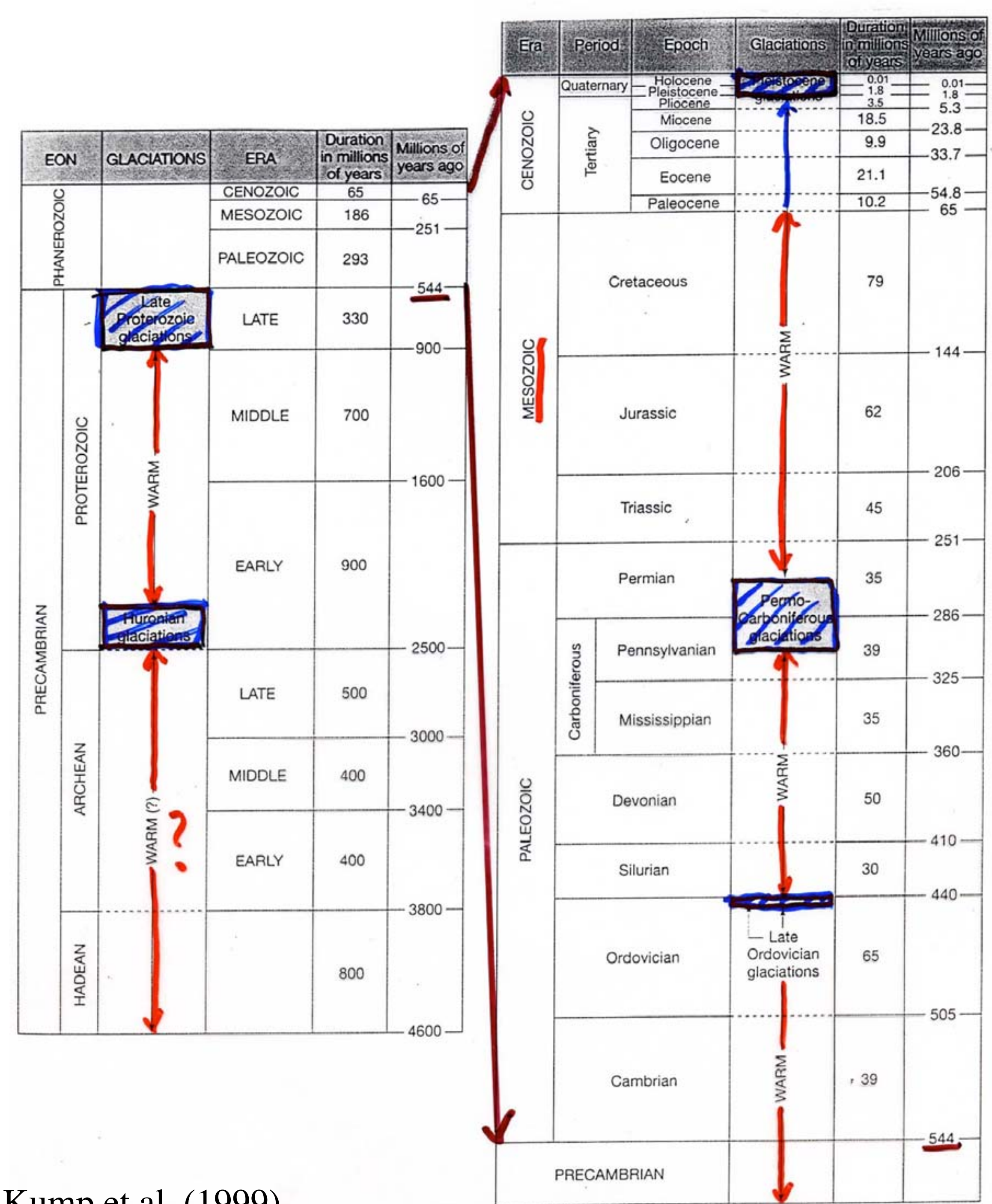
Earth's Climate: the 1st 4 Billion Years

OCEAN 355
Prof. Julian Sachs
Lecture Notes #6
Autumn 2008

Earth's Climate History:

Mostly sunny with a 10% chance of snow



Kump et al. (1999)

Climate Controls - Long & Short Timescales

•Solar output (luminosity): 10^9 yr

•Continental drift (tectonics): 10^8 yr

•Orogeny (tectonics): 10^7 yr

•Orbital geometry (Earth -Sun distance): 10^4-10^5 yr

•Ocean circulation (geography, climate): 10^1 -10^3 yr

•composition of the atmosphere (biology, tectonics, volcanoes): 10^0-10^5 yr

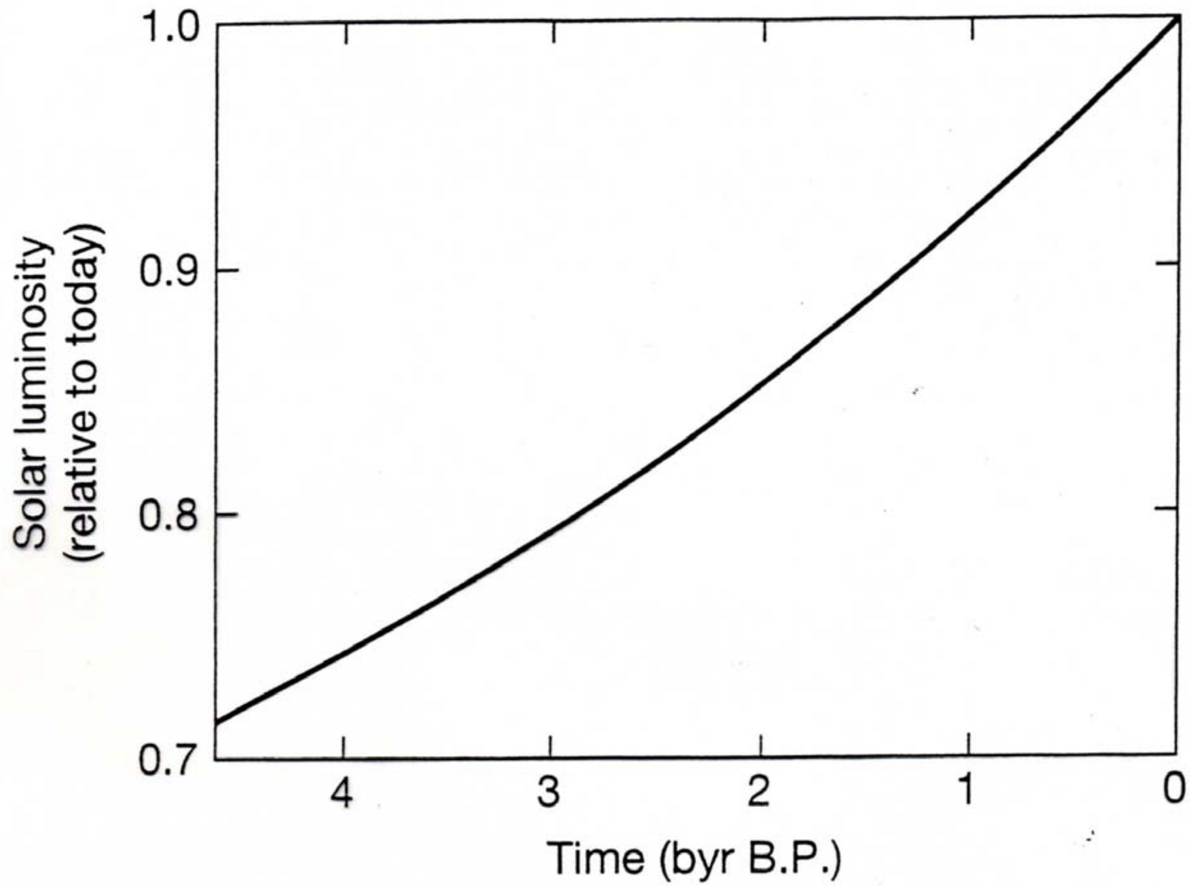
Outline

- Overview of Earth's climate history

- Climate feedbacks: what keeps climate away from extremes?
  - Planetary Energy Balance
  - Greenhouse Effect
  - Geochemical Carbon Cycle, CO_2
  - Temperature, Precipitation-Weathering Feedback

- Case studies:
  - Neoproterozoic glaciations (750-580 Ma)
  - Permo-carboniferous Glaciations (300-275 Ma)
  - Mesozoic Warmth (245-65 Ma)
  - Cenozoic Cooling (100-0 Ma)
  - Pleistocene Glaciations (0.5-0 Ma)

The ‘Faint Young Sun Paradox’



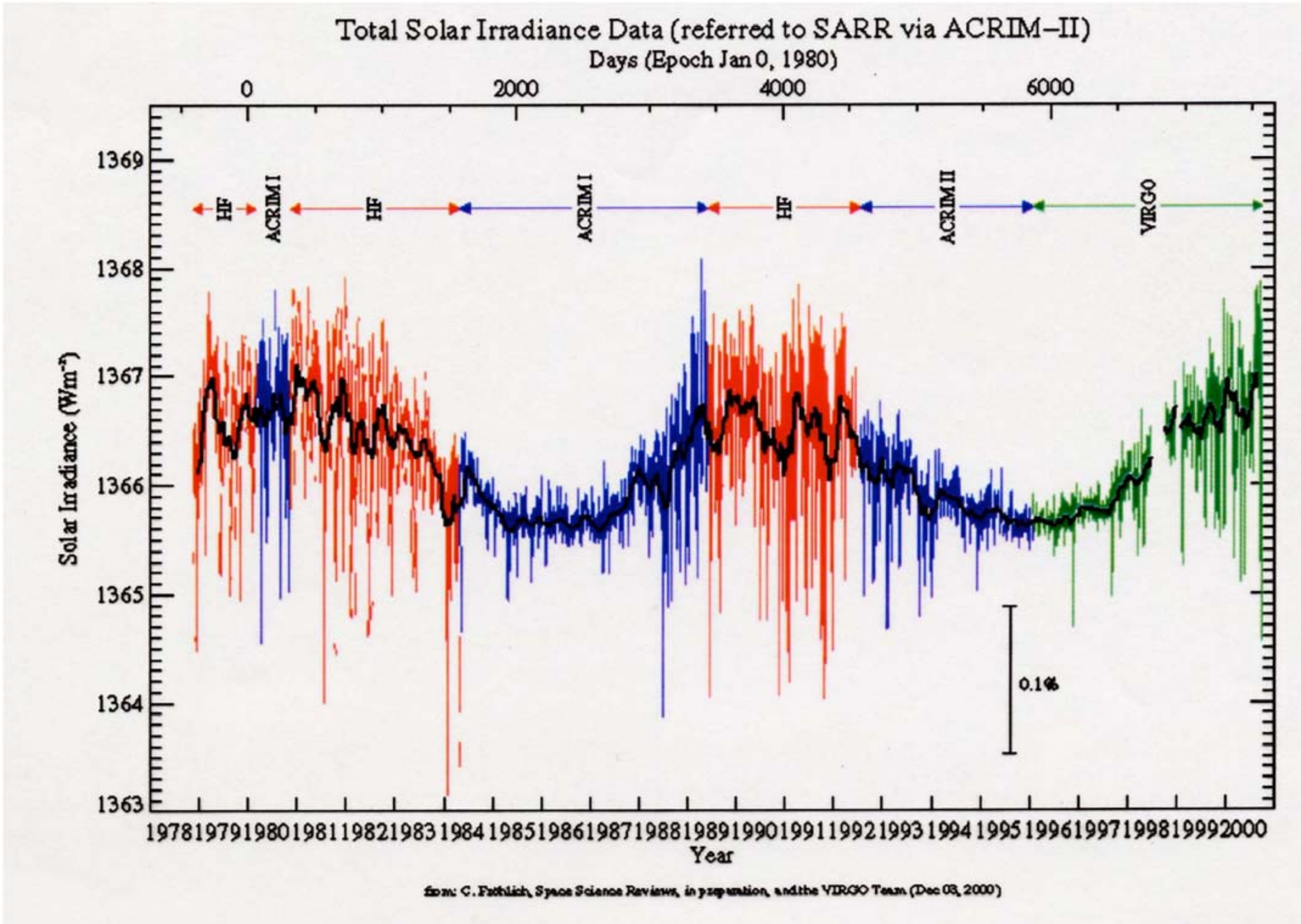
Faint Young Sun Paradox

Solar Luminosty ~30% less 4.6 Byr BP

→ Earth should have been frozen until ~2 Byr BP

4 $^{1}H \rightarrow {}^{4}He$
Incr. density= incr. luminosity

Liquid H_2O existed >3.5 Ga (sed. rocks, life, zircon $\delta^{18}O$)



• Contemporary Solar Variability ~0.1%
• Associated with 11-year sunspot cycle

Simple Planetary Energy Balance

$E_{emitted} = E_{absorbed}$

① $E_{emitted}$

- Blackbody w/ effective radiating temperature, T_e

- Stefan-Boltzmann law

$$E = \sigma T_{eff}^4 \qquad \left(\sigma = 5.67 \times 10^{-8} \frac{W}{m^2 \cdot K^4}\right)$$

→ Energy emitted per unit area

- For entire surface of Earth

$$E_{emitted} = 4\pi R_{Earth}^2 \times \sigma T_{eff}^4$$

• Likely solution to FYSP requires understanding of Earth's energy balance (& C cycle)

• Blackbody: emits radiation w/ 100% efficiency @ all λ

(Multiply by area of sphere)

Adapted from Kump et al. (1999)

Energy Balance (cont'd.)

② Energy Absorbed

$$E_{absorbed} = E_{intercepted} - E_{reflected}$$

$$= \pi R_E^2 \times S - \pi R_E^2 \times S \times A$$

Cross section of Earth = area of circle with Earth radius

$$= \pi R_E^2 S (1-A)$$

$$E_{emitted} = E_{absorbed}$$

$$4\pi R_E^2 \times \sigma T_{eff}^4 = \pi R_E^2 S (1-A)$$

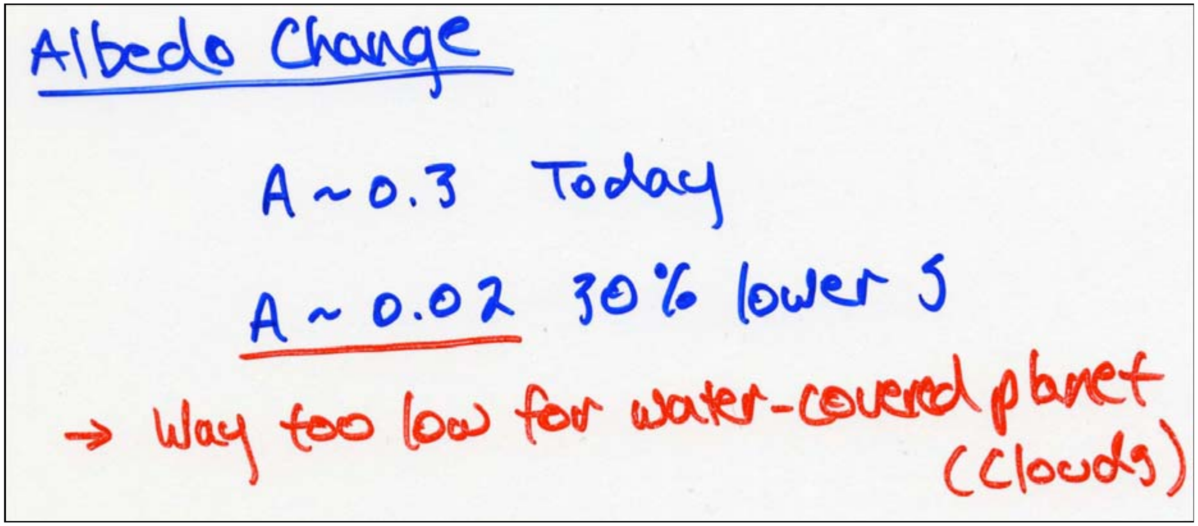
$$\sigma T_{eff}^4 = \frac{S}{4}(1-A)$$

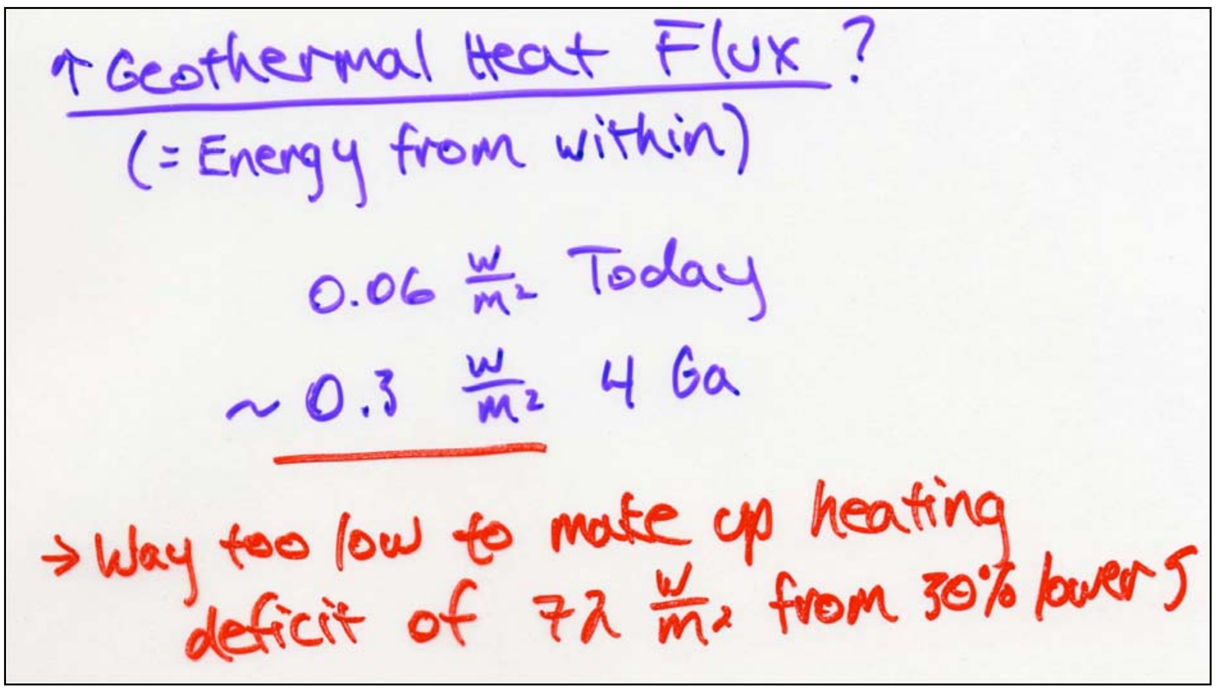
$\Rightarrow$ If $\downarrow S$, Then $\downarrow T_{eff}$ or $\downarrow A$

S = solar radiation received at the radius of the planet's orbit around star (so S is a function of the luminosity of the star and the distance the planet is from the star)

A = albedo; the fraction of solar radiation reflected back to space from clouds, ice, deserts, etc.

Adapted from Kump et al. (1999)





Neither Albedo or Geothermal Heat Flux Changes Can Keep the Earth from freezing w/ 30% lower S

Adapted from Kump et al. (1999)

Lower Solar Output Compensated by Larger Greenhouse Effect

$$\sigma T_{eff}^4 = \frac{S}{4}(1-A)$$

× Geothermal Ht. Flux

× Mass Loss of Sun

$$T_{eff} = \sqrt[4]{\frac{S}{4\sigma}(1-A)}$$

Today: $= 255\,K = -18°C$

Earth surface Temp $= 15°C$

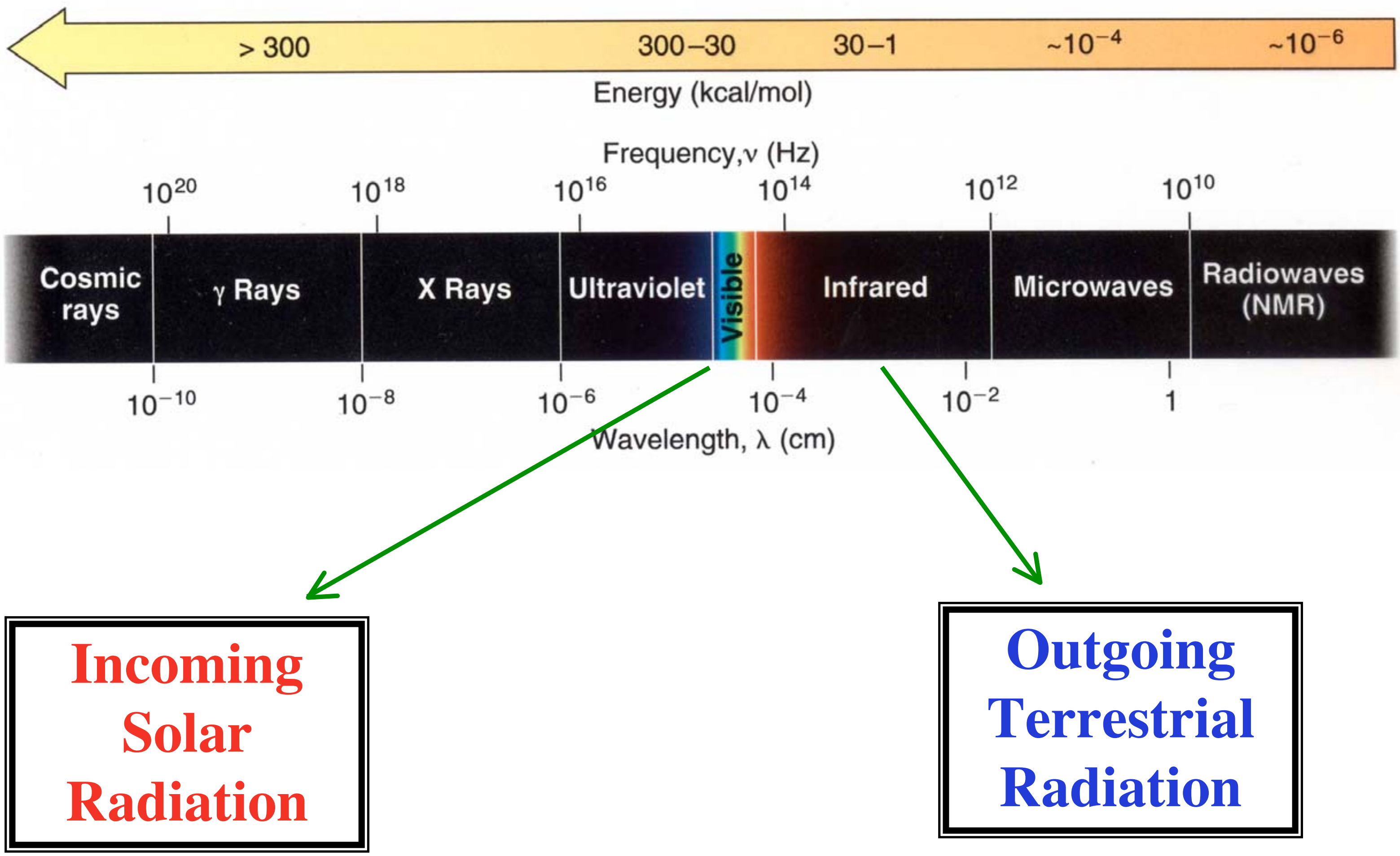
$T_s - T_{eff} = \Delta T_g$ Greenhouse Effect

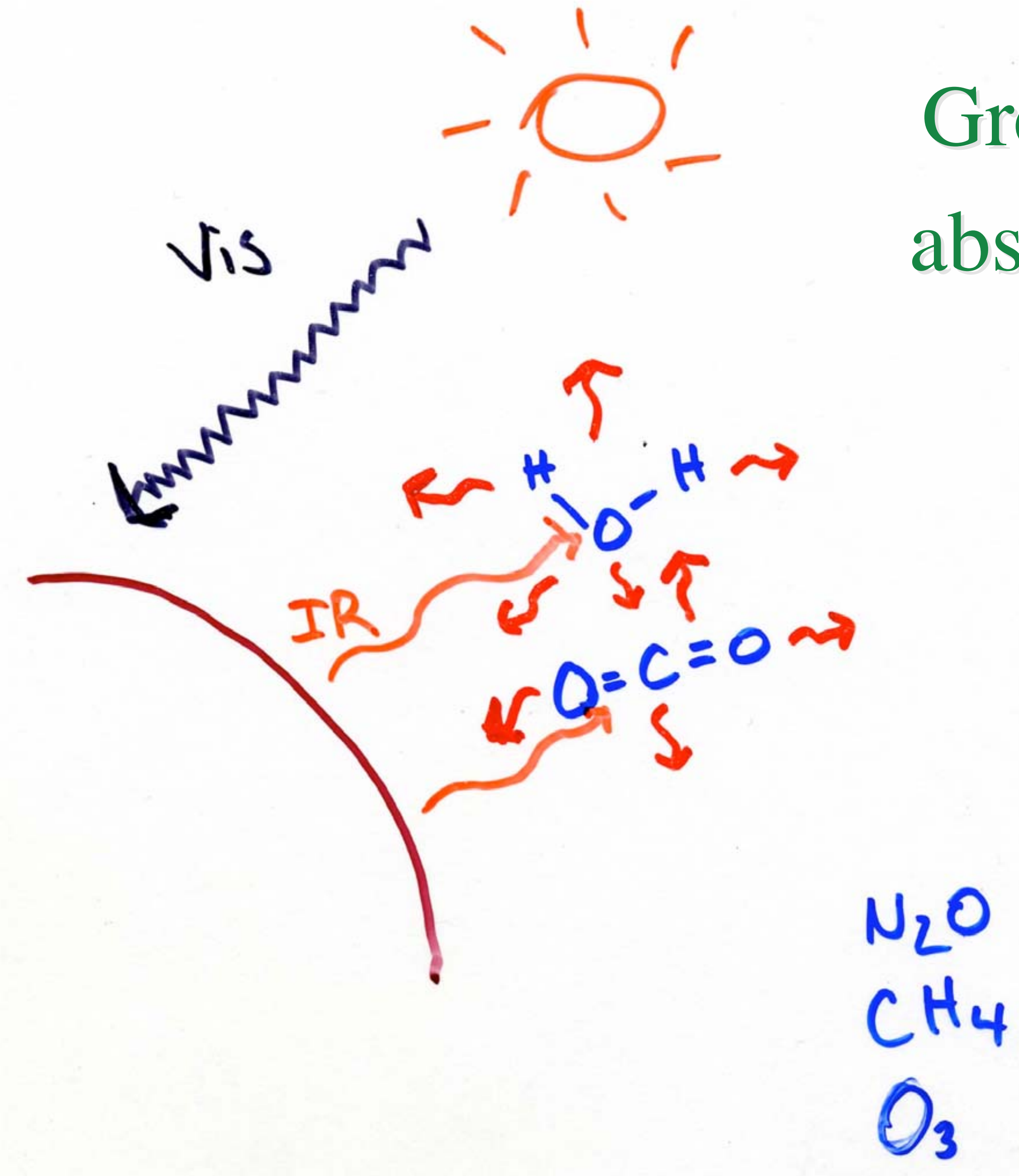
$15° - (-18°) = 33°C$

↓S Compensated by ↑ΔT_g

Adapted from Kump et al. (1999)

