Erschienen in: Physics of Life Reviews. Elsevier. 2020, 34-35, pp. 89-91
https://doi.org/10.1016/j.plrev.2020.06.004

Comment

Mineral self-organized structures in pre-biotic chemistry Comment on: "Mineral self-organization on a lifeless planet" by J.M. Garcia-Ruiz et al.

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Mineral self-organized structures (MISOS) are fascinating silica hybrid structures with either alkaline earth metal carbonates or metal oxy-hydroxides. Many of us know the beauty of chemical gardens [1] already from our childhood when grains of metal salts start to "grow" in a water glass solution. And as scientists, we are intrigued by the beautiful and complex structures of the silica – alkaline earth metal composites called biomorphs [2] with their structures resembling those made by Nature in form of biominerals [3]. The purely inorganic biomorphs were an important example to prove the assumption wrong that such complex morphologies with curved crystalline structures can only be synthesized by living organisms in the process of biomineralization [4].

Although biomorphs have a very complex structure, which can hardly be produced by the common nanoparticle self-assembly methods known to chemists, they do not have an obvious function so that some might consider them more a lab curiosity rather than a useful material. In recent years, scientists have attempted to change this by adding function to biomorphs in form of their chemical modification or the attachment of nanoparticles. This includes the addition of functional molecules or nanoparticles via silane-based coupling molecules [5], doping with fluorescent molecules [6], the polymerization of conducting polymers on the biomorph structure [7], the topotactic conversion of biomorphs into lead halide perovskite semiconductors [8] and the nucleation of magnetic mesocrystals, which transformed the biomorph-mesocrystal hybrid structures into microswimmers with complex shape [9]. For silica-metal membranes electrochemical materials appear feasible [10]. These applications are exciting and show the potential and relevance of MISOS for advanced materials science requiring further investigations in this field. However, biomorphs and silica-metal membranes might also have played an important role in the history of our earth and for the origin of life.

This is the topic of the review paper by Garcia-Ruiz, van Zuilen and Bach who introduced the concept that silica and MISOS have played a key role in the Hadean Earth as catalysts for the generation of simple organic compounds in prebiotic chemistry and therefore for the origin of life. Unfortunately, there are no rocks old enough to check what has happened during the first 500 million years of our planet, but the authors claim a Hadean geochemical scenario with the starting point of silica-rich alkaline oceans from serpentinization reactions of ultramafic minerals producing

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reducing H_2. This leads to the formation of methane and other alkanes from atmospheric CO_2 and H_2 by Fischer-Tropsch type reactions resulting in a reduced atmosphere with CO, CH_4 and H_2 as important constituents, which is supportive for the generation of organic molecules. The interaction of the alkaline silicas with metal hydroxides resp. alkaline earth metal carbonates forms MISOS as silica-metal membranes and biomorphs and these are discussed as catalysts for the formation of organic compounds essential for life such as amino acids and nucleobases. This could be demonstrated experimentally with amino acids forming on the silica side of the membrane and nucleobases at the metal hydroxide side of the silica-metal membrane [11]. Corresponding catalytic reactions on biomorphs are yet less investigated. However, chemically, there is no reason to believe that the silica in biomorphs should not have a similar catalytic effect to that in the silica-metal membranes, although biomorphs are formed in a pH region 1 – 2 pH units lower than the silica-metal membranes.

What is important to investigate now are the catalytic mechanisms on MISOS containing silica as key component since they need to be considered as potentially important catalysts in prebiotic chemistry and the question about the origin of life. There have been a number of laboratory experiments, which demonstrated the formation of organic compounds under prebiotic chemistry conditions. The question is, however, what these conditions were precisely. It is a big difference if the oceans were acidic or alkaline as claimed by the authors. Only the study of rocks from Mars might be able to reveal the likely geochemical scenario on earth. Until then, all plausible geochemical scenarios should be considered. Thus, it is a very exiting research question, which organic molecules can be obtained by MISOS catalysis and the promising results on formamide conversion to amino acids and nucleobases [11] imply an important catalytic role where formamide could have formed from more simple compounds like CO_2, H_2 and NH_3 by condensation.

It is also interesting to note that neither the formation of the silica-metal membranes nor the silica-carbonate biomorphs has been fully revealed yet. In case of biomorphs, the coupled coprecipitation of carbonate and silica at the growth front as a result of pH cycling and the reverse solubility of silica and carbonate is an important factor for the formation of the observed complex structures. However, important questions still remain unanswered. One of these questions is the oligomerization state of silica. The interaction of the different condensation stages of silica with the metal carbonates can certainly be different and can therefore be a factor in morphogenesis and local composition. The same is true for the formation of silica-metal membranes. Therefore, it becomes even more important to reveal the formation of these MISOS as this would not only shed light onto the potential role as prebiotic catalysts, but could also gain information on the chemistry of Precambrian waters, the potential formation of claimed Archean microfossils and thus the correct interpretation of morphological patterns in the search of the earliest forms of life on our planet. All of this remains to be experimentally demonstrated using the Hadean and Early Archean environmental conditions, which is a significant chemical and also analytical challenge.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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