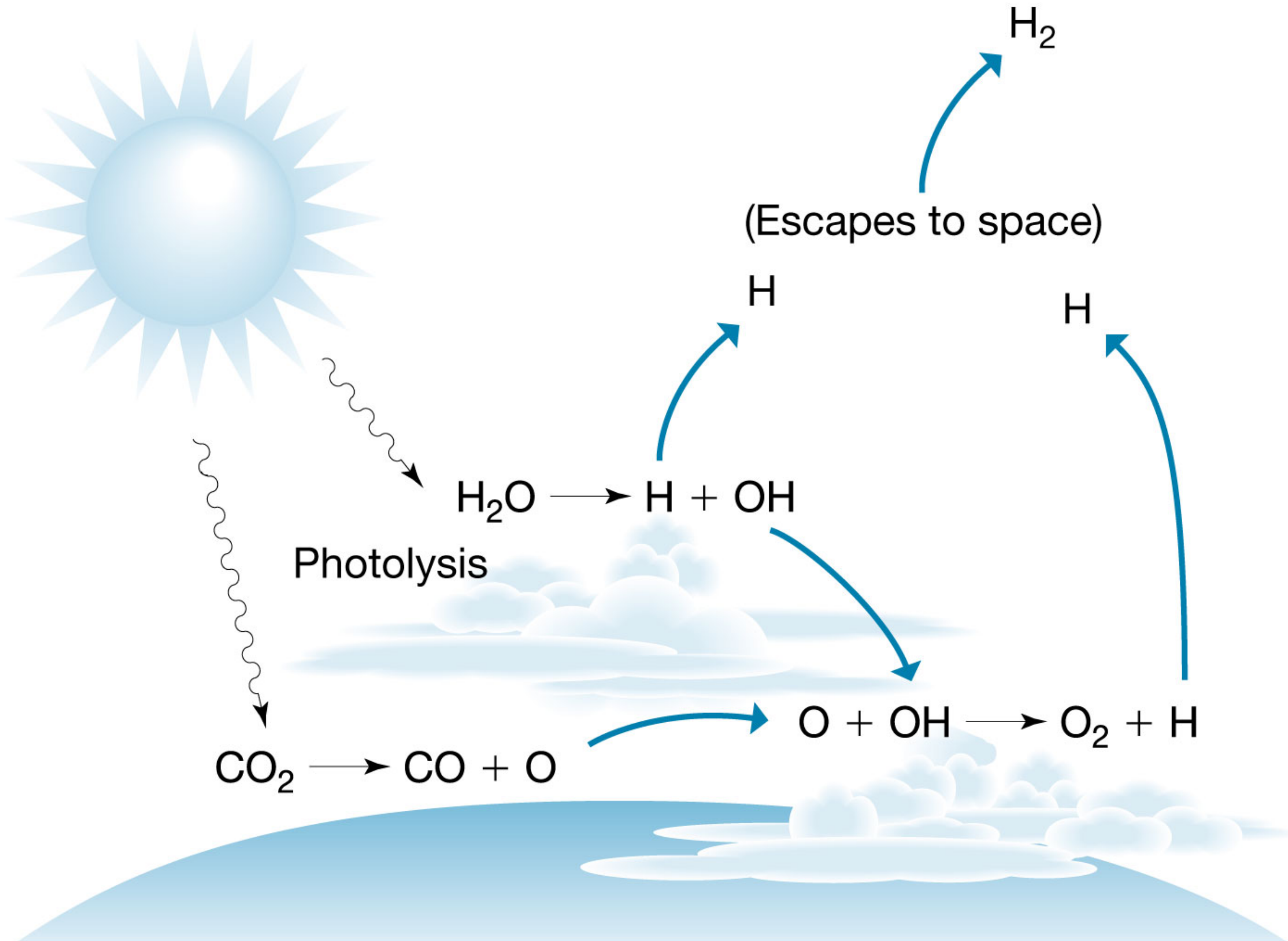
Chapter 11
Bankruptcy…no, wait…

Effect of Life on the Early Earth Atmosphere



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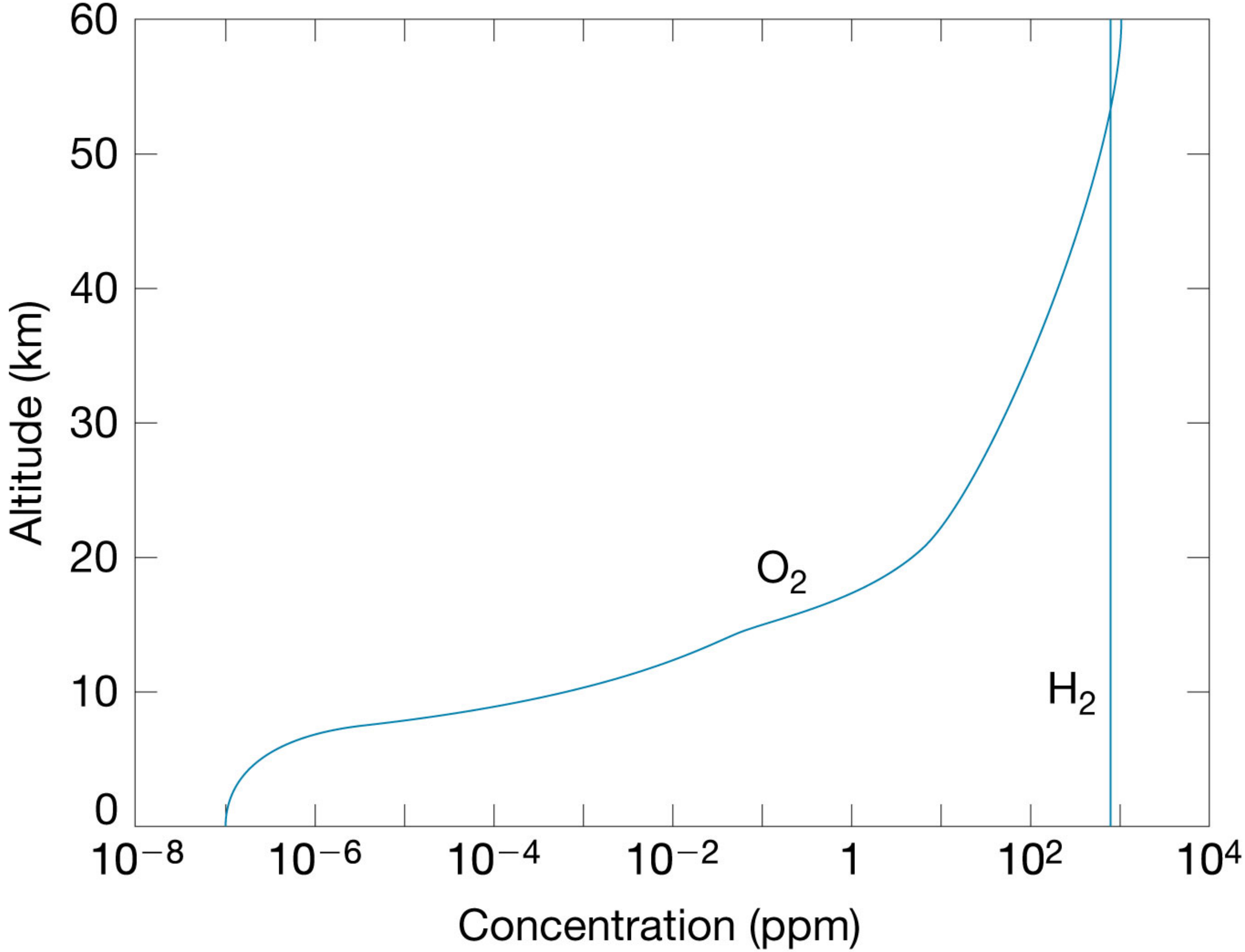

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Fig. 11-1: Stromatolites from the 3.5 billion year old Warrawoona formation in Australia. “Algal” mats?

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Note: Book committed a “no-no” by providing no scale…

If so, not like modern analogs (here)_ because oxygenic photosynthesis had not evolved yet

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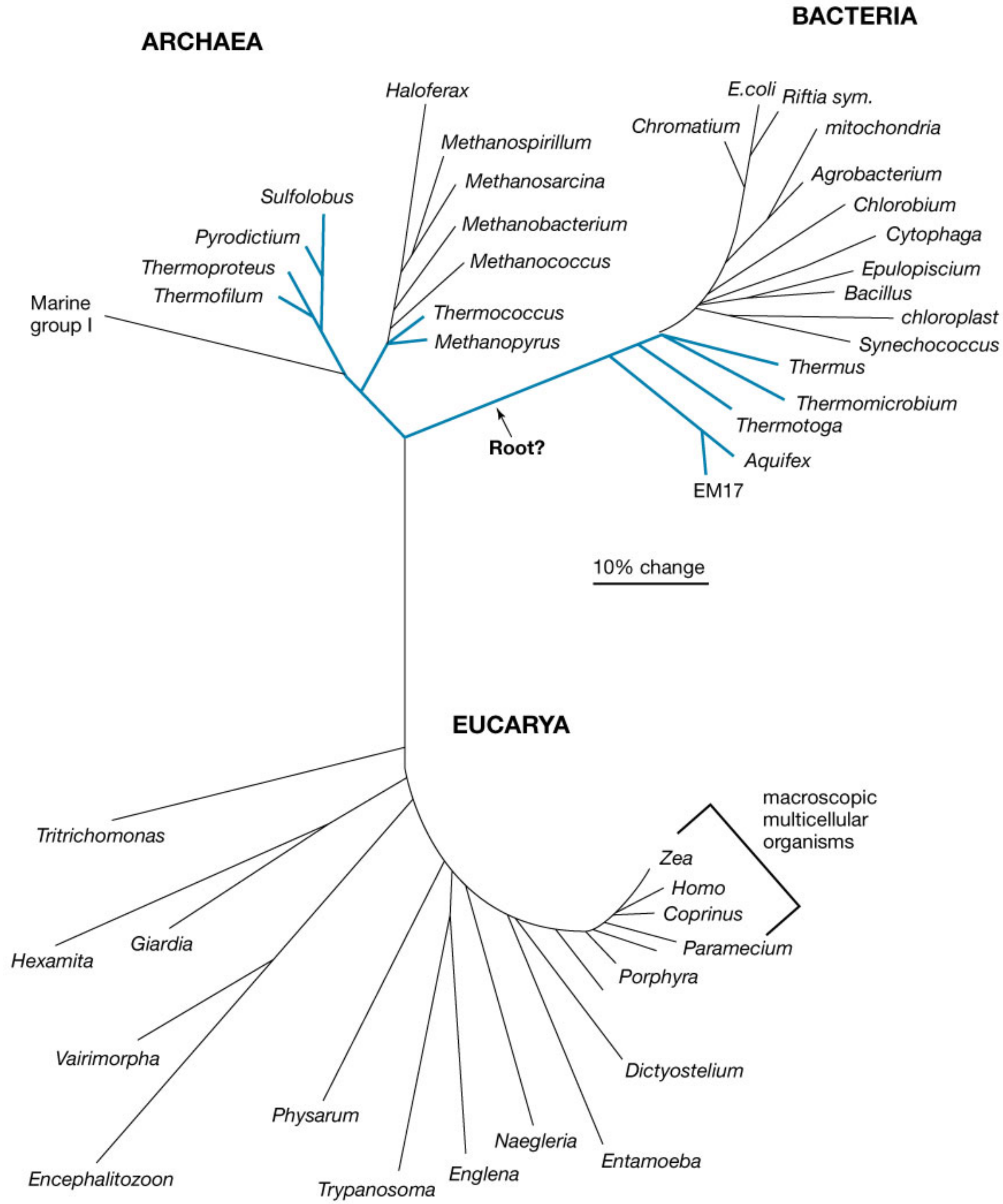
- Hyperthermophilic chemoautotrophs
- Evidence from C isotope fractionation - but how?
- Anoxygenic photosynthesis, perhaps iron reducers very early
- Methanogens occur fairly close to the root of the molecular "tree of life"
- Is there a modern analog?



