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Reduced sulfur–carbon–water systems on Mars may yield shallow methane hydrate reservoirs

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ABSTRACT

Methane clathrate hydrate reservoirs capped by overlying permafrost have been proposed as potential sources of atmospheric methane plumes on Mars. However, the surface flux of methane from hydrate dissociation is limited by the diffusion rate of methane through the overlying ice. Assuming hydrates underlay the entire plume footprint, the maximum diffusion path length is expected to be less than 15 m, depths too shallow to stabilize pure methane hydrates under Mars geothermal and lithostatic conditions at low to mid latitudes. Therefore, pure methane hydrates confined within permafrost could not produce methane surface fluxes of the magnitude observed near the equator. However, the addition of 10% H_2S, a secondary gas commonly associated with methane production on Earth, expands the hydrate stability field, with clathrates expected within 10 m of the surface at the equator and at depths less than 1 m at higher latitudes. This indicates that H_2S would also be expected to be released as well as methane if the plumes have a confined hydrate reservoir source.

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1. Introduction

Recent reports of atmospheric methane plumes with 10–40 ppbv concentrations suggest that methane is being actively released from the surface of Mars (Formisano et al., 2004; Mumma et al., 2009). The short lifetime of methane in the atmosphere of Mars combined with high spatial variability suggests that methane is released through discreet surface pathways from subsurface reservoirs on a seasonal basis (Lefevre and Forget, 2009). Working hypotheses for methane production on Mars include inorganic reaction between hydrogen produced through olivine serpentenization and CO_2 to form methane (Lyons et al., 2005; Oze and Sharma, 2005), biogenic production of methane through anaerobic methanogenesis from hydrogen reacting with carbon dioxide or acetic acid (Chapelle et al., 2002; Geminale et al., 2008; Krasnopolsky et al., 2004), or thermal diagenesis of ancient organic matter.

Closed methane clathrate hydrate reservoirs capped by overlying permafrost could provide a potential concentrated source of methane in the near-subsurface of Mars (Chastain and Chevrier, 2007; Elwood Madden et al., 2007; Prieto-Ballesteros et al., 2006; Thomas et al., 2009). The origin of methane within hydrate reservoirs could be inorganic, biological, or of mixed source. In addition, methane could have been generated at any time in Mars history and trapped within the hydrate reservoir for tens to billions of years prior to release. In order to test this hypothesis, the thermodynamic and kinetic properties of gas hydrates must be evaluated within the context of Mars-relevant permafrost deposits to determine if clathrate reservoirs are a plausible source for the methane plumes observed on Mars.

1.1. C–S–H₂O systems

Terrestrial carbon and sulfur cycles are integrally linked through both inorganic and biological processes. The coexistence of carbon and sulfur on Mars, with sulfur likely in higher concentrations than on Earth (King and McLennan, 2010), suggests the Martian carbon and sulfur cycles are linked as well. Observations of sulfide, sulfate, and carbonate minerals within martian meteorites further support this model (Farquhar et al., 2007; Lorand et al., 2005; Niles et al., 2009). Thermodynamics predicts that both methane and hydrogen sulfide will form under anaerobic, acidic–neutral conditions (Fig. 1) over a wide range of temperatures. On Earth, shallow and deep methane production is often associated with sulfate reduction through both inorganic and biological processes. Inorganic fluid–rock interactions generate hydrogen, which in turn reduces CO_2 and SO_4^{2-} to CH_4 and H_2S, respectively, via the following reactions.

