Life on Mars: a clue to life on Earth?

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A martian meteorite has recently been claimed to show evidence of life and certainly shows the presence of organic matter. What might we learn about how life on Earth developed from studies of Mars?

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The recent paper by McKay *et al.* [1] reported possible relic biogenic activity in a Martian meteorite, giving a new impetus to the search for ancient life on Mars. Although this discovery is certain to be controversial, it highlights two basic questions: first, does our knowledge of primitive terrestrial life and of the early history of Mars allow us to expect life to have developed on Mars? And second, would the discovery of Martian life or organic matter on Mars help us to understand the early forms of life on Earth?

Primitive terrestrial life can be considered to have arisen when the first aqueous chemical systems that were able to copy the information contained within their molecules, and to evolve, emerged. We do not know what this first system was and unfortunately the direct clues which might help chemists to identify it have been erased in the four billion years since life began. But by analogy with contemporary life, it is generally believed that primitive life on Earth originated from the processing of reduced organic molecules by liquid water. The idea that primitive chemical information may also have been stored in mineral crystals has been developed by Cairns-Smith [2], but has, as yet, received almost no experimental support. The question is, where did the reduced organic molecules come from? Simply answering this question with certainty would be a major step forward in understanding the very early steps in the evolution of life. Can we expect this question to be answered by studies of Mars?

How might organic molecules have arisen on Earth?

Oparin [3] suggested that the small reduced organic molecules needed for primitive life were formed in a primitive atmosphere dominated by methane. This idea was tested in the laboratory by Miller [4], who exposed a mixture of methane, ammonia, hydrogen and water to electric discharges. In his initial experiment, he obtained 4 of the 20 naturally occurring amino acids, via the intermediary formation of hydrogen cyanide and formaldehyde. Miller's laboratory synthesis of amino acids occurred efficiently when a reducing gas mixture, containing significant amounts of hydrogen, was used. Although the true composition of primitive Earth's atmosphere is still unknown, geochemists currently favour a neutral or weakly reducing atmosphere dominated by carbon dioxide [5]. Under such conditions the production of amino acids appears to be very limited [6].

More recently, Wächtershäuser has suggested [7] that the carbon source for life was carbon dioxide. He proposes that the energy source required to reduce carbon dioxide was provided by the oxidative formation of pyrite (FeS_2) from iron sulfide (FeS) and hydrogen sulfide. An attractive point in this hypothesis is that pyrite has positive surface charges and binds the products of carbon dioxide reduction, giving rise to a two-dimensional reaction system, which would be more efficient than a system in which the products can freely diffuse away. This hypothesis is currently being tested.

Deep-sea hydrothermal systems have also been examined as possible environments for the synthesis of prebiotic organic molecules. Experiments have been carried out to test whether amino acids can be formed under conditions simulating the hydrothermal alteration of oceanic crust [8]. No convincing explanation for the production of large quantities of organic matter has yet been found.

Extraterrestrial delivery of organic molecules

The study of meteorites, particularly the carbonaceous chondrites that contain up to 5% by weight of organic matter, has allowed a close examination of extraterrestrial organic material. Eight proteinaceous amino acids have been identified, among more than 70 amino acids, in the Murchison meteorite [9]. Engel [10] reported that L-alanine was 18% more abundant than D-alanine in the Murchison meteorite. This rather surprising result has been recently confirmed by Cronin (unpublished observations). Cronin found a racemic composition (equal mixture of L- and D-enantiomers) for norvaline and α-amino-n-butyric acid, two amino acids which can racemize by abstraction of the C_α hydrogen atom. More interestingly, Cronin found enantiomeric excesses of about 10% for isovaline, α-methyl norvaline and α-methyl isoleucine, which cannot racemize by proton abstraction. The enantiomeric excesses found in the Murchison meteorite may help us to understand how a primitive homochiral life emerged. Indeed, homochirality of present-day life is now believed to be not just a consequence of life, but also a prerequisite for life. This is because stereoregular polymers such as β-sheet polypeptides do not form from racemic mixtures of amino acids. The chiral excess of amino acids found in the Murchison meteorite may result from the processing of the organic mantles of interstellar grains by circularly polarized synchrotron radiation from a neutron star remnant of a supernova [11].

Recently, a large collection of micrometeorites has been extracted from Antarctic old blue ice and analyzed by Maurette [12]. A constant, high percentage of unmelted chondritic micrometeorites in the size range 50–100 μm has been observed, indicating that a large fraction of the micrometeorites crossed the terrestrial atmosphere without undergoing drastic changes in temperature. In this size range, the carbonaceous micrometeorites represent 80% of the samples and contain on average 7% carbon. They might, therefore, have brought ~10^{20} g of carbon to Earth during the late terrestrial bombardment phase, a period of 300 million years. Micrometeorites could thus have delivered more carbon than that engaged in the biomass, currently estimated to be ~10^{18} g. Amino acids such as α-amino isobutyric acid have been recently identified in these Antarctic micrometeorites, which may have functioned as tiny chondritic chemical reactors when reaching oceanic water. It seems plausible, therefore, that this is where a large fraction of the organics required to start life on Earth came from. So, what are the next steps required to produce life, and could they have occurred on Mars?

