The Chemical Origin of Life

Thomas Lunkenbein
Berlin, 15.12.2017
The Concepts

Different starting points

**Evolution**
- ~14 billion years ago
- **Human Reason**

**Creation**
- ~6000 years ago
- **God’s Word**

Different views

Creation Museum, Petersburg, KY, USA.
Creationism

DID HUMANS LIVE WITH DINOSAURS?

God made Adam and Eve on the same day as land animals. So dinosaurs and people lived at the same time.

HOW DID DINOSAURS FIT ON NOAH’S ARK?

Most dinosaurs were reasonably small—the size of a sheep or pony, on average. Even large sauropods, as young adults, were not overly large. So Noah’s Ark had plenty of room for all the land animal kinds, including every dinosaur “kind.”

CAN YOU TELL HOW OLD THIS FOSSIL IS?

Fossils don’t come with tags on them that tell us how old they are. We have to study the clues we find to try to figure out their ages. Use the Bible as your starting point, see if you can figure out about how old this fossil is.

Can you think of an event in the Bible where lots and lots of water flooded the whole earth? Noah’s Flood, when God judged the world.
The earth
• History of earth:
  o <4.6 GA: proto-earth → coalescence of various sized planetesimals
  o 4.567 GA: Mars-sized object crashed into the earth → Ni-Fe core + moon from silicon-vapor atmosphere
  o Severe meteor bombardment → energy sufficient to keep rocks in a molten state
  o 4.56 GA: segregation into different, density dependent layers (core, mantel, atmosphere)
  o Water and other volatiles bubbled upwards and heavier ones sank.
  o - 3.8GA: Late Havey Bombardment meteor impact; cooling down, earth day 10 h: early atmosphere (CO2, H2S, H2O, CH4)
  o Sky color: orange to brick red, oceans: muddy brown (gas, liquid water, minerals)
An earthlike planet

• Rare Earth Hypothesis:
  microbial life \(\rightarrow\) common in the universe
  animal equivalents: systems with planetary environmental stability for
  a certain time \(\rightarrow\) are rare
• Many potentially habitable planets \(\rightarrow\) only one
  many possible chemical recipes
• What are the needs?
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 atmosphere)
- Duration: millions of years
- Planetary thermostat: Controls temperature via greenhouse effect
- Subduction controlled process (CO2 household)

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 components

• 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 $\rightarrow$ 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 mechanism, copy of the replication apparatus
• Life develops: copy is made $\rightarrow$ 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

Nucleic acids — genetic information
Build up from nucleotides
DNA/RNA
DNA double helix
RNA single strand (DNA’s slave) → translates information into action

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

Carbonhydrates — Building blocks for larger molecules

lipids

peripheres Membranprotein
integrales Membranprotein
Glykolipide
The tree of life
requirements

• 3.4 - 3.5 GA oldest fossils 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 environment (cell)
• Ability to replicate
How did it work?
Miller-Urey-Experiment

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

<table>
<thead>
<tr>
<th>Source</th>
<th>Energy (cal cm² yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total radiation from sun</td>
<td>260,000</td>
</tr>
<tr>
<td>Ultraviolet light</td>
<td></td>
</tr>
<tr>
<td>λ &lt; 2500 A</td>
<td>570</td>
</tr>
<tr>
<td>λ &lt; 2000 A</td>
<td>85</td>
</tr>
<tr>
<td>λ &lt; 1500 A</td>
<td>3.5*</td>
</tr>
<tr>
<td>Electric discharges</td>
<td>4†</td>
</tr>
<tr>
<td>Cosmic rays</td>
<td>0.0015</td>
</tr>
<tr>
<td>Radioactivity (to 1.0 km depth)</td>
<td>0.8‡</td>
</tr>
<tr>
<td>Volcanoes</td>
<td>0.13§</td>
</tr>
</tbody>
</table>

* Includes the 1.9 cal cm⁻² yr⁻¹ from the Lyman a 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 × 10⁶ years ago, was 2.9 cal cm⁻² yr⁻¹ (41). § Calculated on the assumption of an emission of lava of 1 km³ (Cp = 0.25 cal/g, P = 3.0 g/cm²) per year at 1000°C.

