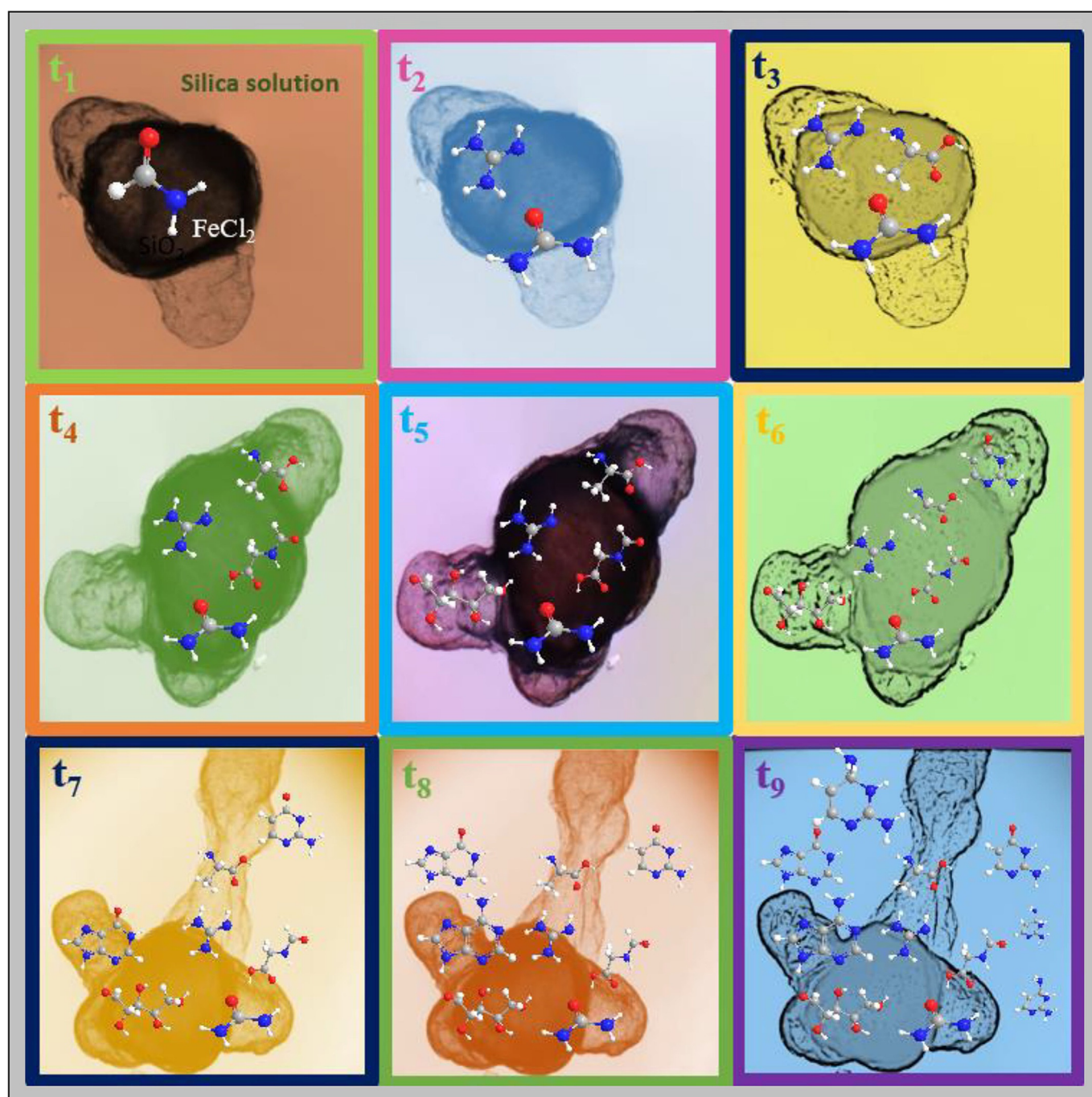ChemPubSoc
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▌ **Prebiotic Chemistry**

A Universal Geochemical Scenario for Formamide Condensation and Prebiotic Chemistry

Raffaele Saladino,*[a] Ernesto Di Mauro,[a] and Juan Manuel García-Ruiz*[b]

Abstract: The condensation of formamide has been shown to be a robust chemical pathway affording molecules necessary for the origin of life. It has been experimentally demonstrated that condensation reactions of formamide are catalyzed by a number of minerals, including silicates, phosphates, sulfides, zirconia, and borates, and by cosmic dusts and meteorites. However, a critical discussion of the catalytic power of the tested minerals, and the geochemical conditions under which the condensation would occur, is still missing. We show here that mineral self-assembled structures forming under alkaline silica-rich solutions are excellent catalysts for the condensation of formamide with respect to other minerals. We also propose that these structures were likely forming as early as 4.4 billion years ago when the whole earth surface was a reactor, a global scale factory, releasing large amounts of organic compounds. Our experimental results suggest that the conditions required for the synthesis of the molecular bricks from which life self-assembles, rather than being local and bizarre, appears to be universal and geologically rather conventional.

