Synthesis and preservation of organic molecules with homochiral excess by adsorption on carbon in carbonaceous chondrites

Abstract. The nature of carbon, initial components, molecules of organic and homochiral abiogenic synthesis and their preservation from decay and racemization for more than 4.5 billion years in carbonaceous chondrites has not been established. In the oxygen-free atmospheres of the nebula and the early Earth, H_2 and gases with H were oxidized with CO and CO_2 to form carbon and H_2O and intermediates H_2CO and HCOOH, which together with NH_3 were the initial components of organic synthesis. According to the Rebinder rule, carbon adsorbs hydrogen well. Its adsorption properties in organic molecules with radicals of CH are close to hydrogen due to a small difference in electronegativity in CH, so experiments with the assumed conditions of the early Earth were carried out by adsorption on carbon. R-(rectus, Latin) ribose was obtained from H_2CO, and S-(sinister) serine from three initial components. For other S-amino acids, a stereo chemical justification of their formation based on S-serine is given. For carbonaceous chondrites, the experiments results were confirmed by the correlation between the amount of hydrogen and homochiral excess with a coefficient of 0.94 for aldonic acids and lactic acid and 0.85 for amino acids. Justification of the homochiral process will allow costs of searching for life on planets, for scientific research, for the production of medicines, perfumes, food, and so on. Basically, doubts about the extraterrestrial origin of homochiral enantiomers in carbonaceous chondrites are caused by ignorance of the reasons for their appearance. This work will significantly reduce such skepticism.

Keywords: *nebula, chondrites, carbon, adsorption, enantiomers, homochirality, preservation*.

1. INTRODUCTION

The preservation of organic matter is provided by a thin vitreous heat-protective crust, which is identified in meteorites after a fall. The problems of the nature of carbon, the initial components of organic synthesis, the appearance and preservation of homochiral molecules from racemization remain unresolved. In the absence of oxygen, H_2 and gases with H could be oxidized by CO_2 and CO to form of H_2O and carbon (reactions 1 – 4, 7, Table 1) or intermediates HCOOH (formic or methane acid) and H_2CO (reactions 5, 6, 8, 9, Table 1), which with NH_3 were the initial components of abiogenic organic synthesis [1]. In experiments, formaldehyde was a universal starting component in the synthesis of amino acids and sugars. The formation of amino acids racemates has been established with a content from 10^{-4} to $5x10^{-3}$ mol in a solution with 2.5% H_2CO (formaldehyde or methanal) and 1.0 – 1.5% NH_4NO_3 or NH_4C1 at a temperature of 313 – 318 K [2]. For the first time, sugars from H_2CO were obtained in 1861 by A.M.

Butlerov. Ribose from H_2CO was synthesized with high yield in the presence of apatite as a catalyst in an Ar atmosphere at pH-7.3 and a temperature of 313 K and [3]. Previously, the possibility of the formation of fatty acids and nitrogenous bases was shown with the disproportionation of H2 CO [3]. H_2CO is installed in the atmosphere of Mars [4] in the interstellar medium and comets [5] in carbonaceous chondrites [6] and in volcanic gases.

According to the Rebinder rule, carbon adsorbs hydrogen well, and in organic molecules its adsorption properties [7] are close to hydrogen due to a small difference in electronegativity in CH. This made it possible to obtain R-ribose and S-serine (reaction 10, Table 1) in experiments by adsorption on carbon with stereo chemical justification [1, 8].. Other S-amino acids were formed on the basis of S-serine during the disproportionation of $H_2C(OH)_2$ (metanediol, H_2CO in water) molecules, as shown by the example of the formation of alanine (reaction 11, Table 1) and phenylalanine (reaction 12, Table 1). Homochirality in other optical isomers (for example, in glucose) could arise during evolution. Adsorption on carbon provided for organic synthesis: the concentration of the initial components, the formation of only R-ribose and S-amino acids, hydrophobic-hydrophilic properties, protection from hydration, decomposition and racemization [1, 8]. Racemization of free homochiral molecules depends on many factors and proceeds rapidly, therefore, their preservation in carbonaceous chondrites for more than 4.5 billion years is paradoxical. The appearance and preservation of enantiomers with homochiral excess in nebula is discussed below in comparison with terrestrial processes.

