Janda lab

By Kathy Marvin
K – 12 Teacher Outreach
2010

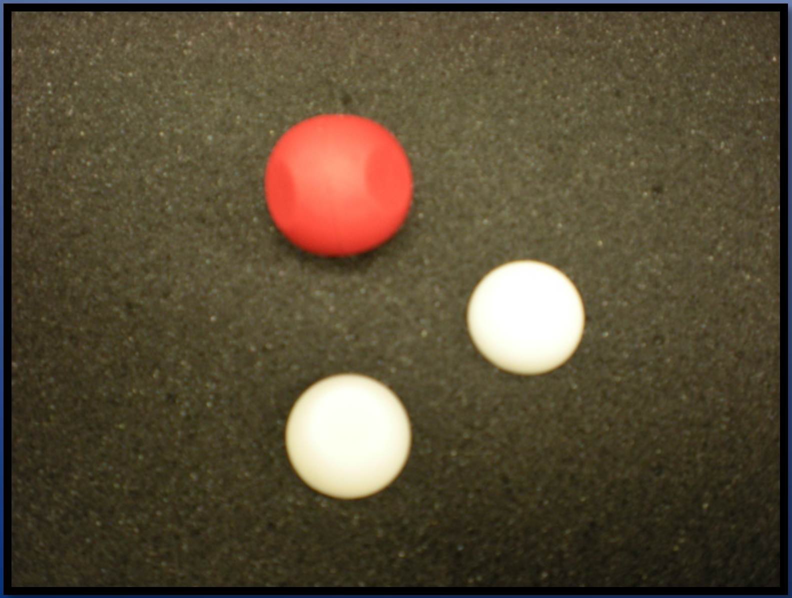
Understanding the Clathrate Hydrate

Some Facts About Water (H2O)

- Ice floats in water
- Water molecules share electrons and are “polar”, with a positive and a negative side
- All 3 phases of water are present in great abundance
- 70% of the earth’s surface is solid or liquid water
- Over ½ our body mass is water
- Lightning is due to collisions between ice particles
- There are 13 known phases of ice
- It is one of the most difficult substances for theory to simulate or model

Molecular Structure of H_2O

- Basic components of water contain 1 oxygen (O) atom and 2 hydrogen (H) atoms



- Single bonded molecule of water containing 1 oxygen (O) and 2 hydrogen (H) atoms

Structure of H_2O as a Gas

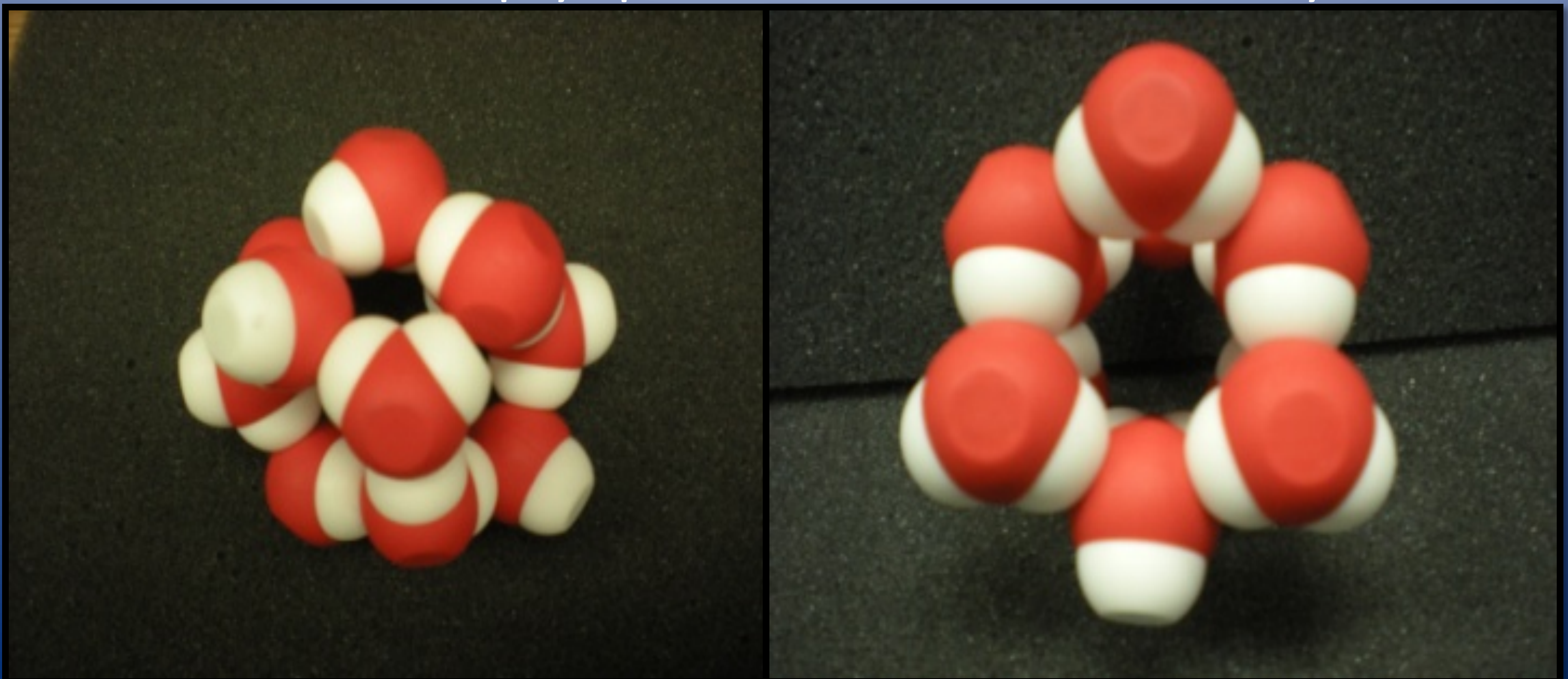
- Molecules are randomly arranged both close together and far apart
- Molecules spread out as far as they can
- No definite shape or volume

