The Global Oxygen Cycle

Presentation on “Geobiology”

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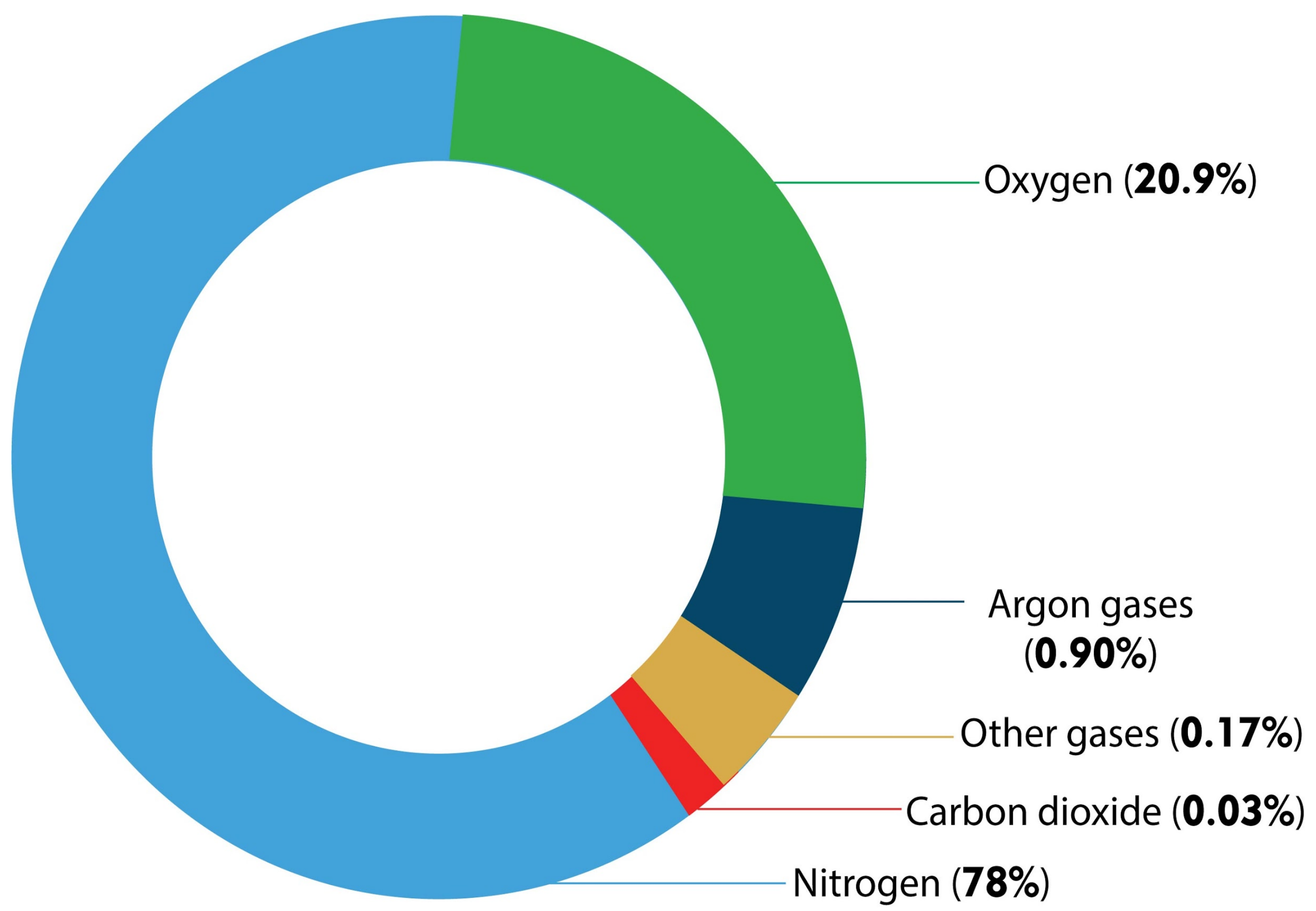
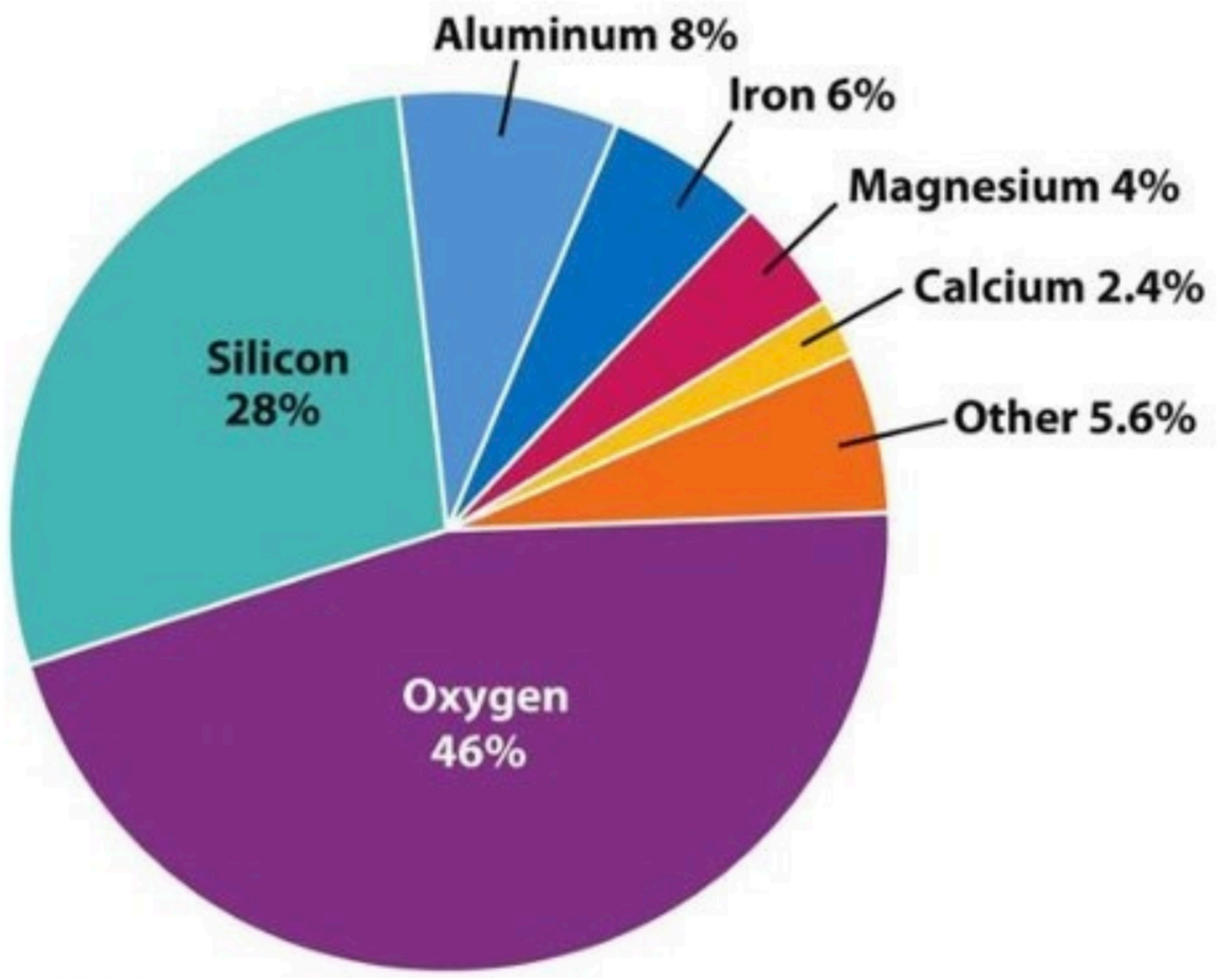
Introduction

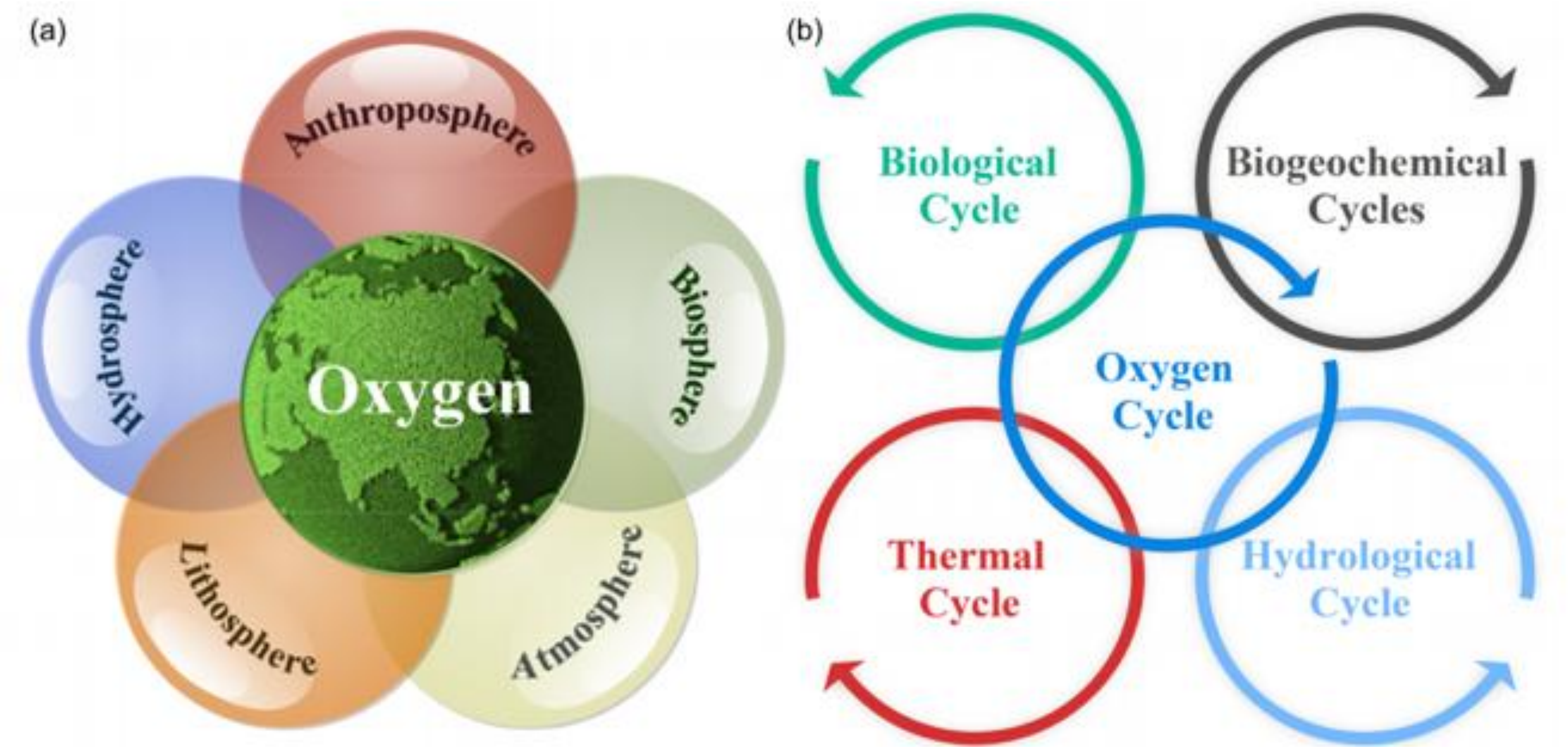
Why Study Oxygen?