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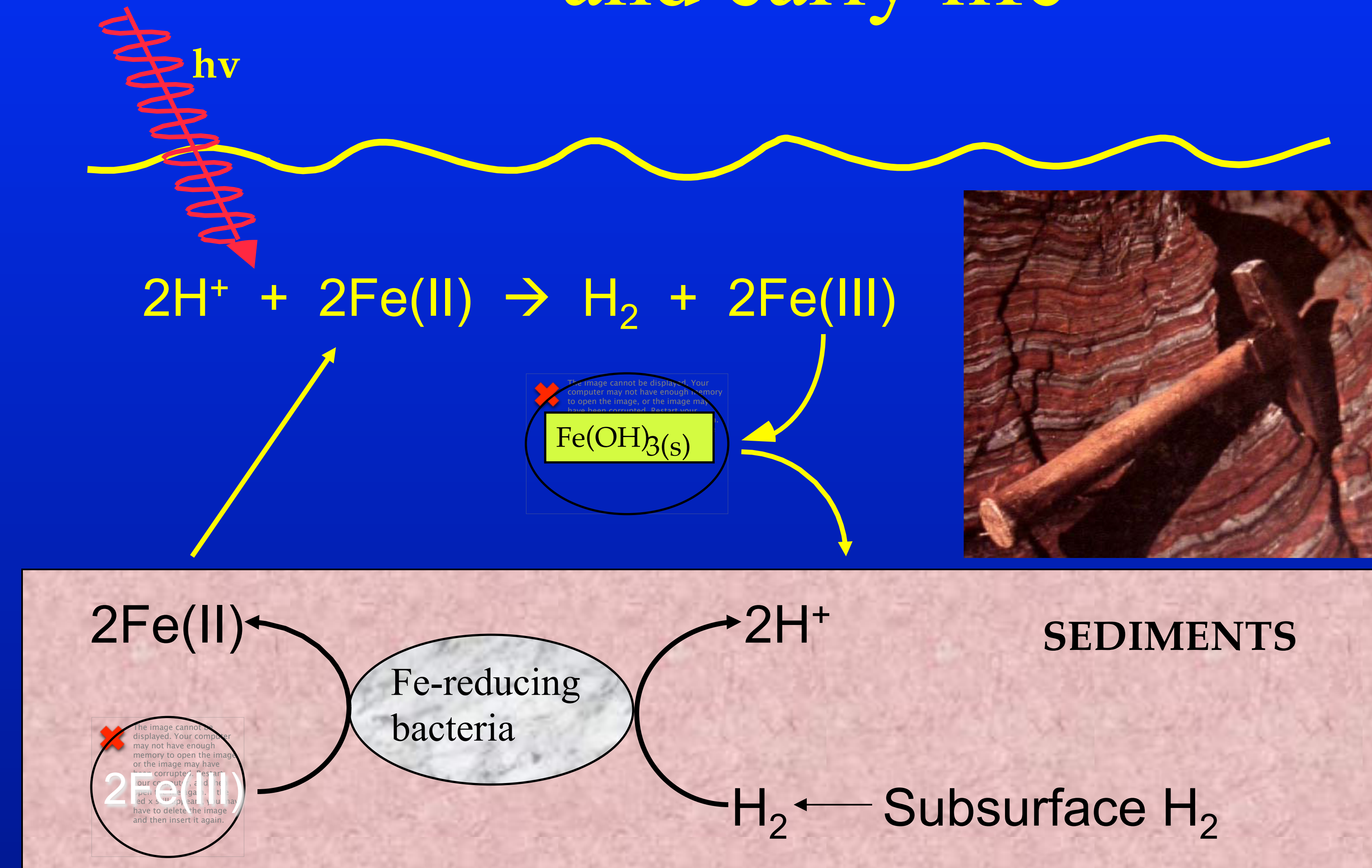
Example: $Fe^{II/III}$ cycling and early life



Characteristics of early life…

- Organisms closes to “last common ancestor” are chemoautotrophs (get fuel from inorganic sulfide, hydrogen, etc.)
- They are also hyperthermophilic – they live at high temperature (current record for growth is about 123°C)

Carbon isotope fractionation

- ^{12}C, ^{13}C are stable isotopes
- Different masses lead to slightly different chemical reaction rates

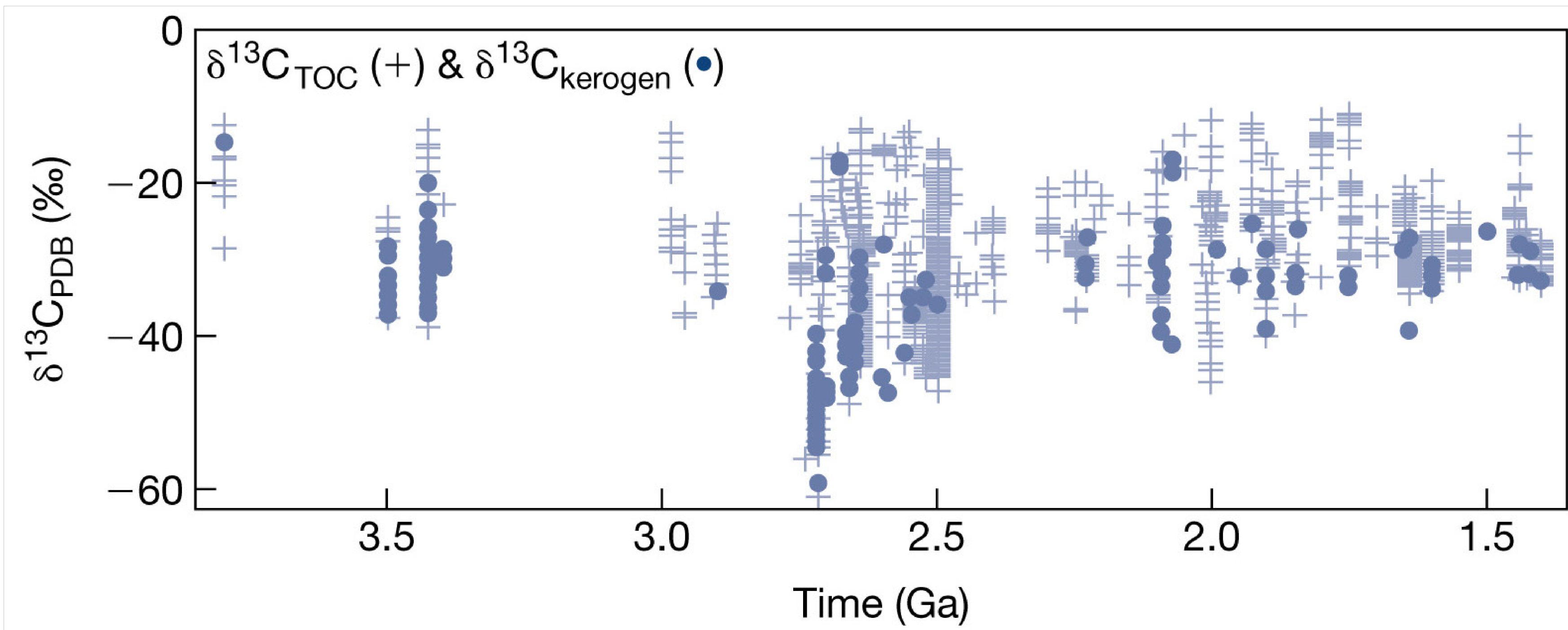
$$\delta^{13}\mathrm{C}_{sample} = \left(\frac{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{sample} - \left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{s\tan dard}}{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{s\tan dard}} \right) \times 1{,}000$$

Methanogenesis

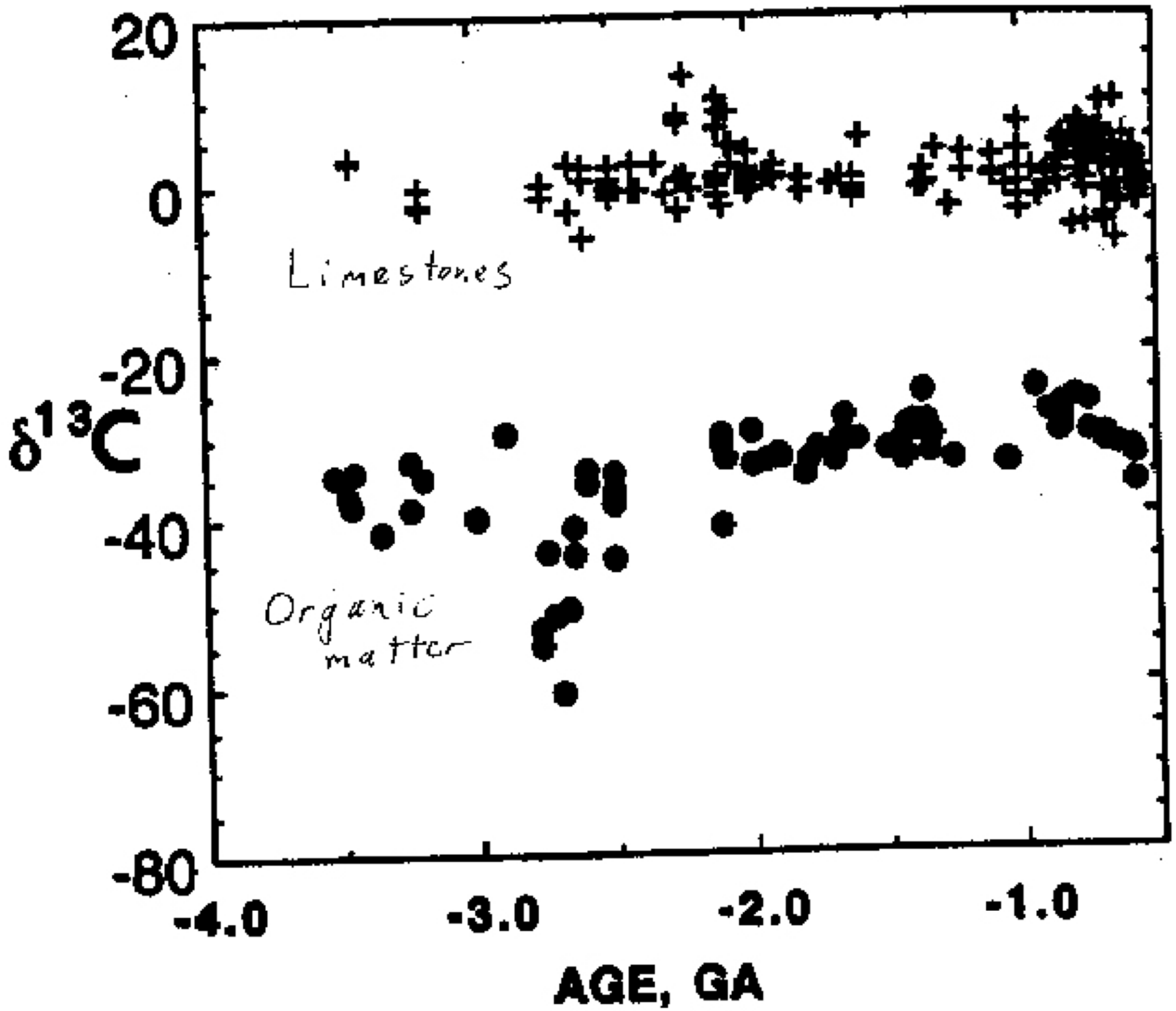
- $CO_2 + 4H_2 \text{-->} CH_4 + 2H_2O$
- Some methanogens metabolize other chemicals, like formate ($HCOO^-$)
- Without much oxygen in the atmosphere, could have had 1000 ppm methane from methanogens!
- Methane is ~23 times better as a greenouse gas than CO_2, would have kept Earth pretty toasty despite dimmer sun

Methanogenesis:

- $CO_2 + 4H_2 \text{-->} CH_4 + 2H_2O$
- C isotope fractionation
- Used by other organisms, making its way into organic matter? Or like Titan (hydrocarbon particles)?



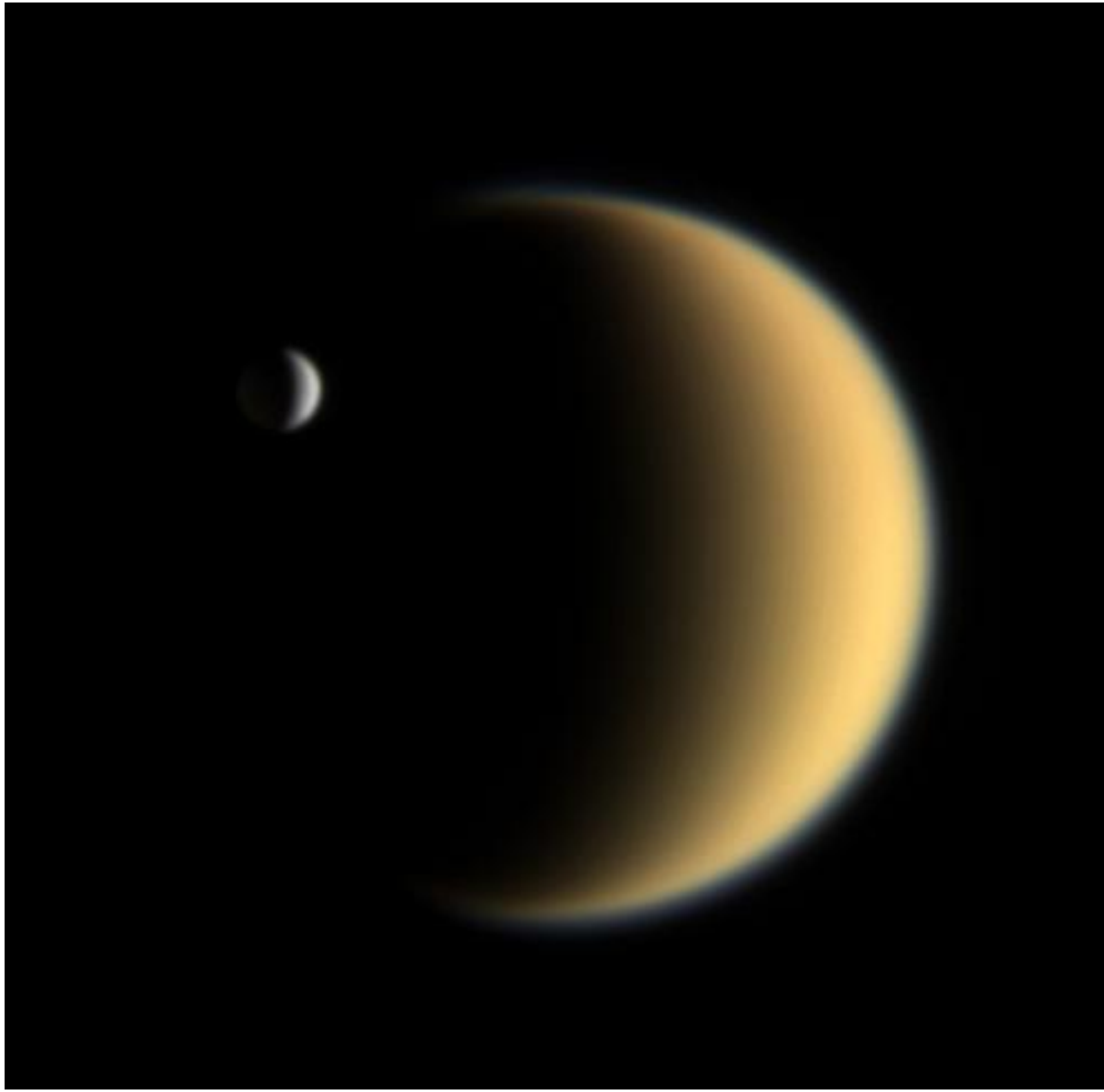
- Fractionation between inorganic and organic carbon all the way back…

