Organics on Mars?

Inge L. ten Kate

Abstract

Organics are expected to exist on Mars based on meteorite infall, *in situ* production, and any possible biological sources. Yet they have not been detected on the martian surface; are they there, or are we not capable enough to detect them? The Viking gas chromatograph–mass spectrometer did not detect organics in the headspace of heated soil samples with a detection limit of parts per billion. This null result strongly influenced the interpretation of the reactivity seen in the Viking biology experiments and led to the conclusion that life was not present and, instead, that there was some chemical reactivity in the soil. The detection of perchlorates in the martian soil by instruments on the Phoenix lander and the reports of methane in the martian atmosphere suggest that it may be time to reconsider the question of organics. The high-temperature oxidizing properties of perchlorate will promote combustion of organics in pyrolytic experiments and may have affected the ability of both Phoenix's organic analysis experiment and the Viking mass spectrometer experiments to detect organics. So the question of organics on Mars remains open. A primary focus of the upcoming Mars Science Laboratory will be the detection and identification of organic molecules by means of thermal volatilization, followed by gas chromatography–mass spectrometry—as was done on Viking. However, to enhance organic detectability, some of the samples will be processed with liquid derivatization agents that will dissolve organics from the soil before pyrolysis, which may separate them from the soil perchlorates. Nonetheless, the problem of organics on Mars is not solved, and for future missions other organic detection techniques should therefore be considered as well. Key Words: Mars—Organic degradation—Search for Mars organics—Laboratory investigations—Interpretation of planetary mission data. Astrobiology 10, 589–603.

1. Introduction

Oᴿɢᴀɴɪᴄ ᴍᴏʟᴇᴄᴜʟᴇs have been detected in the interstellar medium (Ehrenfreund and Charnley, 2000; Millar, 2004; and references in both), comets (see Crovisier, 2004, for a review), meteorites (Botta and Bada, 2002; Sephton, 2002; and references in both), and interplanetary dust particles (Flynn, 1996), and are highly abundant on Earth. Mars seems to be a next logical place to search for organic material in that Mars experienced a long history of bombardment (Marcus, 1968; Werner, 2008) by comets, meteorites [an estimated yearly accumulation rate of 5×10^2 to 5×10^5 meteorites greater than 10 g in mass per square kilometer (Bland and Smith, 2000)], and dust particles. The total mass accretion rate by comets, meteorites, and dust particles is estimated between 1.8×10^{-5} and 4×10^{-4} g m^{-2} per year (Flynn and McKay, 1990), which corresponds to an annual arrival of organic material at the martian surface on the order of 10^6 kg (Flynn, 1996). Another possible source of organic matter is through production on, or beneath, the martian surface. Several mechanisms for endogenous production of organic material on early Earth have

been suggested, which may have played a role on early Mars as well, such as lightning, coronal discharge, UV radiation, and atmospheric shocks (Chyba and Sagan, 1992). Even though the presence of organics on Mars seems likely, based on the above, organic matter has not yet been detected on the martian surface. Is it there at all, or are investigators simply incapable of detecting it? In this paper, I offer an overview of the search for organics on Mars by the Viking mission and, to a lesser extent, the Phoenix mission; the conclusions drawn, in particular, from the Viking mission; and the ways in which these conclusions have shaped laboratory studies on organics under martian environmental conditions.

2. Before the Viking Mission

By the early 1970s, several missions had visited the planet Mars with varying results. Data obtained by Mariner 4 in 1964 and Mariners 6 and 7 in 1969 caused pessimism about the possibility of life on Mars (Klein, 1974). However, the Mariner 9 orbiter and its terrestrial observations showed that (1) Mars is a geologically active planet; (2) the 3–10 mbar

atmosphere is primarily composed of CO_2 with small amounts of CO, O_2, H_2O, and some other traces gases, including O (Barker, 1972); (3) there is 10–20 mm precipitable water; and (4) the surface contains about 1% H_2O (Mariner Mars, 1973; Oró and Flory, 1973). Present martian atmospheric chemical conditions are believed to be hostile with respect to abiotic organic synthesis, but conditions may have been favorable in the distant past (Fanale, 1971). Laboratory simulations have indicated that relatively simple organic compounds could be produced by the direct interaction of UV radiation with the martian atmosphere (Young *et al.,* 1965) in the presence of catalytic surfaces (Hubbard *et al.,* 1971, 1973). Tyson and Oyama (1973) showed that CO_2 can be incorporated into already present amino acids under simulated martian radiation conditions. More-complex organics are known to be present in carbonaceous chondrites (Anders, 1964; Oró, 1972; Nagy, 1975), and Dycus (1969) calculated the mass loss of meteorites that occurs while they travel through the atmosphere and the mass of meteorites after impact on the martian surface, his findings implying that it is likely organic matter has been delivered to the martian surface over the course of billions of years. Since the Mariner missions were not designed to look for organic material or small forms of life (such as microorganisms) and could only scan the surface remotely, the Viking mission was launched in 1975 to land on Mars and analyze the surface.

3. The Viking Mission

The Viking mission consisted of two spacecraft, Viking 1 and Viking 2, each composed of an orbiter and a lander and carrying a range of instruments designed for analysis of soil, rock, and atmosphere (Soffen, 1977). On July 20, 1976, the Viking 1 lander landed at Chryse Planitia (22.48°N, 49.97°W). The Viking 2 lander landed at Utopia Planitia (47.97°N, 225.74°W) on September 3, 1976. Biemann *et al.* (1977) described the aim of the Viking mission as follows:

> One of the major goals of the Viking mission was to find out whether or not organic compounds exist on the surface of the planet Mars and, if they do exist, to determine their structures and measure their abundances. This seemed important because we hoped that the nature of martian organic molecules would provide a sensitive indicator of the chemical and physical environment in which they were formed. Furthermore, we hoped that the details of their structures would indicate which of many possible biotic and abiotic syntheses are occurring on Mars.

For this purpose, the Viking landers were equipped with a biological and a molecular analysis experiment (Soffen, 1977).

3.1. The Viking molecular analysis experiment

The molecular analysis experiment, also known as the Viking gas chromatograph–mass spectrometer (GCMS), was designed to heat soil samples to 200°C, 350°C, and 500°C, and analyze the gases that were released upon heating. The molecular analysis experiment had the following goals (Anderson *et al.,* 1972):

> (1) A qualitative and semi-quantitative determination of the organic compounds present in the top 10 cm layer of

the surface of Mars; (2) qualitative and quantitative composition (including isotope abundances) of the atmosphere at the surface; (3) semi-quantitative determination of water (and its physical state, if possible) in the surface; and (4) whatever information on the inorganic (mineralogical) composition of the surface that can be obtained in the course of the measurements performed to satisfy (1)–(3) above.

