Workshop Outline

- Finding gas hydrate in nature
- Characterizing gas hydrate occurrences
- Can methane be extracted for profit?
- Gas hydrate formation & breakdown
  (Geologic time)
Gas hydrate formation: what is needed?

Ruppel et al. (2017), Rev of Geophysics
Gas hydrate formation: what is needed?

In addition to high pressure and low temperature, methane gas hydrate needs ... **methane**

Ruppel et al. (2017), Rev of Geophysics
Gas hydrate requires a concentration of methane

\[ \sim 6 \text{ water molecules per methane in hydrate} \]
Gas hydrate requires a concentration of methane

\sim 6 \text{ water molecules per methane in hydrate}

\sim 750 \text{ water molecules per methane in water contacting hydrate}
Methane solubility in water

Solubility (moles CH₄/kg water)

Temperature (°C)
Methane solubility in water

Solubility (moles CH₄/kg water)

Temperature (°C)

[Graph showing the decrease in methane solubility with increasing temperature]
Methane solubility in water

Solubility (moles CH\textsubscript{4}/kg water)

Temperature (°C)

High Pressure

Low Pressure
Methane solubility in water

Solubility (moles CH₄/kg water)

Temperature (°C)

High Pressure
Low Pressure
Methane solubility in water
Methane solubility in marine sediment

Location of free gas and gas hydrate is limited by the concentration of methane in the pore water

Xu and Ruppel (1999), JGR
Gas hydrate needs a continuous supply of methane.
Gas hydrate needs a continuous supply of methane

NOAA Okeanos Explorer Exp. 1402 (2014)
Gas hydrate needs a continuous supply of methane

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Gas hydrate needs a continuous supply of methane

NEPTUNE Canada, Dive R1546 (2012)
Where does the methane come from?

Methane requires organic carbon to break down

Ruppel et al. (2017), Rev of Geophysics
How does organic material break down?

Beaudoin et al. (2014), UNEP
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Pohlman et al. (2009), EPSL
How does organic material break down?

- Microbial: shallow, near gas hydrate

Pohlman et al. (2009), EPSL
How does organic material break down?

- **Microbial**: shallow, near gas hydrate
- **Thermogenic**: very deep, so methane needs to be transported up to form hydrate

Pohlman et al. (2009), EPSL
Much of what we find is microbial

Offshore India (NGHP)

Kida et al. (2018), JMPG
Much of what we find is microbial

- Offshore Japan (Nankai) (Uchida et al. (2009), AAPG)
- Offshore Korea (UBGH) (Ryu et al. (2013), JMPG)
- Gulf of Mexico (GC955) (Phillips et al. (2019), AAPG)

Offshore India (NGHP)

Kida et al. (2018), JMPG
What do microbes need to produce methane?

Organic material provides "electron donors"

Whiticar et al. (1986), Geochim. Cosmo. Acta
What do microbes need to produce methane?

Organic material provides “electron donors”

Reaction also needs “electron acceptors”

\[ \text{O}_2 > \text{NO}_3^- > \text{MN(II)} \]

\[ > \text{Fe(III)} > \text{SO}_4^{2-} > \text{CO}_2 \]

(Reeburgh (2007), ChemRev)

Whiticar et al. (1986), Geochim. Cosmo. Acta
Where are the electron donors and acceptors?

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(Reeburgh (2007), ChemRev)

Interfaces where grain size changes!

D’Hondt et al. (2004), Science
Coarse/fine interfaces can be within the “reservoir”

Fujii et al. (2015), JMPG
Faults can provide fluid to thin sands above the reservoir

Boswell et al. (2018), JMPG
Solubility dependence on pressure, temperature... and pore size

Liu and Flemings (2011), JGR
Solubility dependence on pressure, temperature... and pore size

Additional methane required to form hydrate in small pores

Liu and Flemings (2011), JGR
Solubility difference provides a way to make hydrate!

Malinverno (2010), EPSL
Solubility difference provides a way to make hydrate!

Concentration difference makes methane diffuse into the sand

Malinverno (2010), EPSL
Solubility difference provides a way to make hydrate!

Daigle et al. (2018), FITI
Solubility difference provides a way to make hydrate!

Methane-rich fluid can get pumped into the sand due to compaction in the fines

Daigle et al. (2018), FITI
Open research question: where ARE the microbes most active?

Organic material provides \textit{“electron donors”}

Reaction also needs \textit{“electron acceptors”}

\begin{align*}
O_2 & > NO_3^- > MN(II) \\
> Fe(III) & > SO_4^{2-} > CO_2
\end{align*}

(Reeburgh (2007), ChemRev)

How fast is methane being produced?
What would cause hydrate to dissociate?

