

# Methane clathrate hydrates as a potential source for martian atmospheric methane

Brendon K. Chastain, Vincent Chevrier\*

*W.M. Keck Laboratory for Space Simulations, Arkansas Center for Space and Planetary Sciences, University of Arkansas, MUSE 202, Fayetteville, AR 72701, USA*

Received 23 August 2006; received in revised form 9 February 2007; accepted 14 February 2007  
Available online 25 February 2007

## Abstract

Small amounts of methane have been detected in the atmosphere of Mars, though the actual sources of the gas remain unknown. Thermodynamic conditions on Mars suggest that gas clathrate hydrate deposits might exist at the polar caps and in some areas of the planetary subsurface. We review the literature available on the detection of methane in the martian atmosphere and the presence of gas clathrate hydrates on Mars. The possibility of martian methane clathrate deposits is established, and initial sources for the sequestered methane are discussed. Based on correlated data and information from disparate sources, we conclude that subsurface methane clathrate deposits are a possible immediate source for the observed atmospheric methane on Mars.

© 2007 Elsevier Ltd. All rights reserved.

*Keywords:* Mars; Atmosphere; Methane; Clathrates; Astrobiology

## 1. Introduction

Considerable attention has been given recently to the methane detected in the martian atmosphere (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2004). It is indeed an interesting phenomenon, as its short half-life in the atmosphere due to photolysis would indicate the need for either an active primary source for the methane, a release of methane from some type of reservoir, or a combination of both. Some of the related literature presents the possibility of subsurface methanogenic archaea being the immediate source for the martian methane (Kral et al., 2004; Formisano et al., 2004; Krasnopolsky et al., 2004; Krasnopolsky, 2006). Methanogenic organisms are responsible for a large amount of the methane found on Earth, and it is exciting to speculate that the same is true on Mars. While this is certainly a plausible possibility, other alternatives should not be overlooked in the effort to champion the most exciting explanation. The amount of

methane detected is extremely small (~10 ppb) and other possible sources can easily account for its presence.

One viable and simple immediate source for the methane may be the dissociation of the gas from methane clathrate reservoirs present in the martian subsurface and polar caps. Gas clathrates are expected on Mars and might play an important role in the climatic and geological evolution of the planet (Miller and Smythe, 1970; Milton, 1974; Dobrovolskis and Ingersoll, 1975; Musselwhite and Lunine, 1990; Jakosky et al., 1995; Musselwhite and Lunine, 1995; Kargel and Lunine, 1998; Kargel et al., 2000; Komatsu et al., 2000; Baker et al., 2000; Baker, 2001). Max and Clifford (2000) specifically propose the possibility of methane clathrate deposits on Mars, and Formisano et al. (2004) mention methane clathrate as a possible source for the atmospheric methane they detected. Large amounts of methane can be stored for long periods of time in these clathrate structures (Max and Clifford, 2000), with slow release due to many naturally occurring processes. It is also possible that significant events might have released large amounts of methane from clathrates and the atmospheric methane is simply the declining remnant of these events. Future studies on how the

\*Corresponding author. Tel.: +1 479 5753170.

*E-mail addresses:* [bkchasta@uark.edu](mailto:bkchasta@uark.edu) (B.K. Chastain), [vchevrie@uark.edu](mailto:vchevrie@uark.edu) (V. Chevrier).

methane abundance and distribution vary over time will hopefully provide much needed insight into whether the martian atmospheric methane is increasing, decreasing, or relatively stable. That information will be vital as scientists continue to investigate possible sources of the gas.

Below we present a brief review of clathrate hydrate compounds in general and discuss their pertinence to Mars. The main focus is on methane clathrate and its potential as an immediate source for the observed atmospheric methane. Possible methods for detection of martian methane clathrate are also discussed. It should be noted that the intention is not to dispel the idea of biogenic martian methane. The release of methane from clathrate deposits does not rule out the possibility of a biosphere existing in the martian subsurface. The sequestered methane must have had some initial originating mechanism, and it may well have been biological. But there are many other potential sources, and the idea of a clathrate reservoir extends the time frame available for initial methane generation. This extended time frame allows for initial source mechanisms that current researchers might be discounting as too ancient.

## 2. Methane in the martian atmosphere

Methane has been observed in the martian atmosphere by both ground-based and space-based research efforts (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2004). Mumma et al. (2004) and Krasnopolsky et al. (2004) both reported detection of methane in the martian atmosphere using state of the art ground-based Fourier transform IR spectroscopy. Their findings were supported by Formisano et al. (2004) using Planetary Fourier Spectrometer IR data obtained by ESA's Mars Express orbiter. The presence of this methane was unexpected due to its short lifetime in the martian atmosphere. Indeed, methane is quickly dissociated into various products when exposed to solar radiation, and its expected photochemical mean lifetime in the martian atmosphere is listed variably as about 300–600 years (Formisano et al., 2004; Krasnopolsky et al., 2004). This requires that the observed methane be relatively recently produced or released, or that a significant amount of methane was released sometime in the martian past and is currently declining.

The average global concentration of methane was found to be roughly 10 ppb of the martian atmosphere, but observations seem to support some strongly localized sources of up to 30 ppb or more (Formisano et al., 2004; Mumma et al., 2005, Fig. 1). Though the two most comprehensive pieces of literature available on the detection of martian methane agree on the average global concentration, they differ on how much methane would need to be produced each year to account for that amount. Krasnopolsky et al. (2004) posit a yearly requirement of approximately 270 tons, while Formisano et al. (2004) calculate 126 tons. This difference appears to be driven by their differing assumptions about methane's mean lifetime in the martian atmosphere.

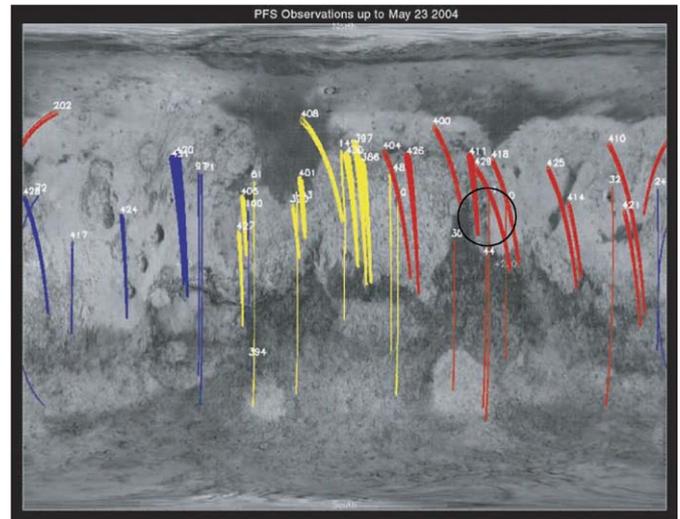


Fig. 1. Relative atmospheric methane concentrations derived from the data acquired by the Planetary Fourier Spectrometer onboard Mars Express (Formisano et al., 2004). The data were collected on orbital passes of Mars Express, and the red, yellow, and blue colors correspond to high, medium, and low methane mixing ratios. The circled area includes a portion of Syrtis Major Planum and encompasses Nili Fossae.

The discrepancy in estimations of atmospheric lifetime is indicative of the complex and sparsely characterized interplay of methane sources, sinks, and photochemistry on Mars. Potential sources have been fairly well documented, but comprehensive information about possible sinks is lacking. Some theoretical work has been done on diffusion of methane through the martian regolith (Weiss et al., 2000; Krasnopolsky et al., 2004; Onstott et al., 2006), but experimental study of methane's adsorption by, potential reactions with, and diffusion through various types of martian regolith is required to more accurately describe its potential paths from formation to destruction on Mars. If the methane production is indeed ongoing, these studies would also assist in characterizing more accurate yearly production estimates.

