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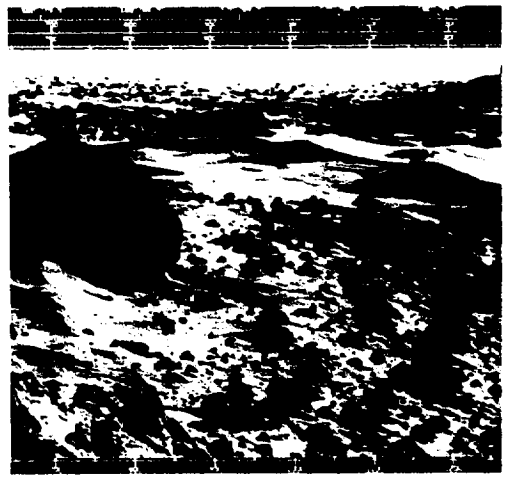

The unambiguous detection of amino acids on Mars could be pivotal in understanding the origin of life

Understanding the events that led to the origin of life on Earth is complicated by the lack of geological evidence from the period around 4 billion years (4 Gyr) ago when the transition from prebiotic chemistry to biochemistry is believed to have occurred. Although erosion and plate tectonics have since erased the terrestrial geological record from the time of the origin of life, there is a possibility that information about this period of Earth history may still be preserved on Mars.

Compared with Earth, Mars is a more placid planet. Surface alteration rates are minimal, and there is no known plate tectonic activity. Extensive areas of the Martian surface may date to > 4 Gyr ago (*1*). Geomorphologic evidence suggests that liquid water existed on the Martian surface at some point in the past and that early Mars may have had an atmosphere similar to that of early Earth (*2*). If this is the case, then at least some of the steps leading to the origin of terrestrial biochemistry may have also taken place on Mars (*3*). Thus, traces of prebiotic chemistry, or organic compounds derived from an extinct Martian biota (*4*), could be present on Mars. Although deemed unlikely, life may still exist today on Mars in some protected subsurface environments (*5*).

The processes thought to be involved in the origin of life on Earth are summarized in Figure 1. The first requirement is the presence of a prebiotic soup consisting of a rich variety of organic compounds, although the exact composition of a soup necessary for the origin of life is not known. The components of the soup may have been made directly on Earth or supplied from space by comets, asteroids, micrometeorites, or interplanetary dust (*6*). A large variety of organic compounds—including those that play a major role in biochemistry, such as amino acids, purines, and pyrimidines—have been identified in one class of meteorites, the carbonaceous chondrites (Figure 2). In addition to demonstrating that important biomolecules can be synthesized by abiotic reactions in extraterrestrial environments, the presence of these organic compounds in meteorites also suggests that exogenous compounds were periodically delivered to the surface of the Earth or other planetary bodies by various processes (*6*).

The subsequent transition from the abiotic chemistry of primitive Earth to the first self-replicating molecular systems capable of Darwinian evolution marked the point of the origin of life. On Earth, subsequent evolution of the first self-replicating molecules gave rise to the RNA world and finally the DNA–protein world characteristic of all modern life.

A major goal of the NASA Space Exploration Program is to search for evidence of abiotic chemistry and extinct or extant life on Mars. During the next decade, spacecraft will orbit Mars, land on the surface, and return with surface samples for analysis. The question is what compounds should we search for, either directly on the planet or in samples returned to Earth, that will answer unambiguously whether abiotic and/or biotic organic molecules are present.

Previous organic analyses

The detection of organic material on Mars was attempted in 1976 by the Viking 1 and 2 landers, which carried GC/MS systems (*8*). No organic compounds were detected above the part-per-billion level in the upper few centimeters of the Martian surface, but the results of other experiments aboard the landers indicated that the Martian surface is saturated with an unidenti-

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fied oxidant that probably destroyed any organics within a short time frame (*9*). Because the oxidizing layer may only extend a few meters below the surface (*10*), the preservation of organics in the subsurface is still a possibility.

Aside from the Viking missions, the only other opportunities to directly analyze Martian samples came from the SNC (shergottites, nakhlites, and Chassigny) meteorites. Because they contain trapped noble gases that are similar to those measured in the Martian atmosphere by the Viking spacecraft (*11*), the SNC meteorites are thought to be fragments of the Martian crust ejected by impact events.

