

# Chapter 1

## The Early Earth Atmosphere and Early Life Catalysts

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### Contents

ABSTRACT .....	1
1 THE EARLY EARTH ATMOSPHERE AND LITHOSPHERE .....	2
1.1 Earth's Internal Structure .....	3
2 CATALYSTS IN THE EARLY EARTH .....	4
3 CLAYS AS POSSIBLE CATALYSTS IN THE SYNTHESIS OF BIOMOLECULES .....	6
4 GENERAL CONCLUSIONS .....	12
ABBREVIATIONS .....	13
ACKNOWLEDGMENT .....	13
REFERENCES .....	13

**Abstract** Homochirality is a property of living systems on Earth. The time, the place, and the way in which it appeared are uncertain. In a prebiotic scenario two situations are of interest: either an initial small bias for handedness of some biomolecules arouse and progressed with life, or an initial slight excess led to the actual complete dominance of the known chiral molecules. A definitive answer can probably never be given, neither from the fields of physics and chemistry nor biology. Some arguments can be advanced to understand if homochirality is necessary for the initiation of a prebiotic homochiral polymer chemistry, if this homochirality is suggesting a unique origin of life, or if a chiral template such as a mineral surface is always required to result in an enantiomeric excess. A general description of the early Earth scenario will be presented in this chapter, followed by a general description of some clays, and their role as substrates to allow the concentration and amplification of some of the building blocks of life.

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## 1 The Early Earth Atmosphere and Lithosphere

The solar system condensed out of an interstellar cloud of gas and dust, known as the primordial solar nebula, about  $4.6 \times 10^9$  years ago. The formation of the inner planets was the result of innumerable impacts of small, rocky particles in the solar system's protoplanetary disk. Over a period of a few million years, neighboring dust grains and pebbles in the solar nebula coalesced into larger objects called planetesimals. Their mutual gravitational attraction brought a few of them together to form larger objects, known as protoplanets. The accretion of more material continued for another 100 million years and led to the formation of the terrestrial planets: Mercury, Venus, Earth, and Mars [1].

The theory of planet formation and the models that attempt to reproduce the early history of Earth indicate that the actual atmosphere is the third atmosphere to evolve [1]. The earliest Earth's atmosphere was composed of trace remnants of dihydrogen ( $H_2$ ) and helium (He) left over from the formation of the solar system, but it did not last very long as these gases are too light to be kept. They gained enough energy from the sunlight to overcome the Earth's gravitational attraction and moved away into space [1]. The gases of the second atmosphere came from inside the Earth, vented through volcanoes and cracks in its surface. The evidence indicates that this was a mixture of carbon dioxide ( $CO_2$ ), dinitrogen ( $N_2$ ), and water vapor ( $H_2O_v$ ), with trace amounts of  $H_2$  [2]. There was roughly 100 times as much gas in that second atmosphere as there is in the atmosphere today. Molecules such as  $CO_2$  and  $H_2O_v$  stored much more heat than the atmosphere does today, creating a greenhouse effect. The Sun had not reached its full intensity at that time, thus the high concentrations of these gases helped to prevent the young Earth from freezing.

Most of the water vapor that outgassed from the Earth's interior condensed out of the atmosphere to form the oceans. The rain absorbed and carried down lots of  $CO_2$  that was absorbed in the oceans. As life evolved most likely in the primitive oceans, much of the dissolved  $CO_2$  was transformed into carbonates ( $CO_3^{2-}$ ) that were trapped in the shells of many organisms [1]. It is estimated that for each molecule of  $CO_2$  presently in the atmosphere, there are about  $10^5$   $CO_2$  molecules incorporated as carbonates in sedimentary rocks [2]. What remained in the air were mostly  $N_2$  and  $H_2O_v$  [1]. Since  $N_2$  is chemically inert, sparsely soluble in water, and noncondensable, most of the outgassed  $N_2$  accumulated in the atmosphere over geologic time to become the atmosphere's most abundant constituent [2]. Some of the oxygen that entered into the early Earth atmosphere

came from oxygen-rich molecules, like  $\text{CO}_2$ , that were broken apart by the Sun's ultraviolet radiation. Then came the dioxygen ( $\text{O}_2$ ) released as a by-product of plant life activity. Early plant life in the oceans removed most of the remaining  $\text{CO}_2$  by converting it into dioxygen by photosynthetic processes. As  $\text{O}_2$ , in the triplet groundstate, is a thermodynamically highly reactive molecule, the early atmospheric  $\text{O}_2$  combined quickly with many elements on the Earth's surface, notably metals, to form metallic oxides such as iron oxides or silicon oxides. About  $2 \times 10^9$  years ago, after all of the surface minerals that could combine with  $\text{O}_2$  had done so, the atmosphere began to fill with this gas, and it became the nitrogen-oxygen mixture that we breathe today [1].

The early Earth atmosphere was a mildly reducing chemical mixture, whereas the present atmosphere is strongly oxidizing. It has been estimated that the current level of  $\text{O}_2$  in the atmosphere was achieved about 400 millions years ago [3].

