The Possibility of the Formation of Protocells and Their Structural Components on the Basis of the Apatite Matrix and Cocrystallizing Minerals

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Abstract. This paper presents the author's theory on the possibility of simultaneous hard-phase synthesis of various organic molecules from gas-phase elements on the basis of the apatite matrix and cocrystallizing minerals (carbonate-apatite, calcite, mica). These molecules and their ensembles gave rise to living systems and protocells of the pro- and eukaryotic types. Synthesis might have occurred through gradual substitution of the mineral matrix by crystal organic matter. The structure and size of the molecules synthesized were determined by the structure, physical parameters, and arrangement of organizing centers in the crystal lattice. Apatite phosphates were embedded in a synthesized nucleic helix and their size and purine–pyrimidine complementarity were determined. Apatite and cocrystallizing minerals were seen to be involved in the synthesis of four basic classes of cell components: apatite-DNA and nucleoproteid complexes; carbonate-apatite–enzymes, other proteins involved in DNA replication, all RNA types and their complexes with the specific proteins and enzymes of transcription and translation; calcite–cytoskeletal proteins; and mica–membrane lipids and proteins. The evidence supporting this theory is presented. A possible mechanism to account for the transition from crystal through organo-mineral crystal to liquid crystal (protocell) and a model of the occurrence of the matrix mechanism of transcription and translation are proposed. Some principal problems in the biochemistry and molecular biology of the origin of life on the Earth are discussed.

Key words: origin of life, protocells, minerals, organo–mineral crystal, liquid crystal, molecular evolution, matrix mechanism

Abbreviations: NA, nucleic acid; NP, nucleoprotein; EC, elementary cell; Ap-DNA, apatite DNA (hypothetical model based on the apatite crystal structure)

Introduction

The problem of the origin of life has been challenging the human mind for thousands of years. Oparin and Bernal were the first to attempt to theorize on the subject. They independently formulated a hypothesis of the abiogenic synthesis of organic compounds under the conditions of the primeval Earth. Interest in the problem of the origin of life continues to attract the attention of researchers [1, 2]. The

key to answer the question seems to be the revolutionary idea proposed by John Bernal in 1939 that the living cell is *per se* a liquid crystal. If we could answer the question of how and why a cell is an aperiodic, homeostatic, self-regenerational liquid crystal we could answer the question of how the life originated. In light of modern knowledge about the cell structure and the mechanisms of its reproduction, the problem of the origin of life must be examined in terms of the problem of the origin of cells, but not the problem of the origin of cell fragments. The cell is a united liquid crystalline complex. Some fragments of that complex, including viruses or phages, are not viable.

Author's attention was drawn to some peculiarities of apatite, and suggested that it could have played a critical role in the process of the abiogenic synthesis of organic molecules.

Why Must it Have Been Apatite?

Apatite is the only considerable source of phosphorus on the Earth's surface. Its typical forms are fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$, chlorapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$, hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, and carbonate-apatite $\text{Ca}_5(\text{PO}_4, \text{CO}_3\text{OH})_3\text{F, OH}$. Apatite minerals take the shape of crystals each with a different nature. The apatite group is characterized by isomorphism; that is, the incorporation of several ions in the crystal lattice with no change in essential structural parameters. Calcium may be partially substituted by Sr^{2+} (up to 11%), Mn^{2+} , Mn^{3+} , Mg^{2+} , U^{4+} , Th, Na^+ , K^+ , Zn^{2+} . The PO_4^{3-} group may be substituted by SO_4^{2-} , SiO_2 , AsO_4 , CO_3^{2-} , Al_2O_3 [3, 4]. There is experimental evidence that OH^- , F^- , Cl^- , and CO_3^{2-} ions are capable of diffusion along the hexagonal axis of the apatite crystal [5]. Some living beings are capable of assimilating PO_4^{3-} , Ca, Si, Sr, Mg, Ge, K, Na, and other elements from minerals of the apatite group. The peculiarities of the incorporation of phosphorus into organic compounds comprising living systems (nucleic acids (NA), phosphorus-containing proteins, and others) are determined by its being a component of the prebiotic apatite lattice. Structurally similar to proteins and NA, apatite is widely used in biochemistry and molecular biology for the separation of these biopolymers [6–10]. Chromatography using hydroxyapatite (HA) shows that the adsorption of organic matter has a stereospecific nature. There are 2 types of adsorbing sites on the surface of HA: P and C sites [11, 12]. These sites exist in the different domains of the HA elementary cell (EC) and depend on the spatial disposition of ions. The P site corresponds to the flat crystal surface and the C site corresponds to the side faces [12, 13–15]. The P site consists of 6 oxygen ions, which belong to 3 phosphates of the HA crystal [11]. These sites are arranged hexagonally on the HA crystal surface with a minimum distance 9.42 Å and they may adsorb the basic groups of basic polypeptides and basic proteins [11]. C sites are located at the hydroxyl positions devoid of hydroxyl ions, and they have the ability to adsorb nucleoside phosphates, NA and acid polypeptides [12, 15]. The

existence of 2 different surfaces has been corroborated experimentally from the different adsorption capacities for proteins and NA and X-ray structural measurements of the HA crystal angles [11–14]. Kawasaki [11] suggested a space-filling model of poly-L-lysine adsorption in chain form on the HA surface. Each amino group of the polypeptide is situated at the center of the phosphate site of the hexagon. Thus a total spatial correspondence of the HA surface to poly-L-lysine is attained. The inorganic components of the bones and teeth of higher animals, of some prokaryotes, and of unicellular eukaryotes are represented by compounds of the apatite group [16, 17]. The periods of the apatite lattice and the DNA double helix are similar, equalling 3.4 Å. Apatite PO_4^{3-} groups are able to catalyse the abiogenic synthesis of D-ribose from ammonia, methane, and water [18, 19]; of nucleotides from nucleosides, condensing agents and ammonium oxalate [20]; and of polynucleotides with a 3',5'-phosphodiether bond [20] under conditions similar to those of the primeval Earth. In addition to apatite, the inorganic components of extant organisms are composed of calcites, aragonites and cristobalites. The lattices of apatite, calcite, aragonite and cristobalite are characterized by similar physico-chemical properties [16, 17].

Proceeding from these and other observations, in 1981 we proposed a model of the abiogenic biosynthesis of the nucleoprotein (NP) complex or its fragments (NA and proteins) on the apatite matrix, suggesting that it would have been the major source of inorganic phosphate under the anhydrous conditions of the primeval Earth [21]. In 1999, the model was substantially improved. In the same year, based on this new model we developed a theory of the origin of life through the formation of protocells and their structural components on the basis of the apatite matrix and cocrystallizing minerals [22]. Recently, indirect geological evidence has been obtained suggesting the involvement of apatite in the origin of life on Earth more than 3.85 billion years ago [23].

To substantiate the theory, we compared the results of the X-ray diffraction analysis of apatite [13, 14], on the one hand, and of chains of Z-form DNA [24, 25], collagen, polyglycine II, and polyproline II [26–29], on the other, and we developed a model of an apatite lattice with an incorporated fragment of Z-form DNA.

