Earth Syst. Dynam., 2, 37–51, 2011
www.earth-syst-dynam.net/2/37/2011/
doi:10.5194/esd-2-37-2011

Earth System Dynamics

Thermodynamic dissipation theory for the origin of life

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Received: 9 February 2010 – Published in Earth Syst. Dynam. Discuss.: 4 March 2010
Revised: 27 July 2010 – Accepted: 24 February 2011 – Published: 11 March 2011

Abstract. Understanding the thermodynamic function of life may shed light on its origin. Life, as are all irreversible processes, is contingent on entropy production. Entropy production is a measure of the rate of the tendency of Nature to explore available microstates. The most important irreversible process generating entropy in the biosphere and, thus, facilitating this exploration, is the absorption and transformation of sunlight into heat. Here we hypothesize that life began, and persists today, as a catalyst for the absorption and dissipation of sunlight on the surface of Archean seas. The resulting heat could then be efficiently harvested by other irreversible processes such as the water cycle, hurricanes, and ocean and wind currents. RNA and DNA are the most efficient of all known molecules for absorbing the intense ultraviolet light that penetrated the dense early atmosphere and are remarkably rapid in transforming this light into heat in the presence of liquid water. From this perspective, the origin and evolution of life, inseparable from water and the water cycle, can be understood as resulting from the natural thermodynamic imperative of increasing the entropy production of the Earth in its interaction with its solar environment. A mechanism is proposed for the reproduction of RNA and DNA without the need for enzymes, promoted instead through UV light dissipation and diurnal temperature cycling of the Archean sea-surface.

1 Introduction

Only 27 years after the publication of "On the Origin of Species" (Darwin, 1859), Boltzmann (1974) recognized that the struggle for existence was not a struggle for raw material, neither for energy, but rather a struggle for entropy (low entropy) which became available through the dissipation of high energy photons to low energy ones (entropy production) through irreversible processes occurring within the biosphere. It is now well established that non-equilibrium structuring of matter in space and time – from molecules to hurricanes to living systems – is contingent on entropy production (Prigogine, 1967; Prigogine et al., 1972). Such irreversible processes are known as "dissipative structures" since, although they exist at low entropy, they arise spontaneously to provide new pathways to a greater sampling of the enormous multitude of microstates that underlie Nature and, thus, their formation increases the entropy of the Universe.

Onsager (1931) has shown how diverse irreversible processes can couple in order to remove impediments to greater global entropy production (Morel and Fleck, 1989). In general, the more complex the dissipative structuring in space and time (i.e. involving many coupled irreversible processes with embedded hierarchal levels and interactions of long spatial and temporal extent) the greater the overall entropy production in the systems interaction with its external environment (Onsager, 1931; Prigogine et al., 1972; Lloyd and Pagels, 1988).

Empirical evidence from the fossil record of the evolutionary history of Earth indeed suggests that living systems, from cells to the biosphere, have generally increased in complexity over time, and correspondingly, there has been an increase in their total entropy production, as well as in the net entropy production per unit biomass (Zotin, 1984). Onsager's principle, and variations thereof, have been useful in describing the existence and stability of abiotic and biotic dissipative systems on Earth (Lorenz, 1960; Paltridge, 1979; Ulanowicz and Hannon, 1987; Swenson, 1989; Kleidon and Lorenz, 2005; Michaelian, 2005; Martyusheva and Seleznev, 2006; Kleidon, 2009).

The ubiquity of the empirical evidence suggesting that Nature tends to find new abiotic, biotic, and coupled abiotic-biotic pathways to entropy production, is taken here as sufficient justification for the proposition that RNA and DNA, and their coupling to the water cycle, arose originally as

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structuring of material in space and time to provide a new route to augmenting the entropy production of the Earth in its interaction with its prebiotic solar environment.

The nucleic acids RNA and DNA are efficient absorbers of photons in the 200–300 nm ultraviolet region of the Sun's spectrum (Chang, 2000); just that important part of the spectrum which could have filtered through the early Earth's dense atmosphere. These molecules, in the presence of water, are extraordinarily rapid at dissipating the high energy photons to heat. It is then plausible that life arose as a catalyst for absorbing sunlight at the surface of the shallow seas, dissipating it into heat and, thereby promoting still other irreversible processes such as the water cycle (evaporation/rain), and wind and ocean currents, all of which contribute to the entropy production of the biosphere (Peixoto et al., 1991; Kleidon 2009). This suggests a thermodynamic imperative for an origin of life which can be related to its thermodynamic function of entropy production (Michaelian, 2009, 2011).

Prevailing scenarios for the origin of life center on the replication first "RNA World" (Gilbert, 1986) hypothesis (see Orgel, 2004, and Rauchfuss, 2008, for a review), and "metabolism first" followed by replication proposals (see Shapiro, 2007, for a review) including hydrothermal vent proposals (Wächtershäuser, 2006; LaRowe and Regnier, 2008; Nitschke and Russell, 2009). The scenario presented here is more akin to the RNA World hypothesis but shares with the metabolism first theories the idea of a gradual genetic take-over of a metabolic process. However, replication and metabolism are linked from the very beginning; the first molecules of life, RNA and DNA, are suggested to be UV light metabolizing photoautotrophs.

From within the framework of the "RNA World", Orgel (2004) recognizes several severe problems related to low yields in the individual steps of RNA synthesis and replication but is cautiously optimistic with regard to the abiogenic synthesis of RNA, suggesting that other, undiscovered, routes to these molecules may eventually be found. The most difficult current problems with abiogenisis are; (1) the production and stability of ribose competing with other more easily synthesized and more stable sugars, (2) the difficulty of the polymerization of nucleotides to form polynucleotides, (3) the problem of the racemic mixture of chiral nucleotides frustrating the template-directed copying of polynucleotides and, perhaps the most difficult, (4) the replication of RNA without the assistance of enzymes.

The theory presented here offers a consistent framework within which each of the above mentioned difficulties is alleviated. It recognizes a non-equilibrium thermodynamic imperative for producing RNA and DNA, irrespective of the difficulty of producing these in the laboratory, due to the great entropy producing potential of these molecules given the initial conditions of the primitive Earth; a high flux of UV photons and a high sea-surface temperature. Considering these thermodynamic forces not only alleviates the difficulty with the abiogenic yields of the primary molecules of life but, at the same time, provides an UltraViolet and Temperature Assisted mechanism for Reproduction (UVTAR) of RNA and DNA, without the need for enzymes.

2 Ambient conditions of insipient life

Since life obtains its vitality only in the context of its interaction with its external environment, establishing the ambient conditions of the primitive Earth is essential to any theory on the origin of life. It has been hypothesized that the early Earth's seas, existing at the very beginnings of life some 3.8 billion years ago (Schidlowski et al., 1983; Schidlowski, 1988), were hot (Knauth and Lowe, 2003) soups of organic material. Inspired by Oparin's (1924) materialistic ideas on the origin of life, Miller and Urey (1959) experimentally tested and confirmed the idea that the organic molecules could have been created by lightning strikes and photochemical reactions on a reducing Archean atmosphere containing much hydrogen in the form of ammonia (NH_3) and methane (CH_4). Oró (1961) and Oró and Kimball (1962) have demonstrated that all the nucleic acid bases can be obtained by mixing hydrogen cyanide (HCN) with cyanogen (C_2N_2) and cyanoacetylene (HC_3N) in an aqueous solution (see also Matthews, 2004). These precursor cyano-molecules are common products of a reducing atmosphere subjected to UV photons (Stribling and Miller, 1987; Orgel, 1994).

