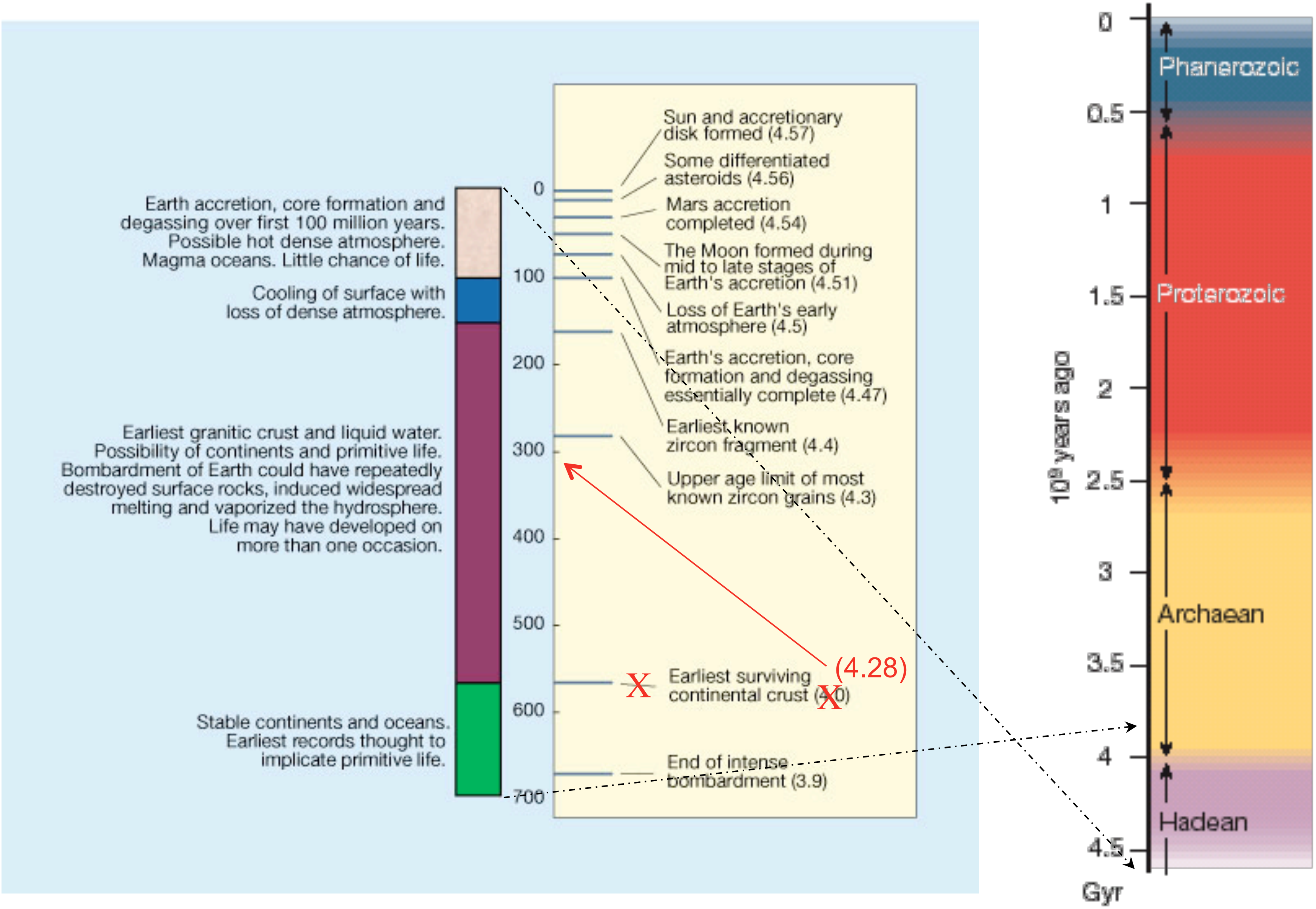
Geologic Evidence for the Antiquity of Life

OCEAN 355, Prof. Julian Sachs, Lecture Notes #3

J.W. Schopf, 1983

Early Earth History & Time Scale



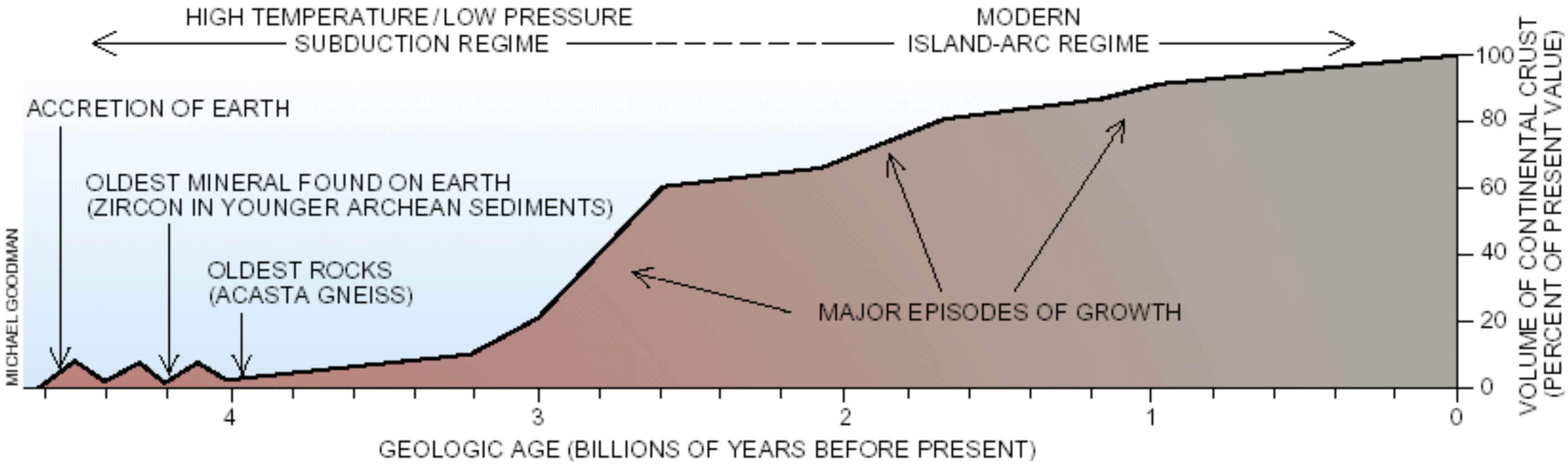
O'Neil et al. (2008) *Science*, Vol. 321: 1828-1831 (Sept. 26, 2008)

Summary of Geologic Evidence for the Antiquity of Life

- ✓ Earth formed 4.567 Ga
- ✓Oldest minerals - zircons 4.4 Ga
- ✓ Evidence for liquid water 4.3 Ga - $^{18}O/^{16}O$ in zircons
- ✓ Oldest terrestrial rocks 4.28 Ga; cooked
- ✓ Oldest microfossils 3.5 Ga - Western Australia's Pilbara Craton (Warrawoona); contentious
- ✓ Next oldest known & convincing microfossils from a 3.2 Ga hydrothermal vent setting in Pilbara craton
- ✓ Oldest molecular fossils ("biomarkers") 2.7 Ga
- ✓ Humans begin to ask this question 0.00001 Ga ?

Origin and Early Evolution of Life

- The lost record of the origin of Life?
- Few crustal rocks from > 3 Ga
- Half life of sediments 100-200 Ma 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.

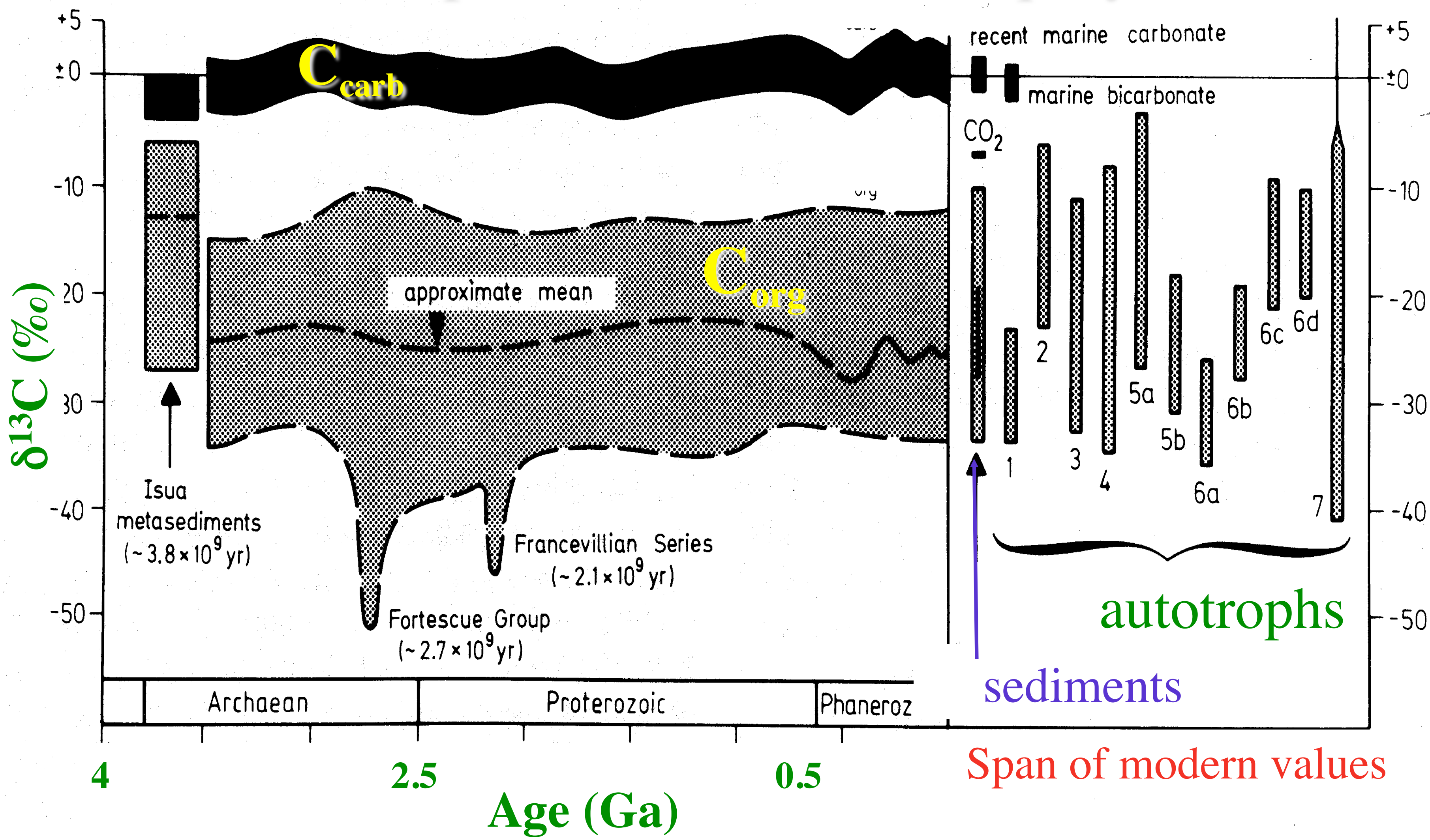
Taylor & McLennan (1996)

The Inhospitable Hadean Eon (4.6-3.8 Ga)

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**. 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.

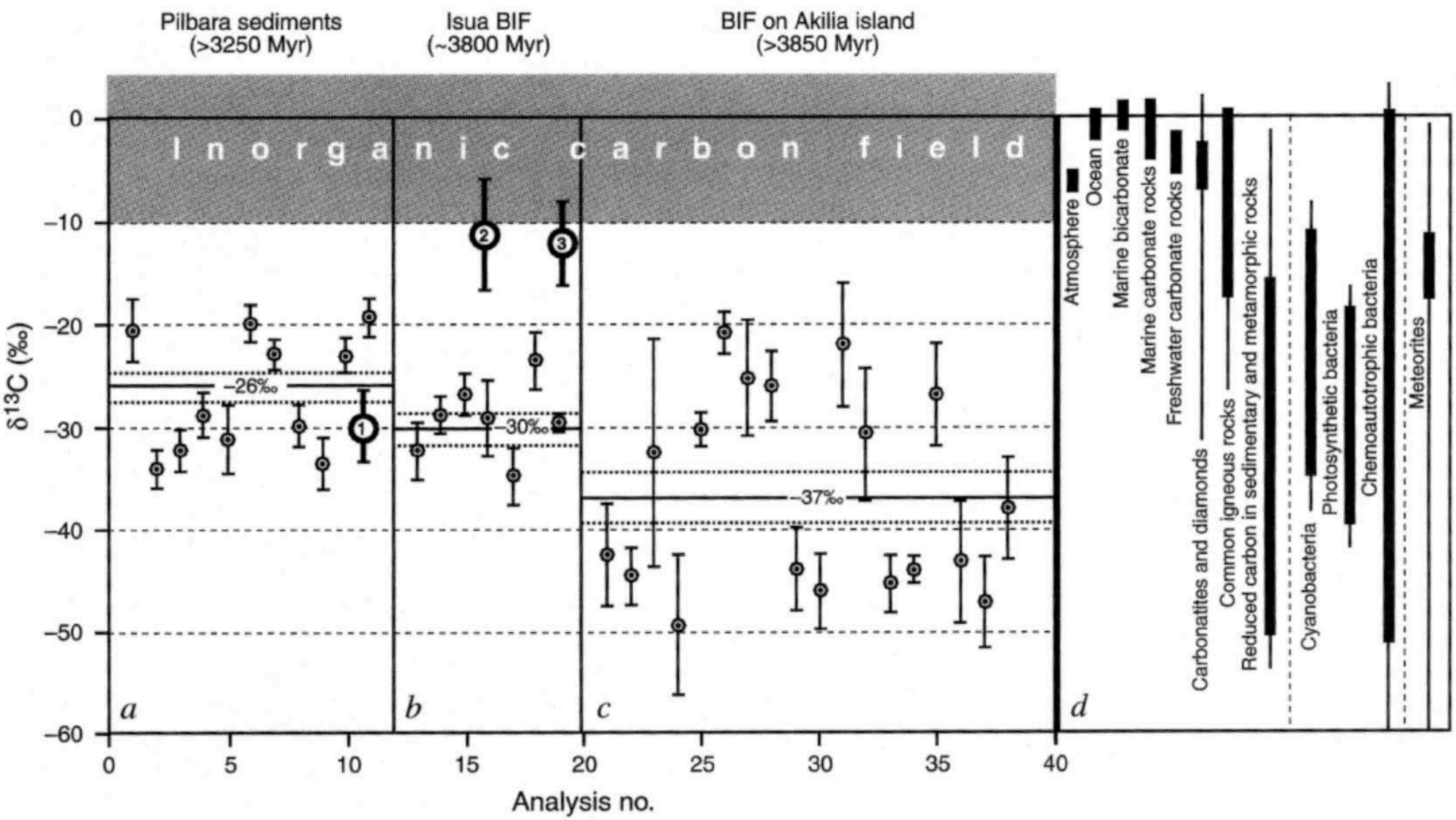
Zahnle (2001) The Hadean Atmosphere, *EOS*, AGU Fall Mtg, U51A-10

Carbon Isotope Evidence for Antiquity of Life

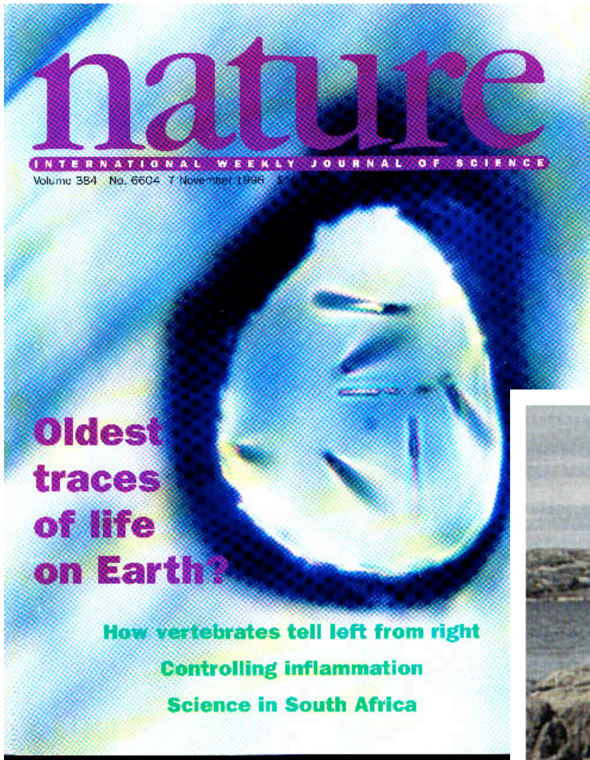


- $\delta^{13}C = [(^{13}C/^{12}C_{smpl} - {}^{13}C/^{12}C_{std}) / {}^{13}C/^{12}C_{std}] * 1000‰$
- $^{12}C = 98.93\%$, $^{13}C = 1.07\%$
- Plants & Phytoplankton preferentially take up ^{12}C relative to ^{13}C when they use CO_2 & HCO^-

Carbon Isotopic Evidence for Life >3.85 Ga



Mojzsis et al. (1996) Evidence for life on Earth before 3,800 million years ago. *Nature*, Vol. 384: 55-59.



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.

A chip off the old block. A geologist's hammer leans against the oldest-known sediments in the world, on the bleak Akilia island off the Greenland coast. Despite metamorphism, they show signs of ancient life.

Mojzsis et al. (1996) *Nature*, Vol. 384: 55-59.

Hayes (1996) *Nature* Vol. 384: 21-22.

3.85 Ga Akilia Rocks

Partially metamorphosed Banded Iron Formation (BIF)

- Carbonaceous (graphite) inclusions within grains of apatite (calcium phosphate)
- Organic carbon?
- Remnant of life?

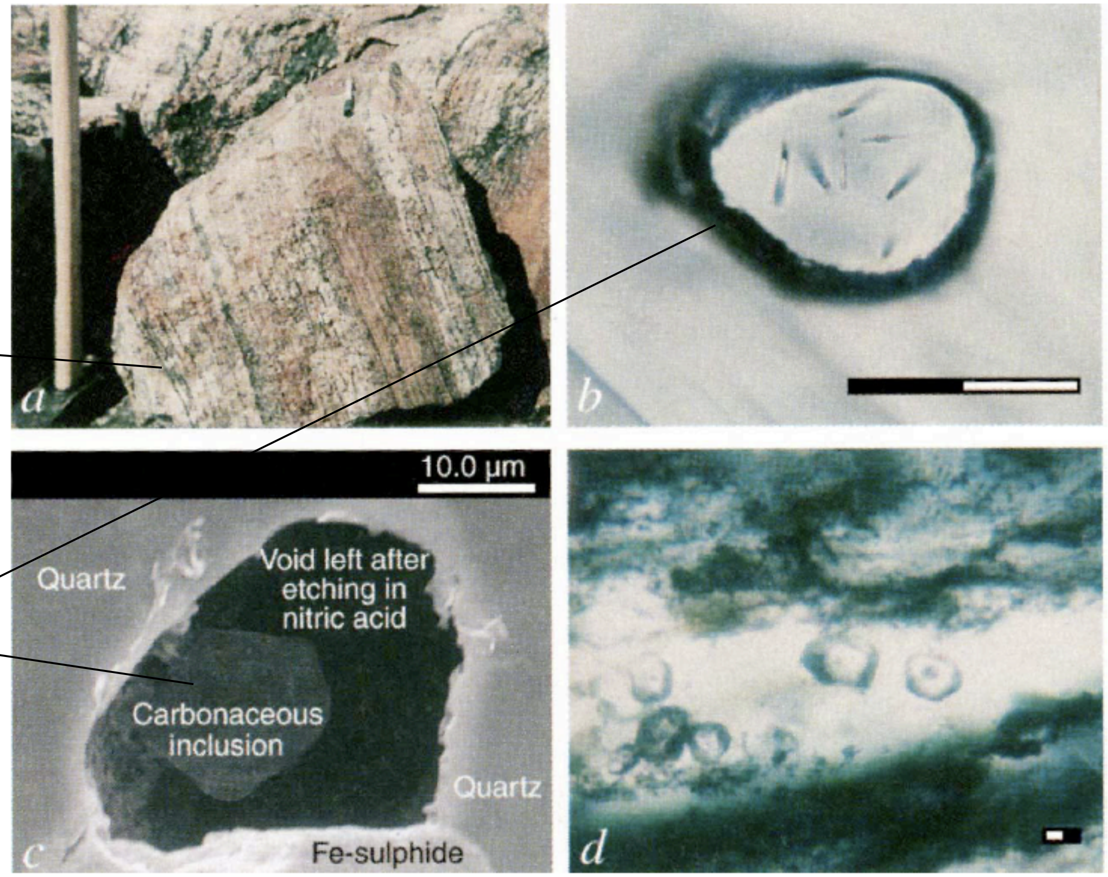
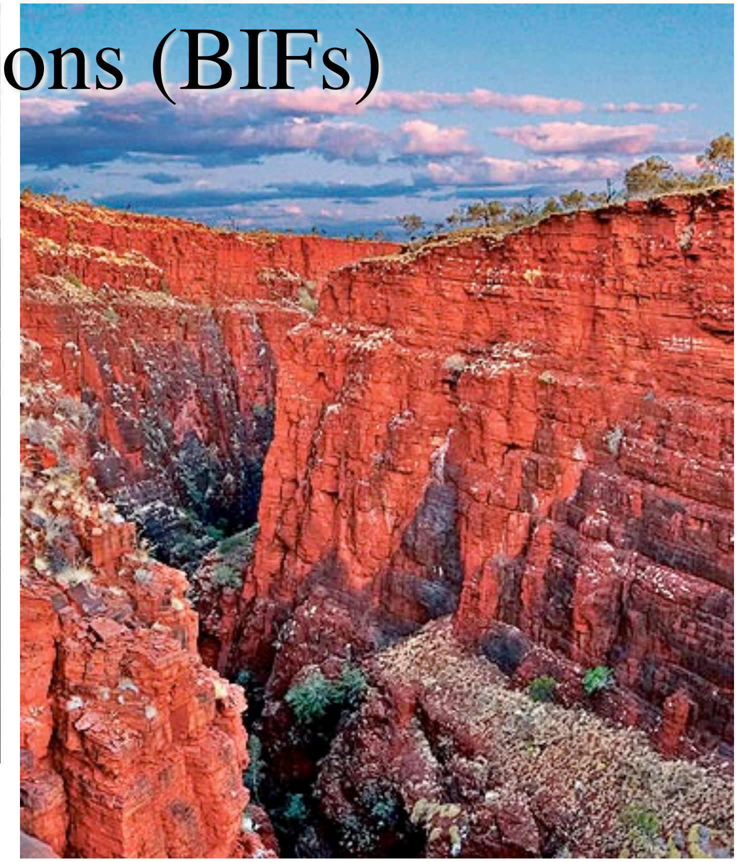


FIG. 1 *a*, Field exposure of the ⩾3,850-yr-old Akilia island BIF[3] (collected 150 km south of Isua, 63° 55′ 40″ N, 51° 41′ 30″ W; photograph by A. Nutman) in southern West Greenland. Finely alternating bands of magnetite (dark) and silicates (light) are evident on the broken-off boulder which is part of a ~5-m-thick section of BIF (background) on the island; the rock hammer is ~40 cm tall. *b*–*d*, micrographs of anhedral, oblate apatite grains and associated carbon in early Archaean BIF. *b*, View of an apatite crystal in amphibole (grunerite), from the Akilia island BIF. The apatite was etched in 2% HNO_3 (120 s at room temperature) to uncover an envelope of opaque carbonaceous matter at the grain boundary; linear features in the crystal are fission tracks from the decay of intrinsic radionuclides revealed by the etching process (*b* and *d* are optical micrographs in transmitted light, oil immersion lens, plane polarized). *c*, Scanning electron micrograph of void left after treating apatite in 2% HNO_3 (1,800 s at room temperature), revealing an acid-resistant carbonaceous inclusion (centre) typical of those analysed by ion microprobe. *d*, Quartzitic microband from the Pilbara craton sediments, Western Australia, containing groupings of apatites with cores of organic matter along thin laminae of organic rich chert. Scale bars in *b* and *d*, 20 µm: scale bar in c, 10 µm.

