ATMOSPHERIC CHEMISTRY

Lecture No.: 2

Organisation of study

- Lecturer:
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  https://e-learning.vscht.cz/course/view.php?id=106

- Scale of subject:
  winter semester

  14 lectures, 14 weeks, 2 hours/week

- Classification:
  Exam - written + oral form (depending on result of the test)

Scope of lecture 2

History of Earth's atmosphere

- Chronostratigraphic history of Earth

- Evolution of Earth's atmosphere

- Fluctuations in oxygen concentration

- Fluctuations in planetary temperature

How does the environmental information system work?

- Description of essential conditions for operation of environmental information systems

- Main automated analytical techniques

- Development of computers and network

- Life cycle of information within the EIS

Chronostratigraphic history of Earth

- The age of Earth is ca. 4.54 billion ± 70 mil. years (Source: Wilde, S. A., Valley, J. A., Peck, W. H., Graham, C. M. (2001))

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

Chronostratigraphic history of Earth

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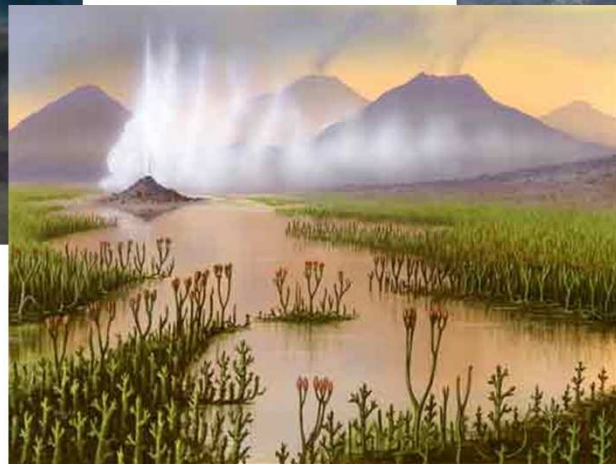
Eon	Era	Period	Epoch	Time [mil. years]		Organisms
Phanerozoic	Paleozoic	Cambrian		541 -	485	Cambrian explosion, genesis of trilobites
		Ordovician		485 -	443	Growth of invertebrates
		Silurian		443 -	419	First terrestrial plants
		Devonian		419 -	359	Genesis of amphibians (salamanders etc.)
		Carboniferous		359 -	299	Growth of insect, genesis of reptiles
		Permian		299 -	252	Growth of reptiles

Chronostratigraphic history of Earth

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| Eon	Era	Period	Epoch	Time [mil. years]		Organisms
Phanerozoic	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	
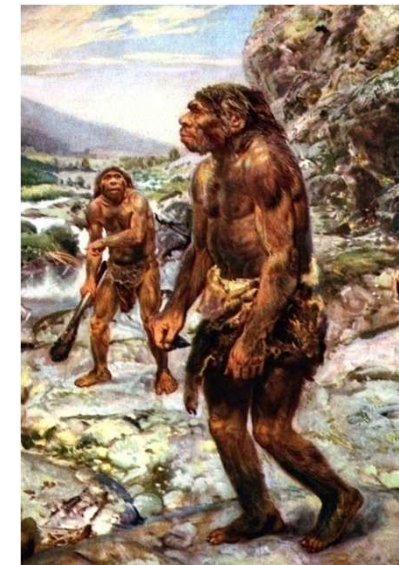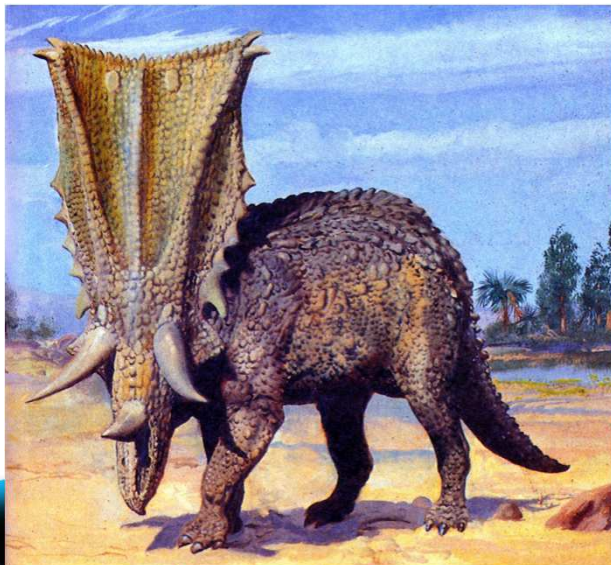
Chronostratigraphic history of Earth

- The age of Earth is ca. 4.54 billion ± 70 mil. years
  (Source: Wilde, S. A., Valley, J. A., Peck, W. H., Graham, C. M. (2001))

Legend (in million years):

