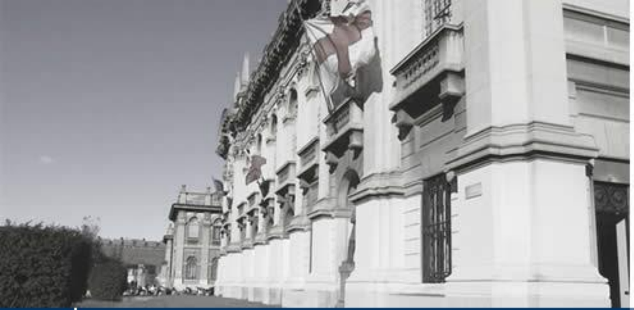


School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Gas Hydrates.

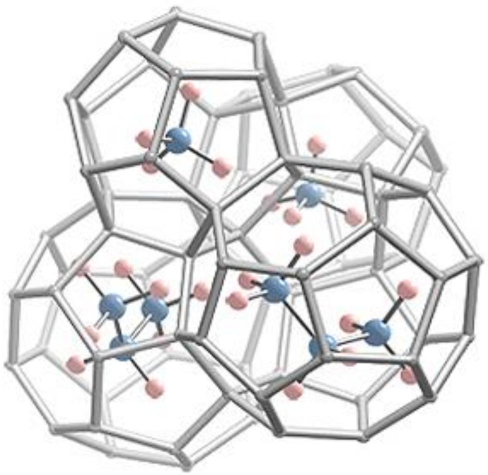
Prof. Attilio Citterio

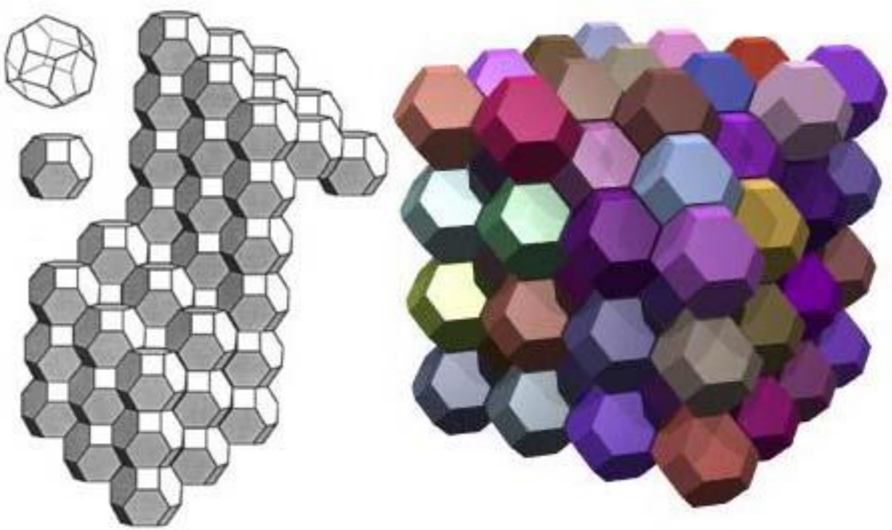
Dipartimento CMIC “Giulio Natta”

http://iscamapweb.chem.polimi.it/citterio/education/**course-topics**/

Overview.

- Hydrates – What they are?
- Clathrates and Supramolecular Chemistry
- Structure and Stoichiometry of gas hydrates
- Example: methane hydrate
- Other gas hydrates
- Occurrence and distribution
- Uses

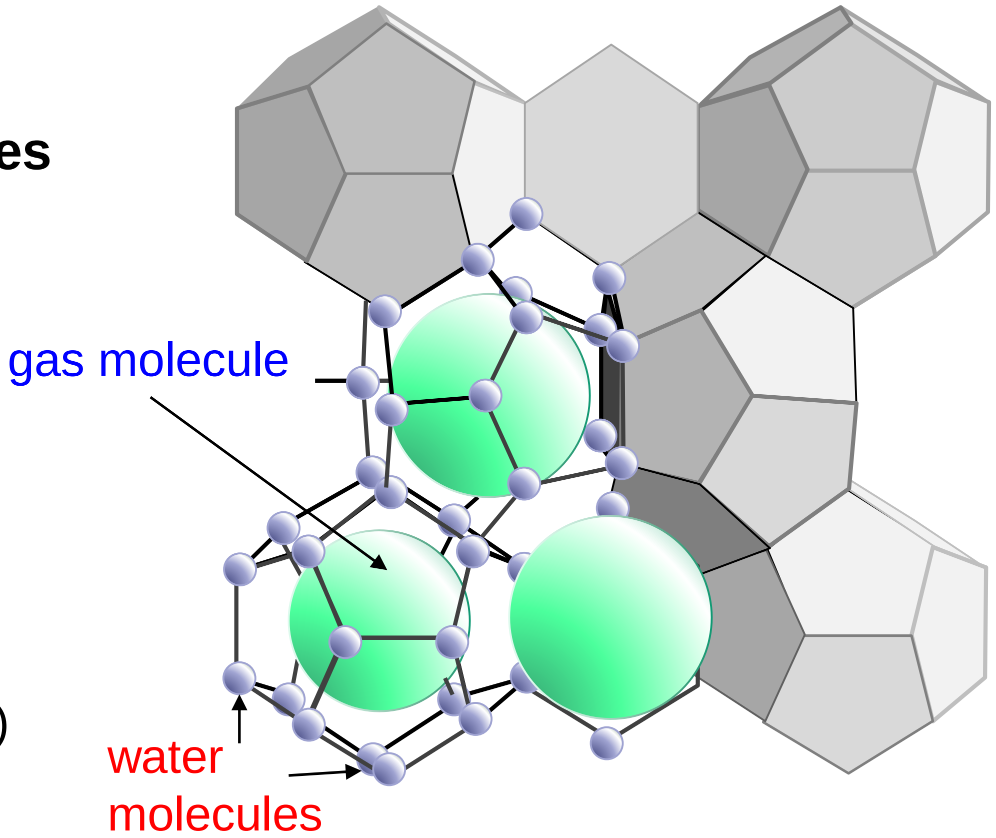




Gas Hydrates: Examples of Clathrates.

Gas hydrates: They are solids formed from hydrocarbon gas and liquid water. They resemble wet snow and can exist at temperatures above the freezing point of water.

They belong to a form of solid complexes known as **clathrates** inclusion compounds, existing at low T and high P.



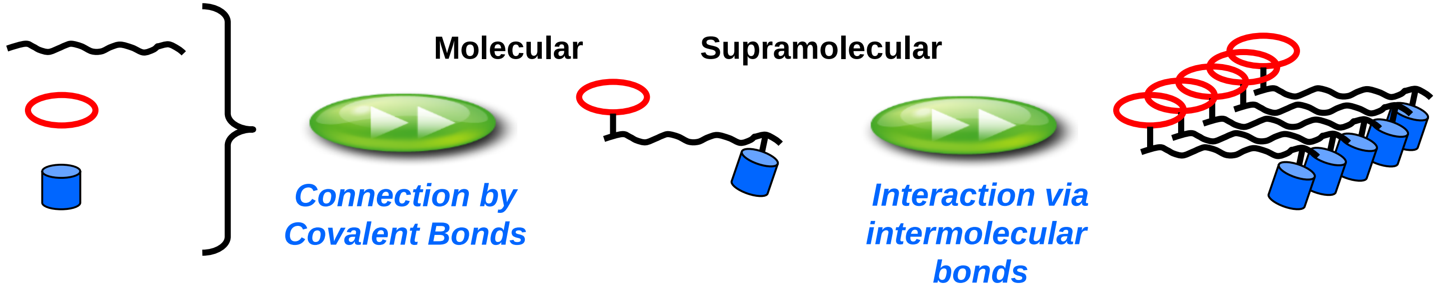
The supramolecular assembly is made by two parts:

1) Host molecules of water arranged in rigid cages
2) Mobile guest molecules (gas) of appropriate dimensions

Supramolecular Connections :

- wide aggregates of molecules
- Weak non covalent interactions
- Interactions by association

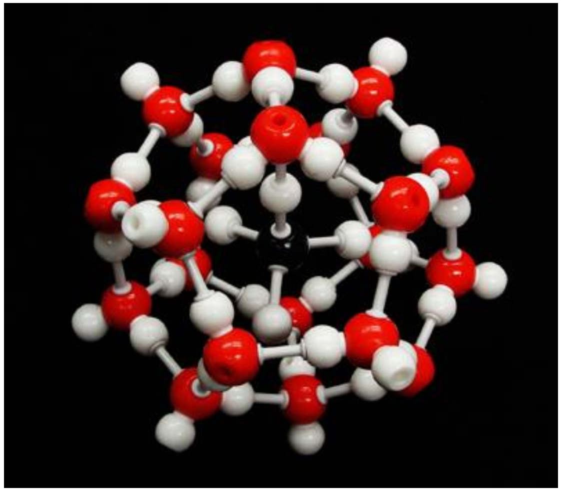
→ Auto organization
Auto assembling



Structure of Gas Hydrates.