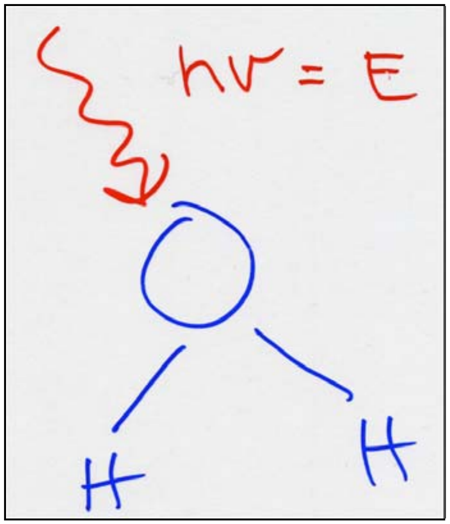
Earth's Incoming & Outgoing Radiation

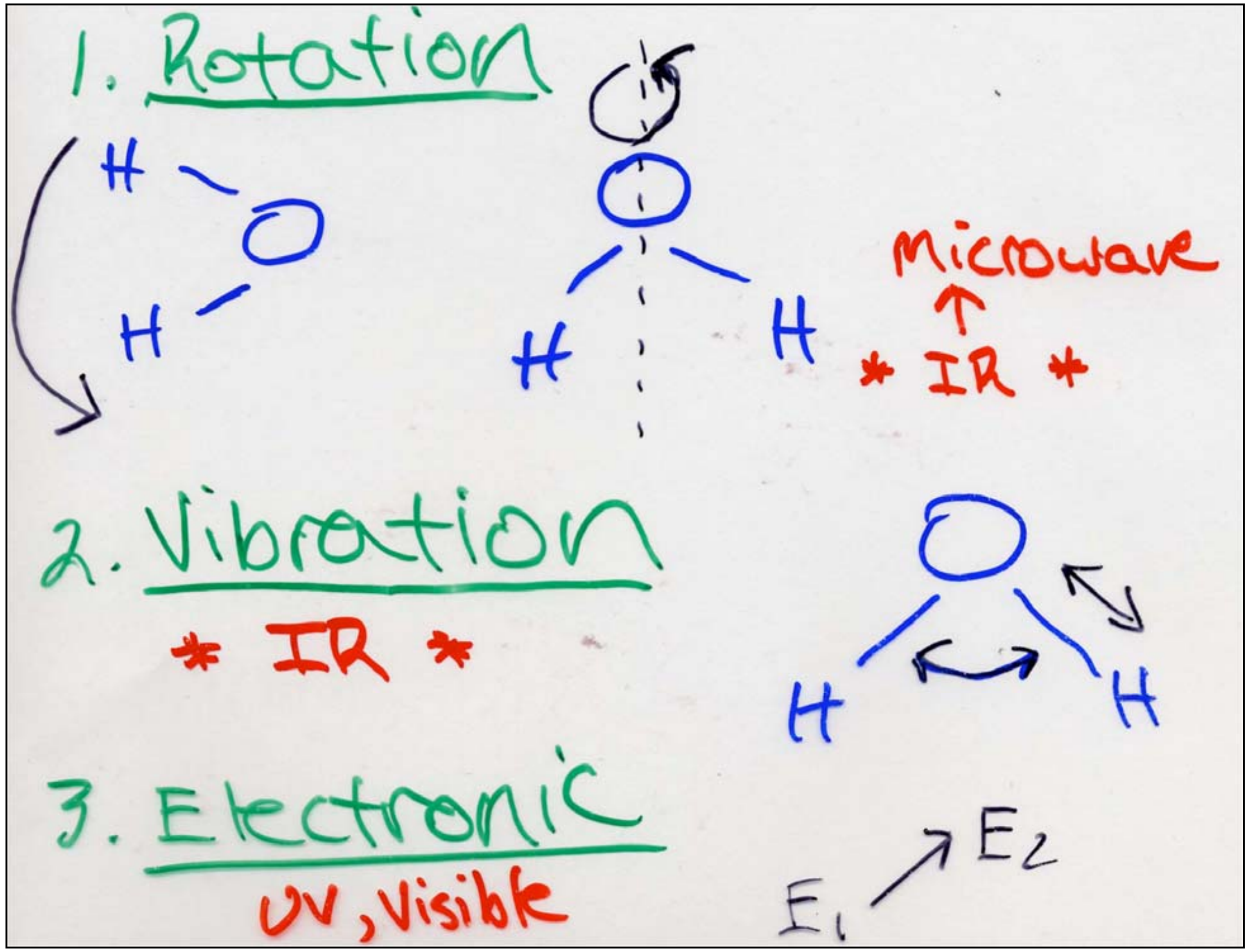




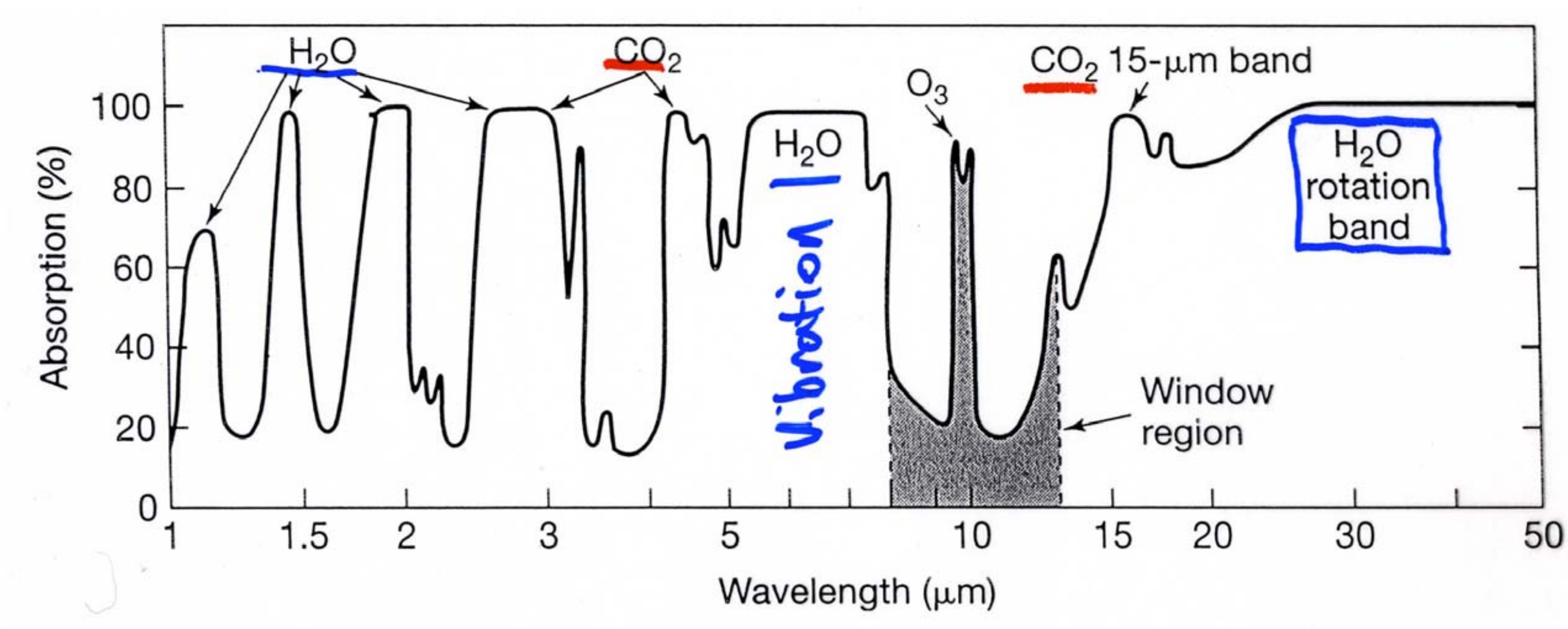
Greenhouse Gases absorb IR radiation efficiently

Molecules Acquire Energy When They Absorb Photons



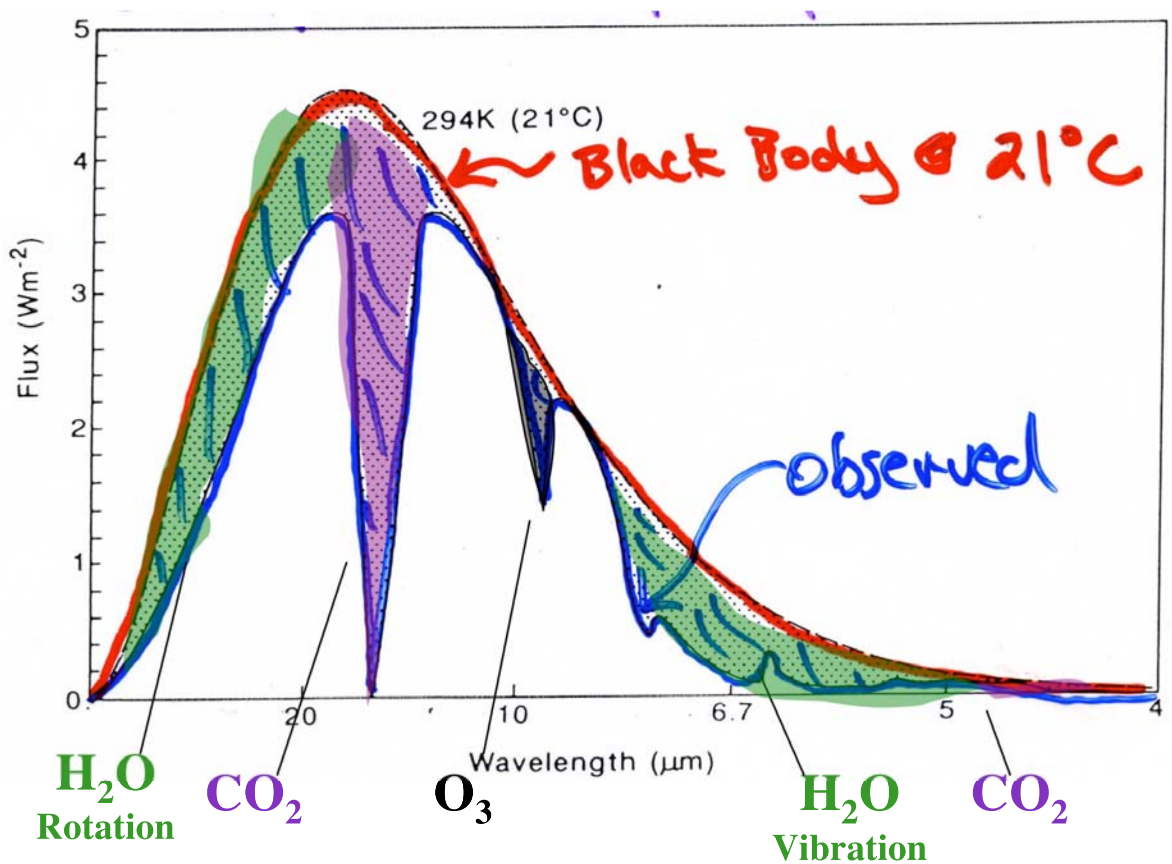


Radiation Absorbed by Atmosphere



Kump et al. (1999)

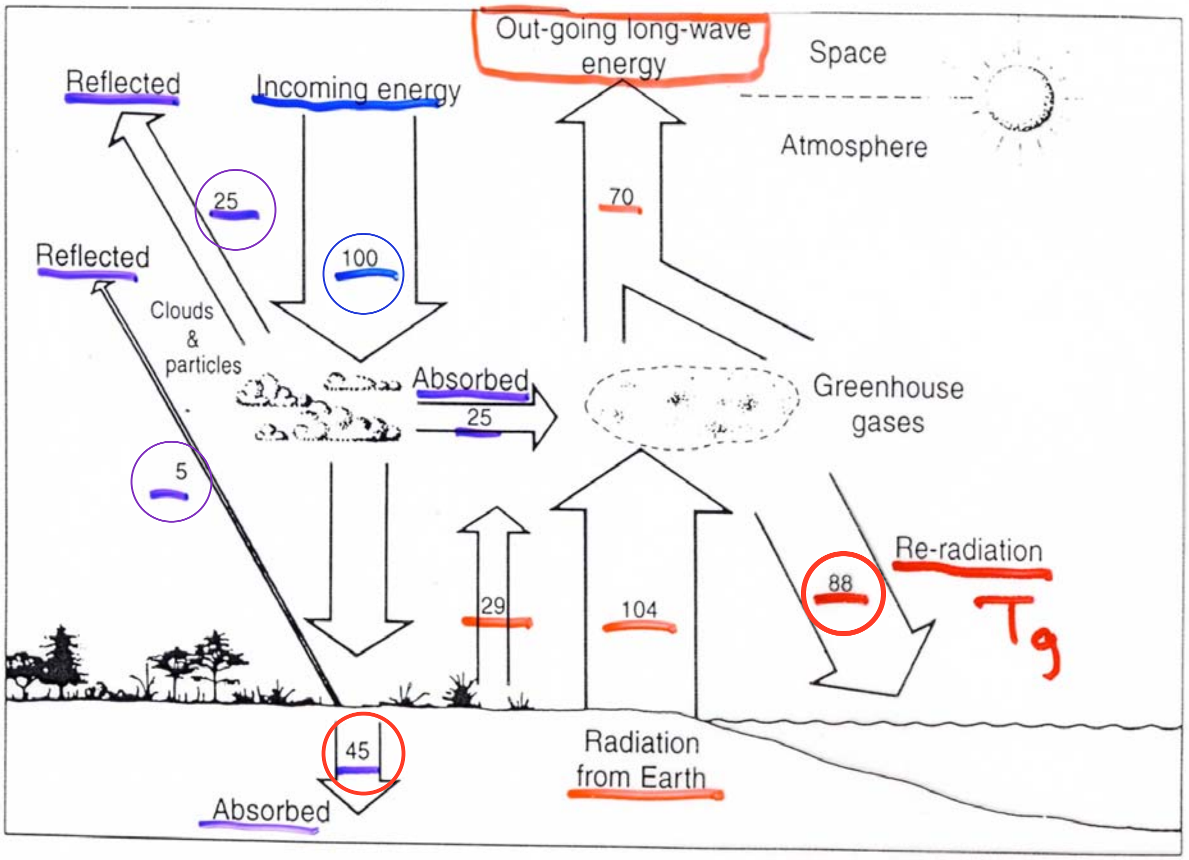
Earth's Surface Radiation Spectrum @ Top of Troposphere



"The Greenhouse Effect"

Adapted from Bigg (1996)

Global Average E Balance



Top of Atmosphere:

$E_{in} - E_{reflected} = E_{Out}$

100 - (25 - 5) = 70

100 - 25 - 5 = 70 % Incident solar radiation available

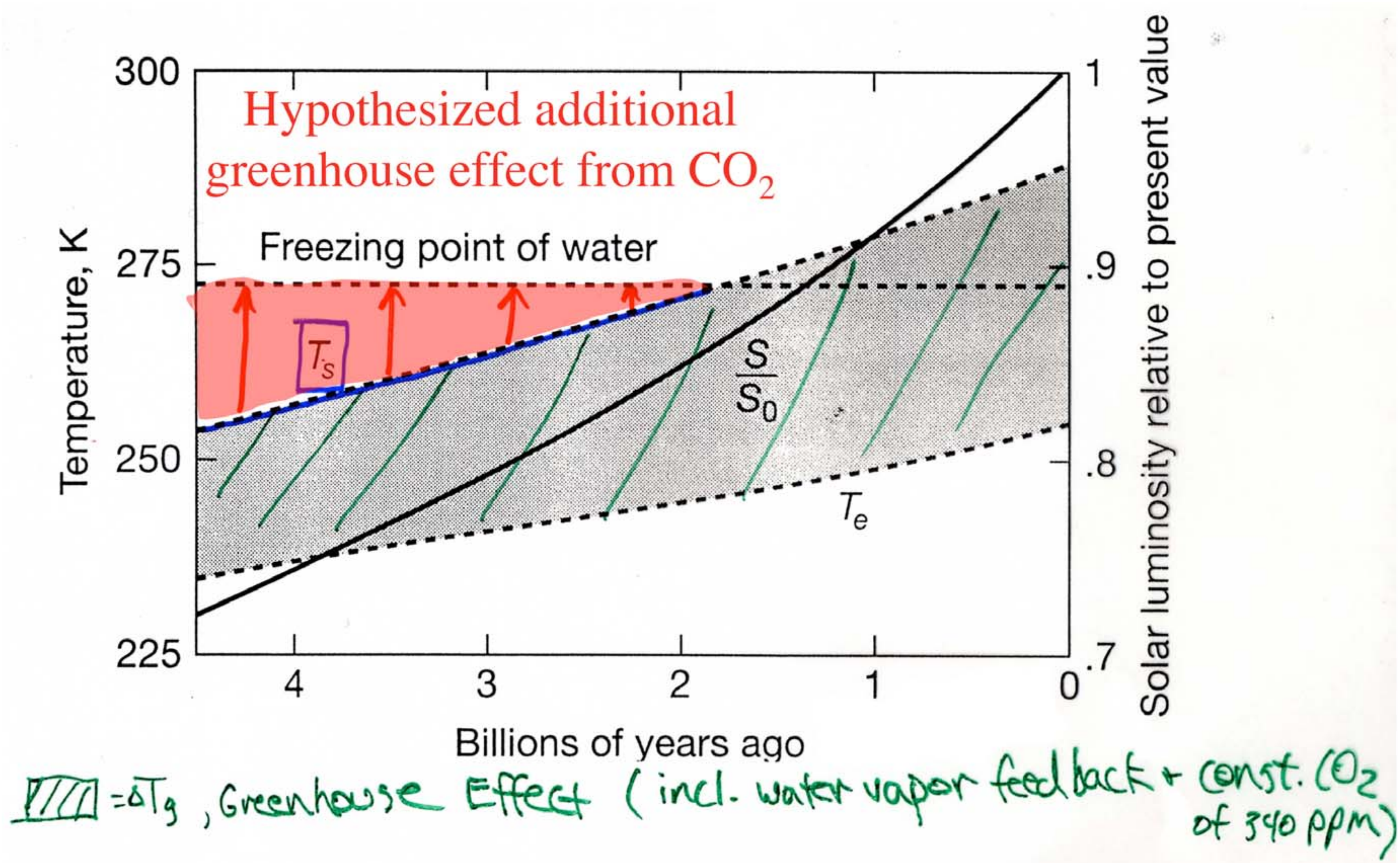
45 + 88 = 133 % Incident rad. avail. at surf. w/ grnhse. gases

Direct absorption by land

Absorption or re-radiated heat by atmospheric greenhouse gases

Adapted from Bigg (1996)

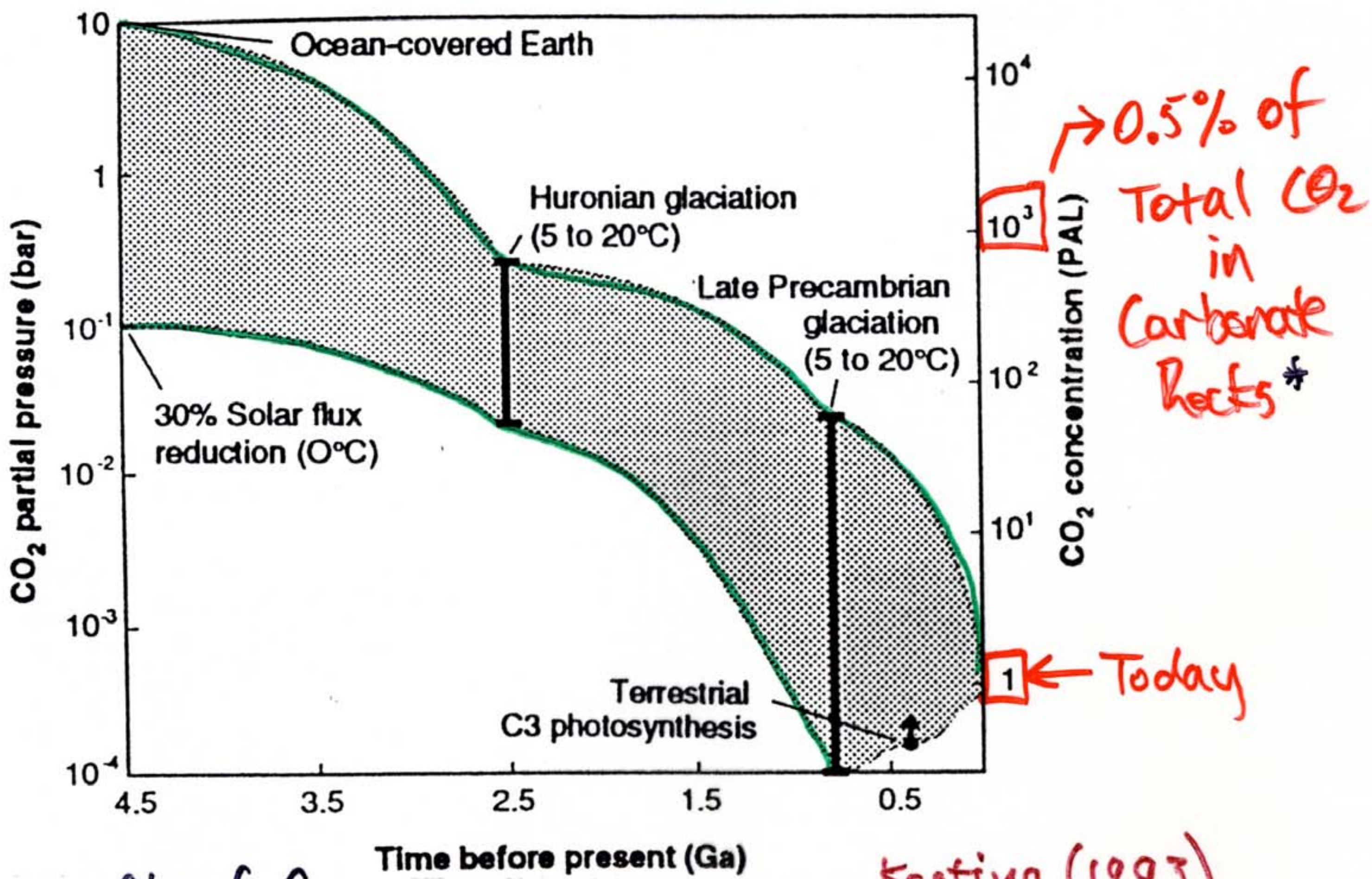
Enhanced CO_2 Greenhouse Effect Seems Necessary to Keep Earth from Freezing > 2 Ga



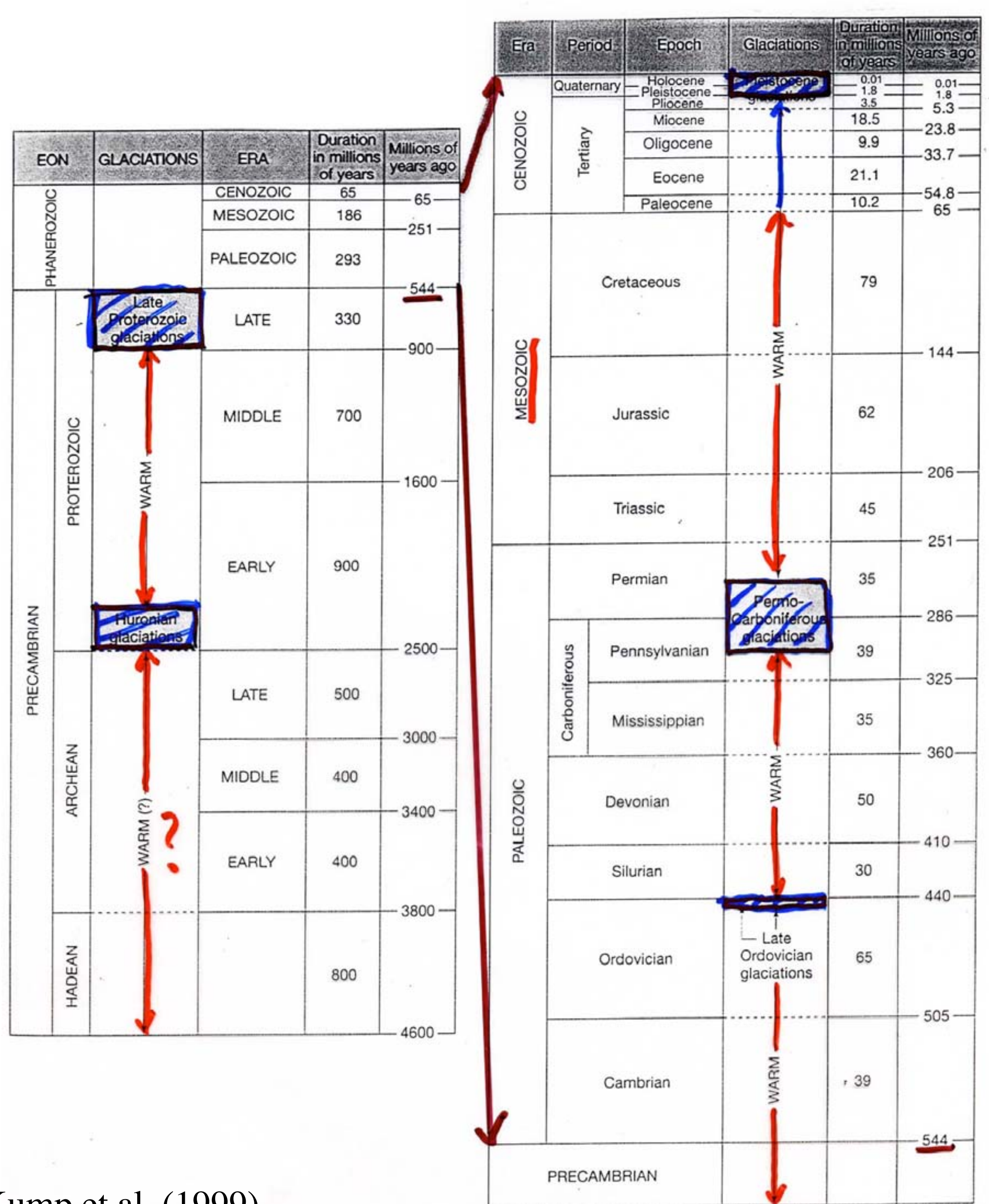
Adapted from Kasting et al. (1988)

How much CO_2 Required for $T_{Surface} > 0° C$?

--> About 1,000x PAL of 385 ppmV



* Venus : Same qty of C as Earth ; All in atmos ⇒ $T_s \leq 450°C$



Kump et al. (1999)

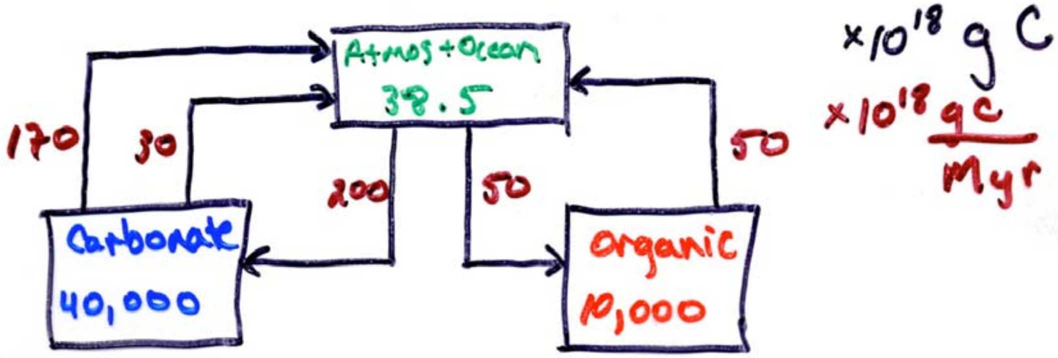
Earth's Climate History:

Mostly sunny with a 10% chance of snow

- What caused these major global climate perturbations?

