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METHANE HYDRATE ON MARS; A RESOURCE-RICH STEPPING STONE TO THE OUTER PLANETS?

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ABSTRACT

The recent detection of plumes of seasonal methane venting into the Martian atmosphere indicates the likely presence of a significant subjacent gas resource. The venting of methane requires a deep, long-term source that, whether originating from biogenic or abiogenic processes, appears to require the existence of an aqueous environment at depth. This methane may reside within and beneath the Martian cryosphere as natural gas hydrate within the hydrate stability zone. Shallower deposits may be easily accessible from the surface. An accessible natural gas hydrate resource would provide the basis for the production of high density liquid fuels and serve as a chemical industry feedstock for constructing facilities and products from local Martian resources. A resource-rich Mars, based on indigenous methane hydrate, water, CO_2, and minable minerals, would make Mars and its moons an ideal base for the exploration of the outer solar system.

Keywords: gas hydrates, Mars, solar system, human space exploration, resources, space flight

NOMENCLATURE

Cryosphere: frozen ground.
NGH: Natural gas hydrate.
HNG: Hydrate natural gas is gas produced from converted hydrate.
GHSZ: Gas hydrate stability zone
BGHSZ: Base of GHSZ

INTRODUCTION

Despite the best efforts of a number of authors to give Mars a human-like, if somewhat threatening personality, from the time of the first spacecraft flyby of Mars in 1965 until the late 1970s, Mars has been characterized as a resource-poor planet. The thin CO_2 atmosphere and numerous craters made it seem more closely related to the Moon than the Earth [1]. Until the active exploration of our Solar System beyond the Moon began, using robotic spacecraft, it was thought that the major planets and moons consisted of only three main types of bodies: the rocky terrestrial planets of the inner solar system and asteroid belt, the four large gas giants of the outer solar system, and a large retinue of icy moons and small bodies, a class that also includes comets, Europa, Ganymede, Callisto, Titan, Triton Pluto (which is no longer considered

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a planet) and its moon Charon – along with a host of intermediate objects. Modern robotic exploration has brought us an extraordinary picture of our Solar System. There is an astounding variety of planets, moons and small bodies, all of whom were once thought to be rather similar. Although the information returned by a host of robotic spacecraft has essentially disproved the old concept of a dead and resource-poor Solar System, the planning for the human exploration of space still appears to be constrained by decision makers mired in this outdated paradigm.

The concept for human exploration beyond the Moon has been largely based on the concept that -- with the exception of water ice, some metals (e.g., nickel and iron) and a few rare elements -- Earth would have to provide the bulk of the resources needed to explore the Solar System – including food, oxygen, the fuel for the outbound and return trips, as well as everything else needed to establish and maintain a base on a moon or plane. This paradigm places a heavy logistical demand and cost on any human exploration initiative, precluding any serious consideration since the close of the Apollo program.

More recent spacecraft investigations have dramatically changed this view. Although, at first glance, the surface of Mars appears barren, remote sensing information from orbital spacecraft and in-situ investigations by both fixed landers and rovers has revealed a geologically active surface that has been modified by the effects of volcanism, impact cratering, fluvial erosion, periglacial processes, tectonics, chemical weathering and quasi-periodic climate change. Evidence of these processes ranges from the presence of the largest volcanoes, impact basins, dry river beds, and canyon in the Solar System, to the presence of large dune fields debris-covered glaciers, and gullied slopes that may reflect erosion by the flow of liquid water in the geologically recent past..

In addition, large amount of water ice, mixed with a small amount of entrained dust, are present at both poles as extensive (~1000 km diameter) layered deposits as much as ~3-4 km deep [2]. There is also geophysical evidence that ice is widespread in the shallow (top meter) subsurface at mid- to high-latitudes [3] and also possibly present at slightly greater depths where nutron activation will not reveal its presence, even near the equator [4].

It is now known that considerable natural resources, including accessible hydrocarbons, exploitable concentrations of minerals and metals, and abundant water, exist not only on Mars but elsewhere in the Solar System. Is it not then time that knowledge of these resources be factored into the exploration in the Solar System?

GEOLOGICAL EPOCHS OF MARS

The density of impact craters on the Martian surface has been used to define a geochronological time scale for Mars, with the most heavily cratered terrain believed to date back to >4 by. This timescale has been divided into three geological epochs, named after the locations on Mars that are most representative of this kind of surface. The precise timing of these epochs is not known, but has been estimated based on comparisons with the crater densities observed on the Moon, which have been determined by the isotopic dating of samples that were returned by the Apollo astronauts. Therefore, the following dates are approximate.

Amazonian epoch (named after Amazonis Planitia) (3000 my to present):. Characterized by the lowest density of impact craters found on the planet; including sedimentary (primarily Aeolian), volcanic and fluvial landforms, as well as the polar ice deposits..

Hesperian epoch (named after Hesperia Planum) (from 3700 to 3000 my ago): Characterized by extensive volcanic plains and areas of erosion, interpreted to be the result of catastrophic floods resulting from the discharge of subpermafrost groundwater.

Noachian epoch (named after Noachis Terra) (from before -4500 to -3700 my): Inferred age of the oldest, most heavily cratered surfaces on Mars, including the very largest impact basins, which are >100 km in diameter.. These terrains are often dissected by integrated networks of small valleys, resembling terrestrial runoff channels, that may have been formed by rainfall associated with the existence of a massive early greenhouse atmosphere and climate..