Next steps towards life

For many decades, it was believed that primitive life emerged as a cell, thus requiring boundary molecules such as phospholipids, catalytic molecules such as protein enzymes and informative molecules such as nucleic acids. Some of these components may also have arrived from space. Vesicle-forming fatty acids have been identified in the Murchison meteorite [13]. Primitive membranes could also have initially been formed by simple isoprene derivatives [14]. Primitive catalysts may have been easy to produce. Selective condensation of amino acids in the presence of liquid water has been experimentally documented. When hydrophobic and hydrophilic amino acids coexist within the same polypeptide chain, the duality generates interesting topologies such as stereoselective and thermostable β-sheet structures. Short peptides have been shown to exhibit catalytic properties [15]. Thus, given that the relevant binding blocks could have been delivered by micrometeorites, two out of three of the components needed for the evolution of life might have been present. But the theory of the cellular origin of life was weakened when nucleotide chemists failed to demonstrate that accumulation of significant quantities of natural nucleotides, the building blocks of RNA, was a plausible chemical event on the primitive Earth. To attempt to address this problem, intense experimental work is being carried out in the field of RNA analogs that might be easier to form under the conditions of the primitive Earth and might provide a transition to RNA itself. Eschenmoser's pyranosyl-RNA is a prime example of these studies [16].

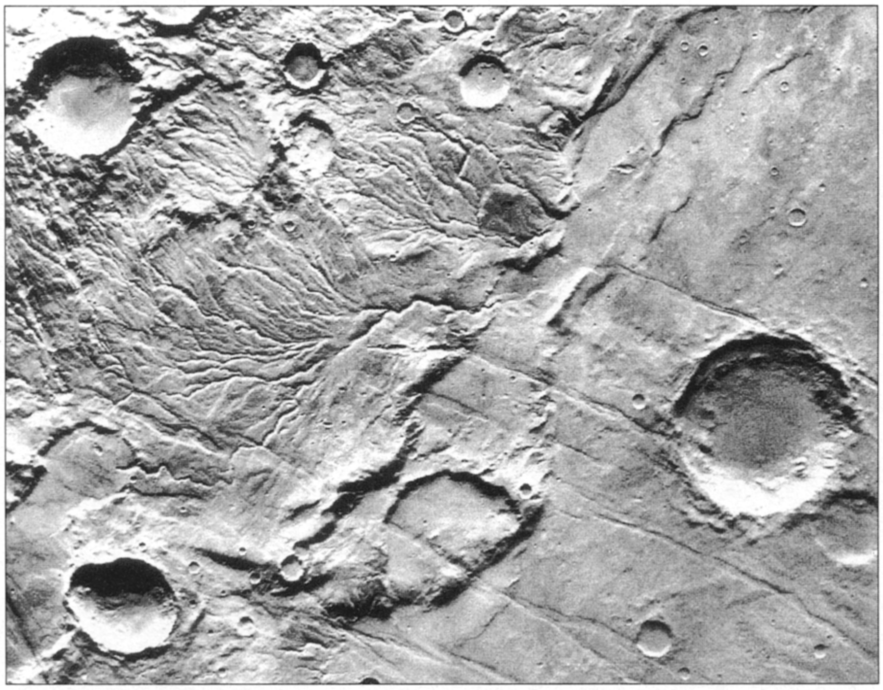
As RNA can act as genetic material and perform catalysis, the notion that the first living system on the primitive Earth was composed largely of RNA (the RNA world) is attractive and has gained wide currency. One should remember, however, that no plausible synthesis of RNA under prebiotic conditions has yet been found. Many chemists are now tempted to consider that primitive life was supported by simpler informative molecules. For this reason much work is being devoted to autocatalytic systems including simple organic molecules [17,18] and micelles [19].

Was Mars similar to the Earth?

Obviously conditions on Mars are now very different from conditions on Earth. The question is, were conditions on Mars and Earth sufficiently similar at the time when life evolved for the essential steps in the generation of life to have occurred on Mars as well. In considering the timing of life emergence the geological record provides important information. The isotopic signatures of the organic carbon of the Greenland metasediments bring indirect evidence that life may be 3.85 billion years old [20]. This conclusion is fully consistent with the remarkable diversity of the 3.465 billion year old fossilized microflora reported by Schopf [21]. Thus, the relevant period is between 4 and 3.5 billion years ago.