2. MATERIALS AND METHODS

2.1 The extraterrestrial nature of enantiomers with homochiral excess in carbonaceous chondrites

Organic substances are known in the interstellar medium and comets [5], therefore their extraterrestrial nature in carbonaceous chondrites, and hence homochiral molecules, is beyond doubt. Doubts about the nature of enantiomers with homochiral excess in carbonaceous chondrites arise most often due to the lack of clarity of the processes of their appearance, which is justified below. In addition, the extraterrestrial nature of these enantiomers is confirmed by the isotopic ratios of C, N_2 and H_2 [5, 9 – 11]. The same nature is indicated by the complete absence of high-molecular organic compounds in carbonaceous chondrites (peptides, proteins, organophosphorus compounds, RNA, etc.). The ice of Antarctica in meteorite impact sites and beyond contains organic matter in trillionths, which is most likely due to meteorite dust [12], and the content of various amino acids in carbonaceous chondrites is millions of times higher than in ice. Carbonaceous chondrites contain about 15 sugar acids and about 75 amino acids not found in the biosphere [10], as well as bio-inverse enantiomers. One meteorite may contain racemates, molecules with bio- and reverse excess, which is not typical of the biosphere.

2.2. Initial components and products of homochiral synthesis in carbonaceous chondrites

The conditions in the nebula make it possible to study planetary regularities and the composition of carbonaceous chondrites. Differentiation of gases in the nebula caused the maxima of their relative abundances (mass of atmospheric gas / mass of the planet) with distance from the Sun for Venus (v) - CO_2, Earth (e) - H_2O (taking into account exospheres) and Jupiter (j) - H_2 [13]. Mathematically, it is expressed in close ratios of the molecular masses of gases (M) to the distances to the Sun (R): $(M_{CO2}/M_{H2O})/(Re/Rv) = (44/18)/(149.5 \text{ x } 10^6)/(108 \text{ x } 10^6) = 1.77$, $(M_{H2O}/M_{H2})/(Rj/Re) = (18/2)/(778 \text{ x } 10^6)/(149.5 \text{ x } 10^6) = 1.73$ or $(M_{H2O}/M_{H2})/(M_{CO2}/M_{H2O}) = 3.69$ and $(Rj/Re)/ (Re/Rv) = 3.77$.

Carbonaceous chondrites are divided into several types depending on the composition and the formation temperature from ~ 1150 – 1200 K to the temperature of the existence of liquid water [14, 15]. These chondrites contain carbonates [14, 15] that indicate the presence of CO_2 in the nebula. The average contents of carbon and water in the main types of carbon chondrites [14] has an almost direct linear relationship. Such dependence could be realized in the nebula in the reactions of H_2 and gases with H with CO and CO_2 with their activation by solar radiation [16] and optimal temperatures. The products of the reactions (reactions 1 – 6, Table 1) were carbon, H_2O, or intermediates of H_2CO and HCOOH, the yield of which increased at temperatures below 970 – 940 K. Like reactions could occur in water (reactions 7 – 9, Table 1). H_2CO and HCOON together with NH_3 were the initial components for organic synthesis during adsorption on carbon [3] and which were identified in the investigated carbonaceous chondrites.

The existing classifications of carbonaceous chondrites take into account an increase in the content of carbon and organic substances with a decrease in temperature in the nebula [14, 15], which reflects the recovery of CO_2 and the mutual relationship of the formation of carbon and organic substances (reactions 1 – 7, Table 1). H_2CO was found in 12 carbonaceous chondrites studied from 0.1 to 18 mg/g [6, 11], and HCOOH in chondrite of Lake Tagish from 209 to 378 mg/g [11] and in the composition of monocarboxylic acids in other chondrites [5]. Ammonia was identified in 6 carbonaceous chondrites from 0.5 to 10 mg/g [9] and in the composition of amino acids. Organophosphorus compounds with H_3PO_4 have not yet been identified. These initial components were in the nebula at pressures from lgP = –3 to –5 bar [14] in gaseous state or in solution in carbonaceous chondrites with condensed water.

Carbonaceous chondrites contain pentoses, sugar alcohols, acids, and more than 100 types of amino acids, as well as other organic compounds. Among them, a homochiral excess is often found. For example, amino acids with S-excess are found in 24 out of 24 studied carbonaceous chondrites, and in one of them R-alanine predominates by 12% [5]. 33 amino acids were found in Lake Tagish chondrite, but homochiral S-excess was studied and revealed in 10 types, and its excess is in alanine (%) 22, in isovaline - 13 and in valine - 97.7 [11]. According to the review [10], out of 101 identified amino acids in carbonaceous chondrites S-excess was found in 23 from 1 to 99% of 28 studied and 5 are represented by racemates, 13 were achiral, homochirality not studied in 60. In the composition of 101 amino acids, 75 types are characteristic only for meteorites. Homochiral R-excess found in 2 aldonic acids with 3 CH (or CH_2) radicals from 33 to 55%, in 4 with 4 radicals from 47 to 100%, and in 6 with 5 radicals of 100% each. S-excess of 3 to 12% is noted in lactic acid. S-excess of 7% and an R-excess of 3% identified in the alanine of one meteorite. R-excess is present in allo-isotreonine up to 8% and from 12 to 60% in allo-isoleucine. The listed compounds with a biologically inverse homochiral excess contain an asymmetric CH_3 radical relative to hydrogen at the central carbon atom (H^1, Fig. a) and two radicals in allo-isoleucine.