Table 2. Yields from sparking a mixture of CH₄, NH₃, H₂O, and H₂; 710 mg of carbon was added as CH₄.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield [moles (× 10⁶)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycine</td>
<td>63.</td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>56.</td>
</tr>
<tr>
<td>Sarcosine</td>
<td>5.</td>
</tr>
<tr>
<td>Alanine</td>
<td>34.</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>31.</td>
</tr>
<tr>
<td>N-Methylalanine</td>
<td>1.</td>
</tr>
<tr>
<td>α-Amino-n-butyric acid</td>
<td>5.</td>
</tr>
<tr>
<td>α-Aminoisobutyric acid</td>
<td>0.1</td>
</tr>
<tr>
<td>α-Hydroxybutyric acid</td>
<td>5.</td>
</tr>
<tr>
<td>β-Alanine</td>
<td>15.</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>4.</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>0.4</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>0.6</td>
</tr>
<tr>
<td>Iminodiacetic acid</td>
<td>5.5</td>
</tr>
<tr>
<td>Iminoacetic-propionic acid</td>
<td>1.5</td>
</tr>
<tr>
<td>Formic acid</td>
<td>233.</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>15.</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>13.</td>
</tr>
<tr>
<td>Urea</td>
<td>2.0</td>
</tr>
<tr>
<td>N-Methyl urea</td>
<td>1.5</td>
</tr>
</tbody>
</table>

At the end of the run the solution in the boiling flask was removed and 1 ml of saturated HgCl₂ 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
Figure 2 | a) Impact shock and meteorite fragments and inclusions, dissolution from the atmosphere, and meteorite evaporation. b) Ferrocyanide, phosphate and chloride salts from the atmosphere, least soluble salts over a wide area, and further evaporation deposits the most soluble salts in smaller, lower-lying areas. c) Bedrock and meteorite inclusions, evaporite layer, and no reaction occurs, but that residual cyanamide still reacts rapidly with bedrock and other meteoritic oxides and salts.
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) Biology did not select all of its building blocks, but was simply presented with a precursor of Val and Leu, whereas phosphorylation of glycerol (the more stable isomer of glyceraldehyde) for subsequent ribonucleotide assembly (bold blue arrows), but also leads to precursors of Gly, Ala, Ser and Thr.

b) Asp, Gln and Glu. Pd11, Reductive homologation of which gives precursors of Pro and Arg.

c) The degree to which the syntheses of ribonucleotides, amino acids and lipid sugars—needed for subsequent ribonucleotide assembly (bold blue arrows), but also leads to precursors of Gly, Ala, Ser and Thr.

d) N-acetylglutamate serves as a precursor to Asn, Gln, Glu. Then the network does not produce a complete set of compounds, however, which suggests that the network does not produce a complete set of compounds, which suggests that

www.nature.com/naturechemistry DOI: 10.1038/NCHEM.2202
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: separation 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 \(\rightarrow\) Several kilometers away from volcanic origin
- Effluent circulated through the crust (\(\sim 200^\circ\text{C}\)) \(\rightarrow\) 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 H2, CH4 and other low-molecular-mass hydrocarbons, but almost no dissolved CO2
- Carbonate precipitation \(\rightarrow\) growth of chimneys (60 metres)
- Alkaline pH is important for the origins of life.
Lost City Hydrothermal field

7-20°C
pH 9-11, CH₄: 1-2 mM, H₂ = 10-15 mM

Poseidon
60-91°C
pH 10-11, CH₄: 1-2 mM, H₂ = 10-15 mM

Serpentinization
110-150°C

Fissures
Caprock
Breccia

Conductive cooling

(Mg, Fe)₂SiO₄ + H₂O + C → Mg(OH)₂ + Fe₃O₄ + H₂ + CH₄ + C₂-C₅

Mg₃SiO₄(OH)₄ + CO₂ → (Mg₂Mn₃)H₂ + ((H/C)n)CnHm + 2H₂O

POSEIDON
Anaerobic methane-oxidizing archaea

SEEPS

Fluids migrating into the massif interact with olivine-rich ultramafic rocks at temperatures up to 200°C. This process results in the generation of pH 9-11 fluids, rich in methane, hydrogen and hydrocarbons. Aragonite, calcite and brucite are deposited to form chimneys as the metal-poor, 40-91°C hydrothermal fluids mix with cold seawater. The warm porous interiors of the chimneys host dense biofilms dominated by a single phylotype related to Methanosarcinales. Surprisingly, animal communities are mostly limited to meiofauna, < 1-2 cm in size that are dominated by gastropods and amphipods, a variety of polychaetes, and rare bivalves. Image produced in collaboration with the Center for Environmental Visualization, University of Washington, USA.
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 microalgal metabolic reactions and potential energy yields in hydrothermal vent environments

