Università di Trieste
Corso di Laurea in Geologia

Anno accademico 2016 - 2017

Geologia Marina

Parte IV

Modulo 4.3 Identificatori di movimento di fluidi: Idrati del metano

Docente
A. Camerlenghi

B2 - Outline

Review of main mechanisms of fluid flow:

- Mud diapirs and mud volcanoes
- Gas chimneys
- Pockmarks
- Seafloor vents in general
- Polygonal fault systems
- Diagenetic fronts
- **Gas hydrates**

NATURAL GAS HYDRATES ARE CONSIDERED AS:

- **Natural controllers of climatic change**
- **Geo-hazards**
- **Potential energy source**
- **Controllers of deep sea eco-systems**
- **Potential safe and effective way of methane transport**
- **Problem in pipelines**
- ***Possible cause of ship and airplane disappearance in the Bermuda triangle***

METHANE

Is the simplest saturated hydrocarbon gas (alkane):

$$\mathbf{CH_4}$$

Other common hydrocarbon gases are:

ethane (C_2H_6), **propane** (C_3H_8) **butane** (C_4H_{10})

When the number of carbon atoms exceeds 5, the name of gases is from Greek numbers: **pentane**, **hexane**, **heptane**...

The general formula of hydrocarbon gases is:

$$\mathbf{C_nH_{2n+2}}$$

Human-related sources

- **Landfills** *(waste disposal)*
- **Natural gas and petroleum systems** *(natural gas production)*
- **Coal mining**
- **Livestock enteric fermentation**
- **Livestock manure management**
- **Wastewater treatment**
- **Rice cultivation**

Natural sources

- **Wetlands**
- **Termites**
- **Oceans** *(anaerobic digestion in marine zooplankton and fish, and also from methanogenisis in sediment)*
- **Hydrates**
- ***Juvenile***

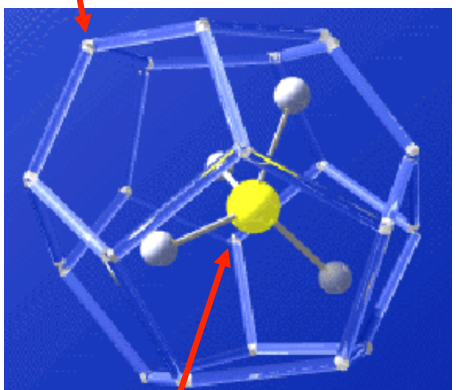
HYDRATES OF NATURAL GAS

(discovered in 1810)

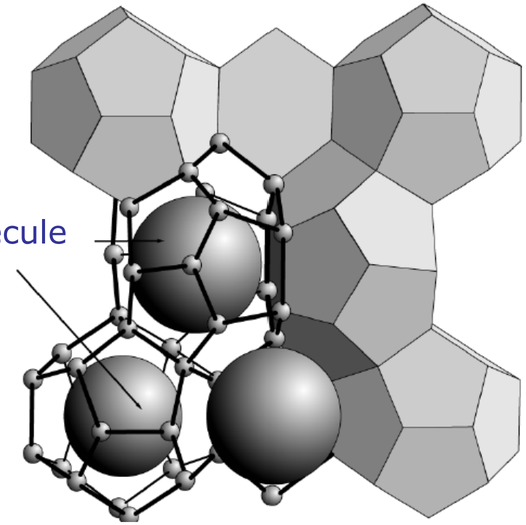
- Gas hydrates are a **solid phase** composed of **water** and low-molecular weight **gases** (predominantly methane)
- Water molecules form an ordered crystalline solid matrix which includes gas molecules with weak electro-static bounds
- The state of **saturation of hydrates is a function of pressure and temperature**. They form under conditions of low temperature, high pressure, and adeguate gas concentration
- The ion content of water and the type of gas (methane, propane, pentane…) affect the phase diagram of the gas hydrate

Hydrate crystal

Water molecule



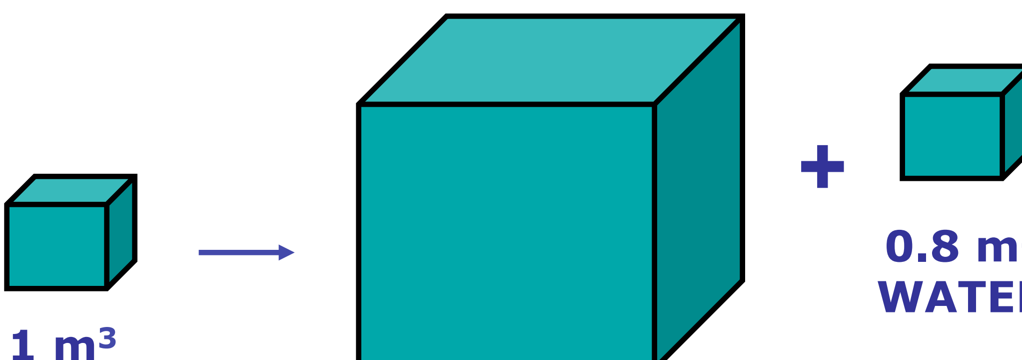
Methane molecule



Methane molecule

Water molecule

Bohrmann and Torres, 2006, in Schulz, Horst D.; Zabel, Matthias (Eds.) Marine Geochemistry



1 m³ GAS HYDRATE → **164 m³ GAS** + **0.8 m³ WATER**

@ standard pressure and temperature

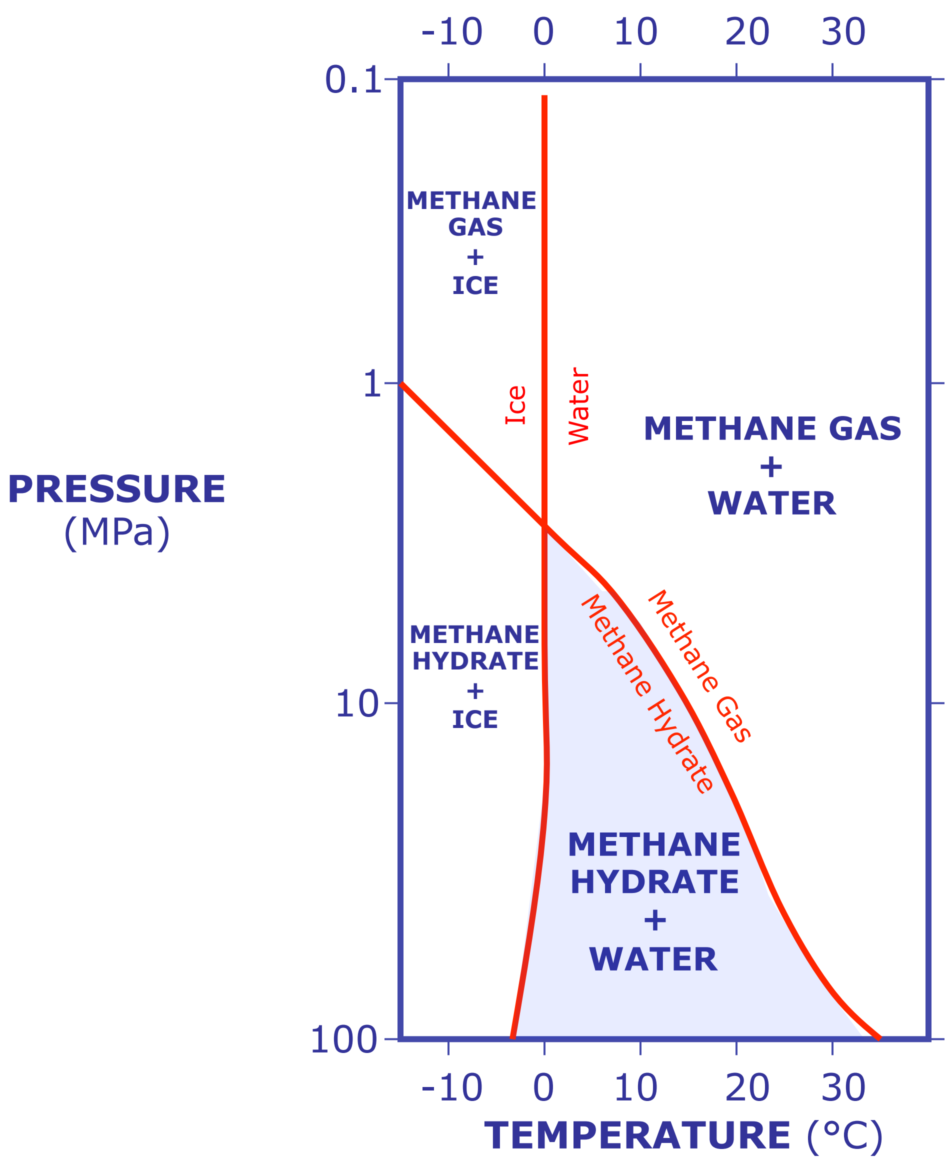
CH4 metro RCOM - University of Bremen

Courtesy:

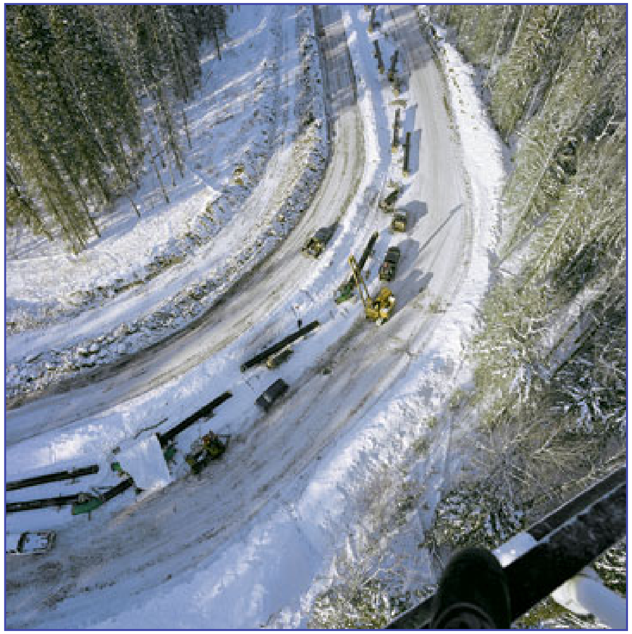
Carlo Giavarini, Filippo Maccioni and Maria Laura Santarelli

Università di Roma "La Sapienza" Dipartimento di Ingegneria Chimica.

PHASE DIAGRAM OF METHANE HYDRATES



Hydrate formation in arctic gas pipelines reduces or blocks methane flow. Chemical additives are necessary to prevent hydrate formation.



Alaska Highway Pipeline TransCanada

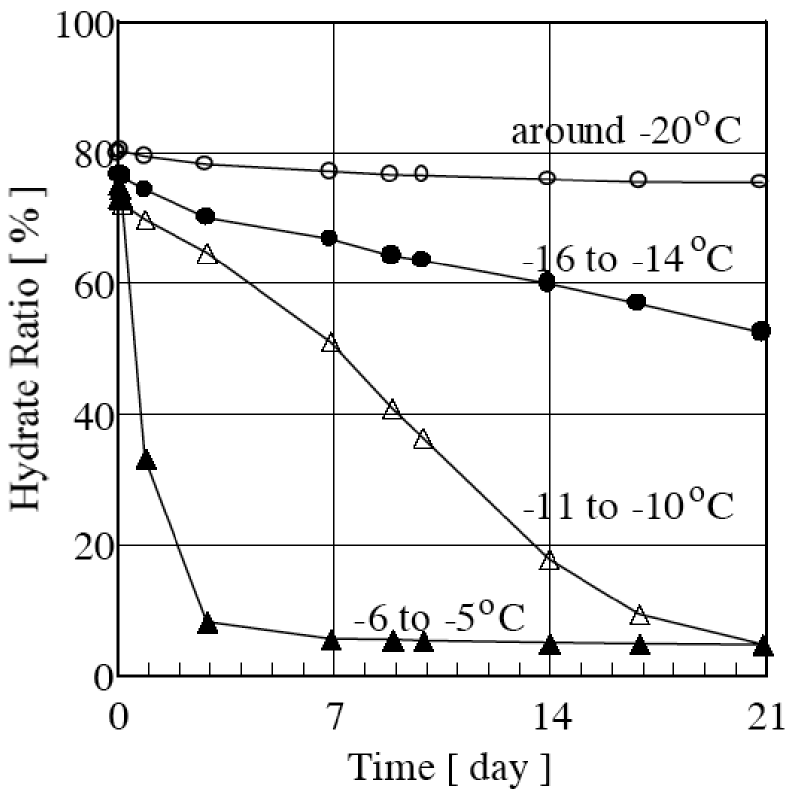
LIQUID NATURAL GAS TRANSPORT IS EXPENSIVE AND DANGEROUS

Methane is condensed into a liquid at almost atmospheric pressure (**Maximum Transport Pressure set around 25 kPa**) by cooling it to approximately -163° C.

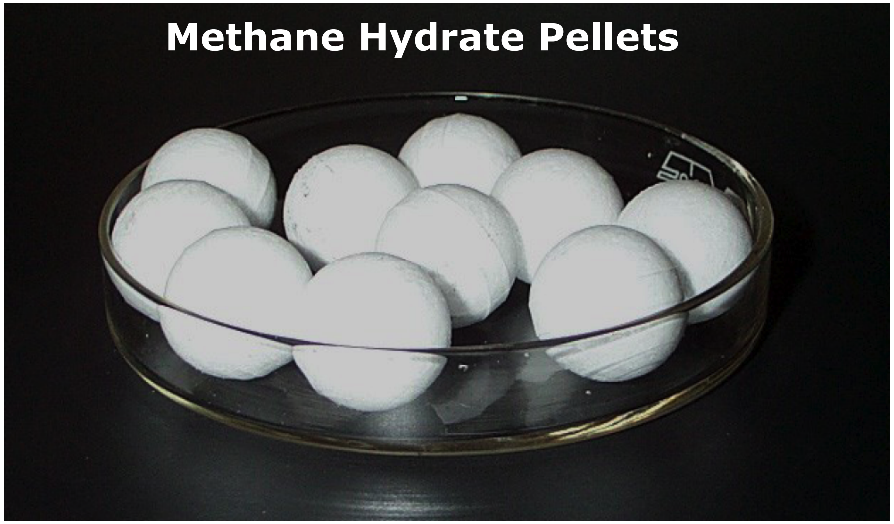
LNG is transported by specially designed **cryogenic sea vessels** and cryogenic road tankers, and stored in specially designed tanks.

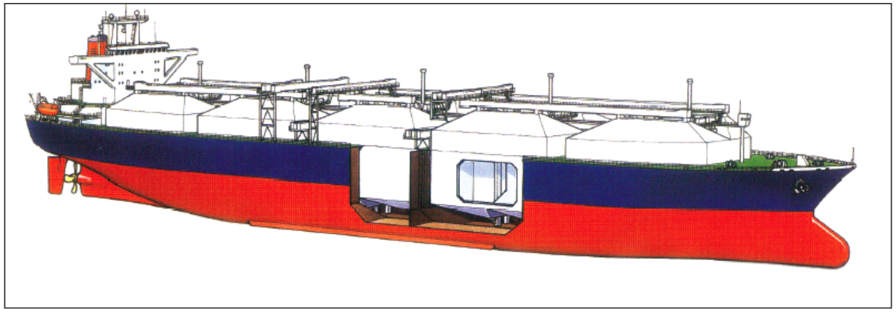
self-preservation

At 1 Atm, CH_4 Hydrates are stable below -20°C.



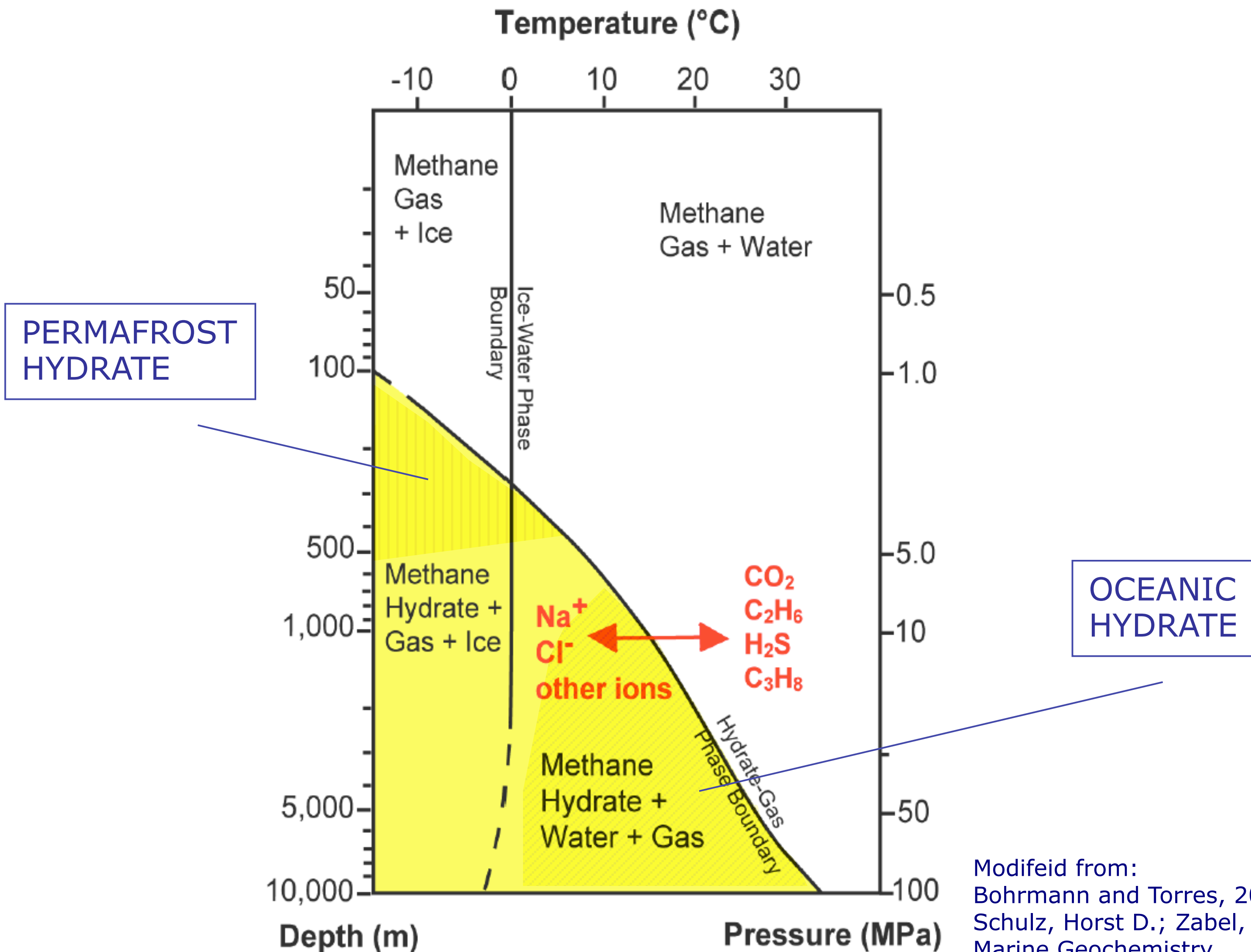
Self-preservation is thought to be caused by a layer of ice from dissociated hydrate; this layer coats the hydrate and seals it from further dissociation.





