

Methane and Carbon Dioxide Hydrates on Mars: Potential Origins, Distribution, Detection and Implications for Future in-situ Resource Utilization

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Abstract

There is high probability for the long-term crustal accumulation of methane and carbon dioxide on Mars. These gases can arise from a variety of processes: either deep biosphere activity, abiotic mechanisms, or, like water, could exist as a remnant of planetary formation and byproducts of internal differentiation. CH_4 and CO_2 would tend to rise buoyantly toward the planet's surface, condensing with water under appropriate conditions of temperature and pressure to form gas hydrate. Gas hydrates are a class of materials created when gas molecules are trapped within a crystalline lattice of water ice. The hydrate stability fields of both CH_4 and CO_2 encompass a portion of the Martian crust that extends from within the water-ice cryosphere, from a depth as shallow as ~ 10 - 20 meters, to as great as a kilometer or more below the base of the Martian cryosphere.

The presence and distribution of methane and carbon dioxide hydrates may be of critical importance in understanding the geomorphic evolution of Mars, the geophysical identification of water and other volatiles as stored in the hydrates. Of critical importance, Martian gas hydrates would ensure the availability of key in-situ resources for sustaining future robotic and human exploration, and the eventual colonization, of Mars.

Introduction

Methane, other gases, and water would almost certainly have concentrated on and in the near-surface of the proto-planet during the formation of Mars. Further, methane is known to be one of the stable gases that is produced by chemical activity early in the history of planetary formation. Thus, some abiotic methane may be expected to have appeared in the earliest Martian

atmosphere, largely as a product of fractionation of magmatic and other rocks. In addition, however, any early life on Mars would almost certainly have been methanogenic, and this biota is likely to have persisted as deep biosphere (Max and Clifford, 2000).

Mapping of the three-dimensional distribution of methane, water, carbon dioxide, and other materials in the crust of Mars, initially by remote sensing from Mars-orbiting vehicles (Mellon, et al., 2000) will provide the first perspectives of an Earth-like planet whose condensative, tectonic, and biosphere development appears to have been arrested early in its history. Understanding the apparently truncated evolutionary geologic history of Mars should provide considerable information about the early history of the Earth, the record of which has been largely obliterated by subsequent terrestrial tectono-biologic activity.

In addition to the contribution that knowledge of the nature and distribution of subsurface components such as methane could shed light on the early history of Mars, rapid acquisition of some of this information will be crucial to the design of a program for exploration of the Red Planet. Mars is presently regarded as an essentially cold, dry, 'dead' planet and as such could contribute little to the eventual human colonization of the planet. Where gas hydrates of carbon dioxide and methane occur, however, finding, extracting, and utilizing the constituents of these gas hydrates would alter not only our understanding of the early development of the planet, but would allow a much earlier and less energy-intensive colonization of Mars than is currently envisaged.

Water is a most basic requirement for human habitation of Mars and it is likely that water is currently present not only in the Martian Polar Regions but also abundantly in the Martian cryosphere. In addition to water, however, other materials are required for the establishment of a self-sustaining human presence on Mars. Oxygen and hydrogen (for fuel) can be produced by electrolysis of hydrate-derived water, using electricity produced either from small nuclear reactors and/or photovoltaics. Utilization of methane either in fuel cells or combustion engines of various types not only produces energy, but also water and CO₂ and other gases. These gaseous products not only act to increase the Martian atmospheric greenhouse character, but also could be captured to support the extension of human activity.

In addition to its utility as a fuel, however, methane and carbon dioxide (the primary constituent of Mar's atmosphere and presumably more common in the sub-surface) are a potential primary feedstock for the synthesis of plastics and other synthetic materials (including

higher-energy-density liquid fuels) from which virtually every object necessary for human habitation of Mars can be manufactured. Existing chemical engineering, and manufacturing, technologies can be miniaturized, optimized for Martian conditions, and used to fabricate virtually everything necessary, in-situ, on Mars. This local materials fabrication technology could be the final element required to permit and support the permanent human habitation of Mars.