Mojzsis et al. (1996) *Nature*, Vol. 384: 55-59.

Banded Iron Formations (BIFs)

Iron Ore Mine, W. Australia



- Most BIFs > 1.9 Ga
- Laminated sedimentary rocks
- Alternating layers of magnetite / hematite & chert (SiO_2)
- Most Fe in steel comes from BIFs in Canada & Australia

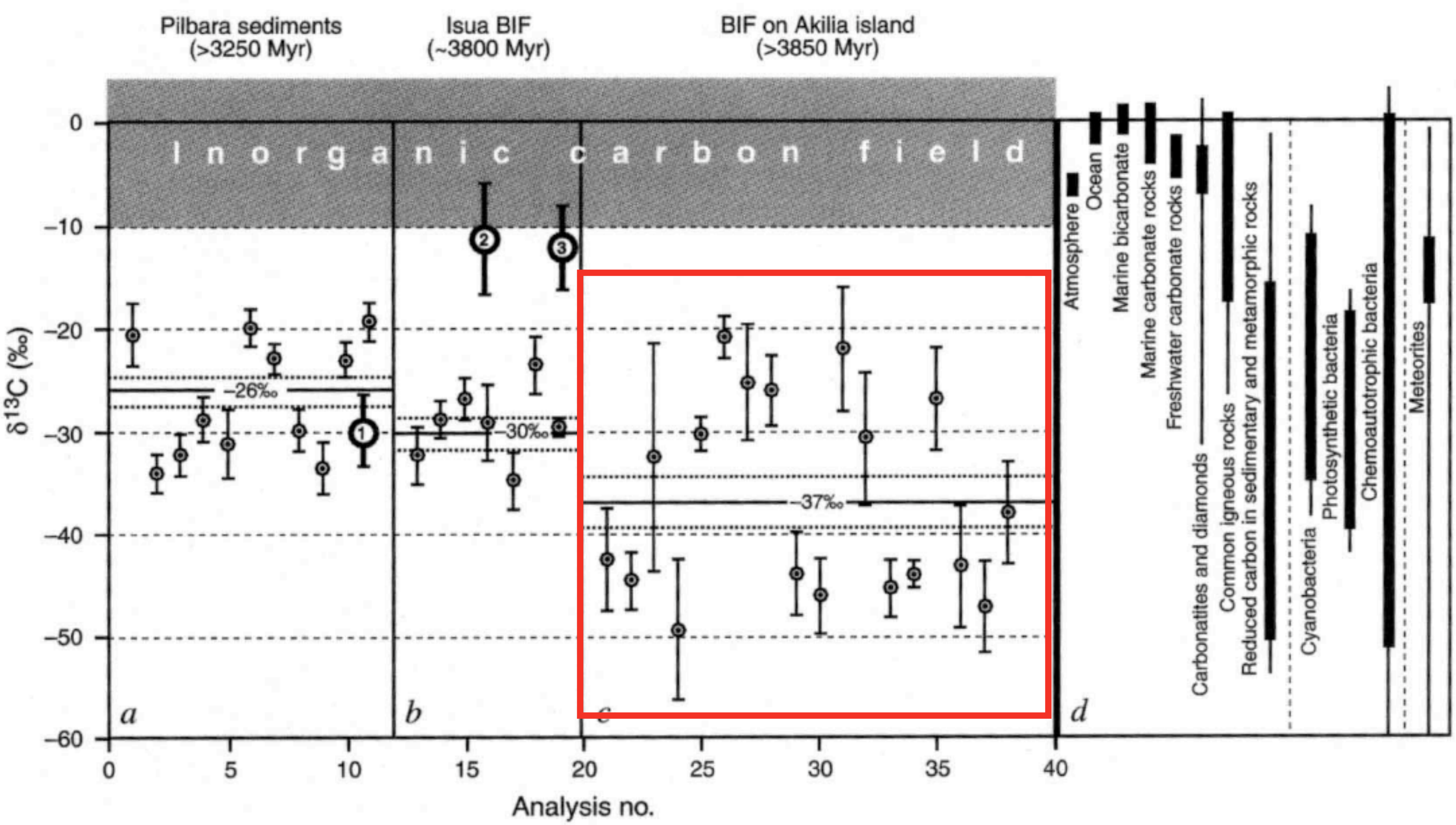
- Hematite (Fe_2O_3) & magnetite (Fe_3O_4) :

  Fe^{2+} --> Fe^{3+}

  $\mathbf{O_2}$ --> H_2O
- Requires free O_2 to oxidize Fe(II)

http://www.geo.utexas.edu/courses/381R/images/381Rphoto3.jpg; http://www.riotinto.com/library/reviewmagazine/common/images/77/article1-1.jpg

Low $^{13}C/^{12}C$ Ratios in >3.85 Ga Graphite (Carbonaceous Inclusions) from Akilia BIFs



Mojzsis et al. (1996) Evidence for life on Earth before 3,800 million years ago. *Nature*, Vol. 384: 55-59.

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

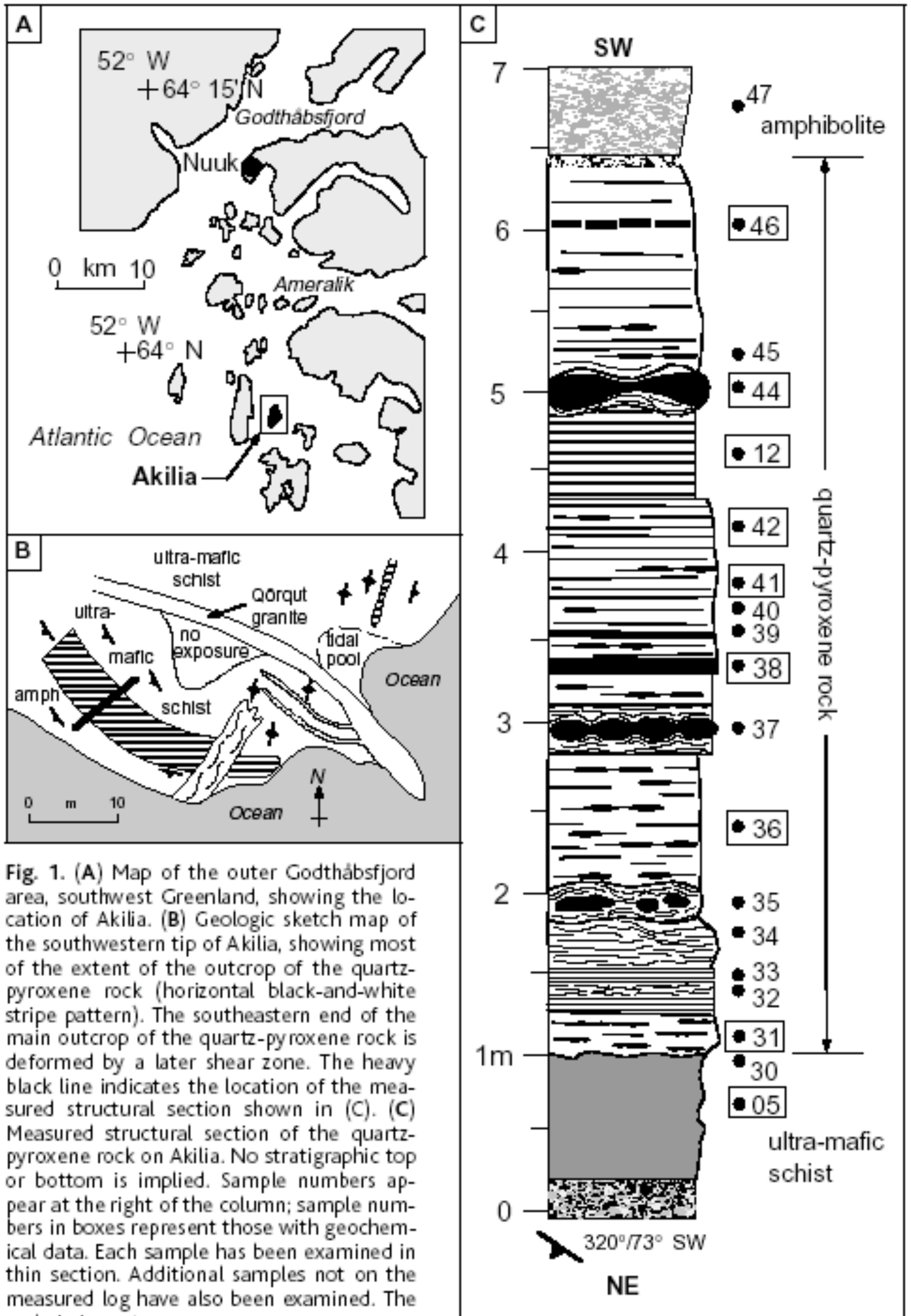


Fig. 1. (A) Map of the outer Godthåbsfjord area, southwest Greenland, showing the location of Akilia. (B) Geologic sketch map of the southwestern tip of Akilia, showing most of the extent of the outcrop of the quartz-pyroxene rock (horizontal black-and-white stripe pattern). The southeastern end of the main outcrop of the quartz-pyroxene rock is deformed by a later shear zone. The heavy black line indicates the location of the measured structural section shown in (C). (C) Measured structural section of the quartz-pyroxene rock on Akilia. No stratigraphic top or bottom is implied. Sample numbers appear at the right of the column; sample numbers in boxes represent those with geochemical data. Each sample has been examined in thin section. Additional samples not on the measured log have also been examined. The scale is in meters.

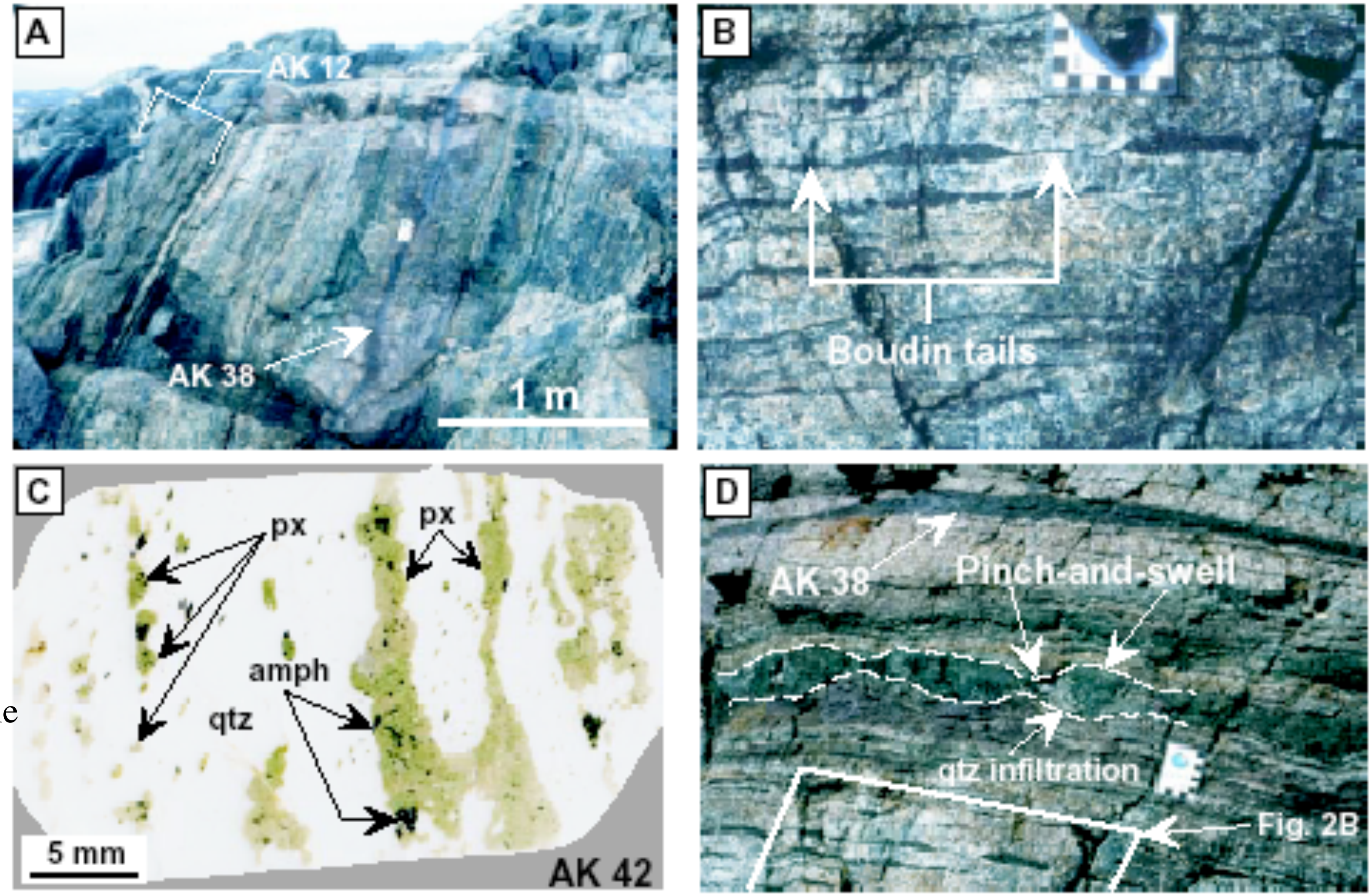
- Re-mapping of Akilia Island & new petrologic & geochemical analyses do not support sedimentary origin for these rocks.
- They appear instead to be metasomatized ultramafic ***igneous rocks*** (not BIFs).
- Therefore highly improbable that they hosted life at the time of their formation.

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

Geology Matters: 2

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

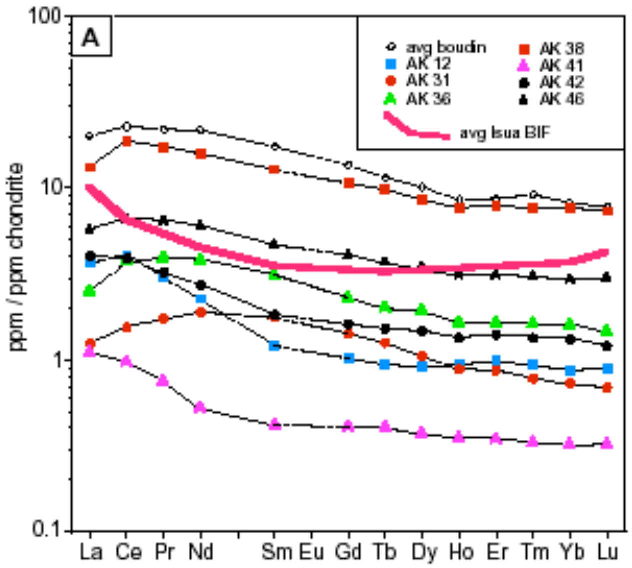
- Quartz-pyroxene outcrop originated as igneous rock, compositionally modified during repeated episodes of **metasomatism (= hot rock + water)** & **metamorphism (= high T +P)**
- Deformational petrologic features inconsistent with BIF

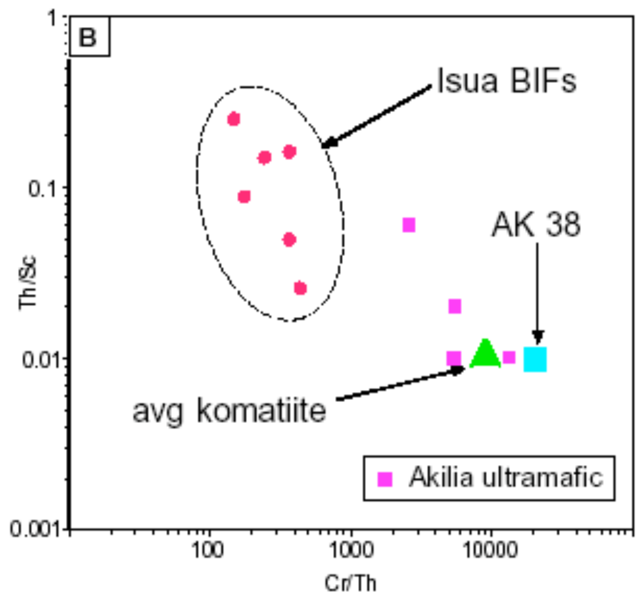


- Quartz
- Pyroxene
- Amphibole

• Geochemical evidence against Akilia rocks being BIFs

• REE pattern, elemental ratios & mineralogy all consistent with Akilia rocks being **igneous** & not sedimentary BIFs





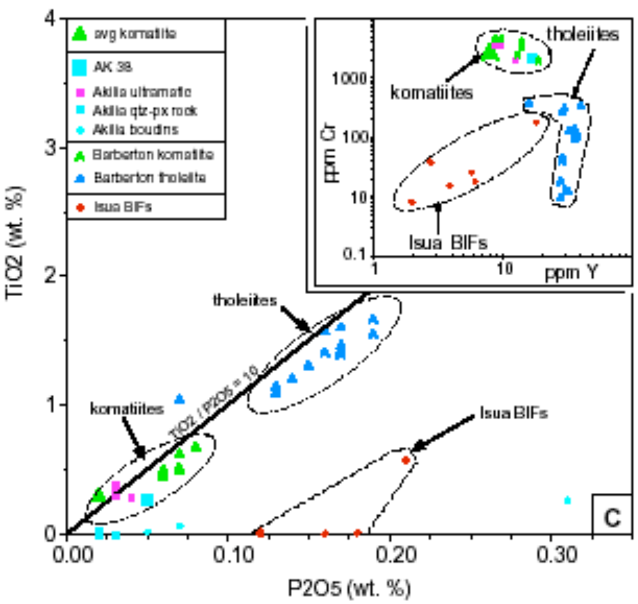
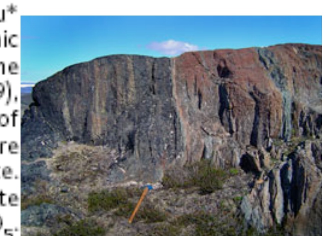


Fig. 3 (A) Plot of chondrite-normalized (*39*) REE abundances for the quartz-pyroxene rock. Note the concave-down behavior of the LREEs in the Akilia quartz-pyroxene samples and the concave-up behavior of the LREEs and the entire pattern for average Isua BIF (heavy red line). The scatter of REE abundances in the quartz-pyroxene samples is due to quartz dilution (AK 46 has 71.9 wt % SiO_2; AK 41 has 95.5 wt % SiO_2). The average value of extracted boudins from the quartz-pyroxene rock is similar to AK 38 in composition and abundance of REEs. Analyses for Eu are not plotted because of very inconsistent behavior of Eu. Eu/Eu* (chondrite-normalized) ranges from 0.25 to 1.61, suggesting that metamorphic conditions may have fluctuated near the Eu(II)-Eu(III) valence boundary. (B) The plot shows the relationships of the six BIF groups from Isua, average komatiite (*19*), AK 38, and four samples of ultramafic schist from Akilia. None of the six groups of Isua BIF have Cr/Th or Th/Sc ratios near those of AK 38 (a proxy for the entire quartz-pyroxene lithology), which are very similar to those of average komatiite. (C) The main plot shows data from Akilia, BIFs from Isua, and tholeiite-komatiite compositions from the Barberton greenstone belt (*18*) for TiO_2 versus P_2O_5. Tholeiites and komatiites plot in consistent positions where $TiO_2/P_2O_5 \leq 10$. AK 38 and Akilia ultramafic samples plot in the komatiite field; all samples of the quartz-pyroxene rock (except for a single boudin) plot near this field. Isua BIFs all lie in an unrelated field. The outlier point in the BIF data represents an aluminous BIF group, which has been interpreted to represent an admixture of BIF and mafic volcaniclastic component and so is not an exclusive BIF composition (*17*). The inset plot shows distinct fields for the different lithologies. Akilia ultramafic samples and AK 38 lie in the komatiite field. Note the distinct position of the Isua BIFs.

