

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

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Received and published: 6 May 2015

We thank Prof. dr. Frank Veroustraete for his interesting and relevant comments on our manuscript.

1. o Comment: It is written in the abstract: ...the thermodynamic imperative of increasing the entropy production of the biosphere... Can entropy be produced?

Answer: Entropy is an extensive thermodynamic variable for which, unlike energy, no conservation law exists. The second law of thermodynamics, however, states that for an isolated system the entropy must increase until reaching a maximum, at which the system is in thermodynamic equilibrium. Equilibrium thermodynamic formalism is only

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valid for isolated systems. For open systems, those allowing an exchange of matter, energy, momentum, angular momentum, etc. with their environment, Prigogine developed an extension of equilibrium thermodynamic formalism known as Classical Irreversible Thermodynamics (Prigogine, 1967). This formalism assumes local (in space and time) equilibrium in small, but still macroscopic, regions of the system, and the normal thermodynamic variables such as energy, entropy, temperature, pressure, etc. retain their meaning, but now locally, i.e. they become functions of space and time. Within this formalism, for open systems, the change in entropy of any system  $dS/dt$  can be written as a sum of two parts, that due to the exchange of entropy with its environment  $d_e S/dt$  and that due to the production of entropy for any irreversible process occurring within the system  $d_i S/dt$ .

$$dS/dt = d_e S/dt + d_i S/dt \quad (1)$$

An irreversible process arises (e.g. flow of heat, matter, electrical current, chemical reaction, etc.) within a system to produce entropy, i.e.  $d_i S/dt > 0$ . Each living organism in the biosphere produces entropy (because life is an irreversible process), and the sum (entropy is an extensive variable) of all the entropy productions due to all the organisms, plus the entropy production due to abiotic processes such as the water cycle, winds, currents, etc., is the total entropy production of the biosphere. If we now assume that the biosphere has arrived at a stationary state, i.e.  $dS/dt = 0$ , (a good approximation at human time scales) then by equation (1), the flow of entropy into the biosphere must be negative and equal to the net positive production of entropy due to all the irreversible processes occurring within the biosphere,

$$d_e S/dt = -d_i S/dt. \quad (2)$$

In the stationary state, the entropy of the biosphere is not changing, entropy is being produced due to irreversible processes, but at the same time it is being expelled to

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space by the same amount, see equation (2). Since, basically, it is only the flow of light which exists over the open biosphere, then the net entropy entering the biosphere  $d_e S/dt$  is just the entropy of the light being brought in per unit time minus the entropy of the light being emitted per unit time. The incident light has a black-body spectrum at a temperature of the surface of the sun, 5800 K, and the emitted light has a black-body spectrum at the temperature of the cloud tops at about  $-15\text{ }^\circ\text{C}$  (258 K). There is empirical evidence that the entropy production of the biosphere has increased since the beginning of life on Earth (Zotin, 1984) and Onsager has shown that irreversible processes couple to reduce impediments to greater entropy production (Onsager, 1931; Morel and Fleck, 1989). This does not mean that the entropy of the biosphere has increased, but that the entropy expelled to space has increased over evolutionary time, equivalent to a red-shifting in evolutionary time of Earth's emitted photon spectrum.

o Comment: Additionally, each living organism in the biosphere internally reduces its entropy. Since these organisms are part of the biosphere, how does this add up to an increase in biosphere entropy? Did the authors take account of this phenomenon?

Answer: As explained above, there is no increase in the biosphere entropy, there is instead an increase in the entropy production of the biosphere and this entropy is expelled to space in the form of an emitted spectrum ever more (over evolutionary time) red-shifted.

It is true that living organisms exist at reduced internal entropy, and the whole biosphere persists at very low entropy. But this reduction in entropy and increased internal order is more than compensated for by the high entropy of heat that biological activity emits to its surroundings and eventually to outer space (Lehninger, 1993).

Life, as any other dissipative structure (ex: Belousov-Zhabotinsky reaction, Benard cells, lasers, hurricanes, etc.), persists at low entropy because only in this state it is able to efficiently dissipate the thermodynamic potential that drives its existence (in the case of life that being the solar photon potential).

