

The State, Potential Distribution, and Biological Implications of Methane in the Martian Crust

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Abstract

The search for life on Mars has recently focussed on its potential survival in deep (>2 km) subpermafrost aquifers where anaerobic bacteria, similar to those found in deep subsurface ecosystems on Earth, may have survived in an environment that has remained stable for billions of years. An anticipated byproduct of this biological activity is methane. The detection of large deposits of methane gas and hydrate in the Martian cryosphere, or as emissions from deep fracture zones, would provide persuasive evidence of indigenous life and confirm the presence of a valuable in situ resource for use by future human explorers.

Introduction

With 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, 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 km-deep channels, tens of kilometers wide and hundreds of kilometers long, 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 (Baker, 1982; Carr, 1996). Additional evidence is provided by the presence of integrated networks of small valleys (that resemble terrestrial run-off channels) in the planet's oldest terrains. Although the interpretation of such features are still debated (Malin and Carr, 1999), this finding has been interpreted as evidence of rainfall associated with a more Earth-like greenhouse climate that may have existed in the distant past (<4 bya) (Masursky et al., 1977; Carr, 1999).

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 organic molecules and eventual emergence of life. 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 (Farmer, 1996). 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 the potential presence of groundwater has enabled it to persist to the present day (Boston et al., 1992; Gold, 1997). 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 deposition, alteration, and possible indirect evidence of microbial life within the 1.3-4.5 billion year old SNC meteorites (McKay et al., 1996, McSween and Harvey, 1998; Warren, 1998, Treiman, 1999).

Although current mean annual surface temperatures on Mars are well below freezing (ranging from ~ 154 K at the poles to ~ 218 K at the equator), radiogenic heating is expected to result in progressively warmer temperatures at depth. Given reasonable estimates of the thermal conductivity of the crust ($\sim 2 \text{ W m}^{-1} \text{ K}^{-1}$), geothermal heat flux ($\sim 30 \text{ mW m}^{-2}$), and the potential freezing point of highly mineralized and saline groundwater (252 - 273 K), the current thickness of frozen ground on Mars is expected to vary from ~ 2 -3 km at the equator to ~ 6 -8 km at the poles, a region that has is called the cryosphere (Fig. 1) (Rosbacher and Judson, 1981; Clifford, 1993).

Theoretical models of the geothermal evolution of Mars suggest that the planet's heat flux was substantially higher in the past (Schubert et al., 1992), having been as much as 5 to 6

time greater 4 billion years ago. 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 H₂O (Clifford, 1993). 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 (Lucchitta, 1981; Squyres et al., 1992).

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.

Biogenic vs. abiotic sources of methane

If life arose on early Mars, and thereafter successfully established itself in the deep subsurface, then it may well resemble the anaerobic bacterial communities found in the recently recognized deep biosphere of present-day Earth (Boston et al., 1992; Parkes et al., 1994; Stevens and McKinley, 1996). If so, then methane has likely been produced in substantial quantities within the Martian subsurface (Fisk and Giovanni, 1999). This expectation is consistent with the origin the vast majority of methane produced on Earth, which arises from either the metabolism of methanogenic bacteria (such as *Methanococcus Jannaschii*), the decay of organic matter, or from subsequent chemical reactions involving the thermogenic alteration of coal and petroleum (Walker, 1977; Parkes et al., 1994; Kargel and Lunine, 1998; Fisk and Giovanni, 1999).

But could large quantities of methane on Mars be produced abiotically? For example, one possibility is that CH₄ might arise as a fractionation product of magma crystallization. Yet, methane emissions from terrestrial volcanoes are low (Kasting, 1993), suggesting that the yield from this process on Mars is likely to be minimal.

Alternatively, methane may also result from the alteration of Martian basalts in a subpermafrost aquifer, sequestered from contact with the ambient CO₂ atmosphere by several kilometers of ice-saturated frozen ground. This possibility has recently been advanced by Wallendahl and Treiman (1999), who calculate that as much as 0.2 bars of CH₄ could have been produced if the only source of carbon available beneath the permafrost was the atmospheric CO₂ initially present in the crustal pores. This abiotic production of methane would be greatly enhanced if the crust contained substantial deposits of carbonate. Such deposits may have been generated by the reaction of atmospheric CO₂ with standing bodies of liquid water very early in the planet's history (Pollack et al., 1987). However, to date, no sizable deposits of carbonate have been detected at the surface, which raises some doubt about the potential size of the inventory that may be present at depth.

