REVIEW

The evolution of organic matter in space

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Carbon, and molecules made from it, have already been observed in the early Universe. During cosmic time, many galaxies undergo intense periods of star formation, during which heavy elements like carbon, oxygen, nitrogen, silicon and iron are produced. Also, many complex molecules, from carbon monoxide to polycyclic aromatic hydrocarbons, are detected in these systems, like they are for our own Galaxy. Interstellar molecular clouds and circumstellar envelopes are factories of complex molecular synthesis. A surprisingly high number of molecules that are used in contemporary biochemistry on the Earth are found in the interstellar medium, planetary atmospheres and surfaces, comets, asteroids and meteorites and interplanetary dust particles. Large quantities of extra-terrestrial material were delivered via comets and asteroids to young planetary surfaces during the heavy bombardment phase. Monitoring the formation and evolution of organic matter in space is crucial in order to determine the prebiotic reservoirs available to the early Earth. It is equally important to reveal abiotic routes to prebiotic molecules in the Earth environments. Materials from both carbon sources (extra-terrestrial and endogenous) may have contributed to biochemical pathways on the Earth leading to life’s origin. The research avenues discussed also guide us to extend our knowledge to other habitable worlds.

Keywords: astrobiology; early Universe; interstellar chemistry; solar nebula processes; extra-terrestrial delivery; hydrothermal vents

1. The evolution of carbon in the Universe

The Universe is currently estimated to be approximately 13.7 Gyr old [1]. During Big-Bang nucleosynthesis, only H and He and traces of a few other light nuclei, such as D, T, Li and Be, were formed. Since the Universe was expanding, cooling and decreasing in density, heavier elements (called metals by astronomers) could not be formed during its early history, up to 500 Myr after the Big Bang. The

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triple-\(\alpha\) process \((3 \times ^4\text{He} \rightarrow ^{12}\text{C})\) in the cores of stars is the fundamental source of carbon, the basis of organic chemistry. After hydrogen is exhausted, further nuclear reactions start in the core of stars with masses greater than half a solar mass leading to carbon and heavier elements, and up to \(^{56}\text{Fe}\) for the more massive stars. Heavier elements than iron are formed during the final stages of stars in stellar explosions by neutron absorption (\(s\) and \(r\) processes). In this phase, no equilibrium can be reached: the stars undergo mass loss either in a smooth way or in violent way, leading to the enrichment of the interstellar medium. Analytical arguments [2], as well as numerical simulations [3], showed that a significant amount of star formation could have occurred when the Universe was only 100 Myr old in the standard cold dark matter theory. The high opacity to Thomson scattering of the Universe found by the Wilkinson Microwave Anisotropy Probe provides support for this theory. The first stars (so called population III or zero metallicity stars) are expected to form in dark matter halos, growing from primordial fluctuations, in which the baryonic gas could cool efficiently enough. Although atomic cooling can ensure temperatures down to 10,000 K, molecular cooling is necessary to reach lower temperatures. The dominant cooling molecule at these stages is believed to be molecular hydrogen, \(\text{H}_2\), formed through \(\text{H} + e^- \rightarrow \text{H}^-\) and \(\text{H}^- + \text{H} \rightarrow \text{H}_2 + e^-\) [4].

First stars are believed to be more massive than present day ones because \(\text{H}_2\) cooling could not decrease the temperature as low as metals do. The Jeans mass is therefore higher, up to 100–1000 solar masses [5]. These massive stars are very short lived, with life times of less than 30 Myr and can no longer be observed. When they explode, large amounts of metals, in particular carbon and oxygen, are distributed. Subsequently, dust is synthesized and dispersed throughout the Universe [6]. There is evidence that a copious amount of molecules, such as \(\text{O}_2\), \(\text{CO}\), \(\text{SiS}\), \(\text{SO}\), \(\text{CO}\) and \(\text{SiO}\), may form in the ejecta of Pop III progenitor supernovae [7] that can be recycled in the next generation of forming stars. The recent detection of hyper metal-poor stars (HMPs) in the Milky Way halo also provides important constraints for early star formation processes [8,9]. The observed HMP stars have an Fe/H ratio less than 1/100,000 of the solar ratio. They have an overabundance in C and O relative to Fe, and are slightly less massive than the Sun. Their modest masses allow them to exist for longer than 10 Gyr, and thus to act as ‘fossil’ record. Investigations of those stars may provide clues regarding the properties of the initial generation of stars and supernovae that distributed the first heavy elements in the early Universe. The star BD+44 493 has been recently identified as the brightest extremely low-metallicity star among all objects reported [10]. Carbon appears to be favoured as a formation product of the first generation of stars. Molecules like CO and water, formed once oxygen and carbon atoms were present (less than 1 Gyr after the Big Bang), as well as very small grains, cool interstellar gas much more efficiently than \(\text{H}_2\). This stimulates cloud fragmentation and triggers the formation of low-mass stars like our Sun [11–14].