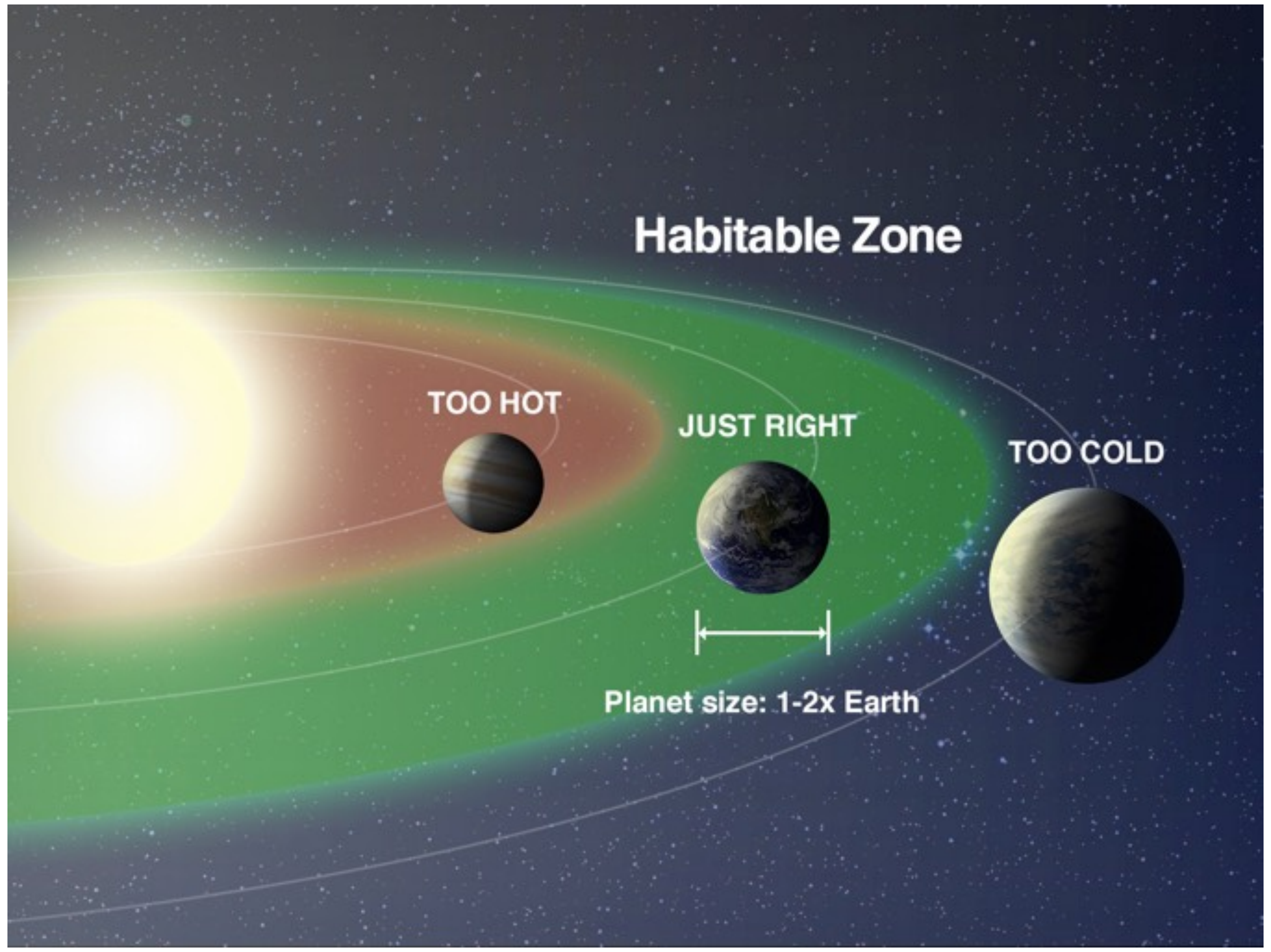


Atmosphere



Crust



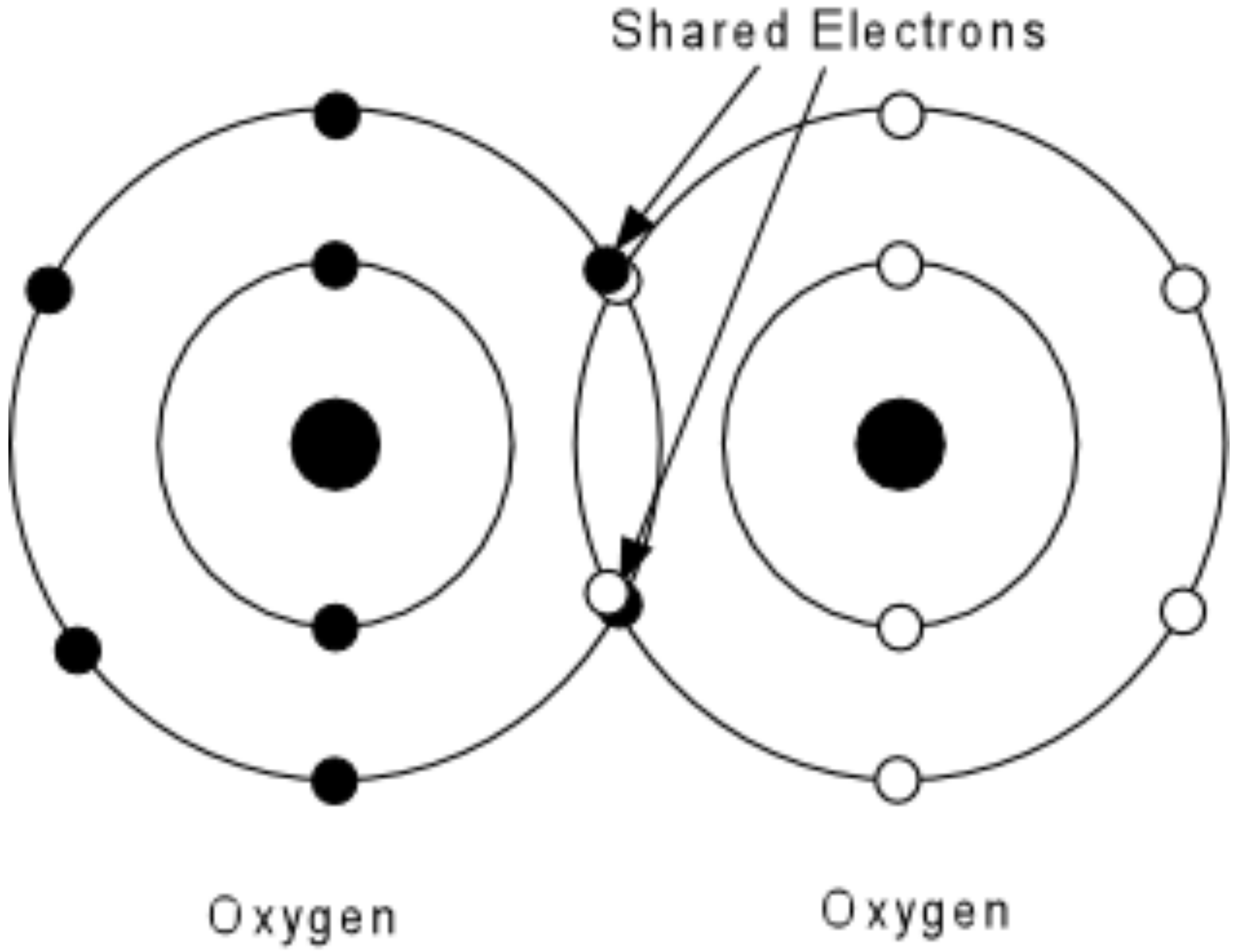


Habitability?

