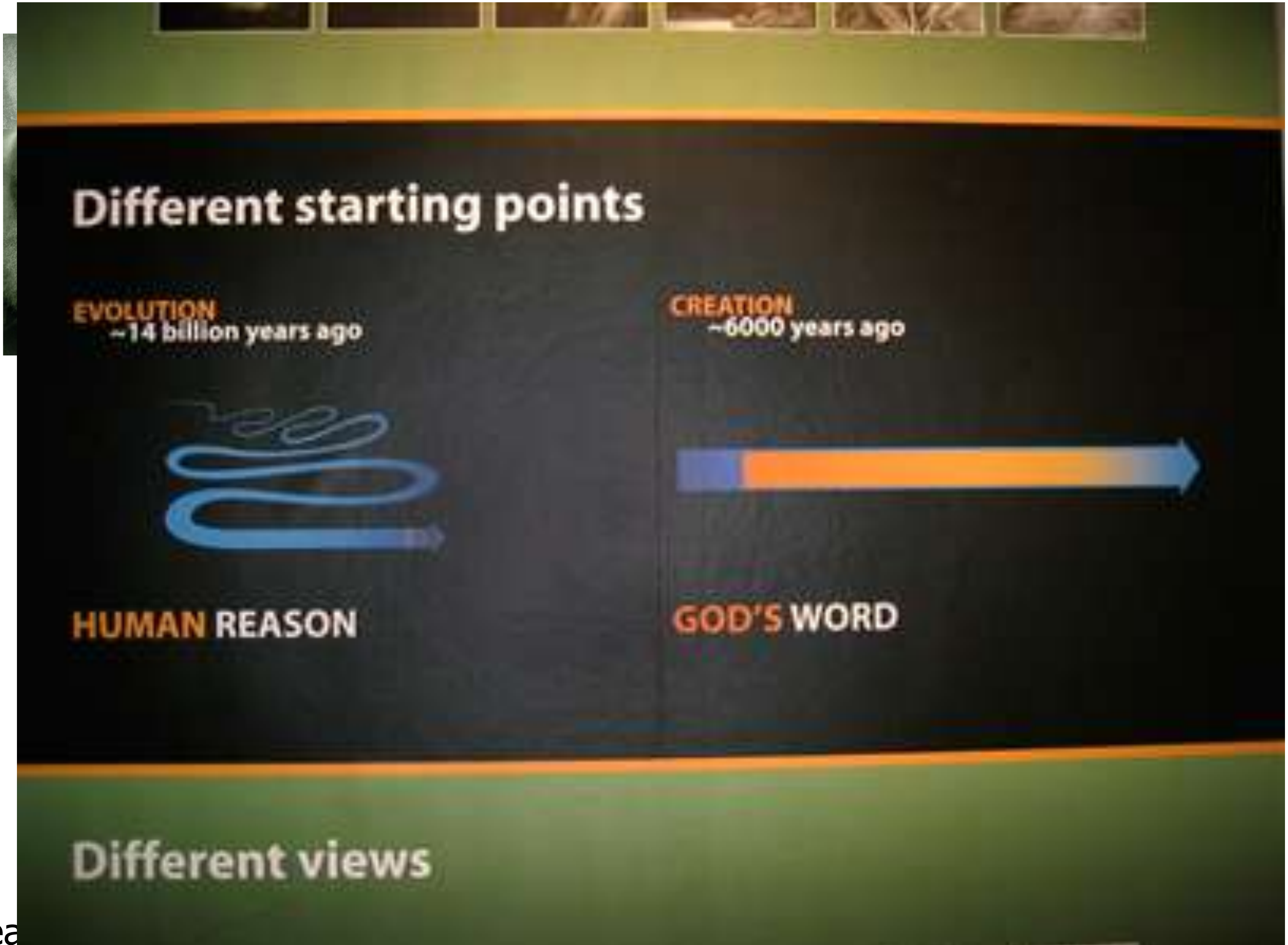
The Chemical Origin of Life

Thomas Lunkenbein

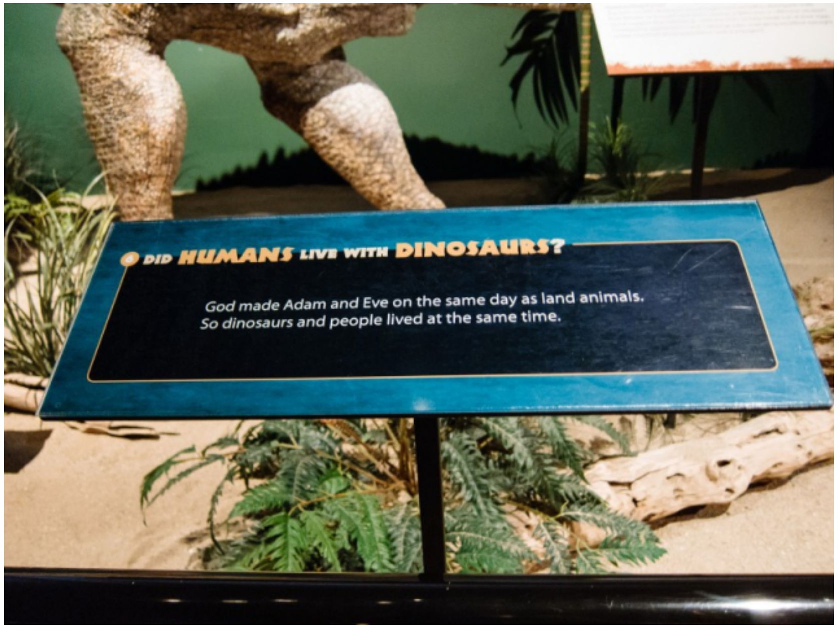
Berlin, 15.12.2017

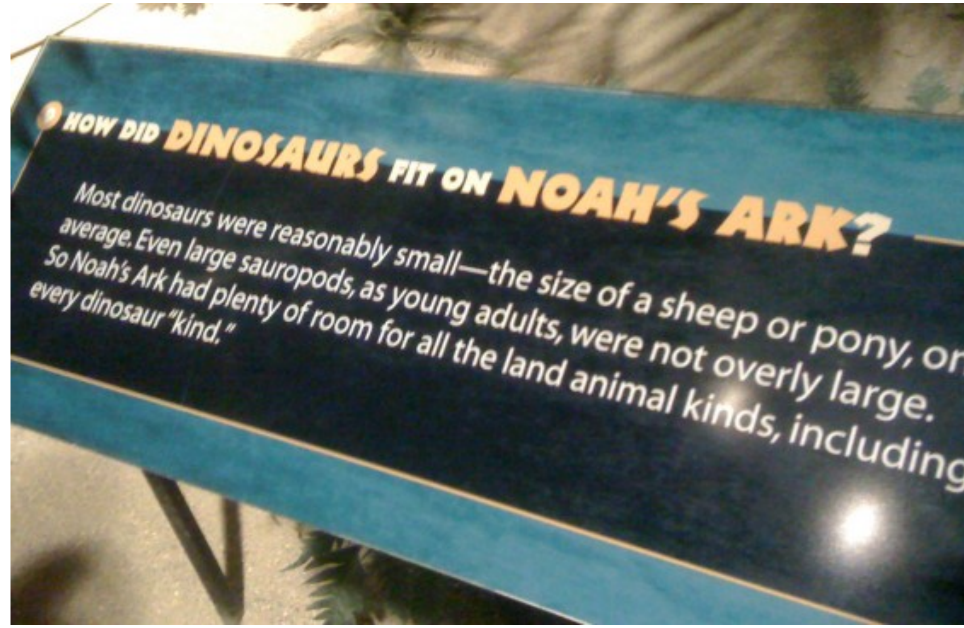
The Concepts

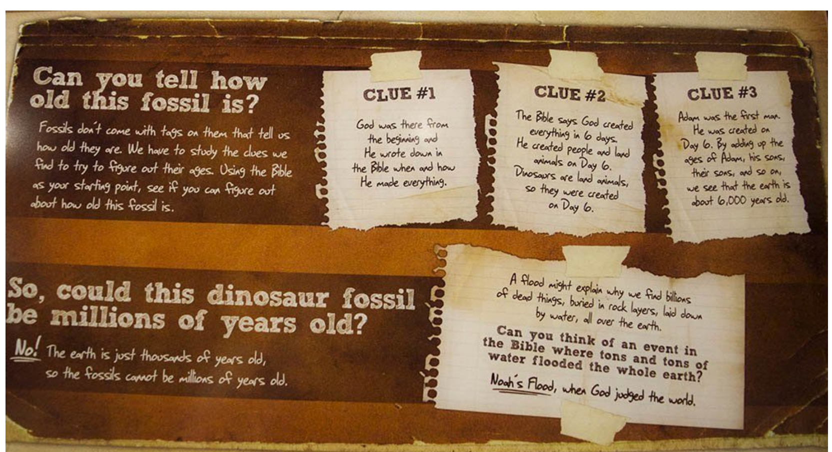


Crea

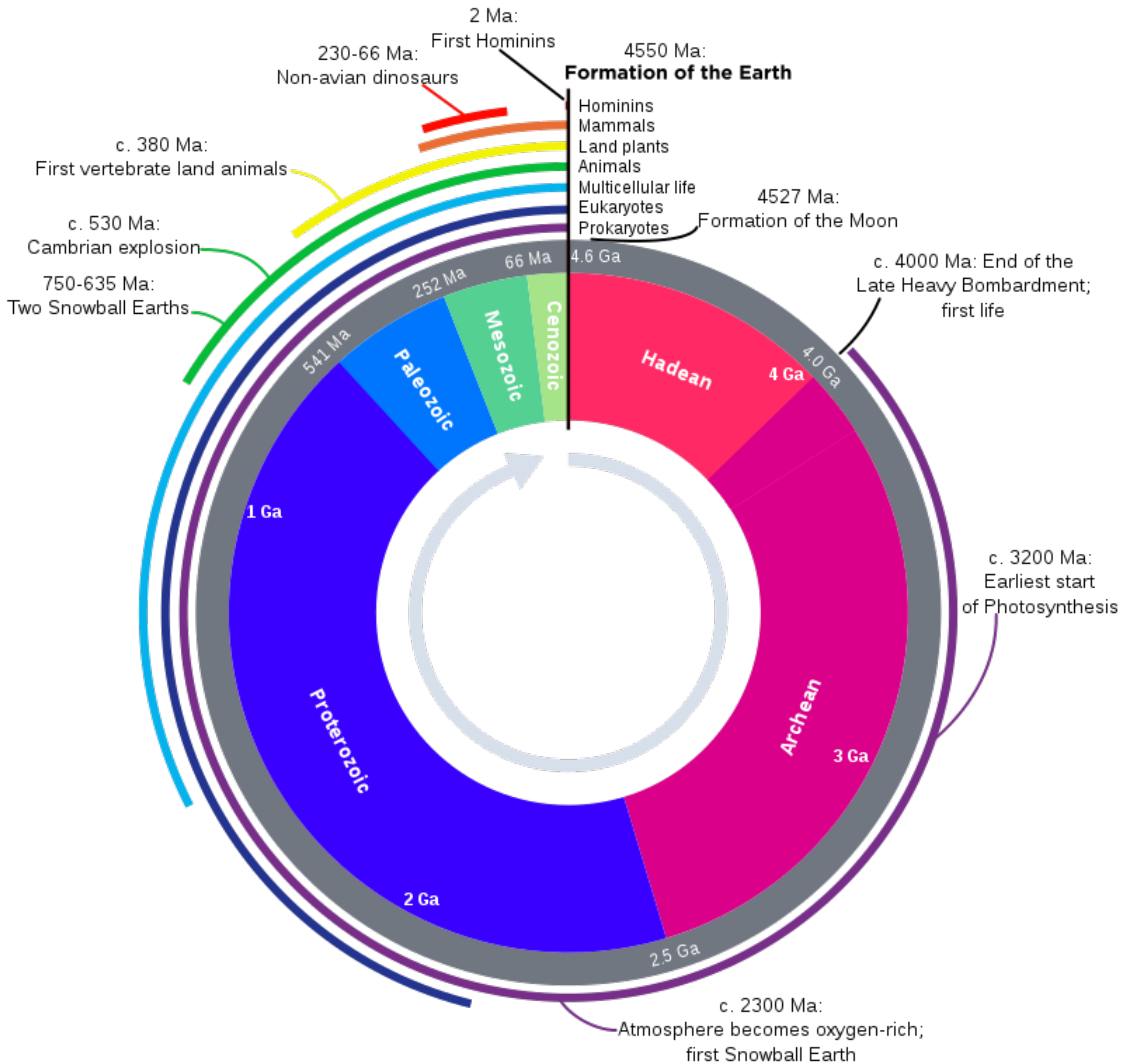
Creationism







The earth


2 Ma:
First Hominins
230-66 Ma:
Non-avian dinosaurs
4550 Ma:
Formation of the Earth
Hominins
Mammals
Land plants
Animals
Multicellular life
Eukaryotes
Prokaryotes
4527 Ma:
Formation of the Moon
c. 380 Ma:
First vertebrate land animals
c. 530 Ma:
Cambrian explosion
750-635 Ma:
Two Snowball Earths
c. 4000 Ma: End of the
Late Heavy Bombardment;
first life
66 Ma
4.6 Ga
252 Ma
541 Ma
Cenozoic
Mesozoic
Paleozoic
Hadean
4 Ga
4.0 Ga
1 Ga
Proterozoic
Archean
3 Ga
2 Ga
2.5 Ga
c. 3200 Ma:
Earliest start
of Photosynthesis
c. 2300 Ma:
Atmosphere becomes oxygen-rich;
first Snowball Earth

An earthlike planet

- History of earth:
  - <4.6 GA: proto-earth → coalescence of various sized planetesimals
  - 4.567 GA: Mars-sized object crashed into the earth → Ni-Fe core + moon from silicon-vapor atomsphere
  - Severe meteor bombardment → energy sufficient to keep rocks in a molten state
  - 4.56 GA: segregation into different, density dependent layers (core, mantel, atmosphere)
  - Water and other volatiles bubbled upwards and heavier ones sank.
  - - 3.8GA: Late Havey Bombardment meteor impact; cooling down, earth day 10 h: early atmosphere (CO2, H2S, H2O, CH4)
  - Sky color: orange to brick red, oceans: muddy brown (gas, liquid water, minerals)

An earthlike planet

- Rare Earth Hypothesis:

microbial life → common in the universe

animal equivalents: systems with planetary environmental stability for a certain time → are rare

- Many potentially habitable planets → only one many possible chemical recipes
- What are the needs?

