

## A Global Scale Scenario for Prebiotic Chemistry: Silica-Based Self-Assembled Mineral Structures and Formamide

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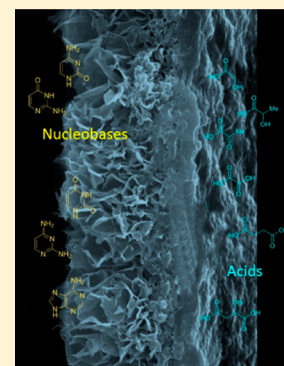
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### S Supporting Information

**ABSTRACT:** The pathway from simple abiotically made organic compounds to the molecular bricks of life, as we know it, is unknown. The most efficient geological abiotic route to organic compounds results from the aqueous dissolution of olivine, a reaction known as serpentinization (Sleep, N.H., et al. (2004) *Proc. Natl. Acad. Sci. USA* 101, 12818–12822). In addition to molecular hydrogen and a reducing environment, serpentinization reactions lead to high-pH alkaline brines that can become easily enriched in silica. Under these chemical conditions, the formation of self-assembled nanocrystalline mineral composites, namely silica/carbonate biomorphs and metal silicate hydrate (MSH) tubular membranes (silica gardens), is unavoidable (Kellermeier, M., et al. In *Methods in Enzymology, Research Methods in Biomineralization Science* (De Yoreo, J., Ed.) Vol. 532, pp 225–256, Academic Press, Burlington, MA). The osmotically driven membranous structures have remarkable catalytic properties that could be operating in the reducing organic-rich chemical pot in which they form. Among one-carbon compounds, formamide ( $\text{NH}_2\text{CHO}$ ) has been shown to trigger the formation of complex prebiotic molecules under mineral-driven catalytic conditions (Saladino, R., et al. (2001) *Biorganic & Medicinal Chemistry*, 9, 1249–1253), proton irradiation (Saladino, R., et al. (2015) *Proc. Natl. Acad. Sci. USA*, 112, 2746–2755), and laser-induced dielectric breakdown (Ferus, M., et al. (2015) *Proc Natl Acad Sci USA*, 112, 657–662). Here, we show that MSH membranes are catalysts for the condensation of  $\text{NH}_2\text{CHO}$ , yielding prebiotically relevant compounds, including carboxylic acids, amino acids, and nucleobases. Membranes formed by the reaction of alkaline (pH 12) sodium silicate solutions with  $\text{MgSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  show the highest efficiency, while reactions with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  showed lower reactivities. The collections of compounds forming inside and outside the tubular membrane are clearly specific, demonstrating that the mineral self-assembled membranes at the same time create space compartmentalization and selective catalysis of the synthesis of relevant compounds. Rather than requiring odd local conditions, the prebiotic organic chemistry scenario for the origin of life appears to be common at a universal scale and, most probably, earlier than ever thought for our planet.



