



## Review

## Mineral self-organization on a lifeless planet

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## Abstract

It has been experimentally demonstrated that, under alkaline conditions, silica is able to induce the formation of mineral self-assembled inorganic-inorganic composite materials similar in morphology, texture and nanostructure to the hybrid biomineral structures that, millions of years later, life was able to self-organize. These mineral self-organized structures (MISOS) have been also shown to work as effective catalysts for prebiotic chemical reactions and to easily create compartmentalization within the solutions where they form. We reason that, during the very earliest history of this planet, there was a geochemical scenario that inevitably led to the existence of a large-scale factory of simple and complex organic compounds, many of which were relevant to prebiotic chemistry. The factory was built on a silica-rich high-pH ocean and powered by two main factors: a) a quasi-infinite source of simple carbon molecules synthesized abiotically from reactions associated with serpentinization, or transported from meteorites and produced from their impact on that alkaline ocean, and b) the formation of self-organized silica-metal mineral composites that catalyze the condensation of simple molecules in a methane-rich reduced atmosphere. We discuss the plausibility of this geochemical scenario, review the details of the formation of MISOS and its catalytic properties and the transition towards a slightly alkaline to neutral ocean.

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## 1. Introduction

Earth is the only known planet where matter self-organized into micron size structures able to display complex behavior and shapes that can evolve by replication. We call these self-organized structures living organisms, and organic chemistry the carbon-based set of reactions that govern their function and growth. It is nowadays fully accepted that life has had a fundamental influence on geochemical processes since its establishment on the planet [1,2]. That influence occurs via different pathways, namely: a) the massive production of gases such as oxygen, methane or carbon

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dioxide, derived from biochemical reactions; b) the production of polymeric compounds that largely affect the nucleation and growth of crystals – and therefore the morphology and textures – of minerals; c) the creation of inorganic or organic solid structures that significantly contribute to the inventory of rock-forming materials; and d) and in the last century, humans who are actually shaping at large scale the atmosphere, the hydrosphere and the surface of the crust, so much that a new geological era, the Anthropocene, has been named to mark their impact [3,4]. Ubiquitous as life is today and it was during most of geological history, it is obvious that this planet was once devoid of life. It is unknown when life first appeared on Earth, and thus we do not know for how long the planet was entirely abiotic and driven by geochemical processes alone. With the information currently available it seems reasonable to state that for several hundreds of millions of years, minerals nucleated and grew without the additives supplied by life. Scientific reconstruction of that part of geological history is a formidable task because of two main reasons. First, we cannot apply actualism, the best methodological tool that geologists use every day to unveil the past history of the planet: the present, which is strongly affected by life, cannot be the key to a lifeless past. Second, there are no observational objects to study. The oldest known rocks on Earth that could harbor traces of early life are ca. 3.8 Ga [5–12], and have been strongly deformed and recrystallized under high pressure and temperature, complicating inferences of life [13–19]. Any geochemical and biological interpretations from the period older than that have to be inferred from some rare preserved zircon crystals [20–25].

For the above reasons, i.e. for the critical role that life plays in most geochemical processes, it is hard to imagine the geological processes at work during the first millions of years when the planet was devoid of life. The very name that geologists have given to that time or eon, the Hadean – a Greek name that refers to the hell – is illustrative of the kind of physical landscape that we had imagined. The classical view that was widely accepted until a few years ago was a landscape of high temperature, mildly reducing atmosphere, devoid of condensed water, with partially melting crust, ubiquitous volcanic activity and intense meteoritic bombardment. This view has drastically changed in the last years. With the currently available information on the Hadean it seems most probable that water condensed on the surface of the planet soon after solidification of the first ultramafic crust [20,24]. The thermally-driven interaction between water and ultramafic minerals – serpentinization – unavoidably created an alkaline, and reduced hydrosphere [26–31]. Because of the higher geothermal gradient this serpentinization reaction was likely a strong driver for Fischer-Tropsch type synthesis of organic molecules [31]. During the Hadean, the Earth's crust also became more differentiated, forming tonalite-trondjemite-granite (TTG) series, alongside ultramafic and mafic rocks. This could have been caused by intense intraplate melting [32–34], or could have resulted from arc-like settings at the onset of early plate-tectonics (e.g. [25]). The interaction of alkaline waters with granites and gabbro produced alkaline silica rich water. This unavoidably led to the formation of mineral self-organized structures (MISOS) of two types, namely silica/carbonate nanocomposites with biomimetic morphology and textures, and mineral membranous vesicles made of silica and metal oxy-hydroxides. The impact of meteorites on the alkaline silica rich “oceans” provoked further large scale MISOS formation and a reduced atmosphere and hydrosphere. We develop here the geochemical foundations of this view of the Hadean times and discuss how the transition from geochemistry to organic chemistry and prebiotic chemistry scenarios may have occurred.

## 2. Mineral self-organization based on silica

Calcium carbonates, either calcite or aragonite, crystallize in the laboratory or in nature from inorganic solutions as single or twinned crystals exhibiting flat faces and perfect cleavage. These calcium carbonate crystals are brittle and their fracture exhibits smooth surfaces at fixed angles that reflect the point symmetry of their crystal structures [35–37]. The faces of these crystals grow by classical mechanisms of step motion, which are generated by screw dislocation and/or two-dimensional nucleation [38,39]. However, when calcite or aragonite crystals grow in living organisms – a process called biomineralization – they do in a very different way. For instance, marine exoskeletons, such as shells of clams or mollusks, display complex morphologies that are shaped by surfaces of continuous curvature rather than by flat facets [40–42]. When these biomineral structures are broken they display a glassy fracture that does not show flat but curved surfaces [43]. These shells are made of millions of nanocrystals that self-assemble with excellent co-orientation forming a mesocrystalline structure that sometimes even retains the point symmetry of the calcite or aragonite structure [44–46]. Visual records of the *in situ* growth of biominerals show that the crystals do not grow by classical growth mechanisms as abiotic calcite and aragonite do, but by accumulation of disordered nanodots of an amorphous precursor or a high-density cation-rich solution that afterwards recrystallized to a stable crystal polymorph

[42,47,48]. It is now well known that amino acids, polypeptides, proteins and other biological molecules are able to substantially modify the precipitation and properties of calcium carbonate and other biominerals [48–50]. Such an effect is thought to be so conspicuous that it has even been proposed as a way to detect life elsewhere [51]. All these studies are strengthening our understanding of the way biomineral structures form and how we can use that knowledge in the design and fabrication of advanced nano-materials [52–54].

Interestingly, this ability of biochemical compounds to induce mineral organization is matched by silica ( $\text{SiO}_2$ ), a ubiquitous compound in the crust throughout Earth's history including the time when the planet was devoid of life (see below). Like biological molecules do, silica dramatically affects the precipitation of carbonate at many levels, including the morphology, texture, fracture, and even the growth mechanism by which carbonate crystals form. Increasing evidence has been gathered during the last thirty years indicating that silica species in alkaline aquatic environments are able to chemically interact with metals to form fascinating self-assembled mineral structures, which show the ability to control shapes and textures of minerals, similar to that of organic matter and life. These self-organized structures form far from equilibrium [55], and on the basis of mineral composition and functionality, they can be classified in two main groups, namely silica biomorphs and silica gardens [56] (Fig. 1). Both of them occur in aqueous solutions with high pH values where the solubility of solid-state amorphous silica increases dramatically, from 180–200 ppm at acidic and circumneutral pH to values of a few grams per liters at pH higher than 10. The solubility of silica increases above pH 8.3 due to the first deprotonation of silicic acid and then increases even more when the second deprotonation event starts [57–59]. The formation of either silica/carbonate biomorphs or silica gardens depends on the pH and  $\text{CO}_2$  concentration, and is determined by the dominance of either of  $\text{H}_3\text{SiO}_4^-$  or  $\text{H}_2\text{SiO}_4^{2-}$  species. Considering the pKs of the two equilibria,  $\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_3\text{SiO}_4^-$  and  $\text{H}_3\text{SiO}_4^- \rightleftharpoons \text{H}_2\text{SiO}_4^{2-}$  the boundary between the two types of MISOS can be estimated to be at a pH value of ca.11.3.

### 2.1. Silica/carbonate biomorphs

As shown in Fig. 1 there are two regions where the effect of silica is quite different. In region of lower pH range, barium, strontium and calcium carbonate/silica biomorphs form, provided there is enough  $\text{CO}_2$  in the environment. These biomorphs are self-organized materials that spontaneously form biomimetic complex structures upon simple mixing of an alkaline silica solution with solutions of alkaline-earth metal [60,61]. They are non-hybrid but purely inorganic composite materials made by millions of nanocrystals of carbonate and a small amount of amorphous silica. Biomorphs have two main biomimetic properties. One is the ability to display morphologies with continuous curvature reminiscent of primitive living organisms at the same micron-size scale, and under geochemically plausible conditions (see below). In addition, biomorphs also build textures of high complexity that mimic extremely well the hybrid organic-carbonate textures of biominerals and biologically induced minerals, and bio-inspired artificial organic-inorganic hybrid materials [62–64].