Bottom water warming (heating)
Distributions of hydrate and future warming

Global distribution of methane hydrate

Bottomwater temperature trend for the next 100 years

Not all hydrate is at risk from warming

Deepwater hydrates:
Assume 1°C bottom water warming per 1000 years,
Assume 1000 m water depth

Beaudoin et al. (2014), U.N. Environmental Programme
Not all hydrate is at risk from warming

Sediment thermal conductivity: 1-2 W/(m·K)

- Heat takes a *long* time to reach the base of hydrate stability.

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Sediment thermal conductivity: 1-2 W/(m·K)

- Heat takes a long time to reach the base of hydrate stability.
- Slow thermal process likely allows system to equilibrate, with hydrate slowly dissociating and reforming higher in the sediment column.

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Assume 1000 m water depth

Beaudoin et al. (2014), U.N. Environmental Programme
Shallow and high-latitude hydrates are more at risk

Global distribution of methane hydrate (present day)

Global distribution of methane hydrate (100-year prediction)

Shallow and high-latitude hydrates are more at risk

Global distribution of methane hydrate (present day)

Global distribution of methane hydrate (100-year prediction)

Why are the high-latitude hydrates at risk?

Arctic gas hydrates are generally found in permafrost environments, stable because of the cold temperatures rather than the high pressures experienced in marine environments.

Ruppel et al. (2016), Geochem., Geophys., Geosystems
Why are the high-latitude hydrates at risk?

~13,500 years ago: low sealevel, extensive permafrost, hydrate likely stable to the shelf break.
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Present day – flooding of the shelf mostly destabilized the permafrost and underlying hydrate.

Alternative present-day view has all permafrost and hydrate gone.

Brothers et al. (2016), Geochem., Geophys., Geosystems
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Ice-bearing permafrost (IBPF) has high velocity, like hydrate. Velocity break indicates the extent of IBPF.

Brothers et al. (2016), Geochem., Geophys., Geosystems
Similar permafrost breakdown seen in the Russian Arctic

Gas flares in the water indicate the presence of gas migrating up through the discontinuous permafrost seal.

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Breaking down permafrost via “warm” water flooding

Shallow, Arctic hydrates:
Assume ~15°C ground surface increase ~13,500 years ago.

- Like the deepwater case, there is a small amount of dissociation at the base of hydrate stability.
  - Slow to develop
  - Gas can recycle upward to reform as stable hydrate.

Beaudoin et al. (2014), U.N. Environmental Programme
Breaking down permafrost via "warm" water flooding

• Flooding the shelf provided quick access to a large, relatively warm, salty heat reservoir:
  • Large thermal gradient to drive heat downward.
  • Chemical gradient to reduce ice and hydrate stability.
  • Dissociation at the top of the reservoir that cannot trap released gas.

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Another “at-risk” region: the shallowest marine hydrates

Deeper, colder water allows for a thicker stability zone

Modified by Dillon, USGS
Another “at-risk” region: the shallowest marine hydrates

In shallow water, the stability zone is very thin

At this edge of stability, small temperature changes can destabilize hydrate near the seafloor

Modified by Dillon, USGS
Another “at-risk” region: the shallowest marine hydrates

- Unlike the deepwater case:
  - Dissociation occurs in tens of years.
  - Gas can not recycle upward to reform as stable hydrate.

Shallow hydrates, no permafrost:
Assume +3°C per 100 years bottom water temperature, and only ~320 m water depth.

Beaudoin et al. (2014), U.N. Environmental Programme
Another “at-risk” region: the shallowest marine hydrates

- Unlike the deepwater case:
  - Dissociation occurs in tens of years.
  - Gas can not recycle upward to reform as stable hydrate.

- Globally, the hydrates at risk in this region represent less than 3.5% of the global hydrate distribution, but methane released likely does not reach the atmosphere.

Shallow hydrates, no permafrost:
Assume +3°C per 100 years bottom water temperature, and only ~320 m water depth.

Ruppel (2011), Nature Knowledge
A faster cause for hydrate dissociation

Drop in sea level (depressurization)
Do the possible dissociation mechanisms cause debris flows?

Model reconstructions of slumps suggest slump failures are not at the base of hydrate stability.

Hornbach et al. (2007), Geochem., Geophys. Geosystems
Do the possible dissociation mechanisms cause debris flows?