The released gases were subsequently analyzed by a gas chromatographic column-detector system, a mass spectrometer with a range of 12–200 dalton, or a combination of both in which the mass spectrometer served as a detector for the gas chromatograph. Direct atmospheric measurements were made with the mass spectrometer (Anderson *et al.,* 1972). The detection limits of the GCMS were in the parts per billion range for compounds containing more than two carbon atoms and in the parts per million range for compounds containing one or two carbon atoms (Biemann, 1979). In the four samples taken from surface and subsurface material from both landing sites, water (0.1–1.0 wt%), carbon dioxide (0.05–0.6 ppm), and some organics were detected, including benzene and toluene. Furthermore, Viking 1 detected traces of chloromethane at 15 ppb at 200°C and Viking 2 detected dichloromethane at 0.04–40 ppb at 200–500°C. However, these chlorohydrocarbons were all considered to be terrestrial contaminants, although they had not been detected at those levels in the blank runs. Therefore, the conclusion was drawn that no organic compounds of martian origin were detected (Biemann *et al.,* 1976, 1977).

3.2. The Viking biology investigations

The Viking biology instrument was equipped with three experiments that could test four different hypotheses: (i) an active martian metabolism is limited by the availability of water; (ii) biological activity is best detected under conditions that approximate those on Mars; (iii) an active martian metabolism (the chemical reactions in a cell that convert "food" into energy) is heterotrophic (in need of an external source of "food") and uses a very dilute aqueous solution of simple organic compounds; and (iv) an active martian metabolism is heterotrophic and uses a concentrated mixture of many organic compounds (Klein, 1977). The Viking biology package included a gas exchange (GEx) experiment (Oyama and Berdahl, 1977) that measured the production of CO_2, N_2, CH_4, H_2, and O_2 and the uptake of CO_2 by soil samples; a pyrolytic release (PR) or carbon assimilation experiment (Horowitz *et al.,* 1977) that measured the incorporation of carbon-14 (^{14}C, radioactive carbon) from ^{14}CO or $^{14}CO_2$ into organic matter; and a labeled release (LR) experiment (Levin and Straat, 1977) that measured the production of ^{14}C labeled gas upon addition of nutrient containing ^{14}C labeled organics. Table 1 gives an overview of the three experiments and their results.

The *GEx experiment* consisted of an 8.5 cm^3 sample cell that could be heated and two gas chromatographic columns with two thermal conductivity detectors, which could measure H_2, Ne, N_2, O_2, Ar or CO, NO, CH_4, Kr, CO_2, N_2O, and H_2S (Oyama *et al.,* 1976; Oyama and Berdahl, 1977). Soil samples of ~1 cm^3 were incubated in the presence of Mars atmosphere in the cell that was filled up to 200 mbar with a test gas composed of additional CO_2, Kr, and He. This higher

TABLE 1. THE VIKING BIOLOGY EXPERIMENT[a]

Experiment	Measurement	Nutrients added	Water added	Illumination	Results
Pyrolytic Release	Incorporation of ^{14}C from ^{14}CO or $^{14}CO_2$ into organic matter[b]	None	None	Light and dark	Small ^{14}C yield Heating to 90°C has hardly any effect.
		None	Trace	Light and dark	Heating to 175°C reduced yield by 90%.[c,d,e]
Gas Exchange	Production of CO_2, N_2, CH_4, H_2, and O_2 and the uptake of CO_2 by soil samples[f]	None	Moist	Dark	Release of some CO_2, N_2, and Ar
		Concentrated solution of organic and inorganic compounds	Wet	Dark	Rapid release of O_2 upon humidification[f] Same as moist Additional CO_2 release upon recharge[f]
Labeled Release	Production of ^{14}C-labeled gas upon addition of nutrient containing ^{14}C-labeled organics[g]	Dilute solution of simple organic compounds	Moist	Dark	^{14}C-bearing gas produced Heating to 18°C had no effect. Heating to 40–50°C slowed production. Heating to 160°C stopped production. Storage at 10°C for 4 months stopped production.[h,i,j]

[a]Adapted from Klein, 1977.
[b]Horowitz et al., 1972.
[c]Hubbard, 1976.
[d,e]Horowitz et al., 1976, 1977.
[f]Oyama and Berdahl, 1977.
[g]Levin and Straat, 1976a.
[h]Levin and Straat, 1976b.
[i]Levin and Straat, 1977.
[j]Levin and Straat, 1979.

pressure was necessary for the gas to be sampled into the gas chromatographic columns. The experiment tested two hypotheses and an aqueous nutrient solution described in Oyama et al. (1976). The first hypothesis was based on the assumption that nutrients were already present in the martian soil and that martian organisms only needed water to grow. Therefore, in the humid, non-nutrient mode a small amount ($\sim 0.5\,cm^3$) of the nutrient solution was added in such a way that the solution would not touch the soil but would only saturate the atmosphere with water. This way the soil would only be humidified by the atmospheric water in the cell, and no interaction with the nutrients would take place. The atmosphere was then analyzed to measure the generation and loss (desorption) of gases. Nonbiological activity was differentiated from biological activity by repetitive charges of fresh medium and prolonged incubation cycles (Oyama, 1972). The second hypothesis assumed that organisms on Mars are heterotrophic. This was tested in the wet mode, where enough ($\sim 2\,cm^3$) nutrient solution was added to the soil sample to wet the soil and let it interact with the nutrient. The samples were incubated for 0.1 to 103 sols (martian days; 0.1 to 106 Earth days). During the incubation, the gas chromatographs analyzed the atmosphere in the cell to measure the production of CO_2, N_2, CH_4, H_2, and O_2 and the uptake

of CO_2 by soil samples (Oyama and Berdahl, 1977). The results showed that, upon both humidification and wetting of the soil samples, an immediate release of N_2, CO_2, O_2, and Ar was measured. The release of N_2, CO_2, and Ar was associated with surface desorption caused by water, and the O_2 release with decomposition of superoxides (O_2^-) inferred to be present in the soil (Ballou et al., 1978). When fresh nutrient solution and test gas were added to the wet samples, only additional CO_2 was released, but at a rate that decreased with each recharge (Oyama and Berdahl, 1977). If microorganisms had been present, a recharge of the samples with fresh nutrient solution would have led to a similar gas production, assuming they had survived the first dose of nutrient. This CO_2 evolution in the wet samples was, therefore, thought to have come from the oxidation of organics present in the nutrient by γ-Fe_2O_3 in the surface samples (Oyama and Berdahl, 1977). A control experiment with a sterilized sample, which was heated to 145°C for 3.5 h, was conducted and also showed the release of O_2. From these results, the overall conclusion clearly excluded a biological explanation of the results (Oyama and Berdahl, 1977).

