Is it life or not? Experimental insights into interpreting biosignatures in rocks from the early Earth and Mars

Tom McCollom

The Center for Astrobiology at the University of Colorado

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3.5 billion year old Apex chert "microfossil" site

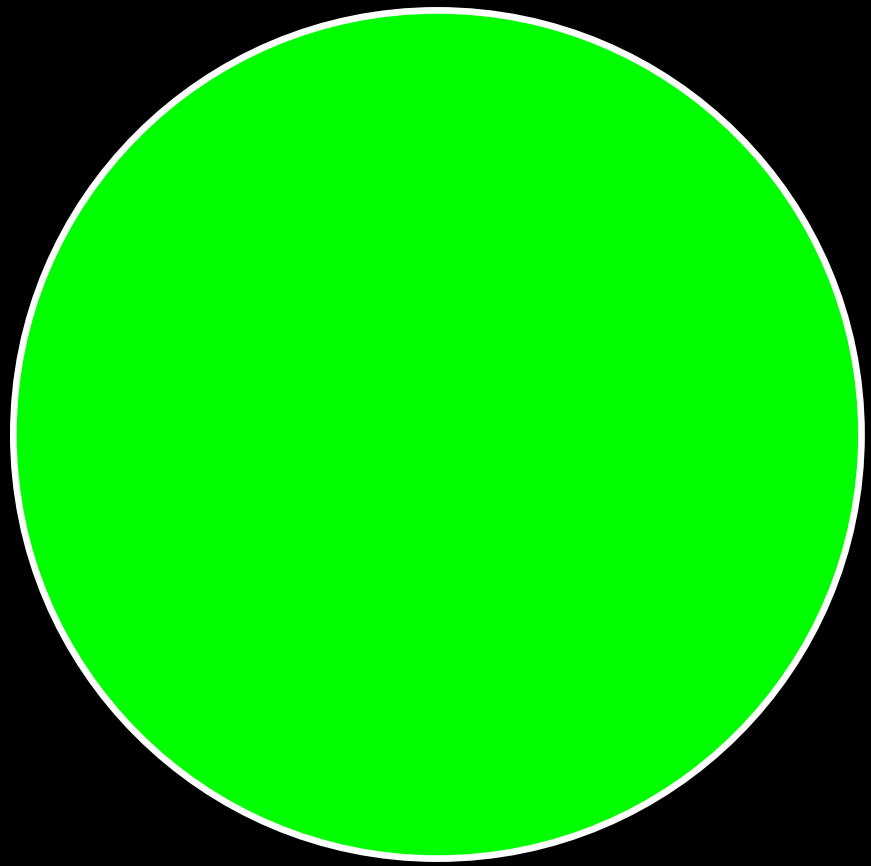
(photo from Brasier et al., 2005)

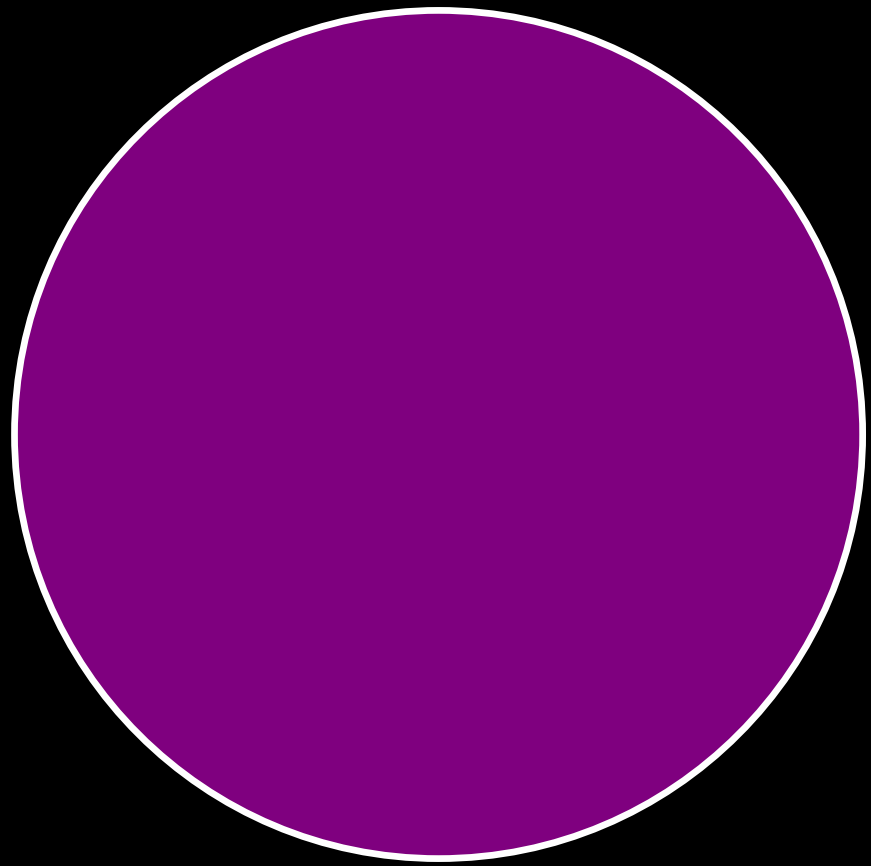
ALH84001

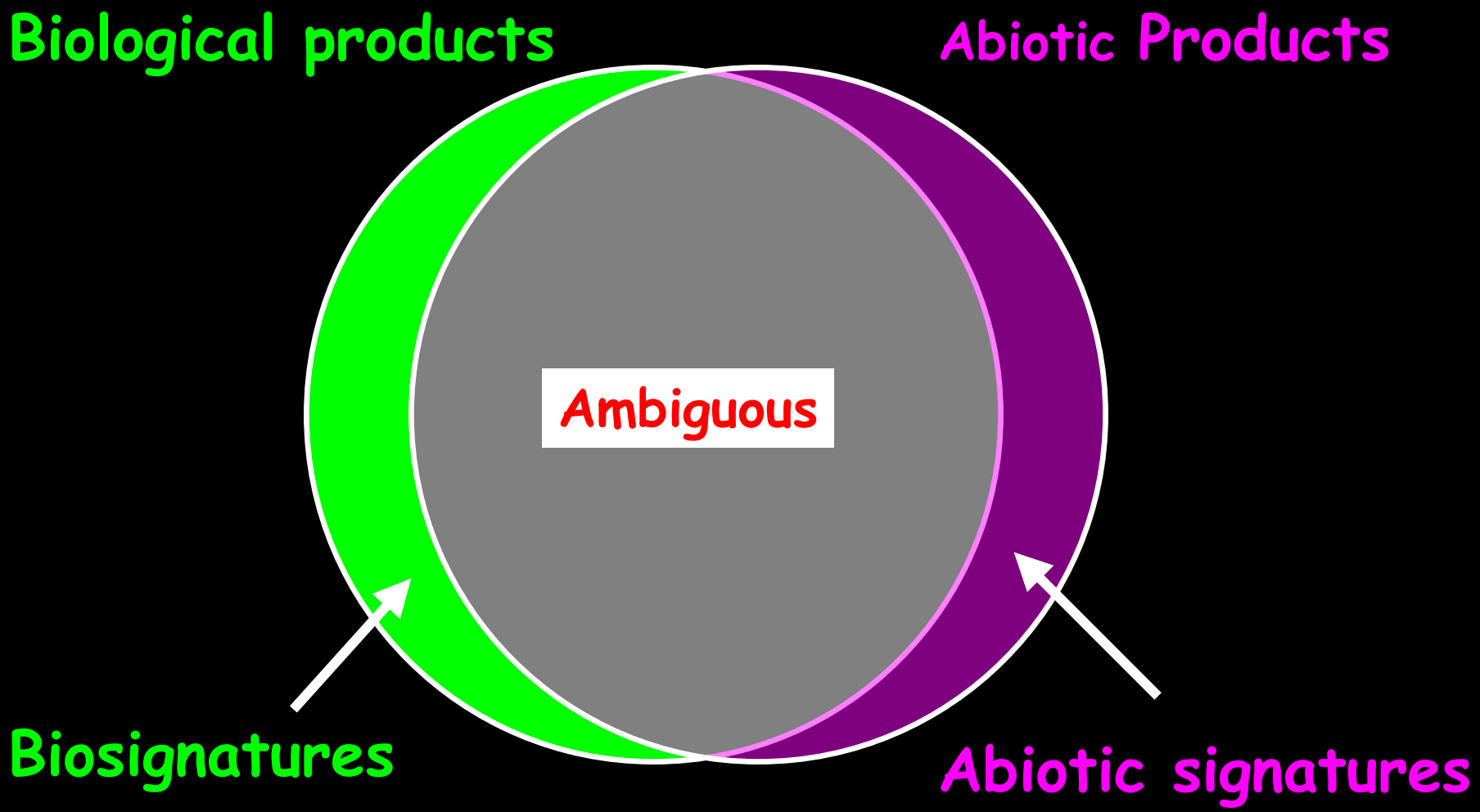
>4.3 billion year old rock from Mars

Biological products

Abiotic products







Valid biosignatures must be *exclusively* biological in origin

Outline

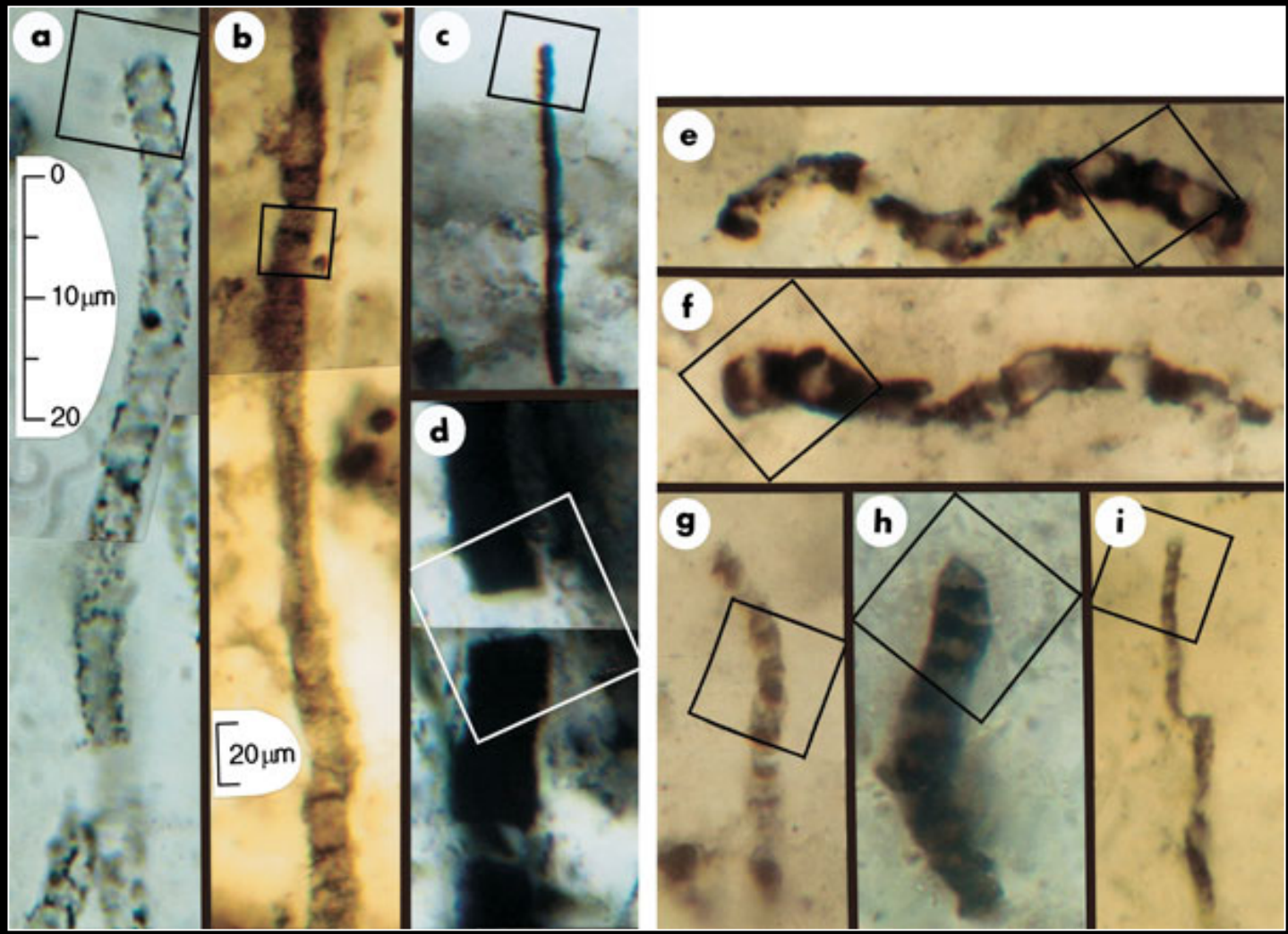
- ♣ Carbon compounds as potential biosignatures
- ♠ The skeptics view: "biosignatures" that might not be biological
- ♦ Three examples:
  - 3.5 billion-year-old Apex Chert
  - Mars meteorite ALH84001
  - >3.8 b.y.o. rocks from Greenland: "the oldest evidence of life on Earth"

The oldest fossil evidence of life (?)

(photo from Brasier et al., 2005)

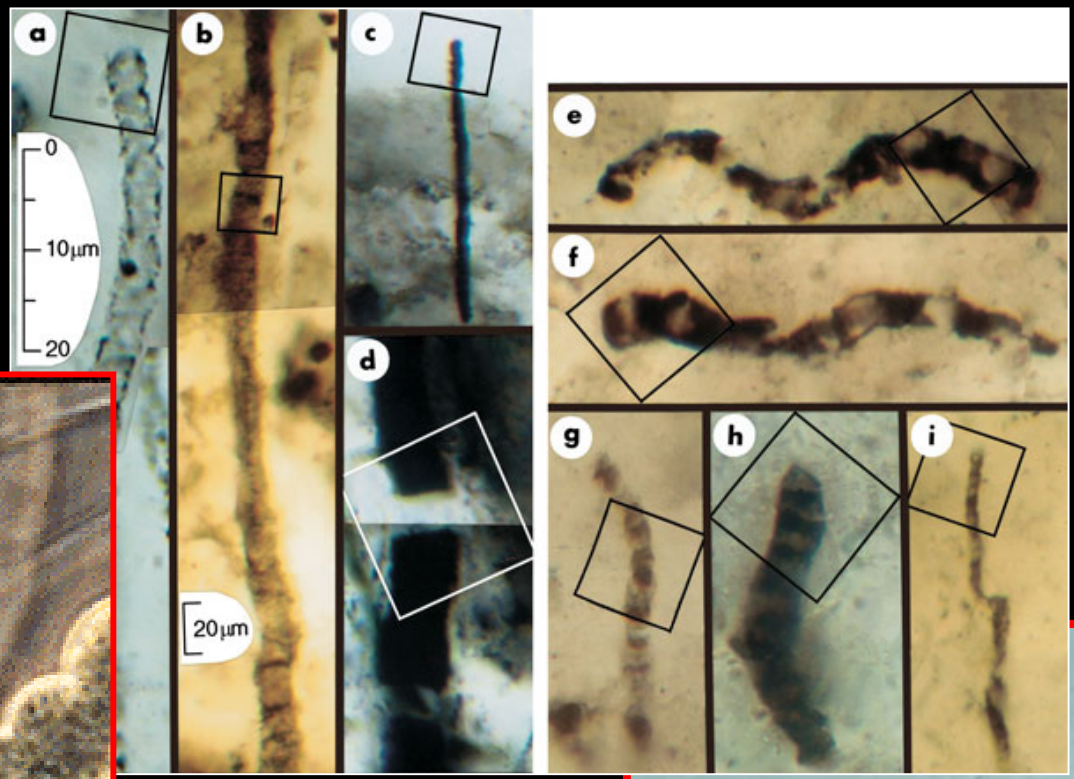
~3.5 billion year old Apex chert,
Warrawoona group, Pilbara, western Australia

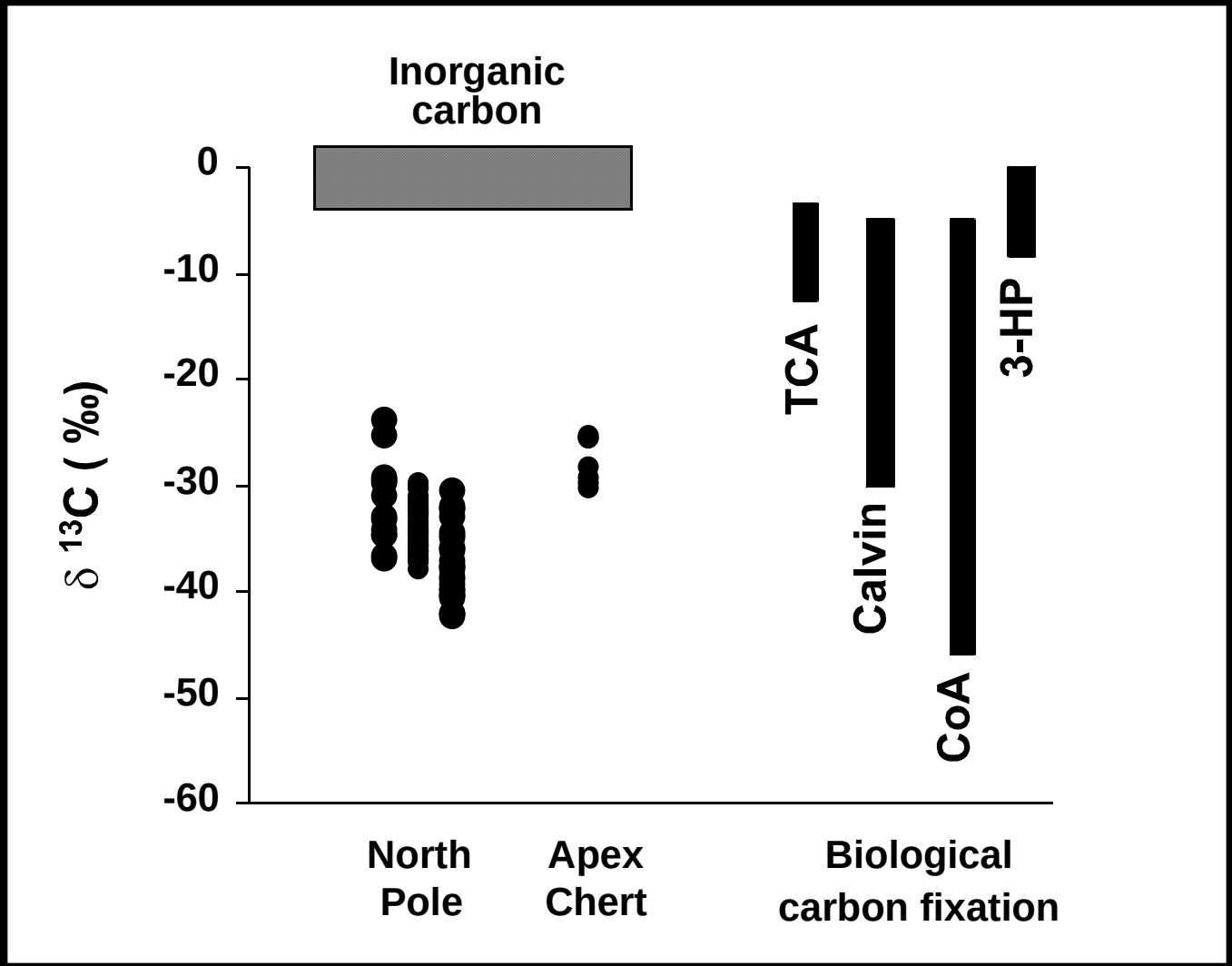
Microfossils (?) in >3.46 billion year old Apex chert



Schopf et al. *Nature* (2002)

Fossilized 3.5 b.y.o. cyanobacteria (?)

