What Earth probably was, and most likely was not, in the earliest times

Stephen Mojzsis
University of Colorado at Boulder
Department of Geological Sciences

as amended and presented by:

Stephen Macko
University of Virginia
Events that Shaped the Earth

The Origin of Life

Stephen Macko
University of Virginia
What were the conditions for life on the early Earth?
Are there clues to the origins of homochirality?
• **Stromatolites**
  - Living: colonies of bacteria living in outer layer of sedimentary rocks
  - 3.5 Byr old rocks: almost identical layered structure
  - Inconclusive evidence: sedimentation layering may mimic stromatolites

• **Fossil evidence**
  - 3.5 Byr old Australian rock shows “cells”
  - Could this form naturally from minerals?
  - Younger sites: at least two more (3.2-3.5 byr old)
  - Older sites: sedimentary rock too altered to be useful
• $^{13}$C/$^{12}$C ratio
  – Normal abundance ratio 1/89
  – Living tissue and fossils show less $^{13}$C
  – Some rocks older than 3.85 Gyr show the low $^{13}$C abundance
Domains of Life

Charles Darwin  1809-1882 Hot Ponds
The Origin of Life on Earth
"primordial soup"
1924

Alexander Ivanovich Oparin
1894-1980
The Miller Urey Experiment

HC Urey

SL Miller

Diagram: A diagram showing a setup with various compartments labeled as 'Water vapor,' 'Oceanic compartment,' and 'Atmospheric compartment.' The diagram includes reactions with gases such as $\text{N}_2$, $\text{NH}_3$, $\text{H}_2$, $\text{H}_2\text{O}$, $\text{CH}_4$, and $\text{CO}_2.$ Sparks stimulate lighting, and a condenser cools the gas. The "ocean" is sampled and its composition analyzed.
No Oxygen!
(Not in the Early Earth’s Atmosphere)

http://www.ucsd.tv/miller-urey/
Primitive molecules

Hydrogen cyanide

Cyanogen

Cyanoacetylene

Formaldehyde

Acetaldehyde

Propionaldehyde
More complex molecules

NOT nucleotides
So...Is it *Right*?

- Rocks don’t reflect such a strange atmosphere (hydrogen, ammonia, methane)
- Chemistry of products don’t reflect LIFE in the amino acids (L-amino acids)
- So where to look for “Origins”?
Stereoisomers of amino acids
Mammoth Hot Springs
Alvin

Sea Link

Hot Vents 250 C
An Ocean on Europa
Meteorite Impacts
Meteorites from Mars

Organized microstructures
Comets

Kuiper Belt and outer Solar System planetary orbits

The Oort Cloud (comprising many billions of comets)

Orbit of Binary Kuiper Belt Object 1998 WW31

Oort Cloud cutaway drawing adapted from Donald K. Yeoman's Illustrator (NASA, JPL)
Still looking
What Earth probably was, and most likely was not, in the earliest times

Stephen Mojzsis
University of Colorado at Boulder
Department of Geological Sciences
Collaborative for Research in Origins (CRiO)
isotope.colorado.edu
crio.space
A short glossary for a diverse audience

**Hadean** (eon; from 4.56 – 3.85 billion years ago)

**Oxygen fugacity** ($fO_2$) – a measure of redox

**Zircon** ($\text{Zr(SiO}_4\text{)}$) – a very useful mineral!

**Granite** (composed of ≥10% quartz, feldspar, +other minerals)

(Basalt, komatiite, peridotite, andesite, etc.) – different rocks expected on the early Earth

**Closure temperature** – retentivity of a mineral

**Chemical partitioning** – how a mineral gets its composition
Can we modify our four criteria for “Planets as Cradles of Life”?

Hypothesis: Life will arise when the above conditions are met “but the first steps are the hardest” (Mike Russell, 2014)
A visual representation summarizing the relative contributions of some major sources of organic molecules.

Prebiotic Soup(s)?

- UV light, reducing atmosphere
- Lightning, reducing atmosphere
- UV light, neutral atmosphere
- Hydrothermal vents
- Input from cometary and asteroidal dust particles (IDPs)
- Lightning in a CO₂/H₂ = 10 atmosphere
2 themes to this presentation

1. Evolution of mantle redox state and what this means for the origin of life

2. The crust as a platform for early life – its antiquity, volume and complexity
1. Mantle redox evolution
The evolution of oxygen fugacity in Earth’s silicate mantle affects the speciation and mobility of volatile elements in the interior and has controlled the character of degassing species from the Earth since the planet’s formation.