An alternative hypothesis is that organic molecules are formed in circumstellar envelopes of stars which shed much of their early atmospheres into interstellar space (Hoyle and Wickramasinghe, 1978; Kwok, 2004). In corroboration, it has been found that cosmic regions of high organic molecular densities are often associated with regions of stellar formation (Ehrenfreund and Charnley, 2000). Over 140 organic molecules have now been found in space, although the nucleobases have yet to be detected (Kwok, 2009). The dispersed organic molecules are then suggested to have been deposited into the Earth's oceans through the vehicle of colliding comets, asteroids, or space dust. Amino acids and nucleobases have been found in carbonaceous chondrite meteorites, believed to be derived from comets, such as the Murchinson meteorite (Martins et al., 2008).

Both theories for the origin of the original organic materials are thus viable and supported by empirical evidence, but which of the two theories is the most plausible in rendering the high concentration of organic molecules required in the original soup depends on how reducing the atmosphere was at the beginnings of life, a topic still highly debated with new insights often changing the balance (Sagan and Chyba, 1997; Tian et al., 2005; Cleaves et al., 2008). For example, recent analysis by Tian et al. (2005) indicates that the Earth's early atmosphere may have been colder than originally assumed and, thus, could have retained up to 30% hydrogen by mass. In this case, the most likely scenario would have been the production of organic molecules through lightning and

photochemical reactions on H_2 and CO_2 rather than on the ammonia and methane atmosphere assumed in the original Miller experiments (Tian et al., 2005). Cleaves et al. (2008) have shown that even in a very neutral atmosphere, the abiogenic yields of the amino acids can be increased by up to two orders of magnitude if oxidation inhibitors, such as ferrous iron, are present.

It is generally believed that Earth's early atmosphere was perhaps twice as dense as today (Walker, 1977, 1983, 1985), and containing a similar amount of nitrogen as today, but significantly greater amounts of CO_2 and water vapor, perhaps some ammonia and methane, and probably hydrogen (Cnossen et al., 2007; Haqq-Misra et al., 2008).

Both the composition and density of the early Earth's atmosphere have relevance to the spectrum of sunlight that could have penetrated to the Earth's surface. CO_2 has a very large photon extinction coefficient at wavelengths shorter than approximately 202 nm (at one atmosphere and 295 K). For longer wavelengths it is found that the optical extinction demonstrates a $1/\lambda^4$-like behavior typical for Rayleigh scattering (Ityaksov et al., 2008). Water vapor absorbs strongly in the ultraviolet below approximately 170 nm, and strongly in the infrared above about 1000 nm, but is basically transparent between these limits (Chaplin, 2009). Ammonia, NH_3, also absorbs strongly below 200 nm.

The early Earth was probably much more volcanically active than it is today due to the internal heat of accretion, asteroid bombardment and a higher internal radioactivity. The most important components of volcanic out-gassing are carbon dioxide CO_2, sulfur dioxide SO_2, and water vapor H_2O. Sulfur dioxide has a photon absorption cross section that is large at wavelengths less than 225 nm with a smaller absorption peak at 290 nm at 1 atmosphere and 295 K (Rufus et al., 2003). As in the case of present day Venus, photochemical reactions on carbon dioxide, sulfur dioxide and water vapor can produce sulfuric acid which condenses in a cold upper atmosphere to produce a fine aerosol that is highly reflective in the visible region of the Sun's spectrum. Venus has a thin layer of sulfuric acid cloud at a height of around 70 km giving the planet an albedo of 0.77 in the visible and leaving the day-time surface of the planet in considerable darkness (similar to a very dark overcast day on Earth). However, the sulfuric acid clouds do not scatter as strongly in the ultraviolet as in the visible (Shimizu, 1977), a fact made evident by the observation of Venus in the ultraviolet by Franck E. Ross in the 1920's, which finally revealed a structure in the cloud cover of the planet. Such a layer of reflective sulfuric acid clouds probably existed on the early Earth. It is known, for example, that a single strong volcanic eruption on Earth can decrease the global temperature by as much as 0.7 °C for several years due to an increase in albedo in the visible region (Stothers, 1984).

Water vapor and dense clouds of water on the hot early Earth, although reflecting uniformly over all wavelengths (hence the whiteness of clouds) would have absorbed preferentially in the infrared region of the solar spectrum.

The early Sun was more active due to a higher rotation rate and its spectrum was probably more intense than it is now in the ultraviolet (Tehrany et al., 2002) and up to 25–30% less intense in the visible (Sagan and Chyba, 1997). A larger magnetic field, due to a higher rotation rate, would mean that gamma and X-ray bursts would also have been much more prevalent and, through degradation in the Earth's atmosphere, would have lead to an additional important component of ultraviolet light on the Earth's surface. A near-by massive star producing up to 10^{10} the amount of UV light as the Sun could also have been an important contributor to the UV flux on Earth (Zahnle et al., 2007).

With the water vapor and clouds absorbing strongly in the infrared and the clouds of sulfuric acid reflecting strongly in the visible, and carbon dioxide, water, and ammonia absorbing strongly in the ultraviolet below about 200 nm and sulfur dioxide absorbing below 225 nm, it is probable that an enthropically important part of the Sun's spectrum reaching the surface of the Archean Earth was that in the ultraviolet between approximately 200 nm to 300 nm.

By considering the probable existence of hydrogen sulfide, being the thermodynamically stable sulfur-containing gas under reducing conditions, and the probable formation of aldehydes (formaldehyde and acetaldehyde) through UV photochemical production, Sagan (1973) calculated a somewhat reduced window of transparency of between 240 and 290 nm.

Cnossen et al. (2007) have carried out detailed simulations of photon absorption and scattering for various hypothetical models of the Earth's early atmosphere. Their models consider different CO_2 concentrations at different pressures and include absorption, Rayleigh scattering, and an estimate of the effects of multiple scattering, besides taking into account the best estimates for the increase in UV intensity expected for a young Sun. Their conclusions are that the Earth's surface during the Archean (4–3.5 Ga) was subjected to ultraviolet radiation within the 200 nm to 300 nm region of up to 10^{31} times (at 255 nm) that of present. This is not surprising since today less than one part in 10^{30} of the incident solar radiation at 250 nm penetrates the Earth's ozone and O_2 atmosphere (Chang, 2000).

The question has arisen as to whether this intense ultraviolet light had a detrimental effect; through photolysing, prejudicial photochemical reactions, and too large informational mutation rates (Biondi et al., 2007), or beneficial effect; through promoting necessary photochemical reactions, such as abiogenic synthesis of the nucleic acid bases, ribose and other carbohydrates (Schwartz, 1995), as well as a favorable selective pressure (Sagan, 1973), on the first molecules of life (Cockell, 1998; Cnossen et al., 2007; Martín et al., 2009). It is argued below, that, apart from inducing useful photochemical reactions and providing favorable selective pressure, ultraviolet light was crucial to the origin of life

for another reason; RNA and DNA are unparalleled ultraviolet light absorbing molecules (photon extinction coefficient of $13\,000\,M^{-1}\,L\,cm^{-1}$ at peak absorption at 260 nm) which, in the presence of water, convert this light rapidly into heat (Middleton et al., 2009) thereby promoting evaporation. The replication of RNA and DNA on the sea-surface would thus have been thermodynamically favored in the intense UV light environment of early Earth since, by coupling to the water cycle, it supplied a new route to greater entropy production (Michaelian, 2009, 2011).