Structure of H2O as a Liquid

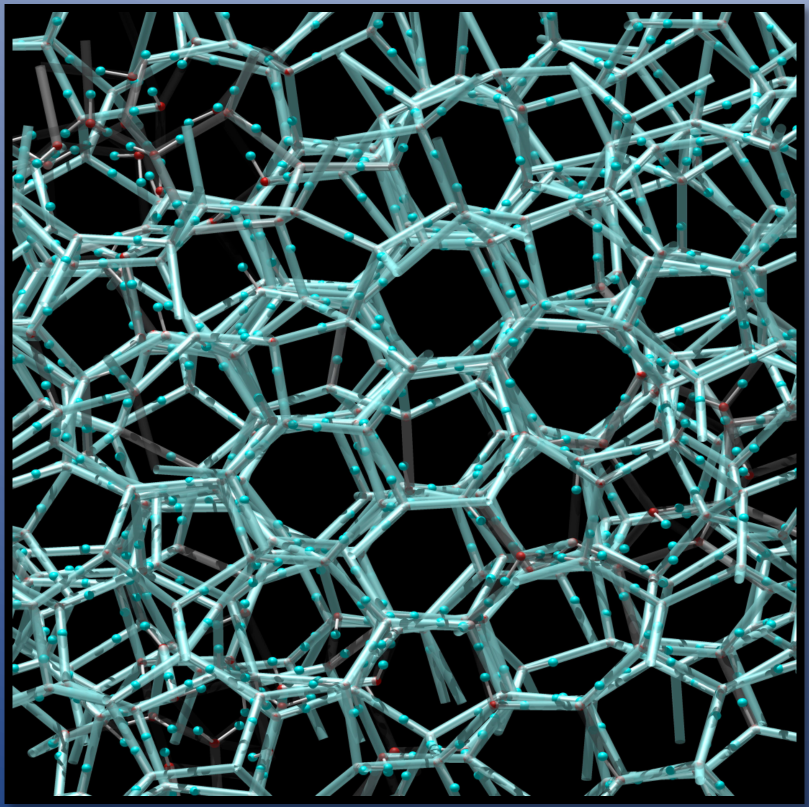
- Water molecules touch but are able to move around easily and slip and slide past other molecules
- Liquid H2O is able to take on shape of its container

Structure of H_2O as a Solid (Ice)

- This is the structure of ice from your freezer
- Repeating pattern of uniform crystals
- Notice the empty space in the center of the crystal



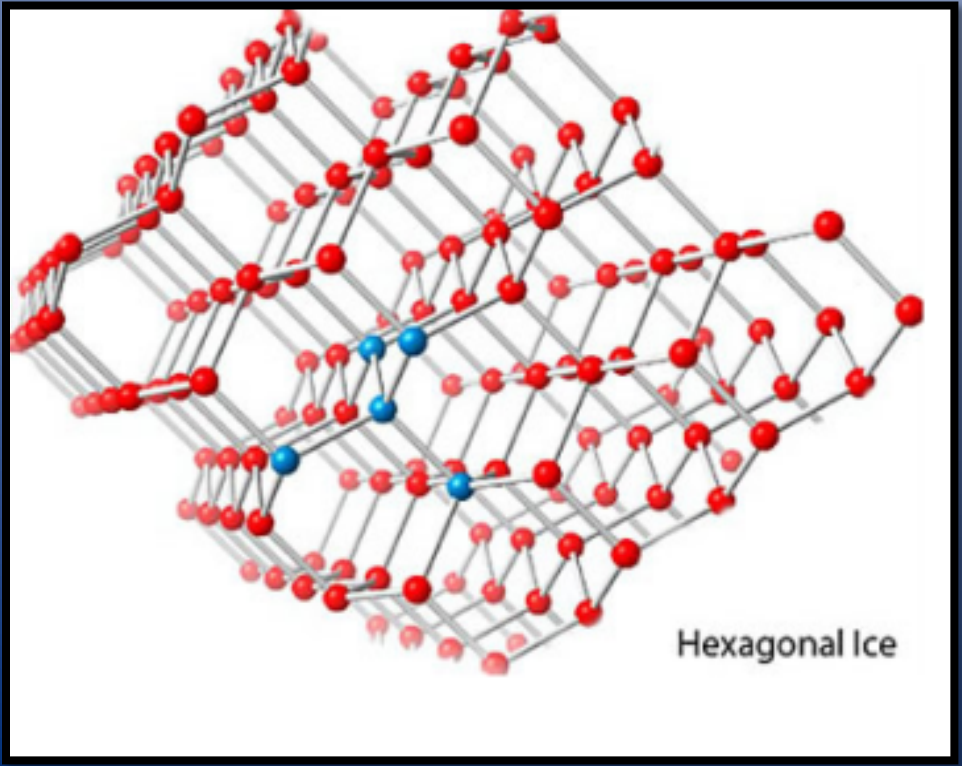
Structure of Solid H2O



Frozen water creates a lattice work of repeating crystalline structures that trap air as they freeze.

Ice From Your Freezer

- Ice from your refrigerator is made of icosohedrons and forms hexagonal structures



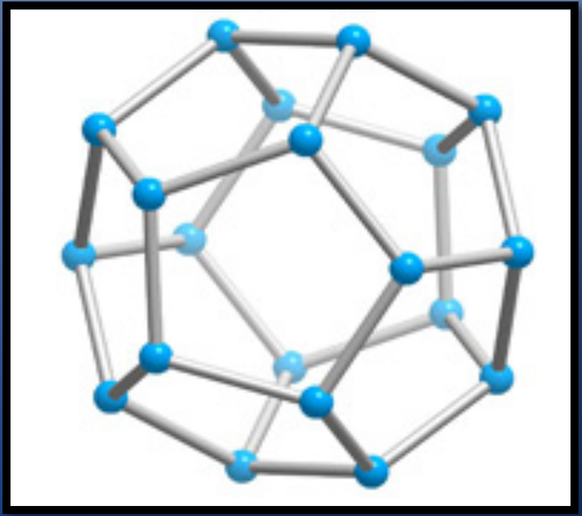
- Notice the long repeating tubes of crystal lattice work
- Any other type of molecule trapped in these tubes could ‘slip’ through

Some Facts About Air & Solid H2O

- Ice floats
- As H_2O freezes and crystallizes, it traps tiny particles of air within it's structure
- Frozen water is less dense than fresh H_2O
- If ice didn't float there would be no life on earth
  - Think about it! WHY????

