Gas Hydrates and Microbiological Processes*

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Abstract

Gas hydrates are an energy resource composed of natural gas in a solid state, in which water molecules, in a relatively stable composition, surround the gas molecules. One volume of gas hydrates is equivalent to approximately 164 volumes of methane. Gas hydrates may represent more than double the energy content of all other hydrocarbon resources. Gas hydrates are found in equilibrium under conditions of high pressures and low temperatures; they occur in arctic regions (permafrost) and on the continental shelf - in marine surface and subsurface deposits, above seismically observable bottom-simulating reflectors (BSR). The importance of gas hydrates is related to their potential for exploration and production as a source of natural gas; to the known problems they cause in drilling and production systems; to their climate-change effects - negative (GHG) and positive (CO_2 sequestration); to the clathrate gun hypothesis effect; and to their potential as a logistics solution for natural gas transportation. Various microbiological investigations of gas hydrates suggest the potential of biological applications for producing hydrates through destabilization. Among these are processes involving microbial conversion of CO_2, biological in-situ methane production, and organisms that produce antifreeze proteins (AFPs), which inhibit the crystallization of hydrates and eliminate more rapid recrystallization or "memory effect". These concepts require more research to explore techniques to uncover "green inhibitors" for hydrates. This represents a challenge to researchers involved in projects related to monetization of the very significant gas hydrate accumulations worldwide: microbiological processes may be the key to their economical recovery.

Introduction

Natural gas reserves are more widely distributed worldwide than oil reserves, and natural gas reserve to production (r/p) indicators are generally higher than for oil. Favorable technical, environmental, and strategic issues favor the growth of natural gas consumption among major world economies (Figure 1). Projected world demand for natural gas is sufficiently high that new unconventional sources must meet most of that demand, in the next few decades (Figure 2).

The energy content of natural gas contained in gas hydrate accumulations is also estimated to be much greater than that of all other hydrocarbon accumulations, plus other naturally occurring carbon fuels (Figure 3). Various studies suggest that total world hydrate accumulations range from 10^{15} to 10^{16} m^3 (Santos Neto, 2004), to 5 x 10^{15} m^3 (Buffett and Archer, 2004). In Brazil such accumulations could be 22 x 10^{12} m^3 just in the Amazonas Delta (Sad, 1998), and 13 x 10^{12} m^3 in the Pelotas Basin. In the USA, accumulations could be 10 x 10^{15} m^3 (Collett, 1995), and in Canada, 1 x 10^{15} m^3. The distribution of considerable gas hydrate resources is rather closely aligned with regions of high consumption (Figure 4).

The future of gas hydrates would thus seem to include the likelihood of increasing participation of gas hydrates in the world natural gas supply. It is also expected that future demand for natural gas will spur efficient technologies to recover gas hydrates, and new technological frontiers will include ever more innovative production methods for gas hydrate recovery.

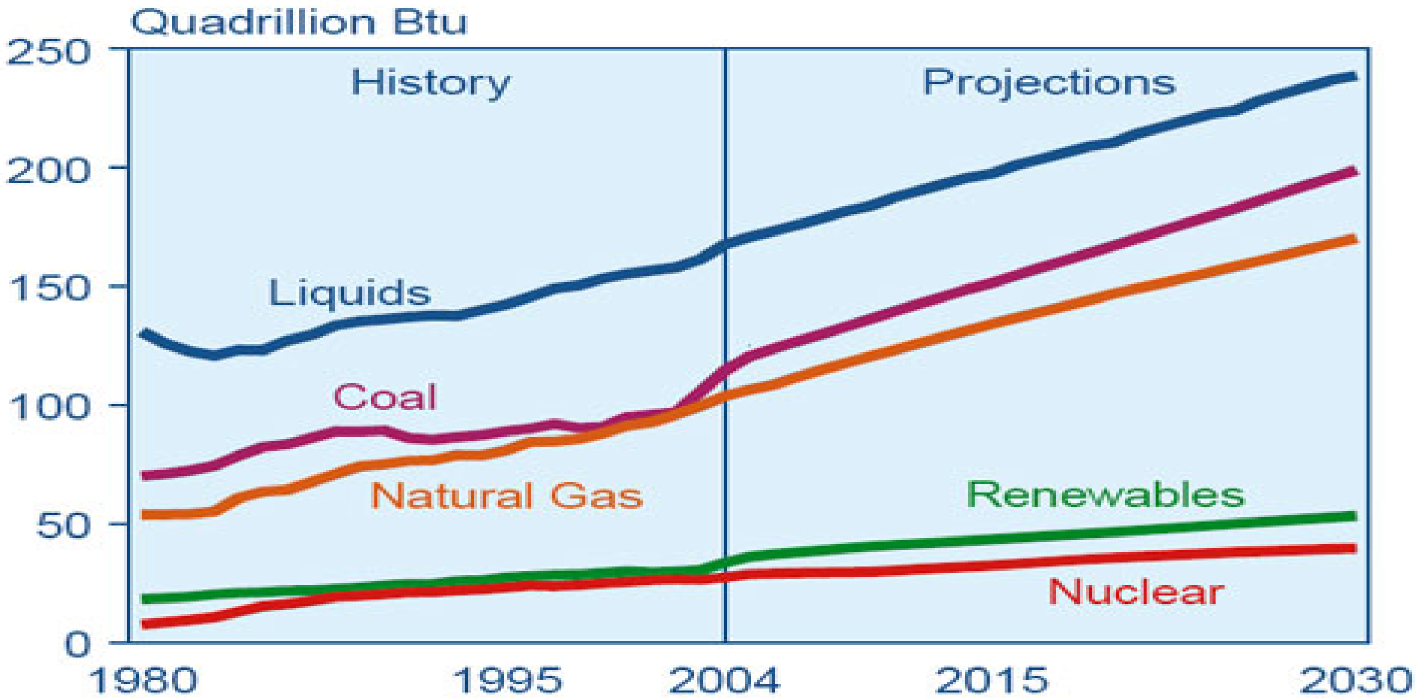

Figure 1. Projected world demand for natural gas (US DOE-EIA, 2008).

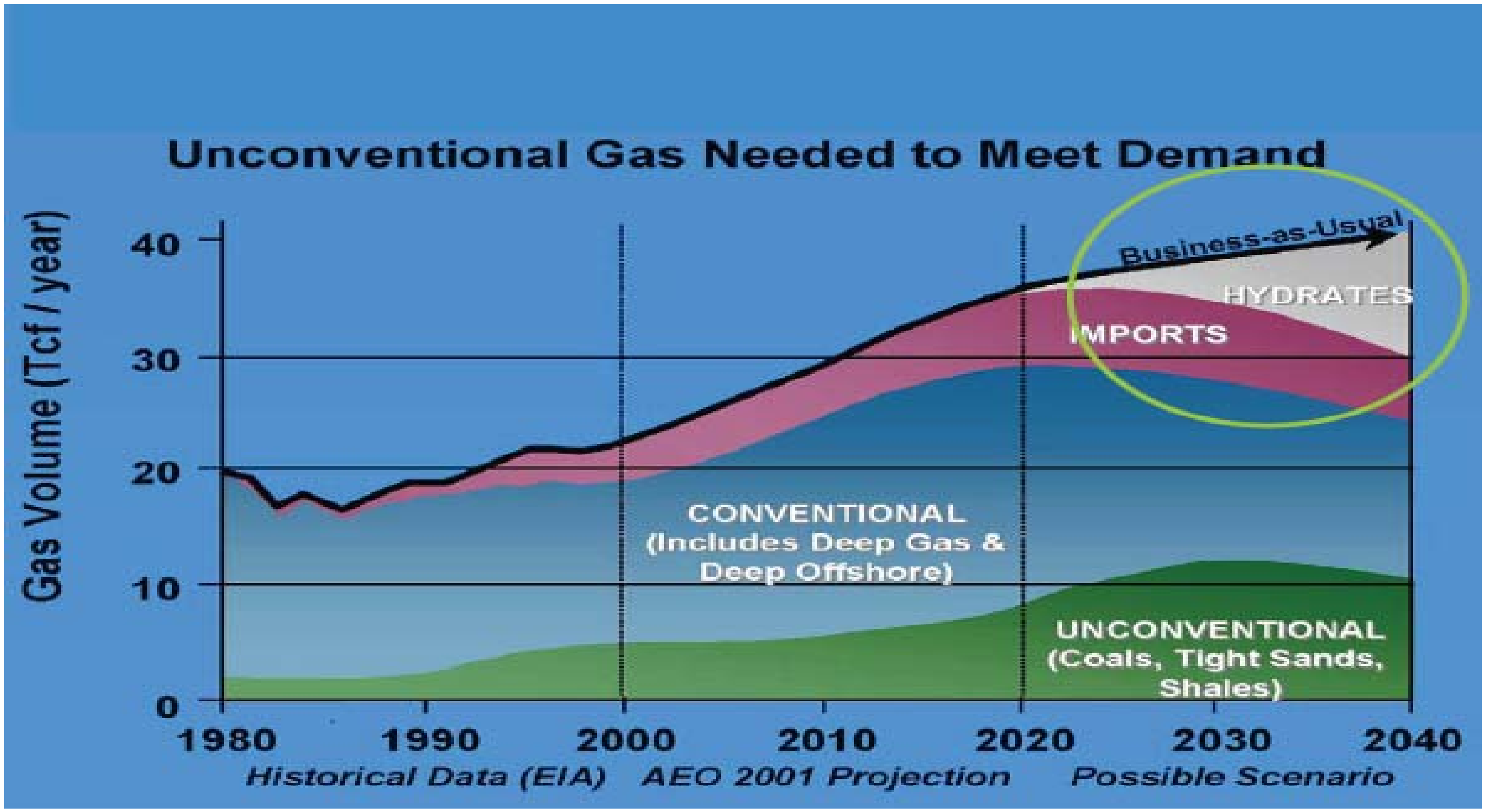

Figure 2. Unconventional gas needed to meet demand for natural gas of major consuming countries (US DOE-EIA, 2008).

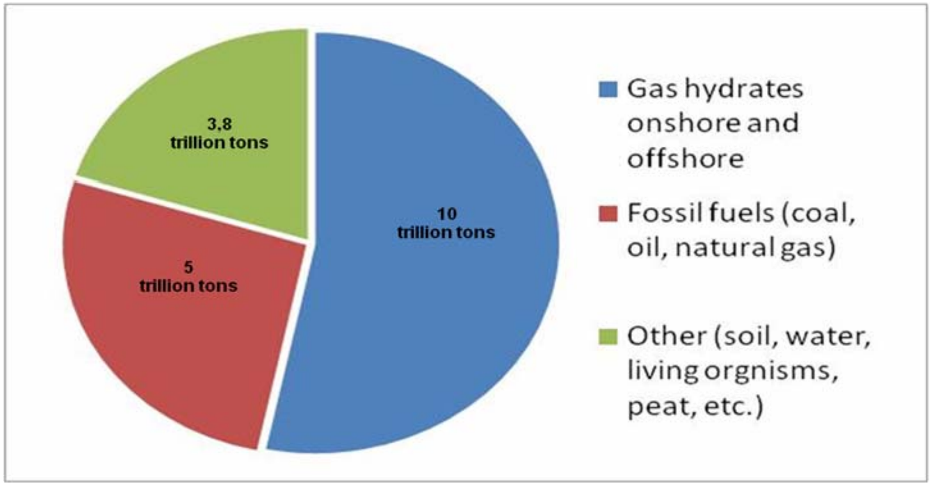

Figure 3. Gas hydrate availability in relation to world carbon fuels (adapted from R. Fisk, T. Collett, and J. Clough).