Chemical Peculiarities of the Apatite Crystal

Our analysis of the apatite crystal lattice and the composition of gas-phase elements that could presumably interact with it in primeval times suggests that due to some peculiarities of the apatite crystal [3, 4] the only DNA form that could be synthesized based on the apatite matrix would be that comprised by complementary pairs of the four purine and pyrimidine bases ($\text{G}\equiv\text{C}$ and $\text{A}=\text{T}$) and characterized by a helix diameter of 18 Å. Our analysis also suggests the possibility of the synthesis of the left-hand DNA helix based on PO_4^{3-} groups in the apatite lattice (Figures 1A, B, 2A, B and 3; Table 1) [21, 22]. The above-mentioned peculiarities of the structure of apatite include its hexagonal syngony with the spatial group $\text{C}_{6n}^2-\text{P}6_{3/m}$; the EC of fixed

size ($a = 9.36\text{--}9.52\text{ \AA}$, $c = 6.85\text{--}6.93\text{ \AA}$); a double set of EC structural units with the period of translation along axis c of $3.4\text{ \AA}$; the presence of PO_4^{3-} helices and two types of Ca-polyhedrons: the nine-apex one (CaO_9), called CaI, and the seven-apex one (CaO_6), called CaII. In both cases, Ca might have been substituted by OH, F, Cl, CO_3 , O^{2-} . The positions of these polyhedrons in EC were heights of 0 and 50, and 25 and 75 in the case of CaI and CaII, respectively. The height of the polyhedrons relative to the phosphorus atoms was 25 and 75 for CaI and CaII, respectively. Emphasis should be also placed on the isomorphism of apatite minerals, i.e., a considerable variation in apatite stoichiometry ($\text{Ca/P} = 1.67/1.50$), depending on pH, with the principal parameters of the apatite structure remaining unchanged. There are some other peculiarities of apatite structure that favour our theory, but this will not be considered here owing to a lack of space. PO_4^{3-} groups occupy similar sites in the apatite crystal and in Z-form DNA (Table 1). The following facts suggest the correspondence of the crystallochemical characteristics of apatite with those of Z-form DNA:

Figure 1. (A) Scheme of the structure of apatite (a single hexagonal apatite cell, plane view) according to X-ray crystal analysis [Kay *et al.* 1964; Sudarsanan, Young 1969]. The direction of the complementary pairs of DNA is indicated in scheme. (B) The structure of apatite (a single hexagonal apatite cell, plane view) containing dGpC (the pair taken from DNA of the Z-form) and a fragment of peptide chain (at center) (Kostetsky 1981, 1999). (C), (D), (E) The apatite structure according to N.B. Belov [Gilinskaya, Scherbacova 1975]: (C) prisms with Ca II cations; (D) prisms with Ca I cations; (E) PO_4 anions. (F) The apatite was from the Vitosh mountain, Bulgaria (4/5 natural size) [Kostov 1971, p. 454]. Figures indicate fractions of the elementary cell height: 0, 25, 50, 75, 100; $\rightarrow$, $\Rightarrow$, direction of polynucleotide chains.

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(B)

(C)

Figure 1. (Continued)

the existence of the left-hand PO_4^{3-} spiral in the apatite lattice; the inter-phosphate distances (about 9 Å) from the helix axis are similar in apatite and DNA; the equal number of phosphate residues (12 pairs) per one helix turn; the helix pitch in Z-form DNA (44.6 Å or 12 nucleotide pairs) corresponds well with the joint height of six ECs (41.3 Å); the turning angle (30°) and translation period (3.4 Å) of apatite polyhedron chains correspond well, respectively, with the turning angle of neighbouring

Figure 2. (A) Scheme of structure of apatite (side view) according to X-ray crystal analysis [Kay *et al.* 1964; Sudarsanan, Young 1969]; (B) Scheme of apatite structure (side view) with DNA chains introduced into its structure. (A), (B) Schemes constructed by Hyperchem 6 (Hypercube Inc.). Numbers indicate fractions of the height of the elementary cell: 0, 25, 50, 75, 100.

nucleotides in Z-form DNA (30°) and the shortest distance between a nucleotide and the helix axis (3.4–3.7 Å); the inter-phosphate distance in complimentary pairs of Z-form DNA (15 Å and 12.5 Å in the case of dCpGp and dGpCp, respectively) is close to the distance between neighbouring phosphates in apatite (15.3 and 13.1 Å), and finally, the distance between phosphorus atoms corresponding to one «polynucleotide» chain in apatite is close to that in nucleic acid (~ 6 Å) [21, 22].

The crystallochemical peculiarities of apatite permit the simultaneous synthesis of DNA, histones, collagen, and other proteins (Figures 1B and 4).

Due to its crystallochemical peculiarities, a single hexagonal apatite cell may be simultaneously involved in the synthesis of one basic complementary chain and 6 supplementary chains at the between the cell and the neighbouring cells

Figure 3. The bond structures in complementary Ap-DNA chains (Figure 2B). Nucleotide pairs are shown at small angle. *Syn* and *anti* designate the type of the torsion angle of the C1'—N glycosidic bond; $\parallel$ or $\perp$ indicate, respectively, the parallel or perpendicular position of the d-ribose C1'—C4' plane to the helix axis at the transition from one phosphate to another through guanine or cytosine; γ , the torsion angle of the C4'—C5' bond is in *gauche-trans* conformation. Note that in this case C2' has an *endo* conformation or is situated farther from the C1'—O1'—C4' plane than C3' and is located on the same side as C5'. The O1' of d-ribose of both chains that are in the *syn* conformation is always directed towards the helix axis, while d-ribose O1' atoms with *anti* conformation have opposite directions in the different chains.

resulting in the formation of a nucleoprotein complex with a complicated structure (Figure 5). We suppose that the different quantity of the apatite EC could participate to form DNA of the future protocells. This might result in the different quantity of chromosomes in protocells.

Table I. Comparison of helices of B-, Z-DNA and Ap-DNA

Helix sense	B- DNA ¹ [14,15] Right-handed	Z-DNA [*] [14,15] Left-handed	Ap-DNA Left-handed
Residues per turn	10	12 (6 dimers)	12 (3 tetramer)
Diameter, Å	~20	~18	~18
Rise per residue, Å	3, 4	3, 7	3, 44
Helix pitch, Å	34	45	41, 3
Base pair tilt	6°	7°	0°
Rotation per residue	36°	60° (per dimer)	120 (per tetramer)
Glycosidic torsion angle			
Deoxyguanosine	Anti	Syn	Anti, Syn
Deoxycytidine	Anti	Syn	Anti, Syn
Sugar pucker			
Deoxyguanosine	C _{2'} endo	C _{3'} endo	C _{2'} endo
Deoxycytidine	C _{2'} endo	C _{2'} endo	C _{2'} endo
Torsion angle around C _{4'} –C _{5'}			
Deoxyguanosine		an (gauche-trans)	an (gauche-trans)
Deoxycytidine		+ck (gauche-gauche)	an (gauche-trans)
Distance of P from axis, Å			
d G _p C	9	8	8
d C _p G	9	6, 9	8, 5
d G _p G	9	–	5, 8
d C _p C	9	–	3, 6
Distance between P complementary pairs, Å			
d (G _p C)	17, 5	15	15, 3
d (C _p G)	17, 5	12, 5	13, 1
d (G _p G)	17, 5		8, 9
d (C _p C)	17, 5		7, 9

Analysis of the Model of Apatite-Synthesized DNA (Ap-DNA)