Also in dispute is the overall distribution of methane in the martian atmosphere. While Mumma et al. (2004) and Formisano et al. (2004) report heterogeneous distributions (Fig. 1) and suggest localized methane production or sinking, Krasnopolsky (2006) presents information to suggest that the apparent heterogeneity is due to spectroscopic limitations caused by surface reflectance. Further observations and new missions should shed more light on the issue. Despite any questions about yearly production amounts and planet-wide distribution, two facts seem to be agreed upon: methane does exist in the martian atmosphere, but the total amount is sparse.

## 3. Clathrate hydrates

In various low temperature/high pressure conditions, liquid water in the presence of certain gases will solidify into a non-stoichiometric crystalline structure called a gas

clathrate hydrate (Buffett, 2000; Max and Clifford, 2000). In oversimplified terms, a gas clathrate hydrate is a lattice of hydrogen bonded  $\text{H}_2\text{O}$  molecules forming cage-like cavities that contain gas molecules (Fig. 2). The water molecules and the included gas molecule interact through weak Van der Waals forces, lowering the free energy of the water molecules and adding to the clathrate's stability (Buffett, 2000).

The clathrate structure allows the normally volatile gas to be trapped in a type of solid solution, storing a large amount of gas in a very stable and compact configuration. This structure has many aliases in scientific literature, including gas hydrate, clathrate hydrate, clathrate, and inclusion compound. Many different gases, including methane, are able to occupy the clathrate cages. The crystalline clathrate cage lattice can take many complex forms, but only three are known to be naturally occurring: structure I, structure II, and structure H (Buffett, 2000). They may alternately be referred to as S-I, S-II, and S-H, respectively. The geometry of the clathrate lattice in each form results in multiple cage sizes. Simplified representa-

tions of the S-I cavities are shown in Fig. 2, and some relevant structural data are provided in Table 1. The superscripted numbers in Table 1 refer to the numbers of face geometries present in a cavity. For example, the  $4^35^66^3$  listed for the medium-sized cavity in S-H refers to a cavity made up of three square faces, six pentagonal faces, and three hexagonal faces. Understanding this notation is important when reading literature dealing with clathrates.

Generally, only one gas molecule occupies a given cage, but multiple occupancy can occur under extreme conditions (Buffett, 2000; Tanaka et al., 2004). S-I and S-II clathrates have two different cage sizes comprising their crystal lattices, while S-H has three (Buffett, 2000). S-I and S-II are the most commonly occurring clathrates, though S-I is favored in environments where methane is the only gas present (Buffett, 2000). The methane molecule fits into the large and small cavities of both S-I and S-II clathrates, but S-I is more stable due to a tighter and more structurally favorable spatial fit within the large cavities of S-I (Buffett, 2000).

Clathrates containing only one gas species are denoted as simple clathrates. The terms binary, ternary, or compound clathrate are used when more than one gas species occupies the cavities of the structure. Compound clathrates, occasionally referred to as multicomponent clathrates, can often be much more stable than simple clathrates due to larger molecules preferentially occupying the large cages of the structure and lowering the free energy (Sloan, 1998). This is often the case with binary  $\text{CO}_2/\text{CH}_4$  clathrate, which can form at much higher temperatures and lower pressures than a simple methane clathrate (Sloan, 1998). The actual composition of a compound clathrate is based on the aforementioned interactions of the included gas molecules with the clathrate cages, as well as the partial pressures of the gases present during and after formation (Lunine and Stevenson, 1985; Sloan, 1998; Osegovic and Max, 2005; Max et al., 2006).

#### 4. Methane clathrates on Mars

Three things are needed for gas clathrate formation:  $\text{H}_2\text{O}$ , the included gas of interest, and a proper temperature/pressure combination. It has already been established that methane is present on Mars.  $\text{H}_2\text{O}$  is also known to exist on Mars. The residual polar caps that persist after the seasonal sublimation of solid  $\text{CO}_2$  have been shown to

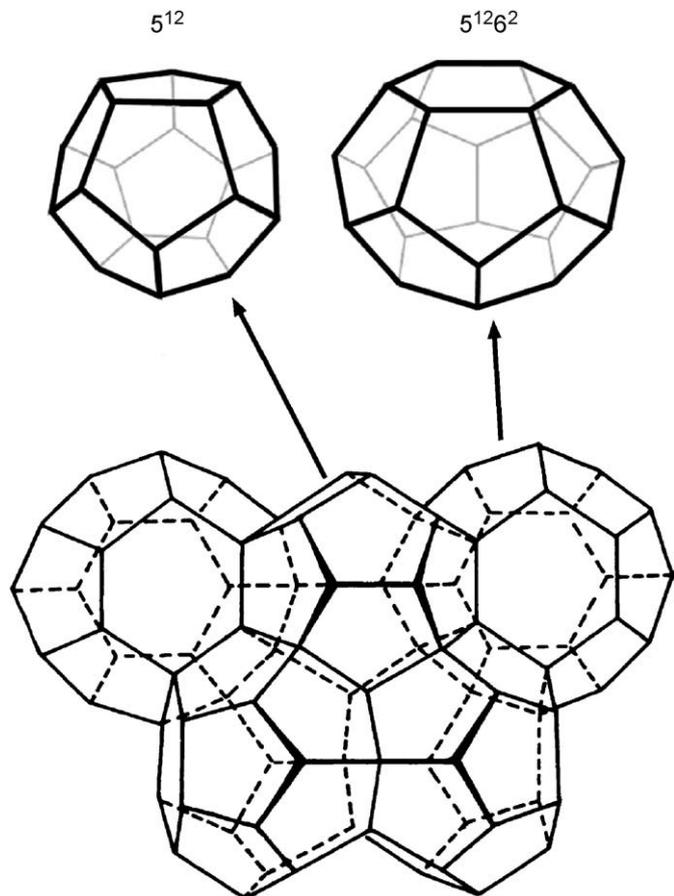


Fig. 2. Structure of the S-I clathrate (Lunine and Stevenson, 1985) with representations of the small ( $5^{12}$ ) and large ( $5^{12}6^2$ ) cavities of S-I clathrate (Buffett, 2000). The line intersections represent the locations of oxygen atoms. Most of the hydrogen atoms are oriented along the lines and form the intra-cage hydrogen bonds, but some extend outward to facilitate hydrogen bonding between the cages.

Table 1  
Clathrate cage information and dimensions (Sloan, 1998)

Property	Structure I		Structure II		Structure H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Cavity geometry	$5^{12}$	$5^{12}6^2$	$5^{12}$	$5^{12}6^4$	$5^{12}$	$4^35^66^3$	$5^{12}6^8$
Avg. cavity radius (nm)	3.95	4.33	3.91	4.73	3.91	4.06	5.71

The cage geometries are described in the text. Stylized representations of the Structure I cavities are provided in Fig. 1, but 3-D visualizations are better suited to accurately depict overall crystal lattice configurations.

contain either water ice or H<sub>2</sub>O in clathrate form (Kargel and Lunine, 1998). Moreover, data gathered by the Mars Odyssey neutron spectrometer have been interpreted as indications of the presence of H<sub>2</sub>O in the martian subsurface extending from the poles to near the equator (Boydton et al., 2002; Feldman et al., 2004; Jakosky et al., 2005; Milliken et al., 2006). Finally, Mars Express has observed water ice in the northern polar cap (Langevin et al., 2005). Fig. 3 shows a geographic distribution of subsurface hydrogen interpreted as being a proxy of water on Mars (Feldman et al., 2004). A part of this hydrogen could be linked to methane trapped into clathrates, especially since the related water is mostly subsurface ice.

