Geobiology Lecture 3

The story so far:

Our solar system formed from a disc of dust and gas about 4.6 billion years ago.

Some of the components, especially elements larger than iron incl. radionuclides, were formed in earlier massive star systems (Supernovae) that exploded and spewed debris into the interstellar medium.

Dense, less volatile materials (metals, silicate minerals) accumulated closer to the sun and accreted in violent collisions to form molten (rocky) planets. More volatile substances (eg ices) accumulated at the outer edges

The inner planets, and especially the Earth, cooled and differentiated early. We now recognise this in the separation of core, mantle and crust. Earth's oversized moon formed as a result of a late impact with a Mars-sized planet

Volatile materials not lost during the accretion process, combined with some material from comets and other impactors, to form an early hydrosphere and atmosphere

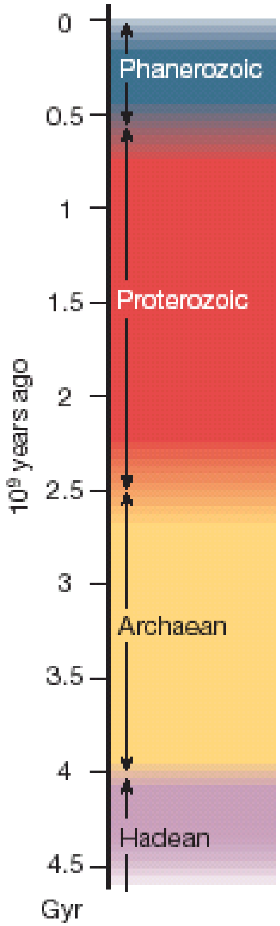
Earth cooled more slowly than other inner planets (eg Mars) and is tectonically active due to interior heat generation by radioactivity. This activity has contributed to retention of the atmosphere and hydrosphere.

Geobiology 2011 Lecture 3

Theories pertaining to the Origin of Life

John Valley: Elements Magazine Vol 2 #4
Early Earth

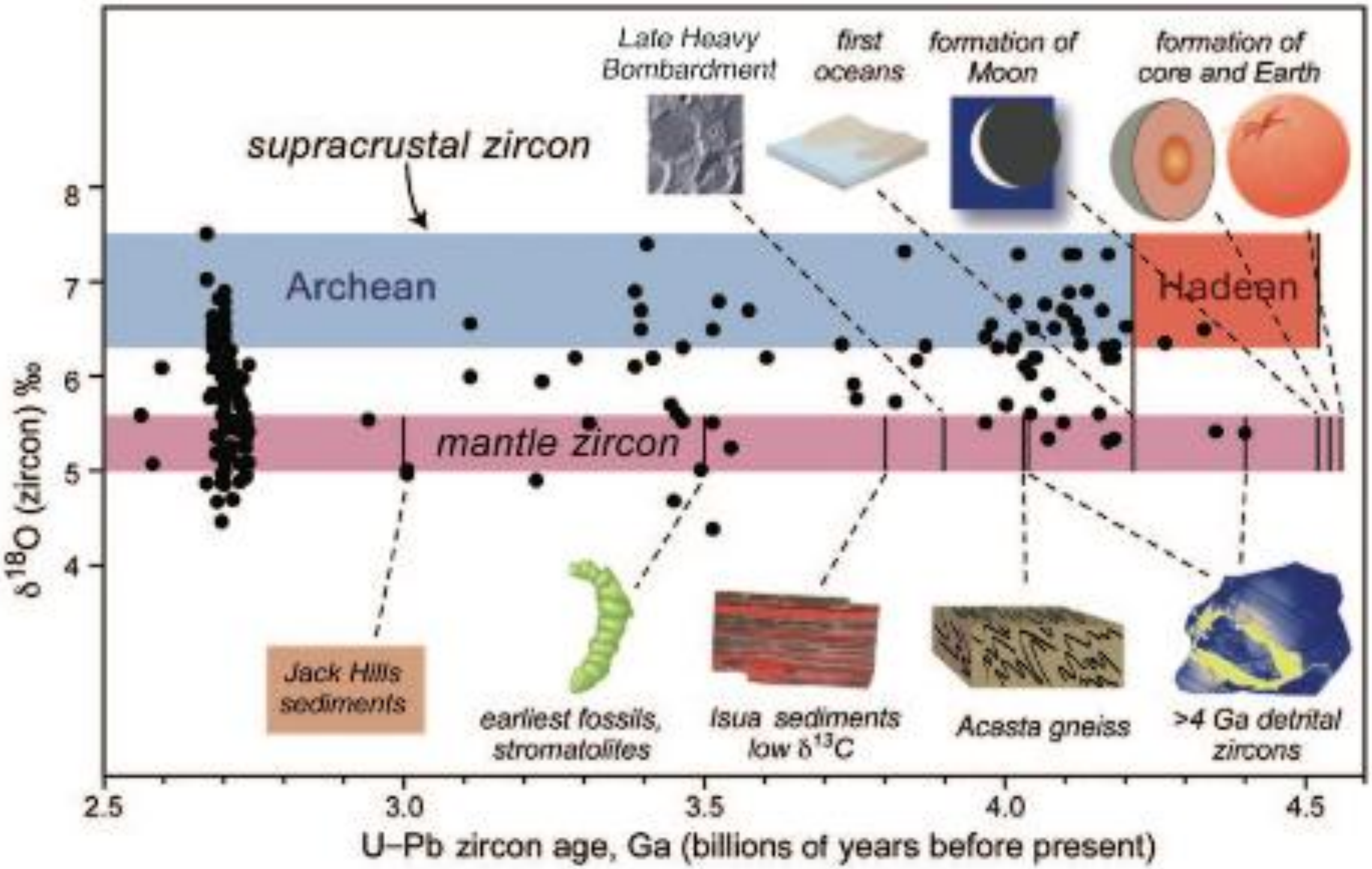
Life Magazine cover from December 8, 1952 removed due to copyright restrictions.



In discussing geological time, 1 Gyr is 10^9 years, 1 Myr is 10^6 years (the 'ago' is implicit and often omitted, such that Gyr and Myr refer to both time before present and duration). There are four aeons. The Hadean is taken here as the time from the formation of the Solar System and early accretion of the planet (4.6–4.5 Gyr), to the origin of life (probably sometime around 4.0 ± 0.2 Gyr). The Archaean, or time of the beginning of life, is from about 4–2.5 Gyr; the Proterozoic from 2.5 Gyr to about 0.56 Gyr; and the Phanerozoic since then.

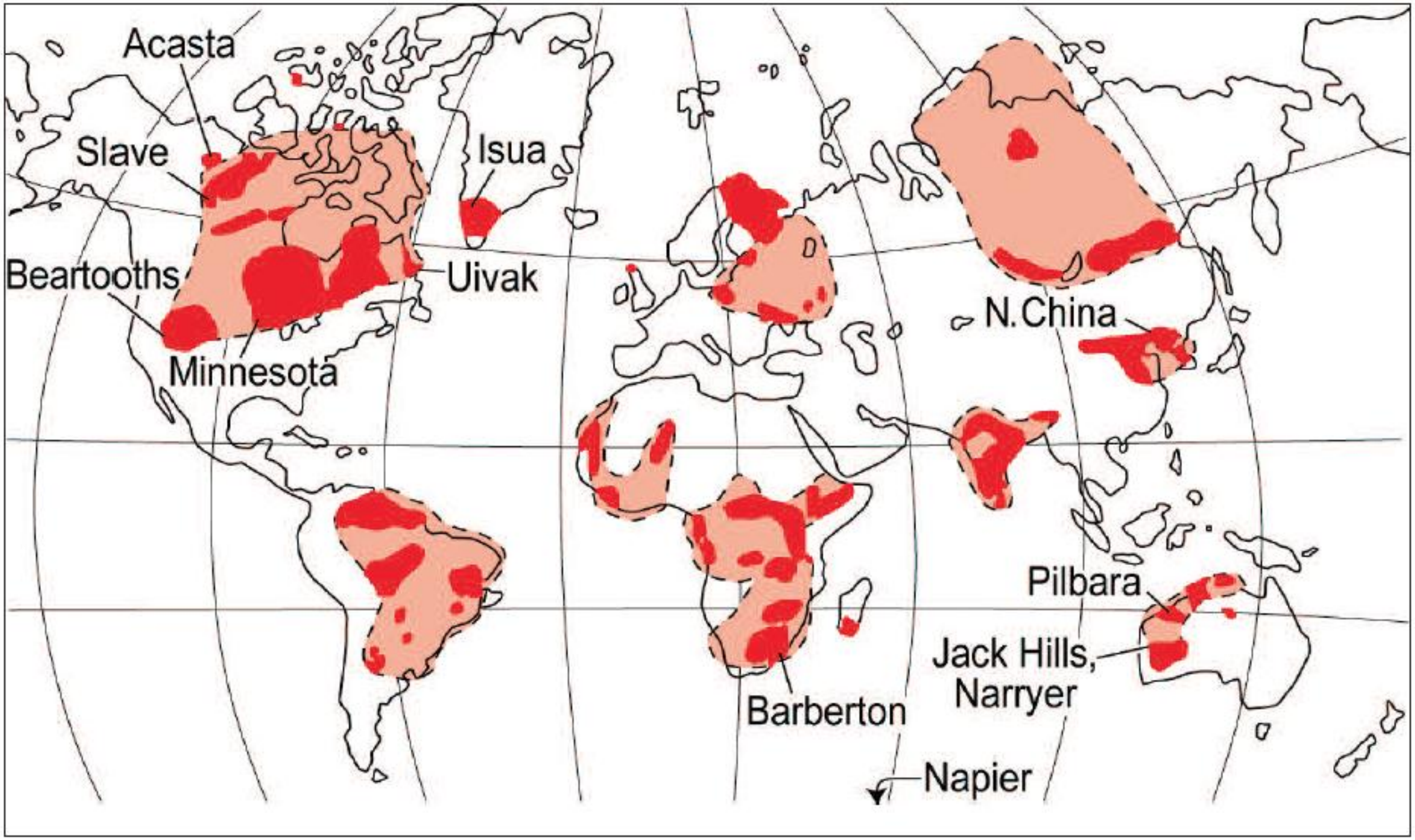
Valley, John W. "Early Earth." *Elements* 2, no. 4 (2006): 201-204.

Timescales 1: The Hadean



Timeline for the first billion years of Earth history. Key events are shown along with oxygen isotope ratios (**$\delta^{18}O$)** of zircons from igneous rocks and their U–Pb age. Primitive rocks in equilibrium with the Earth's mantle have average δ^{18}**O of 5.3‰ (Valley** et al. 2005). Higher "supracrustal" values (6.5 to 7.5) result from processes that require liquid water on the surface of the Earth. Thus, the end of the Hadean was at or before 4.2 Ga.

Valley, John W. "Early Earth." *Elements* 2, no. 4 (2006): 201-204.



Source: Valley, John W. "Early Earth." *Elements* 2, no. 4 (2006): 201-4.

Map showing known (dark orange) and suspected (light orange) areas of rocks older than 2.5 billion years. Areas with >3.6 Ga rocks or zircons are labeled by name.

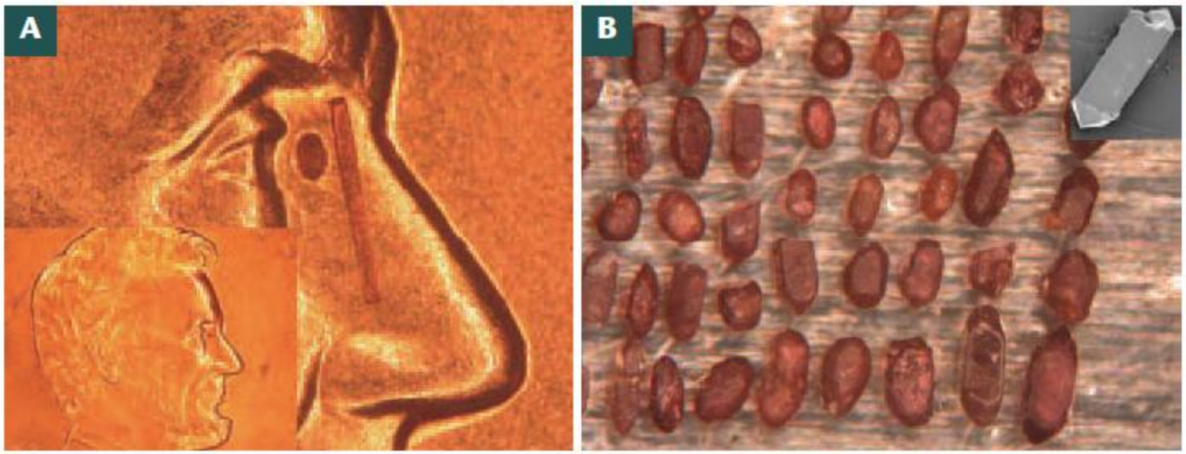


FIGURE 4 Tiny 100–300 μm detrital zircons from the Jack Hills, Western Australia. (**A**) A single zircon with a human hair for scale on Lincoln's nose from a US penny. (**B**) Zircons laid out for casting in epoxy, polishing, and analysis. Note the variable rounding due to abrasion during transport by wind and rivers. A younger, unrounded, volcanic zircon is shown in the upper right for comparison. (**C**) Cathodoluminescence images of polished zircons showing ages (Ma, >85% concordant) and oxygen isotope ratios ($\delta^{18}O$) obtained from ion microprobe analysis at various spots. Scale bar is 100 μm. FROM CAVOSIE ET AL. 2005

Source: Valley, John W. "Early Earth." *Elements* 2, no. 4 (2006): 201-4.

GLOSSARY

Archaea – A recently recognized domain of prokaryotic life. Single-celled organisms, similar in structure to bacteria, but different in metabolism and genotype. They include methanogens and hyperthermophiles that may be similar to the first life.

Archean – Precambrian Eon older than 2.5 Ga and younger than the Hadean

Banded iron formation (BIF) – Layered rock composed of centimeter-scale bands of quartz and iron oxide precipitated from ocean water. The earliest known BIFs formed at 3.8 Ga, whereas the largest BIFs formed between 2.5 and 1.8 Ga, at the same time as the rise of atmospheric oxygen.

Carbon isotopes – The ratios of the stable isotopes of carbon ($^{13}C/^{12}C$) are normalized to a marine carbonate standard and expressed as $\delta^{13}C$ in per mil (‰). Low $^{13}C/^{12}C$ results from metabolism and is commonly cited as evidence for biogenicity. Questions arise in ancient rocks regarding the source of carbon, its preservation, and abiogenic reactions.

Cathodoluminescence (CL) – Light emitted by minerals during electron bombardment. Commonly viewed with an electron microscope. CL imaging of zircons can detect growth zoning, inherited cores, and damaged domains.

Hadean – Geological time before the Archean Eon, ~4.5 to 4.2 Ga

Ga – Billions of years before the present

Giant Impact Theory – Widely accepted hypothesis that the Moon was formed when the Earth was struck by a Mars-size planet at ~4.5 Ga

Late Heavy Bombardment (LHB) – Event characterized by a sharp increase in the size and number of meteorites striking the Earth and other bodies in the inner solar system; proposed to have occurred at ~3.85 Ga

Lithophile – Refers to elements that concentrate in silicate minerals and melts and are more abundant in the Earth's crust than in its mantle and core

Ma – Millions of years before the present

Magma ocean – Worldwide ocean of molten rock, initially at the Earth's surface during accretion but later covered by newly formed crust; may have been hundreds of kilometers deep in the Hadean

Oxygen isotopes – The ratios of the most common stable isotopes of oxygen ($^{18}O/^{16}O$) are normalized to an ocean water standard and expressed as $\delta^{18}O$ in per mil (‰). Fractionations are generally mass dependent and used to determine the temperature of geological events. The ratios of $^{17}O/^{16}O$ are measured in rocks from extraterrestrial bodies and sometimes Earth to study mass-independent processes.

Planetesimals – Small kilometer-scale rock bodies orbiting the young Sun

Radioisotopes – Isotopes that undergo radioactive decay. The parent–daughter isotope ratio and half-life can be used to determine the age of a rock.

Siderophile – Refers to elements that concentrate in metal and are more abundant in the Earth's core than in its outer parts

SIMS, secondary-ion mass-spectrometer – Also called the ion microprobe, an analytical instrument capable of dating zircons and measuring isotope ratios from microscopic spots (typically 10–20 μm) in individual crystals using a highly focused ion beam

Stromatolite – Typically, a finely laminated sedimentary feature formed in shallow water by photosynthetic microbial communities

TIMS, thermal-ionization mass-spectrometer – An analytical instrument most often used for U–Pb geochronology of single zircons and larger samples. Since precision increases with sample size, ages may be more precise than those obtained with the ion microprobe; however, the ability to analyze zoned or heterogeneous zircons is lost.

Tonalite – Granitic plutonic rock with dominant quartz (>20%) and plagioclase [Plagioclase/(Alkali feldspar + Plagioclase) >90%]

Zircon – Common trace mineral ($ZrSiO_4$) that is highly resistant to mechanical and chemical alteration. It yields the most reliable estimates of the U–Pb age and oxygen isotope ratio for ancient rocks. In situ analysis by ion microprobe can resolve the ages of inherited cores and younger overgrowths.

