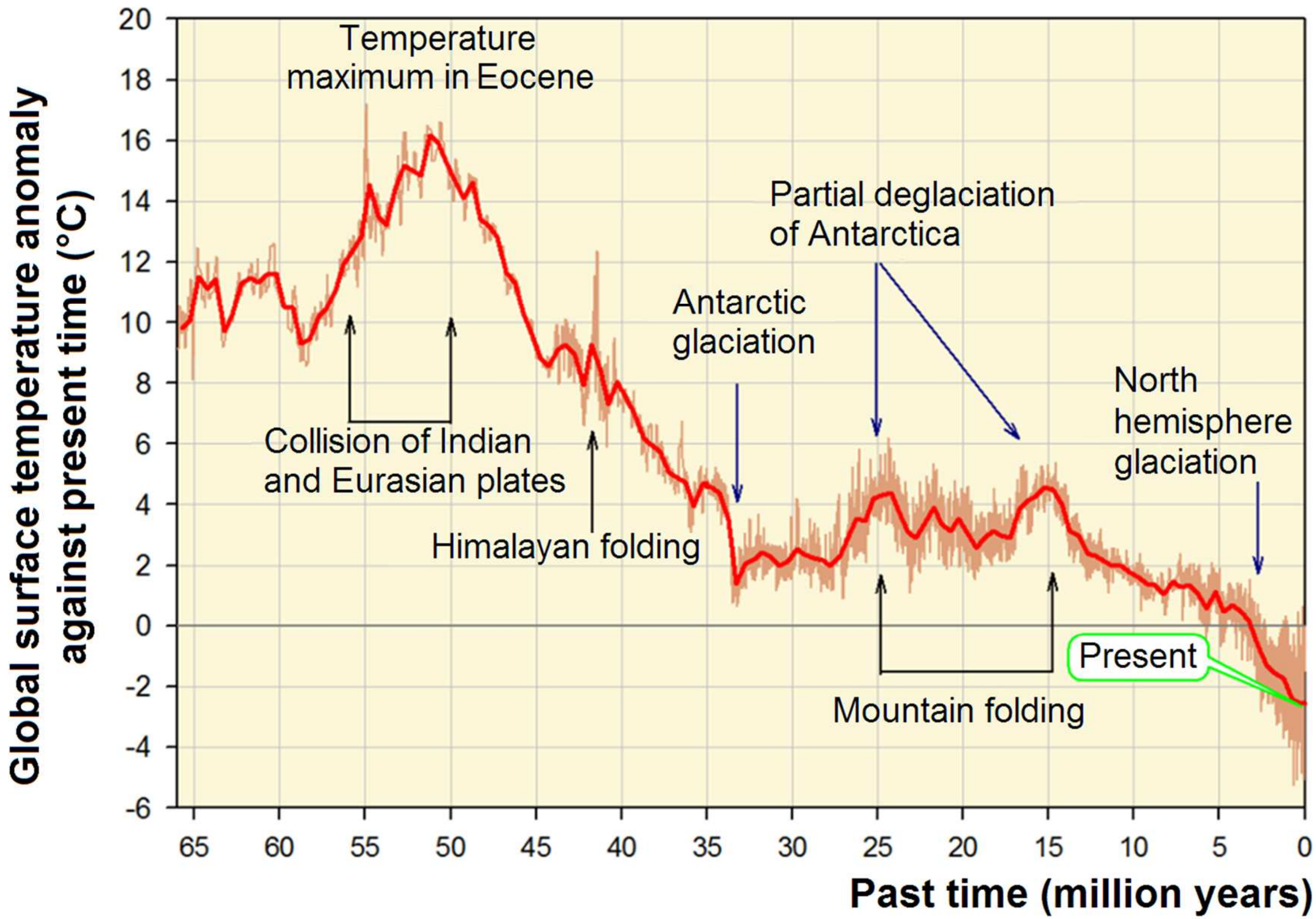
# Evolution of global temperatures

- Several models elaborated
- Changes in global average temperatures between Cambrian and present
  - 30-years average between 1960 and 1990 taken as the zero line