For most of its history, from about the end of the Noachian, the surface of Mars appears to have been frozen [5]. However, we know virtually nothing about the time of the initial onset of subfreezing conditions, the rate of cooling, or the time at which the depth of the cryosphere grew sufficiently great that climatic variations in surface temperature were effectively damped out.

NGH

Natural gas hydrate (NGH) is unique among gas resources because in its natural state it is a solid crystalline material. Especially in permafrost hydrate, NGH will have the character of some mineral deposits. NGH is comprised of cage structures of water molecules having gas molecules within the voids, made stable in the crystalline structure by the weak electrical van der Waals force. Naturally occurring gas hydrate on Earth is composed of mainly biogenic methane, with some higher density hydrocarbon gases where thermogenic gas is part of the leaky gas system. Formation of gas hydrate compresses gas within the hydrate crystalline structure with a compression factor of about 164 (for methane), as the gas molecules are held closely together in the crystalline structure. NGH fills porosity by reacting with either water or water-ice.

NGH forms spontaneously when certain gases contact water under suitable conditions of pressure, temperature and concentration. Once gas hydrate has formed, it is stable within its field of pressure and temperature so long as gas flux remains sufficiently high in its immediate media. NGH is a transitory mineral deposit that forms in a highly reversible reaction that can cause the hydrate to dissolve or dissociate almost as rapidly as it can form.

ICE CRYOSPHERE AND GHSZ ON MARS

The NGH on Mars will be similar in its expression to permafrost hydrate on Earth in that it occurs in frozen ground, but it's origin may be very different owing to the different geological and climate histories of Earth and Mars. On Earth, permafrost is restricted to polar latitudes and high altitude (or 'Alpine' permafrost [6]). Permafrost regions enlarge during glacial maximums and become smaller during interglacials, although near the end of the Proterozoic, a freeze-up of the entire of the Earth's surface may have taken place. The important lesson from Earth's history of glacial episodes is that the oceans have been important buffers of the Earth's climate and that astronomical controls such as changes in the planet's orbital eccentricity and axial inclination, solar output, and other factors can cause the onset and decline of glaciation and the waxing and waning of the aerial distribution of frozen ground.

NGH is stable in the subsurface within a region of appropriate temperature and pressure called the gas hydrate stability zone (GHSZ) which occurs in both permafrost and some areas of the Earth's ocean floor. In both types of deposit, hydrate is most stable and has the highest driving force of crystallization near its uppermost contact with the cold atmosphere or deep ocean water. Within these regions, NGH and water ice form a compound cryogenic zone (cryosphere) 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. The GHSZ occurs within the region of the crust determined by these conditions, below which methane persists solely as a gas.

Current mean annual surface temperatures on Mars are well below freezing (ranging from ~154 K at the poles to ~218 K at the equator). At the 200 K average surface temperature of Mars, methane hydrate is not stable at a confining pressure of less than ~140 kPa [7], corresponding to the lithostatic pressure at a depth of ~15 m in. This depth defines the top of the Martian gas hydrate stability zone. At the colder temperatures characteristic of latitudes >60°, it may be found at shallower depths [8].

The stability field of methane hydrate is imperfectly known at the ~200 K average surface temperature of Mars because of the uncertainty in the effective pore and lithostatic pressure at depth. In addition, because of the low chemical potential of the hydrate reaction at low temperatures, laboratory measurements of NGH stability are very limited. Thus, on Mars, the depth of the top of the GHSZ may be anywhere from 15-30 m deep – or effectively at the surface at the scale of Fig. 1. In contrast, on Earth, with its higher mean annual surface temperatures, NGH is only stable below about 200 m [9].

In contrast, the base of the GHSZ (or BGHSZ) on Earth is only on the order of 1100 m [10] but on Mars it is much deeper, due to the much colder mean annual surface temperatures and the expected smaller geothermal gradient. Based on an estimated geothermal heat flux of ~15-30 mW m^2 and a reasonable estimates of the thermal conductivity of the crust (~2-3 W m^{-1} K^{-1}), the base of the GHSZ is expected to lie at a depth of from ~5-10 km at the equator, to ~12-24 km at the poles (Fig. 1, [10]). This suggests that if groundwater currently survives on the planet, it would be restricted to depths of greater than 5 km at the equator and >12 km at the poles)

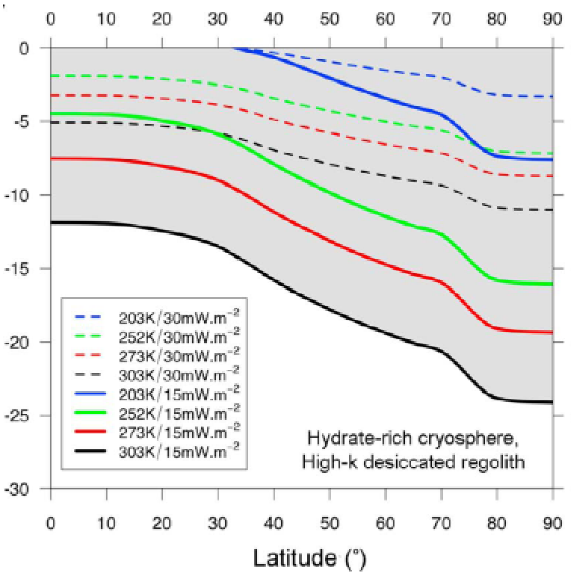

Figure 1. Schematic diagram of a GHSZ for Mars, illustrating the relative positions of the base of the water ice cryosphere (dashed line) and gas hydrate stability zone (solid line) for a mean global geothermal heat flux of ~15-30 mW m^2. Figure after [9].