Chemistry & Biochemistry of Oxygen

Electron Acceptor

- Oxygen has six valence electrons, needs two more for a stable octet
- Molecular oxygen stably exists as O_2, each atom shares two electrons



- Highly electronegative, a strong electron acceptor
- Eg. Oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+})
- $2FeO + \frac{1}{2}O_2 \rightarrow Fe_2O_3$

Chemistry & Biochemistry of Oxygen

Biological Role of O_2

- Respiration / Decay
  - $CH_2O + O_2 \rightarrow CO_2 + H_2O$
  - Release energy stored in organic compounds
- Photosynthesis
  - $CO_2 + H_2O \rightarrow CH_2O + O_2$
  - Sunlight provides energy
- Anoxygenic Photosynthesis
  - Use H_2 or H_2S instead of H_2O

Redox Balance

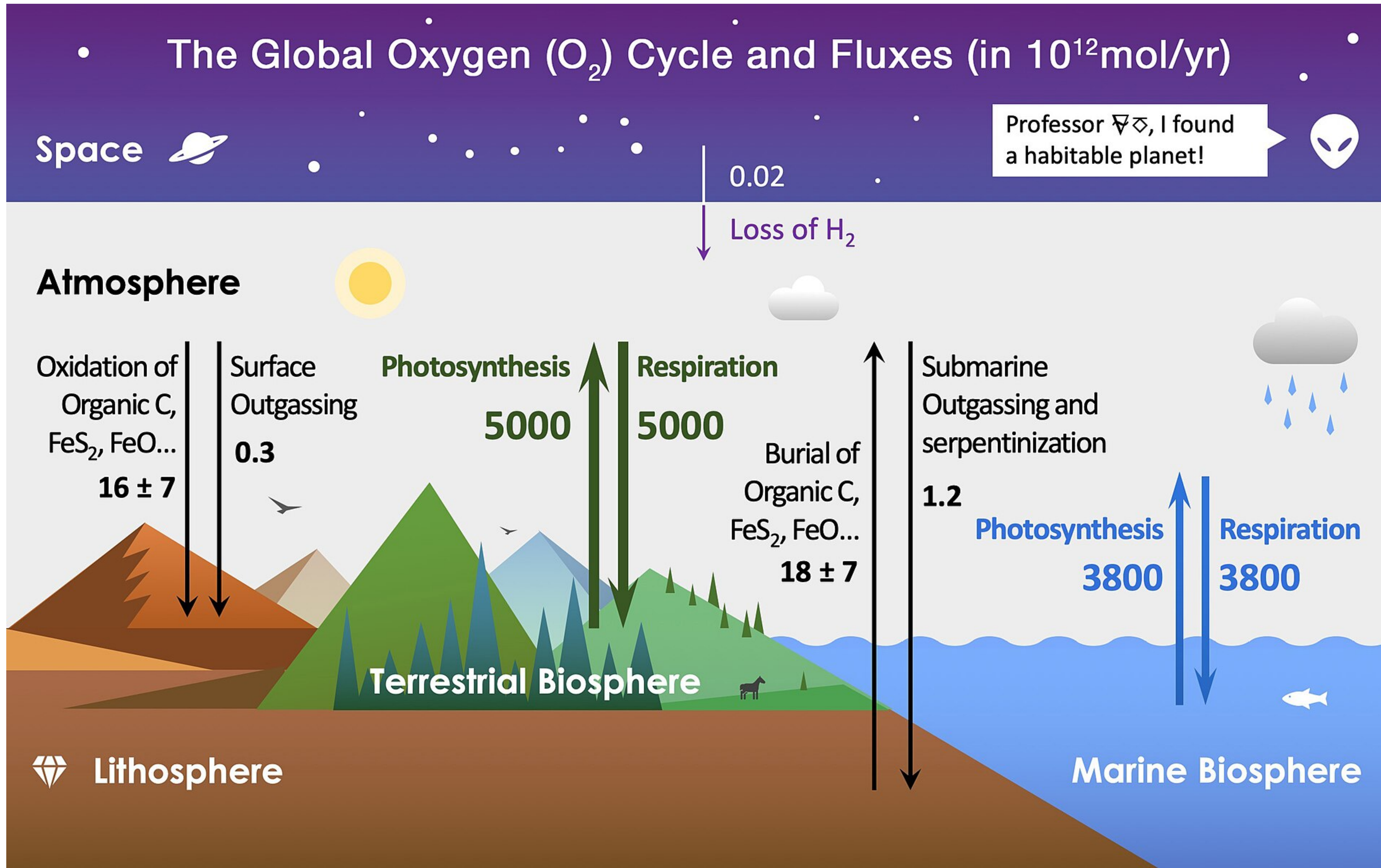
The Concept & Global Redox Budget

- Redox Balance = Conservation of Electrons
- Oxidation of one requires reduction of another
- Global Redox Budget= $\sum$ (Oxidation Fluxes) $-$ $\sum$ (Reduction Fluxes)

Modern Oxygen Cycle

The Biological O_2 Cycle

- Source: oxygenic photosynthesis
  - Land photosynthesis: 60 Gt C yr^{-1}, 5×10^{15} mol O_2 yr^{-1}
  - Marine photosynthesis: 45 Gt C yr^{-1}, 3.8×10^{15} mol O_2 yr^{-1}
- Sink: respiration & decay (nearly balanced)
- Atmospheric O_2: 3.6×10^{19} mol
  - Residence time: $3.6 \times 10^{19} / 5 \times 10^{15} \approx 7000$ yr
  - (Each O_2 cycle once every 7000 yr)
  - (CO_2 residence time: 10 yr, preindustrial)



Modern Oxygen Cycle

The Geological O_2 Cycle: Source for O_2

Source process	**Effect on O_2 (×10^{12} mol/yr)**	**Notes**
Organic C burial	10 ± 3.3	Burial of reduced carbon in marine sediments (≈0.25% of marine NPP)
Pyrite (FeS_2) burial	7 ± 3.6	Produced by bacterial sulfate reduction
FeO burial	0.9 ± 0.4	Sedimentary FeO contributes
H escape	0.024	Loss of H to space → net oxidation.
Total	**≈ 18 × 10^{12} mol/yr**	—

- $CH_2O + O_2 \rightarrow CO_2 + H_2O$
- Understand: reduced species are buried, releasing O_2 equivalents
- $4\,FeS_2 + 15\,O_2 + 14\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,H_2SO_4$
- $4\,FeO + O_2 \rightarrow 2\,Fe_2O_3$
- $2\,H_2O \xrightarrow{h\nu} O_2 + 4\,H \uparrow$

Modern Oxygen Cycle

The Geological O_2 Cycle: Sinks for O_2

Sink process	Effect on O_2 (×10^{12} mol/yr)	Notes
Oxidation of organic C during weathering	7.5 ± 2.5	Continental weathering
Oxidation of FeS_2	7.0 ± 3.6	Produces H_2SO_4 → consumes O_2
Oxidation of FeO	1.0 ± 0.6	Minor contribution
Surface volcanic gases (H_2, SO_2, H_2S)	0.3	Converted to sulfate via oxidation
Submarine H_2S oxidation	1.0	Hydrothermal vent processes
Serpentinization (Fe oxidation)	0.2	H_2 generation at mid-ocean ridges
Total	**≈ 17 × 10^{12} mol/yr**	nearly balanced with production.

Modern Oxygen Cycle

The Geological O_2 Cycle: Volcanic and Seafloor O_2 Sinks

- Volcanic gas oxidation
  - $SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$
  - Subaerial volcanism: $\sim 1 \times 10^{11}$ mol H_2/yr
  - Mid-ocean ridge fluxes dominate ($\sim 80\,\%$ of total)
  - Combined net “volcanic” O_2 sink $\approx 1.5 \times 10^{12}$ mol H_2/yr
- Serpentinization（蛇纹石化）：
  - $3FeO + H_2O \rightarrow Fe_3O_4 + H_2$
  - Reaction of ultramafic(超镁铁质) rocks(olivine橄榄石, pyroxene辉石) with hot sea water
  - Generates H_2, consumes O_2 equivalents
  - Minor today, possibly major in early Earth

Modern Oxygen Cycle

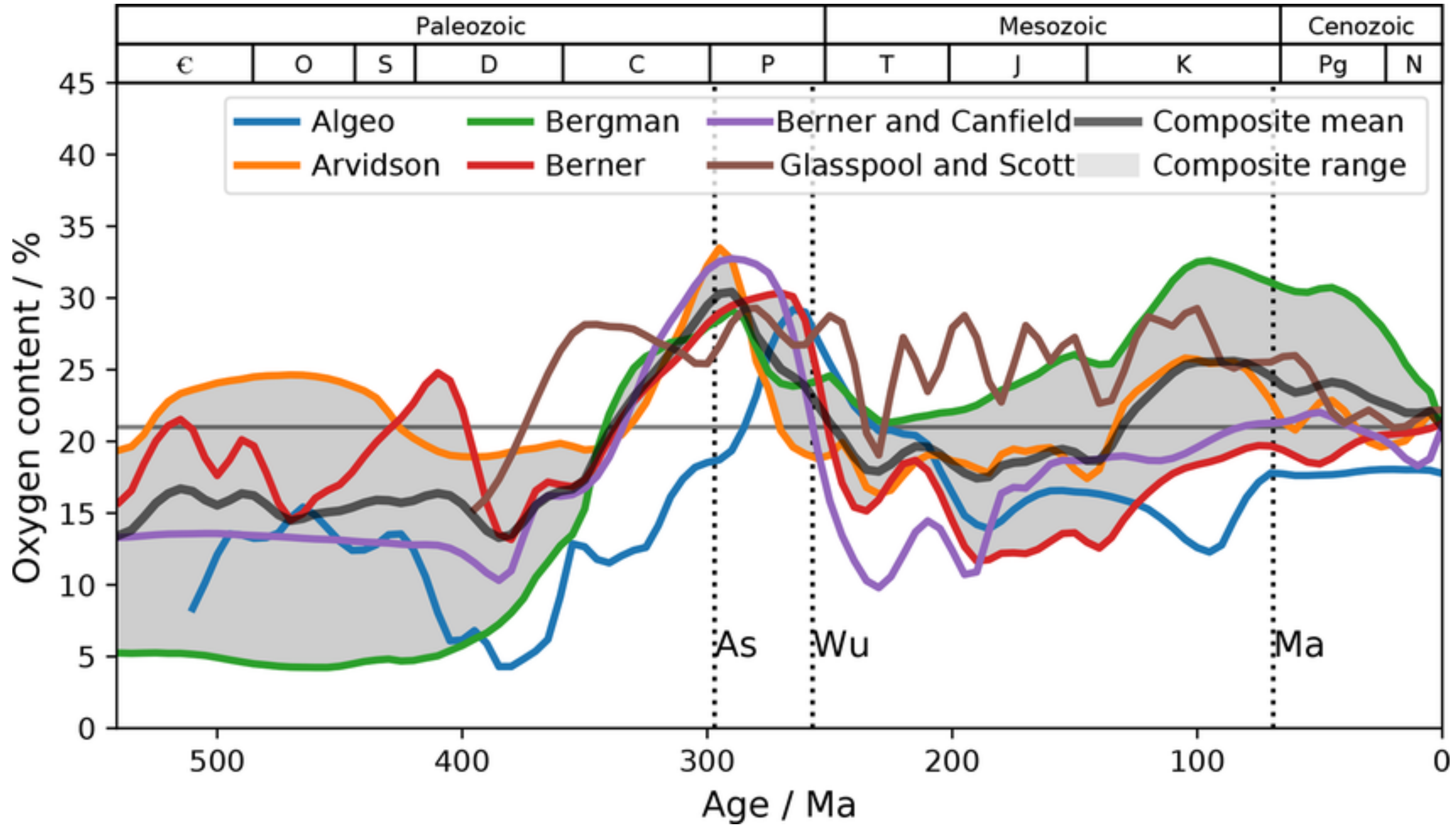
The Geological $\mathrm{O_2}$ Cycle: Balance and $\mathrm{O_2}$ Lifetime