- **Ice like crystalline substances made up of two or more components**
- **Host molecule - forms an expanded framework with void spaces**
- **Guest component(s) - fill the void spaces**
- Van der Waals forces hold the lattice together

- **Natural gas hydrates**
  - Host - water
  - Guest - one or more gases
  - pure methane hydrates REQUIRE - 4-6^{o}C, 50 Atm (500 m), AND correct concentration of gas
  - Guest gases in marine seds. - methane, ethane, propane, butane, carbon dioxide, hydrogen sulfide



Methane **I Hydrate**
ideal formula is X(gas):5.75 water

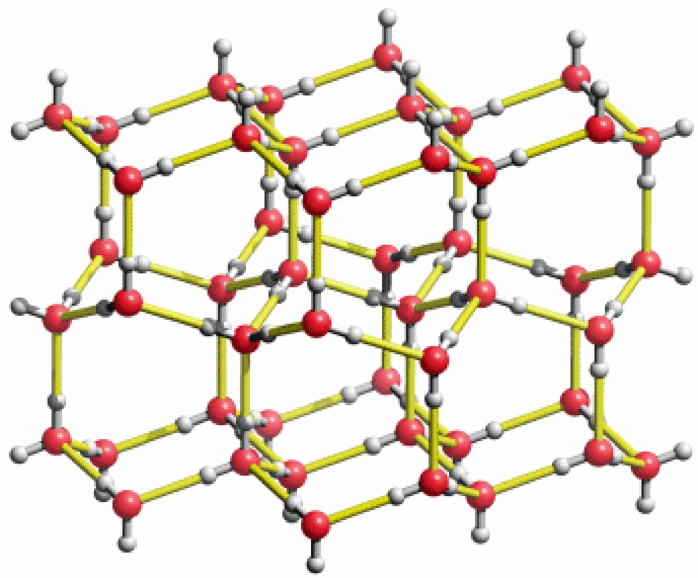
Rules for Solid Water.

According to some authors the crystal structure of ice follows these two rules:

1. tetrahedral O atoms surrounded by H atoms

2. H atoms insert between two adjacent O atoms.

These geometrical constrains allow to produce several different network.

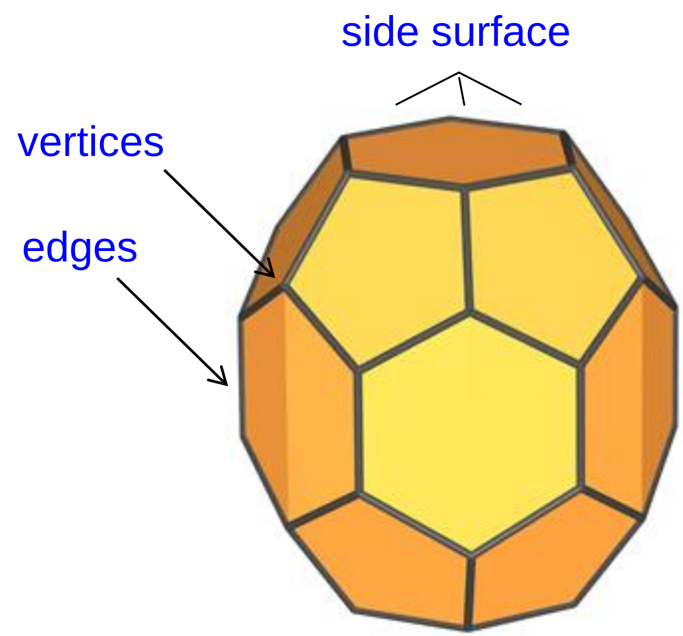


Normal Ice structure

Nomenclature.

Edges – hydrogen bonds

Vertices – oxygen atoms



$5^{12}\ 6^{8}$

Nomenclature X^n

X: Number of edges of side surfaces

n: Number of sides with X edges in the cage

5^{12} 2 pentagonal dodecahedra (12 sides)

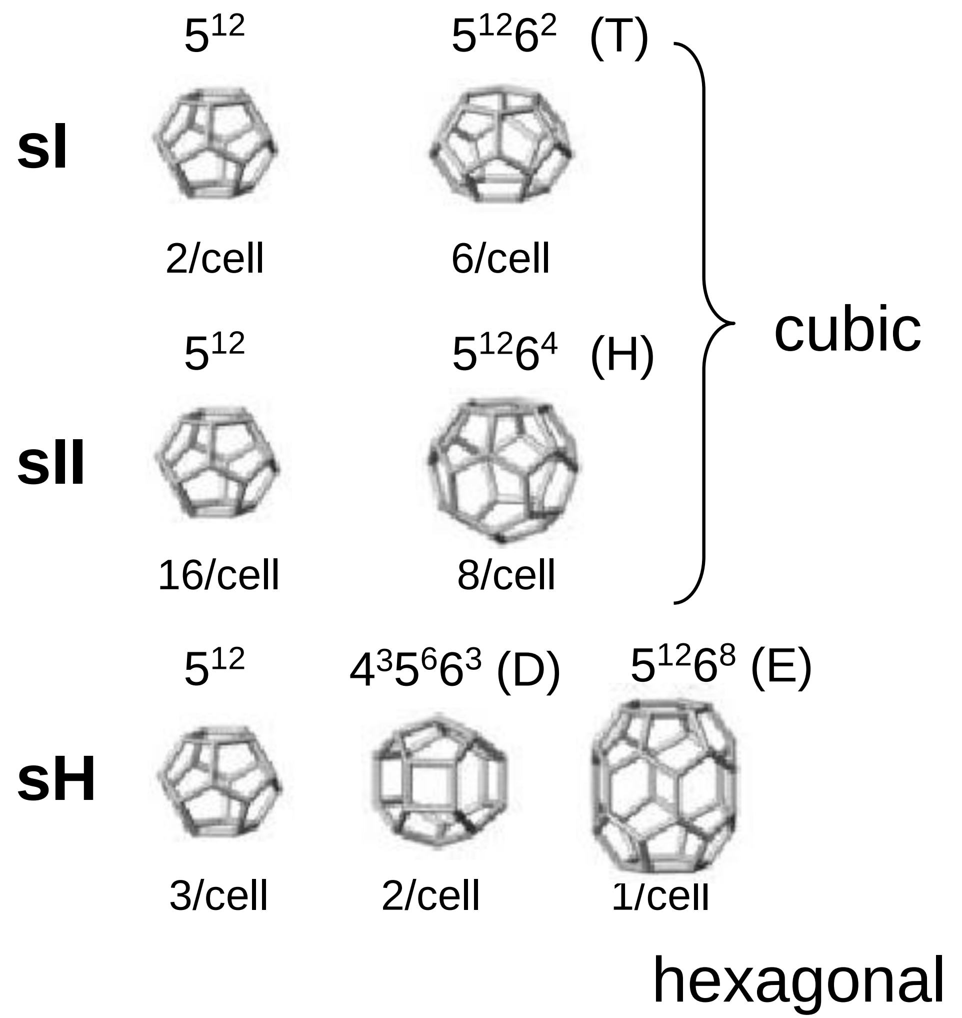
$5^{12}6^{2}$ 6 tetrakaidecahedra (14 sides)

- methane and ethane can be accommodated - nothing bigger
- ideal formula is X(gas):5.75 water
- only one third of spaces need to be filled
- rarely are voids - 100% filled
- non-stoichiometric structures