The *PR experiment* or carbon assimilation was designed to detect life in the martian soil by measuring the incorporation of carbon-14 from ^{14}CO or $^{14}CO_2$ into organic matter

(Horowitz *et al.,* 1972). The experiment was based on the hypothesis that potential martian life, like terrestrial life, is carbon based and exchanges carbon with the atmosphere. The experiment consisted of a closed sample cell with a window and a heater, a trapping column, and a radiation detector. A sample was inserted into the sample cell together with captured martian atmosphere, which was enriched with ~ 20 ml of ^{14}CO and $^{14}CO_2$ (ratio 2:98). Some samples were illuminated with a xenon lamp during incubation to simulate sunlight, while others were left in the dark. After an incubation time of 120 h, the cell was heated to 120°C and vented to remove the nonreacted ^{14}CO and $^{14}CO_2$. The cell was then heated to 635°C to pyrolyze potential organic compounds and release ^{14}CO and $^{14}CO_2$ that was adsorbed onto the soil. This gas passed through a column, which trapped potential organics, but the adsorbed ^{14}CO and $^{14}CO_2$, the "pyrolysis CO_2," continued into the radiation detector for analysis. By heating the trap to 700°C, the "trapped organics" were released and oxidized into CO_2, and subsequently analyzed in the radiation detector as well. If ^{14}CO and $^{14}CO_2$ were assimilated by martian microorganisms, they would appear in the analysis of the "trapped organics" (Horowitz *et al.,* 1972, 1977). The results showed that the amount of fixed carbon-14 was small compared to terrestrial standards and that illuminated samples seemed to have produced the highest carbon-14 yields. Furthermore, multiple samples from the same scoop of soil were analyzed: one sample directly after retrieval and the others after a period of storage at elevated temperatures. Data from these samples showed that heating the surface material to 90°C for nearly 2 h had no effect on the reaction, but heating to 175°C for 3 h reduced the reaction by nearly 90% (Horowitz *et al.,* 1976, 1977; Hubbard, 1976). Initially, the results of the PR experiments were explained as weak but significant presumptive positives (Horowitz *et al.,* 1976). However, later laboratory experiments designed to reproduce and further explain these results appeared to rule out a biological explanation. In combination with results from the other biological as well as the molecular analysis experiments, it was concluded that it is unlikely that the reaction is biological (Horowitz *et al.,* 1977).

The *LR experiment* was based on radiorespirometry, a technique in which a ^{14}C radioactively labeled nutrient solution is added to a sample, in this case martian soil, in a closed environment (sample cell), and any radioactive carbon dioxide subsequently detected in the atmosphere in the cell is used as evidence for the presence of life (see below). The experiment consisted of four incubation cells, a nutrient reservoir, and two solid-state beta detectors, and was designed to measure carbon-14 produced by potential microorganisms (Levin and Straat, 1976a). The assumptions on which the experiment was based were (Levin, 1972) (a) although possible life on Mars may not be limited to microorganisms, the latter must be present to accomplish the biodegradation required for recycling of the organic matter; (b) the biochemical reactions at the cellular level are aqueous; (c) the organisms assimilate compounds from their environment and produce gas as an end product; (d) such compounds include any or all of the following: relatively simple carbon molecules, ions, sulfate. First LR results showed—at both landing sites—rapid evolution of radioactive counts upon addition of the nutrient to a fresh surface sample (Levin and Straat, 1976b). Analysis of a second set of samples

showed a similar behavior. In summary, the initial production of gas from the LR nutrient was uniform; when the reaction approached completion, addition of more nutrient resulted in a net loss of the carbon-14 labeled gas. Furthermore, when the samples were heated to moderate temperatures (40–50°C) the reaction slowed down, whereas raising the temperature to 160°C caused the reaction to end. In contrast, exposure to 18°C for 2 sols (1 sol = 1 martian day ≈ 24.6 Earth hours) did not appear to affect the reaction (Levin and Straat, 1977). The final experiments, which involved two soil samples that were stored at the spacecraft at ~ 10°C for several months, showed that the reactions had strongly diminished (Levin and Straat, 1979). The first conclusion drawn from these experiments was that "the results are consistent with a biological response and also greatly narrow the number of possible chemical reactants" (Levin and Straat, 1977). Later, laboratory experiments showed that addition of hydrogen peroxides might have led to similar results as measured on the martian surface. These laboratory results, however, were only obtained in the presence of certain minerals, some of which are not found on Mars, and assumed a much higher hydrogen peroxide content than had been measured up to then in the martian atmosphere. This led to the conclusion that "the presence of a biological agent on Mars must still be considered" (Levin and Straat, 1981).

3.3. Overall conclusions

The main conclusions drawn from the experiments were that there is neither organic material nor life present on the surface of Mars at the two Viking landing sites. "The molecular analysis experiment has demonstrated the absence of organic compounds in the surface material at two Viking sites. This fact has had a very important impact on the interpretation of the data received from the biology experiments (Klein, 1977; Klein *et al.,* 1976) and put some boundaries on the chemical and physical environment at the surface" (Biemann, 1979). The biology experiments were then interpreted by Klein (1977) as follows: "For each experiment, except for the LR experiment, we must conclude that there were no organisms present within the limits of detectability for these experiments and that all of the observed reactions for these were the results of nonbiological phenomena." However, Klein (1977) then continued, "we must not overlook the fact, in assessing the probabilities of life on Mars, that all of our experiments were conducted under conditions that deviated to varying extents from ambient martian conditions, and while we have accumulated data, these and their underlying mechanisms may all be coincidental and not directly relevant to the issue of life on that planet."

