12.842 / 12.301 Past and Present Climate
Fall 2008

The early geochemical evolution of the earth and the origin of life

12.842 Paleo Lecture 2

Formation of Atmosphere and Ocean

TWO HYPOTHESES

I. Internal: degassing of Earth's interior (volcanic gases)

II. External: comet impacts add H_2O, CO_2, and other gases

- Impact Degassing (Widely Accepted)

-Planetesimals rich in volatiles (H_2O, N_2, CH_4, NH_3) bombard Earth

-Volatiles accumulate in atmosphere

-Energy of impact + Greenhouse effect = Hot surface (>450 km impactor would evaporate ocean)

- Steam Atmosphere?

-Or alternating condensed ocean / steam atmosphere

- Heavy Bombardment (4.6-3.8 Byr BP)

-1st 100 Myr main period of accretion

Outgassing of radiogenic ^{40}Ar

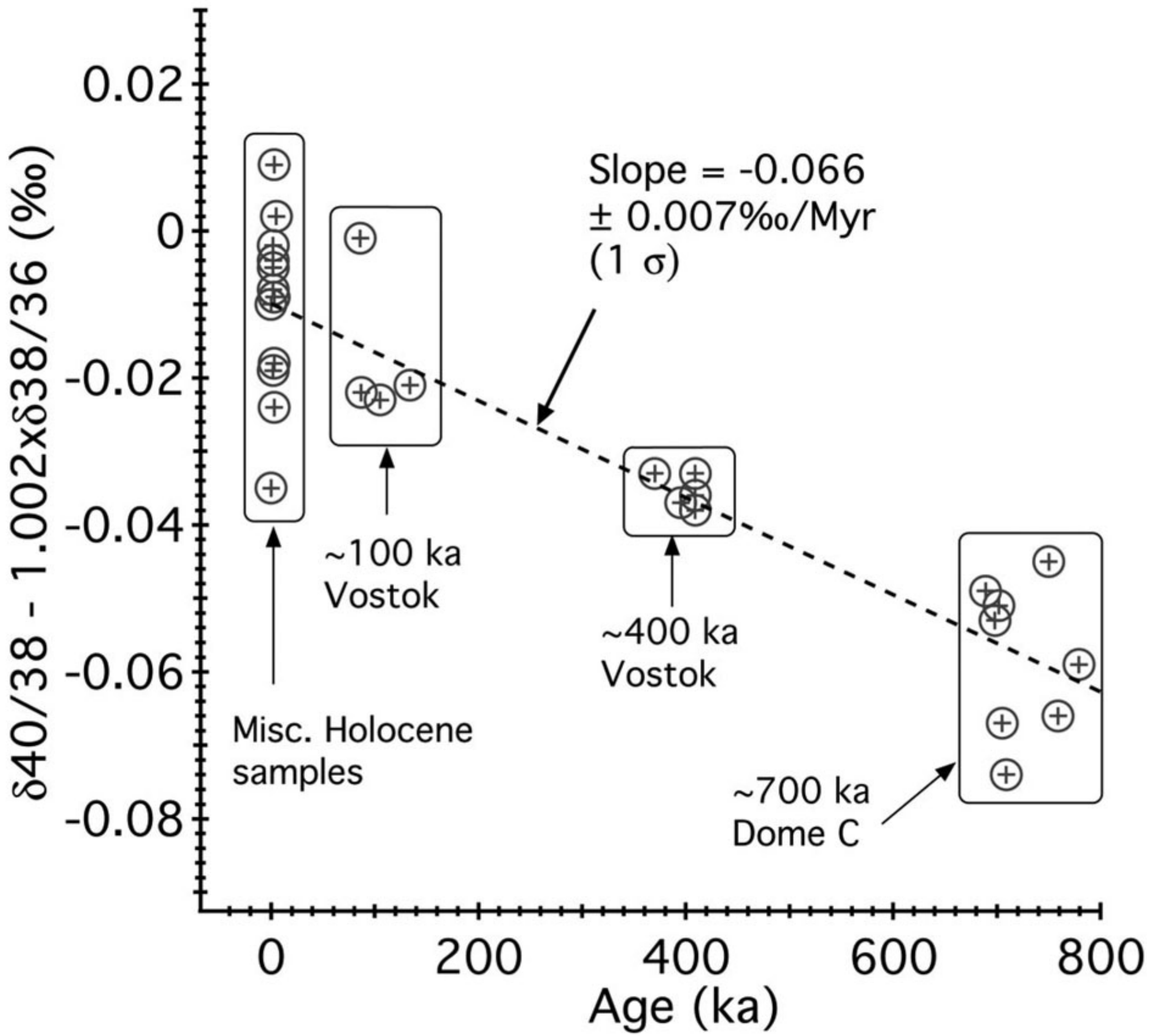

Fig. 1. Paleoatmospheric $\delta^{40/38}$Ar ratio plotted versus age.

Where did the water on earth come from?

Images removed due to copyright restrictions.
Citation: See the image of "an isotopic enigma" and the image of "water from meteors". Robert (2001) Science 293: 1056.

Earth's Early Atmosphere

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Composition of Earth's Early Atmosphere

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Allegre & Schneider (1994)

Geologic Evidence for the Antiquity of Life

Early Earth History

Image removed due to copyright restrictions.

Nisbet & Sleep (2001) "The habitat and nature of early life" *Nature* Vol. 409: 1083-1091.

Evolution of early life on earth

Image removed due to copyright restrictions.
Citation: Canfield (2005) Ann. Rev. Earth Planet. Sci. 33:1-38.

Summary of Geologic Evidence for the Antiquity of Life

- The lost record of the origin of life. ? Happened >3.5 Ga ?
  - –Oldest minerals – zircons 4.2 Ga
  - –Oldest terrestrial rocks 3.98 Ga (Bowring, MIT)
