

Methane and related trace species on Mars: Origin, loss, implications for life, and habitability

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Accepted 8 February 2006

Available online 22 August 2006

Abstract

One of the most puzzling aspects of Mars is that organics have not yet been found on the surface. The simplest of organic molecules, methane, was detected in the Martian atmosphere for the first time in 2003. The existence and behavior of methane on Mars is of great significance, as methane is a potential biomarker. In this paper we review our current understanding of possible sources and sinks of methane on Mars. We also investigate the role of other trace species in the maintenance and removal of methane from the atmosphere, as well as of other organic material from the surface. In particular, we examine the exogenous, hydrogeochemical—especially serpentinization—and biological sources, for supplying methane to Mars. We suggest that comets and meteorites are the least likely, whereas low-temperature serpentinization is the most plausible of all candidates to explain the methane observations. Nevertheless, it is premature to rule out the role of biology in producing methane on Mars, in view of available data. It is important to note that the loss of methane to surface must also be factored into any “source” scenarios for methane. Ordinary heterogeneous loss process to surface tends to be very slow. On the other hand, a reactive surface could potentially accelerate the destruction of methane. If correct, it would imply that a larger source of methane is present than currently estimated on the basis of photochemical loss alone. A reactive surface can also explain why no organic material has ever been detected on the Martian surface. The surface could become reactive if some oxidizer were present. We suggest that vast quantities of a powerful oxidant, hydrogen peroxide, can be produced in electrochemistry triggered by electrostatic fields generated in the Martian dust devils and dust storms, and in normal saltation process close to the surface. Finally, current observations are inadequate to prove or disprove the existence of life on Mars, now or in the past. The question of extraterrestrial life is a fundamental one, and it should be addressed meticulously on future missions to Mars. Measurements planned on the Mars Science Laboratory (MSL), especially carbon isotopes and chirality, will go a long way in meeting this goal. A brief overview of the MSL Mission and measurements relevant to the question of life and habitability of Mars is also presented in this paper.

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Keywords: Mars; Methane; Life; Habitability; Oxidants; Hydrogen peroxide; Electrochemistry; Triboelectricity; Dust devils; Serpentinization; Mars Science Laboratory; Sample Analysis at Mars

1. Introduction

Trace quantities of methane gas have been detected by the Planetary Fourier Spectrometer (PFS) on Mars Express (Formisano et al., 2004). The Fourier Transform Spectrometer (FTS) at Canada-French-Hawaii Telescope (CFHT) yields similar (10 ppbv) *global* abundance (Krasnopolsky et al., 2004). However, a high-resolution spectrograph (CSHELL) at the Infrared Telescope Facility (IRTF) and

the Gemini telescope data imply substantially greater (>250 ppbv), *localized* amounts (Mumma et al., 2004), which is puzzling. The PFS and IRTF/Gemini data also indicate that methane is variable over the planet. This too is puzzling, considering the relatively long lifetime of CH₄ on Mars (300–600 years, Wong et al., 2003; Krasnopolsky et al., 2004). It is tantalizing to surmise that widely dispersed microbial colonies—extinct or extant—may be responsible for the existence and non-uniform distribution of methane on Mars. After all, between 90% and 95% of methane on Earth has a biological origin, either from living things now, organic waste, or fossilized matter, as

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illustrated in Fig. 1. For Mars, the biological source viewpoint may be bolstered by the mineralogical evidence of past (liquid) water at the Mars Exploration Rover (MER) sites, especially Meridiani Plenum and the non-uniformly distributed subsurface ice reported by the Mars Odyssey researchers (Feldman et al., 2002).

A microbial source could indeed be one possible scenario for the existence and non-uniform distribution of methane on Mars. However, it is by no means the only one (Atreya et al., 2004; Atreya and Wong, 2004; Atreya, 2005). In fact, methane production through serpentinization is a common occurrence on Earth, and the interior of Mars poses no unusual challenge (Atreya et al., 2004; Atreya and Wong, 2004; Atreya, 2005). An effective surface sink could also be responsible for non-uniform CH₄. Oxidizers in the surface

could scrub not only the methane gas from the atmosphere, but may also destroy or transform (Benner et al., 2000; McDonald et al., 1998) any organic material that is present in the soil. Electrochemistry triggered by the Martian aeolian processes—dust devils, storms, and normal saltation—is potentially a large source of an oxidant, hydrogen peroxide (Atreya et al., 2006; Delory et al., 2006). In this paper we will summarize the current state and discuss missing links in the above story, especially the isotope data (e.g., ¹²C/¹³C), organics, oxidants, sulfur and halogen species, and more. We will also discuss briefly the tests required for determining the existence of life on Mars, together with the measurements planned by the Sample Analysis at Mars (SAM) Suite on the 2009 Mars Science Laboratory (MSL) Mission.

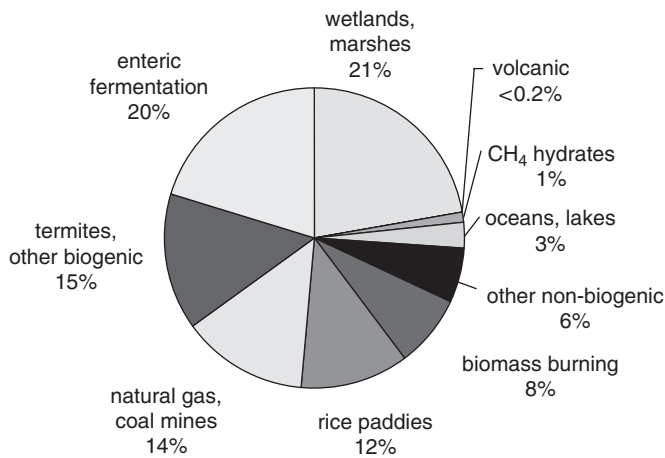


Fig. 1. Methane sources on Earth. Values shown in the figure were adapted largely from Paul and Clark (1996).

2. Methane sources and sinks

Methane on Mars could be produced from any one of the four potential sources:

1. Internal, such as volcanoes.
2. Exogenous, such as meteorites, comets, or interplanetary dust particles.
3. Internal, such as a hydrogeochemical process involving serpentinization.
4. Biological.

We illustrate these sources in Fig. 2.

In order to understand how realistic the source is, it is important to know how methane is destroyed, as it places a constraint on the required source strength.