$$4H_2 + CO_2 = CH_4 + 2H_2O \tag{1}$$

$$3H_2 + SO_2 = H_2S + 2H_2O \tag{2}$$
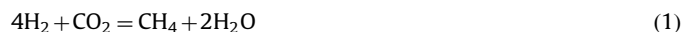
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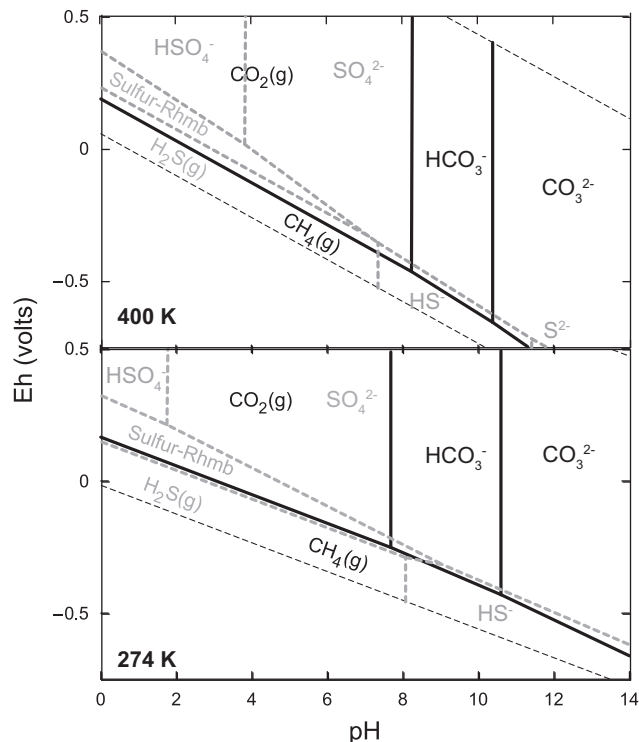
Fig. 1. Eh–pH phase diagrams for C–S–H_2O system at 274 and 400 K. Gray dashed lines and labels represent S species while black solid lines and labels represent carbon species. Methane and hydrogen sulfide are predicted to coexist at neutral–low pH and reducing conditions over the entire range of temperatures investigated. Diagram was constructed using standard thermodynamic dataset in Geochemist's Workbench (Bethke, 1996)

Table 1
Hydrogen sulfide in terrestrial methane hydrate deposits.

Location	H_2S (%)	Reference
S. Australia ODP Leg 182	10–15	Swart et al. (2000)
Vancouver	2–2.5	Hester et al. (2008)
Black Sea	5–6	Popescu et al (2006)
Cascadia	0–10	Kastner et al. (1998)

Microbes can also use the hydrogen produced via fluid–rock interactions to produce methane through methanogenesis (Chapelle et al., 2002). If sulfate is also present in the system, methanogens and sulfate reducers will compete for the hydrogen available. Due to physical heterogeneity, organisms capable of both processes can coexist in the presence of hydrogen and sulfate producing CH_4 and H_2S simultaneously (Lovley et al., 1982). Organic matter and hydrocarbon deposits can also be degraded by low temperature microbial sulfate reduction and higher temperature inorganic thermal sulfate reduction to produce sour gas, a mixture of CH_4 and H_2S (Goldstein and Aizenshtat, 1994).

This overlap in methane and hydrogen sulfide stability is reflected in terrestrial natural gas and gas hydrate deposits, which can contain significant concentrations of hydrogen sulfide, up to 15% in some cases (Table 1). Microbial methane produced in situ as well as thermogenic natural gas transported from deeper reservoirs are often trapped as gas hydrates within seafloor sediments and permafrost on Earth. Gas hydrates form in regions with high methane concentration where the geothermal gradient

intersects the methane hydrate stability field. Methane is released into the overlying pore water or permafrost as hydrates actively decompose at the top of the hydrate stability zone. However, little of this methane ever reaches the atmosphere, as it is consumed by methanotrophic microbes, which oxidize the methane to bicarbonate. Methane oxidation releases hydrogen, which in turn is consumed via microbial sulfate reduction within shallow sediments. Coupled microbial methane respiration and sulfate reduction (reaction (3)) is a common metabolic process in anaerobic sediments associated with gas hydrate deposits on Earth, producing hydrogen sulfide gas and sulfide minerals (Housen and Musgrave, 1996). Similar processes are thought to occur within permafrost systems as well (Dallimore and Collett, 1995; Stotler et al., 2009).

$$CH_4 + SO_4^{2-} = CO_2 + H_2S + 2OH^- \qquad (3)$$

2. Methane clathrate hydrates on Mars

In order to test whether one or more closed gas hydrate reservoirs could produce the methane fluxes observed on Mars, the maximum diffusion path length (thickness of overlying permafrost) was compared to the thermodynamic stability field of mixed CH_4–H_2S hydrates under Mars-relevant geothermal and lithostatic gradients.