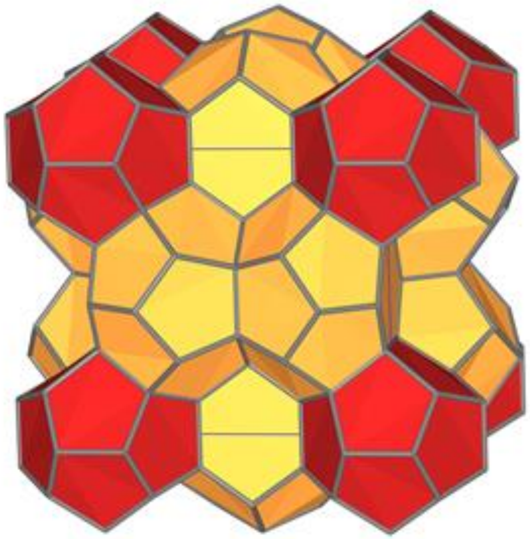
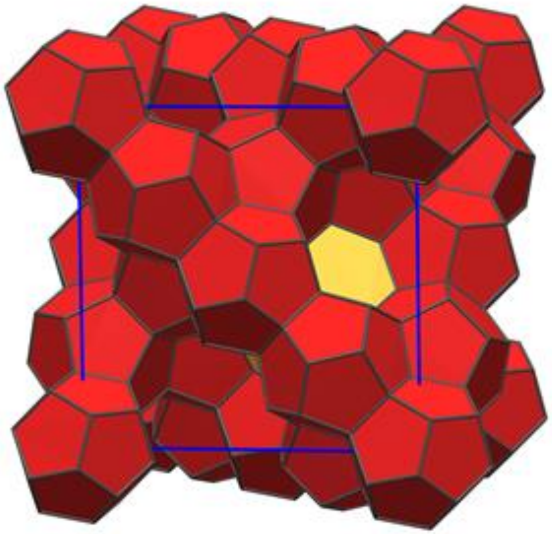
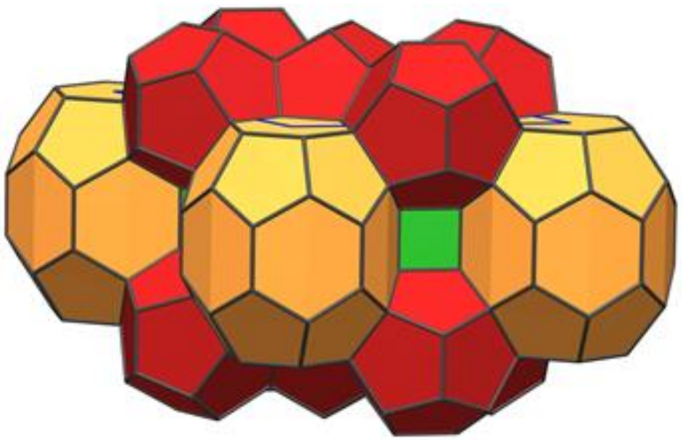
Structure of Gas Hydrates (2).

- Three non stoichiometric cage structures

- S-H host two molecules
  - Double hydrates

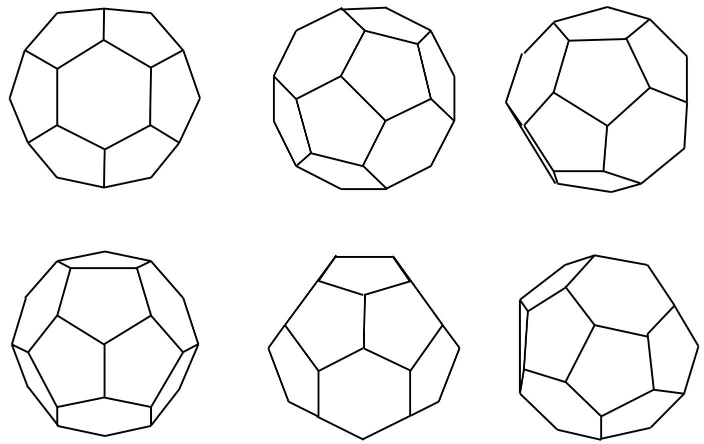


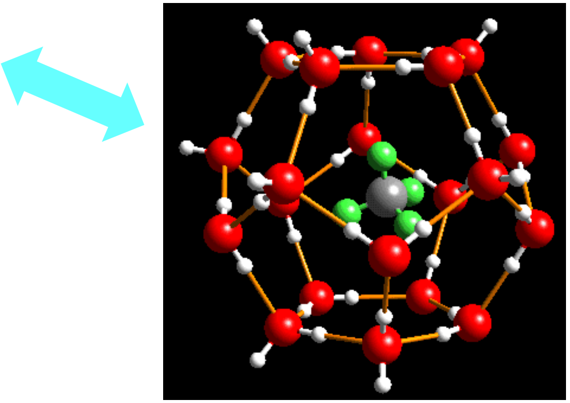
Structure of Gas Hydrates (3).

S-I	S-II	S-H
		
46 H_2O	136 H_2O	34 H_2O

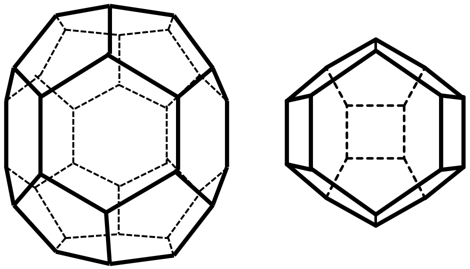
II Hydrate Structure.

- II Hydrate





- II Hydrate
  - 17-angstrom cell, 136 water molecules,
  - 5^{12} pentagonal dodecahedra (12 sided)
  - $5^{12}6^{8}$ hexakaidecahedra (16 sided)
    - accommodates molecules up to 4.8 and 6 Å
    - 16 small, 8 large void spaces
  - X(gas):17 water molecules
    - ideal formula will not occur because when all 8 large spaces are filled the small ones can't be filled
    - void spaces are diamond shaped - can accommodate propane and isobutane.



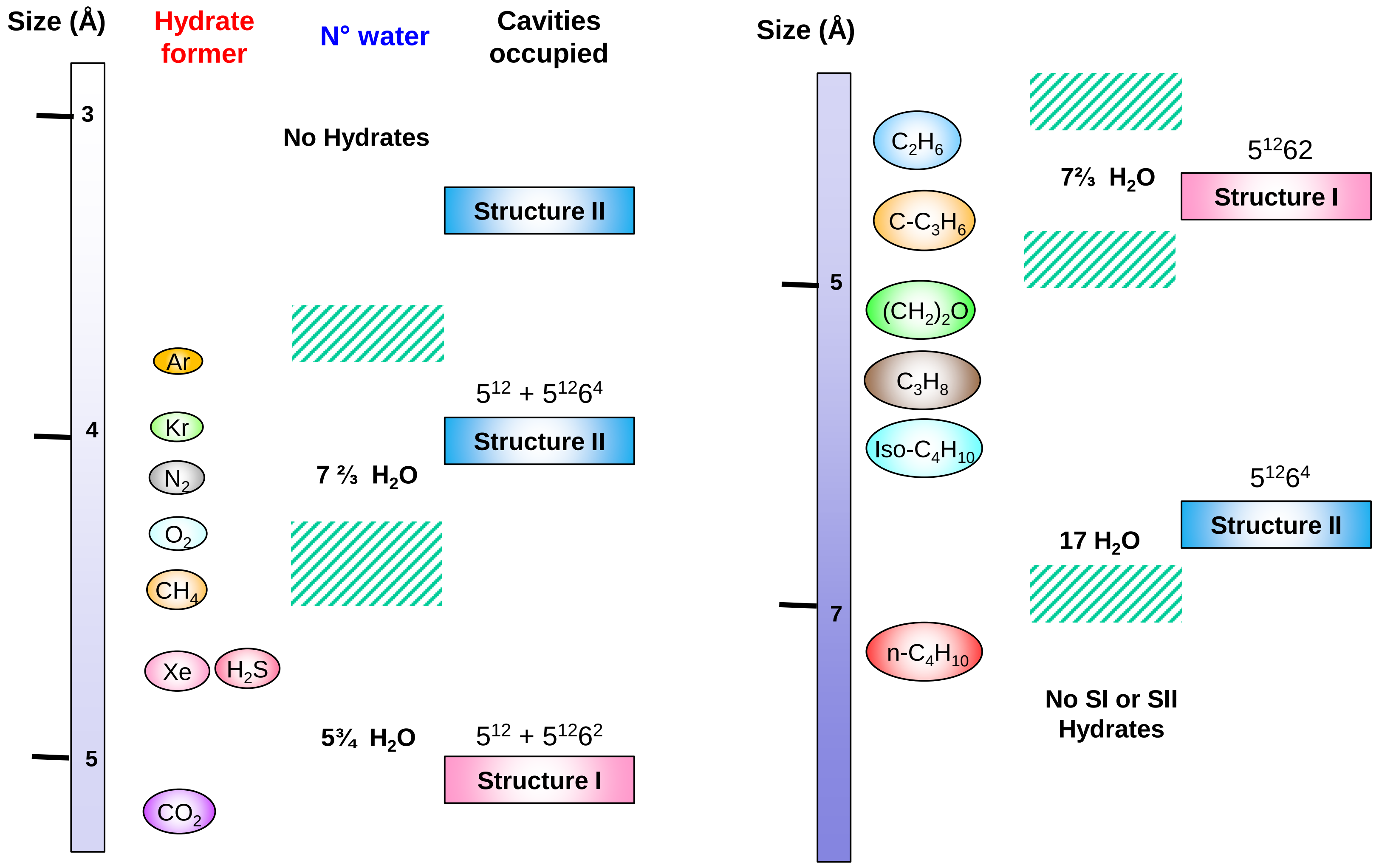
$5^{12}6^{8}$ $4^{3}5^{6}6^{3}$

Property of Gas Hydrates.