3 The sea-surface and entropy production

The sea-surface skin layer, of a thickness of 1 mm, being the region of mass, energy and momentum transfer with the atmosphere (Hardy, 1982; Soloviev and Lukas, 2006), is of particular importance to the theory presented here. The upper 50 µm of this layer (the microlayer) hosts an ecosystem of a particularly high organic density, up to 10^4 the density of that in water only slightly below (Hardy, 1982; Grammatika and Zimmerman, 2001). The organic material consists of cyanobacteria, diatoms, viruses, free floating RNA and DNA and other living and non-living organic material such as lipids, aldehydes, chlorophyll and other pigments. A high enrichment of trace metals, so important to many biological molecules, is also found in the microlayer (Hardy, 1982). The high density of material at the surface is attributed to natural buoyancy and surface tension, but most notably to the scavenging action of rising air bubbles from breaking waves and rain drops (Grammatika and Zimmerman, 2001; Aller et al., 2005).

The sea-surface skin layer, in particular the microlayer, is subject to strong diurnal variations in temperature, salinity, pH, and concentrations of aldehydes and other organic molecules as a result of photochemical and photobiochemical interactions at the air-sea interface (Zhou and Mopper, 1997; Wootton et al., 2008).

Most of the heat and gas exchange between the ocean and the atmosphere of today occurs from within the skin layer. The emitted infrared radiation from the sea originates from within the upper 100 µm (Soloviev and Schlüssel, 1994).

During the day, infrared (700–10 000 nm), visible (400–700 nm), and ultraviolet (290–400 nm) light is absorbed at the sea-surface. Pure water has a low absorption coefficient for visible and near-UV light, as can be surmised from its transparency at these wavelengths. However, the organic and inorganic material at the sea-surface alters its optical properties such that an important part of the total energy absorbed in the skin comes, in fact, from visible and UV light. Although, to the authors knowledge, no measurements of the optical density of the sea-surface skin layer have yet been published, an estimate can be made given the fact that the sea-surface microlayer has a density of organic material roughly 10^4 that of water slightly below (Grammatika and Zimmerman, 2001), which is somewhat greater than the ratio of that for very turbid coastal waters to deep ocean water (Wommack and Colwell, 2000). Using, as a surrogate, the largest frequency dependent absorption coefficient measured for turbid coastal waters of Bricaud et al. (1981) and assuming the solar spectrum at the Earth's surface for cloudless skies (Gates, 1980), one can calculate that the organic material in the sea-surface skin layer augments the absorption of energy in this layer by about 13.3% (9.1% attributed to 290–400 nm UV absorption, 4.2% attributed to 400–700 nm visible absorption) over that of pure water, which absorbs predominantly in the infrared (Michaelian, 2010a). Under cloudy skies, or atmospheres of high water vapor content (the probable condition on prebiotic Earth), infrared light is blocked and the effect of organic material is much more important, increasing the energy absorption in the sea-surface skin layer by a remarkable 400% (200% UV, 200% visible) (Michaelian, 2010a).

Absorption of infrared, visible, and UV light at the sea-surface today increases the daytime temperatures at the skin surface by an average of 2.5 K (up to 4.0 K) relative to the practically constant temperature at a depth of 10 m (Schlüssel et al., 1990). Night time temperatures, on the other hand, are reduced on average by 0.5 K (up to 0.8 K) due to evaporation, radiation, and conduction to the colder atmosphere. Cyanobacterial blooms have been shown to cause considerable additional heating of the sea-surface (Kahru et al., 1993). The effect of a nutrient enriched phytoplankton bloom on the energy exchange at the surface of a lake has been quantified by Jones et al. (2005). They found a 1.8 K increase in the daytime surface temperature of the lake.

Simulations by Gnanadesikan et al. (2010) using coupled climate models indicate that chlorophyll-dependent solar heating has a first-order impact on the spatiotemporal distribution of tropical cyclones. Not only the location of the cyclone, but both frequency and intensity are affected by chlorophyll surface concentration.

Since the accumulation of organic material at the sea-surface is attributed to surface tension, natural buoyancy and the scavenging effect of rising bubbles, it is reasonable to assume that an organically rich surface skin layer would also have existed in prebiotic oceans. An estimate of the optical density of the skin layer in the Archean can be made by assuming concentrations of $1.5 \times 10^{-5}\,M\,L^{-1}$ for the nucleic acid bases, based on estimates by Miller (1998) obtained from calculations by Stribling and Miller (1987) of photochemical production rates of prebiotic organic molecules under somewhat reducing conditions. Although these concentration estimates have since been considered as optimistically large, the recent discovery of new non-equilibrium abiogenic routes to these molecules (see below, and Powner et al., 2009), and the possibility of oxidation inhibitors increasing yields substantially in a more neutral atmosphere (Cleaves et al., 2008), plus the existence of an organically enriched sea-surface skin layer, may, in fact, imply that

they are underestimates. Using measured photon extinction coefficients of the bases of around $13\,000\,\mathrm{M}^{-1}\,\mathrm{L\,cm}^{-1}$ at 260 nm (Chang, 2000), leads to an absorption coefficient of $0.78\,\mathrm{cm}^{-1}$. Using the Archean solar spectrum at the Earth's surface as determined by Cnossen et al. (2007), the above determined UV absorption coefficient, and that of today for the visible (probably an overestimate since pigments in the visible such as chlorophyll did not exist in prebiotic oceans), leads to an increase in the energy absorbed in the Archean sea-surface skin layer due to the nucleic acid bases and other organics, over that of pure water, of about 19% (11% attributed to 200–300 nm UV absorption, 8% attributed to 400–700 nm visible absorption) for a cloudless day, and a remarkable 490% (260% UV, 230% visible) for an overcast day, or for an atmosphere with high water vapor content (Michaelian, 2010a).

Increased absorption of high energy photons at the Archean sea-surface due to organic material would imply lower albedo and an increase in the size of the water cycle. Today, about 46% of the incoming solar radiation is absorbed at the surface of the Earth. About 53% of this absorbed radiation is re-emitted into the atmosphere in the form of latent heat through evaporation and transpiration, while emitted long-wave radiation accounts for 32%, and direct conduction 15%. Water vapor, on reaching the cloud tops condenses, releasing its latent heat of condensation in a black-body spectrum at $-14\,^{\circ}\mathrm{C}$ (Newell et al., 1974). Without organic material at the sea-surface, more photons would be reflected, increasing the albedo, or penetrate deeper into the ocean, augmenting the bulk temperature of the oceans while leaving less heat available at the surface for evaporation. More energy would then be emitted by the Earth as long-wave radiation in a spectrum corresponding to the temperature of the ocean surface of about $18\,^{\circ}\mathrm{C}$, rather than at the lower temperature of the cloud tops, implying less global entropy production. Terrestrial ecosystems would also become less efficient at photon dissipation with less water in the global water cycle. Incident angle and frequency dependent albedo for sunlight on ocean water of today has been measured by Clarke et al. (1970) and Jin et al. (2004). They find that organic material in ocean water reduces the albedo at all incident angles and wavelengths and that this effect increases significantly towards the shorter wavelengths of the ultraviolet.

