

# Long-Term Climate Cycles & The Proterozoic Glaciations (‘Snowball Earth’)



## Assigned Reading:

- Hoffman & Schrag (2002) *Terra Nova*, Vol. 14(3):129-155.
- Lubick (2002) *Nature*, Vol. 417: 12-13.

**12.842 FALL 2004  
PALEOCLIMATE READING LIST #2:  
CLIMATE ON GEOLOGIC TIME SCALES**

**Snowball Earth & Pre-Cenozoic Glaciations**

**Assigned Readings:**

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

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

**Recommended Readings:**

Christie-Blick, N. (1982) Pre-Pleistocene glaciation on Earth: Implications for climatic history of Mars. *Icarus*, **50**, 423-443.

Crowell, J. (1978) Gondwana glaciation, cyclothems, continental positioning, and climate change. *Am. J. Sci.*, **278**, 1345-1372.

Crowley, T.J. & North, G.R. (1991) *Paleoclimatology*. Oxford University Press, New York. (Especially ch.10-12.)

Edmond J. M., Palmer M. R., Measures C. I., Grant B., and Stallard R. F. (1995) The fluvial geochemistry and denudation rate of the Guyana Shield in Venezuela, Columbia, and Brazil. *Geochimica et Cosmochimica Acta* **59**, 3301-3326.

Evans, D., Beukes, N. & Kirschvink, J. (1997) Low-latitude glaciation in the Palaeoproterozoic era. *Nature*, **386**, 262-266.

Frakes, L. (1979) *Climates throughout geologic time*, 310 pp. Elsevier, New York.

Frakes, L.A., Francis, J.E., Syktus, J.I. (1992) *Climate Modes of the Phanerozoic*, 274 pp. Cambridge University Press, Cambridge, UK.

Hambrey, M. & Harland, W. (1981) *Earth's Pre-Pleistocene Glacial Record*, pp. 1004. Cambridge University Press, New York.

Hoffman, P.F. & Schrag, D.P. (2000) Snowball Earth. *Sci. Am.*, **January**, 68-75.

Hoffman, P.F., Kaufman, A.J., Halverson, G.P. & Schrag, D.P. (1998) A Neoproterozoic snowball Earth. *Science*, **281**, 1342-1346.

Meert, J. & van der Voo, R. (1994) The Neoproterozoic (1000-540 Ma) glacial intervals: no more snowball earth? *Earth Planet. Sci. Lett.*, **123**, 1-13.

**CO<sub>2</sub>-Climate Connection**

**Assigned Readings:**

Veizer J., Godderis Y., and François L. M. (2000) Evidence for decoupling of atmospheric CO<sub>2</sub> and global climate during the Phanerozoic eon. *Nature* **408**, 698-701.

Questions CO<sub>2</sub>-climate link b/c Phanerozoic tropical SST record doesn't agree with simple energy balance model results driven by paleo-CO<sub>2</sub> proxy data.

Kump L. R. (2000) What drives climate? *Nature* **408**, 651-652.

Skeptical of Veizer results; questions SST proxy record and paleo CO<sub>2</sub> proxy record.

Rothman, D.H. (2002) Atmospheric carbon dioxide levels for the last 500 million years. *Proceedings of the National Academy of Sciences* **99**(7), 4167-4171.

Berner R. A. (1997) The rise of plants and their effect on weathering and atmospheric CO<sub>2</sub>. *Science* **276**, 544-547.  
Suggests evolution of rooted vascular plants caused Devonian (~400 Ma) CO<sub>2</sub> drawdown by enhancing chemical weathering rates. Supports CO<sub>2</sub>-climate link through Phanerozoic. Exception is Late Ordovician glaciation, explained by "unique paleogeographic circumstances".

Royer D. L., Berner R. A., and Beerling D. J. (2001) Phanerozoic atmospheric CO<sub>2</sub> change: evaluating geochemical and paleobiological approaches. *Earth-Science Reviews* **54**, 349-392.  
Excellent review of paleo-CO<sub>2</sub> proxies.

Crowley, T. J., Carbon dioxide and Phanerozoic climate. in *Warm Climates in Earth History*, edited by Huber, B. T., K. G. MacLeod and S. L. Wing, pp. 425-444, Cambridge University Press, Cambridge, UK, 2000.

**Recommended Readings:**

Retallack G. J. (2001) A 300-million-year record of atmospheric carbon dioxide from fossil plant cuticles. *Nature* **411**, 287-290  
Stomatal indices on fossil leaves during last 300 Myr indicate that the only two periods of low CO<sub>2</sub> were associated with known ice ages, in support of the CO<sub>2</sub>-climate link.

Royer D. L., Wing S. L., Beerling D. J., Jolley D. W., Koch P. L., Hickey L. J., and Berner R. A. (2001) Paleobotanical evidence for near present-day levels of atmospheric CO<sub>2</sub> during part of the Tertiary. *Science* **292**, 2310-2313.  
Leaf stomatal indices through "known" warm intervals (Miocene 15-17 Ma, and Paleocene/Eocene boundary (53-59 Ma) indicate low CO<sub>2</sub>, refuting CO<sub>2</sub>-climate link.

Tanner L. H., Hubert J. F., Coffey B. P., and McInerney D. P. (2001) Stability of atmospheric CO<sub>2</sub> levels across the Triassic/Jurassic boundary. *Nature* **411**, 675-677.  
Paleosol δ<sup>13</sup>C data across Triassic/Jurassic boundary (208 Ma) suggests only small CO<sub>2</sub> increase associated w/ that mass extinction. Argue therefore that deposition of large flood basalts at that time (volcanic events) did not cause high CO<sub>2</sub> and runaway greenhouse, as previously hypothesized.

Pagani M., Arthur M. A., and Freeman K. H. (1999) Miocene evolution of atmospheric carbon dioxide. *Paleoceanography* **14**, 273-292.  
Phytoplankton δ<sup>13</sup>C indicates low CO<sub>2</sub> through Miocene warm interval (~14-18 Ma) and no sharp drop associated with the expansion of the East Antarctic Ice Sheet, refuting strong CO<sub>2</sub>-climate link.

Berner, R.A. (1990) Atmospheric carbon dioxide levels over Phanerozoic time. *Science*, **249**, 1382-1386.

Berner, R.A. (1992) Palaeo-CO<sub>2</sub> and Climate. *Nature*, **358**(6382), 114.

Freeman, K.H. & Hayes, J.M. (1992) Fractionation of Carbon Isotopes By Ancient Phytoplankton and Estimates of Ancient CO<sub>2</sub> Levels. *Glob. Biogeochem. Cycles*, **6**(2), 185-198.

Hayes, J.M., Strauss, H. & Kaufman, A.J. (1999) The abundance of <sup>13</sup>C in marine organic matter and isotopic fractionation in the global biogeochemical cycle of carbon during the past 800 Ma. *Chem. Geol.*, **161**, 103-125.

Popp, B.N., Takigiku, R., Hayes, J.M., Louda, J.W. & Baker, E.W. (1989) The Post-Paleozoic Chronology and Mechanisms of <sup>13</sup>C Depletion in Primary Marine Organic Matter. *Am. J. Sci.*, **289**, 436-454.

**Tectonics and Cenozoic Climate**

**Assigned Readings:**

Raymo, M.E. & Ruddiman, W.F. (1992) Tectonic Forcing of Late Cenozoic Climate. *Nature*, **359**(6391), 117-122.

Edmond, J.M. (1992) Himalayan Tectonics, Weathering Processes, and the Strontium Isotope Record in Marine Limestones. *Science*, **258**, 1594-1597.

**Recommended Readings:**

McCaughey, S. & DePaolo, D. (1997) The marine <sup>87</sup>Sr/<sup>86</sup>Sr and δ<sup>18</sup>O records, Himalayan alkalinity fluxes, and Cenozoic climate models. In: *Tectonic Uplift and Climate Change* (Ed. by W. F. Ruddiman), pp. 427-467. Plenum Press, New York.

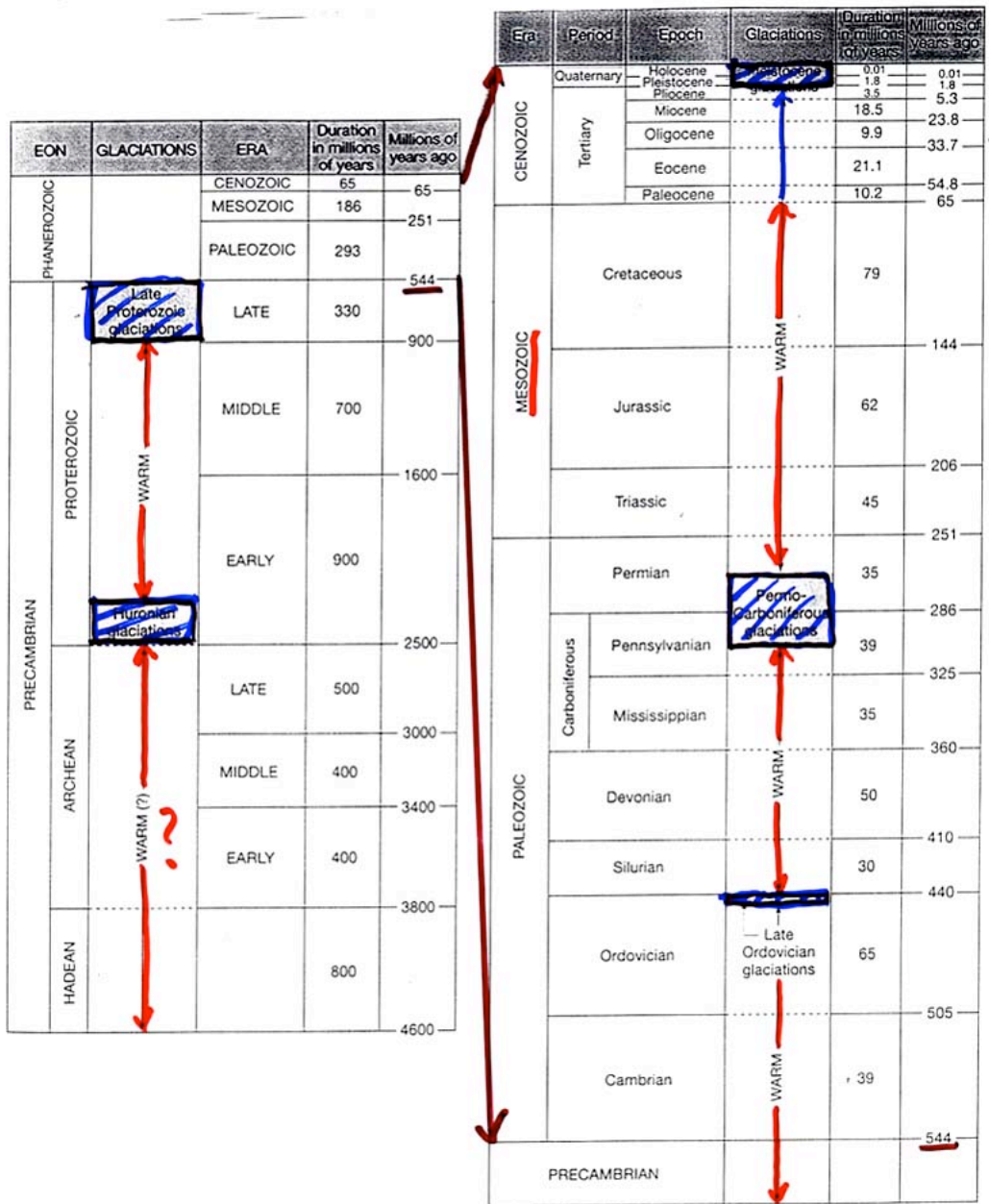
Richter, F.M., Rowley, D.B. & DePaolo, D.J. (1992) Sr Isotope Evolution of Seawater: the Role of Tectonics. *Earth Planet. Sci. Lett.*, **109**, 11-23.

Shackleton, N.J. (1987) The Carbon Isotope Record of the Cenozoic: History of Organic Carbon Burial and of Oxygen in the Ocean and Atmosphere. In: *Marine Petroleum Source Rocks, Geological Society Special Publication No. 26* (Ed. by J. Brooks & A. J. Fleet), pp. 423-434.

# 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
- Atmospheric composition (biology, tectonics, volcanoes):  $10^0$ - $10^5$  yr

"Mostly Sunny with a 10% Chance of Snow"



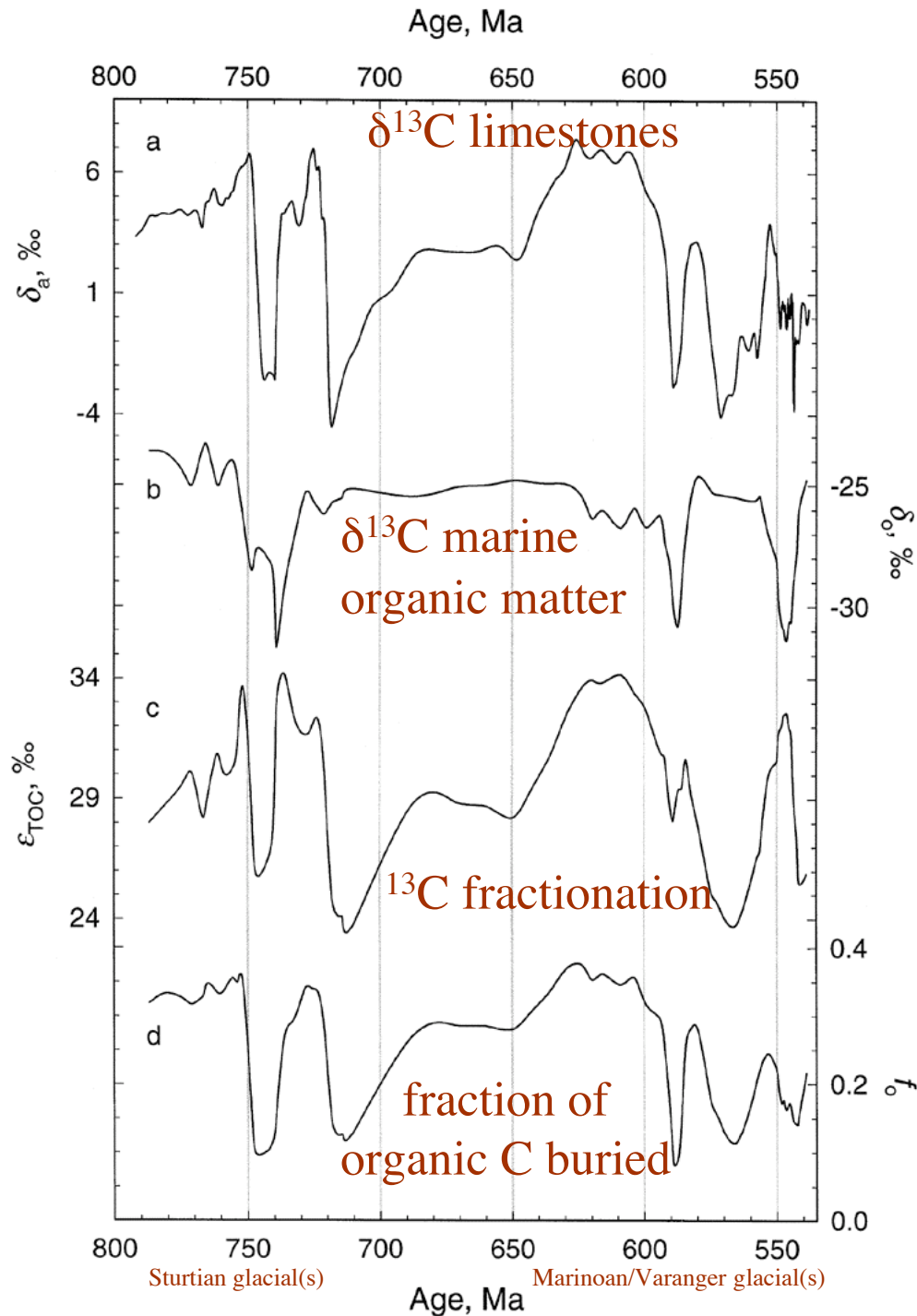
# Earth's Climate History:

## *Mostly sunny with a 10% chance of snow*



- What caused these climate perturbations?

