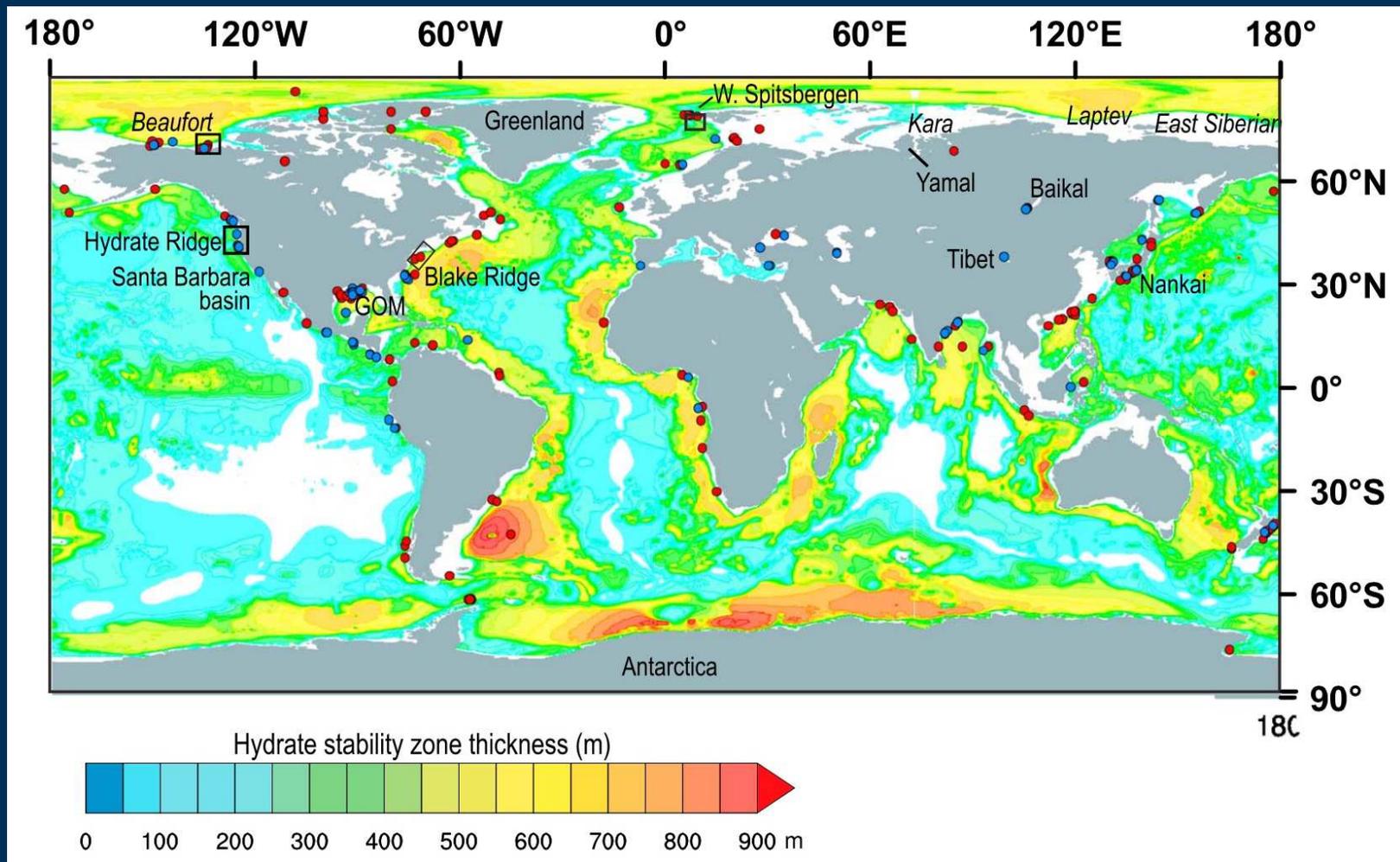


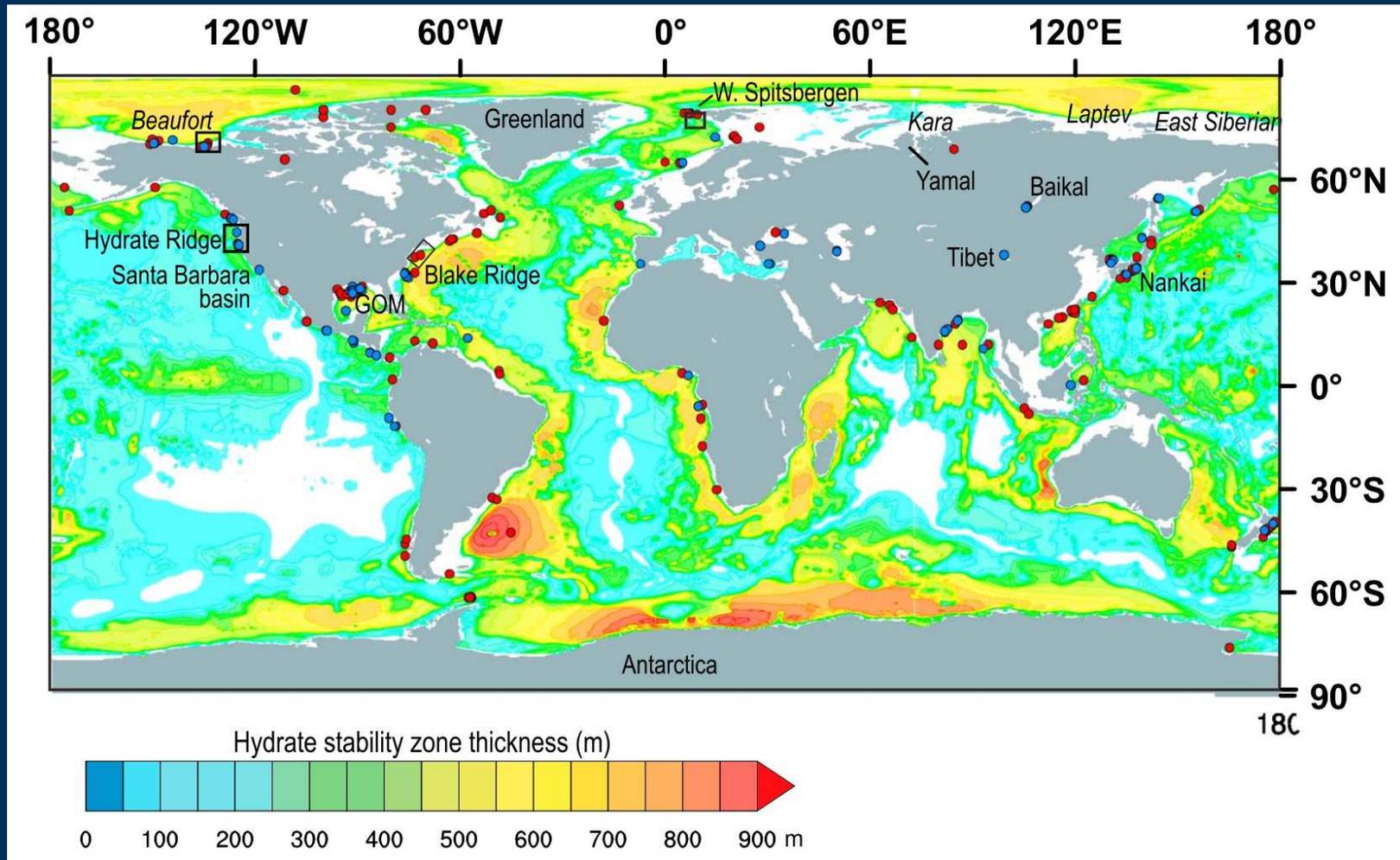
# Workshop Outline

- **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?



# Gas hydrate formation: what is needed?

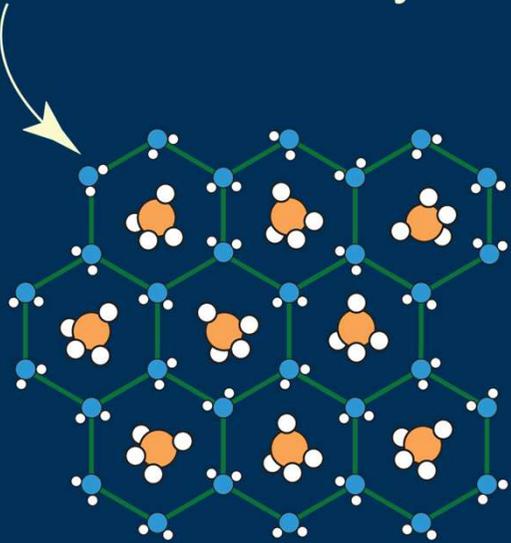


In addition to high pressure and low temperature, methane gas hydrate needs ... ***methane***

Ruppel et al. (2017), Rev of Geophysics

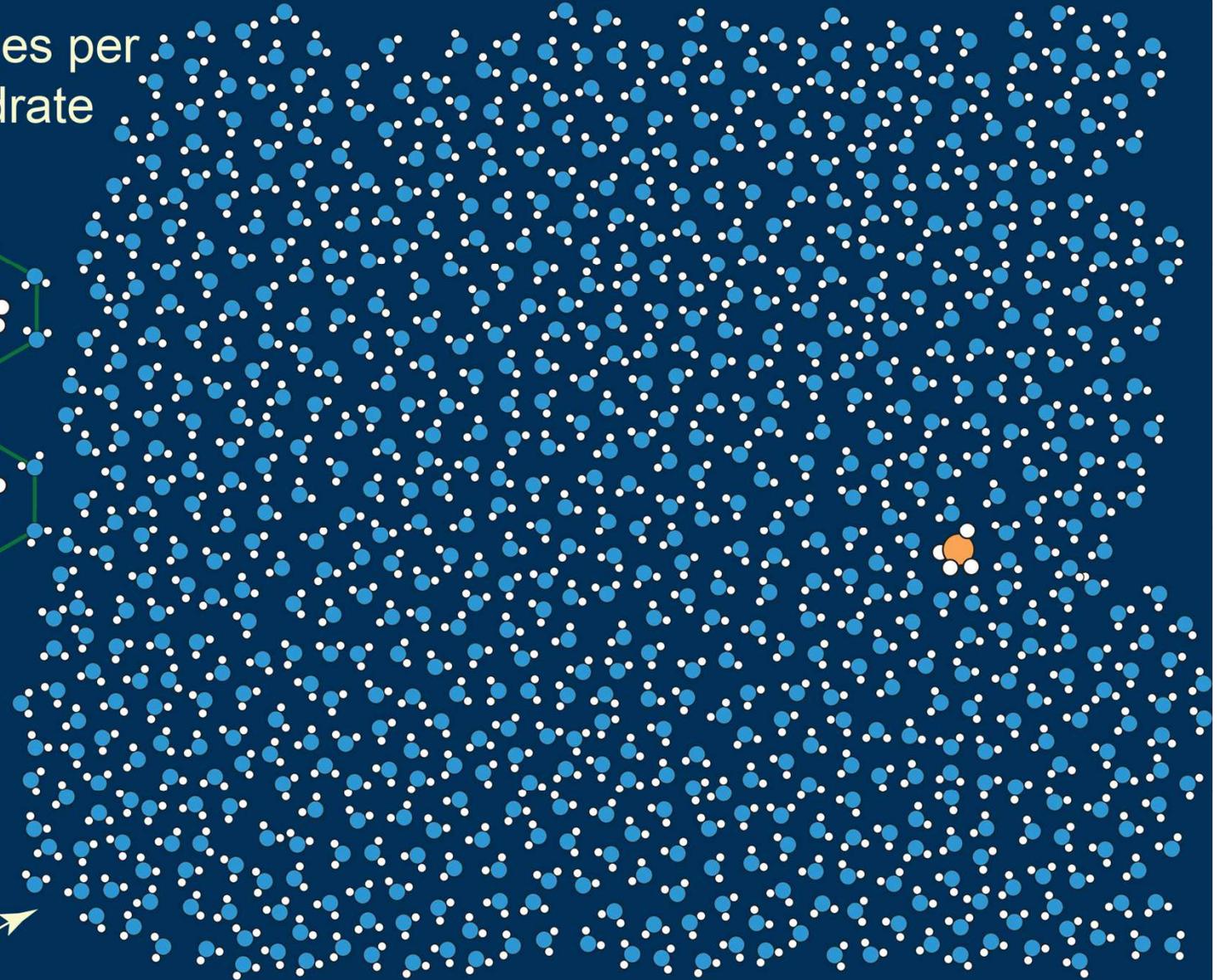
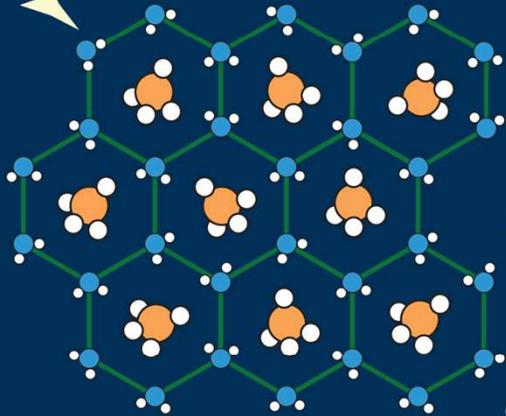
# Gas hydrate requires a concentration of methane

~6 water molecules per  
methane in hydrate



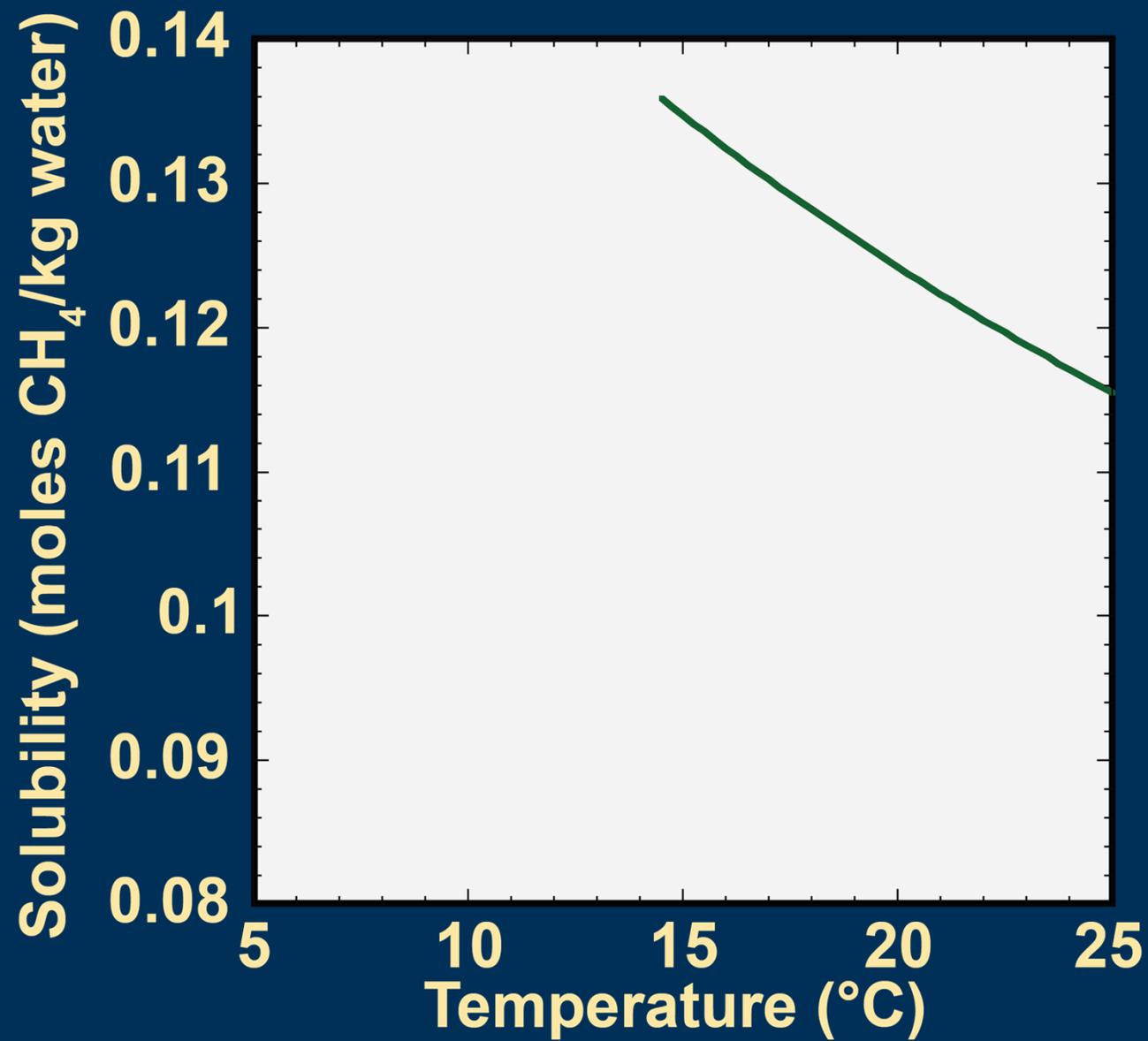
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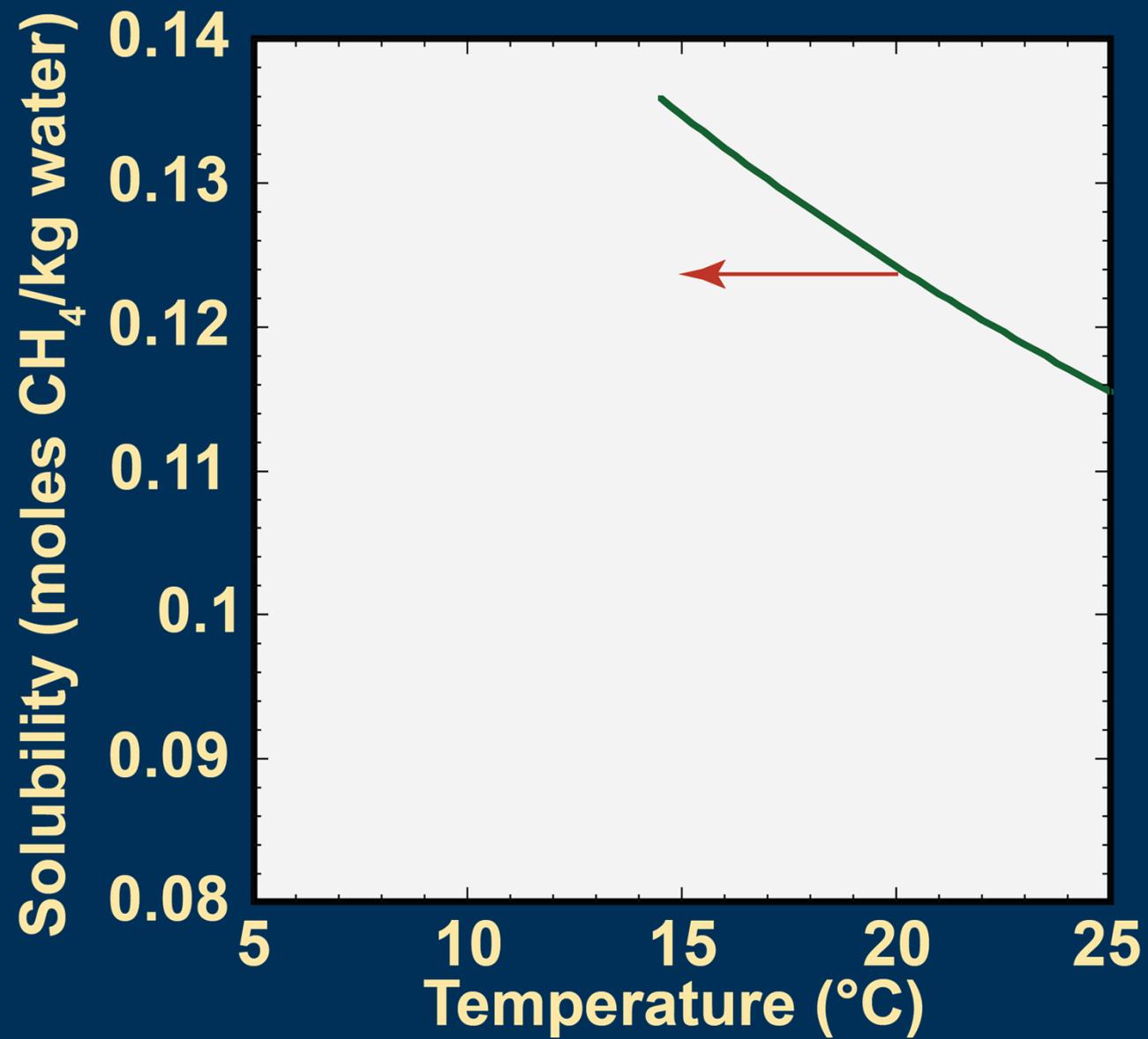


