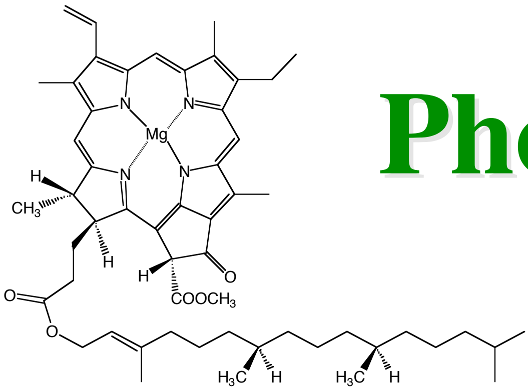
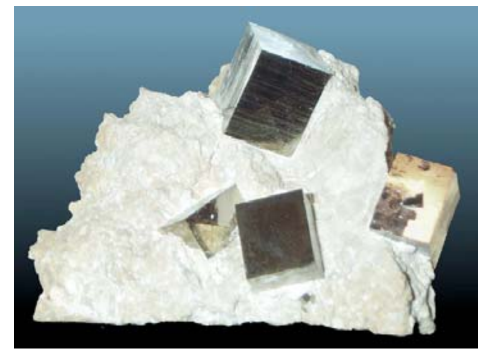


Photosynthesis & the Rise of Atmospheric O_2

$CO_2 + H_2O \longleftrightarrow CH_2O + O_2$

OCEAN 355 - Fall 2008

Lecture Notes #5



"The concentration of oxygen in the atmosphere is a kinetic balance between the rates of processes producing oxygen and the rates of processes consuming it."*

$$\frac{dO_2}{dt} = Fborg - Fworg + 15/8(Fbpy - Fwpy) - Fv$$

Organic carbon burial	Organic carbon weathering	Pyrite burial & weathering	Oxidation of mantle gases

→ We will discuss those processes & explore the geologic record for evidence of their influence on atmospheric O_2 levels through time.

→ Bearing in mind that **"A sparse geologic record, combined with uncertainties as to its interpretation, yields only a fragmentary and imprecise reading of atmospheric oxygen evolution."** *

* D.E. Canfield (2005) *Ann. Rev. Earth Planet. Sci* Vol. 33: 1-36.

Overview of The Rise of Atmospheric Oxygen

- Photosynthesis by cyanobacteria began ~3.5 Ga

  $CO_2 + H_2O \text{ ---> } CH_2O + O_2$
- No evidence for atmospheric O_2 before ~2.4 Ga
- Reduced gases in atmosphere & reduced crustal rocks consume O_2 produced during 1.2 Gyr
- Hydrogen escape irreversibly oxidizes atmosphere
- Mantle dynamics & redox evolution reduce O_2 sink over time
- Geologic & geochemical evidence for O_2 :

  Oxidized Fe & Mn mineral deposits

  Detrital uraninite & pyrite

  Paleosols

  Redbeds

  Sulfur & Iron isotopes

  Eukaryotes
- **Conclusion: Rapid rise of free O_2 2.4-2.2 Ga**

Geologic, Geocehmical & Biologic Evidence for Rise of Atmospheric Oxygen

Kalahari Manganese Member, Hotazel Fm., Manatwan Mine, S. Africa

Oxidation (+2 to +4)

Mn^{+2} → Mn^{+4} insoluble

O_2 → H_2O

Reduction (0 to -2)

© Kjell Gatedal

Caryopilite

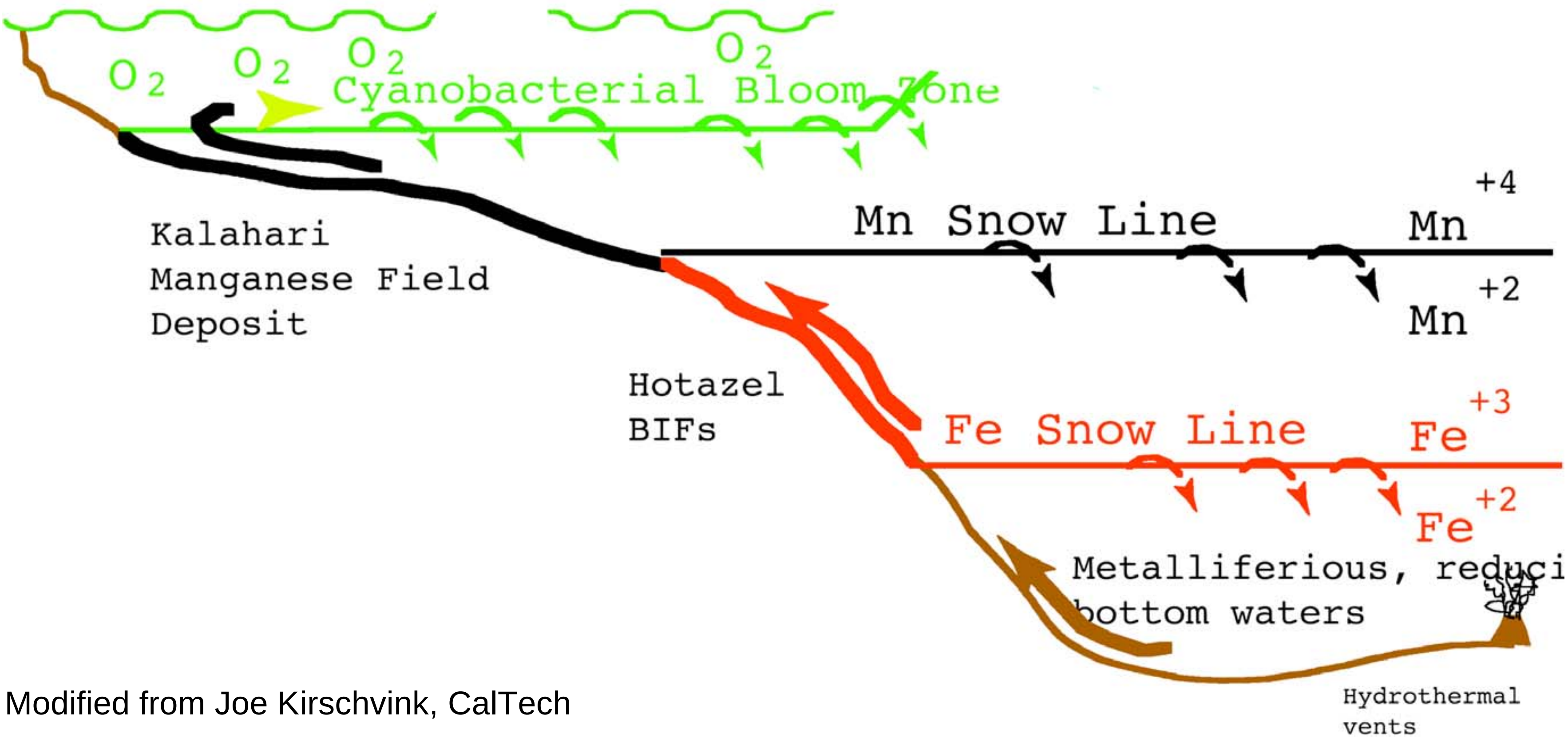
$(Mn,Mg)_3Si_2O_5(OH)$

At 2.4 Ga this is the oldest constraint on free O_2 in earth history…

Modified from Joe Kirschvink, CalTech

Cyanobacteria Bloom Causes Electrochemical Stratification in Ocean, Depositing Manganese in Upwelling Areas on Continental Shelves

- Reduced Mn(II) is dissolved in seawater
- When upwelled into water enriched with O_2 from photosynthesis it's oxidized to Mn(IV)
- Precipitates out & preserved on continental shelves



Modified from Joe Kirschvink, CalTech

Red Beds

- Hematite: Fe_2O_3

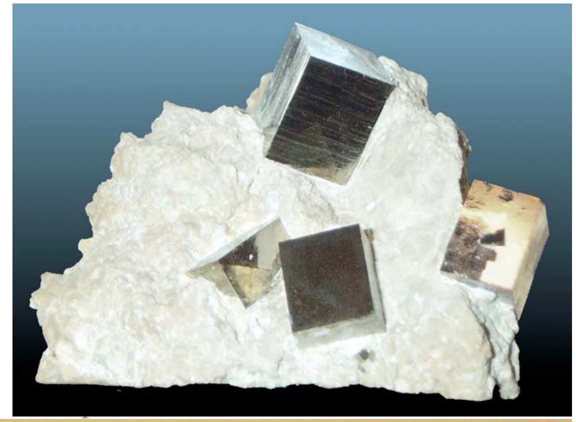
  Fe^{2+} --> Fe^{3+}

  O_2 --> H_2O
- Requires free O_2 to oxidize Fe(II) & produce (red) iron oxides

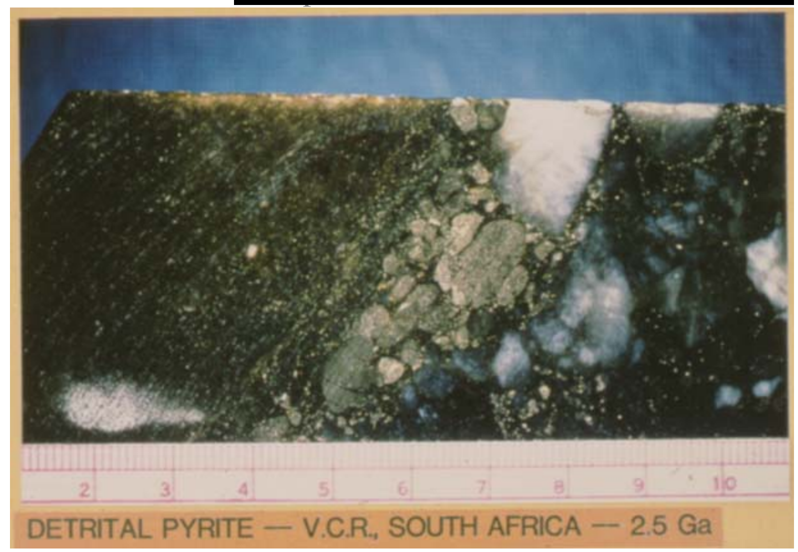
- Oldest red beds ~ 2.2 Ga
- Sedimentary rock
- Reddish, sandy sediment deposited by rivers &/or windblown dust.

Photos: Kansas Geological Survey

Detrital Uraninite & Pyrite



- Uraninite: **UO_2**
- Reduced U(IV)
- Highly radioactive
- Important ore of uranium & radium.



- Pyrite: **FeS_2**
- Reduced Fe(II)

- > 2.2 Ga, these ***reduced*** minerals existed as ***detrital*** minerals in Archean sedimentary rocks.
- In other words, they survived weathering process intact & were transported as solid particles. (I.e., not dissolved).
- Preservation of UO_2 and FeS_2 requires ***anoxia***. They are unstable in the presence of free O_2, which oxidizes & dissolves them.

