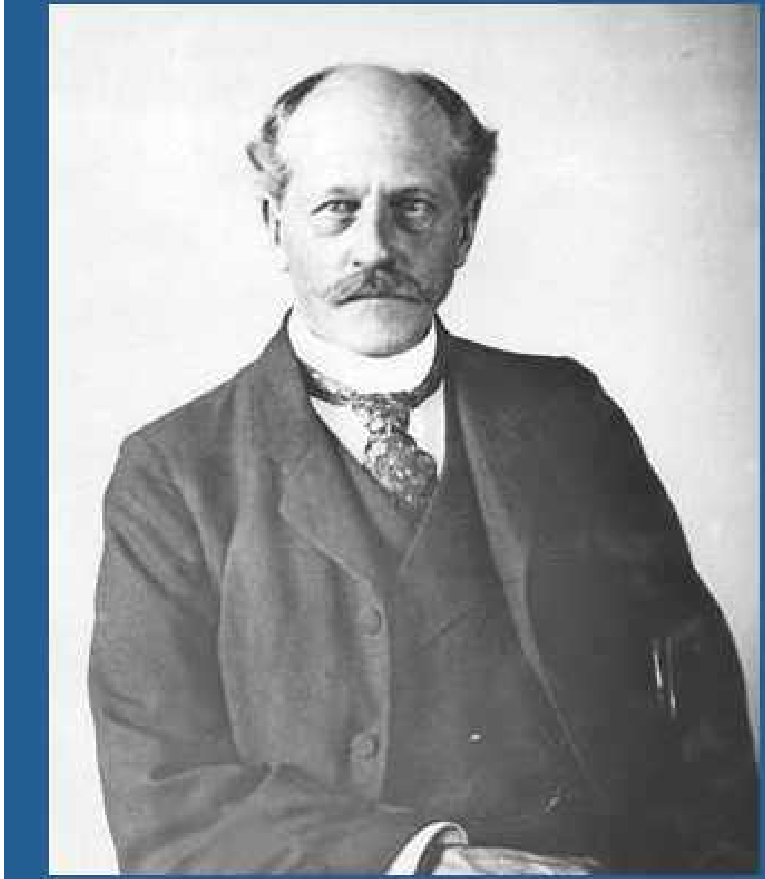
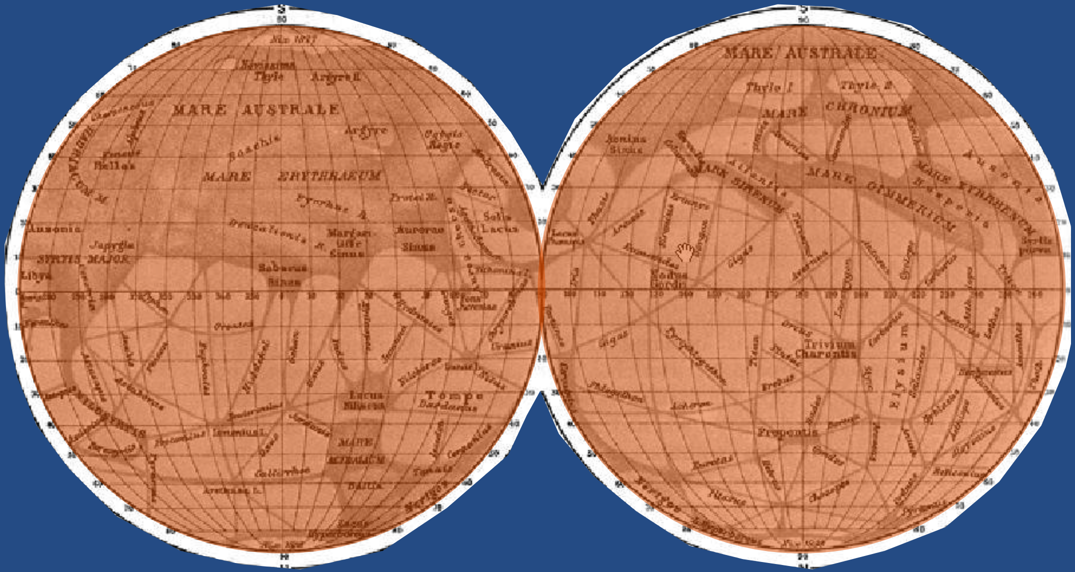
Evolution of Atmospheres

A message from Our Founder

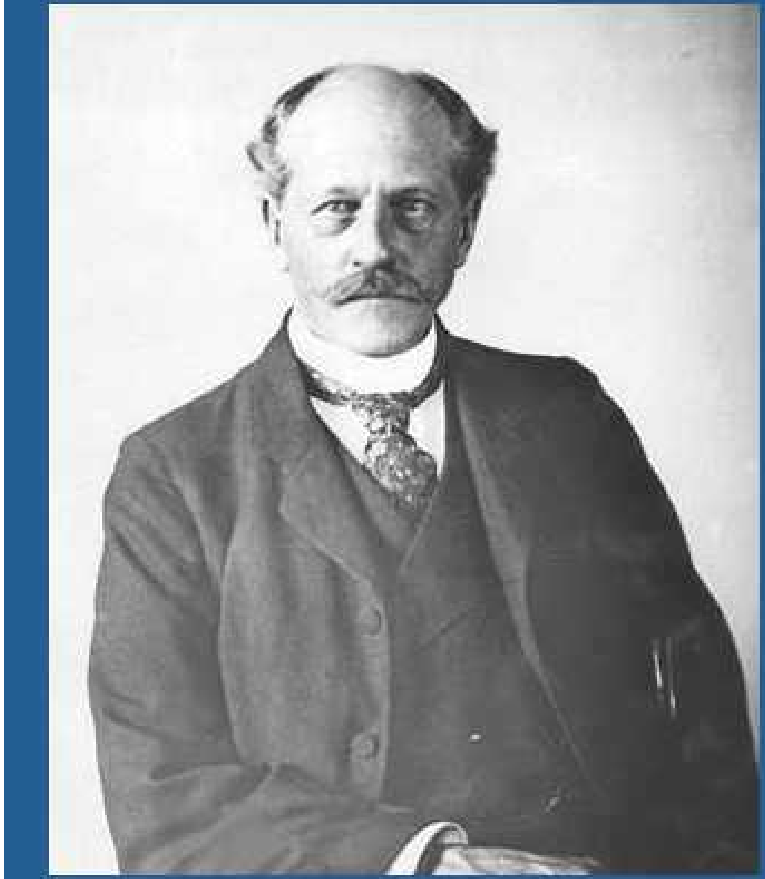


Percival Lowell's planetology: Worlds form hot and dry out as they age.

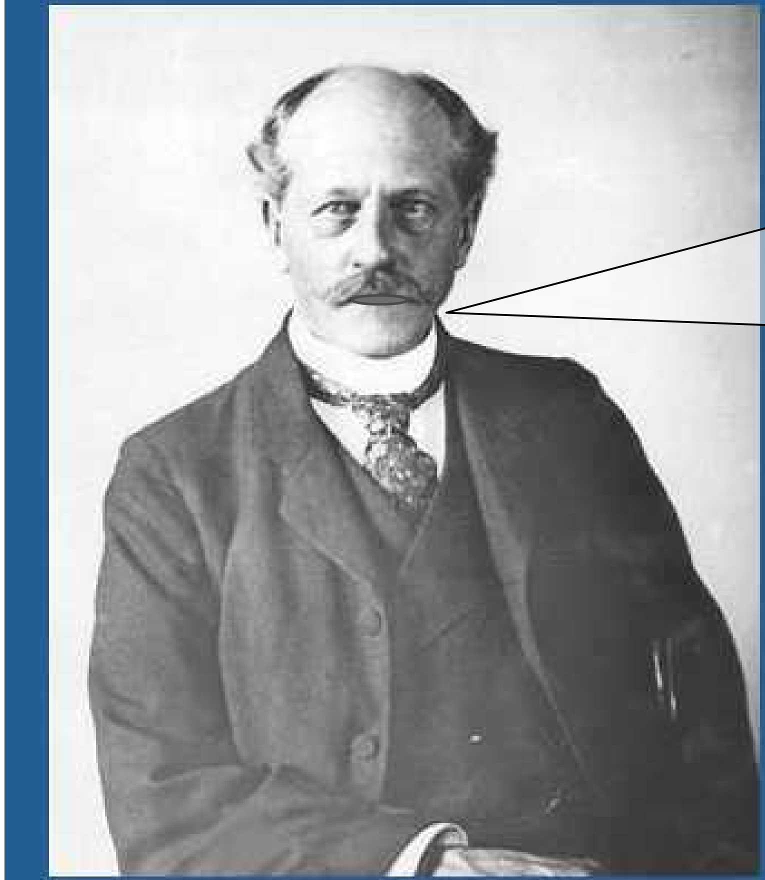


"Canaliform features" on 19th century Mars

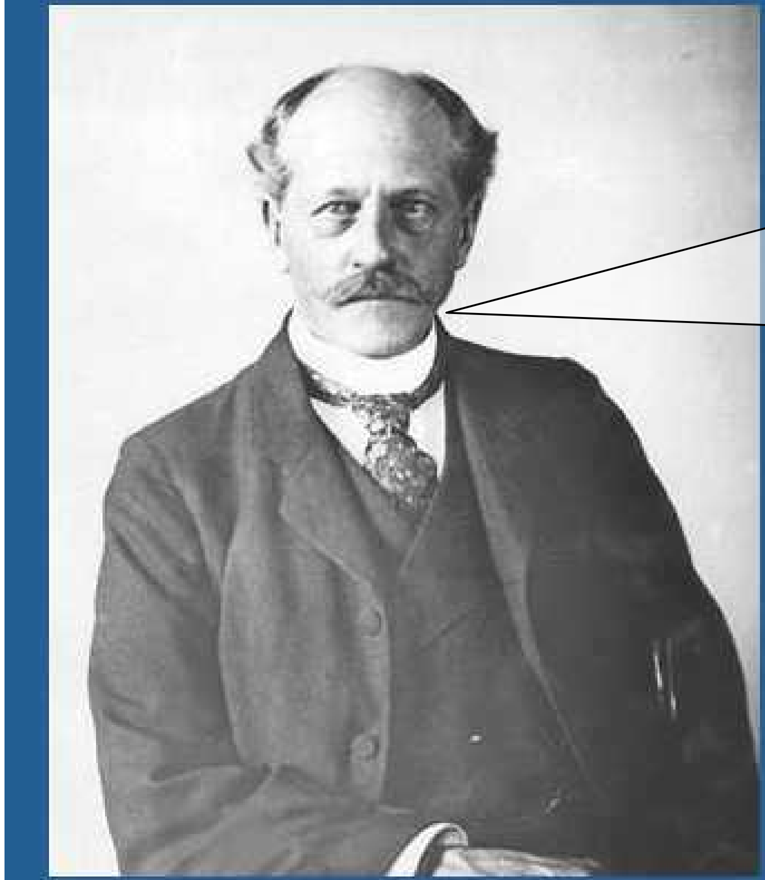
A message from Our Founder



Large worlds cooled slowly, and were still evolutionarily young in 1895,

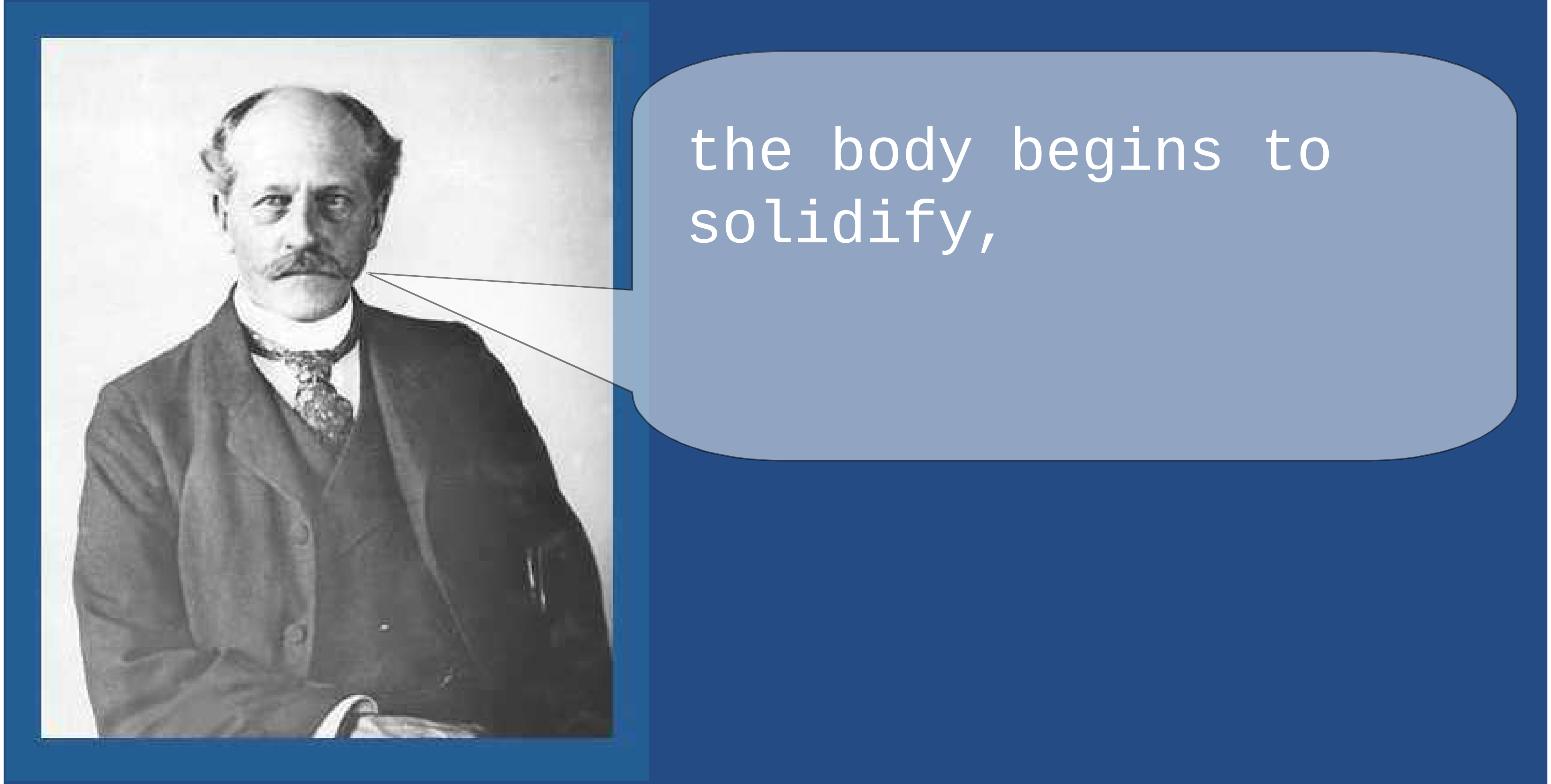


"while in the moon we gaze upon the last sad age of decrepitude…"



"…a world almost sans air, sans sea, sans life, sans everything."

“As the heat dissipates,



the body begins to solidify,

starting with the crust.

For cosmic purposes

it undoubtedly remains plastic,

but cracks of relatively small size

are both formed and persist.

Into these the surface water seeps.

“With continued refrigeration the crust thickens,

more cracks are opened,

and more water given lodgement within

to the impoverishment of the seas."

Lowell accepted Kelvin’s chronology

1. The Earth cooled by thermal conduction. The thermal gradient at the surface indicated an age of 25 Ma

2. The Sun shone by gravitational contraction. Energy conservation indicated an age of 25 Ma

Earth's Moon formed by the impact of a Mars-sized planet with the Earth.

The impact took place 30 to 100 million years after the origin of the solar system.

That was 4.5 billion years ago, give-or-take

The planet that hit the Earth seems to have resembled Mars in many ways, not just its size

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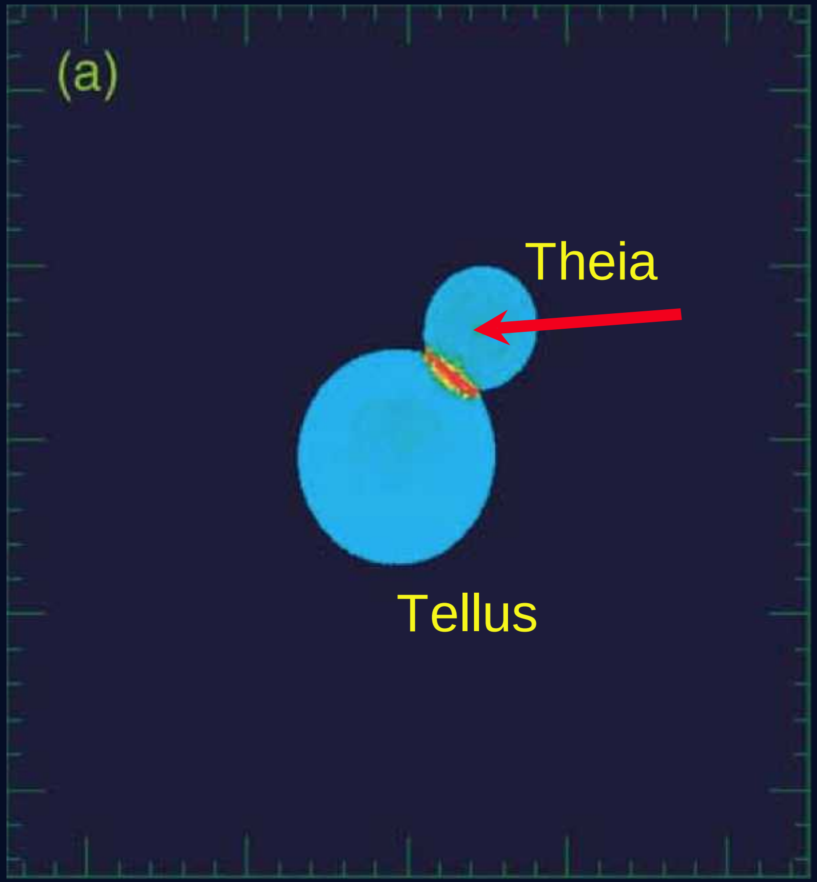
The planet that hit the Earth seems to have resembled Mars in many ways, not just its size

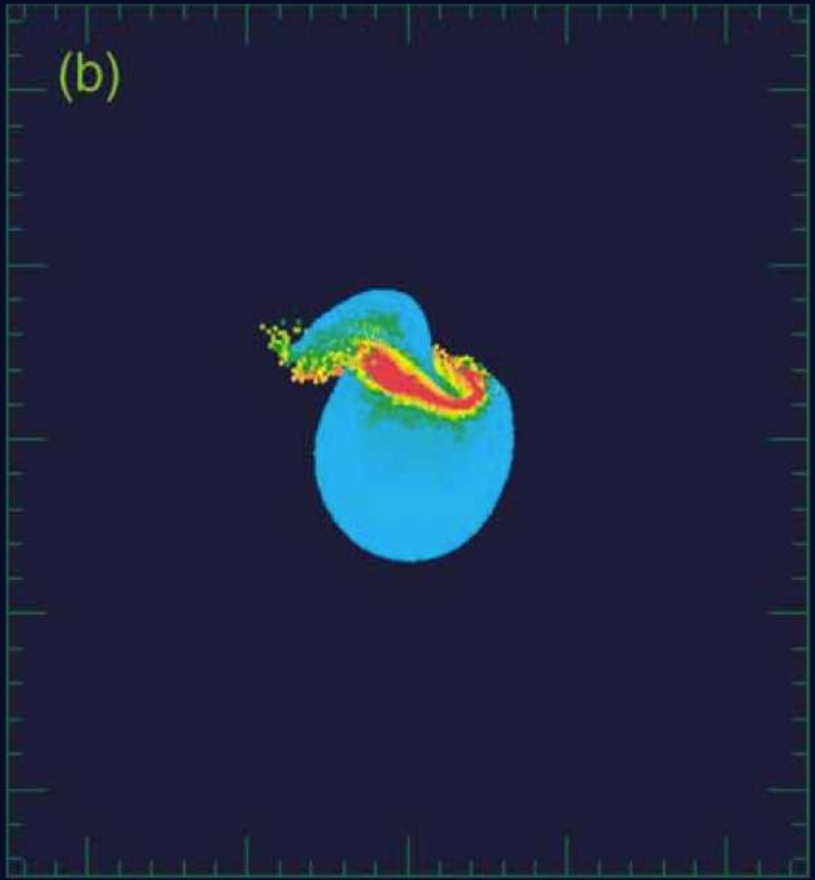
This is what happened to it:

Moon-forming impact



(Canup 2004)