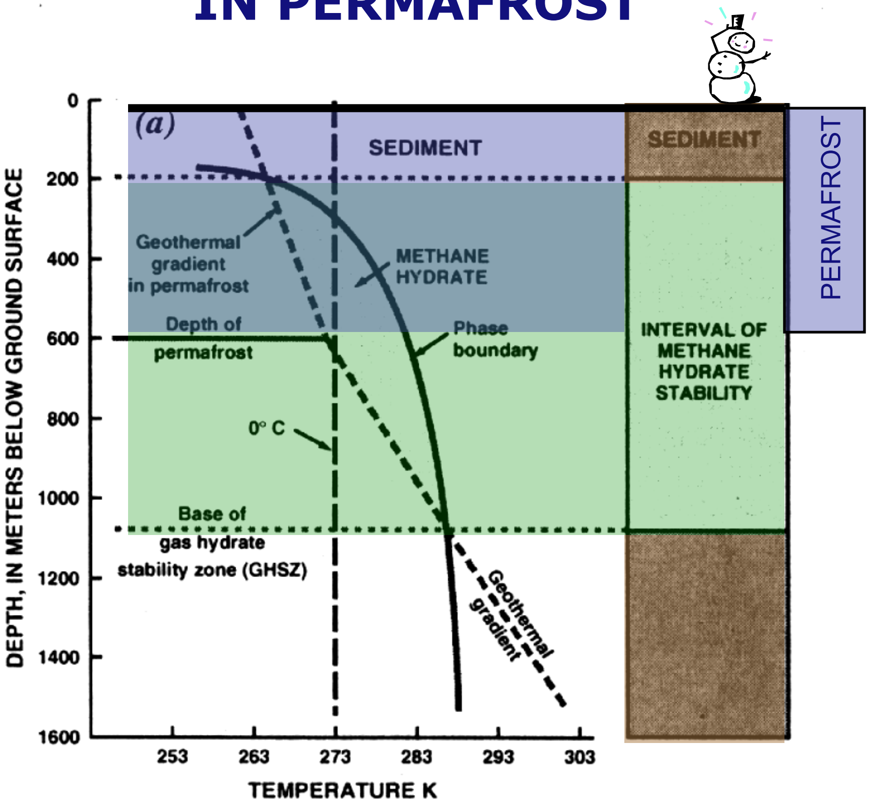
Possible ship specifically designed to carry natural gas **hydrate pellets** @ **-20°C and atmospheric pressure** (National Maritime Research Institute, Mitsui Shipbuilding & Engineering, and Osaka University)

PHASE DIAGRAM OF METHANE HYDRATES IN THE NATURAL ENVIRONMENT



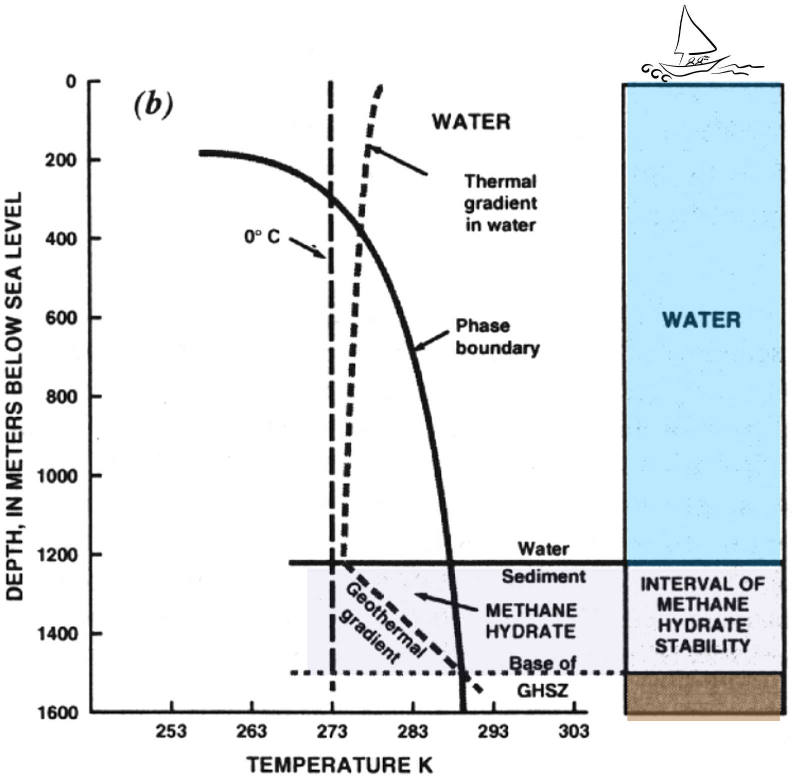
Modifeid from:
Bohrmann and Torres, 2006, in
Schulz, Horst D.; Zabel, Matthias (Eds.)
Marine Geochemistry

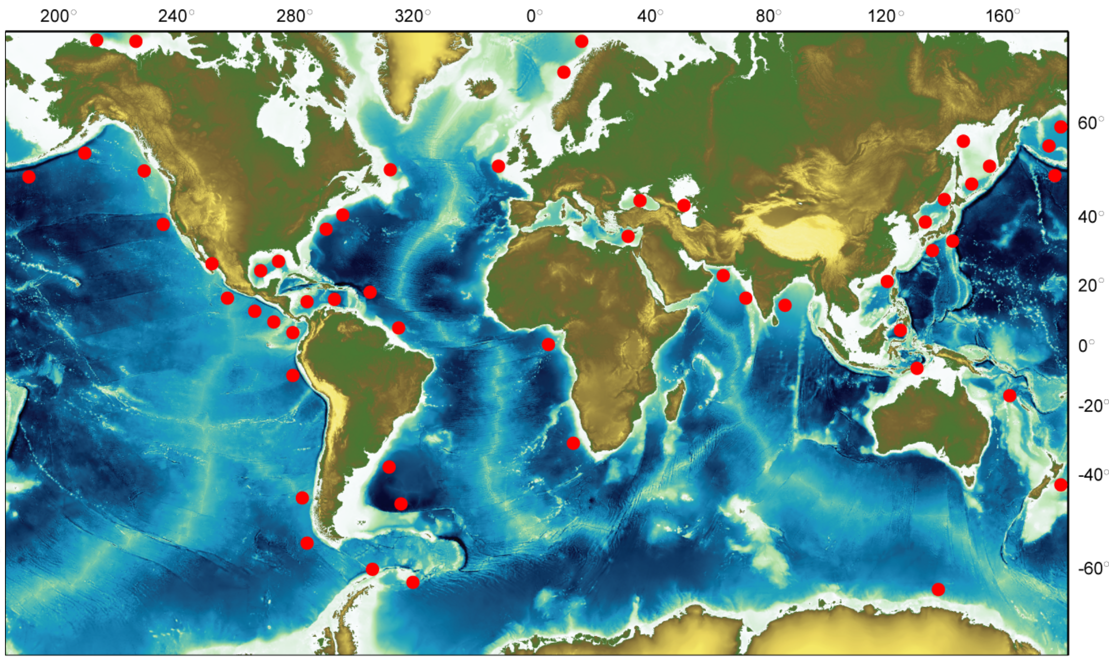
METANE HYDRATES **IN PERMAFROST**



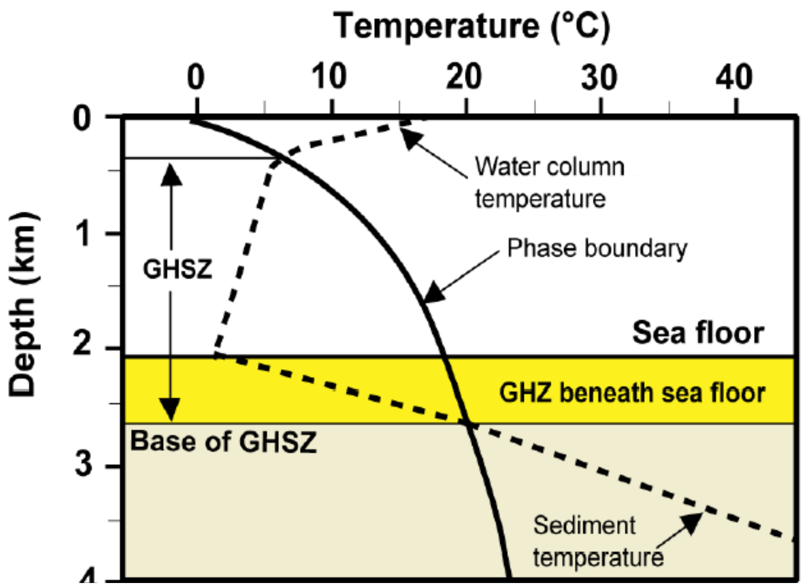
Permafrost is defined as soil, sediment or rock whose temperature is continuosly below 0°C for at least two years

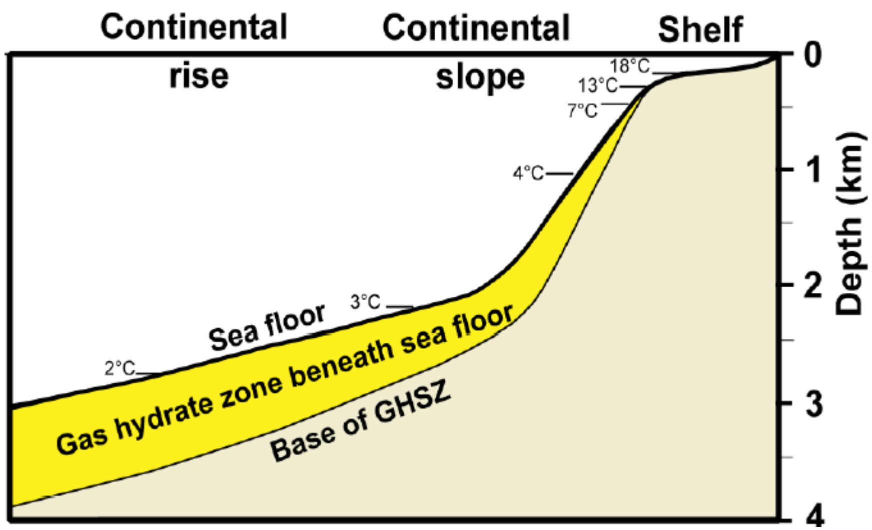
METHANE HYDRATES
IN OCEANIC SEDIMENTS

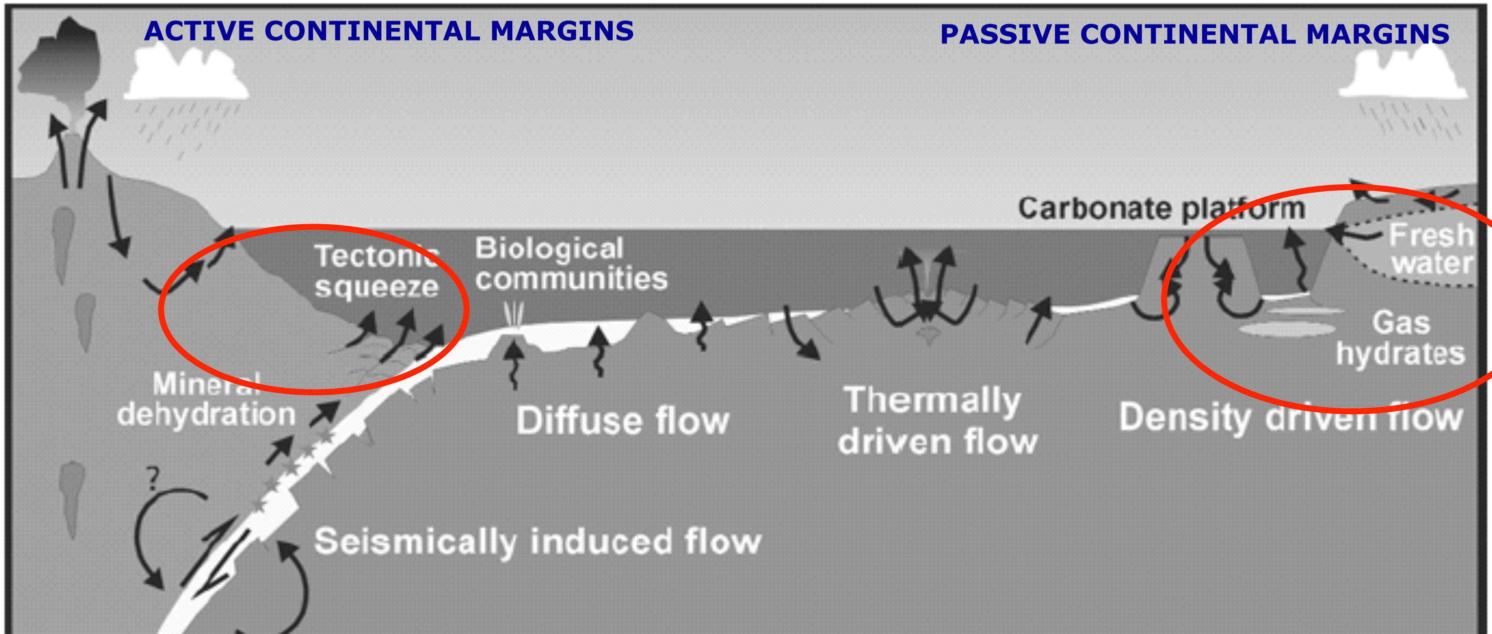




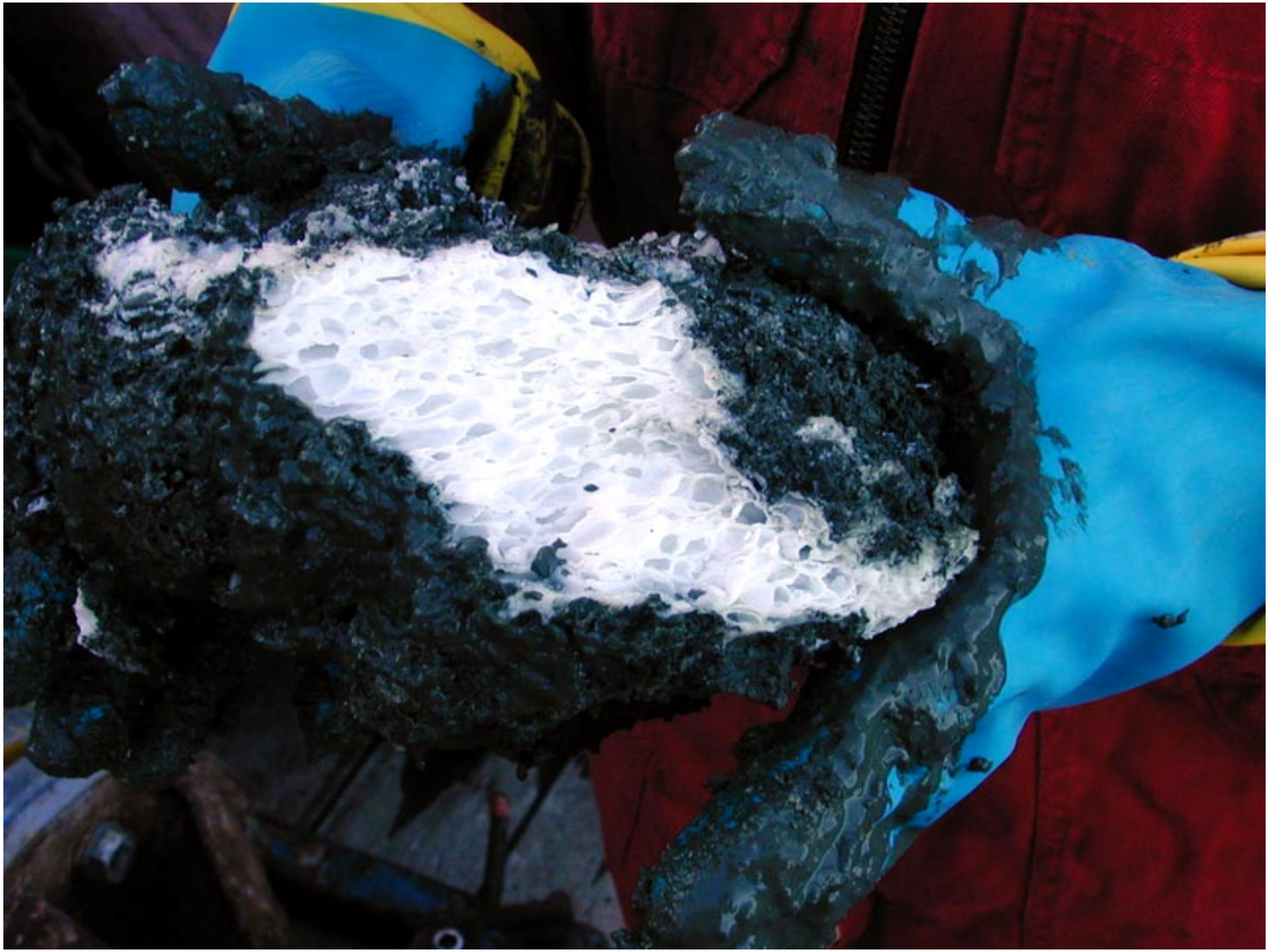
Natural gas hydrates are distributed along the ocean margins world wide within the Gas Hydrate Stability Zone (GHSZ), that ranges from the seafloor down to a maximum of 700-800 m

