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Role of Clay Minerals in Chemical Evolution and the Origins of Life

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<http://dx.doi.org/10.5772/50172>

1. Introduction

A number of hypotheses have been proposed regarding the origins of life on Earth. In the Russian text of 1924, Oparin (1938) suggested that simple molecules (e.g., CH₄, NH₃) in the early Earth, reacted to form small bio-molecules and complex bio-polymers (e.g., nucleoside, nucleotide, peptide, polynucleotide) which then evolved into multimolecular functional systems, and finally 'life' [1]. A few years later, Haldane (1929) independently proposed a similar hypothesis for the origins of life [2]. It was Bernal (1951), however, who first suggested that clay minerals played a key role in chemical evolution and the origins of life because of their ability to take up, protect (against ultraviolet radiation), concentrate, and catalyze the polymerization of, organic molecules [3]. Indeed, Cains-Smith (1982) has suggested that clay minerals can store and replicate structural defects, dislocations, and ionic substitutions, and act as 'genetic candidates' [4]. Thus, intercalation of organic molecules and monomers into the layer structure of clay minerals, such as montmorillonite and kaolinite, would favor the formation and replication of biopolymers with specified sequences (e.g., enzymes, polynucleotides).

The composition of the primitive atmosphere is an important factor influencing the formation of small biomolecules. Urey (1952) and Miller and Urey (1959) proposed that the early Earth had a reducing atmosphere, and conducted their experiments on chemical evolution accordingly [5, 6]. Computer simulation, however, would indicate that the primitive atmosphere was not reducing. Moreover, it was very difficult to synthesize bio-organic molecules under reducing conditions.

In this review we describe the environment of the primitive Earth, outline the clay-induced formation of small molecules and simple bio-molecules, discrimination of optical isomers, and polymerization of bio-molecules, and then briefly remark on the RNA world and the origin of cells.

2. Environment of the early Earth

In discussing the origins of life, it is important to know the state of the early Earth. Cosmic dust grains, rotating around the primitive Sun, coalesced to form planetesimals, and then larger bodies (e.g., planets) through gravitation, giving rise to the solar system about 4.6 billion years ago [7]. The surface of the primitive Earth was molten to a depth of 1000 km [8]. The light elements had disappeared into space but various gases were retained on the surface by gravitation. As the temperature decreased, the surface of the magma ocean gradually solidified. Water vapor, carbon oxide, nitrogen gas began to cover the Earth surface, forming the primitive atmosphere. Water vapor gave rise to clouds which turned into rain, feeding rivers and oceans. Dissolved metal ions from rocks entered into the primitive ocean. Lightnings and volcanic eruptions often occurred. Small and large meteorites also bombarded the early Earth. These events and light from the sun were conducive to creating simple organic compounds and small bio-molecules.

2.1. Atmosphere

In an early paper, Urey (1952) suggested that Earth's primitive atmosphere was mainly composed of anoxic gases (e.g. NH_3 , CH_4) and water vapor [5]. On the other hand, Levine et al. (1982) proposed that non-reductive gases (e.g. CO , CO_2 , N_2) made up the paleoatmosphere [9]. More recently, Owen (2008) argued for a composition between anoxic and non-reductive gases [10].

2.2. Meteorite

There are basically two types of meteorites: primitive and fractionated. Table 1 shows a classification scheme for meteorites. Carbonaceous (C-)chondrite is considered to be the earliest type of meteorite, containing a 'memory' of the primitive solar system. C-chondrites are mainly composed of Mg-rich minerals including a hydrous silicate, serpentine. They also contain organic and bio-organic molecules (e.g., amino acids). When such meteorites rained down on the early Earth, the energy of collision would convert simple organic molecules to bio-organic compounds. Table 2 lists the range and variety of organic molecules in space.

2.3. Bombardment by meteorites and asteroids

The craters on Moon were formed about 3.8–4.0 billion years ago through bombardment by meteorites and asteroids [11]. At the same time, huge numbers of meteorite and asteroids would have hit the relatively larger Earth because of its proximity to Moon. As a result, the surface temperature of Earth would markedly increase, and most liquid water would have evaporated. Likewise, many simple organic compounds or large bio-molecules that were present, or formed through meteorite impact, would have volatilized or decomposed.

Stony chondrites
Enstatite chondrites
H(high-Fe) chondrites
L(low-Fe) chondrites
LL(low Fe and low metal) chondrites
Carbonaceous chondrites: Type I No Chondrule, & Type II Chondrule
Achondrites
Ca-poor: Aubrites, Diogenites, Ureilites, Chassignite
Ca-rich: Angrite, Nahlites, Eucrites, Howardites
Stony- Irons
Pallasites, Mesosiderites
Irons
I AB, II AB, IIAB, IVA, IV B

Table 1. Classification of meteorites [59].

Nitryl and acetylene derivative etc.
HCN, HC ₃ N, HC ₅ N, HC ₇ N, HC ₉ N, HC ₁₁ N, HC ₂ CHO, CH ₃ CN, CH ₃ C ₃ N, CH ₃ C ₂ H, CH ₃ CH ₂ CN, CH ₂ , CHCN, HNC, HNCO, HNCS, HNCCC, CH ₃ NC, HCCNC
Aldehyde, Alcohol, Ether, Ketone, Amine, etc.
H ₂ CO, H ₂ CS, CH ₃ CHO, NH ₂ CHO, H ₂ CCO, CH ₃ OH, CH ₃ CH ₂ OH, CH ₃ SH, (CH ₃) ₂ O, (CH ₃) ₂ CO, HCOOH, HCOOCH ₃ , CH ₃ COOH, CH ₂ NH, CH ₃ NH ₂ , NH ₂ CN, H ₂ C ₃ , H ₂ C ₄ , H ₂ C ₆
Allene
c-C ₃ H ₂ , c-SiC ₂ , c-C ₃ H, c-C ₂ H ₄ O
Molecular ions
HCS ⁺ , CO ⁺ , HCO ⁺ , HOCO ⁺ , H ₂ COH ⁺ , HCNH ⁺ , HC ₃ NH ⁺ , HOC ⁺
Radical
OH, CH, CH ₂ , NH ₂ , HNO, C ₂ H, C ₃ H, C ₄ H, C ₅ H, C ₆ H, C ₇ H, C ₈ H, CN, C ₃ N, C ₅ N, CH ₂ CN, CH ₂ N, NaCN, C ₂ O, NO, SO, HCO, MgNC, MgCN, C ₂ S, NS

Table 2. Organic molecules in space [60]. c- (Allene): circular.