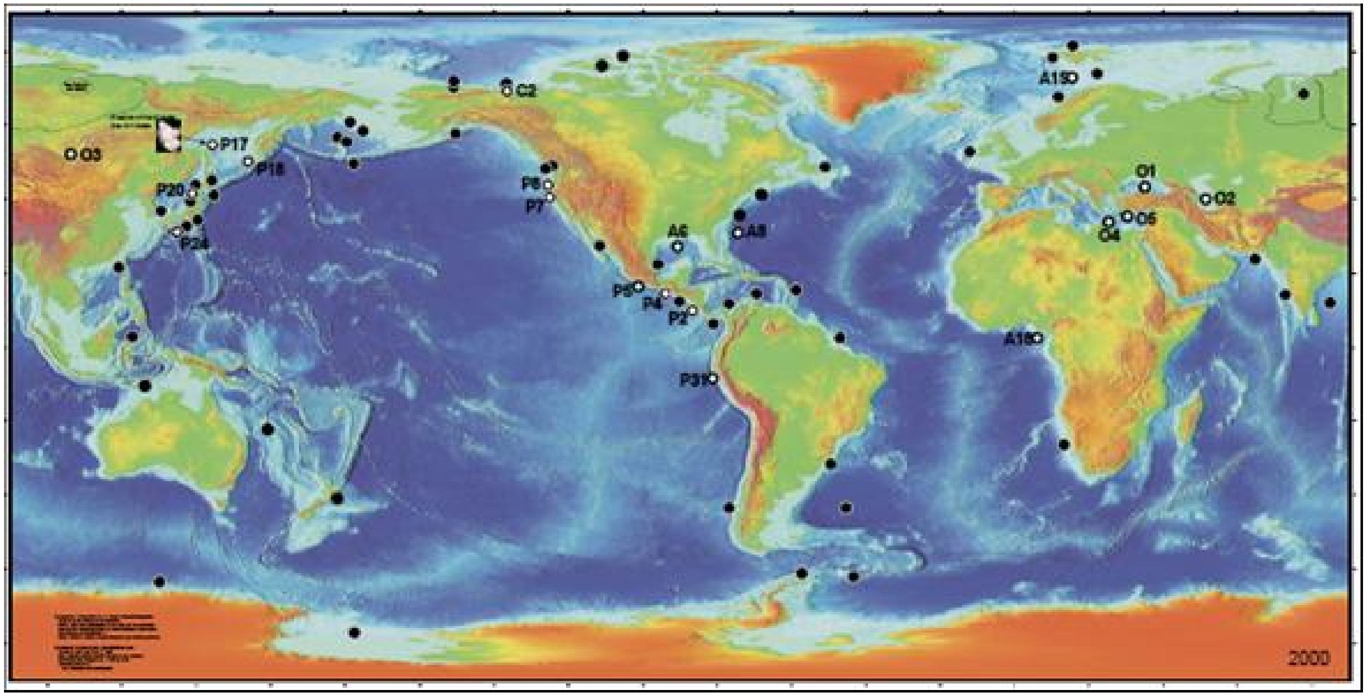

Figure 4. Estimated world gas hydrate distribution (USGS).

Structure, Formation, and Importance of Gas Hydrates

Gas hydrates (clathrates) are a crystalline solid consisting of gas molecules, usually (but not always) methane, each surrounded by a cage of water molecules, in a relatively stable and compact composition (Figures 5, 6, and 7). One volume of gas hydrates is equivalent to approximately 164 volumes of methane.

Gas hydrates are found in equilibrium under conditions of high pressures and low temperatures (Figure 8). Gas hydrates occur in arctic regions (permafrost) and on the continental shelf – in marine surface and subsurface deposits, above BSRs (Figures 9, 10, 11, and 12).

Hydrates are formed when bacteria produce methane at shallow depths (<1000m) or when organic material is decomposed to methane in deep zones, with temperatures 80-100°C (Figures 13, 14, and 15). The main biogenic gas is methane (>99% C1, $\delta^{13}C$ between -80‰ and -100‰), while thermogenic gases ($\delta^{13}C$ between -30‰ and -40‰) have a mixture of hydrocarbons (C2-C5). Biogenic methane is produced in hydrate stability zones, while thermogenic gases migrate from deep source rocks (Clennell, 2000) (Figures 14 and 16).

Methanogenic bacteria in sediments can reduce CO_2 or acetate, from other biological activity, to methane. However, for this to happen, there must be no reducing compounds, such as sulfates, which are present in seawater. Thus, methanogenesis starts at the base of the zone of sulfate reduction, some meters below sea bottom (Figure 15). Organic matter must be between 0.5% and 1.0%, in order for significant hydrate production to occur (Clennell, 2000). An example of a section of gas hydrates on a well log is shown in Figure 17.

During crystallization of hydrates, all salts are excluded from the formation water incorporated into the hydrate structure. Thus, the mineral will consist only of water and methane. After crystallization, the excluded salts outside the clathrates are removed by diffusion and advection. When samples are brought to the surface, the crystals melt and low-salinity water is observed, as pure water mixes with remaining pore water (Clennell, 2000).

Gas hydrates are of great importance for several reasons:

- potential for exploration and production of gas reserves
- prevention of hydrate formation in production facilities
- geohazards in drilling
- climate change effects – negative (GHG) and positive (CO_2 sequestration)
- disaster concerns - clathrate gun hypothesis effect
- potential for conversion of produced gas into hydrate, as a logistics solution (pellets, slurry, etc.)

The clathrate gun hypothesis considers some hydrate accumulations as a cocked gun, waiting to be fired by several possible mechanisms, which could bring about disastrous consequences (Figure 18). Some effects due to human activities are shown in Figure 19.

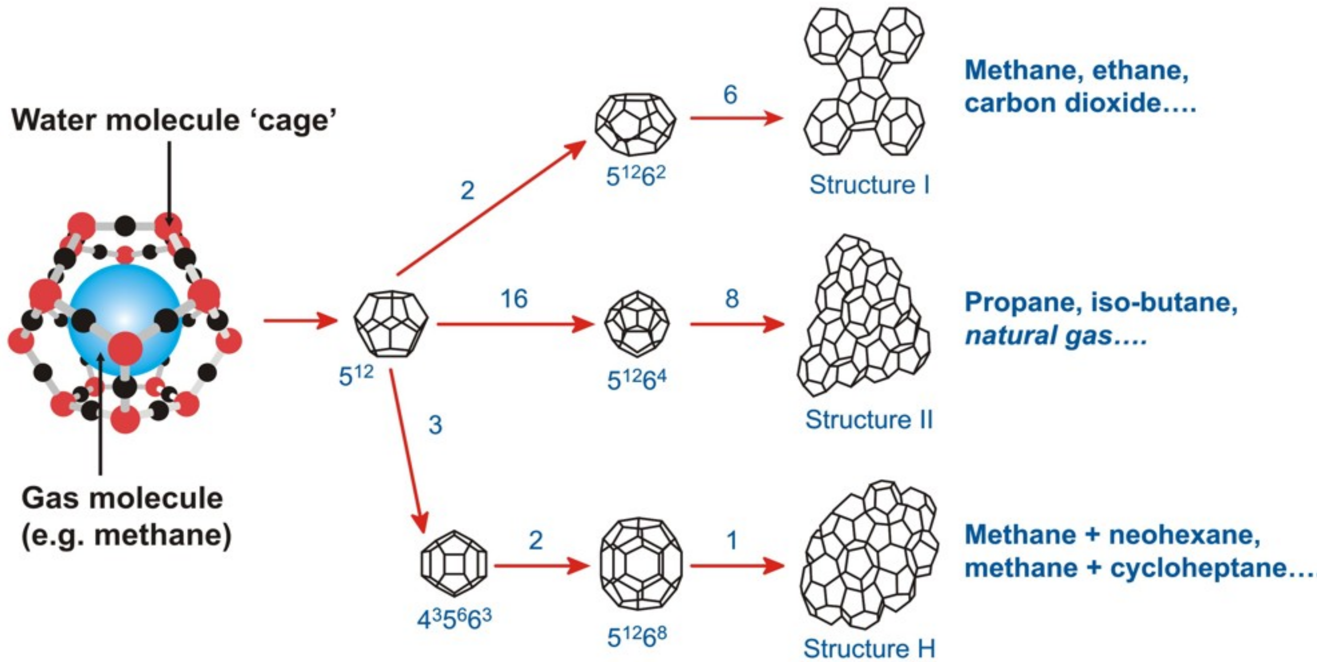

Figure 5. Various gas hydrate types (Herriot-Watt University. Edinburgh, UK).

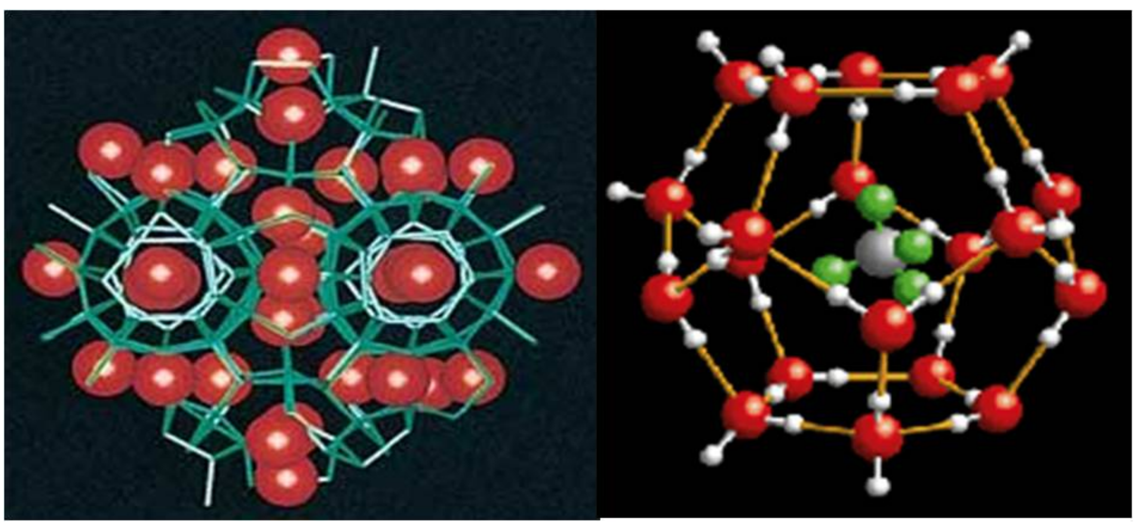

Figure 6. Examples of gas hydrate structure (Schlumberger).