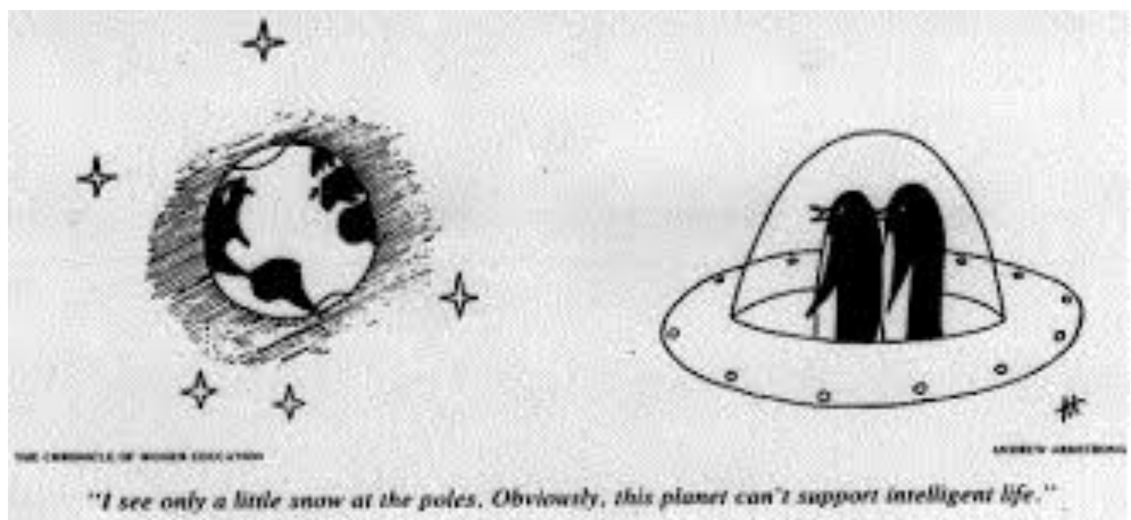
An earthlike planet

- Life as we know it:

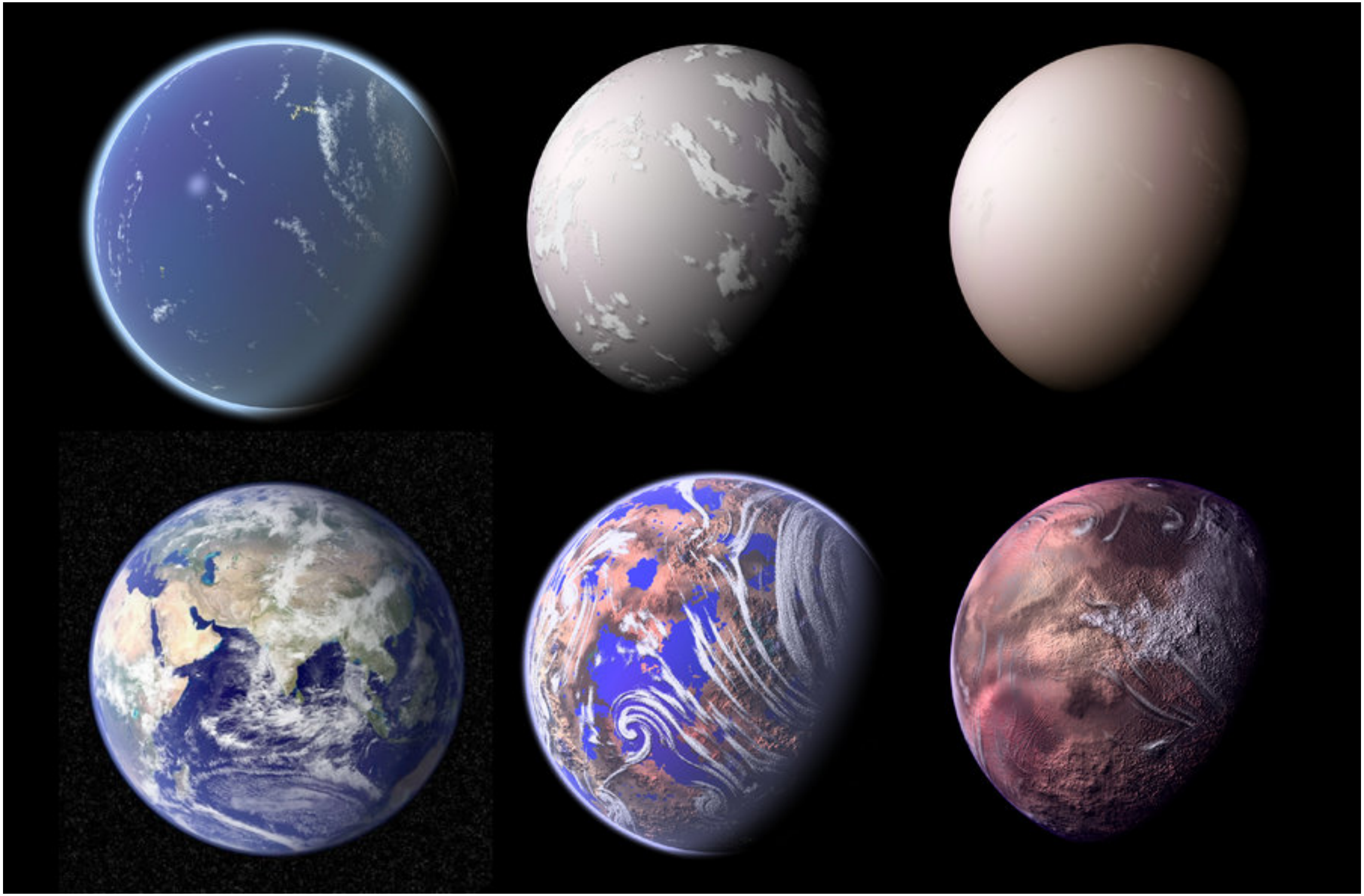
  Temperature and atmosphere, which allows liquid water to form on the surface → picture of modern earth

- Earth has changed greatly in the last 4.567 billion years:

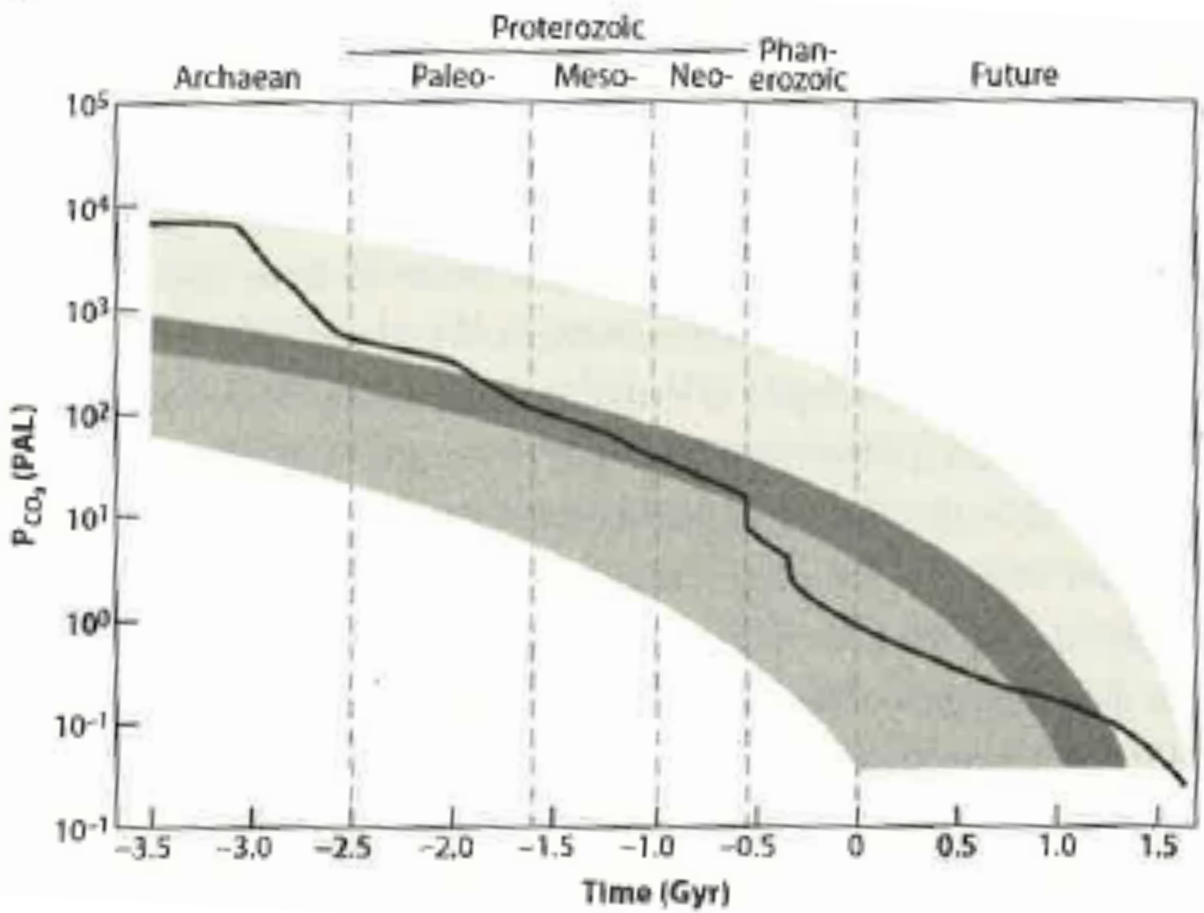
  half of its history complex life (animals, higher plants) was impossible



An earthlike planet

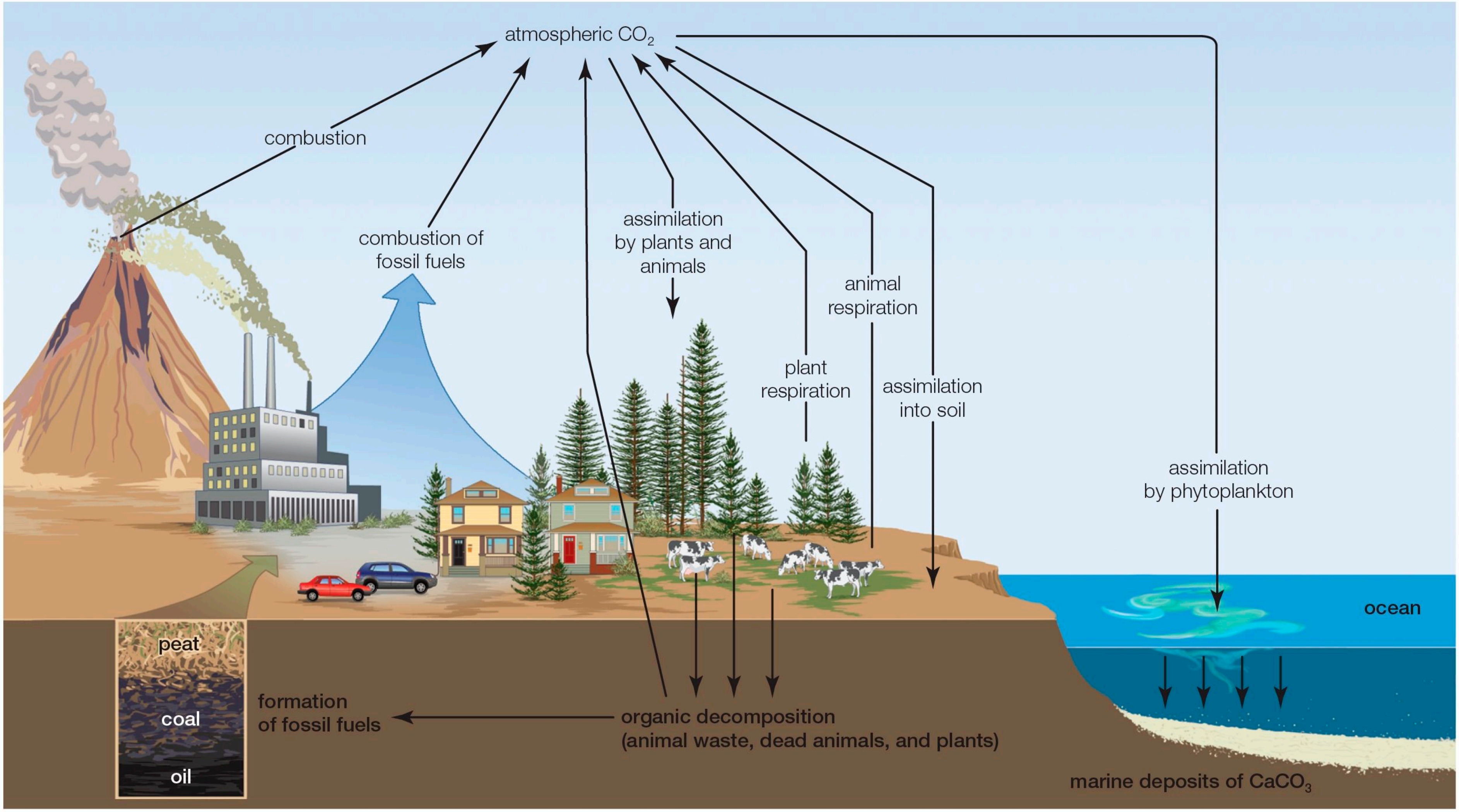


An earthlike planet –the atmosphere-



Element cycles control global temperature

e.g. C cycle (transfer between ocean, atmosphere and life)