The Antarctic shergottite EETA79001 is of considerable interest because it contains a carbonate component with 600–700 ppm combustible carbon, which was suggested to be endogenous Martian organic material (*12*). However, analyses of a small fragment of the EETA79001 carbonate (*13*) found < 1 ppb of α-aminoisobutyric acid (Aib), an amino acid considered to be primarily of abiotic origin (*14*). Aib is one of the most abundant amino acids in carbonaceous meteorites and is readily synthesized in laboratory-based prebiotic experiments, but it is not one of the major amino acids found in the proteins of terrestrial organisms.

Although trace quantities of abiotic amino acids were not detected in EETA-79001, part-per-million quantities of the L-enantiomers of the amino acids commonly found in the proteins of living organisms were found (*13*). The L-amino acids in this Martian meteorite appear to be terrestrial contaminates probably derived from Antarctic ice meltwater that had percolated through the meteorite. Failure to detect endogenous amino acids in this one meteorite does not necessarily rule out the presence of amino acids on Mars, because the extreme temperatures during the impact ejection should have destroyed any amino acids originally present (*14*). However, these results do suggest that the transfer of organic compounds such as amino acids from Mars to Earth, or vice versa, by impact ejecta appears unlikely.

The carbonate component of another Martian meteorite collected in the Antarctic, ALH84001, has recently been reported to contain endogenous polycyclic aromatic hydrocarbons (PAHs), which are suggested to be of biotic origin (*4*). The part-per-million levels of PAHs reported in this meteorite greatly exceed the part-per-billion upper limit for organic compounds determined by Viking. The presence of only L-amino acids of apparent terrestrial origin in EETA79001 (*13*) suggests that organic compounds associated with Earth-based contamination could generate misleading conclusions about whether organic molecules derived from extinct life are indeed present in Martian meteorites.

What should we look for in future missions?

Any strategy for investigating the presence of organic molecules on Mars should focus on compounds that are readily synthesized under plausible prebiotic conditions, are abundant in carbonaceous meteorites, and play an essential role in biochemistry. Amino acids are one of the few compound classes that fulfill all these requirements. They are synthesized in high yields in prebiotic simulation experiments (*15*), are one of the more abundant types of organic compounds in carbonaceous meteorites (Figure 2), are the building blocks of proteins and enzymes, and are ubiquitous on Earth (*14*).

In future organic analyses of Martian samples, a major challenge is not just identifying and quantifying the organic compounds that may be present, but also determining whether the molecules were produced by abiotic reactions or are the product of extinct or extant life. Amino acid homochirality provides an unambigu-

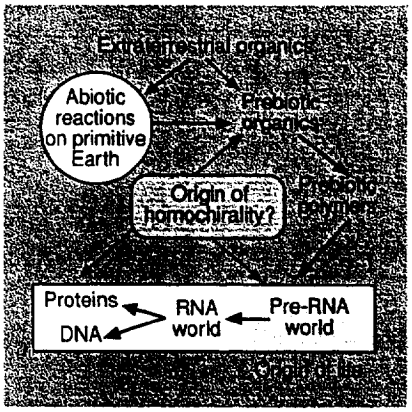

Figure 1. General scheme depicting the key steps in the origin and early evolution of life on Earth.

Life is defined as an autonomous replicating system that evolves by natural selection.

ous way of distinguishing between abiotic and biotic origins. All known laboratory abiotic synthetic processes yield racemic mixtures of amino acids, and the amino acids in carbonaceous chondrites are racemic when terrestrial contamination is absent (*16*). In contrast, terrestrial organisms use L-amino acids almost exclusively in protein biosynthesis.

Amino acid homochirality is an important aspect of biology, because proteins cannot fold into bioactive configurations such as the α-helix or β-sheets if the amino acids are racemic. However, enzymes made up entirely of D-amino acids function just as well as those made up of only L-amino acids, but the two enzymes use the opposite stereoisomeric substrates (*17*).

There are no biochemical reasons that L-amino acids would be favored over D-amino acids. On Earth, the use of only L-amino acids by life was probably simply a matter of chance (*16*). We assume that if proteins and enzymes were a component of extinct or extant life on Mars, amino acid homochirality would have been a requirement. However, the possibility that Martian life was (or is) based on D-amino acids would be equal to the possibility that it is based on L-amino acids.

