Homework #5

Topics (choose 1): Describe criteria for biogenicity in microscopic fossils. How do the oldest describes fossils compare? Use this to argue one side of the Brasier-Schopf debate

OR

What are stromatolites; where are they found and how are they formed? Articulate the two sides of the debate on antiquity and biogenicity.

Up to 4 pages, including figures.

Due 3/31/2009
Need to know

• How C and S- isotopic data in rocks are informative about the advent and antiquity of biogeochemical cycles
• Morphological remains and the antiquity of life; how do we weigh the evidence?
• Indicators of changes in atmospheric pO$_2$
• A general view of the course of oxygenation of the atm-ocean system
Readings for this lecture


Nature and Habitats of Early Life

- Evidence for Earth’s earliest life forms and validity of that evidence
  - Stable isotopic tracers especially C & S
  - Microfossils
  - Stromatolites

- Facts about redox couples
- Consequences of oxygenic photosynthesis? Respiration
- Early record of preserved organic carbon and carbon isotopes
- Early record of molecular oxygen in the environment

- The Earliest Biogeochemical Cycles
Oldest Microfossils on Earth?

Warrawoona Group, N. Pole Dome/ Marble Bar, WA; 3.5 Ga

Lowe & Hoffman stromatolite

Courtesy Joe Kirschvink, CalTech

Courtesy of Joe Kirschvink. Used with permission.
3.5-2.3 Ga Pilbara Craton, NW Australia

### Zircon age of host rock
- 3,458 million years
- 3,465 million years
- 3,468 million years
- 3,469 million years
- 3,515 million years

### Stratigraphy of the North Pole area
- Euro Basalt
- Strelley pool chert
- Panorama Formation
- Apex Basalt
- Chert
- Dresser formation
- Talga Talga Subgroup
- Coonterunah group

### Fossils
- Trendall locality stromatolites (best preserved)
- Schopf locality microfossils
- Awramik locality microfossils
- North Pole stromatolites (first discovery)

### Precise age from U-Pb isotope geochronology
(accurate to about 3 million years)

### Figure by MIT OpenCourseWare.
Black Chert Breccia

black chert veins and clasts

Complex ‘Dyke’ Breccia
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- In shards, clasts  ○ Around shards, clasts  ■ In matrix  □ In veins
* Arsenic-rich
A-C, Fabrics recognized in thin section  Open box, not analysed

Figure by MIT OpenCourseWare. After Brasier et al., 2002.
WARRAWOONA PROKARYOTIC MICROFOSSIL
PILBARA CRATON WA ~ 3.5 Ga (J.W. SCHOPF, 1983)

Image removed due to copyright restrictions.
Image of the original Warrawoona microfossil (J.W. Schopff, 1983).
What Constitutes Compelling Evidence?

- Geologic source of material and probable age limits well-defined... eg pedigree and a sediment and not an igneous rock!
- Provenance of several comparably-aged assemblages similarly well established
- Fossils demonstrably indigenous to, and syngenetic, with deposition
- Demonstrably biogenic
  - ‘biological’ size distribution
  - morphologically comparable to specific modern taxa

from: Schopf, Hayes and Walter, Ch 15 Earth’s Earliest Biosphere, 1983
Text and image removed due to copyright restrictions.
Fig. 1. Optical images (column 1), Raman images (column 2), and spectral bands used for Raman imaging (column 3) of permineralized carbonaceous fossils at or near the upper surfaces of polished chert thin sections: (A) Cell wall in the conductive tissue (lignified xylem) of an aquatic fern cf. *Dennstaedtia* from the essentially unmetamorphosed 45-Ma-old Clarno Formation of Oregon. (B) Tangential section of the tubular sheath of a *Lyngbya*-like oscillatoriacean cyanobacterium in a conical stromatolite (*Conophyton gaubitza*) from the subgreenschist facies 650-Ma-old Chichkan Formation of Kazakhstan. (C) Transverse cell wall of a broad cellular trichome (*Gunflintia grandis*), and (D) a narrow prokaryotic filament (*G. minuta*), in domical stromatolites of the greenschist facies 2,100-Ma-old Gunflint Formation of Ontario, Canada. Each Raman image was produced by combining several hundred pixel-assigned point spectra ("spexels"), like those shown for each specimen in column 3, acquired over a small square part of the total area analyzed. The resolution of the Raman images is defined by the pixel dimensions of their component spexels; for A-C, 2 µm per pixel, and for D, 0.5 µm per pixel.