V/Sc ratios of peridotites and basalts from the Archean cover a similar range to present-day samples, with the inference that upper mantle $f_{O_2}$ could have risen by no more than 0.3 log units over the last 3.5 Gyrs of Earth's history (Li & Lee 2004). Delano (2001) reached a similar conclusion by studying Cr.

SOME IMPORTANT RECENT PROGRESS
Evolution of terrestrial mantle oxygen fugacity from $[\text{Ce}/\text{Ce}^*]_{\text{zircon}}$

- MH (Trail et al. 2011) n=29
- FMQ
- △ FMQ (log$_{10}$ units)
- 207$^{Pb}$/206$^{Pb}$ zircon age (Ma)
- LW (Archean and modern upper mantle)
- △ log $f_{\text{O}_2}$
- Buffer capacity
- $\text{Fe}^{3+}/\text{Fe}^{2+}$ control
- $\text{Fe}^{0}/\text{FeO}$ control
- Rohrbach & Schmitt (2011)
Evolution of terrestrial mantle oxygen fugacity from [Ce/Ce*]$_{\text{zircon}}$

- (Trail et al. 2011) $n=29$
- (Mojzsis et al. 2014) $n=37$
- (Cates et al. 2013) $n=8$
- (Cates & Mojzsis 2009) $n=1$
- Lunar (Taylor et al. 2009) $n=27$

$\Delta$ FMQ (log$_{10}$ units)

$^{207}$Pb/$^{206}$Pb zircon age (Ma)

Mojzsis (2018)
Comparative mantle oxygen fugacities (Earth vs. Moon)

![Graph showing comparative mantle oxygen fugacities with data points from various sources.](image)

- MH (Trail et al. 2011) n=29
- FMQ (Mojzsis et al. 2014) n=37
- IW (Cates et al. 2013) n=8
- IW (Cates & Mojzsis 2009) n=1
- Lunar (Taylor et al. 2009) n=27

**Notes:**
- △ FMQ (log₁₀ units)
- Archean and modern upper mantle

*Mojzsis (2018)*
Frost et al., 2008

- Fraction of impactor core that re-equilibrates
- Surface
- Magma ocean
- Silicate solidus
- Solid lower mantle
- Core
- Liquid core
- Core-forming metal
- Rains through magma ocean
- Metal ponds at silicate solidus
- Disproportionated liquid metal
- Trapped in the lower mantle
- Region of raised O/Fe
NWA7034 martian meteorite
Identified as a polymict regolith breccia
Data below from Humayun et al. (2013)
Speciation of volcanic gases on early Earth and early Mars

Hirschmann (2012); Frost & McCammon (2008)
Oldest terrestrial zircon (n=210,000) is 4.38 Ga
Oldest martian zircon (n=15) is 4.43 Ga
Oldest lunar zircon (n=300) is 4.40 Ga
Putting aside highly reduced global geochemical scenarios actually *leads* to the RNA World hypothesis

Prebiotic chemistry: synthesis of biological molecules necessary for the birth of the first living cell. The above time-line is a little arbitrary, everything from 4.2 to 3.6 Ga on it could be pushed back and squashed into a smaller time span.

THIS IDEA IS GEOCHEMICALLY COMPELLING for a number of reasons.

What is the RNA World?

1. catalytic - react with one another
2. templating - copy each other
   → RNA viruses have RNA genomes
   → have very high mutation rates \((10^5-10^6 \times \text{bacteria})\)
   → RNA viruses not found in Hyperthermophiles
   → use nucleotides from some source

3. Sugars are fundamentally more oxidized chemistry

4. Does not require a Miller-Urey (highly reduced) atm
Problems with The RNA World

1. RNA is not very stable
   - breaks down with heat (>50°C)
   - breaks down in the presence of Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Fe$^{2+}$  
     (stabilized with phosphate; did RNAs need endorheic or lacustrine environments?)
2. The reactions RNA can catalyze are limited  
   (but that might just be because of our limited experimental space)
3. Has to have some external source of nucleotides  
   (same problem with all sugar scenarios, also requires selection of sugars)
4. RNA world would have eventually given rise to The DNA/Protein world.  
   (WHY? Was it an evolutionary innovation to resist heat and salts?)