So far, biomorphic materials have been successfully synthesized for alkaline-earth carbonates with orthorhombic structure, namely for witherite ( $\text{BaCO}_3$ ) and strontianite ( $\text{SrCO}_3$ ) [61,65–70] as well as for aragonite, which is the orthorhombic polymorph of  $\text{CaCO}_3$  [66,71–74]. Biomorphs of monohydrocalcite, the hexagonal monohydrate of calcium carbonate have also been found within a narrow range of temperature between 40 and 80 °C, demonstrating that the crystal structure of the carbonate phase is not fundamental for the self-assembly.

The morphogenesis of these structures has been described phenomenologically [75] but the underlying morphogenetical mechanisms are still debated [62,69,76–78]. From the chemical point of view the phenomenon of biomorph formation is explained by a self-feeding mechanism triggered by the reverse solubility of silica and carbonate with respect to pH provoking a coupled co-precipitation at the growth front [79] (Fig. 2).

The panoply of shapes displayed by biomorphs is clearly reminiscent of those of primitive biological organisms [63]. Unlike crystalline precipitates, they show not only fractal structures but also morphologies with continuous curvature once thought to be exclusive for life. The comparison of biomorphic structures with Precambrian microfossils in terms of morphology is striking [60,81] but the proposal of biomorphs as an alternative explanation for the origin of the microstructures considered Precambrian microfossils or putative microfossils is based not only in morphology but also in the following features:

- 1) Silica/carbonate biomorphs are self-organized structures that form without any external input.

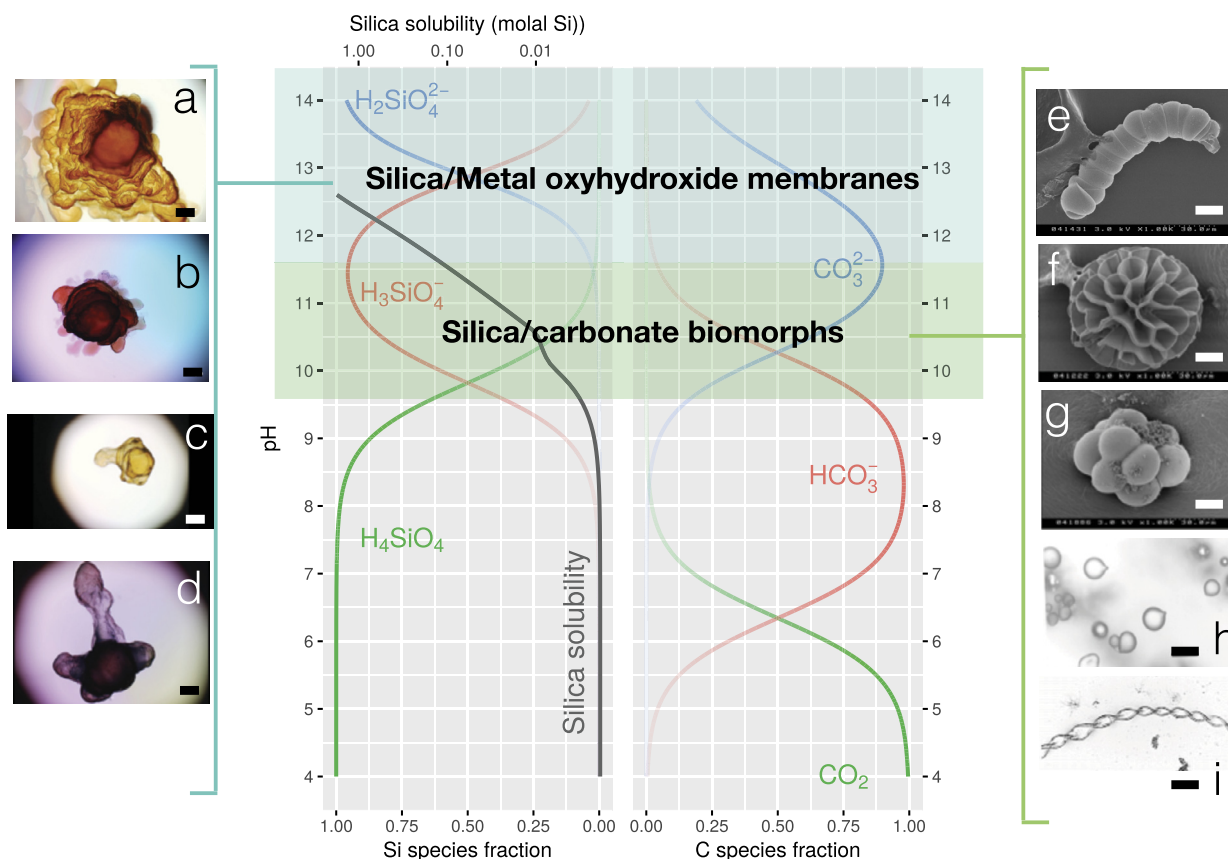


Fig. 1. Mineral self-organization induced by silica. Typical examples of silica biomorphs and mineral vesicle gardens, and the location of both phenomena of self-organization in pH versus silica and pH versus carbonate speciation diagrams. Also shown are the total solubility of silica and hydroxide concentration in solution as a function of pH. The shaded areas represent pH ranges in which the two types of structures were reported to form. In the green area, at moderately alkaline pH (ca. 9–11) silica biomorphs grown by crystallization of barium carbonate, strontium carbonate, or calcium carbonate. Dissolved silica species carry a relatively low number of charges and are prone to condensation reactions [58]. This effect lowers their solubility, and leads to the formation of amorphous silica next to carbonate. The dominant morphologies are shown to the right of the plot. In the blue area, at higher pH values (pH > 11) the solubility of silica increases due to the formation of silicate from the second deprotonation of silicic acid. Upon reaction with acidic metal solutions, amorphous silica and metal silicates form, while the higher concentrations of  $\text{OH}^-$  ions favors the formation of metal hydroxides and oxides. A double sided metal-rich/silica-rich membrane is formed. Typical vesicular and tubular structures are shown to the left of the plot. Scale bars: a) 300  $\mu\text{m}$ ; b-d) 200  $\mu\text{m}$ ; e-g) 20  $\mu\text{m}$ ; h) 100  $\mu\text{m}$ ; i) 50  $\mu\text{m}$ .

- 2) Almost all the Archean putative microfossils reported until now are found in cherty rocks, i.e. rocks that either formed from silica sols or were silicified by silica-rich fluids. And more astonishingly, in several cases the rocks containing the oldest putative remnants of life are barium-rich cherts [82,83].
- 3) Laboratory experiments [60] have demonstrated that carbonaceous compounds - for instance, those that form from decomposition of siderite [84] - can be adsorbed or coated on the surface of the silica skin of biomorphs, thereby creating organic structures that mimic organic microfossils [85].
- 4) Biomorphs and Precambrian putative microfossils have the same scale but they have distinctive size distribution [60,81,86].
- 5) As we will show below, silica/carbonate biomorphs are synthesized from a simple chemical cocktail that is not only geochemically plausible but also physico-chemically similar to the petrogenesis of the rocks in which Archean microfossils are embedded.