	I	I	II	II	H*	H*	H*
Cavity size	small	med	small	large	small	small	huge
Cavity shape	round	oblate	round	round	round	round	oblate
Cavity Description	5^{12}	$5^{12}6^{2}$	5^{12}	$5^{12}6^{4}$	5^{12}	$4^{3}5^{6}6^{3}$	$5^{12}6^{8}$
Number/ unit cell	2	6	16	8	3	12	1
Average radius (Angstrom)	3.91	4.33	3.902	4.683	3.91	4.06	5.71
Rel. size of CH_4 (%)	88.6	75.7	88.9	67.5	88.6		
Coordination No.	20	24	20	28	20	20	36

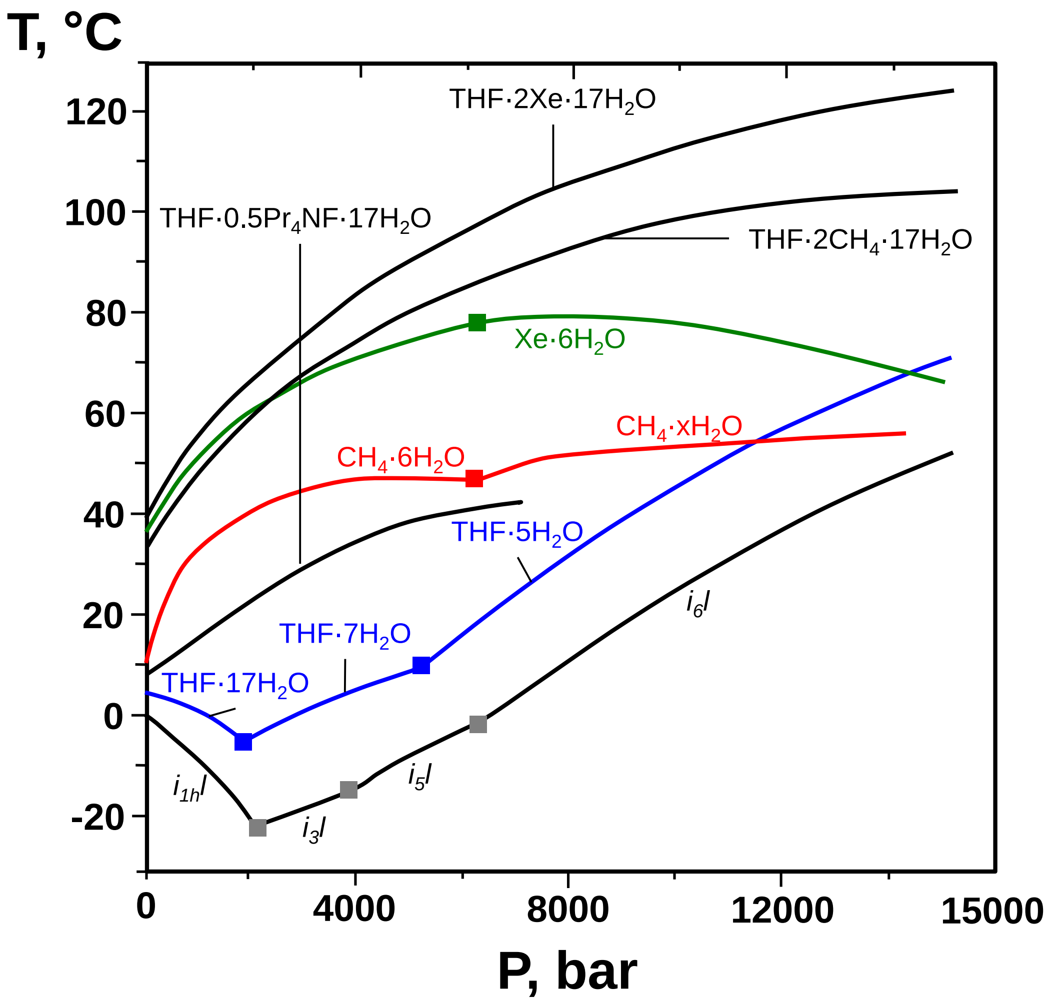
*http://www.netl.doe.gov/scng/hydrate/about-hydrates/chemistry.htm

Influence of Host Molecules.

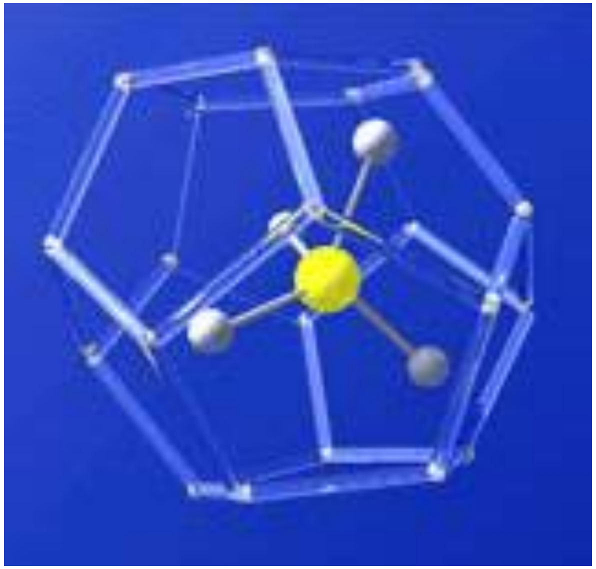


Stoichiometry.

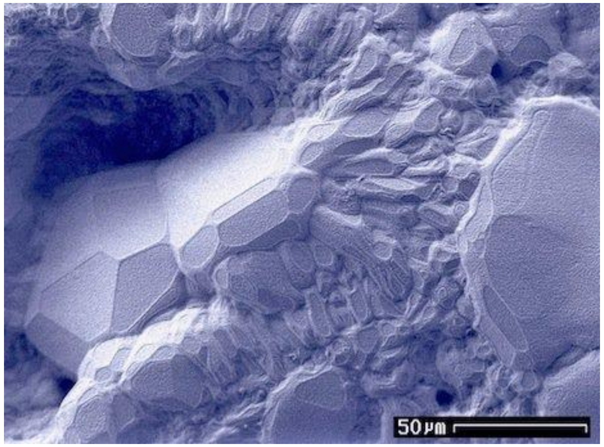
Ratio of occupation dependent on Pressure and Temperature



Example: Methane Hydrate.



Cryogenic SEM images taken at very low T to keep the hydrate stable.
Source: L. Stern / USGS



«firing ice »

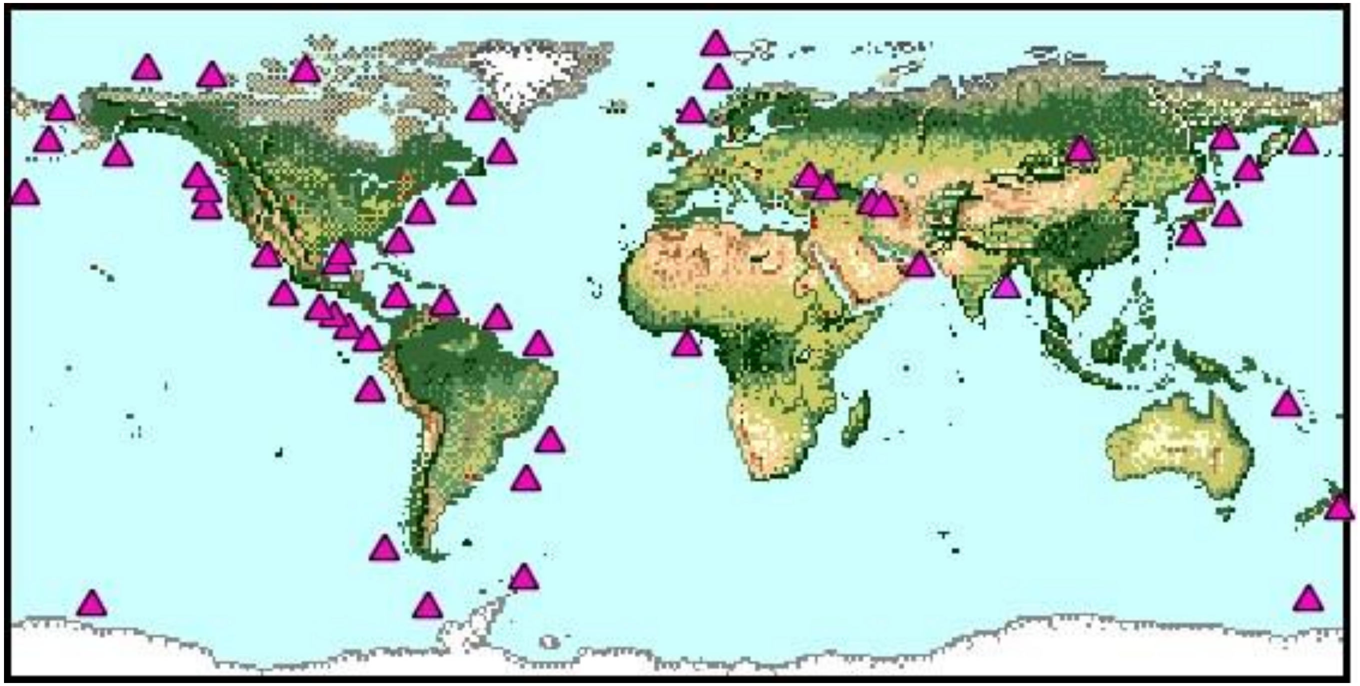
Is a potential Energy Source:

