Biogeosciences Discuss., 12, C1619–C1624, 2015
www.biogeosciences-discuss.net/12/C1619/2015/

Biogeosciences
Discussions
Open Access

Interactive comment on "Fundamental molecules of life are pigments which arose and evolved to dissipate the solar spectrum" *by* K. Michaelian and A. Simeonov

K. Michaelian and A. Simeonov

karo@fisica.unam.mx

Received and published: 24 April 2015

We thank Marko Vitas for his kind remarks and review of our manuscript.

Our description of the proliferation of the fundamental molecules of life as a photochemical autocatalytic dissipative process driven by entropy production is based on a previous thermodynamic analysis of autocatalytic chemical reactions given by Prigogine (1967). In an autocatalytic chemical reaction, one of the products of the reaction acts as a catalyst for the reaction itself. Under the non-equilibrium condition of an imposition of a constant supply of the reactants and a constant sink of the products (a fixed external affinity for the reaction) it can be shown that the steady state concentrations

of the catalyst products grow to many orders of magnitude larger that what would be expected under near equilibrium conditions (Prigogine, 1967). The greater the catalytic activity, the greater the amount of catalyst formed in the steady state and the greater the rate of the dissipation of the chemical potential (defined by the fixed affinity) and, therefore, the greater the rate of entropy production. It is just such an autocatalytic chemical reaction that biochemists have been searching for at the origin of life.

Instead of an "autocatalytic chemical reaction", however, the origin of life would have, most probably, been based on dissipating the prevailing solar photon potential since this potential has always been many orders of magnitude greater (in terms of free energy) than any extinct or extant chemical potential at Earth's surface. If, under the imposition of the solar photon potential (defined by the 5800 K black-body spectrum of the surface of the sun and the 2.7 K cosmic background spectrum of space) and a constant supply of reactants, a photochemical route can be found to the production of a pigment molecule, and if that pigment molecule is efficient at dissipating the same photon potential that "produced" it, then, a similar situation to that of the case of the autocatalytic chemical reaction would exist, only that a photochemical potential, as opposed to a chemical potential, would be dissipated, and, therefore, the concentration of that pigment at the thermodynamic stationary state (when the rate of the dissipative process becomes constant) would become many orders of magnitude larger than which would be expected under near equilibrium conditions. A formal derivation of this is given in Michaelian (2013). The greater the efficacy of the pigment in dissipating the solar photon potential, the greater the amount of pigment existing at the stationary state and the greater the entropy production of the process. Proliferation of the UV-C pigment molecules, such as the nucleic acids, aromatic amino acids, enzymatic cofactors, etc. (see Michaelian and Simeonov, 2015 for a list), on the Archean ocean surface could thus be explained in these general non-equilibrium thermodynamic terms. In the new version of the manuscript, we have included a more detailed discussion of this autocatalytic proliferation.

Regarding the replication of early RNA/DNA polymers in the prebiotic environment and a discussion of template-directed versus autocatalytic scenario, the authors make the following remarks. Although it is not within the scope of the article to delve into the details of this dynamics, the clarification of the relation that Marko Vitas brings up deserves reflection and to this we dedicate the following paragraphs.

Nucleic acid and other fundamental pigment proliferation is assumed to have been generated by the photochemical autocatalytic process as mentioned in the previous paragraph, although the detailed mechanisms of these processes are yet to be determined. Patel et al. (2015) have, in fact, found experimentally plausible routes to the generation of these pigments using UV-C light. RNA molecules have also been found to catalyze the synthesis of nucleotides, i.e. their own building blocks (Unrau and Bartel, 1998).

We believe that a fundamental thermodynamic reason for the polymerization of these nucleic acids into single strands is that they could then act as stereochemical templates for the attachment of other UV-C absorbing pigment molecules (such as, for example, the aromatic amino acids which have affinity to their codons or anticodons) that could act as electronically excited donors to the RNA or DNA single strand polymers which could act as acceptors and provide the rapid radiation-less dissipation of the electronic excitation energy to the ground state (for example, aromatic amino acid excited state lifetimes are of the order of nanoseconds whereas RNA or DNA excited state lifetimes are sub picosecond). The complex of pigment+RNA(DNA) would thus dissipate more UV-C than the sum of its component parts. In this regards, it is interesting that RNA can itself act as a catalyst for nucleotide polymerization (e.g. RNA, in the form of ribozymes; Jonhston et al., 2001; Zaher and Unrau, 2007; Lincoln and Joyce, 2009).