4. Now What?

Although there were many indications that pointed toward the presence of at least organic material on the surface of Mars (as described in the Introduction), Viking did not find them. Absence of evidence, however, is not evidence of absence, and a wealth of papers has argued for reasons of nondetection of organics by this mission. These papers can roughly be divided into two categories, (1) studies that focused on the ability of the Viking instruments and techniques to detect organic matter on the martian surface, and (2) laboratory simulations in which the effects of Mars' environmental conditions, as well as soil composition and min-

eralogy, on organic matter are studied (see Table 2 for an overview). In 2009, two significant events brought new evidence to the search for organics on Mars.

(a) Instruments on the Phoenix lander detected perchlorates in the martian soil (Hecht *et al.*, 2009).
(b) New results (Mumma *et al.*, 2009) on the presence of methane in the martian atmosphere confirmed earlier observations (Formisano *et al.*, 2004; Geminale *et al.*, 2008) that this methane varies both geographically and seasonally, implying a faster production and destruction rate than assumed before.

These events, described in more detail in Section 5, spurred a new wave of laboratory investigations. In Section 6, I will first describe the studies that focus on the ability of the Viking instruments and techniques to detect organic matter on the martian surface. In Section 7, I will give an overview of the laboratory studies in which organic material was investigated under simulated martian conditions; and, in Section 8, I will make some concluding remarks. Another category of research that evolved after Viking focused on microorganisms and potential life on Mars. These studies fall outside the scope of this paper; for overviews of this category see, for example, Jensen *et al.* (2008) and Schuerger and Clark (2008).

5. Methane and Perchlorates

5.1. Methane

In 2004, Formisano *et al.* (2004) and Krasnopolsky *et al.* (2004) published works on the detection of methane in the martian atmosphere, although they used different methods and obtained different mixing ratios. Formisano *et al.* (2004) measured a variable amount of 0–30 ppbv, with a global average of 10 ± 5 ppbv from orbit (the Planetary Fourier Spectrometer, on board Mars Express), whereas Krasnopolsky *et al.* (2004) measured 10 ± 3 ppbv from an Earth-based telescope. The photochemical lifetime of methane was modeled to be 300–600 years (Wong *et al.*, 2003), a lifetime also used by Krasnopolsky *et al.* (2004) to explain their observations. The potential variation in the observations of Formisano *et al.* (2004) is, however, more difficult to explain photochemically and points toward localized sources or sinks. Additional Planetary Fourier Spectrometer observations showed an even stronger seasonal variation, which could not be explained photochemically (Geminale *et al.*, 2008). Earth-based observations by Mumma *et al.* (2009) confirmed this seasonal variation and showed a mixing ratio of nearly 0 ppb in the early northern spring to 45 ppb in the late northern summer. Assuming a cyclic, and not sporadic, seasonal cycle, Mumma *et al.* (2009) derived a production (from equinox to summer) and loss (from summer to equinox) rate of methane of 0.5 kg s^{-1}. However, photochemistry alone is not enough to explain the seasonal variation of methane. Modeling results have suggested that dust-induced electrochemistry can significantly increase the destruction rate of methane, both via direct dissociation and the enhanced production of OH- and H- (Farrell *et al.*, 2006). At electric fields above 10 kV m^{-1}, the destruction of methane is more efficient through electrochemistry than photochemistry. Both destruction processes have, however, been suggested not to be effective enough to explain the seasonal

variation, which suggests an extraordinarily harsh environment for the survival of organics on the planet (Lefèvre and Forget, 2009). Methane-producing processes at work on the martian surface may explain the methane observation by Mumma *et al.* (2009). The presence of biology was suggested by Krasnopolsky *et al.* (2004) as a possible methane-producing process, but there are numerous abiological processes to consider as well. Recent volcanism (Neukum *et al.*, 2004) could be a minor source, although only a few hot spots have been observed by the Thermal Emission Imaging System (THEMIS) on the Mars Odyssey orbiter (Christensen *et al.*, 2003, 2005), and sulfur dioxide, the gaseous counterpart of volcanic methane, has only been observed in trace amounts (Krasnopolsky, 2005). Another process could be the serpentinization of ultramafic crust whereby methane is formed in the presence of limited amounts of water and CO_2, with FeO as a catalyst (Palandri and Reed, 2004). Serpentinization requires temperatures of 40–90°C, which are believed to occur at a depth of as little as 2 km, and stable liquid water, which occurs at depths of 2–20 km (Oze and Sharma, 2005; Atreya *et al.*, 2007). Exogenous sources of methane, from comets and meteorites, have also been considered (Court and Sephton, 2009). Court and Sephton (2009) used pyrolysis to simulate the ablation and pyrolysis of carbonaceous micrometeorites upon atmospheric entry and showed that this process produces twice as much methane as the measured free methane present in the CM2 carbonaceous chondrite, Murchison. This source, however, produces less than 10 kg of methane annually, a mass far below that required to maintain the abundance of methane observed in the atmosphere of Mars.

5.2. The Phoenix lander and the detection of perchlorates

In the late northern spring, the Phoenix lander touched down on Mars on May 25, 2008, inside the arctic circle at 68.22°N, 234.25°E, on a valley floor covered by the Scandia Formation, a deposit that surrounds the northern margin of a shield volcano named Alba Patera (Smith *et al.*, 2009). The main goal of Phoenix was to verify the presence of subsurface water ice (Smith *et al.*, 2008). With regard to the search for organics on Mars, the most important instrument on Phoenix was the Thermal and Evolved Gas Analyzer (TEGA) instrument. TEGA consists of a Thermal Analyzer containing eight separate sample ovens, and a mass spectrometer with a mass range of 2–140 dalton, called the Evolved Gas Analyzer (Boynton *et al.*, 2001). Five samples and two blanks were analyzed by TEGA during the Phoenix mission (Arvidson *et al.*, 2009). The most interesting constituents found in these samples were $CaCO_3$ (Boynton *et al.*, 2009), H_2O (Smith *et al.*, 2009), and O_2 (Hecht *et al.*, 2009). TEGA did not detect any organic material (Ming *et al.*, 2009; Sutter *et al.*, 2009). A second instrument on the Phoenix lander was the Wet Chemistry Laboratory (Hecht *et al.*, 2008; Kounaves *et al.*, 2009), which was designed to add water and specified salts to a sample of the martian soil and then measure the sample's dissolved ionic components and properties; its chemical and mineralogical composition, including sulfates; and its acidity, metal content, and redox pairs (Smith *et al.*, 2008). One of the most interesting finds of the Wet Chemistry Laboratory was the detection of perchlorates (ClO_4^-) in the martian soil, at least some of which were in the form of

TABLE 2. LABORATORY SIMULATIONS ON ORGANICS ON MARS[a]