1. Introduction

Origin of life lacks at present an uncontroversial scenario and unequivocal chemical and physical–chemical frames of reference. Recent progress, however, allow some mote of optimism.

Life is a robust phenomenon. These considerations suggest that its first chemical steps must have been as robust and efficient. Indications that the core chemical frame of the early processes was centered on the properties of hydrogen cyanide HCN and, more diffusely and more abundantly, on those of its hydrolyzed but still highly reactive derivative formamide NH_2COH have been collected during the last twenty years. Here we discuss recent experimental evidences that the geochemical processes of the early earth provided the necessary, efficient, and selective catalytic setup for the transition from one-carbon atom compounds to nucleic bases, amino acids, sugars, and carboxylic acids. The processes which were at the basis of the geochemical evolution of this planet provided at the same time the niche for the formation and the environment for the evolution of biogenic compounds.

Biogenic processes were necessarily preceded by the formation of prebiotic compounds. Occamian logic ("the simplest is the likeliest") suggests that the conditions in which these earliest processes occurred were not rare, occasional, exotic, or fastidious. The solution to the bias of the origin of the prebiotic compounds and to the start of their fertile interactions (summarized by the aphorism: "metabolism-first or genetics-first?") might thus consist on the presence and on the productive interactions of elements of both pre-genetics and pre-metabolism. It is difficult to imagine that metabolic processes of any level of complexity could develop and evolve in the absence of a form of information transmission and that information-containing molecules could form and replicate in the absence of some form of energy harnessing and control. Hence the necessity for prebiotically fertile syntheses to be as rich and variegate as possible, necessarily affording compounds of different type and purport.

Given the elemental composition of biological molecules, largely consisting of H, O, C and N atoms, the starting compound(s) should reflect such composition. One-carbon atom compounds as formaldehyde, formic acid, hydrogen cyanide, and formamide abound in circum- and interstellar space.[1–6] Thus, the conditions under which these syntheses may occur are multiform and potentially diffused at universal scale.[7–13] Reactions from these compounds leading to higher chemical complexity occur under a variety of energy sources, of different chemical mixtures, of catalysts, and of varying physical-chemical conditions.[14]

The logic for individuation of potentially biogenic compounds works top-down: a molecule or a process is prebiotic and biogenic if it is a posteriori possible to recognize its biological role or relevance. In this respect, HCN and NH_2COH have shown their worth. HCN and NH_2COH chemistries are related,[15–17] as predicted and shown by an in-depth computational study of the formation and decomposition reaction channels of NH_2COH by means of ab initio molecular dynamics, allowing the study of reactions both in gas and in liquid phase.[18] This analysis has shown a similar stability of NH_2COH and HCN in solution as well as their relatively facile interconversion. NH_2COH was shown[19] to form in the classical Urey–Miller condensation experiment,[7] along with formic acid but not with HCN. Formamide has in particular shown its versatility[20] owing to the mentioned ubiquity and to its facile formation and possibility of concentration.[21,22]

The geochemical scenario taken into consideration has been chosen based on its geochemical likelihood and its evidence-based consistence. This scenario has been experimentally challenged with NH_2COH synthetic properties (as described below), because of its widespread presence and the experimentally ob-

[a] Prof. R. Saladino, Prof. E. Di Mauro
Dipartimento di Scienze Ecologiche e Biologiche
Università della Tuscia, Via San Camillo De Lellis, 01100 Viterbo (Italy)
E-mail: saladino@unitus.it

[b] Prof. J. M. García-Ruiz
Laboratorio de Estudios Cristalográficos
Instituto Andaluz de Ciencias de la Tierra, CSIC-Universidad de Granada
Av. De las Palmeras 4, Armilla (Granada) (Spain)
E-mail: juanma.garciaruiz@gmail.com

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served flexibility of its chemistry. This approach does not exclude the eventual integration with the possible contribution of other reactants as HCN and/or HCOOH. However, one should consider that the more complex is the prebiotic reaction mixture, the higher is the possibility of encountering the "asphalt problem", as pointed out by S. Benner and co-authors.[23]

We report in Part 2, Figure 1, the biologically most representative compounds that are obtained by reacting NH_2CHO in the presence of various minerals, as fueled by different energy sources. Among the various classifications possible, the compounds obtained are listed as a function of the role that they assume in biological systems (i.e., nucleic bases, amino acids, carboxylic acids, sugars, etc.), rather than more formal chemical principles (for example, chemical composition; number of carbon atoms, etc.).

The result of this series of syntheses boils down to the consideration that NH_2CHO yields mixtures of prebiotic relevant compounds in every energy and catalyst combination tested. Thus, in order to understand the scenario that allowed the biogenic processes on this planet, the question becomes: are the geochemical conditions that bona fide characterized the earliest times of this planet compatible with the production of biogenic molecules? The answer to this question is positive, as described in Part 3.

