



Controls on methane hydrate formation and decomposition

Methane hydrates are ice-like solids composed of rigid cages of water molecules that enclose principally methane under high pressure and low temperature conditions.

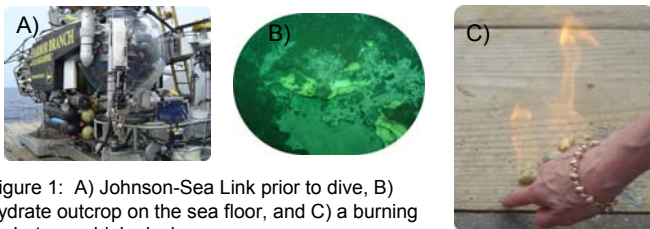


Figure 1: A) Johnson-Sea Link prior to dive, B) hydrate outcrop on the sea floor, and C) a burning hydrate on ship's deck.

OVERVIEW

Methane hydrates are found worldwide in continental shelf sediments and permafrost¹. The global hydrate reservoir may contain around 10^{16} kg of methane carbon, about twice the amount of carbon stored in fossil fuels². If this estimate is correct, hydrates could represent the largest source of hydrocarbons on Earth. It is therefore important to understand the processes controlling gas hydrate formation and dissociation under current sea-floor conditions.

A conceptual model of the processes controlling methane formation and decomposition is proposed in Figure 1. The dissolution and precipitation of methane from the hydrate to the surrounding pore-water (Figure 2A) and biogeochemical processes affecting the methane gas (Figure 2B) will be addressed in this study.

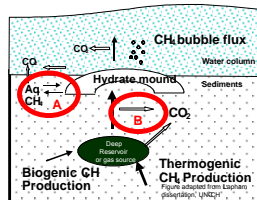


Figure 2: A conceptual model of methane sources and sinks at a hydrate site.

RESEARCH HIGHLIGHTS

A. Goal: To understand the dissolution and precipitation of methane from the hydrate mound.

- In situ gas concentrations are needed to understand dissolution and precipitation of hydrate.
- Traditional coring releases gas upon ascent in water column.
- We need to develop a pore-water device to collect *in situ* samples.

Approach: Develop a sea-floor probe, deployed by submersible.

- Pore-waters are collected at discrete depths and stored in pressure tight chambers for determination of methane concentrations (Figure 3). Samples can be taken adjacent to hydrate.



Figure 3: Probe near hydrate.

Results:

- Probe methane concentrations that were not allowed to decompress were higher than those found in cores (Figure 4A) and in earlier version of probe which decompressed upon ascent (Figure 4B).

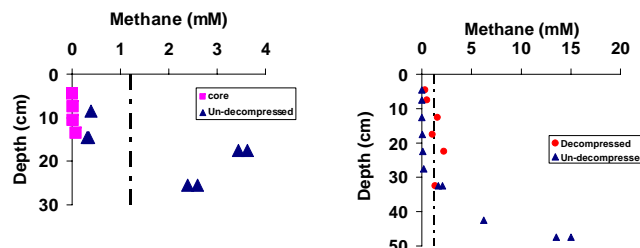


Figure 4: Un-decompressed pore-water probe data compared to A) traditionally collected core and B) an earlier version of the probe which was allowed to decompress. Dashed line represents the saturated concentration at 1-atm.

B. Goal: To understand the biogeochemical processes affecting dissolved methane near the hydrate mounds.

- Methane could be consumed by microbially-mediated anaerobic methane oxidation or produced by methanogens in the shallow sediments surrounding the hydrate mounds.

Approach: Use stable carbon isotopes ($\delta^{13}\text{C}$) to determine the possible biogeochemical processes affecting dissolved methane.

$$\delta^{13}\text{C}(\text{‰}) = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000$$

- where $R = ^{13}\text{C}/^{12}\text{C}$
- As methane is microbially-oxidized, the $\delta^{13}\text{C}$ value of the remaining methane becomes more enriched in the heavy isotope. It becomes more depleted when methane is produced.

Results:

- Figure 5 shows possible microbial activity changing methane isotopic ratio as a transect from mound.

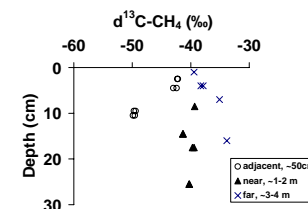


Figure 5: Stable carbon isotopes as a transect from hydrate mound.

GLOBAL SIGNIFICANCE

Gas hydrates are the largest known hydrocarbon source on Earth. However, little is known of what controls their formation and decomposition in shallow sediments. This study begins to shed light on how dissolution and biogeochemical processes may influence the hydrates. By developing the novel submersible-deployed sea-floor probe, future work will quantify these processes and determine their role in hydrate formation and decomposition.

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References: ¹E. Suess, et al. *Sci. American*, 76-83 (1999);
²K. A. Kvenvolden. *Chem. Geol.* 71, 41-51 (1988).