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Hydrocarbon System Analysis for Methane Hydrate Exploration on Mars

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ABSTRACT

The recent detection of plumes of methane venting into the Martian atmosphere indicates the probable presence of a substantial subsurface hydrocarbon reservoir. Whatever the immediate source of this methane, its production (whether by biogenic or abiogenic process) almost certainly occurred in association with the presence of liquid water in the deep (>5+ km [>3+ mi]) subsurface, where geothermal heating is thought to be sufficient to raise crustal temperatures above the freezing point of water. Indeed, a geologic evidence that the planet once possessed vast reservoirs of subpermafrost groundwater that may persist to the present day exists. If so, then methane generation has likely spanned a similar period of time, extending over a considerable part of the geologic history of Mars. As on Earth, the venting of natural gas on Mars indicates that substantial amounts of gas are likely present, either dissolved in groundwater or as pockets of pore-filling free gas beneath the depth where the pressure-temperature conditions permit the formation of gas hydrate. Hydrate formation requires the presence of either liquid water or ice. The amount of water on Mars is unknown; however, the present best geologic estimates suggest that the equivalent of a global layer of water 0.5–1 km (0.3–0.6 mi) deep may be stored as ground ice and groundwater beneath the surface. The detection of methane establishes the subsurface of Mars as a hydrocarbon province, at least in the vicinity of the plumes. Hydrocarbon system analysis indicates that methane gas and hydrate deposits may occur in the subsurface to depths ranging from approximately 10 m (~30 ft) to 20 km (10 mi). The shallow methane deposits may constitute a critical potential resource that could make Mars an enabling

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stepping stone for the sustainable exploration of the solar system. They provide the basis for constructing facilities and machines from local Martian resources and for making higher energy-density chemical rocket fuels for both return journeys to Earth and for more distant exploration.

INTRODUCTION

From the time of the first spacecraft flyby of Mars in 1965 until the late 1970s, Mars was characterized as a resource-poor planet whose thin CO_2 atmosphere and numerous craters made it seem more closely related to the Moon than Earth (Mutch et al., 1976). This early view of Mars was not encouraging for near-term human exploration because all the materials required for a voyage and for establishing a base would have to be transported from Earth, including the fuel for the return trip.

More recent spacecraft investigations have significantly changed this view. Although the surface appears barren, a large amount of water ice, mixed with a small amount of entrained dust, is present at both poles as extensive (~600 mi [~1000 km] diameter) layered deposits as much as 2 to 2.5 mi (~3–4 km) deep (Clifford et al., 2000). Geophysical evidence also indicates that ice is widespread in the shallow (top meter) subsurface at mid- to high latitude (Boynton et al., 2002) and might be present at greater depths near the equator (Clifford, 1993).

Estimates of the total inventory of water on Mars are based in part on the amount of water required to produce the erosion associated with the Martian outflow channels (Carr, 1986, 1996). These are enormous scoured depressions, tens of kilometers wide, hundreds of kilometers long, and as much as 0.6 to 1 mi (1–2 km) deep that generally emanate full born from localized regions of collapsed and disrupted terrain. The scale of the braided and streamlined forms found within their beds, combined with the absence of any identifiable tributaries, indicates an origin by catastrophic floods, apparently fed by the artesian discharge of subpermafrost groundwater (Carr, 1979; Baker, 1982; Baker et al., 1992). Depending on the assumed sediment load of these floods, the size of their original subsurface source regions, and the extent to which the water content of these regions was representative of the rest of the planet, the total inventory of water on Mars has been estimated as equivalent of a global layer approximately 0.5 to 1 km (~0.3–0.6 mi) deep (Carr, 1986, 1996).

The growing evidence for abundant water and the in-situ and remote detection of evaporites (such as sulfates, gypsum, carbonate, and various salts [Clark, 1978]), metals (Fe, Mg, Ti, Na, and Al), and, most recently, methane (Formisano et al., 2004; Krasnopolsky et al., 2004; Geminale et al., 2008; Mumma et al., 2004, 2009), have led to a substantial revision of the resource characterization of Mars. These materials are the basic feedstock of the modern chemical engineering industry and could be harvested and used to support and expand the human exploration of Mars and beyond (Zubrin and Wagner, 1996; Fergus, 2003).

A new paradigm of a resource-rich Mars must now be considered central in future planning for human travel to Mars, where Mars is no longer simply a remote dead-end destination but instead a self-sustaining outpost that can serve as a stepping stone to the outer solar system. A resource-rich Mars will have the natural resources to produce high-energy fuels to return to Earth or travel farther outward in the solar system. Plastics, metals, and many other materials necessary for the sustainable presence of humans on Mars may all be derivable from the natural resources of the planet (Max and Clifford, 2000; Pellenbarg et al., 2003). The question is no longer "Does Mars have resources?" but instead, "How do we assess and exploit the natural resources of Mars?" and "How can these resources support the human exploration of Mars and beyond?"

METHANE IN SUBSURFACE MARS

The possibility that an abundant supply of hydrocarbons may be stored in the Martian subsurface is supported by the apparent subsurface origin of the methane gas recently detected in the Martian atmosphere (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2004, 2009). Earth-based spectroscopic observations suggest that large quantities of methane may have been produced, either biogenically or abiogenically, within the subsurface, where it may occur as pockets of free gas or, under appropriate conditions of temperature and pressure, may have reacted with water ice to form methane hydrate (Kargel and Lunine, 1998; Fisk and Giovannoni, 1999; Max and Clifford, 2000).