## 1.1 Earth's Internal Structure

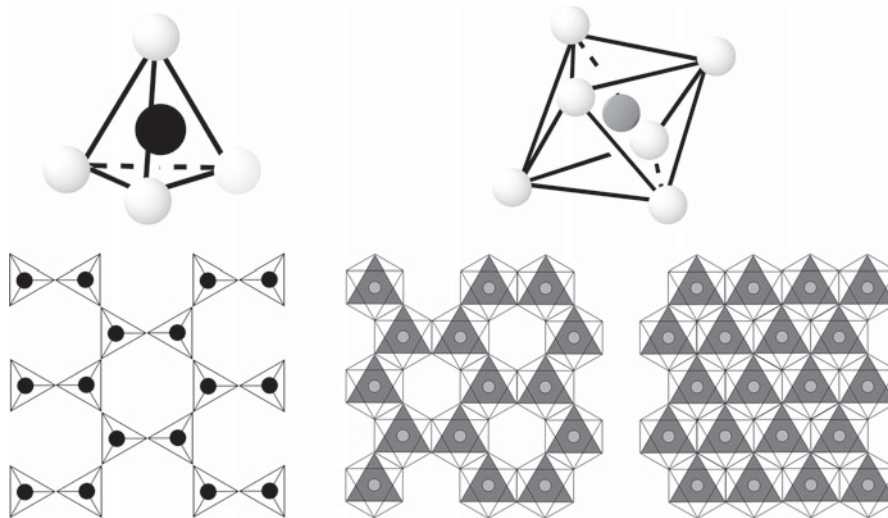
Seismic studies reveal that the Earth's interior is divided into three main layers differentiated by its rheological properties: the core, the mantle, and the crust.

The core is made of material of the highest density. It consists primarily of nickel and iron alloys. The Earth's core has two distinct regions, the solid inner core and the molten outer core. The core's density varies from 13.1 to 9.9  $\text{g/cm}^3$ . The mantle is formed by rocky material of moderate density, mostly silicate minerals rich in silicon, magnesium, and oxygen. Its density varies from 5.6 to 3.4  $\text{g/cm}^3$ . The mantle surrounds the core and makes up most of the Earth's volume. The uppermost layer consist of the lowest-density rocks such as granite and basalt whose density value can vary from 2.9 to 2.2  $\text{g/cm}^3$ , and forms the thin crust that is the Earth's outer skin [4].

In terms of rock strength, geologists define the Earth's outer layer as a relatively cool and rigid rock that floats on warmer, softer rock. This layer is called lithosphere, and encompasses the crust and the upper part of the mantle. The crust occupies less than 1 % of the Earth's volume and can be differentiated into the oceanic crust and the continental crust. The oceanic crust is made of high-density igneous rocks such as basalt, diabase (also called dolorite), and gabbro. It is only 5–10 kilometers thick and radiometric dating shows that it is quite young, with an average age of about 70 million years. Even the oldest seafloor crust is less than 200 million years old [5]. The continental crust thickness varies from 30 to 50 kilometers and is mostly composed of less dense rocks such as granite. The oldest continental crustal rocks on Earth have ages in the range of 3.7 to  $4.28 \times 10^9$  years. The continental crust has an average composition similar to that of andesite. It is enriched in elements such as oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium, principally found as oxides [5, 6].

## 2 Catalysts in the Early Earth

From the geological point of view the Earth's surface is continuously changing. An igneous rock is transformed under the action of high pressure or heat into a metamorphic rock, and both igneous and metamorphic rocks can be eroded into a sedimentary rock, which may be carried deep underground to be melted and then it resolidifies as an igneous rock. As all rocks on the Earth's surface are recycled, a rock's type gives information about the way it was made, while its mineralogical composition informs about its chemical nature. Among the naturally occurring inorganic minerals, phyllosilicate and smectite clays with layered structures are the most abundant [7]. Their generic aluminosilicate structure is composed of multiple silicate plates stacked in layers and crystalline defects with divalent metal species (counterions) in the interlayer galleries (Figure 1). In the smectites, the fundamental units are comprised of two tetrahedral sheets sandwiched with an edge-shared octahedral sheet building a 2:1 structure. Smectites have been well characterized with regard to their chemical composition, lamellar structure with high aspect ratio, geometric shape, surface area, and counter-ion exchange capacity [7]. The most representative phyllosilicate clays of the 2:1 type are montmorillonite, bentonite, saponite, and hectorite. They have conventionally been employed as catalysts, adsorbents, metal chelating agents, and polymer nanocomposites [7].



**Figure 1** Representation of the tetrahedral and octahedral patterns in phyllosilicate clay minerals. The basic tetrahedron and octahedron units are shown on top. The arrangement for the dioctahedral and trioctahedral sheets is also shown. Black circles represent silicon atoms, gray circles correspond to aluminum, magnesium or iron cations, and white circles correspond to oxygen atoms or hydroxyl groups. Based on [13].

Clay minerals could have formed by weathering of volcanic glass and rocks when getting in contact with water [8]. Investigations about Mars soils indicate the occurrence of clay minerals in the planet's surface older than  $3.5 \times 10^9$  years, with a

chemical composition consistent with Al-Si-O-H and Mg-Si-O-H systems [9]. By analogy, clay minerals could have formed in a similar way on the early Earth [8]. Clay minerals might also have formed as an alteration product of silicate minerals by igneous activity and also during diagenesis of sediments. As soon as liquid water appeared on the surface of the primitive Earth, clay minerals could have probably accumulated on the surface and became suspended in the primitive oceans [10].