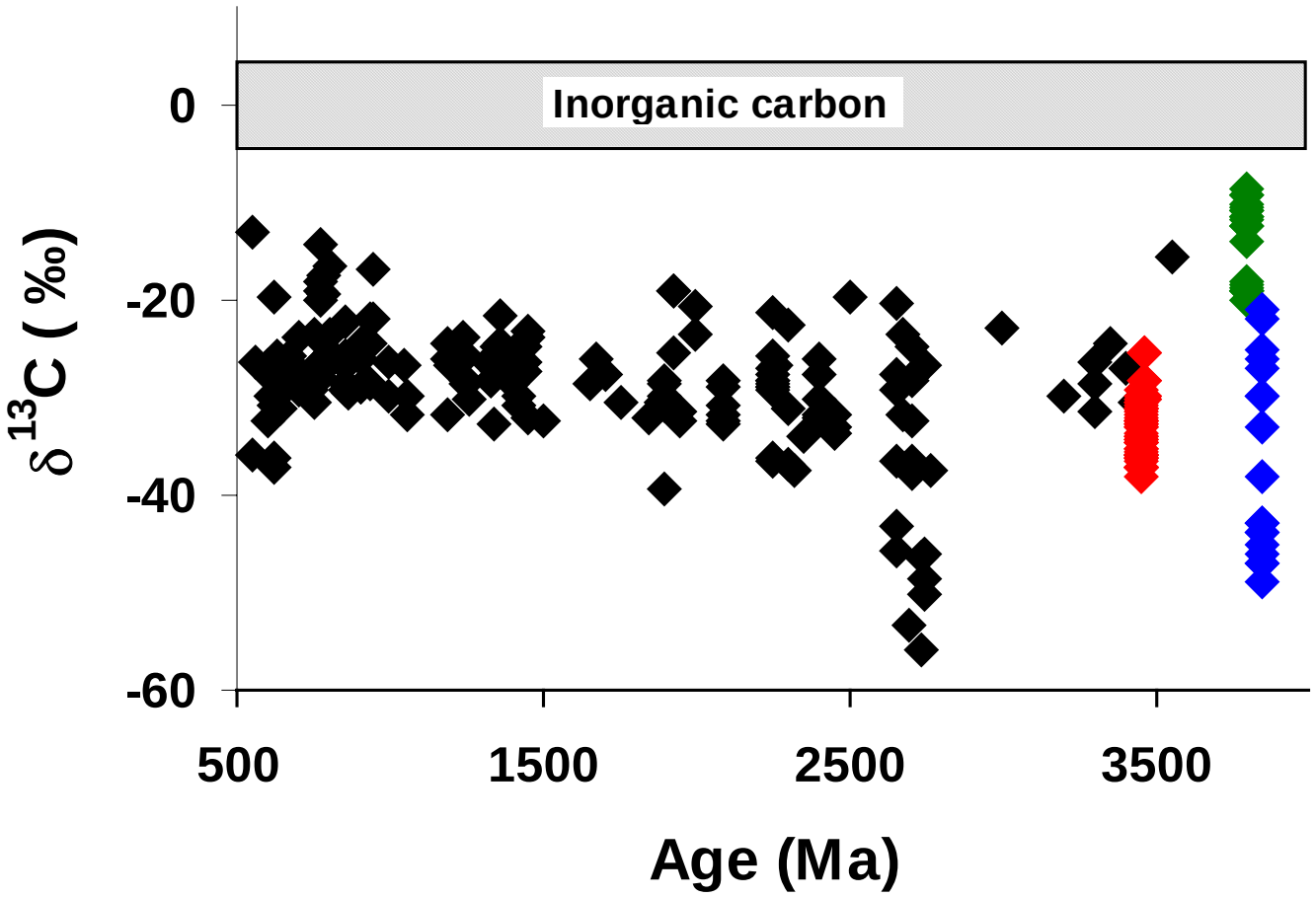




(Data from Hayes et al., 1983; Ueno et al., 2001, 2004; Brasier et al., 2002; House et al., 2003)

Carbon isotopes as a biosignature

C isotope composition of organic matter through time



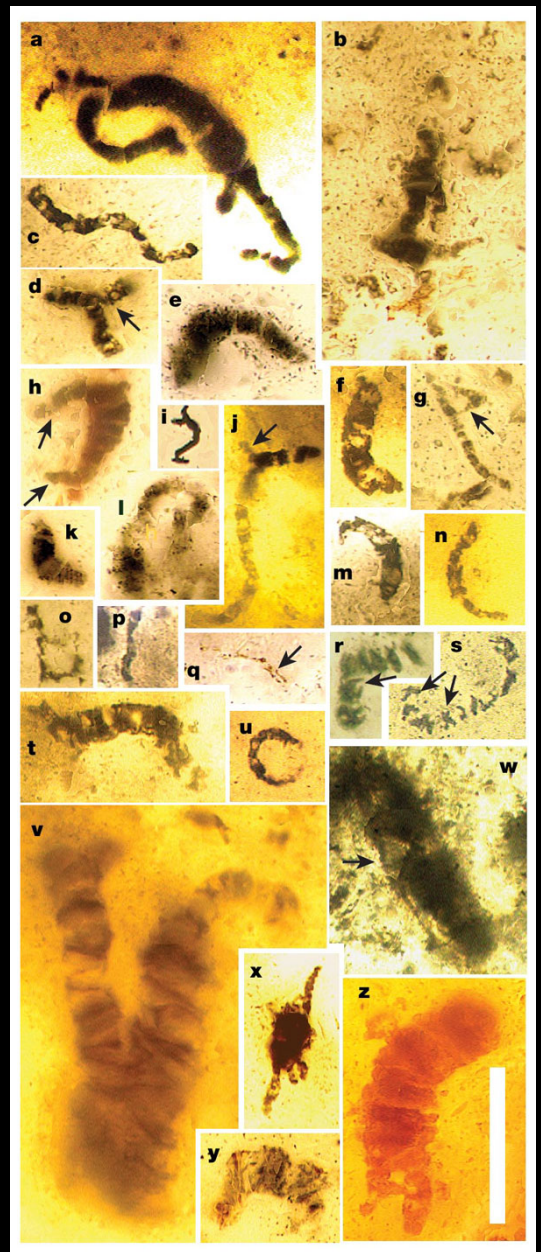
[Data for Greenland & Pilbara: Mozjsis et al., 1996; Ueno et al., 2002, 2004; van Zuilen et al., 2003; Brasier et al., 2002; Rosing, 1999]

The oldest fossil evidence of life (?)

Questioning the evidence for Earth's oldest fossils

Martin D. Brasier*, Owen R. Green*, Andrew P. Jephcoat*, Annette K. Kleppe*, Martin J. Van Kranendonk†, John F. Lindsay‡, Andrew Steele§ & Nathalie V. Grassineau‖

Nature (2002)

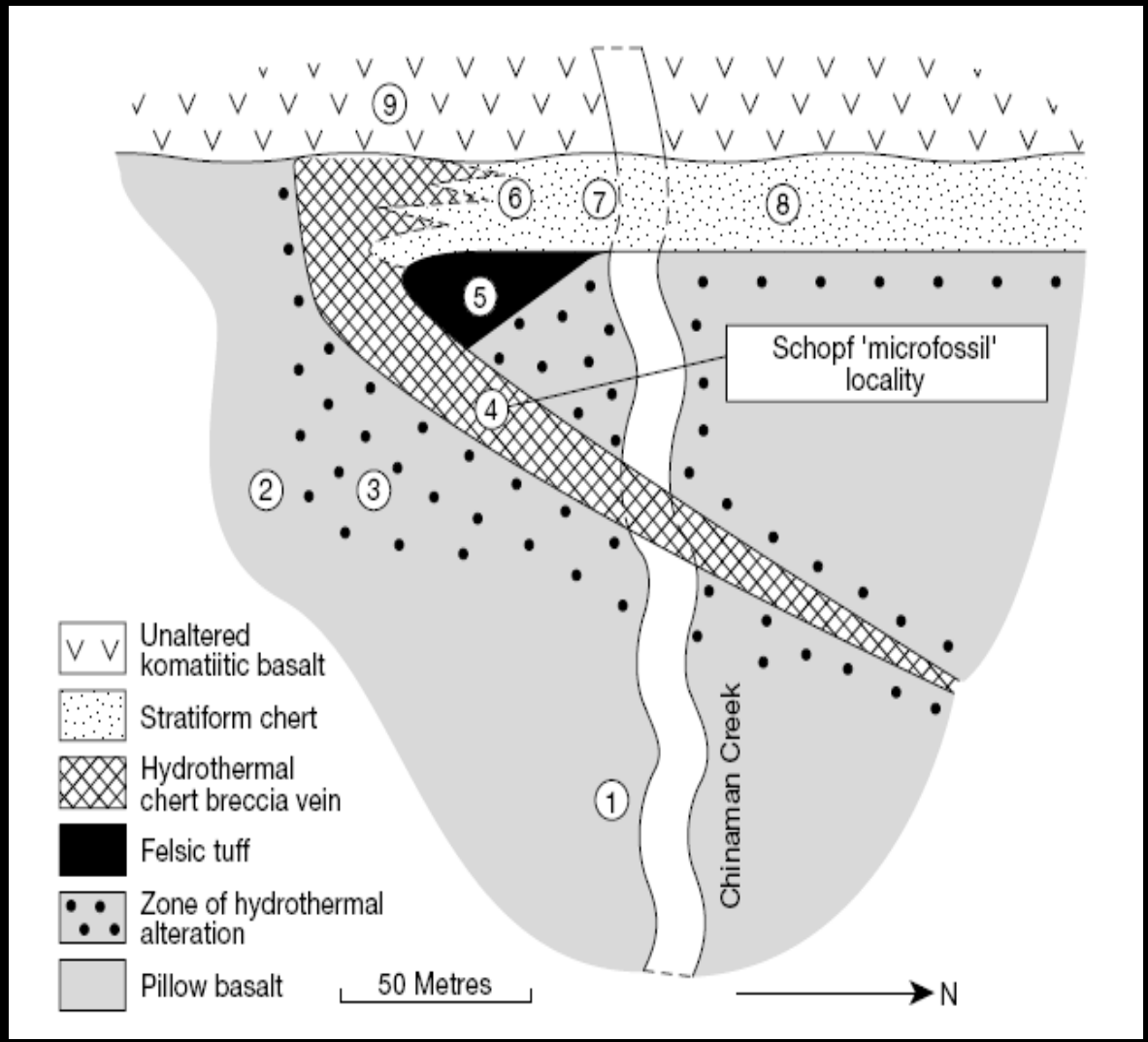


The oldest fossil evidence of life (?)

(photo from Brasier et al., 2005)

~3.5 billion year old Apex chert,
Warrawoona group, Pilbara, western Australia

Apex chert: sediment or hydrothermal vein?



[figure from Brasier et al., 2001]

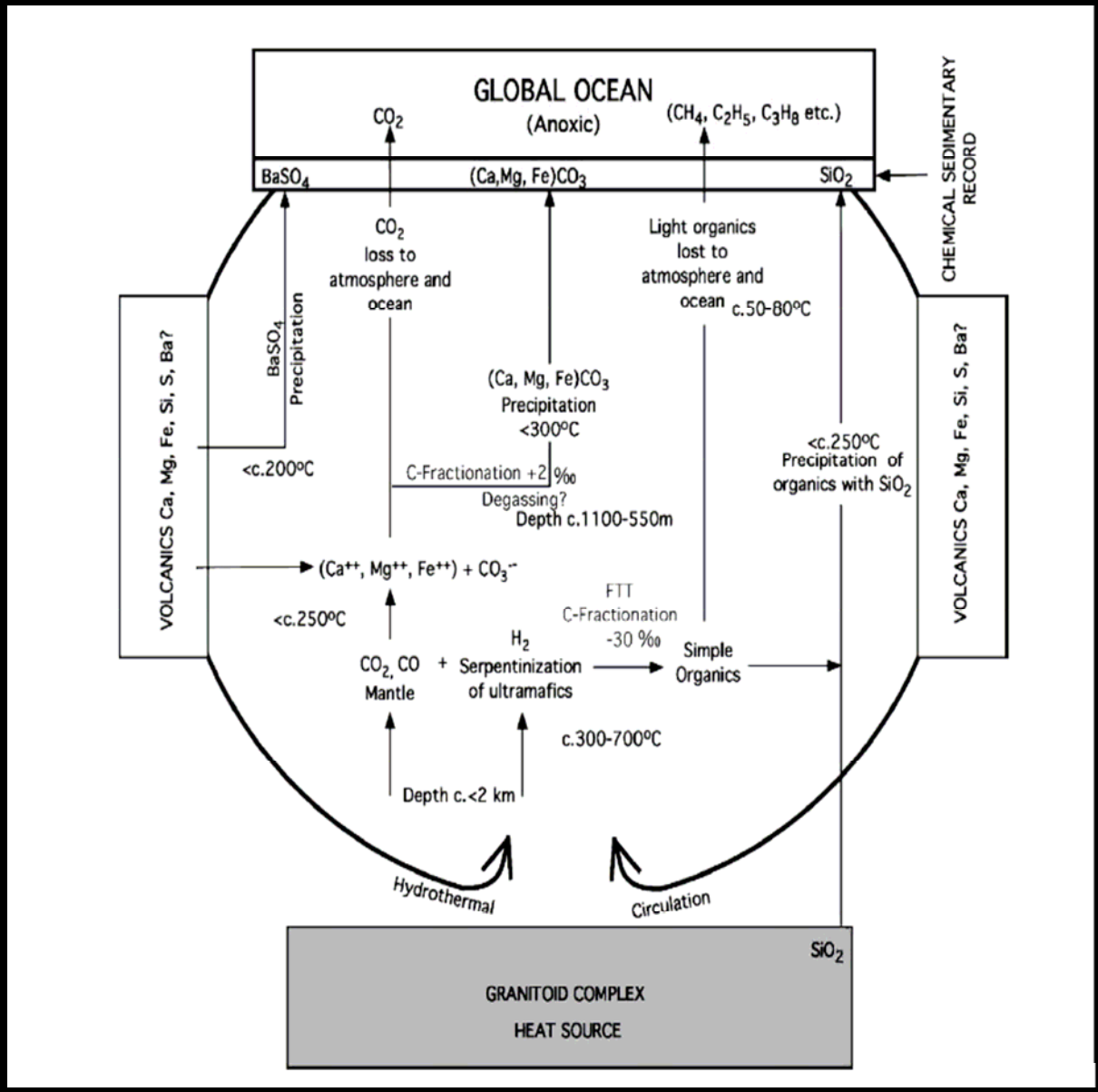
Abiotic organic synthesis in geologic systems:

$(Mg,Fe)_2SiO_2 + H_2O$
olivine

$Mg_6Si_4O_{10}(OH)_8 + Mg(OH)_2 + Fe_3O_4 + H_2$
"serpentine" *brucite* *magnetite*

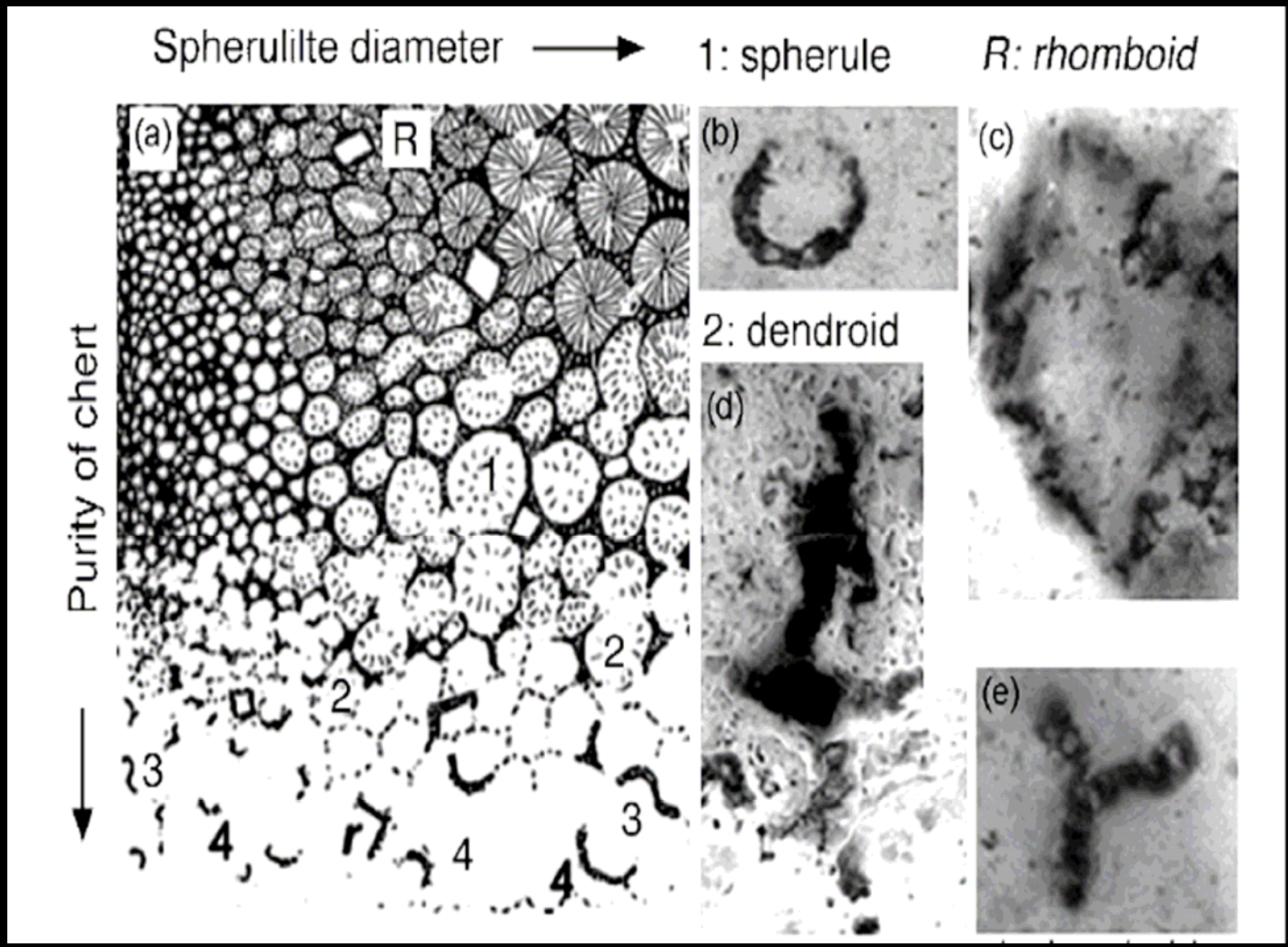
$$CO_2 + H_2 \rightarrow CH_4 + C_2H_6 + C_3H_8 + \ldots$$

Abiotic organic synthesis at Warrrawoona (?)



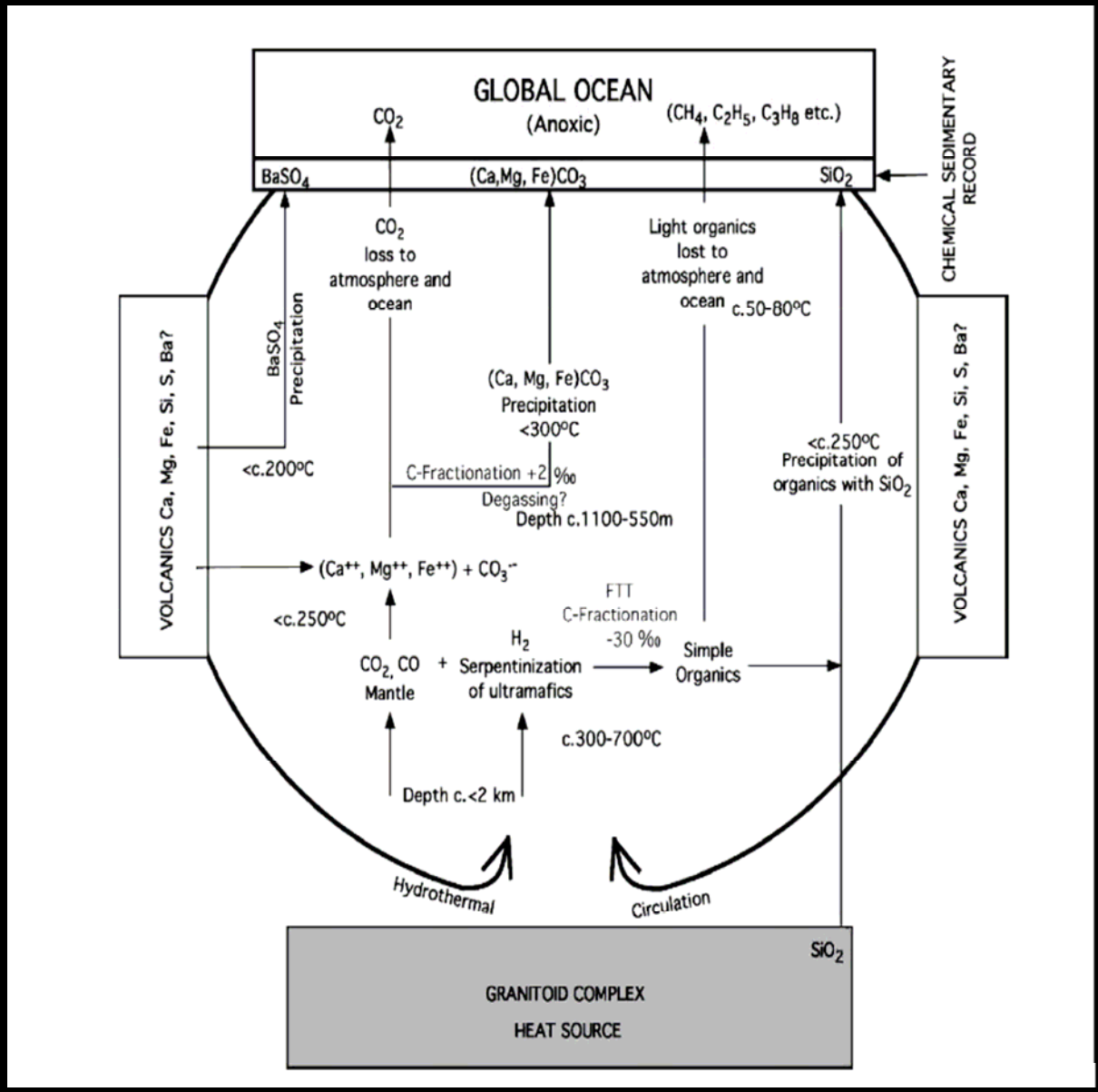
[Lindsay et al., 2005]

Abiotic organic synthesis at Warrrawoona (?)



[Brasier et al., 2005]

Abiotic organic synthesis at Warrrawoona (?)