Source: Valley, John W. "Early Earth." *Elements* 2, no. 4 (2006): 201-4.

http://fallmeeting.agu.org

Abstract #U51A-10 The Hadean Atmosphere Zahnle, K

It is more useful to define the Hadean Eon as the time when impacts ruled the Earth than to define it as the time before the rock record. For decades now it has been obvious that the coincidence between the timing of the end of the lunar late bombardment and the appearance of a rock record on Earth is probably not just a coincidence. I doubt I am pointing out something that the reader hasn't long ago given thought to. While the Moon was struck by tens of basin-forming impactors (100 km objects making 1000 km craters), the Earth was struck by hundreds of similar objects, and by tens of objects much larger still. The largest would have been big enough to evaporate the oceans, and the ejecta massive enough to envelope the Earth in 100 m of rock rain. Smaller impacts were also more frequent. On average, a Chicxulub fell every 10^5 years. When one imagines the Hadean one imagines it with craters and volcanos: crater oceans and crater lakes, a scene of mountain rings and island arcs and red lava falling into a steaming sea under an ash-laden sky.

Zahnle, K. "The Hadean Atmosphere." In *AGU Fall Meeting Abstracts*, vol. 1, p. 10. 2001.

http://www.agu.org/cgi-bin/SFgate

U51A-10 The Hadean Atmosphere Zahnle, K

I don't know about the volcanos, but the picture of abundant impact craters makes good sense --the big ones, at least, which feature several kilometers of relief, are not likely to have eroded away on timescales of less than ten million years, and so there were always several of these to be seen at any time in various states of decay. The oceans would have been filled with typically hundreds of meters of weathered ejecta, most of which was ultimately subducted but taking with them whatever they reacted with at the time --CO_2 was especially vulnerable to this sort of scouring. The climate, under a faint sun and with little CO_2 to warm it, may have been in the median extremely cold, barring the intervention of biogenic greenhouse gases (such as methane), with on occasion the cold broken by brief (10s to 1000s of years) episodes of extreme heat and steam following the larger impacts. In sum, the age of impacts seems sufficiently unlike the more familiar Archaean that came after that it seems useful to give this time its own name, a name we already have, and that, if applied to the Hadean that I have described, actually has some geological value.

http://www.agu.org/cgi-bin/SFgate

U51A-01 Habitability of Terrestrial Planets in the Early Solar System SLEEP, N H

The Protoearth, Mars, Venus, and the Moon-forming impactor were potentially habitable in the early solar system. The interiors of larger asteroids **had habitable circulating water**. To see when the inner solar system became continuously habitable, one needs to consider the most dangerous events and the safest refugia from them. Early geochemical and accretionary processes set the subsequent silicate planet reservoirs and hence hydrospheric and atmospheric masses. **The moon-forming impact made the Moon and the Earth sterile** bodies. Following the impact, the Earth passed through a rock-vapor atmosphere on the scale of 1000s of years and an internally heated steam greenhouse on the scale of 2 m.y. Minerals bearing the principle volatiles (water, Cl, and CO2) were stable at the Earth's surface by the time it cooled to 800K. The mass of reactable shallow material was insufficient to contain the available water and CO_2.

Habitable conditions were established after CO_2 could be deeply subducted into the mantle. Vast quantities of H_2 were vented during accretion and after the moon-forming impact and eventually lost to space.

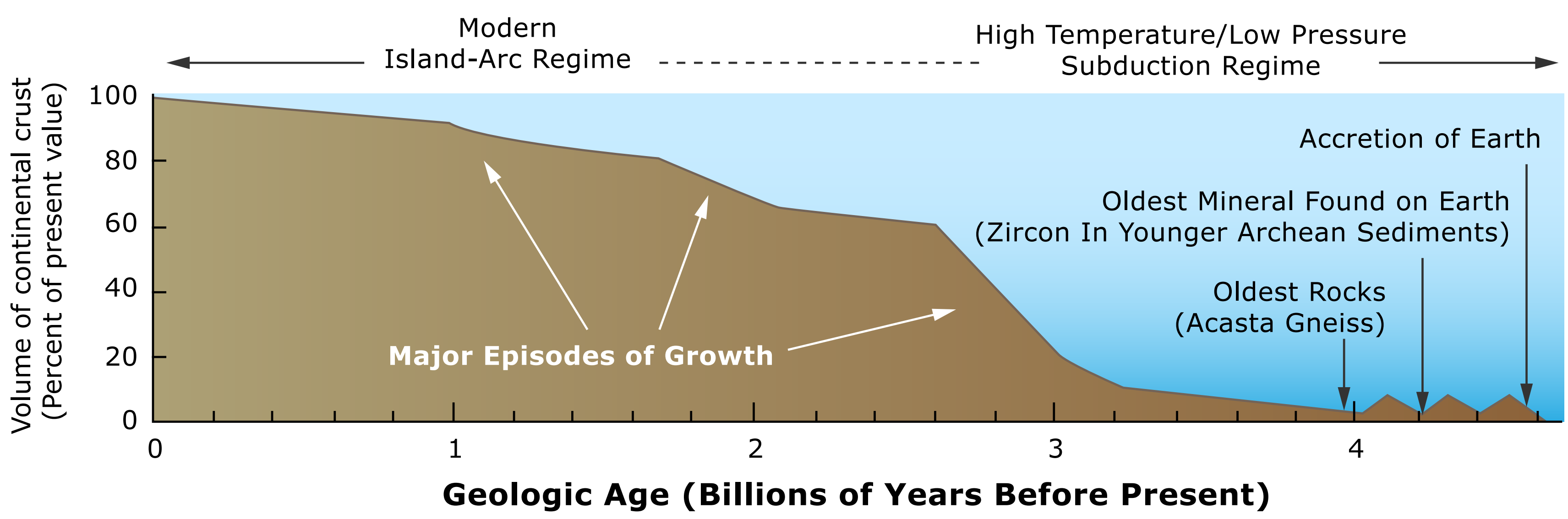
SLEEP, NH. "Habitability of Terrestrial Planets in the Early Solar System." In *AGU Fall Meeting Abstracts*, vol. 1, p. 01. 2001.

U51A-01 Habitability of Terrestrial Planets in the Early Solar System SLEEP, N H

It is unknown whether significant amounts of this gas were present when the Earth's surface cooled into the habitable range. **The moon remained sterile because its interior is essentially devoid of water**. The mantle of the Earth, in contrast, cannot hold the available water, leaving the excess to form oceans. Nitrogen may behave similarly with the excess going into the air. Impacts of large asteroids (and comets) were an ever-present danger on otherwise habitable planets. **The safest niche on planets was a kilometer or deeper crustal rocks habitable by thermophiles**. It is inevitable that several objects, which would have left only thermophile survivors, struck the Earth. Such events were so infrequent that the conditions of such a bottleneck should not be confused with conditions for the origin of life. An **alternative refugium involves ejection of life within rock fragments** and return of such fragments to the surface of the home planet or transfer to another habitable planet. **Mars and the larger asteroids were habitable first** and provide likely sources of seed and also testable places to look for preserved evidence. **Extant terrestrial life appears to have passed through thermophile bottlenecks**. There are subtle hints of space transfer. The need of extant life for Ni may be vestige of life on a young planet covered with ultramafic rocks.

Origin and Early Evolution of Life

- The lost record of the origin of Life? Few crustal rocks from >3 Ga and half life of sediments 100-200Ma so most destroyed



Crustal Growth has proceeded in episodic fashion for billions of years. An important growth spurt lasted from about 3.0 to 2.5 billion years ago, the transition between the Archean and Proterozoic eons. Widespread melting at this time formed the granite bodies that now constitute much of the upper layer of the continental crust.

Image by MIT OpenCourseWare. After Taylor, S. Ross, and Scott M. McLennan. "The Evolution of Continental Crust." *Scientific American* 274 (1996): 76-81.

Extreme Panspermia?

An email once received

- **Dr. Roger Summons**
  Committee on The Origins and Evolution of Life
  National Academy of Sciences

  Dear Dr. Summons:

  Individual solar systems safeguarded from supernova by vigilant intelligent life, and those (in the absence of intelligent life) destined for supernova, are interrelated in the infinite continuum of life: the former an achievement of compassionate reciprocity, the latter vital to life processes through eventual production of chemical elements essential to life.

  Particularly persuasive in the search for extraterrestrial intelligence (SETI), planets secured again! st supernova are a signature of intelligent life - as beneficiaries of steady-state energy supplied by host stars.

  Compassionate reciprocity - setting the standard for life-centered cosmologies - complements the strong version of panspermia (Cosmic Ancestry).
  www.geocities.com/CosmicGenealogy/

Two Points of View

- *"Astrobiology has emerged as a new science for the new millennium. It seeks to understand life in the context of the wider cosmos. The new Centre will continue in the pioneering traditions of astrobiology started in Cardiff over 25 years ago, taking note of the many relevant discoveries that have been made in recent years. The Centre aims to combine the expertise of astronomers, biochemists and microbiologists to generate cutting edge science that would eventually enable us to answer the age-old question: where did we come from?"* **(Professor Chandra Wickramasinghe, director, Cardiff Centre for Astrobiology, and author of *A Journey With Fred Hoyle - The Search for Cosmic Life*, World Scientific, 2005).**

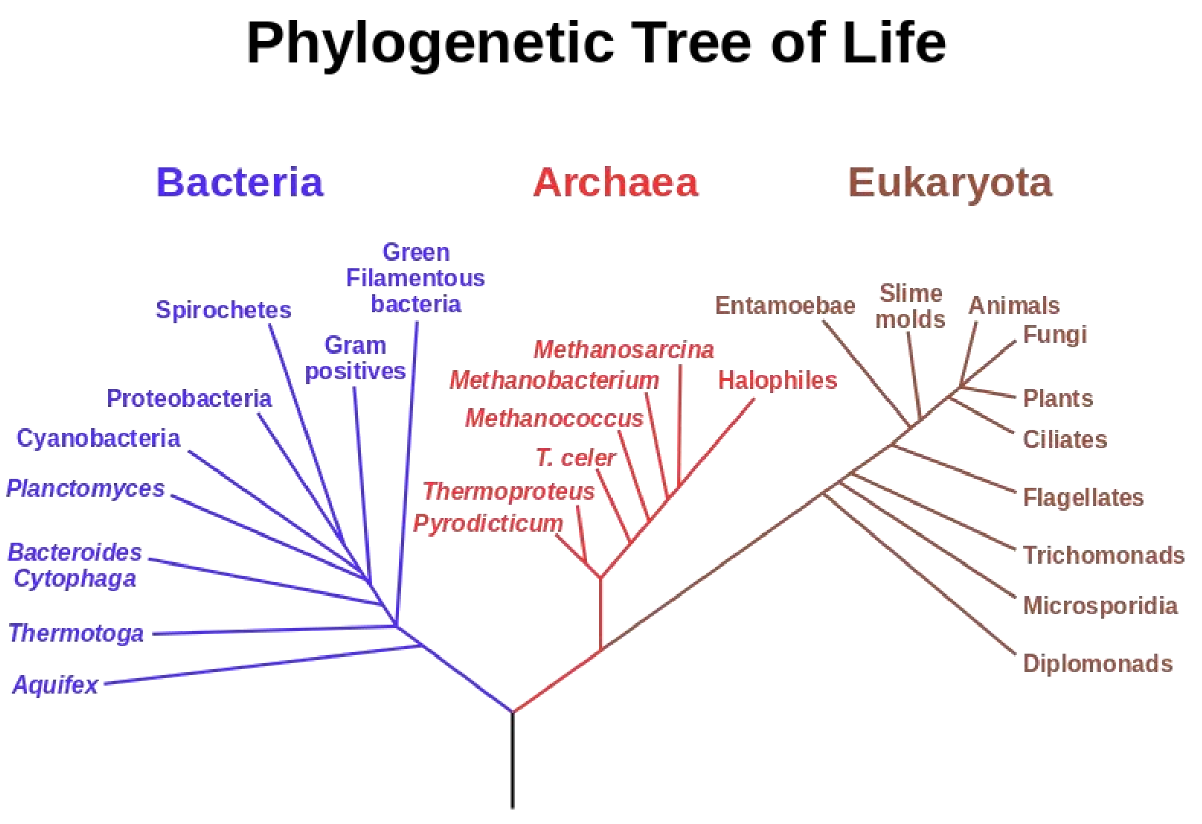
- *"We can soon launch panspermia missions to seed other habitable solar systems. We can target nearby stars and star-forming zones in interstellar clouds. Each mission can seed dozens of new solar systems where local life has not formed."* **(Dr. Michael N. Mautner, Society for Life in Space (SOLIS).**

Theories of the origin of life

"We still have little idea how, when or where life began…. The evidence is circumstantial and can be compared with delving into such records as there are in Massachusetts of the Mayflower, to discern the origins of the English language."

Nisbet, E. G., and N. H. Sleep. "The habitat and nature of early life." *Nature* 409, no. 6823 (2001): 1083-1091.

All known life on Earth descended from a common ancestor



DNA, proteins, rRNA, phylogeny & metabolism all consistent with a universal common ancestor or LUCA

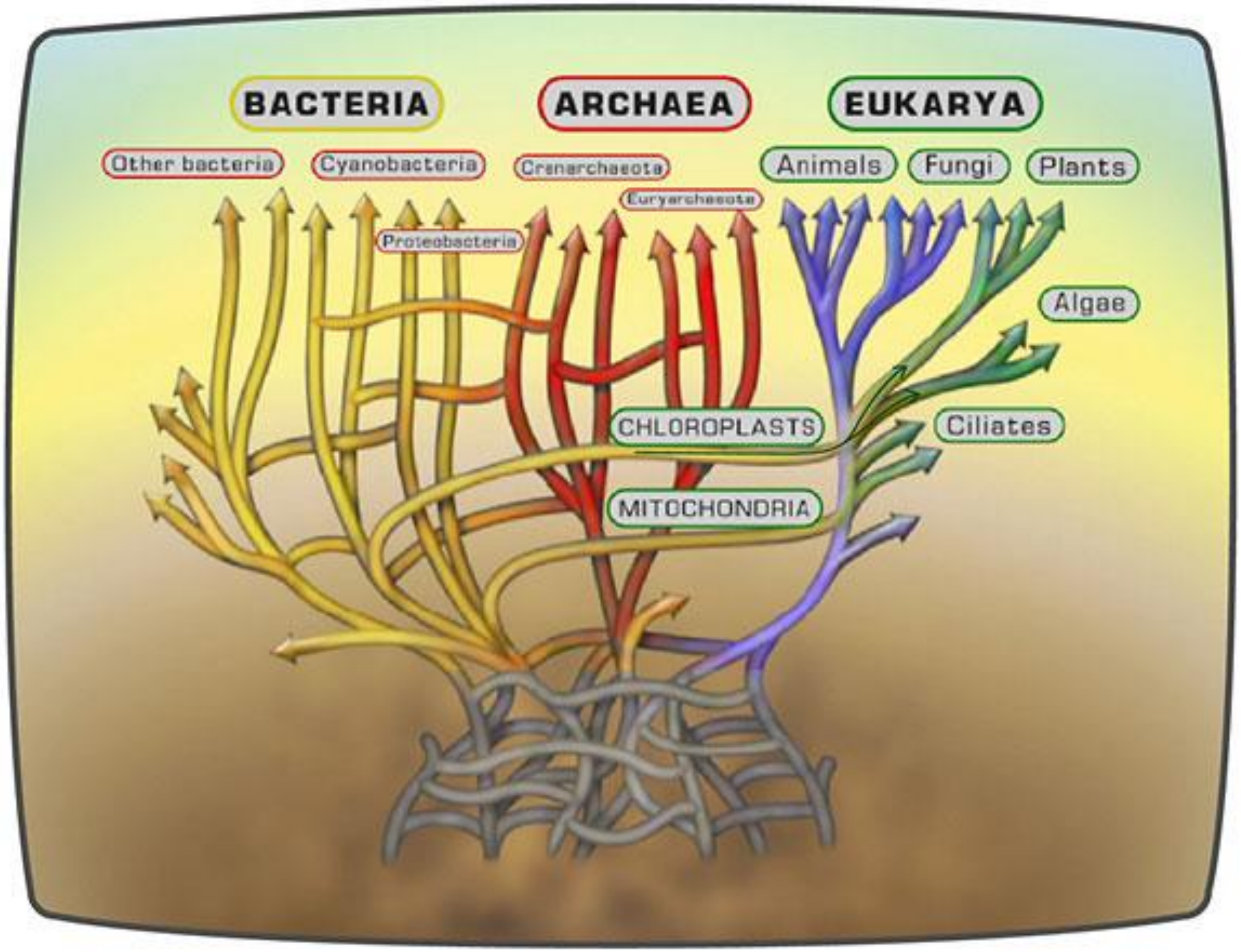
A hyperthermophilic Origin?

The rRNA phylogenetic tree has hyperthermophilic organisms clustered near the base of the Archaeal and Bacterial domains

Figure courtesy NASA Astrobiology Institute.