What is a Clathrate Hydrate?

- Can also be called a gas hydrate
- Water forms into a different geometric shape than hexagonal ice when water and gas come into contact with each other at high pressure and low temperature
- Frozen water 'host' molecules form a cage that can hold a 'guest' gas molecule

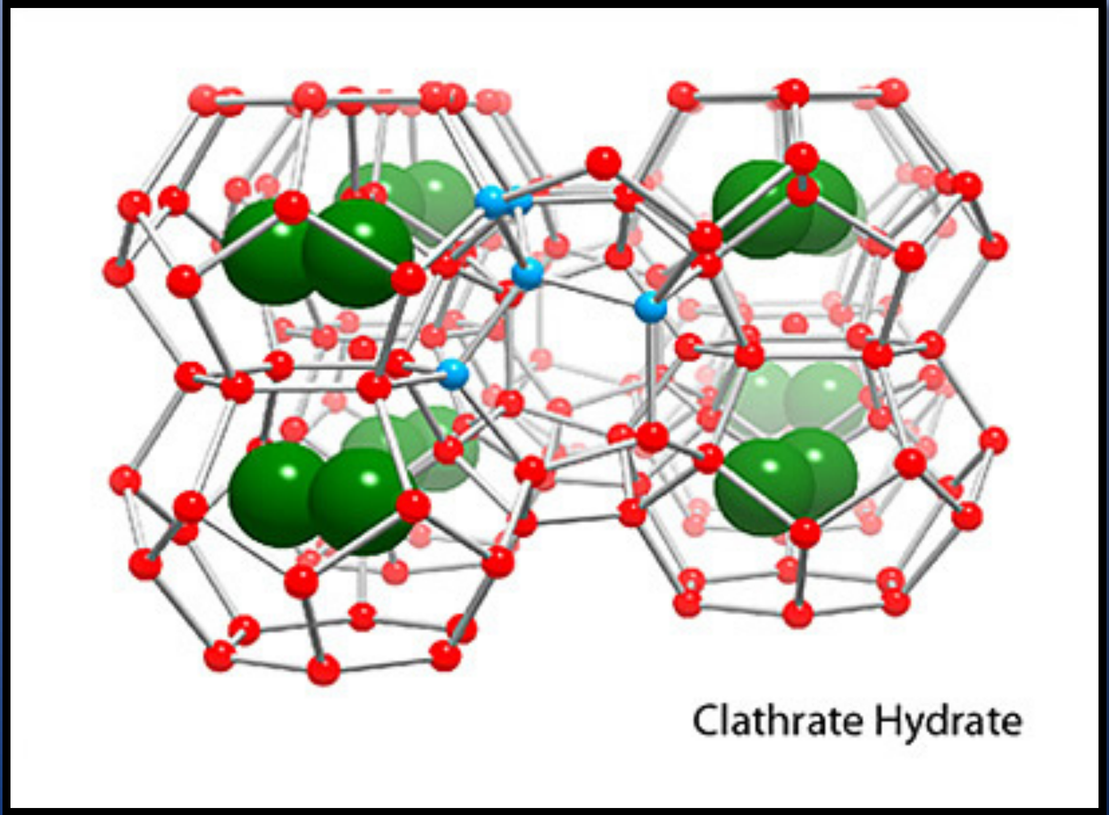


The Gas Hydrate

- Less dense than the original crystalline water structure due to the guest gas molecule
- Forms a differently shaped lattice to accommodate gas molecules
- The cage is held together by hydrogen bonds between water molecules and stabilized by van der Waals forces
  - Van der Waals forces are the forces between the gas and water molecules. It is the Van der Waals force that makes the gas hydrate very stable, in fact the clathrate hydrate is more stable than hexagonal ice
- Gas hydrates are characterized by the shape of their cages

The Gas Hydrate

- Model of a clathrate hydrate with trapped guest molecules of gas inside the ice cages of the host molecules