# Carbon Isotopic Excursions 800-500Ma



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

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

# Late Proterozoic Glaciations: Evidence

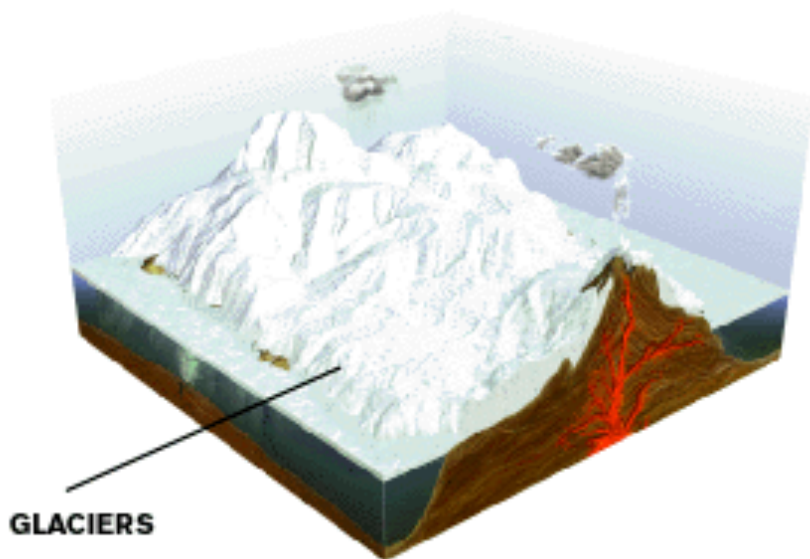
~4 global glaciations followed by extreme greenhouses 750-580 Ma

•Harland (1964); Kirschvink (1992)

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



Stage 3  
**Snowball Earth  
as It Thaws**



## Snowball Events:

- Breakup of equatorial supercontinent 770 Ma
- Enhanced weathering from increased rainfall (more land close to sea)
- Drawdown atmospheric CO<sub>2</sub> → 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<sup>2</sup>) keeps ocean liquid

# Evidence for Glaciers on All Continents

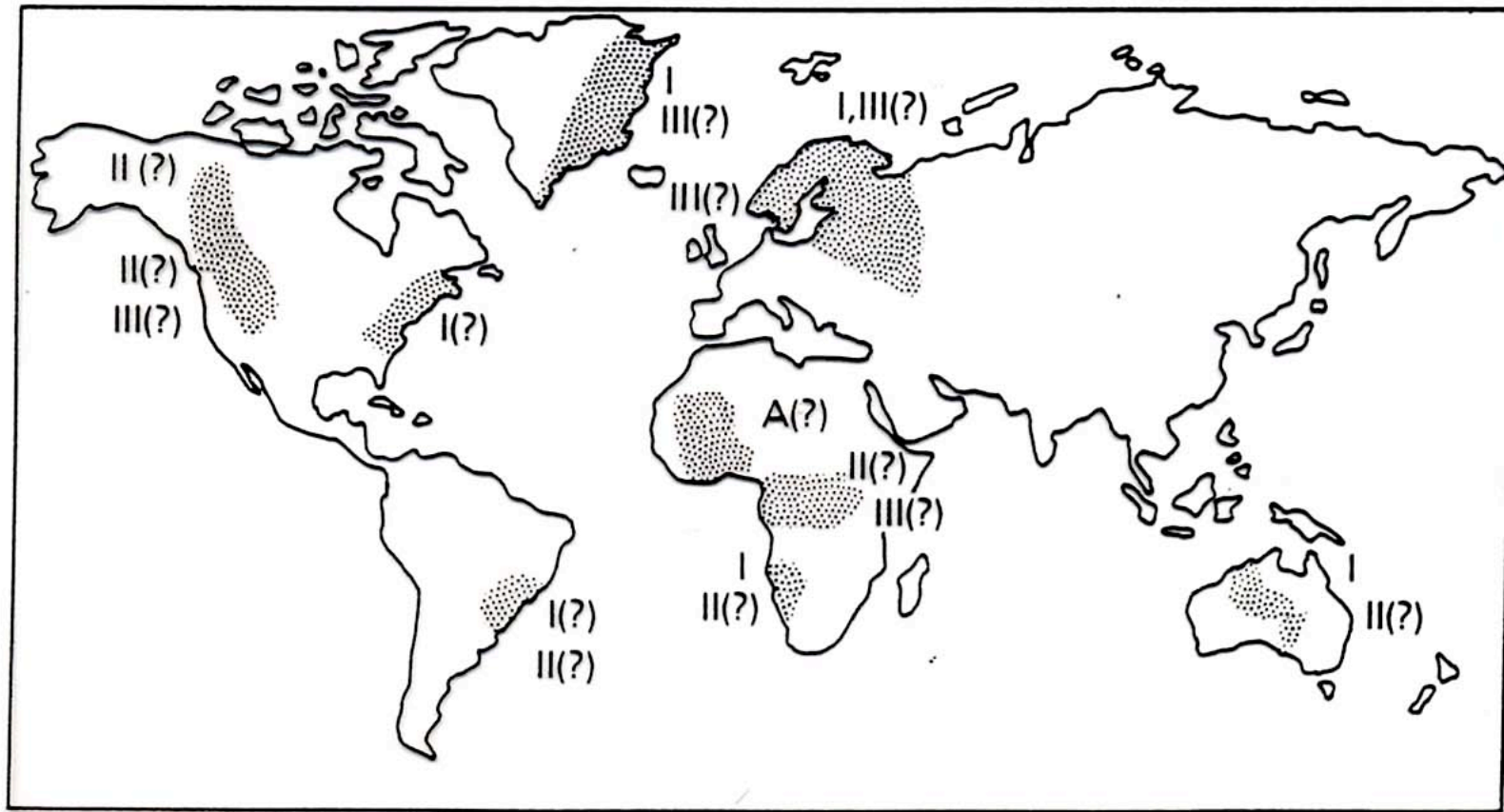


Fig. 12.3. Global distribution of major late Precambrian glacial centers on a map showing the present dispersal of continents. I, II, III refer to glaciations identified by Williams (1975) as centered on ~610 Ma, 750 Ma, and 950 Ma, respectively. A subsequent summary of late Precambrian glaciations (Hambrey 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)

# Late Proterozoic (~0.9-0.6 Ga) Glaciations

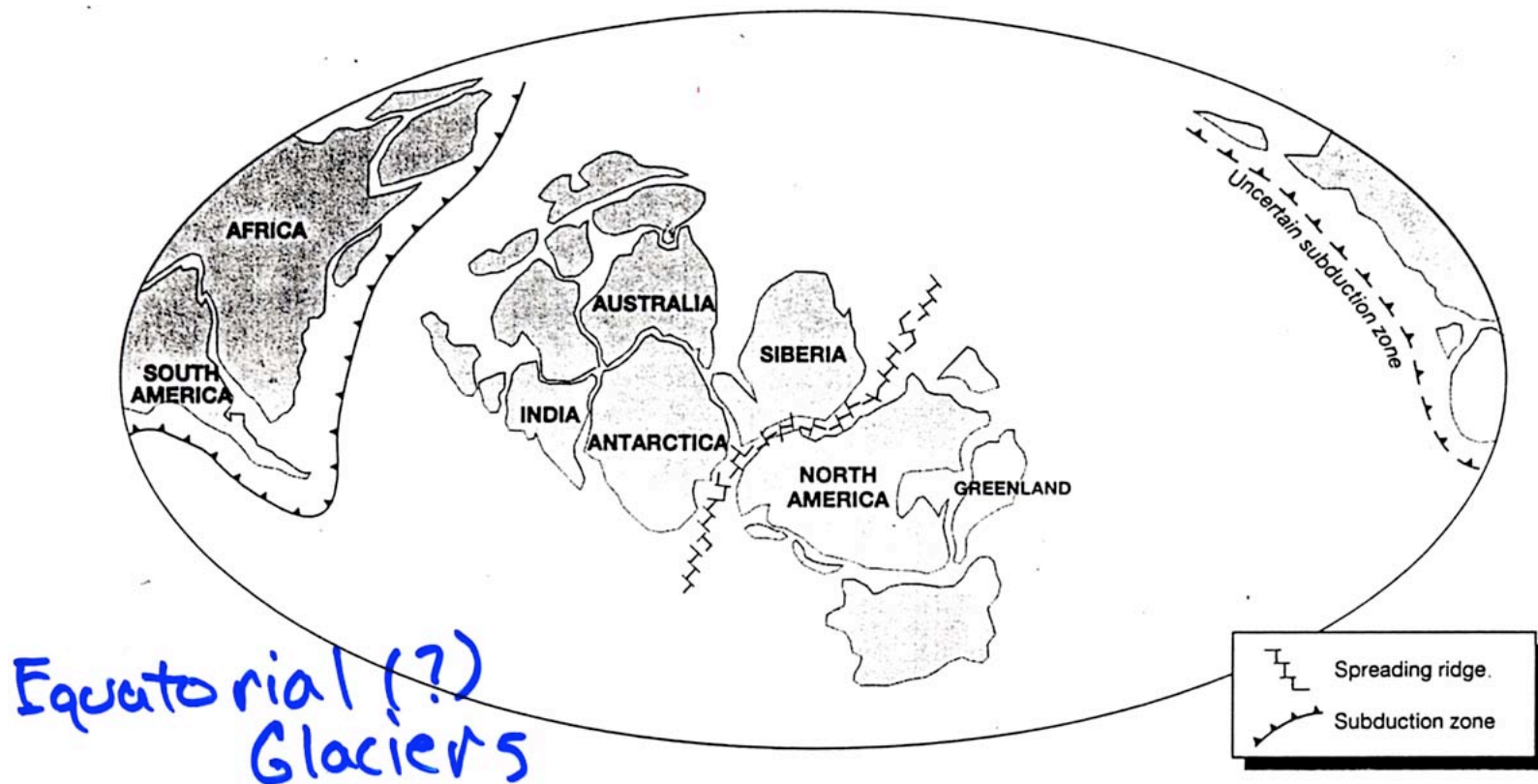
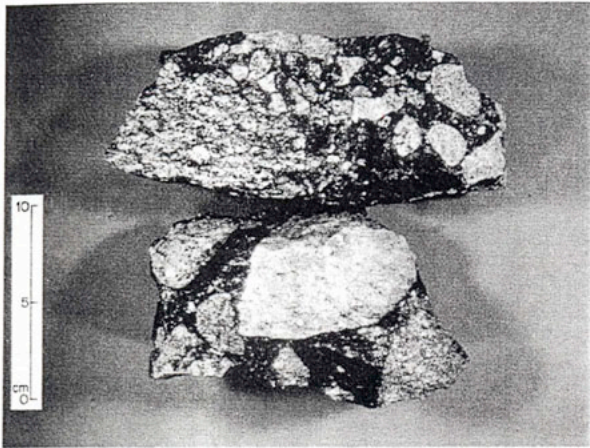


FIGURE 8-12

Possible continental reconstruction for the Late Proterozoic Period. All the continents appear to have been glaciated at that time. (After J.L. Kirshvink in the Proterozoic Biosphere: A Multidisciplinary Study, J.W. Schopf and C. Klein, eds., Ch. 12.1, Cambridge University Press, Cambridge, 1992.)





(a)

Geologic  
Evidence For  
Glaciation

Tillites



(b)

Glacial  
Striations



Dropstones

## Geologic Evidence for Glaciers

- *Tillites*: Packed pebbles, sand & clay. 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



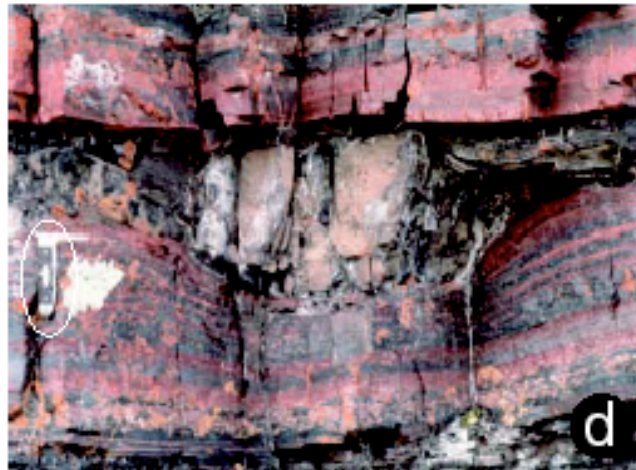
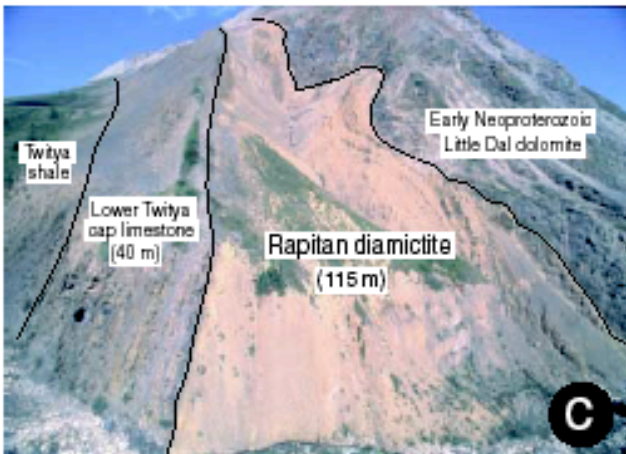
Image: Daniel P. Schrag

# Neo- proterozoic Glacial Deposits

From Norway,  
Mauritania, NW  
Canada, Namibia.

- Glacial striations
- Dropstones

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



# Equatorial Continents?

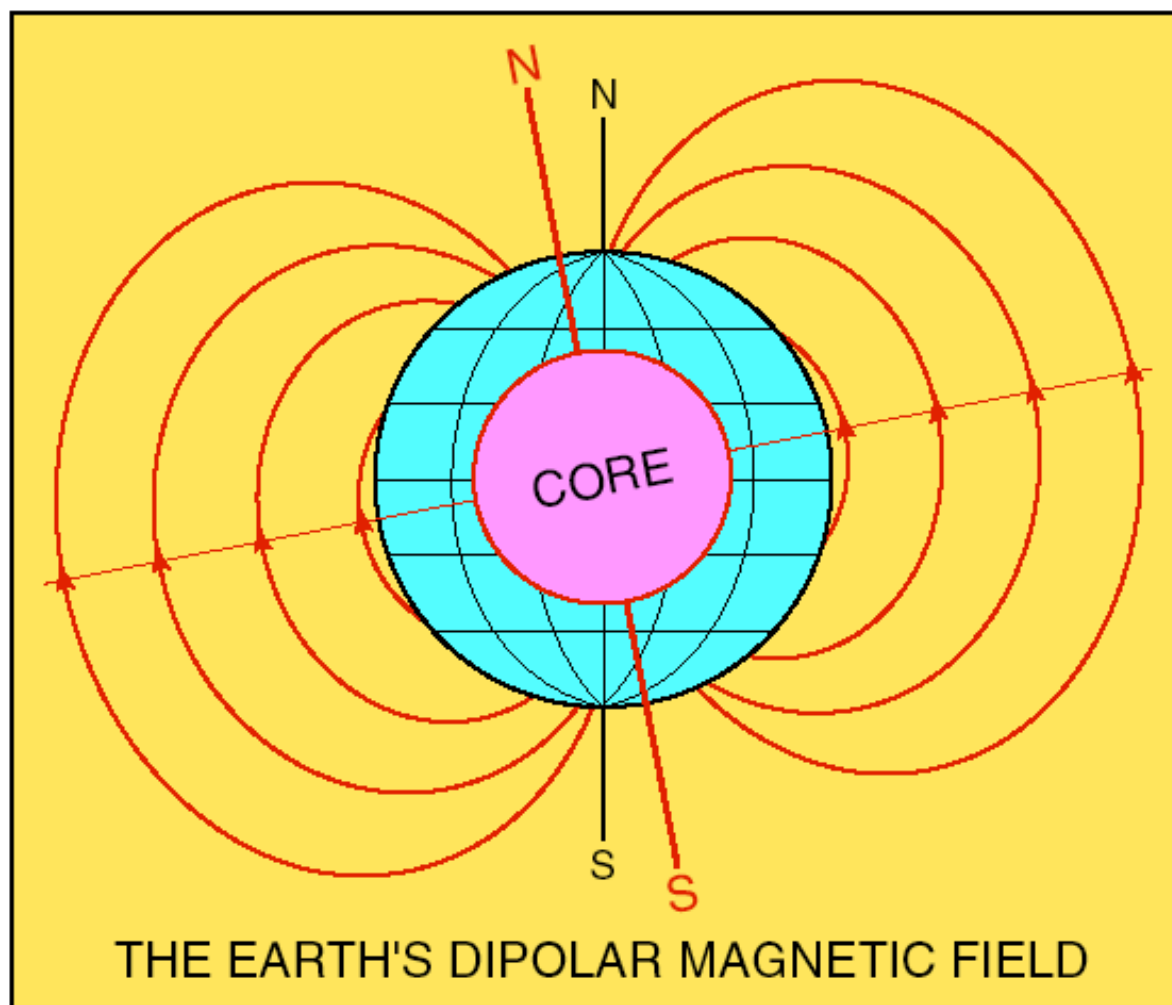


Hoffman  
& Schrag  
(2000)

**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 low a latitude glacial sequence in S. Australia & attributed to episode of extreme obliquity (tilt).