To confirm the above possibility of the synthesis of Ap-DNA based on the apatite crystal with parameters similar to those of Z-form DNA, we developed a spatial model of the apatite crystal with a hypothetical Ap-DNA fragment with a length of 4 nucleotide pairs built into the crystal according to Dreiding's model and a computer model constructed according to X-ray diffraction data [13, 14, 24, 25]. Figures 1A–D, 2 and 3 and Table 1 provide data on several Ap-DNA components. In our model, only guanine and cytosine were used since they are the main components of the structure of Z-form DNA and are able to encode the major amino acids of collagen (glycine – GGG, GGC; alanine – GCG, GCC; proline – CCC, CCG), participating in the apatite synthesis *in vivo*. The model is based on the assumption that the apatite phosphate backbone would determine the position and conformation of d-ribose residues, and that these residues, in turn, would determine the position and conformation of nitrogen bases in the apatite lattice. We also assumed that the

position of oxygen atoms in PO_4^{3-} groups would remain unchanged. The location of PO_4^{3-} groups corresponds to 1/4 and 3/4 of the apatite cell height, and the distance between neighbouring phosphates of one chain to one half of the cell height (3.4 Å) (Figures 1 and 2). All bases are situated at levels 0 and 50 of the apatite cell, i.e., between PO_4^{3-} groups (Figure 2B). Thus, Ap-DNA represents a typical left-hand Z-form DNA helix. Its repetitive element is the tetramer d(GGCC), consisting of two dimers, d(GpGp) and d(CpCp) (or dGpCp and dCpGp) with 120° per tetramer,

Figure 4. (A) Apatite structure according to Bjevers, with chains of polyglycine II (polyproline II, collagen) superimposed over it [Crick, Rich 1955; Rich 1959; Ramachandran Kartha 1955; Ramachandran, Sasisekharan 1965]. The crystalline structure of polyglycine II is similar to the structure of polyproline II and collagen. In the zone of the apatite cell where the formation of protein chains occurs, PO_4^{3-} groups are substituted by CO_3^{2-} groups (Kostetsky 1981; 1999). The structure was found by superposition of the crystalline structure of polyglycine II and apatite as determined by X-ray spectroscopy. (B), (C) Electron microphotograph of the hexagonal arrangement of protein molecules in the crystal of catalase from bull liver (magnification $\times 5 \times 10^5$) (B) and of crystallized leucine-aminopeptidase (C) [Vainstein, 1986].

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(B)

(C)

Figure 4. (Continued)

whereas conventional Z-form DNA consists of alternating dimers dGpCp with 60° per dimer. The diameter of the Ap-DNA helix ($18 \text{ \AA}$) is similar to that of Z-DNA. The phosphate backbone follows a zigzag course, with the PO_4^{3-} groups of complementary chains lying very close to one another (Table 1). Moving along a chain, with the transition from one phosphate to another through guanine or cytosine, the deoxyribose plane is alternately parallel or perpendicular to the main axis of the helix (Figures 2B, and 3). On comparing our data with those for the Z-, A- and B-DNA structures, the results of Saenger [30] and Wang *et al.* [24, 25] will be referred to. In both chains, the relative orientation of a nitrogen base and the sugar ring bound to it is characterized by an alternation of *anti*, *anti*, *anti*, *syn* in the

Figure 5. Proposed scheme of the origin of the different number of chromosomes in future protocells.

5' → 3' chain d(CGGC) chain and *anti*, *syn*, *anti*, *syn* in the complementary 3' → 5' chain d(GCCG), resulting in a zigzag structure of the helix backbone. In Ap-DNA, the dG and dC residues are in the *syn* and *anti* conformation, sugar residues are in the *C2'-endo* conformation; and the torsion angle of the *C4'–C5'* bond is in *an*, *+ck*, *–ck* conformation.

The main difference between Ap-DNA, on the one hand, and Z-, A- and B-DNA, on the other, lies in the position and inclination angle of base pairs in relation to the helix axis. The tilt angle is not equal to zero in Ap-DNA; it is close to the tilt angle in the Z-form of Ap-DNA (7–9°), and differs from unity in A-DNA (13–19°). In Ap- and Z-DNA, the base pairs are shifted to the outer surface of the helix, such that the helix axis lies in the minor groove not running through base pairs, while in A- and B-DNA the axis lies in the major groove or runs across the plane of a base pair, respectively. As a result, the sugar-phosphate backbone in Ap-DNA is

zigzag-shaped, as is the case in Z-DNA. The similarity of some conformational characteristics of Ap-DNA and Z-, A- and B-DNA [24, 25, 30] was confirmed by the present model.

Concerning Protein Chain Synthesis on Apatite and Carbonate-Apatite

The crystallochemical peculiarities of apatite permit a simultaneous synthesis of DNA, histones, collagen, and other proteins (Figures 1B and 4). In the case of histone proteins, the most probable scenario is their synthesis on apatite as NP synthesis proceeds, whereas in the case of collagens and other proteins the most acceptable matrix would be carbonate-apatite or calcite. As noted above, Kawasaki suggested a space-filling model of poly-L-lysine adsorption in the chain form on the HA surface [11]. Each amino group of the polypeptide would be located at the center of the phosphate site of the hexagon. Thus attaining, the total spatial correspondence of HA surface to the poly-L-lysine. The calcite lattice interacts with amino acids like a key to a lock [31]. The author believes that either the synthesis of peptide chains or that of DNA could occur in the apatite crystal on CaII sites. It appears that the synthesis of histone proteins would have occurred simultaneously with that of DNA in the same apatite EC in a "helix to helix" manner, in consistence with the principles of stereospecific complementarity. The crystallochemical characteristics of the peptide chains of polyglycine II, polyproline II, and collagen studied [32, 33] are close to those of the apatite crystal lattice [21, 22]. In the crystal of polyglycine, all chains are parallel, and each has a threefold screw axis at the rotation of one amino acid around the axis by 120° . Seven chains are packed in a hexagonal array, each chain being hydrogen-bonded to each of its six neighbours. The distance between the polypeptide chains is 4.8 Å. The structure of polyglycine II appears to be similar to those of polyproline II and collagen [26, 32–34]. There is a stereospecific complementarity between proteins in the β -form or form II and DNA chains [35]. The configuration, size, and mode of packing of polyglycine II, polyproline II and collagen chains match the pattern of spatial arrangement of CaII-polyhedrons in apatite. The periodicity of the collagen chain (9.5 and 4 Å) [26–29] coincides with the size of the apatite EC (9.5 Å) and the distance between two Ca atoms located at the same level (4 Å) in the trigonal prism of CaII polyhedrons, while the distance between two protein chains (4.8 Å) corresponds to the distance between CaII-polyhedrons. The crystalline structures of the proteins catalase and leucine-aminopeptidase are shown in Figure 4B and C to emphasize the similarity of the proteins possibly formed on apatite, carbonate-apatite or calcite.