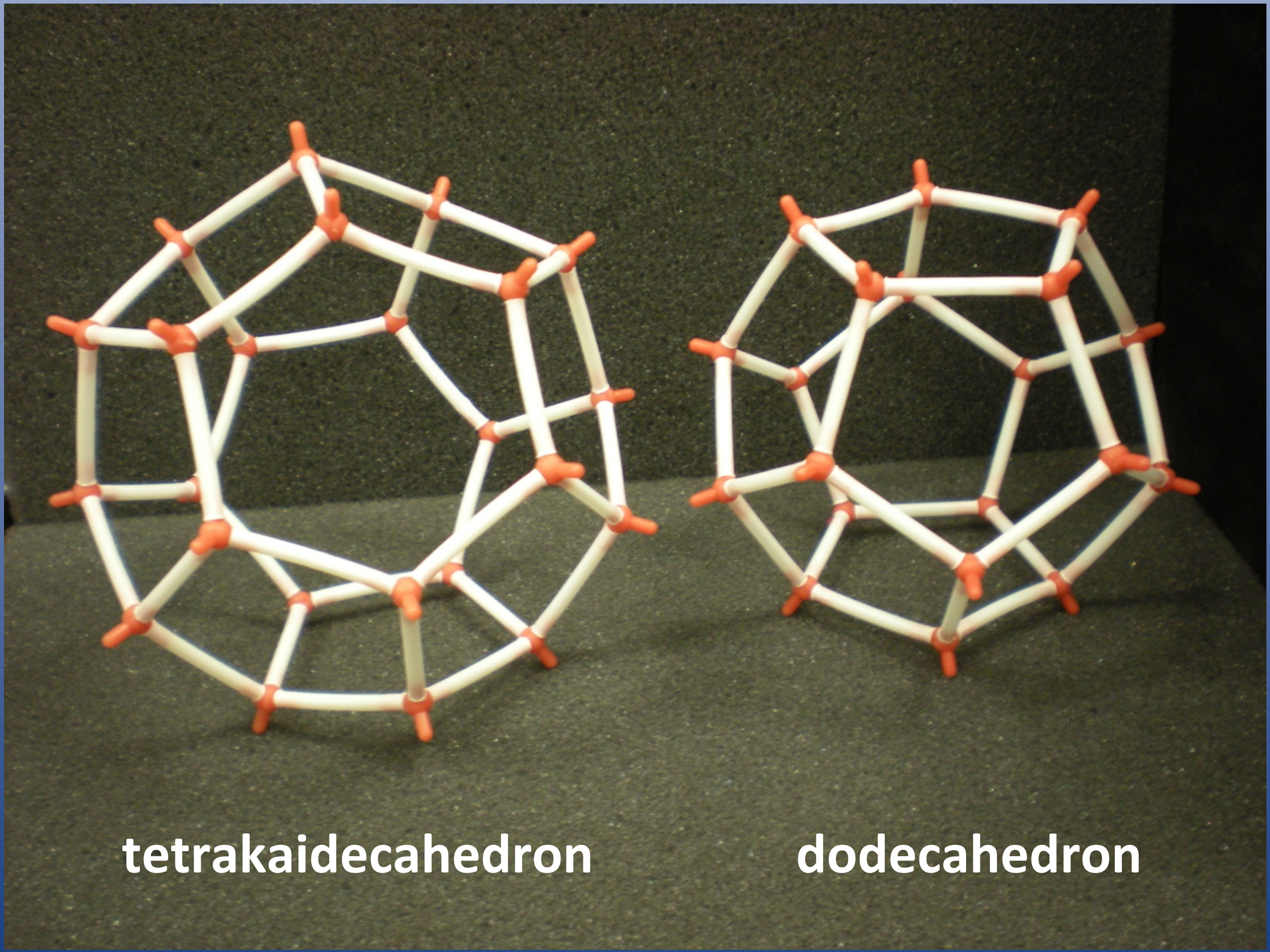
Type I Clathrate Hydrate Structures

- Type I Clathrate Hydrates trap methane gas (CH_4)
- Methane (CH_4) rearranges host molecules (water) to form a cage and remains trapped inside the cage
- Not every cage attracts a gas molecule. Some hosts remain empty. Placement is random and can be in either of the two sized cages however the larger cage is preferred
- When the clathrate hydrate melts, CH_4 is released

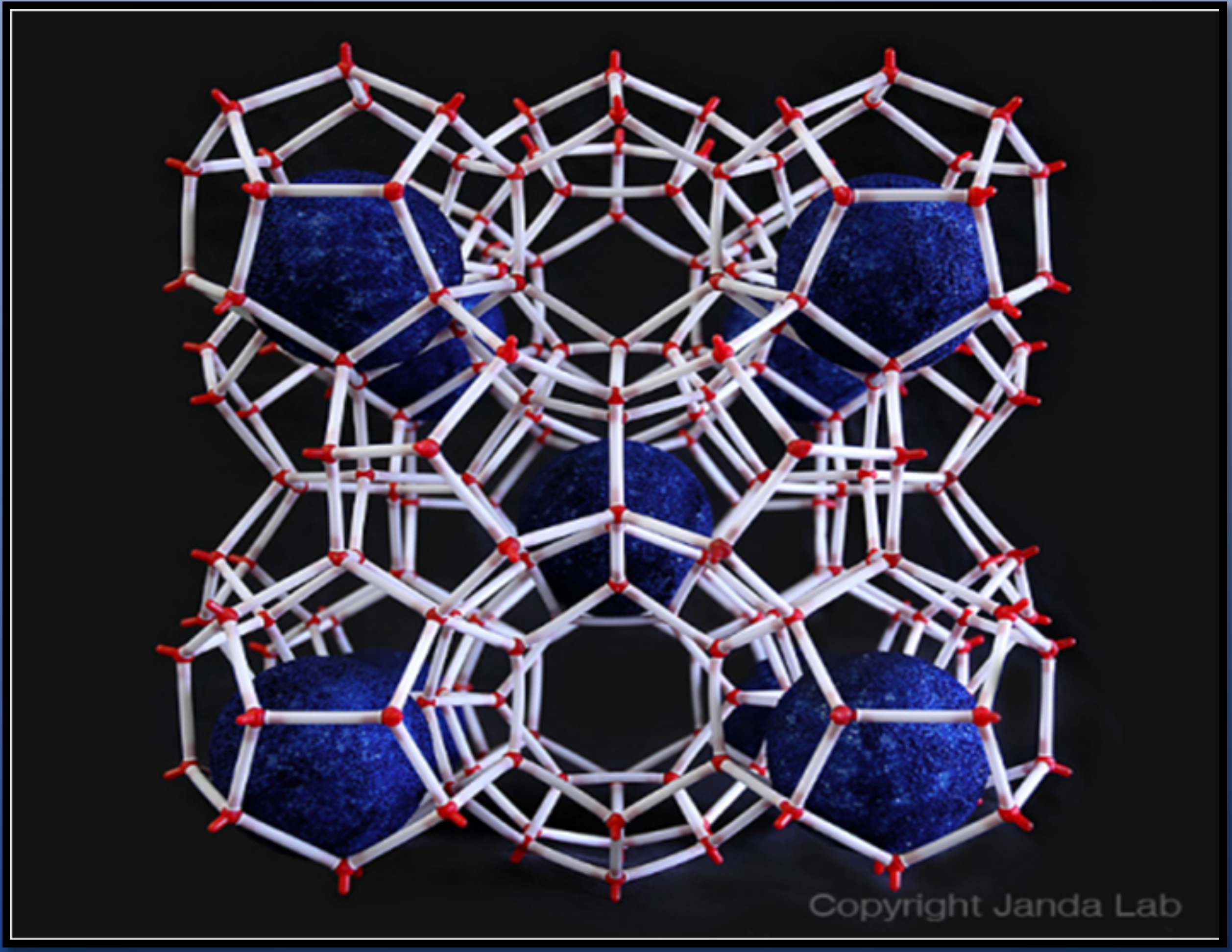
Type I Clathrate Hydrate Structures

- Formed from 2 different shapes of cages
- Small Cages
  - 9 dodecahedrons formed from 12 pentagons (5^{12})
  - Small cages do not touch each other but bond to the larger cages
- Large Cages
  - 12 tetrakaidecahedrons (also called tetradecahedron)
  - Made from 12 pentagons and 2 hexagons ($5^{12}6^{2}$)
  - Small cages join at the large cages to form a cube-like structure

