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COMMENTARY

Abiotic synthesis of organic matter in deep-sea basalt gives clues for the origin of life on Earth and beyond

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A key aspect of deciphering the mystery of the origin of life is how to make organic molecules abiotically, without life. For years, scientists have considered that primordial organic molecules were brought to the early Earth by collisions with asteroids and comets. Afterall, such impacts still occur today, and they are constantly bringing new meteorites on Earth (Fig. 1). Carbonaceous chondrites originating in the asteroidal belt are the most common type of meteorites, accounting for more than 85 per cent of all meteorite falls [1]. Organic matter formed through photochemical dissociation of C-rich precursors was imported to Earth via carbonaceous chondrites [1]. Such rocky remnants dating from the time of accretion of the Solar System can contain several weight percent of organic carbon. For instance, there is more than 3 wt% of organic matter inside rock samples robotically returned from asteroid Ryugu, and organic molecules therein contain various molecular functional groups such as carboxyl (COOH), ketone (C=O), aromatic (C=C), aliphatic

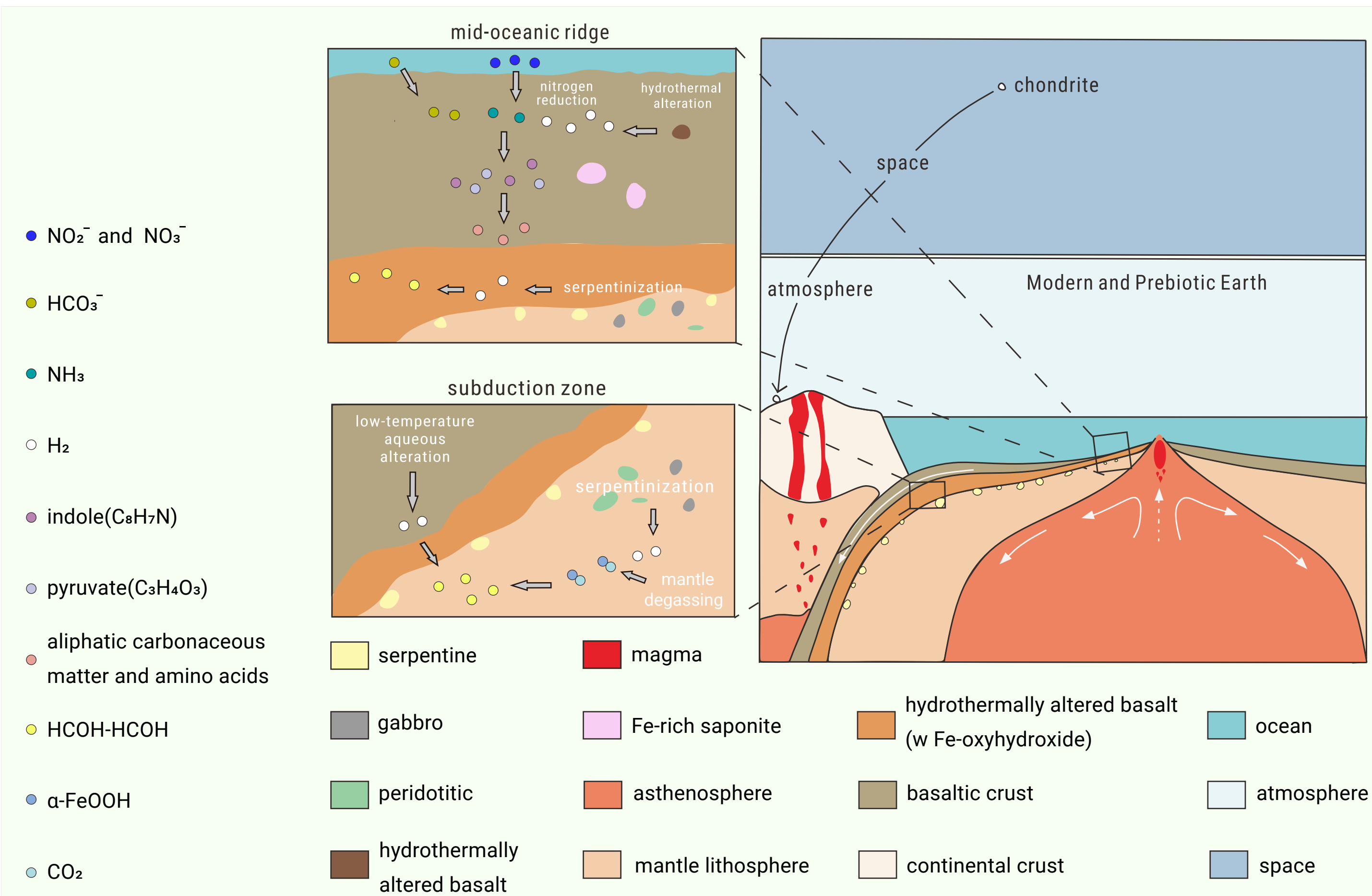

Figure 1. Cartoon model of the context of the discovery of abiotic synthesis of organic matter in serpentinised deep-sea basalt in mid-ocean ridges Processes shown include serpentinization at mid-ocean ridges and in subduction zones where hydrothermal alteration provides H2 for the abiotic reduction of inorganic carbon, which can be catalysed by Fe-oxides, Fe-rich saponite clays, or Fe-oxyhydroxides. These Fischer-Tropsch Type (FTT) reactions are well-known to occur in ultramafic peridotite and gabbro, and they produce methane, aliphatic molecules, and amino acids. The novelty now is that low-temperature aqueous alteration of basalt – the most widespread rock type in the deep-sea – can also lead to the production of HCOH-HCOH polymers through C-C chain elongation. These pathways can collectively produce indole, pyruvate, aliphatic hydrocarbons, and amino acids, which are all organic molecules crucial for biochemistry and the origin of life. Thin arrows represent sources of compounds, whereas thick arrows represent reactions.

(C_nH_m), and amine (C-N) [2]. However, an abiotic supply of organic molecules formed specifically on Earth may be more likely for sustaining a prebiotic carbon cycle, prior to the origin of life and to the proliferation of biological microbial cells. While endogenous and abiotic sources of prebiotic carbon could also have included lightning and photolysis by ultraviolet radiation in the early atmosphere, water-rock interactions should now be viewed as a promising pathway in this context.