The possibility of the formation of the stereospecific NP complex on the apatite matrix is supported by the similarity of this process to those occurring in living beings during the course of biomineralization, when apatite is synthesized in vertebrate bones and teeth as well as in prokaryotic and unicellular organisms: one merely has to reverse the process of interaction between the organic matrix

Figure 6. Scheme of the formation of biogenic crystals. Initially, the organic matrix (1) was formed. It consisted of hexagonal or elliptic polysaccharide plates joined with protein fibrils. Then, both inside and between the fibrils of the polysaccharide matrix, tiny mineral crystals began to grow. Later on, these formed an elementary mineral crystallite (2). In the final stage of mineralization, the formation of the mineralized polycrystal occurred (3). A complex of such polycrystals forms skeletal tissues (bones, shells, armours etc.). Adapted from Golubev [1987].

and the mineral lattice (Figure 6). The formation of mineral crystals is controlled by the organic matrix. In the process of biomineralization most components of the liquid-crystal matrix are “replaced” by mineral crystals, whose orientation retains the liquid-crystal geometry. The size of the “confocal” domains’ of liquid crystals may be an example [16, 17]. Thus we have solid bodies with a crystalline structure, and liquid crystalline properties appear in a mutual orientation of microcrystals. The mechanism of basic skeleton mineral lattice conjugation with organic matter is based on the physics of liquid crystalline confocal textures [16, 17]. Confocal textures in liquid crystals create a united system of unrivalled regulated electromagnetic interactions. They have the ability to fill a space continuously [36], with no breaks. The molecular mechanism for the triggering the biomineralization process is encoded and performed within an organism with the help of special proteins [37–42], enzymes [43], sulfated mucopolysaccharide [44], extracellular matrix vesicles [45] and energetic control [46]. It is possible to present the process of biomineralization by changing the organic matrix [47]. Phosphorylated and sulfated glycoproteins [48–50] play an important role in the initial stage of biomineralization. It has been suggested that they would take part in the formation of biominerals through amorphous liquid-phase precursors [51]. Ions are the reactants during the biomineralization process and ion minerals are the products. The mobile liquid crystalline matrix can allow the ion distance of biogenic crystals to change, but those changes (aragonite) along axis C are no more than 0.1% [16, 52]. All biogenic crystals are

known to contain both mineral and liquid organic crystals. The mineral part is represented by apatite (calcium phosphate) in vertebrates (teeth and bones), prokaryotes, and unicellular organisms; by calcite and aragonite (two crystal modifications of calcium carbonate) in prokaryotes, algae, and invertebrates, and by cristobalite (an amorphous form of silicon oxide) in radiolarians, silicon sponges, and diatoms. The organic part, comprising some 20–30% of the dry mass may be represented by fibrillar proteins (collagen, elastin), polysaccharides (chitin in the bacterial and fungal cell wall and in the arthropod shell; chondroitinsulfate and hyaluronic acid in the connective tissue of many organisms), and phospholipids. Judging by Golubev's data [16], four basic skeleton minerals (apatite, calcite, aragonite and cristobalite) would have coincided and mutually coordinated their proportions, which would have conjugated with liquid crystal matrix confocal structural parameters. The proportions coincide with high but final precision. Since confocal structures are conjugated with dislocations of liquid crystals, the model has some freedom of entropy.

To develop a model of the origin of life based on these observations, one merely has to reverse the process of the interaction between the organic matrix and the mineral lattice [21, 22] and then propose the mechanism for the formation of living systems through the process of the diffusion of free gas-phase radicals and ions into the crystal. When the model is reversed, the matrix is solid, and the reactants are radicals and ions ($\text{CH}_3^\bullet$, $\text{CH}_2^\bullet$, CH_3^- , CH_2^{2-} , CH^{3-} , $\text{C}^{4-(4+)}$, H^+ , N^{3-} , $\text{NH}_2^\bullet$, NH_2^- , NH^{2-} , CO^{2-} etc.), but of smaller radius than the ions in the mineral matrix, and the products are molecules with chemical bonds that are much shorter than the atomic distances of the predecessors. Consequently, epitaxy could not have existed during the formation of organo-mineral complexes in the mineral crystal matrix, and the "volume for volume" (metasomatose) rule of vacancy substitution would have first entered into play with control of orientation from the force fields of the mineral cell (united energetic field created by the atomic environment).

As proposed above, apatite might have served as a matrix for the synthesis of nucleic acids, proteins, NP, and polysaccharides. This hypothesis is sufficient for the explanation of the origin of viruses, including phages. However, it fails to explain the appearance of primary protocells, with their complex set of coding and decoding proteins, and of cell structures capable of the formation of a united liquid-crystal system, matrix biosynthesis of biopolymers, including the processes of replication, transcription, and translation, and able to maintain the homeostasis of the entire system. Such a system is so complex that its state may be affected by separate electrons, protons, light quanta, or changes in ion concentrations. Bearing in mind the relatively young age of the Earth, the successive formation of these complex and closely interconnected cell structures would hardly have occurred through a process of non-solid-phase evolution. In this regard, let us summarize the main characteristics of living cells and attempt to explain their origin and peculiarities.

1. Why are all cell elements and living organism homeostatic liquid-crystal structures?

2. Why do the cells of living beings within a given taxon constitute a peculiar and undivided system? As a rule, the transfer of separate cell elements to other cells, especially phylogenetically distant ones, is impossible.
3. Why is the genetic code universal?
4. Why are the universal character of the genetic code and the similarity of different taxa of the set and arrangement of cell structures and metabolism not accompanied by a universality of cell structures responsible for decoding the genetic code (tRNA- and AA-tRNA-synthases, rRNA- and DNA-polymerases, etc.), controlling the metabolism, participating in the formation of cells, etc.?
5. Why does eukaryote DNA contain unique, moderately repeated, and satellite (ballast, carrying no information) sequences? Non-translated DNA may constitute up to 80% of all DNA and may even exceed this proportion.
6. Why do functionally different proteins have blocks of similar amino acid sequences?
7. Why does the cell contain proteins capable of interacting with calcium, phosphorus, magnesium, strontium, silicon ions, etc.?
8. Why are Ca^{2+} and PO_4^{3-} key elements in all living systems?
9. Why are organic cell components composed mostly of carbon, hydrogen, nitrogen, and oxygen?
10. Why does DNA have strictly determined parameters (the diameter of 18 Å and the distance between base pairs of 3.4 Å)? Why does the base complementarity of only a certain type ($\text{A}=\text{T}$ and $\text{G}=\text{C}$) occur, even though complementarity between a pair of any two bases is also possible? Why are phosphoester bonds in DNA and RNA located between the 3' and 5' ribose atoms, even though other positions are also possible?

Below, we shall try to answer these questions.

According to modern concepts about the nature of living systems, all living systems or their components are considered, with all possible implications, as liquid-crystal structures [53]. Bearing this in mind, the mechanisms of the origin of life may be proposed based on solid-phase effects in mineral and liquid crystals. The participation of minerals in the process of the origin of life makes this process conform to the laws of nature, and the process time is very short. At present, the cell is considered to be a system of closely interrelated elements; the absence of even one of them disturbs the whole system. Primary living systems were seemingly well-arranged and it may be suggested that organo-mineral crystals would have been the precursors of such primary cells. A similar suggestion was made by Carns-Smith [54]. Crystals are known to be capable of self-assembling. Each crystal is characterized by a high regularity and a lattice of a particular type; however, each crystal has some defects in its lattice. The presence of these defects, both small and large, suggests that the crystal lattice would potentially be highly informative. We wondered which type of crystals could serve as a matrix for the formation of primary living systems. The “miracle” properties of apatite seem to be of help in finding the answer.