|		
⬛ (black)	2	first hominids
🟧 (orange)		mammals
🟥 (red)	230–65	dinosaurs
🟨 (yellow)		land plants
🟩 (green)		animals
🔵 (light blue)		multicellular life
🟦 (dark blue)		eukaryotes
🟪 (purple)		prokaryotes
	ca. 2300	first oxygen rich atmosphere
	ca. 3500	photosynthesis starts
	ca 4000	first life
	4527	Moon created
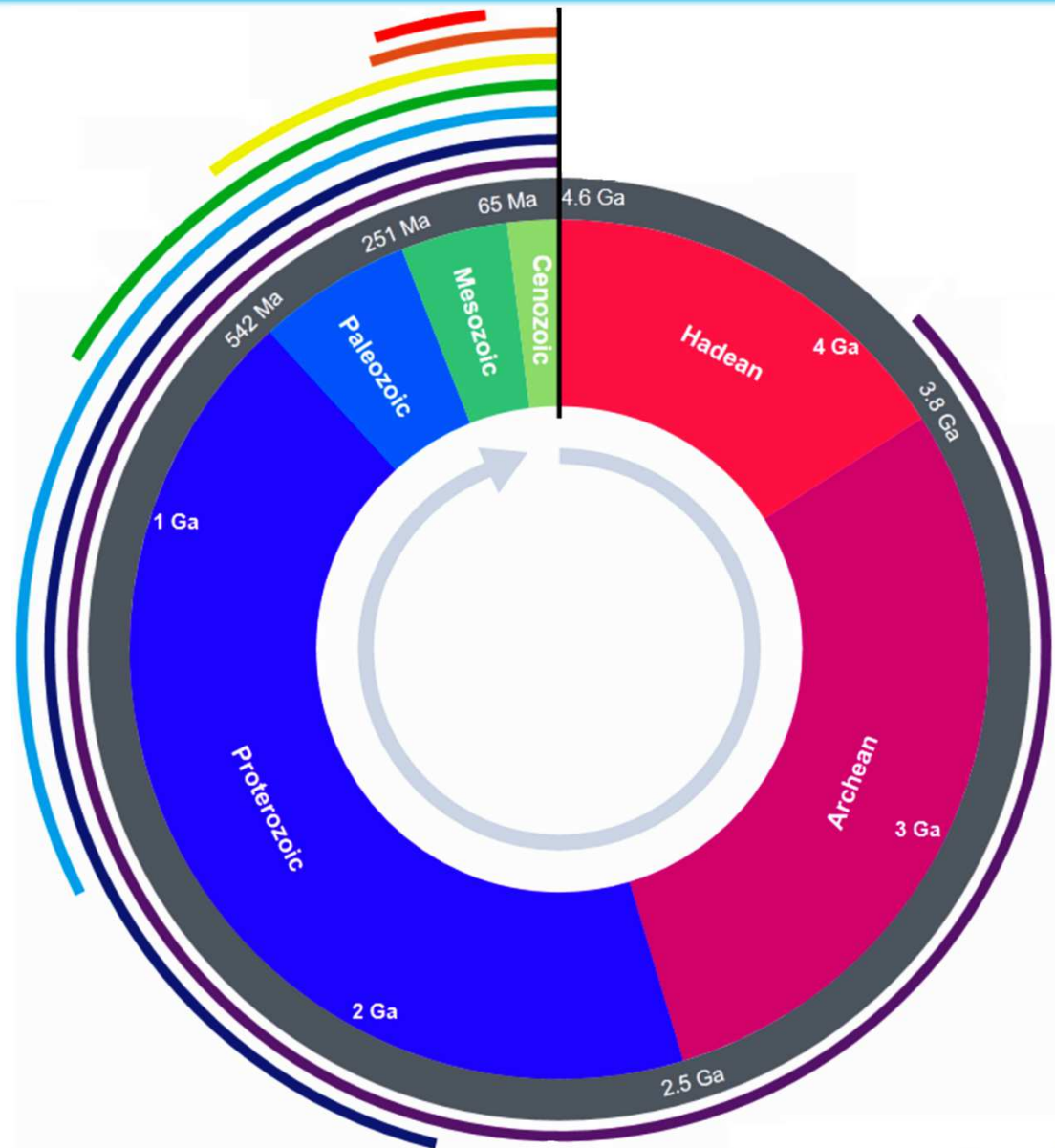
Evolution of Earth's atmosphere

- Primary atmosphere
  - Formation 4.0 – 3.8 billion years ago
  - Absence of heavier molecules – atmosphere mostly consisting of H_2 + He
  - Big leakage to the outer space

- Secondary atmosphere

  - Formed due to volcanic processes and from the planet surface during cooling of the Earth's Crust; it initially contained: CO_2, CH_4, higher C_xH_y, NH_3, H_2O and small quantity of N_2;

  - Maximum greenhouse effect reached ca. 800 mil. years after creation of Earth (t = ca. 44 °C, p = 1.4 times higher than present);

  - Subsequent condensation of water leading to first seas and rivers;

  - As a consequence of absorption of CO_2 in H_2O and following reactions in aqueous solution, formation of carbonate sediments and parallel decrease of CO_2 concentration in atmosphere $\Rightarrow$ suppression of greenhouse effect.
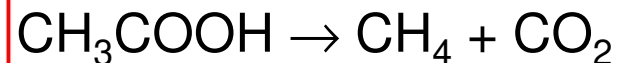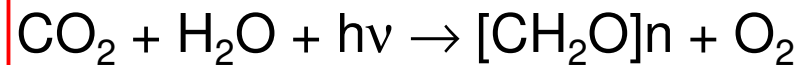
Evolution of Earth's atmosphere

- First organisms

    - Heterotrophic organisms, obtaining energy by the anaerobic process:

    $$NH_4^+ + 2H_2O \rightarrow NO_2^- + 8H^+ + 6e^-$$
    $$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$
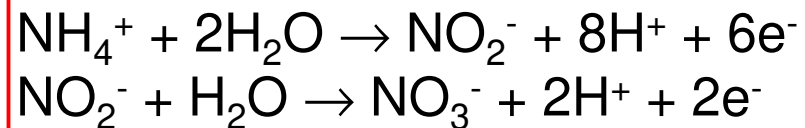
    - Alternative mechanism of cleavage of simple organic molecules:

    $$CH_3COOH \rightarrow CH_4 + CO_2$$

    - Genesis of cyanobacteria - the first life form able to synthesize saccharides via photosynthesis (i.e. photoautotrophs):

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

    - Majority of oxygen bonded by reactions with bivalent iron in ancient oceans (big initial content of Fe^{2+})

    $$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2\ Fe_2O_3 + 8H^+$$

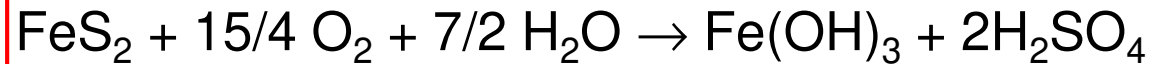   production of $Fe(OH)_3 + Fe_2O_3$

Evolution of Earth's atmosphere

- First organisms

  - Another part of oxygen (after consuming Fe^{2+} ions) was bonded due to the reaction with pyrite

    $$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4$$

  - 2.5 billion years after the formation of Earth, Oxygen produced by photosynthesis removed methane, ammonia and higher hydrocarbons from the atmosphere:

    $$2CH_4 + 4O_2 \rightarrow 2CO_2 + 4H_2O$$
    $$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$
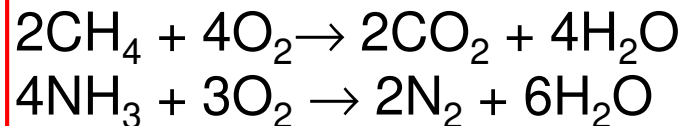
  - The above mentioned processes further reduced the greenhouse effect $\Rightarrow$ 2 billion years ago a low temperature period began (temperature 6 °C, pressure 0.6 of the current value), then gradual stabilization occurred ca. 400 million years ago.

  - In geological history, Oxygen concentration fluctuated.

Evolution of Earth's atmosphere

- Content of O_2 in atmosphere

  - O_2 concentration has probably not been constant since Palaeozoic up to the present.

  - There is no agreement among scientists upon the exact values.

