

Supported by



John
Templeton
Foundation



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

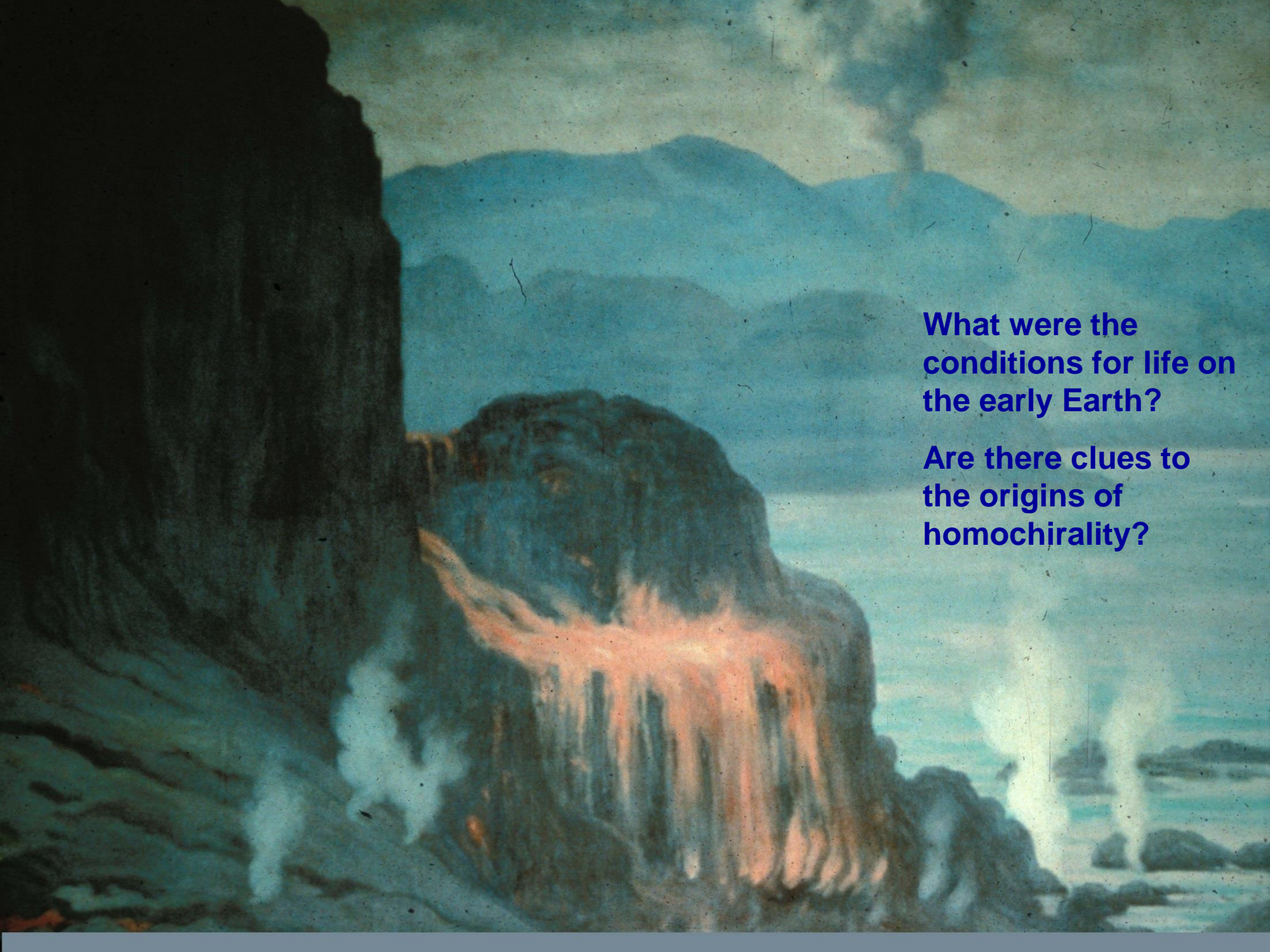
University of Virginia



Events that Shaped the Earth

The Origin Life

Stephen Macko
University of Virginia



**What were the
conditions for life on
the early Earth?**

**Are there clues to
the origins of
homochirality?**

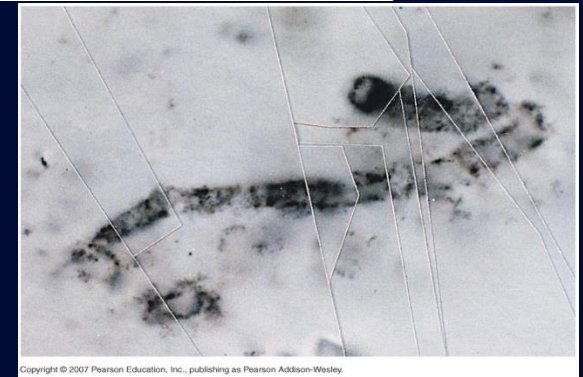
- **Stromatolites**

- 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



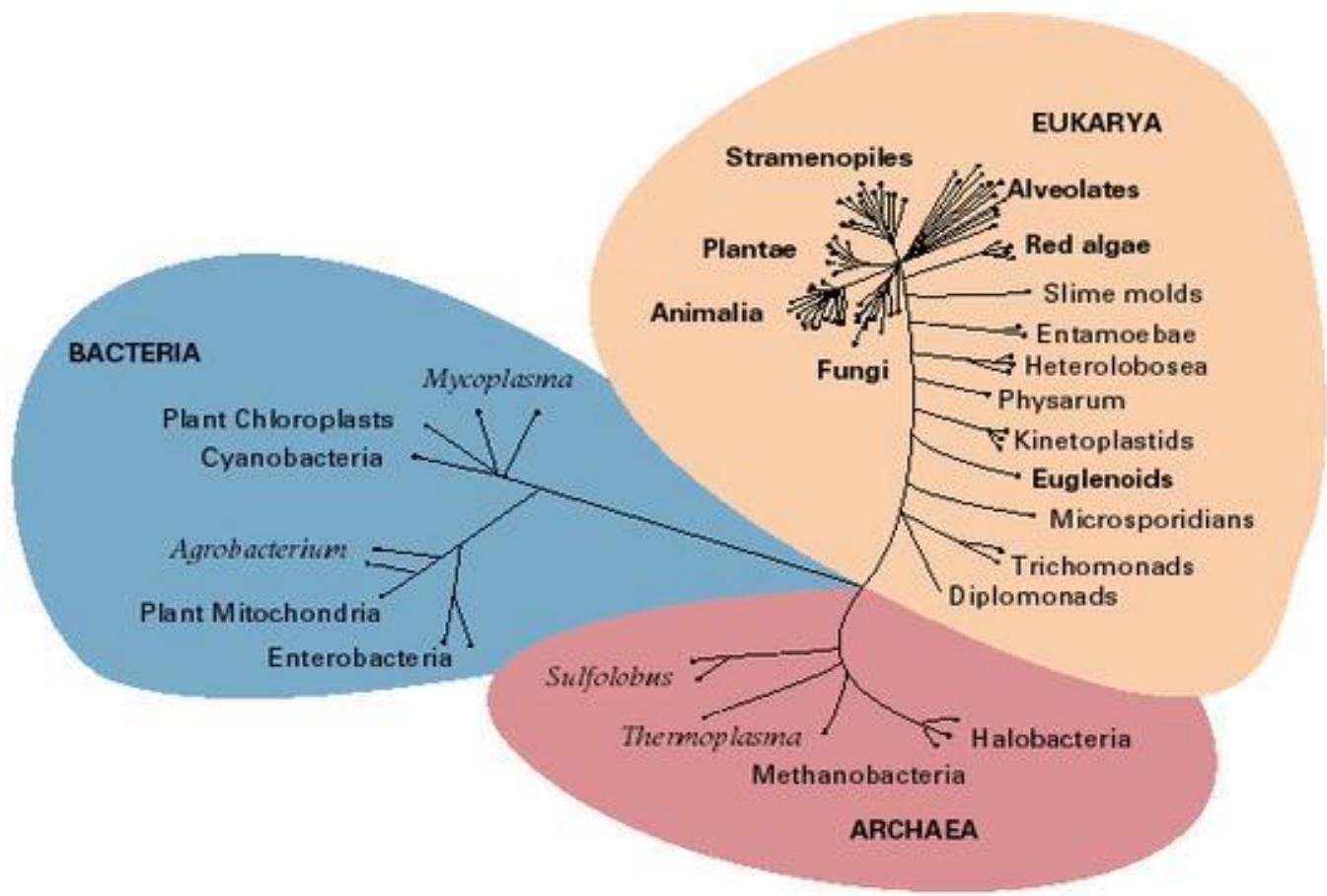
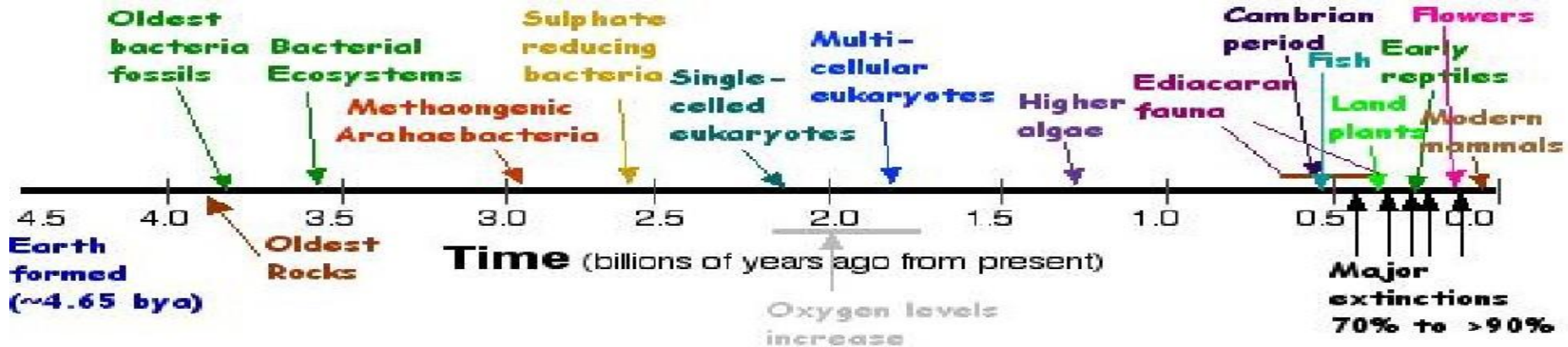
- **Fossil evidence**

- 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



- $^{13}\text{C}/^{12}\text{C}$ 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





Charles Darwin 1809-1882 Hot Ponds

Alexander Ivanovich Oparin

1894-1980

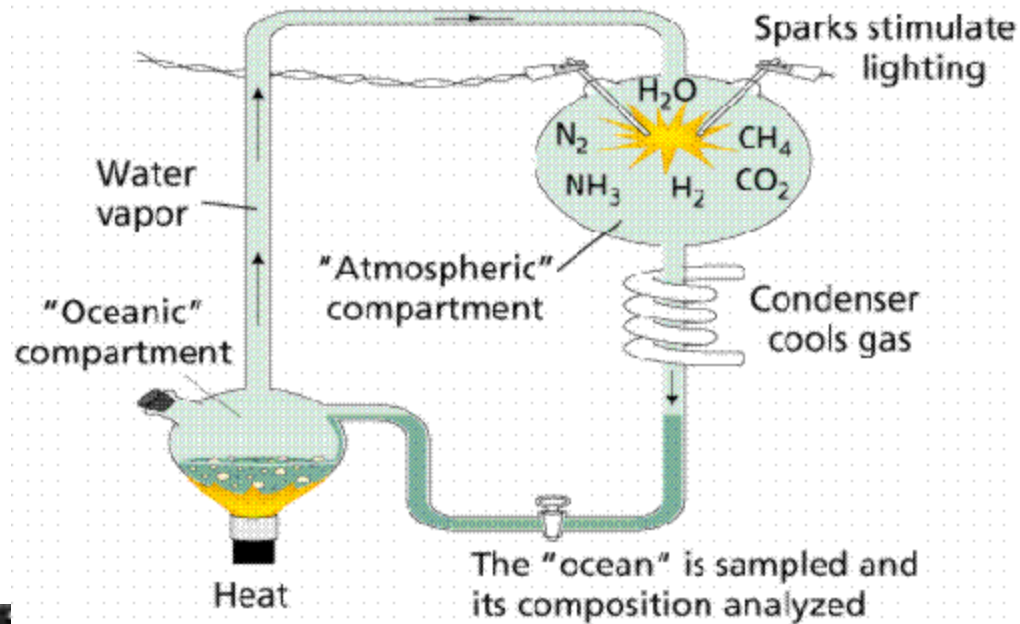


The Origin of Life on Earth
"primordial soup"

1924



The Miller Urey Experiment



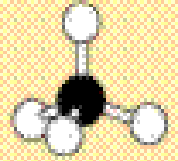
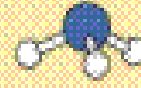
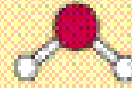
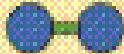
HC Urey



SL Miller



Ingredients in Miller's experiments



Hydrogen
gas

Nitrogen
gas

Carbon
dioxide

Water

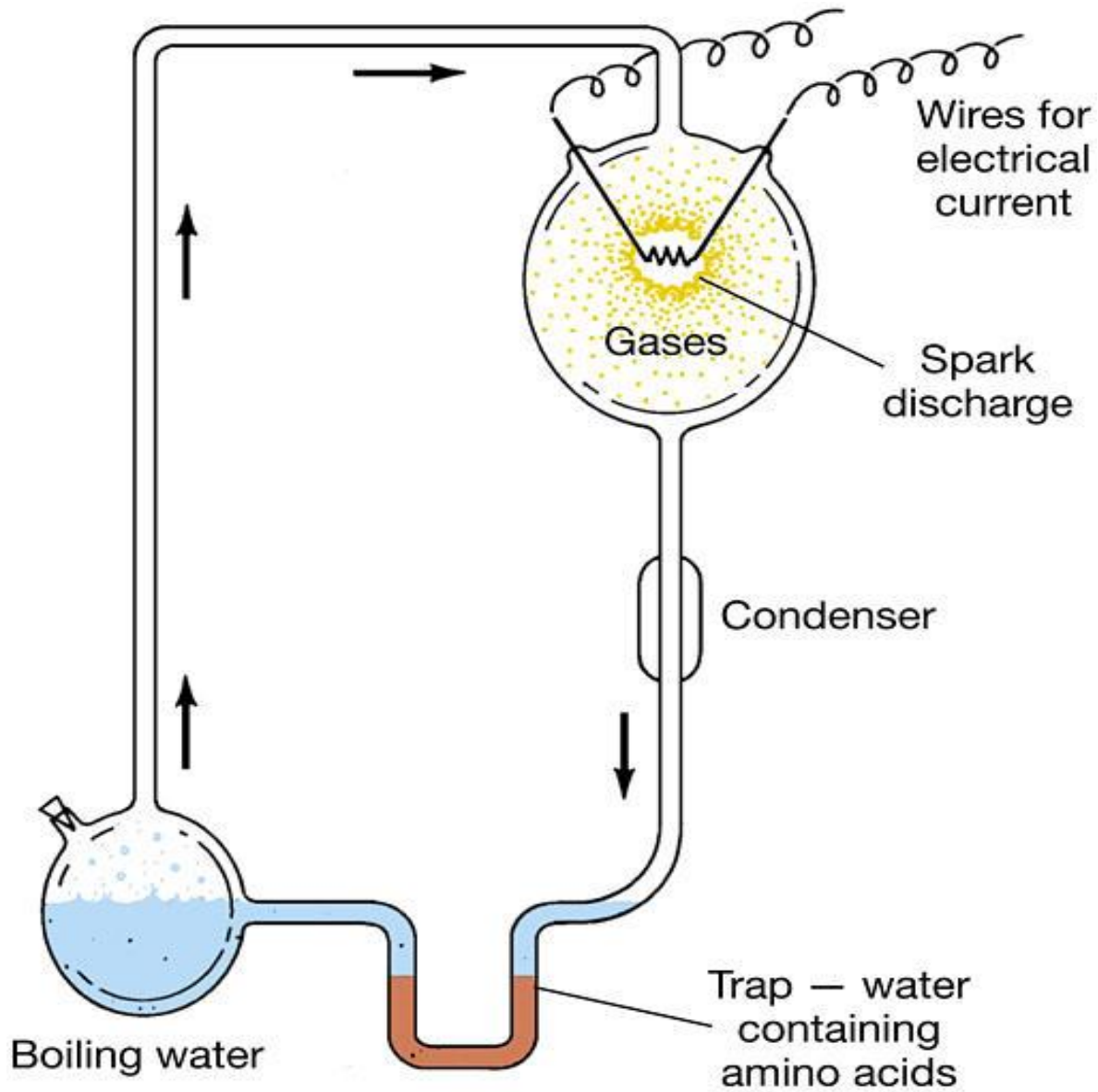
Ammonia

Methane

No Oxygen !