[Lindsay et al., 2005]

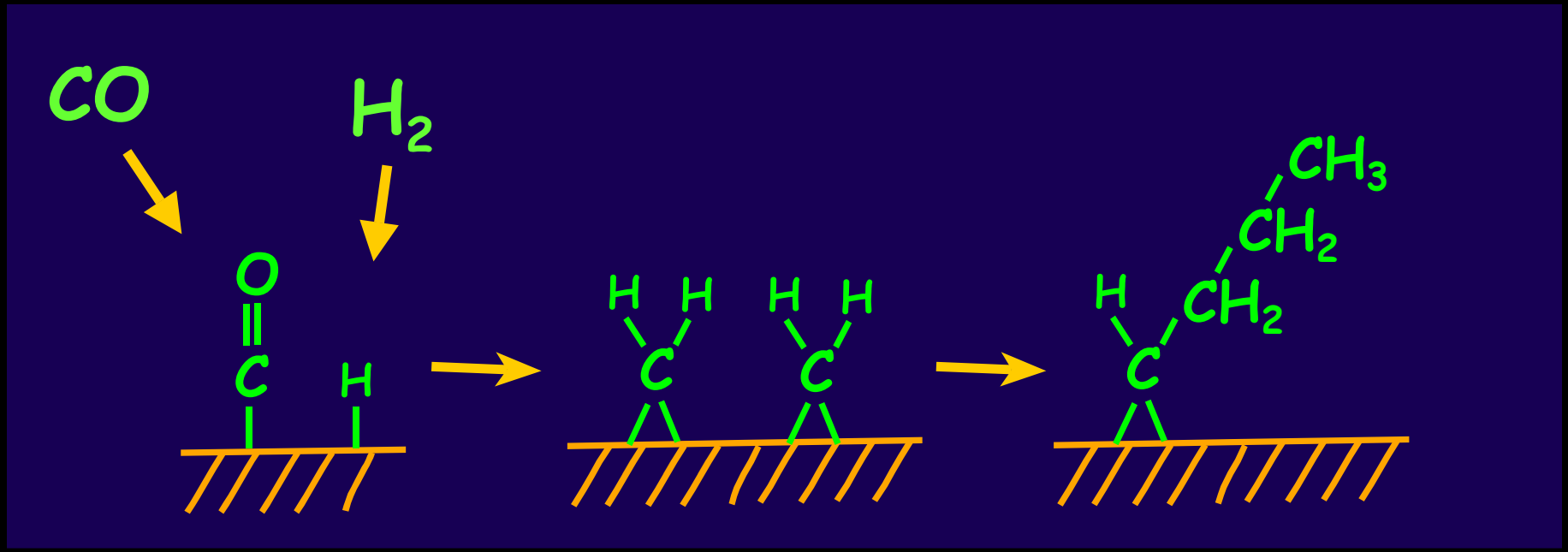
Fischer-Tropsch-type synthesis

$$CO + H_2 \rightarrow CH_4 + C_2H_6 + C_3H_8 + \ldots$$

$$CO_2 + H_2 \rightarrow CH_4 + C_2H_6 + C_3H_8 + \ldots$$

- Surface catalyzed reaction
- Primary products are linear hydrocarbons
  - characterized by decreasing abundance w/ # carbons
- Extensively studied industrial process

Fischer-Tropsch-type synthesis



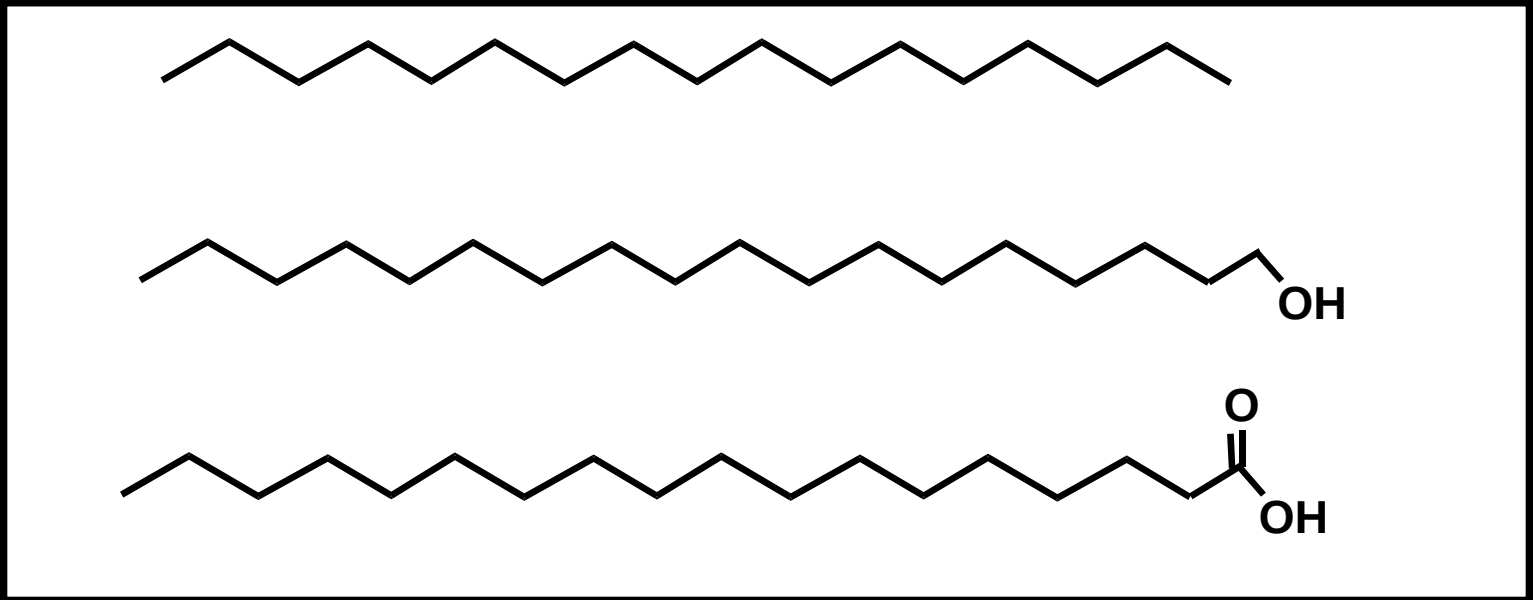
FT products dominated by linear compounds

CH_4 (methane)

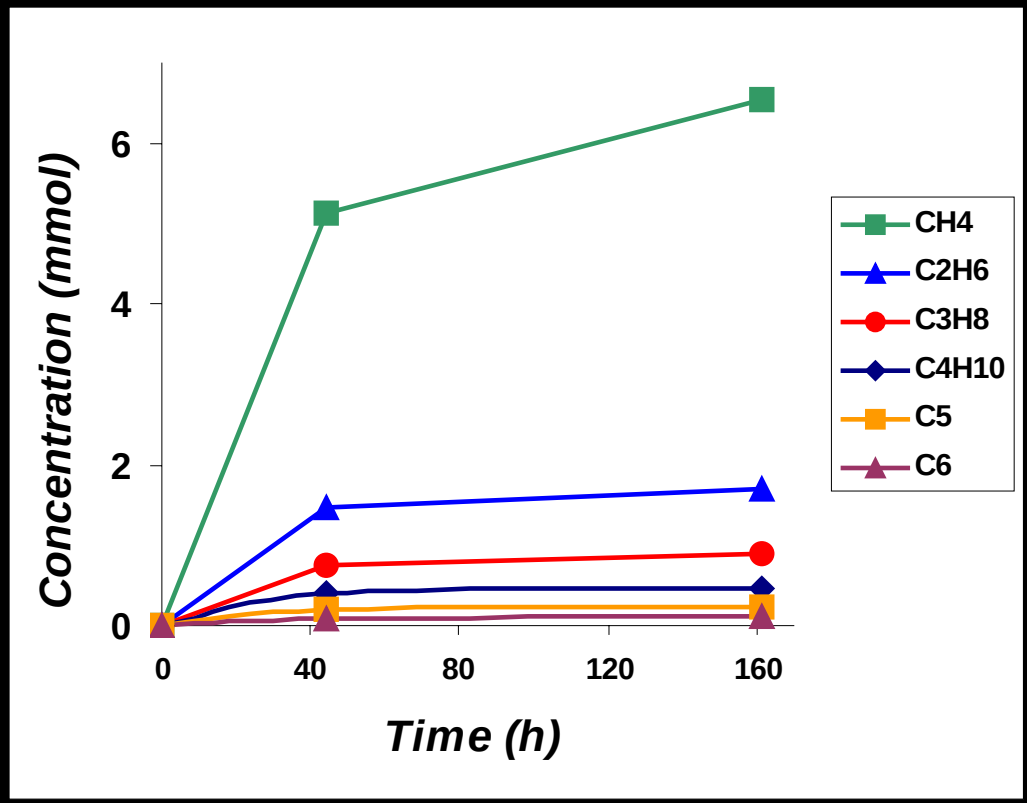
+ C_2H_6 (ethane)

+ C_3H_8 (propane)

+ …



Fischer-Tropsch synthesis (volatile hydrocarbon products)

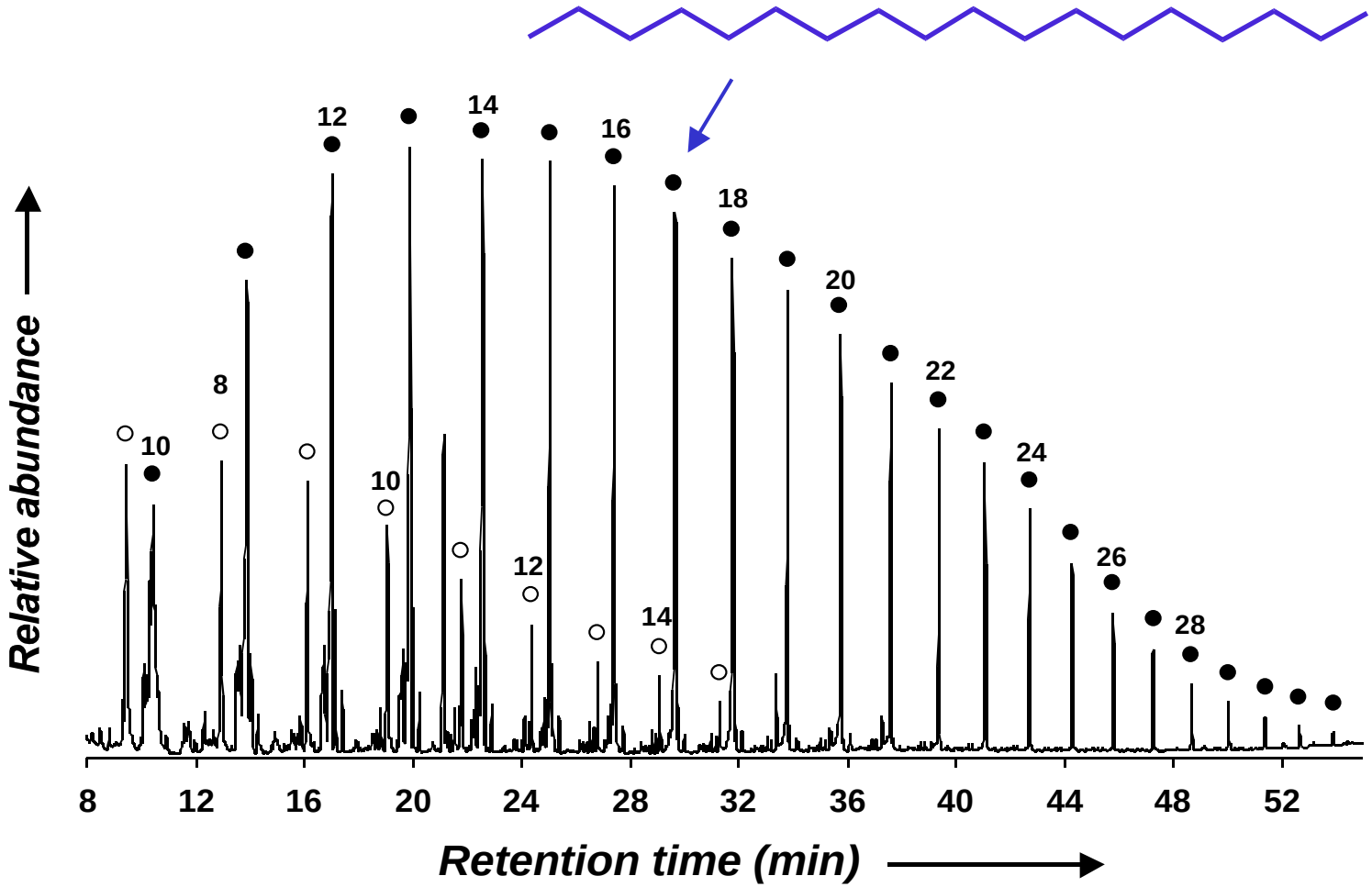


250°C, 325 bars
~1.3 mol% H_2

$Fe + H_2O + HCOOH \rightarrow$

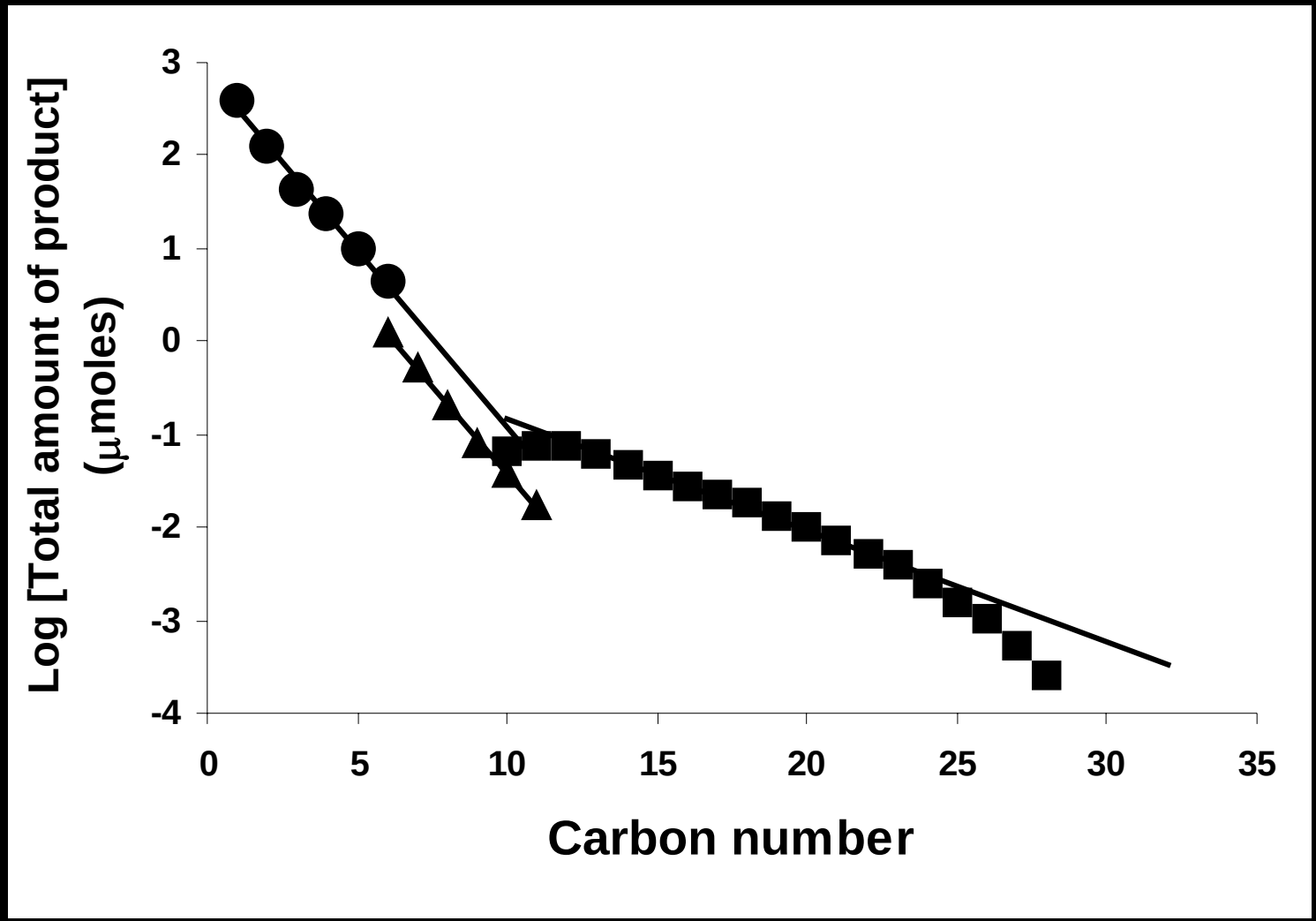
Magnetite (Fe_3O_4) + CO_2 + CO + H_2 + hydrocarbons

Fischer-Tropsch synthesis
(non-volatile hydrocarbon products)



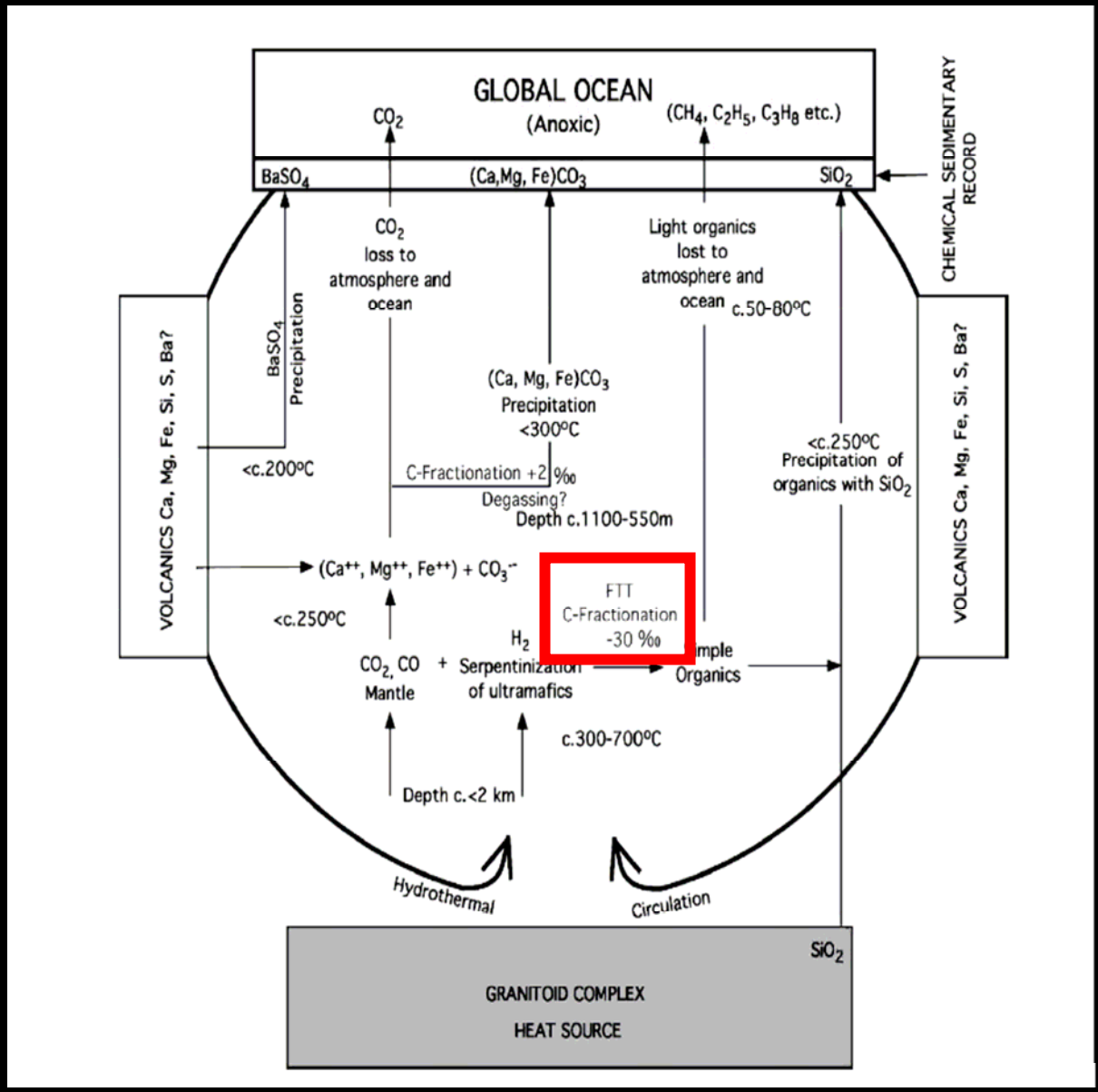
(McCollom & Seewald, *EPSL*, 2006)

FT products follow regular distribution:



(McCollom & Seewald, *EPSL*, 2006)

Abiotic organic synthesis at Warrrawoona (?)



[Lindsay et al., 2005]

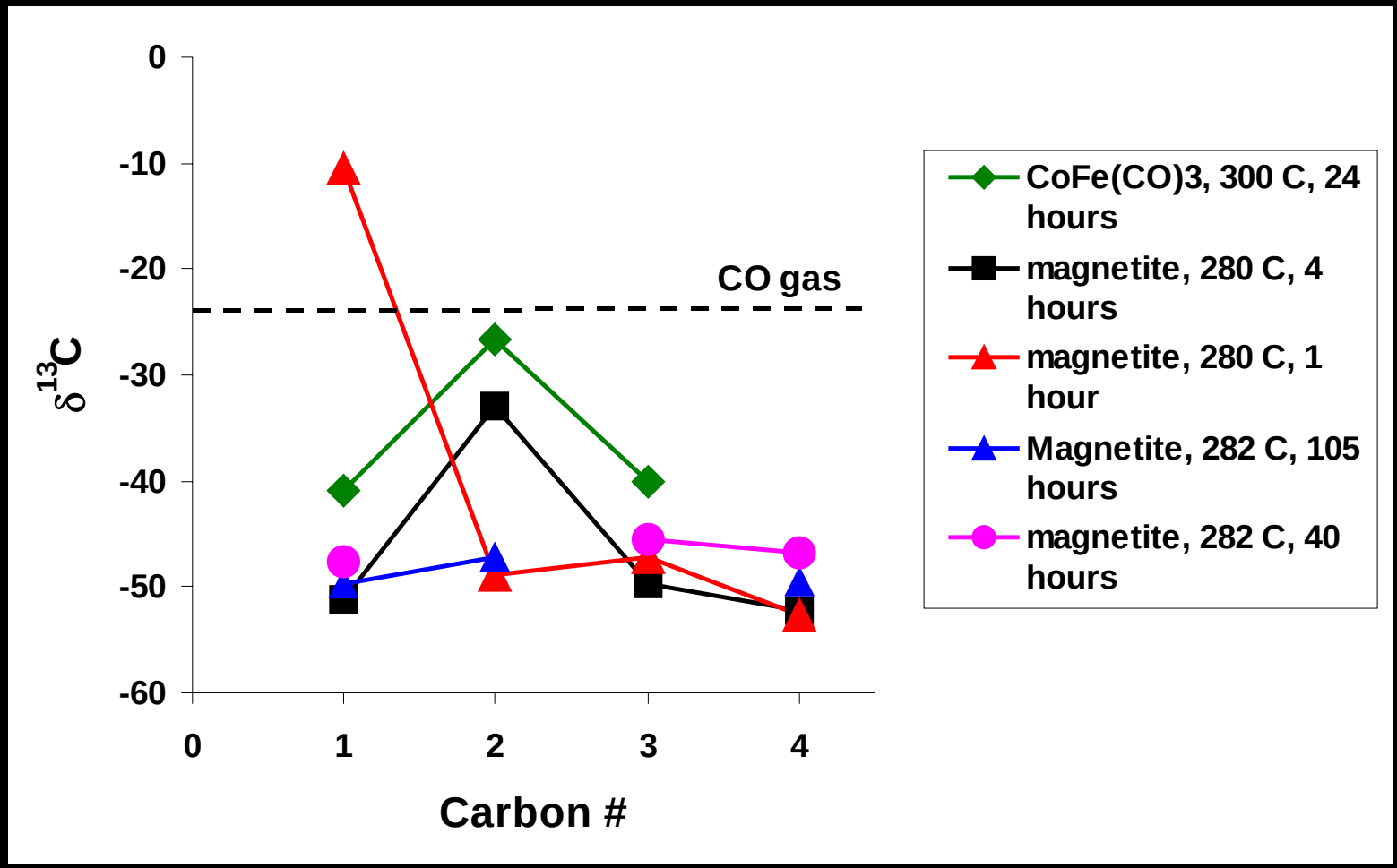
C Isotope fractionation during FT synthesis