Necessary life support systems

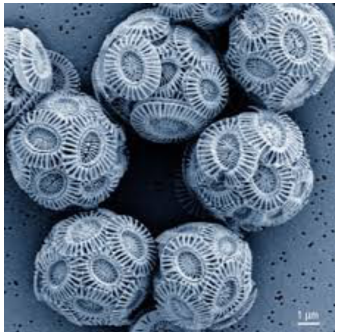
Short term

- Dominated by plants (photosynthesis)
- High energy carbon (reduced carbon)
- Uptake into other living organisms
- Oxidizing (energy will be free)
- Carbon buried without being consumed → cycle closes

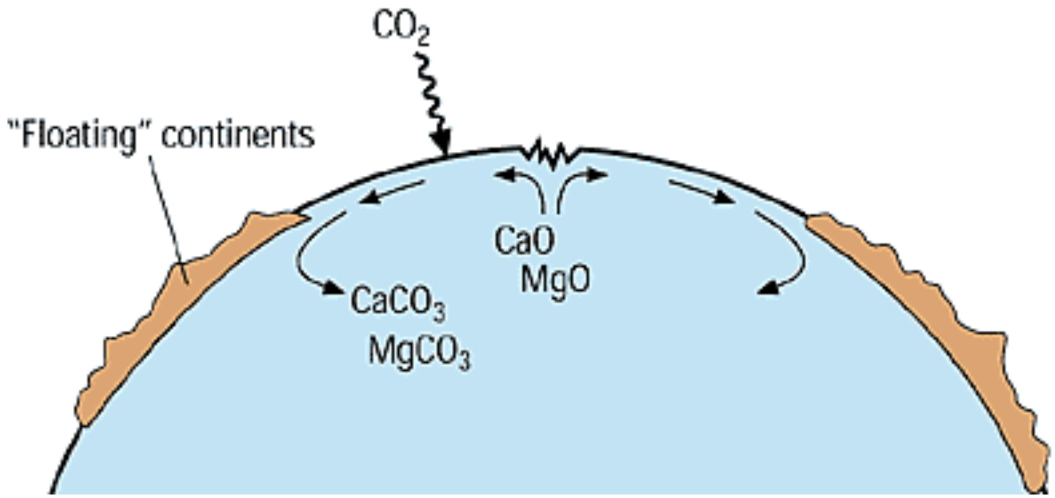
Long term

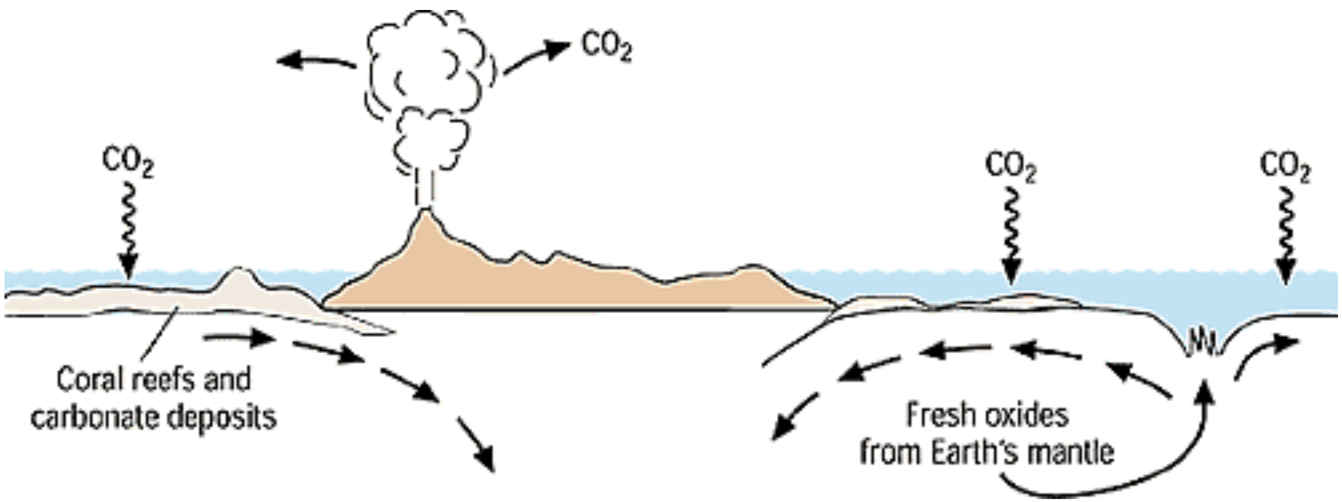
- Different kinds of transformations (between rocks, oceans and atmopshere
- Duration: millions of years
- Plenetary thermostat: Controls temperature via greenhouse effect
- Subduction controlled process (CO2 houshold)

Coccolithophorids,
Planktonic plants



Necessary life support systems

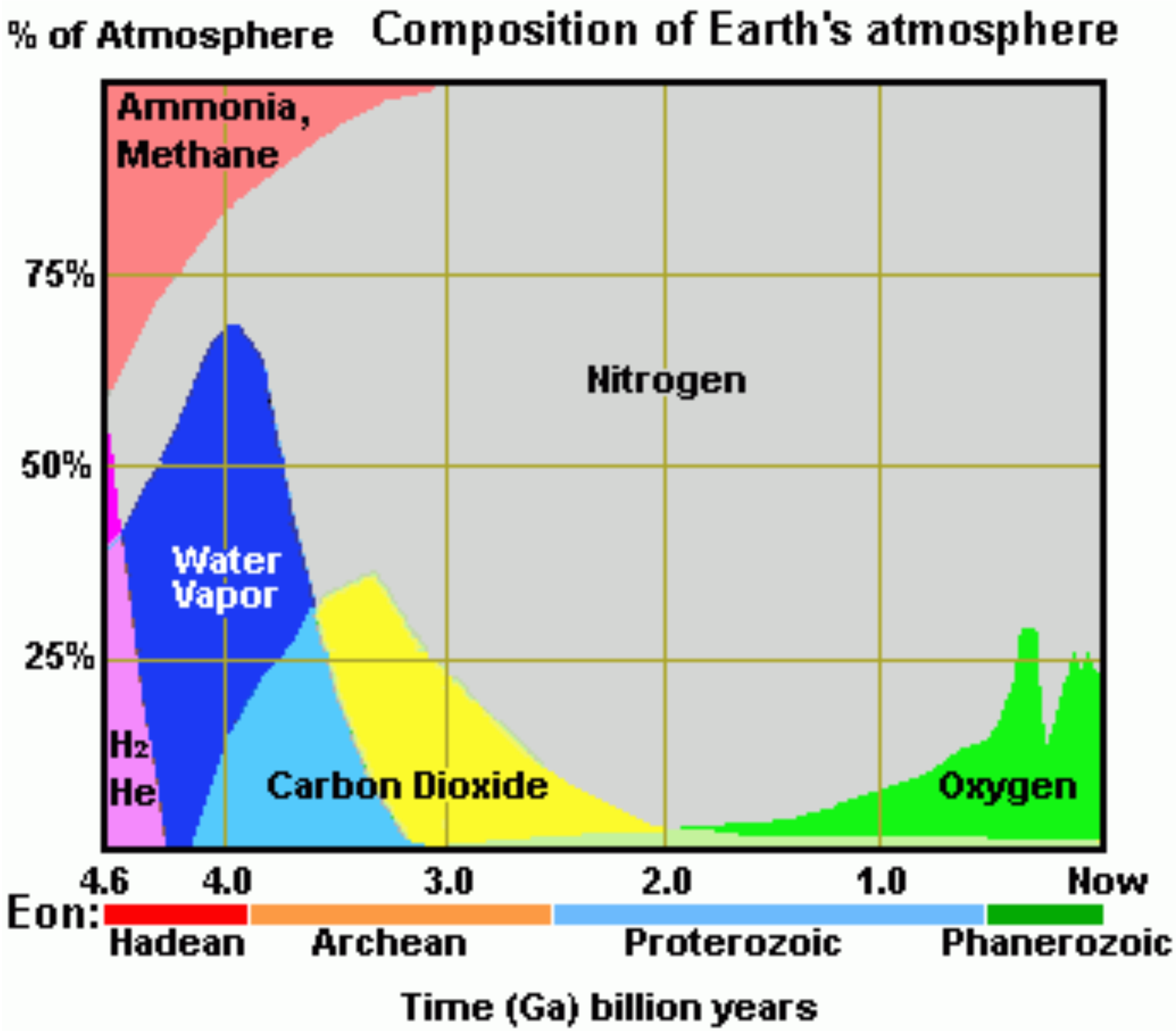




Life – Complex chemical experiments

- Conditions and materials were correct (4 billion years ago
- Interplay and concentrations of various componenets
- Kinetic vs. Thermodynamic products

atmospheric gases reducing enough to permit the building block of life → prebiotic molecules



What is life?

Definition of Life

- Physically:
- Every process that is going on in nature increases entropy → Life an entropical effect?
- Schrödinger:"*Living matter evades the decay to equilibrium*" *and life is maintained by extracting order from the environment (negative entropy)*
- Life: *device by which large numbers of molecules maintain themselves at fairly high levels of order by continually sucking orderliness from their environment*

Definition of Life

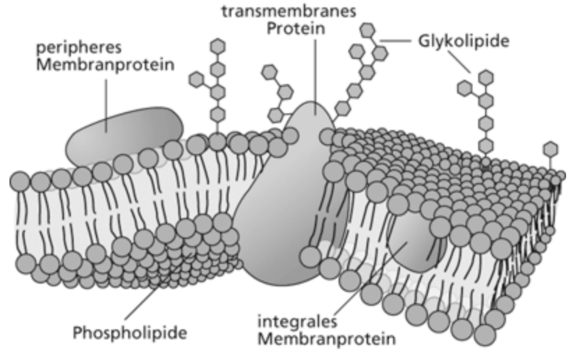
- Life metabolizes: chemicals → energy to harvest negative entropy and maintain internal order
- Life has complexity and organization: complex self-assembled macromolecules
- Life reproduces: copy of itself, copy of the mechnaism, copy of the replication apparatus
- Life develops: copy is made → life continues to change (un-machinelike).
- Life evolves: possibility to adapt
- Life is autonomous: self-determination; can proceed without constant input from other organisms.

Definition of Life

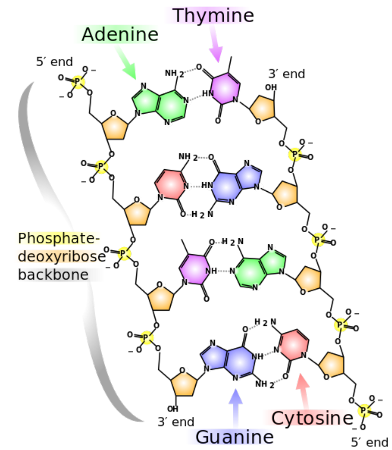
- Energy acquisition and energy dumping
- Self maintaining requires states of nonequilibrium order
- Role of Energy: overcoming thermodynamics
- What is the simplest assemblage of atoms that is alive?
- What is the simplest life form on earth? What does it need to stay alive?