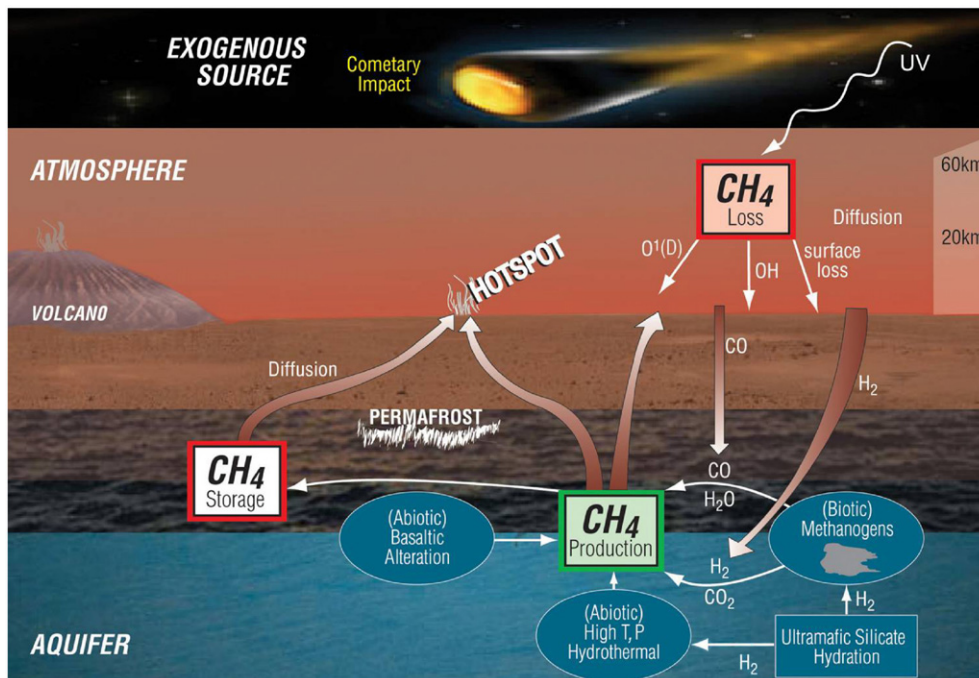


Fig. 2. Potential sources and sinks of methane on Mars, as discussed in this paper.

The conventional loss mechanism for methane on Mars is photolysis by the solar ultraviolet light in the upper atmosphere and oxidation closer to the surface (Fig. 2). This results in a photochemical lifetime (e-folding time) of methane between 300 and 600 years (Wong et al., 2003; Formisano et al., 2004), depending upon the amount of water vapor, solar flux, and ozone. Assuming a CH₄ photochemical lifetime of $\sim 2 \times 10^{10}$ s near the surface, we estimate that a flux of $\sim 1 \times 10^5$ molecules cm⁻² s⁻¹ is required to explain a CH₄ mixing ratio of 10 ppbv on Mars. This implies a disk averaged source strength of ~ 4 g s⁻¹, which is equivalent to approximately 1.26×10^5 kg yr⁻¹ or 126 metric ton yr⁻¹. This is relatively small compared to the source strength of 515×10^6 metric ton yr⁻¹ needed to maintain approximately 1700 ppbv of methane in the Earth's atmosphere (although the destruction mechanisms on Earth are similar to Mars, the methane lifetime is shorter, ~ 10 years, due to greater solar flux and the rate of oxidation on Earth).

2.1. Volcanic source

Volcanoes are not a large source of methane on Earth. Less than 0.2% of all methane on Earth comes from fumarolic sources (Fig. 1). A part of that could ultimately be from the fossilized matter also. A more important consideration is that in the terrestrial fumarolic gases, sulfur dioxide is between 100 and 1000 times more abundant (e.g. Walker, 1977). If the composition of the volcanic gases on Mars were similar to that on Earth, and if the observed 10 ppbv of methane on Mars were of volcanic origin, then one should expect on average 1–10 ppmv of SO₂. However, SO₂ has not been detected on Mars. Only a low upper limit of 3×10^{-8} for SO₂ has been derived from observations from the ground and spacecraft (Encrenaz et al., 1991; Encrenaz, 2001; Table 1). Thus a volcanic origin of methane on Mars is unlikely.

2.2. Meteoritic and cometary source

Only a fraction (<25%) of the approximately 300 g s⁻¹ or ~ 9000 ton yr⁻¹ of micrometeoritic dust is expected to reach the surface of Mars (Flynn, 1996), as most of it would be oxidized in the atmosphere. Moreover, carbonaceous material comprises a very small proportion of the total micrometeoritic dust. There is little likelihood of any surviving organic material to be converted to methane, as we discussed previously (Formisano et al., 2004). Direct infusion of methane carried by meteorites is also negligible.

The only exogenous source with some potential is cometary. With an average impact rate of 1.6×10^{-8} yr⁻¹ for the ecliptic comets at Mars (Levison et al., 2000) and a typical cometary radius of 1 km, the amount of methane delivered to Mars by the comets would be on the order of 1 ton yr⁻¹ on average, i.e. less than 1% of that needed to maintain a steady state mixing ratio of 10 ppbv of methane. Besides, the “average” flux from the comets is not a very

Table 1

Constituent	Mixing ratio	
<i>(a) Composition of the Martian atmosphere</i>		
CO ₂	0.9532 ^a	
N ₂	2.7×10^{-2} a	
⁴⁰ Ar	1.6×10^{-2} a	
O ₂	1.3×10^{-3} a	
CO	7×10^{-4} a	
H ₂ O	2×10^{-4} b	
H ₂ O ₂	4×10^{-8} c	
O ₃	$(1-80) \times 10^{-8}$ d	
CH ₄	$(1 \pm 0.5) \times 10^{-8}$ e	
CH ₂ O	$\leq 5 \times 10^{-7}$ (tentative) ^f	
	$< 3 \times 10^{-9}$ g	
³⁶⁺³⁸ Ar	5.3×10^{-6} a	
Ne	2.5×10^{-6} a	
He	$(1.1 \pm 0.4) \times 10^{-6}$ h	
Kr	3×10^{-7} a	
Xe	8×10^{-8} a	
H ₂	$(1.5 \pm 0.5) \times 10^{-5}$ i	
<i>(b) Global upper limits to possible minor constituents</i>		
C ₂ H ₂	2×10^{-9} j	
C ₂ H ₄	5×10^{-7} j	
C ₂ H ₆	4×10^{-7} j	
N ₂ O	1×10^{-7} j	
NO ₂	1×10^{-8} j	
NH ₃	5×10^{-9} j	
PH ₃	1×10^{-7} j	
SO ₂	3×10^{-8} k	
OCS	1×10^{-8} j	
HCl	2×10^{-9} l	
H ₂ S	1×10^{-7} j	
Ratio	Earth	Mars
<i>(c) Isotope ratio^m</i>		
D/H	1.56×10^{-4}	$(9 \pm 4) \times 10^{-4}$ $(7.8 \pm 0.3) \times 10^{-4}$
¹² C/ ¹³ C	89 (inorganic)	90 ± 5
¹⁴ N/ ¹⁵ N	272	170 ± 15
¹⁶ O/ ¹⁸ O	489	490 ± 25 545 ± 20
¹⁶ O/ ¹⁷ O	2520	2655 ± 25
³⁶ Ar/ ³⁸ Ar	5.3	5.5 ± 1.5
⁴⁰ Ar/ ³⁶ Ar	296	3000 ± 500
¹²⁹ Xe/ ¹³² Xe	0.97	2.5 (+2, -1)

^aOwen et al. (1977).