  - Oxygen concentrations obtained by measurement of ratio of C isotopes in the samples taken from drillings in deep sea rocks and subsequent calculation using bio-geochemical models
  (Source: Falkowski, P.; Science 309: 2202-2204   (2007));

  - Fluctuation as a result of various factors:

    changes in photosynthesis intensity and changes in the 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

Evolution of Earth's atmosphere

- Content of O_2 in atmosphere (Source: Falkowski, P.; Science 309: 2202-2204 (2007));

  – Acquired values:

300 – 350 million years ago	35 %
205 million years ago	10 %
55 million years ago	23 %

  – Possible consequences:

  Influencing biotopes (decrease of Oxygen content below 13 – 16 % suppression of spontaneous growth of forest fires)

  Influencing evolution

  genesis of large forms of terrestrial arthropods

  transition of primitive amphibians and amphibious fish to dry land

  possibility of growth of big mammals (indricotherium, mastodon etc.) due to higher O_2 concentration

Evolution of Earth's atmosphere

- Oxygen content (Source: Falkowski, P.; Science 309: 2202-2204 (2007));

  - Example – gigantic insect: insects generally do not have lungs, but less efficient tracheas $\Rightarrow$ functional only in small bodies (large species may live only at higher concentrations of Oxygen)

Arachnid: Megarachne servinei (50 cm)
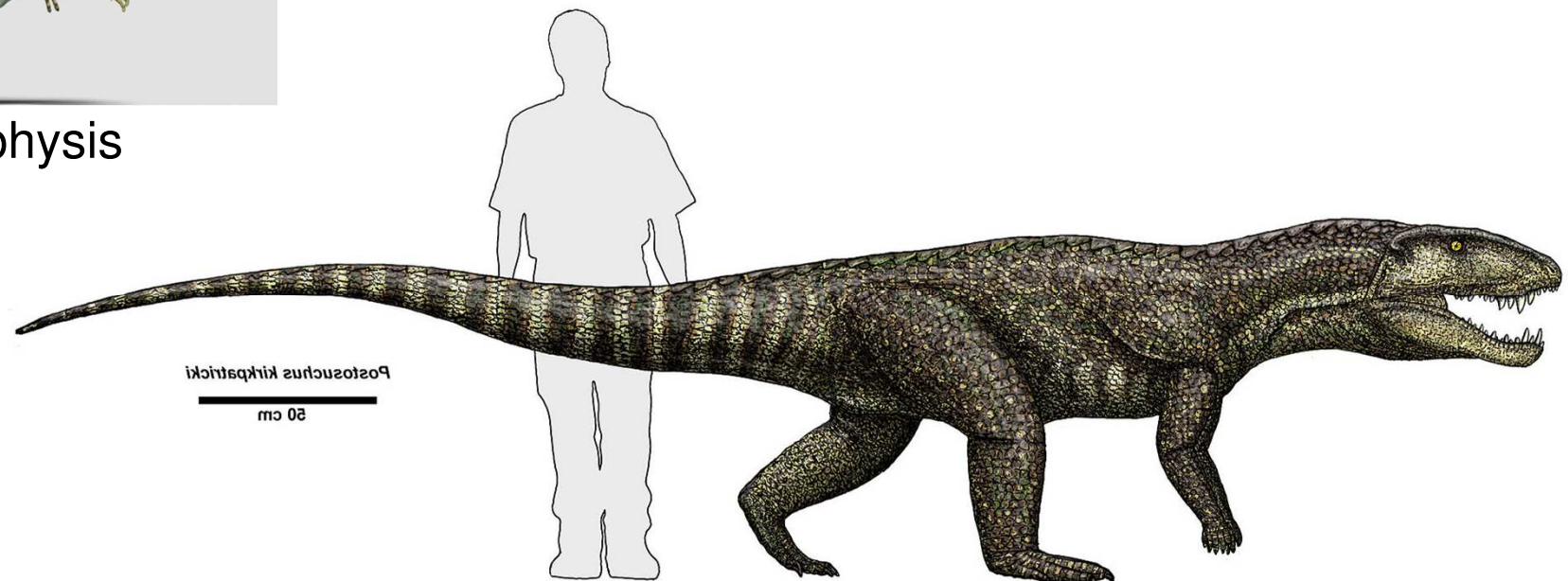

Dragonfly: Meganeura 75 cm)

Arthropleura (200 cm) –biggest millipede ever

Evolution of Earth's atmosphere

- Oxygen content (Source: Falkowski, P.; Science 309: 2202-2204 (2007), pictures https://dinopedia.fandom.com);

    – Example – growth of reptiles in colder, dry Triassic era (good lungs, lower food intake, cold-blooded metabolism)

Coelophysis

Postosuchus kirkpatricki

50 cm

Postosuchus

Evolution of global temperatures

- Changes of global average temperatures between Cambrian and the present (Source: Fergus, G.; Royer et al (2004), Zachos et al (2008), Hansen et al (2013))

- 30-years average between 1960 and 1990 taken as the zero line;

- Temperatures till 0,8 mil. years ago calculated using EPICA model EPICA (European Project for Ice Coring in Antarctica) – core drilling has proceeded in the Dome C area in East Antarctica since 1996; projects realised on the iceberg with the thickness of 3270 m;

- EPICA data summarizes calculated temperatures and measured concentrations of atmospheric CO_2 a CH_4 (back to -0.65 mil. years)

- Due to EPICA climatological data known for 8 glacials (ice ages).
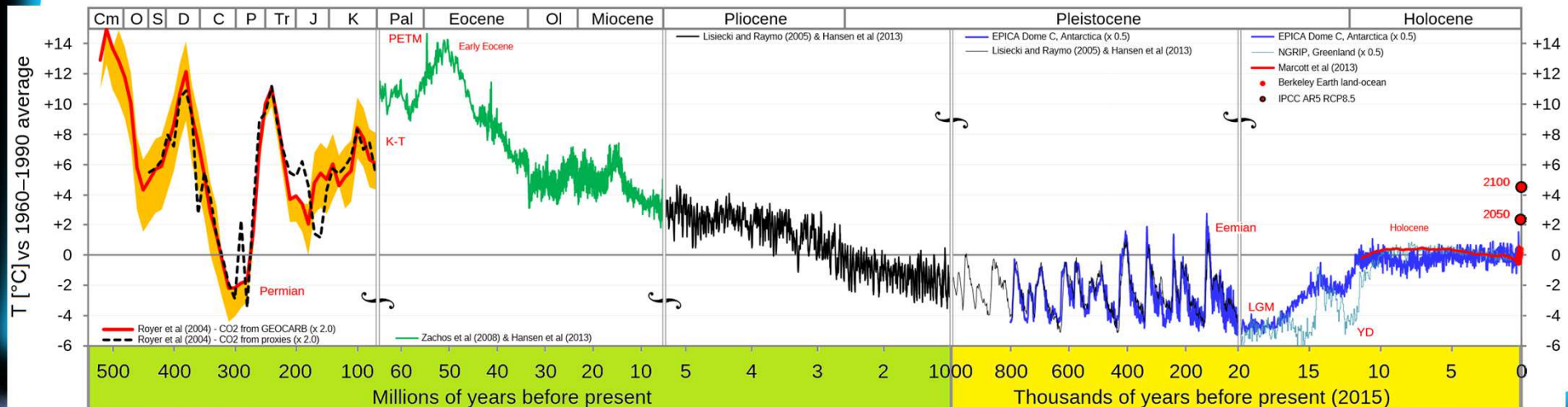
Evolution of global temperatures

