

# Catalysis in the Primordial World

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Review

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## Abstract

Catalysis provides orderly prebiotic synthesis and eventually its evolution into autocatalytic (self-reproduction) systems. Research on homogeneous catalysis is concerned mostly with random peptide synthesis and the chances to produce catalytic peptide oligomers. Synthesis of ribose via formose reaction was found to be catalysed by  $B(OH)_4^-$ , presumably released by weathering of borate minerals. Oxide and clay mineral surfaces provide catalytic sites for the synthesis of oligopeptides and oligonucleotides. Chemoautotrophic or iron-sulphur-world theory assumes that the first (pioneer) organisms developed by catalytic processes on (Fe/Ni)S particles formed near/close hydrothermal vents. The review provides an overlay of possible catalytic reactions in prebiotic environment, discussing their selectivity (regioselectivity, stereoselectivity) as well as geological availability of catalytic minerals and geochemical conditions enabling catalytic reactions on early Earth.

## Keywords

*Chemoautotrophic theory, formose reaction, origin of life, prebiotic chemistry, random synthesis of biopolymers*

## 1 Introduction

The “historical” 1953 Urey-Miller experiment<sup>1–3</sup> may be misleading. The very idea of the emergence of life on Earth by organic synthesis could be traced back to Darwin’s “warm little pond”, expressed in a letter to Hooker, dated February 1, 1871,<sup>4,5</sup> and *Oparin*<sup>6</sup> referred to many ways to obtain organic matter in prebiotic conditions. After all, as Max Bernstein pointed out, “the spark discharge method of making organic molecules is not as important as it was originally thought to be”.<sup>7</sup> Nearly two hundred organic compounds were found in interstellar clouds<sup>8,9</sup> and many more in meteorites (carbonaceous chondrites). There are literally millions of different organic compounds in the Murchison meteorite alone, of which 683 were positively identified.<sup>10</sup> *Chyba and Sagan* estimated an input  $10^7$ – $10^9$  kg yr<sup>−1</sup> of organic material from cometary and asteroidal interplanetary dust particles (IDPs) on early Earth.<sup>11</sup>

The next problem with the Urey-Miller experiment is that primordial Earth’s atmosphere was not Jupiter-like, composed of hydrogen, methane, ammonia and water vapour, as Urey proposed.<sup>12</sup> According to new insights<sup>13,14</sup> it was very much Mars-like, containing mostly carbon dioxide but with traces of volcanic gases (hydrogen, water vapour, hydrogen sulphide, sulphur dioxide and carbon monoxide). Simple molecules ( $H_2O$ , CO,  $NH_3$ ,  $CH_4$ ) along with complex ones were available on Earth from the early stages of its formation, but it seems that Earth’s collision with a Mars-sized body, about 4.5 billion years ago which formed the Moon, removed its pristine atmosphere.<sup>15</sup> This kind of

atmosphere did not easily yield amino acids after being exposed to ionizing agents, like UV radiation or electrical sparking;<sup>16</sup> however the synthesis could have been much improved by buffering reaction solution ( $CaCO_3$ ) and lowering of its oxidation potential ( $Fe^{2+}$ ).<sup>17</sup> For the prebiotic synthesis and eventually emergence of life, it was also necessary to provide suitable geological habitat (increased concentration, temperature or pressure etc.) in the small environment we call Earth.<sup>18</sup> In this respect, the development of the atmosphere and hydrosphere on Earth and also its stratification (formation of core, mantle and crust) was essential, which resulted in the production of the magnetic field around the planet that protects it from dangerous radiation from outer space.<sup>19</sup>

We should also bear in mind that prebiotic synthesis of biologically important compounds (amino acids, sugars, nucleobases, etc.) is not *per se* crucial for the emergence of life. It is also necessary to study the primordial organization of matter in self-sustainable and reproductive systems (*pioneer organisms* and *protocells*). However, to propose such systems, the *persistence principle*<sup>20</sup> firstly needs to be put into effect, *i.e.* make a plausible hypothesis of the mechanisms for the concentration of primordial matter and its orderly (persistent) transformation. In other words, it is necessary to propose a suitable catalysis or catalytic system in the primordial world to be developed into a “primal dynamic steady-state replicative system”, *i.e.* protolife, as it is defined thermodynamically.<sup>20</sup> The obvious fact that the first catalysts were fuzzy and unspecific turned into their advantage because – as theoretical analysis of the development of autocatalytic systems shows – only random novel molecular species enable Darwinian evolution.<sup>21</sup>

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## 2 Oparin's solution: Homogeneous catalysis in coacervate droplets

There are four basic requirements every plausible theory of the origin of life has to fulfil. It has to provide (i) a source of energy to drive molecular and macromolecular synthesis, (ii) a mechanism for the localized concentration of reactants to favour the required chemical reactions, (iii) suitable catalysis, and (iv) a suitable geochemical environment for these reactions and their products. Oparin's theory,<sup>6,22</sup> the first modern and complete theory of life origin, fulfils these requirements, but assuming geochemical environment and chemical processes that in the first half of the 20<sup>th</sup> century seemed much likely to have occurred than they seem now.<sup>23</sup> Oparin, namely, assumed (i) that the source of energy was provided by organic compounds dispersed in the primordial ocean, (ii) that they were concentrated by forming coacervate droplets, (iii) that catalysis was provided by protein or protein-like molecules, and (iv) that the ocean as a whole provided a suitable geochemical environment for the origin and development of life.