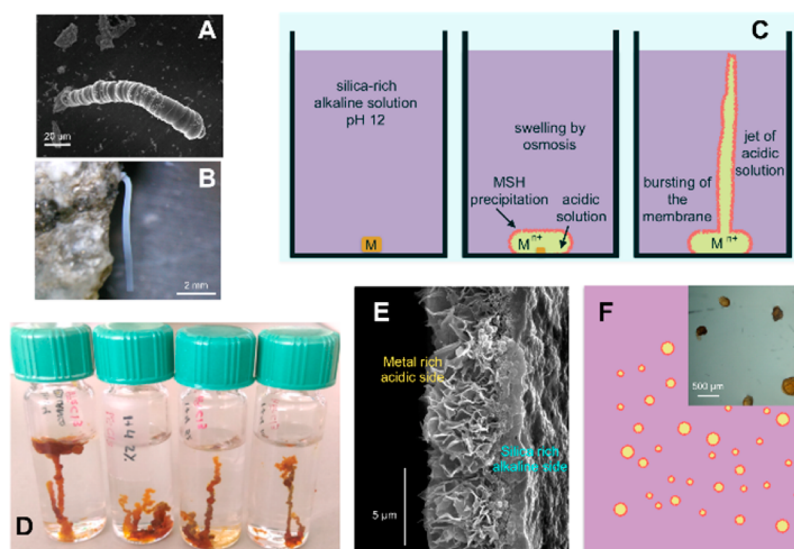
The geological period lasting from the accretion of the planet to 3.8 giga-anni (Ga) is named the Hadean. This name refers to Hades, lord of the Underworld, because that period was thought to be under such infernal conditions as high volcanic activity, high temperature, and intense meteoritic impacts such that even the preservation of rocks was impeded. However, recent isotopic analyses of the zircon crystals found in the Australian localities of Mt. Narryer<sup>6</sup> and Jack Hills<sup>7</sup> have changed that view. These geochemical analyses demonstrated that water might have existed in the liquid state much earlier than currently believed. If the age of the Earth is calculated to be 4.55 Ga,<sup>8</sup> some of these zircon crystals show that water condensed on the rocks of the surface of the planet as early 150 million years later.<sup>9,10</sup> Organic carbon chemistry was thus already plausible 4.4 billion years ago. On such a young planet, water should have condensed on ultramafic rocks, which consisted of a scarce variety of minerals, mostly olivine and

pyroxenes of variable cationic composition. This geochemical scenario intrinsically triggered serpentinization on a global, planet scale.<sup>11</sup> Serpentinization reactions entail a reductive environment rich in  $\text{H}_2$  and  $\text{CH}_4$ , the latter formed upon reaction with  $\text{CO}_2$  outgassing from the inner mantle.<sup>12,13</sup> The Fischer–Tropsch process should have driven chemical reactions, leading to the formation of further complex organic molecules.<sup>14,15</sup> The above-described geological scenario of weathered olivine and pyroxene minerals covering the surface of the planet led to water pools of high pH (about 12) and, upon interactions with plagioclase, quartz, or other silica-rich rocks and minerals, high silica concentration. Under these

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**Figure 1.** (A) Silica/barium carbonate biomorph. (B) Calcium silicate hydrate tubular membranes formed upon the interaction of a highly alkaline fluid with a granitic rock.<sup>20</sup> (C) Interaction of a pellet of a soluble salt with a highly alkaline solution of silica produces the formation around the pellet of a thin membrane of metal silicate and hydroxides. The porous membrane works as a diaphragm, allowing the interchange of ions between the outer strongly alkaline silicate solution and the inner concentrated acidic solutions.<sup>18</sup> Osmosis causes bursting of the membrane and injection of the inner solution into the outer one, which accounts for the formation of the tubular forms. (D) Iron silicate hydrate tubes formed in the presence of (from left to right) 0%, 2%, 5%, and 10% (w/w) formamide. (E) Cross section of the iron silicate hydrate membrane showing the textural and compositional gradient. (F) Iron silicate hydrate hollow microspheres formed by an acidic  $\text{FeCl}_3$  solution being sprayed in the alkaline sodium silicate solution, and a sketch of these structures expected to form in the early, lifeless planet is shown.

alkaline chemical conditions, silica is known to react with metals to form fascinating self-assembled mineral structures. At these pH values, barium, strontium, and/or calcium carbonate form silica biomorphs which are made by self-assembled carbonate nanocrystals, building textures of high complexity and showing morphologies with continuous curvature reminiscent of primitive living organisms and Precambrian microfossils (Figure 1A).<sup>16,17</sup>