However, natural variations in crustal thermal conductivity, heat flow, and the local concentration of potent freezing point depressing salts, such as $CaCl_2$ and $Mg(ClO_4)$, may result in significant local departures from these depths. For instance, at the potential freezing point of highly mineralized and saline groundwater (203 - 273 K), the current thickness of frozen ground on Mars may be reduced to as little as 0 km at the equator and ~6 km at the poles [10], Additionally, high salt or soluble ionic chemicals content in the shallow soil would likely act as an inhibitor, slightly depressing the top of the GHSZ.

While the thickness of the GHSZ can be estimated based on geologically reasonable assumptions, the extent to which this stability zone is actually populated with hydrate or water ice is unknown.

As with a water ice cryosphere, the extent of the methane hydrate stability zone will wax and wane in response to climatic variations in mean annual surface temperature, until the planet's geothermal heat flux has fallen to the point where the depth to the BGHSZ exceeds that at which the climate signal damps to zero [10].

WATER AND RAW MATERIALS ON MARS

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 [11] [12]. These are enormous scoured depressions, tens of kilometers wide, hundreds of kilometers long, and up to 1-2 km deep, that generally emanate from localized regions of collapsed and disrupted terrain.The scale of the braided and streamlined forms found within the channel beds, combined with the absence of any identifiable tributaries, indicate an origin by catastrophic floods, apparently fed by the artesian discharge of subpermafrost groundwater under high hydraulic pressure [11] [13]. [14] have suggested that water and gas derived from the decomposition of NGH may have been responsible for the generation of these high pressures and the consequent disruption of the cryosphere and discharge of groundwater, representing a gas-water blowout.

Theoretical models of the geothermal evolution of Mars suggest that the planet's heat flux was substantially higher in the past [15], having been as much as 5 to 6 time greater 4 billion years ago than it is today. Assuming the present range of mean annual surface temperatures, this implies a proportionately thinner cryosphere. In response to the subsequent decline in planetary heat flow, the freezing front at the base of the cryosphere propagated downward with time -- creating a cold-trap for subsurface water [16]. As a result, the cryosphere is expected to be ice-rich, a belief that is supported by the geomorphic interpretation of a wide variety of surface features, many of which resemble cold-climate features found on Earth [17] [18].

The depth to which significant porosity, permeability, and water persist on Mars is unknown. However, in light of the considerable extent to which impacts, volcanism, tectonics, and the presence of abundant water have affected the evolution of its surface, it is likely that the gross physical and hydraulic properties of the Martian crust will closely resemble those found on Earth – appropriately scaled to reflect the gravitationally induced differences in lithostatic pressure at a given depth. This suggests that the porosity and permeability conditions characteristic of the top 10 km of the Earth's crust may persist to depths as much as ~2 to 3 times greater on Mars. Thus, the potential depth and hydraulic complexity of a subpermafrost hydrosphere on Mars is likely to be substantial. 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 ~0.5 to ~1 km deep [11] [12].

Diagenetic mineralization in sediments concentrates chemicals that may be useful. The discovery of hematite and jarosite by the Opportunity rover, and goethite by the Spirit rover on Mars has led to the conclusion that atmospheric and climatic conditions in the distant past were sufficient to allow liquid water to survive on the surface, which enabled these minerals to form.

The growing evidence for abundant water and the in situ and remote detection of evaporites (such as sulfates, gypsum, carbonate, and various salts [19]), metals (Fe, Mg, Ti, Na and Al), and, most recently, atmospheric methane [20] [21] [22] [23] [24], 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 utilized to support and expand the human exploration of Mars and beyond.

DEEP BIOSPHERE ON MARS?

Mars has an average surface temperature of ~200 K, a CO_2 atmosphere with a surface pressure of ~6 mb, and a high incident flux of UVB. Thus, the present Martian surface environment is hostile to life as we know it. However, there is abundant evidence that conditions on Mars were substantially different in the past. Evidence for past water is widespread, including now dry outflow channels that converge in the planet's northern plains where the tentative identification of paleo-shorelines suggests a former sea or ocean may have once resided [12] [25]. Additional evidence is provided by the presence of valley networks throughout much of the planet's Noachtian terrain – features which are potentially indicative of rainfall associated with an early, more Earth-like past climate.

While the exact nature and genesis of the early Martian climate is uncertain, there is considerable evidence that the early terrestrial and Martian environments shared a number of similarities that may have aided the in situ synthesis of prebiotic and organic molecules. It was during this time that there could have been an emergence of life similar to the early life on Earth. The presence of abundant water, combined with the occurrence of extensive volcanism and the production of large volumes of impact melt, created an environment where hydrothermal activity was likely pervasive [26]. If such conditions gave rise to life on Mars, then it is possible that during the transition to a colder surface environment, this early life adapted to a subterranean existence where warmer temperatures and groundwater may have enabled it to persist to the present day [27]. The existence of a warm, subsurface aqueous environment is supported by the inferred age and origin of the Martian outflow channels and the mineralogical evidence of hydrous mineral deposition and alteration.

METHANE IN SUBSURFACE MARS

[20] [21] [23] [24] have reported spectroscopic observations of the seasonal emissions of atmospheric methane on Mars which they infer is vented from localized subsurface sources (which, for simplicity, we have illustrated as a single vertical system in Fig. 2).