Paleosols

("Ancient Soils")

- > 2.2 Ga: Fe-deficient
- Soluble Fe(II) removed by groundwater

- < 2.2 Ga: Fe-rich
- Fe(III)-oxides insoluble

<u>H. Holland (Harvard)</u>

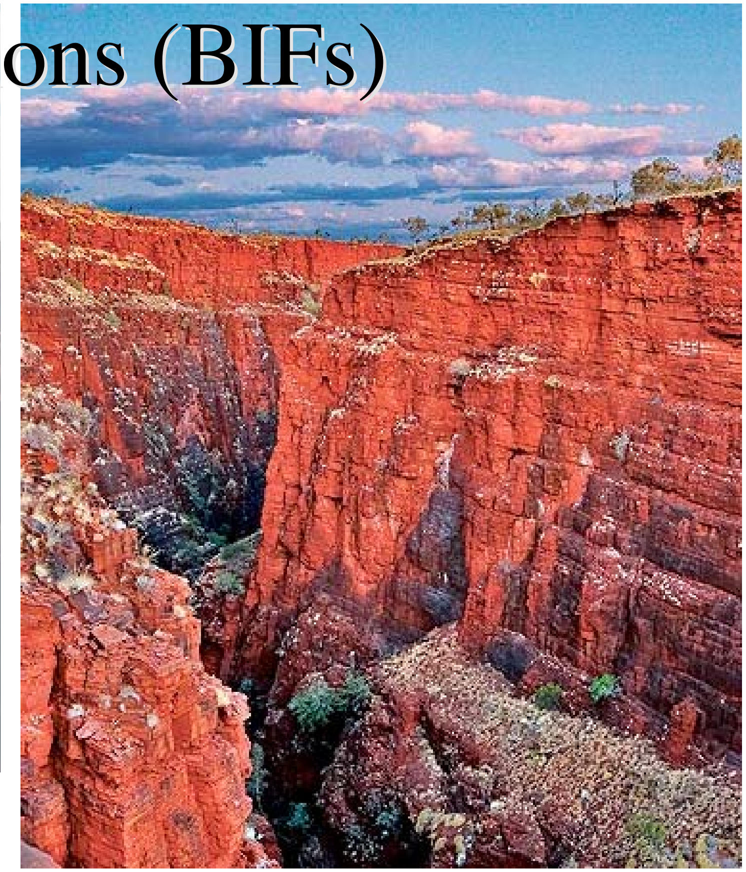
>2.2 Ga: $O_2 < 0.01$ PAL

<1.9 Ga: $O_2 > 0.15$ PAL

- Attempt to develop quantitative indicator of O_2 based on Ref Beds

Kump et al. (1999) *The Earth System,* Prentice Hall.
http://www.gly.uga.edu/railsback/FieldImages.html

Banded Iron Formations (BIFs)



• Most BIFs > 1.9 Ga; indicates free O_2 existed by then

• 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) :

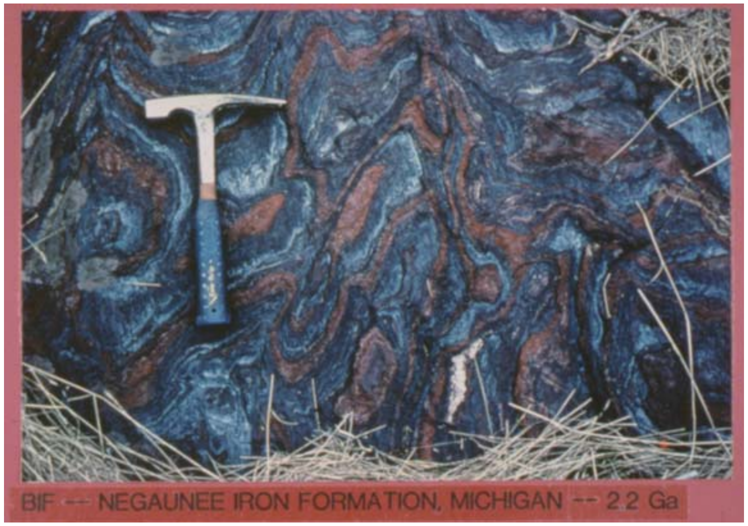
Fe^{2+} --> Fe^{3+}

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

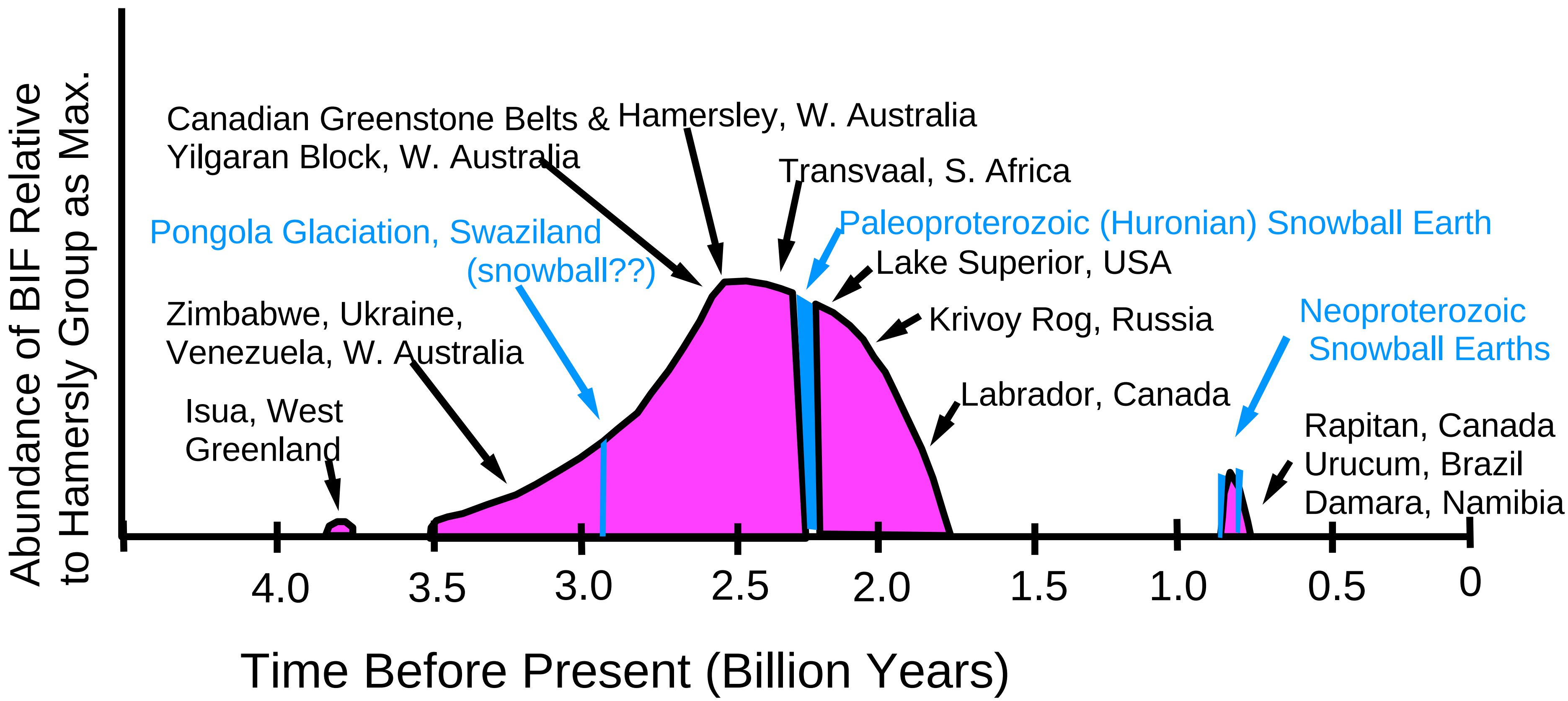
Banded Iron Stones



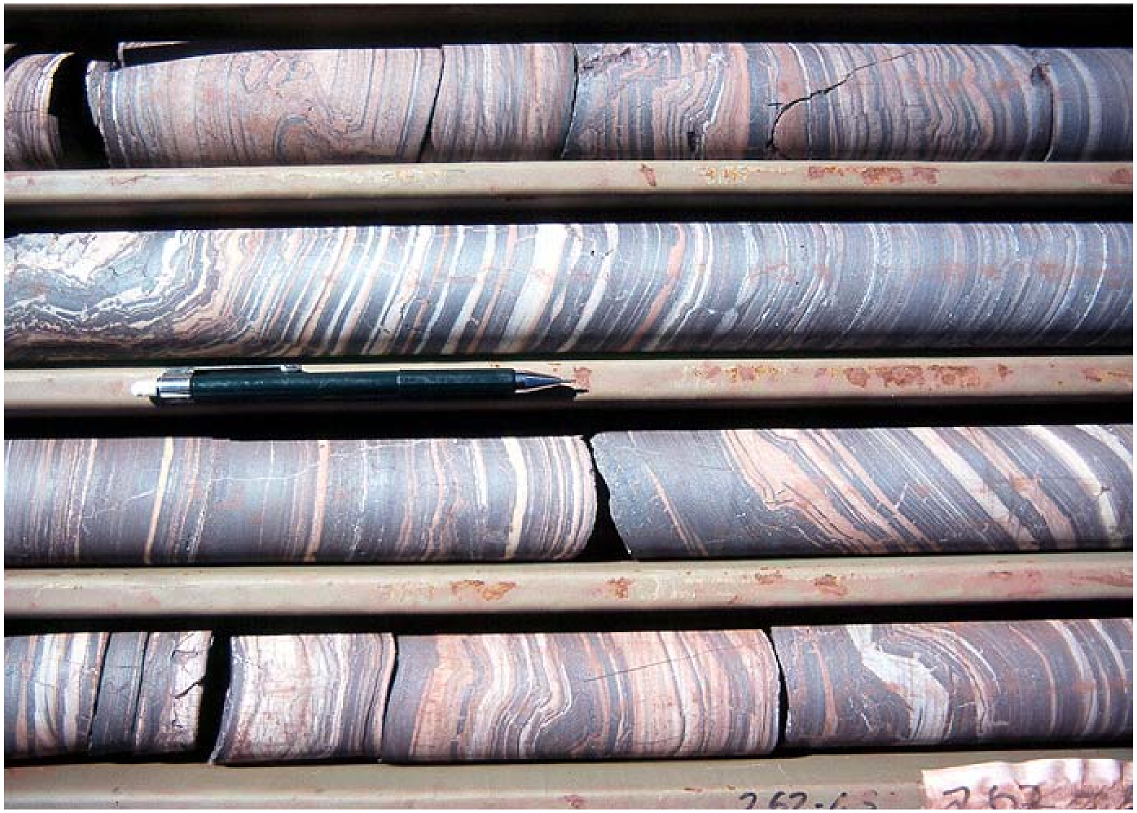
http://www.amnh.org/education/resources/rfl/web/meteoriteguide/images/bandediron_lg.jpg, http://en.wikipedia.org/wiki/Image:Black-band_ironstone_%28aka%29.jpg#file; http://www.cartage.org.lb/en/themes/sciences/Paleontology/FossilsAndFossilisation/FossilsandTime/mich03.gif

Precambrian Banded Iron Formations (BIFs)

(Adapted from Klein & Beukes, 1992)



Courtesy Joe Kirschvink, CalTech



How did BIFs form?

•A big open question in geology!

<u>One favored scenario</u>:

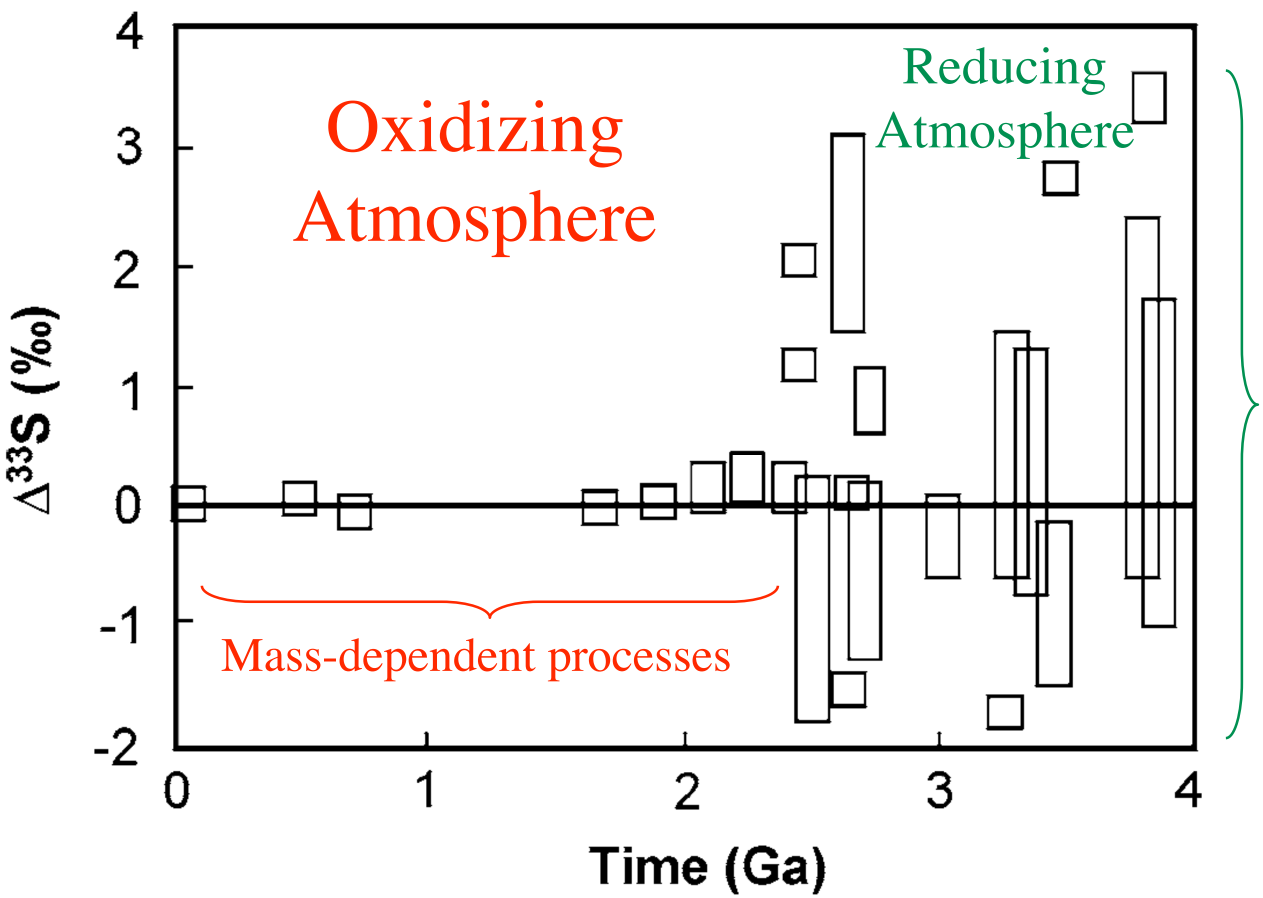
- Anoxic deep ocean containing dissolved Fe(II)
- Seasonal upwelling brings Fe(II) to the surface where it is oxidized to Fe(III) by O_2 produced by cyanobacteria/algae.
- Insoluble Fe(III) precipitates out of seawater
- SiO_2 precipitated by algae during non-upwelling season