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The reduction of internal entropy of the biosphere is mainly attributable to the process of photosynthesis in photoautotrophs which utilizes available free energy in sunlight to fix carbon from carbon dioxide into organic matter. Gates (1980) has estimated that the percentage of available free energy (Gibb's, at constant temperature and pressure) in solar radiation that is used in the net primary production of the biosphere is less than 0.1 percent. The rest of the absorbed energy is dissipated into heat by internal conversion and vibrational relaxation of the excited pigment molecules within photoautotrophs, fomenting evapotranspiration and hence the water cycle (Michaelian, 2012). In conclusion, the internal reduction in entropy of the whole biosphere is negligible when compared to the high entropy produced and emitted as long-wave radiation by coupled biotic-abiotic dissipative processes known as the biosphere.

Specific Comments: 2. It is written on page 2112 (15): From this thermodynamic perspective, one would expect the history of pigment appearance and evolution to be correlated with the evolution of the solar spectrum at Earth's surface. o Comment: Do the authors suggest here that the history of pigment appearance and evolution has taken place outside living organisms or within the biophysical context of a living autotroph or semi-autotroph?

Answer: What we are suggesting is that at the beginning of life on Earth, there were no "living organisms". There only existed molecules which absorbed and dissipated the surface solar photon flux and we have called these molecules "pigments". In another article (Michaelian, 2013) we have suggested how pigment proliferation could have occurred through autocatalytic photochemical reactions under UV-C light. The photochemical product, the pigment, acts as a catalyst for further UV-C photon dissipation, and therefore its concentration under the imposed UV-C light of the Archean could have grown to many orders of magnitude greater than would be expected under near equilibrium conditions. Under UV-C light, there was no need for the pigment to be embedded in a "living organism" in order to proliferate. The free energy available in UV-C photons was sufficient to break and make covalent bonds and the autocatalysis

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argument given above is sufficient to explain the proliferation.

We have suggested that among the first pigments to absorb in the UV-C were the nucleic acid bases and later polymerizations of these that would have chemical affinity to other UV-C absorbing molecules (thereby increasing the size of the antenna for photon capture and dissipation). Our article, in fact, shows that many of the fundamental molecules of life are UV-C absorbing pigments and that many of these also have chemical affinity to RNA and DNA. The complexes RNA/DNA-pigments would have had greater dissipating potential than the separate components because RNA/DNA is extraordinarily fast at dissipating and has the ability to act as an acceptor to the other pigments electronic excitation energy. An example of this is tryptophan chemically binding to its DNA codon. Tryptophan has an electronic excited state life time of nanoseconds, however, if it donates its excitation energy to DNA, which then dissipates it in sub picoseconds, the complex would have greatly increased the efficiency for dissipation compared to tryptophan and DNA acting individually.

The replicating pigment system would tend to evolve towards ever greater entropy production by finding ways for also dissipating the other photon wavelengths arriving at Earth's surface (including the visible). This would imply the evolution of new pigments which could also act as excitation energy donors to RNA and DNA. The formation of protoporphyrin (precursor of chlorophyll which absorbs in the visible) may have had a prior history analogous to other UV-C pigments whose proliferation can be explained through autocatalytic photochemical reactions because protoporphyrin in stacks (which normally occurs in water due to their hydrophobicity) also absorbs in the UV-C. Photon dissipation may, therefore, have been a precursor to photosynthesis.

As oxygen began accumulating due to primitive oxygen photosynthesis, the atmosphere became opaque to UV-C and it was necessary for incipient life to continue using UV-A and visible light to produce pigments. It could have done this once a metabolic route to ATP had been discovered, and this probably occurred within the confines of a cell wall.

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The above is an attempt to provide a plausible description of how the "living organism" gradually evolved in response to dissipating with ever greater efficiency, within an ever greater wavelength range, and over an ever greater Earth surface area, the solar photon potential. Our point is that the focus should be on the dissipating complex and the pigment, not on the "living organism". It is this dissipation that is by far the greatest thermodynamic work that life performs and it is this dissipation that promotes the structuring of material (dissipative structures). The rest of the living organism can be seen as a vehicle by which the dissipating pigments were able to diversify and to proliferate into all new environments and finally to cover the whole of Earth's surface.