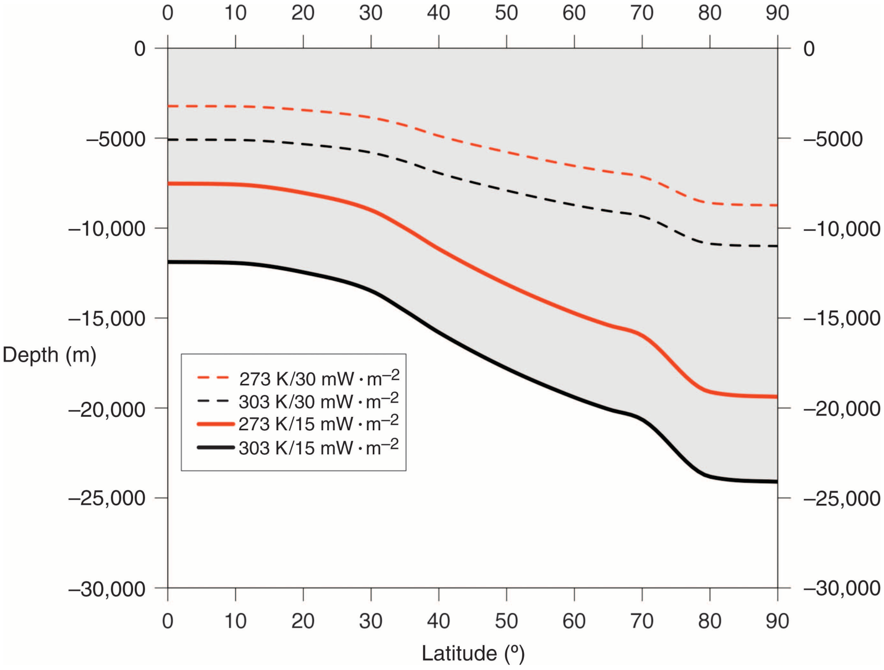

FIGURE 1. **Schematic diagram of a hydrocarbon system for Mars, illustrating the relative positions of the base of the water-ice cryosphere (red lines) and gas hydrate stability zone (black lines), assuming a mean global geothermal heat flux of 15 mW m^{-2} (solid lines) and 30 mW m^{-2} (dashed lines). The figure was adapted from Clifford et al. (2009).**

On Earth, the conditions necessary for the formation of hydrates are found at depth in permafrost and in the subsurface sediments of continental margins. Marine methane hydrate, at least that which is found along the tectonically passive eastern margin of North America, appears to be associated with an active community of anaerobic methanogenic bacteria (Wellsbury and Parkes, 2003). Because the isotopic composition of marine methane hydrate is almost always dominated by an evidence of bacterial production, local production is generally attributed to the metabolism of methanogenic bacteria in the deep biosphere of Earth (Barnes and Goldberg, 1976; Onstott et al., 2006). On active continental margins and accretionary prisms that have no analog on Mars, and in some petroleum deposits, hydrate on Earth also contains some thermogenic methane.

Martian methane may have been produced by both biogenic and abiogenic processes. Although the exact nature of the early Martian environment is still unknown, the presence of abundant water, combined with a higher level of geothermal activity, and the possible presence of an early greenhouse atmosphere may have created the conditions necessary for the emergence of life (Farmer, 1996). If so, Martian organisms may have eventually adapted to a subterranean existence where the combination of warmer temperatures and the presence of groundwater may have enabled them to persist to the present day. It is also possible that methanogenic life also developed entirely in a subterranean environment and did not migrate down from the surface. Such life may resemble the anaerobic bacterial communities found in the deep biosphere of Earth (Boston et al., 1992; Stevens and McKinley, 1996; Onstott et al., 2006). If so, it may have produced comparable quantities of methane (Fisk and Giovannoni, 1999; Max and Clifford, 2000).

Methane may have also been produced abiogenically, as a fractionation product of magma crystallization or by reactions with basalt or carbonate in subpermafrost aquifer-yielding local partial pressures ranging from approximately 0.2 to many bars, depending on the availability of carbon (Wallendahl and Treiman, 1999; Sleep et al., 2004; Schulze-Makuch et al., 2007). Whatever its origin, as the internal heat flow of Mars has declined with time, the resulting downward propagation of the freezing front at the base of the cryosphere would have incorporated any subsurface methane as hydrate in pore space concentrations that may have ranged from dispersed microcrystals to fully saturating the available porosity (Figure 1) (Max and Clifford, 2000).

In permafrost regions on Earth, methane hydrate and water ice form a compound cryogenic zone whose extent is determined by the local mean surface temperature, geothermal gradient, pore water geochemistry, and the increase in confining pressure that occurs with depth. A gas hydrate stability zone (GHSZ) occurs within the region of the crust determined by these conditions, below which methane persists solely as a gas (Dickens et al., 1997; Max and Clifford, 2000; Max, 2003; Kargel et al., 2007).

At the 200 K (−99.7°F) average surface temperature of Mars, methane hydrate is not stable at a confining pressure of less than approximately 140 kPa (20.3 psi) (Sloan, 1997), corresponding to the lithostatic pressure at a depth of approximately 15 m (~50 ft). This depth would define the top of the Martian GHSZ. However, at colder temperatures characteristic of latitudes greater than 60°, it may be found at shallower depths (Chastain and Chevrier, 2007).

Given a reasonable estimate of the thermal properties of the Martian crust, the base of the GHSZ is expected to range from approximately 5 to 10 km (~3–6 mi) at the equator to approximately 12 to 24 km (~7–15 mi) at the poles (Clifford et al., 2009), although, as discussed in the following section, the base of the GHSZ (BGHSZ) can occur at much shallower depths where active venting or other geothermal anomalies are observed. While the size of the GHSZ can be estimated, the extent to which this stability zone is actually populated with hydrate is unknown.

PROBABLE IMPACT OF VENTING ON GEOTHERMS AND THE BASE OF THE ICE AND HYDRATE CRYOSPHERE ON MARS

Recent estimates of the present-day global heat flow of Mars suggest a mean value only half as great as previously thought, effectively doubling the estimated thickness of the cryosphere and GHSZ (Clifford et al., 2009). This suggests that, if groundwater currently survives on the planet, it will generally be restricted to great depth (>5 km [>3 mi] at the equator and >13 km [>8 mi] at the poles). However, natural variations in crustal thermal conductivity, heat flow, and the local concentration of potent freezing-point-depressing salts, such as $CaCl_2$ and $Mg(ClO_4)_2$, may result in significant local departures from these predicted values and may conspire to significantly reduce the expected thickness of frozen ground. We discuss the probable effect of periodically active vents as an additional factor that may contribute to substantial local reductions in the thickness of the cryosphere and GHSZ.

Mumma et al. (2009) report that the distribution of methane in the Martian atmosphere suggests localized sources. One possible explanation for this observation is that they are vents associated with local faults or joint systems, which may provide conduits from reservoirs of methane gas, trapped beneath the BGHSZ, to the surface. In such a leaky system, methane gas migrates upward slowly and irregularly because of buoyancy either as a gas phase or dissolved in fluid. The concentration approaches saturation as the water rises and, at some point, a separate gas phase is formed, possibly accelerating the upward flow of fluid and gas.