Thus, the existence of biomorphs leads to the conclusion that there is no sharp difference in form and point symmetry between structures belonging to the abiotic and the biotic realm and, in turn, that biological origin of any putative

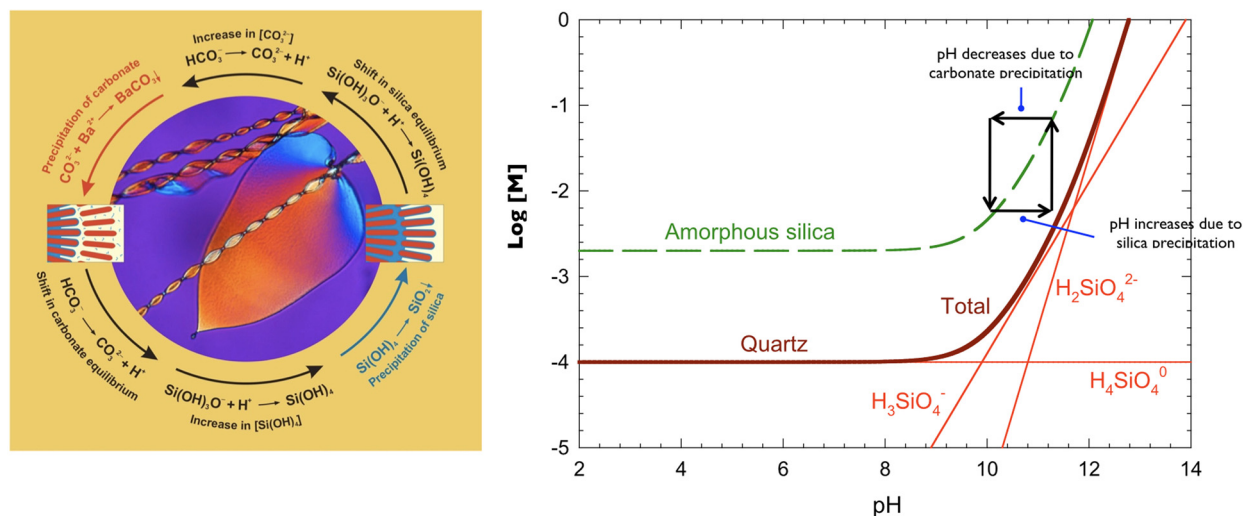


Fig. 2. Mineral complexity requires a feedback mechanism to trigger autocatalysis, schematically shown on the left. In the case of self-assembled silica biomorphs the mechanism is the reverse solubility of silica and carbonate as a function of pH. As shown in the plot at the right, when the carbonate crystals nucleate at the growing front, the pH decreases due to the release of hydrogen ions. This decrease in pH provokes the supersaturation of the surrounding solution with respect to the silicic species dominating at that range of pH and then their precipitation as silica or metal silicates, which inhibits the growth of the carbonates crystallites. The precipitation of silica necessarily provokes an increase in pH that raises the concentration of carbonate ions and eventually provokes a new nucleation of carbonate crystallites. Therefore, the system enters a self-feeding mechanism in which the “impurities” of silicic acid species are produced by the very growth of the carbonate crystalline phase. The existence of these pH oscillations has been demonstrated experimentally [79]. Adapted from reference [75], and reference [80].

remnants of life cannot be identified on the basis of morphological aspects alone. This is particularly true for primitive life when the absence of compartmentalization hinders the application of comparative anatomy. Today, it is accepted that morphology by itself cannot be claimed proof of biogenicity for Archean structures [87–89]. For the same reason, none of the putative Archean microfossils have been demonstrated to be unequivocally silica biomorphs on the basis of morphology either. There are ongoing investigations on deeper characterization of lab-made silica biomorphs, their formation and preservation under different P-T conditions, as well as on the high-resolution structural characterization on adsorbed carbonaceous compounds in laboratory analogues. And, fortunately, recent developments in *in-situ* analysis (isotopic, molecular, compositional, structural) help significantly in the identification of other features of life beyond morphology, allowing a more accurate identification of Archean microfossils [90–100]. The boundary between life and non-life becomes fuzzier and fuzzier as we get further in deep time, when shapes of living organisms were simpler and their preservation was more difficult.

## 2.2. Calcite single crystals with complex shapes

The relevance of silica-induced carbonate biomorphs in life detection is not restricted to the complex polycrystalline microstructures of continuous curvature. It is known that single-crystal and polycrystalline calcite, the trigonal polymorph of calcium carbonate, form in the presence of biological fluids [101,102] or under the effect of extracellular polymeric substance (EPS) films or organic compounds such as amino acids or proteins, and display non-singular faces tautozonal to their c-axis. These bizarre curved crystals have been proposed to be a proxy in life detection studies [51]. However, silica is also able to induce identical morphologies when calcite is grown under alkaline conditions in silica-rich solutions. Under these conditions, they form single crystals displaying complex biomimetic textures and morphologies having memory of the calcite crystal symmetry [103–105]. Noticeably, these calcite single crystals have been shown to be the inorganic alternative to the so-called nanobacteria [101,102].

Even more important for Earth Science studies is the use of silica-carbonate biomorphs as geochemical markers [106]. As discussed in this review, complex shapes with continuous curvature, fractal polycrystalline structures and single crystals of alkaline-earth carbonate with non-singular faces induced by silica are all formed from solutions within a range of pH between 9 and 11. When each of these characteristic morphologies is considered, it can be



possible to determinate the pH with a precision better than one unit [81,107,108]. Therefore, finding these bizarre structures in rocks will provide precious information about the solutions from which they were forming.

In summary, laboratory studies and the search for field evidence of silica biomorphs and fractal carbonates may provide information on: a) the chemistry of Precambrian waters; b) the biological or abiological character of Archean microstructures of debated origin; c) the ability of chemical species derived from silica at high pH to emulate crystal patterns characteristic of biologically induced carbonates and the role that such an emulation might have in explaining processes of biomineralization, and d) the correct interpretation of morphological and textural patterns in the context of the search for life on the earliest Earth and elsewhere.

### 2.3. Self-organized metal hydroxides/silica membranes

At pH higher than 11 (Fig. 1) carbonate is the dominant species of dissolved inorganic carbon and silicate anions dominate the speciation of silica. At these pH values, the mixing of a high-concentration solution of silica with an acidic solution of metals – such as zinc, iron, cobalt, magnesium, nickel, manganese, copper, etc. – results in the formation of permeable diaphragm-like membranes made of amorphous silica and metal oxy-hydroxides nanoparticles, that display chemical and textural gradients. A morphogenetic mechanism based on a combination of fast chemical precipitation, osmosis, and buoyancy results in the formation of hollow tubular or vesicular architectures [109–112]. These structures are known since hundreds of years as silica gardens [63,112]. They were considered in the 19th and early years of the 20th century as vital protoplasm and they are at the root of a Lamarckian trend in synthetic biology [113–116]. Because of their biological-looking morphology and in some cases because of the morphogenetical process, the experimental investigations of these silica/metal membranes and other self-assembled colloidal and osmotic structures were the core of a mechanistic approach to the origin of life [117,118]. The development of biochemistry, cellular theory and evolutionary studies makes evident that this early synthetic biology was a “cul de sac” approach. This experimental mechanistic approach to the origin of life was continued by Sidney Fox [119,120]. His experiments and discussion, mostly seeking a high level of biochemical and cellular organization, were a very modern approach based on self-assembly and far-from-equilibrium self-organization. In addition, based on the morphological chimney-like appearance of classical silica garden experiments, Russell [121] proposed a connection between silica gardens and the theory of the origin of life in hydrothermal vents previously proposed by Baross and Hoffman [122–124].

The discovery of the existence of a voltage between the inner and outer solutions separated by the diaphragmatic membrane of silica gardens raised the interest in these types of structures as microreactors for catalysis studies [55, 56,125–127]. The chemical and diffusion potential across the membrane generates a voltage for several hours of up to 120–550 mV depending on the metal, with ferric iron membranes yielding the highest voltage.

The potential catalytic role of these self-organized mineral membranes in the synthesis of biologically relevant compounds has been tested. These experiments were performed using as chemical precursor, namely formamide ( $\text{NH}_2\text{CHO}$ ), a single-carbon organic molecule that has been demonstrated to be an interesting and well-tested alternative to the classical HCN route used in many prebiotic experiments since the pioneering work of Urey and Miller [128, 129]. The experiments were performed with classical tubular structures [130] but also with mineral vesicles made by pouring drops of metal solution on alkaline silicate solutions [131]. The results of these condensation experiments are outstanding in demonstrating the catalytic power of mineral self-organized membranes induced by silica. Specifically it was shown that a) in addition to three amino acids (glycine, alanine, and N-formyl glycine), and six carboxylic acids, the four nucleobases required as RNA components were synthesized in a single experiment at 80 °C; and b) the catalysis is selective in that the acids are synthesized in the outer, silica side of the membrane, while the nucleobases are in the inner side, made of metal-oxyhydroxide nanoparticles [132]. In addition to their catalytic power, which is higher than in previous studies of minerals tested with formamide, these membranous vesicles provide compartmentalization, and are a very efficient shield against ultraviolet radiation.

In summary, there is documented experimental evidence confirming the ability of alkaline silica to interact with metal carbonates and metal oxyhydroxides to synthesize inorganic self-organized nanocomposite structures, which have relevant geochemical properties, including: a) the formation of shapes with continuous curvature thought to be exclusive of biological organisms; b) the self-assembly of biomineral like textures in which silica plays the role of organic matter in biominerals; c) the use of biological and non-biological morphogenetic processes to create life-like shapes; d) the growth of carbonate crystals by accretion of nanodrops, a mechanism that life uses to grow biominerals; e) the creation of porous membranes that may work as little batteries with plausible catalytic properties; f) the

enhancement of the condensation of formamide with a yield in molecular diversity and concentration unmatched by other previously tested minerals.