Because of the potential importance of gas hydrates in the relatively near-surface Martian cryosphere, we argue that research should be focused on examining our proposition that gas hydrate, especially methane gas hydrate, occurs in quantity on Mars. To confirm this hypothesis, the search for deep biosphere life and its biotypes on Mars is key, because Martian biota is most likely to be methanogenic rather than adapted to an oxygen-rich milieu. In the case of the present ‘dead’ Mars model proving correct, colonization of Mars will await considerable preparation and be much more difficult logistically. In the case of our model for a ‘living’ Mars having storehoused water and large concentrations of useful industrial gases captured from living (likely dominated by bacteria) biota that may still be present in the Martian sub-surface, the timescale for human exploration and colonization of Mars could be shortened considerably.

Gas Hydrate: Controls on Formation and Development; Terrestrial Analogs

The gas-bearing, ice-like solid form of water known as gas hydrate occurs abundantly on Earth in marine sediments and permafrost regions, and sequesters immense amounts of methane. Gas hydrate forms wherever appropriate physical conditions exist — moderately low temperature and moderately high pressure — and the component materials are present: hydrate-forming gas near saturation, and water. These conditions are found at depth in the sea and in underlying sediments, commonly at water depths greater than ~500m in open oceans, ~300m in Polar Regions, and ~600 - 700m in warmer water regimes such as the Mediterranean Sea. Terrestrial permafrost hydrates occur with water-ice in the lower region of a compound, generally polar, cryosphere (Max and Clifford, 2000). Once hydrocarbon (i.e., methane) hydrate is formed in a cryosphere, it may persist even if its ambient pressure conditions drop (Ershov & Yakushev, 1992).

Gas hydrate on Earth is found in the gas Hydrate Stability Zone (HSZ), which extends downward from the a sufficiently deep seafloor surface to a depth where the temperature has risen sufficiently so that hydrate is not stable (even though the pressure increase that comes with greater depth tends to increase gas hydrate stability). The methane in oceanic gas hydrate on Earth is mostly of biogenic origin. A methanogenic deep biosphere in the buried marine sediments of Earth's oceans is the chief reason why gas hydrate occurs in marine sediments. Thermogenic methane produced in association with thermal gas and oil production also occurs, but this methane source is associated with particular tectonic situations and occurs principally in oil-bearing provinces. Without a sufficient positive gas flux from the deep biosphere, no significant accumulation of hydrate will form, and in-place hydrate will tend to dissociate over time if gas flux becomes insignificant, as gas molecules emigrate by solid diffusion mechanisms and thus destabilize the water molecule hydrate cage structure.

Methane on Mars and Its Potential Significance

If the evolution of the Martian surface even marginally paralleled that of Earth, then abundant methanogenic bacteria were likely present in the early anoxic aqueous environment of the Martian surface and near subsurface (see also Boston, et al., 1992). During the transition to the present desiccated, cryogenic crust of Mars, such surface-inhabiting life would likely have adapted to become a deep biosphere form, joining any pre-existing deep biosphere biota, similar to that we now recognize in certain warm, deep anoxic sediments and rocks on Earth. A deep microbial biosphere on Mars would almost certainly also have been at least partially methanogenic, as it is on Earth, and would respire carbon dioxide. In this regard, recent research on unusual terrestrial ecosystems point to the probability of biogenic methane and carbon dioxide. Chapelle, et al., (2002) report on an Idaho (USA) water spring populated by Archea using hydrogen from water to reduce (meteoric?) carbon dioxide to methane.

An abiotic mechanism for the long-term gas (methane or carbon dioxide) concentration exists on Mars as it does on Earth (Max and Lowrie, 1996). For example, biogenic methane gas produced as a waste product tends to migrate buoyantly upward in pore-water rock porosity until it reaches the local Hydrate Stability Zone (HSZ), where the hydrate is stable. On Mars, the particular pressure-temperature and thermodynamic equilibrium associated with the cold Martian

surface is favorable for the formation of a substantial, and deep, HSZ (Max and Clifford, 2000). Methane hydrate and water-ice form a complex cryogenic regime in which water-ice is stable from the Martian surface to about 273 °K at depth, and hydrate is stable from some depth below the surface (depending on average surface temperature, total local pressure, and local geothermal gradient) to some depth below the base of the water-ice stability zone. Under current ambient conditions on Mars, methane hydrate is stable close to, but not at, the surface of the planet. Since the dominant constituent of the Martian crust appears to be Earth-like basalt, and basalt-derived weathering products, the difference in lithostatic pressure at any depth between Mars and the Earth simply scales in proportion to the ratio of gravitational accelerations for the two planets (i.e., ~0.4). At the current 200 °K average surface temperature of Mars, hydrate is not stable at less than about 140 kPa (data from Sloan, 1997), which corresponds to a depth of ~15m (assuming an ice-saturated permafrost density of $2.5 \times 10^3 \text{ kg/ m}^3$). Given a reasonable estimate of the thermal properties of the crust, the base of the Martian HSZ should then extend to depths that lie from several hundred meters to as much as a kilometer below the top of the local HSZ. Thus, the total thickness of the HSZ on Mars is likely to vary from ~3 km at the equator, to ~8 km at the poles (Max and Clifford, 2001).