  - –Oldest putative microfossils – Warrawoona (Pilbara Craton) 3.5 Ga are contentious because of sedimentary relationships
  - –Next oldest known & convincing apparent microfossils from a hydrothermal vent in Western Australia's Pilbara craton 3.2 Ga
  - –Oldest molecular fossils ("biomarkers")-2.7 Ga (Brocks et al.)

Evidence from Zircons for Liquid Water 4.3 Ba

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Wilde et al., *Nature* (2001)

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

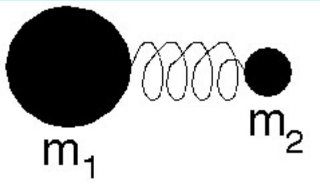
Image removed due to copyright restrictions.

Taylor & McLennan (1996) *Sci. Am.*, January 1996, 76-81.

Two geochemical tools:

1. Stable isotope ratios:

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{standard}} - 1\right] \times 1000$$



2. Triple stable isotope ratios:

$$\Delta^{33}S = \delta^{33}S - 0.515\ \delta^{34}S$$

detects mass-independent isotope fractionation

Global Carbon Isotope Balance

- Mantle carbon emitted by volcanoes has $\delta^{13}C = -5$ ‰
- Photosynthetic carbon (organic carbon) is depleted in ^{13}C ($\delta^{13}C \approx -15$ to -25 ‰)
- The carbon emitted from the mantle is proportioned into two sedimentary rock reservoirs: buried organic carbon ($\delta^{13}C \approx -20$‰) and inorganic carbonate ($\delta^{13}C \approx 0$‰).
- This proportionation follows the rule of isotopic mass balance:

$$\delta^{13}C_{mantle} = f_{organic}\delta^{13}C_{organic} + f_{carbonate}\,\delta^{13}{}_{carbonate}$$

where f = fraction of carbon in the sedimentary reservoir

- In recent geological history, this mass balance tells us that 20% of sedimentary carbon is organic carbon and 80% is inorganic carbonate.
- At times in the past, these proportions have fluctuated and are recorded in the sedimentary record.

Image removed due to copyright restrictions. Citation: Cover of *Nature*. Vol. 384, No. 6604, 1996.