^bSmith (2004), variable.

^cEncrenaz et al. (2004) variable; Clancy et al. (2004).

^dBarth (1974).

^eFormisano et al. (2004); Krasnopolsky et al. (2004).

^fKorablev et al. (1993), equatorial region, solar occultation.

^gKrasnopolsky et al. (1997), southern hemisphere spring.

^hKrasnopolsky et al. (1994).

ⁱKrasnopolsky and Feldman (2001), above 140 km.

^jMaguire (1977).

^kEncrenaz et al. (1991); Encrenaz, 2001.

^lKrasnopolsky et al. (1997).

^mTable compiled by Owen (1992).

meaningful quantity, considering that the probability of a typical size comet (1 km radius) striking Mars is once in every 62 million years. Could it be that a comet did impact Mars in the last few hundred to few thousand years,

injecting methane whose relic we see today? We discuss this possibility below.

In Fig. 3, we show the results of a calculation for the size of comet vs. time of impact, with the constraint that the methane delivered by the comet to Mars at the time of impact has declined to its current value, $2.2 \times 10^{15} \text{ cm}^{-2}$ CH_4 molecules, or 10 ppbv. Assuming an average of 1% CH_4 by weight for the Oort cloud comets (Gibb et al., 2003), together with a methane lifetime of 600 yr, we find that an impact by a comet of radius as small as $\sim 130 \text{ m}$ that impacted Mars as recently as 100 years ago, to an impact by a comet with radius as large as $\sim 360 \text{ m}$ that occurred as long as 2000 years ago, will be required if the 10 ppbv of methane detected on Mars today was supplied by a comet. Although an impact of a few hundred meter comet on Mars in the recent past cannot be ruled out from the observations made from space, such as those by the High Resolution Stereoscopic Camera on board the Mars Express spacecraft, the non-uniform distribution of methane on Mars remains difficult to explain, as it takes only a few months for methane to be redistributed uniformly over the planet. The same difficulty would arise even if there were a constant drizzle of cometesimals bringing in methane. On the other hand, if some localized surface sinks are present to efficiently scavenge methane from the atmosphere, the cometary source could be plausible, but highly unlikely in our opinion.

2.3. Hydrogeochemical (serpentinization) source

Hydration of ultramafic silicates (Mg, Fe-rich) results first in the formation of serpentine (Mg, Fe) $_3\text{Si}_2\text{O}_5(\text{OH})_4$, and molecular hydrogen ($\text{H}_{2(\text{aq})}$),

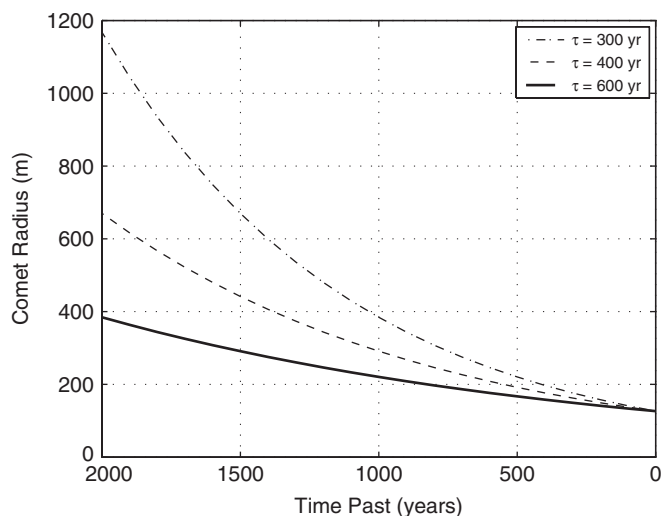
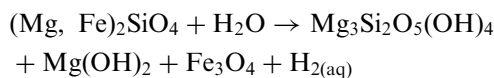
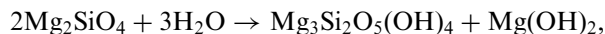
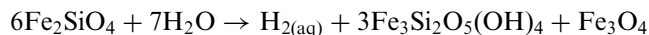


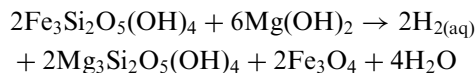
Fig. 3. Comet size vs. time of impact in the past, for different methane lifetimes. The constraint is that the impactor delivered an amount of CH_4 at the time of impact that has declined to its present day global value of 10 ppbv.

or, olivine/pyroxene + water \rightarrow serpentine + brucite + magnetite + hydrogen.

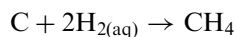
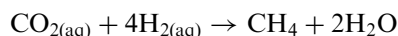
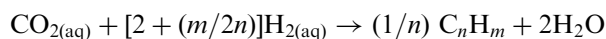
Key hydrogeochemical reactions are:



followed by:



The $\text{H}_{2(\text{aq})}$ produced in above serpentinization process is key to the formation of methane by the hydrogeochemical process. $\text{H}_{2(\text{aq})}$ reacts with carbon grains or CO_2 of the crustal rocks/pores to produce methane and possibly higher order hydrocarbons in decreasing abundances, i.e.



In laboratory experiments simulating the p - T ($\sim 390^\circ\text{C}$, $\sim 400 \text{ bar}$) of the Black Smoker vents, Foustoukos and Seyfried (2004) found a relatively large production of methane in the above reactions catalyzed by Fe-Cr oxide (in addition to being rich in Mg and Fe, oceanic rocks—ultramafic silicates—are also rich in Cr).

Although Black Smokers, first discovered 25 years ago by the submersible Alwyn in the mid-Atlantic Ridge, are commonplace in terrestrial oceans, their occurrence in the interior of Mars is questionable. First, for possible range of Martian geotherms (Fig. 4), Black Smoker type temperatures are expected to be reached 25–50 km beneath the surface of Mars, which is well below the depth where liquid water would be stable (Oze and Sharma, 2005), and the above serpentinization reactions require aqueous phase. Secondly, if by some remote chance methane was produced, it may be nearly impossible for it to push its way out into the atmosphere from such great depths. It is also doubtful that the high temperature-high pressure “aqueous” alteration of silicates to produce methane could have occurred on Mars in the past either.