Lancet & Anders (1970):

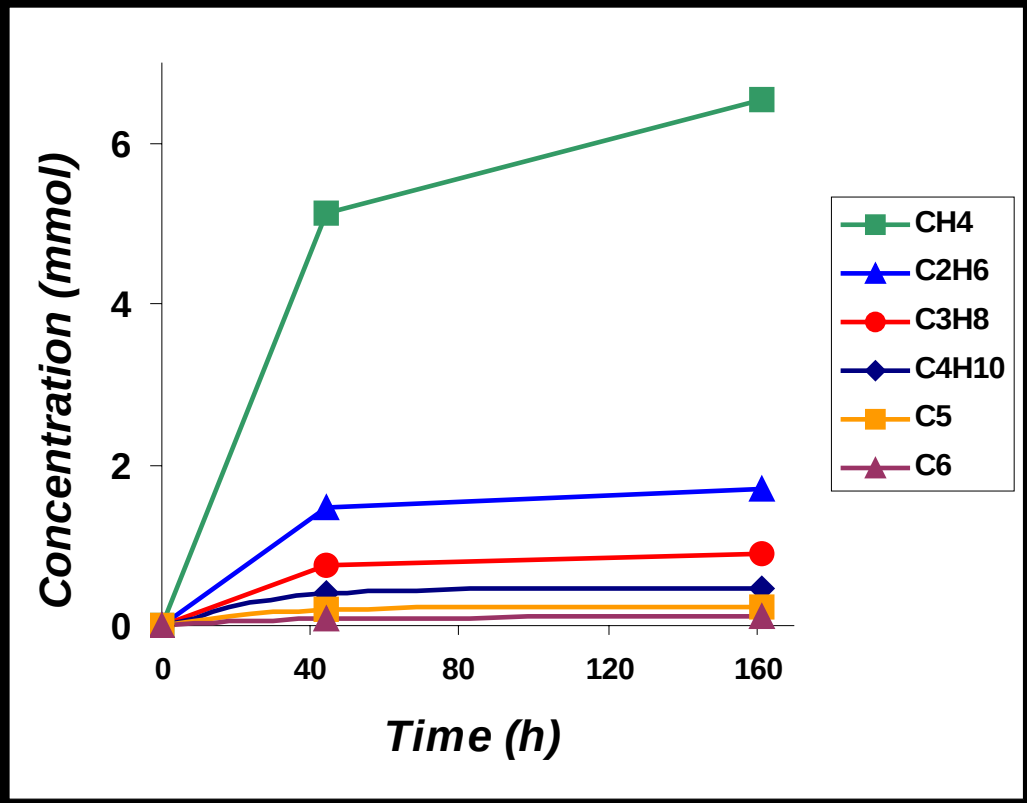
Conditions	$\Delta^{13}C_{CO\text{-}\text{“wax”}}$ (‰)
102°C, Co catalyst	-16
127°C, Co catalyst	-33
177°C, Co catalyst	-33
227°C, Co catalyst	-18
277°C, Fe catalyst	-8.5

C Isotope fractionation during FT synthesis

Hu et al. (Sci. China, 1998):



Fischer-Tropsch synthesis (volatile hydrocarbon products)

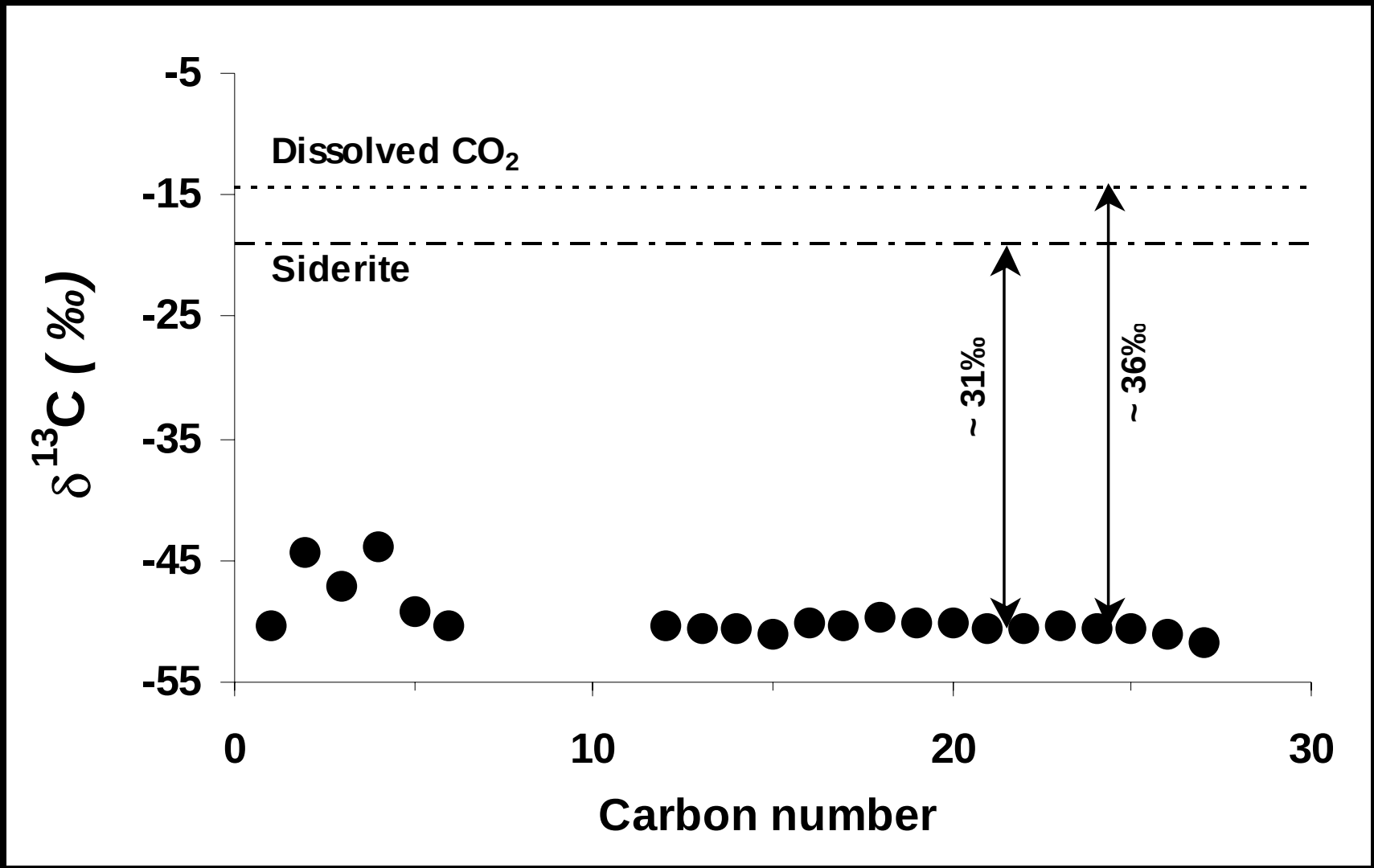


250°C, 325 bars
~1.3 mol% H_2

$Fe + H_2O + HCOOH \rightarrow$

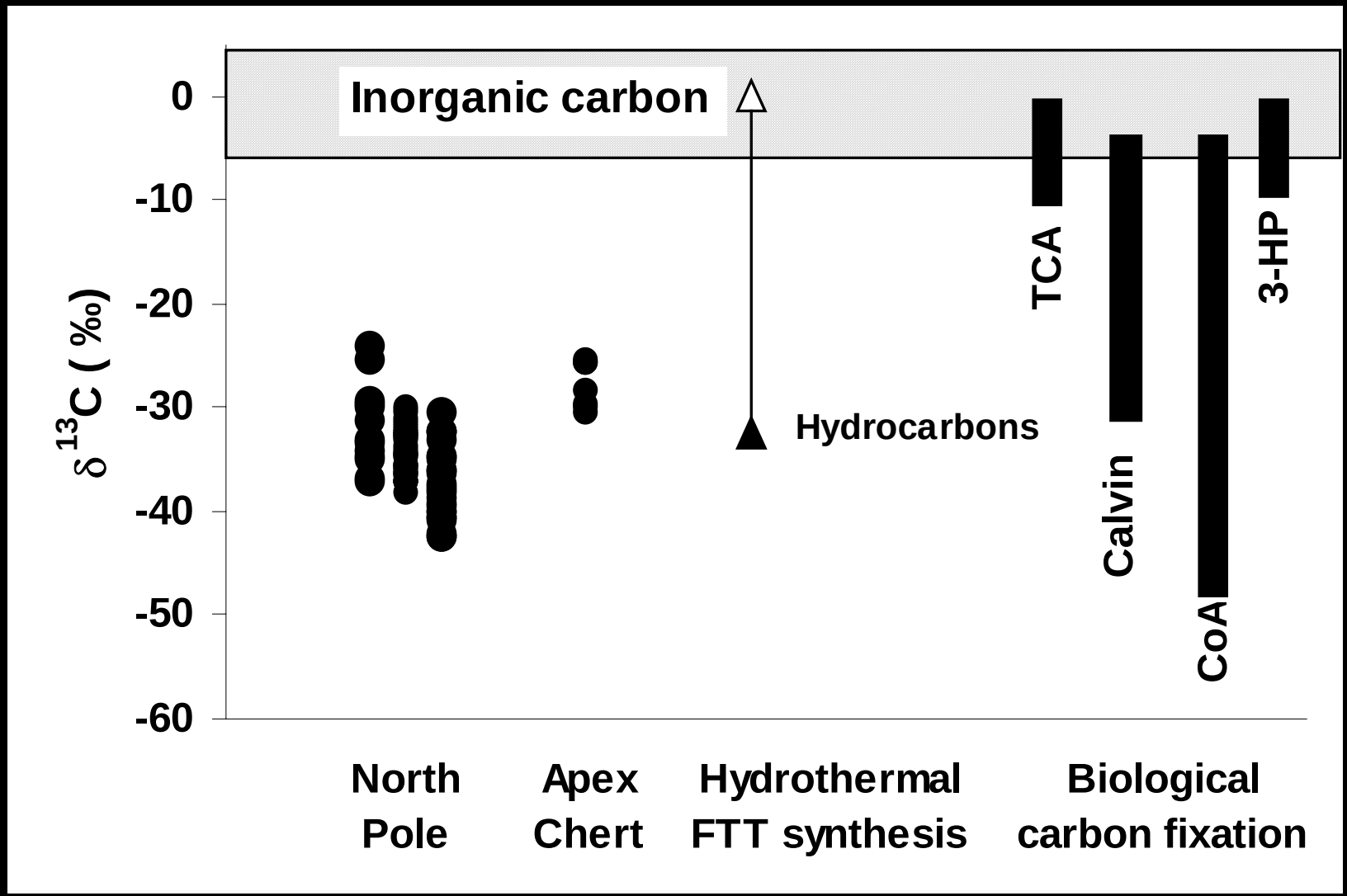
Magnetite (Fe_3O_4) + CO_2 + H_2 + hydrocarbons

C Isotope fractionation during hydrothermal FT synthesis

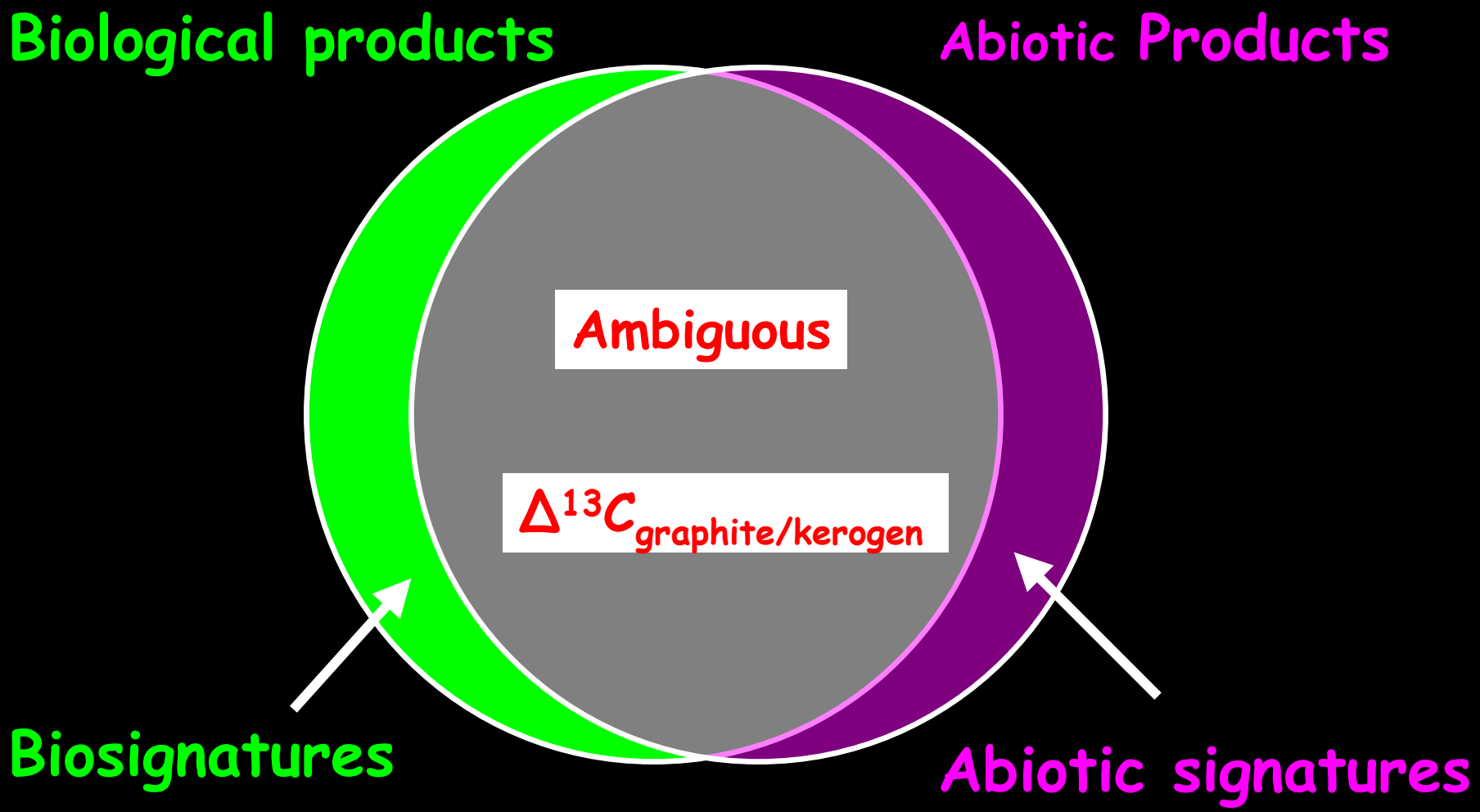


(McCollom & Seewald, EPSL, 2006)

C Isotope fractionation during hydrothermal FT synthesis

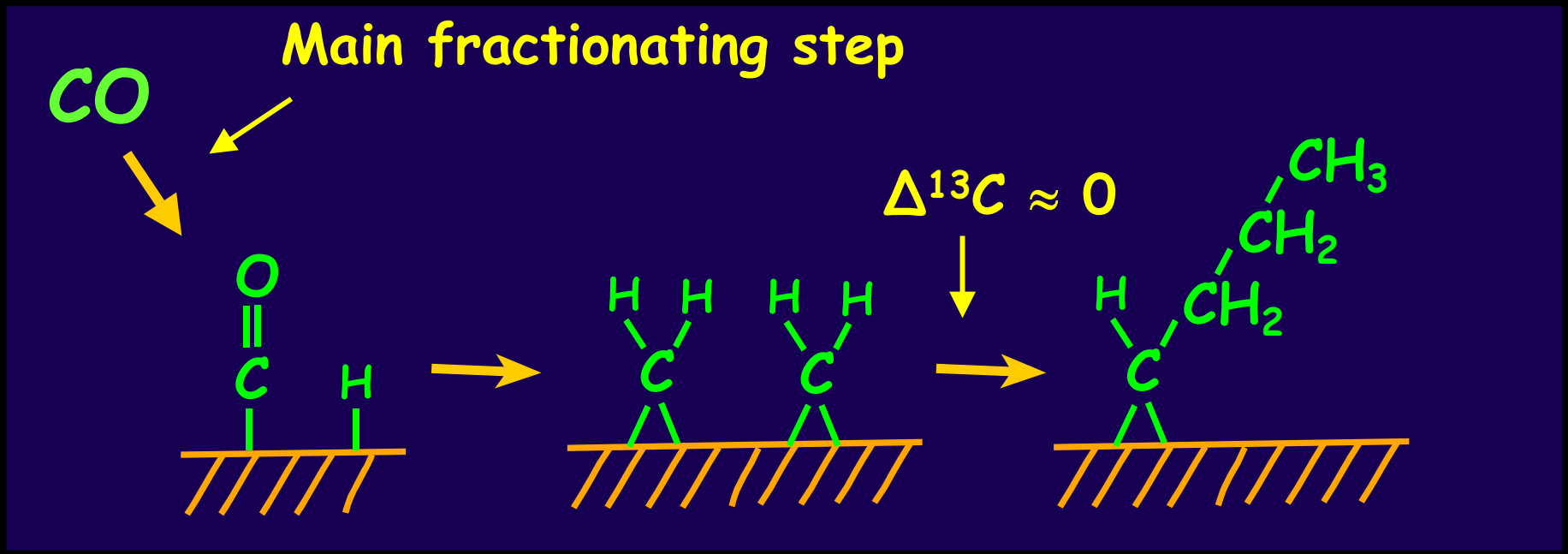


(McCollom & Seewald, EPSL, 2006)



Valid biosignatures must be *exclusively* biological in origin

Fischer-Tropsch-type synthesis

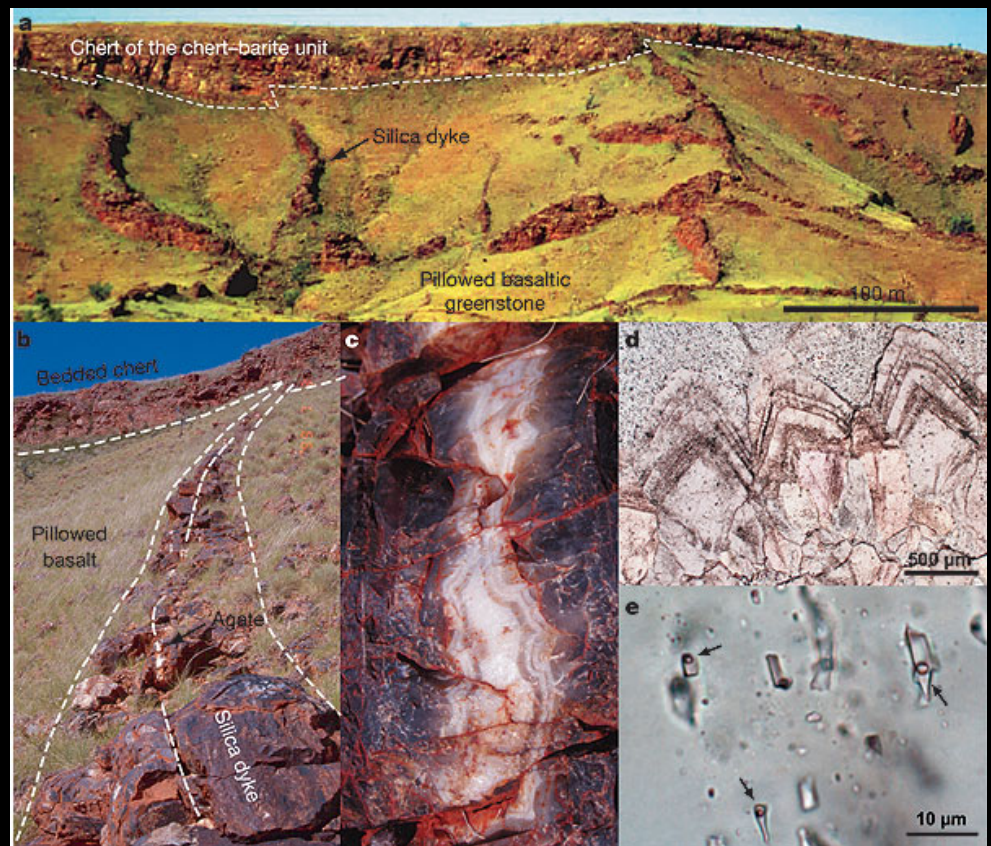


Biological methane formation 3.5 billion years ago (?)