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Text and images removed due to copyright restrictions.
Laser–Raman spectroscopy (Communication arising): Images of the Earth's earliest fossils?
Jill Dill Pasteris and Brigitte Wopenka

Abstract

Text removed due to copyright restrictions.
(Abstract of above article).
Raman imagery: a new approach to assess the geochemical maturity and biogenicity of permineralized precambrian fossils.

Schopf JW, Kudryavtsev AB, Agresti DG, Czaja AD, Wdowiak TJ.

Laser-Raman imagery is a non-intrusive, non-destructive analytical technique, recently introduced to Precambrian paleobiology, that can be used to demonstrate a one-to-one spatial correlation between the optically discernible morphology and kerogenous composition of permineralized fossil microorganisms. Made possible by the submicron-scale resolution of the technique and its high sensitivity to the Raman signal of carbonaceous matter, such analyses can be used to determine the chemical-structural characteristics of organic-walled microfossils and associated sapropelic carbonaceous matter in acid-resistant residues and petrographic thin sections. Here we use this technique to analyze kerogenous microscopic fossils and associated carbonaceous sapropel permineralized in 22 unmetamorphosed or little-metamorphosed fine-grained chert units ranging from approximately 400 to approximately 2,100 Ma old.

Courtesy of Mary Ann Liebert, Inc. Used with permission.
The lineshapes of the Raman spectra acquired vary systematically with five indices of organic geochemical maturation: (1) the mineral-based metamorphic grade of the fossil-bearing units; (2) the fidelity of preservation of the fossils studied; (3) the color of the organic matter analyzed; and both the (4) H/C and (5) N/C ratios measured in particulate kerogens isolated from bulk samples of the fossil-bearing cherts. Deconvolution of relevant spectra shows that those of relatively well-preserved permineralized kerogens analyzed in situ exhibit a distinctive set of Raman bands that are identifiable also in hydrated organic-walled microfossils and particulate carbonaceous matter freed from the cherts by acid maceration. These distinctive Raman bands, however, become indeterminate upon dehydration of such specimens. To compare quantitatively the variations observed among the spectra measured, we introduce the Raman Index of Preservation, an approximate measure of the geochemical maturity of the kerogens studied that is consistent both with the five indices of organic geochemical alteration and with spectra acquired from fossils experimentally heated under controlled laboratory conditions. The results reported provide new insight into the chemical-structural characteristics of ancient carbonaceous matter, the physicochemical changes that accompany organic geochemical maturation, and a new criterion to be added to the suite of evidence by which to evaluate the origin of minute fossil-like objects of possible but uncertain biogenicity.
FIG. 4. Areas of the fossils outlined by white rectangles in Fig. 3, shown here in digitized images (denoted by suffix “1”) and Raman images of the same areas (denoted by suffix “2”), with the prefix letters indicating the geologic source of the fossils as indicated in Figs. 3 and 9.


 Courtesy of Mary Ann Liebert, Inc.
 Used with permission.
Pick the Fossils?

Images removed due to copyright restrictions.

Photographs of real fossils alongside photos of nonliving microstructures that resemble fossils.
Self-Assembled Silica-Carbonate Structures and Detection of Ancient Microfossils
Juan M. Garcia-Ruiz, Stephen T. Hyde, A. M. Carnerup, A. G. Christy, M. J. Van Kranendonk and N. J. Welham

Text removed due to copyright restrictions.
Article abstract.
Self-Assembled Silica-Carbonate Structures and Detection of Ancient Microfossils
Juan M. Garcia-Ruiz, Stephen T. Hyde, A. M. Carnerup, A. G. Christy, M. J. Van Kranendonk and N. J. Welham