2. The Effect of Minerals on Formamide Condensation

Minerals play a key role in the condensation of NH_2CHO. In the absence of minerals, NH_2CHO yields only a very limited panel of compounds, including simple purine, associated with very low amounts of N,N-diethyl formamide, 3-hydroxypyridine, pyruvic acid and 2-propanol, under radiation conditions, and urea, lactic acid, and pyruvic acid, under thermal condition at high pH values.[24]

As reported in Figure 1, the number and variety of condensation products increase enormously in the presence of minerals, encompassing nucleic acid components with different degrees of structural complexity (nucleobases, acyclonucleosides and nucleosides),[25] amino acids, sugars, carboxylic acids, and some organic condensing agents (e.g., carbodiimide), which are essential for the formation of oligomers and polymers. Table 1 summarizes a selected panel of reactions of NH_2CHO performed in the presence of minerals reasonably present in the geochemical scenario of the primitive earth. Simple metal oxides (Al_2O_3, SiO_2, TiO_2), clays, silicates (olivine, forsterite, fayalite, and their derivatives), sulfur–iron and sulfur–copper–iron compounds, zirconia minerals[26] and borate minerals, are all efficient catalysts in the synthesis of biomolecules from NH_2CHO.

In the selected cases, the reactions have been performed from neat NH_2CHO under thermal conditions, mimicking volcanic or hydrothermal scenarios. A comprehensive table, including extraterrestrial minerals (meteorites, cosmic dust samples),[27] as well as energy conditions related to space conditions (proton beam, high energy heavy atom beam) is reported in the Supporting Information. As a general trend, the pre-

biotic mixture is usually rich in products irrespective of the nature of the specific mineral present during the condensation. On the other hand, some selectivity occurs depending on the mineralogical origin and elemental composition of the catalyst. For example, in the silicate family the synthesis of pyrimidine nucleobases is enhanced by the presence of either magnesium and iron (Table 1, entries 7–9).[28] In the case of sulfur-containing minerals, sulfur–copper–iron minerals are generally more active than simple pyrite and pyrrhotine, pyrite being more effective than pyrrhotine (Table 1, entries 10–17).[29] Again, in the case of borates, the so called hydrates containing hydroxyl groups (group A, Dana's classification), and anhydrous borates (group B, Dana's classification), are more efficient in the formation of nucleobases than borosilicates and borocarbonates (Table 1, entries 22–29).[30] Finally, the NH_2CHO condensation works well also in the presence of water, thermal water being a reaction medium better than sea water when the condensation is performed in the presence of the same type of miner-

Raffaele Saladino is President of the Italian Society of Astrobiology. He obtained a Master degree in Chemistry at University "Sapienza" (Rome, Italy), and a Ph.D. in Chemical Sciences at the same University. After post-doctoral training at the University of Montreal (Canada) and teaching and research position at the University of Tuscia, Viterbo (Italy), he is now Full Professor in Organic Chemistry at the same University. He is involved in studies on prebiotic chemistry, green catalysis and oxidative transformations of natural substances mainly focused on bioactive compounds.

Ernesto Di Mauro was born in Valmontone (Italy), in 1945. In 1967 he obtained his degree in Biological Sciences from "Sapienza" University of Rome (Italy). In 1969 he joined the Department of Genetics (Seattle, USA), as a postdoctoral fellow. Appointed in 1978 as an associate professor of Enzymology at the University of Rome, he has been a professor of Molecular Biology since 1987. His research interests are centered on gene regulation, DNA and chromatin structure and topology and, at present, on the various aspects of the origin of life.