~750 water molecules per methane in water contacting hydrate

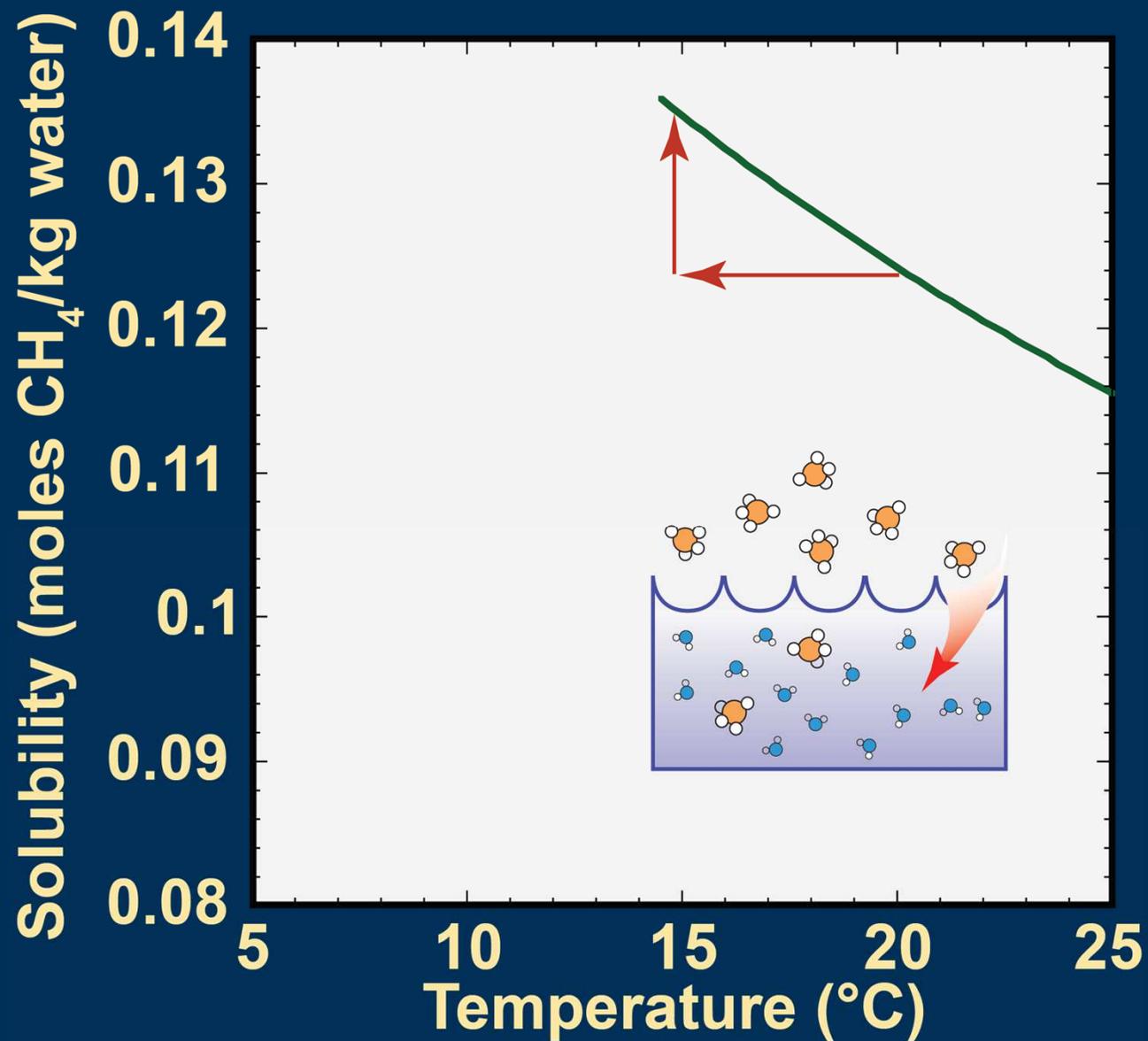
# Methane solubility in water



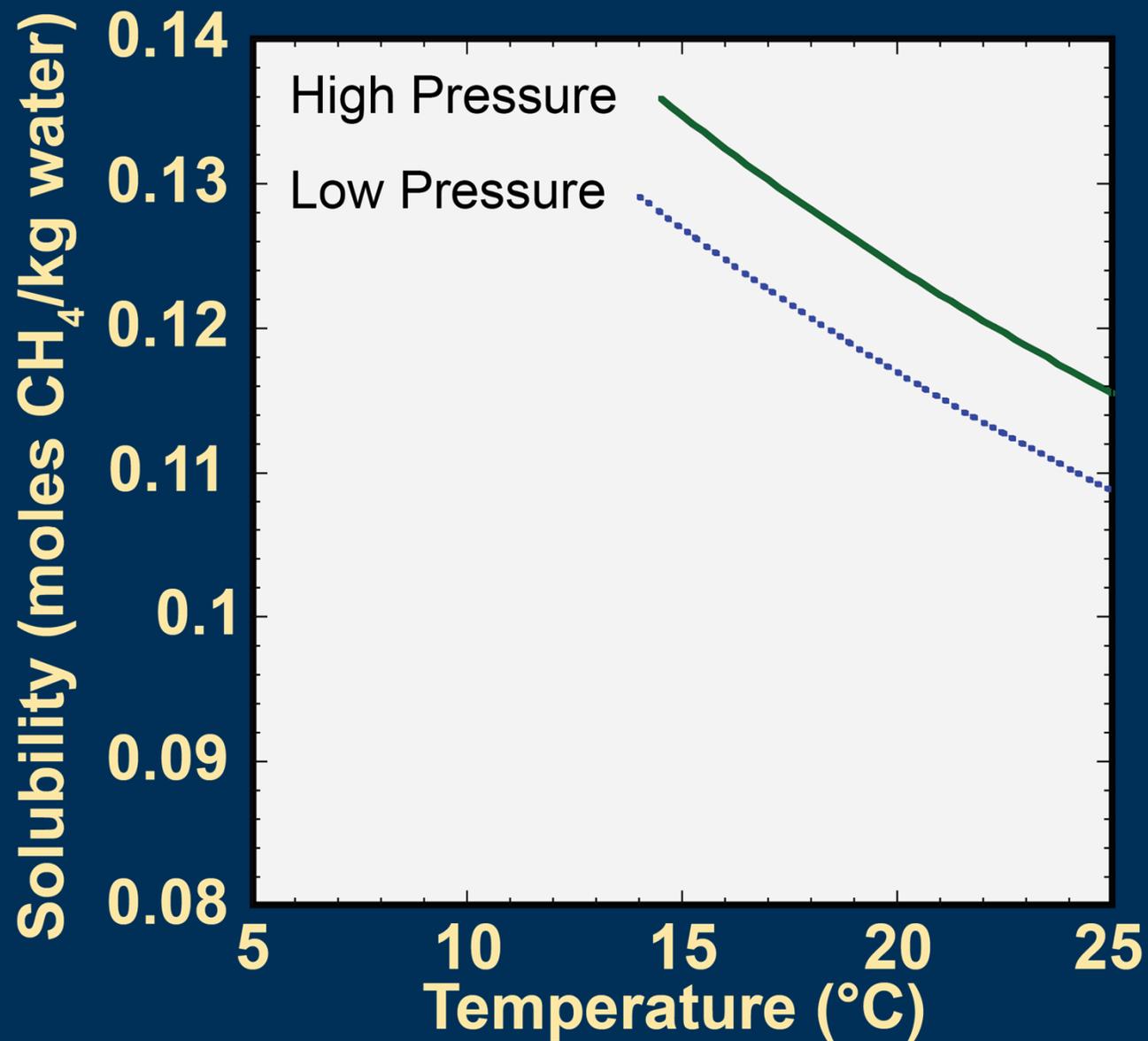
# Methane solubility in water



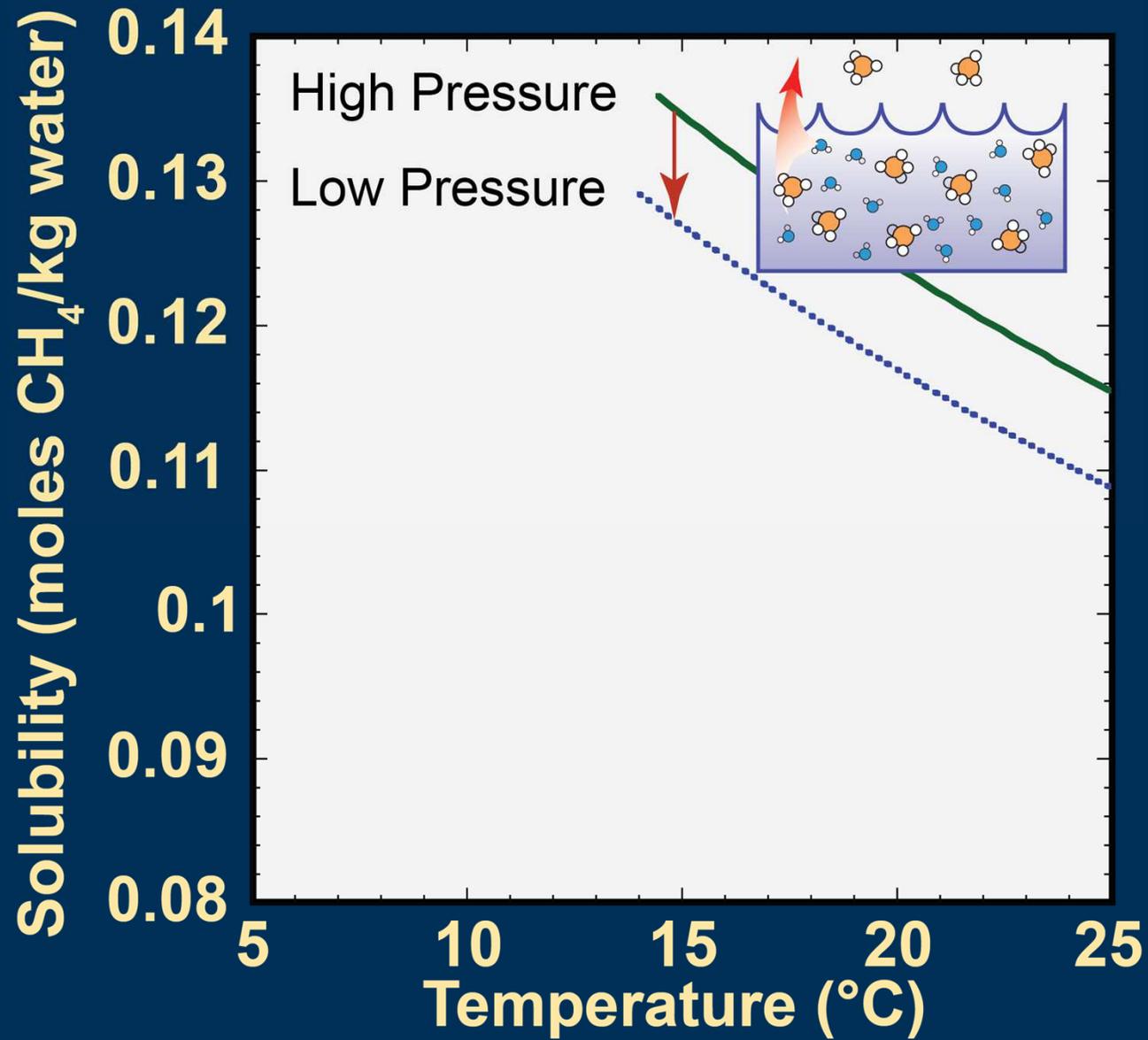
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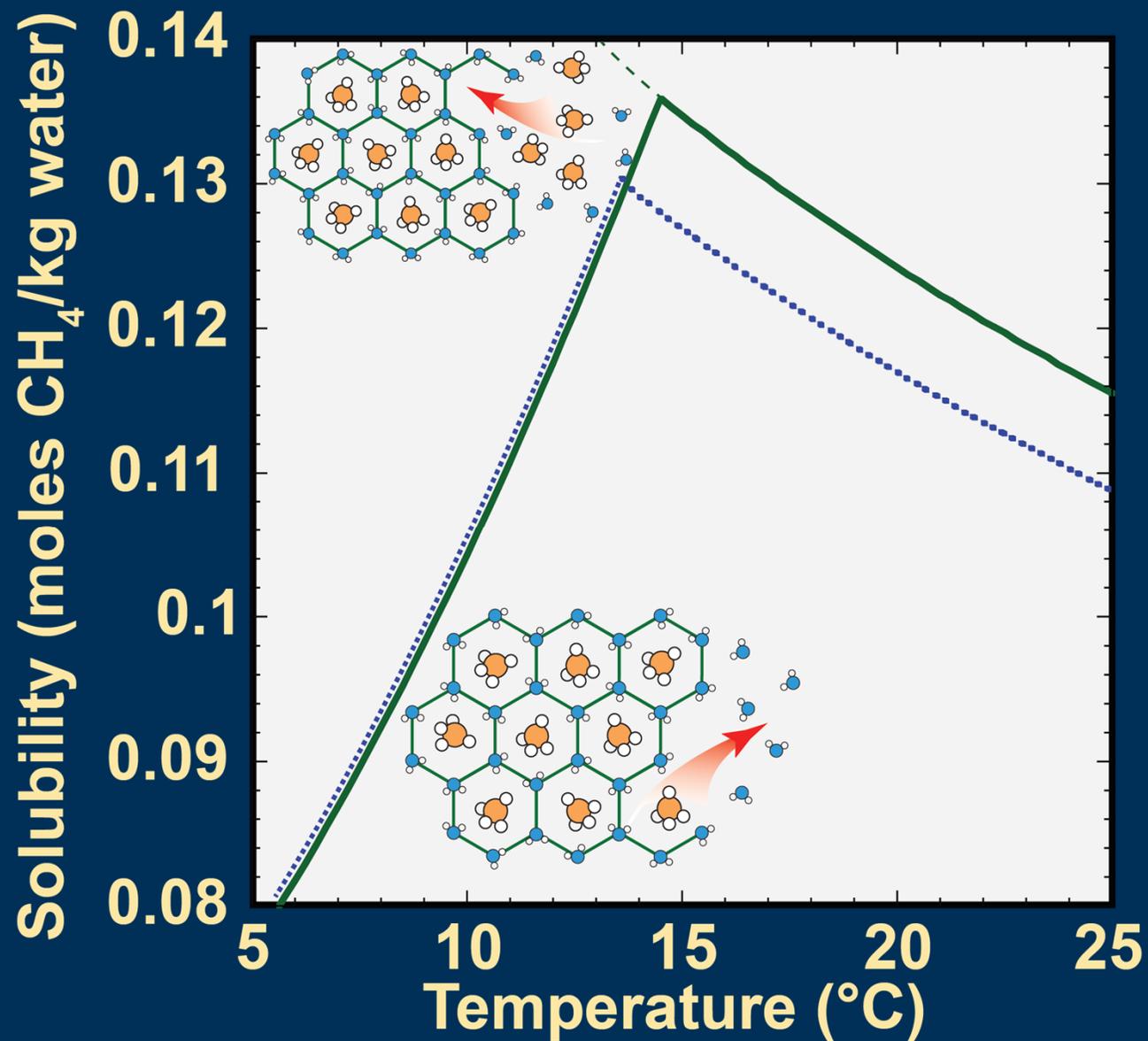
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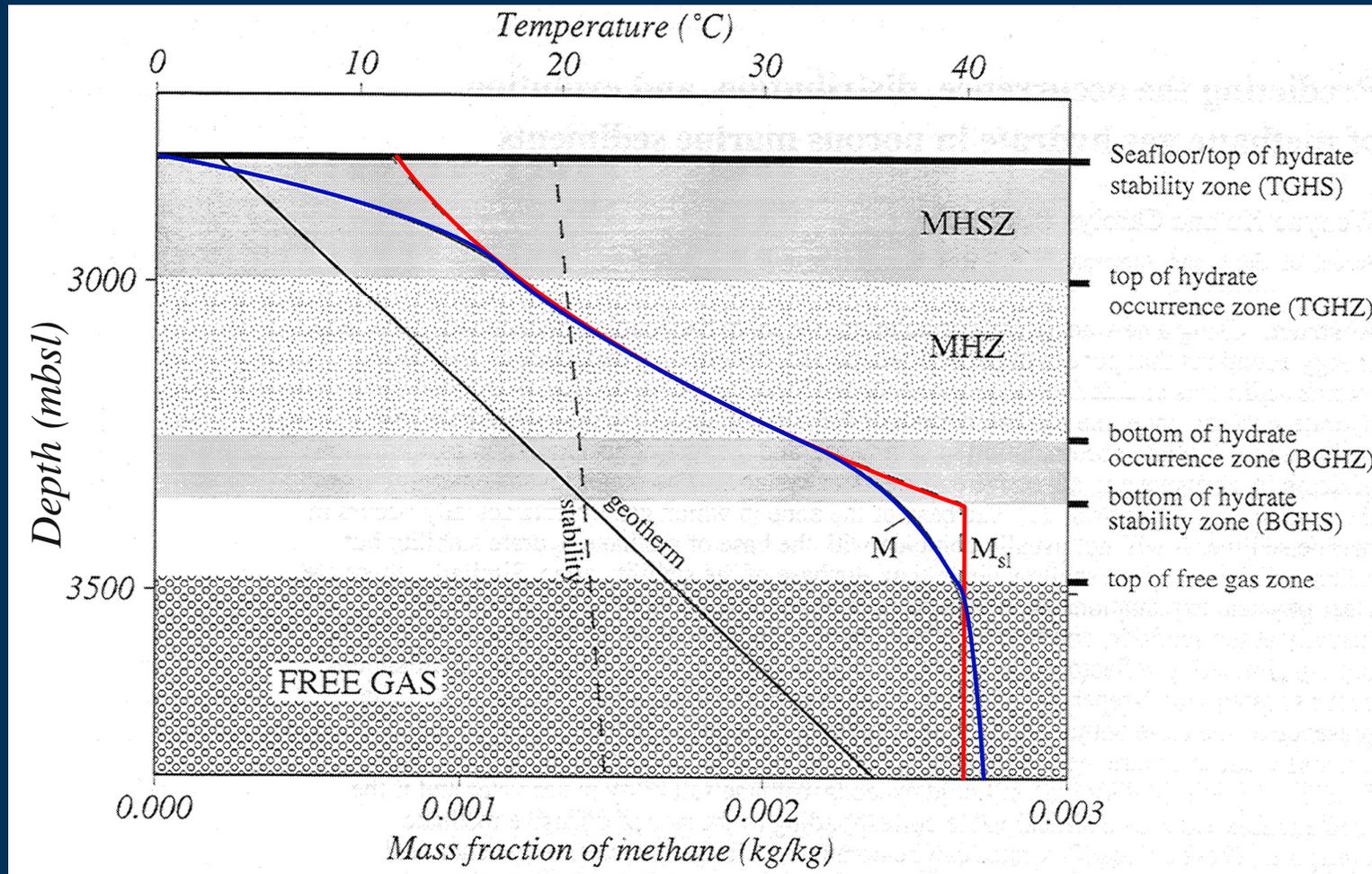
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# Methane solubility in water



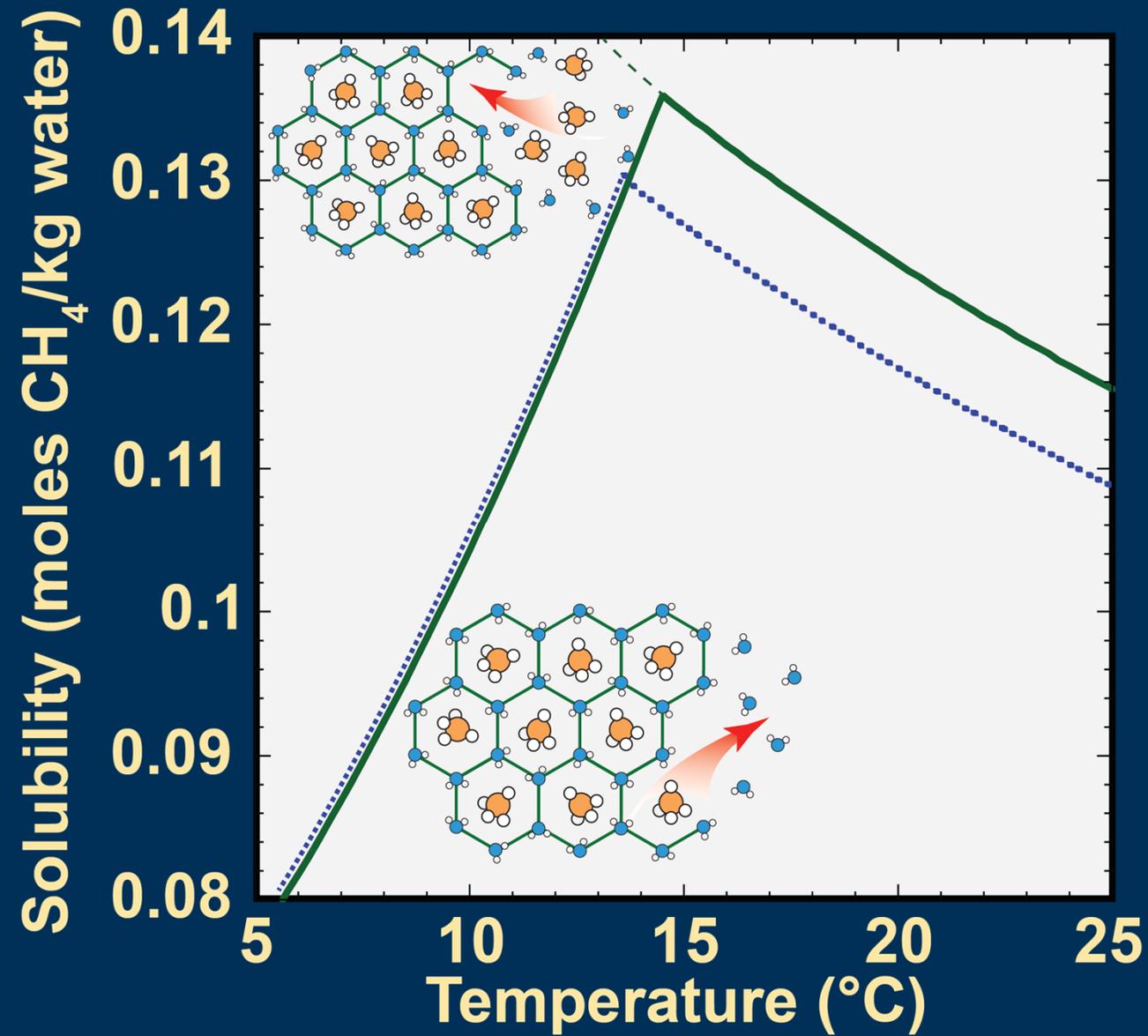
# Methane solubility in marine sediment



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

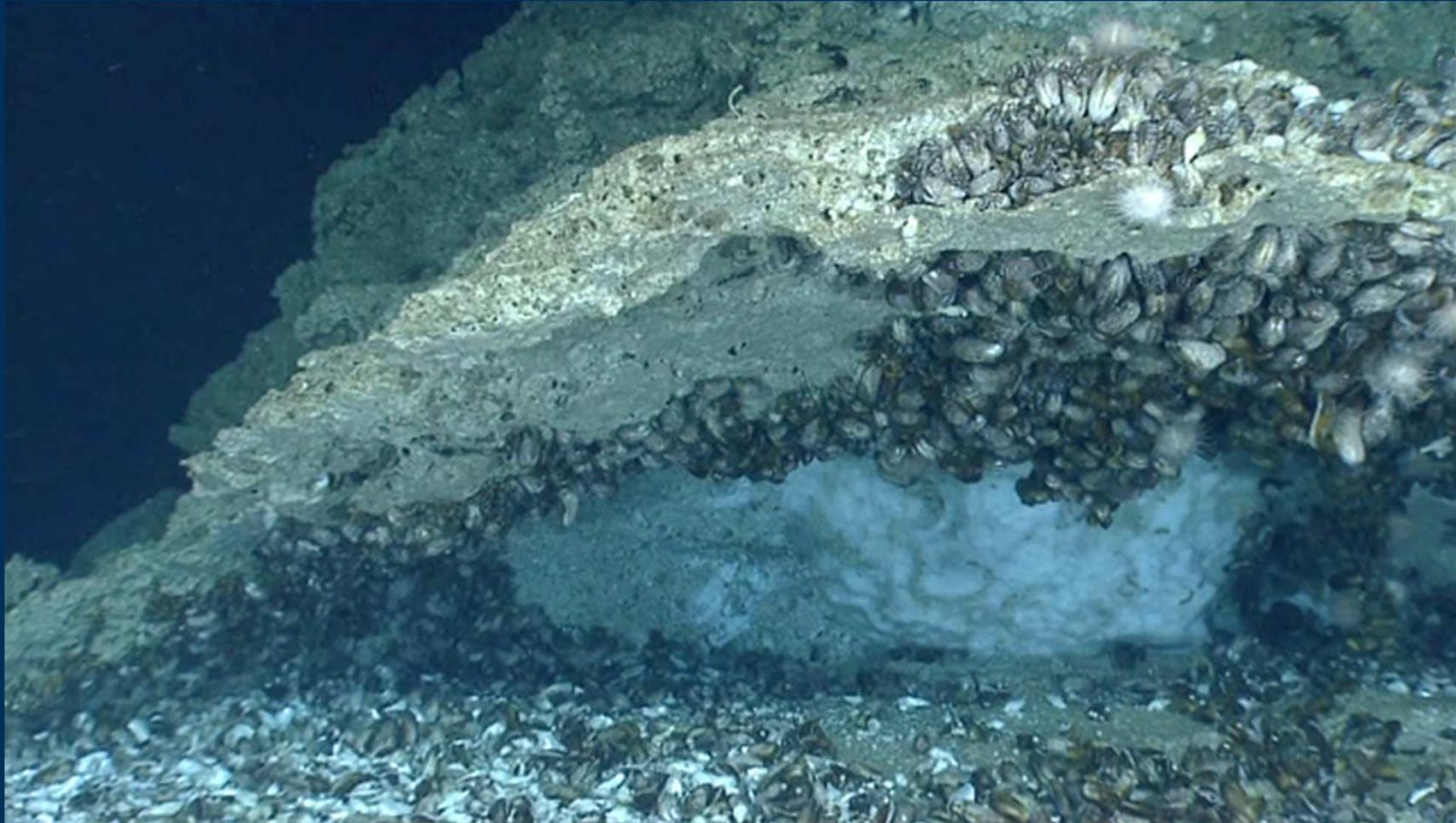


## Gas hydrate needs a continuous supply of methane



NOAA Okeanos Explorer Exp. 1402 (2014)

## Gas hydrate needs a continuous supply of methane



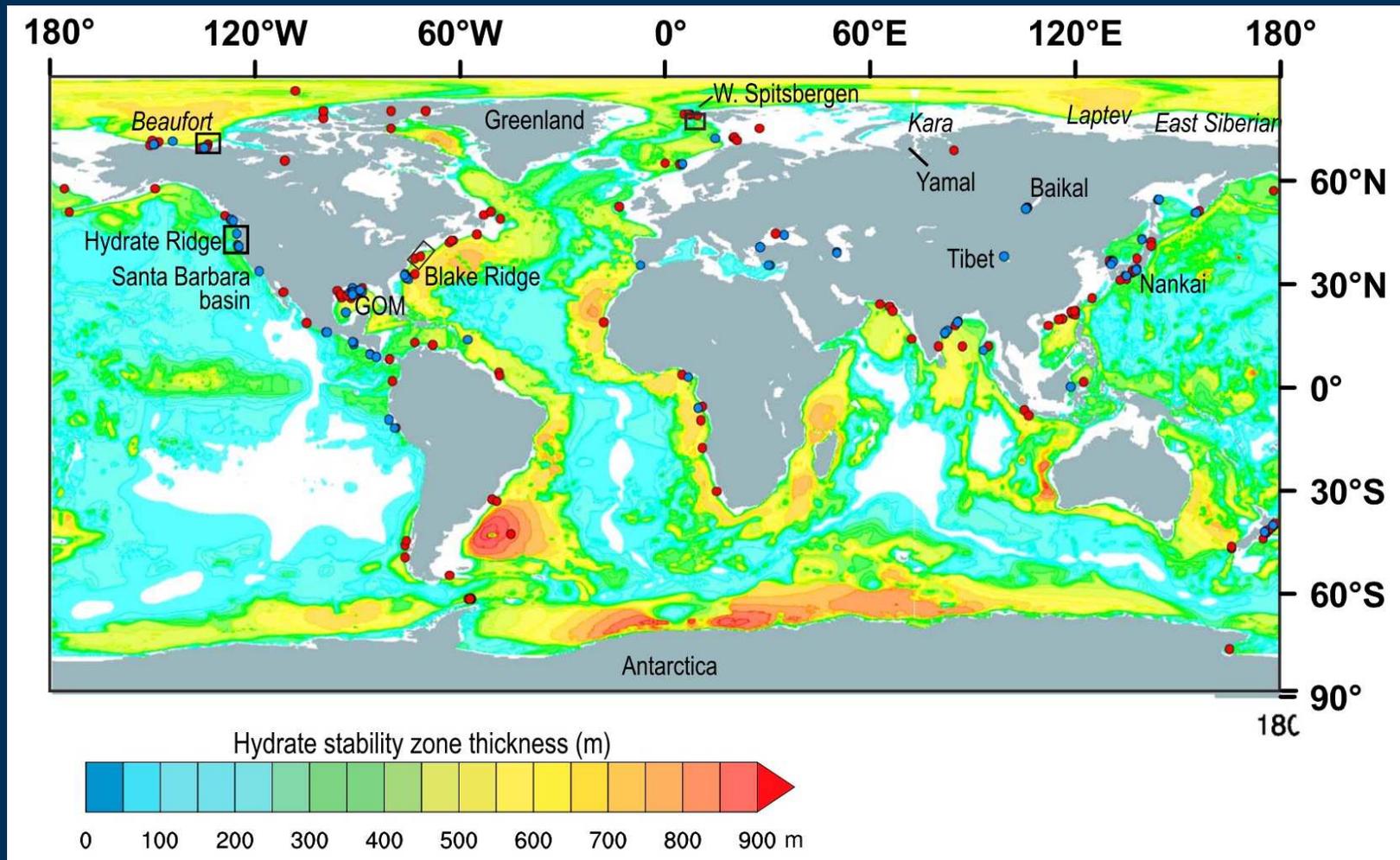
NOAA Okeanos Explorer Exp. 1402 (2014)

# Gas hydrate needs a continuous supply of methane



NEPTUNE Canada, Dive R1546 (2012)

# Where does the methane come from?

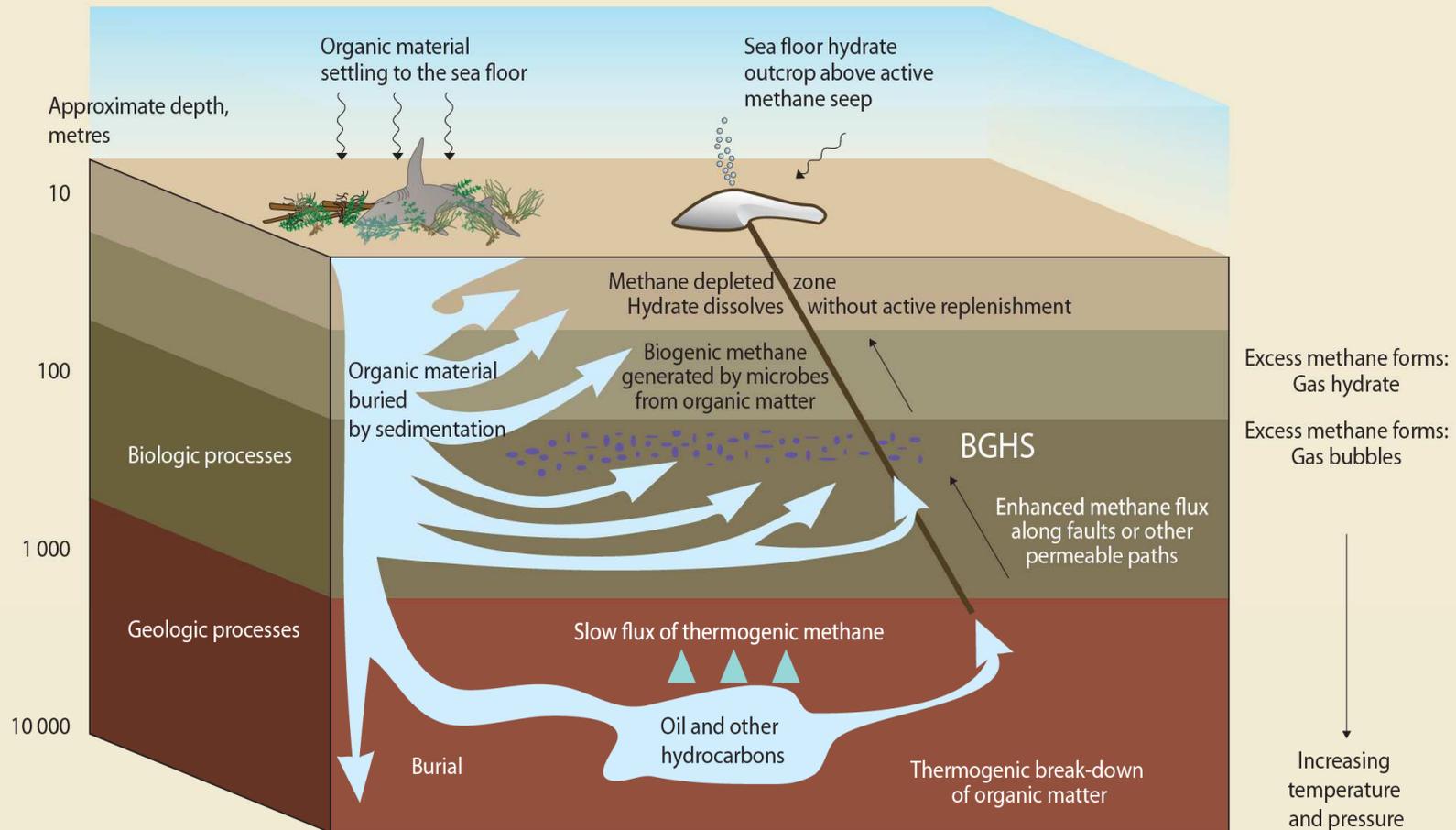


Methane requires organic carbon to break down

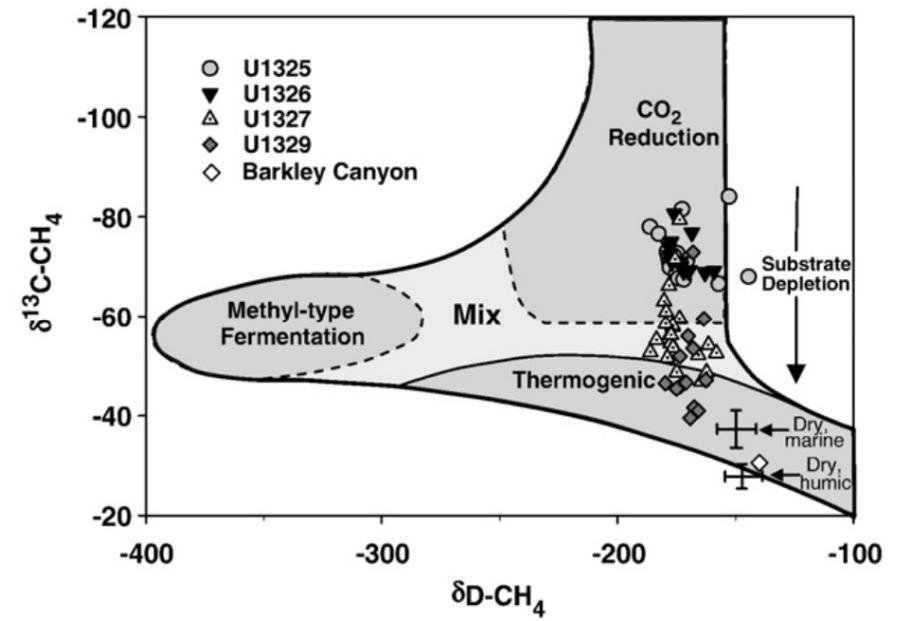
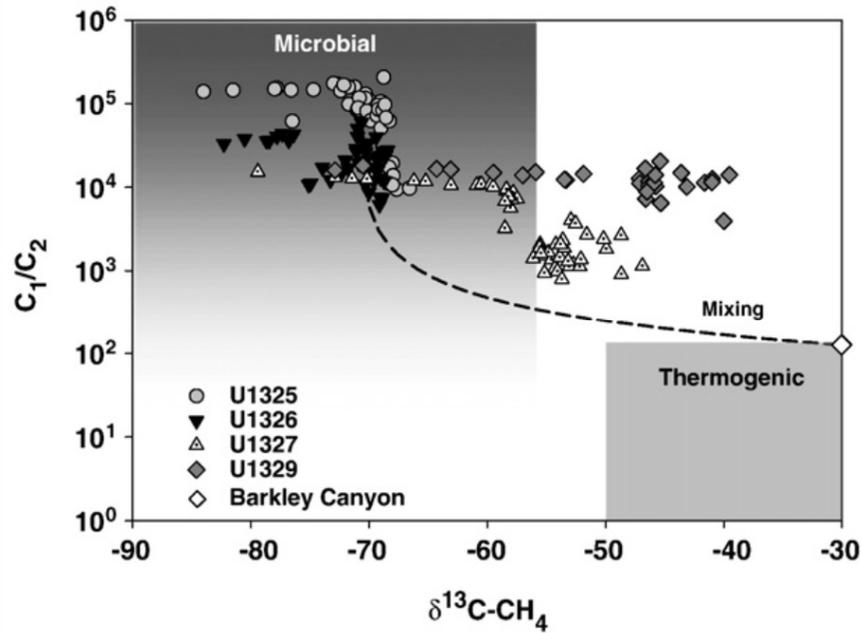
Ruppel et al. (2017), Rev of Geophysics

# How does organic material break down?

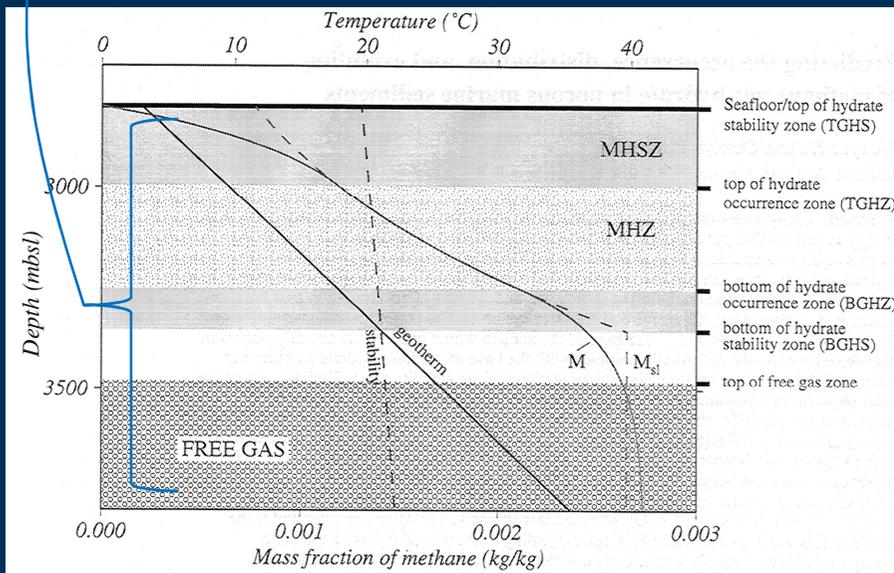
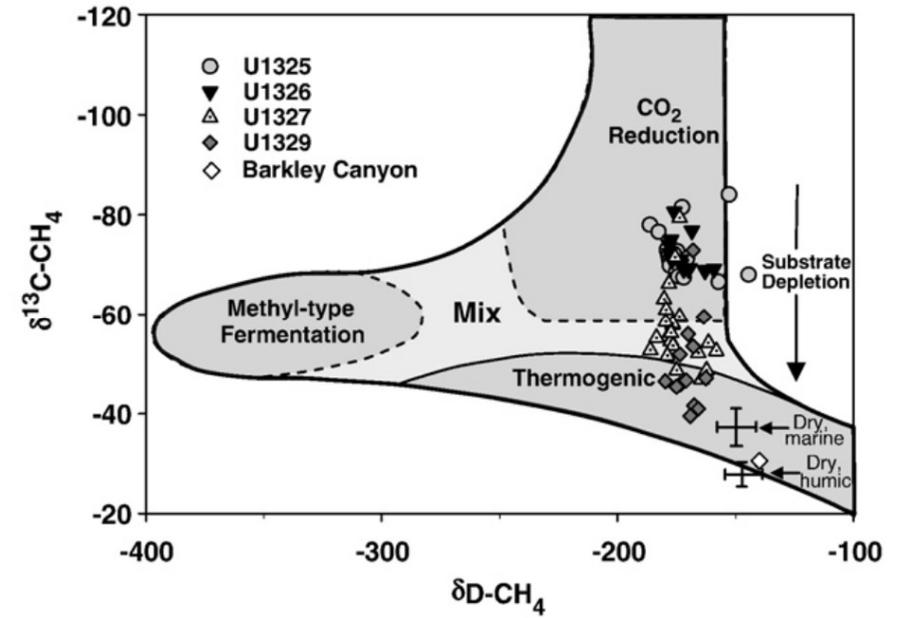
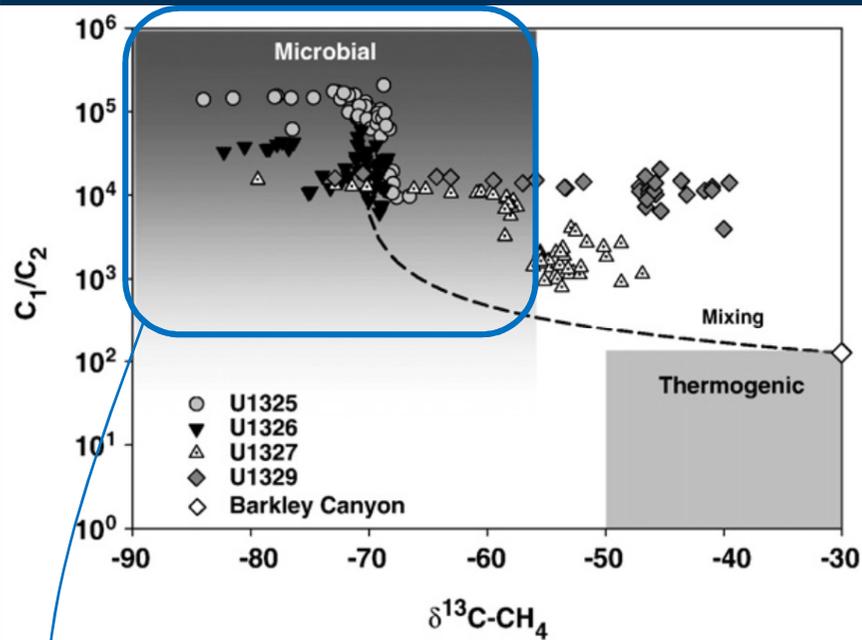
## Fate of buried organic matter



# How does organic material break down?



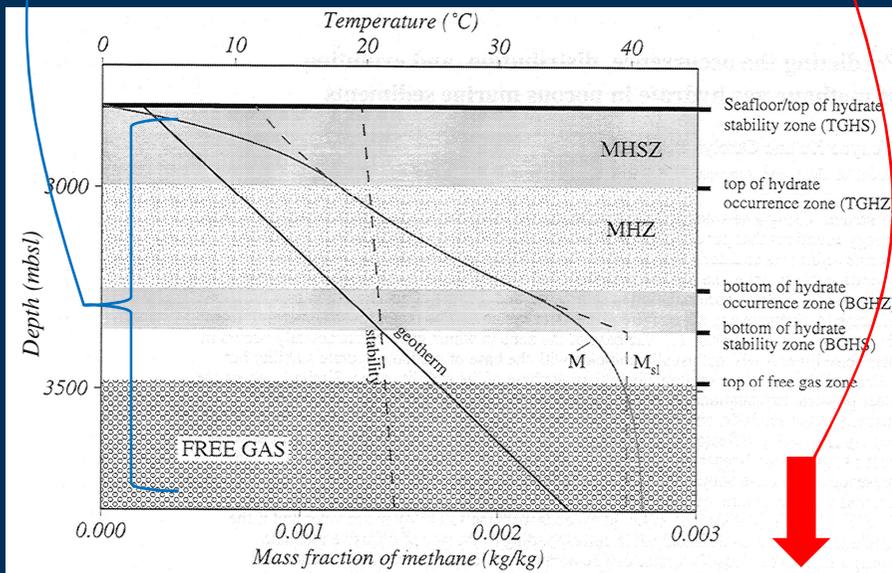
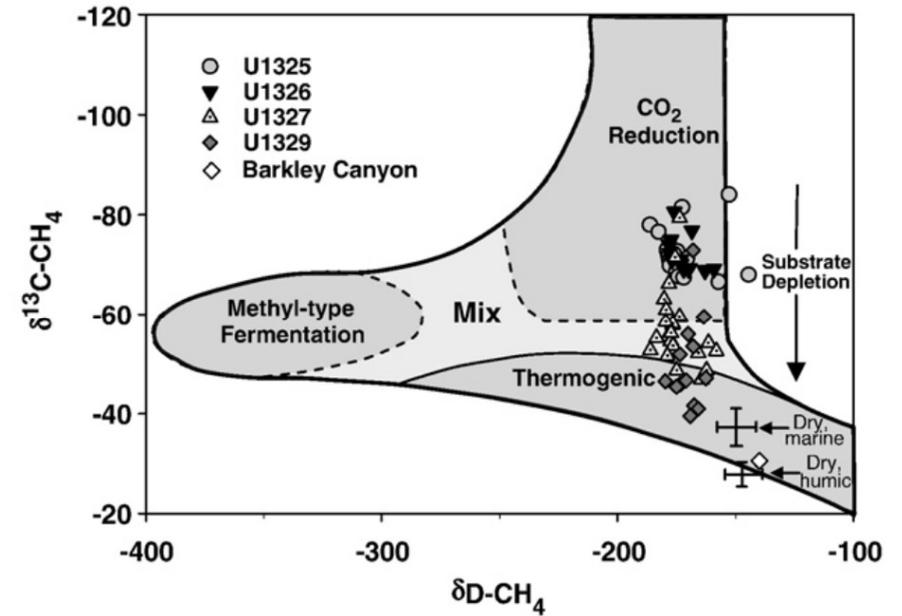
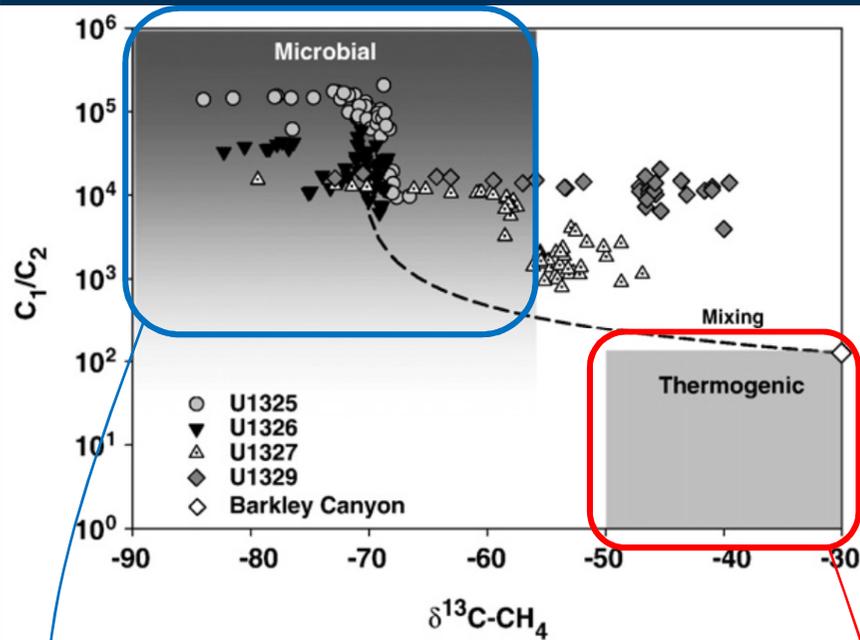
# How does organic material break down?