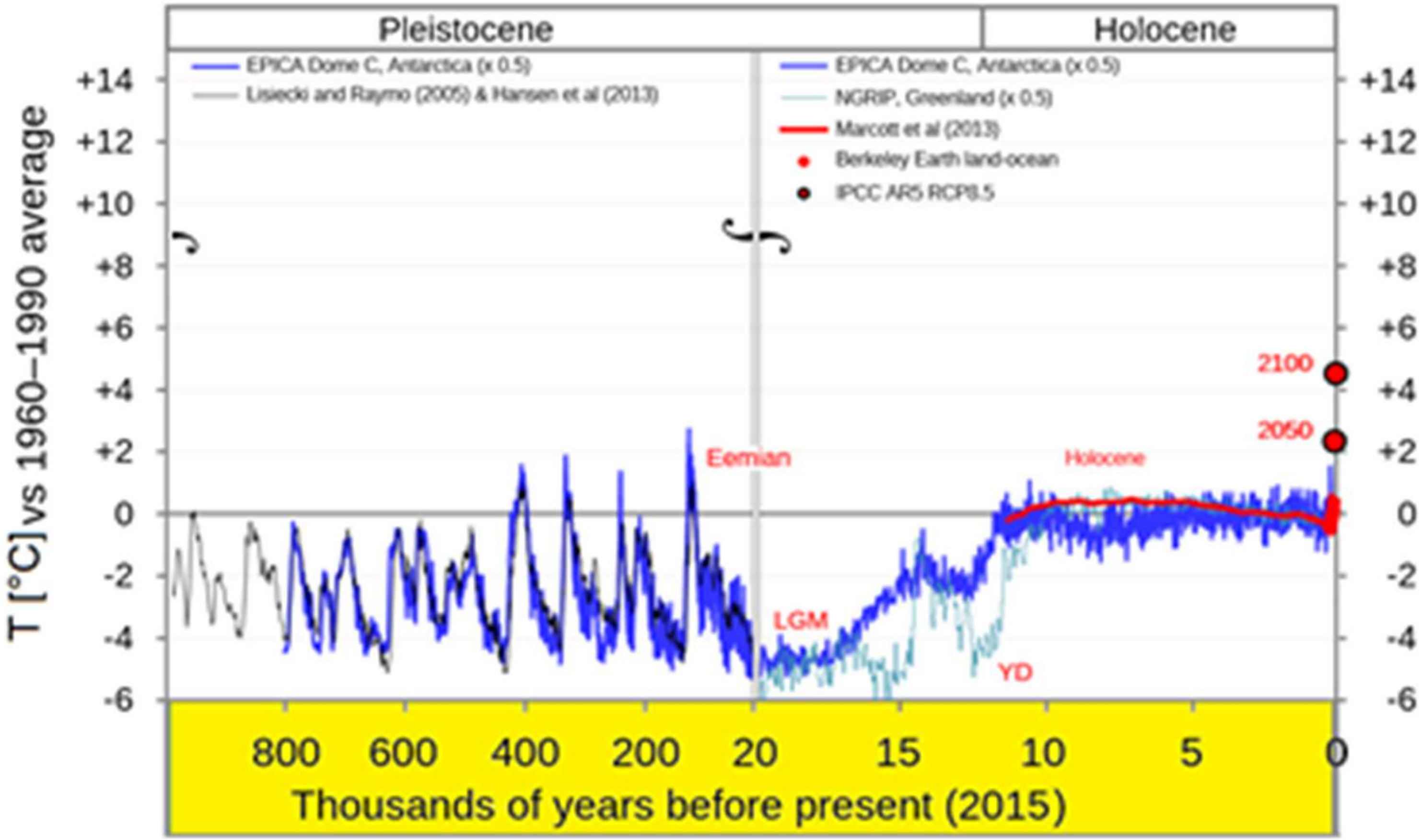
# Evolution of global temperatures

- Global average T estimation (palaeocene - present)