Low-mass stars live much longer, approximately 10 Gyr for the Sun, a duration that enables the formation of terrestrial planets and possibly the emergence of life.

Once the first generation of population III stars had formed and exploded as supernovae about 500 Myr after the Big Bang, the subsequent existence of metals and dust is expected to lead to the efficient formation of molecules like

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Figure 1. The evolution of the intergalactic ion C IV (C\textsuperscript{3+}) abundance as a function of redshift, in units of its contribution to the closing density. The constancy of the curve indicates that vigorous star formation was already underway when the Universe was only 7\% (at redshift $z = 6$) of its present age. Reproduced with permission from Simcoe [19].

CO, water, hydrides and carbon chains [15]. Indeed, high excitation CO emissions from the distant quasar SDSS 114816.64 + 525150.3 at redshift $z = 6.4$ have been detected, indicating that CO, one of the most important coolants of interstellar gas, has been present in the Universe since approximately 800 Myr after the Big Bang [16]. Furthermore, detections of C and C\textsuperscript{+} have been made and upper limits on HCN and water exist [17]. Somewhat more recently, at a redshift $z = 3.9$, the gravitationally lensed quasar APM 08279 allows the inner 200 parsecs of the galaxy to be probed. Large amounts of warm (100 K) CO gas and warm dust (assuming a frequency squared absorption-coefficient dependence) appear to be present, indicative of active star formation [18]. Clearly, carbon and dust surface chemistry was occurring already in the earliest epochs of the Universe. That these objects with a significant amount of carbon are not flukes, is shown in figure 1, where the relative amount of carbon is presented as a function of redshift. In this, redshifts of 1 and 6 mean 35 and 7 per cent of the present age of the Universe, respectively. Clearly, carbon and thus star formation was already very much present in the young Universe [19]. This fits well with the star formation and metal-production history of the Universe [20], where the metals produced by massive stars lead to the formation of molecular gas and thus more stars. For a metallicity of 1 per cent of solar and up, one develops a multi-phase interstellar medium (ISM) that supports a cool dense phase, with a density larger than $100 \text{ cm}^{-3}$ and a temperature less than 100 K, in which stars form and complex (carbon-chain) molecules can be produced [21]. Such a metallicity is certainly reached in the quasar sources mentioned above, and an active carbon chemistry therefore appears to have been in place for at least the past 10 Gyr.

Closer to home, many if not all active galaxies are enjoying an active carbon chemistry, as exemplified by species such as CO, HCN, HNC, HCO\textsuperscript{+}, CH\textsubscript{3}OH, H\textsubscript{2}CO, C\textsubscript{2}H and polycyclic aromatic hydrocarbons (PAHs; e.g. [22–24]). Some galaxies form stars with a very high rate, so-called starburst galaxies like Arp 220
and M82. Carbonaceous molecules are detected in those systems as well, even in the presence of strong mechanical feedback owing to supernova explosions and outflows [25]. UV radiation produced by stars or X-ray photons created by an accreting supermassive black hole can destroy complex molecules in the nuclei of galaxies [26]. Nevertheless, species like CO may survive even such extreme environments, already in the early Universe at metal-enrichment levels of only a few per cent [27]. Also, PAHs have been detected with Spitzer out to high ($z > 1$) redshift (e.g. [28]). The cycle of birth and death of stars that was initiated by population III stars constantly increases the abundance of heavy elements in the interstellar medium, a crucial prerequisite for rocky-planet formation [29,30]. Understanding the early and active Universe is thus extremely relevant to the question of terrestrial-planet formation and consequently life.