Nonliving Building Block of Life

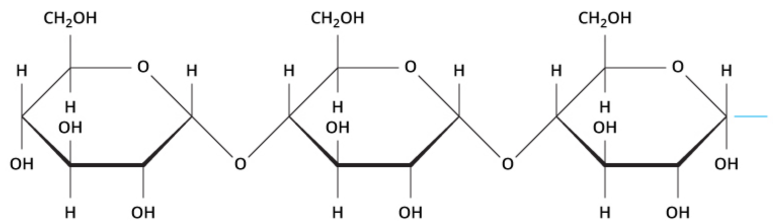
Liquid phase water
(neither solid nor gas) –
the bath tube of life



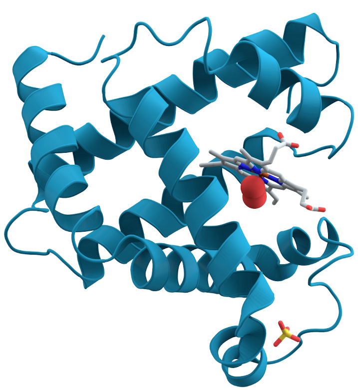
lipids



Nucleic acids –
genetic
information
Build up from
nucleotides



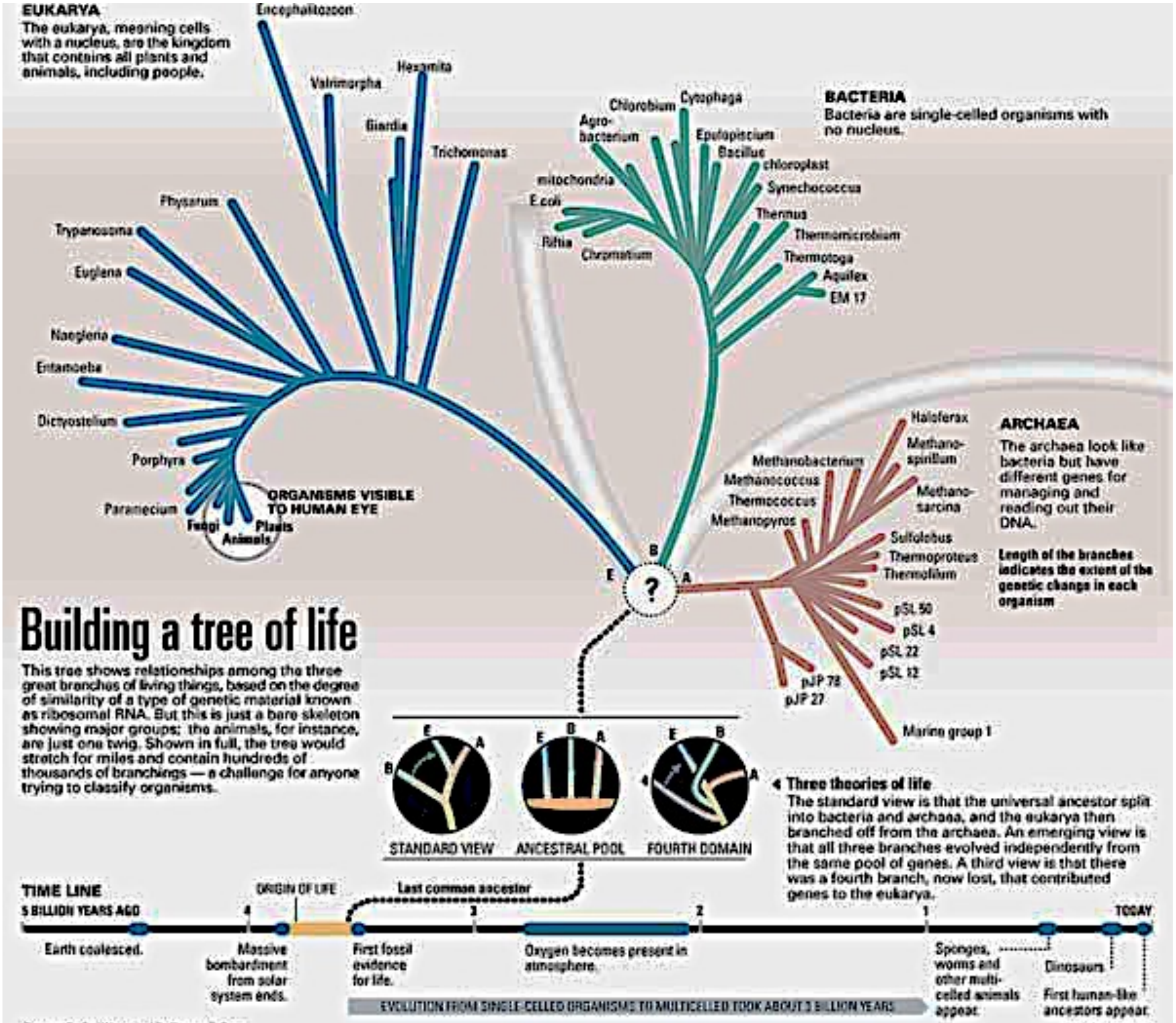
Carbonhydrates –
Building blocks for larger molecules



Proteins:
Building other larege molecules
Repairing other molecules
Transporting materials
Securing energy supply

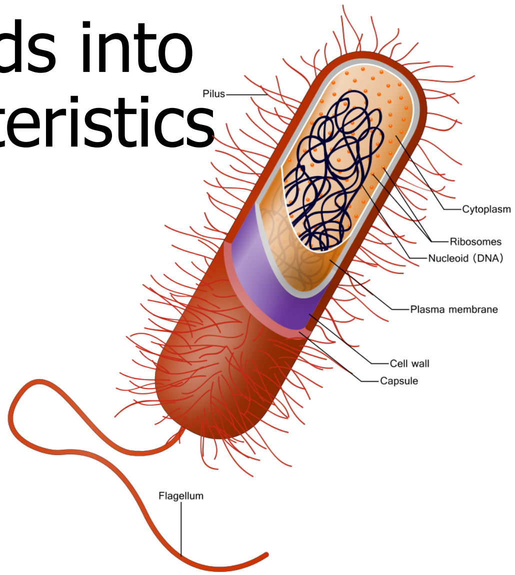
DNA/RNA
DNA double helix
RNA single
strand (DNA´s
slave) →
translates
information into
action

The tree of life



requirements

- 3.4 -3.5 GA oldest fossiles based on sulfur (sulfur bacteria
- Synthesis and accumulation of small organic molecules (amino acids, nucleotides, phosphates)
- Joining of the small molecules into larger molecules (proteins, nucleic acids)
- Aggregation of proteins and nucleic acids into droplets with different chemical characteristics compared to their enivronment (cell)
- Ability to replicate



How did it work?

Miller-Urey-Experiment

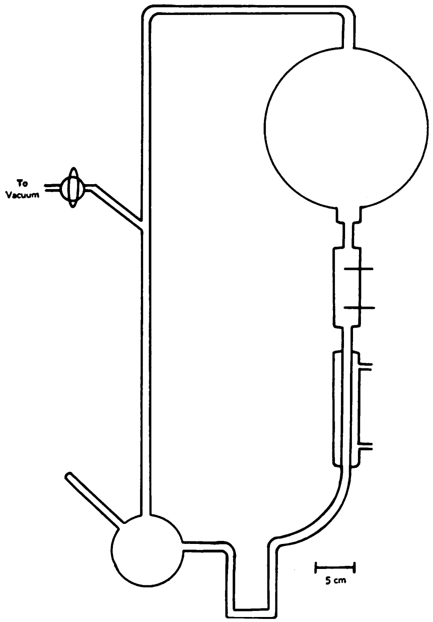


FIG. 1.

Table 1. Present sources of energy averaged over the earth.

Source	Energy (cal cm^{-2} yr^{-1})
Total radiation from sun	260,000
Ultraviolet light	
$\lambda < 2500$ A	570
$\lambda < 2000$ A	85
$\lambda < 1500$ A	3.5*
Electric discharges	4 †
Cosmic rays	0.0015
Radioactivity (to 1.0 km depth)	0.8‡
Volcanoes	0.13§

* Includes the 1.9 cal cm^{-2} yr^{-1} from the Lyman α at 1216 A (*39*). † Includes 0.9 cal cm^{-2} yr^{-1} from lightning and about 3 cal cm^{-2} yr^{-1} due to corona discharges from pointed objects (*40*). ‡ The value, 4×10^9 years ago, was 2.8 cal cm^{-2} yr^{-1} (*41*). § Calculated on the assumption of an emission of lava of 1 km^3 ($C_p = 0.25$ cal/g, $P = 3.0$ g/cm^3) per year at 1000°C.

Table 2. Yields from sparking a mixture of CH_4, NH_3, H_2O, and H_2; 710 mg of carbon was added as CH_4.

Compound	Yield [moles ($\times 10^5$)]
Glycine	63.
Glycolic acid	56.
Sarcosine	5.
Alanine	34.
Lactic acid	31.
N-Methylalanine	1.
α-Amino-*n*-butyric acid	5.
α-Aminoisobutyric acid	0.1
α-Hydroxybutyric acid	5.
β-Alanine	15.
Succinic acid	4.
Aspartic acid	0.4
Glutamic acid	0.6
Iminodiacetic acid	5.5
Iminoacetic-propionic acid	1.5
Formic acid	233.
Acetic acid	15.
Propionic acid	13.
Urea	2.0
N-Methyl urea	1.5

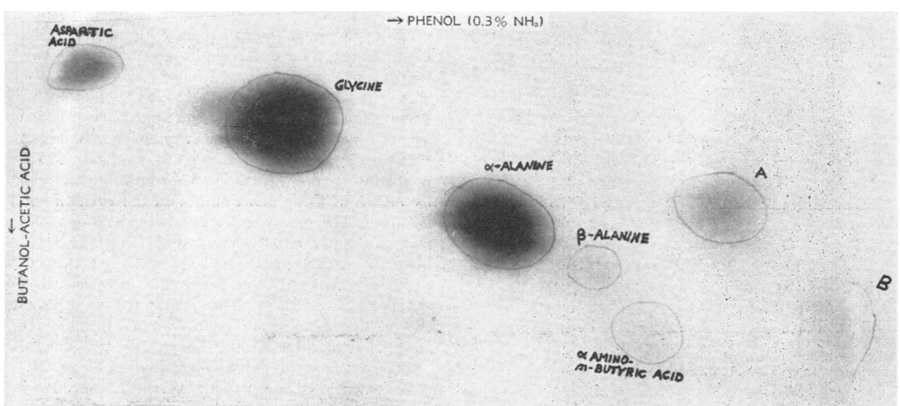
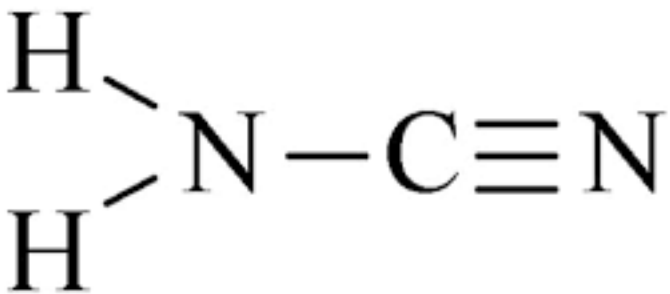


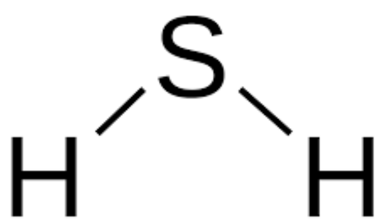
FIG. 2.

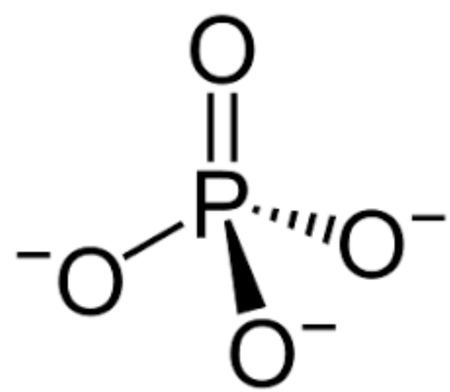
At the end of the run the solution in the boiling flask was removed and 1 ml of saturated $HgCl_2$ was added to prevent the growth of living organisms. The

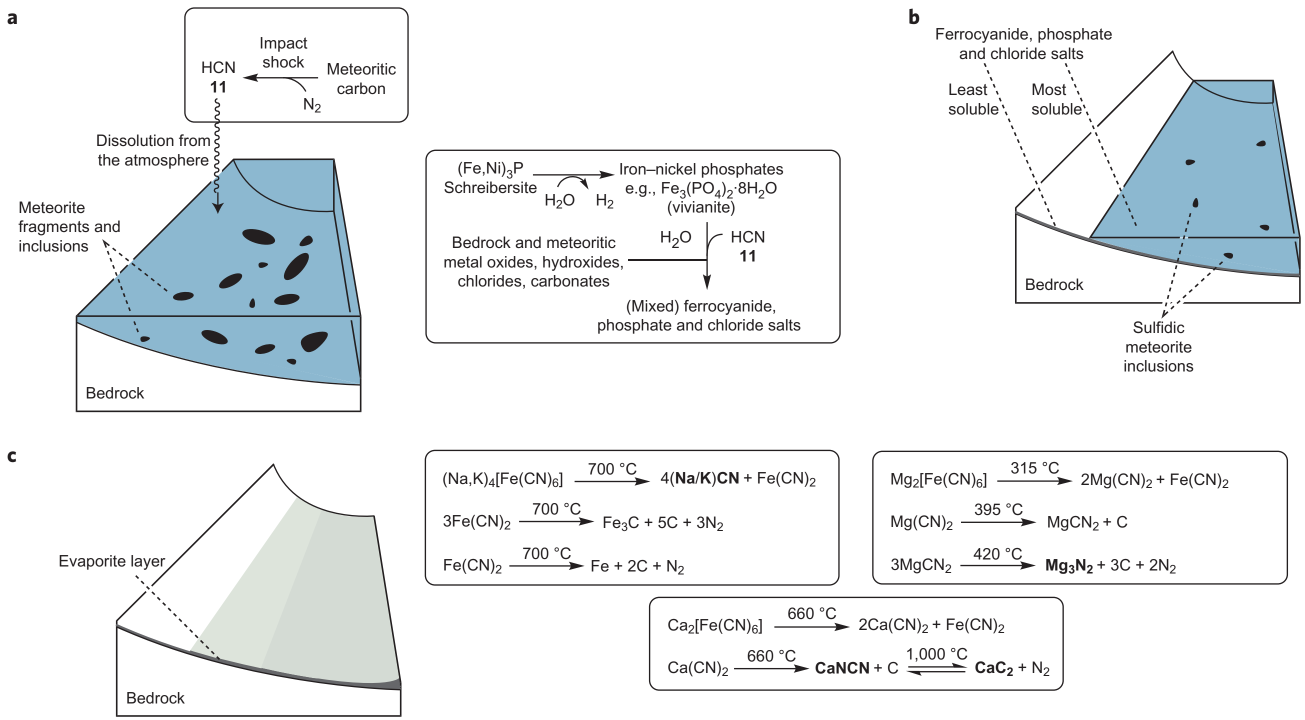
Reaction pathway to educts

- biologically relevant compound: HCN
- reaction network requires: cyanamide, cyanoacetylene, phosphate and hydrogen sulfide