2.4. Clay minerals

Clay minerals would have formed by weathering of volcanic glass and rocks. Also, when the temperature of land and atmosphere decreased, the highly concentrated cations and anions in the primitive ocean would have precipitated on the primitive ocean floor, and there interacted to yield certain compounds. The oldest rock on Earth is sedimentary in origin, suggesting that land erosion by rivers had already happened. Water would have come into contact with volcanic glass and rocks, opening the way to clay mineral formation. The Mars investigation indicates the occurrence in the planet's surface of clay minerals with an age of > 3.5 Ga, and a chemical composition consistent with Al-Si-O-H and Mg-Si-O-H systems [12]. By analogy, clay minerals would have formed on the early Earth.

3. Simple bio-molecules

The bio-organic compounds of 'life' comprise amino acids, nucleic acid bases, sugars, and lipids (Tables 3 and 4; Figure 1). The role of clay minerals in the synthesis of amino acids, nucleic acid bases and sugars is described below.

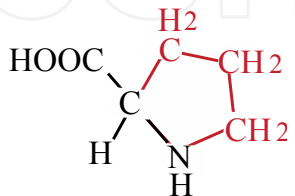
Amino acid	Side chaine (R)	Amino acid	Side chaine (R)
Glycine (Gly)	-H	Aspartic acid (Asp)	$-\text{CH}_2-\text{C} \begin{matrix} \text{= O} \\ \\ \text{OH} \end{matrix}$
Alanine (Ala)	-CH ₃	Glutamic acid (Glu)	$-\text{CH}_2-\text{CH}_2-\text{C} \begin{matrix} \text{= O} \\ \\ \text{OH} \end{matrix}$
Valine (Val)	$\begin{matrix} \text{CH}_3 \\ \\ -\text{C}-\text{H} \\ \\ \text{CH}_3 \end{matrix}$	Asparagine (Asn)	$-\text{CH}_2-\text{C} \begin{matrix} \text{= O} \\ \\ \text{NH}_2 \end{matrix}$
Leucine (Leu)	$\begin{matrix} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}-\text{H} \\ \\ \text{CH}_3 \end{matrix}$	Glutamine (Gln)	$-\text{CH}_2-\text{CH}_2-\text{C} \begin{matrix} \text{= O} \\ \\ \text{NH}_2 \end{matrix}$
Isoleucine (Ile)	$\begin{matrix} \text{H} \\ \\ -\text{C}-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3 \end{matrix}$	Lysine(Lys)	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2$
Phenylalanine (Phe)	$-\text{CH}_2-\text{C}_6\text{H}_5$	Arginine (Arg)	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{C} \begin{matrix} \text{= NH}_2 \\ \\ \text{NH}_2 \end{matrix}$
Tyrosine(Tyr)	$-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$	Histidine (His)	$-\text{CH}_2-\text{C}_4\text{H}_3\text{N}_2$
Serine (Ser)	-CH ₂ -OH	Tryptophan (Try)	$-\text{CH}_2-\text{C}_8\text{H}_6\text{N}_2$
Threonine(Thr)	$\begin{matrix} -\text{CH}-\text{CH}_3 \\ \\ \text{OH} \end{matrix}$	Proline (Pro)	
Cysteine (Cys)	-CH ₂ -SH		
Methionine (Met)	-CH ₂ -CH ₂ -S-CH ₃		

Table 3. Twenty bio-amino acids and their side chains. Proline: the side chaine is red. The structure of the amino acid: R-CH(NH₂)-COOH

Phosphatidate
 Phosphatidylcholine
 Phosphatidylethanolamine
 Phosphatidylglycerol
 Phosphatidylinositol
 Phosphatidylserine
 Cardiolipin
 Sphingomyelin
 Glycolipid
 Cholesterol

Table 4. Main lipids of biological membrane. [61]