2. The complexity of organic matter in space

(a) Interstellar clouds

Interstellar molecular clouds and circumstellar envelopes are factories of complex molecular synthesis [31–33]. Interstellar clouds constitute a few per cent of galactic mass and are composed primarily of H and He. They are enriched primarily by matter ejected from evolved stars and can vary strongly in their fundamental physical parameters such as temperature and density. Dominated by gas, interstellar material also contains approximately 1 per cent of small micron-sized particles. Gas-phase and gas–grain interactions lead to the formation of complex molecules. Surface catalysis on solid interstellar particles enables molecule formation and chemical pathways that cannot proceed in the gas phase owing to reaction barriers [34,35]. H$_2$ is by far the most abundant molecule in cold interstellar regions, followed by CO, the most abundant carbon-containing species, with CO/H$_2$ \sim 10$^{-4}$. CO is characterized by a high binding energy (11.2 eV) and strongly influences the chemistry in interstellar clouds. Two main types of interstellar clouds drive molecular synthesis. In cold dark clouds, the temperature is low (approx. 10 K) and therefore the sticking coefficients of most atoms and molecules are close to unity, leading to a freeze out of practically all species (except H$_2$ and He). The high density in dark clouds (up to approx. 10$^6$ cm$^{-3}$) attenuates UV radiation and offers a protected environment for the formation of larger molecules by gas-phase reactions and ice chemistry on grains. A large number of complex organic gas-phase molecules was identified through infrared, radio, millimetre and sub-millimetre observations (www.astrochemistry.net lists more than 150 molecules). Among them are nitriles, aldehydes, alcohols, acids, ethers, ketones, amines and amides, as well as long-chain hydrocarbons. The main species observed in interstellar ice mantles are H$_2$O, CO$_2$, CO and CH$_3$OH, with smaller admixtures of CH$_4$, NH$_3$, H$_2$CO and HCOOH [36]. A recent c2d (core to disks) Spitzer survey of ices investigated the 6–8 \mu m region that displays the prominent bending mode of water ice. Five independent components that can be attributed to eight different carriers [37] have been identified. Observations of CO$_2$ in low-mass protostars showed high abundances (average of 32% relative to water ice) [38]. CH$_4$ ice was detected in 25 out of 52 targets, with abundances ranging from 2 to 8 per cent relative to water ice and reach 13 per cent in a few sources [39].
Diffuse interstellar clouds are characterized by a low density (approx. $10^3$ atoms cm$^{-3}$) and temperatures less than or equal to 100K. Ion–molecule reactions, dissociative recombination with electrons, radiative association reactions and neutral–neutral reactions contribute to gas-phase processes and influence interstellar chemistry [40]. A variety of small molecules, including CO, CH, CN, OH, C$_2$, C$_3$ and others, are observed [41]. Gaseous PAHs are highly abundant, with fractions of about $10^{-7}$ [42]. Carbonaceous grains composed of macromolecular aromatic networks account for most of the molecular carbon fraction in these clouds as evidenced by a ubiquitous strong UV absorption band at 2175 Å [43].

Amorphous carbon, hydrogenated amorphous carbon, diamonds, refractory organics and carbonaceous networks such as coal, soot, graphite and quenched-carbonaceous condensates have been proposed as possible carbon compounds [31,42,44,45]. PAHs are observed to be widely distributed in galactic and extragalactic regions [42,46–49]. In diffuse interstellar clouds, dust interacts with hot gas, UV radiation and cosmic rays, and evolves or gets destroyed in shocks and by sputtering. Strong differences in the dust component of dense and diffuse interstellar clouds exclude rapid cycling of cloud material [50]. The formation pathway of solid carbonaceous matter is not yet understood. However, circumstellar envelopes are identified as factories of complex molecular synthesis [32]. Figure 2 shows a route to the formation of PAHs and soot material that has been proposed over two decades to occur in the shielded environment of stellar envelopes.