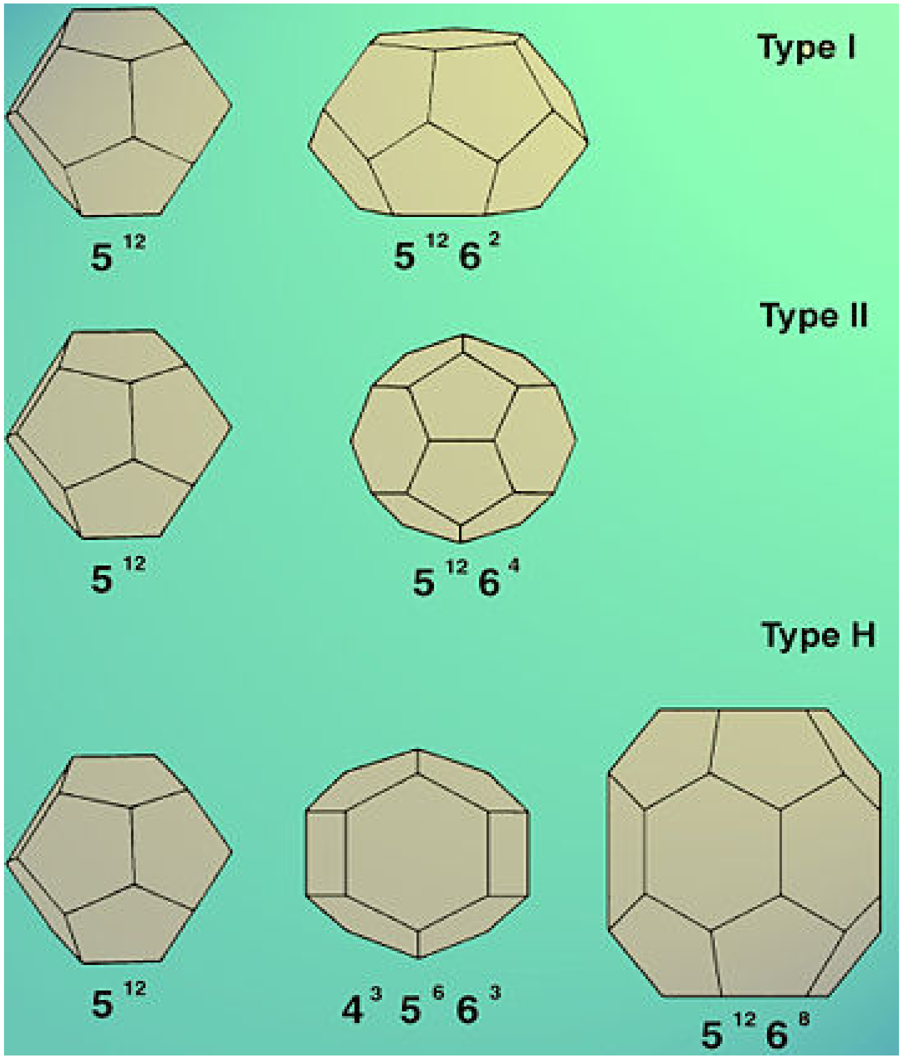

Figure 7. Other examples of gas hydrate structures (University of California, Riverside).

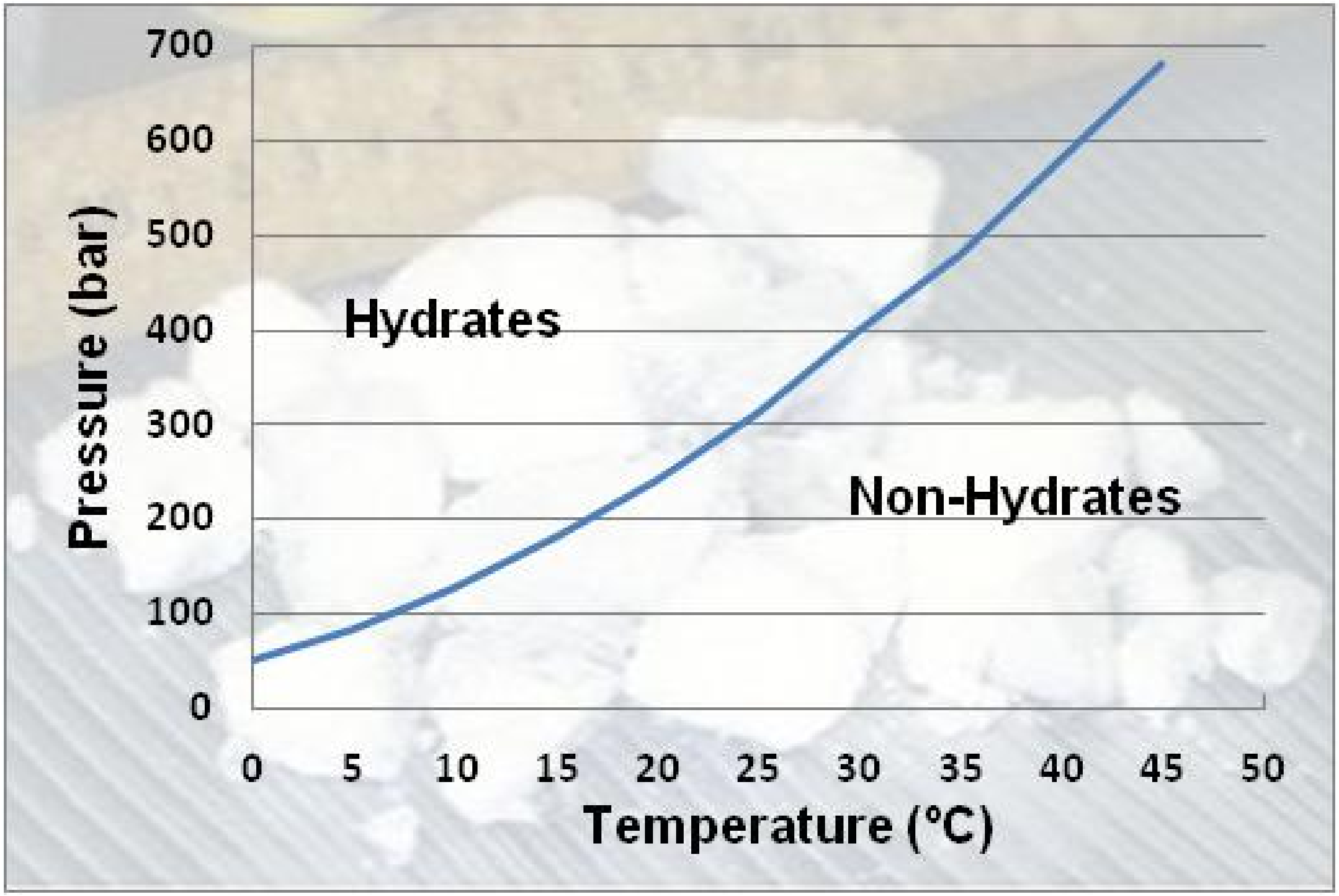

Figure 8. Theoretical stability of gas hydrates (adapted from D.L. Queiroz and K.G. Osadetz).

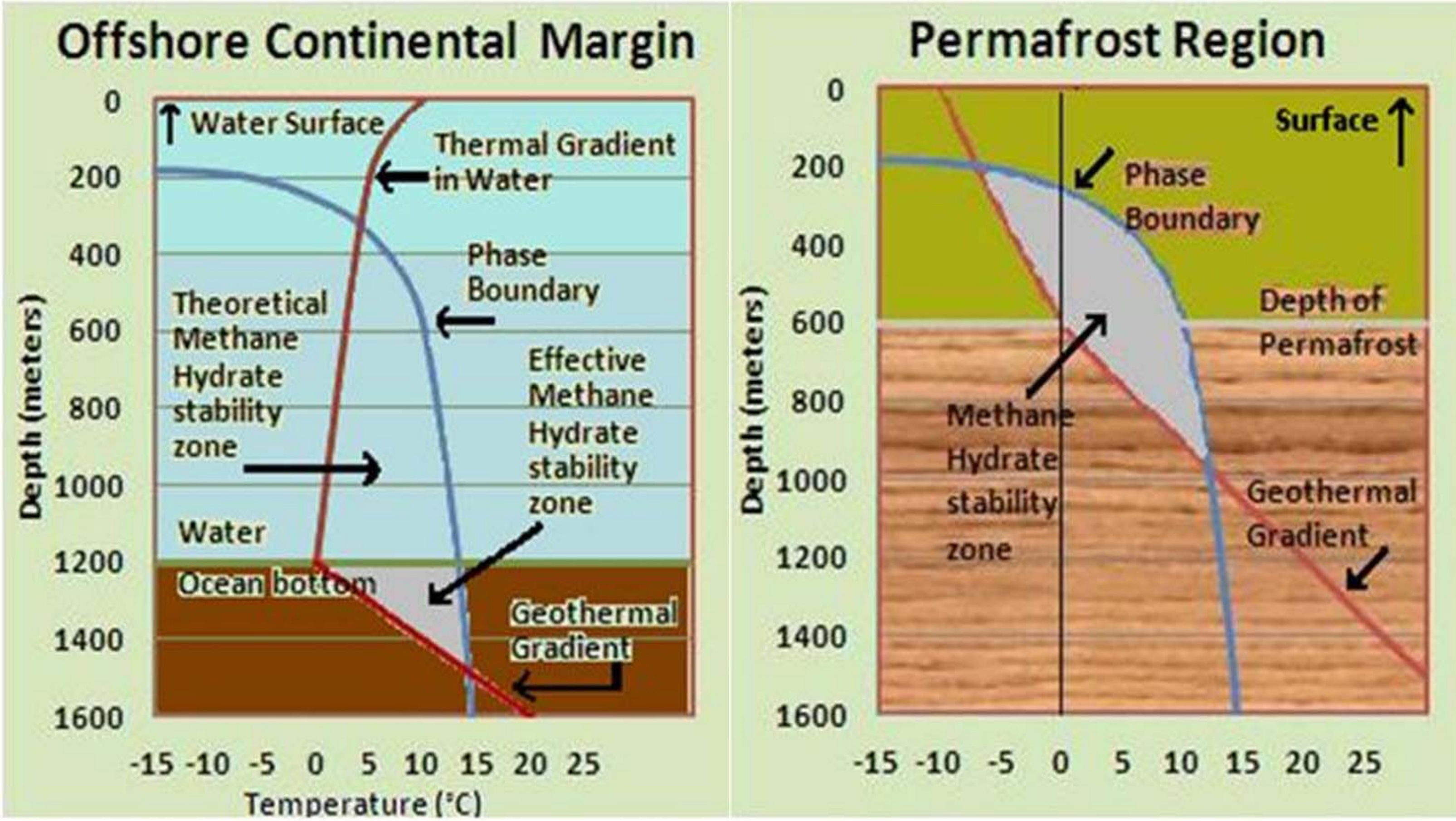

Figure 9. Gas hydrates – in-place stability (adapted from K.G. Osadetz).

Figure 10. Gas hydrate samples.

Figure 11. Gas hydrates on sea-bottom sediments (MIT).

Figure 12. Gas hydrates with associated fauna (source: National Oceanic and Atmospheric Administration, USA).