Once methane has been incorporated within hydrate, it is fixed in place. Because the cryosphere formed over a considerable period, there may be lenses and accumulations of ‘perched’ or stranded gas hydrate that formed in the lower part of an early, thinner cryosphere, even though the zone of water-ice subsequently has penetrated to greater depths. Alternatively, where a hydrate forming gas such as carbon dioxide or methane may migrate into a dry zone in the cryosphere, the gas may persist as a gas pocket where surrounding porosity is filled with ice or hydrate, or the surrounding ice may be converted to hydrate through diffusion of the gas and recrystallization of ice.

At both extremes of water abundance, hydrate may be found on Mars. Gas hydrates have been proposed to occur on the moon, for instance, where the near-surface hydrogen anomalies found by the Lunar Prospector and interpreted as water-ice have been reinterpreted as indicating the possible presence of methane or carbon dioxide hydrate (Duxbury et al., 2001a). At the other extreme, bodies of water similar to Lake Vostok in Antarctica (Duxbury et al., 2001b) that may have occurred below an intermediate stage depth of the Martian cryosphere during its penetration

to its present depth, may have harbored considerable sub-surface life.

Where gas hydrate has formed instead of water-ice, the distribution of the ice-like hydrate will be greater than that of water-ice alone. This is because each cubic meter of hydrate contains only some 0.8 cubic meter of water. In addition, the coefficient of expansion of gas hydrate is about 2/7 greater than the starting volume of water whereas that of water ice is 1/7. Estimates of the proportion of gas hydrate to water ice will strongly affect estimates of the water present in the Martian sub-surface.

The possible existence of methane and carbon dioxide hydrate in the shallow subsurface of Mars offers extraordinary potential to permit and sustain the human habitation of Mars. Thus, identification and quantification of methane hydrate, or proof of its absence, must be regarded as one of the key questions about Mars that must be answered in order to allow for effective planning and preparation for human travel to Mars. The availability of gas hydrates on Mars may prove to be the key to human occupation of the Red Planet.

Hydrate Detection on Mars

Little is currently known about the subsurface character of Martian geology. Virtually nothing is known about the likelihood or location of structural or stratigraphic fluid traps on Mars. The sedimentary and lithic material from which the upper strata of Mars are composed is also little understood. Nonetheless, the cryosphere on Earth exhibits many features, and probable analogs for the situation on Mars, that could be important to providing pathways for gas migration and accumulation, which are vital to recovery of significant volumes of gas on Earth. In addition to primary porosity, extensive secondary porosity in the form of faults, fractures, and 'frost heaving' volume changes owing to ice and hydrate formation may produce pathways for fluid and gas migration in rocks that are otherwise too tight to allow significant gas or fluid flow. Extensive faulting has been observed in gas hydrate bearing strata in many terrestrial regimes, and such faults do show evidence of fluid flow (Dillon, et al., 1998). Both diagenetic water-ice and gas hydrate can form traps in otherwise permeable sediments. Martian analogues of Earth's cryosphere areas would provide significant traps for gases.

Spectroscopic (IR) analysis for atmospheric methane detection may not yield positive results without targeting the likely tectonic and cryogenic features that provide pathways along

which methane may migrate to the planet's surface from depth. Bathed in the strong UV radiation present in the thin atmosphere of Mars, methane may have a half-life much shorter than its approximate 10-year half-life in Earth's atmosphere. Thus, the most likely locations for methane detection are where a subsurface pathway, such as a fault, intersects with the Martian surface. Further, seismic studies could reveal not only the disposition of subsurface rocks and strata but also deposits of diagenetic water-ice and gas hydrate, and free-gas. Remote seismic studies should be designed to reveal likely drilling (exploration) targets (Max & Dillon, 1999) and autonomous drilling rigs that are fully instrumented for chemical (e.g., Raman spectroscopy in water saturated environments, and gas phase methane detectors), biological (e.g., DNA detectors), and physical properties measurements (e.g. full well logging) can penetrate the crust of Mars to reveal the first subsurface information. The collection of subsurface stratigraphic data will be a major advance in the exploration of Mars that will undoubtedly identify the many evidences that are being revealed for past and recent fluid/gas effusion onto the Martian surface from subjacent sources.