In addition, the reaction of alkaline silica solution with metals such as zinc, iron, cobalt, magnesium, nickel, copper, etc., provokes the formation of a metal silicate hydrate (MSH) membrane and the spontaneous separation of two solutions with strong chemical differences.<sup>18</sup> A morphogenetic mechanism based on a combination of osmosis, buoyancy, and chemical reaction results in hollow tubular architectures known as chemical gardens. Their osmotically driven formation and shape look so biological that they have long been linked to the origin of life,<sup>19</sup> and more recently, they helped to develop a theory on the origin of life in white smokers.<sup>20,21</sup> These MSH structures have been made in granitic rocks weathered by highly alkaline fluids<sup>22</sup> (Figure 1B), but their plausible role in prebiotic chemistry has never been tested. The catalytic role of minerals in the prebiotic synthesis of biologically relevant compounds from simple chemical precursors is well-known.<sup>23–25</sup> The novelty and main interest that these self-assembled mineral structures bring to the search for mineral routes to life is twofold. First, the metal silicate hydrate phases have been shown to share the properties of a diaphragm and a membrane, displaying a textural and compositional gradient that allows selective catalytic properties of their inner and outer parts. Second, the membrane separates an enclosed volume of concentrated acidic metal salt solution from the surrounding strongly alkaline silica solution. The existence of an electrochemical potential difference of 20–120 mV that lasts for several hours between the two compartments has been

experimentally demonstrated.<sup>18</sup> Finally, the metal silicate hydrate character of the membrane creates not only a compartmentalized volume but also a shield against ultraviolet radiation.<sup>26</sup>

Among the plausible one-carbon atom chemical precursors that can be produced by purely geochemical pathways ( $\text{HCN}$ ,  $\text{HCOH}$ ,  $\text{HCOOH}$ ,  $\text{NH}_2\text{CHO}$ , and  $\text{HCOONH}_4$ ), we selected formamide for our experiments. Formamide ( $\text{NH}_2\text{CHO}$ ) has been shown to be highly active under mineral catalysis conditions.<sup>3,4,27</sup>  $\text{NH}_2\text{CHO}$  is largely diffused in the universe and has been detected in parsec-wide interstellar clouds.<sup>28,29</sup> The fact that  $\text{NH}_2\text{CHO}$  is liquid between 4 and 210 °C makes it particularly suited to concentration phenomena such as thermoconvection on rock.<sup>30</sup> Space and terrestrial syntheses of  $\text{NH}_2\text{CHO}$  under a large variety of conditions have been previously described and explained.<sup>5,26,30</sup>

## ■ MATERIALS AND METHODS

Formamide (Fluka, >99%) was used without further purification. Fresh commercial water glass (Sigma-Aldrich, reagent grade, containing about 13.8 wt % Na and 12.5 wt % Si) was used as the silica source and was further diluted 1/4 (v/v) with Millipore water. We obtained silica gardens by dipping small pellets of a metal soluble salt into the (diluted) sodium silicate solution containing 2%, 5%, or 10% (v/v)  $\text{NH}_2\text{CHO}$  (see Figure 1 and Supplementary Video 1). Different metal soluble salts were used, namely,  $\text{ZnCl}_2$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{MgSO}_4$ .

To model the chemical environment on the outer side of the tubular structures,  $\text{NH}_2\text{CHO}$  (200  $\mu\text{L}$ ) was mixed with the sodium silicate solution (2.0 mL) in the presence of preformed MSH [ $\text{ZnCl}_2$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{MgSO}_4$ ] (2.0% w/w) at 80 °C for 24 h. In two selected cases [ $\text{FeCl}_2$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ],  $\text{NH}_2\text{CHO}$  (200  $\mu\text{L}$ ) was mixed with the sodium silicate solution (2.0 mL) in the

presence of selected growing MSH (starting from 2.0% w/w of the corresponding salt's pellet) at 80 °C for 24 h. For the inner environment, NH<sub>2</sub>CHO (200 μL) was mixed with distilled water (2.0 mL) in the presence of selected MSH (2.0% w/w) at 80 °C for 24 h. The reaction of NH<sub>2</sub>CHO (10% v/v) with the sodium silicate solution (pH 12) without MSH membranes was also analyzed under similar experimental conditions. The products were analyzed by gas chromatography associated with mass spectrometry (GC-MS) after treatment with *N,N*-bis-trimethylsilyl trifluoroacetamide in pyridine (620 μL) at 60 °C for 4 h in the presence of betulinol (CAS Registry Number 473-98-3) as the internal standard (0.2 mg). Mass spectrometry was performed by the following program: injection temperature 280 °C, detector temperature 280 °C, gradient 100 °C for 2 min, and 10 °C/min for 60 min. To identify the structure of the products, two strategies were followed. First, the spectra were compared with commercially available electron mass spectrum libraries such as NIST (Fison, Manchester, U.K.). Second, GC-MS analysis was repeated with standard compounds. All products have been recognized with a similarity index (SI) greater than 98% compared to that of the reference standards. The analysis was limited to products of ≥1 ng/mL, and the yield was calculated as micrograms of product per starting formamide. For further experimental details, see the [Supporting Information](#).

