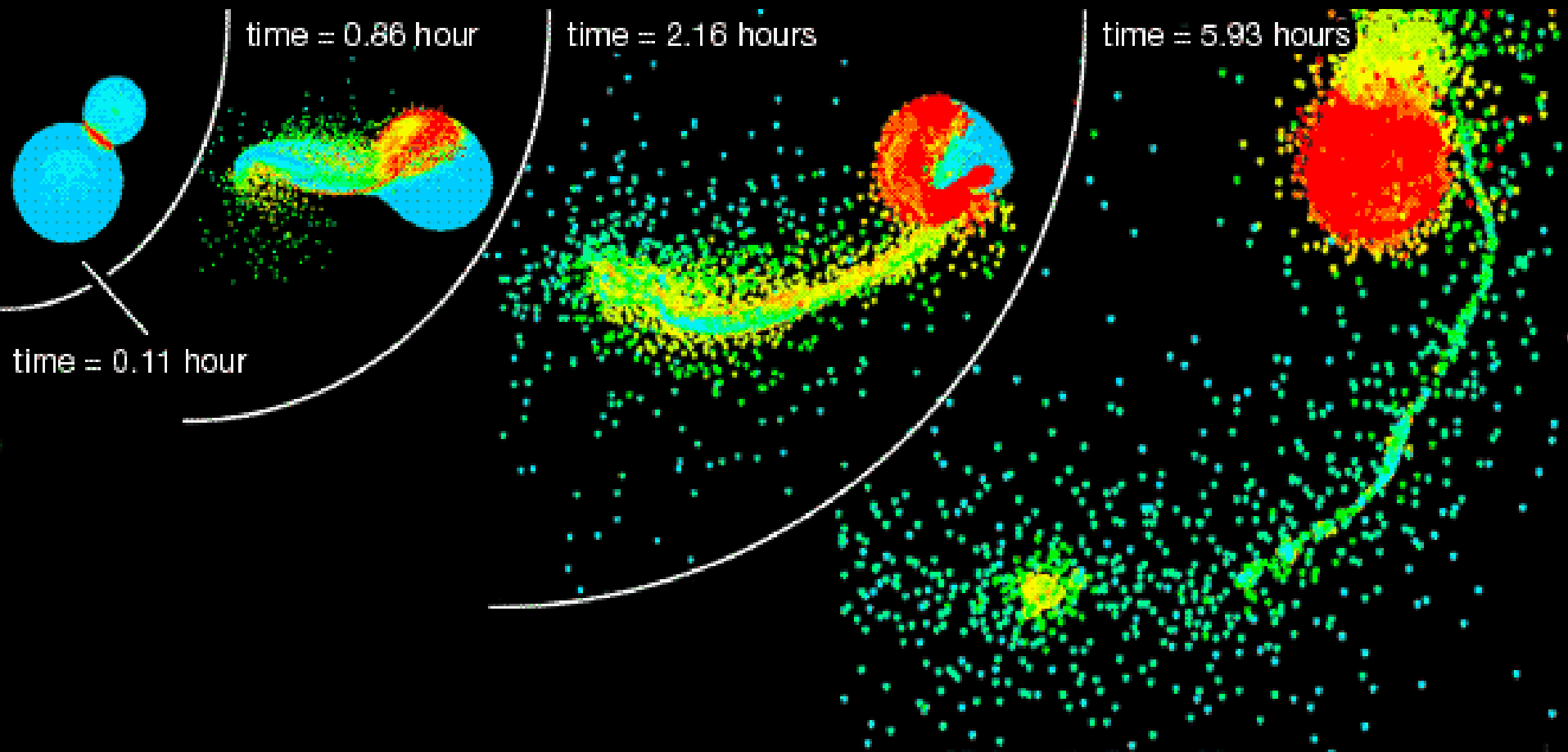


K31: Earth's Paleo-Atmosphere and Climate

R. Nolthenius, PhD

- Earth has larger gravity than Venus, farther from the sun and colder than Venus; So why so little atmosphere today, compared to Venus? It's a great story - To begin...
- ~4.5 billion years ago, a Mars-sized planet ~4,000 mi across likely struck Earth,
- [4 min "Universe" video on impact.](#)
- [3 min impacts, violent Thea impact](#), no narration
- [2 min of impact, Discovery. No narration](#)
- The impact debris ring mostly fell back to Earth, but ~1% self-gravitated to form the moon, spun up the Earth's rotation via impact and early tides
- The moon also stabilized our rotation axis direction, important for a more stable climate long term.
- **Our original atmosphere was lost to space at this moon-creating impact! Today's atmosphere is the result of later outgasing and significant additional chemistry**

Only 6 hrs after Impact, the moon has already formed at the end of the tidal tail of blasted-off material. Most material impacts back onto Earth, creating great heat and liberating much internal volatiles. Moon condenses quickly enough to escape this fate.



Sleep et al. (2014) model the post-impact Earth and find:

- The impact liberates trapped volatiles of water vapor and CO₂ at high density (more than 200 bar?), blocking outgoing IR, raising Runaway Greenhouse at temps > 500K on the surface, for ~10 million years
- Then cooling, ocean formed from H₂O, leaving ~100 bar of CO₂, Lesser amounts of SO₂ (sulfate), HF (hydrogen flouride), and HCl (Hydro-chloride).
- To explain life by 3.8 billion years ago, requires rapid weathering/subduction to sequester CO₂
- How rapid is not certain, but that's a lot of CO₂ in the earliest atmosphere...

Life as Early as 4.1 B yrs ago?

- UCLA researchers studying zircon crystals find good evidence for organic carbon (C13/C12 ratio) graphite in zircons 4.1 B yrs old, suggesting oceans and life this far back ([Bell et al. 2015](#)).
- This is during the hypothesized “late heavy bombardment” period which would seem to make life pretty hard to maintain, although evidence “late bombardment” period was much milder than once thought.
- Not clear the resolution of this data into a consistent and well-accepted picture.
- Other evidence of life 3.8-4.3B yrs ago around hydrothermal vents ([Dodd et al. 2017](#))



Our Later Atmosphere...

- Probably delivered by comets and outgas'ed from our own volcanoes - water, carbon, nitrogen, oxygen, sulfur, and smaller amounts of neon, argon, and other elements
- Volcanoes likely very active in early Earth as crust was still hot and thin, and these light elements were still rising by bouyancy from the the deeper parts of Earth
- Ammonia = NH_3 , likely common and emitted by volcanoes. Ammonia common in Jupiter's atmosphere. Would dissociate over time... it is a greenhouse gas

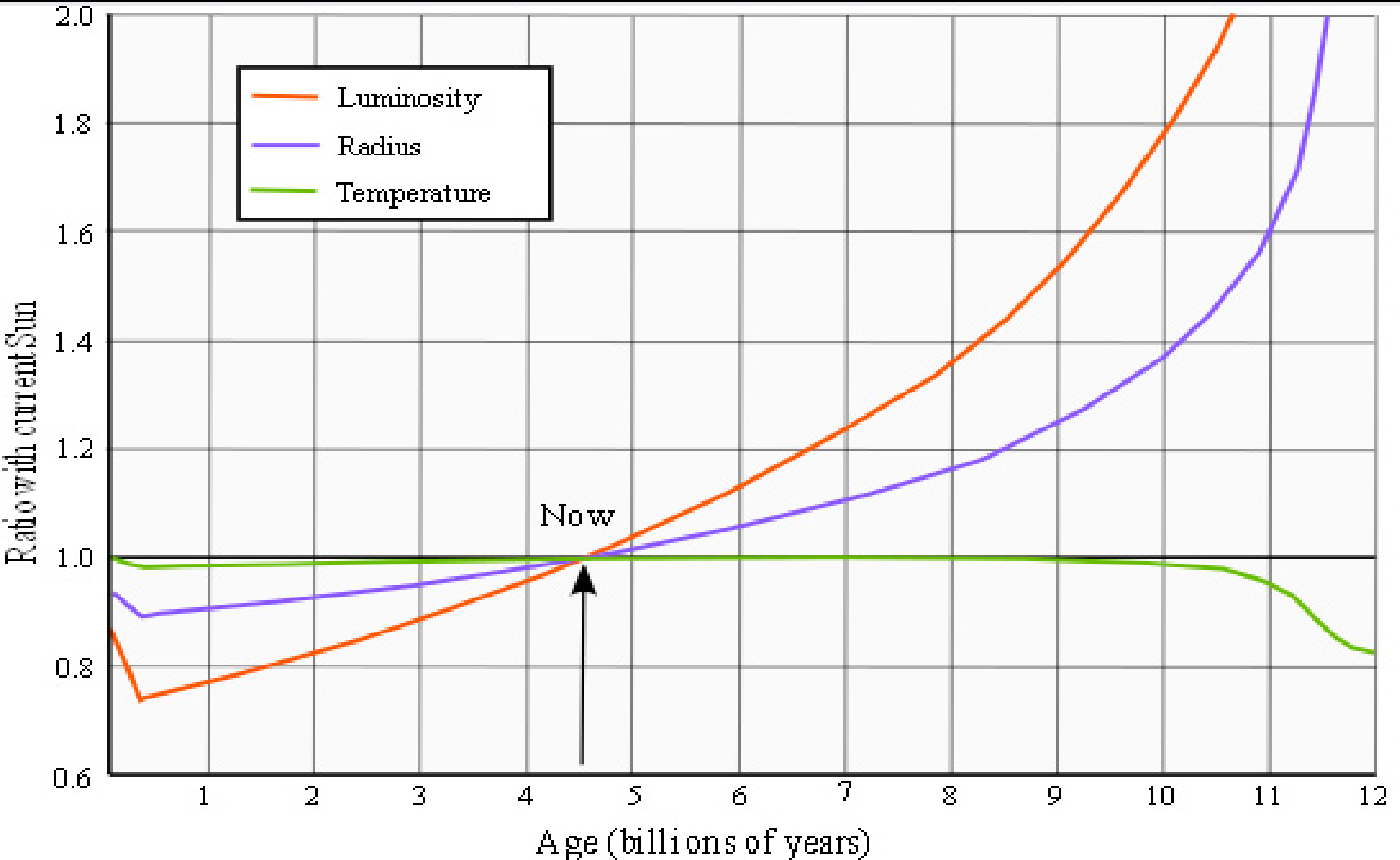
Whence our N₂ Atmosphere?

- Solar UV broke Ammonia into free N and H, and the H was mostly lost to outer space, **and the N combined to make N₂ and enriched the atmosphere.** Also possible volcanoes contributed, giving back nitrogen trapped in the initial condensation of the planet.
- CO₂ also richer than today; heavy and most easily retained by gravity.
- Probably NOT enough CO₂ to fully account for the weaker sunlight of that era and keep Earth from being frozen, as it was NOT frozen. So need a mix of greenhouse gases it seems.

Young Faint Sun Paradox

- The sun, like all stars, increases in luminosity all during its life, until the very late moments before death.
- The sun has increased in luminosity by 30% since shortly after Earth formed, (as the solar core becomes increasingly enriched in denser helium, creating stronger core density and gravity and hence raising the fusion rate. All stars do this, converting their potential energy into kinetic, and then into fusion and outgoing luminosity)
- Yet we have evidence of a liquid ocean going back to ~4.2 billion years ago – almost all the way back to our 4.56 Billion year ago birth, and life almost as far back
- Oceans should have been frozen solid, yet weren't.
- **This is the Faint Young Sun Paradox**
- **Resolution: Probably much more greenhouse gas heat trapping in early atmosphere. Can we make this much additional greenhouse effect and be consistent with the evidence?**

The Luminosity of the Sun has Increased 30% since 4.2 Billion Years Ago



How Do We Know When the Oceans Formed?

- Banded iron amphibolite formations in Greenland and Northern Canada which formed 3.8 billion years ago - can only form in oceans.
- Pillow Lava formations date back to 3.8 billion years, only form underwater.
- Even older - Zircon crystals found in Jack Hills, Australia record O18/O16 ratios, which indicate the onset of weathering (e.g. rain and oceans) at 4.2 billion years ago.
- So – a liquid ocean! But...
- ...this is a weak constraint on temperature then because we could have had higher atmospheric pressure, and at pressure = 10 bars (10 times the pressure you feel around you now), liquid water can exist up to $\sim 177\text{C} = 450\text{K}$.

Modern Undersea Pillow Lava



Boulder from a Banded Iron Formation



Could the Greenhouse Warming ALL be from CO₂? This study says - well, not impossible. But Only If Atmospheric Density is Much Higher Too. Was it? We'll see...

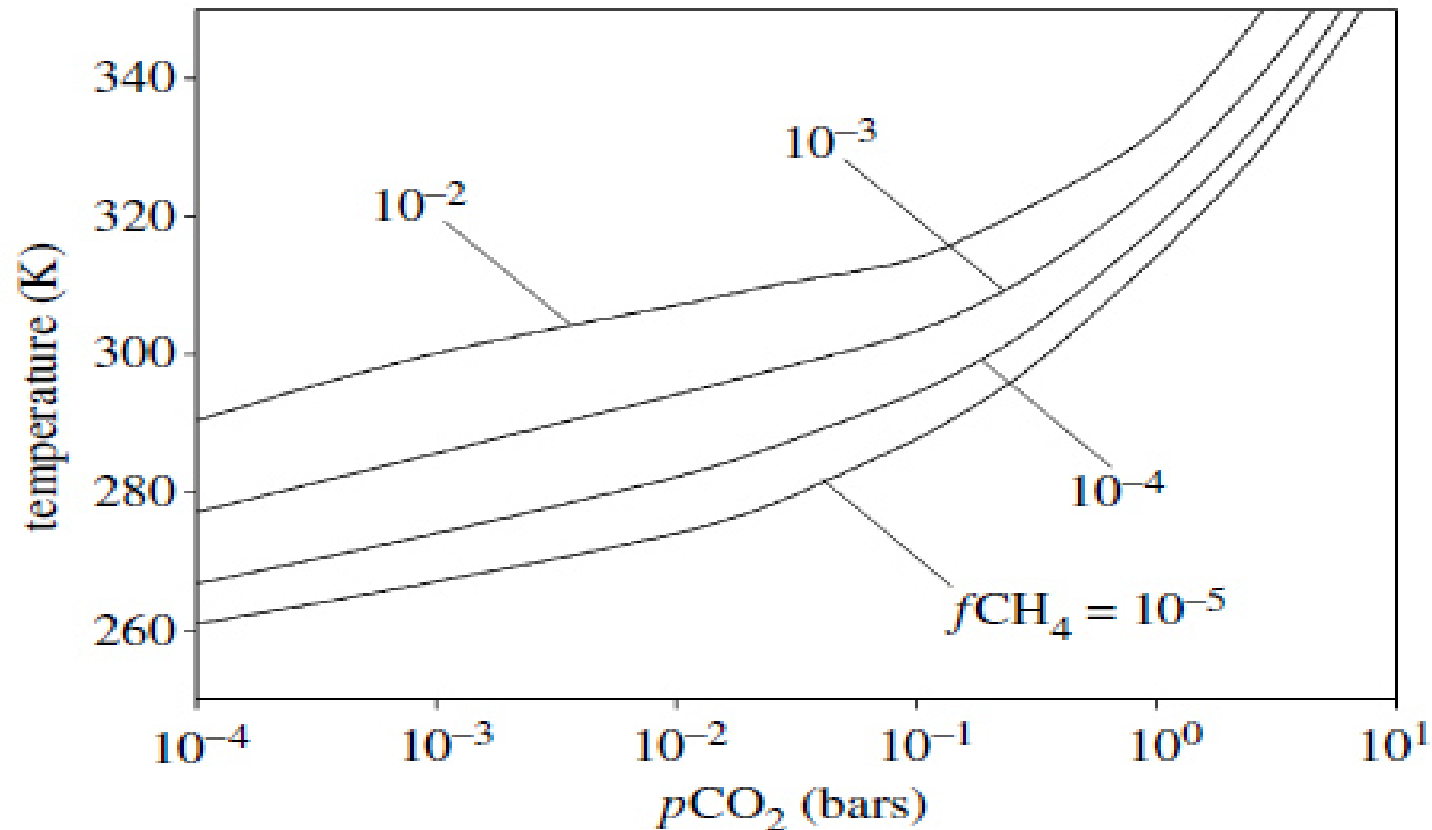


Figure 3. Surface temperature as a function of CO₂ partial pressure and CH₄ mixing ratio. The assumed solar constant was 77% of the present value, which is appropriate for 3.3 Ga. The climate model is from Pavlov *et al.* (2000), with modifications described in the text.