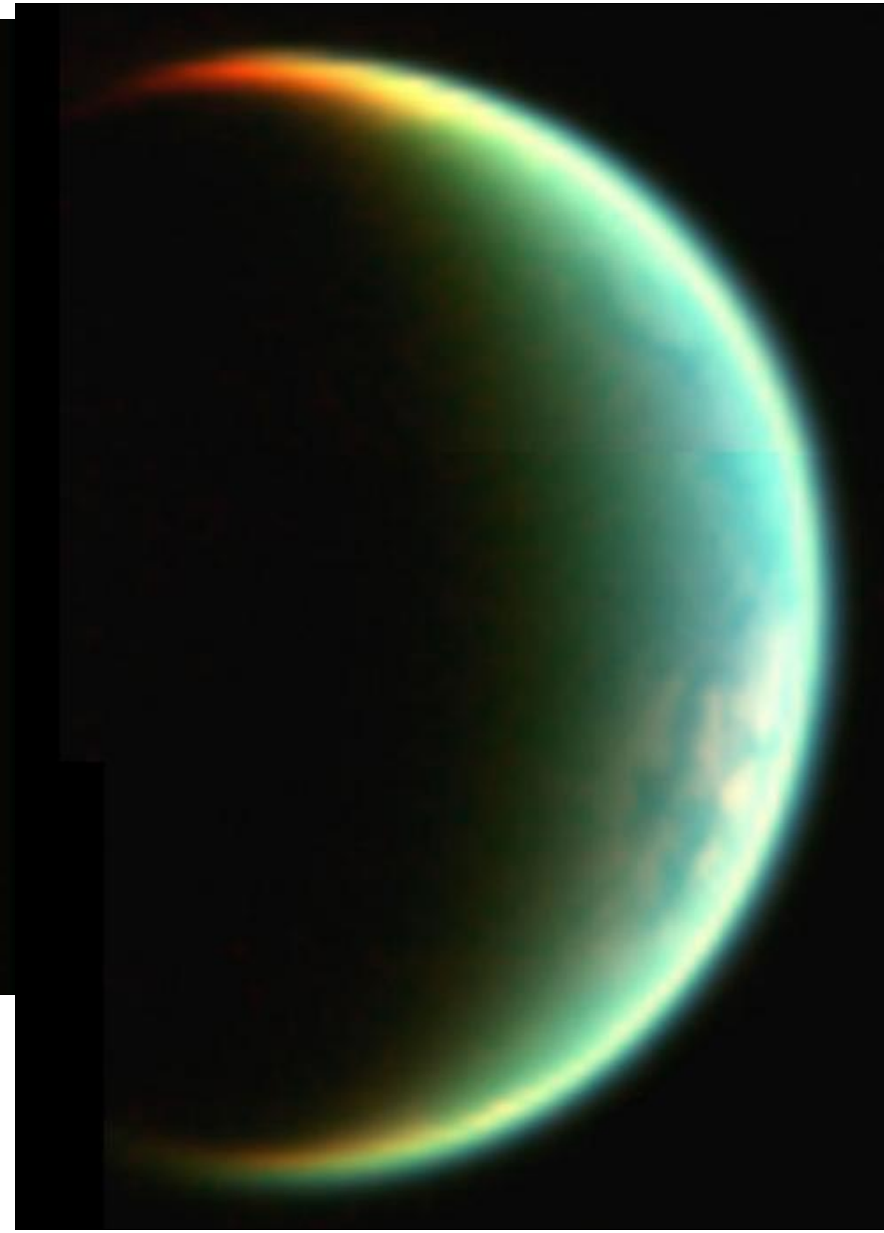


Titan- moon of Saturn

Atmosphere ~98% N_2, 2% CH_4

Orange haze due to photochemical alteration of methane, forming hydrocarbon particles (like smog!)

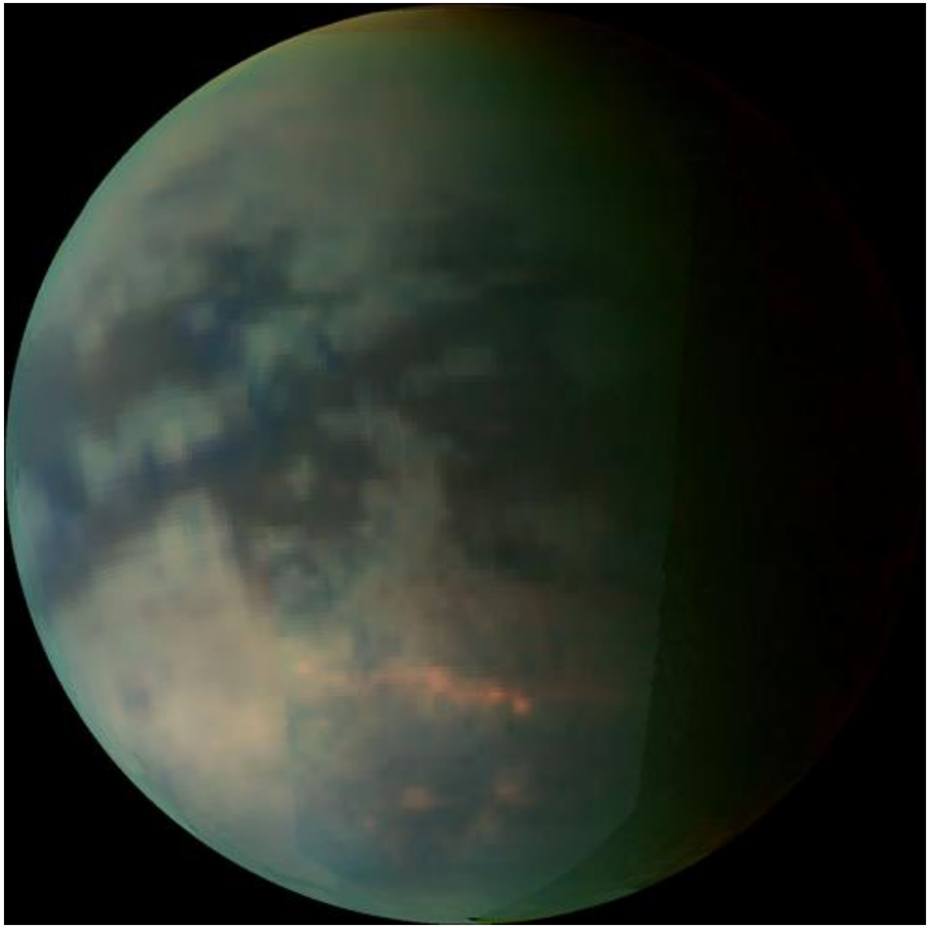


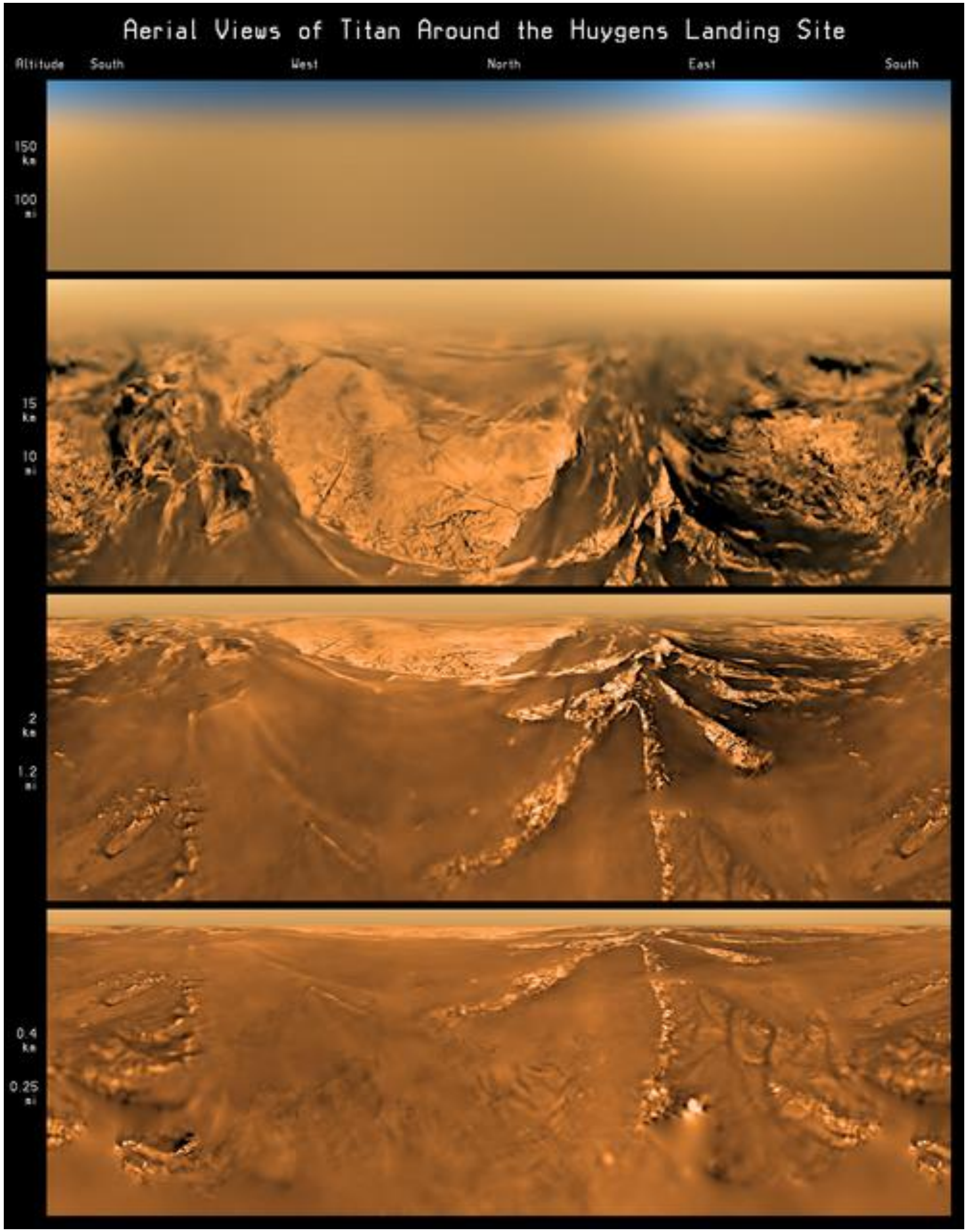


- Titan’s methane-containing atmosphere, from a distance and closer-up…

Titan:

- Close up, shows a changing pattern of clouds in the nitrogen and methane atmosphere

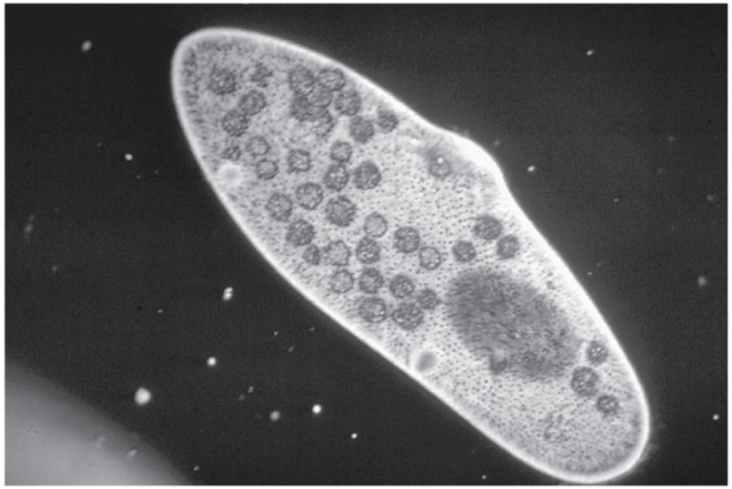



Aerial Views of Titan Around the Huygens Landing Site
Altitude
South
West
North
East
South
150 km
100 mi
15 km
10 mi
2 km
1.2 mi
0.4 km
0.25 mi

Nitrogen Fixation

- Life needs nitrogen to make proteins, but most cannot use N_2 - must use "fixed nitrogen" (NH_3, NO_3^-, etc. because N_2 is quite inert).
- In today's atmosphere, lightning actually provides some fixed nitrogen: $N_2 + O_2 \rightarrow 2\ NO$
- On early Earth, without O_2, another reaction may have provided fixed nitrogen: $N_2 + 2CO_2 \rightarrow 2NO + 2CO$
- NO eventually gets oxidized to nitrate (NO_3^-)
- Prokaryotes can fix nitrogen - and are more resistant to UV radiation! (evolved before much ozone?)
- Bacteria can then use NO_3^- for respiration, reduce it back to N_2

(a)



(b)

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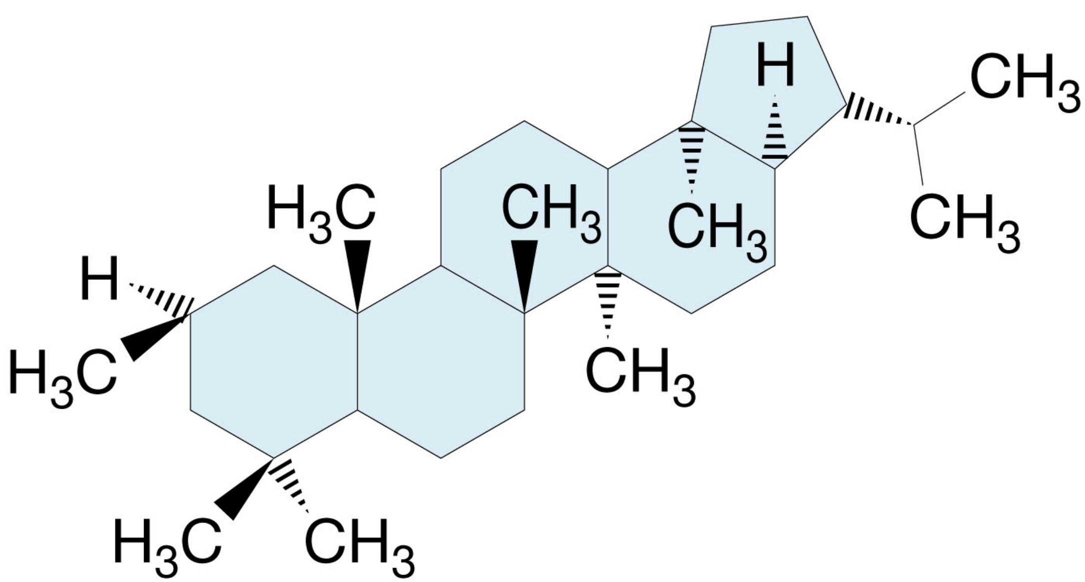
The Rise of Oxygen