- Changes of global temperatures in range Palaeocene - present (Source: Open Science Conference of the World Climate Research Program, 2011, Denver CO, USA)
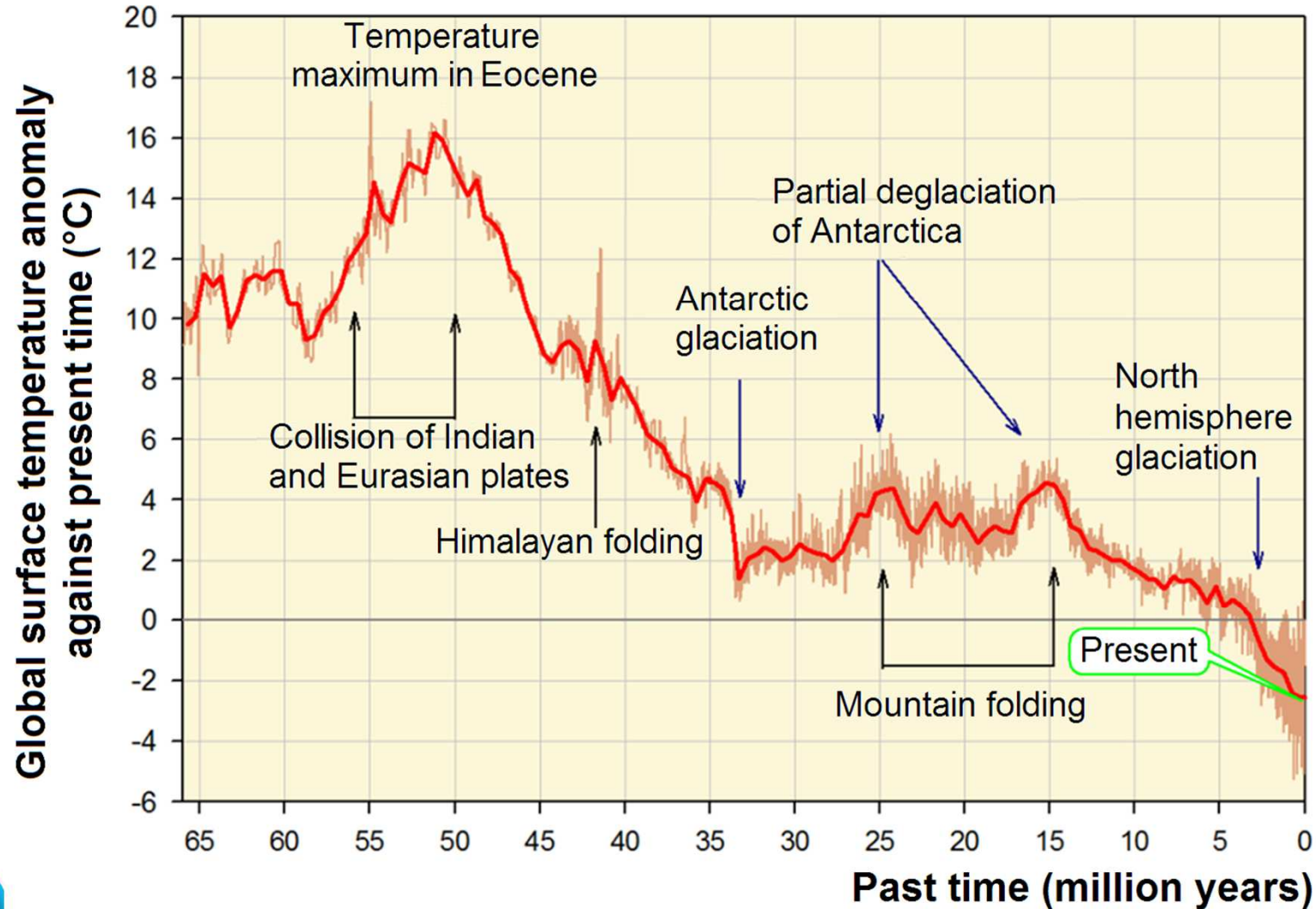
Factors allowing build up the IS

- 1. Public demand for national and international authorities to collect and share environmental data

- 2. Availability of methods for environmental analysis (automated instrumental analysis)

- 3. Availability of electronics to create and store databases = computers

- 4. Availability of systems for sharing of created databases = network

Public demand – 1st condition

- Acceptance of the necessary legislation, based on political consensus, adoption of international agreements etc.

- Example – legal background for stations of imission monitoring system:

    Nationwide system of Automatic Imission Monitoring (AIM) and Manual Imission Monitoring (MIM);

    Budget (in CZ) ensured by Regulation of Government No.: 596/2006 of the Legal Code, Annex No.: 4 (allowable level of public support);

    Operation of IM is supervised, according to law No.: 201/2012 (on the air protection), by Ministry of the Environment and it is technically operated by Czech Hydrometeorological Institute (CHMI).

    Building up the AIM stations done by Regulation No.: 330/2012, on the assessment and evaluation of the level of pollution, scale of public information about level of pollution and during smog situations

    AIM system launched in Prague in 1986 and on the nationwide scale in 1992.