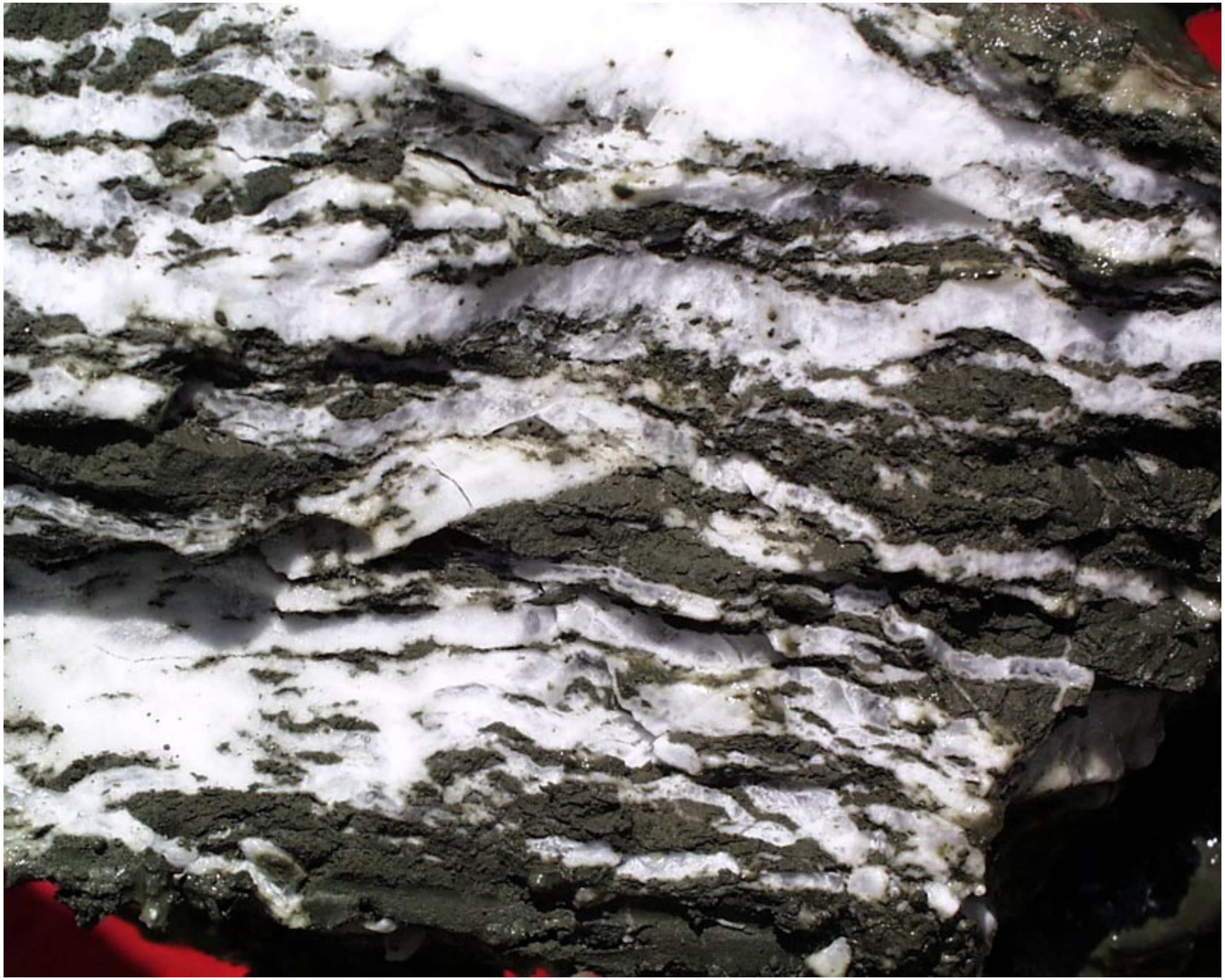


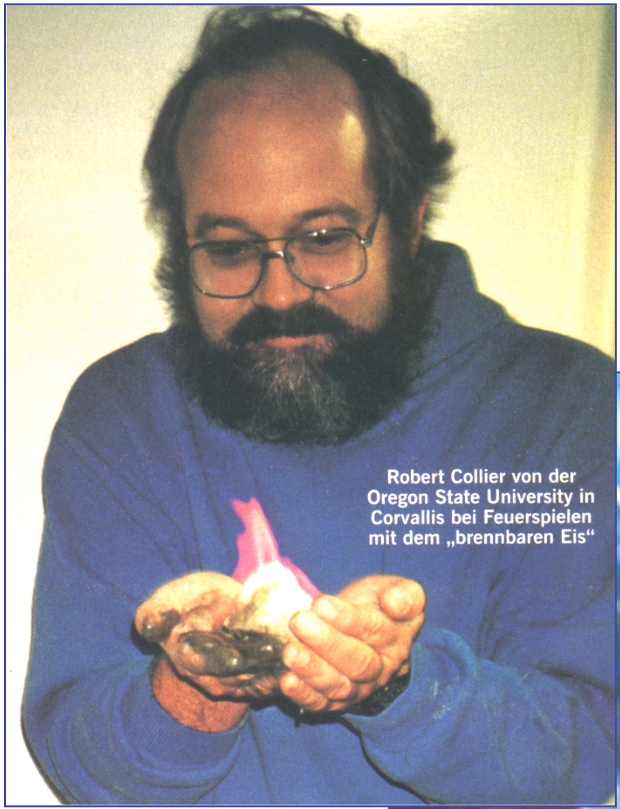


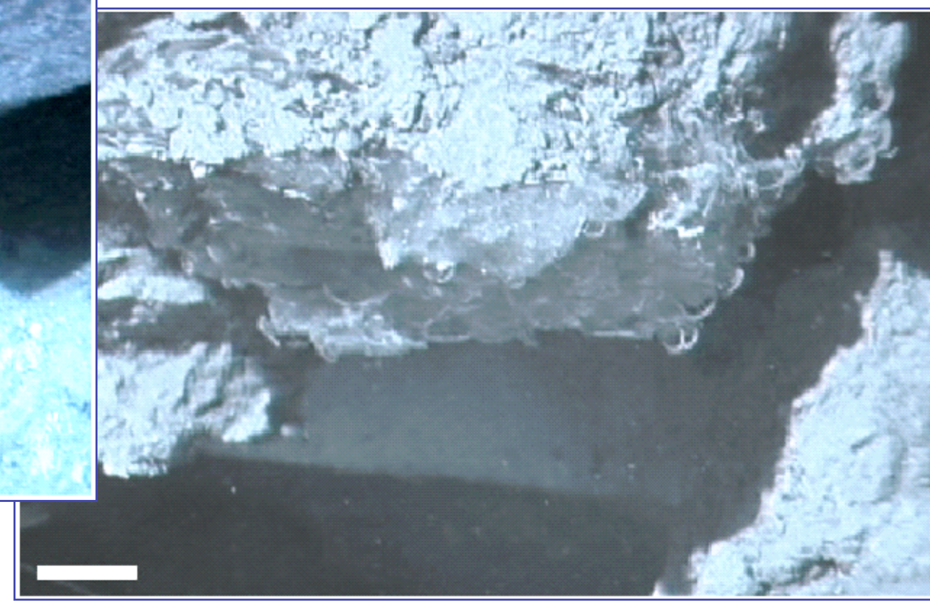


Modified from Ge et alii, Eos,Vol. 84, No. 16, 22 April 2003






Robert Collier von der
Oregon State University in
Corvallis bei Feuerspielen
mit dem „brennbaren Eis"



Van Dover et al. (2003). *Deep Sea Research*

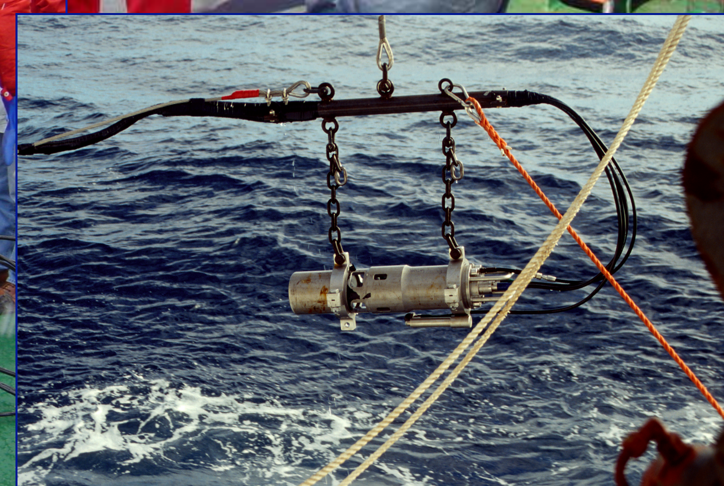
marum http://www.rcom.marum.de

METHODS OF DETECTION OF NATURAL GAS HYDRATES

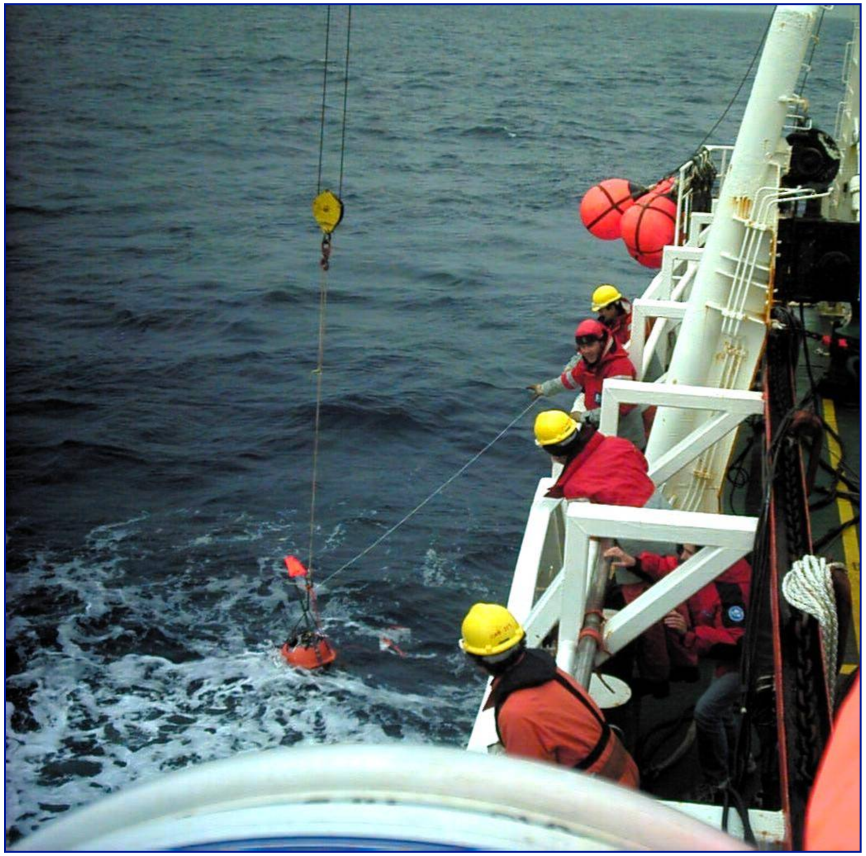
- **SEISMICS**
  (reflection, multichannel, OBS)
- **DRILLING**
  (essentially through scientific drilling)
- **GEOCHEMICAL**
  (inorganic- organic geochemistry)
- **MODELLING**
  (laboratory models - data inversion)
- **BASIN-WIDE ANALYSES**
  (modelling + data)


SEISMIC STREAMER


AIR GUNS



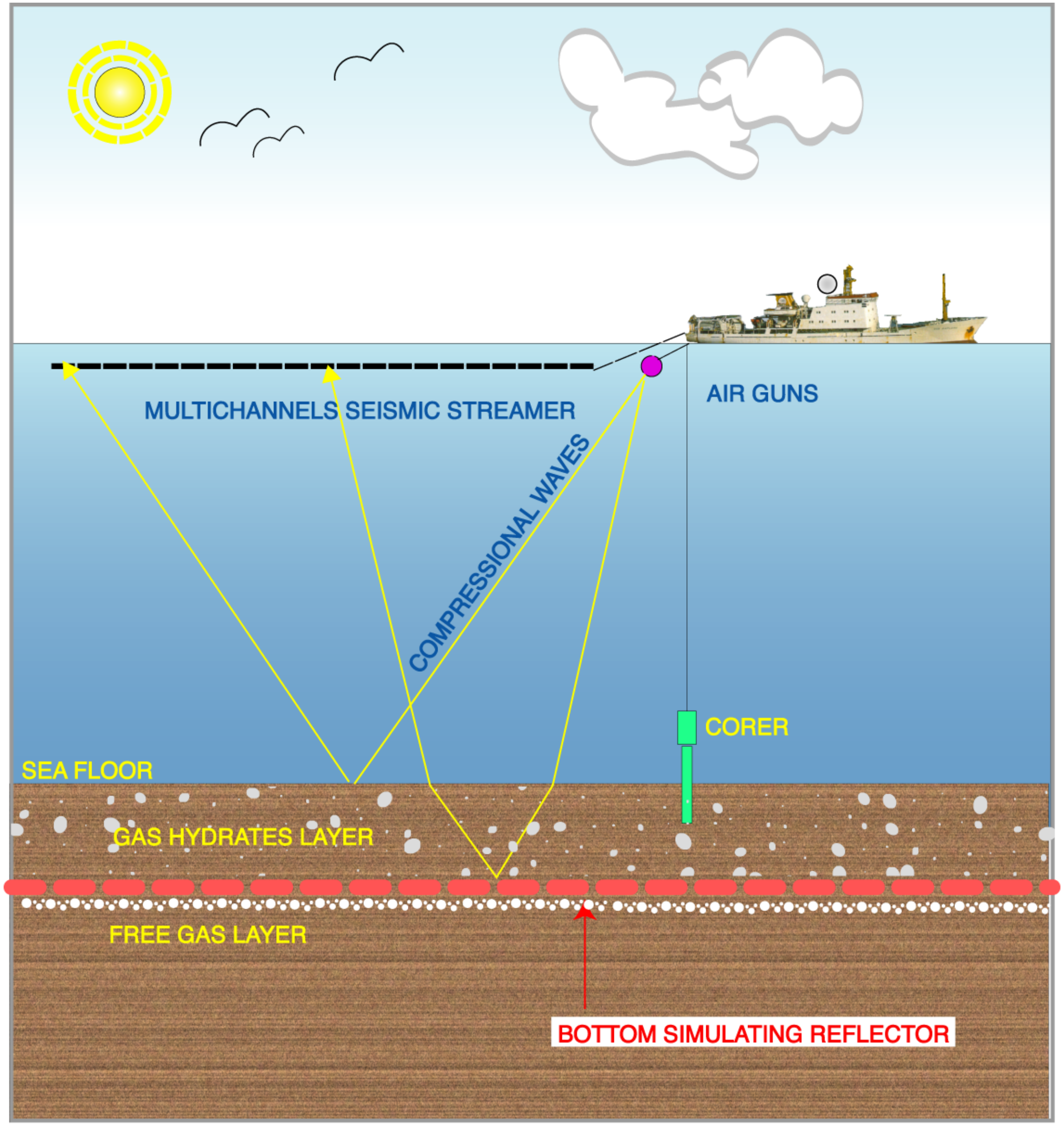
OCEAN BOTTOM SEISMOMETERS (OBS)



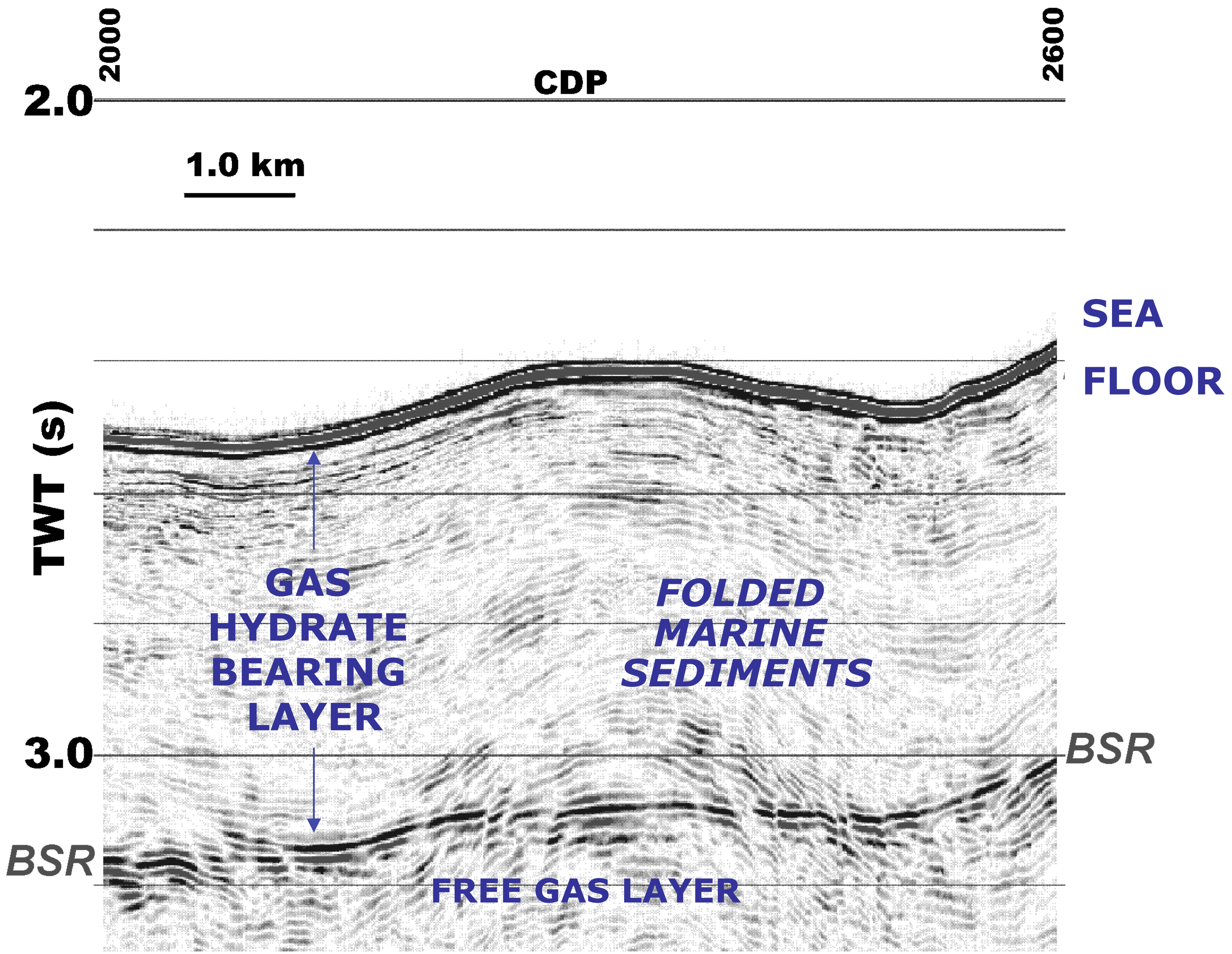
SEISMICS REFLECTION

The concept of **Bottom Simulating Reflector (BSR)**

The BSR is a seismic reflector that simulates the sea bottom reflector. It is produced by the acoustic impedance contrast between sediments with hydrates (above) and sediments with free gas (below).



SEISMC PROFILE

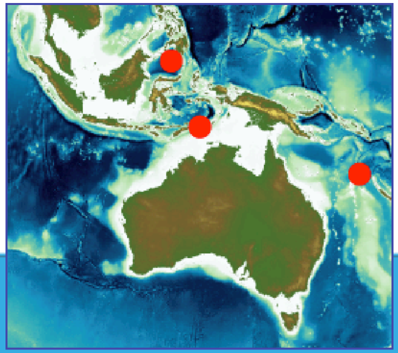


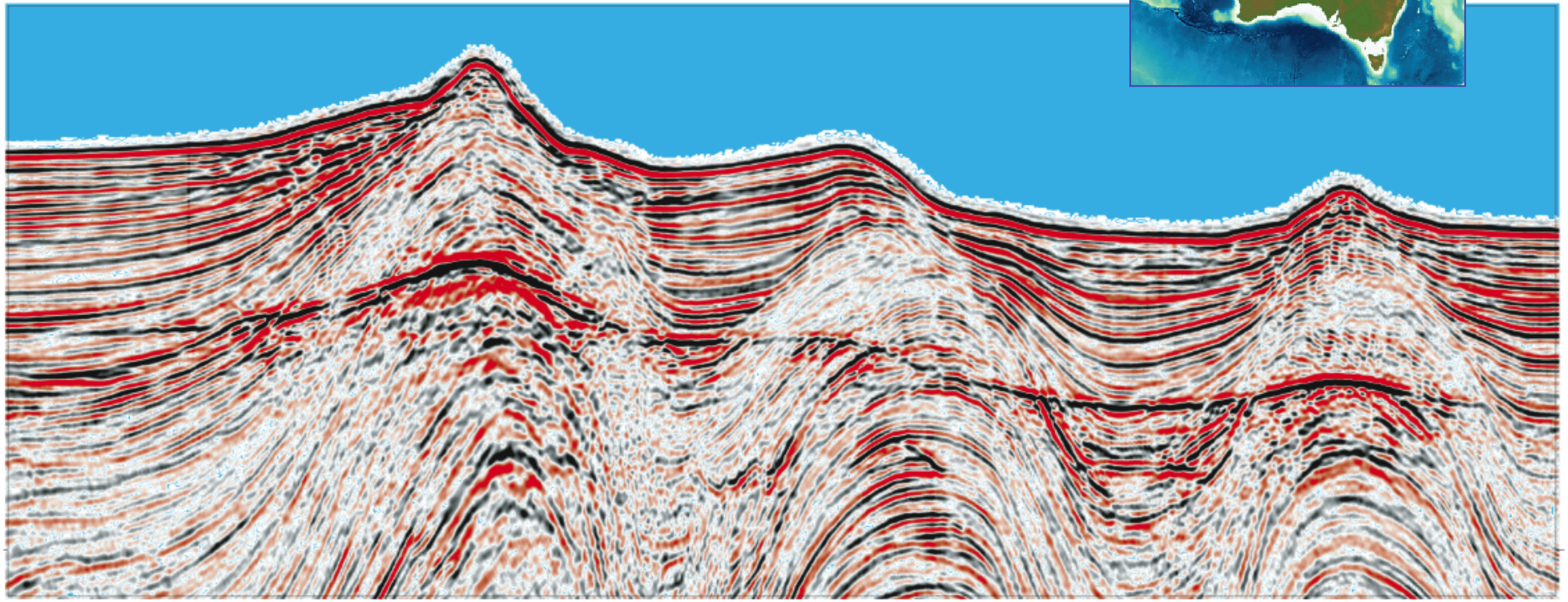
Stratification in Marine Sediments

Turbidite (Gorgoglione Flysch),
Miocene, South Italy

Marne a Fucoidi (Sezione del Bosso)
Cretaceous (Albian), Central Apennines, Italy
FOTO MASSIMO GALLI

Makassar Straits, Indonesia





Data from TGS-NOPEC Geophysical Company, published in Max et al., 2006. Economic Geology of Natural Gas Hydrates, Springer.