Early Greenhouse Clues...

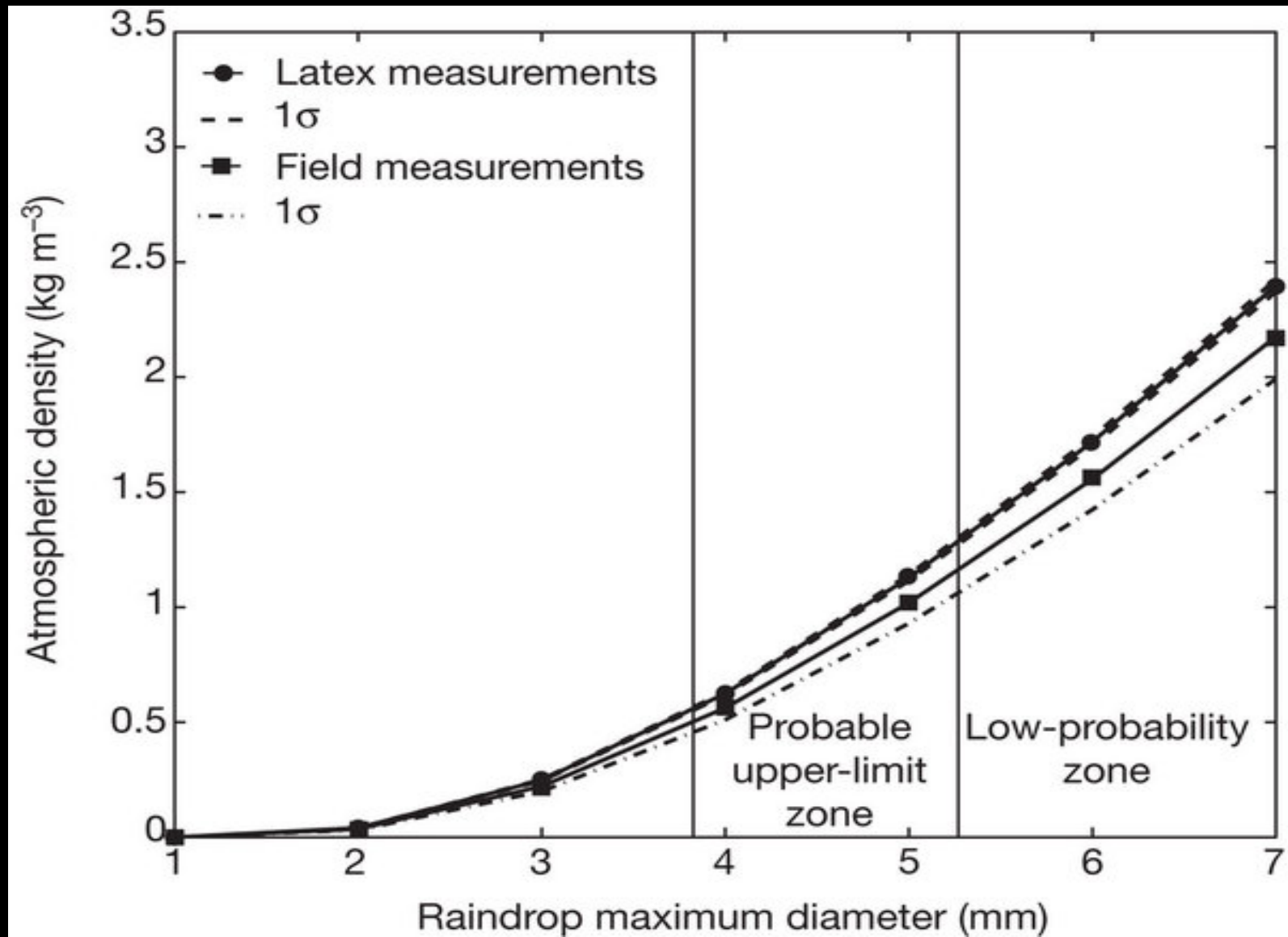
- If we had as high as ~10 bar of CO₂ (10x current atmosphere's pressure, and all of it as CO₂), this would solve low solar luminosity. But, this implies rainwater would have a very acidic pH of 3.7, and this high level acidity would cause extremely high rates of chemical weathering, which we do **not** see in ancient rock
- Also, glaciation ~3 Byrs ago suggests temperatures were more moderate already by then.
- Conclusion – temperatures probably much cooler than a “hot house” ~70C

More Clues...

- If Earth had same 24hr rotation rate and air pressure, we need an atmosphere of ~28% CO₂ to allow the liquid ocean as we know we had.
- But early Earth almost certainly was spinning much faster than this, so soon after planetary collision created the moon, which was much closer to us than today, since subsequent tidal friction has then pushed the moon ¼ million miles away by slowing Earth's rotation.
- The more rapid rotation of Early Earth implies we'd need more like a 100% CO₂ atmosphere at today's pressures. Or more. That's way too much to be consistent with evidence...
- Geochemical analysis of weathering shown in fossilized soil in Minnesota indicates we had only about 1% CO₂ atmosphere during the Archean Era. (Weathering pulls CO₂ out of the atmosphere).
- So CO₂ alone won't work, but methane could – with essentially no oxygen around, methane would be stable and is a ~100x more powerful greenhouse gas than CO₂, pound for pound.
- Higher air pressure would help. But here's an ingenious clue - discovery of [fossilized raindrops on 2.7 billion year old mud](#)...

Raindrop imprint diameter vs. atmospheric density.

Denser atmosphere permits bigger drops, which will drop faster under gravity

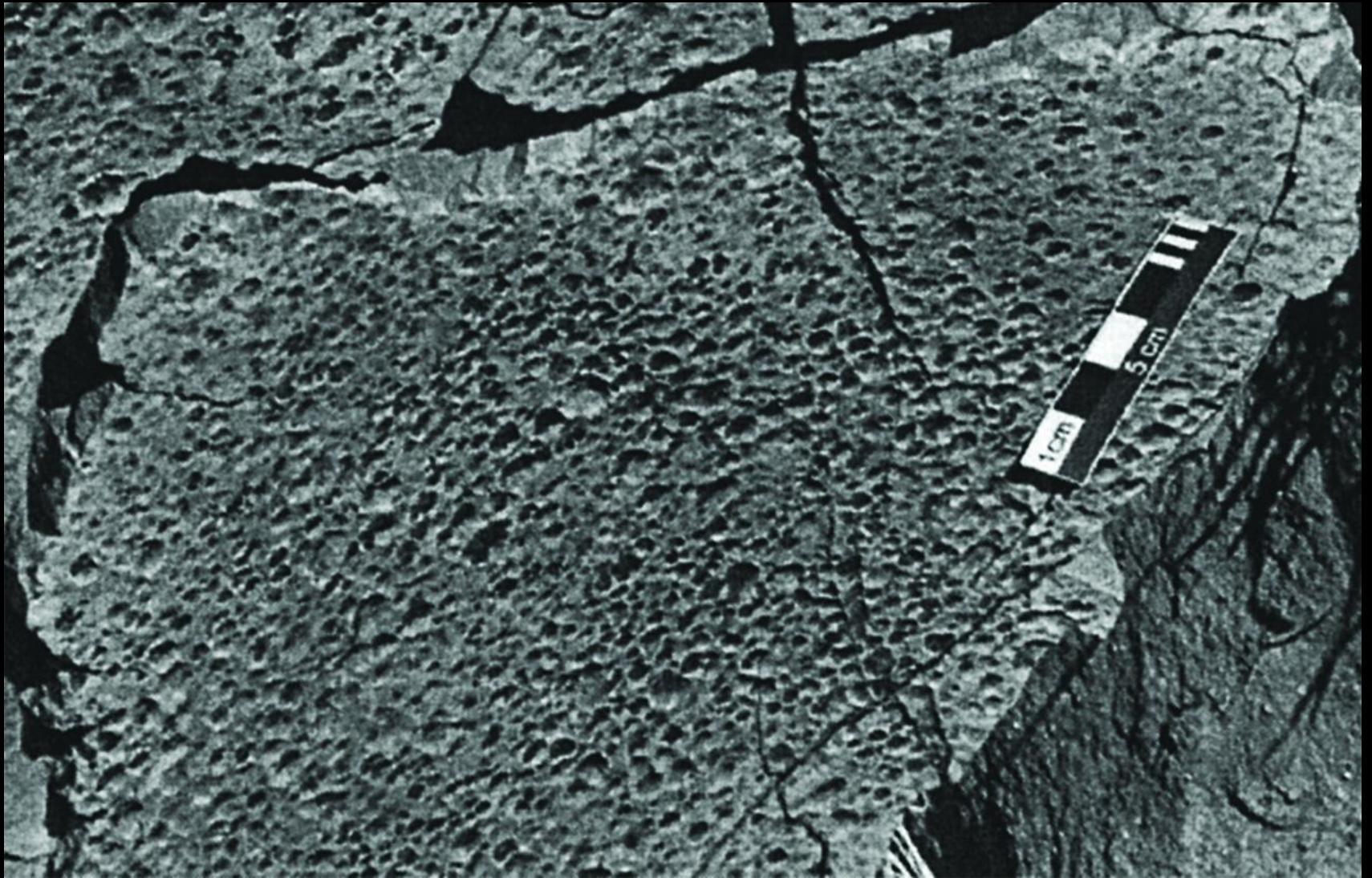


Fossilized imprints of raindrops on volcanic ash mud help determine the density of Earth's atmosphere 2.7 B years ago:

no more than 2x today's (S.M. Som *et al.* [Nature 2012](#))



Fossilized Raindrop Imprints: 2.7 Billion years ago



Late Cambrian (0.5 B yrs ago) fossilized raindrop imprints, similar in size to 2.7 B years ago. Implies similar atmospheric density. But we know the density at 0.5 billion years ago was similar to today.



Working some physics on the raindrops implies air pressure, density then was similar to today's

The Mechanism: Higher density atmosphere permits bigger raindrops due to surface tension considerations, and bigger drops fall faster under gravity, making bigger imprints, which we don't see.

- But 2.7 B years ago the sun was 19% less luminous than today's. So if atmosphere is similar density, still need significant greenhouse to explain unfrozen Earth.
- Adding more greenhouse effect from methane and NH molecule might be enough, but we're not sure of the final answer as yet.

Blattler *et al.* (2016) improve constraints and agrees: ~low CO₂ 2-3 Billion Yrs Ago. Roughly 1% of our atmosphere

ARTICLES

NATURE GEOSCIENCE DOI: 10.1038/NNGEO2844

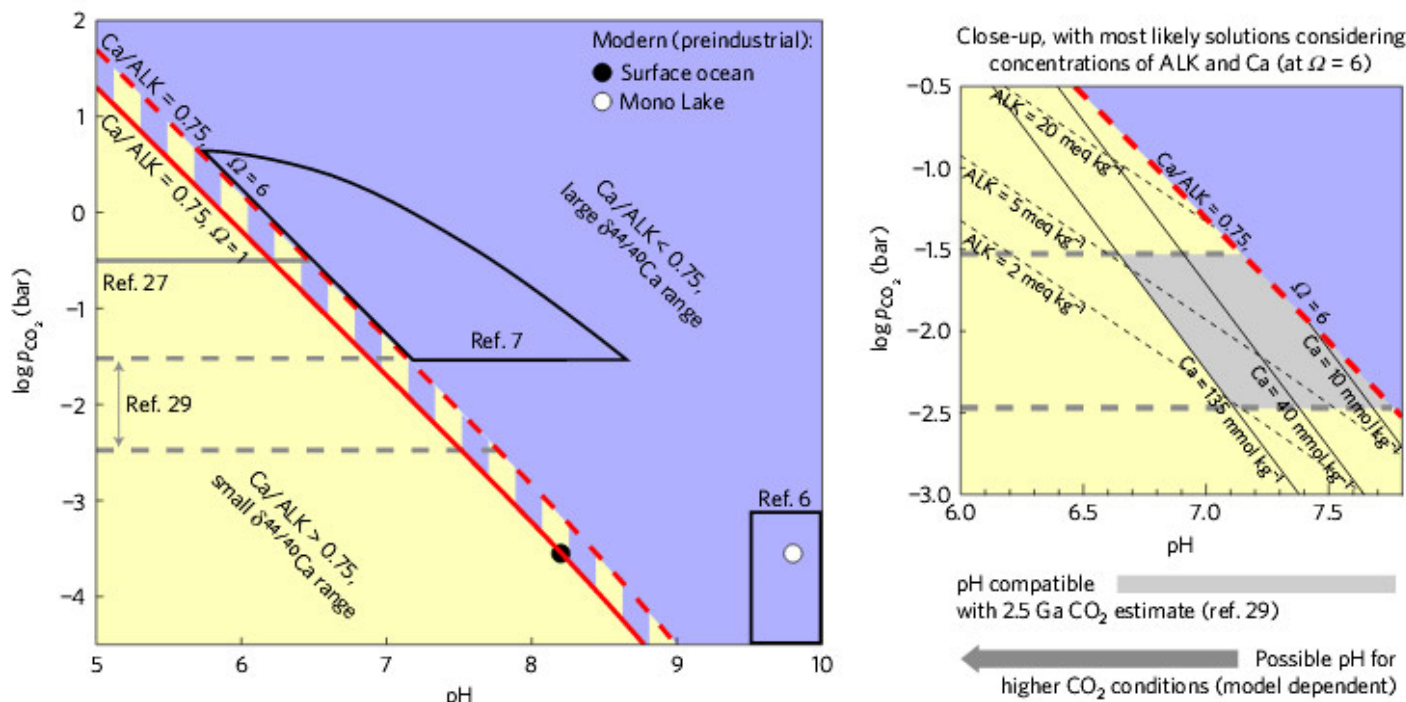


Figure 3 | Equilibrium carbonate chemistry solutions in p_{CO_2} -pH space, divided by the calcium isotope constraint that $\text{Ca}/\text{ALK} > 0.75$. Permissible solutions are shown in yellow; the blue region is inconsistent with data from this study. Uncertainty in the boundary between these regions from assuming different calcite saturation states is reflected in the striped zone between the solutions for $\text{Ca}/\text{ALK} = 0.75$ at $\Omega = 1$ and $\Omega = 6$. Black outlines indicate preferred solution spaces from previous work. Grey horizontal lines show various estimates for p_{CO_2} : solid line is a model result²⁷ for obtaining a mean surface temperature of 288 K (compatible with a mostly ice-free Archaean) at 2.5 Ga with increased CO_2 alone; dashed grey lines reflect upper and lower limits on p_{CO_2} estimated from a 2.5-Ga palaeosol²⁹. The close-up view shows contours of ALK and Ca concentration at $\Omega = 6$, with a reasonable upper limit on Ca (see Supplemental Methods) used to further define the likely solution space.

Currently, the most likely explanation for the warm temps yet colder sun back 4.2 Byrs ago...

