

CCUS Student Week 2018

Fundamentals of Hydrates, Climate Perspectives, and Energy Potentials

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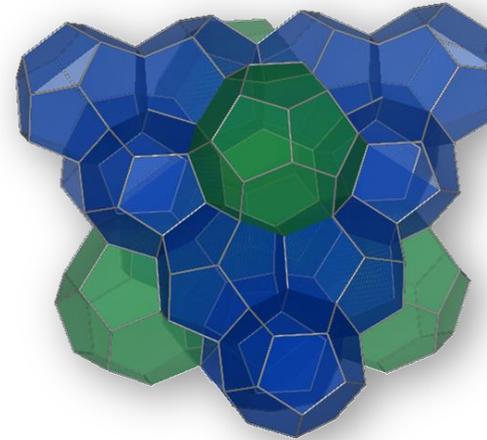
Golden, CO

What are Gas Hydrates?

- Ice-like, crystalline structures
- Common hydrate formers: methane, ethane, propane, carbon dioxide, hydrogen sulfide, nitrogen, hydrogen



crystal structure

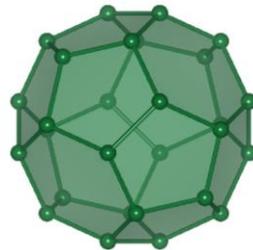
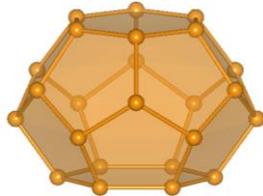
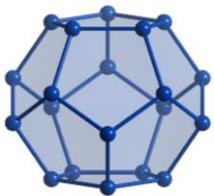


Burning hydrate

5¹²

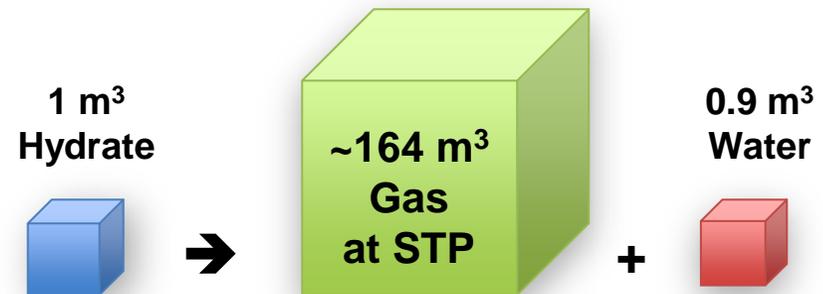
5¹²6²

5¹²6⁸



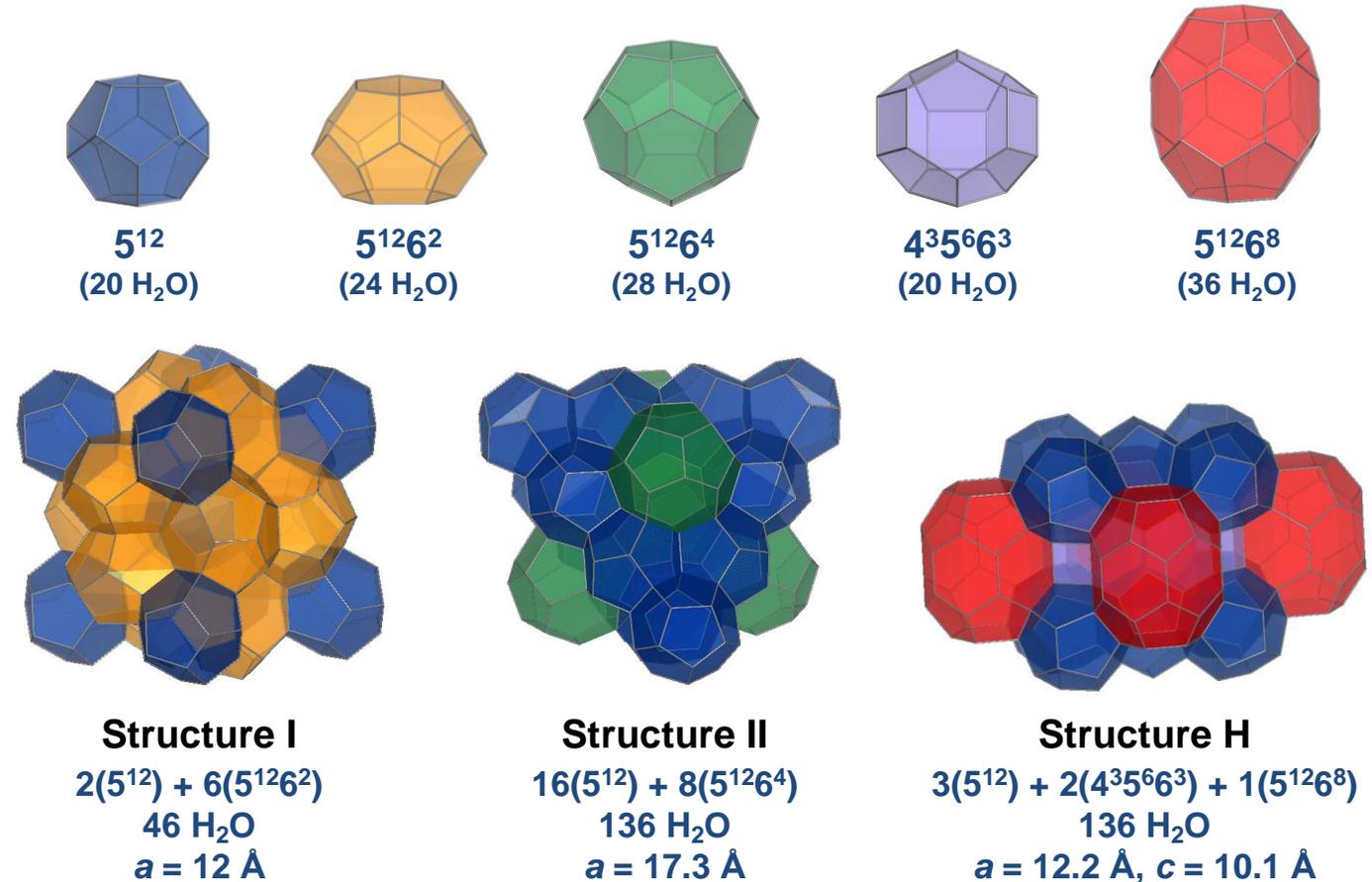
water cages

Gas storage capacity in hydrates



Types of Gas Hydrate Crystal Structures

- The stability of a hydrate structure depends on the fit of the guest molecule inside the host cage
- Small hydrocarbon molecules, like methane and ethane, form hydrate structure I
- Larger hydrocarbon molecules, like propane and iso-butane, form hydrate structure II
- All 3 Structures have:
 - 85 mol% H₂O
 - 15 mol% guests



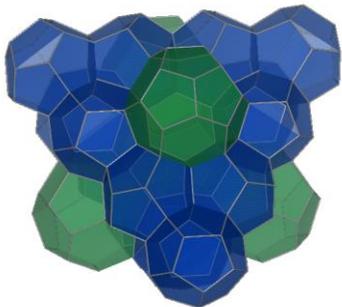
Sloan, E.D., Koh, C.A., 2008. Clathrate hydrates of natural gases. CRC Press, 3rd edition.