Clay minerals are characteristic for near surface hydrous environments including those of weathering, sedimentation, diagenesis, and hydrothermal alteration. Within all of these environments clay minerals may have been newly formed, transformed, or inherited [11, 12]. There are two basic modular components on phyllosilicate clay minerals: (a) sheets of tetrahedrally, and (b) sheets of octahedrally coordinated atoms. Tetrahedral sheets are formed by a cation, usually silicon, surrounded by four oxygen atoms. An octahedral sheet is formed from two planes of closed packed oxygens and/or hydroxyl anions (Figure 1). In the center of such a sheet, and adjacent to every anion, there are three octahedral sites which may be occupied by metal cations, such as aluminum ( $\text{Al}^{3+}$ ), iron ( $\text{Fe}^{3+/2+}$ ), and magnesium ( $\text{Mg}^{2+}$ ), each cation being surrounded by six anions. Two kinds of common octahedral sheets are distinguished according to the cation to anion ratio needed for electrical neutrality. If divalent cations fill all three sites, the octahedral sheet is known as trioctahedral (Tri.). Trivalent cations need only two out of every three sites and thus form a dioctahedral (Di.) sheet. The basic crystal units known as layers, consist of tetrahedral (T) and octahedral (O) sheets. The 1:1 unit, also designated as T-O, is formed by linking one tetrahedral sheet with one octahedral sheet. An octahedral sheet between two tetrahedral sheets forms a 2:1 or T-O-T layer (Figure 1). A detailed description of these structures can be found in [13]. Any substitution in 1:1 layers is fully compensated and there is no net layer charge. Substitutions in a 2:1 layer, however, frequently give rise to a net negative charge, which may be neutralized by cations, or hydrated cations. Most clay minerals host two kinds of layers, such as illite-smectite or chlorite-smectite. Interstratification of three kinds of layers are rarely reported. A classification of some of the most representative phyllosilicate clay minerals based on layer type, and the magnitude of any net charge, is presented in Table 1. Cations required to compensate the net negative layer charges, may be exchanged with others. It is this property which defines the cation exchange capacity of the clay mineral.

**Table 1** Classification of common phyllosilicate clay minerals.<sup>a</sup>

Layer type	Layer charge (q)	Group	Examples
1:1	0.0	Kaolin-Serpentine	Kaolinite, Berthierine
2:1	0.0	Pyrophyllite-Talc	Pyrophyllite, Talc
	0.2–0.6	Smectite	Montmorillonite, Beidellite, Saponite
	0.6–0.9	Vermiculite	Di. Vermiculite*, Tri. Vermiculite*
	1.0	Mica	Illite, Muscovite, Biotite
	Variable	Chlorite	Sudoite, Chamosite, Clinocllore
	Variable	Sepiolite-Palygorskite	Sepiolite, Palygorskite
Variable	Variable	Mixed-layer	Rectorite, Corrensite

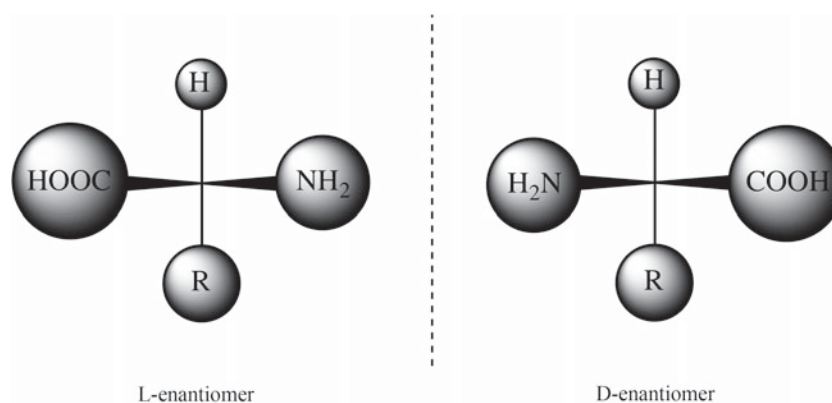
\* Di. = dioctahedral sheet. Tri. = trioctahedral sheet.

<sup>a</sup>Based on [13].

Clays have a particular place in studies related to enzyme immobilization, protein fractionation, soil ecosystem safety, genetic engineering, and specifically in the biochemical evolution and origin of life on Earth. In 1949, Bernal suggested that clay minerals played a key role in chemical evolution and the origins of life because of their uptake capability, their ability to protect against ultraviolet radiation, to concentrate, and to catalyze the polymerization of organic molecules [14]. A number of subsequent reports supported this idea. It was claimed that clay minerals such as montmorillonite, might have played a central role in the formation of proteins and nucleic acids serving as primitive templates to concentrate the primordial biomolecules and to catalyze their polymerization. Furthermore, they helped in the preservation of the first biopolymers that eventually initiated the biological evolution on Earth [15–20].