Putative Mechanism of the Abiogenic Synthesis of Primary Protocells or their Components

Figures 7 and 8 provide a general scheme of environmental effects on mineral crystals that could have served as a matrix in the formation of the organo-mineral crystal complexes of future protocells. Before focusing on the mechanism of the formation of primary protocells or the synthesis of their components, it is necessary to estimate the age of living systems and gain an idea of the geological conditions under which such synthesis occurred. Analysis of the data in the literature reveals that the age of living systems would be 3.85 billion years, differing little from that of the Earth [55]. Eukaryotic and prokaryotic cells are currently believed to have arisen at approximately the same time [56]. The origin of life may have coincided with the progressive metamorphosis of the basaltic crust, the formation of the granite shell, and the disappearance of the dense primary atmosphere. At that time, the temperature at the Earth surface was 600–700°C and an intense emission of several elements in the form of free radicals occurred from the Earth's interior to form the reducing gas-phase. At the same time, the formation of pegmatites (apatite, calcite, cristobalite, mica, quartz, feldspar, etc.) took place from the residual magma melt. Pegmatite minerals have a coarse-grained structure. They may reach sizes ranging from submicroscopic to a meter and are elongated in the C-direction. Apatite normally cocrystallizes with all above minerals. Its lattice was quite flexible at that time. The synthesis of organic substances probably occurred at a temperature of about 200°C.

The model we propose is based on solid-phase effects in mineral and liquid crystals.

HOW DO GAS-PHASE AND MINERAL COMPONENTS INTERACT WITH ONE ANOTHER?

Present in an anhydrous medium, apatite and co-crystallizing minerals were under the permanent and long-term effects of space, nuclear and UV radiation, pressure and high temperature, the reducing gas-phase (NH_3 , CH_4 , HCN , CO , etc.), all of which would have always affected the apatite in one direction – from the center of the Earth to its surface. Under such conditions, the apatite crystal lattice would have loosened, which would have facilitated and accelerated the diffusion of gas-phase components into the apatite crystal. The apatite lattice is extremely “susceptible” to such gas diffusion. There is experimental evidence suggesting the possibility of ion diffusion along the hexagonal axis, the initial apatite structure remaining unchanged [5]. Diffusion might have occurred through free cavities or channels by means of the substitution of other atoms or the filling of vacancies in the lattice. It may also have occurred along the boundaries of the crystal grains. Large anions such as O^{2-} , OH^- , Cl^- can move between separate lattices whereas small ions can penetrate the lattice at the same speed. Alkaline metals strongly decrease in size under pressure and also become highly mobile. The spatial conformation of ions

Figure 7. Scheme of the formation of the organo-mineral complex based on the apatite lattice. Several factors would have elicited a loosening of the lattice and accelerated the diffusion of reducing gas-phase elements into the crystal. The complex grew only in one direction (from the center of the Earth to its surface), occupying the space either of free channels in the lattice or of boundary zones between crystal grains. Growth occurred through substitution of atoms or vacancies in the crystal lattice at 200°C under anhydrous conditions.

in the EC in the lattice determines aliostric features to react with certain elements of the gas-phase. The formation of organic crystals in minerals was completely controlled by force fields of mineral matrix according to the rule of vacancies substitution “volume-for-volume”.

Figure 8. General scheme of the participation of cocrystallizing minerals (apatite-carbonate-apatite-calcite) in the formation of key structures of future protocells.

We consider that atom vacancies must have played the most important role in the formation of organic-mineral complexes. They appear after energy fluctuations of sufficient intensity. Lattice fluctuations have a corporate effect. The main conditions responsible for these fluctuations lie in isomorphous atom substitution of the lattice. Atoms move into the interstitial lattice space characterized by an uncommon valency state. This unusual valency, together with atom dislocations, temperature and outside energetic influences (cosmic, nuclear and ultraviolet radiation) would also have caused such fluctuations. The absorbed energy could have readily been transferred in the lattice from a great distance. Lattice vacancy is an energetic field generated by the atomic environment. Electrons in the vacancy space are delocalized i.e. they belong to the lattice as a whole but not to a single atom. The specific discrete energetic levels of such atoms and packing density would have influenced

the formation of certain structures in the vacancy zones. Free radicals and ions ($\text{CH}_3^\bullet$, CH_3^- , CH_2^{2-} , CH_3^- , $\text{CH}^{4-(4+)}$, H^+ , NH_2^- , CO^{2-} , etc.) would have been produced by diffused gas-phase components substituting the elements of the crystal lattice in agreement with the “volume-for-volume” rule. 7 C^{4+} and N^{5+} atoms (0.15 Å) can fit into the volume of Ca^{2+} (1.05 Å) vacancies. Purine and pyrimidine bases connected to hydrogen bonds can fit into the volume of 2 and more Ca^{2+} vacancies. The position of these molecules in the EC of apatite is predetermined by the position of CaI at levels 0, 50, 100 (Figures 1 and 2). The distance between the atom planes of CaI and DNA base pairs coincide and is equal to 3.4 Å. The same pattern has been found for the atom planes of mineral crystals and polysaccharide plates (chitin, hyaluronic acid, chondroitin sulfate) [16, 17]. The crystal structure forces new atoms and structures to localize in a certain order so that the tension around neighbouring atoms will be compensated, at least in part.

In our model, a particular role in the process of the formation of organo-mineral crystals is played by HCN and the products of its condensation. It is known that HCN derivatives are directly involved in the synthesis of nitrogen bases, carbohydrates, peptides, and also in the process of ion binding [57]. With the participation of the gas-phase elements inside, but not on the surface, of the apatite crystal, the abiogenic synthesis of a polynucleotide helix and/or a protein helix complementary to the polynucleotide helix might have occurred through gradual substitution of part of the mineral matrix (elimination of CaI and CaII) by the crystal organic matter consistent with the rule of “domain” isomorphism.² As a result of the covalent interaction between the atoms and molecules of the gas-phase oriented in the force field of lattice vacancies, organic molecules would have been synthesized. These molecules would have been capable of establishing covalent, ionic or hydrogen bonds with one another.

The size and structure of the organic molecules would have been determined by the structure, parameters, and spatial arrangement of PO_4^{3-} -organizing centers in the crystal lattice. The apatite PO_4^{3-} groups would have been included within a synthesized nucleic helix with no change in their position in the crystal lattice, thus determining the size (diameter) of the helix and limiting the number of possible complementary base combinations to that of the four known combinations of purine and pyrimidine bases. The formation of the organo-mineral complex would have been accompanied by the destruction of ionic and covalent bonds typical of apatite and the formation of predominantly covalent and hydrogen bonds.

ABOUT THE SYNTHESIS OF DNA

The synthesis of NA would have begun with the formation of d-riboses, whose position in the lattice would have been determined by apatite PO_4^{3-} groups. These groups would have thus determined the vector of a synthesized polynucleotide chain. Spatially fixed d-ribose residues would have added nitrogen bases. The location of ribose synthesis in the elementary crystal cell is first determined by the

PO_4^{3-} at levels 25 and 75 of the so-called “interstices” in the crystal structure. It may also have been affected by the rigid fixation of PO_4^{3-} groups in the space of 3 and 5 carbon atoms. “Disadvantages” related to the appearance of the furanose ring would have been followed by adaptive reconstruction of its conformation. The plane of the ring can be parallel or perpendicular to the main axis and can be in 2 conformations: unsymmetrical twist C2'-endo, symmetrical C2'-endo, or C2'-endo envelope conformation (Figure 3).