- Initially, oxygen must have been a poison (life started without it, makes it as a byproduct of photosynthesis)!
- First evidence (though equivocal) is from about 2.7 Ga
- 2a-methylhopanes (a breakdown product of modern cyanobacteria), steranes (from cholesterol, which is unique to eukaryotes that require oxygen)

2α(Me), 17α(H), 21β(H)-hopane



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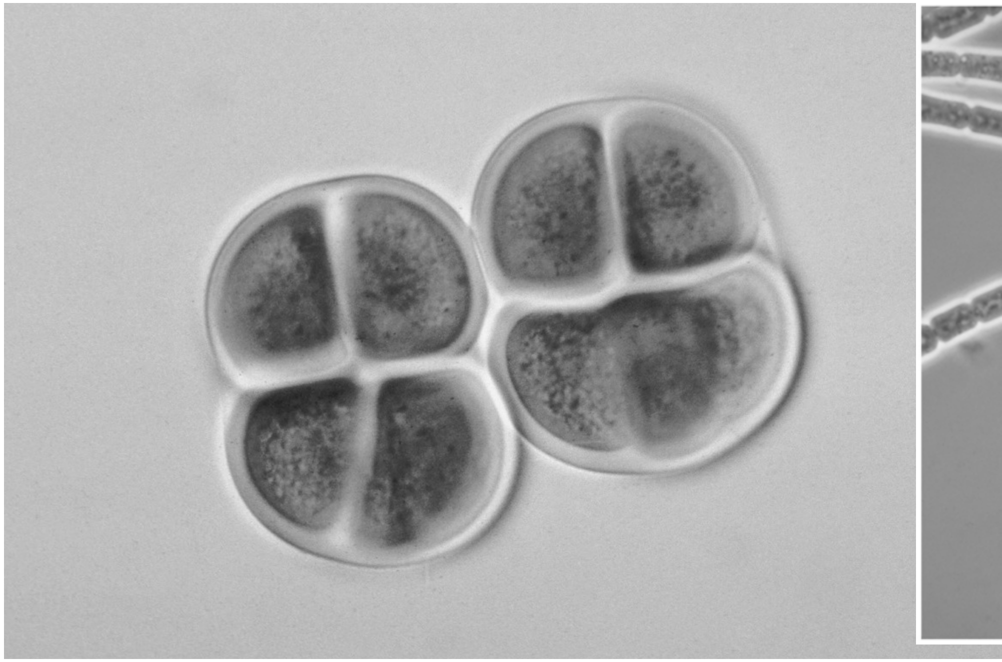
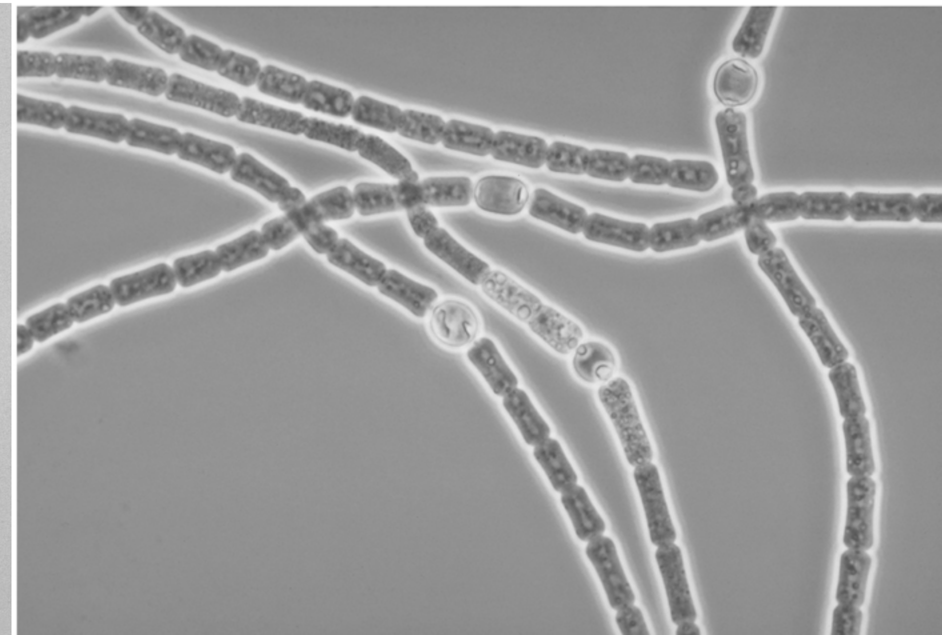
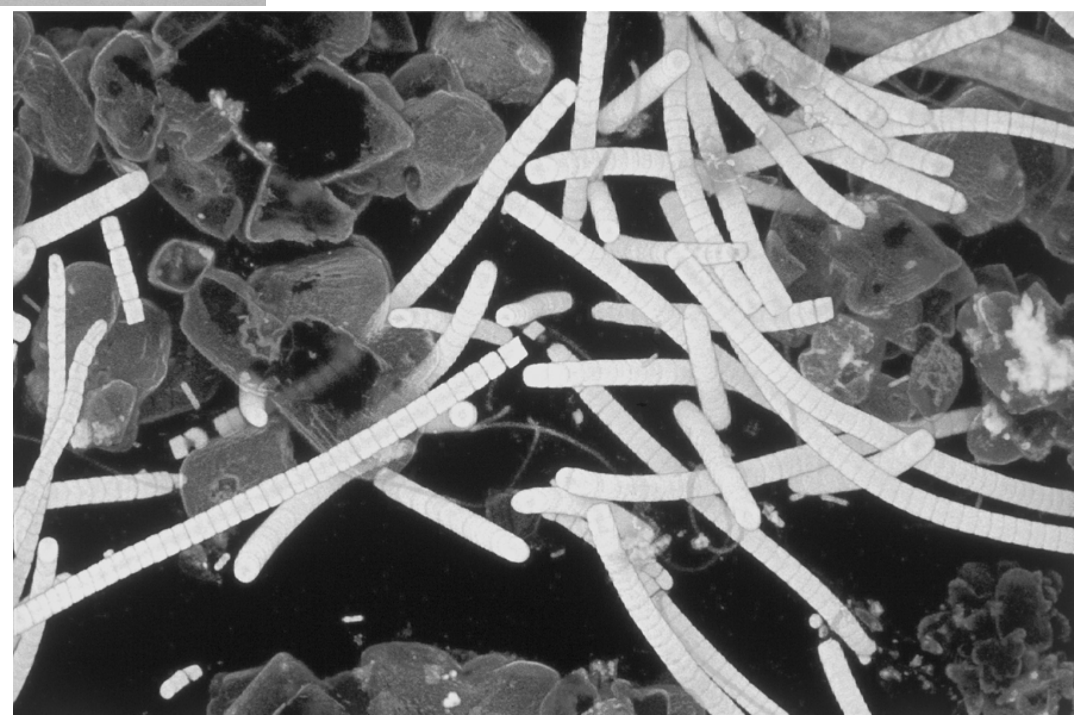




- Coccoid (round)
- Filamentous
- Heterocystic
- Nitrogenase, for N fixation, is poisoned by oxygen
- Specialized cells



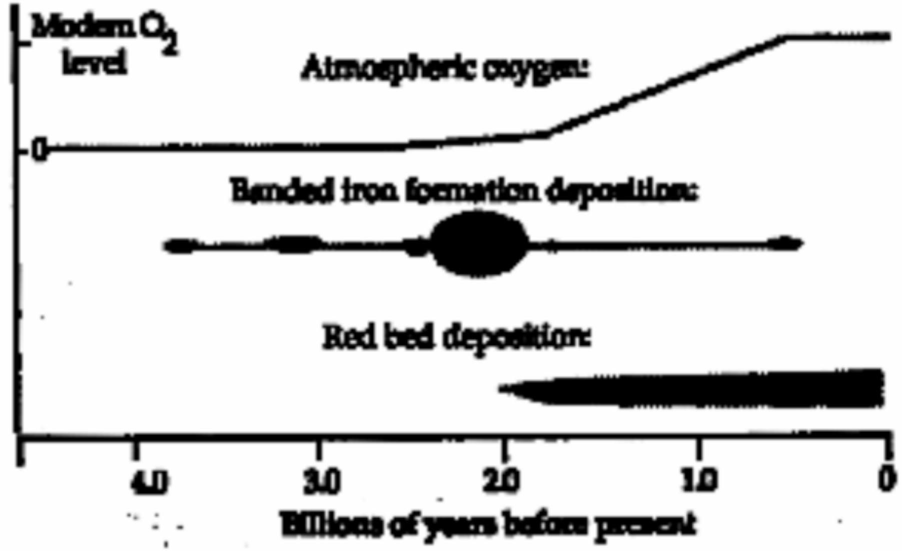
Endosymbiosis

- Chloroplasts are the parts of plant cells where photosynthesis occurs
- Chloroplasts have their own DNA - which closely resembles that of cyanobacteria
- So - modern plants host cyanobacteria, much like modern animals host mitochondria (resembling an organisms that is a disease-causing organism today!)

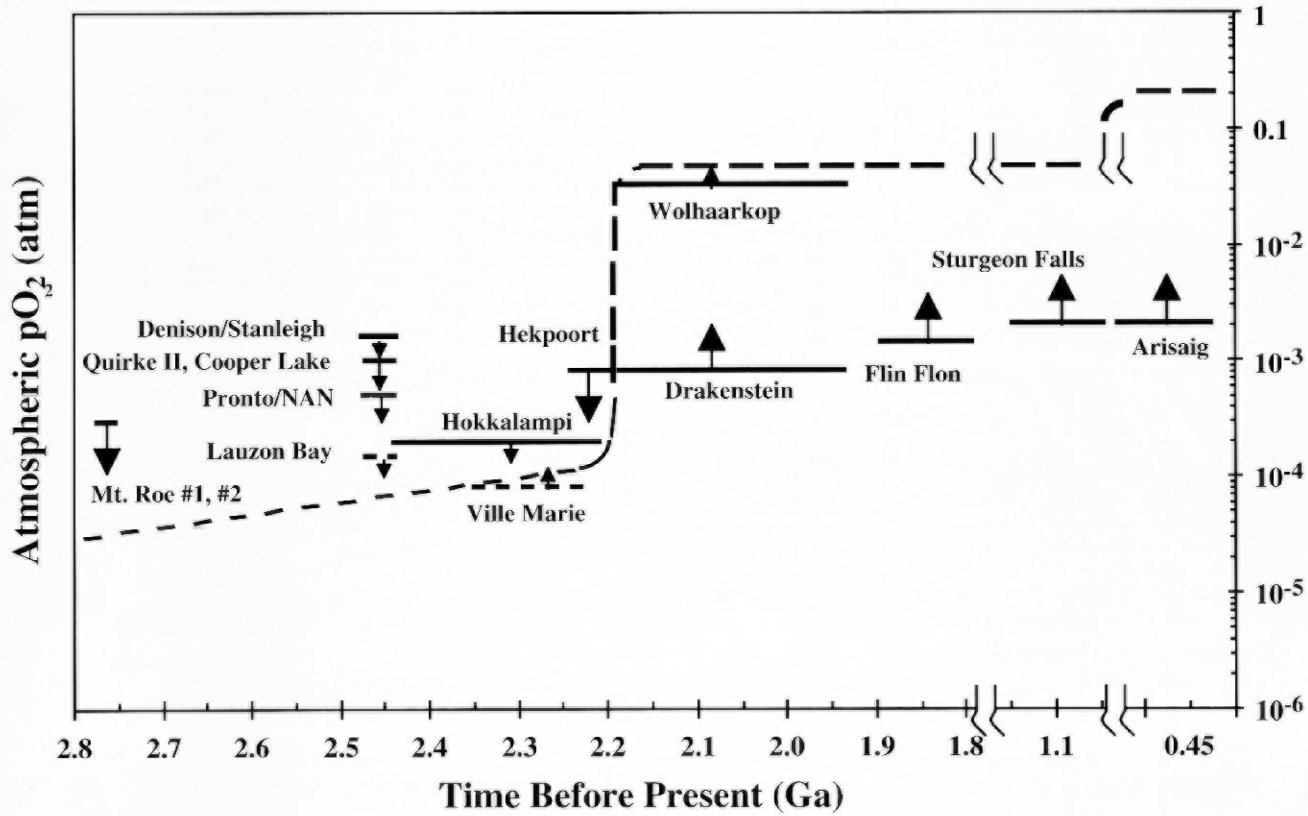
If cyanobacteria were around 2.7 Ga ago, why didn't atmospheric oxygen react modern levels until 300 my ago?