Moon-forming impact



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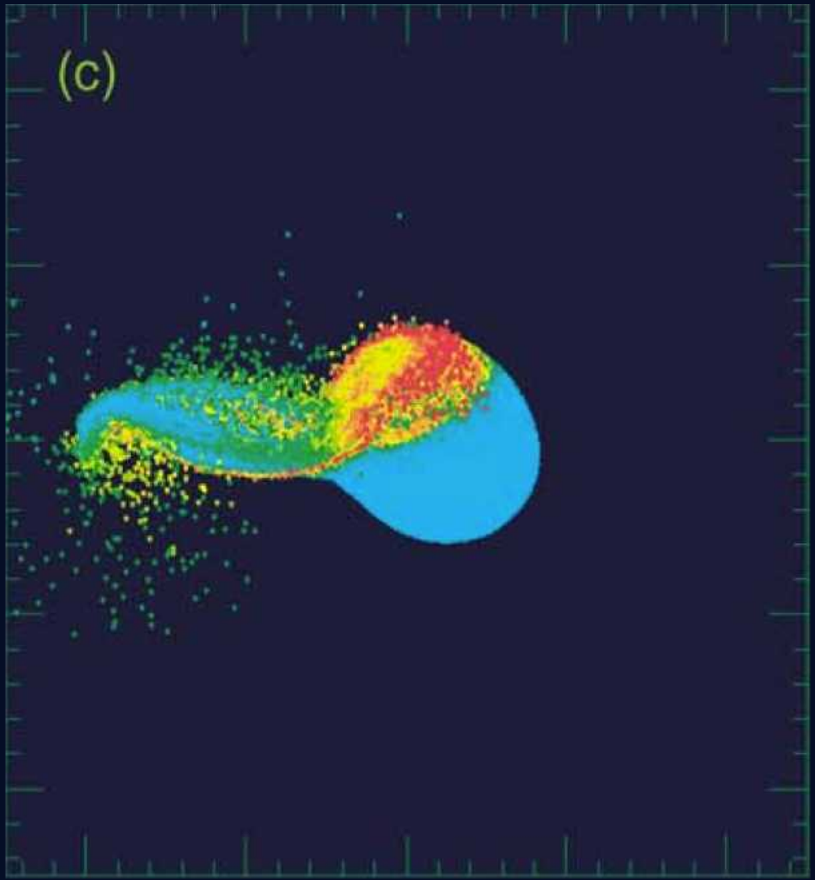
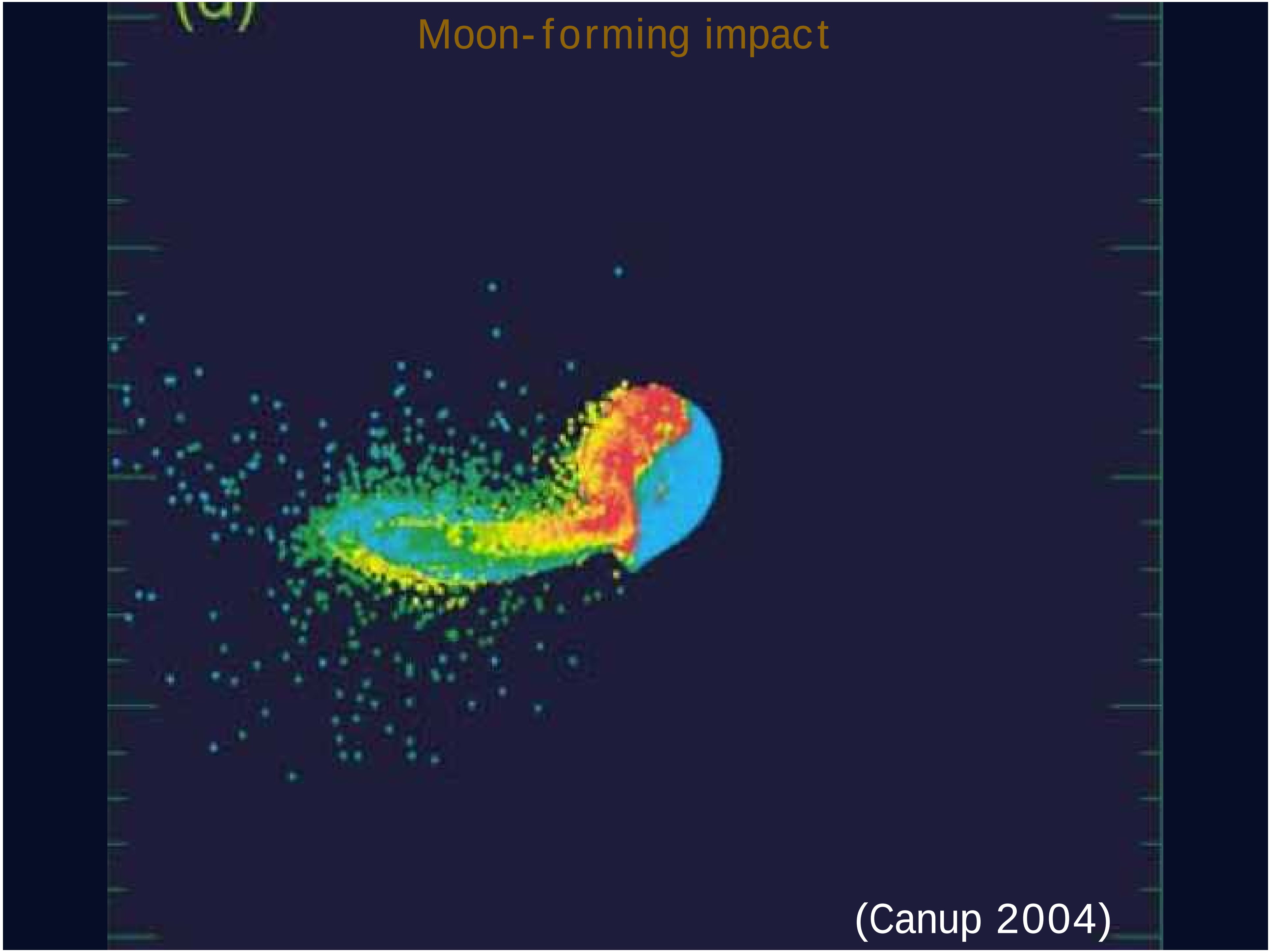
Moon-forming impact



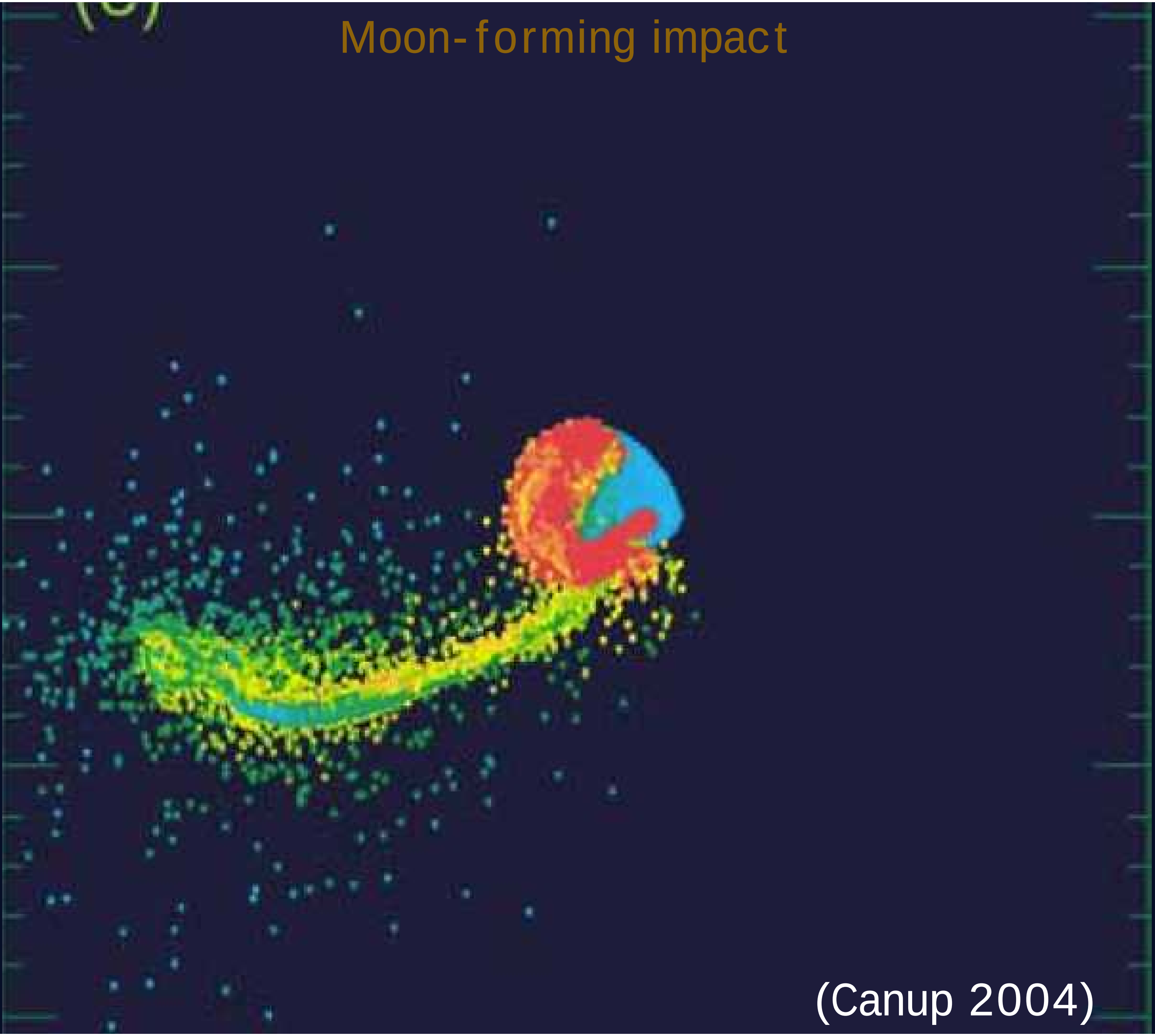
(Canup 2004)

Moon-forming impact



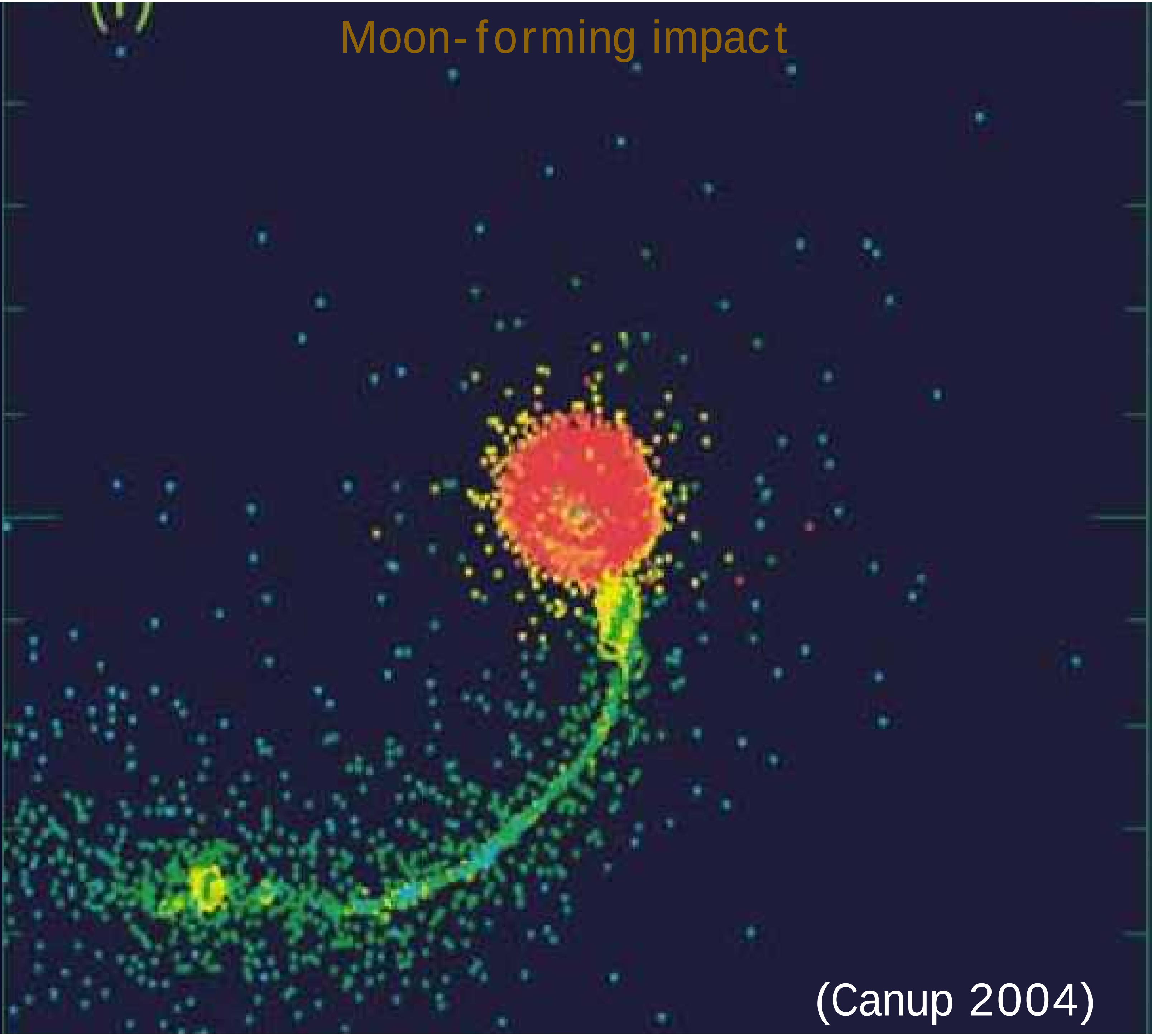
(Canup 2004)

Moon-forming impact



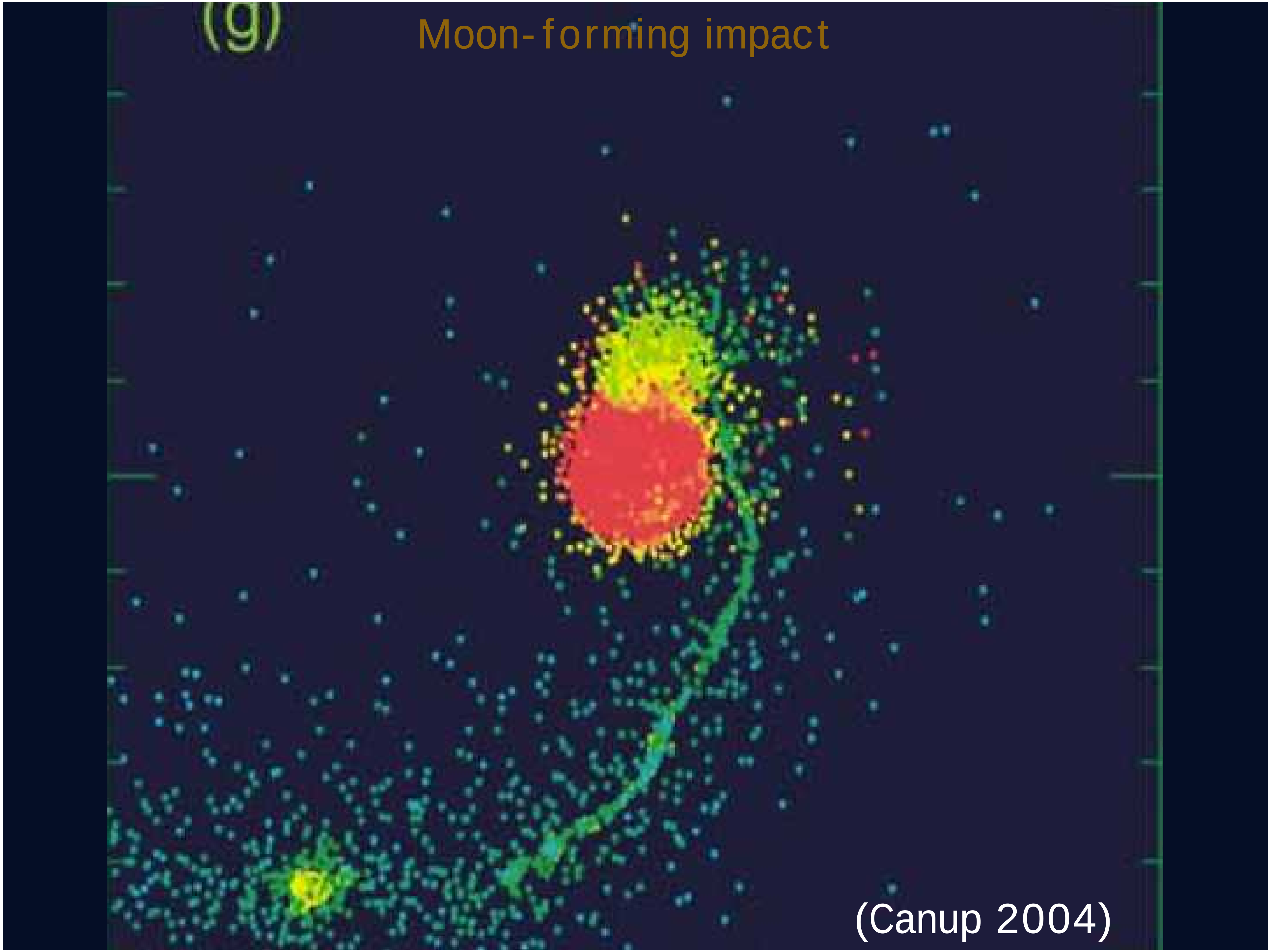
(Canup 2004)

Moon-forming impact



(Canup 2004)

Moon-forming impact



(Canup 2004)

Recap of arguments in favor of the Moon-forming impact:

1. The Moon has the general composition of a planetary mantle, but has only a tiny iron core

- the Moon was made from the mantle of an evolved planet

2. numerical simulations show that a giant impact separates core from mantle

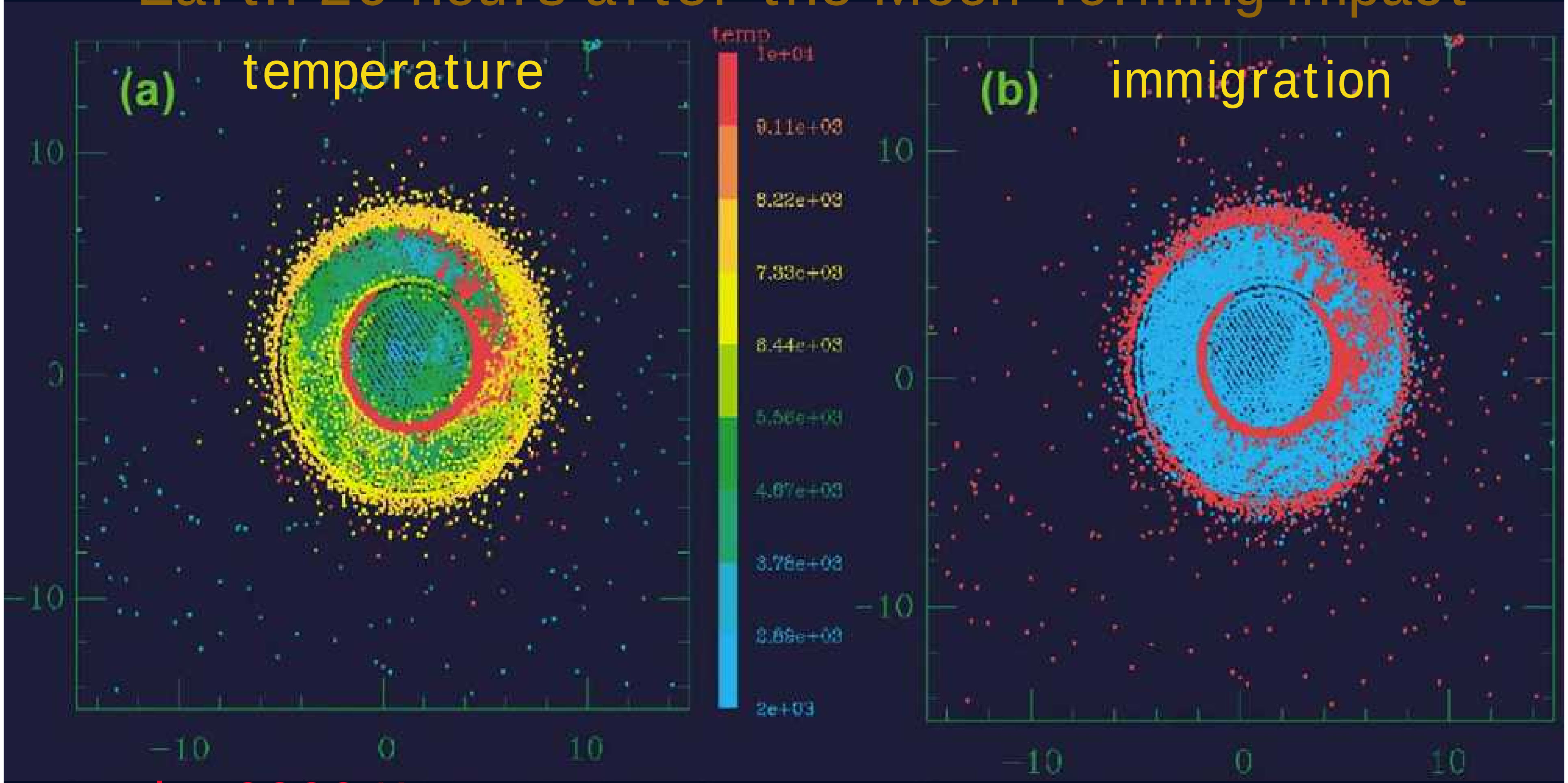
- the core of the evolved planet merged with Earth's core

3. the mechanics work out: the impact gives the right angular momentum and energy

4. All other theories are fatally flawed. (this is a weak argument, but one that people find convincing)

Our focus here will be on the Earth

Earth 20 hours after the Moon-forming impact



temperature

immigration

red: > 9000 K

yellow: 6000-8000 K

green: 4000-6000 K

blue: 2000-4000 K

(Canup 2004)

red = from Theia

blue = from Earth

After the impact

silicate vapor atmosphere

top of core is extremely hot

interior is melted

some atmosphere is lost but oceans are retained (Genda, Abe, 2005.)

day is ~5 hours long , month is slightly longer

and there is a moon

Modeling is based on three constraints:

1. Conservation of Energy
2. The Faint Young Sun
3. The Runaway Greenhouse Effect

The Runaway Greenhouse Effect is usually told as a cautionary tale to young planets:

"If you go too close to the Sun,
you'll end up like Venus!"