Analytics– 2nd condition for IS

- Example – AIM stations in Prague

- 206 stationary stations nationwide 206 (126 CHMI, ca. 39 Public Health Institutes, the rest - other organisations, e.g. Energetic Corporation CEZ)

Prague city:

15 stations AIM

Analytics– 2nd condition for IS

- Example – AIM stations

- 206 stationary stations nationwide 206 (126 CHMI, ca. 39 Public Health Institutes, the rest other organizations, e.g. Energetic Corporation CEZ);

- Prague city: 15 stations AIM + 1 station countryside in Ondřejov

- Standard on-line measurement of: SO_2, NO_x, PM_{10} (Particulate Matter fraction < 10 µm), furthermore, the following substances are measured at selected stations: CO, O_3, BTX fraction (benzene, toluene, ethylbenzene, xylenes)

- Applied on-line methods:
  - SO_2 ultra violet fluorescence spectrometry
  - NO_x $(NO + NO_2)$ chemiluminiscence spectrometry
  - PM_{10} radiometric method
  - CO   IR spectrophotometry
  - BTX fraction   gas chromatography

Analytics– 2nd condition for IS

- Example – AIM station, method overview (examples only)

- SO_2 molecules absorb UV radiation with wavelength in the range of 200 – 240 nm, which makes the atoms excited. During their return to the base level, the particles emit the UV radiation with another wavelength. Its intensity corresponds to the SO_2 concentration and is measured in the right angle to the primary beam.
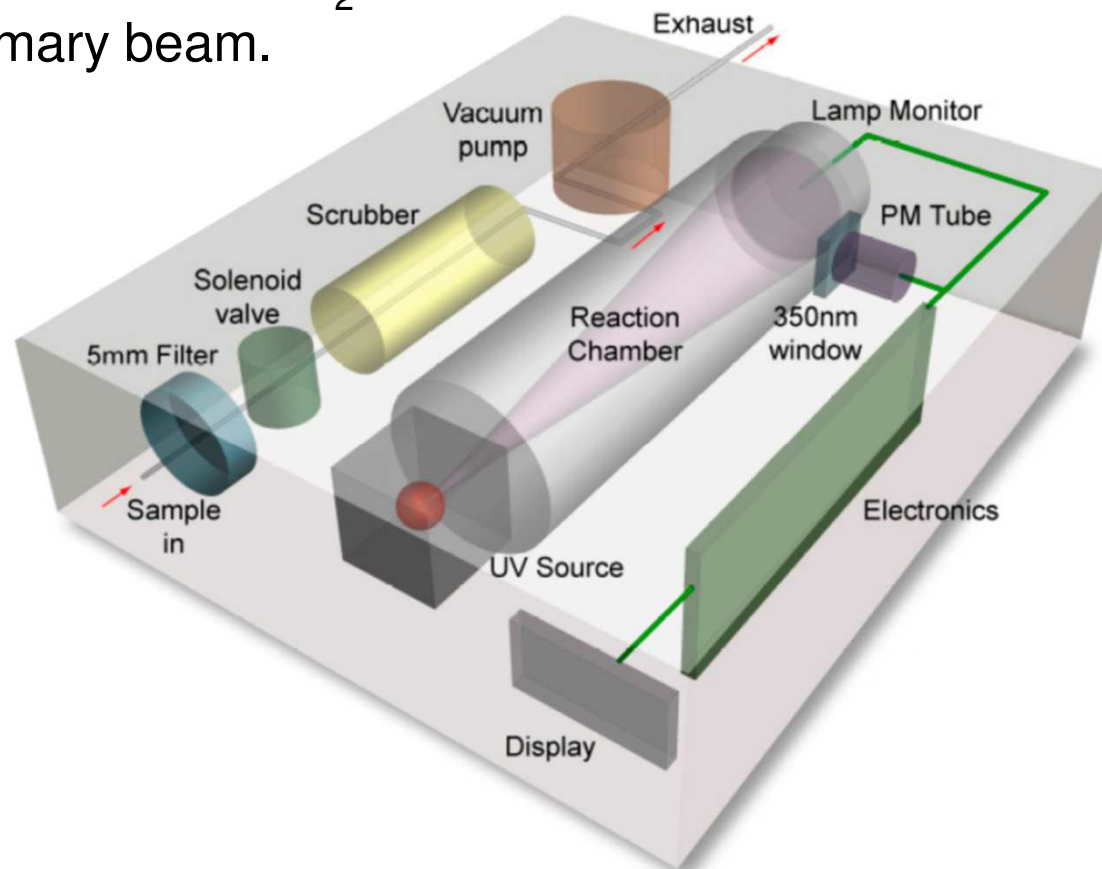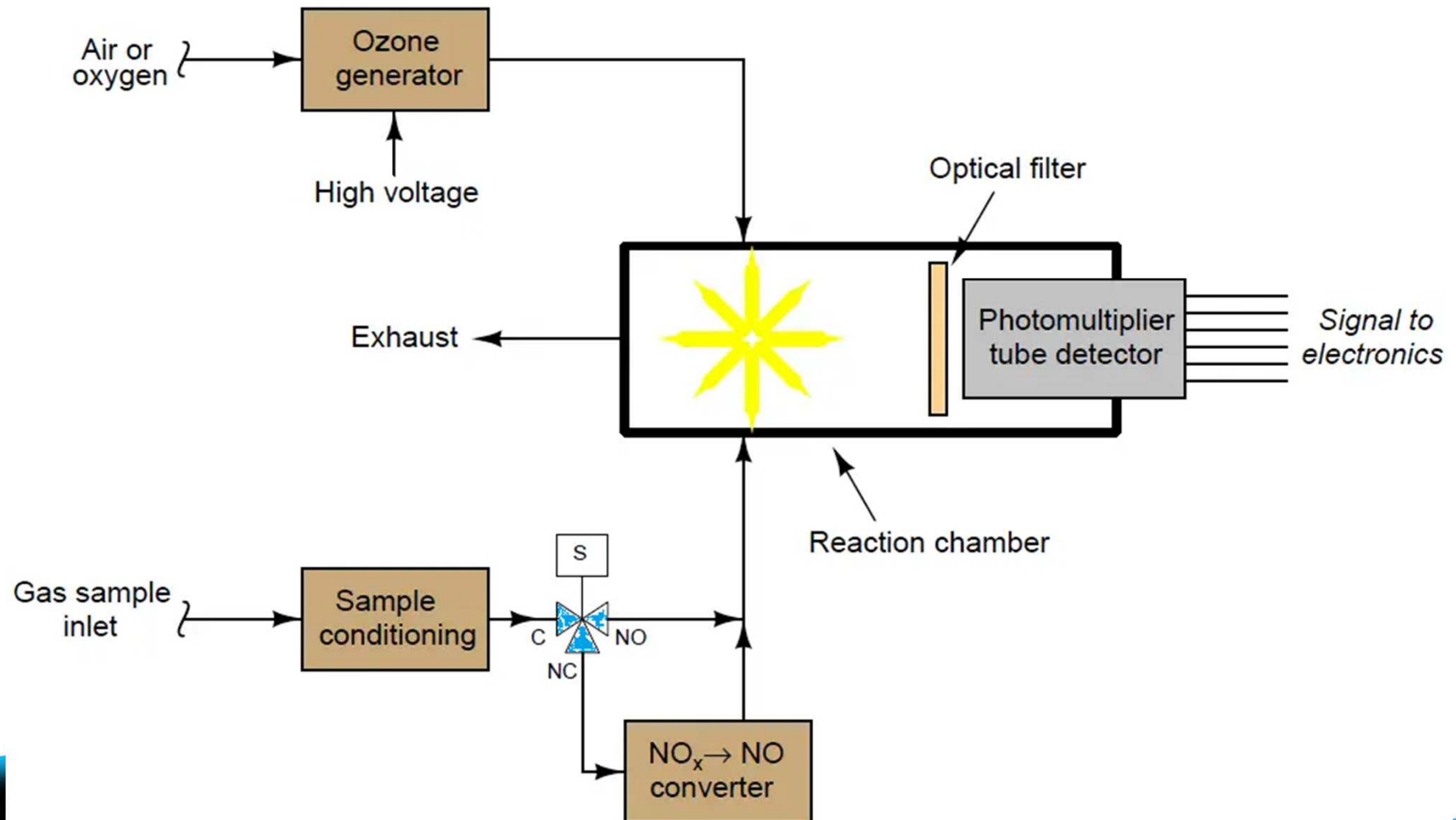
- Example – AIM station, method overview (examples only)