From this perspective, the biosphere is a network of coupled biotic-abiotic dissipative processes for the conversion of low entropy solar photons into high entropy emitted photons, and for reasons of efficiency a hierarchical stratification of groups of organisms with different functions within this network inevitably emerges. This hierarchy would mostly resemble the ecological (or energy) pyramid of biomass but in an inverted form, with the base trophic level of primary producers (autotrophs) at the top, doing the greatest thermodynamic work of dissipating the solar incident energy. Both energy capture and conversion into biomass and energy dissipation occur predominantly inside this first trophic level of the biosphere; more specifically the processes take place inside cyanobacteria, other photoautotrophic and chemoautotrophic bacteria to a lesser extent, and inside the chloroplasts of algae and plants, themselves descendant of cyanobacterial symbiotes. At the molecular level of a cyanobacteria or chloroplast, the primary constituents which are mostly responsible for both of these energy-transformation processes are the different organic pigments (chlorophylls, phycobilins, carotenes, etc), embedded in membrane proteins which serve a secondary role of carriers and catalysts.

If one attempts to formulate a purely thermodynamic or energetic description of biology, one is inevitably pushed toward a pigment-centered description. The authors did not intend to divorce pigments from their autotrophic cellular hosts, but merely to emphasize

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their centrality in the thermodynamics of life. A more detailed account for this pigment-centered view of biological evolution is given in the revised version of the manuscript. Here we provide two relevant evidence favoring our pigment-centered view of biology:

1) Beside the pigments embedded in living phytoplankton, the ocean surface skin layer is rich with free-floating organic material of biological origin and viruses (Michaelian, 2009, 2011, 2012, and references therein). A fraction of this organic material called chromophoric (or colored) dissolved organic matter (CDOM) interacts with solar radiation and appreciably absorbs light in the UVB, UVA and visible regions. It has been demonstrated that CDOM dominates light absorption throughout the blue and especially in the UV spectral regions at the ocean surface, with nearly 50 percent of the total light absorption at 400 nm and more than 70 percent of the total light absorption at 300 nm (Nelson and Siegel, 2013). Phytoplankton absorption apparently does not dominate the open ocean spectral light absorption budget, and its contribution is only equal to that of CDOM absorption for wavelengths greater than 450 nm (Nelson and Siegel, 2013). The chemical composition of CDOM is still ill-defined, mostly due to the great diversity and variability of organic compounds, but analysis so far suggests the presence of aromatic amino acids, humic substances (of aromatic and phenolic nature), lignin phenols, mycosporine-like amino acids (MAAs), etc. (Coble, 1996). Given the above, the contribution of life-derived CDOM to the entropy production at the ocean surface would appear to be greater than the contribution of the pigments embedded in the living phytoplankton population of the ocean surface.

2) Beginning in the 1930's until today, a great body of astronomical data has been accumulating, suggesting that a considerable proportion (> 20 percent) of carbon atoms in the universe is locked up into complex pigment (or chromophoric) organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) or mixed aromatic-aliphatic organic nanoparticles (MAONs) (Kwok, 2012). They have been found in interstellar molecular clouds and circumstellar envelopes, planetary atmospheres and surfaces, satellites, comets, asteroids, meteorites and interplanetary dust particles (Tielens, 2008; Botta

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and Bada, 2002). Many of these environments are expected to be of low temperature and pressure, implying that the Gibb's free energy for the formation of these complex molecules should be positive and large, suggesting that their origin and ubiquity could only be attributed to non-equilibrium thermodynamic processes. We believe that the abundance of these complex organic pigment molecules in the cosmos can only be explained on the basis of their catalytic properties in dissipating photons in the ultraviolet and visible emission spectrum of stars, leading to greater local entropy production. After the absorption of high energy UV photons, the excited aromatic molecules emit specific infrared emission bands by vibrational relaxation to the ground state (Peeters et al., 2004). This photon-dissipation by interstellar carbonaceous material contributes significantly to the so-called interstellar extinction or reddening, which is the decreasing light intensity and shift in the dominant observable wavelengths of light from a star (Clayton et al., 2003). There is also evidence that in the UV-poor environments of protoplanetary (pre-planetary) nebulae, the aliphatic component (less-absorbing component of these organic macromolecules) constitutes a significantly larger percent of the macromolecule when compared to the UV-intense regions of planetary nebulae where almost the entire molecule is aromatic (Yang et al., 2013). Therefore, there is strong reason to suspect that these cosmic "organic pigments" have an origin and dissipative function similar to life on Earth. A difference between them would be the coupling of primordial Earth pigments (chromophores) to liquid water and the water cycle; a "partnership" based on entropy production which "guided" their evolution into the complex organisms we see today. An article on this subject is currently under preparation by the authors.