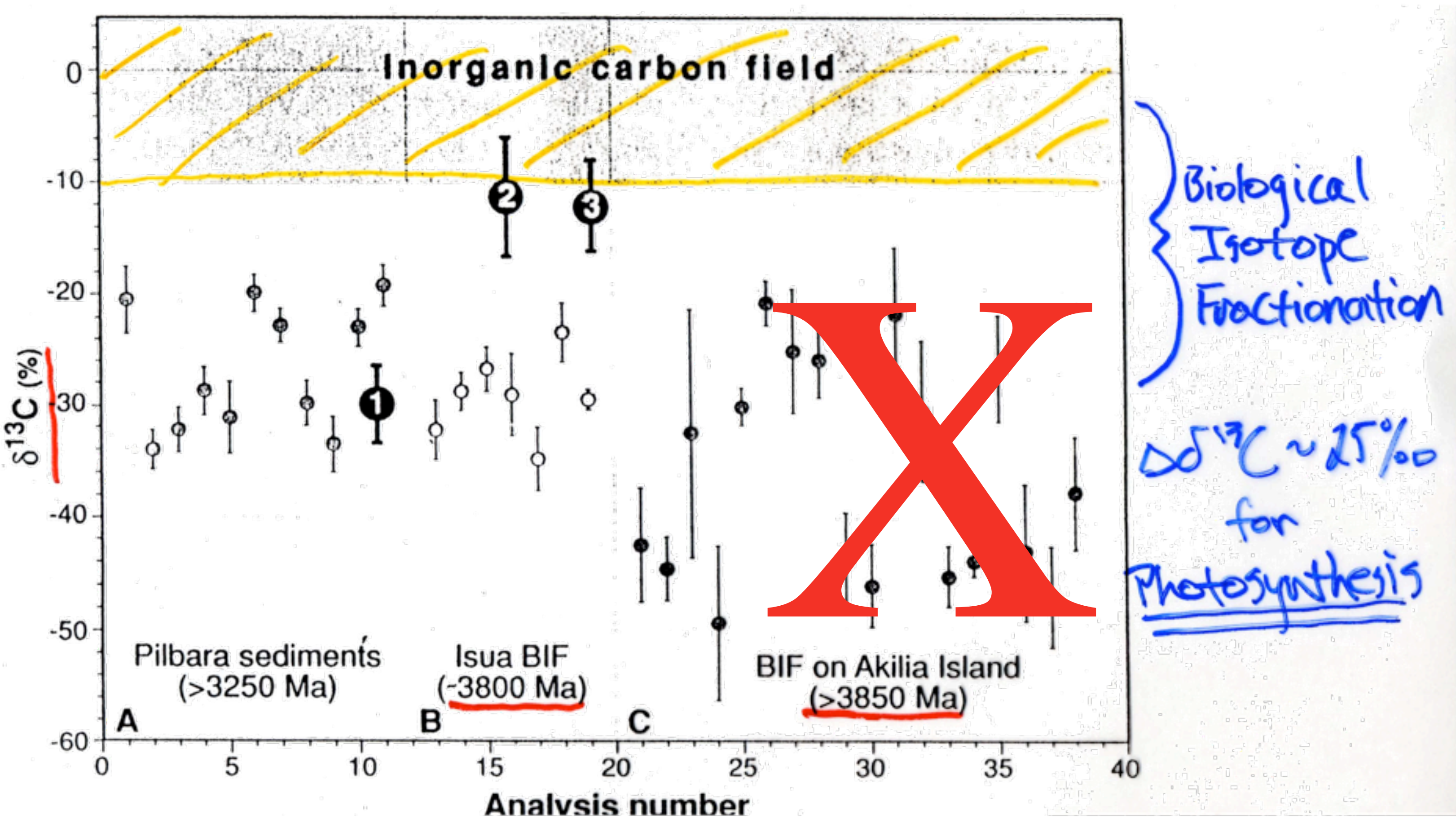
Geology Matters: 3



Isua BIF, SW Greenland (3.7-3.8 Ga)

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

> 3.85 Ga Akilia rocks were igneous (not sedimentary) & unlikely to have hosted life



Tracing Life in the Earliest Terrestrial Rock Record, *Eos Trans. AGU, 82*(47), Fall Meet. Suppl., Abstract P22B-0545 , 2001

(Lepland, A., van Zuilen, M., Arrhenius, G)

The principal method for studying the earliest traces of life in the metamorphosed, oldest (> 3.5 Ga) terrestrial rocks involves determination of isotopic composition of carbon, mainly prevailing as graphite. It is generally believed that this measure can distinguish biogenic graphite from abiogenic varieties. However, the interpretation of life from carbon isotope ratios has to be assessed within the context of specific geologic circumstances requiring (i) reliable protolith interpretation (ii) control of secondary, metasomatic processes, and (iii) understanding of different graphite producing mechanisms and related carbon isotopic systematics. We have carried out a systematic study of abundance, isotopic composition and petrographic associations of graphite in rocks from the ca. 3.8 Ga Isua Supracrustal Belt (ISB) in southern West Greenland. Our study indicates that most of the graphite in ISB occurs in carbonate-rich metasomatic rocks (metacarbonates) while sedimentary units, including banded iron formations (BIFs) and metacherts, have exceedingly low graphite concentrations. Regardless of isotopic composition of graphite in metacarbonate rocks, their secondary origin disqualifies them from providing evidence for traces of life stemming from 3.8 Ga. Recognition of the secondary origin of Isua metacarbonates thus calls for reevaluation of biologic interpretations by Schidlowski et al. (1979) and Mojzsis et al. (1996) that suggested the occurrence of 3.8 Ga biogenic graphite in these rocks. The origin of minute quantities of reduced carbon, released from sedimentary BIFs and metacherts at combustion steps > 700°C remains to be clarified. Its isotopic composition ($\delta^{13}C$ = -18 to -25‰) may hint at a biogenic origin. However, such isotopically light carbon was also found in Proterozoic mafic dykes cross-cutting the metasedimentary units in the ISB. The occurrence of isotopically light, reduced carbon in biologically irrelevant dykes may indicate secondary graphite crystallization from CO_2 or CH_4- containing fluids that in turn may derive from bioorganic sources. If this were the case, trace amounts of isotopically light secondary graphite can also be expected in metasediments, complicating the usage of light graphite as primary biomarker. The possibility of recent organic contamination, particularly important in low graphite samples, needs also to be considered; it appears as a ubiquitous component released at combustion in the 400-500°C range. A potential use of the apatite-graphite association as a biomarker has been proposed in the study by Mojzsis et al. (1996). Close inspection of several hundred apatite crystals from Isua BIFs and metacherts did, however, not show an association between these two minerals, moreover graphite is practically absent in these metasediments. In contrast, apatite crystals in the non-sedimentary metacarbonate rocks were found commonly to have invaginations, coatings and inclusions of abundant graphite. Considering that such graphite inclusions in apatite are restricted to the secondary metasomatic carbonate rocks in the ISB this association can not be considered as a primary biomarker in the Isua Supracrustal Belt

References: Mojzsis,S.J, .Arrhenius,G., McKeegan, K.D.,.Harrison, T.M.,.Nutman, A.P \& C.R.L.Friend.,1996. Nature 384: 55
Schidlowski, M., Appel, P.W.U., Eichmann, R. & Junge, C.E., 1979. Geochim. Cosmochim. Acta 43: 189-190.

Know Thy Rock: 1

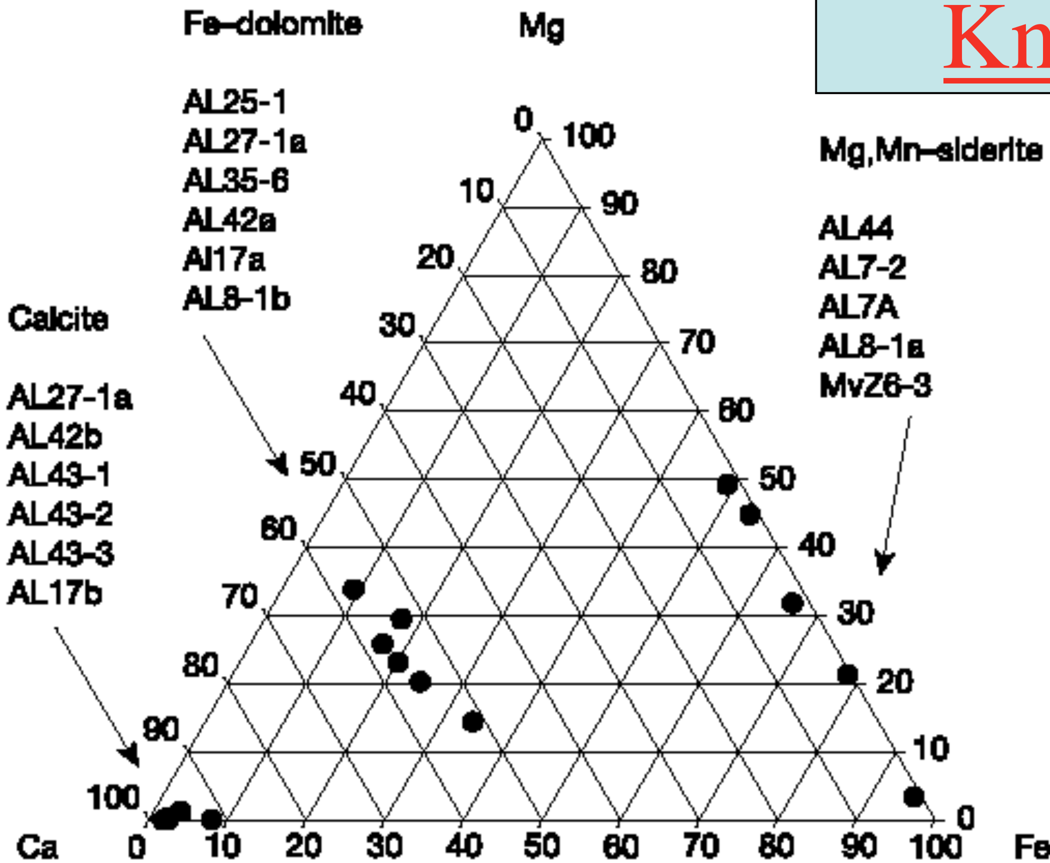


Figure 1 Carbonate phases can be divided into three distinct populations. These are: calcite ($Fe_{0.02–0.08}Mg_{0.00–0.03}Mn_{0.01–0.04}Ca_{0.89–0.97}CO_3$), Fe–dolomite ($Fe_{0.09–0.36}Mg_{0.14–0.34}Mn_{0.00–0.06}Ca_{0.50–0.57}CO_3$), and MgMn–siderite ($Fe_{0.40–0.85}Mg_{0.03–0.40}Mn_{0.09–0.22}CO_3$). AL8-1, AL17, AL27-1 and AL42 contain carbonate minerals with two different compositions (populations a and b) and support an earlier suggestion of the occurrence of multiple pulses of carbonate metasomatism in the ISB[12]. Not shown are AL13-1, AL15-1B, MvZ6.4D1, MvZ6.4D2, because they do not contain carbonate. Samples MvZ6.4D1 and MvZ6.4D2 are highly graphitic, chlorite and magnetite dominated interlayers within MgMn–siderite-rich metacarbonate veins.

- •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.

Isua BIF, SW Greenland (3.7-3.8 Ga)

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

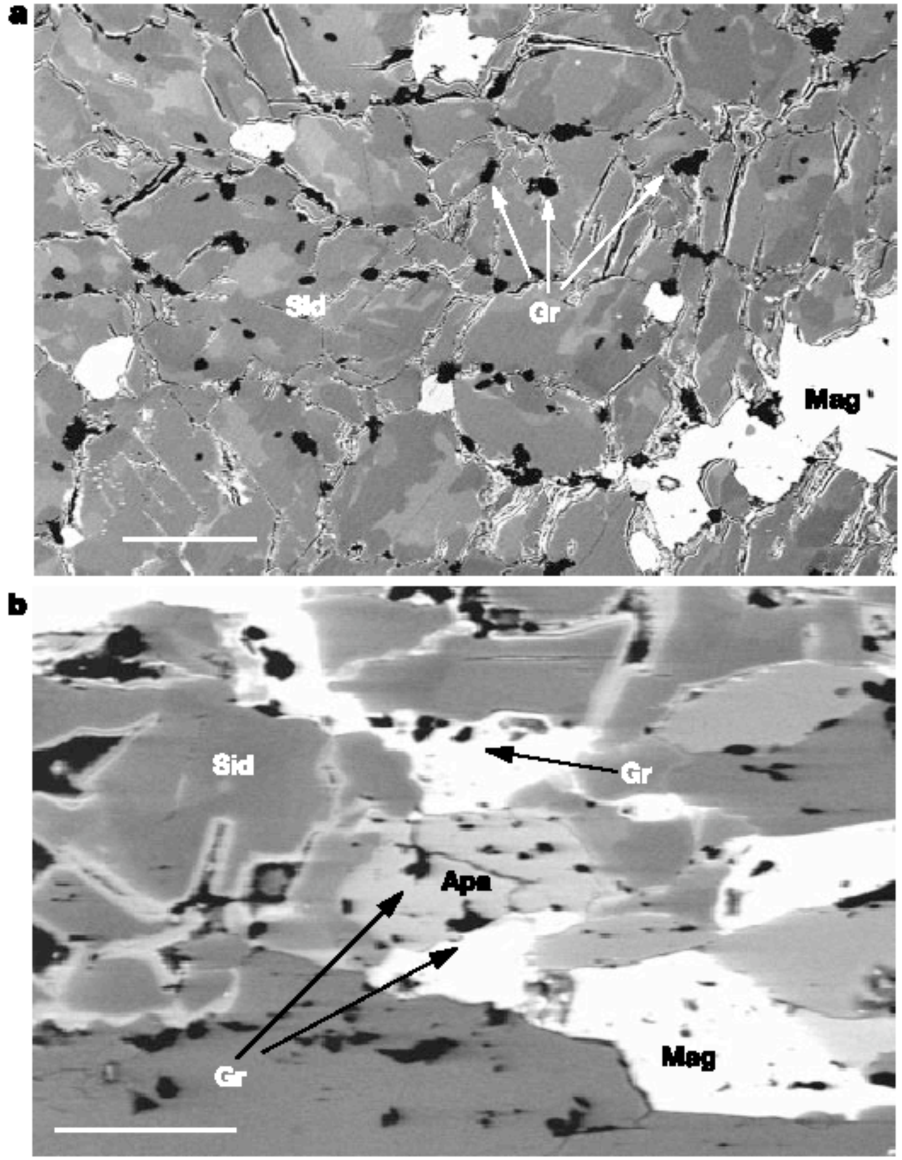


Figure 3 Backscattered electron (BSE) images of samples. **a**, BSE image of AL44, showing the spatial distribution of graphite (Gr) in relation to MgMn–siderite (Sid) and magnetite (Mag). Scale bar, 200 μm. **b**, BSE image of I-3381, showing an apatite crystal with graphite inclusions (Apa) in relation to magnetite, MgMn-siderite and graphite. Scale bar, 50 μm.

Know Thy Rock: 2

Metasomatism: introduction of elements into rock by circulating fluids

• 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.,

$$6FeCO_3 \rightarrow 2Fe_3O_4 + 5CO_2 + C$$

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

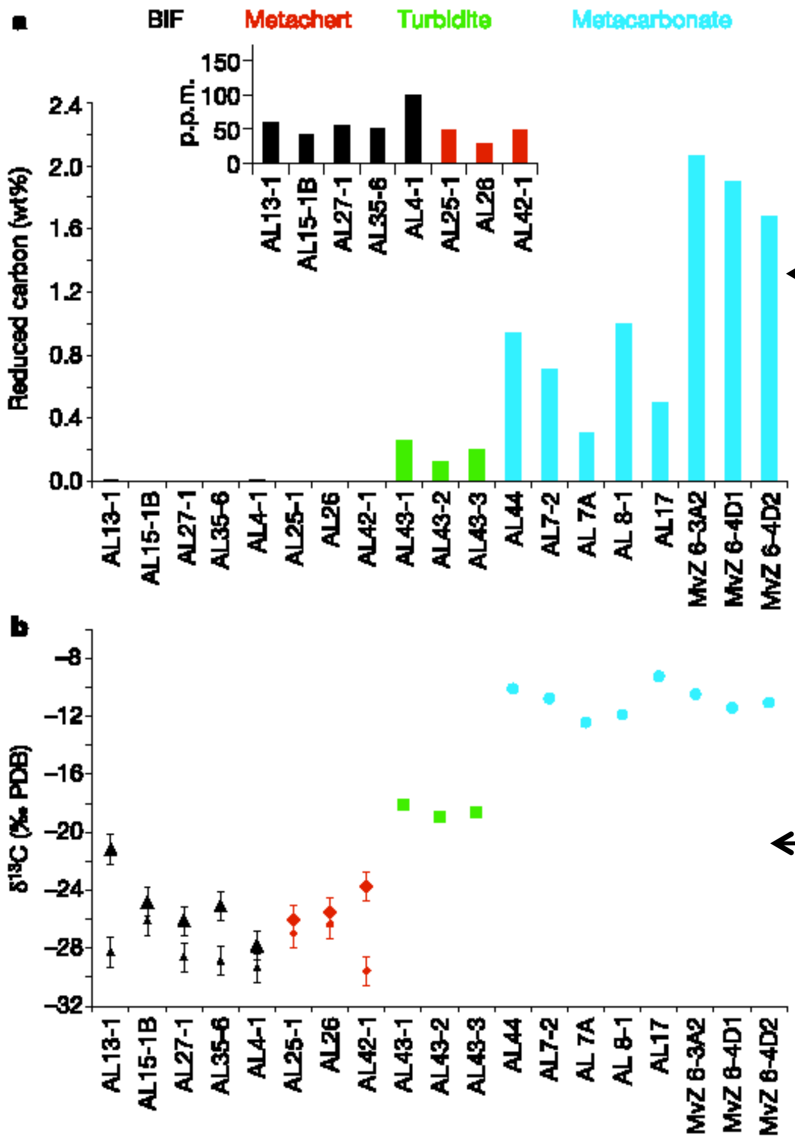


Figure 2 Abundance and isotope composition of reduced carbon. **a**, Abundances (wt%) of reduced carbon in studied samples. In a separate plot a close-up of low concentrations (carbon content in p.p.m.) in BIFs and metacherts is shown. **b**, Carbon isotope composition of total reduced carbon in BIFs (black triangles), metacherts (red diamonds), turbidites (green squares), metacarbonates (blue circles). Isotopic composition for carbon released at 450 °C is shown for BIFs (small black triangles) and metacherts (small red diamonds).

Know Thy Rock: 3

- 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.

*** Ended here - 10/17/08 ***

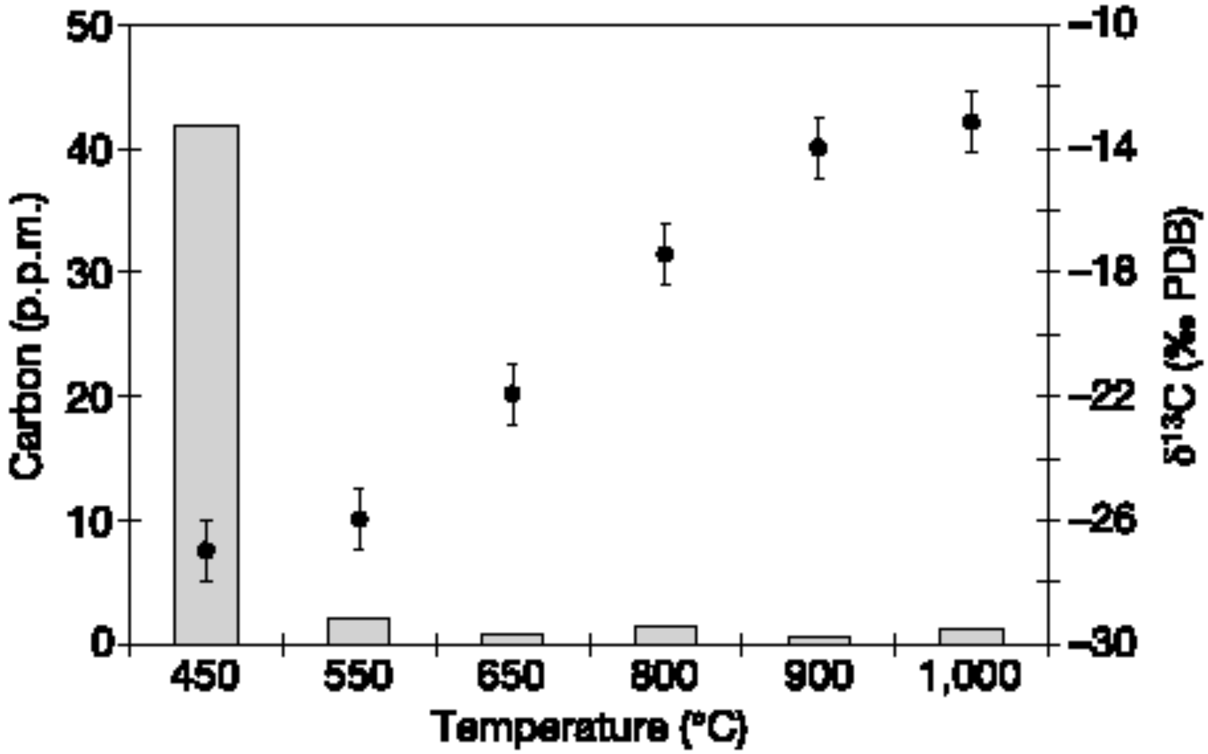


Figure 4 Stepped-heating combustion data for sample AL25. 1-h steps at 450, 550, 650, 800, 900 and 1,000 °C. Abundance of extracted reduced carbon (p.p.m.) and the isotopic composition ($\delta^{13}C$) are shown for each temperature step. The reduced carbon component that dominates in this sample is isotopically light ($\delta^{13}C = -28‰$) and comes off at low temperature.