- Lots and lots and LOTS of Fe (iron) around, most of it *ferrous* (Fe^{2+}) like in many Fe-silicate minerals
- Fe^{2+} is very soluble in water
- The oxidized form, *ferric* Fe (Fe^{3+}) is insoluble in water
- Complex - but production of O_2 in ocean water would lead to oxidation of some ferrous Fe to ferric Fe, deposition
- So, even though oxygen produced, it was used immediately and could not build up in atmosphere, especially if oxygen production limited, "self poisoned", or limited by reduced volcanic emissions

Examples of BIFs…

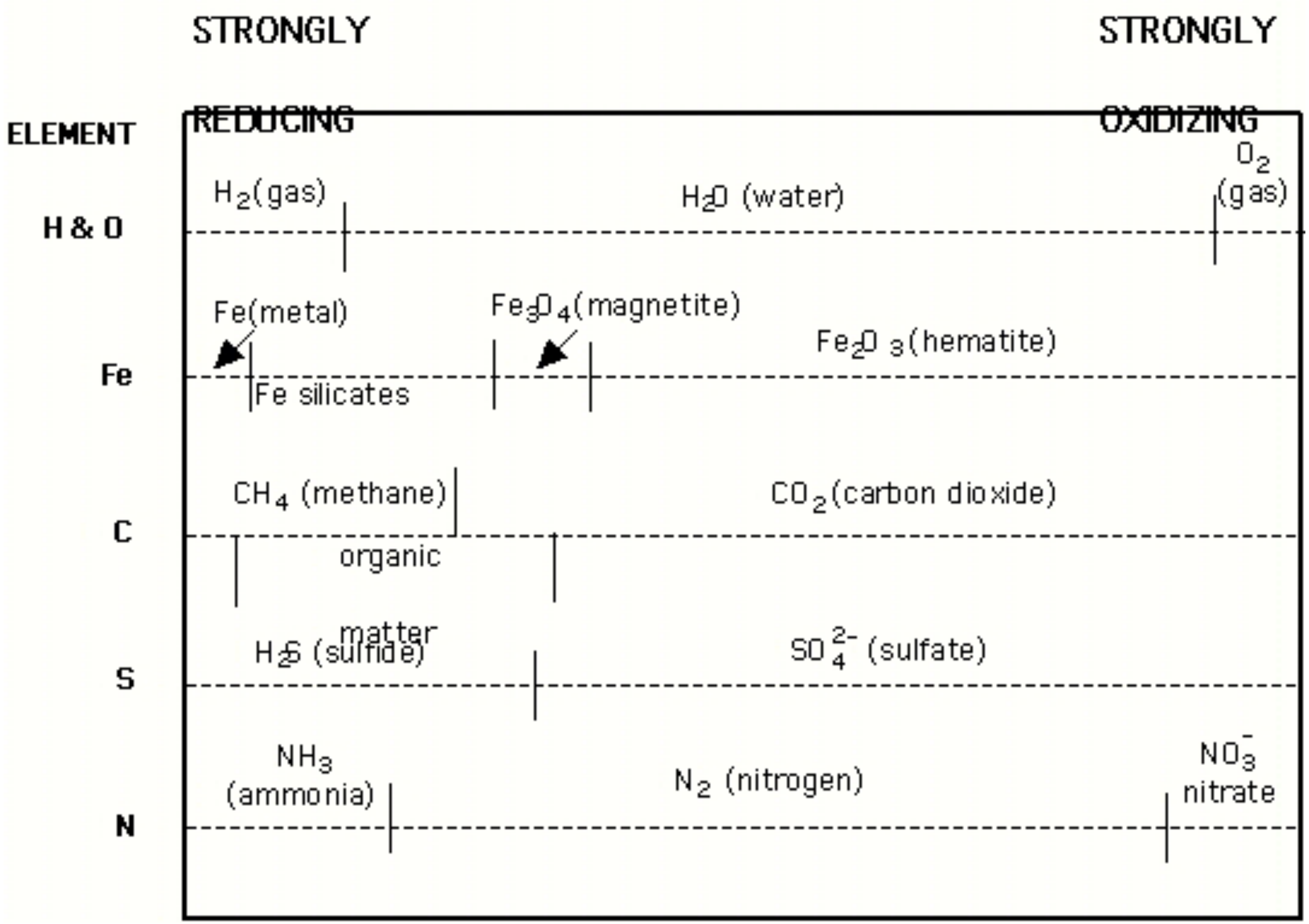


Modern O2 level
0
Atmospheric oxygen:
Banded iron formation deposition:
Red bed deposition:
4.0
3.0
2.0
1.0
0
Billions of years before present



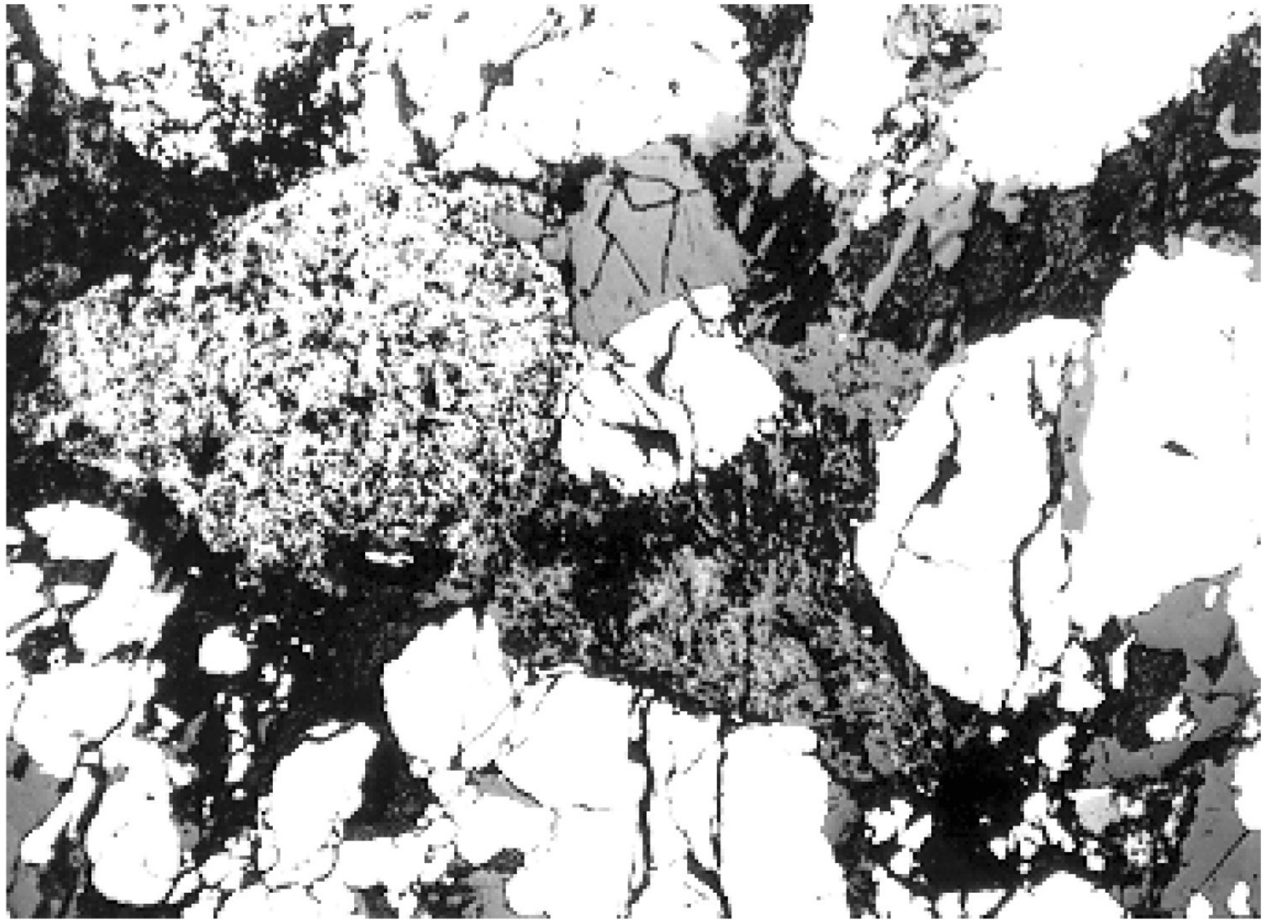
Atmospheric pO2 (atm)
1
0.1
10-2
10-3
10-4
10-5
10-6
Wolhaarkop
Sturgeon Falls
Denison/Stanleigh
Hekpoort
Quirke II, Cooper Lake
Arisaig
Drakenstein
Flin Flon
Pronto/NAN
Hokkalampi
Lauzon Bay
Mt. Roe #1, #2
Ville Marie
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.1
0.45
Time Before Present (Ga)

FORMS OF DIFFERENT ELEMENTS UNDER DIFFERENT CONDITIONS



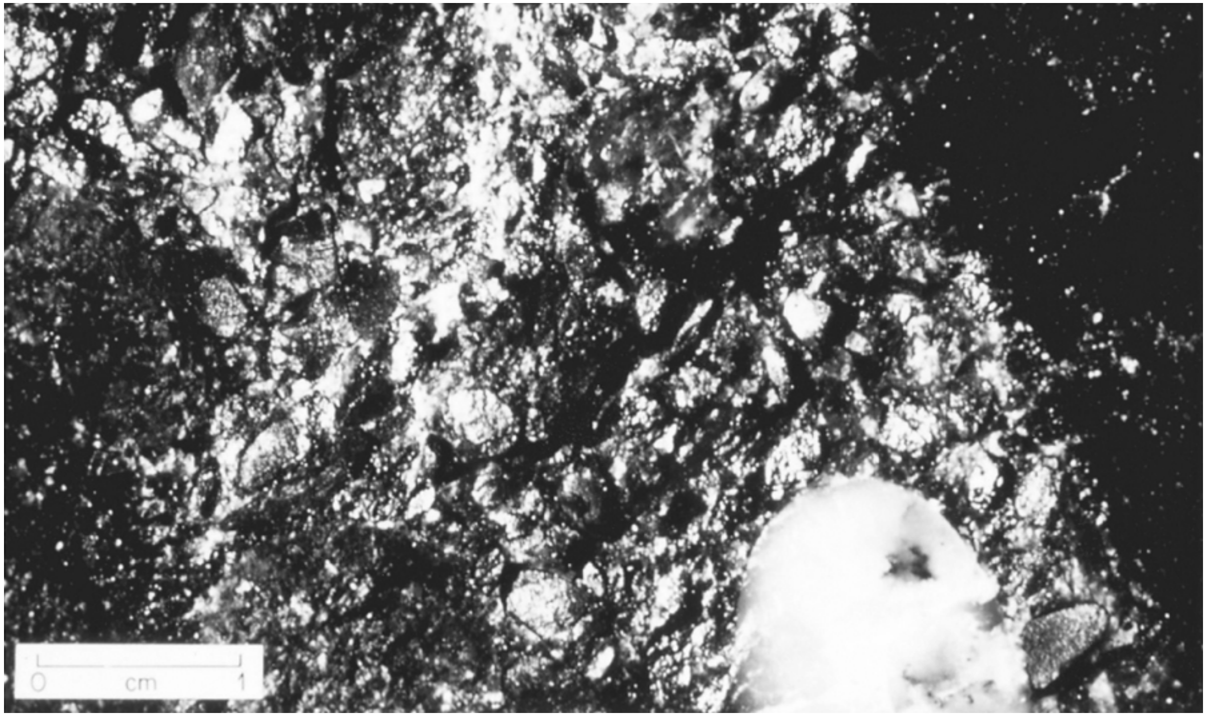
Detrital Uraninite (UO_2)

- U(VI) soluble, U(IV) insoluble



Detrital Pyrite (FeS_2)

- What is the effect of oxygen on pyrite?



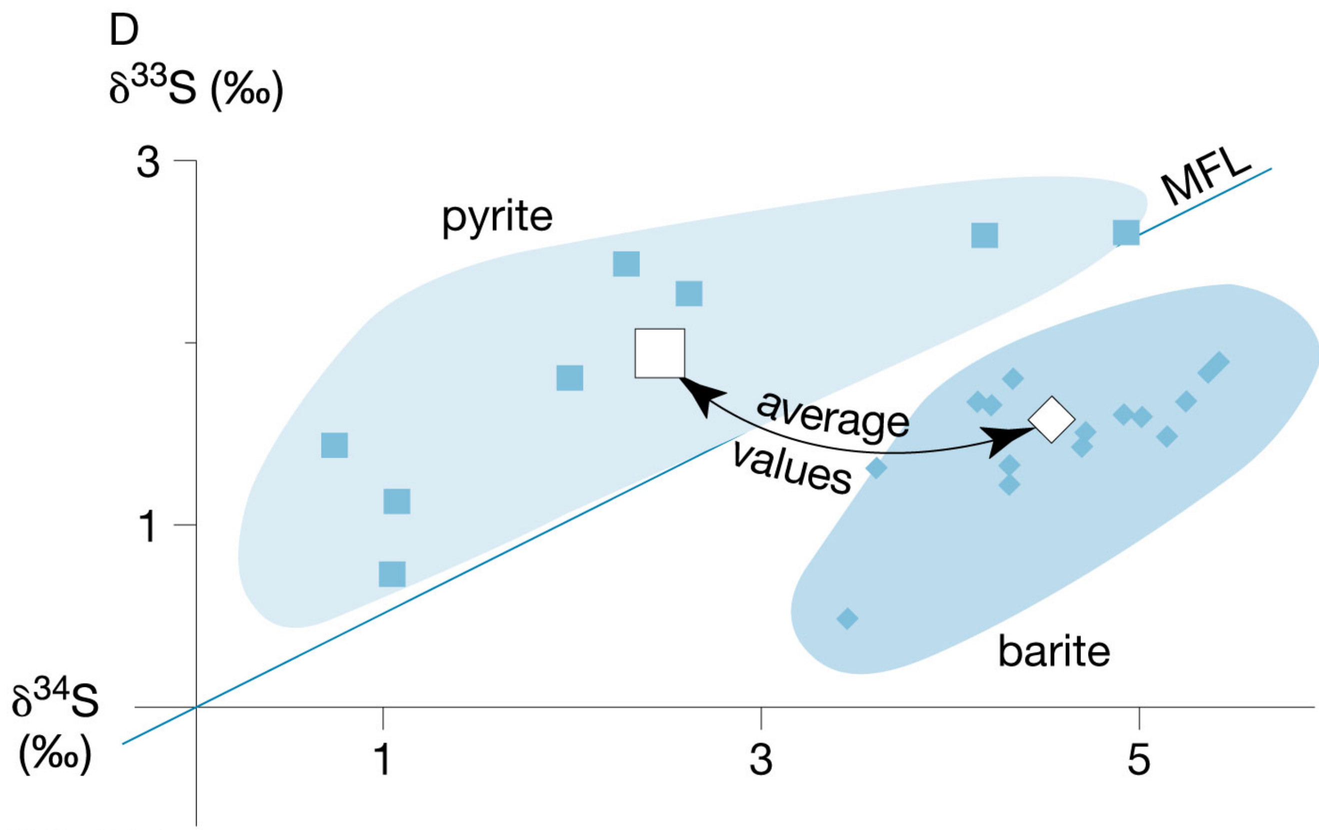
Paleosols, Redbeds

- Hematite (Fe^{3+} mineral) coats these wind-blown sand grains in arid environments, indicate oxygenated atmosphere

Mass-independent S isotopes

- Most chemical processes fractionate S isotopes
- (32, 33, 34, 36)
- Modern S in sediments falls along the MFL line
- Archaean S isotopes are shown - and DO NOT fall on the MFL!

