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Interactive comment on "Thermodynamic origin of life" *by* K. Michaelian

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I thank Prof. Schwartzman for his careful consideration of the manuscript and his insightful observations that have lead to a clearer exposition.

In the new version of the manuscript I now mention the prevailing scenarios for the origin of life, in particular the metabolism first proposal, including the hydrothermal vent scenario. However, I do not confront these scenarios in the manuscript since doing justice to these would require much more space, but worse, would take attention away from the main premise of the paper which is to propose a mechanism for the origin of life based on UV light dissipation. In my view, a debate on the respective merits of one or another scenario would best be left to another article.

I would, however, like to point out to Prof. Schwartzman that light dissipation is the basis of almost all metabolisms occurring in life today. I have not neglected metabolism in the manuscript, on the contrary, the structuring and replication of RNA/DNA is suggested to be mediated through UV light dissipation. I have, therefore, emphasized the most important (thermodynamically speaking) metabolic processes occurring in life which is often neglected; the dissipation of the solar photon flux. (See also submitted Short Comment by A. Makarieva and V. Gorshkov.)

The sea surface microlayer appears to be a very robust entity which reestablishes its integrity rapidly after perturbation. According to Hardy (1982) who cites MacIntyre (1974) "breaking waves will disrupt the microlayer temporarily, but whitecaps cover only 3-4% of the ocean surface at any one time." Also according to Hardy (1982), who cites Dragcevic and Pravdic (1981) "Formation and reorientation of organic surface films at the air/water interface has been established to occur in only about 0.2 sec." The convective mixing of deeper ocean water with the surface microlayer is damped by the large viscosity of this layer and by surface tension (Hardy, 1982). Moreover, Hardy (1982) states "Brownian movement and diffusion are relatively unimportant in determining microlayer residence times." As with breaking waves, rain is a source of bubble formation which, through scavenging action, brings organic material from depths to the sea surface microlayer (Aller et al., 2005). Therefore, "dilution of the environment" by hurricanes, convection, diffusion, or rain, is probably not important. Anyhow, there would be little UV or visible light to dissipate during a hurricane.

The UV absorption characteristics of RNA/DNA are due to the collective electronic excitations of the aromatic rings of the naturally occurring nucleic acid bases. Decay characteristics are very sensitive to the particular electronic structure of the molecule (Serano-Andres and Merchan, 2009). Tautomers of the bases absorb well but often decay through much longer lived channels, making these prone to photoreactions (Serano-Andres and Merchan, 2009). Sagan (1973) has pointed out that the ability of the natural bases to absorb and dissipate rapidly UV photons would have given them a chemical selective advantage at biogenesis over other less UV stable, but more easily produced, compounds in the intense UV environment of the primitive Earth. Through numerical simulations, Mulkidjanian et al. (2003) have validated the proposal of Sagan and have shown that such absorption and dissipation characteristics of the bases allows longer RNA/DNA polymers to persist under high UV irradiation.

It is true that UV light of between 200 and 300 nm can often break the RNA/DNA skeleton at the pentose-phosphate bonds (Biondi et al., 2007), but long RNA/DNA polymers are only required if replication and photon dissipation (or more generally in this scenario, the origin of life) were dependent on RNA/DNA information content. Since I am proposing an enzyme independent UVTAR mechanism for replication, a long RNA/DNA oligonucleotide, which could code for many enzymes, was not a prerequisite for the origin of life. In the same information independent sense, pyrimidine dimers would have little effect on this scenario for the origin of life. Finally, since a particular UV photon is absorbed on generally one or two, but rarely more bases (Takaya et al., 2008), the length of the polymer would not have had much influence on life's early metabolism (UV absorption and dissipation). As the sea surface cooled, replication would have become less reliant on UVTAR and more reliant on information content required for denaturing enzymes. These early enzymes, however, could have been simple antenna type molecules that absorbed and dissipated into heat more of the UV and visible region of the solar spectrum, such as the aromatic amino acids tyrosine and tryptophan, or the mycrosporines of today which are based on the most readily abiogenically synthesized amino acid, glycine (Montero and Lubian, 2003). These first "enzymes" would thus also not require long RNA/DNA polymers for their codification.