					Atmospheric composition (%)					Solar radiation				
Year	Sample	Incubation method	Temperature (°C)	Pressure (mbar)	CO_2	N_2	Ar	O_2	He	(nm)	Light source	Water addition	Oxides	Reference
1979	Adenine, glycine, naphthalene on quartz Murchison	Quartz tubes	−10 to 25[b]	0.001	-	100	-	-	-	200–300	Mercury-xenon	-	-	Oró and Holzer, 1979
1979	Olivine Pyroxene	Mars chamber	−22 to 0	1000[c]	-	-	-	-	100	-	-	<67.8 mbar (to be frozen onto sample)	-	Huguenin et al., 1979
1982	Murchison TiO_2	Pyrex flasks	R.T.[b,d]	3.4	-	-	-	100	-	UV-visible >200	Not mentioned	-	-	Pang et al., 1982
1997	Palagonite Glycine	Mars Jars	R.T.	100	95.59	-	4.21	0.11	-	210–710	Xenon	-	-	Stoker and Bullock, 1997
1998	Tholins Humic acid	Eppendorf tubes	−23 to +10[b]	1000[c]	-	-	-	-	-	-	-	-	H_2O_2	McDonald et al., 1998
2000	Labradorite		−30	6	Mars gas mixture		-	-	-	254 (peak)	Mercury	-	-	Yen et al., 2000
				0.34; 3.4; 23,700	-	-	-	100	-					
2005	Glycine D-alanine	Mars chamber	R.T.	4×10^{-6}	-	-	-	-	-	190–325	Deuterium	-	-	ten Kate et al., 2005
2006	Glycine D-alanine	Mars chamber	−63 and R.T.	10^{-7} and 7	99.9	-	-	-	-	120–180 190–325	Hydrogen Deuterium	-	-	ten Kate et al., 2006
2006	Salten Skov JSC Mars-1	Mars chamber	25	$\sim10^{-5}$	-	-	-	-	-	190–325	Deuterium	-	-	Garry et al., 2006
2006	Amino acids	Pyrex glass vials	−63 R.T.	7 1,000[c]	99.9	100	-	-	-	0.50–5.42 MGy[e]	^{60}Co	-	-	Kminek and Bada, 2006
2008	ATP	Mars chamber	−80, −10, and +20	7.1	Mars gas mixture		-	-	-	200–280	Xenon-arc	-	-	Schuerger et al., 2008

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2009 Brines with amino acids, with and without iron	Silica glass vessels in Mars chamber	−135 to +40	7–15	95.3	2.7	1.6	0.13	-	250–700	Xenon-arc	In suspension	-	Johnson and Pratt, 2010
2009 Aqueous solutions of organics on minerals	Suprasil tubes	R.T. −196	1,000[c]			air			355	Nd:YAG pulsed laser (6 ns)	In suspension	Goethite, hematite, anatase	Shkrob and Chemerisov, 2009
2009 Carboxylic acids	Glass jar	−65	10^{-2}	-	-	-	-	-	190–250	Xenon-arc	-	-	Stalport et al., 2009
2010 Phenanthrene, octadecane, octadecanoic acid, decanophenone, and benzoic acid	Mars chamber	−10 R.T.	6.9	95.5	2.7	1.6	0.13	-	200–280 1,500 V	Xenon-arc Glow discharge	0.03% in atmosphere	-	Hintze et al., 2010
2010 Aqueous solutions of organics on minerals	Suprasil tubes	−196	1000[c]		100				355	Nd:YAG pulsed laser (6 ns)	In suspension	Goethite, hematite, anatase	Shkrob et al., 2010

[a] Adapted from Jensen et al., 2008.
[b] Constant temperature.
[c] Ambient terrestrial atmospheric pressure.
[d] R.T. = room temperature ~20°C.
[e] Applied doses: 0.50, 1.00, 2.05, 5.42 MGy.

$Mg(ClO_4)_2$ or $Ca(ClO_4)_2$ (Hecht *et al.*, 2009). These findings were further endorsed by the detection of O_2 by TEGA, which evolved at temperature ranges consistent with the thermal decomposition of perchlorates (Hecht *et al.*, 2009). This perchlorate finding is particularly interesting because, although perchlorate does not readily oxidize organics under martian conditions, the low water activity associated with such a strongly desiccating substance may inhibit many forms of life. The high-temperature oxidizing properties of perchlorate will, however, promote combustion of organics in pyrolytic experiments (Hecht *et al.*, 2009), which could have affected the ability of both Phoenix's TEGA experiment and the Viking mass spectrometer experiments to detect organics (Biemann, 2007; Ming *et al.*, 2009).

6. The Suitability of Thermal Volatilization Gas Chromatography–Mass Spectrometry for the Detection of Organics on Mars

After the results from the Viking mission were analyzed and did not directly show the presence of organics or life on the surface of Mars, a debate ensued as to whether the instruments on Viking were the best choice for finding organics on Mars, either from an instrument sensitivity point of view or a technique point of view. Biemann (1979) stated the following: "First, the question arises, whether the instruments indeed worked properly. Fortunately, experimental data exists which demonstrates this proper function beyond any doubt." However, he also added that

certain types of organic material can not be detected by the molecular analysis (thermal volatilization GCMS) experiment, which consisted of heating the sample to 500°C in several steps followed by the analysis of organic compounds evolved by volatilization or pyrolysis. Any compound that would be stable at 500°C such as highly cross-linked polymers, would probably not produce detectable material. Compounds of the opposite behavior, namely one that decomposes upon heating into certain molecules, which the Viking GCMS can not detect, would also remain unnoticed (Biemann, 1979).