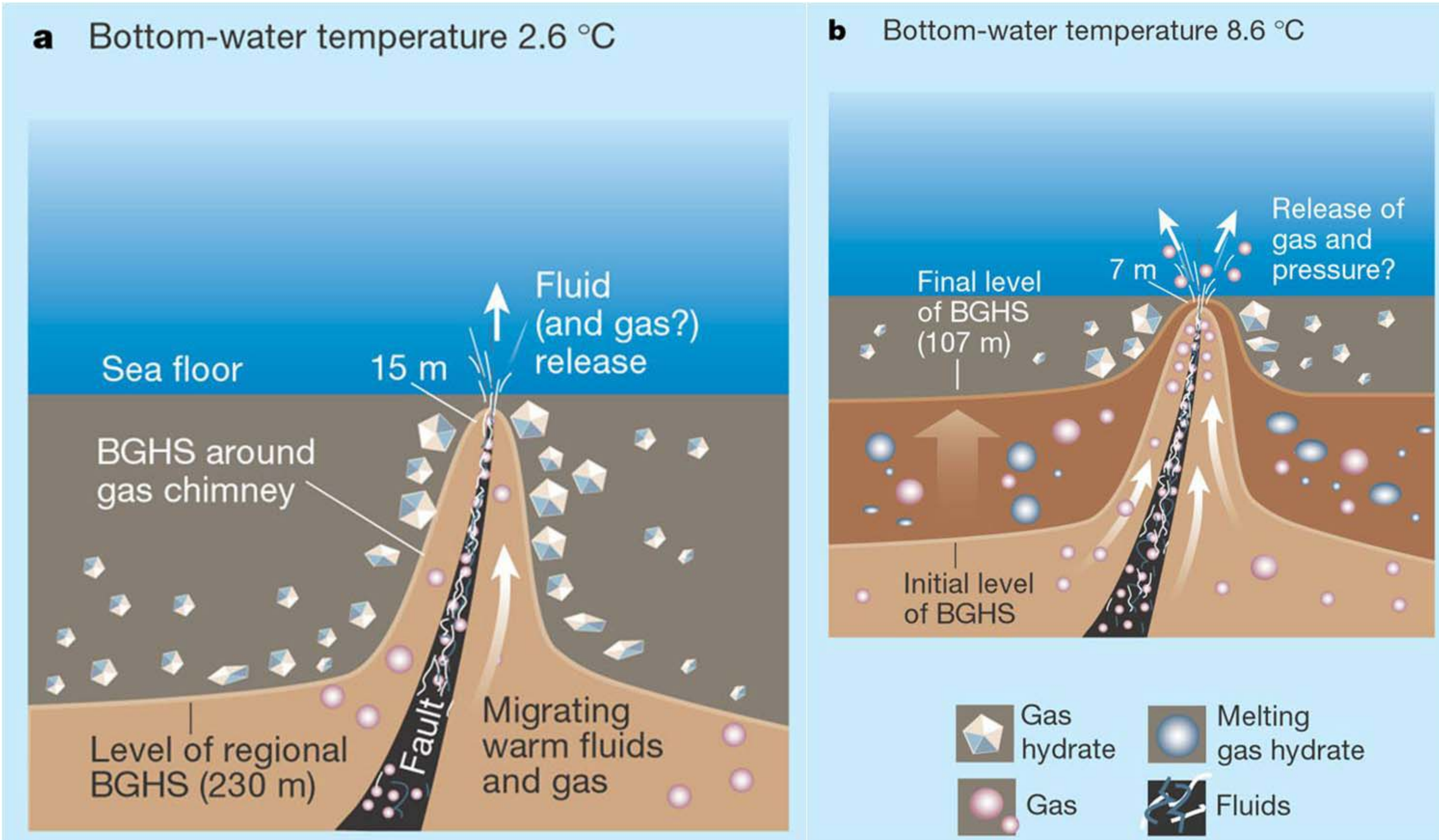

Figure 13. Hydrate formation (source: I.A. Pecher, 2002).

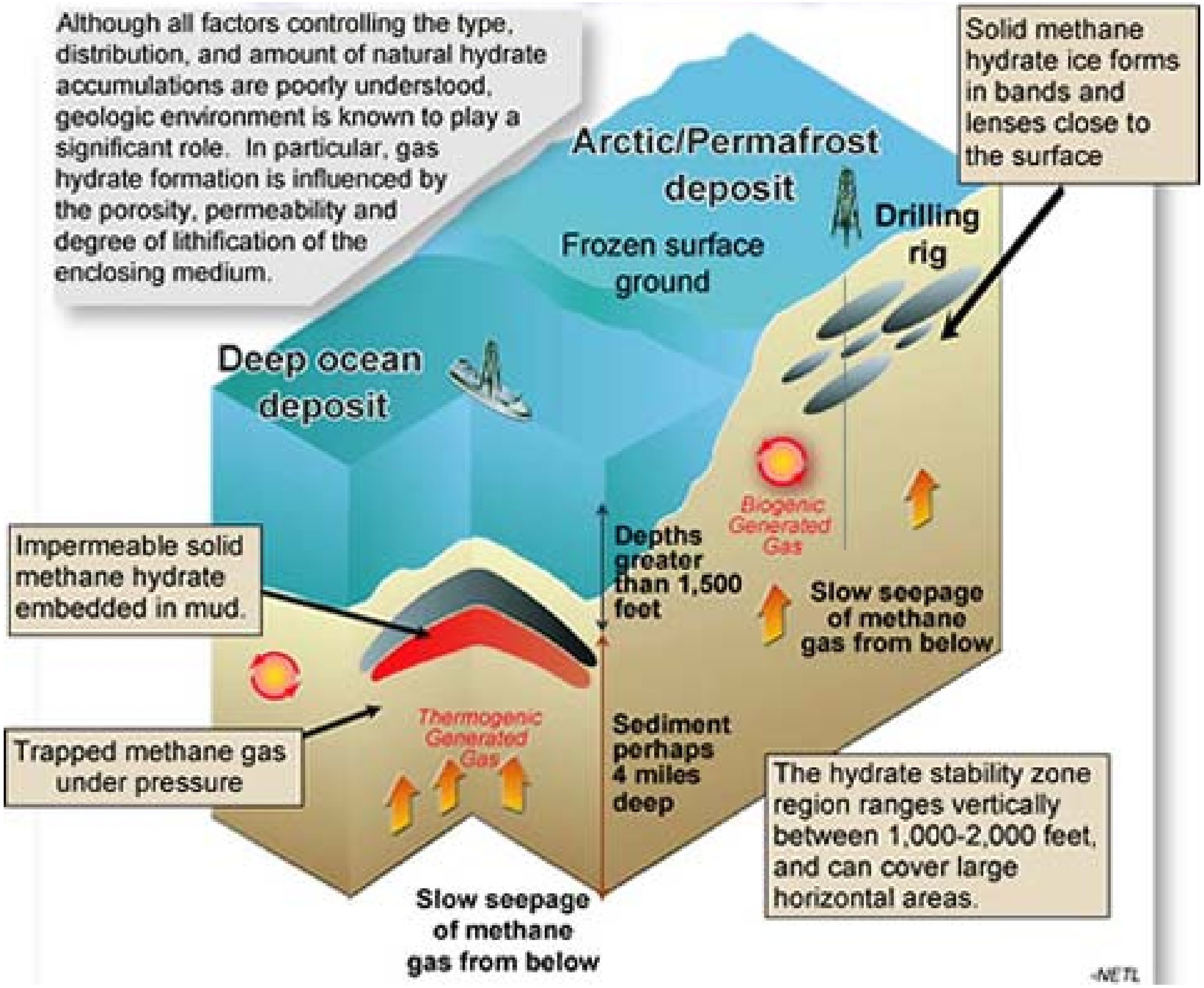

Figure 14. Gas hydrate formation (source: USDOE – NETL).

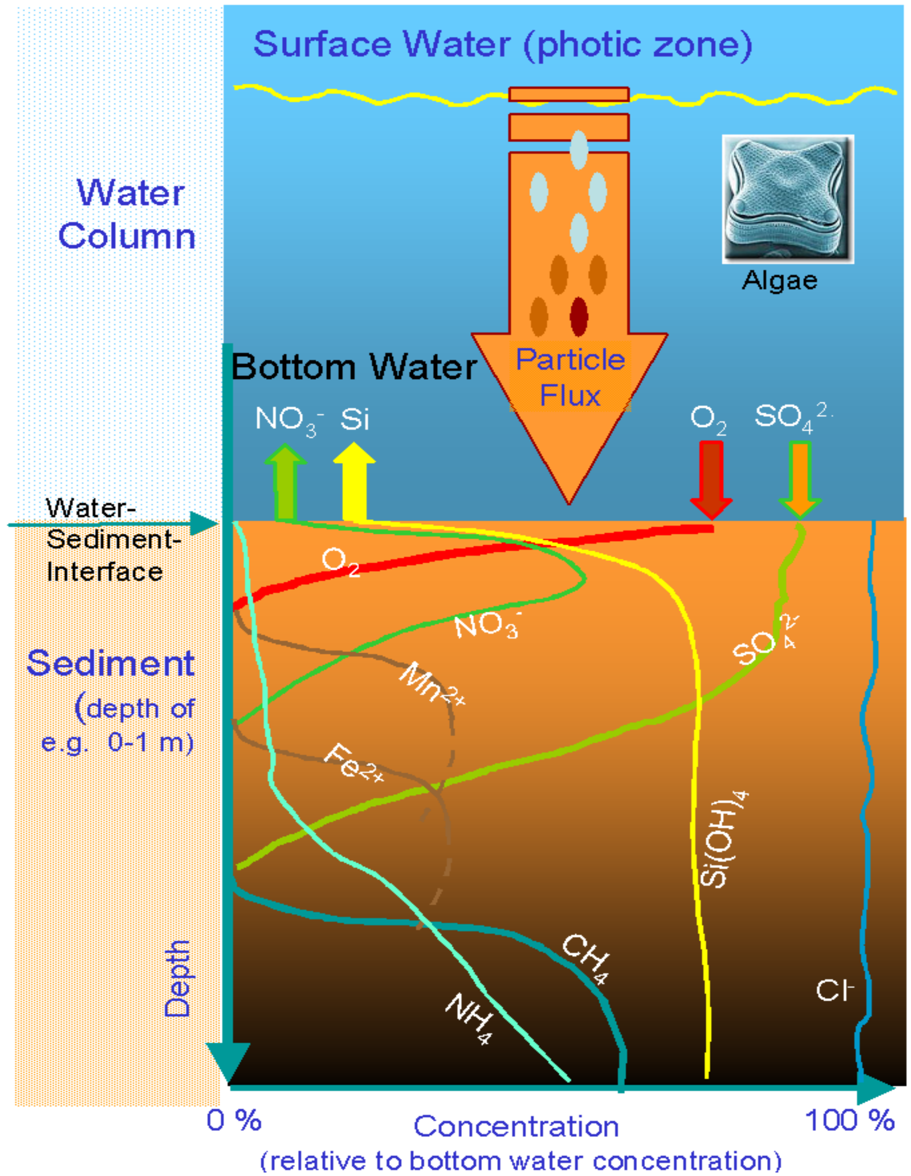

Figure 15. Gas hydrate chemical conditions (source: Alfred-Wegener Institute for Polar and Marine Research, Germany).

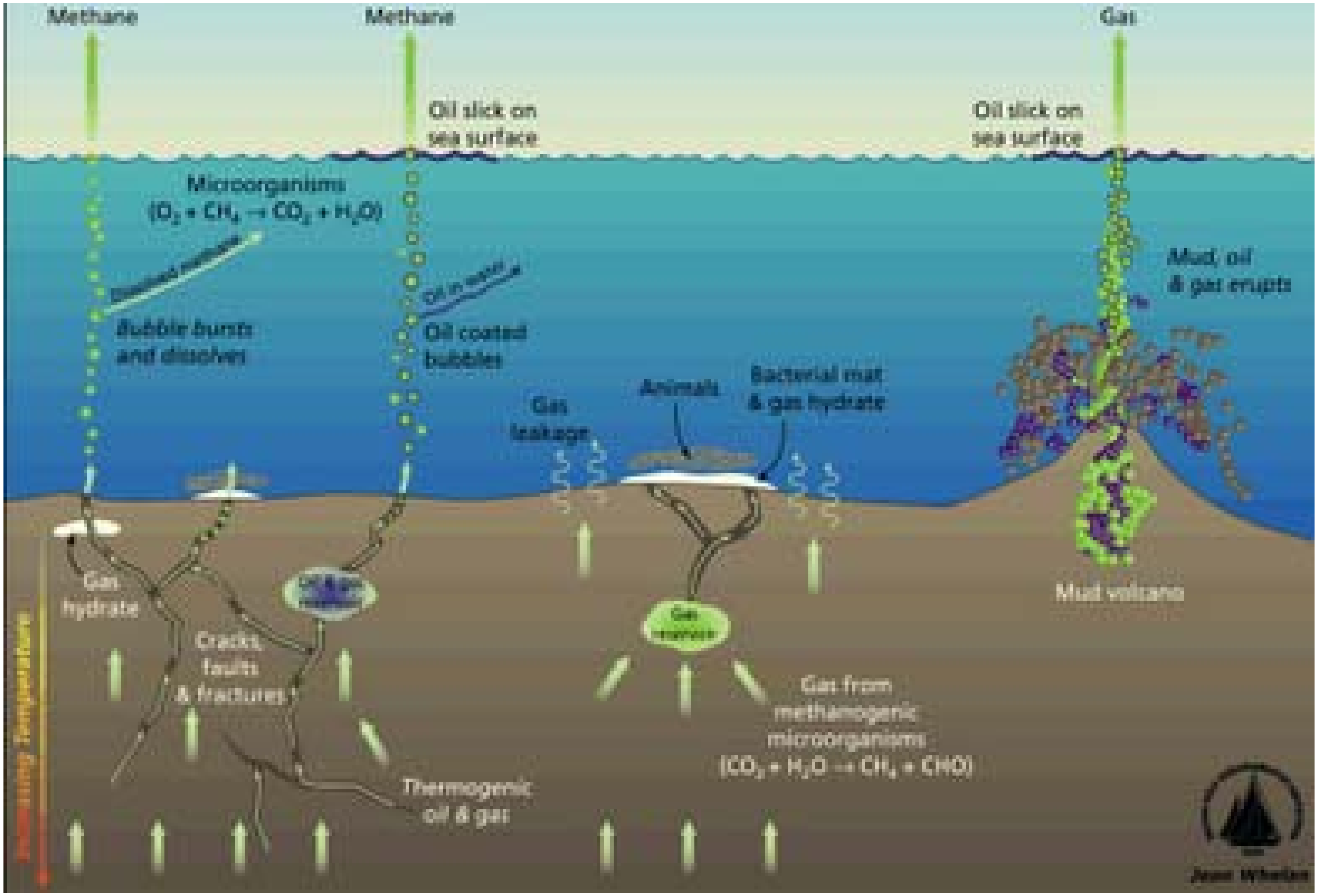

Figure 16. Gas hydrate release (source: J. Whelan, Woods Hole Oceanographic Institute).