# Determining Paleolatitude from Remnant Magnetism



- Paleomagnetism: latitude of formation of rock
- Natural Remnant Magnetism (NRM): inclination varies with “magnetic” latitude
  - vertical @ magn poles
  - horz. @ magn equator (many Neoprot glac deposits)
- Magnetic polar drift averages out on  $T \sim 10$  ky

Image from P. Hoffman

# Paleolatitude from Paleomagnetism

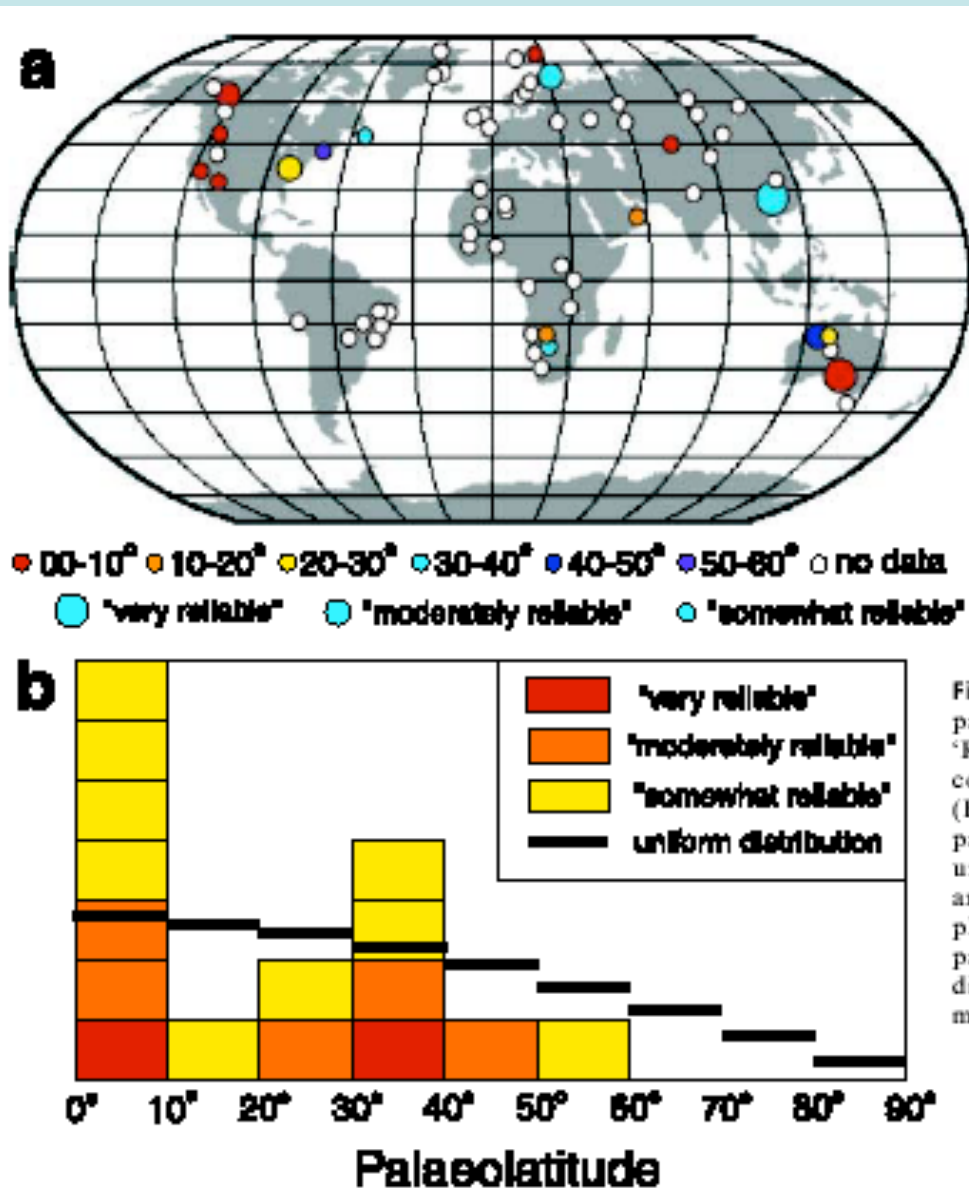


Fig. 1 Global distribution (a) of Neoproterozoic glaciogenic deposits with estimated palaeolatitudes based on palaeomagnetic data (modified from Evans, 2000). 'Reliability' takes into account not only palaeomagnetic reliability but also the confidence that the deposits represent regionally significant, 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-dipole 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.

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

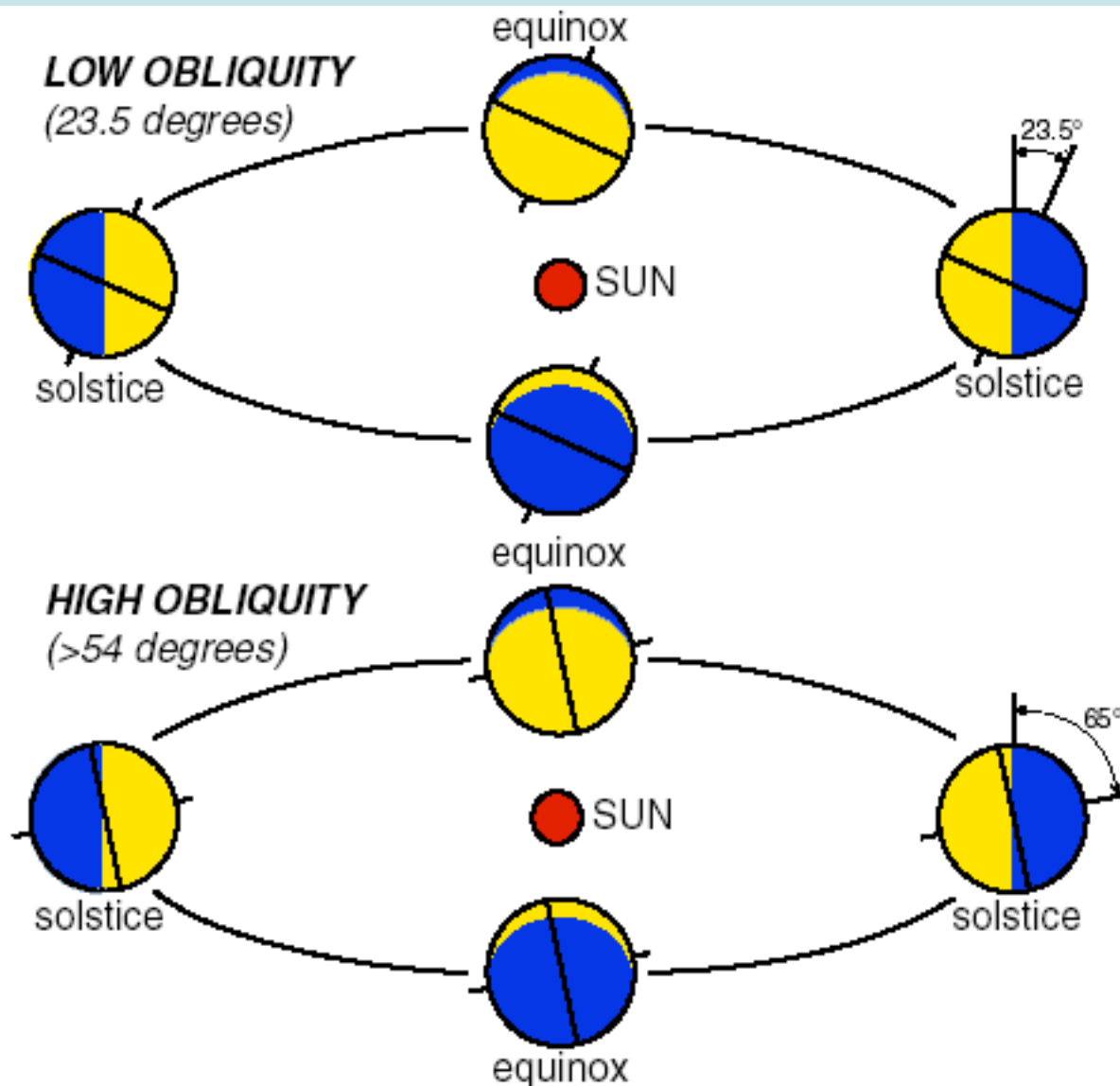
Williams (1975)

- Earth's tilt (obliquity) controls seasonality
- At high tilt angles ( $> 54^\circ$ ) 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

## Problems:

- 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



For obliquities  $> 54$  degrees, mean annual temperatures in the tropics are lower than at the poles, but low-latitude glaciation is unlikely because of very high seasonality.



# Snowball Earth Hypothesis

*~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.

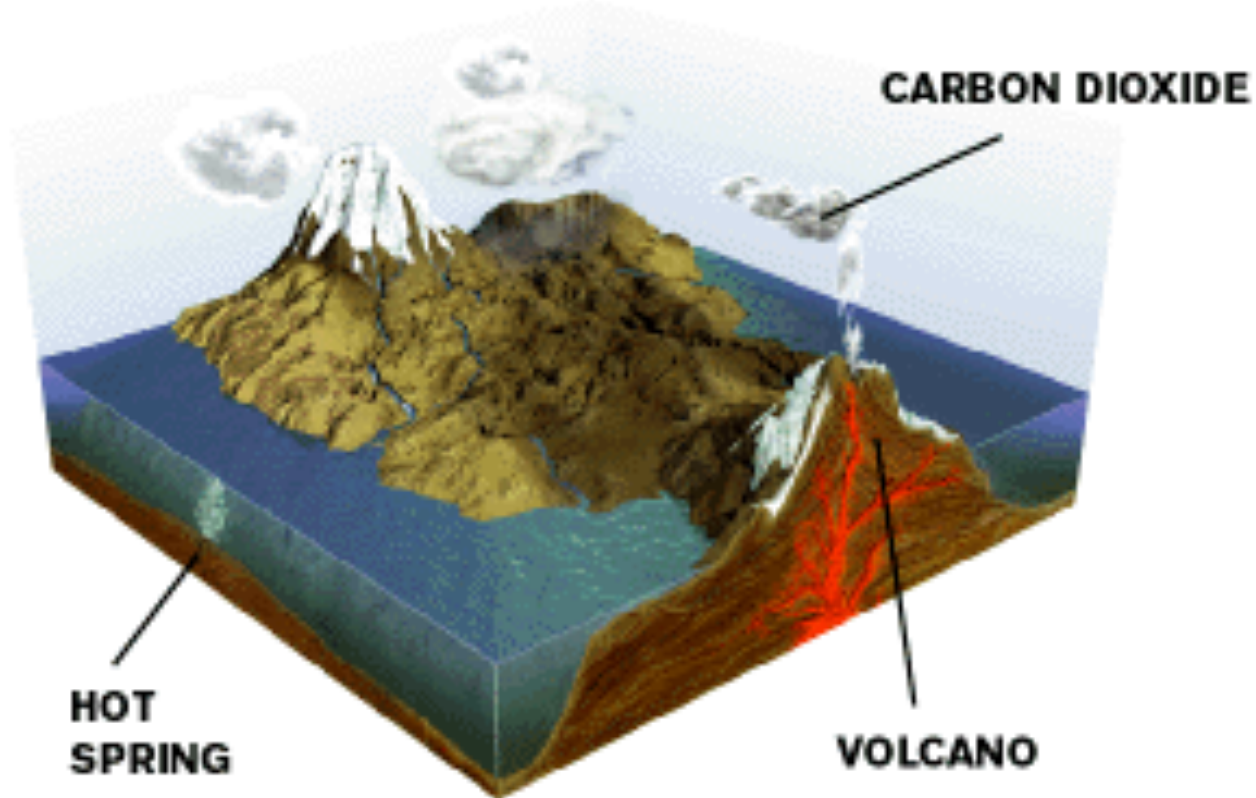


## Snowball Events:

- Breakup of equatorial supercontinent 770 Ma
- Enhanced weathering from increased rainfall (more land close to sea)
- Drawdown atmospheric CO<sub>2</sub> → 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<sup>2</sup>) keeps ocean liquid



## Stage 1 Snowball Earth Prologue

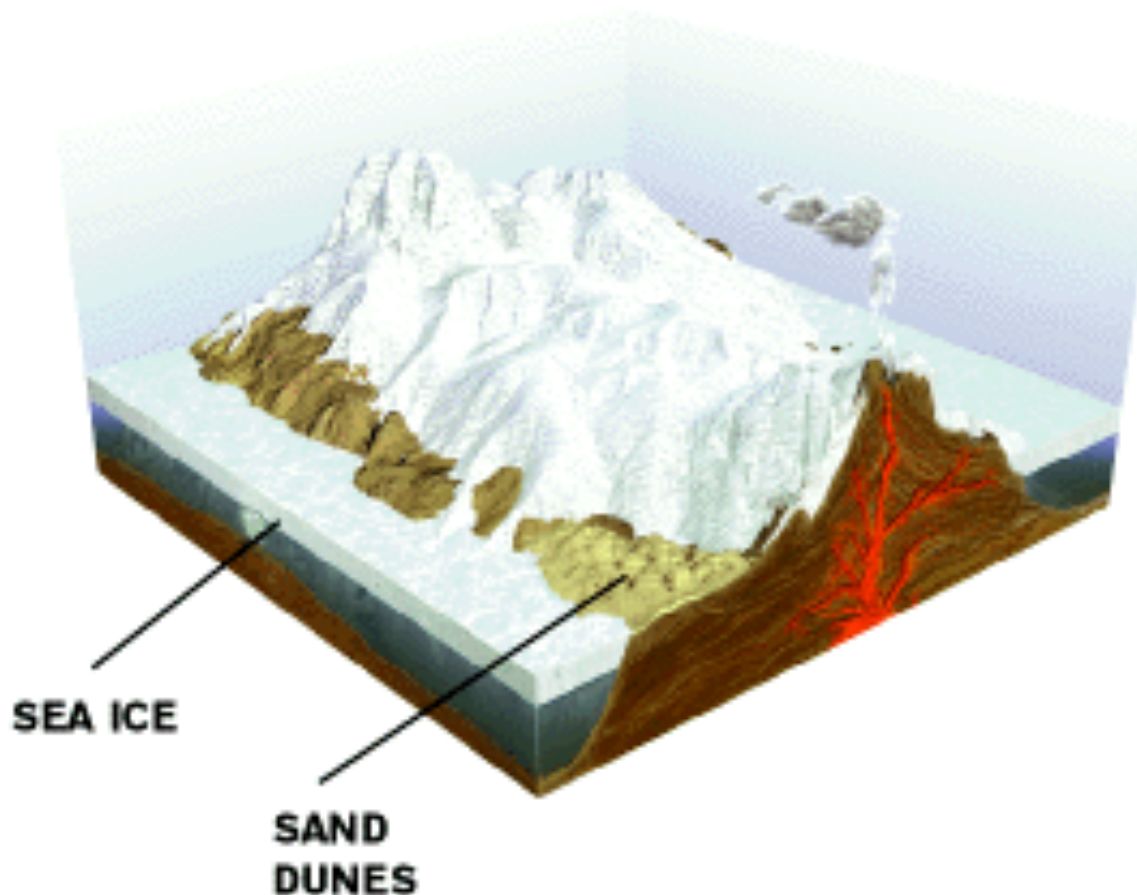


## Prologue to Snowball

- Breakup of equatorial supercontinent
- Enhanced weathering from increased rainfall (more land close to sea)
- Drawdown atmospheric  $\text{CO}_2 \rightarrow$  Global cooling



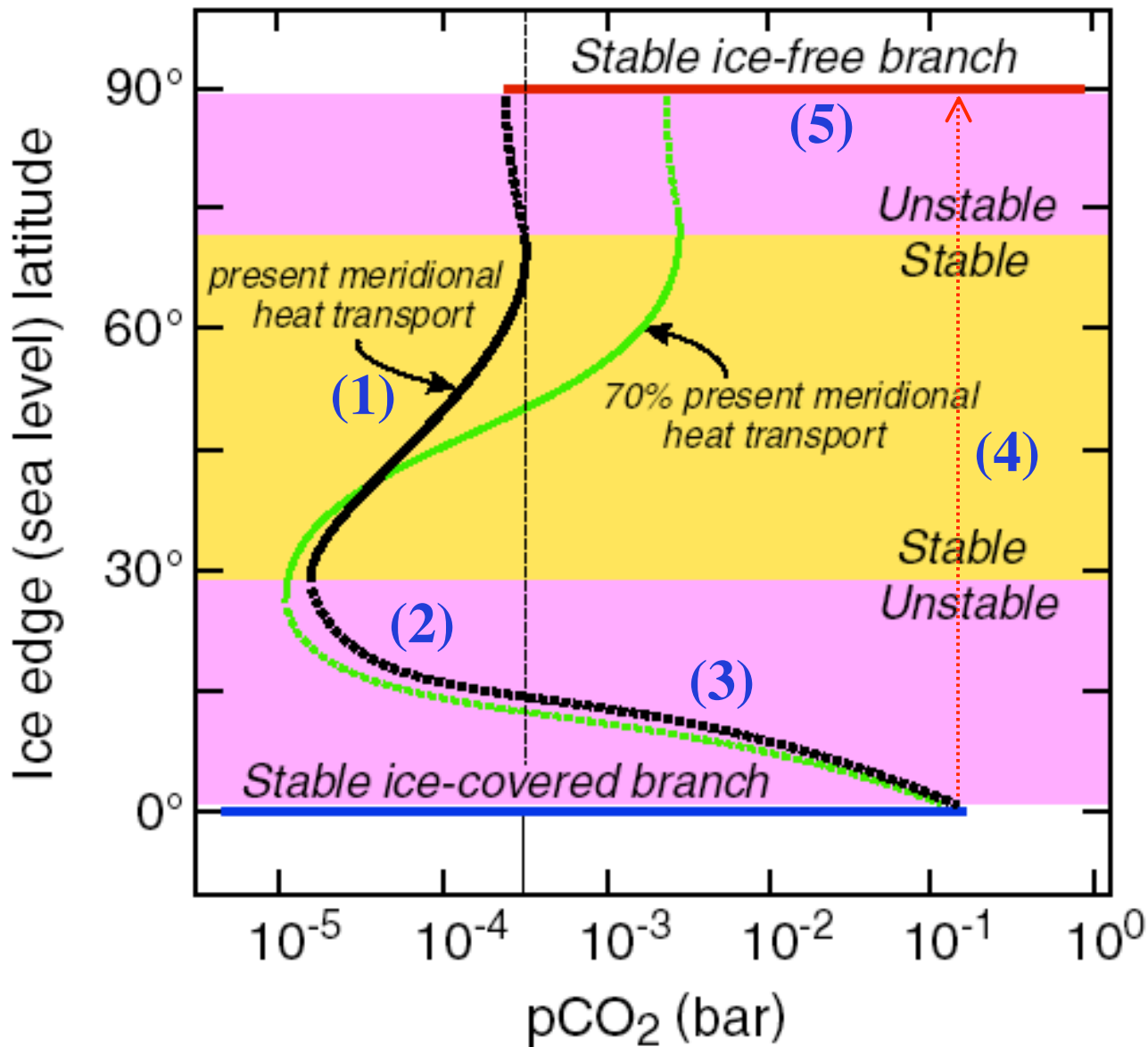
## Stage 2 Snowball Earth at Its Coldest