On Earth, the conditions necessary for the formation of hydrates are found at depth in permafrost and in the seafloor sediments of continental margins. The isotopic composition of marine methane hydrate, at least that which is found along the tectonically passive eastern margin of North America, provides evidence that the bulk of marine methane is produced by an active community of anaerobic methanogenic bacteria in the sediments beneath the GHSZ [28]. Additional methane may result from thermal decomposition of older hydrocarbon deposits present in active continental margins and accretionary prisms that have no analogue on Mars.

The Martian valley networks provide evidence that Mars may have once possessed a warmer, wetter climate, conducive to the origin of life. 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 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 [27]; [29] [30]. If so, it may have produced comparable quantities of methane [31] [32].

Methane may have also been produced abiogenically, as a fractionation product of magma crystallization or by reactions with basalt or carbonate in subpermafrost aquifers – yielding local partial pressures ranging from ~0.2 to many bars, depending on the availability of carbon [33] [34] [35]. 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 crustal pores in concentrations that may have ranged from dispersed microcrystals to fully saturating the available porosity [32].

It is likely that the vents are associated with local faults or joint systems, which may provide conduits to the surface from subjacent reservoirs of methane gas (Fig. 2).

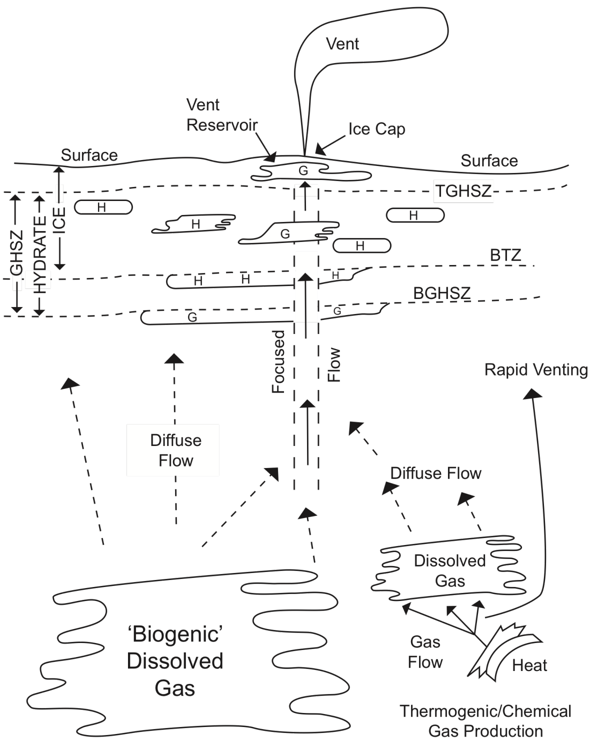

Figure 2. Schematic diagram of the methane production system at depth with venting at surface through GHSZ and ice cryosphere.

In such a leaky system, methane gas migrates upward slowly and irregularly, due to 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. Gas produced over a large area is initially diffuse, but as it concentrates, its flow becomes more focused (Fig. 2)

VENTING AND THE SUBJACENT GAS/HNG RESERVOIRS

Because the methane venting on Mars is seasonal in nature [24], 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 of the surface in order 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 [32]. 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} [24], it is unlikely that it results from the dissociation of gas hydrate due to seasonal warming. The thermodynamics of the GHSZ are such that hydrate is most stable near the surface and least stable near its base [36]. But 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 >105 yrs) and would take ~106 yrs to propagate down to the BGHSZ. Even such dramatic 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.

POTENTIAL IMPACT OF VENTING ON THE ICE BASE AND THE BGHSZ ON MARS

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 (Fig. 3). The vents may be rooted in tectonic faults, fractures, or some type of geothermal anomalies, perhaps associated with deep magma chambers or igneous intrusions.

On Earth, such as in the northern Gulf of Mexico, methane vent sites are common and a few have been extensively studied as part of an assessment of associated ecosystems along with natural gas resources that utilized seismic data, seafloor sampling, drilling, and heatflow measurements, as well as measurements of the temperature and composition of the vent fluids [9].

On Earth, in regions where the GHSZ exhibits an otherwise uniform thickness, the focused upward flow of relatively warmer gas and fluid from depth introduces heat into the region surrounding the vent. This causes a local thermal anomaly 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 (Fig. 3). This updoming of the base of the gas hydrate stability zone (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 venting. The upwarping effect on Mars is unlikely to be as dramatic as the steep upwarping of the BGHSZ in Earth's marine sediments 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. Seafloor venting on Earth is usually transitory in nature because of sedimentation and compaction. Vent systems on Mars may be much more long-lived as the fracture systems the venting is related to are liable to be much more stable. Thus, even though the instantaneous thermal effect of upward movement of warm, wet gas will have a lesser effect than in an Earth oceanic vent system, its much more long-standing nature could generate a comparable upwarping of the base of the cryosphere and BGHSZ over time.

Upwarping of the BGHSZ will depend on the longevity of the vent, the proportion of vented gas to 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 3).