Characteristics of the BSR

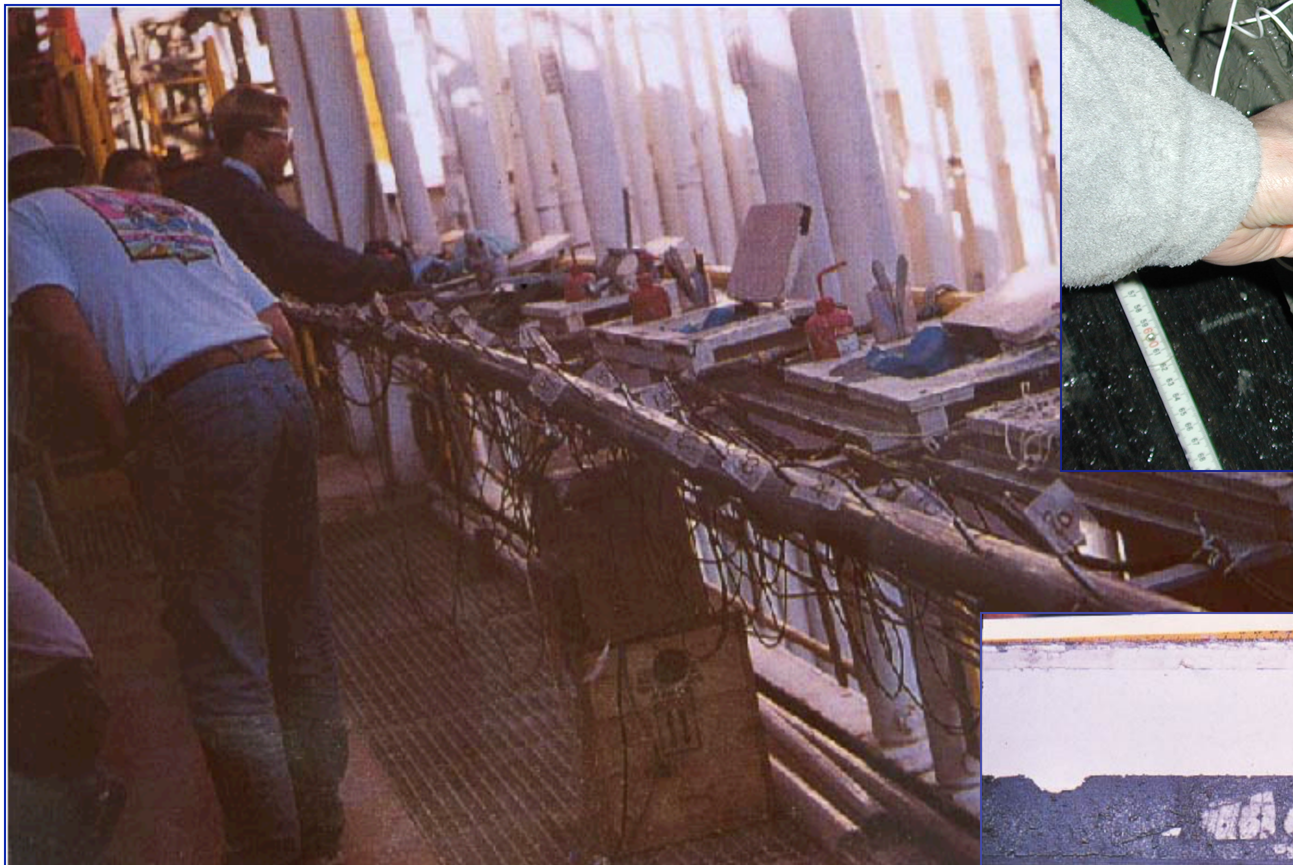
- **High reflection coefficient**
- **Reverse polarity with respect to the seafloor reflector**
- **Cuts through lithologic reflectors**
- **Its depth approximately coincides with the theoretical depth of the base of the hydrates stability zone.**
- **It may be underlined by another reflector produced by the base of the free gas layer (BGR)**

How can the hydrates be identified through drilling?

- Thermal anomaly in cores
- Soupy layers
- Chlorinity anomaly
- Resistivity anomaly
- Seismic velocity anomaly

http://www.jamstec.go.jp/chikyu/

Thermal anomaly in cores

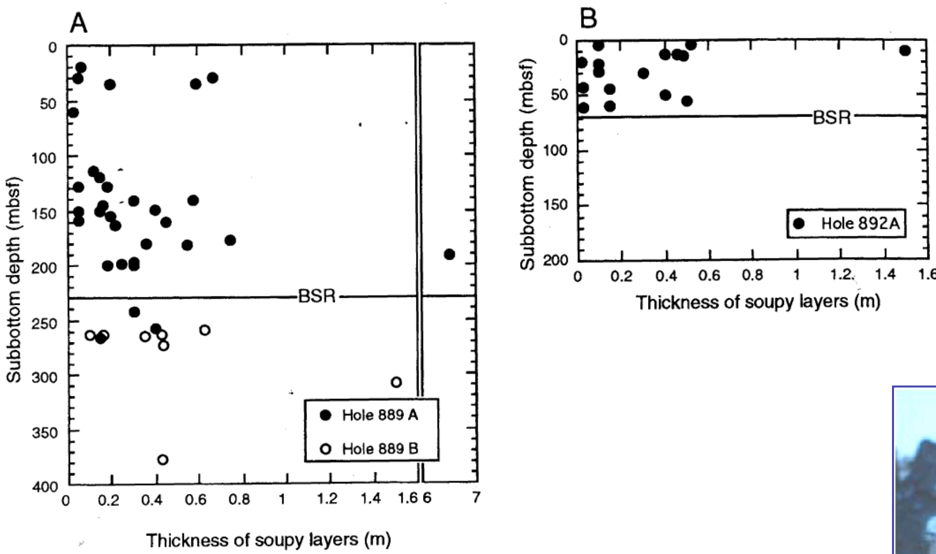


G. Bohrmann, Initial results from M52/1 **MARGASCH**

Gas hydrate dissociation is an **endo-thermic** reaction (it absorbs heat from the surroundings >>>>> decrease in bulk sediment temperature)

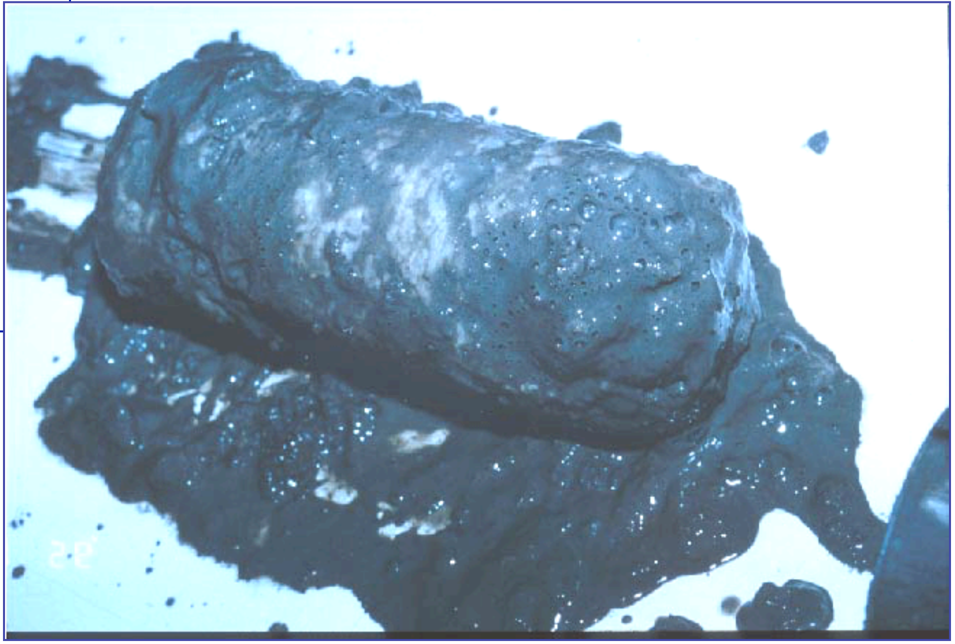
Soupy layers

SOUPY LAYERS: Sedimentological evidence of the presence of gas hydrates layers



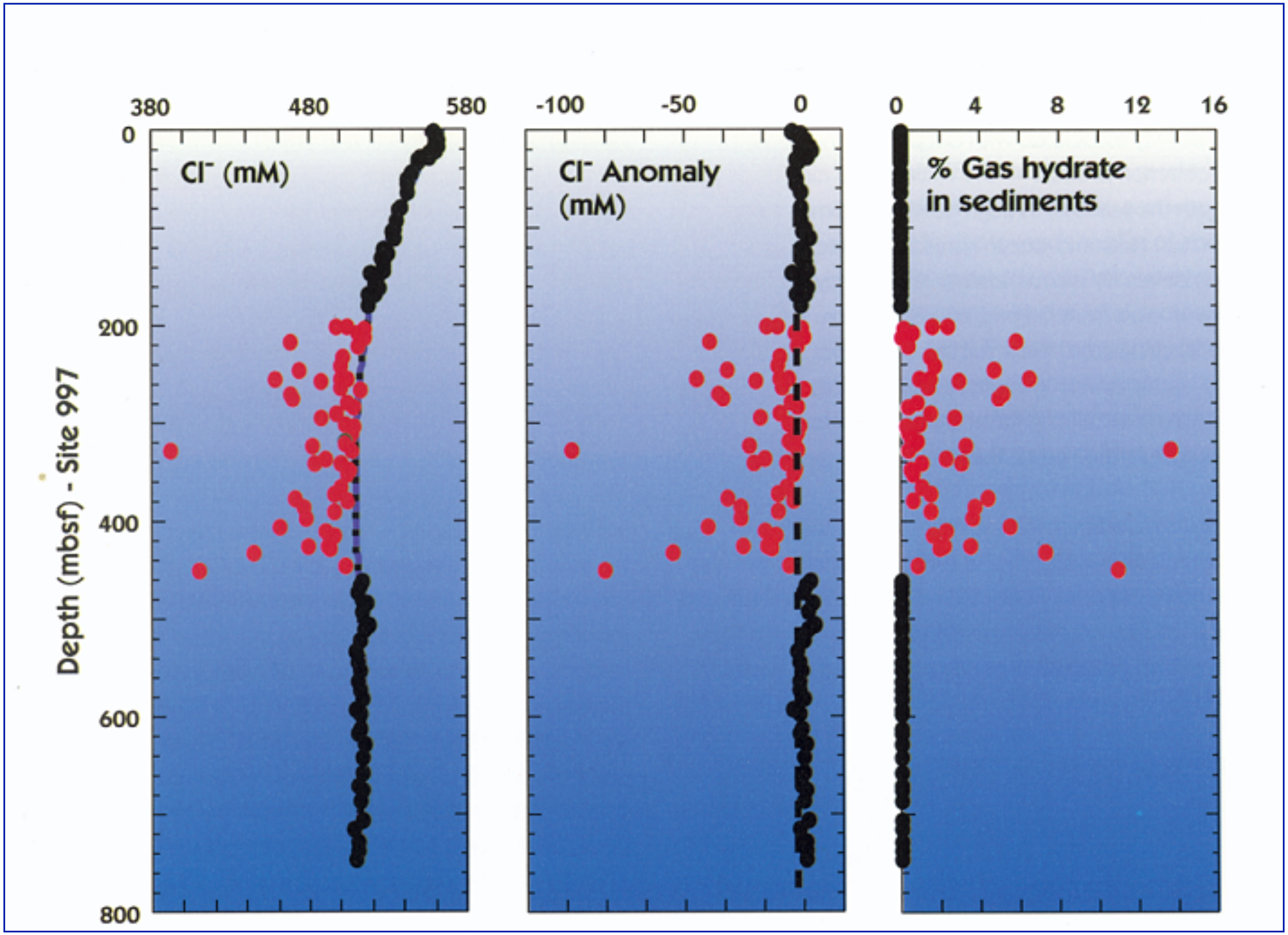
Kastner et al., 1995

Gas hydrate dissociation during core recovery destroys the sediment fabric, producing disturbed, liquified 'soupy' sediment layers in cores



Chlorinity anomaly

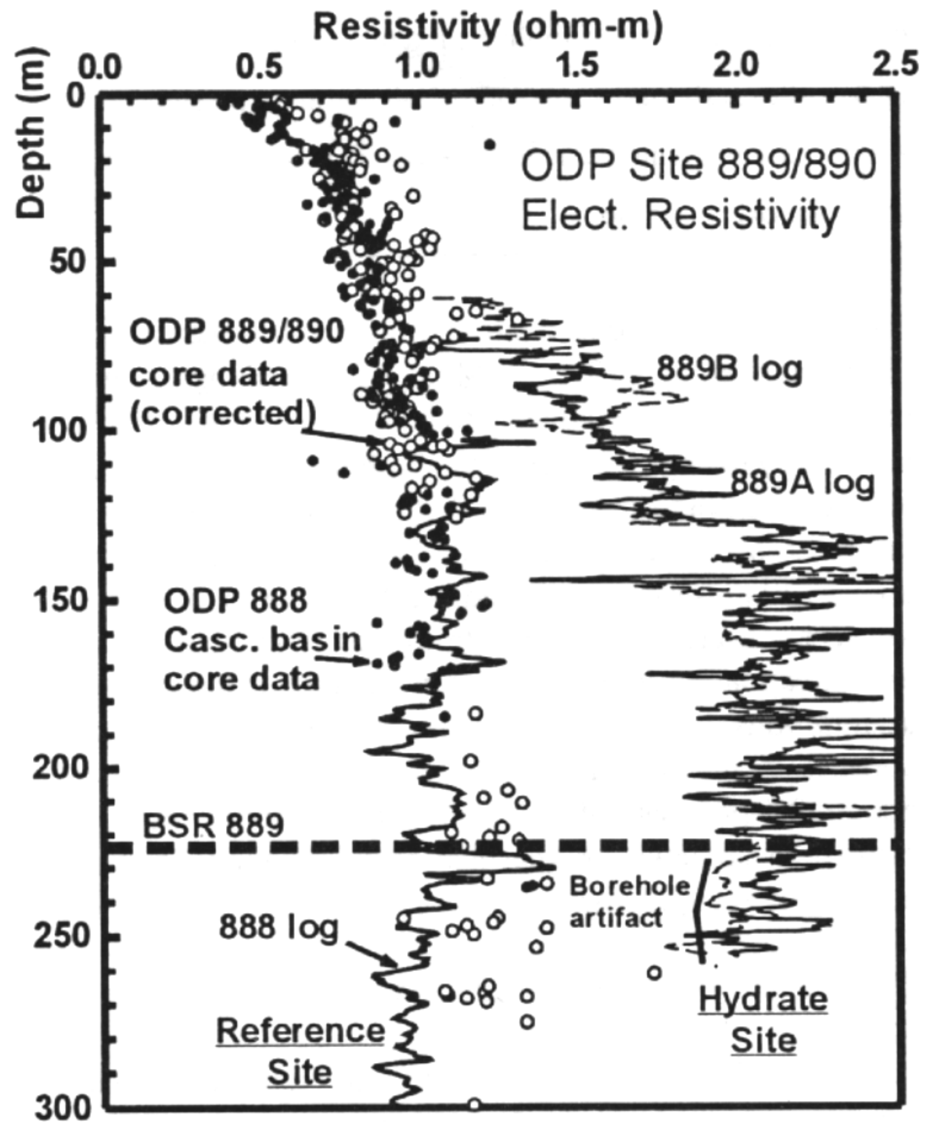
Gas hydrate dissociation during core recovery produces **residual fresh water** that dilutes the ionic concentration of the pore water



In situ Electrical Resistivity anomaly

The electrical resistivity of gas hydrates is **higher** than that of seawater.

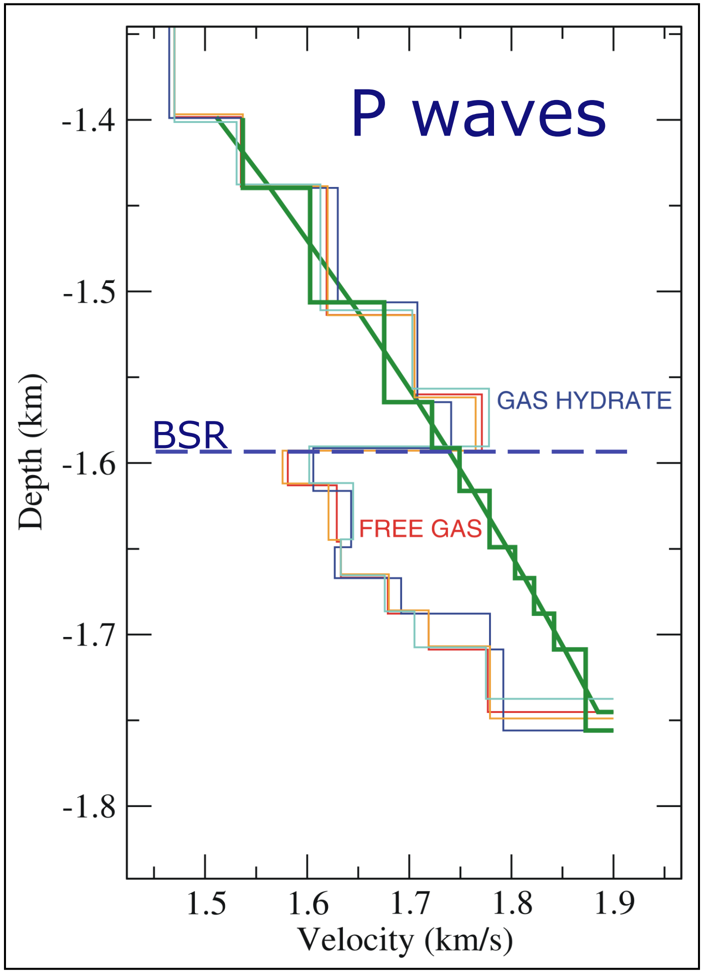
The anomaly is identified with respect to a resistivity profile in a nearby borehole with similar sediment NOT containing hydrates

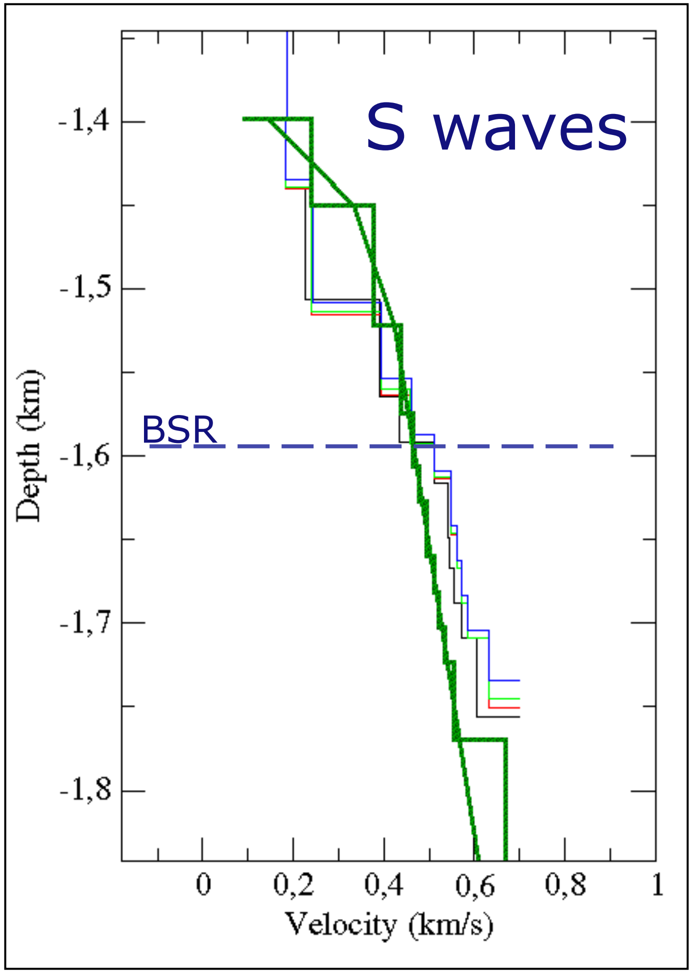


In situ seismic velocity anomaly

The compressional wave velocity of gas hydrates is **higher** than that of seawater.

