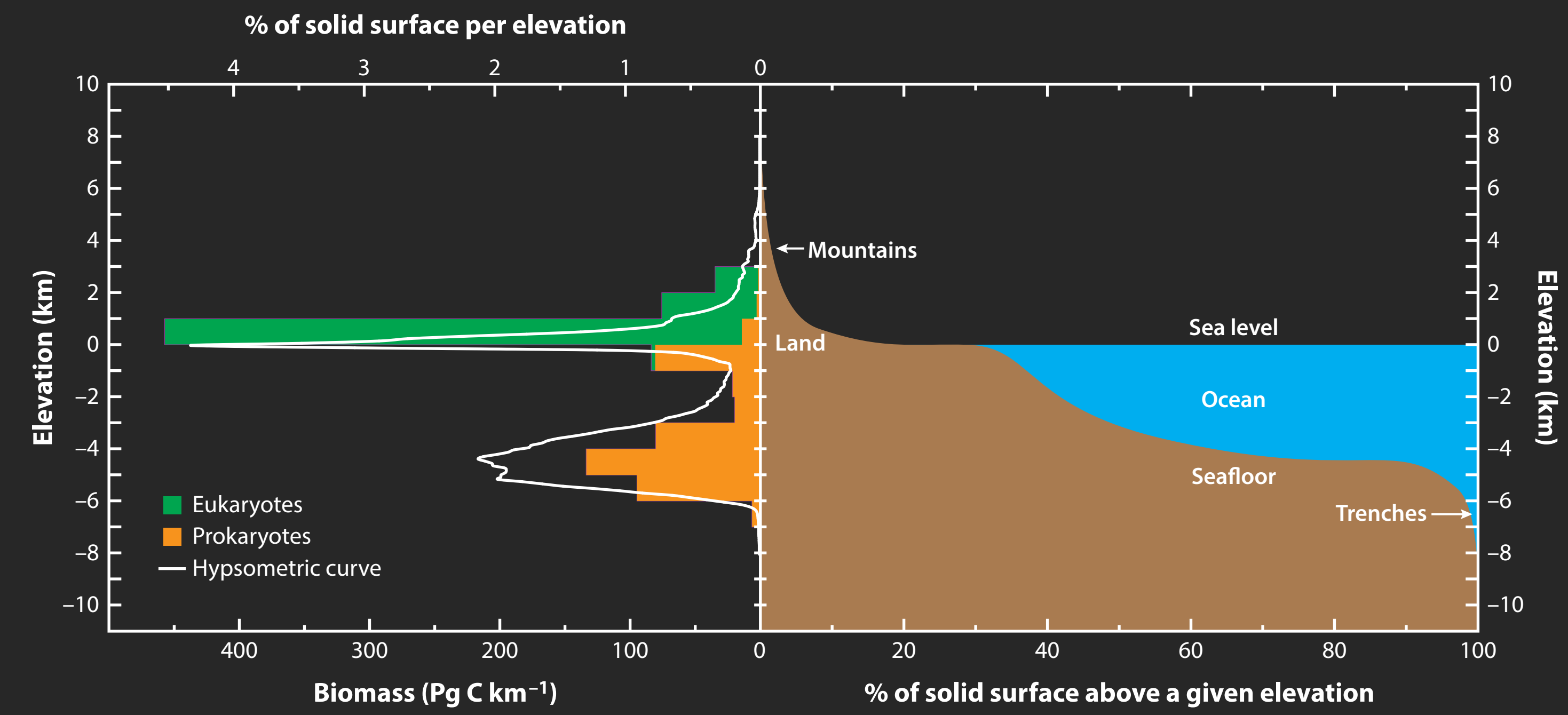


Studying the earliest and most fundamental metabolisms of life on Earth provides an understanding of the energy-transducing metabolisms associated with the emergence of life on Earth and elsewhere. Here we discuss principles that apply to redox and photon gradients used by life on Earth and whether we should expect similar sources of free energy and the metabolisms they induce, to exist on other wet rocky planets.

1. TERRESTRIAL BIOSHELL

Earth's biosphere is a thin bioshell whose thickness is ~10 km. Today, ~65% of the biomass is phototrophic and ~35% is chemotrophic [1]. Thus, the dominant energy source for extant life is the photon flux from the Sun. However, when life emerged approximately 4 billion years ago there was far less dry land than today and the biomass distribution may have more closely resembled the current prokaryotic distribution in which the majority of the biomass is not necessarily in the photic zone.