S.J.Mojzsis et al. (1996), "Evidence for life on Earth before 3,800 million years ago" …based on isotopically light carbon in graphite from apatite in rocks on Akilia Island, SW Greenland.

But …

Sano et al. '99 report the apatite had U/Pb and Pb/Pb ages of only ~ 1.5 Ga.

And…

Geology Matters: 1

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Fedo & Whitehouse (2002) *Science*, Vol. 296:1448-1452.

Akilia Island, SW Greenland

•Evidence for life >3.85 Gyr ago from ^{13}C-depleted graphite
•Rocks interpreted to be sedimentary (Banded Iron Formations--BIFs).
(Mojzsis, 1996)

•BIFs formed early in Earth's history, supposedly by chemical precipitation and settling out of particles from seawater.
•Critical indicators of early life b/c they establish existence of liquid hydrosphere in a habitable T range.

•Re-mapping of Akilia Island & new petrologic & geochemical analyses do not support sedimentary origin for these rocks.
•They appear instead to be metasomatized ultramafic igneous rocks (<u>not</u> BIFs).
•Therefore highly improbable that they hosted life at the time of their formation.

Know Thy Rock: 1

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Citation: See Figure 1. Van Zuilen et al (2002) Nature Vol. 418:627-630.

- Carbonate in 3.8 Ga Isua (SW Greenland) rocks occurs in 3 distinct phases
- Likely formed during multiple injections of fluid across contacts between igneous ultramafic rocks and their host rocks.

Van Zuilen et al (2002)
Nature Vol. 418:627-630.

Know Thy Rock: 2

Metasomatism: introduction of elements into rock by circulating fluids

Image removed due to copyright restrictions. Citation: See Figure 3. Van Zuilen et al (2002) Nature Vol. 418:627-630.

- Graphite is associated primarily with the metacarbonate rocks, NOT with metasedimentary rocks.

- This suggests the reduced carbon formed by thermal disproportionation of the carbonates. E.g.,

$$\mathbf{6FeCO_3 \rightarrow 2Fe_3O_4 + 5CO_2 + C}$$

Van Zuilen et al (2002) *Nature* Vol. 418:627-630.

Know Thy Rock: 3

Image removed due to copyright restrictions.
Citation: See Figure 2.
Van Zuilen et al (2002)
Nature Vol. 418:627-630.

•Most of the reduced C (graphite) in the 3.8 Ga Isua rocks is in the metacarbonate phases and not the metasedimentary phases & likely formed by thermal disproportionation of the carbonate minerals at a later time.

•Most of the reduced C does not have the large ^{13}C-depletion expected from biological materials.
•The isotopically-depleted C is only found in the metasedimentary rocks, where it's concentration is very low & it may be contamination….

Van Zuilen et al (2002) *Nature* Vol. 418:627-630.

Know Thy Rock: 4

Image removed due to copyright restrictions.
Citation: See Figure 4. Van Zuilen et al (2002) Nature Vol. 418:627-630.

- The isotopically-depleted C in this 3.8 Ga Isua sample (of presumed biological origin) combusts at *low* T, suggesting it is unmetamorphosed recent organic material (i.e., contamination)

Bottom Line: No evidence for a Biogenic Origin of Reduced Carbon in 3.8 Ga Isua (SW Greenland) Rocks

A biogenic origin of graphite in carbonate-rich rocks in Isua[1–4] was inferred from the assumption that these rocks had a sedimentary origin. However, recent field and laboratory investigations have shown that most if not all carbonate in Isua is metasomatic in origin. Petrographic and isotopic analyses show that graphite in the metacarbonate rocks, serving as a basis for earlier investigations, is produced abiogenically by disproportionation of ferrous carbonate at high temperature and pressure and at a time later than the formation of the host rock. This type of graphite, including graphite inclusions in apatite, therefore cannot represent 3.8 Gyr-old traces of life. Stepped-temperature combustion accompanied by isotope

Van Zuilen et al (2002) *Nature* Vol. 418:627-630.

With the carbon isotopic evidence for life >/= 3.8 Ga now seriously challenged….