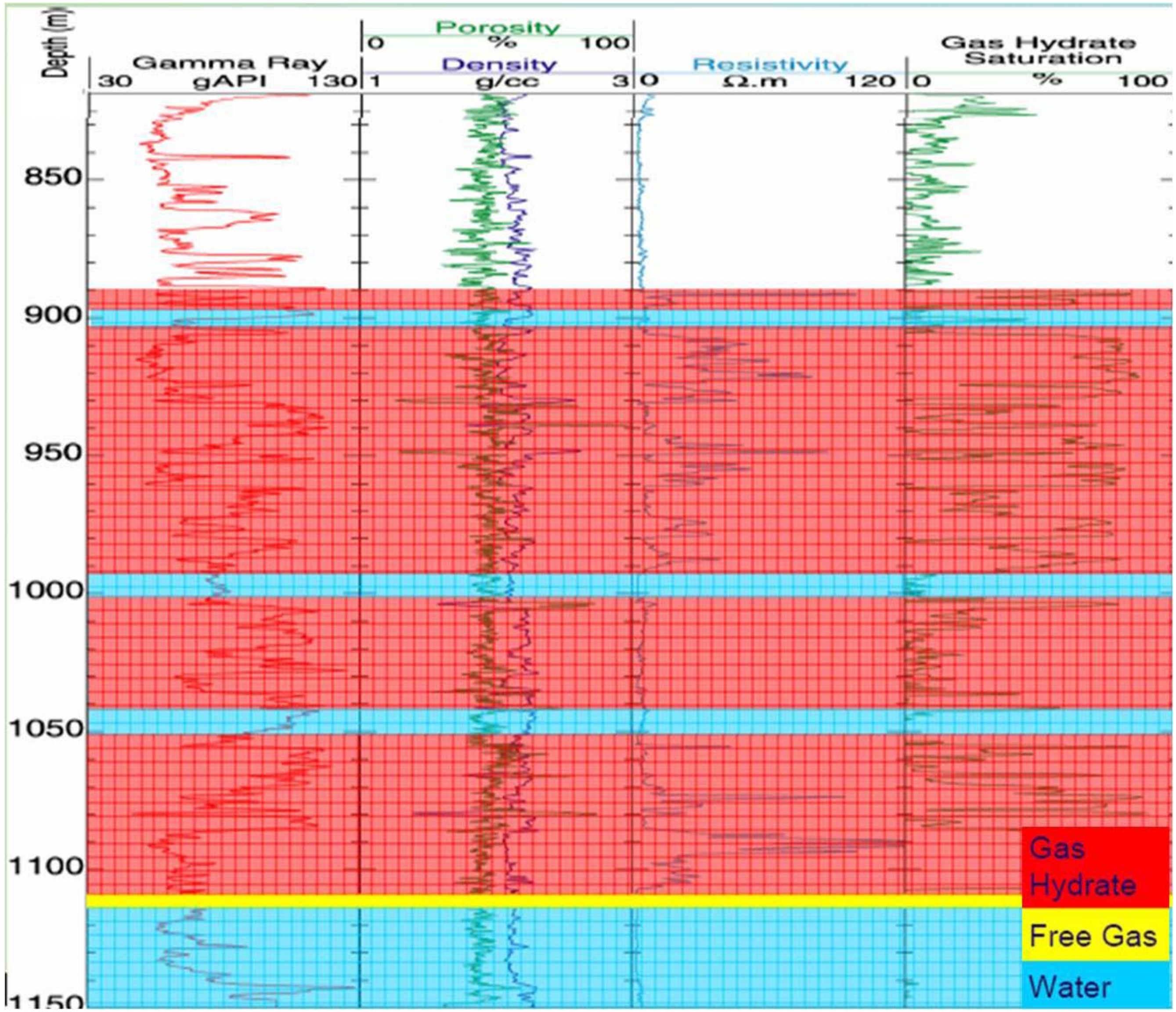

Figure 17. Gas hydrates example at Mallik site (source: K. Osadetz, 2006).

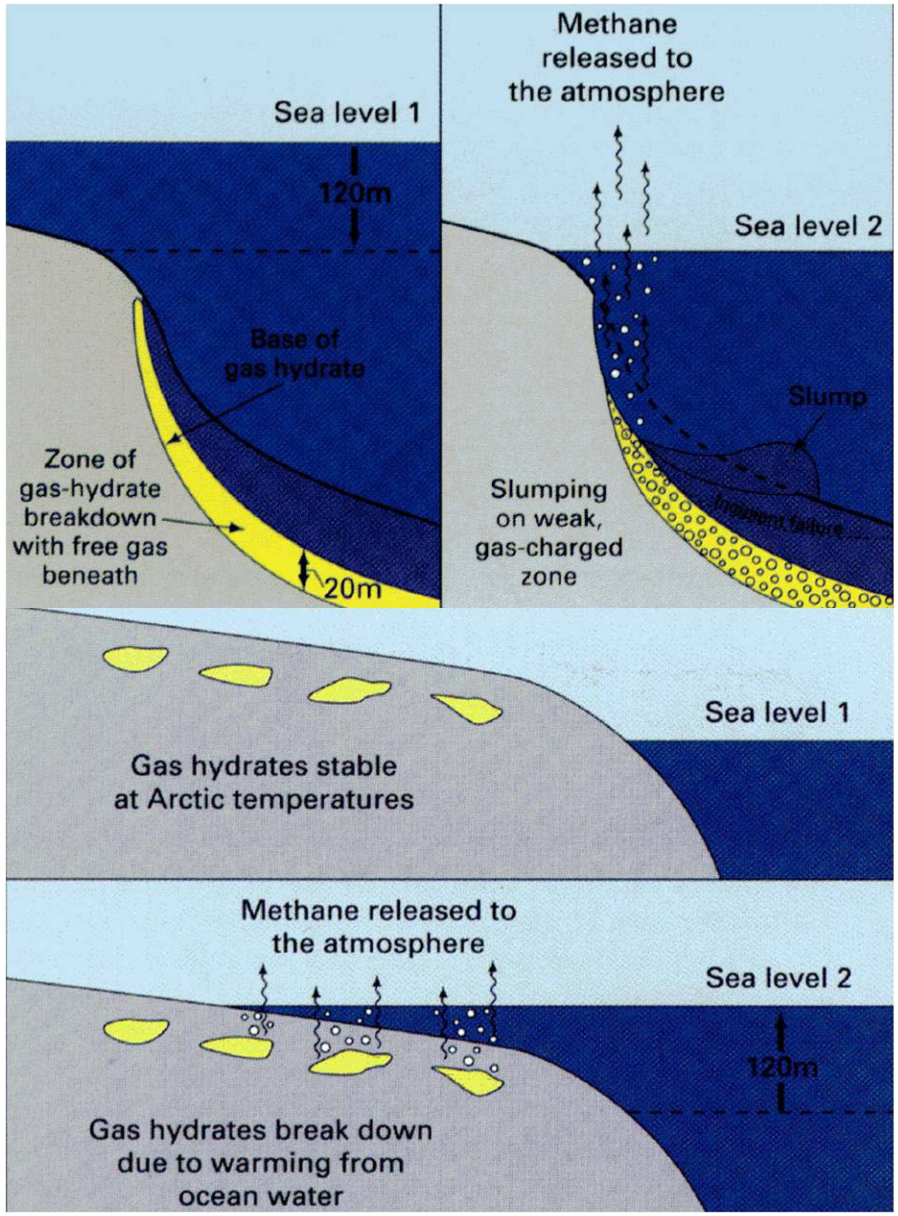

Figure 18. Clathrate Gun Hypothesis, fired by either a rise or a fall in sea level (Source: Dillon, 1998).

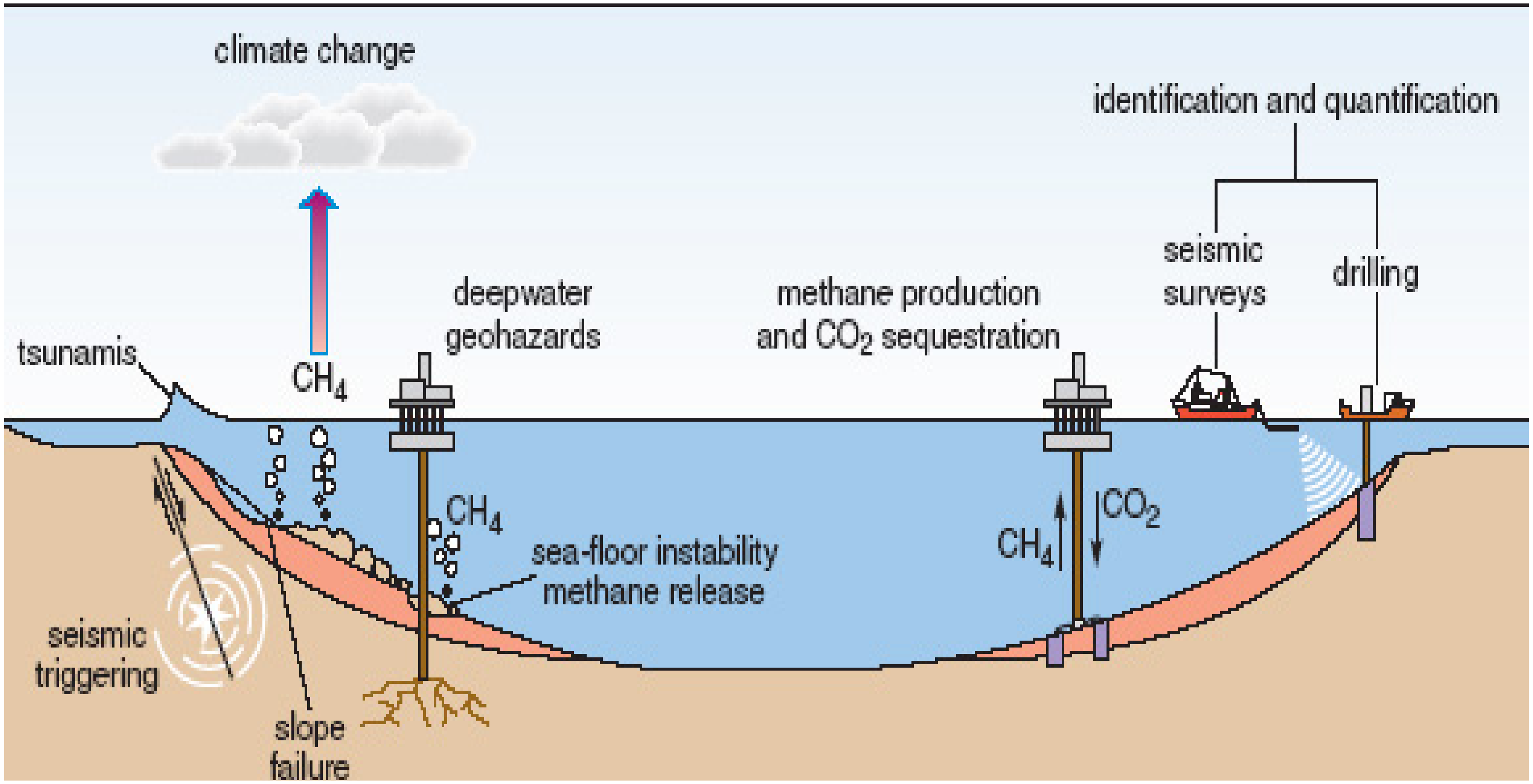

Figure 19. Other gas hydrate effects from human activities (Source: OpenLearn, The Open University, UK)

Gas Hydrates and Microbiological Processes

Gas hydrates are often associated with specialized micro- and macrofauna (Figures 20 and 21). This also raises the possibility of using some of these organisms, or the processes that they carry out, in order to stimulate hydrates towards destabilization, and thus production of natural gas.