FIGURE 1: The hypsographic curve on the right shows the fraction of Earth's solid surface above a given elevation. The hypsometric curve on the left (white line) shows the fraction of Earth's solid surface at any given elevation [2]. The histogram on the left shows our estimate of the vertical profile of terrestrial biomass derived from [3] & [4].

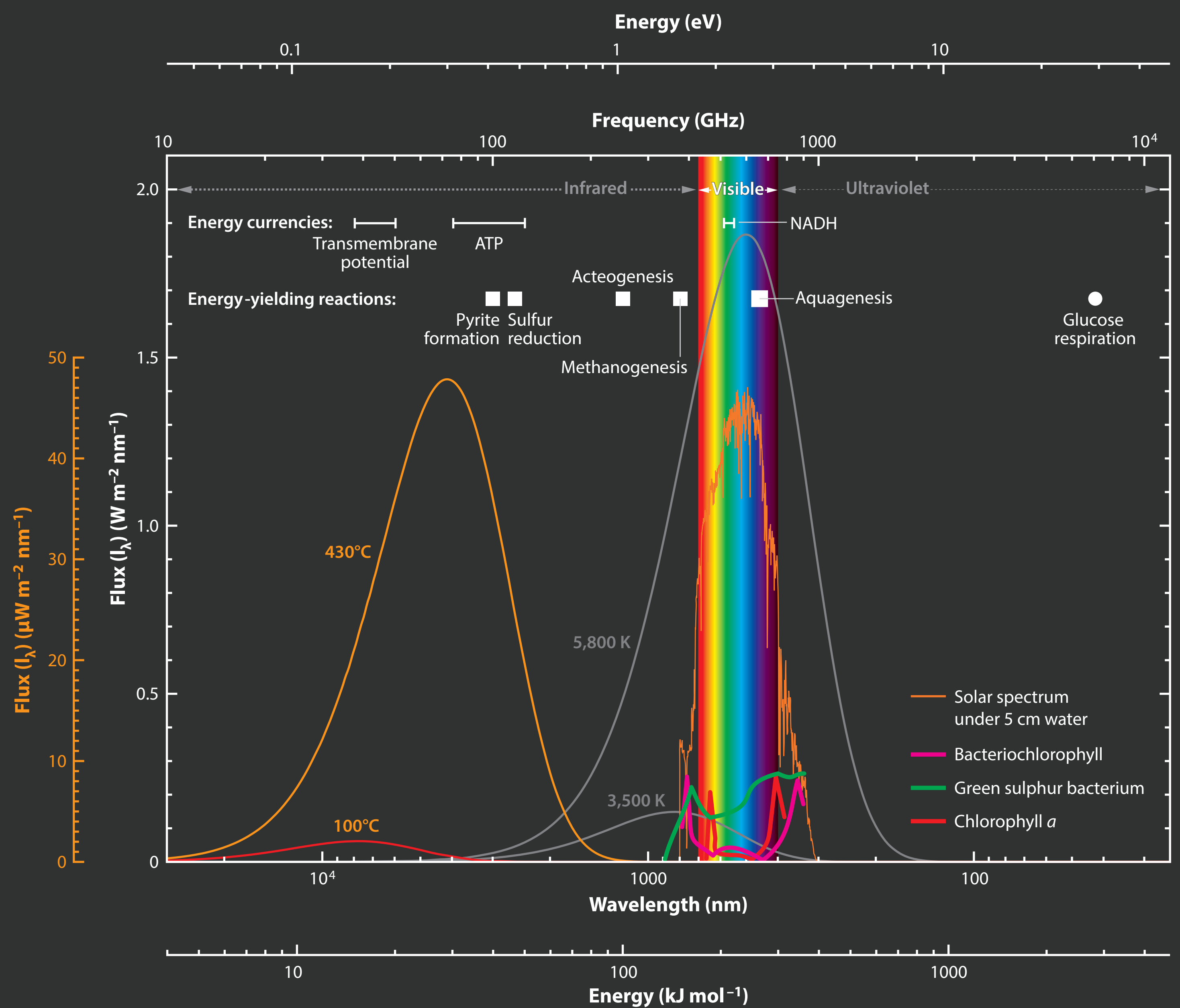


2. HABITABLE ENERGIES

Redox reactions in hydrothermal vents and hot springs probably played a dominant role in early metabolism, particularly since hydrothermal activity was more widespread [5]. The similar free energies of the earliest metabolic pathways and the availability of the reactants in such environments bolsters the case that life began by using energy sources based on commonly available redox gradients and over time evolved to perform higher energy reactions such as oxygenic photosynthesis and oxic respiration.