Thus, the detection of substantial quantities of subsurface methane, as either a gas or hydrate, would by itself provide persuasive evidence that an Earth-like subsurface biosphere

evolved on early Mars. Additional evidence for or against a biogenic origin could also come from any observed fractionation of carbon isotopes. On Earth, isotopically light methane (i.e., methane whose $^{12}\text{C}/^{13}\text{C}$ ratio is higher than is typically found in terrestrial marine carbonates) is widely interpreted as having a biogenic origin, while the origin of heavy methane (which is enriched in ^{13}C) is typically attributed to abiotic processes (e.g., McCabe et al., 1993). There is some debate, however, as to whether such fractionation is necessarily a universal or unique characteristic of life (Gold, 1999).

While the presence of abundant methane on Mars does not require that life be extant now, the comparative isolation and stability of microbial life in a subpermafrost environment makes it difficult to imagine how life once established in this niche could become extinct. The most probable threat to such life would be if the initial inventory of groundwater on Mars was small. In that event, the growth of the cryosphere, in response to the long-term decline in the planet's internal heat flow, may have led to the eventual assimilation of the entire groundwater inventory into the frozen crust (Clifford, 1993).

Stability of methane hydrate on Earth and Mars

On Earth, methane produced by organisms in subsurface sediments is often naturally concentrated by buoyant migration and confinement beneath low permeability strata and ice-sealed traps (Kargel and Lunine, 1998). On Mars, this potential is likely enhanced by the expected widespread occurrence of ice-saturated permafrost subsurface (Fisk and Giovanni, 1999).

The methane trapped in these deposits may occur as both gas pockets or, under appropriate conditions of temperature and pressure, as a hydrate that takes the form of intergrown, poorly-defined ice-like crystals. Hydrocarbons (mostly methane), as well as other gases, are thermodynamically stabilized in gas hydrates by hydrogen bonding (Van der Waals weak electrical forces) within a cubic crystalline lattice of water molecules (Kvenvolden, 1993). Because not all the guest sites within the lattice are generally occupied, gas hydrates are non-stoichiometric compounds of methane and water [$\text{CH}_4 \cdot 6.1 (\pm 0.1\%) \text{H}_2\text{O}$]. Hydrate formation concentrates methane by forcing the molecules into closely packed lattice sites in the hydrate crystals (at a molecular density that exceeds that of even liquified methane). Typically, 1 m^3 of naturally occurring 90% saturated methane hydrate contains 164 m^3 of methane gas (at STP) and 0.8 m^3 of liquid water (Kvenvolden, 1993).

The stability field of methane hydrate is constrained by the increase in crustal temperature and pressure that occurs with depth. On Earth, hydrate is found in the intergranular pore space of rocks and sediments at depths as shallow as 150-200 m in permafrost regions (Collett, 1995; 1998), and in the low-temperature, high-pressure conditions found on the deep ocean floor (Max and Dillon, 1998). Like permafrost, the maximum depth at which hydrate remains stable is limited by crustal temperature, although the pressure-temperature fields of water-ice and methane hydrate differ considerably (Fig. 2). The region of the crust that satisfies the thermodynamic stability criteria for methane hydrate is called the Hydrate Stability Zone (HSZ), whose thickness is governed by the magnitude of the local geothermal gradient (i.e., being greater for shallow gradients and thinner for steeper gradients).

In practice, determining the absolute depth to which methane hydrate will remain stable is a complex issue that is dependent on a variety of factors, including: the salinity and nature of dissolved solids present in any groundwater that it may be in contact with, the local geothermal gradient, the mean annual surface temperature and the recent thermal history of the crust.

Beneath this depth, methane persists as a gas. For example, large gaseous methane deposits associated with water below the HSZ have been identified off the southeastern coast of the United States (Dillon and Paull, 1983; Dillon et al., 1994; 1997). This stratification of methane hydrate within the HSZ and gaseous methane below, is characteristic of all known oceanic hydrate systems on Earth (Max and Dillon, 1998).

The pore pressures that govern the condensation and stability of methane hydrate are determined to a large extent by their saturation state. In hydrate- or ice-saturated pores, the local confining pressure is equal to the lithostatic pressure exerted by the overlying crust. However, in unsaturated pores, the local gas pressure is generally intermediate between the lithostatic value and the sum of the depth-adjusted barometric pressure and local saturated vapor pressure of H₂O. This situation is complicated by the likelihood of considerable heterogeneity in the structure, lithology, and volatile stratigraphy of the crust – both within the cryosphere and within any unsaturated zone that might exist between its base and global water table (Fig. 1).