Image: http://web.uct.ac.za/depts/geolsci/dlr/hons1999/sishen2.jpg

Geochemical Evidence for Atmospheric Oxygen

Sulfur Isotopic Evidence for O_2 After 2.3 Ga

- S cycle > 2.3 Ga controlled by **mass-independent fractionation** of S isotopes



- S has 4 stable isotopes: ^{32}S-95.02%, ^{33}S-0.75%, ^{34}S-4.21%, ^{36}S-0.02%

- Only known source of mass-independent fractionation of S isotopes is gas phase photolysis of SO_2 (from volcanoes) w/ UV light in near absence of O_2

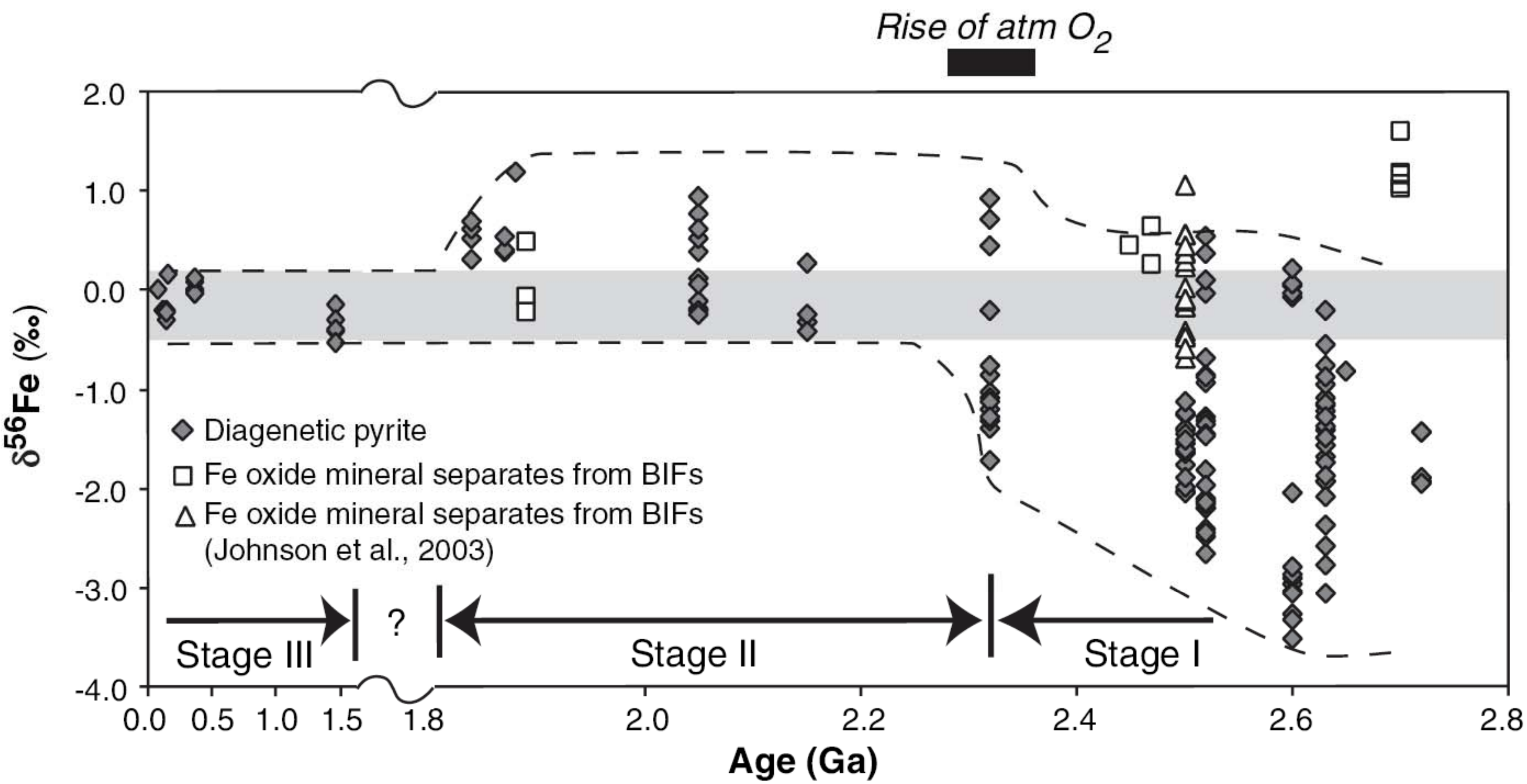
- During biological, thermodynamic & kinetic processes S isotopes are fractionated in a predictable manner according to mass differences (i.e., $\Delta^{33}S=0$)

-measured on sulfates & sulfides

$\Delta^{33}S=\delta^{33}S_{meas}-\delta^{33}S_{exp}= \delta^{33}S_{meas} -0.518*\delta^{34}S_{meas}$

Farquhar & Wing (2003) *Earth Planet. Sci. Lett.* **213** 1-13
in Canfield (2005) *Ann. Rev. Earth Planet. Sci* Vol. 33: 1-36.

Iron Isotope Contraints on Ocean Redox State

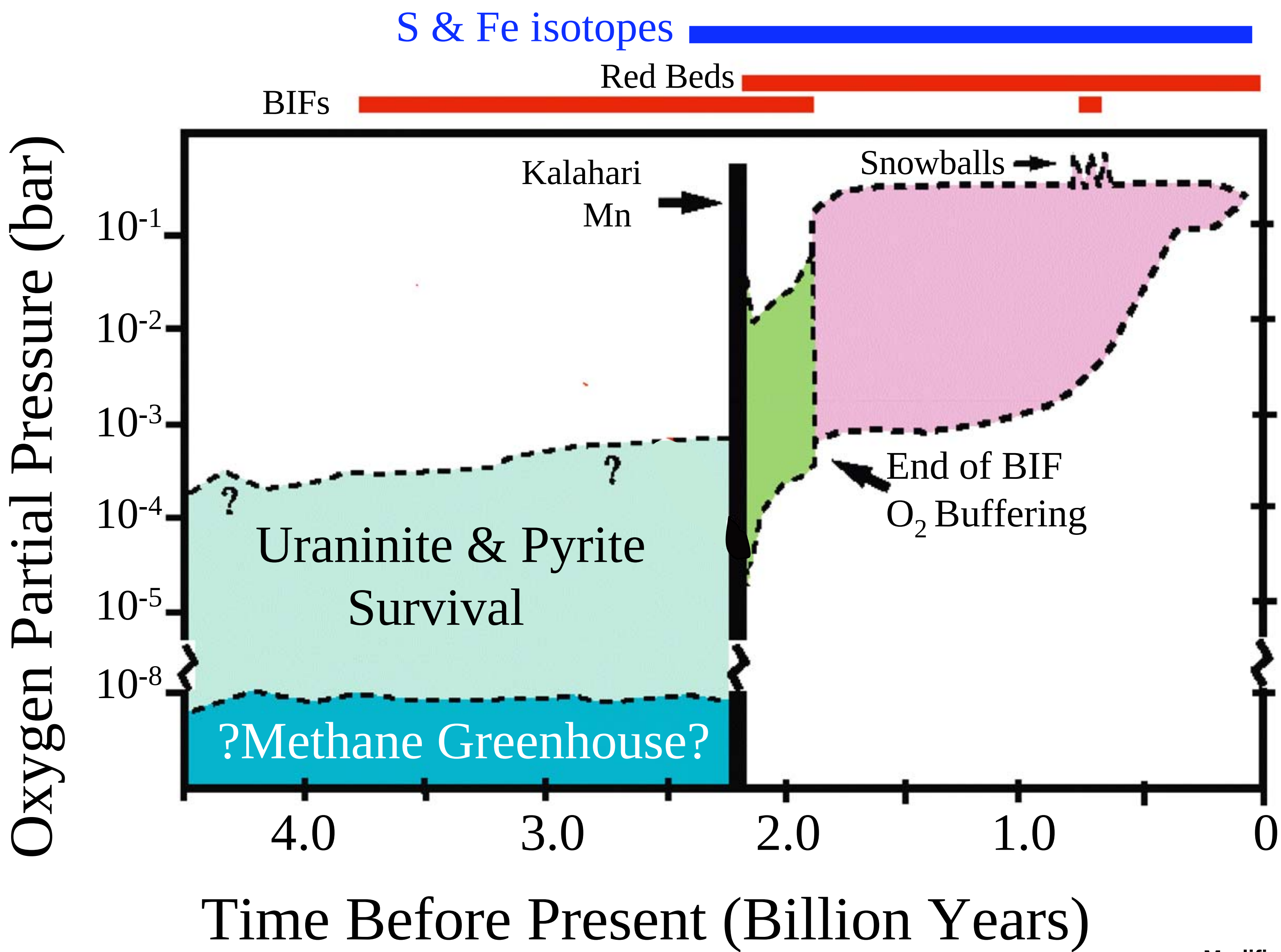


- An oxygenated ocean must accompany an oxygenated atmosphere
- Iron isotope fractionation occurs during Fe mineral formation, primarily oxides & sulfides
- Increase in δ^{56}Fe after 2.35 Ga consistent with well oxygenated (surface) ocean & rapid oxidation of Fe(II) to Fe_xO_y