## RESULTS AND DISCUSSION

We first demonstrated the formation of silica gardens in the presence of NH<sub>2</sub>CHO. As shown in [Figure 1D](#) and

**Table 1. Products Obtained (mg) after the Reaction of NH<sub>2</sub>CHO with Sodium Silicate Solution at Different Temperatures<sup>a</sup>**

product	25 °C	80 °C	120 °C
guanidine (2)	traces	traces	traces
urea (3)	1.0 × 10 <sup>-3</sup>	2.2 × 10 <sup>-3</sup>	0.5 × 10 <sup>-3</sup>
pyruvic acid (4)	1.1 × 10 <sup>-3</sup>	1.9 × 10 <sup>-3</sup>	0.3 × 10 <sup>-3</sup>
lactic acid (5)	0.7 × 10 <sup>-3</sup>	1.0 × 10 <sup>-3</sup>	traces
glycolic acid (6)	traces	traces	

<sup>a</sup>NH<sub>2</sub>CHO (200 μL) was mixed with the sodium silicate solution (2.0 mL) at the reported temperatures for 24 h. The data are the mean values of three experiments with standard deviations of less than 0.1%.

**Table 2. Products Obtained after the Reaction of NH<sub>2</sub>CHO and SSS in the Presence of Selected MSH<sup>a</sup>**

product <sup>b,c</sup>	ZnCl <sub>2</sub>	FeCl <sub>2</sub>	CuCl <sub>2</sub>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	MgSO <sub>4</sub>
guanidine (2)		0.90 (0.40) <sup>d</sup>	traces	0.80 (0.90) <sup>d</sup>	traces
urea (3) <sup>c</sup>	2.0 × 10 <sup>-3</sup>	0.80 (0.32)	0.90	0.015 (nd) <sup>e</sup>	0.01
pyruvic acid (4)	1.9 × 10 <sup>-3</sup>	0.83 (0.24)	traces	0.15 (0.05)	
lactic acid (5)	0.15	0.63 (0.92)	traces	0.16 (0.11)	
glycolic acid (6)	0.11	0.01 (0.12)		traces	0.11
oxalic acid (7)	2.8 × 10 <sup>-3</sup>	0.18 (nd)		0.38 (0.25)	0.12
succinic acid (8)			0.16	0.096 (0.01)	0.071
malic acid (9)				0.02 (0.06)	0.005
<i>N</i> -formylglycine (10)	6.0 × 10 <sup>-3</sup>	traces (nd)		9.0 × 10 <sup>-3</sup> (nd)	2.3 × 10 <sup>-3</sup>
DAMN (11)		0.46 (nd)		0.13 (0.64)	0.09

<sup>a</sup>NH<sub>2</sub>CHO (200 μL) was mixed with SSS (2.0 mL) in the presence of preformed MSH (2.0% w/w) at 80 °C for 24 h. <sup>b</sup>The data are the mean values of three experiments with standard deviations of less than 0.1%. <sup>c</sup>The amount of product is defined as milligrams of compound compared to that of the initial reaction mixture. <sup>d</sup>NH<sub>2</sub>CHO (200 μL) was mixed with SSS (2.0 mL) in the presence of selected growing MSH (starting from 2.0% w/w of the corresponding salt's pellet) at 80 °C for 24 h. <sup>e</sup>nd = not determined.