Hydrate Structure Dependent on Guest Size

Molecular Diameter

No Hydrates

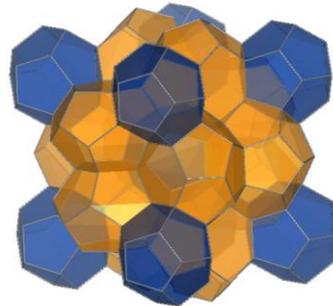
4.0 Å



Structure II

Hydrogen
Argon
Krypton
Nitrogen
Oxygen

5.0 Å



Structure I

Methane
Ethane
Cyclopropane
Carbon Dioxide
Ethylene Oxide
Hydrogen Sulfide
Xenon

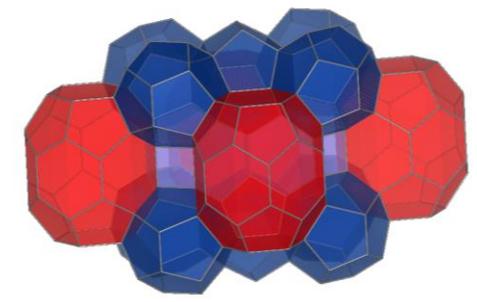
6.0 Å



Structure II

Propane
Isobutane
Cyclopentane
Tetrahydrofuran

7.0 Å



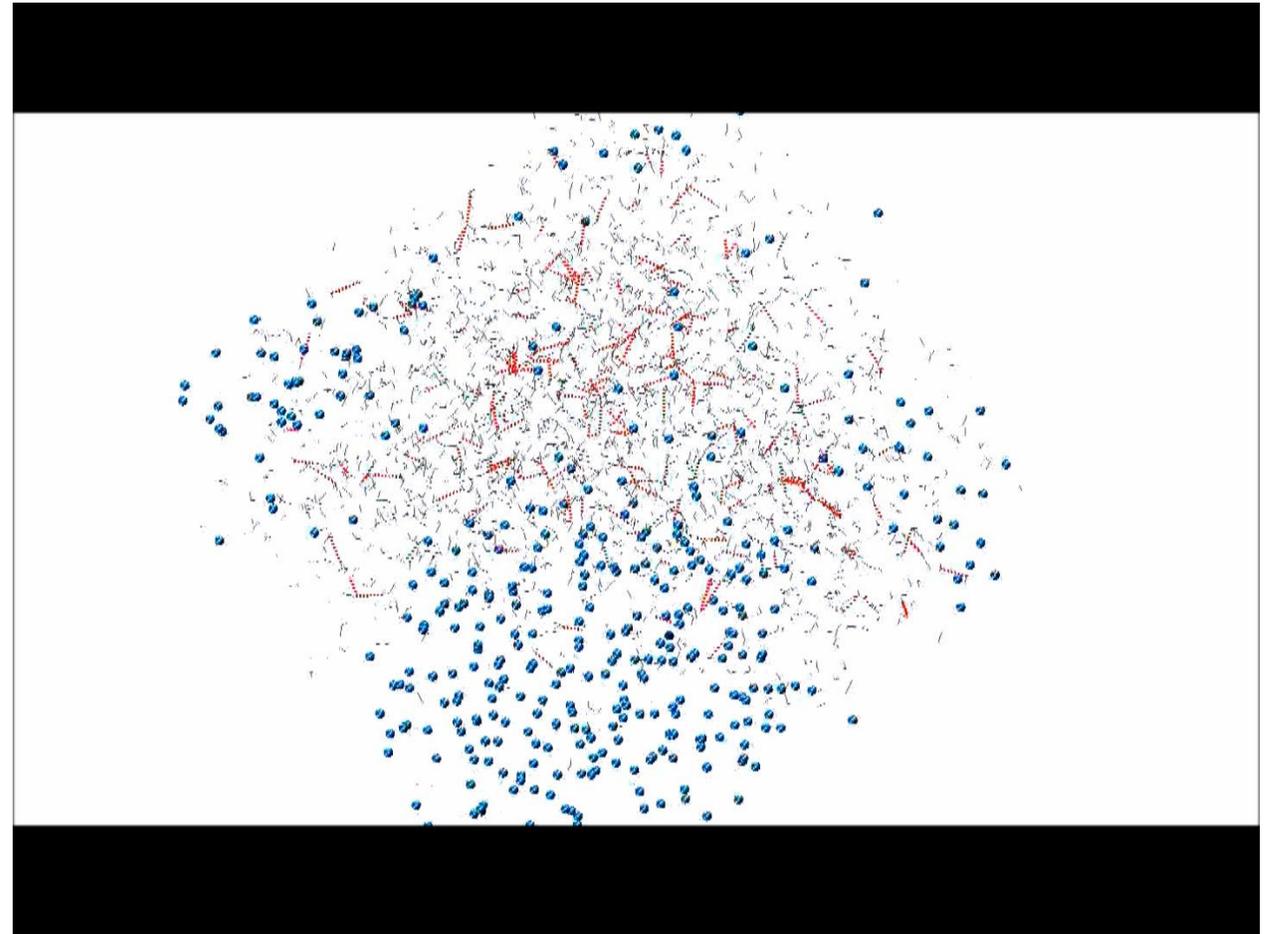
Structure H*

2,2-Dimethylbutane
Methylcyclohexane
Ethylcyclohexane
Cycloheptane
Cyclooctane
Adamantane

Gas Hydrates Formation Mechanisms at Molecular Level

Molecular Dynamics Simulation

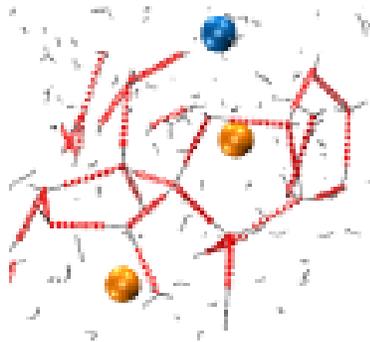
- Water: Grey Lines
- Methane: Blue Spheres
- Hydrogen-bonds: Red Lines



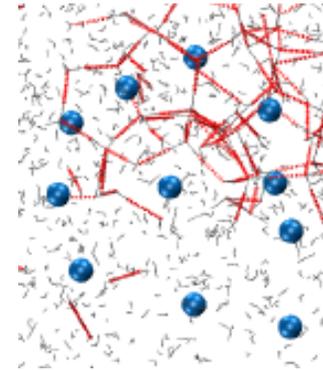
Walsh, M.R., Koh, C.A., Sloan, E.D., Sum, A.K., & Wu, D.T. (2009). Microsecond simulations of spontaneous methane hydrate nucleation and growth. *Science*, 326(5956), 1095-1098.