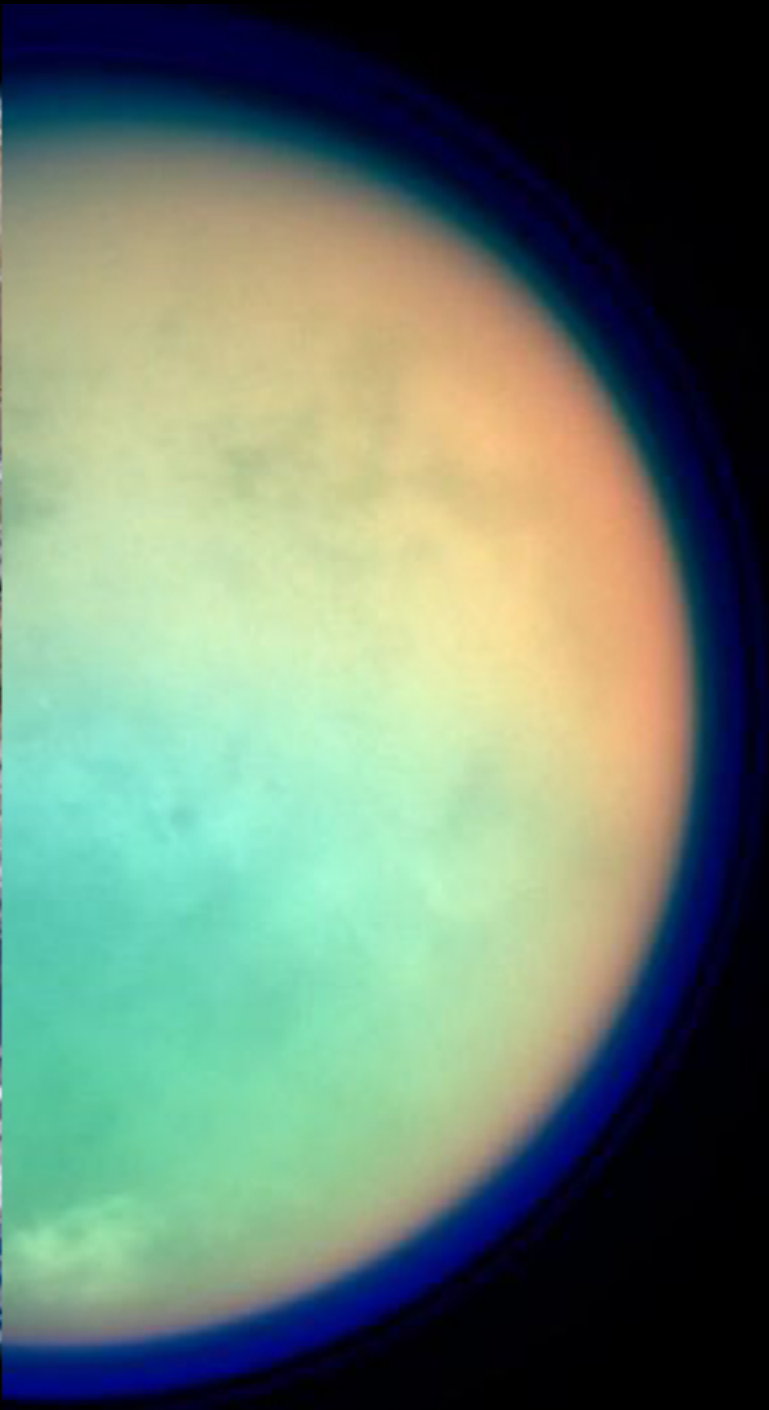
- Is higher greenhouse warming due to ...
- 1. Lots of primordial methane (CH₄) which would be stable given lack of free atmospheric oxygen during first ~billion years of Earth. Methane ~100x greenhouse power as CO₂, pound for pound. Methane doesn't leave easy "fingerprints" to help us, though, so it's a guess.
- 2. Some CO₂, which is a tough, stable molecule, about 40x pre-industrial levels (or 1.2% if atmosphere density then is same as today)
- N₂ at ~2x today's level (i.e. atmosphere twice as dense) will help GHG's widen absorption bands and increase GH effect. (pressure broadening of spectral lines)
- All this is comfortably within observational limits, it'll all work to explain. But, **too much** CO₂ will conflict with weathering data, as does too much N₂
- Minor effect: Possible to also allow the Earth to be a little closer to the sun w/o violating astronomical observations, but not a whole lot.
- H₂O and higher ammonia will also add to greenhouse effect, although they can't add a lot vs. today because water rains out, and ammonia wouldn't survive long in the early atmosphere.
- No big contradictions here, just sparse data and awaiting better data for the precise greenhouse atmosphere we had.
- Nice summary [here](#)

2.7-2.9 billion years ago: Oldest evidence for glaciers

- [Young et al. \(1998\)](#) and [here](#)
- Glaciers push ALL debris regardless of size or mass. So, characteristic glacial deposits are an unsorted mix of all sizes of rocks and sand.
- Such deposits, in a laminated matrix of mudstone is interpreted as ice-rafted glacial debris melted and deposited onto lake/ocean floor sediments.
- We see such deposits 2.9 and 2.75 B yrs ago
- Therefore, Earth temps must have been not too different than today's, with higher greenhouse and dimmer sun to allow it to be this cold

2.6-2.5 Byrs Ago: Unstable Swings in Composition: Methane Haze to Oxygen Clear

- This is suggested by isotope ratios of sulfur and carbon in rocks in a South African formation, showing microbial mats which produced oxygen.
- Could be why pinning down the composition at this time is hard – it transitioned, depending on methane production by early microbes
- From Titan-like haze, to clean up oxygen-rich skies, and back and forth for 100-200 million years, then permanently to oxygen clear skies thereafter
- See [story, Zerkle et al. 2012](#)
- **Methane, again, is a very powerful greenhouse gas**



From National Geo Article on [Zerkle et al. 2012 Paper](#) on this

- “Core samples from these rocks contain microbial mats, which show that some of the tiny creatures in shallow seas were producing oxygen long before the Great Oxygenation of our atmosphere.
- The rocks also contain carbon and sulfur isotopes—chemicals that would have reacted with oxygen. The levels of the different kinds of isotopes present indicate that sometimes oxygen production was happening when the atmosphere was thick with methane—but other times the atmosphere must have been free of methane haze.
- Methane and oxygen won’t co-exist in the atmosphere for long, since methane oxidizes to CO₂ and H₂O.
- The clarity of the early atmosphere seems to flip flop roughly every few million years, Zerkle *et al.* report, hinting at a push and pull between microbes that generated oxygen and those that belched methane.”

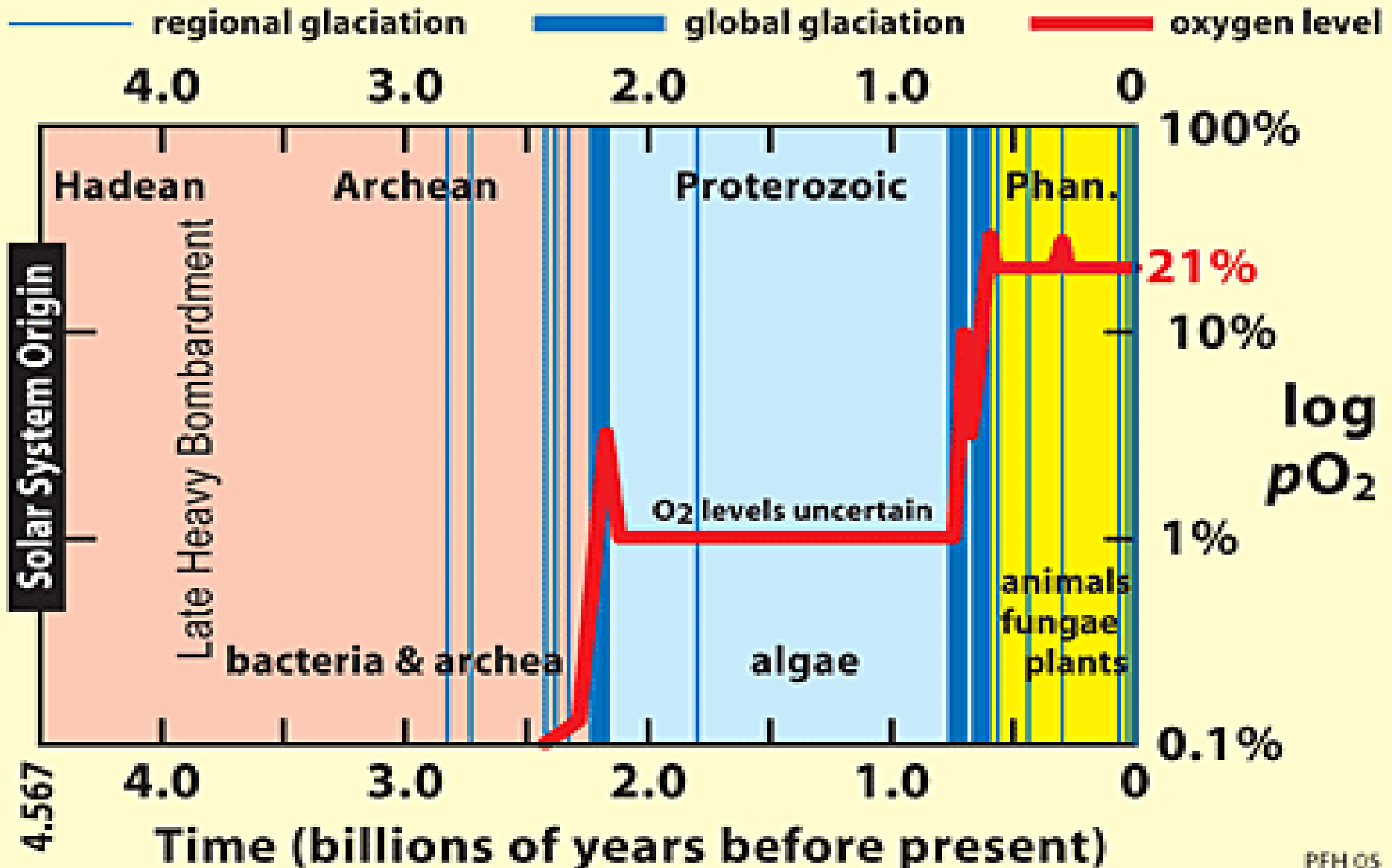
Oxygen Concentration was Low, and Rising Through Earth's History. The Geological Evidence...

- Iron (Fe) is extremely reactive with oxygen. If we look at the oxidation state of Fe in the rock record, we can infer a great deal about atmospheric oxygen evolution.
- **Archean Period** - Find occurrence of minerals that only form in non-oxidizing environments in Archean sediments: Pyrite (Fools gold; FeS_2), Uraninite (UO_2). These minerals are easily dissolved out of rocks under present (high oxygen) atmospheric conditions.
- **Banded Iron Formation (BIF)** - Deep water deposits in which layers of iron-rich minerals alternate with iron-poor layers, primarily chert. Iron minerals include iron oxide, iron carbonate, iron silicate, iron sulfide. BIF's are a major source of iron ore, as they contain magnetite (Fe_3O_4) which has a lower oxygen-to-iron ratio than hematite. These are common in rocks 2.0 - 2.8 B.y. old, but do not form in today's high oxygen environment.
- **Red beds** (continental siliciclastic deposits) are never found in rocks older than 2.3 billion years ago, but are common during Phanerozoic (relatively recent) time. Red beds are red because of the highly oxidized mineral hematite (Fe_2O_3), that probably forms secondarily by oxidation of other Fe minerals that have accumulated in the sediment.

More Evidence for a Low Oxygen Atmosphere: Biological

- **Chemical building blocks of life could not have formed in the presence of atmospheric oxygen.** Chemical reactions that yield amino acids **outside of cells** are inhibited by presence of even very small amounts of oxygen – which is extremely reactive (we love anti-oxidants in our food!).
- Oxygen prevents growth of the most primitive living bacteria such as photosynthetic bacteria, methane-producing bacteria and bacteria that derive energy from fermentation.
- Since today's most primitive life forms are anaerobic, the guess is that the first forms of cellular life probably had similar metabolisms.
- Today these *anaerobic* life forms are restricted to anoxic (low oxygen) habitats such as swamps, ponds, and lagoons.

Studies suggest oxygen at only 1% of our atmosphere or less, until ~700M yrs ago, allowing the “Cambrian Explosion” of life to transform life on Earth



Why did it take so long for oxygen levels to rise?

- The ocean chemistry explanation is complex, but [Scott et al. 2013](#) find that molybdenum, essential for life, was very rare in these ancient ocean sediments, as was oxygen, halting the evolution of complex oxygen-using life for as long as 2 billion additional years.
- Without oxygen in the atmosphere, there also could be no ozone in the stratosphere, no ozone layer and so UV would sterilize and kill any land life.

“Snowball Earth” 2.2B yrs ago. Evidence – glacial deposit strata which were estimated to be at the equator through magnetic field orientation (and tectonic motion studies).



Schrag and Hoffman (both Harvard) in Namibia, Africa. Evidence for Snowball Earth 700 million years ago; ice-rafted shallow oceanic glacial deposit layer poor in carbonates, followed (layer above) of carbonate-rich glacial-free sediments, after CO₂ returned to the atmosphere

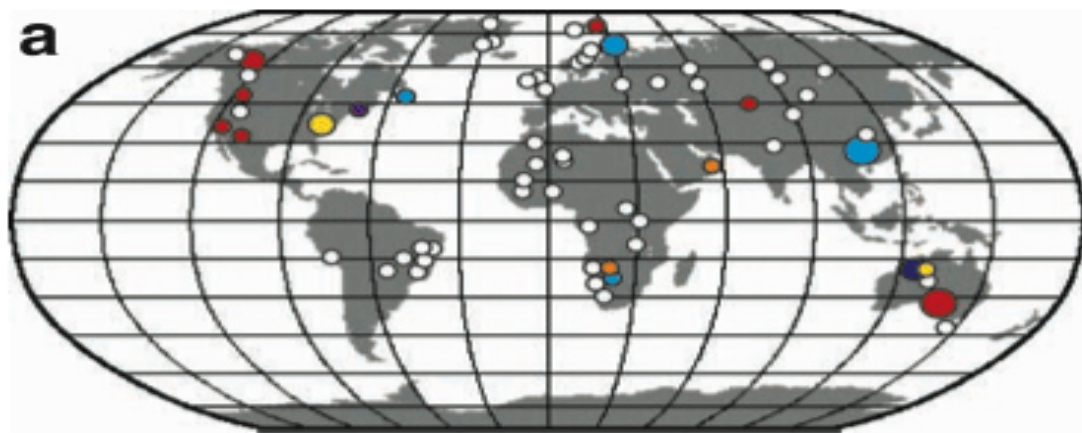


Other evidence for widespread frozen ocean and continents...

- ...is [here](#)
- **My summary of that source:**
 - Glacial deposits show on shallow ocean bottom in these areas, indicating glaciers dumped right into the oceans, and this was again at ~the equator. If it's that cold at sea level at the equator, strongly suggests it is frozen EVERYwhere.
 - Banded iron formations found exclusively in glacial marine strata after 1.9B yrs ago, indicating widespread anoxia (consistent with an ice-covered ocean unable to communicate with the atmosphere) and an increase in the ratio of Fe to S entering the ocean (consistent with ice-covered continents).
 - Deep flooding of previously shallow-water shelves and platforms after the Sturtian and Marinoan meltdowns, sustained after isostatic re-adjustments, reflecting slow tectonic subsidence over millions of years under the ice.

Conclusion: Equatorial ocean glacial deposits say ice existed on the ocean itself; the continental glaciers pushed their moraines and boulder-strewn debris down to sea-level and out onto the ocean as an ice shelf, until it eventually melted (see following slides)

So “SnowBall Earth” Looks Real



● 00-10° ● 10-20° ● 20-30° ● 30-40° ● 40-50° ● 50-60° ○ no data
 ● "very reliable" ● "moderately reliable" ● "somewhat reliable"

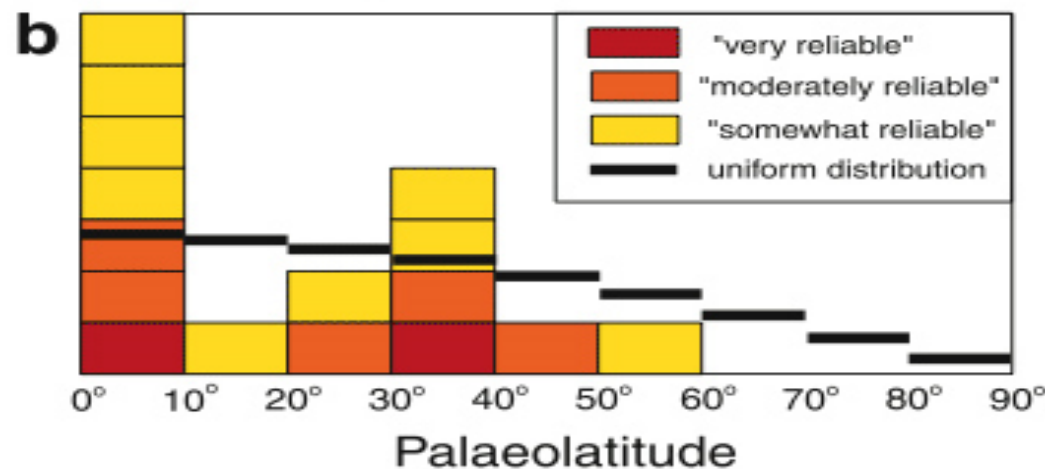


Fig. 1 Global distribution (a) of Neoproterozoic glaciogenic deposits with estimated palaeolatitudes based on palaeomagnetic data (modified from Evans, 2000). 'Reliability' takes into account not only palaeomagnetic reliability but also the confidence that the deposits represent regionally significant,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

Many sites around Earth show glacial deposits when those sites were tropical. Glacial deposits in shallow equatorial ocean floor adjacent to continents indicates glaciers at sea level and ice-covered ocean offshore. Alternative explanations (widely varying obliquity of axis, or Saturn-like rings) are *ad hoc* and conflict with astronomical theory!