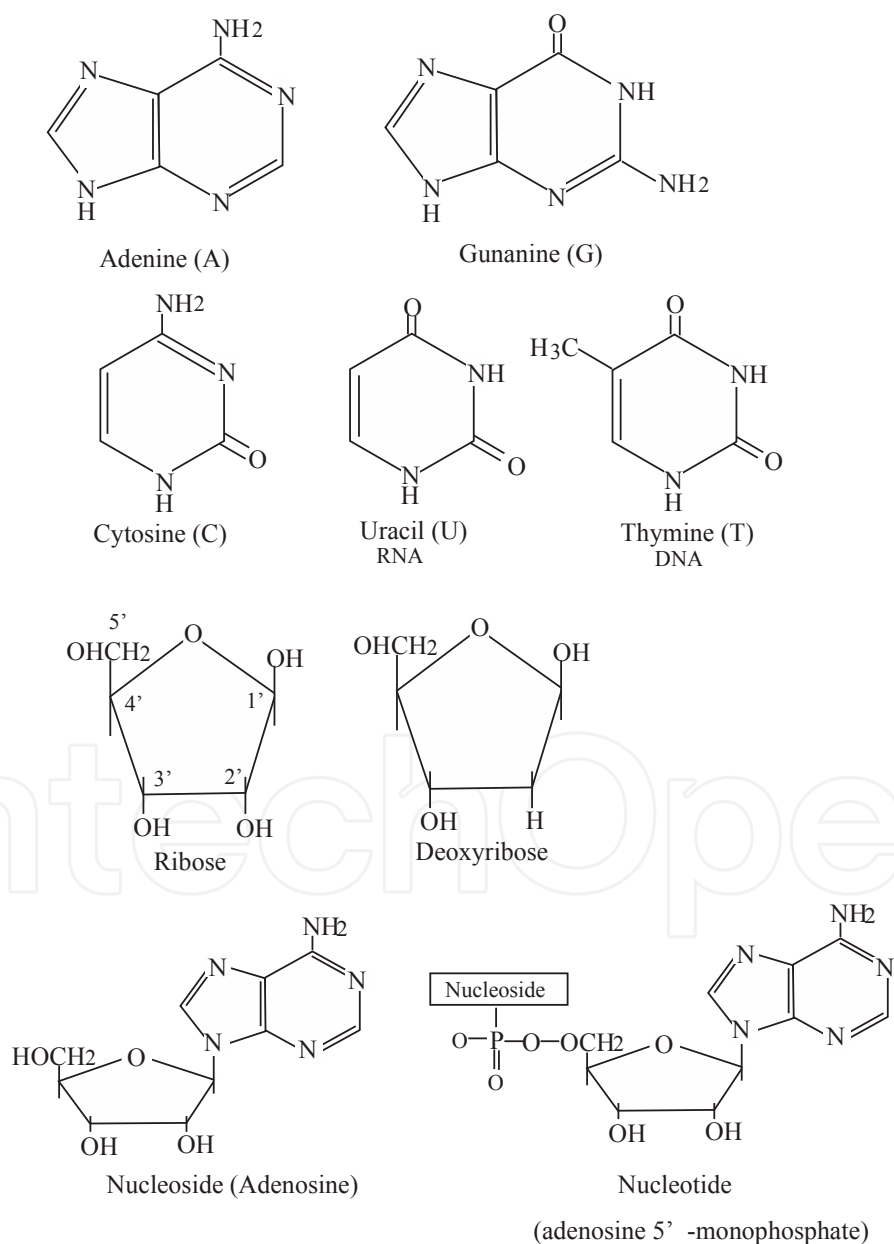


Figure 1. Components of RNA (or DNA) and nucleoside and nucleotide.

3.1. Amino acids

Miller and Urey (1959) were able to synthesize bio-molecules from simple precursors (e.g., NH_3 , CH_4 , water) by circulating the mixture past an electric discharge (“spark”), simulating a lightning strike. Table 5 lists the compounds obtained abiotically under reducing atmospheric conditions. When montmorillonite was added to Miller’s (1953) system, Shimoyama et al. (1978) found that the yield of amino acids with an alkylated side chain increased [13, 14] (Table 5). Subsequently, Yuasa (1989) conducted the sparking experiment using HCN and $\text{NH}_4(\text{OH})$ in the presence of montmorillonite [15], obtaining glycine, alanine, and aspartic acid as the main products.

Glycine	Succinic acid
Glycolic acid	Aspartic acid
<u>Sarcosine</u>	Glutamic acid
<u>Alanine</u>	Iminodiacetic acid
Lactic acid	Iminoacetic-propionic acid
N-Methylalanine	Formic acid
<u>α-Amino-n-butyric acid</u>	Acetic acid
α -Aminoisobutyric acid	Propionic acid
α -Hydroxybutyric acid	Urea
β -Alanine	N-Methy urea

Table 5. Organic compounds detected in Miller’s experiment [5,13]. Bold: bio-amino acid. Red; more of these compounds were obtained in the presence of monmtrillonite [13].

Some components of the primitive atmosphere are soluble in water. Under hydrothermal conditions, as would pertain in a thermal vent, the dissolved components would react to form various amino acids (e.g., glycine, alanine, lysine, isoleucine) as Marshall (1994) has reported [16].

The primitive atmosphere might not have been reducing, however. Further, bio-organic molecules are difficult to obtain under the conditions used by Miller (1953) [14]. In an attempt to make for favorable conditions, Kobayashi et al. (1990) used proton irradiation to produce a reducing atmosphere from an oxidizing one [17]. Nevertheless, the role of clay minerals in the formation of bio-molecules remains uncertain. Infrared spectroscopy suggests that the dust in the diffuse interstellar medium contains aliphatic hydrocarbons [18]. Again, it is uncertain whether clay minerals are involved in their formation.

3.2. Adsorption of amino acids by clay minerals

Clay minerals would be capable of adsorbing bio-organic molecules from the early ocean. The resultant clay-organic complexes would partly be deposited on the ocean floor.

Greenland et al. (1962, 1965) investigated the interactions of various amino acids with H-, Na-, and Ca-montmorillonites [19, 20]. Arginine, histidine, and lysine adsorbed to Na- and Ca- montmorillonites by cation exchange. Other amino acids (alanine, serine, leucine,

aspartic acid, glutamic acid, phenylalanine) adsorbed to H-montmorillonite by proton transfer. The adsorption of glycine and its oligo-peptides by Ca-montmorillonite and Ca-illite increased with the degree of oligomerization (molecular weight). Hedges and Hare (1987) suggested that the amino and carboxyl groups of the amino acids were involved in their adsorption to kaolinite [21], while Dashman and Stotzky (1982, 1984) reported that kaolinite adsorbed less amino acids and peptides than did montmorillonite [22, 23].

Serpentine is a clay mineral, formed by the weathering of olivine and pyroxene. As such, serpentine would be expected to occur on the surface of the early Earth. Serpentine, however, has a limited capacity for taking up amino acids (Hashizume, 2007) although it can adsorb measurable amounts of aspartic and glutamic acids [24]. On the other hand, allophane can take up appreciable amounts of alanine [25]. The adsorption isotherms showed three distinct regions as the (equilibrium) concentration (C_e) of alanine increased: a nearly linear rise at low C_e , a leveling off to a plateau at intermediate C_e , and a steep linear increase at high C_e . The oligomers of alanine were also adsorbed by allophane but the extent of adsorption did not vary greatly with solute molecular weight [26].

3.3. Optical discrimination

Amino acids can exist in two enantiomeric (chiral) types, namely, D (dextrorotatory) and L (levorotatory) (Figure 2). Both enantiomers would have formed, in equal amounts under abiotic conditions, giving a racemic mixture with a D/L molar ratio of 1/1. The amino acids in living organisms, however, are generally of the L-type. This finding is one of the problems associated with the origins of life.

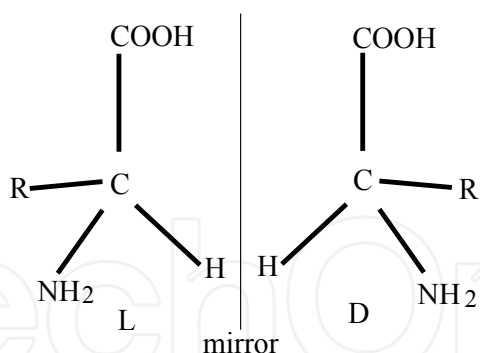


Figure 2. D- and L-enantiomers (“mirror” images) of amino acids. R represents the side chain (Table 3).

The question arises whether clay minerals can discriminate between D- and L-amino acids when placed in contact with a racemic mixture. Using Na-montmorillonite and a racemic mixture of several amino acids, Friebele et al. (1981) did not observe any difference in adsorption between the D- and L-enantiomers [27]. This finding is not altogether surprising since clay minerals have no chirality in their bulk structures although the layer structure of kaolinite may be chiral due to the presence and positioning of vacancies (Figure 3). The edge surface of a montmorillonite layer may also be structurally chiral due to the presence of defects. These chiral structures, however, are not individually separable.

