

Biogeosciences Discuss., author comment AC2
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Reply on RC2

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Author comment on "Reply to Lars Olof Björn's comment on "Fundamental molecules of life are pigments which arose and co-evolved as a response to the thermodynamic imperative of dissipating the prevailing solar spectrum" by Michaelian and Simeonov (2015)" by Karo Michaelian and Aleksandar Simeonov, Biogeosciences Discuss., <https://doi.org/10.5194/bg-2021-199-AC2>, 2022

We thank the reviewer for their interesting questions and for their useful suggestions for our Reply.

Concerning the comparison of the entropy production of an Earth with and without life:

The value of 2.6 times greater entropy production that the reviewer refers to in our Reply is for the Earth/Moon comparison. The Moon is quite different from an Earth without life, since the Moon has no atmosphere and therefore no water cycle, or any other irreversible process occurring at its surface. The Moon thus radiates as an approximate black-body at the temperature of its surface as determined by energy conservation, taking into account its albedo, emissivity, and distance from the Sun. The Moon's entropy production can thus be easily calculated and compared to that of the Earth today.

However, an Earth without life would have an atmosphere, probably more similar to that of Titan than to Earth's non-equilibrium atmosphere of today which has been completely transformed by life. An Earth without life would have little oxygen, little ozone, and therefore intense UV light at the surface. Without life, Earth would probably have lost most of its water since there would be no free oxygen to capture hydrogen freed by UV photolysis. Surface temperatures would be different (probably cooler because of less greenhouse water vapor) and this would affect the albedo through increasing ice at the polar caps. Life is also thought to have had an important effect on plate tectonics (Parnell, and Brolly, 2021), etc. In summary, a fair comparison of the

entropy production of an Earth with and without life would require knowledge of an alternative geochemical history of Earth, as well as knowledge of what irreversible processes could be occurring on such an Earth today without life.

Kleidon et al. (2000) consider a simple, and imaginary, scenario in which life is suddenly removed while maintaining the atmosphere of today relatively unchanged except for the amount of water vapor. This is obviously not representative of what would be the case if life had failed to arise 3.9 billion years ago, and it's not what the reviewer is asking. However, for this scenario they conclude that, "Land surface evapotranspiration more than triples in the presence of the 'green planet', land precipitation doubles (as a second order effect) and near surface temperatures are lower by as much as 8 K in the seasonal mean resulting from the increase in latent heat flux." Higher surface temperatures emitting into space (without the latent heat flux) and less damping of the day-night temperature difference (due to less water vapor) for an Earth without life would mean less entropy production, as we found for the exaggerated case of the Moon.

The ratio of the entropy production of an Earth with life over an Earth without life, would most probably be less than the value of 2.6 found for comparison with the Moon (because an Earth without life would still have secondary dissipative processes occurring at its surface), perhaps similar to our comparison with Venus, Earth/Venus of $1.247 \text{ W K}^{-1} \text{ m}^{-2} / 0.801 \text{ W K}^{-1} \text{ m}^{-2} = 1.557$ (Michaelian 2012). However, there is no conceivable way of obtaining a reliable answer to the reviewer's question without knowledge of the alternative geochemical history.

An incomplete, but more meaningful, answer would be to consider just that part of the entropy production due to absorption and dissipation of incident photons on surfaces with and without life, without considering secondary coupled irreversible process. In Michaelian and Cano (2022) we performed a detailed calculation for the entropy production of a conifer forest and compared it to that of a dry sand and rock desert. The ratio of the entropy production we found, with the sun directly overhead, was, $6.834 \text{ W K}^{-1} \text{ m}^{-2} / 4.714 \text{ W K}^{-1} \text{ m}^{-2} = 1.450$

Since Björn removed his section on the comparison of the albedo of the Moon to that of the Earth from his final published Comment, we have also left this section out in our revised version of our Reply.

Concerning the first enzymes:

We have published a paper (Mejia and Michaelian, 2020) on how UV-C photon dissipation could have led to the specificity (chemical affinity) of amino acids for their codons and anticodons, indicative of a stereochemical era at the beginning of life (Yarus,1998; Yarus et al., 2005). It seems that those amino acids which one could argue have some capacity to increase photon dissipation of the amino acid - nucleic acid complex (e.g., amino acid acting as a UV-C antenna, as an aliphatic anchor to the ocean surface, or as a facilitator for charge transfer catalysis) are precisely those that have strong chemical affinity to their codons or anticodons. We explain in our paper how this may have come about through a thermodynamic selection on photon dissipation. As an example, the aromatic amino acids tyrosine, tryptophan, phenylalanine, and histidine could have acted as antenna molecules when coupled to the nucleic acids (which have conical intersections for rapid internal conversion to the ground state) giving the complex more efficient UV-C dissipation. If reproduction (e.g. denaturing) depended on photon dissipation (for example, through local heating or photon-induced charge transfer - Michaelian and Santillan, 2019) then those DNA or RNA sequences with chemical affinity to the antenna amino acids would be selected more frequently (because they denatured more frequently) than arbitrary sequences.

Bioinformatic studies have shown that enzymes involved in either purine metabolism or porphyrin and chlorophyll metabolism are evolutionarily the oldest (Caetano-Anolles et al. 2008, Caetano-Anolles et al. 2012). Both groups use nucleotides as their cofactors. The second group is specifically involved in pigment metabolism.

Concerning the corrections and inclusions of references:

Line 102-104: "However, they produce.....today". Needs a reference.

The sentence has been reworked so that the value of 1000 for the entropy produced during their lifetime compared with the entropy that could be produced through the burning of the tree as fossil fuel can be understood to come from the value of 0.1% of the solar free energy captured by the tree that goes into covalent bonding (Gates, 1980).

Line 120-124: A reference is needed

Included.

Some words are unnecessary negatively targeting

The negativity has been removed from our revised Reply.

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