At issue is whether the proper thermodynamic conditions exist for clathrates, specifically methane clathrate, to form. Theories supporting the presence of clathrates on Mars initially focused on CO<sub>2</sub> as the sequestered gas but have been extended to include other gases. It was established in 1970 that CO<sub>2</sub> clathrate was thermodynamically stable at the martian poles (Miller and Smythe, 1970). Since that time, others have posited the existence of large CO<sub>2</sub> clathrate deposits and commented on their possible effects on martian climate and geomorphology (Milton, 1974; Dobrovolskis and Ingersoll, 1975; Jakosky et al., 1995; Kargel and Lunine, 1998; Komatsu et al., 2000; Longhi, 2006). Other simple and compound clathrates of atmospheric volatiles might also be stable in the polar caps and permafrost (Lebofsky, 1975; Musselwhite and Lunine, 1990, 1995; Kargel et al., 2000; Max and Clifford, 2000).

Literature specifically proposing methane clathrate deposits on Mars began to appear four years prior to the actual discovery of the atmospheric methane (Max and Clifford, 2000). The body of work specific to

martian methane clathrate remains scarce but has grown since that time (Pellenburg et al., 2003; Duxbury et al., 2004; Max and Clifford, 2004; Onstott et al., 2006; Prieto-Ballesteros et al., 2006). Considering permafrost regions with a density of 2500 kg/m<sup>3</sup> and the thermodynamic properties of the martian crust, Max and Clifford (2004) present evidence for a simple methane clathrate stability zone starting as shallow as 15 m below the surface in some permafrost areas and varying in thickness from 3–5 km at the equator to 8–13 km at the poles. Depending on conditions, methane clathrate could be stable at much shallower depths. Fig. 4 provides a comparison of methane clathrate and water ice stability in conditions similar to those below the surface of Mars. The nature of the subsurface substrate directly controls the geothermal conditions and then the depth of the clathrate formation. An unconsolidated soil acts like a thermal insulator, preventing stability of clathrate at any depth except a very small zone at a few tens of meters. In contrast, sediments like sandstone or ice-cemented soils allow formation of clathrates at a depths shallower than 10 m (Fig. 4) because they are much more efficient in evacuating the heat, thus keep lower temperatures.

Conditions at the poles could be even more favorable to CH<sub>4</sub>-clathrate formation than those on the surface. Sloan (1998) provides a wide range of experimentally determined temperature and pressure combinations at which methane clathrate is stable; the two lowest temperatures provided are 148.8 and 159.9 K. These data points bracket the mean martian polar temperatures estimated by Dobrovolskis and Ingersoll (1975) as 155 K in the north and 154.1 K in the south. Using a linear interpolation of the Sloan (1998) data, a rough polar ice density of 1000 kg/m<sup>3</sup>, and 3.7 m/s<sup>2</sup>

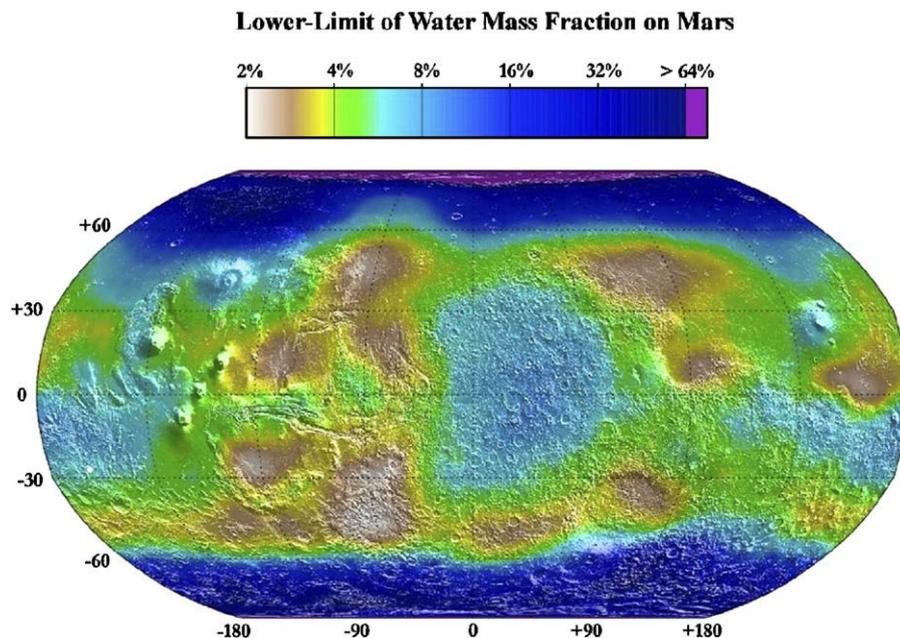


Fig. 3. Percentage water content of soil as derived by Feldman et al. (2004) from the epithermal-neutron analyzed by the Gamma Ray Spectrometer onboard Mars Odyssey. Even if the data strongly suggests a large global supply of H<sub>2</sub>O, some portions of the hydrogen atoms may be linked to the presence of methane in clathrates.

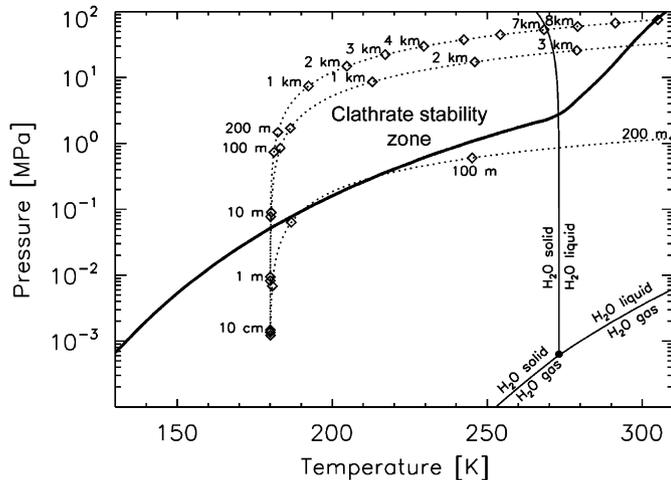


Fig. 4. Pressure, temperature stability diagram of water (thin solid lines) and methane clathrate (thick black curve). The dotted lines represent various models of martian geothermal profiles depending on the surface material, with from top to bottom: ice-cemented soil, dry sandstone and dry, unconsolidated soil. The graph for water and geothermal profiles is reprinted from Mellon and Phillips (2001), the data for the methane clathrate stability curve are determined using the program CSMHYD (Sloan, 1998).

as an estimate for the acceleration due to martian gravity, simple methane clathrate could potentially be stable just 2.46 m below the surface near the martian poles. This is a lower limit example that assumes a temperature of 155 K, a necessary overburden pressure of 9.1 kPa, and the diffusive isolation of the clathrate from the methane-depleted atmosphere, but it illustrates the fact that clathrate deposits do not require enormous pressures and are not limited to the deep subsurface. A similar calculation using 2500 kg/m<sup>3</sup> permafrost density, 170 K temperature, and a requisite overburden pressure of 23.8 kPa yields methane clathrate stability as shallow as 2.57 m, closely corresponding to values reported by Prieto-Ballesteros et al. (2006) for sub-permafrost clathrates at circumpolar latitudes.