The scheme of purine and pyrimidine base synthesis in all living systems is very close what we observe in apatite crystals. Purine nucleotide synthesis begins from 5-ribose-phosphate by the building of an acyclic nucleotide, which then becomes cyclized. Cell synthesis takes place with the same elements of the gas-phase. These elements are N-3 and N-9 of the glutamine amide group, (N-1) from aspartic acid, and (N-7) from glycine. Glycine itself is a derivative of NH_3 , CH_3 and CO_2 . The 4th and 5th carbon atoms also have a glycine origin. The 2nd and 8th carbon atoms are from formyl and the 6th carbon atom is from CO_2 . The biosynthetic pathway of pyrimidine nucleotides resembles the biosynthesis of purine nucleotides but is less complex. Carbamoyl phosphate and aspartic acid are the derivatives of the same gas-phase [58].

A single apatite EC could have been attained by gas-phase elements through many ways, permitting the simultaneous synthesis of several organic molecules. The synthesized molecules could have interacted with one another through the formation of covalent and hydrogen bonds such as $\text{A}=\text{T}$ or $\text{G}=\text{C}$. Depending on the type of organic matrix formed in a given apatite crystal (NA or proteins), either the hexagonal apatite axis (OH^- , F^- , and Cl^- sites) or CaI could have served as a channel for facilitating the diffusion of the gaseous phase elements.

ON THE SYNTHESIS OF RNA, MATRIX APPARATUS PROTEINS AND CYTOSKELETAL COMPONENTS

The synthesis of RNA, matrix apparatus proteins, and cytoskeletal components seems to have occurred through the same scheme but on mixed crystals with proportions that coincided and were coordinated with those of apatite. These are carbonate-apatite, calcite, aragonite, cristobalite and mica. Figure 8 shows a general scheme of the participation of the complex of co-crystallized minerals in the formation of the organo-mineral crystalline complex of future protocells. The proportions inherited from mineral crystals happened to be quite favourable for conjugation with organic structures [16]. Coinciding proportions of different minerals could have helped to create this liquid crystal structure of organo-minerals to gain the ability to combine into a united regulated system. It has been reported that the transition from an apatite to a calcite matrix takes place with no visible harm to the organism (an example is the blue-green seaweed *Mastigocladus*) and in the microgeometry of the compounds [16].

As a result of the matrix principle, all the lattice defects appear in the organic matrix. Highly defective and cocrystallization zones of apatite with carbonate-apatite would have been preferable for the formation of the future matrix apparatus of protocells, since in these zones the crystal lattice is under additional stress due to the absence of coordinators of the PO_4^{3-} groups. A total or partial lack of PO_4^{3-} groups means that the formation of the DNA double helix would be impossible but would permit the formation of RNA chains, nucleotide fragments such as ATP, GTP, CTP, UTP, NAD, or FAD, and proteins associated in a different way with RNA or its fragments (future enzymes, among them those associated with NAD, FAD, or ATP as a cofactor). The regular arrangement of PO_4^{3-} groups or their presence in the crystal lattice are not absolute requirements for the synthesis of the proteins of the future cytoskeleton of protocells. The cocrystallization of apatite, carbonate-apatite and calcite would not have had any influence on the emergence of proteins with proportions or parameters different from proteins of apatite nature, because these mineral lattices have coincident and mutually coordinated proportions. The calcite lattice would have interacted with amino acids, following the “key to lock” principle [31]. Nevertheless, the proposed model of protein synthesis by the diffusion of gas-phase elements inside the crystalline lattice of calcite and carbonate-apatite does not correspond to the epitaxy version described by Ramenskaya [31].

The isomorphism of, and the presence of defective zones in, carbonate-apatite and calcite would have favoured the synthesis of proteins having binding centers specific to Ca, Mg, Sr, Si, and other ions. These proteins might have determined the future structure of the mineral component of living systems, i.e., their apatite, calcium, silicium, or strontium backbone. The peculiarities of the proteins synthesized on the crystal matrix could not change since they were not captured by a future protocell from the environment, but were contained within the crystal complex together with other structural elements. In cocrystallization zones, heme-containing proteins and proteins associated with NAD, FAD, FMN, and some other cofactors might also have been synthesized. Preliminary analysis of the parameters of the porphyrin cycle has revealed their agreement with those of the apatite EC.

THE HERITAGE OF MINERAL CRYSTAL

The structure of minerals has determined the peculiarities and mechanisms of in-crystal diffusion in the organo-mineral complex of the future pro-living system: the effect of light quanta, electrons, protons, nuclear radiation, heat on the diffusion process; the ways of diffusion of the gas-phase elements through free in-crystal cavities or channels and along the boundaries of the crystal grains; the direction and sequence of the intercellular processes underlying cell metabolism and homeostasis. At the level of the apatite crystal, homeostasis appears as the prevention of the formation of voids and vacancies due to external factors, i.e., the maintenance of crystal integrity. The more defects present in the crystal lattice, the more difficult it is to maintain its homeostasis. This principle probably also held in the case of

the probiotic system after its transformation from crystal into liquid crystal. The structural elements of future protocells would have repeated all peculiarities of the crystal lattice, including its defects, isomorphism, and the incorporation of other minerals. The degree of variation in the mineral structure would have determined the diversity of future living systems: isomorphism would have underlain the specificity of proteins to certain ions (Ca, Fe, Ge, Mg, Si, etc.) and would have determined the mineral component of the cytoskeleton (Sr, Si, Ca, etc.). The degree of defectness of the crystal lattice would have caused the adaptive capacities of the future organism, since the higher the degree of defectiveness of the system, the more difficult the maintenance of its homeostasis. We suggest that zones devoid of defects in the apatite crystal lattice would have corresponded to non-informative, mainly satellite DNA tightly packed with histones, while defective zones would have served as a matrix for the synthesis of informative DNA. Large fragments of sparingly defective zones of the apatite crystal might have served as a matrix for the synthesis of NP complexes that comprised, together with non-informative DNA, highly and moderately repetitive and unique DNA sequences.

Regarding the origin of life, the energy from phosphates, the role of calcium in the regulation of the processes inside living systems etc. could go back to the same crystals. The mechanism of hydroxyapatite formation in mitochondria in exchange for ADP oxidizing phosphorylation seems quite interesting. The energetic transfer of electrons can be used by mitochondria either for the formation of hydroxyapatite or for the synthesis of ATP. This ability of mitochondria provides them with an opportunity to take part in the processes of biologic calcination and decalcination, i.e. the general regulation of metabolism inside the cell [59, 60].

The structure of mineral complexes would have supported the formation of organic mineral complexes packed into confocal textures. These textures are necessary for the skeleton mineral formation in living organisms [16].

FROM THE ORGANO-MINERAL COMPLEX TO THE FUTURE PROTOCELLS

As mentioned above, the organo-mineral complex of the future protocells could have been formed inside the mineral matrix under anhydrous conditions. According to [16, 61, 62], the transition from inorganic to organic matter results from the phase transition from mineral crystal to liquid organo-mineral crystal. In the present case, such a transition would have required the presence of liquid water on the Earth, i.e., that the temperature at its surface should have fallen below 100°C. The primary oceans were acid due to the intense release of H₂S and HCl. Apatite fields containing the organo-mineral complexes of future protocells would have entered in contact with the acid waters of the primary oceans. This would have resulted in the extraction from the apatite of the mineral component that was not included within the protocell structure. The protocell membrane was probably formed *in situ*, since the source of the PO₄³⁻ groups required for the synthesis of membrane phospholipids was the same as in the case of other biomolecules, i.e., apatite. The possibility of the synthesis

of phospholipid fatty acids based on minerals from the mica or quartz groups, cocrystallized with apatite, was discussed in our first work on the issue [63].