(b) Solar-System materials

The gravitational collapse of an interstellar cloud led to the formation of the protosolar nebula from which planets and small bodies of our Solar System formed [54]. Observations of protoplanetary disks show that gas and solids drift inward in time. Solids migrate inwards faster than gas, and small particles grow to kilometre-sized bodies that accrete to planets. The chemical composition of protoplanetary disks is expected to hold clues to the physical and chemical processes that influence the formation of planetary systems. Recently, it has been reported that the protoplanetary disks of AA Tauri possess a rich molecular emission spectrum in the mid-infrared, indicating a high abundance of simple organic molecules (HCN, C$_2$H$_2$ and CO$_2$), water vapour and OH [55]. Data from recent space missions, such as the Spitzer telescope, Stardust and Deep Impact, show that the dynamic environment of the solar nebula with the simultaneous presence of gas, particles and energetic processes, including shock waves, lightning and radiation (e.g. [56]) can trigger a rich organic chemistry. Turbulent motion leads to radial mixing of the products within the disk [57,58], which has been confirmed by Stardust data [59]. The carbonaceous inventory of our Solar System therefore contains a mixture of material that was (i) highly processed by exposure to high temperatures and radiation, (ii) newly formed within the solar nebula, and (iii) captured as relatively pristine material with significant interstellar heritage.

Many organic compounds are observed or sampled from our Solar System, including planetary surfaces/atmospheres, comets and interplanetary dust [31,60–62]. More than 50 molecules have been identified in cometary comae [63,64]. The analysis of carbon compounds in fragments of asteroid 2008 TC3
Acetylene chemistry leading to the formation of benzene and small PAHs that subsequently build up larger structures has been proposed to occur in the shielded environments of carbon-rich circumstellar envelopes (e.g. [32,51]). Aromatic materials, in solid and gaseous form, constitute the largest fraction of organic material in the Universe [52,53].

by Jenniskens et al. [65] recently revealed interesting insights into the asteroid chemistry. Carbonaceous chondrites (meteorites) and micrometeorites, which represent fragments of cometary and asteroidal bodies, do contain a variety of organics (e.g. see [62,66] for reviews).

In the soluble fraction of the Murchison meteorite, more than 70 extraterrestrial amino acids have been identified in addition to many other organic compounds, including N-heterocycles, carboxylic acids, sulphonic and phosphonic acids, and aliphatic and aromatic hydrocarbons [67–70]. However, the major carbon component in meteorite samples is composed of a macromolecular organic fraction [71]. A recent study using ultra-high resolution molecular analysis of the solvent-accessible organic fraction of Murchison shows high molecular diversity [72].

The remaining population of planetesimals not incorporated into planets exists until today as asteroids and comets. Most of the asteroids and comets are confined to stable orbits (such as the asteroid belt between Mars and Jupiter) or reservoirs in the outer Solar System (such as the Kuiper Belt) or beyond our Solar System (Oort cloud). In the early history of our Solar-System small bodies, such as comets

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and asteroids, and their fragments impacted the young planets [73]. A destabilized planetesimal disk caused a massive delivery of planetesimals to the inner Solar System at 3.9 Gyr ago. This so-called Late Heavy Bombardment (LHB) phase was likely triggered by rapid migration of giant planets [74]. The large quantities of extra-terrestrial material delivered to young terrestrial planetary surfaces during this period may have provided raw material useful for protocell assembly on the Earth [73,75]. The analysis of extra-terrestrial matter in the Earth laboratories indicates that the dominant form of carbonaceous material that was delivered to young planets must have been aromatic macromolecular matter.

3. Terrestrial planets

(a) Conditions on the early Earth

Planet Earth was formed through a hot accretion process about 4.6 Gyr ago, which allowed only the rocky material from the inner Solar System to survive. Although many interesting geological data of the early Earth were revealed in the last decade, we still have limited knowledge regarding the exact atmospheric composition, the temperature of the oceans and geological activity. Considerable geochemical evidence supports an initiation of plate tectonics on the Earth shortly after the end of the Hadean about 3.9 Gyr ago. It is unclear if the transition to plate tectonics resulted from radioactive decay-driven mantle heating or from cooling to the extent that large lithospheric plates stabilized [76]. Any existing carbon material from the solar nebula (volatile and refractory) was destroyed during the Earth’s formation. Therefore, organic molecules found on terrestrial planets must have formed after the planetary surface cooled, or have been delivered via impacts by small bodies in the young Solar System. All terrestrial planets have been seeded with organic compounds through the impact of small bodies during Solar-System formation. There is a consensus that a combination of exogenous and endogenous sources has provided the first precursor molecules for life on the young Earth. These simple molecules reacted and assembled on catalytic surfaces (such as minerals) and formed more complex structures that later developed into primitive cells (protocells). The endogenous synthesis of prebiotic organic compounds (molecules that are involved in the processes leading to the origin of life) may have been limited to protective environments such as the oceans, owing to the hostile conditions on the young Earth, including volcanism, radiation and bombardment by comets and asteroids.