- Microbial: shallow, near gas hydrate

Pohlman et al. (2009), EPSL

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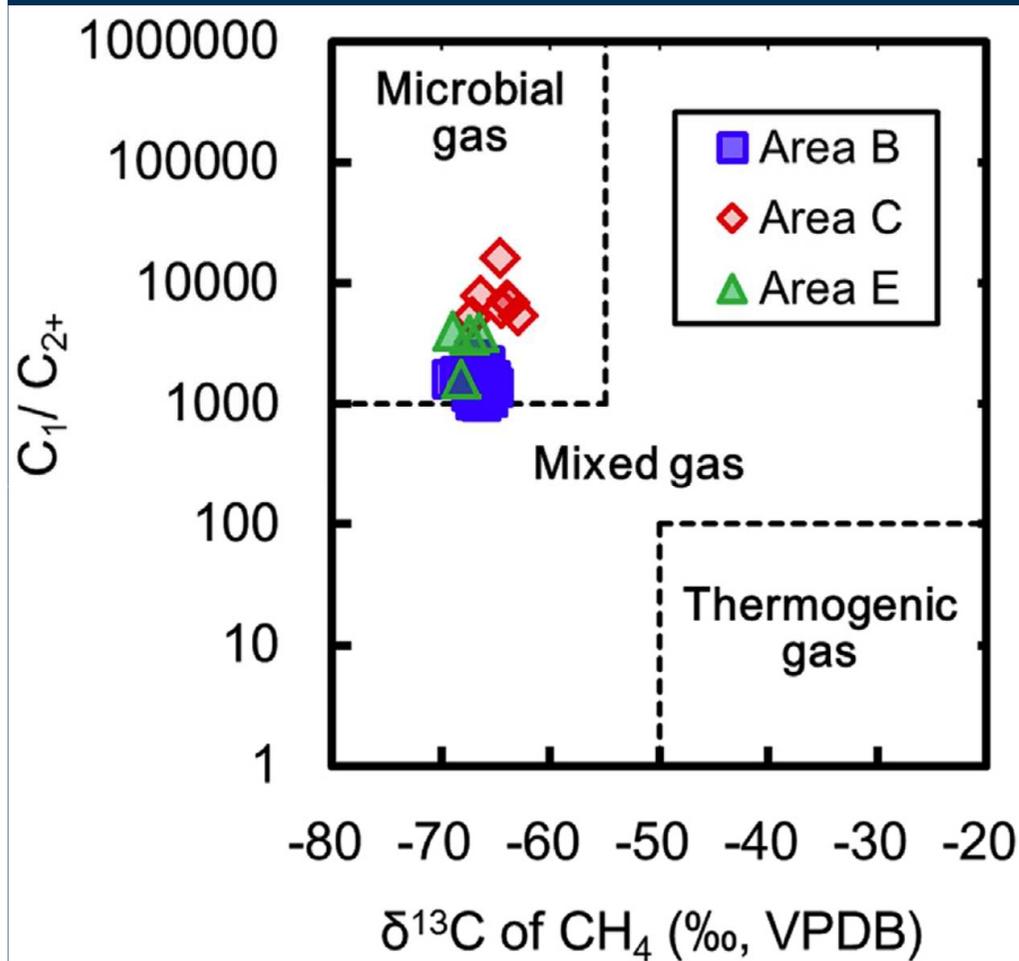


- Microbial: shallow, near gas hydrate
- Thermogenic: very deep, so methane needs to be transported up to form hydrate

Pohlman et al. (2009), EPSL



## Much of what we find is microbial

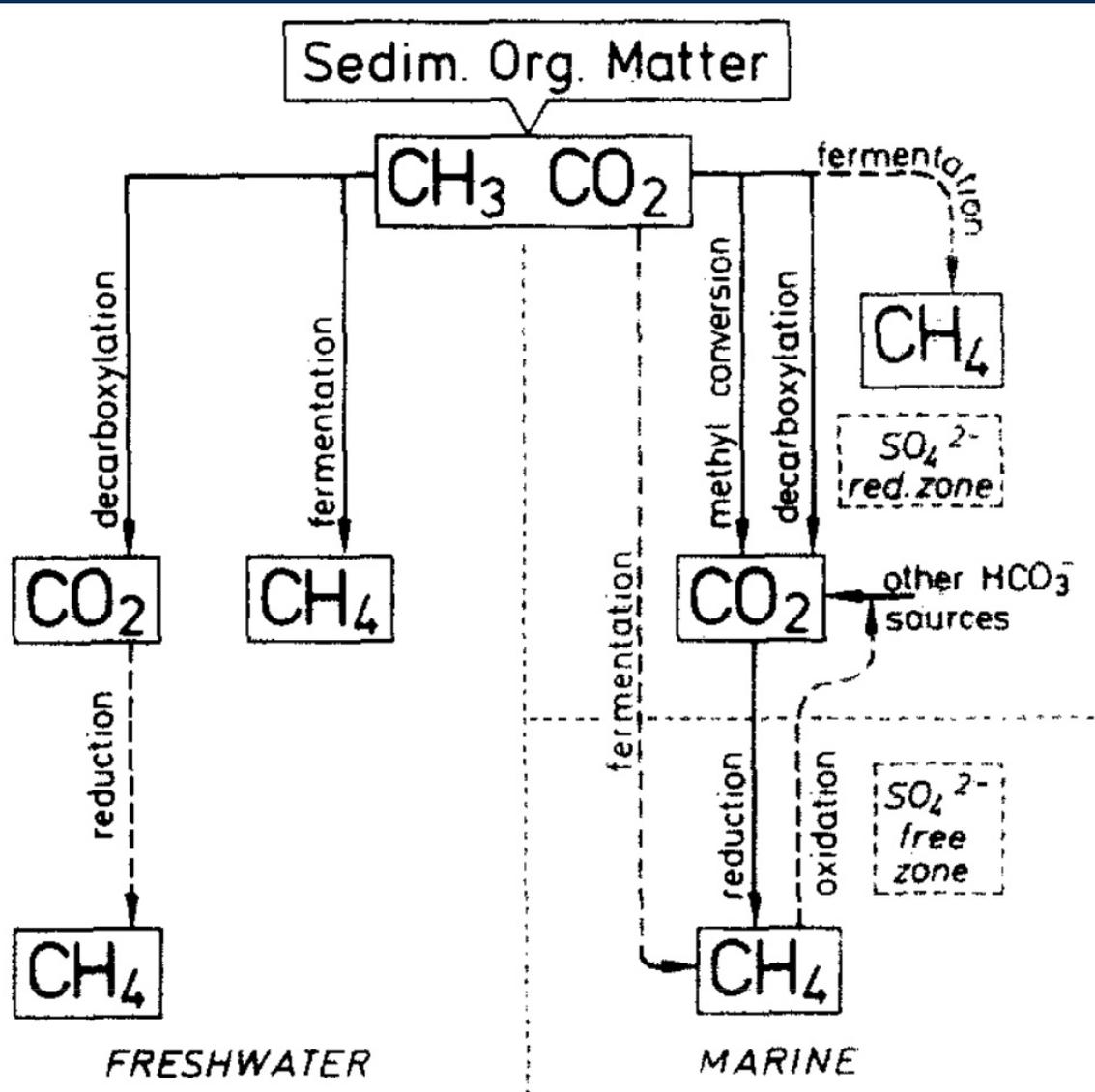


- Offshore Japan (Nankai)  
(Uchida et al. (2009), AAPG)
- Offshore Korea (UBGH)  
(Ryu et al. (2013), JMPG)
- Gulf of Mexico (GC955)  
(Phillips et al. (2019), AAPG)

Offshore India (NGHP)

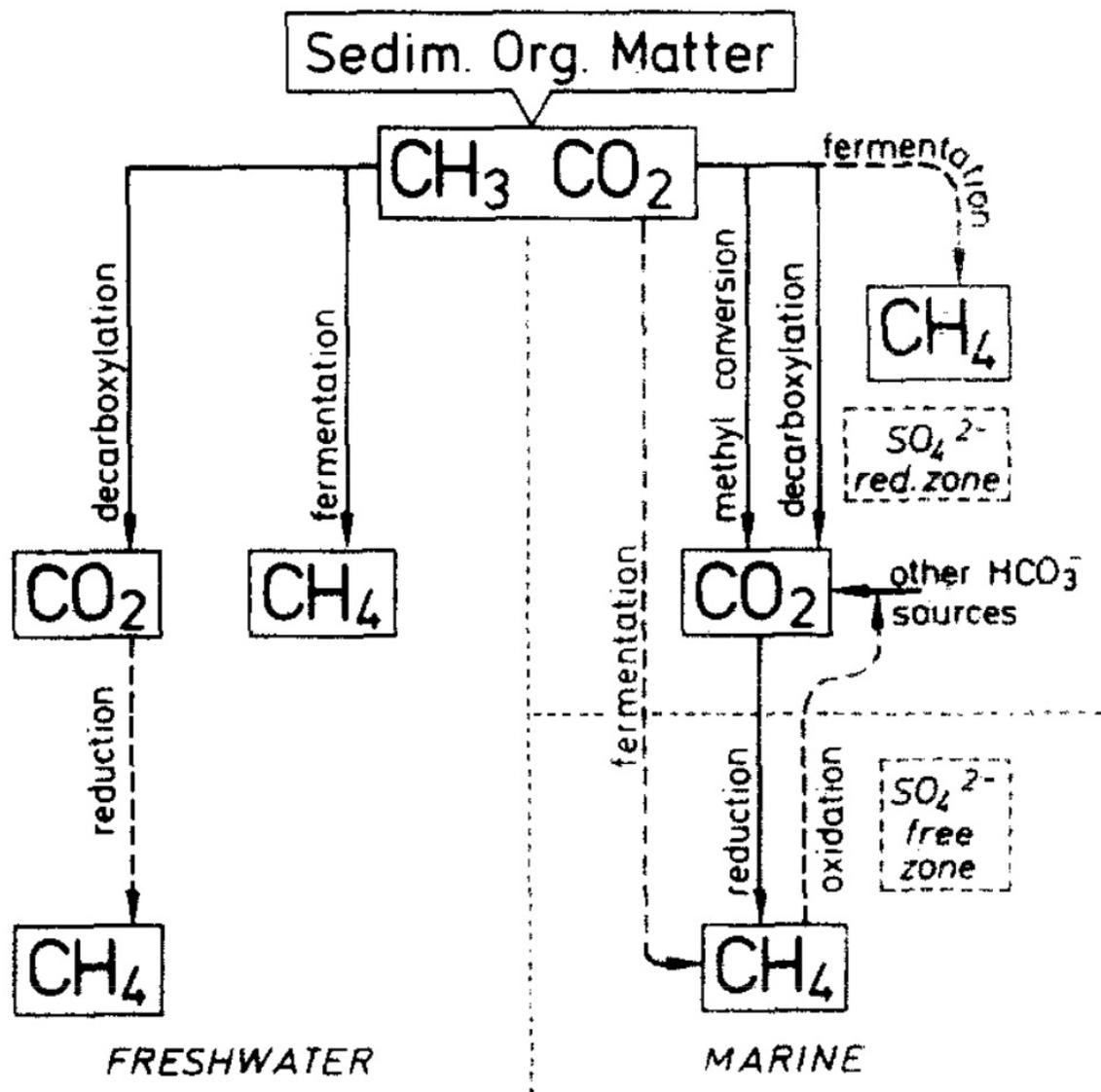
Kida et al. (2018), JMPG

# What do microbes need to produce methane?



Organic material provides  
**“electron donors”**

# What do microbes need to produce methane?



Organic material provides

“**electron donors**”

Reaction also needs

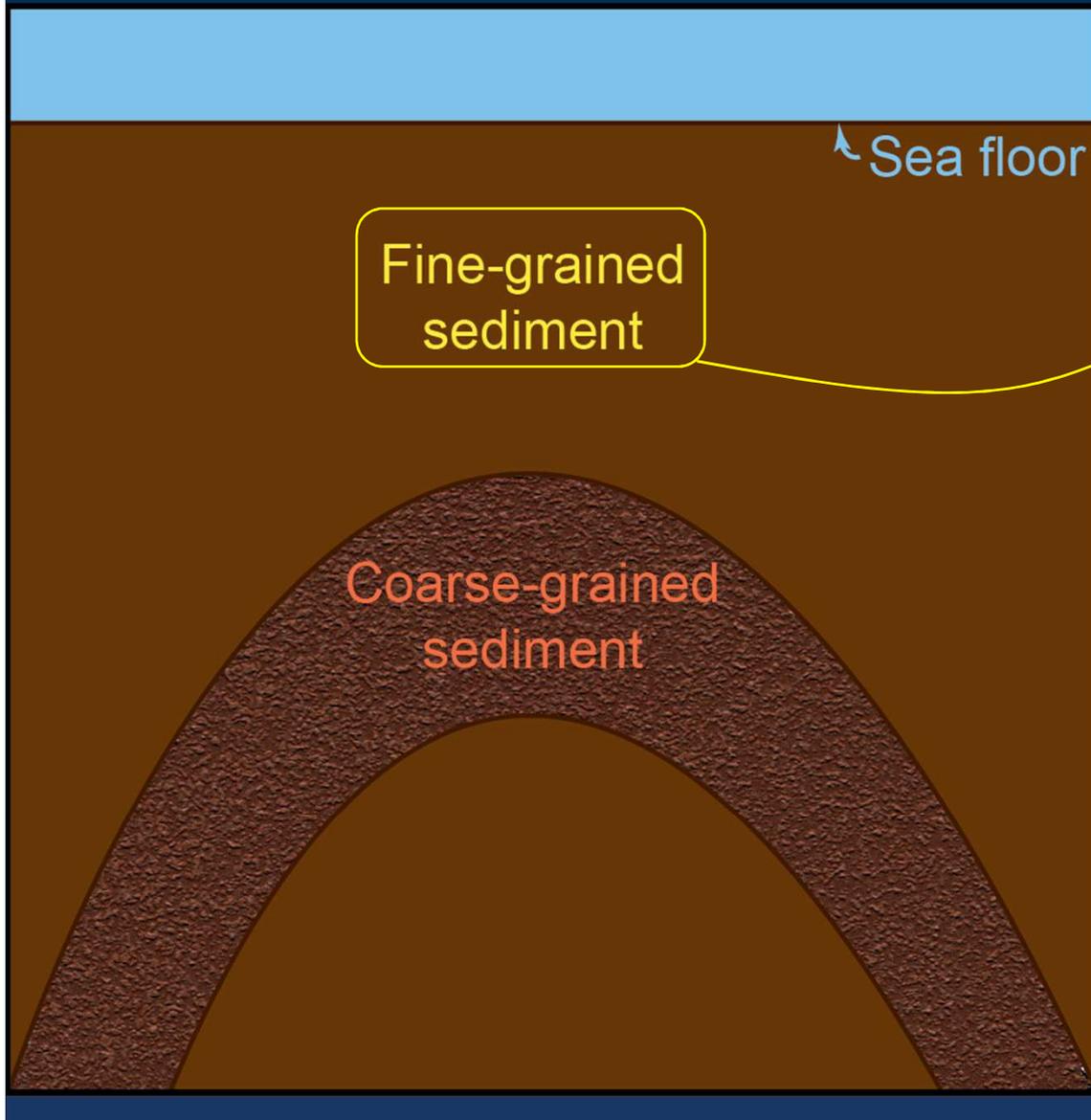
“**electron acceptors**”

$O_2 > NO_3^- > MN(II)$

$> Fe(III) > SO_4^{2-} > CO_2$

(Reeburgh (2007), ChemRev)

# Where are the electron donors and acceptors?



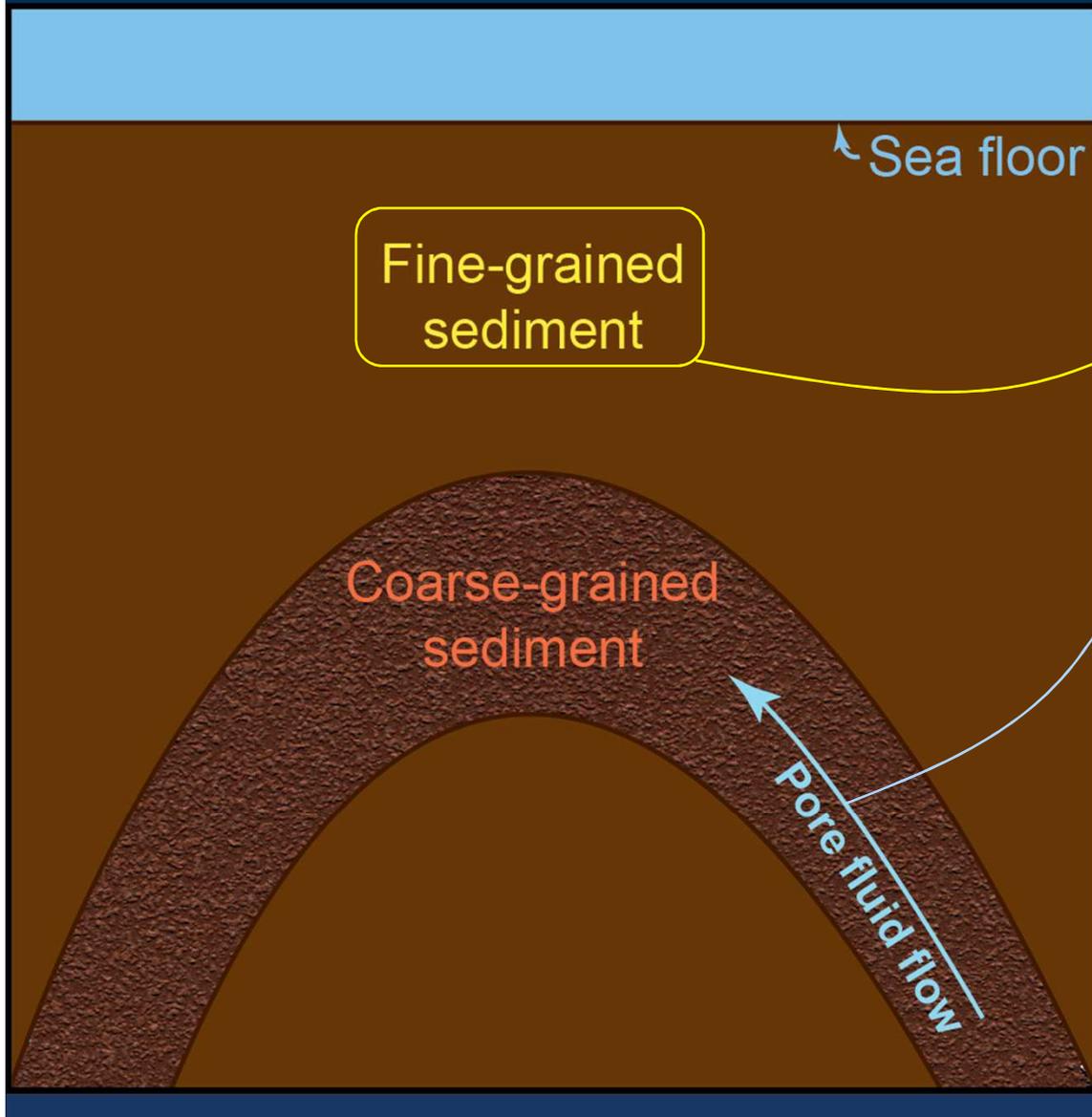
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(Reeburgh (2007), ChemRev)

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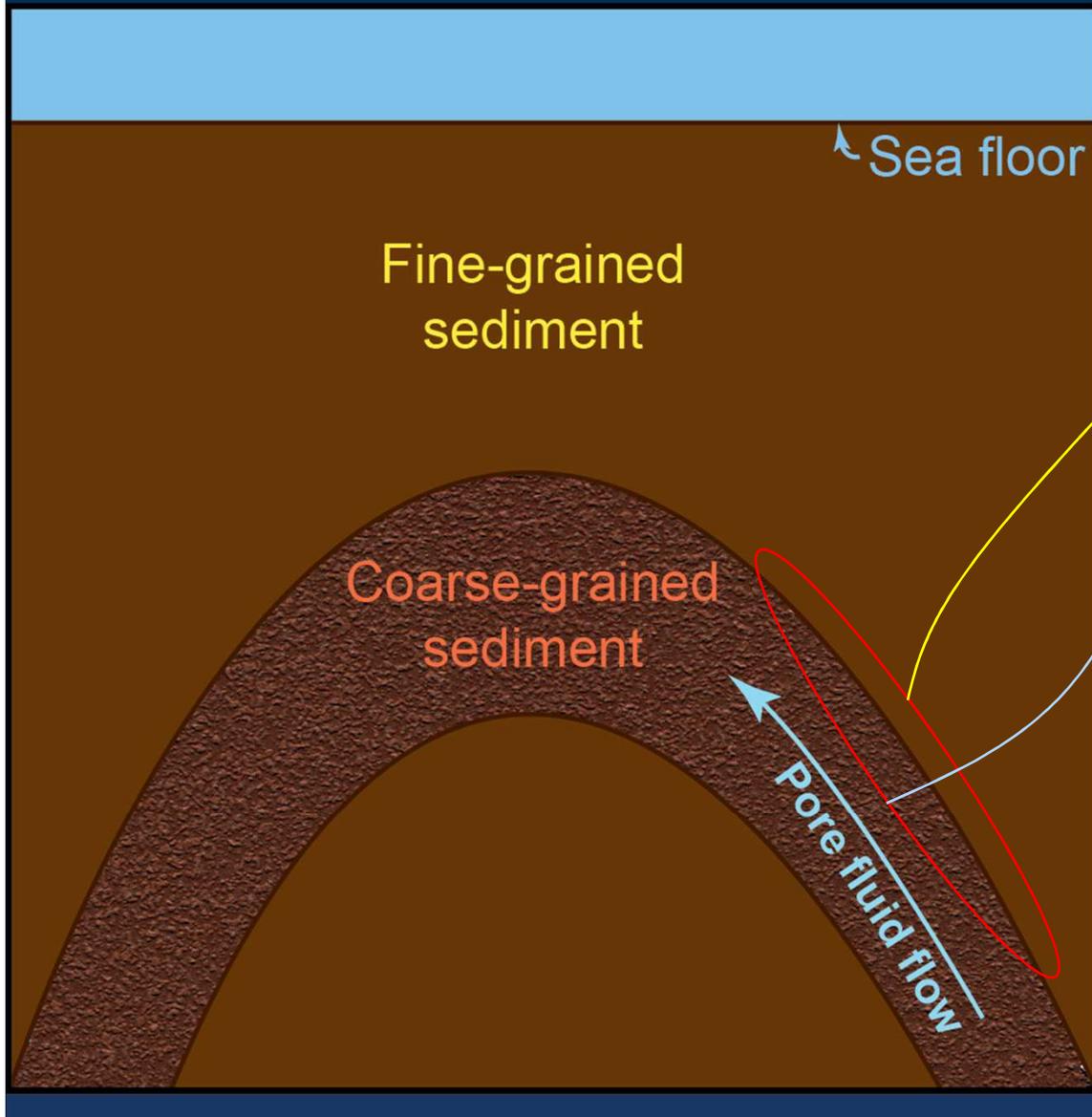
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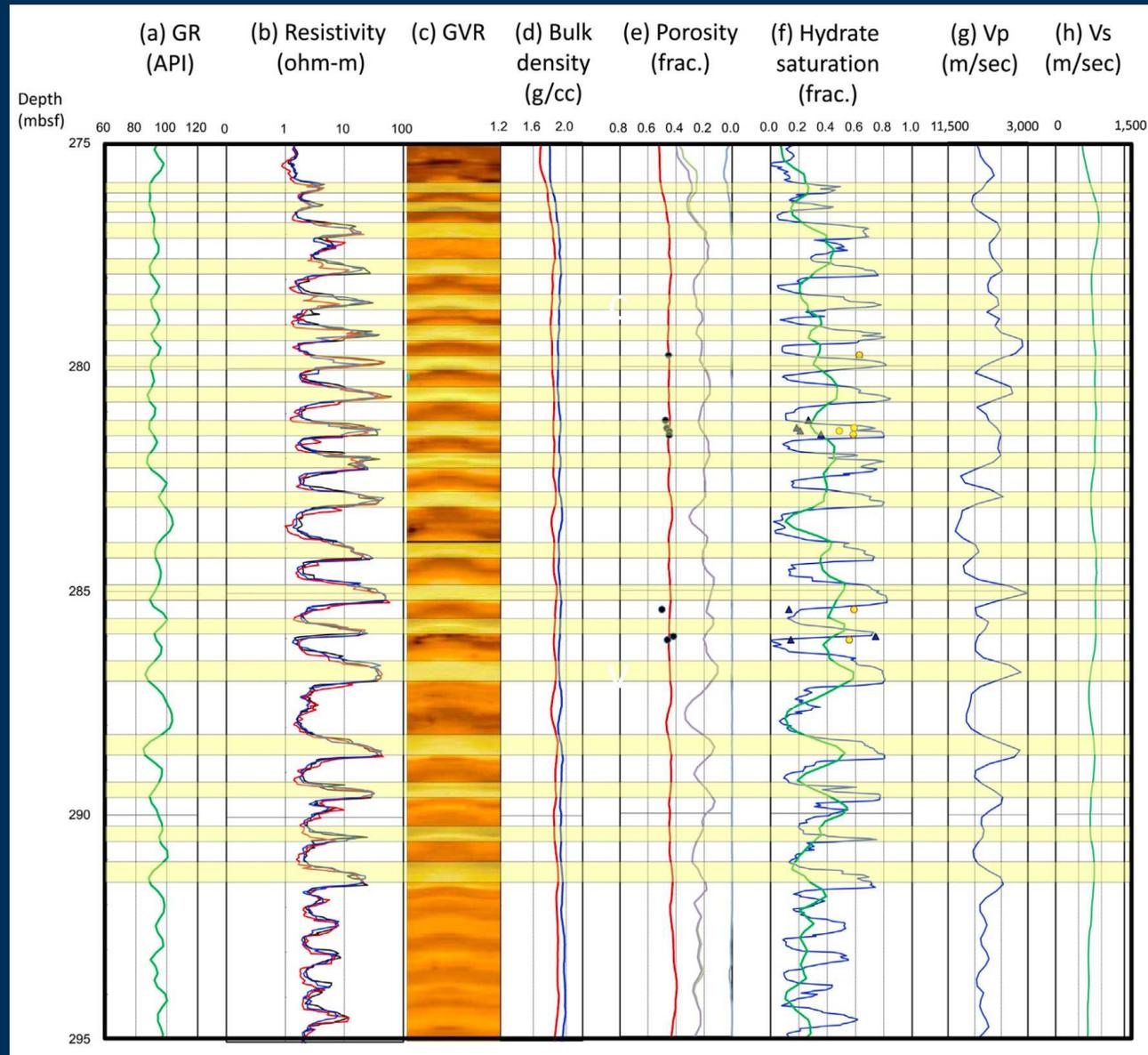


(Reeburgh (2007), ChemRev)

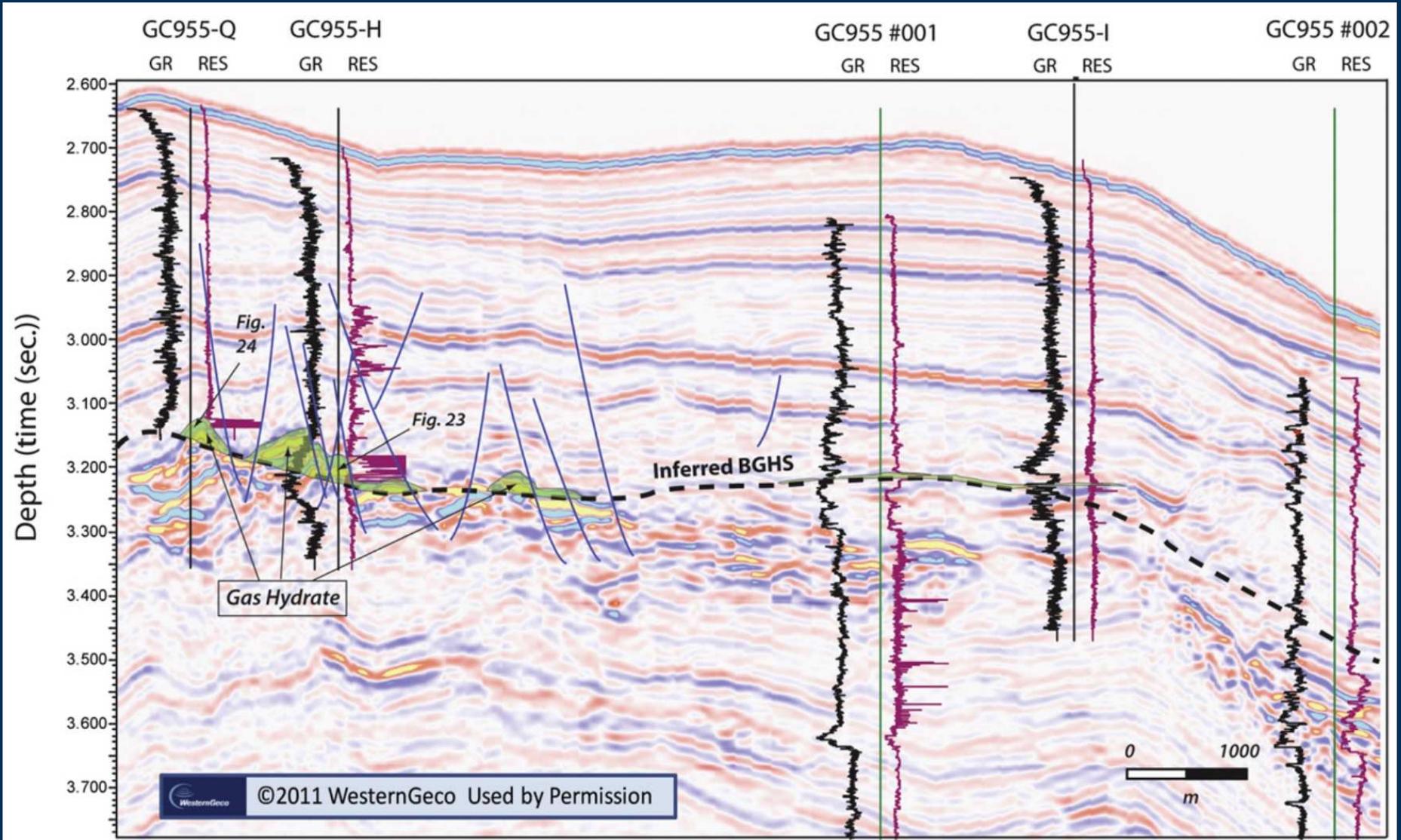
Interfaces where grain  
size changes!