Juan Manuel García-Ruiz is Research Professor at the National Research Council in Granada (Spain). Founder of the Laboratory of Crystallographic Studies, and of the Crystallization Factory, he is an international expert in the crystallization of minerals, drugs and proteins, including self-assembly in natural and synthetic materials. He is currently leading the European Research Council project "Prometheus" on early Earth. Prof. García-Ruiz is the author of the book "The Mystery of the Giant Crystals". In 2006 he initiated the governmental Program Explora.
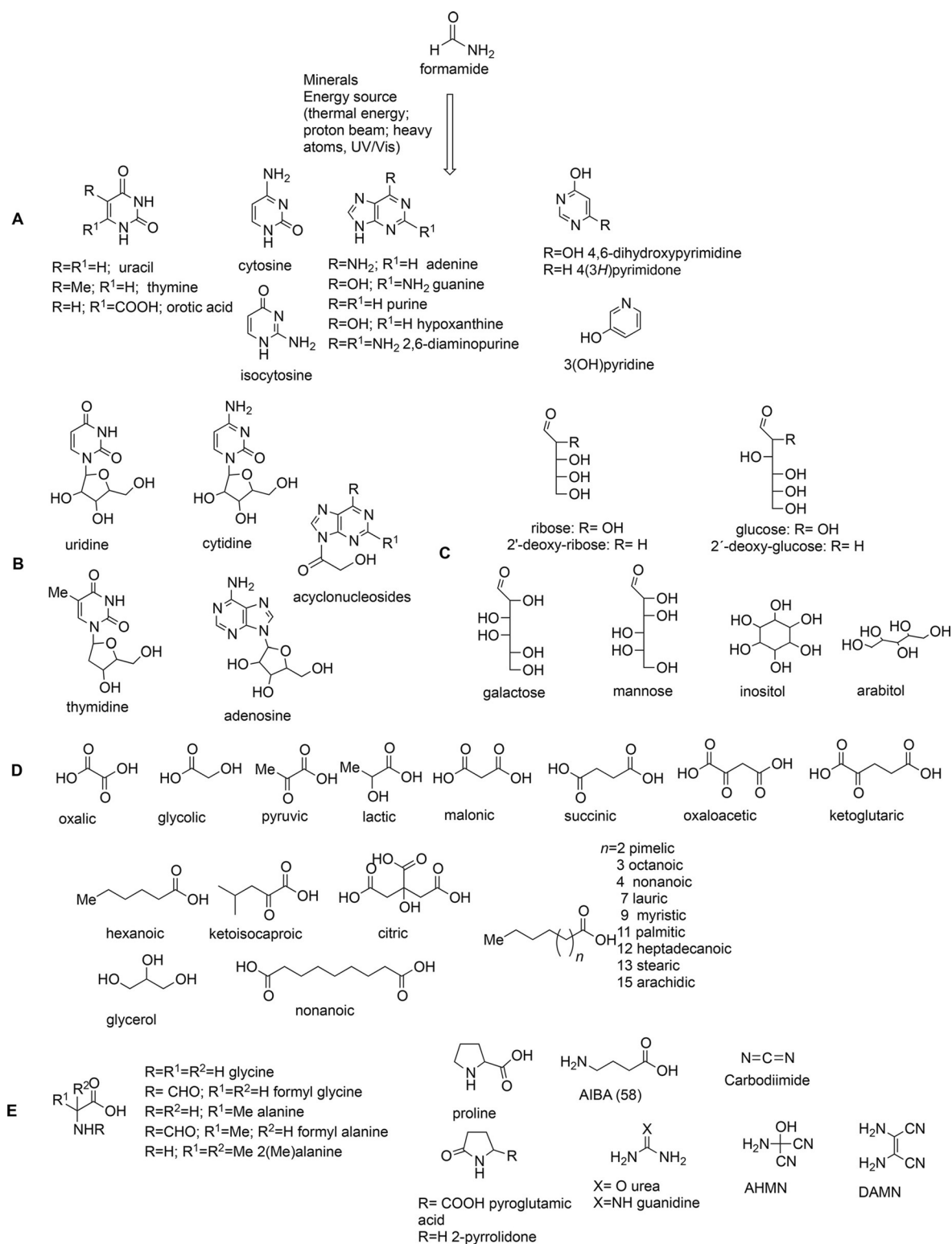
Figure 1. The biologically more relevant compounds obtained by reacting NH_2CHO in the presence of various minerals. A: nucleobases. B: nucleosides and acyclonucleosides. C: sugars. D: carboxylic acids. E: amino acids, condensing agents, and HCN oligomers.

al.[31] At the moment, the high complexity of heterogeneous catalysis, associated to the specificity of the mineral surface chemistry, does not allow to delineate detailed structure–activity relationships able to correlate a specific mineral (and an energy source) to a defined NH_2CHO reaction pathway. The

yield of each compound rarely exceeds 0.1%. This might appear as a major limitation of the system if considered in the logics of preparative chemistry. In the prebiotic perspective, this fact is only apparently a drawback; given the large diversity of compounds formed together (nucleic bases, carboxylic

Table 1. A selected panel of reactions of NH_2CHO performed in the presence of minerals reasonably present in the geochemical scenario of the primitive earth.