Why didn't we **STAY** in SnowBall Earth ?

- After all, this is a pure white globe now, reflecting most sunlight, which is much weaker than today's sunlight as well.
- Amplifying feedback of whitening glaciating Earth would just make it cooler and cooler.
- So why didn't we stay frozen?
- The **Walker *et al.* (1981) mechanism**, elaborated by Richard Alley - let's call it the **Walker/Alley mechanism**

Liquid oceans enforced by the Walker/Alley mechanism

- When the ocean surfaces are frozen everywhere, they have a cap of ice which cuts off communication across that cap.
- Therefore, the atmosphere can no longer transmit CO₂ to the cold oceans and the carbon cycle is halted
- Meanwhile, volcanoes don't care at all about ice and surface temperatures, and continue to erupt, injecting (at today's rate), about 300 million tons of CO₂ per year into the atmosphere, which now has nowhere to go thanks to impenetrable ice-capped oceans
- Greenhouse heating therefore increases... until finally the ocean surface melts, allowing CO₂ to diffuse once again into the oceans, so the long carbon cycle resumes

- This is the only mechanism we have found which explains how the oceans are forced to melt if they become globally frozen.
- “Snowball Earth” phases would therefore be geologically brief, because within a few million years or less the volcanic CO₂ injection would be plenty enough to melt the equatorial oceans.
- Indeed, we only see a few very brief “Snowball Earth” phases in the time lines we just saw
- The last was at 600-700 million years ago.

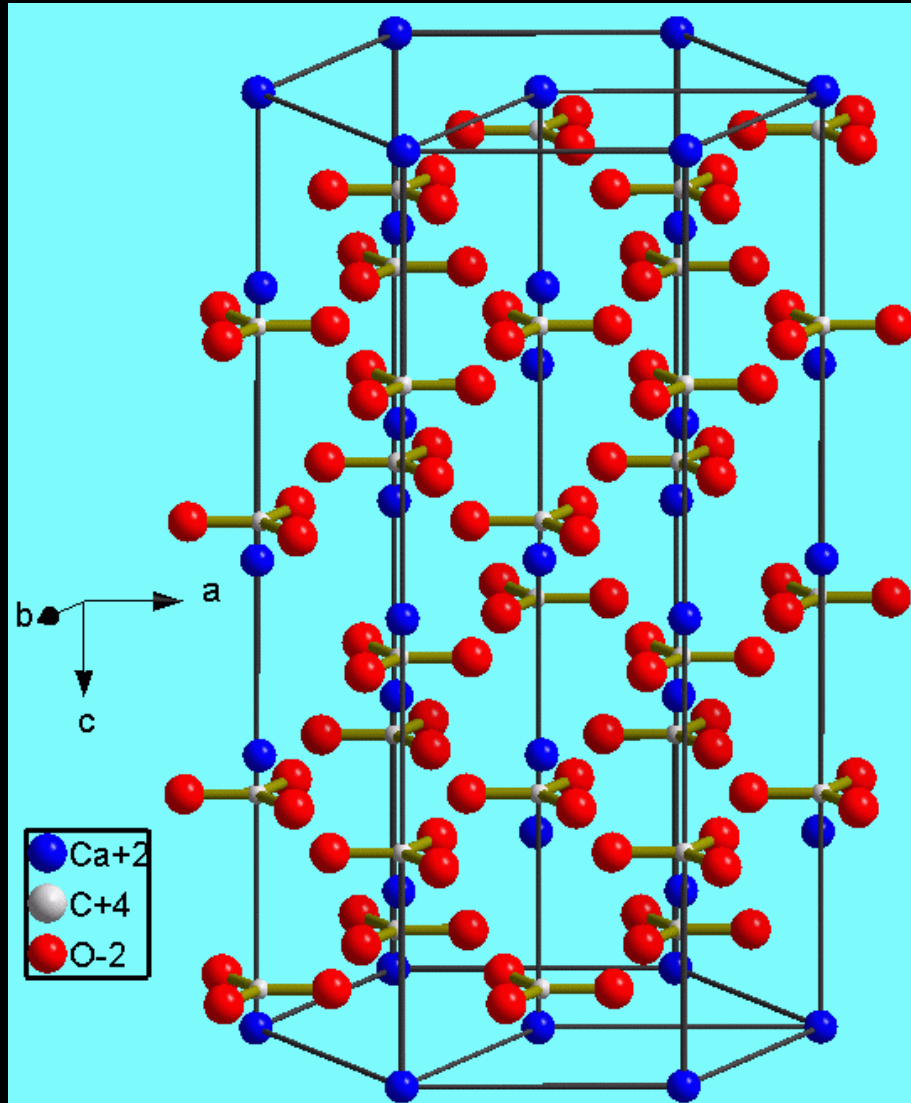
CO₂ and methane – Life plays a major role in GHG levels

- It's believed the nitrogen composition hasn't changed much over the history of the Earth, after very early ammonia-rich atmosphere ended
- It's CO₂ and methane which have changed greatly
- Evidence – these are powerful greenhouse gases, needed to account for relatively warm Earth when sun was only 25-30% less luminous
- Absolute amounts are poorly determined however.
- Still, why did CO₂ and methane concentrations drop so much? Life!

Ocean Life Transformed Our Atmosphere from CO₂-rich, to CO₂-poor, via the “Slow Carbon Cycle”

- CO₂ will dissolve into raindrops, forming carbonic acid, falling on rocks (chem weathering) and then into the rivers and oceans. Then...
- Calcium + dissolved CO₂ in the ocean was used by forams and other sea animals to produce CaCO₃ = calcium carbonate as a protective shell or skeletal material.
- When they die, they carry that CaCO₃ to the ocean bottom where it is eventually subducted into the mantle.
- Only SOME of CO₂ is recycled by outgasing tectonic volcanoes. The rest remains in the mantle

The most stable form of CaCO_3 is Calcite (no, don't memorize the morphology here!). It's the aragonite form which suffers most in acidic oceans



Thus: Net loss of CO₂ from atmosphere and into the mantle: Falling atmospheric CO₂ over geologic time scales

- The lowered CO₂ level in the ocean then pulls CO₂ out of the atmosphere to try to re-attain equilibrium.
- Result: Falling atmospheric CO₂ levels over geologic time.
- There can be other processes that come in, but we expect (and see) that over the billion year time scales, CO₂ has indeed been on a downward path on Earth.

Some Methods of Measuring CO₂ in the Paleo Atmosphere

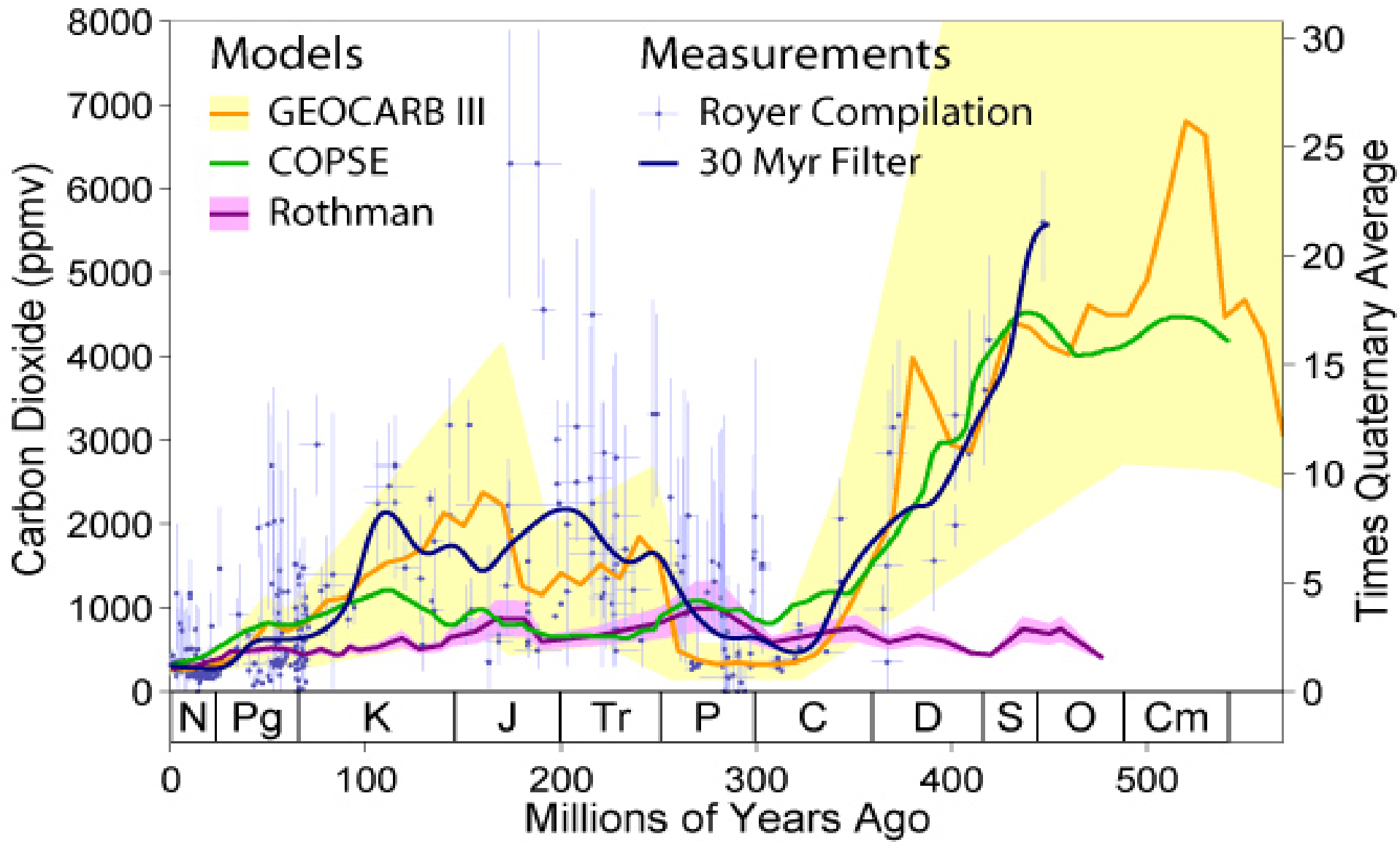
- C¹³/C¹² Carbon isotope ratio, correlates with CO₂ in atmosphere since C¹³/C¹² is different in soil and seawater vs. air. Measure in ancient soil, infer to air. Approximate.
- Boron isotope ratio; from how boron incorporates into oceanic foramanifora with changing pH, which correlates with atmospheric CO₂ levels (are those correlations really that tight?)
- Better: Number density of leaf stomata, which transpire CO₂ for plants – higher CO₂ concentrations require fewer stomata. (e.g. [Beerling 2002](#))
- Unfortunately, there is only qualitative agreement on directions of change in CO₂ from the various proxies, so these are not very precise measures. See for example [Pagani et al. 2004](#)

Recent (Cambrian onward) atmospheric history of CO₂: The Last 500 Myrs

- Shows generally falling CO₂ levels
- Especially during the Carboniferous Period, when plants dominated the Earth's surface and deposition covered the dead biomass so oxygen couldn't reach it
- This produced the great coal and oil deposits we're furiously burning back into the atmosphere today...

←==== Forward Time Direction

Phanerozoic Carbon Dioxide



The First Mass Extinction: the Ordovician End Time: 444 Myrs Ago

- [Cause is uncertain](#), but large climate changes both hot and glaciation are seen changing over periods of a few hundred thousand years.
- Gamma Ray burster within 6,000 lyr of Earth? Might explain the beginning of the period. A direct hit would destroy significant ozone, letting solar UV to kill the base of the food chain, is one candidate
- Purely climate change events perhaps?
- Most life was in the oceans; an ocean extinction, most genera die, 70-80% of all species die

The Second Mass Extinction – The Late Devonian: 377-360 Myrs Ago

- A series of extinctions, mostly in the oceans, where most life existed
- Cause is not clear, but the fossil data show clearly that the oceans were widely anoxic (no oxygen), which encourages sulfide organisms which produce hydrogen sulfide - H_2S ; poisonous for an oxygen-adapted ecosystem.

The Third Mass Extinction – End Permian Event 250 Myrs ago

- Good program on the Permian Extinction is [here](#) (47:24)
- Massive volcanism buried an area the size of the United States in magma a mile deep
- Outgassed CO₂ caused global warming by +5C, shutting down ocean circulation, killing oxygen-producing plants and promoting deadly H₂S organisms, killing most life in oceans
- Pyrites show an anoxic ocean around the globe.
- A second global warming followed when the CO₂-induced initial +5C warming penetrated to the methane hydrates on the continental shelves – the “methane apocalypse” then raised the temperatures a further +5C, giving +10C total.
- **95% of all life died, and it took about 100,000 years**

The 4th mass extinction: End Triassic Period 200 myrs ago

- Steep rise in CO₂ due to volcanism (active period of plate collisions), triggering greenhouse heating, destabilizing massive methane hydrate reservoirs and a sharp rise in Earth temps ([Huynh et al. 2005](#)) and also [here](#)
- And, melting poles lower pole-equator temperature gradient, reducing ocean circulation and turnover, raising further ocean surface temps, lowering oxygenation and ability to absorb atmospheric CO₂, and this cycle continues until...
- 80% of all species, both land and ocean, perished
- **Except for the Asteroid-caused extinction 65.56 million years ago, rapid greenhouse warming is implicated in all other mass extinctions ([Sci Am](#))**

Parallel with Today?

