Methane escape from gas hydrate systems in marine environment, and methane-driven oceanic eruptions

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1. Introduction

[1] Huge quantities of \( \text{CH}_4 \) are stored in marine sediment in the form of methane hydrate, bubbles, and dissolved \( \text{CH}_4 \) in pore water. Here I discuss the various pathways for methane to enter the ocean and atmosphere, including: (i) Methane hydrate dissolution or dissociation as it rises through seawater. The dissociation rate can be 2 to 3 orders of magnitude greater than the dissolution rate. (ii) The dissolution and expansion of a bubble with or without a hydrate shell as it rises through seawater. There is a critical radius (which depends on depth), above which a bubble would reach the surface or even become larger as it rises. I also propose and model the dynamics of a new type of terrestrial gas-driven eruptions: methane-driven oceanic eruptions. Such eruptions not only represent a yet unrecognized geohazard, but also provide a pathway for \( \text{CH}_4 \) to rapidly enter the atmosphere as a greenhouse gas.


2. Stability of Methane Phases in the Marine Environment

[3] Methane can exist in the marine environment as gas hydrate, free gas or dissolved in water. To illustrate the stability of methane hydrate, methane gas, and dissolved methane in seawater, a phase diagram is constructed for the \( \text{CH}_4 \)-seawater system along a T-P-depth profile similar to Blake Ridge (east of the Carolina coast), a site with a large reservoir of methane in the form of hydrate and gas [Holbrook et al., 1996; Dickens et al., 1997]. Figures 1a and 1b show the temperature and pressure profile. Figure 1c shows the phase diagram along the depth and is explained below. From the sea surface to a shallow depth in the water column (<537 m below sea level, mbsl), methane hydrate is not stable. If total \( \text{CH}_4 \) concentration is low, all \( \text{CH}_4 \) would dissolve in water; if total \( \text{CH}_4 \) concentration is greater than the solubility (which increases roughly linearly with depth to 0.127 wt% (0.081 mol/L) at 537 mbsl [Duan et al., 1992]), then extra \( \text{CH}_4 \) would be in the gas phase (bubbles). From 537 mbsl to 3225 mbsl (450 m below seafloor, mbsf), methane hydrate is stable if \( \text{CH}_4 \) concentration in the system is high enough. The formation of methane hydrate limits the solubility of \( \text{CH}_4 \) in water [Dickens and Quinby-Hunt, 1994]. From 537 mbsl to the seafloor (2775 mbsl), temperature decreases slightly with increasing depth and the requisite pressure for hydrate formation decreases. Hence, hydrate becomes more stable with increasing pressure, leading to a slight decrease in the solubility of \( \text{CH}_4 \) from 0.127 wt% at 537 mbsl to 0.107 wt% at 2775 mbsl. From 2775 mbsl to 3225 mbsl (seafloor to 450 m bslf), temperature increases with depth, and hence the formation pressure of methane hydrate increases with depth. Therefore, methane hydrate stability decreases and \( \text{CH}_4 \) solubility in pore water increases with depth to 0.3 wt% at 3225 mbsl. Below this depth, methane hydrate is not stable due to high temperatures. Instead, oversaturation of \( \text{CH}_4 \) leads to the formation of gas bubbles in pore water. For other locations, temperature profiles and water depths can differ, leading to different phase diagrams. For example, if water depth is only 500 m and the temperature-depth profile is the same as the top 500 mbsl at the Blake Ridge, there would be no hydrate stability field.

3. Methane Escape Mechanisms

3.1. Rise of Hydrate

[4] Density of hydrate is smaller than that of seawater. Whether released hydrate would rise depends on how much sediment is mixed in it. If mixing of sediment is insignificant, methane hydrate would rise buoyantly through the water column either individually or collectively with other hydrate
calculated from equilibrium with methane hydrate is more stable, the solubility is calculated based on total CH4 concentration in pore water due to decomposition of organic matters before any modification by mass transport or compaction. See Dickens et al. [1997] for actual total CH4 concentration profile in pore water.

crystals. We have extended the model of Kerr [1995] to high Reynolds numbers to calculate the convective dissociation rate upon buoyant rising, and the model of McLeod and Sparks [1998] to calculate convective dissociation rate upon rising [Zhang and Xu, submitted]. In deep water, hydrate dissociates as it rises. At 4°C (for deep water), a typical calculated convective dissociation rate is 0.2 to 0.3 mm/s. A crystal with an initial radius of 5.2 mm would dissolve completely after a 2000-m rise. In shallow water, hydrate dissociates as it rises. At 20°C (for shallow water), a typical calculated convective dissociation rate is 0.1 mm/s, greater than the dissolution rate in deep water by 2 to 3 orders of magnitude. A crystal with an initial radius of 5 mm would completely dissociate after only a 3-m rise. Modeling using a more realistic temperature-depth profile shows that hydrate chunks larger than 100 mm radius would be able to survive dissociation through a 530-m surface layer and reach the ocean surface [Zhang and Xu, submitted].