1. CO_2 Feedbacks: Geochemical Carbon Cycle

- Transfer of C between rocks and ocean/atmosphere ($>10^6$-yr) can perturb CO_2 greenhouse effect
- Ocean/atmosphere C reservoir small w.r.t. rock reservoir and the transfer rates between them



2. Evidence for Long-Term CO_2-Climate Link

3. Case studies:
   - Neoproterozoic glaciations (750-580 Ma)
   - Permo-carboniferous Glaciations (300-275 Ma)
   - Mesozoic Warmth (245-65 Ma)
   - Cenozoic Cooling (100-0 Ma)
   - Pleistocene Glaciations (0.5-0 Ma)

The Carbon Cycle: Strong driver of climate on geologic timescales

Steady State & Residence Time

<u>*Steady State*: Inflows = Outflows</u>

Any imbalance in I or O leads to changes in *reservoir* size

Inflow:
60 Gton C/yr
Respiration

Atmospheric CO_2

760 Gton C

Outflow:
60 Gton C/yr
Photosynthesis

1 Gton = 10^9 * 1000 kg = 10^{15} g

The <u>*Residence time*</u> of a molecule is the average amount of time it is expected to remain in a given reservoir.

Example: t_R of atmospheric CO_2 = 760/60 = 13 yr

The Geochemical Carbon Cycle

1. Organic Carbon Burial and Weathering

$$CO_2 + H_2O \underset{\text{Weathering}}{\overset{\text{Burial}}{\rightleftharpoons}} CH_2O + O_2$$

2. Tectonics: Seafloor Spreading Rate

   - Mantle CO_2 from Mid-Ocean Ridges

3. Carbonate-Silicate Geochemical Cycle

   - Chemical Weathering Consumes CO_2
   - Carbonate Metamorphism Produces CO_2

The Bio-geochemical carbon Cycle

Geochemical Carbon Cycle #2

Chemical Weathering = chemical attack of rocks by dilute acid

$$CO_2 + H_2O \longleftrightarrow H_2CO_3$$

----

1. **Carbonate Weathering:**

$$CaCO_3 + H_2CO_3 \longrightarrow Ca^{2+} + 2\,HCO_3^-$$

2. **Silicate Weathering:**

$$CaSiO_3 + 2\,H_2CO_3 \longrightarrow Ca^{2+} + 2HCO_3^- + SiO_2 + H_2O$$

- 2x CO_2 consumption for silicates
- Carbonates weather faster than silicates

Granite (silicate)

(a)

Limestone (carbonate)

(b)

⇒ Rivers Transport dissolved ions to Ocean

Carbonate rocks weather faster than silicate rocks!

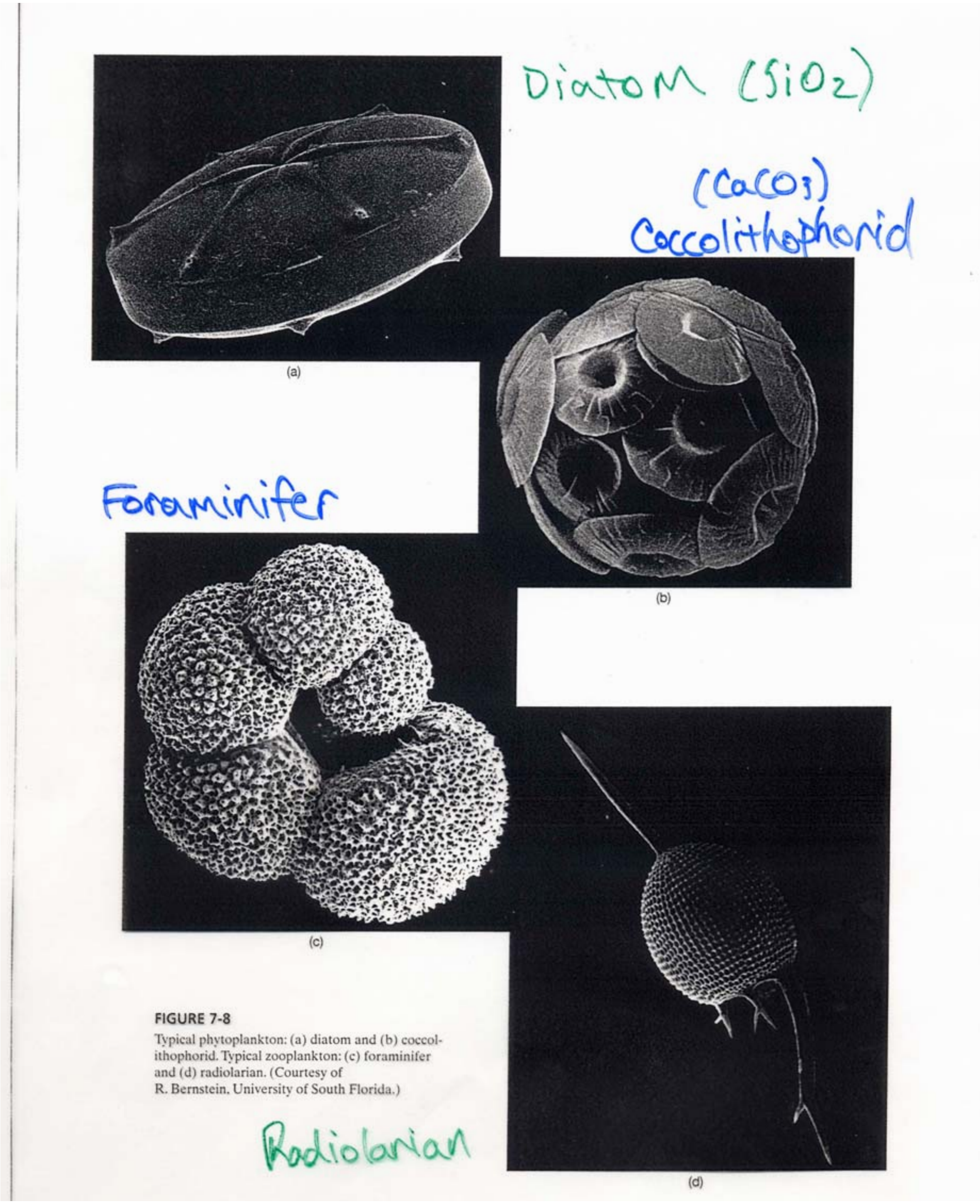


FIGURE 7-8
Typical phytoplankton: (a) diatom and (b) coccolithophorid. Typical zooplankton: (c) foraminifer and (d) radiolarian. (Courtesy of R. Bernstein, University of South Florida.)

Products of weathering precipitaed as $CaCO_3$ & SiO_2 in ocean

Kump et al. (1999)

Net Reaction of Rock Weathering

+

Carbonate and Silica Precipitation in Ocean

$$CaSiO_3 + CO_2 \text{ --> } CaCO_3 + SiO_2$$

- CO_2 consumed (~ 0.03 Gt C/yr)
- Would deplete atmospheric CO_2 in 20 kyr
- Plate tectonics returns CO_2 via Volcanism and Metamorphism

----

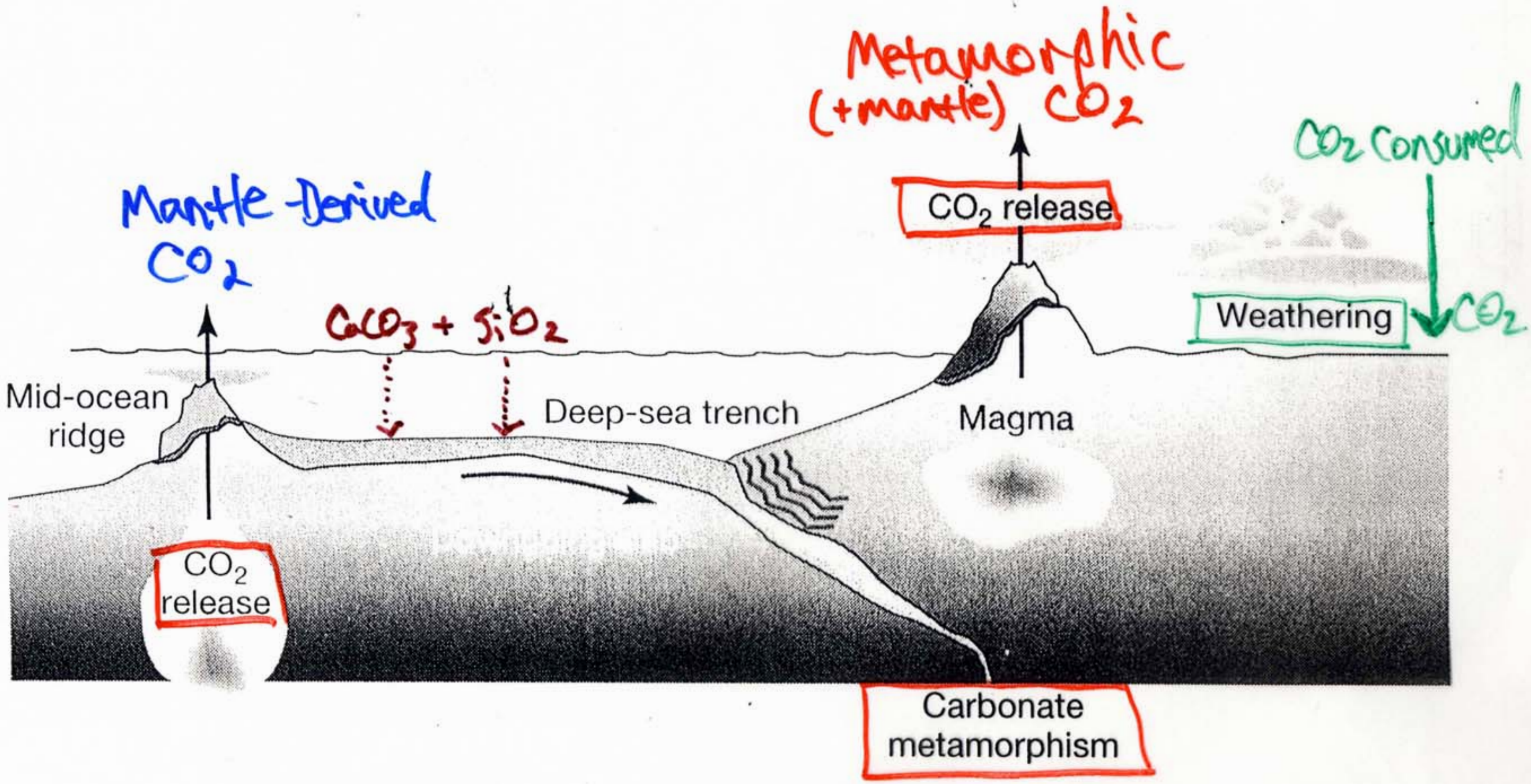
Carbonate Metamorphism

$$CaCO_3 + SiO_2 \text{ --> } CaSiO_3 + CO_2$$

- CO_2 produced from subducted marine sediments

Net reaction of geochemical carbon cycle (Urey Reaction)

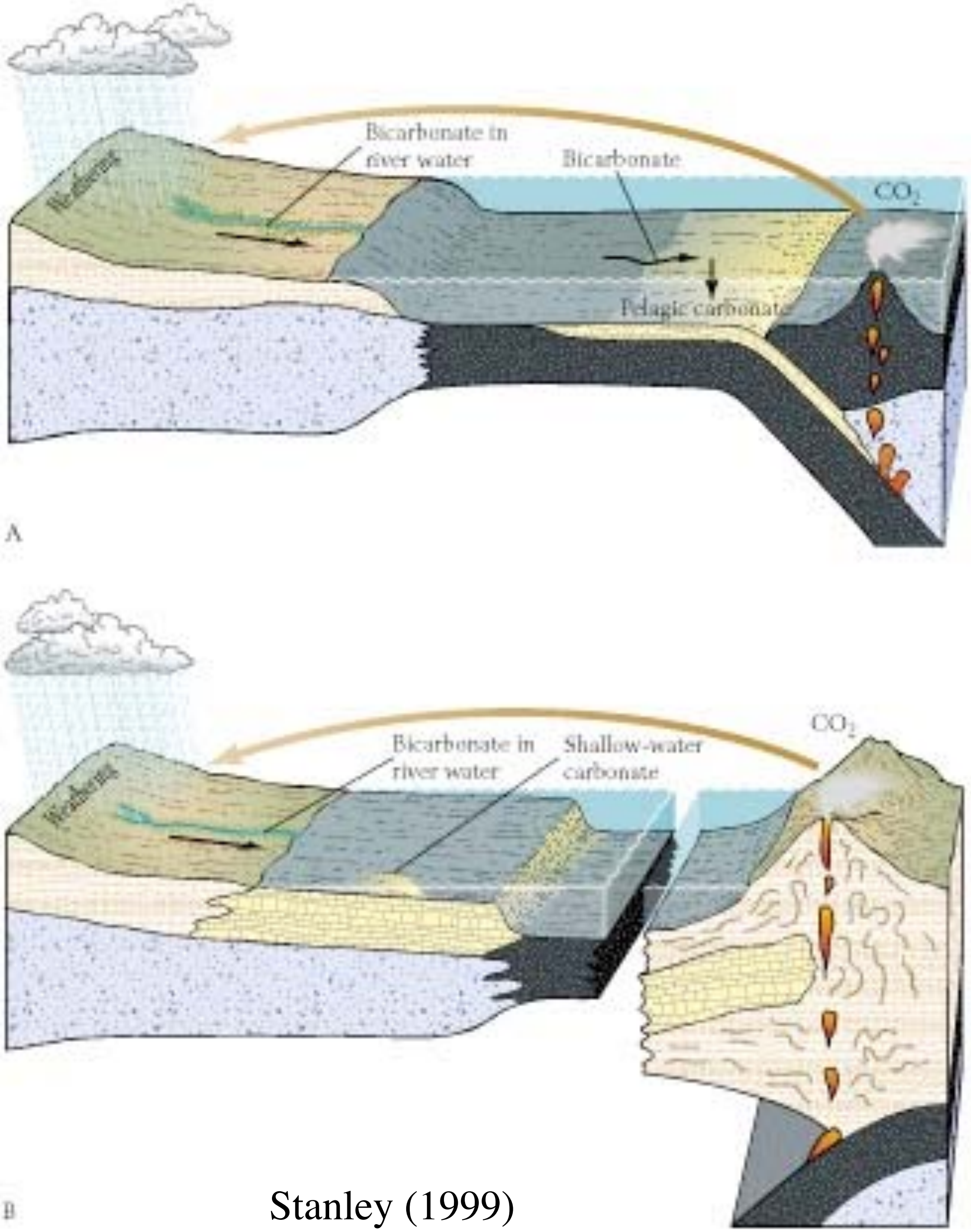
Carbonate-Silicate Geochemical Cycle



$CaCO_3 + SiO_2 \rightleftarrows CaSiO_3 + CO_2$

Weathering

Kump et al. (1999)



Stanley (1999)

Carbonate-Silicate Geochemical Cycle

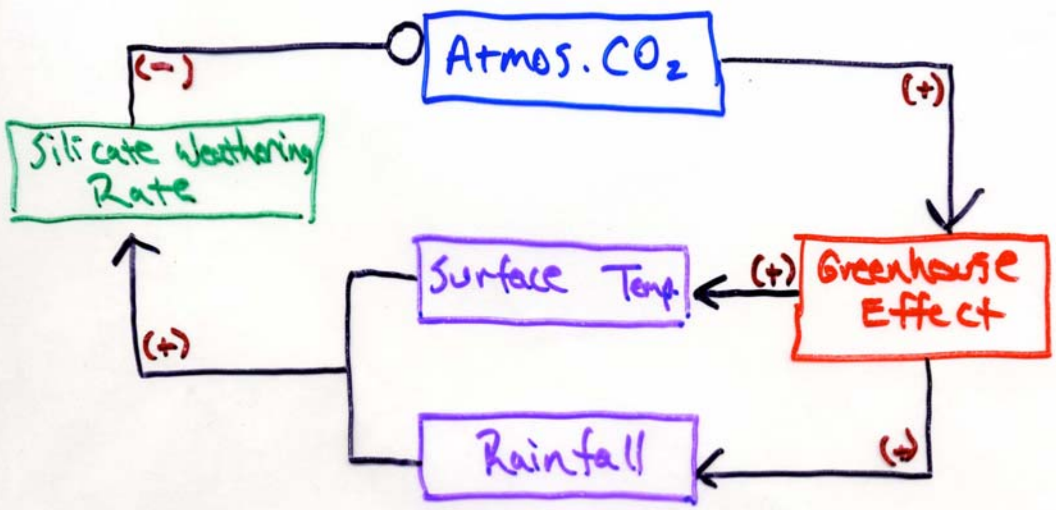
- CO_2 released from volcanism dissolves in H_2O, forming carbonic acid H_2CO_3
- CA dissolves rocks
- Weathering products transported to ocean by rivers
- $CaCO_3$ precipitation in shallow & deep water
- Cycle closed when $CaCO_3$ metamorphosed in subduction zone or during orogeny.

- Geologic record indicates climate has rarely reached or maintained extreme Greenhouse or Icehouse conditions....
- Negative feedbacks between climate and Geochemical Carbon Cycle must exist
- Thus far, only identified for Carbonate-Silicate Geochemical Cycle:

Temp., rainfall enhance weathering rates

(Walker et al, 1981)

(I.e., no obvious climate dependence of tectonics or organic carbon geochemical cycle.)

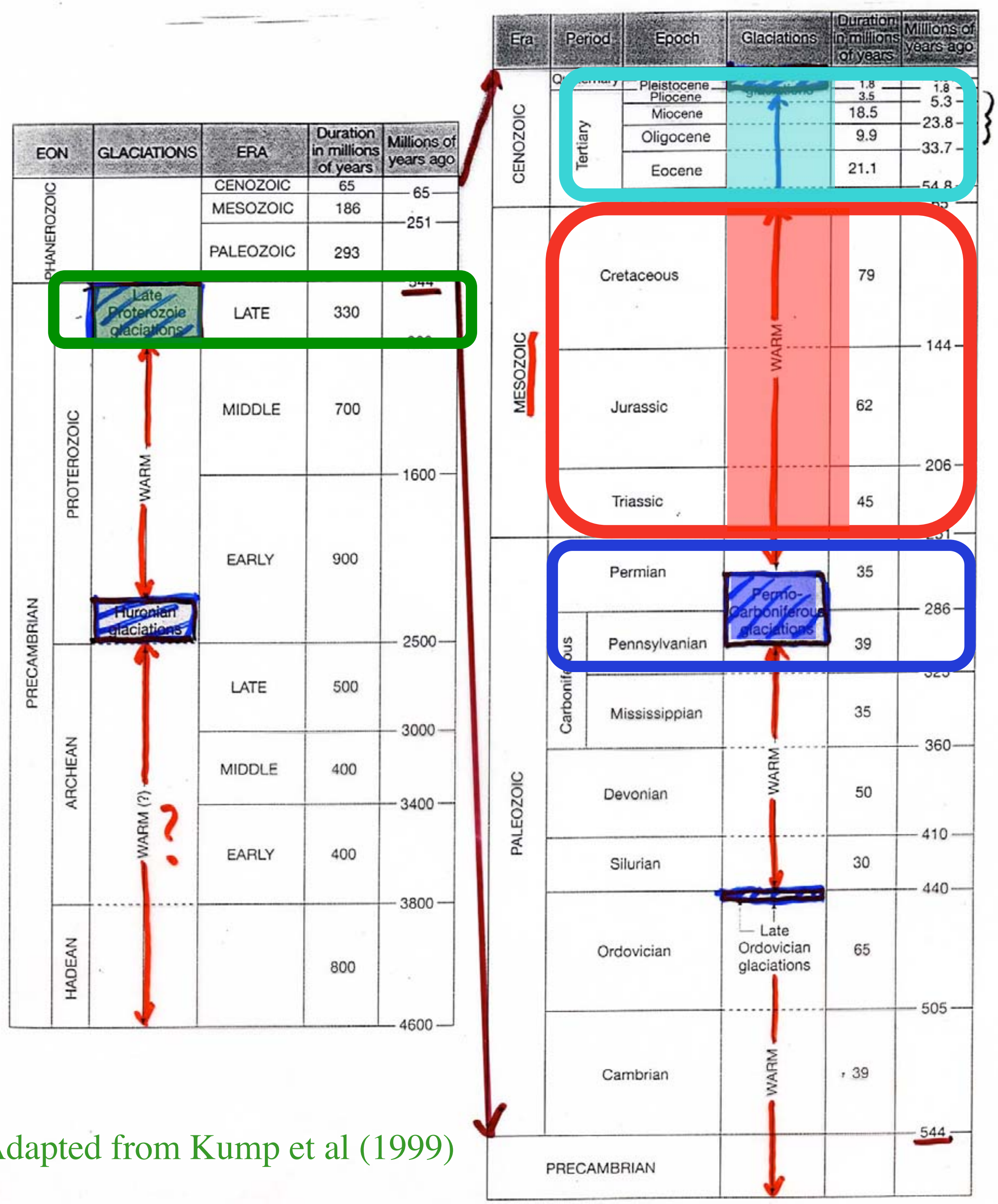


How are CO_2 levels kept in balance?

Feedbacks

Adapted from Kump et al. (1999)

Climate History of Earth: Case Studies



Adapted from Kump et al (1999)

Neoproterozoic Glaciations

Permo-Carboniferous Glaciations

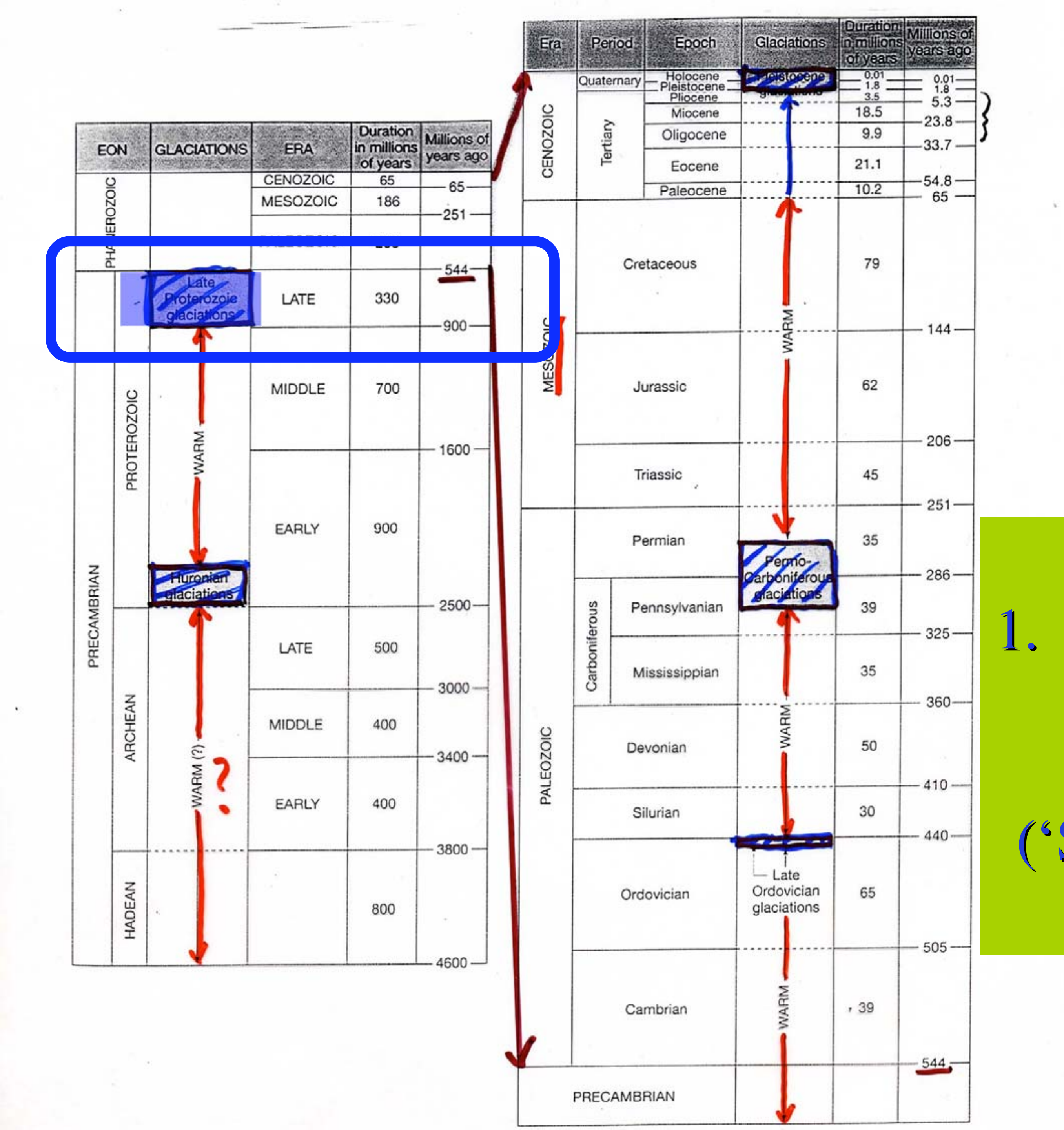
Mesozoic Warmth

Cenozoic Cooling

The Proterozoic Glaciations

('Snowball Earth')

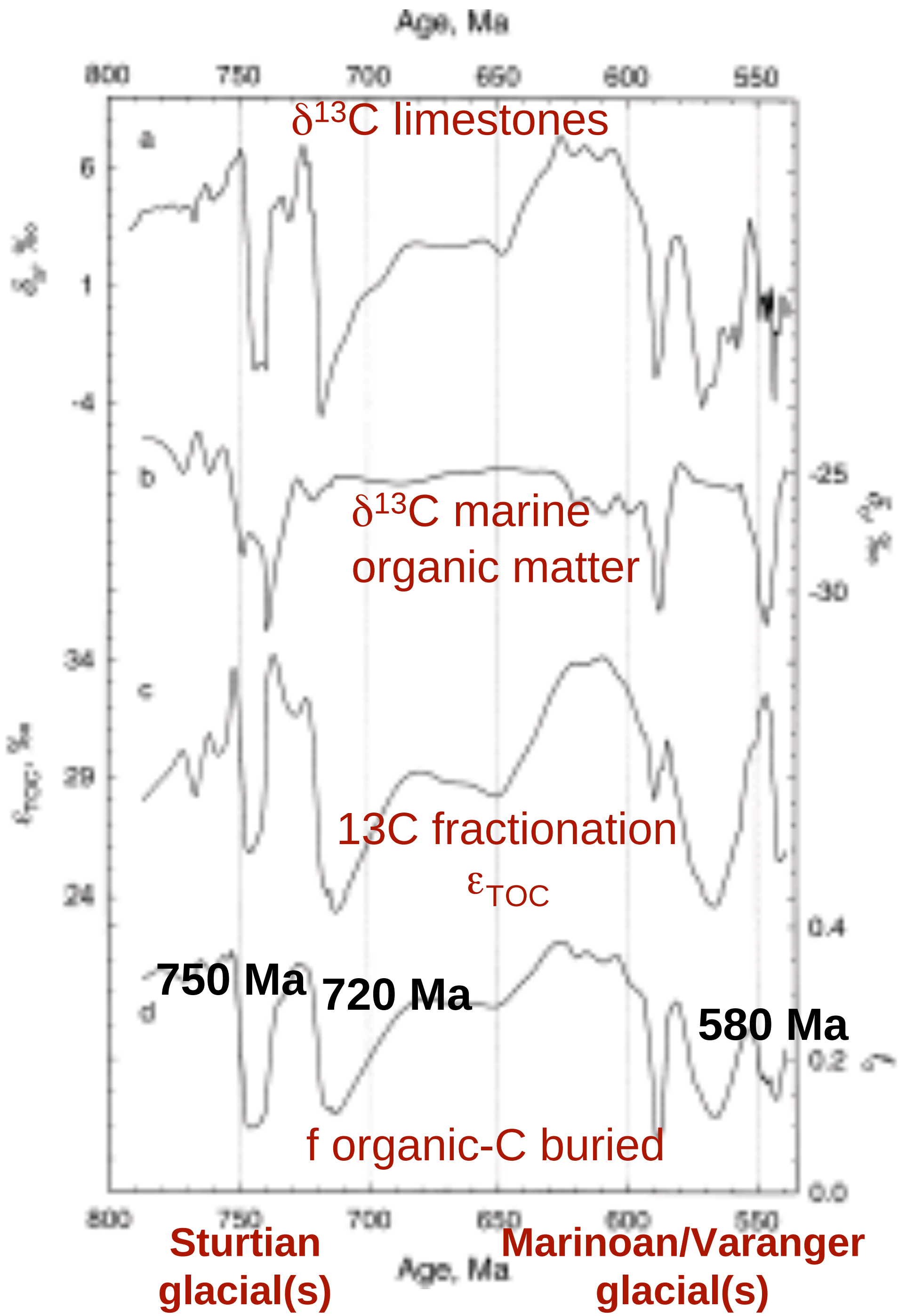
Reading:
•Hoffman & Schrag (2002) *Terra Nova*, Vol. 14(3):129-155.