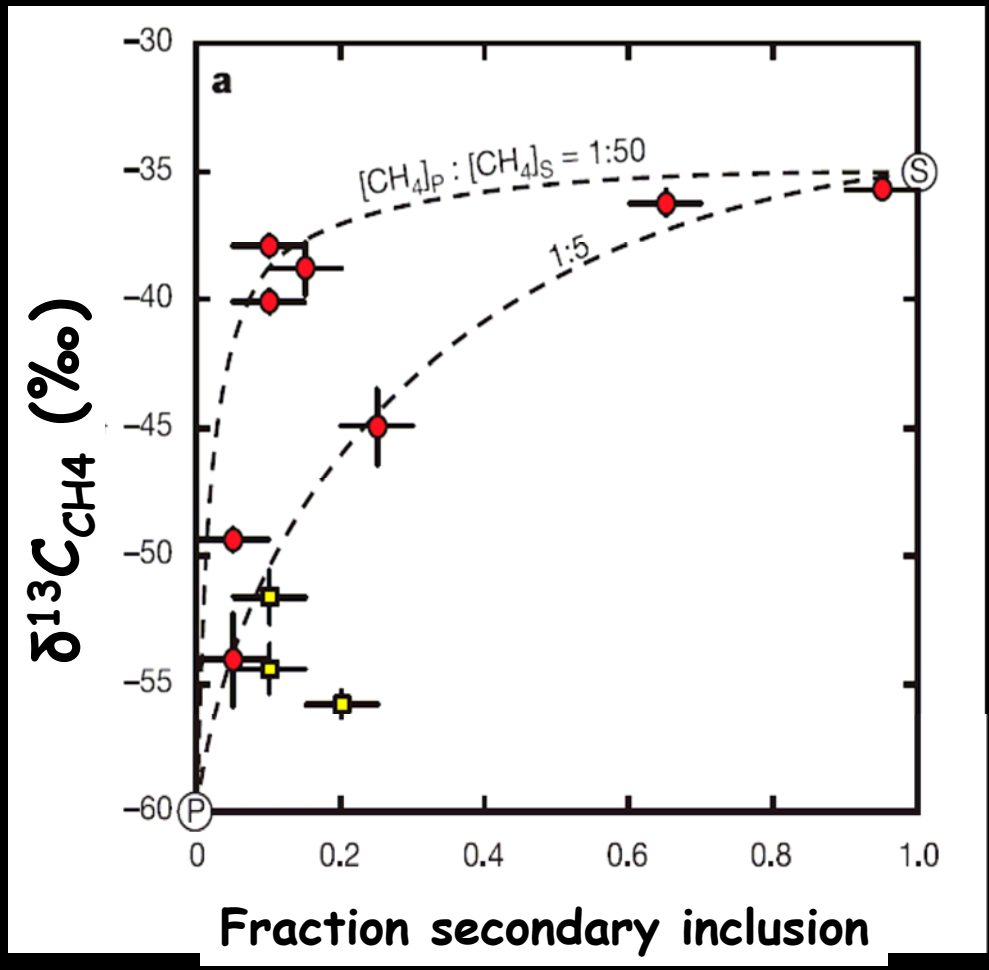
Evidence from fluid inclusions for microbial methanogenesis in the early Archaean era

Yuichiro Ueno[1,3,5], Keita Yamada[4,5], Naohiro Yoshida[1,3,4,5], Shigenori Maruyama[1,2] & Yukio Isozaki[6]

Nature (2006)

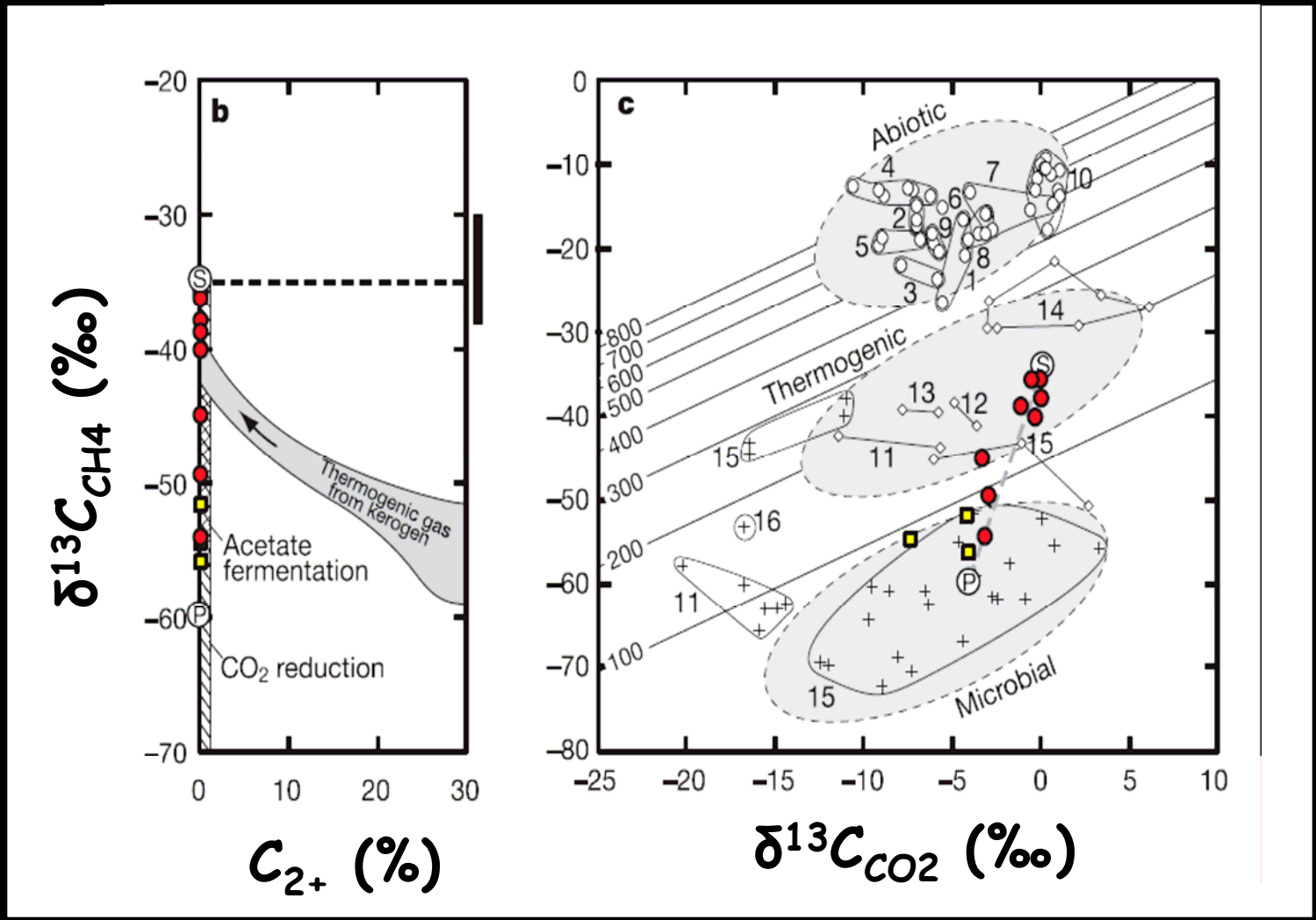


Biological methane formation 3.5 billion years ago (?)



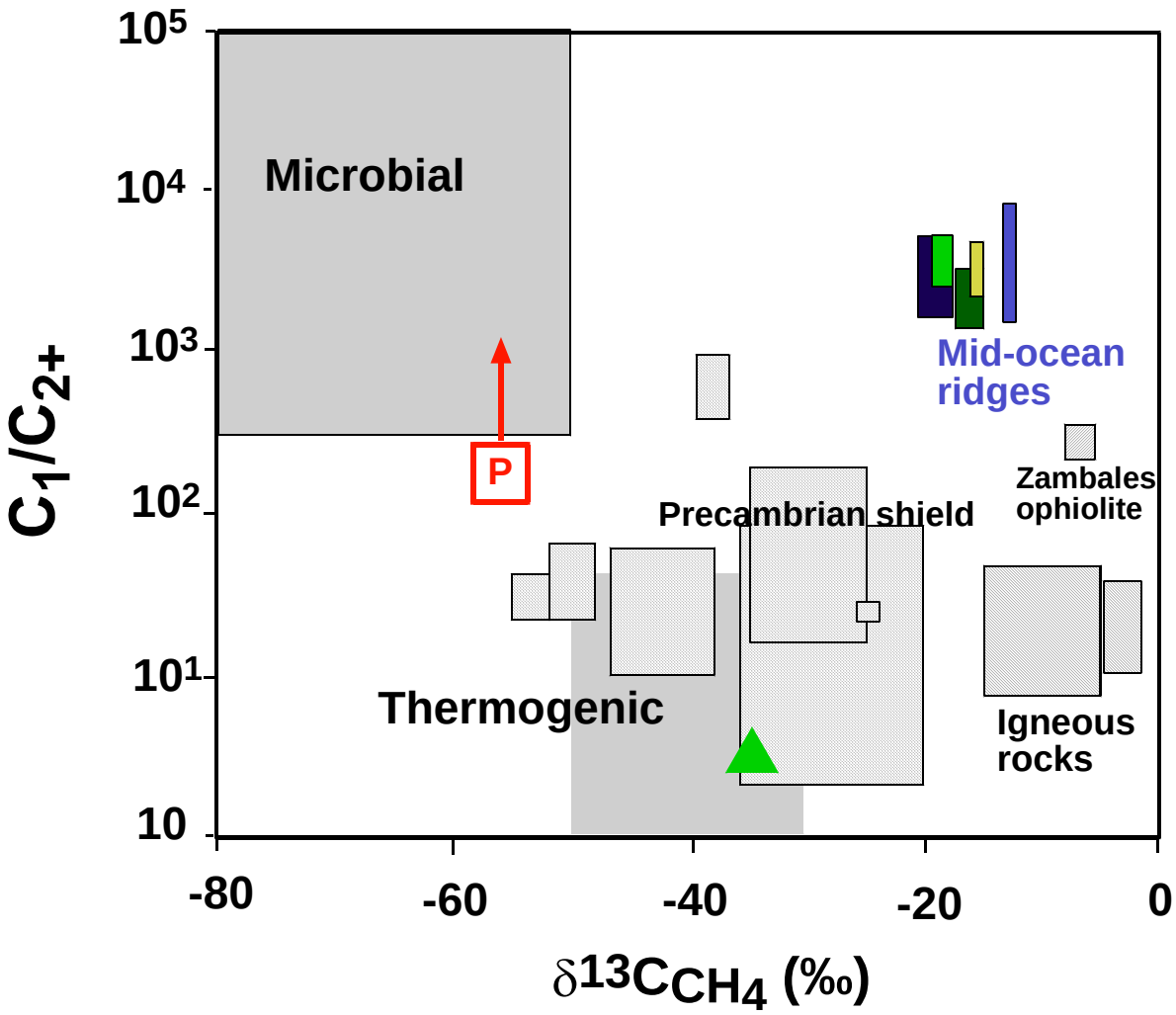
Ueno et al., *Nature* (2006)

Biological methane formation 3.5 billion years ago (?)



Ueno et al., *Nature* (2006)

Biological methane formation 3.5 billion years ago (?)



P Ueno et al., 2006

▲ Fischer-Tropsch synthesis

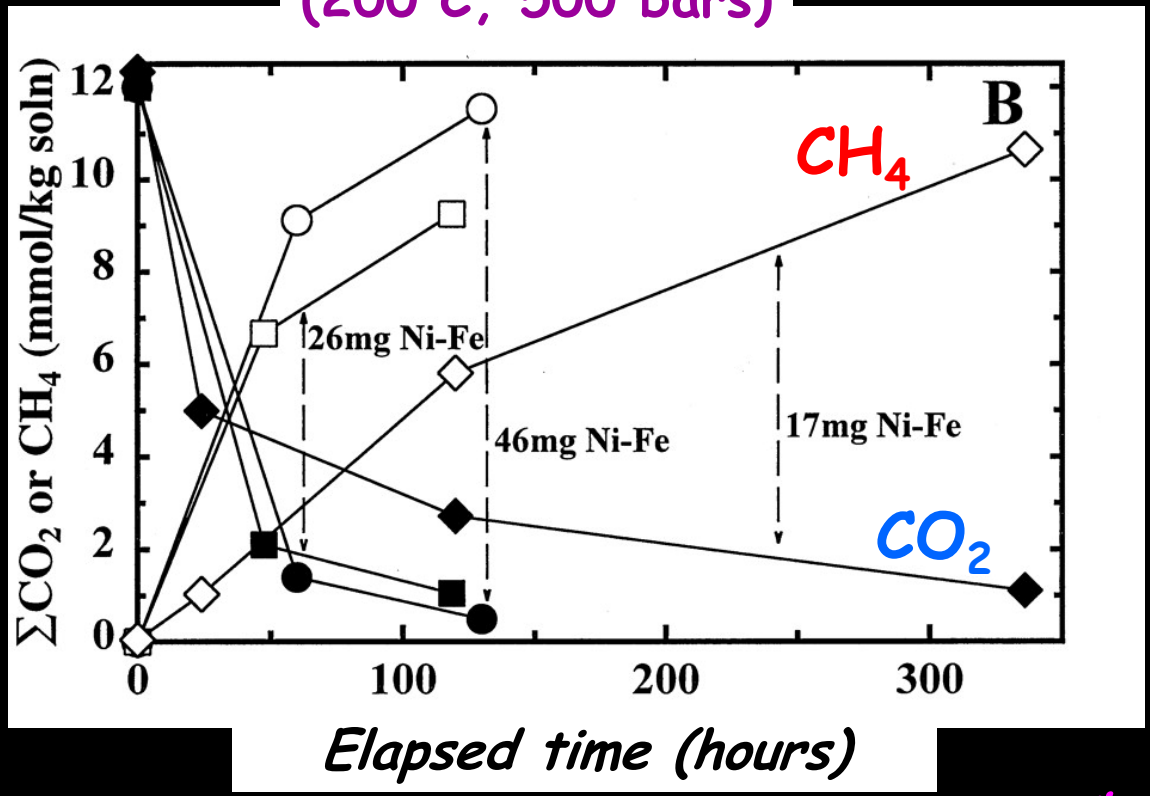
(McCollom & Seewald, 2006)

C Isotope fractionation during abiotic methane formation

Horita & Berndt (1999):

Hydrothermal reduction of CO_2 to CH_4 catalyzed by NiFe-alloy (awaruite)

(200°C, 500 bars)



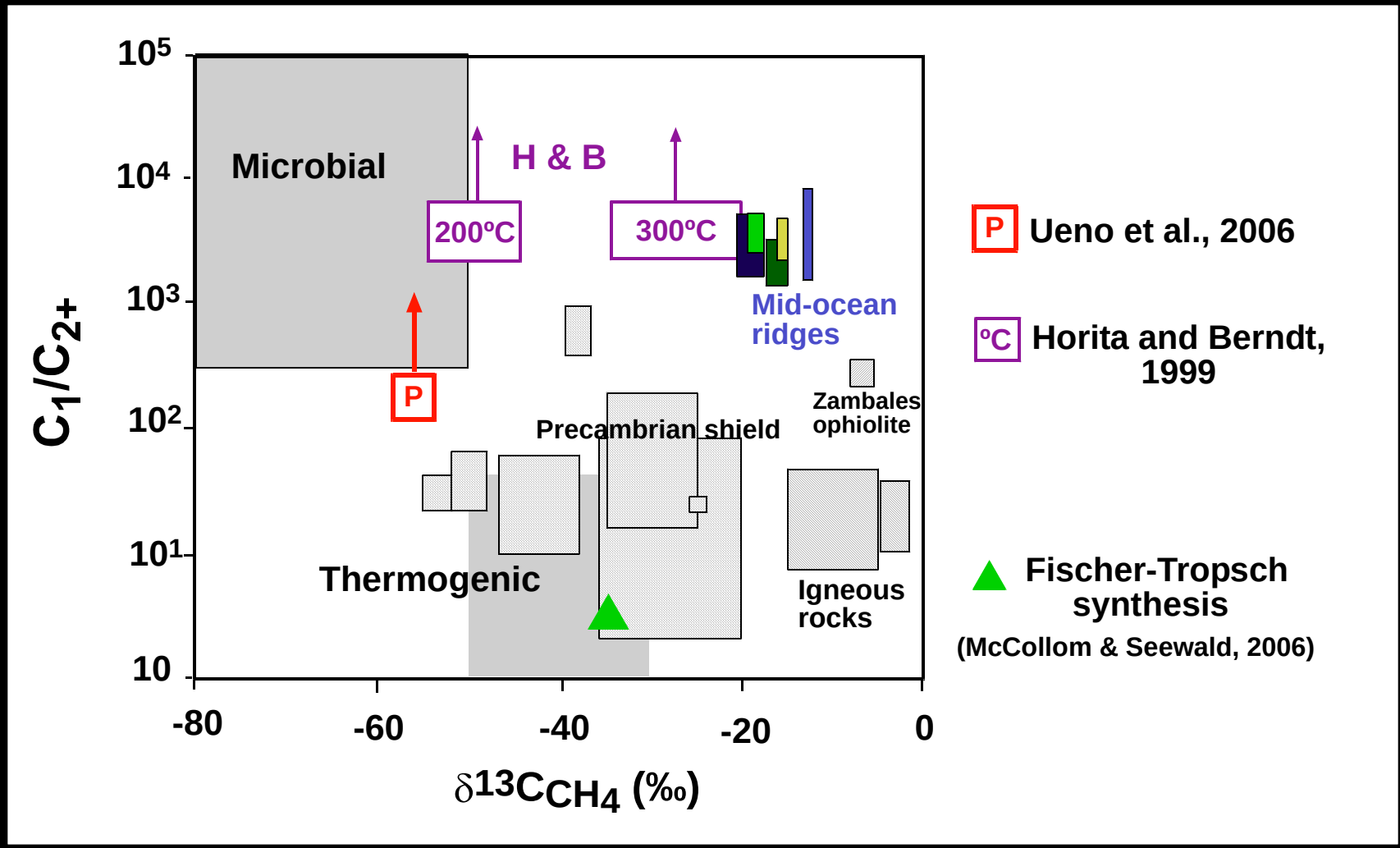
*No ethane, propane, etc. observed**

$\Delta^{13}C_{CO2-CH4}$

-50 to -60‰ (200°)
-35 to -40‰ (300°)

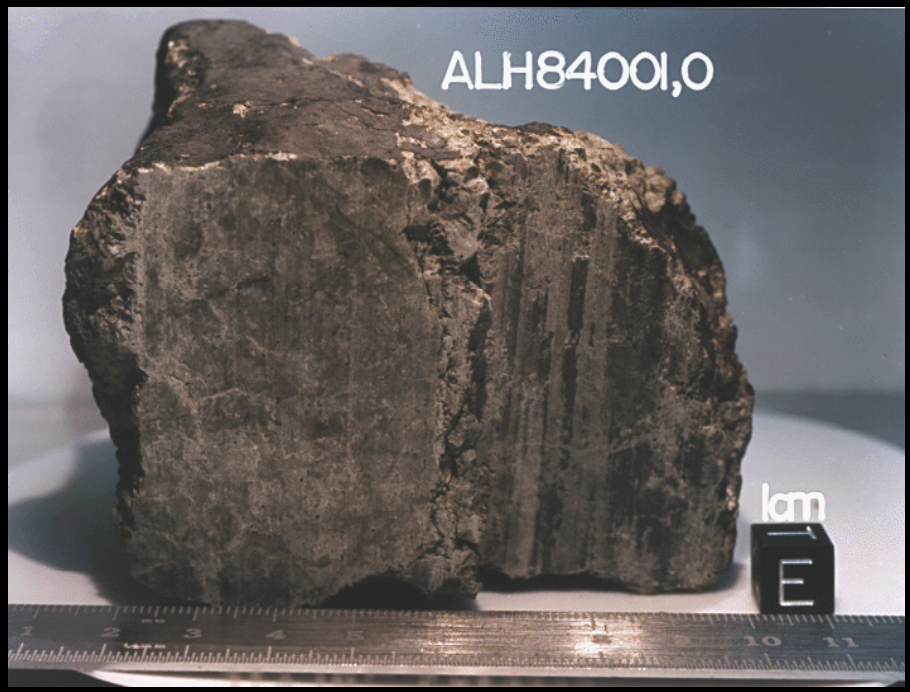
**not Fischer-Tropsch*

Biological methane formation 3.5 billion years ago (?)



(see Sherwood Lollar & McCollom, *Nature*, 2006; Ueno et al., *Nature*, 2006)

Extraterrestrial life in a martian meteorite (?)



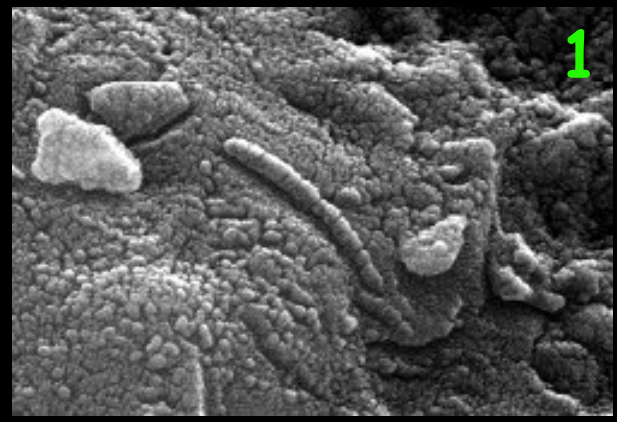
McKay et al. (Science, 1996) proposed that martian meteorite ALH84001 contained traces of life on Mars (!)