D'Hondt et al. (2004), Science

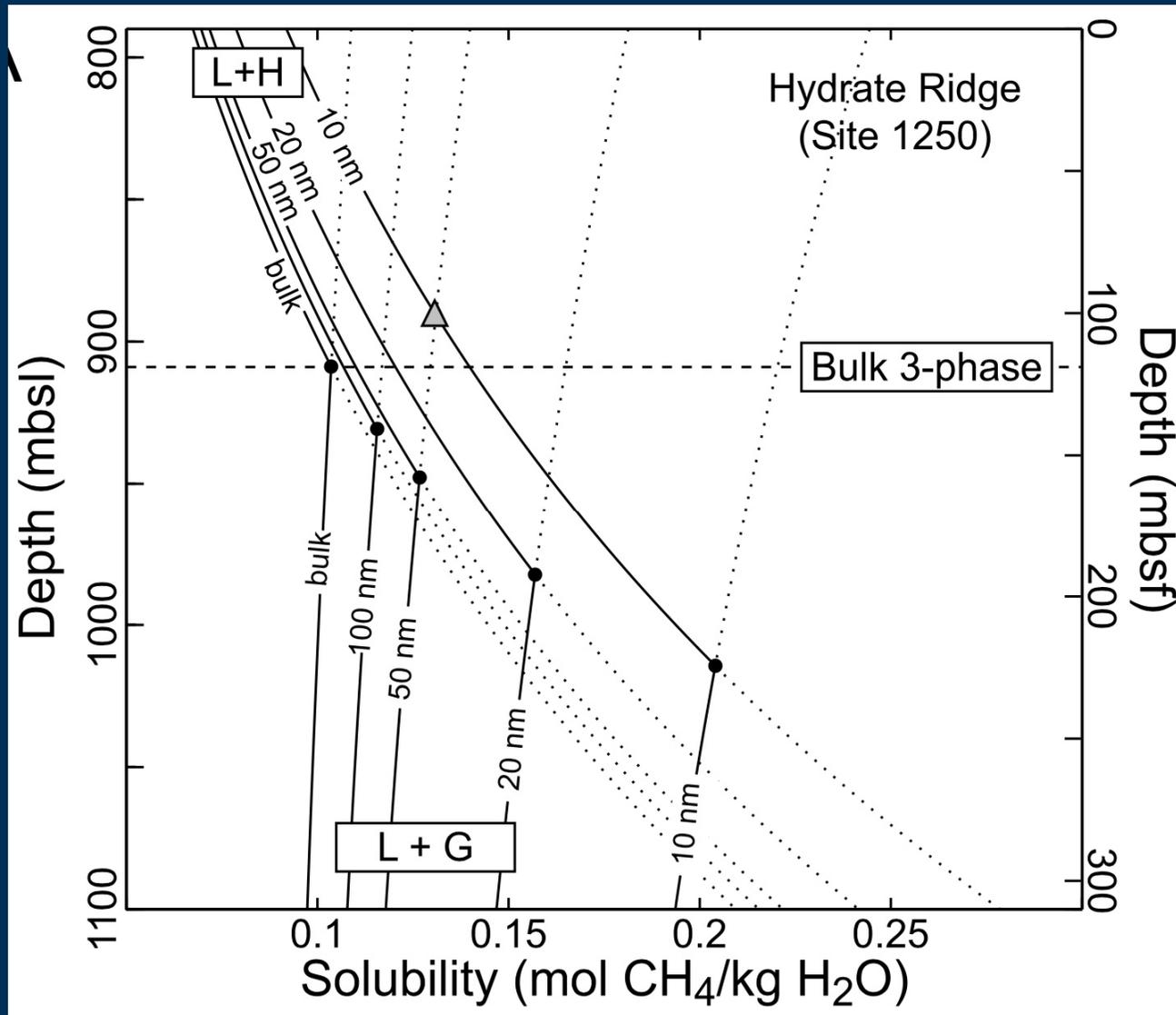
# Coarse/fine interfaces can be within the “reservoir”



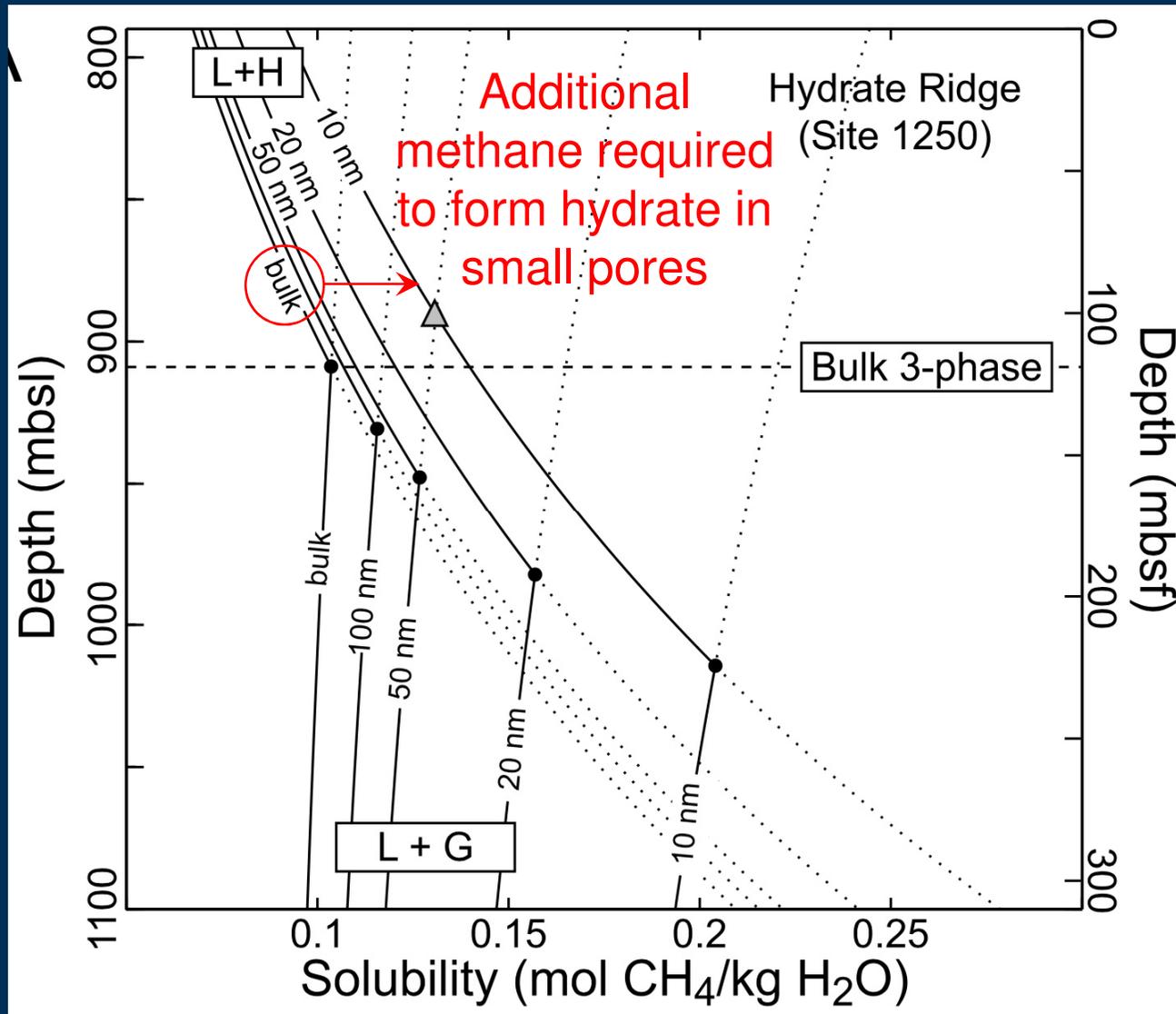
# Faults can provide fluid to thin sands above the reservoir



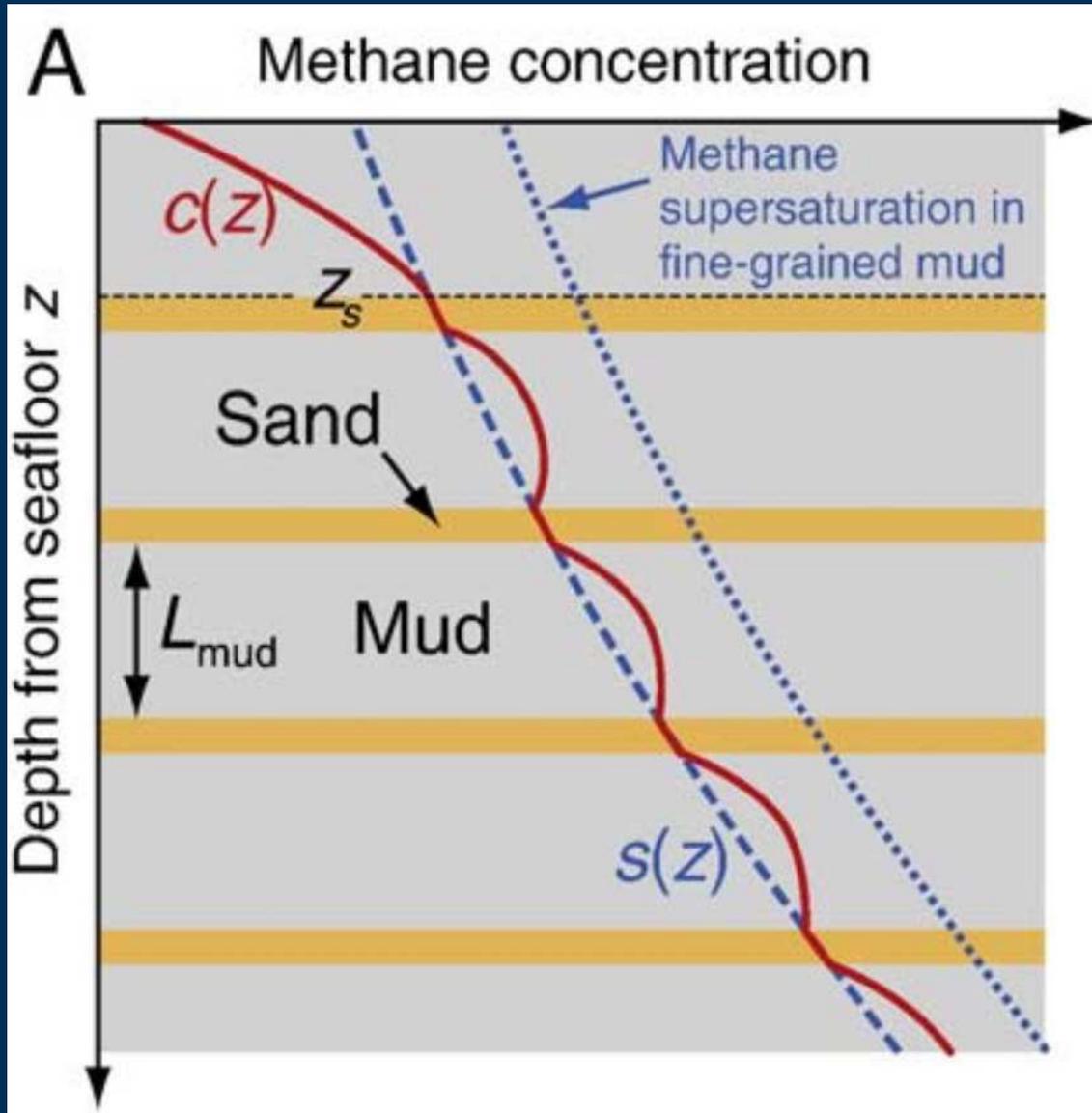
# Solubility dependence on pressure, temperature... and pore size



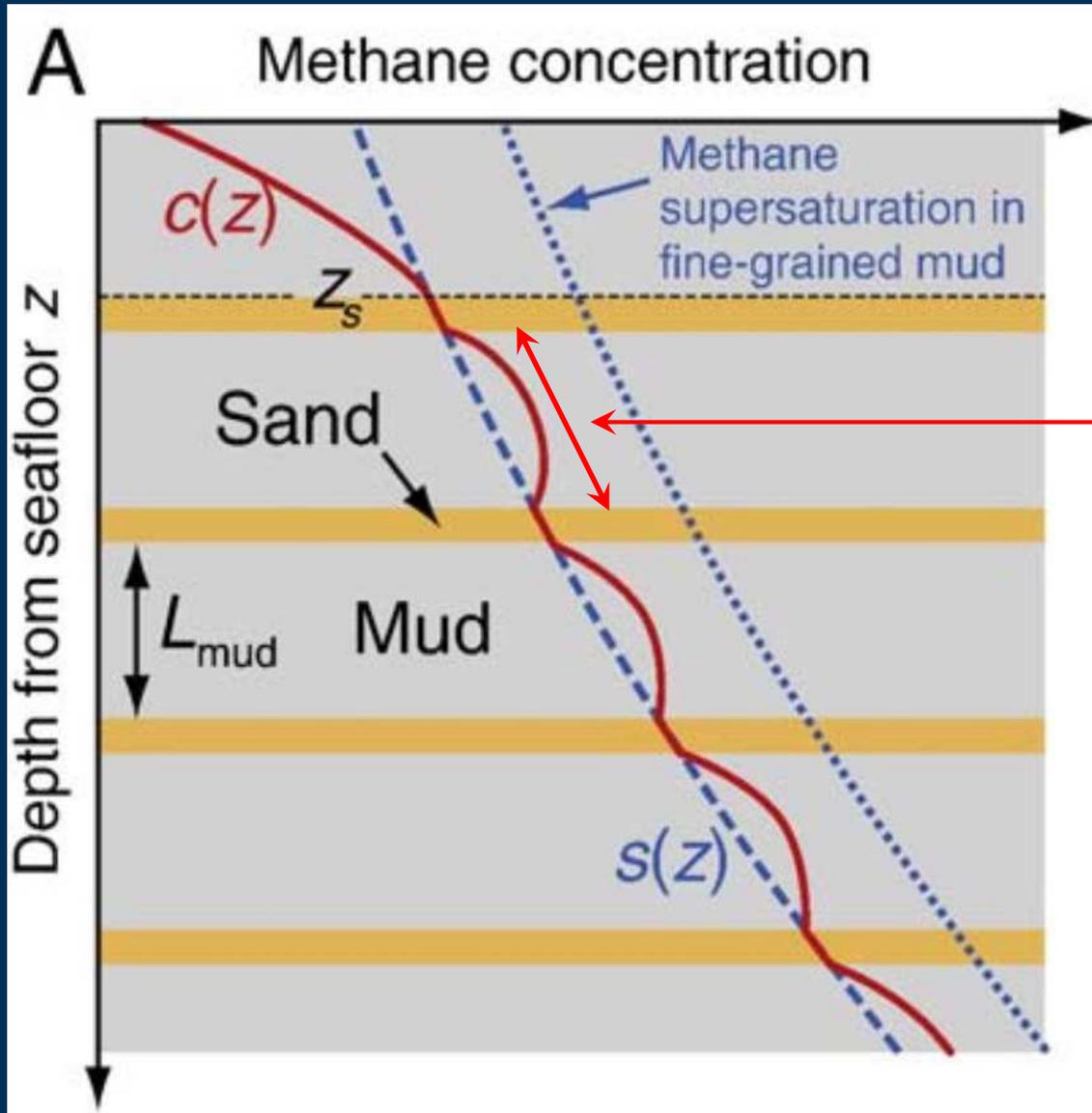
# Solubility dependence on pressure, temperature... and pore size



Solubility difference provides a way to make hydrate!



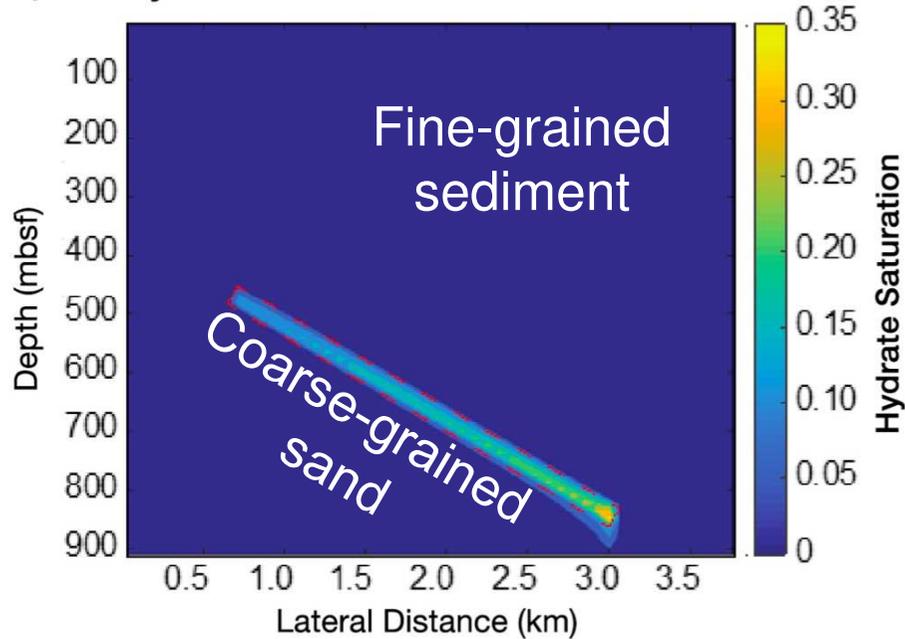
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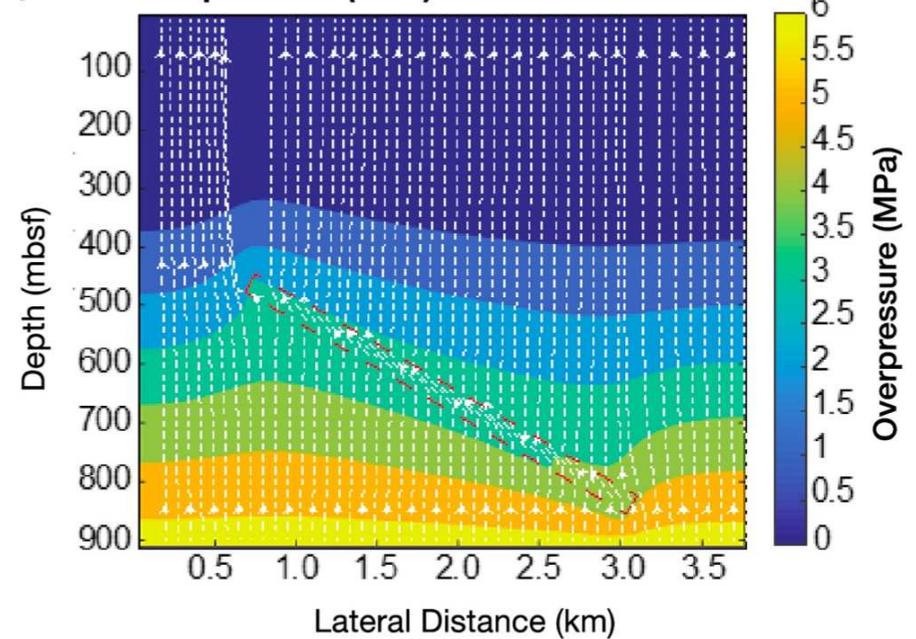
Concentration difference makes methane diffuse into the sand

# Solubility difference provides a way to make hydrate!

a) Hydrate Saturation After  $6.06 \times 10^5$  Years

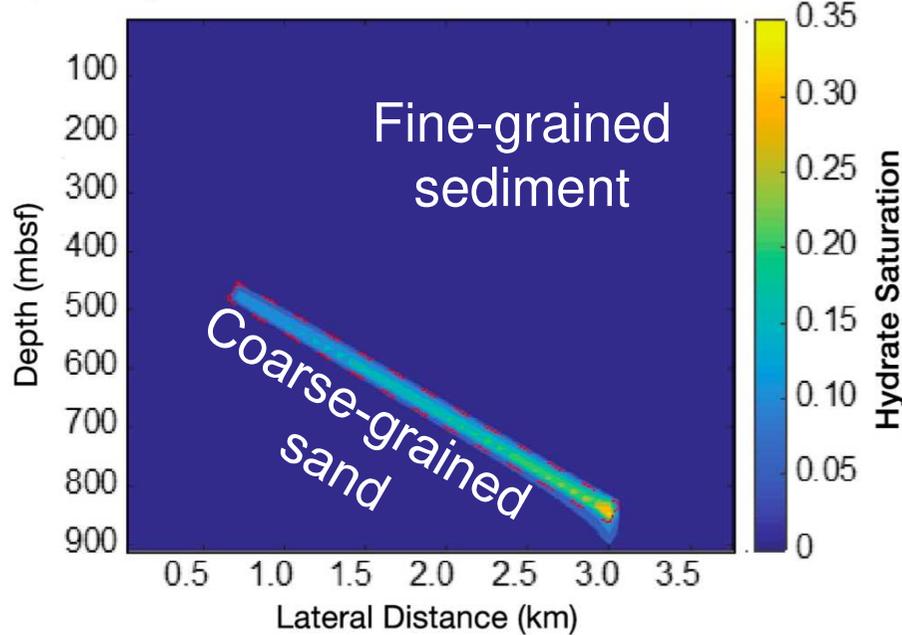


b) Overpressure (MPa) After  $6.06 \times 10^5$  Years

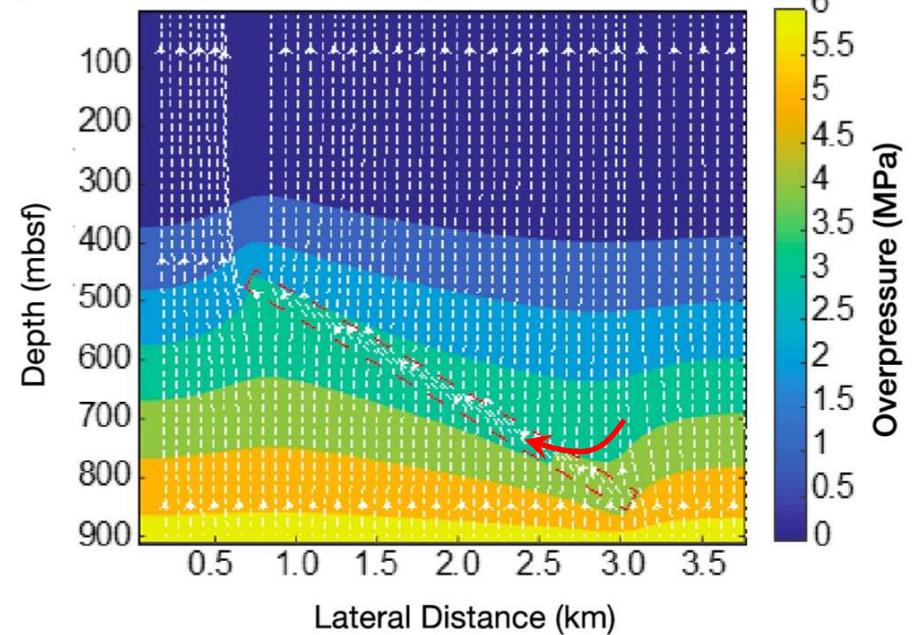


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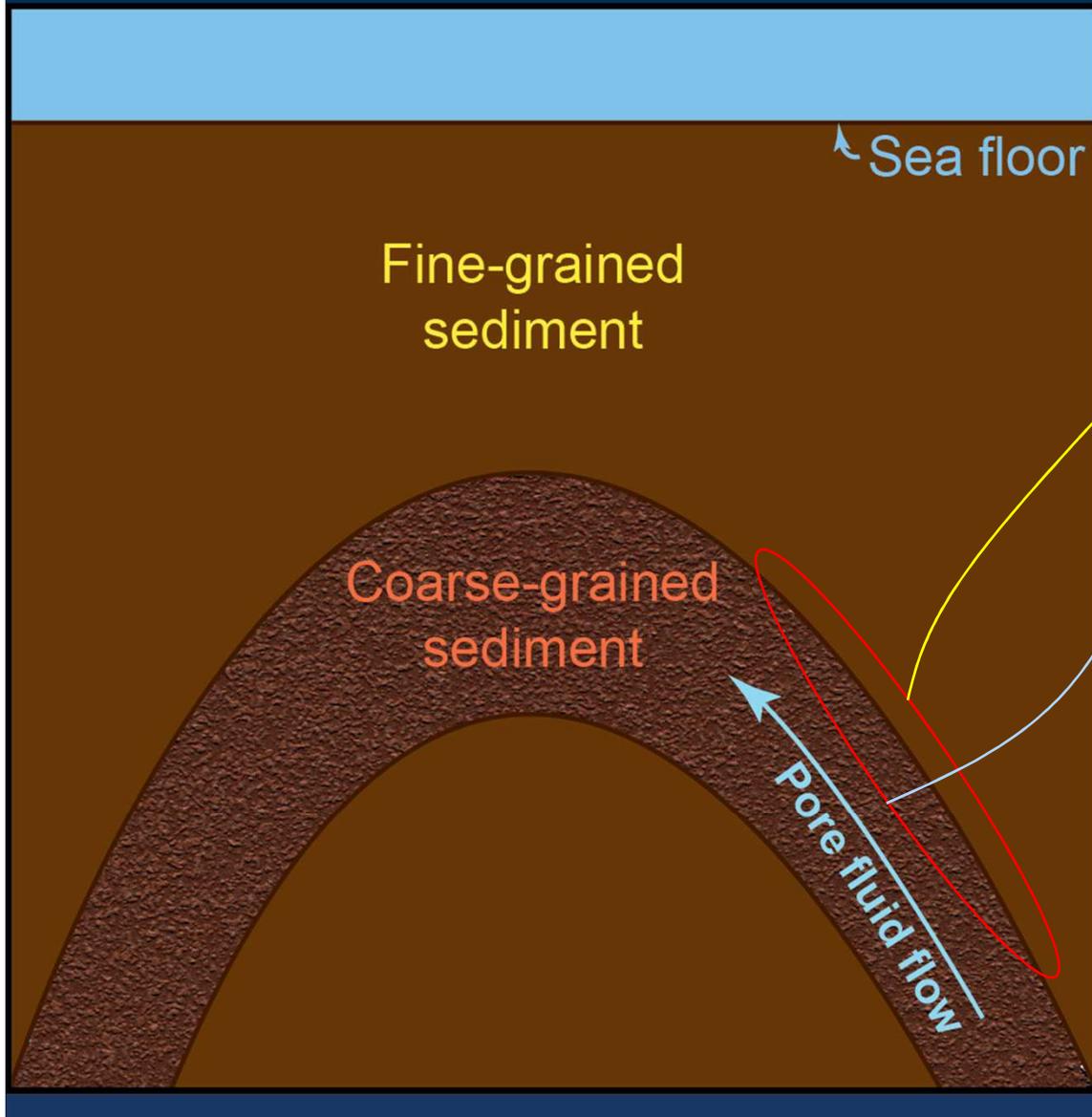


b) Overpressure (MPa) After  $6.06 \times 10^5$  Years



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

# Open research question: where ARE the microbes most active?



Organic material provides “**electron donors**”

Reaction also needs “**electron acceptors**”

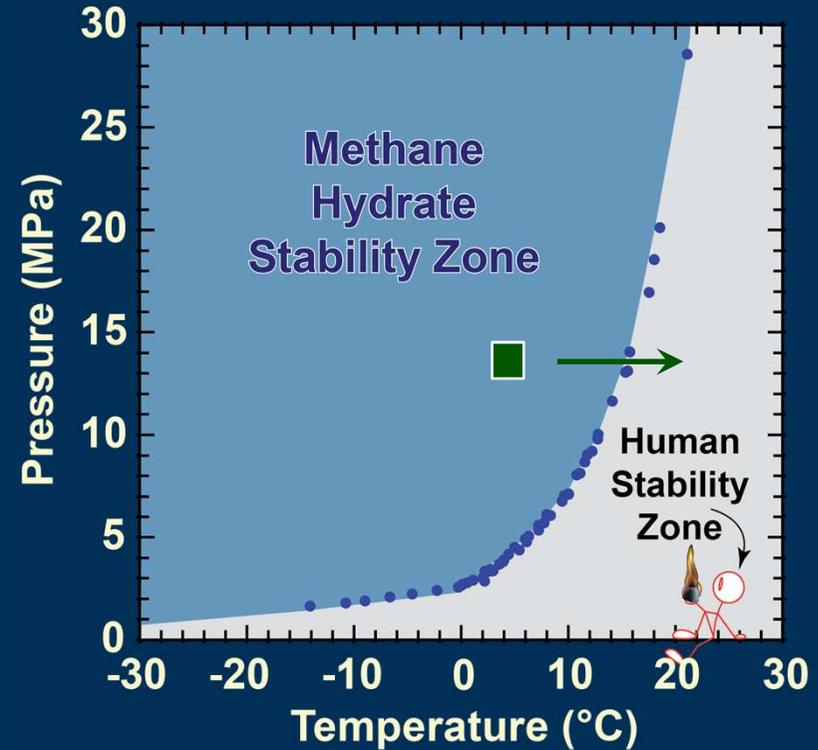
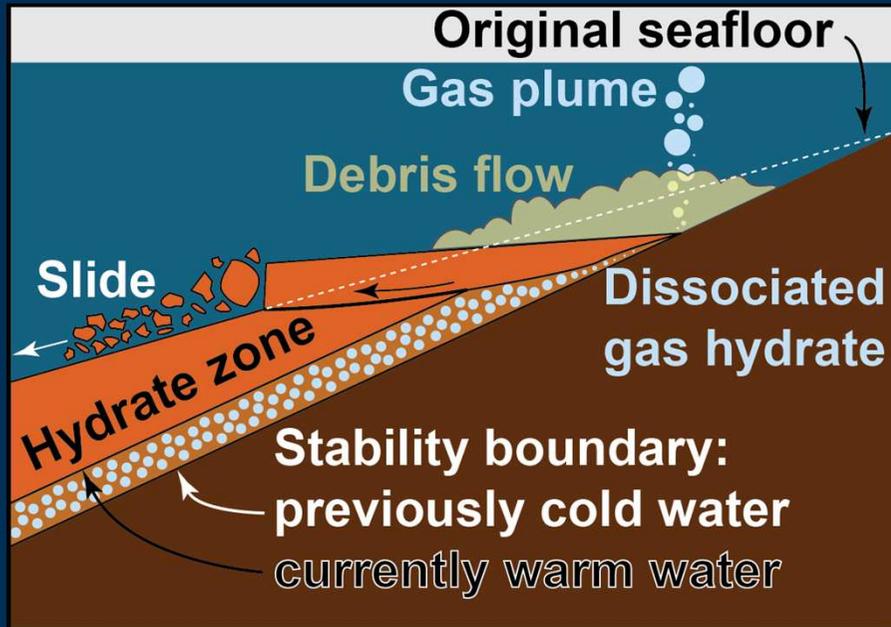


