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Thermodynamic origin of life

K. Michaelian

Instituto de Física, Universidad Nacional Autónoma de México, Cto. de la Investigación Científica, Cuidad Universitaria, Mexico

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Correspondence to: K. Michaelian (karo@fisica.unam.mx)

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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 shallow 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 the ambient temperature conditions of prebiotic Earth.

1 Introduction

Empirical evidence from the fossil record of the evolutionary history of Earth 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). Only 27 years after the publication of “On the Origin of Species” by Charles Darwin, Boltzmann (1886) 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 avail-

ESDD

1, 1–39, 2010

able through the dissipation of high energy photons to low energy ones through the biosphere.

Prigogine and co-workers have shown 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 were given the name "dissipative systems" since, although they exist at low entropy, they arise spontaneously to provide pathways to a greater sampling of the enormous multitude of microstates that underlie Nature and, thus, their formation actually increase the entropy production of the Universe. New dissipative systems arising on Earth augment the overall entropy production, increasing the rate of the natural tendency of Nature to explore all available microstates. In general, the more complex the dissipative structuring in space and time (i.e. involving embedded hierarchal levels and interactions of larger spatial and longer temporal extent) the greater the overall entropy production in the systems interaction with its external environment (Prigogine et al., 1972; Lloyd and Pagels, 1988).

Thus, there is empirical evidence to suggest that Nature tends to find new routes to increasing entropy production, whether abiotic, biotic, or mixed abiotic-biotic, and this has been referred to as the "maximum entropy production principle" (Paltridge, 1979; Ulanowicz and Hannon, 1987). Although there has been an attempt at establishing a statistical mechanical basis for this principle (Dewar, 2003, 2005), the analysis has raised controversy (Grinstein and Linsker, 2007; Bruers 2007). However, such a principle has 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 in favour of this principle, suggesting that Nature finds new abiotic, biotic, and mixed abiotic-biotic pathways to entropy production, is taken here as sufficient justification for the proposition that the reproduction of RNA and DNA and their coupling to the water cycle arose originally as 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.

Aromatic organic molecules, such as the nucleic acid bases of RNA and DNA, due to the de-localized nature of their covalent electrons in π-bonding, 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 high energy region of the spectrum which could have filtered through the early Earth's dense atmosphere. These molecules, in the presence of water, are also extraordinarily rapid at dissipating the high energy photons to low energy ones that can be absorbed by the water molecules as heat. It is then plausible that life arose as a catalyst by 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).

For a review of the current understanding regarding the origin of life see Orgel (2004) and Rauchfuss (2008). Within the framework of the "RNA World" (Gilbert, 1986), Orgel recognizes several severe problems related to low yields in the individual steps of RNA synthesis 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 under the RNA World hypothesis are; 1) the production and stability of ribose over the other more easily synthesized and stable sugars, 2) the difficulty of the polymerization of nucleotides leading to 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 novel and consistent framework within which each of the above mentioned difficulties may be significantly alleviated. In a general sense, it recognizes a non-equilibrium thermodynamic imperative for the reproduction of RNA/DNA due to the great entropy producing potential of these molecules in the

absorption and dissipation of high energy photons. Not withstanding the great difficulty of producing these molecules in the laboratory using catalysts under near equilibrium conditions, a non-equilibrium pathway to the production of these molecules would have been sought out by Nature simply because of their great entropy producing potential given the particular boundary and initial conditions of the primitive Earth; in particular, a high flux of UV photons and a high sea surface temperature. It is shown here that considering these thermodynamic forces may not only alleviate the difficulty with the abiogenic yields of the primary molecules of life but, at the same time, provide an Ultra-Violet and Temperature Assisted mechanism for Reproduction (UVTAR) of RNA/DNA, without the need for enzymes.