[Supplementary Video 1](#), metal silicate hydrate tubular structures can be formed readily in the presence of up to 10% NH<sub>2</sub>CHO by small pellets of different metal soluble salts being dispensed inside a sodium silicate solution (SSS) containing 2%, 5%, or 10% (v/v) NH<sub>2</sub>CHO (see [Methods](#)). Then, we designed two different kinds of experiments to model the chemical environment in the outer and inner parts of the tubular structure according to previous work. In the first experiment, we dipped selected and preformed MSH tubules [ZnCl<sub>2</sub>, FeCl<sub>2</sub>·4H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O, or MgSO<sub>4</sub>] in an alkaline (pH 12) solution of sodium silicate containing 10% (v/v) NH<sub>2</sub>CHO. In two selected cases [FeCl<sub>2</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O], the first experiment was repeated in the presence of the membrane in growth by the addition of the pellets of soluble salts directly inside the sodium silicate solution. In the second experiment, we modeled the chemistry of the inner part of the tubular structures by dipping the selected MSH membrane in a water solution and 10% (v/v) NH<sub>2</sub>CHO. As a control experiment, we also analyzed the output of an alkaline solution (pH 12) of sodium silicate with NH<sub>2</sub>CHO (10% v/v) in the absence of MSH membranes. All of the experiments ran for 24 h at the optimized temperature of 80 °C. The experiments were reproduced three times.

The results of the experiments are shown in [Tables 1–3](#) and [Figure 2](#) (see also the [Supporting Information](#)). As a general trend, the control reaction at 80 °C afforded a panel of compounds larger than that obtained at 25 and 120 °C. Guanidine (2), urea (3), pyruvic acid (4), lactic acid (5), and glycolic acid (6) were observed in small amounts ([Table 1](#)). The temperature of 80 °C was selected for the next reactions. The experiments that used preformed MSH membranes afforded a larger variety of products and did so in higher yields ([Tables 2](#) and [3](#), respectively). In particular, the experiment modeling the catalytic effect of the outer side of the membrane afforded 2, 3, 4, 5, 6, oxalic acid (7), succinic acid (8), malic acid (9), *N*-formylglycine (10), and diamino malonitrile (DAMN) (11) ([Table 2](#) and [Figure 2](#)).

Similar results were obtained in the presence of the growing membrane ([Table 2](#), data in parentheses), suggesting that the “active” silicate membranes do not play a key role when compared to that of preformed membranes.

Interestingly, the chemical environment modeling the inner side of the tubular structures afforded an even larger panel of products. In addition to compounds 2–11, the inner

Table 3. Products Obtained after the Reaction of NH<sub>2</sub>CHO and Distilled Water in the Presence of Specific MSH<sup>a</sup>

product <sup>b</sup>	ZnCl <sub>2</sub>	FeCl <sub>2</sub>	CuCl <sub>2</sub>	MnCl <sub>2</sub>	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	MgSO <sub>4</sub>	CuN <sub>2</sub> O <sub>6</sub>
guanidine 2 <sup>c</sup>	5.2 × 10 <sup>-3</sup>	3.4 × 10 <sup>-3</sup>	1.6	0.1	0.18	0.12	0.67
urea 3	traces		1.7	5.0 × 10 <sup>-3</sup>		traces	
pyruvic acid (4)	4.1 × 10 <sup>-3</sup>	0.01	1.8 × 10 <sup>-3</sup>		0.73	0.7	0.28
lactic acid (5)					0.07	0.05	
oxalic acid (7)	traces		0.10		traces	traces	
succinic acid (8)					0.21	0.17	0.18
malic acid (9)					0.03	0.03	
N-formylglycine (10)	2.5	0.85	traces		1.9	1.8	
DAMN (11)					0.02	traces	
glycine (12)	0.03	0.23	0.76		0.57	0.53	
alanine (13)	traces	traces	traces		0.27	0.23	
parabanic acid (14)			0.59				0.9
4(3H)-Pyr (15)			5.6	0.3	traces	traces	0.05
2,4-DAP (16)			0.3	0.02	0.18	0.17	traces
6(OH)-2,4-DAP (17)			0.3	0.06			traces
2,4-DAP-5COOH (18)			traces		traces	traces	0.14
cytosine (19)		traces	0.13		0.18	0.15	1.2
isocytosine (20)		traces	5.0		0.11	0.11	1.4
uracil (21)	traces		3.8	0.03	0.22	0.23	0.85
adenine (22)			0.01		0.01	0.01	traces