The detection of a nonracemic mixture of amino acids in a Martian sample would be strong evidence for the presence of an extinct or extant biota on Mars. The finding of an excess of D-amino acids would provide irrefutable evidence of unique Martian life that could not have been derived from seeding the planet with terrestrial life. In contrast, the presence of racemic amino acids—along with amino acids such as Aib and racemic isovaline (*14*)—would be indicative of an abiotic origin, although we have to consider the possibility that the racemic amino acids were generated from the racemization of biotic, homochiral amino acids (*18*).

When an organism dies, its amino acids begin to racemize at a rate dependent on the particular amino acid, the temperature, and the chemical environment (*14*). Racemization reactions are rapid on the terrestrial geological time scale, and even at deep ocean temperatures of 2 °C, amino acids are totally racemized in about 5 million to 10 million years. Amino acids from an extinct Martian biota maintained in a dry, cold (< 250 K) environment would not have racemized significantly over the entire 4.5-Gyr lifetime of the planet. However, complete racemization would have taken place in environments where liquid water was present for periods of only a few million years following biotic extinction.

The best preservation of amino acid homochirality associated with extinct Martian life would be in the polar regions. When biogenic amino acids are completely racemized, they are indistinguishable from a chirality point of view from the racemic amino acids produced by abiotic organic syntheses or those derived from exogenous sources. Although α-dialkyl amino acids with a chiral center, which are common in carbonaceous meteorites (*7*), are very resistant to racemization (*14*), these amino acids are not usually found in the proteins of terrestrial organisms. However, we cannot exclude the possibility that α-dialkyl amino acids might be used by life elsewhere. Finding that the amino acids with an α-hydrogen were racemic, whereas for the α-dialkyl amino acids with a chiral carbon there was a significant excess of one enantiomer, could suggest that life did, or still does, exist on Mars.

Preventing cross-contamination between Earth and other solar system bodies is a central concern of the NASA Space Exploration Program (*19*). Although the surface oxidant layer could retard the accumulation of Earth-derived organic contaminates, how widespread the oxidant is over the entire Martian surface is not known. Terrestrial amino acid contamination could greatly compromise assessments of whether any amino acids are endogenous to Mars. Because of the distinctive L-amino acid signature associated with life on Earth, enantiomeric analyses of protein amino acids could be used to monitor the level of contamination on Mars during the course of planetary exploration. This requires that data be acquired as early as possible in the Mars exploration program to provide a useful baseline data set for comparison with future analyses.

Detecting amino acids on Mars

In Table 1 we have evaluated the spacecraft worthiness of amino acid analytical methods routinely used in the laboratory that might be used to perform in situ analyses on Mars. GC/MS and HPLC are about equally suited for spacecraft instrumentation; however, because of the prospects for miniaturization, CE appears to be the best choice of the three methods.

GC/MS is an obvious choice because of the success with similar instrumentation during the Viking missions and because of the long history of amino acid analysis by GC in Earth-based laboratories. However, any GC/MS system on future missions must be able to distinguish between abiotic and biotic origins through enantiomeric resolution. Either chemical derivatization procedures that produce diastereomeric derivatives or a chiral stationary phase that can separate derivatized enantiomers would be required.

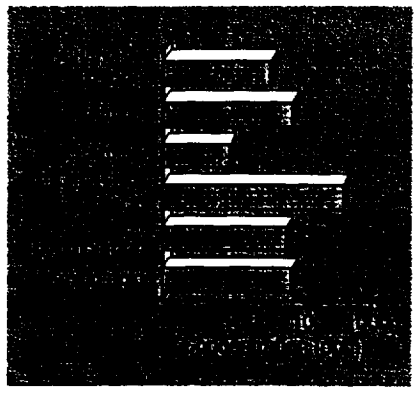

Figure 2. Approximate amounts of several classes of organic compounds detected in carbonaceous chondrites.

Data from Reference 7.

These derivatization procedures require additional hardware such as reaction chambers, valves, and pumps, which can greatly increase the size, weight, and mechanical complexity of the GC/MS system, although there has been some progress in miniaturizing GC components (*20*). MS and thermal conductivity detectors lack the sensitivity needed to detect amino acids at the sub-part-per-billion level, and although flame ionization detectors have greater sensitivity, they are probably too unstable and dangerous for use on a spacecraft.