Benner *et al.* (2000) suggested that organic compounds that arrive on Mars through meteoritic delivery, such as alkanes, alkylbenzenes, naphthalene and higher polycyclic aromatic hydrocarbons, kerogen, and amino acids and hydroxyacids, are most likely to be converted to carboxylic acid derivatives. These compounds would not be easily detected by thermal volatilization GCMS because they are either nonvolatile or generate CO_2, CO, and H_2O, which are present in the martian atmosphere and therefore difficult to distinguish. Attempts to reproduce the Viking LR results led to conclusions that the mechanism for the decomposition of organics in Yungay soils is different from the processes observed in the Viking LR experiment (Quinn *et al.*, 2007) but also that a mysterious oxidant in the martian soil that evolved oxygen when humidified in the LR experiment might have been H_2O_2 of biological origin (Houtkooper and Schulze-Makuch, 2007). Viking GCMS-like experiment results (Navarro-González *et al.*, 2006) suggest that the presence of iron oxides or their salts, or both, in other analyzed soil samples (*e.g.*, jarosites from Río Tinto and Panoche Valley) caused the intrinsic organic material to oxidize to carbon dioxide (CO_2),

which drastically attenuates the detection of organics. Another result from this study, which was that small amounts of organics would fall below the detection limit of the Viking GCMS, was refuted, however, because the equipment used was a thousand times less sensitive than the Viking GCMS and the experimental methods different from the Viking methods (Biemann, 2007). Iñiguez *et al.* (2009) further investigated the usefulness of thermal volatilization for organic detection on Mars and found that there are two sources of strong oxidizers in palagonite soils: hydroxyl radicals and oxygen atoms. These strong oxidizers completely decomposed low levels of stearic and mellitic acids present in the soil samples, which suggests that thermal volatilization may not be the best method for organic detection on Mars. Navarro-González *et al.* (2009) showed that, when organics are present in the soil at levels above 1500 ppm, several characteristic organic fragments can be detected by thermal volatilization mass spectrometry; however, when the levels are below <150 ppm, thermal volatilization oxidizes them, and no organic fragments are released. The most recent experiments that have taken into account both Viking and Phoenix data showed that, upon heating of Atacama soils mixed with 1 wt% of magnesium perchlorate, all the organics present were decomposed to water and carbon dioxide, but that a small amount was chlorinated and formed chloromethane and dichloromethane at 500°C (Navarro-González *et al.*, 2010). "Re-interpretation of the Viking results therefore suggests 0.1% perchlorates and 1.5–6.5 ppm organic carbon at the landing site 1, and 0.1% perchlorates and 0.7–2.6 ppm organic carbon at the landing site 2" (Navarro-González *et al.*, 2010).

7. Laboratory Investigations of Organics on Mars

A few years after Viking, several processes were suggested that could have led to the nondetection of organic material. These processes can roughly be divided into four categories: (i) the potential presence of some oxidizing agents in the martian soil, (ii) the potential effects of electrification and glow discharge, (iii) degradation by UV and other radiation, and (iv) the photocatalytic effects caused by interaction of radiation with mineral surfaces. Table 2 shows an overview of the studies performed that involve either one or a combination of these effects.

7.1. Oxidization

The presence of an *oxidizing source in the martian soil* could have destroyed organics. Klein (1979) suggested that a thermally labile oxidant such as H_2O_2, which is known to destroy organics, could have caused the evolution of CO_2 in the LR experiments by reacting with the formate ($CHOO^-$) in the nutrient solution that was part of the experiment. This H_2O_2 could be produced due to photochemical reactions in the martian atmosphere (Hunten, 1979) but also by frost weathering (interaction of minerals with H_2O frost) of olivine (Huguenin *et al.*, 1979; Huguenin, 1982). Oyama and Berdahl (1979) determined that γ-Fe_2O_3, which has been suggested to be present on the martian surface (Hargraves *et al.*, 1976), could both oxidize organics directly as well as catalyze oxidation through H_2O_2. This could explain the slow CO_2 production in the LR and GEx experiments and the CO_2 production in the LR experiment. Ponnamperuma *et al.*

(1977) had earlier obtained similar results by showing $^{14}CO_2$ production upon adding Viking nutrient mixture to γ-Fe_2O_3. On the other hand, there were also arguments against H_2O_2. Levin and Straat (1981) proposed that H_2O_2 reacted also with compounds in nutrients other than only formate, which suggests that the H_2O_2 hypothesis did not account for the fact that only one compound in LR was oxidized to CO_2. Furthermore, they found that there should by at least 2 wt% of H_2O_2 in the soil to reproduce the LR results. This was considered to be doubtful because there was hardly any H_2O_2 detected in the atmosphere (Hanel and Maguire, 1980, in Levin and Straat, 1981), and H_2O_2 has a short lifetime (10^4 s) against UV destruction.

A different approach suggested that the GEx and LR results may have been caused not by oxidation of organics but by the presence of clays, such as smectites, in the martian soil. These clays may have absorbed compounds from the atmosphere that were released in the GEx experiment, and their catalytic surfaces may have helped in decomposing the formate in the LR nutrient, which would have released ^{14}C to the atmosphere in the LR experiment (Banin and Rishpon, 1979; Banin and Margulies, 1983).

In 1994, Zent and McKay offered that in the most realistic model the martian soil contains oxidants produced by heterogeneous chemical reactions with a photochemically produced atmospheric oxidant. However, most compounds with the capacity to oxidize H_2O to O_2, as seen in the GEx experiment, are thermally labile or unstable against reduction by atmospheric CO_2, and the oxidants most often suggested to explain the LR experiment, including H_2O_2, are expected to decompose rapidly under martian UV (Zent and McKay, 1994). The interaction between absorbed H_2O, (ferric and ferrous) iron, and H_2O_2 leads to very efficient radical production through the (photo-)Fenton reaction (Spacek et al., 1995; Southworth and Voelker, 2003; Möhlmann, 2004; Zhang et al., 2005), although this mechanism still needs the presence of H_2O_2. Other oxidizing mechanisms that are not based on H_2O_2 have been proposed as well. Oxygen radicals (O_2^-) can be formed by the interaction of UV with Mars-analog minerals both at martian temperatures ($-30°C$) and room temperature in the presence of oxygen, either in a Mars-like mixture or as pure oxygen with a partial pressure comparable to that of the oxygen in the martian atmosphere (Yen et al., 2000). In Mars analog environments on Earth, for example, the Atacama Desert, dry acids can be produced photochemically in the atmosphere from SO_2 and NO_x precursors, which then adsorb onto dust and soil surfaces. High relative humidity at night can then trigger oxidative acid soil reactions. These soil acids are expected to play a significant role in the oxidizing nature of the soils, the formation of mineral surface coatings, and the chemical modification of organics in the surface material (Quinn et al., 2005). Garry et al. (2006) reached a similar conclusion based on experiments that showed a decrease in intrinsic amino acid content of cold martian soil analogues ($-60°C$) upon UV irradiation in a CO_2 atmosphere with trace amounts of residual water. In contrast, experiments (Mancinelli, 1989; McDonald et al., 1998) have shown that an extract of terrestrial soil organics as well as organic macromolecules, such as tholins and humic acid, subjected to a H_2O_2–H_2O solution do not decrease measurably, either at $20°C$ or at low temperatures ($-58°C$ and $-123°C$), and might be stable against oxidation on the martian surface, at least in the polar regions, over the entire history of Mars.