Box Fig. 11-1



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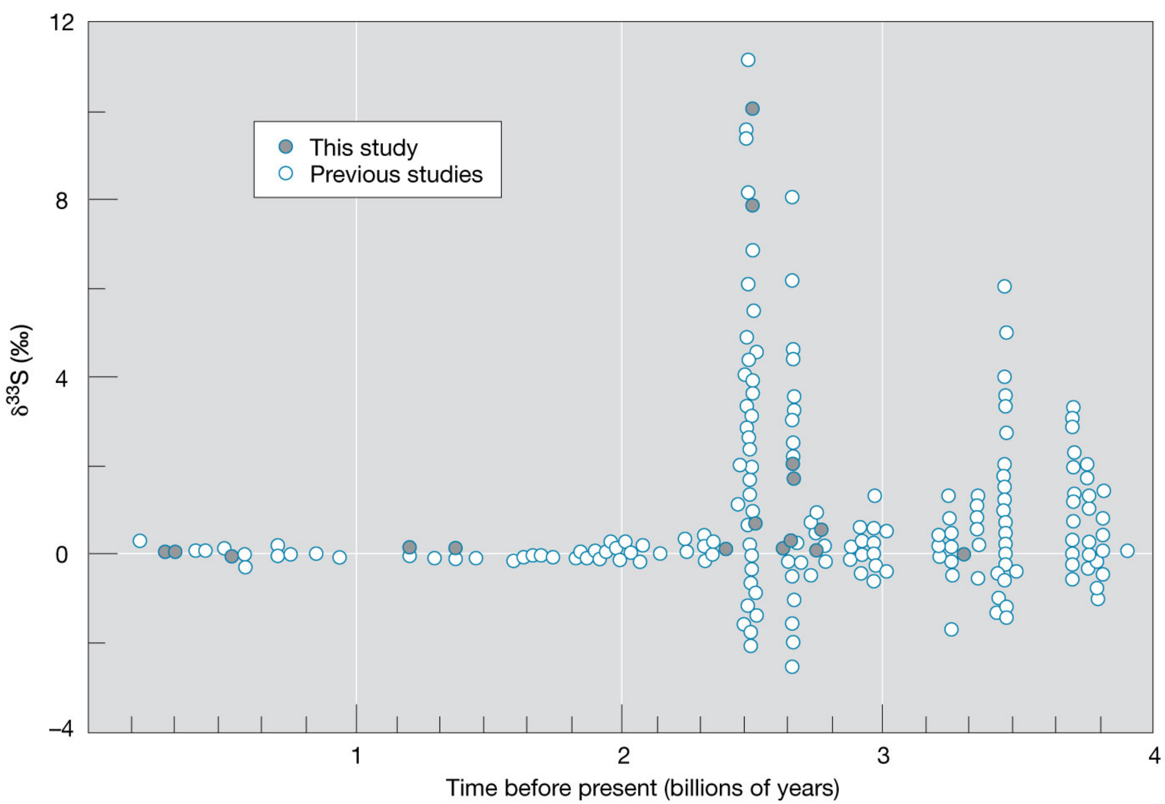
Example S fractionation eqn:

- $\delta^{34}S(^o/_{oo}) = \{[(^{34}S/^{32}S)_{sample} - (^{34}S/^{32}S)_{std}]/[(^{34}S/^{32}S)_{std}]$
- This can only happen photochemically in an atmosphere without much oxygen

Box Fig. 11-2



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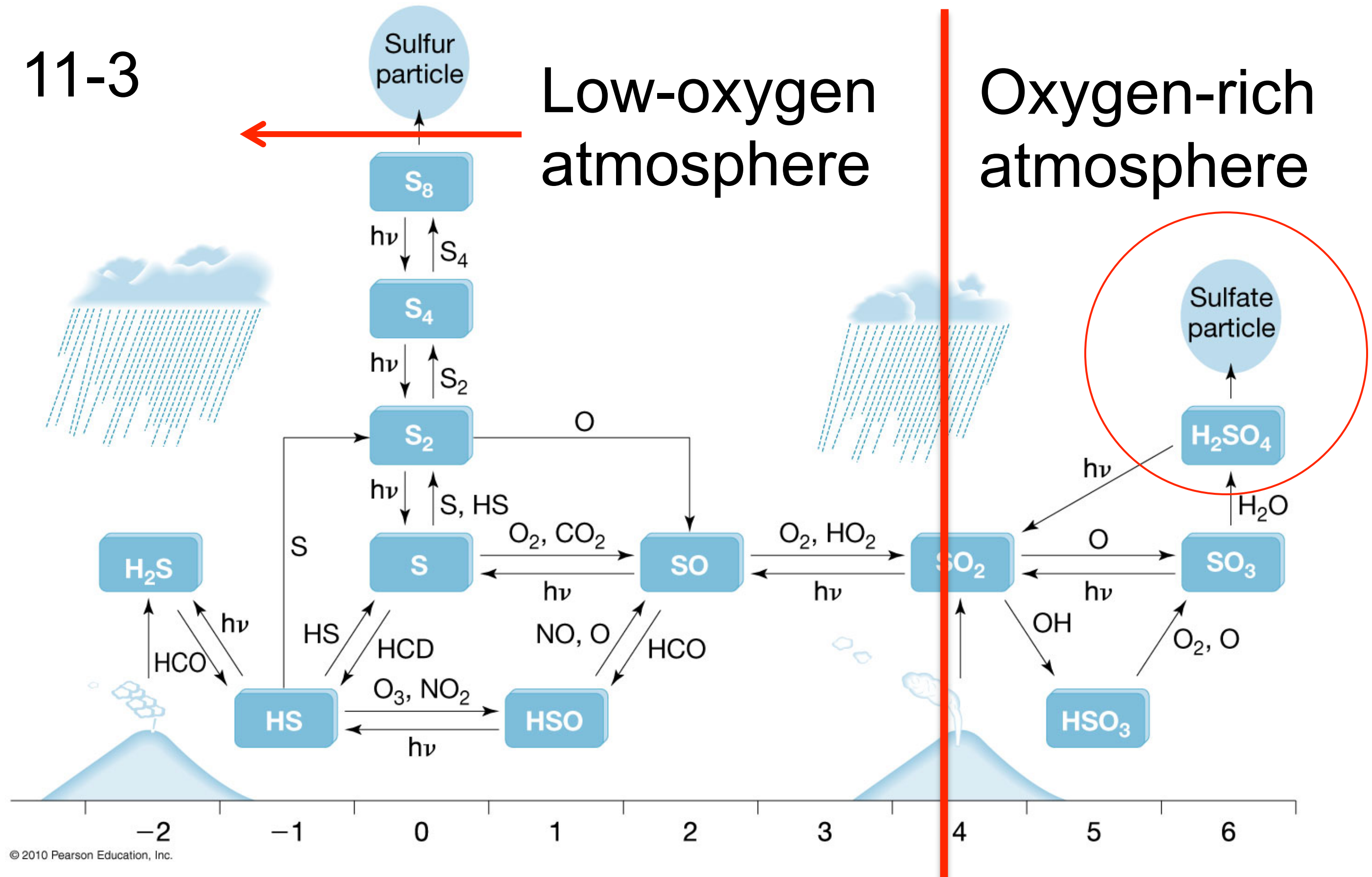
S chemistry complex before atmospheric oxygen…

Box Fig. 11-3



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No oxygen, no ozone…or…

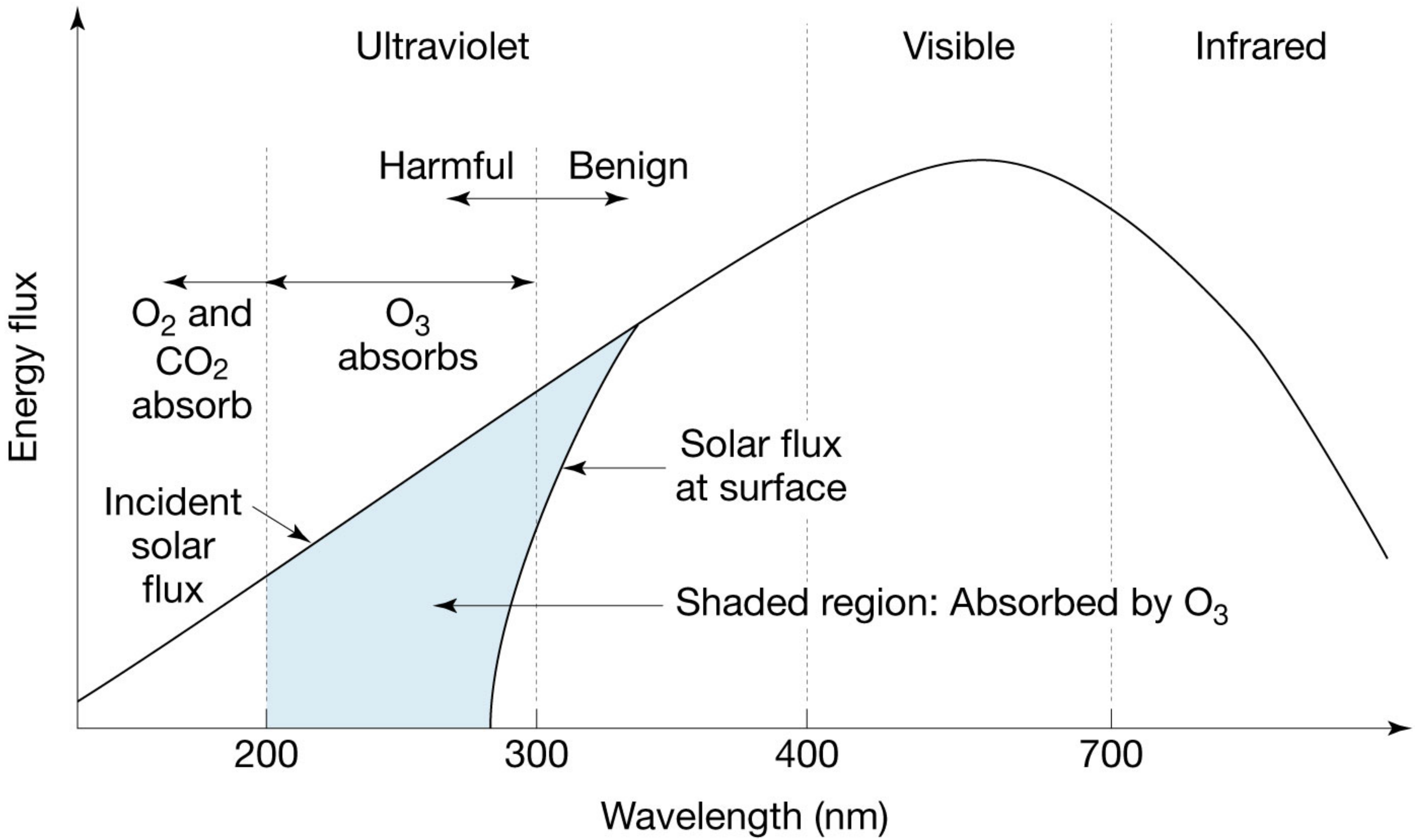

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Fig. 11-12

- Would have had enough oxygen to produce enough ozone for “bioprotection” at about 2 Ga, or 0.01 PAL