This theory was quite in line with the current biochemical doctrine of biocolloidy that regarded life as a colloidal phenomenon based on proteins.<sup>24</sup> Thus, the essence of Oparin's theory is to explain how life as "a form of existence of protein bodies" (p. 136)<sup>6</sup> emerged on Earth; however, this obsolete concept has been revived by the new concept of protoplasmic continuity and the models of organic films and microspheres.<sup>25</sup>

Catalysed reactions inside coacervate droplets provided their stability and thus "only the dynamically most stable colloidal systems secured for themselves the possibility of continued existence and evolution" (p. 191).<sup>6</sup> Further evolution of coacervate droplets was enabled by linking of catalytic, *i.e.*, enzymatic reactions. Evolution pressure has been a gradual depletion of substrates from the environment. This means that the initial catalysed reaction  $A \rightarrow B$  gradually evolved into  $C \rightarrow A \rightarrow B$ ,  $D \rightarrow C \rightarrow A \rightarrow B$ , etc.

There are two critical flaws in Oparin's theory. The first is the regulation of protoenzymatic reactions in his droplets, and the second is the abiotic synthesis of enzymes, *i.e.*, proteinoid homogeneous catalysts. Oparin never solved the first problem; he succeeded in preparing coacervate droplets with enzymes (which, due to accumulation of products, even divided themselves), but never with more than one enzyme.<sup>26</sup> Lately, much more elaborate enzymatic systems have been devised; those based on phospholipid vesicles were even able to synthesize proteins and nucleic acids,<sup>27,28</sup> but the problem of regulation persisted. The second problem, the evolution of catalysis inside the droplets, has two aspects: (1) catalysis of protein synthesis, and (2) abiotic generation of catalytic peptides.

Catalysts for protein synthesis may be such simple substances as sodium and potassium ions, which were abundant in the primordial ocean. It was namely demonstrated that in 1 M concentration, they catalyse polymerization of glutamic acid with 1,1'-carbonyldiimidazole into 9- (Na<sup>+</sup>) and 11-mer (K<sup>+</sup>) oligopeptides.<sup>29</sup> More important, however, is that simple dipeptides Ser-His and Gly-Gly (less efficiently) catalyse polymerization of amino-acid esters,

peptide fragments, and building blocks of peptide nucleic acids (PNA).<sup>30</sup> Basic peptides, polymers of lysine, catalyse hydrolysis of phosphodiester bond, especially if their conformation is  $\beta$ -sheet rather than random coil.<sup>31</sup>

The second problem, abiotic generation of catalytic proteins, could possibly be solved by directed peptide synthesis.<sup>32,33</sup> Firstly, two small families (A and B) of four decapeptides each were synthesized, and by their combinations (A·B), 16 oligopeptides of length 20 were prepared. However, only four of them were soluble in water. By further combination, only one soluble oligopeptide of length 40 was obtained. This scheme could possibly explain the synthesis of long-chain peptides in the prebiotic environment, but it seems quite implausible, as *P. C. Higgs* pointed out, that selection of physical properties (*i.e.* water solubility) alone could generate many identical copies.<sup>33</sup> There are, namely, 20<sup>4</sup> random sequences for 20-oligopeptides, *L* being the number of amino acids, and there is an enormous number of possible water-soluble peptides synthesized in this way to lead evolution to an autocatalytic mechanism.

In line with this research is the [GADV]-protein world hypothesis,<sup>34</sup> stating that the first biological molecules were proteins composed of only four amino acids: glycine (G), alanine (A), aspartic acid (D), and valine (V). In the repeated heat-drying experiments (mimicking processes on primitive Earth) of aqueous solutions of the respective amino acids in equimolar concentrations, a library of random peptides were synthesized, which showed catalytic abilities to hydrolyze  $\beta$ -galactoside and amide (peptide) bond.<sup>35,36</sup> The same was achieved by random [GADV]-octapeptides on BSA substrate.<sup>37</sup> Random synthesis of [GADV]-peptides by microwave heating produced a library of 1–4 kDa peptides,<sup>38</sup> which showed hydrolase- and oxidoreductase-like catalytic activities.<sup>39</sup> Against all odds of combinatorics, it is clear that catalytic peptides could have been easily formed on primordial Earth.

## 3 Prebiotic synthesis by homogeneous catalysis

Despite the fact that the scheme for the prebiotic synthesis of sugars (*formose reaction*) has been known since the 19<sup>th</sup> century,<sup>40</sup> its catalysis by borates is a very new development.<sup>41</sup> It was found that in the uncatalysed reaction, the yield of pentoses was only 30 % (1 % ribose), less than the yield of hexoses (55 %), but more than that of tetroses (10 %) and higher sugars (5 % > C<sub>6</sub>).<sup>42</sup> Moreover, "formose" is not stable, but inclined to "browning" (*asphalt problem*),<sup>43</sup> yielding insoluble organic matter (IOM) besides amino acids (when ammonia was added) and other low-molecular compounds by simulated synthesis on carbonaceous chondrites and comets.<sup>44,45</sup> However, addition of borate in the form of artificially prepared mineral colemanite, Ca<sub>2</sub>B<sub>6</sub>O<sub>11</sub>·5H<sub>2</sub>O, stabilizes formose solutions for months.<sup>46</sup> The effect of borate was attributed mostly to the stabilization of pentoses, and to a lesser extent, of glyceraldehyde, the key autocatalytic reactant, keeping it in the enolate form (Fig. 1). Both substances form bis-complexes with borate anion, B(OH)<sub>4</sub><sup>-</sup>, B(OH)<sub>3</sub> + OH<sup>-</sup> → B(OH)<sub>4</sub><sup>-</sup> (pK = 9.1) in basic solutions, as do many other geminal