A more likely scenario involves serpentinization at relatively “low temperatures”. Recently, Kelley et al. (2005) have observed that in “Lost City”, 15–20 km from spreading centers in terrestrial oceans, methane is found in copious quantities. The process that produces this methane is believed to be serpentinization, as outlined above for the Black Smoker vents. However, the temperatures in Lost City are relatively mild, 40 – 90°C . For possible range of the Martian geotherms, such temperatures are reached at depths as shallow as $\sim 2 \text{ km}$ below the surface (Oze and Sharma, 2005). Moreover, the region of stability of liquid water extends from approximately 2–20 km below the surface (Oze and Sharma, 2005). Although aquifers are yet to be detected on Mars, if present, they would be a fertile

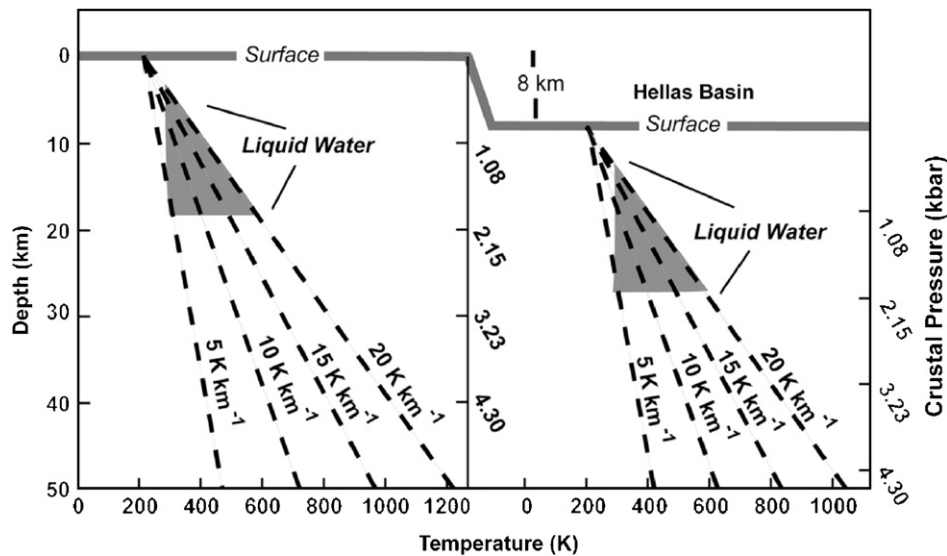


Fig. 4. Possible range of Martian geotherms (Oze and Sharma, 2005). Geotherms of 5, 10, 15, and 20 K km⁻¹ are shown on a T - P -depth diagram where the surface of Mars in relation to Hellas Basin is noted. The depth and T at which H₂O_(l) can be present is shown with a grey polygon. Crustal P s were calculated using a Martian crust density of 2900 kg m⁻³ and the gravity of Mars (3.71 m s⁻²).

ground for the above water-rock reactions to take place, and to produce methane in turn.

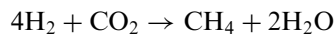
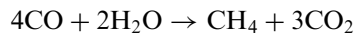
In fact, a chemical equilibrium computer model of basaltic alteration by serpentinization at low temperatures of <150 °C yields as much as 0.2 bar, or approximately 10¹⁵ tons (10¹⁸ kg) of CH₄ (Wallendahl and Triemann, 1999). The process involves wet phase conversion of carbon—initially present as CO₂ in the crustal pores—into CH₄. Such a process could well be active on Mars today. Alternatively, if methane was produced in the past, it could have been stored as stable methane hydrate in subpermafrost aquifer, and gradually risen to the planet's surface (Max and Clifford, 2000). Although the rate of release to the atmosphere is unknown, the above mechanism yields a maximum CH₄ flux of approximately 200,000 tons yr⁻¹, assuming that leaking has been taking place at a uniform rate over the geologic time. This is a factor of 2000 times greater than the 100 tons or so per year needed to maintain a steady state mixing ratio of 10 ppbv of CH₄ on Mars today, thus easily accommodating a slower or non-uniform release.

2.4. Biogenic source

Despite our own enthusiasm for a hydrogeochemical process as the source of methane on Mars, it behooves us to consider the possibility that the methane we see on Mars today could have a biological origin. If the source is biogenic and current, methanogens that use CO or H₂ for energy are candidate sources. The measured abundances of both of these molecules may constrain the global activity of such a biomass (Weiss et al., 2000).

Subterranean and oceanic chemolithotrophic microbial ecosystems are common on Earth. Such microbes are known to produce methane as a product of metabolism (Chapelle et al., 2002; Stevens and McKinley, 1995; Parkes

et al., 1994). The chemical reactions involved are:



Microbial colonies could exist in the subpermafrost aquifer environment of Mars, where microorganisms utilize CO and/or H₂, and produce methane in turn. The Martian atmosphere provides a ready source of CO (~700 ppmv) and H₂ (40–50 ppmv), based on models and observations (Atreya and Gu, 1994, 1995; Nair et al., 1994; Krasnopolsky, 1993). These gases are expected to diffuse through the regolith to the subsurface aquifers. Abundant H₂ may also be made available locally via the hydration of ultramafic silicates. It has been suggested that the source of methane need not be current. If microorganisms existed on Mars only in the past during its (possible) warm and wet phase and produced methane, that methane could have been stored in methane-hydrates for later release, as discussed above. A comparison of the CH₄ source strength at Mars (4 g s⁻¹) with that on Earth (1.67 × 10⁷ g s⁻¹, Yung and DeMore, 1999) indicates that if methane on Mars is microbial in origin, the microbe population must be small. This is because nearly all of the 1700 ppbv of CH₄ in the Earth's atmosphere has its ultimate origin in organisms (Fig. 1), and the Martian source pales in comparison. The quantification of any microbial source on Mars should take into account the possibility of methanotrophs. The latter would consume methane, thus providing another mechanism for the loss of methane from the atmosphere.

2.5. Loss processes: surface oxidants, and organics

As discussed in the introduction to Section 2, the conventional loss mechanism of methane in the Martian

atmosphere is photochemistry, i.e. UV photolysis in the middle and upper atmosphere and oxidation by $O(^1D)$ and OH below. This results in a “photochemical” lifetime of 300–600 years for CH_4 . Wong et al. (2003, 2004) found that CH_4 does react with chlorine species, but its loss rate is quite small, even assuming the maximum possible value of HCl as given by its upper limit in Table 1. Loss due to reaction with other trace constituents (Table 1) is also negligible. On the other hand, there is a distinct possibility of heterogeneous loss to the surface. Generally, such loss processes tend to be slow, so that they do not alter the methane lifetime substantially. This could change significantly if the surface were reactive, as the atmospheric molecules are constantly in the process of diffusing on to the surface. A species that could render the surface of Mars reactive is hydrogen peroxide (H_2O_2). In fact, hydrogen peroxide was proposed as a possible candidate to explain the results of Viking Life Sciences Experiments (LSE). One of the more startling LSE findings was the lack of detection of organics in the Martian surface by the Viking Gas Chromatograph Mars Spectrometer (GCMS; Biemann et al., 1977). Moreover, no convincing evidence of organic material in the surface of Mars has been found to date by remote sensing observations either.