Know Thy Rock: 4

Isua BIF, SW Greenland
(3.7-3.8 Ga)

- The isotopically (^{13}C)-depleted carbon 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)

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

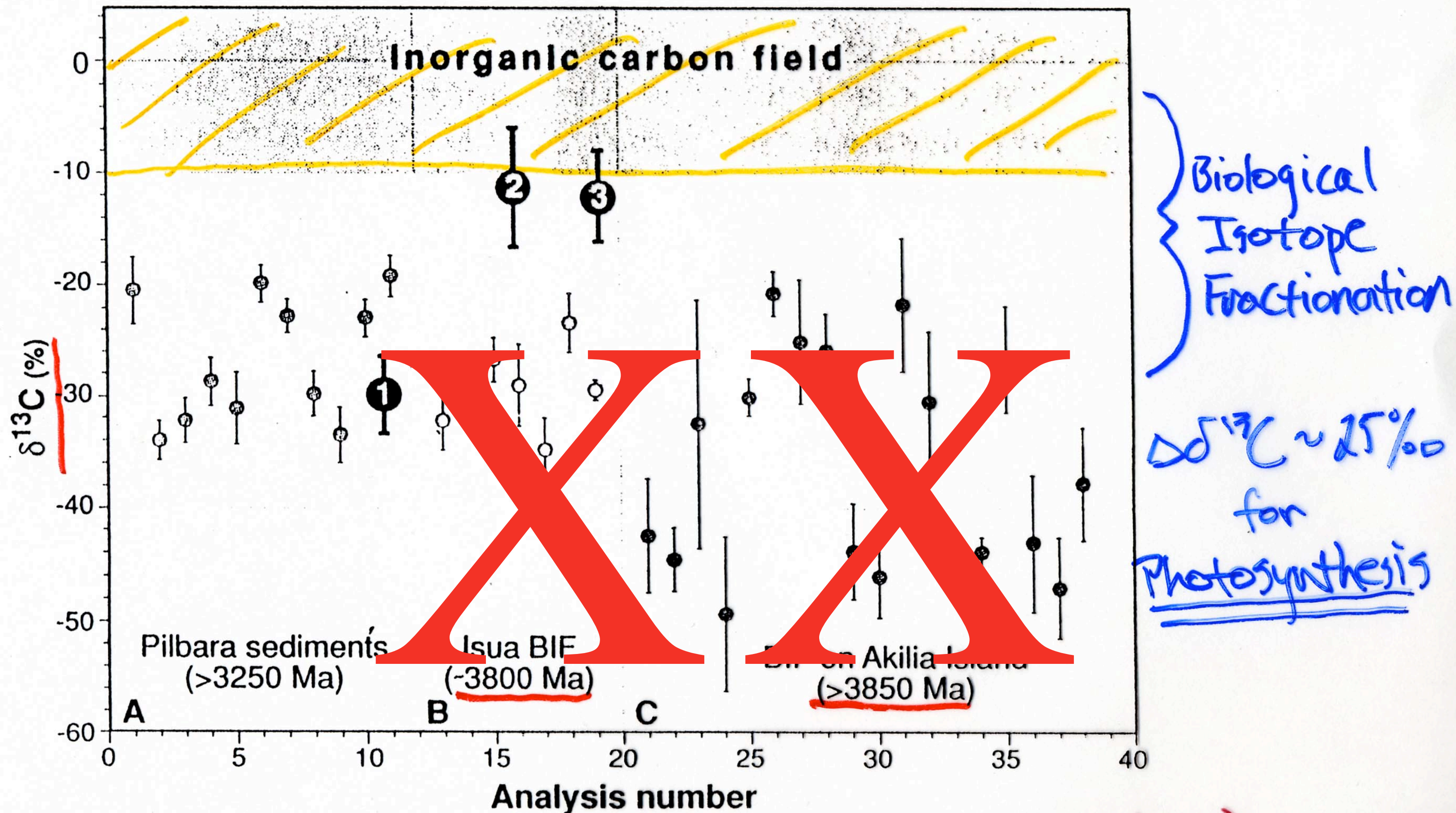
Bottom Line: No evidence for a Biogenic Origin of Reduced Carbon in 3.8 Ga Isua (SW Greenland) Rocks

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

$$6FeCO_3 \rightarrow 2Fe_3O_4 + 5CO_2 + C$$

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

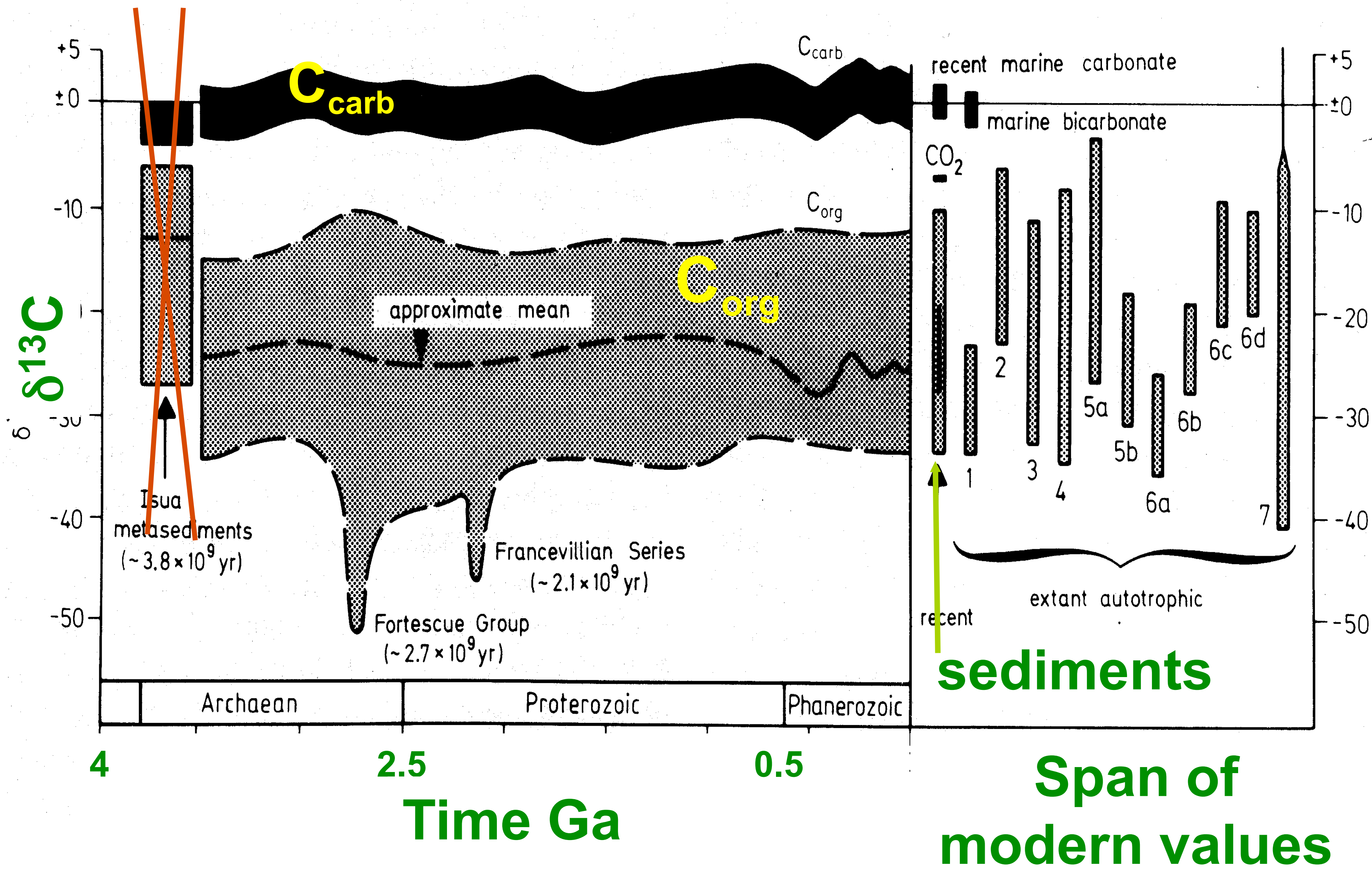
The ~3.8 Ga Isua graphite formed by thermal disproportionation of $FeCO_3$ at a later time than the host rock



Holland (1997)

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1\right] \times 1000 \; (‰)$$

Revised C Isotope Evidence for Life's Antiquity



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

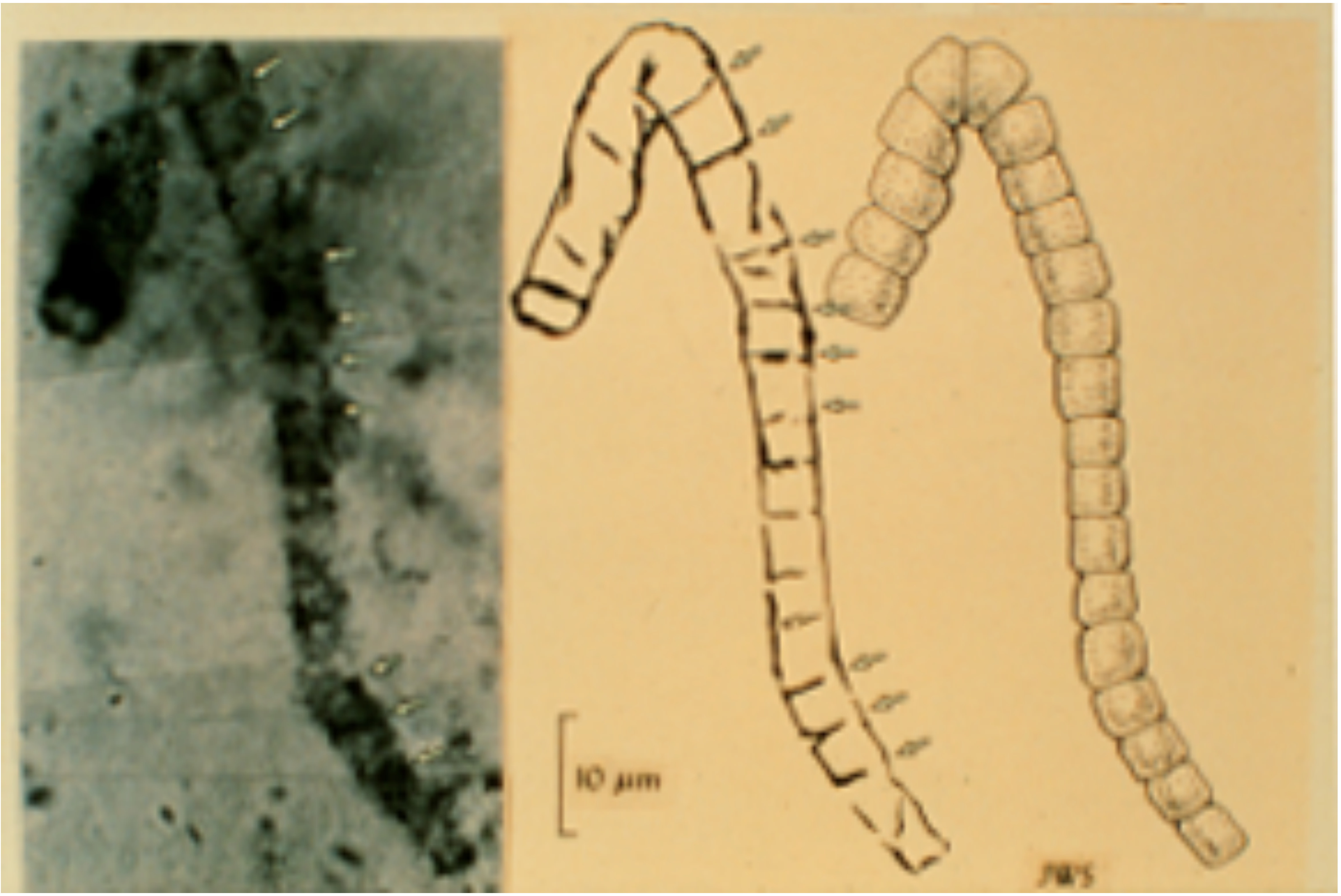
It’s time to look at some fossil evidence for early life….

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

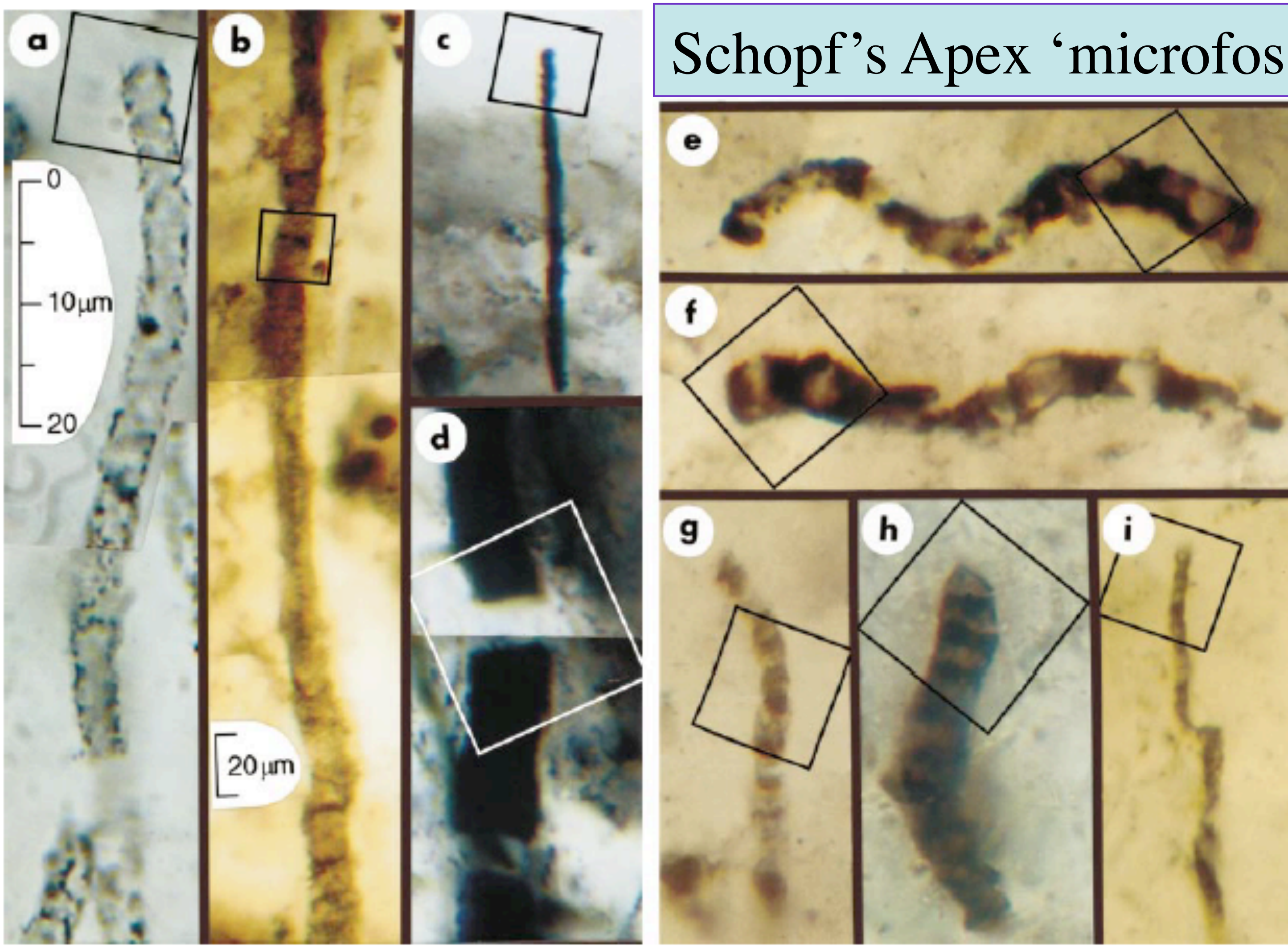
So jump ahead 300 Myr to 3.5 Ga…

Morphological Evidence for Antiquity of Life

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



Schopf's Apex 'microfossils' #1



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

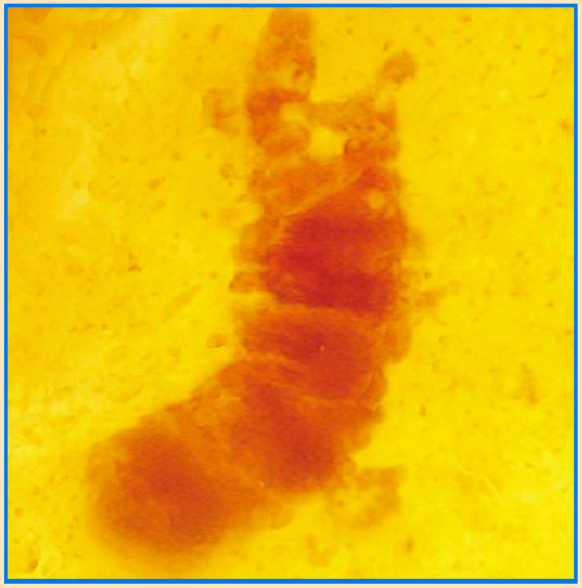
Schopf et al. (2002) *Nature*, vol. 416:73-76.

Figure 1 Optical photomicrographs showing carbonaceous (kerogenous) filamentous microbial fossils in petrographic thin sections of Precambrian cherts. Scale in **a** represents images in **a** and **c–i**; scale in **b** represents image in **b**. All parts show photomontages, which is necessitated by the three-dimensional preservation of the cylindrical sinuous permineralized microbes. Squares in each part indicate the areas for which chemical data are presented in Figs 2 and 3. **a**, An unnamed cylindrical prokaryotic filament, probably the degraded cellular trichome or tubular sheath of an oscillatoriacean cyanobacterium, from the ~770-Myr Skillogalee Dolomite of South Australia[12]. **b**, *Gunflintia grandis*, a cellular probably oscillatoriacean trichome, from the ~2,100-Myr Gunflint Formation of Ontario, Canada[13]. **c**, **d**, Unnamed highly carbonized filamentous prokaryotes from the ~3,375-Myr Kromberg Formation of South Africa[14]: the poorly preserved cylindrical trichome of a noncyanobacterial or oscillatoriacean prokaryote (**c**); the disrupted, originally cellular trichomic remnants possibly of an *Oscillatoria-* or *Lyngbya*-like cyanobacterium (**d**). **e–i**, Cellular microbial filaments from the ~3,465-Myr Apex chert of northwestern Western Australia: *Primaevifilum amoenum*[4,5], from the collections of The Natural History Museum (TNHM), London, specimen V.63164[6] (**e**); *P. amoenum*[4] (**f**); the holotype of *P. delicatulum*[4,5,15], TNHM V.63165[2] (**g**); *P. conicoterminatum*[5], TNHM V63164[9] (**h**); the holotype of *Eoleptonema apex*[5], TNHM V.63729[1] (**i**).

Non-biologic Origin of 3.5 Gyr "Microfossils"?

Biogeochemistry

That's life?



This could be a picture of one of the earliest-known fossils — a microbe, 60 μm long, that is almost 3,500 million years old. On the other hand, it could be just a flaw in the rock. It all depends on whom you talk to, as epitomized by two papers in this issue.

The more optimistic view is taken by William Schopf and colleagues (*Nature* **416,** 73–76; 2002). In the early 1990s, Schopf caused a sensation with reports of a diverse bacterial flora from the 3,465-million-year-old Apex cherts of Western Australia. At the time, all he had to go on was morphology. This was always controversial, given that bacteria have little morphology to begin with. As a consequence, it is hard to tell the difference between a bacterium — especially a fossil bacterium — and a bubble. This is why Schopf has devised authenticity criteria that are based on bacterial habit. If you have one bacterium, for example, you will usually have hundreds: isolated blobs purporting to be bacteria usually turn out to be artefacts.

Since then, Schopf and colleagues have sought to back up the morphology using laser–Raman imaging, a technique in which the chemical composition, as well as the structure of the fossils, can be mapped in two dimensions. After several tests of the technique on less controversial fossils, Schopf *et al.* have used the method on the Apex chert material. They find that the fossils have the composition to be expected if they were made of organically derived carbon.

This will not be the end of the controversy, however, as demonstrated by the report from Martin Brasier and colleagues (*Nature* **416,** 76–81; 2002). Using the original Apex chert material, as well as newly collected specimens, they find that the rocks in which the fossils were found come from a vein that may have been produced hydrothermally, that is, by the action of heated water on minerals. The carbon-isotope signature is consistent with a biogenic origin, one derived from living organisms. But other studies suggest that this was an environment in which carbon dioxide produced by volcanic action was transformed into isotopically light carbon at 250–350 °C. The bottom line is that although the carbon looks organic, it need not be. Similarly, Raman spectroscopy shows that although the material in the fossils could be biogenic, it could equally well be amorphous graphite.

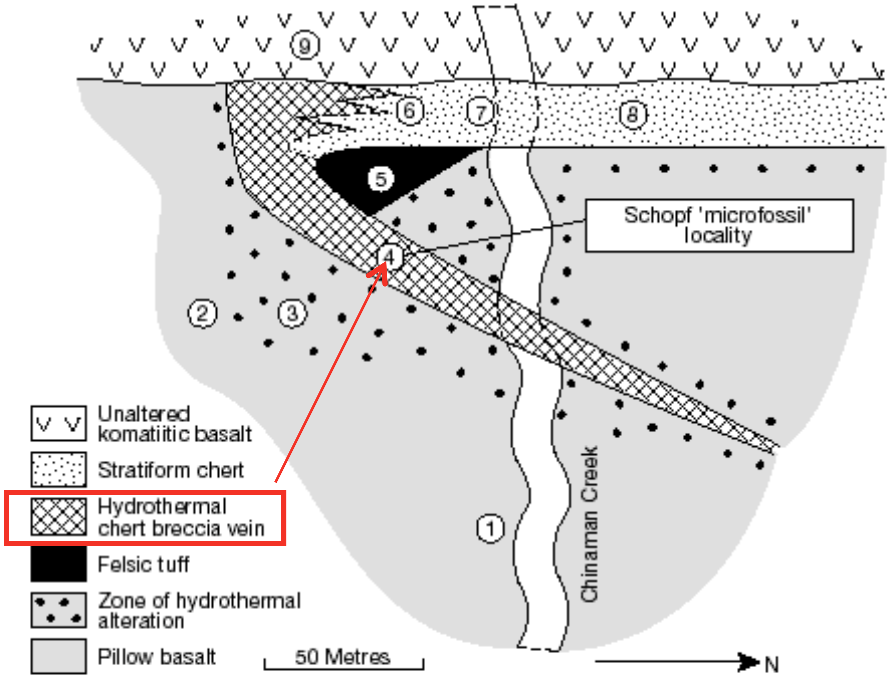
Brasier *et al.* even dismiss the morphology. They suggest that the fossils, as a whole, have a random orientation that is not characteristic of bacterial behaviour, in which the cells tend to line up in one direction or another; the individual cells have a range of strange, even branched, morphologies; and what look like filaments with internal divisions may be the result of interleaving quartz and graphite sheets. Many authors agree that there is isotopic evidence for biogenic activity in the Archaean (that interval of Earth history before 2,500 million years ago). But Brasier and colleagues, at least, say that the Apex chert fossils aren't really fossils at all.

Given that Schopf was one of the first to cast doubt on the biogenicity of another celebrated suite of purported microfossils — in the martian meteorite ALH84001 — it is ironic that his own work should be subjected to such scepticism. But that is the name of the game for claims of life at the extremes of time and space. **Henry Gee**

- 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



	1	2	3	4 A1/B1	4 A2/B2	4 A3/B3	4 C/A4	5	6	7	8	9
Chromite	–	–	–	■	■	■	–	● ■	–	–	–	–
Iron oxide	■	■ □	■	■	■	● ■	–	● ■	■	–	–	■ □
TiO_2	■	■	–	■	● ■	● ■	–	● ■ □	–	–	■	■ □
$BaSO_4$	–	□	–	● ■	■ ■	● ■	■ □	○ ■ □	● ■	○ ■	○ ■	–
Alunite–jarosite	–	–	–	● ■	■ ■	● ■	■ □	–	■ ★	● ■ ★	● ○ ■ ★	–
Aluminosilicates	■	■	■	● ■	● ■	● ■	–	● ○ ■	–	–	–	■ □
Metals, *sulphides*	*Cu* ■	Ni □ Cu □ Zn □ Pb □	–	Fe ● Ni ● Cu ● Zn ● *Pb* ●	Fe ■ ■ *Fe* ■ ■ Ni ● Cu ● Zn ■ Sn ● *Pb* ■	Fe ■ *Fe* ■ Cu ●	*Pb* □	Pb ●	*Fe* ■ *Cu* ■ Zn ■	*Fe* ■ ■ *Ni,As* □ *Cu* ■ ■ *Cu* ○ □	Fe ■ *Fe* ● ○ *Cu* ■ *Zn* ● ○ *Zn* ■ □ *Sb* ● ○ *Sb* ■ □	–
Sulphur (p.p.m.)				–	162	79			–	330	607	
Graphite				● ■	● ■	● ■		● ○ ■	●	●	● ○ ■	
Carbon (p.p.m.)				126–1206	1413	36			34	2545	2162	
$\delta^{13}C_{PDB}$ (‰)				–30.3 –26.5	–29.9	–28.4			–25.6	–29.5	–25.6	
$\delta^{18}O_{SMOW}$ (‰)				+14.5 +14.7	+14.5	+14.6 +14.7			+14.3	+14.1	+13.7	

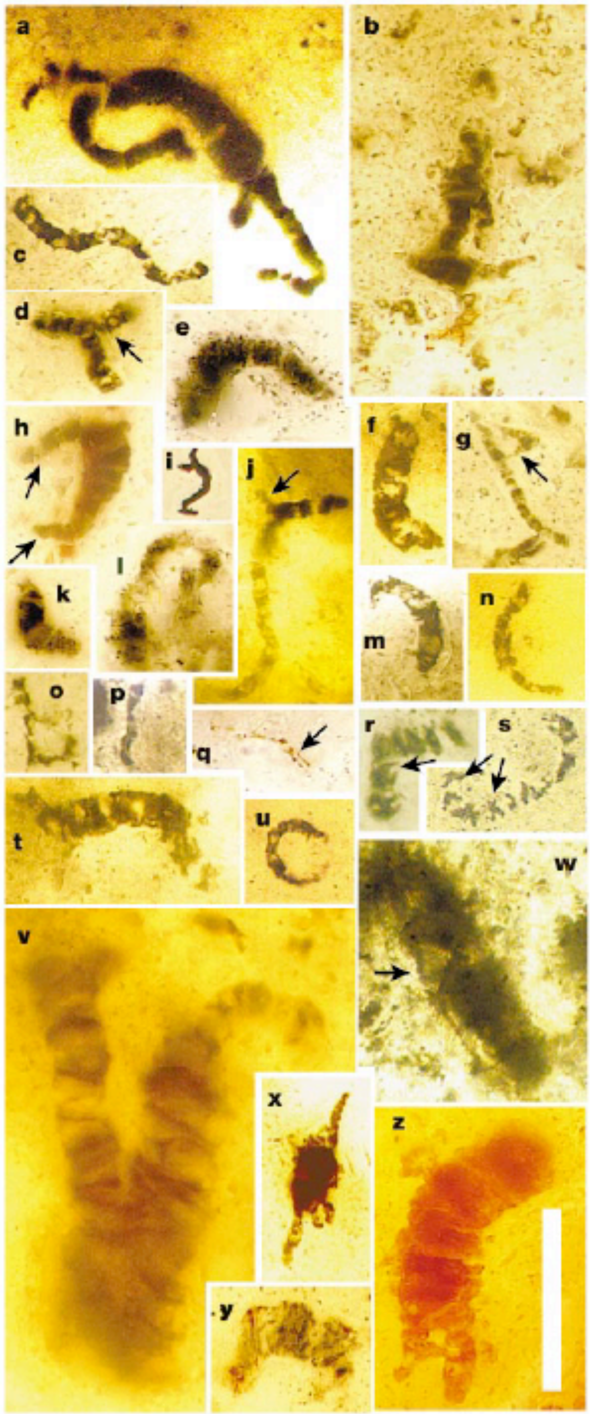
● In shards, clasts ○ Around shards, clasts ■ In matrix □ In veins ★ Arsenic-rich
A-C, Fabrics recognized in thin section Open box, not analysed

Figure 1 Geological sketch map of the Apex chert at Chinaman Creek, showing sample numbers and site of the Schopf 'microfossil' locality (sample 4) from a metalliferous hydrothermal chert breccia vein that cross-cuts hydrothermally altered pillow basalt. Samples 1–9 are from this study. New geochemical data are consistent with a hydrothermal setting (see Methods).