(Not in the Early Earth's Atmosphere)

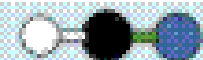
<http://www.ucsd.tv/miller-urey/>



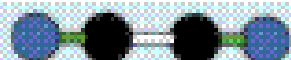
Chicago 1953



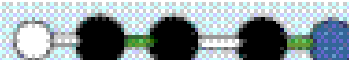
Primitive molecules



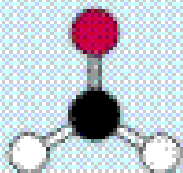
Hydrogen
cyanide



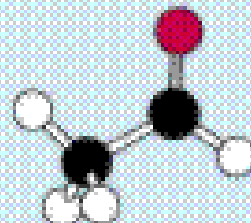
Cyanogen



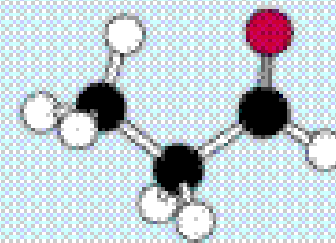
Cyanoacetylene



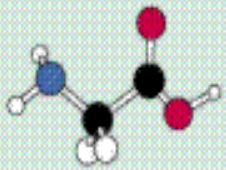
Formaldehyde



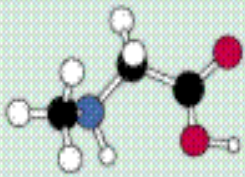
Acetaldehyde



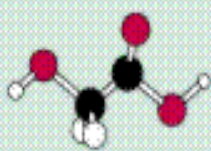
Propionaldehyde



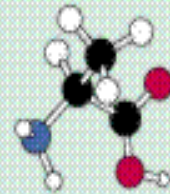
Glycine



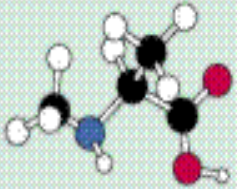
Sarcosine



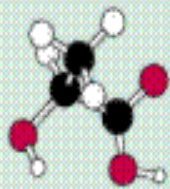
Glycolic acid



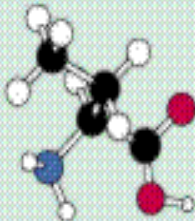
Alanine



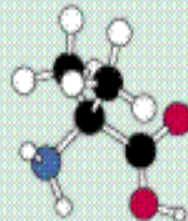
N-Methylalanine



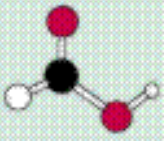
Lactic acid



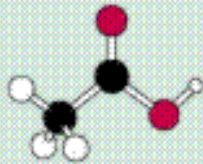
α -Aminobutyric acid



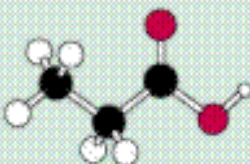
α -Aminoisobutyric acid



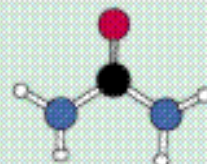
Formic acid



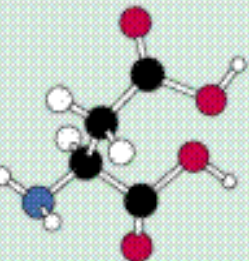
Acetic acid



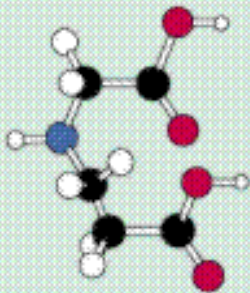
Propionic acid



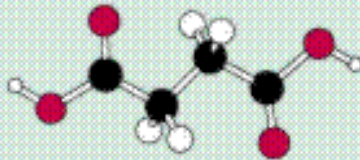
Urea



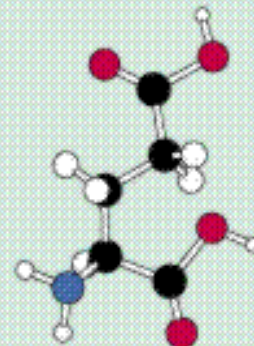
Aspartic acid



Iminoacetic-propionic acid



Succinic acid



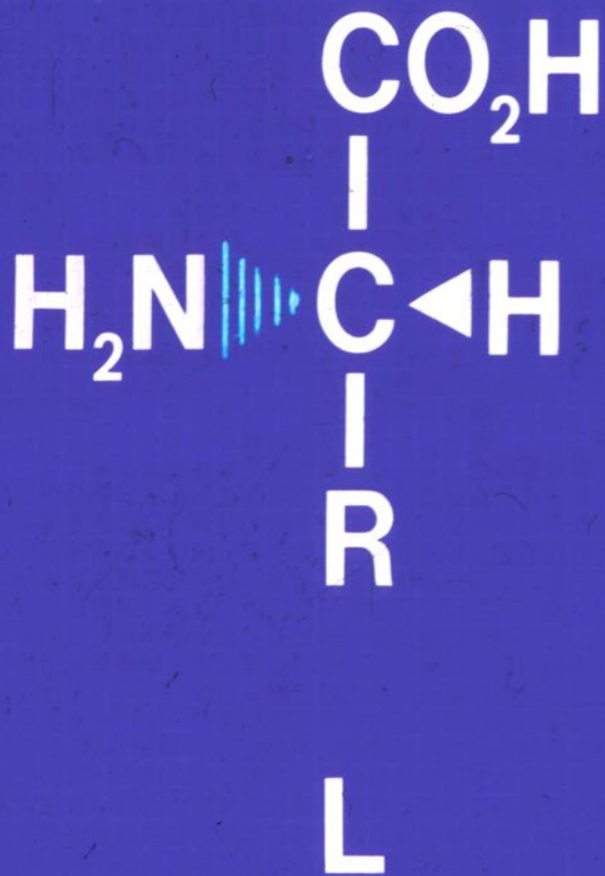
Glutamic acid

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"?

mirror



Stereoisomers of amino acids

Mammoth Hot Springs



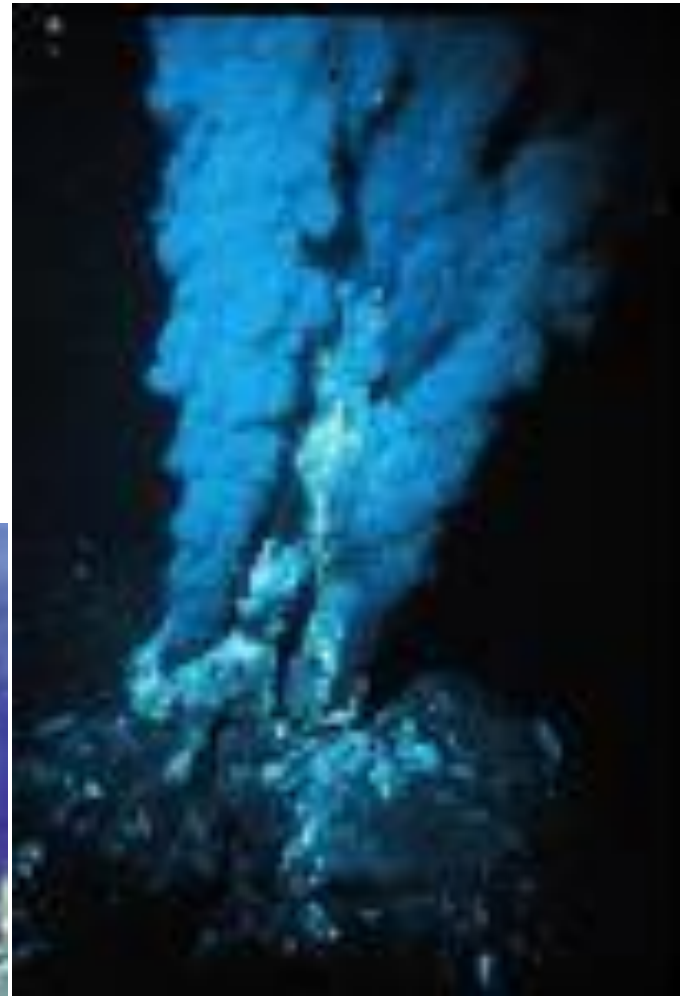
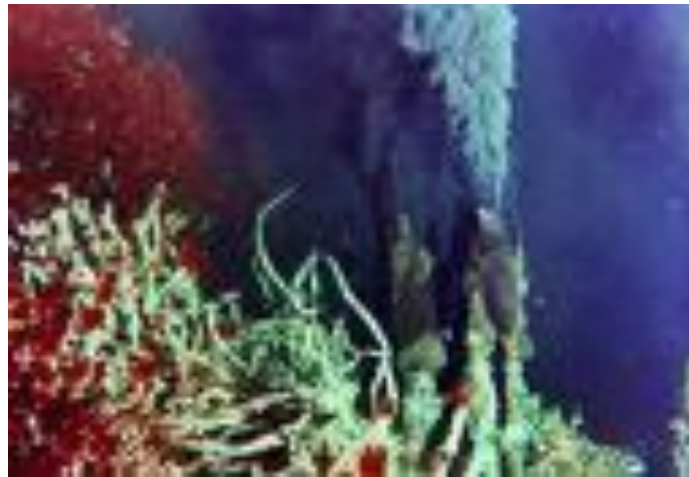


Alvin

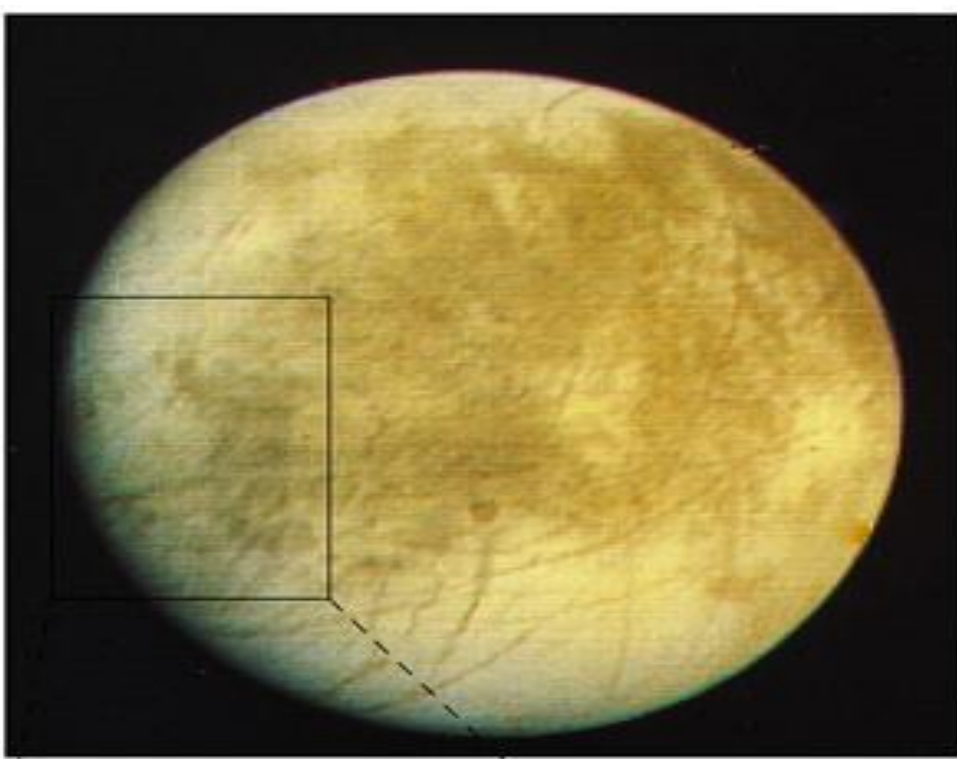


Sea Link

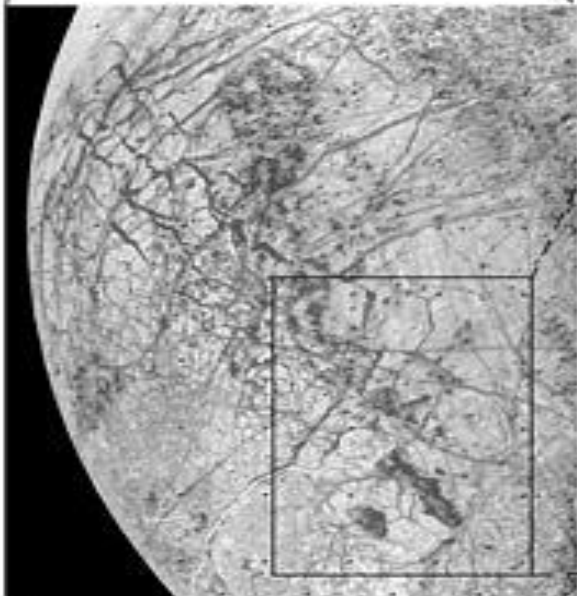
Hot Vents 250 C



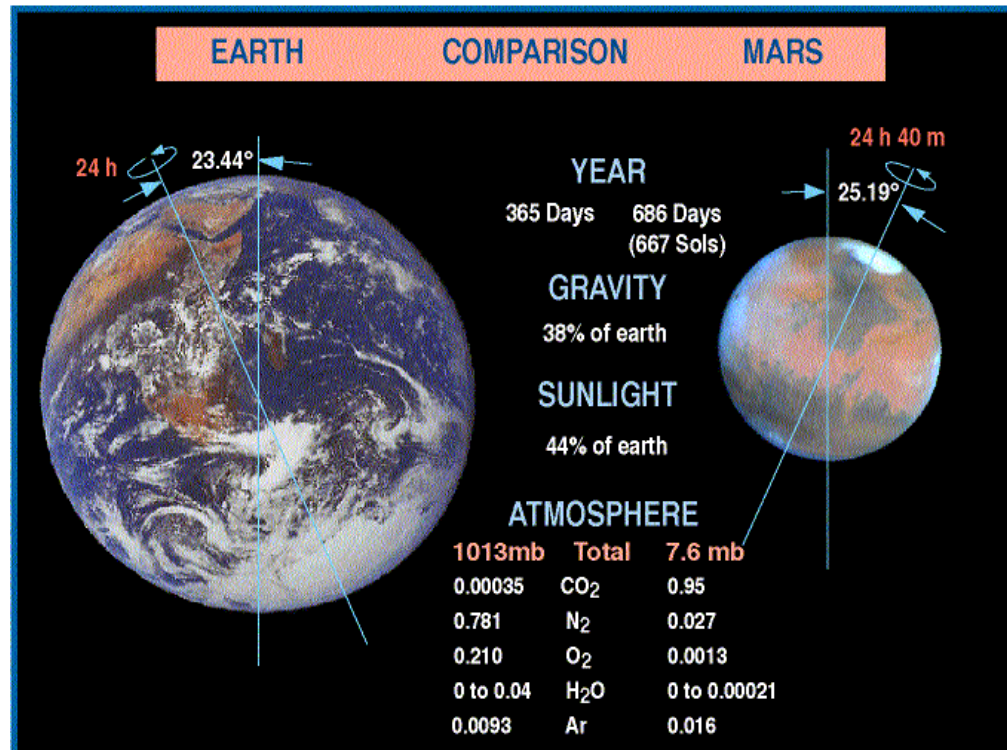
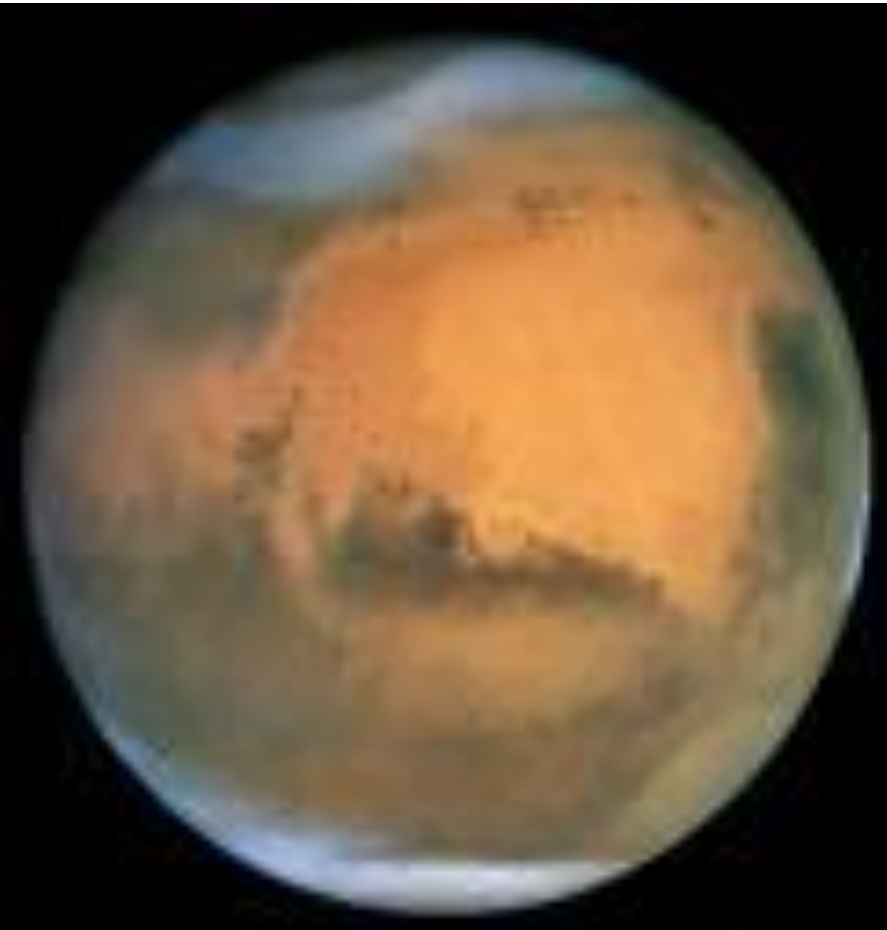
An Ocean on Europa



(a)



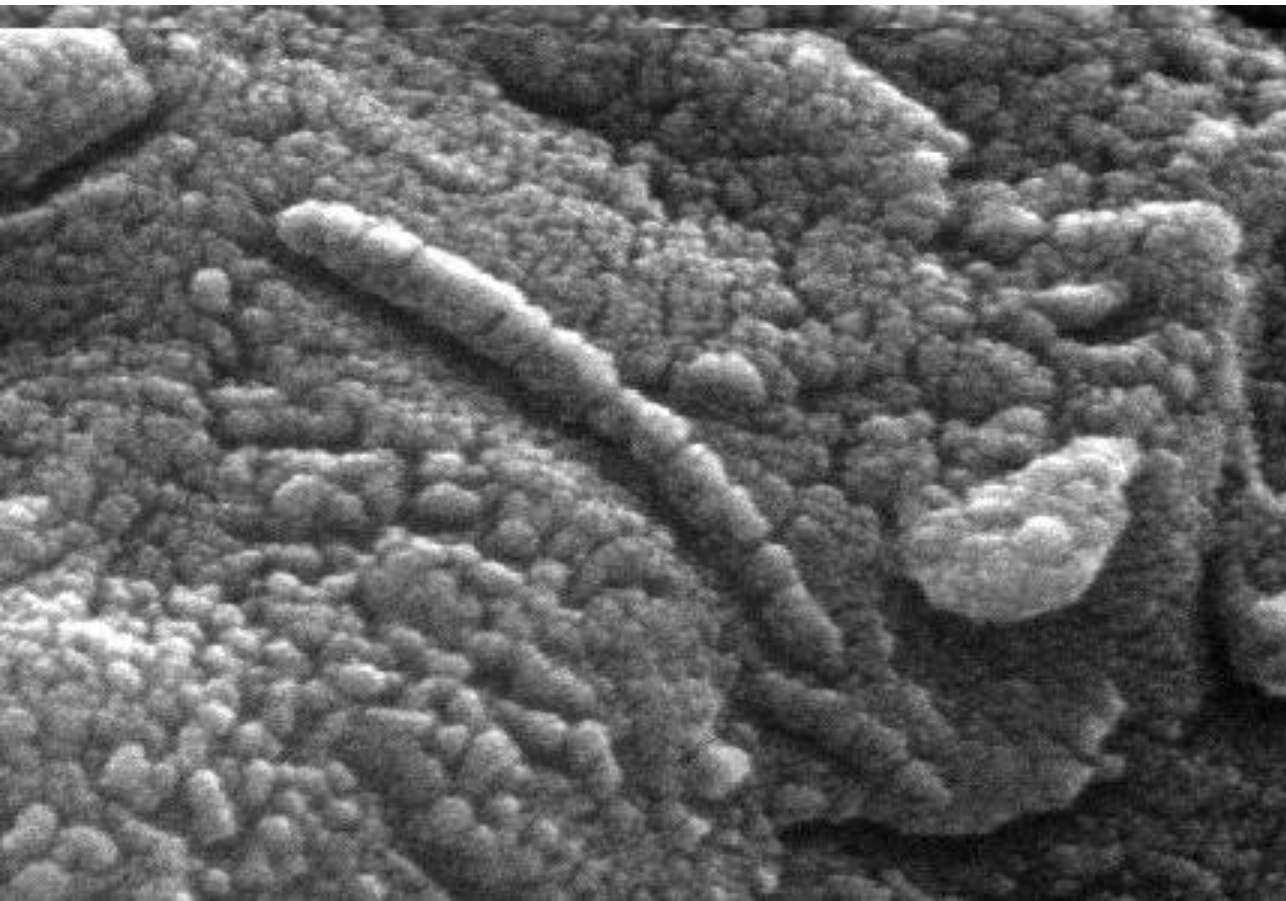
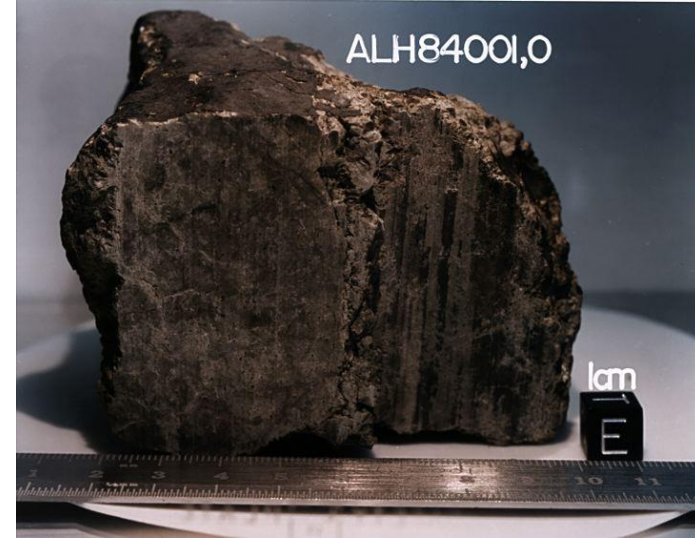
Mars