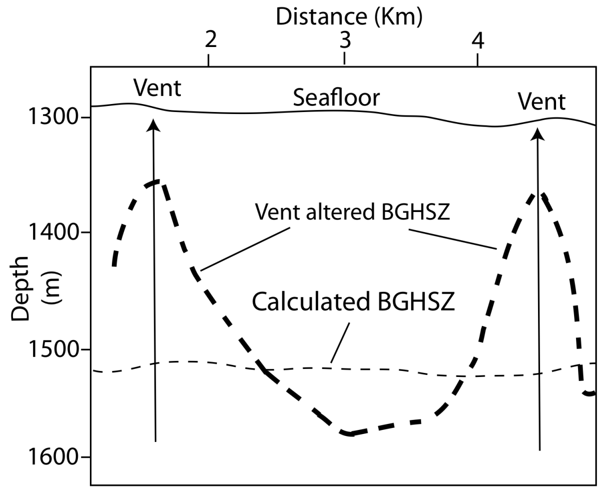

Figure 3 Schematic diagram of the vent-related alteration of the BGHSZ. Redrawn from Figure 4.17 [9] based on USGS Seismic Line shown there in more detail.

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.

HYDRATE PETROLEUM SYSTEM ANALYSIS FOR MARS

The physical and chemical controls governing hydrate formation on Mars, and other bodies in the solar system, are the same as on Earth, although there are individual differences arising from variations in upper crustal and atmospheric composition, environmental conditions, and depositional and erosive environments. Nonetheless, the basic principles of hydrocarbon system analysis apply broadly, and understanding the entire methane system on Mars will be the key to identifying potentially recoverable NGH deposits. In this respect, the Martian methane vents can be considered analogs of the natural oil seeps on Earth that led to the original exploitation of Earth's hydrocarbon resources. On Earth, petroleum system analysis is used as an integrated framework to guide oil and gas exploration, particularly in early stage assessment. On Mars, a special petroleum system analysis for a newly recognized type of NGH deposit can be used.

How and where hydrocarbons are generated, how they migrate, and how they are trapped in a concentration so that they can be economically extracted, are the basis of hydrocarbon exploration. On Earth, petroleum system analysis has been used to identify those regions where exploration for hydrocarbon deposits is most likely to achieve success. The critical elements of a conventional petroleum system consist of: 1) mature source rock that generates hydrocarbons, 2) migration pathways, 3) reservoir, and 4) a trap and seal that prevents further movement of the concentrating hydrocarbons.

Because the rock and sedimentary environments in which a conventional petroleum system exists evolve with time, the relative timing of petroleum system elements is important. For instance, the chemical or biological generation of a large volume of gas in the deep subsurface may be of little consequence if there is no migration path to reservoir rocks at more accessible depths. Modern exceptions of this are unconventional shale gas and coal gas deposits, in which the gas (and oil in oil shale) does not appear to have migrated from its source beds. Likewise, a high capacity reservoir is useless without a cap and seal and a reservoir with good trap and seal but without any hydrocarbons having migrated into it is of no value. But in a conventional petroleum system, generation, migration, concentration, and secure storage all play a role in determining the viability of economic recovery. In a conventional hydrocarbon occurrence, once the hydrocarbons have been trapped, they may persist for a very long time, although some degradation or leakage may take place.

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, shale gas, coalbed methane, structural and stratigraphic traps, hydraulic down-dip traps, etc., 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. Hydrate plays on Earth are described and characterized in [9] [36] along with a new type of hydrate occurrence that has not yet been evaluated for its economic potential [6].

The physical chemistry, paragenesis, and behavior of the NGH system is well understood and can be expected to function in the same way on both Earth and Mars, as well as through the solar system and more widely. A principal attribute of NGH deposits is that they can build up slowly over a long period of time or they can form relatively fast in geological time. The interaction of other hydrate-forming gases with methane in hydrate formation is unlikely to be of much significance on Mars, although it may be important on other bodies in the solar system, such as Titan, where hydrate formation and decomposition may be an important factor in controlling climate [37]. Thus, understanding hydrate processes is important as they can be used to make a number of inferences about the state of subsurface Mars and its hydrate forming potential.

Because weathering, erosion, and other geological processes that produce, transport, and deposit high-porosity, permeable sediments have been so much less active on Mars than they are on Earth, similar reservoir rocks probably do not exist in abundance on Mars. In contrast to the Earth, where sedimentary processes dominate land areas and continental flanks, the geologic history of Mars appears to have been dominated by basaltic volcanism, impacts, and relatively minor tectonic activity in response to crustal loading. Martian geotectonics are believed to have contributed to extensive crustal fracturing, with little geothermally-induced annealing. The extent of precipitation of dissolved minerals is completely unknown. Thus, the geology of Mars may naturally favor the formation of NGH deposits in fracture zones, in contrast to its common occurrence in permeable strata on Earth.

SHALLOW NGH DEPOSITS?

The fundamental issue is not whether hydrate occurs on Mars or not (as methane appears to be venting through the cryosphere, hydrate formation would be difficult to avoid) but whether it is sufficiently concentrated and accessible from the surface to be economically recoverable. Although the hydrate on Mars may provide evidence of a deep biosphere and buffer the release of methane to the atmosphere (moderating its impact on the global climate) as it does on Earth, its greatest significance to the human exploration of Mars and destinations beyond may ultimately be more practical than scientific.

On Earth, the cryosphere is relatively thin compared to estimates of its current thickness on Mars -- and subpermafrost groundwater is generally abundant. On Mars, however, the ice saturation state of the cryosphere is unknown, as is the amount of water beneath it. Although the Martian outflow channels provide persuasive evidence that water was abundant in the past [11],, at a time when the cryosphere was thinner. The amount could survive today is unknown.