Since the major gas in the martian atmosphere and polar caps is CO<sub>2</sub>, the presence of binary clathrates of CO<sub>2</sub> and various other atmospheric volatiles on Mars has been suggested (Musselwhite and Lunine, 1990, 1995). This is also probably true for binary CO<sub>2</sub>/CH<sub>4</sub> clathrates. The presence of CO<sub>2</sub> in the clathrate, while decreasing the amount of CH<sub>4</sub> trapped in the clathrate (Table 2), allows the clathrate to form at lower pressures (Fig. 5, Table 2). Moreover, this effect increases at lower temperatures. For an equimolar mixture of CH<sub>4</sub> and CO<sub>2</sub>, the pressure of clathrate stability is about  $\frac{2}{3}$  of the pressure for CH<sub>4</sub> alone at 273 K, but only  $\frac{1}{3}$  at 173 K (Table 2). Therefore, the CO<sub>2</sub>-dominant atmosphere would allow formation of CO<sub>2</sub>/CH<sub>4</sub>-clathrates at even shallower depths than simple CH<sub>4</sub>-clathrate. Indeed, the pressure required for stability of the binary clathrate decreases as the amount of CO<sub>2</sub> sequestered in the deposit increases.

As previously indicated, the actual composition of a binary clathrate depends heavily on the partial pressures of

the included gases during and after formation. The current dearth of atmospheric methane precludes the active formation of any substantial methane-containing clathrates near the surface without an ongoing subsurface source for the gas. It also limits the possible formation processes for any methane clathrate deposits that might currently exist on Mars. However, in the past of Mars, higher concentrations of methane, linked to various potential processes, could have led to CH<sub>4</sub>-rich clathrates in the martian crust. Therefore, if methane clathrate exists in the martian polar caps, it is likely an ice-sealed remnant of an early atmosphere that was richer in methane. Kargel and Lunine (1998) detail the trapping of atmospheric gases in glaciers on Earth, and the same mechanism could have driven methane into the polar caps of an early Mars. They also discuss the ice-sealing phenomenon that sometimes allows clathrates to exist in conditions that are not thermodynamically favorable. A protective seal could stabilize any sub-polar methane clathrate and slow the diffusion of included gas into the methane-poor atmosphere. Methane clathrate deposits in martian permafrost could be remnants of an earlier time when the gas was supplied from above by the atmosphere or from below by microbial or geological processes. The details of these processes are discussed in the following section. Permafrost clathrates could also be acting as a reservoir for an active methane source, continually being replenished from a deeper source as the gas slowly diffuses out of the upper boundary toward the methane-depleted atmosphere. Deeper subsurface deposits are very unlikely to form today as a result of interactions with the atmosphere and thus require an active or ancient subsurface source. Therefore, if the methane clathrates are the source for the observed methane on Mars, they mostly result from ancient methane-rich conditions and/or are replenished by an active source.

Extensive methane clathrate deposits are not required to account for the small amount of methane detect in the martian atmosphere. Max and Clifford (2000) state that 1 m<sup>3</sup> of methane clathrates holds about 164 m<sup>3</sup> (STP) of methane. That equates to about 116 kg of methane. If the upper bound assumption of a fully occupied simple clathrate lattice is used, the dissociation of a layer 1 m thick with an area of only ~2330 m<sup>2</sup> would release 270 ton of atmospheric methane. The required area decreases with increased clathrate layer thickness, and clathrate deposits on Earth are known to exceed 100 m in thickness (Golmshtok et al., 2000; Dallimore et al., 2003).

Dissociation of clathrate deposits can be driven by any event that increases the temperature in the area of the deposit or decreases the overlying hydrostatic or lithostatic pressure. Milton (1974) first suggested clathrate dissociation due to geological surface alteration and fractures, though he discussed them in relation to ancient large-scale dissociation events. Simple small-scale pitting, faulting, or mass transfer due to seismic events could easily lead to the depressurization and dissociation of subsurface clathrate deposits on Mars. Knapmeyer et al. (2006) provide an

Table 2  
Equilibrium conditions of clathrate (pressure and composition) at various selected temperatures for a binary mixture of CH<sub>4</sub> and CO<sub>2</sub>

Temperature (K)	Pressure (10 <sup>6</sup> Pa)	CH <sub>4</sub> /(CH <sub>4</sub> + CO <sub>2</sub> ) (mol fraction in gas phase)	CH <sub>4</sub> /(CH <sub>4</sub> + CO <sub>2</sub> ) (mol fraction in hydrate phase)
173.15	6.295 × 10 <sup>-3</sup>	0.0	0.0
	6.296 × 10 <sup>-3</sup>	0.0001	<0.0001
	6.229 × 10 <sup>-3</sup>	0.001	0.0003
	6.340 × 10 <sup>-3</sup>	0.01	0.0028
	6.785 × 10 <sup>-3</sup>	0.1	0.0297
	7.365 × 10 <sup>-3</sup>	0.2	0.0624
	8.066 × 10 <sup>-3</sup>	0.3	0.0990
	8.930 × 10 <sup>-3</sup>	0.4	0.1408
	1.002 × 10 <sup>-2</sup>	0.5	0.1897
	1.148 × 10 <sup>-2</sup>	0.6	0.2492
	1.348 × 10 <sup>-2</sup>	0.7	0.3258
	1.650 × 10 <sup>-2</sup>	0.8	0.4336
	2.163 × 10 <sup>-2</sup>	0.9	0.6100
	3.048 × 10 <sup>-2</sup>	1.0	1.0
200	4.170 × 10 <sup>-2</sup>	0.0	0.0
	4.170 × 10 <sup>-2</sup>	0.0001	<0.0001
	4.173 × 10 <sup>-2</sup>	0.001	0.0004
	4.198 × 10 <sup>-2</sup>	0.01	0.0035
	4.464 × 10 <sup>-2</sup>	0.1	0.0365
	4.809 × 10 <sup>-2</sup>	0.2	0.0763
	5.220 × 10 <sup>-2</sup>	0.3	0.1205
	5.717 × 10 <sup>-2</sup>	0.4	0.1705
	6.335 × 10 <sup>-2</sup>	0.5	0.2285
	7.126 × 10 <sup>-2</sup>	0.6	0.2982
	8.181 × 10 <sup>-2</sup>	0.7	0.3859
	9.669 × 10 <sup>-2</sup>	0.8	0.5043
	1.197 × 10 <sup>-1</sup>	0.9	0.6819
	1.557 × 10 <sup>-1</sup>	1.0	1.0
223.15	1.480 × 10 <sup>-1</sup>	0.0	0.0
	1.480 × 10 <sup>-1</sup>	0.0001	<0.0001
	1.481 × 10 <sup>-1</sup>	0.001	0.0004
	1.489 × 10 <sup>-1</sup>	0.01	0.0041
	1.576 × 10 <sup>-1</sup>	0.1	0.0422
	1.688 × 10 <sup>-1</sup>	0.2	0.0880
	1.819 × 10 <sup>-1</sup>	0.3	0.1384
	1.975 × 10 <sup>-1</sup>	0.4	0.1950
	2.165 × 10 <sup>-1</sup>	0.5	0.2600
	2.405 × 10 <sup>-1</sup>	0.6	0.3369
	2.713 × 10 <sup>-1</sup>	0.7	0.4316
	3.129 × 10 <sup>-1</sup>	0.8	0.5548
	3.727 × 10 <sup>-1</sup>	0.9	0.7277
	4.636 × 10 <sup>-1</sup>	1.0	1.0
250	4.835 × 10 <sup>-1</sup>	0.0	0.0
	4.836 × 10 <sup>-1</sup>	0.0001	<0.0001
	4.838 × 10 <sup>-1</sup>	0.001	0.0005
	4.862 × 10 <sup>-1</sup>	0.01	0.0048
	5.123 × 10 <sup>-1</sup>	0.1	0.0490
	5.449 × 10 <sup>-1</sup>	0.2	0.1016
	5.828 × 10 <sup>-1</sup>	0.3	0.1591
	6.272 × 10 <sup>-1</sup>	0.4	0.2228
	6.803 × 10 <sup>-1</sup>	0.5	0.2950