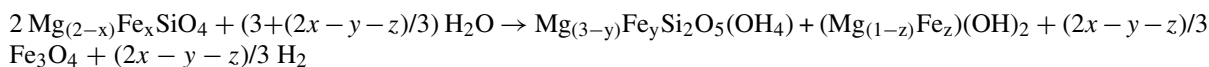
Given these facts, the main question to be asked is whether the laboratory conditions to produce silica based self-organization are geochemically plausible and more importantly if there was a time on the lifeless early Earth in which the conditions to create silica/carbonate biomorphs and metal silicate hydrate membranes were met. In the next section we discuss how plausible these alkaline silica-enriched environments are today, and were in the past.

### 3. Geochemical scenarios for silica induced mineral self-organization

#### 3.1. Geochemical framework of related contemporary processes

As shown in the previous section, the ability of silica to induce complex biomimetic structures such as silica biomorphs and mineral vesicles has been experimentally demonstrated in the laboratory with model solutions. Their synthesis requires highly alkaline solutions, in addition to a high concentration of silica. The relevant question for the significance of this type of mineral self-organization to Earth Sciences is: Are these conditions geochemically plausible? Were there environments on Early Earth where these conditions prevailed? At present, alkaline water with a high silica concentration like the one required to trigger self-organization, i.e. 300 ppm for silica biomorphs and biomimetic calcite and 900 ppm for mineral vesicles (these values depend on pH, salinity and temperature [56]) are scarce. Fig. 3 shows the composition of spring waters from those sites in a plot of pH versus silica concentration. There are two types of geochemical scenarios leading to alkaline natural waters enriched in silica. One of them is serpentinization, Aqua de Ney being an example, and the other one is a soda lake, such as Magadi Lake [133–135].

Serpentinization is one of the few geochemical reactions that creates a highly reduced environment due to the release of molecular hydrogen [26,136]. This reaction is triggered when water interacts with olivine, a silicate mineral, which is a solid solution between two end members, fayalite (iron silicate) and forsterite (magnesium silicate). The reaction produces magnetite and molecular hydrogen together with the hydrous minerals serpentine and brucite:



The distribution of Fe in the reaction products, and hence the yield of  $\text{H}_2$ , is a function of pressure, temperature, and rock composition [29,137,138]. The presence of brucite imposes a high pH and low silica activity to the interacting waters. Thus, spring waters known to derive from serpentinization processes have pH values as high as 12, even in the contemporary presence of a  $\text{CO}_2$  atmosphere acting as acidifying agent (e.g., [139]). On modern Earth, serpentinization is a widespread process, which takes place in many geotectonic settings (e.g., [140]). The presence of serpentine and brucite effectively buffers silica concentrations to low values ( $3 \text{Mg}(\text{OH})_2 + 2 \text{SiO}_2(\text{aq}) = \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{H}_2\text{O}$ ; ignoring Fe). Hence, serpentinization reactions do not release silica. Nonetheless, there are some contemporary sites where serpentinization waters are enriched in silica, as for instance in the Cascades Range, in the contact between the Trinity Ophiolite Complex and Tertiary basaltic-andesitic volcanic deposits, in Northern California. There, high-pH ground waters derived from serpentinization [141], pass through silica-rich rocks and become enriched in silica [142]. One of these alkaline springs is known as Aqua de Ney and is located at the Siskiyou country (California, USA). The water of the Ney spring discharges at 14 °C with pH 12 and up to 4 g/L of dissolved silica [105]. These values fall inside the range of crystallization conditions of silica induced self-assembled structures, which might nucleate and grow from these waters. Therefore, waters from Ney's spring were mixed with solutions of different metals at different temperatures. The experiments clearly demonstrate the production of the three main types of silica-induced mineral self-assembly (Fig. 3), namely a) nanocrystalline self-assembled biomorphic composites of barium carbonate and silica; b) mesocrystals and crystal aggregates of calcium carbonate (calcite) with complex biomimetic textures, and c) osmotically driven metal silicate hydrate membranes. Unfortunately, the Ney spring is located on the border of a fast flowing creek (Ney's creek) of neutral water and the alkaline water from the spring becomes immediately diluted. There are some millimeter-thick travertines made by evaporation of these salts on the artificial wall separating the main well from the creek. The waved texture is mainly made of hydrocalcite. The search for in-situ formation of complex mineral self-organized structures in the wells of Aqua de Ney would require to drill the rocks surrounding the well, in the ruins of the old Ney's Spa. Nevertheless, these investigations demonstrate that silica-based mineral

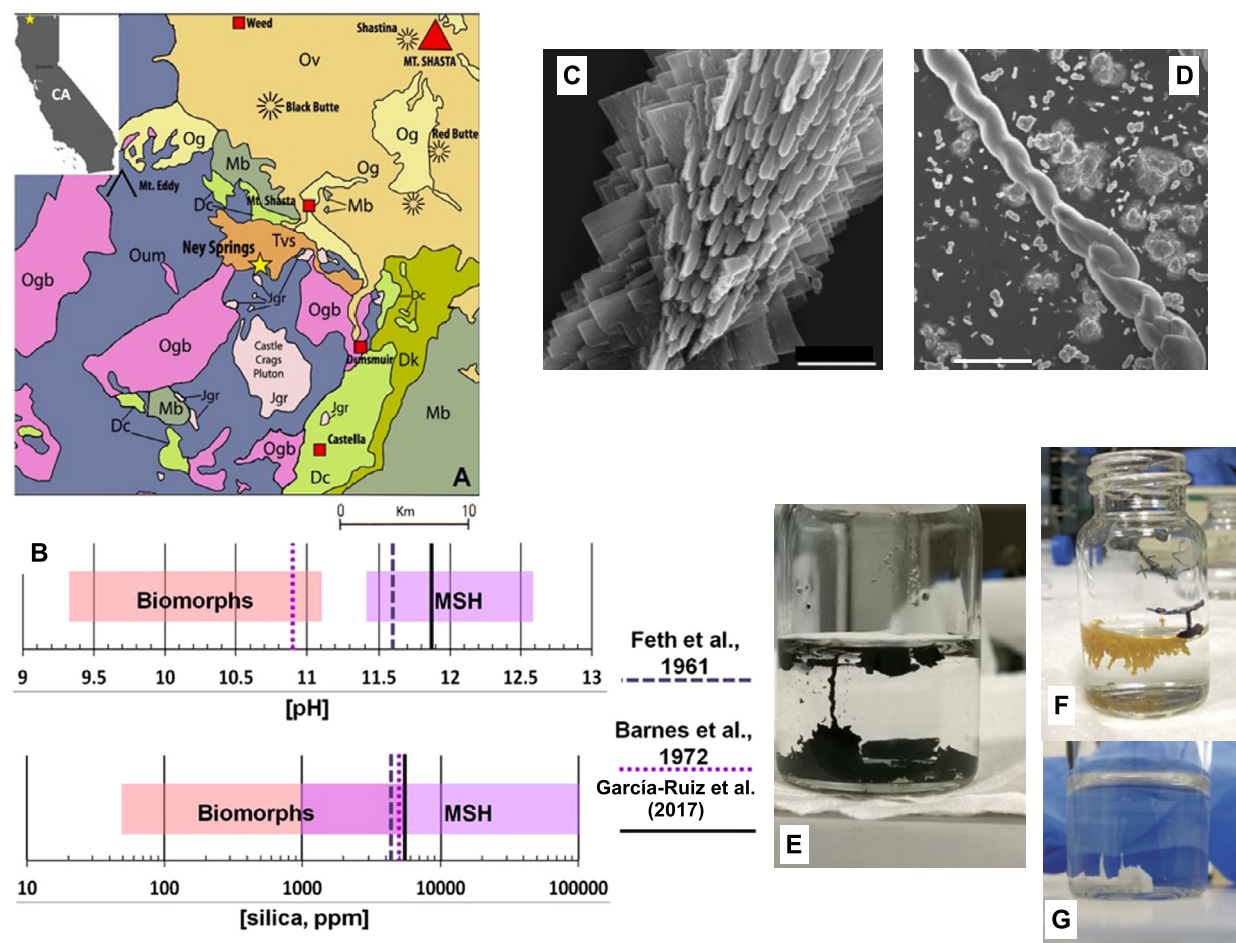


Fig. 3. Aqua de Ney is a hyperalkaline (pH~12) silica-rich (4 mg/l of silica) high-methane mineral spring located in Siskiyou County (North California). A) Simplified geological map of the Ney Springs area. OUM, Ordovician Trinity Ultramafic Sheet; OGB, Ordovician Gabbro and diorite; DC, Early Devonian Copley Greenstone; DK, Early-Middle Devonian Kennett Fm. (interbedded dark siliceous shale, rhyolitic tuff and limestone); MB, Mississippian Bragford Formation; JGR, Jurassic granitoid plutons; TVS, Eocene-Oligocene volcanic and sedimentary rocks. The spring is located at the geological contact of ultramafic rocks of the Trinity ophiolite complex (Oum in the schematic map) with volcano-sedimentary deposits (TVS). The high pH fluids of the Ney are derived from interaction with the serpentinized peridotites, and the enrichment in silica was generated by the dissolution of silica-rich phases in the volcano-sedimentary deposits at high pH [141,143]. B) Comparison of the pH values and the silica concentration (ppm) needed for the synthesis of biomorphs and MSH membranes, with the values found in the Ney natural spring waters [105,144,145]. C-G) Self-organized mineral structures synthesized with Ney waters: Biomimetic textures of calcium carbonate (C); Silica-carbonate biomorphs (D) and silica/metal oxide hydroxide membranes (E-G). Scale bar: c) 1  $\mu$ m; d) 10  $\mu$ m. Adapted from reference [105].

self-organization may occur within the hydrochemical features of natural silica-rich alkaline water derived from serpentinization.