	Mineral	Purine[a] nucleobases	Pyrimidine[a] nucleobase	Carboxylic acids[a] C1/C6	Amino acids[a]	Condensing agents[a]
metal oxides						
1	alumina	40.4	5.7	–	–	–
2	SiO_2	4.9	5.7	–	–	–
3	TiO_2	28.3	1.1	–	–	–
clays						
4	kaolin	51.9.	2.0	–	–	–
5	zeolite	83.1	4.4	–	–	–
silicates						
6	$MgFeSiO_4$	–	5.5	–	–	0.2
7	Fe_2SiO_4	–	5.2	–	–	–
8	Mg_2SiO_4	–	0.13	–	–	–
sulfur iron and sulfur copper/iron minerals						
9	FeS	0.01	0.18	0.01	–	0.01
10	pyrrhotine $Fe_{1-x}S$[b]	0.01	0.13	0.03	–	0.04
11	FeS_2	0.26	1.05	–	–	0.04
12	pyrite FeS_2[c]	0.28	0.73	–	–	0.21
13	chalcopyrite $FeCUS_2$[c]	0.20	6.56	–	–	6.80
14	bornite $FeCu_5S_4$[c]	1.80	1.71	0.50	–	0.05
15	tetrahedrite (Fe,Cu,Sb)S[d]	0.19	3.07	–	–	0.42
16	covellite CuS[d]	–	5.86	0.50	–	0.32
zirconica minerals						
17	ZrO_2[e]	0.08	0.83	0.08	–	0.16
18	$ZrSiO_4$	0.01	0.21	0.04	–	0.07
19	Li_2ZrO_3	0.0001	0.11	0.01	–	0.05
20	$BaZrO_3$	0.05	1.06	0.14	–	0.63
borate minerals						
21	borax $Na_2B_4O_7\cdot5H_2O$[f]	–	< 0.01	0.03	< 0.01	–
22	$CaMgB_6O_8(OH)_6\cdot6H_2O$[f]	–	0.04	0.03	< 0.01	0.18
23	$MgB_3O_3(OH)_5\cdot5H_2O$[f]	–	0.02	0.03	0.05	0.01
24	$Mn_3B_7O_{13}Cl$[g]	0.02	< 0.01	0.20	0.09	–
25	$Mg_2Fe^{3+}BO_5$[g]	0.02	< 0.01	0.61	< 0.01	–
26	$Fe_2^{2+}Fe^{3+}BO_5$[g]	0.66	0.02	3.93	< 0.01	0.21
27	$Al_{6.9}(BO_3)(SiO_4)_3O_{2.5}(OH)_{0.5}$[h]	–	< 0.01	0.08	< 0.01	–
28	$NaFe^{2+}Al_6(BO_3)Si_6O_{18}(OH)_4$[h]	–	0.04	0.41	< 0.01	–
chemical gardens						
29	$ZnCl_2$	–	–	< 0.01 (0.001)	traces	traces
30	$FeCl_2$	–	–	< 0.01 (0.008)	–	0.01
31	$CuCl_2$	–	–	< 0.01 (0.0002)	–	< 0.01 (0.04)
32	$Fe_2(SO_4)_3$	–	–	< 0.01 (0.002)	< 0.01 (0.0003)	< 0.01 (0.003)
33	$MgSO_4$	–	–	< 0.01 (0.001)	< 0.01 (0.0001)	< 0.01 (0.0003)
34	$ZnCl_2$	–	traces	traces	0.01	traces
35	$FeCl_2$	–	traces	traces	< 0.01 (0.005)	traces
36	$CuCl_2$	traces	0.08	< 0.01 (0.004)	–	0.02
37	$MnCl_2$	–	< 0.01 (0.002)	–	–	< 0.01 (0.0005)
38	$Fe_2(SO_4)_3$	traces	< 0.01 (0.004)	< 0.01 (0.005)	0.01	< 0.01 (0.001)
39	$MgSO_4$	traces	< 0.01 (0.003)	< 0.01 (0.005)	0.01	< 0.01 (0.006)
40	CuN_2O_6	traces	0.02	< 0.01 (0.007)	–	< 0.01 (0.003)
silica vesicles						
41	$ZnCl_2$	0.02	0.10	0.46	0.007	0.04
42	$FeCl_2$	–	0.0001	6.6	0.00001	–
43	$CuCl_2$	–	7.94	14.74	–	5.0
44	$MnCl_2$	2.24	11.62	11.90	0.00001	2.67
45	$Fe_2(SO_4)_3$	5.8	29.08	6.28	4.64	1.22
46	$MgSO_4$	2.8	41.3	5.26	3.82	0.42
47	CuN_2O_6	0.94	7.98	11.96	0.32	1.64

[a] Yield defined as mg of product per gram of starting formamide. [b] Highly pure commercially available $Fe_{1-x}S$, in which $0 < x < 0.2$. [c] Natural source: mineral from China. [d] Mineral from Peru. [e] Reaction performed in the presence of high surface area ZrO_2 (surface area 30 m^2g^{-1}). [f] Group A from Dana's classification; hydrates of borates containing hydroxyl or halogen moieties. [g] Group B from Dana's classification; anhydrous borates. [h] Group C from Dana's classification; borosilicates.

acids, amino acids, etc.), the yield of each compound adds up to the amounts of the other compounds, favoring their poten-

tial further interactions during molecular evolution. Anyhow, general trends are observed that require additional analysis

using advanced methods of multivariate statistical treatment of experimental data.