Meteorite Impacts

Meteorites from Mars



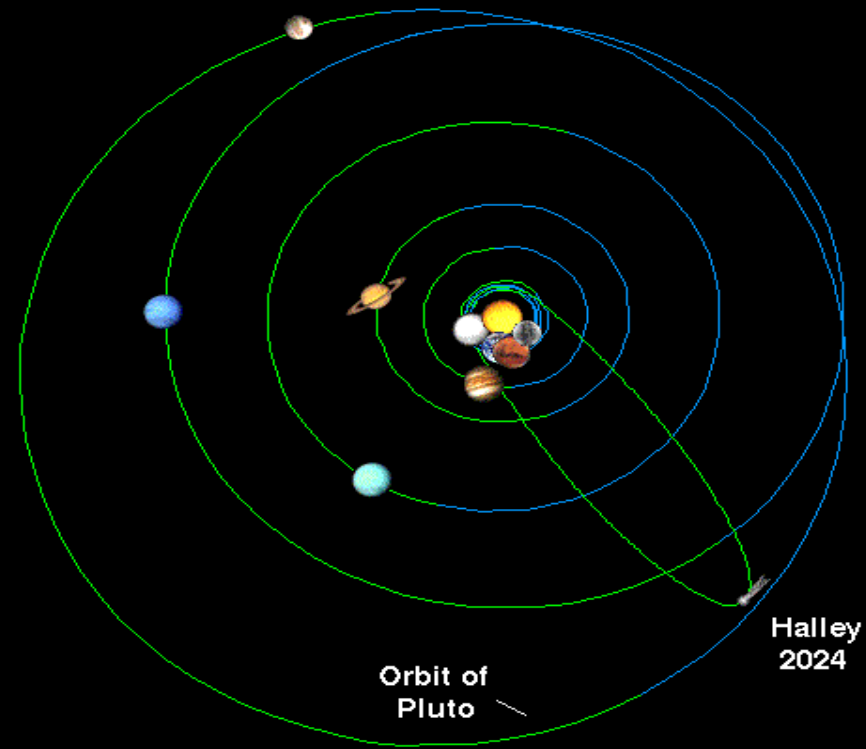
**Organized
microstructures**

Comets



The Oort Cloud (comprising many billions of comets)

Oort Cloud cutaway drawing adapted from Donald K. Yeoman's illustration (NASA, JPL)



Still looking



Supported by



John
Templeton
Foundation



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 ($Zr(SiO_4)$) – a very useful mineral!

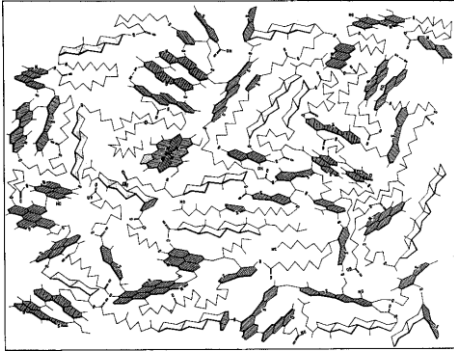
Granite (composed of $\geq 10\%$ quartz, feldspar, +other minerals)

(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

Organic raw materials



*“Free Energy” from disequilibria**



Liquid water



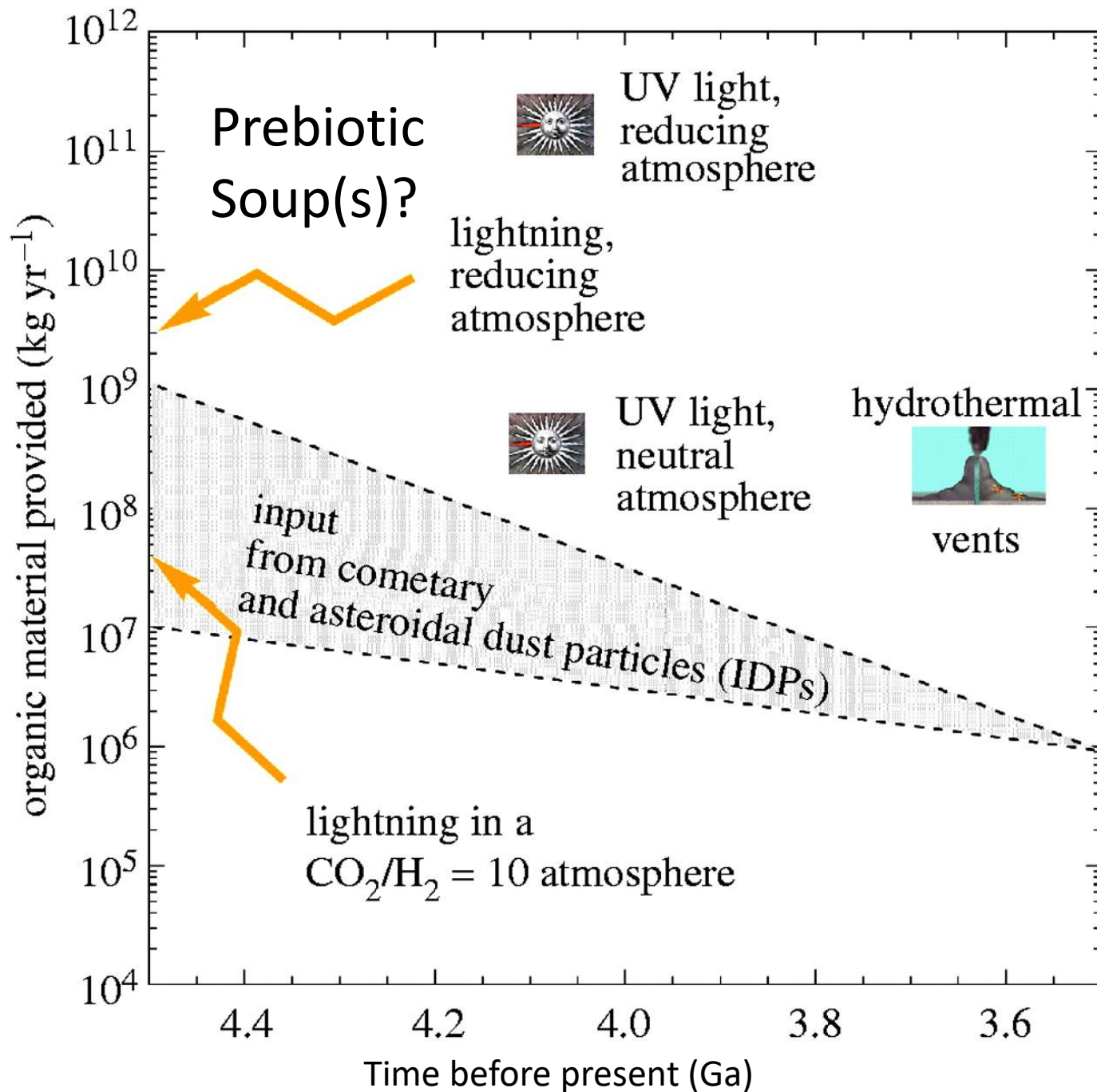
Time



Hypothesis: Life will arise when the above conditions are met
“but the first steps are the hardest” (Mike Russell, 2014)

CAN WE MODIFY OUR FOUR CRITERIA FOR “PLANETS AS CRADLES OF LIFE”?

A visual representation summarizing the relative contributions of some major sources of organic molecules.

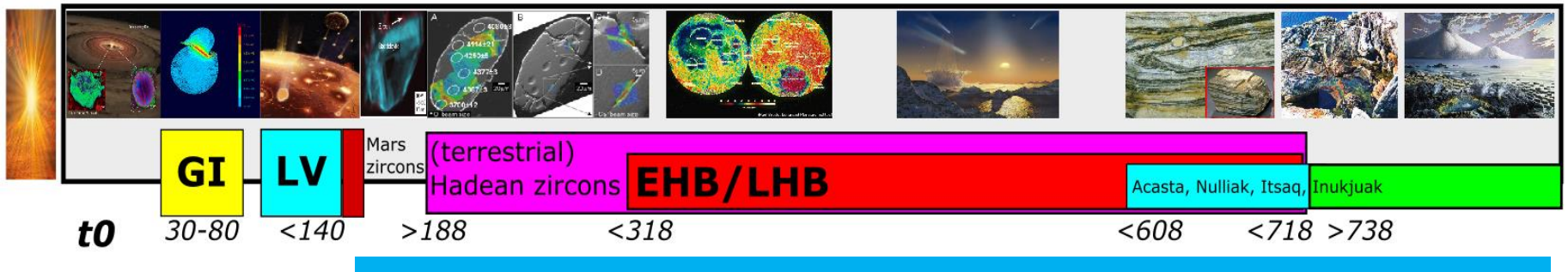


artwork: Cosmographica



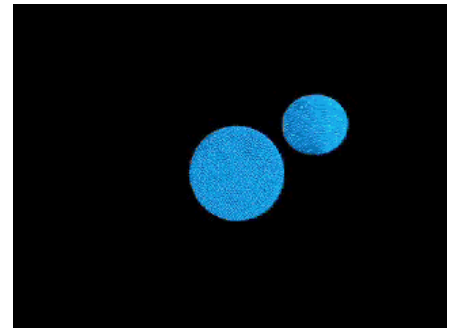
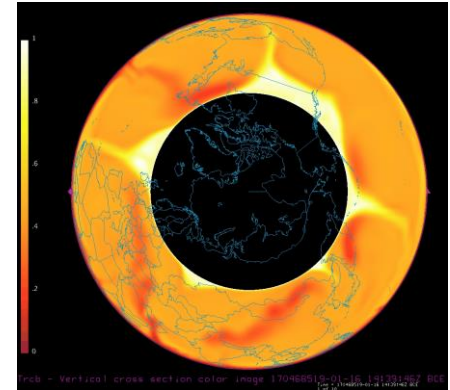
artwork: Don Dixon



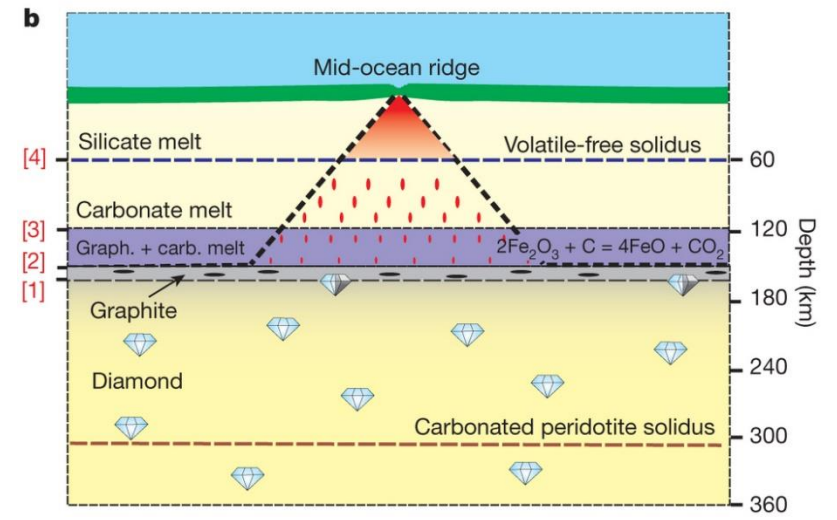
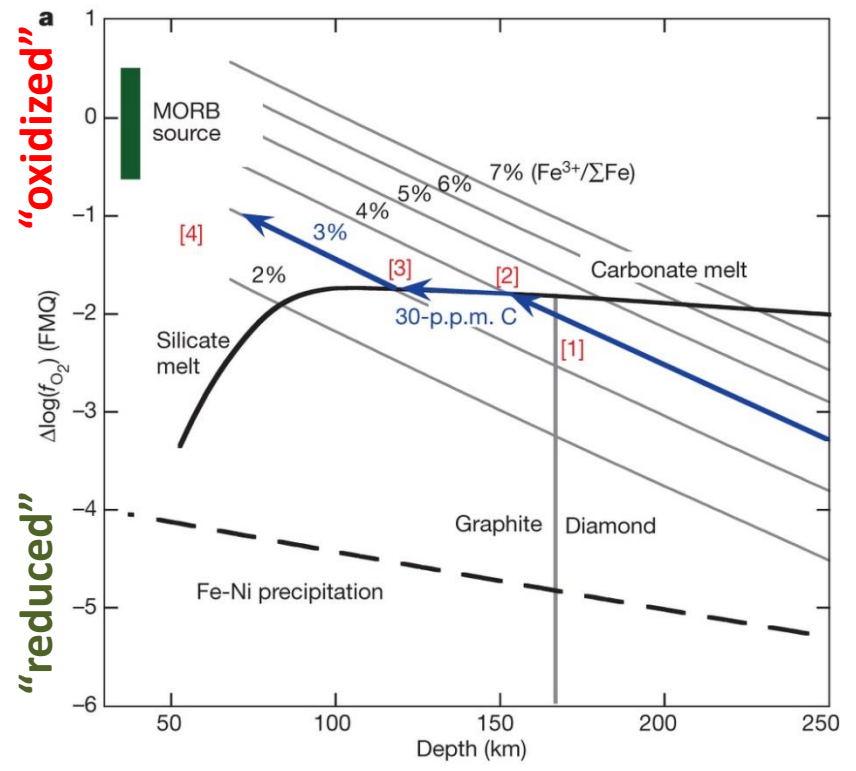


2 themes to this presentation

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



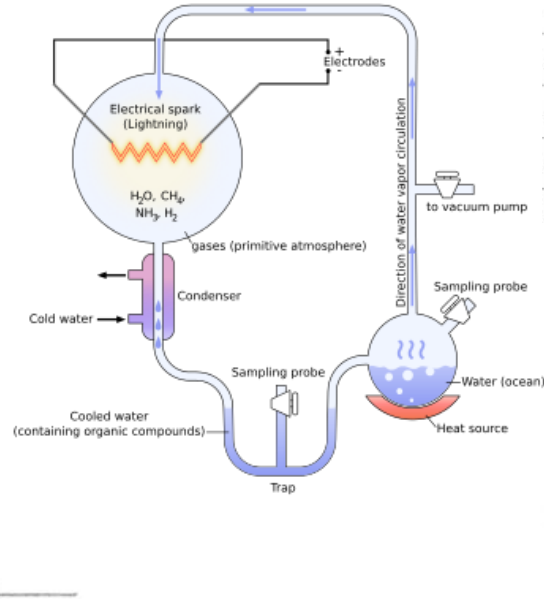
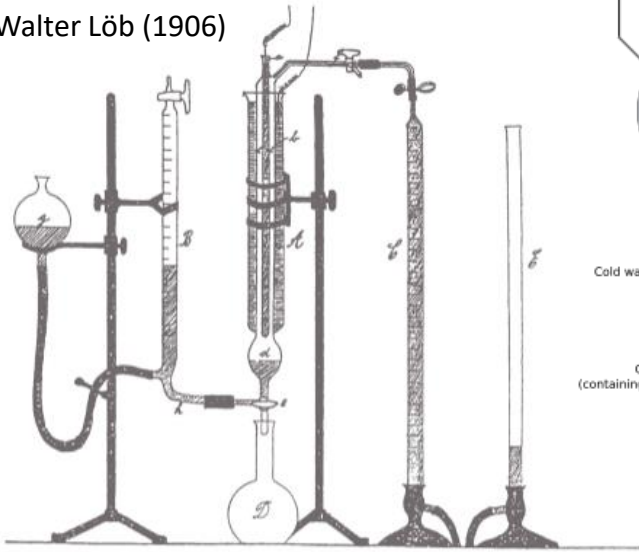
1. Mantle redox evolution



Stagno et al. (2012)

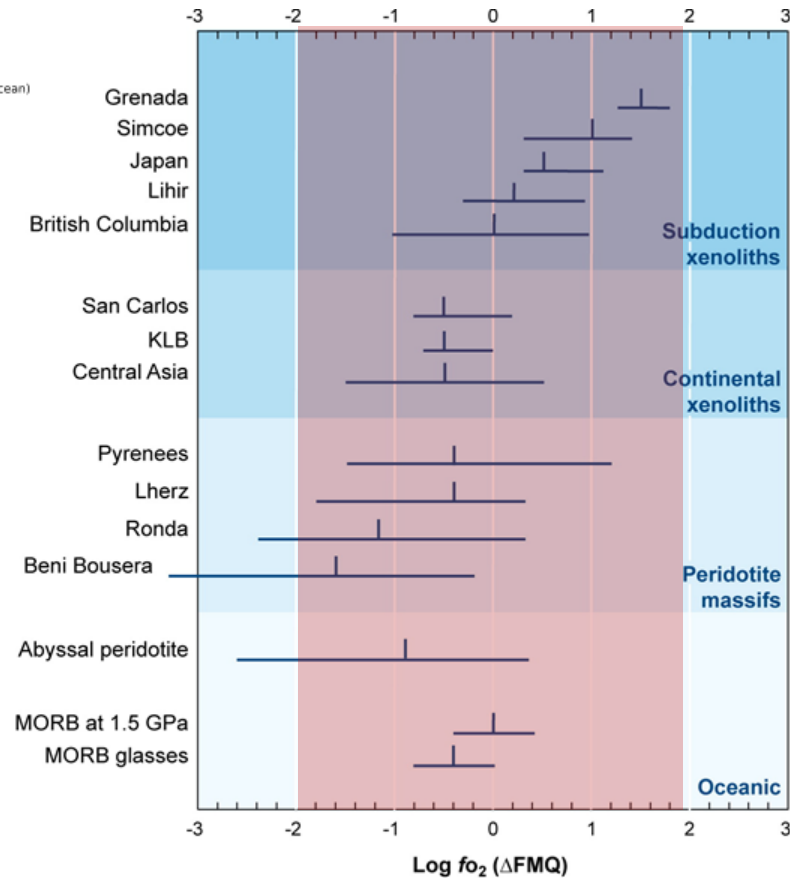
The evolution of oxygen fugacity in Earth's silicate mantle affects the speciation and mobility of volatile elements in the interior and has controlled the character of degassing species from the Earth since the planet's formation.