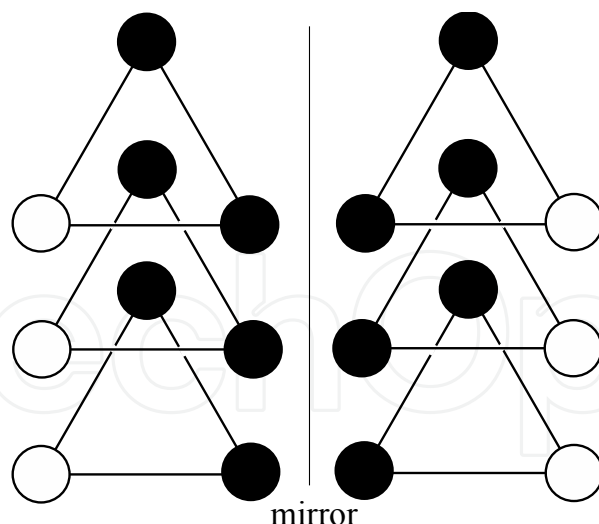


Figure 3. Overlap of Al atoms in stacked layers of kaolinite. Black circles indicate occupied Al site, and white circles indicate vacant Al sites [62].

On the other hand, quartz crystals are intrinsically chiral and, as such, can show stereospecific effects. Bonner et al. (1974), for example, found that L-quartz preferred L-alanine to its D-enantiomer, while D-quartz adsorbed more D- than L-alanine. The difference in preference was about 1%. Interestingly, Siffert and Naidja (1992) reported that montmorillonite showed stereo-selectivity in the adsorption and deamination of aspartic and glutamic acids. Likewise, Hashizume et al. (2002) reported that an allophane from New Zealand, extracted from a volcanic ash soil, showed a clear preference for L-alanyl-L-alanine over its D-enantiomer [30]. They suggested that the size, intramolecular charge separation, and surface orientation of L-alanyl-L-alanine zwitterions combined to confer 'structural chirality' to the allophane-amino acid complex. Although the allophane sample was purified before use, the presence of trace amounts of organic matter might have left a chiral 'imprint'.

3.4. Nucleic acid bases

Nucleic acids contain two purine bases (adenine, guanine), and three pyrimidine bases (cytosine, uracil, thymine) (Figure 1). Uracil and thymine are found in RNA and DNA, respectively.

Adenine could be prebiotically synthesized from hydrogen cyanide, and cytosine from cyanoacetylene, while uracil could arise from cyanoacetylene via malic acid. Chittenden and Schwartz (1976) reported that the addition of montmorillonite increased the rate of adenine formation [32].

No nucleic acid bases were found in the Miller experiment [6]. Adenine was formed, however, when a mixture of HCN and montmorillonite was added to the reaction vessel, and exposed to lightning [15]. Similarly, uracil could be synthesized from CO, N₂ and H₂O by proton irradiation [17].

3.5. Adsorption of nucleic acid bases by clay minerals

The adsorption of nucleic acid bases by montmorillonite has been widely investigated. Lawless et al. (1984) and Banin et al. (1984) reported that the adsorption of adenosine monophosphate (AMP) by montmorillonite, containing different exchangeable cations (Zn, Cu, Mn, Fe, Ca, Co, Ni), generally increased as solution pH decreased [33, 34]. In the case of Zn-montmorillonite, adsorption of 5'-AMP reached a maximum at pH ~7. The extent of adsorption was primarily influenced by the acid dissociation constant of the nucleic acid base. Winter and Zubay (1995) investigated the relative ability of montmorillonite and hydroxylapatite in adsorbing adenine and adenine-related compounds [35]. They found that montmorillonite adsorbed more adenine than the other compounds (adenosine, 5'-AMP, 5'-ADP, 5'-ATP), while hydroxylapatite preferred adenosine phosphate to adenine and adenosine. The extent of adsorption depended on solution pH, and might also be affected by the buffer used.

More recently, Hashizume et al. (2010) investigated the adsorption of adenine, cytosine, uracil, ribose, and phosphate by Mg-montmorillonite [36]. At comparable concentrations in the equilibrium solution, adsorption decreased in the order adenine > cytosine > uracil, while ribose was hardly adsorbed. Hashizume and Theng (2007) found that allophane had a greater affinity for 5'-AMP than for adenine, adenosine, or ribose [37]. Again, very little ribose was adsorbed. The strong adsorption of 5'-AMP accords with the high phosphate-retention capacity of allophane [38].

The adsorption of nucleic acid bases to clay mineral surfaces has also been assessed by computer simulation. An *ab initio* study by Michalkova et al. (2011) suggests that uracil was adsorbed perpendicularly to the kaolinite surface [39]. With montmorillonite, on the other hand, nucleic acid bases tend to adsorb in a face-to-face orientation with respect to the basal siloxane plane [40].

3.6. Sugar

Sugars may be synthesized from formaldehyde through the Formose reaction. Clay and layered minerals (e.g., montmorillonite, brucite) can catalyze the self-condensation of formaldehyde. Further, the sugar oligomers formed are stabilized by adsorption to montmorillonite [41, 42].

4. Polymerization of bio-polymers

4.1. Peptides

Peptides are polymers of amino acids (Table 3; Figure 4). On the early earth, peptides may have formed at places where energy is produced, such as thermal vents on the sea floor. The primitive ocean may have contained small bio-molecules, including amino acids. As already mentioned, clay minerals would have played an important role in concentrating and polymerizing such molecules on their surfaces.

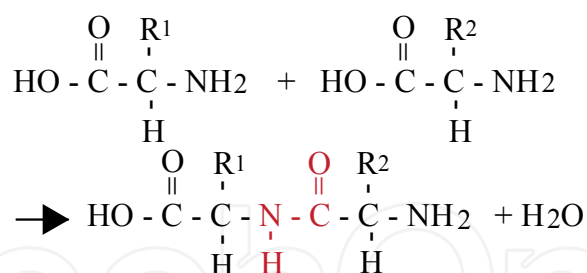


Figure 4. Polymerization of amino acids. Red indicates peptide bonding. R1 and R2 represent amino acid side chains (Table 3).

