

Interactive comment on “Thermodynamic origin of life” by K. Michaelian

K. Michaelian

karo@fisica.unam.mx

Received and published: 14 May 2010

I thank the referee for their comments and suggestions. Although 55 of the 106 references cited are of an empirical nature, in the new version of the manuscript I have included an additional 16 new references to experimental data which further support some of the most crucial points of the hypothesis. For example, I now cite experimental evidence that UV irradiation augments the denaturation rate of DNA held in a water bath at a fixed temperature (Roth and London, 1977) and that there exists a direct route to the promotion of ATP with the protein bacteriorhodopsin and UV light at 280 nm (Kalisky et al., 1981).

I presume that the referee’s suggestion to shorten the paper is directed towards improving the redaction by making the paper more concise. In the new version, I have made numerous rewordings and removed unnecessary descriptions. However, the

C15

new citations to the experimental data and the new calculations suggested by referee 2 (see below), as well as the suggestion by referee 3 to include mention of alternative scenarios for the origin of life, have, in fact, lead to a slightly longer paper.

I have emphasized more strongly the thermodynamic perspective throughout.

In the previous version of the manuscript, I presented a calculation of the increase in energy absorbed in the 1 mm sea surface skin layer due to the absorption of light by RNA/DNA segments based on concentration estimates of these by Miller (1998) obtained from calculations of photochemical production rates of prebiotic organic molecules by Stribling and Miller (1987). (Note that Miller was not aware of recently discovered routes to pyrimidine ribonucleotide production utilizing UV light (Powner et al., 2009), nor of the existence of an organically enriched sea surface skin layer, so his determinations of the concentrations are probably lower limits.) This, therefore conservative, calculation showed that the energy gain in the skin layer due to the absorption of UV light by nucleic acid and other organic molecules would be about 19% higher on clear days and 490% higher on cloudy days (or for an atmosphere containing a lot of water vapor). The difference in this increase in energy absorption between clear and cloudy days is due to the fact that on clear days, direct infrared light from the Sun is by far the major contributor to surface heating. Water in the atmosphere, either in the form of clouds or vapor, strongly blocks infrared light from reaching the surface. Given the probable high surface temperature during the Archean (Knauth and Lowe, 2003), and the fact that there is ample evidence for the existence of oceans at the origin of life (Wilde et al., 2003), it is most probable that there was a large amount of water vapor in the atmosphere and thus little direct infrared light from the Sun was reaching the Earth’s surface. Therefore, the diurnal temperature cycling of the ocean surface would be mostly due to absorption of UV and visible light that could penetrate the atmosphere.

Given that the Archean Sun was brighter in the UV and dimmer in the visible than today, and assuming similar absorption characteristics in the visible of the sea surface micro-

C16

layer as for today (probably an overestimate since pigments such as chlorophyll did not exist in the Archean), it was shown in the manuscript that UV light contributes more than visible light to the energy deposited in the skin layer. Furthermore, since the individual photons are of higher energy, entropy production resulting from UV dissipation in this layer would be greater still than entropy production due to visible dissipation. This, in the context of Onsager's principle (see response to Prof. Schwartzman), seems to be strong thermodynamic incentive for Nature to discover routes to nucleic acid formation in the Archean sea surface skin layer.

In the new version of the manuscript I have estimated the diurnal variation in temperature to be expected within the surface skin layer due to the absorption of UV and visible light attributed to RNA/DNA and other organic molecules. I have also included new evidence of diurnal increases (to late afternoon peaks) of the pH and formaldehyde content of the microlayer (Wootton et al., 2008; Zhou and Mopper, 1997), both of which reduce DNA/RNA denaturing temperatures (Williams et al., 2001; Traganos et al., 1975) and thus facilitate the UVTAR mechanism. Experimental determinations with the PCR technique give optimal (specificity and rate) primer annealing temperatures of about 5 °C below DNA melting temperatures. From these physical-chemical diurnal variations, plus the increase in local temperature due to the direct absorption of a UV photon on RNA/DNA, as well as the much longer times allowed for denaturation and extension by the UVTAR mechanism as compared with the PCR technique (hours instead of seconds), I conclude that an effective UV and temperature assisted replication mechanism could have been operating at the Archean sea surface.