The venting of methane gas has the potential to advect heat upward from beneath the cryosphere, which can result in an updoming of the isotherms in the vicinity of the vents, thinning the regions where both ice and methane hydrate are stable (Figure 2). The occurrence of these vents may be aided both by tectonic faults and fractures or geothermal anomalies, associated with deep magma chambers or igneous intrusions.

On Earth, in the northern Gulf of Mexico, several methane vent sites have been extensively studied as part of an assessment of natural gas resources that used seismic data, sea-floor sampling, drilling, and heat-flow measurements, as well as measurements of the temperature and composition of the vent fluids (Max et al., 2006). In regions where the GHSZ exhibits an otherwise uniform thickness, the focused upward flow of relatively warmer gas and fluid along fractures from depth introduces heat into the region surrounding the vent and distorts the regional geotherms. A hydrate-free halo is defined by thermal conditions in which the methane hydrate is unstable surrounding the vent, with a bell-shaped thermal anomaly centered on the vent (Figure 2). This updoming of the BGHSZ is a product of the virtually instantaneous reversibility of the hydrate reaction that makes mono-gas hydrate supremely responsive to form or dissociate in response to change in either pressure or temperature.

As it is on Earth, venting is a mechanism that has the potential to thin the GHSZ and the ice-rich cryosphere of Mars subjacent to the region of venting. The upwarping effect on Mars is unlikely to be as significant as the steep upwarping of the BGHSZ in the marine sediments of Earth because little, if any, liquid water is likely to be involved, and the amount of heat potentially transported by vapor alone will be significantly less. Sea-floor venting on Earth is commonly transitory in nature whereas the vent systems on Mars may be much more long-lived because no overlying ocean to buffer temperature changes in the crust exists. As a result, significant upwarping of the cryosphere and BGHSZ may occur over time.

Upwarping of the BGHSZ will depend on the longevity of the vent, the proportion of vented gas to

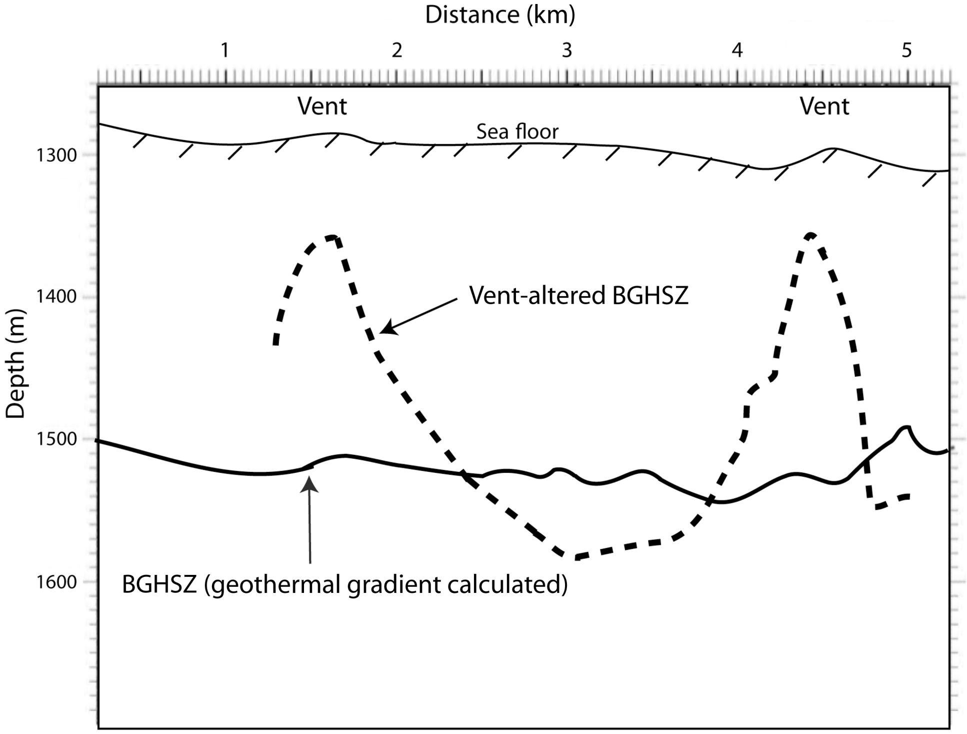

FIGURE 2. Upwarping of the base of the gas hydrate stability zone (BGHSZ; dashed lines) surrounding vents. Redrawn from figure 4.17 of Max et al. (2006), based on the U.S. Geological Survey seismic line shown there in more detail. Note the vertical exaggeration.

liquid, the amount of geothermal heat that is introduced into the system as a function of time, as well as the thermal properties of the cryosphere, which will govern the speed and extent of thermal equilibration. The margins of the bell-shaped unfrozen zone, surrounding the vent, will be defined by a combination of the BGHSZ and the ice-water transition that marks the lower boundary of the cryosphere. These could form a broad-shaped cone at depth (Figure 2). If a vent were of long-standing character, linking a methane-producing area at depth with the surface, liquid water could be present within the unfrozen region surrounding the vent at much shallower depths than predicted by the assumption of a uniform geothermal gradient, based on mean crustal properties, over the same region.

Because water-rich zones underlying abnormally thinned cryosphere may occur beneath vents and the movement of gas and water could be expected to distribute nutrients, as vents do on Earth, the search for deep biosphere life might well first investigate water and pore space in sediments subjacent to vent sites.

VENTING AND THE LOCATION OF THE VENT RESERVOIR

Because the methane venting on Mars is seasonal in nature (Mumma et al., 2009), it may plausibly originate from gas-filled vents that are capped by ice that thaws in the summer and releases the gas. If so, this would indicate that the immediate cap on the source needs to be within 2 m (7 ft) of the surface to be affected by the seasonal thermal wave. The gas reservoir, however, can be anywhere between the surface and the top of the hydrate stability zone, which is almost certainly too deep to be affected by seasonal temperature variations (Max and Clifford, 2000). Although the gas reservoir from which the vent draws the gas is almost certainly subjacent to the vent, the ultimate source of the gas need not be. The migration path from the gas production zone at depth to a gas reservoir near the surface would follow the most permeable path, whose geometry could be quite complex.

Given the inferred amount of methane contained in the principal Martian plume (~19,000 metric tons) and the estimated release rate of 0.6 kg s^{-1} or more (Mumma et al., 2009), it is unlikely that it results from the dissociation of gas hydrate caused by seasonal warming. The thermodynamics of the GHSZ are such that hydrate is most stable near the surface and least stable near its base (Max, 2003). However, the amplitude of the thermal disturbance necessary to result in the dissociation of basal hydrate would need to be huge (with sustained surface temperatures above freezing for more than 10^5 yr) and would take approximately 10^6 yr to propagate down to the BGHSZ. Even such significant surface warming would have little effect as long as the pressure was sufficient for hydrate stability. At best, seasonal warming might result in a slight deepening of the top of the GHSZ, but no mechanism is available to reform significant amounts of hydrate in the near-surface zone on a seasonal basis.