Walter Löb (1906)



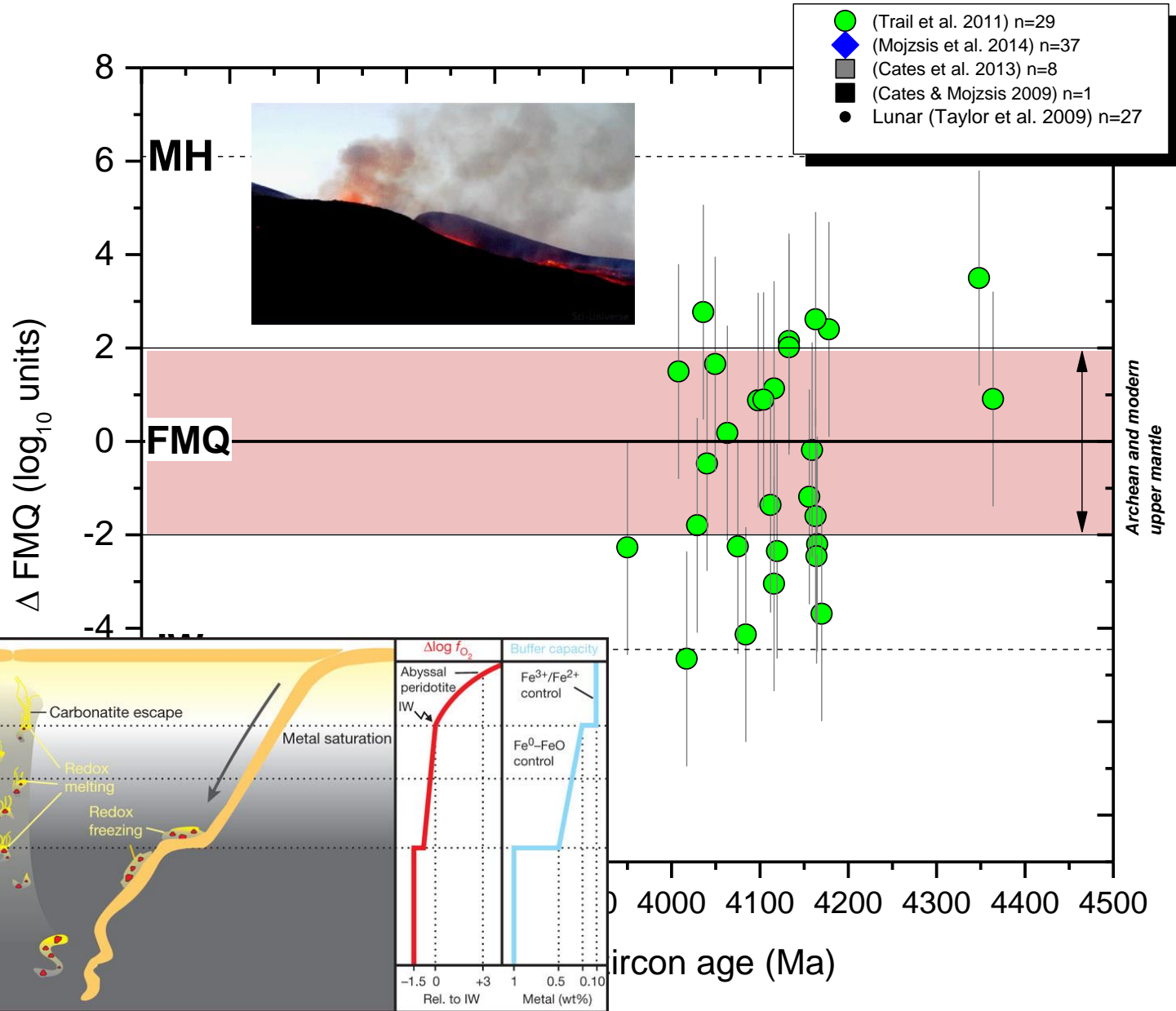
S. Miller & H. Urey (1952)

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.

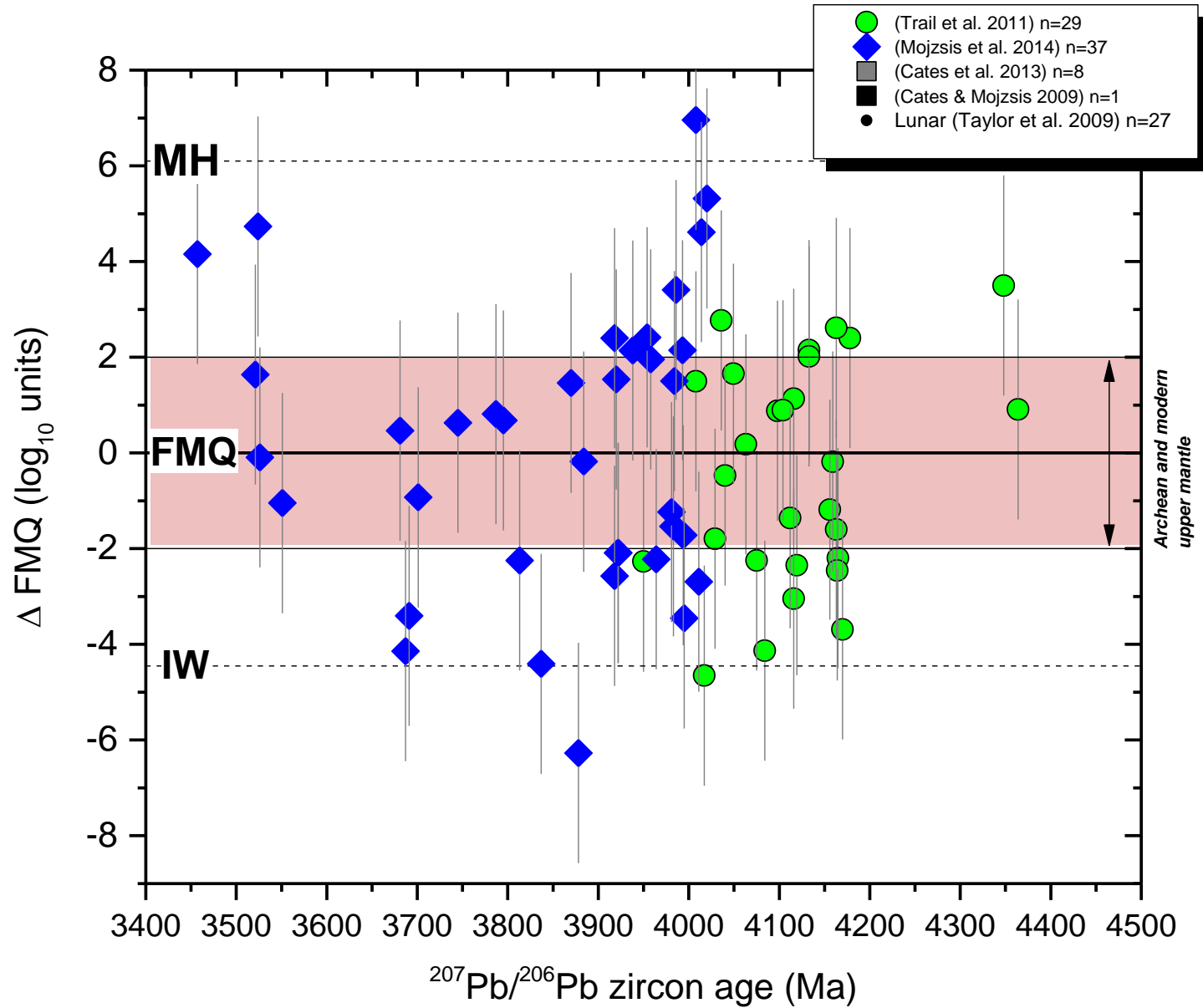


SOME IMPORTANT RECENT PROGRESS

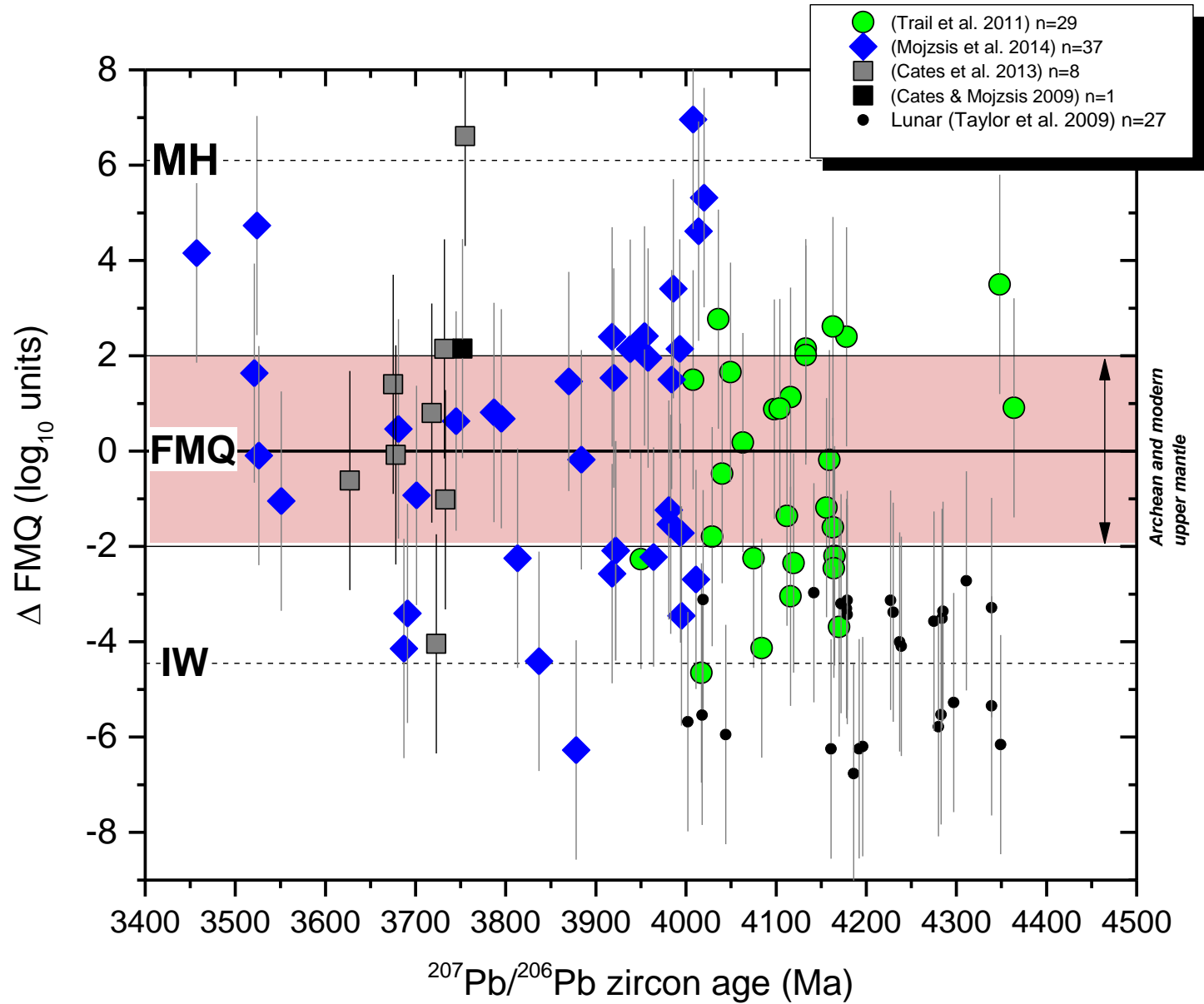
Evolution of terrestrial mantle oxygen fugacity from $[\text{Ce}/\text{Ce}^*]_{\text{zircon}}$

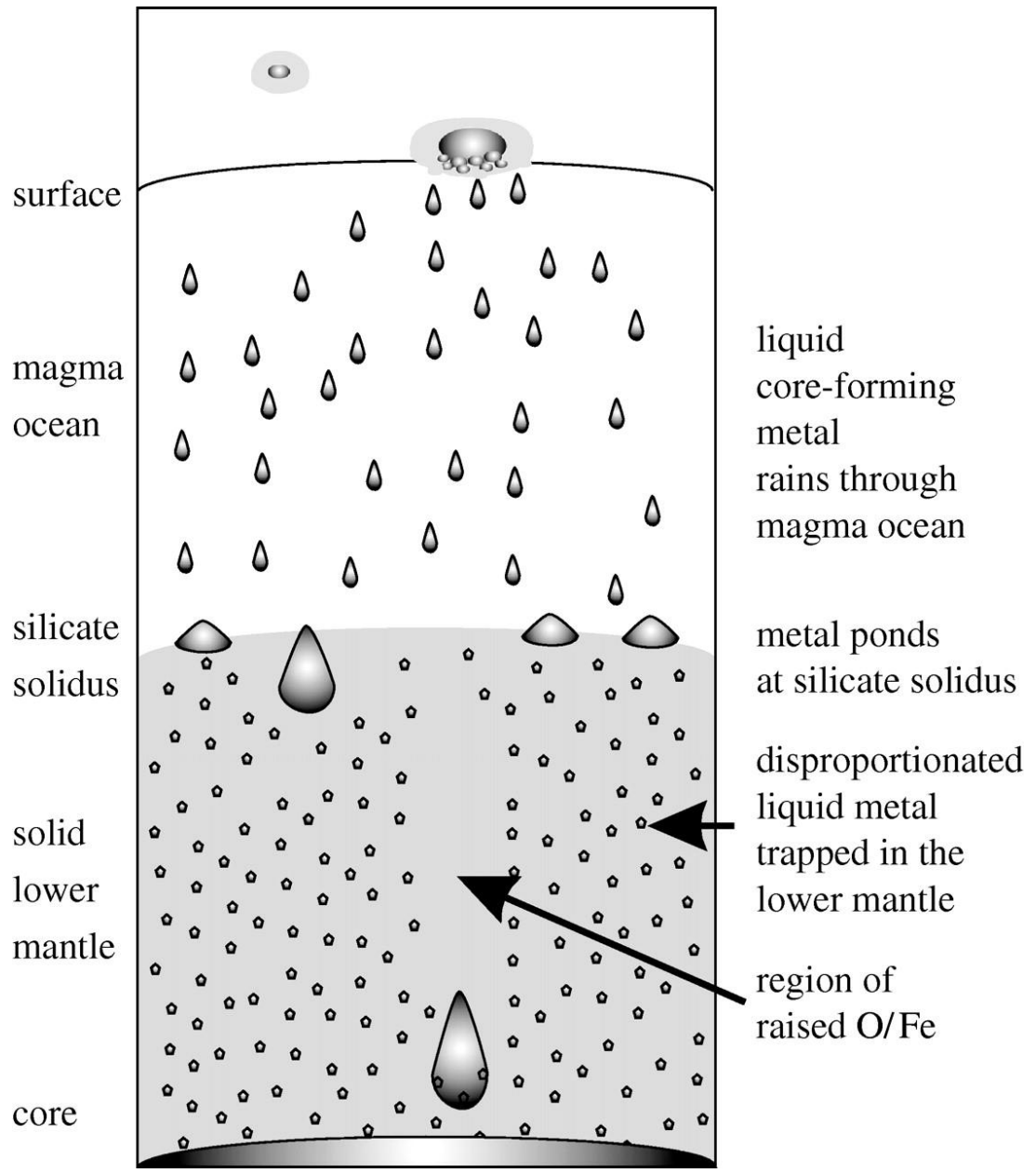
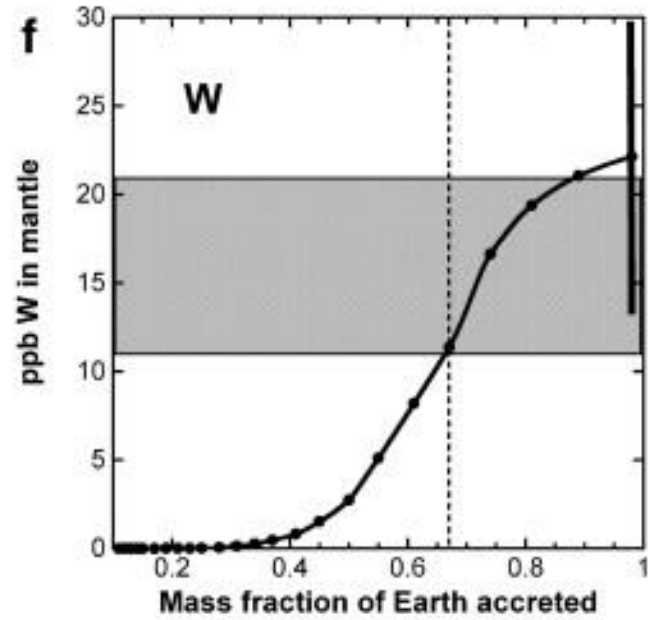
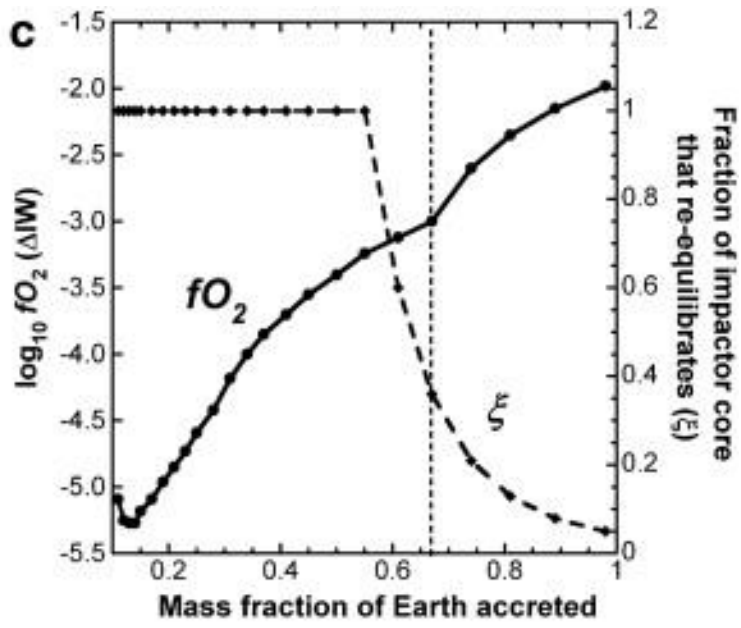