Methane production, by either biotic or abiotic processes, requires the presence of liquid water, whether pore filling or merely adsorbed on mineral surfaces. Martian crustal faults and fractures are believed to persist to great depth (i.e., well-below the inferred maximum depth of the Martian cryosphere), providing diffusive pathways for the upward migration of methane, sourced from even greater depth. At the depth where the methane is being produced, therefore, some liquid water almost certainly exists.

Within the near-subsurface, hydrate may span a range of ages. The oldest would be associated with the establishment of the early cryosphere and its deepening with time as the result of the decline in the geothermal heat flux of the planet. Thus, the oldest deposits were likely formed in the near-subsurface, as vein-like that occupied the primary porosity of Noachtian volcanic rocks and sediments.. The youngest deposits would most likely occur in association with existing vent systems,

SYN-FREEZEUP NGH FORMATION

Although the existence of NGH deposits was proposed on Mars prior to the identification of atmospheric methane [31] [32], based on the hydrate petroleum system on Earth, there are important differences between cryosphere-hydrate systems on Earth and Mars [38].

The geological framework of Earth favors the formation of concentrated hydrate in sediments having high primary porosity and permeability. Vein-type hydrate in secondary porosity in marine sediments has been recognized on Earth, but these form in a liquid pore water media. Shallow hydrate concentrations near the present surface of Mars are unlikely to occur, except as relics of deposits that may have developed when the geothermal heat flux was higher and the base of the cryosphere was closer to the surface.

[32] suggested that Earth-type primary porosity (e.g., stratabound) NGH deposits could have formed close to the Martian surface, following the transition from a warm early greenhouse climate to the subfreezing conditions that characterize the planet today. With that transition, a freezing front would have developed in the near-surface that propagated downward with time, in response to both the colder surface temperatures and the planet's declining geothermal heat flow. Under these conditions, methane, originating from the deep subsurface (whether by the serpentization of olivine or as a byproduct of microbial activity, would have reacted with the water vapor and liquid water freezing at the base of the newly-formed cryosphere, resulting in the formation of the earliest (and shallowest) deposits of hydrate. Once liquid water no longer occupied porosity, it would be unlikely for sediment-related NGH deposits to form, except where there was some ice in porosity and enough porosity and permeability remained for gas utilizing these beds for migration to convert this ice to hydrate.

Climatic temperature variations, in response to changes in the planet's axial inclination and orbital eccentricity, have been superimposed on the longer-term cooling of the crust in response to the decline in planetary heat flow with time. In some instances, this accelerated the advance of the freezing front at the base of the cryosphere and, in others, it warmed the shallowest deposits of NGH, which would have led to their dissociation. It may well be that some of these earliest deposits, having been cutoff from a continuing supply of methane by the continued deepening of the cryosphere, may have eventually grown unstable, dissolving and releasing their dense content of methane, which may have contributed to the localized atmospheric plumes that have been recently detected.

MODERN NGH FORMATION

In contrast to their oceanic hydrate analogues, vein-type permafrost NGH deposits on Earth are not well documented yet, having only been described in one documented location to date – in the Qinghai-Tibet plateau in western China [39]. However, their discovery suggests that this type of deposit may be more widely distributed in permafrost regions than previously believed. [6] but it may have even more relevance to Mars. Although NGH deposits in permafrost have been recognized since the early 1970s, these are essentially conventional deposits of natural gas that was concentrated in geological traps prior to being converted to NGH by the deepening of the cryosphere during the most recent glacial maxima [9]. These types of gas traps may also exist on Mars, but they would depend on the ancient concentration of gas deposits in a geological trap. The probability of deposits of this type is unknown.

To our knowledge, the extent of vein-type NGH deposits in terrestrial permafrost has not been verified, and virtually no exploration for this type of deposits has been conducted, outside of the documented discovery by [39]. Although the extent and effective permeability of the Martian cryosphere are unknown, this terrestrial experience illustrates another potential form in which NGH may occur in the crust.

Perhaps the most important aspect of the potential occurrence of vein type NGH deposits on Mars is that they may exist very close to the surface, where conditions for NGH crystallization and preservation are enhanced because of the extreme cold. There should be a relatively sharp transition at the depth at which methane can form hydrate and above which it will be unstable and vent to the atmosphere.

Under present climatic conditions, the growth of NGH from the freezing of a liquid water solution is not possible in the shallow Martian cryosphere without the aid of potent freezing-point-depressing salts (such as calcium chloride or magnesium perchlorate) whose presence might itself cause chemical interference with the formation of hydrate. In contrast, the presence of open faults and fractures throughout the cryosphere could enable water-ice-natural gas recrystallization anywhere where gaseous methane would come into contact with ice. Because liquid water is not necessary for NGH formation, this process could be forming new NGH deposits even under current environmental conditions.

Gas injection along fractures and the crystallization of ice to NGH offers a mechanism for continuously forming NGH throughout the Martian cryosphere, especially in its upper part, where it would be most accessible from the surface. As these fissures are filled, the mechanically weak rubble zones may become more brittle and susceptible to further fracturing, enabling additional NGH to form. In this way, active fracture zones have the potential to hold considerable NGH over time.

