

Thermodynamics of life on the planetary scale

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Abstract: The generation of organic matter from CO₂ and H₂O is a highly endothermic reaction. Energy for biological carbon fixation can be derived from chemical potential gradients in the environment by chemoautotrophic organisms or it can be harvested from photon energy by photosynthesis. On Earth, the plate tectonically driven carbon flux through the surface environment is of such a magnitude that the chemical free energy production within the Earth is insufficient to support conversion of any significant fraction of the carbon to organic matter through chemoautotrophy. Therefore, the chemical and isotopic fingerprints we observe in the Earth's surface environments are based on the invention of photosynthesis by life. We cannot *a priori* assume that life on any planet will invent photosynthesis and remote life detection should thus not be based exclusively on the expectations from our own ecosystem.

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Earth and the other terrestrial planets are dissipative systems in which heat energy is dissipated over time. The dissipation of heat has caused a steady production of entropy in the system which responded by the formation of chemical heterogeneities which consumed both heat and entropy in an attempt to minimize the rate of entropy production (Prigogine 1967).

The Earth and its sister planets probably accreted as initially more or less homogeneous bodies. During the dissipation of heat the planets have been differentiated into heterogeneous bodies composed of chemically distinct compartments. On Earth the compartments include the oceanic crust, the continents, the depleted mantle, the ocean and the atmosphere. We can regard the compartmentalization of the planets as side effects of the dissipation of heat and the efficiency of the compartmentalization process must be assumed to be controlled by the rate of energy translation in the system.

The planets were born with a finite inventory of nuclear, thermal and chemical energy, which is gradually translated to heat. The rate of nuclear energy translation to heat is exponentially decreasing with time as the radioactive mother nuclides decay. The thermal energy reservoir resulted from translation of potential and kinetic energy during accretion and core segregation. Some is stored as latent heat in the core, and released during crystallization and growth of the inner solid core at the expense of the outer liquid core. This thermal energy is released in response to the cooling of the Earth, and

the rate of heat production at any time is a function of the efficiency of the cooling process. Aside from the latent heat of the liquid core, the chemical energy inventory is difficult to evaluate. The metal part and some fraction of the volatiles are not thermodynamically miscible with the silicate parts of the terrestrial planets even at high temperatures, and some small energy contribution may have been released during unmixing immediately after accretion. However, local thermodynamic equilibrium prevails throughout the terrestrial planets except for thin interfaces between the core and the mantle, and the crust and the hydrosphere/atmosphere. During a steady state such as plate tectonic cycling, we can probably assume that there is no significant net release of chemical energy, because the negative heat of reaction during surface processes such as carbonation and hydration of silicate minerals is balanced by heat consumption during devolatilization, recrystallization or melting of surface materials upon return to the deep Earth.

The energy budget for a planet can be closely approximated by the heat flow, which is a measure of the integrated energy translations and is characterized by a number of nested processes which represent the mechanisms of heat transport. Both the partial melting of mantle material to form basalt and subsequent metamorphic reactions all form links in the heat transport chain that brings heat from the interior of the Earth towards space. At present the Earth's heat flow is $\sim 87 \text{ mW m}^{-2}$ (Stein 1995). Approximately 70–80% of this heat is derived from radioactive decay and the remaining part is drawn from the fossil heat capital (Kellogg *et al.* 1999). This is the energy that fuels the plate tectonic Earth machine,

and it has long been assumed that all the differentiation processes of Earth into different geochemical compartments were inherent effects of the plate tectonic cycles.

Compared to the meagre 87 mW m^{-2} internal energy for Earth and possibly Venus, and the even smaller budget for Mars, the planets receive enormous amounts of light energy at their surfaces. Earth is intersected by 340 W m^{-2} (Wells 1997) of solar energy which is partly scattered and partly converted to heat and back-radiated to space as longer-wavelength radiation. There is some spending of mechanical energy during this heating due to convective stirring of atmospheres and Earth's ocean, which drives erosion on the planetary surfaces. Most of the photons that irradiate the planetary surfaces are incapable of performing chemical work in the surface materials, because individual photon energies are less than the bond strengths of the surface chemical compounds. For example, a blue light photon possesses 298 kJ mol^{-1} photons while the oxygen–hydrogen bond of the water molecule has a strength of 492 kJ mol^{-1} .

With the invention of chlorophylls and photosynthesis by living organisms some time during the Archaean (Buick 1992; Nisbet *et al.* 1995; Des Marais 2000; Russel 2003; Falkowski *et al.* 2004; Olson & Blankenship 2004; Rosing & Frei 2004) the energy budget for Earth was suddenly changed. The concept of photosynthesis covers a broad range of metabolic pathways all of which bestow the capability of organisms to harvest light energy and convert it to chemical energy. The chemical energy is used to synthesize ATP (adenosine triphosphate) which can be utilized to produce organic matter from CO_2 and an electron donor. Photosynthetic organisms are thus able to build chemical potential gradients. In contrast, chemoautotrophic organisms derive the energy for their life activities from catalysing reactions that exploit already existing chemical potential gradients in their environment. In principle, chemoautotrophic organisms do not contribute to Earth's energy budget, since they derive their energy from accelerating the decay of chemical gradients, most of which would decay spontaneously anyway. The photoautotrophic energy harvest is expressed in the biogenic maintenance of chemical disequilibria in the environment. These disequilibria may have a profound effect on planetary evolution and can be distinguished on Earth in the strong oxidation of the surface environment, relative to the reducing mantle (Sleep 2005). On the present Earth, photoautotrophic carbon fixation converts $\sim 268 \text{ mW m}^{-2}$ of photon energy to chemical free energy. This biogenic energy flow is approximately three times greater than the 87 mW m^{-2} of energy dissipated in association with the heat flow. The profound differentiation of Earth's surface environment and the strong chemical disequilibrium between the atmosphere and the rock substrate is to a large extent caused by this phototrophic energy translation. It is plausible that the beginning stabilization of granite continents on Earth 850 million years after accretion of the planet was a response to this dramatic increase in the chemical free energy budget as a result of the emergence of photosynthetic organisms. The causative

link may have been a forcing of the weathering of basalt crust, which is an essential link in the chain of processes responsible for the formation of granite (Rosing *et al.*, in preparation).

Nucleosynthesis in stars determines the elemental and isotopic composition of protostellar nebulae, which probably develop with systematic relationships between nominally reducing and oxidizing components and between stable and radioactive nuclides. Likewise differentiation of the protostellar nebulae into planetary systems probably follows some common rules. The systematic evolution of planetary systems means that all the terrestrial planets in our Solar system must have limited internal free-energy production derived from radiogenic heat relative to their carbon inventories, and that Earth-like planets in general will have limited energy budgets. Therefore chemoautotrophic life will be very scarce on terrestrial planets, and possibly below the detection limit by remote observation, simply because there is not enough energy available to sustain extensive life activities from the internal heat sources. When searching for life on distant planets it must be borne in mind that the environmental impacts that distinguish life on Earth are based on the ability to perform photosynthesis, and that the most significant effect, the oxygenation of the atmosphere, is due to one particular metabolic pathway which evolved only once during the more than 3800 Myr of life's evolution on Earth. It is thus very possible that life can exist without expressing itself significantly in the chemical environment, until it acquires the ability to exploit photon energy.

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