(Reeburgh (2007), ChemRev)

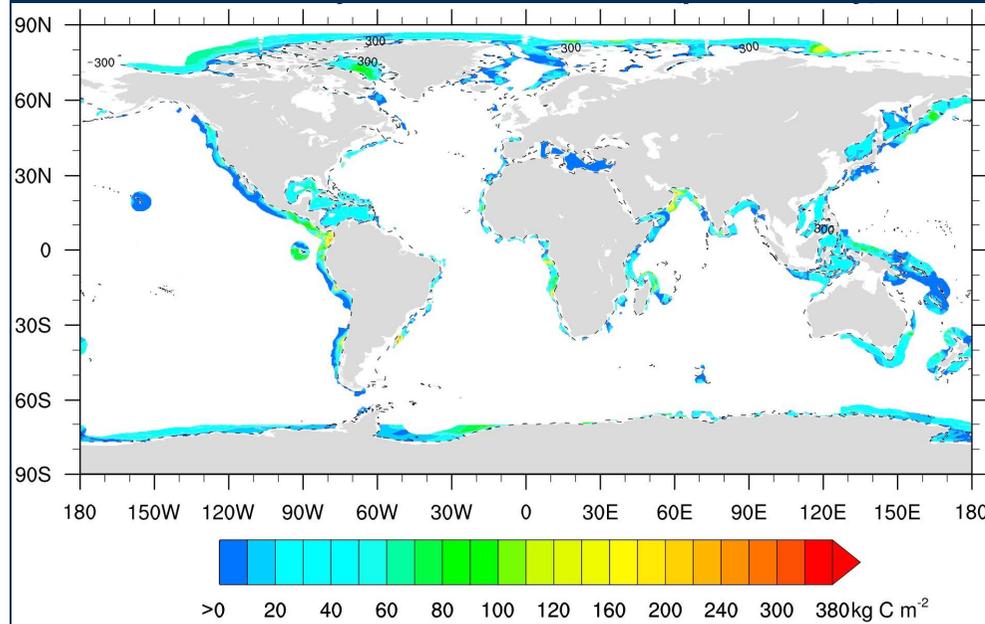
**How fast is methane being produced?**

# What would cause hydrate to dissociate?

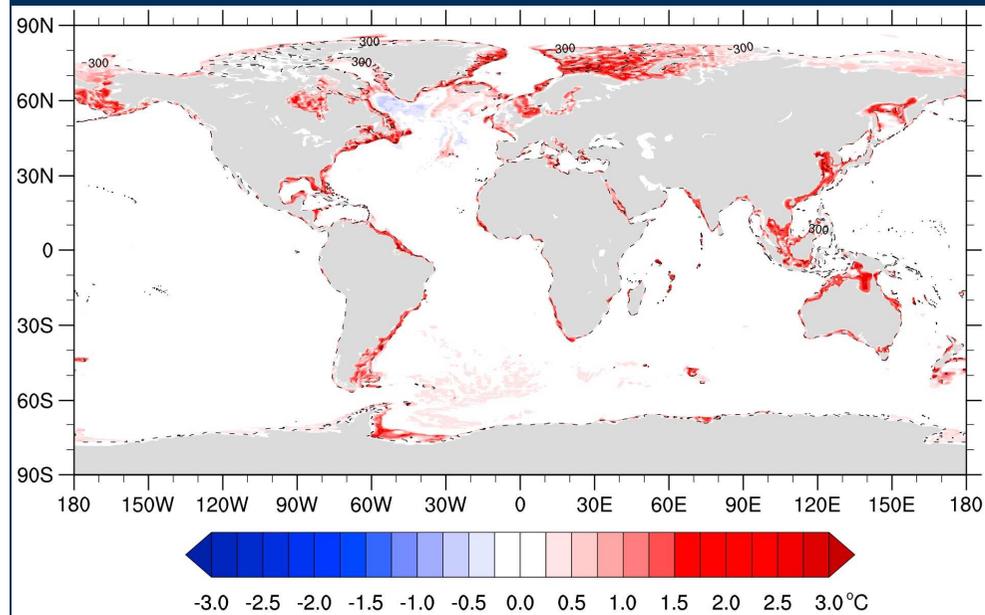
Bottom water warming (heating)



# Distributions of hydrate and future warming



Global distribution of methane hydrate

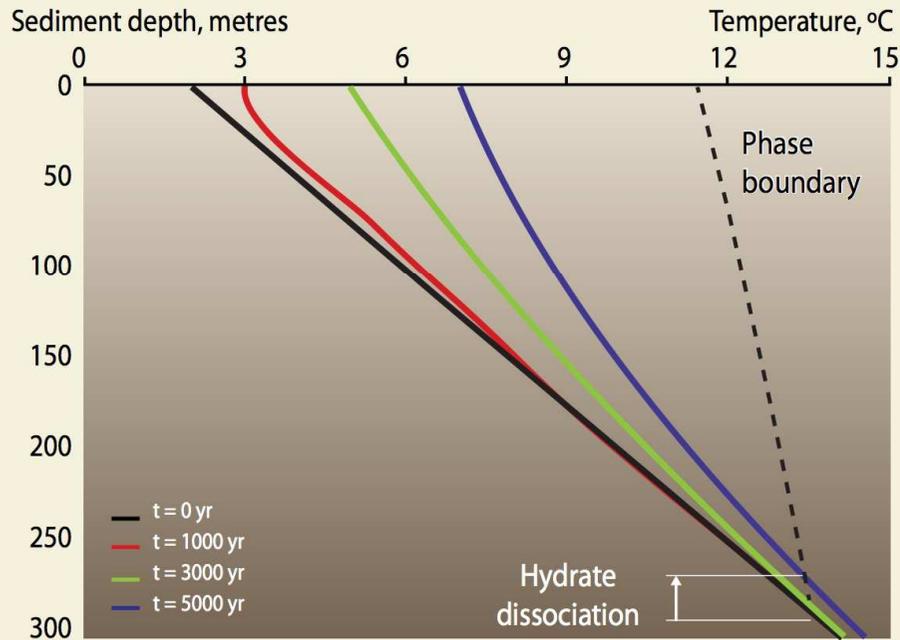


Bottomwater temperature trend for the next 100 years

Kretschmer (2015), Glob. Biogeochem. Cycles

# Not all hydrate is at risk from warming

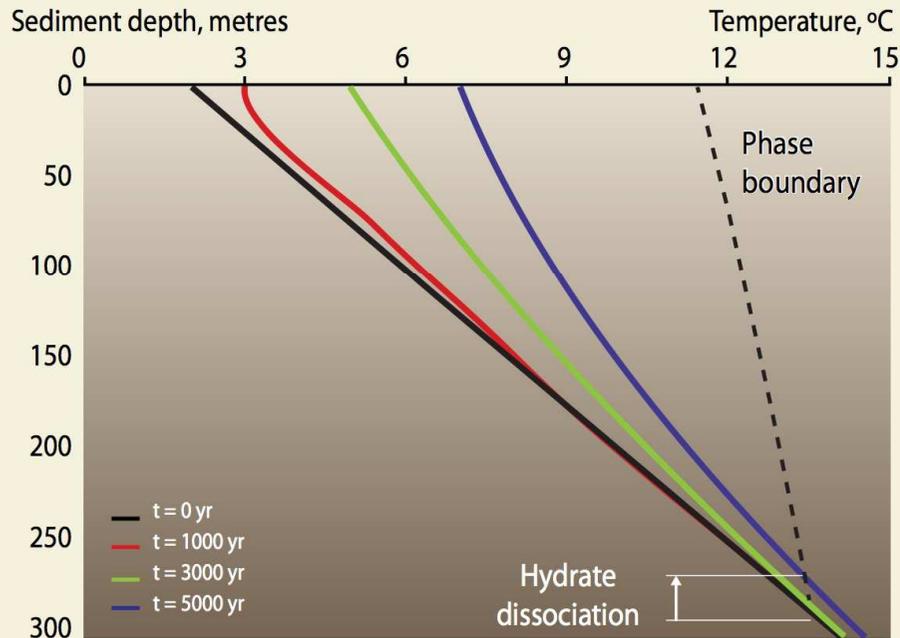
## Deep-water system: penetration of heat into marine sediments beneath 1000 metres of water



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

# Not all hydrate is at risk from warming

## Deep-water system: penetration of heat into marine sediments beneath 1000 metres of water



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

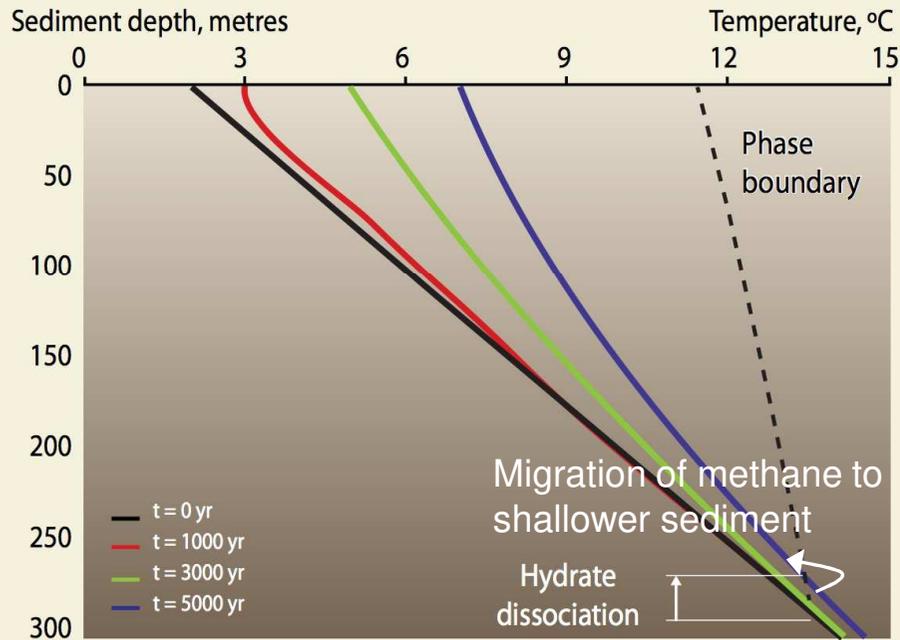
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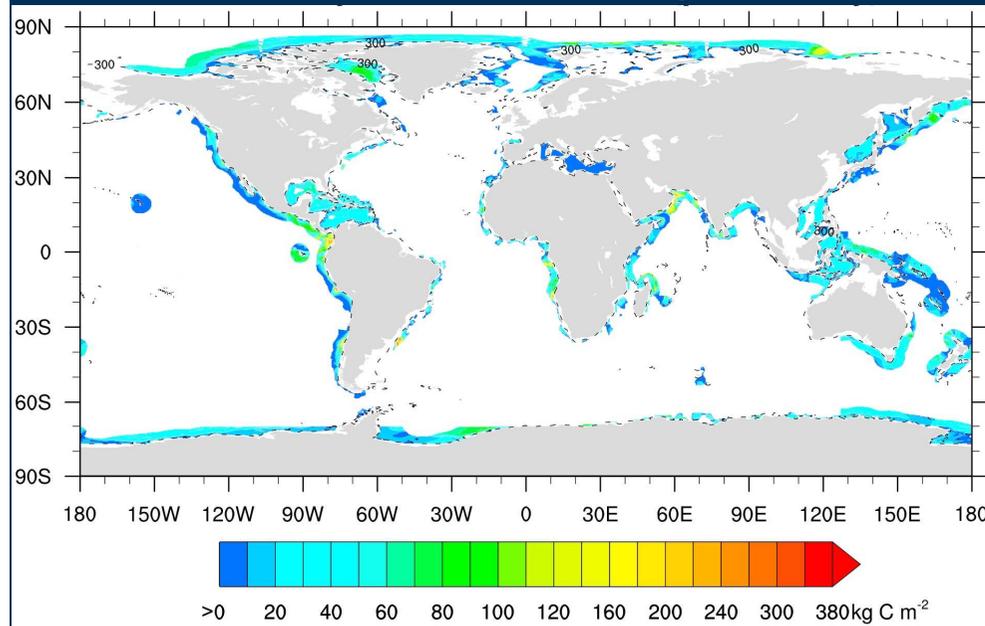
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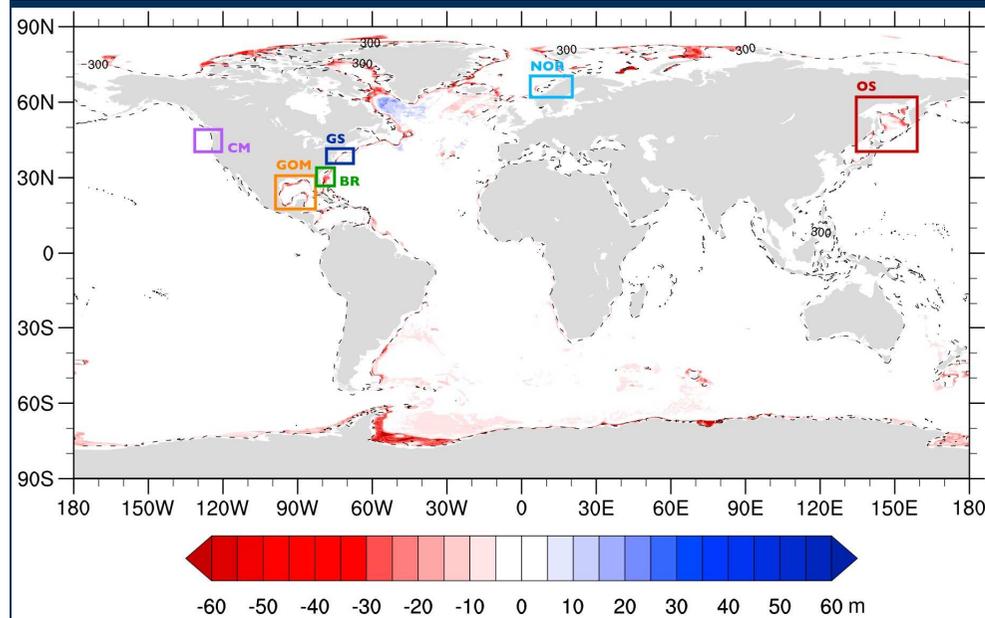
- Heat takes a *long* time to reach the base of hydrate stability.
- Slow thermal process likely allows system to equilibrate, with hydrate slowly dissociating and reforming higher in the sediment column.

# Shallow and high-latitude hydrates are more at risk

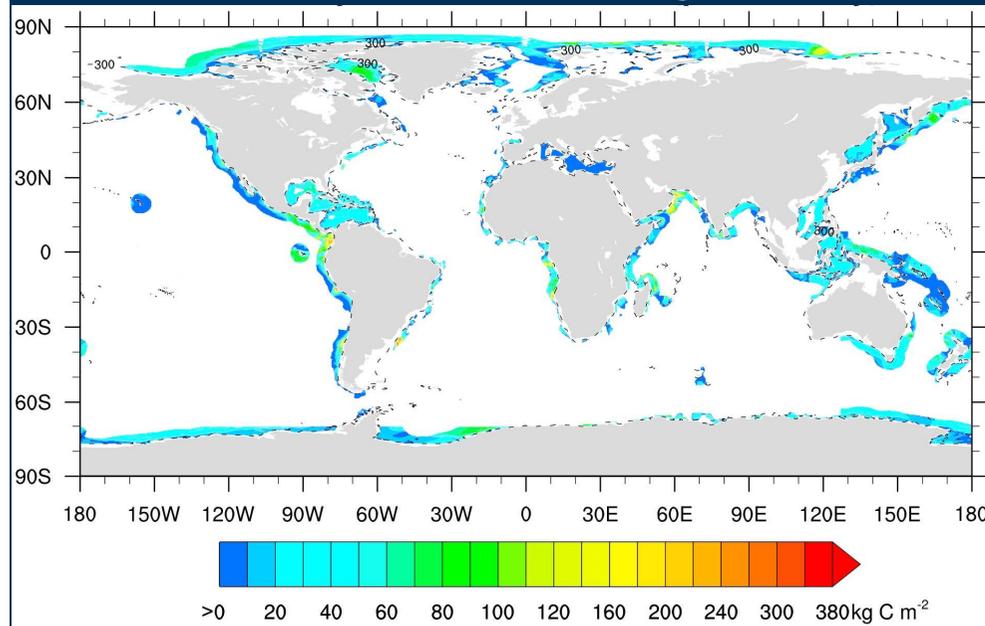
Global distribution of methane hydrate (present day)



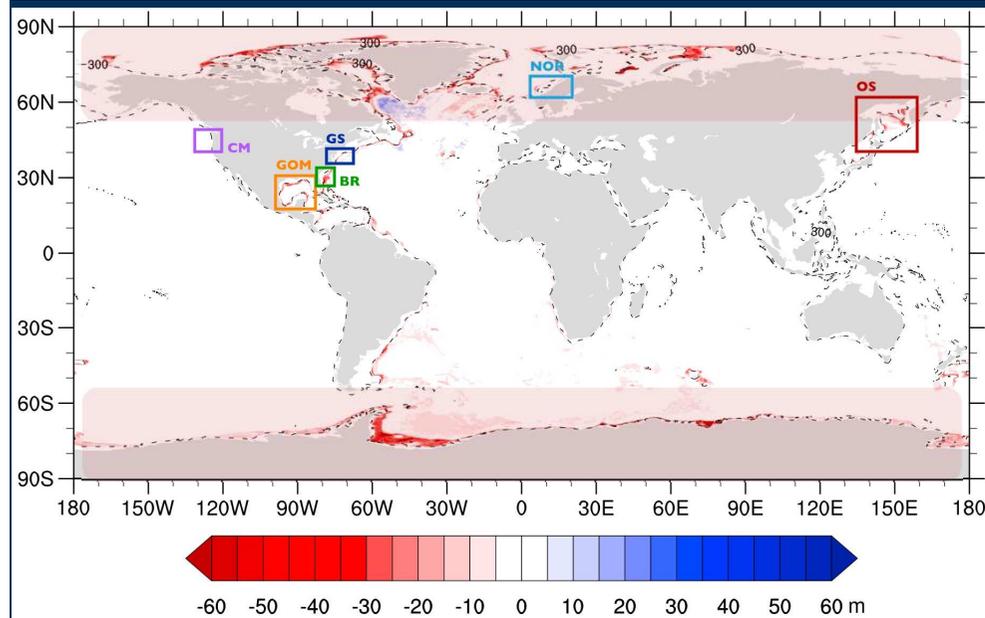
Global distribution of methane hydrate (100-year prediction)



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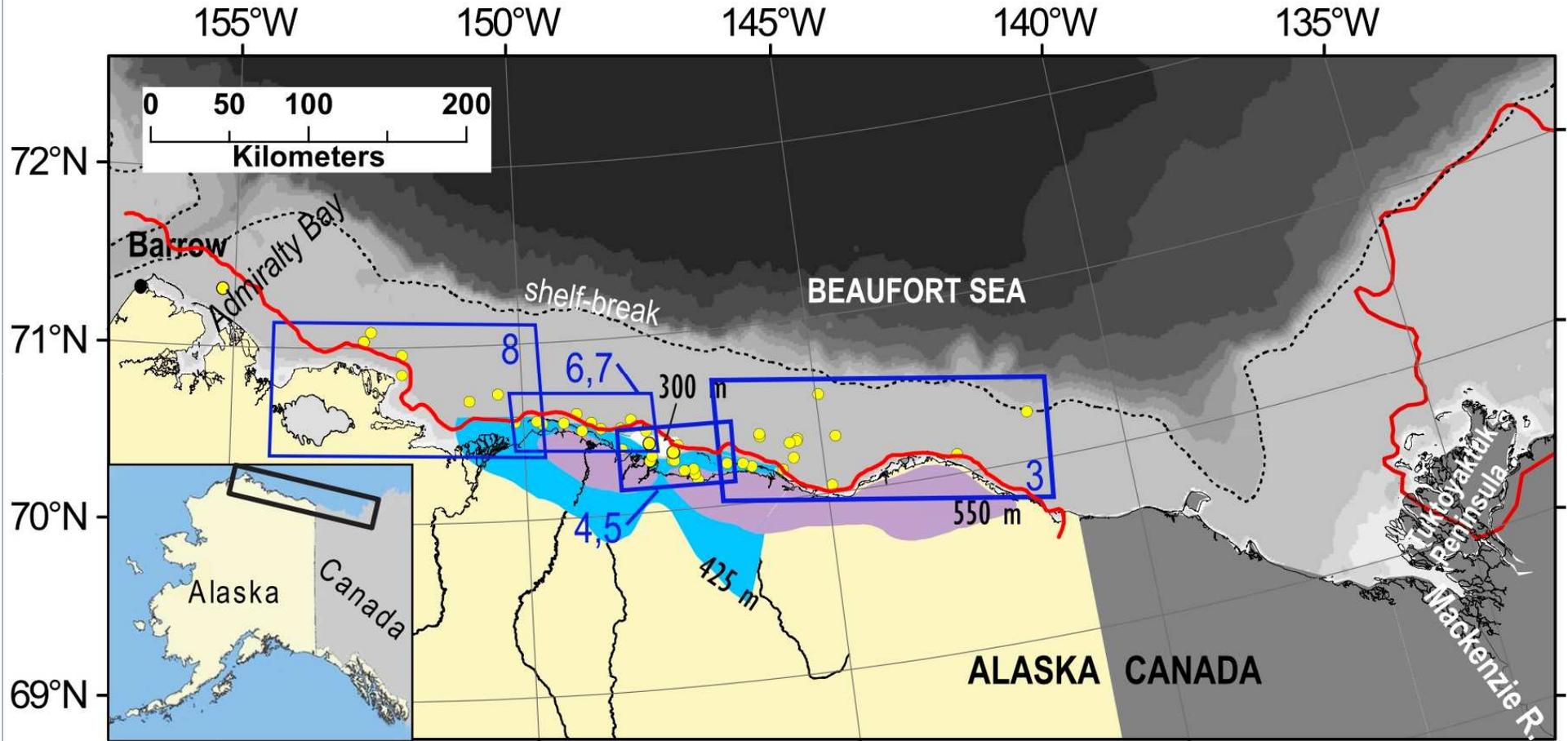


Global distribution of methane hydrate (present day)



Global distribution of methane hydrate (100-year prediction)

# Why are the high-latitude hydrates at risk?

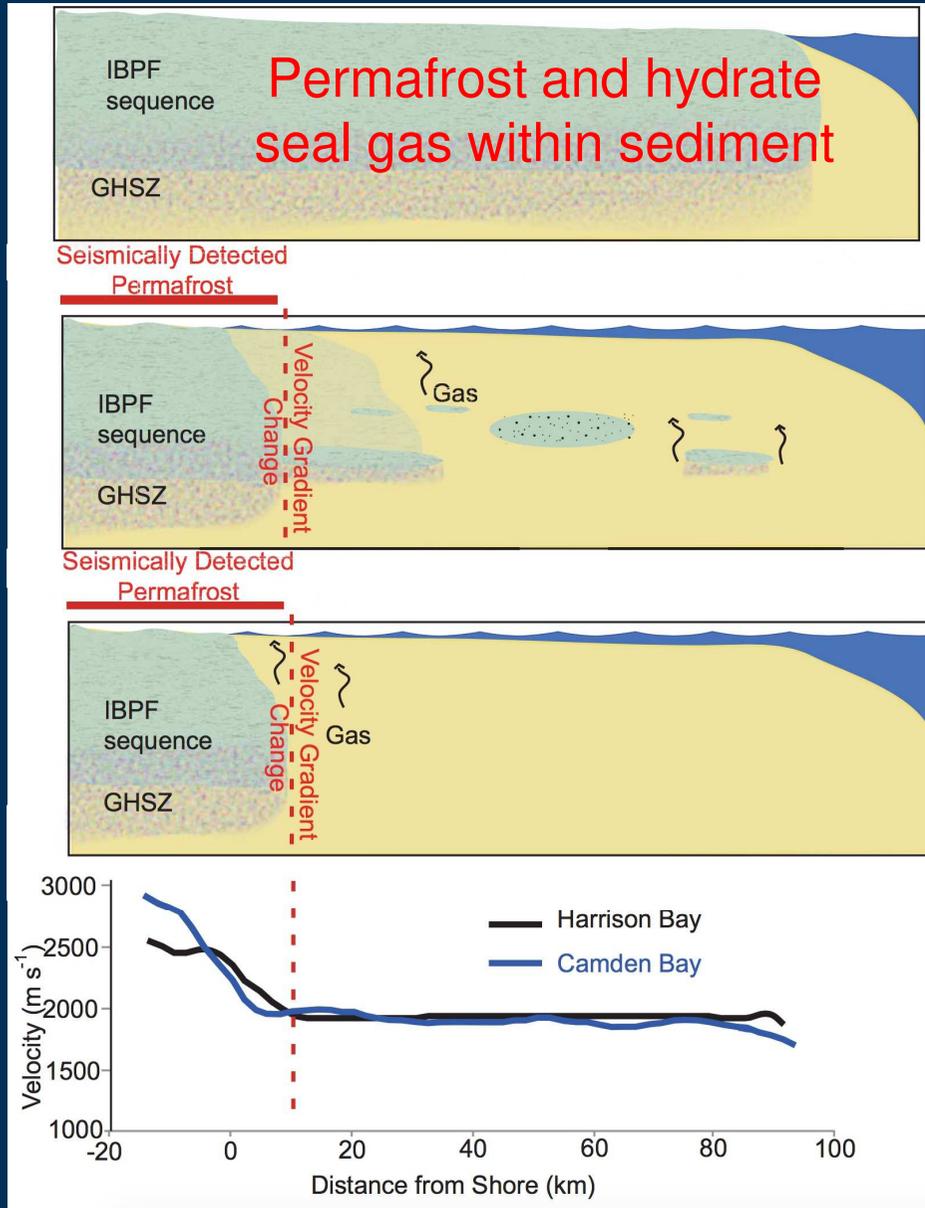


Arctic gas hydrates are generally found in permafrost environments, stable because of the cold temperatures rather than the high pressures experienced in marine environments.

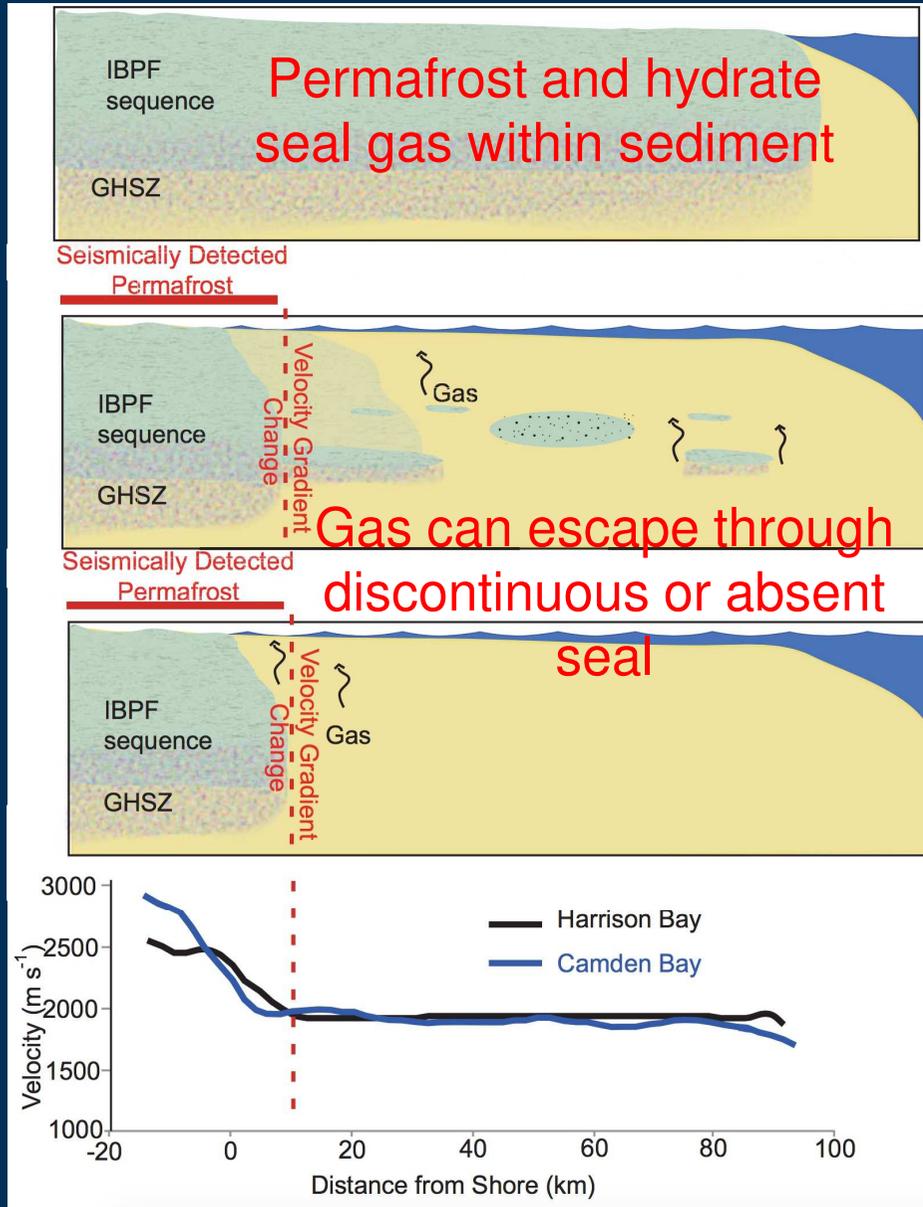
Ruppel et al. (2016), *Geochem., Geophys., Geosystems*

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~13,500 years ago: low sealevel, extensive permafrost, hydrate likely stable to the shelf break.



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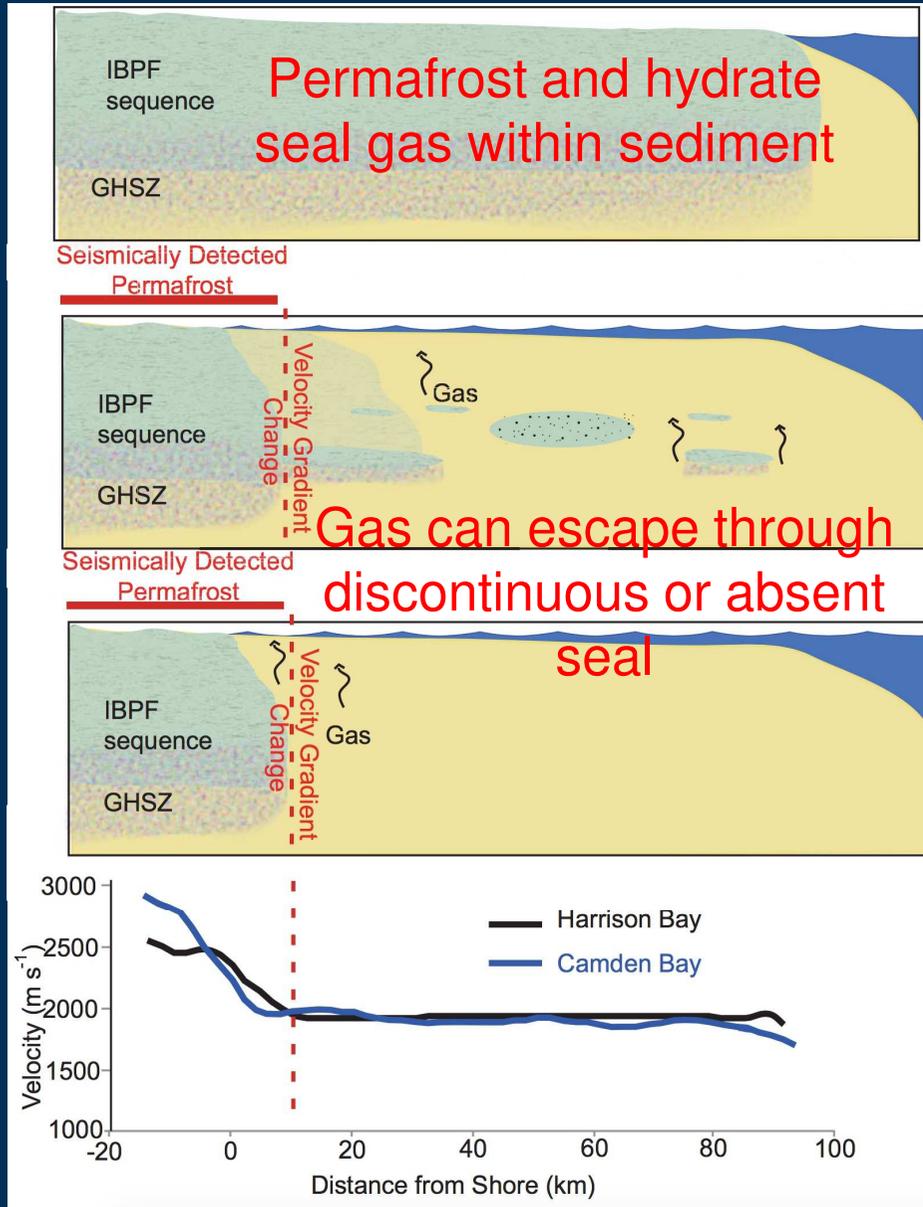


~13,500 years ago: low sealevel, extensive permafrost, hydrate likely stable to the shelf break.