2 Ambient conditions of early 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 shallow seas, existing at the very beginnings of life some 3.8 billion years ago (Schidlowski et al., 1983; Schidlowski, 1988), were hot soups of organic material. Theories on the origin of the organic molecules making up the soup have matured as our geochemical and geophysical understanding of the history of Earth has improved. 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 lightening strikes and photochemical reactions on an Archean reducing 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_2 N_2) and cyanoacetylene (HC_3 N) in an aqueous solution (see also Matthews, 2004). These precursor cyano-molecules are natural 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, through continuous outflow, shed much of their atmospheres into interstellar space (Hoyle and Wickramasinghe, 1978; Kwok, 2004). In corroboration with the idea that the original molecules of life on Earth may have come from interstellar space, it has been found that 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 be deposited into the Earth's oceans through the vehicle of colliding comets or asteroids. Amino acids and nucleobases have been found in carbonaceous chondrite meteorites 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, 1997; Tian et al., 2005). 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 Miller experiments (Tian et al., 2005).

Although the composition of the Earth's early atmosphere at the beginnings of life is still uncertain, it is generally accepted that the atmosphere was denser, 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, water vapour, 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 behaviour typical for Rayleigh scattering (Ityaksov et al., 2008). Water vapour absorbs strongly in the ultraviolet below approximately 170 nm, and strongly in the infrared above about 1000 nm, but is basically transparent between roughly 170 and 1000 nm (Chaplin, 2009). Ammonia, NH_3, also absorbs strongly below 200 nm.

It is generally believed that the early Earth was 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 vapour 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 vapour can produce sulfuric acid which condenses into 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 revealed a structure in the cloud cover of the planet for the first time. 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 through an increase in albedo in the visible region (Stothers, 1984). Dense clouds of water on the hot early Earth may have also been important in reflecting much of the remaining

visible light back into space. The greater amount of water in the prebiotic atmosphere would also imply a significantly greater absorption of solar infrared light than today.

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 wavelengths (Tehrany et al., 2002) and up to 25–30% less intense in the visible. A larger magnetic field, due to a higher rotation rate, would mean that gamma and X-ray 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. Today, the solar spectrum incident at the top of the Earth's atmosphere drops off quickly at wavelengths of less than 200 nm (Sagan and Chyba, 1997). With the water vapour absorbing strongly in the infrared and the clouds of sulfuric acid and water reflecting strongly in the visible and the 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 the 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 in the Early atmosphere, being the thermodynamically stable sulfur-containing gas under reducing conditions, and the probable formation of aldehydes (formaldehyde and acetaldehyde) through photochemical reactions with UV light on a reducing atmosphere, Sagan (1973) suggested a somewhat reduced window of transparency for UV light 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 an early 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 many orders

of magnitude greater than at present. Of considerable interest here is their result suggesting a peak in this excess radiation, of up to 10^{31} times the present values at a wavelength of 255 nm. This is not surprising since today less than one part in 10^{30} of the incidental solar radiation at 250 nm penetrates the Earth's ozone and O_2 atmosphere (Chang, 2000). RNA and DNA absorb very strongly just at these wavelengths with peak absorption at 260 nm (at one atmosphere) due to the electronic excitation of the aromatic rings of their nucleic acid bases. Proteins absorb strongly at 280 nm due to the aromatic ring of the amino acids tyrosine, tryptophan and phenylalanine (Chang, 2000), although with molar absorptions of between one and two orders of magnitude lower than that of RNA/DNA, depending on the percentage of aromatic amino acids in the protein.

The question has arisen as to whether this intense ultraviolet light between 200 nm and 300 nm had a detrimental (causing photolysing and very large mutation rates) or beneficial (through promoting necessary photochemical reactions, such as abiogenic synthesis of the nucleic acid bases, ribose and other carbohydrates; Schwartz, 1995) effect on the origin of life (Cockell, 1998; Cnossen et al., 2007; Martín et al., 2009). It is suggested here that, apart from inducing useful photochemical reactions, ultraviolet light was crucial to the origin of life for another reason; RNA and DNA are unparalleled ultraviolet light absorbing molecules which, in the presence of water, convert this light rapidly into heat (Middleton et al., 2009). This irreversible process, consisting of the dissipation of a high energy photon on the sea surface, leads to evaporation and the water cycle, which together produce great quantities of entropy. The replication of RNA and DNA would thus have been promoted on the early Earth as a route to greater entropy production (Michaelian, 2009).