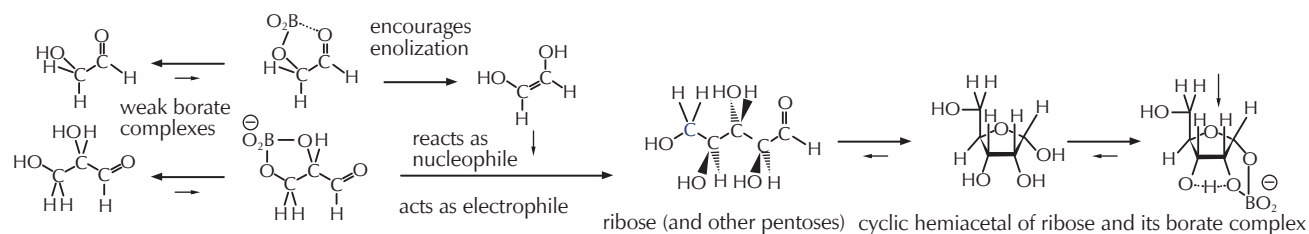


Fig. 1 – Formose reaction catalysed by borates:  $B(OH)_4^-$  stabilizes reactants (glycolaldehyde, glyceraldehyde) and the product (ribose); adapted after Ref. 43.

Slika 1 – Reakcija formoze katalizirana boratima:  $B(OH)_4^-$  stabilizira reaktante (glikolaldehid, gliceraldehid) i produkt (ribozu), preuzeto iz ref. 43.

diols.<sup>47</sup> Systematic study of the stability of pentose complexes with borate (borax) in concentration of 0–80 mM revealed that ribose is the most stable pentose (others are xylose, lyxose and arabinose) in 80 mM borate, but the least stable in the 0 mM solution.<sup>48</sup> It was also found that boric acid increases the thermostability of monosaccharides under acidic (ribose) and basic conditions (glucose).<sup>49</sup> Analogous catalytic activity was found for silicate ions (sodium silicate),<sup>50</sup> but its relevance for prebiotic synthesis is dubious.<sup>51,52</sup>

However, the question is whether boron-catalysed synthesis is possible in a prebiotic environment. Boron is among the rarest elements in the Universe (amount fraction 1 ppb) because it was neither synthesized by nucleosynthesis within stars nor during the Big Bang, but by nuclear fusion in cosmic-ray collisions.<sup>53,54</sup> The catalytic role of boric acid is pointed out in discussions of possible reactions in seawater.<sup>55</sup> The borate concentration in today's seawater is only 4.45 ppm,<sup>56</sup> but the finding of tourmaline in 3.8-billion-year-old rocks<sup>57</sup> and boron minerals in carbonaceous chondrites<sup>58</sup> speaks in favour of moderate borate concentrations in the waters of early Earth. Their abundance has to date increased following evolution of geological environments.<sup>18,59–61</sup>

However, the occurrence of its soluble minerals (evaporites, e.g. colemanite) demands a developed and rare environment like basic lakes, or boron-rich lakes. *Benner et al.*<sup>43</sup> envisaged such a geochemical environment in subaerial intermountain desert valleys with borate-rich aquifers (pH = 10–11), which collect runoff from a watershed containing serpentinizing olivines and igneous tourmalines, being also rich in formaldehyde, formamide, ammonium formate, and similar chemicals. Due to  $CO_2$  adsorption, the pH of aquifers dropped to 6, which enabled further prebiotic synthesis and prevented formation of macromolecular material (*asphalt*).

Boric ions also catalyse amino acid polymerization.<sup>55</sup> This kind of catalytic activity was also found for sodium and potassium ions,<sup>29</sup> but the systematic study of the influence of pH, temperature, and metal concentration on the polymerization of glycine revealed a negative influence of other divalent metals.<sup>62</sup> Namely, metal ions, which easily form complexes with glycine and its oligomers ( $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Co^{2+}$ ,  $Hg^{2+}$ ), inhibit Gly polymerization in contrast to  $Fe^{2+}$  and  $Mg^{2+}$ , which have virtually no influence.

That led to the conclusion that these metals were immobilized in the form of respective sulphides, supporting this way the chemoautrophic (or “iron-sulphur-world”) theory of life origin (see the fifth paragraph). Metallic cations like  $UO_2^{2-}$ ,<sup>63,64</sup>  $Pb^{2+}$ ,  $Zn^{2+}$  and those of lanthanides<sup>65,66</sup> catalyse nucleotide polymerization, and even non-enzymatic template directed synthesis of RNA oligomers.<sup>67,68</sup> However, because of the scarcity of these ions in modern as well as in early Earth's geological habitat, their role in prebiotic synthesis could hardly be important.

#### 4 Heterogeneous catalysis: Synthesis on clay minerals

The hypothesis that clays played a decisive role in the origin of life, expressed originally by *J. D. Bernal* in 1949<sup>69</sup> and later elaborated by *C. Ponnamperna*,<sup>70</sup> is still very popular (Table 1). Clays were easily found on early Earth because they are produced by weathering of silicate rocks through different processes involving liquid water and vapours. Montmorillonite, the most interesting clay mineral in the context of the origin of life, is formed by weathering of volcanic ash, and the first occurrence of kaolin in geological environment is connected to the activation of hydrothermal alteration of feldspar-containing rocks.