Present day – flooding of the shelf mostly destabilized the permafrost and underlying hydrate.

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

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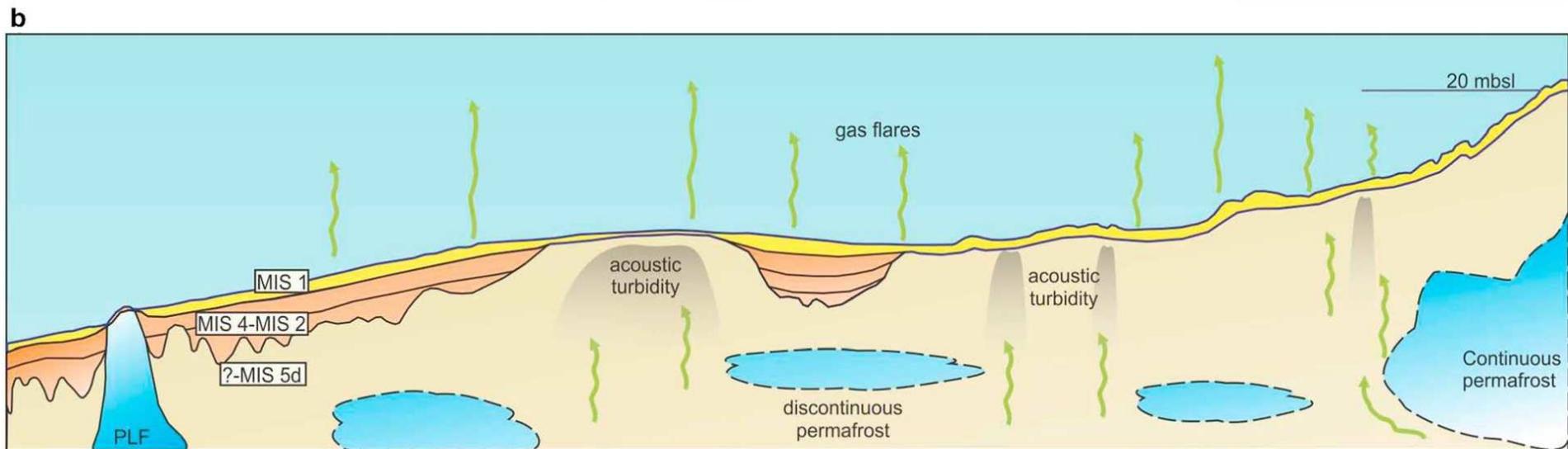
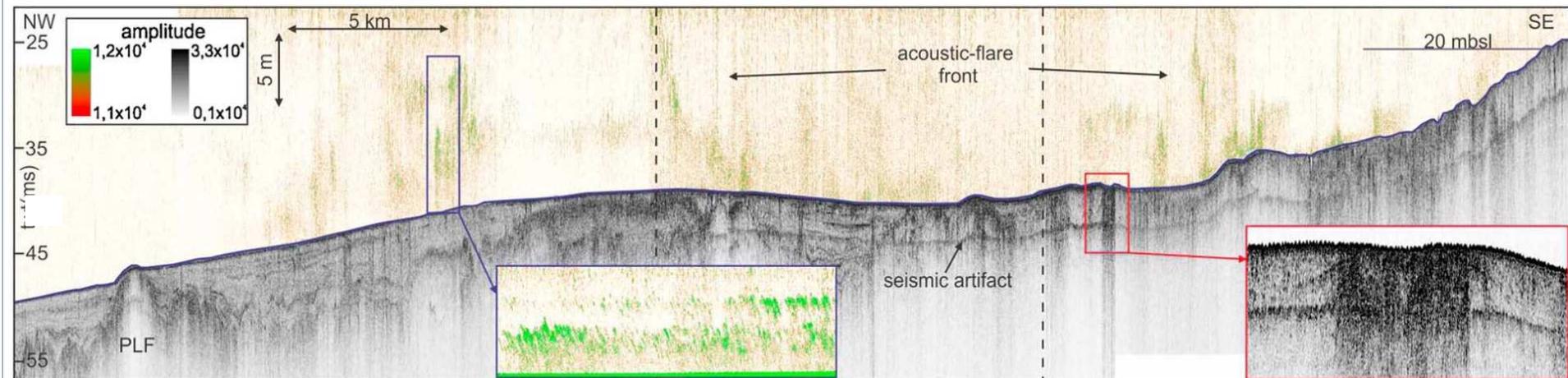
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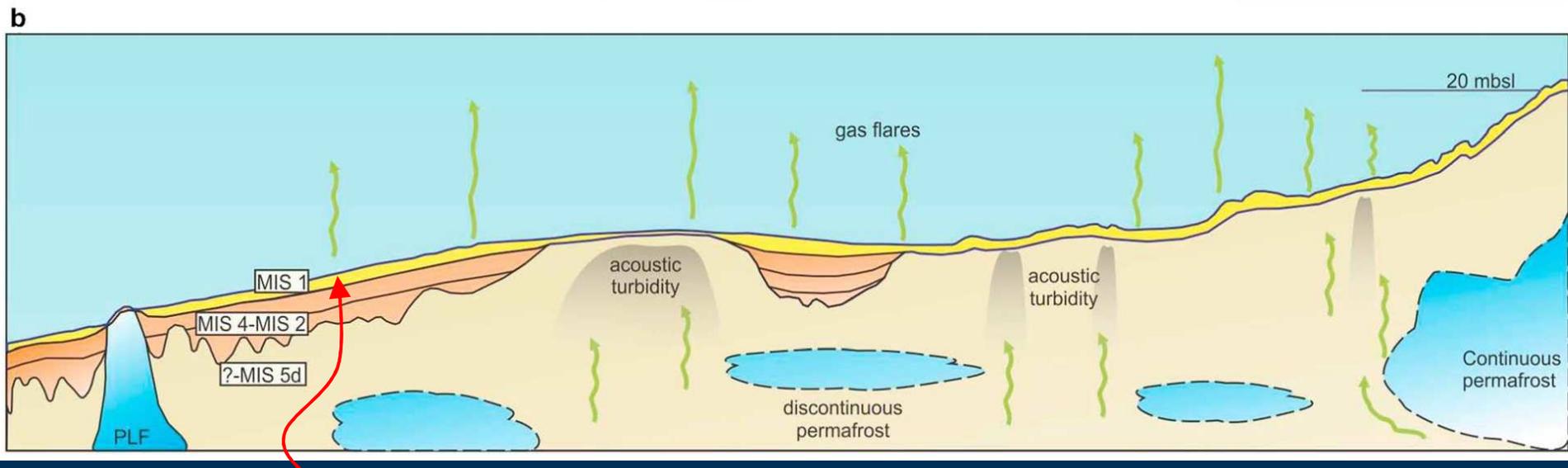
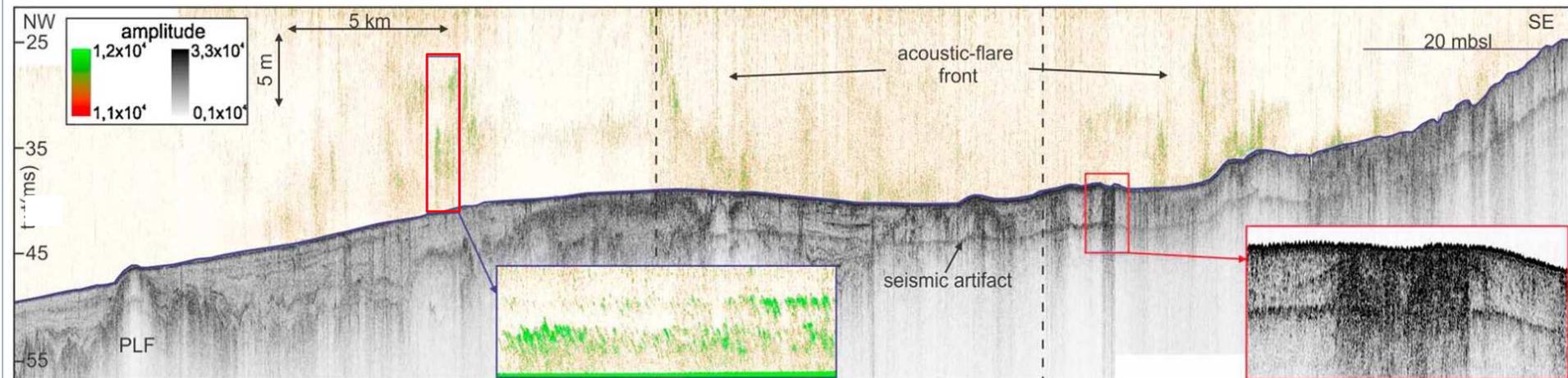
Ice-bearing permafrost (IBPF) has high velocity, like hydrate. Velocity break indicates the extent of IBPF.

# Similar permafrost breakdown seen in the Russian Arctic



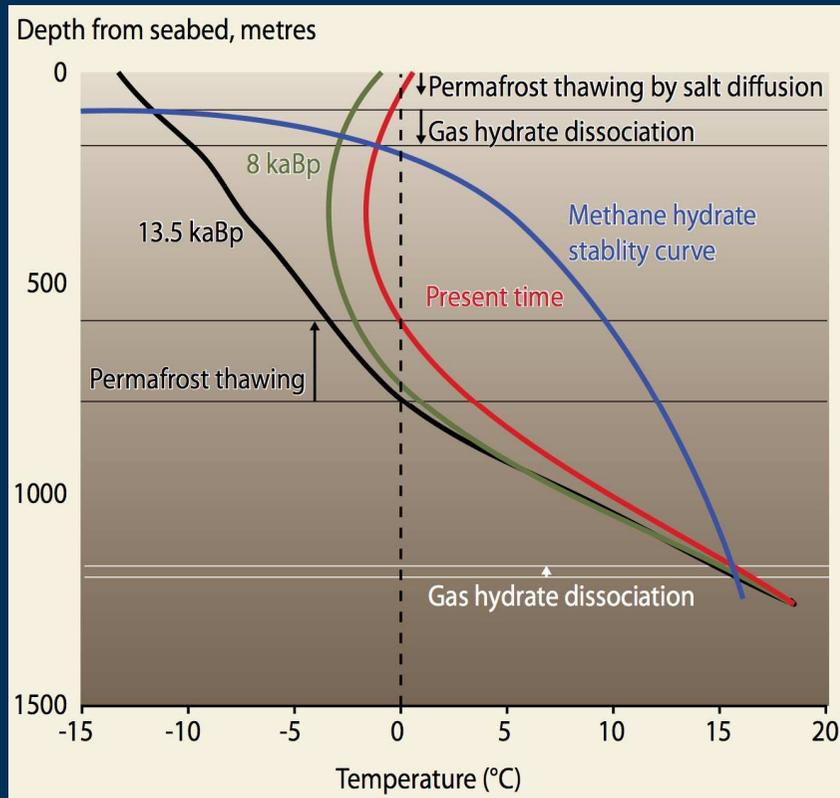
Gas flares in the water indicate the presence of gas migrating up through the discontinuous permafrost seal.

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

# Breaking down permafrost via "warm" water flooding

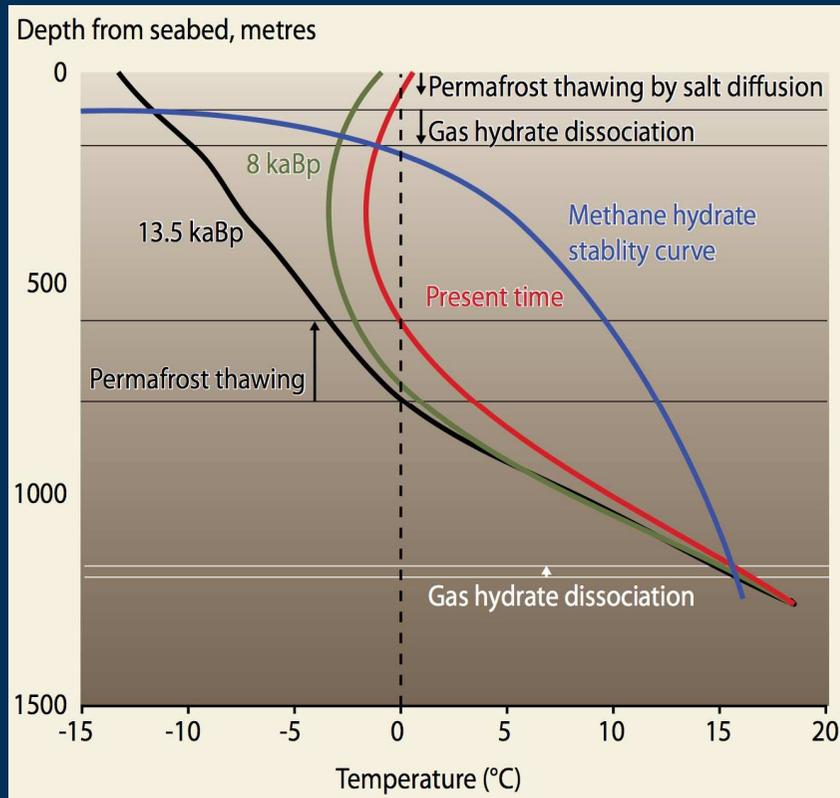


**Shallow, Arctic hydrates:**  
Assume  $\sim 15^{\circ}\text{C}$  ground surface  
increase  $\sim 13,500$  years ago.

- 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

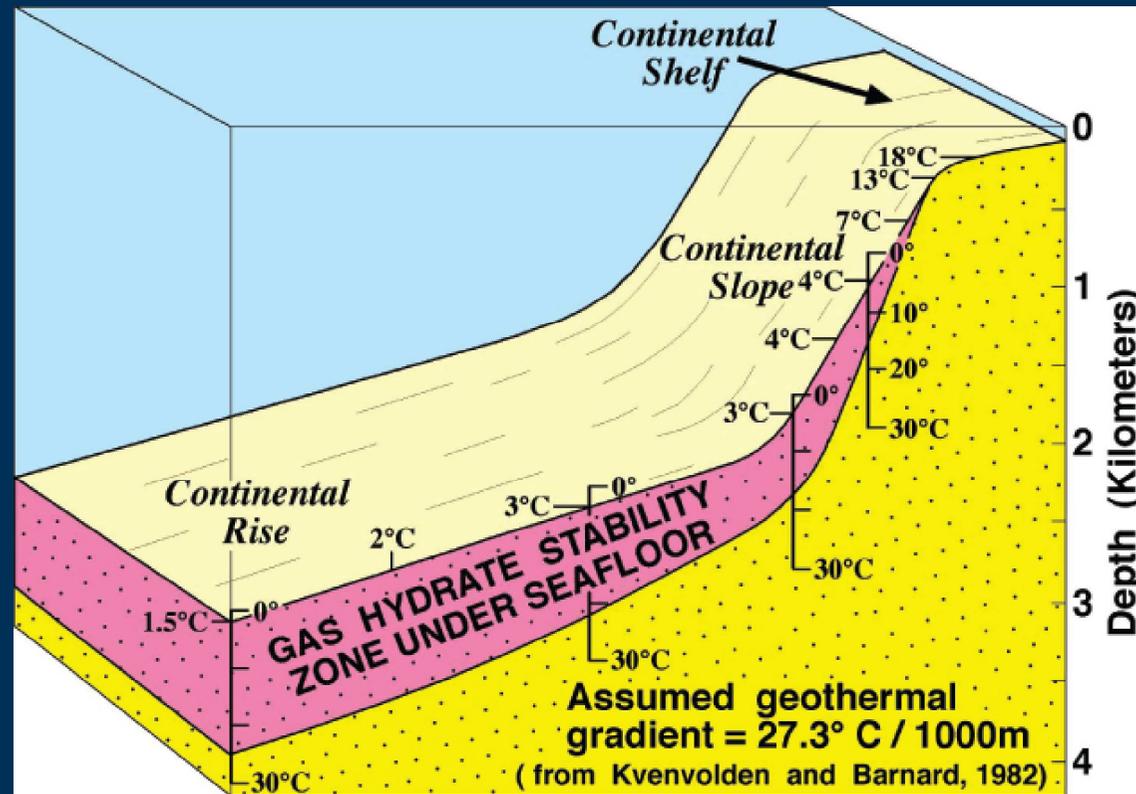


**Shallow, Arctic hydrates:**  
Assume ~15°C ground surface  
increase ~13,500 years ago.

- 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.
- 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.

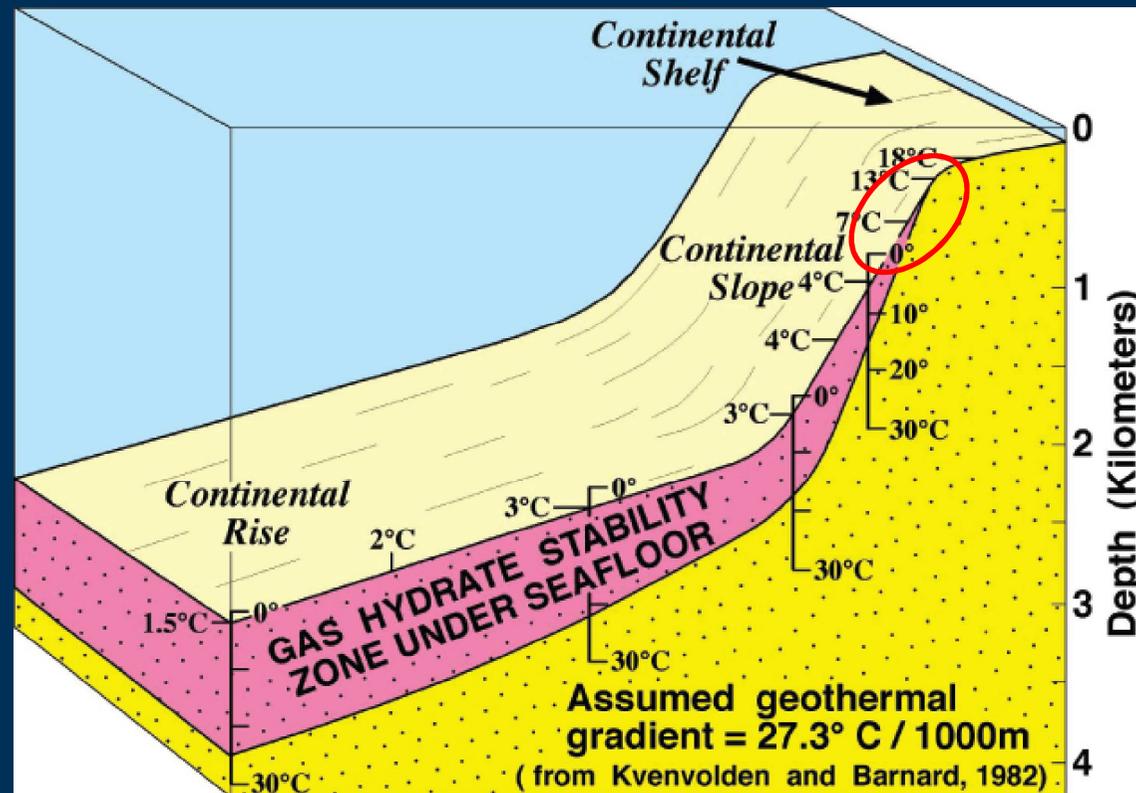
# Another “at-risk” region: the shallowest marine hydrates

Deeper, colder water allows for a thicker stability zone



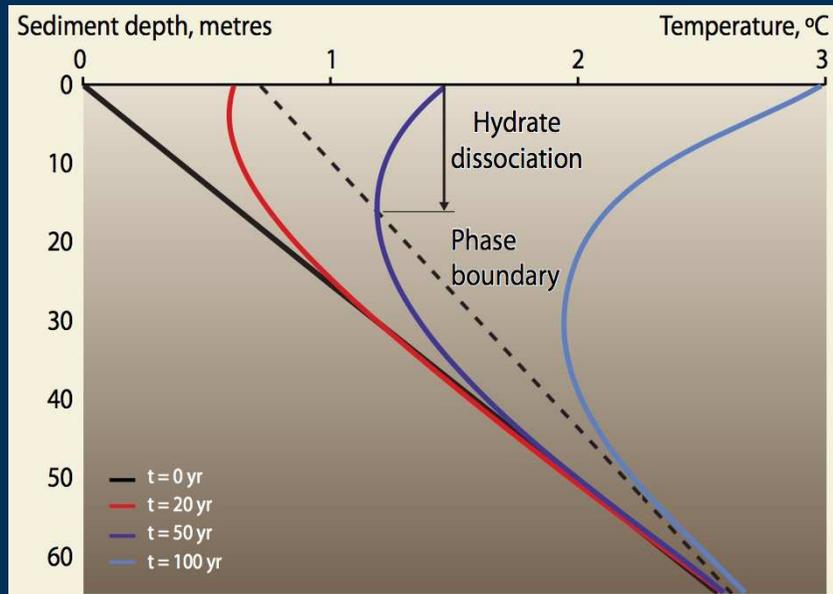
## Another “at-risk” region: the shallowest marine hydrates

In shallow water, the stability zone is very thin



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

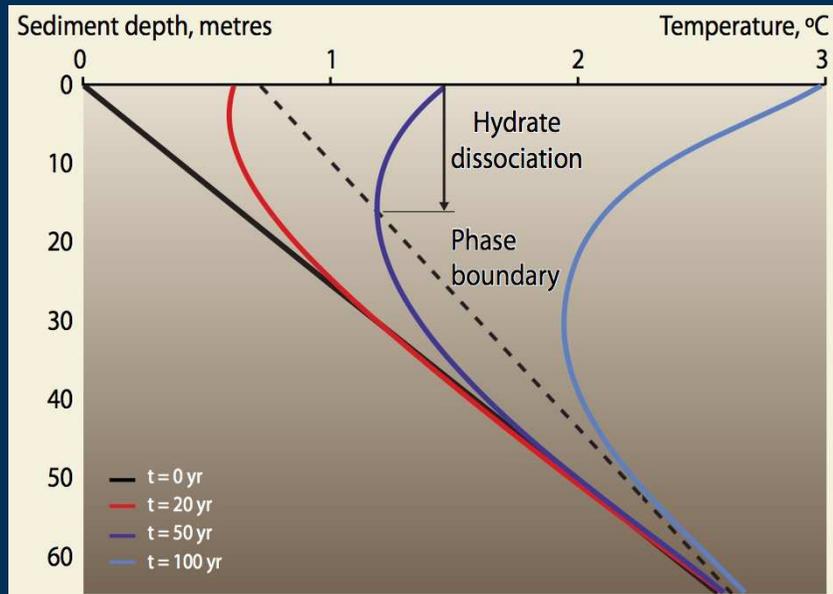
## Another “at-risk” region: the shallowest marine hydrates



- 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.

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



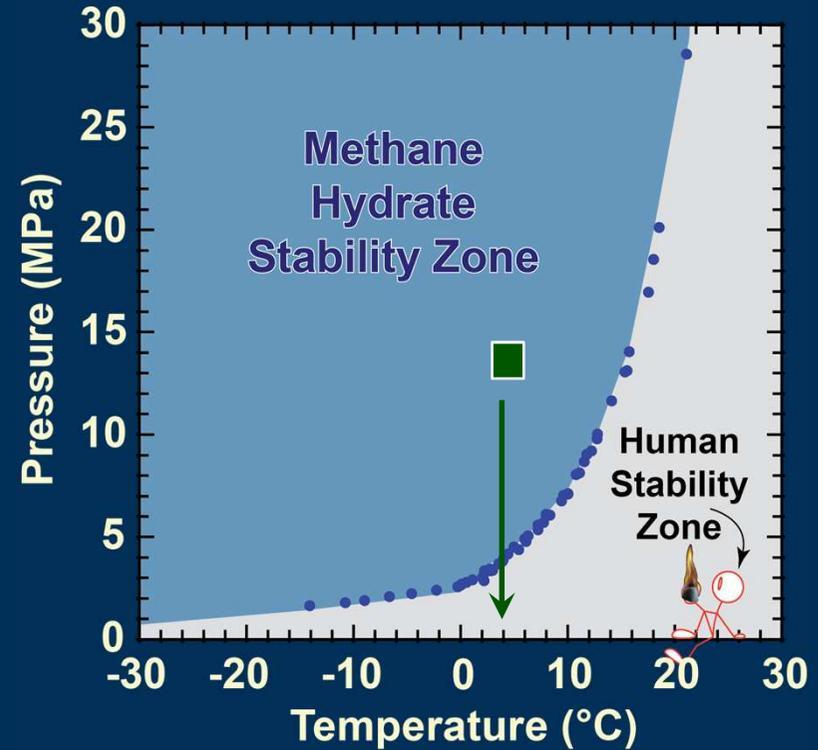
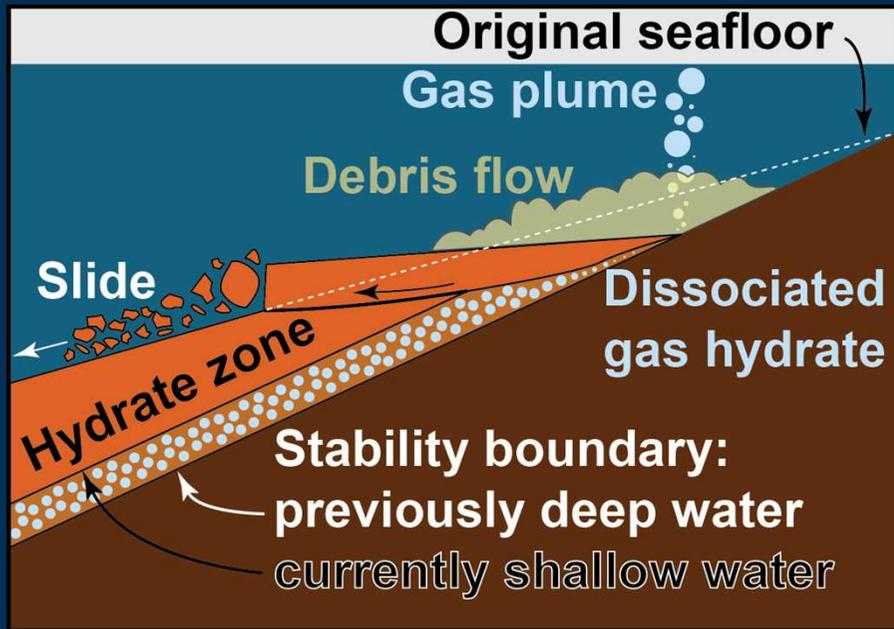
- Unlike the deepwater case:
  - Dissociation occurs in tens of years.
  - Gas can not recycle upward to reform as stable hydrate.
- Globally, the hydrates at risk in this region represent less than 3.5% of the global hydrate distribution, but methane released likely does not reach the atmosphere.

### Shallow hydrates, no permafrost:

Assume +3°C per 100 years  
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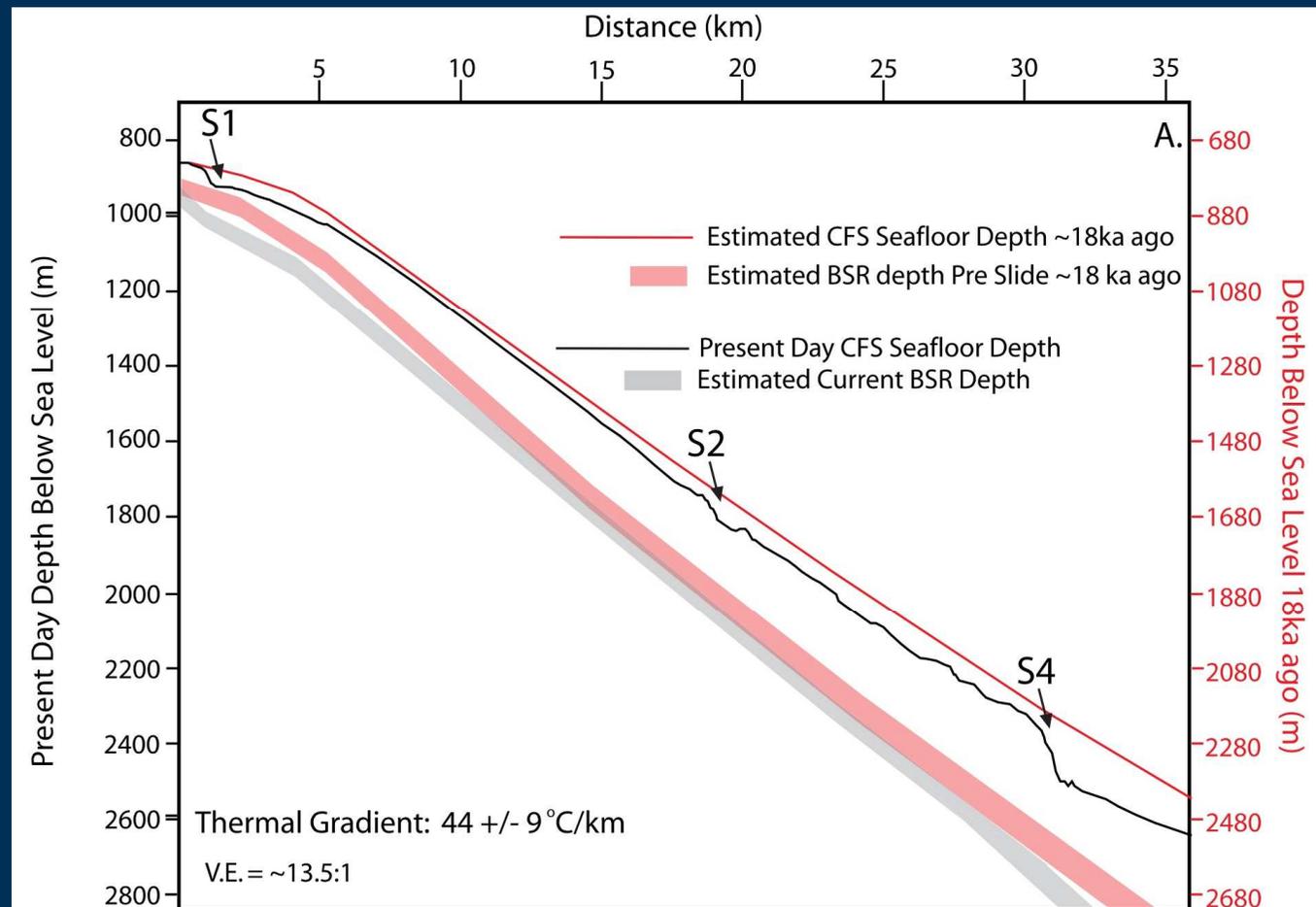
# A faster cause for hydrate dissociation

Drop in sea level (depressurization)



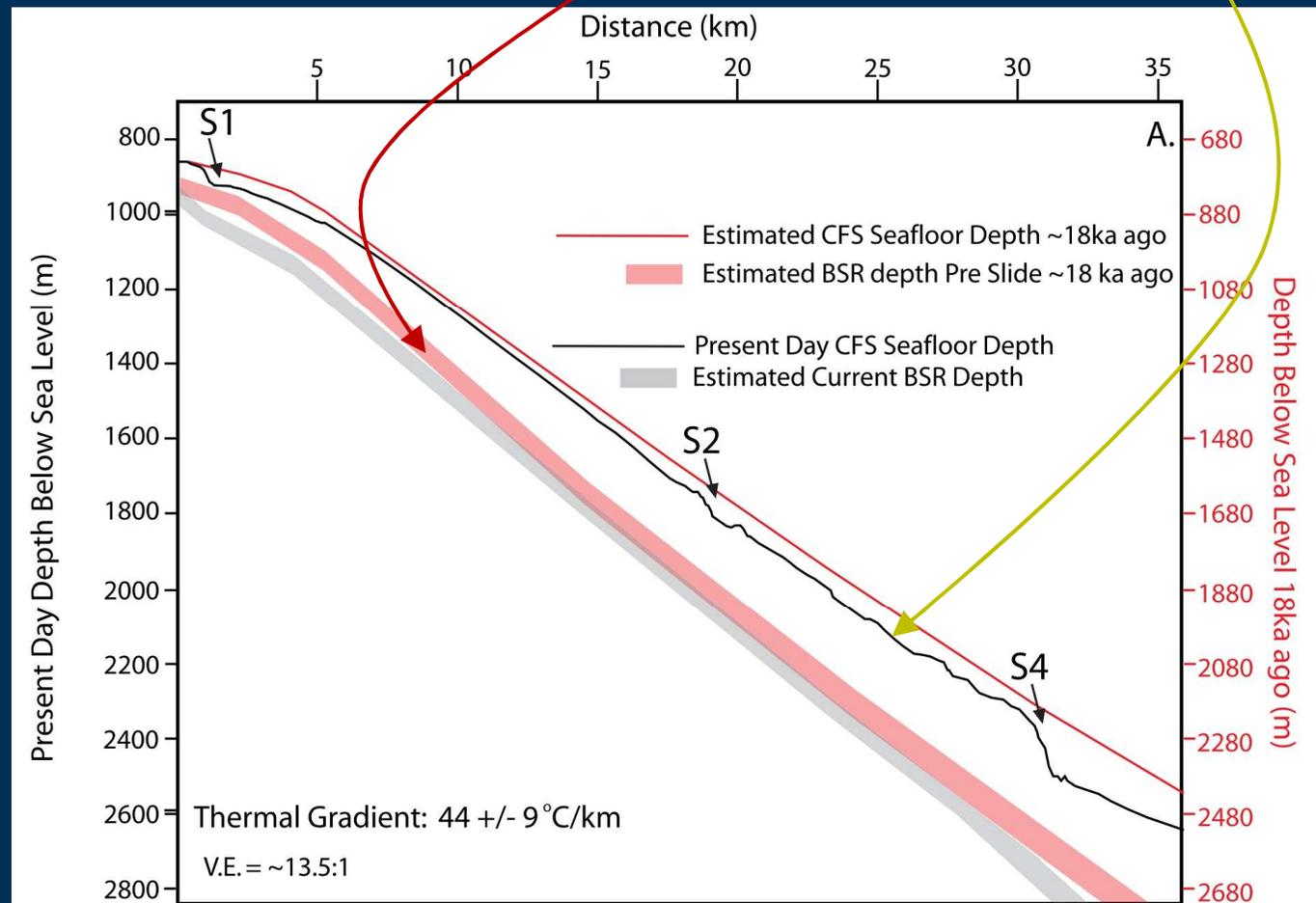
# Do the possible dissociation mechanisms cause debris flows?