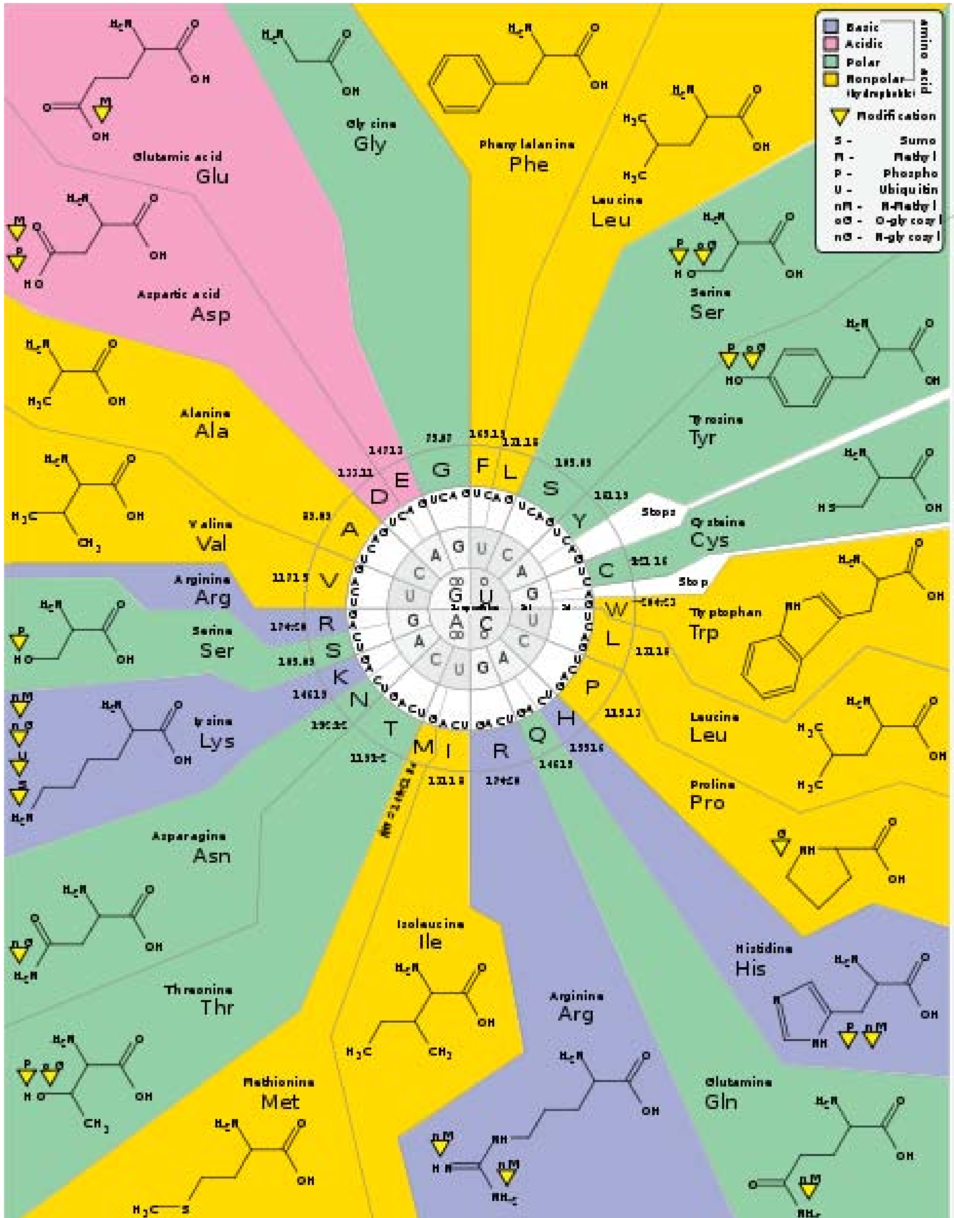
THE SHRUB OF LIFE

Doolittle, W. Ford. "Uprooting the tree of life." *Scientific American* 282, no. 2 (2000): 90.



Proposed by W. Ford Doolittle, this view of early evolution suggests multiple primitive cells as ancestors to the three domains, and illustrates lateral gene transfer among early organisms.

All known life on Earth descended from a common ancestor



Seond letter

First letter	U	C	A	G	Third letter
U	UUU Phe UUC Phe UUA Leu UUG Leu	UCU Ser UCC Ser UCA Ser UCG Ser	UAU Tyr UAC Tyr UAA Stop UAG Stop	UGU Cys UGC Cys UGA Stop UGG Trp	U C A G
C	CUU Leu CUC Leu CUA Leu CUG Leu	CCU Pro CCC Pro CCA Pro CCG Pro	CAU His CAC His CAA Gln CAG Gln	CGU Arg CGC Arg CGA Arg CGG Arg	U C A G
A	AUU Ile AUC Ile AUA Ile AUG Met	ACU Thr ACC Thr ACA Thr ACG Thr	AAU Asn AAC Asn AAA Lys AAG Lys	AGU Ser AGC Ser AGA Arg AGG Arg	U C A G
G	GUU Val GUC Val GUA Val GUG Val	GCU Ala GCC Ala GCA Ala GCG Ala	GAU Asp GAC Asp GAA Glu GAG Glu	GGU Gly GGC Gly GGA Gly GGG Gly	U C A G

Figures courtesy Arapacana and NIH.

Origin-of-Life: Evolving concepts #1

•>2,000 yrs ago: *The Bible* states God created humans & higher organisms.
•< mid 1800's: Creationism + insects, frogs & other small creatures arise spontaneously from mud & rot.
•mid 1800's: (1) **Pasteur** demonstrated bacteria & other microorganisms arise from parents resembling themselves. Spontaneous generation is dead. (2) **Darwin** proposes natural selection, the theory that environmental pressure results in the perpetuation of certain adaptations. Evolution of complex organisms therefore possible, & all current life forms could have evolved from a single (last) common ancestor.
•Darwin (privately) suggested life could have arisen from chemistry: "in some warm little pond, with all sorts of ammonia and phosphoric salts, light, heat, electricity, etc., present."

Adapted from Orgel, Leslie E. "The origin of life on the earth." *Scientific American* 271, no. 4 (1994): 77-83.

Origin-of-Life: Evolving concepts #2

•<u>1953</u>: Miller-Urey experiment (U. chicago) demonstrates that amino acids could be formed with atmospheric gases + lightning.
•<u>Late 1960s</u>: Woese (U. Illinois), Crick (England), Orgel (Salk Inst, San Diego) concurrently proposed RNA may have preceded proteins & catalyzed all reactions for survival & replication of 'last common ancestor'. The 'RNA World' hypothesis born.
•<u>1977</u>: Hydrothermal vents on the seafloor discovered teaming with diverse life. Evidence for the possibility life may not have evolved at the surface.
•<u>1983</u>: Thomas Cech (U. Colorado) & Sidney Altman (Yale) independently discovered *ribozymes*, enzymes made of RNA. Heritability & reproducibility possible with a single molecule.

Origin-of-Life: Evolving concepts #3

- 1988: Günter Wächtershäuser (German patent lawyer!) theorizes that Fe & Ni sulfide *minerals* at hydrothermal vent systems provided the template & catalyst for formation of biological molecules.
- 1996: Everett Shock hypothesizes that chemical disequilibria existing where seawater reacts with hot rocks are conducive to organic synthesis from CO_2 or H_2CO_3.
- 1997: Jay Brandes (Carnegie Inst.) demonstrates that N_2 is converted to NH_3 in the presence of H_2 & magnetite (Fe_3O_4), at T & P typical of hydrothermal vents. Mineral surfaces & HT vent environments can produce biologically-useful form of N.
- 2000: George Cody et al. demonstrate synthesis of pyruvate using mineral catalysis under hydrothermal conditions. Pyruvate is branch point for many extant biosynthetic pathways.
- 2003: McCollom demonstrates organosynthesis from $FeCO_3$ at 300° C

What is Life?

Passage removed due to copyright restrictions.
See the insert titled “What Is Life?” in this article:

Sagan, Carl. “The Search for Extraterrestrial Life."
Scientific American 271, no. 4 (1994): 92-99.

What is Life?

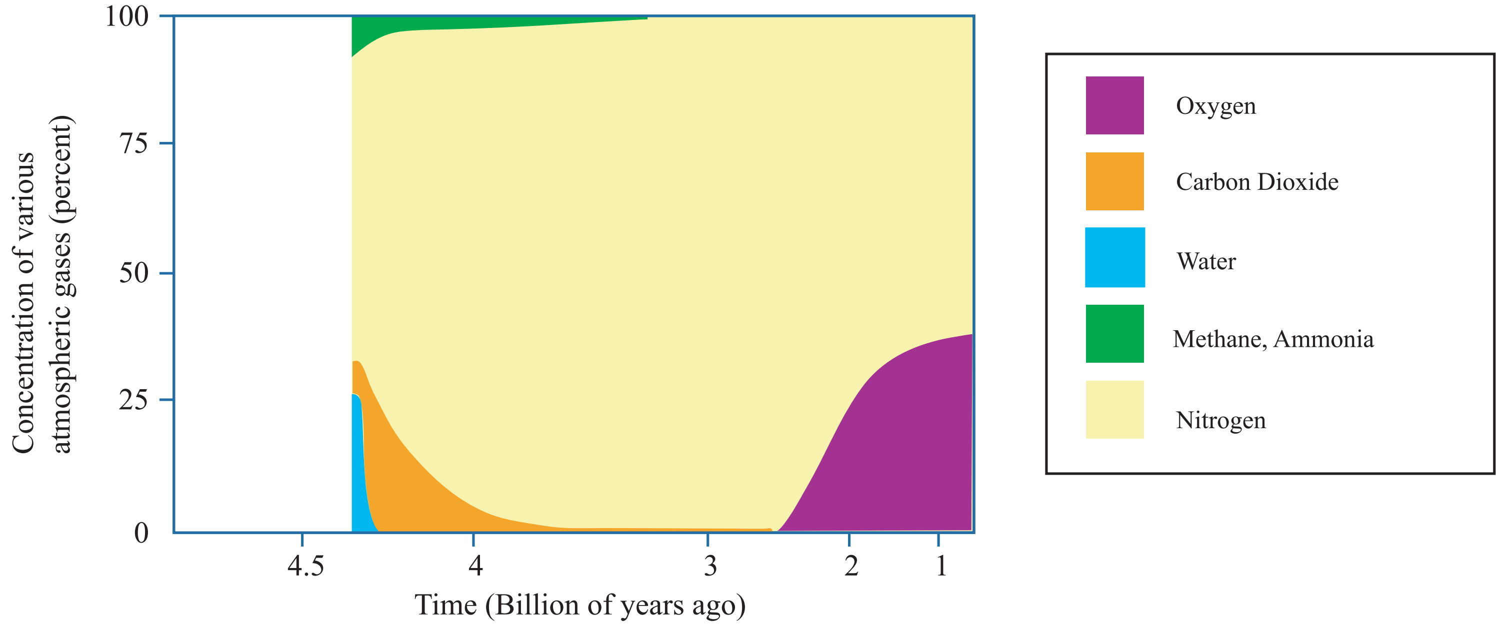
“Life can be recognized by its deeds — life is disequilibrium, leaving behind the signatures of disequilibrium such as fractionated isotopes or complex molecules. It is more besides, but the larger question ‘what is life?’ is perhaps beyond natural science. Continuum exists between chemistry, autocatalysis and what every one would agree is life. But defining the point at which autocatalysis becomes life is like searching for the world’s smallest giant.”

Nisbet, E. G., and N. H. Sleep. "The habitat and nature of early life." *Nature* 409, no. 6823 (2001): 1083-1091.

What is Life?

- Life is based on carbon chemistry operating in an aqueous environment
  - carbon is the only element that is sufficiently abundant, ubiquitous and chemically suited for life
- It will process chemicals for carbon and energy, make copies of itself, be autonomous and evolve in concert with its environment
- Biochemical pathways will operate as above
  - comprise energy yielding and replication reactions
  - construct complex molecules from simple, universal precursors
  - evolve

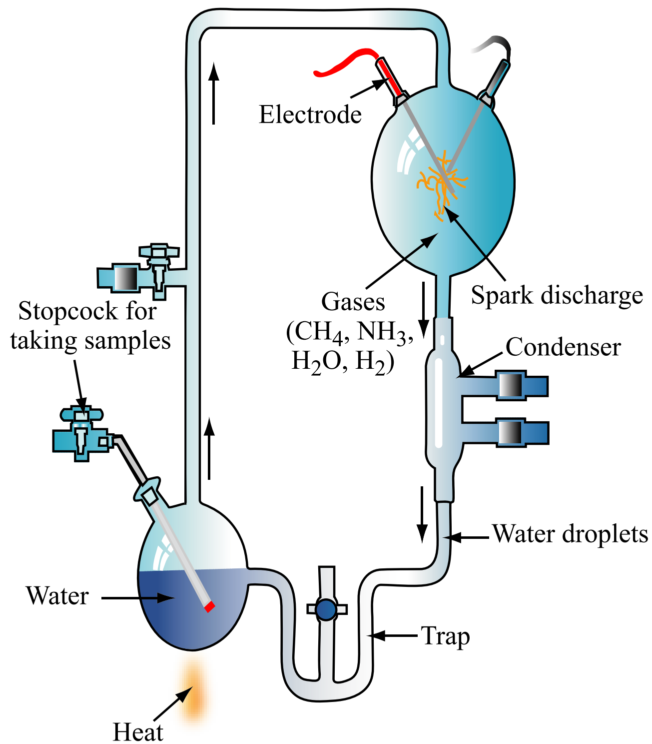
Composition of Earth's Early Atmosphere



Atmospheric composition, shown by the relative concentration of various gases, has been greatly influenced by life on the earth. The early atmosphere had fairly high concentrations of water and carbon dioxide and, some experts believe, methane, ammonia, and nitrogen. After the emergence of living organisms, the oxygen that is so vital to our survival became more plentiful. Today carbon dioxide, methane and water exists only in trace amounts in the atmosphere.

Figure by MIT OpenCourseWare. After figure on page 74 of Allegre, Claude J., and Stephen H. Schneider. "The evolution of the Earth." Scientific American 271 (1994): 44-51.

Formation of the Building Blocks for Biomolecules Miller-Urey Expt



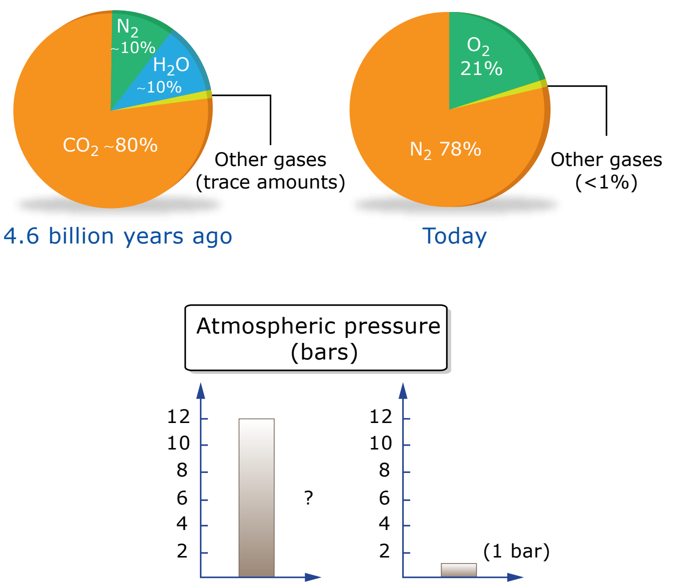
Amino Acid	Murchison Meteorite	Discharge Experiment
Glycine	● ● ● ●	● ● ● ●
Alanine	● ● ● ●	● ● ● ●
α–Amino-*N*-Butyric Acid	● ● ●	● ● ● ●
α–Aminoisobutyric Acid	● ● ● ●	● ●
Valine	● ● ●	● ●
Norvaline	● ● ●	● ● ●
Isovaline	● ●	● ●
Proline	● ● ●	●
Pipecolic Acid	●	●
Aspartic Acid	● ● ●	● ● ●
Glutamic Acid	● ● ●	● ●
β–Alanine	● ●	● ●
β–Amino-*N*-Butyric Acid	●	●
β–Aminoisobutyric Acid	●	●
γ–Aminobutyric Acid	●	● ●
Sarcosine	● ●	● ● ●
N-Ethylglycine	● ●	● ● ●

Image by MIT OpenCourseWare. After table on page 79 in Orgel, Leslie E. "The origin of life on the earth." *Scientific American* 271, no. 4 (1994): 77-83.

The Building Blocks for Biomolecules: The Miller-Urey Experiment (c.)

Orgel (1994) *Sci. Am.*, Oct. 1994, 77-83.

Atmospheric composition



Possible atmospheric composition and pressure during the heavy bombardment period. Compared with today.

Changes in Atmospheric Composition over time

	Prebiotic Atmosphere	Archean Atmosphere	Modern Atmosphere
Surface pressure	1-10 bars	1-2 bars	1 bar
N_2	10-80%	50-80%	78%
O_2	about 0	about 0	21%
CO_2	30-90%	10-20%	0.036%
CH_4	10-100 ppm	1000-10,000 ppm	1.6 ppm
CO	100-1000 ppm	–	0.1-0.2 ppm
H_2	100-1000 ppm	–	0.5 ppm

Image by MIT OpenCourseWare.