2.3. Initial components and conditions of the origin of life on Earth

Planetary regularities show that the Earth's atmosphere in the early Archean did not qualitatively differ from the atmospheres of Venus and Mars and consisted of CO_2, N_2 and other gases in descending order, as on Venus: SO_2, CO, Cl_2, HCl, H_2S, CH_4, H_2, NH_3 [17]. The Martian atmosphere contains H_2, CH_4, NH_3, and H_2CO [4]. The volcanic gases of the Earth have a similar composition. Of 108 samples for 6 volcanoes [18], the average content of gases without H_2O is (%): CO_2 - 58.7, SO_2 - 20.1, H_2 - 7.7, HCl - 6.7, CO - 5.1, HF - 0.58, H_2S - 0.41, NH_3 - 0.16, CH_4 - 0.016, sometimes OCS, CS_2 H_2CO and others are noted. Carbon, carbohydrates and amino acids were found in the products of volcanic eruptions with an abiogenic nature according to isotopic data [18]. Volcanoes during the degassing of terrestrial planets determined the composition of the atmospheres in the Archean. The composition of volcanic gases is

Table 1. The most likely reactions the formation organic molecules and carbon.

№	Reactions	$\lg K_T^*$ at T, K		
		298	323	348
1	$CO_g+H_2O_g=CO_{2g}+H_{2g}$	5.1	4.6	4.1
2	$CO_{2g}+2H_{2g}=2H_2O_{liq}$	14.0	11.6	8.9
3	$CO_{2g}+CH_{4g}=2H_2O_{liq}+2C_{gr}$	5.1	3.7	2.5
4	$3/2CO_{2g}+2NH_{3g}=3H_2O_{liq}+3/2C_{gr}+N_{2g}$	15.1	12.7	10.7
5	$3/2CO_{2g}+2NH_{3g}=H_2CO_g+2H_2O_{liq}+1/2C_{gr}+N_{2g}$	7.1	7.0	6.9
6	$2CO_{2g}+2NH_{3g}=HCOOH_{fl}+2H_2O_{liq}+C_{gr}+N_{2g}$	2.7	1.1	-0.3
7	$CO_{2s}+2H_2S_s=2H_2O_{liq}+C_{gr}+2S_{cr}$	5.7	4.6	3.7
8	$HCO_3^-+2HS^-+H^+=H_2CO_s+2H_2O_{liq}+2S_{cr}$	7.1	7.2	7.3
9	$2HCO_3^-+HS^-+2H^+=HCOO^-+CO_{2s}+2H_2O_{liq}+S_{cr}$	8.7	8.6	8.5
10	$CH_2(OH)CH(OH)_{2a}+HCOONH_4={}^+NH_3CHCH_2OHCOO_a^-+2H_2O_{liq}$	-	-	-
11	▬$CH_2OH+H_2C(OH)_2+HCO_3^-=$ ▬$CH_3+HCOO^-+H_2O_{liq}+H_2CO_3$	pH 6.3-7.5		
12	▬$CH_2OH+12H_2C(OH)_2+12HCO_3^-=$ ▬$CH_2C_6H_5+6HCOO^-+13H_2O_{liq}+12H_2CO_3$	pH 6.3-7.5		

*Notes: g-gas, s-solution, gr-graphite, liq-liquid, cr-crystal a-adsorbed.*Approximate values.* ▬*chemical bond.* ▬*CH_2OH serine radical. (Thermodynamic potentials [19 – 21].*

similar to the composition of comets [5], gases in carbonaceous chondrites and their minerals [14, 15], therefore, the initial components of the abiogenic synthesis of the Earth and the nebula were identical.