The anomaly is identified with respect to a resistivity profile in a nearby borehole with similar sediment NOT containing hydrates



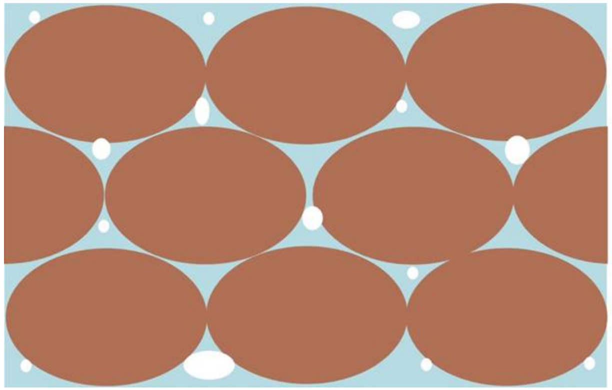


Rossi et al., ICGH (2005)

VELOCITY MODEL

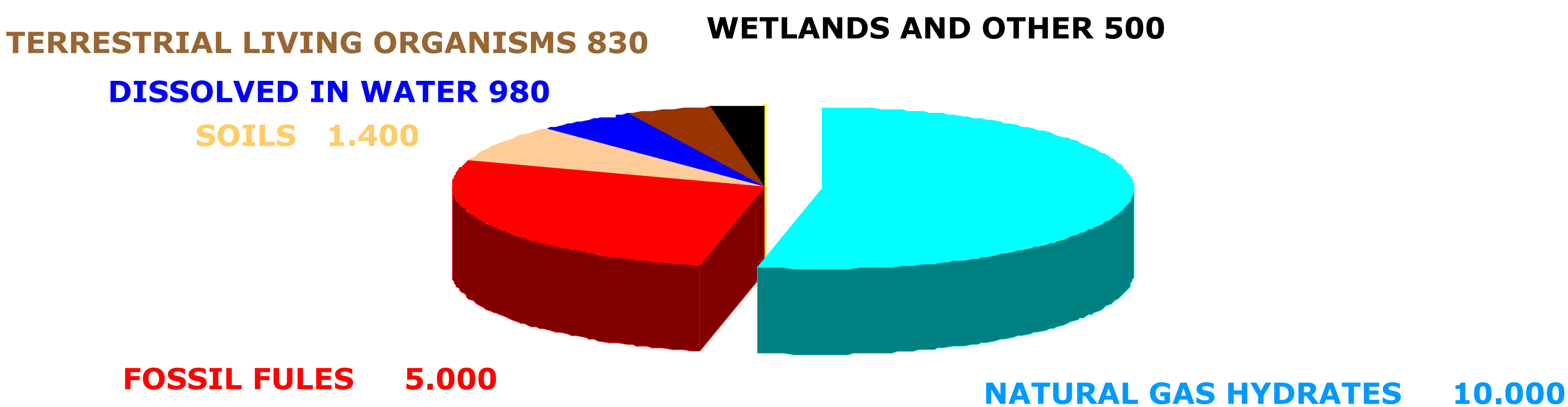
Biot-Geerstma-Smit equations

$$V_p = \left\{ \left[\left(\frac{1}{C_m} + \frac{4}{3}\mu \right) + \frac{\frac{\phi_{eff}}{k}\frac{\rho_m}{\rho_f} + \left(1 - \beta - 2 \cdot \frac{\phi_{eff}}{k}\right) \cdot (1-\beta)}{(1 - \phi_{eff} - \beta) C_b + \phi_{eff} C_f} \right] \cdot \frac{1}{\rho_m \left(1 - \frac{\phi_{eff}}{k}\frac{\rho_f}{\rho_m}\right)} \right\}^{1/2} \qquad (1)$$



GLOBAL ESTIMATES

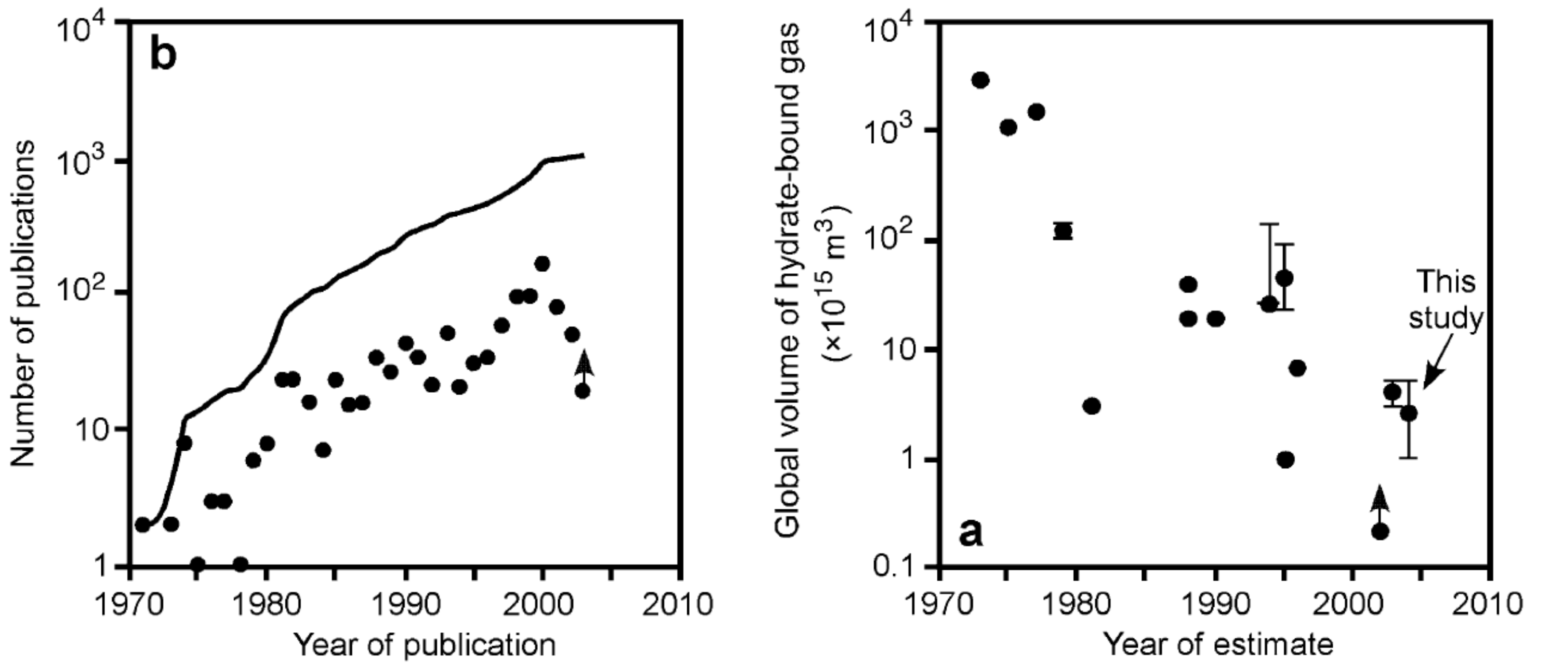
Estimation as amount of Carbon atoms · 10^{15} g



Kvenvolden, various sources

HOWEVER……..

Global estimates of the volume of hydrate-bound gas in marine sediments versus the year in which the estimate was made.

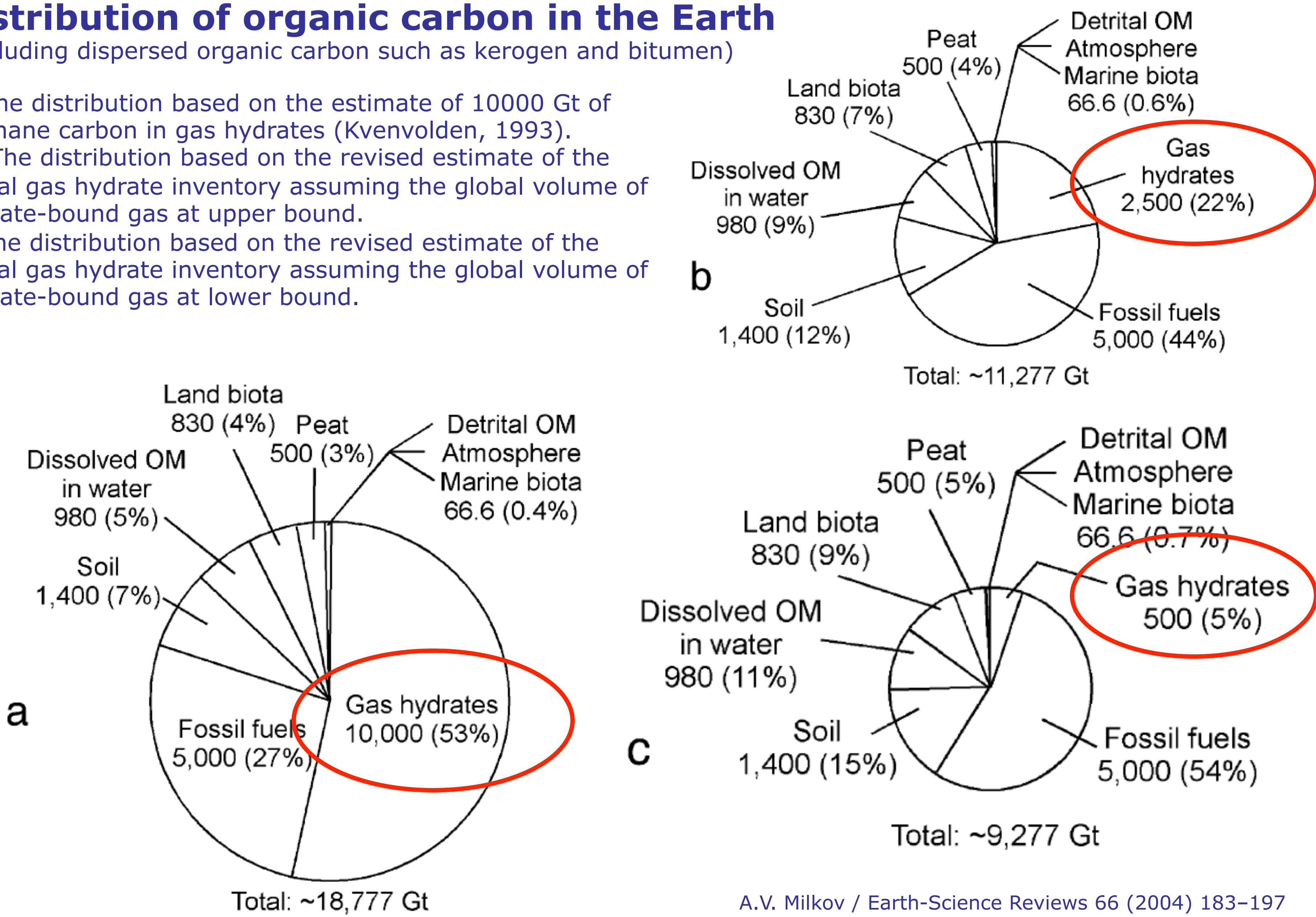


A.V. Milkov / Earth-Science Reviews 66 (2004) 183–197

Distribution of organic carbon in the Earth

(excluding dispersed organic carbon such as kerogen and bitumen)

a) The distribution based on the estimate of 10000 Gt of methane carbon in gas hydrates (Kvenvolden, 1993).
b) The distribution based on the revised estimate of the global gas hydrate inventory assuming the global volume of hydrate-bound gas at upper bound.
c) The distribution based on the revised estimate of the global gas hydrate inventory assuming the global volume of hydrate-bound gas at lower bound.



A.V. Milkov / Earth-Science Reviews 66 (2004) 183–197

In spite of changing global hydrates estimates…….

- Methane is the cleanest fossil fuel:

$$CH_4 + 2O_2 \longrightarrow 2H_2O + CO_2 + heat$$

- Methane is presently the preferred fossil fuel for power generation in OECD countries,

- Methane demand is increasing also in other regions such as the Middle East, China and India

- Despite current high prices, the vast majority of new power generation on line in the review period will be gas-fired.

Methane Hydrates are considered as NON CONVENTIONAL HYDROCARBONS by most oil companies

- There is not an established extraction technology .

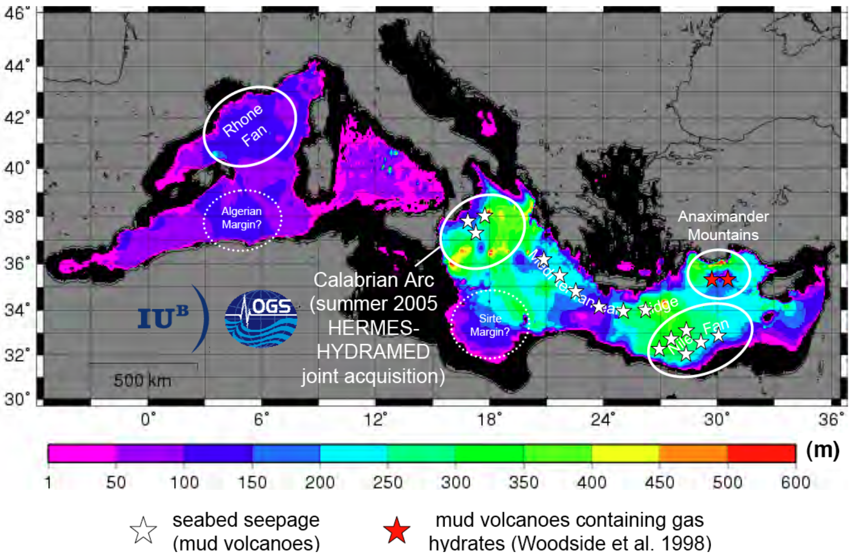
- The hydrates must be dissociated in situ by:
  - Heat injection
  - Injection of chemical inhibitors
  - depressurization
  -
- There are severe environmental implications and the methods will not be considered as economically feasible until the gas price will rise considerably.

- **USA, Japan, India, Korea** and other countries of the Pacific Area have started National Plans for the gas hydrates assessment in their Economic Exclusive Zones.

What Happens in Europe?

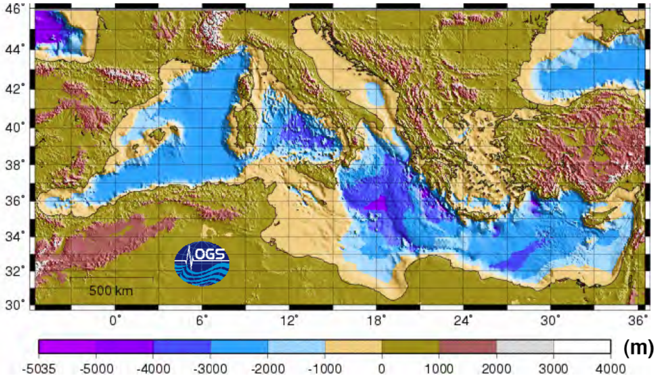
- No policy has been established so far
- Several EC projects have been dedicated to the matter from a purely scientific point of view (see next part of this talk)
- Oil companies and academia have focussed don this issue regarding the implications for submarine slope stability (see next part of this talk)
- **Regional evaluations of gas hydrate potential** of European Margins are in due course:
    - Atlantic European Margins
    - Mediterranean
    - Black Sea

HYDRATES PROSPECTIVIY in the Mediterranean Sea

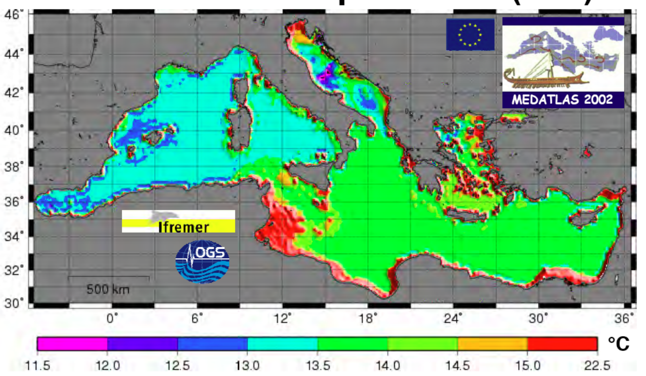


D. Praeg, V. Unnithan, and A. Camerlenghi, American Geohpysical Unions Fall Meeting, December 2006

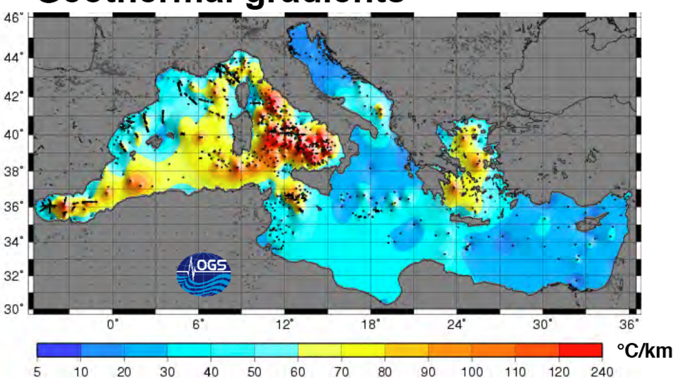
Bathymetry



Bottom water temperatures (bwt)



Geothermal gradients



Due to:

- High temperature of bottom water
- High salinity of pore water
- Presence of a salt seal (Messinian) preventing deep fluid migration

The thickness of the Gas Hydrates Stability Zone is reduced in the Mediterranean Sea with respect to world Oceans.

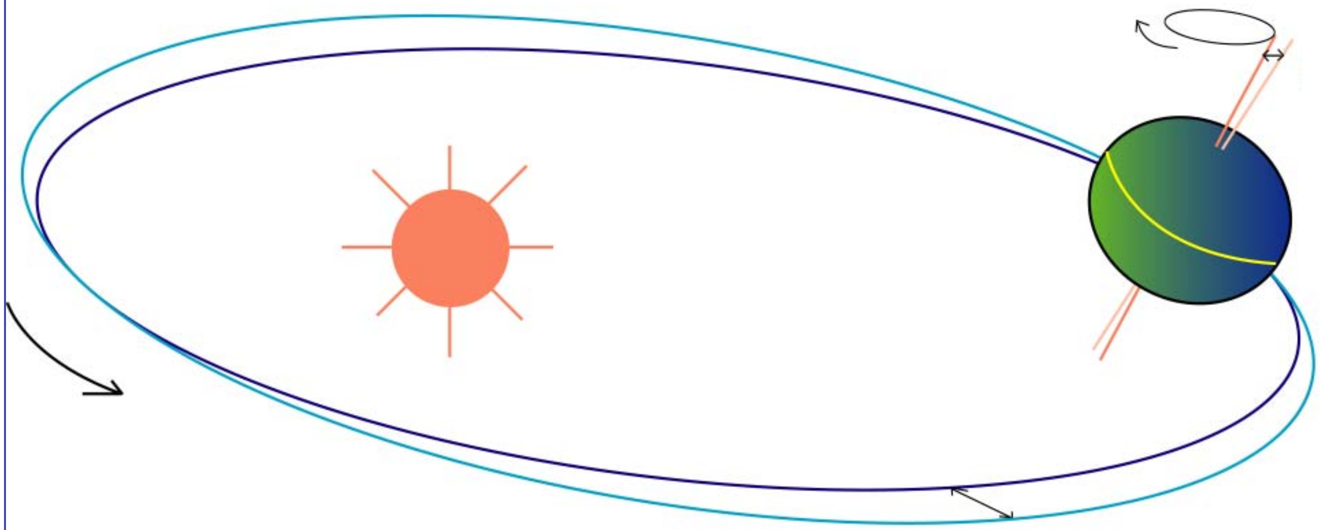
EU HYDRAMED Project. Praeg et al. in progress

MARIE CURIE ACTIONS

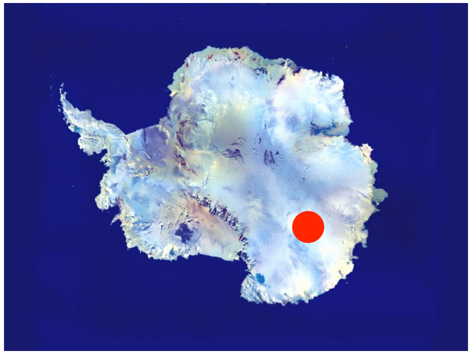
METHANE HYDRATES AND GLOBAL CLIMATE

MILANKOVITCH ORBITAL CYCLES

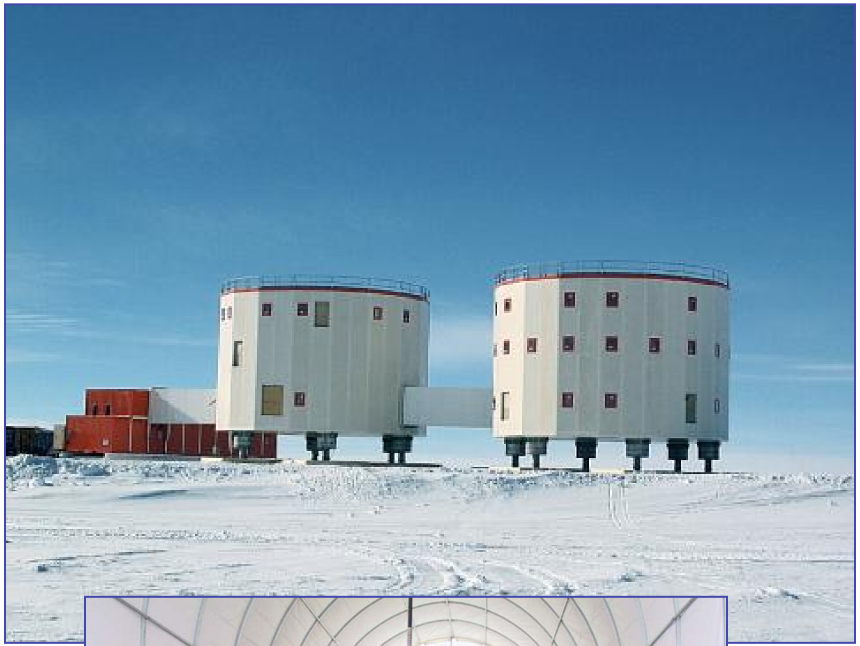
Frequencies of the main Earth orbital variations



The mean Solar radiation received by the earth changes through time. Such changes are the primary cause of glacial interglacial epochs and other climatic stages.