Table 2 (continued)

Temperature (K)	Pressure (10 <sup>6</sup> Pa)	CH <sub>4</sub> /(CH <sub>4</sub> + CO <sub>2</sub> ) (mol fraction in gas phase)	CH <sub>4</sub> /(CH <sub>4</sub> + CO <sub>2</sub> ) (mol fraction in hydrate phase)
	7.449 × 10 <sup>-1</sup>	0.6	0.3787
	8.255 × 10 <sup>-1</sup>	0.7	0.4790
	9.295 × 10 <sup>-1</sup>	0.8	0.6040
	1.069	0.9	0.7682
	1.269	1.0	1.0
273.15	1.243	0.0	0.0
	1.243	0.0001	0.0001
	1.243	0.001	0.0005
	1.248	0.01	0.0055
	1.300	0.1	0.0560
	1.364	0.2	0.1153
	1.438	0.3	0.1791
	1.522	0.4	0.2487
	1.621	0.5	0.3262
	1.737	0.6	0.4143
298.15	1.876	0.7	0.5171
	2.047	0.8	0.6409
	2.263	0.9	0.7959
	2.546	1.0	1.0
	178.070	0.0	0.0
	177.920	0.0001	0.0006
	176.639	0.001	0.0060
	164.857	0.01	0.0549
	102.706	0.1	0.3090
	75.968	0.2	0.4328
62.613	0.3	0.5096	
54.702	0.4	0.5685	
49.438	0.5	0.6212	
45.649	0.6	0.6744	
42.818	0.7	0.7332	
40.720	0.8	0.8028	
39.284	0.9	0.8890	
38.527	1.0	1.0	

Data are calculated using the program CSMHYD (Sloan, 1998).

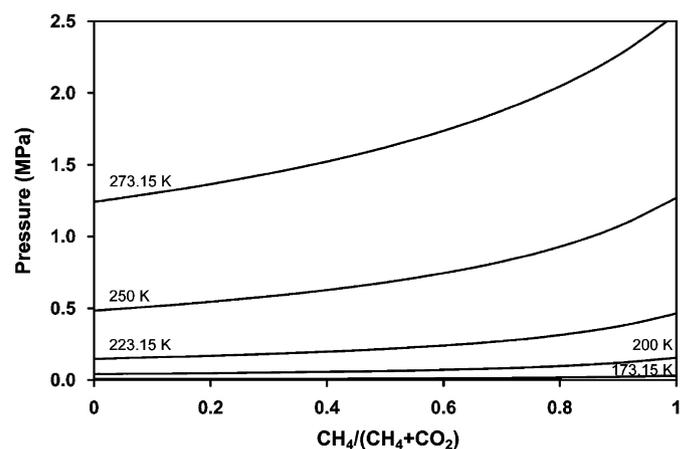


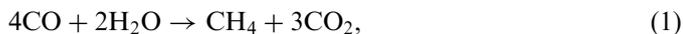
Fig. 5. Pressure of clathrate formation as a function of the composition of the gas for a binary system CO<sub>2</sub> + CH<sub>4</sub>, at different temperatures ranging from 173 to 273 K. Data are determined using the program CSMHYD (Sloan, 1998). Increasing the CO<sub>2</sub> content of the gas decreases the pressure of clathrate formation, allowing it to form at shallower depth.

outstanding overview of the martian seismic profile along with predictions of current seismic activity levels. Small impactors could also have stimulated recent clathrate dissociation and methane release. A crater with a diameter as small as 16 m could mean excavation of over 1000 m<sup>3</sup> of material, lowered lithostatic pressures over substantial surface area, and shock-heating of the underlying strata. There would be little to distinguish a crater such as this from the myriad other small primary and secondary craters found on Mars. Finally, climate changes can also drive dissociation of clathrate deposits. Prieto-Ballesteros et al. (2006) suggested obliquity-driven climate change as the driving force for slow, long-term clathrate dissociation. They proposed that Mars is in an interglacial period where ice-rich deposits are retreating poleward (Head et al., 2003), possibly releasing trapped methane from clathrates or exposing deeper methane clathrate deposits to low atmospheric methane partial pressures. This exposure prompts the diffusion of methane out of the clathrate (Max et al., 2006). The biggest advantage of this mechanism is that it would allow only a very slow release of methane, and thus very low concentrations in the atmosphere, especially if considering the destruction mechanisms that prevent any accumulation of methane in the atmosphere.

## 5. Origin of the methane in the clathrates

By far the most exciting aspect in regard to discussions of methane clathrates on Mars is the idea of a biological methane source. Viability of subsurface methanogenic organisms on Mars was suggested before the atmospheric methane was even discovered (Boston et al., 1992; Weiss et al., 2000; Kral et al., 2004). Biogenic mechanisms are generally considered the most abundant source of methane on the Earth, so it is natural to consider them as a methane source on Mars.

The biological source most often discussed in association with Mars is that of chemolithotrophic methanogenic organisms. It is known that methanogenic archaea actively reduce CO and CO<sub>2</sub> to methane in the following reactions (Formisano et al., 2004):



A subsurface biosphere including methanogens existing below the clathrate stability zone on Mars could produce methane that would then seep upward into the stability zone and be sequestered in methane clathrate. This sequestration of methane does not need be associated with a currently active biosphere on Mars. It may have occurred on an early Mars when conditions were more favorable to life as we know it. Alternatively, any biosphere currently active on Mars could produce methane, even if the concentrations remain very low in the atmosphere, since the clathrate stability zone would act like a buffer of

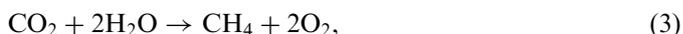
methane release. Therefore, this would allow the presence of a potentially important biosphere in the martian subsurface, which is impossible on the surface due to the paucity of methane, indicating only small oases of methanogens on Mars (Krasnopolsky et al., 2004).

It is also possible that the methane was produced by the anaerobic decay of deceased organisms deep in the subsurface. This would require an incredibly robust and large biosphere to be extant or to have once existed in the martian subsurface. Some authors have completely ruled this scenario out based on Viking Lander information about organics at the martian surface and current martian surface conditions (Krasnopolsky et al., 2004), but the existence of a subsurface methane clathrate reservoir would make this a possible scenario.

Regardless of any time spent in a clathrate intermediary, methane released to the atmosphere would still retain its isotopic information. Assuming the same biological metabolism on both Earth and Mars, any biogenic organic gases should tend to be isotopically light. If data pertaining to the isotopic makeup of the atmospheric methane can be obtained, they might provide an indication of whether the martian methane is biogenic or abiogenic. If that information strongly supports biogenic methane, then research should focus on whether it was an ancient and now extinct or an extant biosphere that is responsible for the gas. Unfortunately, another mission to Mars with proper equipment is required to obtain isotopic fractionation information and there are no guarantees that the data would be conclusive, especially since the very low concentrations in the atmosphere make any measurement and interpretation much more complicated (Krasnopolsky, 2006).