<table>
<thead>
<tr>
<th>Metabolism</th>
<th>Reaction</th>
<th>( \Delta G^\circ ) (kJ per mole)*</th>
<th>Examples in vent environments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anaerobic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>( 4 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} )</td>
<td>(-131)</td>
<td>\textit{Methanococcus} spp. common in magma-hosted vents; Methanosarcinales at Lost City</td>
</tr>
<tr>
<td></td>
<td>( \text{CH}_3\text{CO}_2^- + \text{H}_2 \text{O} \rightarrow \text{CH}_4 + \text{HCO}_3^- )</td>
<td>(-36)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 4 \text{HCO}_3^- + \text{H}^+ \rightarrow 3 \text{HCO}_3^- + \text{CH}_4 )</td>
<td>(-106)</td>
<td></td>
</tr>
<tr>
<td>S(^0) reduction</td>
<td>( \text{S}^0 + \text{H}_2 \rightarrow \text{H}_2\text{S} )</td>
<td>(-45)</td>
<td>Lithotrophic and heterotrophic; hyperthermophilic archaea</td>
</tr>
<tr>
<td>Anaerobic CH(_4) oxidation</td>
<td>( \text{CH}_4 + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O} )</td>
<td>(-21)</td>
<td>\textit{Methanosarcina} spp. and epsilonproteobacteria at mud volcanoes and methane seeps</td>
</tr>
<tr>
<td>Sulfate reduction</td>
<td>( \text{SO}_4^{2-} + \text{H}^+ + 4 \text{H}_2 \rightarrow \text{HS}^- + 4 \text{H}_2\text{O} )</td>
<td>(-170)</td>
<td>Deltaproteobacteria</td>
</tr>
<tr>
<td>Fe reduction</td>
<td>( 8 \text{Fe}^{3+} + \text{CH}_3\text{CO}_2^- + 4 \text{H}_2\text{O} \rightarrow 2 \text{HCO}_3^- + 8 \text{Fe}^{2+} + 9 \text{H}^+ )</td>
<td>Not calculated(\textit{f})</td>
<td>Epsilonproteobacteria, thermophilic bacteria and hyperthermophilic Crenarchaeota</td>
</tr>
<tr>
<td>Fermentation</td>
<td>( \text{C}<em>6\text{H}</em>{12}\text{O}_6 \rightarrow 2 \text{C}_2\text{H}_6\text{O} + 2 \text{CO}_2 )</td>
<td>(-300)</td>
<td>Many genera of bacteria and archaea</td>
</tr>
<tr>
<td><strong>Aerobic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur oxidation(\textit{g})</td>
<td>( \text{HS}^- + 2 \text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+ )</td>
<td>(-750)</td>
<td>Many genera of bacteria; common vent animal symbionts</td>
</tr>
<tr>
<td>CH(_4) oxidation</td>
<td>( \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{HCO}_3^- + \text{H}^+ + \text{H}_2\text{O} )</td>
<td>(-750)</td>
<td>Common in hydrothermal systems; vent animal symbionts</td>
</tr>
<tr>
<td>H(_2) oxidation</td>
<td>( \text{H}_2 + 0.5 \text{O}_2 \rightarrow \text{H}_2\text{O} )</td>
<td>(-230)</td>
<td>Common in hydrothermal systems; vent animal symbionts</td>
</tr>
<tr>
<td>Fe oxidation</td>
<td>( \text{Fe}^{2+} + 0.5 \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 0.5 \text{H}_2\text{O} )</td>
<td>(-65)</td>
<td>Common in low-temperature vent fluids; rock-hosted microbial mats</td>
</tr>
<tr>
<td>Mn oxidation</td>
<td>( \text{Mn}^{2+} + 0.5 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2 \text{H}^+ )</td>
<td>(-50)</td>
<td>Common in low-temperature vent fluids; rock-hosted microbial mats; hydrothermal plumes</td>
</tr>
<tr>
<td>Respiration</td>
<td>( \text{C}<em>6\text{H}</em>{12}\text{O}_6 + 6 \text{O}_2 \rightarrow 6 \text{CO}_2 + 6 \text{H}_2\text{O} )</td>
<td>(-2,870)</td>
<td>Many genera of bacteria</td>
</tr>
</tbody>
</table>
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 N₂ and CO₂ (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. c | Microbial sampling at the Lost City hydrothermal field. These habitat-rich hydrothermal vents are typical of the 20–30°C cool Re Union
CH4 and H2 as energy source