Mars mapping by Mariner 9 and by Viking 1 and 2 revealed channels resembling dry river beds (Fig. 1). Three major classes of channels were identified: (1) dendritic runoff channels and valleys primarily associated with cratered terrain older than 3.8 Ga and also generally associated with fluvial water erosion; (2) outflow channels suggestive of large-volume flows in cataclysmic events; and (3) fretted channels which are steep walled with smooth, flat floors suggestive of erosion by debris flows. It is difficult to estimate the total amount of water that may have existed on the surface of Mars; the estimated depth of surface coverage ranges from a few meters to several hundred meters. The climatic conditions required for the formation of the valley networks are also poorly understood. The most plausible picture is that the CO_2 atmosphere was relatively thick (1–5 bars) in the early history of Mars, giving rise to a greenhouse effect that allows the mean global surface temperature to remain above the freezing point of water. Recently, it has been suggested [22] that the valley networks, like the fretted channels, formed mainly by mass wasting, aided by groundwater seepage into the mass-wasted debris, between 3.8 and 3.7 Ga ago. Liquid water therefore seems to have been restricted to the very early stages of Martian history. By about 3.8 Ga ago, atmospheric CO_2 was probably irreversibly lost due to carbonate formation and, as a result, the pressure and temperature declined. Nevertheless, in the crucial period when life probably developed on Earth conditions on Mars appear to have been at least broadly similar to those on Earth.

Figure 1



Martian dendritic valley system, most probably formed by surface water flow.

Life on Mars?

The Viking 1 and 2 lander missions were designed to address the question of existing life on Mars. Three experiments were selected to detect metabolic activity such as photosynthesis, nutrition and respiration of potential microbial soil communities. All three biology experiments gave 'positive' results, although no organic carbon was found in the Martian soil by gas chromatography– mass spectrometry. It was concluded that the most plausible explanation for these positive results was the presence of highly reactive oxidants at the Martian surface, for example H_2O_2, which would have been photochemically produced in the atmosphere [23]. But since the Viking lander could not sample soils below 10cm, the depth of this apparently organic-free and oxidizing layer is unknown. Bullock *et al.* [24] have calculated that the depth of diffusion for H_2O_2 is less than 3 meters, so, experiments carried out at a greater depth than this might yield more informative results about organic molecules and possibly fossilized microorganisms.

The early histories of Mars and Earth clearly show similarities. Geological observations collected from Martian orbiters suggest that liquid water was once stable on the surface of Mars, attesting to the presence of an atmosphere capable of decelerating micrometeorites. Despite the interpretation of Viking results, chemical evolution may have been possible on Mars.

The two meteorites EETA79001 [25] and ALH84001 [1,26] supply new and very interesting information. The most direct evidence for their Martian origin is the trapped gas component (rare gases, nitrogen and CO_2) which has element and isotope ratios very different from those observed in any other meteorites, but closely matching the Martian atmosphere analyzed by Viking. A subsample of EETA79001 excavated from deep within the meteorite has been subjected to stepped-combustion. The CO_2 release from 200°C to 400°C suggests the presence of organic molecules. The carbon is enriched in ^{12}C, like the carbon of terrestrial biogenic material, with $\delta^{13}C$ of about –27‰ ($\delta^{13}C = [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard} - 1] \times 1000$; $\delta^{13}C$ expresses the permil deviation of the $^{13}C/^{12}C$ ratio of the sample relative to that of a conventional standard, the carbonate skeleton of a fossil cephalopod which has a $^{12}C/^{13}C$ ratio of 88.99). A high concentration of organics has also been found in ALH84001 with $\delta^{13}C$ of about –22‰ [23]. McKay *et al.* [1] reported the presence of polycyclic aromatic hydrocarbons (PAHs), carbonate globules and ovoid features which may represent a signature of relic biogenic activity on Mars. From a list of observations about the carbonates and PAHs, the authors stated: 'when considered collectively...we conclude that [these phenomena] are evidence for primitive life on early Mars'.

Taken individually, the observations about the carbonates and PAHs can, however, be explained by non-biological means. For instance, there are conflicting values for the formation temperature of the carbonates: major-element chemistry implies a temperature of more than 500°C, which is incompatible with bacterial life, whereas oxygen isotope composition gives less than 100°C. PAHs are not synthesized in any biological system but are produced by metamorphism of marine plankton and early plant life. Their presence in the unmetamorphized ALH84001 cannot therefore be taken as a convincing biomarker. No analysis of the composition of the ovoid feature edges has been performed to show whether they are organic or not. The carbonates that contain the microfossils are found in igneous rock rather than in a sediment [27]. Although the evidence for ancient life in ALH84001 is not conclusive, the two Martian meteorites clearly show the presence of organic molecules. Thus, it is plausible that the ingredients required for the emergence of a primitive life were present on the surface of Mars. If so, microorganisms may have developed on Mars until liquid water disappeared. Since Mars probably had no plate tectonics and since liquid water seems to have disappeared from the surface of Mars very early, the Martian sub-surface perhaps keeps a frozen record of the very early forms of a terrestrial-like life. Drilling into the Martian sediments will be the way to explore its biological past and to search for organic remnants of meteoritic and cometary bombardment.

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