Except on Earth, clay minerals were found on Mars,<sup>71,72</sup> in meteorites, especially liquid-water-altered CI1 carbonaceous chondrites,<sup>73,74</sup> as well as on asteroids.<sup>75</sup> It was hypothesized that clay minerals are present on comets, making them allegedly places for prebiotic synthesis and even for the origin of life (*interstellar panspermia*).<sup>76</sup> Clay minerals are characterized by very small particles or crystals that increase the active surface of the particles, and make clay mineral more efficient in processes of adsorption and exchanging ions. They have layered structures, sometimes expandable (like in smectite group minerals), with enough space between the layers to accommodate ions, and even organic molecules making them catalysts in organic synthesis.<sup>77,78</sup> Therefore, clay deposits, in combination with plate tectonics, might play an important role in the production and concentration of prebiotic organic molecules crucial for the emergence of life.

As *J.-F. Lambert* pointed out, clay and similar minerals (silicates,  $SiO_2$ ,  $Al_2O_3$ ,  $TiO_2$ ) are not, strictly speaking, catalysts

Table 1 – Prebiotic reactions catalysed by clay minerals  
 Tablica 1 – Predbiološke reakcije katalizirane mineralima gline

Reaction Reakcija	Catalyst Katalizator	References Referencije
formose reaction	kaolinite, illite	173, 174
polymerization of Gly	kaolinite, bentonite	175
polymerization of Gly	kaolinite	176
polymerization of Gly	phyllosilicates (kaolinite montmorillonites, nontronites)	177
polymerization of Gla, Ala	mono-ionic bentonites	88
polymerization of Gly and Gly <sub>2</sub>	Ca <sup>2+</sup> - and Cu <sup>2+</sup> -montmorillonite	178
polymerization of negatively charged amino acids (Glu, Asp, O-phospho-Ser)	illite	179, 180
polymerization of pyroGlu	kaolinite, montmorillonite	181
polymerization of Gly, Ala, (Ala+Gly), (Ala+Gly <sub>2</sub> ), (Ala+DKP)	montmorillonite, hectorite	87
polymerization of Gly, Tyr, (Gly+Tyr)	Cu <sup>2+</sup> -hectorite, montmorillonite	182
polymerization of Gly, Ala, (Ala+Gly), Pro, (Pro+Gly), (Pro+Gly <sub>2</sub> ), (Pro+Ala), Val, (Val+Gly), (Val+Gly <sub>2</sub> ), (Val+Ala), Leu, (Leu+Gly), (Leu+Gly <sub>2</sub> ), (Leu+Ala)	hectorite	97
polymerization of AMP with EDAC	Na <sup>+</sup> -montmorillonite	183
polymerization of ImpU	montmorillonite	184, 185
polymerization of ImpC	montmorillonite	186
polymerization of ImpA	montmorillonite	179, 187
polymerization of ImpA	Na <sup>+</sup> -montmorillonite	122
polymerization of ImpA, ImpU	montmorillonite	115
polymerization of ImpA + ImpC	montmorillonite	112, 187
polymerization of MeadpA, MeadpU	montmorillonite	188, 189
polymerization of ImpX +XmP (X = A, C, G, U, Im)	montmorillonite	190
polymerization of ImpA, ImpU, ImpA + ImpU	Na <sup>+</sup> -montmorillonite	116, 117, 191
polymerization of Imp(A, C, U, G)	montmorillonite	119, 120

(*pseudo-enzymes*) in peptide synthesis since the polymerization of amino acids is an endergonic process.<sup>79</sup> The function of clays in prebiotic synthesis was to concentrate reactants on mineral surfaces enabling thermal polymerization by the drying/wetting process. The adsorption of amino acids on mineral surfaces was not yet sufficiently explained, but three possible mechanisms were proposed (Fig. 2). The first was the “formation of an anhydride” with surface hydroxyl groups; that is, formation of Si–O–CO–R moieties on the surface of silicate minerals.<sup>80</sup> The second mechanism was the formation of complexes with Ti<sup>4+</sup> (TiO<sub>2</sub>)<sup>81</sup> or Al<sup>3+</sup> and Cu<sup>2+</sup>.<sup>82</sup> The third proposed mechanism was the formation of hydrogen bonds between –COOH groups of amino acids and Si–OH groups of silicate mineral.<sup>83,84</sup> The study of the glycine intercalation into kaolinite silicate layer found the drop of activation energy by heating, from 21 kJ mol<sup>-1</sup> (20–65 °C) to 5.8 kJ mol<sup>-1</sup> (65–80 °C).<sup>85</sup>

Adsorption of an amino acid depends on its chemical form. Amino acids, as neutral molecules (H<sub>2</sub>N–CHR–COOH) dominate in the adsorption from gas phase on dried surfaces, whereas they are adsorbed better as zwitterions (+H<sub>3</sub>N–CHR–COO<sup>-</sup>) from aqueous solutions. In ad-

dition, with charged groups in side chains, they are better adsorbed than those with uncharged side chains.<sup>86</sup> That finding, however, speaks against the theory of prebiotic synthesis on clay minerals, because amino acids with neutral side chains prevail in proteins. It also contradicts the [GADV]-theory, because it includes three amino acids, out of four, with neutral side chains (G, A, V).