Organic synthesis could have arisen on Earth with the appearance of sedimentary rocks and water basins 3.7 – 3.8 billion years ago. Typical sedimentary rocks of this period are rare and contain carbon and carbonates [22], apparently due to the small amount of water and basins on the planet. The CO_2 pressure in the atmosphere was about 50 – 60 kPa, and the temperature was close to 310 – 320 K [23, 24]. The height of the Archean troposphere could be about 6.5 km, which is 1.7 times less than its current average height of 11 km (from the comparison of the modern homogeneous atmosphere with the atmosphere from CO_2 at pressure of 55 kPa by the formula $H=P_0/\rho \times g$, where P_0 and ρ are the pressure and density at sea level, g - is the acceleration of gravity). These factors provided sharp daily temperature changes up to 25 – 35 K (as in tropical deserts) with change in the solubility of gases and pH (hydrogen index) in small pools.

The totality of the above data allows us to identify the main factors the emergence of life on Earth. During the accretion of planets, the distance of the Earth from the Sun determined the maximum concentration of water on it and, together with the content of greenhouse gases in the atmosphere, the optimal temperature for its existence in liquid form. The appearance of H_2CO and HCOOH was facilitated by the mass of the planet, which prevented dispersion of H_2 into space, as well as the predominance of CO_2 pressure in the atmosphere over the sum of pressures of H_2 and gases with H (but with P_{H2} exceeding the minimum for reactions with CO_2, at $P_{CO2} = 0.55$ bar, $P_{H2} > 10^{-6.8}$ from reaction 2 of Table 1).

3. RESULTS AND DISCUSSION

3.1. Synthesis and preservation of enantiomers with homochiral excess by adsorption on carbon in carbonaceous chondrites

The age of chondrites varies from 4.5 to 4.575 billion years [14]. The time of racemization of asparagine at 252 K is estimated at 20 million years, and in the shell of mollusks with an age of one million years, the ratio of R to S amino acids was: for asparagine - 0.88, alanine - 0.95, valine - 0.85 [10]. Half of the racemization cycle varies from 500 to 180,000 years for 11 amino acids from the composition of proteins [25]. Long-term conservation of homochirality in enantiomers could be achieved by fixing them on a solid material and at low temperatures. The most accessible method of fixation is adsorption, and the most effective adsorbent in carbonaceous chondrites is carbon. An increase in the number of hydrogen atoms in 3 alkanes and 5 alcohols was accompanied by an increase in their adsorption from solutions (experiments with alkanes were performed 4 times on 4 brands of coal, and with alcohols 5 times on 5 brands of coal) [7]. Therefore, in the homochiral synthesis of molecules by adsorption on carbon, there must be a correlation between the number of hydrogen atoms and the homochiral excess.

The significant correlation coefficients between the number of hydrogen atoms in aldonic acids and lactic acid and the average values of the homochiral excess are 0.94 and 0.85 for amino acids (Table 2). The correlation coefficients show that the homochiral synthesis of enantiomers was carried out by adsorption on carbon. Correlation is also noted for homochiral excesses and molecular weights of aldonic

Table 2 Initial data for calculating the correlation coefficients and the regression equations.

№	Enantiomers	Quantity H atoms	Average homochiral	Number determinations	References
	Lactic and aldonic acids		% R-excess		
1	Lactic acid	3	- 6 (S-excess)	4*	[10]**
2	Erythronic acid	4	54.0	1	– // –
3	Threonic acid	4	43.7	4	– // –
4	Ribonic acid	5	57.0	1	– // –
5	Arabinonic acid	5	53.5	2	– // –
6	Xylonic acid	5	91.0	2	– // –
7	Lyxonic acid	5	80.5	2	– // –
8	Allonic acid	6	100.0	1	– // –
9	Altronic acid	6	100.0	1	– // –
10	Gluconic acid	6	100.0	2	– // –
11	Idonic acid	6	100.0	1	– // –
12	Galactonic acid	6	100.0	2	– // –
13	Talonic acid	6	100.0	2	– // –
	Amino acids		% S-excess		
1	Serine	5	46.4	8***	[5, 10, 11]
2	Aspartic	5	57.5	14	[5, 10,11]
3	Alanine	6	35.5	11	[5, 10, 11]
4	Threonine	7	68.0	3	[10]
5	Glutamic	7	67.4	16	[5, 11]
6	Proline	8	65. 0	2	[10]
7	Valine	10	96.0	2	[11]

*Notes. *Sample from 24 lactic and aldonic acids, and 53 amino acids. **The accuracy of the definition is not given. ***Values were excluded if the accuracy of the determination was close to racemates.*

acids and lactic acid due to their proportionality to the amount of hydrogen, but in its absence there is no correlation in amino acids. Enantiomers with homochiral excess could not appear and persist in the nebula without carbon protection from radiation and collisions. Complex organic molecules (sugars, amino acids, etc.) are unknown in interstellar [5].