Cages of the Type I Gas Hydrate



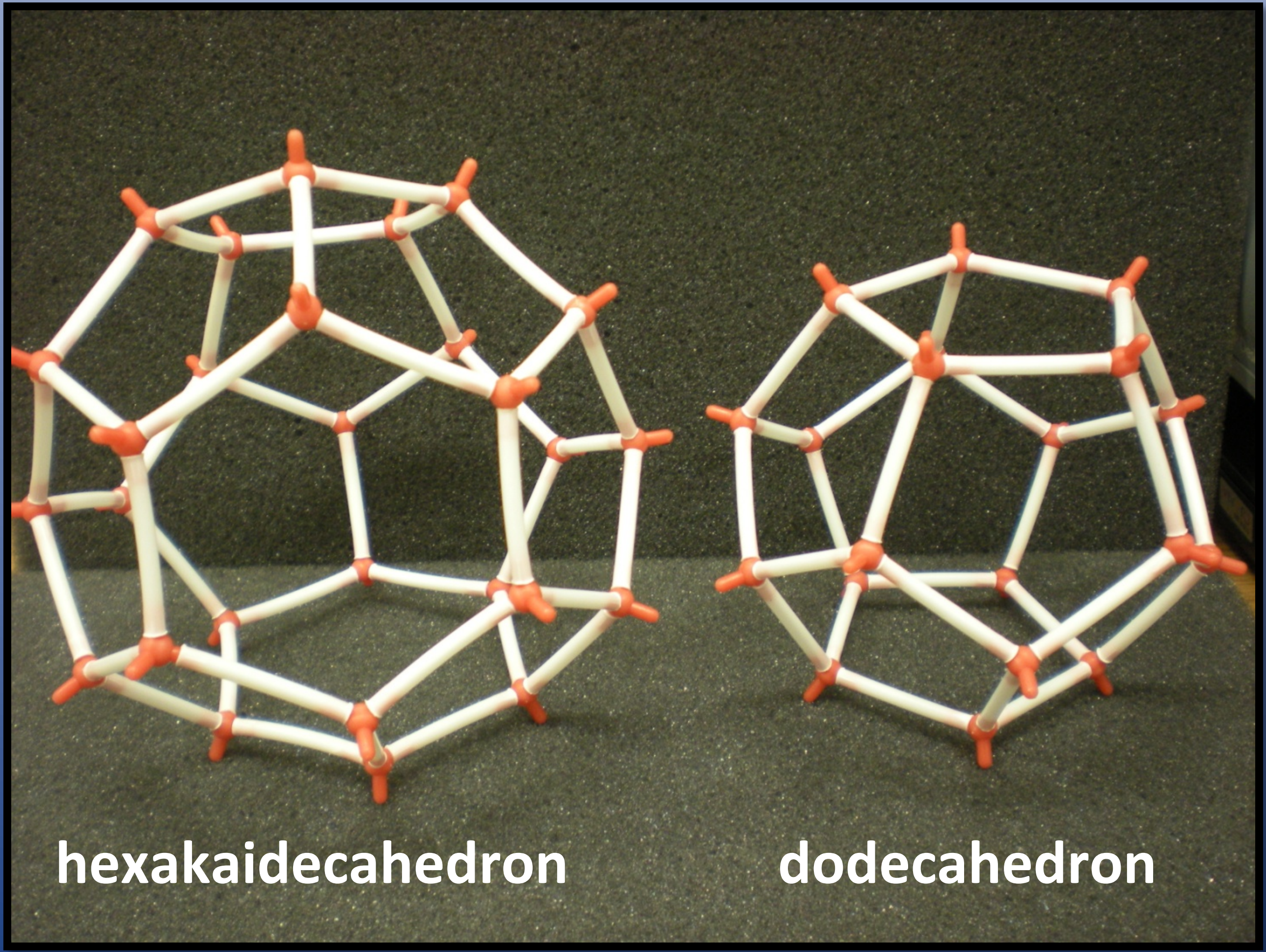
Model of Methane Gas Inside the Type I Clathrate Hydrate