3.2. Rise of a Bubble

If methane bubbles are released slowly into shallow seawater where hydrate is not stable (e.g., <537 mbsl, Figure 1c), bubbles rise through water individually or in streams [Brewer et al., 1997; Clark et al., 2000; Leifer et al., 2000]. As a bubble rises, it dissolves in seawater (which is almost always CH4-undersaturated), and expands as the pressure decreases. The dissolution makes the bubble smaller. The expansion makes the bubble larger. Whether the size of the bubble would increase or decrease depends on the interplay between dissolution and expansion. Zhang and Xu [2001] developed a model for the convective dissolution rate of a spherical bubble as it rises buoyantly through seawater, but nonspherical bubbles (those with radius greater than 1.5 mm) can only be roughly treated. For a given depth, there is a critical bubble size, above which bubble size increases, and below which the bubble size decreases as it dissolves and rises. The critical radius for a bubble to survive 50-m rise is 0.9 mm. Bubble rise velocity is typically <0.3 m/s.

3.3. Rise of a Bubble With Hydrate Shell

If a methane bubble is released into deep water where methane gas and water would react to form hydrate (≥537 mbsl, Figure 1c), a thin hydrate shell may form on the bubble. As the bubble with a thin hydrous shell rises, hydrate would dissolve. Furthermore, gas in the bubble would expand, cracking the hydrate shell. Nevertheless, any new contact between CH4 in the bubble and seawater would lead to new hydrate formation. Hence there would be a delicate balance between dissolution of methane hydrate shell, and its reformation, leading to a steady-state CH4 mass loss from the bubble. Since hydrate is more stable than CH4 gas, the solubility of hydrate in seawater is smaller than that of a CH4 bubble. Hence the formation of a hydrate shell slows down the dissolution. Calculation shows that if the initial bubble radius is 3 mm or greater, the bubble with hydrate shell would be able to survive from any depth to shallow water.

3.4. Methane-Driven Ocean Eruptions

In the special case of a sudden release of a large amount of pore water that is oversaturated with methane (containing hydrate and bubbles), such as during a large landslide, a methane-driven ocean eruption may occur. This would be similar to CO2-driven lake eruptions [Kling et al., 1987; Sigurdson et al., 1987; Sigvaldason, 1989; Zhang, 1996; Halbachwaich and Sabroux, 2001]. Gas-driven ocean eruptions have also been hypothesized to resurface Europa [Crawford and Stevenson, 1988].

If CH4-bearing water is released to shallow seawater (e.g., <537 mbsl, Figure 1c), methane hydrate is unstable. With a high bubble number density (number of bubbles per unit volume of water), bubbles would rise collectively as a bubbly water plume because bubbly water has a lower overall density than the surrounding water. As the bubbly plume rises, the volume of the gas phase expands due to pressure reduction. Hence, the density of the bubbly water decreases further, leading to more rapid buoyant rise of the bubbly water plume (Figure 2). This strong positive feedback is similar to what happens in CO2-driven lake eruptions [Zhang, 1996], although the smaller solubility of CH4 in water means that the eruption velocity would be smaller under the same saturation pressure.

If hydrate- and bubble-bearing pore water oversaturated in CH4 is released to deep water (>537 mbsl, Figures 1c and 2), methane hydrate is stable, and CH4 gas bubbles may react rapidly with water to form hydrate shells. Although there is always relative motion between hydrate, bubbles and
are modeled below, following the analyses for CO2-driven eruptions. Combining equation 1 and the gas-water Bernoulli equation, and integrating, the following equation can be obtained:

\[
\frac{1}{2} u^2 = \lambda \frac{\rho'}{\rho} \ln \left( \frac{P_0}{P_{\text{exit}}} \right) - \lambda \frac{P_0}{P_{\text{exit}}} - \lambda \frac{\rho'}{\rho} \frac{RT}{P_0} \ln \left( \frac{P_0}{P_{\text{exit}}} \right) + \delta_0 \left[ RT \ln \left( \frac{P_0}{P_{\text{exit}}} \right) - \frac{P_0}{P_{\text{exit}}} \right].
\]  

where \( P_{\text{exit}} \) is the exit pressure at the sea level, \( u \) is the velocity of the bubbly flow as it exits the ocean surface, and \( g \) is acceleration due to gravity.