Chemical Engineering Opportunities and Constraints on Mars

If concentrated water, methane, carbon dioxide and metal salts exist on Mars, the basis of virtually all manufactured items required for shelter, transport, and eventually permanent habitation of the planet can be produced on Mars, rather than being transported from Earth. Fuel for return journeys or for travel further away from Earth can be produced on Mars. Basic chemical engineering processes can be applied to convert simple starting materials into useful products (see Folger, 1992). Polystyrene (see Appendix 1), for instance, can be formed into structural shapes such as "I" beams, or foamed with CO₂ to give insulating materials. Items such as furniture, construction panels, elements of housing and hydroponic farming structures and equipment, amongst the wide variety of 'things' that a technology outpost depends upon, are relatively easily fabricated from polystyrene and other plastics. The key to this opportunity is availability of simple chemical feedstock (dominantly methane and carbon dioxide from hydrates) from which these things can be fabricated.

At the beginning of any manufacturing activity based on materials found on Mars, there must be an energy source to support chemical engineering processes that will produce useful

products, and to provide power in general. Synthetic chemistry, even on the restricted industrial scale required by initial Martian colonies, will require power for heating, pressurizing, and irradiating chemical reaction vessels, for example. Dependable high-energy-density power sources, at first, can be provided either by nuclear- or solar-electric installations.

Although nuclear power is attractive from the standpoint of power density and dependability, any reactor and its nuclear fuel would have to be transported from Earth. However, a reactor need not be brought to the Martian surface. It could be placed in a stable orbit around Mars, or emplaced on either Deimos or Phobos, from where power could be beamed to the surface of Mars. However, nuclear power has three prime concerns that must be dealt with. First is the cost of transporting a relatively heavy reactor from Earth to Mars. Second is the possibility of a nuclear accident in the Earth's atmosphere or in the vicinity of Mars. Third is the problem of what to do with the spent nuclear fuel.

If concerns about nuclear power prove to be overwhelming, solar energy is likely to be the initial power source for a Martian colony. A key factor in this energy equation is the fact that Mars is roughly twice as far from the Sun as is Earth, and thus receives roughly one-quarter the energy per unit area as does Earth. Solar collectors on Mars would thus need to be some four times as large as they would need to be on Earth for the same energy output.

Discussion

We have discussed broad chemical engineering concepts confined to producing useful organic compounds containing mainly carbon, hydrogen, and oxygen. There are myriad other organic materials which incorporate such atoms as chlorine, sulphur, phosphorus or nitrogen, for instance, which would allow for the manufacture of very sophisticated materials on Mars. Martian colonists may wish to engineer polyvinyl chloride (PVC) as a structural material. For PVC, the colonists would need a source of chlorine, which is easily produced by the electrolysis of salt (NaCl). Are there salt deposits on Mars? If there was standing water on an ancient Mars, there may well be salt deposits related to ocean evaporation. Such deposits could also contain nitrate (e.g., NaNO_3) or phosphate (e.g., K_3PO_4), which would provide readily usable industrial feedstock. Our concept is to build virtually all necessary products from raw materials found on Mars. Thus, a schedule of exploration by geologists must be initiated at an early stage.

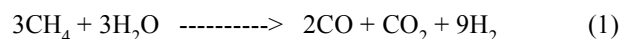
In the longer term, use of methane as a fuel and in other chemical processes will produce CO₂ gas, and thus will increase the Martian greenhouse character over time, even without a planned, intentional atmospheric remediation plan. Increasing atmospheric density and thus enhancing the greenhouse effect of the atmosphere should eventually render Mars more amenable to habitation in the longer term. Both methane and carbon dioxide are strong greenhouse gases, and if released in sufficient quantities, could lead to marked warming on the planet. Of course, it is highly probable that enough CO₂ and other greenhouse gases would be released into an enclosed space (e.g. large greenhouses) to allow the cultivation of biomass on Mars without modifying the planetary atmosphere as a whole. We support the proposition that release of virtually all gases into the atmosphere of Mars provides for a beneficial increase in the greenhouse character of the planet, and these releases should be encouraged.