The lack of organics on the surface of Mars is puzzling! It is important to attempt to unravel this mystery as the answer could also affect our thinking about the source of methane gas in the atmosphere. Even if there were no organics indigenous to Mars, organic material must have been delivered in vast quantities by meteorites, comets, and interplanetary dust particles over the past 4.5 billion years. While the Viking GCMS failed to find organics, other life detection devices on the Lander, in particular the Gas Exchange (GEX) and Labeled Release (LR) experiments, indicated a reactive surface. In the LR experiment, gas was given off when nutrients were added to the soil (Levin and Straat, 1979). In the GEX experiment, both O_2 and CO_2 were released from the soil (Oyama, et al., 1977; Oyama and Berdahl, 1977), but the rate of release was fast. In the beginning, presence of microorganisms was invoked, but the rapidity of reactions implied an unrealistic metabolism. A simpler solution was proposed, instead. The seemingly contradictory findings of the Viking GCMS: absence of organics, and the GEX and LR experiments: possible presence of microorganisms, hence organics, could be reconciled if a powerful oxidizer were present in the Martian surface. This led to a suggestion that H_2O_2 was that oxidizer (Oyama et al., 1977).

After three decades of relentless pursuit, H_2O_2 was detected finally in 2003. Encrenaz et al. (2003, 2004) detected it at a dozen lines in the 8.04–8.13 μm range, and Clancy et al. (2004) at a single submillimeter line at 362.156 GHz with JCMT. The H_2O_2 mixing ratio was found to vary between 20 and 40 ppbv over the planet (Encrenaz et al., 2004), in reasonable agreement with photochemical models (Krasnopolsky, 1993; Atreya and Gu, 1994; Nair et al., 1994) corresponding to the time of

observation (southern spring, $L_s = 206^\circ$). The observed abundance of H_2O_2 is at least a factor of 1000–10,000 too small compared to the amount of oxidizer in the surface estimated from the reactivity of soil measured by Viking (Mancinelli, 1989), even after accounting for H_2O_2 vapor diffusion from atmosphere on to the surface (Atreya et al., 2006). Could there be another mechanism responsible for the presence of excess oxidant in the surface?

Reaction between H_2O frost and ultramafic silicate rock, such as pyroxene or olivine, may produce H^+ and OH^- ion pair, and eventually H_2O_2 , from the recombination of residual OH after surface neutralization (Huguenin et al., 1979). Electrical discharges between wind-blown sand particles could produce alkali earth and alkali metal superoxides, peroxides, etc. (Oyama and Berdahl, 1979). Smectite clays could also catalyze oxidation of organics (Banin and Rishpon, 1979). And, recently, taking a cue from the medical literature on silicosis and toxicity of mineral dust (Fubini and Hubbard, 2003), Hurowitz et al. (2005) have found that a large quantity of H_2O_2 is produced from aqueous suspension of freshly ground samples of labradorite, augite, foresterite, and fayalite. It is surmised that cleavage of mineral surfaces during grinding and crushing results in radical species, whose solution in water gives rise to highly reactive oxidants such as H_2O_2 (Fubini and Hubbard, 2003; Fenoglio et al., 2000). However, it is not apparent how minerals will undergo crushing on Mars in order to produce reactive species, and then how they would become suspended in aqueous solution as aquifers may be present only several kilometers below the Martian surface. Nonetheless, above geologic processes for producing oxidants on Mars are promising, but their quantification and the test of their efficacy for producing H_2O_2 or other oxidants would require controlled laboratory measurements under appropriate Martian environmental and interior conditions. On the other hand, aeolian processes that are so prevalent on Mars may turn out to be a potent source of oxidants, as discussed below.

Atreya et al. (2006) have investigated this new mechanism for producing oxidants, especially H_2O_2 , on Mars. Large-scale electrostatic fields generated by charged sand and dust in the Martian dust devils and storms and in the normal saltation process, can induce chemical changes near and above the surface of Mars. The most dramatic effect is the production of H_2O_2 , as illustrated in Fig. 5. The normal photochemical process requires self-recombination of two HO_2 radicals. The triboelectric process results in excess OH, and subsequently excess H, followed by excess HO_2 , which in turn gives rise to excess H_2O_2 .

In fact, the calculated abundance of H_2O_2 could reach 10^4 times that produced by photochemistry alone, assuming the production rates of the CO/O^- and OH/H^- pairs from electric fields as calculated by Delory et al. (2006) using a collisional plasma physics model. With large electric fields of 20 kV/m based on terrestrial analogs, H_2O_2 abundance can get so large that saturation would

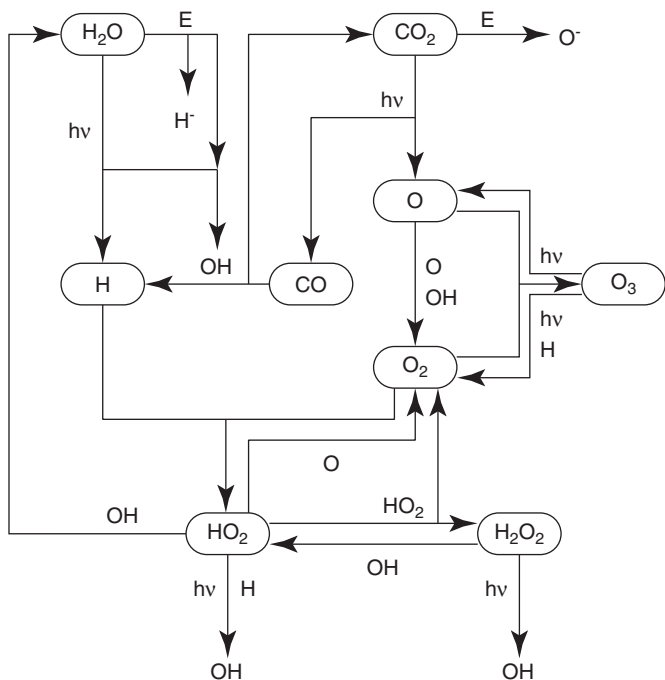


Fig. 5. Electro-photochemical scheme in the atmosphere of Mars. Normally, H_2O_2 is produced by the self-recombination of two HO_2 radicals; HO_2 results from the reaction between H and O_2 . In photochemistry, H comes from the UV dissociation of H_2O , and O_2 comes from the UV dissociation of CO_2 . In electrochemistry, triboelectric processes break down H_2O to produce additional OH , which when combined with CO produces additional H . The rest of the chemistry proceeds as normal, with the end result being excess H_2O_2 production.

occur (at 200 times the photochemical value of approximately 20 ppbv). This would lead to the condensation of H_2O_2 , followed by its precipitation out of the atmosphere on to the surface in the form of H_2O_2 ice adsorbed on airborne dust particles. We suggest that this hydrogen peroxide “dust”, or another superoxide processed from it in the surface, may be responsible for scavenging organic matter from the surface of Mars.