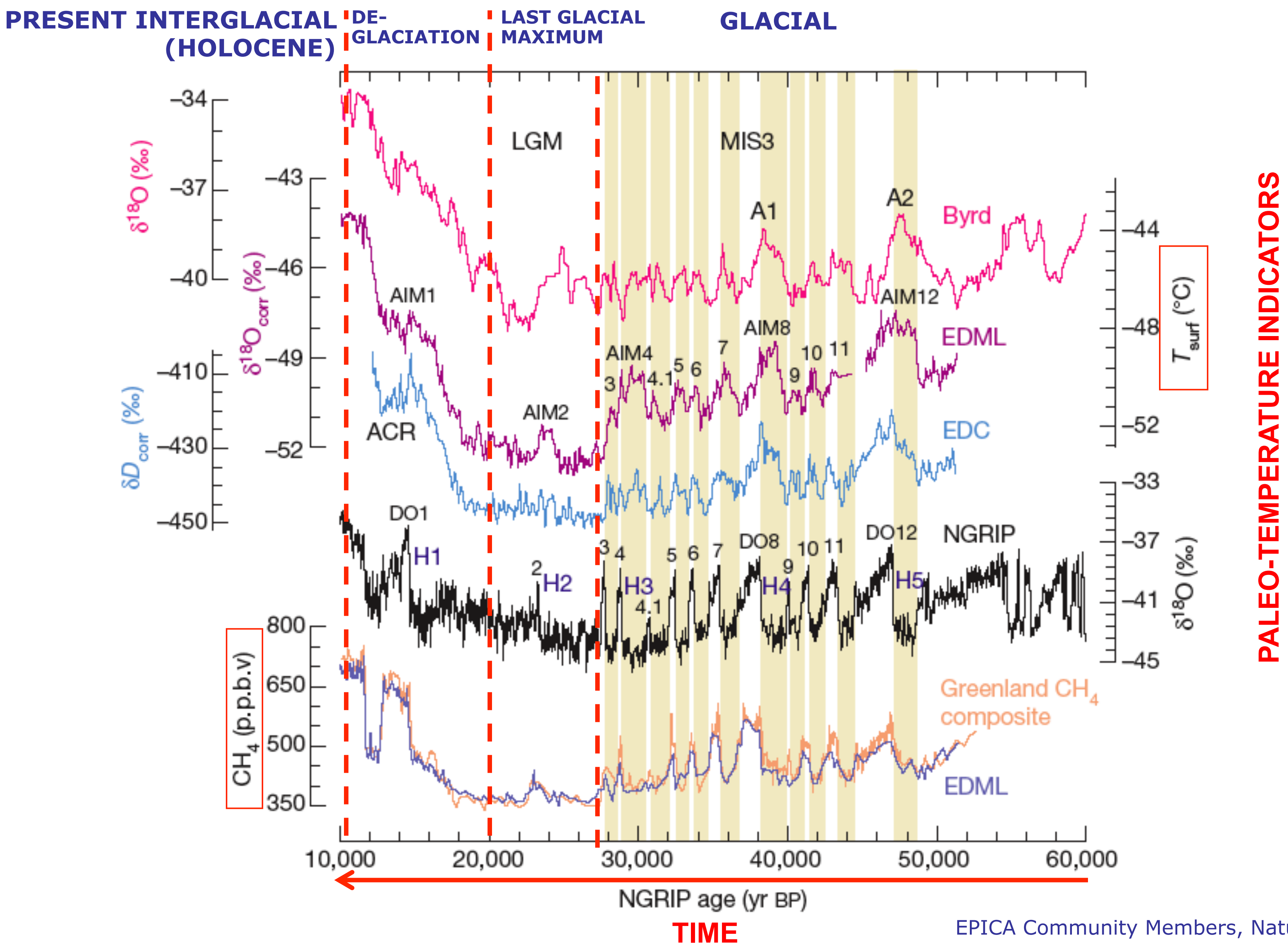


Dome-C Station, Antarctica



Programma Nazionale di Ricerche in Antartide (PNRA)

European Project for Ice Coring in Antarctica (EPICA)



EPICA Community Members, Nature, 2006

METHANE HYDRATES STORED IN PERMAFROST AND MARINE SEDIMENTS ARE HIGHLY SENSITIVE TO AMBIENT TEMPERATURE AD PRESSURE CHANGES

IN MARINE SEDIMENTS:

- WHEN OCEAN BOTTOM WATER TEMPERATURE RISES (DE-GLACIACION) SOME METHANE CHANGES FROM HYDRATE FORM TO GASE FORM AND ESCAPES FROM TEH SEAFLOOR INTO THE WATER COLUMN, AND FROM THERE TO THE ATMOSPHERE.
- HOWEVER, BECAUSE SEALEVEL CHANGES ACCORDING TO CLIMATIC CHANGES, THE INFLUENCE OF PRESSURE HAS TO BE TEKEN INTO ACCOUNT.

Anaerobic oxidation of methane (AOM) via sulfate reduction.

Microbial consortia of **methanotrophic archaea** and **sulfate-reducing bacteria** identified on gas hydrate-bearing samples (Boetius et al. 2000).

The archaea oxidize methane:

$\mathbf{CH_4} + 2H_2O >>> \mathbf{CO_2} + 4H_2$

And sulfate reducing bacteria may act in two ways, indicated by reactions:

$SO_4^{2-} + 4H_2 + H^+ >>> HS^- + 4H_2O$

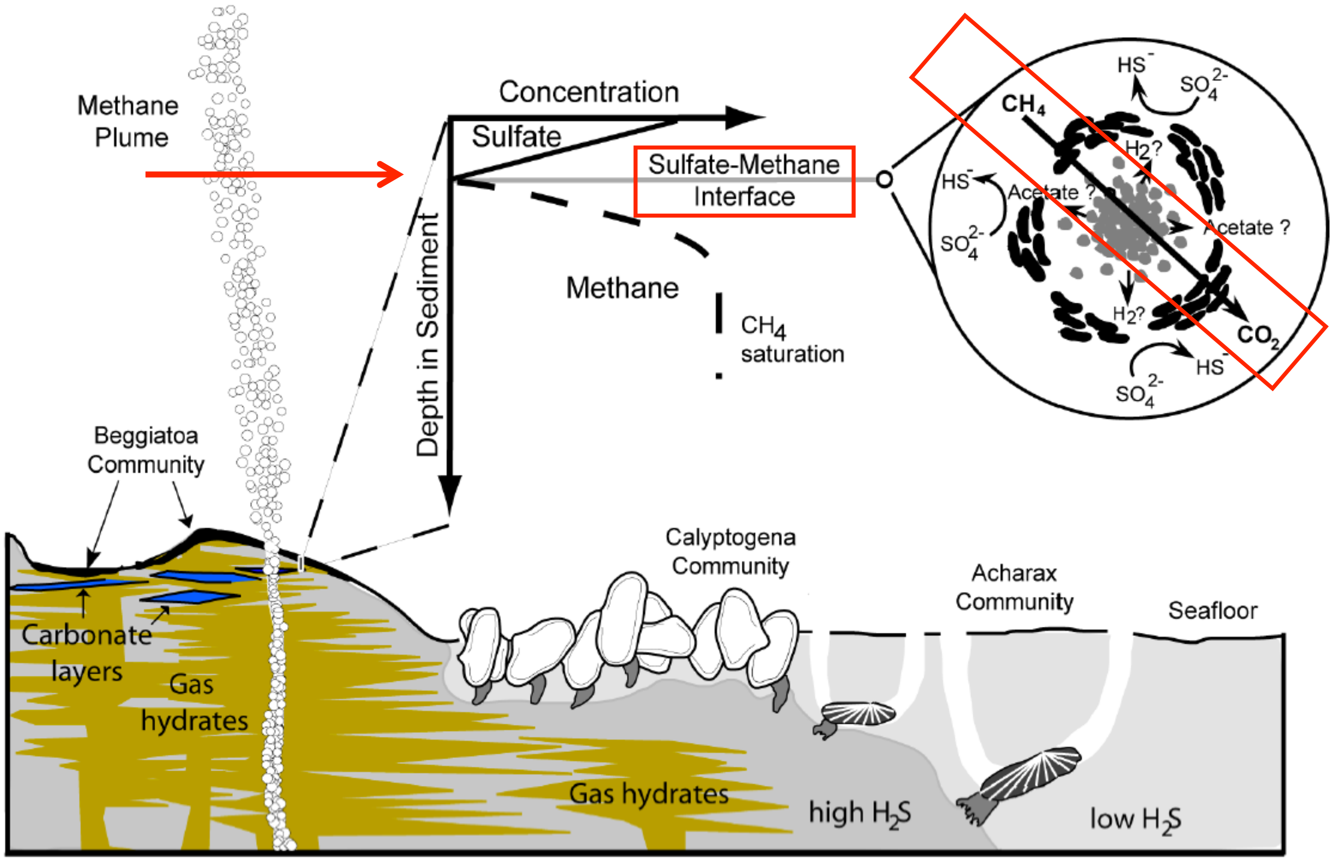
$SO_4^{2-} + CH_3COOH + 2H^+ >>> 2CO_2 + H_2S + 4H_2O$

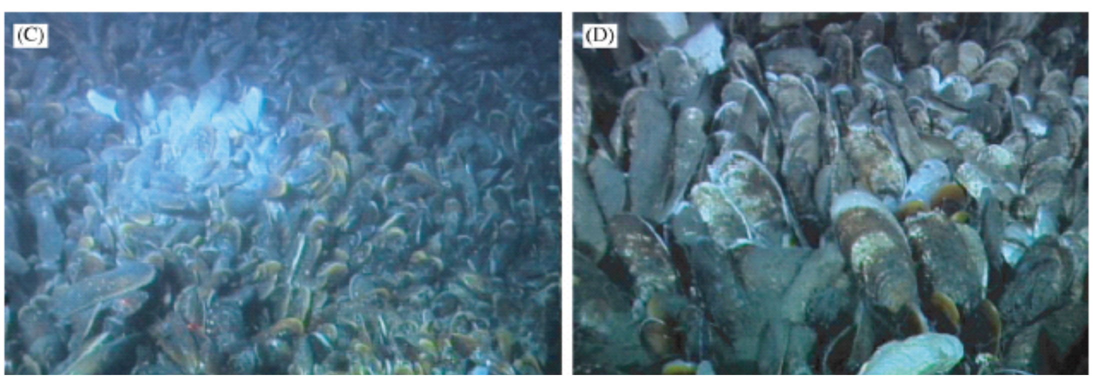
$\mathbf{CH_4} + SO_4^{2-} >>> \mathbf{HCO_3^-} + HS^- + H_2O$

Authigenic carbonate precipitation
Methane-derived Calcium Carbonate.

HCO3- + OH- + Ca2+ → CaCO3(*s*) + H20 + C02

HCO3- +	OH- +	Ca2+ →	CaCO3(*s*) + H20 + C02
Bicarbonate from bacterial action	alkaline seawater	calcium ions present in seawater	calcium carbonate deposited





Bathymodiolus heckerae mussel beds. (A) Juvenile and adult mussels at Marker 'E'. (B) Dead mussels and octopus. (C) Extensive bed of live mussels of relatively uniform size, partially covered by bacterial mats, at Marker 'B'. (D) Dead mussels at the eastward periphery of Marker 'B'. (E) Mussels with a chiridotid holothurian and Alvinocaris sp. (F) Mussels with Alvinocaris sp. And ophiuroids. Scale bars: A–D : 10 cm, E; F : 5 cm.

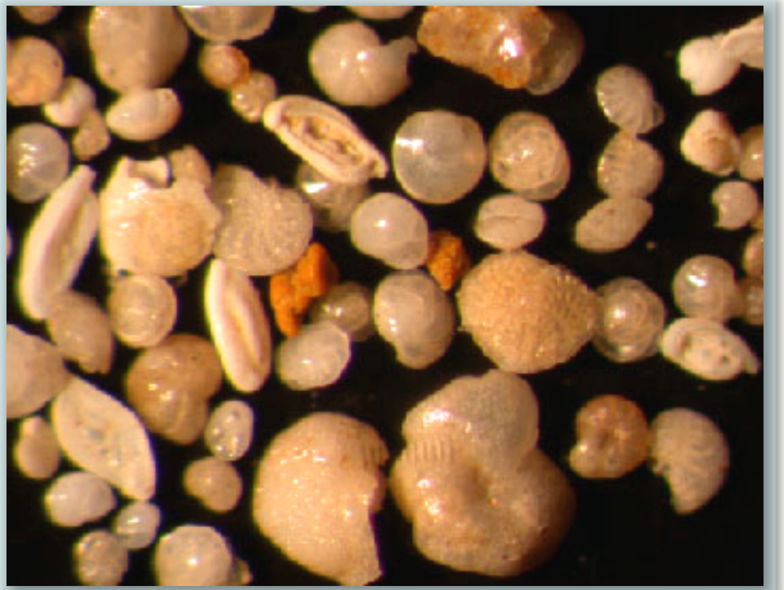
Van Dover et al. (2003). *Deep Sea Research*

FORAMINIFERA (Marine zooplankton)

- **Protists: Unicellular marine organisms**
- **They live in all marine environments**
- **They have existed since the Cambrian**
- **Size: from 0.01 to 5 mm (> 50 mm)**

Shell composition:

- Agglutinated
- Tectine
- **Calcium Carbonate ($CaCO_3$)**



- Foraminifera form their skeleton in **isotopic equilibrium** with ambient seawater
- The isotopic composition of the skeleton of benthic foraminifera reflects the **micro-habitat** where they live

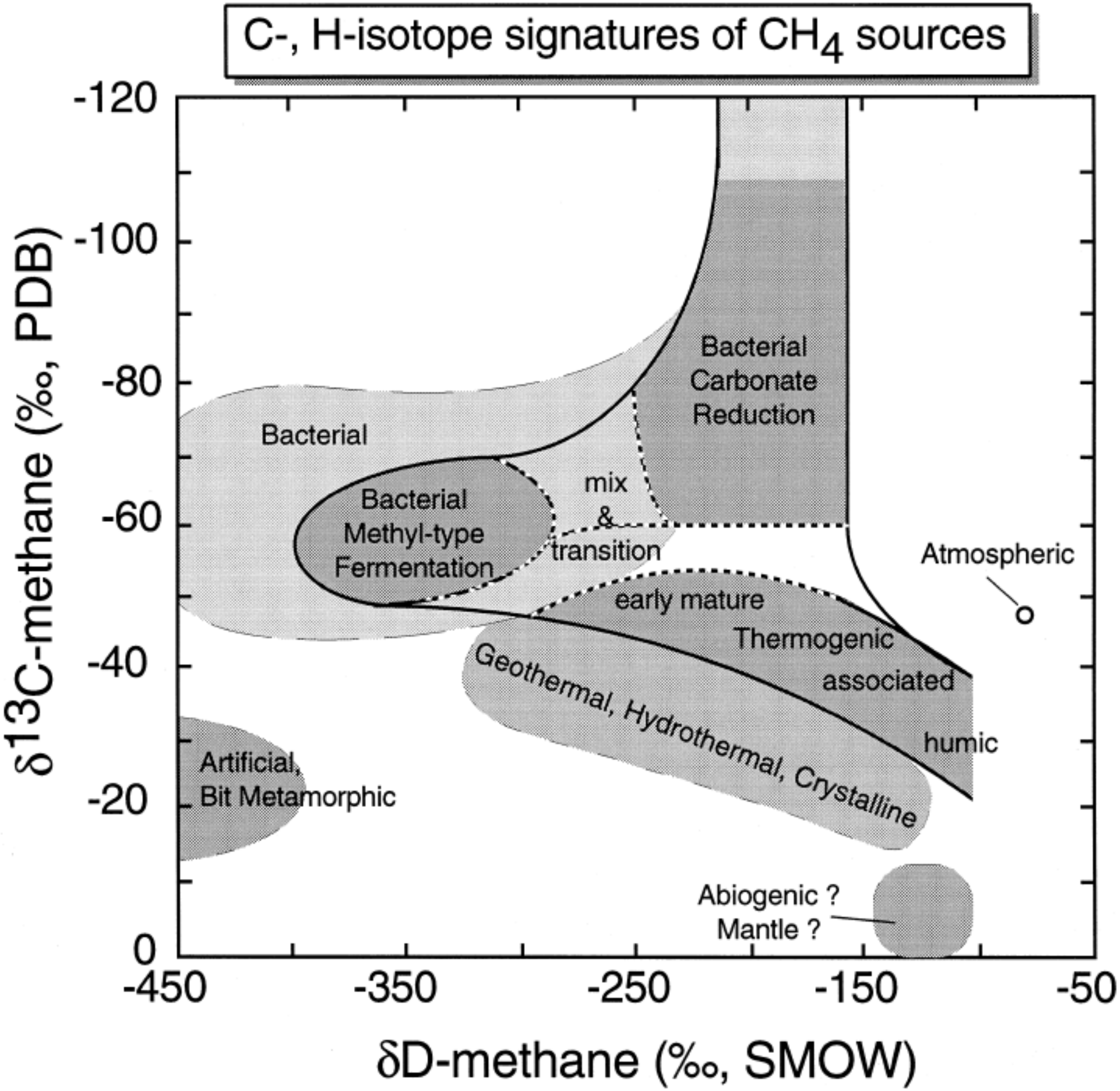
The $\delta^{13}C$ of foraminifera depends on the $\delta^{13}C$ of the Dissolved Inorganic Carbon (DIC) of the water in which they live:

Normal marine environment: $\delta^{13}C_{DIC} \cong 0‰$

(Peterson e Fry, 1987)