### 3 Clays as Possible Catalysts in the Synthesis of Biomolecules

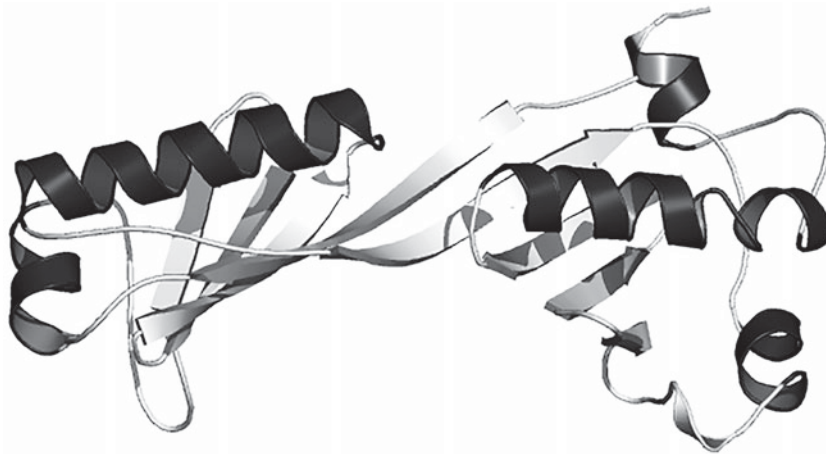
A distinctive feature of life's chemistry is its homochirality illustrated by amino acids and sugars, fundamental biomolecules for the construction of proteins and nucleic acids. A chiral molecule is a type of molecule that has a non-superimposable relationship with its mirror image. The feature that is most often the cause of chirality in molecules is the presence of one or several asymmetric carbon atoms. Chiral molecules can exist in two distinguishable mirror-image forms, designated as L- or D-enantiomers (optical isomers) (Figure 2).



**Figure 2** The two enantiomers of a generic  $\alpha$ -amino acid,  $\text{H}_2\text{N-CH(R)-COOH}$  ( $\text{R}$  = side-chain, see Table 2); L,D assignment is done with reference to glyceraldehyde,  $\text{HO-CH(CH}_2\text{OH)-CHO}$ . The structures are drawn as chemical standard structures, not as the typical zwitterionic forms that usually exist in aqueous solution.

Pairs of enantiomers are often described as right- and left-handed. To name the enantiomers of a compound unambiguously, their names must include the handedness of the molecule according to the R,S nomenclature (Cahn-Ingold-Prelog rules). Enantiomers have, when present in a symmetric environment, identical chemical and physical properties except for their interaction with polarized light (so-called optical activity). For example, an enantiomer will absorb left- and right-circularly polarized light to differing degrees, which is the basis of circular dichroism spectroscopy. To illustrate the three-dimensional structure of a chiral molecule by a two-dimensional drawing, one can use the projection already introduced by Emil Fischer in 1891. It is still in use today, particularly in the case of carbohydrates and amino acids [21].


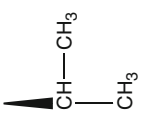
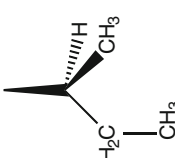

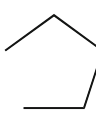
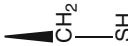
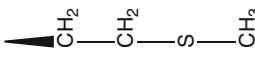
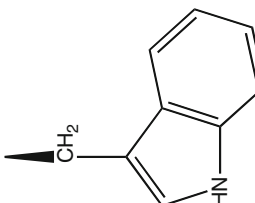
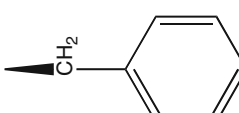
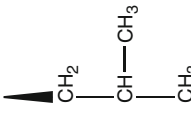
Proteins are all exclusively made of a series of L-amino acids, whose order dictates the primary structure. This homochirality leads to homochirality in higher-order structures such as the right-handed  $\alpha$ -helix found in some secondary structures or the way in which some proteins are folded to originate its tertiary structure (Figure 3). Table 2 presents the side-chain structures of the twenty standard amino acids.