According to the thermal vent model, organic molecules sink to the sea floor around a thermal vent, and polymerize under conditions of high pressure and temperature [43]. The polymers formed would then move away from the thermal vent. Imai et al. (1997) have attempted to synthesize oligopeptides in a flow reactor, simulating a submarine hydrothermal system [44]. Details of the instrumentation have been given by Matsuno (1997) [45]. With glycine as the monomer, both di- and tri-glycine were formed. The effect of metal cations on amino acid oligomerization was also investigated but that of clay minerals has not been assessed.

The temperature of seawater on the early Earth is expected to be appreciably higher than that at present, a condition that would favor organic molecule polymerization. The thermal copolymerization of various amino acids (aspartic acid, glutamic acid, glycine, alanine, leucine) has been reported by Fox and Harada (1958). Indeed, they were able to synthesize a protenoid microsphere [46].

Plate tectonics would have been operative in the early Earth. When organic-rich sediments moved into a trench where the temperature and pressure are higher than at the surface, the water in the sediments would be depleted. As a result, the concentration of organic molecules would increase, promoting their polymerization [47]. The synthesis of glycine peptides with montmorillonite under trench-like hydrothermal conditions (5–100 MPa pressure; 150 °C temperature) has been reported by Ohara et al. (2007) who obtained up to 10-mers of glycine [48].

Clay mineral particles on the beach undergo repeated drying and wetting, being dried at low tide, and wetted at high tide. This condition would favor polymerization of the clay-associated organic molecules. Using kaolinite and bentonite as the clay minerals, and glycine as the organic species, Lahav et al. (1978) obtained measurable amounts of glycine oligomers up to the 5-mer [49], as shown in Table 6. Ferris et al. (1996) obtained about 50-mers of glutamic acid [50] by incubating (activated) glutamic acid with illite.

In a “shock” experiment, simulating collision of meteorite and asteroids with Earth, by Blank et al. (2001) amino acids were polymerized into oligo-peptides (mostly dimers and trimmers) [51].

Cycles No.	Net heating period (days)	Yields (nmol/mg clay)			
		Dimer	Trimer	Tetramer	Pentamer
Kaolinite					
11	33.7	2.27	0.45		
21	55.0	1.99	0.79	0.29	trace
27	67.4	2.25	1.01	0.33	trace
33	77.3	2.21	0.83	0.32	trace
27	67.4	0.97	0.38	0.10	trace
27	67.4	1.31	0.55	0.15	trace
27	67.4	3.50	1.58	0.60	trace
Bentonite					
11	32.8	6.37	0.20	n.d.	n.d.
21	55.0	7.99	0.60	n.d.	n.d.
27	67.4	4.92	0.61	trace	n.d.
27	67.4	2.92	0.20	n.d.	n.d.
27	67.4	12.7	1.90 trace	n.d.	
11	57.0	36.7	8.2	2.5	
1	10.6	11.9 trace	n.d.		
5	25.4	26.9	1.9	n.d.	
11	57.0	40.1	7.9	1.2	0.8

Table 6. Yields of glycine oligomers in the presence of kaolinite and bentonite, subjected to wetting and drying cycles [49]. n.d. = not detected

4.2. Nucleotide polymers (RNA world)

One hypothesis concerning the origins of life involves the 'RNA world' in which RNA molecules acted as both enzyme-like catalysts and genetic materials [52]. The four nucleic acid bases in RNA have a complementary function. Thus, RNA would be able to behave like DNA, although uracil (U) and ribose were used in RNA instead of thymine (T) and deoxyribose in DNA [53]. The molecule of RNA is composed of a nucleic acid base, ribose and phosphate. Combination of a nucleic acid base with 1'-ribose gives rise to a nucleoside, and the addition of phosphate at the 3'- and 5'- positions of ribose yields a nucleotide (Figure 1). RNA is therefore a polynucleotide.

The clay-catalyzed synthesis of polynucleotides has been investigated by Ferris and coworkers. Using the 5-phosphorimidazolidine of adenine (ImpA) as the activated RNA monomer, Ferris and Ertem (1993) were able to obtain oligomers containing 6–14 monomer units in the presence of montmorillonite [54]. The formation of RNA oligomers, however, is but the first step towards preparing RNA with more than 40 monomers that are theoretically required for the initiation of the RNA world. Long-chain (elongated) RNA can be obtained using the “feeding” procedure; that is, by daily addition of ImpA to the decanucleotide (10-mer primer) adsorbed to Na-montmorillonite. Polynucleotides containing more than 50-mers are formed after 14 feedings although the principal products contain 20–40 monomer units [55]. Using activated adenosine-, uridine-, guanosine- or cytosine-5'-phospho-1-methyladenine, Joshi et al. (2009) obtained the corresponding 40 to 50-mers [56].

5. Cell origin

Lipids make up part of the living cell (Table 4). In water lipids form a micelle structure where that the outer hydrophilic part is in contact with water, and the hydrophobic part is turned inside (Figure 5). The cell wall has a trans-membrane protein through which nutrients enter the cell.

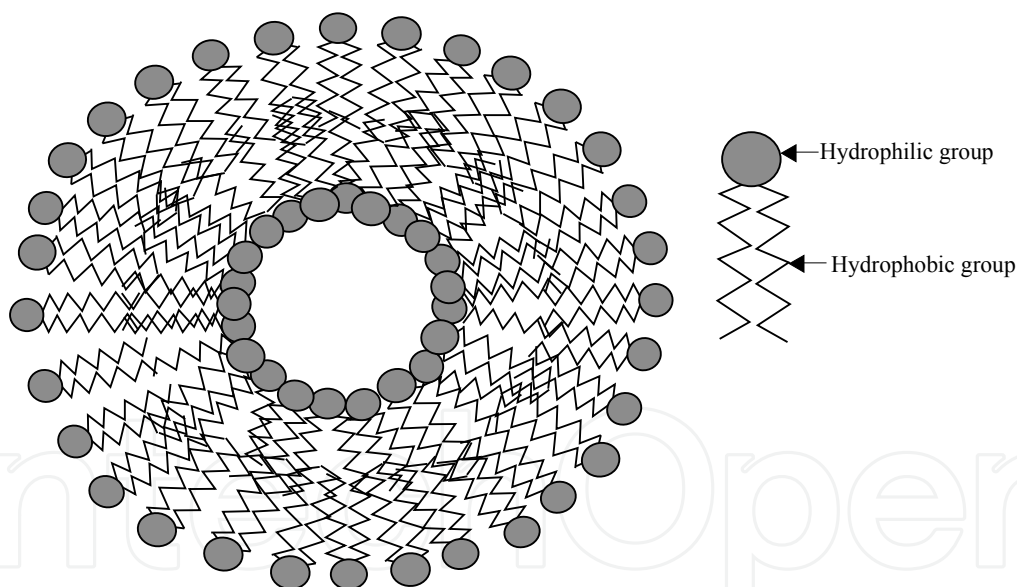


Figure 5. Micelle structure. Hydrophilic group: phosphate group, choline group, phosphocholine group etc. Hydrophobic group: stearate, oleate, linoleate etc.