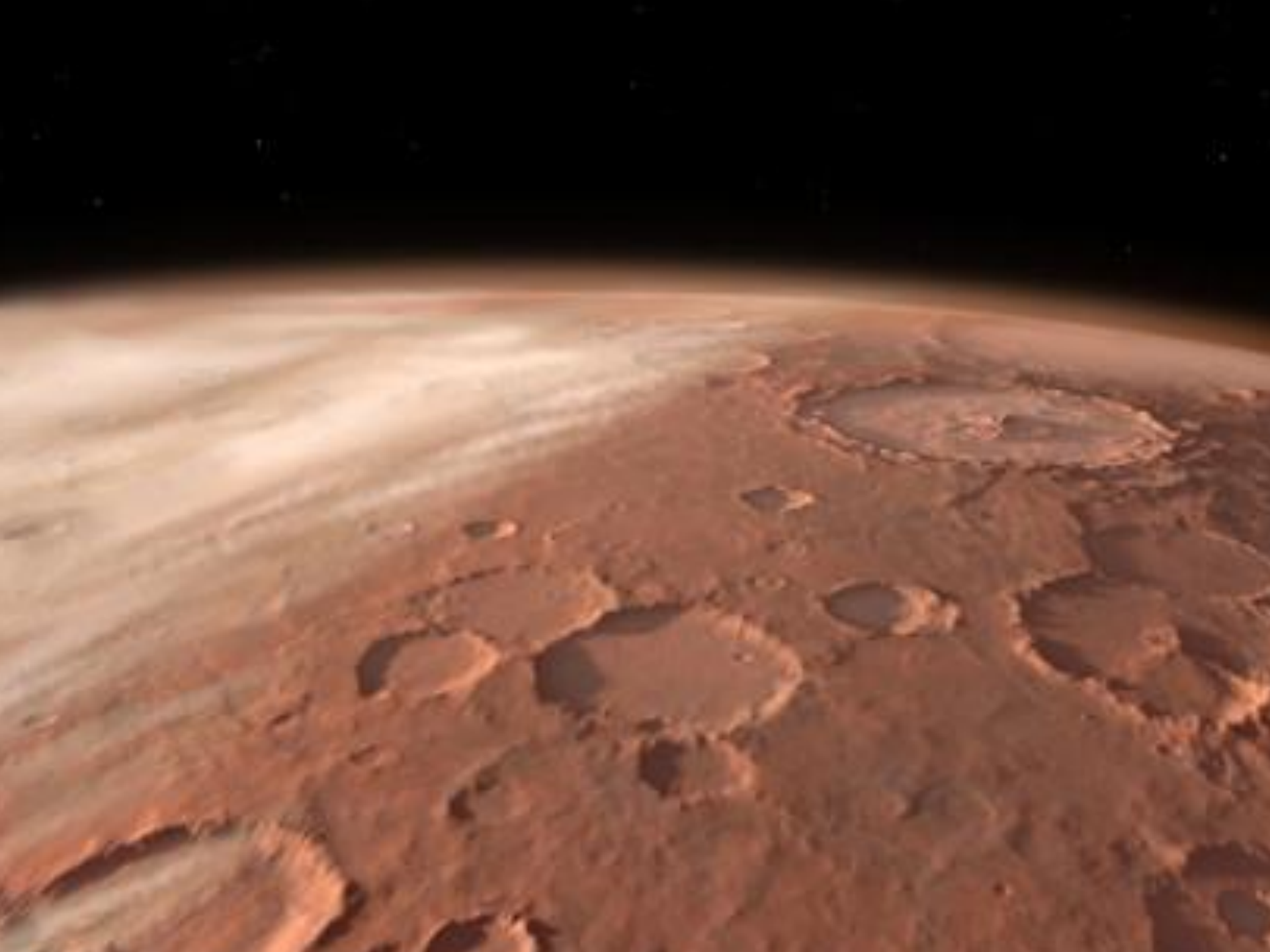
Evolution of terrestrial mantle oxygen fugacity from $[\text{Ce}/\text{Ce}^*]_{\text{zircon}}$



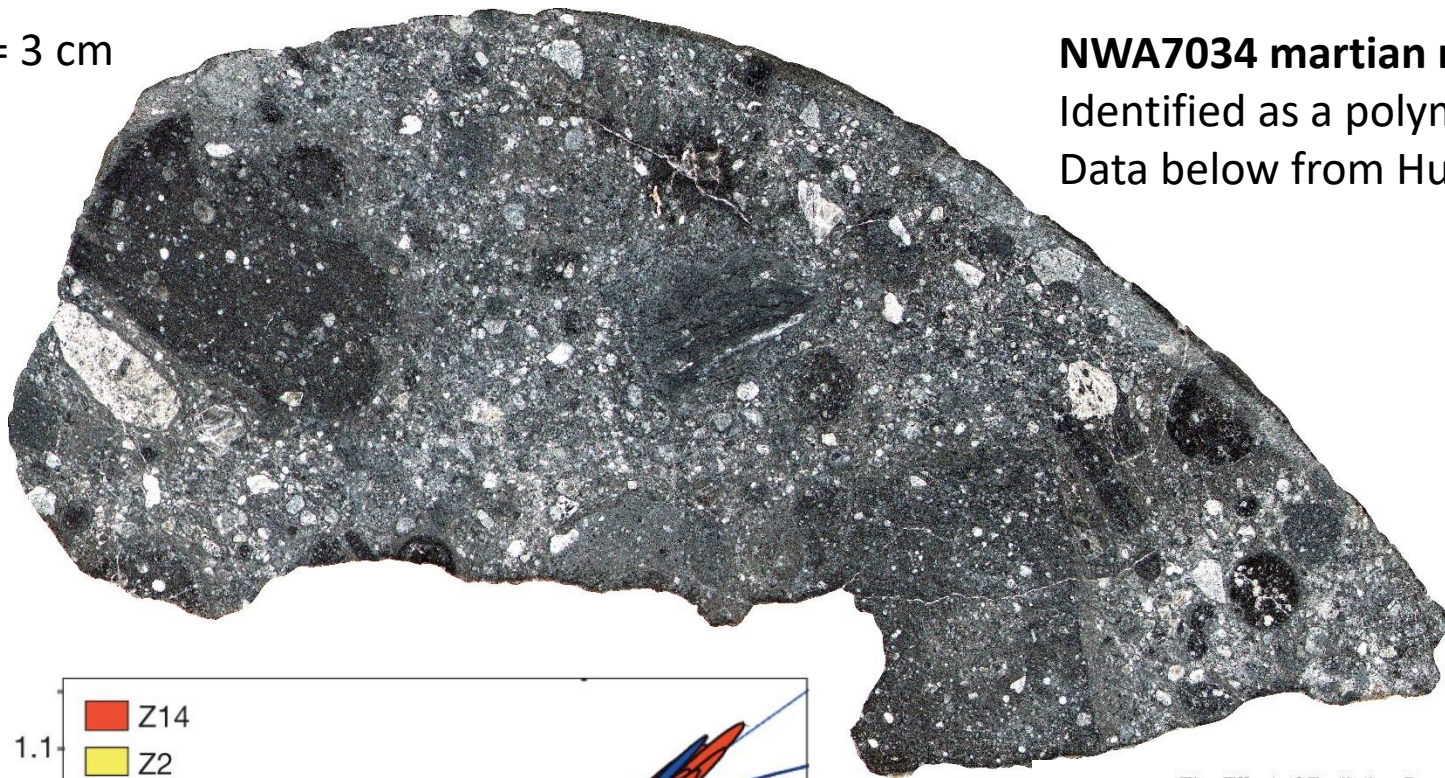
Comparative mantle oxygen fugacities (Earth vs. Moon)



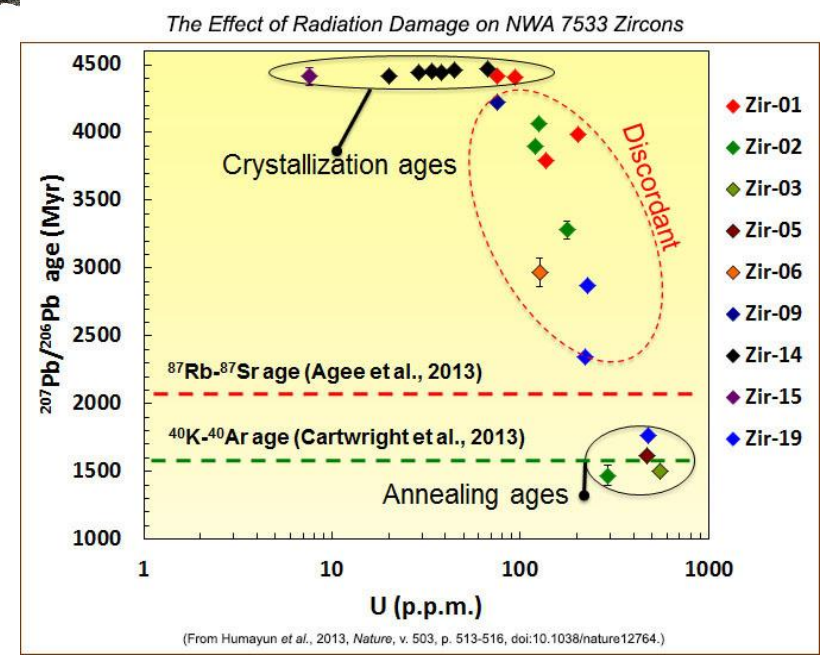
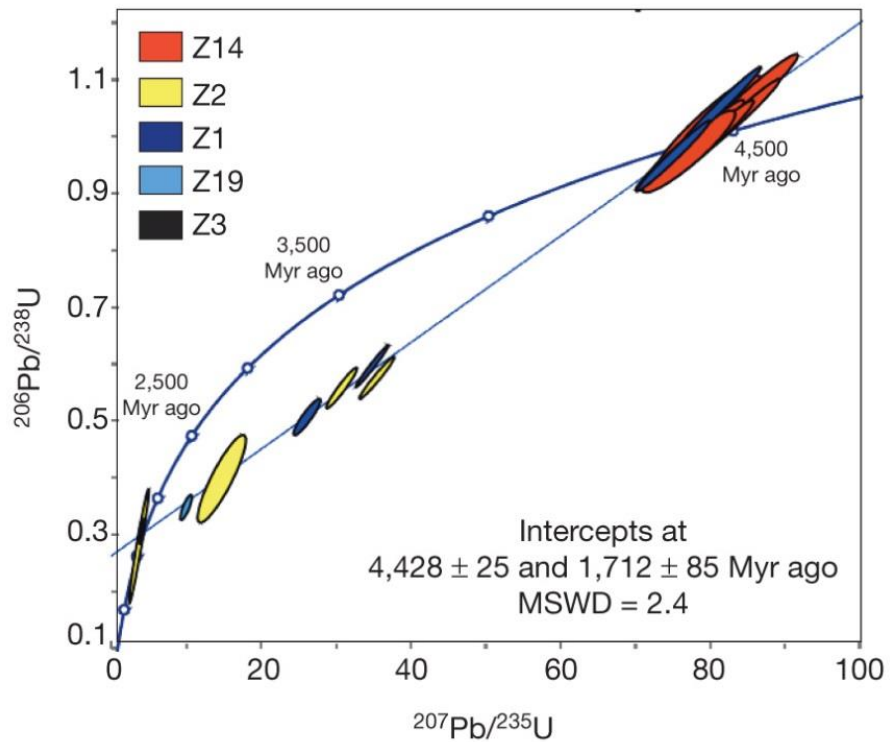




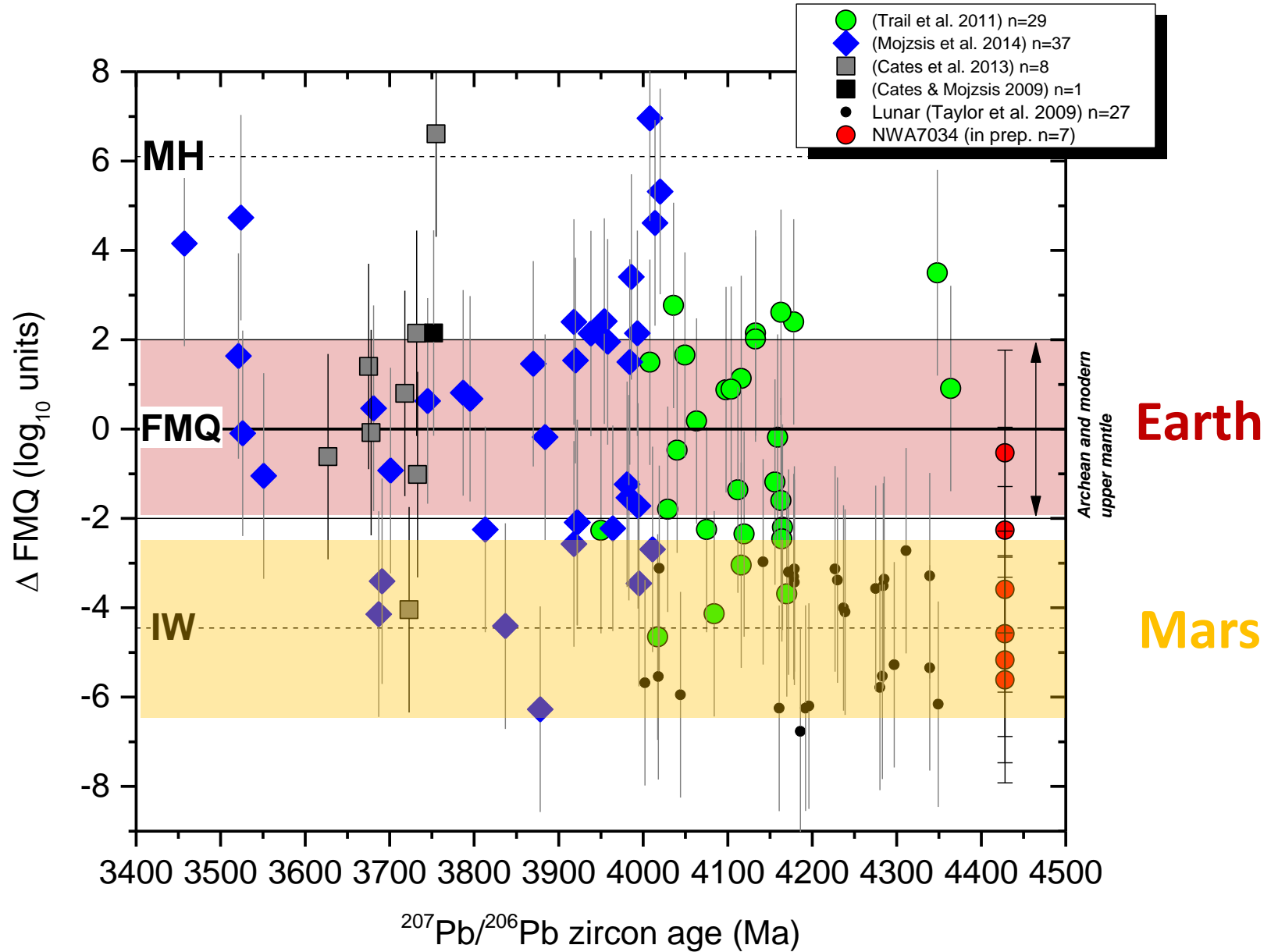
l = 3 cm



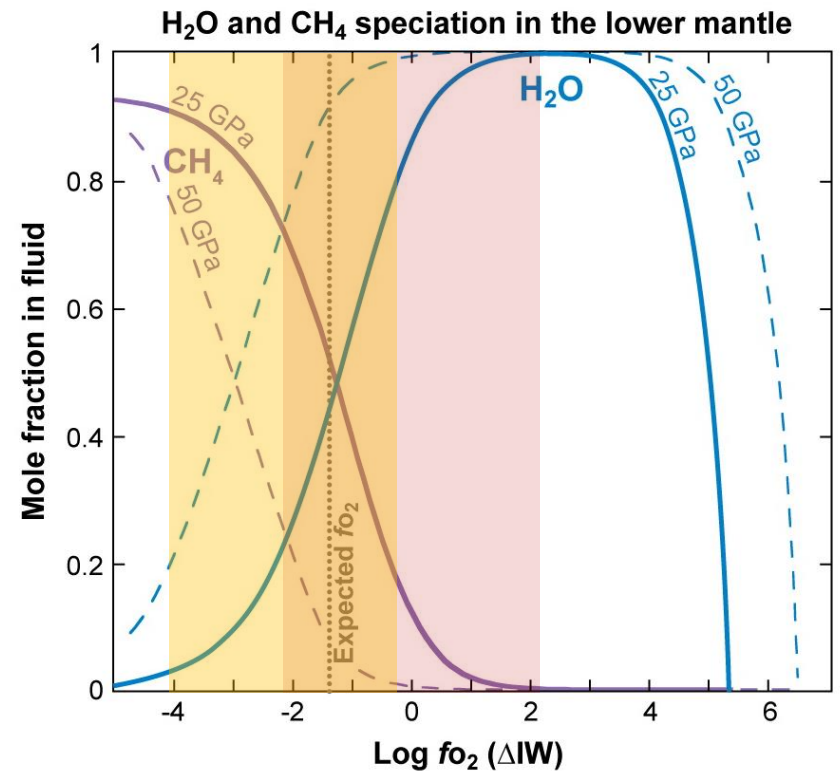
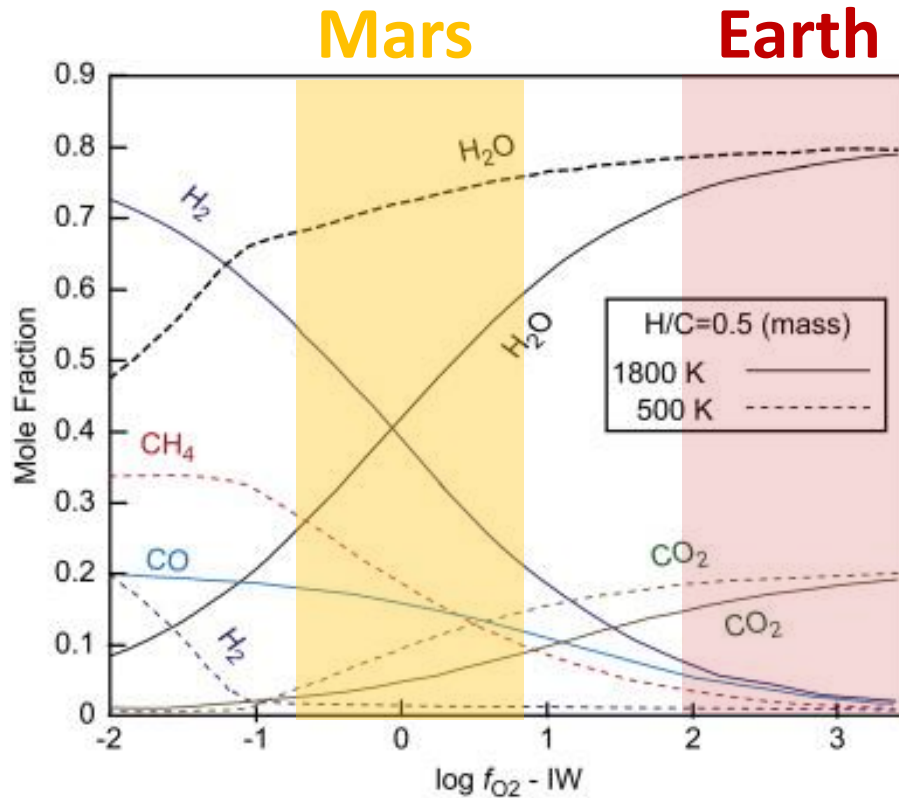
NWA7034 martian meteorite
Identified as a polymict regolith breccia
Data below from Humayun et al. (2013)