The transition of life from a redox-only energy source to a redox and photon energy source is suggested by comparing the energies of different metabolic reactions. The earliest redox reactions; pyrite formation, sulfur reduction, methanogenesis and acetogenesis provide less energy than photosynthesis. However, these early reactions do provide enough energy to charge trans-membrane potentials in a chemiosmotic coupling and convert low energy molecules such as ADP, NAD⁺ and NADP⁺ to higher energy molecules such as ATP, NADH and NADPH [6]. These molecules are universal energy currencies and likely to have been adopted by the earliest organisms.

FIGURE 2: Comparison of the photon and redox energy sources with the dominant energy currencies of life. Blackbody curves are shown for Sun-like G stars and for the most common star in the universe, low-mass M stars such as Gl581. The blackbody spectra of a 430°C hydrothermal vent fluid and a 100°C fluid represent the native environment of hyperthermophiles. Absorption spectra are shown for two candidates for the earliest anoxygenic photosynthesis. Eukaryotic chlorophyll *a* and the maximum energy available from oxic glucose respiration are shown for comparison.



3. THERMODYNAMIC CONSTRAINTS

The ΔG energies of all redox reactions in Figure 2, are above the peak energy of the 100°C ambient temperature of a hyperthermophile environment. An upper limit for the temperature at which metabolic activity can take place is defined by the temperature at which protein molecules and membranes dissociate. If solvents are required for biochemistry, then the temperature at which the solvent remains a liquid, will set the energies of the reactions that biological catalysts can control.