Methane hydrate and water-ice form a compound cryogenic zone (Fig. 3). Water-ice is stable from the surface to about 0 °C and hydrate is stable from some depth below the surface (depending on average surface temperature, total pressure, and geothermal gradient) to some depth below the base of the water-ice stability zone (Fig. 4). In Alaskan permafrost, variations in the local thermal properties of the crust can yield maximum hydrate stability depths of 600 - 1075 m with associated crustal temperatures of ~285 - 287 K (Dallimore et al., 1988; Kvenvolden, 1988, 1993).

Under ambient conditions on Mars, methane hydrate is stable close to, but not at, the surface. Since the dominant constituent of the crust appears to be basalt (or 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 planet's (i.e., ~0.38 g). At the 200 K average surface temperature of Mars, hydrate is not stable at less than about 140 kPa (data from Makogan and Sloan in Sloan, 1997), which corresponds to a depth of ~15 m (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 base of the cryosphere (whose extent is depicted in Fig. 1). Thus, the total thickness of the Hydrate Stability Zone on Mars is likely to vary from ~3 km at the equator, to ~8 km at the poles.

Migration and distribution of methane within the cryosphere

Whether methane on Mars is derived from biological activity or simply inorganic chemical reactions between groundwater and basaltic rock, it will reside in the water-saturated fracture and intergranular pore space that lies beneath the cryosphere. On Earth, the upward migration of gaseous methane occurs in response to its natural buoyancy in a fluid-filled medium. However, in solution, methane diffuses through the crustal fluids in response to local solubility gradients, which are steepest near where it is produced. In both cases, the direction of net transport is from deeper to shallower depths within the crust.

The rate and path of ascent of methane is subject to variations in the porosity and permeability of the crust. In this regard the complexity and heterogeneity of the Martian crust is likely to be similar to that of the Earth. Thus, methane will rise where the transport properties of the crust permit and move laterally or stagnate where it encounters obstacles such as less-permeable strata. During the course of billions of years, even strata possessing extremely small

diffusion rates will permit considerable transport and create the potential for substantial deposits of methane and hydrate at shallower depths within the crust.

Condensation of water ice in the fracture and intergranular pore space of the cryosphere will substantially reduce, if not eliminate, the gaseous permeability of any rocks in which it forms. Because the depth of the cryosphere reflects the local thermal structure of the crust, it follows the first-order variations in local surface topography. For this reason, as methane diffuses upward from below, it will be concentrated in topographic traps at the base of the cryosphere that correspond to elevated regions at the surface. Although Figure 1 illustrates that the base of the cryosphere slopes upward from polar regions (a product of the higher mean annual surface temperatures at low latitude), this trend occurs over such a large scale that it may have little impact on the lateral migration or global distribution of methane.

Of course, the depth of the cryosphere has not remained static with time. As the interior of the planet cooled, the freezing front at the base of the cryosphere has propagated deeper into the crust -- forcing any subsurface biosphere, or inorganic aqueous-based reactions, to greater depths as well.

The rate at which the freezing front propagated into the crust has important consequences for the concentration and distribution of subsurface methane -- a fact that remains true whether it had a biological origin or not. If the freezing front descended rapidly (as it may have, following the sudden transition from a hypothetical warm to cold early climate), methane would have been assimilated into the cryosphere as a dispersed gas (or hydrate). However, if it descended slowly, then there would have been a greater time for methane to have accumulated at the base of the cryosphere, where it may have ultimately been incorporated as an extended deposit of gas or hydrate. This potential may have been enhanced by the unsteady local production of methane, which may have arrived at the base of the cryosphere in pulses -- rather than as a diffuse, constant flux.

Of course, it is highly unlikely that the progressive cooling of the Martian crust, and growth of the cryosphere, has been a monotonic or globally universal process. Long-term variations in solar luminosity, climate, surface albedo, and obliquity, can be expected to have induced changes in surface temperature that would have propagated through the crust and caused the zone of hydrate stability to thicken and thin with time. Temporal and spatial variations in the thermal structure of the crust may also have arisen from local igneous and volcanic activity, as well prolonged surface deposition or erosion. Such changes may have had a significant impact on the stability and subsurface distribution of hydrate. For example, on Earth, higher temperatures can cause hydrate to dissociate, forming pockets of highly-pressurized gas and water that generate enough force to breach the surface or, at depth, drive flow against the local hydraulic head (Max and Chandra, 1998).