A recent fluid-rock interaction experiment highlighted the geochemical plausibility of silica-metal-oxyhydroxide membranes [146]. It was shown that the interaction of granitic rocks with highly alkaline solutions results in the formation of silica induced mineral complexity. As shown in Fig. 4, when a cement model solution (pH 13, [0.3] KOH, [0.22] NaOH; [0.22]  $\text{CaCl}_2$ ) flows through a granitic rock at 80 °C with residence times of hours, the fluid leaving the rocks is enriched in silica, and there is also the precipitation of calcium/silica tubular membranes. The inner part of the membrane is enriched in silica whereas the outer part is enriched in calcium. In other words, reverse silica gardens are formed.

These experiments were actually designed to study the interaction of underground water with large cement-made underground structures. However, the results are also relevant for picturing the kind of fluid-rock interaction that, as shown below, was probably widespread for a long period of time during the early Hadean, and led to the enrichment



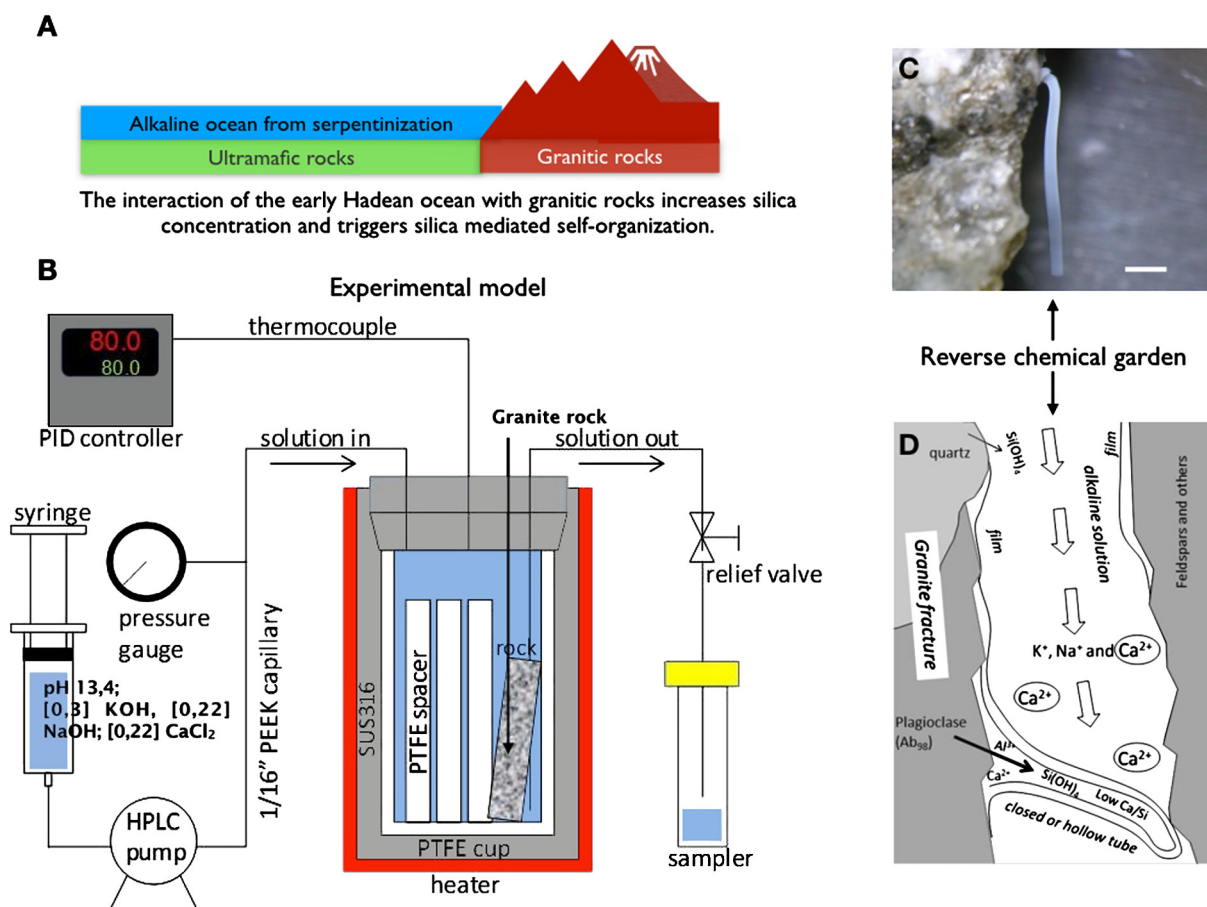


Fig. 4. Laboratory analogues of the interaction of an alkaline ocean with a granitic rock in the early Hadean. A) Sketch of the geological situation; B) Experimental model; Initial pH 13.2; Reactor temperature 80 °C; Flow rate: 10-30 ml/min, duration of the experiment 737 hours). C) Tubular forms created in the fractures of granite rocks when the highly alkaline fluid passes through; D) Explanation of the tubular structures as an inverse silica garden. Scale bar in c) 1 mm. Adapted from reference [146].

in silica in the primordial alkaline lakes and seas, and to the physico-chemical conditions required for the formation of mineral self-organized structures.

### 3.2. Early Earth ocean and atmosphere evolution

As was discussed in the Introduction, the Earth formed ca. 4.56 billion years ago [147], but the rock record can only be traced to ca. 4.0 Ga ago [148]. The conditions on the Earth's surface during the first 500 million years are therefore poorly constrained, hampering the reconstruction of the origin and early evolution of life. Several key processes occurred in this period: core/mantle separation, the Moon-forming impact event, formation of the first crust, and the condensation of atmospheric water vapor and formation of the oceans. Also in the Hadean, the intensity of the meteorite-flux decreased and chemical differentiation of the crust-mantle led to changes in the compositions of Earth's oceans and atmosphere, which profoundly affected habitability of the Earth and likely created the first niches for prebiotic chemistry and the dawn of life. A brief summary is given here on the theoretical constraints and rare observables we have on these key events.

#### 3.2.1. Core-Mantle differentiation and moon-forming impact:

Geochemical models suggest that the initial Earth had the composition of carbonaceous chondrites and that cold accretion of the Earth was followed by complete melting and core segregation within the first 50-100 m.y. (e.g., [149]). During or shortly after core/mantle separation, a Mars-sized planetesimal impacted the Earth, leading to the

formation of the Moon (e.g., [150–152]). In the direct aftermath of this event, the silicate Earth was essentially molten and contained a hot silica vapor atmosphere [153]. Thermodynamic computations [154] suggest that the main gas constituents forming an atmosphere in the aftermath of impacting of a body with the composition of a carbonaceous chondrite were  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . If the impactor had an ordinary chondrite composition, the main gases would have been  $\text{CO}$  and  $\text{H}_2$ . As the magma ocean cooled and solidified the surface temperature dropped from ca. 1500 K to <500 K and steam condensed to form a hot, salty ocean. This is suggested to have happened within the first 2 m.y. after the Moon forming impact [153,155].