4 Abiogenic synthesis of the molecules of life

A central problem with all theories on the origin of life has been the difficulty in demonstrating efficient abiogenic reaction pathways for producing high yields of the primary molecules of life (Orgel, 2004). High yields are important since the half-lives of these molecules are relatively short at high temperature, on the order of hours for ribose, and years or days for nucleic acid bases ($t_{1/2}$ for A and $G \approx 1\,\mathrm{yr}$; $U \approx 12\,\mathrm{yr}$; $C \approx 19\,\mathrm{days}$ at $100\,^{\circ}\mathrm{C}$; Levy and Miller, 1998). Many of these molecules require chemical reactions which are "uphill", corresponding to overall positive changes in the Gibb's free energy, while others have large activation barriers that require special enzymes in order to proceed. Near equilibrium pathways to these molecules have been found but do not lead to high yields.

Prigogine (1967), however, has shown that the yield of a product of a chemical reaction can be increased enormously over its expected near-equilibrium value by coupling the nominal reaction to other entropy producing irreversible processes (Chang, 2000). Irreversible processes can be coupled as long as the net production of entropy is positive and Curie's principle is respected; macroscopic causes must have equal or fewer elements of symmetry than the effects they produce. For example, a chemical reaction (scalar) cannot give rise to a directed heat flow (vector). These routes, under far from equilibrium conditions, have scarcely been explored and may offer alternative pathways to efficient abiogenisis (Wicken, 1978, 1979; Pulselli et al., 2009).

For example, the second difficulty mentioned by Orgel (2004), the polymerization of polynucleotide from mononucleotides is an endergonic reaction (positive free energy change) which will not proceed spontaneously. However, this reaction can be coupled with a second irreversible process, the absorption and dissipation of a high energy photon, such that the overall reaction is exergonic (negative free energy change). McReynolds et al. (1971) have shown that the polymerization of oligonucleotides occurs under the action of UV light on an aqueous solution of nucleoside phosphates. Such coupled photochemical reactions would have been prevalent at the beginning of life given the great amount of UV light reaching the Earth's surface. Spontaneous polymerization of polynucleotide under UV light is entropy driven since single strand RNA and DNA in water is more efficient (rapid) in quenching the excitation energy of the absorbed UV photon directly to the ground state through vibrational cooling than are single (particularly pyrimidine) bases, which lose efficiency by decaying to longer lived $^1n\pi^*$ states about 40% of the time (Middleton et al., 2009).

Another important characteristic of ultraviolet light is that it can readily destroy other organic molecules that have the potential for either catalyzing the break-down of RNA and DNA, or for competing for reactants needed for their synthesis. For example, Powner et al. (2009) have found a promising new route to pyrimidine ribonucleotide production, bypassing the difficult production of ribose (the first problem mentioned by Orgel) and free pyrimidine nucleobases, by employing UV light (254 nm) and a heating and cooling cycle to enhance ribonucleotide synthesis over other less endergonic products.

Other experimental data also support the assertion that the prevalent conditions on Archean Earth – intense UV light, high temperature, and temperature cycling – relieve the problem of the low yield of nucleotide synthesis. Ponnamperuma

et al. (1963) have reported the detection of small amounts (0.01%) of adenosine when a 10^{-3} M solution of adenine, ribose and phosphate was irradiated with UV light. Folsome et al. (1983) report on anoxic UV photosynthesis of uracil, various sugars, including deoxyribose, and amino acids. Kuzicheva and Simakov (1999) have shown that much larger yields ($\sim$4%) of nucleotides can be synthesized by including temperature cycling along with UV light. Their data were obtained by flying basic compounds on board a spacecraft exposed to the UV and gamma environment of space. The rotation of the spacecraft caused temperature cycling, an effect to which they attribute higher yields than obtained in their laboratory experiments with only UV light.

Finally, even though some reactions on the road to nucleotide synthesis may be exergonic, their rates may be very low due to large activation barriers. In this case, yields may be considerably increased by augmenting the temperature (Ponnamperuma and Mack, 1965; de Graaf and Schwartz, 2005) or employing catalysts, such as enzymes.

The thermodynamic forces of intense UV radiation and temperature cycling not only appear to alleviate the difficulty with yields of the primary molecules, but are essential to a proposed mechanism of ultraviolet and temperature assisted reproduction of RNA/DNA without the need for enzymes.

5 UV and temperature assisted RNA and DNA reproduction

It is generally believed that RNA preceded DNA in life's evolutionary history (RNA World hypothesis; Gilbert, 1986). This belief is based in part on the fact that, because it is less stable, RNA exists more often in single strand and shorter length segments than DNA, and can, therefore, fold in on itself or pack together to form three dimensional structures akin to proteins, which, under certain conditions, can catalyze chemical reactions. For example, the active surfaces of ribosomes, the molecular machinery of the cell where proteins are made, consist of RNA known as ribosomal RNA (rRNA). An important catalytic activity of rRNA, which points to RNA as the first molecule of life, is its demonstrated ability to catalyze peptide bonds between amino acids to form proteins (Chang, 2000). In fact, it is becoming apparent that RNA has many extraordinary characteristics pointing to its pioneering status (Spirin, 2002). DNA, on the other hand, is less poly-faceted and lacks a hydroxol group on its ribose sugar, allowing it to obtain its full three-dimensional conformation and to coil up to fit within the nucleus of more modern eukaryote organisms, suggesting relevance to life at a later date. It has, therefore, been reasonable to presume that RNA preceded DNA. However, both molecules are produced with similar abiogenic yields in vitro and both appear to have similar ultraviolet absorbing and dissipating characteristics. Therefore, within the present framework, there is no overwhelming reason why DNA could not have replicated con-temporarily alongside RNA, performing the same function of catalyzing the water cycle and entropy production through UV light absorption and dissipation. The two molecules eventually forming a symbiosis allowing new possibilities for more efficient reproduction and evolution, and correspondingly, greater entropy production.

The two naturally occurring molecules RNA and DNA will, thus, be treated here on equal footing by denoting both inclusive possibilities as "RNA/DNA", while acknowledging that future data may favor one over the other as the first molecule of life in the context of the proposed theory. Simpler synthetic molecules, postulated as pre-RNA candidates, such as PNA, TNA and GNA (Egholm et al., 1993), do not occur naturally and, therefore, probably have little to do with photon absorption and dissipation in the biosphere.

At temperatures above 90 °C (at one atmosphere and pH 7), almost all of double strand RNA or DNA is denatured into flexible single strands (Haggis, 1974). At lower temperatures, the amount of denaturing depends on the relative proportion of $G-C$ base pairs, the length of the strand, the pH of the solvent (very low and very high pH correlates with more denaturing; Williams et al., 2001), and the salt concentration (higher salt concentration correlates with less denaturing). RNA has generally lower denaturing temperature than similar length DNA. Random nucleotide sequences and smaller length segments also have lower denaturing temperature. For example, random RNA formed from equal concentrations of A, G, C, and U has a melting temperature (defined as that temperature at which half of the double strands are denatured) of 50 °C, while calf thymus DNA has a melting temperature of 87 °C (Haggis, 1974). At the higher atmospheric pressures thought to have existed at the beginning of life (up to twice the present value) these denaturing temperatures may have been somewhat higher.