It's time to look at some fossil evidence for early life….

But don't be surprised to find plenty of controversy there too!

So jump ahead 300 Myr to 3.5 Ga…

Morphological Evidence for Antiquity of Life

WARRAWOONA PROKARYOTIC MICROFOSSIL PILBARA CRATON WA ~ 3.5 Ga (J.W. SCHOPF, 1983)

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Schopf's Apex 'microfossils' #1

Image removed due to copyright restrictions.
Citation: Figure 1. Schopf et al. (2002) Nature, vol. 416:73-76.

- Photo-montages of inferred microfossils from rocks ranging in age from 0.7-3.5 Ga.

Schopf et al. (2002) *Nature*, vol. 416:73-76.

Non-biologic Origin of 3.5 Gyr “Microfossils”?

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•Schopf’s “microfossils” seem to have formed hydrothermally (hot water + rock)

Gee (2002) *Nature*, 416:28.
Brasier et al. (2002) *Nature*, 416:76-81.

Questioning the authenticity of 3.465 Ga Apex fossils: 1

Image removed due to copyright restrictions.
Citation: Figure 1. Brasier et al. (2002) Nature, Vol. 416: 76-81.

- Rather than emanating from a sedimentary rock, the Schopf ‘microfossils’ came from a hydrothermal rock vein created by the interaction of hot rock + H_2O

Brasier et al. (2002) *Nature*, Vol. 416: 76-81.

Questioning the authenticity of 3.465 Ga Apex fossils: 2

"Many of these filamentous structures [from the apex chert] are branched or formed in ways not shown in the original descriptions because of the choice of focal depth and/or illustrated field of view."

Image removed due to copyright restrictions.
Citation: Figure 2. Brasier et al. (2002) Nature, Vol. 416: 76-81.

Questioning the authenticity of 3.465 Ga Apex fossils: 3

• It would appear as though Schopf (1993) “left out” some essential morphological features of his ‘microfossils’…

Image removed due to copyright restrictions.
Citation: Figure 3. Brasier et al. (2002) Nature, Vol. 416: 76-81.

Schopf's 'microfossils' #2: Raman Spectroscopy to the rescue?

D G

Images removed due to copyright restrictions.
Citation: Figures 2 & 3. Schopf et al. (2002) Nature, vol. 416:73-76.

- Raman spectra & spectral maps (G band) of 0.7-3.5 Ga 'microfossils'
- Indicates presence of reduced carbon (graphite) associated with 'microfossils'.

Questioning the authenticity of 3.465 Ga Apex fossils: 4

Brasier et al. (2002) *Nature*, Vol. 416: 76-81.

Image removed due to copyright restrictions.
Citation: Figure 4. Brasier et al. (2002) Nature, Vol. 416: 76-81.

- Unfortunately for Schopf et al., Raman spectra of dark specks within surrounding host (quartz) rock of Apex 'microfossils' give same Raman spectrum.
- The spectroscopic results therefore provide no support for the "biogenicity" of Schopf's 'fossils'.

Abiotic origin of microfossil-like structures #1

Image removed due to copyright restrictions.

Garcia Ruiz et al. (2002) *Astrobiology*, Vol. 2(3):353-369.

- Morphology is at best an ambiguous indicator of biogenicity.
- Evidenced here by inorganic aggregates precipitated from a simple solution of $BaCl_2$, Na_2SiO_3, NaOH

Abiotic origin of microfossil-like structures #2

Image removed due to copyright restrictions.

Garcia Ruiz et al. (2003) Science, Vol. 302: 1194-1197.

a,b: Apex chert (3.5 Ga, WA) microfilament images from Schopf et al (2002) & Brasier et al. (2002), respectively (10 µm and 40 µm scale bars, respectively).
C,d: SEM micrographs of self-assembled silica-carbonate aggregates (scale bars = 40 µm)

Abiotic origin of microfossil-like structures #3

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Garcia Ruiz et al. (2003) Science, Vol. 302: 1194-1197.