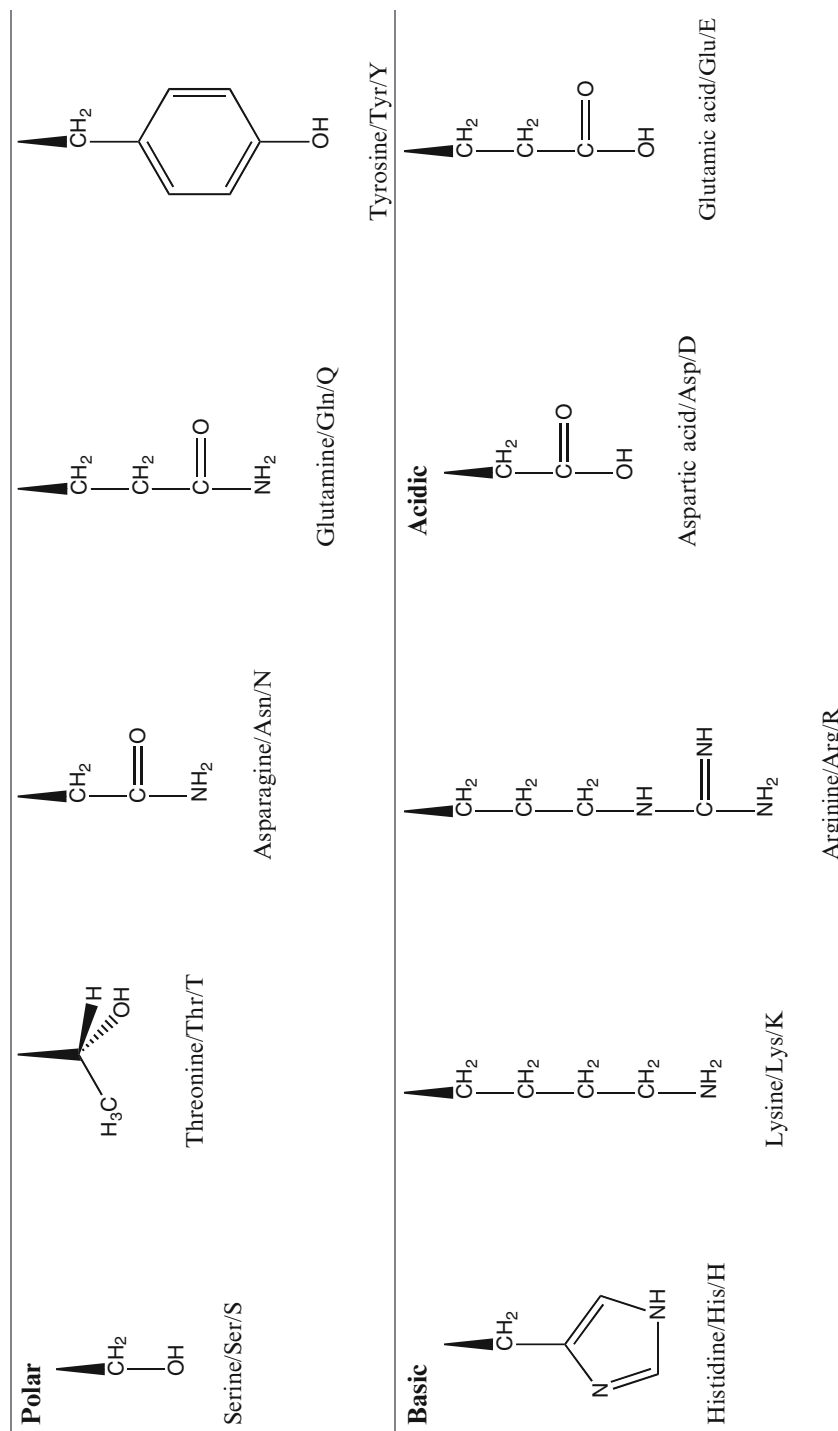
**Figure 3** Ribbon diagram for the tertiary structure of the TATA binding protein from *Taenia solium* showing its right-handed  $\alpha$  helices (in black). Redrawn from [48] by permission of R. Miranda.

On the other hand, nucleic acids consist of chains of deoxyribonucleosides (for deoxyribonucleic acid, DNA) or ribonucleosides (for ribonucleic acid, RNA), connected by phosphodiester bonds, all based exclusively on the D-deoxyribose or D-ribose sugar ring, respectively [22]. The homochirality in the monomeric sugar building blocks of nucleic acids leads to homochirality in their secondary structures such as the right-handed B-type DNA double helix, as shown in Figure 4.

**Table 2** Side chain residues (R) of the twenty standard amino acids,  $\text{H}_2\text{N}-\text{CH}(\text{R})-\text{COOH}$ .<sup>a</sup>

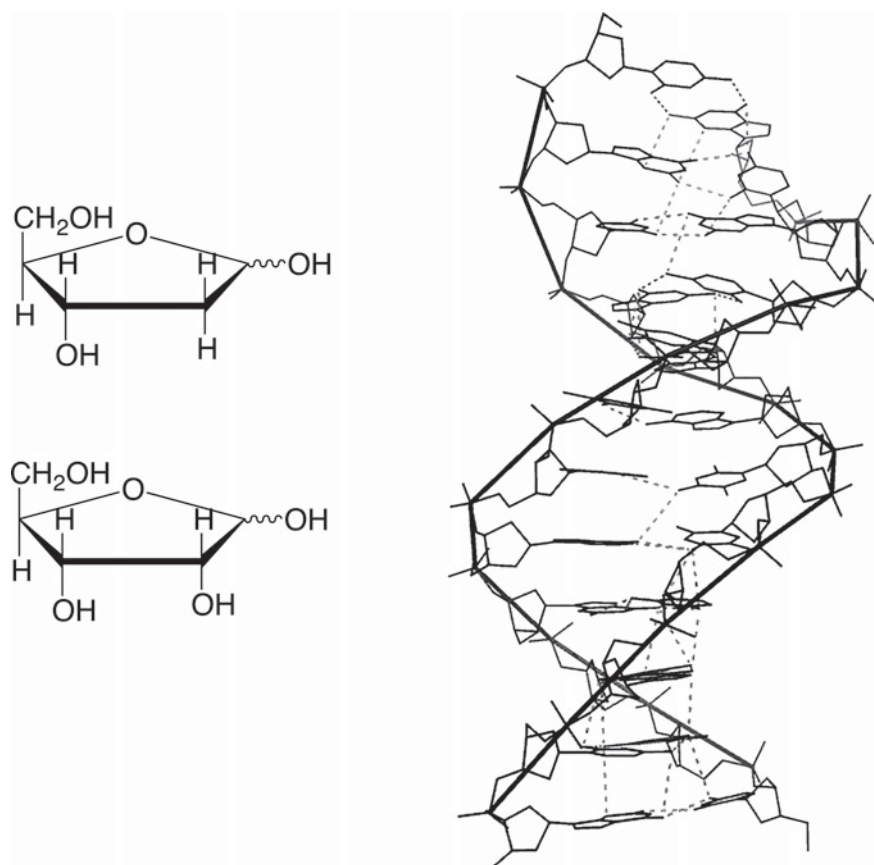
<b>Non polar</b>			
Glycine/Gly/G		Valine/Val/V	Isoleucine/Ile/I
			