At the high temperatures of the surface of the seas existing before the beginnings of life on Earth, the nucleotides probably floated independently, unable to stack through Van der Waals and hydrophobic interactions, or pair conjugate through hydrogen bonding, because of their large Brownian motion. However, the Earth's surface gradually began to cool, and when the sea-surface temperature cooled to below that of the melting temperature of RNA or DNA (relevant to the local prevailing ambient pressure, pH, and salinity) a phenomenon, which may be called "ultraviolet and temperature assisted RNA/DNA reproduction" (UVTAR), could have occurred.

One estimate has the surface temperature of the Earth descending below 100 °C about 4.4 billion years ago (Schwartz and Chang, 2002). Giant impacts, extending into the "late lunar bombardment era" of ca. 3.9 Ga, may have periodically reset ocean temperatures to above the boiling point (Zahnle et al., 2007). There is geochemical evidence in the form of $^{18}O/^{16}O$ ratios found in cherts of the Barberton greenstone belt of South Africa indicating that the Earth's surface temperature was around 80 °C at 3.8 Ga (Knauth, 1992; Knauth

and Lowe, 2003), falling to $70 \pm 15\,^{\circ}\mathrm{C}$ during the 3.5–3.2 Ga era (Lowe and Tice, 2004). These surface temperatures, existing at the beginnings of life (ca. 3.8 Ga), are suggestively close to the denaturing temperatures of RNA/DNA.

During daylight hours, the water at the Archean sea-surface absorbed some solar infrared light, and the aromatic bases of RNA/DNA and amino acids absorbed solar ultraviolet light, while other organic molecules absorbed visible light. It is then probable that the sea-surface skin temperature in the local neighborhood of the RNA/DNA would heat up beyond the denaturing temperature and these would separate into single strands by breaking the hydrogen bonds between conjugate base pairs.

RNA/DNA strongly absorb ultraviolet radiation at around 260 nm at 1 atmosphere pressure (Haggis, 1974; Chang, 2000) due to the $^1\pi\pi^*$ electronic excitation of the bases (Voet et al., 1963; Callis, 1983). The relaxation to the ground state of UV excited DNA has been studied in detail by Middleton et al. (2009, and references therein). An ultra-fast, sub-picosecond, decay of the $^1\pi\pi^*$ excited state is observed for the unstacked bases in single strand RNA/DNA through vibrational cooling to the ground state by coupling to the high frequency modes of the water solvent (Pecourt et al., 2000, 2001). Water appears to be the most efficient of many tested solvents (Middleton et al., 2009). Such ultra-fast de-excitation does not appear to exist for stacked bases in double strand RNA/DNA, which normally form long-lived, 100-picosecond, exciton states. This may be partly due to the fact that hydrophobic interactions exclude water from the interior of stacked double strand RNA/DNA (Pecourt et al., 2000, 2001).

It has been suggested that these surprising characteristics are not fortuitous, but rather remnants from earlier days when life was exposed to significantly higher doses of UV radiation. The argument is that these characteristics would have been favored by natural selection since such a highly efficient non-radiative decay significantly lowers the rate of RNA/DNA damage through photo-reactions, thereby reducing the need for frequent repair (Crespo-Hernández et al., 2004; Middleton et al., 2009).

Sagan (1973) pointed out that the rapid UV photon dissipation characteristics of nucleic acid bases would provide an important selective advantage to RNA and DNA over other more easily synthesized organic molecules under the harsh UV conditions of prebiotic Earth. Mulkidjanian et al. (2003) have confirmed this using simple Monte Carlo simulations. However, the interpretation given here of these surprising absorption and relaxation characteristics of RNA/DNA is more profound; apart from conferring stability to these molecules under intense UV radiation, these characteristics confer remarkable entropy producing potential to these molecules due to the efficient absorption of UV light and its rapid dissipation into heat.

As night came, with no light to absorb, the surface of the sea would cool through evaporation, radiation, and conduction of heat to the atmosphere, to a temperature below which the single strands of RNA/DNA could begin to act as templates and hydrogen bond through their bases with conjugate nucleotides or oligonucleotide segments floating nearby. New, complementary double-strand RNA/DNA would thus be formed at the sea surface during the cool periods overnight. An alternative form of cooling of the ocean surface may have been provided by hurricanes which are known to have an important effect on reducing the surface temperatures of seas (Manzello et al., 2007). Given the high sea-surface temperatures existing on early Earth, and a cold upper atmosphere (Tian et al., 2005), hurricanes would have been much more prevalent than at present.

As the Sun rose, about 7 h after setting (the rotation of the Earth was more rapid 3.8 billion years ago) the sea-surface skin layer would again heat up through the absorption of ultraviolet and visible light on the organic material, and the absorption on water of some infrared light that could penetrate the clouds and water vapor in the atmosphere. Using the Archean solar intensity spectrum at the Earth's surface as determined by Cnossen et al. (2007) and the absorption coefficient for UV light between 200 nm and 300 nm of $0.78\,\mathrm{cm}^{-1}$ determined from estimated prebiotic concentrations of the nucleic acids (Miller, 1998; see Sect. 3), while assuming similar absorption in the visible as that of today's oceans of $8.0 \times 10^{-3}\,\mathrm{cm}^{-1}$, and that the diffuse downward and upward long-wave energy flux approximately cancel (Webster, 1994) it can be estimated that diurnal temperature cycling at the Archean sea-surface skin layer could have had an amplitude as large as 4 K (Michaelian, 2010a). Schlüssel et al. (1990) have measured a diurnal temperature variation at the skin surface of today's oceans as large as 5 K.

Direct absorption of a UV photon of 260 nm on RNA/DNA (which occurs preferentially on one or two of the nucleic acid bases; Middleton et al., 2009) would leave 4.8 eV of energy locally which, given the heat capacity of water, would be sufficient energy to raise the temperature by an additional 3 K of a local volume of water that could contain up to 50 base pairs (Michaelian, 2010a). Given that the full width of the denaturing curve for RNA/DNA is between 4 and 10 K (depending on the $G-C$ content) the sea-surface temperature in the neighborhood of the segment which absorbed the UV photon would be raised again beyond the denaturing temperature of RNA/DNA and the double strand would separate, providing, in this way, a new generation of single strand RNA/DNA that could serve as new template for complementary strand polymerization during the subsequent cool period. Experimental evidence (Hagen et al., 1965; Roth and London, 1977) indicates that UV irradiation does indeed induce denaturation of DNA held in water baths at a fixed temperature, and that the denaturing effect of UV light increases as the temperature of the bath approaches DNA melting temperature.

A temperature assisted mechanism for RNA/DNA reproduction is not hypothetical; the procedure of repetitive

heating and cooling is a process known as polymerase chain reaction (Mullis, 1990) that is used today in the laboratory to amplify exponentially a particular DNA or RNA segment of interest. The enzyme polymerase is used to speed up the polymerization of nucleotides on the single strand templates during the low temperature period.