The liquid-crystal organo-mineral complex would have contained all the components necessary for intermediate metabolism in the future protocells. The organic substances that were not included within the structure of the future protocells-phages or viruses – due to having being synthesized based on a related or the same mineral matrix would have favoured the maintenance of the homeostasis of the future protocells. It seems that the driving force of the future evolution of protocells mainly involved such changeable environmental factors as pH, temperature, ion and oxygen concentrations in seawater, the availability of organic matter, symbiotic processes, and catastrophic processes.

The Assumed Scheme of Origin Through a Matrix Mechanism in Protocells in the Case of the Transcription-Translation Apparatus

In 1936, Koltsov [64] developed a principle of matrix reproduction based on crystal similarity. The mechanism suggested here is a further step of that principle. Upon deciding this question, we had the following problems: how did the matrix mechanism appear; how was it triggered, and where did primal proteins (ribosomal) and protein-enzymes (AAtRNA synthetase and DNA-dependent RNA polymerase) come from for this trigger? Picking up on the above hypothesis of primal protocell emergence, let us try to understand how the matrix mechanism of the transcription-translation apparatus could have appeared. Let us take a prokaryotic system, e.g., that of *E. coli* as a basic model. The gene disposition order of *E. coli* is well known: there are 75 identical or different tRNA genes united in clusters; 7 rRNA genes, including the 16s-, 23s- and 5s-rRNA fragments, separate tRNA and spacers. Then mRNA comes. Gene size and nucleotide specificity in genes increase from tRNA (73–93 n) to rRNA (1500–2900 n) and mRNA (thousands of nucleotides). This system repeats over and over again in eukaryotic cells and the so-called nontranslated zone of satellite DNA can be added to it. How could this order appear in the genome in crystals? High periodicity is typical for all crystals, but this structure has up to 5–6% of defects in each real crystal. The presence of defects renders them potentially highly informative and could have led to the formation of the huge amount of stable alternative configurations, which is a necessary condition for the storage of information. Non-defective zones in the crystalline lattice do not hold any information.

HOW AND WHY, ARE THEN, THE DEFECTS LOCALIZED IN THE CRYSTAL?

Defects in the crystal first of all mean the presence of isomorphic substitutions and vacancies. Vacancies appear next to the emergence of sufficient energy fluctuations. The causes of such fluctuations are isomorphic substitutions of the crystalline lattice

atoms; atoms in an abnormal valency condition; atoms from the main substance removed into the internodes, and dislocations. Electrons present in the vacancy volume are relocated, i.e. they belong to the crystal in general, and not to the individual atom. Specific to these atoms, discrete energetic levels and packing density will affect the formation of fairly fixed structures in the vacancy zones.

The matrix mechanism may have originated in the defective zone of apatite and in the cocrystallizing carbonate apatites, calcite and mica. The system of coordinated proportions of these lattices together with the presence of defective zones would have given rise to unique construction pathways, creating the molecular and supramolecular complexes in the future protocells. Rhythmic changes in the chemical composition of mixed crystals often result in zoning organization. Crystal impurities show a good macrolevel of this stratification. The rhythmic appearance of strats can be described as ordered in this case. The energetic properties of these inclusion crystal defects in a certain order comprise the regular repeating zones of stratification. Figure 1E depicts the modulation structures, which have accumulating properties of energetic fluctuations in the defective zones. The energetic fluctuations of the heat variations of atoms are especially high in the defective zones of the lattice. This state is not stable and is assumed to generate disorder points for the energetic potential to be emitted. Strats, which are necessary for smoothing crystal disorders, have been found in all natural crystals having defects. The transition of a non-defective zone to defective zone is accompanied by increasing entropy, and hence a self-organization of the crystal stratification zone occurs. All these features occurring in organic-mineral complexes can also be found in the structure of nuclear-protein complexes and the cell transcription-translation apparatus.

The evolution of the matrix mechanism on the apatite, carbonate-apatite, and calcite lattice would have occurred in two stages. In the first stage, an organo-mineral crystal complex would have been formed. In the second stage, the organo-mineral crystal complexes would have been transformed into a liquid-crystal complex as a component of the protocell. A fragment of a crystal defective zone is shown in Figure 9. The process of matrix apparatus formation would have occurred in this zone. DNA, and informationally connected with it RNA and protein molecules, can occur as one-dimensional structures consisting of a huge number of monomeric units. The genes in DNA are not distributed in a random way; they are in a certain place. A triple complex of DNA, RNA, and proteins would have been formed in the apatite and carbonate-apatite zone. Such complex self-organization comes naturally from the fact that its synthesis occurs simultaneously on the complex of co-crystallizing minerals, which have mutually coordinated proportions.

The interaction between the components of the triple complex would have occurred at the level of the primary structure and would have followed the principle of helix-to-helix complementarity. The backbone of the complex would be a double DNA helix. DNA, RNA and proteins were interacting among themselves at the level of the primal structure. At that stage, all proteins necessary for replication,

Figure 9. The presumptive scheme of the evolution of the matrix (transcription-translation) mechanism in protocells suggests that the following events would have occurred in the zones of defect accumulation and cocrystallization: (1) Formation of the triple DNA–RNA–protein complex. (2) Initiation of the matrix mechanism. This might have been induced by a change in ion concentrations and may have occurred through the despiralization of the helix complex; (3) Inverted repeats in the tRNA and rRNA structure, together with complex proteins, would have promoted the formation of the secondary and tertiary rRNA and tRNA structures. (4) Several amino acids migrated from the calcite zones to bind with AA-tRNA-synthetase. (5) The hybridization of mRNA and ApDNA was disturbed owing to conformational changes in the nucleic acids caused by their association with 30sRb and 50sRb particles.

transcription, and translation were present, although the ribosomal apparatus was not yet formed and functionally active.

A transition between the defective (chaos enhancement) and non-defective zone would have come about through the peculiarities of the nucleotide sequences in the synthesized DNA chains. A gradual transition would have occurred from the satellite zone (non-informative DNA zone of eukaryotes) to highly (tDNA zone), moderately repetitive (rDNA zone) and unique genes zone of mDNA. Transcripts of tRNA, rRNA and mRNA would have been located complementary to these zones of the carbonate-apatite in precisely that sequence, which was specified for them in the prokaryotic genome (Figure 9). The length of RNA transcripts would have increased along with the “chaos enhancement” on the apatite from tRNA (dozens) to rRNA (thousands) and mRNA (hundreds of thousands of nucleotides). It should also be noted that RNA transcripts were not only associated with DNA, but would also have formed complementary bonds (helix-to-helix) with proteins, among them future enzymes. A RNA-protein complex would have been synthesized in carbonate-apatite zones cocrystallized with apatite. It was the substitution of PO_4 groups by CO_3 groups in the crystal lattice of carbonate-apatite that ensured the formation of the RNA-protein complex. PO_4^{3-} groups that were not involved in the synthesis of RNA could have played an active role in the formation of phosphorylated proteins and other compounds. Each pre-tRNA fragment in the crystal matrix would have come into association with a specific protein, future AA-tRNA-synthetase, which had already been associated with ATP and an appropriate amino acid. The ATP and amino acid would have been synthesized on the carbonate-apatite and on the carbonate-apatite and calcite matrix, respectively. It is worth mentioning that (*E. coli*) bacterial synthetase structural genes are dispersed along the chromosome and do not adjoin the genes that define synthesis of respective amino acids and tRNA. There must be 40 AA-tRNA-synthetase molecules *per* each tRNA in each *E. coli* cell, but why?