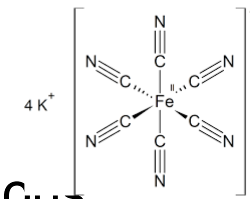




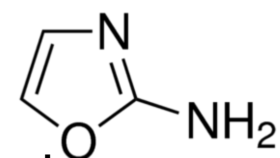
a
Impact shock
HCN 11
Meteoritic carbon
N2
Dissolution from the atmosphere
Meteorite fragments and inclusions
Bedrock
(Fe,Ni)3P Schreibersite
H2O
H2
Iron–nickel phosphates e.g., Fe3(PO4)2·8H2O (vivianite)
Bedrock and meteoritic metal oxides, hydroxides, chlorides, carbonates
H2O
HCN 11
(Mixed) ferrocyanide, phosphate and chloride salts
b
Ferrocyanide, phosphate and chloride salts
Least soluble
Most soluble
Bedrock
Sulfidic meteorite inclusions
c
Evaporite layer
Bedrock
(Na,K)4[Fe(CN)6] → 700 °C → 4(Na/K)CN + Fe(CN)2
3Fe(CN)2 → 700 °C → Fe3C + 5C + 3N2
Fe(CN)2 → 700 °C → Fe + 2C + N2
Mg2[Fe(CN)6] → 315 °C → 2Mg(CN)2 + Fe(CN)2
Mg(CN)2 → 395 °C → MgCN2 + C
3MgCN2 → 420 °C → Mg3N2 + 3C + 2N2
Ca2[Fe(CN)6] → 660 °C → 2Ca(CN)2 + Fe(CN)2
Ca(CN)2 → 660 °C → CaNCN + C ⇌ 1,000 °C ⇌ CaC2 + N2

Educt formation

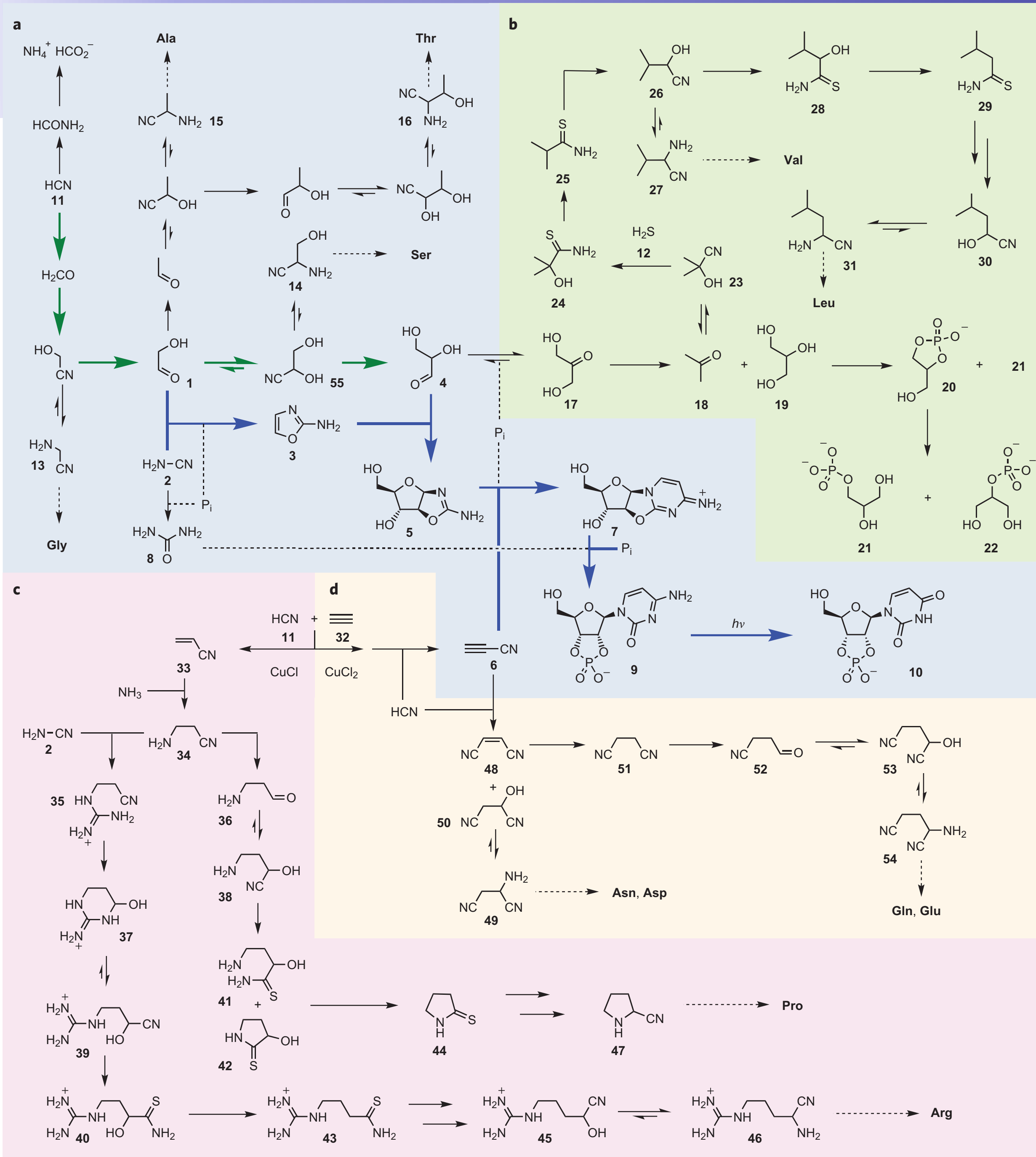
- HCN: high-temperature → carbonaceous meteors + atmospheric nitrogen
- Phosphate: schreibersite ((Fe,Ni)3P) + surface water



- gaseous HCN dissolved in surface water; coordinated by ferrous ions → ferrocyanide
- Group I salts of ferrocyanide + high temperatures → sodium or potassium cyanide + iron carbide and carbon.
- group II ferrocyanide salts: magnesium ferrocyanide → magnesium nitride (Mg3N2), calcium ferrocyanide → calcium cyanamide (CaNCN) → calcium carbide (CaC2) + nitrogen

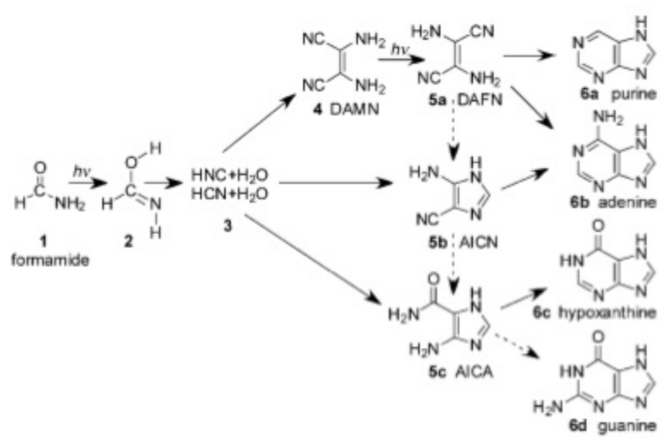


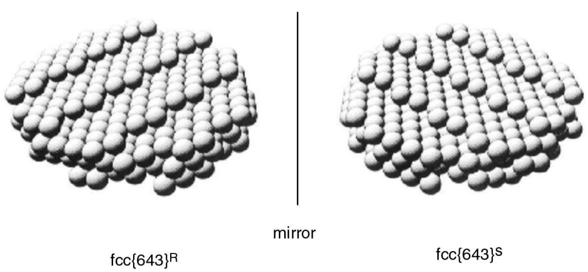
- hydrolysis of calcium cyanamide → cyanamide → 2-aminooxazole
- hydrolysis of calcium carbide → acetylene; oxidatively coupled with hydrogen cyanide → cyanoacetylene
- Hydrolysis of magnesium nitride → ammonia + HCN → Strecker synthesis of α-aminonitriles from aldehydes
- sodium or potassium cyanide solution + metal sulfides → hydrosulfide, the stoichiometric reductant (photochemistry)


a
b
c
d
NH_4^+ HCO_2^-
$HCONH_2$
HCN 11
H_2CO
Ala
Thr
Ser
Gly
Val
Leu
H_2S 12
P_i
hν
HCN 11 + 32
CuCl
$CuCl_2$
NH_3
H_2N-CN 2
HCN
Asn, Asp
Gln, Glu
Pro
Arg
1 2 3 4 5 6 7 8 9 10 11 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55

Origin of life

- Oparin + Haldane: prebiotic soup or primeval broth that covered the Earth;
- Miller + Urey: simulated lightning on H2O, CH4, NH3 and H2 → organic compounds (aldehydes + amino acids) + HCN
- Strecker synthesis: amino acids through the hydrolysis of the reaction products of HCN, ammonium chloride and aldehydes
- polymerization of HCN produced the nucleic acid bases adenine and guanine
- further condensation and polymerization of organic precursor requires concentration (evaporation of tidal pools, adsorption to clays, concentration in ice through eutectic melts and giant oil slicks, temperature cycling)
- Chiral surfaces: seperation of enanotiomers





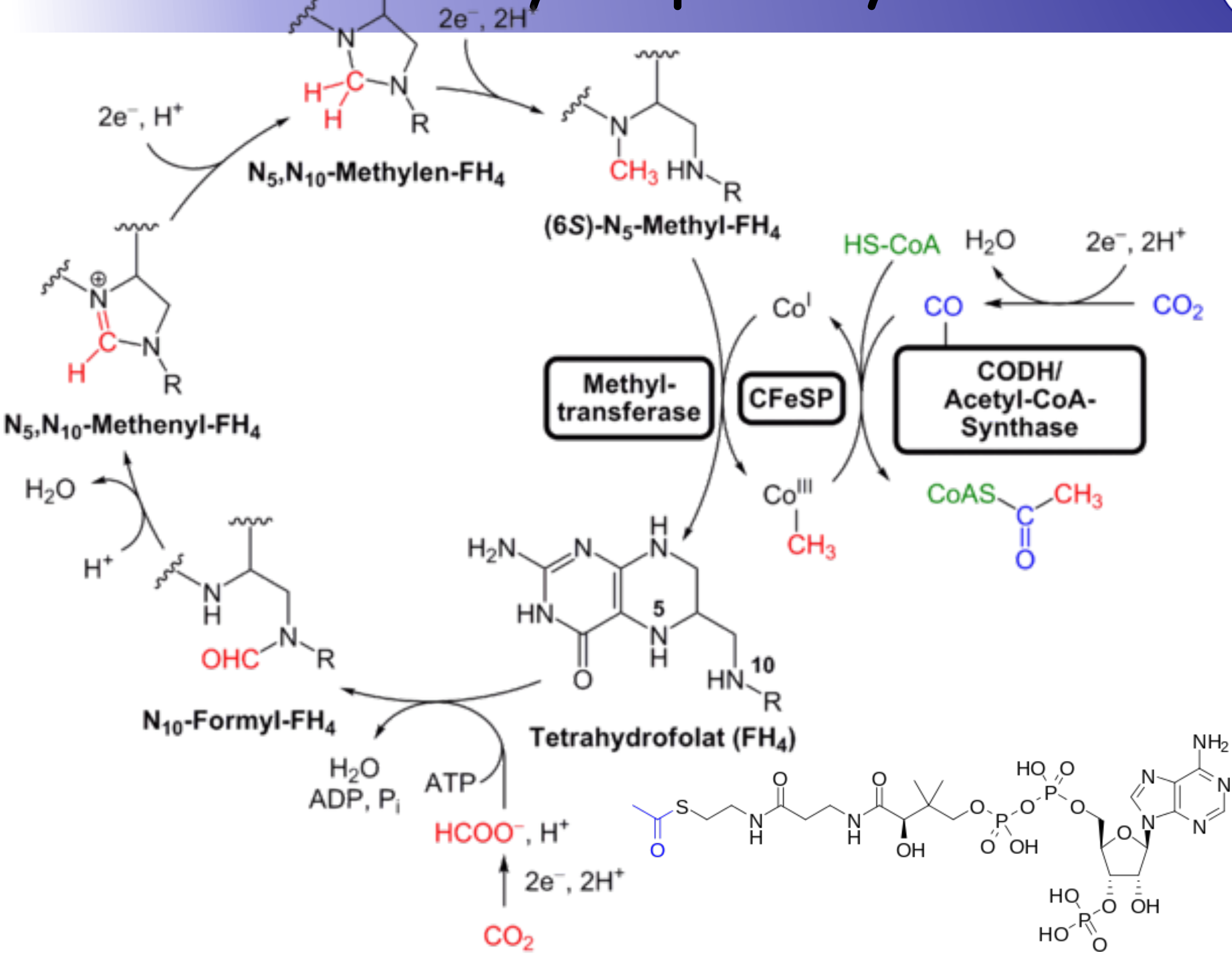
Origin of Life

- The concepts:
- information first' (or RNA world) versus a 'metabolism first' (or autotrophic origins)
- information-first: evolutionary transition occurred from peptide, nucleic acids to tetrose nucleic acids and to RNA
- tetrose was derived from formaldehyde condensations and bases were derived from HCN condensations
- essential building blocks of life were synthesized in space and reached early Earth by comets.
- → organic soup, but without the help of lightning