- 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



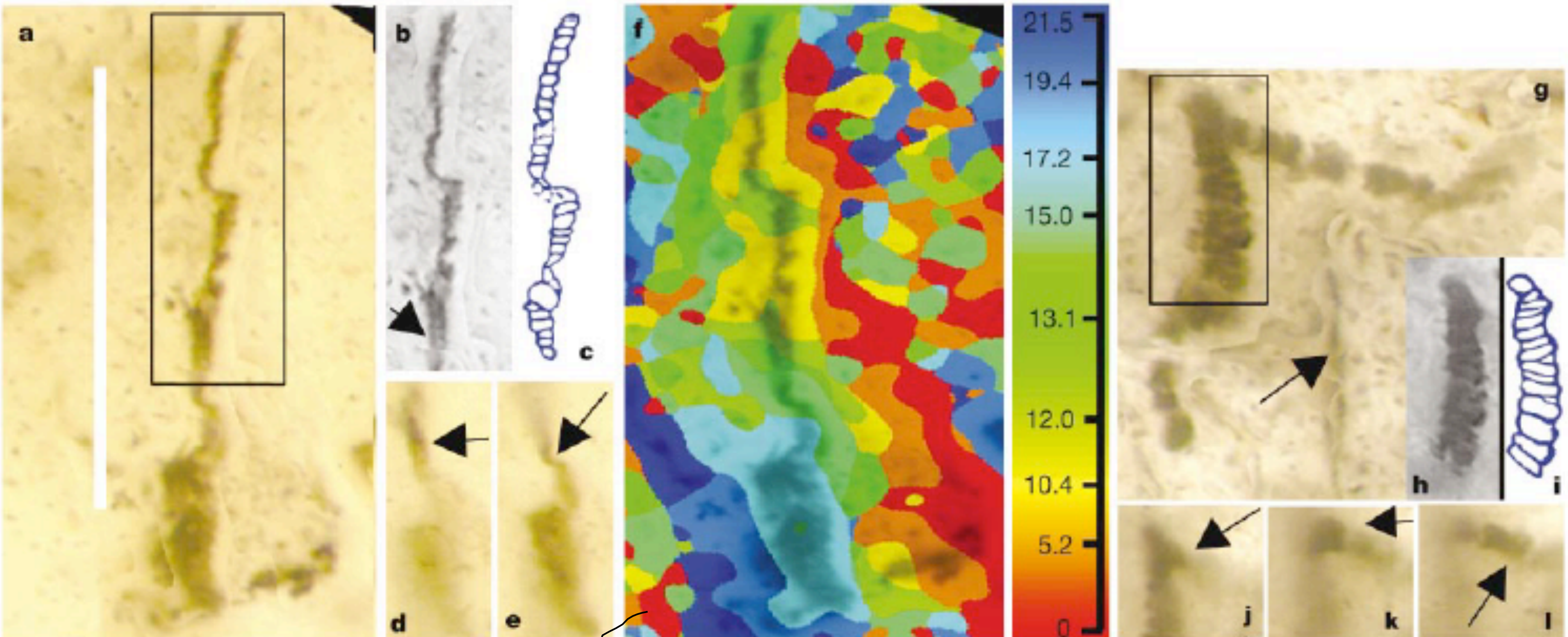
> "Many of these filamentous structures [from the apex chert] are branched or formed in ways not shown in the original descriptions because of the choice of focal depth and/or illustrated field of view."

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

Figure 2 Automontages of inferred artefacts from the Apex chert. **a**, **b**, **o**, **u**, **v**, **x**, Pseudoseptate and branched filamentous artefacts from vein chert (NHM V.63127, 63164, 63165, 63127, 63164, 63164). **i**, Artificial graphite filament (63166). **e**, **k**, **l**, Filamentous artefacts from felsic tuff (**e** and **k** from chalcedony matrix; **l** from within devitrified rim of volcanic glass shard). **p**, Pseudoseptate filament from clast in stratiform chert. **c**, **d**, **f–h**, **j**, **m**, **n**, **q–t**, **w**, **y**, **z**, New images of previously illustrated structures (refs 2, 3; holotypes*): **c**, *Primaevifilum amoenum*; **d**, *A. disciformis*; **f**, *P. laticellulosum**; **g**, *P. delicatulum**; **h**, *P. attenuatum**; **j**, *P. amoenum**; **m**, *P. conicoterminatum**; **n**, type C narrow filament; **q**, *Archaeotrichion septatum**; **r**, **s**, 'trichome showing bifurcated cells'; **t**, type A broad filament; **w**, cf. *A. grandis**; **y**, 'type B' broad filament; **z**, *Archaeoscillatoriopsis maxima**. Bright-field transmitted light. Scale bar, 40 μm; arrows indicate anomalies (see the text).

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'…



Focal planes used to create montage of most sharply focused images in (a)

Figure 3 Automontages of inferred artefacts from the Apex chert. **a**, New image of putative beggiatoan *Eoleptonema apex* Holotype (ref. 3), combining the most sharply focused images from successive focal planes; **b**, **c**, digital image and interpretative sketch in the style of ref. 3 that omits the lower structure; **d**, **e**, new single image frames showing continuity of original and newly imaged structures. **f**, Topographic map showing computer-selected focal planes (plus scale in µm) of **a**; **g**, new image of putative cyanobacterium *Archaeoscillatoriopsis disciformis* Holotype (ref. 3) showing rhombic ghost (arrow); **h**, **i**, digital image and interpretative sketch in the style of ref. 3 that omits the lower structure and side branch; **j**, **k**, **l**, new single image frames showing continuity of original and newly imaged structure. Scale bar, 40 µm.

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

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

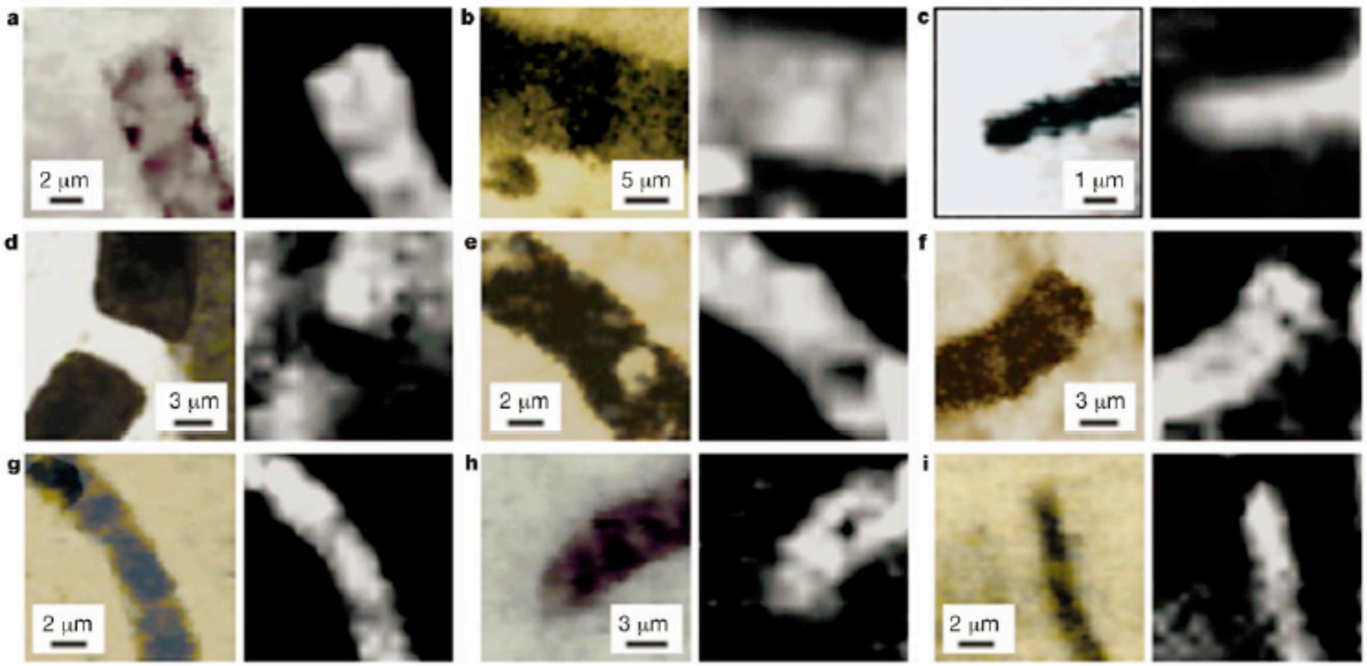
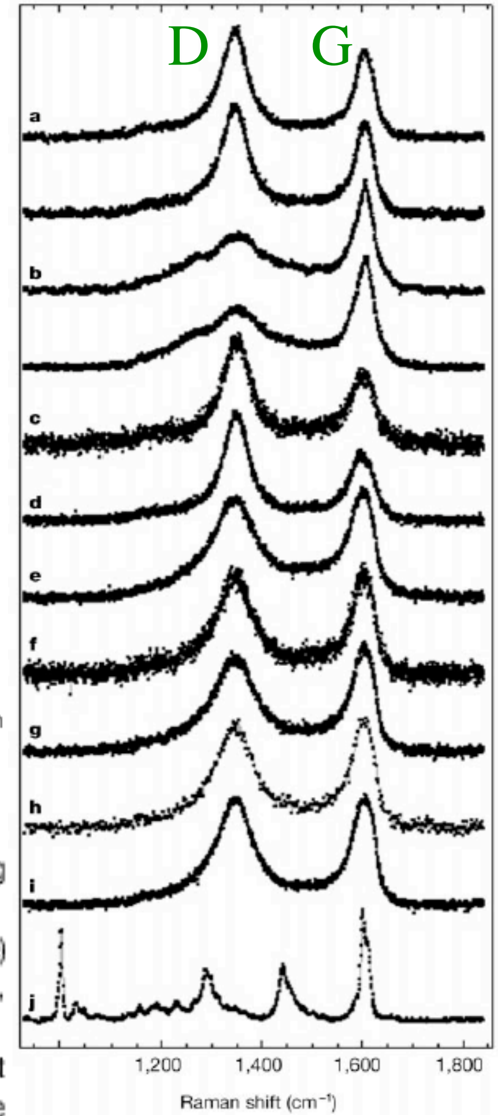


Figure 2 Digital optical images and corresponding Raman images. **a–i**, Optical images (left) and Raman 'G' band intensity maps (right), of areas of fossils indicated by the squares in Fig. 1a–i, respectively.



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

Figure 3 Typical spectral bands of parts of fossils shown in Fig. 1 used for Raman imaging (Fig. 2) and the spectrum of immersion oil used to enhance the optical image of some specimens. **a**, **b**, Point spectra of the Skillogalee filament shown in Fig. 1a, without (above) and with (below) a covering veneer of immersion oil; and of *Gunflintia grandis* (Fig. 1b), without (above) and with (below) an oil veneer (showing a broad 'D' band and its substructure, typical of the kerogen in this relatively unmetamorphosed, subgreenschist facies, geologic unit). **c–i**, Point spectra of other fossils from which Raman images were acquired: unnamed filamentous prokaryotes from the Kromberg Formation (**c**, **d**; shown in Fig. 1c, d, respectively); cellular filamentous prokaryotes from the Apex chert (**e–i**; shown in Fig. 1e–i, respectively). **j**, Spectrum of immersion oil used to enhance the optical image of some specimens.

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

Questioning the authenticity of 3.465 Ga Apex fossils: 4

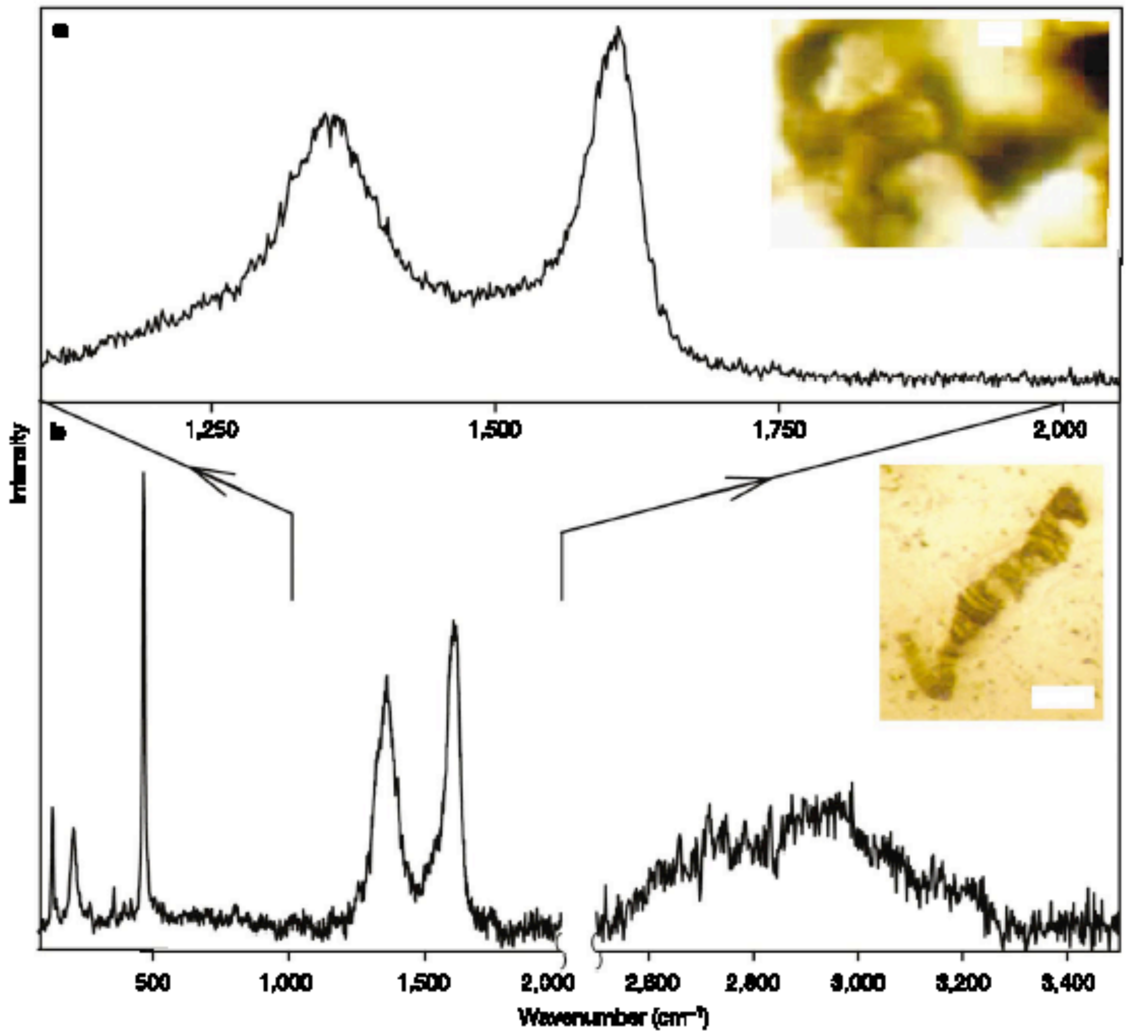


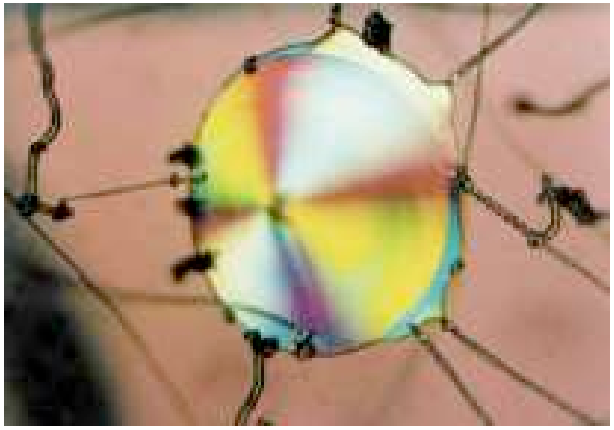
Figure 4 Raman spectra of associated graphitic objects (<1 mm apart) within NHM V.63165. **a**, Spherulitic mass in B2; **b**, pseudofossil identified as a 'degraded cellular filament or wrinkled sheath' (Fig. 1.5.4B in ref. 2) within fabric A1, showing quartz modes (128, 206, 355 and 464 cm^{-1}) plus first- and second-order graphitic carbon peaks. Comparable spectra are also produced by dark microclasts within fabric A2 and dendritic pseudoseptate mullions within fabric B2. Background has been subtracted. Scale bar for insets, 10 μm.

- Unfortunately for Schopf et al., Raman spectra of dark specks within surrounding host (quartz) rock of Apex 'microfossils' give same Raman spectrum.

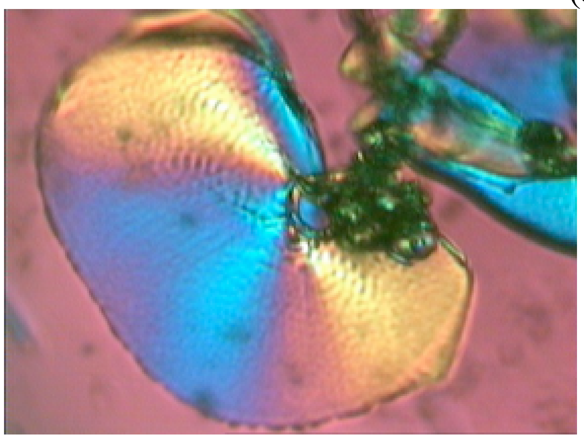
- The spectroscopic results therefore provide no support for the "biogenicity" of Schopf's 'fossils'.