Three main production methods exist: production of gas hydrates with pressure destabilization, production with methanol, and thermal destabilization. Experimental results point to operating conditions at least sufficient to cover operating costs (Figure 22).

The expected course for microbial processes used to destabilize hydrates involves the potential for methanol to drive hydrate dissociation and methane production. Other innovations in techniques and equipment could also help bring about major innovations in natural gas production from hydrate accumulations:

- Gas Hydrate and Sediment Test Lab Instrument (GHASTLI)
- Hydrate Autoclave Coring Equipment (HYACE)
- New Pore Pressure Tools
- IR imaging
- X-Ray CT
- Pressure Core Sampling
- Nuclear Magnetic Resonance
- Dipole Acoustic Tool
- Fiber Optic Temperature Sensor
- Electrical Conductivity & Resistivity
- Magnetic stratigraphy

Several useful microbial processes are envisioned as possible aids in hydrate conversion to natural gas. *Methylococcus capsulatus* Bath with soluble methane monooxygenase (sMMO) coding gene can be cultivated and utilized at elevated temperatures, and their copper tolerant MMO activity makes them good candidates for future biotechnological use in methane conversion (L. Bodrossy - Hungary, and Hakemian and Rosenzweig – Northwestern University.). The same is true for *Methylosinus trichosporium* (J. C. Murrell – Warwick University). Bacterial communities in the methane hydrate-bearing sediments were dominated by members of the JS1 group, Planctomycetes, and Chloroflexi (Inagaki et al, 2006). The implications are there for potential applications to hydrates destabilization.

“We anticipate that future studies of the microbes in nearshore deep marine sediments will clarify their role in the formation and STABILITY of methane hydrates, and determine how they affect the cycling of carbon in subsurface strata.” – personal contact, Mark Delwiche, Biological Sciences, Idaho National Laboratory, USA.

Excess CO_2, when introduced into a methane hydrate reservoir, displaces CH_4 in favor of the formation of stable CO_2 hydrate. This raises the possibility of using geologic CO_2 sequestration as hydrate, and coincident CH_4 production from natural gas hydrate reservoirs, according to researchers in this area. “The potential for using microbial communities which convert CO_2 could possibly allow controlled destabilization of CH_4 hydrate” (personal contact, Dr. Fred Wright, Geological Survey of Canada). Other researchers are also involved in work in this area (e.g., Dr. P. R. Bishnoi, University of Calgary). *Acidimethylosilex fumarolicum* SolV grows under oxygen limitation on methane as the sole source of energy, down to pH 0.8 (K. Heijmans, Radboud University, Netherlands). T. Yan (Oak Ridge National Laboratory), found a great diversity of functional genes for methanotrophs in sediments associated with gas hydrates in the Gulf of Mexico. The implications are there for a considerable number of novel methanotrophic species with potential applications to hydrates.

A study by Pacific Northwest National Laboratory (Comparative Assessment of Advanced Gas Hydrate Production Methods) involved processes such as phase saturation modification, hydrate dissociation and others, including via microbial methods (White, 2008). Certain organisms produce either antifreeze proteins (AFPs) which can inhibit the crystallization of hydrates and eliminate more rapid recrystallization or "memory effect". One such organism is *Chryseobacterium* sp. C_{14}. (E. I. Huva, Queen's University, Ontario). The apparent potential for these products to perturb hydrate growth suggests exploring new techniques to uncover "green inhibitors" for hydrate, including methane production with such bioproducts. Methanol production from methane is a mature technology, ever since methanotrophs were isolated that convert methane into methanol. Biocatalytic conversion offers the advantages of good thermal efficiency and high-product yield in a single-step reaction, and methanol is basically the only product.

Gas Hydrate Research

Several world experiences have also shown that the possible exploitation of gas hydrates may not be indefinitely far off into the future (Figures 23, 24, 25, 26, and 27).

Significant research and development funds have been applied worldwide towards hydrate research. The total is estimated at over US$1 billion over five years.

- In 2005, US DOE allocated $165 million over 5 years, with funding through Department of Energy and National Energy Technology Lab (NETL)
- Japan – invested an estimated US$50 million per year
- India – US$56 million over 5 years
- China and Korea combined – US$49 million per year

Among the main research and development sponsors involved in this research have been:

- Natural Resources Canada
- US DOE
- UK DTI
- Statoil
- Petrobras
- Total
- Clariant Oil Services
- Others

Other researchers and their research and development institutes involved have been:

- Yosuke Higashi, National Institute of Advanced Industrial Science and Technology (AIST)
- Leena D. Palekar, Scripps Institution of Oceanography, University of California, San Diego

- Saskatchewan Research Council
- Institute of Biophysics, Hungary
- Pacific Northwest National Laboratory
- Japan Marine Science and Technology Center

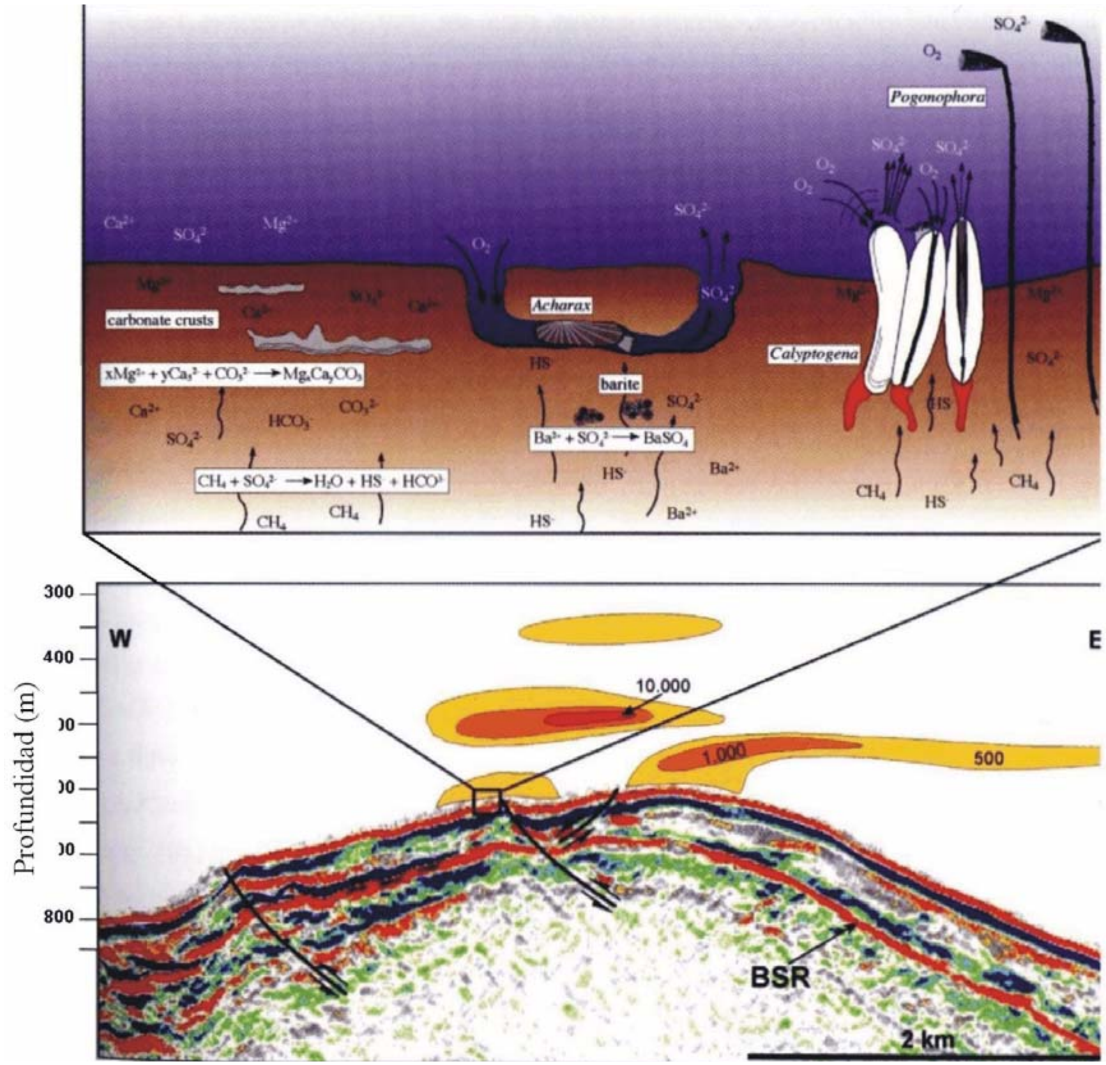

Figure 20. Biological processes related to gas hydrates (Source: Universidad Catolica de Valparaiso, Chile).

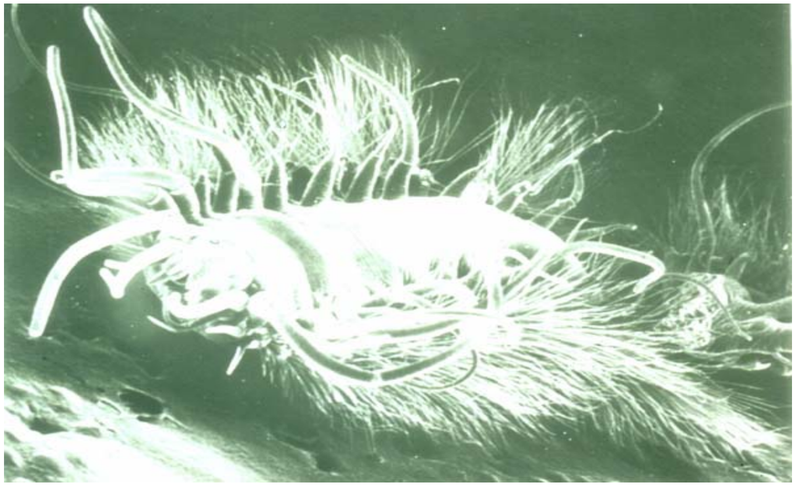

Figure 21. Micrograph of ice worm, *Hesiocaeca methanicola*, discovered living in a hydrate bed at 800 m depth during 1997 submersible dives in the northern Gulf of Mexico (Credit: C. Fischer, Source: NOAA).