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3 The early sea-surface environment

The sea-surface skin layer, of a thickness of about 1 mm, being the region of mass, energy and momentum transfer with the atmosphere, is of particular importance to the theory presented here. A quantitative understanding of the ocean surface microlayer of today has emerged over the past decade (Soloviev and Lukas, 2006). This skin surface layer has its own ecosystem of a particularly high density in organic material, about 10^4 the density of water only slightly below (Grammatika and Zimmerman, 2001). The organic material at the surface skin layer consists of cyanobacteria, diatoms, viruses, free floating RNA/DNA and other living and non-living organic material such as lipids, chlorophyll and other pigments. The high organic density 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.

Most of the heat exchange between the ocean and the atmosphere of today occurs from within this upper 1 mm of ocean water. For example, most of the radiated infrared radiation from the sea comes from the upper 100 µm (Soloviev and Schlüssel, 1994). About 52% of the heat transfer from ocean to atmosphere is in the form of latent heat transfer (evaporation), radiated longwave radiation accounts for 33%, and sensible heat through direct conduction accounts for the remaining 15%.

During the day, infrared (700–10 000 nm), visible (400–700 nm), and ultraviolet (290–400 nm) light is absorbed at the sea-surface skin layer. 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 material in the sea-surface microlayer alters its optical properties considerably, so that an important part of the total energy absorbed is in fact due to visible and UV light. Although, to the authors knowledge, no measurements of the optical density of the sea-surface microlayer 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 costal 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 microlayer augments the absorption of energy in this layer by about 13.3% (9.1% attributed to 290–400 nm UV absorption, 4.2% to 400–700 nm visible absorption) with respect to pure water absorption, which is predominantly in the infrared (Michaelian, 2010a). Under cloudy skies, or atmospheres of large water vapour content (the probable condition on prebiotic Earth), 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), due principally to the fact that infrared light from the Sun is strongly absorbed by water vapour and water droplets in the clouds.

Absorption of infrared, visible and UV light at the sea-surface microlayer increases the daytime temperatures at the skin surface by approximately 2.5 K (up to 4.0 K) compared to the practically constant temperature at an ocean depth of 10 m (Schlüssel et al., 1990). Night time temperatures at the surface are decreased on average by 0.5 K (up to 0.8 K) with respect to the constant temperature at 10 m depth. Cyanobacterial blooms have also been shown to cause considerable additional heating of the sea surface (Kahru et al., 1993). The effect of increasing phytoplankton densities on energy exchange at the surface of a lake has been quantitatively measured by Jones et al. (2005). They found that an enriched phytoplankton community increased the daytime surface temperature of the lake by 1.8 K given their particular experimental conditions.

Since the accumulation of organic material at the sea-surface microlayer is attributed to surface tension, natural buoyancy and the scavenging effect of rising bubbles from breaking waves (Grammatika and Zimmerman, 2001), it is reasonable to assume that an organically rich surface microlayer would also have existed in prebiotic oceans. An estimate of the optical density of this surface layer in the Archean can be made by

assuming concentrations of up to 1.5×10^{-5} M/L for the nucleic acid bases in prebiotic oceans based on estimates by Miller (1998) obtained from calculations of photochemical production rates of prebiotic organic molecules by Stribling and Miller (1987). Although these concentration estimates have been considered as optimistically large, the recent discovery of the sea-surface microlayer and other non-equilibrium abiogenic routes to these molecules (see below, and Powner et al., 2009), may, in fact, imply that they are underestimates. Given photon extinction coefficients of the bases of around 13 000 M^{-1} L cm^{-1} at 260 nm (Chang, 2000), leads to an absorption coefficient of 0.78 cm^{-1}. Using the Archean solar spectrum at the Earth's surface as determined by Cnossen et al. (2007) and 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 microlayer due to the nucleic acid bases, over that of pure water, by 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 (Michaelian, 2010a).

Such increases in the high energy photon absorption in the Archean sea-surface skin layer due to organic material would imply lower albedos and increases in the entropy production resulting from the dissipation of UV and visible light within this layer. Incident angle and frequency dependent albedos for sunlight on ocean water of today have been measured by Clarke et al. (1970). 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 smaller wavelengths of the ultraviolet. Similar results have also been obtained more recently by Jin et al. (2004).