- Rapidly rising atmospheric CO₂
- Rapidly rising methane levels
- Melting permafrost due to loss of Arctic Ocean ice
- Rapidly dropping pole/equator temp gradient
- Slowing ocean circulation
- Dropping oxygenation of oceans and atmosphere
- “dead zones” proliferating
- Massive species extinctions happening

Atmospheric CO₂: Last 500 Myrs; Proxies Differ. Brecker et al. 2009. Note the low levels of CO₂ during the Carboniferous era 350-300 million years ago, when much of the fossil fuels we're burning today were laid down

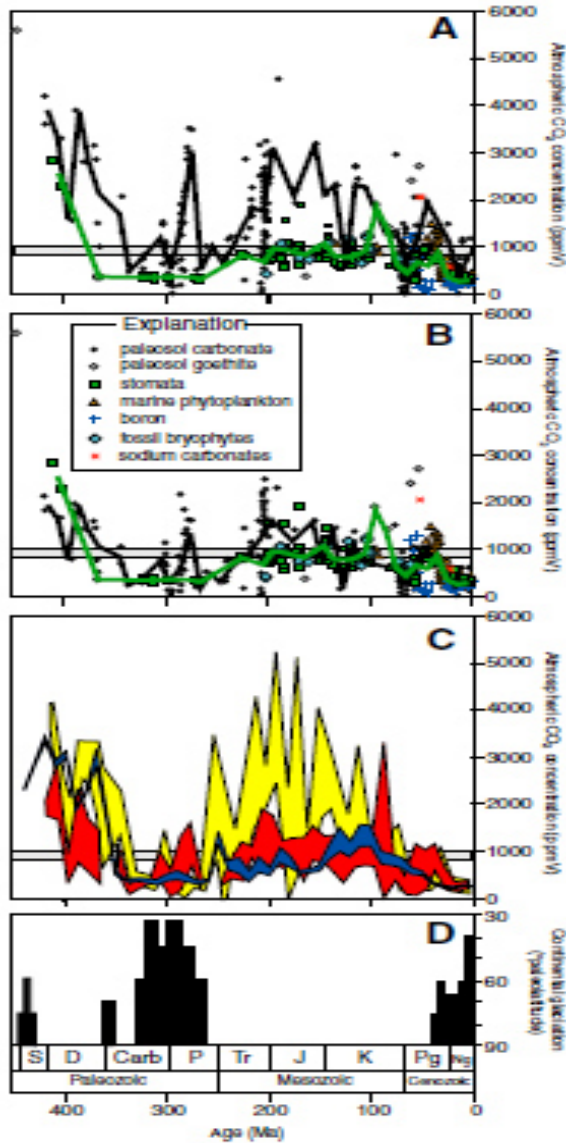


Fig. 2. A compilation of Phanerozoic atmospheric CO₂ records. (A) A compilation of atmospheric CO₂ records from different proxies. Paleosol carbonate-based estimates are from original papers in which $S(z)$ values between 4,000 and 10,000 ppmV were used in Eq. 2. Compilation from (5) with additional proxy-based CO₂ estimates (6, 8, 37, 39–48, D. Royer, pers. comm.). 10 million year bin means of the paleosol carbonate-based estimates and of all the other proxy-based estimates are shown by the black and green lines, respectively. (B) Same as Fig. 2A with $[CO_2]_{atm}$ estimates from paleosol carbonate re-calculated using $S(z) - 2500$ ppmV (see Methods). The estimates from paleosol carbonate (black curve) and all other proxies (green curve) are in far better agreement than they are in Fig. 2A (two goethite data points at 6,300 ppmV (174 and 188 Ma) were not included in the 10 million year bin means shown in Fig. 2A and Fig. 2B because these outliers have a strong influence on the averages and may represent transient fluctuations rather than typical Mesozoic atmospheric conditions). (C) Comparison of the $[CO_2]_{atm}$ estimates from proxies with $[CO_2]_{atm}$ estimates from GEOCARBSULF (38). The region shown for GEOCARBSULF output (the blue region in front) incorporates the full range of temporal variability in granite $^{87}Sr/^{86}Sr$ values considered in the model. The most recently published compilation of proxy-based $[CO_2]_{atm}$ estimates (9) is shown in yellow (10 million year bins means $\pm 1\sigma$). The revised proxy-based estimates (10 million year bin means $\pm 1\sigma$ shown in red) are generally in good agreement with the GEOCARBSULF model results and are substantially lower than the most recent compilation of proxy-based estimates. (D) Paleolatitudinal extent of Phanerozoic glaciations (49) showing the strong correlation between $[CO_2]_{atm}$ and glaciation. CO₂ concentrations predicted for the year A.D. 2100, assuming a heterogeneous world in which technological advancements spread slowly, population grows continuously, and economic development is primarily regional rather than global (2) (SRES anthropogenic emissions scenario A2), are shown as the horizontal gray bar in A, B, and C. Figure modified from (5).

Atmospheric CO₂ levels for the past 60 million years, and 25 million years (Pearson & Palmer 2000). The last microscopic sliver, when humans drove CO₂ over 400ppm, not shown. LEFT is forward time direction

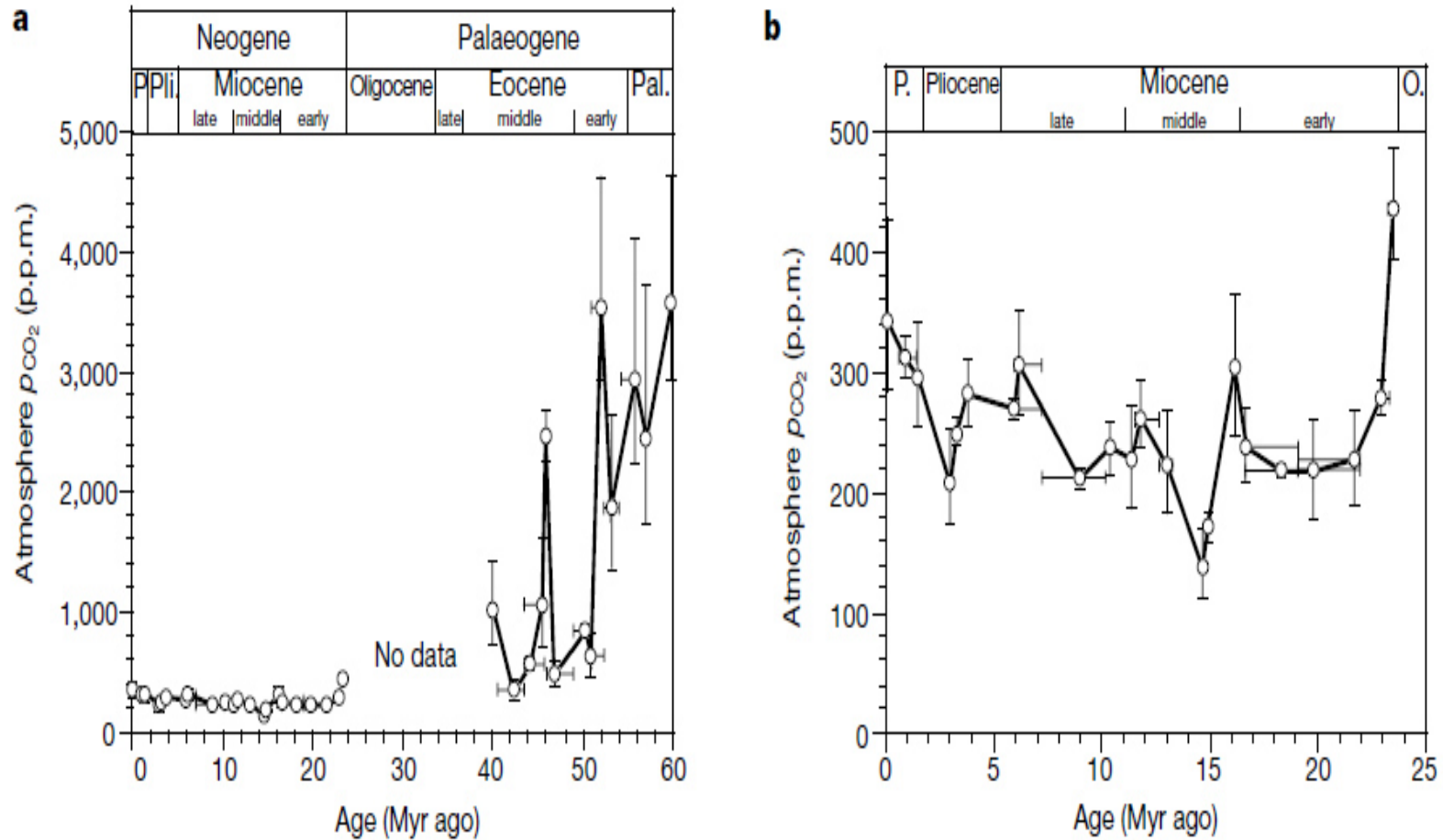


Figure 3 Record of atmospheric carbon dioxide for the past 60 Myr. **a**, The whole record; **b**, expansion for the past 25 Myr. We note that the nature of the pH- $\delta^{11}B_{CC}$ relationship means that analytical errors result in much larger uncertainties in the calculated p_{CO_2} at

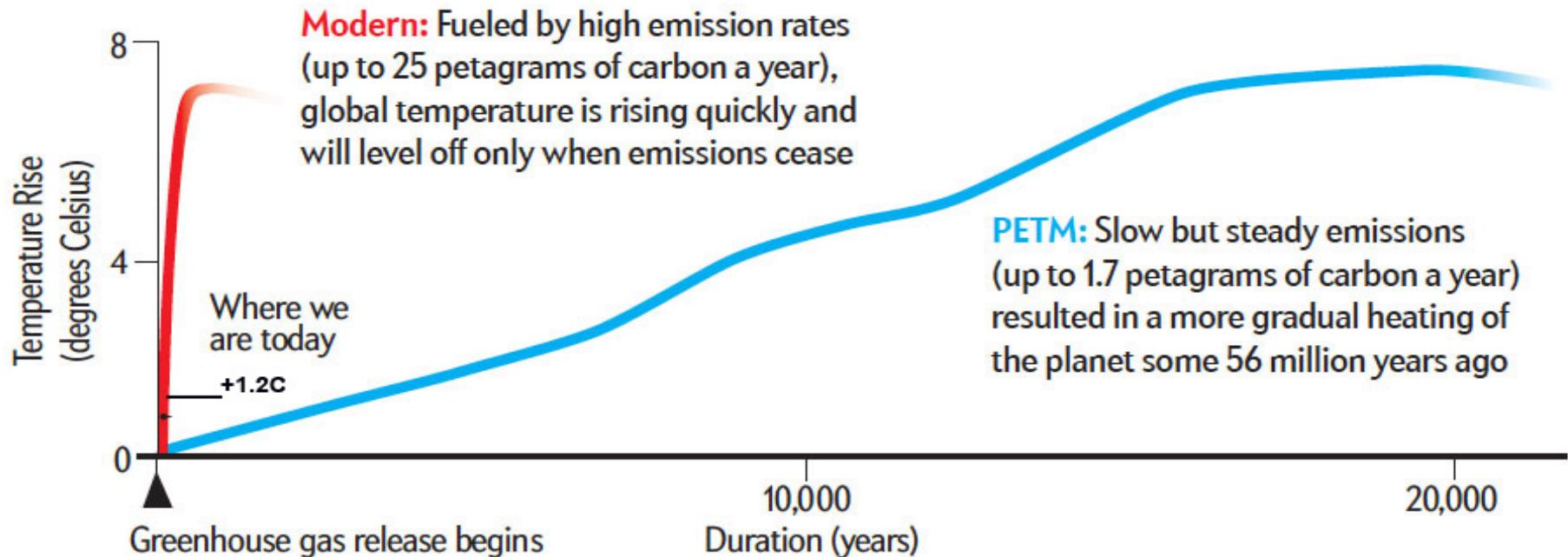
lower pH values. These values were calculated using a modified version of the carbonate equilibria presented in ref. 33. Epochs as for Fig. 1; O., Oligocene.

The Paleocene-Eocene Thermal Maximum (PETM)

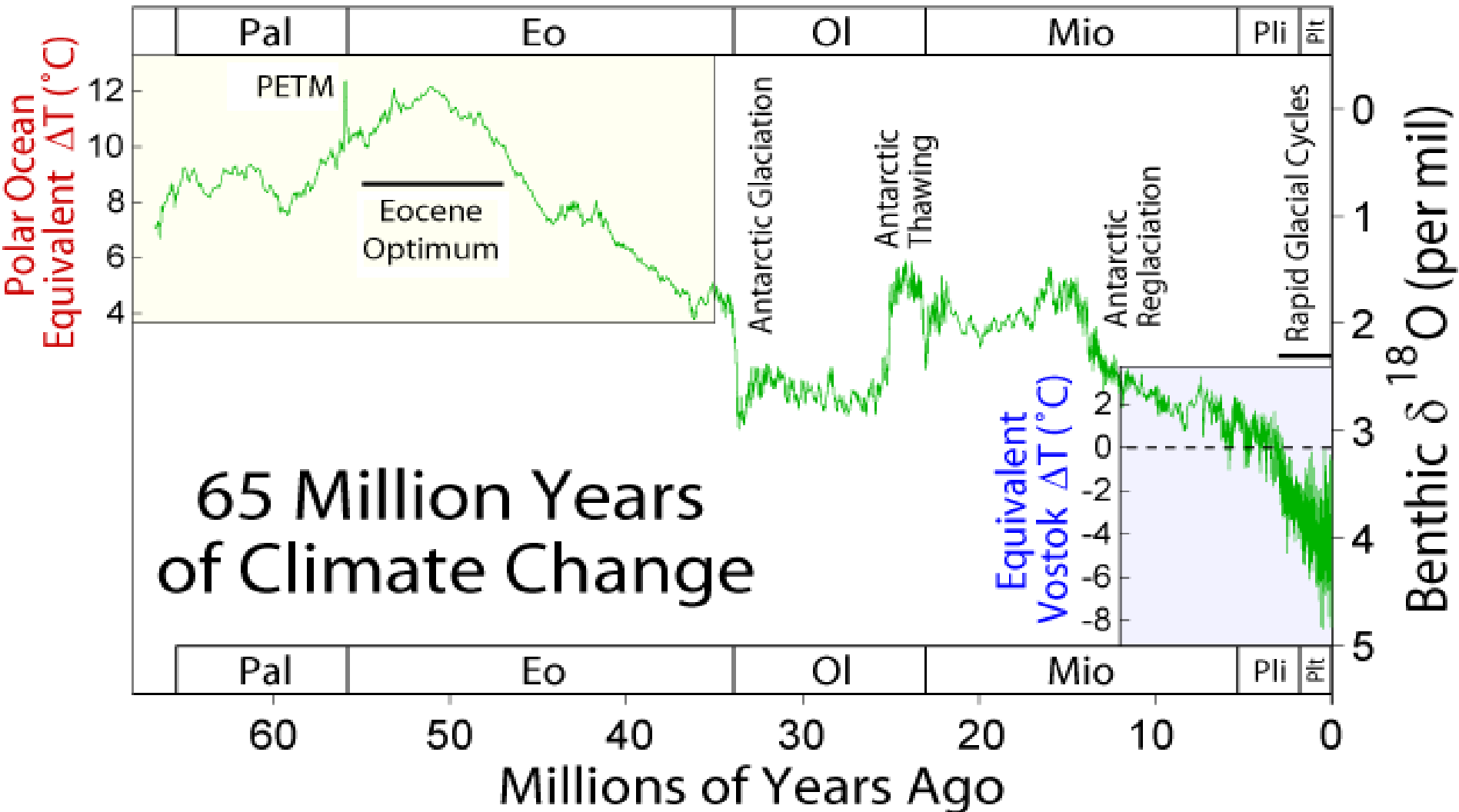
- A brief period 55.5 million years ago, of massive carbon release, steeply rising CO₂, +5C in global temperatures, ocean acidification, within a few thousand years, followed by fall back to “normal” levels
- Earth was already ice-free at this time
- The cause of the PETM is controversial. One recent [study \(deConto et al. 2012\)](#) indicates it was induced by ordinary Milankovitch changes causing insolation at the Arctic Circle warm enough to melt the permafrost and release carbon into the atmosphere. But the speed and cause are both perhaps even more dramatic...

How fast was the PETM? Did it take 20,000 years or only 12 years, as one study suggests. The trigger increasingly looks like an extra-terrestrial impact

Global temperature is rising much more quickly today than it did during the PETM



Temperature proxy O_{18}/O_{16} ratio shows dropping temps goes with dropping CO_2 , over past 65 million years



The Most Recent ~3 Million Years

- Dominated by Ice Ages – Two key causes:
- Primarily: The **periodicity** of the Ice Ages appears to be caused by periodicities in solar forcing near the Arctic Circle – the **Milankovich Cycles**
- Secondly: The **ability to lay down additional reflective snow** and ice in such Ice Age amounts was aided by the closing off of Panama about 3 million years ago, forcing the equatorial warm waters to divert northward – today’s “Gulf Stream” – which brings warmer water and air and hence more humid and wetter air capable of delivering more snow to the far North

The Key Driver of Ice Ages is:

- ...How much melting of winter snow is done in the summer, in the latitudes near the Arctic Circle +65N
Remember this!
- If summer **insolation** (incoming solar energy) is not sufficient to melt everything, then it will accumulate
- More snow means more reflectivity of the Arctic region, causing further cooling, more snow... albedo feedback is amplifying, as are these additional ones: Colder ocean pulls more CO₂ out of atmosphere, amplifying cooling, and freezing ground sequesters methane in permafrost. Until you have a full blown Ice Age
- It's **not** how cold it gets in winter that matters; it's always cold enough in winter there to make snow and ice. **Instead, it's how much summer heating and snow melting there is, that's the key!**

Why the Arctic Circle?

- Because in the past ~10-30 million years, the continents positions have been about the same as today, and the Arctic Circle happens to correspond to the boundary of the Arctic Ocean.
- At the Arctic Circle and south, ice can be anchored on land, which has low thermal capacitance and can freeze completely and stay frozen if covered.