Problems with a Miller-Urey-type origin for biomolecules

- Hadean atmosphere now thought to have been much less reducing than in Miller-Urey atmosphere (predominance of CO_2 relative to CH_4 and NH_3)
- 50-50 mixture of right- & left-handed molecules is synthesized; natural molecules are 100% left- or right-handed…

Homochirality

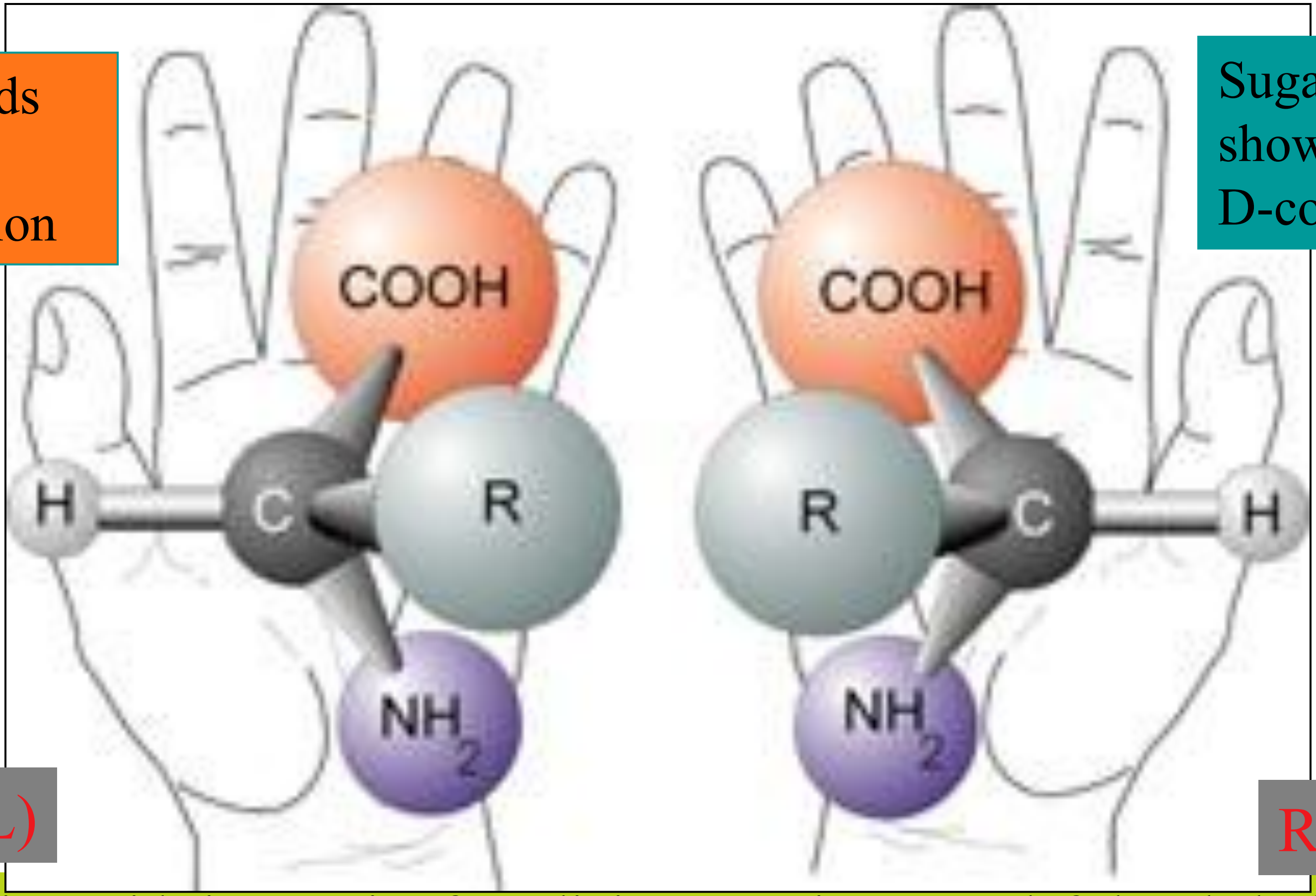
From Wikipedia:

Homochirality is a term used to refer to a group of molecules that possess the same sense of chirality. Molecules involved are not necessarily the same compound, but similar groups are arranged in the same way around a central atom. In biology homochirality is found inside living organisms. Active forms of amino acids are all of the L-form and most biologically relevant sugars are of the D-form. Typically, the alternative form is inactive and sometimes even toxic to living things. The origin of this phenomenon is not clearly understood. Homochirality is said to evolve in three distinct steps: **mirror-symmetry breaking** creates a minute enantiomeric imbalance and is key to homochirality, **chiral amplification** is a process of enantiomeric enrichment and **chiral transmission** allows the transfer of chirality of one set of molecules to another.

Chirality of Biomolecules

Amino acids have an L-configuration

Sugars (not shown) have a D-configuration



Left (L)

Right (D)

- All amino acids in proteins from living organisms are "left-handed" (L-enantiomers), while sugars are "right-handed". (Chirality was yet another discovery by Louis Pasteur ~150 yr BP!)
- The Miller-Urey experiment, and all similar organic synthetic experiments, produce a 50-50 (racemic) mixture of biomolecules.

Figure courtesy of NASA.

How did homochirality arise?

- It may have occurred in the solar nebula during the formation of the solar system.
- Amino acids with a slight L-enantiomeric excess is observed in the many meteorites incl Murchison
- (Although beware of contamination, since all Earthly aa's begin with L configuration. But note: during natural decomposition processes, protein aa's revert to a 50-50 (racemic) mixture over time.)
- Crystal faces have surface structures that are mirror-images. Experiments show that crystal faces can select L or D amino acids quite efficiently (40% excess) (Hazen, 2001). While this mechanism can explain the propagation of the L or D configuration, it cannot explain the *origin* of that preference.

Chiral Amino Acids in the Murchison Meteorite

Table 2 and Figure 4 removed due to copyright restrictions.

Cronin, John R., and Sandra Pizzarello. "Enantiomeric excesses in meteoritic amino acids." Science 275, no. 5302 (1997): 951-955.

Photograph courtesy U.S. Department of Energy.

- Murchison fragment (Martin Horejsi)
- Carbonaceous chondrite
- Struck 9/28/69, near Murchison, Victoria, Australia.

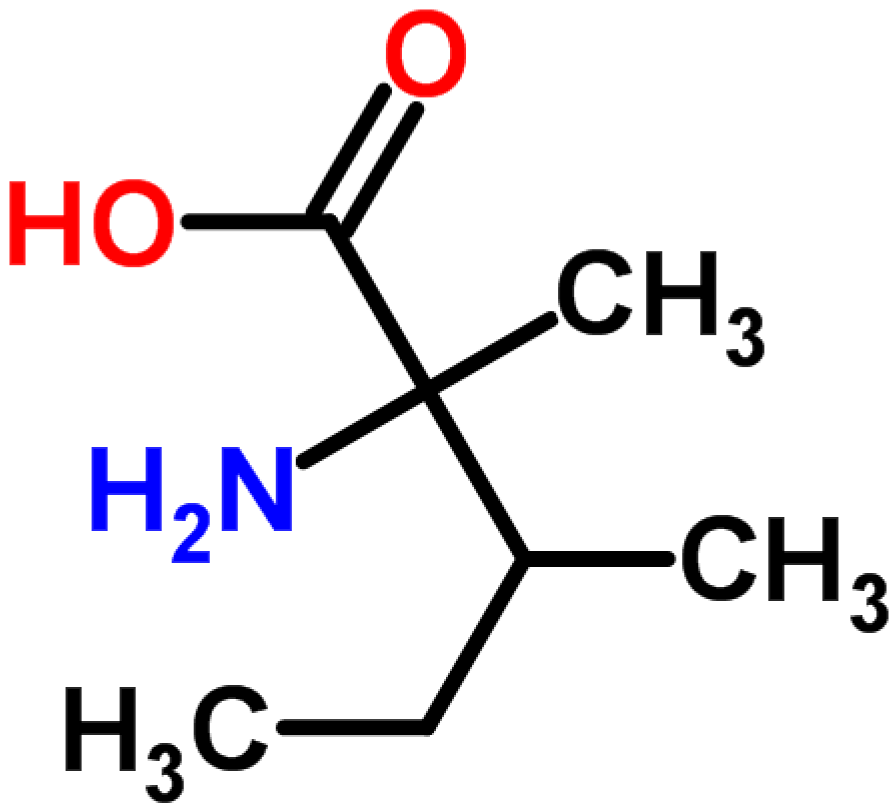
- Non-protein aa's analyzed to avoid contamination (previous L-excesses were shown to be the result of terrestrial contamination)

Enantiomeric Excesses in Meteoritic Amino Acids

John R. Cronin and Sandra Pizzarello

Gas chromatographic–mass spectral analyses of the four stereoisomers of 2-amino-2,3-dimethylpentanoic acid (DL-α-methylisoleucine and DL-α-methylalloisoleucine) obtained from the Murchison meteorite show that the L enantiomer occurs in excess (7.0 and 9.1%, respectively) in both of the enantiomeric pairs. Similar results were obtained for two other α-methyl amino acids, isovaline and α-methylnorvaline, although the α hydrogen analogs of these amino acids, α-amino-*n*-butyric acid and norvaline, were found to be racemates. With the exception of α-amino-*n*-butyric acid, these amino acids are either unknown or of limited occurrence in the biosphere. Because carbonaceous chondrites formed 4.5 billion years ago, the results are indicative of an asymmetric influence on organic chemical evolution before the origin of life.

Cronin, John R., and Sandra Pizzarello. "Enantiomeric excesses in meteoritic amino acids." Science 275, no. 5302 (1997): 951-955.



Structure of 2-amino-2,3-dimethylpentanoic acid (2-α-2,3-dmpa). This amino acid has two chiral centers and, consequently, four stereoisomers: the D and L forms of α -methylisoleucine and α-methylalloisoleucine

CSID:10652963, http://www.chemspider.com/Chemical-Structure.10652963.html (accessed 15:53, Aug 27, 2013)

Figure 3 A removed due to copyright restrictions.

Cronin, John R., and Sandra Pizzarello. "Enantiomeric excesses in meteoritic amino acids." Science 275, no. 5302 (1997): 951-955.

Fig. 3. (**A**) Total-ion chromatogram of 2-α-2,3-dmpa stereoisomers from the Murchison meteorite run as *N*-PFP isopropyl esters on Chirasil-L-Val.

Isotopic evidence for extraterrestrial non-racemic amino acids in the Murchison meteorite

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Many amino acids contain an asymmetric centre, occurring as laevorotatory, L, or dextrorotatory, D, compounds. It is generally assumed that abiotic synthesis of amino acids on the early Earth resulted in racemic mixtures (L- and D-enantiomers in equal abundance). But the origin of life required, owing to conformational constraints, the almost exclusive selection of either L- or D-enantiomers[1,2], and the question of why living systems on the Earth consist of L-enantiomers rather than D-enantiomers is unresolved[3]. A substantial fraction of the organic compounds on the early Earth may have been derived from comet and meteorite impacts[4-6]. It has been reported previously that amino acids in the Murchison meteorite exhibit an excess of L-enantiomers[7], raising the possibility that a similar excess was

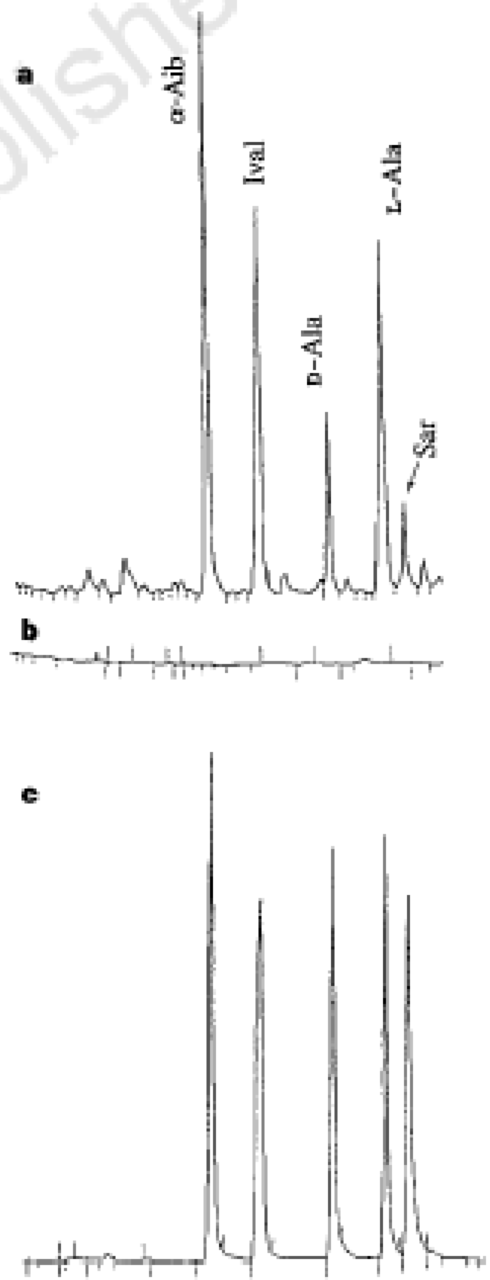


Figure 1 a, Gas chromatogram showing the resolution of D-alanine and L-alanine in the Murchison meteorite. **b**, Procedural blank chromatogram that preceded the meteorite analysis. **c**, Chromatogram of a standard mixture of the amino acids. Abbreviations are as follows: α-Aib, α-aminoisobutyric acid; Ival, isovaline; D-Ala, D-alanine; L-Ala, L-alanine; *Sar*, sarcosine. For GC, GC/MS and GC/C/IRMS, the separation of the trifluoroacetyl isopropyl esters of the amino acid stereoisomers was accomplished using a Chirasil-Val 50 m × 0.25 mm (internal diameter) fused-silica capillary column (Alltech, Deerfield, IL). The GC/C/IRMS consists of a Hewlett Packard 5890 GC coupled to an OPTIMA (Micromass, Manchester, UK) stable-isotope mass spectrometer through a cupric oxide/nichrome wire oxidation furnace, a copper reduction furnace and a liquid-nitrogen carbon dioxide/water cold trap[21]. The GC and GC/MS analyses were performed using a Hewlett Packard 5890A GC and a Hewlett Packard GC/MSD.

Engel, Michael H., and S. A. Macko. "Isotopic Evidence for Extraterrestrial Non-Racemic Amino Acids in the Murchison Meteorite." *Nature* 389, no. 6648 (1997): 265-8. Courtesy of Nature Publishing Group. Used with permission.

Table 1 Amino-acid abundances and $\delta^{15}N$ values

Amino acid	Concentration ($nmol\,g^{-1}$)	$\delta^{15}N$ (‰)*
α-Aminoisobutyric acid	20.1	+184
Sarcosine	ND†	+129
Isovaline	8.0‡	+66
Glycine	24.5	+37
β-Alanine	12.8	+61
D-Alanine	−§	+60
L-Alanine	10.4‡	+57
L-Leucine	2.5§	+60
D,L-Proline	ND†	+50‖
D,L-Aspartic acid	4.7§	+61‖
D-Glutamic acid	−§	+60
L-Glutamic acid	10.9§	+58

* The $\delta^{15}N$ values are an average of four GC/C/IRMS analyses, the average error being about ±1‰. Values are reported relative to the standard, atmospheric N_2: $\delta^{15}N(‰) = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{standard} - 1] \times 10^3$.

† Not determined. Sarcosine was not sufficiently resolved by HPLC; the HPLC method did not detect secondary amines such as proline.

‡ The value for isovaline includes a contribution from valine that co-eluted with isovaline during HPLC analysis.

§ Concentrations reported for L-alanine, L-leucine, D,L-aspartic acid and L-glutamic acid represent the total contribution of both enantiomers for the respective amino acids.

‖ $\delta^{15}N$ value reflects contribution of both enantiomers.

An extraterrestrial origin for homochirality?

Figure of polarization in Orion OMC1 has been removed due to copyright restrictions. See "Chirality and the Origin of Life."

•In the model 1st proposed by Rubenstein et al. (1983) (*Nature*, Vol. 306:118) the action of circular polarized light on interstellar chiral molecules introduced a left handed excess into molecules in the material from which the solar system formed. Some of this organic material then finds its way onto Earth via impacts of comets, meteorites and dust particles during the heavy bombardment phase in the first few hundred million years of the solar system. These molecules were then part of the prebiotic material available for the origin of life, and tipped the scales for life to develop with L-amino acids and D-sugars.

•Rubenstein et al. originally proposed that synchrotron radiation from neutron stars in supernova remnants would be a suitable source of the required UV circularly polarized light. However, this interpretation is not supported by theory or observation which show that the circular polarization of these sources is very low.