If methane or carbon dioxide hydrate deposits can be identified on Mars, their location may provide the determining factor in selecting habitation and colonization sites there because they will contain the basic elements necessary for human habitation: water, power, synthetic carbon-based materials for shelter, and, eventually, foodstuffs. Thus, early research such as seismic experiments for determining the character and distribution of sedimentary and diagenetic materials (such as water-ice, gas hydrates, and other mineral deposits) and exploratory drilling, should, in our view, be undertaken as a matter of urgency. Any locally derived materials used in the inhabited installations will not accrue the huge energy costs of bringing such materials from Earth. For true colonization to be contemplated, the inhabitants of Mars must become as self-sustaining as possible, as rapidly as possible.

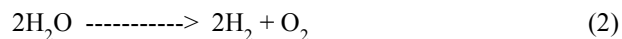
Although a great deal of scientific research can be usefully carried out on Mars that will provide new perspectives about the formation and history of Earth, focusing a research effort first on the question of the existence and character of deep biosphere, and then on the likely byproducts of this biosphere, if it exists, would accelerate our basic and practical knowledge of Mars. The nature of the research schedule itself should be conditioned by research planned to test particular models of Martian formation and geologic evolutions, and the schedule should be reset when models can be modified - proved or disproved - so as to rapidly move the exploratory efforts to the next important stage. At present, designing a research schedule for Mars may more represent a program designed by a committee which spreads the work overly amongst a wide

range of interests. In contrast, we propose that focusing on a paradigm-shifting issue, such as identifying deep biosphere, with all of the biological implications that alone would have, may be of greater value than a broader but thinner program, especially if our model for the interaction of deep biosphere with the development of cryosphere on Mars is found to exist.

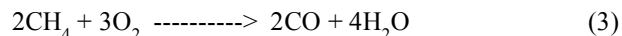
Appendix 1. Examples of potential structural materials that can be derived from gas hydrate.



(1) is desirable because the reaction converts reduced carbon (CH_4) to oxidized carbon (CO and CO_2) which is a useful industrial feedstock. Alternatively, water from gas hydrate could be electrolyzed, as in (2):



where the resultant oxygen (O_2) can be further reacted as in (3):



The net desirable result of reactions (1) and (3) is to produce carbon monoxide. Keep in mind that carbon dioxide could be available on Mars directly from CO_2 hydrate, but it is useful to have the chemical technology to convert CH_4 to CO , even if abundant CO_2 were available. Thus, (4):



produces CO and H_2 so that the Fischer-Tropsch Process (FTP) can be employed (5, intentionally left unbalanced):

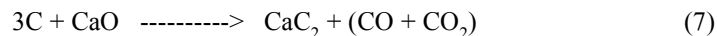


with an appropriate metallic catalyst(s). With proper selection of these chemical participants, the FTP will yield liquid hydrocarbon fuels, oils, waxes, and a variety of other organic chemicals.

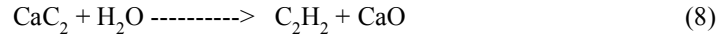
For the purposes of colonization of Mars, access to a synthetic structural material, such as plastics, is critical. Polystyrene, for use as an structural plastic can be produced as follows (initially, consider the water gas reaction, 6):



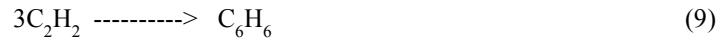
which when driven in the reverse yields elemental carbon. Carbon will react with calcium oxide (a Martian ore?) in an electric furnace to give calcium carbide (7):



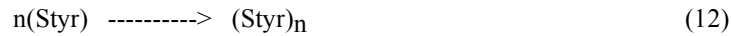
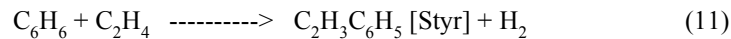
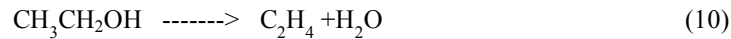
and calcium carbide will react with water to give acetylene (8):



and acetylene can be condensed to benzene (9):



which will react with ethylene (from dehydration of ethyl alcohol [10] from the FTP) to give styrene (11). Styrene can be polymerized to a rigid plastic (12):



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