$\delta^{56}Fe=[(^{56}Fe/^{54}Fe)_{smpl}/(^{56}Fe/^{54}Fe)_{std} -1]*1000$

Rouxel et al. (2005) *Science* Vol. 307: 1088-1091

History of Atmospheric Oxygen on Earth



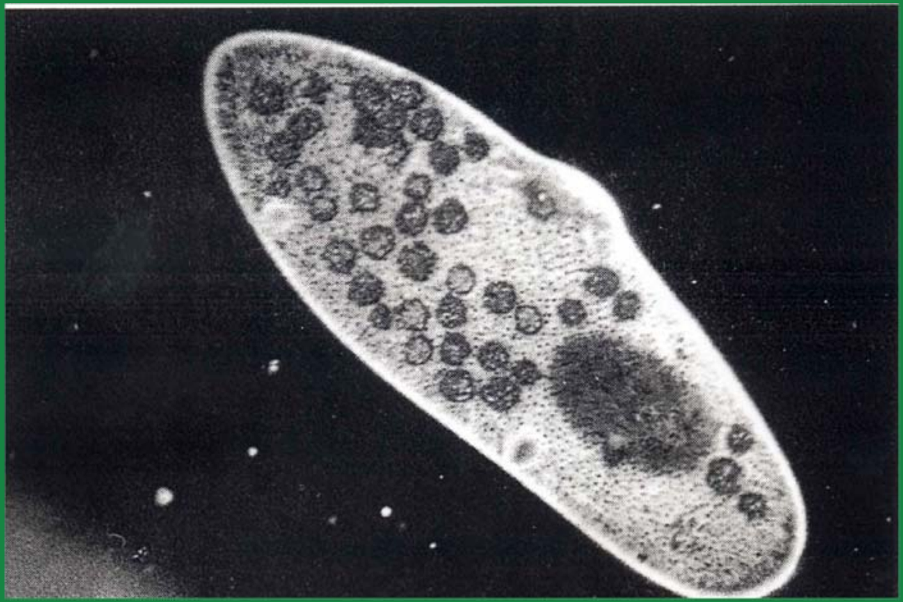
Modified from Joe Kirschvink, CalTech

Biotic Evidence for Atmospheric Oxygen

Evolution of Eukaryotes

• Eukaryotes require free O_2 in excess of 0.1% PAL for respiration

• Prokaryote



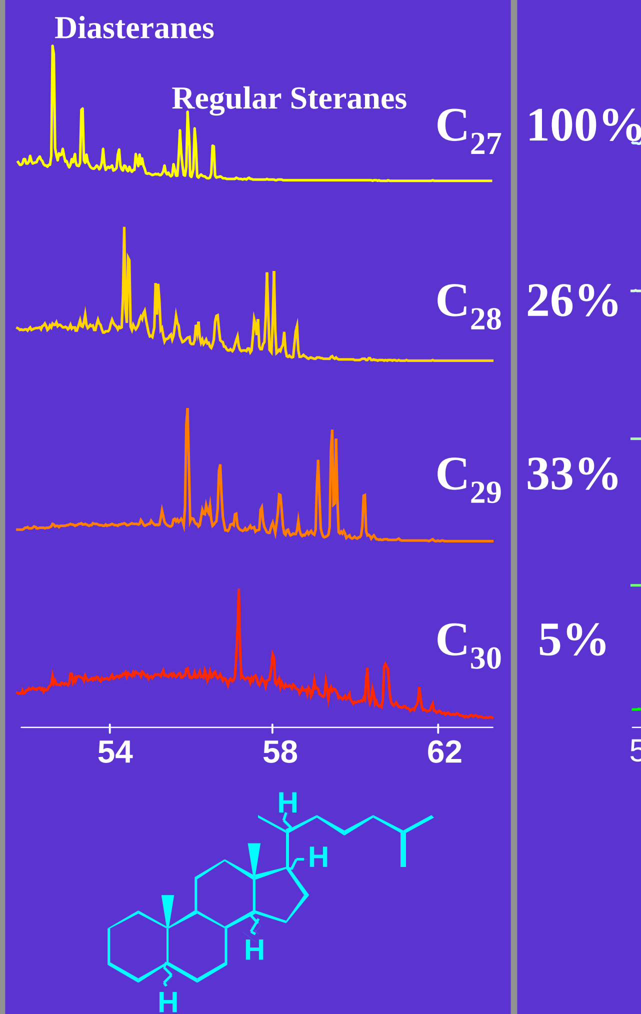
• Eukaryote

Kump et al. (1999)

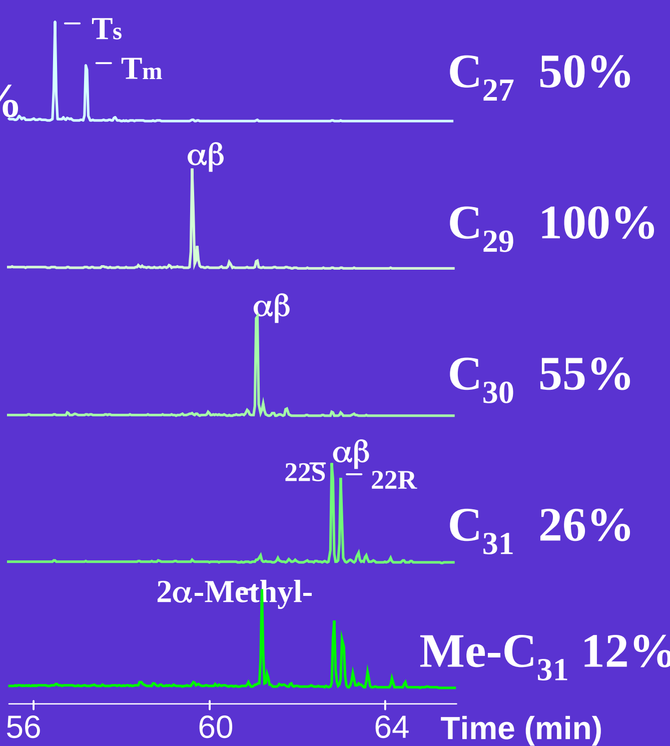
2.7 Ga Cyanobacterial (Prokaryote) & Eukaryote Biomarkers

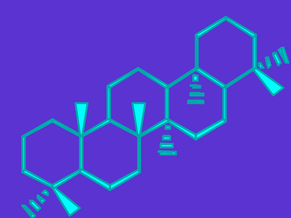
- Diagenetic products of **Hopanols** & **Sterols**

Steranes



Hopanes





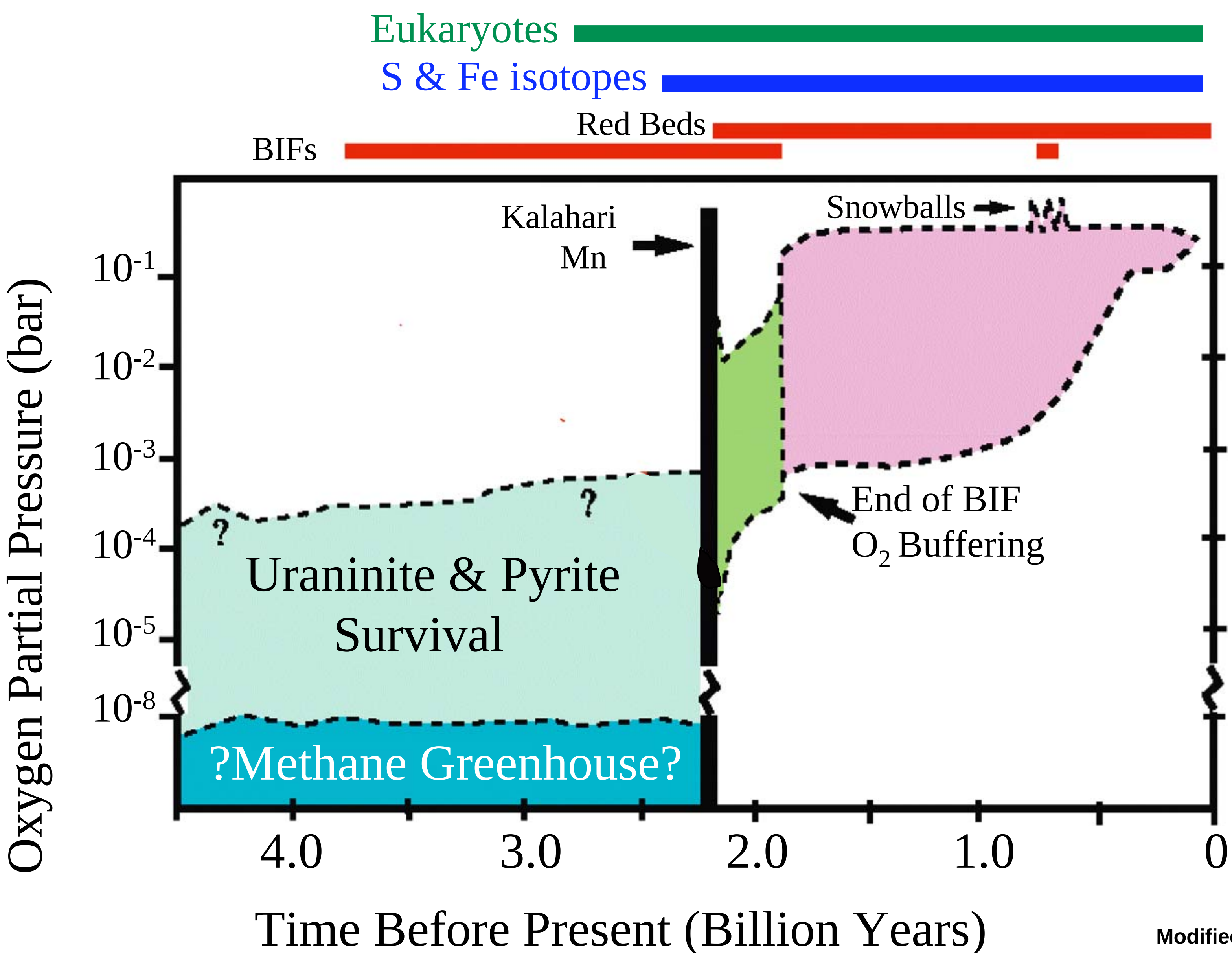
Brocks, et al. (1999)

Multicellular Algal Fossils--2.1 Ga

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

Stanley (1999)