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Runaway

not enough

there is an upper limit to how much Earth can radiate to back to space if there is liquid water

too much

QuickTime™ and a
TIFF (Uncompressed) decompressor
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the oceans evaporate

Runaway

not enough

there is an upper limit to how much Earth can radiate to back to space if there is liquid water

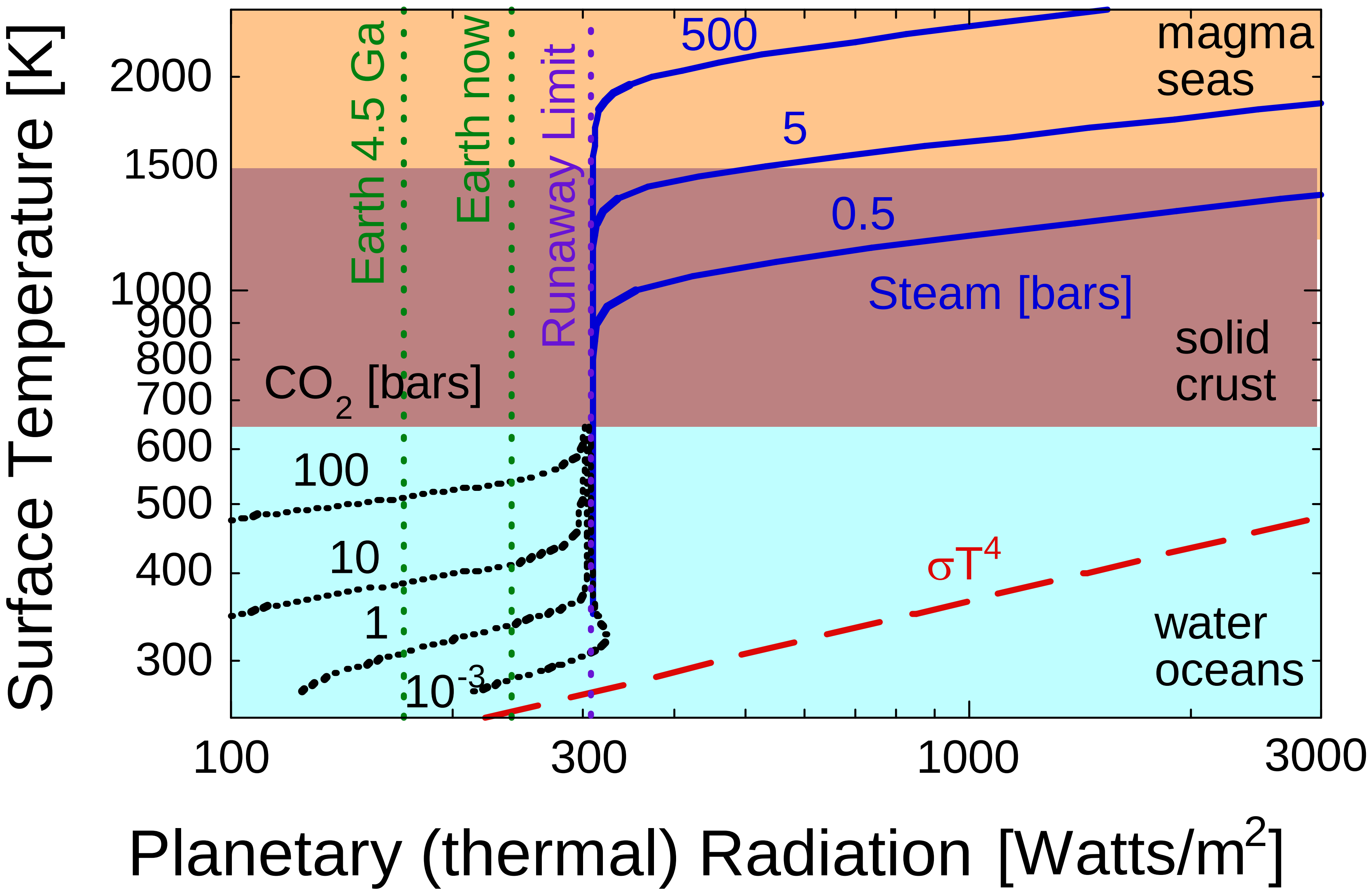
too much

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

the oceans evaporate

until it begins to melt

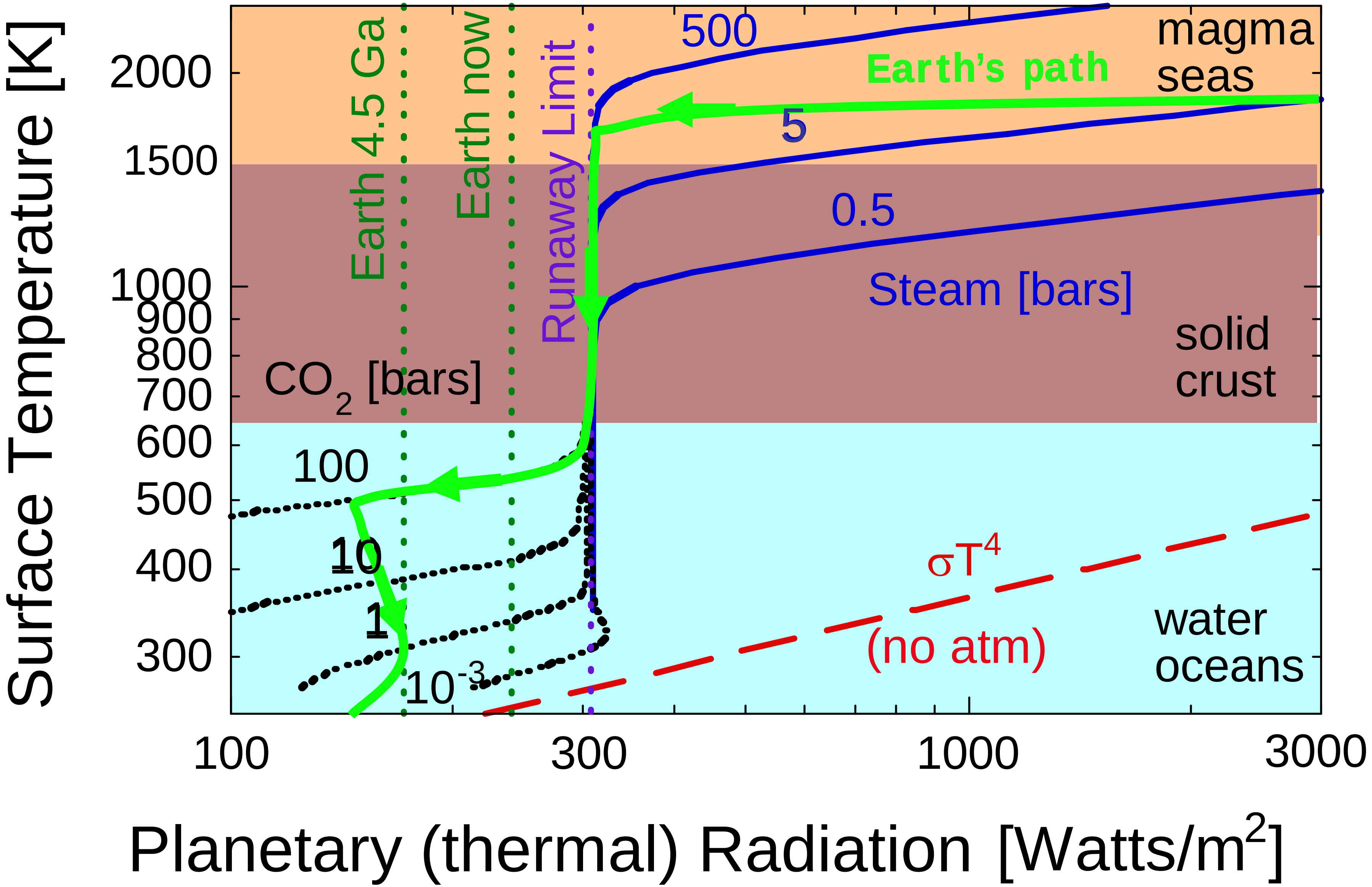
The Runaway Greenhouse Effect



adapted from work by Yutaka Abe

When Earth cools after the Moon-forming Impact, the Runaway Greenhouse Effect runs backwards

The Runaway Greenhouse Effect



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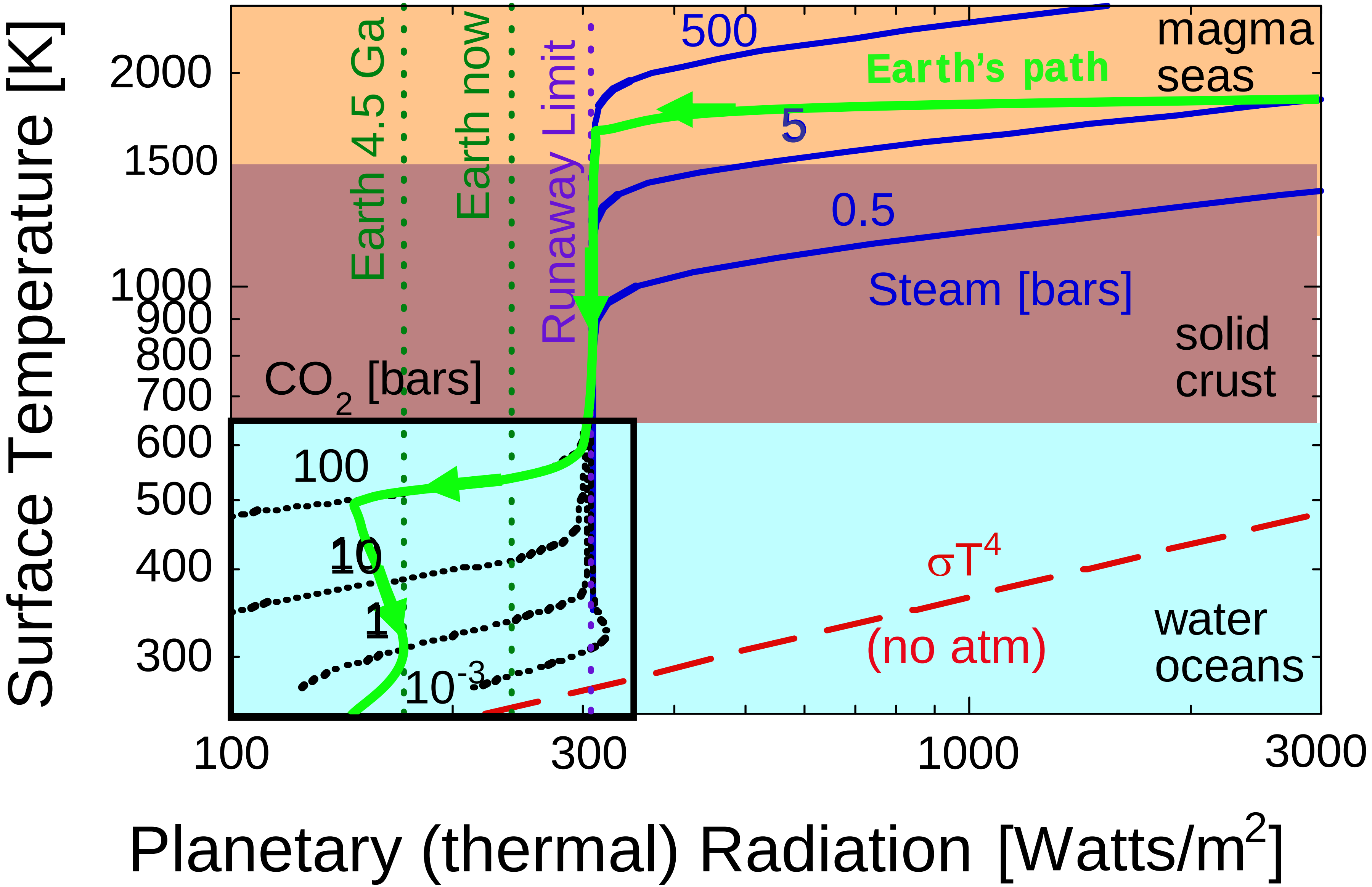
The Runaway Greenhouse Effect



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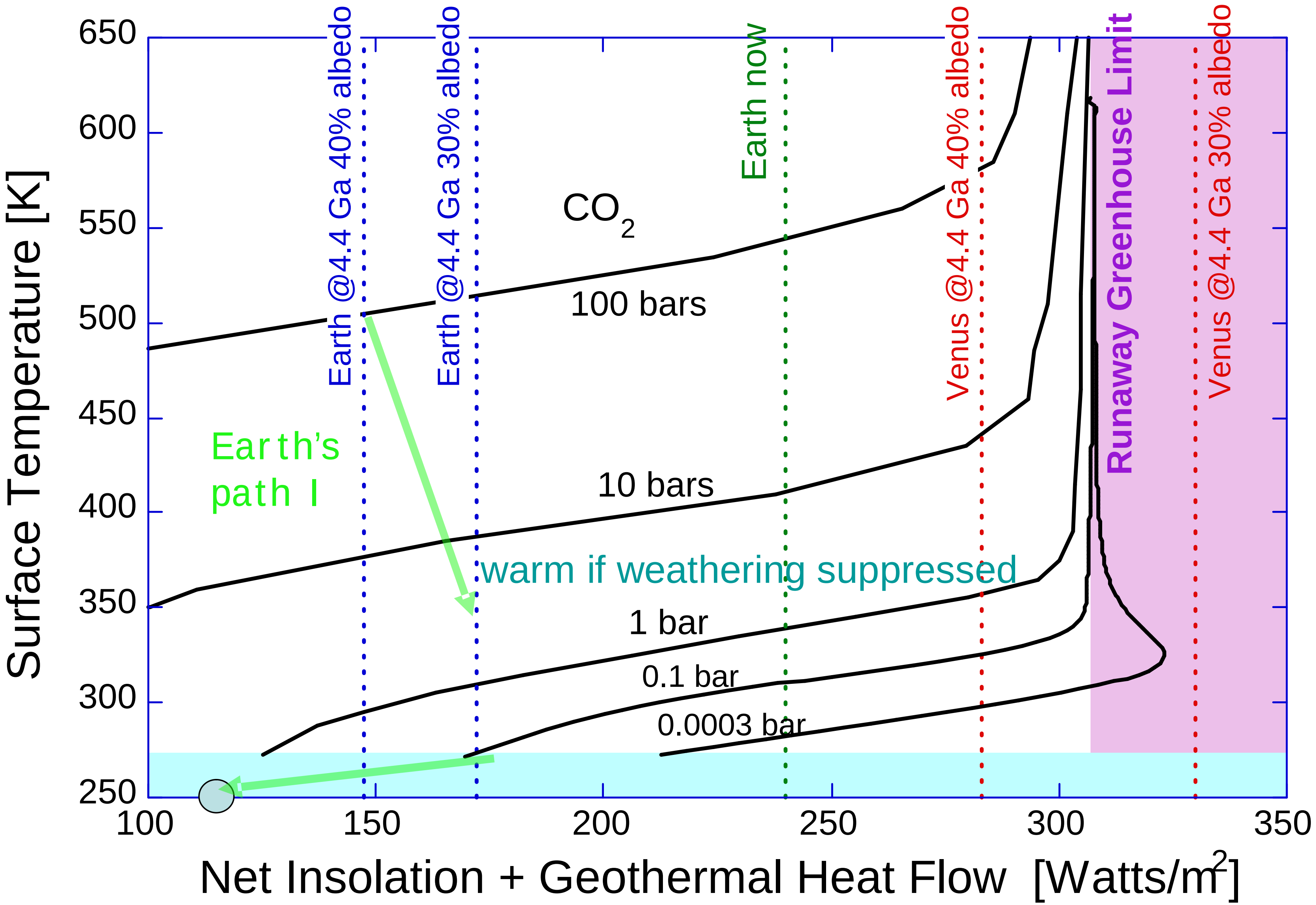

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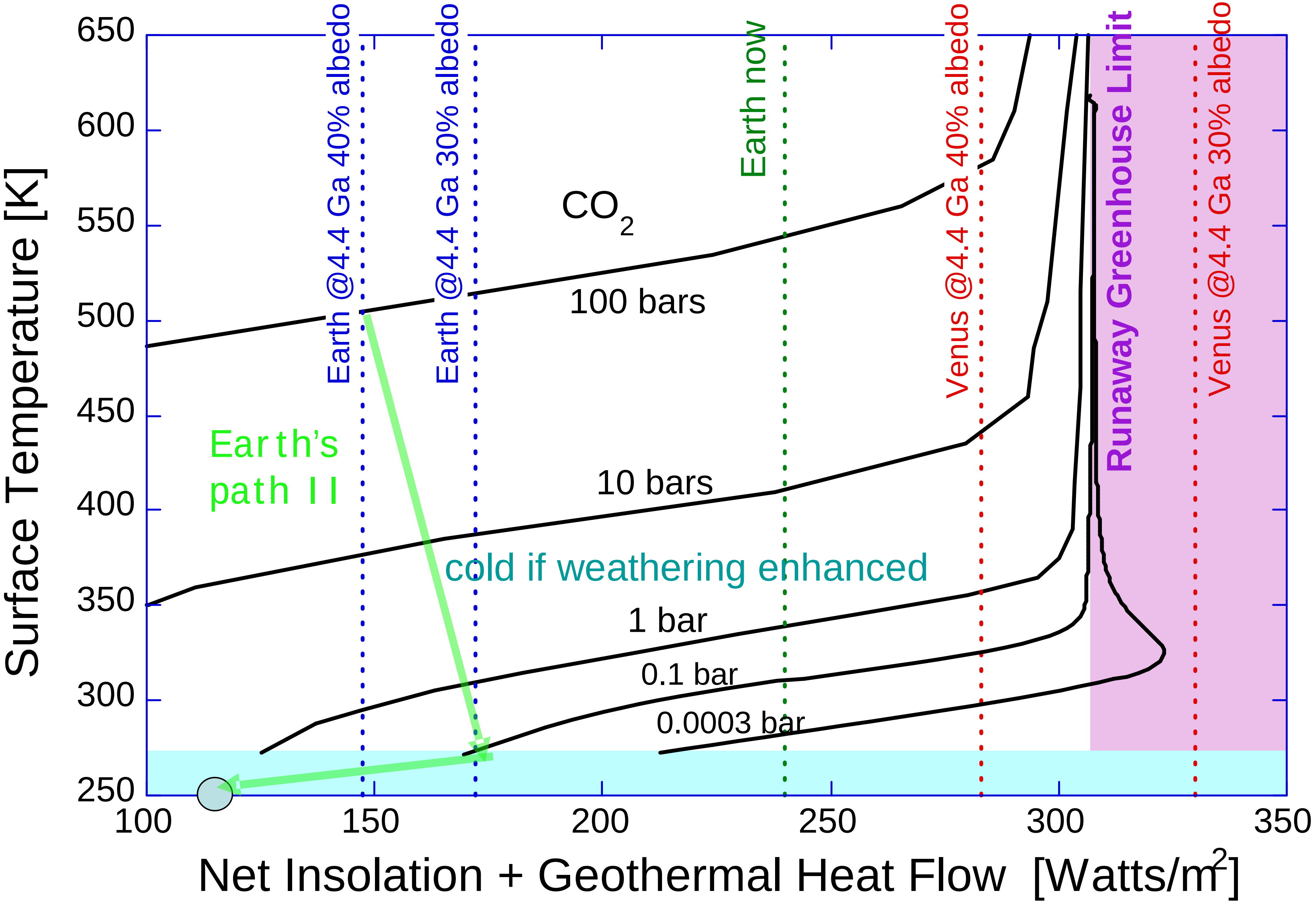