Type II Clathrate Hydrate Structures

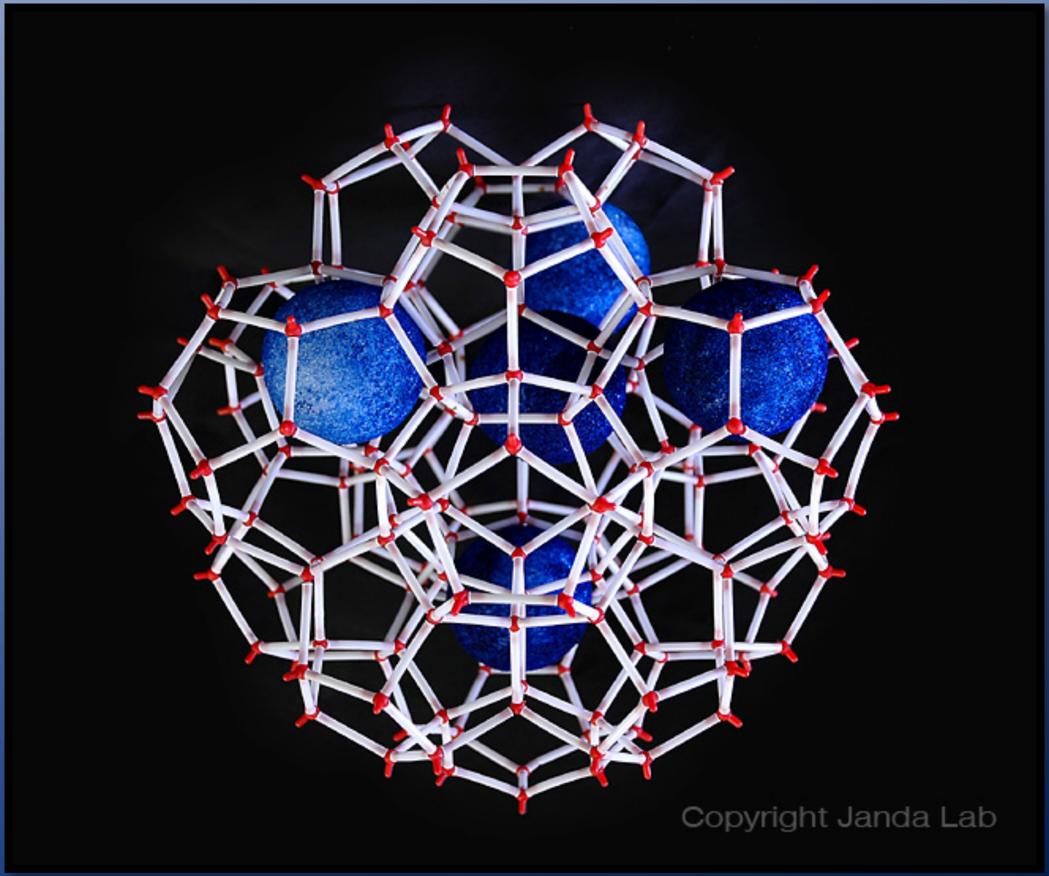
- Formed from 2 different shapes of cages
- Small Cages
  - 16 dodecahedrons formed from 12 pentagons (5^{12})
- Large Cages
  - 8 hexakaidecahedrons (also called hexadecahedron)
  - Made from 12 pentagons and 4 hexagons ($5^{12}6^{4}$)

Cages of the Type II Gas Hydrate



Type II Clathrate Hydrates

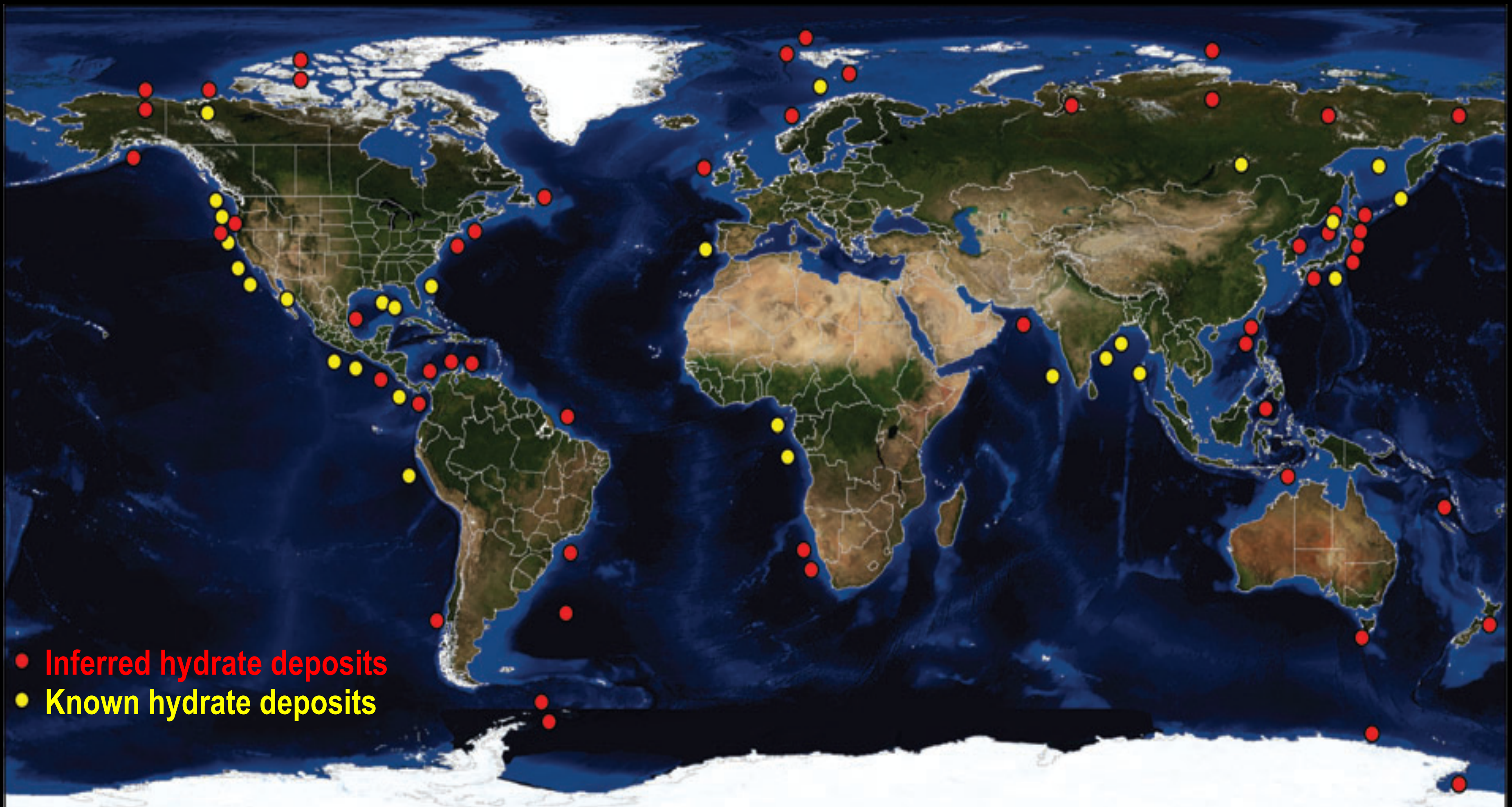
- Trap propane (C_3H_8) gas in their cages
- Can only occupy the larger of the two cages
  - The dodecahedron cages are too small for the larger propane molecule