History of Atmospheric Oxygen on Earth



Modified from Joe Kirschvink, CalTech

Sources of Oxygen to the Atmosphere

General Photosynthetic Equation

Photosynthesis

$$6CO_2 + 6H_2O + \text{Solar Energy} \longrightarrow C_6H_{12}O_6 + 6O_2$$

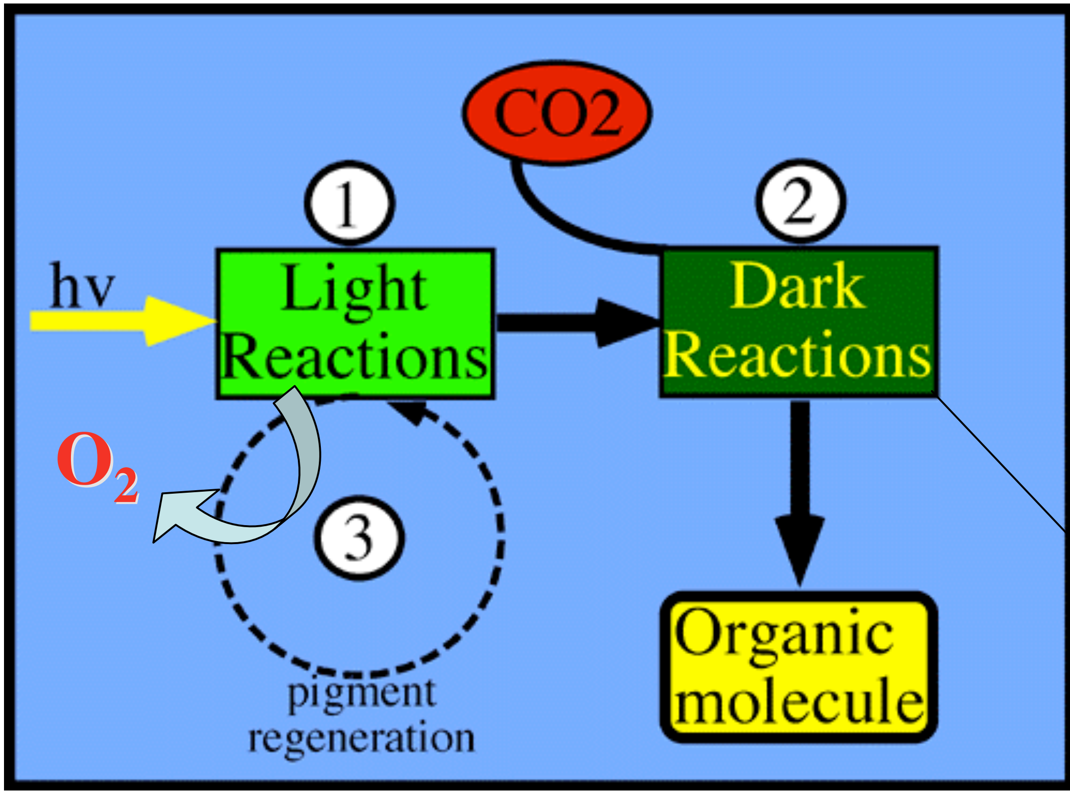
ie. algae

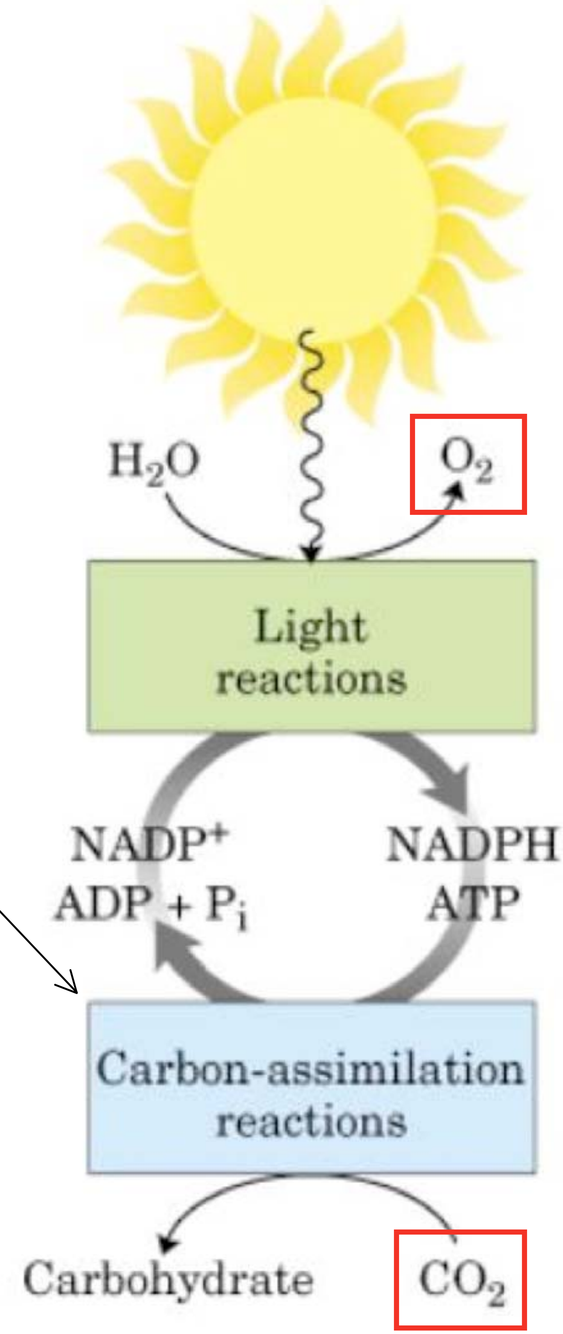
Carbohydrates + Oxygen as products

1 mole of CO_2 consumed
as 1 mole of O_2 produced

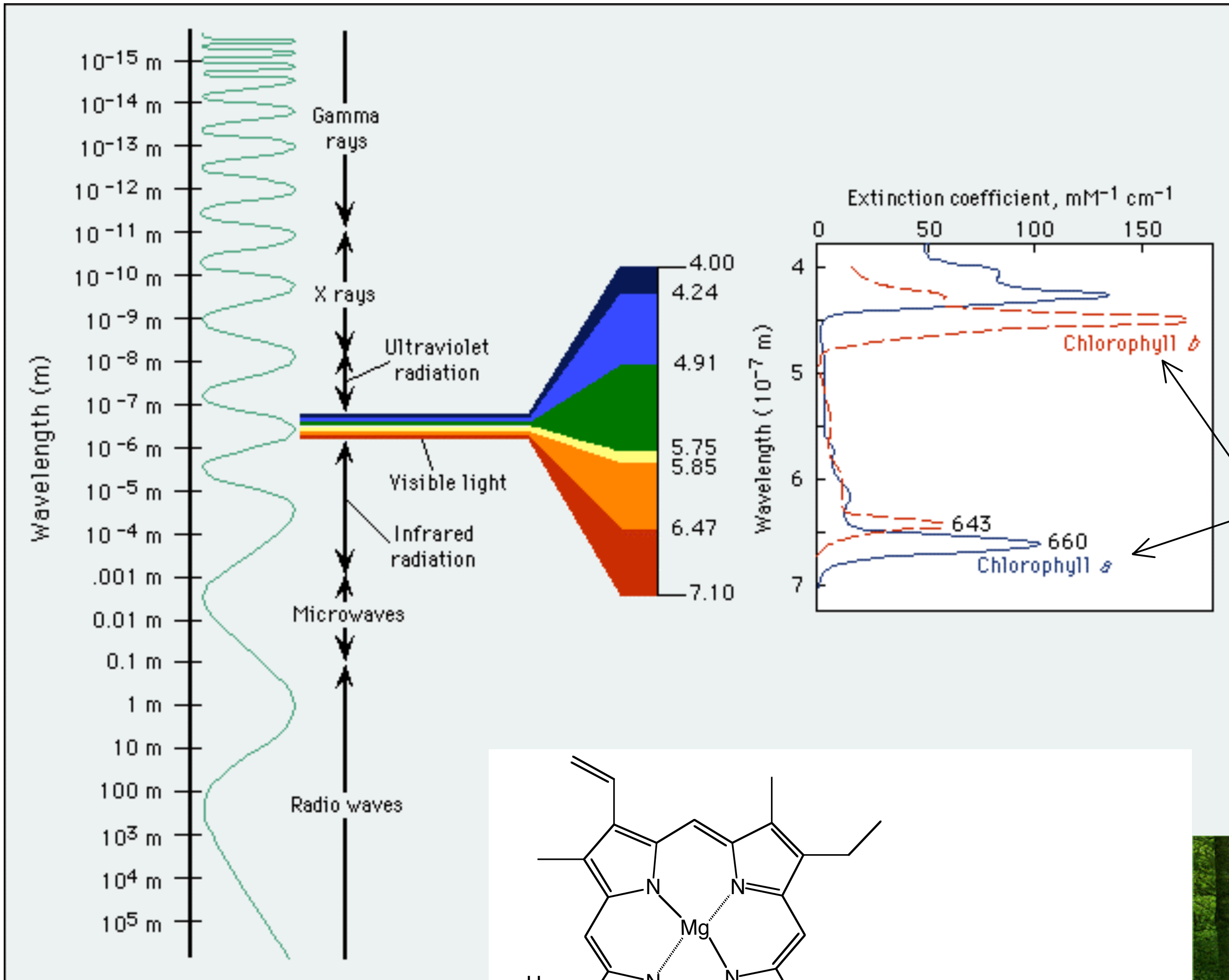
→ Controls surface water ocean chemistry of inorganic carbon and nutrients and, when combined with respiration, controls atmospheric CO_2 concentration.

3 Steps of Photosynthesis





http://courses.cm.utexas.edu/emarcotte/ch339k/fall2005/Lecture-Ch19-3/Slide2.JPG



Light Absorption by Chlorophyll

- Chlorophylls absorb strongly in the blue & red portion of the visible spectrum of light, making plants appear green

Chlorophyll *a*

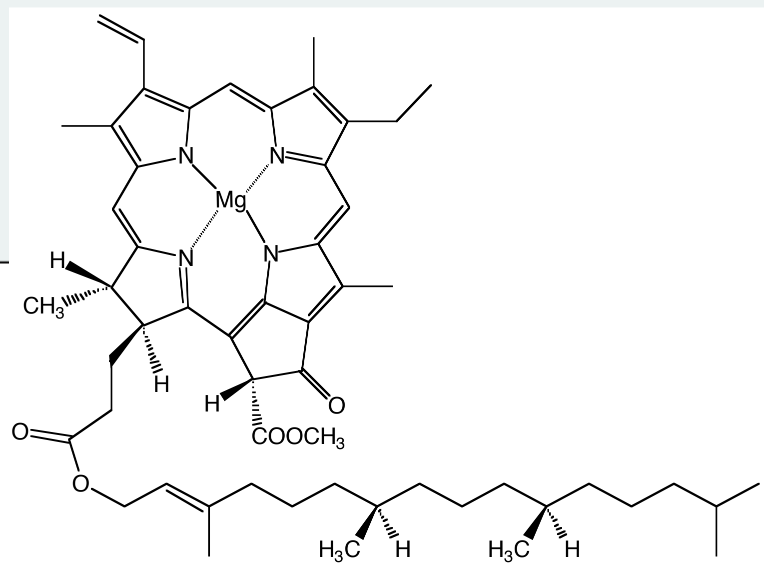
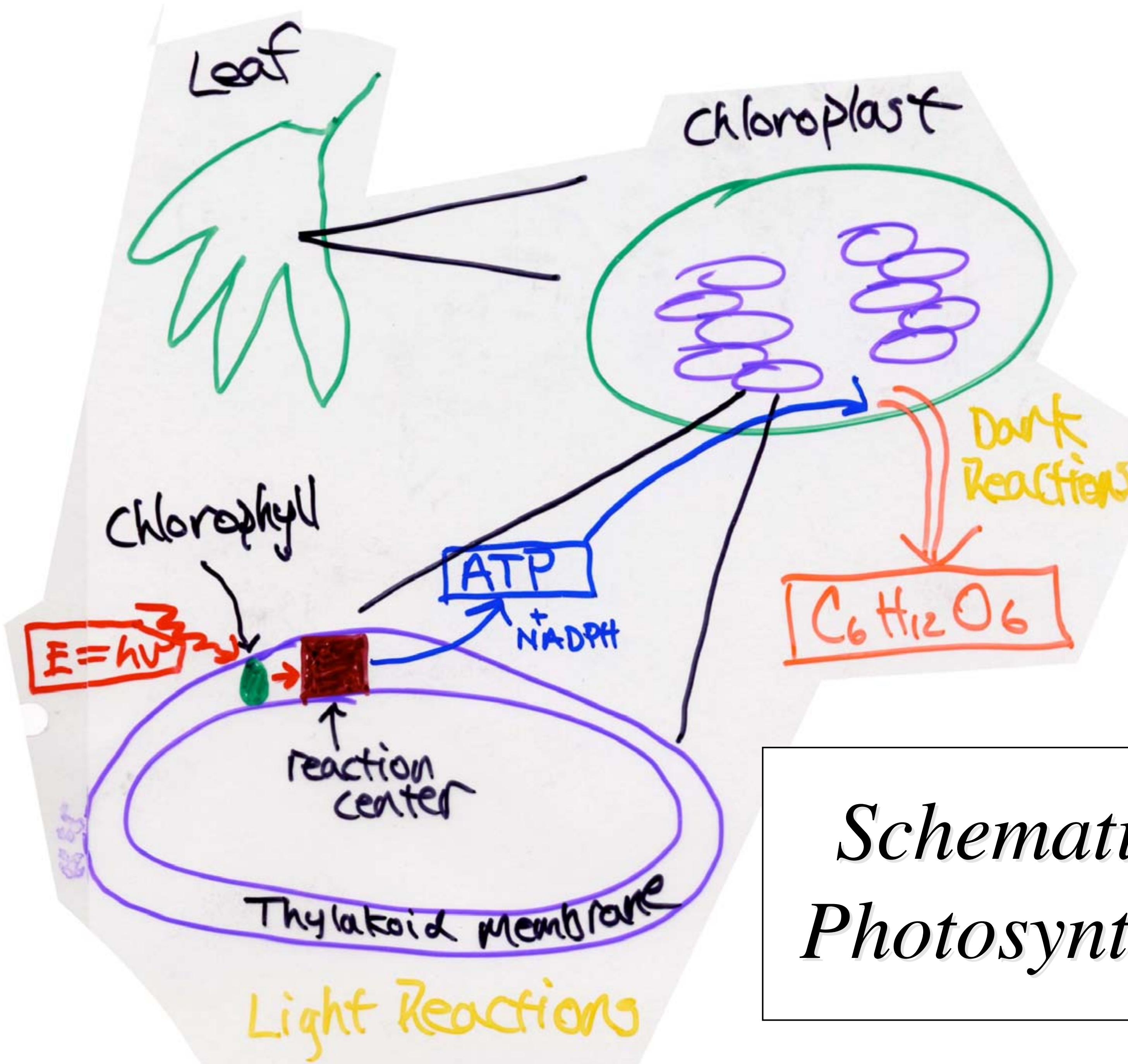


