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Reply to comment

The convergence of minerals and life
Reply to comments on “Mineral self-organization on a lifeless planet”

Juan Manuel García-Ruiz [a,*], Mark A. van Zuilen [b], Wolfgang Bach [c]

[a] *Laboratorio de Estudios Cristalográficos, Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada, Av. de las Palmeras 4, Armilla (Granada), Spain*
[b] *Equipe Géomicrobiologie, Université de Paris, Institut de Physique du Globe de Paris, CNRS, F-75005 Paris, France*
[c] *Geoscience Department and MARUM, University of Bremen, Klagenfurter Str. 2, 28359 Bremen, Germany*

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Since our review covers a very long time of the less known, earliest eon in Earth history, and we approached it with tools and information from different disciplines, we hardly expected to receive comments to the entire scope of the review. Fortunately, we have gathered with gratitude six excellent comments from different perspectives and different fields of expertise. The topic itself - what happened at the surface of the planet in a period from which there are no rocky remnants - is obviously very controversial. As Javaux and Sforna say in their comment [1], “the Hadean is a fascinating and mysterious time.” So far, we have approached the Hadean from speculations and modeling. We think that it is time for an experimental approach. It is time to design experiments to help reveal the plausible scenarios that most probably hide the secrets of the conquest of the planet by organic self-organization, and ultimately by life. Therefore, we thank our commentators for the elegance with which they wrote their criticisms, their supports, and their views. Although it is a highly controversial topic, the comments are very constructive and allow us to address issues that had been left in the pipeline due to lack of space or to maintain the readability of the text. In what follows, we discuss the most important issues and observations raised by Cölfen [2], Javaux & Sforna [1], Pereto [3], Ruiz-Mirazo [4], Šponer & Šponer [5], and Vago & Westall [6].

Cölfen focuses primarily on the physicochemical aspects of biomorph formation and their implications in the geochemical context of the first few hundred million years of Earth history. Cölfen recalls the different applications of silica-carbonate biomorphs in the field of materials science, in particular the recent successes in the functionalization of biomorphs [7]. That leads him to suggest further investigation of the interaction between the silica-carbonate biomorphs and organic molecules. Indeed, we agree that this is a field with an undoubted future due also to the different types of applications that can be anticipated. For instance, what has been called reverse biomineralization,

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[*] Corresponding author.
E-mail address: jmgruiz@ugr.es (J.M. García-Ruiz).

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i.e., the replacement of inorganic compounds forming silica/carbonate biomorphs by organics, while keeping shape and textures intact [8]. Or the use of surface properties of biomorphs to enhance tissue regeneration [9]. But we agree that it is a subject that has not been explored enough for its implications in protobiochemistry [10,11]. It is known that silica/carbonate biomorphs are a racemic mixture; therefore, it would be of great interest to induce in them a left-handed or right-handed character. Inducing chirality could be possible by screening the effect of chiral macromolecules during their synthesis. The inverse is also interesting, i.e., would it be possible to carry out a selection of amino acids and their chirality through selective absorption on the nanostructured walls of the biomorphs? And of course, it is necessary to investigate the catalytic effects that biomorphs might have on the condensation of key prebiotic molecules like formamide, and the formation of peptide bonds, particularly considering that these biomorphs grow at about two pH units lower than silica/metal oxides membranes.

Another important issue that Cölfen points out is the necessity for a better physical and chemical explanation of the formation of biomorphs. Despite the advances made in recent years, we are still far from understanding in depth the physicochemical processes governing the morphogenesis of biomorphs, i.e., to understand how and why pure inorganic compounds solubilized in a homogeneous solution can self-organize in these mesmerizing nanocrystalline architectures. The work of research groups in Harvard [12,13], Florida [14,15], México City [16,17], Konstanz [18,19], Torino [20], Yokohama [21,22], Canberra, Regensburg [23–25], and Granada [26–30] has shown that the problem of the morphogenesis of silica/carbonate biomorphs is a formidable theoretical challenge that certainly cannot be solved by classical approaches of crystal growth. This is a fundamental issue because unlike other famous self-organized structures such a Belousov-Zhabotinsky reaction, cellular automata, physical instabilities, or Turing patterns ([31–37] that have been produced only as faded liquid patterns or just *in silico*, biomorphs are stable solid architectures forming in wet chemistry that takes place in plausible geochemical environments. Certainly, we have progressed in the phenomenological understanding of the morphogenesis, in the control of the shapes, and even the control of biomorphic and crystalline textures to produce complex architectures. But we still need to understand the fundamental mechanisms behind this extraordinary self-assembly. Only such a deep comprehension will allow us to explore the possibility of farther complex levels of self-organization at different scales. In other words, to push farther the actual limits of inorganic mineral self-organization.