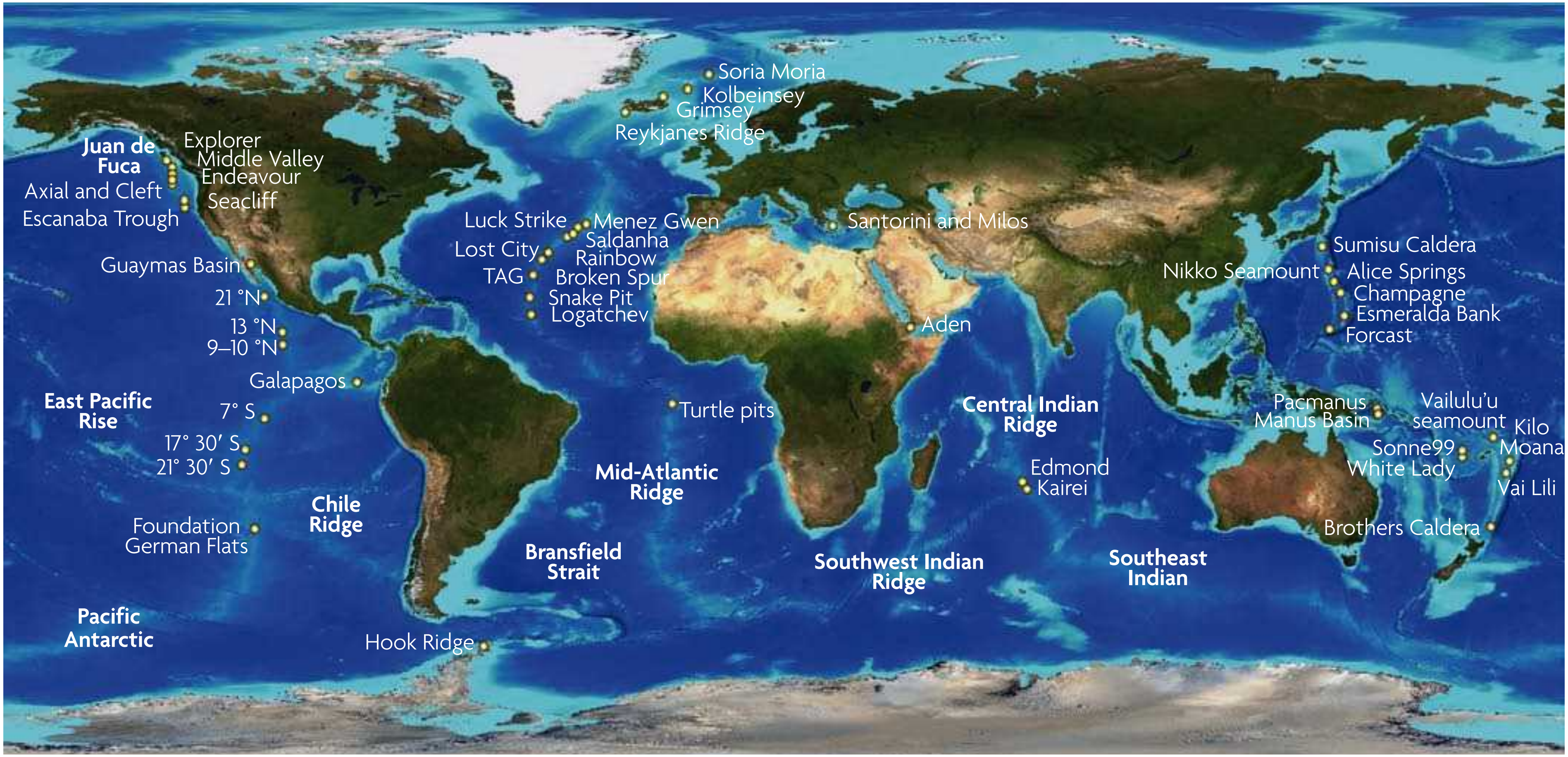
Vents

- Metabloism first: H2-dependent chemistry of transition-metal sulphide catalysis in a hydrothermal-vent
- Chemical conversion similar to biochemical CO2 reduction biochemistry of modern microorganisms → Wood–Ljungdahl acetyl-coenzyme A (acetyl-CoA) pathway → plausible starting point for biochemical evolution
- Evidence: acetyl-CoA, an energy-rich thioester, most central carbon backbone in microbial metabolism
- Synthesis of acetate and CH4 from H2 and CO2 releases energy → energy need not derived from lightning or conditions in space
- Reactions take place readily on the Earth
- thermodynamics of CH4 and acetate formation support synthesis of more complicated biomolecules

Coacteyl-A pathway



Distribution of vents



Black smokers

- directly above magma chambers (1–3 kilometres beneath the sea-floor)
- emit hot (up to 405°C) chemically modified sea-water
- sea-water comes into close contact with the magma chamber
- Water moves through the crust to reemerge at the vents
- acidic (pH 2–3) effluent and rich in dissolved transition metals (Fe(II) and Mn(II))
- fueled by volcanoes, fluids contain high concentrations of magmatic CO2 (4–215 mmol per kg), H2S (3–110 mmol per kg) and dissolved H2 (0.1–50 mmol per kg), with varying amounts of CH4 (0.05–4.5 mmol per kg)

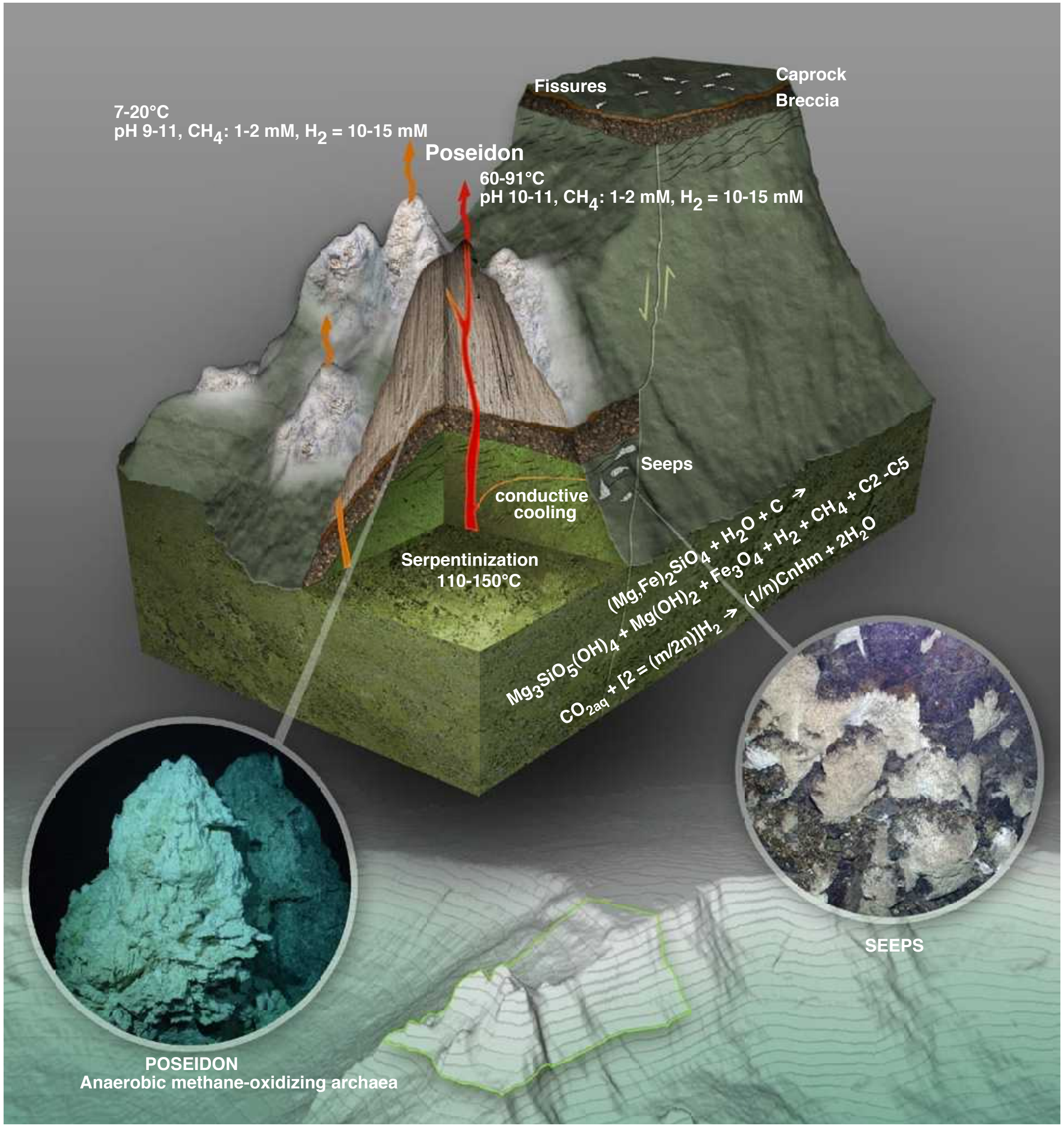
Black smokers

- Temperature gradient from the hot interior to the cold (2°C), oxygenated sea-water
- dissolved gases and metals in black smokers fuel the microbial communities → base of the food chain in these ecosystems
- some of the archaea can replicate at temperatures up to 121°C, (upper limit of temperature to form life)
- Example of fossilized black smokers: 3,235-million-year-old sulphide deposits in Western Australia that contained filamentous microfossils

Other vents

- Lost city hydrothermal fields → Several kilometers away from vulcanic origin
- effluent circulated through the crust (~200˚C) → no contact to magma chamber
- Fluid circulation: convection that dissipates heat from the underlying mantle rocks + exothermic chemical reactions between the circulating fluids and host rocks
- rocks have different compositions compared to black smokers (dominated by the magnesium- and iron-rich mineral olivine).
- highly alkaline (pH 9–11) effluent and high concentrations of dissolved H_2, CH_4 and other low-molecular-mass hydrocarbons, but almost no dissolved CO_2
- Carbonate precipitation → growth of chimneys (60 metres)
- alkaline pH is important for the origins of life.

Lost City Hydrothermal field



What grows at Lost City?

- anaerobic methanogens from the Lost City Methanosarcinales (LCM) order
- methanogens use several organic compounds, for anaerobic methane oxidation (AMO)
- LCM possess nearly all of the genes necessary for methanogenesis,
- little or no active venting: phylotype of the anaerobic methanotrophic clade AnME-1.
- T>80˚C: LCMs group → dense biofilms (>10 µm thickness)
- chimney exteriors: sulphur-oxidizing + methane-oxidizing bacteria (oxygenated sea-water) Interface: sulphate-reducing Firmicutes
- Effluent: no oxygen → only anaerobes; contact to sea water: aerobes
- LCMs and AnME-1 can be sources or sinks of CH4

What grows at Lost City?

- sulphate-reducing eubacteria cooccur in tightly coupled consortia
- Consortia: syntrophic metabolic relationship
- Thermodynamically: AMO is not energetically feasible unless sulphate-reducing bacteria are present to use H2 that is generated from the anaerobic oxidation of CH4
- AMO has been shown to occur at cold, sediment-hosted environments that are supported by CH4 hydrates, CH4 seeps
- CH4 and associated short hydrocarbons in the effluent of LCHF are not formed by biological activity, but instead are of geochemical origin
- LCMs and AnME-1 can oxidize CH4 at LCHF in the presence of abundant environmental H2
- methyl sulphide was inhibitory → important role methyl sulphide

Table 1 | Anaerobic and aerobic microbial metabolic reactions and potential energy yields in hydrothermal vent environments

Metabolism	Reaction	$\Delta G^{0\prime}$ (kJ per mole)*	Examples in vent environments
Anaerobic			
Methanogenesis	$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O$ $CH_3CO_2^- + H_2O \rightarrow CH_4 + H\,CO_3^-$ $4\,HCOO^- + H^+ \rightarrow 3\,HCO_3^- + CH_4$	−131 −36 −106	*Methanococcus* spp. common in magma-hosted vents; Methanosarcinales at Lost City
S° reduction	$S° + H_2 \rightarrow H_2S$	−45	Lithotrophic and heterotrophic; hyperthermophilic archaea
Anaerobic CH_4 oxidation	$CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$	−21	*Methanosarcina* spp. and epsilonproteobacteria at mud volcanoes and methane seeps
Sulfate reduction	$SO_4^{2-} + H^+ + 4\,H_2 \rightarrow HS^- + 4\,H_20$	−170	Deltaproteobacteria
Fe reduction	$8\,Fe^{3+} + CH_3CO_2^- + 4\,H_2O \rightarrow 2\,HCO_3^- + 8\,Fe^{2+} + 9\,H^+$	Not calculated‡	Epsilonproteobacteria, thermophilic bacteria and hyperthermophilic Crenarchaeota
Fermentation	$C_6H_{12}O_6 \rightarrow 2\,C_2H_6O + 2\,CO_2$	−300	Many genera of bacteria and archaea
Aerobic			
Sulfide oxidation§	$HS^- + 2\,O_2 \rightarrow SO_4^{2-} + H^+$	−750	Many genera of bacteria; common vent animal symbionts
CH_4 oxidation	$CH_4 + 2\,O_2 \rightarrow HCO_3^- + H^+ + H_2O$	−750	Common in hydrothermal systems; vent animal symbionts
H_2 oxidation	$H_2 + 0.5\,O_2 \rightarrow H_2O$	−230	Common in hydrothermal systems; vent animal symbionts
Fe oxidation	$Fe^{2+} + 0.5\,O_2 + H^+ \rightarrow Fe^{3+} + 0.5\,H_20$	−65	Common in low-temperature vent fluids; rock-hosted microbial mats
Mn oxidation	$Mn^{2+} + 0.5\,O_2 + H_2O \rightarrow MnO_2 + 2\,H^+$	−50	Common in low-temperature vent fluids; rock-hosted microbial mats; hydrothermal plumes
Respiration	$C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 6\,H_2O$	−2,870	Many genera of bacteria