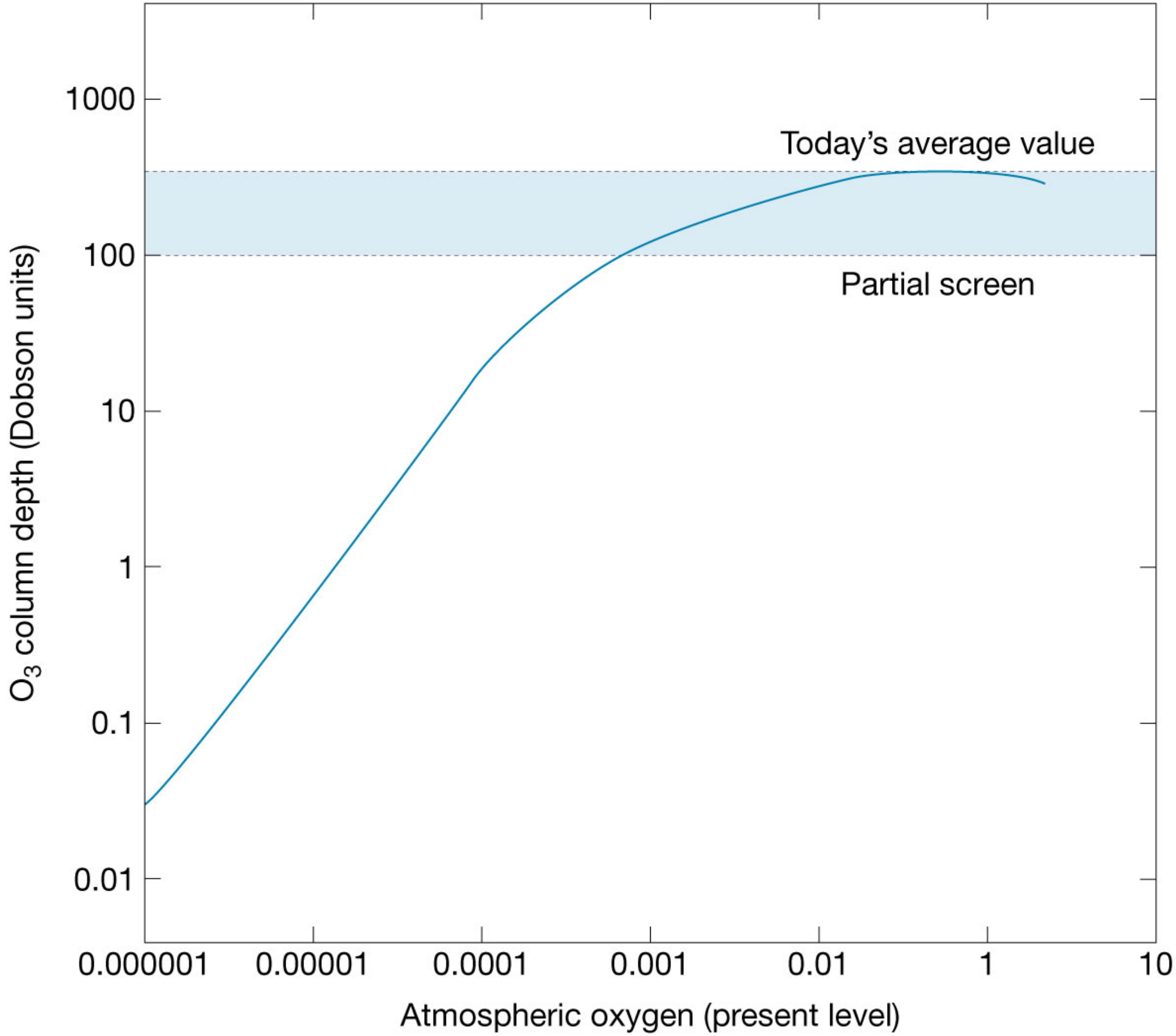

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Fig. 11-13

So…

- At 2.7 Ga, evidence for cyanobacteria (that photosynthesize and make oxygen) and eukaryotes that require it.
- Oxygen in atmosphere isn't that great until about 2.3 up to 1.9 Ga, however
- Oxygen didn't reach near-PAL levels until perhaps as late at 300 my!
- Paleontology (Ediacaran fauna, 600 my): These precambrian animals would have required at least 0.1 PAL, but there was probably not much more than this.

C isotopes in limestone get *heavy*…

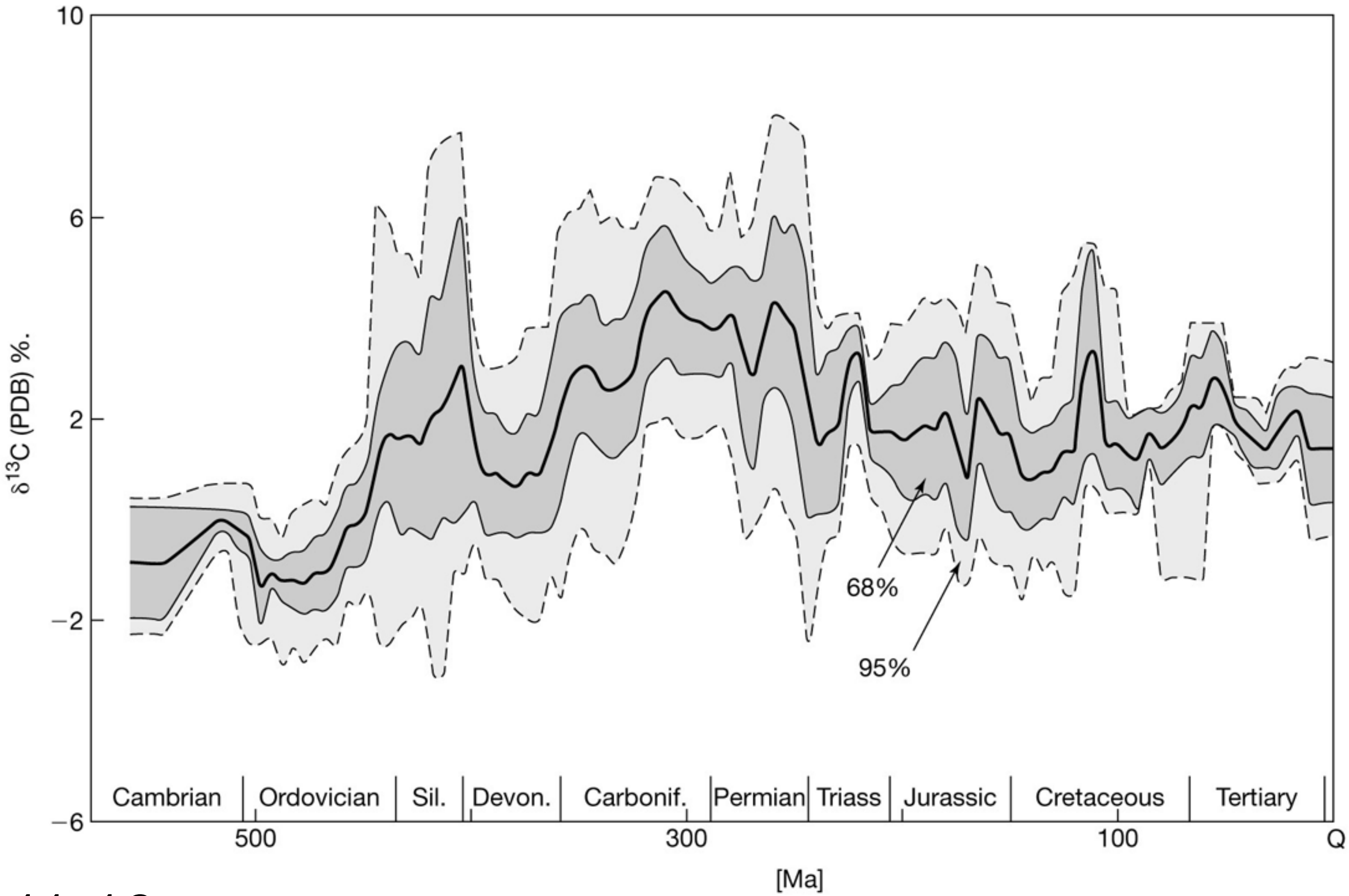

Fig. 11-16

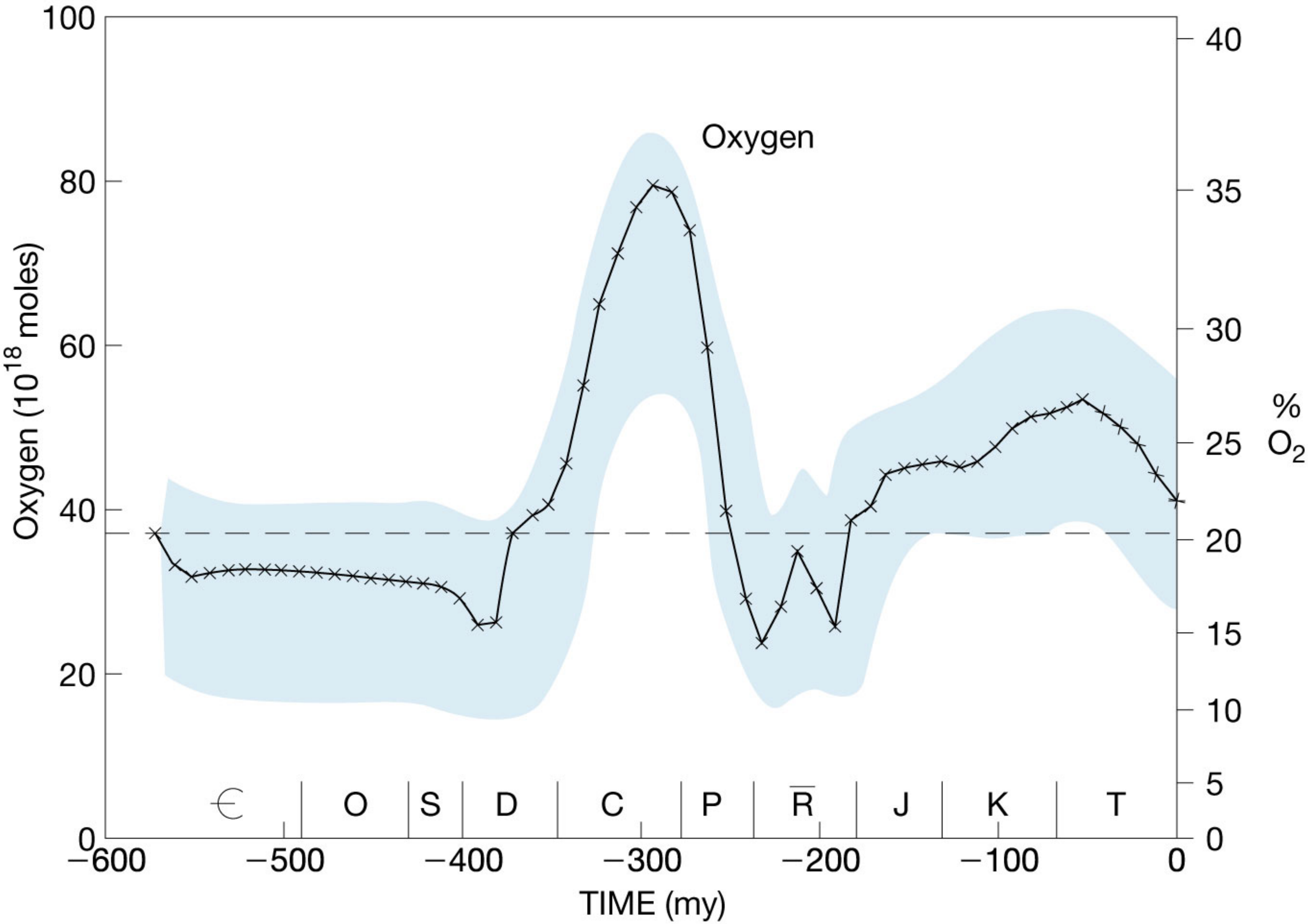

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Fig. 11-17

Other constraints on atm O_2…

- O_2 levels < 13%, no forest fires
- O_2 level > 35%, everything would burn and we wouldn't be here!

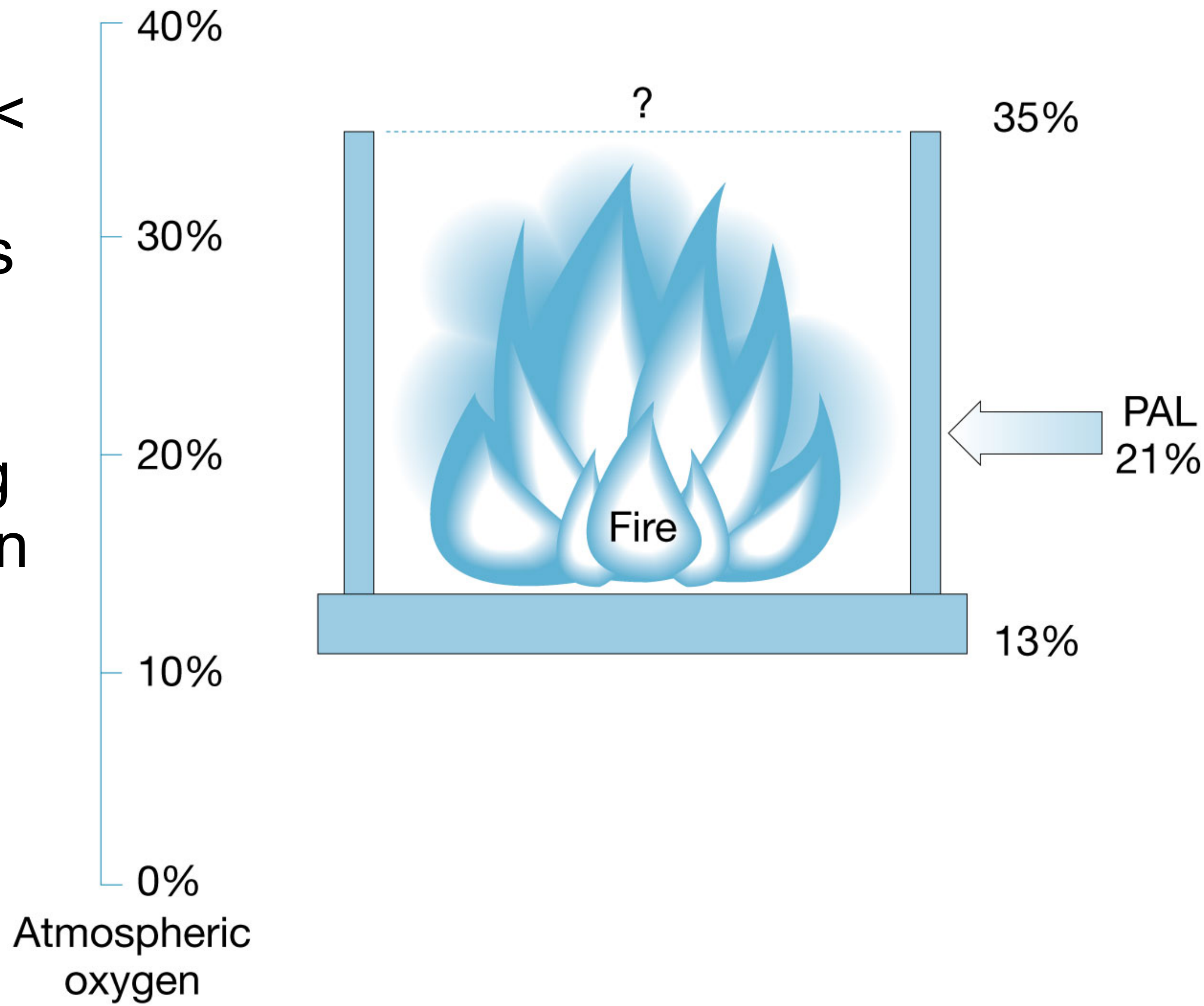

Fig. 11-19

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Do low-oxygen zones aid preservation of organic carbon and lead to increased atmospheric oxygen?