- A 1 m^3 block of hydrate at normal temps and pressures will release ~ 163 m^3 of methane (if filled to 90%)
- Methane hydrate energy content of ~ 6860 $Mj \cdot m^{-3}$
- Can occur at water T up to 30°C (↑P)

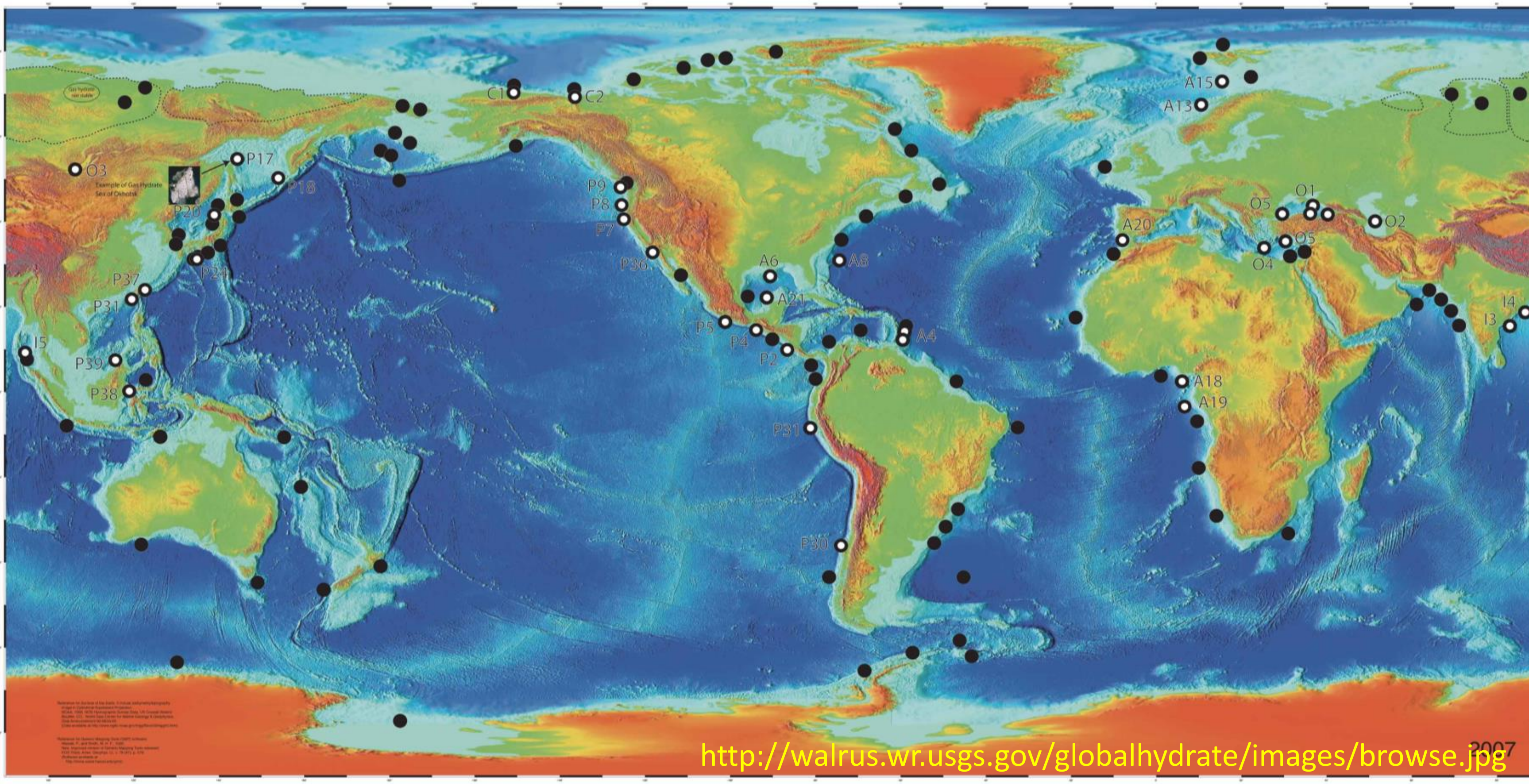
Methane Hydrate Sample.

Methane Hydrate Deposits.

- Deposits in permafrost regions (1.4×10^{13} to 3.4×10^{16} m^3)
- Submarine sediments in oceans (3.1×10^{15} to 7.6×10^{18} m^3)
  - kerogen is the only pool of carbon greater than hydrates
  - natural gas in hydrates 2 times greater than total fossil fuel reserves



Distribution of Gas Hydrate.



Thomas D. Lorenson and Keith A. Kvenvolden

white dot = gas samples recovered
black dot = hydrate inferred from seismic imaging
dotted lines = hydrate-containing permafrost

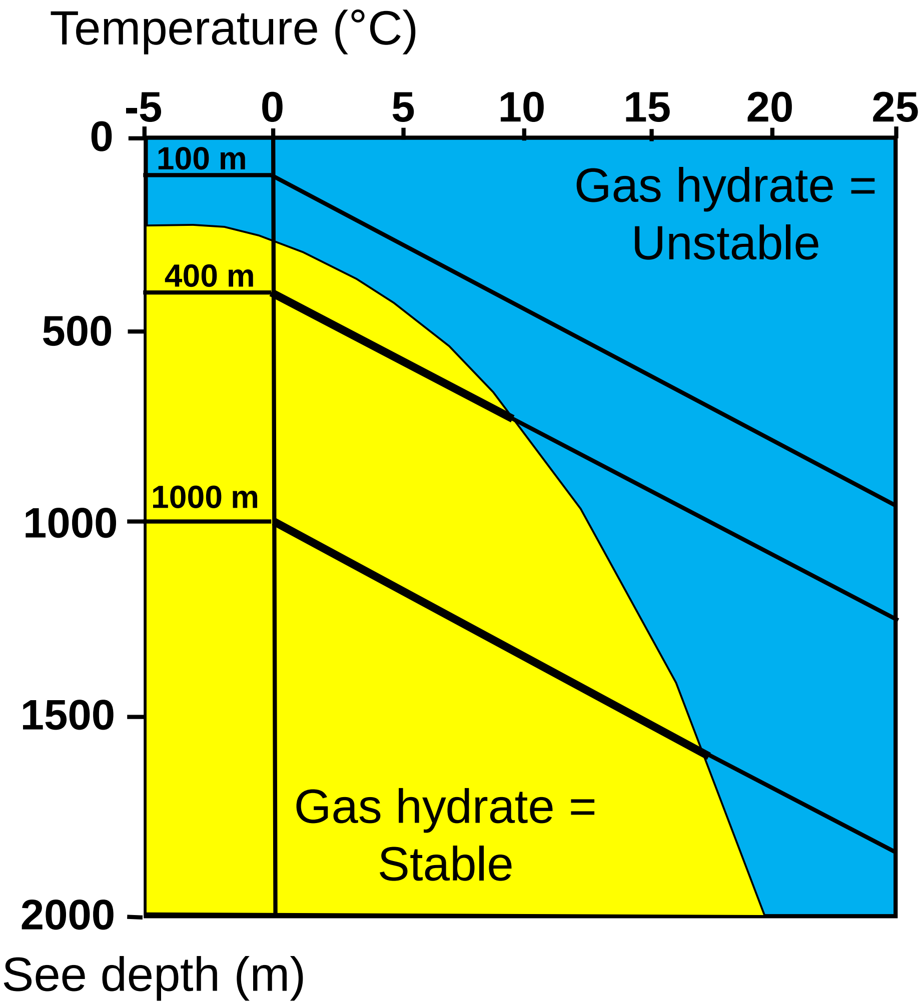
Methane Hydrate Formation.