## Deep Freeze

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

Hoffman & Schrag (2000)



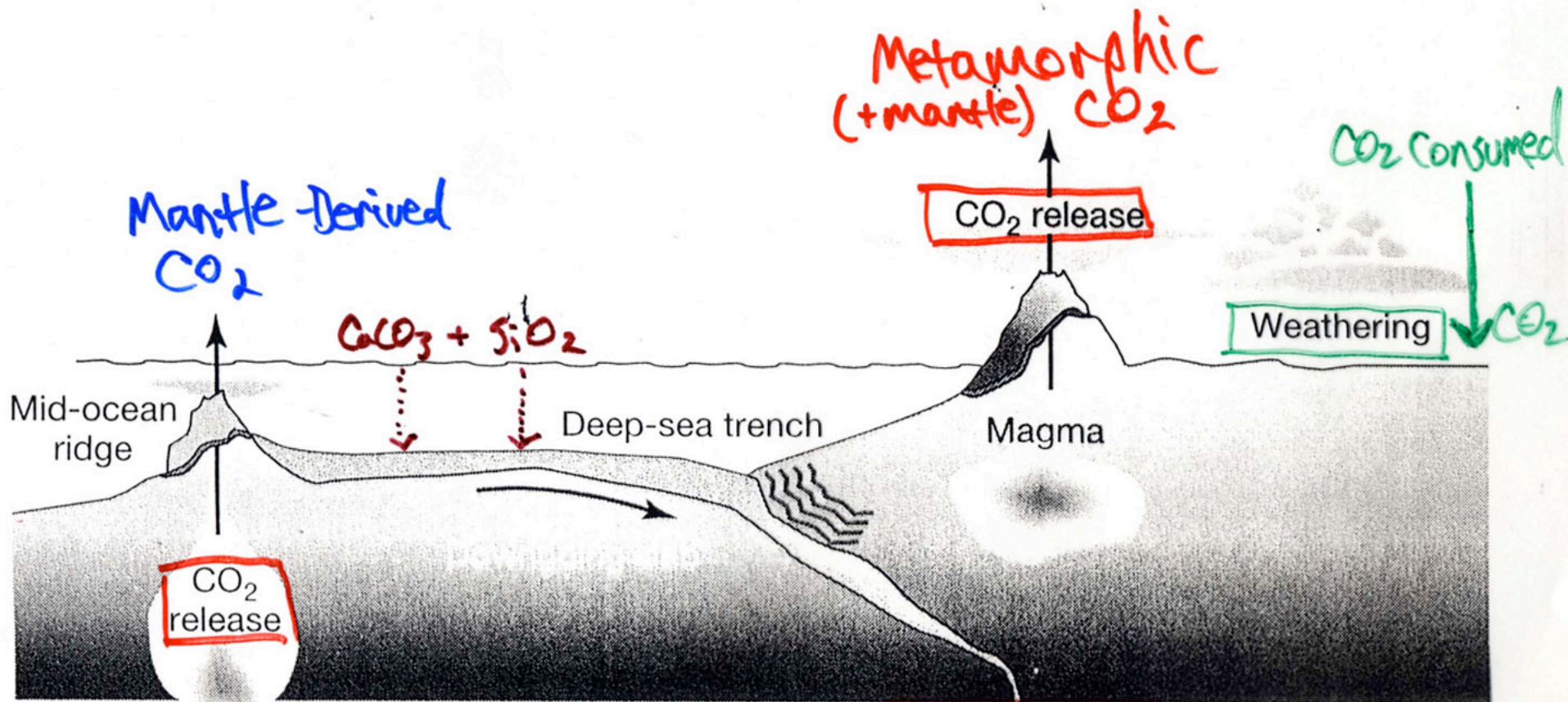
## •Runaway Albedo Feedback

1. Eq. continents, incr. weathering, lowers CO<sub>2</sub>, slow cooling, equatorward movement of ice.
2. Runaway albedo
3. Weathering shuts down
4. Slow buildup of CO<sub>2</sub> from volcanoes
5. Rapid decay of ice in 10<sup>2</sup> yr. High T<sub>s</sub> from enhanced H<sub>2</sub>O-T feedback.
6. Slow CO<sub>2</sub> drawdown from weathering

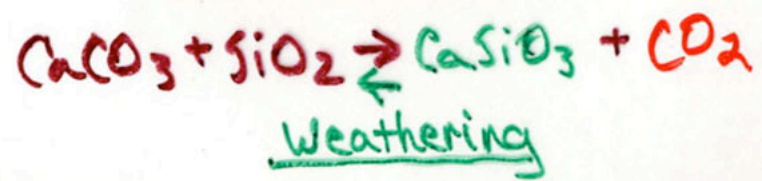
Steady-state ice lines as a function of atmospheric pCO<sub>2</sub>, see Caldeira and Kasting (*Nature* **359**: 226, 1992), and Ikeda and Tajika (*Geophys. Res. Lett.* **26**: 349, 1999).

Image from P. Hoffman

# Carbonate-Silicate Geochemical Cycle



Carbonate metamorphism

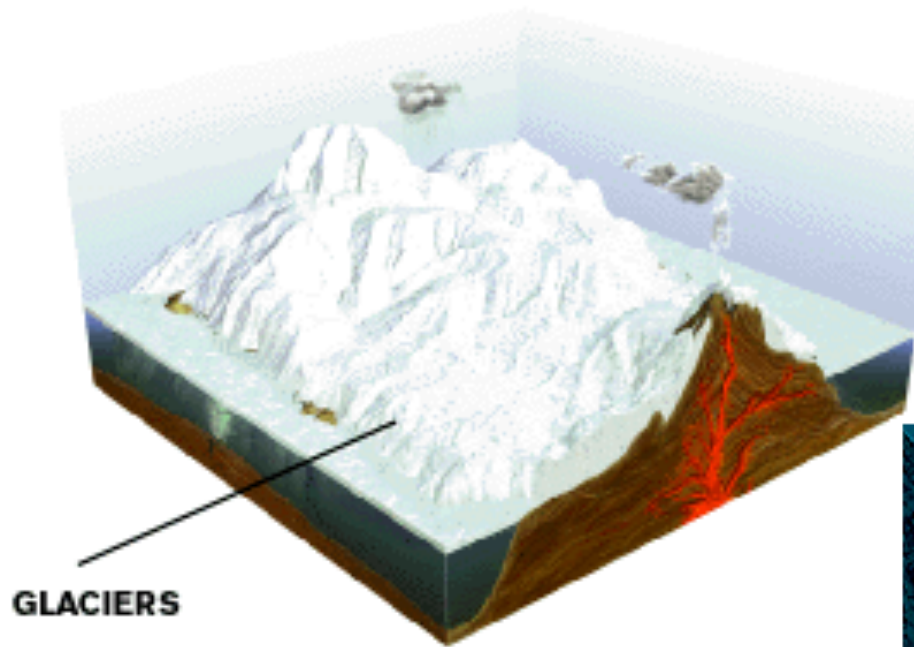




### Stage 3 Snowball Earth as It Thaws

## *Snowball?*

- Global glaciation for ~10 Myr (avg T ~ -50°C)
- Sea ice ~1000 m thick, geothermal heat flux (0.07 W/m<sup>2</sup>) keeps ocean liquid



Hoffman & Schrag (2000)



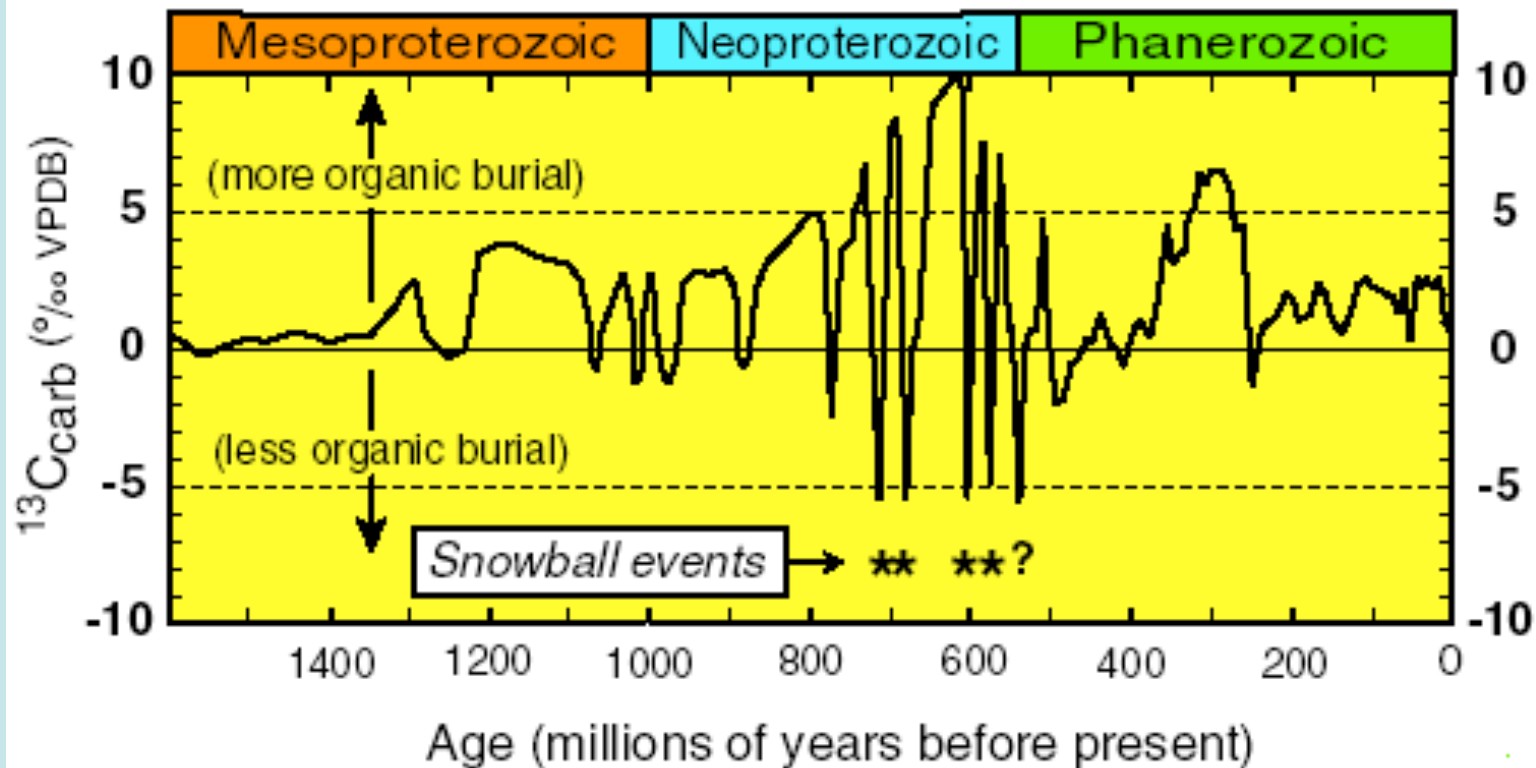
*The Vallee Blanche, Mont Blanc, French Alps*

# Evidence cited for Snowball

- *Stratigraphy*: globally-dispersed glacial deposits.
- *Carbon isotopes*: negative  $\delta^{13}\text{C}$  excursions through glacial sections (inorganic  $\delta^{13}\text{C}$  reaches  $\sim -5$  to  $-7\text{‰}$ ). Little or no biological productivity (no light).
- *Banded iron formations w/ice-rafted debris (IRD)*: only BIFs after 1.7 Ga. Anoxic seawater covered by ice.
- *Cambrian explosion*: 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

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

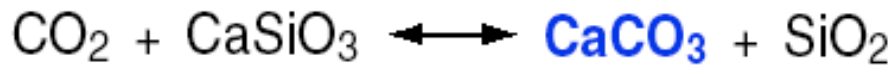


*Secular variation in carbon isotopic composition of shallow marine carbonates over the last 1600 million years (adapted from Kaufman, 1997; Kah et al., 1999).*