[10] A more realistic model for the dynamics of CH4-driven water eruptions would require consideration of entrainment and disequilibrium. Entrainment is especially important if the volume of release is small. Owing to the simplifying assumptions, equation 2 and the results below should be considered semi-quantitative. Figure 3 shows calculated maximum exit velocity as a function of the initial depth (at which methane hydrate dissociates to methane gas and water) for several \( \delta_0 \) values and with \( \lambda = 0.034 \). Because the Ostwald solubility coefficient for CH4 is smaller than that for CO2 by a factor of about 30, CH4-driven eruptions are much less violent under the same saturation conditions. For example, if initial water depth is 208 m and \( \delta_0 = 0 \), the maximum exit velocity would be only 18 m/s for CH4-driven water eruptions, compared to 89 m/s calculated for CO2-driven Lake Nyos eruption [Zhang, 1996]. However, the oceans are much deeper than lakes and mass and concentration of CH4 in released pore water can be very large. For example, a 2000 km² landslide [Bugge et al., 1987; Maslin et al., 1998; Rothwell et al., 1998] might release pore water containing \( \geq 1 \) Gt CH4, 1000 times the volume of CO2 released in the 1986 eruption of Lake Nyos [Kling et al., 1987]. The dissociation of thin hydrate shells and small hydrate crystals can also contribute initial CH4 gas \( (\delta_0 > 0) \) in a large volume of water. Consequently, CH4-driven oceanic eruptions have the potential to achieve greater exit velocities than CO2-driven lake eruptions. Direct measurements show that pore waters in marine sediment may average

Figure 2. A schematic diagram for the dynamics of methane-driven eruptions. Rectangles represent methane hydrate crystals and aggregates; circles represent bubbles; double circles represent bubbles with methane hydrate shell.

Figure 3. Calculated maximum exit velocity (using equation 2) as a function of initial depth. Fraction on each curve indicates the initial mass fraction of the gas phase \( (\delta_0) \). The calculation is done for an exit pressure of 1 bar, \( T = 280 \) K, and \( \lambda = 0.034 \). The results are semi-quantitative because shallow water entrainment and disequilibrium between the gas phase and water are ignored.
1.1 wt% total CH₄ [Dickens et al., 1997]. With such a concentration at 500 mbsl, the maximum exit velocity would be 110 m/s. With high exit velocity and large amounts of gas, oceanic eruptions could be very violent.

[12] In addition to the solubility difference between CO₂-driven and CH₄-driven water eruptions, another difference between them is that CH₄ gas is less dense than air whereas CO₂ gas is denser than air. Hence erupted CH₄ gas is expected to rise buoyantly into the atmosphere, instead of forming a ground-hugging “ambioructic” flow [Zhang, 1996], which was the killing agents in CO₂-driven eruptions. Therefore, CH₄-driven eruptions would only impact on those in the direct path of the rising column. Such eruptions would also provide a pathway for CH₄ in marine sediment to rapidly enter the atmosphere as a greenhouse gas.

[13] Methane-driven oceanic eruptions requires major slumps or other major disturbances. Such conditions are more easily met when there was wholesale warming of ocean bottom water. Hence, the thermal maximum at the Paleocene-Eocene boundary would be an optimum time for such eruptions, leading to rapid CH₄ transfer to the atmosphere. Furthermore, the magnitude of δ¹³C excursion (about −3%) [Dickens et al., 1995; Kennett et al., 2000]) is quantitatively consistent with CH₄ reaction with dissolved oxygen in deep seawater, as shown below. The concentration of dissolved O₂ is about 0.00022 M and that of HCO₃⁻ is 0.0023 M, with a [O₂]/[HCO₃⁻] concentration ratio of about 0.1. One mole of CH₄ reduces two moles of O₂. Hence complete depletion of deep water O₂ by oxidation of CH₄ would contribute 5% of total dissolved HCO₃⁻ in seawater. Assuming an average of δ¹³C of −60‰ for CH₄ and 0‰ for HCO₃⁻, the resulting extent of δ¹³C is 0.05 × (−60‰), about −3‰. Locally the excursion can be greater or smaller because both dissolved O₂ content and the δ¹³C value of CH₄ may vary. The depletion of dissolved O₂ in deep seawater would have major environmental consequences.

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References


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