Image from http://chapmannd.org/images/Healing_Green_Pat.gif



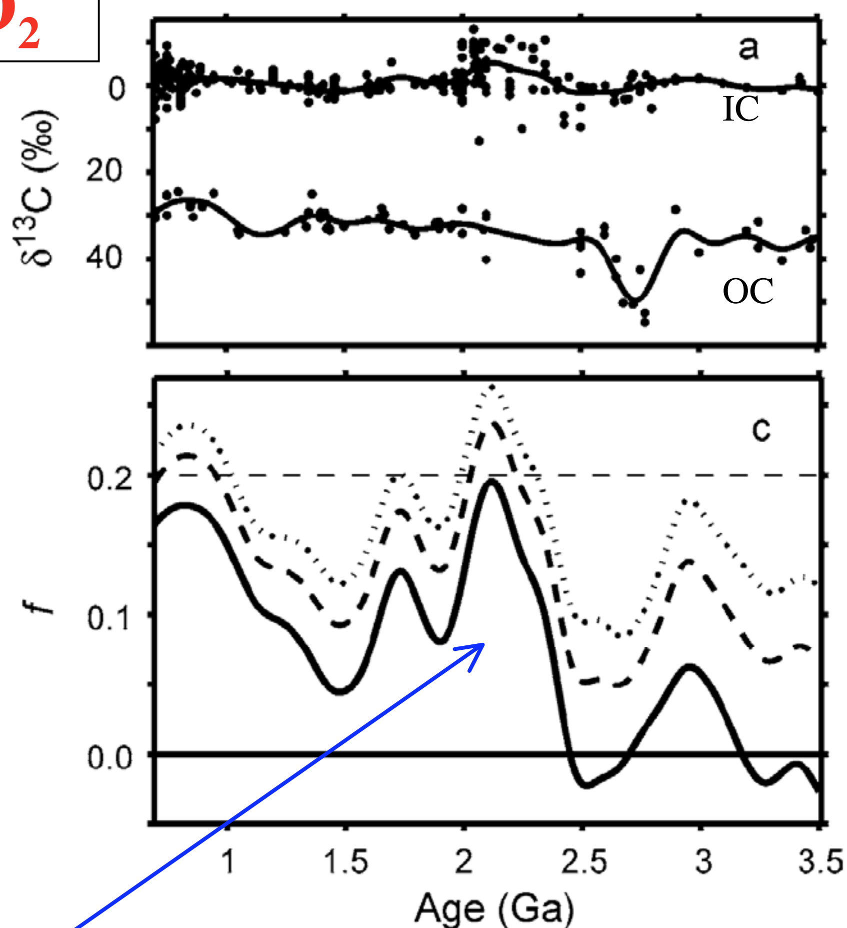
Schematic of Photosynthesis

$C_{organic}$ Burial Allows O_2 to Remain in Atmosphere/Ocean

$$CO_2 + H_2O \dashrightarrow CH_2O + O_2$$

• Massive C_{org} burial

• Rapid Oxygen production



• *f* is the fraction of total carbon buried that is organic

Canfield (2005) *Ann. Rev. Earth Planet. Sci* Vol. 33: 1-36.

http://thescarletbeard.com/Indonesian_coal_mine.jpg
http://www.theonlyoblong.com/oil_field/images/postcards/robinson/keeley_oil_well_rob.jpg

Pyrite Burial: Removal of Reduced Fe(II) & S(-II) (I.e., electrons) from Ocean / Atmosphere Leaves it Oxidized (with fewer electrons)

$CO_2 + H_2O$ ---> $\mathbf{CH_2O + O_2}$

$2H^+ + SO_4^{2-} + 2(\mathbf{CH_2O})$ --> $2CO_2 + H_2S + 2H_2O$
(sulfate reduction)

$FeS + H_2S$ --> $\mathbf{FeS_2} + 2H^+ + 2e^-$

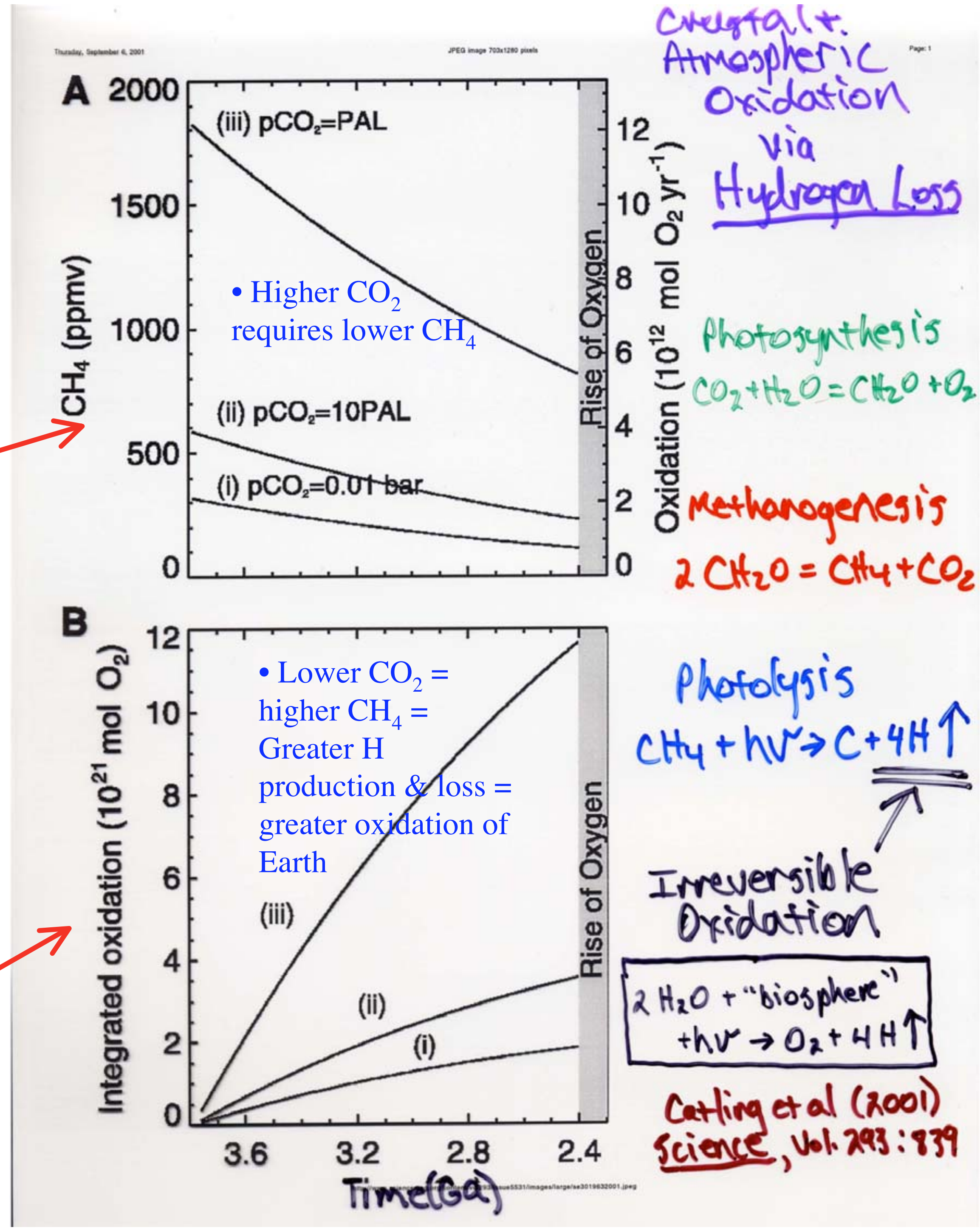
Fe(III) --> Fe(II), S(+VI)O_4^{2-} --> $\mathbf{H_2S}$(-II) (reductions)
H_2O --> $\mathbf{O_2}$, $\mathbf{CH_2O}$ --> CO_2 (oxidations)

Crustal & Atmospheric Oxidation via *Hydrogen Escape*

- H_2 is only molecule light enough to escape Earth's gravity

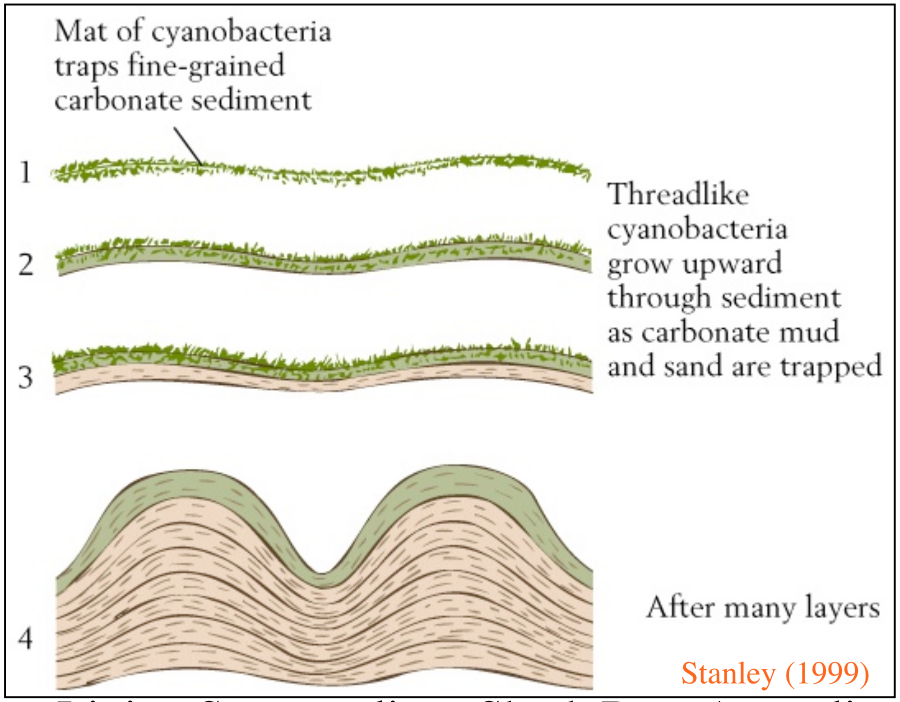
• Calculated mixing ratio of CH_4 needed to maintain surface T of 290 K.

• Integrated oxidation of Earth by H escape for scenarios i-iii.

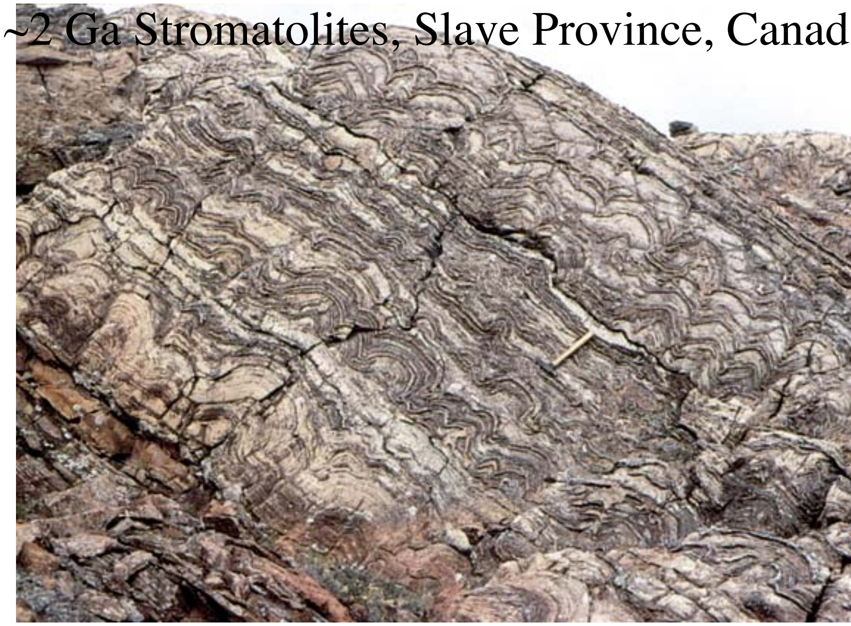


We previously established (i.e., Origin of Life lectures) that the Photosynthetic Machinery has been around for ~3.5 Gyr…