### 3.2.2. Hadean meteorite impacts

Later bombardment by meteorites may also have affected the oxygen fugacity of the mantle. While the flow of meteoric impacts and their time distribution is under debate, there is no doubt that the Hadean Earth suffered an intense bombardment of meteorites [150,156–158]. It is well known from lunar cratering records that there was a spike in meteorite flux to the Earth around 3.9 Ga ago [156,159]. Bottke et al. calculated that ca.  $10^5$  giant-basin sized impacts occurred between 4.1 and 3.8 Ga ago [156]. The temporal evolution of the meteorite flux prior to this Late Heavy Bombardment, however, is debated. As summarized in Hopkins and Mojzsis [157] and Norman [152], this flux could have been a steady exponential decay throughout the Hadean [160], a classical Late Heavy Bombardment representing a unimodal cataclysm ca. 3.9 Ga ago [161,162], a ‘Sawtooth’ cataclysm with an increase in intensity around 4.1 Ga ago [163], or a scatter of multiple bombardment episodes [153,164].

### 3.2.3. Controls of mantle $f\text{O}_2$ and impacts on atmospheric composition

The atmosphere and oceans were subsequently modified by interactions with the newly formed crust and degassing fluxes coming off the interior of the planet. The issue of oxygen fugacity of this mostly molten Earth’s silicate shell is of particular relevance to this communication, as it determines the nature of the outgassing flux and hence the composition of the Hadean atmosphere and oceans. In the mantle of modern Earth, oxygen fugacity is strongly pressure-dependent as increasing pressure favors the stability of  $\text{Fe}_2\text{O}_3$  components, which lowers  $f\text{O}_2$  with depth and leads to the predominance of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  in terms of C-O-H volatile species [165]. The disappearance of  $\text{Fe}_2\text{O}_3$  components into garnet and spinel causes  $f\text{O}_2$  to increase from fugacities similar to the IW-buffer at 8 GPa to fugacities close to QFM-buffered conditions at 2 GPa [165]. The C-O-H volatile speciation changes from  $\text{CH}_4$ - to  $\text{CO}_2$ -dominated along this decrease in pressure and this is why melts produced in the upper mantle of modern Earth degas  $\text{CO}_2$  and not  $\text{CH}_4$  [166].

What was the oxidation state of the upper mantle of our planet in the early Hadean? Based on trace element studies of mantle-derived rocks and minerals it had been suggested that the oxidation state of the uppermost mantle has been within  $\pm 2$  log units of the QFM buffer for the past 3.8 Ga [167–169]. This has led to the idea that the Earth’s mantle has had a similar redox state as today very early in its evolution and that gases released from the mantle would create a mildly reducing atmosphere consisting primarily of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{N}_2$ , with only minor amounts of  $\text{CO}$  and  $\text{H}_2$  [155, 170,171]. Cerium partitioning into Hadean zircons indicate that the magma from which the zircons crystallized also had  $f\text{O}_2$  values close to QFM [172]. It is important to realize that those zircons do not tell us about oxygen fugacities of the mantle. Only phases that are in chemical equilibrium have identical gas fugacities. A melt crystallizing zircon, however, cannot be in equilibrium with the mantle and the zircons can hence not be used to infer mantle  $f\text{O}_2$  values. We therefore do not know what  $f\text{O}_2$  in the Hadean mantle was.

The idea of constant mantle redox since the early days of our planet’s evolution has created a conundrum, as it would suggest that the subduction of  $\text{H}_2\text{O}$  and oxidized materials, in particular after the Great Oxidation Event (2.3 Ga) has not affected the oxidation state of the mantle. Indeed, more recent work has suggested that  $f\text{O}_2$  deduced for the upper mantle from the V/Sc redox proxy is about one order of magnitude lower for samples from the Archean mantle when compared to post-Archean samples [173]. In the light of these new results, it appears quite unlikely that the oxidation state of the Hadean and modern mantle were similar. Results of a comprehensive modeling study also suggest that the oxygen fugacity was low (<IW) in Earth’s mantle after its accretion was completed [174]. It is certain that during core formation 4.5 Ga ago, the silicate shell of Earth must have been in equilibrium with Fe and Ni, which would correspond to low  $f\text{O}_2$  (4.5 log units below FMQ [165] and high degassing fluxes of  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{H}_2$  [175]. This is consistent with the IW-like  $f\text{O}_2$  conditions deduced from Martian samples [176] and with modeling results for Earth accretion and core-mantle formation [174]. Therefore, at some time within the first billion years of Earth’s evolution, the mantle must have become more oxidized. The amount of incurred oxidation corresponds to an

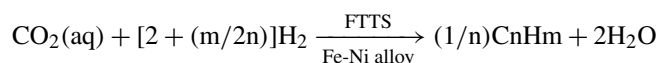
increase in Fe<sub>2</sub>O<sub>3</sub> in the upper mantle from zero after core formation to 0.2 wt.% in the Archean [165]. The cause of this oxidation is not known, but degassing loss of H<sub>2</sub>, which is ultimately lost to space, is one likely scenario. Subduction of water-rich oxidized material [177] or disproportionation of FeO and loss of Fe to the core [165] are other possibilities.

Although it is perhaps impossible to reliably reconstruct mantle redox states for the Hadean, it appears likely to us that the early Hadean atmosphere may have been less CO<sub>2</sub>-rich than in the Archean and that it quite possibly had significant amounts of CO and CH<sub>4</sub> that were released from a mantle that was more reduced than that of modern Earth. In addition, impacts may have given rise to transient reduced atmospheres where CO, H<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub>S were the major volatile constituents [154,155,175,178,179]. Large impact events throughout the Hadean could have also caused perturbations in the mantle redox state, driving oxygen fugacity down to several orders of magnitude below the QFM-buffer [178,179]. These meteorite impacts therefore had a profound effect on the Earth, but they likely did not completely sterilize the habitable surface [159].

### 3.2.4. Serpentinization of the Hadean ultramafic crust

There is evidence from Hadean zircon crystals preserved in younger rocks, that water had condensed on crustal rocks as early as 4.4 Ga ago [20,24,181]. Once oceans had formed, CO<sub>2</sub> would be gradually removed from the atmosphere by carbonate formation (via hydrothermal interaction with mafic/ultramafic crust) [153,155,182].

The first crustal rocks that formed from the early Hadean magma ocean likely were mafic/ultramafic in composition [33,183]. Based on the composition of Archean komatiites [184], the ultramafic rocks likely had 30–35% MgO. The ultramafic rocks of the Hadean have probably been even more MgO-rich given that the mantle adiabatic temperature was higher in the Hadean and hence mantle melts were more magnesian [185]. Therefore, the water that started to condensate on the crust of the planet after the Moon-forming event would interact with these ultramafic rocks and serpentinite would form from these interactions [26,106,186–188]. Because the serpentinization reactions outlined in section 3.1, turn the interacting water alkaline, the liquid water that covered most of the surface of the planet likely had a high pH. The OH<sup>−</sup> produced by water-rock reactions converts CO<sub>2</sub>(aq) (from exchange with CO<sub>2</sub>(g) in the atmosphere) into bicarbonate and carbonate, which will bind with alkaline earth ions released from the rocks to form carbonate precipitates. This is observed on modern Earth at low temperatures in ultramafic exposures on land (e.g., [189]) and under hydrothermal conditions (100–150 °C) in submarine vents (e.g., [190,191]). As predicted by Sleep and Zahnle [182], CO<sub>2</sub>-levels of the atmosphere were likely low in the Hadean because of the efficiency of ultramafic crustal rocks as CO<sub>2</sub> sink. Sleep et al. calculated that atmospheric CO<sub>2</sub>-levels controlled by reactions with basaltic rocks would be much higher [171]. Serpentinization of ultramafic rocks (komatiites) may hence have played a key role in removing CO<sub>2</sub> from the atmosphere and cooling Earth's climate in the Hadean. Also, the serpentinization processes in the Hadean oceans are expected to have produced copious amounts of H<sub>2</sub>, which slowed down the oxidation of the atmosphere from H<sub>2</sub> loss to space. As suggested by Shock [192] CO<sub>2</sub> is not stable in a system in which the H<sub>2</sub> fugacity is controlled by ultramafic lithologies (FMQ-buffered) at temperatures below 250–350 °C. It is hence likely that CO<sub>2</sub> degassed from the planetary interior will either form carbonate or methane and other organic molecules after reduction. Indeed, experimental work has demonstrated that CO<sub>2</sub> is efficiently converted to CH<sub>4</sub> during serpentinization of komatiite [193]. These authors pointed out that methane production by this reaction may have been large enough to affect atmospheric composition and climate on Early Earth. Methane formation may have taken place by the Sabatier reaction or by Fischer-Tropsch-type (FTT) synthesis which can also produce larger molecular weight organics (e.g., [194,195]). FTT synthesis is favored at relatively high temperature (>300 °C) and pressure (500 bars) and maybe catalyzed by Ni-sulfide, awaruite (Ni<sub>3</sub>Fe) or Cr-spinel (e.g., [193,196]):



Based on these considerations, we envisage the earliest Hadean crust and the associated hydrothermal systems as a producer of very alkaline, reduced fluids with potentially high contents of organic compounds. It is also important to realize that serpentinization, although it creates a highly reduced environment, leaves behind a highly oxidized rock (2/3rd of the Fe is ferric in magnetite, which is the principal Fe-host in serpentinites). Subduction or delamination of serpentinized seafloor [33] could hence have contributed to the oxidation of the upper mantle within the Hadean and perhaps early Archean.