The second problem with the clay theory is a very low yield of polymers. Performing the drying/wetting cycles (80 °C) on montmorillonite and hectorite, yields far below 1 % were obtained for glycine and alanine<sup>87</sup>, and < 2 % alanine had converted to dialanine after 56 days of drying/heating/wetting cycles (45/94 °C) on mono-ionic bentonites.<sup>88</sup> Obviously, a higher temperature gives a better yield, but the decomposition of adsorbed material takes place at about 200 °C.<sup>89</sup>

It was hypothesized that clay minerals had been the key chiral agents for the preference of L-amino acids in proteins. The hypothesis has been strongly supported by the finding that heating of aspartic acid on kaolin at 90 °C yielded 25 % polymerization of L- but only 3 % of D-iso-

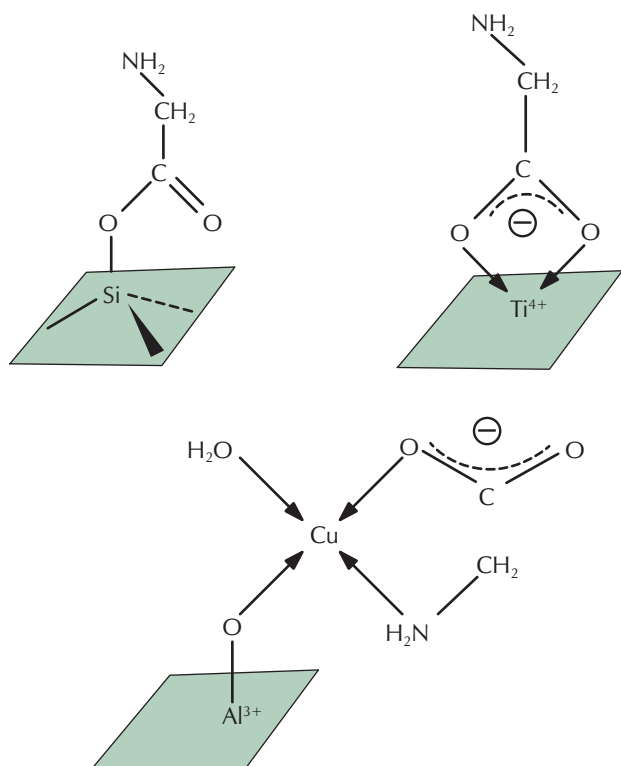


Fig. 2 – Proposed mechanisms for amino-acid adsorption on mineral surfaces; formation of an anhydride with surface hydroxyl groups, formation of complexes with  $Ti^{4+}$  or with  $Al^{3+}$  and  $Cu^{2+}$

Slika 2 – Pretpostavljeni mehanizmi za adsorpciju aminokiselina na površine minerala: stvaranje anhidrida s hidroksilnim skupinama na površini te nastajanje kompleksa s  $Ti^{4+}$  i s  $Al^{3+}$  i  $Cu^{2+}$

mer.<sup>90</sup> However, the problem is far from simple. In 1971, better adsorption of L- than D-phenylalanine on kaolin was found,<sup>91</sup> but this has not been confirmed.<sup>92</sup> L-glutamic acid is better adsorbed on  $Na^+$ -montmorillonite (pH = 6.0) than its D-isomer, but quite opposite holds for aspartic acid, and both amino acids proved more reactive to deamination in their L-forms.<sup>93</sup> The problem is complex not only because of the different mechanisms of adsorption and polymerization of different amino acids, but also because different enantioselectivity could be observed even on different crystal faces of the same mineral.<sup>94</sup> At any rate, enantioselective adsorption and polymerization of amino acids on mineral surfaces cannot be denied, and it was even explained by “occasional chirality” of clay crystal lattice<sup>70</sup> or by stacking of the optically active ions in the interlayer space,<sup>95,96</sup> but the connection with biological homochirality remains obscure.

Research on other non-clay minerals revealed that the most efficient catalyst for amino acid polymerization is alumina, showing a yield of even 13.06 % for glycine dimerization,<sup>97</sup> which is not at all surprising as alumina is a well-known industrial catalyst. In addition to silica, alumina is a very common product of weathering and hydrothermal alteration of silicate rocks. A systematic study of the polymerization of glycine on mineral surfaces showed the order of catalytic efficiency: rutile > anatase >  $\gamma$ -alu-

mina > forsterite >  $\alpha$ -alumina > magnetite > hematite > quartz > amorphous silica.<sup>98</sup> Martra and coworkers prepared poly-Gly up to 16 units long by condensation of the amino acid vapour (130 °C) on  $TiO_2$  (anatase) and amorphous  $SiO_2$  surfaces.<sup>99</sup> That line of research<sup>100</sup> opens a number of possibilities for prebiotic synthesis, but it has to be taken into consideration that there is a quite significant difference in polymerization efficiency for different amino acids on different minerals, e.g. 0.07–13.06 % for dimerization on alumina.<sup>97</sup> Also, many of the studied minerals were, and still are, rare. Forsterite,  $Mg_2SiO_4$ , was the most abundant; magnetite, rutile and anatase were not so plentiful, because they are accessory minerals. Amorphous silica was also present, but as a new, weathering and alteration product.

The problem of nucleic acid synthesis on clay minerals<sup>101,102</sup> has gained importance since RNA-world hypothesis came to the fore. This hypothesis<sup>103–105</sup> implies that RNAs were molecules on which all original biological functions of proto-organisms were based; from them developed both DNA and proteins. Such a hypothesis put many requirements on the theory of prebiotic synthesis. In contrast to proteins, which were presumably synthesized by polymerization of amino acids, which were in turn produced by simple Miller-like synthesis, prebiotic synthesis of RNA monomers is much more complex both chemically<sup>106–108</sup> and geochemically.<sup>109–111</sup> However, it has to be pointed out that experiments aimed at clay-catalysed synthesis seem much more convincing than those designed for the synthesis of peptides. Polymerization reactions were exergonic because they were performed by using condensing agents (EDAC) or activated nucleotides, mostly ImpA. The second reason is that only one mineral has been successfully employed, i.e. montmorillonite, one of the most abundant clay minerals on Earth as well as Mars.<sup>71</sup>