- NO_x ($NO + NO_2$)   chemiluminiscence method

NO measurement: The device generates the ozone, which oxidises NO to form NO_2. Ca. 10 % of the generated NO_2 is obtained in excited state. During the transition back to the initial state the particles produce the radiation, which corresponds to the NO_2 concentration. This secondary radiation is detected by a photodiode.

Measurement of NO_2: In the first step molecules of NO_2 are reduced to NO, which is measured by the same mechanism as described above. Then the sum of NO_x is done by counting $NO + NO_2$.

- Example – AIM station, method overview (examples only)

- NO_x (NO + NO_2)   chemiluminiscence method
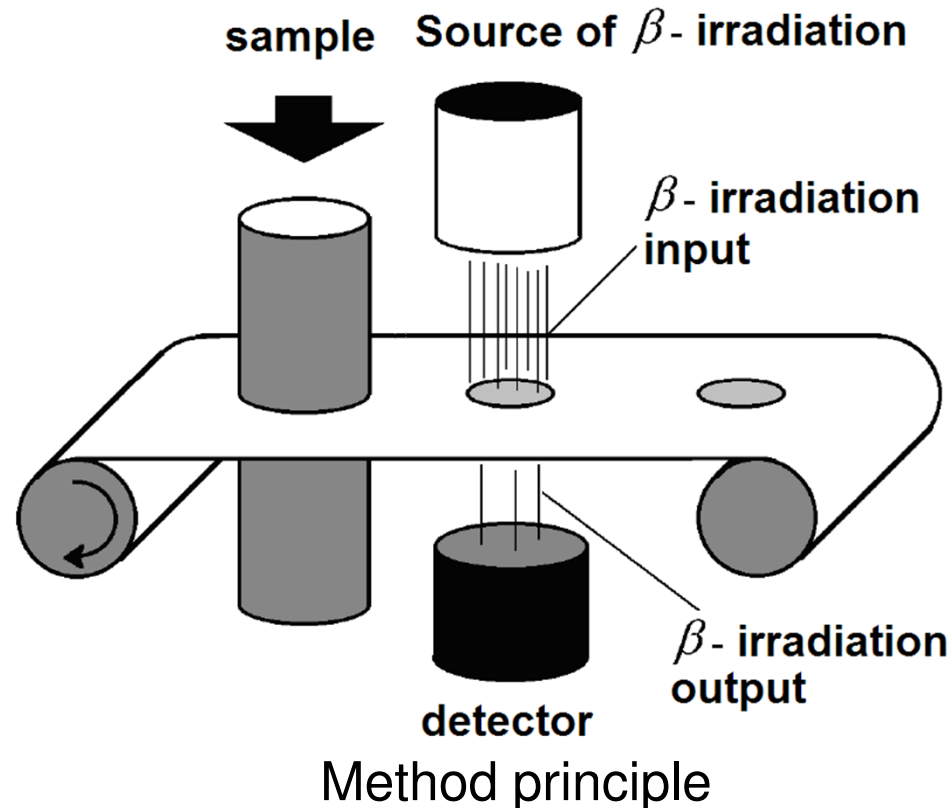
- Example – AIM station, method overview (examples only)

- PM$_{10}$ radiometric method
  Absorption of β-irradiation in the sample captured by a flat filtering material. Differences in absorbance between exposed and unexposed filters correspond to the concentration of particulate matter in the air.

Sampling head

Method principle

- Example – AIM station (Source: Ekologické centrum Most)

- Conventions and possibilities of AIM distribution according to the purposes:

  - traffic AIM stations – installed within 50 m from the road with high traffic intensity (it should represent the line with the maximum length);

  - industrial AIM stations – installed inside industrial company premises or in the area with supposed impact by the smoke (due to predominant wind direction);

  - background AIM stations – installed in the localities with no direct influence of industry or traffic; it measures the tropospheric background in the cities, countryside or industrial districts:

    - representative radius for downtown and suburban AIM: more than 1 – 1.5 km,

    - representative radius fro countryside AIM: more than 5 – 60 km (usually 10 – 20 km).

Computers – 3rd condition for IS

- Development of computers

  (Source: http://www.fi.muni.cz/usr/pelikan/ARCHIT/TEXTY/HISTOR.HTML)

- Division into generations; each generation has a characteristic configuration, performance and basic construction element:

Generation	Beginning	Cases	Configuration	Operations
0.	1940	many	relays	units/s
1.	1945-52	tenths	tubes	100 – 1 000
2.	1958	< 10	transistors	10^3
3.	1964	< 5	circuits SSI, MSI	10^4
3½.	1972	1	circuits LSI	10^5
4.	1981	1	circuits VLSI	10^7 and more