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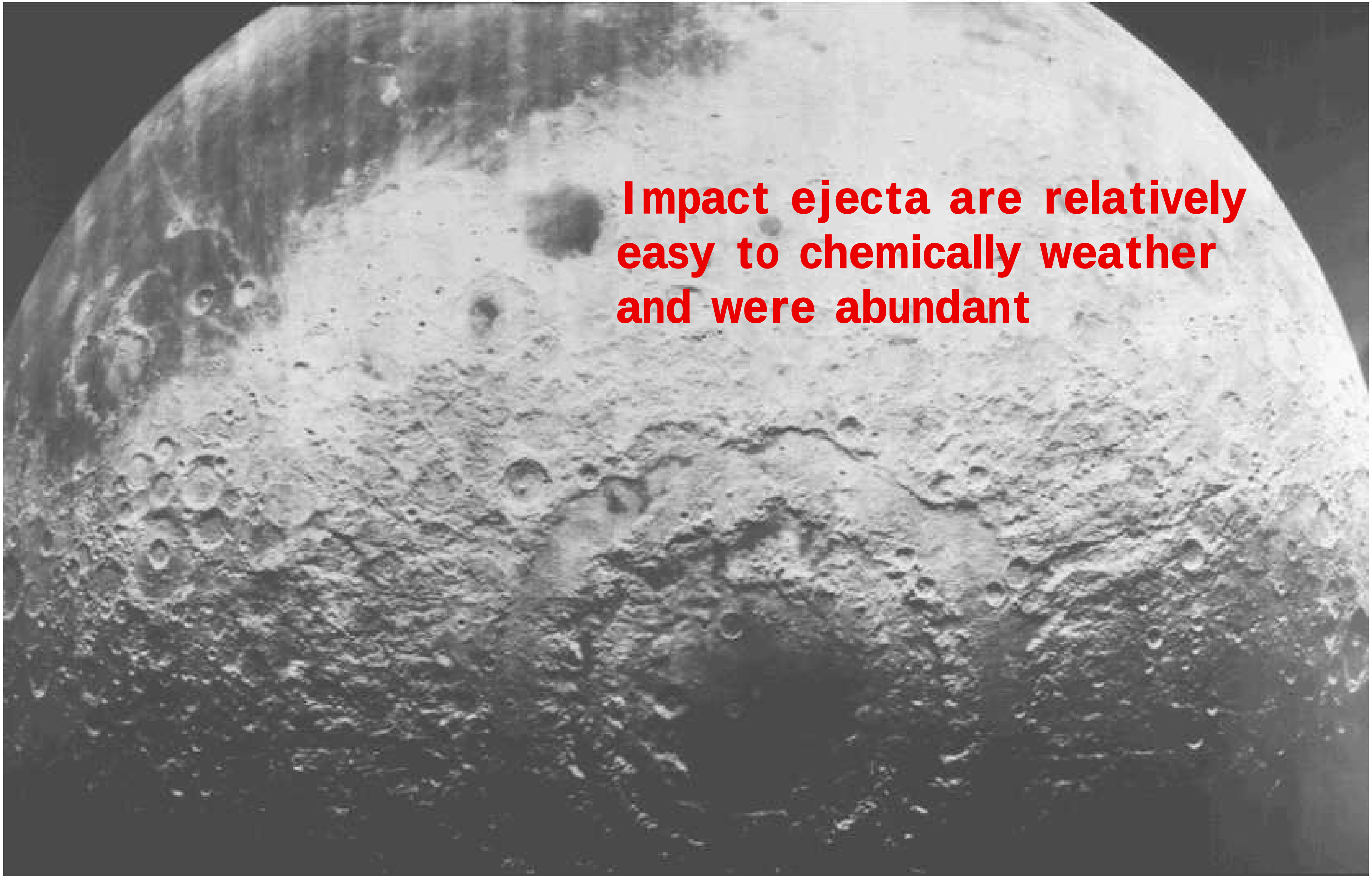
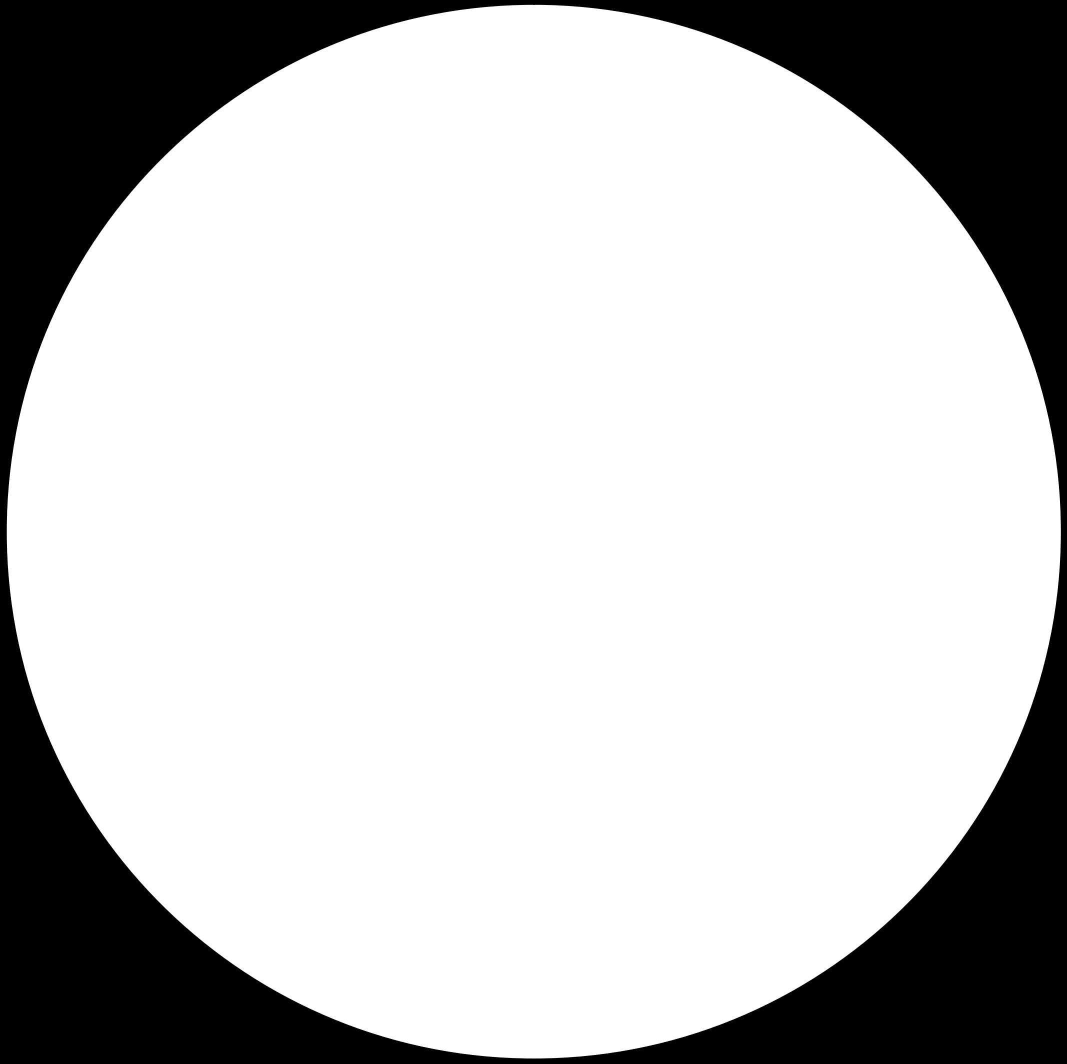
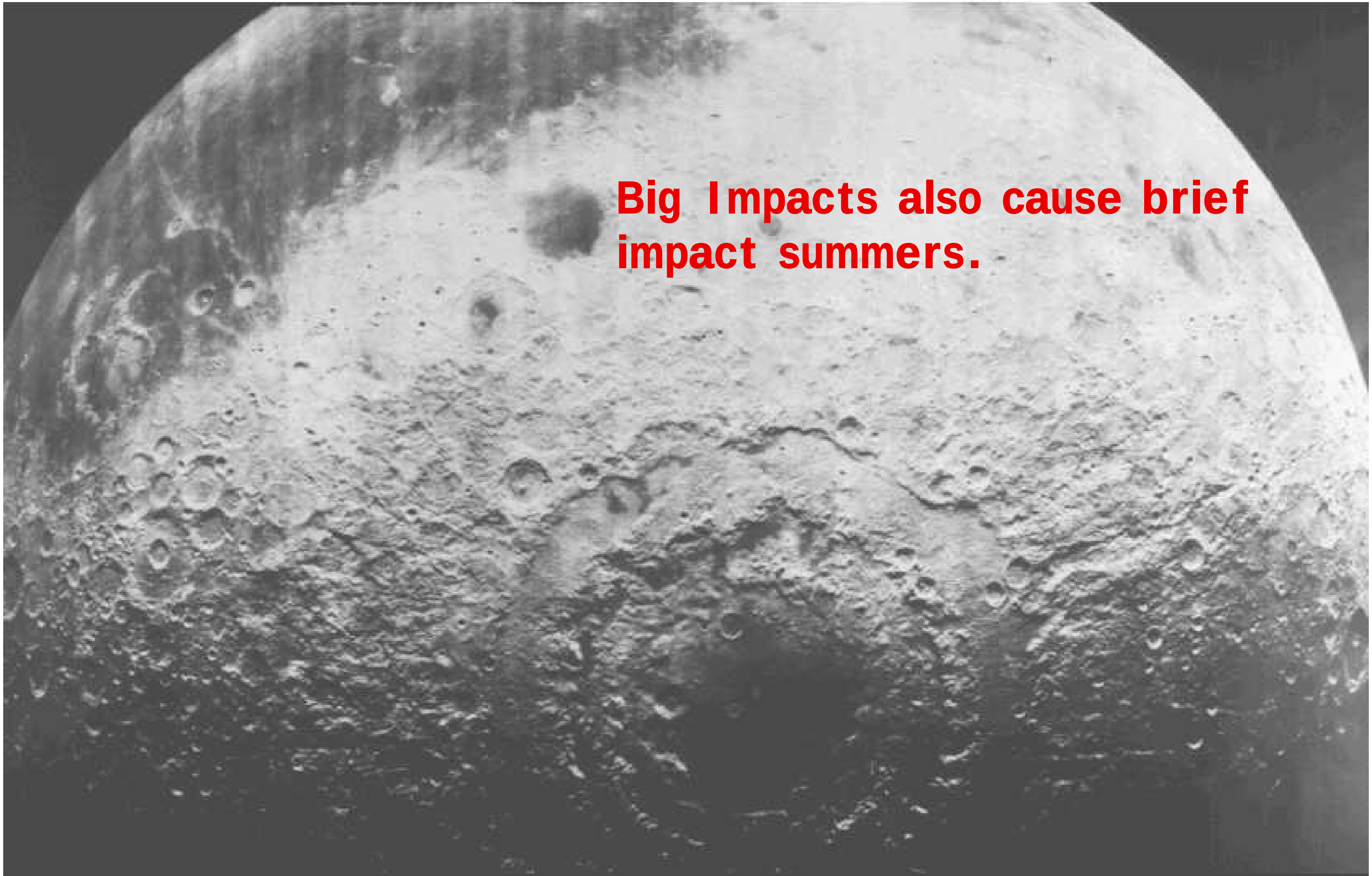


Impact ejecta are relatively easy to chemically weather and were abundant

Mare Orientale

Hadean Iceball Earth (tentative model)

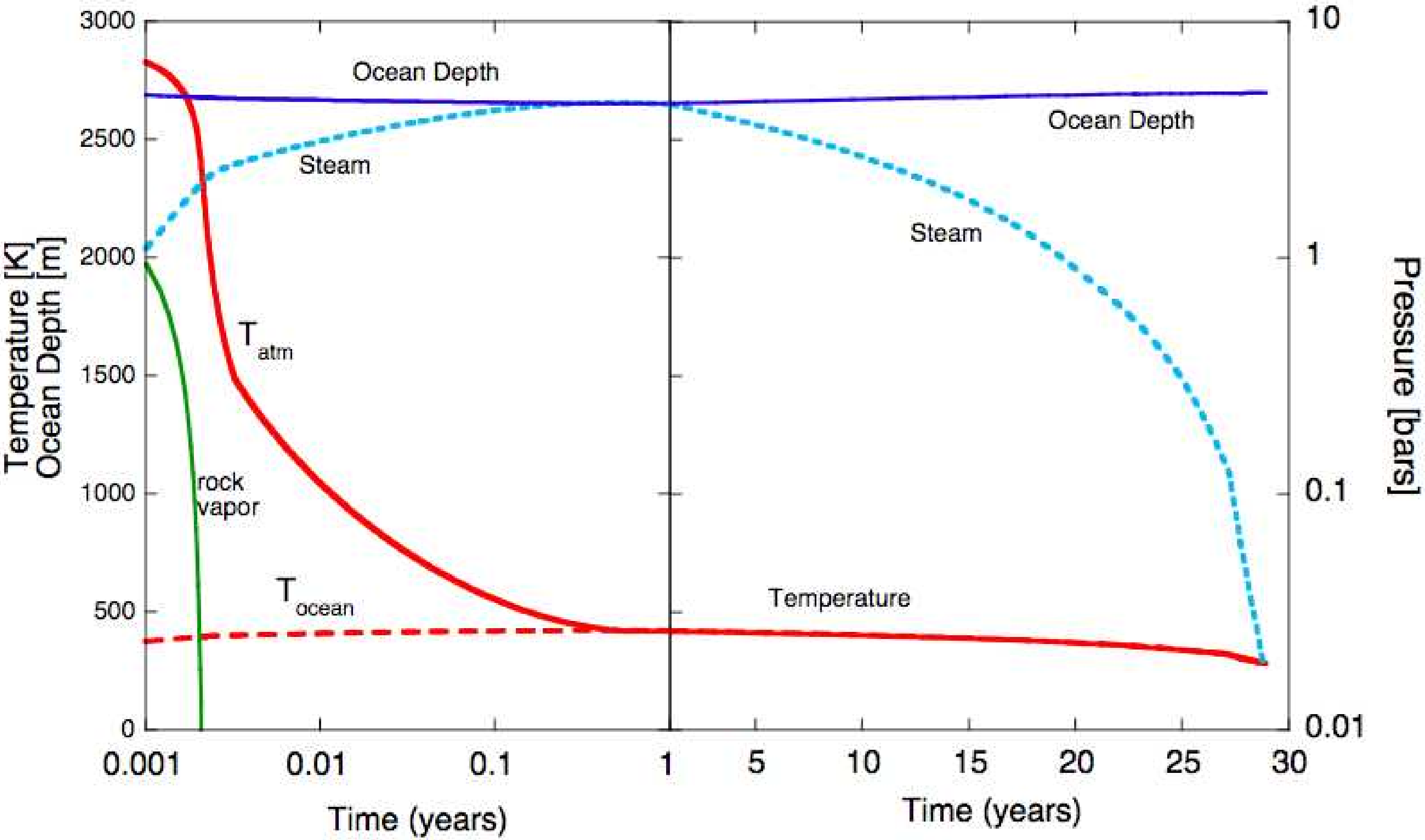


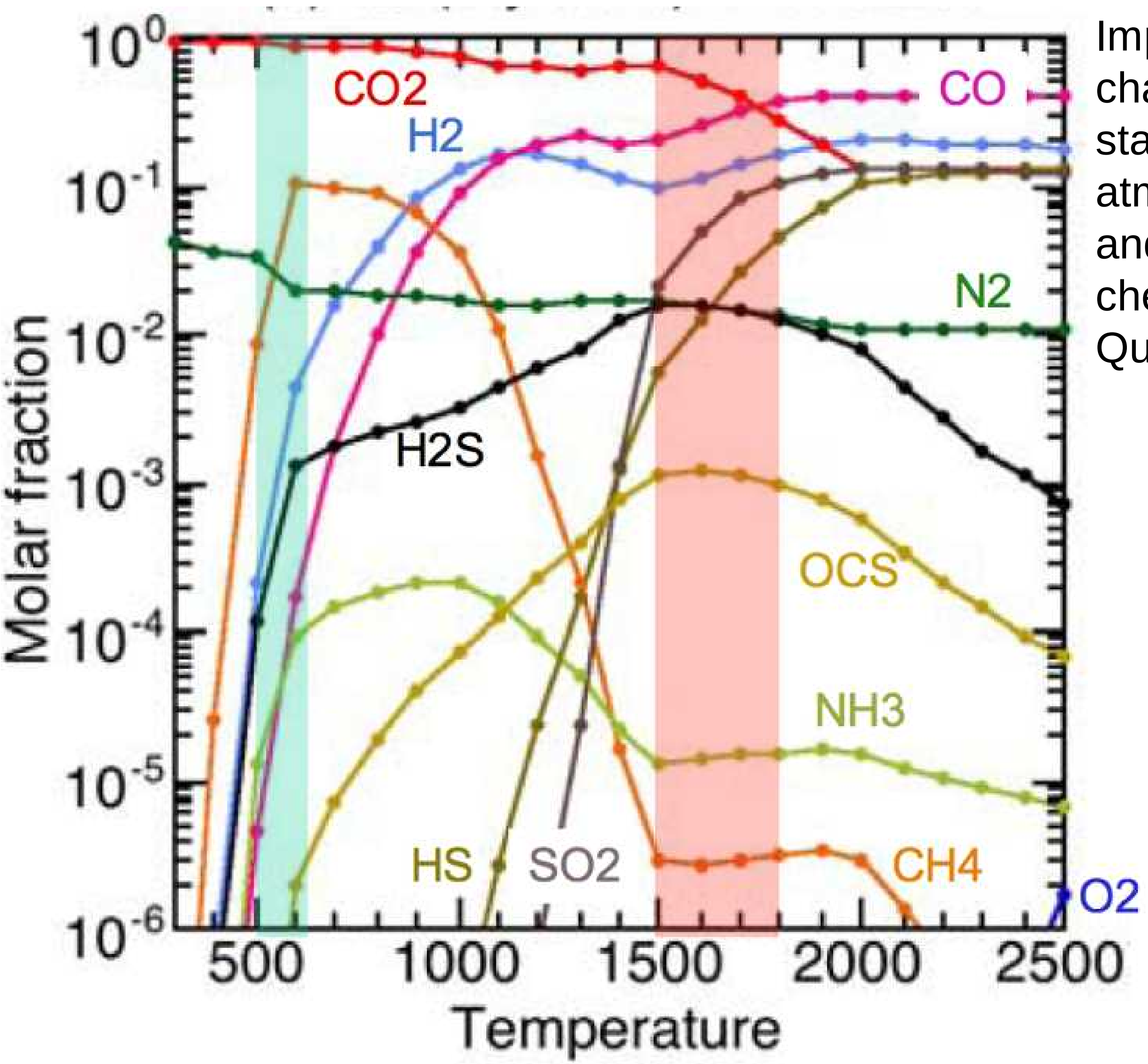


Big Impacts also cause brief impact summers.

Mare Orientale

10^{33} ergs - Orientale size impact on Earth

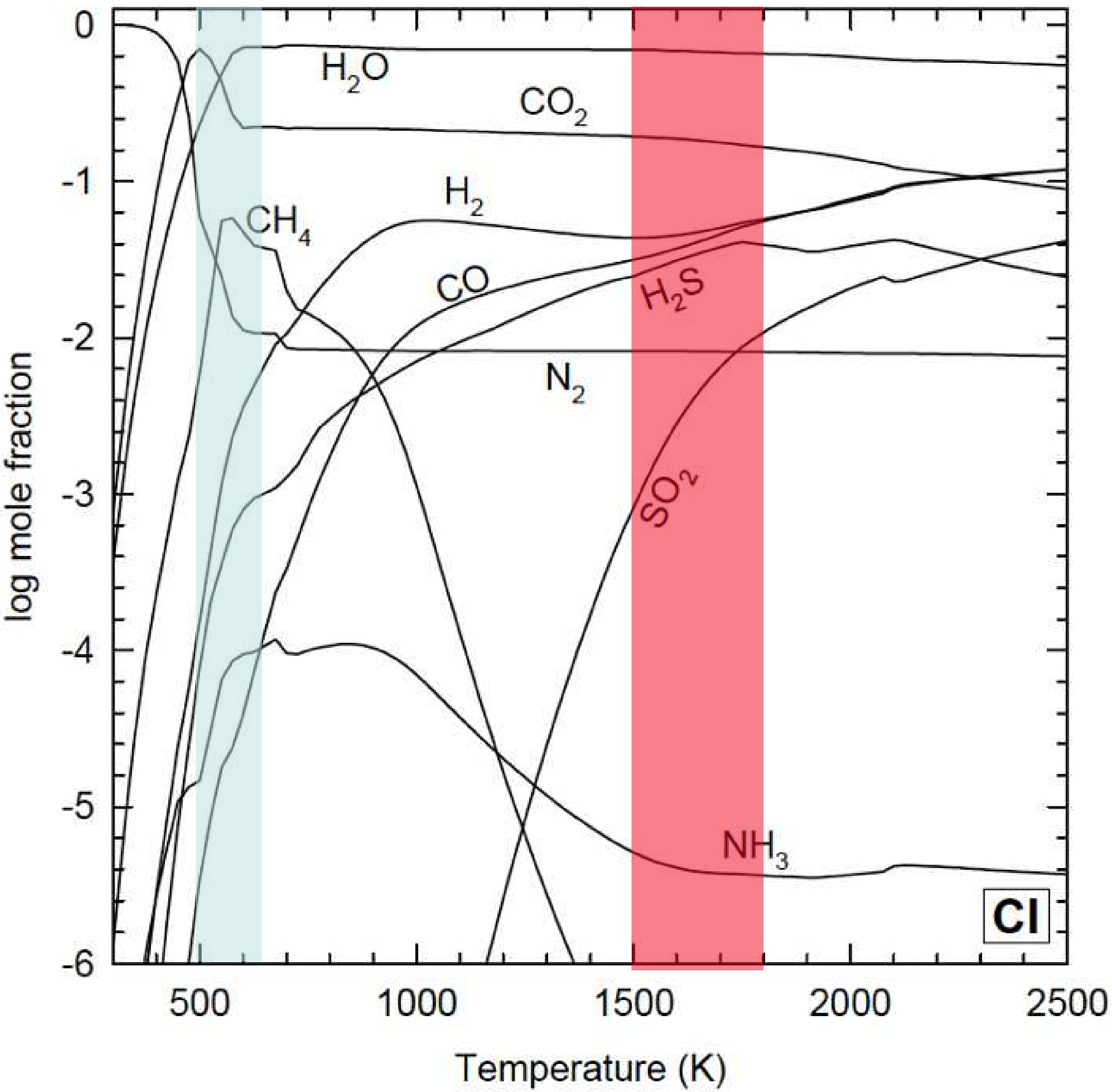




Impacts can
change the redox
state of the
atmosphere
and cause shock
chemistry.
Quench T ~ 1500

Hashimoto
et al 2007

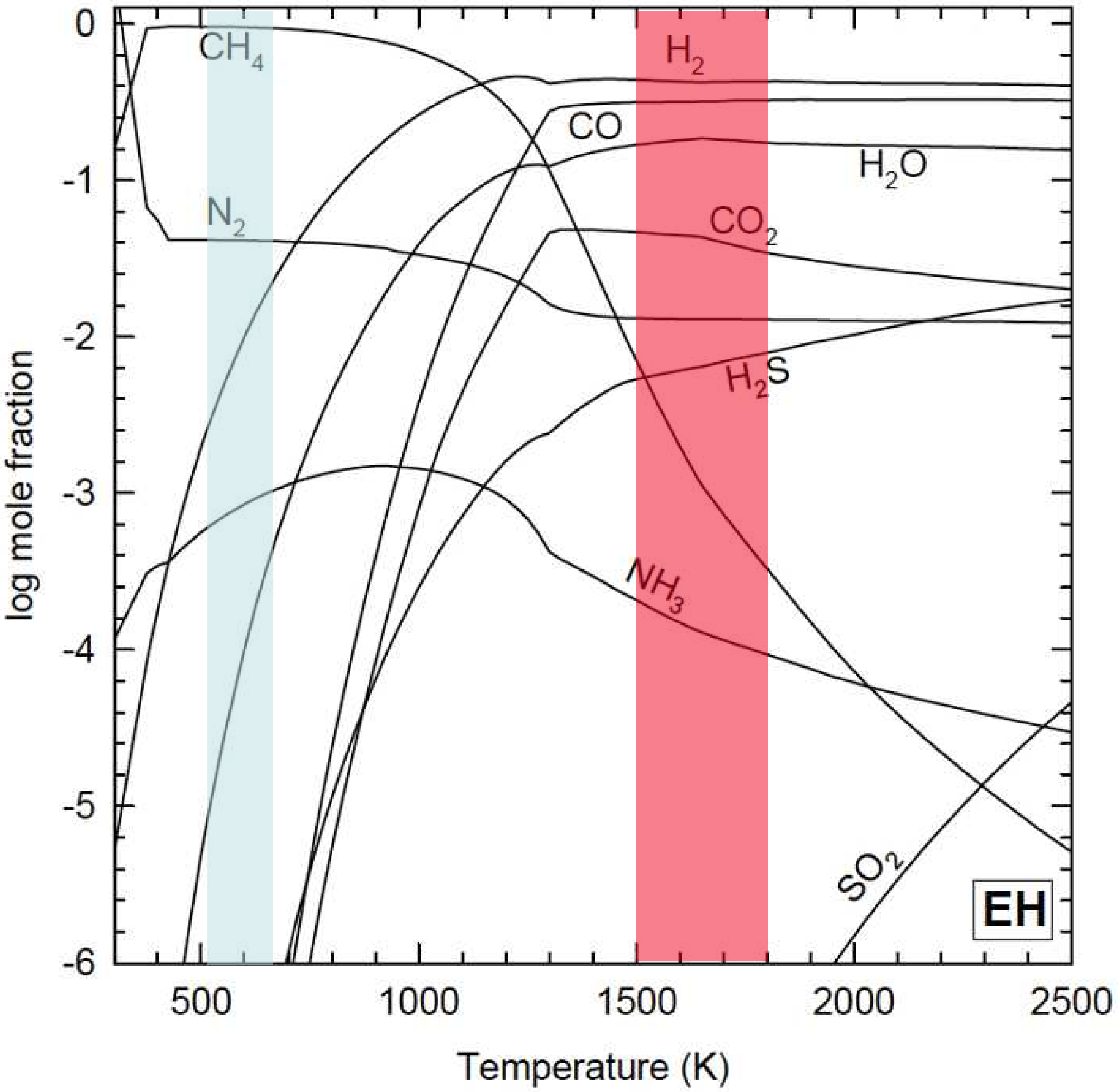
100 bars



Schaefer and
Fegley 2009

Carbonaceous
Chondrites

More oxidized



Schaefer and Fegley 2009

Enstatite Chondrites

More reduced

Life on CO

Carboxydotrophy:

$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$

e.g. Rhodospirillum rubrum

Methanogenesis:

$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$

e.g. Methanobacterium thermoautotrophicum

They eat water!