Fig. 2. Comparison of synthetic filaments with purported ancient microfossils. (A to D) FESEM images of inorganic in vitro filaments. (A), (B), and (D) As-prepared filaments, containing silica and witherite. [Adapted with permission from \(12\).] (C) Bare barium carbonate (witherite) crystallite aggregate after dissolution of silica in mild alkaline solution. (D) Silica skin, coating the exterior of the aggregates. (E and F) Microfilaments found in the Warrawoona chert. [(E) Adapted with permission from \(6\); (F) adapted with permission from \(19\).] (G to I) Optical micrographs of synthetic filaments, showing the progressive dissolution of the solid (witherite) interior of the biomorphs in dilute ethanoic acid, leaving a hollow silica membrane whose morphology is that of the original witherite-silica composite. [Adapted with permission from \(12\).] Scale bars in (A) and (B), 40 µm; in (C), 10 µm; in (D), 4 µm; in (F) to (I), 40 µm [(G) and (I) are at the same magnification as (H)]. A more detailed sequence is available in movie S3.
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Fig. 3. (A to C) Optical micrographs of the silica-witherite structure before and after exposure to organic species, all taken under identical illumination. (A) Inorganic structure as prepared. (B) Structure after hydrothermal adsorption of organics. (C) Cured material produced by baking the sample that was preexposed to the organic mixture [as in (B)]. Scale bars, 50 µm. (D) (Upper curve) Raman spectrum of heatcured biomorphs (similar to Fig. 3C) compared with kerogen-like Raman spectrum reported by Schopf et al. (lower curve), collected from a microfilament in the Archean Warrawoona chert [reproduced with permission from fig. 3H of (6)]
3.2 Ga Hyperthermophilic Microbes from W.Aust. Rasmussen 2001

Image removed due to copyright restrictions.

Putative cyanobacteria and anaerobic bacteria from the 3.1 Gy Fig Tree Group overlying the Swaziland Group of South Africa.
Barghoorn, E.S. and Tyler, S.A.

Schopf, J.W.
The oldest unequivocal visible remains of a diversity of microorganisms occur in the 2.0 BYO Gunflint Chert of the Canadian Shield.

Images removed due to copyright restrictions.

Gunflint Chert Fossils. A-C. blue-green algae; *Animikia, Entosphaeroides*, and *Gunflintia*; *D. Huroniospora*, an algal spore; *E. Gunflintia* and *Hurionospora*; *F. Euastrion*, a bacterium, and enigmatic forms, *G. Kakabekia*; *H. Eosphaera*.
Stromatolites

Images removed due to copyright restrictions.

Photographs of stromatolites. See these examples:
http://upload.wikimedia.org/wikipedia/commons/1/1b/Stromatolites_in_Sharkbay.jpg
http://upload.wikimedia.org/wikipedia/commons/0/02/Lake_Thetis-Stromatolites-LaRuth.jpg

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Conical stromatolites
Domical stromatolites
Precise age from U-Pb isotope geochronology (accurate to about 3 million years)
Microfossils


Figure by MIT OpenCourseWare.
‘Classic’ picture of stromatolites, Telegraph Station, Hamelin Pool WA. These are effectively stranded above high water and ‘dead’.

1m domal subtidal stromatolites, Carbla Point, Hamelin Pool

‘Reef’ of 1m stromatolites, Carbla Point
Examples of 800 million year-old stromatolites from the Officer Basin, Western Australia.

**LEFT:** *Acaciella australica* - a form with narrow columns in bioherms up to 1 metre in diameter.

**ABOVE:** *Baicalia burra* - a form with broad, irregular branching columns
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- Conical stromatolites
- Domical stromatolites
- Precise age from U-Pb isotope geochronology (accurate to about 3 million years)
- Microfossils

**Warrawoona Group**

3.5-3.4 Ga volcanics & sediments

Figure by MIT OpenCourseWare.
Warrawoona Stromatolites Are Perhaps the Oldest Evidence for Life on Earth.

Adapted from The Carl Sagan Lecture by Joe Kirschvink

http://www.gps.caltech.edu/users/jkirschvink/

Grotzinger & Knoll ’99 argue that Archean stromatolites could be simple inorganic precipitates!
cones ca 1m high with lensoid laminae

Image removed due to copyright restrictions.

Stromatolite photograph.
**RIGHT:** Detail of a branching column formed on the side of a stromatolite cone. Complex structures such as these rule out formation by means such as the folding of soft sediments.