Formation:

- Sufficient gas molecules
- Water saturated by methane
- Appropriately low temperatures
- Appropriately high pressures

if we know where these conditions are met, it is possible to predict where gas hydrates will form.

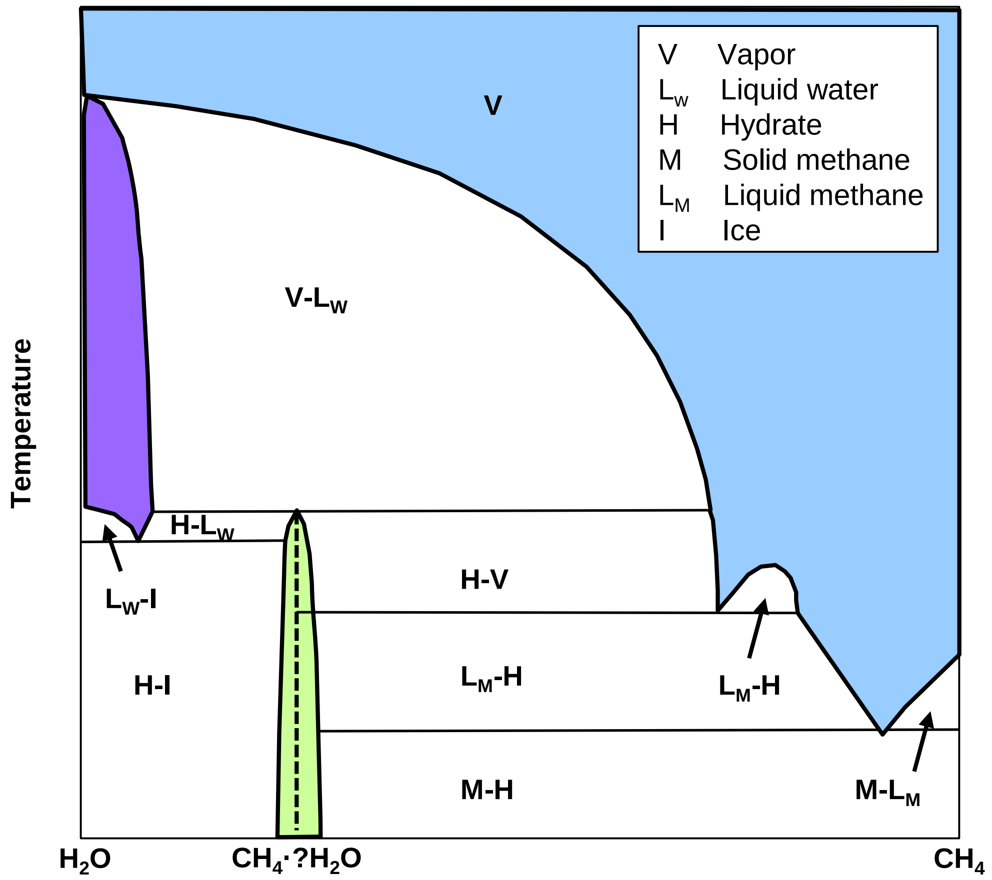
Not fully understood and is dependent on methane source.



Phase Diagram.

Scheme: isobars in the phase diagram.

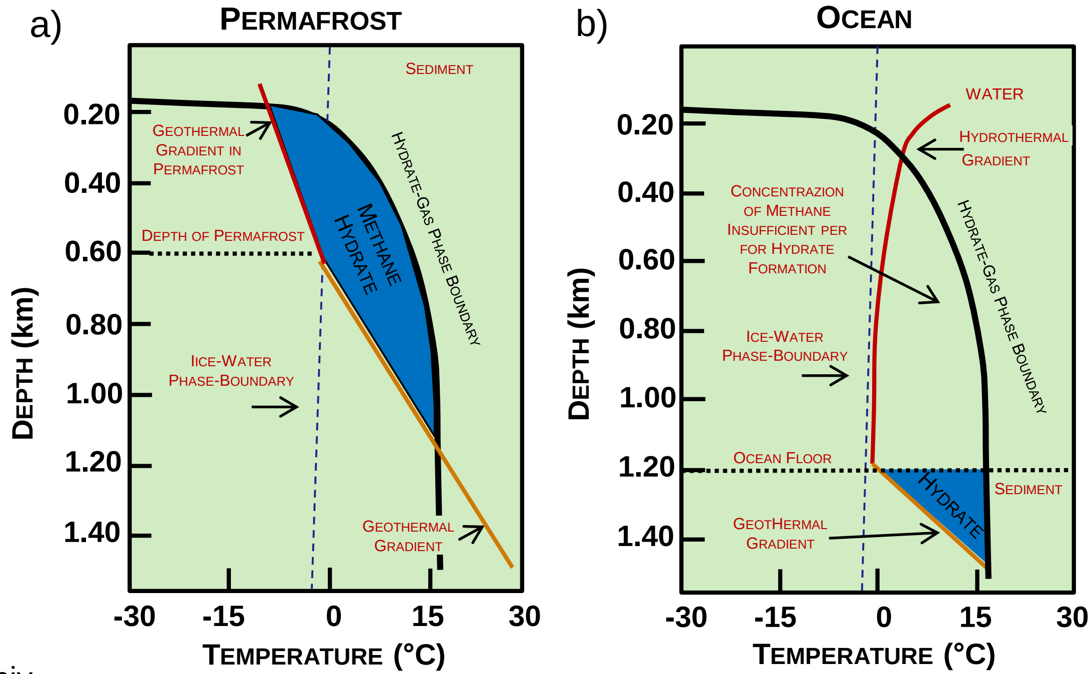
In green the methane hydrate region.



Gas Hydrate Formation.

- Thermogenic gas produced at high temperatures
  - migrates from place of origin to the ‘**HYDRATE STABILITY ZONE**’
- Hydrates - most likely form at the ‘gas-liquid’ interface
- BUT - could also form from gases dissolved in the liquid phase
- Gas must migrate to the ‘ZONE’ and be presented in ‘SUPERSATURATED’ quantities

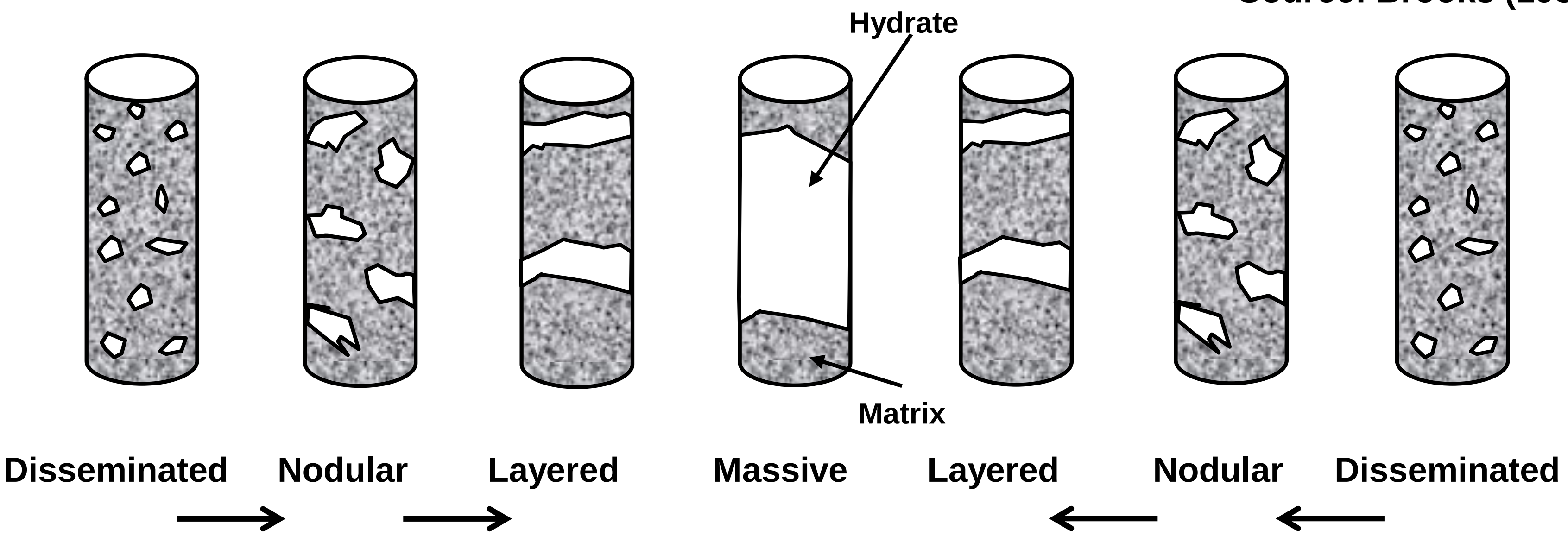
- Hydrates can form as - finely disseminated crystals, nodules, layers and mass accumulations
- Progression of smaller to larger accumulations



Source: Stanford Univ.