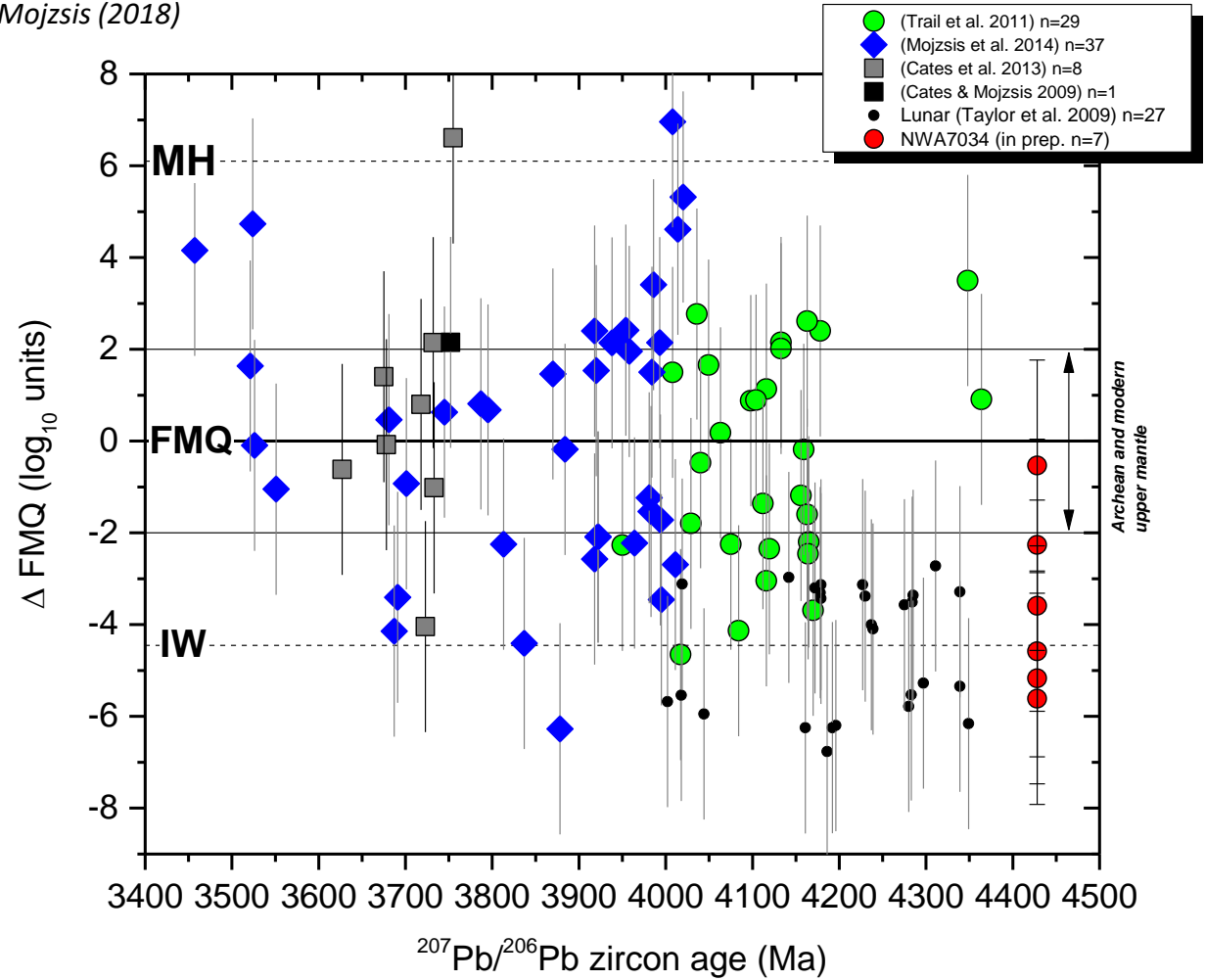
Comparative mantle oxygen fugacities (Earth vs. Moon vs. Mars)



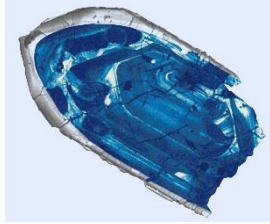
Speciation of volcanic gases on early Earth and early Mars



Mojzsis (2018)



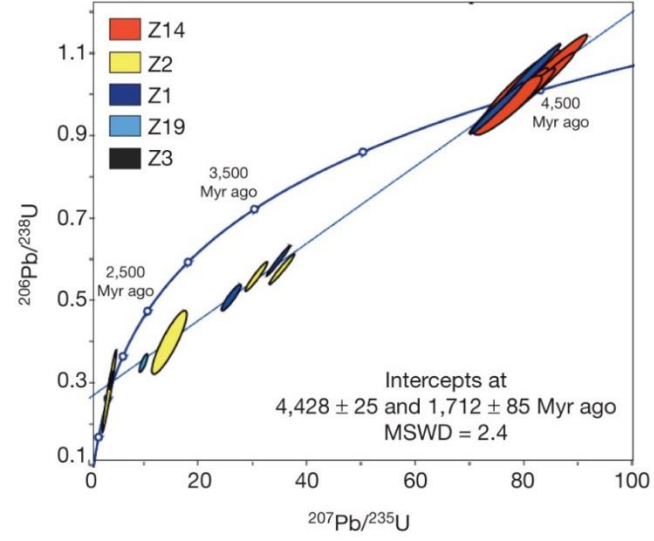
Valley et al. 2014



Mojzsis et al. 2016



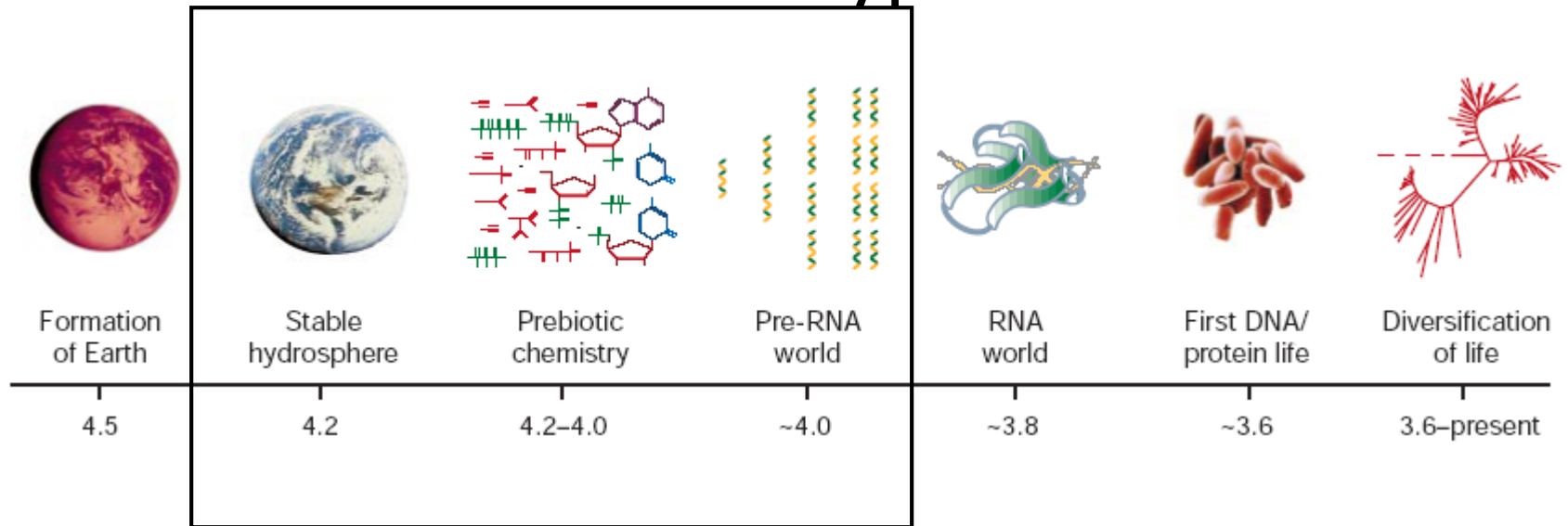
Nemchin et al. 2010



Humayun et al. (2013)

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



Joyce, G.F. (2002) *Nature* **418**, 214-221.

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

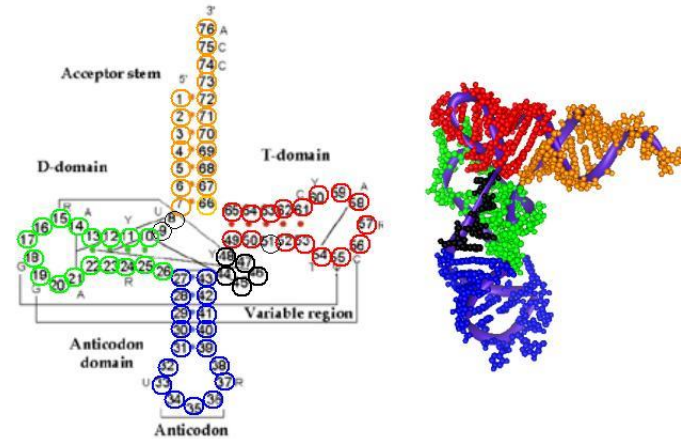
→ have very high mutation rates (10^5 - $10^6 \times$ bacteria)

→ RNA viruses not found in Hyperthermophiles

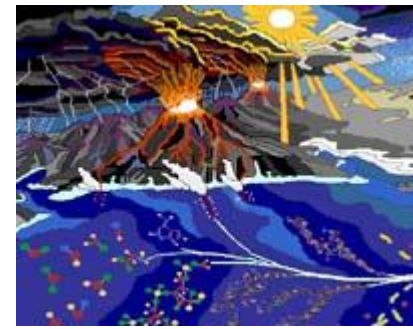
→ use nucleotides from some source

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 ($>50^{\circ}\text{C}$)

-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!)

1.4×10^{24} g of water in the hydrosphere

Bulk D/H of this water is 1.557×10^{-4}

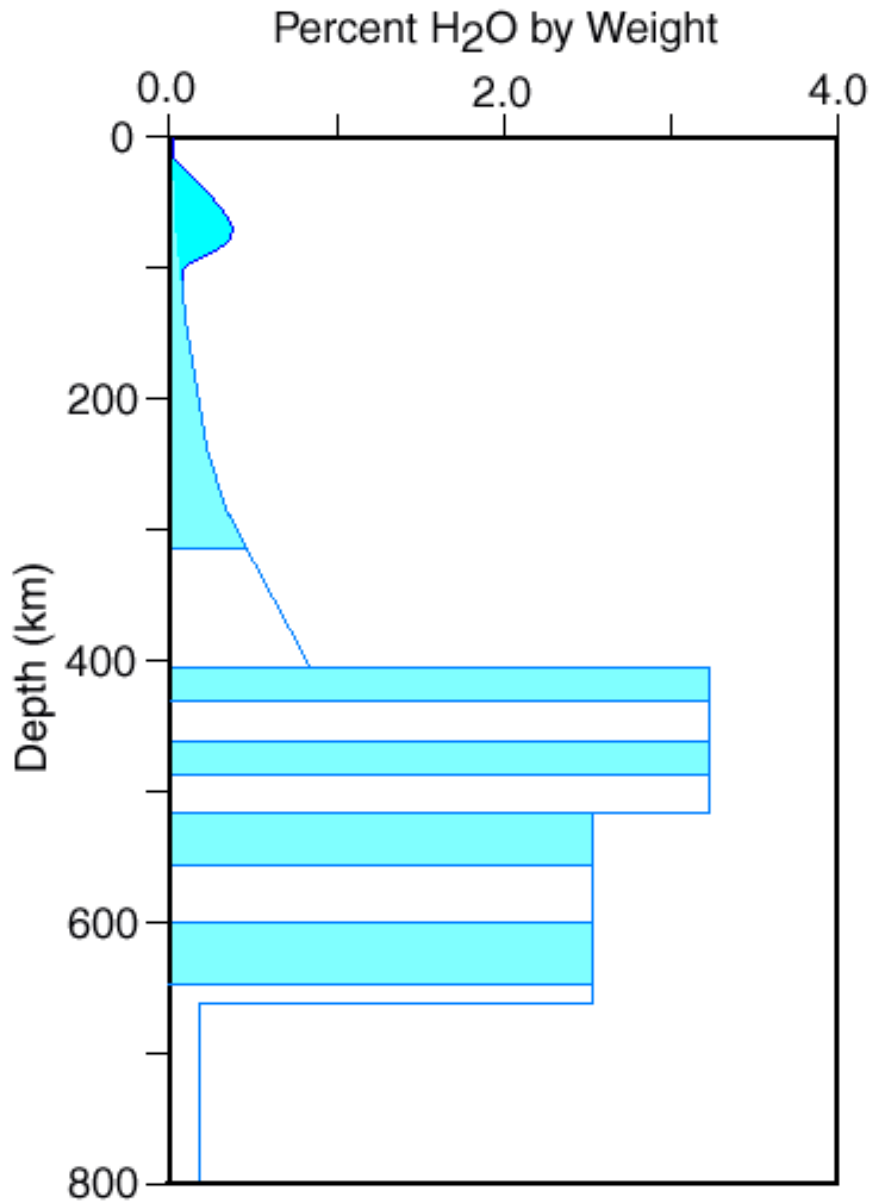
The depleted mantle appears to have a water content between 100 and 500 ppm, with the lower value preferred (Sobolev and Chaussidon, 1996) and consistent with measurements of mantle xenoliths (Bell and Rossman, 1992).

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



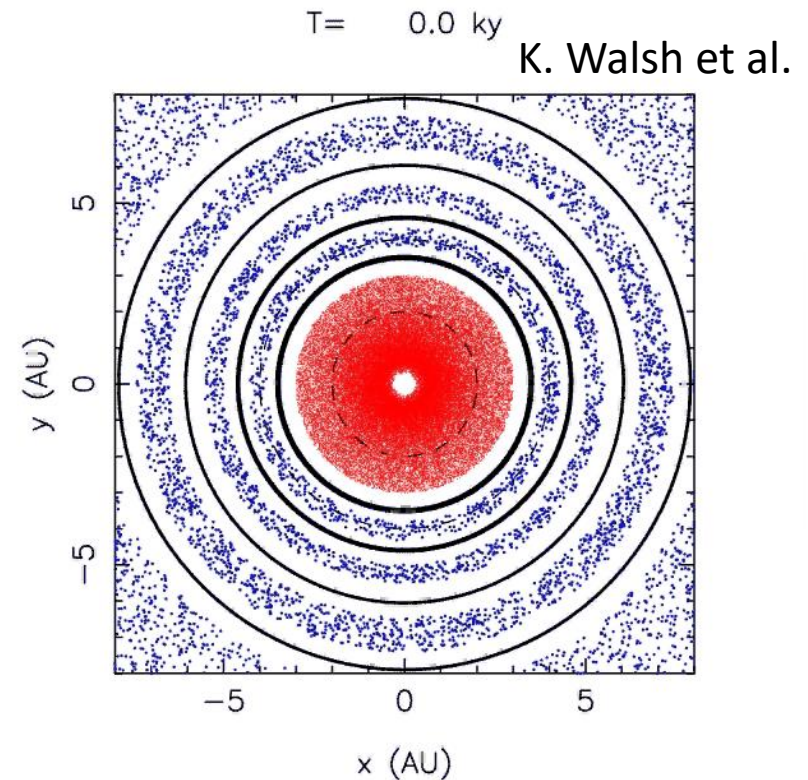
By these estimates, present-day water for the bulk Earth is at least 2.6×10^{24} g with D/H = 1.5×10^{-4}
Or about 4.4×10^{-4} Me

Water storage capacity (Ocean units)



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

Courtesy: J. Smyth



The “Grand Tack” hypothesis can explain this

Water delivery in Grand Tack

- Planets > 0.5 Earth mass accrete median value of $\sim 1\%$ Earth mass of C-type material (2-3% is not rare)
- Assuming 10% water by mass (consistent with carbonaceous chondrites), this gives $\sim 1 \times 10^{-3}$ Earth masses of water
 - Earth has (low estimate) $\sim 5-20 \times 10^{-4}$ Earth masses of water

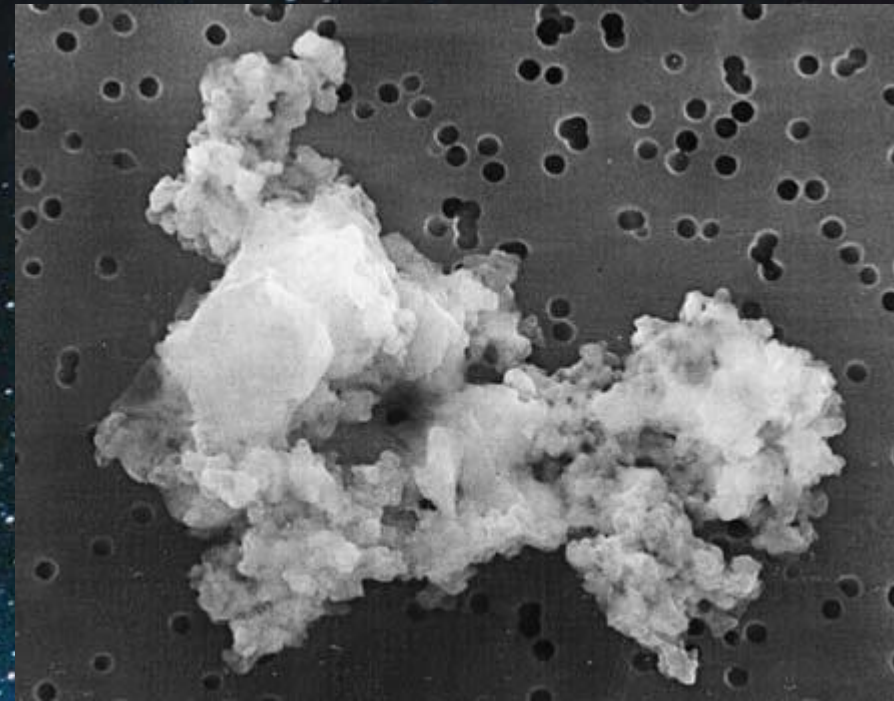
Additional water may be delivered through more massive embryos that were not included in the simulations

Murchison
(CM meteorite)



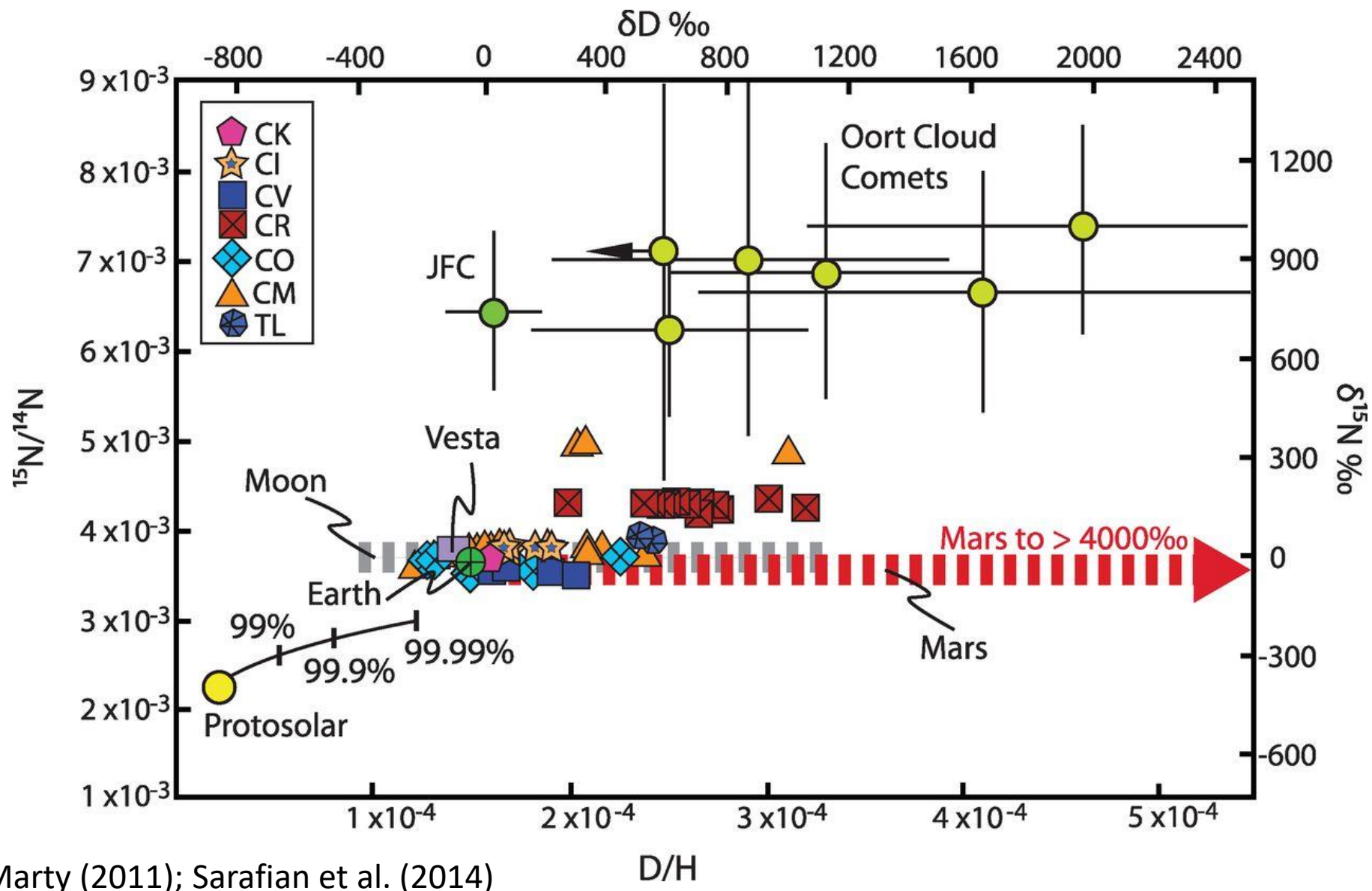
What about comets?