Suggested Hydrate Nucleation Mechanism

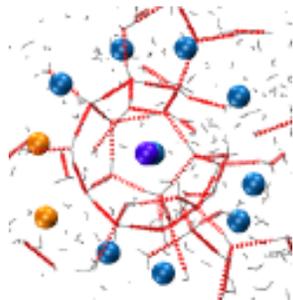
1. Dissolved methane slows down water



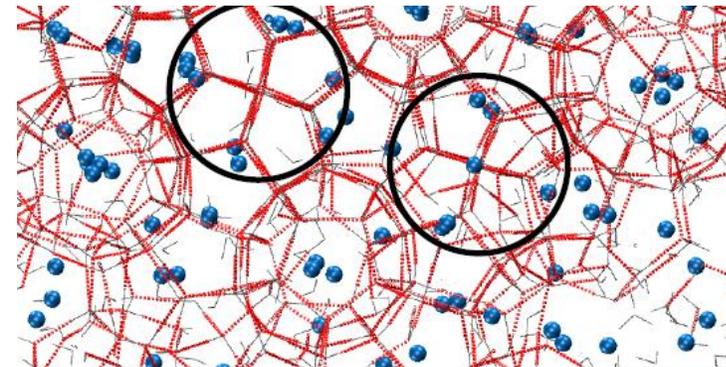
3. Fluctuating initial cages



2. Initial structure gradually forms a hydrate cage

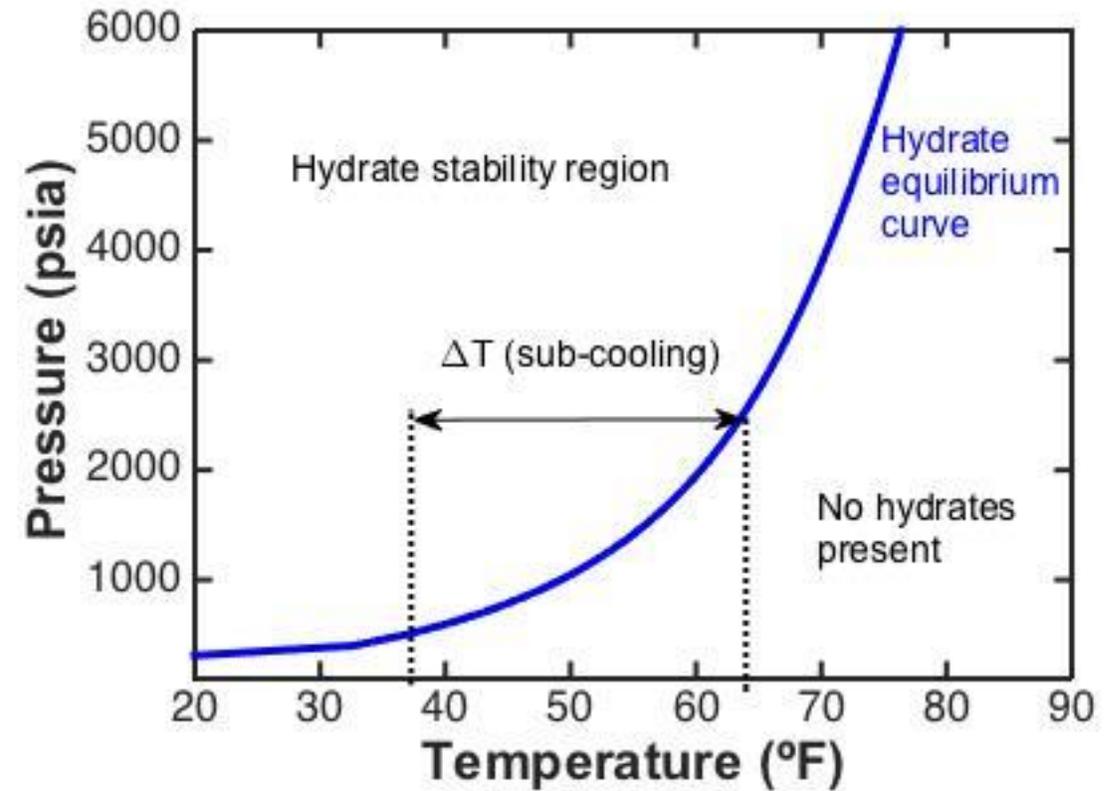
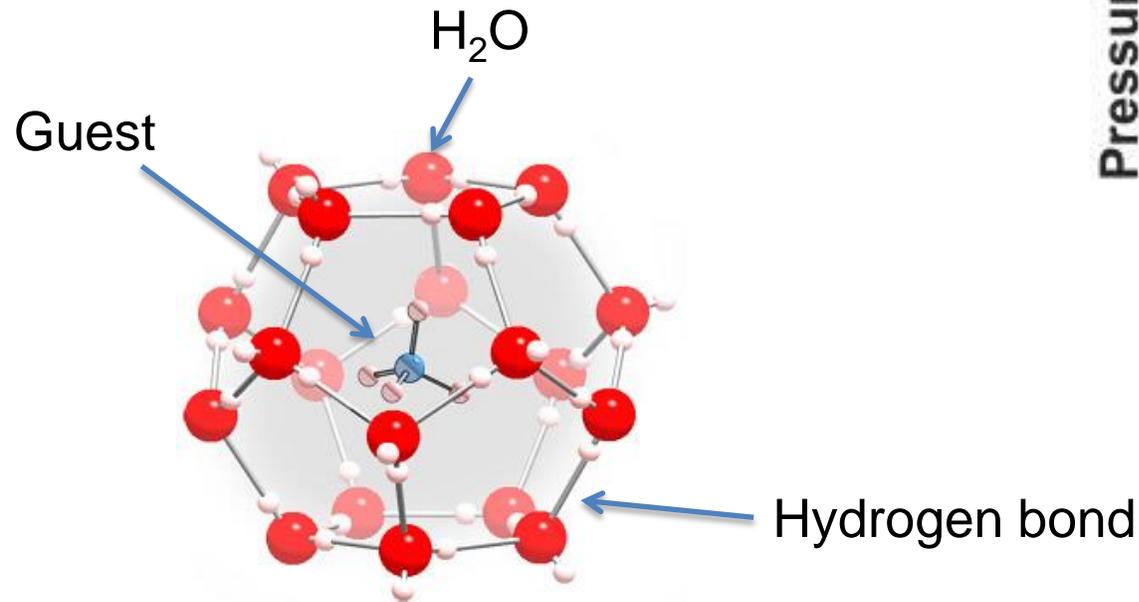


4. $5^{12}6^3$ cages allow for sl to grow

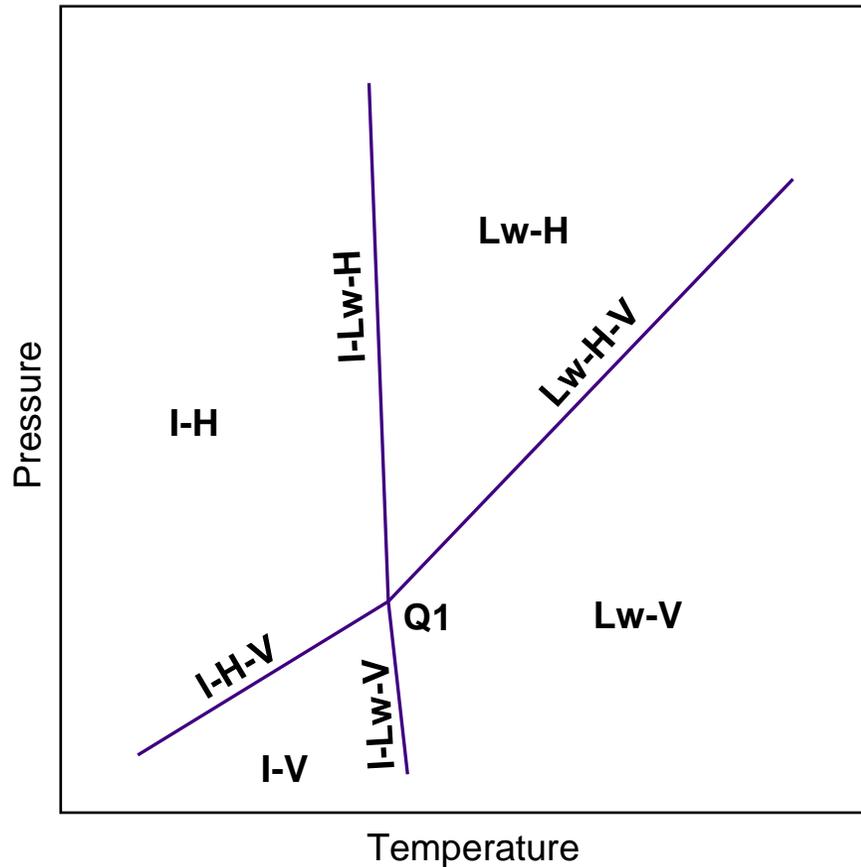


Hydrate Forming Conditions

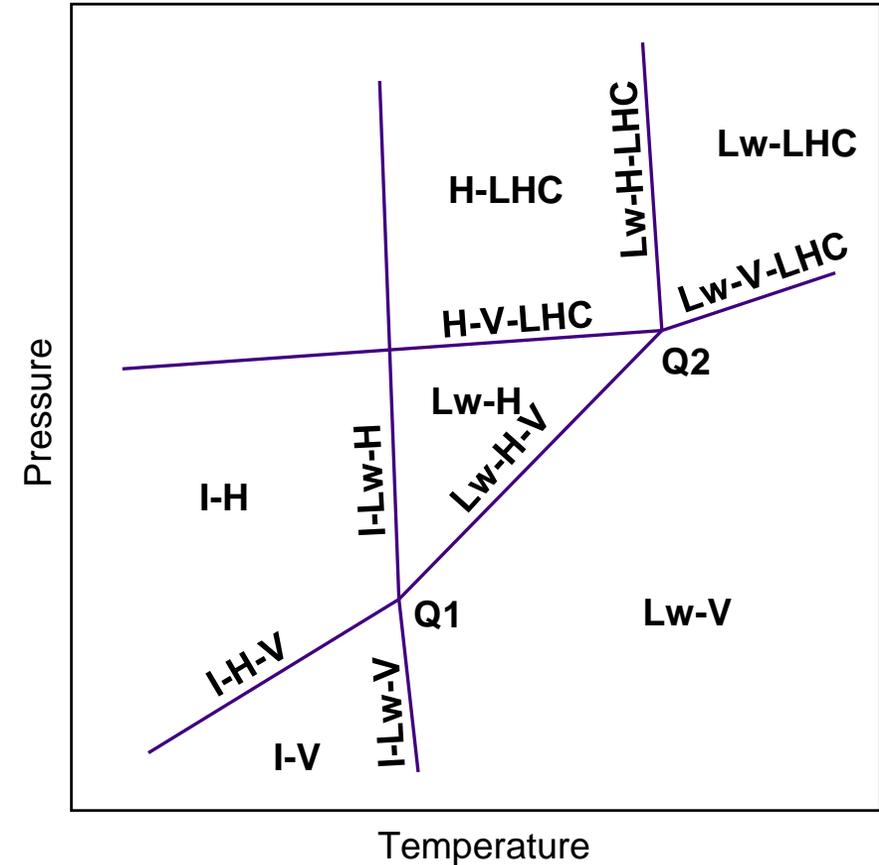
- High pressure
- Low temperature
- Liquid water
- Small gas molecule