This challenge connects directly with the problem that several of our commentators have pointed out, namely the fascinating subject of the differentiation between the morphological patterns of the inorganic world and those of the living world. Javaux and Sforna [1], citing Bruylants et al. [38], argue that the boundaries between life and non-life are blurred in the computational sense of the term, i.e., fuzzy. Indeed, we wholeheartedly agree. As illustrated by Peretó [3] (see also [39,40]), the history of paleontology is well-stocked with examples of the misuse of morphology in detecting remnants of life. In terms of morphology and texture, biomorphs are an excellent demonstration of how diffuse that boundary is, mainly because of their geochemical plausibility. The morphological convergence of biomorphs with primitive life is evident. The fact that their size and size distribution are similar to those of the reliable remains of primitive life, is also undeniable. Many Archean rocks that contain proposed microfossil remains have a geochemical background compatible with that of the synthesis of biomorphs. Nevertheless, we agree with Javaux and Sforna that the use of a combination of analytical and statistical techniques can help to differentiate life remnants from their inorganic counterparts [41–44]. It is beyond any doubt that detecting unequivocally the earliest, oldest remains of life on Earth is a fundamental goal in establishing the timing of the origin of life on our planet. But it is also essential to detect biomorphic mineral structures and reveal their actual origin because they are excellent geomarkers that could provide valuable information about the geochemical environments of early Earth [31]. And most importantly, they would shed light on the possibilities of self-organization of the abiotic mineral world, an issue that Ruiz-Mirazo brought to the discussion [4].

Ruiz-Mirazo touches on a delicate subject usually avoided in the framework of the origin of life studies. He wonders why organic matter has triumphed over inorganic matter; why should there be any *in principle* barrier for 'inorganic life'? He asks for more for our review: why are we not claiming that mineral biomorphs could develop further to a higher level of complexity? Indeed, the following question is licit: How would this planet has evolved if life as we know it did not emerge 4 billion years ago? Would biomorphs have developed into self-sustaining, authocatalytic objects capable of evolving into selective complexity? We hope that the source of our caution is now clear. As we say above, we still miss a theoretical framework for understanding the genesis of that complexity. We frankly don't know yet in detail how the textural and morphological complexity of silica/carbonate biomorphs emerges from a simple homogenous aqueous solution. Of course, purely theoretical approaches are valid. For instance, the smart hypothesis of Cairns-Smith of genetic takeover [45] has an outstanding internal logic, although it is experimentally difficult to verify [46,47]. In the case of silica-induced biomorphs, we prefer to jump to the next step of inorganic complexity, including inorganic selectivity, chirality, and metabolism with the feet resting on the stones of experimentation, on experimental design driven by knowledge.

From a chemical point of view the formamide route is today considered one of the best-founded pathways to the origin of life [48]. The condensation of formamide produces an outstanding variety of prebiotic key molecules with unbeatable yielding. However, the probability of formamide to concentrate in the surface of the early Earth is still a matter of discussion [49–53]. Sponer and Sponer focused on this crucial issue [5]. They argue that liquid formamide could have been accumulating in the early ocean through the dissociation of ammonium formate, a compound that could have formed by the gas-phase reaction of formic acid with ammonia [54,55]. Interestingly, their experimental studies also suggest that minerals such as Fe-Ni thiospinel catalyze the Fischer-Tropsch-type conversion of carbonate to formate, an alternative but a parallel route to formamide production in a Hadean geochemical scenario as the one proposed in our review. Interestingly, Shtyrlin at al., [56] has also explored the condensation of formamide under meteoritic shock in the water-formamide-potassium bicarbonate-sodium hydroxide system. The hydrochemistry used in their experiments is similar to the water of the soda lakes of the African Rift Valley where recently the formation of MISOS has been demonstrated [57]. There is certainly a promising research venue to the exploration of the role of mineral catalysis in the condensation of formamide but also in the synthesis of formamide. So far, we have devoted much attention to the composition of the atmosphere in prebiotic chemistry experiments. We strongly believe that it is time for rock-fluid interaction experiments to enter the scene with well-designed ad-hoc experiments.