Comet 67P/Churyumov–Gerasimenko



Nov. 13, 2014 at 1:02 AM JST

Stable isotopes suggest that terrestrial planets' volatiles are mainly chondritic

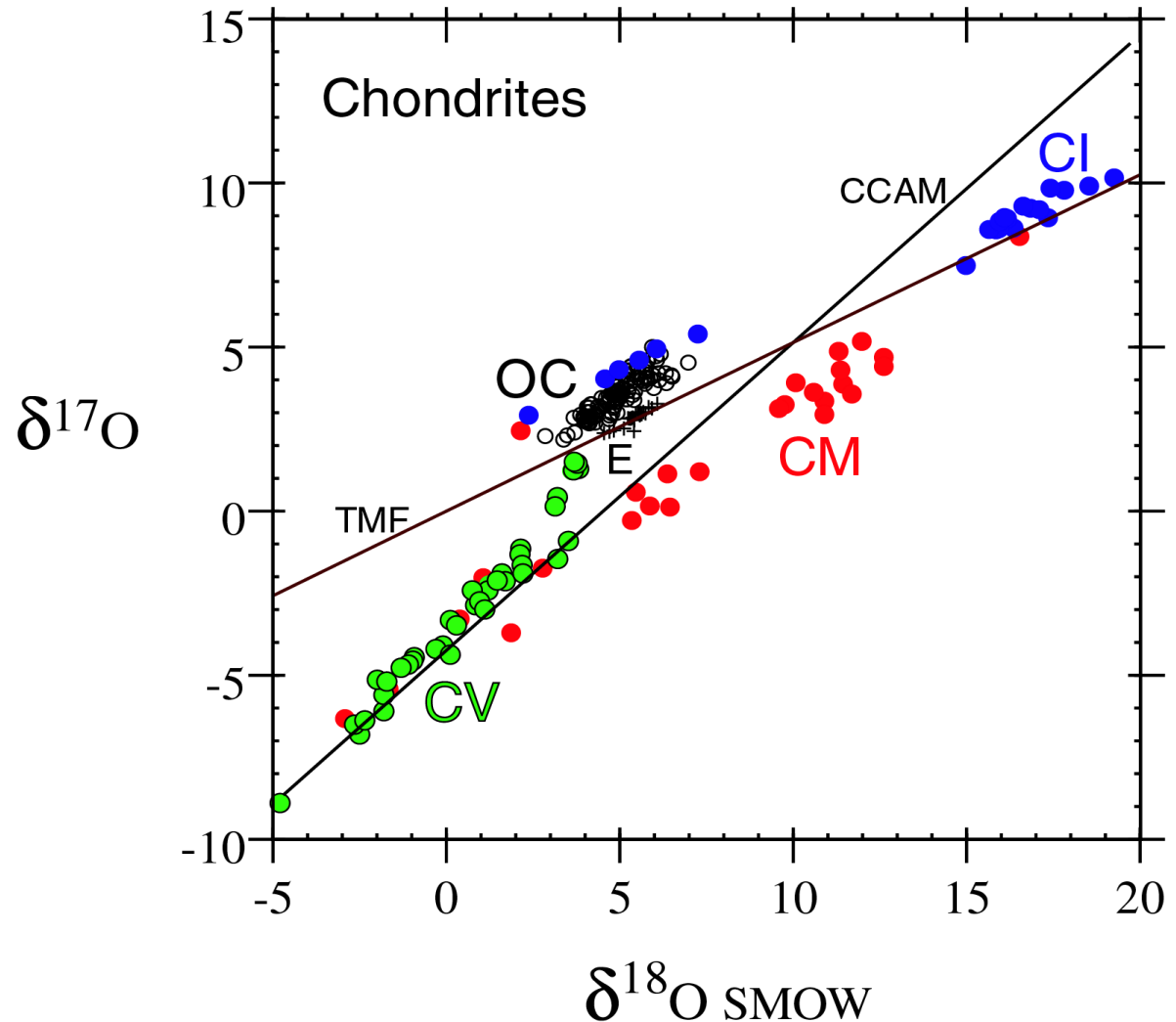


Timing of water/volatile accretion

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 Vener”) would have made the Earth and the Moon easily distinguishable in oxygen isotopes!



Copyright 2009
© 2009 The Authors
North Ridge



Water (and volatile elements) argue for an heterogeneous accretion of the Earth. This is well-accepted.

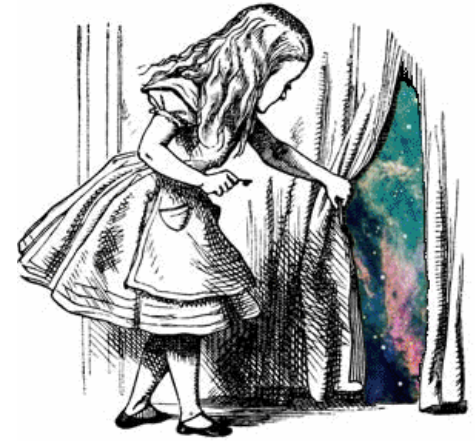
Volatiles were delivered towards the end of the Earth accretion, not by comets and as we will see, not in a Late Veneer fashion, and not in a late heavy bombardment.

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

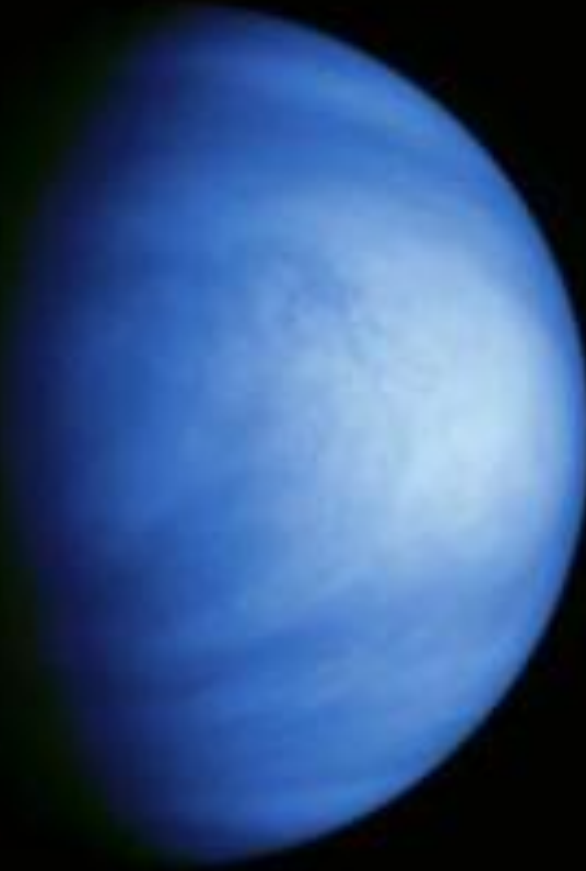
**WATER WAS MOSTLY DELIVERED AT
TIME OF PLANET FORMATION, NOT BY
COMETS AND NOT IN BOMBARDMENT**

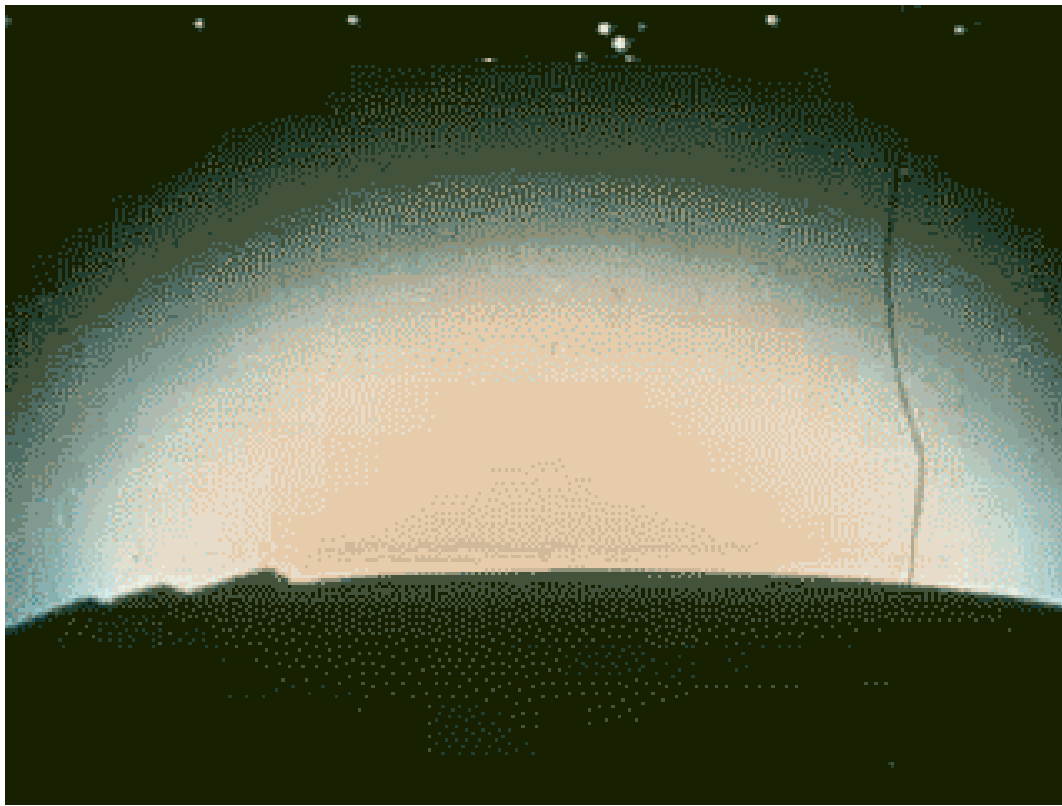
2. Nature of the crust



**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

$\tau_{1/2} = 37.8 \text{ Ga}$

Lu \rightarrow mantle, Hf \rightarrow crust

Principally in felsic rocks



MAFIC ROCKS = things like basalt

FELSIC ROCKS = things like granite

Lu/Hf zircon studies - concepts

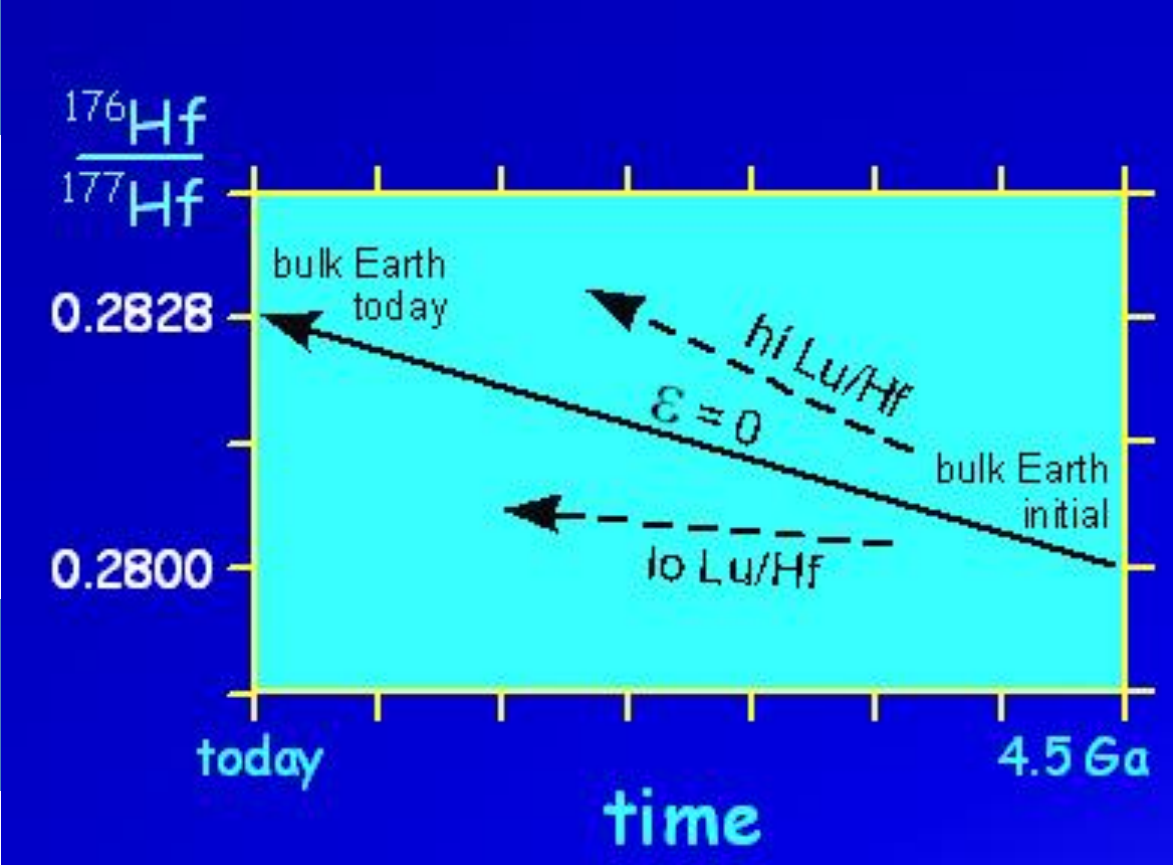


^{176}Lu decays to ^{176}Hf with $\tau_{1/2} = 37.8 \text{ Ga}$

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

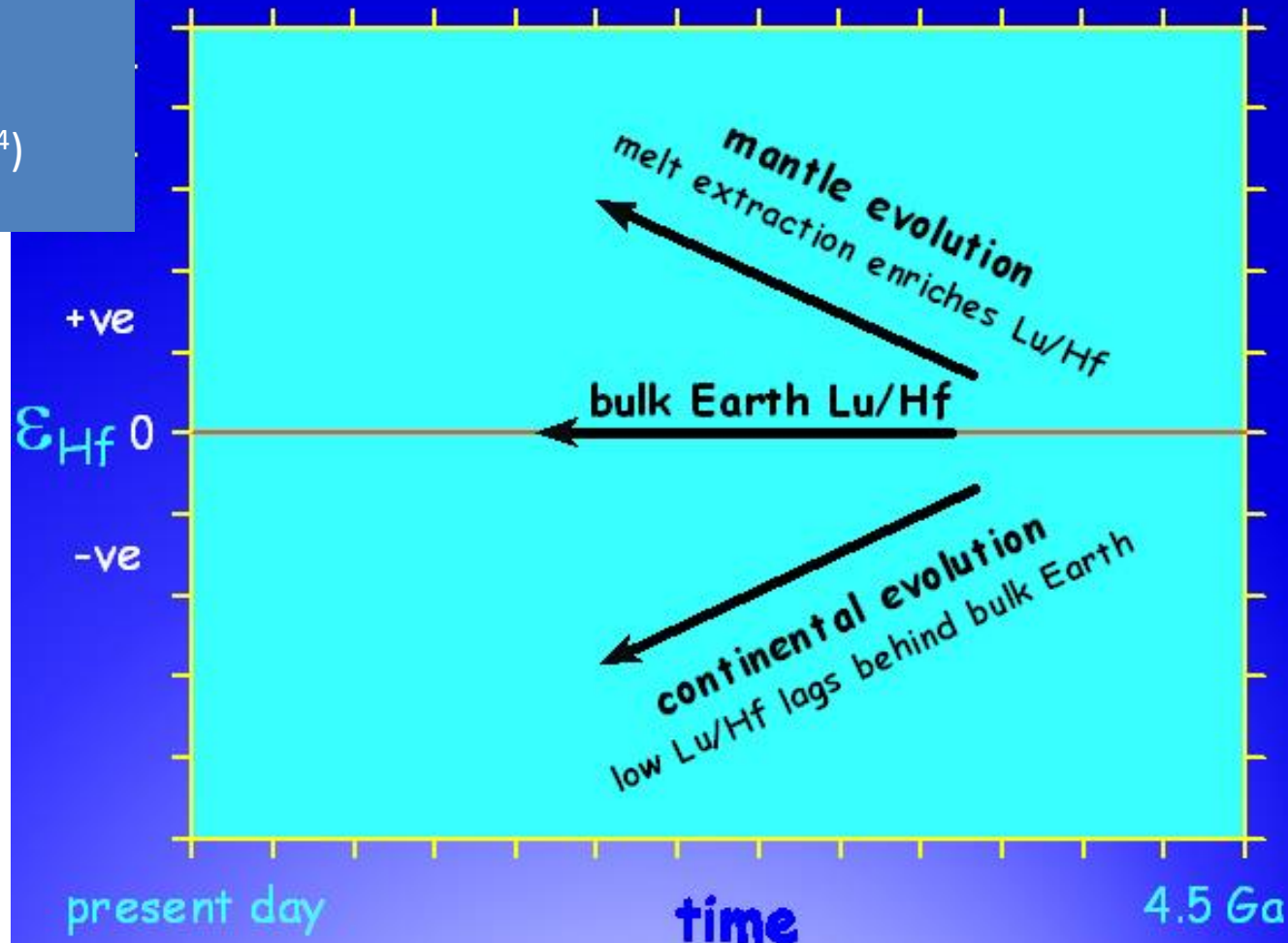
^{177}Hf is the stable reference isotope