Whatever the inventory of endogenous organic compounds on the ancient Earth was, it would have been augmented by extra-terrestrial material. It is estimated that these sources delivered approximately $10^9$ kg of carbon per year to the Earth during the heavy bombardment phase of 4.5–3.9 Gyr ago [73].

Life on Earth is one of the outcomes of the formation and evolution of our Solar System and has adapted to every possible environment on planet Earth. Life on Earth can be found in extreme environments, such as hydrothermal vents, in dry deserts, the Earth atmosphere and in polar regions. These findings challenge the definition of the ‘planetary habitable zone’. Primitive life, in the form of bacteria, emerged approximately 3.5 Gyr ago [77,78]. The homologous series of long-chain aliphatic hydrocarbons found in old sedimentary rocks
characterized by odd-over-even carbon-number predominance is only consistent with a biological origin and indicates that, despite the hostile conditions, planet Earth was habitable in its early history [79].

Today, the Earth provides an ideal environment for life to sustain. Dynamic processes in the interior of the Earth have established a magnetosphere that protects the Earth from harmful cosmic radiation. Oceans and atmosphere enable a stable climate and temperature cycle. Our neighbour planets are less fortunate. Venus, with an average surface temperature of 500°C and a steamy atmosphere, is unable to sustain life at its surface. Mars, with an average surface temperature of −60°C and a thin toxic atmosphere, provides a hostile surface environment, but may harbour life in the subsurface.

Nitrogen is an essential element of both nucleotides (genetic code, energy transfer) and proteins. Systems containing NH₃/NH₄⁺ are more efficient in abiotic organic synthesis than those dominated by N₂ in both aqueous and gaseous environments [80]. The reason is that the triple bond between the atoms in molecular nitrogen is very stable and hard to break. Geochemically plausible abiotic synthesis pathways of prebiotic molecules and concentration mechanisms for nitrogen-containing molecules must eventually be found since nitrogen-based life is likely to have existed on the Earth from early Archean about 3.8 Gyr ago and onwards [81]. High ammonium contents (54–95 ppm) have been found in authigenic clays of the Isua supracrustal rocks of western Greenland, suggesting that clays were major sinks of NH₄⁺ or other nitrogen compounds on the Earth’s surface already at 3.8 Gyr ago [82]. Ward & Brownlee [83] have argued that plate tectonics is necessary for the origin of life on terrestrial planets and have listed a number of reasons in support of their opinion. However, one argument that they have never mentioned is the connection between plate tectonics, hydrothermal geochemistry, and reduction of simple carbon and nitrogen compounds suitable for abiotic organic chemistry. The best location where such processes could occur would be at convergent margins during the early phases of subduction of oceanic plates. As a plate descends, fluids distilled from the plate influence, and even control, fundamental processes in the subduction zone [84]. The subducting plate, along with its fluids and altered igneous rock, interact with the over-riding plate along the subduction zone. Fluids originating in the subducting plate will rise through the upper plate containing hydrated ultramafic mantle material in its lower parts. The fluids may thus move from a relatively acidic environment in weathered basalt into an alkaline environment in serpentinized peridotite.

The strong pH increase promotes the formation of carbohydrates like ribose from simple organic compounds. It also supports the synthesis of amino acids and purine nitrogen bases, as well as their condensation to nucleotides in the presence of phosphorylated ribose.