- Net budget:
  - $\mathrm{O_2}$ production: 17.9×10^{12} mol/yr
  - $\mathrm{O_2}$ consumption: 17.0×10^{12} mol/yr
    - Effectively balanced within uncertainties($\pm 50\,\%$)
- Geologic lifetime of $\mathrm{O_2}$
  - $\tau_{O_2} = \dfrac{3.6 \times 10^{19} \text{ mol}}{1.8 \times 10^{13} \text{ mol/yr}} \approx 2 \times 10^{6}$ years
  - $\approx$ 2 million years
  - Timescale for large $\mathrm{O_2}$ variations if sources/sinks shift
  - **Atmospheric $\mathrm{O_2}$ is geologically stable**

Modern Oxygen Cycle

O_2 over Phanerozoic Time

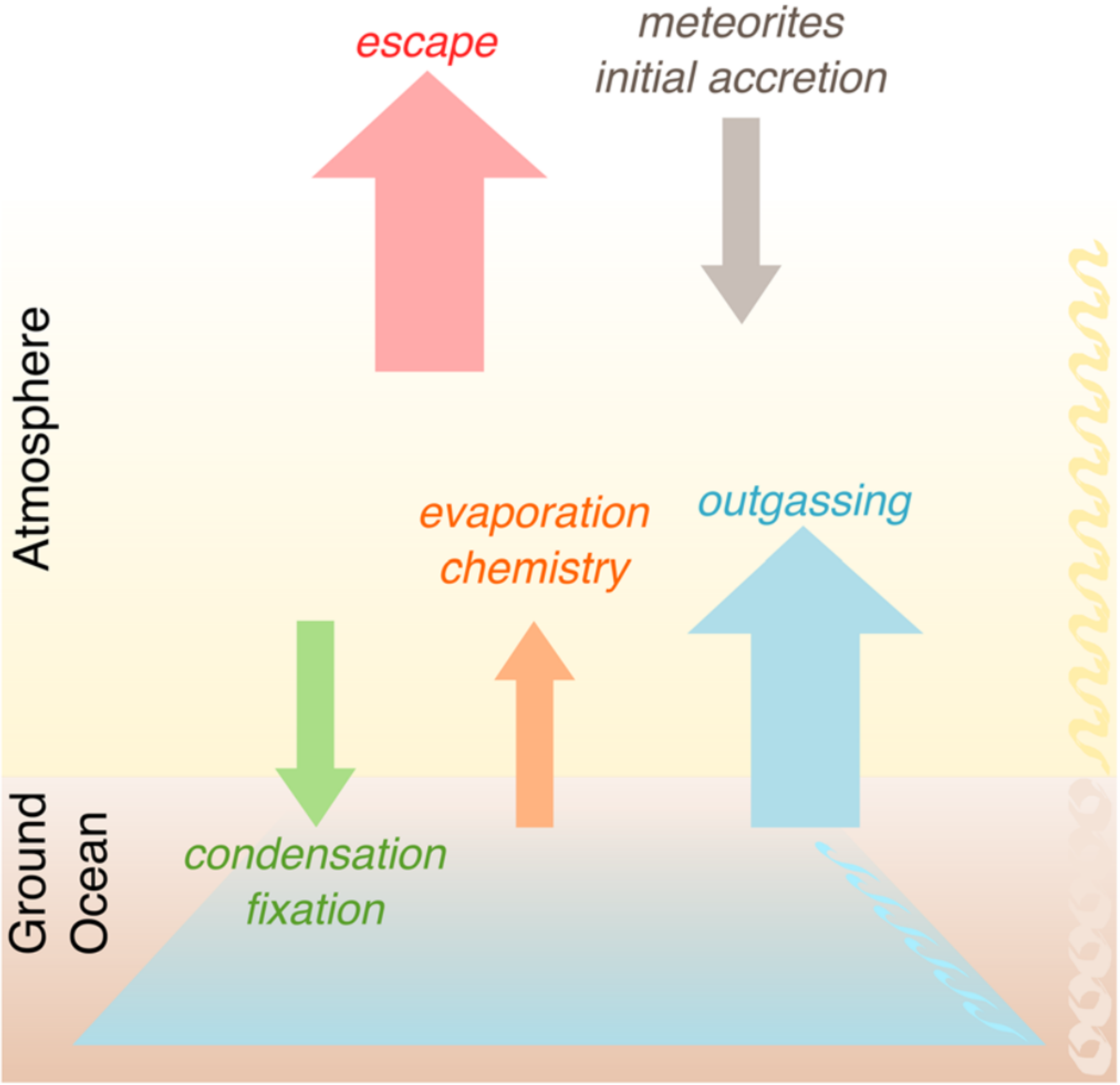
- High O_2 overall: Animal persistence implies O_2 never $< \sim 10\,\%$ of present
- Most of time O_2 stayed $\sim \pm 50\,\%$ of present: fires give the upper bound
- Stabilizing feedbacks
  - weathering depends on O_2
  - pyrite burial inversely depends in O_2
  - newest sediment weather first



Modern Oxygen Cycle

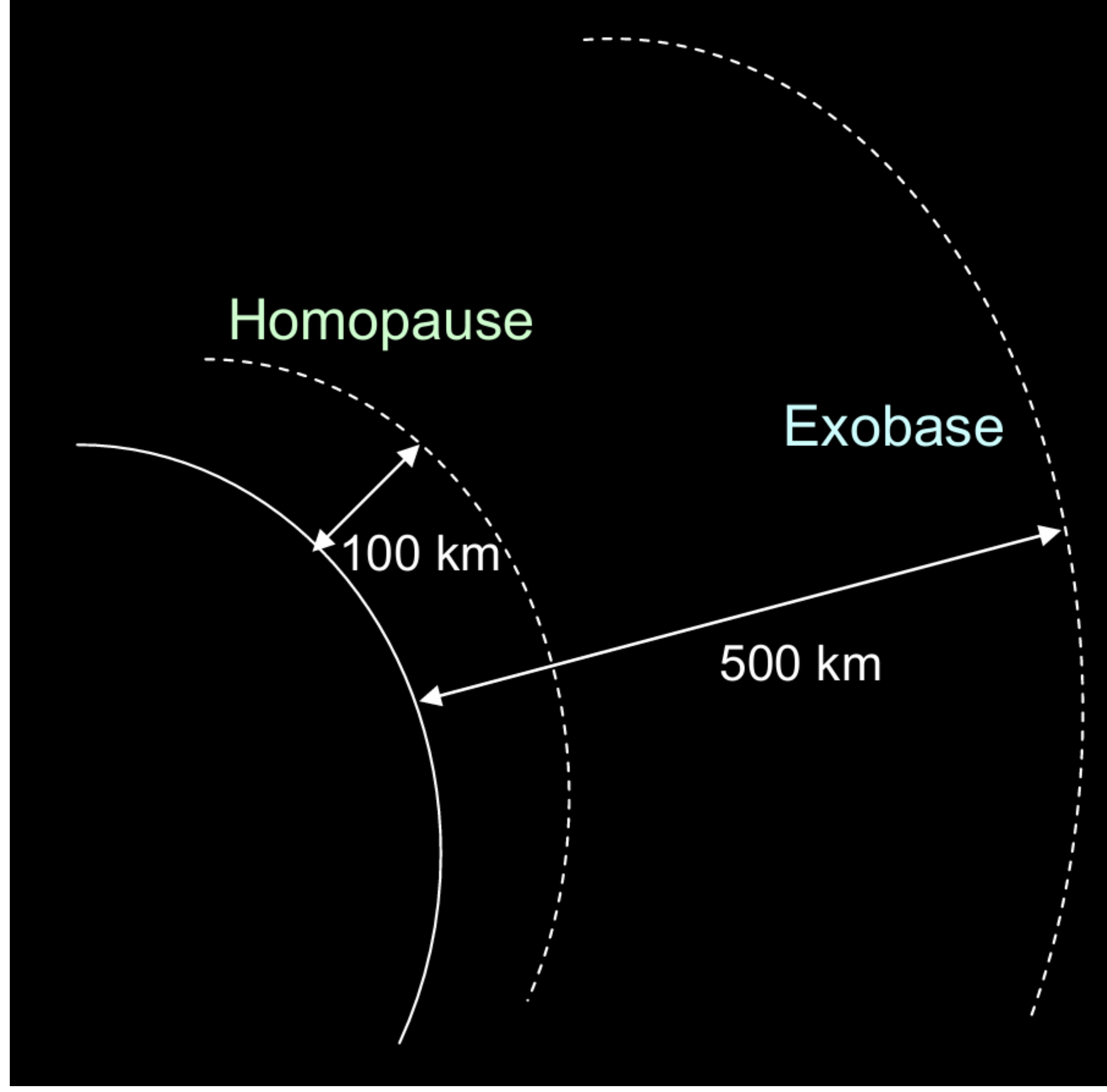
Loss of Hydrogen to Space: Concept & Redox Effect

- Global Redox Budget:
  - Internal O_2 sources/sinks
  - Top boundary: Hydrogen escape to space
- Most H on Earth is H_2O, the loss of H leaves O_2 behind, producing a net oxidation of the planet

