Abiotic synthesis of complex organics in the Universe

Complex organics are now observed throughout the Universe, forming in the circumstellar environments over thousands of years and providing materials for star formation. Did the Earth inherit any of these organics at the time of its formation?

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When people think of organic compounds on Earth, most naturally think of the biosphere. The total amount of carbon in the living biosphere, which includes Earth's crust, atmosphere and oceans, is about 1,000 gigatons (GT). In comparison, there are about 4,000 GT of carbon in fossil fuels and 15,000,000 GT in kerogen, a macromolecular compound found in sedimentary rocks[1]. As coal, oil, natural gas and kerogen are remnants of past living organisms, almost all known organics on Earth are derived from life.

The first evidence for the existence of extraterrestrial organics came from meteorites. It began with the detection of paraffins in the Orgueil meteorite in 1961 (ref. [2]), followed by aromatic and aliphatic hydrocarbons, amino acids, carboxylic acids, amines, alcohols, carbonyl and other organic compounds in the 1970s. Since then, most molecular building blocks of life have been found in the soluble component of carbonaceous chondrites[3], which are primitive stony meteorites with carbon atoms residing mostly in organic compounds. Most notably, over 100 amino acids have been discovered, far more than the 20 amino acids in terrestrial proteins[4].

However, the largest fraction of organics in carbonaceous chondrites comes in the form of insoluble macromolecular solids. These solids are amorphous in structure and consist of small aromatic rings connected by short aliphatic chains mixed with other heavy elements, such as oxygen, nitrogen and sulphur. The relative abundance of elements in the insoluble material is $C_{100}H_{46}N_{10}O_{15}S_{4.5}$ (ref. [4]).

In addition to occurring in meteorites, complex organic matter has also been detected in comets, interplanetary dust particles and planetary satellites[5,6]. The chemical structures of organics in comets and interplanetary dust particles are similar to those of the insoluble component of meteorites. The amount of hydrocarbons in Titan's lakes and sand dunes is estimated to exceed the total oil and gas reserves on Earth[7].

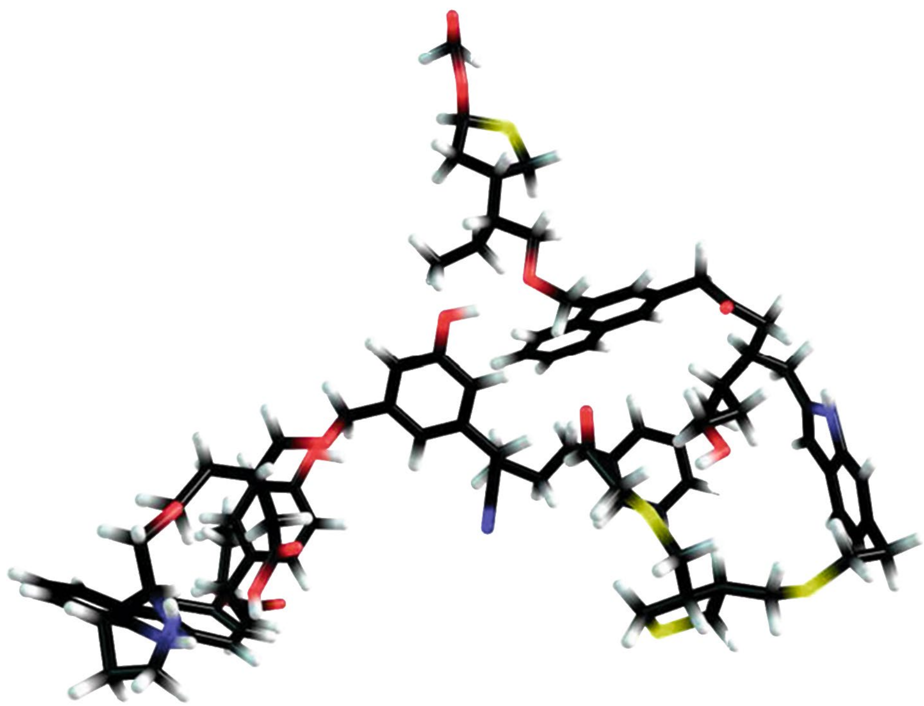

Fig. 1 | A three-dimensional illustration of a possible partial structure of a MAON particle. Carbon atoms are represented in black, hydrogen in light grey, sulphur in yellow, oxygen in red and nitrogen in blue. There are 101 C, 120 H, 14 O, 4 N and 4 S atoms in this example. The number of heavy elements has been intentionally exaggerated for the purpose of illustration. Figure reproduced from ref. [12], IOP.