Abiotic organic molecules are already known to form in modern ultramafic rocks – rocks rich in magnesium and iron coming from Earth's mantle – as well as in their hydrothermally altered serpentinite products. However, these rock types are generally much less common than basaltic rocks – rocks that form in volcanic eruptions on Earth's surface and seafloor. In fact, today the seafloor is predominantly composed of basalt, which typically originates from volcanic eruptions located on the edge of diverging tectonic plates in the deep sea, where pieces of oceanic crust are spreading away from each other. As a result, seafloor basalt is the most common rock type in Earth's oceans, covering about 70% of Earth's surface area. Could seafloor basalt be an abiotic source of organic molecules?

In a new discovery, an international team of scientists reported the existence of various organic molecules in volcanic basalt from the seafloor [3]. The rocks came from the Southwest Indian Ridge and were collected using robotic arms fitted on the human-occupied submersible '*Shenhaiyongshi*'. During this deep-sea expedition between 2.6 and 2.8 km below sea level, the scientific team collected basaltic volcanic rocks located in the vicinity of active hydrothermal chimneys that exhale hot and black gases and minerals. While these hydrothermal systems are home to various animals and microorganisms, the team documented that the organic matter inside their basalt samples did not contain any trace of life. Instead, they documented organic molecules with various molecular bonds and elements including hydrogen, nitrogen, and oxygen atoms. Their spectroscopy analyses showed specific types of organic bonds including C_nH_m, alcohol (C-OH), and C-N. These kinds of molecular functional groups bonded to organic carbon are known to form abiotically under experimental hydrothermal conditions, at $T < 300°C$, from simple abiotic precursor organic molecules [4].

In ultramafic systems, the abiotic synthesis of organic molecules is known to begin with the process of serpentinization during which water molecules in contact with the mineral olivine ($(Fe,Mg)SiO_4$) are spontaneously reduced to dihydrogen (H_2) and where ferrous iron (Fe^{2+} – in olivine) is oxidised to ferric iron (Fe^{3+}) oxides. Subsequently, carbon dioxide (CO_2), carbon monoxide (CO), and bicarbonate (HCO_3^-) in hydrothermal fluids can react with H_2 on metal catalysts to produce methane (CH_4) and longer C_nH_m molecules. These spontaneous phenomena occur in ultramafic systems with peridotite (an olivine-rich rock) such as in the Mid-Atlantic Ridge, or in serpentinites where abiotic C_nH_m molecules with various functional groups have been observed [5]. Such observations point to ultramafic rocks as loci for the abiotic production of organic molecules, however these rock types are not as common as basalt on the global oceanic seafloor. Besides, Friedel-Crafts-type reactions can also lead to the abiotic formation of aromatic amino acids during hydrothermal alteration of oceanic peridotites, a reaction catalysed by iron-rich saponite clays [5].