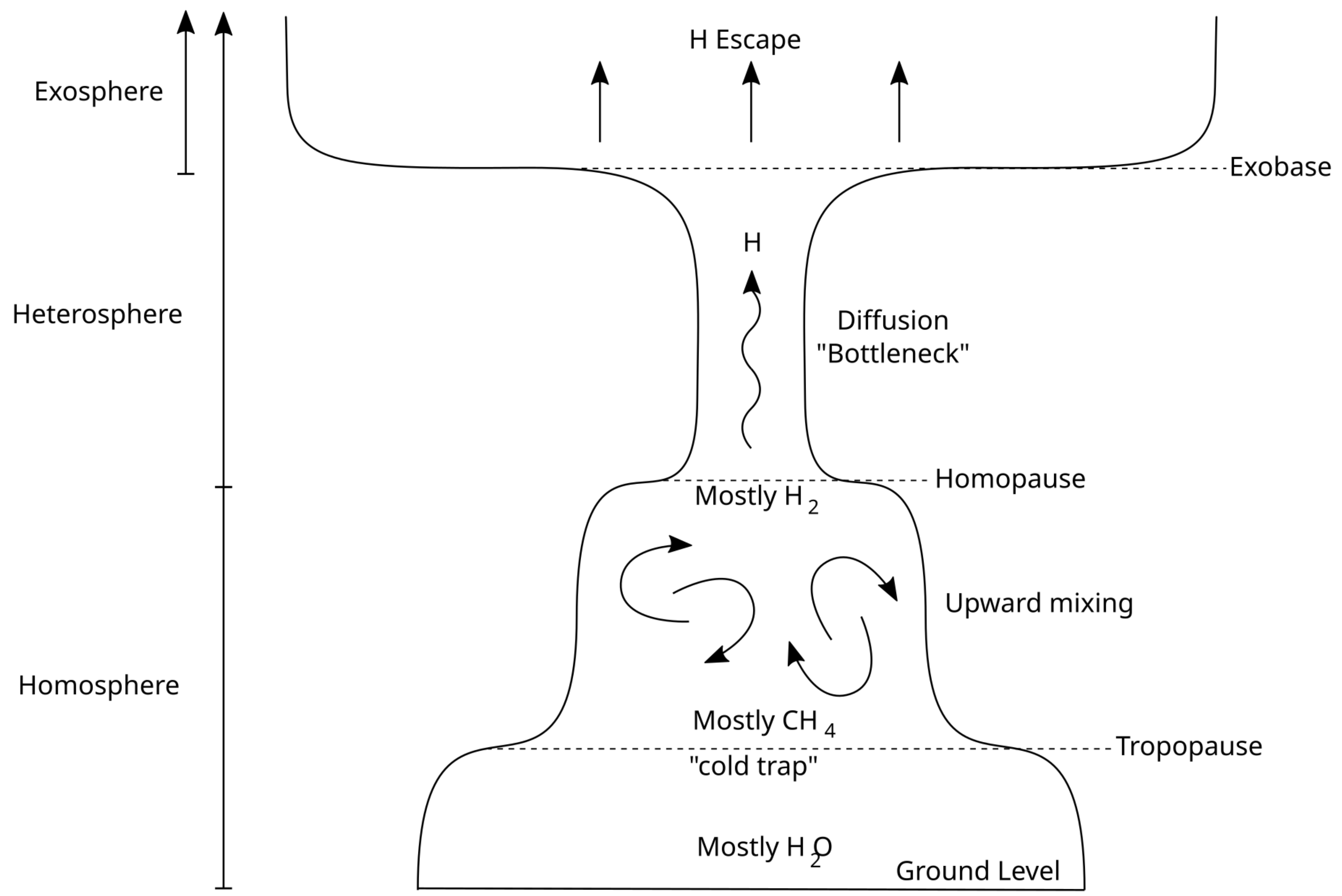


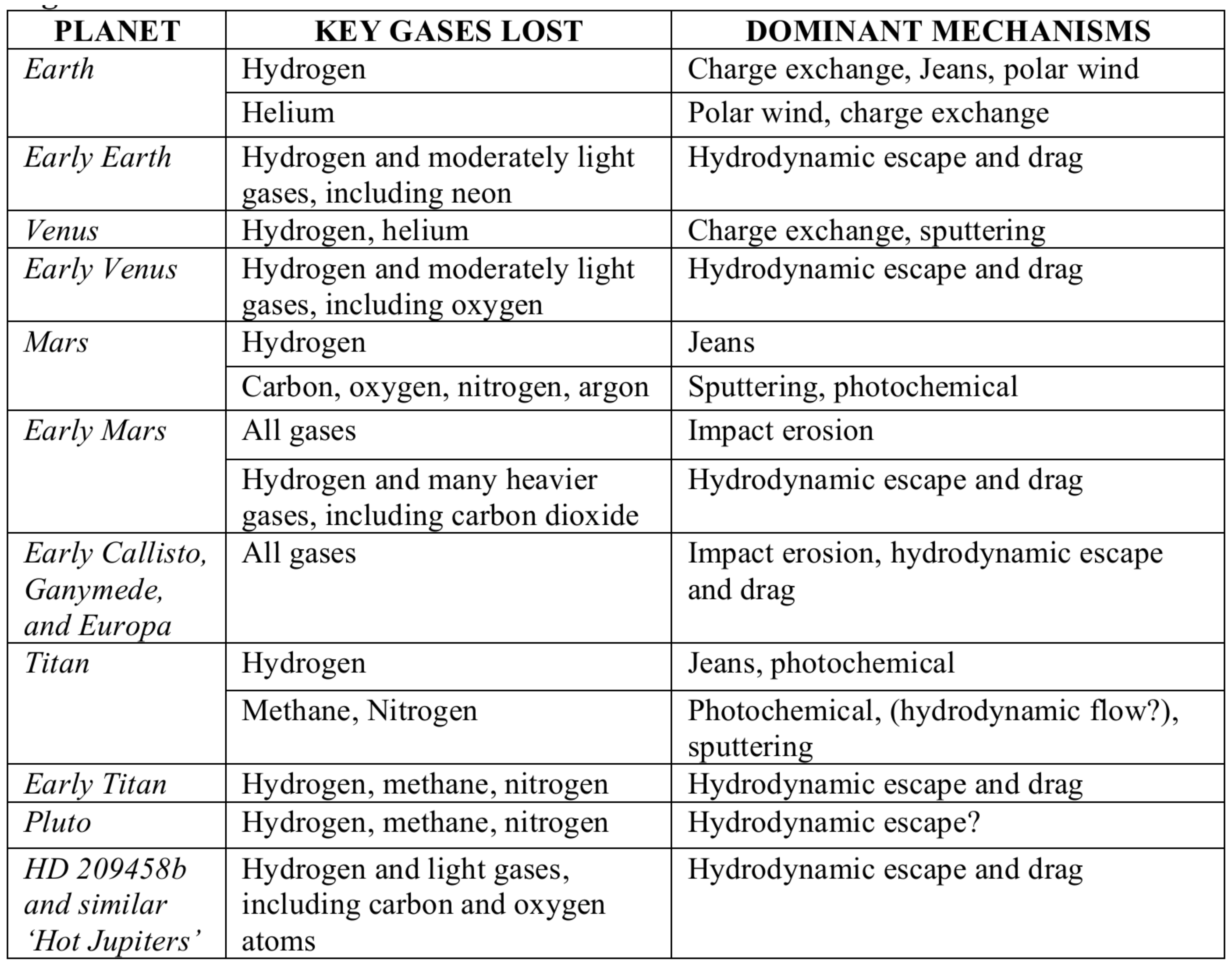
Modern Oxygen Cycle

Loss of Hydrogen to Space: Mechanism



- Escape occurs above the Exobase
  - (by thermal & non-thermal mechanisms)
- On Modern Earth, the escape rate is limited by diffusion through homopause





PLANET	KEY GASES LOST	DOMINANT MECHANISMS
Earth	Hydrogen	Charge exchange, Jeans, polar wind
	Helium	Polar wind, charge exchange
Early Earth	Hydrogen and moderately light gases, including neon	Hydrodynamic escape and drag
Venus	Hydrogen, helium	Charge exchange, sputtering
Early Venus	Hydrogen and moderately light gases, including oxygen	Hydrodynamic escape and drag
Mars	Hydrogen	Jeans
	Carbon, oxygen, nitrogen, argon	Sputtering, photochemical
Early Mars	All gases	Impact erosion
	Hydrogen and many heavier gases, including carbon dioxide	Hydrodynamic escape and drag
Early Callisto, Ganymede, and Europa	All gases	Impact erosion, hydrodynamic escape and drag
Titan	Hydrogen	Jeans, photochemical
	Methane, Nitrogen	Photochemical, (hydrodynamic flow?), sputtering
Early Titan	Hydrogen, methane, nitrogen	Hydrodynamic escape and drag
Pluto	Hydrogen, methane, nitrogen	Hydrodynamic escape?
HD 209458b and similar 'Hot Jupiters'	Hydrogen and light gases, including carbon and oxygen atoms	Hydrodynamic escape and drag

Modern Oxygen Cycle

Loss of Hydrogen to Space: Mechanism of Thermal Escape

- Neutral constituents in the upper atmosphere are in local thermodynamic equilibrium(LTE, 局部热力学平衡). Maxwellian function:
  - $f(\vec{x}, \vec{v}) = N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} = N\left(\frac{1}{u_i\sqrt{\pi}}\right)^3 e^{-v^2/u_i^2}$
    - $u_i = \sqrt{\frac{2kT}{m_i}}$, thermal speed for species
- Flux of Jeans Escape:
  - $\Phi_i(\text{escape}) = \int_0^{2\pi}\int_0^{\pi/2}\int_{v_\text{esc}}^{\infty} v_i \cos(\theta) f(v_i) v_i^2 \sin(\theta)\, dv_i\, d\theta\, d\Psi$
    - $= N_i\left(\frac{kT_e}{2\pi m_i}\right)^{1/2}\left(1 + \frac{m_i v_\text{esc}^2}{2kT_e}\right) e^{-\frac{m_i v_\text{esc}^2}{2kT_e}} = N_i\left(\frac{u_i}{2\sqrt{\pi}}\right)\left(1 + \frac{v_\text{esc}^2}{u_i^2}\right) e^{-\frac{v_\text{esc}^2}{u_i^2}}$
  - use the values of $v_{esc} = \sqrt{2GM/r}$ and u_i at the exobase (collisionless).