4 th generation has remained till the present, only miniaturization and increase of performance.
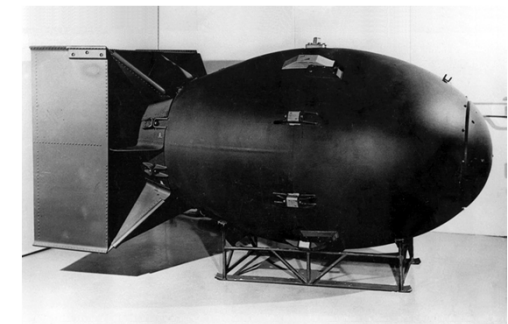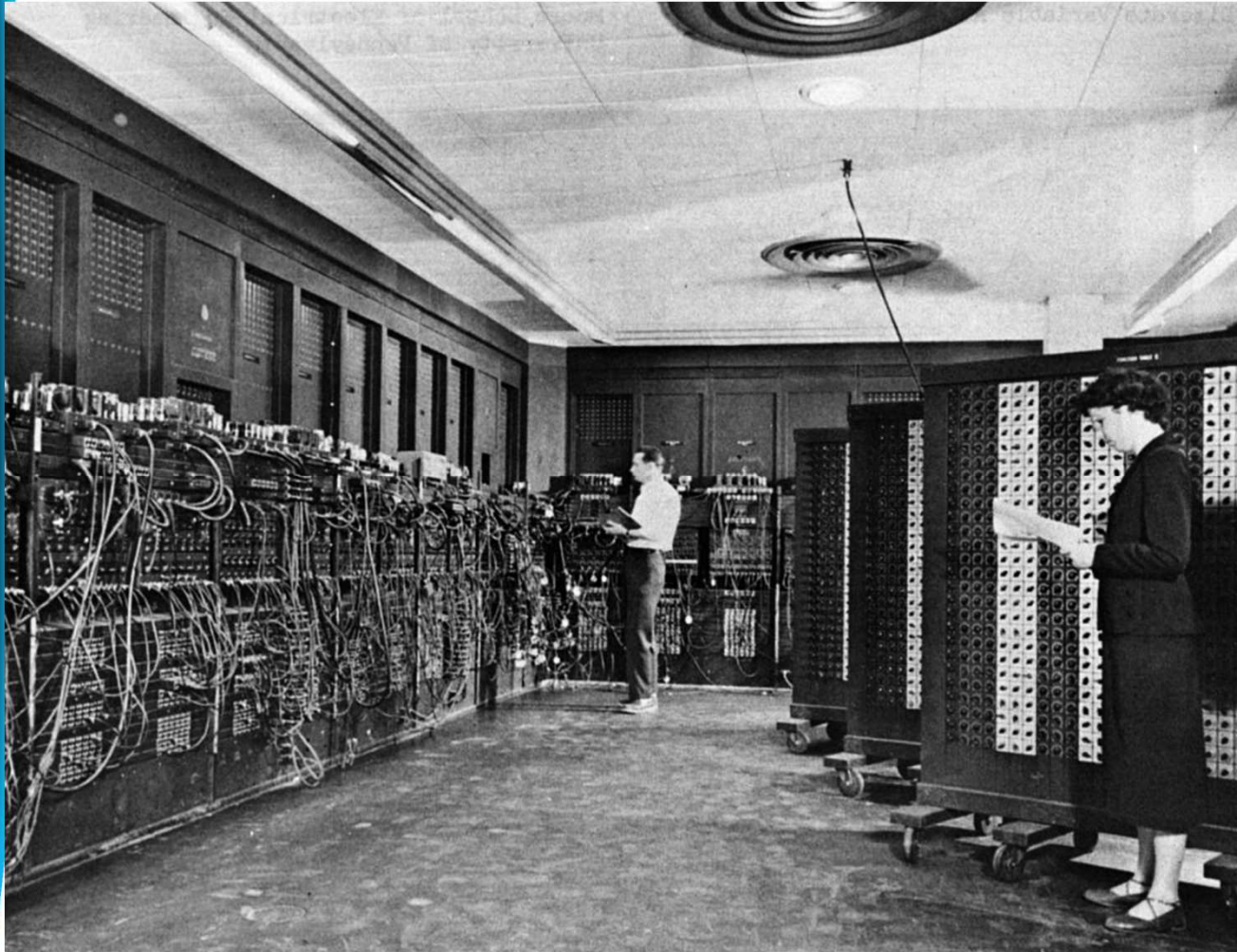
5th generation = artificial intelligence; not available

Note. Circuits according to logical members: SSI = Small Scale Integration, MSI = Middle Scale Integration, LSI Large Scale Integration, VLSI Very Large Scale Integration

- Development of computers – ENIAC 1946 (1st generation) –

military purposes

■ Development of computers

IBM 7090 – 2nd generation

IBM 360 – 3rd generation

Computers – 3rd condition for IS

- Development of computers – beginning of 4th generation
- One of the very first laptops:

Osborne 1

Introduced	1981
Contemporary price	1795 $
CPU frequency	4 MHz
RAM	64 kB
HDD	none

HP Spectre Pro x360 G1 ultrabook

1490 $ in the year 2014

CPU frequency (dual core)	2.7 GHz
RAM DDR3	4 GB
HDD SSD	128 GB

- Progress in computers – increase of performance, so called Moore's law (from 1965: number of transistors in an integrated circuit has doubled each 18 months). However, currently the multiplication of transistors occurs every 2 years and the validity of the law is estimated for next ca. 20 years.
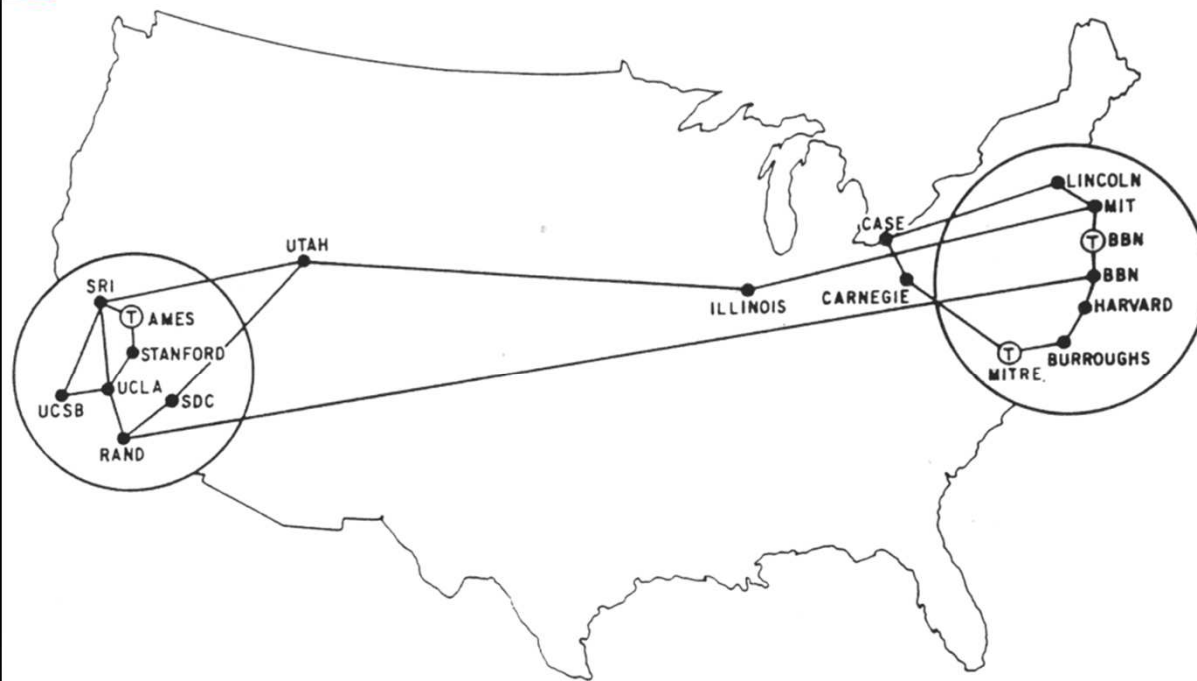
Network – 4th condition for IS