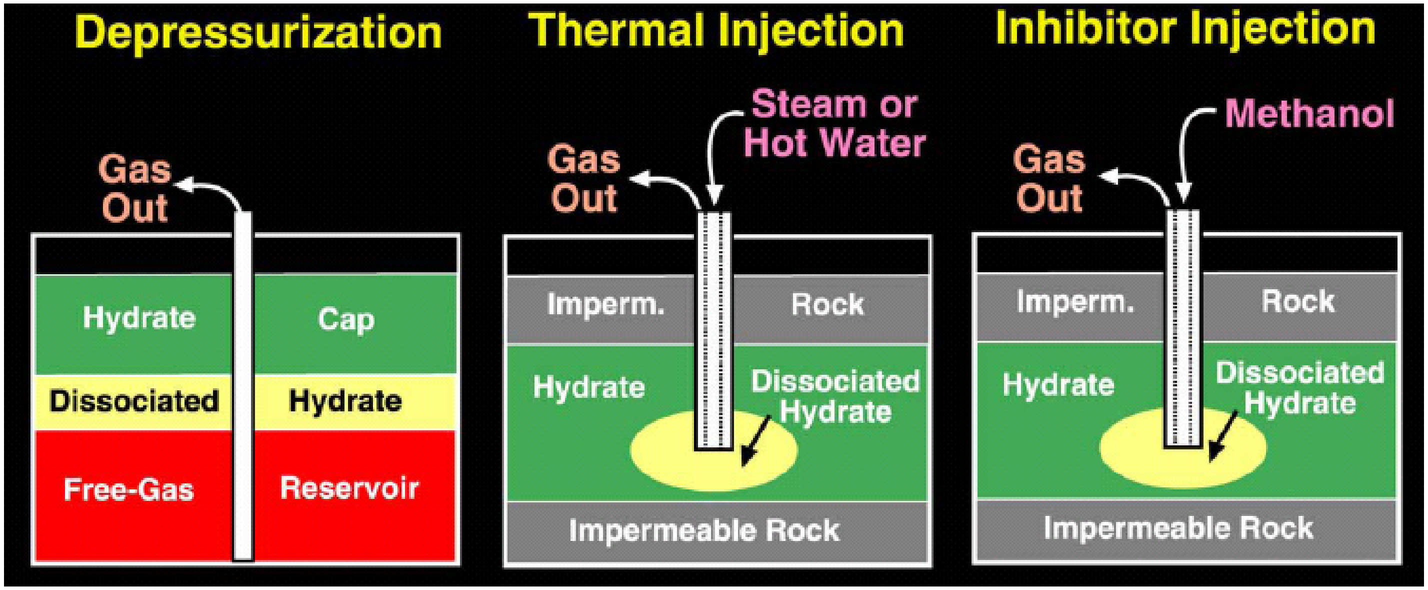

Figure 22. Gas hydrate production methods (source: K.G. Osadetz, 2006).

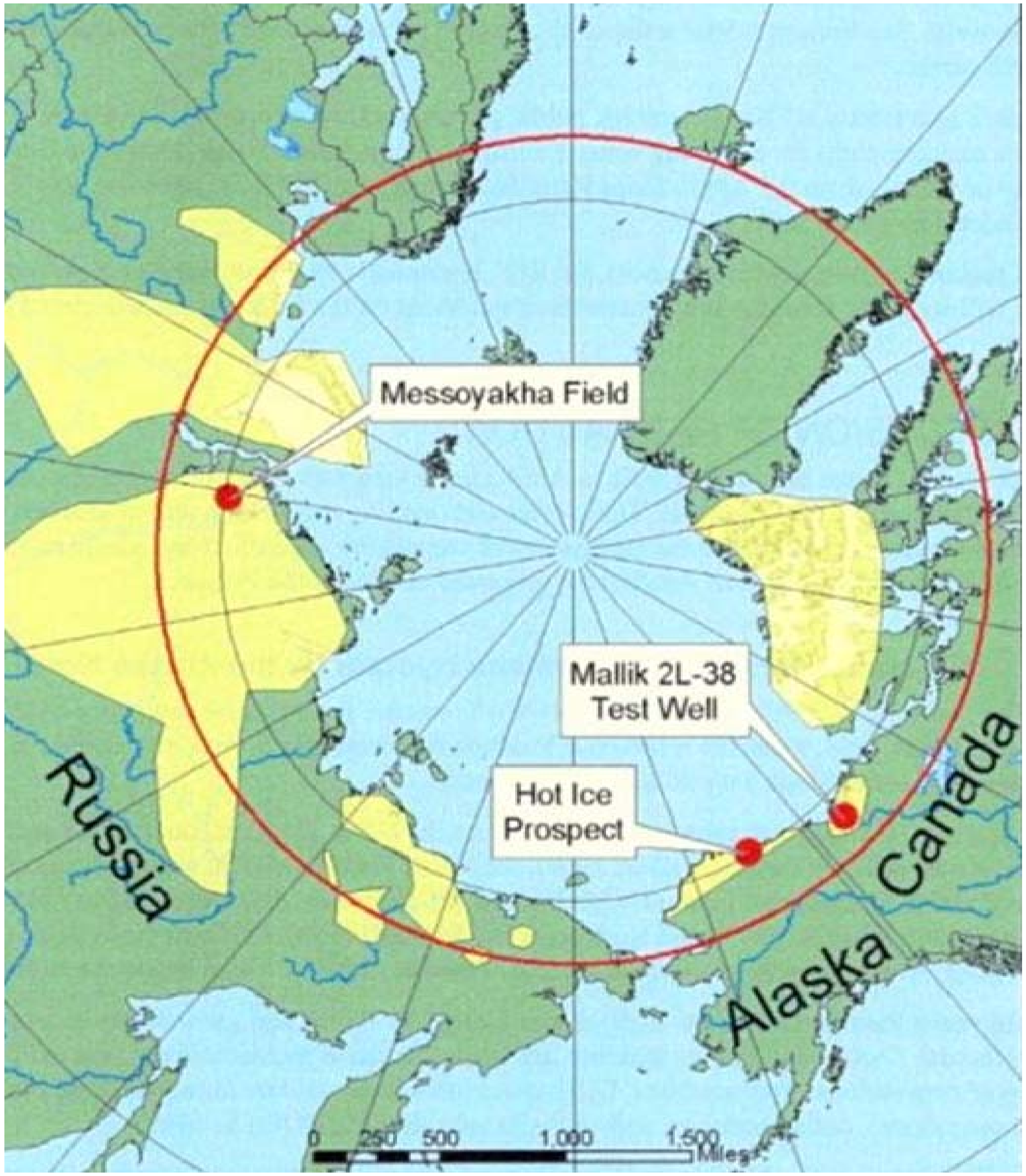

Figure 23. World experiences in gas hydrate production efforts.

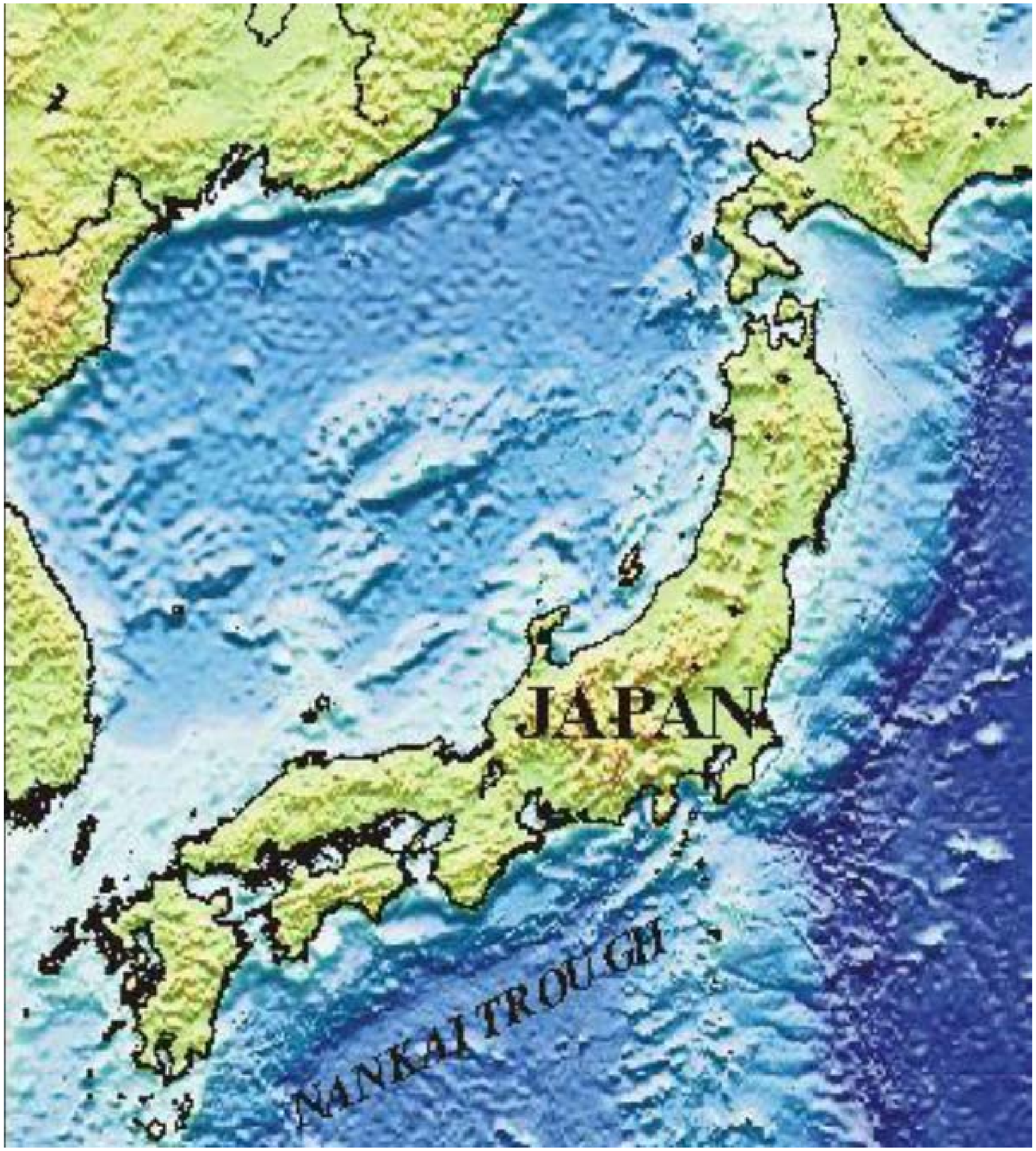

Figure 24. World experiences: Nankai Trough, Japan - 50km from coast; water depth 950m; bsr at 290m below seabottom; total 5m of productive zone; estimates of 500 million m^3 of accumulations per km^2.