Modern Oxygen Cycle

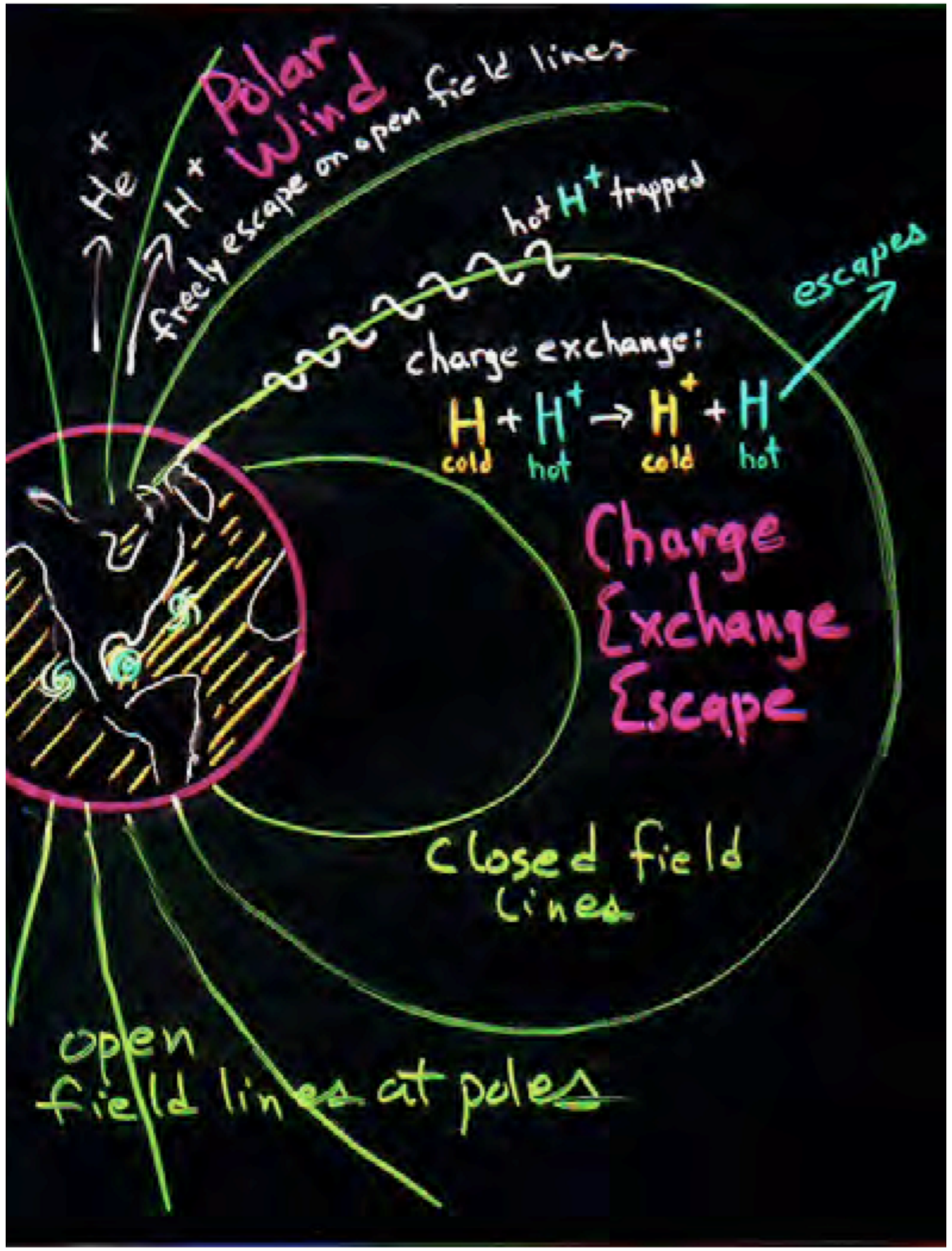
Loss of Hydrogen to Space: Mechanism of Thermal Escape

- We define Jeans parameter: $\lambda_{\text{ex}} = \dfrac{GMm_i/r}{kT} = \dfrac{v_{\text{esc}}^2}{u_i^2}$
  - (Gravitational Potential Energy/Thermal Energy)
- $\Phi_i(\text{escape}) = N_i \left(\dfrac{u_i}{2\sqrt{\pi}} \right) (1 + \lambda_{\text{ex}}) e^{-\lambda_{\text{ex}}}$
  - $\lambda_{\text{ex}} \uparrow$, $\Phi_i(\text{escape}) \downarrow$ exponential decay
- Light particles' λ_{ex} is small, easy to escape (H & O ?)

Modern Oxygen Cycle

Loss of Hydrogen to Space: Mechanism

- Hydrodynamic escape can be regarded as an extreme form of Jeans escape, where the bulk flow carries gas away.
- For non-thermal escape, particles also need to exceed the local escape velocity v_{esc}.
- Since lighter species have higher thermal velocities at a given temperature, they are more likely to reach or exceed v_{esc} , and hence are more easily lost to space.



Modern Oxygen Cycle

Loss of Hydrogen to Space: Diffusion Limited Escape

- If the escape rate is efficient at exobase, the escape process is “limited” by the diffusion through homopause
- The vertical flux of a molecule is $\Phi_i = \Phi_i^{\text{mol}} + \Phi_i^{\text{eddy}}$
  - (molecular diffusion+eddy diffusion)
- Above the homopause, we only consider Φ_i^{mol}: (a light gas 1 diffuse through background gas 2)
  - $\Phi_1^{\text{mol}} = -D_{12}\, n_1 \left(\frac{n^2}{n_1 n_2}\frac{df_1}{dz} + \frac{(m_2 - m_1)\, g}{kT} + \frac{\alpha_T}{T}\frac{dT}{dz} \right)$
    - (mixing ratio gradient+gravitational separation+thermal diffusion)
    - D_{12} is binary diffusion coefficient, $f_1 = n_1/n$ is mixing ratio
  - Under steady state condition approximation: $\Phi_l = D_{12}\, n_1 \frac{(m_2 - m_1)g}{kT}$
  - $D_{12} = b_{12}/n$, where b_{12} is binary diffusion parameter, $\Phi_l = \frac{b_{12}(m_2 - m_1)g}{kT} f_1$
  - In the end, we get: $\Phi_{\text{esc}} \approx \frac{b f_{\text{tot}}(H)}{H_a}$

Modern Oxygen Cycle

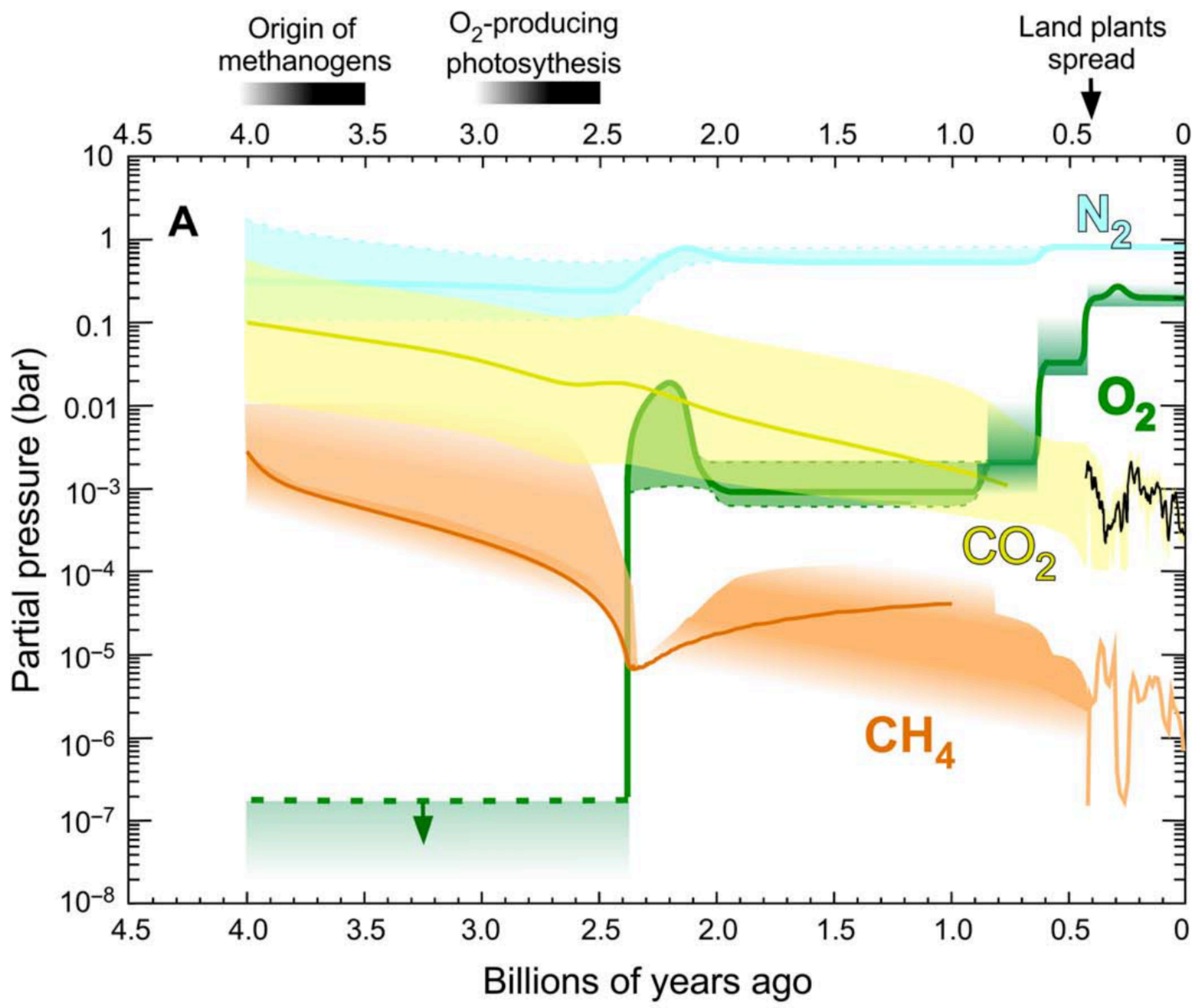
Loss of Hydrogen to Space: Diffusion Limited Escape

- $\Phi_{\text{esc}}(H_2) \approx 2.5 \times 10^{13} f_{\text{tot}}(H_2)$ molec cm^{-2}s^{-1}
  - $f_{\text{tot}}(H_2) = f(H_2) + \frac{1}{2} f(H) + f(H_2O) + 2f(CH_4) + \ldots$
- At the homopause: H_2O (~4ppm), CH_4 (~1.6ppm)
  - $f_{\text{tot}}(H_2) \approx 7.2 \times 10^{-6}$
  - $\Phi_{\text{esc}}(H_2) \approx 1.8 \times 10^{8} H_2$ molec cm^{-2}s^{-1}
    - Converted to global flux: $\approx 4.8 \times 10^{10}$ mol H_2 yr^{-1}
    - Equivalent O_2 production: $\frac{1}{2} \Phi(H_2) \approx 2.4 \times 10^{10}$ mol O_2 yr^{-1}
    - Compare to geologic O_2 production: $\approx 1.8 \times 10^{13}$ mol yr^{-1} → negligible ($\sim 0.1\%$)

Modern: O_2-rich atmosphere prevents H accumulation
Early Earth???