Ultraviolet and temperature assisted RNA/DNA reproduction would have been enhanced by a number of natural phenomenon. First, single strand RNA/DNA absorbs from 20% to 40% more ultraviolet light than does double strand. This effect, known as hypochromism (Bolton and Weiss, 1962; Chang, 2000), is related to the orientation of the electric dipoles of the bases, stacked in fixed relation one above the other in the double helix. On denaturation, the orientation of the dipoles is random and the absorption intensity increases. Double strand RNA/DNA is also less efficient (rapid) at transforming the electronic excitation energy into heat than single strand randomly stacked DNA (Middleton et al., 2009). Both these effects would provide positive feedback for augmenting entropy production by stimulating denaturation under solar UV light and by reducing the possibility of recombination of the separated strands.

A second class of phenomena that could have enhanced UVTAR is the diurnal variation of the chemical properties of the sea-surface microlayer. Both the pH and formaldehyde concentration of the microlayer peak in late afternoon due, in part, to causes predicted to be more relevant during the Archean; lower CO_2 dissolution in warmer water (Wootton et al., 2008) and increased UV photochemical reaction rates (Zhou and Mopper, 1997), respectively. Both high pH and formaldehyde concentration promote lower DNA/RNA denaturing temperatures (Williams et al., 2001; Traganos et al., 1975). Salinity also reaches a maximum at late afternoon due to increased water evaporation in the microlayer (Zhang et al., 2003), but this would produce a lesser effect opposing denaturation.

Since experimental determinations with the PCR technique give optimal (specificity and rate) annealing temperatures of primers of about 5 K below DNA melting temperatures, these thermal and chemical diurnal variations, as well as the longer denaturation and annealing times allowed for by the UVTAR mechanism (hours instead of minutes for PCR), suggest that an effective UV and temperature assisted RNA/DNA replication mechanism could have been operating at the Archean sea-surface. RNA/DNA at the beginning of life did not require enzymes for its replication, reproduction was instead promoted by the day/night fluctuation of the sea-surface skin temperature about the denaturing temperature of RNA/DNA.

6 Entropy production, information storage, and fidelity

The link between entropy and information has been made by Shannon and Weaver (1949). However, information only has thermodynamic relevance in the context of its ability to catalyze irreversible processes. In a non-equilibrium environment with thermodynamic forces over the system, information is thus more correctly associated with entropy production.

As the seas began to cool further, competition for free floating nucleotides would imply that those RNA/DNA segments which, through particular base sequences along their length, had lower denaturing temperatures or could absorb more ultraviolet light and transfer this energy more efficiently to the molecular degrees of freedom of the surrounding sea-surface water, would be those favored for reproduction because of a higher denaturing probability. For example, favored segments would be those with more adenine-uracil ($A-U$) pairs for RNA, or adenine-thymine ($A-T$) pairs for DNA, as opposed to those with more guanine-cytosine ($G-C$) pairs, since the later have higher denaturing temperatures due to stronger van der Waals interactions between neighboring $G-C$ pairs and because the later are joined by three hydrogen bonds while $A-T$ pairs have only two. For example, a DNA segment containing 30% of $G-C$ pairs has a denaturing temperature of 82 °C while that containing 60% denatures at 96 °C (Chang, 2000).

This might lead to the conclusion that, as the sea temperature cooled to below the denaturing temperature of RNA/DNA, the composition of the organic soup would consist of mainly long double-strand RNA/DNA containing a high percentage of $G-C$ pairs that could no longer replicate, and many more very short-strand RNA/DNA containing a preference for $A-U$ or $A-T$ pairs that could continue replicating, and thereby increase their proportionate representation. However, there is an important possibility which may have arisen to counter this bias. If, by chance, a codon of the longer RNA/DNA strands coded for a simple enzyme that could help it denature at a lower temperature, then these longer strand RNA/DNA would retain their replicating ability and thus their selective advantage even in an ever colder sea. For example, the easily abiogenically synthesized aspartic amino acid (ASP) is a metabolite of the urea cycle that can produce urea from ammonia. Urea (and also formamide and formaldehyde) in the presence of magnesium ions can reduce DNA melting temperatures by about 0.6 °C for every 1% increase of the denaturing substance (Jungmann et al., 2008). The thermodynamic advantage of maintaining, and even enhancing, the entropy production in ever colder seas could thus have been the origin of the information content and the associated need for reproductive fidelity of RNA/DNA.

The association of a RNA/DNA molecule with an enzyme, or protein, is still in very common existence today, known as a virus. Poteins absorb strongly at 280 nm due to the aromatic ring of their constituent amino acids tyrosine,

tryptophan and phenylalanine (Haggis, 1974; Chang, 2000). They could thus have first served as antenna molecules by providing a larger cross section for UV absorption, and thereby more local heating, favoring denaturing and thus still greater entropy production.

7 Evolution

With greater cooling of the oceans came greater selection pressure for longer RNA/DNA segments that could code for still more complex enzymes that could facilitate denaturing at still cooler temperatures. Just as urea and formamide require the presence of magnesium ions to lower the denaturing temperature of DNA, a denaturing enzyme existing today, helicase, requires a magnesium ion for coupling adenosine triphosphate (ATP) hydrolysis to nucleic acid unwinding (Frick et al., 2007). Proteins and other molecules containing a magnesium ion would have had a natural affinity to RNA/DNA because of their ionic attraction to the negatively charged phosphate groups of the backbone.

Magnesium ions are also an important component of the pigment chlorophyll. The most readily abiogenically synthesized amino acid glycine reacts with succinyl-CoA from the citric acid cycle to form a porphyrin which, when coordinated with a magnesium ion, forms chlorophyll.

Another possible product of information for promoting UV and temperature assisted RNA/DNA reproduction as the seas cooled is the coding for sequences of RNA that promote self-splicing (e.g. self-splicing introns), or in the case of DNA, for a primitive topoisomerase enzyme which can break lengths of DNA into shorter parts for a transient time, effectively giving a large RNA/DNA the lower denaturing temperature of the smaller length segments. The catalytic residue of the topoisomerase enzyme is based on the amino acid tyrosine (TYR). This amino acid is also used in the photosystem II of chloroplasts, acting as the electron donor of the oxidized chlorophyll. Tyrosine, because of its aromatic ring, absorbs strongly at 280 nm (Chang, 2000) and, like RNA/DNA in water, has demonstrated chemical stability under high doses of UV radiation (Barbiera et al., 2002), suggesting that its initial association with RNA/DNA may have been as a robust antenna type of photon absorber to augment the local water temperature sufficiently for denaturation.