The increase in homochiral excesses and the number of hydrogen atoms in the molecules indicates the fixation of hydrogen on carbon, what ensured their preservation for more than 4.5 billion years in carbonaceous chondrites at low temperatures. 99.8% of meteorites come from the asteroid belt, where the temperature varies depending on the distance of the orbit to the Sun from 165 to 190 K. It was even lower at the early luminosity of the Sun. At these temperatures, racemization of enantiomers could occur in molecules with weak adsorption adhesion after desorption, which depends on the number of adsorbed hydrogen atoms. Desorption of enantiomers could occur due to the penetration of high-energy cosmic rays and internal radioactive decay, or due to strong heating of the frontal part and impact during falls.

3.2. Synthesis and preservation of enantiomers with biologically reverse homochirality

The asymmetric position of CH_3 radicals in the structure of enantiomers relative to H^1, as in alanine (Fig. a), could lead to bio-inversion and fixation of the reverse homochiral excess only on non-mobile molecules, that is, by adsorption on carbon. Otherwise, only equilibrium racemates would be preserved. The effect of asymmetry in the structure of the enantiomer on its inversion confirmed by an increase in the homochiral R-excess from 3 – 12% in amino acids with one asymmetric CH_3 radical to 60% with two such radicals in allo-isoleucine. In valine, the excess of S reaches 97.7% [11] with the symmetrical position of two CH_3 radicals. The radical appears after all groups in amino acids upon adsorption on carbon [3]. H^4 was formed instead of serine hydroxyl (Fig. a, reaction 11, Table1) with an asymmetric position relative to H^1. The asymmetric position of H^4 in the carbon adsorption force field and the dipole effect of O^1 could lead to the rotation of groups C^1 and C^2 counterclockwise (from C^2) with the

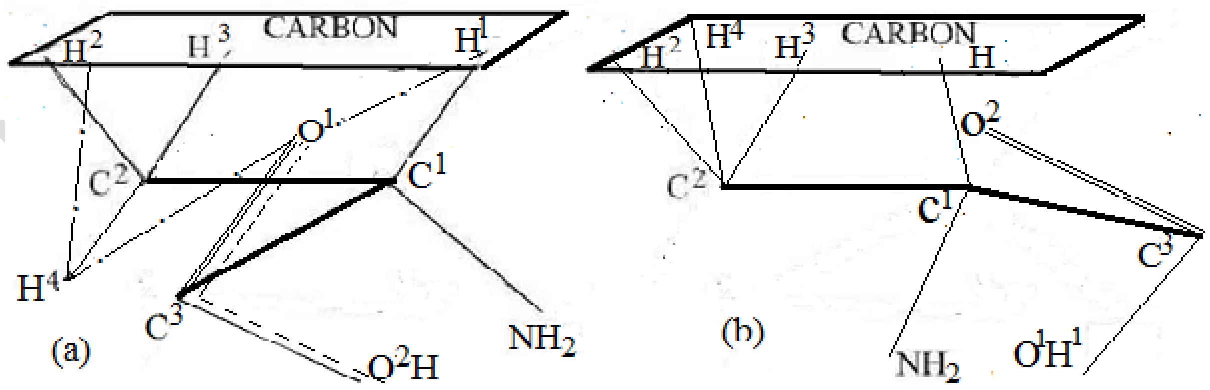

Figure. Structural diagram of the formation of R-alanine during adsorption on carbon. (a) S-alanine at the time of formation of H^4 (dash-dotted lines - directions of interaction, dash line - direction of electron transfer at the time of formation hydroxyl O^1H^1), (b) R-alanine after inversion of group C^3.

convergence of O^1 with H^1 due to the delay of H^1 adsorption. This led to the homolytic break of the C^1-H1 bond with the formation of hydroxyl O^1-H^1 and the C^1-C^3 bond instead of C^1-H1. At the same time, an excess electron appeared, the transfer of which from O^1 to O^2 determined the occurrence of a C^3-O^2 bond and a C^1-H bond instead of C^1-C^3 (Fig. b), probably as during racemization, but with the fixation and preservation of a new structure by adsorption on carbon.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

4. CONCLUSIONS

The processes of abiogenic homochiral synthesis on the early Earth and in carbonaceous chondrites were carried out by adsorption on carbon and were identical. The difference, apparently, was in the volume of water and in the absence of organophosphorus compounds in the nebula.

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