2.1. Diffusion

Using a methane diffusion rate of 1.7×10^{-13} m^2 s^{-1} (D_1) Table 2 from the literature determined at $T_1 = 271$ K (Komai et al., 2004) and an activation energy (Ea) of 20 kJ mol^{-1} (Takeya et al., 2002), the Arrhenius equation was used to estimate the rate of methane diffusion (D_2) through ice at Mars-relevant temperatures ($T_2 = 220$ K, Clifford and Parker, 2001), where R is the ideal gas constant:

$$\ln\left(\frac{D_1}{D_2}\right) = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (4)$$

Fick's Second Law of Diffusion, in finite difference form, was applied to estimate the maximum diffusion path (thickness) of overlying ice ($\Delta depth$) which could be present for a range of reservoir sizes:

$$J = -D\frac{\Delta concentration}{\Delta depth} \qquad (5)$$

The flux from the hydrate reservoir (J, mol m^{-2} s^{-1}) is the total number of moles of methane (1.2×10^9) observed in the March 2003 plume (Mumma et al., 2009) divided by the lateral surface area (1–10^{13} m^2) of a potential hydrate reservoir, assuming all the gas was released over a 120 day period. The diffusion coefficient

Table 2
Summary of values used in the model.

Variable	Value	Source
T_1	271 K	Komai et al. (2004)
T_2	220 K	Clifford and Parker (2001)
D_1	1.7×10^{-13} m^2 s^{-1}	Komai et al. (2004)
D_2	2.1×10^{-14} m^2 s^{-1}	This work, Eq. (4)
Ea	20 kJ mol^{-1}	Takeya et al. (2002)
CH_4 in plume	1.2×10^9 mol	Mumma et al. (2009)
Maximum plume footprint	10^{13} m^2	Mumma et al. (2009)
Δ concentration	7700 mol CH_4 m^{-3}	Sloan and Koh (2008)
Heat flow	30 mW m^{-2}	Clifford and Parker (2001)
Permafrost density	2.5 g/cm^3	Clifford and Parker (2001)
Thermal conductivity	2.0 ± 1.0 W m^{-1} K^{-1}	Clifford and Parker (2001)
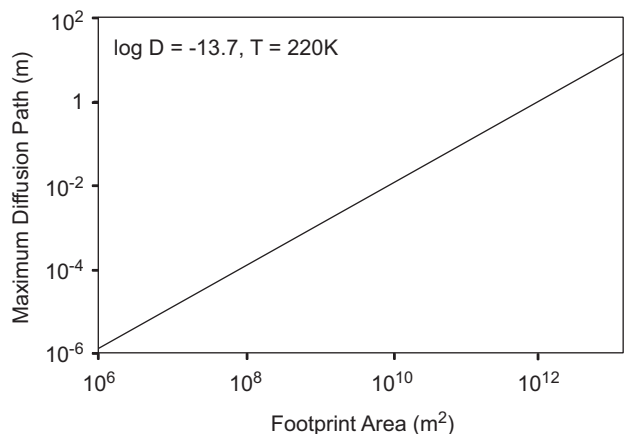
Fig. 2. Maximum diffusion path length for methane through overlying permafrost. Assuming total methane abundance as measured by Mumma et al. (2009), the maximum thickness of overlying permafrost was calculated for hydrate reservoirs with lateral areas ranging from 10^6 to 10^{13} m^2 and the physical footprint of the plume at 220 K.