It is thus possible that RNA/DNA segments containing the codons specifying for one or more of these amino acid cofactors, acting as primitive denaturing enzymes, gradually mutated into one specifying for a primitive chlorophyll molecule. From a phylogenetic reconstruction of photosynthesis genes from all photosynthetic lineages, Xiong et al. (2000) have determined that purple bacteria are the most ancient photosynthetic organisms. These bacteria employ bacteriochlorophyll in a reaction center that absorbs UV light strongly at 280 nm and 400 nm, with very limited absorption in the visible and a small absorption peak in the infrared at 800 nm (Nozawa et al., 1987). The absorption in the infrared has led to the suggestion (Nisbet et al., 1995) that the first living organisms were chemotrophs living around hydrothermal vents and using the faint infrared light from the vent for phototaxis (orientation) which later developed into photosynthesis as an adjunct to chemotrophy. However, it seems more probable that the peaks in the ultraviolet were used in a primitive photosynthesis at the surface of the seas and that later these organisms spread to hydrothermal vents where the absorption of the faint infrared light emanating from these vents powered photosynthesis before chemotrophy could be properly developed. Indeed, photosynthetic activation spectrum of bacteria employing bacteriochlorophyll extends into the ultraviolet with photosynthetic inhibition increasing with shorter wavelength but reaching only about 10% at 280 nm (Halldal, 1967).

With some modification of bacteriochlorophyll, leading to chlorophyll, the efficacy of the light absorption and dissipation process would be still further enhanced as the skies cleared of organic haze, aldehydes, cyano-molecules, sulfur dioxide and sulfuric acid and water clouds, permitting more visible radiation to penetrate. Chlorophyll absorbs strongly at 430 nm, just where water is most transparent.

RNA/DNA segments that mutated to code for enzymes that could help it capture, join, and polymerize with individual free floating nucleotides would then find even greater selective advantage in still colder seas. Due to reduced Brownian motion, an accidental, and correctly aligned, meeting of a RNA/DNA single strand with a free floating nucleotide or oligonucleotide would become ever more improbable. It is relevant again here that the nucleic acid polymerase of today contain Zn^{++} and Mg^{++} ions as cofactors for their enzymatic activity (Rauchfuss, 2008). As the rain of the nucleic acid bases and other organic molecules from the sky began to dry up, RNA/DNA segments that coded for enzymes that could not only capture but also synthesize the bases from more primitive but more prevalent organic molecules such as hydrogen cyanide (Matthews, 2004), would be increasingly more favorably selected.

Since ATP is synthesized in the chloroplasts of plants of today by a process known as photophosphorylation, there may have existed a more primitive direct photochemical rout to its synthesis involving UV light and heat. For example, Muller (2005) suggests that thermosynthesis of ATP may be possible through temperature cycling in hydrothermal vents. However, UV light absorption and dissipation by the nucleic acid bases during daylight hours and cooling of the sea surface at night by evaporation and radiation, might have provided a similar heat engine for the abiogenic synthesis of ATP. For example, Kuzicheva and Simakov (1999) have measured significant yields of 5'AMP from nucleosides and inorganic phosphates due to the action of UV light and temperature cycling on spacecraft experiments.

It is a remarkable fact that the protein bacteriorhodopsin, that promotes ATP production in archea by acting as a proton

pump through the absorption of a photon at 568 nm in the visible, also works perfectly well by absorbing at 280 nm in the ultraviolet (Kalisky et al., 1981). The UV photon energy is absorbed on the aromatic amino acids tyrosine and tryptophan and the energy transmitted to the chromophore. It may thus have been that ATP originally obtained its free energy for formation directly from UV light and that life found a means to harvest this stored free energy for endergonic reactions that required a softer mode (or delayed mode) of energy transfer that could not be provided by direct UV or visible photons.

Thus may have begun the history of the evolution of amino acids, proteins, ATP, and chlorophyll with RNA/DNA; first as simple catalysts to help it denature at colder sea temperatures, as complements that aided in the absorption of UV and visible light, and finally as more active catalysts in attracting cyano-molecules, synthesizing nucleotides, and polymerizing RNA/DNA, as well as providing an active unwinding mechanism as RNA/DNA grew in length and sea temperatures cooled. The increasing competition between the reproducing RNA/DNA segments for organic molecules produced in the Earth's early atmosphere, or delivered from outer space by the comets and meteorites, and the importance of this reproduction to the entropy production of the Earth, could thus have constituted the first steps of evolution through natural selection.

Since the life induced changes in the composition of the Earth's atmosphere, the rain of organic molecules from the sky has now ceased. Viruses, which may thus have been the remnants of the very beginnings of life, and which were able to obtain their component molecules from abiogenisis and reproduce through the UVTAR mechanism, have now evolved to parasitize the complex nucleic acid production of existing life within the protected environment of the cell (Smith, 1965). Their associated proteins may have evolved from simple denaturing enzymes to vehicles that facilitate entry across cellular membranes. Their principal function appears to have also changed from being dissipators of ultraviolet light to agents that cause mortality through lysing in bacteria and higher organisms, allowing their nutrients to be recycled into photosynthetic life. It has been suggested that viruses have co-evolved with primordial cells, stimulating them to produce rigid walls, which caused genetic privacy, allowing vertical evolution (Jalasvuori and Bamford, 2008). Vertical evolution has also augmented entropy production on Earth through the water cycle by producing higher mobile life forms which by transporting nutrients allowed the photon dissipating molecules to spread into regions initially inhospitable to their reproduction (Michaelian, 2009, 2011).

Viruses have recently been found to be much more prevalent in sea water than suspected; being the major component by number of the organic material in ocean water (Wommack and Colwell, 2000). These so called "virioplankton" are found in concentrations of 10^4 to 10^8 per ml of ocean water, usually about one to two orders of magnitude more common than the bacterial phytoplankton that they parasitize. They are also found in highest abundance within the first 20 µm of still lake water (Wommack and Colwell, 2000). Viral DNA appears to account for only approximately 20% of the dissolved DNA found in ocean water. The rest appears to be soluble DNA of roughly 500 base pairs in size (viral DNA has greater than 20 thousand base pairs) of still unknown origin but probably the result of virus lysing bacteria (Wommack and Colwell, 2000). Bacterial lysing by viruses augments the production of cyanobacteria and other phytoplankton by cycling through necessary nutrients such as phosphor and nitrogen (Wommack and Colwell, 2000; and references therein). This floating organic material, in effect, increases the absorption and dissipation of sunlight at the surface of lakes and oceans today (Jones et al., 2005; Michaelian, 2010a).

8 Comparison with prevailing scenarios for the origin of life

Traditional views of the origin of life see it as an extraordinary event, persisting for a kind of inherent self-indulgence. The present theory sees the origin of life as a thermodynamic imperative; a new irreversible process, arising once environmental conditions became appropriate, that coupled to existing abiotic irreversible processes to augment the global entropy production of the Earth in its interaction with its solar environment. Although prevailing theories recognize the necessity of a free energy source for the metabolism of self-perpetuation, such as that derived from the chemical potential or thermal gradients of a hydrothermal vent (Wächterhäuser, 2006), they fail to acknowledge a greater thermodynamic function of life beyond self-perpetuation; dissipation of the solar photon flux through life's coupling to the water cycle.

The solar photon flux would have been the most intense and extensive free energy source available during the Archean. The present theory suggests how the visible photon dissipation by life of today may be directly linked with UV photon dissipation at life's beginnings in the Archean. Chemical and thermal gradient sources of free energy would have been limited in size and extent and a theory of the origin of life based on these sources would still have the difficult problem of explaining how photon dissipation (including photosynthesis), appearing very shortly after the origin of life (Rosing and Frei, 2004), could have evolved rapidly from chemical or thermal dissipation.