A template-directed mechanism for the primordial non-enzymatic replication of RNA/DNA, which we called UVTAR (Ultra-Violet and Temperature Assisted Replication) was given in an earlier work (K. Michaelian , 2009; 2011). In this scenario, the local heat generated by the dissipation of a UV-C photon by the nucleic acid bases

of RNA or DNA is sufficient to disrupt the hydrogen bonds between complementary bases and allow separation into single strands. This hypothesis has been supported by recent experimental data (Michaelian and Santillan Padilla, 2014) showing that double-stranded DNA effectively denatures when exposed to UV-C light. Enzyme-less extension to form a complementary strand is plausible when performed overnight at colder sea surface temperatures and using Mg2+ ions as cofactors. Some experimental evidence for this kind of enzyme-less extension has already been given (Szostak, 2012 and references therein).

One could look at the overall process of production and replication of RNA or DNA in terms of the individual steps or mechanisms, for example;1) autocatalytic photochemical production of the nucleic acid bases and other pigment molecules, 2) polymerization of the bases into single strands, 3) attachment of other pigment molecules to coding sections on the RNA or DNA polymers, 4) UV-C induced denaturing, and 5) enzyme-less extension. Alternatively, one could look at the process as one large autocatalytic photochemical reaction in which the net result is the proliferation of specific (coding) RNA or DNA segments which have large photon dissipation capacity. The latter view is a more general thermodynamic view while the former view, considering the individual steps in the overall reaction, is a more detailed mechanistic view. A still more detailed view of the actual mechanisms operating in each step has yet to be delineated, particularly with regard to mechanisms (routes) to the UV-C photochemical production of the pigments (point (1) above). However, the general view of the proliferation of coding segments of RNA and DNA, as an autocatalytic photochemical reaction which proceeds and evolves through thermodynamic selection based on the efficacy of the organism to dissipate the solar photon potential is the most useful view for giving a physical-chemical description of evolution through natural selection and avoids having to include an ad hoc "will (drive) to survive" (the Darwinian postulate) in the description of evolution.

We hope that this clarifies the relation between template-directed and autocatalytic

proliferation that Marko Vitas was concerned about without bringing up too many new issues. We have endeavored to make this relation clear in the revised version of the manuscript.

The spectral classification of our sun, the "G0-V" term, has been replaced by the term of more common usage of "G-type" and the "primitive gases" term has been replaced by the term "primordial gases".

We sincerely thank Marko Vitas for his comments which have led to an improved version of our manuscript.

References:

Johnston, W. K., Unrau, P. J., Lawrence, M. S., Glasner, M. E., Bartel, D. P.: RNA-Catalyzed RNA Polymerization: Accurate and General RNA-Templated Primer Extension, Science 292 (5520), 1319–1325, 2001.

Lincoln, T.A., Joyce, G.F.: Self-sustained replication of an RNA enzyme, Science, 323(5918), 1229-1232, 2009.

Michaelian, K. Thermodynamic origin of life. Cornell ArXiv, arXiv:0907.0042 [physics.gen-ph] (2009) .

Michaelian, K.: Thermodynamic dissipation theory for the origin of life, Earth Syst. Dynam., 2, 37–51, doi:10.5194/esd-2-37-2011, 2011.

Michaelian, K.: A non-linear irreversible thermodynamic perspective on organic pigment proliferation and biological evolution, J. Phys.: Conf. Ser. 475, 012010, 2013. doi:10.1088/1742-6596/475/1/012010

Michaelian, K., Santillán Padilla, N., DNA Denaturing through UV-C Photon Dissipation: A Possible Route to Archean Non-enzymatic Replication, BioRxiv. Cold Spring Harbor Labs Journals, 2014. doi:http://dx.doi.org/10.1101/009126

Michaelian, K. and Simeonov, A. Fundamental molecules of life are pigments which

arose and evolved to dissipate the solar spectrum. Biogeosciences Discuss. 12, 2101-2160, 2015. www.biogeosciences-discuss.net/12/2101/2015/ doi:10.5194/bgd-12-2101-2015.

Patel, B.H., Percivalle, C., Ritson, D. J., Duffy. C.M., Sutherland, J.D., Common origins of RNA, protein and lipid precursors in a cyanosulfidic protometabolism, Nature Chemistry 7, 301–307, 2015. doi:10.1038/nchem.2202

Prigogine, I.: Thermodynamics of Irreversible Processes, Wiley, New York, 1967.

Szostak, J.W., The eightfold path to non-enzymatic RNA replication, J. Sys. Chem. 3:2, 2012.

Unrau, P. J., Bartel, D. P.: RNA-catalysed nucleotide synthesis, Nature, 395 (6699), 260–263, 1998.

Zaher, H.S., Unrau, P.J.: Selection of an improved RNA polymerase ribozyme with superior extension and fidelity, RNA, 13, 1017-1026, 2007.

Interactive comment on Biogeosciences Discuss., 12, 2101, 2015.