Progression of Hydrate Formation/Stabilization.

Source: Brooks (1986)



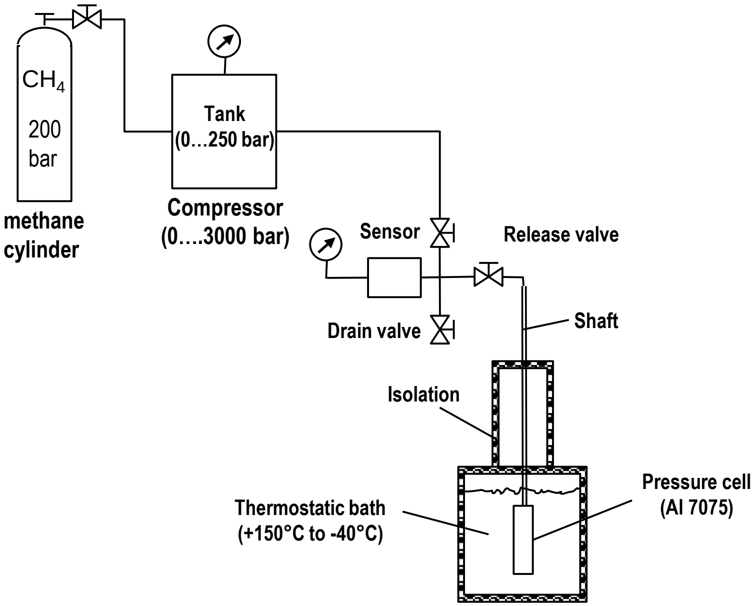
- hydrate lattices stabilized OR de-stabilized by co-occurring organic and inorganic pore water constituents
- hydrate is effectively ‘freshened’ as these are ‘excluded’ from the lattice
- in the presence of propane hydrates can be stable at higher T and lower P
- clays can stabilize hydrates (and other solids)
- rapid sedimentation rates and influenced by sediment texture
- authigenic carbonate rubble formation with shallow fracturing of sediments

Inhibition of Formation.

- NaCl - “anti-freeze” - lowers the temp at which a hydrate can form
  - 3.5% solution reduces stabilization temp by 2-3 °C
- Inclusion of heavier gases increases temp (hence off-sets the salinity problem)
- Gas hydrates can alter the concentrations of pore waters by excluding salts or melting (’freshens’ the pore water)
- >50% Nitrogen can increase pressure required by 30%
- butane (1 - 5.8%) is included in a hydrate when pressures are less than 10^3 Atm
  - does not form hydrates at its own vapor pressure
  - does not inhibit the formation of methane hydrates

Lab. Experiment on Methane Hydrate.

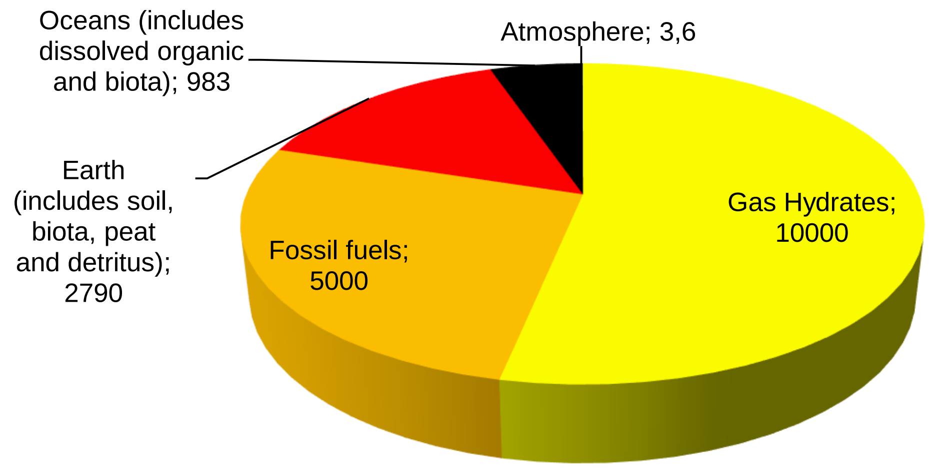
- Feeding of water and methane
- Hexagonal Ice and Gas



Uses of Gas Hydrates.

As energy source

- Relevant reserves of methane
- Country mainly interested: Siberia and Canada
- Possible use as fuel storage



Distribution of organic carbon in Earth reservoirs (excluded dispersed carbon in rocks and sediments, which equals nearly 1000 times this amount. Numbers in gigatons (10^{15} tons) of carbon

- Methane hydrate energy content of ~ 6860 MJ·m^{-3}
- Methane gas – 42.8 MJ·m^{-3}
- Liquefied natural gas 16000 MJ·m^{-3}

1 cubic meter of gas hydrate (90% site occupied) = 163 m^3 of gas

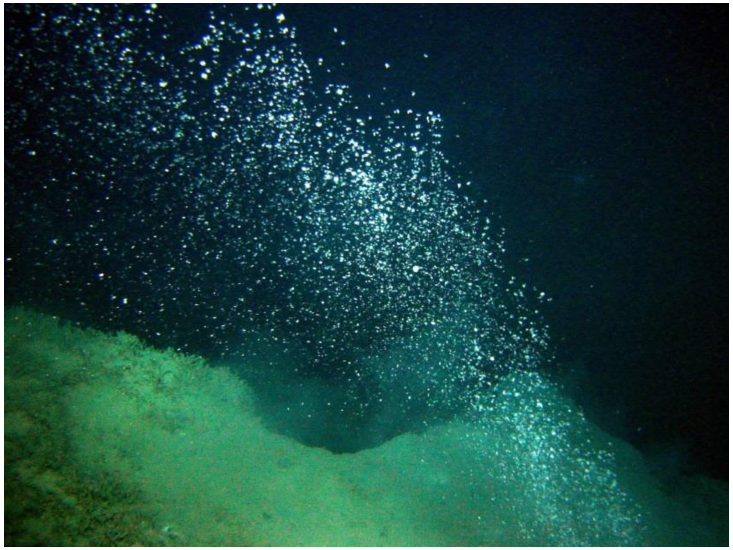
PROBLEMS with Methane Hydrates.

- hydrate dissociation upon recovery; engineering challenge
- expense of long pipelines across continental slope, subject to blockage with solid hydrate
- methane release into atmosphere problem for climate change (20x more potent than CO_2)
- fragile ecosystems surround sediment surface hydrates & seeps

Environmental issues:

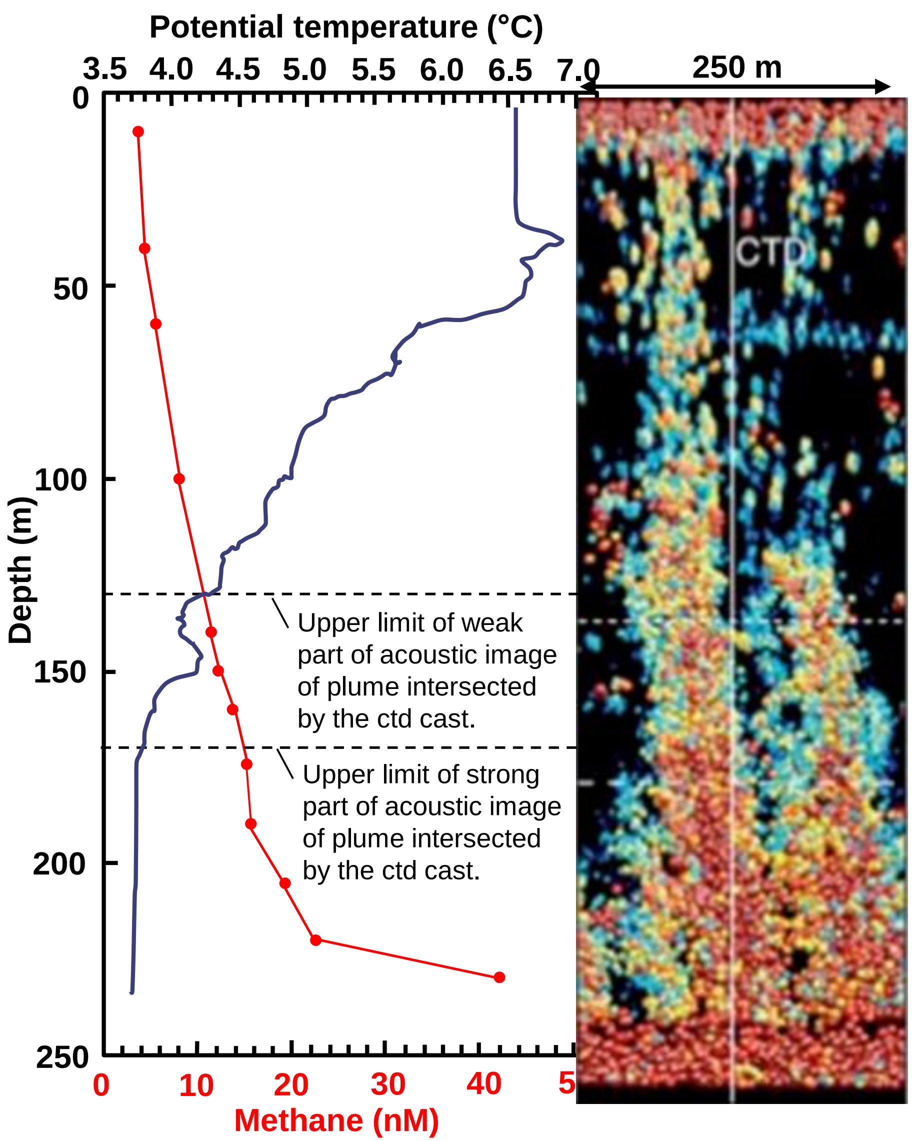
Increase in temperature on Earth will induce significant release of methane from methane hydrates.