3. It is written on page 2112 (20): ...an important hallmark of the evolution of life on Earth is the proliferation of organic pigments over Earth's surface... o Comment: Are we dealing here with the proliferation of organic pigments over Earth's surface or the proliferation of living organisms carrying organic pigments over Earth's surface? It is my opinion that living organisms are the drivers of proliferation since a pigment cannot reproduce itself. Proliferation is a typical property of living organisms. It are the first

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autotrophs that colonized the Earth's oceans (most probably), not their pigments on its own, but always embedded in the organisms biophysical structures (membranes). It is only in that context that thermodynamics have to be considered as well, and not outside the organism except maybe the ecosystem it lives in. o Therefore I would replace pigments or organic pigments everywhere in the manuscript by pigment containing organisms.

Answer: Our answer to this question is mainly contained within the answer of question No. 2. Here we want to emphasize that according to the evidence presented above, the hallmark of biological evolution would indeed seem to be the proliferation of organic pigments (or chromophoric organics) over Earth's surface, whether they are inside living cells or outside of them. From this thermodynamic standpoint, living cells can be regarded as vehicles for pigment proliferation over Earth's surface, a complex self-replicating system ensuring their catalyzed synthesis, support, sustenance, recycling and fast dispersal. Today with only visible light to dissipate, one cannot exist without the other but this is a chicken and egg problem. Only when one includes solar photon dissipation into this problem does the centrality of the pigments become apparent.

4. It is written on page 2113 (25): ...the fundamental molecules of life (nucleic acids, aromatic amino acids, enzymatic cofactors) are actually organic pigments in the UVC-UVB range. o Comment: I have a problem with the expression 'organic pigments in the UVC-UVB range. I assume the authors intend to express that nucleic acids, aromatic amino acids and enzymatic cofactors absorb and dissipate solar radiation in the UVC-UVB spectral range. o Comment: I don't consider nucleic acids, aromatic amino acids and enzymatic cofactors as pigments, but as organic molecules. It is my opinion that an organic pigment has to absorb (and dissipate) electromagnetic (EM) energy in the visible part of the solar spectrum to be named a pigment, at least in chemical terms. If not, one simply speaks of organic molecules, not pigments. A pigment is a material that changes the color of reflected or transmitted light as the result of wavelength-selective absorption in the visible part of the spectrum. Hence a

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pigment is by definition visible by the human eye and this terminology is not chosen by coincidence, but by the biochemistry of human vision and the photosynthetically active part of the solar spectrum, the PAR spectral region from 400 to 700 nm.

Answer: Prof. Veroustraete is correct in that the common definition of a "pigment" is a substance which selectively absorbs wavelengths in only the visible region of the spectrum, and having the color of the reflected or transmitted wavelengths. However, the term "accessory pigments" have for a long time been associated with organic molecules which dissipate photons, including photons in the UV; for example, "mycosporine-like amino acid pigments" (see for example Bohm et al., 1995 and Carreto et al., 2011). These pigments have mostly been considered as providing a "protective" function to the photosynthetic apparatus. In the perspective that we present in the article, these "pigments", independent of their absorption ranges, are seen as the primary focus of life and evolution due to the dissipative function that they perform and it would be confusing to call those molecules that absorb in the visible as "pigments" while those that absorb elsewhere in the spectrum as "something else". The only other term, to our knowledge, which may be suitable is "chromophore" but this term refers to a particular unit of covalently bound atoms that absorbs at a particular wavelength and not to molecules in general. The term "pigment" has, in fact, been used before to describe molecules which absorb in the UV-C; see for example Skulachev (1996) who used the term "UV-pigment" to describe adenine. We therefore see no valid reason for not using the extended definition of the term pigment if this helps to avoid confusion. After all, it is clear that our paper discusses photon absorption and dissipation and not human vision. However, taking Prof. Veroustraete's criticism into account, we now make a clear definition of what we mean by the word "pigment" in the introduction to our revised article.