**LEFT:** The outcrop of "egg-carton" stromatolites when first discovered, before removal of the overlying rocks.

(Click to enlarge.)

**RIGHT:** The "egg-carton" rock face after the overlying rocks were removed. Although today the "egg-cartons" are tilted at an angle of about 70 degrees, they were originally flat lying.
Large Domical Stromatolite
Dresser Fm
Large Dresser Fm dome from above
Wave ripples
Dresser Fm
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- Precise age from U-Pb isotope geochronology (accurate to about 3 million years)
- Microfossils

Figure by MIT OpenCourseWare.
Oldest Marine Transgression??

Domal stromatolite growing on in situ pebbles of Marble Bar Chert
Mathematical models have ... been used to cast doubt on the biotic origin of stromatolites. Here ... we propose a biotic model for stromatolite morphogenesis which considers the relationship between upward growth of a phototropic or phototactic biofilm ($v$) and mineral accretion normal to the surface ($\lambda$). These processes are sufficient to account for the growth and form of many ancient stromatolites. Domical stromatolites form when $v \leq \lambda$. Coniform structures with thickened apical zones, typical of Conophyton, form when $v >> \lambda$. More angular coniform structures, similar to the stromatolites claimed as the oldest macroscopic evidence of life, form when $v >>> \lambda$.


Variation modeled by two processes, upward growth and vertical accretion, applied at different rates.
Biogeochemical Redox Couples

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \\
\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \\
\text{CO}_2 + 2\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
\text{CO}_2 + \text{HS}^- + \text{H}_2\text{O} \rightarrow \text{biomass} + \text{SO}_4^{2-}
\]

- Oxygenic photosynthesis
- Interdependency?
- Aerobic respiration
- Methanogenesis
- Oxidative methanotrophy
- Anoxygenic photosynthesis
The electron tower...........

Strongest reductants, or e donors, on top LHS

Electrons ‘fall’ until they are ‘caught’ by available acceptors

The further they fall before being caught, the greater the difference in reduction potential and energy released by the coupled reactions

Note electron fall from CH₂O to O₂ is the among the largest here

\[ \Delta G = \Delta G^\circ (T) + RT \cdot \ln K \]

Adapted from TheCarlSaganLecture By Joe Kirschvink

http://www.gps.caltech.edu/users/jkirschvink/
Biogeochemical Redox Couples

aerobic respiration

\[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

- 1 mole glucose $\rightarrow$ 32 mole ATP

- 1 mole glucose $\rightarrow$ 2-4 mole ATP

Biosynthesis requires approx. 1 mole ATP per 4g of cell carbon
Biogeochemical Redox Couples

oxygenic photosynthesis

CO$_2$ + H$_2$O $\rightarrow$ CH$_2$O + O$_2$
\(^{13}\text{C} \) Evidence for Antiquity of Earthly Life

Figure by MIT OpenCourseWare.
Biogeochemical Redox Couples

oxygenic photosynthesis

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \]
<table>
<thead>
<tr>
<th>AGE (Ga)</th>
<th>4</th>
<th>3</th>
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<tr>
<td>Banded Iron Formations</td>
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<td><img src="image2" alt="Graph" /></td>
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<td><img src="image4" alt="Graph" /></td>
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<td>Conglomeratic Au and U</td>
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<td><img src="image7" alt="Graph" /></td>
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<td>Bedded Cu in clastic strata ‘Red-Bed Cu’</td>
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</tbody>
</table>

(Adapted from Lambert & Groves, 1981)
A Typical Banded Iron Stone (BIF)

Image courtesy of William Schopf. Used with permission.

Courtesy of Joe Kirschvink. Used with permission.
Precambrian Banded Iron Formations (BIFs) (Adapted from Klein & Beukes, 1992)

Time Before Present (Billion Years)

Canadian Greenstone Belts & Hamersley, W. Australia
Yilgaran Block, W. Australia
Transvaal, S. Africa
Pongola Glaciation, Swaziland (snowball??)
Zimbabwe, Ukraine, Venezuela, W. Australia
Isua, West Greenland
Krivoy Rog, Russia
Lake Superior, USA
Labrador, Canada
Neoproterozoic Snowball Earths
Rapitan, Canada
Urumuc, Brazil
Damara, Namibia

Abundance of BIF Relative to Hamersly Group as Max.