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

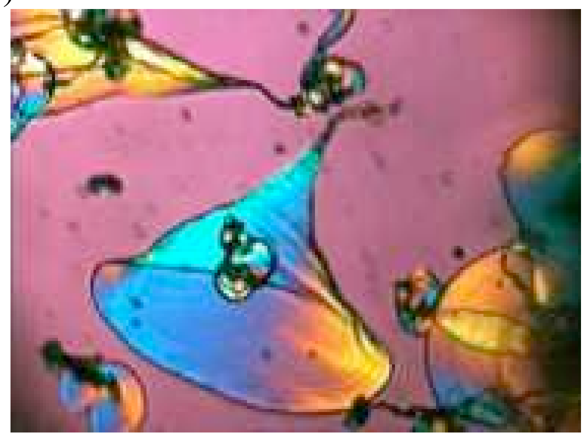
Abiotic origin of microfossil-like structures #1



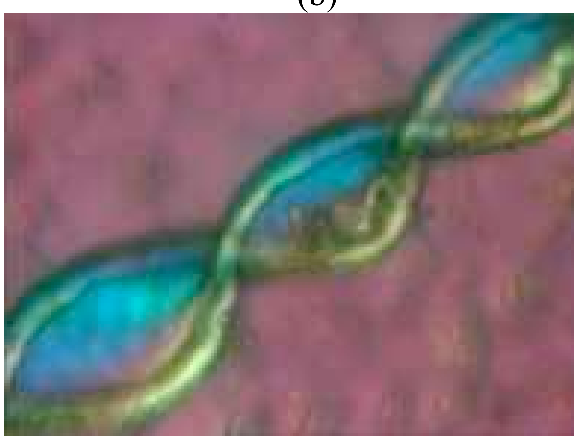
(a)



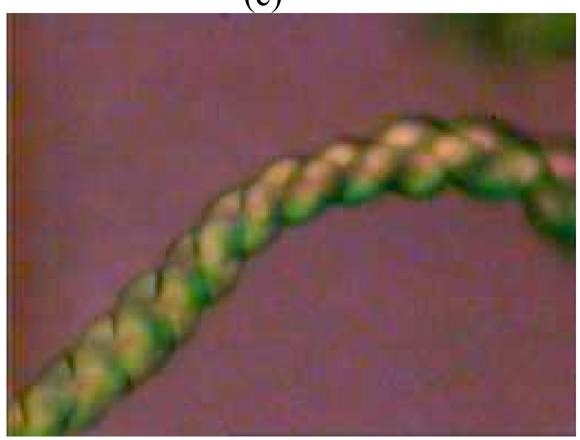
(b)



(c)



(d)

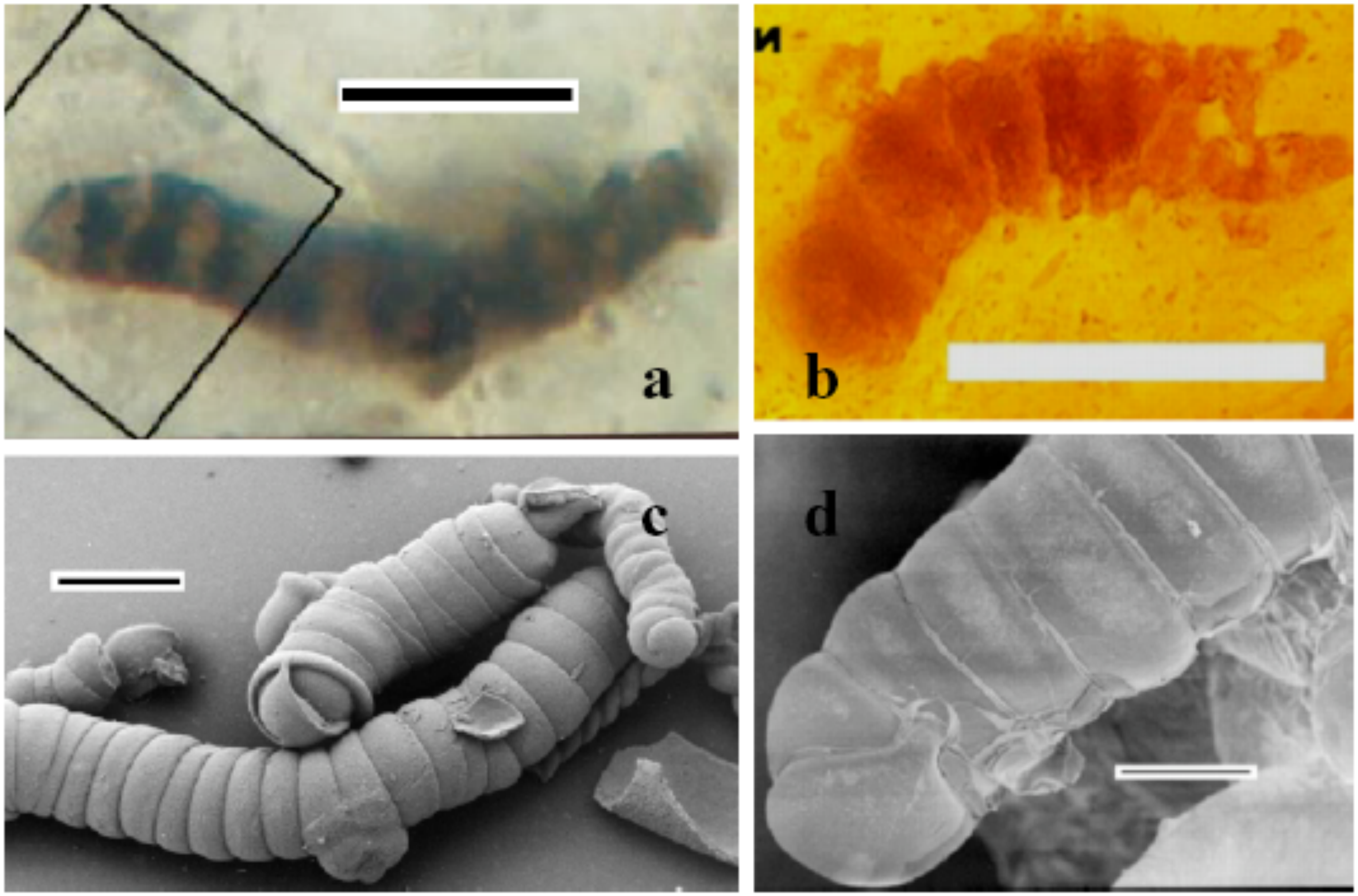


(e)

- 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

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

Abiotic origin of microfossil-like structures #2

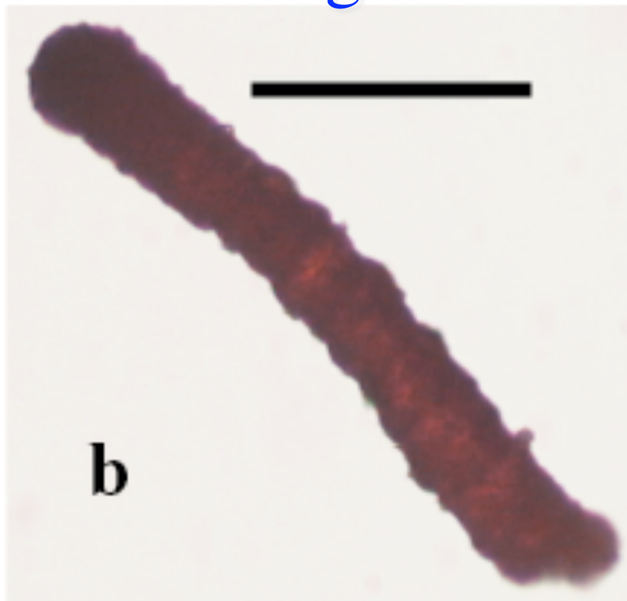


a,b: Apex chert (3.5 Ga, WA) microfilament images from Schopf et al (2002) & Brasier et al. (2002), respectively (10 μm and 40 μm scale bars, respectively).

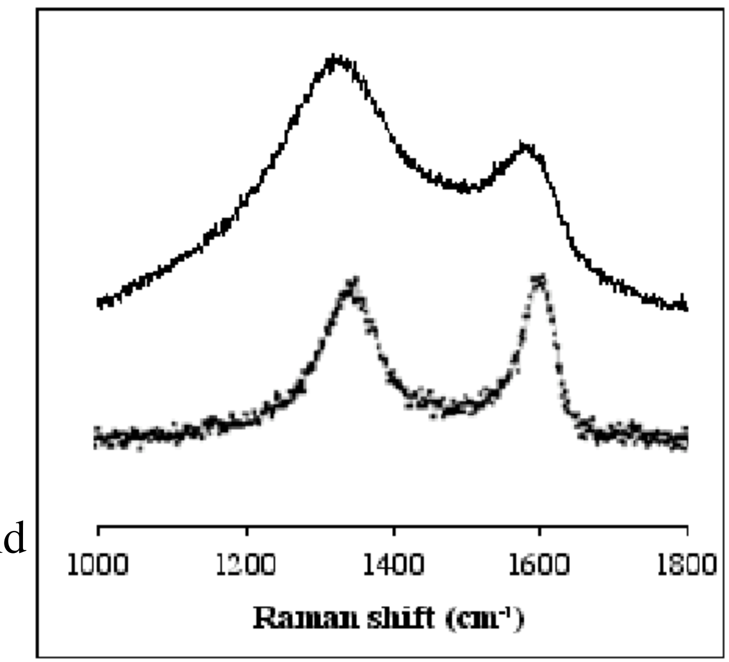
c,d: SEM micrographs of self-assembled silica-carbonate aggregates (scale bars = 40 μm)

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

Abiotic origin of microfossil-like structures #3



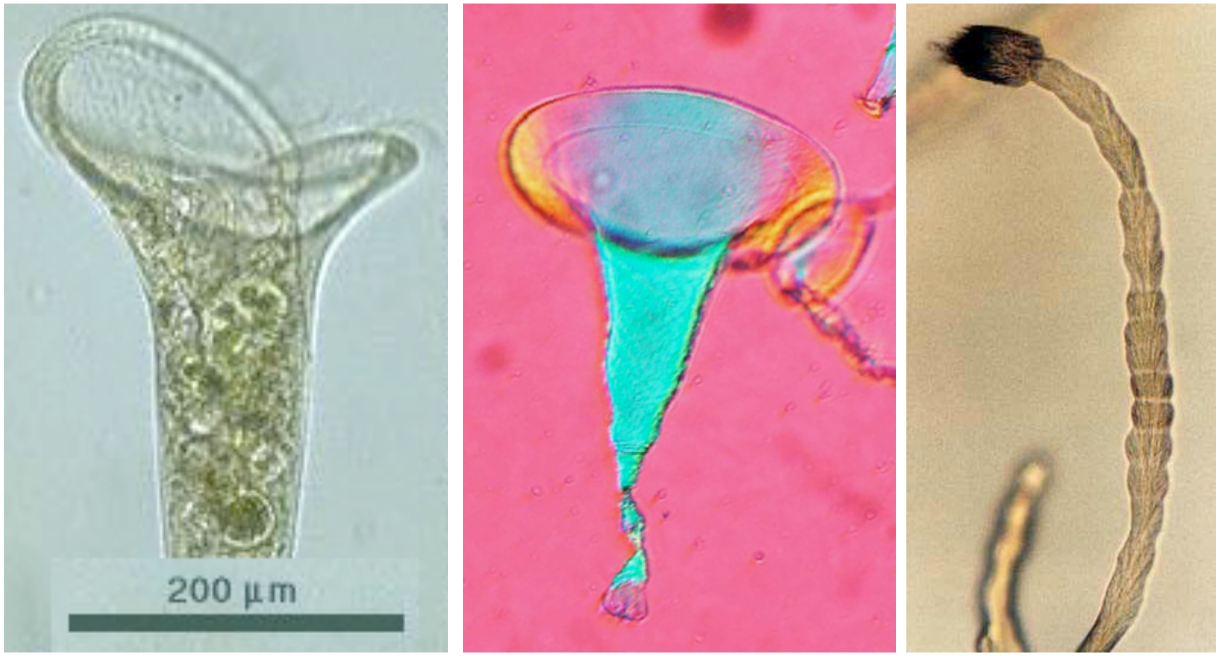
<u>Above</u>: Optical micrographs of silica-carbonate 'biomorphs' taken under same illumination (scale bars = 50 μm)
(a) As prepared; (b) after hydrothermal absorption of organics; (c) baked after exposure to organics (as in b).



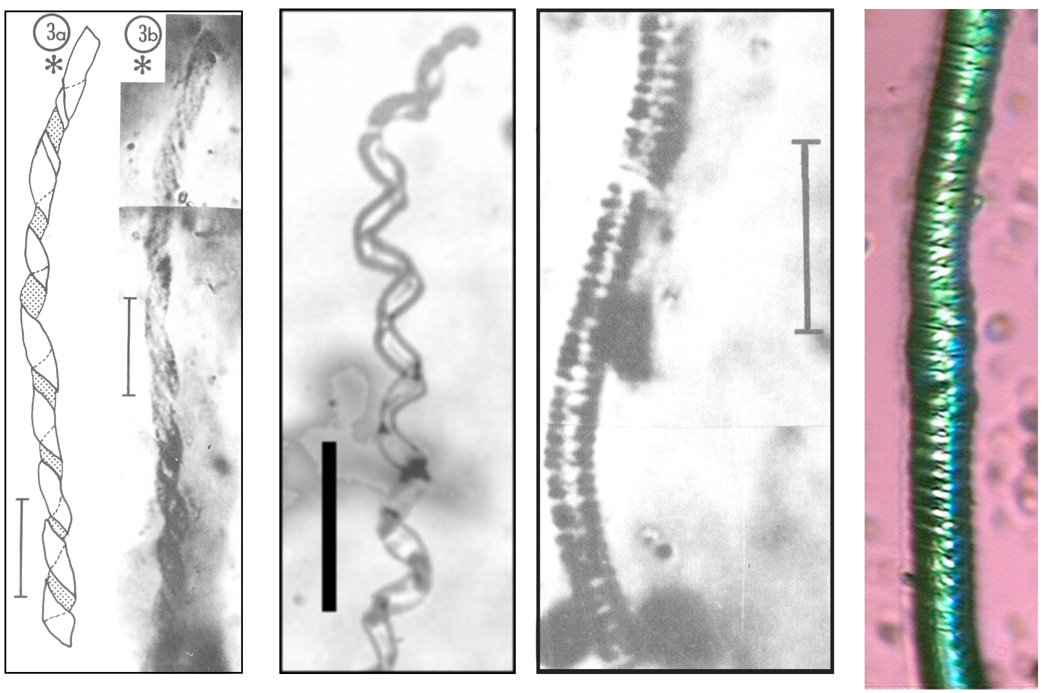
<u>Right</u>: Raman spectra of (Top) heat-cured biomorph and (Bottom) Schopf et al. (2002) 3.5 Ga Apex microfilament.

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

(a-c)



(d-g)

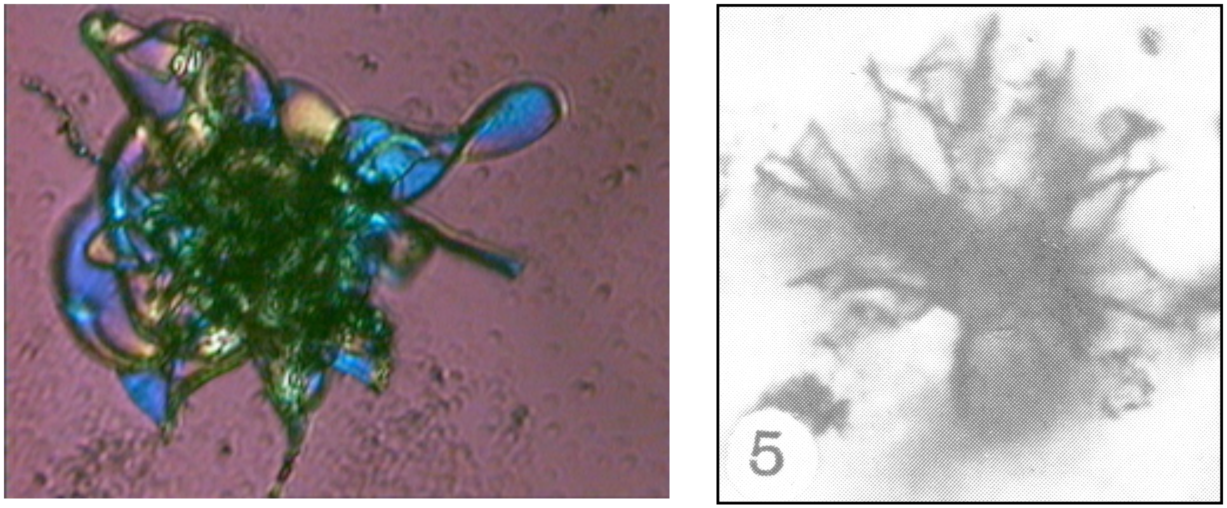


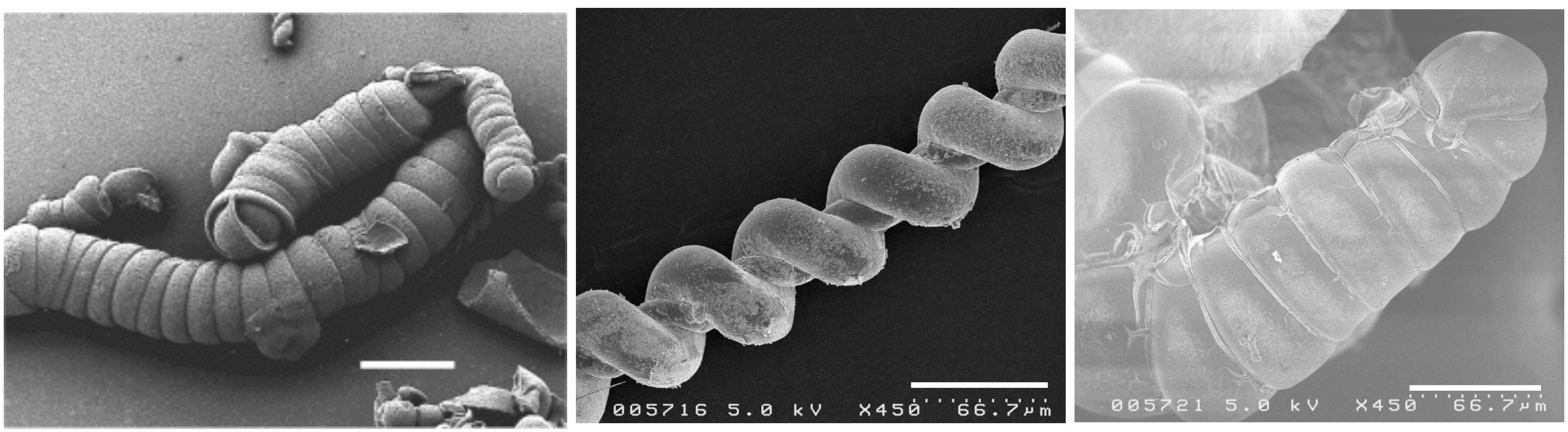
Animal, Vegetable or Mineral (“Biomorph”) #1 ?

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

Animal, Vegetable or Mineral #2?

(h-i)

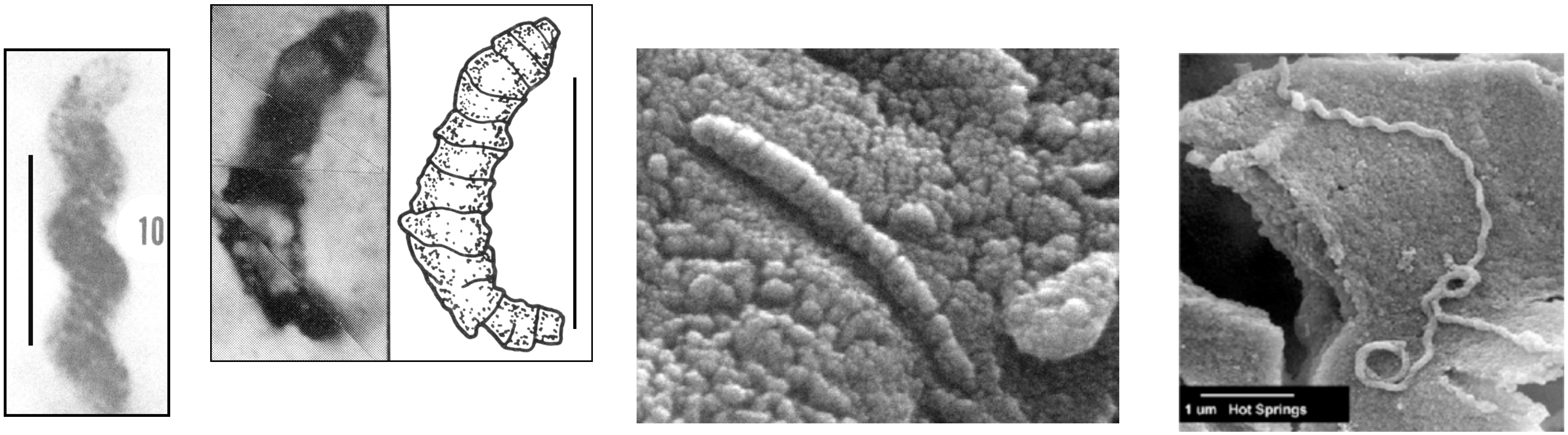




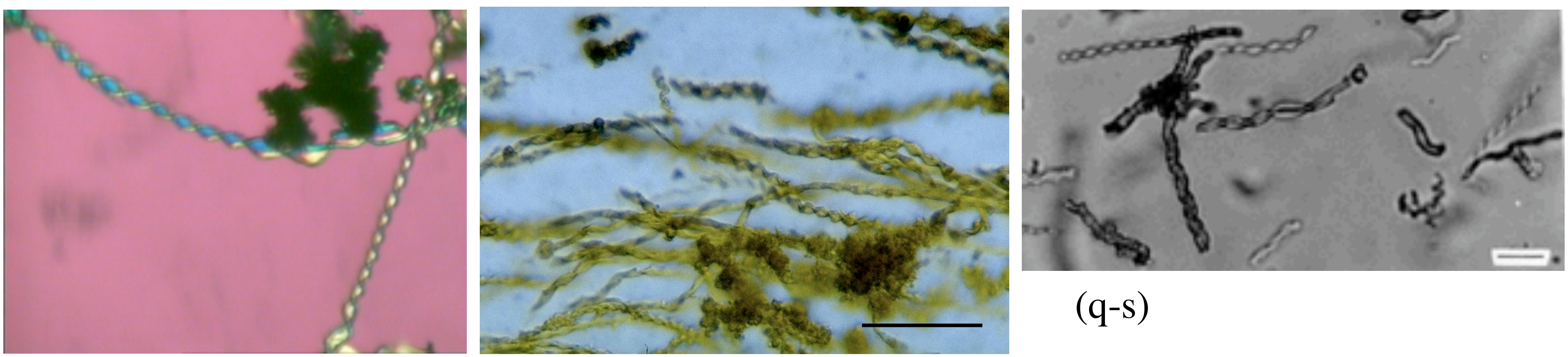
(j-l)

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

Animal, Vegetable or Mineral #3?



(m-p)



(q-s)

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

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

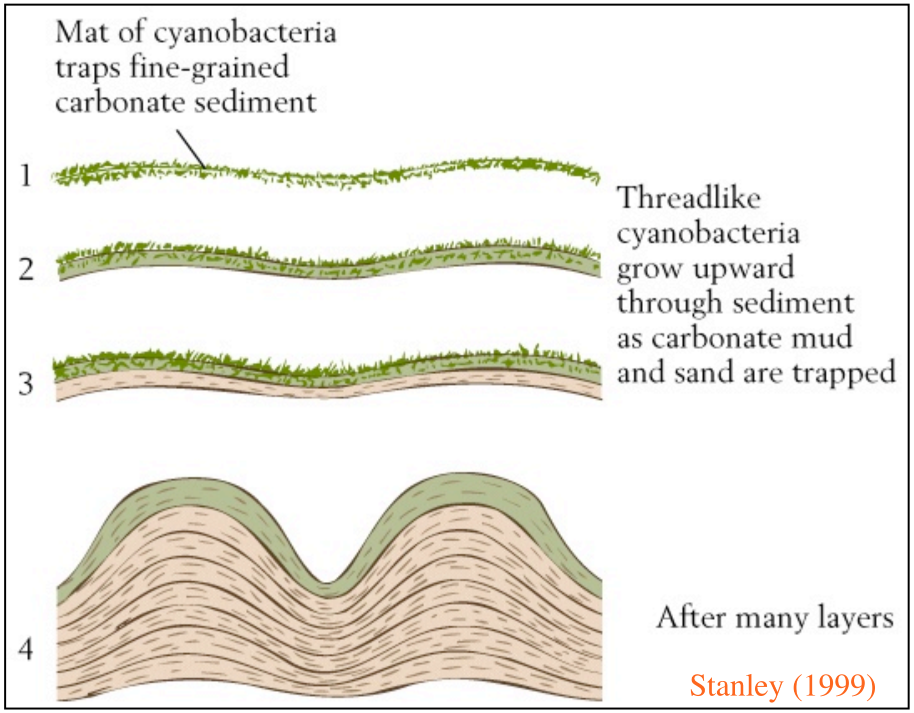
As can Raman spectrospcopy.