3. A Geological Setting for Formamide Condensation
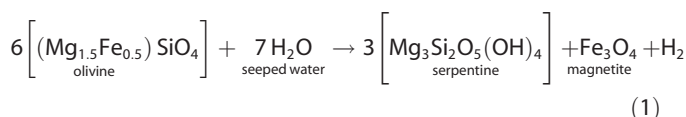
3.1. Mineral self-assembly

The solubility of silica in water strongly depends on pH.[32] From pH 2 to pH 8.3, the solubility of silica is almost constant and varies from 120 ppm to 180 ppm depending on the solid phase at equilibrium, either quartz (or any of the other polymorphs of silicon oxide) or amorphous silica. Within that range of pH, dissolved silica is present mainly as silicic acid. Above pH 8.3, the solubility of silica increases dramatically with pH due to the first and the second deprotonation of the silicic acid. Thus, at pH 12, the concentration of silica could reach values about 4000 ppm. Interestingly, the precipitation of silica from alkaline solutions may couple chemically with the precipitation of metal carbonate and hydroxide creating self-assembled nanocrystalline materials with interesting physical and chemical properties.[33] We can distinguish two main regions of chemical coupling. In the range of pH from 9.5 to 11.5, a chemical coupling of silica and alkaline-earth carbonate precipitation (specifically barium, strontium or calcium carbonate) occurs yielding a particular type of nanocrystalline materials that develop non-crystallographic morphologies through a self-assembly mechanism. These materials, named "silica/carbonate biomorphs", closely resemble typical biologically induced mineral textures and shapes, and have been proposed as an alternative explanation to some of the oldest putative remnants of life.[34] At higher pH, when high concentrated silica solutions are mixed with metal solutions, a totally different phenomenon appears, namely the spontaneous formation of tubular structures known for many years as chemical gardens.[35] The tubules are the results of the interaction of a chemical reaction with osmotic and buoyant forces. The wall of the tubules consists of a metal–[hydroxide/silica(te)] membrane[36] that separates two solutions with fundamentally different compositions. The kinetics of the overall process varies depending on the type of metal cation used, essentially due to the different solubilities of the hydroxides, oxyhydroxides, or hydroxyanions forming during the precipitation of the tubular membranes.[37]

The phenomenon of a chemical garden has been unconvincingly proposed almost two hundred years ago to be related with the origin of life[38] on the basis of its biomimetic appearance: tubular shapes, membrane formation, and osmotic forces. Nevertheless, three main characteristics of these structures made them particularly interesting in the framework of prebiotic chemistry. First, the membrane has a textural and compositional gradient, the outer part being made of a region rich in amorphous silica and the inner part made of nano- and microcrystalline metal oxyhydroxides. Second, while the formation of the tubular structures occurs almost immediately after mixing, there is an experimentally demonstrated diffusion of ions across the membrane[39] that triggers a reorganization process of the texture of the membrane lasting more than one day.[37] Third, during the first half of that time, a considerable electrochemical potential difference across the tubular precipitates occurs, which enhances the catalytic properties of the membrane.[40]

3.2. Serpentinization

It seems reasonable to expect that the loci for prebiotic chemistry in a lifeless planet should be close to the geological setting in which organic compounds form from raw mineral reactions. One of the few geochemical reactions known to create a reduced environment and to form molecular hydrogen is the so-called serpentinization[41] (Figure 2). This reaction is triggered when water interacts with olivine, a mineral silicate, which is a solid solution between two end members, fayalite (the iron silicate) and forsterite (the magnesium silicate). The reaction produces magnetite, molecular hydrogen and a clay mineral called serpentine [Eq. ()]:

$$6\left[(Mg_{1.5}Fe_{0.5})SiO_4\right]_{olivine} + 7H_2O_{seeped\ water} \rightarrow 3\left[Mg_3Si_2O_5(OH)_4\right]_{serpentine} + Fe_3O_4_{magnetite} + H_2 \quad (1)$$

The reaction also produces an environment of low oxygen fugacity that favors the formation of carbon-based organic compound. Thus, upon reaction of H_2 and CO_2, the so-called Sabatier reaction produces methane (CH_4). When the reaction occurs at relatively high temperature (300 °C) and pressure (500 bars) several high-carbon number hydrocarbons are produced by the so-called Fischer–Tropsch-type (FTT) synthesis,[42] which is catalyzed by magnetite and aweurite (Ni_3Fe) [Eq. (2)]:

4.4 billion years ago
Water condensed on the first solid crust

It reacts on peridotite and ultramafic rocks triggering serpentinization

$Fe_2SiO_4 + 5Mg_2SiO_4 + 9H_2O \longrightarrow 3Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 + 2Fe(OH)_2$
fayalite + forsterite + water —> serpentine + brucite + iron hydroxide

Serpentinization reaction yields alkaline fluids that could be enriched in silica allowing the formation of mineral self-assembled structures.

Mineral vesicles

Serpentinization also creates a reduced environment: the abiotic formation of organic compounds is triggered

$3Fe(OH)_2 \longrightarrow Fe_3O_4 + 2H_2O + H_2$
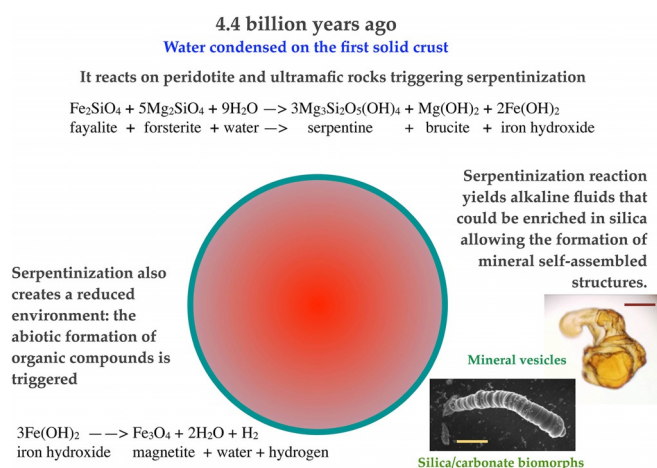iron hydroxide   magnetite + water + hydrogen