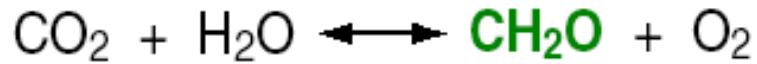
Image from P. Hoffman



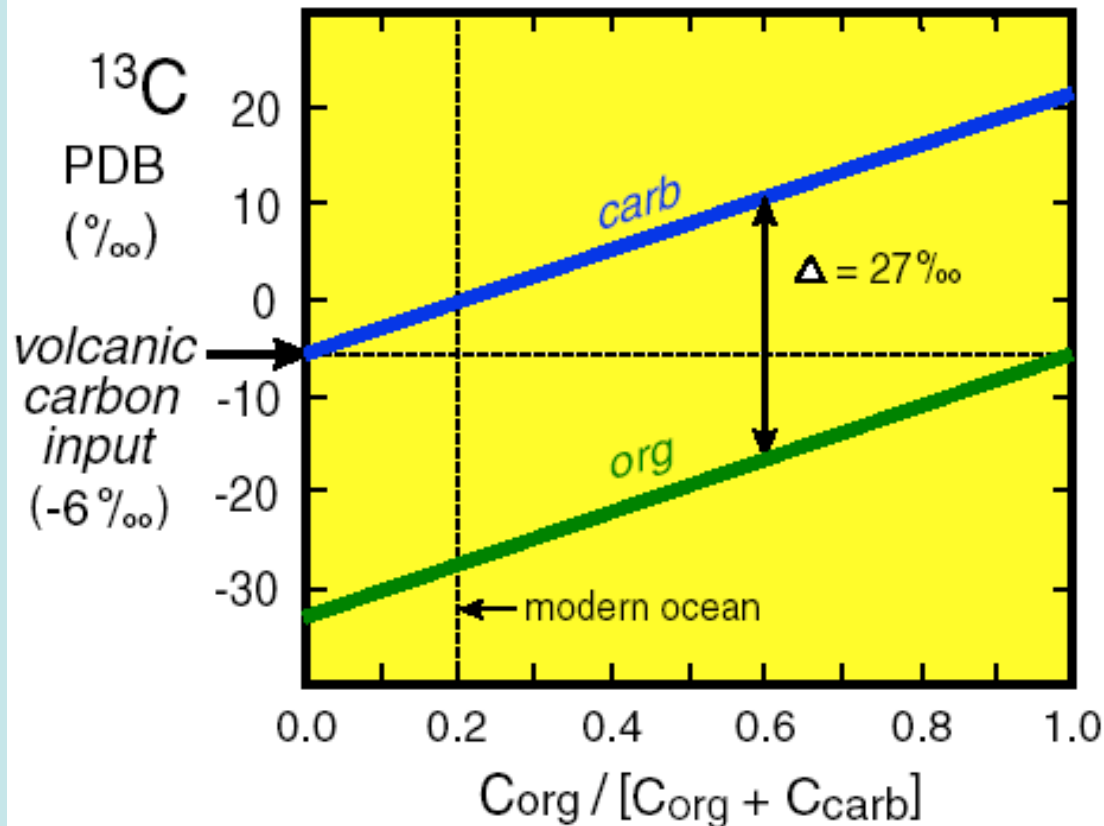
*inorganic carbon burial:*



*organic carbon burial:*



# Carbon Isotope Fractionation

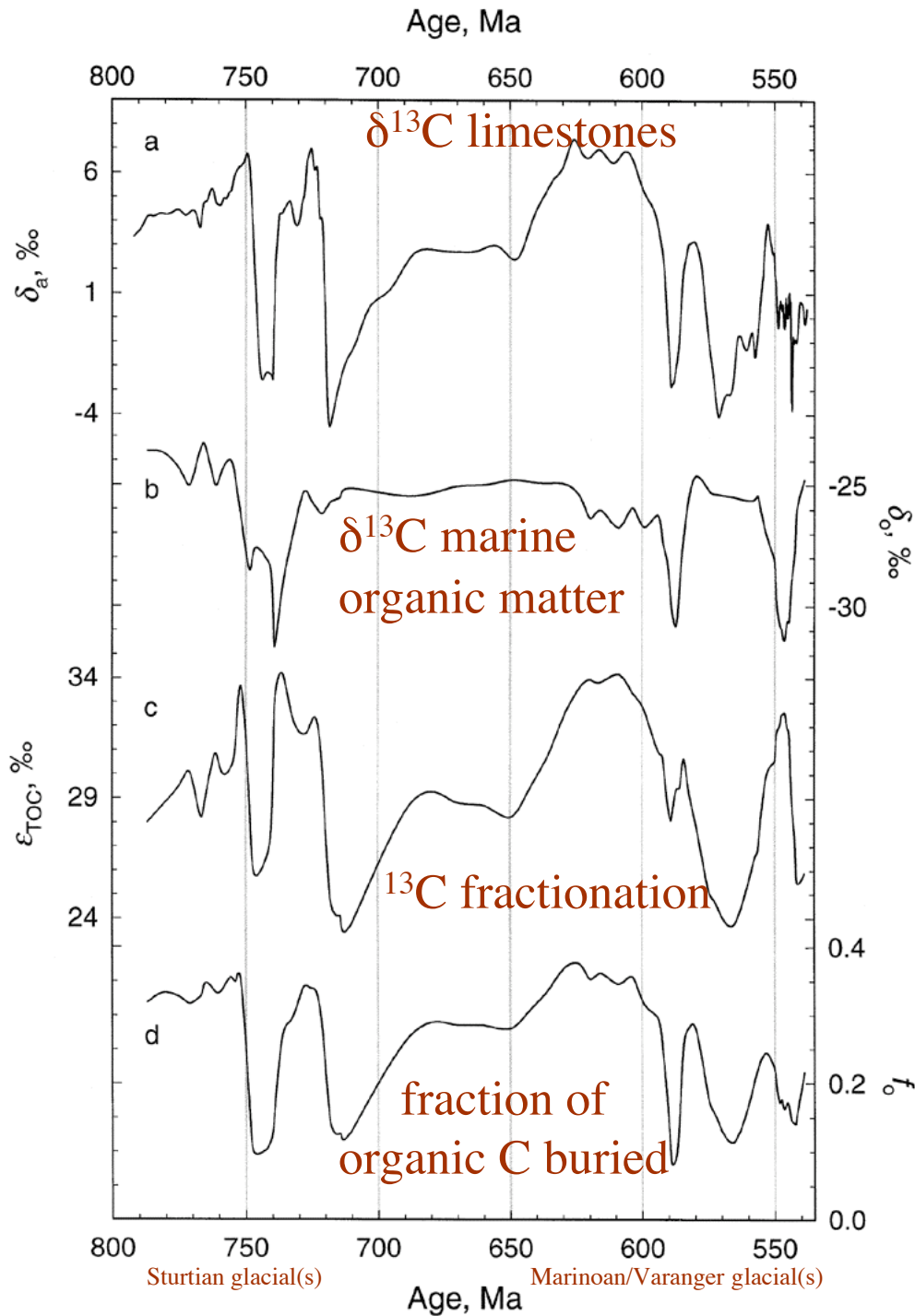


- As fraction of carbon buried approaches zero,  $\delta^{13}\text{C}$  of  $\text{CaCO}_3$  approaches mantle (input) value

$$^{13}\text{C}_{\text{PDB}}(\text{sample}) = \left[ \frac{R_{\text{sample}} - R_{\text{PDB}}}{R_{\text{PDB}}} \right] \times 10^3$$

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

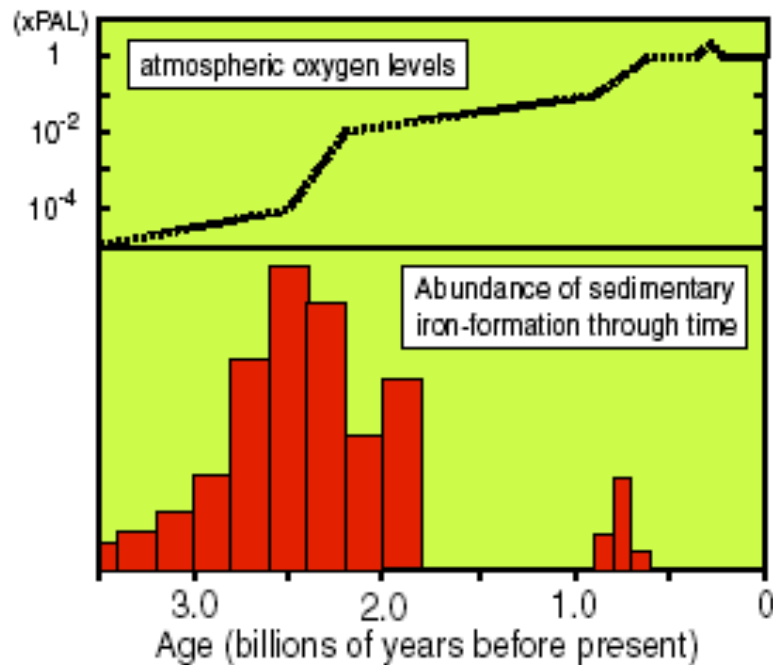
Image from P. Hoffman



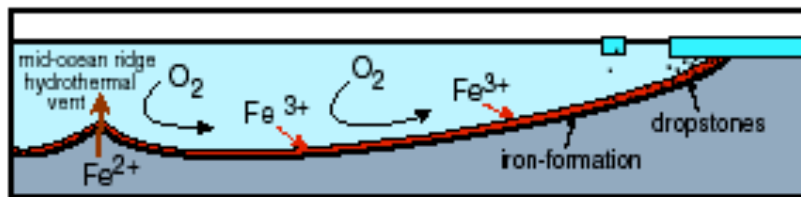
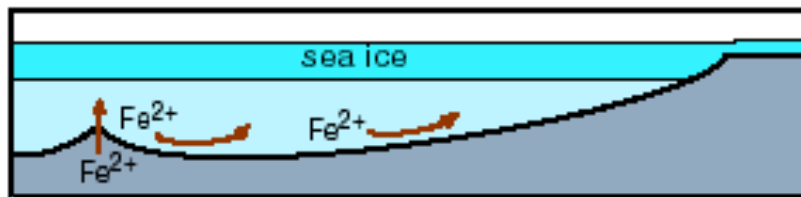
# Extreme Carbon Isotopic Excursions 800-500Ma Require Massive Perturbation of Global carbon Cycle

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

If  $O_2$  is absent, iron is soluble as ferrous ( $Fe^{2+}$ ) ion.  
If  $O_2$  is present, iron is insoluble as ferric ( $Fe^{3+}$ ) ion.



Snowball earth: anoxic ocean



Deglaciation: ocean ventilation

## 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?

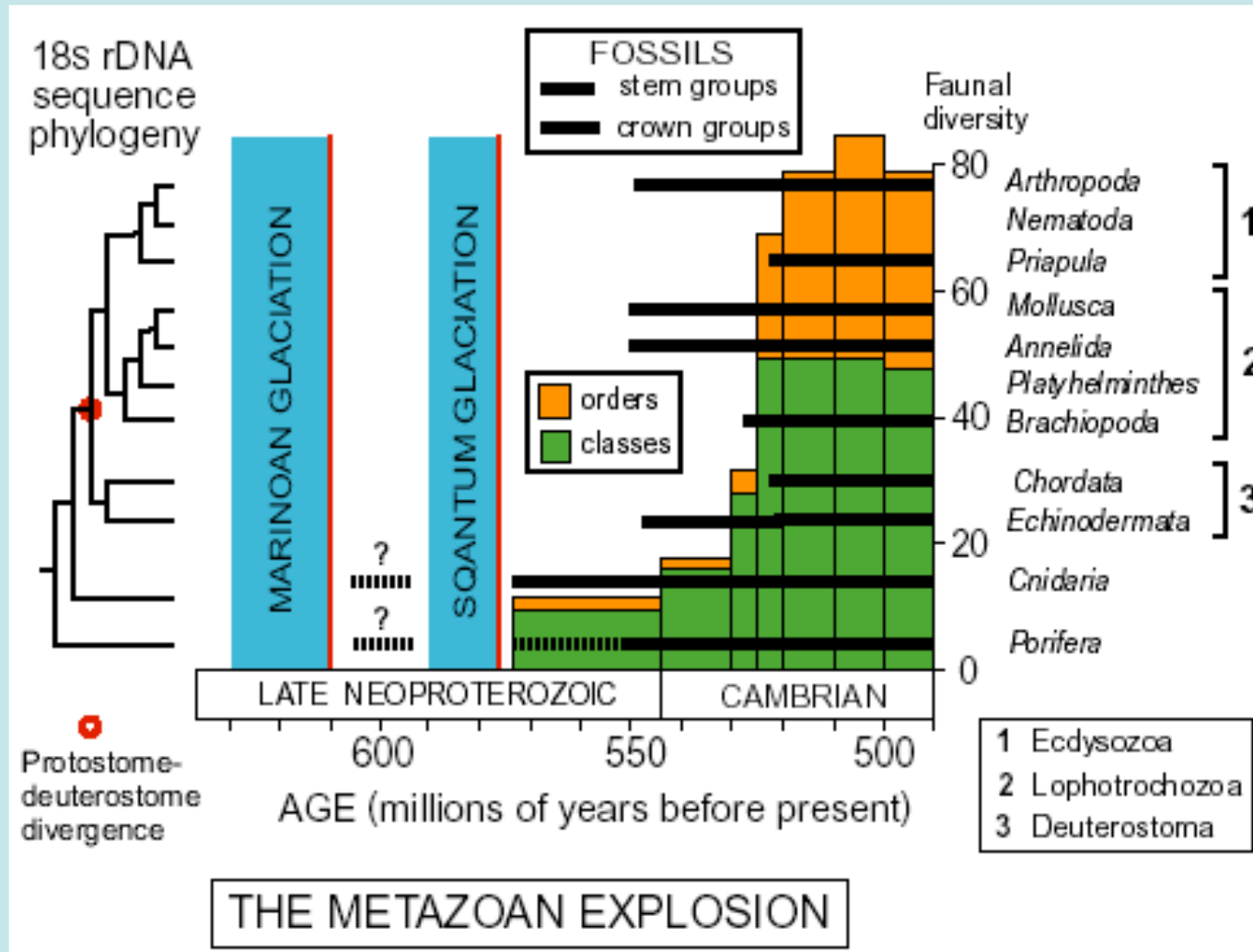


Image from P. Hoffman

# Breaking out of the Snowball



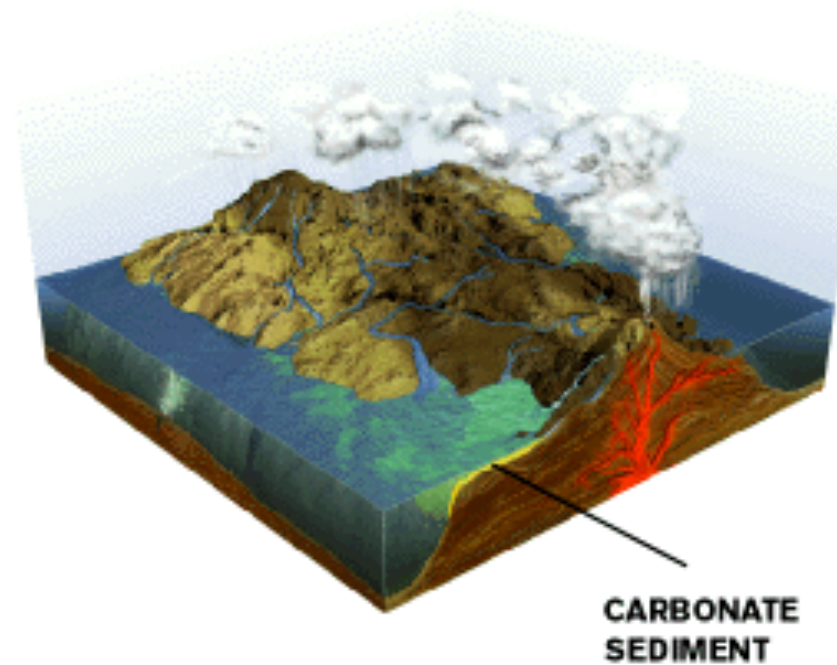
- Volcanic outgassing of  $\text{CO}_2$  over  $\sim 10^6$  yr may have increased greenhouse effect sufficiently to melt back the ice.

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

# Bring on the Heat: Hothouse follows Snowball?



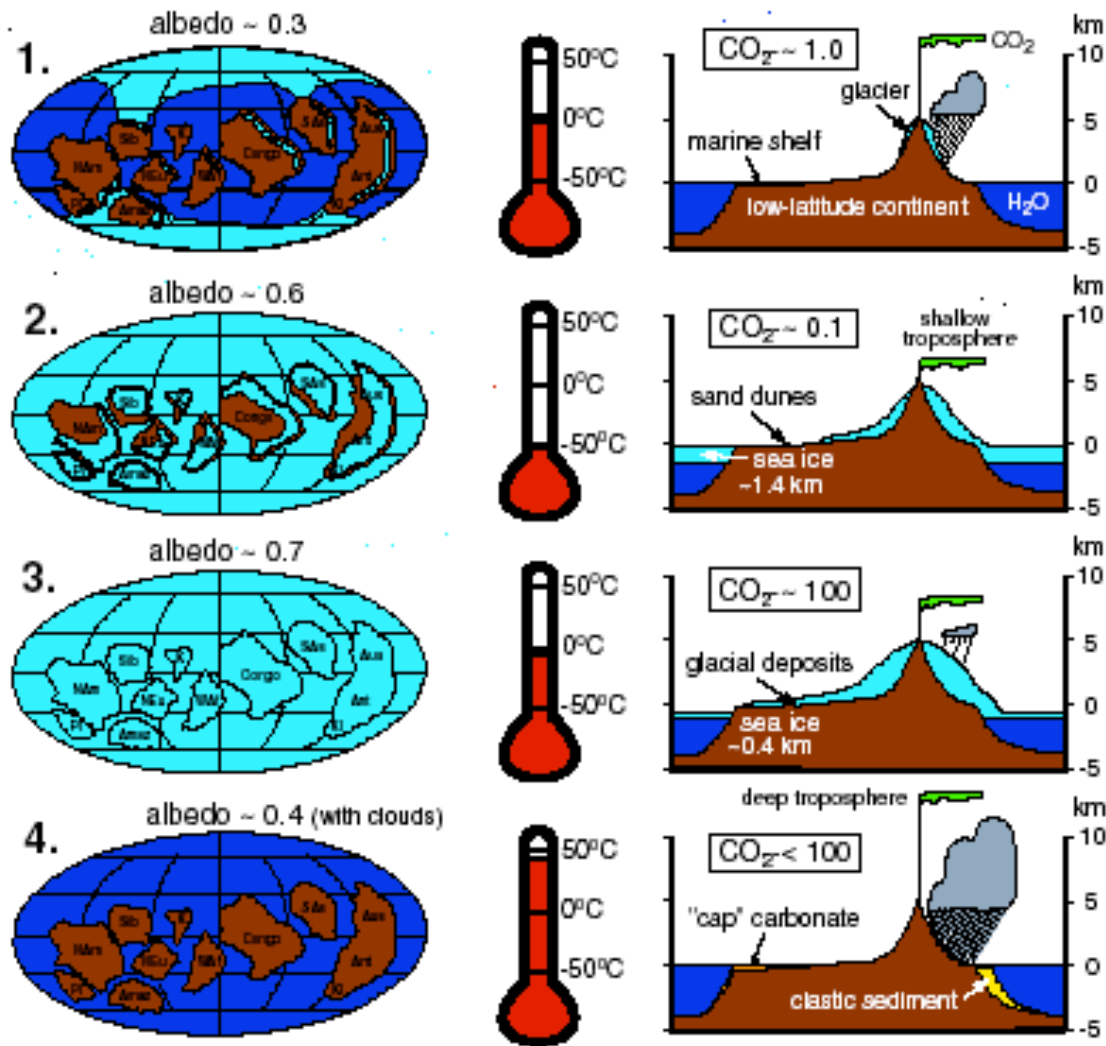
## Stage 4 Hothouse Aftermath



### Hothouse Events

- Slow  $\text{CO}_2$  buildup to  $\sim 350$  PAL from volcanoes
- Tropical ice melts: albedo feedback decreases, water vapor feedback increases
- Global T reaches  $\sim +50^\circ\text{C}$  in  $10^2$  yr
- High T & rainfall enhance weathering
- Weathering products +  $\text{CO}_2 =$  carbonate precipitation in warm water