You can build miles of ice on top of land, not ocean

- Land has poor conductivity of heat, so ice will not get much heat from below to melt it.
- The layer of ice on an ocean, however, cannot build from below because the warmer liquid water can convect with essentially the entire depth of water, rather easily, and water has very high thermal capacitance. It would just take too much cold to freeze the entire Arctic Ocean so as to then build a thick ice sheet on top

The Amount of Incoming Solar Energy Here is Determined by Small Changes in our Orbit & Tilt

- The **tilt of our axis** determines how directly the sun's rays impact the ground
- The **ellipticity of our orbit** determines how much our distance from the sun varies during the year.
- The **orientation of our orbit** determines when the date of closest approach to the sun compares to the Northern summer solstice
- You get maximum summer insolation when we have maximum ellipticity, maximum axis tilt, and when the date of closest approach to the sun is around the time of the summer solstice

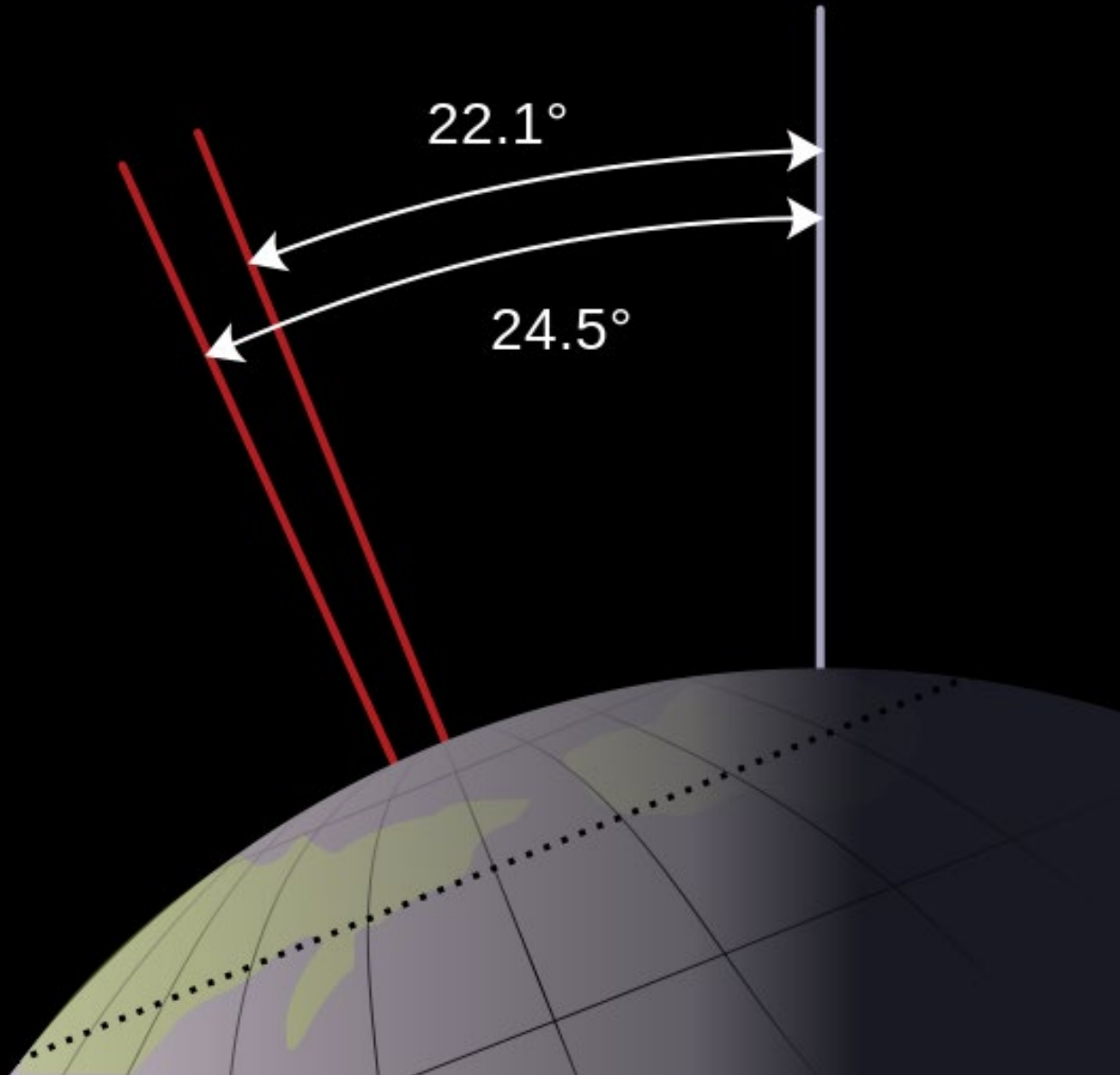
Earth axis tilt, orbital parameters (for next slides)

- ε – tilt of Earth's rotation axis relative to the orbital plane
- e – eccentricity of the orbit. Varies due mostly to resonances with the gravity of Jupiter and Saturn
- ω - Longitude of perihelion

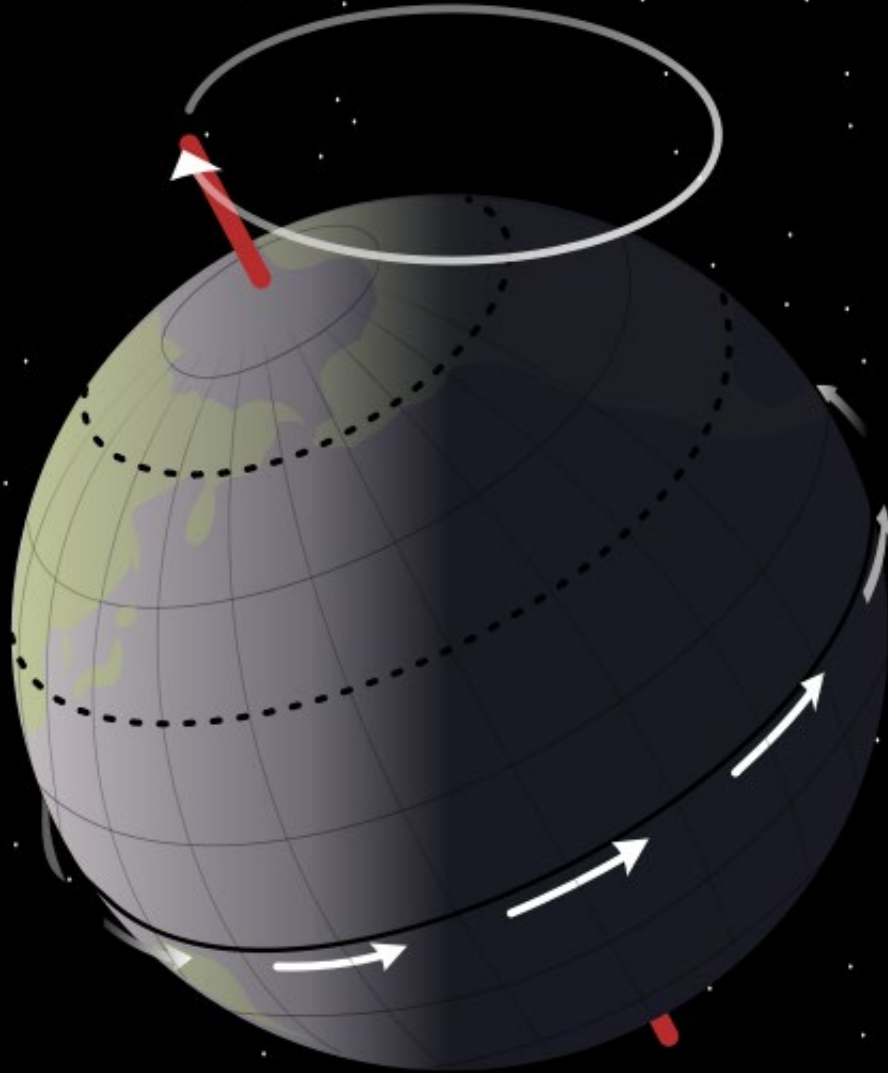
$\varepsilon \sin \omega$ - precessional index

(No, you don't want to memorize these!)

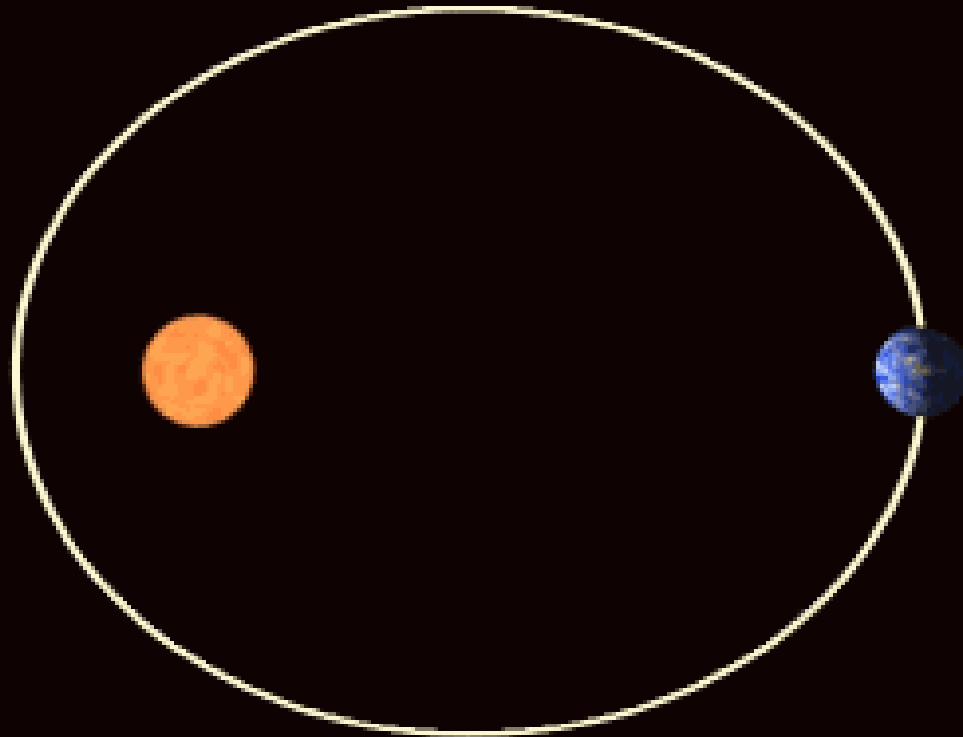
Range of Axis Tilt (kept in narrow range by the existence of our Moon): 41,000 year period



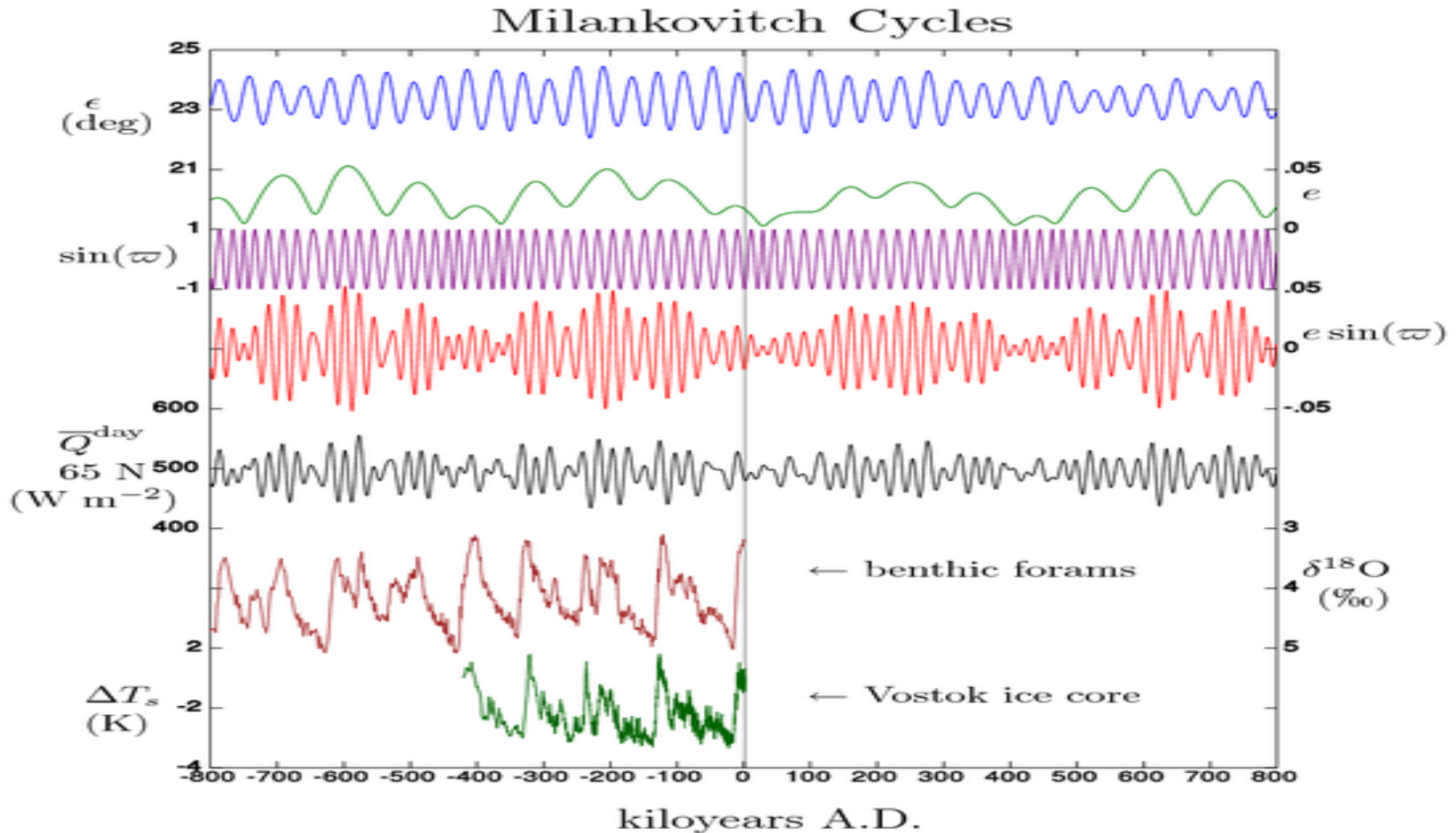
Precessional Motion: 26,000 yr Period. Affects when the seasons occur within our elliptical orbit



Precession of Orbital Major Axis: 21,600 years

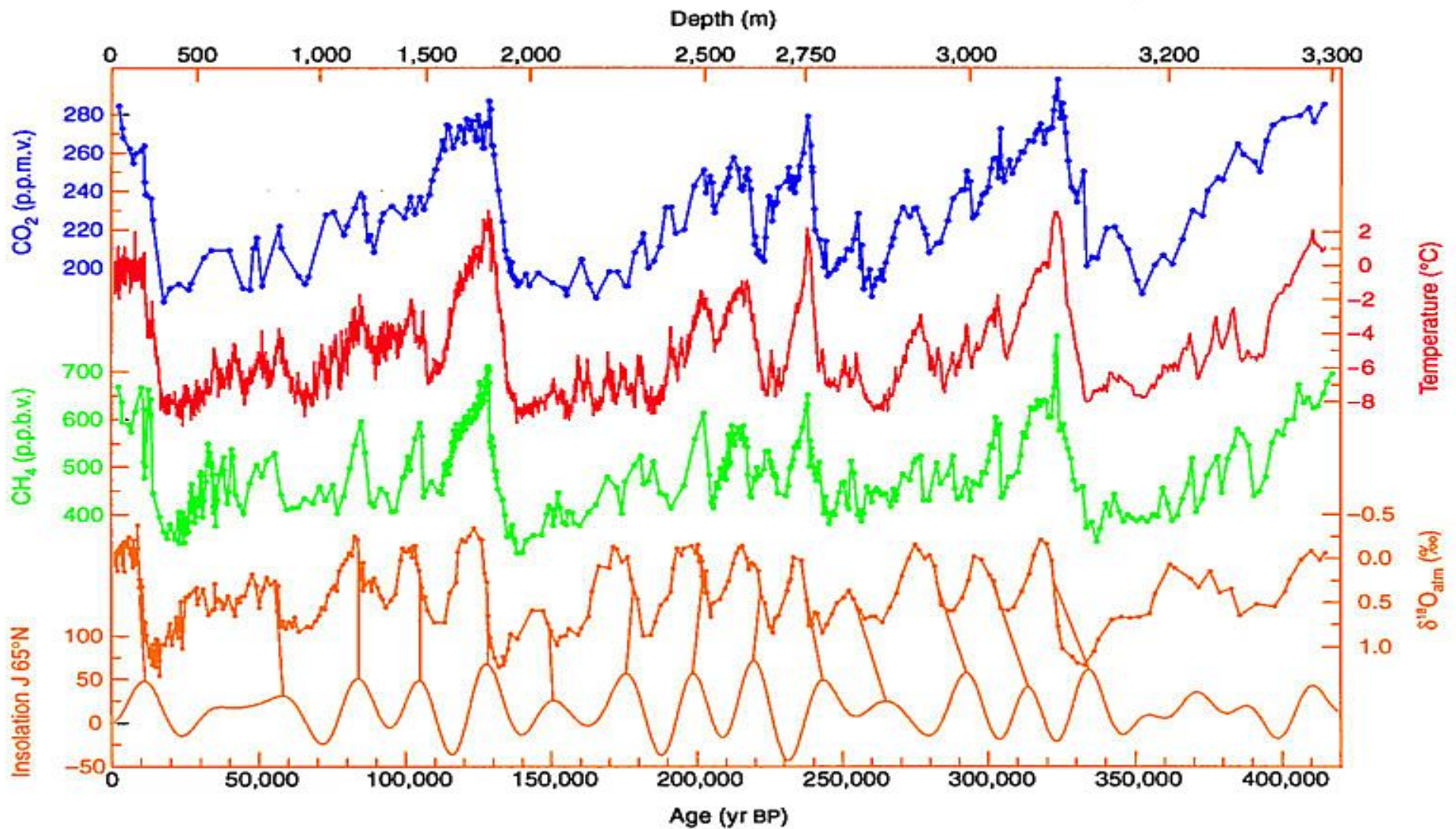


Most recent ~3 million years dominated by Ice Ages
– **Caused by cycles in Earth's tilt and orbit, affecting insolation (4th curve below) at Arctic Circle**



Going INTO an Ice Age...