The observed seasonality of methane release on Mars is different from that seen in permafrost regions on Earth, where large sudden methane releases from the tundra occur during the onset of freezing (Mastepanov et al., 2008) as methane derived from near-surface biota and organic matter is apparently expelled during the phase change from water to ice.

ECONOMIC GEOLOGY OF MARS

Generally speaking, any natural materials that are present in usable quantities have probable economic or practical value. However, in the context of the human exploration of Mars, the greatest value is placed on those materials that are most critical for sustaining and expanding human settlements and capabilities, not for commercial sale and revenue, although that could come later.

Some economically important minerals may be associated with Martian volcanic and fumarole deposits. The rocks on Mars appear to be almost entirely of basaltic origin, having undergone little differentiation that would lead to mineral deposits such as those typically associated with diorites and granitic rocks. However, some of the high-temperature magmatic metals, such as iron and titanium, are known to be present. Martian volcanoes are very large and their development almost certainly involved hydrothermal interactions with water in the crust (Gulick and Baker, 1990; Schulze-Makuch et al., 2007). Mineralization at fumaroles may have produced local mineral deposits similar to those found in similar environments on Earth. Restricted metamorphic deposits may be present but at depths that are probably too great to be of interest, although some may outcrop in the deepest layers exposed in Valles Marineris and in other faulted and fractured terrains. In addition to potential igneous and volcanic mineral deposits, an extensive evidence of widespread sedimentary deposits of both eolian and aqueous origin is observed, the latter yielding a variety of minerals (such as sulfates, carbonate, gypsum, salts, and phyllosilicates) indicative of their water-related origin.

Hydrocarbon concentrations are an integral part of economic geology, although gas and liquid hydrocarbon accumulations are commonly regarded as a separate discipline from the economic geology of solid crystalline-ore materials. Methane hydrate and hydrate-derived gas straddle the line between classical economic geology and hydrocarbon geology. This is because hydrate is a solid crystalline material, but one whose formation and dissociation are part of a highly reversible reaction that may either sequester gaseous and dissolved CH_4 into hydrate or release it as gas. The observational evidence now suggests that substantial reservoirs of subsurface methane may exist on Mars. Thus, an understanding of the factors that govern methane formation, migration, and concentration (which define a hydrocarbon system) is important to the eventual recovery and use of Martian methane.

HYDROCARBON SYSTEM ANALYSIS

The physical and chemical controls governing hydrate formation on Mars, and other bodies in the solar system, are the same as on Earth, although individual differences arising from variations in upper crustal composition, environmental conditions, and depositional and erosive environments exist. Nonetheless, the basic principles of hydrocarbon system analysis apply broadly, and understanding the entire methane system on Mars will be the key to identifying recoverable methane deposits. The natural oil seeps on Earth that led to the original exploitation of the hydrocarbons of Earth have, as a Martian analog, the methane vents; however, the recovery strategy of drilling straight down to tap the subjacent deposit that has worked on Earth may not work as well as on Mars. Oil and gas on Earth are produced from organic matter by either biogenic or thermogenic means. Nonhydrocarbon gases, of which N_2, CO_2, and SO_x are the most common, may also be produced and will migrate with the hydrocarbons. On Earth, petroleum system analysis is used as an integrated framework to guide oil and gas exploration, particularly in early stage assessment (Okui et al., 2008).

How and where hydrocarbons are generated, how they migrate, and how they are concentrated and trapped so that they can be economically extracted are the foundations of hydrocarbon exploration on Earth. Petroleum system analysis is used to identify those regions where exploration for hydrocarbon deposits is most likely to achieve success. The critical elements of a petroleum system consist of a mature source rock, a migration pathway, a reservoir, and a trap and seal. Because rock and sedimentary environments in which the petroleum system exists evolve with time, the relative timing is important. For instance, the chemical or biological generation of a large volume of gas in the deep subsurface is of little consequence if no migration path to reservoir rocks at more accessible depths is observed. Likewise, a high-capacity reservoir is useless without a cap and seal. Generation, migration, concentration, and storage are all significant factors in determining the viability of economic recovery. Once the hydrocarbons have been trapped, they may persist for a very long time, although some degradation may occur. Natural leakage of hydrocarbons out of reservoirs may also occur. Exploration prospects are typically similar in basins or regions that have undergone a similar process of sedimentation, tectonics, and thermal history. Generally speaking, particular trapping mechanisms, such as those for tight sands, shales, coalbed methane, structural and stratigraphic traps, hydraulic downdip traps, and others, are referred to as plays. The nature and effectiveness of these plays may exhibit considerable local variation, although they may be related on a larger scale (Selly, 1998). Hydrate plays on Earth are described and characterized in Max (2003) and Max et al. (2006).

PROPOSED HYDROCARBON SYSTEM FOR MARS

Suitable Source Rock/Hydrocarbon Generation

If methane on Mars was solely the product of primordial degassing, then it could reasonably be concluded that, as the magmatic activity of the planet died down, the volume of gas released to the atmosphere would have experienced a significant decline. However, if the present level of venting represents a long-standing process, such as relic biosphere, then the production of subsurface methane would have been an ongoing process over a considerable part of the geologic history of Mars.

Different thermal histories produce different hydrocarbons. For instance, low temperatures commonly are conducive to the production of biogenic gas deposits. Serpentinization of basic rocks will also produce methane (Wallendahl and Treiman, 1999; Sleep et al., 2004; Schulte et al., 2006), and this also commonly occurs as part of a low-temperature metamorphic history that allows water to bond in the serpentine structure. At higher temperatures, serpentine either will not form or will dehydrate. At still higher temperatures, thermogenic gas deposits will form. Thus, the methane that is now seen venting from the Martian surface may be the product of either ancient serpentinization or the continuing reactions between water and basalt at depth, producing methane that has managed to escape cryosphere-hydrate system sequestration.