(b) Hydrothermal environments

Hydrogen cyanide is a key compound in abiotic synthesis of organic molecules. HCN is formed by a variety of processes driven by thermal energy, but is normally present in trace amounts [85]. HCN is, for instance, readily formed by the reaction of CO or CH₄ with NH₃ (figure 3) [84]. Hydrothermal systems represent regions of the highest conversion rates of nitrate and nitrite to ammonium on the Earth [86]. In general, the purine-coding elements of RNA (adenine and guanine) can be
Figure 3. Cartoon showing a cross-section of oceanic lithosphere, extending from the spreading centre to the subduction zone. Off-axis hydrothermal flow in the oceanic lithosphere causes oxidation of Fe(II) to Fe(III) and reduction of water to molecular hydrogen. Some Fe(II) and Ni(II) is reduced to native metals. Carbon dioxide is reduced to carbon monoxide and methane, while nitrate and nitrite may be reduced to ammonium and adsorbed on secondary minerals like smectite and zeolites. During early subduction the descending plate is heated and dehydrated. Adsorbed carbon monoxide and methane may react with ammonia and form hydrogen cyanide. The released fluid carrying hydrogen cyanide rises from an environment of relatively low pH into hydrated mantle rock of high pH. At the high pH hydrogen cyanide may form HCN oligomers as well as amino acids, purine bases, nucleosides and, perhaps, nucleotides (adapted from [84]).

synthesized in the same abiotic reactions that yield amino acids [87–90]. Adenine is likely to have been the first nucleobase formed abiotically, and has been shown to remain in detectable concentrations still after 200 h at 300°C under fugacities of CO₂, N₂ and H₂ that are supposedly representative of those in marine hydrothermal systems on the early Earth [91]. The purines are formed from HCN via two routes. One route is via HCN oligomers, which may also form amino acids; the second one is via the HCN tetramer diaminomaleonitrile (DAMN) [87,88]. DAMN formation is accelerated by the presence of formaldehyde under mildly alkaline conditions (pH 9.2) [92]. Amino acids can be released by hydrolysis of HCN oligomers that form by the self-condensation of hydrogen cyanide in aqueous solution [88]. Furthermore, amino acids may be synthesized in putative prebiotic chemistries like Strecker-type reactions (synthesis of amino acids from cyanide and aldehyde in the presence of ammonia) in hydrothermal environments at fairly low temperatures (150°C) [93,94]. In order to participate in abiotic organic reactions, HCN must first be concentrated. One possibility is the concentration to a reservoir of ferrocyanide at relatively low pH from which free HCN can be released upon local elevation of the pH [81,95]. HCN reacts with ferrous ions to give ferrocyanide, provided that the concentration of hydrogen sulphide is low [96], like in the Lost City serpentinite-hosted hydrothermal field off the Mid-Atlantic Ridge [97]. The elevation of pH would lead to oxidation of Fe(II) and precipitation of the iron as FeOOH. This would avoid the ‘Miller paradox’,
which refers to the side reaction of glycolonitrile (cyanohydrin of formaldehyde) formation from free HCN and ubiquitous formaldehyde [98]. Formaldehyde and HCN, if present in the same environment, tend to react to form stable glyconitrile. On the other hand, Schwartz & Goverde [92] have shown that admixture of solutions enriched in cyanohydrins (like glyconitrile) with solutions of HCN permits oligomerization of HCN to DAMN, even under dilute conditions.

An alternative model to avoid the ‘Miller paradox’ involving alkaline hydrothermal mounds as flow reactors in which strongly polar compounds such as the cyanide ion is retained by fresh FeS/Fe₃S₄ membranes has been presented by Russell et al. [99–102]. According to their model, the fluctuations in pH at the interface between hydrothermal fluid and sea water would determine adsorption and desorption of the cyanide. In natural environments, the occurrence of ferrocyanides in hydrothermal systems has so far been reported only from the Kurile Islands and the Kamchatka Peninsula in the northwest Pacific Ocean [103,104].

Cohn et al. [105] have shown that adenine is far displaced towards adsorption onto pyrite, quartz and pyrrhotite, which are all common minerals of hydrothermal environments. It would, therefore, normally be useless to search for the purine bases in the fluid phase of hydrothermal systems [106]. The observed coding effect of adsorbed purine bases [107] may indicate that the role of phosphate as a constituent of polynucleotides is a secondary property, and that phosphate was originally incorporated in prebiotic systems because of its energy-transfer capacity.