4 Abiogenic synthesis of the molecules of life

A central problem with 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 ≈1 yr; U ≈12 yr; C ≈19 days at 100 °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, and 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, 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 (Prigogine, 1967). Irreversible processes can be coupled as long as the net production of entropy is positive and Curie's principle is respected; that macroscopic causes always 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.

For example, the second difficulty mentioned by Orgel (2004), the polymerization of polynucleotide from mononucleotides at constant temperature and pressure 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). The free energy required to chemically transform bonds in the substances comes from the free energy available in the photon. Such coupled photochemical reactions would have been much more frequent at the beginning of life

because of the greater amount of UV light reaching the Earth's surface. Spontaneous polymerization of polynucleotide under UV light is, in fact, entropy driven since single strand RNA/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).

Thermosynthesis is another example of a coupled irreversible process; thermocycling of molecules in convection cells provides free energy for chemical reactions which are endergonic. Muller (2005) has suggested that hotsprings could provide the source of heat for a convection cycle that could couple to ATP production. Similarly, the absorption of UV photons by RNA/DNA and their dissipation to heat during daylight hours and the cooling of the sea surface at night would also provide thermocycling that may, just as well, have been coupled to abiogenic synthesis of ATP and other organic molecules important to life.

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 more probable end products.

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 or employing catalysts, such as enzymes.

Significant experimental data have been collected over time to support the above assertion that the prevalent conditions on Archean Earth, intense UV light and high temperature cycling, relieve the problem of low yield of nucleotide synthesis.

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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 desoxyribose and amino acids. Kuzicheva and Simakov (1999) have shown that much larger yields (~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. Concerning activation barriers, Ponnamperuma and Mack (1965) and de Graaf and Schwartz (2005) have found high temperature to be useful in different routes to nucleotide synthesis.

Intense UV radiation and temperature cycling are the non-equilibrium conditions of primitive Earth assumed in the proposed theory of non-equilibrium, thermodynamically driven RNA/DNA replication. These thermodynamic forces not only appear to alleviate the difficulty with yields of the primary molecules but are essential to the central theme of the present paper which is the ultraviolet and temperature assisted reproduction of RNA/DNA without the need for enzymes.

5 UV and temperature assisted RNA and DNA reproduction

Assuming that more efficient pathways to the production of the nucleotides and polynucleotides will eventually be found, ostensibly by considering non-equilibrium coupling to irreversible entropy producing processes such as UV light dissipation, we now address perhaps the most difficult problem presented by Orgel (2004) which is the replication of polynucleotides without the help of enzymes.

If the salt concentration of an aqueous solution is raised above a certain threshold (for example Mg^{++} ions at concentrations of 10^{-2} molar), single strand RNA and DNA will spontaneously base pair through hydrogen bonding of the conjugate pairs and

through van der Waals and hydrophobic interactions to form RNA or DNA double helix (Haggis, 1974). The magnesium ions cancel the electrostatic repulsion of the negatively charged phosphate groups on the backbone of the two strands, allowing them to come together. Double helix strands are more rigid than single strands, and their secondary structures are no longer randomly folded.

At temperatures above 90 °C (at one atmosphere and pH 7), almost all of double strand RNA or DNA is denatured, separated into flexible single strands (Haggis, 1974). At lower temperatures, the amount of denaturing depends on the relative amounts of the base pairs G-C and A-U (or A-T), the length of the strand, the pH of the solvent (higher pH correlates with more denaturing), 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 could have been significantly higher.

It is generally believed that the RNA molecule preceded DNA in life's evolutionary history (RNA World hypothesis). 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 instance, 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 molecules of life, is their demonstrated ability to catalyze peptide bonds between amino acids and so form proteins (Chang, 2000). On the other hand, the lack of a hydroxol group on the ribose sugar of DNA allows 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 much later date. It is, therefore, reasonable to presume that RNA preceded DNA. However, both molecules are produced with similar abiogenic yields in vitro (until recently, RNA was somewhat easier to synthesize than DNA because ribose is easier to produce than deoxyribose, however, non-ribose routes to nucleoside synthesis have been discovered; Powner et al., 2009), and both appear to have similar ultraviolet absorbing characteristics. Therefore, within the framework of the theory presented here, there is no overwhelming reason why DNA could not have coexisted alongside RNA in the early organic soup, performing the same function of catalyzing entropy production through UV light absorption and dissipation.