•New observations with the Anglo-Australian Telescope (above) have shown surprisingly high circular polarizations (the red and white regions in the image) in the infrared light from reflection nebulae in the star forming regions Orion OMC1 (a region in the Orion nebula M42) and NGC 6334. Although we can only observe these regions at infrared wavelengths which can penetrate the thick dust clouds in which they are embedded, it is predicted that circular polarization should also be present at the ultraviolet wavelengths needed for asymmetric photolysis of molecules such as amino acids. If our own solar system formed in such a region of high circular polarization, it could have led to the excess of L-amino acids which we see in meteorites and to the homochirality of biological molecules. It is possible that without such a process operating it would not be possible for life to start. This may have implications for the frequency of occurrence of life in the universe.

http://www.phys.unsw.edu.au/~jbailey/chirality.html

Exogenous delivery of chiral building blocks of biomolecules

Carbonaceous Chondrites: A Window on Organic Chemistry in the Early Solar System
J. R. Cronin
Arizona State University
http://astrobiology.arc.nasa.gov/workshops/1996/astrobiology/speakers/cronin

∝

"Analyses of selected chiral amino acids from the Murchison meteorite suggest L-enantiomer excesses of the order of 5-10%. In general, the finding of enantiomeric excesses in extraterrestrial molecules supports the hypothesis that exogenous delivery made a significant contribution to organic chemical evolution leading to the origin of life. The finding of these enantiomeric excesses specifically in substituted amino acids may have implications for the chemistry of a pre-RNA world insofar as it suggests the possibility that these unusual, but meteoritically abundant, amino acids were early biomonomers. "

[1] Cronin J. R. and Chang S. (1993) in The Chemistry of Life's Origins (J.M. Greenberg et al., eds.) Kluwer, pp. 209-258. [2] Epstein S. et al. (1987) Nature, 326, 477-479. [3] Bonner W. A. and Rubenstein E. (1987) BioSystems, 20, 99-111

ASYMMETRIC AUTOCATALYSIS AND HOMOCHIRALITY OF BIOMOLECULES

Kenso Soai* and Itaru Sato

Abstract

"Asymmetric automultiplication of chiral compounds by asymmetric autocatalysis is realized for the first time where a chiral product acts as a chiral catalyst for its own production."

In other words, a miniscule chiral excess in a compound can propagate when those compounds are catalyzing reactions involving themselves.

Soai, Kenso, and Itaru Sato. "Asymmetric autocatalysis and the homochirality of biomolecules." *Viva Orig* 30 (2002): 186-198.

Role of Mineral Mineral Surfaces in Biochemical Evolution

Mineral surfaces can serve as templates for chiral molecules

Image of calcite crystal attracting left- and right-handed amino acids removed due to copyright restrictions. See "Templates" figure of "Crystal Power" inset on page 80 of Hazen, Robert M. "Life's Rocky Start." *Scientific American* 284, No 4, (2001): 77-85.

Hazen, Robert M. "Life's Rocky Start." *Scientific American* 284, No 4, (2001): 77-85.

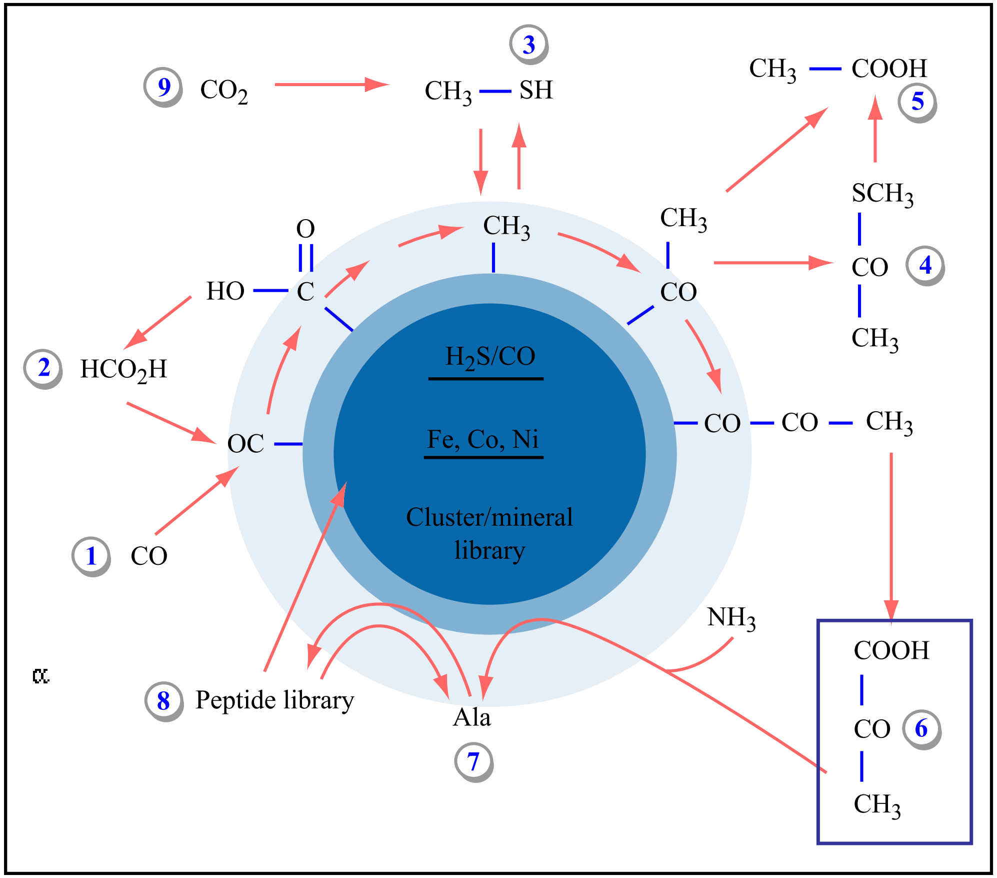


Image by MIT OpenCourseWare. After figure in Wächtershäuser, Günter. "Life As We Don't Know It." *Science* 289, no. 5483 (2000): 1307-1308.

Mineral-surfaces can also catalyze organic syntheses under hydrothermal conditions

Wächtershäuser comment on, Cody et al. (2000) *Science* 289:1337.

Conditions for Reactions in the Figure			
Reaction	*Catalyst*	*Temp.*	*Pressure*
(1) → (2)	(Fe,Ni)S	100°C	0.2 MPa
(1) → (3)	(Fe,Ni)S	100°C	0.2 MPa
(9) → (3)	FeS	100°C	0.2 MPa
(1) → (5)	(Fe,Ni)S	100°C	0.2 MPa
(3) → (4)	(Fe,Ni)S	100°C	0.2 MPa
(2) → (6)	FeS	250°C	200 MPa
(6) → (7)	FeS	100°C	0.2 MPa
(7) → (8)	(Fe,Ni)S	100°C	0.2 MPa

Image by MIT OpenCourseWare.

•Iron-sufide minerals catalyze production of **pyruvate** & other biomolecules under conditions existing in hydrothermal vent systems.

Mineral surfaces can protect fragile molecules

Image of microscopic pits on the surface of feldspar removed due to copyright restrictions. See “Containers” figure of “Crystal Power” inset on page 80 of Hazen, Robert M. "Life’s Rocky Start." *Scientific American* 284, No 4, (2001): 77-85.

Hazen, Robert M. "Life’s Rocky Start." *Scientific American* 284, No 4, (2001): 77-85.

Further evidence for mineral catalysis of simple organic molecules

Image of magnetite triggering the recombination of nitrogen and hydrogen gasses into ammonia removed due to copyright restrictions. See "Catalysts" figure of "Crystal Power" inset on page 80 of Hazen, Robert M. "Life's Rocky Start." *Scientific American* 284, No 4, (2001): 77-85.

$N_2 + H_2 + Fe_3O_4$(magnetite) →→ **NH_3**

$FeCO_3$ (Siderite) + H_2O →→ hydrocarbons (PAH + alkanes)

- Sealed vessel at 300˚C Tom McCollom (GCA and in press).

Hazen, Robert M. "Life's Rocky Start." *Scientific American* 284, No 4, (2001): 77-85.

Mineral surfaces can act as scaffolds in the synthesis of complex molecules

Image of clay layers trapping stray organic molecules removed due to copyright restrictions. See “Scaffolds” figure of “Crystal Power” inset on page 80 of Hazen, Robert M. "Life’s Rocky Start." *Scientific American* 284, No 4, (2001): 77-85.

Hazen, Robert M. "Life’s Rocky Start." *Scientific American* 284, No 4, (2001): 77-85.

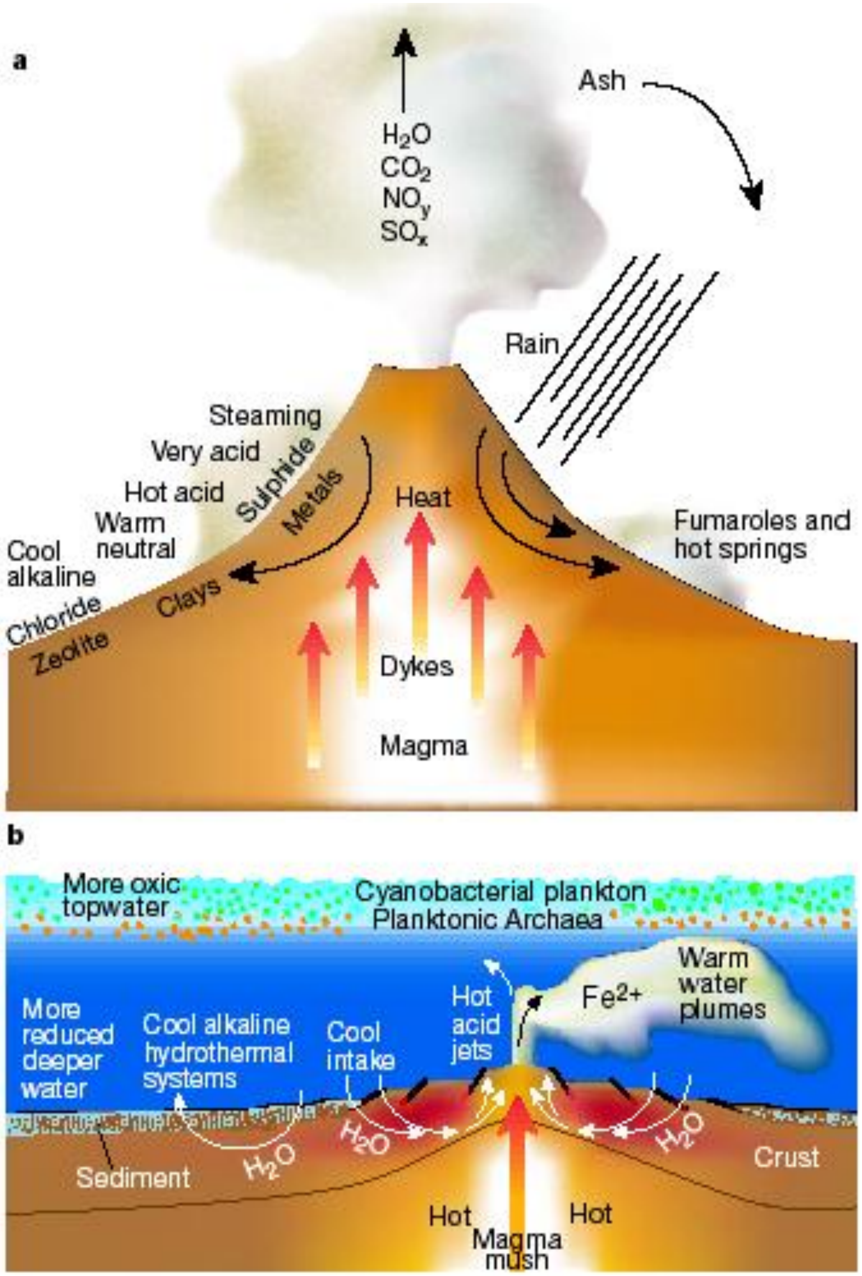
A Hyperthermophilic Beginning for Life?

- Given the inhospitable surface environment on Earth >3.8 Ga, when the intense bombardment likely melted the crust & vaporized the ocean, perhaps repeatedly, it is frequently proposed that life began in a sub-surface environment, perhaps a hydrothermal system where hot water, CO_2 & a variety of metals are readily available.

- The recognition that many of the essential enzymes for life require metals common in hydrothermal settings (Fe, Ni, Mo, Cu, Co, Zn) supports this supposition.

c.f., Nisbet & Sleep (2001) *Nature*, Vol. 409:1083-1091.

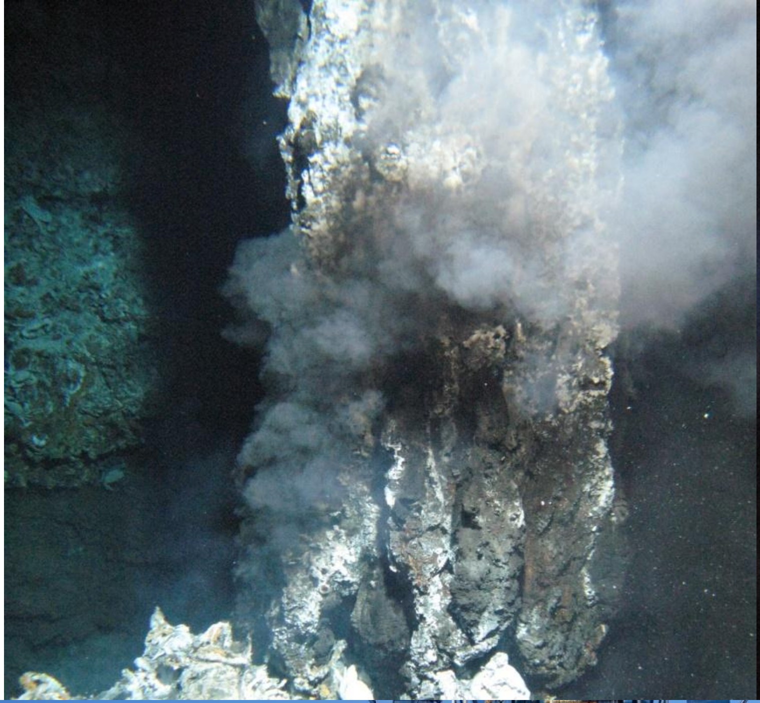
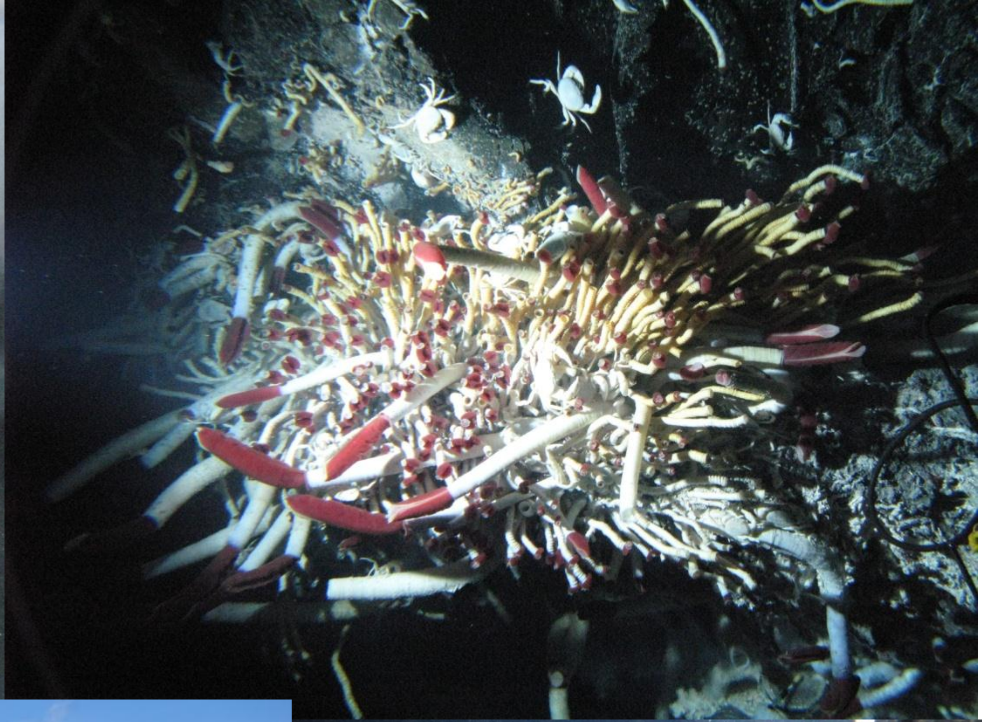
Hydrothermal Habitats for Early Life

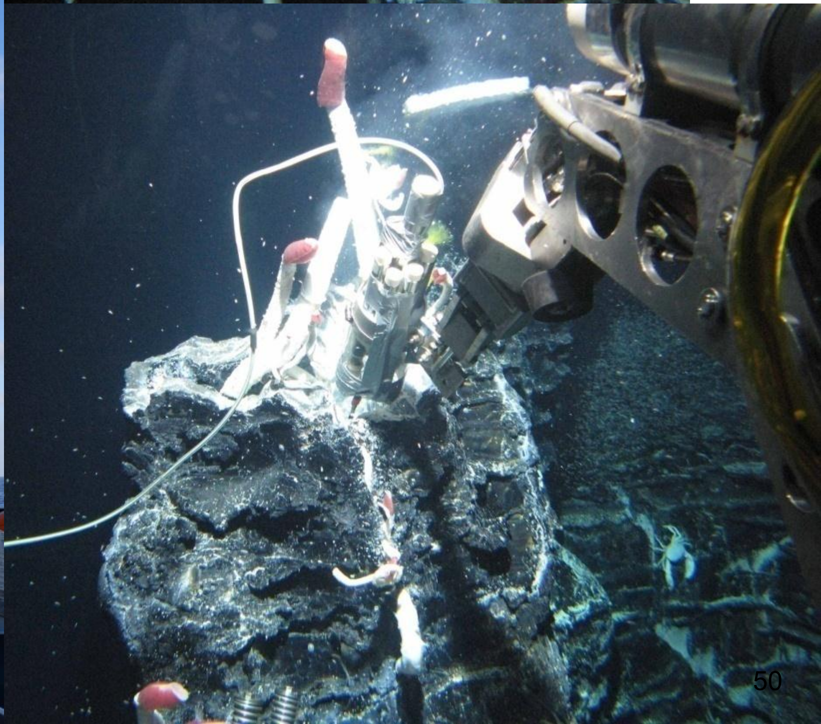


On Land, around a volcano.