Oxygen

From each according to their ability
To each according to their need

or

microbes control the means of production

A general trend: oxidation of planetary surfaces/atmospheres

Mars - O_2 atmosphere, strongly oxidized surface:
  $MgSO_4$, $KClO_4$, CaO_2, H_2O_2…
  Oxidation is from photolysis. But photolysis does not explain net oxidation of surface.
  What is needed is
    H_2O -> O (crust, atm) + 2H (space)

Meteorite Parent Bodies (asteroids) are more oxidized than the solar nebula.
  Also requires H escape

A general trend: oxidation of planetary surfaces/atmospheres

Earth - O_2 atmosphere.

O_2 is from photosynthesis. But photosynthesis does not explain net oxidation of crust.

Either:

CO_2 -> O_2 (atm) + C (mantle)

or

$2H_2O$ -> O_2 (atm) + 4H (space)

Loss of H to space is irreversible

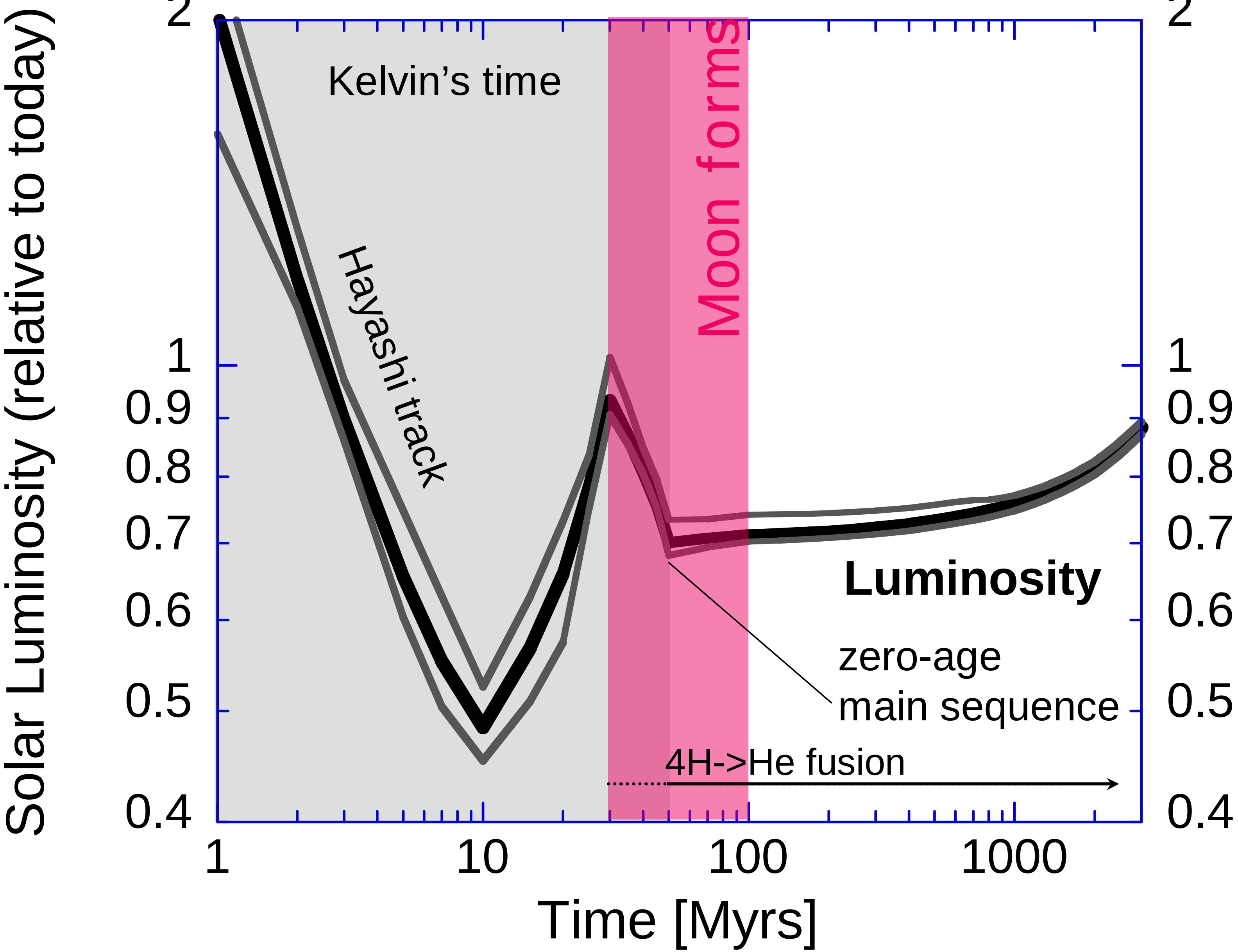
A general trend: oxidation of planetary surfaces/atmospheres

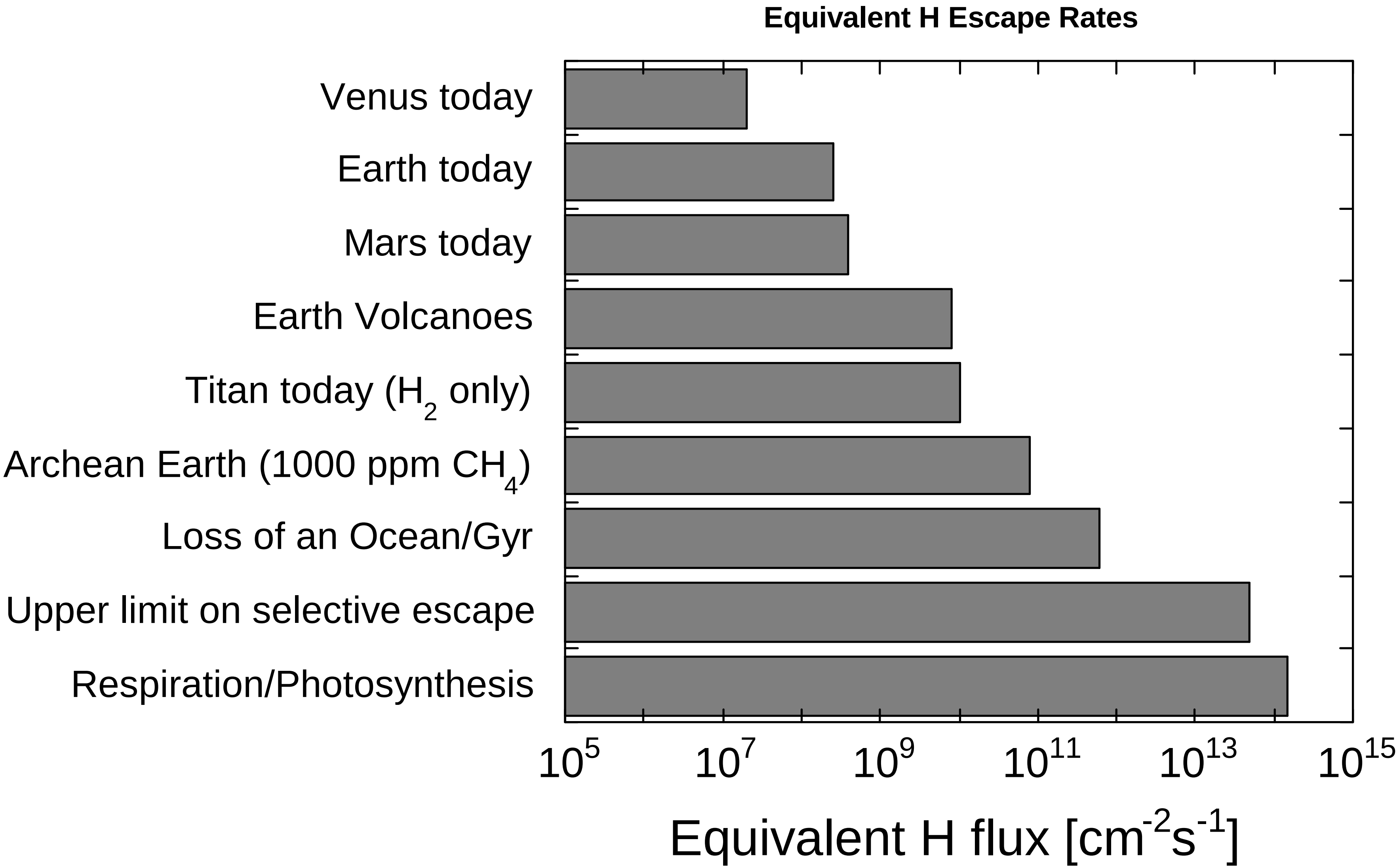
Titan: H_2 escape is observed.
C_2H_2 etc are more oxidized than CH_4

Europa, Ganymede, Callisto all have very thin O_2 atmospheres. Europa is most evolved and apparently more oxidized. H escape.

Venus? High D/H, very little H_2O. Where did O go? If very early in solar system, O can escape. Otherwise, O must be in crust/mantle

Luminosity Evolution of the Young Sun




Equivalent H Escape Rates
Venus today
Earth today
Mars today
Earth Volcanoes
Titan today (H_2 only)
Archean Earth (1000 ppm CH_4)
Loss of an Ocean/Gyr
Upper limit on selective escape
Respiration/Photosynthesis
10^5
10^7
10^9
10^{11}
10^{13}
10^{15}
Equivalent H flux [$cm^{-2}s^{-1}$]

Current H escape fluxes - Earth

ϕ_{lim} (H) ~ 2.5×10^{8} $cm^{-2}s^{-1}$

diffusion-limited (ΣH = 12ppm in stratosphere)

~ 1 m of lost H_2O per Gyr

~ 0.1 bar O_2 per Gyr

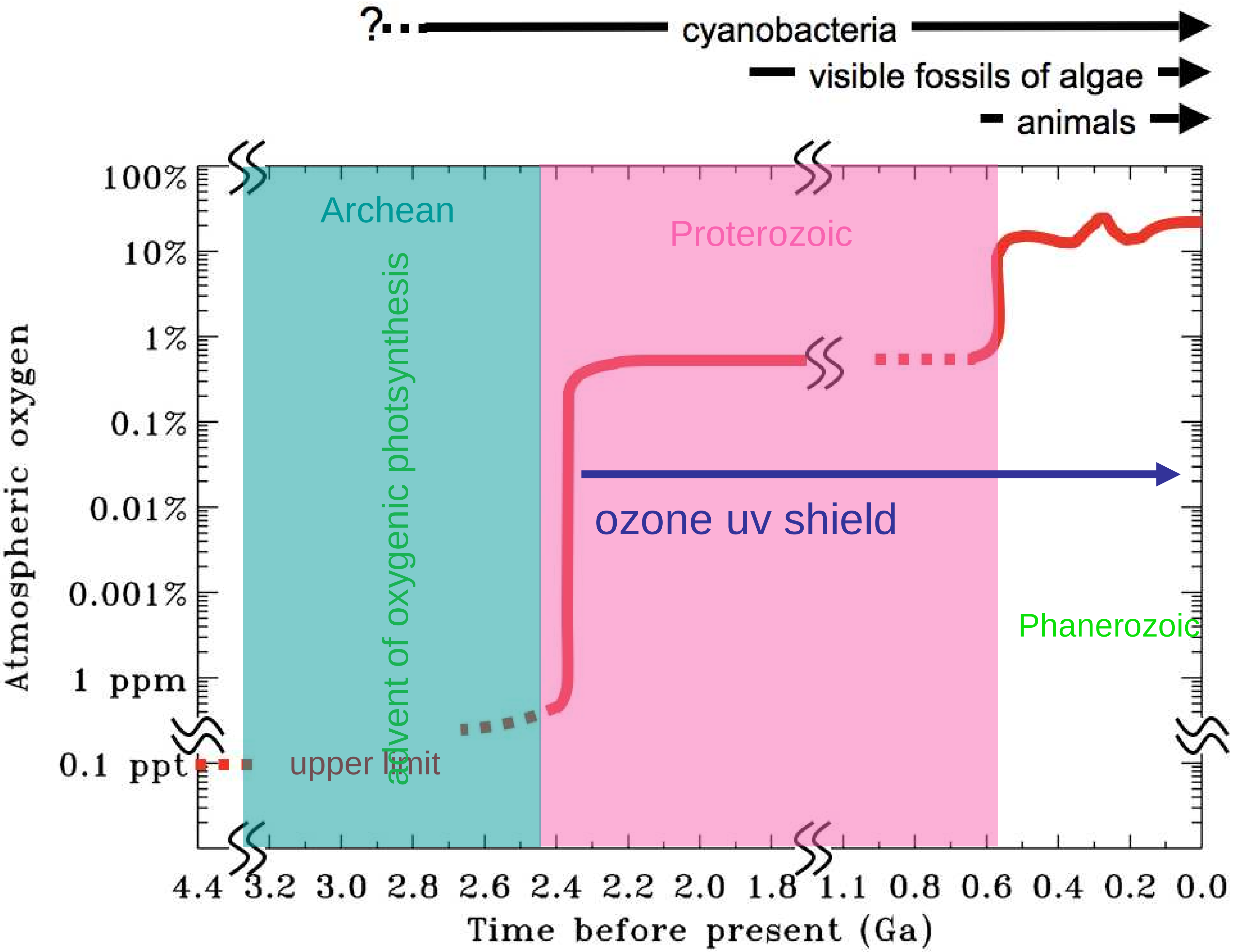
if 1000 ppm CH_4 greenhouse in late Archean,

ϕ_{lim} (H) ~ 8×10^{10} $cm^{-2}s^{-1}$

~ 400 m of lost H_2O per Gyr

~ 40 bars of O_2 generated per Gyr

Behold the Power of Escape!


?
cyanobacteria
visible fossils of algae
animals
Archean
Proterozoic
Phanerozoic
advent of oxygenic photsynthesis
ozone uv shield
upper limit
100%
10%
1%
0.1%
0.01%
0.001%
1 ppm
0.1 ppt
Atmospheric oxygen
4.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.1
0.8
0.6
0.4
0.2
0.0
Time before present (Ga)

Classic Indicators of a rise of free Oxygen ca. 2.3 Ga:

- first appearance of rusty soils:
  - change from greybeds to redbeds
  - Ce^{+4} appears in paleosols
  - siderite ($FeCO_3$) disappears from paleosols
- disappearance of abundant detrital reduced minerals:
  - siderite, pyrite, uraninite (insoluble U^{+4})
- delayed disappearance of BIFs

Newer, better Indicator of a rise of O_2 2.46 Ga:

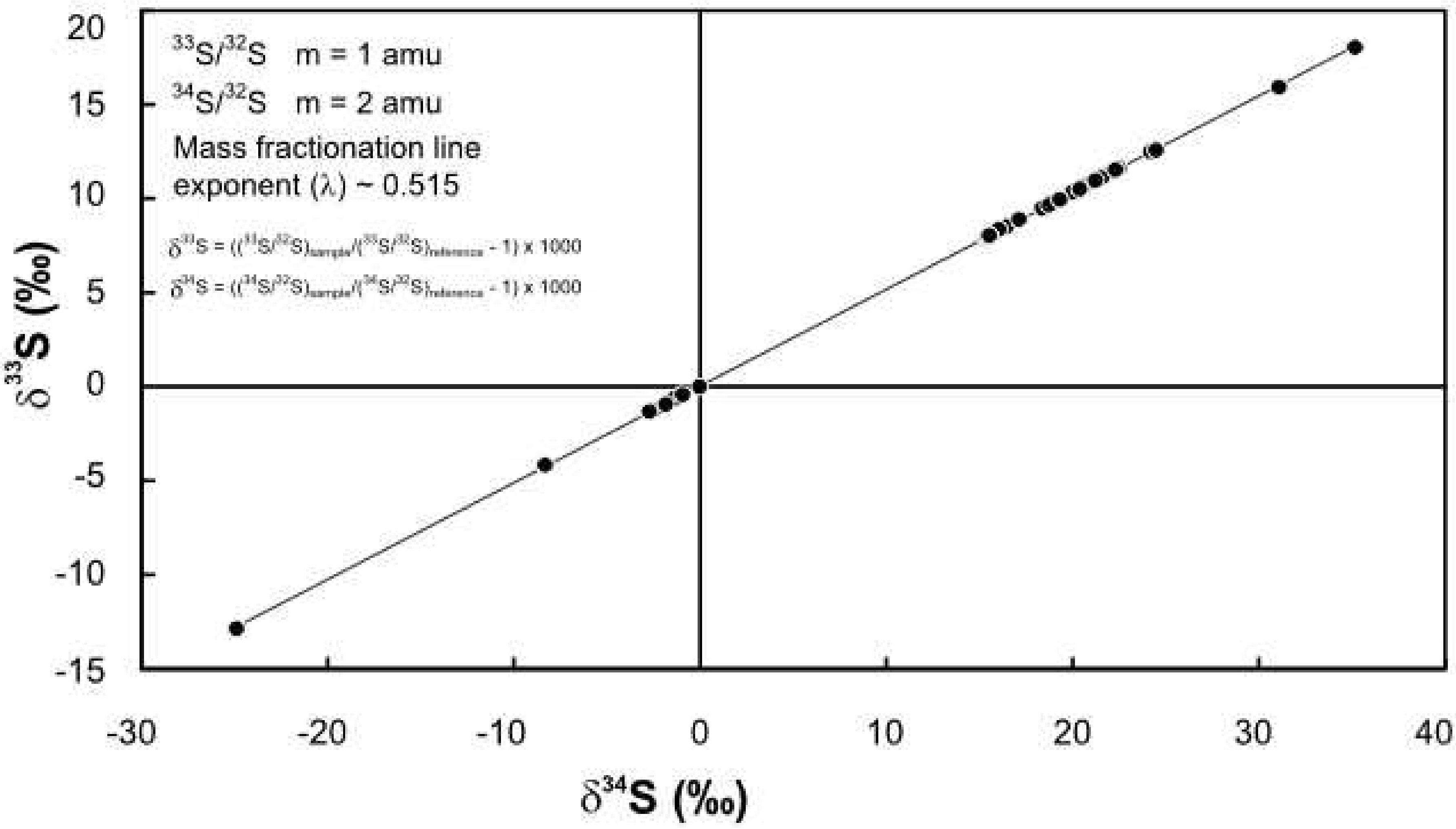
- change in sulfur isotope fractionation at 2.46 Ga

There are 4 stable isotopes of sulfur: 32, 33, 34, 36.

Most reactions fractionate in proportion to mass.
Often the heavy isotope accumulates in the strongest bond.

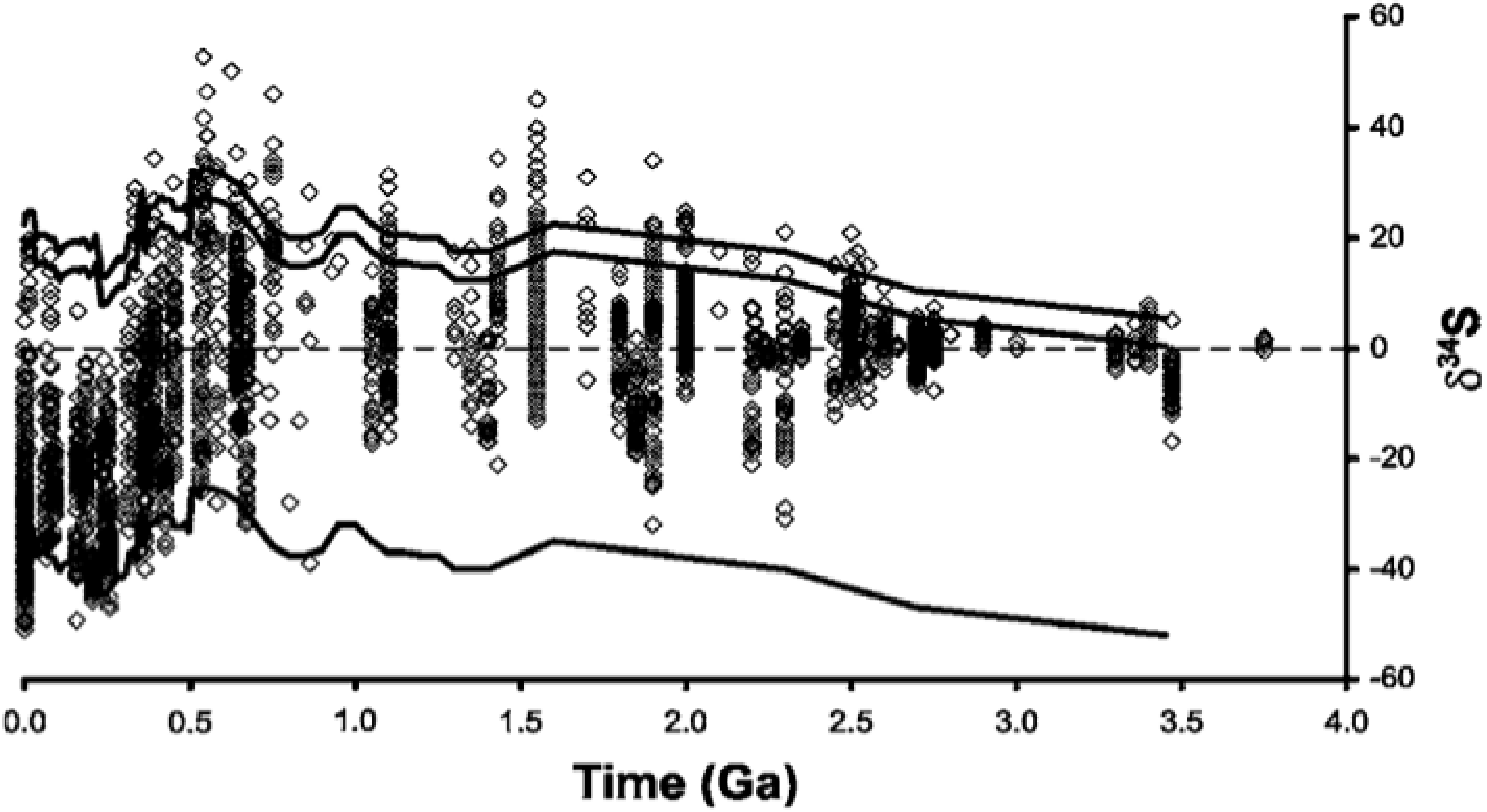
E.g., if for some reason an organism prefers ^{33}S to ^{32}S,
it will prefer ^{34}S twice as much.