I appreciate the information theory oriented perspective of Wicken and Pulselli et al. on the origin of complex organic molecules. Clearly, as emphasized by these authors, the structuring of molecules can occur simply due to the increases in entropy of the environment that is promoted by their structuring. Such is the case of the structuring of hydrophilic-hydrophobic lipid bilayers in water, for example, which, by the bonding of adjacent molecules, allow for an increase in orientation randomization of the

C17

surrounding water molecules (Chang, 2000) and thus, in fact, lipid structuring augments the entropy of the system plus environment. A more familiar example is the non-homogeneous equilibrium formation of droplets of oil in water. However, many of these near-equilibrium routes to molecular structuring in the context of RNA/DNA and the origin of life have already been explored in many different experiments. What I am suggesting in the paper is that non-equilibrium routes to the structuring of molecules should also be explored (for example, the pyrimidine ribonucleotide production using UV and temperature cycling (Powner et al., 2009)). The suggestion of non-equilibrium coupling of irreversible processes leading to the structuring of molecules has been made by Prigogine (1967) and was cited as such in the manuscript. This same idea has been re-emphasized by Wicken and Pulselli et al. In the new version of the manuscript I make reference to these authors in section 4 on the abiogenic synthesis of the molecules of life.

The paper of Biondi et al. concerning the UV protective effects of clay is based on the assumption that UV radiation was harmful to the beginnings of life. This, in turn, is based on the assumption that protecting the information content and the secondary structure (for enzymatic activity) of RNA was a necessary first ingredient of life. However, I point out in my article that neither information content nor enzymatic capabilities are required for RNA/DNA replication if the ambient conditions are such that they permit an ultraviolet and temperature assisted replication (UVTAR) mechanism to operate. One of the characteristics of UVTAR is precisely the existence of a large flux of UV light to dissipate into heat. UV dissipation is the suggested thermodynamic incentive for the origin of life. Replication without some form of dissipation does not make thermodynamic sense and almost all life today is based on visible light dissipation. Therefore, the suggestion that prebiotic RNA/DNA needed to be shielded from UV light runs contrary to the hypothesis of my manuscript. I have, however, included a reference to the Biondi et al. paper in section 2 on the ambient conditions of early life where I mention the opposing perspective of those that suggest UV light may have been detrimental to the origin of life.

C18

I do not think that a change of title is appropriate.

References;

Kalisky, O., Feitelson, J., and Ottolenghi, M. (1981) Photochemistry and Fluorescence of Bacteriorhodopsin Excited in Its 280-nm Absorption Band, *Biochemistry* 20, 205-209.

Knauth, L.P., Lowe, D. R. (2003) High Archean climatic temperature inferred from oxygen isotope geochemistry of cherts in the 3.5 Ga Swaziland group, South Africa, *Geol. Soc. Amer. Bull.* 115: 566–580.

Miller, S.L., (1998) The endogenous synthesis of organic compounds. In “The Molecular Origins of Life”, André Brack, ed., Cambridge University Press, Cambridge.

Powner, M.W., Gerland, B., Sutherland, J.D. (2009), Synthesis of activated pyrimidine ribonucleotides in prebiotically plausible conditions. *Nature* 459, 239-242.

Prigogine, I. (1967) *Thermodynamics of Irreversible Processes*. Wiley, New York.

Roth, D. and London, M. (1977) Acridine probe study into synergistic DNA-denaturing action of heat and ultraviolet light in squamous cells. *J. Investigative Dermatology* 69: 368-372.

Stribling, R. and Miller, S.L. (1987) Energy yields for hydrogen cyanide and formaldehyde syntheses: the HCN and amino acid concentrations in the primitive ocean. *Origins of Life and Evolution of the Biosphere* 17: 261-273.

Traganos, F., Darzynkiewicz, Z., Sharpless, T., Melamed, M. R. (1975) Denaturation of deoxyribonucleic acid in situ effect of formaldehyde. *J. Histochemistry and Cytochemistry*, 23: 431-438.

Wilde et al. (2003) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature*, 409: 175-178.

C19

Williams, M. C., Wenner, J. R., Rouzina, I., Bloomfield, V. A. (2001) Effect of pH on the overstretching transition of double-stranded DNA: evidence of force induced DNA melting. *Biophysical Journal*, 80: 874-881.

Wootton, J. T., Pfister, C. A., Forester, J. D. (2008) Dynamic patterns and ecological impacts of declining ocean pH in a high-resolution multi-year dataset. *PNAS*, 105: 18848-18853.

Zhou, X. and Mopper, K. (1997) Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange. *Marine Chemistry* 56: 201-213.

Interactive comment on Earth Syst. Dynam. Discuss., 1, 1, 2010.

C20