HPLC is more suited to chiral amino acid analysis than GC. Simple chiral derivatization procedures and fluorescence detection can be used to achieve sensitivities well below the part-per-billion level. Reversed-phase LC with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatization and fluorescence detection has been used to search for extraterrestrial amino acids in meteorites (*13*), lunar samples (*21*), sediments from the Cretaceous–Tertiary boundary (*22*), and polar ice core samples (*23*). However, the hardware is heavy and mechanically complex and requires large volumes of solvents, which are all disadvantages when designing instrumentation for a spacecraft.

A relatively new technology that shows promise for spacecraft-based amino acid analysis is microchip-based CE (*20, 24, 25*), which can be used with the same chiral derivatization reagents and detection techniques used in HPLC, such as laser-induced fluorescence or electrochemical detection, to achieve the same level of sensitivity. The separation hardware, including buffer reservoirs and derivatization reaction chambers, can be etched onto microchips with dimensions on the order of centimeters (*26*). In these systems, multiple reactions can be performed under computer control in a few minutes, consuming only 100 nL of reagents.

The reagents, sample, and solvents can also be manipulated using the electroosmotic forces that effect the separation, with no need for mechanical pumps or valves. Such a system has great advantages over GC or LC systems in weight, size, and power requirements. Although the enantiomeric resolution of amino acids using microchip-based CE has not yet been extensively investigated, it appears that this methodology offers the best potential for a compact, rugged, low-mass instrument package for in situ amino acid analyses on Mars.

Table 1. Evaluation of amino acid analytical techniques for spacecraft operation.

	GC/MS	HPLC	CE
Sensitivity	1	3	3
Analysis time	1	2	3
Weight	2	1	3
Mechanical complexity	1	1	3
Reagent volume and storage	2	1	3
Ease of derivatization	1	3	3
Confirmation of peak identity	3	1	1
Proven space worthiness	3	1	1
Enantiomeric resolution	2	3	3
Miniaturization potential	2	1	3
Total score	18	17	26

Scoring: 1 = least suitable, 2 = suitable, 3 = most suitable

Sample acquisition and preparation

Before the amino acid content can be determined, a sample of Mars must be acquired, prepared, and delivered to the in situ analytical instrument. Simple scooping up of loose soil and dropping it into a receptacle on the analytical instrument was used by the Viking landers. However, because of the highly oxidizing conditions on the Martian surface (*9*), this method would not likely yield samples containing amino acids, and other sampling methods are needed.

One possibility is the removal of intact fragments from the interior of rocks, although a remotely operated technology to do this has not been developed. To obtain samples not affected by the oxidant layer, it will probably be necessary to penetrate to the deep subsurface. Although sample collection by drilling to depths of a meter or more was achieved by Russian unmanned lunar vehicles, drilling equipment capable of reaching depths of 10 m or more may be necessary for Mars; this presents major logistical and technological problems. Sampling geologically recent impact craters or exposing fresh material by using explosive projectiles offers alternative subsurface sampling strategies.

Once a sample has been taken, the amino acids must be separated from the rock or mineral matrix. The extraction procedure could parallel that used in laboratories on Earth for the analyses of amino acids in carbonaceous meteorites (*27*). A pulverized sample is extracted with hot water, and a portion of the supernatant is desalted by ion-exchange chromatography, derivatized, and analyzed. Another portion of the water extract can be hydrolyzed in HCl to convert amino acid precursors to amino acids, which are subsequently analyzed. Although this procedure is suitable for laboratory-based analyses, in a spacecraft instrument package, a complex series of valves, reagent reservoirs, and reaction chambers would be required.

Another possible extraction procedure would be to sublime the amino acids directly from the sample. Amino acids have appreciable vapor pressures at temperatures in the range 150–250 °C (*28*). Thus, amino acids could be isolated by heating the sample under partial vacuum (easily obtained on Mars where the surface pressure is only 4–6 torr) in a closed chamber interfaced with the sample acquisition component of the analytical system maintained at the Martian surface temperature. This would require no extensive sample manipulation procedures or reagents. However, the possible decomposition of amino acids during sublimation needs to be carefully investigated. (We recently conducted an experiment with alanine at 500 °C and about 1 torr and found that it readily sublimed. Although there was some decomposition, it could be minimized by using lower temperatures.)

Samples returned to Earth

A complete evaluation of the inventory of organic compounds that may be present on Mars requires that samples be returned, especially if prior in situ analyses are positive. Theoretically, samples returned to Earth could be analyzed by any suitable technique; however, there are limitations in returned-sample analyses.