The lower denaturing temperature of RNA would mean that, if it replicated simultaneously along with DNA, it would be found at somewhat different (cooler) sea depths. Since the temperature profile of the ocean is not monotonically decreasing with depth (maximum daytime temperatures are reached at depths of slightly less than 1 mm), these depths may have been either greater or smaller. At some later date, the two molecules may have formed a symbiosis which allowed new possibilities for more efficient reproduction 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 favour 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 and, thus, have little probability of relevance to the proposed theory.

At high temperatures of the surface of shallow seas existing during the very beginnings of life on Earth, the nucleotides containing the purine and pyrimidine bases probably floated independently in the sea, unable to pair conjugate bases through hydrogen bonds because of the large Brownian motion. However, the earth and the seas gradually began to cool, and when the sea surface temperature became close to that

of the denaturing temperature of RNA or DNA (at the existing ambient pressure) 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 at 70 ± 15 °C during the 3.5–3.2 Ga era (Lowe and Tice, 2004). These surface temperatures, existing around the time of the beginnings of life (ca. 3.8 Ga), are incitingly close to the denaturing temperatures of RNA/DNA. During daylight hours, the sea surface absorbed solar infrared light and the RNA/DNA molecules absorbed ultraviolet light and degraded it into infrared light which could then also be absorbed by water. It is then probable that the surface skin temperature of the sea in the local neighborhood of the RNA/DNA would heat up above their denaturing temperature and these would spontaneously 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). Most noteworthy, these molecules are ultra-fast at converting the electronic excitation energy into heat through internal conversion; that is, into vibrational motion of the atoms of the surrounding water molecules (Pecourt et al., 2000, 2001). This non-radiative process occurs on the sub-picosecond time scale, making RNA/DNA a very efficient absorber since the molecule promptly returns to the ground state, ready to absorb another photon. It has been suggested that this surprising ability is not fortuitous, but rather a remnant from earlier days when life was exposed to significantly higher doses of UV radiation. The argument is that this ability would have been favoured by natural selection since such a highly efficient nonradiative decay significantly lowers the rate of RNA/DNA damage through photoreactions,

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thereby reducing the need for frequent repair (Crespo-Hernández et al., 2004; Middleton et al., 2009). Sagan (1973) pointed out long ago that the rapid UV photon dissipation characteristics of nucleic acid bases would imply an important selective advantage to RNA and DNA over other more easily synthesized organic molecules under the harsh UV conditions of a prebiotic Earth. Mulkidjanian et al. (2003) have confirmed these ideas 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 through the efficient absorption of UV light and its dissipation into heat, heat which could be further harvested by other entropy producing processes such as the water cycle and ocean and wind currents.

An incoming ultraviolet photon, of wavelength between approximately 200 nm and 300 nm (of energy around 5 eV, corresponding to a Boltzmann temperature of 2500 K for thymine; Middleton et al., 2009) would then be efficiently absorbed and be degraded directly and rapidly to heat of the surrounding water. 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. Water appears to be the most efficient of many tested solvents (Middleton et al., 2009). Liquid water absorbs strongly at wavelengths greater than 1000 nm with a particularly strong absorption peak at 3000 nm. 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).

Other organic molecules such as melanin (responsible for pigment in skin and hair) also absorb ultraviolet radiation and convert the energy directly into heat. However, within the 200 to 300 nm range, there is no molecule, natural or man-made, that has the remarkable ability of single strand RNA/DNA to strongly absorb and covert ultraviolet light rapidly into heat. The RNA/DNA molecule, thus, has great entropy producing potential in that intense part of the early Sun's spectrum that could have penetrated into the surface of the Earth's early seas.

As night came, with no light to absorb, the surface of the shallow sea would cool through evaporation, radiation and conduction of heat to the atmosphere and earth, to a temperature below which the single strands of RNA/DNA could hydrogen bond through their bases with conjugate nucleotides floating nearby. Favoured by the template effect of single strand RNA/DNA, 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 extraordinary effect on reducing the surface temperatures of seas (Manzello et al., 2007). At the high sea-surface temperatures existing on early Earth, and with a cold upper atmosphere (Tian et al., 2005), hurricanes would have been much more prevalent than at present. Such torments would also have had relevance in stirring up and mixing organic cyano-molecules and metallic ions lying at the bottom of the shallow seas or floating in the atmosphere, making these available for the abiogenic synthesis of nucleotides, more complex amino acids, and other important organic molecules.