Detectability and accessibility of subsurface methane

Given the possible permutations of local structure and thermal evolution that may be encountered on Mars, the subsurface distribution of gas and hydrate is likely to be both exceedingly complex and inherently unpredictable. Indeed, because the stability zones of water-ice and methane hydrate overlap, and their seismic and electrical properties are similar, they are virtually impossible to differentiate with standard geophysical techniques -- although, if gas is present at the base of the hydrate stability zone, a Bottom Simulating Reflector (BSR) similar to those commonly seen on Earth (Singh et al., 1993) may be detected.

While no unambiguous technique for the remote detection of subsurface methane has yet been developed, identification by direct means is possible where element- and isotope-specific, solid-state devices can be placed in intimate contact with a source or vent. Such an approach might be implemented by imbedding electronic sniffers in a recent fault zones to detect methane emissions from the deep subsurface. However, the identification of such conduits is likely to be difficult -- because any opening in the crust that is in diffusive communication with a subsurface reservoir of H₂O, is likely to be rapidly sealed by the thermal redistribution and condensation of ice (Clifford, 1993). Alternatively, localized methane emissions may be identified from orbit using high-resolution spectrometers that possess bands specifically chosen for the detection of methane (National Aeronautics and Space Administration, 1995).

A more likely method of directly accessing and identifying subsurface methane is by drilling. Drilling investigations of both the shallow and deep subsurface of Mars have been identified as principal objectives in the search for evidence of past or extant life (Morrison and Schmidt, 1999; Farmer and Des Marais, 1999). Beyond their potential exobiologic significance, such investigations will also yield important insights into the planet's geologic and climate history, and could provide an important means of accessing and exploiting *in situ* resources in support of future human exploration.

Although drilling to depths of several 10s to 100s of meters might conceivably be undertaken by advanced robotic spacecraft, the technical and logistical challenges involved in reaching greater depths would almost certainly require a human presence. Because a subpermafrost aquifer represents the most promising environment for finding extant life on Mars, and because access to a local supply of water is vital to sustain any prolonged human exploration of the surface, groundwater is likely to be the primary objective of any deep-drilling effort.

Thermal and hydraulic considerations suggest that the depth to any potential reservoir of groundwater will be minimized at low-latitude and low-elevation (Clifford, 1996). However, selecting a drill site based solely on these criteria provides no guarantee that groundwater will actually be found. The potential for significant crustal heterogeneity, combined with the enormous technical and logistical challenges facing any effort to drill to depths of 3 - 5 km, necessitates that the presence of a local reservoir of groundwater be confirmed before drilling commences. Fortunately, the seismic and electrical characteristics of groundwater make it considerably easier to identify than either methane hydrate or gas. Thus, a comprehensive geophysical survey is a mandatory first step in the evaluation of any potential drill site.

This analysis suggests that if a deep microbial biosphere did establish itself on early Mars, then evidence of its presence, in the form of methane hydrate or gas, could well be detectable in the shallow subsurface. As noted earlier, a biogenic vs. abiotic origin of such deposits could potentially be determined by the detection of any isotopic fractionation of carbon relative to the ambient environment. Deeper investigations of the crust, targeting groundwater, would have the greatest potential for encountering large reservoirs of gaseous methane. Of course, the penetration of an over-pressurized gas reservoir or the destabilization of methane hydrate (at shallower depths), could itself pose a significant hazard to any deep-drilling activity - necessitating continuous down-hole monitoring.

The discovery of substantial deposits of subsurface methane, whatever its form or origin, could represent an invaluable resource to future human explorers. On Earth, recent drilling in a permafrost hydrate in the Mackenzie Delta of northern Canada has yielded 150 billion cubic feet of methane per km² over tens of km² in an anticlinal concentration (Collett and Dallimore,

1998). The presence of similar deposits on Mars could provide an important in-situ source of energy (either by combustion with oxygen derived from atmospheric CO₂, or by direct use in fuel cells) and serve as a local feedstock for the production of more complex hydrocarbons and other organic molecules (Ash et al., 1978; Meyer and McKay, 1996).

Conclusions

The apparent presence of abundant water on Mars, combined with the recent discovery of deep lithoautotrophic bacteria on Earth raises the possibility that early Martian life may have established itself in deep subpermafrost aquifers, where it may survive to the present day. If so, methane is a likely by-product of that metabolism.