- Lowering summer insolation causes summer heating to fail to melt all winter snow in the high north, causing ongoing buildup of snow and ice, raising albedo and cooling the planet further – an amplifying feedback
- Colder oceans can dissolve and hold more CO₂, pulling it out of the atmosphere, lowering greenhouse warming further – another amplifying feedback
- Colder atmosphere can hold less water vapor, lowering greenhouse warmth still further – another amplifying feedback
- All these effects amplify the insolation trigger, and we are sent into an **Ice Age**
- See how CO₂ tracked the Ice Ages on the next slide...



CO₂, Temperature, CH₄, and Insolation During Past Several Ice Ages.

Bubbles tell atmosphere composition. O¹⁸ ratio tells us temperature of atmosphere

Note how well CO₂ and methane correlate with temperature. Looking carefully at the timing indicates the CO₂ and methane rise lag the temperature by roughly 800 years. This is because the initiating cause of warming is the Milankovitch-related insolation at the Arctic Circle. Rising ocean temps then release CO₂ into the atmosphere; a positive feedback which amplifies the weak Milankovitch forcing into significant climate change

Coming OUT of an Ice Age... CO2 Levels Rise as a Response to the Arctic Circle Insolation Forcing

- Unlike current climate change, the forcing agent for the Ice Ages was summer insolation at the Arctic Circle. We'll remind you of this when we get to climate denialist bogus claims, so take note.
- Melting Arctic ice lowered albedo for the Earth, raised global temperatures, including those in the ocean, bringing dissolved CO2 up and into the atmosphere, and thawing methane out of the permafrost
- Rising atmospheric CO2, methane and water vapor caused greenhouse warming, amplified the insolation effect, and brought us out of the Ice Age

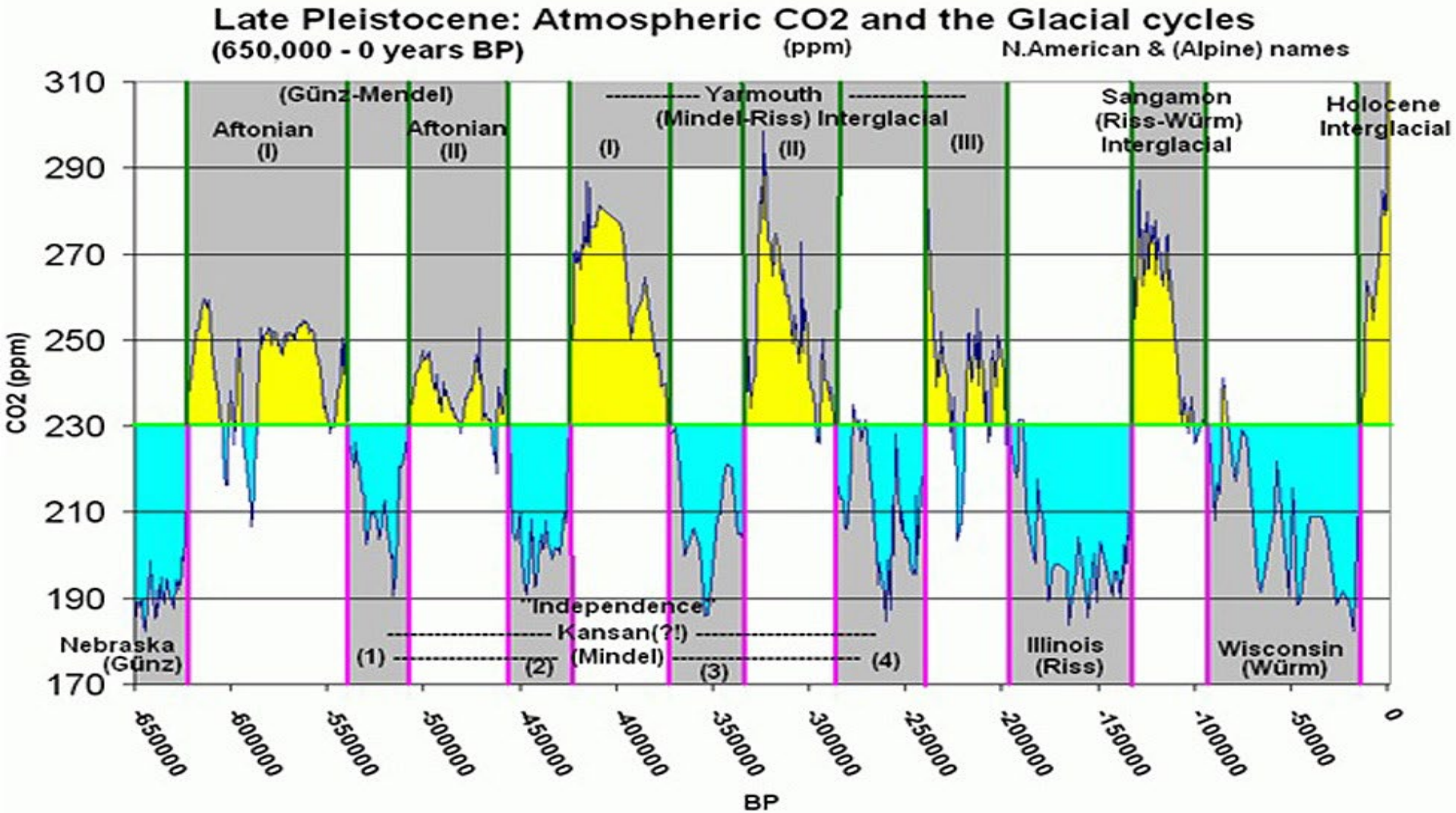
Vostok (Antarctica) and Other Ice Cores Tell Us:

- Ice Ages are the rule for the past 3 million years or so. Most of the time we're in one.
- We are in an inter-glacial warm period right now
- The past 4 Ice Ages fit well with a very rough $\sim 100,000$ year period.
- These Milankovitch cycles are theoretically reasonable and fit the periods, and are likely the main triggers.

The Ice Ages are Recent, due to low Atmospheric CO₂, Likely from Rise of Himalaya and Washing of CO₂ out of the atmosphere

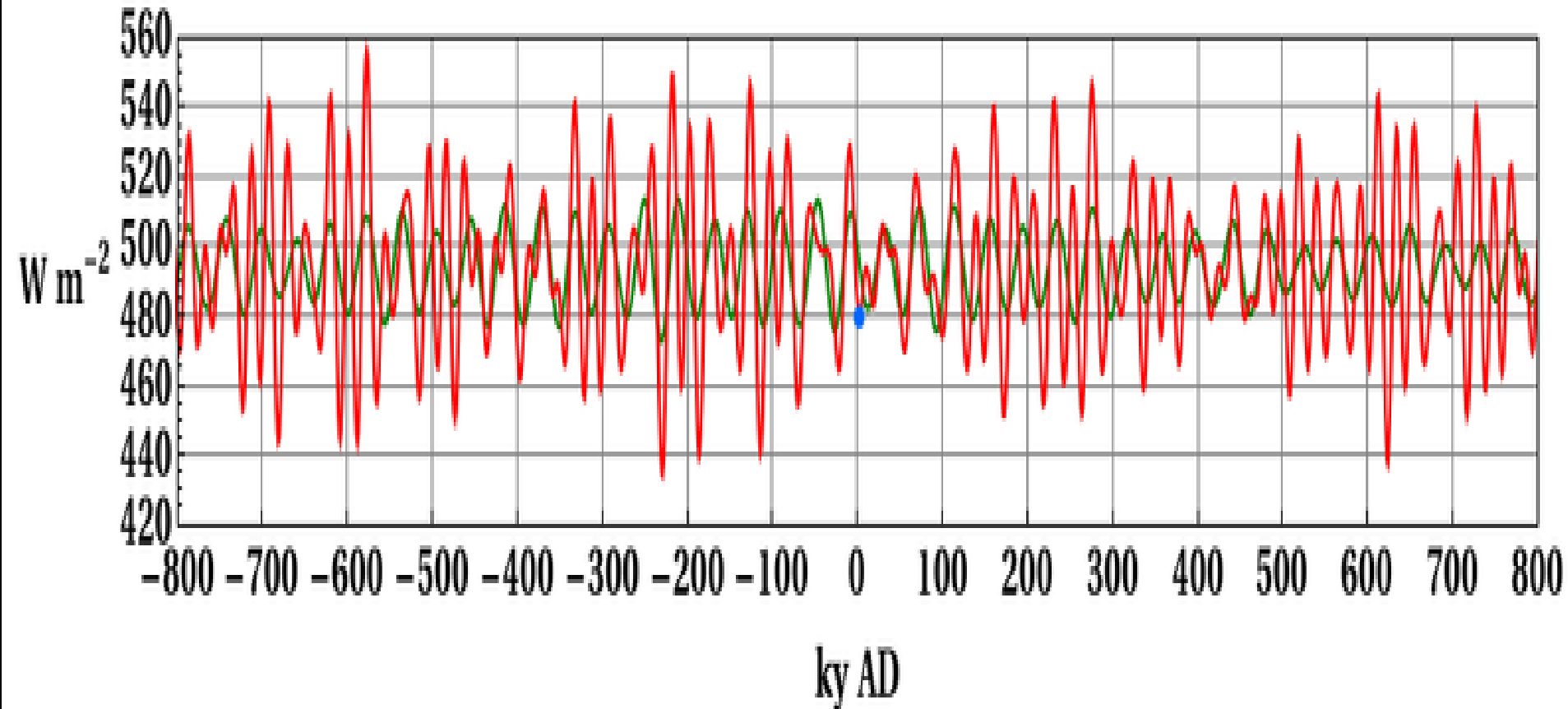
- But there are other climate determiners as well, so the cycles aren't perfect. See the [Wikipedia entry](#) for more.
- While Ice Ages are the rule right now, this is recent.
- We need to have climate in a cool enough state that it is possible for these small orbital effects to cause the incomplete melting of summer snow in the Arctic Circle. Otherwise, no periodic Ice Ages

Note that in 2020 our CO2 is at 417 ppm, FAR above the top of the graph

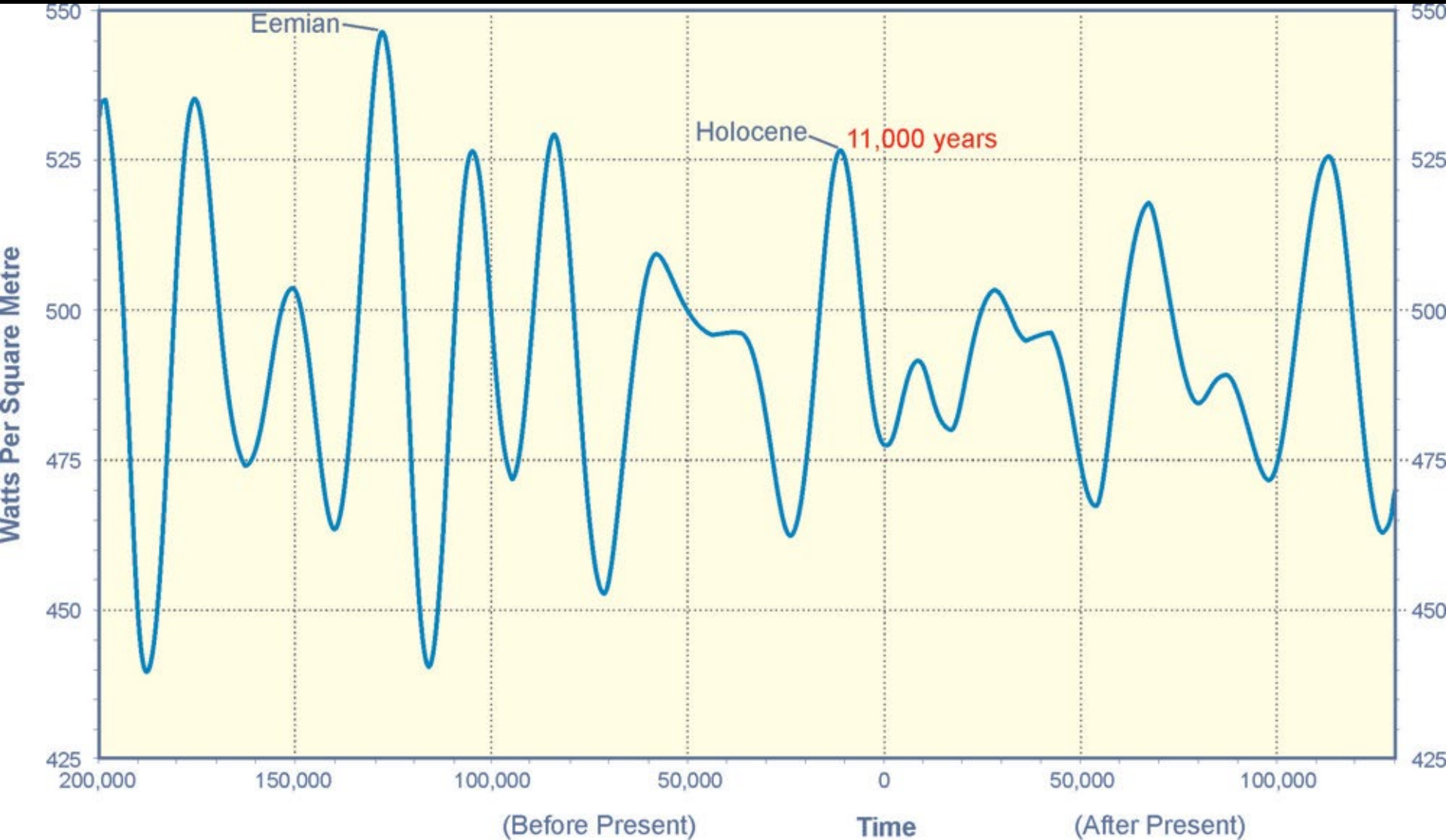


Past and Future 800,000 years of Milankovitch cycles. Insolation in Red. Note the “beat frequency” of about 100,000 yrs, due to the combination of odd cycle lengths “beating” against each other, and that we are currently in a benign low-amplitude period with no Ice Age triggering expected for at least 45,000 years and perhaps 145,000 years.