5. It is written on page 2114 (15-20): Therefore, the coupling of nucleobase photon dissipation to the water cycle... o Comment: I do see the contribution of nucleobase photon dissipation to the evaporation of water. But how does this lead to a coupling

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with the water cycle? What hydrological process balances out the mass of evaporated water so that one can actually speak of a water cycle with a closed mass balance? Precipitation? And if it is precipitation, wouldn't the Earth's atmosphere in that case not be covered with dense clouds? And do dense clouds not attenuate solar radiation drastically? Hence, the solar radiation reaching the Earth through the atmospheric windows, wouldn't it be strongly determined by the balance of this Hadean ocean primitive hydrological cycle?

Answer: Precipitation is indeed the process that closes the mass balance in the water cycle. Precipitation does indeed require the existence of clouds, and clouds do indeed attenuate the solar radiation reaching the Earth's surface. It might therefore seem counterintuitive that the coupling of photon dissipation to the water cycle increases photon dissipation. However, the situation is much more complex than as seen at first sight. In response to Prof. Veroustraete, we quote what we have previously published in an article entitled "Biological catalysis of the hydrological cycle: life's thermodynamic function" (Michaelian, 2012). For references and tables cited, please consult the original article.

"Clouds are an integral part of the water cycle; however, their formation may seem to have a detrimental effect on evaporation since cloud cover on Earth reflects approximately 20 percent of light in the visible and ultraviolet regions of the Sun's spectrum (Pidwirny and Budikova, 2010). Clouds absorb the major part of the direct infrared radiation from the Sun, thereby reducing the potential for evaporation at the Earth's surface. However, evapotranspiration is a strong function of the local relative humidity of the air around the leaves of plants or above the surface of the oceans. By producing local cool regions during the day, and local warm regions during the night, clouds are able to maintain the average wind speed at the Earth's surface within dense vegetation at values above the threshold of 0.25 ms<sup>-1</sup> required to make the boundary-layer resistance to water loss almost negligible in a plant leaf (see for example, Speck; 2003), thereby procuring maximal transpiration rates (Gates, 1980). Other indications sug-

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gesting that a partially clouded Earth may, counter-intuitively, be beneficial to global evaporation are (1) the condensation of water vapor into clouds reduces the absolute amount of water vapor in the atmosphere, meaning reduced humidity at the surface. (2) Clouds bring water to inland regions which allows plants to grow and thus increment land evapotranspiration and thus the size of the water cycle over land. In any case, without clouds, there simply would be no hydrological cycle.

The important question, however, within the context of the hypothesis presented here, is not the evaporation rate, but rather the global entropy production rate under a partly cloudy sky as compared to a clear sky. This is a much more complex issue, because all coupled irreversible processes operating in the ecosphere must be taken into account. As mentioned in Sect. 3, even Lambertian reflection of light produces entropy (on Venus it accounts for half of the total entropy production; see Table 1). Finally, and most importantly, the potential for entropy production is biased towards the visible and UV regions, so the strong absorption of clouds in the infrared, although having an important effect on the incident energy flow, will have a reduced effect on global entropy production."

6. It is written on page 2115 (5): ...cystine (Pace et al., 1995; Edelhoeh,1967)... o  
Comment: cystine. Isn't it cysteine which is meant here?

Answer: The amino acid in question is cystine, formed by the oxidation of two cysteine molecules that covalently link via a disulfide bond, with the formula (SCH<sub>2</sub>CH(NH<sub>2</sub>)CO<sub>2</sub>H)<sub>2</sub>. The amino acid cysteine also absorbs in the UV at around 250 nm, and it will be added in the revised version of the manuscript.

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

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