Clay minerals might function as a primordial cell [4]. When clay minerals are deposited on the ocean floor (or dried), the particles form a pile, enclosing small spaces (Figure 6). It is conceivable that the small spaces behave like cells. Further, when clay minerals are dispersed in water, bubbles form in water or the surface of water, while the clay particles gather at the boundary between water and air, as shown in Figure 7 [57]. In such a case, clay minerals make a cell-like spherule.

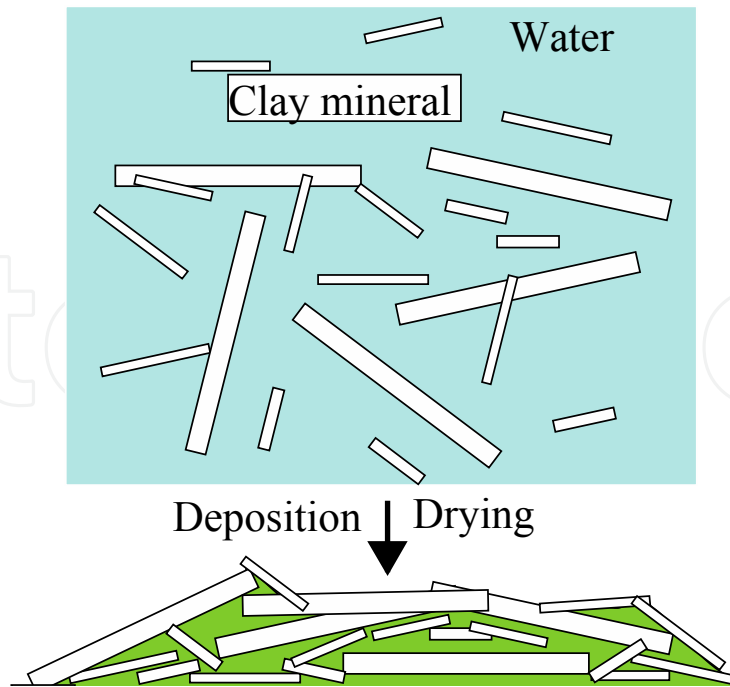


Figure 6. Schematic figure of the room (green) to function like the cell. Clay mineral layers were dispersed in water and then dry water but small rooms play the role like the cell [4].

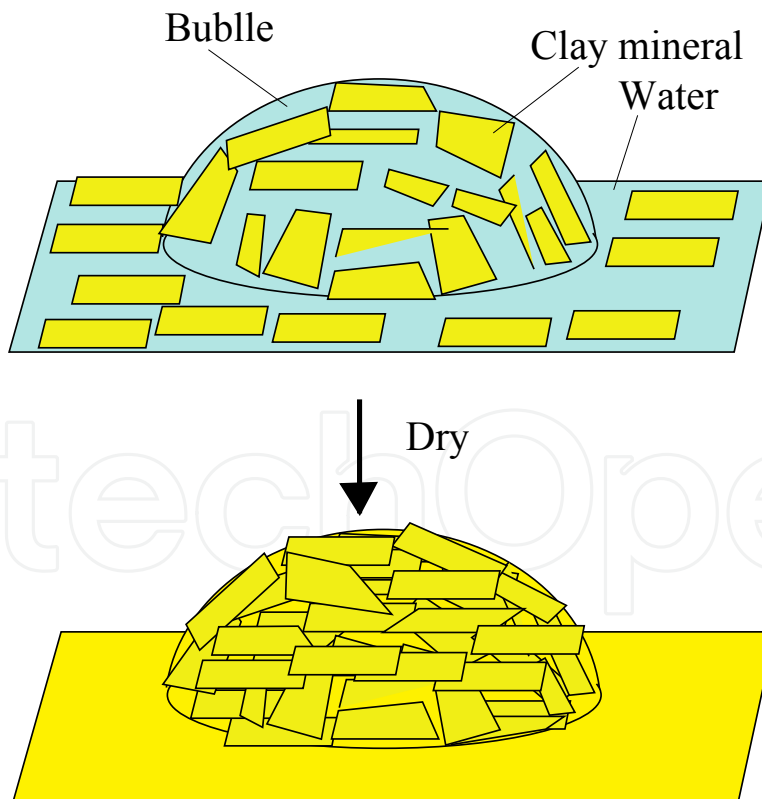


Figure 7. Schematic figure of a bubble shape sheet clay mineral micelle [57].

Unlike surfactants, lipids are difficult to synthesize. Surfactants may transform into lipids. Apatite has been reported to be capable of catalyzing the formation of a proto-lipid [58].

6. Conclusions

This article describes the role of clay minerals in chemical evolution although various other materials in the early Earth would have participated in the formation of life-like structures. Most experiments related to the origins of life on Earth use specific clay minerals, such as montmorillonite and kaolinite. Volcanic rocks from the magma ocean would be enriched in Mg^{2+} ions. On this basis, we have investigated the interactions of Mg-rich clay minerals (e.g., talc, serpentine) with organic molecules, including bio-organic compounds. It is further suggested that the atmosphere of the early Earth contained little oxygen. This condition would be conducive to the formation of Fe^{2+} -rich clay minerals which, therefore, might have played an important part in the synthesis of simple bio-organic molecules.

Besides being able to concentrate organic molecules, clay minerals can also control the surface arrangement of adsorbed nucleic acid bases or amino acids. By using a mixture of different clay mineral species, it may be possible to select a given bio-molecule over another for adsorption and polymerization. Although there is an element of trial and error in investigating the role of clay minerals in chemical evolution and the origins of life, we may yet be surprised by the outcome.

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Acknowledgement

We thank the editor Dr. M. Valaskova and the co-editor Dr. G. S. Martynkova for a chance to write this review. We also thank Dr. B. K. G. Theng (Landcare Research, New Zealand) for useful discussions and polishing English.