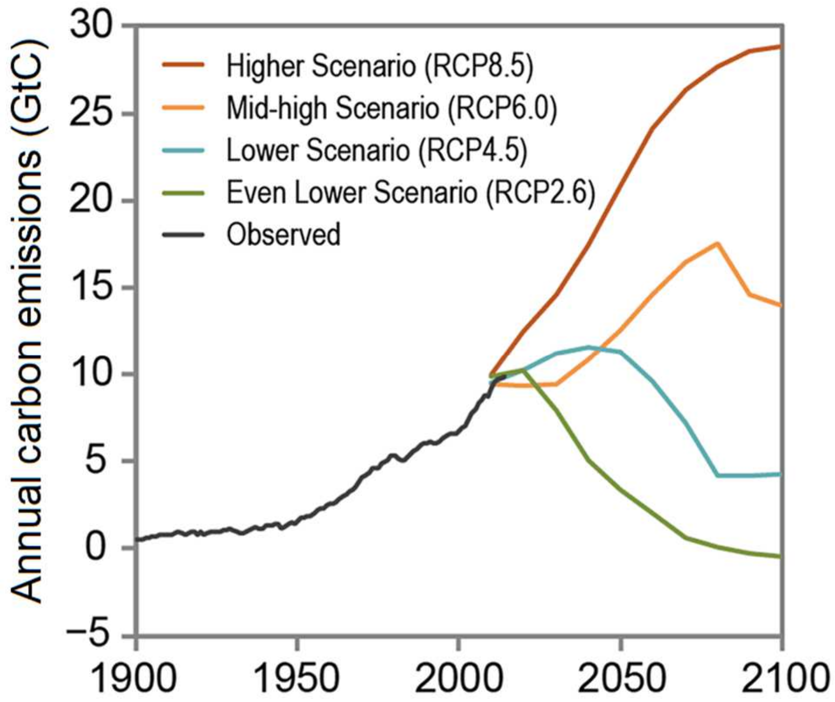


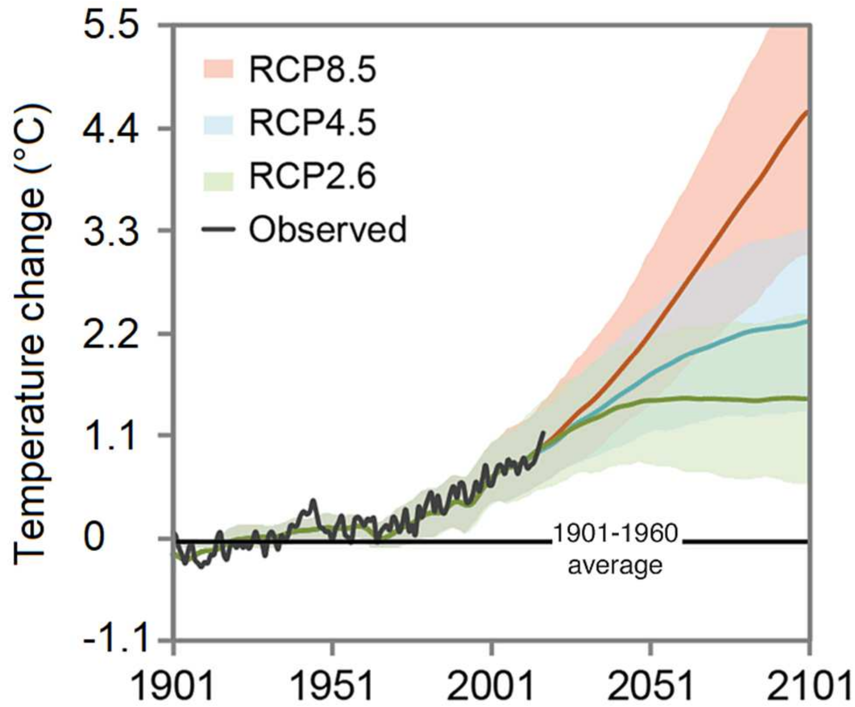
# Evolution of global temperatures

- Global average T according to EPICA model (pleistocene-holocene)
  - 30-years average between 1960 and 1990 taken as the zero line
  - 8 glacials/interglacials detected



- Made by several authorities, e.g. U.S. Global Change Research Program
- Calculation based on hypothetical pathways of global C emissions
  - called representative concentration pathways (RCP)
  - The dispersion of values in each scenario depends, among other things, on the change in the amount of aerosol in the air.