Early Earth Oxygen Cycle

Overview & Timing of O_2 Rise



- Before the GOE, atmospheric O_2 was very low
    - (MIF-S,硫同位素质量无关分馏)
- Oxygenic photosynthesis likely invented by 2.7-2.5Ga, but O_2 stayed low
- Why the delay between photosynthesis and rise of O_2?

Early Earth Oxygen Cycle

Evidence & Biosignatures

- Evidence for early oxygenic photosynthesis:
  - Mo, U, N isotopes in black shales(页岩)
  - Biomarkers(2-methylhopanes, steranes)
  - Microfossils / stromatolites(叠层石)
- Overall data support cyanobacterial evolution before GOE
- ? Biology was ready, but environmental sinks kept O_2 low

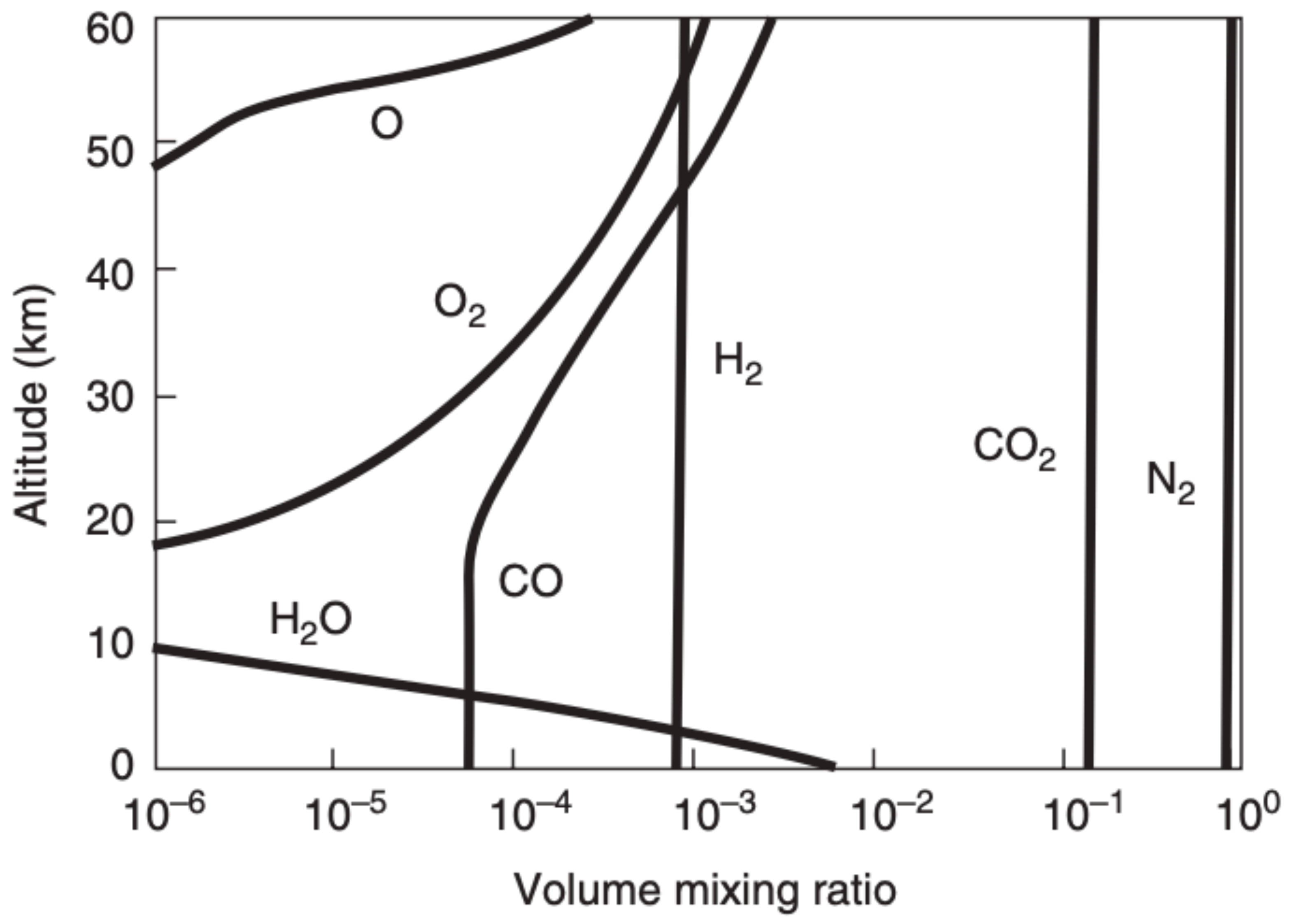
Early Earth Oxygen Cycle

Prebiotic / Very-low-O_2 Redox Budget

- Consider the abiotic Earth (no organic burial, negligible abiotic organic production)
- With low oceanic sulfate in the Archean, H_2S formation at ridges was limited, volcanic gases became dominant O_2 sinks (surface + submarine outgassing)
- Sources of O_2 prebiotically are few: effectively only H escape to space (from H_2O photolysis)
  - Modern-style calculation gives O_2 eq. ~1.3×10^{10} mol/yr
  - (from H_2O-sourced H escape)
- Net: sinks ≫ sources → O_2 remains trace

Early Earth Oxygen Cycle

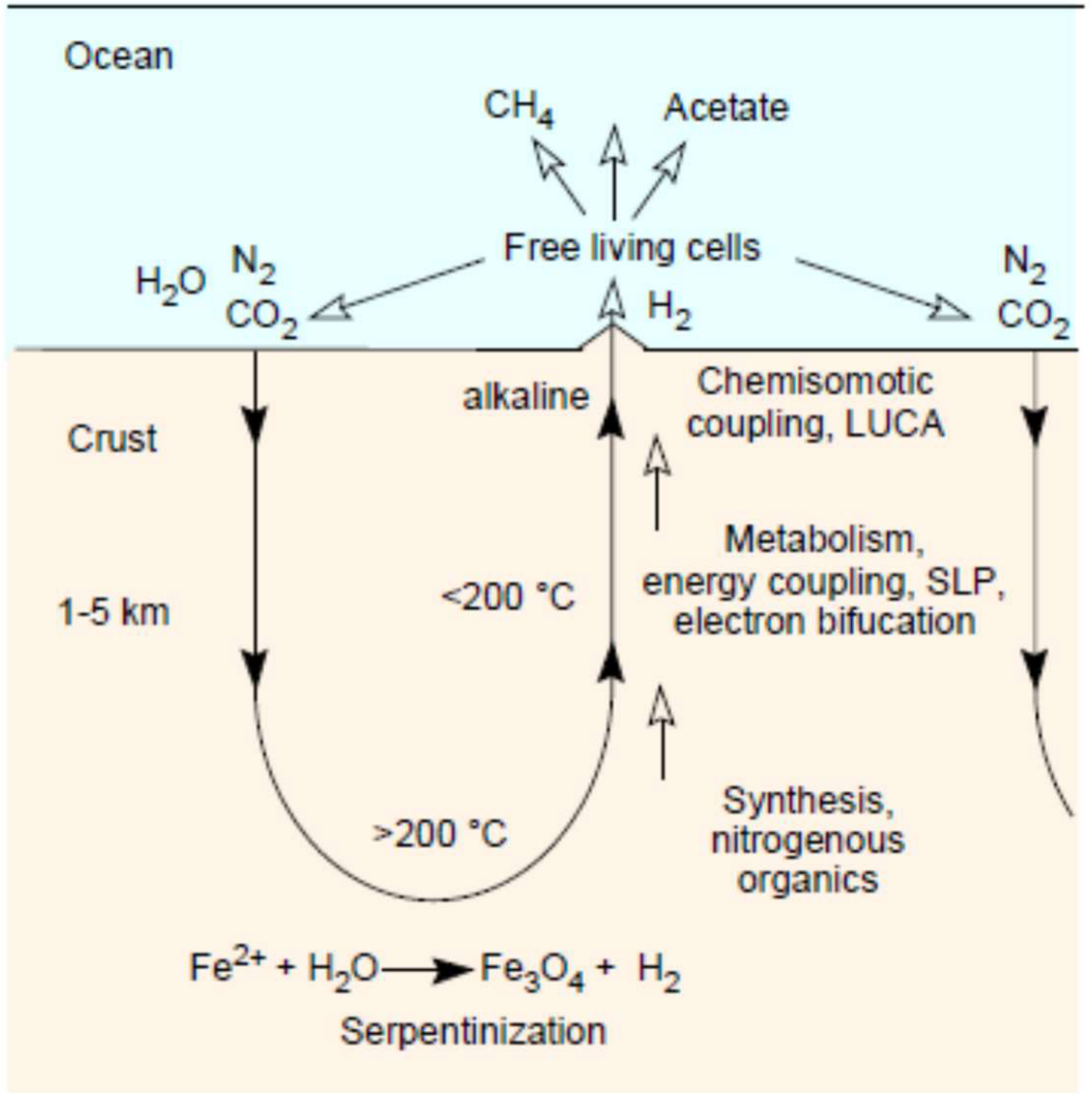
H_2 escape controls & expected H_2, O_2 levels



- H escape on early Earth is diffusion-limited at the homopause
  - (flux ∝ total H mixing ratio)
- Photochemical models predict H_2 mixing ratio ~10^{-3} (order-of-magnitude), consistent with enhanced H outgassing
  - (by higher Archean geothermal heat flow and serpentinization)
- O_2: a trace species
  - ~10^{-3} in the upper stratosphere, but near zero at the surface
  - (rapidly consumed by H_2).