<sup>a</sup>NH<sub>2</sub>CHO (200 μL) was mixed with water (2.0 mL) in the presence of selected MSH (2.0% w/w) at 80 °C for 24 h. <sup>b</sup>The data are the mean values of three experiments with standard deviations of less than 0.1%. <sup>c</sup>The amount of product is defined as milligrams of compound compared to that of the initial reaction mixture.

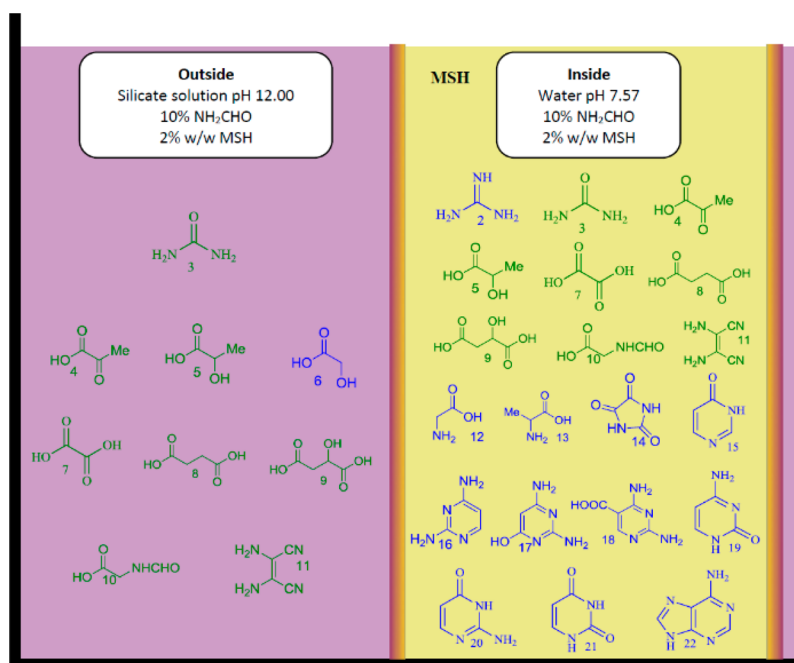


Figure 2. Schematic representation of products obtained with different MSH from NH<sub>2</sub>CHO outside (left) and inside (right) of the membranous structure. Color codes: compounds synthesized at both sides of the membrane (green); compounds synthesized only inside the membrane (blue).

environment of the membranes also catalyzed glycine (12), alanine (13), parabanic acid (14), 4(3H)pyrimidinone [4(3H)-Pyr] (15), 2,4-diamino pyrimidine (2,4-DAP) (16), 6-hydroxy-2,4-diamino pyrimidine [6(OH)-2,4-DAP] (17), 2,4-diamino pyrimidine-5-carboxylic acid (2,4-DAP-5COOH) (18), cytosine (19), isocytosine (20), uracil (21), and adenine (22) (Table 3 and Figure 2). MgSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O, CuN<sub>2</sub>O<sub>6</sub>·3H<sub>2</sub>O, and CuCl<sub>2</sub>·2H<sub>2</sub>O were the most active MSH in the synthesis of nucleobases 19, 21, and 22. Amino acids 12 and 13 were also produced in acceptable amounts