The methane plumes detected on Mars appear over several Northern Hemisphere locations, including a region east of Arabia Terra, the Nili Fossae region, and the southeast quadrant of the Syrtis Major volcanic province, which is 1200 km (700 mi) in diameter (Mumma et al., 2009). These areas also show evidence of ancient ground ice or flowing water, which suggests that water or ice may be present at depth. As on Earth, subsurface water on Mars is almost certainly not uniformly distributed. As liquid water is required for both the biogenic and abiogenic productions of methane, the location of the plumes may indicate where groundwater persists below the base of the cryosphere.

HYDROCARBON PROVINCING

The first requirement for hydrocarbon exploration is determining whether conditions for the generation of sufficient hydrocarbons to compose a hydrocarbon province exist. Identification of a gas province is based on both direct and indirect evidences. On Earth, direct evidence might consist of the detection of large vents of natural gas from the sea floor or, on land, subaerial mud volcanoes, both of which are good signs that large reservoirs may be present in the subsurface. Indirect methods consist of drill core analyses or remote survey methods such as seismic, magnetic, gravitational, and electrical methods, among others. In this context, the detection of methane plumes on Mars is a direct evidence of the probable presence of extensive natural gas provinces in the subsurface.

MIGRATION

The permeability and porosity of the source rock, the migration path, and the characteristics of any probable reservoirs are unknown on Mars. The Martian subsurface is believed to be frozen to depths of approximately 5 to 20 km (~3–12 mi), and the existing geophysical data are insufficient to permit an understanding of the variation of its physical and compositional properties with depth or the extent to which these properties have been affected by the variable effects of the secondary development of ice, hydrate, and possible gas deposits in the cryosphere.

Evidence of extensive sedimentary deposits, which are generally characterized by high values of primary porosity, are found across the surface of the planet (Malin and Edgett, 2000; Lewis et al., 2008), but the depths to which sedimentary deposits persist are difficult to predict in the absence of in-situ measurements and processes such as plate tectonics which, on Earth, has recycled tens of kilometers of sediments over geologic time. However, at depth, it is likely that secondary joint and fracture system permeability has been produced by both extensive impact cratering and mild tectonism (Clifford, 1993; Clifford and Parker, 2001; Hanna and Phillips, 2005)— secondary porosity that might provide significant pathways for fluid and gas migration, even at depth.

Expulsion of the hydrocarbons from the source rock requires a sufficient level of permeability and porosity along the entire migration path. Migration is commonly driven up-structure by buoyancy in a water-dominated porous system. That porosity may take the form of faults and fractures, or be manifested through coarser sediments that are sufficiently porous and permeable. The migration can occur on the scale of meters or thousands of kilometers. Artesian systems in which complex diffusion and mixing occur (Anderson, 2007) may also contribute to the transport and concentration of gas.

On Mars, the level of tectonic activity appears to have always been less than on Earth, although Valles Marineris (an equatorial rift ~4000 km [~2500 mi] long and ~100 to 600 km [~60 to 370 mi] wide) and the radial and concentric fractures associated with the Tharsis Bulge (a dome that is ~4000 km [~2500 mi] in diameter and rises ~10 km [~6 mi] above the mean elevations of the planet) provide evidence that the geology of the planet has evolved in response to enormous lithospheric stresses in the past. However, the active plate tectonics of the Earth that periodically recycle the crust of Earth and upper mantle are not seen on Mars. On Mars, therefore, water movement occurs within a mostly passive environment driven by gravitational and thermal forces, originating from the buildup of long-term tectonic stresses, seismic disturbances associated with earthquakes and infrequent large impact, long-term decline in global heat flow, and local thermal disturbances associated with magmatic activity and the impact melt generated by large impacts.

Other probable drives of groundwater movement include centripetal effects, which will be relatively greater on Mars than on Earth because of the lower gravity of Mars, and differences in groundwater composition, which can result in variations in density. For instance, CO_2-rich water can be as much as 2 to 3% heavier than pure water and will sink as a gravity mass whereas methane-rich water will be less dense and more buoyant. Diffusion forces will probably predominate, although local water percolation may occur, especially in association with the taproots and migration path of vent-related gas and water.

Hydrate is metastable, readily forming and decomposing as part of a highly reversible reaction. In a manner similar to the sublimation of ice, during which the solid ice yields a vapor phase to a gas envelope, hydrate may dissolve in the presence of water instead of forming gas. In a frozen zone, a transition from hydrate to ice and methane gas may occur, but this would be very slow and, without a gas reservoir being formed, the gas could not be generated abruptly enough to form a vent of the scale that has been recently observed. In the presence of water and methane gas, the growth dynamic for crystallization would cause hydrate to form. Hydrate only dissolves by diffusion when the vapor pressure of the methane in the hydrate is greater than the media with which it is in contact. As the vapor pressure at which gas forms from dissolved methane is greater than that of hydrate, no gas will evolve directly from hydrate. Gas does not form until the level of saturation in the aqueous phase rises above that required for hydrate formation.

Diffusion of methane molecules in either water or ice can drive hydrate formation, although the processes are somewhat different. Hydrate growth from solution is favored by percolation in which the fluids reach lower pressure zones while they cool. Fluid or gas flow has the capability to move methane most quickly, and is probably the mechanism that favors the methane penetrating the GHSZ, instead of forming hydrate.

ACCUMULATION AND TRAP

Hydrocarbons that are not mobilized from their source beds and have not successfully navigated a migration path to a trap are commonly not sufficiently concentrated to justify extraction. Shale gas on Earth is an example of an unconventional gas deposit that lateral drilling and fracturing have now rendered into recoverable deposits. A trap consists of a subsurface reservoir that has sufficient porosity and permeability to be suitable for containing hydrocarbons but which is also sealed by a relatively impermeable formation through which the hydrocarbons cannot easily escape. Sands and other sediments having good porosity and permeability typically serve as reservoirs. The porosity and permeability may be either primary or secondary. Sedimentary rocks are the most common reservoir rocks because they have more porosity and permeability than most igneous and metamorphic rocks, and they form under temperature conditions at which hydrocarbons may be preserved. Fine-grained rocks, however, typically have insufficient permeability to form effective reservoirs. A seal is a relatively impermeable rock, commonly shale, anhydrite, or salt that forms a barrier or a cap above and around a reservoir rock such that fluids cannot easily migrate beyond the reservoir.