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 by perhaps 5 K (Schlüssel et al., 1990) through the absorption of ultraviolet, visible and some infrared light that could penetrate the clouds. 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, 2010b).

Given that the full width of the denaturing curve for RNA/DNA is about 8 K, the sea surface temperature in the neighborhood of the segment which absorbed the UV photon would, thus, 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 a new template for complementary strand polymerization during the subsequent cool period.

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 the new strand of nucleotides on the template during the low temperature period.

Ultraviolet and temperature assisted RNA/DNA reproduction would have been enhanced by a phenomenon known as hypochromism (Bolton et al., 1962; Chang, 2000). Double strand RNA/DNA absorbs from 20% to 40% less ultraviolet light than it does when separated into single strands. This effect 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 significantly. The strong absorption at 260 nm and the hypochromism of RNA/DNA is used in the laboratory with great efficacy to determine the denaturing temperature of a particular RNA/DNA segment (Haggis, 1974; Chang, 2000). As mentioned above, 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 further stimulating denaturation under solar UV light and by reducing the possibility of rapid recombination of the separated strands.

6 RNA/DNA catalyzing the water cycle and entropy production

Ultraviolet and temperature assisted RNA/DNA replication is in accord with the premise that the main thermodynamic function of life is to act as a catalyst for entropy production (Michaelian, 2009). It ties the beginnings of life to irreversible abiotic processes still occurring within the biosphere today. By absorbing UV light and dissipating it as heat, RNA/DNA was producing entropy. By heating the ocean surface, the floating strands of polynucleotide were enhancing the evaporation of water and, thus, acting as a catalyst for the water cycle, itself an important entropy producing process. The establishment of temperature gradients also leads to hurricanes, and ocean and wind currents, and even to the possibility of producing ribonucleotides from simpler molecules by thermosynthesis (Muller, 2005), or to non-ribose routes to the nucleotides such as that described by Powner et al. (2009). RNA/DNA did not require any enzyme for its replication, reproduction was instead promoted by the day/night fluctuation of the shallow sea surface skin temperature about the denaturing temperature of RNA/DNA (at the existing ambient pressure) due, in large part, to the absorption of ultraviolet light by these molecules.

As the seas began to cool further, the competition for free nucleotides would imply that those RNA/DNA segments which, through particular sequences of the different base pairs along their length, had lower denaturing temperatures and could absorb more ultraviolet light and transfer this energy more efficiently to the surrounding sea surface water, would be those favoured for reproduction. For example, favoured 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 de Waals interactions between neighboring G-C pairs and because the later pairs 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% of G-C pairs denatures at 96 °C (Chang, 2000). These short length,

predominantly A-U or A-T, segments would more easily denature during daylight and be available as templates for nucleotide polymerization at night (or during cooling periods brought on by hurricanes) and thus their replication would be favoured.

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 many 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 representation with respect to the long strand, or mainly G-C RNA/DNA. However, there is an important possibility which could have arisen to counter this bias towards shorter length and mainly A-U/A-T, RNA/DNA. If at least some of the codons of the longer RNA/DNA strands could code for an enzyme that would help it denature at a lower temperature, then these longer strand RNA/DNA could retain their replicating ability and thus increase 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) in the presence of magnesium ions can reduce DNA melting temperatures significantly, 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 reproduction fidelity of RNA/DNA.