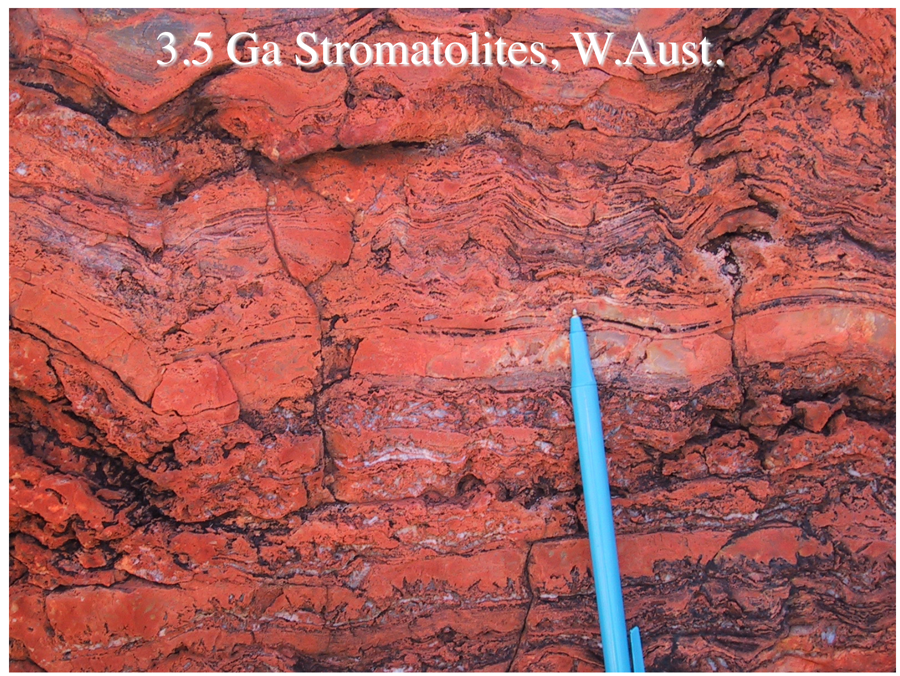
And carbon isotopes.

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

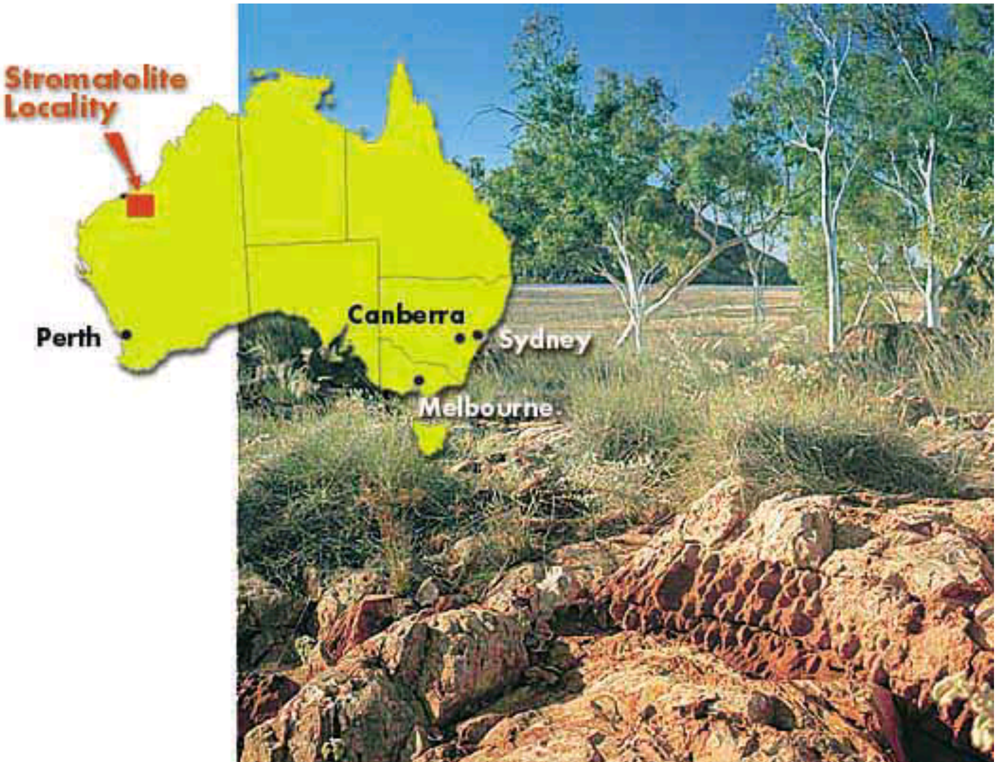
We need to take a look at… Stromatolites

What are Stromatolites & how do they form?

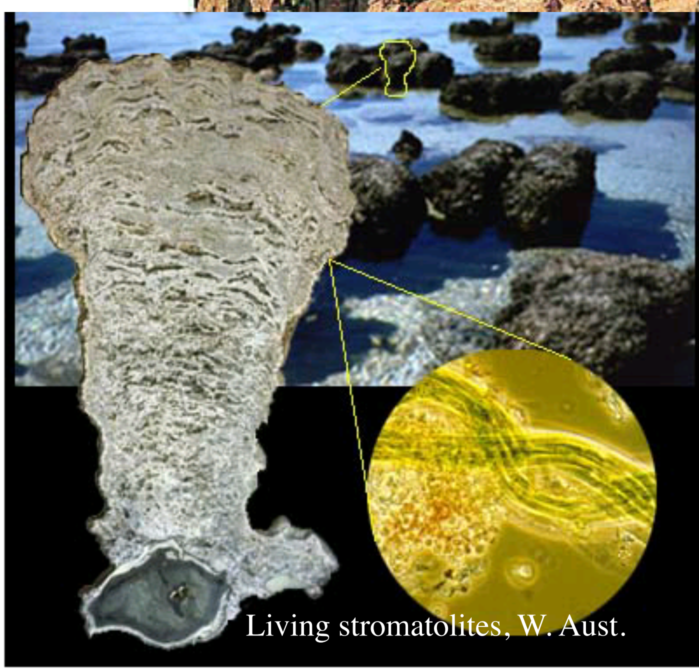




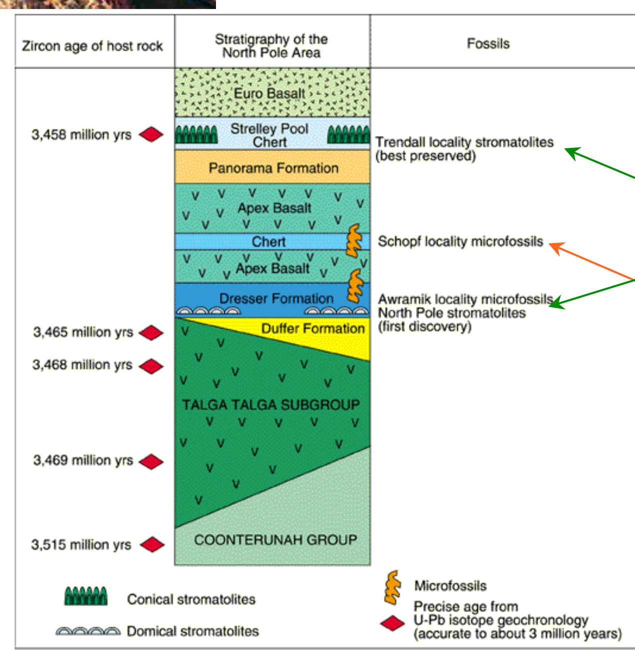
*** Ended Here - 10/20/08 ***



Stromatolites

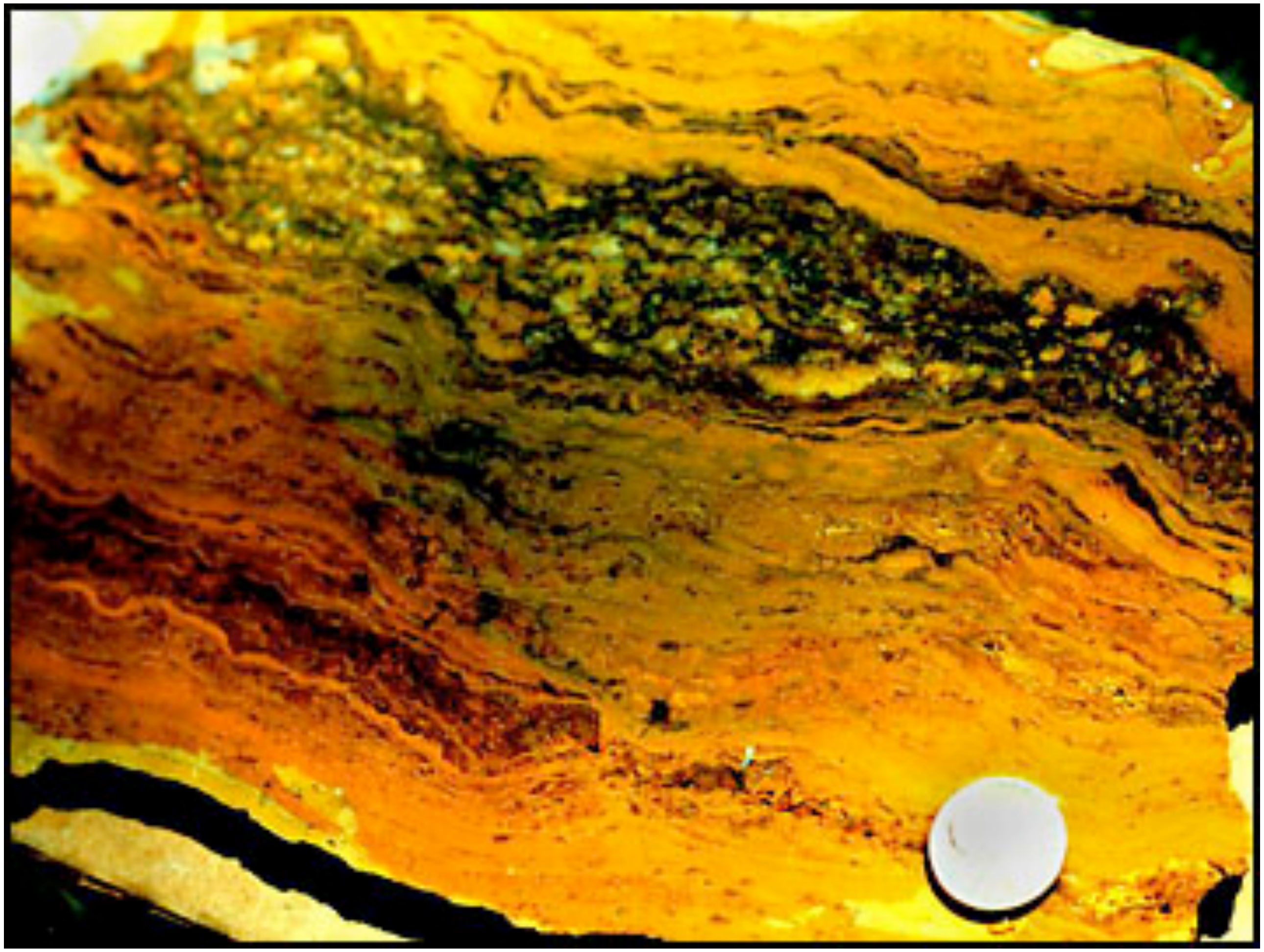


Living stromatolites, W. Aust.



- W. Australia location of stromatolites & Schopf 'microfossils'

•Hofman et al. (1999) *Geol. Soc. Am. Bull.* Vol. 111(8): 1256-1262.
•http://www.dme.wa.gov.au/ancientfossils



Stromatolites-1

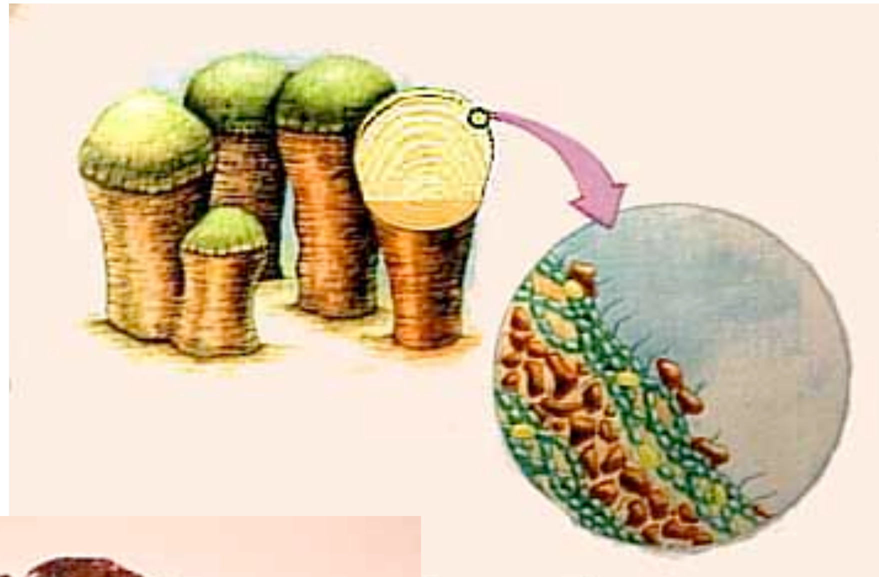
- 1.5 Ga stromatolite from Ozarks

http://www.stlcc.cc.mo.us/fv/geology/text/25.html

- Stromatolites are fossils which show the life processes of cyanobacteria (fomerly called blue-green algae). The primitive cells (Prokaryotic type), lived in huge masses that could form floating mats or extensive reefs. Masses of cyanobacteria on the sea floor deposited calcium carbonate in layers or domes. These layered deposits, which have a distinctive "signature" are called laminar stromatolites. This is an example of a layered stromatolite from the Ozark Precambrian. Most often, stromatolites appear as variously-sized arches, spheres, or domes. *Ozarkcollenia*, a distinctive type of layered Precambrian stromatolite, pushes the appearance of life in the Ozarks to well over 1.5 Ga.

Stromatolites-2

• Kona Dolomite (Michigan) 2.2 Ga stromatolite



• Schematic of stromatolite structure

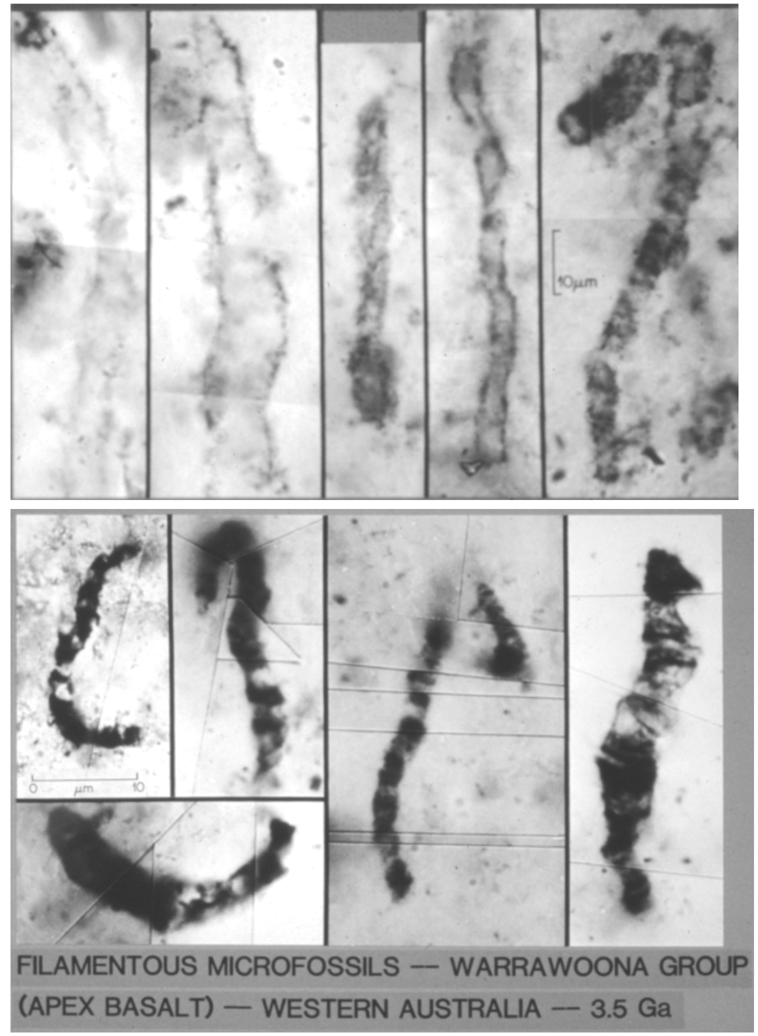
• Mary Ellen Jasper (Minnesota) 2.1 Ga stromatolite

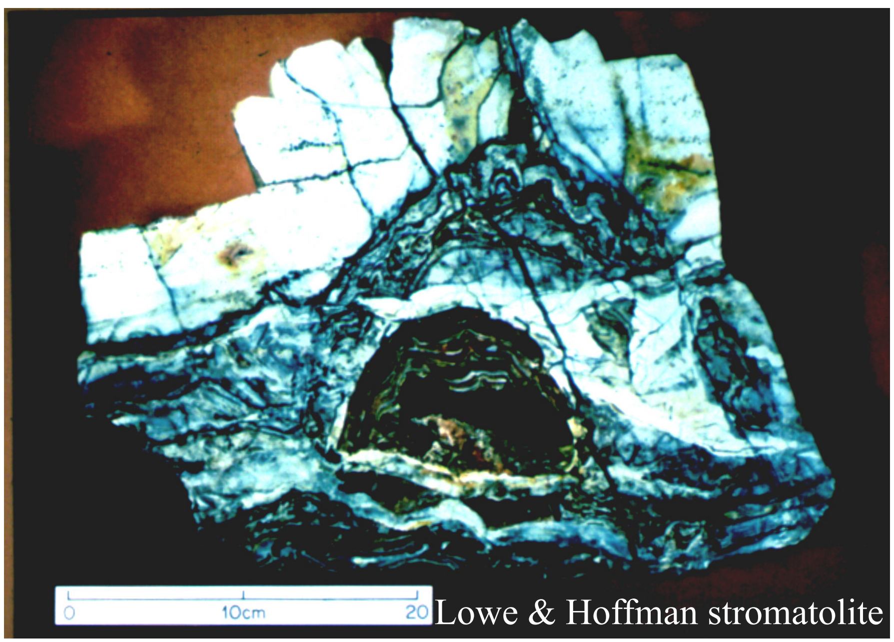
• Stomatolites are colonial structures formed by photosynthesizing cyanobacteria and other microbes. Stromatolites are prokaryotes (primitive organisms lacking a cellular nucleus) that thrived in warm aquatic environments and built reefs much the same way as coral does today.

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

Oldest Microfossils on Earth?

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





Lowe & Hoffman stromatolite

Courtesy Joe Kirschvink, CalTech

Warrawoona Stromatolites May be the Oldest Convincing Evidence for Life on Earth*

**My opinion & that of many geologists*

Grotzinger & Knoll '99
argue that Archean stromatolites could be simple inorganic precipitates!

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*.

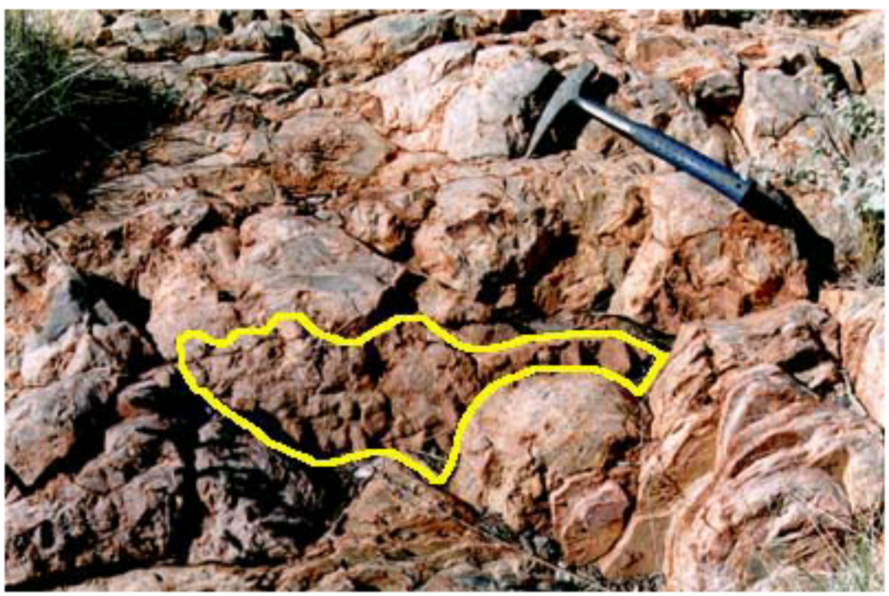
ABOVE: *Baicalia burra - a form with broad, irregular branching columns*

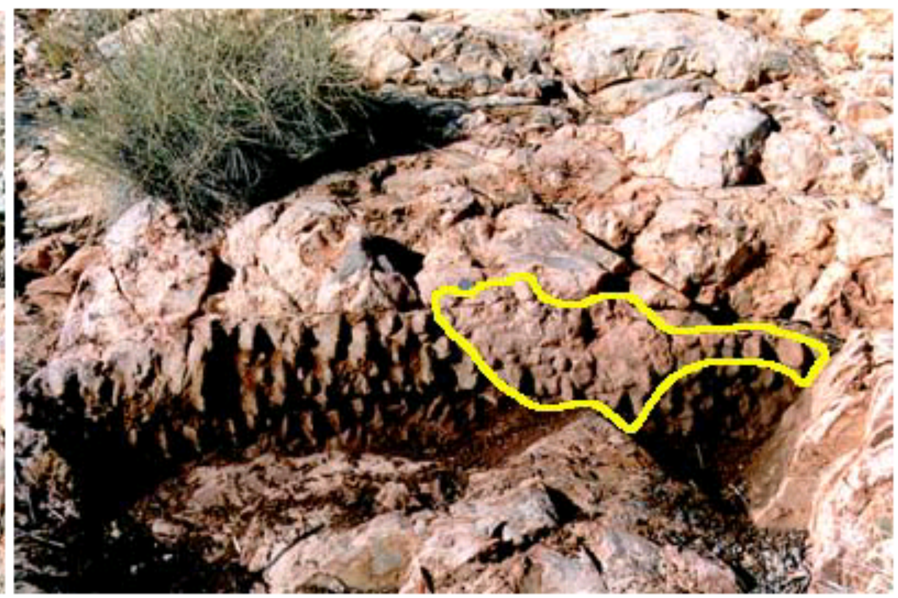
More W. Australian Stromatolites

LEFT: *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.*

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

BELOW 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.*





Macroscopic Remains of Proterozoic Stromatolites

CONOPHYTON STROMATOLITES

McARTHUR BASIN, AUSTRALIA ~ 1.6 Ga (M.R. WALTER)

Caveat: A possible abiotic origin for stromatolites?

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

Grotzinger & Rothman (1996) "An abiotic model for stromatolite morphogenesis," *Nature*, Vol. 382: 423-425.

A **Modern Analog**, though, provides support for the interpretation of stromatolites as fossil life forms:
Modern Living Stromatolites in Shark Bay, Australia

http://www.sharkbay.org/terrestial_enviroment/page_15.htm

- 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**.

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.

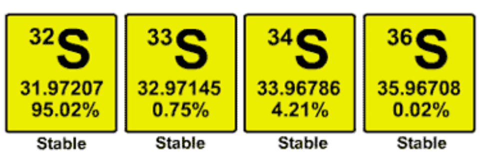
By 3.47 Ga there is additional evidence for microbial life in the form of isotopically-depleted sulfur minerals….