### 3.2.5. Crustal differentiation and consequences for ocean composition

The geodynamic driving forces of the crust-mantle system during the early evolution of Earth are not well understood. We refer to a recent review on this topic by O'Neill and Zhang [197] and summarize only very briefly some of the possible scenarios and consequences for ocean and atmosphere composition. The first crust was likely thin, extremely hot at its base, and affected by the incidence of strong plumes rising up in the mostly molten mantle. Giant meteorite impacts would constitute an additional mechanical driving force that could have driven active subduction. Most workers (e.g., [197,198]) consider it unlikely that plate tectonics as we know it from modern Earth is a good model for the Hadean Earth. More likely the Hadean crust was governed by a stagnant lid regime that could have switched intermittently to short-lived plate tectonics [198]. There are also geochemical arguments for questioning the early onset of plate tectonics in the Hadean.  $^{142}\text{Nd}$  anomalies in rocks as young as 2.67 Ga [199] suggest that mantle mixing took as long as 2 Ga since the formation of the Earth. These long mixing times are supported by  $^{182}\text{Hf}$ - $^{182}\text{W}$  systematics [200] and by platinum-group element concentrations in komatiites [201]. Such long mixing times are not consistent with continuous plate tectonics, but rather indicate stagnant lid convection, punctuated with tectonic episodes [198]. Harrison et al. [25] argued that the Hadean zircons must have formed in an arc-like setting, because the melts from which the zircons crystallized were affected by the addition of water [24]. If that addition of water had taken place within a subduction zone, then that means that plate tectonics was already active 4.4 Ga. Other workers argued that the water could have been assimilated by magma in a long-lived mafic intrusive body, parts of which differentiated to the granites from which these zircons were derived. This scenario is more consistent with a stagnant plate regime.

It is important to note that the more differentiated crustal rocks (tonalite-trondjemite-granite (TTG) series) that we find in the oldest rock record alongside ultramafic and mafic rocks of the Early Archean (e.g., [183]) could have been generated during the Hadean by crustal melting in a stagnant lid regime by intraplate remelting (delamination and recycling) (e.g., [33,34,197]). So regardless of the geodynamic model (stagnant lid or plate tectonics), it is clear that the Earth's crust became more differentiated, hydrated, and oxidized as magmatic differentiation and interactions with the oceans proceeded in the Hadean (Fig. 5). Recent silicon isotope studies [202,203] have shown that Archean crustal rocks were unusually rich in  $^{30}\text{Si}$ , which is enriched in cherts. This signature is interpreted to indicate subduction of cherts and mass transfer of silica from the downgoing slab into the newly formed felsic crust. If this interpretation is correct, these results indicate that the global pre-Archean ocean must have been very high in silica.

### 3.3. Implications for silica-induced biomimetic structures on Early Earth

Although serpentinization fluids are buffered to low silica activities, they have the potential of dissolving large quantities of silica due to their high pH. In the first billion years of Earth's evolution, TTG rocks probably became more abundant crustal materials with time, as their formation required complex differentiation processes in a thickened crust [198]. These differentiated rocks consist of minerals such as quartz and plagioclase that dissolved in the alkaline seawater controlled by serpentinization reactions. As a result the concentration of silica in seawater would increase. The increased silica input into the early oceans [204] caused a global silicification of the Early Archean seafloor, as evidenced by abundant chert and underlying strongly silicified volcanic rocks in the Barberton Greenstone Belt (e.g., [205–207]), the Pilbara Granitoid-Greenstone Belt [207–209], and other areas of exposure of Archean seafloor [207,210]. The mantle at this time was less molten than in the Hadean, so that tholeiites became more abundant than komatiites [184] and serpentinization was less common. Indications for high partial pressures of  $\text{CO}_2$  in the Archean atmosphere have been presented in the form of temperature models and paleosol reconstructions [211,212]. If these estimates are correct, then the implication is that high outgassing fluxes of  $\text{CO}_2$  must have led to a steady state and a high  $p\text{CO}_2$  of the atmosphere. Perhaps this shift from a presumed alkaline ocean (and corresponding low  $p\text{CO}_2$  of the atmosphere) to higher  $p\text{CO}_2$  (and corresponding lower pH of the oceans) is due to a combination of decreased serpentinization and increased  $f\text{O}_2$  of the mantle (similar to or slightly lower than today). This alkaline high  $\text{CO}_2$  scenario could correspond in some way to the so-called soda ocean proposed for the Archean by Kempe and Degens [213,214].

The slowdown of global serpentinization rate and the change of atmospheric composition to higher  $p\text{CO}_2$  caused the pH of seawater to decrease. This led to further silicification until a new steady state had established itself. In a transitional period the increased  $\text{CO}_2$  flux into an ocean-atmosphere system that was still heavily affected by serpentinization reactions may have boosted methanogenesis ( $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ ). But eventually the increasing



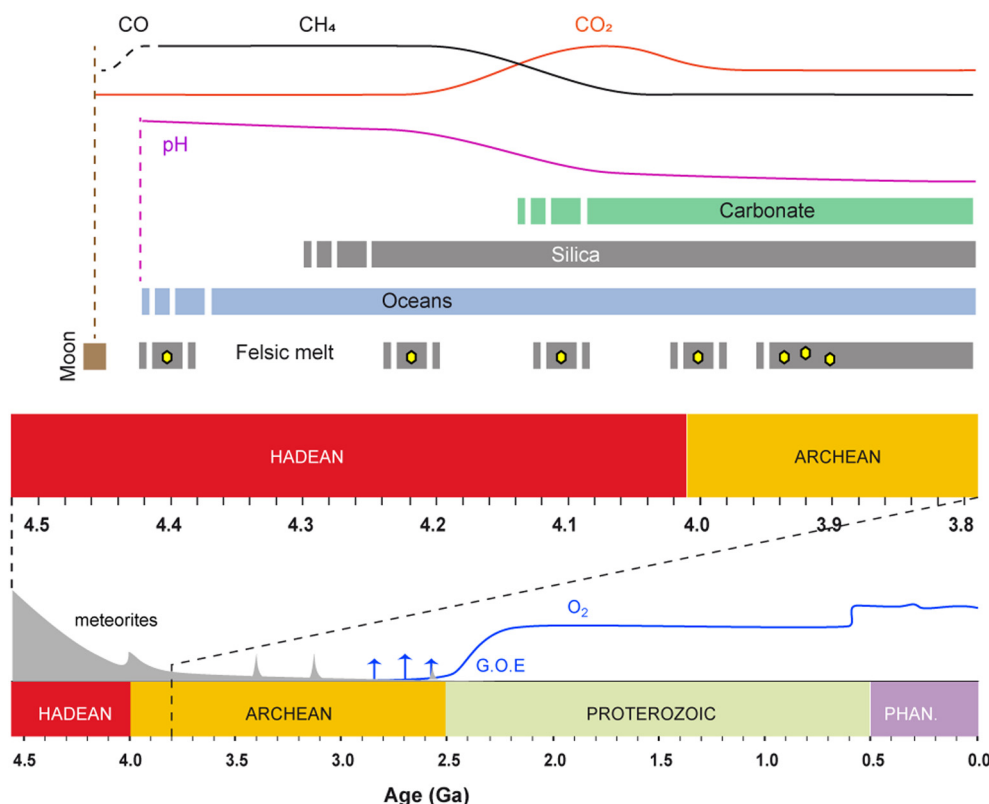


Fig. 5. Timeline of early Earth, showing key steps for the conditions of life, from initial sterile conditions during high meteorite bombardment in the early Hadean to the rise of atmospheric oxygen during the Neoproterozoic (G.O.E., Great Oxidation Event). The evolution of oxygen was redrawn from reference [180]. In the period between these two events, several critical changes took place that are described in the main text and are summarized in the inset: A large impact between ca. 4.53–4.45 Ga created the Moon, and subsequent outgassing of the mantle created the first reducing atmosphere. Oxygen-fugacity was controlled by the IW-buffer, leading to significant CO in the high-temperature atmosphere. Cooling of the atmosphere stabilized CH<sub>4</sub> and caused H<sub>2</sub>O to condense and form the first oceans at ca. 4.4 Ga. Serpentinization of the ultramafic crust led to global release of H<sub>2</sub> and CH<sub>4</sub> to the atmosphere and overall high ocean alkalinity. Evidence from rare zircon crystals suggests crustal melting events that led to the formation of felsic rocks (TTG's). As a result of these events, silica started to accumulate in a worldwide alkaline ocean. The onset of plate tectonics had relative wet, oxidized crustal rocks subduct into the mantle, causing the release of more oxidized gases, particularly CO<sub>2</sub>, into the atmosphere which led to acidification, accelerated silicate weathering, and the formation of carbonate platforms. In this overall scenario, there must have been a period in the Hadean when relatively alkaline, silica-rich aquatic environments existed that were dominated by silica-polymerization and the formation of complex silica-organic interactions.