Conventionally expressed relative to epsilon



Lu/Hf studies tell us about the origin and evolution of the crust

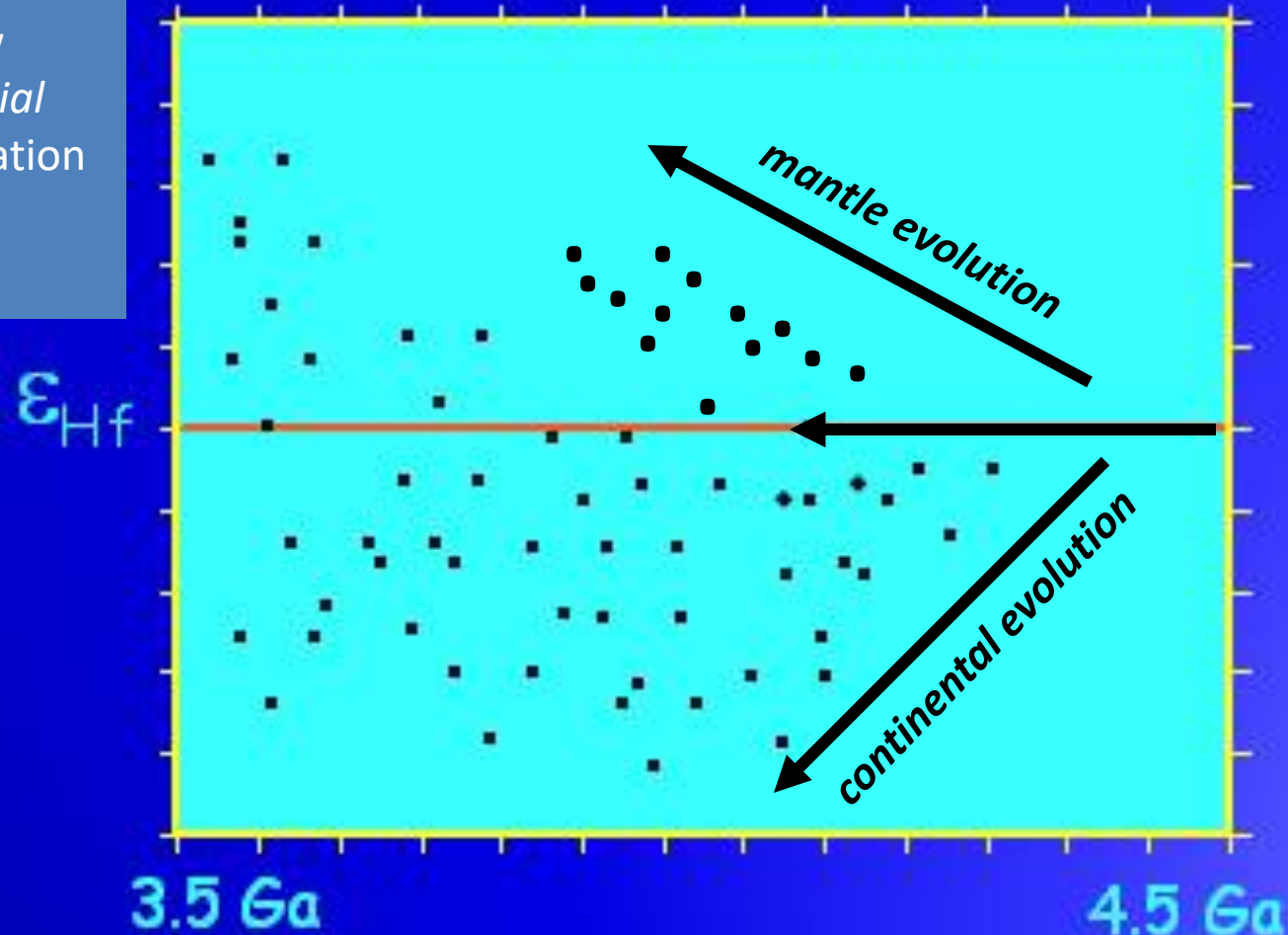
ϵ_{Hf} denotes deviations in $^{176}\text{Hf}/^{177}\text{Hf}$ from Bulk Earth (in parts per 10^4)





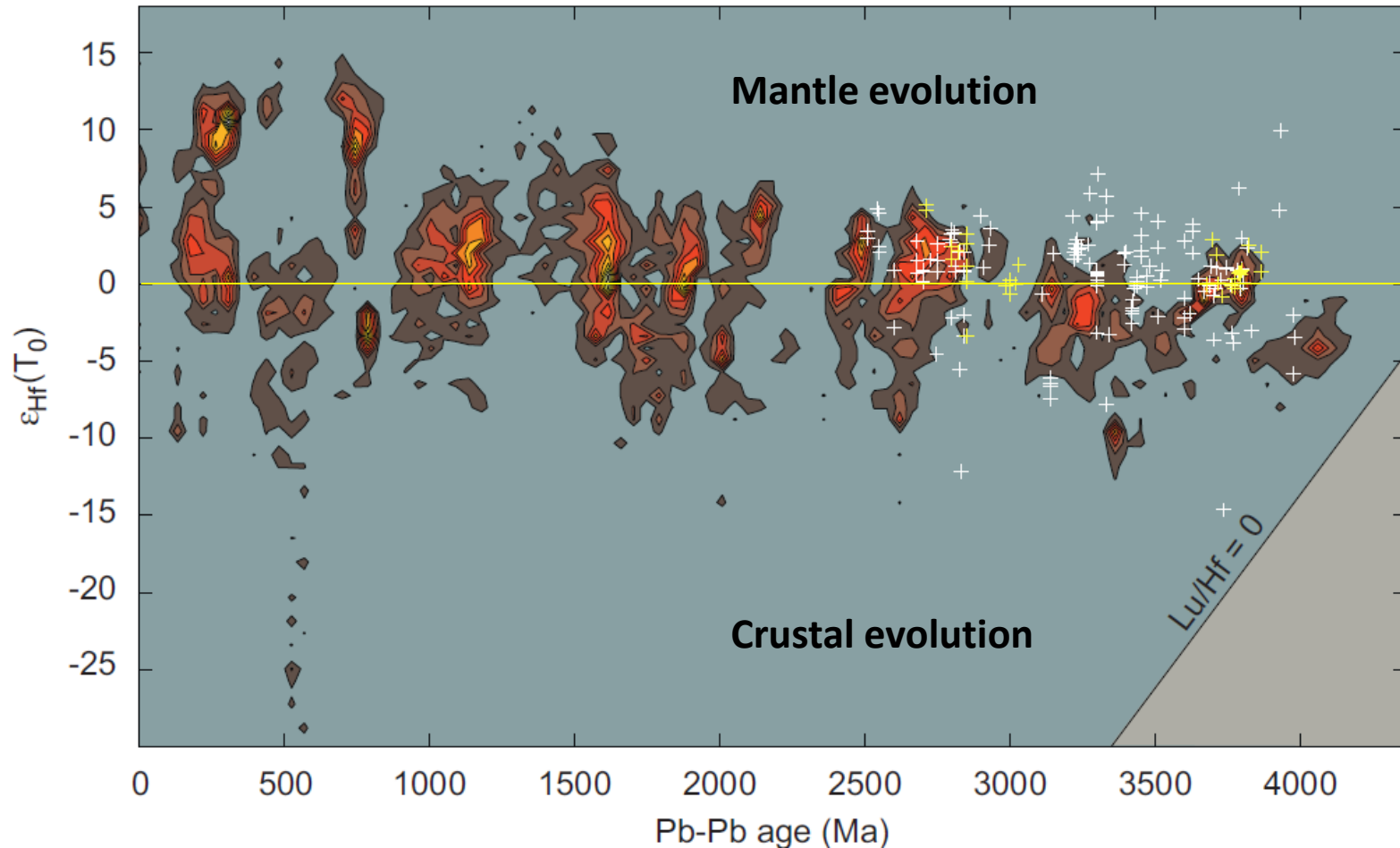
Lu/Hf studies lead us to...

Zircons have extremely low Lu/Hf, thus they record *initial* $^{176}\text{Hf}/^{177}\text{Hf}$ 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.



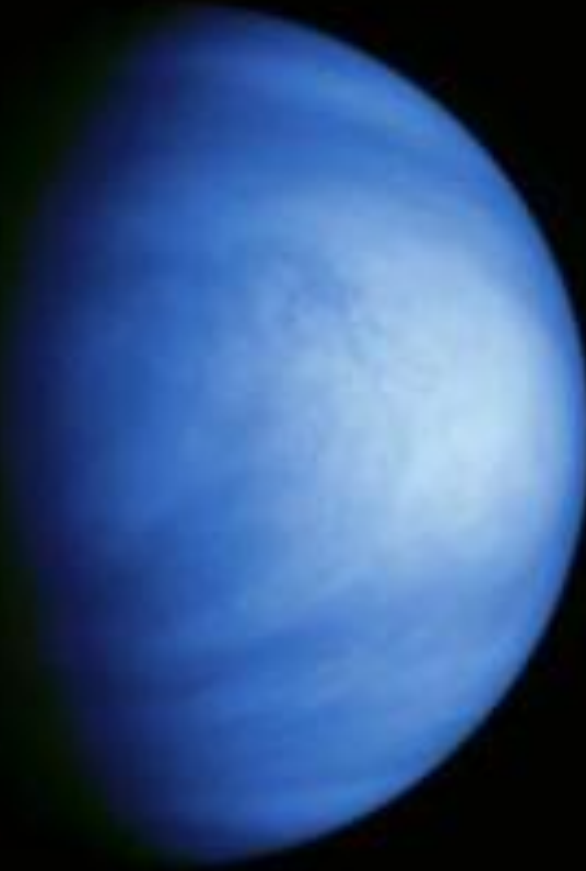
This result means that Earth's mafic (ocean crust) & felsic (continental crust) has grown in “pulses” since the earliest times, and probably is a reflection of **crust-hydrosphere** interactions since the beginning

Continental volume estimates

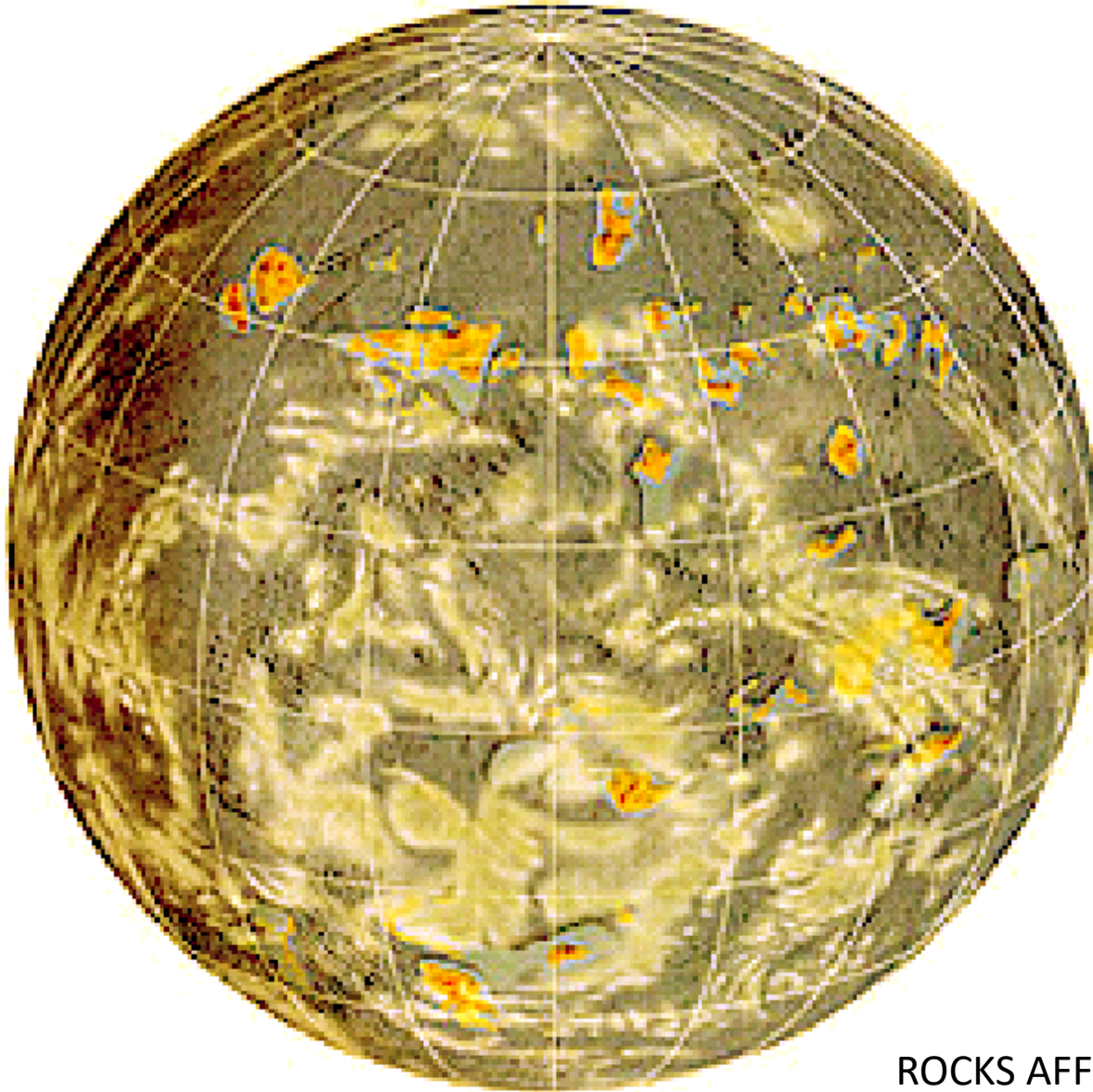


5% of present continental area \approx 0.9 Australia

Hadean Earth as a Water Planet?



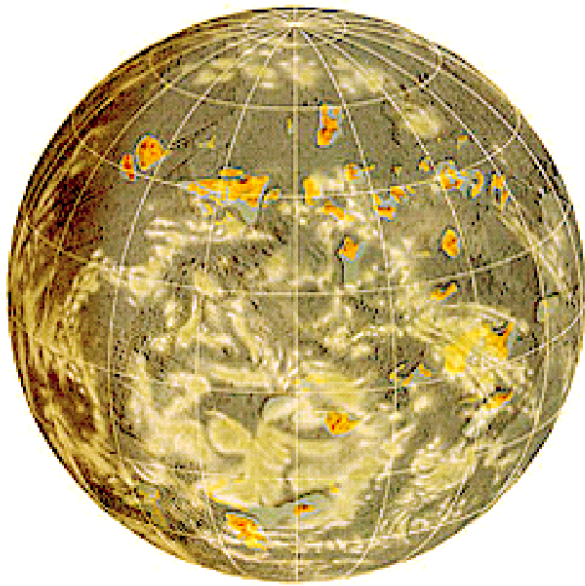
A conceptual model of the Hadean Earth



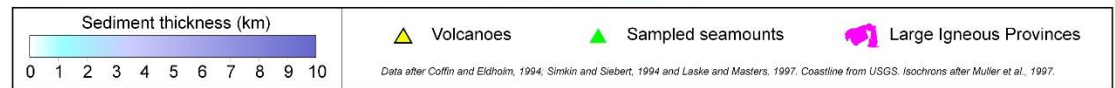
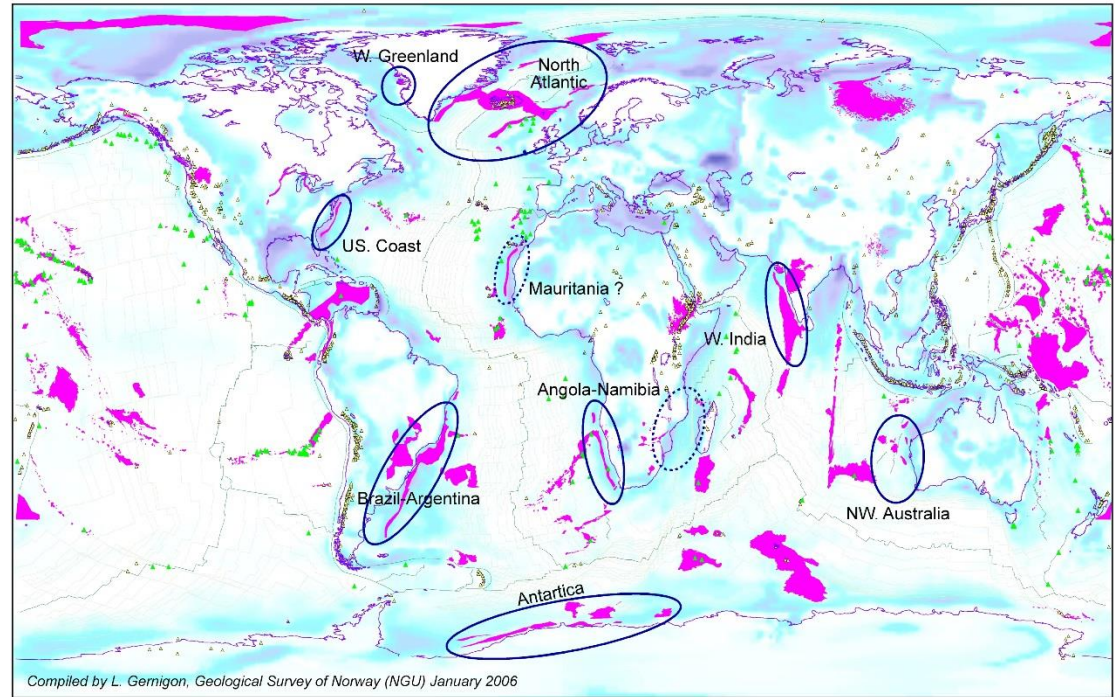
Abundant small proto-continental masses, akin to immature-to-mature island arcs at ocean-ocean subduction zones and plume-related edifices.

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

ROCKS AFFECTED BY WATER = Dry land

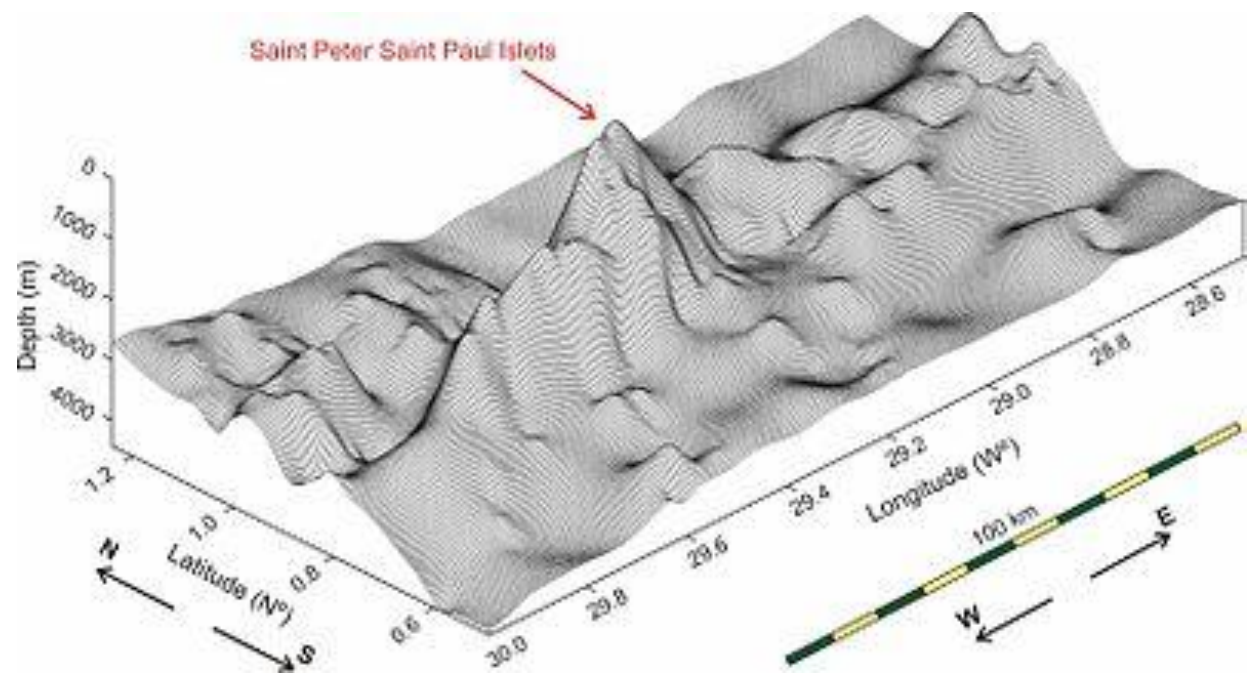


World sedimentary basins, Large Igneous Provinces and distribution of volcanic rifted margins



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!