Presence of an oxidizer in the surface could have important consequences for methane also. A reactive surface could remove methane much more efficiently than the photochemical loss processes mentioned earlier. This would place a greater burden on the source, as the production rates are inversely proportional to the methane lifetime. In other words, a faster loss rate would imply a faster production rate in order to maintain the same amount of methane in the atmosphere. It could also mean greater non-uniformity in methane.

3. Life and habitability

Present observations of methane neither prove nor disprove the existence of extant or extinct life on Mars. The observed non-uniformity in methane could be due to localized microbial colonies or localized hydrogeochemical sources. The habitability of Mars is another matter, however. Oxidants in the surface, widespread aeolian

processes and associated electrical storms, harmful solar ultraviolet radiation passing through the thin Martian air and constantly bombarding the surface, all have the effect of sterilizing the surface and possibly rendering it inhospitable to life. If life exists on Mars today, or if it ever existed in the past, e.g. during or after any warm, wet phase, the subsurface is a more friendly environment. We should stress that, life in this context means life *as we know it*.

3.1. Life tests: carbon isotopes

Several tests need to be carried out to determine the existence of life on Mars, now or in the past. One such test is based on the carbon isotopes. Life on Earth has evolved to favor “light” carbon, ^{12}C . This is because when organic molecules, including the simplest of organic molecules, CH_4 , combine, it takes less energy to form a bond between ^{12}C and ^{12}C elements than between ^{12}C and ^{13}C elements. This kinetic “preference” led to amino acids combining to form protein molecules, the building blocks of life, in such a way that the resulting organic molecule contained more ^{12}C than ^{13}C , hence a deficiency in ^{13}C . Such an isotopic fractionation in organic matter is a good indicator of life, *as we know it*. The isotopic fractionation relative to some known “inorganic” standard is expressed as $\delta^{13}\text{C}$. For example, $\delta^{13}\text{C}$ for methane is given by:

$$\delta^{13}\text{C} (\text{CH}_4)_{\text{bio}} \text{ vs. } [\text{std}] = (R_{\text{bio}} - R_{\text{std}}) / R_{\text{std}} \times 1000,$$

where $R_{\text{std}} = ^{13}\text{C}/^{12}\text{C} = 0.0112372$, is the PDB (Pee Dee Belemnite) Inorganic Standard value, so that $^{12}\text{C}/^{13}\text{C} = 89.0$ (inorganic).

With a -60% fractionation of $\delta^{13}\text{C} (\text{CH}_4)_{\text{bio}} =$, one obtains $R_{\text{bio}} = 0.010563$, or $^{12}\text{C}/^{13}\text{C} = 94.7$ (biogenic).

The typical range of $\delta^{13}\text{C} (\text{CH}_4)_{\text{bio}} \text{ vs. } [\text{PDB std}]$ for extant autotrophs including methanogens, methanotrophs, cyanobacteria, etc., is -10% to -40% , with average around -30% (Schidlowski, 1988), resulting in $^{12}\text{C}/^{13}\text{C} = 92$. Values even lower than -85% have been found for some microorganisms, with corresponding $^{12}\text{C}/^{13}\text{C}$ of approximately 97. Thus, for all organic molecules associated with life on Earth, the $^{12}\text{C}/^{13}\text{C}$ ratio is greater than the inorganic standard value of 89. Note, however, the inorganic standard for ^{13}C is based on Belemnite of the Pee Dee Belemnite formation in South Carolina (PDB) that originally came from the bones (carbonate) of a marine animal, which is no longer available. A new reference standard, Vienna-PDB, or simply V-PDB, has been defined, based on the US National Bureau of Standards (now NIST) limestone material NBS19. The V-PDB reference standard is only very slightly different from the previous (PDB) reference, and is agreed to be $^{13}\text{C}/^{12}\text{C} = 0.0111797$. Note that both V-PDB and PDB standards are used in the literature, often without making any distinction.

The above discussion on the carbon isotope fractionation in organic molecules illustrates a monumental

challenge for determining the existence of life on Mars. The mere detection of methane on Mars is not sufficient. Precise carbon isotopic measurement will be required. The average mixing ratio of CH₄ is 10⁻⁸, so that the ¹³CH₄ would be only approximately 1% of this, or a mixing ratio of ~10⁻¹⁰ for ¹³CH₄. Thus the ¹³C/¹²C determination would require measurement capability of *at least* 0.1 ppbv, which is quite difficult. But even that will not suffice, because it is the deficiency of ¹³C due to biology, if any, that needs to be measured. The ¹³C fractionation due to biology, δ¹³C (CH₄)_{bio}, could be as low as -3‰ relative to an inorganic standard. Thus a very accurate and precise determination of the ¹²C/¹³C ratio is essential, and requires an instrument that is capable of measuring methane at 0.01 ppbv levels.

The second challenge is to determine an inorganic standard “reference” value for ¹²C/¹³C *at Mars*, again with a very high degree of precision. Present values using CO₂ are hopelessly uncertain. Even if ¹²C/¹³C could be determined from CO₂ accurately in the future, there is no guarantee it will represent the inorganic standard reference, as this ratio could have been altered due to escape, for example, leading to an “excess” of ¹³C over geologic time. The trick is to measure the carbon isotopes in CO₂ and CH₄ (possibly CO as well) in the atmosphere, along with the same in (yet to be found) organic material and carbonates and in the surface, subsurface and the rocks.

3.2. Life tests: chirality

Although the carbon-isotope ratio can provide a critical test for the presence of life on a planet, it is not a good discriminator between extant (present) or extinct (past) life. One possible test for present life is chirality, or handedness, of organic molecules. Life on Earth has evolved to favor “left handed” organic molecules. All of the amino acids used to make proteins are chiral, although in nature (non-life) they can exist in equal numbers of left- and right-handed configurations. The origin of such chirality is obscure. However, amino acids in meteorites rich in organic material (carbonaceous chondrites, such as Murchison and Orgueil) are also left-handed. Organic molecules associated with life can exist either as left-handed, as on Earth, or right-handed, but not both. Could it be that life on Earth was started by extraplanetary material? Could it be that the chirality of organic material was fixed in the dense molecular clouds before the formation of the solar system? In such clouds, the absorption characteristics of molecules with left and right circularly polarized ultraviolet light are different. Although it is not apparent how and when chirality of organic molecules was determined, chirality is test of life, but only for present life. This is because over time a racemic mixture will be formed, i.e. one with equal number of left-handed and right-handed configurations. The chirality test at Mars is difficult technically, but crucial. The MSL mission is designed to address the important questions of life and habitability on Mars, and considerable effort will be made to carry out

precise measurements of chirality and isotope abundances amongst other things, as we discuss below.