- mM concentrations of CH4 in the Lost City effluent do not originate from marine CO2
- Originate from leached inorganic carbon in the mantle
- H2 from *serpentinization* is the reductant for CH4 synthesis
- the overall reaction that produces CH4 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 synthesize ATP
Autotrophic

- Life had autotrophic origins and started from CO2
- reduced carbon from CO2 and other simple C1 compounds, H2 as main electron donor
- *Central to the autotrophic origins hypothesis is the view that the acetyl-coenzyme A (acetyl-CoA) pathway of CO2 fixation is the most ancient among the 4 CO2-fixing pathways*
- acetyl-CoA pathway provides a source of carbon and the source of ATP
- During the reduction of CO2 with electrons from H2, acetogens and methanogens use the acetyl-CoA pathway to generate an ion gradient
- CO for methanogenesis or acetogenesis instead of CO2 provides more energy
- C1 metabolism for origin of life
• 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
Serpentinization

- 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, olivine (Mg1.6Fe0.4SiO4)
- At ca. 300°C Fe2+ reduces H2O

\[(\text{Mg}, \text{Fe})_2 \text{SiO}_4 + \text{H}_2\text{O} + \text{C} \rightarrow \text{Mg}_3 \text{SiO}_3(\text{OH})_4 + \text{Mg(OH)}_2 + \text{Fe}_3 \text{O}_4 + \text{H}_2 + \text{CH}_4 + \text{C}_2-\text{C}_5 \]

\[\text{CO}_{2\text{aq}} + [2 + (m/2n)]\text{H}_2 \rightarrow (1/n)\text{C}_n\text{H}_m + 2\text{H}_2\text{O} \]

- 1m³ olivine produces 500 mol H2
- Oceans volume circulate through hydrothermal vents every 100000 years
- Fe2+ earth electron reservoir for H2 production
- Energy releasing reactions
- Serpentenization: Acidic and alkaline conditions
Serpentinization

- 1 m$^3$ of peridotite composed of 70% olivine (10% Fe), (density of 4.4 g/cm$^3$)
- 755 mol of fayalite (the iron end-member of olivine) would have been consumed
- 3 mol of fayalite produce 2 mol of H$_2$
- $3\text{Fe}_2\text{SiO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2$
- $\rightarrow$ 500 mol H$_2$ are formed.
- Transformation duration: 150 million years $\rightarrow$ hydrogen production of 8.6 nmol/day/m$^3$ of rock.
- Hydrogen: electron donor and energy source
- H$_2$ flux delivers 15–345 J/day/m$^3$ 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)
How did it continue

- 3.5 GA old fossils
• Archean $\rightarrow$ Proterozoic: photosynthesis $\rightarrow$ oxygen occurred
• Banded iron formations
Oxygen Atmosphere

- UV: $\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{O}_2 + \ldots$
- Precambrian glaciation: 0.1% ice was made of $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 +$ 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 $\rightarrow$ last common ancestor of all eukaryotes
- 200 million years of evolution to response to the intrinsically poisonous oxygen
- 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 formation?
• 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 $R_{\text{bolide}} = 2.0$. Model ages younger than $\sim3.0$ Gyr are proportional to $1/R_{\text{crater}}$ (which is roughly proportional to $1/R_{\text{bolide}}$) 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 elements 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.
The diagram shows the concentration of \( \text{CO}_2 \) over time (Ma) with different time markers such as C, O, S, D, Carb, P, Tr, J, K, Pg, and Ng. The y-axis represents \( \text{CO}_2 \) concentration in parts per million (ppm), ranging from 0 to 8000 ppm. The x-axis represents time in millions of years (Ma), ranging from 0 to 550 million years. The data is plotted using different lines and shaded areas to represent Proxies (LOESS) and GEOCARB III.