Both relatively shallow methane hydrate and gas concentrations may be accessible from the Martian surface. The cryosphere is not cold enough to liquefy methane and no evidence of heavier hydrocarbon gases that might have been formed by thermogenic processes exists as yet. Hydrate deposits can only exist in the GHSZ, which is a zone extending downward from near the surface (Max and Clifford, 2000) to some depth determined by temperature and pressure. The gas deposits could exist in the surface-accessible cryosphere, but it would be more likely that initial gas deposits would have been converted to gas hydrate as the cryosphere conditions penetrated downward, especially where the methane was in contact with subjacent water (Max et al., 2006).

Significant differences in the tectonics and geology of Mars that almost certainly result in less varied subsurface conditions and more restricted opportunities for hydrocarbon generation than those that occur on Earth are observed. In particular, it is likely that little liquid hydrocarbon is, or has been, generated on Mars. The same general elements of a hydrocarbon system will apply on Mars (Figure 1). A deeper zone where temperature and pressure promote the production of gas is connected with migration paths from those depths into the upper reaches of the crust of the planet whose properties are dominated by the presence of a cryosphere. Large accumulations of methane are most likely to occur within or just below this frozen zone.

As on Earth, hydrate itself is both a reservoir and a trap. No geologic seal is necessary on the reservoir because the hydrate is a solid crystalline substance and not a gas or liquid that will migrate away. Once it is formed, and in the presence of sufficient hydrate forming gas in the surrounding media to resist its dissolving, hydrate itself creates an effective seal. This is the main difference from a petroleum system that requires a seal on the reservoir. Any suitable porous and permeable host rock that lies along a migration path for methane, especially where water is present, can serve as a host for the formation and storage of hydrate. Geologic data on the scale required to make any judgments of migration or reservoir character are yet to be acquired.

EXPLORATION FOR METHANE HYDRATE

A need to increase the success of exploration and to not only reduce costs but to develop a sustainable base of natural resources most quickly is observed. Exploration for methane hydrate and gas deposits on Mars can be conducted with the full panoply of exploration techniques used on Earth, many of which are suitable for autonomous or robotic use. In addition, because of the absence of near-surface liquid water and the extremely cold near-surface temperatures, some techniques, such as ground-penetrating radar (GPR), may be more useful on Mars than they are in all but a few areas of Earth. Extensive remote sensing and physical modeling to increase our understanding of subsurface conditions will promote the economy of exploration.

Major advances in our understanding of the sources, distribution, concentration, and dynamic behavior of atmospheric methane, as well as several other important atmospheric gases and photochemical by-products, are expected from the data that will be returned by the European Space Agency (ESA) ExoMars Trace Gas Orbiter mission, which is scheduled to fly in 2016. The distribution of these gases will be mapped with a detection sensitivity of 1 to 10 ppb (and as much as 1–10 parts per trillion for spot measurements taken during solar occultation), with a surface spatial resolution of approximately 1 m (~3 ft).

GEOLOGIC/HYDROGEOLOGIC ANALYSIS

In conventional petroleum system analysis, accumulations of different materials (water, oil, gas) separate and occupy different parts of traps. In a contiguous reservoir, gas will overlie oil, which overlies water. Water movement in porous beds provides the media from which gas and oil separate and then is mostly responsible for pressurizing reservoirs. Gravity is the driving mechanism, and buoyancy is the process by which hydrocarbon deposits form in traps. Groundwater generally occupies a complex system of porous beds or zones of both primary and secondary porosities that are generally interlinked.

Exceptions, where aquifers are isolated from neighboring systems, are generally rare, limited in areal extent, and not commonly associated with either hydrocarbon or mineral deposits.

As part of a general geologic modeling of a region in which hydrocarbon deposits are thought to exist from identification of source beds and appropriate thermal history, an appreciation of the hydrogeologic setting is critical to early exploration. Initially, this analysis involves the identification of porous strata or zones of significant secondary porosity in which groundwater and hydrocarbons may accumulate and be transported. In the second part of the analysis, these porous zones must be shown to be oriented so that fluids and gases can migrate upward into traps.

Hydrocarbon system analysis for hydrate (hydrate system) is fundamentally different in some important ways that reflect the essential nature of methane hydrates as solid, crystalline mineral deposits instead of as fluid and gas. Hydrates in high-grade mineral deposits appear to form most readily from slowly flowing or percolating water that is saturated to a level that allows hydrate to crystallize from it (Max et al., 2006). A porous bed or zone remains a focus of the hydrate system even more than in conventional hydrocarbon exploration. Whereas a conventional trap may contain economic hydrocarbons and the porosity may be decreased by secondary mineralization, the porosity of a zone associated with methane hydrate deposits will probably remain high because hydrate concentrations are typically associated with active groundwater systems.

The concentration of dissolved methane in growth media such as pore water solutions must be higher than the vapor pressure of methane in hydrate for methane hydrate to grow. If the vapor pressure of dissolved methane (its concentration) falls much below that which supports the existence of hydrate, the hydrate will dissolve. Therefore, continued supplies of high concentrations of dissolved methane in the pore water is the best way to insure the existence of a hydrate deposit in a porous zone open to source and to the surface. Where solid hydrate, ice, or other mineralization sufficiently tightens the porosity, however, methane can only move through solid diffusion processes, which are much slower. Hydrate in contact with a solid diffusion barrier may persist for considerable periods of time, without methane-saturated water in contact.

Hydrate system analysis, after hydrate provincing, focuses on identifying porous horizons or zones that can act as conduits for migrating pore water or gas having high concentrations of dissolved methane that migrates from a warmer area at depth to a colder area near the sea floor (in oceans on earth) or permafrost zones. Orientation of the porous zones is important if pore water has to pass upward into the zone of hydrate stability, but this may only be in the very end of the hydraulic pore water system in which hydraulic head may actually force fluids downward. The path of the migrating methane-rich pore water need not always have been generally upward, depending on several factors. Pore water moves because of recharge overpressures that are generally driven from depth. Water movement may be part of an artesian system, dewatering of packing sediment, driven by heating by igneous rocks, or induced by tectonics. Water movement may also be driven by dissociating gas hydrate, as has been suggested for driving subsurface water to the surface of Mars (Max and Clifford, 2001).

Hydrate system analysis puts most emphasis on porous beds and zones and groundwater movement. The actual formation of the hydrate may be viewed as merely the final component of the process of forming hydrate concentrations. Methane hydrate may occur anywhere in a GHSZ. The hydrate concentration is simply the location of the crystallization of hydrate from solution. The results of the drilling program on the Cascadia margin of North America (Tréhu et al., 2004) show hydrate concentrations occurring at multiple levels within the GHSZ, but always in association with a porous horizon that would sustain relatively high water movement. Tracking methane source to hydrate concentration is a fundamental aim of hydrate exploration on Earth or in the subsurface of any planet or moon. Whereas hydrate concentrations on Earth are dynamic and currently active, relict hydrate systems and concentrations may occur elsewhere in the solar system, where they would represent the presence of one-time dynamic hydrate systems.