4. Tests for habitability with the Mars Science Laboratory

The sensitive detection of the trace atmospheric species CH₄ and H₂O₂ from Earth and from Mars orbit motivates not only the systematic investigation of sources and sinks for these molecules but also, a broader exploration of the range of geochemical conditions and processes that impact habitability. The combination of the increasingly comprehensive imaging, spectroscopy, altimetry, and neutron measurements available from present and future Mars orbital platforms together with the ground truth provided by the MER rovers provide a good basis for the selection of optimal sites for future landers and rovers that can most directly address the question of the likelihood of past or present life on Mars. For example, prime candidates for such surface sites might be those that contain evidence of sedimentary layers or those that show morphological or chemical evidence for previous transport of ice or liquid water.

The MSL currently under development with a planned launch date of 2009 is designed to achieve a more detailed exploration of habitability. Its goals are to assess and characterize over the period of a full Martian year (1) the biological potential of the target environment, (2) its geology and geochemistry (3) planetary processes that influence habitability, and (4) the surface radiation. A payload for this mission was recently selected that is designed to enable a more detailed in situ analysis of the chemical state of elements such as C, H, O, N, S, P, Ca, and Fe that are essential for terrestrial life. In a significant step forward in analytical capability from the Mars Exploration Rovers, the MSL is designed to provide resources for a capable chemical and mineralogical Analytical Laboratory to sample the atmosphere and processed solid phase samples of regolith or rock cores. The Analytical Laboratory includes the suite of instruments to analyze volatiles that is described in the next section and an X-ray diffraction/X-ray fluorescence (XRD/XRF) instrument that will be able to establish definitive mineralogy of powders delivered by the MSL sampling tools. A diverse set of contact and remote surface and subsurface survey tools will establish context for measurements of this Analytical Laboratory and will facilitate sample identification and selection.

4.1. The Sample Analysis at Mars suite

The primary MSL investigation for organic, volatile, and light isotope analysis is the Sample Analysis at Mars (SAM) Suite Investigation. The primary scientific objectives of the SAM investigation are (1) to take inventory of carbon compounds including those relevant to terrestrial life to determine their sources and processing, (2) to determine the chemical state of light elements through

analysis of volatiles from minerals that trace aqueous and geological processes, (3) to examine oxidation chemistries that might play a role in the destruction of organic compounds, and (4) to establish isotope ratios in noble gases and light elements that may constrain models of atmospheric evolution and past habitability conditions.

SAM consists of three instruments (Mahaffy et al., 2005), a 2-535 Dalton Quadrupole Mass Spectrometer (QMS), a 6-column Gas Chromatograph (GC), and a 4-channel Tunable Laser Spectrometer (TLS). The effluent from the GC is sent to the QMS to enable GCMS analysis. The SAM instrument interrelationships and sample flow is illustrated in Fig. 6 and a model of the current baseline configuration of the SAM instruments and subsystems is illustrated in Fig. 7.

4.2. SAM analysis of methane and hydrogen peroxide

The TLS of SAM employing quantum-cascade and inter-cascade infrared lasers in a 10m Harriot cell is the primary MSL tool for the analysis of both hydrogen peroxide and methane since both of these species fall in a spectral region of the mass spectrometer that is likely to contain interferences from the ion fragments from other species. The TLS technique has been used extensively for measurements of water D/H, $^{18}\text{O}/^{16}\text{O}$, and $^{17}\text{O}/^{16}\text{O}$ isotope ratios in the Earth's atmosphere (Webster and Heysfield, 2003) and the technique for the measurement of water and trace methane in the atmosphere of Mars has also been

developed (Webster et al., 2004, 2005; Webster, 2005). Although, several parts per billion volume mixing ratio (ppbv) of these species can readily be measured directly by the TLS, the SAM Chemical Separation and Processing Laboratory (CSPL) is able to substantially enrich methane for detections substantially below the ppbv mixing ratio. This enrichment will allow the $^{13}\text{C}/^{12}\text{C}$ isotope ratio in methane to be obtained.

4.3. SAM analysis of other organic compounds

SAM provides the capability to search for carbon compounds in MSL delivered samples by three different measurement protocols.

- (1) Pyrolysis of the sample with direct QMS measurements followed by GCMS
- (2) Solvent extraction of organics followed by chemical derivatization and GCMS analysis, and
- (3) Combustion of carbon compounds followed by TLS analysis of the CO_2 produced and its isotopic composition in both carbon and oxygen.

In the first measurement protocol, several tens of cubic millimeters of a crushed sample of Mars regolith or rock delivered from the MSL sample processing tools are heated in an inert carrier gas stream from the ambient temperature to 1000–1100 °C in a programmed temperature ramp. As volatiles are released, these are detected by introducing

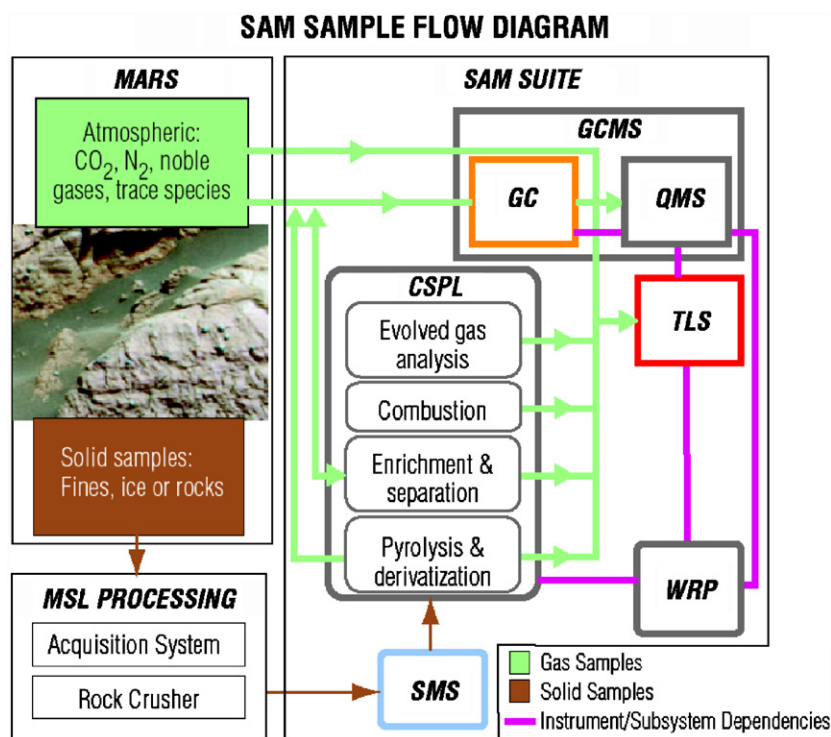


Fig. 6. Flow of solid or gas samples through the instruments and major subsystems of the SAM suite including the quadrupole mass spectrometer (QMS), the gas chromatograph (GC), the tunable laser spectrometer (TLS), the sample manipulation system (SMS), the wide range pump (WRP), and the Chemical Separation and Processing Laboratory (CSPL).