Earth's Climate History

1. Late Proterozoic Glaciations

('Snowball Earth')



Carbon Isotopic Excursions 800-500Ma

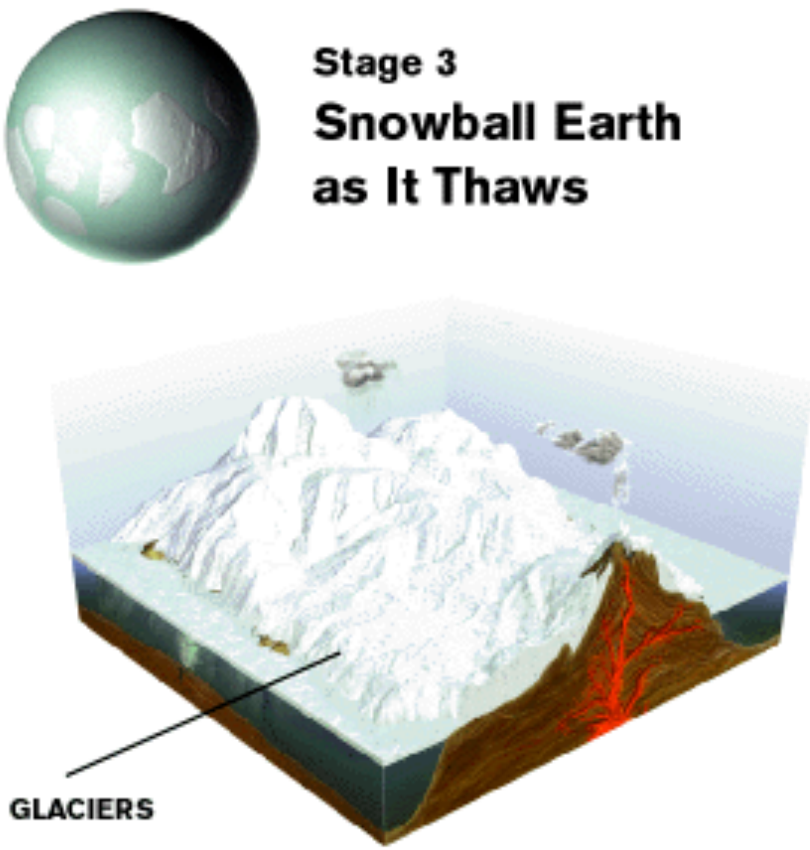
- **What caused these massive perturbations to the carbon cycle during the late Proterozoic?**

Hayes et al. (1999) *Chem Geol*. Vol. 161: 37.

Late Proterozoic Glaciations: Evidence

~4 global glaciations followed by extreme greenhouses 750-580 Ma

•Harland (1964); Kirschvink (1992)
•Hoffman et al. (1998) *Science*, v. 281: 1342-6; Hoffman & Schrag (2000) *Sci. Am.*, Jan: 68-75.



Snowball Events:

•Breakup of equatorial supercontinent 770 Ma
•Enhanced weathering from increased rainfall (more land close to sea)
•Drawdown atmospheric CO_2 → Global cooling
•Runaway albedo effect when sea ice < 30° latitude
•Global glaciation for ~10 Myr (avg T ~ -50°C)
•Sea ice ~1000 m thick, geothermal heat flux (0.07 W/m^2) keeps ocean liquid

Evidence for Glaciers on All Continents

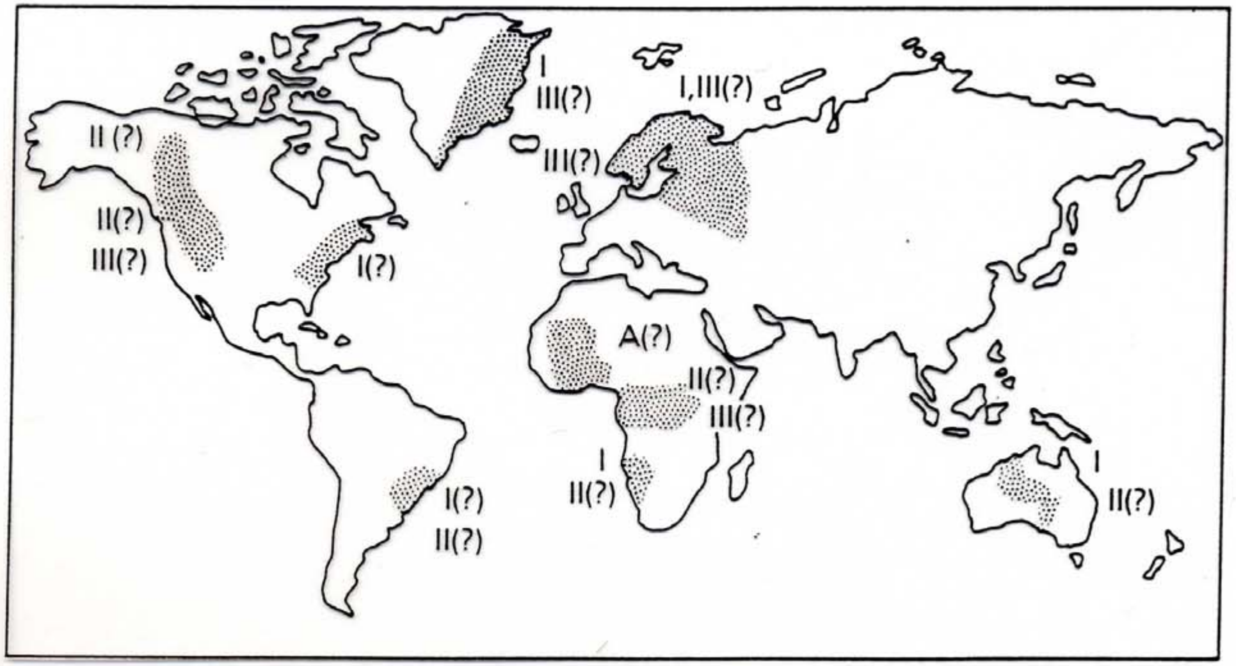


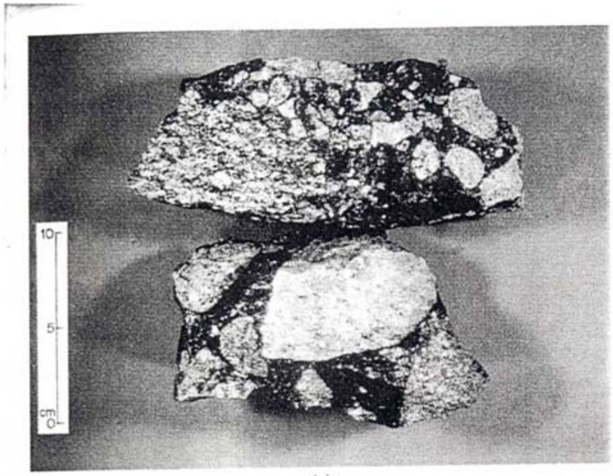
Fig. 12.3. Global distribution of major late Precambrian glacial centers on a map showing the present dispersal of continents. I, II, III refer to glaciations identified by Williams (1975) as centered on ~610 Ma, 750 Ma, and 950 Ma, respectively. A subsequent summary of late Precambrian glaciations (Hambrey and Harland, 1981a) suggests that these glaciations may not be as episodic as inferred by Williams. The letter A signifies that all three time intervals may be represented. [Modified from Frakes, 1979] *Reprinted by permission from L. Frakes, "Climates Throughout Geologic Time," copyright, 1979, Elsevier Scientific Publishers.*

Frakes (1979), in Crowley + North (1991)

Evidence for Glaciers on All Continents: 0.9-0.6 Ga

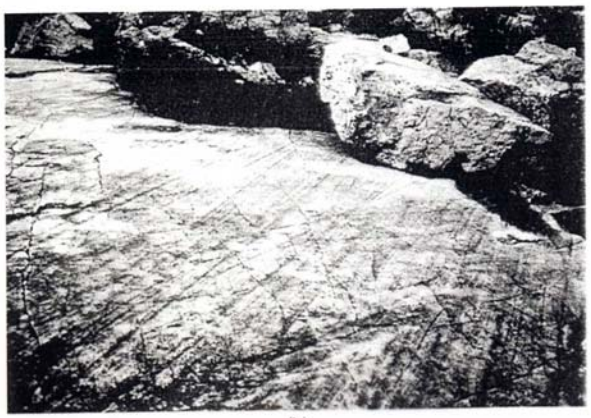
Geologic Evidence for Glaciers

Geologic Evidence For Glaciation



(a)

Tillites



(b)

Glacial Striations

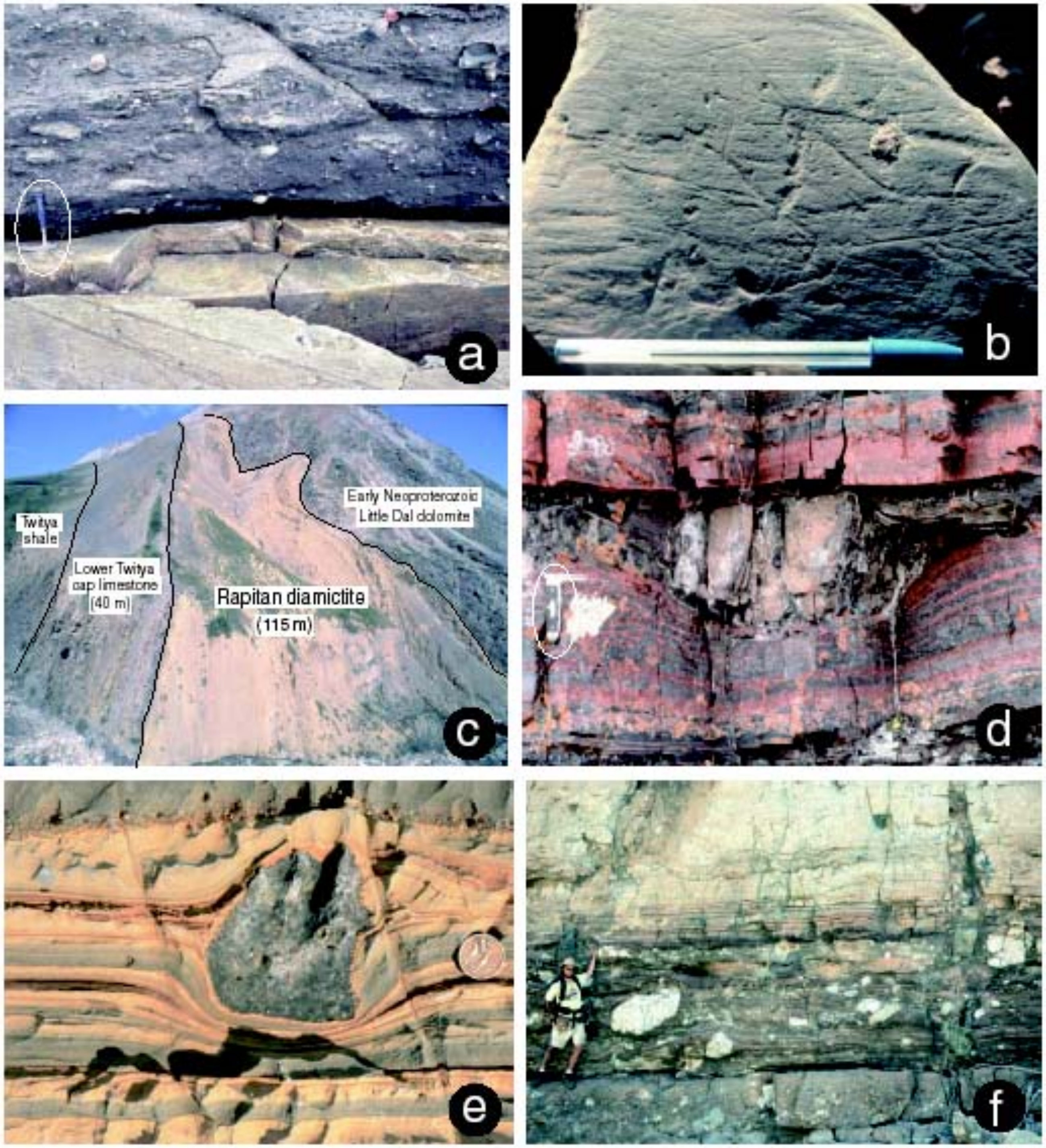
Dropstones

- *Tillites*: Packed pebbles, sand & mud. Remnants of moraines
- *Glacial Striations*: Scratches from rocks dragged by moving ice
- *Dropstones*: Rocks transported by icebergs and dropped into finely laminated sediment (IRD).

Kump et al. (1999)

Glacial sediments – poorly sorted, angular clasts including dropstones – Namibia c. 750 Ma

Image: Daniel P. Schrag



Neo-proterozoic Glacial Deposits

From Norway, Mauritania, NW Canada, Namibia.

- Tillites (a)
- Glacial striations (b)
- Dropstones (d,e,f)

Hoffman & Schrag (2002) *Terra Nova*, Vol. 14(3):129-155.

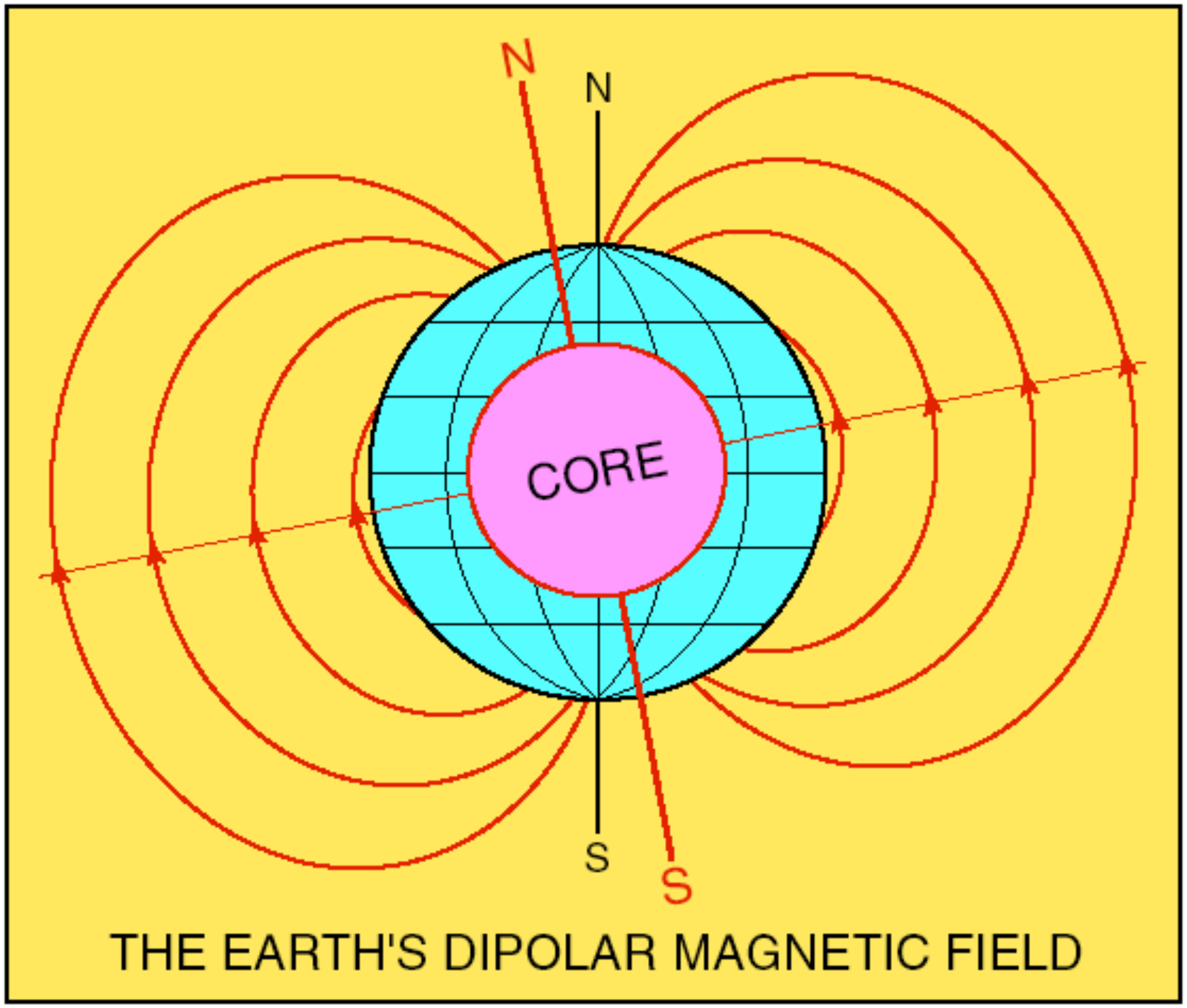
Equatorial Continents 600 Ma ?

Hoffman & Schrag (2000)

EARTH'S LANDMASSES were most likely clustered near the equator during the global glaciations that took place around 600 million years ago. Although the continents have since shifted position, relics of the debris left behind when the ice melted are exposed at dozens of points on the present land surface, including what is now Namibia (*red dot*).

•Harland & Rudwick (1964) identified glacial sediments at what looked like equatorial latitudes by paleomagnetism.
•George Williams (1975) identified a low latitude glacial sequence in S. Australia & attributed to episode of extreme obliquity (tilt).

Determining Paleo-latitude from Remnant Magnetism



- Paleomagnetism: latitude of rock formation
- Natural Remnant Magnetism (NRM): inclination varies with "magnetic" latitude
  - vertical @ magn poles
  - horz. @ magn equator (many Neoprot. glacial deposits)
- Magn polar drift avgs out on T~10 ky

Image from P. hoffman

Paleolatitude of Neoproterozoic Glacial Deposits Determined from Paleomagnetism

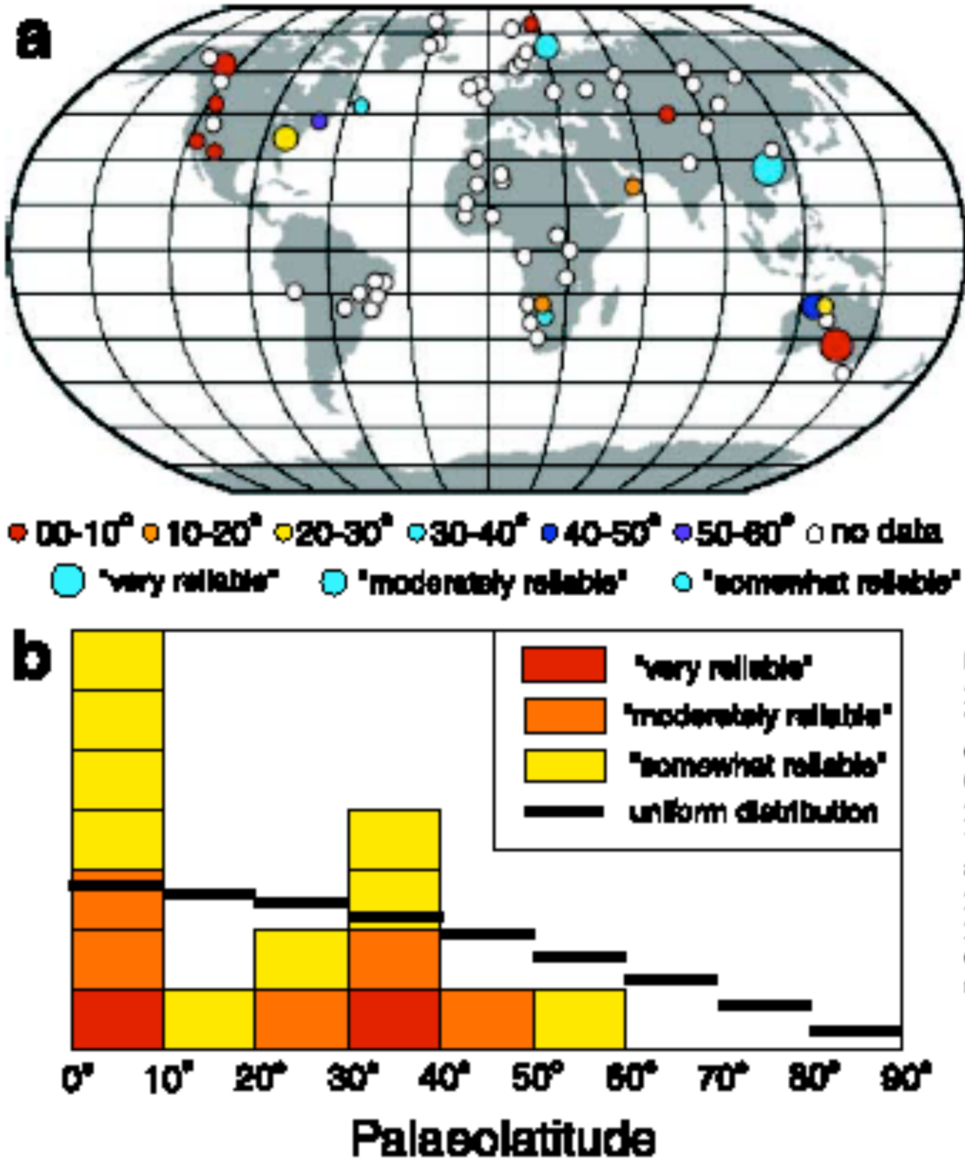
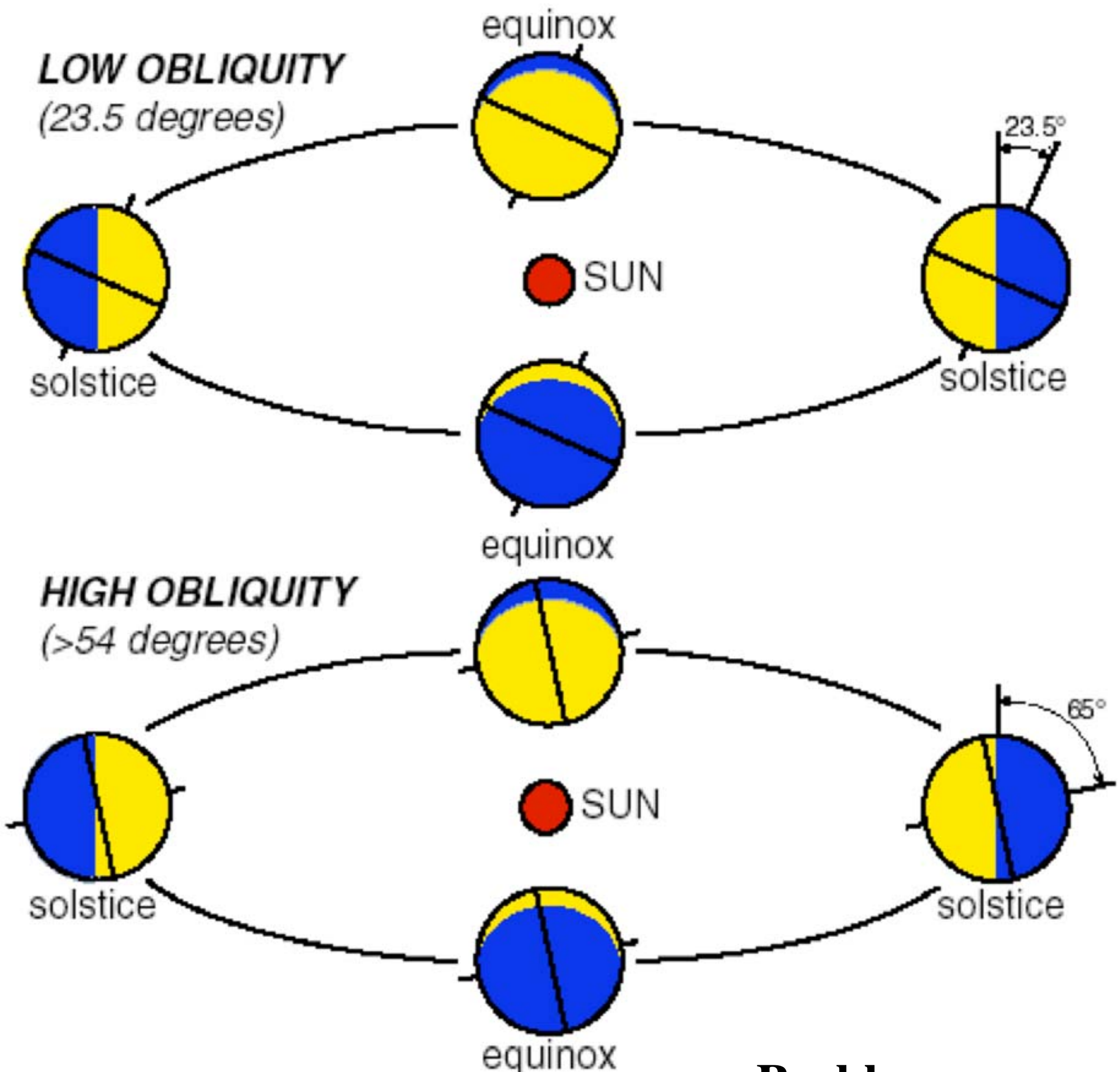


Fig. 1 Global distribution (a) of Neoproterozoic glaciogenic deposits with estimated palaeolatitudes based on palaeomagnetic data (modified from Evans, 2000). 'Reliability' takes into account not only palaeomagnetic reliability but also the confidence that the deposits represent regionally significant, low-elevation ice sheets (Evans, 2000). Histogram (b) of the same glaciogenic deposits according to palaeolatitude. The discontinuous steps show the expected density function of a uniform distribution over the sphere. Note the preponderance of low-latitude deposits and absence of high-latitude deposits. This finding would not be invalidated by plausible non-diploe components of the field, which would effectively raise the palaeolatitudes of only the mid-latitude results (Evans, 2000). The minimum in the distribution in the subtropics may reflect the meridional variation in precipitation minus evaporation due to the Hadley cells.

- Many glacial deposits appear to have been formed near the equator

Hoffman & Schrag (2002) *Terra Nova*, Vol. 14(3):129-155.

How to Explain Glaciers on all Continents when those continents appear to have been close to the equator?