Silica/carbonate biomorphs

Figure 2. 4400 Million years ago, water condensed on the first solid crust of the planet, which was made of peridotites and ultramafic rocks. The reaction of water with the mineral olivine triggers serpentinization reaction at large scale and creates the reduced environment required for the formation of organic compounds of geological origin. Alkaline pH and subsequent enrichment in silica allows the formation of mineral self-organized structures, such as silica/carbonate biomorphs and mineral vesicles, which are illustrated. Scale bar of silica/carbonate biomorphs: 25 microns; Scale bar of mineral vesicles: 300 microns.

$$CO_2(aq) + [2 + (m/2n)]H_2 \xrightarrow[Fe-Ni\ alloy]{FTTS} (1/n)C_nH_m + 2H_2O \qquad (2)$$
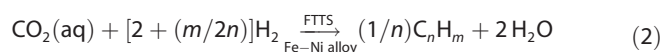
Interestingly, intermediate stages of the serpentinization reaction produce brucite, a mineral composed of magnesium hydroxide that increases the pH and leads to alkaline aquatic environments. Nowadays, waters known to derive from serpentinization processes may contain a high concentration of OH^- at which pH reaches values higher than 12. In fact, serpentinization is a widespread process and there are several places in the world where it can be found at work. As shown by the above equations, serpentinization does not release silica, because the silica dissolved from the olivine at high pH values will be as silicate species and will quickly precipitate as serpentine. However, when high pH waters derived from serpentinization infiltrate through silica-rich rocks, such as granite, they will produce silica-rich solutions. One of the contemporary sites where serpentinization waters are enriched in silica is located in the Cascades Range, in the contact between the trinity ophiolite complex and a tertiary basaltic–andesitic volcanic deposits, in Northern California. In these mountains there are some springs with waters of pH 12 and up to 4 gr L^{-1} of silica.[43] We collected waters from Aqua de Ney spring (Siskiyou country, California, USA) and demonstrated that mixing these waters with metallic solutions can produce all the three main types of mineral self-assembly induced by silica. These experiments confirm that silica/carbonate biomorphs, silica/metal oxyhydroxide mineral vesicles, and calcite mesocrystals with biomimetic textures are geochemically plausible phenomena.[44]

3.3. Serpentinization in the earliest earth

Today, there are few geological sites with alkaline water and a silica concentration higher than the one required to trigger self-organization, that is, 300 ppm for silica biomorphs and biomimetic calcite and 900 ppm for mineral vesicles, depending on pH, salinity and temperature.[33b] In addition to the springs in the Cascades Range mentioned above, most of the so-called soda lakes in the Rift Valley fulfill these conditions.[45] Even though we have to admit that the geological scenarios for the chemical coupling of silica with carbonate and hydroxides are today rare and bizarre, these alkaline geochemical scenarios could have been widespread during the first billion years of this planet.[46]

The earth is 4.5 billion years old. The first five hundred million years are called the Hadean era, the Greek word for the hell, because it was thought until recently that during that time the planet was full of volcanic activity, underwent huge meteoric bombardment and high ultraviolet radiation, and had a very hot surface, that is, conditions that would not only sterilize the planet, but also hinder any prebiotic relevant chemistry. However, recent studies have shown that water condensed on the rocks of the crust 4.4 Ga ago, that is, just after the formation of the moon.[47] At such an early time, it is currently thought that the planet was still in the first stage of differentiation of a solid crust.[42a] There are no rock remnants from that earliest earth, but geochemical and petrological models sustain that the planet should already have a thin crust of ultramafic rocks, that is, rocks mostly composed of olivine and pyroxenes. Therefore, the water that started to condense on the crust of the planet 4.4 billions years ago would interact, mostly, with the rocks required to trigger serpentinization. Note that we are talking of a serpentinization process at global scale, at the scale of the planet. The serpentinization reaction would release a huge amount of hydrogen that upon reaction with CO_2 degassed from the inner of the planet would form methane through the Sabatier reaction. Thus, a reduced atmosphere would set in for a long time until the production of H_2 becomes smaller than the flow of CO_2 released by the inner core.[48] Under these reduced conditions formamide would easily form from HCN. As the serpentinization process progresses, it would provoke a distinct mechanical difference between the ultramafic rocks and the clay minerals formed during the reaction. This in turn would facilitate rock alteration, triggering crack formation and the infiltration of water to deeper and hotter rocks, which could be the origin of the very first and simplest hydrothermal systems. The chemistry of these hydrothermal waters would be basically derived from fluid/olivine interactions at temperatures hot enough for Fischer–Tropsch-type synthesis. Therefore, we can envisage the earliest crust of the planet at that time as a huge factory recycling an extremely alkaline fluid full of organic compounds. It is important to note that contemporary serpentinization is framed by an atmospheric composition rich in CO_2 that buffers the pH of serpentinization waters as soon as they reach the surface. An atmosphere rich in methane stabilizes high pH values derived from serpentinization reaction and makes the kinetics of silica release faster than the production of clays. Further rock differentiation would connect these waters with minerals such as quartz and plagioclase that would be dissolved by the high pH alkaline waters from serpentinization, increasing their concentration in silica. Then, the chemical conditions for the formation of biomorphs (that require lower pH values and smaller silica concentrations) but also of metal silicate hydrate membranes and mineral vesicles would be available.[49] Fatty acids, polycyclic aromatic hydrocarbons, and other organic compounds pumped by the very first hydrothermal vents would interact with the product of the condensation of NH_2CHO. We predict that the textural properties of the membranes forming self-assembled mineral vesicles and the small but continuous energy generated during their formation will catalyze NH_2CHO condensation and carbon-based reactions to form organic compounds of increasing diversity and complexity.