Clathrate Hydrates in Nature

- Both CH_4 and C_3H_8 gas hydrates exist in the natural world
- Large deposits of methane (CH_4) exist on earth
  - Arctic hydrates are found under the permafrost layer
  - Oceanic hydrates are found along continental margins around the world
- Studies of gas hydrates began in the early 1800's
- In the 1930's it was discovered that CH_4 and water could plug oil and gas pipelines
- Gas hydrates may make up as much as 12x that of conventional fossil fuels including coal, oil, and natural gas combined
- Potential energy resource <u>OR</u> potential geo-hazard

Methane Hydrate Deposits in Nature

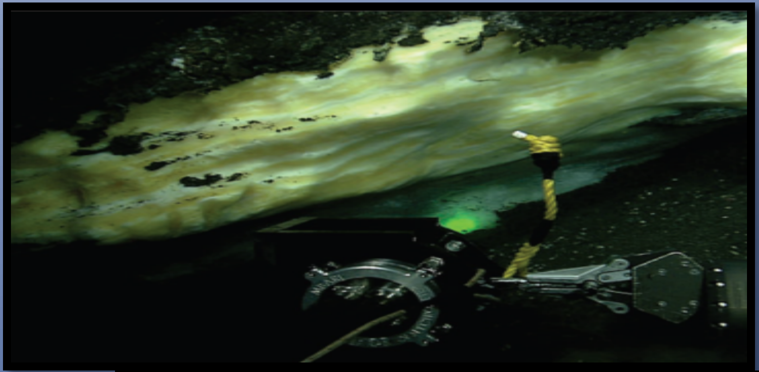


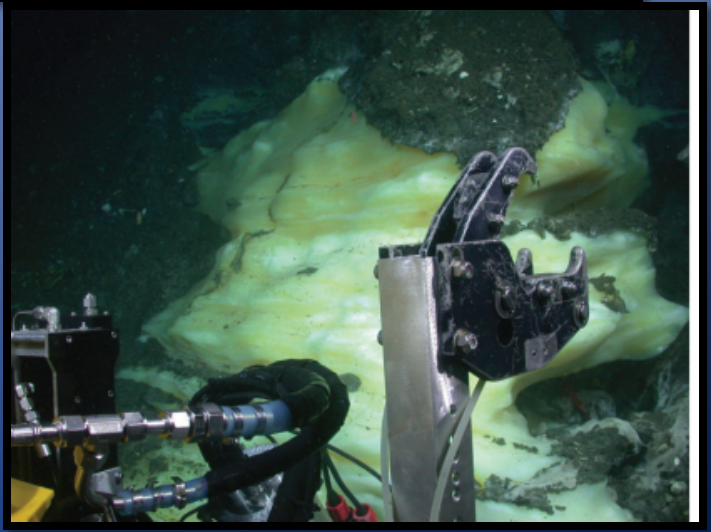
http://arjournals.annualreviews.org/doi/pdf/10.1146/annurev.marine.010908.163824

Methane Hydrates in Nature

Hydrate mound studied at Barkley Canyon, Vancouver Island, Canada at a depth of 850 m

Seafloor Mound Releasing CH_4





** Barkley Canyon deposits contain both Type I & Type II Clathrates

Methane Hydrates in Nature

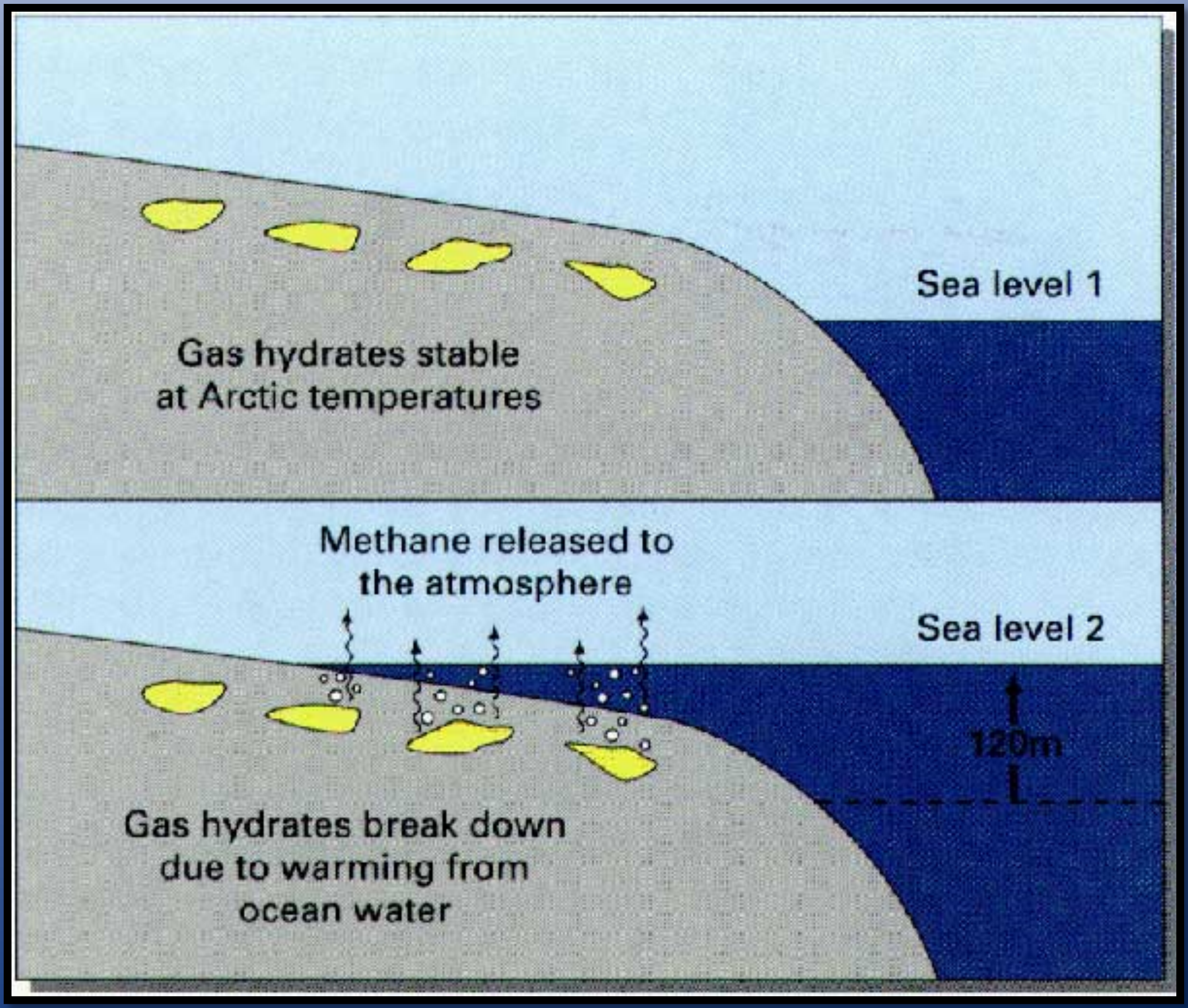
Near-sea floor hydrates recovered.