The cost of a sample return mission could limit sampling to only a few geologi-

cally distinct sites. The size of sample that can be returned using presently available space transportation technology may limit the number of laboratory-based analyses that can be performed and may eliminate techniques with large sample requirements. Compound-specific organic analyses of a returned sample might be limited to techniques that are compatible with other areas of investigation, such as mineralogical and stable isotope analyses.

The main limitation of organic analyses of returned samples will be the omnipresent problem of terrestrial contamination. Even the best and most sensitive analytical methods are limited by contaminants that will affect detection limits of extraterrestrial organic compounds. Although this could also be a potential problem for in situ Martian analyses, there are ways to minimize it. Any spacecraft landing on the Martian surface would be required to undergo rigorous decontamination to ensure that the planet is not inoculated with terrestrial organisms and organic compounds (*19*). Reagents used in in situ analytical systems would be extensively purified and sterilized before the mission and probably transported dry. Water required for aqueous buffers and sample processing could be made using an H_2/O_2 fuel cell directly on the Martian surface.

Terrestrial contamination has limited the detection of Aib in lunar soils to ~ 0.1 ppb (*21*) and to ~ 1 pptr in polar ices (*23*). For example, results our of analyses of small samples of the organic-rich Murchison meteorite are shown in Figure 3. With a 10-mg sample, the extraterrestrial amino acids Aib and racemic isovaline are clearly present, whereas in the 100-µg sample, Aib is only barely detected compared with the blank.

Contamination problems are even more crucial in the detection of the protein amino acids in extraterrestrial samples (*16*). To detect part-per-billion levels of endogenous amino acids with a S/N

Zare's Martian measurements

The announcement in August of possible fossils of early life on Mars far smaller than even the smallest bacteria on Earth will undoubtedly accelerate the search for more signs of life on the surface of the Red Planet itself. Whether or not the claim of ancient life stands up under further scrutiny, Richard N. Zare, a chemist at Stanford University, is confident that the PAHs in the meteorite, which his group found using their microprobe two-step laser MS method (μL^2MS), represent the first measured organic compounds of Martian origin (*4*).

Although the overall project was headed by David S. McKay of NASA Johnson Space Center, Zare led the team responsible for the mass spectral analysis of ALH84001, a meteorite found in the Allan Hills of Antarctica in 1984 that has been determined to be of Martian origin. The MS technique they used was developed by Zare for the study of interplanetary dust particles. "It's only because of the reputation we got for our work [with interplanetary dust] that we were approached by the people from NASA," said Zare. "The idea to study this Martian meteorite did not originate with me." The μL^2MS technique can measure the PAHs in the sample with 40-µm spatial resolution and subattomole sensitivity without requiring a separation step. It is a "soft" ionization technique that results in little fragmentation of the analytes.

What is the technique? A pulse from an IR laser is used to desorb molecules from the sample surface. The IR pulse heats the surface without ionization, and the low power density minimizes decomposition. A second laser pulse, this one UV, uses 1 + 1 resonance-enhanced multiphoton ionization, in which a first photon promotes the molecule to an excited state and a second photon ionizes it, to ionize preferentially gas-phase organic molecules. Analytes can be selectively ionized by adjusting the UV wavelength used, 266 nm in this case. The ions are detected with a time-of-flight mass spectrometer.

Zare and his co-workers identified two collections of PAHs in the mass spectra of the meteorite samples. One mass envelope covered the mass range of 178–276 and was assigned to phenanthrene (178), pyrene (202), chrysene (228), perylene or benzopyrene (252), and anthanthracene (278). The second mass envelope ranges from 300 to > 450 with periodicities of both 14 and 2, indicating the presence of alkylated side chains. The concentration profile of the PAHs increases with sampling depth, ruling out terrestrial or laboratory contamination.

Despite being the first organic molecules associated with Mars and despite the fact that PAHs are well-known biomarkers for prehistoric life on Earth, the discovery of PAHs in the Martian meteorite does not in itself suggest the existence of life. "We've got organics," said Zare. "But you can find organics in meteorites that you don't necessarily think are alive. We've got PAHs. Does this itself prove life? It does not."