Courtesy of Joe Kirschvink, CalTech
Pyrite ($\text{FeS}_2$) is Unstable in $\text{O}_2$-Rich Environments
Multicellular Algal Fossils--2.1 Ga

_Grypania:_ genus of coiled multicellular eukaryotic algae. From 2.1 Ga rocks in Michigan.

Stanley (1999)
Likely sequence of critical evolutionary events leading to multicellular forms

- Eukaryotes likely arose from union of two prokaryotic cells.
- Internalized cell became mitochondrion (where E from food derived by respiration).
- DNA & RNA in mitochondrion is different than in surrounding cells.
- Protozoan consumed & retained cyanobacterium that became chloroplast.
- Chloroplasts contain own DNA & RNA (like mitochondrion) and are remarkably similar to cyanobacteria.

Stanley (1999)
Life’s History on Earth

- **Prokaryote World**
- **First Eukaryotes**
- **First Invertebrates**
- **Multi-cell Life**
- **Humans**

**PO₂ (atm)**

**Time before Present (Ga)**

Images removed due to copyright restrictions.
Steroids and O$_2$

Jahnke & Klein 1983 showed epoxidase synthesis stimulated at 0.03% (c. 300nM)

Need to determine the levels of dissolved O$_2$ which enables these steps in living cells
Multiple sulfur isotopes

$\delta^{33}S = 0.515 \delta^{34}S, \delta^{36}S = 1.91 \delta^{34}S$
Mass-independent isotopic signatures for $\delta^{35}S$, $\delta^{34}S$, and $\delta^{36}S$ from sulfide and sulfate in Precambrian rocks indicate that a change occurred in the sulfur cycle between 2090 and 2450 million years ago (Ma). Before 2450 Ma, the cycle was influenced by gas-phase atmospheric reactions. These atmospheric reactions also played a role in determining the oxidation state of sulfur, implying that atmospheric oxygen partial pressures were low and that the roles of oxidative weathering and of microbial oxidation and reduction of sulfur were minimal. Atmospheric fractionation processes should be considered in the use of sulfur isotopes to study the onset and consequences of microbial fractionation processes in Earth's early history.

Mass Independent Fractionation

New insights into Archean sulfur cycle from mass-independent sulfur isotope records from the Hamersley Basin, Australia

Shuhei Ono b,c, Jennifer L. Eigenbrode b, Alexander A. Pavlov c, Pushker Kharecha b, Douglas Rumble III a, James F. Kasting b, Katherine H. Freeman b

Fig. 3. A conceptual model of Archean sulfur cycle. Photochemistry in the atmosphere causes MIF in sulfur isotopes, and aerosols of S8 and H2SO4 carry sulfur with positive (*S) and negative (#S) v33S signatures, respectively. The preservation of MIF signatures in the sediments implies incomplete oxidation of S8 in the ocean (dashed arrow).

Mass Independent Fractionation

Data from 3.3-3.5 Ga sedimentary sulfides and sulfates. All Phanerozoic sulfides and sulfates plot along the MFL line.

Figure by MIT OpenCourseWare. After Farquhar et al., 2001.
Mass-Independent Fractionation of Sulfur Isotopes in Archean Sediments: Strong Evidence for an Anoxic Archean Atmosphere
A.A. PAVLOV and J.F. KASTING ASTROBIOLOGY Volume 2, Number 1, 2002
Sulfur Isotopic Evidence for $O_2$

Image removed due to copyright restrictions.

Conundrum: If oxygen-producing photosynthesis was occurring by 3.5-2.7 Ga, why doesn’t free O$_2$ appear until 2.3 Ga, a 1200-400 Myr delay?

The BIG question in geobiology today!!
Conundrum: If oxygen-producing photosynthesis was occurring by 3.5-2.7 Ga, why doesn’t free O2 appear until 2.3 Ga, a 1200-400 Myr delay?

**Sources**
- Photosynthesis
- Hydrogen escape

**Vs.**

**Sinks**
- Respiration
- Reduced minerals in rocks
- Reduced volcanic gases
- Reduced hydrothermal vent fluids