Typical Hydrate Phase Diagram

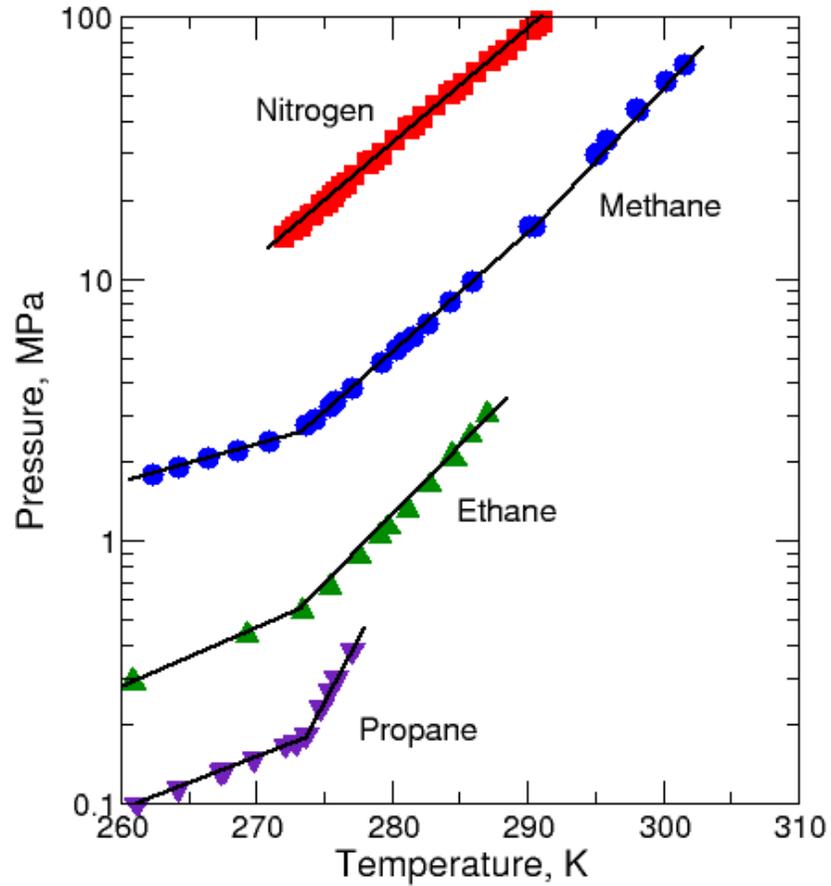


Quadruple point Q1
I-Lw-H-V

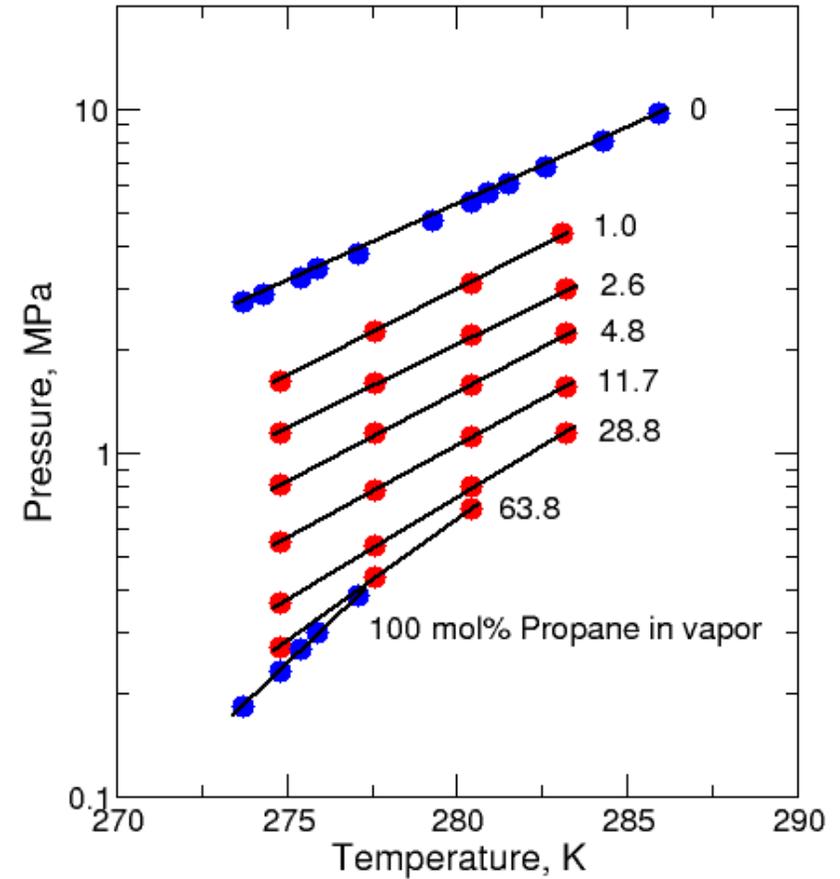


Quadruple point Q2
Lw-H-V-LHC

Typical Hydrate Phase Diagram



Methane+Propane Mixture



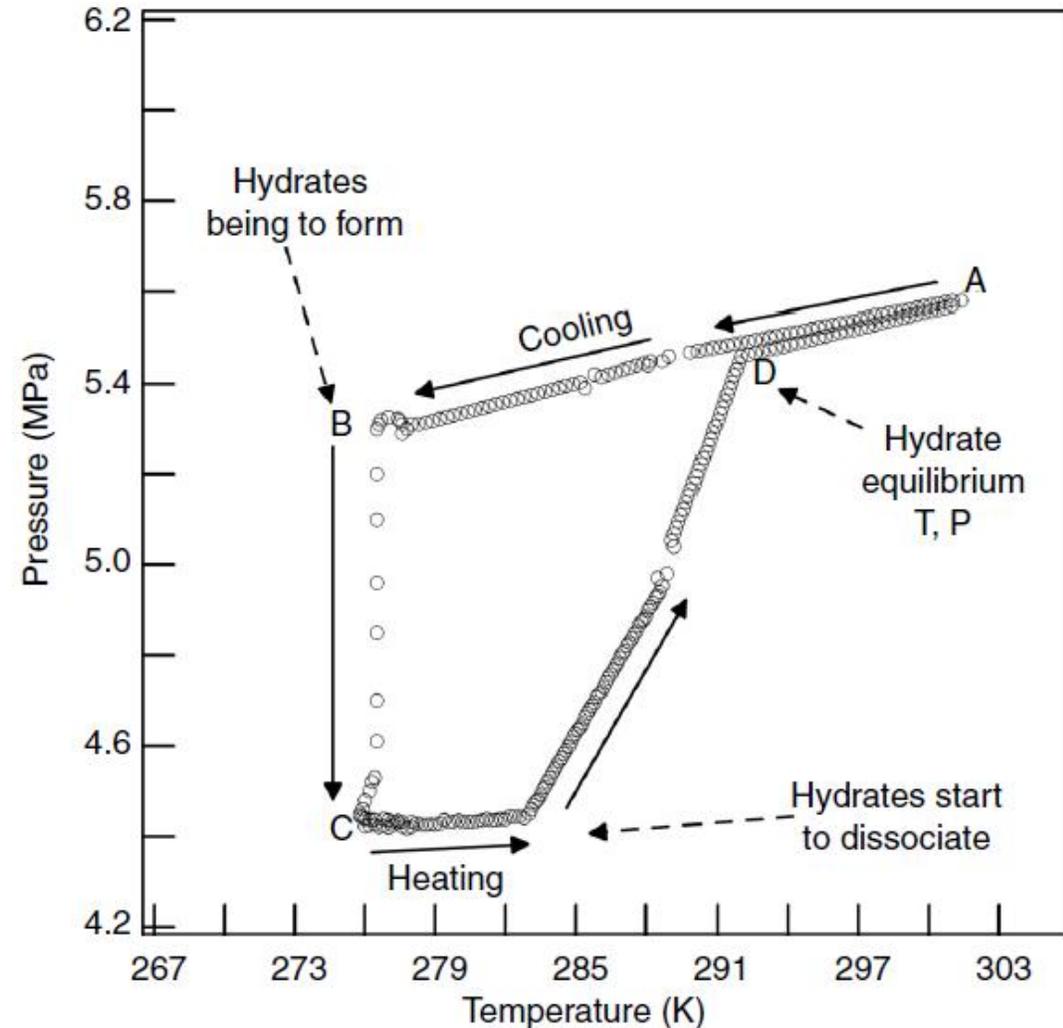
Methods for Determining Hydrate Conditions