$\delta^{34}S$ ("little delta 34S") measures the preference.



^{33}S vs. δ^{34}S for terrestrial sulfide and sulfate younger than 2.0 Ga [7–9,26,50]. The array defin
ith $^{33}\lambda = 0.515$. This terrestrial mass fractionation line does not reflect a single fractionation pr
e effects of the various mass-dependent fractionation processes that have operated over Earth's hi
ects the mass differences among ^{32}S, ^{33}S, and ^{34}S and arises because the drive for mass-dependent
alf as strong for δ^{33}S variations as it is for δ^{34}S variations.

Mass Dependent Sulfur Fractionation



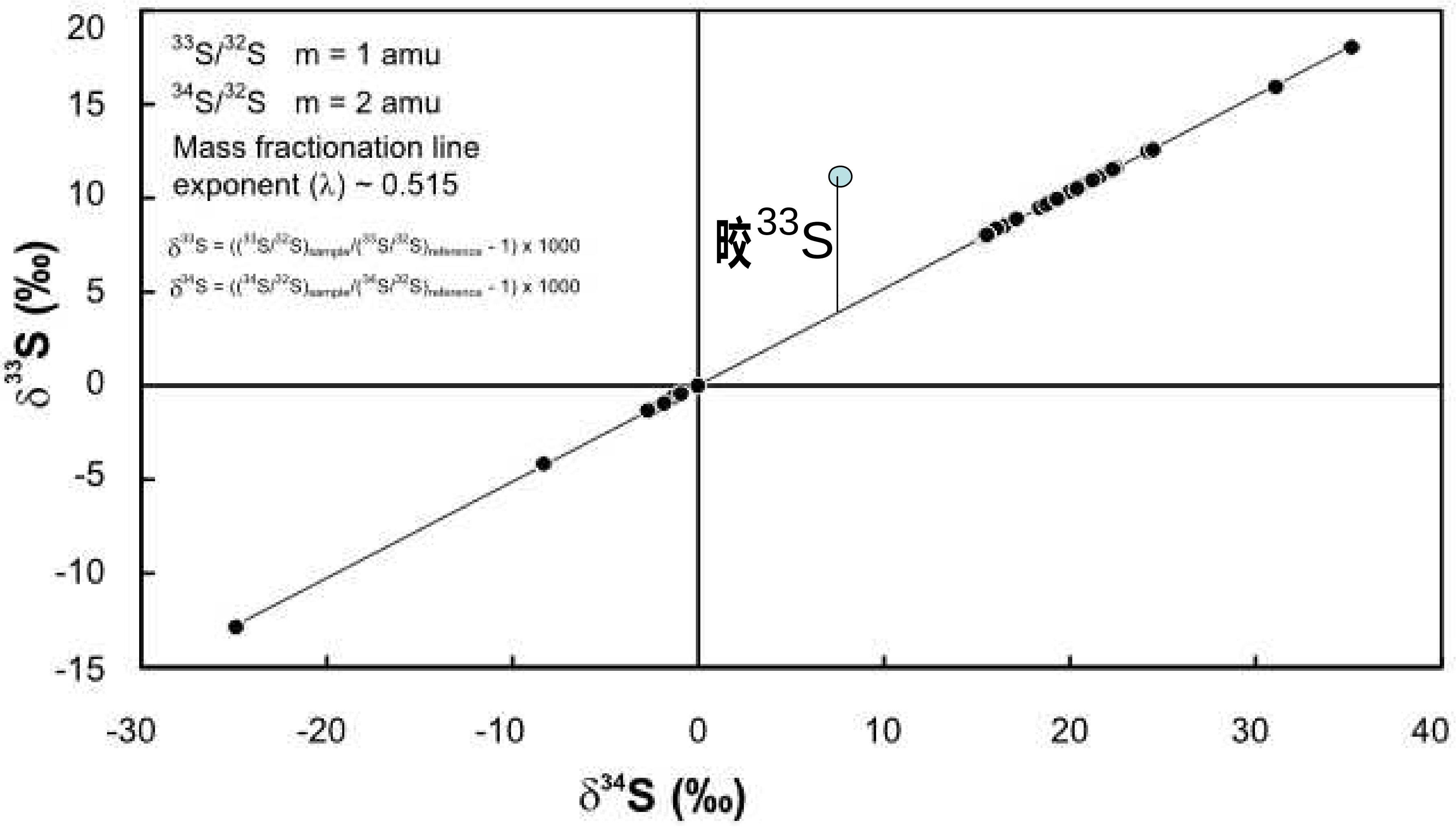
The widening envelope of sulfur fractionation implies that sulfate becomes more available. Sulfate reducers outcompete methanogens, and sulfate can be used eat methane.

Some atmospheric photochemical processes do not fractionate according to mass.
This is called “mass-independent fractionation”
even though the fractionations are a function of mass.
For sulfur these occur when there is no O_2 or O_3 in air

Δ^{33}S (“Big Delta 33S”) is the deviation of δ^{33}S (little delta 33S) from fractionation in proportion to mass.

Δ^{36}S (“Big Delta 36S”) is the equivalent for ^{36}S.

J. Farquhar, B.A. Wing / Earth and Planetary Science Letters 213 (2003) 1–13



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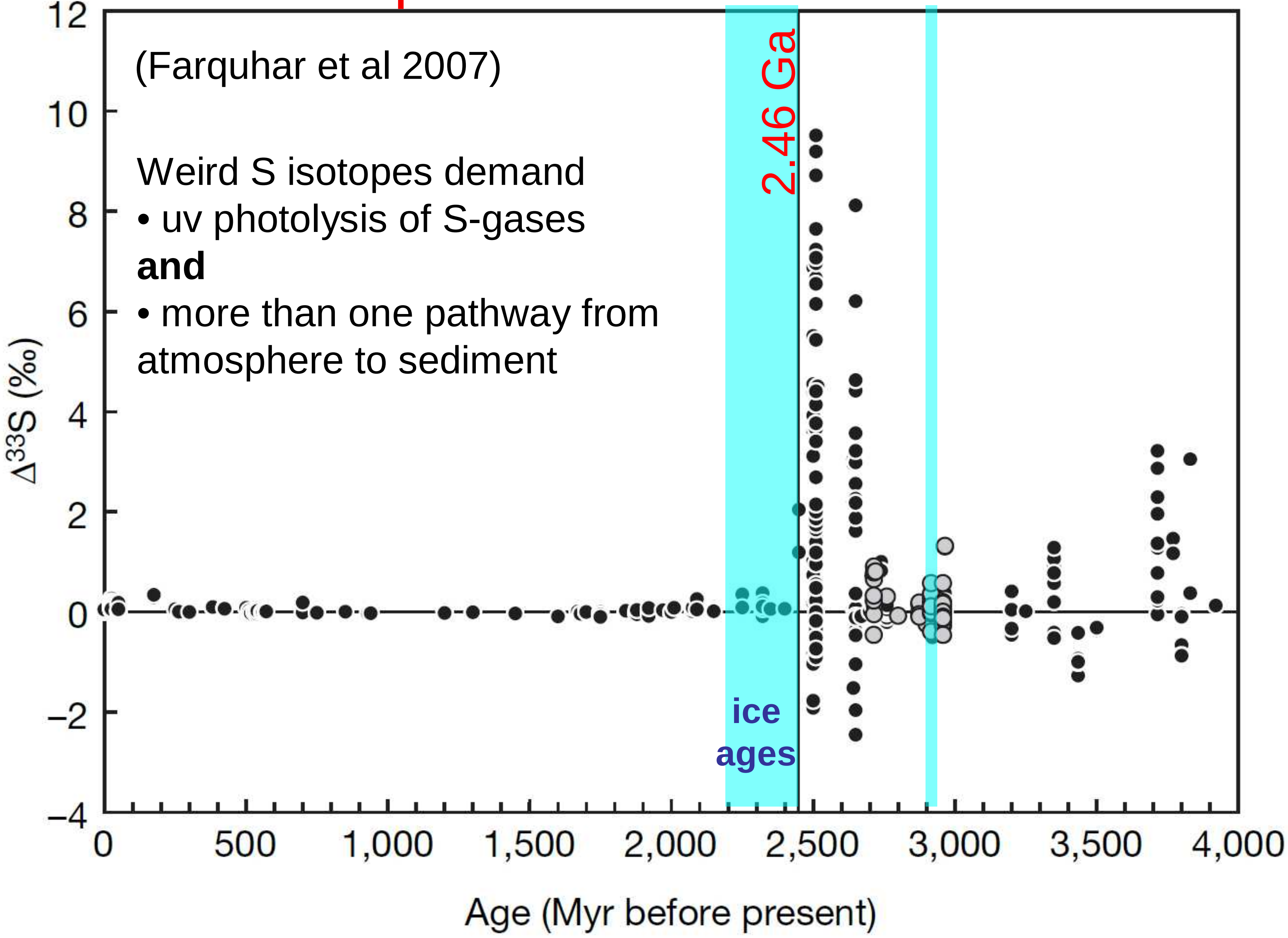


(Farquhar et al 2007)

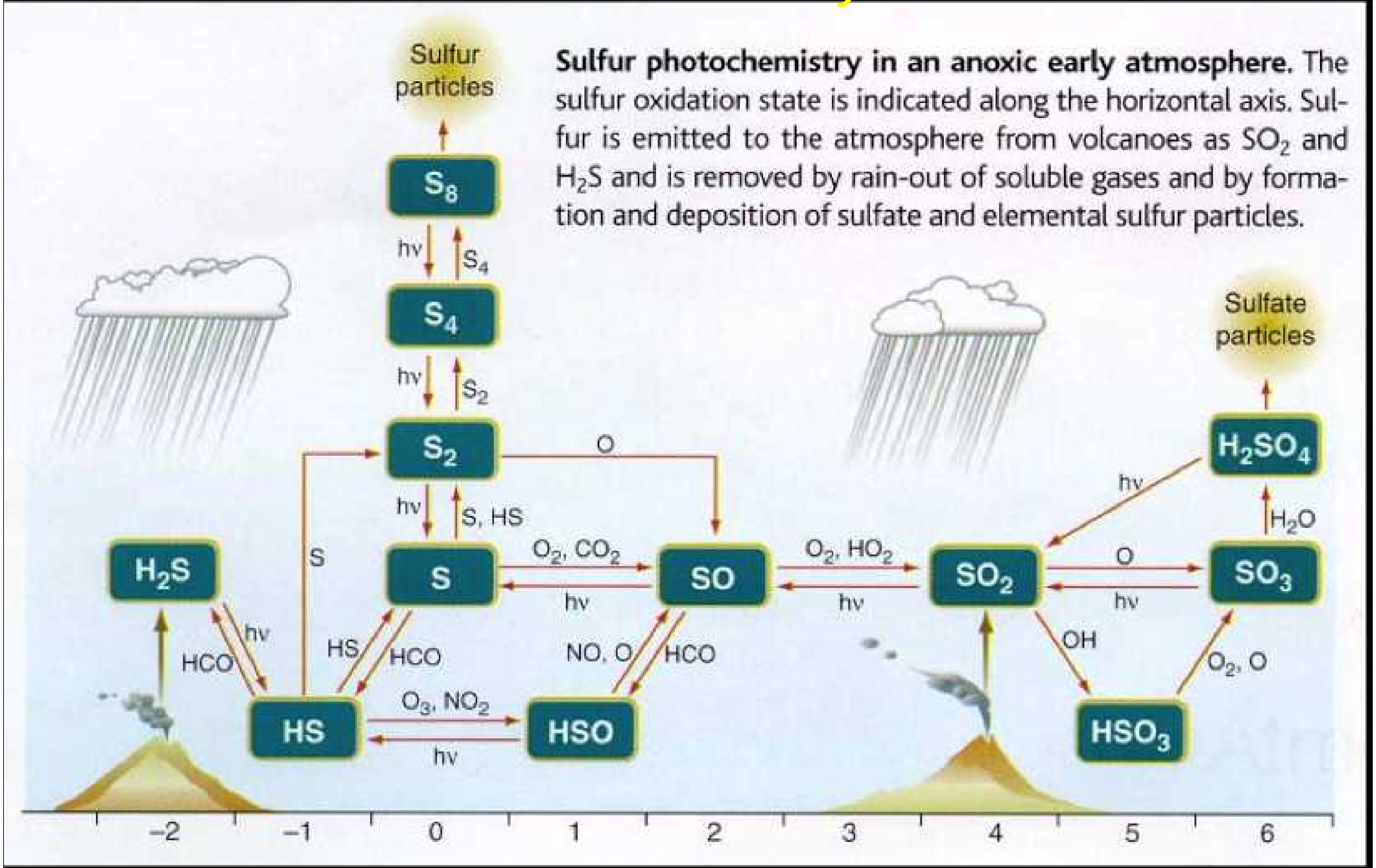
Weird S isotopes demand

- uv photolysis of S-gases

and

- more than one pathway from atmosphere to sediment

Archean Sulfur Cycle



Sulfur photochemistry in an anoxic early atmosphere. The sulfur oxidation state is indicated along the horizontal axis. Sulfur is emitted to the atmosphere from volcanoes as SO_2 and H_2S and is removed by rain-out of soluble gases and by formation and deposition of sulfate and elemental sulfur particles.

Kasting, *Science* (2001) Redrawn from Kasting et al., *OLEB* (1989)

photochemical modeling assumptions

1-D time-dependent integrations to steady-state

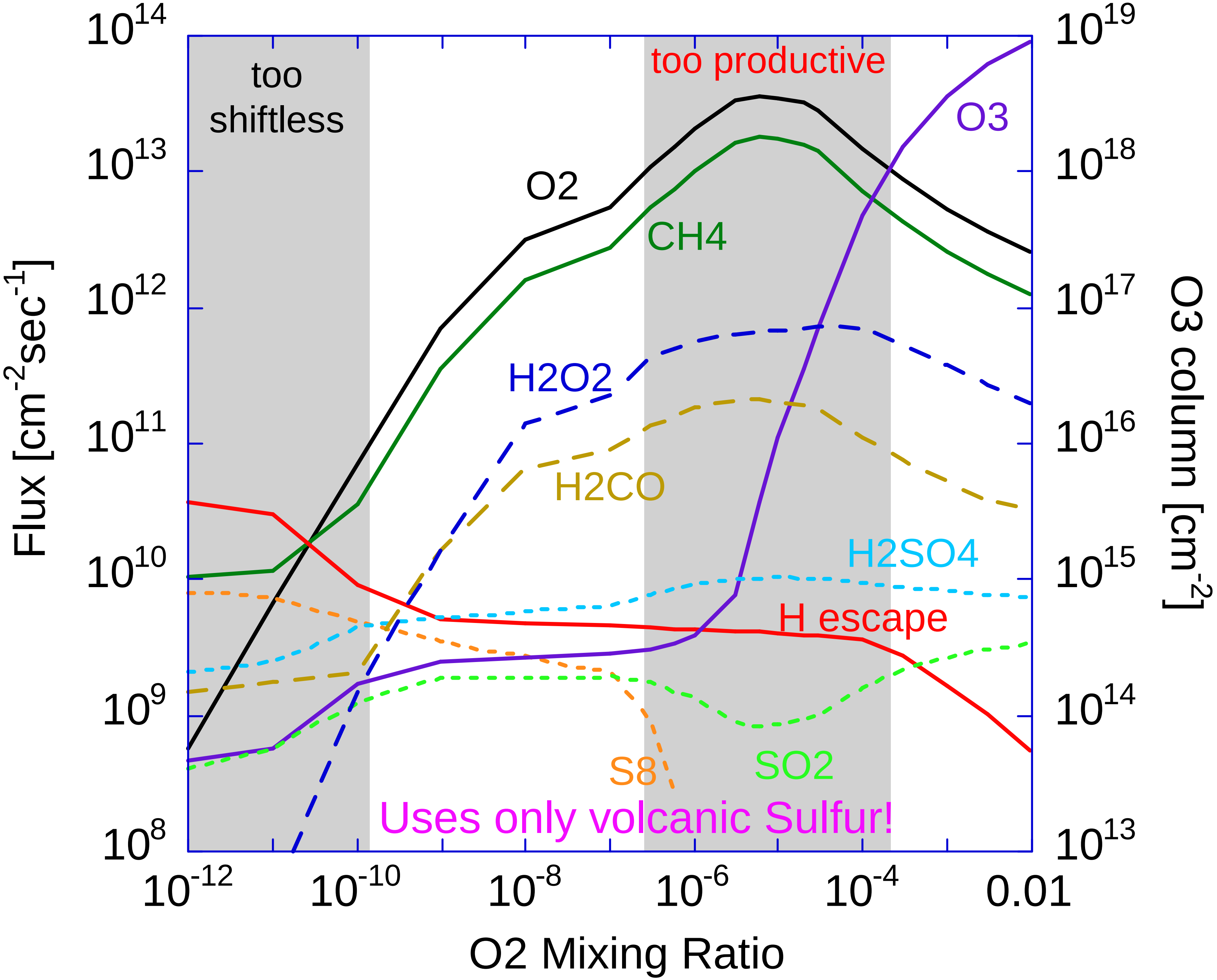
hydrogen escape by diffusion-limited flux

SO_2, H_2, CO from volcanic sources

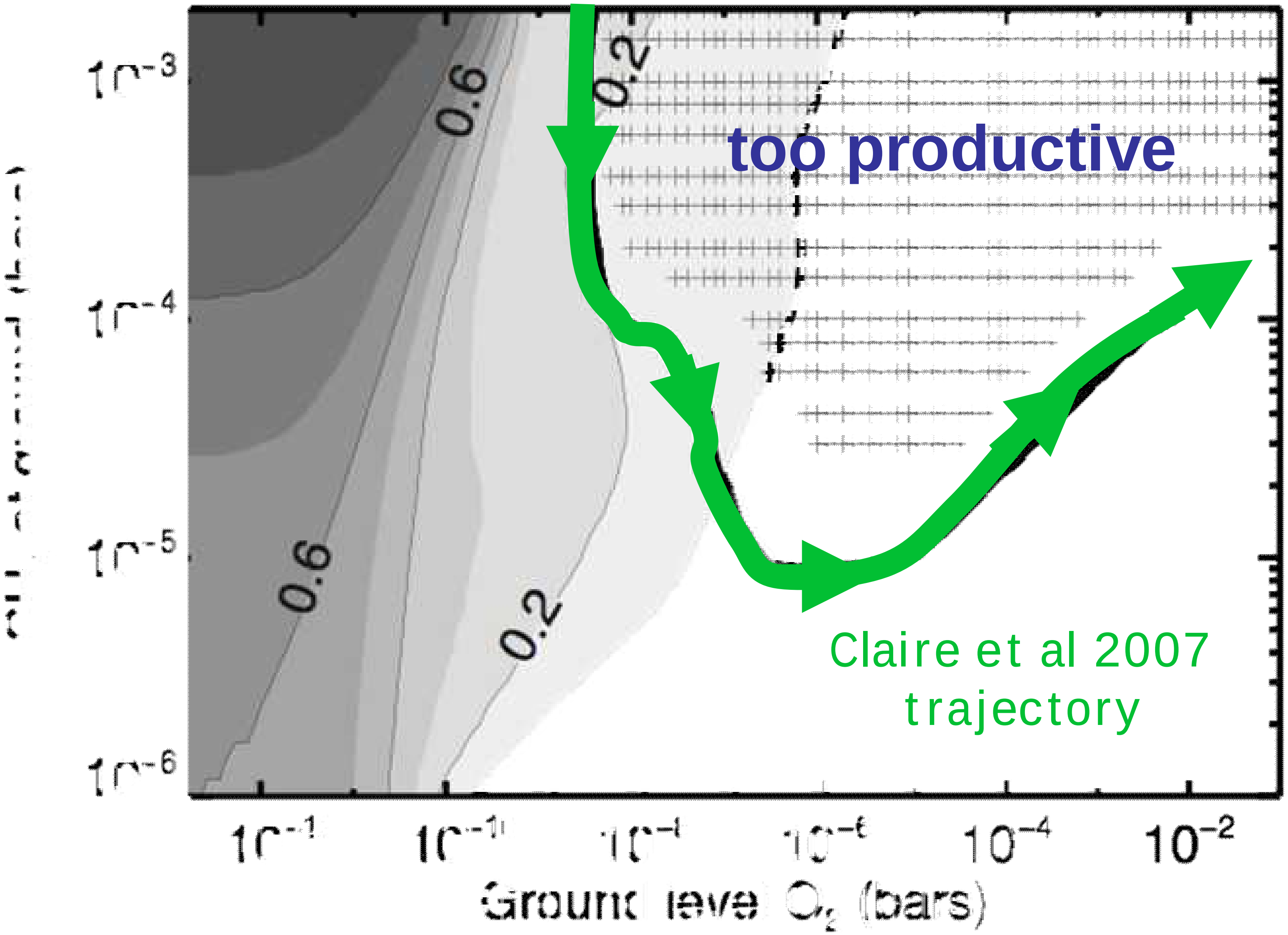
Either
    O_2 and CH_4 held at constant mixing ratios
or
    O_2 and CH_4 are supplied by sources at the surface

S_8 and H_2SO_4 can form particles that fall to the surface
SO_2, H_2SO_4, HCHO, H_2O_2 etc. can rain out

N_2, CO_2, and tropospheric H_2O are held constant


too shiftless
too productive
O2
CH4
O3
H2O2
H2CO
H2SO4
H escape
S8
SO2
Uses only volcanic Sulfur!
Flux [cm^{-2}sec^{-1}]
O3 column [cm^{-2}]
O2 Mixing Ratio
10^{14}
10^{13}
10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
10^{14}
10^{13}
10^{-12}
10^{-10}
10^{-8}
10^{-6}
10^{-4}
0.01