We acknowledge Vago and Westall [6] for their suggestion to extend our view of the Hadean times to the earliest days of other celestial bodies. It is an exciting venue to extrapolate these considerations to other planets and moons in our solar system and beyond. Ultimately, insight into our own origin on Earth may be derived from observations made on other celestial bodies. The serpentinization process appears to be ubiquitous on most Earth-like planets and moons as soon as water condensed on ultramafic rocks in their crust [58]. In fact, highly alkaline environments likely related to serpentinization have been suggested to exist on different moons of the solar system, including Enceladus, Europa, Ganymede and Titan [59–63]. The evidence of a pleiad of organic compound, in some cases at concentrations high enough - e.g. in Titan - to predict a planetary scale factory as the one we propose in our view of the earliest Earth is worth to be explored in detail. More observational and analytical data are required to envisage a clear geochemical framework for these moons. In the case of Mars, it is now well-established that it contained bodies of liquid water early in its history. Indeed, we agree that it will be of critical interest to study water-rock interactions under these early Martian environmental conditions. Given that the Martian surface did not evolve plate tectonics, ancient surface features such as water-lain sediments [64,65] and hydrothermal sinter deposits [66] have remained largely intact without any histories of high-grade metamorphism. It is therefore entirely possible that important steps in prebiotic chemistry, mineral self-organization processes, organic synthesis, and early evolution of life, are preserved in these Martian deposits. Based on these considerations, we would argue that the search for traces of life on Mars should be extended with a search for prebiotic molecules and self-assembled mineral aggregates.

Vago and Westall [6], as well as Javaux and Sforna [1] raised concerns about the likelihood of alkaline oceans in the Hadean. Indeed, the perception of an acidic Archean ocean is more widely accepted and is explained by high atmospheric pCO_2 (e.g. [67,68]) or high contents of dissolved iron [69]. Albarede et al. [69] argued that the scarcity of limestone in the Early Archaean means low ocean alkalinity due to both little weathering and low atmospheric pCO_2. These authors suggest that Earth prior to the great oxidation event had perhaps only 20% of today's landmass, and hence much lower alkalinity fluxes to the oceans can be expected. Javaux and Sforna [1] employed this argument to suggest that a Hadean world without continental surfaces would mean even smaller alkalinity fluxes to the oceans, which would hence have low pH. Low alkalinity flux, however, does not equate to low pH. For instance, serpentinization of the ultramafic crust will also directly affect the pH of the interacting fluids. In high-temperature hydrothermal systems, such interaction leads to acidic fluids, but in low-temperature hydrothermal systems, highly alkaline fluids are produced even in the presence of a contemporary CO_2-bearing atmosphere (e.g., [70]). These fluids have high pH but low alkalinity [71].

The views on ocean-atmosphere chemistry in the Archean are diverse. The cherished hypothesis of a high-pCO_2 and fairly oxidized atmosphere has been challenged in several recent studies [69,72,73]. The hypothesis of a ferruginous, low-pH ocean [69] was developed to help explain the common occurrence of BIFs in the Mesoarchean. Likewise, the idea of high pCO_2 in the atmosphere was advanced to account for Paleoarchean siderite beds ([67] and references therein). But the ubiquitous silicification of Eoarchean seabed rocks cannot be explained by either scenario. It calls for different ocean chemistry, one in which silica concentrations were high. High silica concentrations require high pH (just like high Fe concentrations require low pH). Discharge of acidic high-temperature vent fluids into an alkaline, silica-rich ocean would cause massive localized silicification, which is a hallmark of Archean hydrothermal deposits. So, in order to explain the ubiquitous occurrence of extreme silicification of the seabed around and away from hydrothermal vents, it makes good sense to consider that the earliest oceans were alkaline and silica-rich. It is this specific setting that we see as a global-scale factory for MISOS-catalyzed prebiotic chemistry and the origin of life.

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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