Each pre-rRNA and pre-mRNA would have also been associated with specific proteins, whose large numbers were a consequence of the greater length of the RNA fragments as compared to pre-tRNA. The proteins directly interacting with DNA and RNA would have in turn formed complementary bonds with many other proteins. There cannot be fewer than 55 proteins *per* pre-rRNA in *E. coli*. Might this not be an answer to the question of where primal proteins for ribosome formation and the acylation of tRNA came from? It has been reported that pre-rRNA would have stimulated the polymerization of amino acids, while isolates from the 30s- and 50s- subunits of rRNA would not have had such an effect. Bacteria have been found to have polyribosomes that synthesize at least 15 out of 55 ribosomal proteins. [65]. The question of the origin of 40 proteins remains open. In *E. coli*, the ratio between ribosomal proteins and free pre-rRNA is zero. It has been suggested that ribosomal and other proteins would be necessary for the processing of the transcription units of rRNA [66]. The triggering of the transcription-translation apparatus in cells is not possible without such proteins.

In a second stage, the organo-mineral complex would have passed into the liquid-crystal state in the presence of water. This process would have been accompanied by a partial untwisting of the complex, its transition into the strained state or an unstable equilibrium. In this system, the ion concentration would have played a key role, and any, even local, change in ion concentration might have changed the equilibrium and induced the launching of the matrix mechanism. This, in turn, might have led to further untwining and other conformational changes of some enzymatic reaction in the components of the complex, together with the restriction of a zone of complementary interaction. The compacting of the complex would have been accompanied by that of all its compounds. Conformational changes in RNA and neighbouring proteins would have been accompanied by the movement of the components of the complex along the DNA chain.

The presence of water and the change in ion concentration would have had the most profound effect on protein folding. The protein-stereospecific complementary dependence of RNA would have been less than the RNA dependence on the DNA double helix. This is why the protein primary structure was readily transformed into other types of structures, having an active influence on stereospecifically connected RNA fragments. Simultaneous changes in the conformation of an AA-tRNA-synthase and its respective tRNA would have occurred, as a result, the tRNA would have been aminoacid-acylated with the participation of ATP associated with AA-tRNA-synthase. Any change in tRNA conformation would have been facilitated by the presence of a large number of inverted repeats [67]. The primary structure of tRNA readily transformed into a tertiary one. Both the tertiary structure of tRNA and the specificity of its anticodon to an amino acid would have depended on the AA-tRNA-synthase. Being a larger and conformationally more active part of the complex, the enzyme would have adjusted the conformation of the tRNA molecule and determined its anticodon specificity by shaping the anticodon loop and exposing the anticodon triplet. This could be an answer to the issue of how different isoacceptor tRNAs were recognized by AA-tRNA-synthase of a single type. No conclusions can be drawn from the differences between isoacceptor tRNA. Sometimes they are minimal; sometimes they are so huge, that comparison of the primary structures of tRNA does not allow the detection of any signs of its similar specificity.

Unlike pre-tRNA, pre-rRNA would have been associated with many proteins, which were bound both to rRNA and to each other. This may be an answer to the question of how specific ribosomal proteins might have been synthesized prior to starting to perform their functions. Ribosomal RNAs are characterized by numerous inverted repeats [74], causing their transition from a linear to a “caterpillar” conformation at the untwining of the helix. These caterpillar rRNAs would have come into association with complementary proteins to form ribosomal subunits crawling along the DNA chain and interacting with mRNA. The 16S rRNA was the first to be synthesized. It would have formed, together with its proteins, the 30S subunit. The subunit prevented Ap-DNA from complementarily associating

with mRNA and came into complementary interaction with Ap-DNA. This process would have corresponded to the formation of the primary complex of the 30S Rb subunit and mRNA during the course of translation. Later on, the 23S and 5S rRNAs with their unique proteins would have joined this complex to form a complete mRNA-ribosome complex. This complex would then have come into contact with many AA-tRNA complexes. We suggest that AA-tRNA, together with AA-tRNA-synthase, would have been part of the ribosomal complex. It should be mentioned that such an arrangement of tRNA, rRNA and mRNA on the DNA *E.coli* chain is consistent with a gradual accumulation of defects in apatite and cocrystallizing minerals.

The cancellation of factors launching the matrix mechanism might have led to the return of the mechanism into the initial state. It is suggested that since the DNA matrix did not change, in DNA sites formerly occupied by the earlier tRNA and rRNA there would have occurred an active self-assembly of new tRNA and rRNA chains. The RNA chains synthesized would have come into contact with their specific proteins. It is possible that these proteins might not have been synthesized with the participation of ribosomes, but came from the next protein generation and were thus complementary to the proteins with tRNA and rRNA. The laminar packing of complementary proteins would have allowed the transcription apparatus to function in an assembly line-like manner without the participation of ribosomes. Subsequent generations of rRNA-associated proteins might have been synthesized with the participation of ribosomes. After one cycle of synthesis was finished, the matrix mechanism would have returned to its initial stable homeostatic state.

Conclusion

The proposed mechanism for the formation of the organo-mineral complexes of future protocells based on the mineral complex allows one to answer the main questions and solve some of the problems related to the origin of life: how and why the cell is an aperiodic, homeostatic, self-regenerational liquid crystal. Questions related to a thermodynamic barrier in the form of water on the path leading to synthesis of protobiopolymers are no longer relevant. Mineral chirality, the unidirectionality of the synthesis process (from bottom to top) and synthesis through the "spiral in a spiral" principle would have determined the structural asymmetry of the monomeric units of NA, proteins and the aperiodicity of all the molecules synthesized. Future protocells would have inherited from minerals: 1) matrix synthesis; 2) the universal genetic code (the united matrix of apatite) and the absence of the universality of the structures participating in the implementation of this code in several living systems; 3) the peculiarity of the eukaryotic DNA structure; 4) the key role played by Ca^{2+} and PO_4^{3-} groups in the vital activity of living systems as well as the need of such elements as Si, Sr, Ge, and others for certain groups of living systems; 5) the presence of proteins specifically binding only Ca^{2+} or some

other ions; 6) the appearance of living systems building their skeletons based solely on Sr, Si, Ca, Ca^{2+} and PO_4^{3-} , or other elements.

We would like to point out that the proposed model provides a universal mechanism of the origin of organic matter on Earth or Earth-like planets. The biomolecules of living systems, the humic skeleton of soils, oil hydrocarbons were all synthesized through the interaction of gas-phase elements with the lattices of different minerals. In the case of biomolecules, such minerals were apatite, calcite, cristobalite, and aragonite; in the case of humus, aluminosilicates; in the case of oil hydrocarbons, minerals with the linear structure of the crystal lattice.

Notes

1. Confocal domains represent one of the possible ways of supramolecular organization of liquid crystals.
2. "Domain" isomorphism is a phenomenon of the substitution of part of the crystal lattice by regular submicroscopic blocks of other substances.

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