The third reason is that a much better degree of polymerization has been achieved with nucleotides than with amino acids, and even selectivity has been observed. In the experiment of copolymerization of ImpA and ImpC<sup>112</sup> 8, 10, 5 and 4 isomers with 2, 3, 4, and 5 mers, respectively, were detected, obviously much less than the number of isomers predicted in random synthesis (8, 32, 128 and 512). By binding of decameric primer on  $Na^+$ -montmorillonite, oligomers up to 50 monomer units were prepared.<sup>113</sup> Enantioselectivity was also observed because D-D and L-L dimers were preferentially formed starting from racemic (D,L) nucleotides.<sup>114</sup> However, it holds true only for purine nucleotides (ImpA), which gave 66.9 % homochiral dimers in contrast to 39.2 % homochiral dimers for ImpU;<sup>115</sup> quaternary reactions (ImpA + ImpU) gave 63.5 % homochiral dimers and 74.5 % homochiral trimers.<sup>116</sup> Similar results were obtained for tetramers and pentamers.<sup>117</sup>

Molecular modelling revealed that the decisive factor in enantioselectivity are dipole interactions between nucleotide anion and zwitterion (Fig. 3) on clay surface.<sup>115</sup> Coulombic interactions are also dominant for the montmorillonite catalytic activity. It was shown that montmorillonites with smaller surface layer charges are better catalysts.<sup>118–120</sup> By studying the oligomerization reaction of ImpU and ImpA inhibited by  $N^6,N^6$ -dimethyladenine and  $dA^{5'}$  pppA on montmorillonite, it was found that activated RNA mon-

omers (ImpU and ImpA) bind only to the silicate surface of the clay interlayer, on catalytic sites about 1.5 nm apart ( $1-2 \cdot 10^{14}$  sites per milligram).<sup>121</sup> On clay surfaces, purine nucleotides bind more strongly and are oriented differently than those of pyrimidine. This may account for the observed regioselectivity (3',5' vs. 2',5' links), but the exact mechanism of selective binding and polymerization is not yet known.

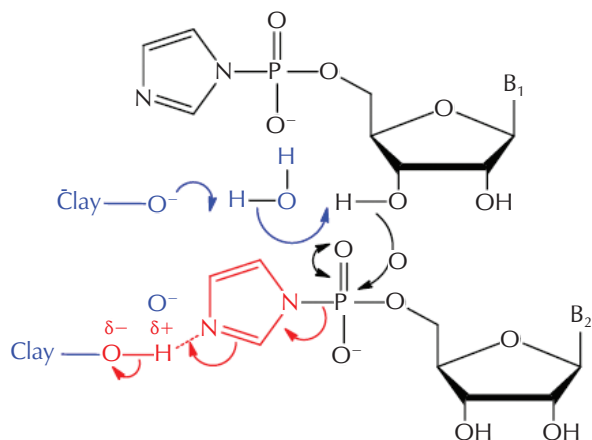


Fig. 3 – Mechanism of polymerization of nucleotides on clay surfaces (adapted from Ref. 115)

Slika 3 – Mehanizam polimerizacije nukleotida na površinama glina (preuzeto iz ref. 115)

The catalytic properties of montmorillonite depend also on the background electrolyte, *i.e.*, on its salt form. Catalytic activity is higher for smaller ions ( $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$ ,  $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ ).<sup>120</sup> The best catalytic activity for  $\text{Na}^+$ -montmorillonite was observed in 1 M NaCl solution,<sup>122</sup> close to salt concentration ( $c = 0.9 - 1.2$  M) of the primordial ocean.<sup>123</sup>

## 5 Reactions on sulphide surfaces

Chemoautotrophic (or iron-sulphur-world) theory of life origin<sup>124-127</sup> rests on two assumptions. The first is that the first prebiotic catalytic reactions took place on Fe/Ni sulphide particles evolving gradually to autocatalytic systems, and ultimately to the first (pioneer) organisms. The second assumption is that the driving power for all prebiotic processes has been the oxidative formation of pyrite,  $\text{FeS}_2$ , by reaction of FeS with  $\text{H}_2\text{S}$ .<sup>128</sup> The hypothesis is supported by its correlation with iron-sulphur proteins,<sup>129</sup> *i.e.*, proteins with iron-sulphide and similar metal-sulphide catalytic centres,<sup>130-132</sup> which constitute the group of phylogenetically oldest enzymes, *e.g.* nitrogenases.<sup>133</sup> As early as 1974, R. Österberg hypothesized that the first electron carriers were in the form of  $\text{FeS}/\text{FeS}_2$  particles.<sup>134</sup>

This theory is also concordant with the hypothesis that all life forms evolved from hyperthermophilic organisms, because the oldest extant life forms (*e.g.* Crenarchaeota, Nanoarchaeota) are chemoautotrophic hyperthermophiles.<sup>135</sup>

Hyperthermophiles<sup>136</sup> were in turn found near the underwater hydrothermal vents at Mid-oceanic ridges rich in dissolved hydrogen sulfide,<sup>137,138</sup> the possible geological habitat of pioneer organisms.<sup>126</sup> (Other habitats might also be magnesium-rich komatiite lava deposits<sup>139</sup> and hydrothermal systems developed as a consequence of asteroid impacts on early Earth,<sup>140</sup> but in our opinion, such events were rare.) Hyperthermophiles had possibly evolved from pioneer organisms, and were later adapted to “milder” surface conditions.<sup>141,142\*</sup>