As the sea temperature decreased to less than a critical value at which even very small segments could only very rarely denature (about 65 °C for DNA at one atmosphere and pH 7), then those longer RNA/DNA segments with a section coding for a primitive denaturing enzyme would begin to increase their proportionate representation, being the only ones able to continue multiplying through the UV and temperature assisted mechanism in colder seas. The rest of the RNA/DNA segment not coding for the denaturing enzyme would still be of use for absorbing and dissipating ultraviolet light which, according to our proposition, was the primordial thermodynamic function

of these molecules at that point in their evolutionary history. Apparently non-coding DNA exists today, constituting what is colloquially known as "junk" DNA, or introns, which are very prevalent in archea (Balbas, 2002). It may be that this non-coding DNA found in all organisms, and even floating independently today in natural water bodies in great quantities (Wommack and Colwell, 2000), is conserved because it retains its UV light absorbing and dissipating entropy production function for the biosphere, particularly after bacterial breakdown and viral lysing of the organism leads to the release of its RNA/DNA (Michaelian, 2009). Such a hypothesis must however be tempered with the fact that very little UV light between 200 and 300 nm is today reaching the Earth's surface.

Such an association of a RNA/DNA molecule with an enzyme, or protein, is still in very common existence today, known as a virus. Proteins, apart from their chemical catalytic activity in helping to denature RNA/DNA, are also efficient absorbers of ultraviolet radiation within the range of 200 to 300 nm (Haggis, 1974). 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 still greater entropy production.

7 Information, fidelity and evolution

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 cooled, and the Earth's surface environment was removed ever further from the natural regime of UV and temperature assisted RNA/DNA reproduction, this molecule had to begin to store information in order to continue reproducing and thereby maintain or augment entropy production. Simple enzymes for facilitating denaturation were probably the first products of information storage. Other

early products of information storage could have been antenna molecules which absorbed and dissipated ever more of the Sun's spectra that made it to the Earth's surface as the sky became more transparent.

With greater cooling of the oceans came greater selection pressure for larger 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). It is known that magnesium ions facilitate the formation of the double helix conformation by canceling out the negative charges on the phosphate groups of opposite backbones. Thus, proteins and other molecules containing a magnesium ion would have a natural affinity to RNA/DNA because of this ionic attraction.

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. There is little doubt that the ubiquity of the magnesium ion in biological function today has to do with its chemical affinity to RNA/DNA, in particular it may have played a historical role, in conjunction with the amino acid aspartic, in aiding UV and temperature assisted RNA/DNA reproduction, and later in the formation of antenna molecule chlorophyll used to capture and dissipate more of the Sun's spectrum.

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 (eg. 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 catalyitic 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, also 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 a primitive denaturing enzyme, gradually mutated into one specifying for a primitive Chlorophyll molecule. With the new molecule Chlorophyll allied with RNA/DNA, 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 and be absorbed by the new RNA/DNA-Chlorophyll pigment complex floating at the surface of the seas.

Single strand RNA/DNA, maintained in their non-stacked conformation by the sugar and phosphate groups, coupled with chlorophyll, provided a potent absorber of the most intense portion of the early Sun's photon spectrum that leaked through the Earth's early atmosphere and which could not be easily absorbed by the water surface (chlorophyll absorbs strongly at 430 nm, just where water is most transparent). The surfaces of the seas were then well heated, allowing convection mechanisms (upwelling) to bring up from the depths of the shallow seas new organic materials and minerals, such as the very useful magnesium ion. Similarly, evaporation occurring between the hot sea surface and the cool upper atmosphere allowed heat to be carried into the upper atmosphere and radiated into space through the water cycle. The energy involved (latent heat of condensation) being emitted at a wavelength much longer than that of the light absorbed by the organic molecules at the surface, thereby contributing to the global entropy production of the Earth.

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 where, due to reduced Brownian motion, an accidental, and correctly aligned, meeting of a RNA/DNA single strand with a free floating nucleotide 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, it is suggested here that infrared light absorption by water and UV light absorption and dissipation by the nucleic acid bases during daylight hours and cooling of the surface at night may have provided a heat engine for the abiogenic synthesis of ATP. 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 may have been that ATP originally obtained its free energy for formation directly from sunlight and that life found a means to harvest this stored free energy for reactions that required a softer mode (or longer storage mode) of energy transfer that could not be provided by direct UV or visible photons. Such a source of energy, together with new denaturing enzymes, would have aided life in its reproduction in ever colder seas.