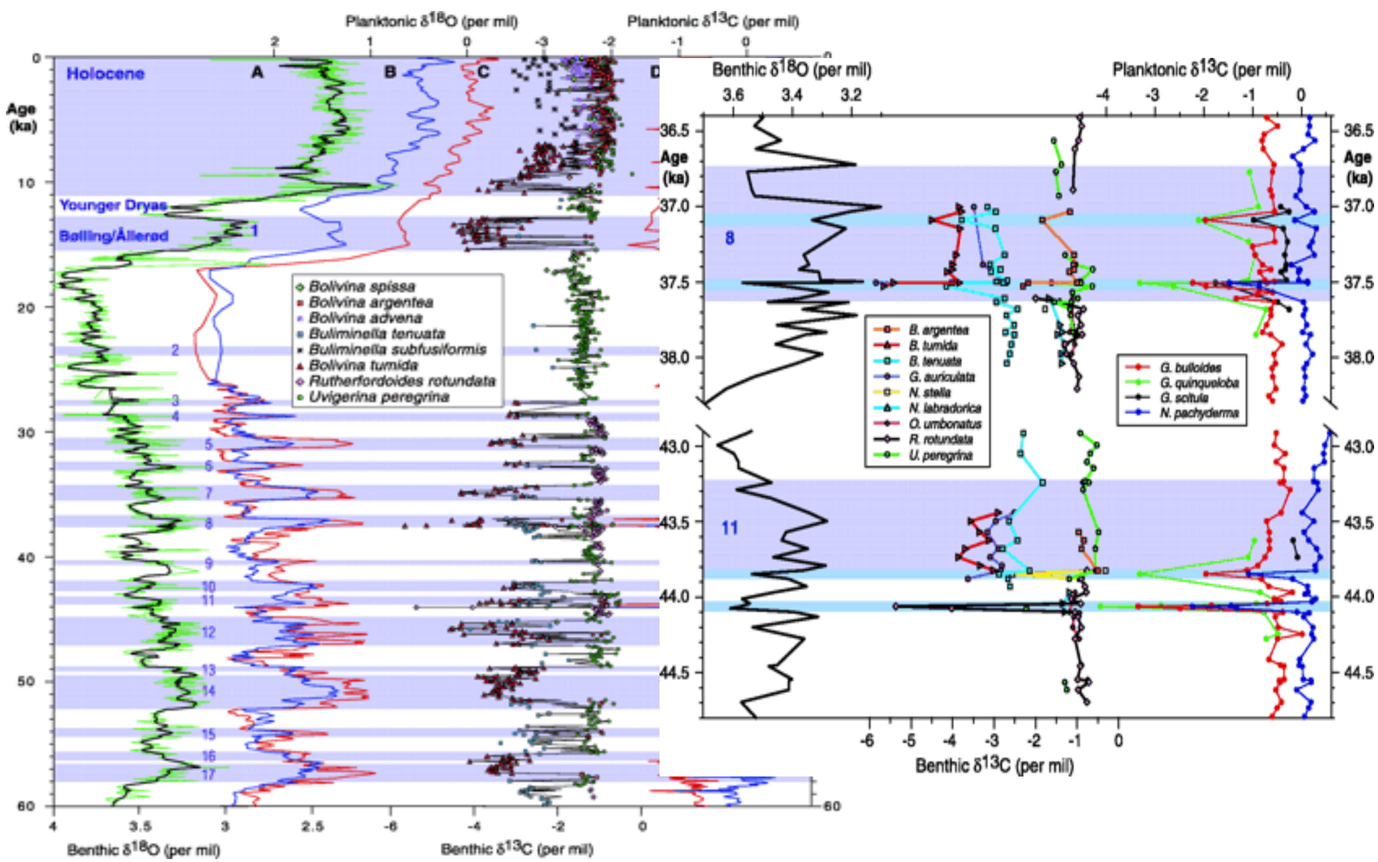
Methane seeps environment: $\delta^{13}C_{DIC} \cong -30/-60‰$

(Aharon *et al*., 1992)

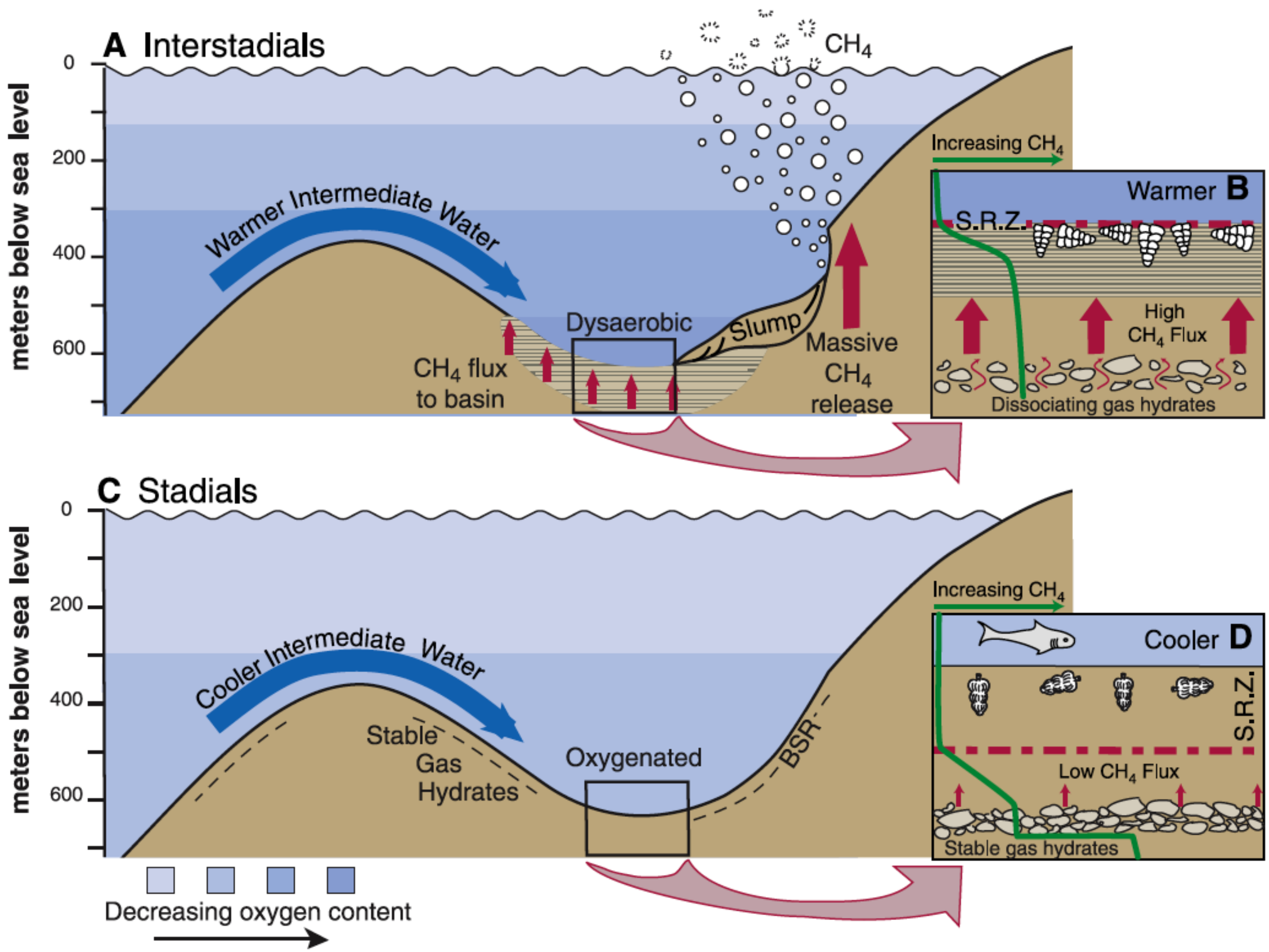


Whiticar 1999_ Marine Geology

Negative excursions of $\delta^{13}C$ in marine sediments during warm periods can be explained ONLY with massive emissions of Methane from the seafloor

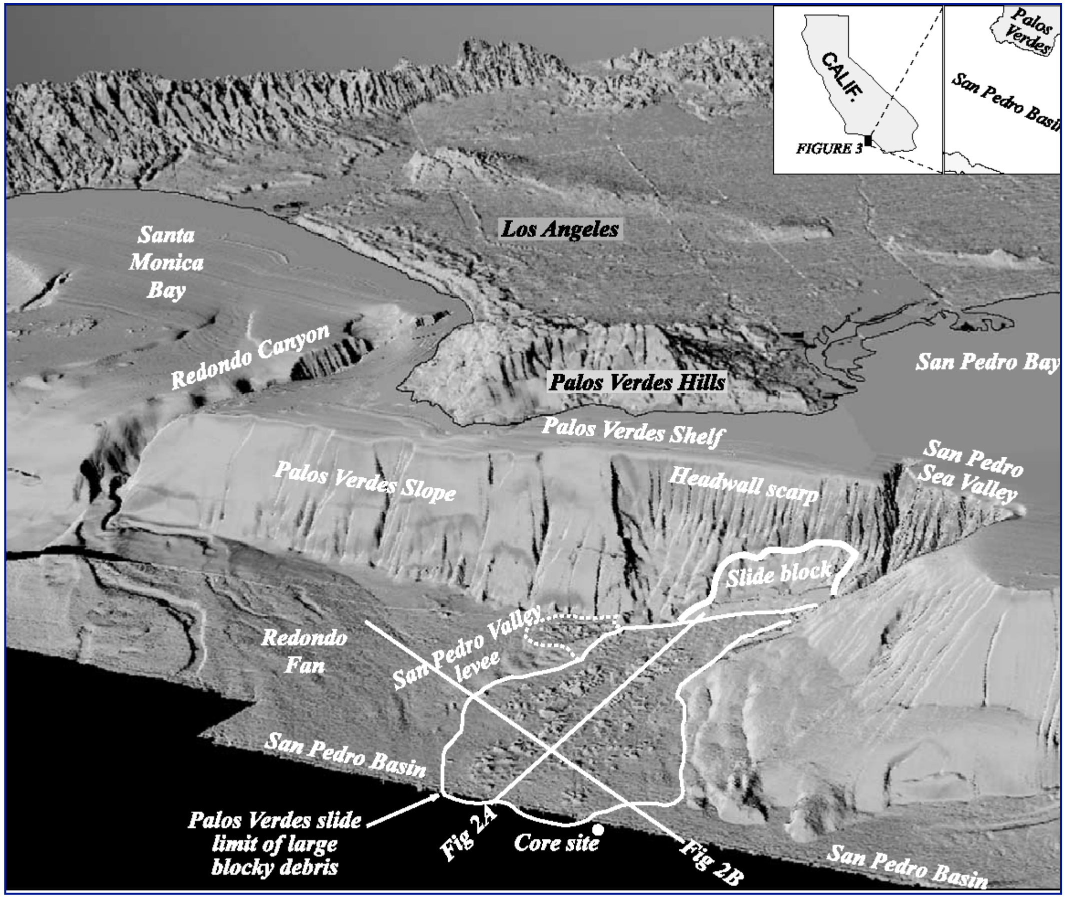


The Clathrate Gun Hypothesis



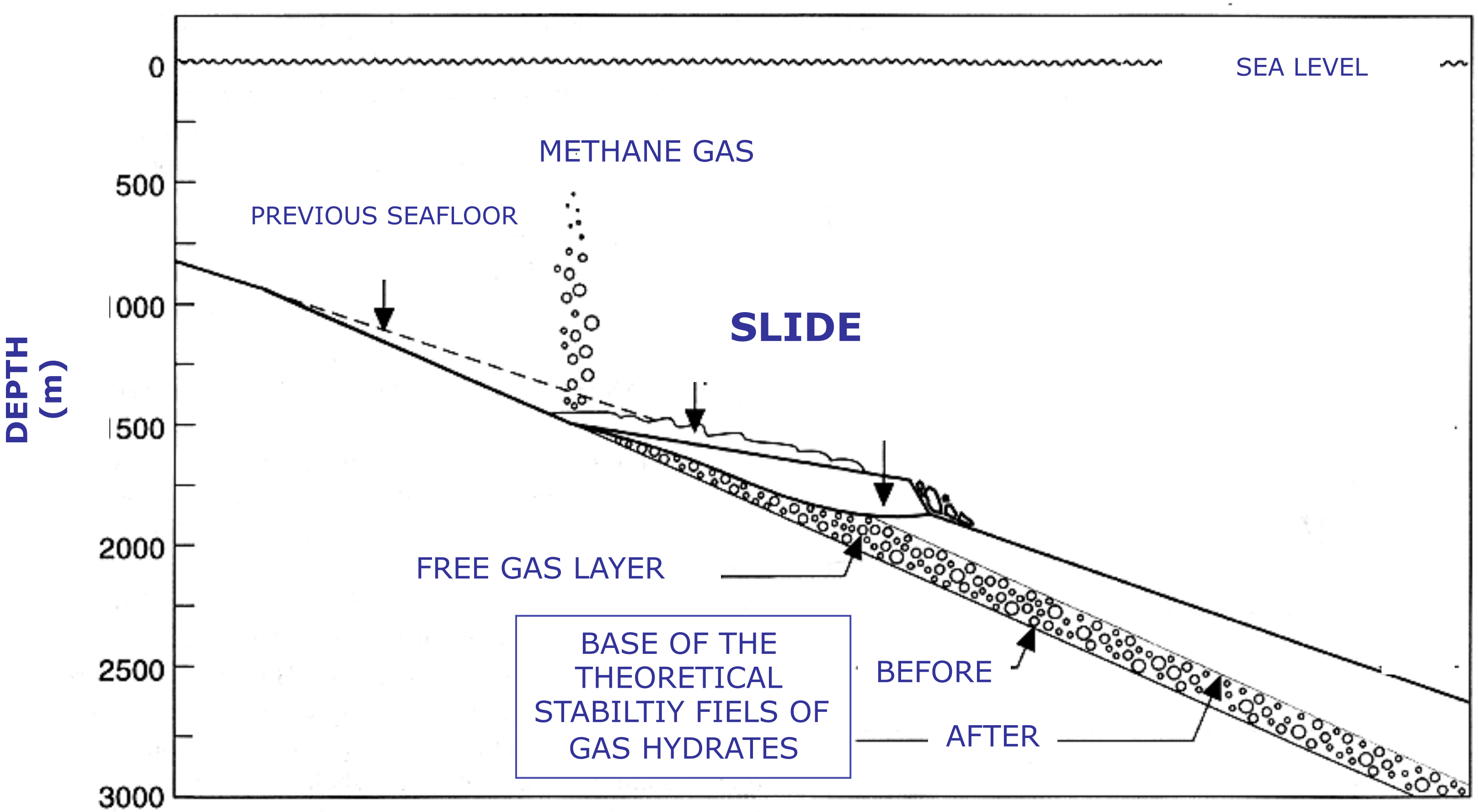
Kennett *et alii*, Science, 2000

Methane hydrate dissociation as source of submarine slope instability

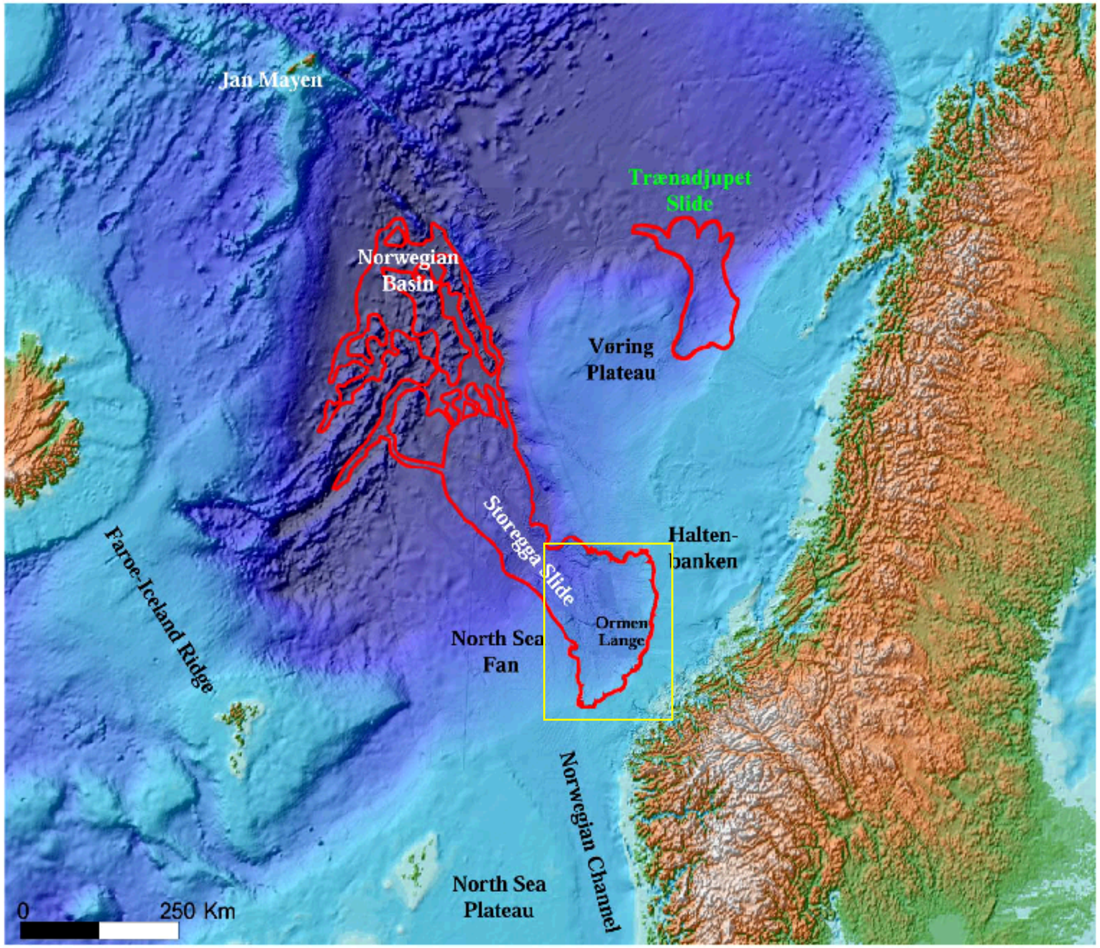


Normark et al. Marine Geology 203 (2004) 247-259

GLOBAL WARMING

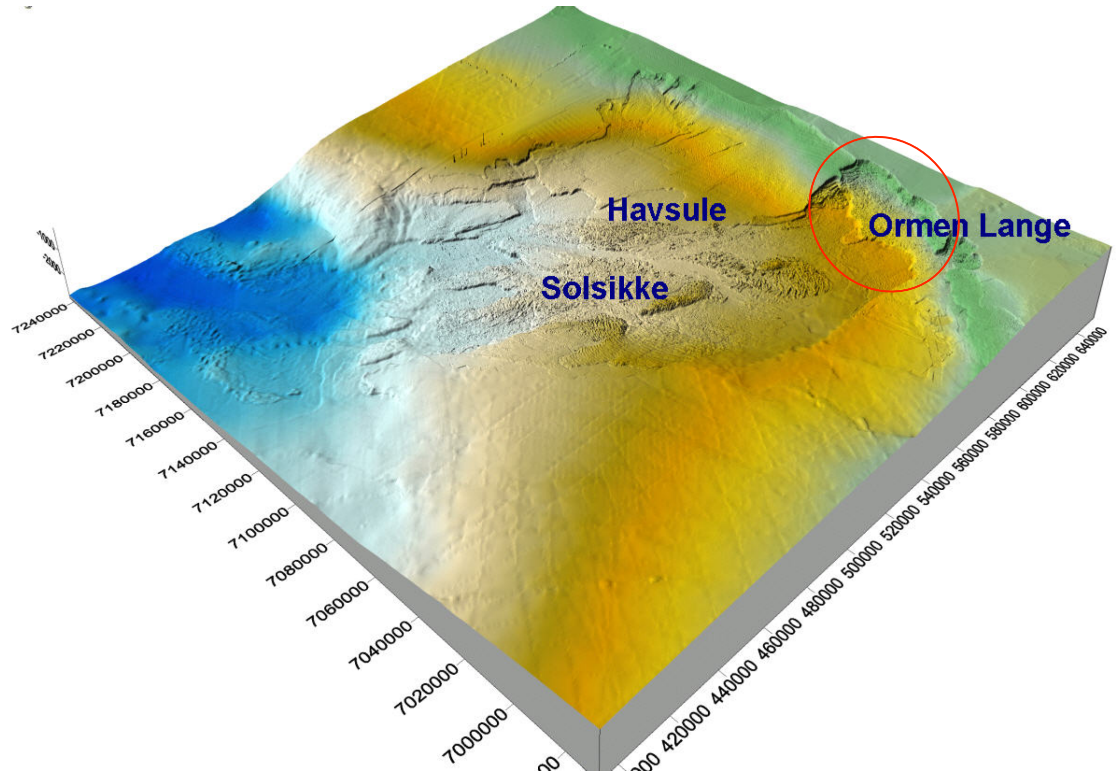


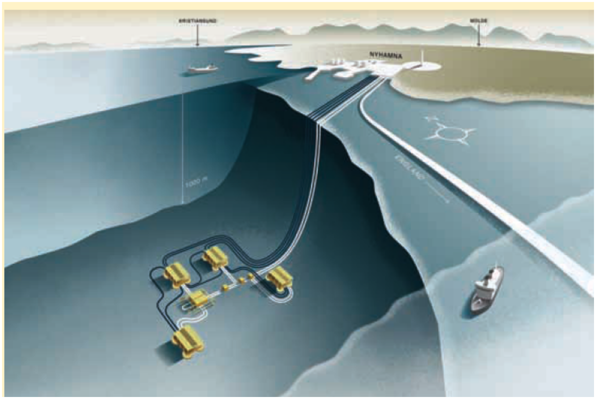
THE STOREGGA SLIDE ON THE NORWEGIAN CONTINENTAL MARGIN(7000 yr)