It is interesting to note that the salts of the two metals that form the olivine solid solution, MgSO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O, are the most efficient salts, while CuCl<sub>2</sub>·2H<sub>2</sub>O, ZnCl<sub>2</sub>, FeCl<sub>2</sub>·4H<sub>2</sub>O, and MnCl<sub>2</sub>·4H<sub>2</sub>O showed a low reactivity. Carboxylic acids 4–9 were obtained in larger amounts in the outer environment with the exception of only MgSO<sub>4</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O. Therefore, this process is selective in terms of mineral properties because different metal silicate hydrated membranes afford different panels of products. Even more interesting is the fact that the panels of compounds formed inside and outside

the tubular membrane are specific, as shown in Figure 2. Thus, nucleobases (19, 21, and 22), nucleobase bioisosteres (16 and 20), and nucleobase analogues (15, 17, and 18) are produced only inside the membrane (Figure 2). Amino acids 12 and 13 are also synthesized only inside the membrane.

Carboxylic acids 4–9 were obtained in the inner and outer environments. The prebiotic roles of DAMN<sup>31</sup> and the nucleobase bioisosteres and analogues have been reviewed previously.<sup>32</sup> The ability of formamide to trigger the synthesis of compounds representative of the major classes of prebiotic precursors in the presence of a number of minerals (including boron-, iron-, sulfur-, zircon-, titanium-, and phosphorus-based minerals, metal oxides of various types, and meteorites) has been previously shown to be particularly efficient under proton irradiation and the simulated impact of an extraterrestrial body. Our results provide the first example of a catalytic process endowed with (a) selective catalysis of the synthesis of biogenic relevant compounds by a textured membrane, (b) intrinsic compartmentalization ability, and (c) a shielding environment against ultraviolet radiation. Interestingly, in the reported experiments, the nucleic acid precursors were located on the inner side of the membranes. However, we have not found significant differences in either the number or the yield of biochemically relevant compounds when comparing the reactivities of active versus passive metal silicate hydrate membranes. This means that the electron voltage reported in previous silica garden<sup>18</sup> experiments does not play a differential role in the catalysis of prebiotic compounds. The geological niche proposed here for the transition from inorganic to organic geochemistry, a silica-rich, alkaline, aqueous solution in contact with metal-bearing minerals in the presence of NH<sub>2</sub>CHO, was highly plausible during the Hadean and Archean times. This niche was settled most likely as early as 4.4 Ga, i.e., almost one billion years earlier than the oldest putative remnants of life on our planet. Therefore, the existence of biological compounds such as carboxylic acids, amino acids, and nucleobases, or their carbon-like derivatives in Hadean zircon crystals or in Archean rocks, is rather plausible. It is worth noting that in these organic geoniches, silica biomorphs that mimic primitive organisms readily form in the presence of alkaline earth metals.<sup>16</sup> This geological niche is not exclusive to our planet. It should also exist, or have existed, on Earth-like planets, meteorite parent bodies, and comets, as well as in the interstellar dust made of olivine that are or were in contact with enriched regions of NH<sub>2</sub>CHO in the universe. These results suggest that the conditions required for the synthesis of the molecular bricks from which life self-assembles, rather than being local and bizarre, seem to be universal and geologically conventional.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.biochem.6b00255.

Detailed experimental conditions of the reactions, GC-MS chromatograms, mass-to-charge ratio (*m/z*) value, and the abundance of mass spectra peaks of the products (PDF)

Video of growing silica gardens (AVI)

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### Author Contributions

R.S., G.B., and B.M.B. performed the condensation experiments with formamide, and J.M.G.R. performed the silica garden experiments. E.D.M. and J.M.G.R. conceived the work. J.M.G.R., R.S., and E.D.M. analyzed the results and wrote the manuscript.

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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

MSH, metal silicate hydrate; SSS, sodium silicate solution; DAMN, diamino malonitrile; [4(3H)-Pyr], 4(3H)-pyrimidinone; (2,4-DAP), 2,4-diamino pyrimidine; [6(OH)-2,4-DAP], 6-hydroxy-2,4-diamino pyrimidine; (2,4-DAP-SCOOH), 2,4-diamino pyrimidine-5-carboxylic acid

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