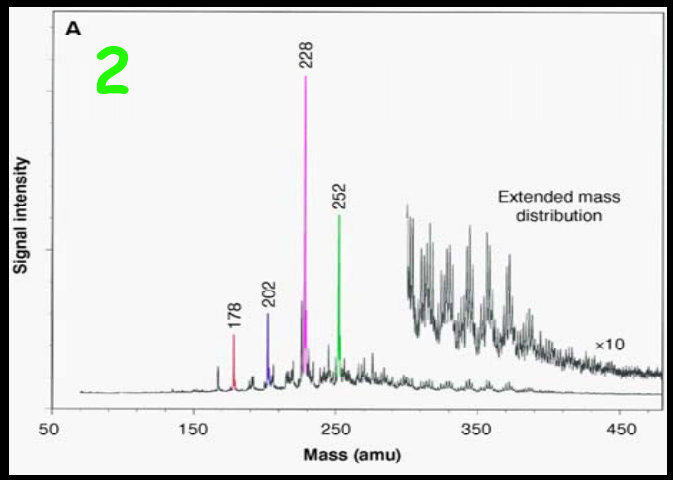
Evidence for life in ALH84001
(McKay et al., 1996):

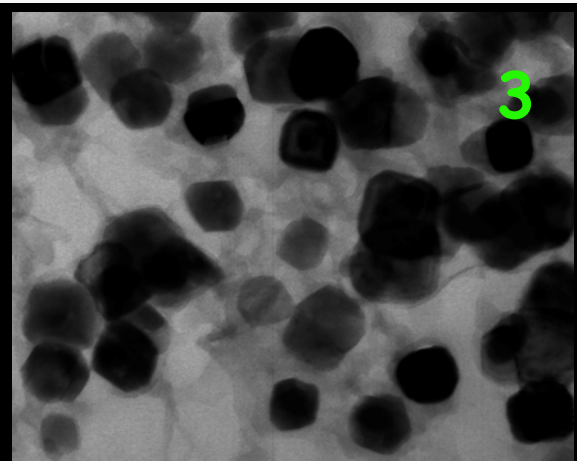
1) Bacteria-like morphologies

2) Organic compounds (PAH)

3) Magnetite grains







Formation of magnetite rims by siderite decomposition

$$\underset{\text{Siderite}}{FeCO_3} \rightarrow \underset{\text{magnetite}}{Fe_3O_4} + CO_2 + CO + C$$

$$\underset{\text{Siderite}}{FeCO_3} + H_2O \rightarrow \underset{\text{magnetite}}{Fe_3O_4} + CO_2 + CO + H_2$$

Magnetite formed by siderite decomposition closely resemble those in the ALH84001:

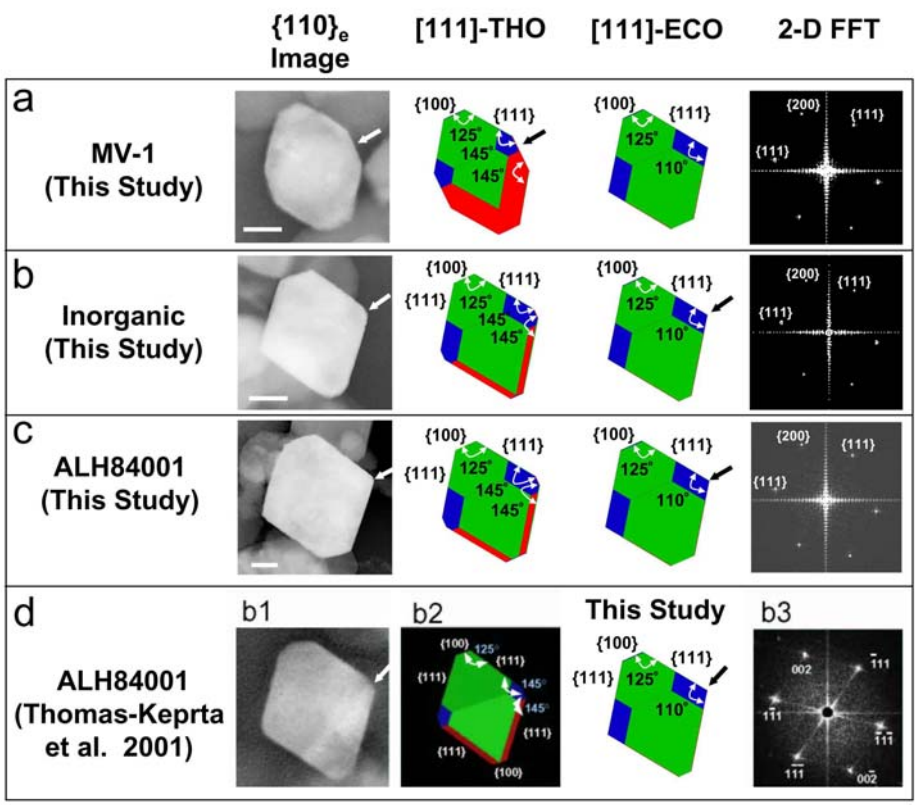


Figure 16, Golden et al.

(D.C. Golden et al., *Amer. Mineral.*, 2004)

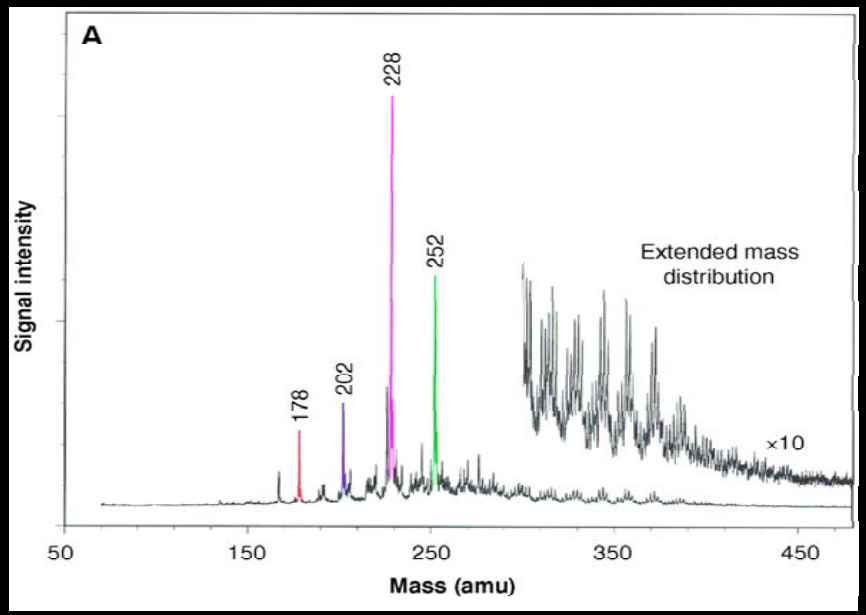
Abiotic organic synthesis during siderite decomposition??

$$\underset{\text{Siderite}}{FeCO_3} + H_2O \rightarrow \underset{\text{magnetite}}{Fe_3O_4} + CO_2 + CO + H_2$$

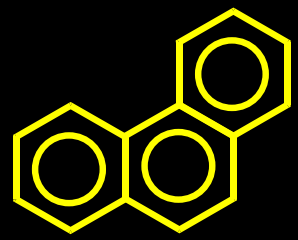
$$CO_2 + CO + H_2 \rightarrow \text{Organic compounds}$$

Organic compounds in the ALH84001:

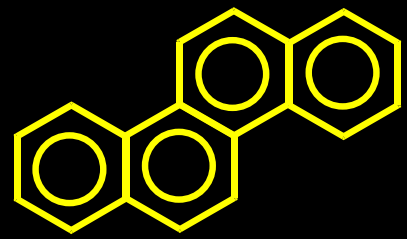
Primarily polycyclic aromatic compounds (PAH)



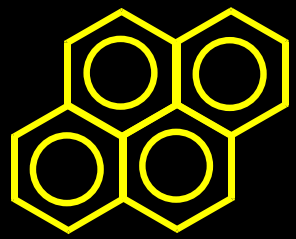
(McKay et al., 1996)



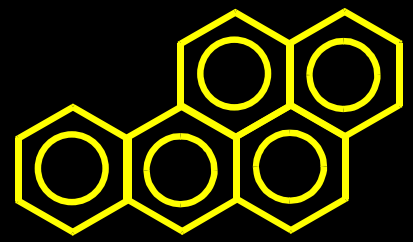
Phenanthrene (178)



Chrysene (228)

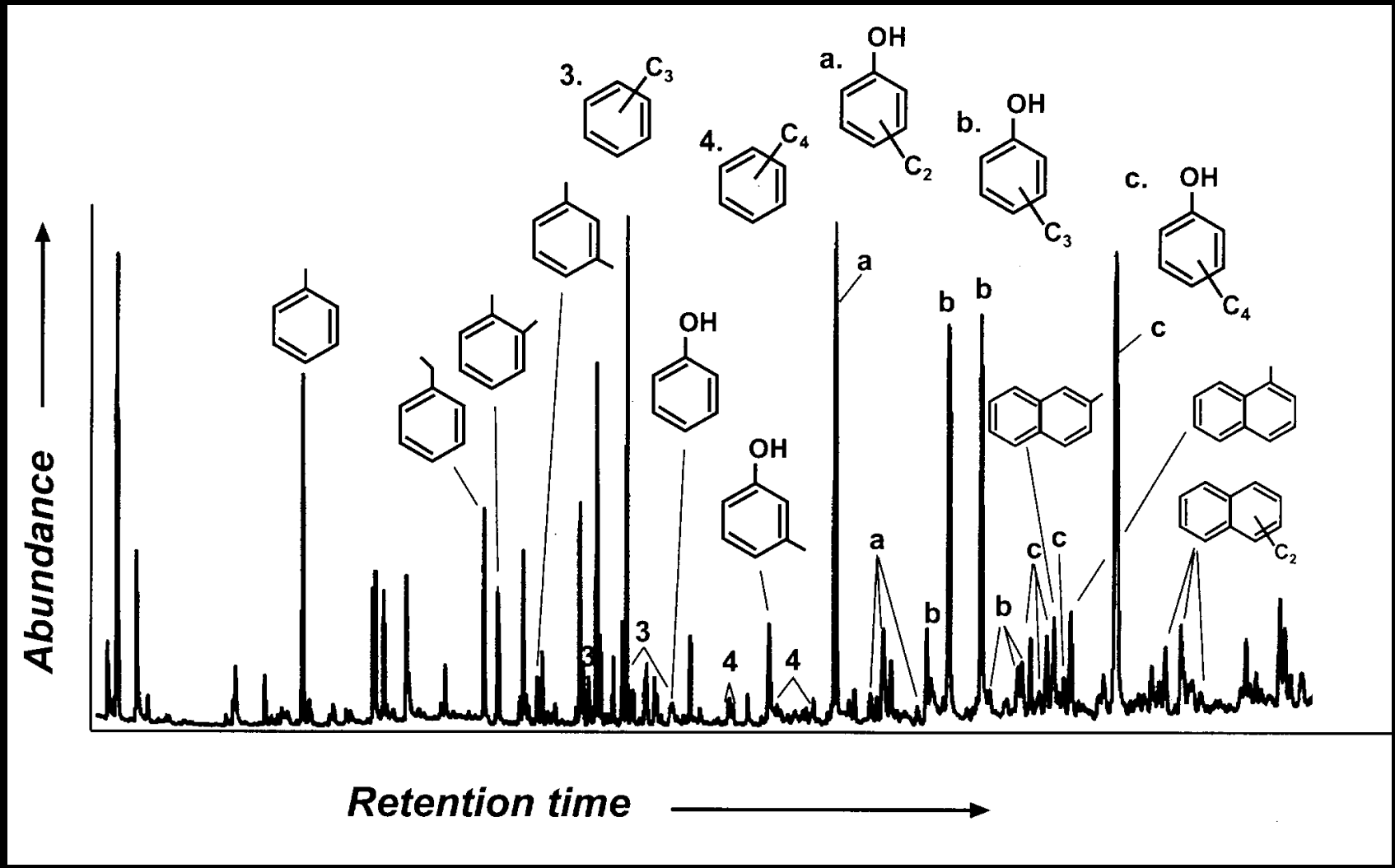


Pyrene (202)



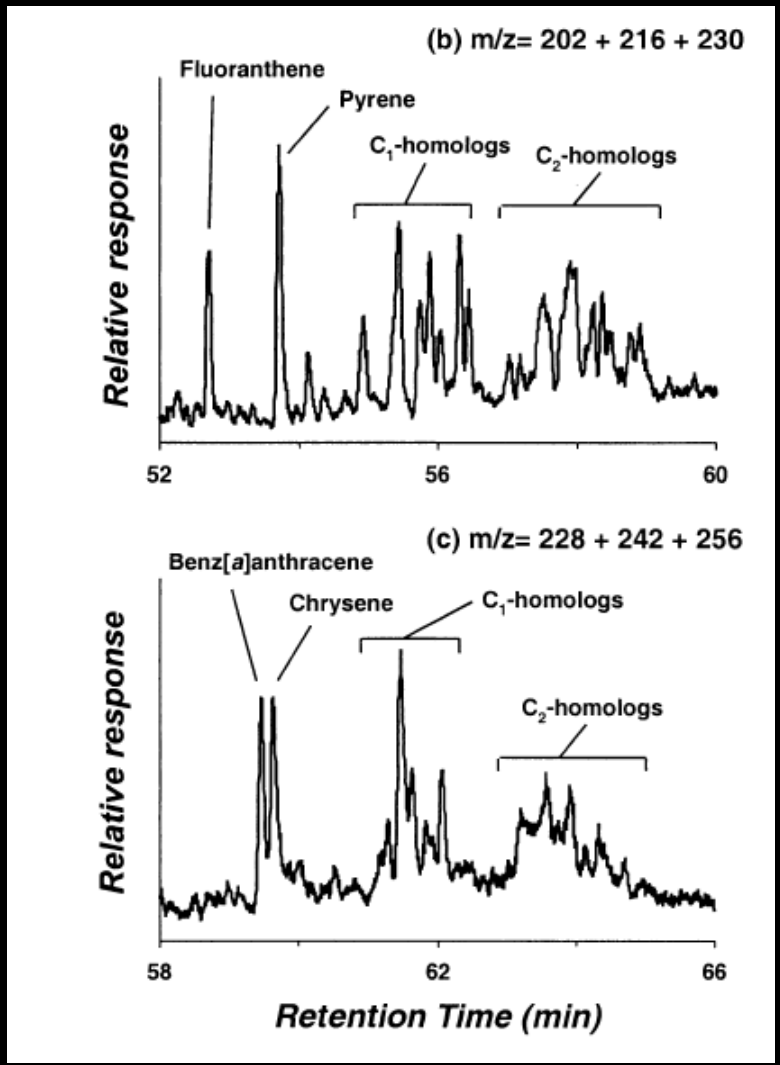
Benz[a]pyrene (252)

Siderite + H_2O (48 hours @ 300°C)

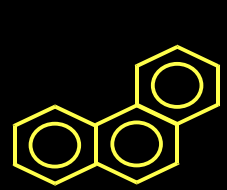


(McCollom, *GCA*, 2003)

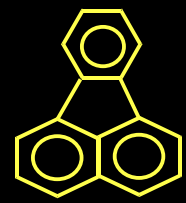
PAH produced during thermal decomposition of $FeCO_3$



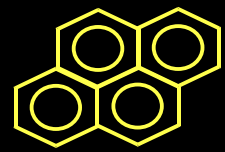
Polycyclic products:



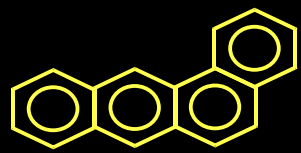
Phenanthrene



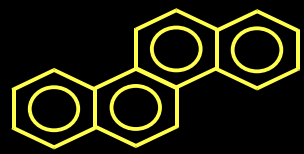
Fluoranthene



Pyrene



Benz[a]anthracene

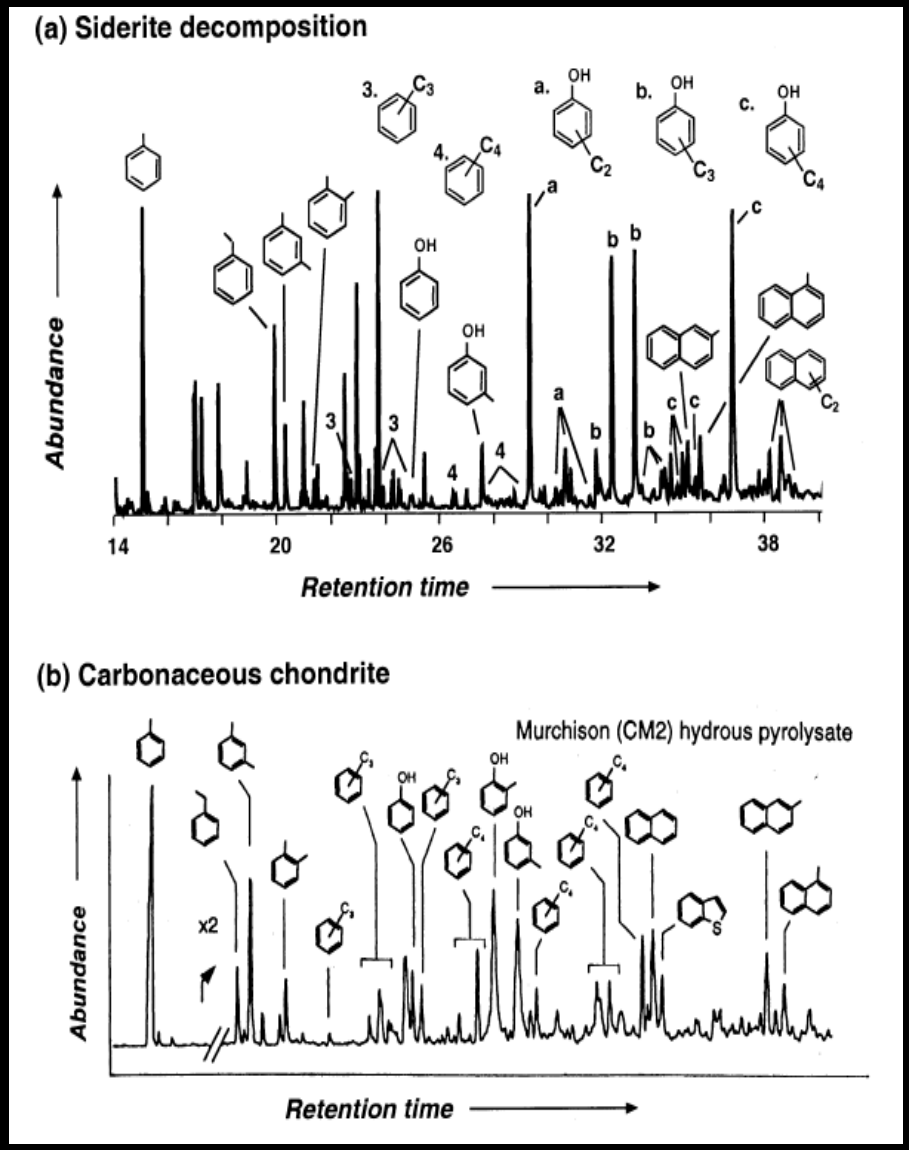


Chrysene

plus alkylated homologs...

(McCollom, *Geochim. Cosmochim. Acta*, 2003)

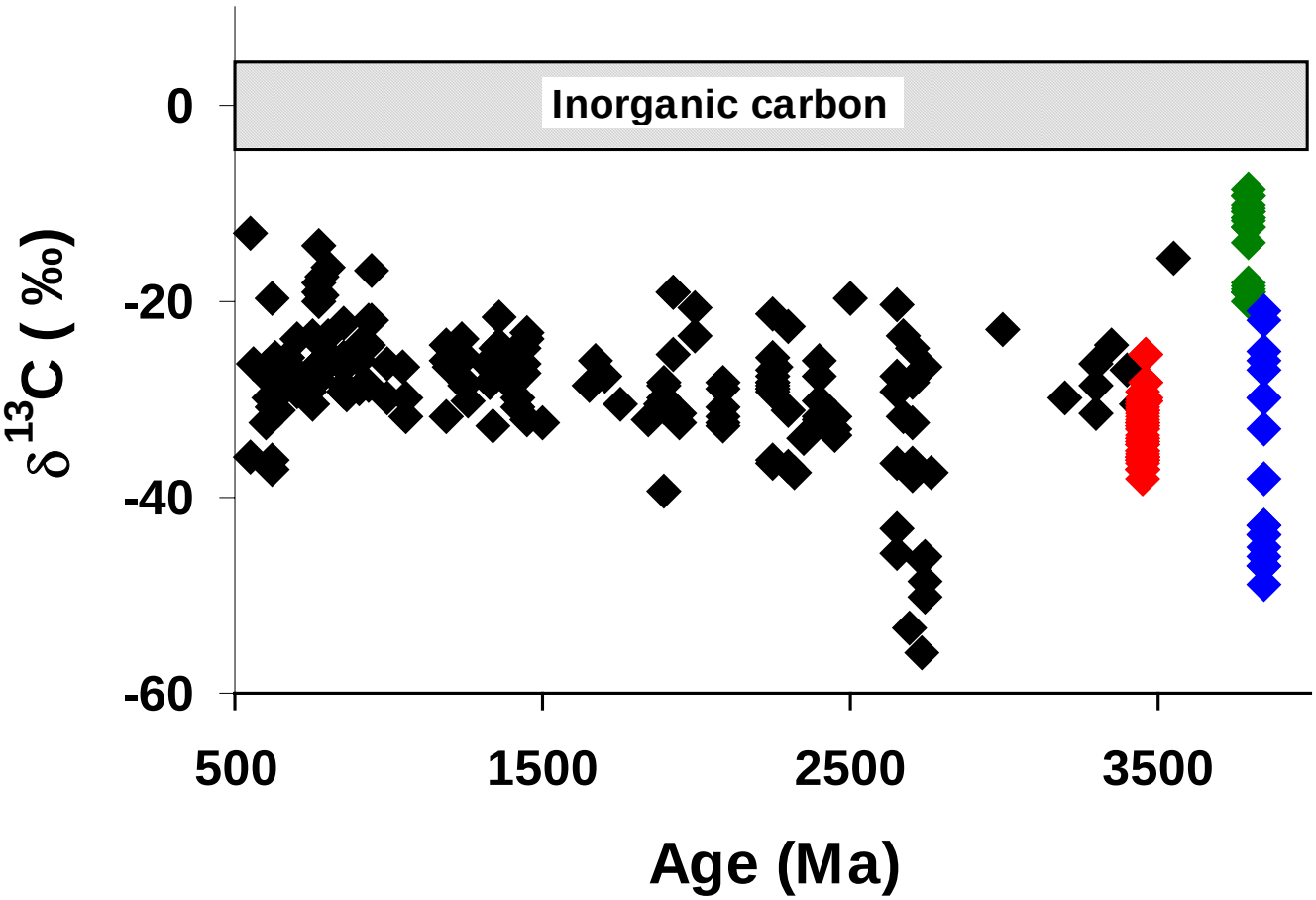
Siderite decomposition products closely resemble organic matter in non-martian meteorites



(Murchison meteorite; Sephton et al., 2000)

Carbon isotopes as a biosignature

C isotope composition of organic matter through time



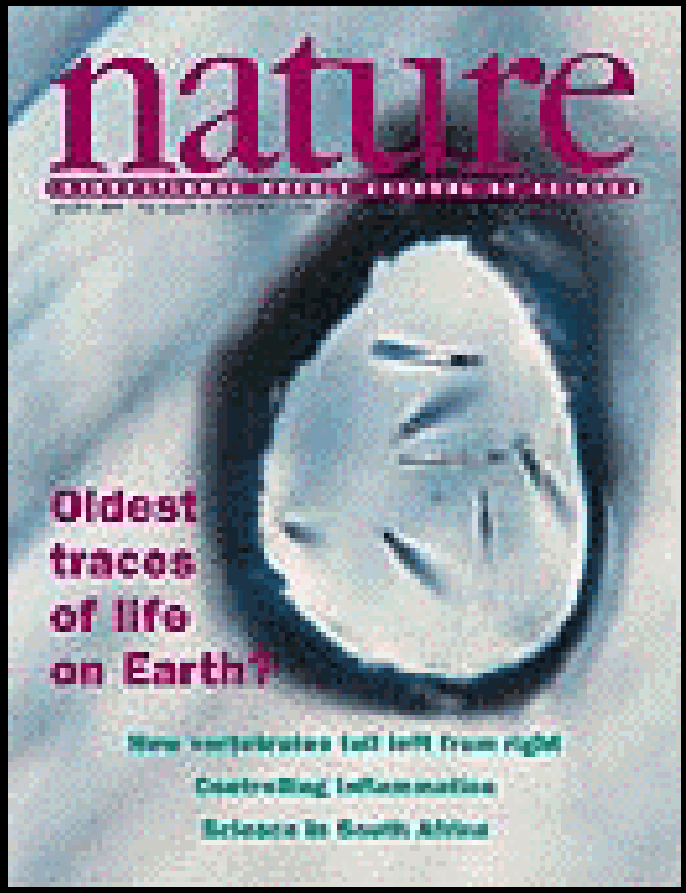
~3.8 b.y.o. rocks Greenland:

Isua

Akilia Island

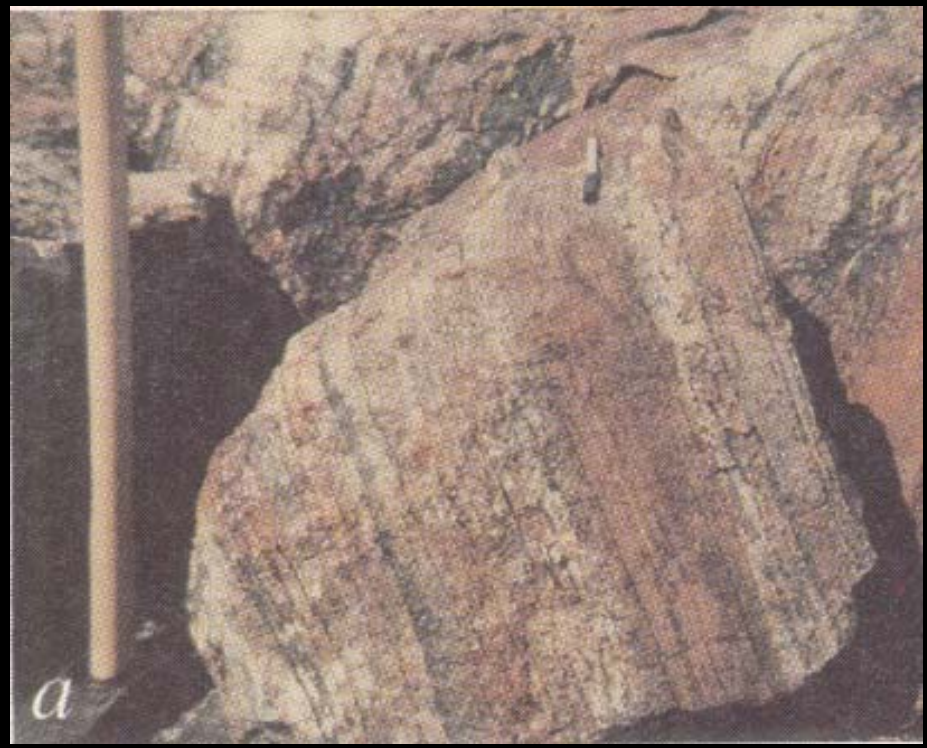
[Data for Greenland & Pilbara: Mozjsis et al., 1996; Ueno et al., 2002, 2004; van Zuilen et al., 2003; Brasier et al., 2002; Rosing, 1999]

The oldest traces of life on Earth (?)