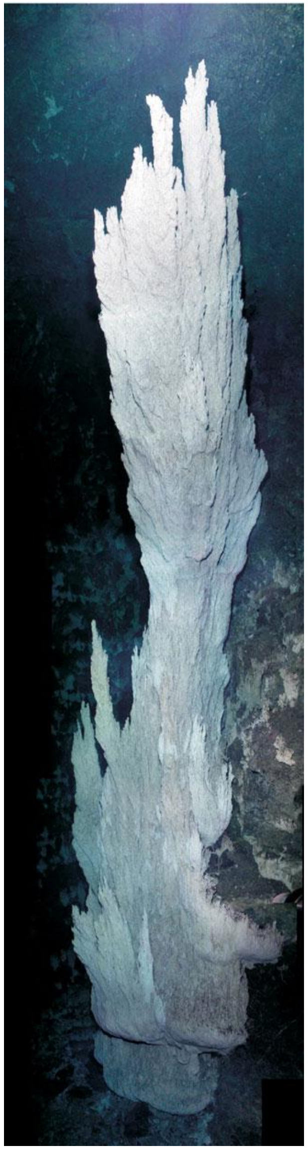
On the seafloor, at a mid-ocean ridge.

Source: Nisbet, E. G., and N. H. Sleep. "The Habitat and Nature of Early Life." *Nature* 409, no. 6823 (2001): 1083-91.



Serpentinization: source of H_2 and alkalinity



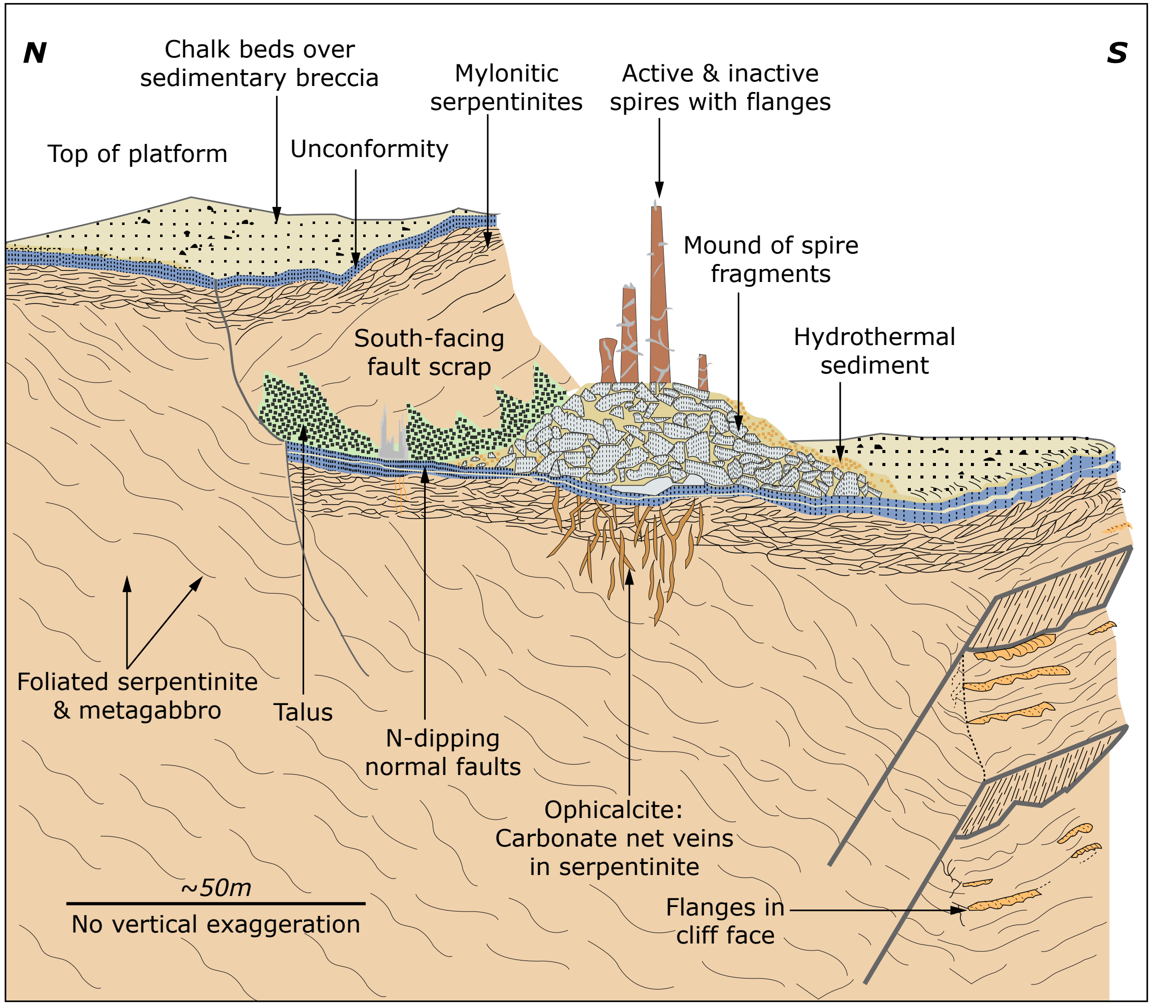
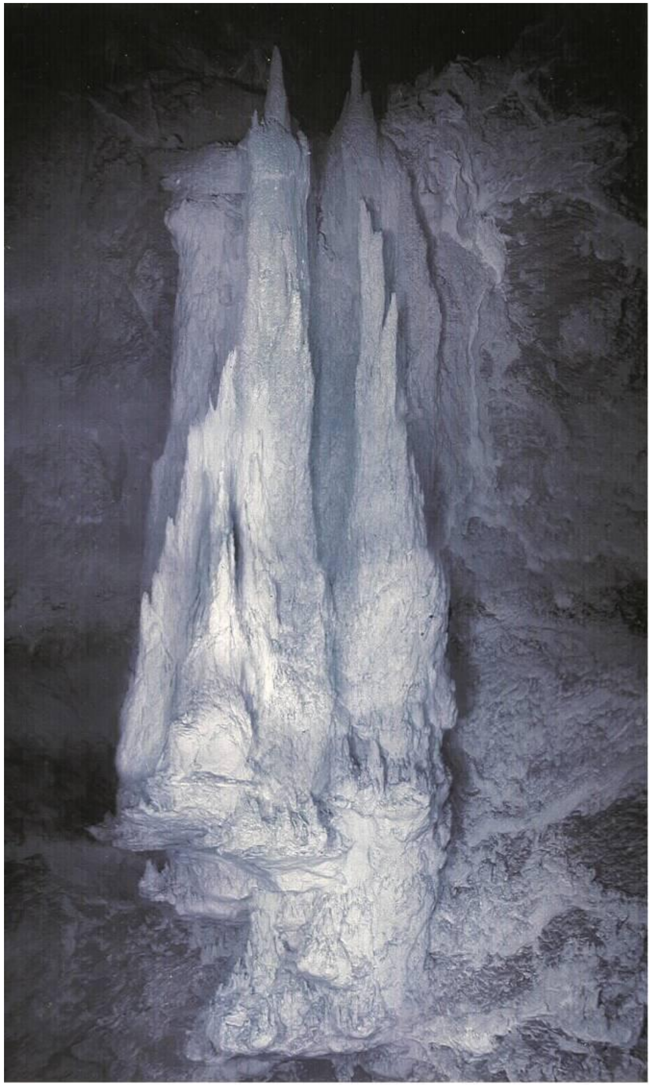


Image by MIT OpenCourseWare. After figure 3 in Kelley, Deborah S., Jeffrey A. Karson, et al. "A serpentinite-hosted ecosystem: the Lost City hydrothermal field." *Science* 307, no. 5714 (2005): 1428-34.

Olivine + water → Serpentine + brucite + magnetite + H_2

Kelley, Deborah S., Jeffrey A. Karson, Gretchen L. Früh-Green, Dana R. Yoerger, Timothy M. Shank, David A. Butterfield, John M. Hayes et al. "A serpentinite-hosted ecosystem: the Lost City hydrothermal field." *Science* 307, no. 5714 (2005): 1428-1434.

Lost City Hydrothermal Field



Vent Fluids

Hydrogen – up to 15 mmol/kg

Methane – up to 2 mmol/kg

Calcium – up to 30 mmol/kg

pH – 9 to 11

Low temp volatile production:
Proskurowski et al., Chem. Geology 2006

Abiogenic Hydrocarbon Production at
Lost City Hydrothermal Field:
Proskurowski et al., Science 2006

Shock, E.L. “Geochemical habitats in hydrothermal systems.” In: *First Steps in the Origin of Life in The Universe, Proceedings of the Sixth Trieste Conference on Chemical Evolution*, ed. J. Chela-Flores, Kluwer (2001).

http://geopig.asu.edu

- Organic synthesis from dissolved inorganic carbon (DIC) is favored by the chemical disequilibria that exists between hot hydrothermal fluids and seawater

Shock, Everett L. "Geochemical habitats in hydrothermal systems." In *First Steps in the Origin of Life in the Universe*, pp. 179-185. Springer Netherlands, 2001.

Universal phylogenetic tree of life based on 16s rRNA data removed due to copyright restrictions. See figure 1 in Shock, Everett L. "Geochemical habitats in hydrothermal systems." In *First Steps in the Origin of Life in the Universe*, pp. 179-185. Springer Netherlands, 2001.

rRNA tree suggests hyper-thermophiles are ancient

Summary

- Synthesis of ‘organic compounds is pervasive throughout the cosmos.
- Simple organic compounds with many of the attributes of ‘biological’ building blocks have been delivered on dust and larger impactors since beginning of the solar system.
- Similar organic compounds are made abiologically under conditions existing at different stages of earth history.
- Homochirality is a ‘biochemical’ quality but likely had its origins in cosmochemistry and prebiotic chemistry
- The ‘when’ and ‘how’ of the transition from prebiotic chemistry to biochemistry remain unsolved.

The ‘RNA World’ Hypothesis

Commonality & the Central Problem of Origin-of-Life Research

•Insight into the character of the 'last common ancestor' can be gained by identifying *commonalities* in contemporary organisms. I.e., intricate features common to all modern organisms are unlikely to have evolved independently.

•Examples: similar C compounds, same 20 amino acids make all proteins, genetic information in nucleic acids (RNA & DNA).

"our last common ancestor stored genetic information in nucleic acids that specified the composition of all needed proteins. It also relied on proteins to direct many of the reactions required for self-perpetuation. Hence, the central problem of origin-of-life research can be refined to ask, By what series of chemical reactions did this interdependent system of nucleic acids and proteins come into being?"

Orgel, Leslie E. "The origin of life on the earth." Scientific American 271, no. 4 (1994): 77-83.

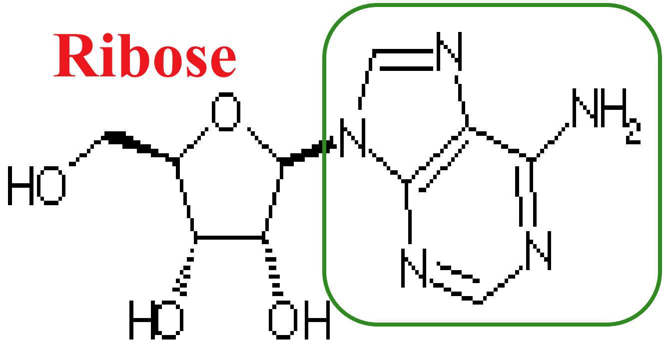
The ‘RNA World’ Hypothesis

Image of RNA molecules removed due to copyright restrictions. See page 80 in Orgel, Leslie E. "The origin of life on the earth." Scientific American 271, no. 4 (1994): 77-83.

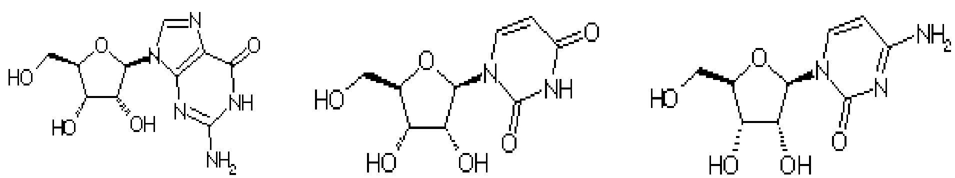
- Late 1960s: Woese (U. Illinois), Crick (England), Orgel (Salk Inst, San Diego) concurrently proposed RNA may have preceded proteins & catalyzed all reactions for survival & replication of ‘last common ancestor’.
- 1983: Thomas Cech (U. Colorado) & Sidney Altman (Yale) independently discovered *ribozymes*, enzymes made of RNA.
- Previously all biomolecules that catalyzed reactions (enzymes) were thought to be proteins (sequences of amino acids).

How to make subunits of RNA?

- Phosphate: rock weathering
- Ribose: $CO_2 + h\nu \rightarrow 5\ COH_2$ (formaldehyde) $+ H_2O \rightarrow$ **Ribose**
- Base: $CH_4 + N_2 + h\nu \rightarrow 5\ HCN \rightarrow$ **Adenine**



Other 3 RNA Bases: guanine uracil cytosine



Ricardo, A., M. A. Carrigan, A. N. Olcott, and S. A. Benner. "Borate minerals stabilize ribose." *Science* 303, no. 5655 (2004): 196-196.

Figure of pentose formation in the presence of borate removed due to copyright restrictions.

See figure 1 of Ricardo, A., M. A. Carrigan, A. N. Olcott, and S. A. Benner. "Borate minerals stabilize ribose." *Science* 303, no. 5655 (2004): 196-196.

Ricardo, A., M. A. Carrigan, A. N. Olcott, and S. A. Benner. "Borate minerals stabilize ribose." *Science* 303, no. 5655 (2004): 196-196.

Ribose

- Evidence for an "RNA world," an episode of life on Earth during which RNA was the only genetically encoded component of biological catalysts, is found in the ribosome , catalytic RNA molecules, and contemporary metabolism. That RNA could form has been doubted, however. **Ribose** and its sister pentoses (arabinose, xylose, and lyxose) are made under alkaline conditions from simple organic precursors (formaldehyde and glycolaldehyde) known in interstellar space and presumably available on early Earth. Pentoses do not accumulate under these conditions, however; they rapidly decompose in a "browning" reaction to generate largely undescribable polymeric mixtures.

Ricardo, A., M. A. Carrigan, A. N. Olcott, and S. A. Benner. "Borate minerals stabilize ribose." *Science* 303, no. 5655 (2004): 196-196.

Ribose

- These experiments suggest that the formation of pentoses appears to be the natural outcome of the chemical transformation of organic molecules present in the nebula that form stars and planets in the presence of borate minerals. Because neither borate minerals nor interstellar organics are excluded from the early Earth, we also cannot exclude the availability of **ribose** formed prebiotically at the time when life emerged on Earth.