DNA is much more stable.  
   - less sensitive to heat  
   - stable in the presence of Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Fe$^{2+}$
Proteins with 20 amino acids can catalyze a much larger variety of chemical reactions

The RNA world hypothesis is a temporary phase in the origin of life.
"You were right, sir. It was dishwater. The chef regrets the error."
(Apr 26, 1952) by Syd Hoff

Parochial conclusion #1

IN ANY SCENARIO, THE ‘PREBIOTIC SOUP’ ON EARTH WAS ALWAYS FANTASTICALLY DILUTE IN A RELATIVELY OXIDIZED SETTING
Earth’s water and other volatiles

Hydrogen:

Two major terrestrial reservoirs of water: Hydrosphere & Mantle (see review paper by Mike Mottl on this!)

1.4 x 10^{24} g of water in the hydrosphere
Bulk D/H of this water is 1.557 x 10^{-4}

The depleted mantle appears to have a water content between 100 and 500 ppm, with the lower value preferred (Sobolev and Chaussidon, 1996) and consistent with measurements of mantle xenoliths (Bell and Rossman, 1992).

The DM estimate corresponds to 0.4-2 x 10^{24} g of water, with D/H = 4 – 8‰ lighter than SMOW.

By these estimates, present-day water for the bulk Earth is at least 2.6 x 10^{24} g with D/H = 1.5 x 10^{-4}
Or about 4.4 x 10^{-4} Me
Water storage capacity (Ocean units)

Nominally Anhydrous Minerals (NAMs) can incorporate up to 10 times the total Ocean mass if saturated.

The “Grand Tack” hypothesis can explain this
Water delivery in Grand Tack

- Planets > 0.5 Earth mass accrete median value of ~1% Earth mass of C-type material (2-3% is not rare)

- Assuming 10% water by mass (consistent with carbonaceous chondrites), this gives ~1x10^{-3} Earth masses of water
  - Earth has (low estimate) ~5-20x10^{-4} Earth masses of water

Additional water may be delivered through more massive embryos that were not included in the simulations
What about comets?

Comet 67P/Churyumov–Gerasimenko

Nov. 13, 2014 at 1:02 AM JST
Stable isotopes suggest that terrestrial planets’ volatiles are mainly chondritic.
The Earth and the Moon have indistinguishable oxygen isotope composition.

All carbonaceous meteorites (with the exception of CI) have clearly different Oxygen isotope composition.

The delivery of water AFTER the Moon forming event (in something like a “Late Veneer”) would have made the Earth and the Moon easily distinguishable in oxygen isotopes!
Water (and volatile elements) argue for an heterogeneous accretion of the Earth. This is well-accepted.
Volatile were delivered towards the end of the Earth accretion, not by comets and as we will see, not in a Late Veneer fashion, and not in a late heavy bombardment.

All of this is consistent with the latest dynamical models. But we have to know the DIFFERENCE between the Late Veneer and LHB.

Parochial conclusion #2

WATER WAS MOSTLY DELIVERED AT TIME OF PLANET FORMATION, NOT BY COMETS AND NOT IN BOMBARDMENT
2. Nature of the crust

WHEN DID THE CRUSTAL PLATFORM FOR LIFE APPEAR?
Hadean Earth as a Water Planet?
Last part of the talk, with a heavy dose of radiogenic isotope geochemistry

WHEN DID ALL OF THIS HAPPEN?
A word (or two) about isotopic systems

- $^{176}$Lu-$^{176}$Hf
  - $\tau_{1/2} = 37.8$ Ga
  - $\text{Lu} \rightarrow \text{mantle, Hf} \rightarrow \text{crust}$

**Principally in felsic rocks**

MAFIC ROCKS = things like basalt

FELSIC ROCKS = things like granite
Lu/Hf zircon studies - concepts

$^{176}\text{Lu}$ decays to $^{176}\text{Hf}$ with $\tau_{1/2} = 37.8$ Ga

$\epsilon_{\text{Hf}}$ denotes deviations in $^{176}\text{Hf}/^{177}\text{Hf}$ from Bulk Earth (in parts per $10^4$)

$^{177}\text{Hf}$ is the stable reference isotope

Conventionally expressed relative to epsilon
Lu/Hf studies tell us about the origin and evolution of the crust

e_{Hf} denotes deviations in $^{176}\text{Hf}/^{177}\text{Hf}$ from Bulk Earth (in parts per $10^4$)
Zircons have extremely low Lu/Hf, thus they record initial $^{176}$Hf/$^{177}$Hf at time of formation established by Pb ages.
When did crust recycling begin?