Isotopic evidence for microbial sulphate reduction in the early Archaean era

Yanan Shen*, Roger Buick† & Donald E. Canfield*

* *Danish Center for Earth System Science (DCESS) and Institute of Biology, Odense University, SDU, Campusvej 55, 5230 Odense M, Denmark*
† *School of Geosciences FO5, University of Sydney, Sydney, NSW 2006, Australia*

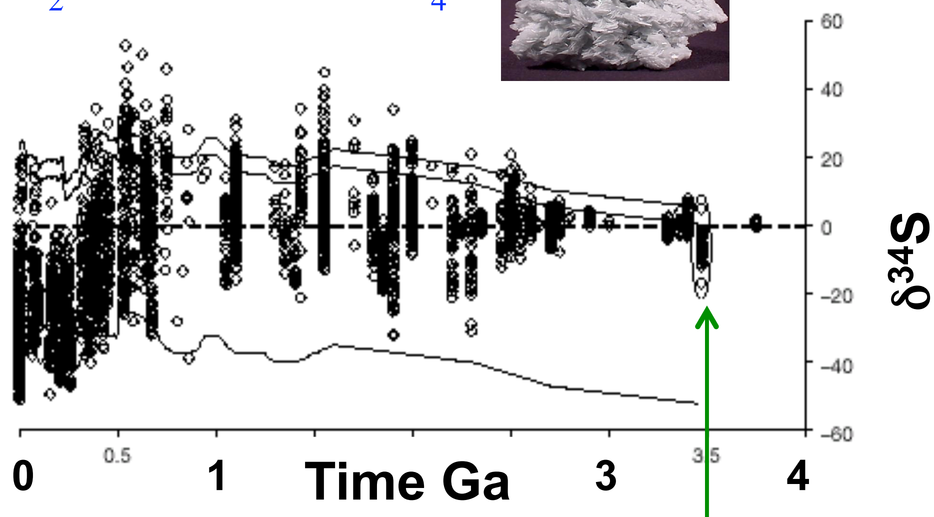
Sulphate-reducing microbes affect the modern sulphur cycle, and may be quite ancient[1,2], though when they evolved is uncertain. These organisms produce sulphide while oxidizing organic matter or hydrogen with sulphate[3]. At sulphate concentrations greater than 1 mM, the sulphides are isotopically fractionated (depleted in ^{34}S) by 10–40‰ compared to the sulphate, with fractionations decreasing to near 0‰ at lower concentrations[2,4–6]. The isotope record of sedimentary sulphides shows large fractionations relative to seawater sulphate by 2.7 Gyr ago, indicating microbial sulphate reduction[7]. In older rocks, however, much smaller fractionations are of equivocal origin, possibly biogenic but also possibly volcanogenic[2,8–10]. Here we report microscopic sulphides in ~3.47-Gyr-old barites from North Pole, Australia, with maximum fractionations of 21.1‰, about a mean of 11.6‰, clearly indicating microbial sulphate reduction. Our results extend the geological record of microbial sulphate reduction back more than 750 million years, and represent direct evidence of an early specific metabolic pathway—allowing time calibration of a deep node on the tree of life.



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

Microbial Activity ~3.47 Ga Suggested by Sulfur Isotopes

H_2S in Barite = $BaSO_4$



Microbial sulphate reduction?

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

- *Sulfide is depleted in heavy isotope (^{34}S) relative to sulfate precursor when biological enzymes reduce it.*

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 Au
Nedlands, Western Australia 6907, Australia

letters to nature

"A biogenic origin is inferred for the filaments from their sinuous morphology, length-wise uniformity and intertwined habit…"

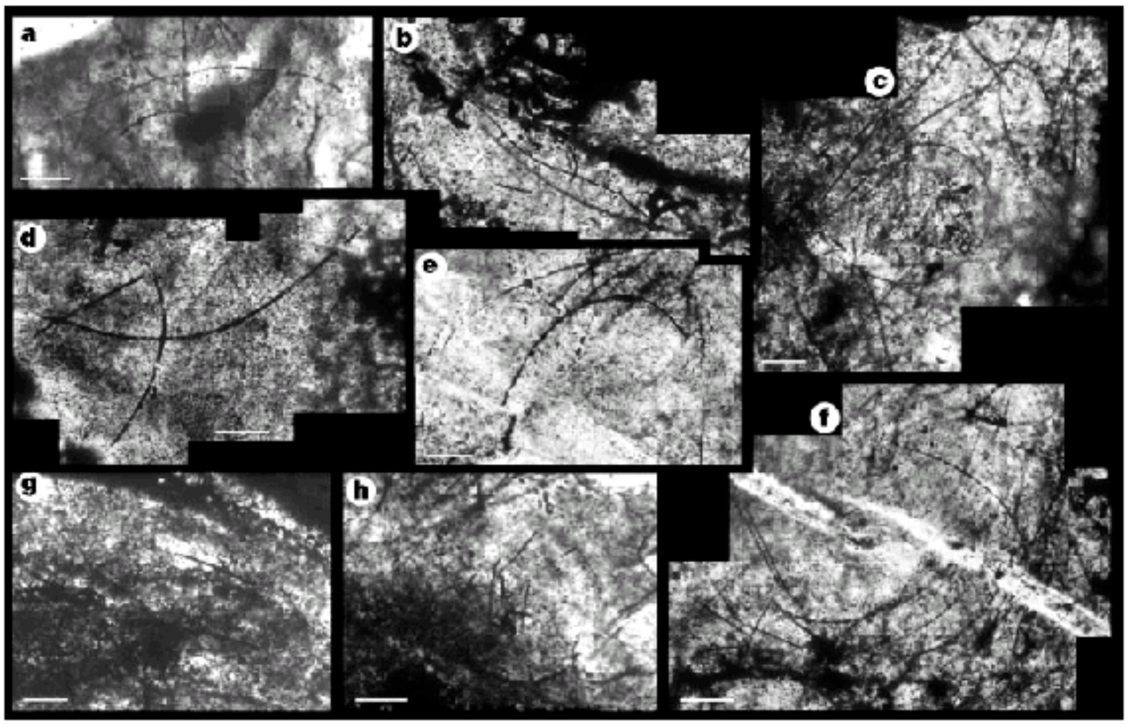


Figure 3 Photomicrographs of filaments from the Sulphur Springs VMS deposit. Scale bar, 10 μm. **a**–**f**, Straight, sinuous and curved morphologies, some densely intertwined. **g**, Filaments parallel to the concentric layering. **h**, Filaments oriented sub-perpendicular to banding.

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

Location & Images of 3.2 Ga hydrothermal microbes

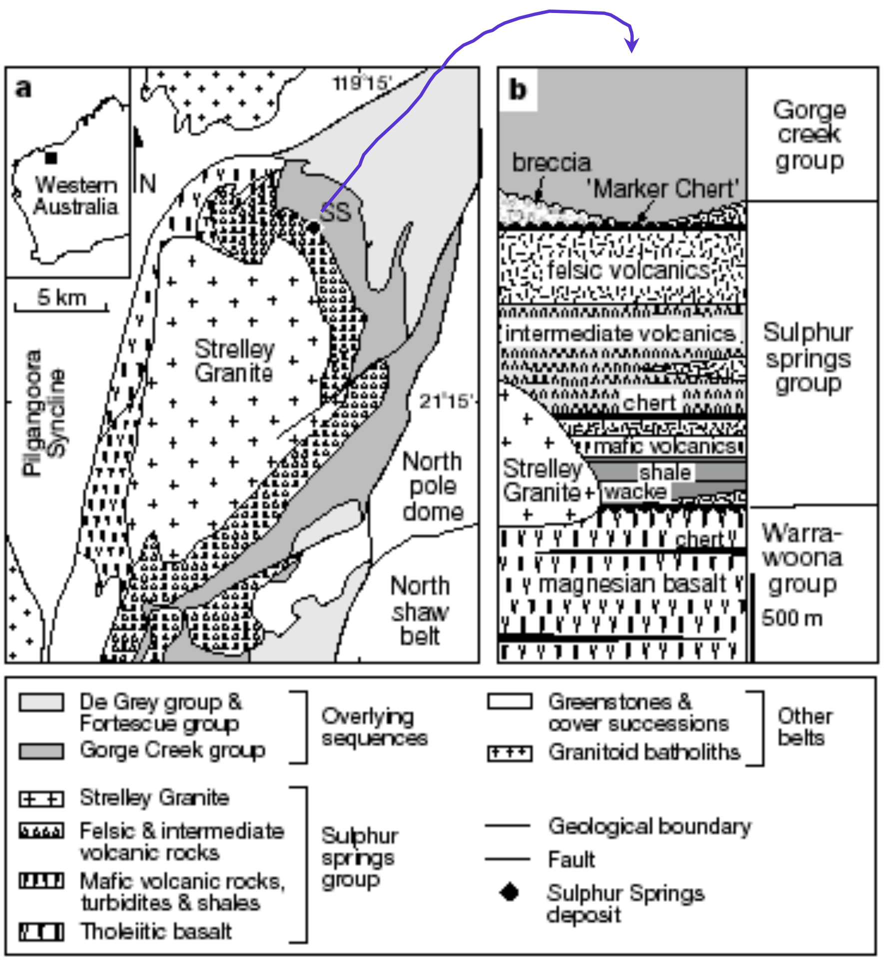


Figure 1 Location and geology of the Sulphur Springs deposit. **a**, Map showing the geology of the northern Soanesville belt and the location of the Sulphur Springs deposit (after ref. 16). **b**, Stratigraphic column of the Sulphur Springs group (after ref. 18).

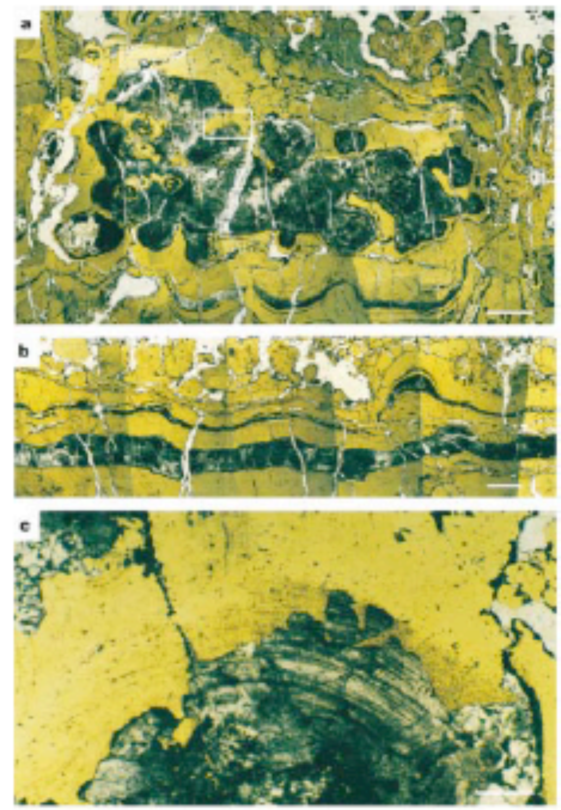
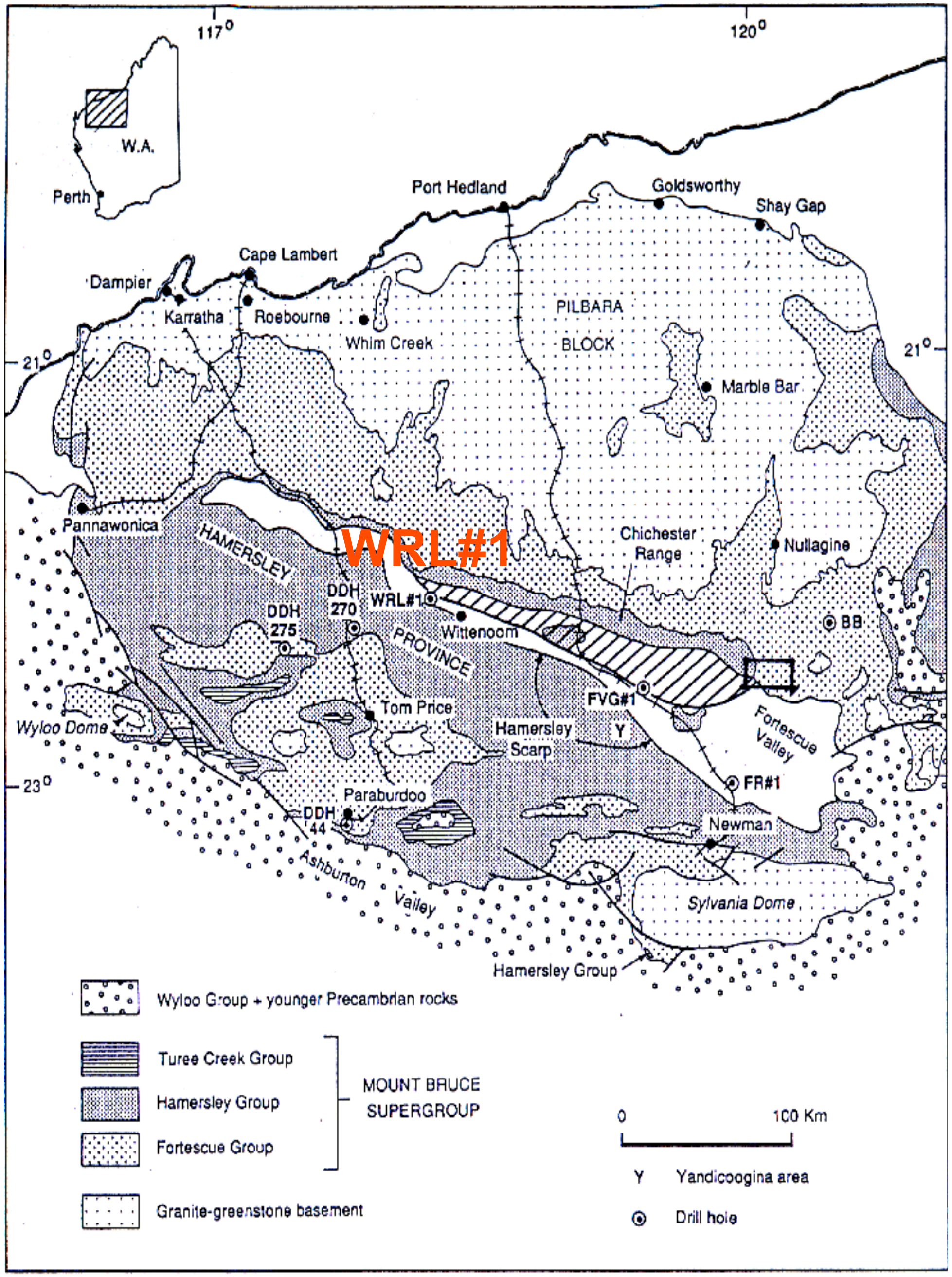


Figure 2 Remnant cores and bands containing filaments. **a**, Silica-rich colloform cores containing filaments, surrounded by replacive pyrite (gold). Combined transmitted and reflected light (TL and RL) photographic montage. **b**, Thin banded layer containing filaments within paragenetically early chert (TL and RL). **c**, Detail of **a** showing the partial replacement of quartz-rich colloform structures displaying fine-scale lamination (TL and RL). Scale bar is 1 mm for **a**, **b** and 0.1 mm for **c**.

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.*

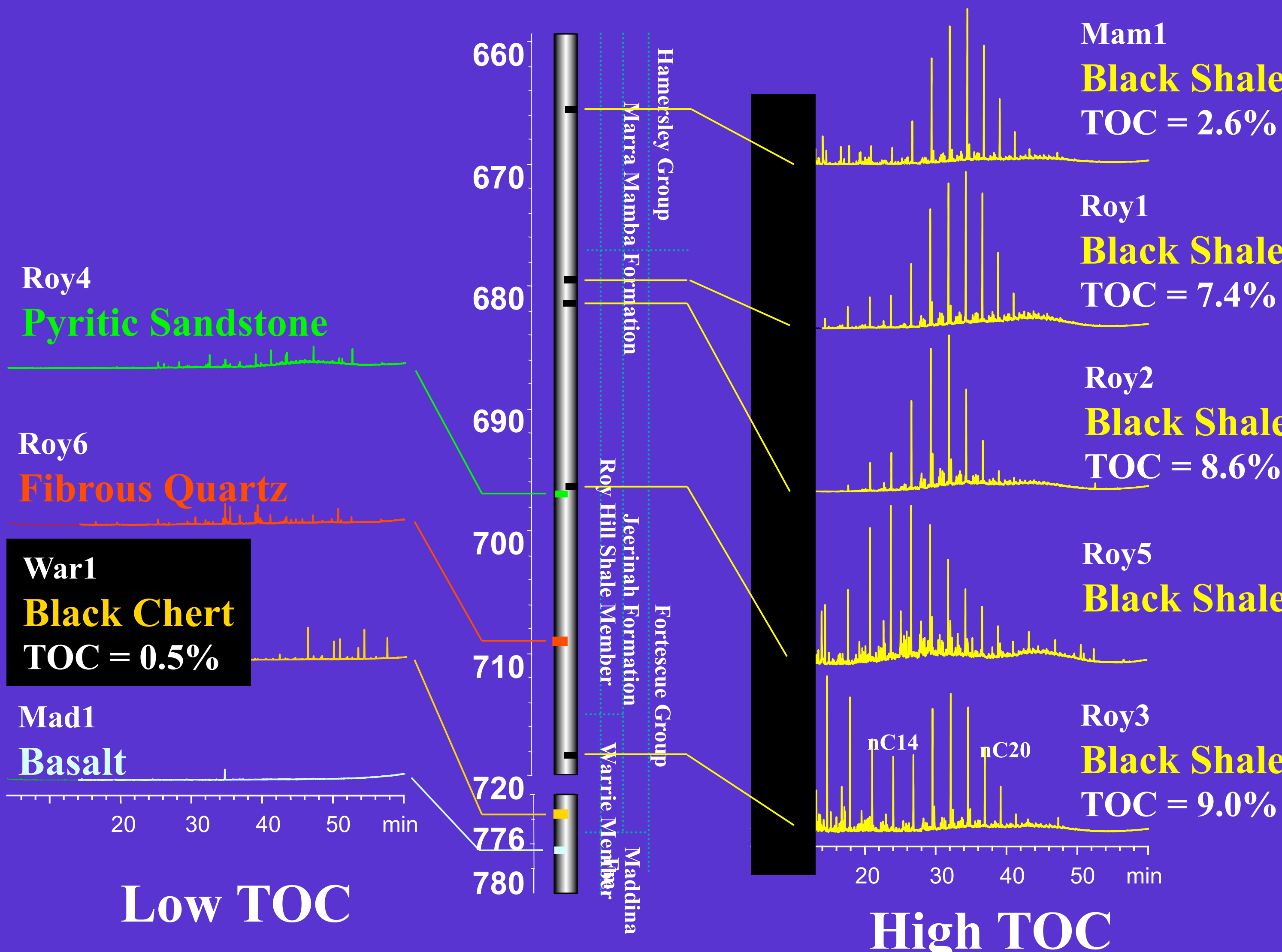


•Archean Molecular Fossils from the 2.7 Ga Roy Hill Shale

PILBARA CRATON

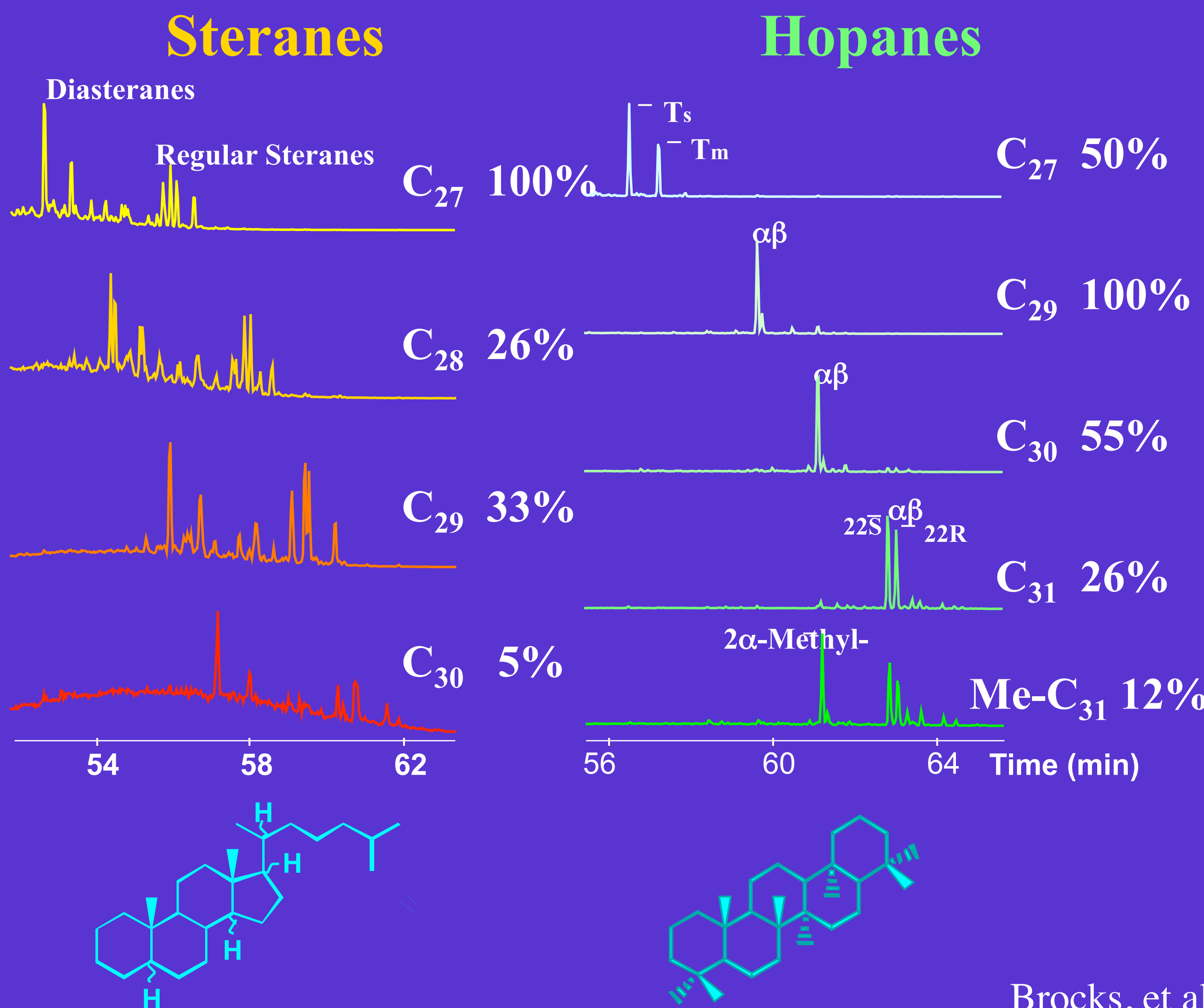
“Archean Molecular Fossils & The Early Rise of Eukaryotes”
Jochen J. Brocks, Graham A. Logan, Roger Buick & Roger E. Summons
Science, 285, 1033, 1999

•GEOCHEMISTRY vs STRATIGRAPHY



Summons, Brocks, et al.

2.7 Ga Cyanobacterial & Eukaryote Biomarkers



Brocks, et al. (1999)