# SNOWBALL FREEZE-FRY SCENARIO



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

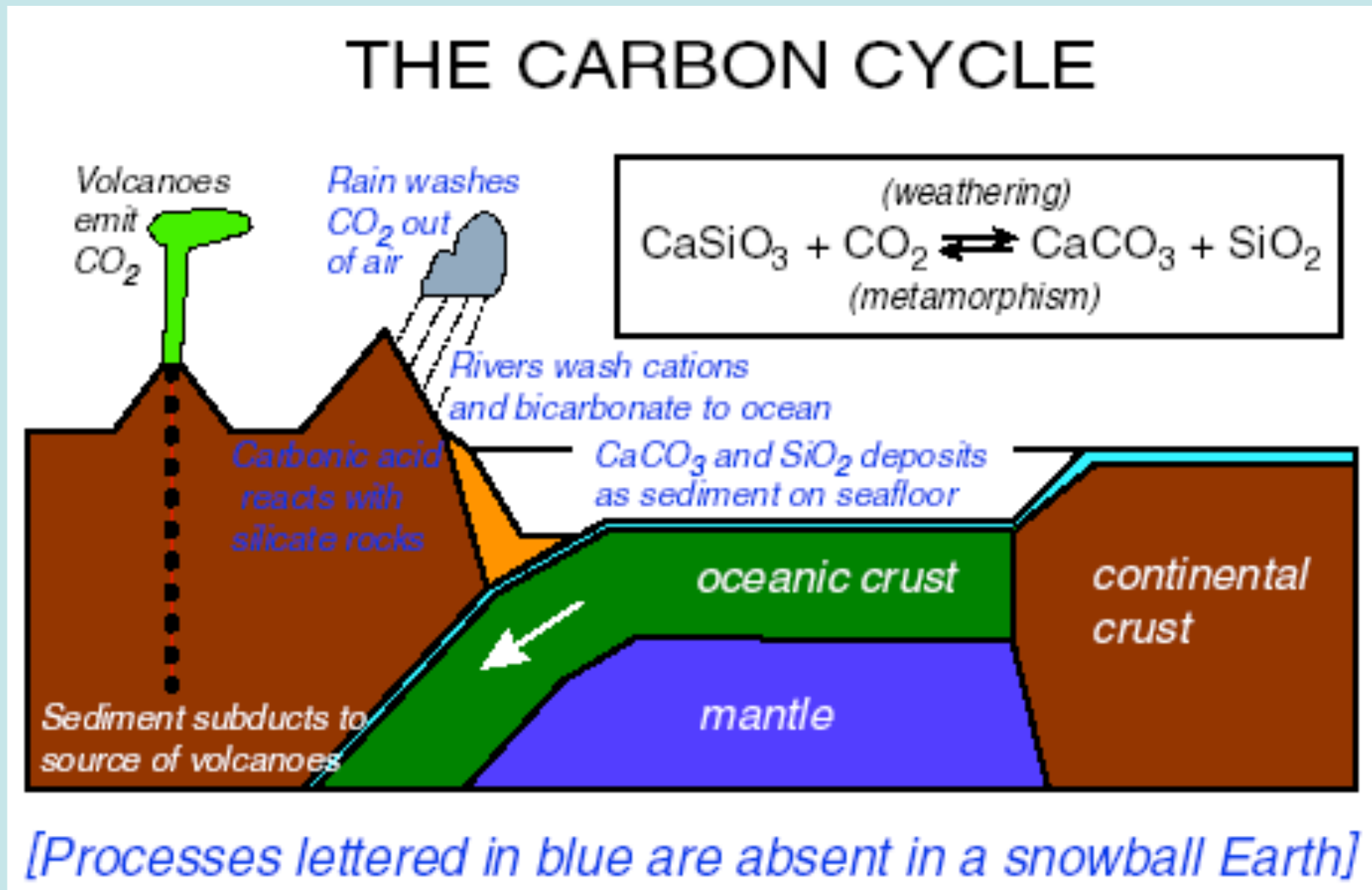
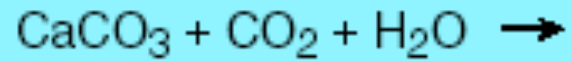


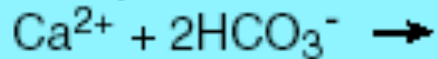
Image from P. Hoffman

## CARBONATE WEATHERING

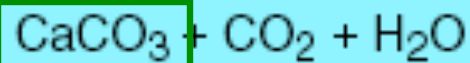
*weathering:*



*transport:*

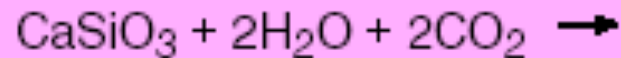


*sedimentation:*

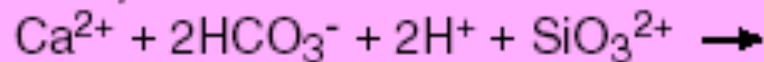


## SILICATE WEATHERING

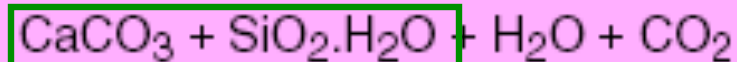
*weathering:*



*transport:*



*deposition:*



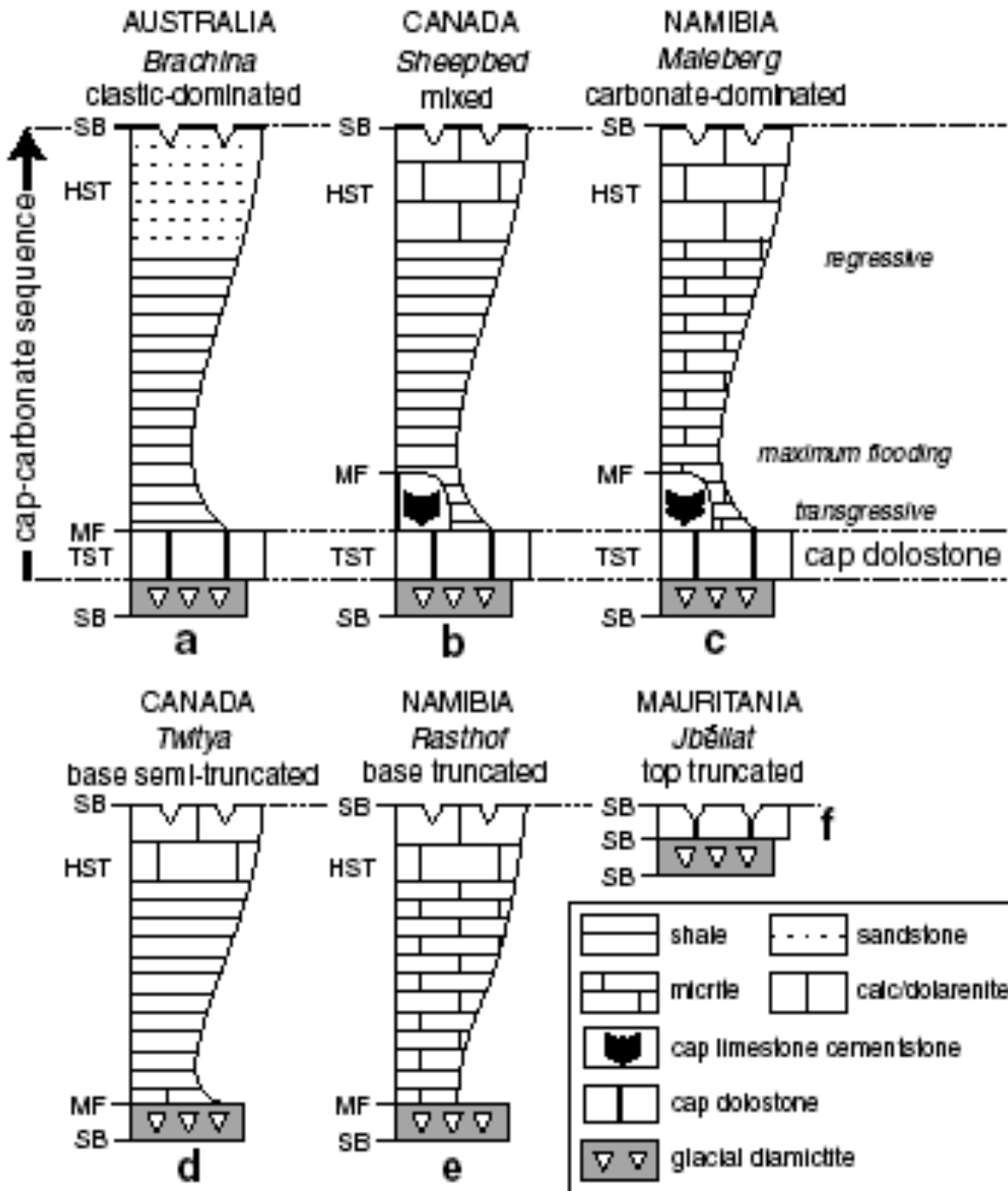
# Enhanced Weathering of Rocks Results in Precipitation of Minerals in Ocean

- High T & CO<sub>2</sub> cause increase in weathering rate of continents
- Products of weathering carried to ocean by rivers
- Precipitated as CaCO<sub>3</sub> and SiO<sub>2</sub> minerals in ocean

# **Geologic Evidence for Hothouse Aftermath: “Cap Carbonates”**

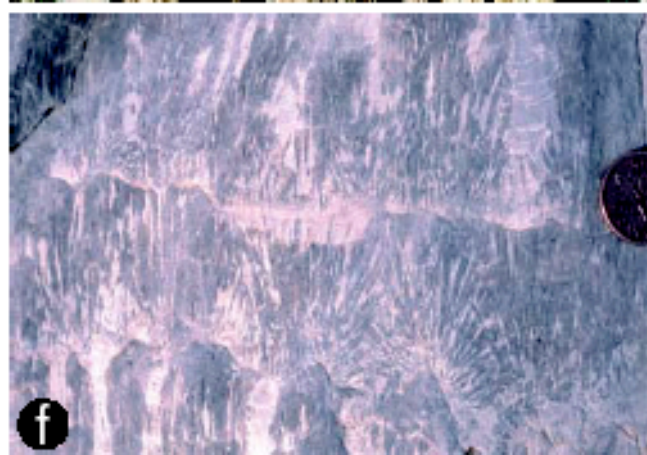
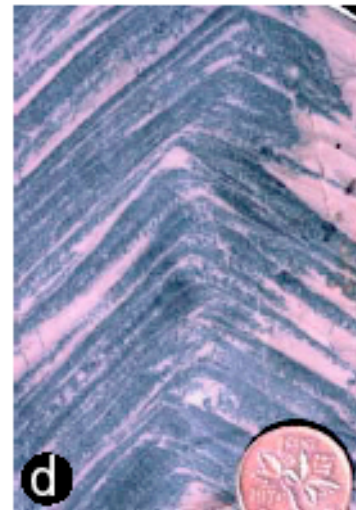
**Thick sequences of inorganically  
precipitated  $\text{CaCO}_3$  overly  
Neoproterozoic glacial deposits  
globally.**

# Neo-proterozoic Cap Carbonates-1



- Thick sequences of inorganically precipitated carbonate minerals are found over 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.



## Neoprot. Cap Carbonates: 2

- Ripples, storm waves
- Aragonite crystal fans

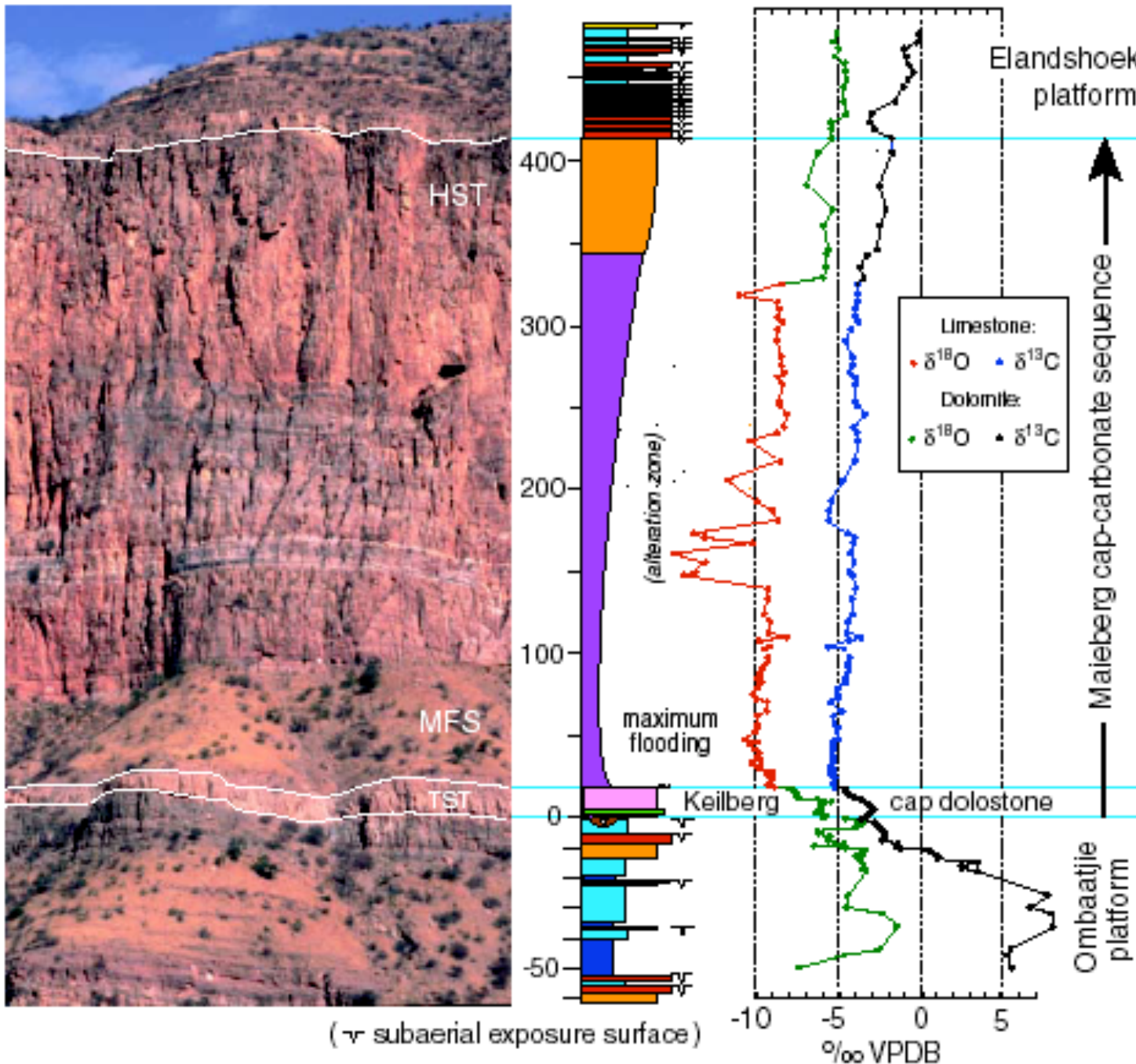
Hoffman & Schrag  
(2002) *Terra Nova*,  
Vol. 14(3):129-155.

# Aragonite Fan in Namibia



- Carbonate fans form when  $\text{CaCO}_3$  is rapidly precipitated from water.

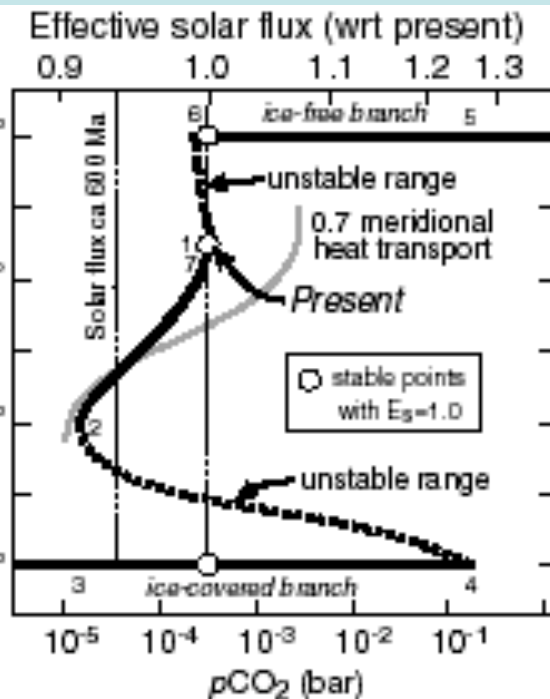
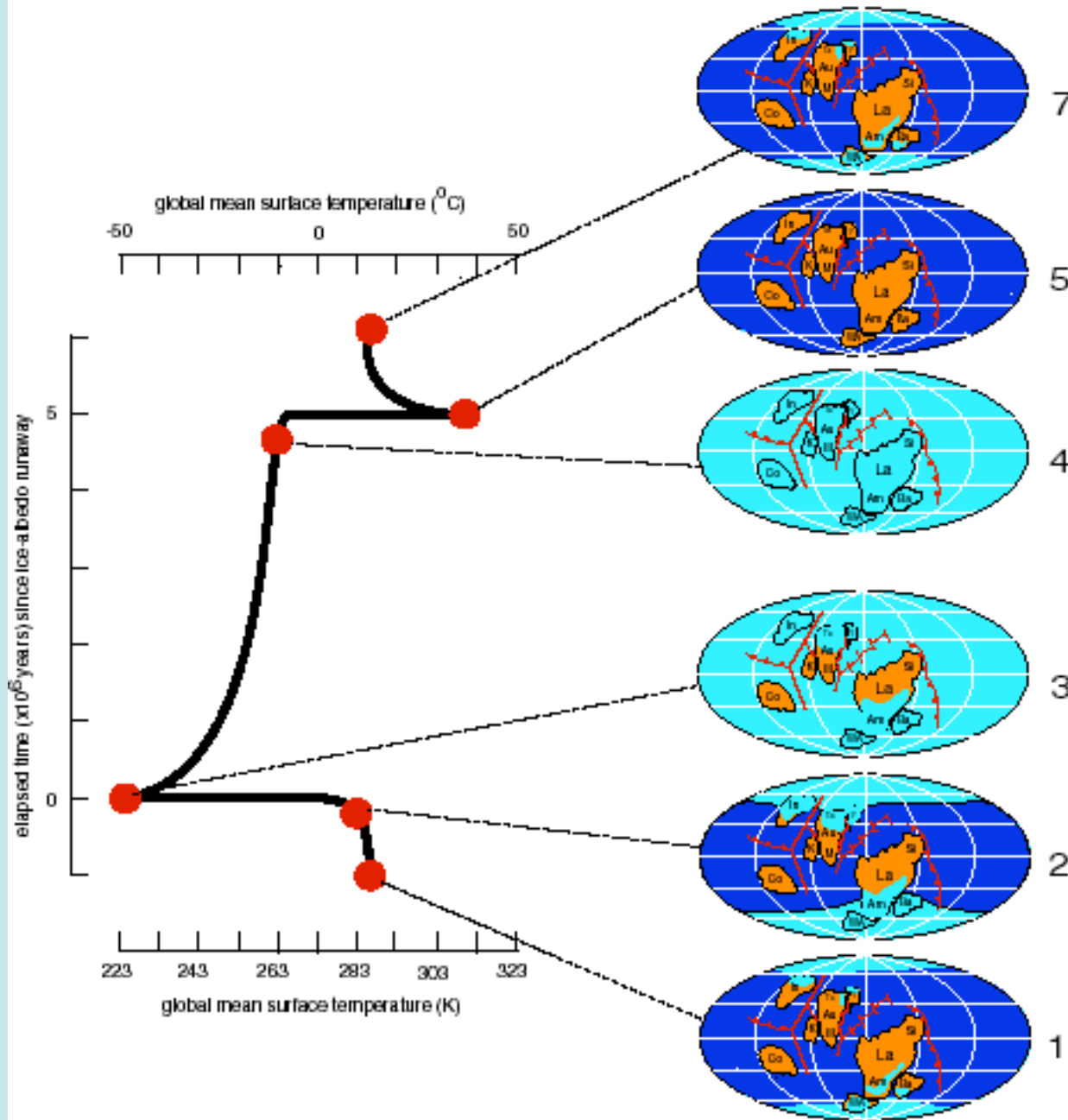
Image from P. Hoffman