Abiological mechanisms for methane production on Mars might be less exciting than the biological possibilities, but they are no less likely to have occurred. The amount of literature available on possible abiogenic sources of methane on Mars has grown as scientists search for alternative explanations for the atmospheric methane. The most frequently discussed abiotic mechanisms are (1) volcanic or hydrothermal reactions (Krasnopolsky et al., 2004), (2) low-temperature alteration and serpentinization of basalts (Oze and Sharma, 2005), (3) comet or meteorite impacts (Kress and McKay, 2004), and (4) atmospheric reactions (Bar-Nun and Dimitrov, 2006).

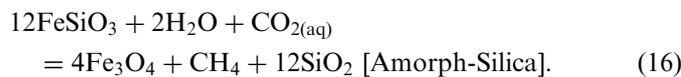
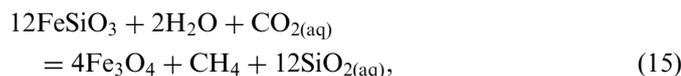
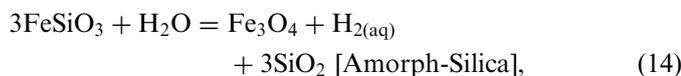
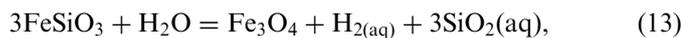
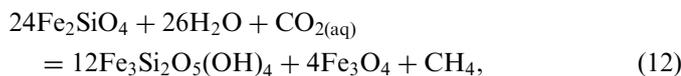
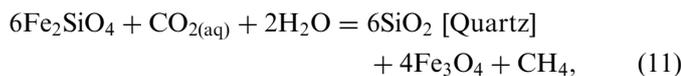
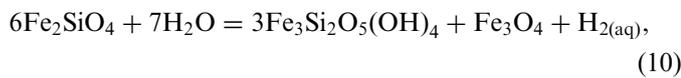
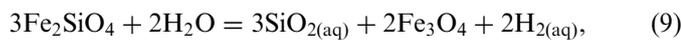
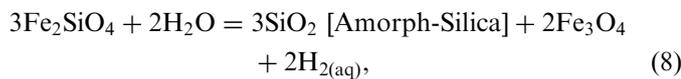
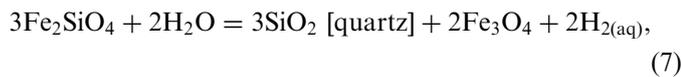
Krasnopolsky et al. (2004) discuss volcanic and hydrothermal reactions and list the following possible pathways for methane production:



They dismiss these geochemical possibilities based on slow low-temperature reaction rates and lack of current

volcanism or areas of significant heat on Mars (Krasnopolsky et al., 2004). Additionally, some studies have used terrestrial analogues to show that martian volcanoes could not account for the amount of methane observed (Ryan et al., 2006). However, it is certainly possible that ancient subsurface volcanism or hydrothermal activity created an early atmosphere that was rich in methane compared to today. That methane could have been trapped in subsurface binary clathrates as the planet cooled.

Oze and Sharma (2005) give a good overview of geochemical alteration of basalts on Mars and present numerous reactions where serpentinization of olivine fayalite ( $\text{Fe}_2\text{SiO}_4$ ) or Fe-rich pyroxene ( $\text{FeSiO}_3$ ) leads to the production of methane or hydrogen gas with silica, magnetite ( $\text{Fe}_3\text{O}_4$ ) and greenalite ( $\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ):



Some of these reactions produce molecular hydrogen  $\text{H}_2$  that can further react with  $\text{CO}_2$  to form more methane:



Methane is a favored end product when olivine-rich rocks react with liquid water at low temperature, suggesting that methane produced by this process on early Mars could have been stored in subsurface clathrates for future release (Oze and Sharma, 2005). Hamilton and Christensen (2005) used data supplied by the Mars Odyssey Thermal Emission Imaging System (THEMIS) to confirm a 113,000  $\text{km}^2$  area of high olivine concentration in the Nili Fossae region of Mars. Also using THEMIS data, Christensen et al. (2003)

report extensive olivine in the walls of the Ganges Chasma in Vallis Marineris. Additionally, Mustard et al. (2005) report on the Mars Express Observatoire pour la Mineralogie, l'Eau, les Glaces, et l'Activite (OMEGA) results that indicate substantial amounts of olivine and pyroxene in crater floors and older terrain on Mars.

Researchers have indicated and commented on localized areas of anomalously high atmospheric methane concentrations on Mars (Formisano et al., 2004; Mumma et al., 2004; Atreya, 2005; Mumma et al., 2005). The circled region in Fig. 1 includes a portion of the Syrtis Major Planum and the Nili Fossae, which are located under an area of high methane concentration. As more information is released about localized abundances of methane, it will be interesting to see if there are specific correlations between large olivine deposits and high atmospheric methane concentrations.

Planetary impacts by comets and meteorites can also create methane on impact, deliver exogenous methane, or dissociate existing subsurface methane clathrate deposits (Kress and McKay, 2004; Sugita and Schultz, 2005). Krasnopolsky (2006) provides a relatively thorough probabilistic dismissal of recent impact-related methane generation or delivery accounting for all of the observed atmospheric methane. His findings are based on the amount of gas detected and martian impactor size and frequency data. The findings do not rule out ancient impact-related methane being stored in clathrates as the planet evolved or address possible dissociation of existing methane from clathrates.

## 6. Detecting the presence of clathrates on Mars

Regardless of what methods are used to try to detect martian clathrate deposits, a return trip to Mars with new equipment is likely required. One possible method that comes to mind is simply drilling into the subsurface. While effective, this method is not cost efficient even here on Earth and delivering that type of equipment to another planet would be a monumental task. Drilling is also a power intensive process that is rife with potential mechanical problems. These concerns increase with deeper target depths and longer drilling times. Literature regarding drilling on Mars appeared as far back as 1980 (Mitchell and Harris, 1980), but early papers generally dealt with extremely shallow target depths. Finally, in 2000, a NASA technical report presented a conceptual analysis of drilling to a depth of 200 m (Blacic et al., 2000).

Literature and research on martian drilling has been plentiful since that time, and momentum seems to be building for a deep drilling mission to Mars. This type of mission could have enormous benefits for a space program. Pellenberg et al. (2003) highlight the potential of using subsurface methane clathrate deposits as a fuel and water source for future exploration and colonization of Mars. They also discuss the additional greenhouse effect of  $\text{CO}_2$  released from clathrates or generated as a byproduct of

methane fuel utilization. They consider the identification of methane clathrates on Mars to be of utmost importance. The discovery of substantial deposits would allow Mars to be modeled as a resource-rich environment when planning future colonization efforts.

A deep drilling mission to Mars does not appear likely until well into the next decade. The Phoenix mission (to be launched in August 2007) that will land in the polar regions will be equipped with a small drilling arm that will allow investigations in the upper centimeters, eventually down to 0.5 m (Smith, 2006). While unlikely to reveal clathrates, (which would rather require a few meters), this would constitute a first step toward a drilling project and eventually bring some useful information regarding clathrate presence, such as the concentration of methane in the upper regolith. If confirmation of clathrate deposits is to be obtained before that time, other methods need to be examined. Unfortunately, finding clathrates with non-drilling methods is difficult, and most work in the area revolves around locating deposits below Earth's seafloors. This is done primarily with seismic probing. Seafloor sediment laced with clathrate has a different density and seismic profile than that of gas-saturated sediment beneath it, and there is often a pocket of gas trapped just beneath the clathrate stability zone (Sloan, 1998). When detected with seismic exploration below the seafloor, this gas pocket shows prominently and runs parallel to the seafloor and is an indicator of methane hydrate deposits (Sloan, 1998; Max and Clifford, 2003). Max and Clifford (2003) suggest that variations of this seismic probing might be used to locate methane clathrate deposits on Mars.