Early Earth Oxygen Cycle

Oxidation of Mantle & Crust (delaying GOE)

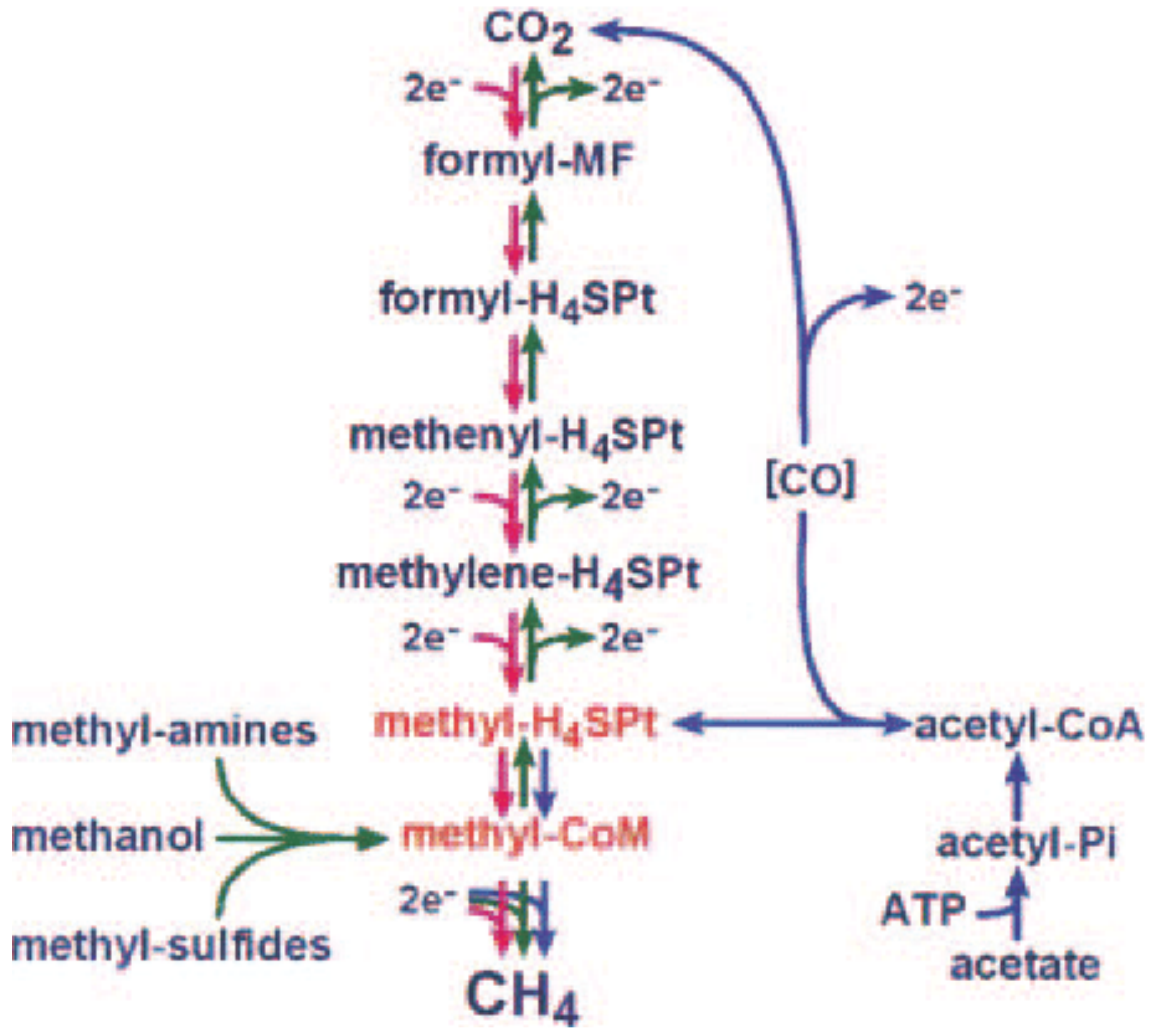


- An H_2-rich atmosphere implies O must go somewhere
  - oxidation of crust and mantle can store O_2-equivalents.
- Processes:
  - serpentinization (蛇纹石化,$Fe^{2+} \rightarrow Fe^{3+} + H_2$)
  - weathering and subduction of ferric iron
  - progressive crustal oxidation.
- Large O sinks in the solid Earth: delay atmospheric O_2 rise until these sinks diminish.

Early Earth Oxygen Cycle

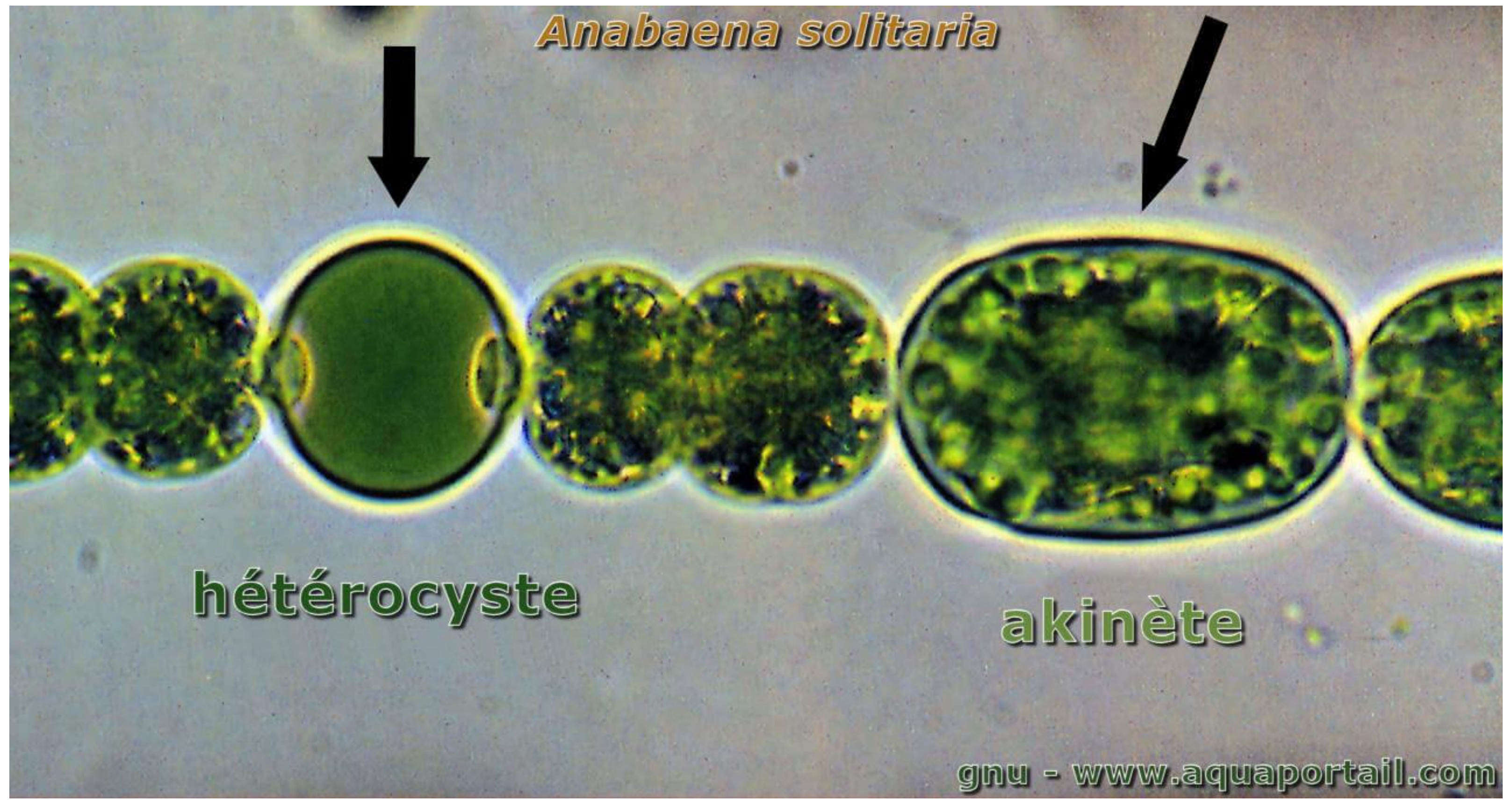
Biotic Archean & Role of CH_4

- After life becomes widespread
  - methanogens(甲烷菌): H_2 + organic $C \rightarrow CH_4$
- High CH_4:
  - greenhouse warming
  - affects redox budget



Rise of Atmospheric Oxygen

Why O_2 stayed low before GOE?



- O_2 producers (cyanobacteria) likely existed earlier, but O_2 remained low.
- Biological “brake”:
  - nitrogenase(固氮酶) is O_2-sensitive (anaerobic, 厌氧)
  - early cyanobacteria may have lacked protection, like heterocysts(异形胞)
  - limited spread
- Geochemical sinks dominated:
  - reduced volcanic/hydrothermal gases
  - crust & mantle oxidation
  - low sulfate → less pyrite burial (smaller O_2 source)
- Global redox budget net ≈ zero or negative → O_2 cannot accumulate.

Rise of Atmospheric Oxygen

Why did O_2 rise at GOE?

- Biology improves:
  - cyanobacteria evolve nitrogenase protection
    - broader spread
- Sources strengthen / sinks weaken:
  - increased: S & C recycling, organic burial
  - declined: abiotic H_2 supply, hydrothermal(热液) sinks
  - seafloor shifts ultramafic(超镁铁质) → mafic(镁铁质), less reduced gas production
  - volcanism shifts to more subaerial
- Small, long-term positive redox imbalance → atmospheric O_2 rises
- Still uncertain, need improved tectonic–Earth-system models……

Q&A