DISCUSSION

The recent detection of plumes of methane venting into the Martian atmosphere indicates the potential presence of a substantial subsurface hydrocarbon reservoir. Whatever the immediate source of this methane, its production (whether by biogenic or abiogenic processes) almost certainly occurred in association with the presence of liquid water in the deep subsurface, where temperatures are above the freezing point of water. Depending on the geothermal heat flux, thermal conductivity of the crust, and the presence of any potent freezing point depressing salts, liquid water may be restricted to depths in excess of 10 km or at significantly shallower depths where the venting of methane has advected heat and thinned the cryosphere around the vent.

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 deep may be stored as ground ice and groundwater beneath the surface. There is geologic evidence that the planet once possessed vast reservoirs of subpermafrost groundwater that may persist to the present day, either as ground ice or groundwater. If so, then methane generation has likely spanned a similar period of time, extending over a considerable part of Mars' geologic history. 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, on the other hand, requires the presence of either liquid water or ice.

The detection of methane establishes the subsurface of Mars as a hydrocarbon province, at least in the vicinity of the plumes. Methane gas and hydrate deposits may occur in the subsurface at shallow depths on the order of ~15 - 30 m. Shallow methane gas deposits could constitute the most important near-term in-situ resource. Utilizing the natural resources of Mars could significantly reduce the cost of human exploration when compared with what would be required if these same resources were transported from Earth. In fact, the availability of these natural resources may prove to be the critical factor that will enable the continued human exploration of the solar system.

A new paradigm of a resource-rich Mars should now be considered the basis for the planning of future human exploration, whether on Mars or beyond – turning Mars from a remote, dead-end destination to a self-sustaining outpost that can serve as a stepping stone to the outer Solar System. A resource-rich Mars can be tapped for the production of high-energy fuels to return to Earth or travel further outward in the Solar System. Plastics, metals, and many other materials necessary for the sustainable presence of humans on Mars may also be secured from the planet's natural resources [32] [40]. The question is no longer "does Mars have resources?" but rather, "how do we assess and exploit the natural resources of Mars?", and "how can these resources support the human exploration of Mars and beyond?"

REFERENCES

[1] Mutch T, Arvidson RE, Binder AB, Huck FO, Levinthal EC, Liebes S, Morris EC, Nummendal D, Pollack JB, Sagon C. *The Surface of Mars: The View from the Viking 2 Lander.* Science 194, 1976, 1277–1283.

[2] Clifford SM and 52 others, *The state and future of Mars polar science and exploration*: Icarus 144, 2000, 210-242.

[3] Boynton WV, Feldman WC, Squyres SW, Prettyman TH, Bruckner J, Evans LG, Reedy RC, Starr R, Arnold JR, Drake DM, Englert PAJ, Metzger AE, Mitrofanov I, Trombka JI, d'Uston c, Wanke H, Gasnault O, Hamara D, Janes DM, Marcialis RL, Maurice S, Mikheeva I, Taylor GJ, Tokar R, Shinohara C. *Distribution of Hydraogen in the near surface of Mars: Evidence for subsurface ice deposits.* Science 297, 2002, 81-85. DOI: 10.1126/science.1073722.

[4] Clifford SM. *A model for the hydrologic and climatic behavior of water on Mars.* Journal Geophysical Research 98(E6), 1993, 10,973–11,016.

[5] Shuster DL, Weiss BP. *Martian Surface Paleotemperatures from Thermochronology of Meteorites.* Science 309, 2005, 594-597. DOI: 10.1126/science.1113077,

[6] Max MD, Johnson AH. *Diagenetic Methane Hydrate Formation in Permafrost: A New Gas Play?* Offshore Technology Conference. Proceedings, OTC Arctic Technology Conference, Houston, Texas, USA, 7–9 February 2011, 7pp.

[7] Sloan ED. *Clathrate hydrates of natural gases* (2nd Ed.). Marcel Dekker. Inc. New York, 1998, 628pp.

[8] Chastain BK, Chevrier V. *Methane clathrate hydrates as a potential source for martian atmospheric methane.* Planetary and Space Science 55, 2007, 1246–1256.

[9] Max MD., Johnson AH, Dillon, WP. *Economic Geology of Natural Gas Hydrate:* Springer, Berlin, and Dordrecht, 2006, 341pp.

[10] Clifford S, Lasue J, Heggy E, Boisson J, McGovern P. Max MD. *The depth of the Martian cryosphere: revised estimates and implications for the existence and detection of subpermafrost goundwater.* Journal of Geophysical Research 115, 2010, E07001, doi:10.1029/2009JE003462, 2010, 17pp.

[11] Carr MH. *Mars: A water-rich planet?*: Icarus 68, 1986, 187–216.

[12] Carr MH. *Water on Mars.* New York, Oxford University Press, 1996, 229 pp.

[13] Baker VR, Carr MH, Gulick C, Williams CR, Marley MS. *Channels and valley networks, in Mars.* In: H. H. Kieffer HH, Jakosky BM, Snyder CW, M. S. Mathews MS (eds) Tucson, University of Arizona Press, 1992, 493–522.

[14] Max MD, Clifford SM, *Initiation of Martian outflow channels: Related to the Dissociation of Gas Hydrate.* Geophysical Research Letters. 28, 2001, 1787-1790.

[15] Schubert G, Solomon SC, Turcotte DL, Drake MJ, Sleep NH, *Origin and thermal evolution of Mars.* In: *Mars.* Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds), 147-183, Univ. of Arizona Press, Tucson, 1992.

[16] Clifford SM. *A model for the hydrologic and climatic behavior of water on Mars.* Journal Geophysical Research 98(E6), 1993, 10,973–11,016.