# Geologic & Isotopic Change Associated with Snowball Event:

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

# Summary of Snowball-Hothouse Sequence



Note: T estimated from  
E balance model

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

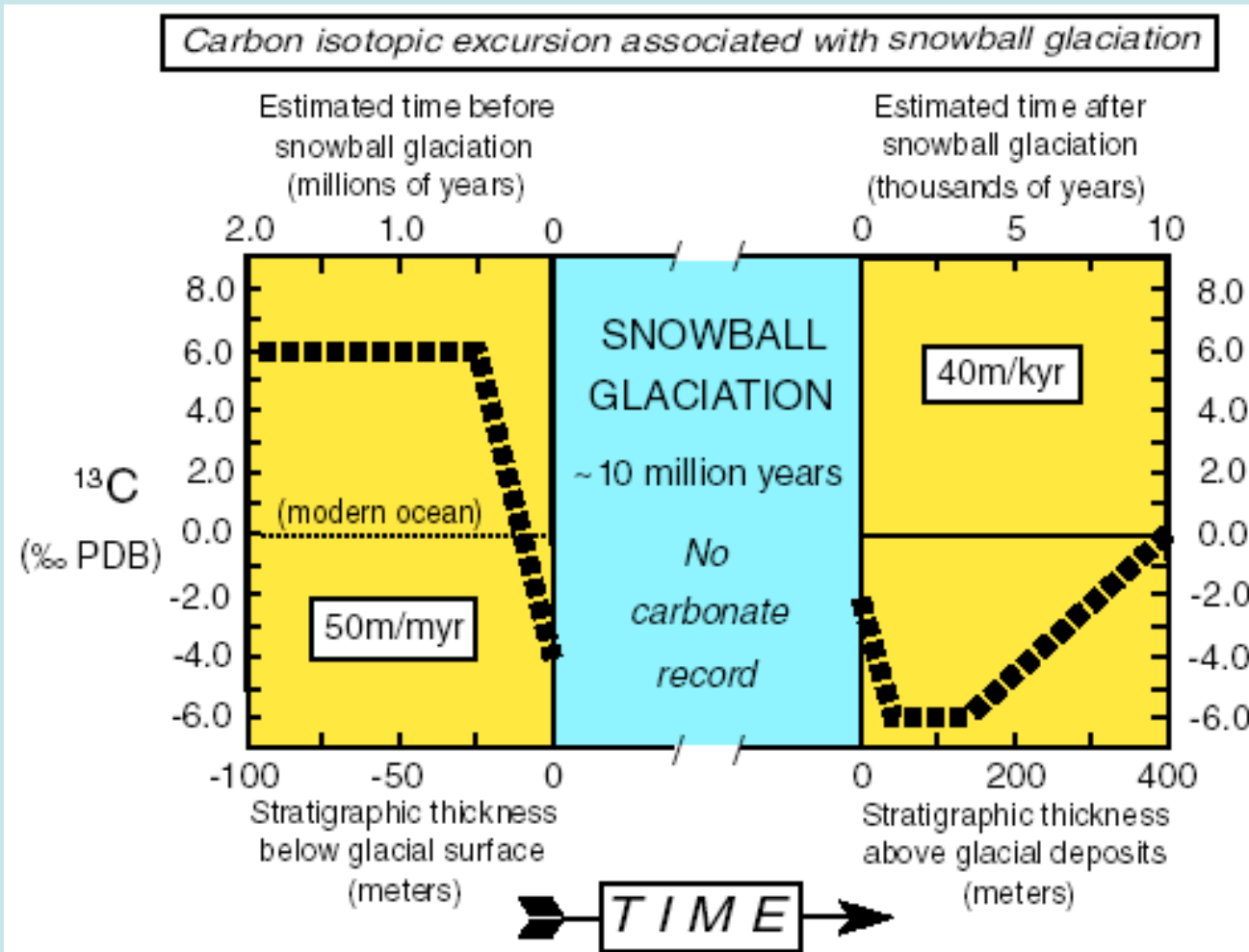


## Evidence for Snowball / Hothouse

- *Stratigraphy*: globally-dispersed glacial deposits overlain by thick sequences of inorganic (cap) carbonates.
- *Carbon isotopes*: negative  $\delta^{13}\text{C}$  excursions through glacial sections ( $\delta^{13}\text{C}$  reaches  $\sim -5$  to  $-7\text{‰}$ ). Little or no biological productivity (no light). Remain low through most of cap carbonate deposition.
- *Banded iron formations w/IRD*: only BIFs after 1.7 Ga. Anoxic seawater covered by ice.
- *Cambrian explosion*: Rapid diversification of multicellular life 575-525 Ma expected to result from long periods of isolation and extreme environments (genetic "bottleneck and flush").

# 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

# What kept this from happening after ~580 Ma?

- Higher solar luminosity (~5% increase)
- Less landmass near equator = lower weathering rates (?)  
→ John Edmond: weathering rates limited by abundance of fresh rock, not temperature.
- Increased bioturbation (eukaryote diversity following re-oxygenation of ocean): Less C accumulation in sediments sequesters less atmospheric CO<sub>2</sub>, offsetting lower weathering rates (from higher-latitude continents).
- lower iron and phosphorus concentrations in better-oxygenated Phanerozoic ocean [Fe(II) is soluble; Fe(III) is less so]: Decreased 1° production = Decreased CO<sub>2</sub> drawdown.

→ What we would like to know:  
CO<sub>2</sub> concentrations through snowball/hothouse cycle.

## 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.

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<sup>1</sup>.

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 dur-



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

ing 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<sup>2</sup>. 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 atmos-



Volcanic CO<sub>2</sub> may have caused a greenhouse effect that freed snowball Earth from its ice age.

phere, eventually creating enough greenhouse warming to melt the ice sheets.

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<sup>3</sup>. 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

# Potential Problems with the 'Snowball Earth hypothesis'

- Ocean/atmosphere climate models cannot seem to keep entire ocean covered with ice.
- No evidence for lower sea level.
- Weathering reactions are slow..... Maybe too slow to be the source of cap carbonates.

P. L. SMITH/ISTOCK PHOTO

MORIGUNI/ISTOCK

# Climate dynamics of a hard snowball Earth

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Department of Geophysical Sciences, University of Chicago, Chicago, Illinois, USA

Received 25 June 2004; revised 12 October 2004; accepted 12 November 2004; published 15 January 2005.

[1] The problem of deglaciating a globally ice-covered (“hard snowball”) Earth is examined using a series of general circulation model simulations. The aim is to determine the amount of  $CO_2$  that must be accumulated in the atmosphere in order to trigger deglaciation. Prior treatments of this problem have been limited to energy balance models, which are incapable of treating certain crucial physical processes that turn out to strongly affect the conditions under which deglaciation can occur.  $CO_2$  concentrations up to .2 bars are considered in the general circulation model simulations, and even at such high  $CO_2$  content the model radiation code is found to perform well in comparison with codes explicitly designed for high  $CO_2$ . In contrast to prevailing expectations, the hard snowball Earth is found to be nearly 30 K short of deglaciation, even at .2 bars. The very cold climates arise from a combination of the extreme seasonal and diurnal cycle, lapse rate effects, snow cover, and weak cloud effects. Several aspects of the atmospheric dynamics are examined in detail. The simulations indicate that the standard scenario, wherein snowball termination occurs after a few tenths of a bar of  $CO_2$  has built up following cessation of weathering, is problematic. However, the climate was found to be sensitive to details of a number of parameterized physical processes, notably clouds and heat transfer through the stable boundary layer. It is not out of the question that other parameterization suites might permit deglaciation. The results should not be construed as meaning that the hard snowball state could not have occurred, but only that deglaciation requires the operation of as-yet undiscovered processes that would enhance the climate sensitivity. A brief survey of some of the possibilities is provided.

**Citation:** Pierrehumbert, R. T. (2005), Climate dynamics of a hard snowball Earth, *J. Geophys. Res.*, *110*, D01111, doi:10.1029/2004JD005162.

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

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

- $\text{CaCO}_3$  precipitation does not require increased weathering flux of minerals.
- Can be caused by increased seawater alkalinity resulting from  $\text{CH}_4$  consumption by sulphate-reducing bacteria.



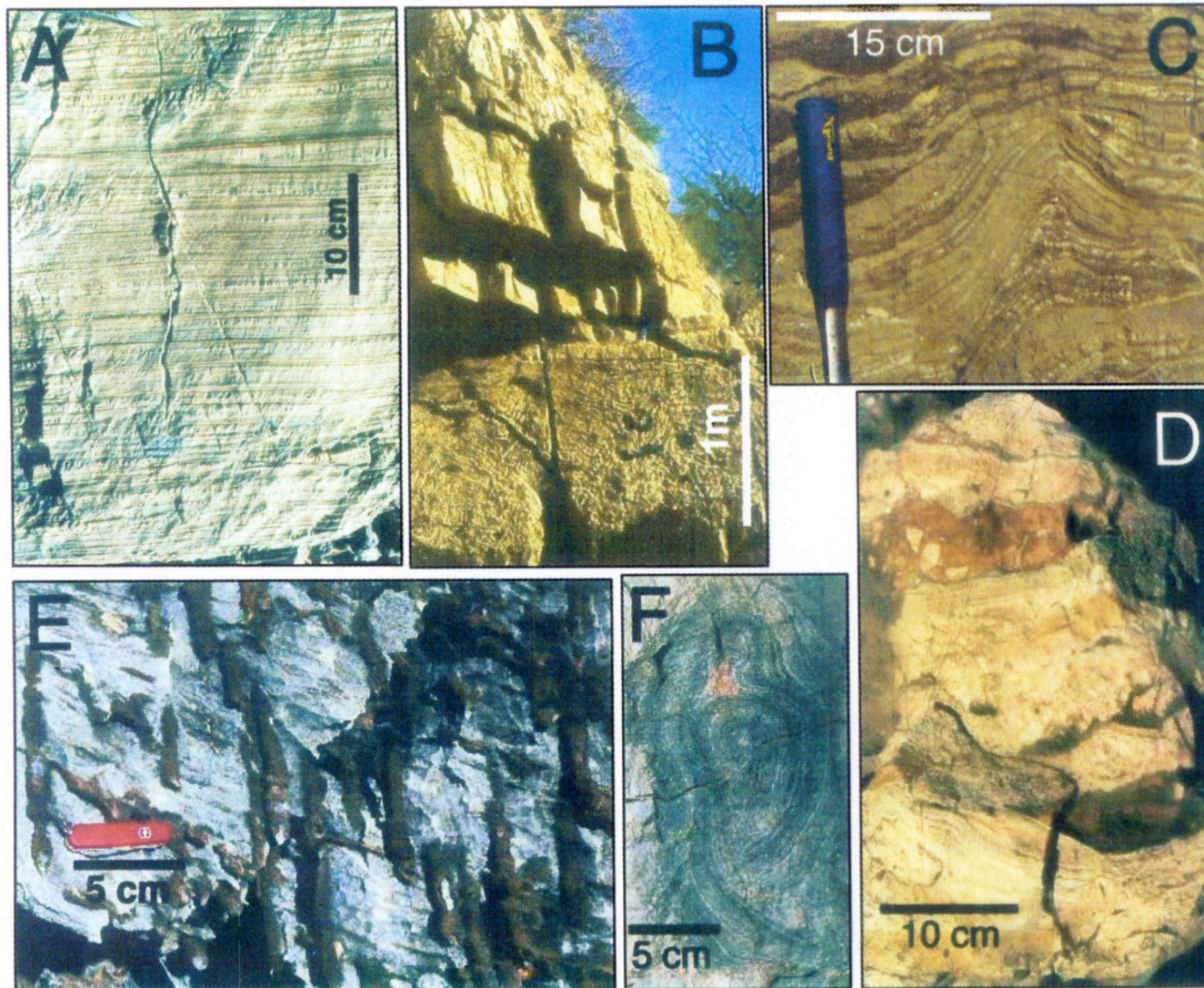


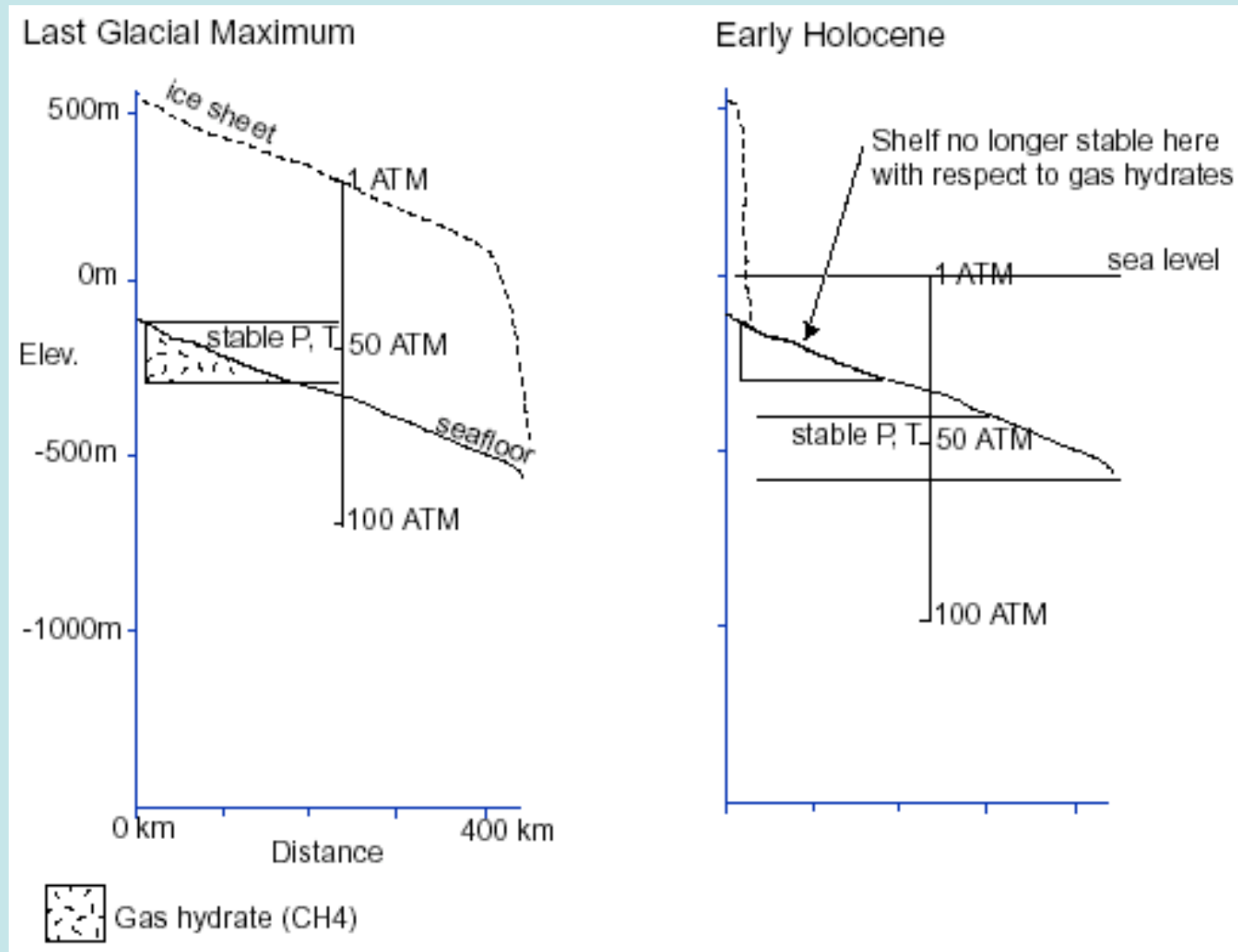
Figure 1. Cap carbonate lithofacies: A: Typical laminated dolomiticrite. B: Facies with domal and tepee-shaped structures and abundant cement, overlain by laminated dolomite. C: Detail of B showing growth of tepee-shaped structure and sheet cracks lined by isopachous cement. D: Brecciation in core of 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).

