

Methane hydrates: A source for slow methane release on Mars? M.E. Elwood Madden¹, J. R. Leeman¹, B. Guttery¹, ¹School of Geology and Geophysics, University of Oklahoma 100 E Boyd, Norman, OK, melwood@ou.edu.

Introduction: Gas hydrates (clathrates) are ice-like materials in which a guest molecule (CO₂, CH₄, ethane, butane, H₂S, etc.) is encapsulated within a rigid cage-like structure of water molecules. At elevated pressure, hydrates can form at temperatures above the freezing point of water, reaching temperatures >300K at pressures exceeding 10 MPa. On Earth, gas hydrates form in organic-rich pore waters along the continental shelf, as well as at the base of permafrost deposits associated with conventional natural gas reservoirs. Gas hydrates are also a likely phase on Mars, forming in carbon-rich regions of the subsurface [1-4]. Colder temperatures at the surface of Mars expand the latitudinal extent of hydrate-favorable regions and shift the top of the hydrate stability zone to shallower depths, relative to terrestrial environments.

Implications: Due to their composition and range of stability, hydrates have the potential to be significant subsurface reservoirs for water and carbon on Mars. The concentration of CH₄ molecules in hydrates far exceeds that in the gas phase alone- one unit volume of CH₄ hydrate contains the equivalent of 168 units of free CH₄ gas at 100 kPa and 273 K. Therefore, only 2000 m³/yr of CH₄ hydrate would be needed to account for recent observations of CH₄ in Mars' atmosphere [5], thus small volumes of hydrates may affect atmospheric composition through formation and dissociation fluxes tied to changes in seasons, obliquity [6, 7] and/or subsurface fluid chemistry [5].

Gas hydrates may also serve as both a sink and a source of biogenic gases and/or nutrients for subsurface biological communities. Terrestrial hydrates form at the base of permafrost deposits when gas concentrations exceed the solubility limits of the hydrate phase. These environments are also likely habitability zones for subsurface microbial communities on Earth and Mars. CH₄ produced through methanogenesis may be trapped as hydrates, thus preventing biogenic gases from reaching the surface [8]. Likewise, dissociation of recent or ancient CH₄ hydrate deposits may release carbon that is then utilized by surrounding biological communities, much as CH₄ hydrate deposits support diverse ecosystems on Earth [9].

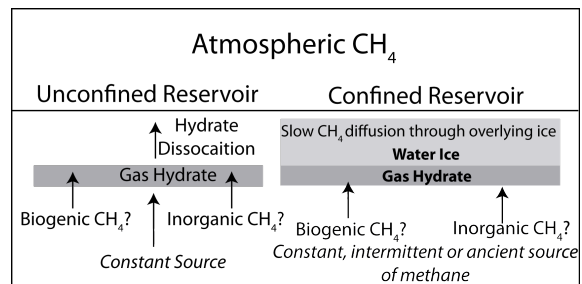
Geologic models of hydrate reservoirs on Mars:

While pressure and temperature conditions within the subsurface of Mars are conducive to gas hydrate formation, P-T conditions alone are not sufficient. CH₄ concentration must be great enough that gas hydrate is a thermodynamically stable phase, and the rate of nucleation must be sufficient for hydrates to form within a geologic timescale. The juxtaposition

of water and guest molecules of sufficient concentration within the same pore-space or fractures requires biologic or geologic processes that produce gas-saturated water or ice within a sealed, closed system [2]. Alternatively, the system could be open to the atmosphere, but in this case, a *constant* source of gas to replenish the hydrate reservoir must also exist [8].

In order to test hydrate reservoir models with observations of CH₄ flux and surface features on Mars, the kinetics of hydrate formation and dissociation processes at Mars-relevant conditions must be determined. Data available for ice-hydrate transformations is very limited and often contradictory since terrestrial hydrate forms predominantly through liquid-gas interactions. The Gas Hydrates Laboratory at the University of Oklahoma is currently conducting low temperature, moderate pressure experiments to determine the rate of hydrate formation and dissociation below the freezing point of water.

Terrestrial analog experiments have demonstrated that hydrate formation and dissociation are both self-limiting processes. The endothermic nature of hydrate dissociation requires additional heat flow to sustain hydrate dissociation. In addition, the large volume change coupled with gas release from hydrate dissociation results in elevated pressures within closed or semi-closed systems, effectively halting further hydrate dissociation. Therefore, natural hydrate melting rates are likely to be slow, especially at low temperatures.



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