Proline/Pro/P	Cysteine/Cys/C	Methionine/Met/M	Tryptophan/Trp/W
			
		Phenylalanine/Phe/P	Leucine/Leu/L





<sup>a</sup>Name of amino acid/3-letter code/1-letter code

Elucidating the origin of biological homochirality has occupied a central position on studies of the origin of life since the discovery of chiral symmetry by Pasteur [23, 24]. There is, however, no consensus on how an initial small bias for handedness arose and how a slight excess of handedness led to such a dominance of biological evolution on Earth. Researchers in this area have agreed to redefine the question of how homochirality arose into a search for an advantage factor that was capable of ensuring a large quantitative excess of one of the enantiomers over the other [24]. There exist many diverse suggestions for the nature of advantage factors, but they can be globally grouped into two classes, local and global. Local advantage factors might have existed in a particular region on the Earth's surface. They could have varied from region to region and/or might have existed during a definite period of time. On the other hand, global advantage factors are caused by the parity nonconservation in weak interactions. The action of the advantage factor might, in principle, lead to an almost chirally pure state of the medium [25].



**Figure 4** Structural model of a B-DNA right-handed double helix. The structural formula for 2-deoxy-D-ribofuranose (top), and D-ribofuranose (bottom) are shown on the left. They are the sugar components in DNA and RNA, respectively. The carbohydrate-phosphate “backbone” in the DNA dodecamer is highlighted in black. Hydrogen bonding between complementary bases is shown with dotted lines. Redrawn using the sequence PDB CODE = 156D reported in [49].

Although complete homochirality in the prebiotic chiral monomers may not be necessary for the initiation of prebiotic homochiral polymer chemistry, a small initial enantiomeric excess may be required. This small enantiomeric excess could be produced by some physical chiral influence. On a cosmic scale, enantioselective mechanisms depending on parity violation or circularly polarized light, are the only ones that could predetermine a particular handedness. In all other mechanisms, like a local chiral environment induced by a mineral surface, the ultimate choice would arise purely by chance [22]. That life evolved to use L-amino acids in proteins, and D-sugars in nucleic acids after it began remains a possibility, but there is considerable evidence that the formation of these biopolymers from homochiral material is necessary for them to function. Usually, in laboratory synthesis, unless special experimental conditions are used, a racemic (50:50) mixture of the D- and its L-enantiomer will be obtained when chiral molecules are formed from achiral starting materials. When a particular reagent or catalyst is added, an excess of one of the enantiomers can be used to direct the formation of more homochiral molecules. However, by which mechanism and when the first one-handed building block for life arose, still remains an open question [26].

Clay minerals have long been postulated to play a role in concentrating the products of non-biological organic processes leading to the Huxley-Darwin-Oparin-Haldane model for the origin of living systems. Because of their large surface areas and adsorption characteristics, clays can act as catalysts for the formation of RNA oligomers from activated nucleotide precursors. Furthermore, montmorillonite clay and alumina both catalyze polymerization of amino acids in peptide formation reactions [27]. Chiral selectivity has been demonstrated in experimental and theoretical studies. The layered structure of clays could also allow them to play a key role in concentrating, shielding and catalyzing the assembly of some of the most important molecules necessary for the development of living systems.

Clay minerals such as montmorillonite, kaolinite and illite (Table 1) represent a naturally abundant class of layered aluminum-silicates that are important in the context of prebiotic chemistry due to their good biocompatibility, strong adsorption, ion exchange ability, and expansibility [28], ancient origin and wide distribution. Different studies have demonstrated that they can absorb a variety of biomolecules including proteins, DNA, RNA, lipids, purines, pyrimidines [29–31].

Miller-Urey type experiments have been performed in the presence of montmorillonite, resulting in an increased yield of alkylated amino acids [32], or in the preferred synthesis of some specific compounds such as glycine, alanine, or aspartic acid [33]. Greenland and coworkers [34, 35] investigated different adsorption mechanisms of amino acids on  $H^+$ -,  $Na^+$ -, and  $Ca^{2+}$ -montmorillonite. They noticed that basic amino acids, such as arginine, histidine, and lysine (Table 2) were preferentially adsorbed on  $Na^+$ - and  $Ca^{2+}$ -montmorillonite by cation exchange, whereas non-polar amino acids such as alanine, serine, leucine, or phenylalanine, and acidic amino acids like aspartic acid and glutamic acid were adsorbed on  $H^+$ -montmorillonite by proton transfer. They also noticed that the adsorption of glycine and its oligopeptides onto  $Ca^{2+}$ -montmorillonite and  $Ca^{2+}$ -illite increased with the degree of oligomerization. Hedges and Hare [36] suggested that the amino and

carboxyl terminal groups of the amino acids were involved in their adsorption to kaolinite. Dashman and Stotzky [37, 38] reported that kaolinite was less efficient in the adsorption of amino acids and peptides than montmorillonite. Other clay minerals, such as serpentine, can adsorb measurable quantities of aspartic and glutamic acid [39], whereas allophane can take up appreciable amounts of alanine [40].