Combinations of seismic probing and other methods can also be used to locate clathrate deposits in subsurface areas. In a NASA technical brief put out by Jet Propulsion Laboratory, Duxbury and Romanovsky (2003) suggest combining electromagnetic prospecting methods with their own "thermo-prospecting" procedure to detect methane clathrate deposits. They give a detailed breakdown of how the difference in latent heat of methane clathrate formation/dissociation and the latent heat of permafrost freezing/thawing creates a signature in the electrical resistivity profile of the permafrost/thawed zone boundary and suggest this signature as a proxy for clathrate presence. The brief presents both magneto-telluric sounding and subsurface electrical resistivity as applicable electromagnetic prospecting methods (Duxbury and Romanovsky, 2003).

In a paper related specifically to non-drilling detection methods for methane clathrates on Mars, Duxbury et al. (2004) suggest a combination of RADAR data and thermal properties similar to those in the NASA briefly mentioned above for indicating the presence of subsurface methane clathrates. They claim that their method can be used in conjunction with radar data provided by the Shallow Subsurface Radar (SHARAD) instrument on NASA's Mars Reconnaissance Orbiter (MRO) and potential

Ground Penetrating Radar data from NASA's planned Mars Science Laboratory (MSL).

## 7. Conclusions

Gas clathrate deposits are expected to be present on Mars due to favorable thermodynamic conditions on the planet. With the discovery of methane in the martian atmosphere and numerous viable subsurface or ancient methane production avenues existing in concert with very few plausible current external and surface production mechanisms, there is a strong possibility of methane clathrate or binary CO<sub>2</sub>/CH<sub>4</sub> clathrates existing in the martian subsurface and/or polar caps. The existence of these clathrates would extend the possible time frame for the initial production of the trapped methane and allow for many feasible initial sources that might otherwise be dismissed. Subsurface methane clathrates on Mars could be the remnant of an extinct subsurface biosphere on the planet or might even serve as a repository for methane currently being produced by microbes in the martian subsurface. As exploration of Mars continues, efforts should be made to obtain both the isotopic signature of the atmospheric methane as well as confirm the existence of any methane-bearing clathrates that might be present in the subsurface. They are both vitally important clues in the continuing quest toward establishing whether life exists or ever arose on Mars.

## Acknowledgments

We thank the two anonymous reviewers whose comments helped to improve the quality of this manuscript.

## References

- Atreya, S.K., 2005. Methane, organics, and related trace constituents on Mars: sources, sinks, implications. AAS/Division for Planetary Sciences Meeting Abstracts 37.
- Baker, V.R., 2001. Water and the martian landscape. *Nature* 412, 228–236.
- Baker, V.R., Strom, R.G., Dohm, J.M., Gulick, V.C., Kargel, J.S., Komatsu G., Ori, G.G., Rice, J.W., 2000. Mars oceanus borealis, ancient glaciers, and the MEGAOUTFLO hypothesis. Lunar and Planetary Science Conference XXXI, #1863.
- Bar-Nun, A., Dimitrov, V., 2006. Methane on Mars: a product of H<sub>2</sub>O photolysis in the presence of CO. *Icarus* 181, 320–322.
- Blacic, J.D., Dreesen, D.S., Mockler, T., 2000. Report on conceptual systems analysis of drilling systems for 200-m-depth penetration and sampling of the martian subsurface. NASA STI/Recon Technical Report N 01, 31709.
- Boston, P.J., Ivanov, M.V., McKay, C.P., 1992. On the possibility of chemosynthetic ecosystems in subsurface habitats on Mars. *Icarus* 95, 300–308.
- Boynton, W.V., Feldman, W.C., Squyres, S.W., Prettyman, T.H., Brückner, J., Evans, L.G., Reedy, R.C., Starr, R., Arnold, J.R., Drake, D.M., Englert, P.A.J., Metzger, A.E., Mitrofanov, I., Trombka, J.I., d'Uston, C., Wänke, H., Gasnault, O., Hamara, D.K., Janes, D.M., Marcialis, R.L., Maurice, S., Mikheeva, I., Taylor, G.J., Tokar, R., Shinohara, C., 2002. Distribution of hydrogen in the