- Development of networks
  - The oldest network using data packs and having decentralized conception and possibility to be accessed by various types of computers was reserved for U.S. government computers:

ARPANET
solution published in1964
commissioned in 1969

State of ARPANET in 1971

Network terminal
(end of sixties)

Network – 4th condition for IS

- **Development of network, milestones**

- 1969 ARPANET — Note: stopped in 1990
- 1971 introduced email
- 1972 introduced Telnet — terminal program, which allows remote working on the selected servers
- 1973 widely used FTP — File Transfer Protocol (first version published in 1971)
- 1977 introduced mailing list
- 1979 Usenet, uucp — fundamentals of chat groups, based on architecture Unix-To-Unix Copy
- 1982 TCP/IP expansion — Transmission Control Protocol/Internet Protocol, primary protocols for internet
- 1984 DNS — Domain Name System
- 1986 NSFNET — National Science Foundation Network, fundamentals of internet between 1986–1995
- 1991 WWW, Gopher — Gopher service had similar purpose as www, (later overcome commercially by www)
- 1992 Veronica — search engine for Gopher servers …….

Life cycle of information

- Level of permissions for working with database according to authorization: basic users should not have the full access ⇒ they download available data only through online applications – better for data safety (Source: Hřebíček J.: Environmentální informační systémy)
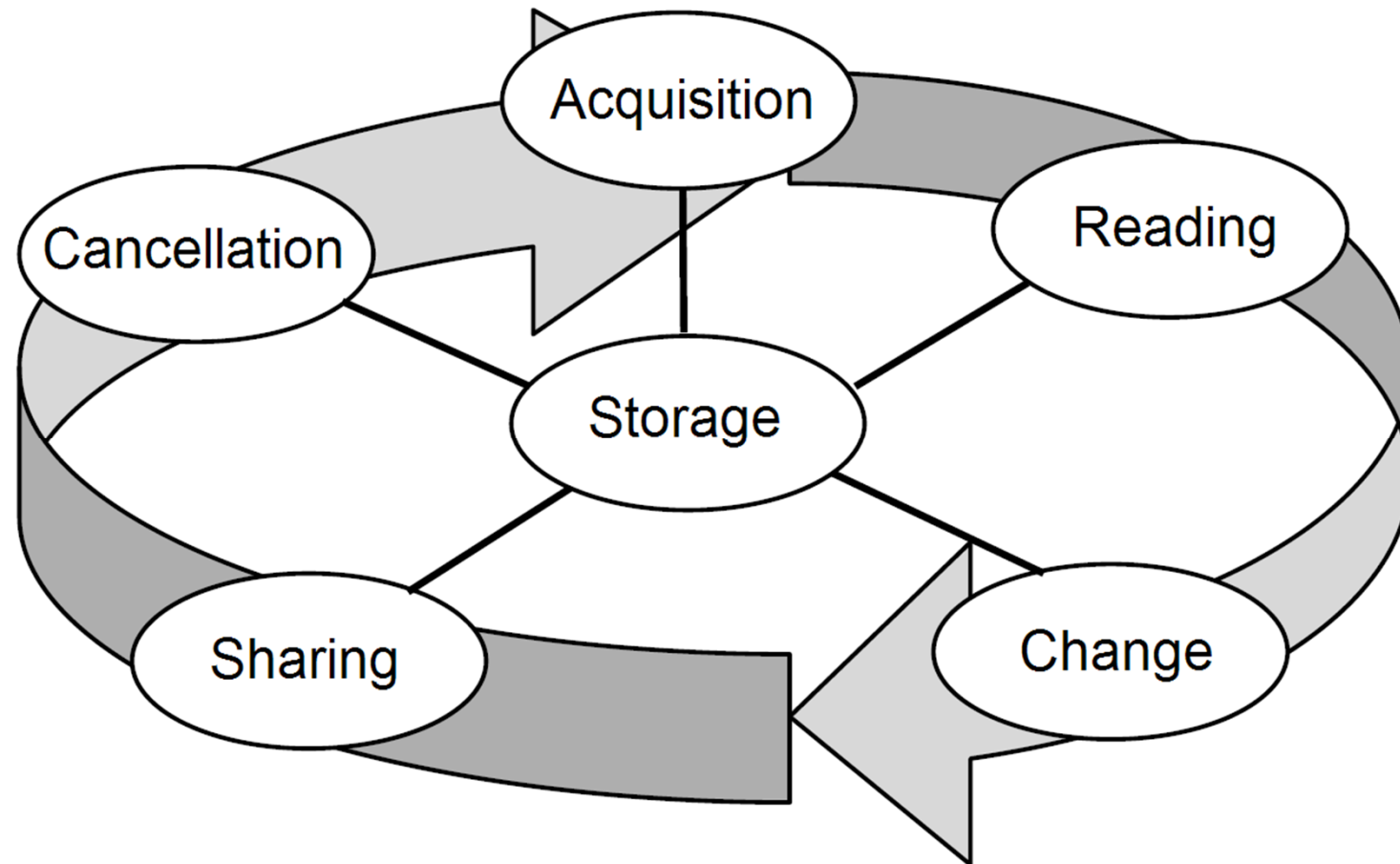
Purpose of environmental IS

- European model for influencing the environmental pollution by the state authority (Source: Hřebíček J.: Environmentální informační systémy)

- In the EU model DPSIR has been proposed (Driving force-Pressure-State- Impact-Response)

- Model DPSIR is actually applied for handling the environmental data by European Environment Agency – EEA.

- Model DPSIR depicts relationships among those factors, which influence the environment, and the tools available for their regulation.

Purpose of environmental IS

- Model DPSIR (Driving force-Pressure-State-Impact-Response)

(Source: Hřebíček J.:   Environmentální informační systémy)