7.2. Glow discharge

A second mechanism for organic degradation could be the formation of electrostatically generated *glow discharge plasmas* in martian dust storms, which could alter the local atmospheric chemistry on Mars to produce reactive species, such as hydrogen peroxide, and breakdown species, such as organic compounds (Mills, 1977; Oyama and Berdahl, 1979). In Earth's atmosphere, anhydrous electrical currents are generated in dust devils and dust storms (Freier, 1960; Crozier, 1964; Ette, 1971). In terrestrial dust devils, dust particles generate and transfer electric charge through collisions with each other and with the surface (Ette, 1971; Eden and Vonnegut, 1973; Farrell et al., 2003). In this process, smaller particles get charged negatively and are eddied up in dust storms, whereas larger grains become positively charged and stay close to the surface (Ette, 1971; Gierasch and Goody, 1973; Melnik and Parrot, 1998; Farrell et al., 2003; Krauss et al., 2003). This displacement in grain charge types creates a dust storm–sized electric dipole moment, which results in the development of coherently varying electric fields that extend well outside the dust storm. Field strengths near 500 V m^{-1} at a distance of many 10s of meters from the features have been measured (Freier, 1960; Crozier, 1964). In desert tests that combined electrical, magnetic, and meteorological measurements, electric fields were found to be coherent, and large scale, and to exceed 20 kV m^{-1} (Farrell et al., 2004; Renno et al., 2004). Unsaturated electric fields near 120 kV m^{-1} were measured from dust devils in the Mojave Desert (Jackson and Farrell, 2006), and simple saltating grains were found to generate electric fields exceeding 160 kV m^{-1} (Schmidt et al., 1998). These coherent electric fields from dust devils are not impulsive "discharge fields" or lightning, but long-lasting electrostatic fields associated with the buildup of vertical, well-separated charge centers in the feature. Discharges occur when these electrostatic fields become anomalously large, which creates "breakdown" conditions and leads to increased impulsive electron flow.

It is anticipated, with Earth as an analogy, that martian dust storms are also electrical in nature, as long as (1) vertical winds exist to mass stratify grains and (2) the lifted grains vary in size and composition [required for efficient grain-grain charge generation (Desch and Cuzzi, 2000)]. Both required conditions exist with the easily lifted iron mineral/basalt grain mix on Mars. Melnik and Parrot (1998) modeled these electrical processes in dust storms and found that the macroscopic electrostatic fields within a martian dust cloud could reach breakdown levels of $\sim$20 kV m^{-1}. The analytical model of Farrell et al. (2003) compared the development of a terrestrial and a martian dust storm of similar sizes and found that both would ultimately develop comparable electric field strengths ($>$20 kV m^{-1}), with the martian storm's temporal development about 15% slower due to current leakage into the more conductive martian atmosphere. Modeling has suggested that this dust-induced electrochemistry can significantly increase the destruction rate of methane, both via direct dissociation and the enhanced production of OH- and H- (Farrell et al., 2006). Furthermore,

Delory *et al.* (2006) found that under near-breakdown conditions the dissociation of H_2O via electron collisions produces negative ions (OH- and H-) at much higher rates than photochemical processes, which will lead to a ~ 200 times larger subsequent production of H_2O_2 (Atreya *et al.*, 2006). Within this context, Hintze *et al.* (2010) subjected five organic compounds—phenanthrene, octadecane, octadecanoic acid, decanophenone, and benzoic acid—to a glow discharge plasma in a simulated martian atmosphere. The plasma contained cations and excited neutral species, including carbon dioxide, carbon monoxide, and nitrogen. After exposure to the plasma, oxidized, higher-molecular-weight versions of the parent compounds containing carbonyl, hydroxyl, and alkenyl functional groups were identified.

7.3. UV degradation

The third proposed organic destruction mechanism focuses on the relatively *high UV flux* into short wavelength ranges (190–400 nm, compared to 290–400 nm on the Earth's surface) that may efficiently destroy organic compounds. Oró and Holzer (1979) exposed adenine, glycine, naphthalene, and the Murchison meteorite to UV in the presence of varying amounts of oxygen and measured their decomposition. Adenine and glycine were found to be more stable than naphthalene, and the degradation rates increased with the amount of oxygen present. Another mechanism could be titanium oxide–catalyzed photooxidation, where the organics are oxidized through interaction with a combination of UV radiation, gaseous oxygen (present at 0.13% in the martian atmosphere), and a catalyzing surface, such as TiO_2, which is also present on Mars (Chun *et al.*, 1978; Pang *et al.*, 1982). Stoker and Bullock (1997) UV irradiated samples in which glycine was mixed with a Mars analogue (palagonite from the Mauna Kea Volcano on Hawaii). They measured the headspace gases over the samples during irradiation for traces of methane, assuming that the destruction of one glycine molecule produced one methane molecule. They found destruction rates of $2.24 \pm 1.2 \times 10^{-4}$ g of carbon m^{-2} per year when scaled to martian surface conditions and concluded that the surface of Mars should be depleted of organics, based on the annual influx of organic material (Flynn, 1996). Ten Kate *et al.* (2005, 2006) also studied the effects of UV radiation on glycine as well as on alanine, in the form of thin layers of the pure amino acids. They found as well that glycine and alanine have a short lifetime on the martian surface, with half-lives of 22 ± 5 h for glycine and 3 ± 1 h for alanine (~ 500 and ~ 81 h, respectively, in the lab), when extrapolated to martian surface conditions. Furthermore, they found that these rates slowed down by a factor of ~ 10 when the samples were cooled to an average Mars' surface temperature of $-60°$C. A similar approach was used by Stalport *et al.* (2009), who irradiated cold ($-55°$C) thin films of mellitic, benzoic, and oxalic acids in vacuum. The half-lives of benzoic and oxalic acid as observed in the lab are 0.8 ± 0.2 and 1.8 ± 0.5 h, respectively, which is considerably shorter than that of the amino acids studied by ten Kate *et al.* (2005, 2006). Mellitic acid, on the other hand, produces a UV radiotolerant compound identified as benzenehexacarboxylic acid–trianhydride ($C_{12}O_9$). This result led the authors to conclude that, in spite of the eventual presence of oxidation

processes and UV radiation on the martian surface, compounds produced by photolysis of benzenecarboxylic acids (such as mellitic acid) may have accumulated into the martian regolith (Stalport *et al.*, 2009). This conclusion is in line with predictions by Benner *et al.* (2000). Schuerger *et al.* (2008) studied the response of thin films of adenosine triphosphate (ATP), a molecule essential for life, to UV irradiation in a Mars-like atmosphere. They found a half-life for ATP of ~ 4 days in the lab, which corresponds to ~ 22 sols (≈ 22.6 Earth days) when extrapolated to martian surface conditions. In the same facility, Hintze *et al.* (2010) exposed the same five organic compounds as used in their glow discharge experiments—phenanthrene, octadecane, octadecanoic acid, decanophenone, and benzoic acid—to Mars-like UV radiation in a simulated martian environment. The UV degradation reactions also produced oxidized, higher-molecular-weight compounds as compared to the starting materials; however, this process seemed to be less efficient than glow discharge.