Archer et al., 2007



dissociating methane hydrate at sediment/water interface

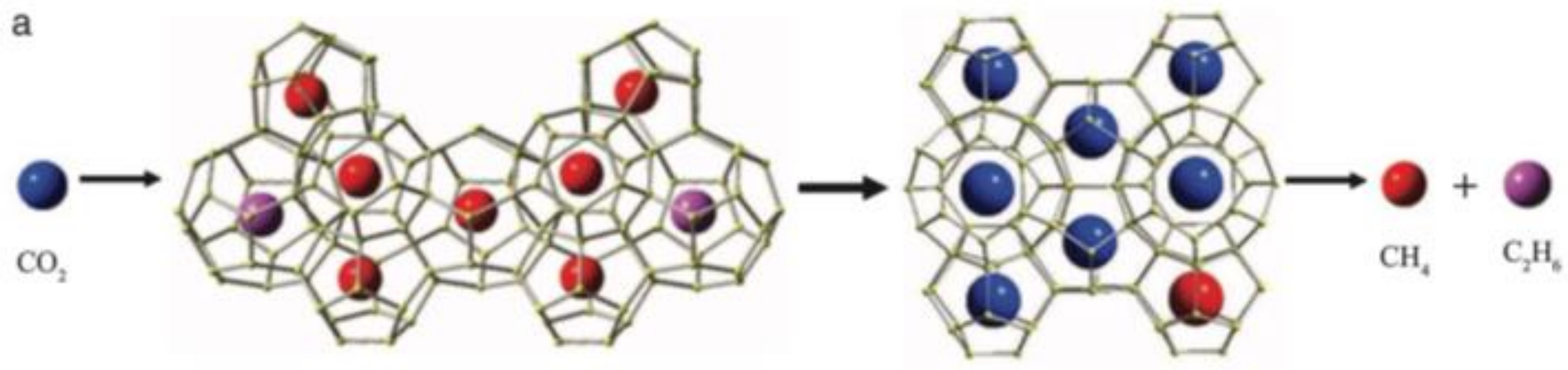
Environmental Concern on Methane Escape.

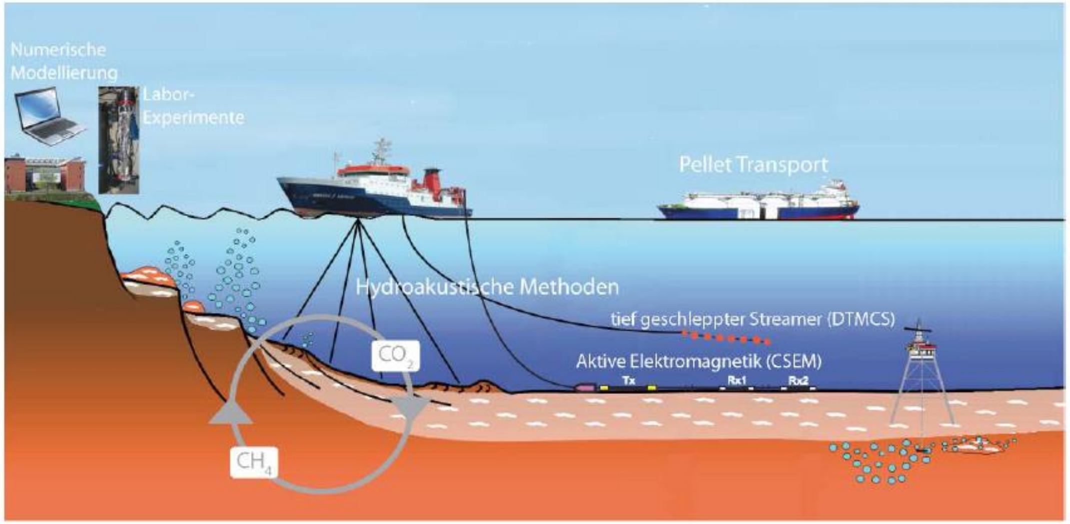


- lots of CH_4 escaping from melting gas hydrates
- powerful **positive feedback** on global warming
- CH_4 is a powerful greenhouse gas
- most likely oxidizes to CO_2 before it enters the atmosphere… but still!
- A detailed investigation of methane hydrate dissociation during global warming was reported (Archer et al., 2007)

Westbrook et al., 2009

Recovery of Methane with Sinking of CO_2.





Park et al., PNAS, 2006

Extractive Activities.

Large, expensive pilot programs focus on drilling in frozen permafrost areas

Ex: Mallik, Canada

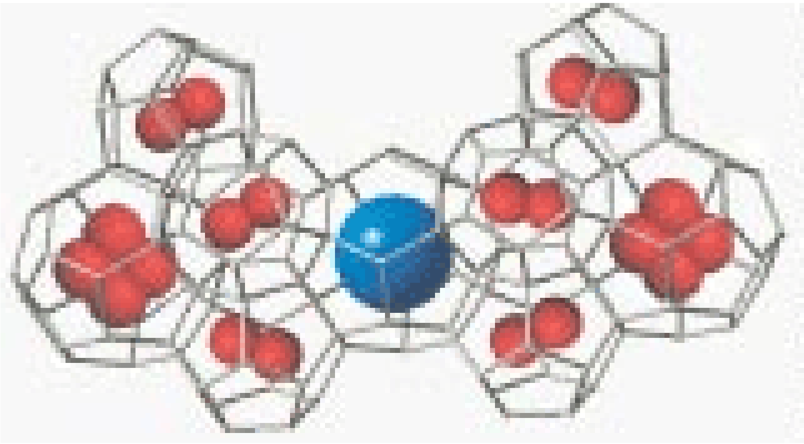
http://energy.usgs.gov/other/gashydrates/mallik.html

Hydrogen Storage Potential

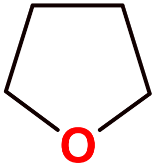
- Binary inclusions of gas hydrate and THF

- Cage occupation

$(2\ H_2)_2 \cdot (4\ H_2)_x \cdot THF_{(1-x)} 17H_2O$



- Capacity: 4 % by weight

THF = 

Source: Nature 434, 743-746, 2005

References.

1. E. Dendy Sloan, Jr., Nature, 426, 353-363, 2003

2. H. Lee, J.-w. Lee, D. Y.Kim, J. Park, Nature 434, 743-746, 2005

3. Dr. Jörg Bialas, IFM-GEOMAR, Submarine Gashydratlagerstätten als Deponie für die CO_2-Sequestrierung, 2007

4. Gabitto, J. F. and Tsouris C. "Physical Properties of Gas Hydrates: A Review." J. of Thermodynamics, Hindawi Pub., Vol. 2010, ID271291.

5.] J. Caroll. Natural gas hydrates. A Guide for Engineers. Gulf Professional Publishing, ISBN 0-7506-7569-1, 2003

6. E. D. Sloan and C. A. Koh. Clathrate hydrates of natural gases. Third edition, CRC Press, 6000 Broken Sound Parkway NW, Suite 300, Boca Raton, FL 33487-2742, U.S.A., 2008

7. www.ifm-geomar.de

8. http://www.imc.tuwien.ac.at/download/supramolekular_01.pdf

9. http://www.sfv.de/lokal/mails/wvf/methanhy.htm

10. http://www.cup.uni-muenchen.de/ac/kluefers/homepage/L_ac1.html