A couple of decades ago, many scientists believed that the abiotic formation of ribose, a constituent of RNA, occurred through the formose reaction [87,108]. The formose reaction was discovered and first described by Butlerow [109]. In this reaction, pentoses like ribose can be formed under alkaline conditions from simple organic precursors (formaldehyde and glycolaldehyde) [87,88]. The condensation of formaldehyde to sugars is catalysed by divalent cations and layered minerals, such as clays. The reaction proceeds by the stepwise condensation of formaldehyde to dimer (glycolaldehyde), trimer, etc. Under experimental conditions, it has been possible to convert as much as 50 per cent of the original formaldehyde to glycolaldehyde [110]. However, this reaction has, for a while, been an outdated concept in prebiotic chemistry. A major reason for this is that the reaction, as we have known it, is non-selective and leads to a large variety of aldoses, ketoses and sugar alcohols with only small fractions of potentially bioactive compounds such as ribose [90,111,112]. A general opinion has been that if ribose were used in the first RNA, an unknown selection process must have operated to segregate ribose from the other sugars that were formed. A second reason why the formose reaction has been outdated is that the reaction proceeds at a significant rate only under naturally ‘improbable’ conditions, like under highly alkaline conditions [81,87,108,113].

Natural environments with the pH conditions required for the abiotic formation of carbohydrates have previously been considered to be relatively rare on the Earth. However, the recent discovery of alkaline hydrothermal systems in ultramafic rocks, such as the Lost City Hydrothermal Field on the Mid-Atlantic Ridge [97,114–116] and the Mariana Trench [94,84], indicates that alkaline environments may be much more common on the Earth than was thought just a few years ago.
Because of the postulated difference in requirements for the formation of the ribose and the nitrogen base, the spontaneous formation of RNA under prebiotic conditions on the Earth has been doubted [90]. The differences in required environment may, however, be illusive. It was mentioned earlier that formaldehyde is necessary for the formation of carbohydrates in the formose reaction. Schulte & Shock [117] have shown that aldehydes may be intermediates in the formation of carboxylic acids from hydrocarbons in sedimentary basin brines, as well as in hydrothermal systems. Furthermore, they concluded that the presence of aldehydes should normally be difficult to detect in natural systems if metastable equilibrium is reached between aldehydes and carboxylic acids at expected redox conditions. On the other hand, this suggests that aldehydes are always present as reaction intermediates in cases when organic acids and hydrocarbons both exist in natural hydrothermal systems. In fact, low concentrations of formaldehyde have been identified in hot-spring environments in Iceland, Mexico and southern California [118].

At equilibrium in hydrothermal systems, carboxylic acids, aldehydes and hydrocarbons will all be present in parallel, although at different levels of concentration.

4. Conclusion

The cycle of birth and death of stars that is initiated by population III stars constantly increases the abundance of heavy elements in the interstellar medium. Observations of the oldest stars show that carbon has been formed already in the very early Universe. The central star of our Solar System, the Sun, was formed many billion years after this time, and therefore contains several generations of supernova-produced metals. Tracing the earliest stars provides important insights into the origin of the elements necessary for life. The wide range of organic molecules identified by astronomical observations, space probes and by laboratory analysis of carbonaceous meteorites, suggests that the basic building blocks of life, at least as recognized on the Earth, must be widespread in planetary systems in our Galaxy and beyond [119]. There is a consensus that both exogenous and endogenous carbon sources have provided the raw material for the first building blocks of life on the early Earth.

The extra-terrestrial contribution arrived via comets, asteroids and small fragments during the LHB phase 3.9 Gyr ago. The large quantities of extra-terrestrial material delivered to young terrestrial planetary surfaces provided organic material predominantly in the form of aromatic networks that could have been used in biochemical pathways on the young Earth. Endogenous prebiotic carbon compounds may have formed in the early oceans. The connection between plate tectonics, hydrothermal geochemistry and reduction of simple carbon and nitrogen compounds has shown to be very suitable for abiotic organic chemistry. The best location where such processes could occur would be at convergent margins during the early phases of subduction of oceanic plates.

Understanding the early and active Universe is extremely relevant to the question of terrestrial-planet formation. How heavy elements assemble to complex molecules and evolve in interstellar and circumstellar regions and how they are incorporated into forming planetary systems and are used on young planets.
to form life are major research avenues that are investigated under the interdisciplinary umbrella of astrobiology. Understanding the constraints when defining the chemical composition of life’s raw material from the viewpoints of different scientific disciplines is essential.

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