Mojzsis et al. *Nature* (1996)

^{13}C-depleted graphite inclusions in apatite in >3.83 billion year old rocks, Akilia Island, SW Greenland



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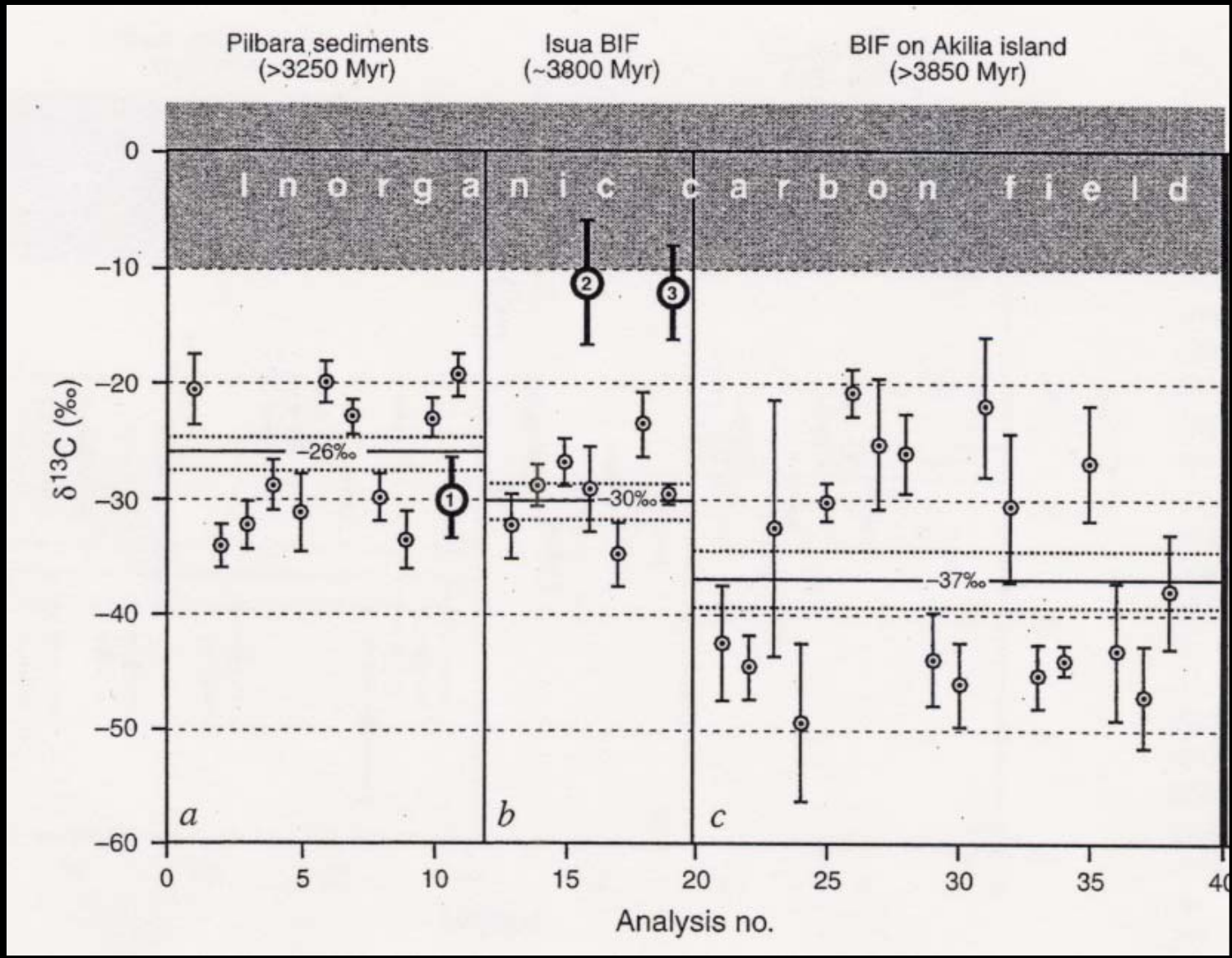
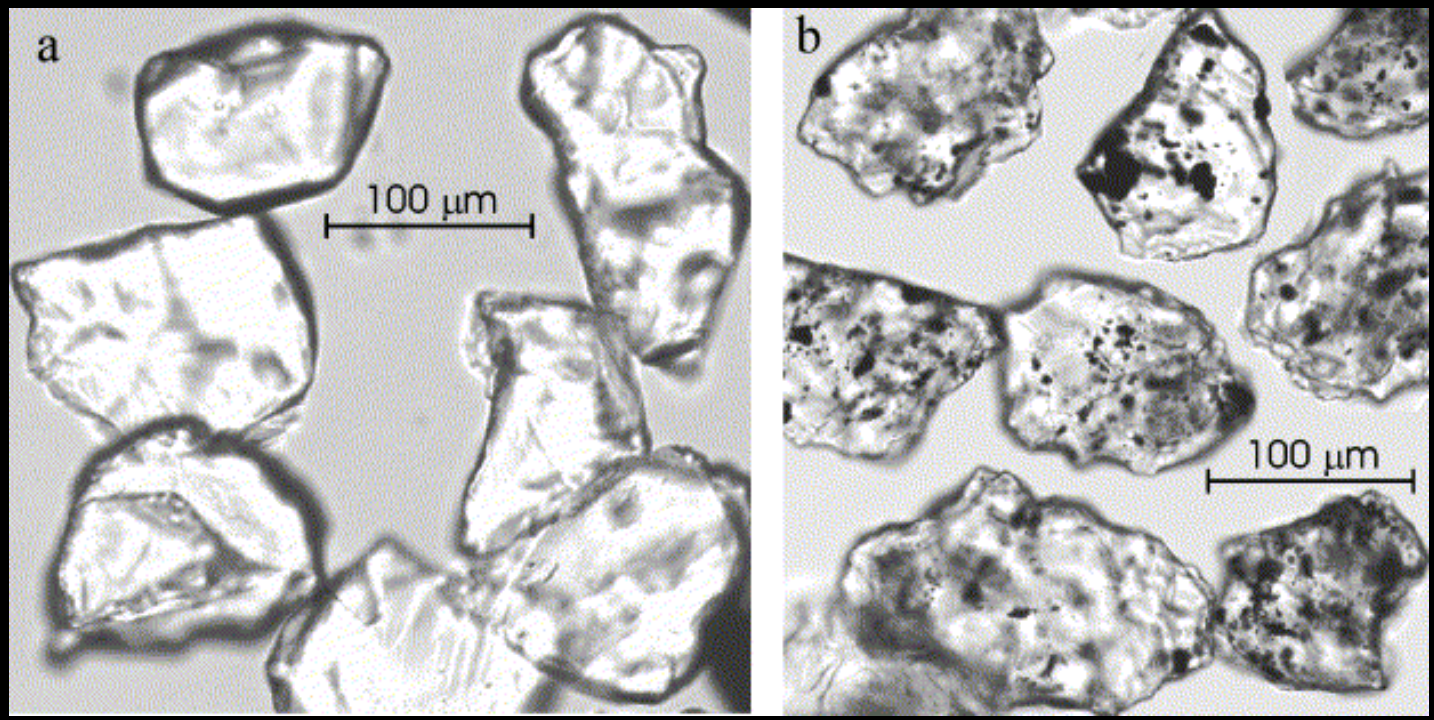
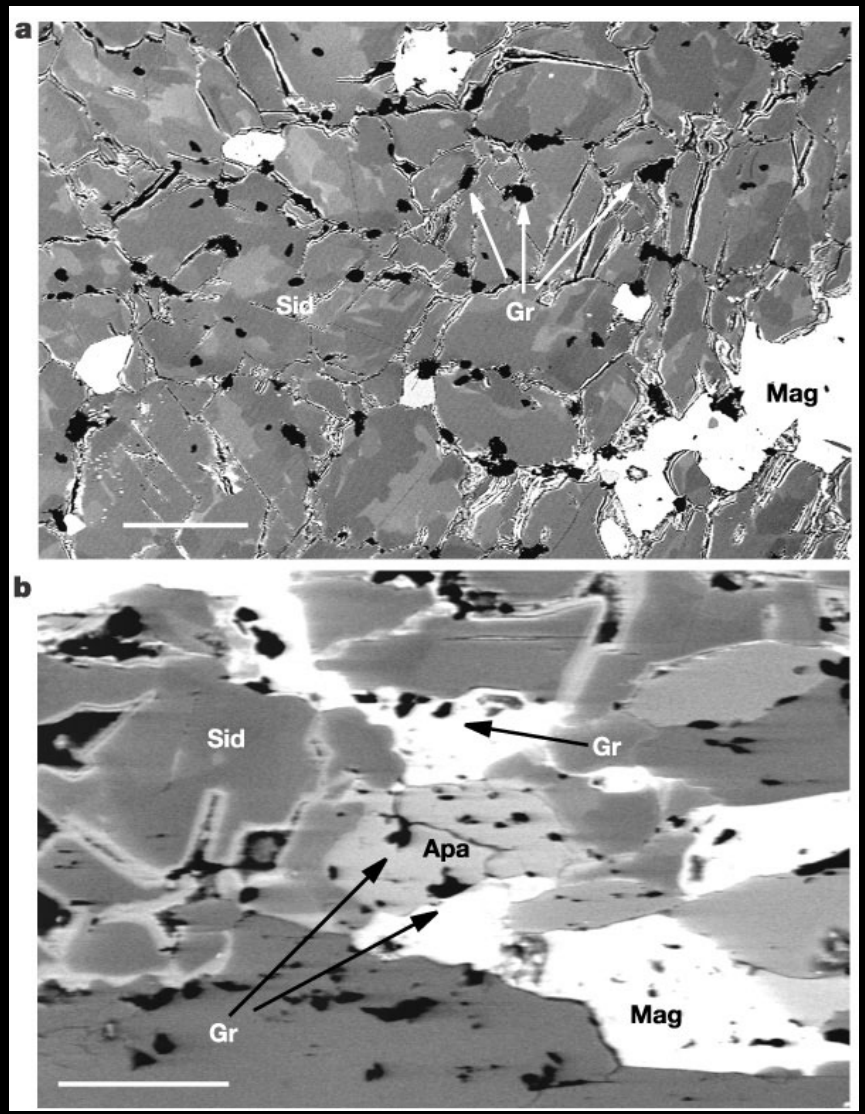


Mojzsis et al. *Nature* (1996)

Two populations of apatite at Isua; One has graphite, the other doesn't …



Lepland et al. *Precambrian Research* (2003)



… and ones that do are from decomposition of siderite

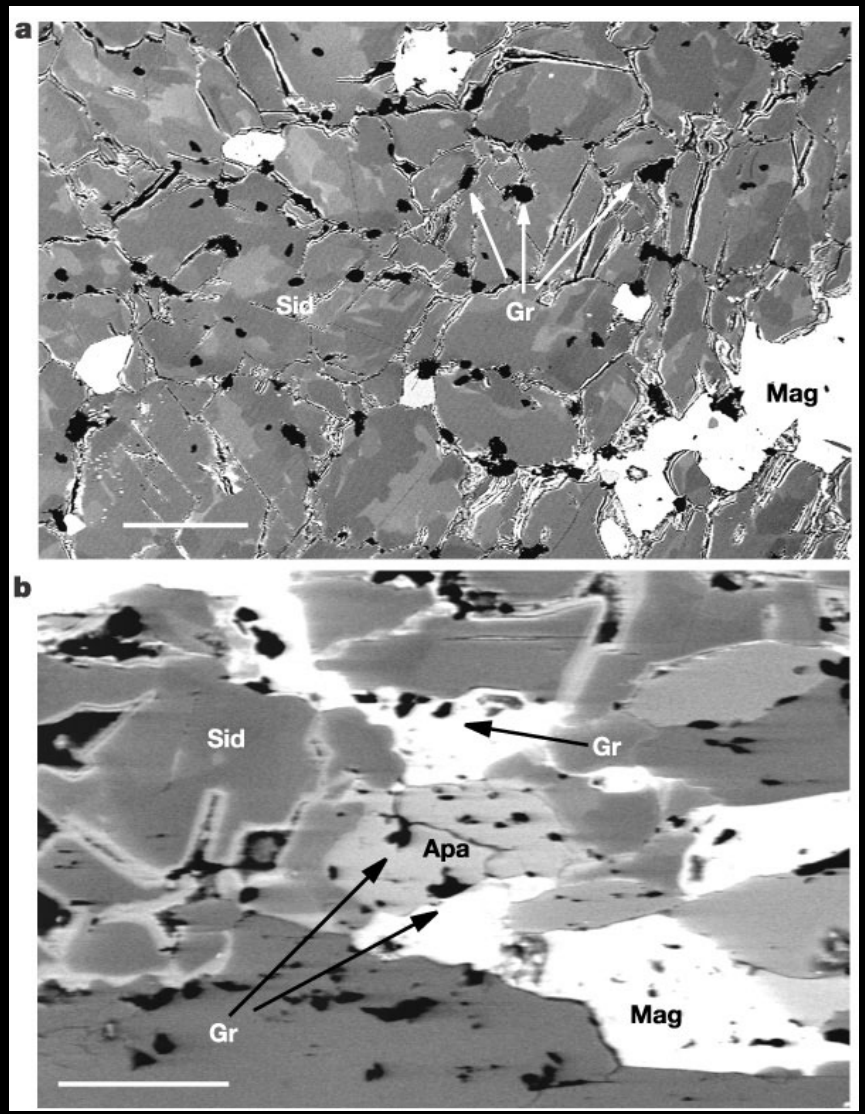
$FeCO_3$ ➔

Siderite

$Fe_3O_4 + CO_2 + C$ (graphite)

magnetite

Van Zuilen, Lepland & Arrhenius, *Science* (2002)



… and ones that do are from decomposition of siderite

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Siderite

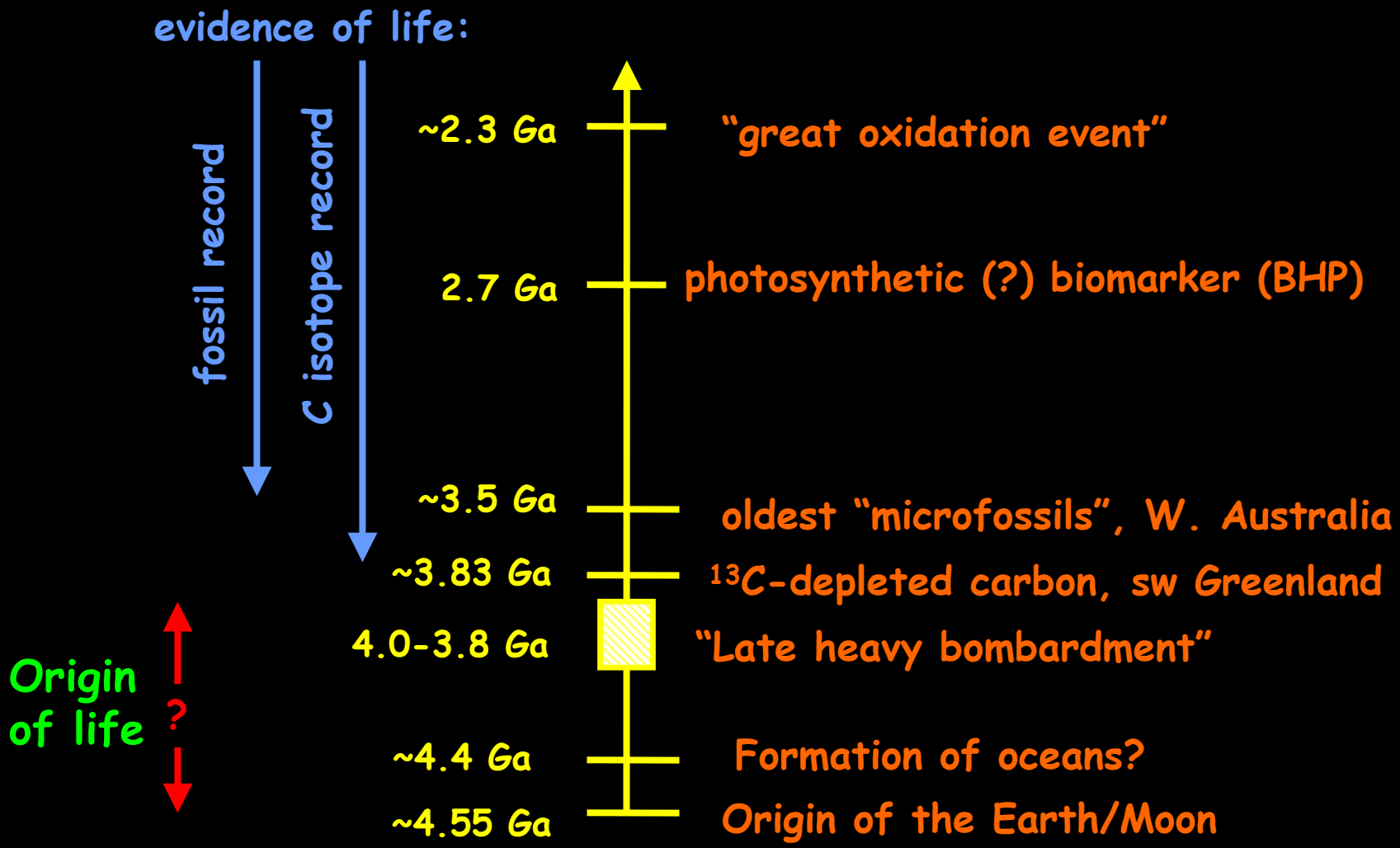
$Fe_3O_4 + CO_2 + C$ (graphite)

magnetite

$\Delta^{13}C$ = ????