Very early. Lu-Hf isotope systematics allows us to “see” back to about 4500 Ma. This result means that Earth’s mafic (ocean crust) & felsic (continental crust) has grown in “pulses” since the earliest times, and probably is a reflection of crust-hydrospere interactions since the beginning.
Continental volume estimates

5% of present continental area ≈ 0.9 Australia
Hadean Earth as a Water Planet?
A conceptual model of the Hadean Earth

Abundant small proto-continental masses, akin to immature-to-mature island arcs at ocean-ocean subduction zones and plume-related edifices.

(What happens with an Exo-Earth that has 100 oceans? Into core?)

ROCKS AFFECTED BY WATER = Dry land

Figure modified from one that appeared in Cassell’s “Atlas of Evolution” (2001)
NO: IT IS HIGHLY LIKELY THAT EMERGENT LAND EXISTED IN THE HADEAN
Motoki et al. (2007)
Some conclusions to discuss & debate

• The first habitats for life could have been a mere 50-100 Myr after solar system formation.

• Cosmochemically Earth-like planets tend to have oxidized mantles.

• Liquid water is primordial to Earth; hardly any was supplied later by comets. Primary accretion source.

• GI>>LV>>>LHB; only magma ocean-forming events matter in the historical continuity of the biosphere.

• Planets form hot. Any time hot rock interacts with liquid water = hydrothermal alteration of that rock.

• Disequilibrium is maintained over geologic timescales by melting rock, and an atmosphere is probably necessary (planetary oxidation – reduction couple)
Some conclusions to discuss & debate

- The first habitats for life could have been a mere 50-100 Myr after solar system formation.
- **Cosmochemically Earth-like planets tend to have oxidized mantles.**
- Liquid water is primordial to Earth; hardly any was supplied later by comets. Primary accretion source.
- GI>>LV>>>LHB; only magma ocean-forming events matter in the historical continuity of the biosphere.
- Planets form hot. Any time hot rock interacts with liquid water = hydrothermal alteration of that rock.
- Disequilibrium is maintained over geologic timescales by melting rock, and an atmosphere is probably necessary (planetary oxidation – reduction couple)
Some conclusions to discuss & debate

• The first habitats for life could have been a mere 50-100 Myr after solar system formation.

• Cosmochemically Earth-like planets tend to have oxidized mantles.

• **Liquid water is primordial to Earth**; hardly any was supplied later by comets. Primary accretion source.

• GI>>LV>>>LHB; only magma ocean-forming events matter in the historical continuity of the biosphere.

• Planets form hot. Any time hot rock interacts with liquid water = hydrothermal alteration of that rock.

• Disequilibrium is maintained over geologic timescales by melting rock, and an atmosphere is probably necessary (planetary oxidation – reduction couple)
Some conclusions to discuss & debate

• The first habitats for life could have been a mere 50-100 Myr after solar system formation.

• Cosmochemically Earth-like planets tend to have oxidized mantles.

• Liquid water is primordial to Earth; hardly any was supplied later by comets. Primary accretion source.

• GI>>LV>>>LHB; only magma ocean-forming events matter in the historical continuity of the biosphere.

• Planets form hot. Any time hot rock interacts with liquid water = hydrothermal alteration of that rock.

• Disequilibrium is maintained over geologic timescales by melting rock, and an atmosphere is probably necessary (planetary oxidation – reduction couple)
Some conclusions to discuss & debate

- The first habitats for life could have been a mere 50-100 Myr after solar system formation.
- Cosmochemically Earth-like planets tend to have oxidized mantles.
- Liquid water is primordial to Earth; hardly any was supplied later by comets. Primary accretion source.
- GI >> LV >>> LHB; only magma ocean-forming events matter in the historical continuity of the biosphere.
- Planets form hot. Any time hot rock interacts with liquid water = hydrothermal alteration of that rock.
- Disequilibrium is maintained over geologic timescales by melting rock, and an atmosphere is probably necessary (planetary oxidation – reduction couple)
Some conclusions to discuss & debate

• The first habitats for life could have been a mere 50-100 Myr after solar system formation.

• Cosmochemically Earth-like planets tend to have oxidized mantles.

• Liquid water is primordial to Earth; hardly any was supplied later by comets. Primary accretion source.

• GI>>LV>>>LHB; only magma ocean-forming events matter in the historical continuity of the biosphere.

• Planets form hot. Any time hot rock interacts with liquid water = hydrothermal alteration of that rock.

• Disequilibrium is maintained over geologic timescales by melting rock, and an atmosphere is probably necessary (planetary oxidation – reduction couple)
Thank you!

With apologies to Stepen Mojzsis
Still looking
Thank you!