Gas Hydrates as a Geo-Hazard

- Methane is a 21 times more powerful greenhouse gas than CO_2
- Increase of global temperatures could destabilize natural gas hydrates causing the release of trapped gases from oceans and permafrost into the atmosphere
- Increased greenhouse gases could then cause further increase of global temperatures causing ongoing destabilization of gas hydrates on earth
- Release of gas hydrates presents a significant drilling hazard in the petroleum industry
- Most recent example is the Deep Horizon Oil Rig in the Gulf of Mexico

Methane is a More Powerful Greenhouse Gas Than $C0_2$

Warm ocean water from rising sea levels causes the Arctic ice to rise in temperature and melt. The resulting breakdown of the otherwise stable gas hydrates trapped within the sediment are released into the atmosphere.



URL: http://pubs.usgs.gov/fs/gas-hydrates/figures/fig5.html

Geo-Hazards of Gas Hydrates

Inferring What May Have Caused the Deep Water Horizon Oil Well Disaster

- Fact- Workers on the platform were performing the task of pumping cement around the pipe shaft to seal the space between the pipe and the hole in the ground
- Fact- Although this has been done harmlessly in shallow water, it involves risk when performed at great depths in clathrate hydrate zones
- Fact- The curing process for cement creates heat as it solidifies
- Fact- Heat created during the cement curing process can cause the deep water methane hydrates to heat enough to release gas
- The release of gas quickly moved up the pipeline and into the drilling rig on the surface of the ocean
- Although it is possible that spontaneous combustion from the quickly escaping methane gas ignited, it seems more likely that a spark on the rig ignited the methane and caused the explosion and fire.

Why Study Clathrate Hydrates?

- A better understanding of interactions within the hydrate structure on a molecular level
- Pressure and temperature studies provide information about the mechanisms of a clathrate hydrate
- Understanding effects of global warming on marine methane deposits
  - A major release of natural methane deposits could cause a major climate change in a short amount of time
- Potential global implications of gas hydrates as a future sustainable energy source
- Safety in deep oil drilling operations both for human life and our planet
- Potentially safe, efficient method for storing and transporting gases because almost any molecule that is not too polar can fit into a clathrate water cage

Sources Used

- Clathrate Hydrates in Nature
  - Keith C. Hester and Peter G. Brewer
  - Monterey Bay Aquarium Research Institute, Moss Landing

  http://arjournals.annualreviews.org/doi/pdf/10.1146/annurev.marine.010908.163824

- Clathrate Hydrates
  - Peter Englezos
  - *Department of Chemical Engineering, The ‘niversity of British Columbia, 2216*
  - *Vancouver, British Columbia V6T 124, Canada*

- Mallik2002, short-term production test showing the gas flare from gas produced from hydrate under the permafrost. Reprinted with permission from S. R. Dallimore, T. S. Collett, eds., Scientific Results from the Mallik 2002 Gas Hydrate Production Research Well Program.
  - Copyright © 2005 by Scott Dallimore and Tim Collett.

Sources Used

- http://commons.wikimedia.org/wiki/File:Methane_Clathrate_Location_Map_USGS.gif

- http://www.google.com/imgres?imgurl=http://images.cdn.fotopedia.com/flickr-4068936199-hd.jpg&imgrefurl=http://www.fotopedia.com/items/flickr-4068936199&usg=__UxBKQ6bh-bbGV654P7sJPWAnxYs=&h=645&w=840&sz=91&hl=en&start=0&sig2=8LwtdnWR7zBCgyvit0w1qg&tbnid=ZKomw0OdBIUEcM:&tbnh=138&tbnw=180&ei=r1dkTNzCJtHinQfWlpCYDQ&prev=/images%3Fq%3Dmethane%2Bclathrate%26hl%3Den%26as_st%3Dy%26biw%3D1280%26bih%3D606%26tbs%3Disch:1,iur:f&itbs=1&iact=hc&vpx=517&vpy=112&dur=31&hovh=197&hovw=256&tx=154&ty=82&oei=r1dkTNzCJtHinQfWlpCYDQ&esq=1&page=1&ndsp=5&ved=1t:429,r:2,s:0

- http://articles.latimes.com/2010/may/12/nation/la-na-oil-spill-cause-20100512
- May 12, 2010|By Jill Leovy, Los Angeles Times

- http://blog.accelrys.com/2010/05/undersea-hydrates/
- May 17, 2010 by George Fitzgerald, PhD

- http://dana.ucc.nau.edu/~mlz8/Hydrates/greenhouse.html

Sources Used

- http://seminal.firedoglake.com/diary/44349
- http://www.aade.org/houston/study/Fluids/11182009/F%20Tahmourpour%20Deepwater%20Cementing.pdf
- http://pubs.usgs.gov/fs/gas-hydrates/figures/fig5.html
- http://chem.ps.uci.edu/~kcjanda/Group/index.html
- http://chem.ps.uci.edu/~kcjanda/Group/Makogon.html
- http://commons.wikimedia.org/wiki/File:Burning_hydrate_inlay_US_Office_Naval_Research.jpg
- http://www.chem1.com/acad/sci/aboutwater.html
- http://news.mongabay.com/2005/0906-gas_hydrates.html
- http://www.visionlearning.com/library/flash_viewer.php?oid=1381&mid=57#
- http://en.academic.ru/dic.nsf/enwiki/7039581