Prof. Schwartzman's preoccupations concerning the problems inherent in the application of the maximum entropy production principle are valid. In fact, there has recently been much discussion on the issue (apart from the special issue in Philisophical Transactions Royal Society B 2010:365, see the special issues of Entropy 2009:11 and 2010:12). It appears that obtaining predictive utility from such a principle requires a careful consideration of the "boundary" of the system, its ergodicity (ability to equate information entropy with thermodynamic entropy) (Virgo, 2010), and, as it seems to me, a careful consideration of the dependence on initial conditions (even at the microscopic level, if the system is very non-linear). The position I have taken in the revised version of the manuscript has been to remove reference to the maximum entropy production principle. This has been done without any ensuing debility of argument since such a general principle was not needed for the thesis of the paper. Instead, it is sufficient to invoke the ample empirical evidence that Nature tends to find new routes to entropy production, whether abiotic, biotic, or mixed abiotic-biotic. Rather than a "maximum entropy production principle", the thesis of the paper can be wholly supported on a much weaker, but empirically established, principle such as that suggested by Lars Onsager (1931); that thermodynamic processes arise to reduce impediments to increasing entropy production.

Thus, Prof. Schwartzman is correct in asserting that "Multiple possible pathways in the biosphere and biotic evolution are possible and the actual history does not necessarily have a greater entropy flux to the environment relative to alternative histories." Indeed, any complex non-equilibrium system may have many attractors (Prigogine, 1967) and the system may evolve from one to another attractor due to perturbation (perturbation at even the microscopic level if the system is very non-linear). Given this inherently probabilistic nature of the evolution of non-linear, non-equilibrium systems, it clearly makes little sense to assert that the particular evolutive history of the Earth's dissipative systems is the one that maximizes global entropy production given the boundary conditions imposed by the external space environment.

The use of the much weaker "Onsager principle" in the manuscript is justified solely on the empirical evidence that living systems have tended to evolve towards states of increasing complexity and entropy production over time, and thus life, since it does indeed contribute to the global entropy production of Earth (judging from the lower albedos and temperatures measured over biotic areas, and from life's important effect on the water cycle (Kleidon, 2008)), has at least a "reason for coming into being and for evolving". It is not suggested that life is the only possible entropy producing process, and much less that it is the best of all possible processes for the given boundary and historical conditions. The working hypothesis of the manuscript is that any process has a net positive probability to come into being and to persist for which adequate boundary and initial conditions exist, which is consistent with all constraints, and for which the global entropy production of the Earth in its solar environment is increased. Of course, this does not say much since it cannot be used to make detailed predictions; however it does provide a general framework for understanding the phenomena of the origin and evolution of life. Without a thermodynamic principle such as the “Onsager principle” one has only the traditional view that life arose as an accident and persists for its own sake, which says even less and is in conflict with what is known of all other non-equilibrium processes which do arise and persist to produce entropy.

Apart from the physical constraints imposed by the Earth-Sun system (Earth’s magnetic field is perhaps the most important physical constraint allowing Earth to retain its water; Barabash et al., (2007)) life, by recombining atomic hydrogen with atomic oxygen has played a part in retaining water on the planet (Lovelock, 2005). Also, life appears to have played a non-trivial part in maintaining water in a liquid state by controlling the amount of greenhouse gasses in the atmosphere (Ventura et al., 2007). Thus, as Prof. Schwartzman states, entropy flux is constrained by the initial and evolving characteristics of the planet, but it is plausible that life has had a function in determining the evolution of those evolving characteristics. It is precisely the liquid water environment that permits life to have an important entropy producing function. Dry trees are dead trees with high albedo and no transpiration. Going back in time, in the context of the hypothesis of the manuscript, RNA/DNA which is not in water cannot as effectively dissipate UV photons into heat (Middleton et al., 2009).

Given the empirical support for the “Onsager principle”, the longevity of life and the water cycle on Earth suggest that it is probably a good (stable) mixed biotic-abiotic system for producing entropy as compared to other unknown possible systems compatible with Earth’s initial and boundary conditions. Without life, there would probably be no water cycle. There would, however, still be an atmosphere due to gravity. Would the atmosphere be like that of Venus? Difficult to say, but if it were, our planet would have a much higher albedo than at present. It is an interesting fact, perhaps not to be taken too seriously, that solar system bodies like comets devoid of atmospheres but which can sustain liquid water near their surface as they approach the intense UV and visible light field of the Sun, have extremely low albedos (∼0.03). This appears to be due, in no small part, to the formation of light absorbing organic molecules on their surfaces (Hoover, 2006).

I have attended to the "Specific Comments" of Prof. Schwartzman in the context of the above response to his three principle observations. I would only like to emphasize once again here that replication coupled with metabolism, is described in the paper. I am suggesting that the first living "organisms" were RNA/DNA phototrophs and that their structuring and replication was completely dependent on UV light dissipation.

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