- Experimental
- Graphical
- Analytical
- Computational

Methods for Determining Hydrate Conditions

Experimental

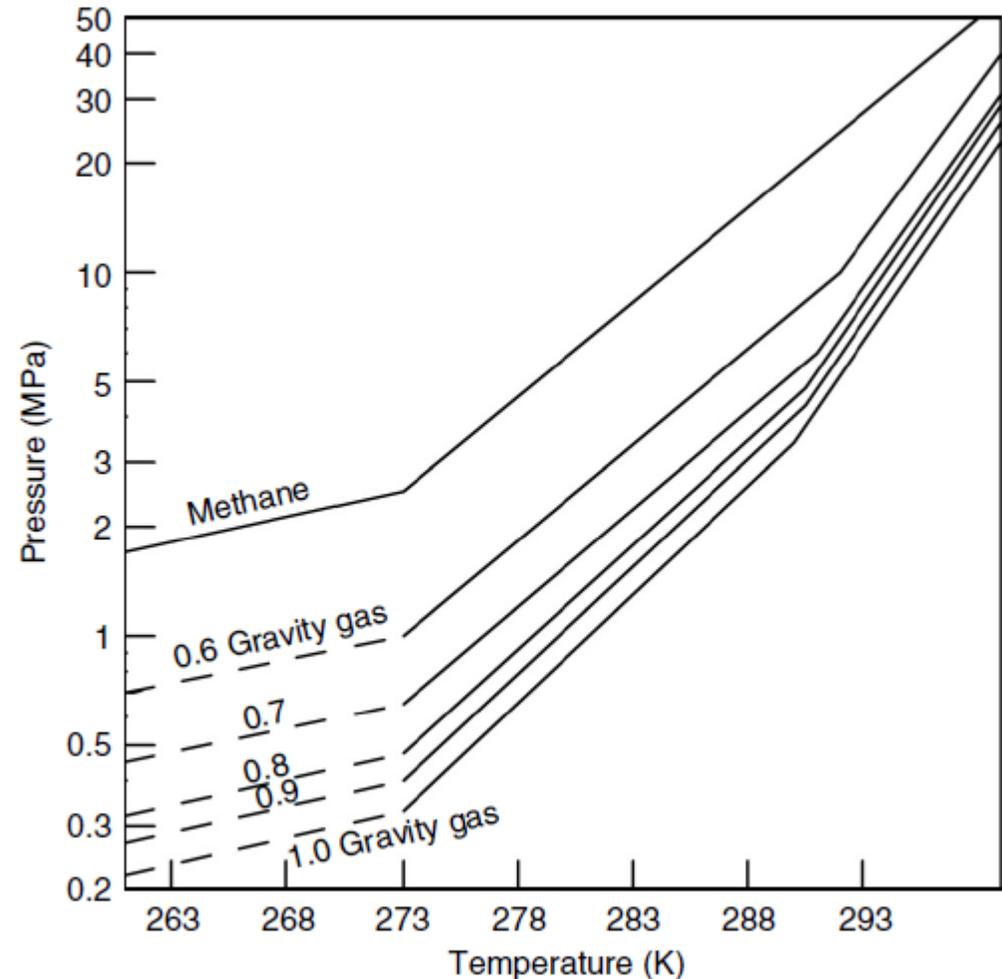
- Constant volume
- Point A: initial T and P
- Cooling until hydrates beginning to form (B)
- Heating until hydrates dissociate completely (D)



Methods for Determining Hydrate Conditions

Graphical

- Gas gravity charts of Katz (1945)
- Estimate hydrate formation pressure, given temperature and gas gravity
- For gas mixtures
- Should be used with caution for gases with non-hydrocarbon components (CO_2 , H_2S , N_2)



Methods for Determining Hydrate Conditions

Analytical

Gas	Temperature interval (°C)	Equations (P in atm, T in °C)
Methane, CH ₄	-11 < T < 0	$\ln P = 5.5414 - 1154.61/T$
	0 < T < +23	$\ln P = 1.415 + 0.417(T + 0.01T^2)$
	+24 < T < +47	$\ln P = 1.602 + 0.0428T$
Ethane, C ₂ H ₆	-10 < T < 0	$\ln P = 6.9296 - 1694.86/T$
	0 < T < +14.5	$\ln P = 0.71 + 0.0547T$
Propane, C ₃ H ₈	-12 < T < 0	$\ln P = 5.4242 - 1417.93/T$
	0 < T < +8.5	$\ln P = 0.231 + 0.0576T$
CO ₂	-6 < T < 0	$\ln P = 13.4238 - 3369.1245/T$
	0 < T < +9.8	$\ln P = 1.08 + 0.056T$
H ₂ S	-32 < T < 29.6	$\ln P = 2.844 + 0.0466T$
Mixtures	0 < T < +25	$\ln P = \beta + 0.0497(T + kT^2)$

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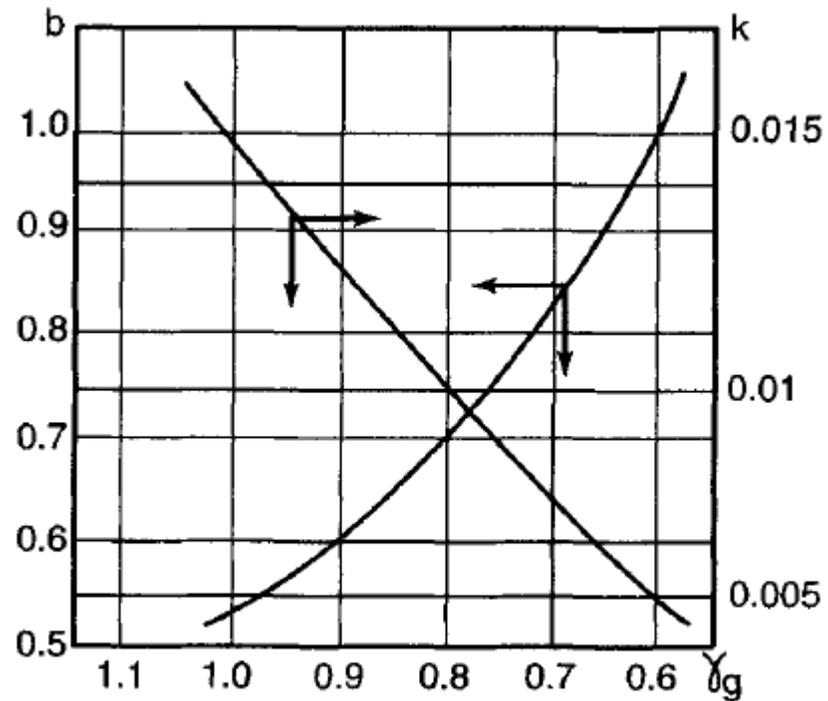


Figure 6.7.11 Dependence of coefficients β and k on the relative density (SG_d) [8].

Methods for Determining Hydrate Conditions

Computational

- Commercial thermodynamic programs based on the van der Waals and Platteeuw model (1959)
 - Multiflash[®] from KBC Advance Technologies
 - PVTsim[®] from Calsep
- Colorado School of Mines program based on the Gibbs energy minimization method
 - CSMHyd
 - CSMGem
- The composition of the fluids is used as input to calculate the hydrate equilibrium conditions