On addressing evolution, prevailing theories are subject to the same criticism of circularity of argument that inflicts Darwinian theory. What is natural selection selecting? The present theory suggests that natural selection selects biotic-abiotic coupled systems leading to ever greater global entropy production, in accordance with the Onsager principle and empirical evidence.

The present theory shares with hydrothermal vent proposals congruency with evidence supporting a thermophilic

origin of life (Schwartzman and Lineweaver, 2004). Any irrefutable evidence indicating that the surface of the Earth was cold at the time of the origin of life would render the theory inviable. The present theory suggests that life as we know it may be less universal than prevailing ideas might indicate, since, besides the requirements of liquid water, a concentration of appropriate chemical constituents, and a free energy source, the theory also imposes stringent requirements on the evolution of the external boundary and initial conditions; an atmospheric window allowing a high UV flux to reach the surface, temperatures descending gradually below the melting temperature of RNA/DNA, temperature cycling, and a water cycle. Of course, other "life" in the Universe may be based on a coupling to other irreversible processes, such as, for example, other solvent phase cycles, but water has many extraordinary properties that may make it unique in this regard.

The present theory avoids the difficulty of the RNA World hypothesis that has made it most vulnerable to criticism; that of requiring a priori sufficient RNA information content and reproductive fidelity (Shapiro, 2007), employing instead the particular environmental conditions of Archean Earth. A temperature cycling mechanism for amplification of RNA and DNA indeed has been shown to function in the laboratory (polymerase chain reaction).

In contrast to prevailing theories, the present theory does not require the unlikely discovery of an abiotic mechanism that produced an initial high enrichment of chiral enantiomers to explain the homochirality of life today. Instead, the present theory argues that homochirality arose gradually over time due to a small asymmetry in the environmental conditions that promote the UVTAR mechanism. In particular, if indeed life emerged when the sea-surface temperature had cooled to below the denaturing temperature of RNA/DNA, then, since the sea-surface temperature would be greatest in the late afternoon, the absorption of the slightly right-handed circularly polarized atmospheric light (Angel et al., 1972), or submarine light (Wolstencroft, 2004), of the afternoon, could have contributed to the abundance of RNA/DNA with D-enantiomer nucleotides. Double strands containing predominantly L-enantiomer nucleotides would absorb less well the right-handed circularly polarized light, and thus could not raise local water temperatures as often for denaturation, thereby curtailing their replication and evolution (Michaelian, 2010b).

9 Discussion and conclusions

Competition for organic molecules in itself could not have led to evolution through natural selection, or even to simple reproduction. This has been made clear from the numerous experiments of Orgel and others which have failed to create self replicating systems in the laboratory (Orgel, 1994, 2004). Ignoring the entropy producing function of life is, in fact, the basis of the tautology in Darwin's theory of evolution through natural selection. As Boltzmann hinted 150 years ago, the vital force of life and evolution is derived from photon dissipation, i.e. through entropy production. Greater numbers of RNA/DNA in the Archean absorbed more sunlight and catalyzed the early Earth water cycle, besides driving ocean and wind currents. Reproduction and evolution were thus synonymous with increases in the entropy production of the coupled abiotic and biotic biosphere. Naturally selected mutations of the RNA/DNA-protein complexes, and later that of complex animals and ecosystems, would be those allowing for ever greater increases in absorption of high energy photons and greater efficiency at converting these into heat.

The non-equilibrium thermodynamics of the abiogenisis of the primary molecules and their polymerization has hitherto not been duly considered in theories and experiments addressing the origin of life. High temperatures, temperature cycling, and UV light have been demonstrated to be useful in augmenting the abiogenisis of the nucleotides and the polymerization of the polynucleotides.

The problem of RNA/DNA replication without the help of enzymes has been addressed through an ultraviolet and temperature assisted mechanism involving cycling of the primitive sea-surface skin temperature around the denaturing temperature of RNA/DNA and the remarkable ability of these molecules to absorb and dissipate rapidly into heat the intense UV light that penetrated the primitive Earth's atmosphere. A corroborating fact is the evidence indicating that the Earth's surface temperature at the beginning of life was around the denaturing temperature of DNA and RNA. The formation and replication of RNA/DNA would be thermodynamically favored because of the overall increase in entropy production that these molecules afforded to coupled biotic-abiotic irreversible process occurring in the biosphere, in particular, to the water cycle.

The origin of information content and replication fidelity of RNA/DNA could be conceived of within the framework of the proposed theory if particular polynucleotide sequences coded for enzymes that facilitated denaturation at colder sea temperatures, or for light harvesting antenna molecules, leading to a differential replication success and entropy producing potential of different sequences. This may have been the beginnings of evolution through natural selection.

The problem discussed by Orgel (2004) of the racemic product of nucleotides frustrating the copying of stable polynucleotides has also been addressed by the present theory. The slightly right-handed circularly polarized light of the late afternoon would have led to homochirality before surface temperatures had cooled to a point at which enzymes and, therefore, reproductive fidelity, were necessary (Michaelian, 2010b). This completes the consideration from within the proposed framework of the major problems concerning the origin of life as reviewed by Orgel (2004).

A first step in probing the veracity of the proposed theory would be to test experimentally if polymerase chain reaction (PCR) could be carried out by substituting the heat cycling thermostat with UV light cycling, with the thermal bath held constant at a few degrees below the melting temperature of the short (<50 BP) strand RNA/DNA segment, or with slight temperature cycling ($\sim$4 °C) representing day and night temperature fluctuations of the Archean sea-surface.

The origin of life and beginnings of evolution, as depicted by this theory has the general feature of an auto-catalytic cycle involving a strong coupling between biotic and abiotic processes, driven by the goal oriented and universal process of increasing the entropy production of Earth in its interaction with its solar environment. This great auto-catalytic cycle involving life and abiotic entropy producing processes remains to this day, and appears to be evolving towards still greater efficiency at producing entropy. Since the appearance of chlorophyll, new pigments capable of capturing ever more of the Sun's spectrum have been incorporated into the photosynthesizing systems of today's plant and bacterial life. Examples are the carotenoids in green plants, the phycobilins in phytoplankton, and the recently discovered mycosporine-like amino acids (MAA's) in phytoplankton which absorb across the ultraviolet (Whitehead and Hedges, 2002). Most of these pigments are known not to have a direct role in photosynthesis. Furthermore, a number of complex mechanisms exist in plants today to dissipate into heat photons absorbed in excess. These pigments and mechanisms have hitherto been considered merely as "safety valves" for photosynthesis (Niyogi, 2000). Alternatively, they may now be explained on thermodynamic grounds through their importance to photon dissipation and the water cycle (Michaelian, 2009, 2011).

The net effect of the origin and evolution of life on Earth has been to gradually increase the Earth's entropy producing potential, or, in other words, to reduce the Earth's albedo and effective temperature at which it emits infrared radiation, making it ever more a blackbody of lower temperature.

Acknowledgements. The author is grateful to the editor, A. Kleidon, and a number of reviewers who's comments (see http://www.earth-syst-dynam-discuss.net/1/1/2010/esdd-1-1-2010-discussion.html) have served to improve the manuscript. The financial assistance of DGAPA-UNAM, grant numbers IN118206 and IN112809 is greatly appreciated.

Edited by: A. Kleidon

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