CO<sub>2</sub> flux from the mantle overwhelmed the H<sub>2</sub> production by the throttled serpentinization and pCO<sub>2</sub> was able to build up in the atmosphere. As a consequence of the pH drop of the oceans, the solubility of Fe<sup>2+</sup>, which was formerly tied up in secondary minerals as Fe(OH)<sub>2</sub>, increased and the oceans became enriched in Fe. This trend was reversed during the Great Oxidation Event when Fe<sup>2+</sup> was oxidized and the pH of the oceans further decreased (Fe<sup>2+</sup> + 0.25 O<sub>2</sub>(aq) + 2.5 H<sub>2</sub>O → Fe(OH)<sub>3</sub> + 2H<sup>+</sup>) leading to more silica precipitation (H<sup>+</sup> + H<sub>3</sub>SiO<sub>4</sub><sup>−</sup> = SiO<sub>2</sub> \* 2 H<sub>2</sub>O; opal).

It is important to realize that our model of Hadean ocean evolution implies that throughout much of the early evolution of our planet, waters of an alkaline ocean interacted with the granitic rocks of newly formed crust. Note that this is the same chemical scenario as in the experiment reported by Satoh et al. [146], in which it was demonstrated that the inflow of hyperalkaline water within a reactor containing granitic rocks yields an enrichment in silica of the water and the formation of silica/calcium self-organized tubular membranes and vesicles in the cracks of the rocks. These inorganic membranes could have played a vital role in prebiotic chemistry and perhaps the origin of life.

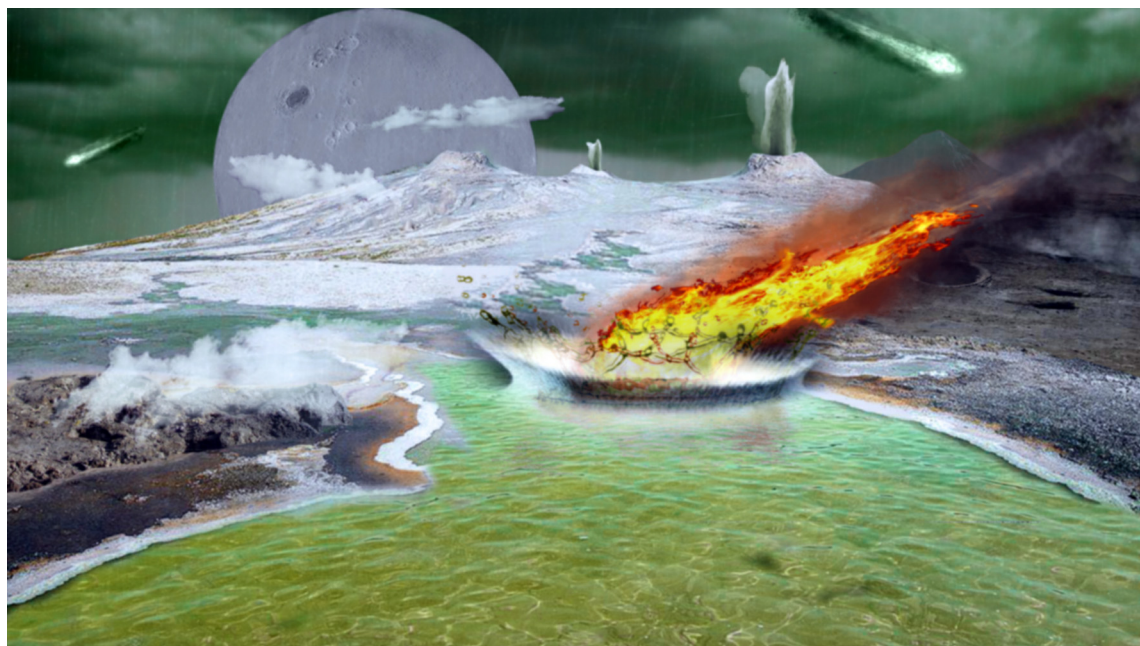


Fig. 6. An artist's view of Earth's surface during the Hadean. Condensed water covered most of the planet, with expansive and shallow oceans. Crustal rocks were mostly ultramafic (dark rocks in foreground), and ubiquitous serpentinization caused the oceans to be alkaline and rich in  $H_2$  and  $CH_4$ . Early crustal differentiation caused silicic rocks to form (bright rocks in background), which released silica and salts to the oceans. A young, closer moon triggered tidal pumping. Meteorites were a source of metals, silica and carbonaceous matter and their impact created complex prebiotic molecules relevant for the origin of life. The impact of meteorites along with phreatomagmatic volcanism created a hazy atmosphere of rock nanoparticles, water vapor and complex organic compounds. Geysers and springs were the first hydrothermal systems in which organic molecules were synthesized by Fischer-Tropsch type processes. Silica-induced mineral self-organized structures catalyzed high yielding condensation reactions of crucial precursor compounds of biomolecules. In summary, the Hadean Earth was a global-scale reactor and breeder of compounds required for origin of life. Artist: Lucas Chacon.

#### 4. Summary

The conclusion can be drawn that particularly during the Hadean eon, Earth-surface conditions could have arisen for mineral-self organization. Highly alkaline, silica-rich waters are nowadays only found in some exceptional settings, such as particular ophiolite complexes where high-pH fluids are generated by serpentinization of ultramafic rocks, which then passed through more felsic, silica-rich rocks. Alternatively, similar conditions can arise in soda lakes where evaporation leads to silica enrichment of high-pH salt brines. We argue that during the Hadean eon there were periods when these types of conditions were not just possible, but actually were dominating the Earth surface environments.

After core-mantle differentiation and the Moon-forming event, ca. 4.4 Ga ago the first oceans condensed from the newly formed atmosphere, and interacted with a predominantly ultramafic crustal surface. The resulting global-scale serpentinization, enhanced by intense volcanism and effective hydrothermal circulation, caused hydrogen release, triggered FTT-type synthesis, and generated highly alkaline fluids (Fig. 6). It has been argued in the past that the early atmosphere was  $CO_2$ -dominated and consequently the oceans were acidic. Here we have shown that there were at least three possible drivers for a more reduced atmosphere, in which  $CH_4$ ,  $CO$ , and  $H_2$  were important constituents. First, recent studies have demonstrated that the redox state of the Hadean upper mantle must have been more reduced than that of the Archean and younger rocks, with an oxygen fugacity as low as 4.5 log units below the QFM-buffer. Second, large meteorite impact events could have temporarily perturbed the redox state of the upper crust, leading to more reduced transient atmospheric conditions. Third, serpentinization of a predominantly ultramafic crust led to global-scale production of  $H_2$  and a removal mechanism for  $CO_2$  (carbonate formation and/or FTT-synthesis). These effects, taken together, must have led to an atmosphere that was less dominated by  $CO_2$ , and contained more  $CH_4$  than most current models anticipate. Moreover, serpentinization as the dominant mechanism of crust-ocean exchange would have created strongly alkaline hydrothermal fluids and hence have caused a high-pH ocean.

It is known that already early in the Hadean felsic crustal rocks such as TTG's could develop. Even in the absence of plate tectonics such high-silica rocks could be generated by enhanced intraplate melting in a stagnant lid regime. It is therefore entirely possible that during the Hadean eon conditions were established were highly alkaline, silica-rich aquatic environments developed in which ubiquitous processes of silica-based mineral-self organization could have occurred. Our claim for a Hadean geochemical scenario of a reduced, alkaline ocean that subsequently becomes enriched in silica, can be extended to most Earth-like planets and moons. Certainly the kinetic aspects will vary with size, distance to the sun, orbits, etc., and therefore the time scale of the different stages of our geological story will vary. Fortunately, the next Exomars mission to Mars [215] will offer the possibility to test our ideas. Hopefully, Exomars will provide for the first time the possibility to study rocks of the Martian Noachian, i.e. rocks formed at the time when our geochemical scenario proposed in this manuscript could be working for both planets.

### 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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