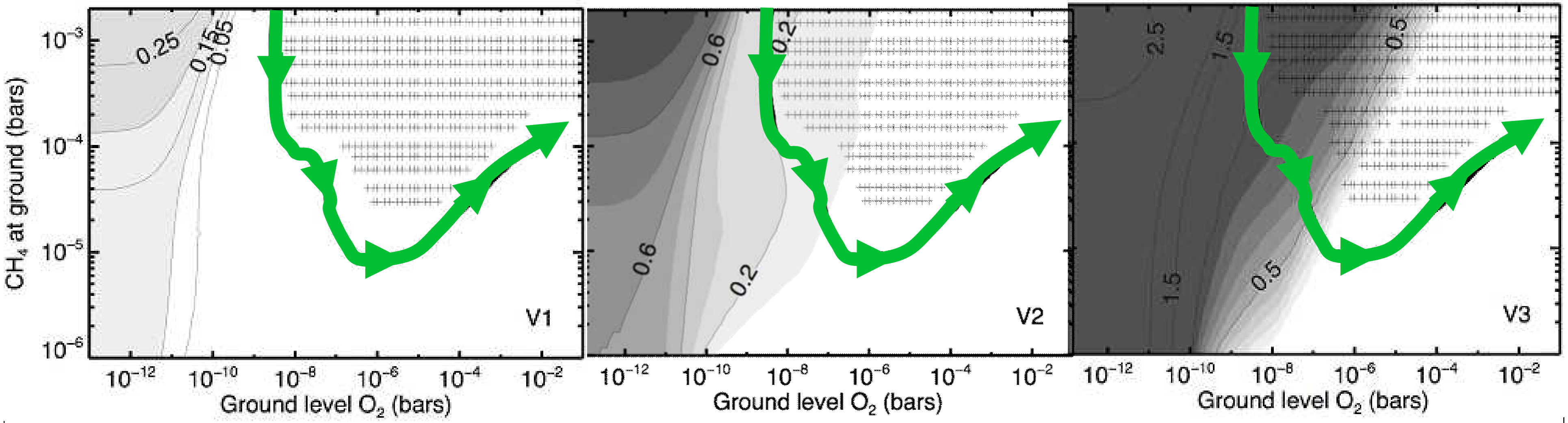
Fraction of volcanic SO_2 that falls out as elemental sulfur



too productive

Claire et al 2007
trajectory

Fraction of volcanic SO_2 that falls out as elemental sulfur



Weak SO_2 Source (low estimate for modern Volcanoes)

Strong SO_2 Source (high estimate for modern Volcanoes)

Archean SO_2 Source (Exuberant Volcanoes)

Big SO_2 fluxes into the atmosphere produce big S_8 fluxes out of the atmosphere.
All cases produce big H_2SO_4 fluxes

sulfate reduction outcompetes methanogenesis

autotrophy

$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

$4H_2 + SO_4^{-2} + H^+ \rightarrow 4H_2O + HS^-$

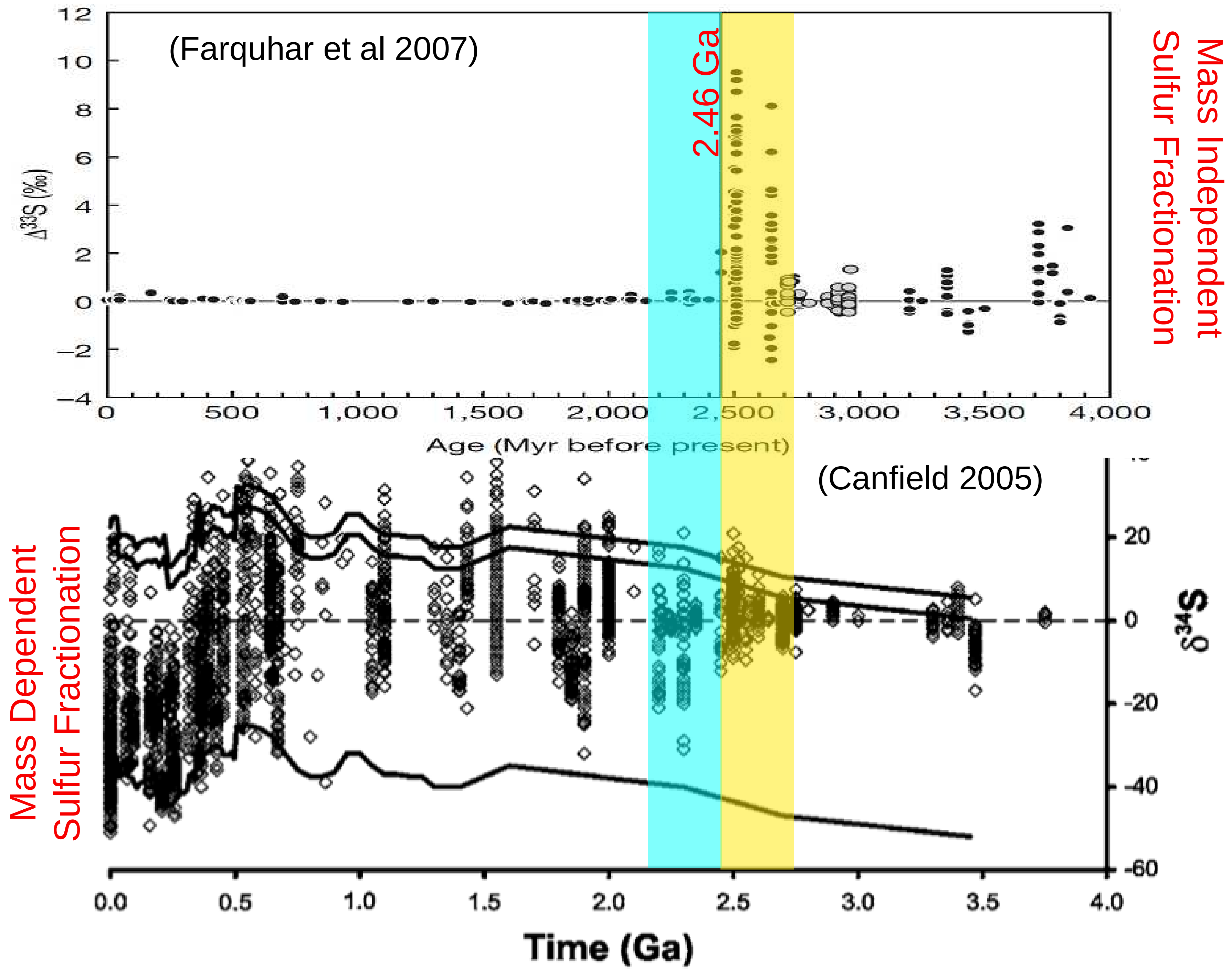
heterotrophy

$CH_3COOH \rightarrow CH_4 + CO_2$

$CH_3COO^- + SO_4^{-2} \rightarrow 2HCO_3^- + HS^-$

direct action (theory)

$CH_4 + SO_4^{-2} \rightarrow HCO_3^- + H_2O + HS^-$



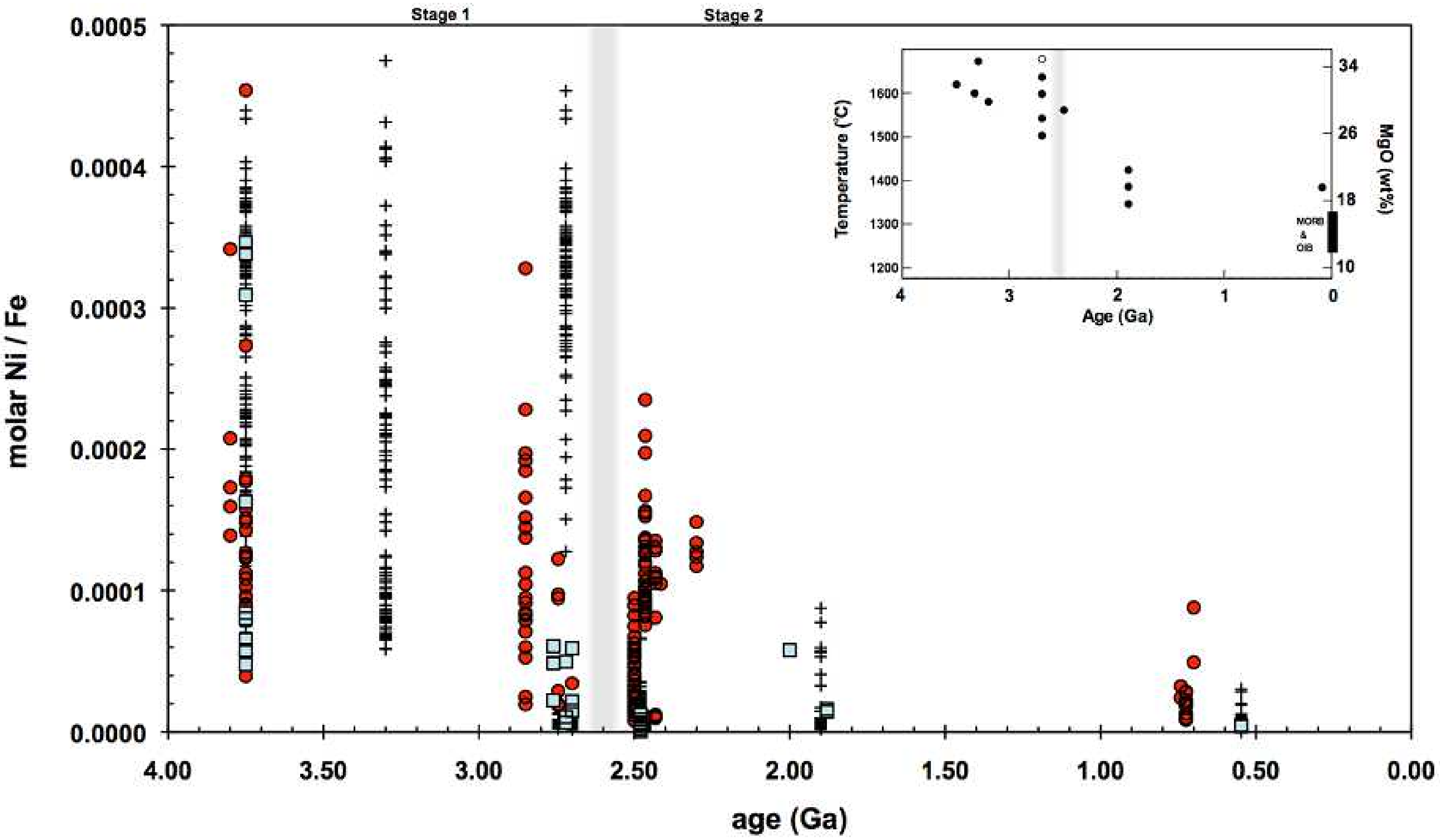
(Farquhar et al 2007)

2.46 Ga

Mass Independent Sulfur Fractionation

(Canfield 2005)

Mass Dependent Sulfur Fractionation



Methanogens use Ni to make methane from CO, CO_2.
Konhauser et al 2009 show that seawater Ni decreased monotonically and relate this to mantle cooling. Less Ni, less methane formation.

Atmospheric chemistry: CH_4 or O_2 wins

CH_4 production = reaction w/ O_2 + photolysis loss

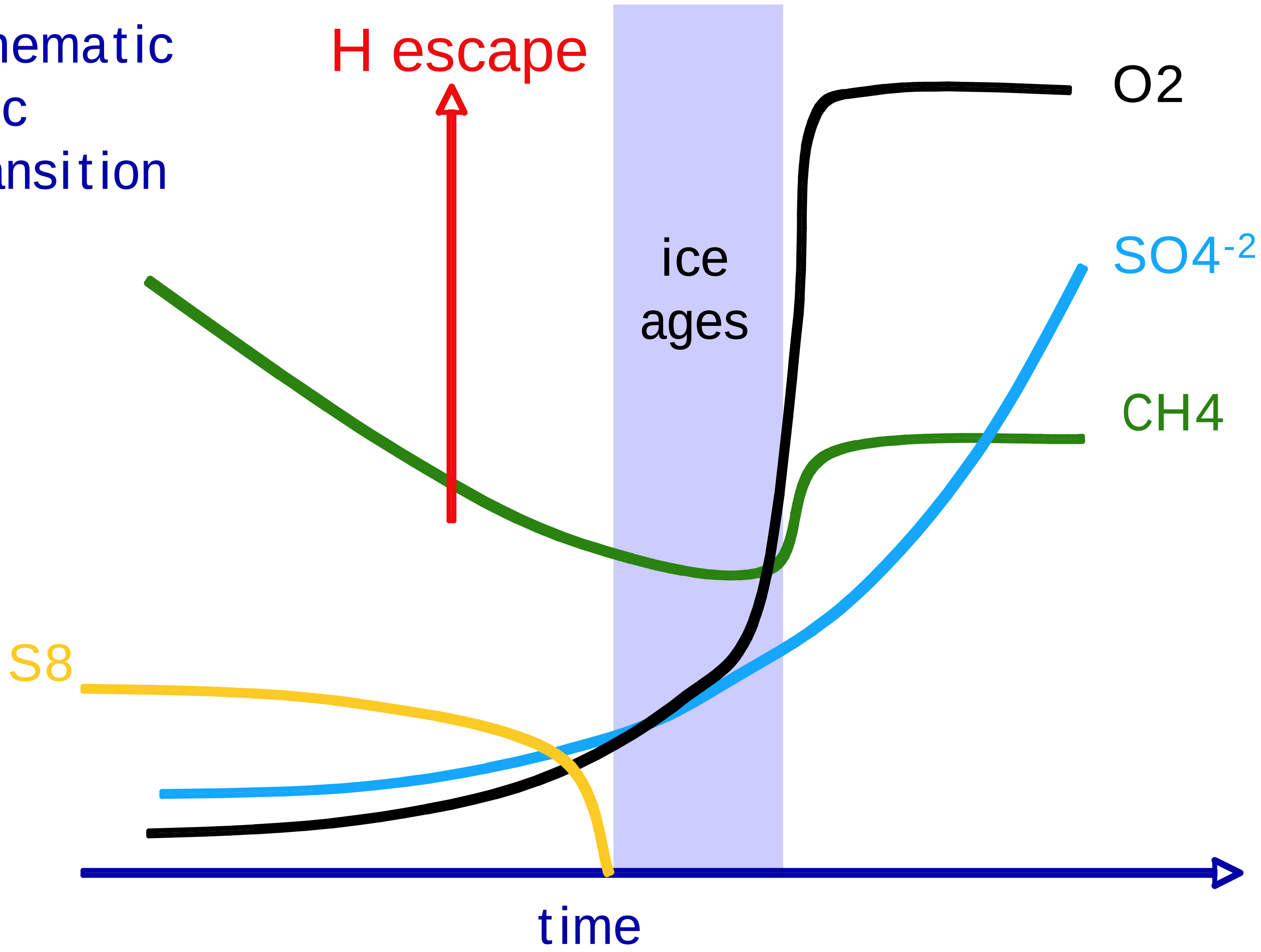
O_2 production = reaction w/ CH_4 + reaction w/ rocks

With oxygenic photosynthesis…

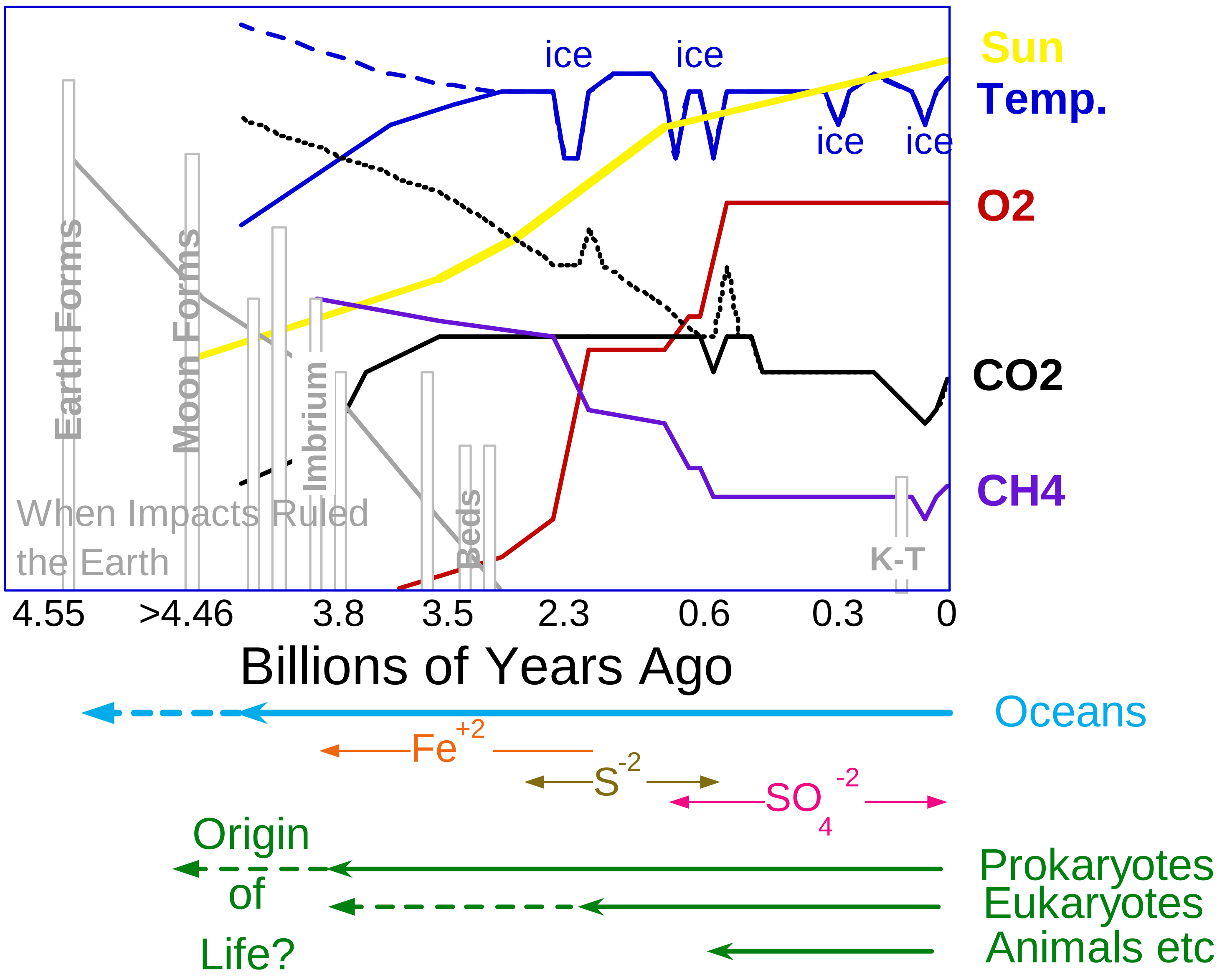
1. more growth = more death = more CH_4
2. CH_4 is less reactive with rocks than O_2
3. The first consequence is an Age of Methane

Eventually (i.e. ~500 Myr) the easily oxidized rocks get oxidized and O_2 becomes more stable