(*D*) at 220 K (the average surface temperature near the equator Clifford and Parker, 2001) was determined using the Arrhenius equation described above (D_2 in Eq. (4)). Δ *concentration* over the diffusion path was set at 7700 mol m^{-3} methane based on the assumption that the concentration of CH$_4$ is 1: 5.75 H$_2$O molecules (7700 mol m^{-3} hydrate based on a density of 0.95 g/cm^3) at the top of the methane hydrate stability zone (Sloan and Koh, 2008) and the concentration of methane at the base of the atmosphere is negligible. Using these values, the maximum diffusion path through the overlying permafrost (Δ *depth*, m) was determined as a function of reservoir footprint from 10^6 m^2 to the maximum footprint of the observed plume ($\sim 10^{13}$ m^2); (Fig. 2).

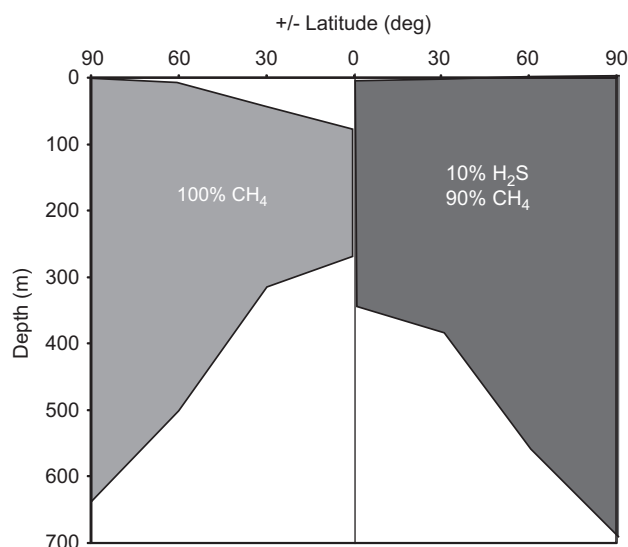### 2.2. CH$_4$–H$_2$S hydrate stability zone

The depth to the top of the hydrate stability zone was predicted by combining geothermal and lithostatic gradients appropriate for water–ice cemented regolith (Clifford, 1993; Clifford and Parker, 2001) calculated at 1 m resolution to determine the *P–T* conditions at depth at $\pm 0°$, $\pm 30°$, $\pm 60°$, and $\pm 90°$ latitudes. Mixed CH$_4$–H$_2$S hydrate stability data from the HYDOFF statistical thermodynamic model (http://hydrates. mines.edu/CHR/Software.html; Sloan and Koh, 2008) were compared to Mars subsurface P–T conditions (Clifford, 1993; Clifford and Parker, 2001) following the technique of Elwood Madden et al. (2007) to determine the depth and thickness of the hydrate stability field for 0%, 1%, 5%, and 10% H$_2$S concentrations.