- near surface of Mars: evidence for subsurface ice deposits. *Science* 297, 81–85.
- Buffett, B.A., 2000. Clathrate hydrates. *Annu. Rev. Earth Planet. Sci.* 28, 477–507.
- Christensen, P.R., Bandfield, J.L., Bell III, J.F., Gorelick, N., Hamilton, V.E., Ivanov, A., Jakosky, B.M., Kieffer, H.H., Lane, M.D., Malin, M.C., McConnochie, T., McEwen, A.S., McSween Jr., H.Y., Mehall, G.L., Moersch, J.E., Neelson, K.H., Rice, J.W., Richardson, M.I., Ruff, S.W., Smith, M.D., Titus, T.N., Wyatt, M.B., 2003. Morphology and composition of the surface of Mars: Mars Odyssey THEMIS results. *Science* 300, 2056–2061.
- Dallimore, S.R., Collett, T.S., Uchida T., Weber, M., 2003. Overview of the science activities for the 2002 Mallik gas hydrate production research well program, Mackenzie Delta, N.W.T., Canada. EGS-AGU-EUG Joint Assembly, Nice, France, 6–11 April 2003, Abstract #8100.
- Dobrovolskis, A., Ingersoll, A.P., 1975. Carbon dioxide–water clathrate as a reservoir of CO<sub>2</sub> on Mars. *Icarus* 26, 353–357.
- Duxbury, N.S., Romanovsky, V.E., 2003. Methane clathrate hydrate prospecting. *NASA Tech. Briefs* 27 (12).
- Duxbury, N.S., Abyzov, S.S., Romanovsky, V.E., Yoshikawa, K., 2004. A combination of radar and thermal approaches to search for methane clathrate in the Martian subsurface. *Planet. Space Sci.* 52, 109–115.
- Feldman, W.C., Prettyman, T.H., Maurice, S., Plaut, J.J., Bish, D.L., Vaniman, D.T., Mellon, M.T., Metzger, A.E., Squyres, S.W., Karunatillake, S., Boynton, W.V., Elphic, R.C., Funsten, H.O., Lawrence, D.J., Tokar, R.L., 2004. Global distribution of near-surface hydrogen on Mars. *J. Geophys. Res.* 109, #09006.
- Formisano, V., Atreya, S., Encrenaz, T., Ignatiev, N., Giuranna, M., 2004. Detection of methane in the atmosphere of Mars. *Science* 306 (5702), 1758–1761.
- Golmshtok, A.Y., Duchkov, A.D., Hutchinson, D.R., Khanukaev, S.B., 2000. Heat flow and gas hydrates of the Baikal Rift zone. *Int. J. Earth Sci.* 89, 193–211.
- Hamilton, V.E., Christensen, P.R., 2005. Evidence for extensive, olivine-rich bedrock on Mars. *Geol.* 33 (6), 433–436.
- Head, J.W., Mustard, J.F., Kreslavsky, M.A., Milliken, R.E., Marchant, D.R., 2003. Recent ice ages on Mars. *Nature* 426, 797–802.
- Jakosky, B.M., Henderson, B.G., Mellon, M.T., 1995. Chaotic obliquity and the nature of the Martian climate. *J. Geophys. Res.* 100, 1579–1584.
- Jakosky, B.M., Mellon, M.T., Varnes, E.S., Feldman, W.C., Boynton, W.V., Haberle, R.M., 2005. Mars low-latitude neutron distribution: possible remnant near surface water ice and a mechanism for its recent emplacement. *Icarus* 175, 58–67.
- Kargel, J.S., Lunine, J.I., 1998. Clathrate hydrates on earth and in the solar system. In: Schmitt, B., DeBergh, C., Festou, M. (Eds.), *Solar System Ices*. Kluwer Academic Press, Boston, pp. 97–117.
- Kargel, J.S., Tanaka, K.L., Baker, V.R., Komatsu, G., Macayal, D.R., 2000. Formation and dissociation of clathrate hydrates on Mars: polar caps, northern plains and highlands. *Lunar and Planetary Science Conference XXXI*, #1891.
- Knapmeyer, M., Oberst, J., Wahlich, M., Deuchler, C., Wagner, R., 2006. Working models for spatial distribution and level of Mars' seismicity. *J. Geophys. Res. (Planets)* 111, E11006.
- Komatsu, G., Kargel, J.S., Baker, V.R., Strom, R.G., Ori, G.G., Mosangini, C., Tanaka, K.L., 2000. A chaotic terrain formation hypothesis: explosive outgas and outflow by dissociation of clathrate on Mars. *Lunar and Planetary Science Conference XXXI*, #1434.
- Kral, T.A., Bekkum, C.R., McKay, C.P., 2004. Growth of methanogens on a Mars soil simulant. *Origins Life Evol. Biosphere* 34, 615–626.
- Krasnopolsky, V.A., 2006. Some problems related to the origin of methane on Mars. *Icarus* 180, 359–367.
- Krasnopolsky, V.A., Maillard, J.P., Owen, T.C., 2004. Detection of methane in the martian atmosphere: evidence for life? *Icarus* 172, 537–547.
- Kress, M.E., McKay, C.P., 2004. Formation of methane in comet impacts: implications for Earth, Mars, and Titan. *Icarus* 168, 475–483.
- Langevin, Y., Poulet, F., Bibring, J.-P., Schmitt, B., Douté, S., Gondet, B., 2005. Summer evolution of the north polar cap of Mars as observed by OMEGA/Mars Express. *Science* 307, 1581–1584.
- Lebofsky, L.A., 1975. Stability of frosts in the solar system. *Icarus* 25, 205–217.
- Longhi, J., 2006. Phase equilibrium in the system CO<sub>2</sub>–H<sub>2</sub>O: application to Mars. *J. Geophys. Res.* 111, E06011.
- Lunine, J.I., Stevenson, D.J., 1985. Thermodynamics of clathrates at low and high pressures with application to the outer Solar System. *Astrophys. J. Suppl. S.* 58, 493–531.
- Max, M.D., Clifford, S.M., 2000. The state, potential distribution, and biological implications of methane in the Martian crust. *J. Geophys. Res.* 105, 4165–4172.
- Max, M.D., Clifford, S.M., 2003. Methane hydrate exploration on Mars: a test bed for development of strategies for planetary exploration. *Sixth International Conference on Mars*, Abstract #3160.
- Max, M.D., Clifford, S.M., 2004. The origin and distribution of methane hydrate in the martian crust. *Second Conference on Early Mars: Geologic, Hydrologic, and Climatic Evolution and the Implications for Life*, Abstract #8083.
- Max, M.D., Johnson, A., Dillon, W.P., 2006. *Economic Geology of Natural Gas Hydrate*. Springer, Berlin, Dordrecht, 341pp.
- Mellon, M.T., Phillips, R.G., 2001. Recent gullies on Mars and the source of liquid water. *J. Geophys. Res.* 106 (10), 23165–23180.
- Miller, S.L., Smythe, W.D., 1970. Carbon dioxide clathrate in the martian ice cap. *Science* 170, 531–533.
- Milliken, R.E., Mustard, J.F., Poulet, F., Bibring, J.-P., Langevin, Y., Gondet, B., Pelkey, S., 2006. The H<sub>2</sub>O content of the martian surface as seen by Mars Express OMEGA. *Lunar and Planetary Science Conference XXXVII*, #1987.
- Milton, D.J., 1974. Carbon dioxide hydrate and floods on Mars. *Science* 183 (4125), 654–656.
- Mitchell, D.C., Harris, P.T., 1980. Study of sample drilling techniques for Mars sample return missions. *Martin Marietta Corp. Report*, Denver, CO.
- Mumma, M.J., Novak, R.E., DiSanti, M.A., Bonev, B.P., Dello Russo, N., 2004. Detection and mapping of methane and water on Mars. *American Astronomical Society, DPS Meeting #36*, #26.02; *Bull. Am. Astron. Soc.* 36, 1127.
- Mumma, M.J., Novak, R.E., Hewagama, T., Villanueva, G.L., Bonev, B.P., DiSanti, M.A., Smith, M.D., Dello Russo, N., 2005. Absolute abundance of methane and water on Mars: spatial maps. *Bull. Am. Astron. Soc.* 37, 669.
- Musselwhite, D.S., Lunine, J.I., 1990. Clathrate storage of volatiles on Mars. *Lunar and Planetary Science Conference XXI*, 831.
- Musselwhite, D.S., Lunine, J.I., 1995. Alteration of volatile inventories by polar clathrate formation on Mars. *J. Geophys. Res.* 100, 23301–23306.
- Mustard, J.F., Poulet, F., Gendrin, A., Bibring, J.-P., Langevin, Y., Gondet, B., Mangold, N., Bellucci, G., Altieri, F., 2005. Olivine and pyroxene diversity in the crust of Mars. *Science* 307, 1594–1597.
- Onstott, T.C., McGown, D., Kessler, J., Lollar, B.S., Lehmann, K.K., Clifford, S.M., 2006. Martian CH<sub>4</sub>: sources, flux, and detection. *Astrobiology* 6, 377–395.
- Osegovic, J.P., Max, M.D., 2005. Compound clathrate hydrate on Titan's surface. *J. Geophys. Res. Planets* 110, E08004.
- Oze, C., Sharma, M., 2005. Have olivine, will gas: serpentinization and the abiogenic production of methane on Mars. *Geophys. Res. Lett.* 32, L10203.
- Pellenbarg, R.E., Max, M.D., Clifford, S.M., 2003. Methane and carbon dioxide hydrates on Mars: potential origins, distribution, detection, and implications for future in situ resource utilization. *J. Geophys. Res.* 108 (E4).
- Prieto-Ballesteros, O., Kargel, J.S., Fairen, A.G., Fernandez-Remolar, D.C., Dohm, J.M., Amils, R., 2006. Interglacial clathrate destabilization on Mars: possible contributing source of its atmospheric methane. *Geology* 34 (3), 149–152.

- Ryan, S., Dlugokencky, E.J., Tans, P.P., Trudeau, M.E., 2006. Mauna Loa volcano is not a methane source: implications for Mars. *Geophys. Res. Lett.* 33, L12301.
- Sloan, E.D., 1998. *Clathrate Hydrates of Natural Gases*. Marcel Dekker, New York.
- Smith, P.H., 2006. Science considerations driving the choice of the Phoenix mission landing site. *Lunar and Planetary Science Conference XXXVII*, Abstract #1910.
- Sugita, S., Schultz, P.H., 2005. An efficient methane producing mechanism due to iron meteorite impacts. *Lunar and Planetary Science Conference XXXVI*, #1621.
- Tanaka, H., Nakatsuka, T., Koga, K., 2004. On the thermodynamic stability of clathrate hydrates IV: double occupancy of cages. *J. Chem. Phys.* 121 (11), 5488–5493.
- Weiss, B.P., Yung, Y.L., Neelson, K.H., 2000. Atmospheric energy for subsurface life on Mars? *Proc. Nat. Acad. Sci. U.S.A.* 97 (4), 1395–1399.