The adsorption of nucleic acid bases on clay minerals has also been investigated. Lawless et al. and Banin et al. [41, 42] described the adsorption of adenosine monophosphate (5'-AMP) by montmorillonite in the presence of different metal cations and variation of the medium acidity. They found a maximum adsorption on  $Zn^{2+}$ -montmorillonite at a pH value close to neutrality. Winter and Zubay [43] found that montmorillonite adsorbed more adenine than adenosine, 5'-AMP, 5'-ADP, or 5'-ATP, while hydroxyapatite preferably adsorbed 5'-AMP compared to adenine or adenosine. They also found an adsorption dependence on the acidity of the medium. Other types of clay minerals have also been examined. Hashizume and Theng [44] found that allophane exhibited a greater affinity for 5'-AMP over adenine, adenosine or ribose.

The transformation of formaldehyde, the simplest aldehyde (HCOH), into complex sugars like ribose and from there to nucleic acids (e.g., RNA) in experiments simulating the early Earth conditions was proposed by Butlerov in 1861 under the name of formose reaction [45]. Clay minerals, such as montmorillonite and brucite can catalyze the self-condensation of formaldehyde and even more important, montmorillonite can stabilize several of the formed oligomers [46, 47].

Fraser and colleagues [27] have shown that vermiculite clay gels with large interlayer spacing act as amplifiers that sequentially change the D/L ratios of solutions containing the amino acids alanine, lysine, and histidine. A proposed natural ancient scenario for their results could be a clay-rich lagoon containing simple prebiotic molecules. The continuous repetition of D/L fractionation like the one they found, over geological periods of time, could lead to clay/solution nanofilm multilayers with amino acids having a chiral excess. Alternatively, chiral excess could have originated under the physicochemical conditions of interstellar space, or could have been produced in a modified type of Miller-Urey synthesis in the presence of polarized light or dust particles with chiral centers. Such activated clay films have the capacity to concentrate and to induce significant chiral separation of amino acids. They propose that such a mechanism could be the reason for the chiral selectivity observed for the rare amino acid isovaline in the Murchinson or Orgueil meteorites [27]. The discovery of isovaline (2-amino-2-methylbutanoic acid) in the biosphere suggests an extraterrestrial origin of amino acids and has been linked to the homochirality of life on Earth [50].

## 4 General Conclusions

Clay minerals formed since early geological times on Earth and were widely distributed. Due to their catalytic and adsorption properties, they have played a significant role in the search for an explanation of a biology dominated by L-amino

acids and by D-sugars. Clays have also offered a catalytic surface beneficial to the aggregation and preservation of the first biopolymers. Even when an extensive number of experiments have validated these functions, the specific conditions dominating the early Earth scenario are difficult to find in laboratory simulations. Perhaps a definitive answer for the specific role of clays in the prebiotic chemistry of the early Earth will never be found. Whether they offer an initial bias for handedness or just a surface that preferentially favored the domination of handedness on Earth, is a question that still requires further investigation.

## Abbreviations

5'-AMP	adenosine monophosphate
5'-ADP	adenosine diphosphate
5'-ATP	adenosine triphosphate
H <sub>2</sub> O <sub>v</sub>	water vapor

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## References

1. N. F. Comins, W. J. Kaufmann, *Discovering the Universe*, W. H. Freeman and Co., New York, 2008.
2. J. H. Seinfeld, S. N. Pandis, *Atmospheric Chemistry and Physics. From Air Pollution to Climate Change*, 2nd edn., John Wiley & Sons Inc., Chichester, UK, 2006.
3. P. Cloud, *Sci. Amer.* **1983**, *249*, 176–189.
4. T. H. Jordan, *Proc. Natl. Acad. Sci. USA* **1979**, *76*, 4192–4200.
5. T. Tanimoto, in *Global Earth Physics: A Handbook of Physical Constants*, Ed T. J. Ahrens, American Geophysical Union, Washington, D. C., 1995, pp. 214–224.
6. R. L. Rudnick, S. Gao, in *The Crust*, Vol. 3 of *Treatise on Geochemistry*, Eds H. D. Holland, K. K. Turekian, Elsevier-Pergamon, Oxford, UK, 2003, pp. 1–64.
7. C.-W. Chiu, J.-J. Lin, *Progr. Polymer. Sci.* **2012**, *37*, 406–444.
8. H. Hashizume, in *Clay Minerals in Nature: Their Characterization, Modification and Application*, Eds M. Valaskova, G. S. Martynkova, *InTech*, **2012**, pp. 191–208.
9. T. F. Bristow, R. E. LMilliken, *Clays Clay Miner.* **2011**, *59*, 339–358.
10. C. Ponnampuruma, A. Shimoyama, E. Friebele, *Orig. Life* **1982**, *12*, 9–40.
11. G. Millot, *The Geology of Clays*, Masson, Paris, 1970.
12. D. D. Eberl, *Phil. Trans. Roy. Soc.* **1984**, *A311*, 241–257.
13. S. Hillier, in *Clay Mineralogy, Encyclopaedia of Sediments and Sedimentary Rocks*, Eds G. V. Middleton, M. J. Church, M. Coniglio, L. A. Hardie F. J. Longstaffe, Kluwer Academic Publishers, Dordrecht, 2003, pp. 139–142.
14. J. D. Bernal, *Proc. Phys. Soc. B London*, **1949**, *62*, 597–618.
15. R. Saladino, C. Crestini, U. Ciambecchini, F. Ciciriell, G. Costanzo, E. Di Mauro, *Chembiochem* **2004**, *5*, 1558–1566.