High Obliquity Hypothesis

Williams (1975)

- **Earth's tilt (obliquity) controls seasonality**
- **At high tilt angles (> 54°) the poles receive more mean annual solar radiation than the tropics (sun constantly overhead in summer)!**
- **Glaciers *may* be able to form at low latitudes**

<u>Problems</u>:

- **Even the tropics get quite warm at the equinoxes**
- **Moon stabilizes obliquity**
- **Would need v. large impact to destabilize; moon orbit doesn't support this**

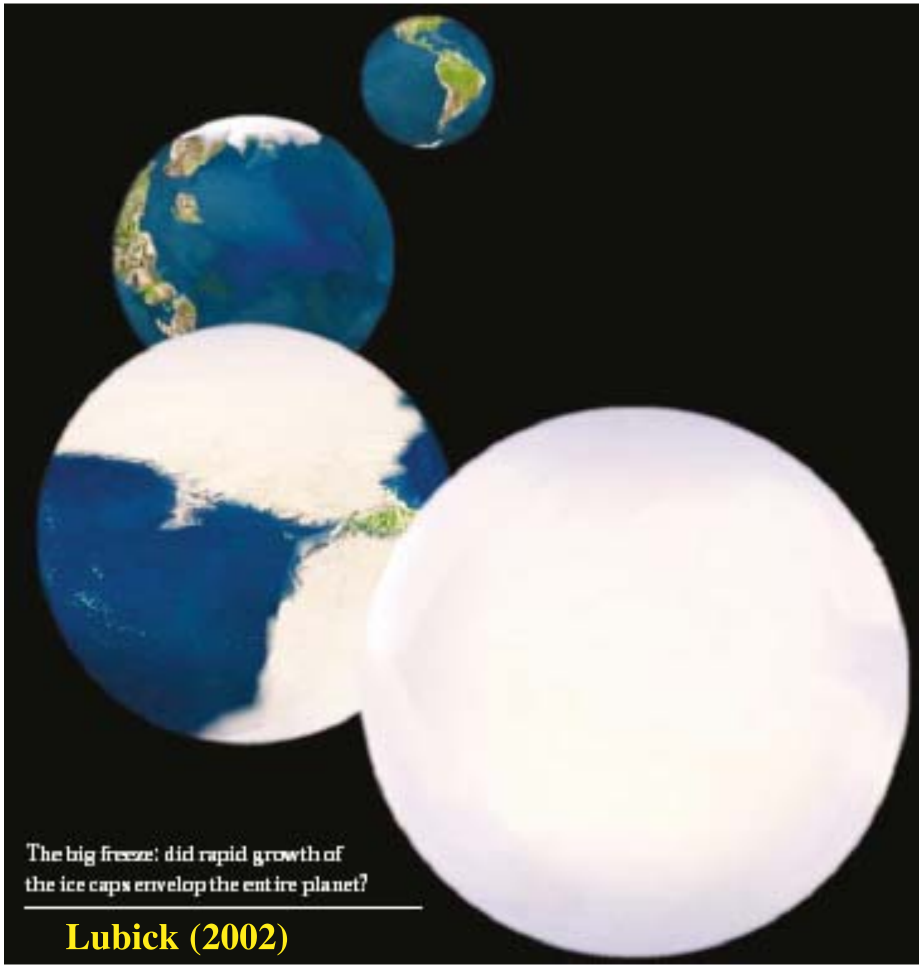
Image from P. hoffman

Snowball Earth Hypothesis: Geochemical C Cycle, Water Vapor-T & Ice-Albedo Feedbacks

~4 global glaciations followed by extreme greenhouses 750-580 Ma

• Harland (1964); Kirschvink (1992)

• Hoffman et al. (1998) *Science*, v. 281: 1342-6; Hoffman & Schrag (2000) *Sci. Am.*, Jan: 68-75.



Snowball Events:

• Breakup of equatorial supercontinent 770 Ma

• Enhanced weathering from increased rainfall (more land close to sea)

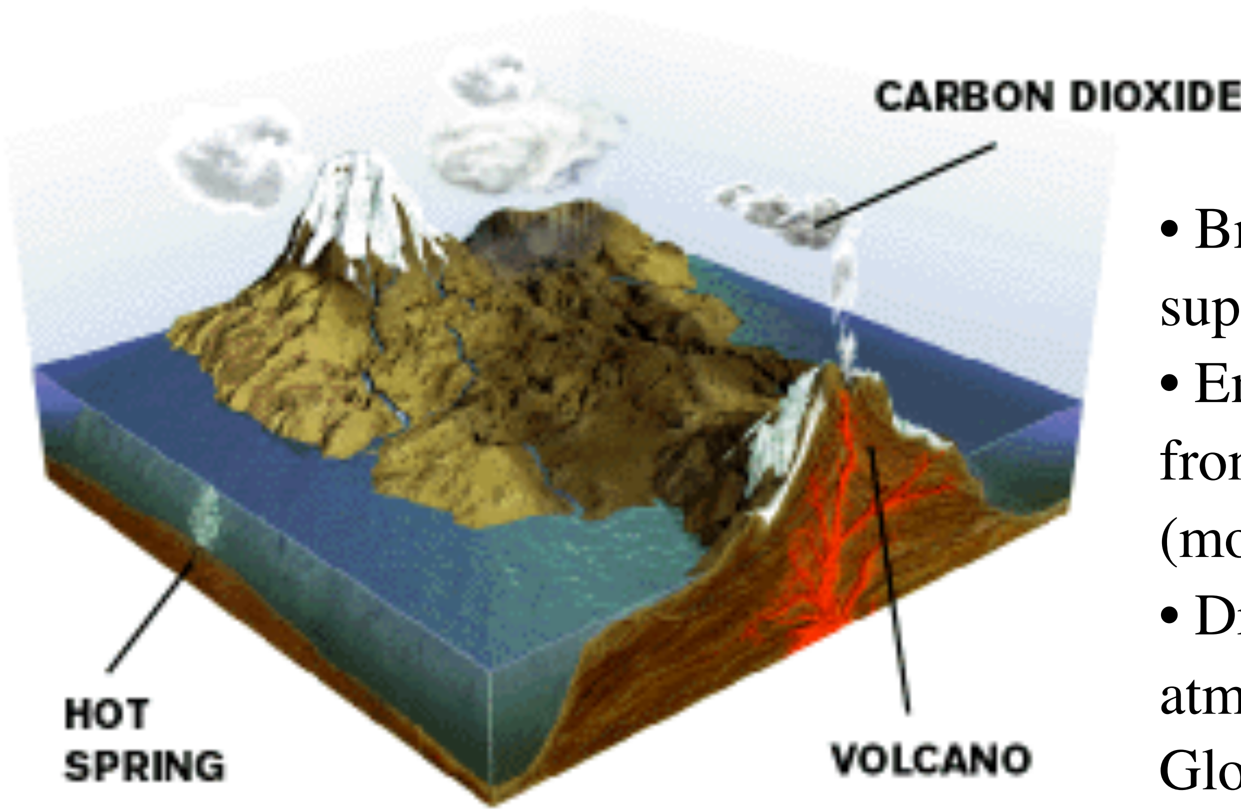
• Drawdown atmospheric CO_2 → Global cooling

• Runaway albedo effect when sea ice < 30° latitude

• Global glaciation for ~1-10 Myr (avg T ~ -50°C)

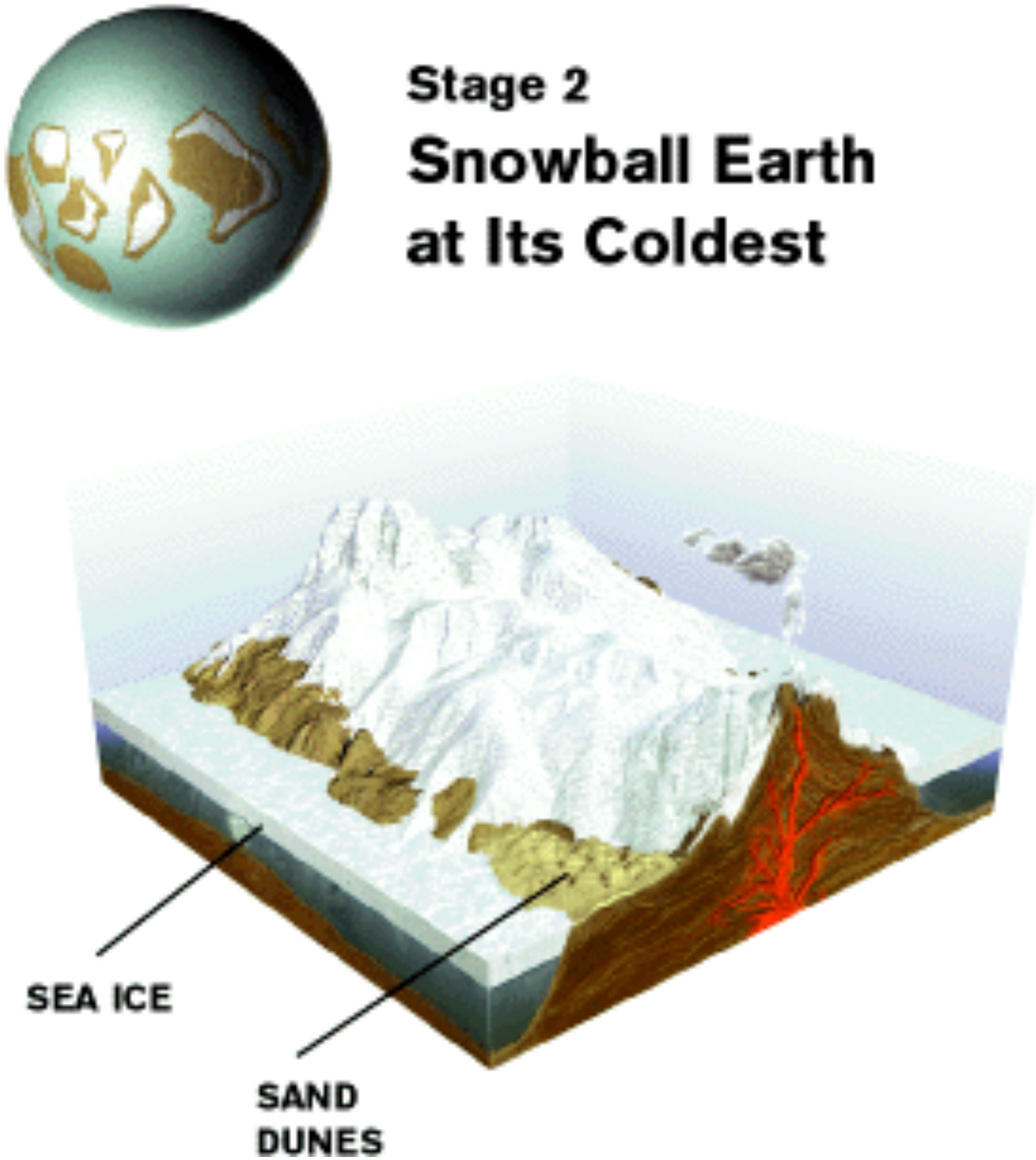
• Sea ice ~1000 m thick, geothermal heat flux (0.07 W/m^2) keeps ocean liquid

Prologue to Snowball



- Breakup of equatorial supercontinent
- Enhanced weathering from increased rainfall (more land close to sea)
- Drawdown atmospheric CO_2 → Global cooling

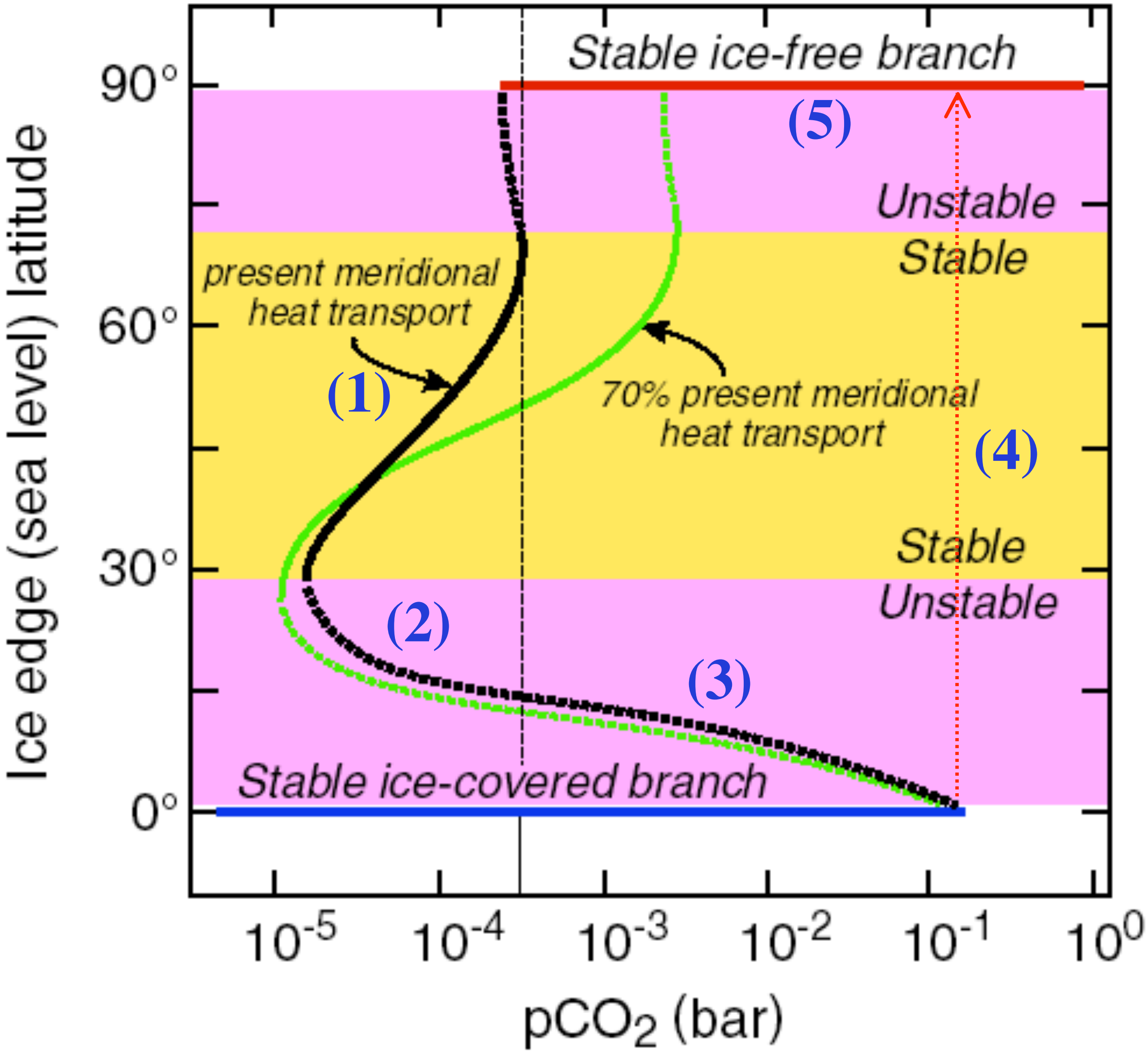
Hoffman & Schrag (2000)



Hoffman & Schrag (2000)

Deep Freeze

- Global cooling causes sea ice margin to move equatorward
- Runaway albedo effect when sea ice <30° latitude
- Entire ocean possibly covered with ice

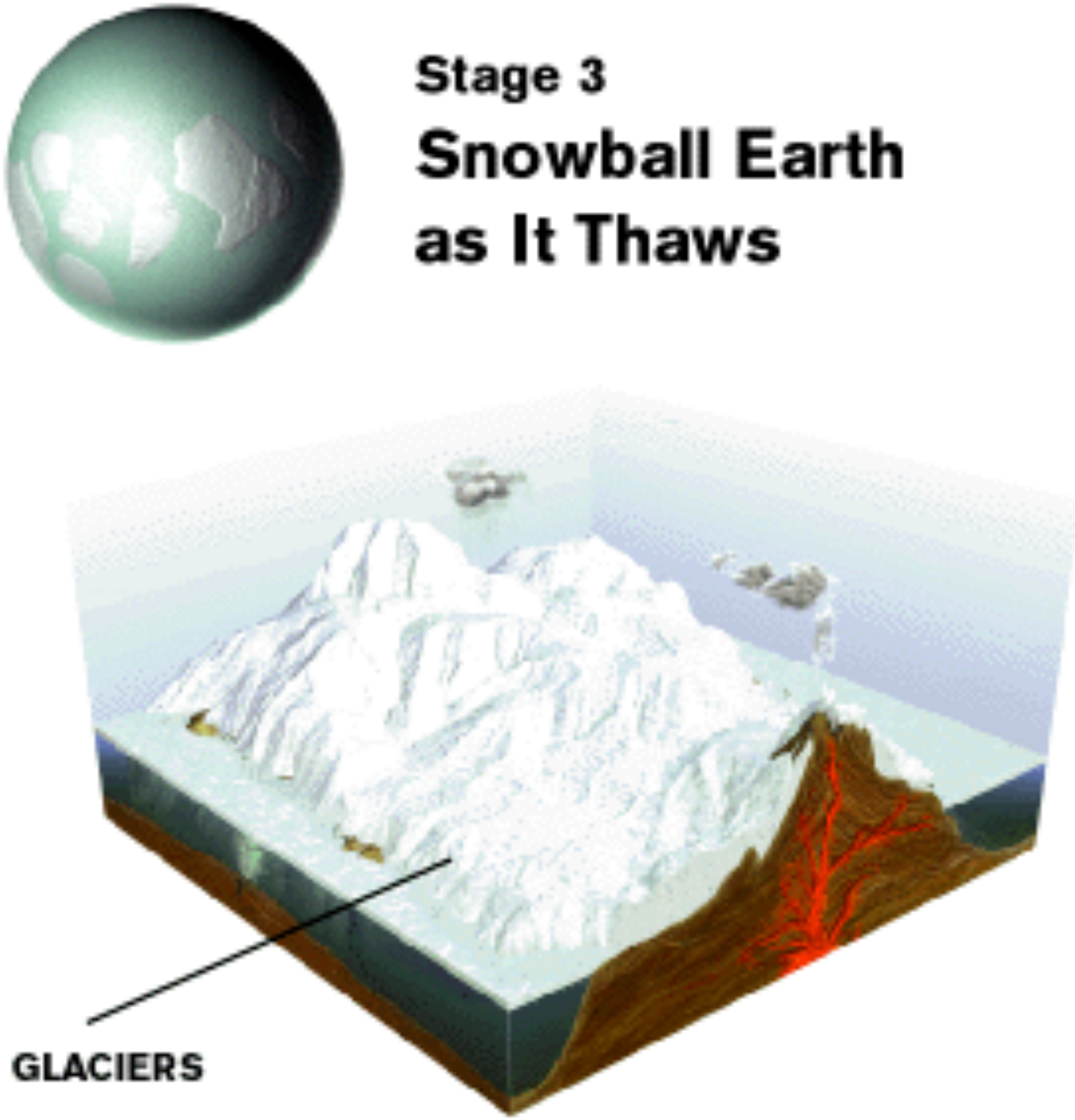


Steady-state ice lines as a function of atmospheric pCO_2, *see* Caldeira and Kasting (*Nature* **359**: 226, 1992), and Ikeda and Tajika (*Geophys. Res. Lett.* **26**: 349, 1999).

Runaway Albedo Feedback

1. **Eq continents, incr weathering, lowers CO_2, slow cooling, equatorward movement of ice.**
2. **Runaway albedo**
3. **Slow buildup of CO_2 from volcanoes**
4. **Rapid decay of ice in 10^2 yr. High T_s from enhanced $H_2$0-T feedback.**
5. **Slow CO_2 drawdown from weathering**

Image from P. hoffman



Hoffman & Schrag (2000)

Snowball

- Global glaciation for ~1-10 Myr (avg T ~ -50°C)

- Sea ice ~1000 m thick, geothermal heat flux (0.07 W/m^2) keeps ocean liquid

Glaciated Terrain

The Vallee Blanche, Mont Blanc, French Alps

Evidence for Snowball

• *Stratigraphy*: globally-dispersed glacial deposits.

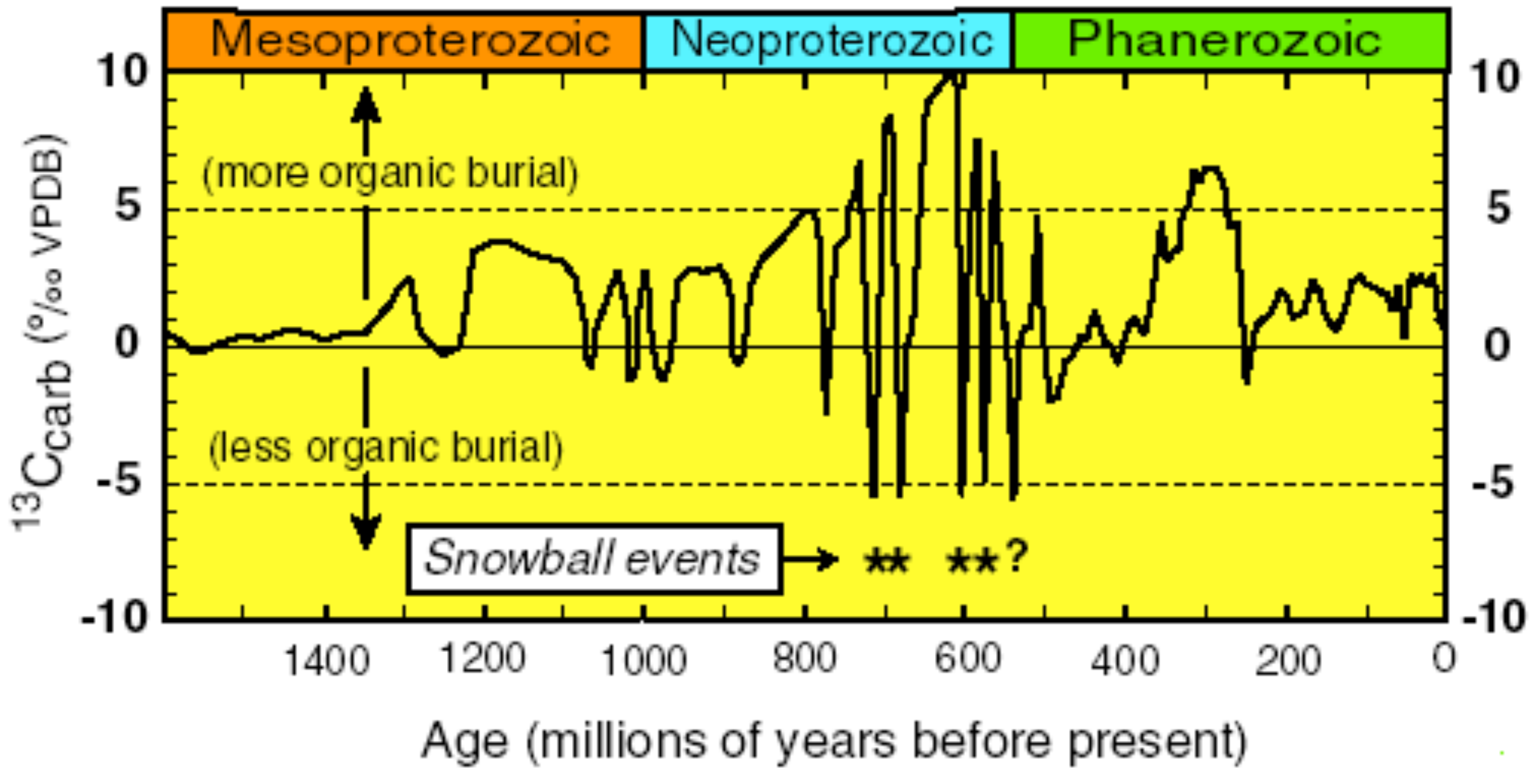
• *Carbon isotopes*: negative $\delta^{13}C_{CaCO3}$ excursions through glacial sections ($\delta^{13}C$ reaches ~ -5 to -7‰). Little or no biological productivity (no light).

• *Banded iron formations w/IRD*: only BIFs after 1.7 Ga. Anoxic seawater covered by ice.

• *Cambrian explosion (circumstantial)*: Rapid diversification of multicellular life 575-525 Ma expected to result from long periods of isolation and extreme environments (genetic "bottleneck and flush").

Carbon Isotopic Evidence for Snowball

- $\delta^{13}C$ values of -5‰ (mantle value) consistent with "dead" ice-covered ocean



Secular variation in carbon isotopic composition of shallow marine carbonates over the last 1600 million years (adapted from Kaufman, 1997; Kah et al., 1999).