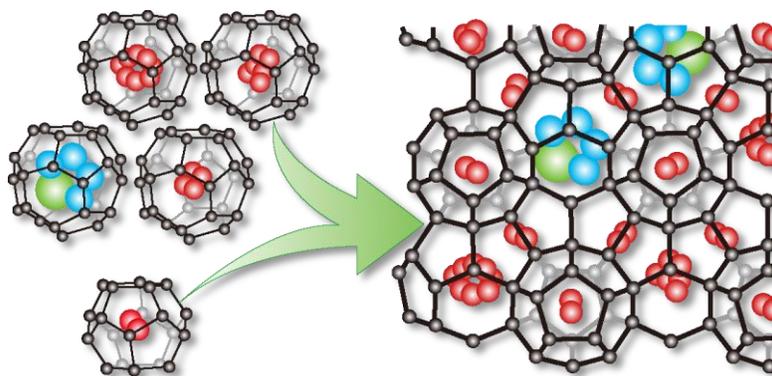
Gas Hydrates in Energy Applications

Center for Hydrate Research – Colorado School of Mines

Hydrates in *Flow Assurance*



Hydrates in *Science*

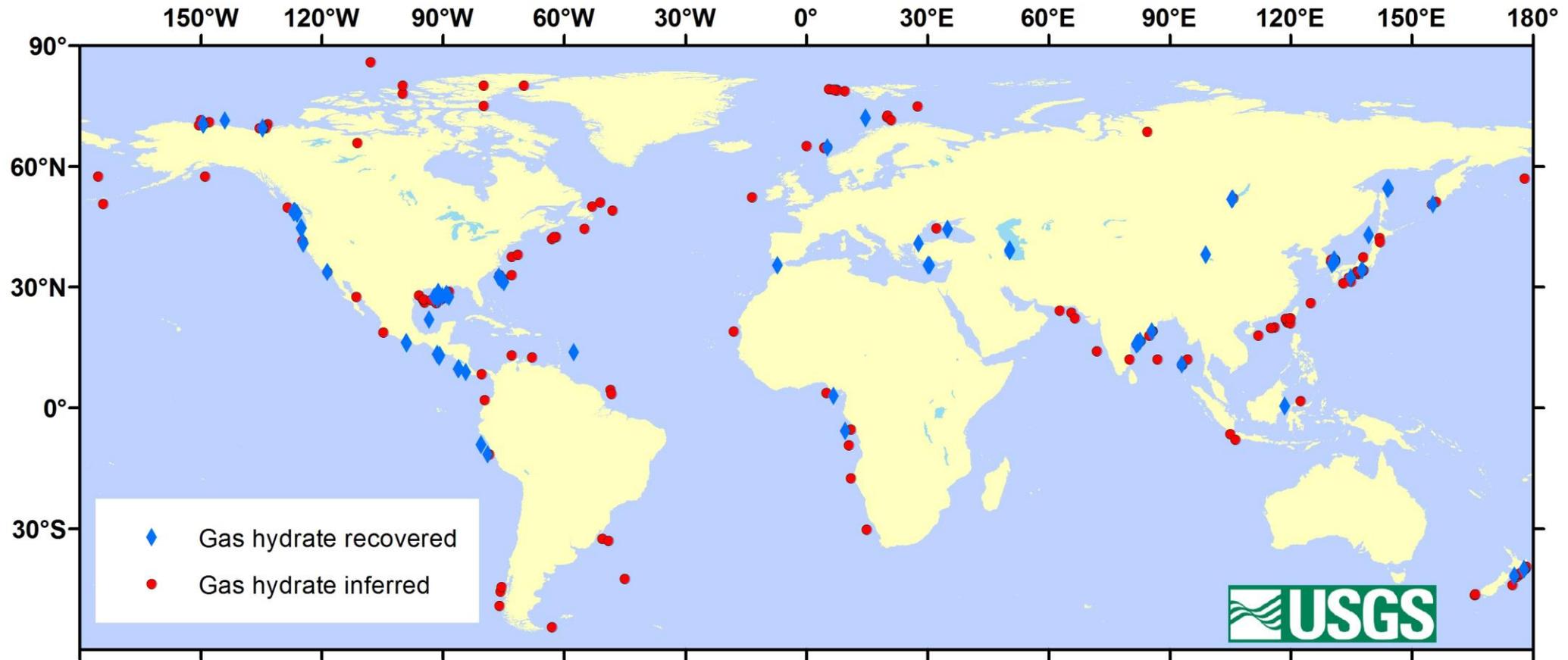


Hydrates in *Nature*



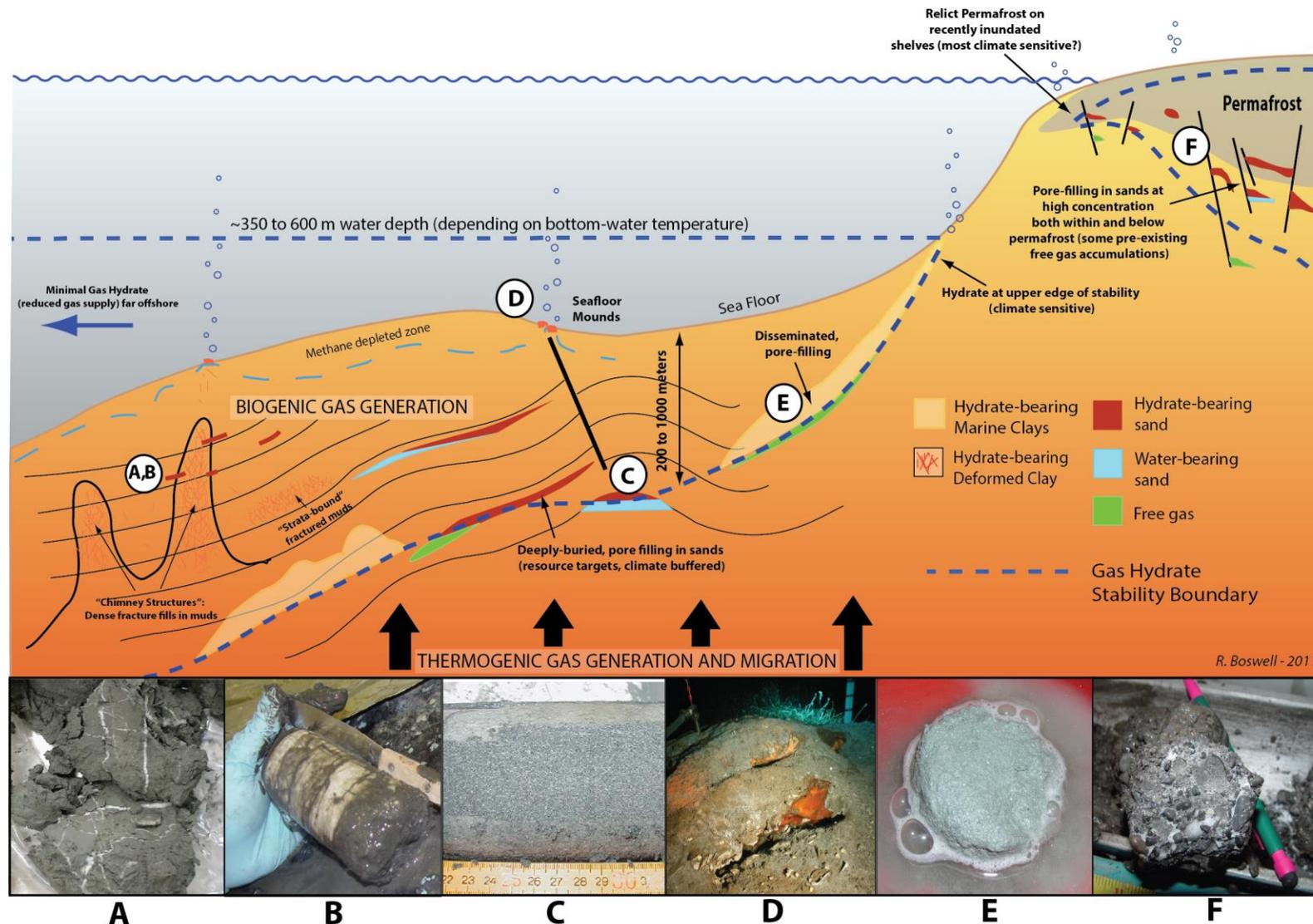
Hydrates as Energy Resource

- Current Estimates 10^{15} - 10^{17} m³ (35,700 – 875,000 TCF)
(Energy in Hydrates = 2 × total from fossil fuels available)
- Annual US Consumption ~ 650 billion m³ (23 TCF)