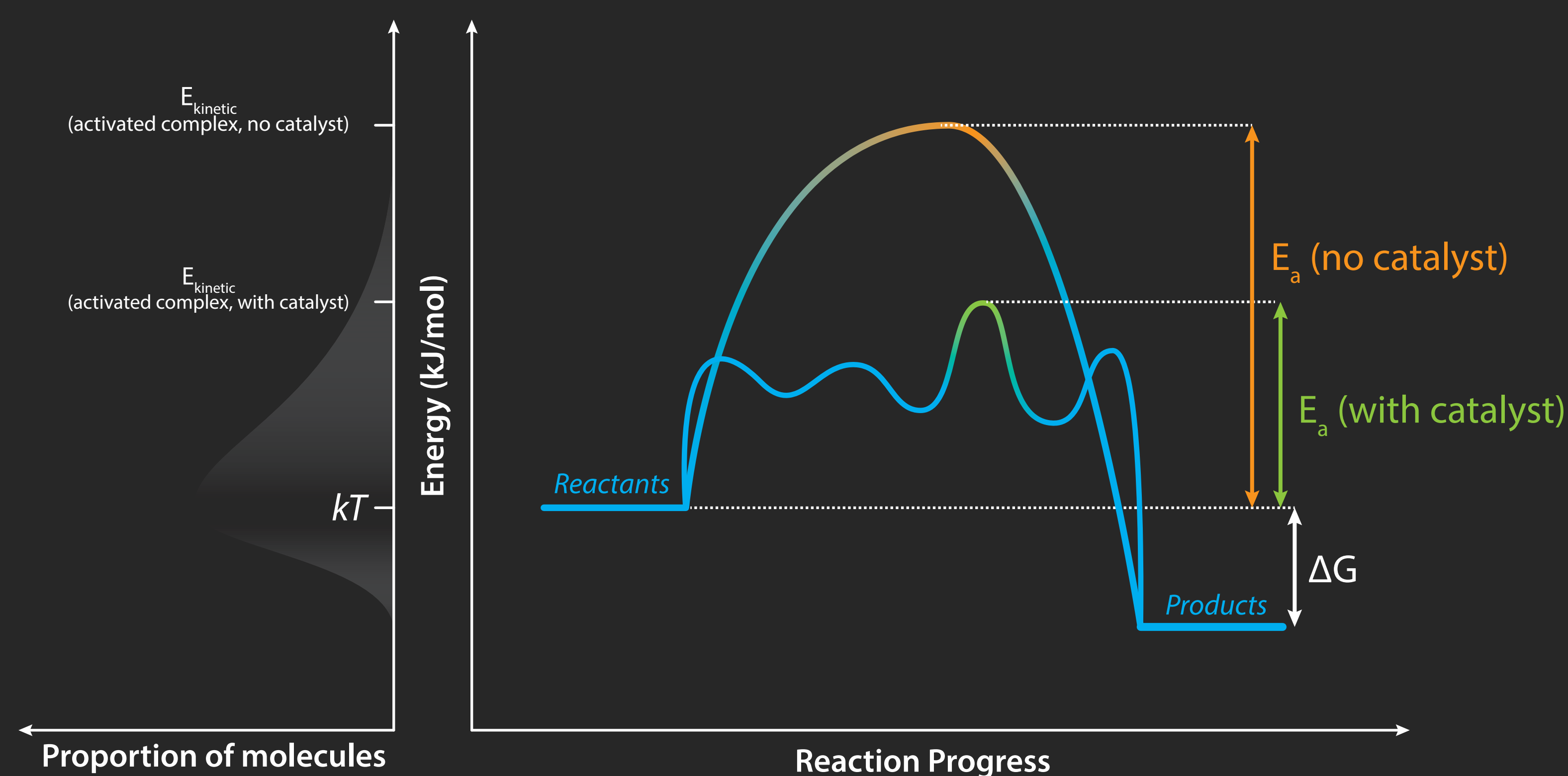


FIGURE 3: The relationship between environmental kinetic energy kT (represented by the Maxwell-Boltzmann distribution on the left), and energies associated with chemical reactions (on the right). Any metabolic reaction used by life must have activation energies higher than kT (the average energy of reactant molecules and the environment) otherwise the reaction would proceed to equilibrium without being mediated by the bio-catalysts of life [7]. Life makes a living by developing bio-catalysts to lower the activation energy of the reactions of available redox pairs. Metabolism is based on the ability to control the presence of these bio-catalysts [8]. Life elsewhere could extract energy in the same way from a variety of abiotically produced chemical disequilibria.

Typically in terrestrial biochemistry, $E_a(\text{no catalyst}) / E_a(\text{with catalyst})$ is greater than 10, so the choice of catalyst provides a strong control of the reaction rate [9]. When life was first emerging on Earth and the first catalysts were evolving, this ratio must have been ≈ 1 , and then gradually evolved to the much larger values (10 - 30) that are typical of catalysts used by biota today.

CONCLUSION: NO FREE ENERGY BOTTLENECK FOR E.T.

- Life elsewhere could extract energy from a variety of abiotically produced chemical disequilibria since both the ingredients and the free energy sources (redox or photon based) should be available at the atmosphere:rock-surface or the ocean:rock-surface interfaces on Mars, Titan, Europa and other exoplanetary systems [10].
- Energy sources based on redox gradients should be plentiful on rocky planets in circumstellar habitable zones because of the ubiquity of differentially oxidised minerals in the presence of water heated by radiogenic or convective sources in the first approximately 0.5 to 1 billion years of an active wet rocky planet. Over time, life would evolve new catalysts that give access to a wider range of redox pairs and photons, plausibly resulting in a remotely detectable atmospheric biosignature [11].

[1] Lineweaver CH & Chopra A (2012) The Habitability of Our Earth and Other Earths: Astrophysical, Geochemical, Geophysical, and Biological Limits on Planet Habitability. *Annu. Rev. Earth Planet. Sci.* 40:597–623 [2] Perotti CR & Rinaldi M (2011) Mars and Earth topography: a preliminary comparative analysis. *Mem. Soc. Astron. It.* 82:334–40 [3] Whitman WB, Coleman DC & Wiebe WJ (1998) Prokaryotes: the unseen majority. *Proc. Natl. Acad. Sci. USA* 95:6578–83 [4] Houghton RA (2003) The contemporary carbon cycle. In *Treatise on Geochemistry*, Vol. 8: Biogeochemistry, pp. 473–513. [5] Nisbet EG & Sleep N (2001) The habitat and nature of early life. *Nature* 409:1083–91 [6] Mitchell P (1961) Coupling of phosphorylation to electron and hydrogen transfer by a chemi-osmotic type of mechanism. *Nature*, 191, 144–148 [7] Shock EL & Holland ME (2007) Quantitative habitability. *Astrobiology*, 7, 389–851. [8] Nealson KH & Conrad PG (1999) Life: past, present and future. *Phil. Trans. R. Soc. Lond. B* 354, 1923–1939 [9] Quinn DM & Sikorski RS (2014) Enzymatic Rate Enhancements. eLS. [10] Lineweaver CH & Chopra A (2012) What can Life on Earth Tell Us about Life in the Universe? In Seckbach J. (Ed.), *Genesis - In The Beginning: Precursors of Life, Chemical Models and Early Biological Evolution*, 799–815, Springer. [11] Chopra A & Lineweaver CH (2015, *in prep.*) Estimates of the Universal Patterns of Biochemical Metabolism.