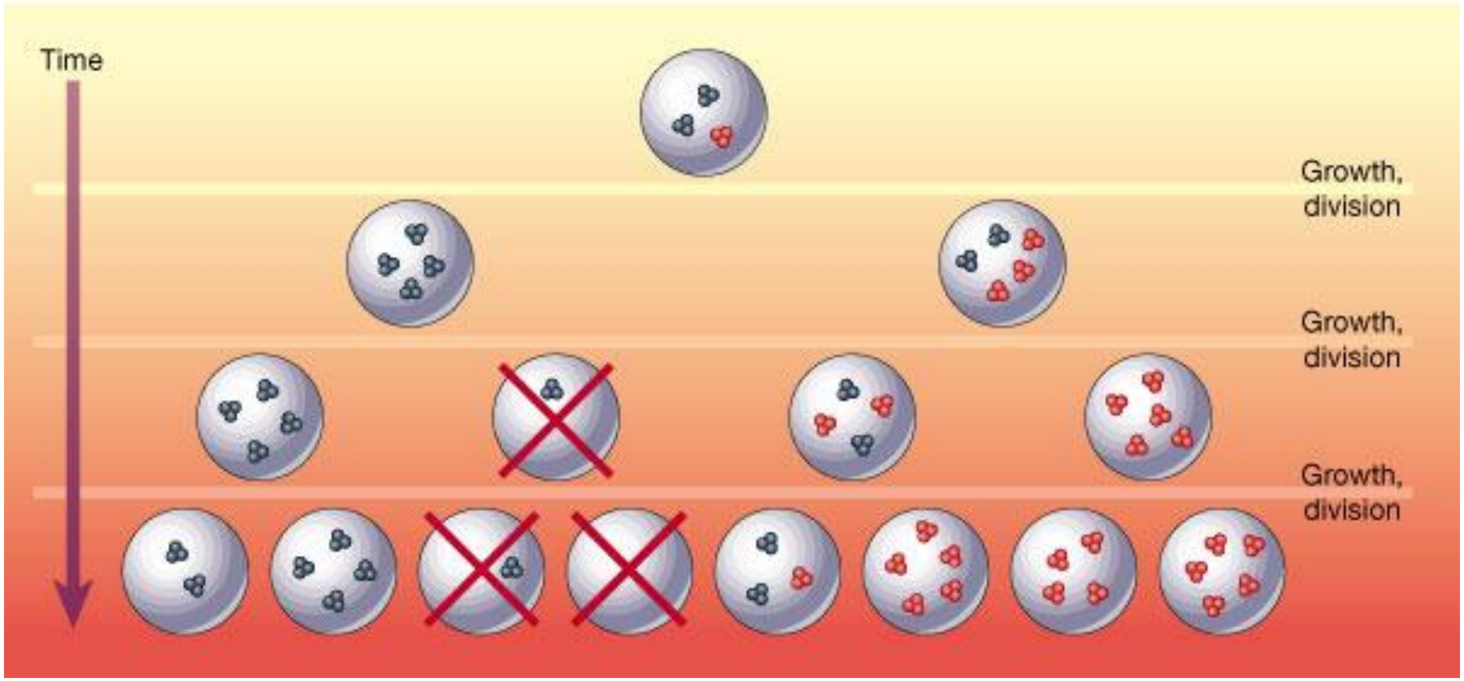
insight feature

Synthesizing **life**

Jack W. Szostak, David P. Bartel & P. Luigi Luisi

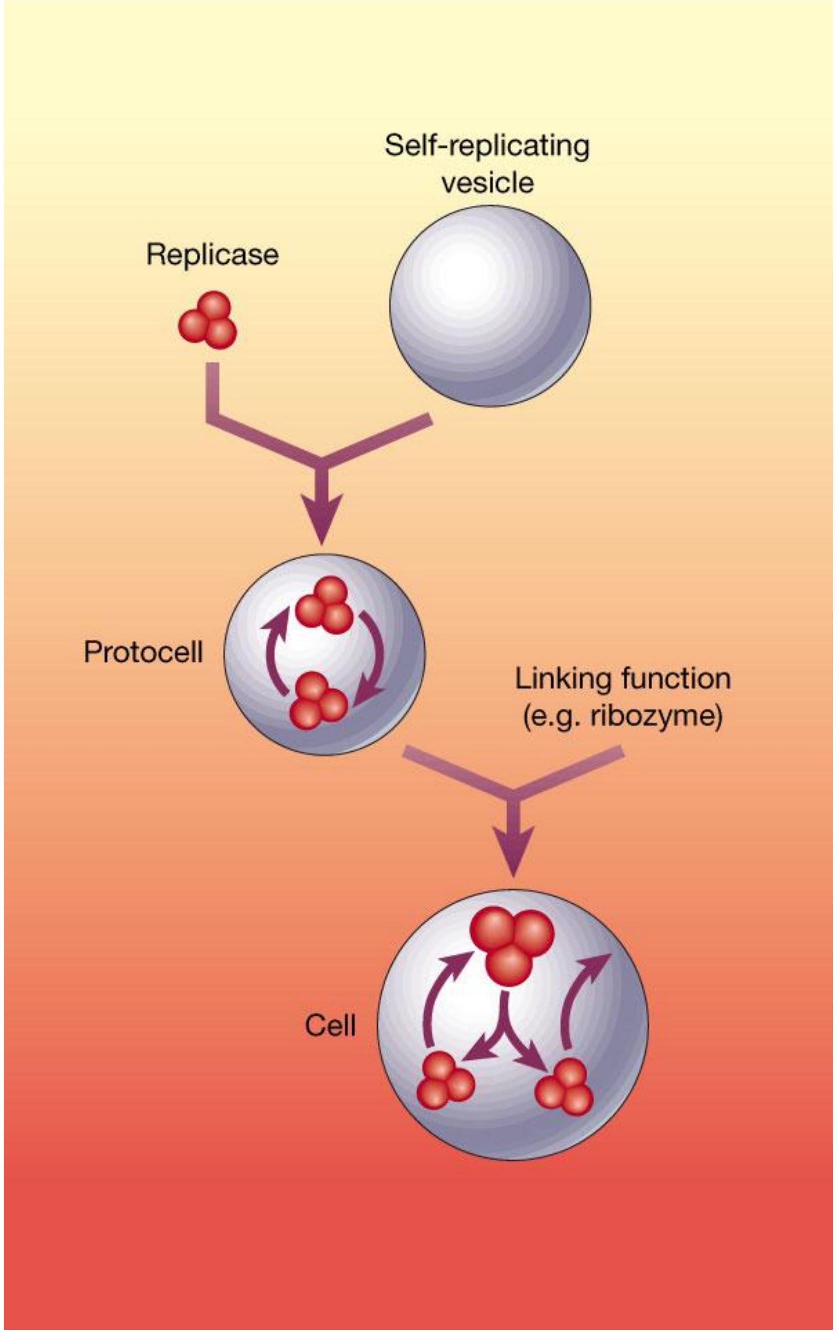
Advances in directed evolution and membrane biophysics make the synthesis of simple living cells, if not yet foreseeable reality, an imaginable goal. Overcoming the many scientific challenges along the way will deepen our understanding of the essence of cellular life and its origin on Earth.

Szostak et al, 2001

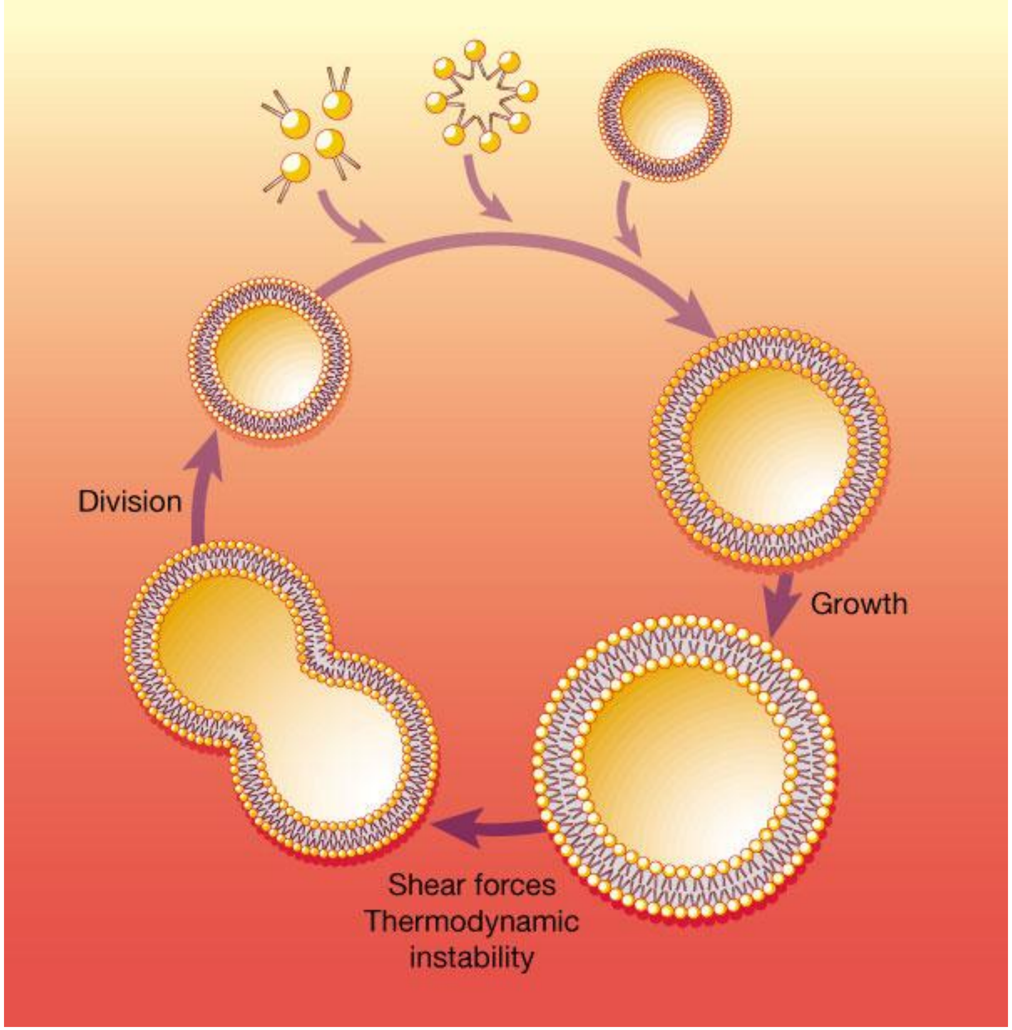


Courtesy of Nature Publishing Group. Used with permission. Source: Szostak, Jack W., David P. Bartel, et al. "Synthesizing Life." *Nature* 409, no. 6818 (2001): 387-90.

The vesicular compartment ensures that molecules related by descent are, on average, kept in physical proximity to each other, allowing a superior mutant replicase (red) to preferentially self-replicate, in comparison to the parental replicase (black). The evolutionary advantage of increased replication is amplified as vesicles with superior replicase molecules are more likely to give rise to vesicles with at least two replicase molecules (or a replicase and a template molecule). Vesicles with less than two replicase molecules (indicated by an X) and the progeny of these vesicles cannot continue RNA self-replication. In this way, vesicles with superior replicase molecules become an increasing fraction of the vesicles that maintain replicase activity.



The first major synthetic intermediates are an RNA replicase and a self-replicating vesicle. These are combined into a protocell, enabling rapid evolutionary optimization of the replicase. Addition of an RNA-coded linking function, such as a lipid-synthesizing ribozyme, completes the cellular structure.



Self-replicating membrane vesicles can grow either gradually or in discrete steps, and may divide either spontaneously or under the influence of external environmental forces.

The Search
for Extraterrestrial Life

The earth remains the only inhabited world known so far, but scientists are finding that the universe abounds with the chemistry of life

by Carl Sagan

Sagan, Carl. "The Search for Extraterrestrial Life." *Scientific American* 271, no. 4 (1994): 92-99.

Panspermia 1

Planetary perspective on life on early Mars and the early Earth

by Dr. Norman Sleep

Sleep, Norman H., and Kevin Zahnle. "Planetary Perspective on Life on Early Mars and the Early Earth." (1996).

Large (400 km) projectile
Ocean completely boiled
230 m rock rain
Return to normal
(100 years Mars)
(3000 years Earth)

Small (70 km) projectile
Dry land surface (Earth and MArs) heated to melting point of rock
All lakes boiled on Mars
25 m of ocean boiled on the Earth
1 meter of rock rain
Planet returns to normal in 25 years
Sample projectile - Orientale basin on moon

Refugia from 400-km projectile
Moderate to deep subsurface (Mars)
Deep subsurface (Earth)
Only thermophile survivors on Earth
Nonthermophiles probably survive on Mars

Refugia from 70-km projectile
Subsurface (Earth and Mars)
Moderate to deep ocean (Earth)
Thermophile and nonthermophile survivors on both planets

Panspermia 2

Planetary perspective on life on early Mars and the early Earth

by Dr. Norman Sleep

http://astrobiology.arc.nasa.gov/workshops/1996/astrobiology/speakers/sleep/sleep_index.html

Biological evidence

Life may root in thermophile on Earth - one or more almost sterilizing events

Possible Martian fossils come from safe subsurface environment

Space transfer

Unshocked Mars meteorites fall today on the Earth

Current transfer rate is 107-108 rocks per million years

10-4 of rocks arrive within 10,000 years of impact

Rate of transfer of fresh rocks is 104 per million years

Early solar system rate 103 higher

Billions of fresh rocks transferred

Conclusions

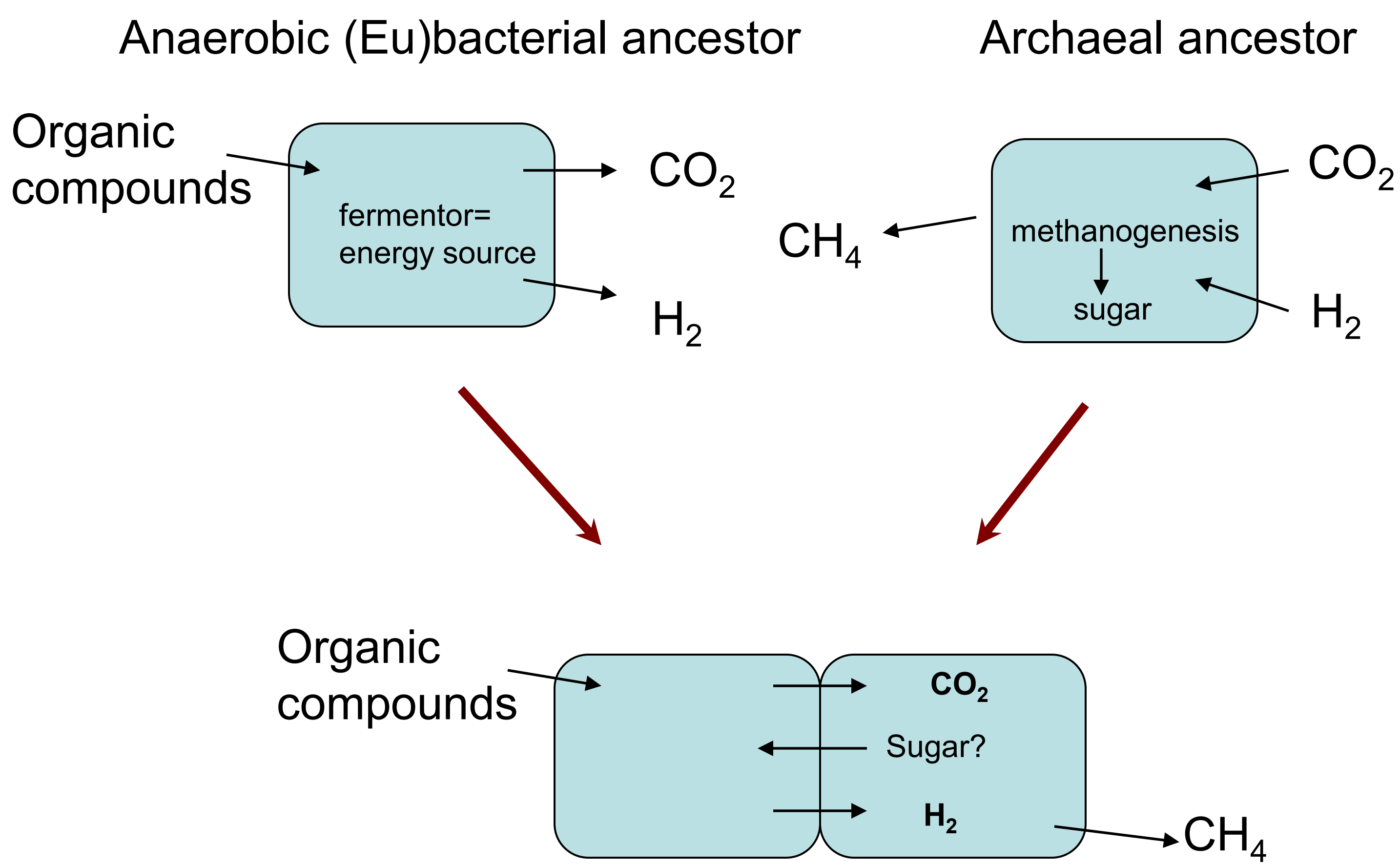
Subsurface of Mars was safer from the Earth