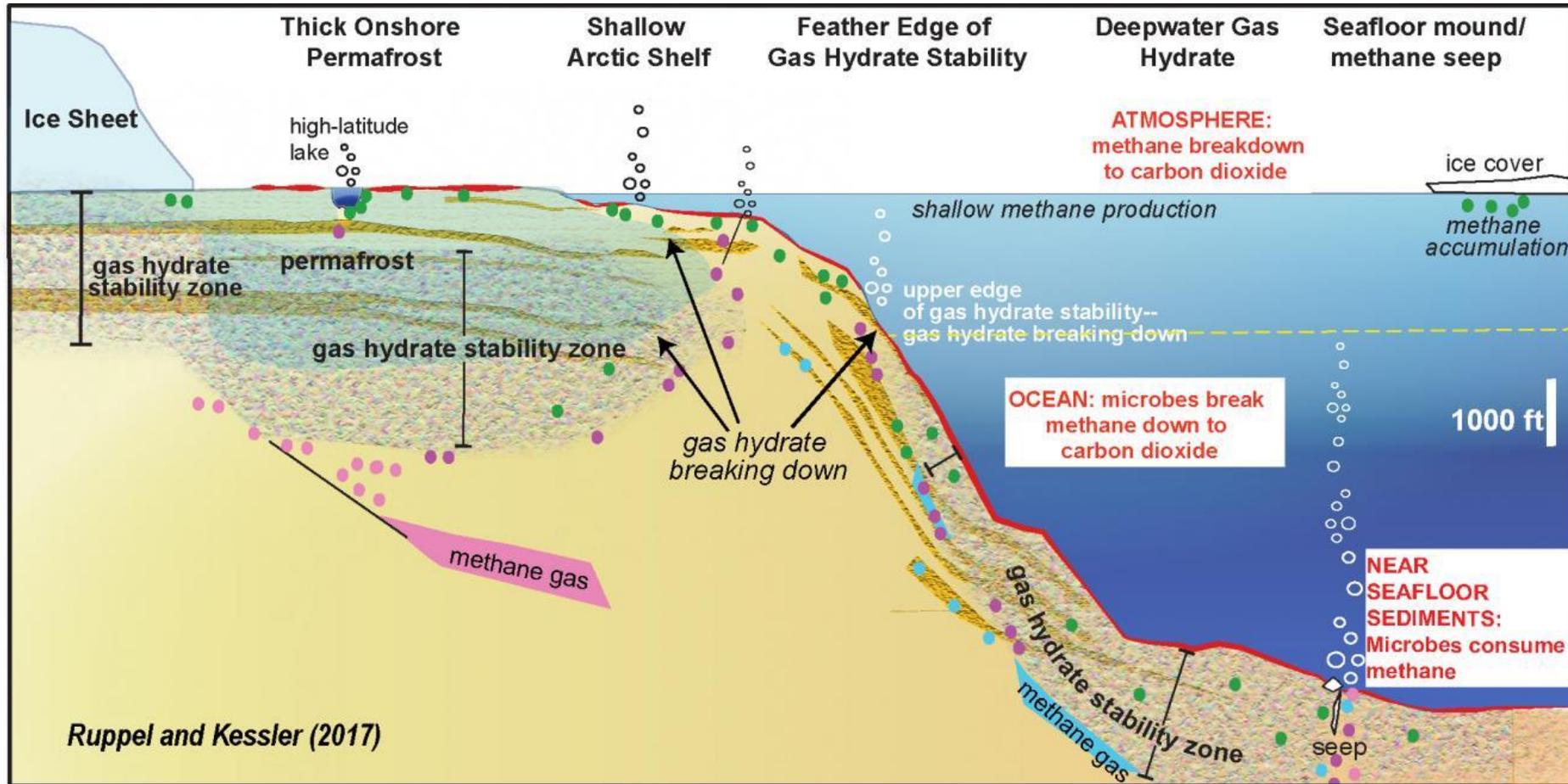
USGS Gas Hydrates Project

Gas Hydrate Occurrence in Nature



Boswell, 2011, NRC Topical Paper 1-11

Climate-Hydrate Interactions

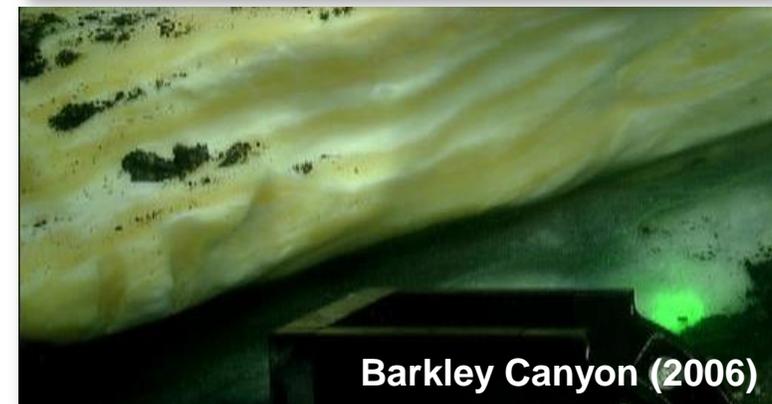


Recovered Natural Hydrates Samples

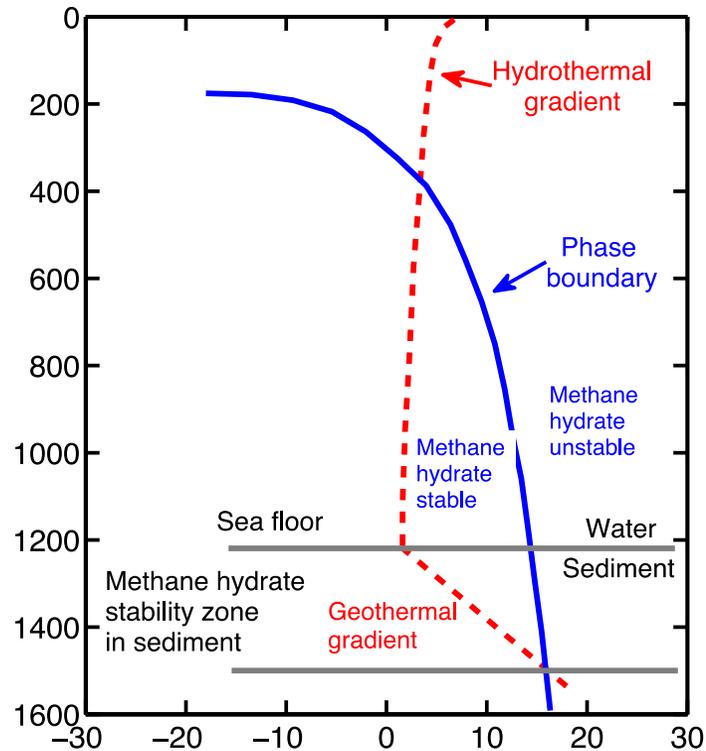
Permafrost Hydrates



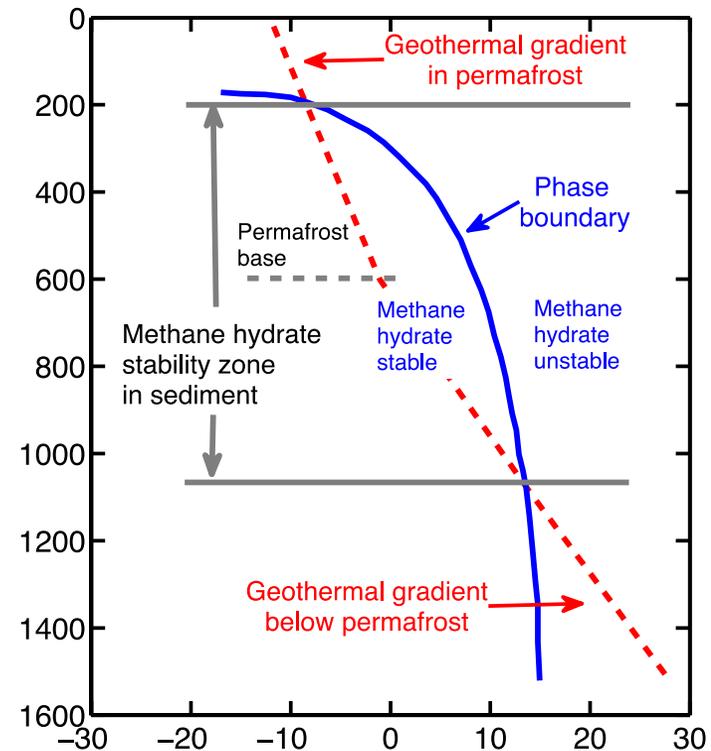
Oceanic Hydrates



Hydrate Formation Conditions in Sediments

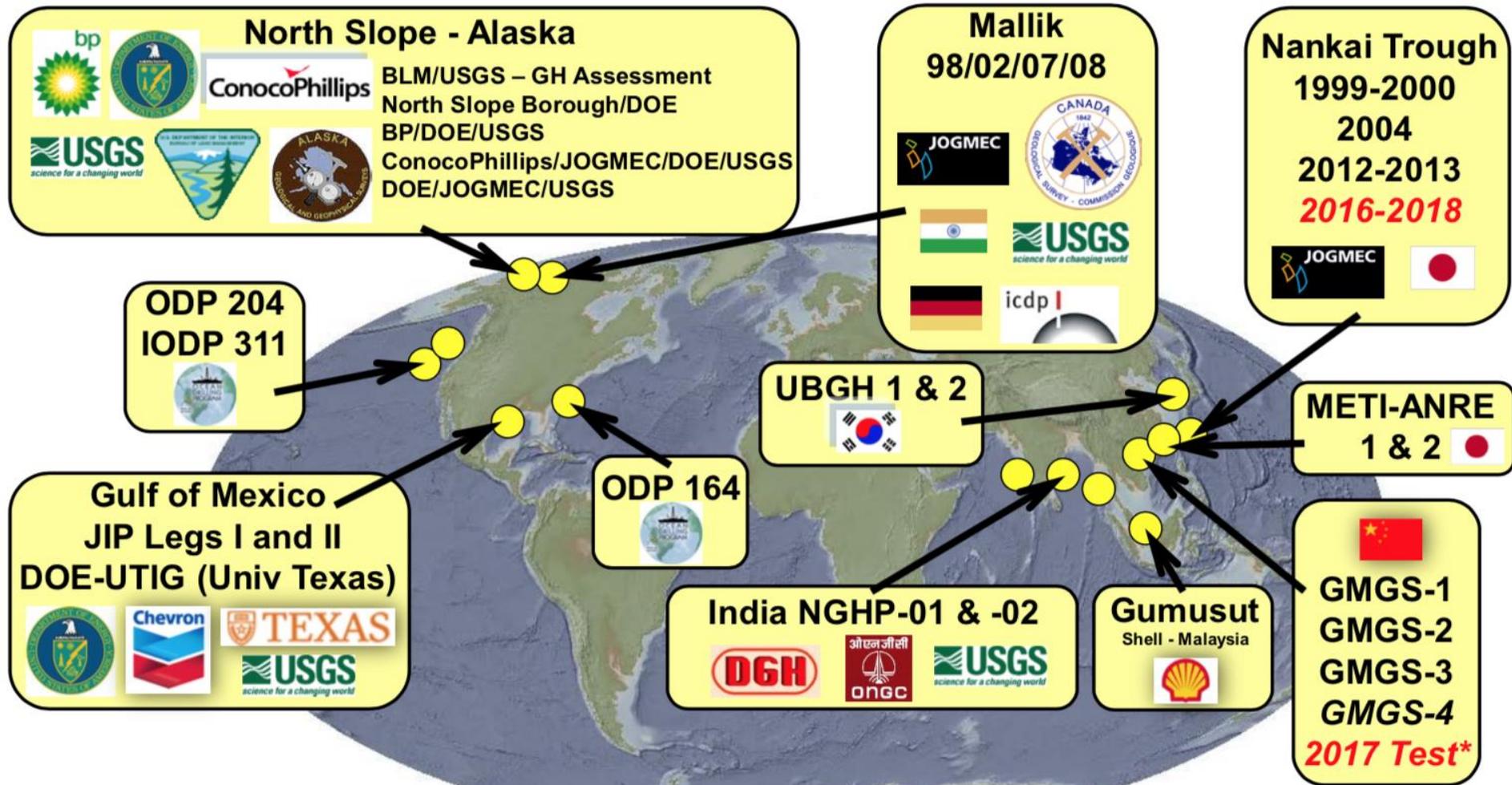


Marine environment



Permafrost regions

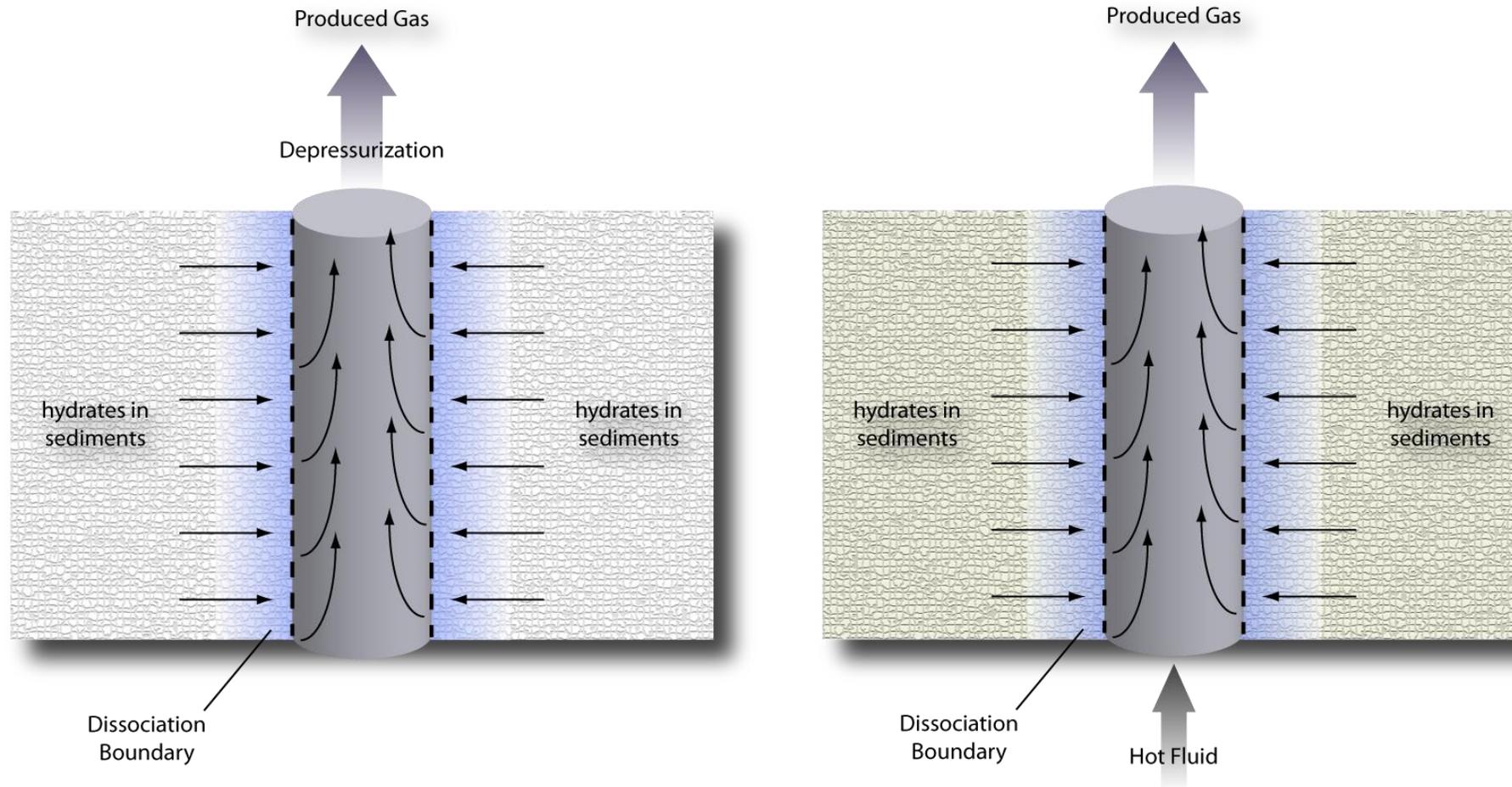
Gas Hydrate Scientific and Industry Drilling Programs



Collett, USGS, 2018

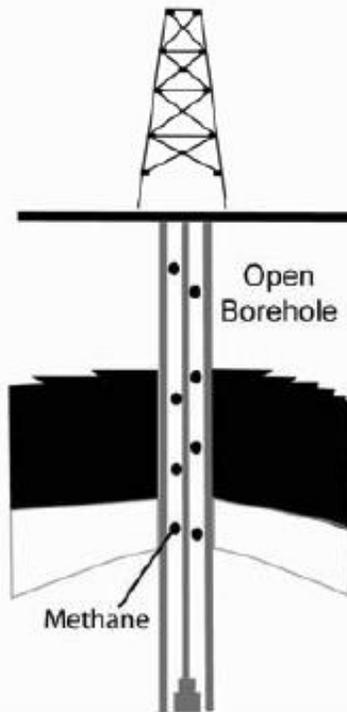
*China Ministry of Land and Resources