Catalytic particles were formed by reaction of hydrogen sulphide with metal ions ( $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{W}^{4+}$ ) dissolved in ocean water. They very probably formed protocell-like “monosulphide bubbles”,<sup>143,144</sup> by “chemical-garden” (*chemobrionics*) reactions.<sup>145</sup> This provided the first (inorganic) membranes, as well as catalytic surfaces (mineral substructure). Simple molecules from volcanic liquid water phase ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{COS}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{HCN}$ ) were adsorbed on a mineral substructure making an organic superstructure<sup>126</sup> prone to all kinds of chemical transformations. This hypothesis is supported by the finding that iron and copper sulphide minerals (pyrrhotite, pyrite, covellite, bornite, chalcopyrite, tetrahedrite) proved to be efficient catalysts in converting formamide ( $\text{H}_2\text{NCHO}$ ) into purine, adenine, and other heterocyclic bases under simulated prebiotic conditions.<sup>146</sup> It was also shown that pyrite and greigite ( $\text{Fe}_3\text{S}_4$ ) catalyse  $\text{CO}_2$  reduction, converting it respectively into formate<sup>147</sup> and methanol, formic, acetic and pyruvic acid.<sup>148</sup> FeS also appears to be a suitable agent for reducing nitrates and nitrites to ammonia under primordial acidic conditions.<sup>149</sup>

The basic idea of the iron-sulphur-world theory is that the electrons released by oxidation of iron(II) sulphide were used for reduction of simple molecules from liquid water phase and synthesis of complex organic compounds on (Fe,Ni)S surfaces. Many such reactions were proven experimentally,<sup>124,126</sup> like reduction of nitrogen into ammonia at 1 bar, 80 °C, and  $\text{pH} = 3-4$ :<sup>150</sup>



synthesis of methanethiol (along with other sulphur compounds,  $\text{CS}_2$ ,  $\text{Me}_2\text{S}$ ,  $\text{R-SH}$ ) from carbon dioxide at 1 bar and 75 °C:<sup>151</sup>



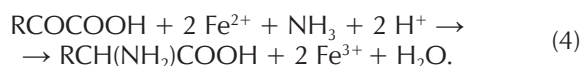
and the synthesis of pyruvic acid from carbon monoxide at 2000 bar and 250 °C:<sup>152</sup>



Other reactions, not directly involving the formation of pyrite, could also be catalysed by such a mineral substructure. Using FeS and/or  $\text{Fe}(\text{OH})_2$  as a catalyst,<sup>153,154</sup> amino acids (Ala, Glu, Phe, Tyr) were synthesized in the maxi-

\* There is, however, an alternative explanation for the evolution from hyperthermophilic organisms, namely that these organisms were the only survivors after large asteroid impacts in early Earth's history, Ref. 129,171,172.

mum 35–58 % yield from corresponding keto acids (1 bar, 75–100 °C, pH = 9–11):



Even more complex schemes were devised, like oligopeptide and purine synthesis from carbon monoxide,<sup>155</sup> and – quite speculative – anaerobic citric acid cycle on (Fe,Ni)S catalyst.<sup>156</sup> The hypothesis of the evolution of bacterial (acetogens) and archaea (methanogens) metabolisms by carbon (CO<sub>2</sub>) fixation on catalytic (Fe,Ni)S minerals in alkaline hydrothermal vents is also based on such a speculative scheme.<sup>157</sup>

Wächtershäuser also proposed a theory of evolution on the surface of (Fe,Ni)S catalyst<sup>126</sup> from the assumption that some ligands may dramatically increase the activity of (metal) catalyst.<sup>158</sup> This led to the development of autocatalytic systems, which in turn led to coevolution of proteins and nucleic acid synthesis by autocatalytic feedback. The theory also explains the formation of the first protocells, by the process of surface lipophilization and the establishment of pH gradient across membrane (chemiosmosis). The hypothesis is experimentally supported by studying vesicle formation in the presence of various minerals, e.g., pyrite and montmorillonite.<sup>159,160</sup> However, experiments aimed at synthesis of amino acids and nucleic bases from CO<sub>2</sub> using FeS/H<sub>2</sub>S system failed,<sup>161</sup> and it was shown that sulphide minerals stimulate degradation of RNA by catalysing the hydrolysis of phosphodiester bonds.<sup>146</sup>

## 6 Conclusion

The troubles with the theories of life origin stem from the very nature of the scientific research: the problem of higher complexity has to be divided into a set of less complex ones. Thus, the riddle of the emergence of life on Earth should be solved by answering questions concerning the potential catalytic substances available on early Earth, composition of its primordial hydrosphere, lithosphere and atmosphere, efficiency of mineral catalysts in synthesizing biopolymers, evolution of autocatalytic systems, self-assembly of molecules in nanostructures, e.g. nanovesicles,<sup>162–164</sup> evolution of the protocells and the first anaerobic metabolism<sup>165</sup>, and so forth. Despite much effort in solving these problems, it is not yet possible to comprise all the experimental data in a consistent theory; however, the general shape of the evolution leading to the first protoorganisms can be envisaged.

Evolution of organic matter is dependent on the evolution of inorganic matter; the diversification of minerals opened new possibilities for catalysed reactions, and consequently for greater diversity of prebiotic forms (Table 2). The origin of life, viewed as the result of the development of catalysis, is intimately connected with clays and sulphides, so the emergence of life as we know it, was impossible before these minerals had appeared, *i.e.* before Earth differentiation and plate tectonics.<sup>19</sup> This opens a possibility that some kind of prebiotic forms existed before the conditions for the iron-sulphur world had been met, suggesting the gradual evolution from biopolymers into autocatalytic (metabolic) systems. At any rate, the emergence of life on Earth before 3.8 Ga<sup>166</sup> was not caused by long-term evolu-

Table 2 – Early history of Earth (adapted after Ref. 18)

Tablica 2 – Rana povijest Zemlje (sastavljeno prema ref. 18)