7. References

- [1] Oparin A. I (1938) *The Origin of Life*. New York: MacMillan. (Original: (1924) *Proiskhozhdenie zhizny*. Moscow: Izd. Moskovski Rabochii.
- [2] Haldane J. B. S (1929) *The Origin of Life*. *The Rationalist Annual* 148: 3–10.
- [3] Bernal J. D (1951) *The Physical Basis of Life*. London: Routledge and Kegan Paul. 364p.
- [4] Cains-Smith A. G (1982) *Genetic Takeover*. Cambridge: Cambridge University Press. 133p.
- [5] Urey H. C (1952) *On the Early Chemical History of the Earth and the Origin of Life*. *Proc. Nat. Acad. Sci. USA* 38: 351–363.
- [6] Miller S. L, Urey H.C (1959) *Organic Compound Synthesis on the Primitive Earth*. *Science* 130: 245–251.

- [7] Taylor S. R, Norman M. D (1990) Accretion of Differentiated Planetesimals to the Earth. in Newsom H. E, Jones J. R, editors, *Origin of the Earth*. New York: Oxford University Press, pp. 29–43.
- [8] Davies G. F (1990) Heat and Mass Transport in the Early Earth. in Newsom H. E, Jones J. R, editors, *Origin of the Earth*. New York: Oxford University Press, pp. 175–194.
- [9] Levine J. S, Augustsson T.R, Natarajan M (1982) The Prebiological Paleoatmosphere: Stability and Composition. *Origin Life* 12: 245–259.
- [10] Owen T (2008) The contributions of Comets to Planets, Atmospheres, and Life: Insights from Cassini-Huygens, Galileo, Giotto, and Inner Planet Missions. *Space Sci. Rev.* 138: 301–316.
- [11] Chyba C, Sagan C (1992) Endogenous Production, Exogenous Delivery and Impact-Shock Synthesis of Organic Molecules: an Inventory for the Origins of Life. *Nature* 355: 125–132.
- [12] Bristow T. F, Milliken R.E (2011) Terrestrial Perspective on Authigenic Clay Mineral Production in Ancient Martian Lakes. *Clays Clay Miner.* 59: 339–358.
- [13] Shimoyama A, Blair N, Ponnamperna C (1978) Synthesis of Amino Acids under Primitive Earth Conditions in the Presence of Clay. In Noda N. H editor, *Origin of Life*. Tokyo: Center for Academic Publisher, pp. 95–99.
- [14] Miller S. L (1953) A Production of Amino Acids under Possible Primitive Earth Conditions. *Science* 117: 528–529.
- [15] Yuasa S (1989) Polymerization of Hydrogen Cyanide and Production of Amino Acids and Nucleic Acid Bases in the Presence of Clay Minerals –In Relation to Clay and the Origin of Life. *Nendo Kagaku* 29: 89–96 (in Japanese).
- [16] Marshall W. L (1994) Hydrothermal synthesis of amino acids. *Geochim. Cosmochim. Acta* 58: 2099–2106.
- [17] Kobayashi K, Tsuchiya M, Oshima T, Yanagawa H (1990) Abiotic Synthesis of Amino Acids and Imidazole by Proton Irradiation of Simulated Primitive Earth Atmospheres. *Origin Life* 20: 99–109.
- [18] Sandford S. A, Pendleton Y. J, Allamandola L. J (1995) The Galactic Distribution of Aliphatic Hydrocarbons in the Diffuse Interstellar Medium. *Astrophys. J.* 440: 697–705.
- [19] Greenland D. J, Laby R. H, Quirk J. P (1962) Adsorption of Glycine and Its Di-, Tri-, and Tetra-Peptides by Montmorillonite. *Trans. Farad. Soc.* 58: 829–841.
- [20] Greenland D. J, Laby R. H, Quirk J. P (1965) Adsorption of Amino-Acids and Peptides by Montmorillonite and Illite. *Trans. Farad. Soc.* 61: 2024–2035.
- [21] Hedges J. I, Hare P. E (1987) Amino Acid Adsorption by Clay Minerals in Distilled Water. *Geochim. Cosmochim. Acta* 51: 255–259.
- [22] Dashman T, Stotzky G, (1984) Adsorption and Binding of Peptides on Homoionic Montmorillonite and Kaolinite. *Soil Biol. Biochem.* 16: 51–55.
- [23] Dashman T, Stotzky G (1982) Adsorption and Binding of Amino Acids on Homoionic Montmorillonite and Kaolinite. *Soil Biol. Biochem.* 14: 447–456.
- [24] Hashizume H (2007) Adsorption of Some Amino Acids by Chrysotile. *Viva Origino* 35: 60–65.