BASIN ANALYSIS

Strictly speaking, no recognized Martian analogs to the many depositional basins of Earth, which are the result of tectonic activity and abrupt weathering associated with the continuous action of weathering and erosion, exist. However, certain areas of Mars are known to contain laminated sedimentary material to considerable depths, whereas an ocean may have once occupied the northern plains and a large sea may have occupied the interior of the Hellas impact basin. Where the putative ocean was adjacent to the southern highlands, considerable erosion and sedimentary deposition may have occurred in the early history of Mars when liquid water may have been stable on its surface. Secondary porosity in Martian strata may be formed from impact activity that is not reannealed over time by active tectonism and plate tectonics. In addition, extensional tectonic activity created Valles Marineris and its associated chasmata, some of which have trapped many kilometers of layered sediments within their interiors. Such basins have no known counterpart on Earth.

GEOPHYSICAL EVALUATION

Reflection and refraction seismic exploration could be conducted on Mars as it is on Earth, with human participation on the ground. At present, relatively simple robotic apparatus is having spectacular success in revealing the near-surface geologic history of Mars. More complex robots will be able to attack the issues of revealing subsurface geology. Seismic exploration offers the opportunity not only for resolving reflectors defined by the reflection coefficient of sure-wave velocity differences, but also for determining both pressure-wave velocities that depend on bulk modulus and shear velocities that depend on shear modulus, as well as attenuation characteristics. Data of this type can be used to infer subsurface lithology, stratigraphy, porosity, and perhaps permeability, and other factors that could control the existence of methane deposits. A great inventory of analyses and successful techniques, particularly in permafrost areas, that can be applied directly to seismic interpretation on Mars is observed.

Techniques that are analogous to Martian conditions have been developed for sea-floor seismic data acquisition in which sea-floor geophone arrays are used to determine the fine-scale response of subsea-floor materials. In this type of work, no human hand is directly applied to the laying out of the geophone string. In particular, techniques for coupling geophones to the sediment (Caiti et al., 1995) can be applied to the autonomous deployment of geophone arrays on Mars. Several methods for moving geophone arrays, using more than one array to provide three-dimensional subsurface information, and optimizing location of both sources and receiver arrays can be proposed because of the relatively benign surface, atmospheric, and weather conditions of Mars. It is envisaged that seismic analysis, for both reflection (including interval velocity analysis) and refraction, will provide the basic subsurface information for the disposition of geologic and material elements in any hydrocarbon exploration.

DRILLING

Drilling is one sure way to reach the subsurface to identify its composition by sampling and downhole logging techniques. Autonomous drilling and coring of at least short boreholes have been proven on Earth sea floors — an exploration technique that could readily be adapted to the special conditions of the surface of Mars. The first attempt to conduct such an investigation will be made by the ExoMars rover of ESA, which is scheduled to fly in 2018 with a payload that includes a GPR and a 2 m (7 ft) drill.

GROUND-PENETRATING RADAR

Radar is an increasingly important tool in the investigation of a wide range of solar system objects and is particularly well suited to the investigation of ice-rich (and, thus, dielectrically low-loss) environments, such as the Martian polar layered deposits, the icy satellites of the outer planets, and comets. The Mars Advanced Radar for Subsurface and Ionosphere Sounding (MARSIS) (Picardi et al., 2005) and Shallow Subsurface Radar (SHARAD) (Seu et al., 2007) radar sounding investigations of Mars, conducted from the Mars Express and Mars Reconnaissance Orbiter spacecraft, have resolved details of subsurface structure ranging from depths of hundreds of meters (Campbell et al., 2008; Phillips et al., 2008) up to several kilometers (Picardi et al., 2005; Watters et al., 2007; White et al., 2009). These orbital investigations have been conducted over a frequency range of approximately 2 to 5 MHz (MARSIS) and 15 to 25 MHz (SHARAD), yielding in-ground vertical spatial resolutions of approximately 20 to 100 m (~70–300 ft). The next radar that will be sent to Mars will be the Water Ice Subsurface Deposit Observation on Mars (WISDOM) GPR on the 2016 ExoMars mission of ESA (Ciarletti et al., 2009). The WISDOM has an operational frequency range of 0.5 to 3 GHz and is expected to achieve maximum penetration depths of up to several meters with a best vertical resolution of as little as several centimeters. Together, these three instruments offer the opportunity to investigate and characterize the lithologic and structural properties of the subsurface, over a wide range of depths, by their electromagnetic reflection and attenuation properties.

For a radar pulse reaching the boundary between two materials of differing dielectric properties, a part of the incident energy is reflected back, whereas the remainder continues to propagate into the subsurface, in a manner similar to that of acoustic propagation. Additional losses can be caused by scatter and absorption. As successive dielectric interfaces are encountered, the signal suffers additional reflections and losses, until its strength is attenuated so that the reflected energy is less than the ambient noise. Neither refraction studies nor interval velocity studies can be undertaken with GPR from an orbiting satellite, although both reflection structure and attenuation may be determined using GPR.

Water and gas hydrate differ from each other in their structure in one major way, apart from their different crystal structures (ice is hexagonal whereas methane hydrate is cubic). Water ice is monomolecular, being composed of water molecules, apart from any included material such as rock dust and larger particles. Hydrates are container compounds that are composed of water molecules disposed in a cage structure that is stabilized by a gas molecule within the void, the entire of which is stabilized by van der Waals weak electrical bonding. From core analyses of ice and CH_4 samples on Earth, it is known that the attenuation in hydrate is higher than in ice (Guerin et al., 1999), and it is likely that the same condition pertains on other bodies in the solar system. If the attenuation effect can be calibrated closely enough, it may be possible to distinguish between subsurface CH_4 and CO_2 hydrate using a yet undefined processing technique using GPR or seismic data.