The PAH evidence was used in combination with electron microscopy of "carbonate globules" found in the meteorite, which are similar in shape and texture to carbonate precipitates induced by bacteria on Earth. The carbonate globules are associated with magnetite and iron sulfides. The coexistence of noncorroded iron sulfides and magnetite with partially dissolved carbonate is not easily explained with inorganic models but can be explained with a biogenic model. The concentration of PAHs also peaked at the location of the carbonate globules.

Zare and his colleagues are quick to acknowledge that no one line of evidence points to biological origins, but they believe that the combination is difficult to explain in any other way. "Each thing has a 'maybe' associated with it," said Zare. "When you put 'maybes' together, you still have 'maybe,' but at some point, your 'maybe' gets your confidence up to the point where you say it's likely. Finally, you get to a stage where you say 'I don't know another way. There may be another way, but I don't know what it is.' Still, a healthy skepticism is an important part of the scientific process."

Celia Henry

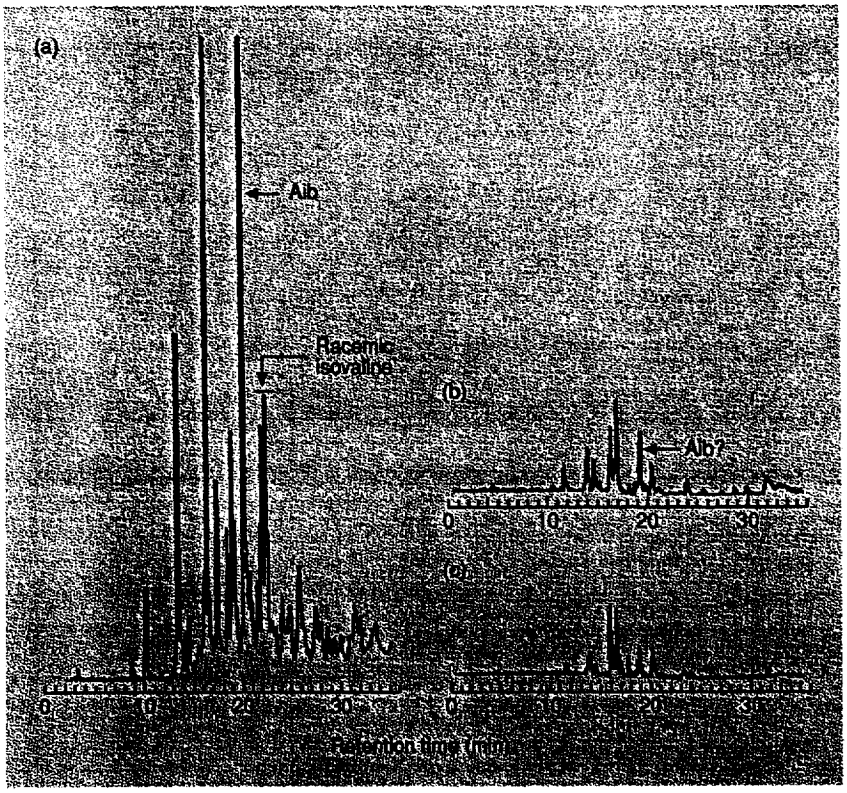

Figure 3. Murchison meteorite samples analyzed by HPLC with OPA/NAC derivatization and fluorescent detection.

(a) 10 mg, (b) 100 μg, (c) blank. The analytical method can be found in Reference 22.

of two, approximately 0.5–1 g of a Martian sample could be required. This would likely be considered a large sample, and the portions of returned samples available for analysis could be restricted to much smaller amounts.

To detect trace levels of amino acids in returned samples, the background contamination from terrestrial amino acids and other interfering compounds would need to be greatly reduced. Because any returned sample from Mars would be quarantined to ensure that any Martian organisms did not contaminate the Earth (*19*), facilities would also be set up to prepare the super-clean reagents, glassware, etc., necessary to reduce terrestrial background contamination levels.

Into the next century

The next couple of decades will be exciting times with respect to the question of whether life existed or exists elsewhere in the solar system and the resolution (we hope) of how life originated on Earth. The exploration and the results from organic analyses of the surface of Mars will undoubtedly be pivotal in these questions, and state-of-the-art analytical chemistry techniques will play a major role.

Abiotic organic compounds detected on the Martian surface could provide information about the possible composition of the prebiotic soup on early Earth. Finding convincing evidence of extinct life on Mars would be, to put in mildly, sensational. The demonstration of extant life on Mars would be even more so and could revolutionize our understanding of the chemistry on which life is based.

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