16. J. P. Ferris, *Orig. Life Evol. Biosph.* **2002**, *32*, 311–332.
17. J. P. Ferris, A. R. Hill, R. Lis, L. E. Orgel, *Nature* **1996**, *381*, 59–61.
18. M. Franchi, E. Gallori, *Gene* **2005**, *346*, 205–214.
19. W. Huang, J. P. Ferris, *Chem. Commun.* **2003**, *21*, 1458–1459.
20. M. M. Hanczyc, S. M. Fujikawa, J. W. Szostak, *Science* **2003**, *302*, 618–622.
21. N. E. Schore, K. P. C. Vollhardt, *Organic Chemistry Structure and Function*, 6th edn., W. H. Freeman and Co., New York, 2011, pp. 169–214.
22. L. D. Barron, *Space Sci. Rev.* **2008**, *135*, 187–201.
23. L. Pasteur, *C. R. Acad. Sci. Paris* **1848**, *26*, 535–538.
24. L. Pasteur, *Anal. Chim. Phys.* **1848**, *24*, 442–459.
25. V. A. Avetisov, V. I. Goldanskii, V. V. Kuz'min, *Physics Today* **1991**, 33–41.
26. S. P. Fletcher, *Nat. Chem.* **2009**, *1*, 692–693.
27. D. G. Fraser, H. G. Greenwell, N. T. Skipper, M. V. Smalley, M. A. Wilkinson, B. Demé, R. K. Heenan, *Phys. Chem. Chem. Phys.* **2011**, *13*, 825–830.
28. C. H. Zhou, *Appl. Clay Sci.* **2011**, *53*, 87–96.
29. P. Cai, Q. Huang, M. Li, W. Liang, *Colloids and Surfaces B: Biointerfaces* **2008**, *62*, 299–306.
30. E. Biondi, S. Branciamore, L. Fusi, S. Gago, E. Gallori, *Gene* **2007**, *389*, 10–18.
31. L. Perezgasga, A. Serrato-Díaz, A. Negrón-Mendoza, L. de Pablo Galán, F. G. Mosqueira, *Orig. Life Evol. Biosph.* **2005**, *35*, 91–110.
32. A. Shimoyama, N. Blair, C. Ponnampereuma, in *Synthesis of Amino Acids under Primitive Earth Conditions in the Presence of Clay. Origin of Life*, Ed. N. H. Noda, Center for Academic Publisher, Tokyo, 1978, pp. 95–99.
33. S. Yuasa, *Nendo Kagaku*, **1989**, *29*, 89–96.
34. D. J. Greeland, R. H. Laby, J. P. Quirk, *Trans. Faraday Soc.* **1962**, *58*, 829–841.
35. D. J. Greeland, R. H. Laby, J. P. Quirk, *Trans. Faraday Soc.* **1965**, *61*, 2024–2035.
36. J. I. Hedges, P. E. Hare, *Geochim. Cosmochim. Acta* **1987**, *51*, 255–259.
37. T. Dashman, G. Stotzky, *Soil Biol. Biochem.* **1982**, *14*, 447–456.
38. T. Dashman, G. Stotzky, *Soil Biol. Biochem.* **1984**, *16*, 51–55.
39. H. Hashizume, *Viva Origino* **2007**, *35*, 60–65.
40. H. Hashizume, B. K. G. Theng, *Clay Minerals* **1999**, *34*, 233–238.
41. J. G. Lawless, A. Banin, F. M. Church, J. Mazzurco, R. Huff, J. Kao, A. Cook, T. Lowe, J. B. Orenberg, *Orig. Life* **1985**, *15*, 77–87.
42. A. Banin, J. G. Lawless, J. Mazzurco, F. M. Church, L. Margulies, J. B. Orenberg, *Orig. Life* **1985**, *15*, 89–101.
43. D. Winter, G. Zubay, *Orig. Life Evol. Biosph.* **1995**, *25*, 61–81.
44. H. Hashizume, B. K. G. Theng, *Clays Clay Miner.* **2007**, *55*, 599–605.
45. M. A. Butlerov, *C. R. Acad. Sci. Paris* **1861**, *53*, 145–147.
46. N. W. Gabel, C. Ponnampereuma, *Nature* **1967**, *216*, 453–455.
47. R. Saladino, V. Neri, C. Crestini, *Philos. Mag.* **2010**, *90*, 2329–2337.
48. R. Miranda, *Estudio de la región carboxilo terminal de la proteína de unión a caja TATA de Taenia solium*, Bachelor thesis, Universidad Nacional Autónoma de México, México, 2013.
49. H. R. Drew, R. M. Wing, T. Takano, C. Broka, S. Tanaka, K. Itakura, R. E. Dickerson, *Proc. Natl. Acad. Sci. USA* **1981**, *78*, 2179–2183.
50. J. R. Cronin, S. Pizzarello, *Adv. Space Res.* **1999**, *23*, 293–299.