Image from P. hoffman

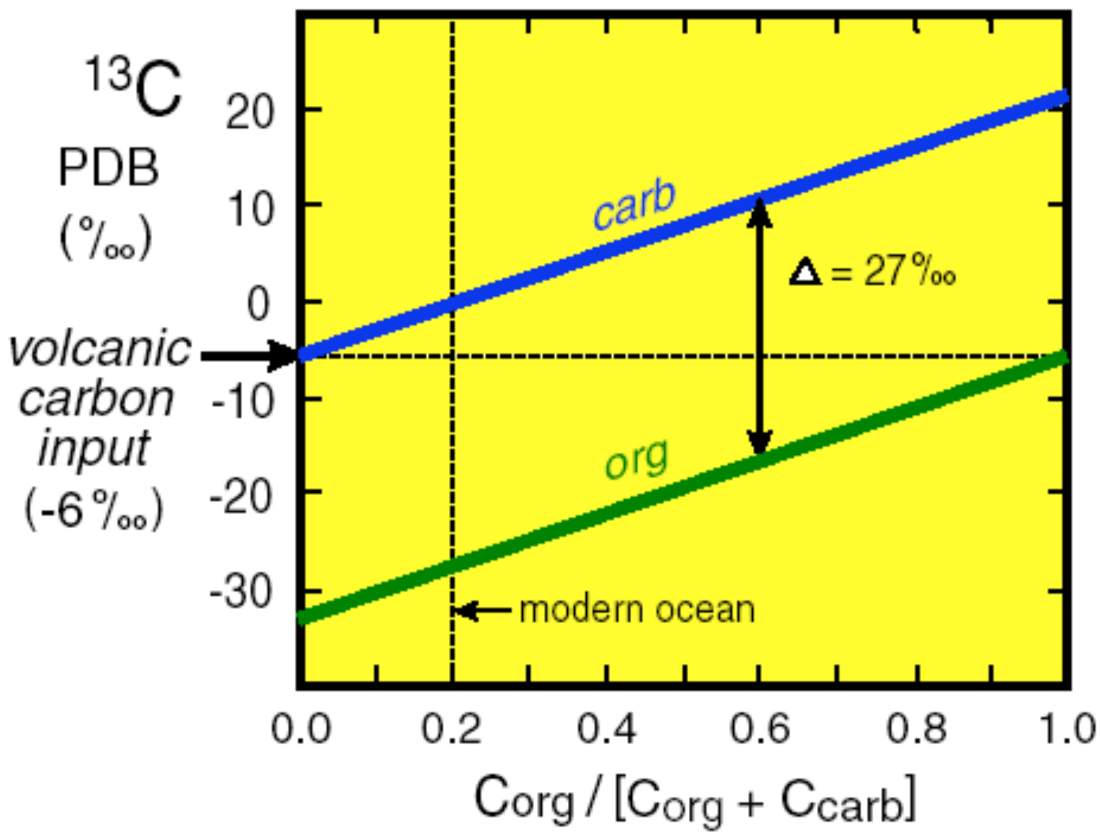
Carbon Isotope Fractionation

inorganic carbon burial:

$CO_2 + CaSiO_3 \longleftrightarrow CaCO_3 + SiO_2$

organic carbon burial:

$CO_2 + H_2O \longleftrightarrow CH_2O + O_2$

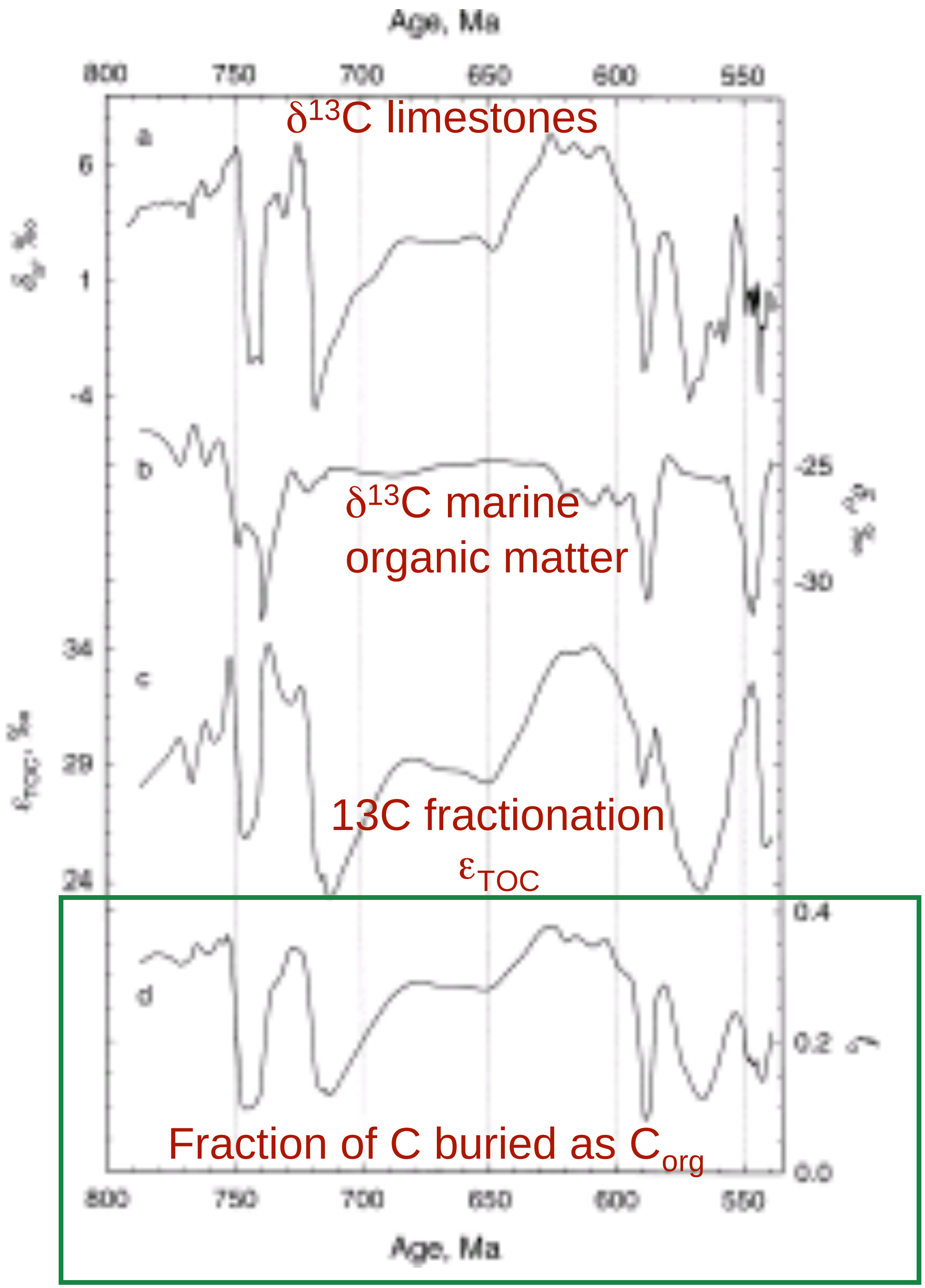


$^{13}C_{PDB}(sample) = [(R_{sample} - R_{PDB}) / R_{PDB}] \times 10^3$

(where $R = {}^{13}C / {}^{12}C$)

- As fraction of carbon buried approaches zero, $\delta^{13}C$ of $CaCO_3$ approaches mantle (input) value

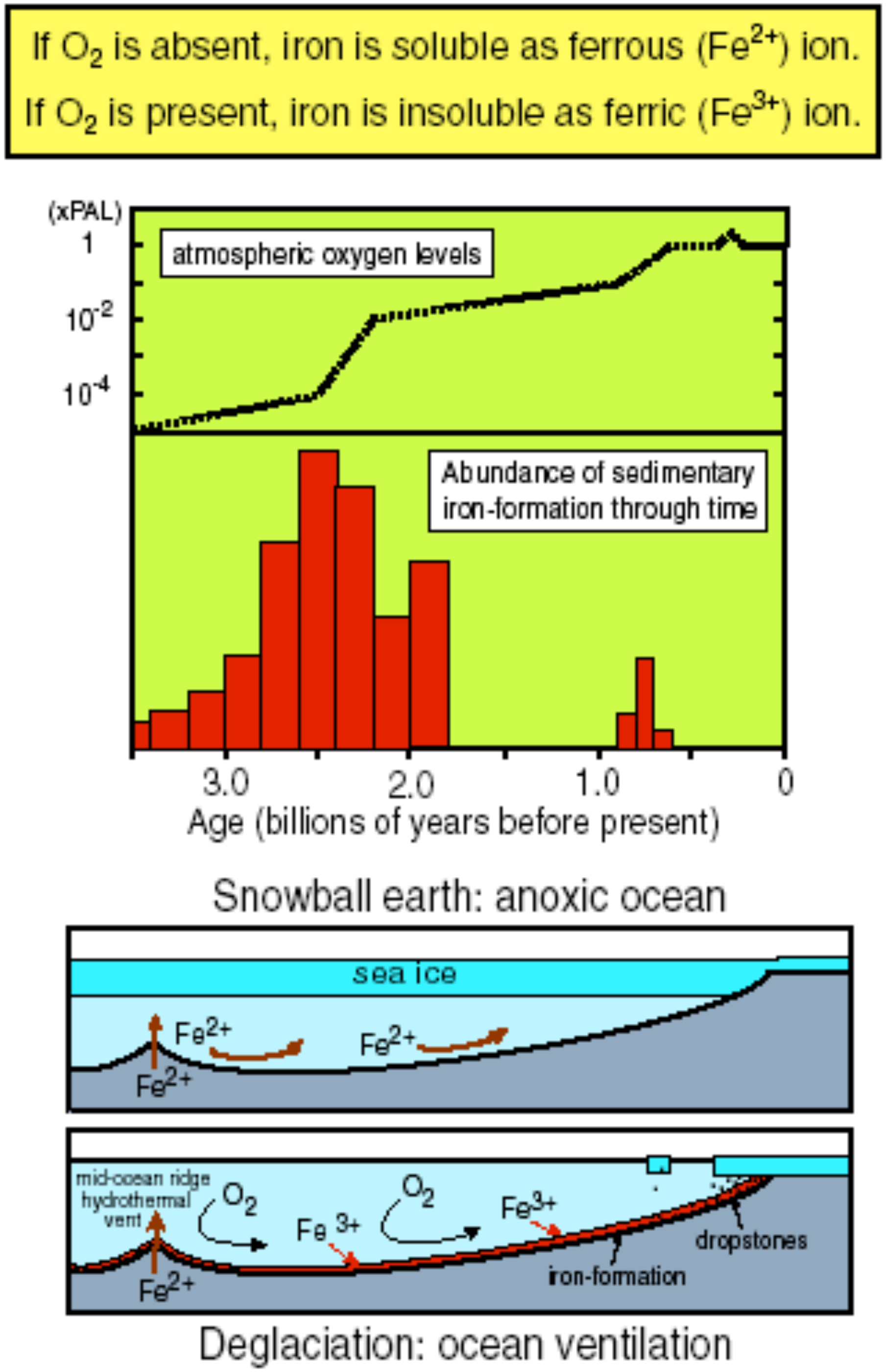
Image from P. hoffman



Carbon Isotopic Excursions 800-500Ma

- Carbon isotopes in organic and inorganic carbon from the Neoproterozoic indicate 4 periods when 10% or less of the carbon buried in the rock record was organic.
- Consistent with very low primary productivity in an ice-covered ocean

Hayes et al, Chem Geol. 161, 37, 1999



The Return of Banded Iron Formations

- After a ~1 Gyr absence, BIFs return to the geologic record
- Implies anoxic ocean
- Consistent with ice-covered ocean

Image from P. hoffman

BIF + Dropstone = Ice-covered, anoxic ocean?

McKenzie Mtns., Western Canada

Image from P. hoffman

Metazoan Explosion: Response to genetic bottlenecks & flushes?

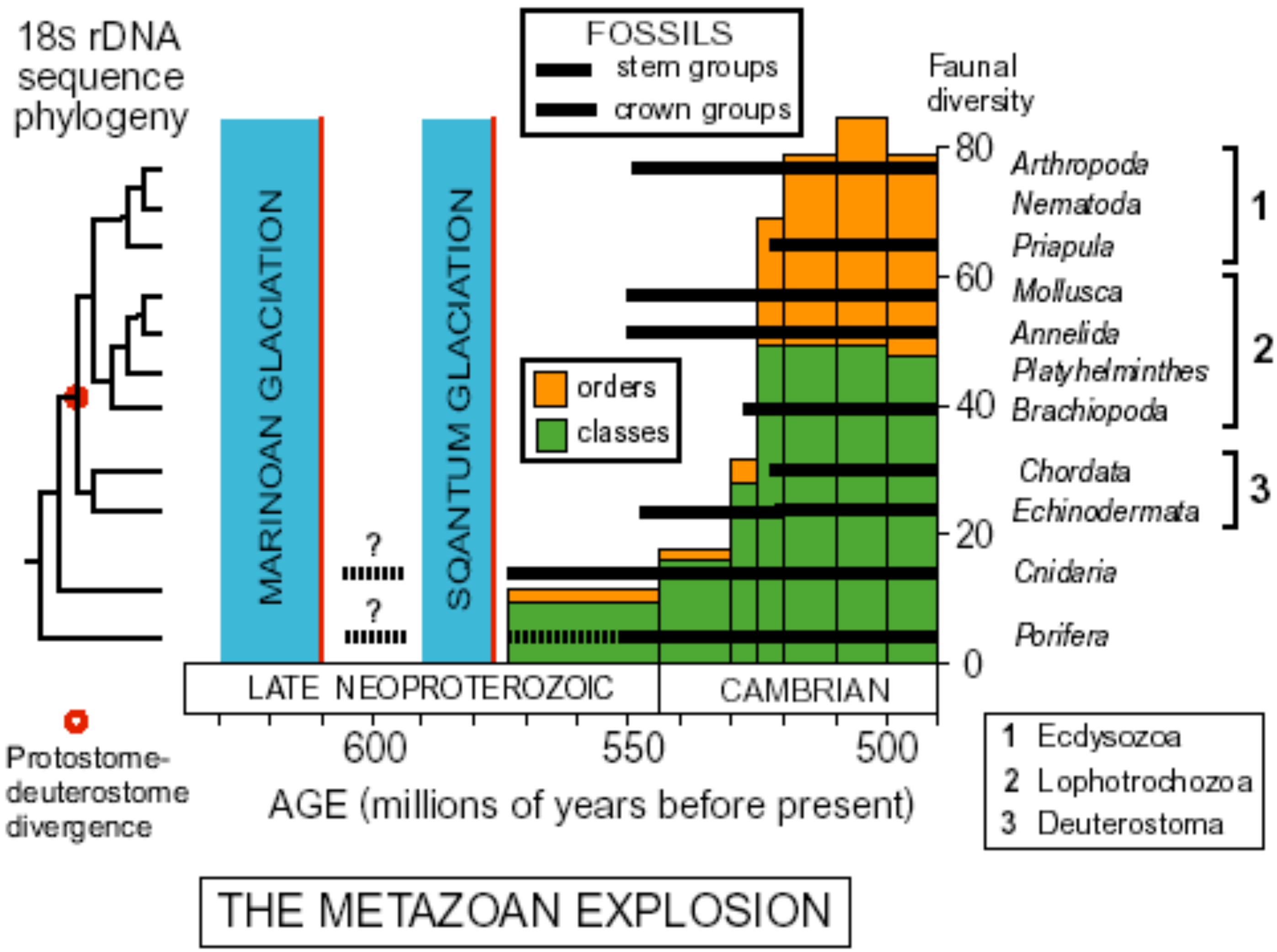


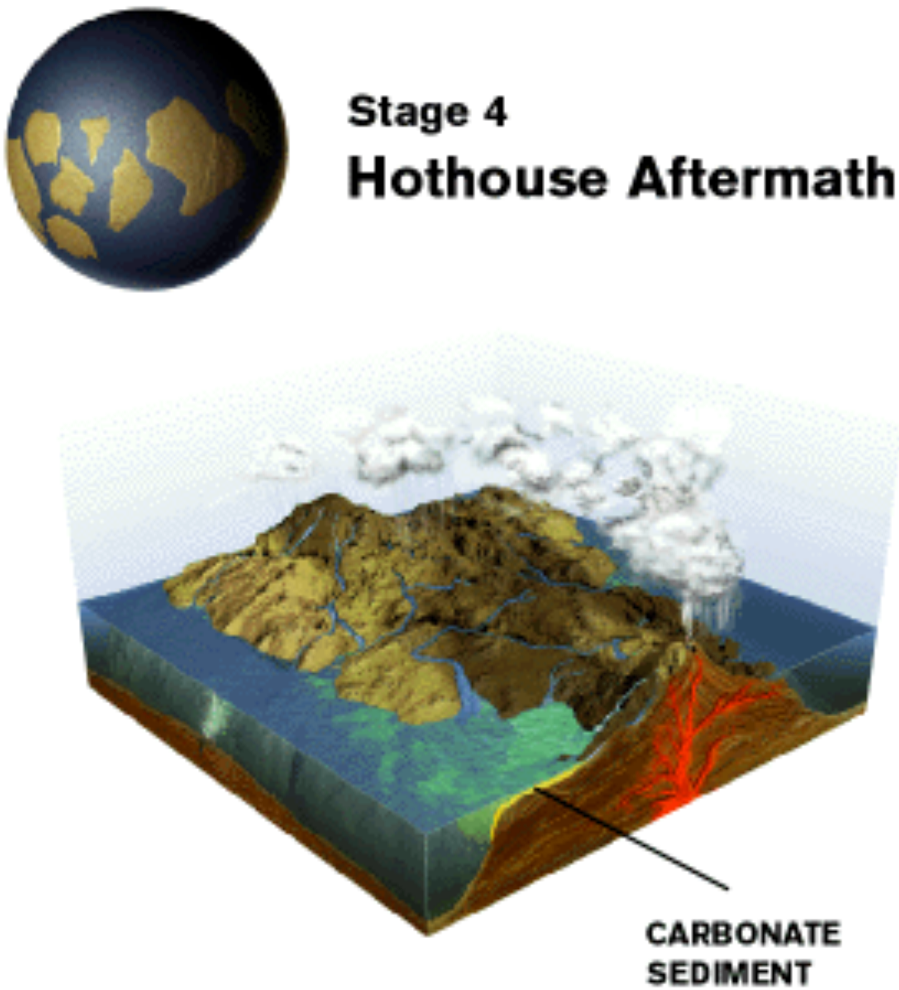
Image from P. hoffman

Breaking out of the Snowball

- Volcanic outgassing of CO_2 over $\sim 10^6$ yr may have increased greenhouse effect sufficiently to melt back the ice.

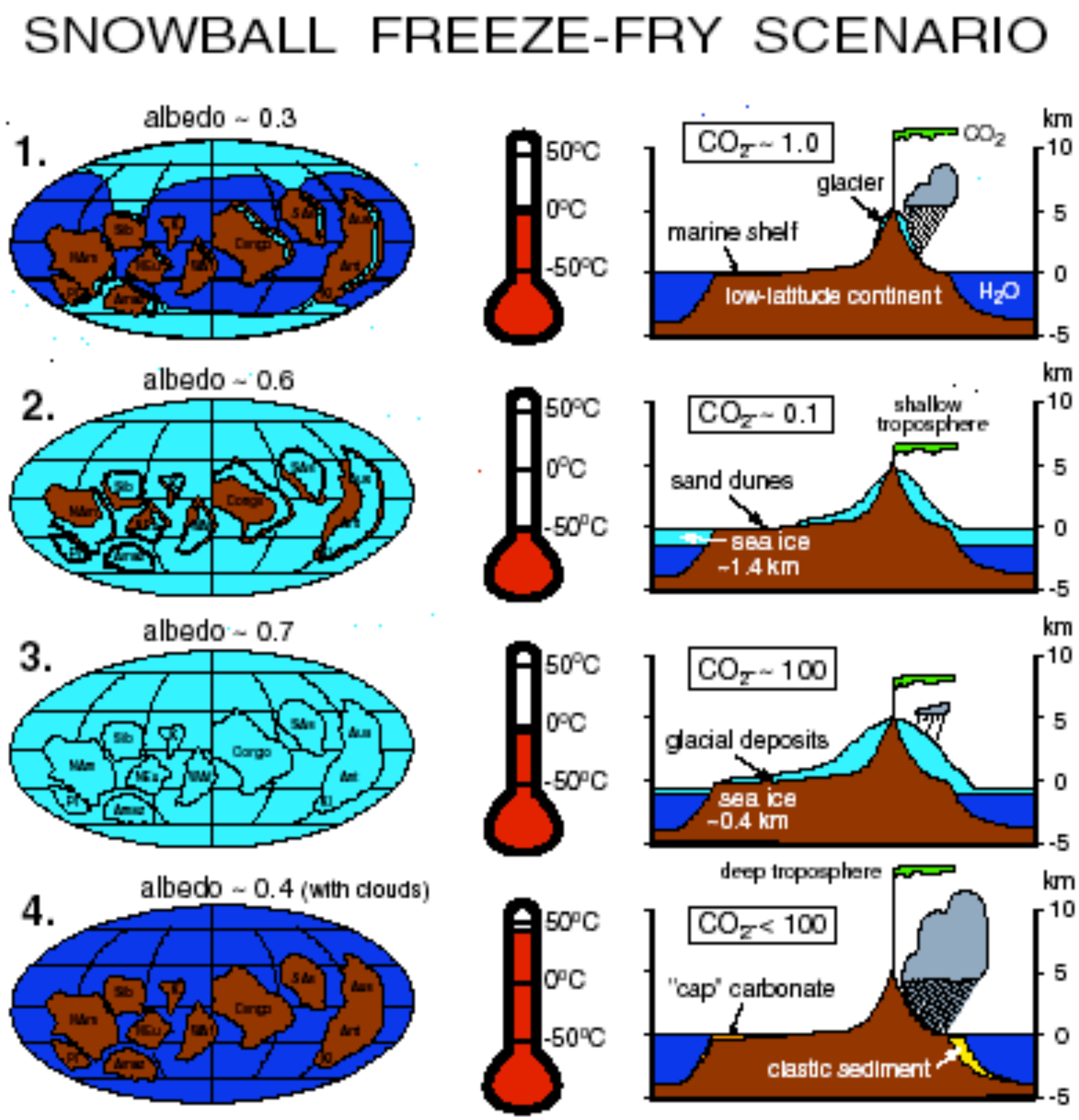
Image from Lubick (2002) *Nature*, Vol. 417: 12-13.

Bring on the Heat: Hothouse follows Snowball?



Hothouse Events

- Slow CO_2 buildup to ~350 PAL from volcanoes
- Tropical ice melts: albedo feedback decreases, water vapor feedback increases
- Global T reaches ~ +50°C in 10^2 yr
- High T & rainfall enhance weathering
- Weathering products + CO_2 = carbonate precipitation in warm water

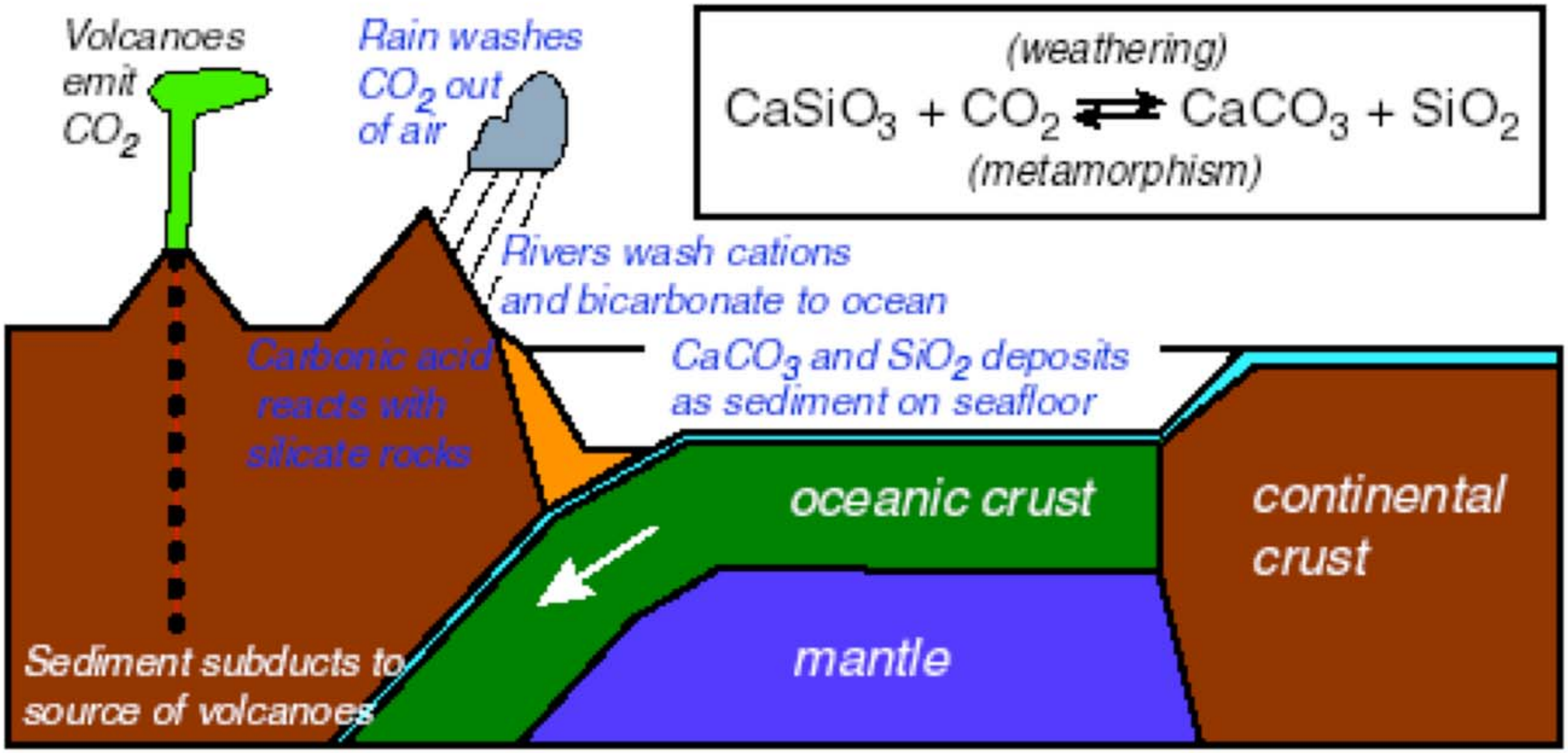


Cartoon of one complete 'snowball' episode, showing variations in planetary albedo, atmospheric carbon dioxide, surface temperature, tropospheric depth, precipitation, glacial extent, and sea ice thickness. Stage 1. incipient glaciation; 2. runaway ice-albedo (onset of 'snowball'); 3. end of 'snowball'; 4. transient 'hothouse' aftermath.