[17] Lucchitta BK. *Mars and Earth: Comparison of cold-climate features.* Icarus 45, 1981, 264–303.

[18] Squyres,SW, Clifford SM, Kuzmin RO, J. R. Zimbelman JR, Costard FM. *Ice in the Martian regolith*. In: *Mars.* Kieffer HH, , Jakosky BM,

Snyder CW, Matthews MS (eds), 523–554, University of Arizona Press, Tucson, 1992.

[19] Clark BC. *Implications of abundant hygroscopic minerals in the Martian regolith*. Icarus 34, 1978, 645–665.

[20] Formisano VS, Atreya T, Encrenaz N, Ignatiev M, Giuranna M. *Detection of Methane in the Atmosphere of Mars*. Science 306, 2004, 1758–1761.

[21] Krasnopolsky VA, Maillard JP, Owen TC. *Detection of methane in the Martian atmosphere: evidence for life?*. Icarus 172, 2004, 537–547.

[22] Geminale A, Formisano V, Giuranna M, *Methane in Martian atmosphere: Average spatial, diurnal, and seasonal behavior*. Planetary and Space Science 56, 2008, 1194–1203.

[23] Mumma MJ, Novak RE, DiSanti MA, Bonev BP, Dello Russo N, *Detection and Mapping of Methane and Water on Mars*. Bulletin American Asronomical Society 36, 2004, 1127.

[24] Mumma MJ, Villanueva GL, Novak RE, Hewagama T, Bonev BP, DiSanti MA, Mandell AM, Smith MD. *Strong release of methane on Mars in northern summer 2003*. Scienc express, 2009, 10.1126/science.1165243, 7pp.

[25] Clifford SM, Parker TJ. *The evolution of the Martian hydrosphere: Implications for the fate of a primordial ocean and the current state of the northern plains*. Icarus 154, 2001, 40-79.

[26] Farmer JD. *Hydrothermal Processes on Mars: An Assessment of Present Evidence*. pp. 273-299. In: Bock G, Goode, J, (eds). *Evolution of Hydrothermal Ecosystems on Earth (and Mars?)*. New York, John Wiley and Sons, 1996, 334 pp.

[27] Boston PJ, Ivanov MV, McKay CP. *On the possibility of chemosynthetic ecosystems in subsurface habitats on Mars*. Icarus 95, 1992, 300-308.

[28] Wellsbury P, Parkes RJ. Deep biosphere: Source of mehtane for oceanic hydrate. In: Max MD (ed) 2003. *Natural Gas Hydrate in Oceanic and Permafrost Environments*. Kluwer Academic Publishers, The Netherlands, 2003, 91-104.

[29] Stevens TO, McKinley JP. *Lithoautophic microbial ecosystems in deep basalt aquifers*. Science 270, 1996, 450-455.

[30] Onstott TC, McGown Kessler DJ, Lollar BS, Lehmann KK, Clifford SM. *Martian CH_4: Sources, Flux, and Detectio*.: Astrobiology 6, 2006, 377-395.

[31] Fisk MR, Giovannoni SJ. *Sources of nutrients and energy for a deep biosphere on Mars*. Journal Geophysical Research 104, 1999, 11805–11815.

[32] Max, M.D. & Clifford, S. *The state, potential distribution, and biological implications of methane in the Martian crust*. Journal of Geophysical Research-Planets 105/E2, 2000, 4165-4171.

[33] Wallendahl A, Treiman AH, *Geochemical models of low-temperature alteration of Martian rocks*. Lunar Planetary Science 30, 1999, Abstract 1268.

[34] Sleep NH, Meibom A, Fridriksson Th, Coleman RG, Bird DK. *H_2-rich fluids from serpentinization: Geochemical and biotic implications*. Proc. National Academy Sciences 101, 2004, 12818–12823.

[35] Schulze-Makuch DJ, Dohm M, Fana C, Fairénd CAG, Rodriguez JAP, Baker VR, Fink W. *Exploration of hydrothermal targets on Mars*. Icarus189, 2007, 308-324.

[36] Max MD (ed). *Natural Gas Hydrate: In Oceanic and Permafrost environments (2nd Edition)*. Kluwer Academic Publishers (now Springer), London, Boston, Dordrecht, *2003,* 422pp.

[37] Osegovic JP, Max MD. *Compound clathrate hydrate on Titan's surface*. Journal of Geophisics Research-Planets 110, 2005, E08004, doi:10.1029/2005JE002435.

[38] Max MD, Clifford SM, Johnson AH. *Hydrocarbon System Analysis for Methane Hydrate Exploration on Mars*. In: Ambrose WA, Reill, JF, Lauretta DS, Peters DC (eds), Energy Resources for Human Settlement in the Solar System and Earth's Future in Space, American Association of Petroleum Geologists, Special Publication (in press for 2011).

[39] Lu Z, Zhu,Y, Zhang Y, Wen H. Li Y, Jia, Z., Liu C, Wang P, Li, Q. *Gas Hydrate features in the /qilian Mountain permafrost, Qinghai Province, China*. In: Boswell R. Fire in the Ice, March 2010, National Energy Technology Center, Morgantown, WV. 6-9.

[40] Pellenbarg RE, Max MD, Clifford SM. *Methane and carbon dioxide hydrates on Mars: Potential origins, distribution, detection and imlications for future in-situ resource utilization.* Journal of Geophysical Researches – Planets 108 (E4), 2003, DOI 10.1029/2002JE001901, 5pp.