When and where were these organics made? It is clear that the organics in both soluble and insoluble components of meteorites are not products of life, but were synthesized abiotically. The common view in the planetary science community is that these organics were made in situ within the Solar System. With carbonaceous chondrites being the most primitive meteorites, the origin of the organics dates back to at least the beginning of the Solar System 4.6 billion years ago.

Among astronomers, the prevailing opinion in the 1960s was that the low-density and high-ultraviolet background of interstellar space would not allow the formation or survival of molecules beyond simple short-lived radicals. After the development of millimetre-wave and infrared spectroscopic observational capabilities in the 1970s, a large number of gas-phase molecules was detected through their rotational and vibrational transitions. The list of detected interstellar molecules now includes almost every family of organic molecules, with examples ranging from biomolecule precursors, such as acetamide, a molecule with a peptide bond, to glycolaldehyde, the first step towards sugar[5].

Although organic molecules have also been detected in interstellar clouds, the timescale of their formation is unknown. Our most definite knowledge of molecular synthesis comes from circumstellar envelopes of evolved stars in the evolutionary stage, from asymptotic giant branch (AGB) stars to planetary nebulae. After carbon is synthesized in the core of AGB stars and dredged up to the surface, molecules and minerals have been observed to form in the stellar winds ejected from these stars[5]. Molecules detected include rings, chains, radicals, molecular ions and fullerenes (C_{60}). The dynamic timescale of the stellar winds puts a limit of about 10^4 years on chemical reactions. This range indicates that molecules and solids can form very quickly under very low-density conditions[8].

The most mysterious phenomenon for me is the unidentified infrared emission (UIE) bands — a set of infrared features commonly observed in planetary nebulae, H II regions, reflection nebulae and active galaxies. The UIE bands are frequently attributed to emissions from polycyclic aromatic hydrocarbon molecules, but they have also been proposed to originate from mixed aromatic/aliphatic organic nanoparticles[9] (MAON), an example of which is illustrated in Fig. 1. Laboratory simulations have shown that when a mixture of gas-phase hydrocarbons is subjected to various forms of the energy injection, MAON-like materials showing UIE-like spectra can form naturally[6]. If the carriers of UIE bands are indeed complex organics, then their detection in distant galaxies suggests that organics were synthesized in the Universe as early as 10 billion years ago.

The UIE bands are commonly seen in planetary nebulae, short-living (about 20,000 years) descendants of AGB stars. They are not detected in AGB stars but are first seen in the spectra of proto-planetary nebulae, a short (10^3 years) phase of stellar evolution between AGB stars and planetary nebulae, suggesting that the carrier of UIE bands is first synthesized there. By observing the spectral evolution from AGB stars to proto-planetary nebulae to planetary nebulae, we learned that the chemical synthesis pathway is from acetylene to benzene to MAONs[8]. The observation of circumstellar organic synthesis is the most direct evidence that complex organics can be made by stars abiotically over very short timescales.

As the chemical structure of MAONs is similar to that of the insoluble organic matter in meteorites, is it possible that the early Solar System inherited complex organics ejected by stars? The Earth was formed from planetesimals. Is it possible that the Earth also inherited primordial organics?

The most well-known proponent of the existence of primordial hydrocarbons on Earth was Tommy Gold. In his book *The Deep HotBiosphere*[10], Gold proposed that primordial methane deep inside the Earth offered a huge, untapped fuel reserve. As the Earth condensed from a hot molten state after a period of coalescence of smaller bodies through accretion, the high temperature and collisional shock would make it very difficult for simple hydrocarbons to survive. For this reason, Gold's theory was never taken seriously by geologists. However, if the primordial hydrocarbon was in the form of a macromolecular compound, its chances of survival during Earth's formation would have been much higher.

Gold hypothesized that complex organics are synthesized from primordial methane in the Earth's deep interior and flow to the surface in the form of coal and oil. Our current established links between petroleum and life are nickel- and vanadium-porphyrin complexes, which can be traced to iron-porphyrin and haemoglobin in animals and magnesium chlorophyll in plants. But we do know that not all hydrocarbons on Earth are biological in origin, as evidenced by the discovery of methane in hydrothermal vents. The amount is small. But if the primordial material were MAONs, then coal and oil could be their natural processed products over time[11]. It is interesting to ponder whether, in addition to the biological fossil fuels near the Earth's surface, there are any reserves of primordial organics deep inside the Earth.

From the detection of complex organics in Solar System objects, stars and galaxies, we now know that complex organics are prevalent in the Universe and synthesized abiotically on a large scale. Such synthesis, although observed directly in circumstellar envelopes, is difficult to understand theoretically due to the low density and short timescale of the environment. There is something missing in our fundamental understanding of chemistry that underlies the manufacturing of molecules, minerals and organics in space. Circumstellar chemistry therefore offers a new arena for us to explore chemical processes beyond those in the terrestrial laboratory. ❐

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