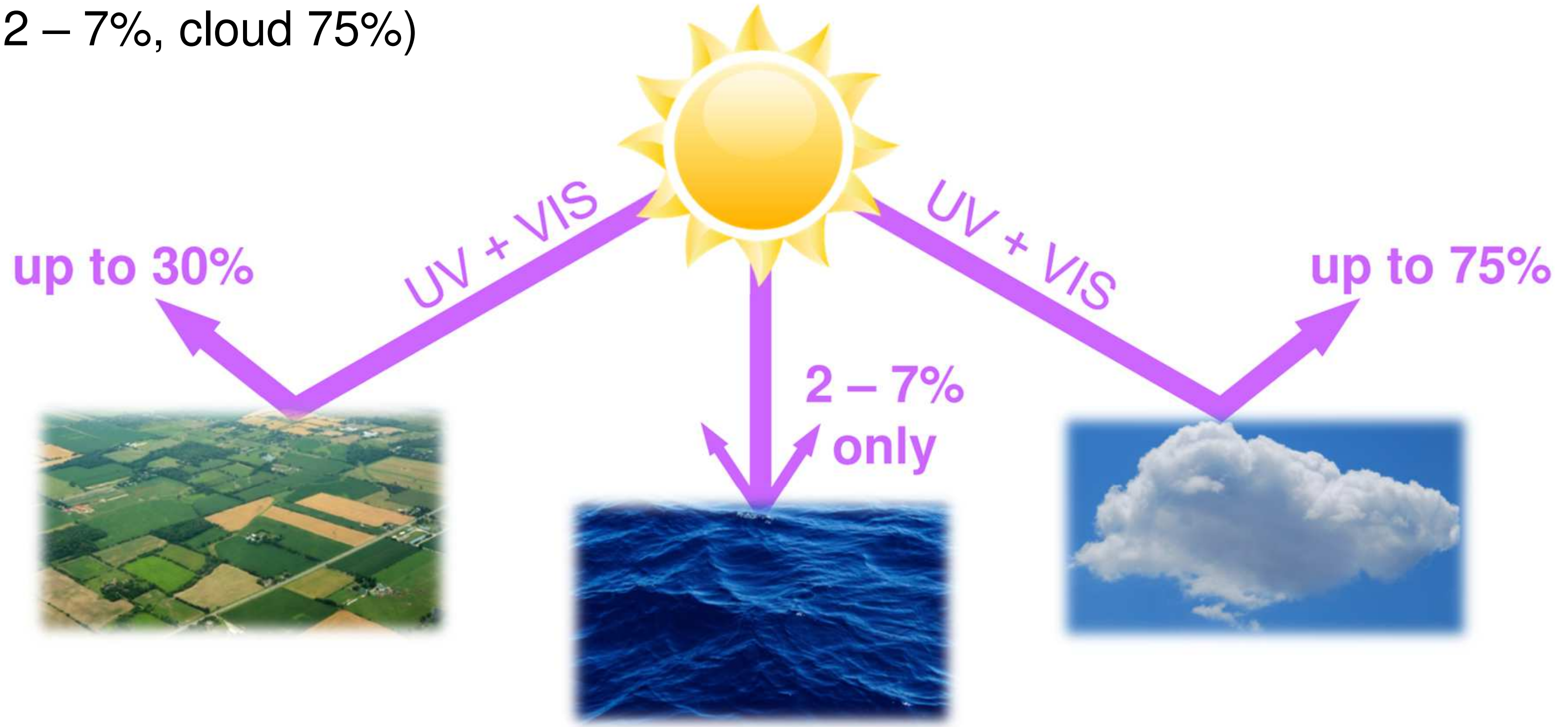


# How aerosols influence the global climate?

- Diameter of typical aerosol particles in the air = ca. 0.01 mm
- Cloud = visible conglomeration of particles of liquid water or ice
- Cloud cover = ratio of square covering of the visible sky by clouds
  - ► global value of cloud cover = ca. 54 %
  - ► important factor for energetic balance due to high **albedo** (reflection coef.)

(land 30%, sea 2 – 7%, cloud 75%)



# How can we save global climate?

- Relationship between economic development and $CO_2$ production
- Y. Kaya proposed the equation:

$$CO_2\uparrow_{total} = POP \times (GDP_{PC}) \times (BTU/GDP) \times (CO_2\uparrow/BTU) - CO_2\downarrow$$

| | |
|---|---|
| ► $CO_2\uparrow$ | total $CO_2$ released to atmosphere |
| ► CO2↓ | total $CO_2$ captured by geosphere and biosphere |
| ► POP | worldwide population |
| ► $GDP_{PC}$ | gross domestic product per capita |
| ► GDP | total gross domestic product |
| ► BTU/GDP | energy consumption per GDP |
| ► $CO_2\uparrow$/BTU | $CO_2$ released per consumed energy |

- In general, the equation tells what must be changed if other parameters remain unaffected.

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