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



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

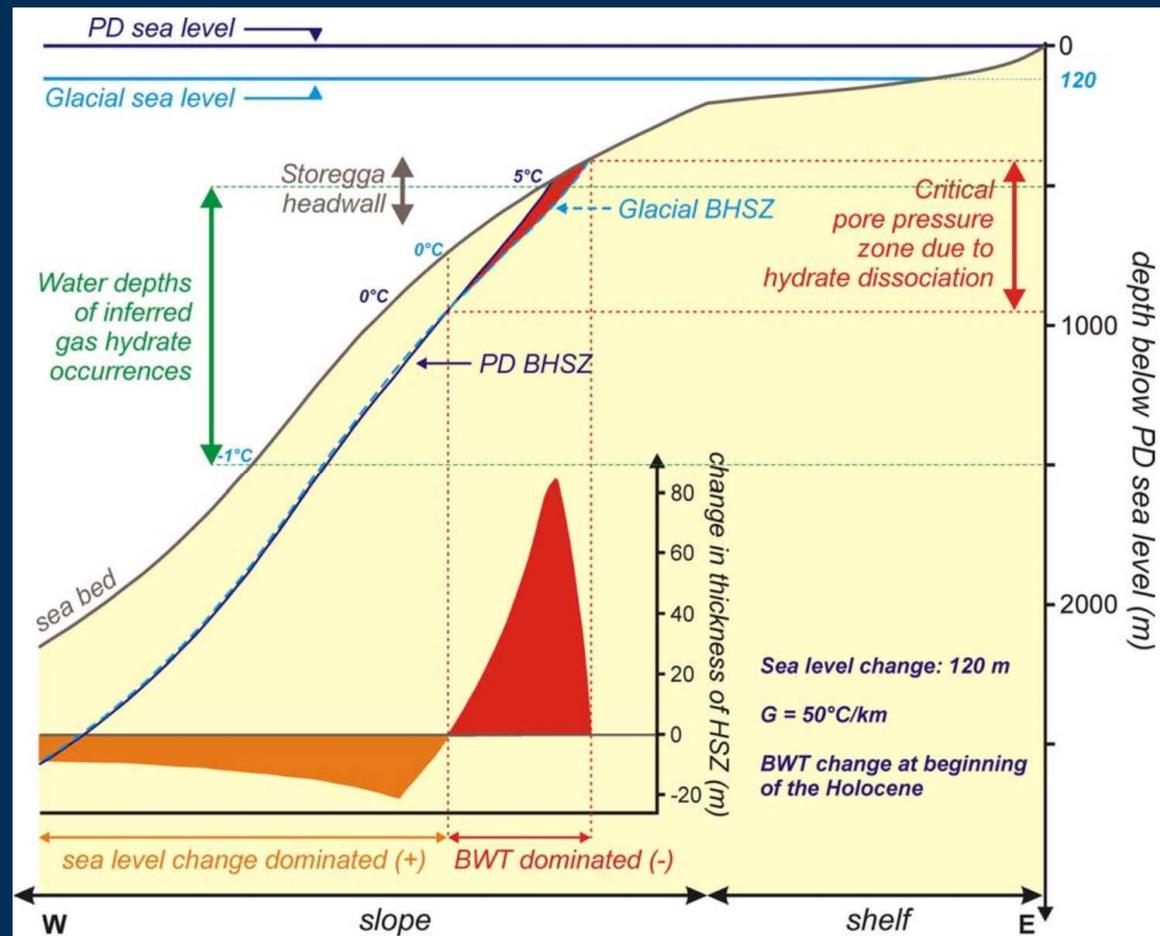


Cape Fear Slide (offshore USA)

Hornbach et al. (2007), *Geochem., Geophys. Geosystems*

Do the possible dissociation mechanisms cause debris flows?

Model reconstructions of slumps suggest some slump failure mechanisms could not have involved hydrate



Storegga Slide (offshore Norway)

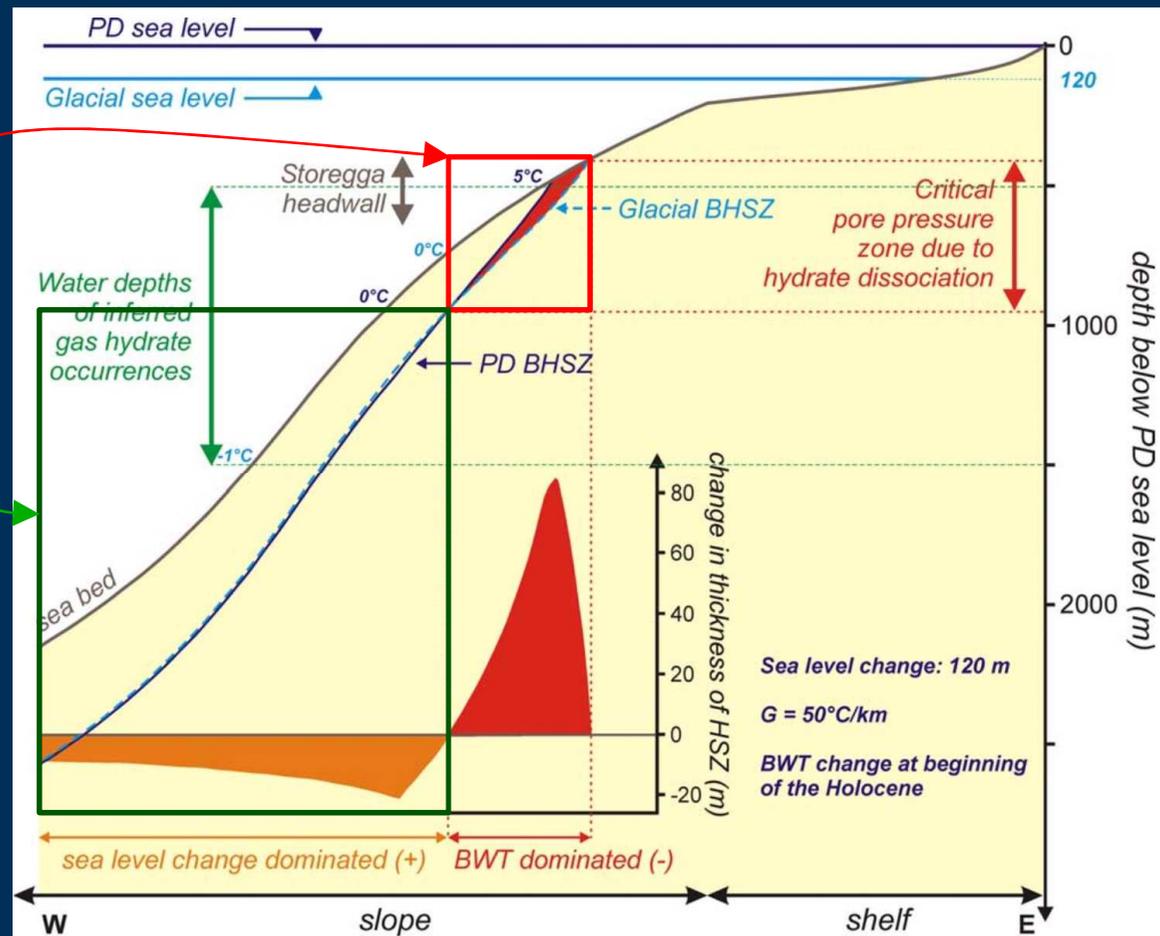
Mienert et al. (2005), Marine Petroleum Geology

# Do the possible dissociation mechanisms cause debris flows?

Model reconstructions of slumps suggest some slump failure mechanisms could not have involved hydrate

Upper portion dominated by bottom-water warming (destabilizing for hydrate)

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



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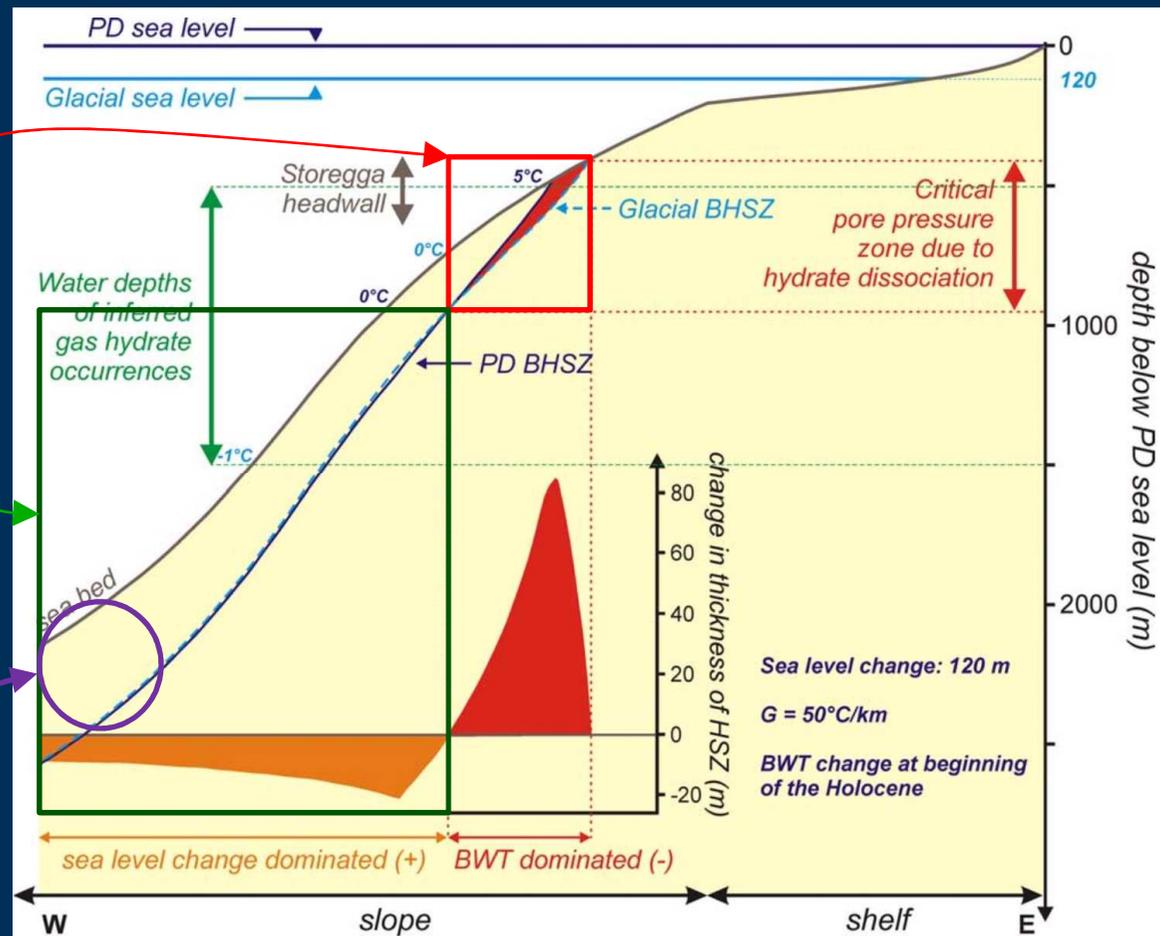
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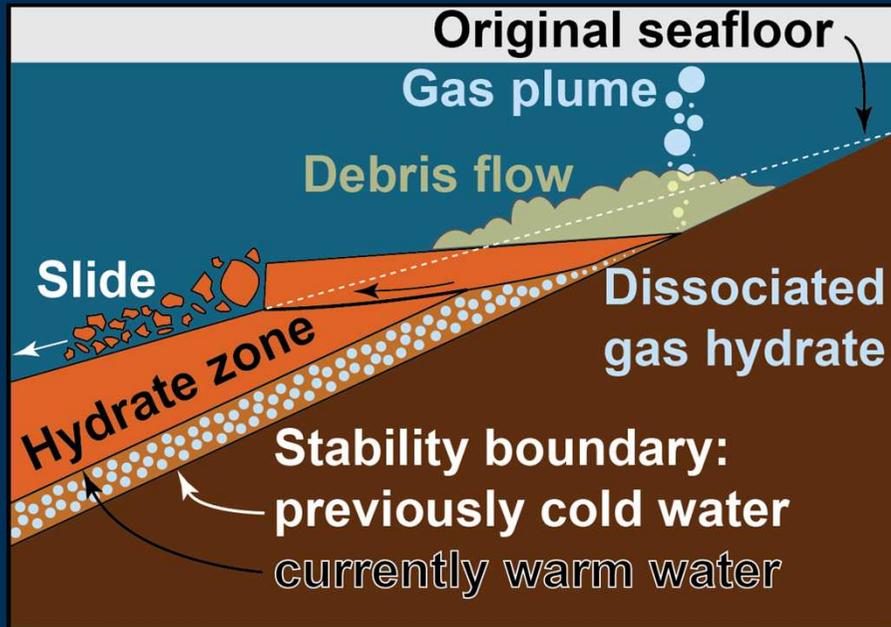
Slide began near the toe, where hydrates were becoming *more* stable.



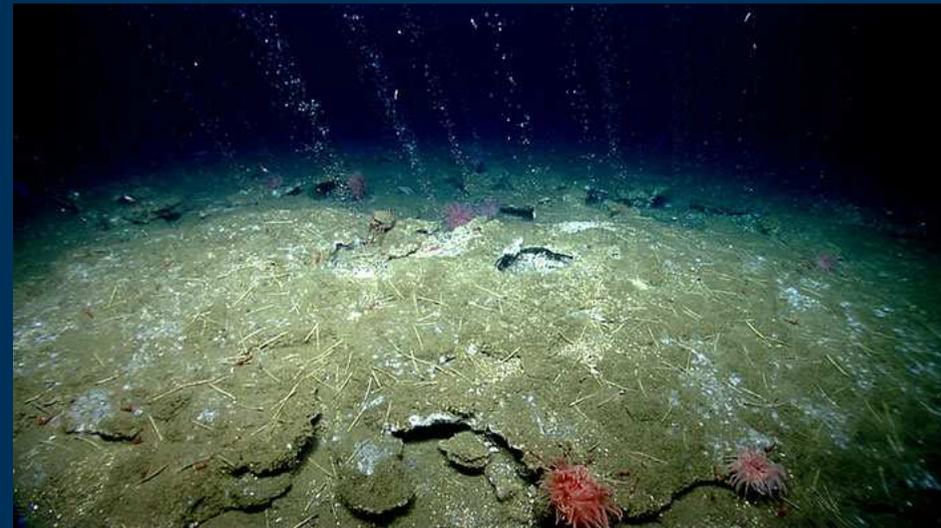
Storegga Slide (offshore Norway)

Kvalstad et al. (2005), Marine Petroleum Geology

Catastrophic release does not seem likely.  
What about sustained release of methane?



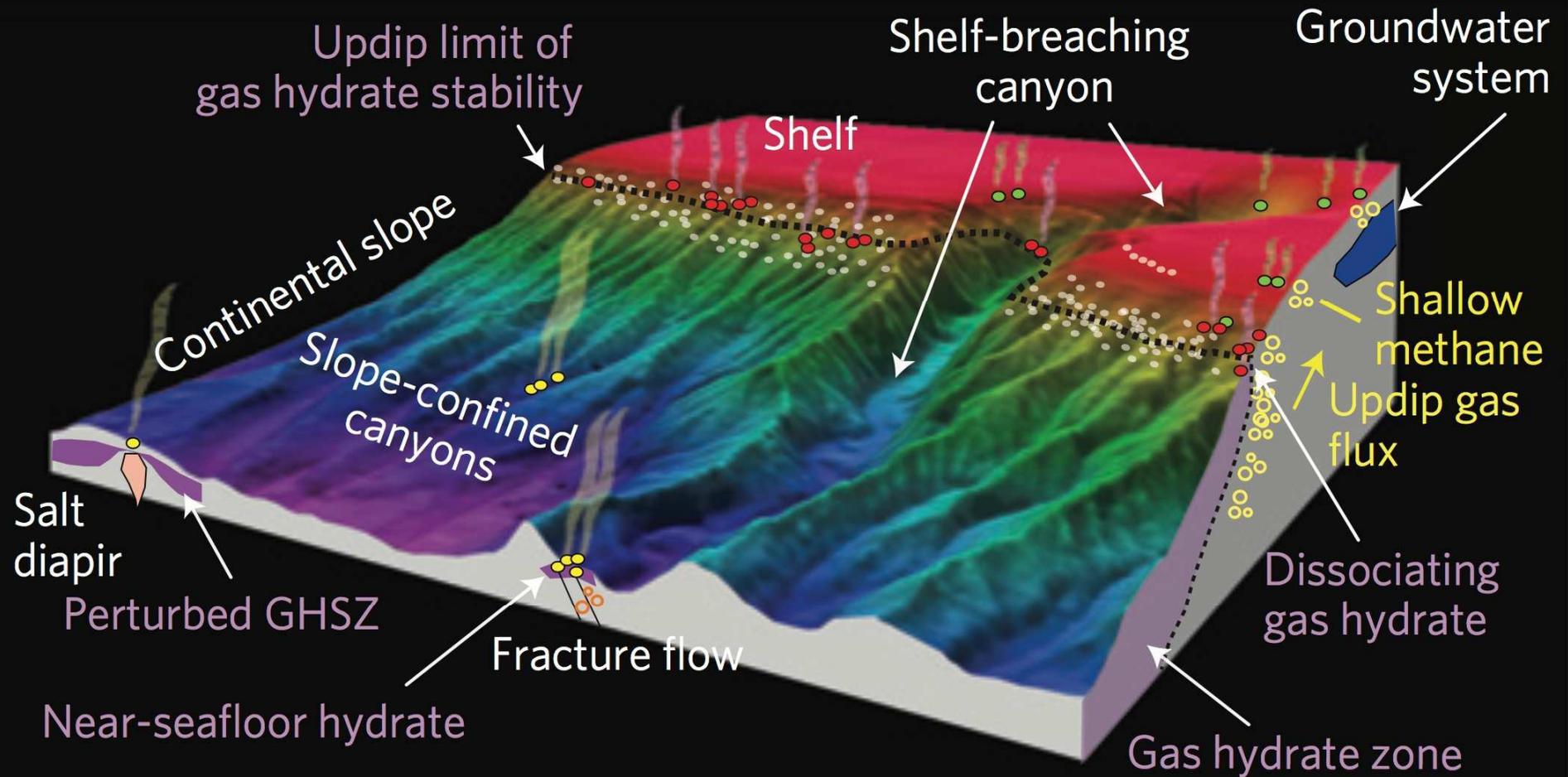
Catastrophic methane release



Atlantic Margin gas plumes  
(offshore USA)

Chronic, long-term methane release

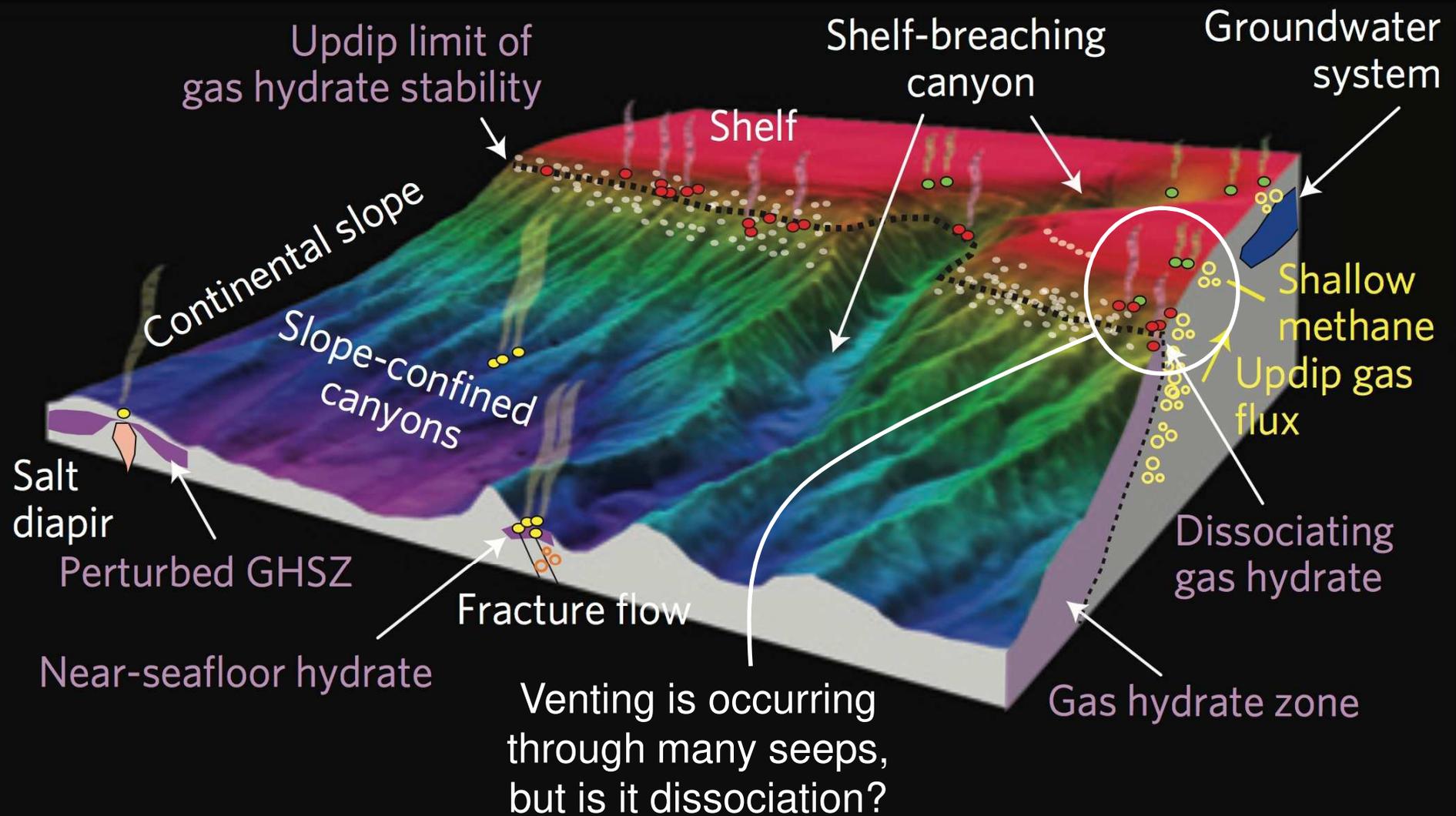
# Is modern climate change destabilizing the shallow-water hydrate?



Atlantic Margin gas plumes (offshore USA)

Skarke et al. (2014), Nature Geoscience

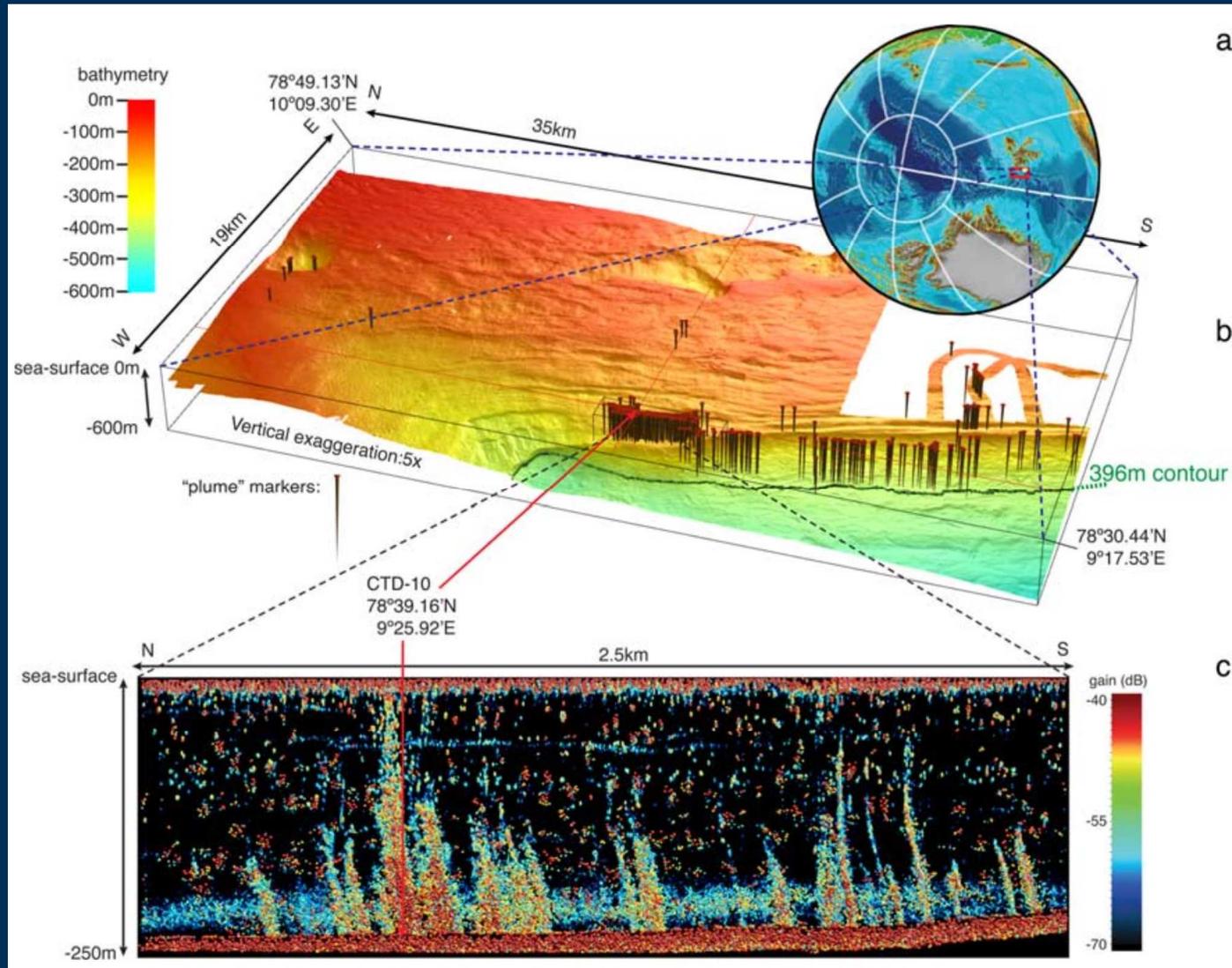
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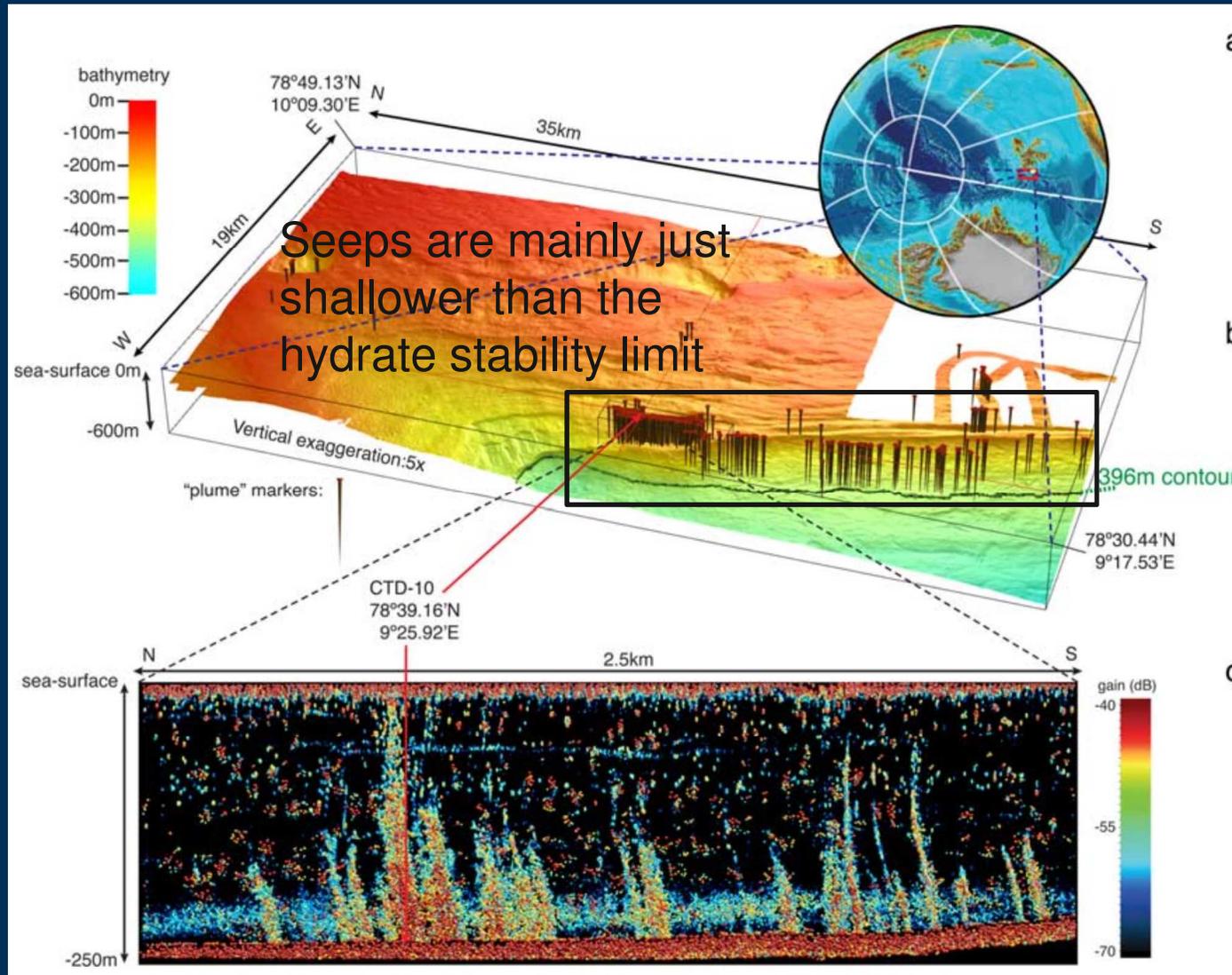
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West Spitsbergen Margin (offshore Svalbard, Norway)