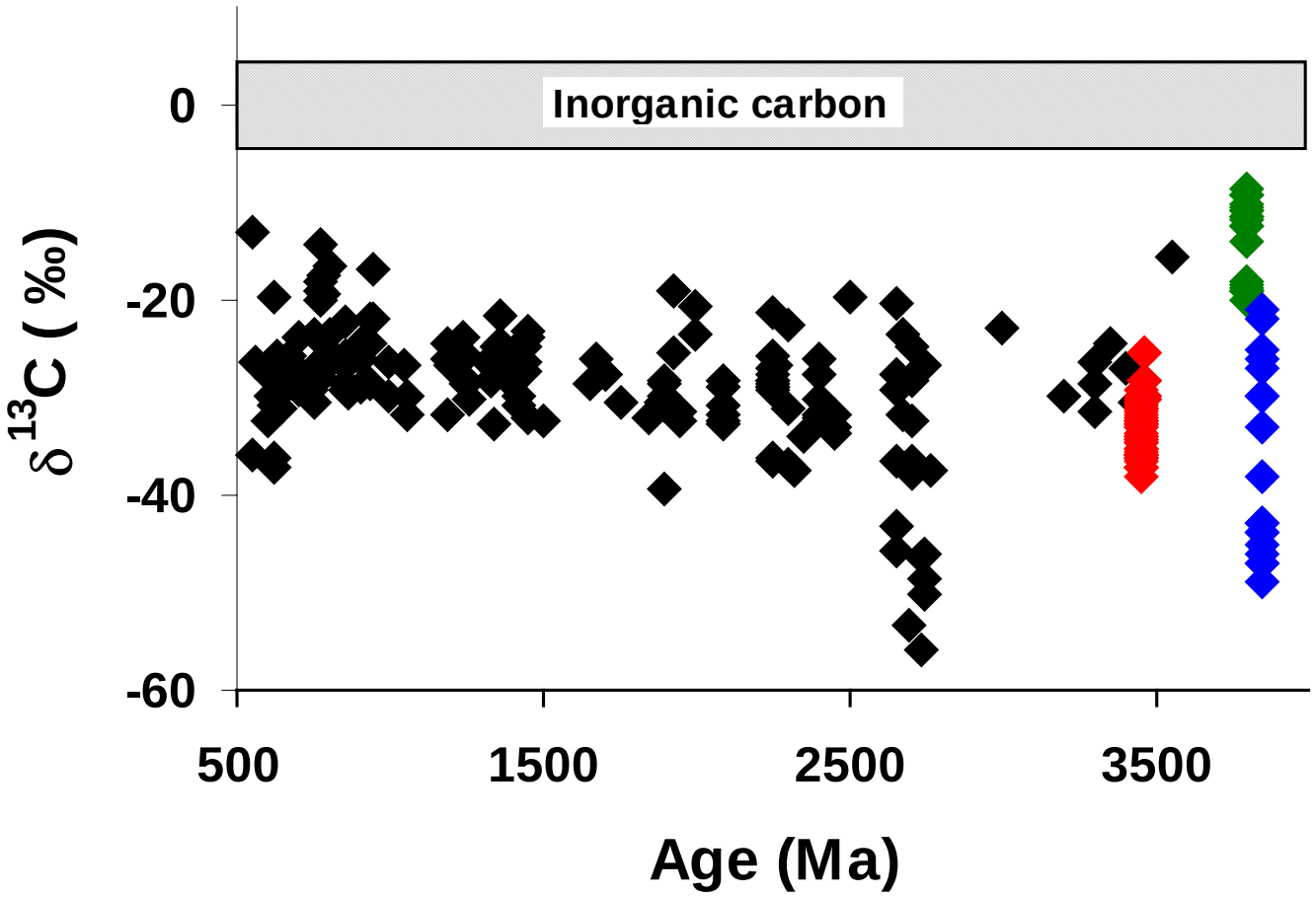
Van Zuilen, Lepland & Arrhenius, *Science* (2002)

Timeline of the early Earth



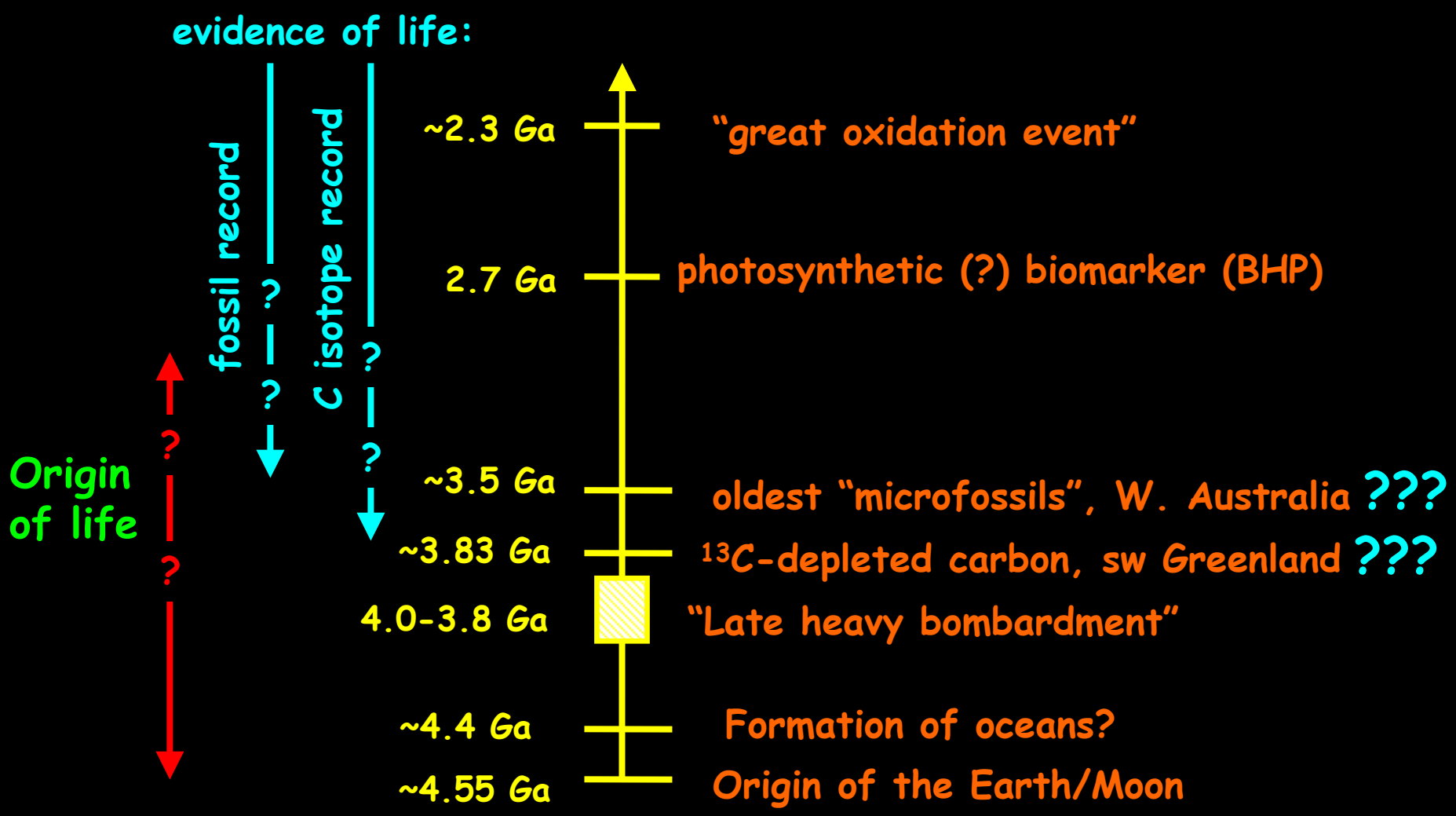
Carbon isotopes as a biosignature

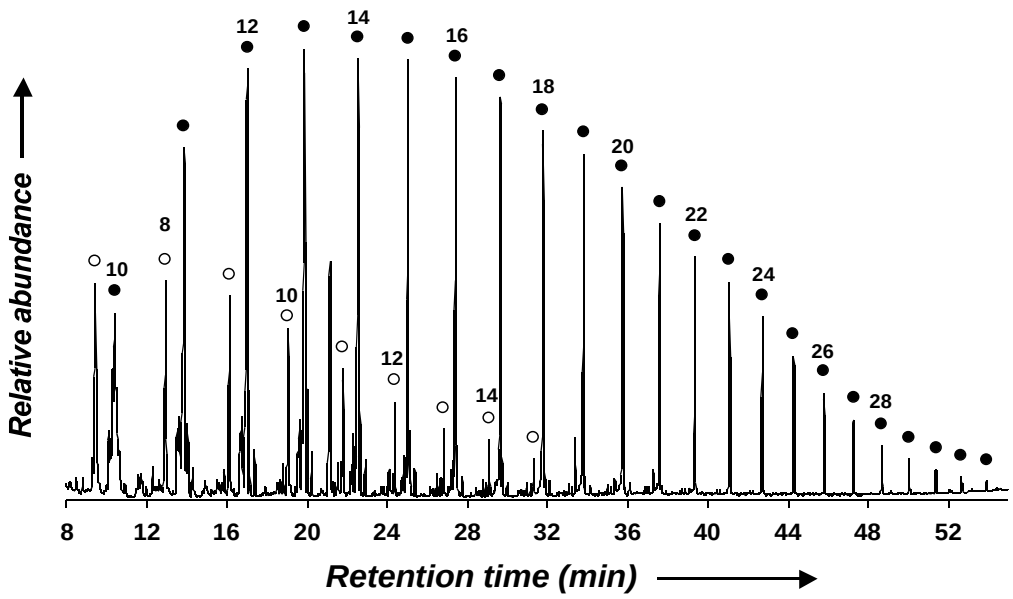
C isotope composition of organic matter through time

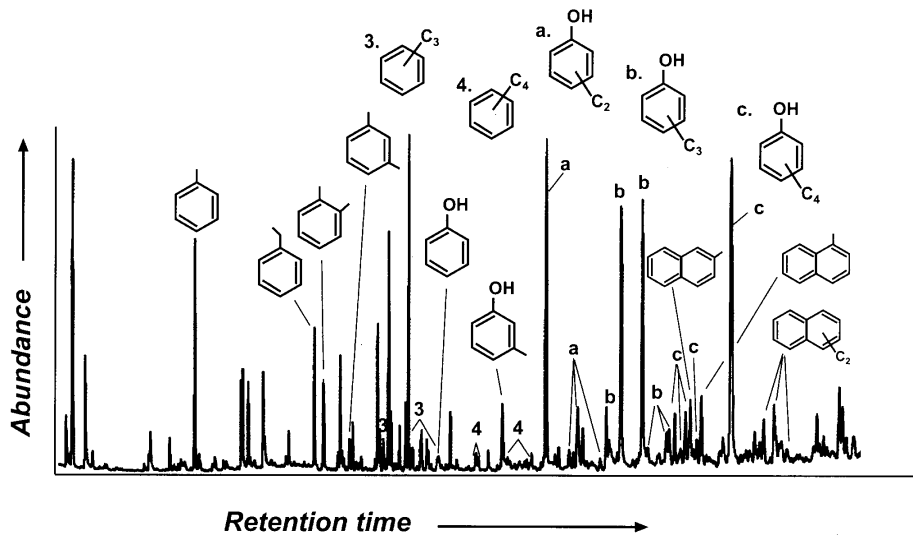


[Data for Greenland & Pilbara: Mozjsis et al., 1996; Ueno et al., 2002, 2004; van Zuilen et al., 2003; Brasier et al., 2002; Rosing, 1999]

Timeline of the early Earth



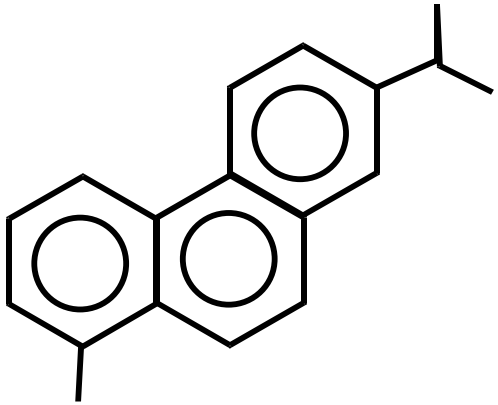




Common features of abiotic synthesis pathways:

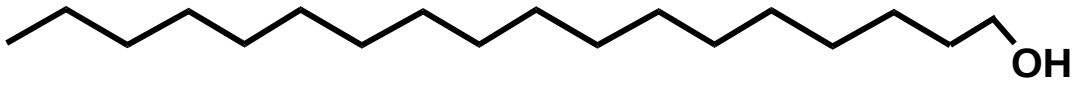
- ♠ Products occur as families of structurally related compounds (homologs)
- ♣ Products have "randomized" structural distributions

Examples of hydrocarbons that would NOT be good biomarkers

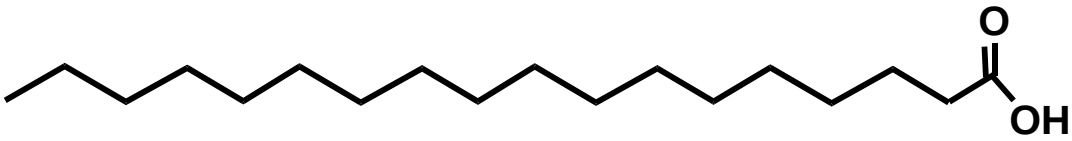


retene

heptadecane

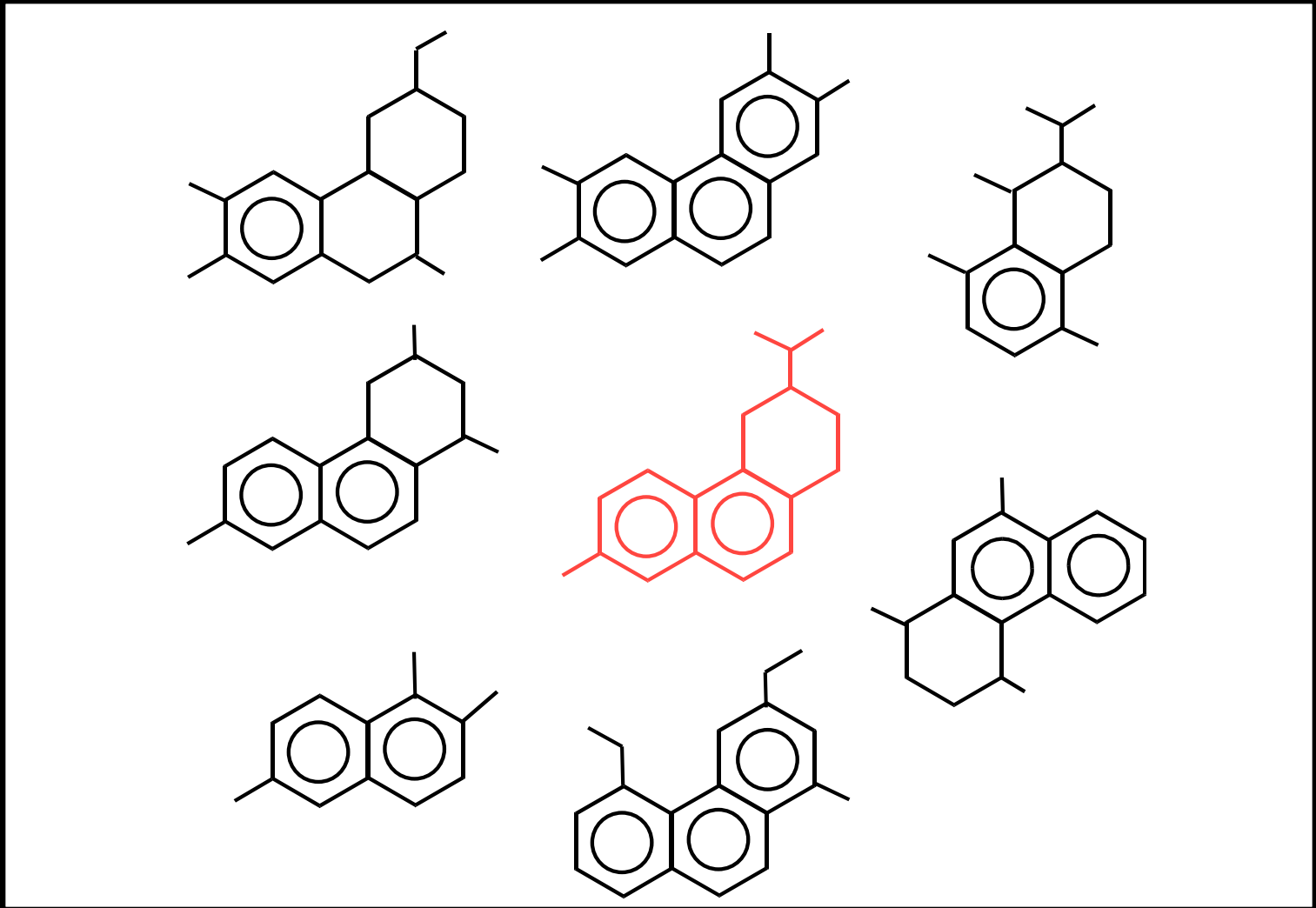


heptadecanol

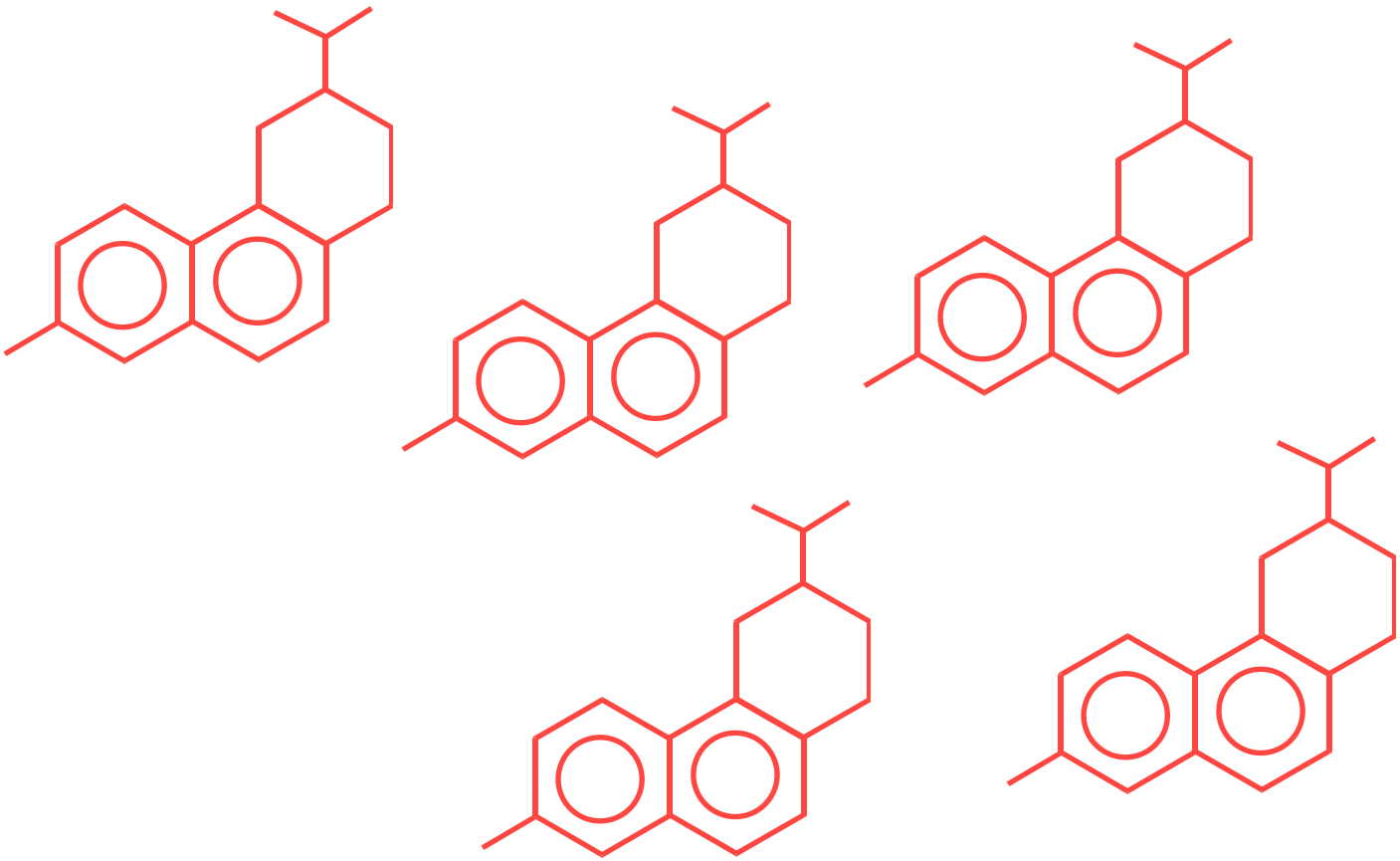


Stearic acid
(octadecanoic acid)

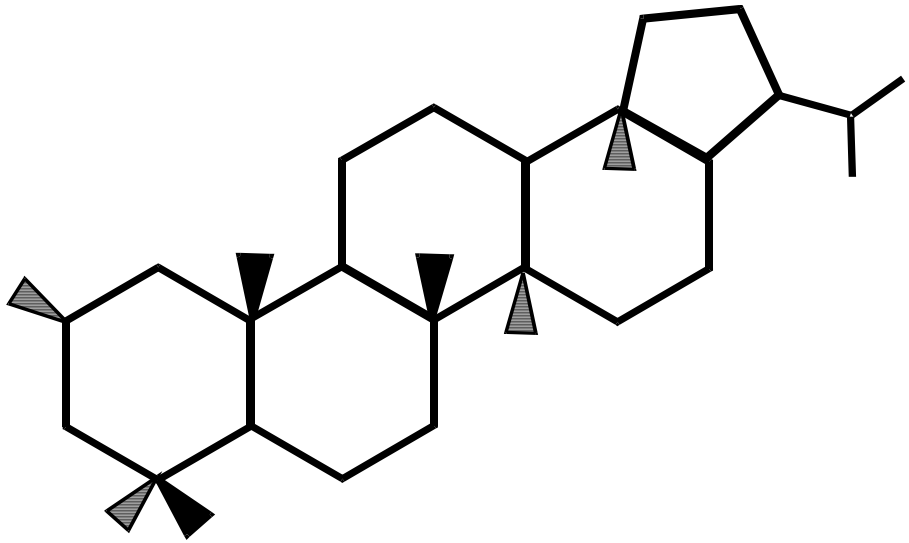
Structurally complex compounds are not necessarily a biosignature …



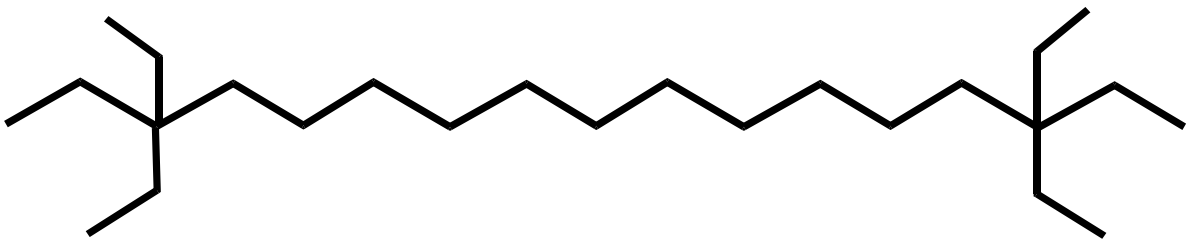
EXCEPT if they occur without related compounds:



Examples of hydrocarbons that may be good biomarkers



hopane



Quaternary-branched compound