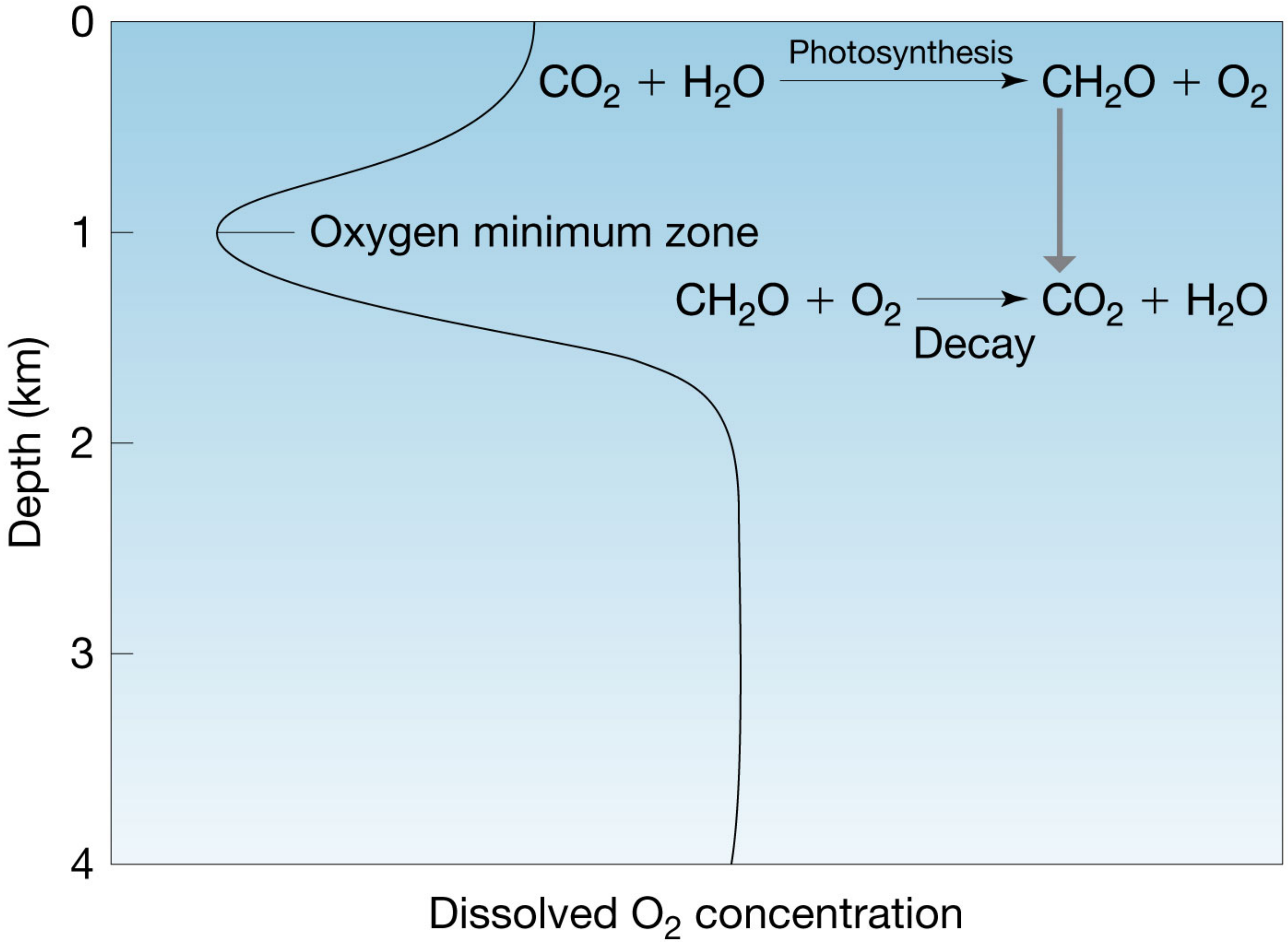

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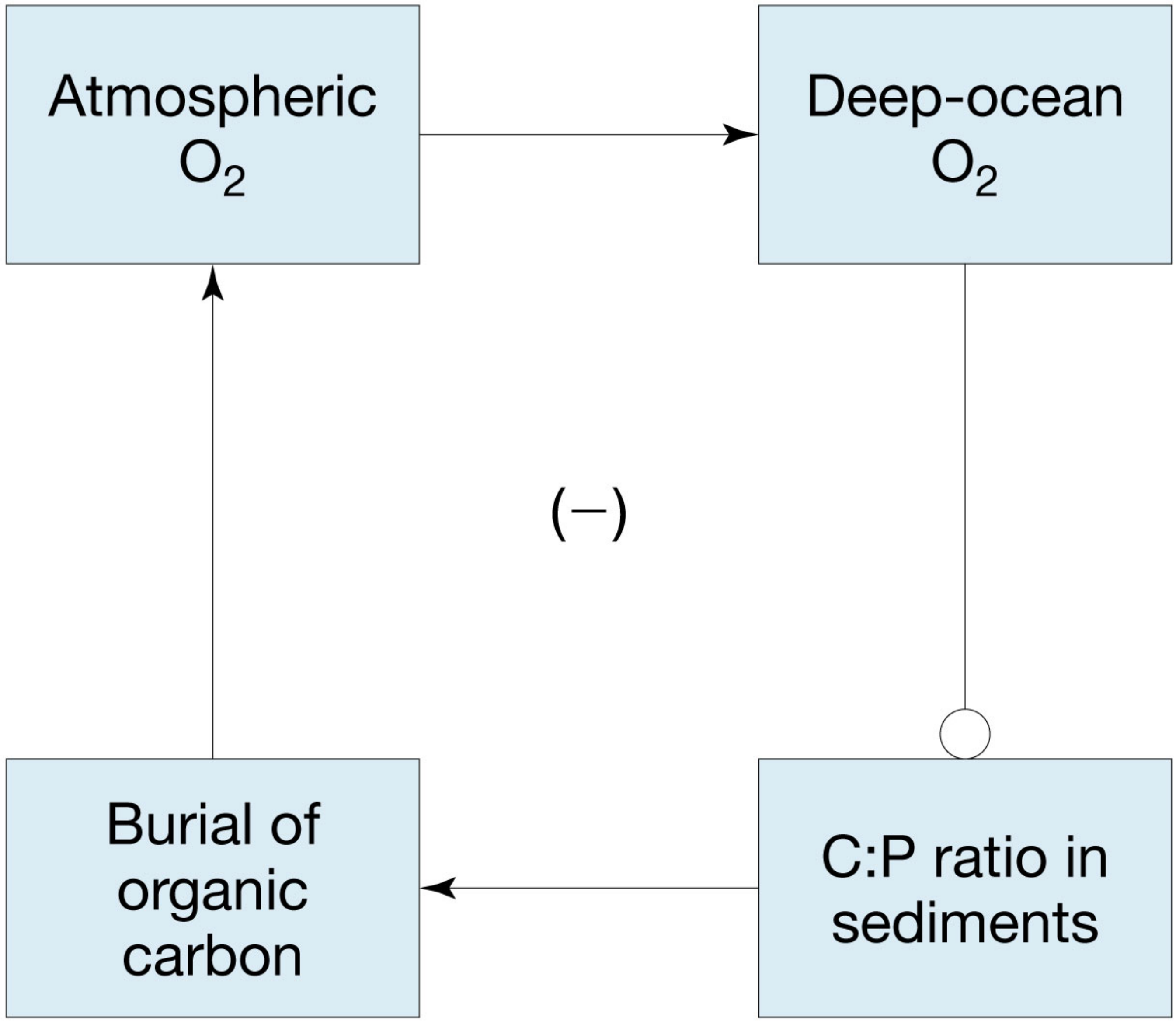
Fig. 11-20



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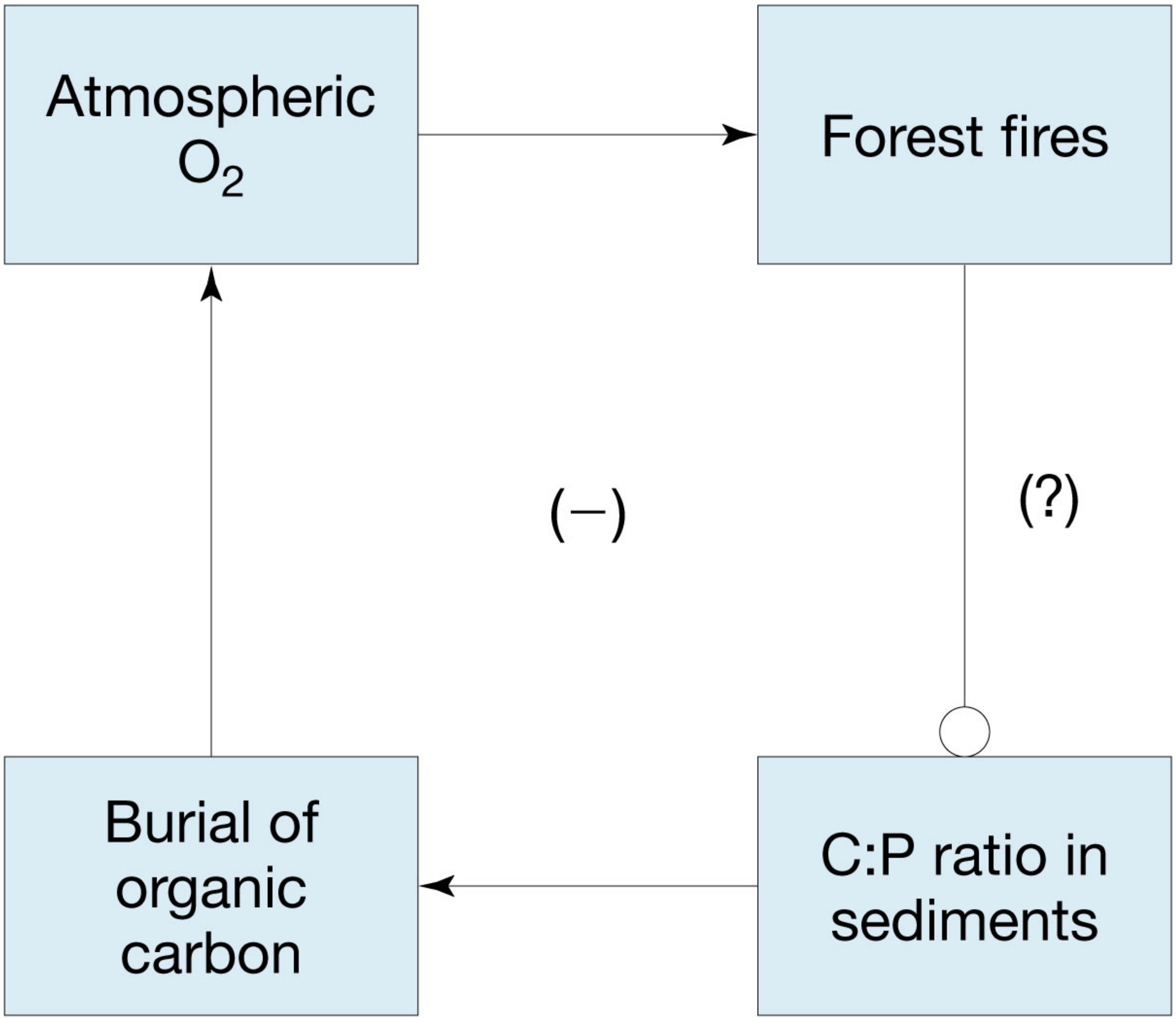

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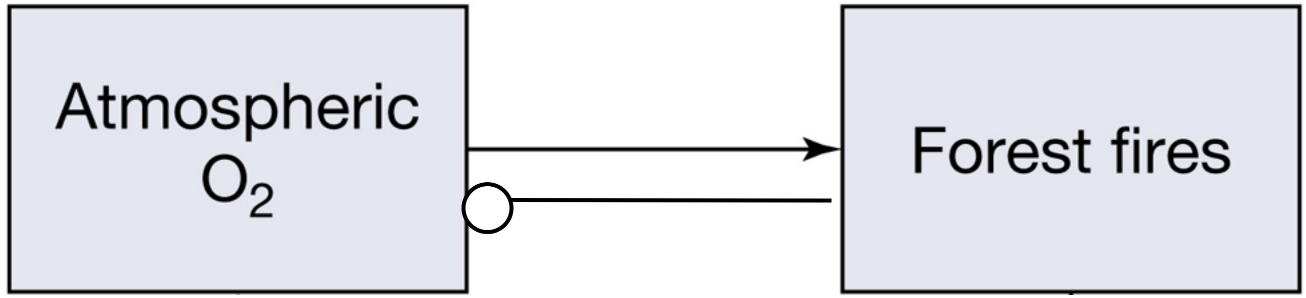

Alternatively, we can simplify this to the negative feedback Above, keeping in mind the following:

$$CO_2 + H_2O = CH_2O + O_2$$