schematic oxic transition

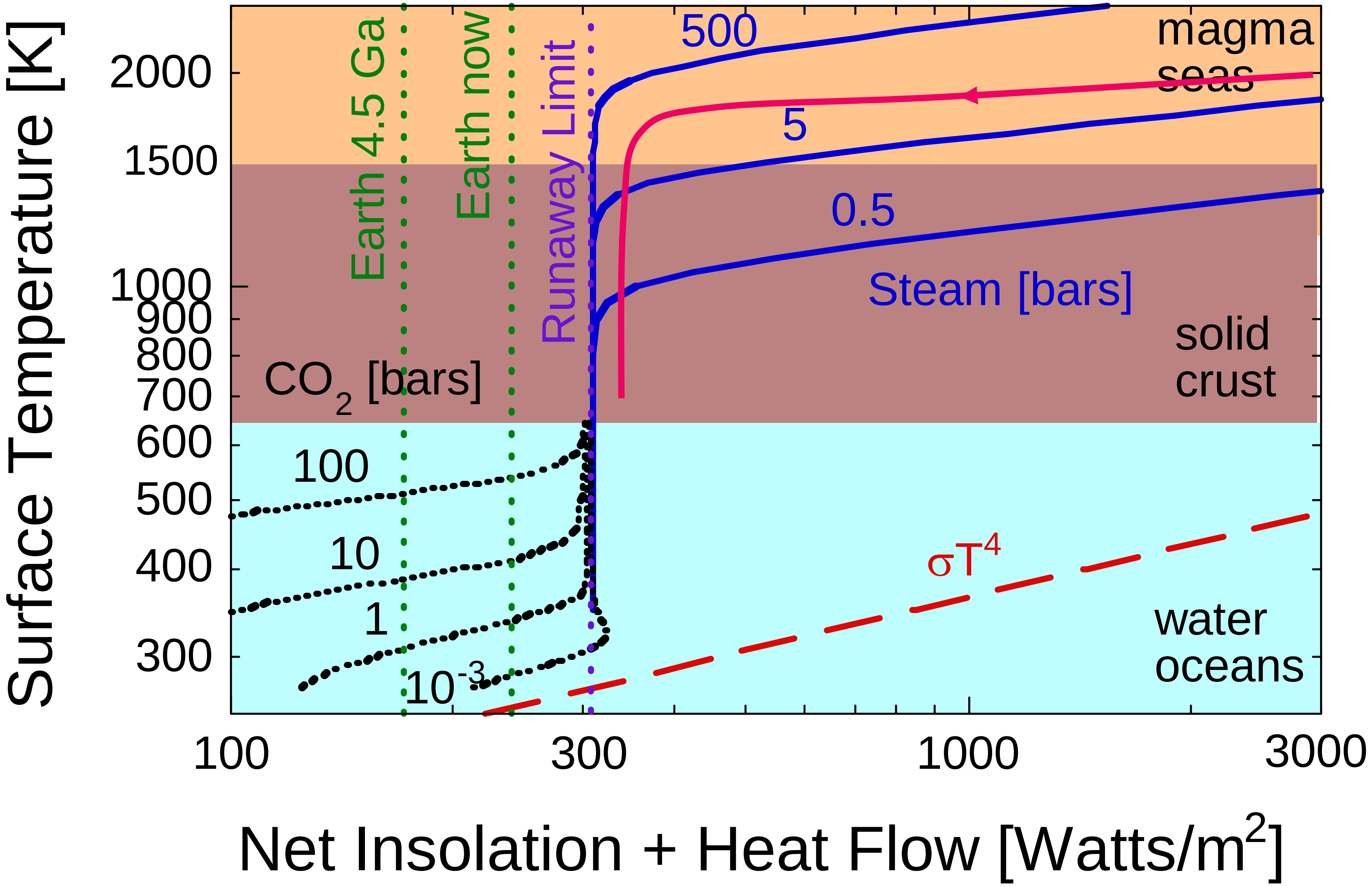


Everything All at Once Together

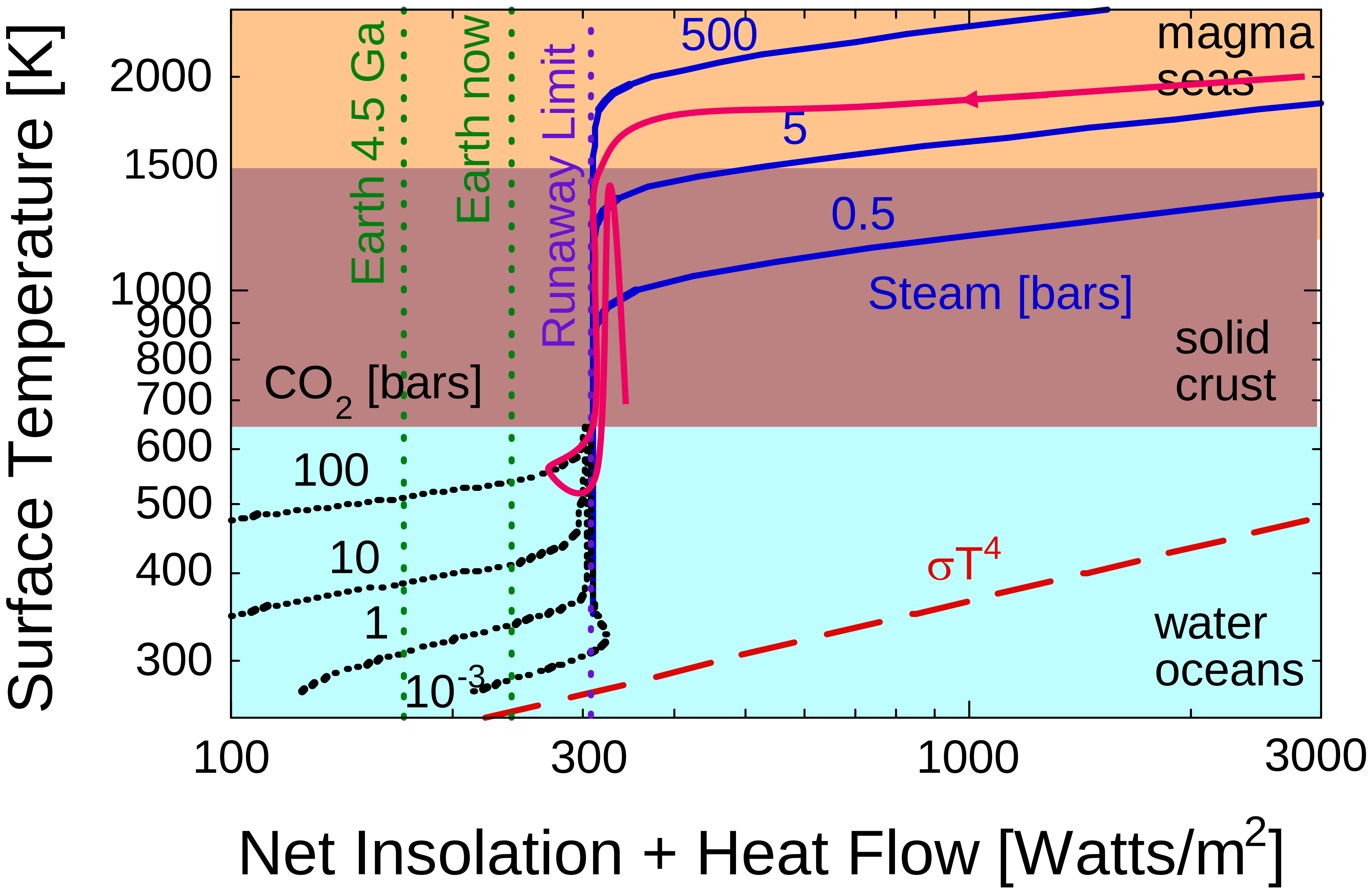


Venus

Venus - dry evolution after a giant impact



Venus - wet evolution after a giant impact



Mars

Mars Atmospheric Photochemistry

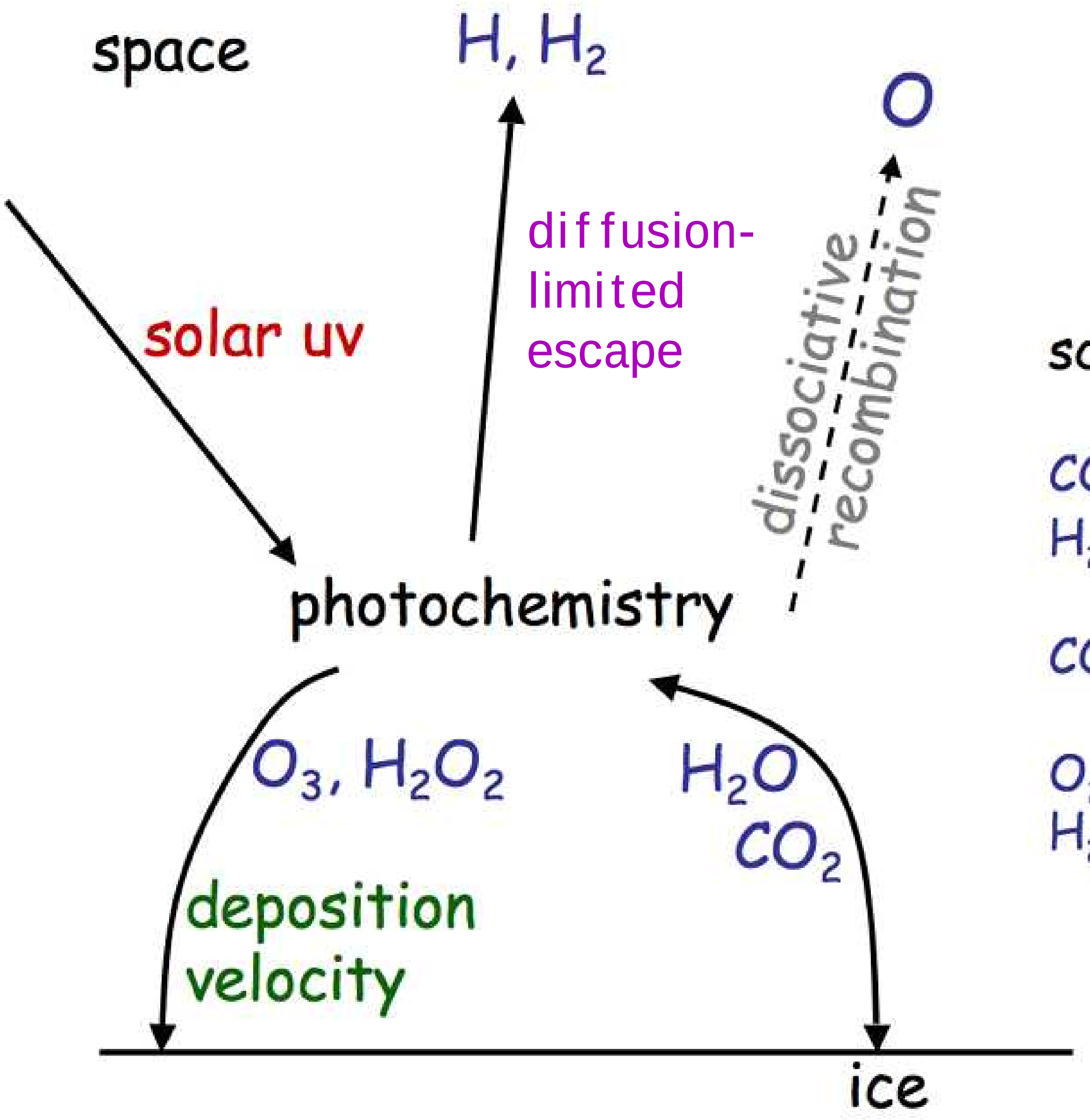
Classic problem: stability of CO_2

Solution: H_2O photolysis produces OH radical that destroys CO, remakes CO_2
(McElroy, Hunten, Donahue ca 1972)

Classic problem: hydrogen escape

Neat idea: nonthermal O escape, such that one O escapes for every 2H:
$O_2^+ + e \rightarrow O + O +$ lots of kinetic energy
"dissociative recombination" *(McElroy 1972)*

Our Model



schematic photochemistry:

CO_2 + uv → $\frac{1}{2}O_2$ + CO
H_2O + uv → $\frac{1}{2}O_2$ + H_2 (to space)

$CO + H_2O \rightarrow CO_2 + H_2$ (to space)

$O_2 + O \rightarrow O_3$ → to surface
$H_2O + \frac{1}{2}O_2 \rightarrow H_2O_2$ → to surface

Mars Atmospheric Photochemistry

Revisionist problem I: stability of CO.

Why is there so **much** CO?

Solution?

- increase vertical mixing (1970s)
- non-gas-phase chemistry (1990s)
- change the chemical reactions (1990s)
- expect it to go away with 3D models (2000s)

or • invoke very dry “stratosphere”

Mars Atmospheric Photochemistry

Neoclassic problem I: O doesn’t escape very fast

What happens to H_2O when H escapes?

Solution?

- O_2 oxidizes soils (1970s, just before Viking)
- H_2O_2, O_3 oxidize soils (just after Viking)
- ignore the problem (1980s and 1990s)
- or non-gas-phase chemistry (1990s and 2000s)

Today Now: *Mars atmosphere is oxidized*

$f(O_2)$ = 1200-2000 ppm
$f(CO)$ = 800 ppm
$f(H_2)$ = 17 ppm

net oxidation vs CO_2 and H_2O is

$2*f(O_2) - f(H_2) - f(CO) = 1600 - 3200$ ppm O excess

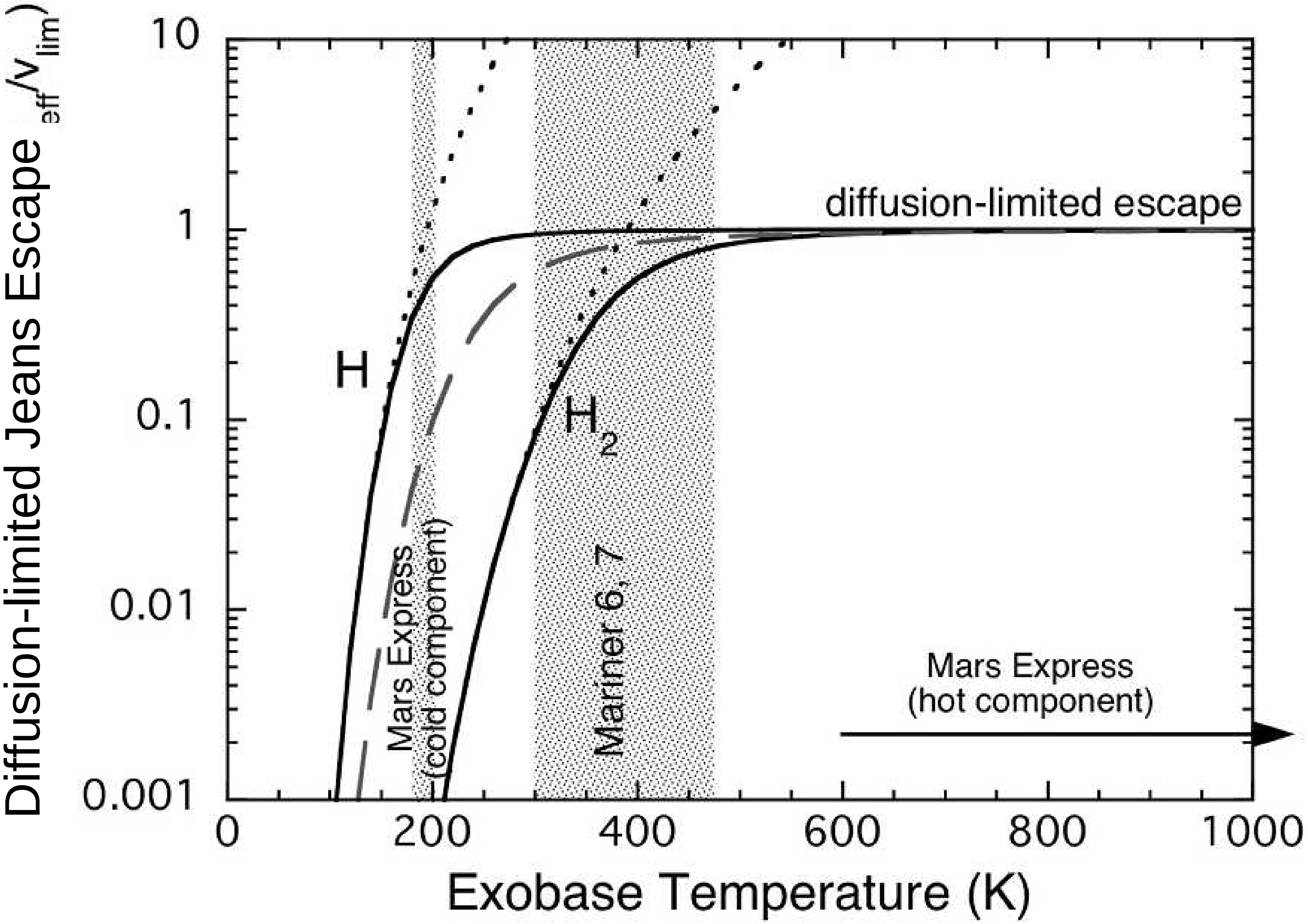
expressed as a pressure, this is 10 - 20 microbars of O

It takes ~10^5 yrs to build up this much excess O by H escape at current rates

Our Model

The lower boundary condition is to set deposition velocities v_{dep} on reactive species.

On Modern Mars, the key gases are H_2O_2 and O_3
Successful models use $v_{\mathrm{dep}} = 0.02$ cm/s
This is 3% of v_{dep} on Earth for these same gases

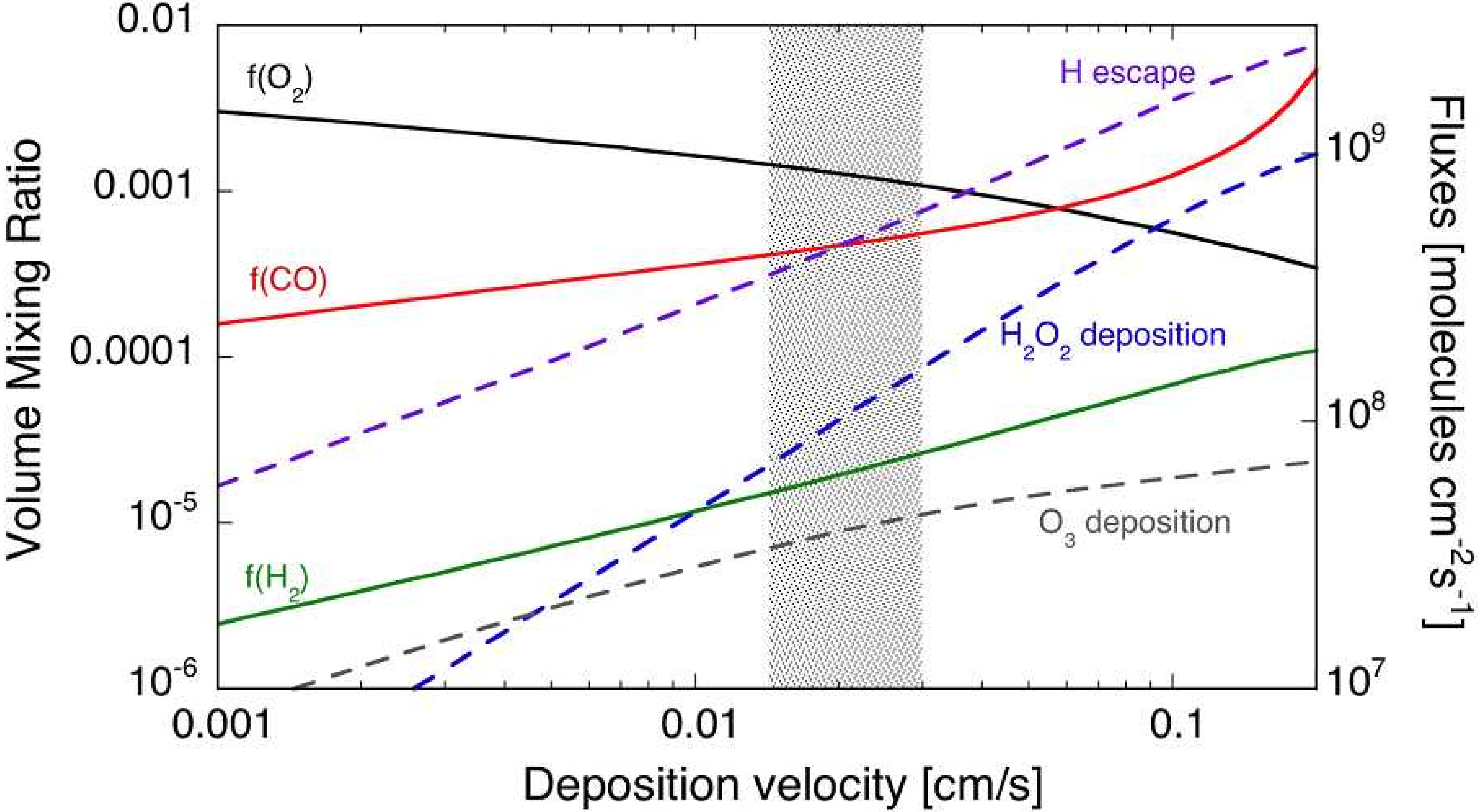

Diffusion-limited Jeans Escape (v_{eff}/v_{lim})
10
1
0.1
0.01
0.001
0
200
400
600
800
1000
Exobase Temperature (K)
diffusion-limited escape
H
H_2
Mars Express (cold component)
Mariner 6, 7
Mars Express (hot component)

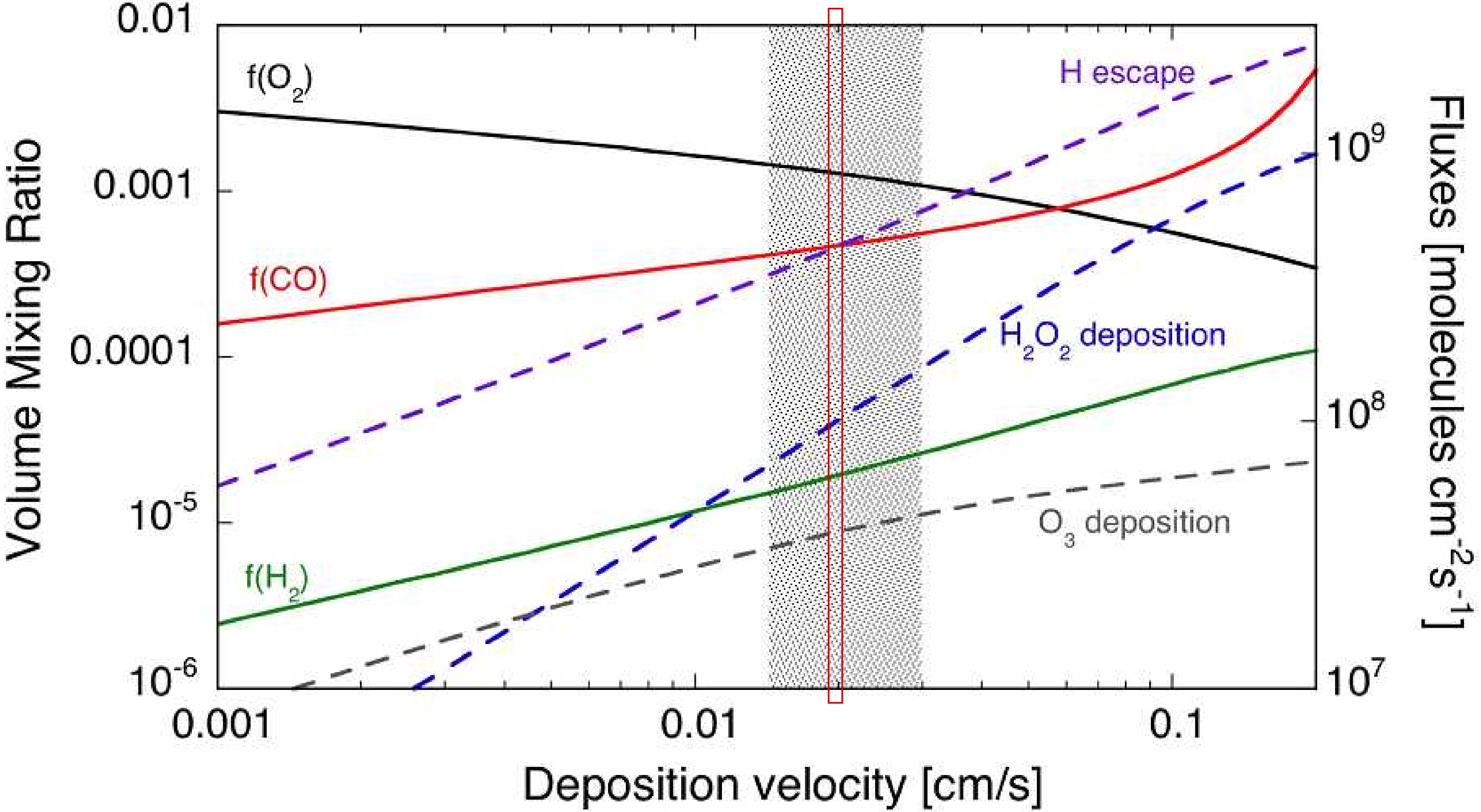
Our Model

The upper boundary condition is to set diffusion limited escape velocities v_{esc} on H and H_2

If H escape from Mars is diffusion-limited, then

1) aeronomical details don't matter
2) H, D escape is probably not strongly fractionating
3) easy to put into photochemical models
   and
4) easy to put into models of ancient Mars
5) Our Model is left with a single family of free parameters: the deposition velocity v_{dep}


Volume Mixing Ratio
0.01
0.001
0.0001
10^{-5}
10^{-6}
Fluxes [molecules cm^{-2}s^{-1}]
10^9
10^8
10^7
0.001
0.01
0.1
Deposition velocity [cm/s]
f(O$_2$)
f(CO)
f(H$_2$)
H escape
H$_2$O$_2$ deposition
O$_3$ deposition


f(O$_2$)
H escape
f(CO)
H$_2$O$_2$ deposition
f(H$_2$)
O$_3$ deposition
Volume Mixing Ratio
0.01
0.001
0.0001
10^{-5}
10^{-6}
Fluxes [molecules cm^{-2}s^{-1}]
10^9
10^8
10^7
0.001
0.01
0.1
Deposition velocity [cm/s]

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