Stromatolites: 3.5 Ga - Present

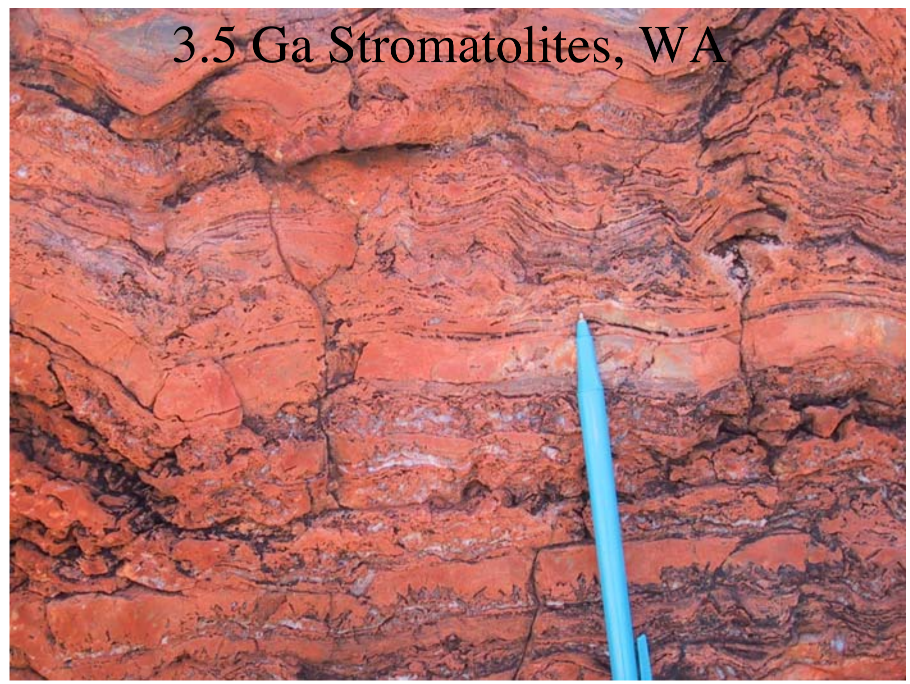


~2 Ga Stromatolites, Slave Province, Canada

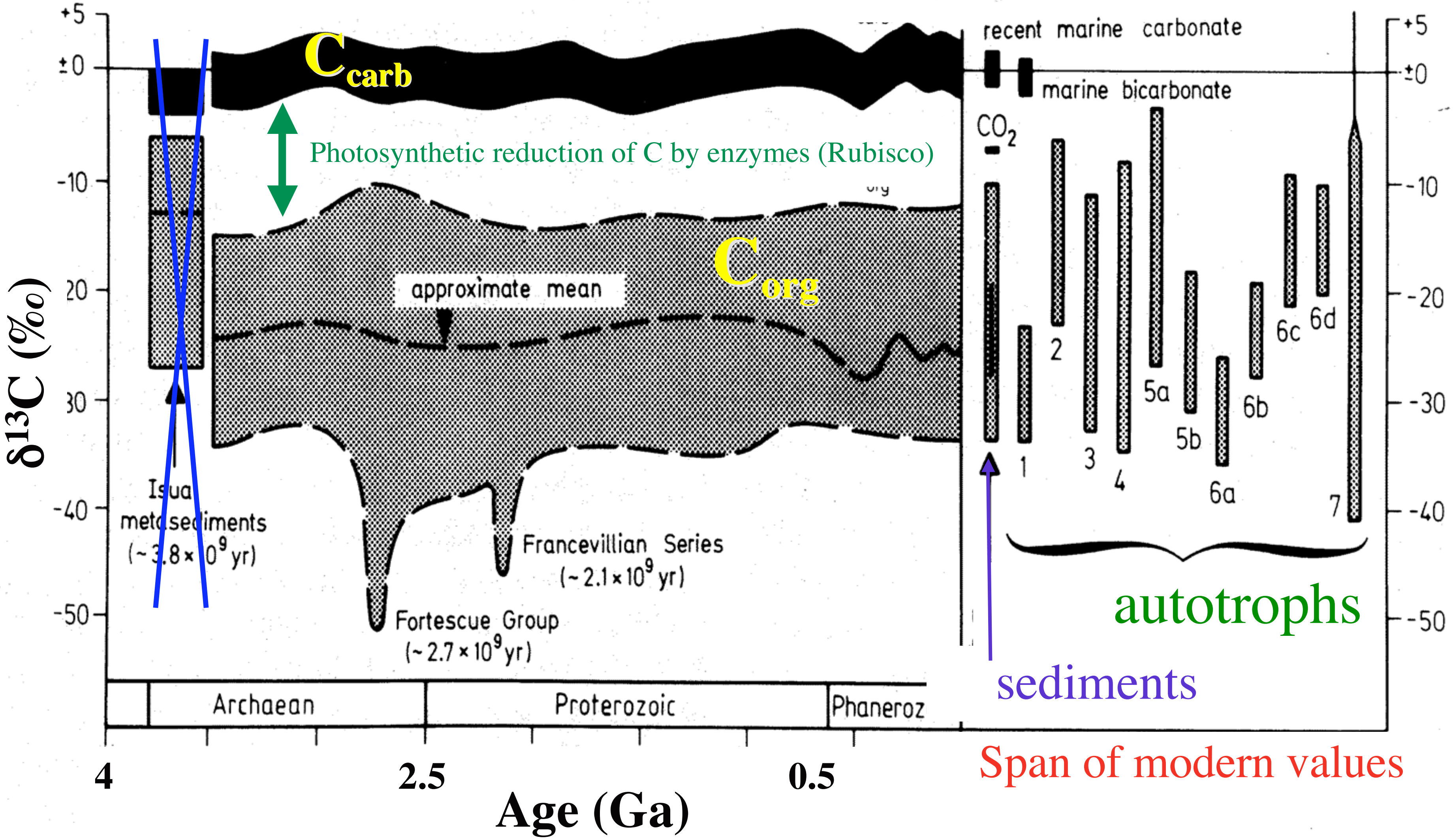


Living Stromatolites, Shark Bay, Australia

3.5 Ga Stromatolites, WA



~3.5 Gyr of Photosynthetic Carbon Fixation

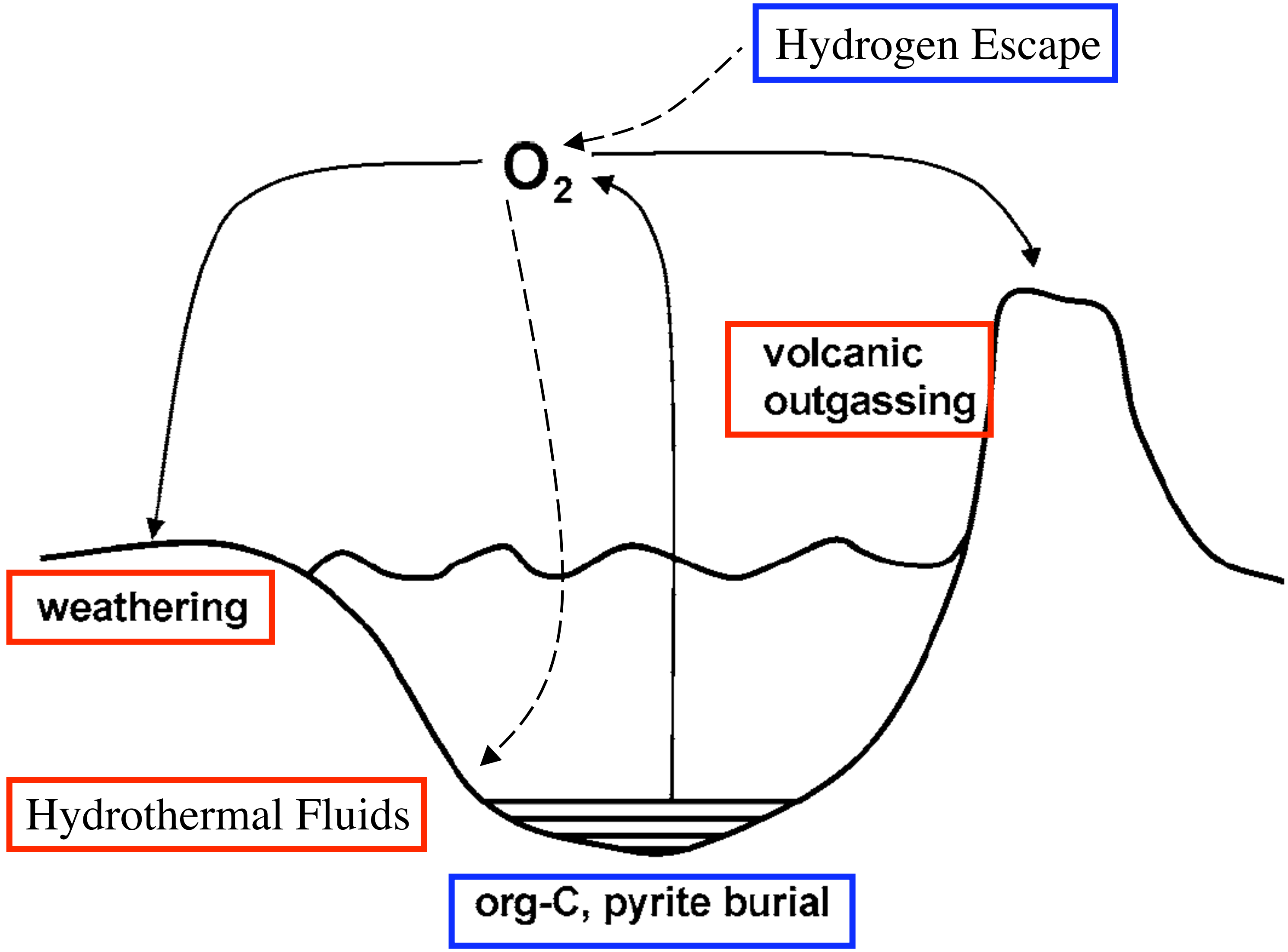


• $\delta^{13}C = [(^{13}C/^{12}C_{smpl} - ^{13}C/^{12}C_{std}) / ^{13}C/^{12}C_{std}] * 1000‰$

•Plants & Phytoplankton preferentially take up ^{12}C relative to ^{13}C when they use CO_2 & HCO^-

Conundrum: If oxygen-producing photosynthesis was occurring by 3.5 Ga, why doesn't free O_2 appear until 2.3 Ga, a 1.2 Gyr delay?

Must Consider the Sources & Sinks of O_2



Adapted from Canfield (2005) *Ann. Rev. Earth Planet. Sci* Vol. 33: 1-36.

What caused the atmosphere to become oxygenated 2.4-2.2 Ga?

Sources

✓ Photosynthesis

✓ $C_{organic}$ burial

• Pyrite burial

✓ Hydrogen escape

versus

Sinks

• Respiration

• Reduced minerals in rocks

• Volcanic gases

• Hydrothermal vent fluids

Sinks for Atmospheric Oxygen

Respiration

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{Biochemical Energy}$$

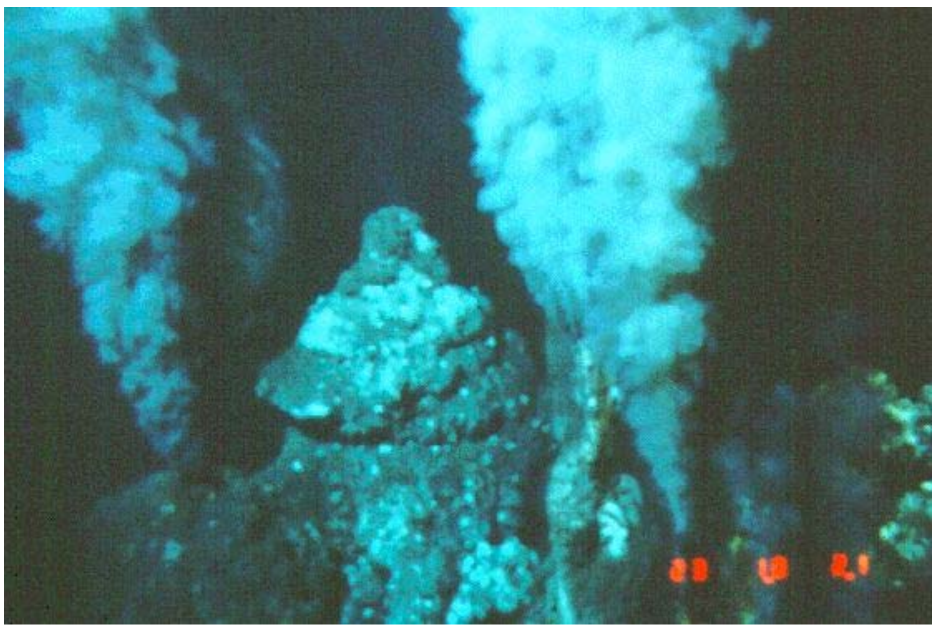
Carbon dioxide + water + Energy as products

1 mole of O_2 consumed
as 1 mole of CO_2 produced

- Cellular respiration, the counter point to photosynthesis, is carried out by all eukaryotes & converts carbon compounds & O_2 into CO_2 & ATP.
- The trick is to extract high-energy electrons from chemical bonds and then use these electrons to form the high-energy bonds in ATP.
- Some bacteria can break down organic molecules in the absence of O_2 (anaerobic respiration).