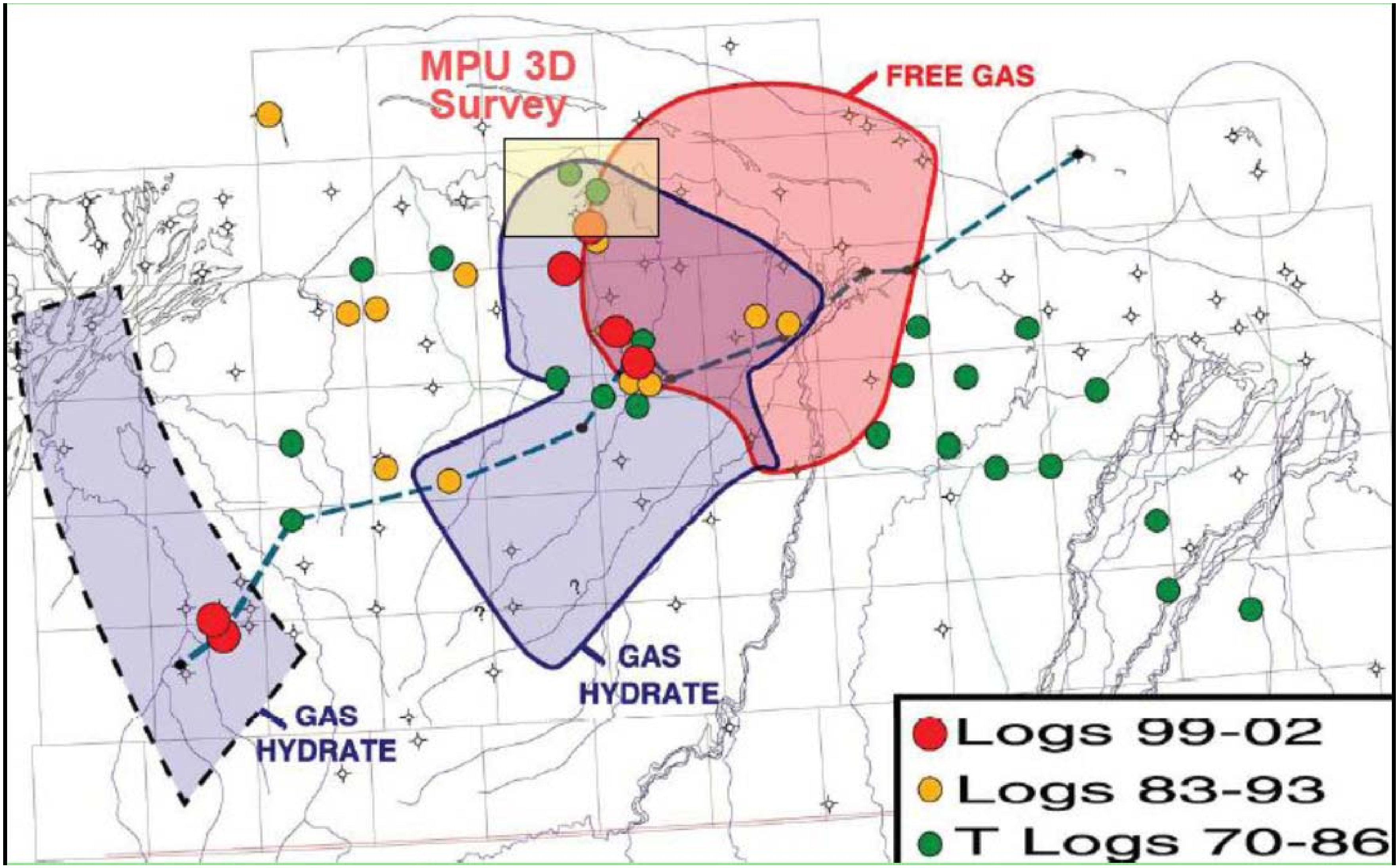

Figure 25. World experiences: Hot Ice Prospect - NPRA (National Petroleum Reserve, Alaska), EUA.

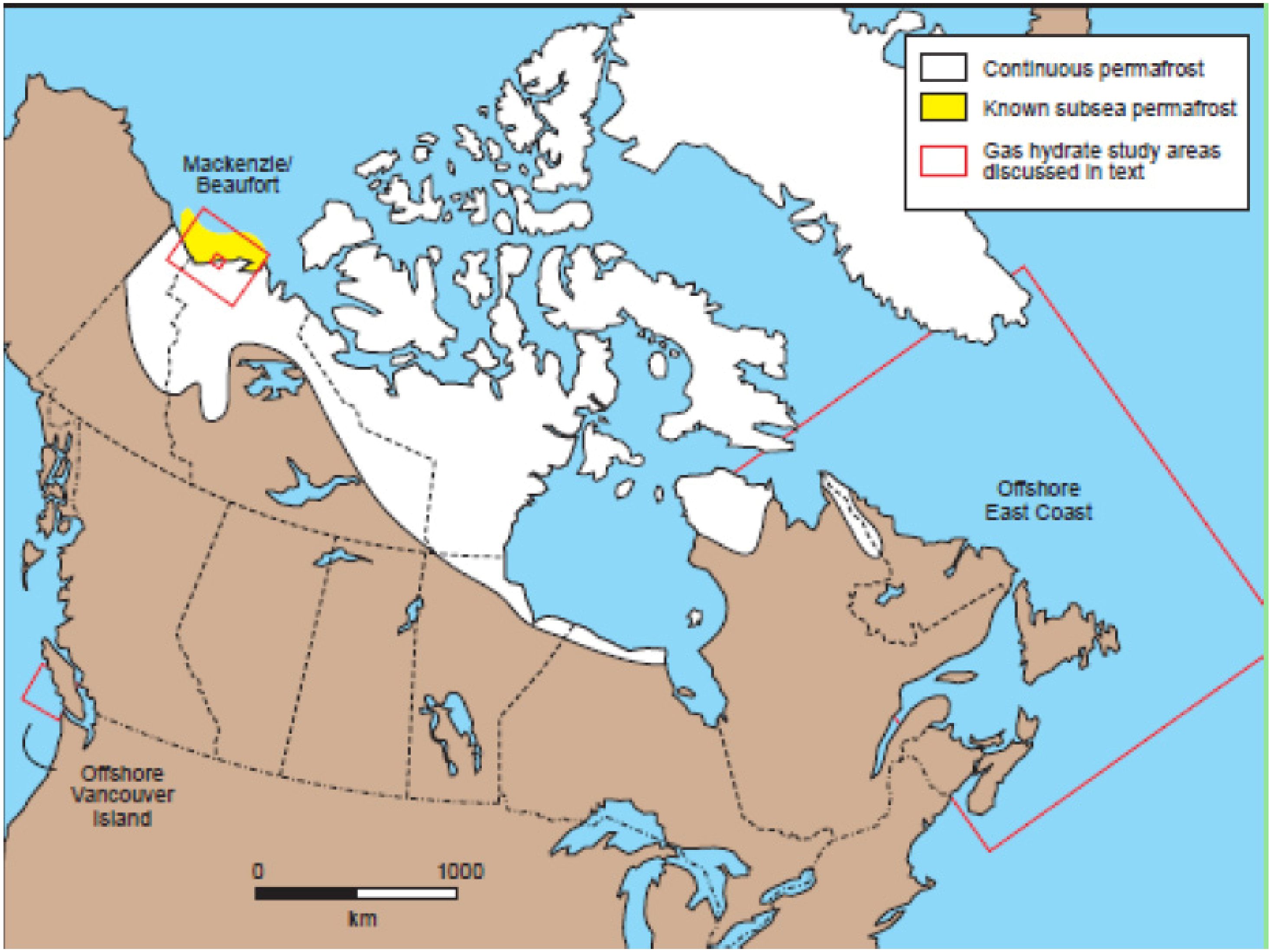

Figure 26. World experiences: Mallik, NW Territories, Canada - region with the best samples of gas hydrates in the world production of hydrates via destabilization by heating and pressure reduction (Majorowicz and Osadetz, 2001).

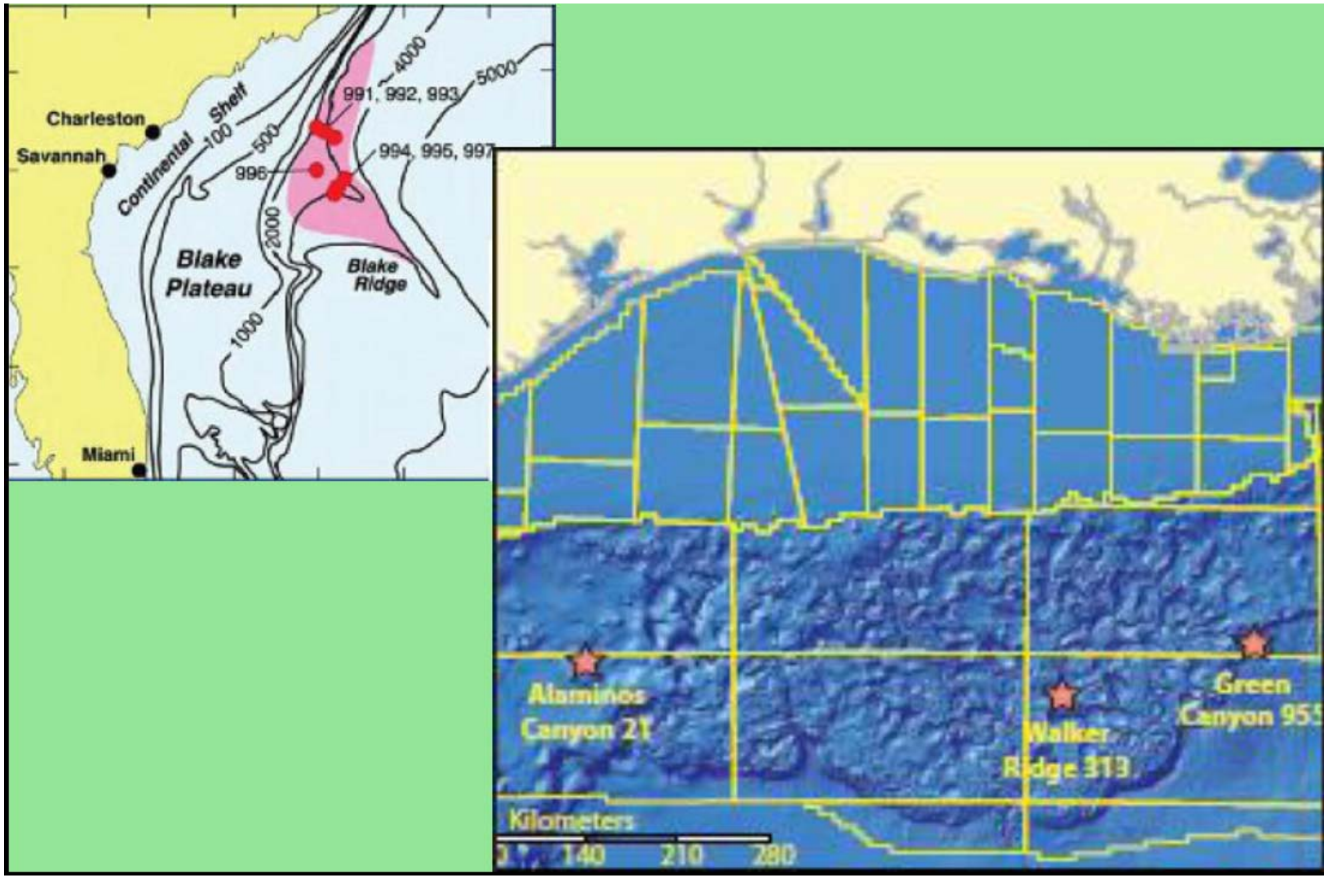

Figure 27. World experiences: Blake Ridge, eastern continental platform of North America and Walker Ridge Gulf of Mexico (JIP Expedition) – the first "commercial" quality discovery in the Gulf of Mexico (water depth ~ 2200m; depth below seabottom ~200-800m; thickness of hydrate zone up to 230m; hydrate saturation of 50-90%) (National Energy Technology Laboratory, US-DOE).

Conclusions

The production methods for making gas hydrates commercially available are still being developed. Given the wide scope of biological effects observed, microbiological processes involved are strong candidates for current studies and pilot projects, and in the longer term, production from hydrates will likely incorporate biological processes.

However, there are significant challenges along this road, although the potential returns are sure to provide better than average prospects for funding, as there is an attractive future for commercial applications:

- The need to be ahead of the innovation curve, which is constantly moving forward.
- The need to pursue, direct or redirect research efforts towards discovering, understanding, and applying microbiological processes and organisms involved in dissociation and formation of methane hydrates.

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