Above: Optical micrographs of silica-carbonate 'biomorphs' taken under same illumination (scale bars = 50 μm)
(a) As prepared; (b) after hydrothermal absorption of organics; (c) baked after exposure to organics (as in b).

Right: Raman spectra of (Top) heat-cured biomorph and (Bottom) Schopf et al. (2002) 3.5 Ga Apex microfilament.

So… morphology can be be a poor indicator of biogenicity.

As can Raman spectrospcopy.

And carbon isotopes.

Yet our quest for for evidence of life 3.5 Ga does not end here.

We need to take a look at… Stromatolites.

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Modern Living Stromatolites: Shark Bay, Australia

- Hamelin Pool's stromatolites result from the interaction between microbes, other biological influences and the physical and chemical environment.
- The cyanobacteria trap fine sediment with a sticky film of mucus that each cell secretes, then bind the sediment grains together with calcium carbonate which is separated from the water in which they grow. Because the cyanobacteria need sunlight to grow and they have the ability to move towards light, their growth keeps pace with the accumulating sediment.

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Stromatolites-2

Kona Dolomite (Michigan) 2.2 billion years old stromatolite fossil

Image removed due to copyright restrictions.

http://www.wmnh.com/wmel0000.htm

Schematic of stromatolite structure

Mary Ellen Jasper (Minnesota) 2.1 billion years old fossil stromatolite

Stomatolites are colonial structures formed by photosynthesizing cyanobacteria and other microbes. Cyanobacteria are prokaryotes (primitive organisms lacking a cellular nucleus) that thrived in warm aquatic environments and built reefs much the same way as coral does today.

An abiotic origin for stromatolites?

-->Grotzinger, J. and Rothman, D.H., "An abiotic model for stromatolite morphogenesis," *Nature*, 382, 423-425, October 3, 1996.

- Statistically feasible that the morphology of stromatolites can occur through non-biological processes.

-->Grotzinger & Knoll, 1999

- Argue that Archean stromatolites could be simple inorganic precipitates.

The majority view seems to be that stromatolites are the first good evidence for life, placing its origin in the vicinity of 3.5 Ga.

By 3.47 Ga there is additional evidence for microbial life in the form of isotopically-depleted sulfur minerals….

Microbial Activity ~3.47 Ga Suggested by Sulfur Isotopes

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Microbial sulphate reduction?

$$SO_4^{2-} + 2CH_2O = S^{2-} + 2CO_2 + 2H_2O$$

Shen et al (2001) *Nature*, Vol. 410:77-81)

By 3.5 Ga then there is evidence for life from stromatolites (Warrawoona, NW Australia) & isotopically-depleted sulfur in barite (N. Pole, Australia).

By 3.2 Ga there is new and different evidence for life… Only this time it did not form at the surface….

Rather microbial life seems to have evolved in a submarine thermal spring system…

3.2 Ga Hyperthermophilic Microbes from W. Australia

Filamentous microfossils in a 3,235-million-year-old volcanogenic massive sulphide deposit

Birger Rasmussen

Department of Geology and Geophysics, University of Western Australia, Nedlands, Western Australia 6907, Australia

Rasmussen (2000) *Nature*, Vol. 405:676-679.

Image removed due to copyright restrictions.
Citation: Figure 3. Rasmussen (2000) Nature, Vol. 405:676-679.

Location & Images of 3.2 Ga hydrothermal microbes

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Citation: Figures 1 & 2. Rasmussen (2000) Nature, Vol. 405:676-679.

Rasmussen (2000) *Nature*, Vol. 405:676-679.

By 2.7 Ga there is excellent evidence for both microbial life, eukaryotes & oxygenic photosynthesis from *molecular fossils*.

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•Archean Molecular 7 Ga Roy Hill Shale Fossils from the <u>PILBARA CRATON</u>

"Archean Molecular Fossils & The Early Rise of Eukaryotes"

Jochen J. Brocks, Graham A. Logan, Roger Buick & Roger E. Summons
***Science*, 285, 1033, 1999**

Will we ever find unambiguous evidence for life on earth?