Other Archean O_2 Sinks #1

- Volcanic Outgassing
  H_2, CO, SO_2
- Hydrothermal Vent Fluids
  Fe^{2+}, S^{2-}



Monolith Chimney, Juan de Fuca Ridge

lhttp://www.pmel.noaa.gov/vents/

Mt. Pinatubo, Philippines

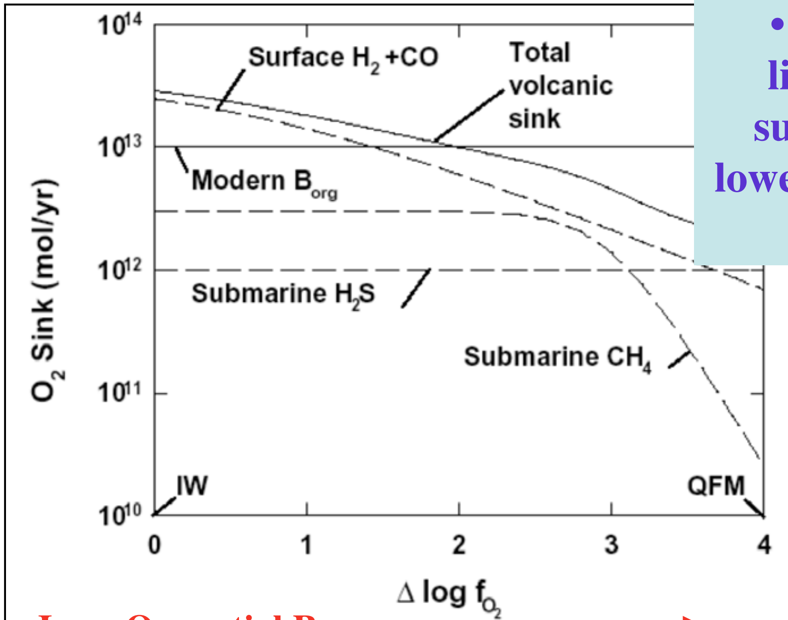
http://eos.higp.hawaii.edu/index.html

Today: Whereas oxidative weathering of reduced minerals in rocks (i.e., Fe^{2+}, S^{2-}, CH_2O) removes 75% of O_2 generated by C_{org} burial today (the other ~ 25% sink consists of volcanic outgassing at 14% & hydrothermal vents at ~10%), it was not quantitatively important during Archean.

-Holland (1978) *The Chemistry of the Atmosphere and Oceans*. John Wiley, NY, 351 pp.
-Holland (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press, Princeton, NJ, 582 pp.

Other Archean O_2 Sinks #2

Archean mantle dynamics & redox evolution-1



Incr. O_2 partial P →

Figure 1. Magnitude of the volcanic O_2 sink as a function of the oxygen fugacity of mantle source regions. B_{org} is the organic carbon burial rate and the presumed rate of oxygen production if most of the organic matter came from oxygenic photoautotrophs. $\Delta \log fO_2$ is relative to the iron-wustite (IW)

- O_2 sink decreases with increasing oxygen partial pressure in mantle source region.

- **Oxidized lithosphere subducted to lower mantle (O_2 sink)**

- **Reduced upper mantle erupted at MORs oxidized by O_2 (sink)**

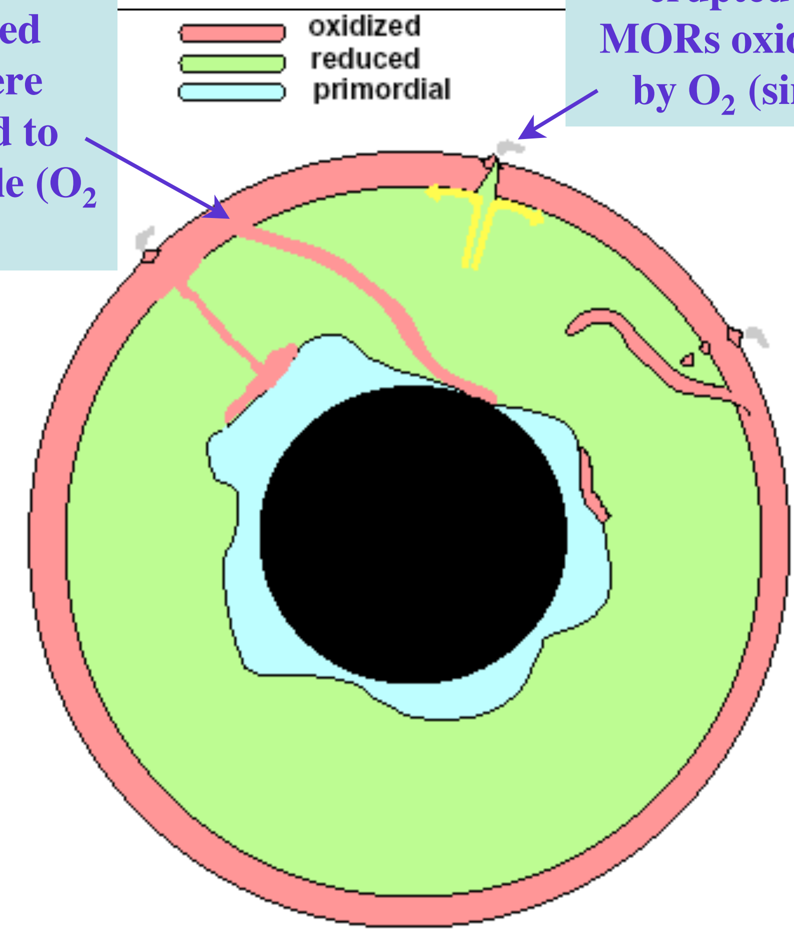


Figure 2. Model of Late Archean mantle structure and dynamics, depicting heterogeneity of mantle redox states. Basalts erupted at Earth's surface become oxidized. The oxidized slabs of oceanic lithosphere are subducted, penetrating into the lower mantle and accumulate at the core-mantle boundary. Plumes carry oxidized mantle back to the surface. Source regions for mid-ocean ridge basalts remain reduced through the Archean. Interior structure (but not redox characteristics) after *Albarede and van der Hilst* [1999].

Kump et al. (2001) *Geophys Geochem. Geosyst.*, Vol. 2: 2000GC000114

The Rise of Atmospheric Oxygen

- Photosynthesis by cyanobacteria began ~3.5 Ga

  $CO_2 + H_2O \text{ ---> } CH_2O + \mathbf{O_2}$

- No evidence for free O_2 before ~2.4 Ga
- Reduced gases in atmosphere & reduced crust consume O_2 produced during 1.2 Gyr
- Hydrogen escape irreversibly oxidizes atmosphere
- Mantle dynamics & redox evolution reduce O_2 sink over time
- Geologic & geochemical evidence for O_2 :

  Oxidized Fe & Mn mineral deposits

  Detrital uraninite & pyrite

  Paleosols

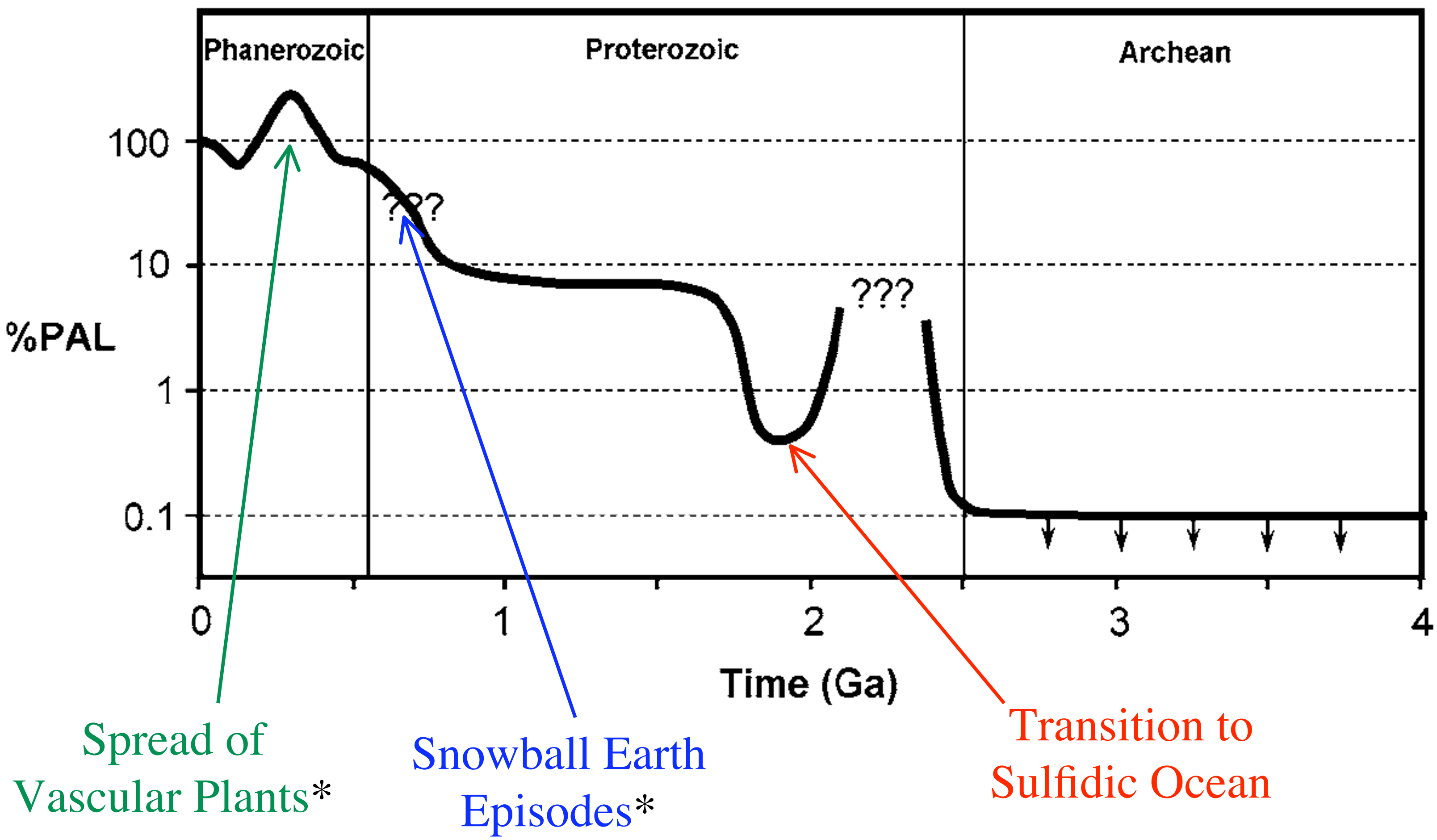
  Redbeds

  Sulfur & Iron isotopes

  Eukaryotes

- **Conclusion: Rapid rise of free O_2 2.4-2.2 Ga**

Atmospheric O_2 did not rise steadily from 2.3 Ga: There were Bumps & Dips!



* Stay tuned… we'll talk about these in the upcoming lectures!

Canfield (2005) *Ann. Rev. Earth Planet. Sci* Vol. 33: 1-36.