THE ENERGETICS AND EVOLUTION OF METABOLISM ON EARTH AND ELSEWHERE. Aditya Chopra[1] and Charles H. Lineweaver[1], [1]Planetary Science Institute, Research School of Earth Sciences and Astronomy & Astrophysics, Australian National Univ., aditya.chopra@anu.edu.au, charley.lineweaver@anu.edu.au

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.

On Earth 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 ~4 billion years ago there was much less dry land and the terrestrial 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. Redox reactions in hydrothermal vents and hot springs probably played a dominant role in early metabolism, particularly since hydrothermal activity was more widespread [2]. The similar free energies of the earliest metabolic pathways and the availability of the reactants in environments such as hydrothermal vents 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 (Fig. 1).

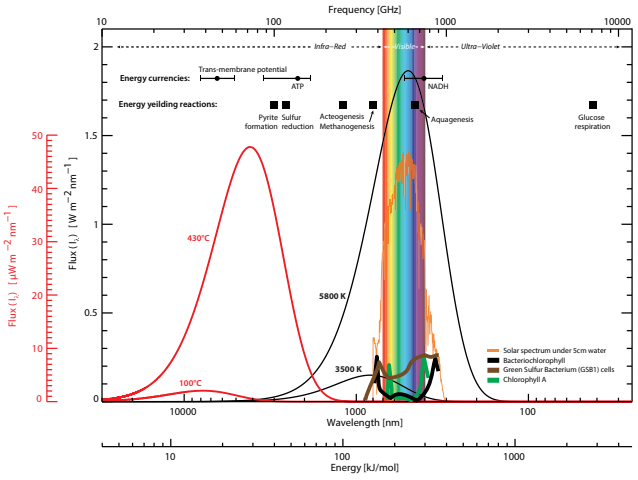

Fig. 1: Comparison of the photon and redox energy sources of early life with the dominant energy currencies of life [1].

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 [3]. These molecules are universal energy currencies and likely to have been adopted by the earliest organisms.

Note that the ΔGs of all redox reactions in Fig. 1, are above the peak energy of the 100°C ambient temperature of a hyperthermophile environment. Any redox reaction that is used by life must satisfy the constraint that the non-catalyzed activation energy must be higher than what is available as background energy in the environment [4]. Biological catalysts may reduce the activation energy such that the random thermal vibrational energy in the system drives the reaction forward in a controlled manner.

An upper limit for the temperature at which metabolic activity can take place is defined by the temperature at which the molecular dissociation of proteins and membranes takes place. We suggest that if solvents are required for biochemistry, then the temperature at which the solvent remains a liquid, will set the energies of the reactants, and the type of redox reactions that biological catalysts can control.

Life elsewhere could extract energy in the same way 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 [5]. In particular, energy sources based on a redox gradients should be plentiful on rocky planets in the CHZ because of the ubiquity of differentially oxidised minerals in the presence of water heated by radiogenic or convective sources in the first ~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.

References: [1] Lineweaver, C.H. & Chopra, A. (2012) *AREPS, 40,* 597–623. [2] Nisbet E.G. & Sleep N. (2001) *Nature*, 409, 1083-1091 [3] Mitchell P. (1961) *Nature*, 191, 144–148 [4] Shock E.L. & Holland M.E. (2007) *Astrobiology*, 7, 389-851. [5] Chopra, A. & Lineweaver, C.H. (2015, *in prep).*