One Complete Snowball-Hothouse Episode

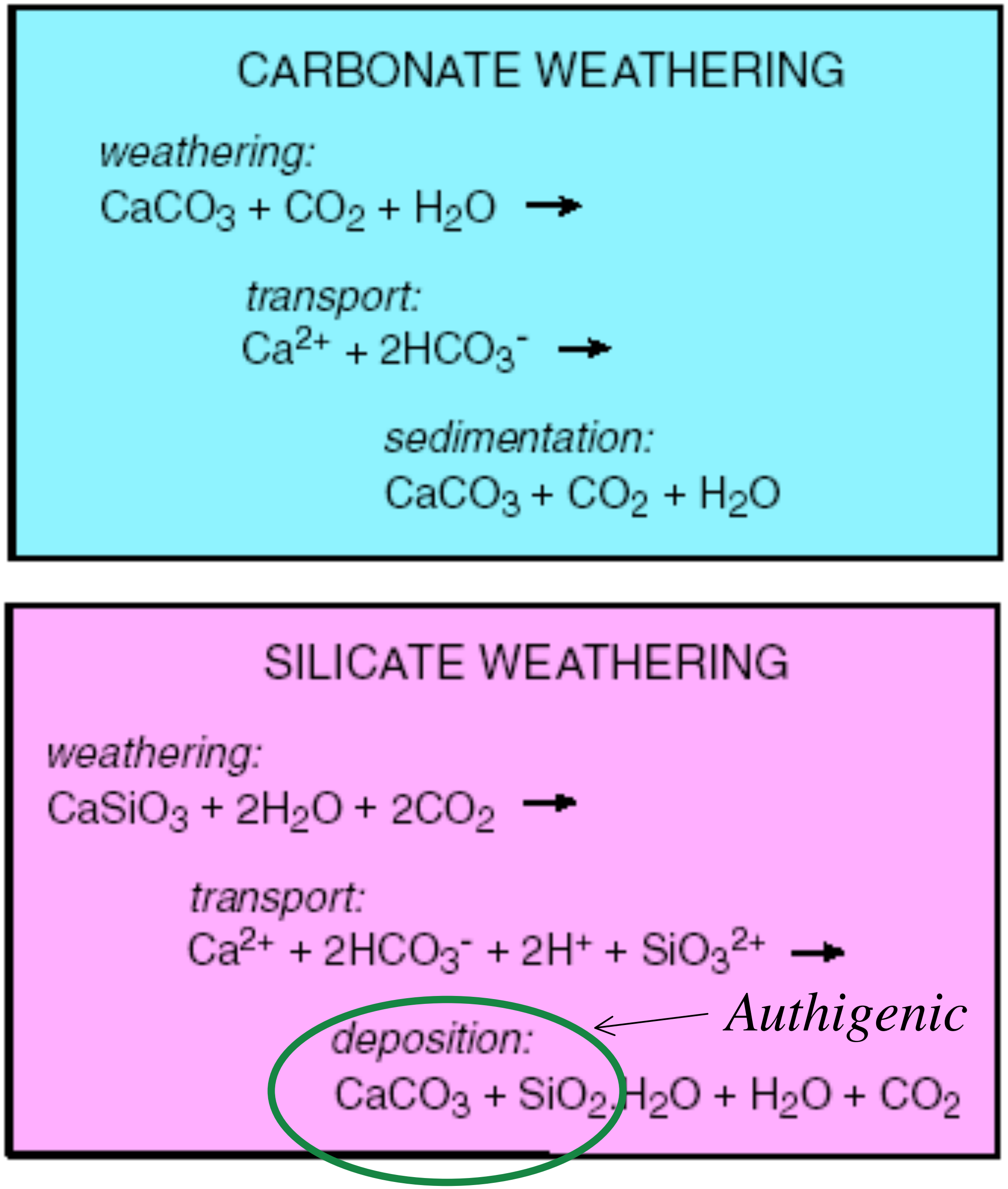
Image from P. hoffman

The Geochemical Carbon Cycle



[Processes lettered in blue are absent in a snowball Earth]

Image from P. hoffman



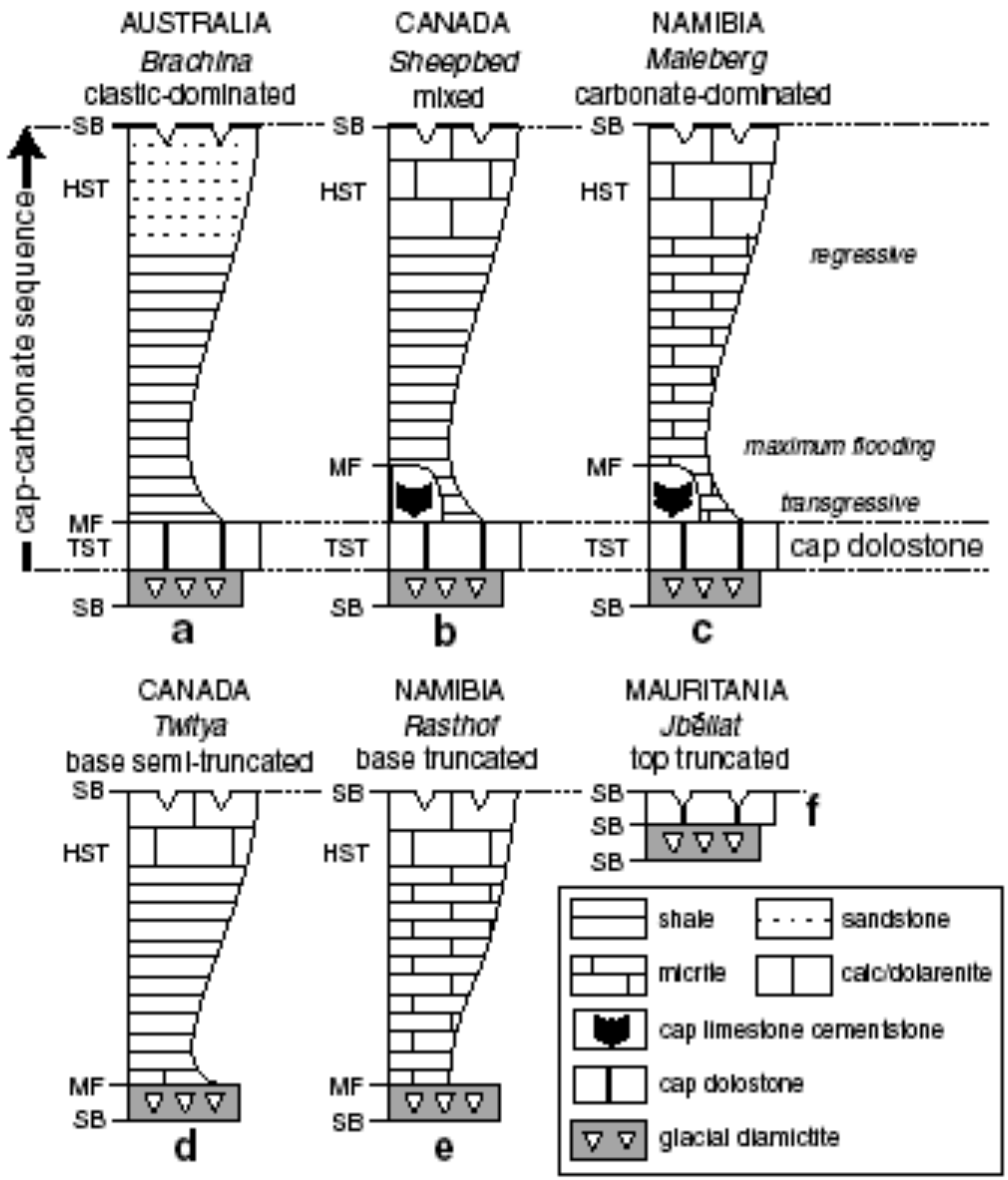
Enhanced Weathering of Rocks Results in Precipitation of Minerals in Ocean

- High T & CO_2 cause increase in weathering rate of continents
- Products of weathering carried to ocean by rivers
- Precipitated as $CaCO_3$ & SiO_2 minerals in ocean

Geologic Evidence for Hothouse Aftermath: "Cap Carbonates"

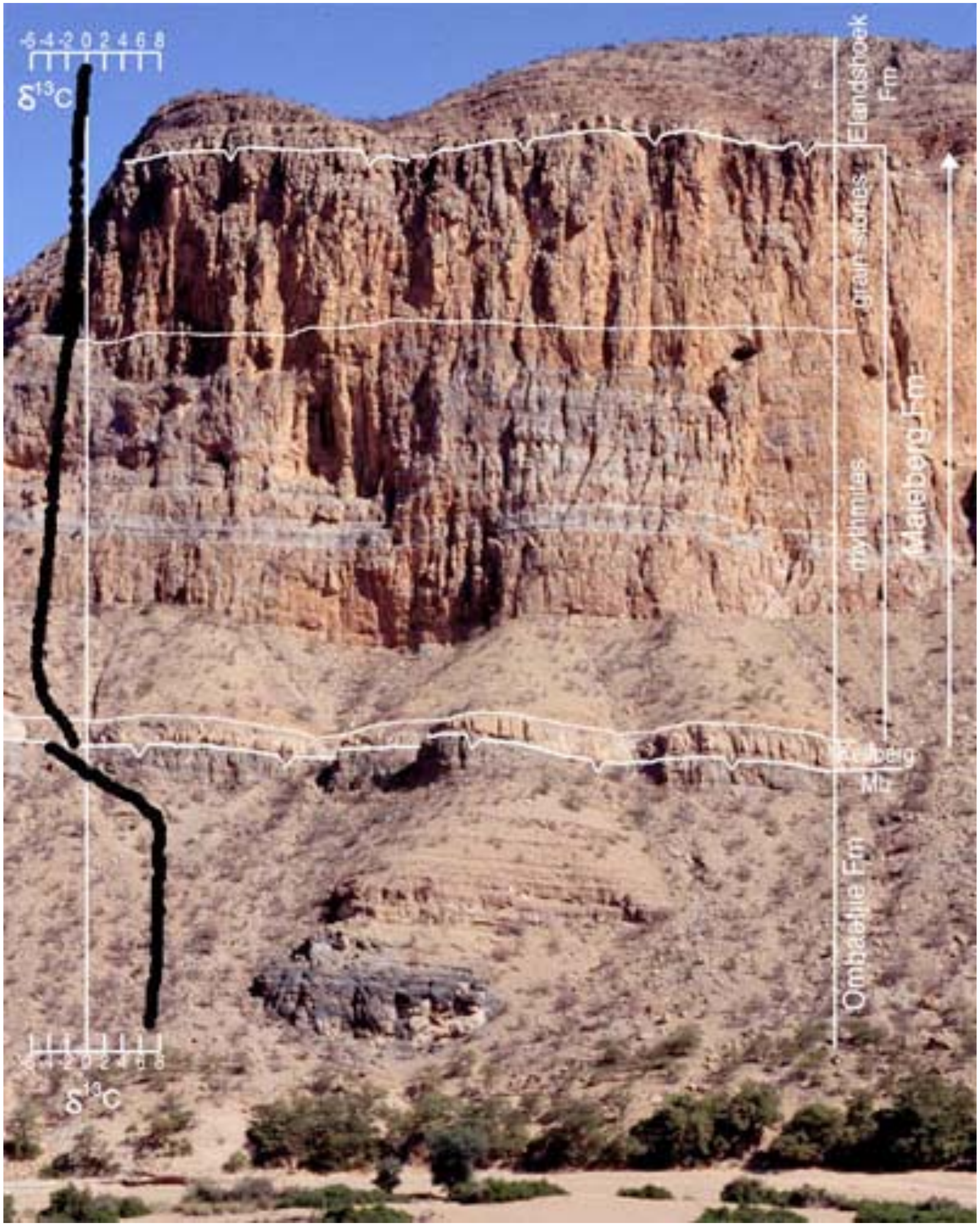
Thick sequences of inorganically precipitated $CaCO_3$ cover Neoproterozoic glacial deposits globally.

Neo-proterozoic Cap Carbonates



- Thick sequences of inorganically precipitated carbonate minerals cover Late Proterozoic glacial deposits.
- Consistent with massive flux of weathering products to ocean in snowball aftermath.

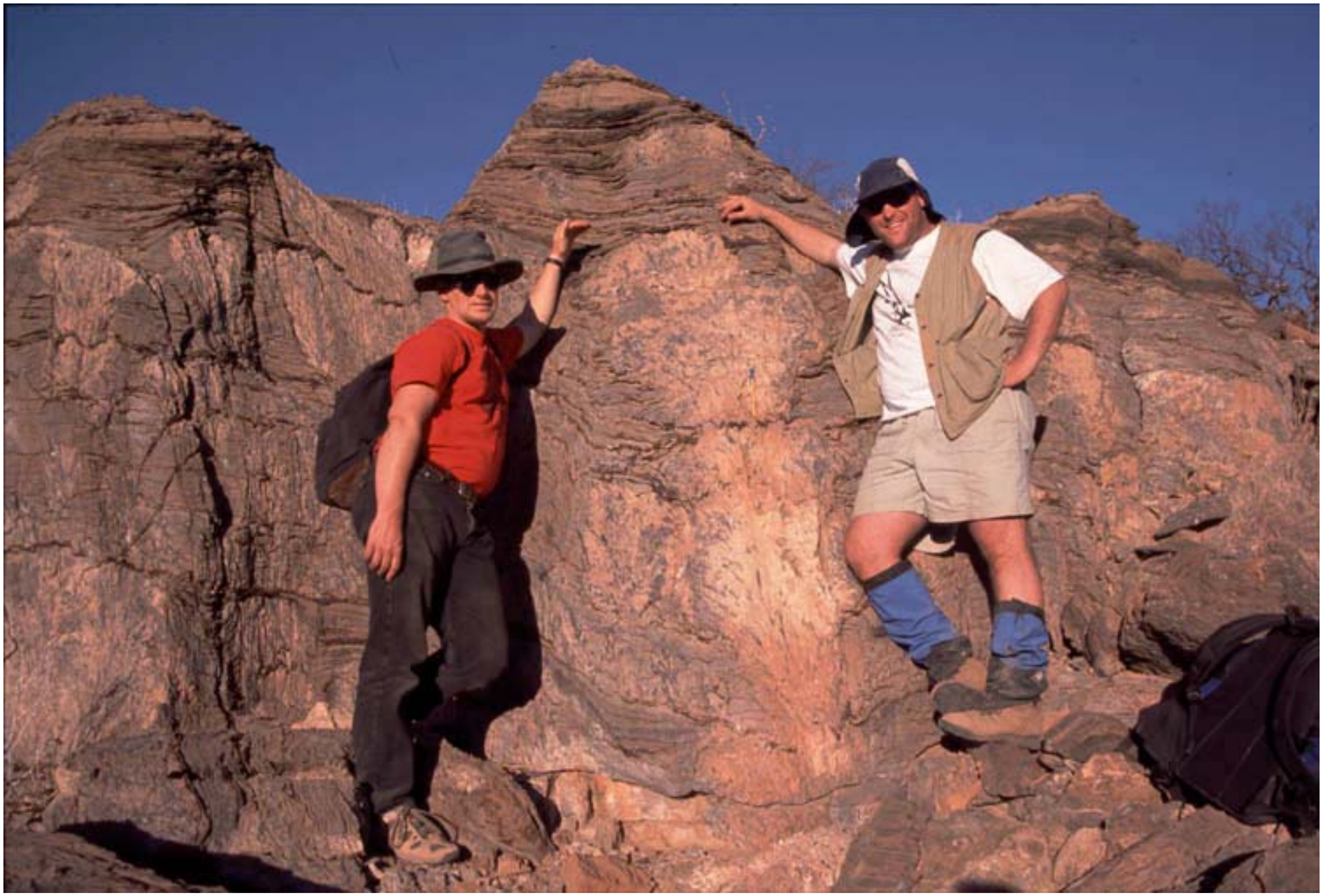
Hoffman & Schrag (2002) *Terra Nova*, Vol. 14(3):129-155.



Glacial Deposit Overlain by **Cap Carbonate** in Namibia (~700 Ma)

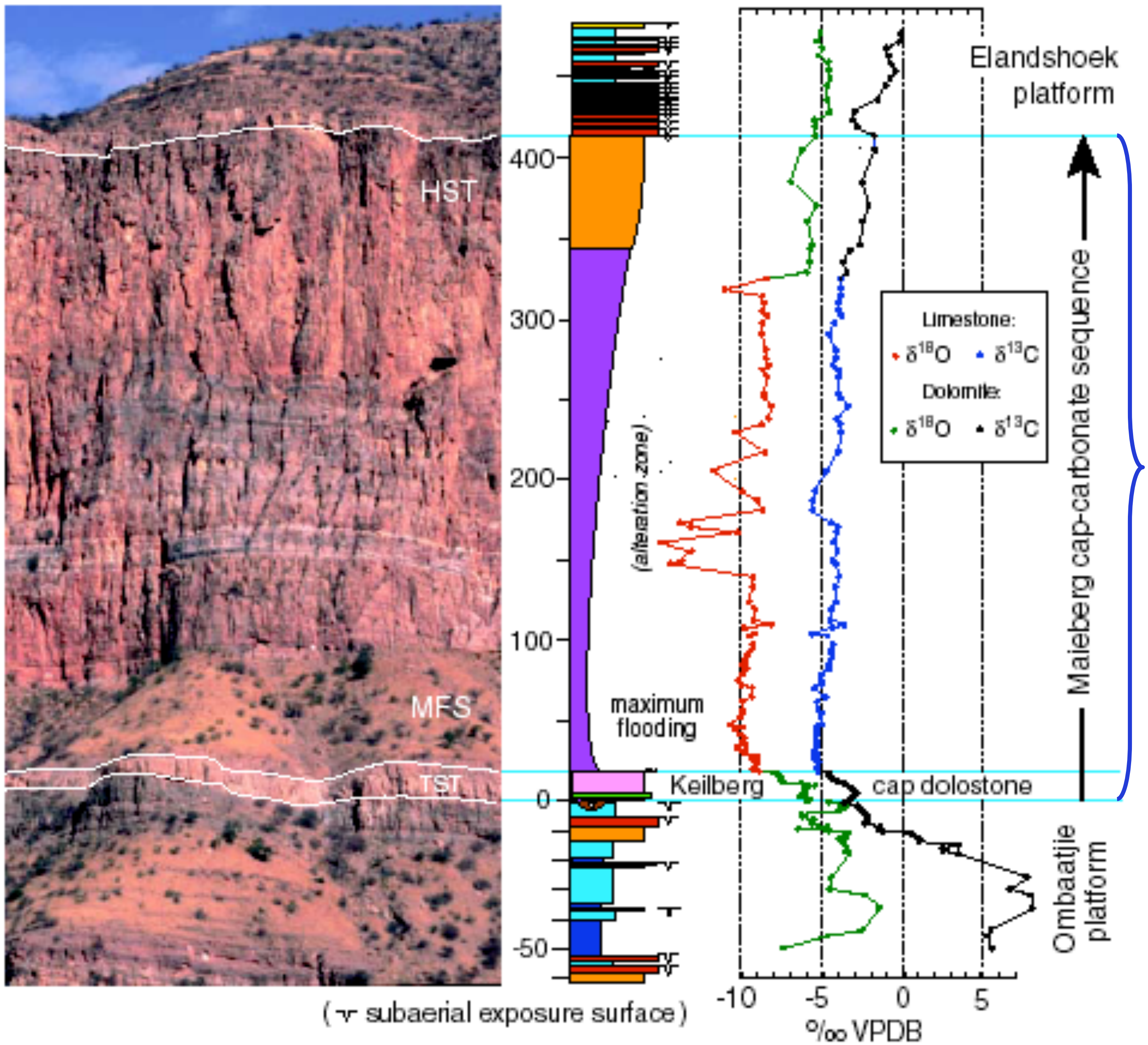
Hoffman & Schrag (2000)

Aragonite ($CaCO_3$) Fan in Namibia



- Carbonate fans form when $CaCO_3$ rapidly precipitates from water

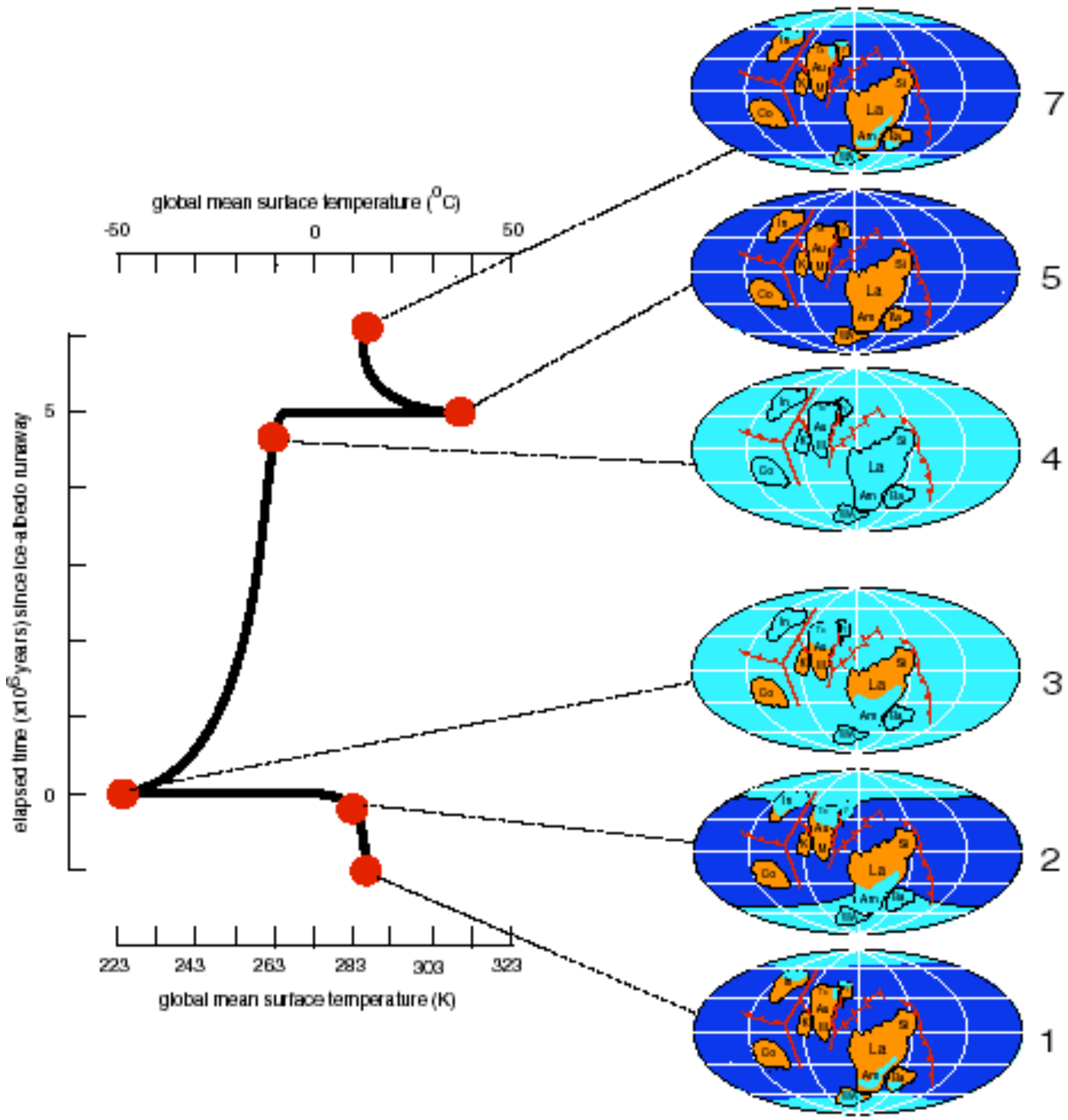
Image from P. hoffman

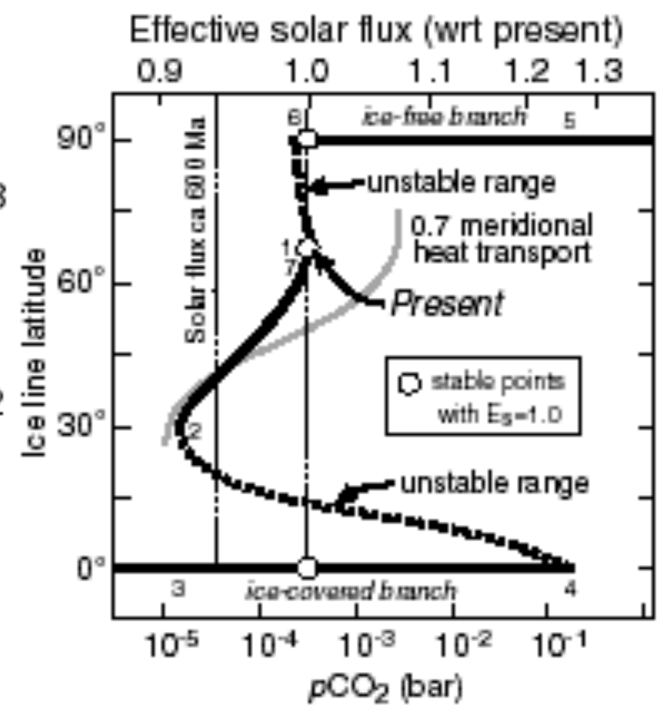


Geologic & Isotopic Change Associated with Snowball Event (Namibia)

Hoffman & Schrag (2002) *Terra Nova*, Vol. 14(3):129-155.

Summary of Snowball-Hothouse Sequence



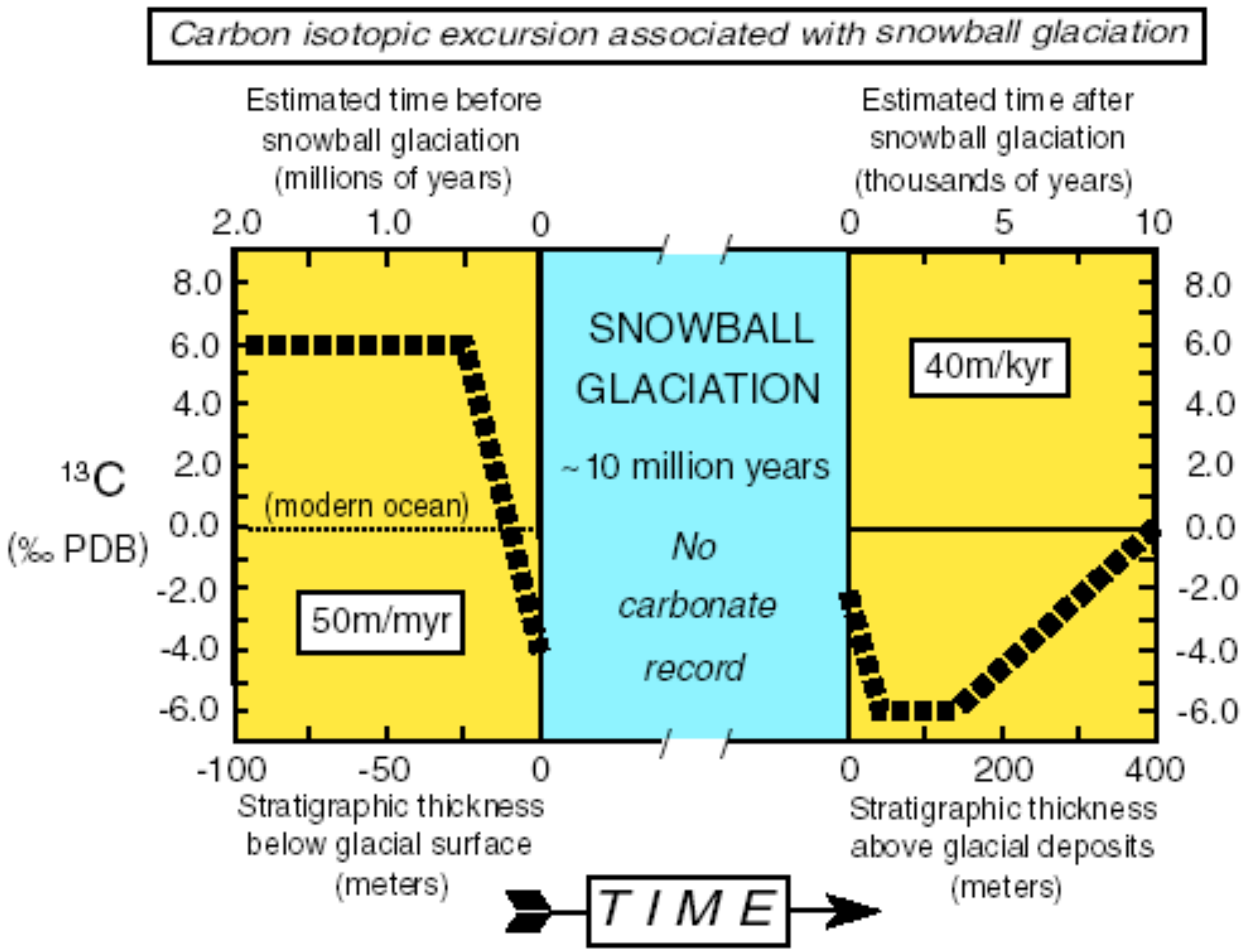


Note: T estimated from E balance model

Hoffman & Schrag (2002) *Terra Nova*, Vol. 14(3):129-155.

How Long Did it Last?

• *Big open question! Recent work by Sam Bowring (MIT) suggests glacial episode lasted < 1 Myr*



• Glacial episodes probably lasted < 1 Myr

• Cap carbonates likely deposited within 10^3-10^4 yr

Image from P. hoffman

What kept this from happening after ~580 Ma?

• Higher solar luminosity (~5% increase)
• Less landmass near equator = lower weathering rates (?)

→*Caveat:* John Edmond, a highly regarded geochemist at MIT (now deceased) found that weathering rates were limited by abundance of fresh rock, not temperature. Based on analyses of dissolved major & minor elements in Siberian and tropical rivers.

• Increased bioturbation (eukaryote diversity following re-oxygenation of ocean) = higher rates of remineralization: Less C accumulation in sediments offsets lower weathering rates, so atmospheric CO_2 may be kept from reaching extremes
• Lower iron & phosphorous concentrations in better-oxygenated Phanerozoic ocean [Fe(II) is soluble; Fe(III) is less so]: Decreased 1° production = Decreased CO_2 drawdown.

→ What we would like to know:
CO_2 concentrations through snowball/hothouse cycle.

Potential Problems with the ‘Snowball Earth hypothesis’

Snowball fights

Did the world freeze over some half a billion years ago? Two Harvard scientists think so, but convincing other climatologists is proving difficult. Naomi Lubick tracks the latest twists and turns in the snowball Earth debate.

The big freeze: did rapid growth of the ice caps envelop the entire planet?

Paul Hoffman and Daniel Schrag have had a busy few years. In 1998, the two Harvard University geologists rekindled a radical idea: that on at least one occasion between 580 million and 750 million years ago, the Earth lay entirely encrusted in ice for tens of millions of years. This ‘snowball Earth’ hypothesis seemed to explain some puzzling geological data. But it was controversial then, and the debate shows no sign of letting up.

Sceptics first asked how the Earth could freeze and thaw in such a short geological time. Climate modellers have since questioned whether ice sheets could have reached the Equator. And last year came an assault on Hoffman and Schrag's central line of geological evidence. The proponents of snowball Earth, it seems, are on the defensive once more.