HYDRATE AND GAS LOCALIZATION IMPACT ON EXPLORATION

1) Migration may be offset laterally by dipping porous strata or secondary porosity zones in a structural framework quite different from that of Earth. Because plate tectonics is not active on Mars, explorationists must be ready to identify new source, migration, and localization paradigms.
2) Hydrate deposits may not lie immediately below vent sites if the local geothermal gradients are steep enough, although gas deposits may occur. Vents characteristically tap fluids and gases from beneath the GHSZ, which pass upward through the zone without necessarily forming hydrate. Cooler porous beds, adjacent to the vents, could host both gas and hydrate.
3) Hydrate deposits can occur anywhere in the GHSZ as can gas that has migrated into the cryosphere, especially where the porosity is not yet saturated with ice. Methane deposits depend on the flux of gas (and possibly fluid) into the most porous and permeable zones and are not directly related to the distance from the BGHSZ. The high concentrations of hydrate that occur immediately above the BGHSZ in locations such as the Blake Ridge area of the United States East Coast continental margin are the result of a diffusion model that applies to muddy, poorly bed-differentiated sediments. Similar sediments are not likely to be found on Mars.
4) Methane hydrate formation can be of longstanding character. If the gas supply remains sufficient, the hydrate will reside in place for long periods of time. It is not known how shallow near-surface hydrate deposits can be found away from the vicinity of the Martian vents. However, the possibility exists that both methane and hydrate deposits may occur at shallow depths on Mars, reflecting a former location of the BGHSZ as the phase boundary propagated deeper into the crust of the planet in response to the decline in planetary heat flow.
5) Development of new remote signal analysis methods for distinguishing water, ice, and methane hydrate from each other using GPR radar and seismic acquisition should be attempted.

THE MARTIAN NATURAL GAS PLAY

The subsurface conditions anticipated on Mars have important implications for the generation of methane and its sequestration within the region extending from the shallow cryosphere to immediately beneath the hydrate stability zone. If sufficient deposits of these compounds can be found on Mars, they could be used to fabricate virtually everything necessary to support human habitation. In this way, Mars might also serve as a stepping stone for the human exploration of the rest of the solar system, providing access to the additional resources present on other planets, moons, asteroids, and comets. In this context, the presence of methane hydrate on Mars may provide one of the resource cornerstones for human exploration and sustainability.

The venting indicates that significant amounts of gas exist on Mars. The reservoir from which this venting occurs is almost certainly larger than the reservoirs are on Earth. The energy and material content of the observed gas provides a baseline or floor for the subjacent gas resource. Within a single Martian plume, approximately 1 billion standard ft^3 of methane has been observed (Mumma et al., 2009), potentially providing the feedstock necessary to produce the energy equivalent of approximately 13,200 barrels ($\sim$950,000 Btu/ft^3) of jet or diesel fuel (assuming an average composition of $C_{12}H_{23}$ and 0.84 kg/L density for diesel fuel). In the process of making this amount of fuel, large amounts of hydrogen (2.65×10^9 kg) would also be released. The reactions necessary to accomplish the conversion of basic feedstock into useful fuels and products require multiple steps that may tie up the hydrogen in other types of compounds instead of being available for use in its own right. We have not modeled this in detail because a full engineering solution would require consideration of the energy consumed in the production and manufacturing process. These numbers are estimates only, based on averages and recognition that diesel fuel is a mixture of hydrocarbon chemicals. This same amount of methane, combined with other more readily available materials, could also be used to fabricate tons of plastic, depending on its type.

Although the volume of methane venting from the reservoir is large enough to produce a large volume and a wide array of useful materials, the most important aspect of the scale of the venting is what it indicates about the likely size of the reservoir that still resides beneath the Martian surface. As on Earth, only a relatively small amount of a natural resource, such as methane, may be present in sufficient concentration to make extraction a useful or profitable exercise. Exploration based on hydrocarbon system analysis is the key to the identification of economic energy and other resources. Once these assessments are made, the necessary recovery systems can be developed, such as those used to access unconventional gas deposits on Earth, such as coalbed methane and shale gas.

BEYOND MARS: A HYDROCARBON KEY TO THE HUMAN EXPLORATION OF THE SOLAR SYSTEM

Hydrocarbons in the solar system are important for human exploration and habitation because they will provide essential high energy-density fuels, and feedstock for plastics from which buildings, implements, transportation systems, and other manufactured goods can be produced, as they presently do on Earth.

Arguably, the knowledge base of the hydrocarbon and chemical industries on Earth, which know how to find and process natural resources, forms the basis for industrialization on Mars. Existing technology is probably already able to deal with many of the Martian challenges inherent in off-Earth sustainable exploration.

The large icy moons of the outer planets (especially Europa, Callisto, Ganymede, and Enceladus) may all possess mantle oceans, covered by icy crusts many kilometers to tens of kilometers thick; Tethys, Dione, Rhea, Mimas, and Iapetus also exhibit evidence that they may now possess, or at some time in the past, have possessed similar subsurface oceans. Methane is also known to exist on some of these icy bodies. Where an ice-covered ocean may exist on one of these bodies, the zone of hydrate stability will straddle the lower part of the ice zone and extend into the ocean beneath it for a distance determined by the local hydrothermal and/or geothermal gradient. An ocean heated from below, however, may have significant overturn zones and complex water movements that could locally control methane gas hydrate and ice thickness.

Until we began the active exploration of our solar system with robotic spacecraft, it was expected that the major planets and moons consisted of essentially three types of bodies: the rocky terrestrial planets of the inner solar system, the four large gas giants of the outer solar system, and their large retinue of icy moons associated with the gas giants (a class that also included Pluto and Charon). The astounding dissimilarity of the planets and moons of bodies in the solar system that were once thought to be similar instead, however, has essentially destroyed the old concept that planets and moons except for Earth were essentially dead and were probably resource poor, except for the possibility of metals and rare elements. The concept for human exploration beyond the Moon has been mostly based on the concept that Earth will have to provide the bulk of the logistics necessary to support human life throughout the course of the exploration. In other words, water, food, and fuel for each entire two-way trip would have to be provided at the outset. This places a heavy logistical demand upon any operation, and hence, the concept of human exploration of the solar system has not been seriously considered since the close of the Apollo program.

Using the natural resources of Mars will inevitably result in lower costs for supporting human exploration there than if we had to rely on transporting those same resources from Earth. In fact, the availability of these natural resources may prove to be the critical enabling factor for the continued human exploration of the solar system.

The identification of substantial reservoirs of water and hydrocarbons on Mars, as well as on the moons of Jupiter and Saturn, means that the old paradigm of a resource-poor solar system is no longer valid. Instead, we have the foundations of a new and more dynamic paradigm, based on the knowledge that these bodies possess the natural resources to support and sustain the human exploration and settlement of space so that no destination in the solar system is beyond our reach.

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