Gas Production from Hydrates

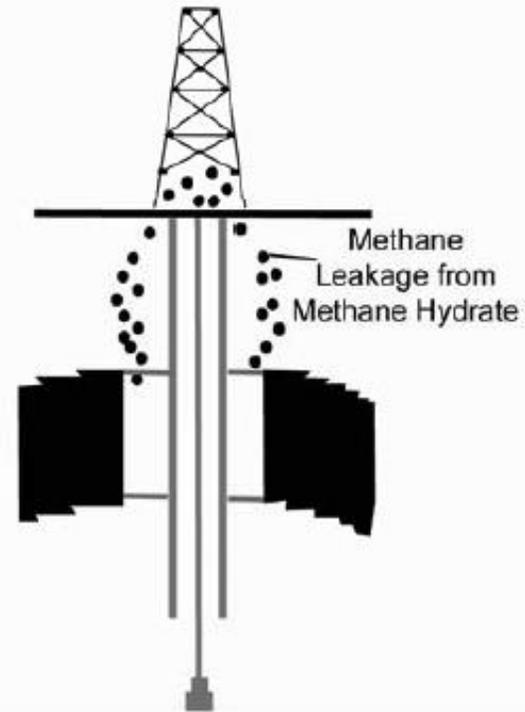


Potential Conditions During Drilling for Methane Hydrate or Oil/Gas Exploration/Production

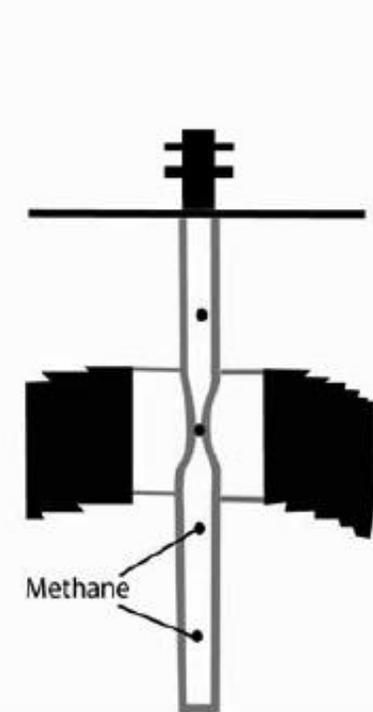
A Methane Gas Release



B Methane Gas Leakage



C Potential Collapsed Casing



Collett & Dallimore, 2002

Conclusions

- Gas hydrates are ice-like crystals of water cages trapping small gas molecules
 - which form at high pressure and low temperatures
- Methods to determine hydrate forming conditions
 - Experimental, graphical, analytical and computational
- Gas hydrates occurrences in nature are a potential energy resource
- Gas hydrate effects on climate related to CO₂ emissions