Model reconstructions of slumps suggest slump failures are not at the base of hydrate stability

Cape Fear Slide (offshore USA)

Hornbach et al. (2007), Geochem., Geophys. Geosystems
Do the possible dissociation mechanisms cause debris flows?

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Storegga Slide (offshore Norway)

Mienert et al. (2005), Marine Petroleum Geology
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Upper portion dominated by bottom-water warming (destabilizing for hydrate)

Lower portion dominated by sea level rise (stabilizing for hydrate)

Mienert et al. (2005), Marine Petroleum Geology
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Upper portion dominated by bottom-water warming (destabilizing for hydrate)

Lower portion dominated by sea level rise (stabilizing for hydrate)

Slide began near the toe, where hydrates were becoming more stable.

Storegga Slide (offshore Norway)

Kvalstad et al. (2005), Marine Petroleum Geology
Catastrophic release does not seem likely. What about sustained release of methane?
Is modern climate change destabilizing the shallow-water hydrate?

Atlantic Margin gas plumes (offshore USA)

Skarke et al. (2014), Nature Geoscience
Is modern climate change destabilizing the shallow-water hydrate?

Atlantic Margin gas plumes (offshore USA)

Chronic, long-term methane release at sea-floor seeps, but is it dissociation?

Atlantic Margin gas plumes (offshore USA) by Skarke et al. (2014), Nature Geoscience
Is modern climate change destabilizing the shallow-water hydrate?

West Spitsbergen Margin (offshore Svalbard, Norway)

Westbrook et al. (2009), GRL
Is modern climate change destabilizing the shallow-water hydrate?

Seeps are mainly just shallower than the hydrate stability limit

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Westbrook et al. (2009), GRL
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• Modern bottom water warming was thought to be causing hydrate breakdown and methane release….

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- Carbonate dating suggests the venting here and on the Atlantic Margin has been going on for thousands of years.

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Kvalstad et al. (2005), Mar. and Pet. Geol.; Skarke et al. (2014), Nature Geoscience
Is modern climate change destabilizing the shallow-water hydrate?

- Modern bottom water warming was thought to be causing hydrate breakdown and methane release….

- Carbonate dating suggests the venting here and on the Atlantic Margin has been going on for thousands of years.

- Hydrate dissociation due to modern climate change may contribute to observed methane releases, but is not likely the sole or even the primary source.

Kvalstad et al. (2005), Mar. and Pet. Geol.; Skarke et al. (2014), Nature Geoscience
Does the methane make it to the atmosphere?

- Surface water and air sampling do not show any methane contribution from the underlying seeps on the West Spitsbergen Margin.

West Spitsbergen Margin
(offshore Svalbard, Norway)

Myhre et al. (2016), GRL
Does the methane make it to the atmosphere?

- Surface water and air sampling do not show any methane contribution from the underlying seeps on the West Spitsbergen Margin.

- Beyond 30-m water depth, methane from seafloor seeps was only ~10% of the overall methane detected in surface waters for water offshore northern Alaska.

U.S. Beaufort Sea Shelf (offshore Alaska, USA)

Sparrow et al. (2018), Science Advances
Microbial consumption of dissolved methane

Methane appears to be getting converted to carbon dioxide by microbes in the sediment and water column.

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

Valentine et al. (2001), Geochim et Cosmochim Acta
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- Oxygen depletion

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- Acidification

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Valentine et al. (2001), Geochim et Cosmochim Acta
Big Ideas: gas hydrate over geologic time

- Formation: sediment index properties, solubility and organic carbon are all important, but we still don’t know where methane is being formed, or at what rates.
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- Dissociation: “Feather edge” hydrates most at risk from climate, but released methane is consumed in the water column.
Big Ideas: gas hydrate over geologic time

- Formation: sediment index properties, solubility and organic carbon are all important, but we still don’t know where methane is being formed, or at what rates.

- Dissociation: “Feather edge” hydrates most at risk from climate, but released methane is consumed in the water column.

- Methane release:
  - Oxygen loss
  - Acidification
  - Potential secondary hydrate

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]
Opportunity to present your own ongoing work

Gordon Research Conference
Natural Gas Hydrate Systems

• ~100 people
• Galveston, Texas, USA
• Abstracts Due January 25/26, 2020

Gordon Research Seminar: Feb. 22-23, 2020

• Graduate students and early career researchers only


• Researchers at all levels, from all over the world
• Goal – foster collaboration, get feedback on your ideas
• 5 talks per day, posters remain up 2-3 days each, a lot of time for discussions