3.4. Formamide condensation enhanced by mineral vesicles

To prove the proposed catalytic effect of silica-induced mineral self-organization, we have tested two experimental set-ups. First we used classical chemical gardens made by inserting pellets of soluble metallic salts within sodium silicate solutions at pH 12.[50] The osmotic-driven membranous structures catalyzed the condensation of NH_2CHO to yield nucleobases, amino acids, and carboxylic acids. Membranes formed from sodium silicate solutions in the presence of magnesium and iron salts

[$MgSO_4$ and $Fe_2(SO_4)_3 \cdot 9H_2O$] showed the highest efficiency with respect to copper-, zinc- and manganese-based compounds ($CuCl_2 \cdot 2H_2O$, $ZnCl_2$, and $MnCl_2 \cdot 4H_2O$). It is worth noting that the collections of compounds formed inside and outside the membrane were clearly site-specific, nucleobases prevailing inside and carboxylic acids prevailing outside, demonstrating that the mineral self-assembled membranes simultaneously provide space compartmentalization and selective catalysis of the synthesis of relevant compounds. In a second set of experiments we used mineral vesicles as catalysts.[51] The micro vesicles were synthesized by mixing microdrops of a solution of the metallic salts with solution of sodium silicate. They can be made either by pouring the drop on top of the silicate solution or immersing the drop into the silicate solutions. In both cases metal/silicate membranes formed at the interface of the acidic or neutral drop of the metallic solution and the surrounding alkaline silicate solution. Then, after few minutes, the initial quasi-spherical membranous vesicle starts to corrugate and it bursts as a result of the osmotic forces. The vesicle is observed to break expelling a jet of the inner solution into the outer silicate solution, creating new membranous bulbs or tubules that severely modified their shape. Thus, NH_2CHO condensation occurs during the time at which the membrane formation and reorganization is going on. Our experiments clearly show that the four nucleobases required for RNA synthesis, three amino acids (glycine, alanine, and N-formyl glycine), and six carboxylic acids can be synthesized from NH_2CHO in a single geochemical scenario. In particular, the condensation of NH_2CHO is catalyzed during the formation of silica-oxyhydroxide membranes of different metals (iron, magnesium, manganese, and copper) that are common components of the ultramafic and komaititic rocks of the earliest crust of the planet, able to interact with water to start the serpentinization process.[42a] Moreover, mineral vesicles are more efficient in term of both yielding and diversity than classical chemical gardens. This is due to several factors, but mostly to the fact that they were active during NH_2CHO condensation and that the crystallinity of the membrane of mineral vesicles—as seen by X-ray powder diffraction—is demonstrated to be smaller than the crystallinity of the garden membranes, thus increasing catalytic efficiency.

4. Outlook

The main conclusion of our ongoing investigation is that the chemical molecules that we know are the bricks of the life can be easily formed under geological conditions that were widely distributed in the primitive earth. We propose that the crust of the early earth was a factory of organic compounds working at planetary scale, as much as 4.4 billion years ago. This geochemical niche should also exist, or have existed, on earth-like planets (on which water condensed after the first differentiation of an ultramafic crust), on meteorite parent bodies, on comets, and on the interstellar dusts made of olivine that are and were in contact with enriched regions of formamide in the universe. Thus, we claim that the transition from inorganic geochemistry to organic geochemistry and even to prebiotic geochemistry was an unavoidable and universal phenomenon.

However, the mechanism by which some of the molecules of the organic mixture self-assembled to create complex molecules able to self-reproduce is still unknown. The geological niche proposed here for the transition from inorganic to organic geochemistry was settled most likely as early as 4.4 Ga, that is, almost one billion years earlier than the oldest putative remnants of life on our planet. Once more, time shows to be again a key parameter for origin of life studies.

Conflict of interest

The authors declare no conflict of interest.

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