Insolation at 65 N, Summer Solstice (green is obliquity contribution)



We're today at a (mild) minimum in Arctic summer insolation. Assuming (for the sake of argument) we do not permanently damage our atmosphere, the next chance for an Ice Age onset isn't for another ~45,000 years. Plotted below - Insolation at Arctic Circle on Summer Solstice



Post-Glacial Sea Level Rise

Present Rate of Increase

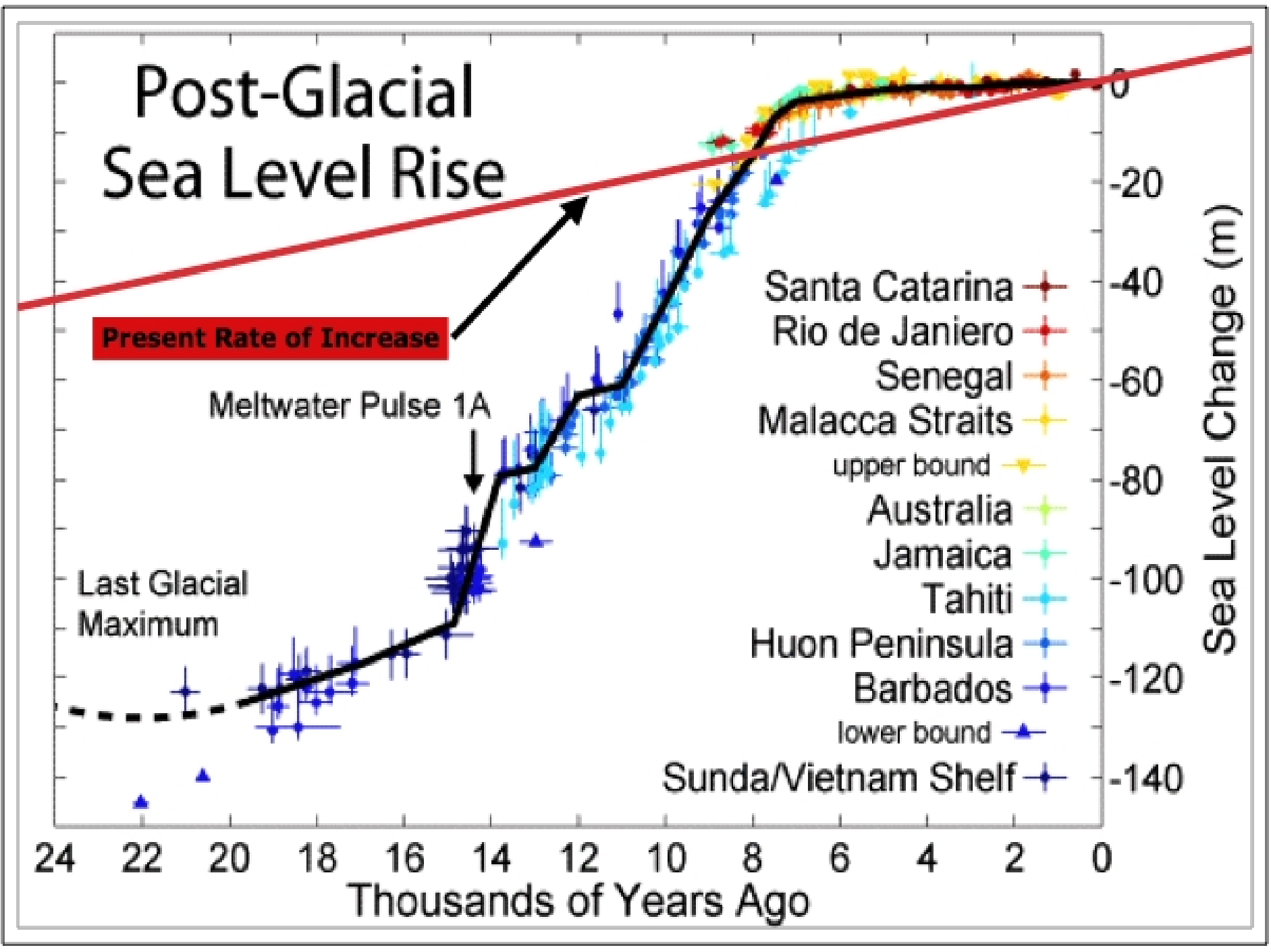
Meltwater Pulse 1A

Last Glacial
Maximum

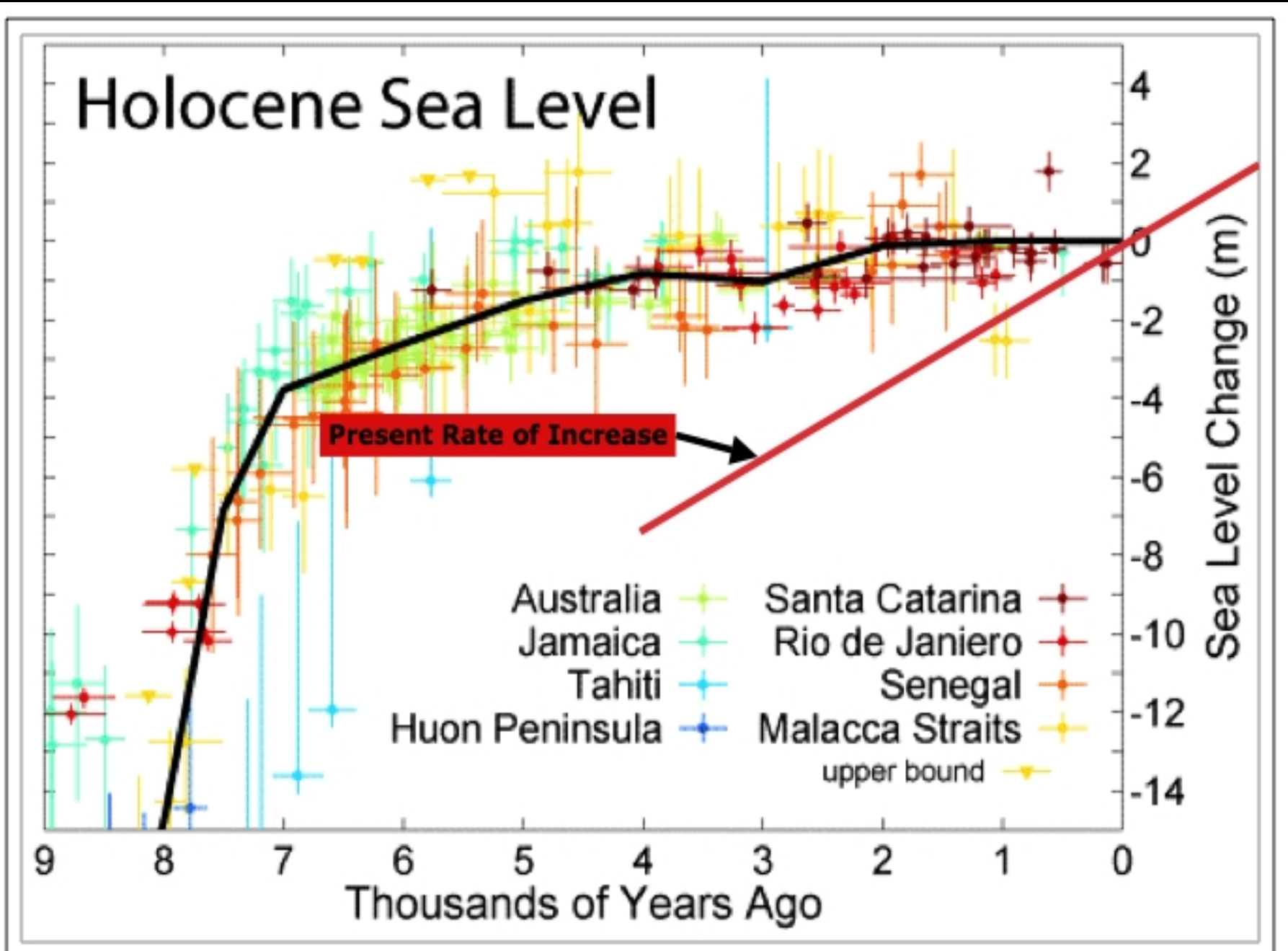
- Santa Catarina +
- Rio de Janiero +
- Senegal +
- Malacca Straits +
- upper bound +
- Australia +
- Jamaica +
- Tahiti +
- Huon Peninsula +
- Barbados +
- lower bound ▲
- Sunda/Vietnam Shelf +

Sea Level Change (m)

Thousands of Years Ago



Same, only zoomed in on last 9,000 years



The Maunder Minimum and The “Little Ice Age” (LIA). Only a Weak Connection

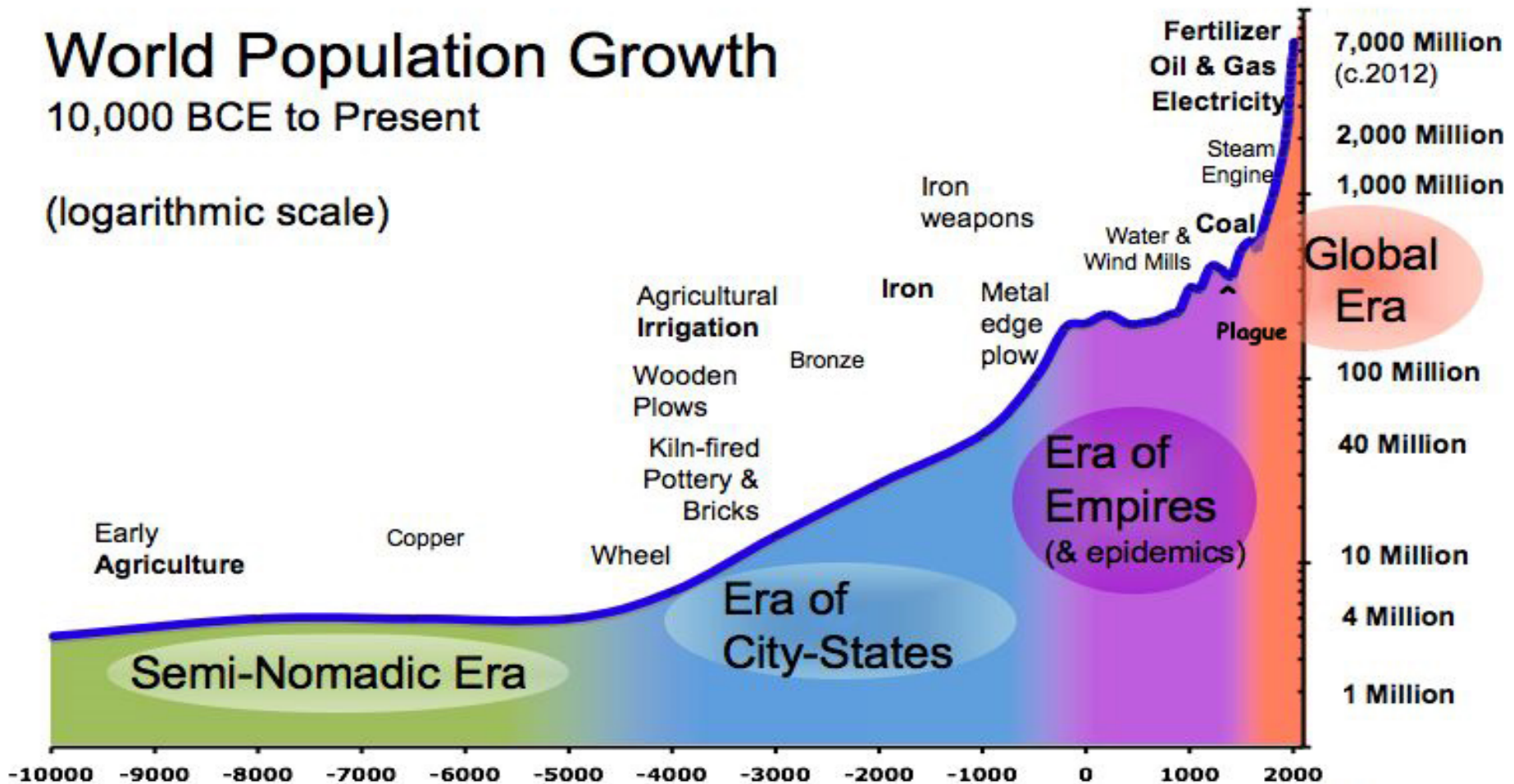
- The **Maunder Minimum** in sunspot numbers in the late 1600's corresponds roughly to a cool period in climate on Earth.
- But careful [research finds several causes](#) of the LIA...
- 1. Unusually intense volcanic ash/dust period
- 2. Disease killed ~20% of human population in the Americas, abandoned land reforestation took up extra CO₂ out of the atmosphere.
- 3. Lower solar luminosity (now seen to be a minor contributor, from satellite correlations of sunspot number vs TSI)
- 4. Reduced thermohaline circulation failing to efficiently distribute equatorial warmth to European and North American latitudes, and Maunder Minimum stories are primarily from Europe.

Population, on a logarithmic Scale. The Plague of the 1300's is Considered a Starting Point for the Little Ice Age. There's Another Drop in Human Population Just before Coal Discovery

World Population Growth

10,000 BCE to Present

(logarithmic scale)



To Emphasize the Relation between Paleo Climate and Life

- Every past mass extinction is caused by climate change (even the K-Pg asteroid event)
- **THE** criterion astronomers study in order to judge the life-harboring ability of exo-planets is – **the Stability of its Climate**
- When you de-stabilize climate over geologically short time scales, as we're doing today – you kill living systems. They can't adapt fast enough

The Sixth Mass Extinction: It's Happening Now

**Caused by Human Domination
of Planet Earth, with Multiple
Causes, Including Climate
Change
(more on this later)**

Key Points – K31: PaleoClimate

- Earliest atmosphere; 4.567 B yrs ago, brought by comets, asteroids
- Earliest atmosphere blown away by moon-forming impact ~100myrs after our formation
- Secondary atmosphere then formed; more comets, and volcanoes; Likely N₂, methane, water vapor, CO₂, some ammonia, no oxygen
- Oceans as early as 4.2 billion years ago: from zircons and O₁₈ ratios
- Sun ~25-30% less luminous back then, yet liquid water – must have had much stronger greenhouse warming. Methane most likely, with help from CO₂. Evidence indirect only
- Today's N₂ atmosphere formed from solar UV converting ammonia NH₃ into N₂ + water. After formation, N₂ is fairly stable
- Oxygen created by cyanobacteria. Oxygen very low until 2.2B yrs ago, Life only possible on land when sufficient oxygen in stratosphere to make ozone, blocking solar UV.
- Snowball Earth at ~2.2Bya and ~600 Mya, evidence from oceanic ice-rafted glacial deposits at ~equatorial latitudes, and widespread anoxic sediments.
- CO₂ likely a strong component of early atmosphere, but conversion into CaCO₃ limestone by sea life has steadily lowered CO₂ and its greenhouse effect compensating very well for rising solar luminosity for over past 4 billion years.
- Walker/Alley mechanism, volcanic atmospheric CO₂ can't dissolve into iced-over ocean, causing rising greenhouse until ocean melts – forces SnowBall epochs to be very short.
- Nearly all of our mass extinctions due to rapid climate change
- Last 3 million years CO₂ greenhouse warming has been low enough to allow these weak Milankovitch cycles to induce regular Ice Ages
- Milankovitch climate driver: does all winter snow at ~65deg (Arctic Circle) latitude melt in summer? If not, Ice Age can result from positive feedbacks: CO₂ pulled from warming ocean, methane from melting permafrost – amplify Milankovitch to take us out of Ice Ages.
- Today Earth is near a local minimum in Milankovitch insolation; will slowly rise beginning in a few centuries. No possible Ice Age for over 40,000 years. Ancient Man's impact on CO₂ levels has been gracefully accommodated by a COOLING Milankovitch period. Those days are OVER! No more help from Nature to keep things cool. We're on our own now – and doing badly.