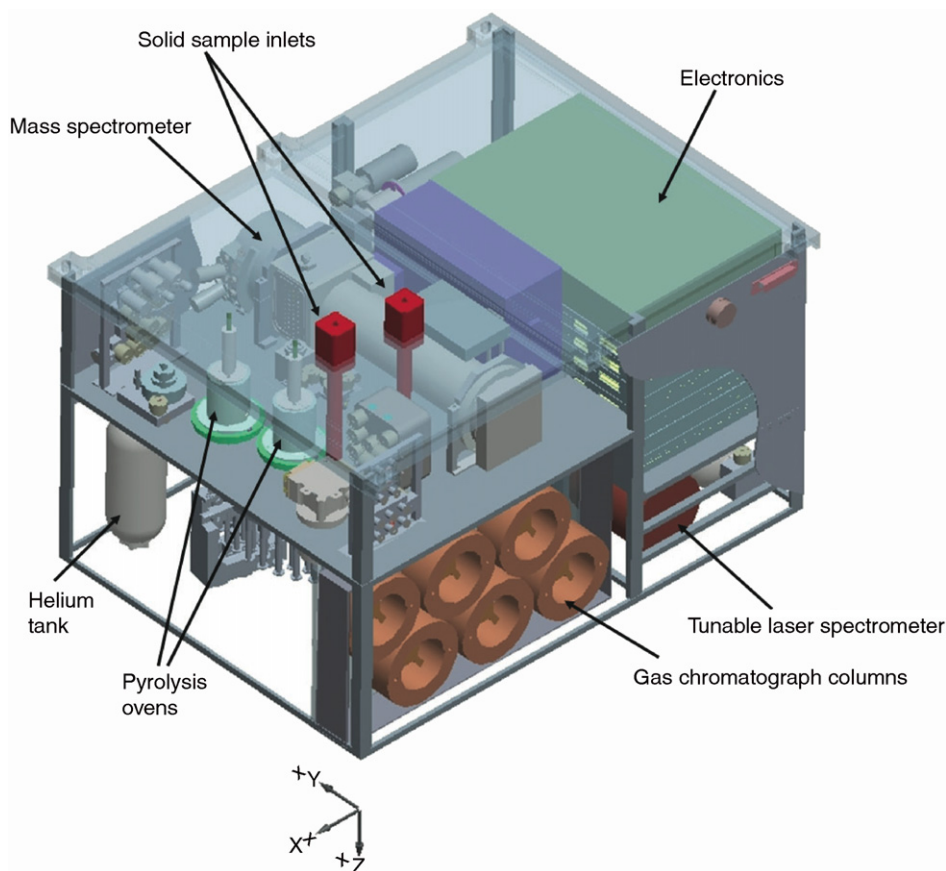


Fig. 7. The baseline mechanical configuration of the SAM suite of instruments is illustrated without the external contamination and shielding covers.

a small volume of the gas stream into the ion source of the QMS. The QMS will ionize a fraction of all gases that are sufficiently volatile and inert to be transported through the heated transfer tubes of the gas manifold to the ion source. Simultaneously, the gas containing thermally evolved and pyrolyzed products is directed over a trap that selectively removes hydrocarbons from the gas stream. Subsequently, the trapped hydrocarbons are injected by a sharp thermal pulse into one of the SAM capillary chromatograph columns and a GCMS measurement is implemented by continuously scanning the QMS while ramping the temperature of the column. Even if a sample is delivered that contains no organic compounds, the evolved gas analysis will reveal the hydration state of the sample as water is evolved and signatures of the mineralogy as inorganic compounds break down at higher temperatures into simple gases such as CO_2 , SO_2 , and nitrogen oxides that can be detected by the SAM QMS and/or the TLS.

In the second organics measurement protocol, the solid sample is delivered into a cup containing both a solvent and a chemical derivatization agent. As organics are extracted from the samples, certain classes of compounds will react with the derivatization agent, in this case the *N, N* Methyl, (dimethyl ter-butylsilyl) trifluoro acetamide. We have demonstrated that this reagent successfully produces volatile species for a range of amino and carboxylic acids

and nucleobases. Non-volatile compounds, such as carboxylic acids (Benner et al., 2000), to which the Viking GCMS was not sensitive, can also be detected with a single step derivatization (Cabane et al., 2001).

Finally, SAM will bring to Mars an oxygen containing reservoir that can be used to combust kerogen-like organic material that may be difficult to analyze without this destructive chemistry. The CO_2 produced in a stepped combustion process will be analyzed in the TLS for both abundance and $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, and $^{17}\text{O}/^{16}\text{O}$. Comparison of the stepped combustion products with the release of CO_2 from the direct pyrolysis, will help distinguish organic carbon from the carbon released as carbonates decompose. Independent measurements from the XRD/XRF may also provide information on carbonates. Of particular interest will be a comparison of the $^{13}\text{C}/^{12}\text{C}$ ratios in carbonates and organic material, as this could be diagnostic of the origin of the organic compounds.

The SAM chemical processing that removes hydrocarbons for injection into the GC after a pyrolysis sequence, will also be used to trap trace species from a stream of atmospheric gas that is driven through the system by the pressure differential produced by the turbomolecular pumps. The ratio of methane to other trace hydrocarbons such as ethane and more complex species may provide another clue in understanding the origin of the atmospheric

methane. A search will be carried out for other potential atmospheric biomarkers such as dimethylsulfide, methanethiol, or hydrogen sulfide (Pilcher, 2003) with this gas enrichment technique.

5. Summary

The detection of methane in the atmosphere of Mars has rejuvenated interest in the possibility of life on the planet, now or in the past. Life and habitability are fundamental reasons for the exploration of solar *systems*. Current data sets on methane are inadequate for answering these issues for Mars. One of the first measurements to be carried out is to confirm the high, localized methane sources and to map them. Methane could be biological in origin, or it could just as well be a product of hydro-geochemistry in the interior. Many coordinated measurements with a high degree of accuracy need to be carried out to answer this and related questions. Measurements of the isotopes of carbon and other elements, together with chirality, organics, oxidants, and other trace species, in samples of the surface, rock, and the atmosphere are essential. The Analytical Laboratory on board the MSL Mission will carry a suite of instruments whose combined results are expected to assess whether Mars is biologically active today, or if it was ever habitable.

Acknowledgments

Part of the research discussed here was performed under the auspices of NASA's MSL Project. SKA's research was supported in part also by NASA's Jet Propulsion Laboratory for his participation as a US Investigator on ESA's Mars Express Mission, and by NASA's Planetary Atmospheres Program for development of a generalized numerical photochemistry code. Discussions with Thérèse Encrenaz, Christopher Webster and Ricardo Amils have been valuable to this research.

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