As the search for life on Mars expands to include investigations of the deep subsurface, the presence and vertical distribution of methane hydrate and gas may provide important clues regarding both the origin of life and its subsequent evolution. Deep-drilling efforts, directed at the retrieval of groundwater from beneath the cryosphere, would provide an ideal opportunity for investigating the distribution of these deposits throughout the top several kilometers of the crust and could well provide unambiguous evidence of life at much shallower depths. The successful retrieval of methane and water from beneath the Martian cryosphere may not only confirm the presence of native life, but may also provide the basic elements of fuel and water necessary to support the eventual expansion of human life across the surface of the planet.

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Figure Captions

Figure 1. A hypothetical pole-to-pole cross-section of the Martian crust (along 300° W longitude), illustrating the potential relationship between surface topography, ground ice, and groundwater. Elevations are based on the USGS Mars Digital Terrain Model.

Figure 2. Generalized methane hydrate and water ice stability fields on Earth (both water-ice and hydrate are stable to the left of their respective phase boundaries). Gas hydrates are stable and naturally occur in the pressure-temperature conditions of the deep-oceans and polar permafrost areas. In the open oceans they are stable below about 45 atmospheres total pressure; in cold polar areas they occur as part of a compound permafrost horizon at lower pressures (but are not stable at the surface). Natural gas, primarily methane, is held within a water molecule crystal lattice and thermodynamically stabilizes the structure through hydrogen bonding. In the ocean, the Hydrate Stability Zone (HSZ) extends downward from the sediment surface at the sea bottom to a maximum a depth determined by both the local heat flow and water depth (which determines the ambient pressure). The HSZ is thicker in deeper water where hydrostatic pressure is higher. Gas generated in the sediment below the HSZ rises buoyantly in the sediment fluids and can be trapped as hydrate in the HSZ. The resulting reduction in porosity and permeability can turn the base of the HSZ into a gas trap. For this reason, as gas continues to rise from the underlying sediment (or is created by the decomposition of existing hydrate due to the upward migration of the stability field in response to local sedimentation), gas is frequently encountered within the lower part of the HSZ. Approximately 160 to 180 volumes of gas (STP) are concentrated in one volume of solid hydrate.

Figure 3. Detailed diagram of the pressure/temperature phase boundary of methane hydrate in permafrost (from Kvenvolden, 1993). Note that at the mean annual temperatures characteristic of cold climate regions on Earth, the depth to the upper boundary of the hydrate stability zone (HSZ) is effectively determined by lithostatic pressure, while the depth to the base of the zone is determined by the local geothermal gradient. On Mars, the combination of lower mean annual surface temperatures and the expectation of a smaller geothermal gradient are likely to increase the vertical extent of the HSZ by a factor of several.

Figure 4. A combined permafrost and methane hydrate stability zone (HSZ) diagram for the Alaskan North Slope.

Figure 1.