Besides UV, other ranges of the solar spectrum could affect the martian surface as well. UV radiation will penetrate only a few microns into the martian surface, which implies that organics are safe from UV radiation when buried under even a thin layer of soil (*e.g.*, ten Kate *et al.*, 2005). However, cosmic rays will produce a higher dose-rate than they produce on Earth, since the martian atmospheric column density at normal incidence is only $16–27$ g cm^{-2} compared to Earth's atmospheric shield of 1000 g cm^{-2}, which is equivalent to a depth of 9 m below ground on Mars (Clark, 1979). Other studies have suggested that influence of galactic cosmic rays and solar energetic particles reaches much deeper (several meters), compared to UV (Pavlov *et al.*, 2002; Dartnell *et al.*, 2007a, 2007b). Laboratory experiments in which amino acids were irradiated with γ rays indicated that amino acids buried in the first meter of the martian subsurface would be destroyed through radiolysis. Below a radiation shielding depth of $400–500$ g cm^{-2}, amino acids would not be degraded substantially (Kminek and Bada, 2006).

7.4. The interaction of UV with organics absorbed onto minerals

Recent studies have not only focused on the effect of UV by itself but also on the catalytic effects mineral surfaces could have on the interaction of UV with organic matter, a process already suggested by Chun *et al.* (1978) and Pang *et al.* (1982). Apart from radiolytic oxidation, racemization [the process in which one enantiomer of an amino acid converts to the other, *e.g.*, L-alanine to D-alanine, until a 1:1 mixture is reached (Johnson and Pratt, 2010)] has been proposed. Experiments involving five amino acids indicated that the rates of racemization in the presence of metals in solution are an order of magnitude slower than degradation through radiolytic oxidation, and both are several orders of magnitude faster than previously reported by Bada and Schroeder (1975), Snider and Wolfenden (2000), and Li and Brill (2003). Shkrob and Chemerisov (2009) studied UV (355 nm)–induced reactions of carboxylic, hydroxycarboxylic, and aminocarboxylic acids, carboxylated aromatics, and R-amino acids and peptides adsorbed on the hydrated metal oxides anatase (TiO_2), goethite (R-FeOOH), and hematite (R-Fe_2O_3)

at low (-196 to $-73°C$) and room ($22°C$) temperature. The UV wavelength of 355 nm was chosen because at this wavelength the light is completely absorbed by the oxides and no direct photolysis of the organics takes place. They showed that the main photodegradation path in these experiments is decarboxylation catalyzed by the metal oxides. This photocatalytic decarboxylation is inconsistent with the Benner *et al.* (2000) hypothesis that chemical evolution of the organic component of the soil results in the accumulation of stable, nonvolatile carboxylated and polycarboxylated molecules in martian soil. This led the authors to suggest that there may be no "safe haven" for organics on Mars. Further analysis of these experiments, however, indicated that during the process of photocatalytic decarboxylation both CO_2 and CH_4 form via the photo-Kolbe reaction (Shkrob *et al.*, 2010). In the sequence of processes suggested in this work, the ultimate end product of organics delivered by meteorites on the martian surface is CH_4. Therefore, these reactions may account for seasonally variable methane production (Shkrob *et al.*, 2010).

8. Conclusion

After 45 years of research on organic matter on the surface of Mars, which included two missions that could have detected organics, Viking and Phoenix, it is still unclear as to whether organic matter is present on Mars. Work by Navarro-González *et al.* (2006, 2009, 2010) suggested that thermal volatilization gas chromatography–mass spectrometry, the method used on both missions, may not be the best method to look for trace amounts of organics, because organics can be destroyed upon heating in a pyrolysis unit. Organic matter should be detectable by thermal volatilization mass spectrometry (*e.g.,* ten Kate *et al.,* 2010). Very recent work by Shkrob and Chemerisov (2009), and Shkrob *et al.* (2010), suggested that active removal processes take place that could explain the observation that the martian surface is depleted of organics, as well as the production of the CH_4 detected in the martian atmosphere. The best way to determine whether there are organics on Mars would be to look for them *in situ.* The upcoming Mars Science Laboratory scheduled for launch in the fall of 2011 is equipped with the Sample Analysis at Mars (SAM) instrument suite (Mahaffy, 2008). A primary focus of SAM will be the detection and identification of organic molecules by way of thermal volatilization gas chromatography–mass spectrometry. To enhance organic detectability by the GCMS, some of SAM's sample cups are filled with derivatization agents that will dissolve organics from the soil before pyrolysis and make them more volatile (Mahaffy, 2008). Two derivatization methods to be used both react with amines, acids, and alcohols. Moreover, one of the methods is more suitable for free organics, such as amino acids (Buch *et al.,* 2006), the other for bonded macromolecules. The effects of perchlorates on these derivatization steps are currently under investigation (J.L. Eigenbrode, D.P. Glavin, personal communication). Even after a successful Mars Science Laboratory, future missions should incorporate instruments that enable organic detection. For these future missions, other organic detection techniques should therefore be considered as well [*e.g.,* capillary electrophoresis (Skelley *et al.,* 2005)].

Abbreviations

ATP, adenosine triphosphate; GCMS, gas chromatograph–mass spectrometer; GEx, gas exchange; LR, labeled release; PR, pyrolytic release; SAM, the Sample Analysis at Mars; TEGA, Thermal and Evolved Gas Analyzer.

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Address correspondence to:
Inge L. ten Kate
NASA Goddard Space Flight Center
Greenbelt, MD 20771
USA

E-mail: Inge.L.TenKate@nasa.gov