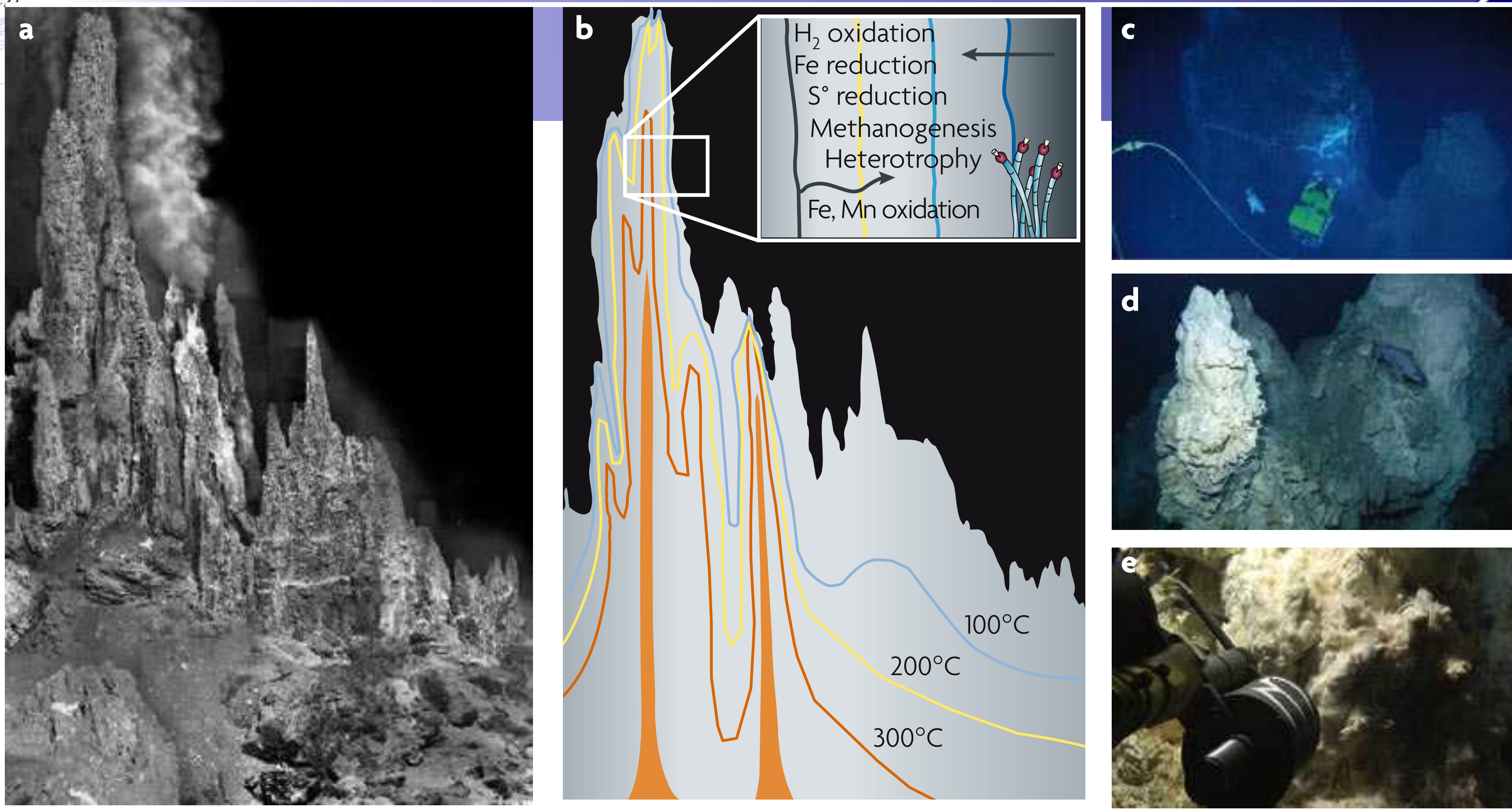


Figure 2 | **Hydrothermal vents.** There are two main types of hydrothermal vent: the black smoker type (**a,b**) and the Lost City type (**c–e**). **a** | A black smoker in the Faulty Towers complex in the Mothra hydrothermal field on the Endeavour Segment of the Juan de Fuca Ridge. The tallest chimney rises 22 metres above the sea-floor. The 'furry' appearance of the chimneys reflects the fact that the chimney walls are encrusted in dense communities of tube worms, scale worms, palm worms, sulphide worms and limpets. The two-pronged chimney in the middle with an active plume is a 300°C chimney called Finn, from which a 121°C organism was cultured that uses Fe(III) as an electron acceptor in the presence of N_2 and CO_2 (REF. 15). **b** | The outer surface of black smoker chimneys is bathed in a mixture of 2°C, oxygenated sea-water and warm vent fluid that escapes from within the structure. The inner walls that form the boundary of the central up-flow conduits commonly exceed 300°C, and temperatures are fixed by a steady supply of rapidly rising, strongly reducing vent fluid. Intermediate conditions exist as gradients between these extremes. Changes in microbial abundance, diversity and community structure have been associated with inferred environmental gradients in the chimney walls[99,100]. **c** | Microbial sampling at the Lost City

CH4 and H2 as energy source

- mM concentrations of CH_4 in the Lost City effluent do not originate from marine CO_2
- Originate from leached inorganic carbon in the mantle
- H_2 from *serpentinization* is the reductant for CH_4 synthesis
- the overall reaction that produces CH_4 in the subsea-floor hydrothermal system is the same as that used by methanogens to fuel carbon and energy metabolism
- all living systems exhibit a main chemical reaction at the core of energy metabolism — the chemical reaction that cells use to synthe-size ATP

Autotrophic

- Life had autotrophic origins and started from CO_2
- reduced carbon from CO_2 and other simple C1 compounds, H_2 as main electron donor
- *Central to the autotrophic origins hypothesis is the view that the acetyl-coenzyme A (acetyl-CoA) pathway of CO_2 fixation is the most ancient among the 4 CO_2-fixing pathways*
- acetyl-CoA pathway provides a source of carbon and the source of ATP
- During the reduction of CO_2 with electrons from H_2, acetogens and methanogens use the acetyl-CoA pathway to generate an ion gradient
- CO for methanogenesis or acetogenesis instead of CO_2 provides more energy
- C1 metabolism for origin of life

Autotrophic

- Black smokers (T>350˚C): carbon that is in equilibrium with water, even in the presence of significant levels of H2 usually occurs as CO2.
- LCHF (T<150˚C): reduced-carbon species are favoured
- no substantial kinetic barriers in the reduction of CO2 to formate formaldehyde and methanol (the reactions proceed quickly), but that kinetic barriers in the reduction to CH4 were appreciable
- simple carbon and energy metabolism at an alkaline hydrothermal vent might have been capable of supporting the origin of microbial life
- alkaline vents offer a possible solution even for this mechanism, because they provide a geochemically generated electrochemical gradient of protons at the vent–ocean interface →chemiosmotic coupling to synthesis ATP

Serpentization

- ultramafic rocks
- produce geological H2
- Sea-water penetrates crust (500m-1000m, 100°C-400°C) through cracks
  → place for serpentinization
- Reactants for serpentinization: CO2 + H2O, olvine (Mg1.6Fe0.4SiO4)
- At ca. 300°C Fe2+ reduces H2O

$$(\mathrm{Mg,Fe})_2\mathrm{SiO}_4 + \mathrm{H_2O} + \mathrm{C} \rightarrow \mathrm{Mg_3SiO_5(OH)_4} + \mathrm{Mg(OH)_2} + \mathrm{Fe_3O_4} + \mathrm{H_2} + \mathrm{CH_4} + \mathrm{C_2}\text{–}\mathrm{C_5}$$

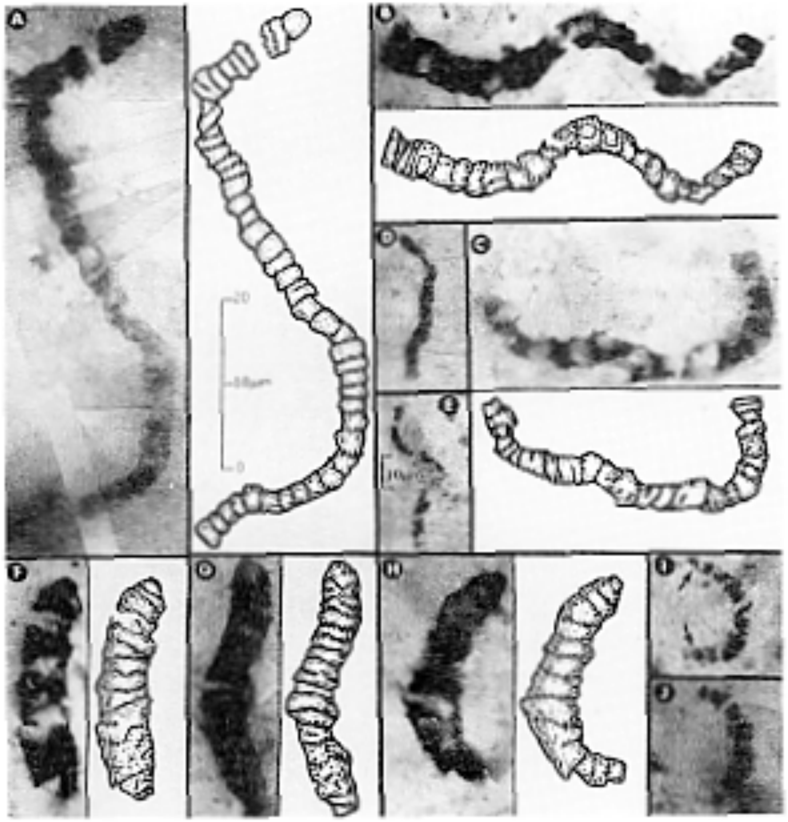
$$\mathrm{CO}_{2\mathrm{aq}} + [2 + (m/2n)]\mathrm{H_2} \rightarrow (1/n)\mathrm{C}_n\mathrm{H}_m + 2\mathrm{H_2O}$$

- 1m^3 olivine porduces 500 mol H2
- Oceans volume circulate through hydrothermal vents ever 100000 years
- Fe2+ earth electron reservoir for H2 production
- Energy releasing reactions
- Serpentenization: Acidic and alkaline conditions

Serpentinzation

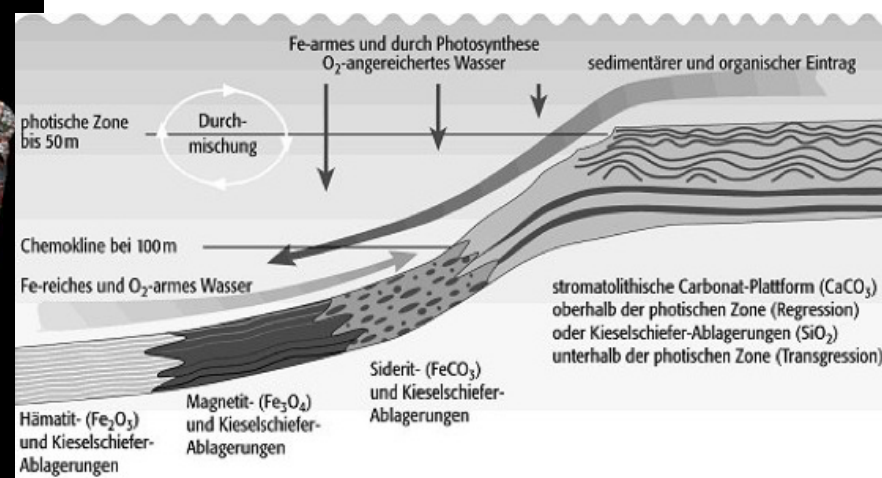
- 1 m^3 of peridotite composed of 70% olivine (10% Fe), (density of 4.4 g/cm3)
- 755 mol of fayalite (the iron end-member of olivine) would have been consumed
- 3 mol of fayalite produce 2 mol of H2
- 3Fe2SiO4 2H2O → 2Fe3O4 3SiO2 2H2
- → 500 mol H2 are formed.
- Transformation duration: 150 million years → hydrogen production of 8.6 nmol/day/m3 of rock.
- Hydrogen: electron donor and energy source
- H2 flux delivers 15–345 J/day/m3 of rock (minimally)
- Lab: maintenance energy for anaerobic microorganisms is about 1,300 J/g of biomass (dry weight)/day at 15°C
- Nature: maintenance energy value of 1.3 J/g of biomass (dry weight)/day,
- each cubic meter of rock could potentially support 12–265 g of biomass (dry weight)