Westbrook et al. (2009), GRL

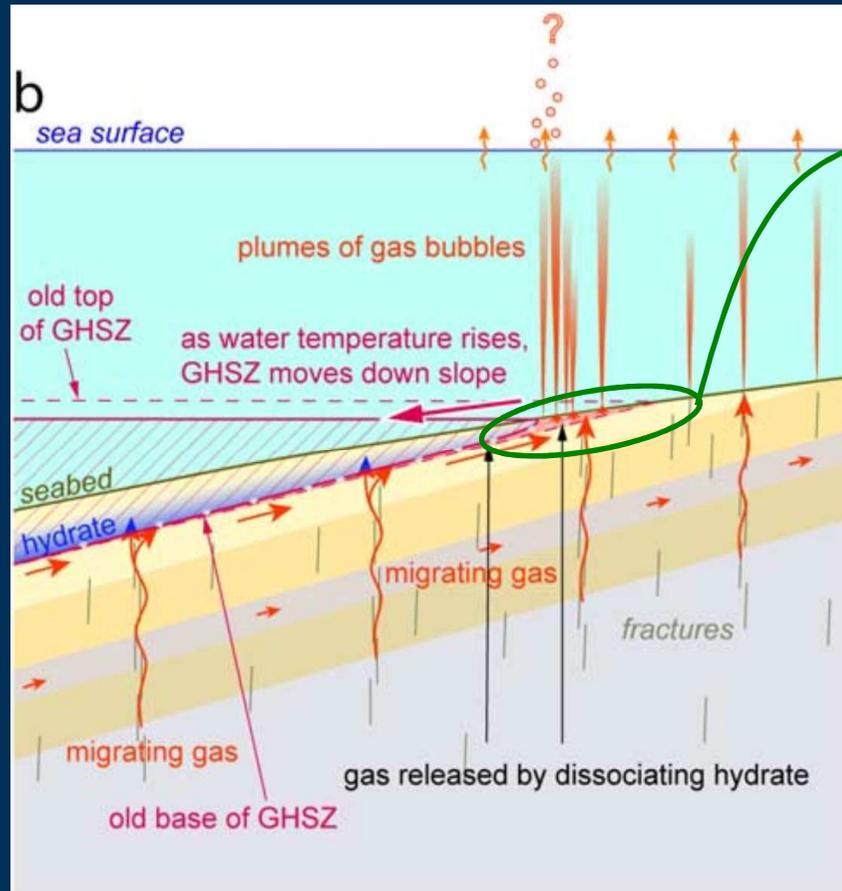
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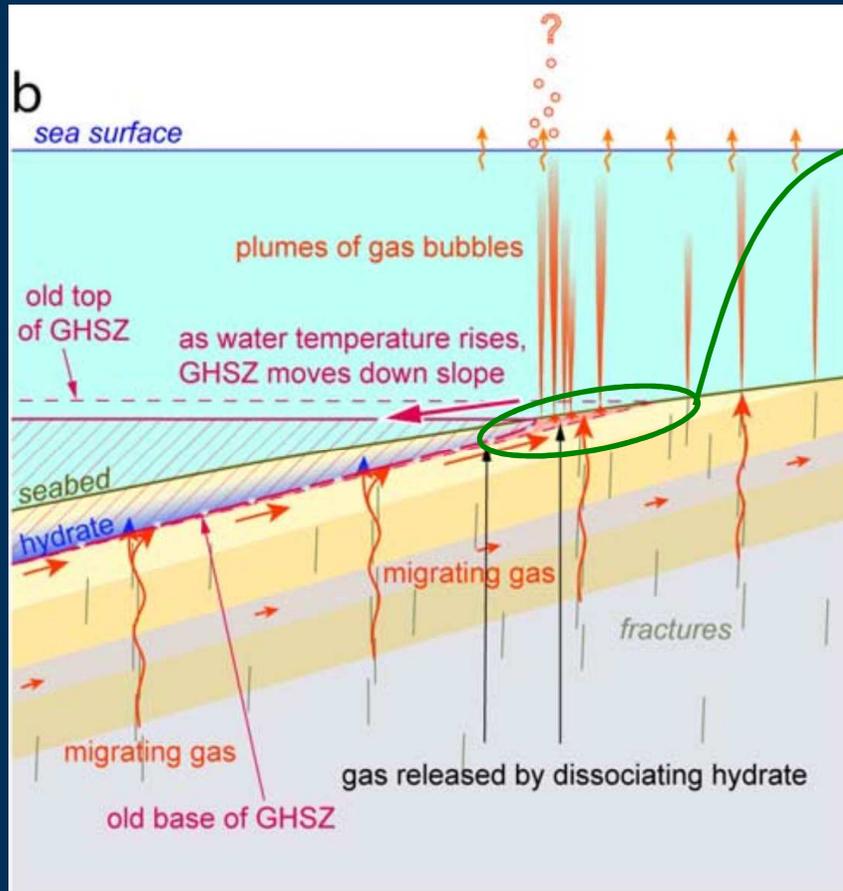
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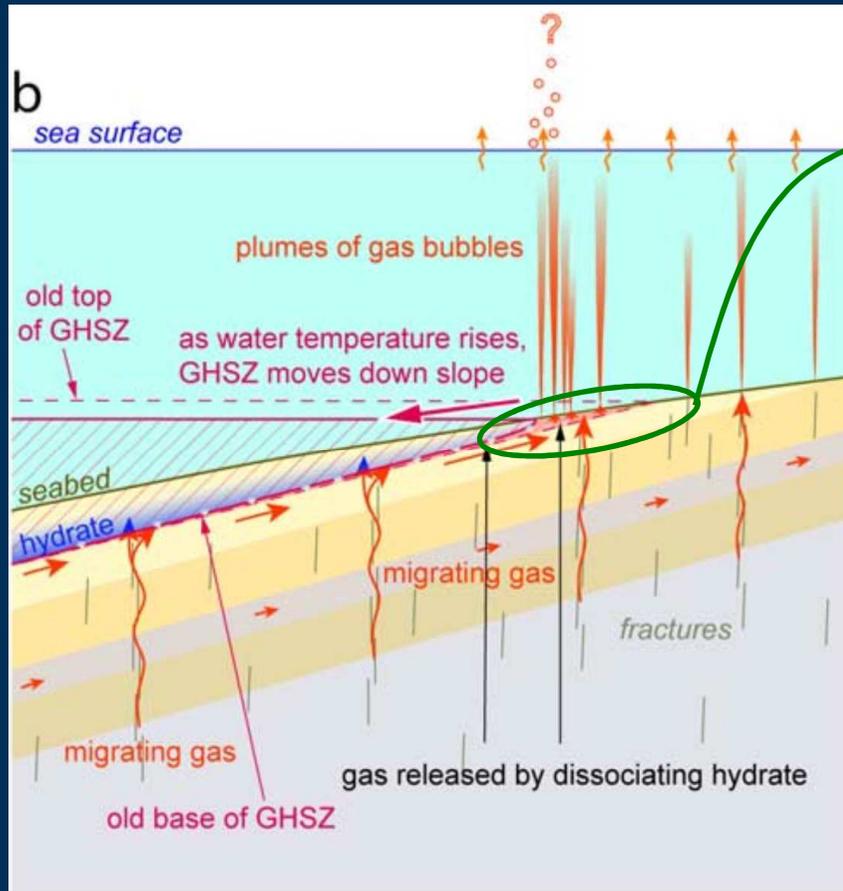
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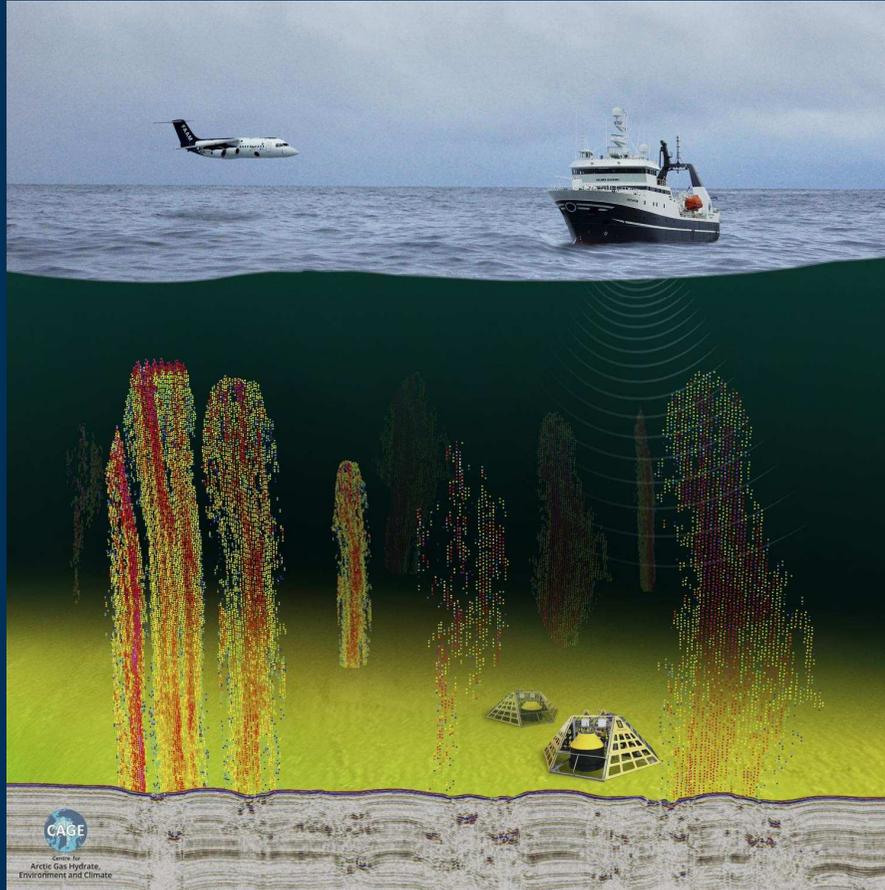
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- Hydrate dissociation due to modern climate change may contribute to observed methane releases, but is not likely the sole or even the primary source.

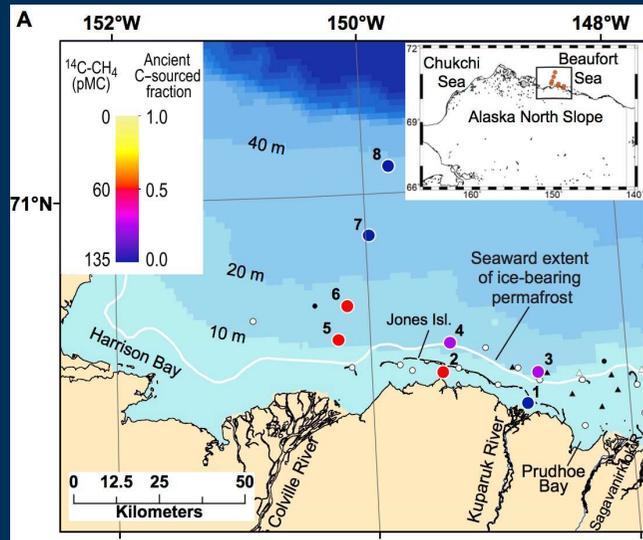
# Does the methane make it to the atmosphere?



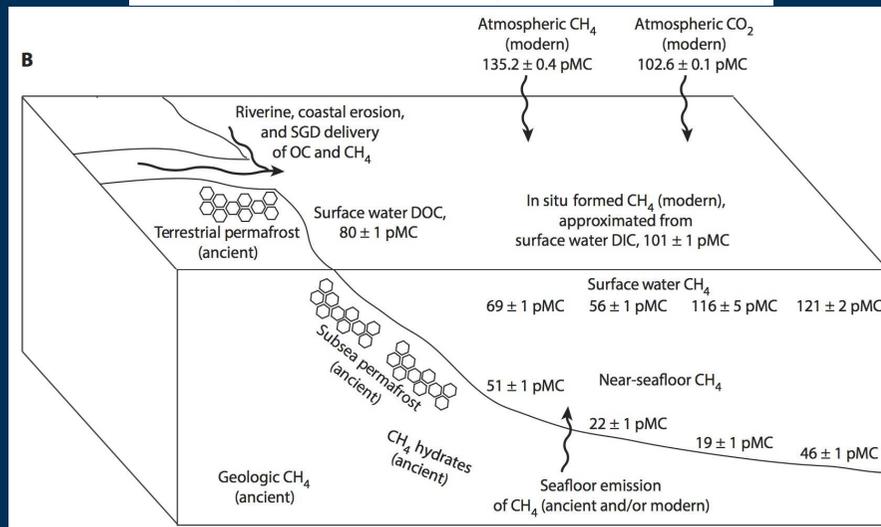
West Spitsbergen Margin  
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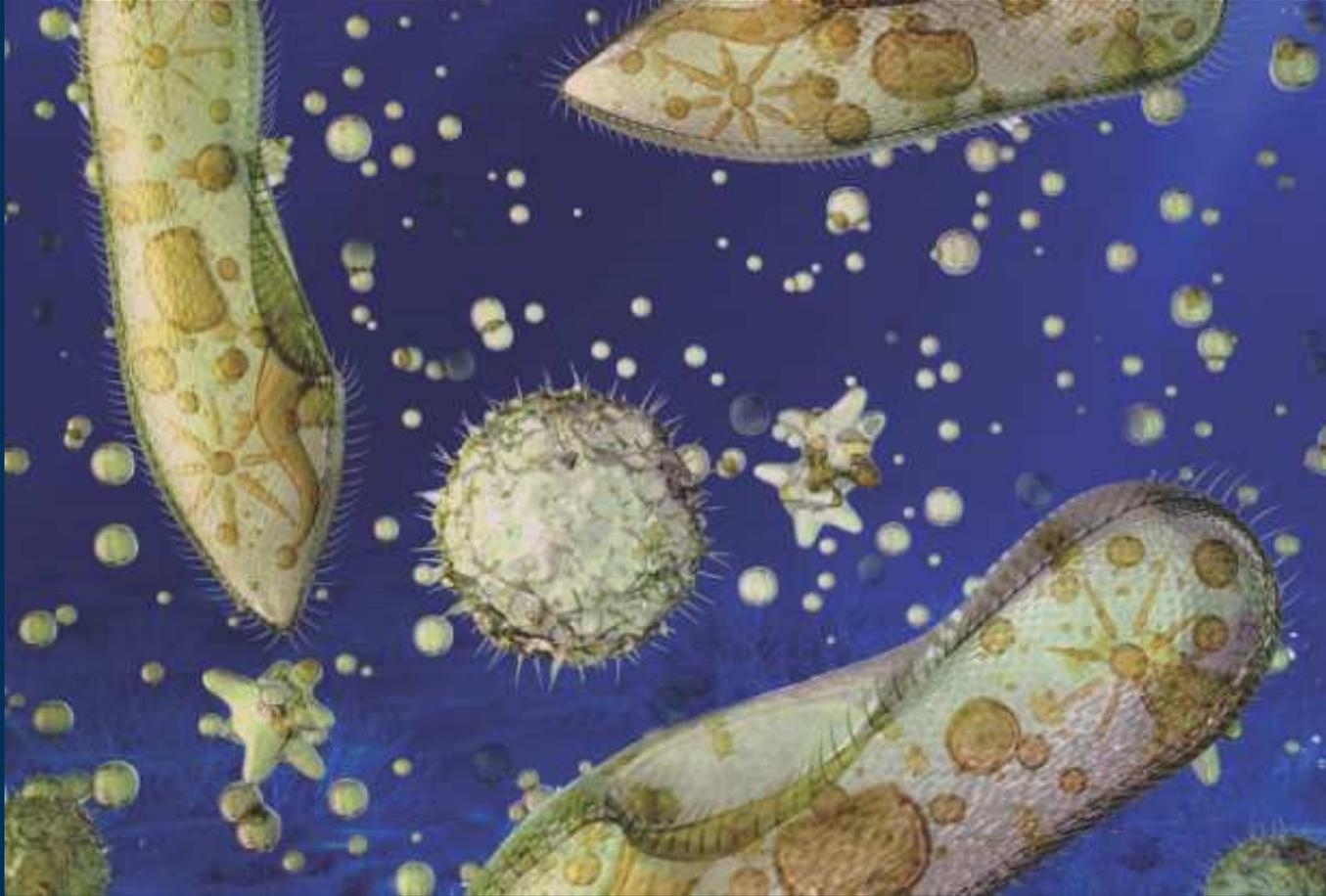
- Surface water and air sampling do *not* show any methane contribution from the underlying seeps on the West Spitsbergen Margin.
- Beyond 30-m water depth, methane from seafloor seeps was only ~10% of the overall methane detected in surface waters for water offshore northern Alaska.



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

Sparrow et al. (2018), Science Advances

## Microbial consumption of dissolved methane

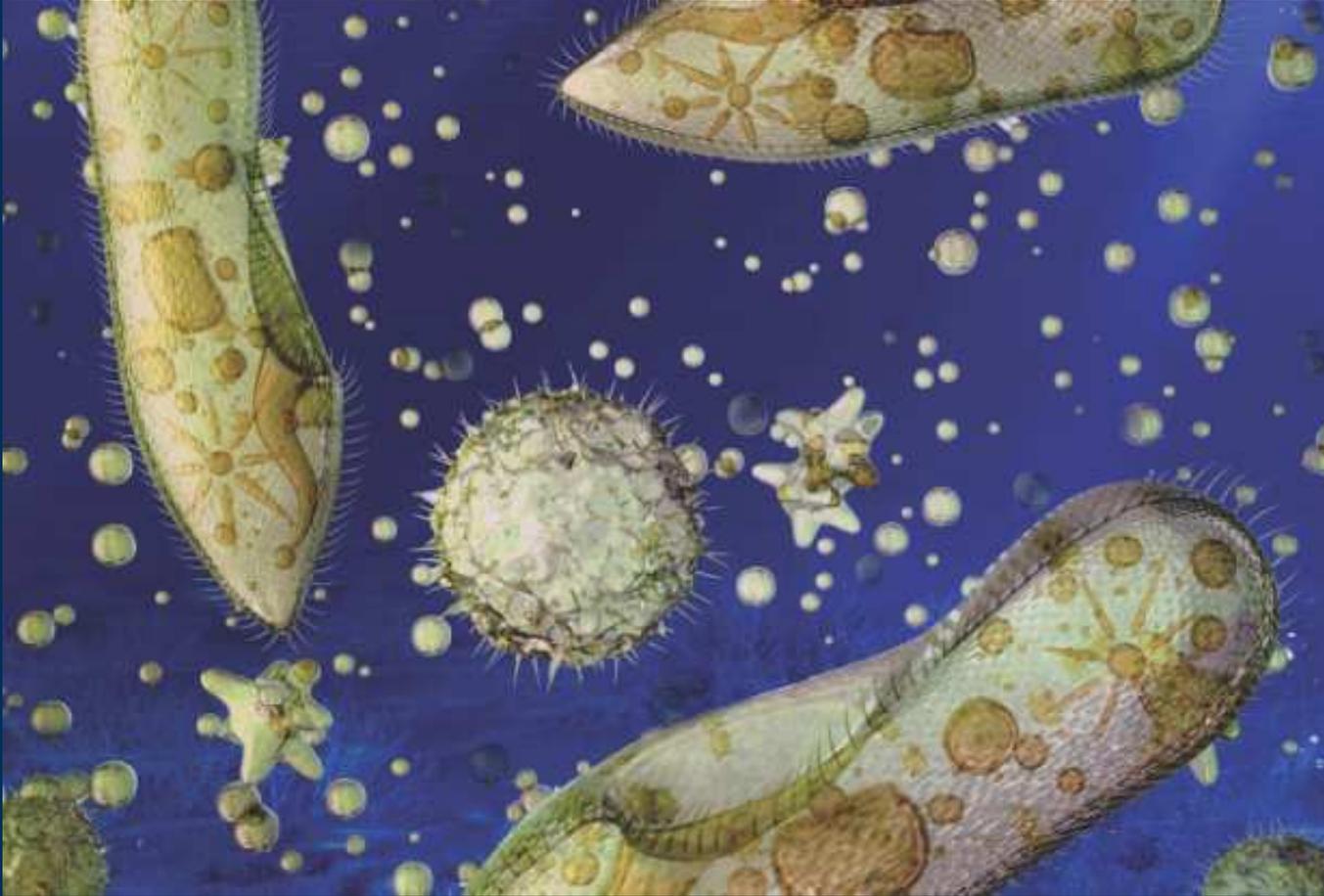


Methane appears to be getting converted to carbon dioxide by microbes in the sediment and water column.



Valentine et al. (2001), *Geochim et Cosmochim Acta*

## Microbial consumption of dissolved methane



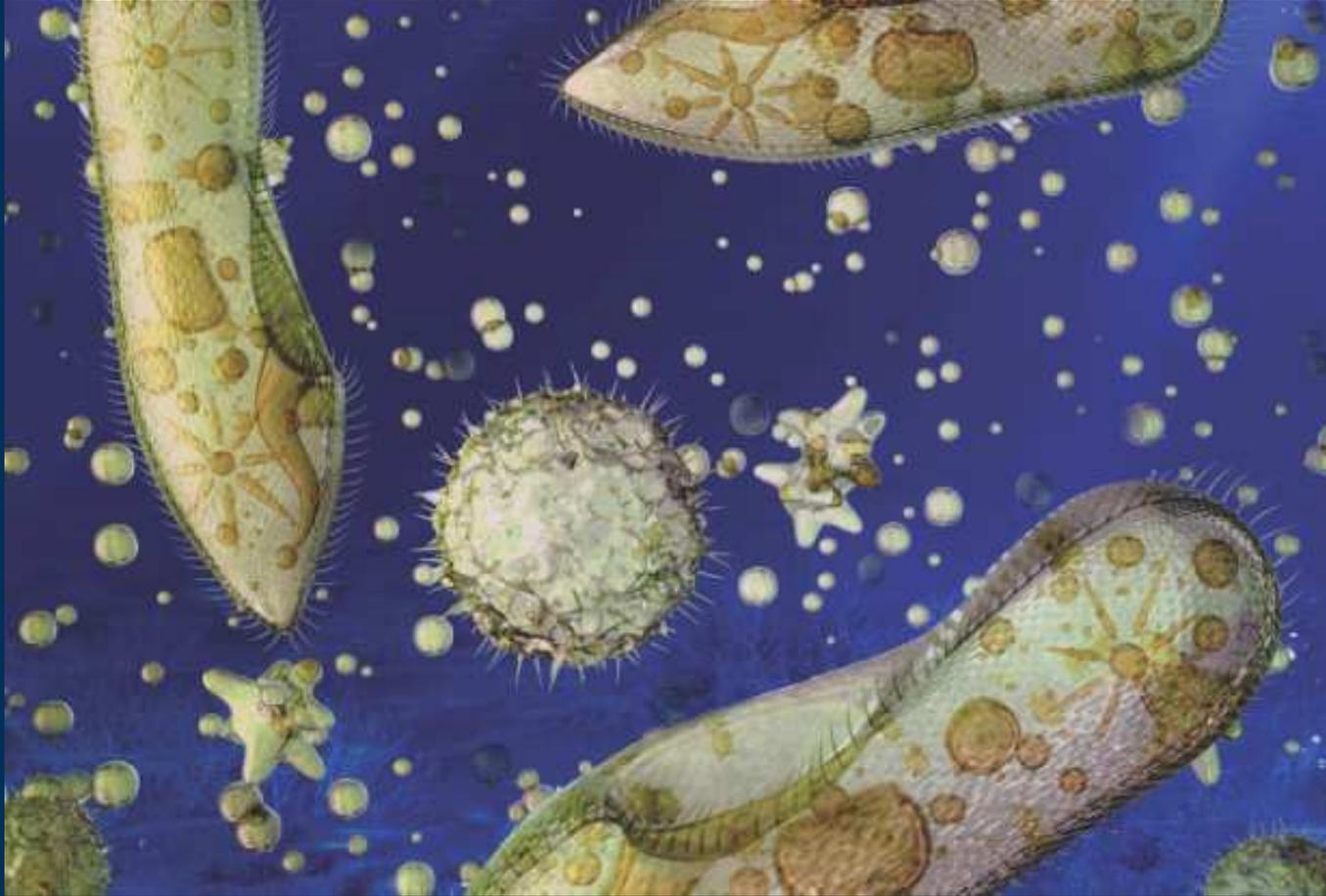
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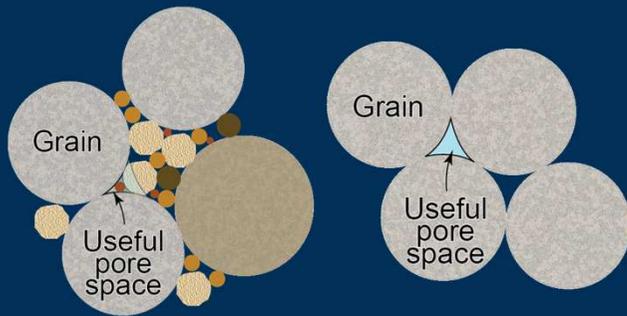
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- Oxygen depletion
- Acidification

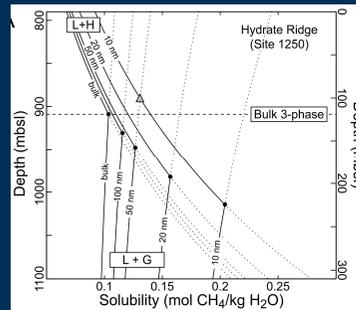


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# Big Ideas: gas hydrate over geologic time



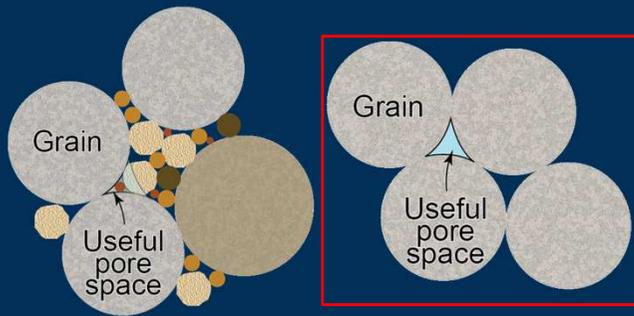
Grain and pore size



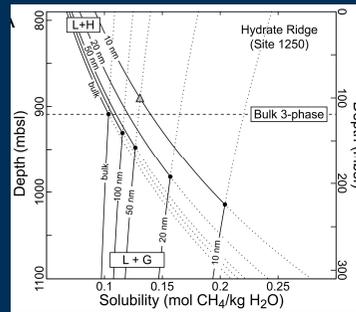
Solubility

- 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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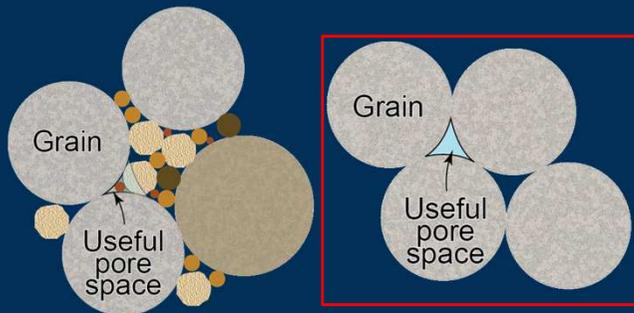
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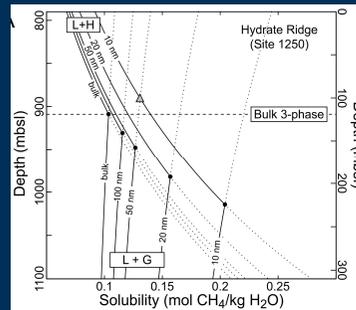
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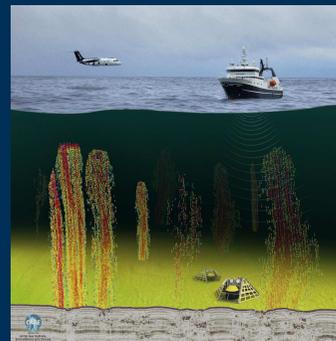
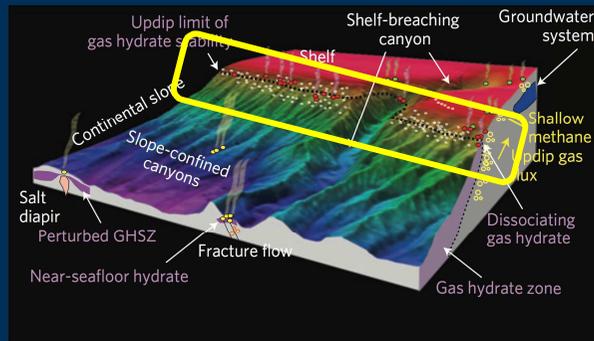


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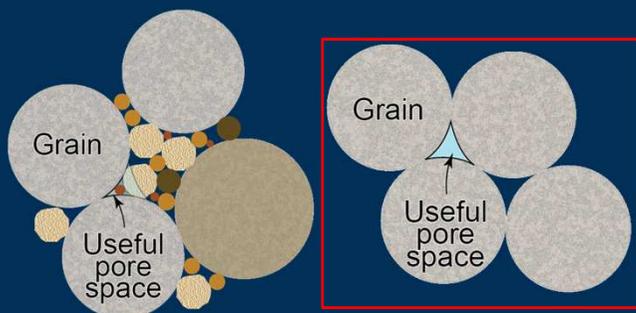
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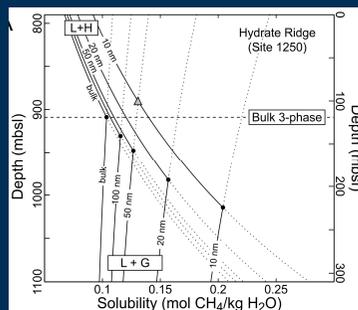


- Dissociation: "Feather edge" hydrates most at risk from climate, but released methane is consumed in the water column.

# Big Ideas: gas hydrate over geologic time

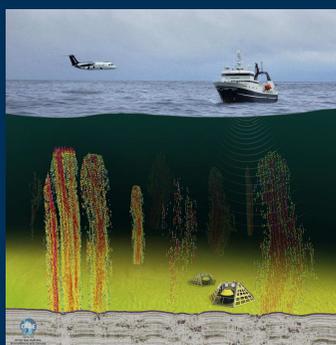
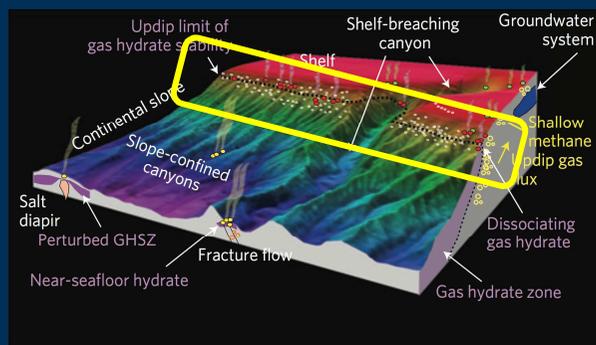


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- Methane release:
  - Oxygen loss
  - Acidification
  - Potential secondary hydrate

# 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
- <https://www.grc.org/natural-gas-hydrate-systems-grs-conference/2020/>

## Gordon Research Conference: Feb. 23-28, 2020

- 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
- <https://www.grc.org/natural-gas-hydrate-systems-conference/2020/>