Space transfer of organisms seems feasible

There is biological evidence for partial sterilization of the Earth

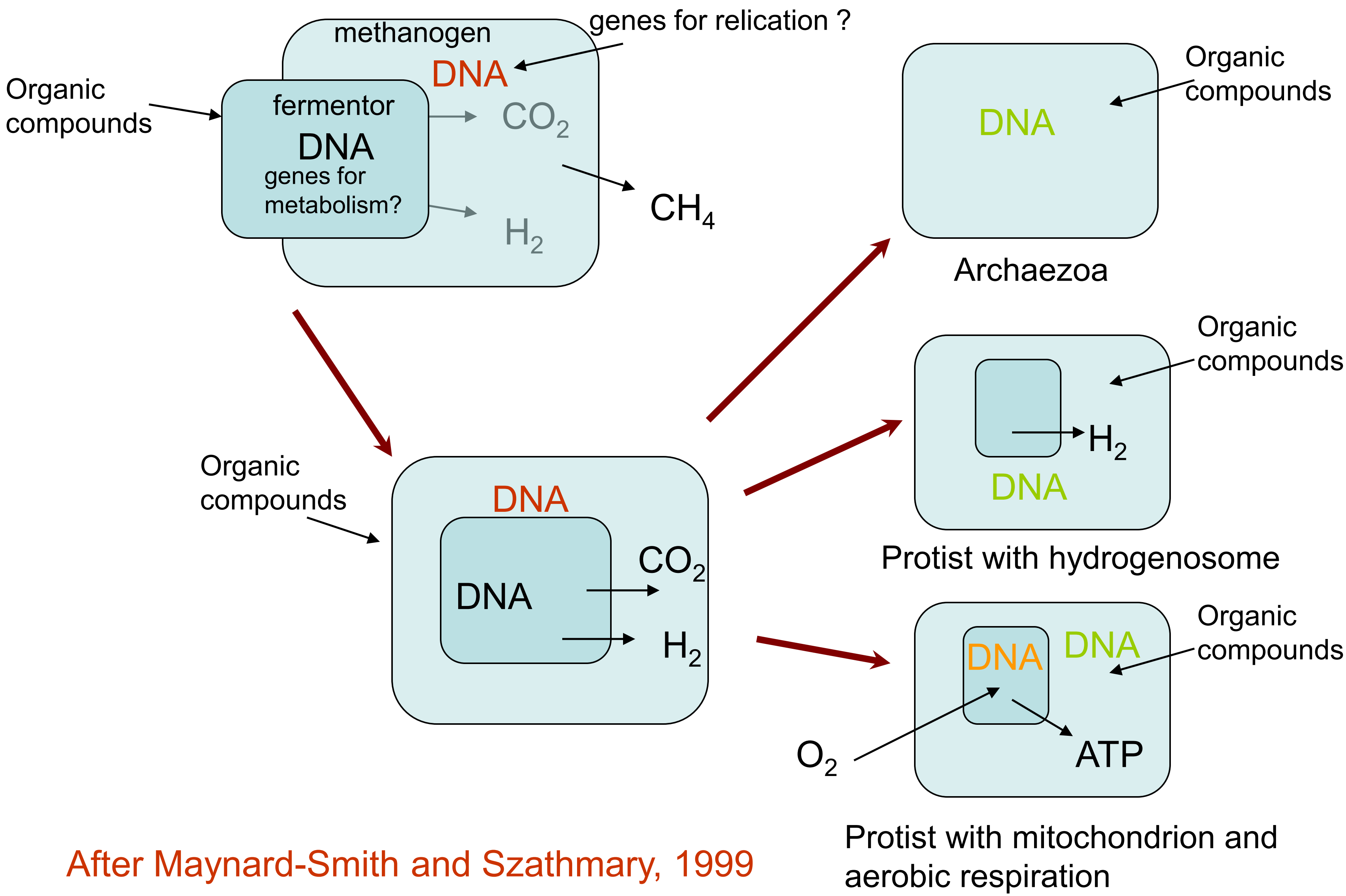
Space transfer of life to Earth is a viable possibility

Symbiosis leading to proto-eukaryote



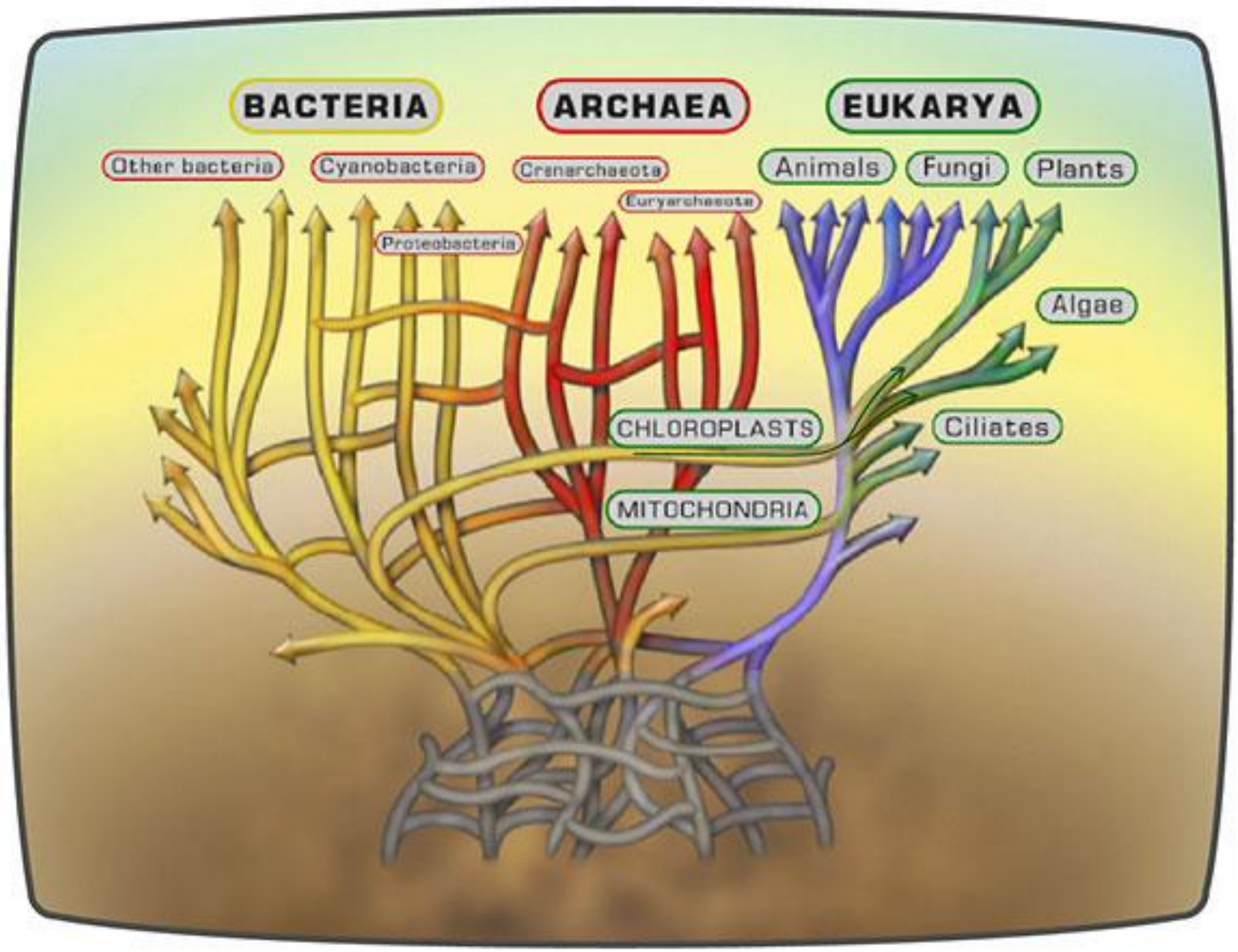
After Maynard-Smith and Szathmary, 1999

Symbioses leading to Eukaryotes



After Maynard-Smith and Szathmary, 1999

THE SHRUB OF LIFE



Proposed by W. Ford Doolittle, this view of early evolution suggests multiple primitive cells as ancestors to the three domains, and illustrates lateral gene transfer among early organisms.

Complexity of Extant Life

Species	**Type**	**Approx. Gene Number**
Prokaryotes E. Coli	 typical bacterium	 4,000
Protists O. Similis S. Cerevisiae Distyostelium discoideum	 protozoan yeast slime mould	 12,000-15,000 7,000 12,500
Metazoan C. Elegans D. melanogaster S. Purpuratas Fugu rubripes Mus musculus Homo sapiens	 Nematode Insect Echinoderm Fish Mammal mammal	 17,800 12,000-16,000 <25,000 50,000-10,0000 80,000 60,000-80,000

After Maynard-Smith and Szathmary, 1999

Major Transitions in Origin/Evolution of Life

replicating molecules	populations of molecules in protocells
independent replicators	chromosomes
RNA as a gene and enzyme	DNA genes, protein enzymes
prokaryotic cells	Cells with nuclei & organelles ie eukaryotes
asexual clones	sexual populations
single bodied organisms	fungi, metazoans and metaphytes
solitary individuals	colonies with non-reproductive castes
primate societies	human societies with language

After Maynard-Smith and Szathmary, 1999

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Hypothesis Article

Signatures of a Shadow Biosphere

Paul C.W. Davies,[1] Steven A. Benner,[2] Carol E. Cleland,[3] Charles H. Lineweaver,[4]
Christopher P. McKay,[5] and Felisa Wolfe-Simon[6]

Abstract

Astrobiologists are aware that extraterrestrial life might differ from known life, and considerable thought has been given to possible signatures associated with weird forms of life on other planets. So far, however, very little attention has been paid to the possibility that our own planet might also host communities of weird life. If life arises readily in Earth-like conditions, as many astrobiologists contend, then it may well have formed many times on Earth itself, which raises the question whether one or more shadow biospheres have existed in the past or still exist today. In this paper, we discuss possible signatures of weird life and outline some simple strategies for seeking evidence of a shadow biosphere. Key Words: Weird life—Multiple origins of life—Biogenesis—Biomarkers—Extremophiles—Alternative biochemistry. Astrobiology 9, 241–249.

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An even more radical departure from known life would be organisms that employ a different set of elements from the familiar C, H, N, O, P, S set. One example that has received some attention (Wolfe-Simon *et al.*, 2009) is arsenic (As), which is chemically similar to phosphorus (P) and could substitute for it in some biochemical roles. The kinetic lability of the arsenic-oxygen bond makes it unlikely that arsenic could entirely replace the structure and function of phosphorus in nucleic acids, lipid membranes, and ATP; but it might serve a transient kinetic role in weird metabolism.

Davies, Paul CW, Steven A. Benner, Carol E. Cleland, Charles H. Lineweaver, Christopher P. McKay, and Felisa Wolfe-Simon. "Signatures of a shadow biosphere." *Astrobiology* 9, no. 2 (2009): 241-249. doi:10.1089/ast.2008.0251.

Sciencexpress Research Article

A Bacterium That Can Grow by Using Arsenic Instead of Phosphorus

Felisa Wolfe-Simon,[1,2*] Jodi Switzer Blum,[2] Thomas R. Kulp,[2] Gwyneth W. Gordon,[3] Shelley E. Hoeft,[2] Jennifer Pett-Ridge,[4] John F. Stolz,[5] Samuel M. Webb,[6] Peter K. Weber,[4] Paul C. W. Davies,[1,7] Ariel D. Anbar,[1,3,8] Ronald S. Oremland[2]

"…Here we describe a bacterium, strain GFAJ-1 of the Halomonadaceae, isolated from Mono Lake, CA, which substitutes arsenic for phosphorus to sustain its growth. Our data show evidence for arsenate in macromolecules that normally contain phosphate, most notably nucleic acids and proteins. Exchange of one of the major bio-elements may have profound evolutionary and geochemical significance."

Wolfe-Simon, Felisa, Jodi Switzer Blum, Thomas R. Kulp, Gwyneth W. Gordon, Shelley E. Hoeft, Jennifer Pett-Ridge, John F. Stolz et al. "A bacterium that can grow by using arsenic instead of phosphorus." *Science* 332, no. 6034 (2011): 1163-1166. doi: *10.1126/science.1197258.*

Wolfe-Simon, Felisa, Jodi Switzer Blum, Thomas R. Kulp, Gwyneth W. Gordon, Shelley E. Hoeft, Jennifer Pett-Ridge, John F. Stolz et al. "A bacterium that can grow by using arsenic instead of phosphorus." *Science* 332, no. 6034 (2011): 1163-1166. doi: *10.1126/science.1197258.*

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Arsenic(III) Fuels Anoxygenic Photosynthesis in Hot Spring Biofilms from Mono Lake, California

T. R. Kulp,[1] S. E. Hoeft,[1] M. Asao,[2] M. T. Madigan,[2] J. T. Hollibaugh,[3] J. C. Fisher,[3*] J. F. Stolz,[4] C. W. Culbertson,[5] L. G. Miller,[1] R. S. Oremland[1]†

Phylogenetic analysis indicates that microbial arsenic metabolism is ancient and probably extends back to the primordial Earth. In microbial biofilms growing on the rock surfaces of anoxic brine pools fed by hot springs containing arsenite and sulfide at high concentrations, we discovered light-dependent oxidation of arsenite [As(III)] to arsenate [As(V)] occurring under anoxic conditions. The communities were composed primarily of *Ectothiorhodospira*-like purple bacteria or *Oscillatoria*-like cyanobacteria. A pure culture of a photosynthetic bacterium grew as a photoautotroph when As(III) was used as the sole photosynthetic electron donor. The strain contained genes encoding a putative As(V) reductase but no detectable homologs of the As(III) oxidase genes of aerobic chemolithotrophs, suggesting a reverse functionality for the reductase. Production of As(V) by anoxygenic photosynthesis probably opened niches for primordial Earth's first As(V)-respiring prokaryotes.

Kulp, T. R., S. E. Hoeft, M. Asao, M. T. Madigan, J. T. Hollibaugh, J. C. Fisher, J. F. Stolz, C. W. Culbertson, L. G. Miller, and R. S. Oremland. "Arsenic (III) fuels anoxygenic photosynthesis in hot spring biofilms from Mono Lake, California." *Science* 321, no. 5891 (2008): 967-970.

Sciencexpress Research Article

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Figure S2 from Wolfe-Simon et al. removed due to copyright restriction.

See the supporting online material in Wolfe-Simon, Felisa, Jodi Switzer Blum, Thomas R. Kulp, Gwyneth W. Gordon, Shelley E. Hoeft, Jennifer Pett-Ridge, John F. Stolz et al. "A bacterium that can grow by using arsenic instead of phosphorus." *Science* 332, no. 6034 (2011): 1163-1166.
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Figure S2. 75As-:12C- versus 31P-:12C- ratio plot from GJAJ-1 cells by NanoSIMS. Data showing the relationships between As, P and C for GFAJ-1 cells grown +As/-P (open circles) and -As/+P (closed squares). Error bars represent 1 standard deviation of analytical variance during a single measurement.

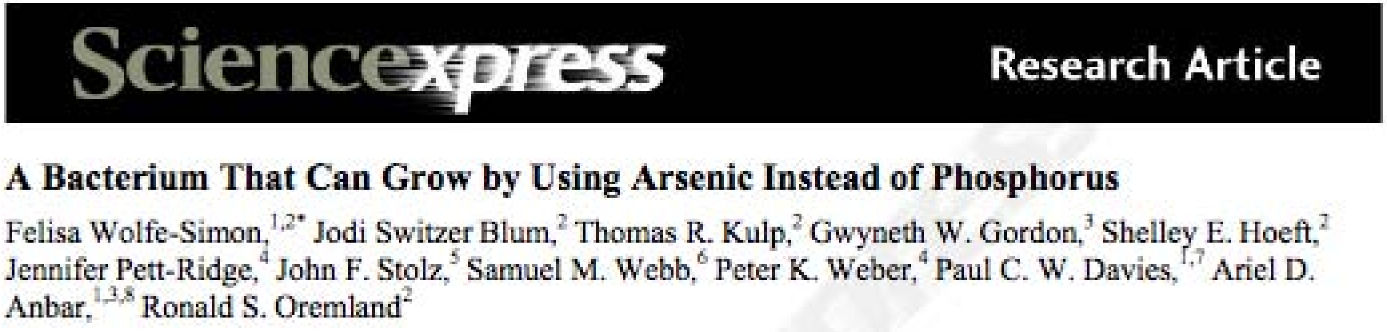
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Fig 2. NanoSIMS analyses of GFAJ-1: extracted DNA and whole cells elemental ratio maps. (A) Agarose gel loaded with DNA/RNA extracted from GFAJ-1 grown +As/-P (lane 2) and -As/+P (lane 3) as compared to a DNA standard (Lane 1). Genomic bands were excised as indicated and analysed by NanoSIMS. Ion ratios of 75As-:12C- of excised gel bands are indicated below with 2 sigma error shown (all values multiplied by 10-6). NanoSIMS images of whole GFAJ-1 cells grown either +As/-P (B, D, and F) or -As/+P (C, E, and G). The ion ratios of 75As-:12C- [(B) and (C)], 31P-:12C- [(D) and (E)], and secondary electron, SE [(F) and (G)]. Ratios in B, C multiplied by 10-4 and D, E multiplied by 10-3. The color bars indicate measured elemental ratios on a log scale as indicated. Length scale is as indicated on images (*11).*

Scientists see fatal flaws in the NASA study of arsenic-based life.

By Carl Zimmer

Posted Tuesday, Dec. 7, 2010, at 10:53 AM ET

On Thursday, Dec. 2, Rosie Redfield sat down to read a new paper called "A Bacterium That Can Grow by Using Arsenic Instead of Phosphorus." Despite its innocuous title, the paper had great ambitions. Every living thing that scientists have ever studied uses phosphorus to build the backbone of its DNA. In the new paper, NASA-funded scientists described a microbe that could use arsenic instead. If the authors of the paper were right, we would have to expand our notions of what forms life can take.

As soon as Redfield started to read the paper, she was shocked. "I was outraged at how bad the science was," she told me.

Redfield blogged a scathing attack on Saturday. Over the weekend, a few other scientists took to the Internet as well. Was this merely a case of a few isolated cranks? To find out, I reached out to a dozen experts on Monday.