3. Results and discussion

Our calculations suggest that the diffusion coefficient (*D*) for methane at 220 K is 2.1×10^{-14} m^2 s^{-1} through water ice. Based on this diffusion coefficient, methane hydrates sealed beneath more than 15 m of permafrost cannot produce the flux of methane observed in the plumes of Mars (Fig. 2), assuming the hydrate reservoir footprint is less than the plume footprint reported by Mumma et al. (2009). Therefore, if the source of the methane plume is a gas hydrate reservoir, the clathrate reservoir must be capped by less than 15 m of permafrost. The thermodynamic stability field for pure methane hydrate requires 40–70 m of overlying permafrost for clathrate to be stable at low latitudes on Mars. Only at mid–high latitudes is pure methane hydrate stable at less than 15 m depth below permafrost
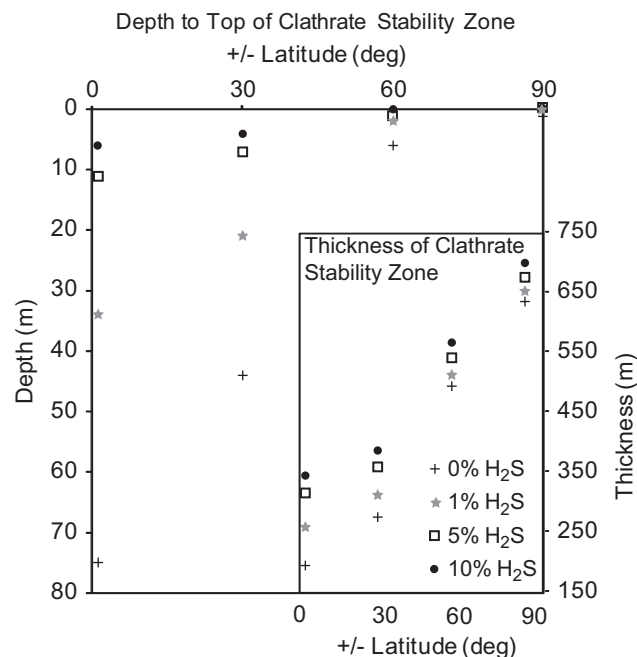
Fig. 3. Depth and thickness of the hydrate stability zone. Thermodynamic modeling predicts CH$_4$–H$_2$S hydrate will be stable at depths within 6 m of the surface at the equator if the hydrate contains 10% H$_2$S. However, pure methane hydrate requires >40 m of overlying permafrost. Addition of H$_2$S also increases the thickness of the hydrate stability zone as the mixed gas clathrate is also stable at elevated temperature. Given the diffusion rate for methane through ice (see Fig. 2), overlying permafrost >15 m thick would limit the flux of methane release to levels below those observed in recent plumes. This suggests that mixed CH$_4$–H$_2$S hydrate may be a potential source for methane plumes observed on Mars.

Fig. 4. Extent of CH$_4$–H$_2$S hydrate stability zone on Mars. The addition of 10% H$_2$S expands the hydrate stability zone, particularly at low latitude relative to the stability zone for pure CH$_4$ hydrate.

(Fig. 3, black crosses). However, the methane hydrate stability field is expanded significantly by adding small concentrations of H$_2$S to the system (Figs. 3 and 4). The addition of small concentrations of H$_2$S is thought to stabilize lattice defects within the clathrate structure as H$_2$S forms hydrogen bonds with the surrounding water molecules. This leads to an expanded

stability field for mixed H_2S hydrate phases (Buch et al., 2009; Kvamme and Forrisdahl, 1993).

Under Mars permafrost conditions, the addition of 1% H_2S to the clathrate structure expands the stability field for methane hydrate to half the depth required for the pure methane phase, bringing the hydrate stability zone within 2 m of the surface at latitudes greater than 60° (gray stars in Fig. 3). At 10% H_2S concentration, methane hydrate is expected to be stable within 6 m of the surface at the equator (black circles in Fig. 3). These H_2S concentrations are well within the range observed for natural methane hydrate deposits on Earth (Table 1). The addition of H_2S also expands the hydrate stability zone to greater depths, allowing a larger volume of methane to be stored within a potential hydrate reservoir (Figs. 3 and 4). The effect of H_2S is particularly large at low latitudes, where methane plumes were observed in 2003 and 2006.

4. Conclusions

Thermodynamics predicts that in C-S-H_2O systems, CH_4 and H_2S will be the dominant species at neutral to acidic pH and reducing conditions. Both phases are commonly observed in terrestrial systems, including gas hydrate reservoirs, and may be produced via both inorganic and biological processes. The abundance CO_2 in the atmosphere and sulfur in the lithosphere on Mars suggests they are both likely present in the subsurface in many environments. Diffusion rates of methane through overlying permafrost suggest that a potential permafrost-capped clathrate source must lie fairly close to the surface to produce the methane plumes observed at low latitudes. While pure methane hydrate requires depths greater than 40 m, the addition of modest concentrations of H_2S expands the hydrate stability zone within 15 m of the surface, depths at which a large hydrate reservoir could produce the observed plume. Therefore, the presence of H_2S in addition to methane in the atmosphere would be expected if the methane is being released from a closed methane hydrate system.

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