The idea of a global glaciation was first proposed in the 1960s by Mikhail Budyko of the Main Geophysical Observatory in St Petersburg, Russia. Budyko looked at what would happen if the Earth's climate were to cool slightly, prompting an increase in the size of the polar ice-caps. Ice reflects heat from the Sun, so this growth would cause further cooling. Runaway growth of the ice-caps could result, Budyko argued, eventually leaving the Earth entirely sheathed in ice[1].

Budyko's ideas explained puzzling evidence, including signs of scouring of rocks by ice, that seemed to imply that glaciers reached the Equator on at least two occasions between 580 million and 750 million years ago, towards the end of the Neoproterozoic period. This was baffling, because ice sheets reached only as far as northern Europe during more recent ice ages. But Budyko's theory had some holes in it. What, for example, eventually caused the ice to thaw?

Iron out

In 1992, Joseph Kirschvink, a geologist at the California Institute of Technology in Pasadena, provided an explanation of how the ice could have receded[2]. Kirschvink, who coined the term ‘snowball Earth’, realized that normal cycles of rain and erosion, which play an important role in removing carbon dioxide from the atmosphere, would have shut down if ice had covered the oceans. Carbon dioxide released by volcanoes would then build up in the atmosphere, eventually creating enough greenhouse warming to melt the ice sheets.

Volcanic CO_2 may have caused a greenhouse effect that freed snowball Earth from its ice age.

Kirschvink also pointed out that a snowball Earth could explain another strange geological deposit — iron-rich rocks that formed near the end of the Neoproterozoic. Iron is added to the ocean at geothermal vents in the sea floor and precipitates out of sea water when it comes into contact with oxygen. But if the oceans had been capped with ice, oxygen levels in water would have fallen and dissolved iron would have built up. Oxygen levels would have increased when the ice melted, causing large amounts of iron to precipitate out and fall to the sea floor.

Six years later, Hoffman and Schrag, together with colleagues at Harvard, published the paper that thrust the hypothesis back into the limelight[3]. They had studied ratios of carbon isotopes in rocks formed when carbon-containing compounds precipitated out of sea water. Photosynthetic marine microorganisms take up carbon, preferring the lighter carbon-12 isotope to the heavier carbon-13 — so photosynthesis causes carbon-12 levels in water to fall, leaving less of that isotope to precipitate out.

But when Hoffman and Schrag looked at ‘cap carbonates’ — sediments that were deposited towards the end of the Neoproterozoic glaciations — they found surprisingly high levels of carbon-12. In fact, the ratio of carbon isotopes suggested that almost no photosynthesis had occurred in the waters from which the rocks precipitated. This, they reasoned, was exactly what would occur if ice had covered the ocean and starved it of light.

Journals' correspondence columns were

MORGUNBLADET/AP

- Ocean/atmosphere climate models cannot seem to keep entire ocean covered with ice
- Weak evidence for lower sea level
- Weathering reactions are slow….. Maybe too slow to be the source of cap carbonates

Lubick (2002) *Nature*, Vol. 417: 12-13.

Alternate Cause for Cap Carbonate Deposition & ^{13}C Depletions: Gas Hydrate Destabilization

- $CaCO_3$ precipitation does not require increased weathering flux of minerals

- Can be caused by increased seawater alkalinity resulting from CH_4 consumption by sulphate-reducing bacteria

Kennedy et al. (2001) *Geology* Vol. 29(5): 443-446.

Structures in Cap Carbonates May Result from Gas Release

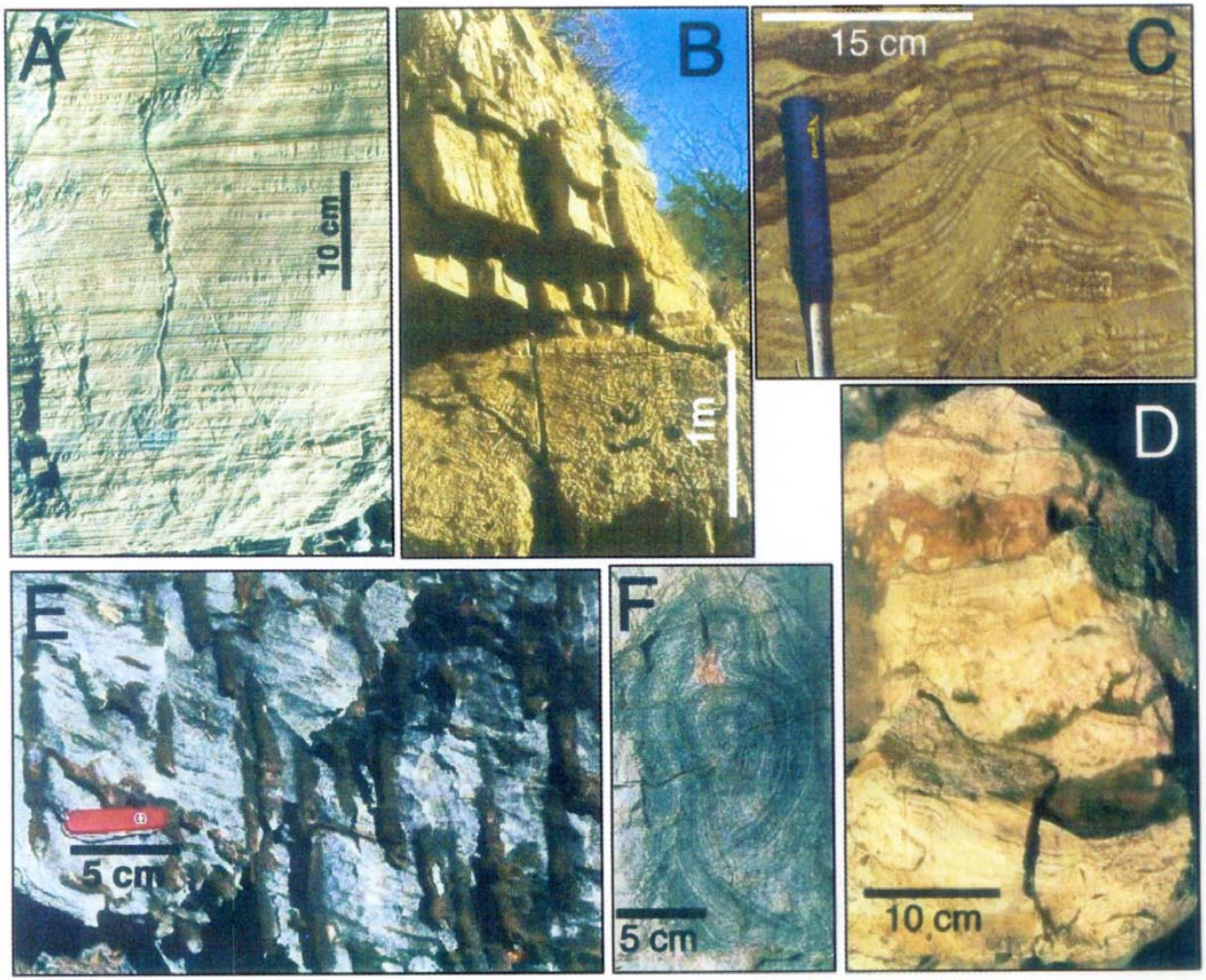
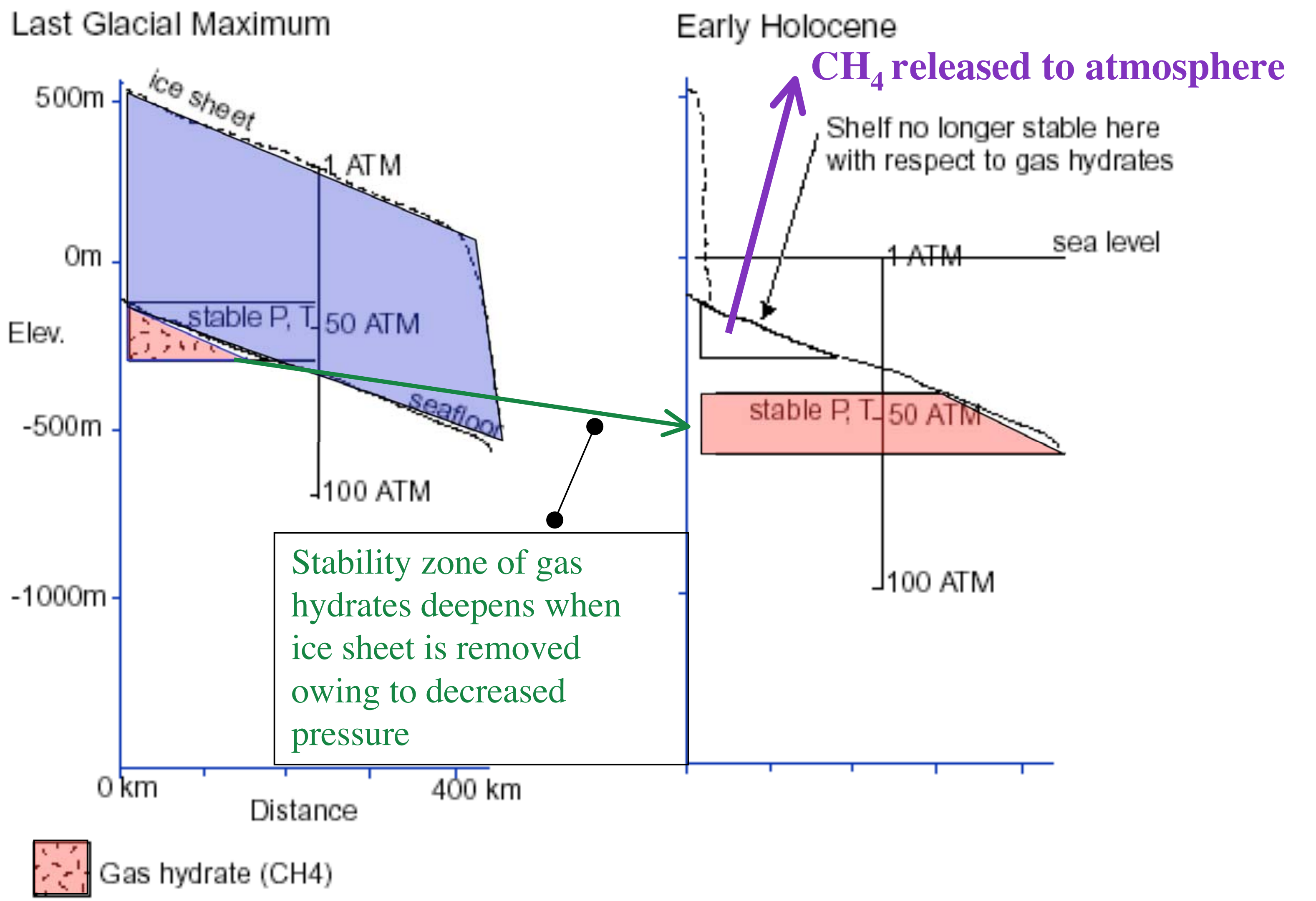


Figure 1. Cap carbonate lithofacies: A: Typical laminated dolomicrite. B: Facies with domal and tepee-shaped structures and abundant cement, overlain by laminated dolomite. C: Detail of B showing growth of tepee-shaped structure and sheet cracks lined by isopachous cement. D: Brecciation in core of structure, related to repeated bedding disruption and cementation. E: Tubestone facies, attributed to outgassing of methane. F: Roll-up structure, interpreted to represent microbial binding by chemosynthetic and/or heterotrophic organisms in deep water. All examples are from northern Namibia, except D (Kimberley region, Australia).

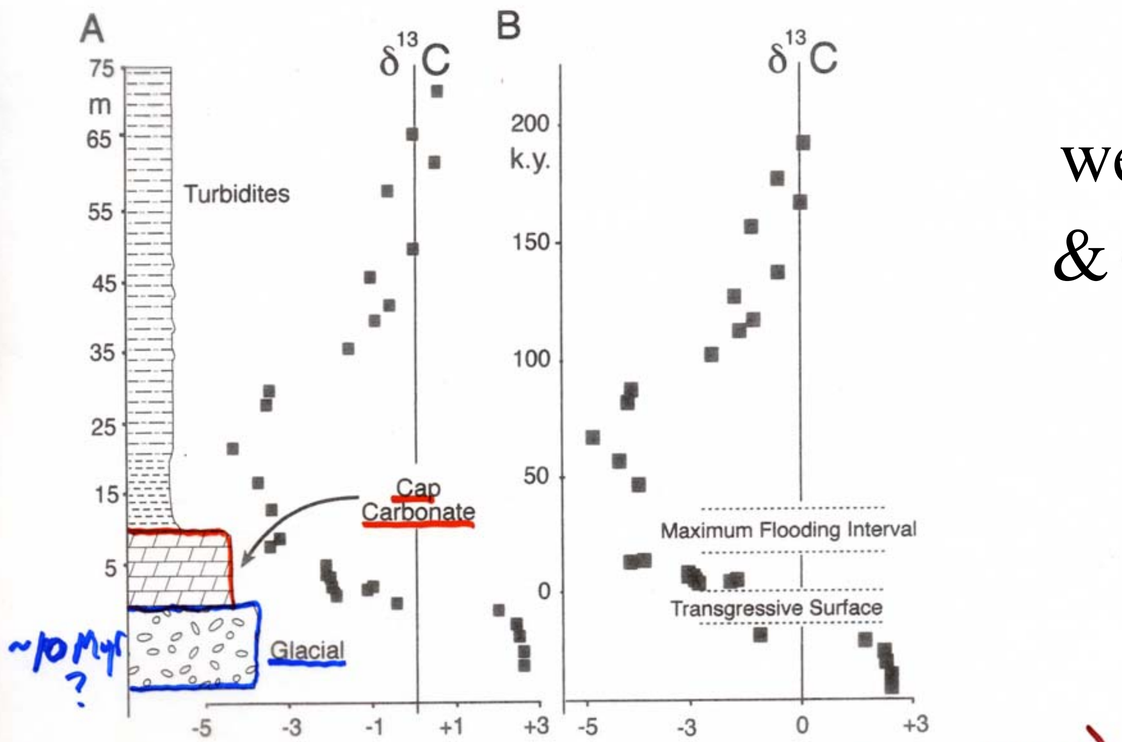
- Gas Hydrate = [H_2O + hydrocarbon (CH_4)] ice
- CH_4 from biogenic + thermogenic decomposition of deeply buried C_{org}
- Biogenic CH_4 has very low $\delta^{13}C$ (-60 to-90‰)
- Sequestered as hydrate in *permafrost* (> 150 m) & along continental margins (> 300 m)
- Destabilized by increased temperature
- CH_4 released from flooded permafrost during deglaciation

Kennedy et al. (2001) *Geology* Vol. 29(5): 443-446.

Gas Hydrate Stability Influenced by T & P



Smith, Sachs, et al. (2001) *Geophys. Res. Lett.*, Vol.28(11): 2217-2220.



Rather than increased weathering flux of cations & HCO_3^- to ocean causing $CaCO_3$ precipitation, increased seawater alkalinity could have caused $CaCO_3$ precipitation

Methane $\delta^{13}C$: -60 to -95 ‰

Low $\delta^{13}C$ → $CH_4 + SO_4^{2-} \rightarrow HS^- + HCO_3^- + H_2O$ → CH_4 consumption by SO_4^{2-} reducers @ seafloor & in flooded permafrost

↓

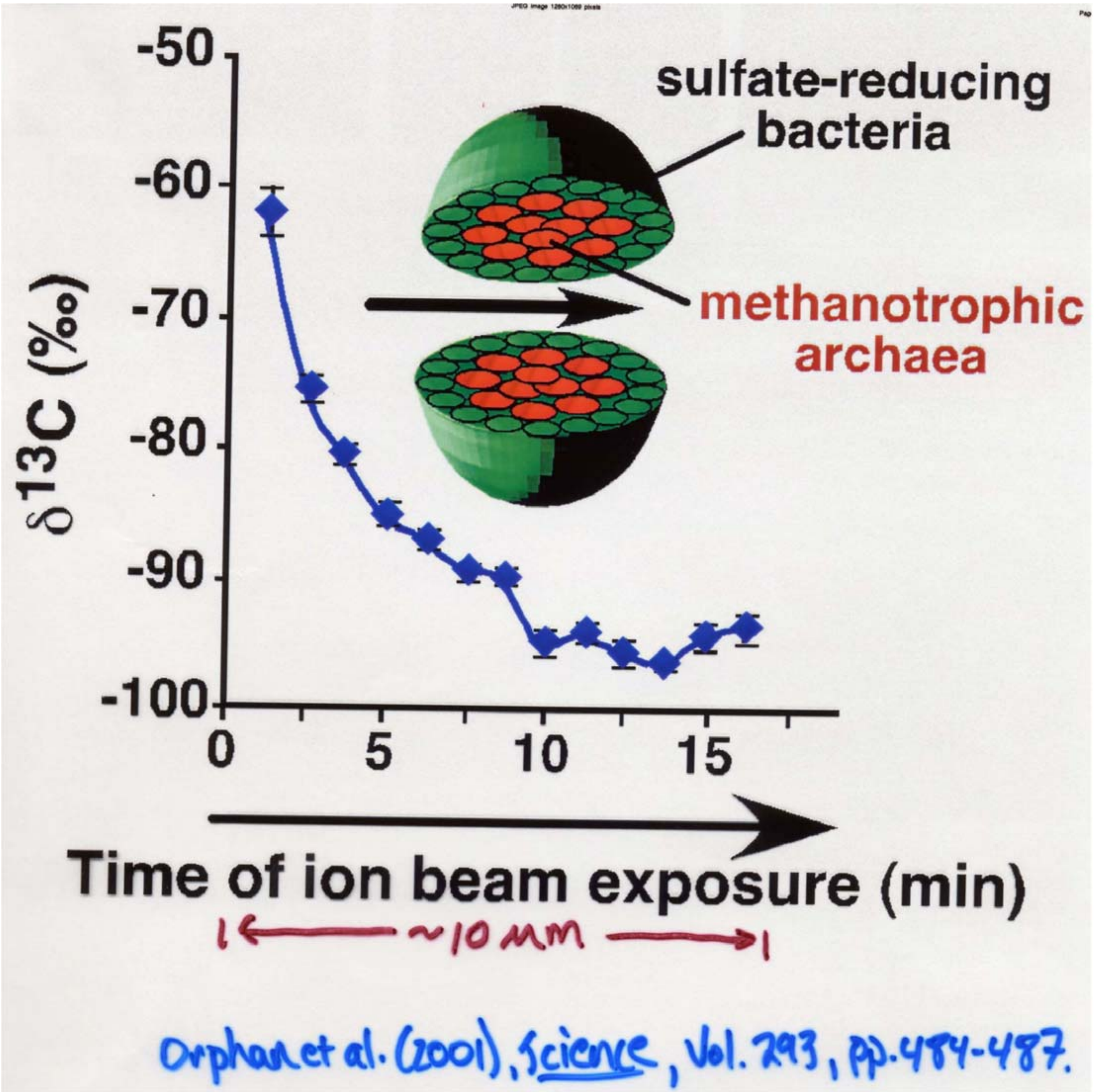
Increase ~~Decrease~~ seawater Alkalinity → Drives ΣCO_2 ($H_2CO_3 + HCO_3^- + CO_3^{2-}$) toward CO_3^{2-}, causing $CaCO_3$ to precipitate out of seawater

↓

Causes $CaCO_3$ to ppt.

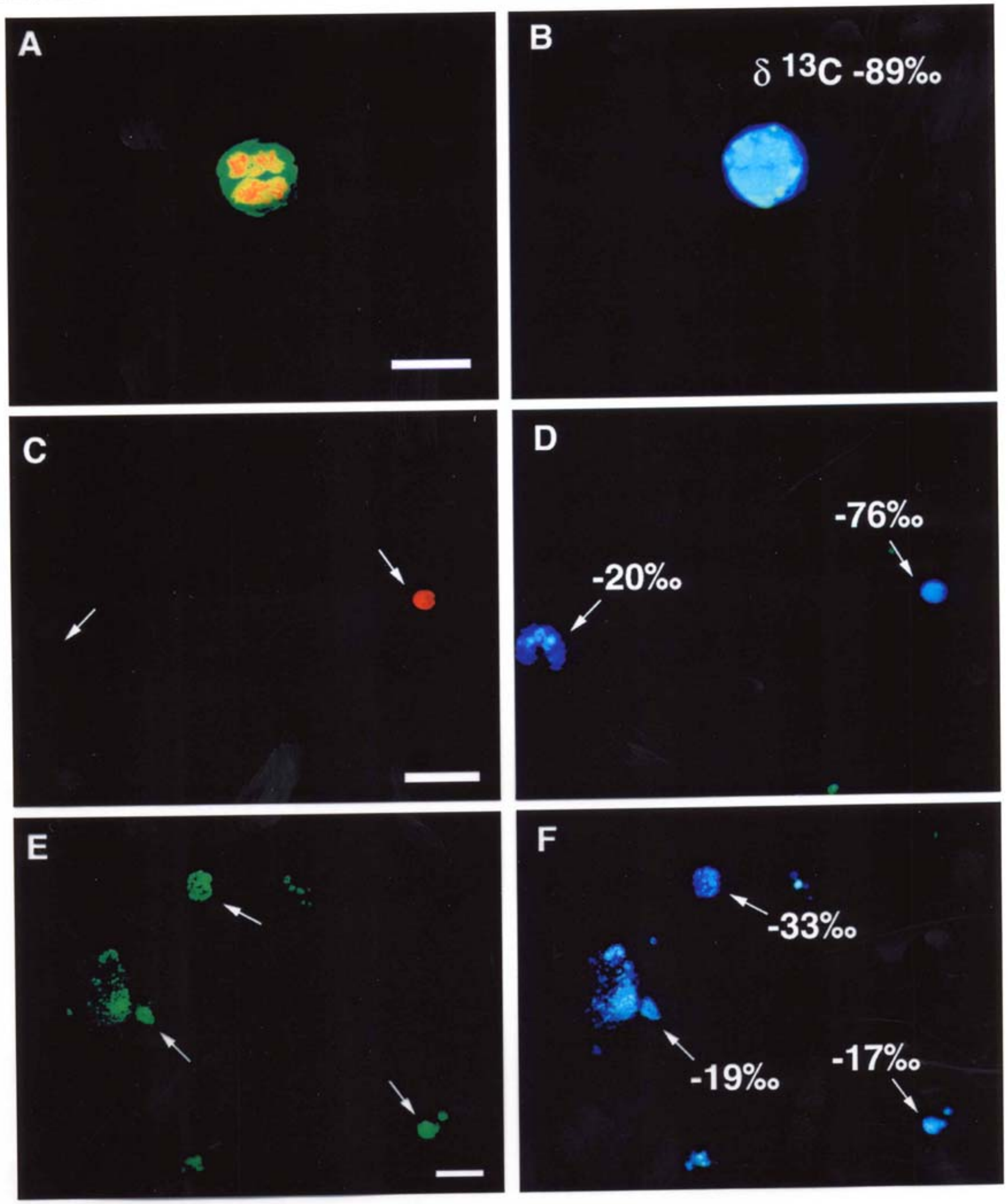
↓

Low $\delta^{13}C$ of ocean/atmosphere = Low $\delta^{13}C_{CaCO_3}$ → CH_4-derived $CaCO_3$ has low $\delta^{13}C$



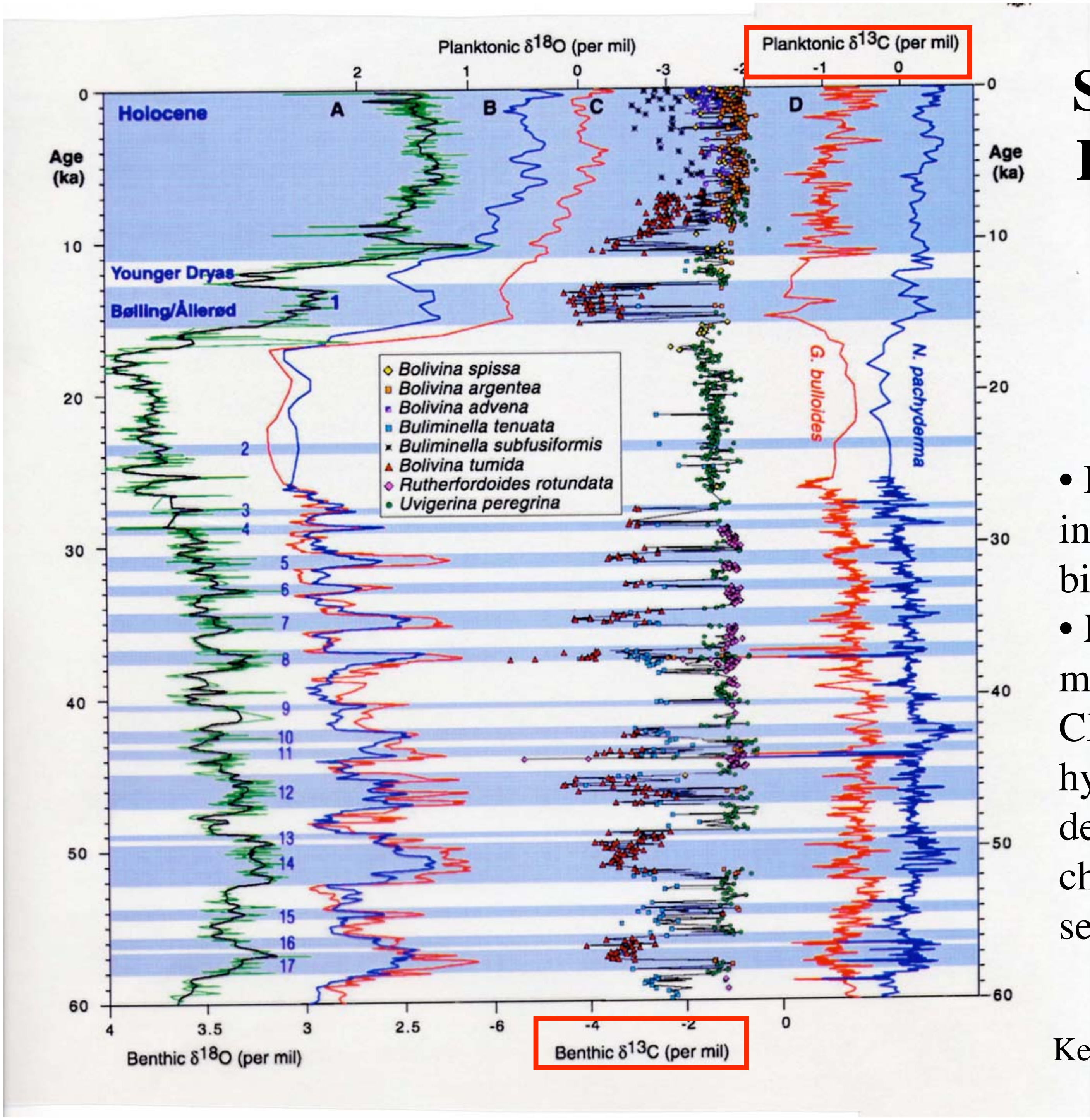
CH_4 consumption by sulphate reducers is observed at methane seeps in modern ocean, & $CaCO_3$ precipitates there as a result

- SO_4^{2-} reducers produce highly ^{13}C depleted HCO_3^- which goes into ocean/atmosphere



Orphan et al. (2001), Science, Vol. 293, pp. 494-487.

Consortia of sulphate reducers & methane-oxidizing microbes from modern CH_4 seep



Santa Barbara Basin: Recent methane hydrate releases?

- Large ^{13}C-depletions in seawater & biogenic carbonates
- Likely resulted from massive releases of CH_4 when gas hydrates were destabilized by changing T & P (I.e., sea level)

Kennett et al. (2000) *Science*, Vol. 288: 128-133.