The organic matter inside the matrix of basaltic rocks from the Southwest Indian Ridge was amorphous in shape and occurrences were only a few micrometres in size [3]. It was noted that it was specifically associated with nanometre size ferric iron oxyhydroxide (FeOOH) minerals [3]. This close association pointed to the role of FeOOH in helping to create hydrogen bonds with precursor CO or CO_2 from the hydrothermal fluids (Fig. 1). Hence, the conclusion was that these organic molecules formed abiotically, which was also supported by their association with olivine and pyroxene that are partly serpentinised. This discovery of serpentinization and abiotic organic synthesis in basaltic rocks thus follows that of abiotic organic synthesis in ultramafic rocks at mid-ocean ridges [5] and in subduction zones [6] (Fig. 1). All these rocks are typically rich in olivine and pyroxene minerals, in which Fe^{2+} is oxidised to Fe^{3+}, forming magnetite and other minerals, and releasing H_2. Fischer-Tropsch reactions can then synthesize organic molecules using H_2 and CO_2. While there may be similarities in the abiotic formation processes of organic molecules in ultramafic rocks, asteroids, and in seafloor basalt, the latter is a much more widespread rock type and therefore greatly expands the known realm of locations for abiotic organic synthesis.

The team also used sophisticated computer models, based on quantum mechanics, to shed light on the reaction pathways starting with CO_2 adsorption, hydrogenation, and the subsequent growth of aliphatic C-C chains [3]. They used these models and observations to further study how these carbon atoms might react with hydrogen in FeOOH to become bound in stable, more complex molecules. Such complex stable molecules, like fatty acids with aliphatic and carboxyl groups, are crucial for the formation of cellular membranes and thus for the origin of life. Hence, this discovery suggests that abiotically formed organic molecules in seafloor volcanic rocks are widespread today on Earth, and by inference, also on the primordial Earth.

Through research of this type, using multiple kinds of innovative correlated microscopy and spectroscopy analytical techniques, significant progress is being made to characterize minuscule levels of organic molecules in the petrographic context of rocks [2,3,5,6]. This approach is important and elegant, because it minimizes chances of airborne contamination through the nanofabrication of thin slices of rock and subsequently analysed by chemical imaging. The petrographic context of the nanofabricated specimen targets can demonstrate that the organic matter is not contamination, which is crucially important for the study of small amounts of rock sample with little organic matter. The major challenge is then to correctly interpret the observations and to understand their implications through space and time. Yet, some of the great remaining challenges in prebiotic chemistry include elucidating the pathways to form complex organic molecules from simple precursors, the distinctions between abiotic or biological precursor organic molecules, and systematically mitigating against contamination risk during sampling and analysis.

In conclusion, it comes as no surprise that the same kinds of visually correlated micro-analytical techniques as used in deep-sea basalt are also used on precious rock specimens returned from asteroids, solar wind, comets, and the Moon. This work not only contributes to build contamination-free approaches that will be used to directly search for traces life in rocks to soon be returned from planet Mars, but it also contributes important scientific observations that help to distinguish between abiotic and biological sources of organic matter. In fact, the discovery that hydrothermally altered basalt is a source of abiotic carbon leads to new questions about possible abiotic carbon synthesis on other planets. To be convincing to the scientific community, any evidence of biosignatures from extraterrestrial life will require the most robust approach to distinguish abiotic signatures from true biological-microbial signatures, and careful considerations of the characteristics of abiotic organic matter. These are the main challenges for a successful search for extraterrestrial life, past or present, on Mars or beyond.

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AUTHOR CONTRIBUTIONS

DP wrote the original draft and MD conceived the figure. All authors contributed to the manuscript and approved the final version

DECLARATION OF INTERESTS

The authors declare no competing interests.