Years from present / Ga Godina od sadašnjosti / Ga	Mineral species Mineralne vrste	Kinds of rocks and minerals Vrste stijena i minerala	Examples Primjeri	Geological events and possible prebiotic processes Geološki događaji i mogući predbiološki procesi
> 4.56	60	chondrules pre-solar grains	olivine forsterite troilite magnetite	formation of the Solar System
4.56–4.55	250	chondrites achondrites iron clay minerals carbonates	smectites feldspars zeolites	accretion and alternation of planetesimals formation of Earth Earth differentiation (core, mantle, crust) clay-mineral catalysis
4.55–4.0	350	igneous rocks evaporites	amphiboles micas halite	plate tectonics hydrothermal vents Miller-like synthesis evaporite catalysis sulphide catalysis
4.0–3.2	1000	granitoids	quartz	the first life
3.2–2.8	1500	granite pegmatite sulphates	quartz alkali feldspars	development of photoautotrophic and anaerobic metabolism
2.5–1.9	4000		secondary oxides oxysalts gypsum	great oxidation development of aerobic metabolism

tion of organic matter in the “primordial soup”, as Oparin viewed it, but has been rather a natural consequence of geochemical evolution.

It is notorious that theories of the evolution of autocatalytic systems are not based on any real chemical system, much less on real geological habitats. Despite a huge number of works on polymerization of amino acids on clay and oxide minerals, it is still unclear how they would have been employed in prebiotic synthesis; this presumes them to be good catalysts for all protein amino acids, which obviously not the case. Most of the prebiotic reactions, such as amino acid synthesis,<sup>167</sup> formose, and iron-sulphur-world reactions need basic conditions, but it is hard to imagine such reactions on early Earth with CO<sub>2</sub>-rich atmosphere and rainwater with pH = 3.7, and temperature of 70 °C.<sup>13</sup> It is, however, highly probable that many different catalyst systems were temporarily active, because, as S. A. Kauñman put it, “the more complex web of coupled reactions, together with the chance that molecules in the web are catalysts for the same reactions, the easier it is to form collectively autocatalytic sets”, *i.e.* protocells.<sup>168</sup> This leads to an obvious conclusion that the development of a geological habitat, *i.e.*, the rising number of mineral species, led to the emergence of life on Earth.<sup>169</sup>

The idea that it is possible to reconstruct Darwin’s “warm little pond”, *i.e.*, that it should be possible to design an experiment from which some kind of proto-organism would emerge by mixing of chemicals, proved unsuccessful,<sup>6,145,170</sup> it is naïve to expect to be able to reproduce processes that took place on thousands of square kilometres and lasted a few hundred million years by a test-tube experiment. However, from another point, it does not seem impossible to find mineral catalysts that would be capable of directing the key prebiotic reactions needed for the emergence of life on this planet.

#### List of abbreviations and symbols Popis kratica i simbola

BSA	– bovine serum albumin – albumin govedeg seruma
DKP	– diketopyranozide (cyclic dimer of amino acids) – diketopiranozid (ciklički dimer aminokiselina)
EDAC	– 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (condensing agent) – 1-etil-3-(3-dimetilaminopropil)karbodiimid (agens za kondenzaciju)
Ga	– gigaannum, 10 <sup>9</sup> years – gigagodina, 10 <sup>9</sup> godina
IDP	– interplanetary dust particle – međuplanetarna čestica prašine
Imp	– imidazole-5'-phosphate – imidazol-5'-fosfat
IOM	– insoluble organic matter – netopljiva organska tvar
Meadp	– 1-methyladenine-5'-phosphate – 1-metiladenin-5'-fosfat
PNA	– peptide nucleic acid – peptidna nukleinska kiselina

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## SAŽETAK

### Kataliza u prvotnom svijetu

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Kataliza omogućuje uređenu sintezu te njezinu evoluciju do autokatalitičkih (samoreproduktivnih) sustava. Istraživanje homogene katalize bavi se većinom nasumičnom sintezom peptida i vjerojatnostima nastajanja katalitičkih peptidnih oligomera. Sinteza riboze reakcijom formoze katalizirana je ionom  $B(OH)_4^-$ , koji se može osloboditi trošenjem boratnih minerala. Površine oksidnih minerala i minerala gline daju katalitička mjesta za sintezu oligopeptida i oligonukleotida. Kemoautotrofna teorija ili teorija želježno-sumpornog svijeta pretpostavlja da su se prvi (pionirski) organizmi razvili katalitičkim procesima na česticama (Fe/Ni)S nastalim blizu hidrotermalnih vrela. Rad daje pregled mogućih katalitičkih reakcija na Zemlji prije nastanka života te razmatra selektivnost (regioselektivnost, stereoselektivnost) i geološku raspoloživost katalitičkih minerala uz osvrt na geološke uvjete koji su omogućili katalitičke reakcije na mladoj Zemlji.

#### Ključne riječi

Kemoautotrofna teorija, reakcija formoze, postanak života, predbiološka kemija, nasumična sinteza polimera

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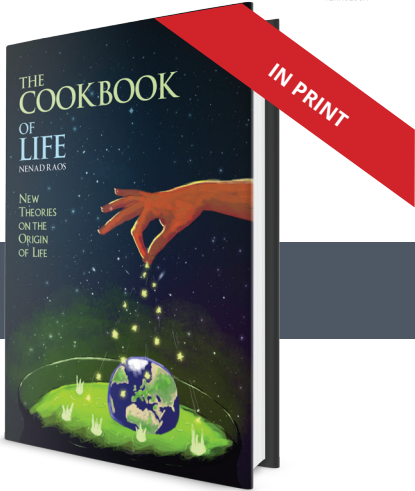
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