- 3.5 GA old fossils



How did it continue

- Archean → Proterozoic: photosynthesis → oxygen occured
- Banded iron formations

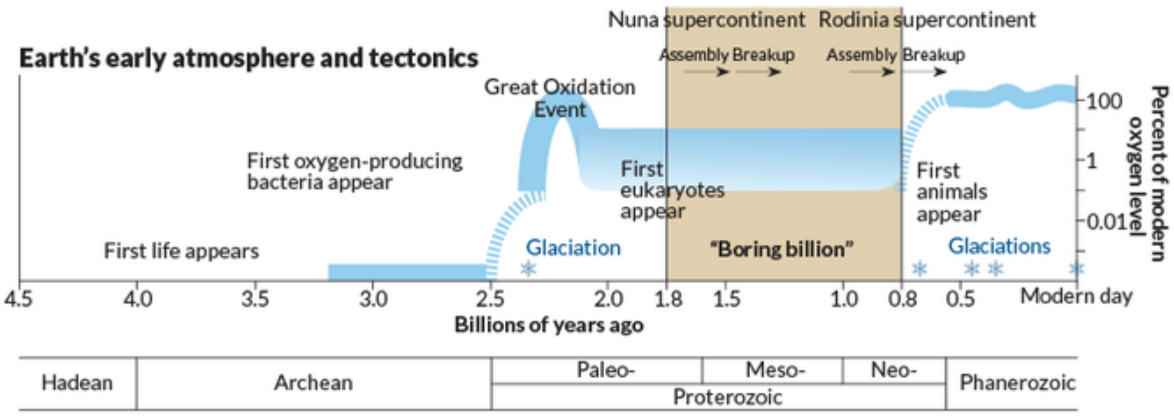


Oxygen Atmosphere

- UV: $H_2O + CO_2 \dashrightarrow O_2 + ...$
- Precambarian galciation: 0.1% ice was made of $H_2O_2 \rightarrow O_2$ + water (no ozone layer) before 2.4 GA ago
- First organism with oxygen „protection"... Evolve in a trial and error approach
- Takes 100s of millions years before atmosphere became significantly oxygenated
- 1.9 billion years → last common ancestor of all eukaryotes
- 200 million years of evolution to response to the intrinsically poisonous oxygen

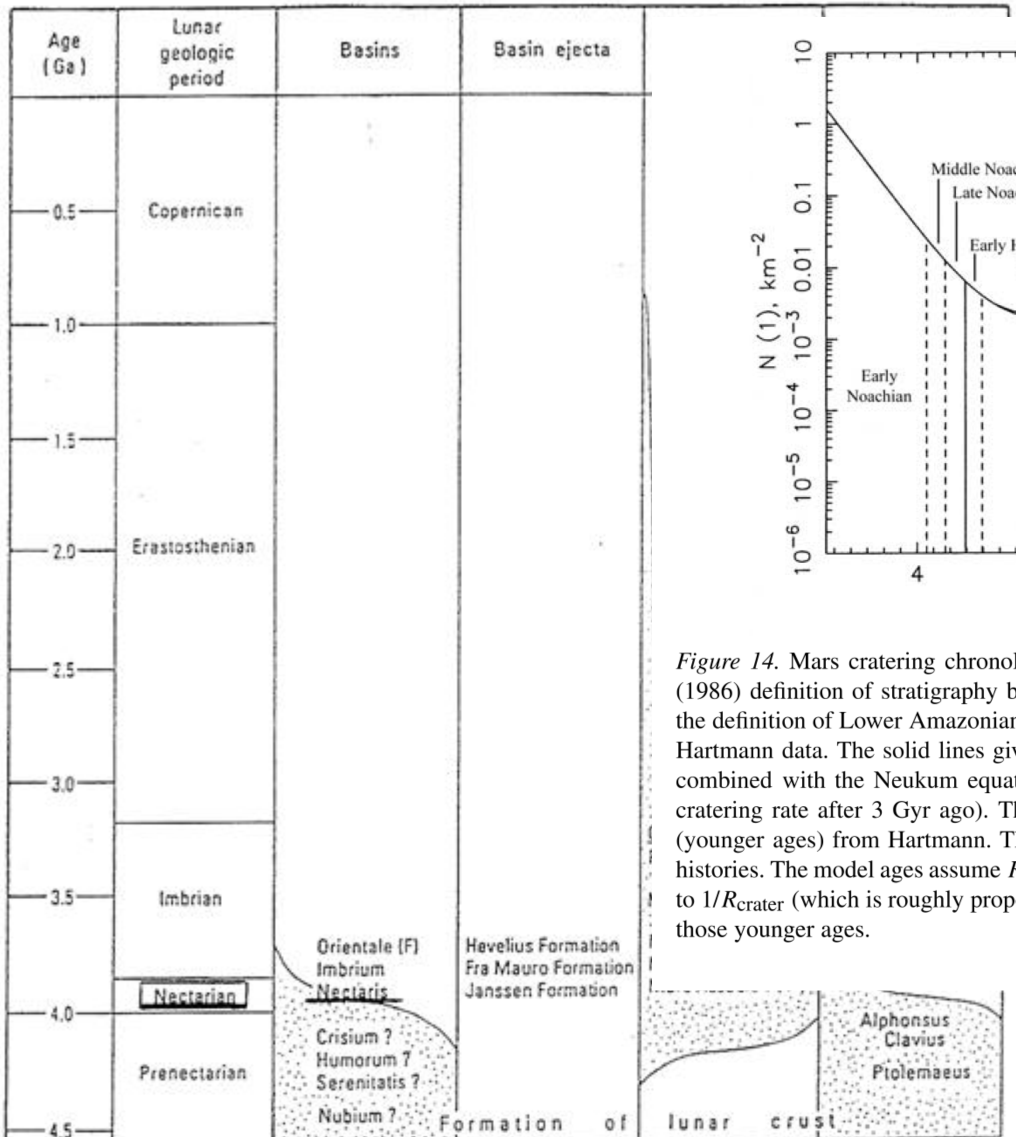
Boring billion

- Great oxygenation → first appearance of common multicellular life (2.0-1.0 GA)
- Overabundance of single-celled sulfur-using bacteria competing with the oxygen releasing forms (sulfur-requiring microobes (green and purble sulfur bacteria) photosynthesis does not split water



- Where new and/or more amino acids required?
- Did oxygen promote their formatin?
- If yes how?

- Thank you very much for your attention



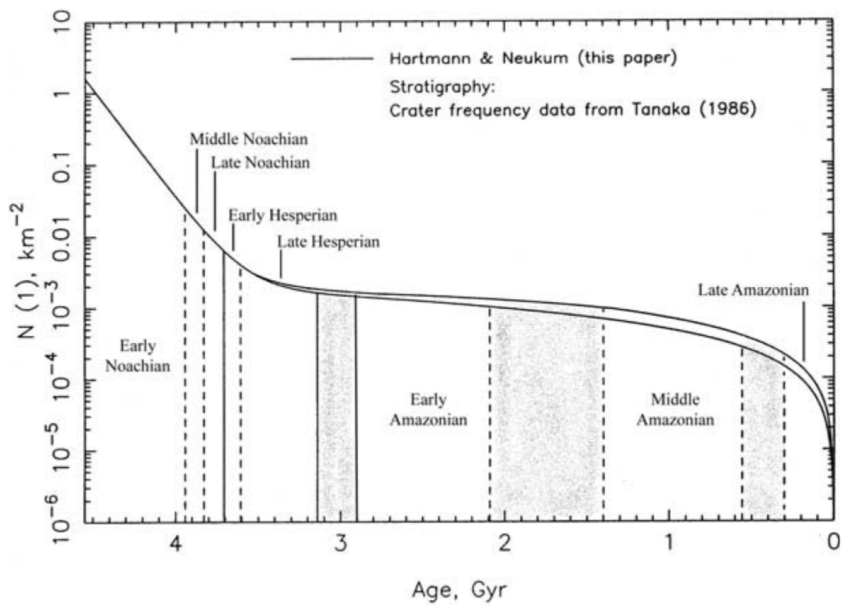
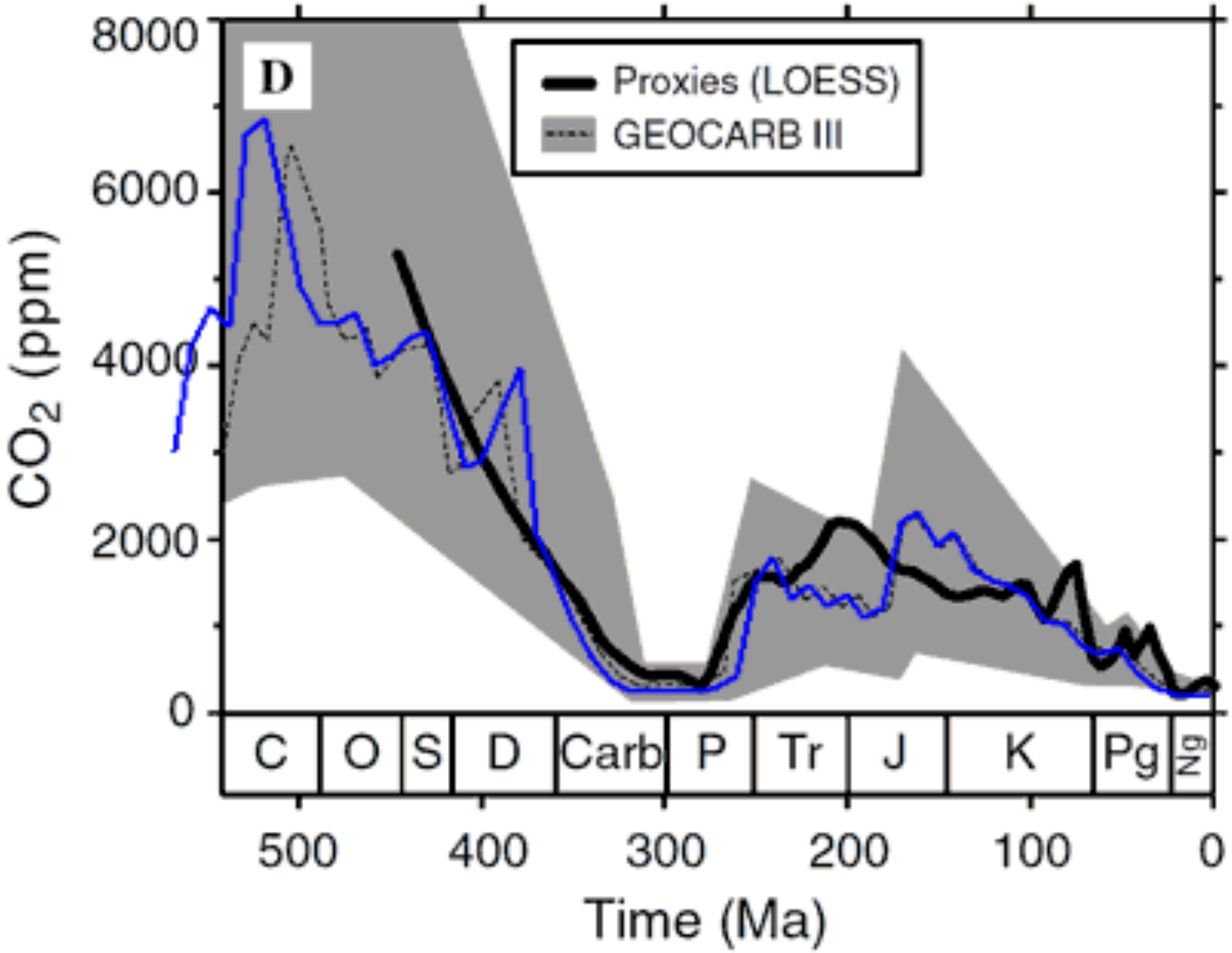


Figure 14. Mars cratering chronology model based on work in the present paper, using Tanaka's (1986) definition of stratigraphy based on crater densities at $D > 1$ km (plus our rediscussion of the definition of Lower Amazonian), and Ivanov's (2001) derivation of isochrons from Neukum and Hartmann data. The solid lines give model ages based primarily on the Ivanov-Neukum isochrons combined with the Neukum equation for time dependence of cratering (with essentially constant cratering rate after 3 Gyr ago). The left curve (older ages) is from Neukum data, the right curve (younger ages) from Hartmann. The diagram shows why uncertainties are greatest in mid-Martian histories. The model ages assume $R_{\mathrm{bolide}} = 2.0$. Model ages younger than ~3.0 Gyr are proportional to $1/R_{\mathrm{crater}}$ (which is roughly proportional to $1/R_{\mathrm{bolide}}$) and thus an additional uncertainty enters for those younger ages.

- The discovery of hydrothermal vent systems profoundly changed how we view the geological, geochemical and ecological history of the Earth. undersea vents are abundant on the floor of the world's oceans and are important sources of many ele- ments and organic compounds that are transferred into the hydrosphere.
- support life without input from photosynthesis
- harbour fascinating life with symbiotic relationships that involve lithoautotrophic microorganisms that use chemical energy to support metazoans.

- geochemical processes of carbon reduction in hydrothermal systems represent the same kind of energy-releasing chemistry that gave rise to the first biochemical pathways.


D
Proxies (LOESS)
GEOCARB III
CO_2 (ppm)
8000
6000
4000
2000
0
C
O
S
D
Carb
P
Tr
J
K
Pg
Ng
500
400
300
200
100
0
Time (Ma)