- [25] Hashizume H, Theng B. K. G (1999) Adsorption of DL-Alanine by Allophane: Effect of pH and Unit Particle Aggregation. *Clay Minerals* 34: 233–238.
- [26] Hashizume H, Theng B. K. G (1998) Adsorption of L-Alanine Monomer, Dimer, Tetramer, Pentamer by Some Allophanes In: Arehart G.B. Hulston J.R editors, Proc. 9th Intern. Symposium Water-Rock Interaction Rotterdam: A.A. Balkema. pp.105-107
- [27] Friebele E, Shimoyama A, Hare P. E, Ponnampereuma C (1981) Adsorption of Amino Acid Enantiomers by Na-Montmorillonite. *Origin Life* 11: 173–184.
- [28] Bonner W. A, Kavasmaneck P. R, Martin F. S (1974) Asymmetric Adsorption of Alanine by Quartz. *Science* 186: 143–144.
- [29] Siffert B, Naidja A (1992) Stereoselectivity of Montmorillonite in the Adsorption and Deamination of Some Amino Acids. *Clay Minerals* 27: 109–118.
- [30] Hashizume H, Theng B. K. G, Yamagishi A (2002) Adsorption and Discrimination of Alanine and Alanyl-Alanine Enantiomers by Allophane. *Clay Minerals* 37: 551–557.
- [31] Fraser D. G, Greenwell H. C, Skipper N. T, Smalley M. V, Wilkinson M. A, Demè B, Heenan R. K (2011) Chiral Interactions of Histidine in a Hydrated Vermiculite Clay. *Phys. Chem. Chem. Phys.* 13: 825–830.
- [32] Chittenden G. J. F, Schwartz A.W (1976) Possible Pathway of Prebiotic Uracil Synthesis by Photodehydrogenation. *Nature* 263: 350–351.
- [33] Lawless J. G, Banin A, Church F. M, Mazzurco J, Huff R, Kao J, Cook A, Lowe T, Orenberg J. B (1985) pH Profile of the Adsorption of Nucleotides onto Montmorillonite I. Selected Homoionic Clays. *Origin Life* 15: 77–87.
- [34] Banin A, Lawless J. G, Mazzurco J, Church F. M, Margulies L, Orenberg J. B (1985) pH Profile of the Adsorption of Nucleotides onto Montmorillonite II Adsorption and Desorption of 5'-AMP in Iron-Calcium Montmorillonite System. *Origin Life* 15: 89–101.
- [35] Winter D, Zubay G (1995) Binding of Adenine and Adenine-Related Compounds to the Clay Montmorillonite and the Mineral Hydroxylapatite. *Origin Life Evol. Biosphere* 25: 61–81.
- [36] Hashizume H, van der Gaast S, Theng B. K. G (2010) Adsorption of Adenine, Cytosine, Uracil, Ribose, and Phosphate by Mg-exchanged Montmorillonite. *Clay Minerals* 45: 413–419.
- [37] Hashizume H, Theng B. K. G (2007) Adenine, Adenosine, Ribose and 5'-AMP Adsorption to Allophane. *Clays Clay Miner.* 55: 599–605.
- [38] Theng B. K. G, Russell M, Churchman G. J, Parfitt R. L (1982) Surface Properties of Allophane, Halloysite, and Imogolite. *Clays Clay Miner.* 30: 143–149.
- [39] Michalkova A, Robinson T. L, Leszczynski J (2011) Adsorption of Thymine and Uracil on 1:1 Clay Mineral Surfaces: Comprehensive Ab Initio Study on Influence of Sodium Cation and Water. *Phys.Chem. Chem. Phys.* 13: 7862–7881.
- [40] Mignon P, Ugliengo P, Sodupe M (2009) Theoretical Study of the Adsorption of RNA/DNA Bases on the External Surfaces of Na⁺-Montmorillonite. *J. Phys. Chem. C* 113: 13741–13749.
- [41] Gabel N. W, Ponnampereuma C (1967) Model for Origin of Monosaccharides. *Nature* 216: 453–455.

- [42] Saladino R, Neri V, Crestini C (2010) Role of Clays in the Prebiotic Synthesis of Sugar Derivatives from Formamide. *Philos. Mag.* 90: 2329–2337.
- [43] Mulkidjanian A. Y, Bychkov A. Y, Dibrova D. V, Galperin M. Y, Koonin E. V (2012) Origin of First Cells at Terrestrial, Anoxic Geothermal Fields. *PNAS*: <http://www.pnas.org/cgi/doi/10.1073/pnas.1117774109>. Accessed 2012 Jan 20.
- [44] Imai E. - I, Honda H, Hatori K, Matsuno K (1997) Autocatalytic Oligopeptide Synthesis in a Flow Reactor Simulating Submarine Hydrothermal Vents. *Viva Origino* 25: 291–295.
- [45] Matsuno K (1997) A Design Principle of a Flow Reactor Simulating Prebiotic Evolution. *Viva Origino* 25: 191–204.
- [46] Fox S. W, Harada K (1958) Thermal Copolymerization of Amino Acids to a Product Resembling Protein. *Science* 128: 1214.
- [47] Nakazawa H, Yamada H, Hashizume H (1993) Origin of Life in the Earth's Crust, a Hypothesis: Probable Chemical Evolution Synchronized with the Plate Tectonics of the Early Earth. *Viva Origino* 21: 213–222 (In Japanese with English abstract).
- [48] Ohara S, Kakegawa T, Nakazawa H (2007) Pressure Effects on the Abiotic Polymerization of Glycine. *Origin Life Evol. Biosphere* 37: 215–223.
- [49] Lahav N, White D, Chang S (1978) Peptide Formation in the Prebiotic Era: Thermal Condensation of Glycine in Fluctuating Clay Environments. *Science* 201: 67–69.
- [50] Ferris J. P, Hill Jr. A. R, Liu R, Orgel L. E (1996) Synthesis of Long Prebiotic Oligomers on Mineral Surfaces. *Nature* 381: 59–61.
- [51] Blank J. G, Miller G. H, Ahrens M. J, Winans R. E (2001) Experimental Shock Chemistry of Aqueous Amino Acid Solution and the Cometary Delivery of Prebiotic Compounds. *Origin Life Evol. Biosphere* 31: 15–51.
- [52] Cech T. R (1986) A Model for the RNA-Catalyzed Replication of RNA. *Proc. Nat. Acad. Sci. USA* 83: 4360–4363.
- [53] Gilbert W (1986) The RNA World. *Nature* 319: 618.
- [54] Ferris J. P, Ertem G (1993) Montmorillonite Catalysis of RNA Oligomer Formation in Aqueous Solution. A Model for the Prebiotic Formation of RNA. *J. Am. Chem. Soc.* 115: 12270–12275.
- [55] Ferris, J. P, Hill Jr. A. R, Liu R, Orgel L. E (1996). Synthesis of Long Prebiotic Oligomers on Mineral Surfaces. *Nature* 381: 59–61.
- [56] Joshi P. C, Aldersley M. F, Delano J. W, Ferris J. P (2009) Mechanism of Montmorillonite Catalysis in the Formation of RNA Oligomers. *J. Am. Chem. Soc.* 131: 13369–13374.
- [57] Subramanian A. B, Wan J, Gopinath A, Stone H. A (2011) Semi-Permeable Vesicles Composed of Natural Clay. *Soft Matter* 7: 2600–2612.
- [58] Ourisson G, Nakatani Y (1998) Molecular Evolution and Origin of Biomembranes. *Protein Nucleic Acid Enzyme* 43: 1953–1962 (in Japanese).
- [59] Henderson P (1982) *Inorganic Geochemistry*. Oxford: Pergamon Press, 353p.
- [60] National Astronomical Observatory (2000) *Rika Nenpyo (Chronological Scientific Table 2000)* Tokyo:Maruzen Co. Ltd. p. 167.

- [61] Vote D, Vote J. G (1990) *Biochemistry* New York: John Wiley & Sons. (Translated into Japanese by Tamiya N, Muramatsu M, Yagi T, Yoshida H (1992) *Vote Seikagaku* (Jo), Tokyo: Tokyo Kagaku Dojin, 546p.
- [62] The Clay Science Society of Japan (2009) *Handbook of Clays and Clay Minerals*, 3rd edition. Tokyo:Gihodo. pp. 28–35 (in Japanese).

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