## Structures in Cap Carbonates May Result from Gas Release

- Gas Hydrate =  $[H_2O + \text{hydrocarbon } (CH_4)]$  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

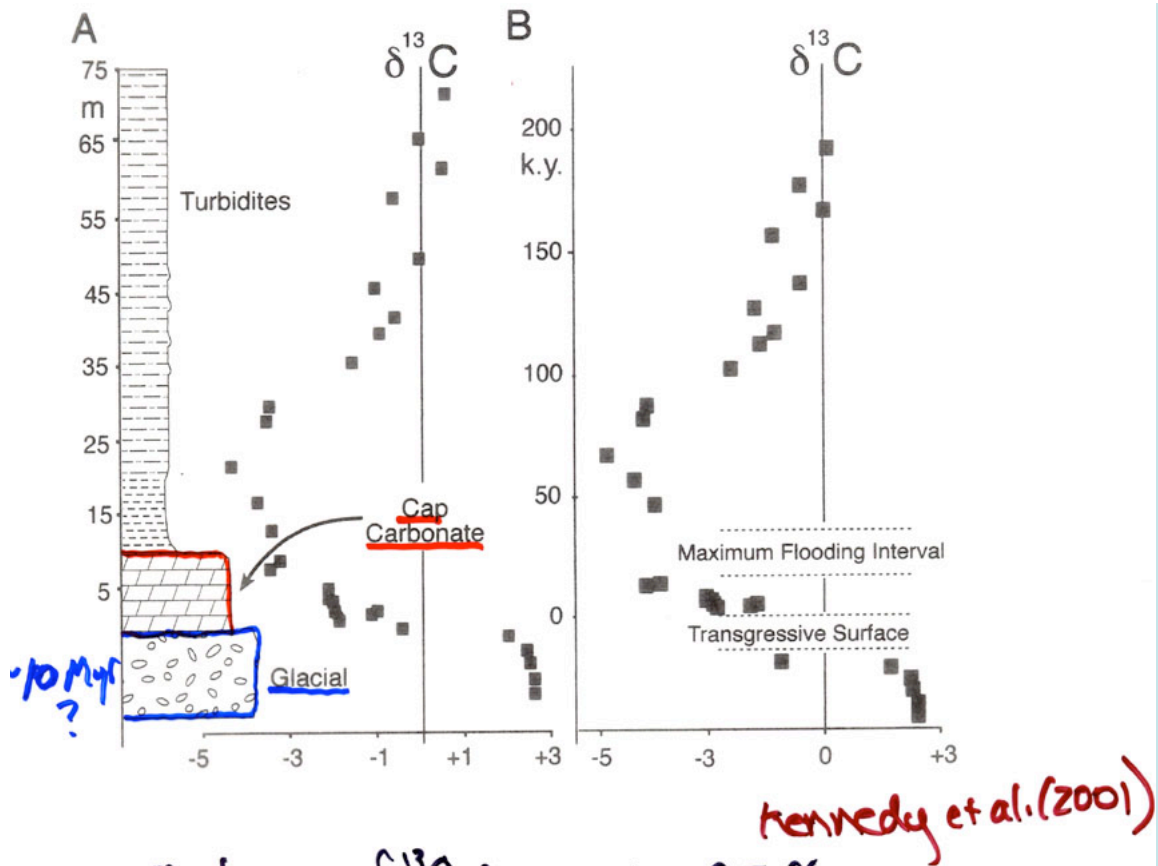
Kennedy et al. (2001)  
*Geology* Vol. 29(5): 443-446.

# Gas Hydrate Stability



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





Methane  $\delta^{13}\text{C}$ : -60 to -95 ‰



Increase ~~Decrease~~ seawater Alkalinity

Causes  $\text{CaCO}_3$  to ppt.

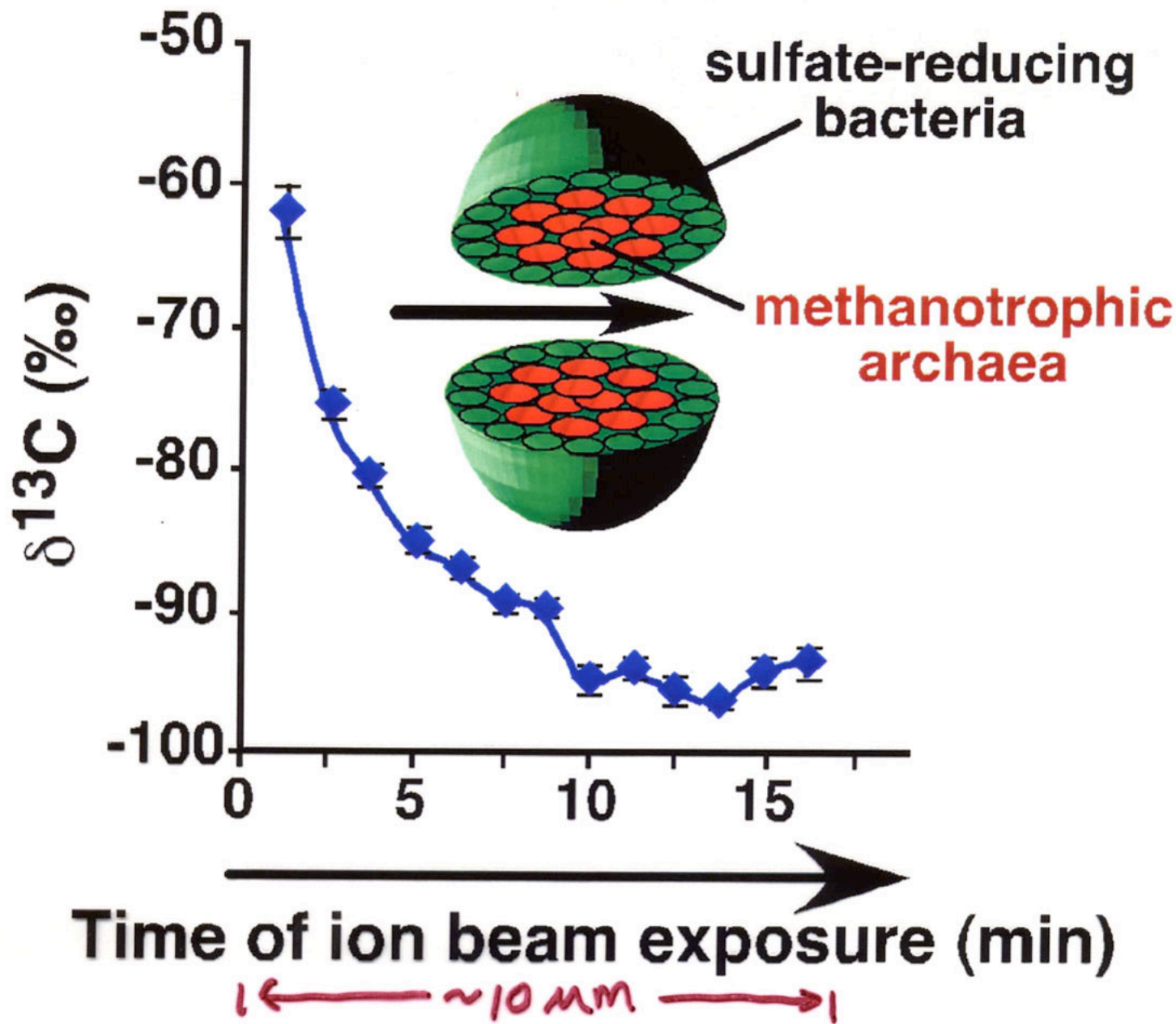
Low  $\delta^{13}\text{C}$  of ocean / atmosphere  
= Low  $\delta^{13}\text{C}$   $\text{CaCO}_3$

Rather than increased weathering flux of cations &  $\text{HCO}_3^-$  to ocean causing  $\text{CaCO}_3$  precipitation, decreased seawater alkalinity could have caused  $\text{CaCO}_3$  precipitation

$\text{CH}_4$  consumption by  $\text{SO}_4^{2-}$ -reducers @ seafloor & in flooded permafrost

Drives  $\Sigma\text{CO}_2$  ( $\text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{2-}$ ) toward  $\text{CO}_3^{2-}$ , causing  $\text{CaCO}_3$  to precipitate out of seawater

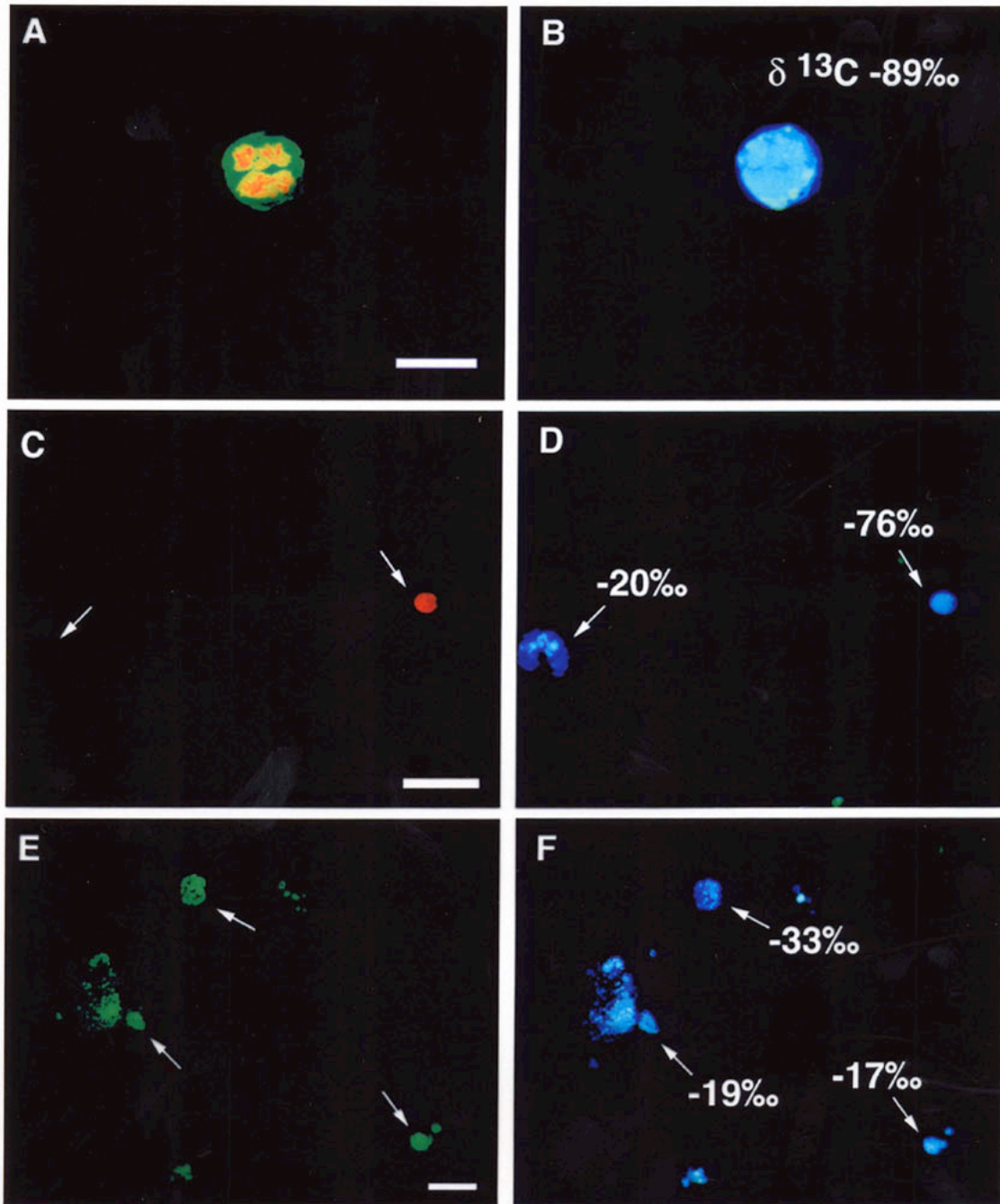
$\text{CH}_4$ -derived  $\text{CaCO}_3$  has low  $\delta^{13}\text{C}$



Orphan et al. (2001), Science, Vol. 293, pp. 484-487.

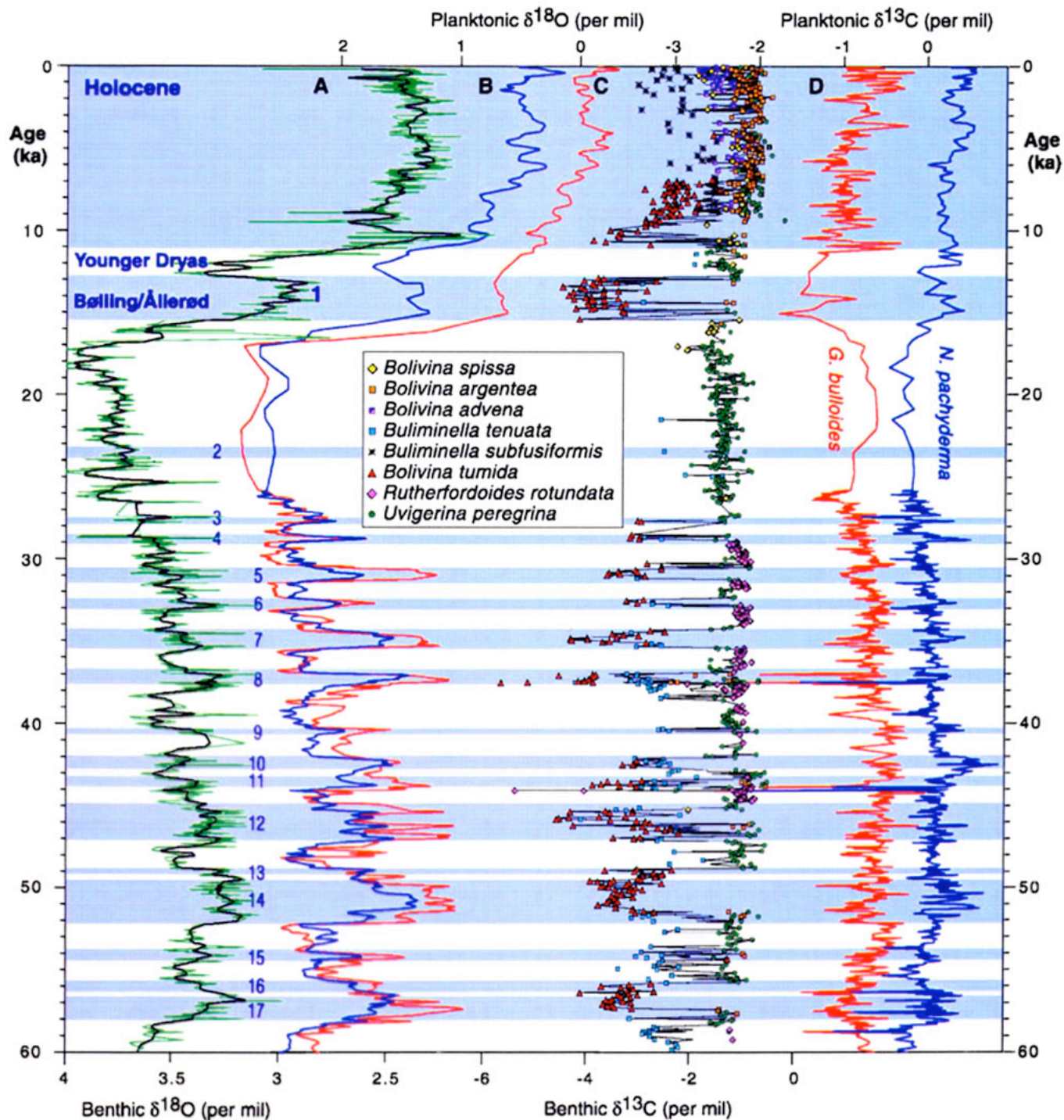
$\text{CH}_4$  consumption by sulphate reducers is observed at methane seeps in modern ocean, &  $\text{CaCO}_3$  precipitates there as a result

•  $\text{SO}_4^{2-}$  reducers produce highly  $^{13}\text{C}$  depleted  $\text{HCO}_3^-$  which goes into ocean/atmosphere



Consortia of  
sulphate  
reducers &  
methane-  
oxidizing  
microbes  
from modern  
CH<sub>4</sub> seep

Orphan et al. (2001), Science, Vol. 293, pp. 494-497.



## Santa Barbara Basin: Recent methane hydrate releases?

- Large  $^{13}\text{C}$ -depletions in seawater & biogenic carbonates
- Suggested as due to massive releases of  $\text{CH}_4$  when gas hydrates were destabilized by changing T & P (i.e., sea level)

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