Thus may have begun the history of the evolution of amino acids, proteins, and ATP 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 then as more active catalysts in attracting cyano-molecules, synthesizing nucleotides, and then polymerizing RNA/DNA, as well as providing an active unwinding mechanism as

RNA/DNA grew 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 entropy production of the Earth, could thus have promoted 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 by abiogenisis and reproduce independently, 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 absorbers 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 coevolved 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).

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 at highest abundance at the surface skin layer of water bodies, for example, in 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). Lysing of bacteria by viruses is now known to be one of the greatest (if not the greatest) contributions to the dissolved organic material pool of natural water bodies. It has been demonstrated empirically that this 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 Discussion and conclusions

It is important to emphasize, however, that simple competition for organic molecules in itself could not have led to evolution through natural selection, or even to simple reproduction. This has been learned from the numerous experiments of Orgel and others which have failed to create self replicating systems in the laboratory (Orgel, 1994, 2004). Such an incorrect vision which ignores non-equilibrium thermodynamics 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 strands 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 biotic and abiotic 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 aspect of the thermodynamics of living systems related to entropy production in the abiogenisis of the primary molecules, their polymerization, and their reproduction, has hitherto not been duly considered in theories addressing the origin of life. High temperatures, temperature cycling, and UV light have been demonstrated experimentally to augment significantly the abiogenic yields of the nucleotides and the polynucleotides. Possibilities for the coupling of these endergonic reactions to other irreversible processes remain to be explored.

The problem of RNA/DNA replication without the use 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 to heat the intense UV light that would have penetrated the primitive Earth's atmosphere. The creation and replication of RNA/DNA would, in general, be thermodynamically favored because of the overall increase in entropy production that these molecules afforded to the coupled biotic-abiotic irreversible process occurring in the biosphere, in particular to the water cycle.

The third problem discussed by Orgel (2004), that of the racemic product of nucleotides frustrating the copying of stable polynucleotides may be alleviated to some extent by considering the possibility of circularly polarized UV light in the present theory. If indeed life emerged when the sea surface temperature had cooled to close to the denaturing temperature of RNA/DNA, then since the sea surface temperature would be greatest in the late afternoon, the scattering of unpolarized UV sunlight from asymmetric volcanic (or other) particles in the atmosphere, oriented preferentially by the Earth's magnetic field, could have contributed to the abundance of RNA/DNA with D-enantiomer nucleotides through the unequal absorption cross sections for left and right-handed circularly polarized light of these chiral molecules. Double strands containing L-enantiomer nucleotides would have been at a disadvantage since they would absorb less well the right-handed circularly polarized light of the late afternoon, and thus could not raise local water temperatures as often for denaturation. These,

therefore, would suffer from a lower probability of reproduction through the proposed UV and temperature assisted mechanism. Once RNA/DNA containing predominantly L-enantiomer nucleotides had formed, they would tend to become locked in the double strand formation, effectively removing the templates for facilitating further production of L-enantiomer nucleotide RNA/DNA from the organic pool. Those with D-enantiomer nucleotides could have continued replicating, and thus evolving. This hypothesis is being considered in detail elsewhere (Michaelian, 2010b) and is only presented here to complete the consideration within the postulated framework of the major problems concerning the origin of life as reviewed by Orgel (2004).

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

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 thermodynamic bath held constant at a few degrees below the denaturing temperature of the short (<50 bp) strand RNA/DNA segment, or with slight temperature cycling (~5 °C) representing day and night fluctuations of the sea surface temperature.

The origin of life and beginnings of evolution, as depicted by this theory has the general feature of an autocatalytic 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 autocatalytic 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 the chlorophyll molecule, new pigments capable of capturing still more of the Sun's spectrum have been incorporated into the more evolved photo-

synthesizing systems of today's plant and bacterial life. Examples are the carotenoids in green plants, the phycobilins in phytoplankton existing at greater ocean depths where only blue-green light can reach, 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 (for example, the photosynthetic activation spectrum of red algae has little relation to its photoabsorption spectrum; Berkaloff et al., 1971). A number of complex mechanisms exist in plants today to dissipate into heat photons absorbed in excess but have hitherto been considered merely as "safety valves" for photosynthesis (Niyogi, 2000). Their existence and evolution, however, may now be justified on thermodynamic grounds through their importance to photon dissipation and evaporation of water (Michaelian, 2009). 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.

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