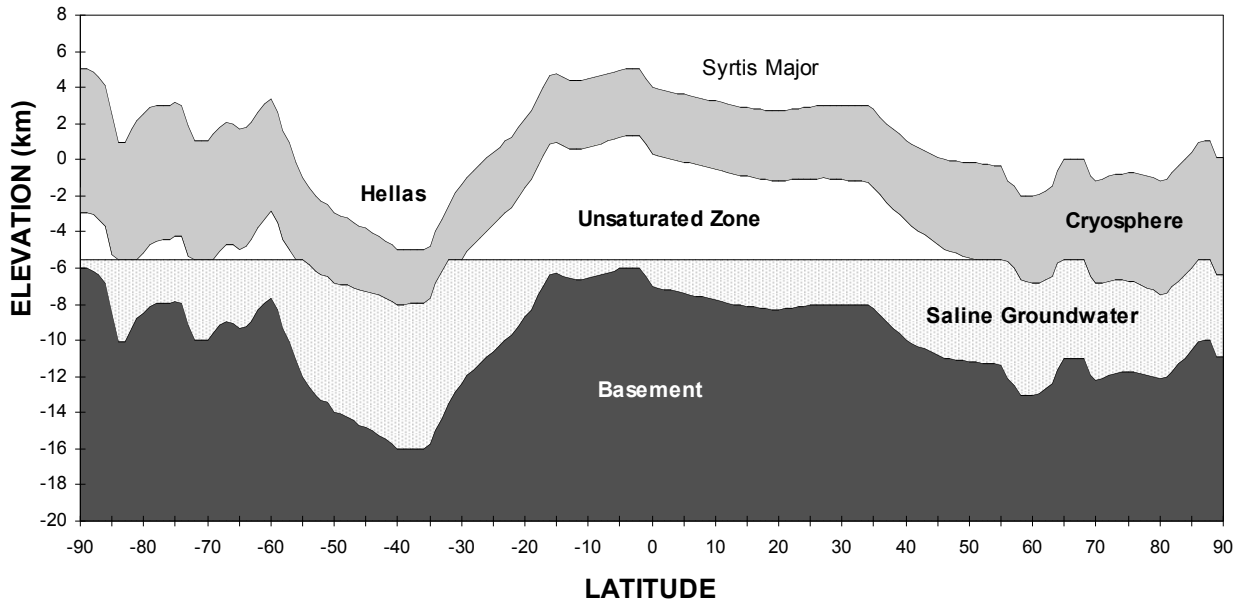


Figure 2.

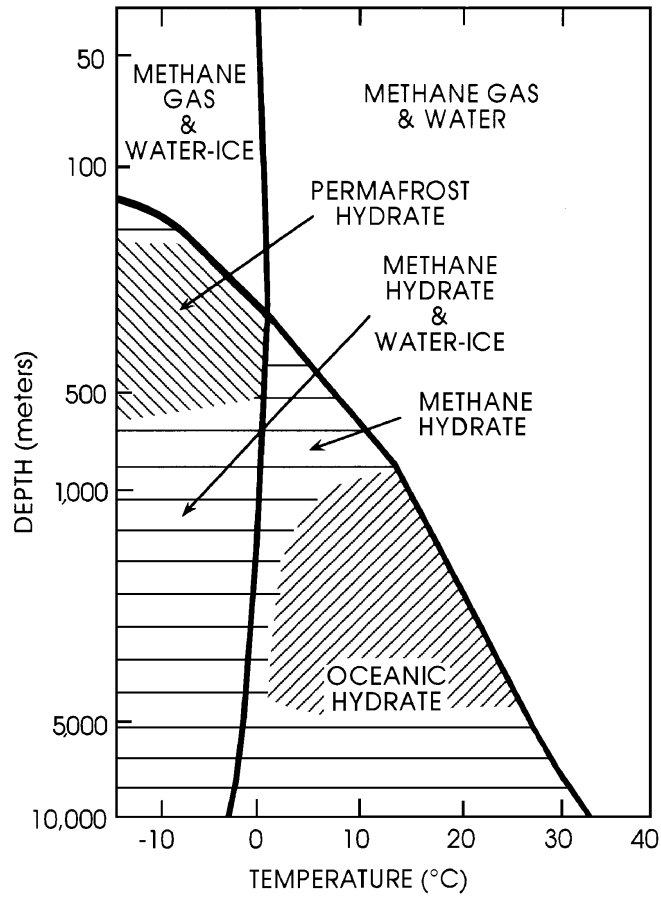


Figure 3.

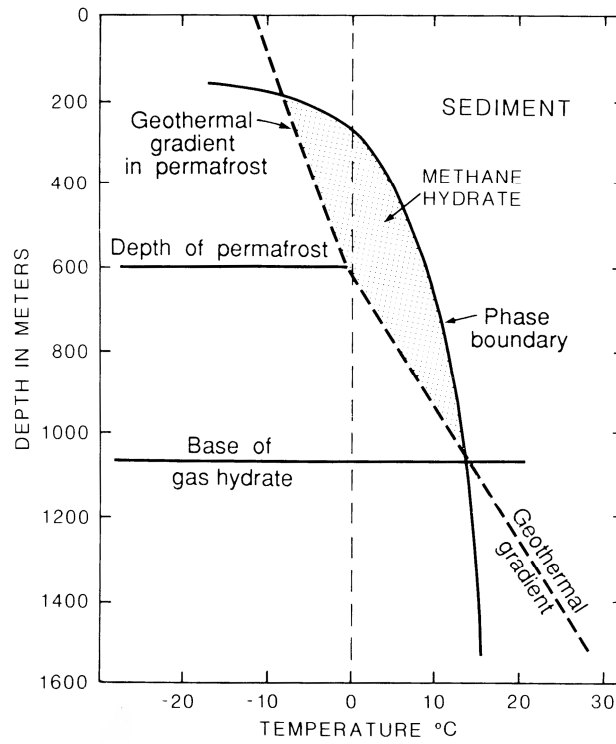


Figure 4.