Norsk Hydro
E&D Norway
Geophysical Operations

Courtesy Petter Bryn





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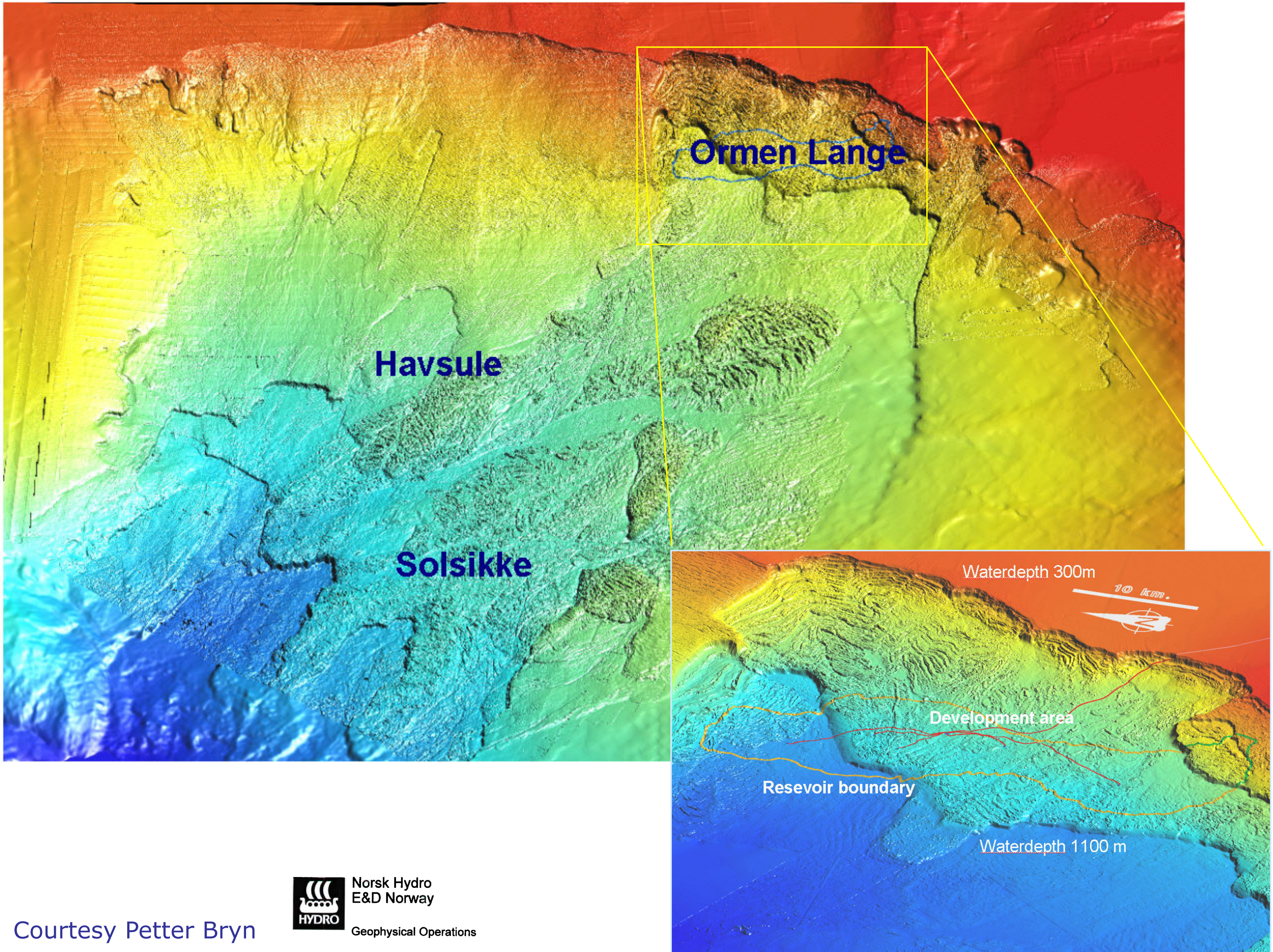

Norsk Hydro
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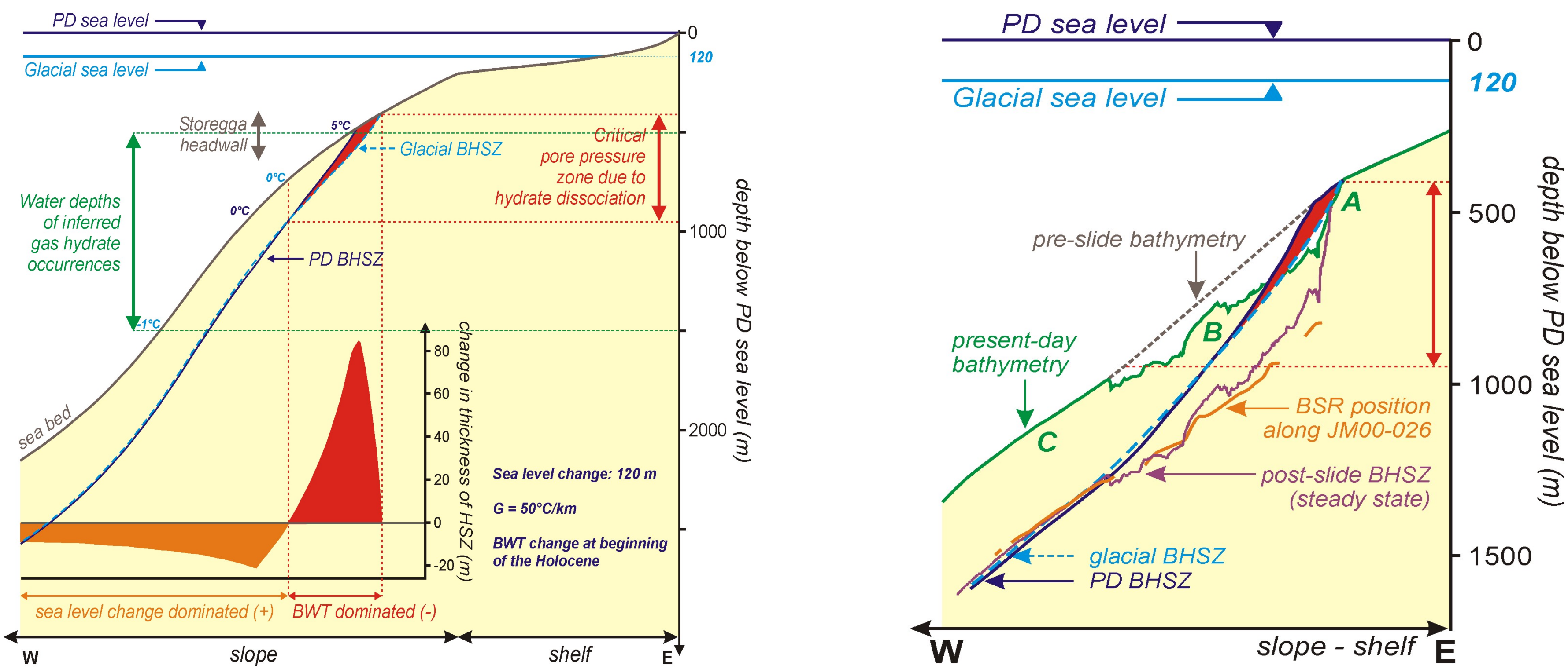
Courtesy Petter Bryn

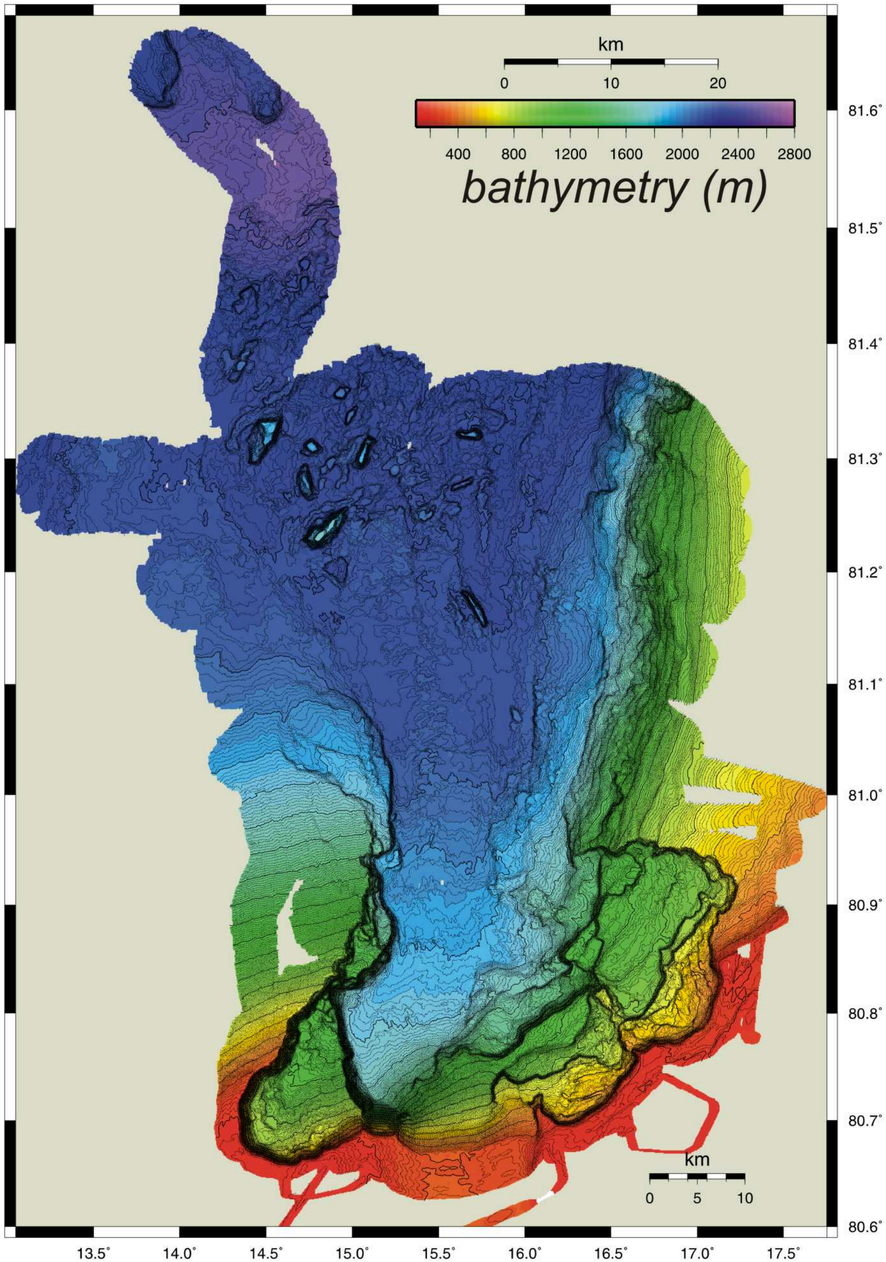
THE STOREGGA SLIDE CAUSED A HUGE TSUNAMI

The effect of gas hydrates

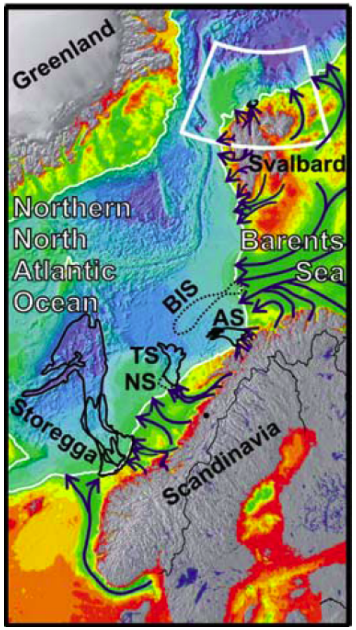


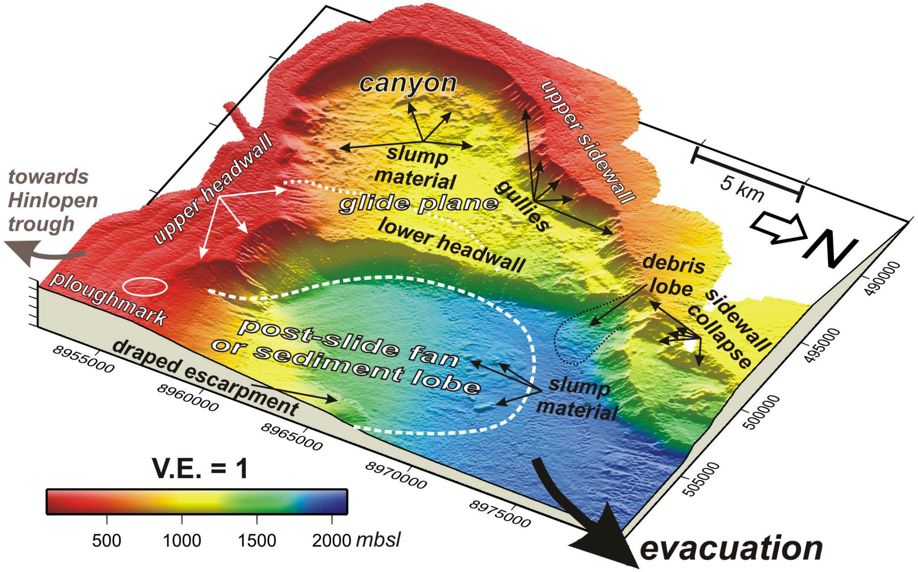
Mienert et al., 2005

Change in theoretical thickness of hydrate stability zone due to sea level change (small, negative) and bottom water temperature (locally large, positive). Biggest effect near upper headwall in Storegga.



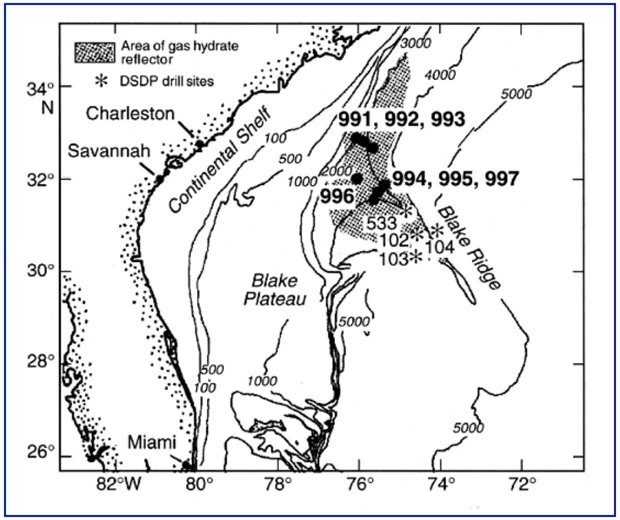
THE NORTH SVALBARD SLIDE

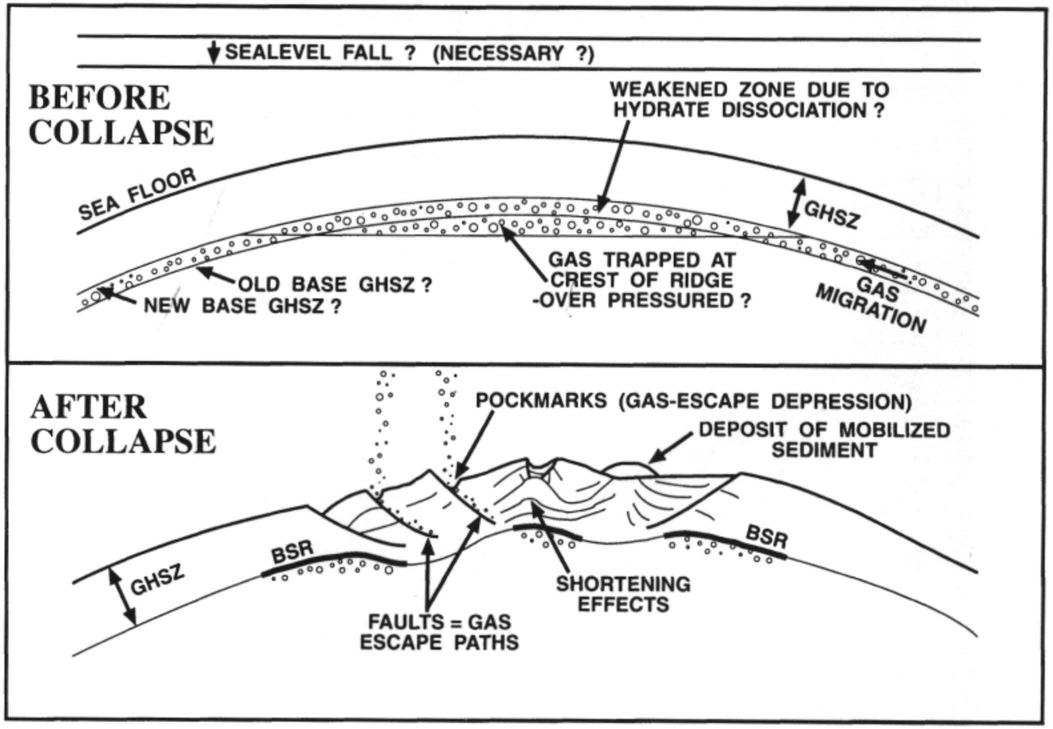


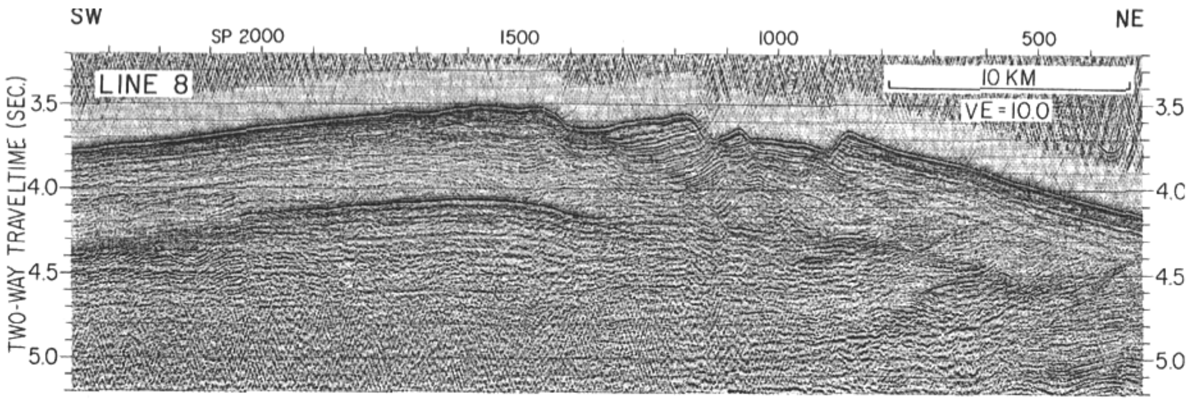


Vanneste et al., EPSL, 2006

BLAKE RIDGE

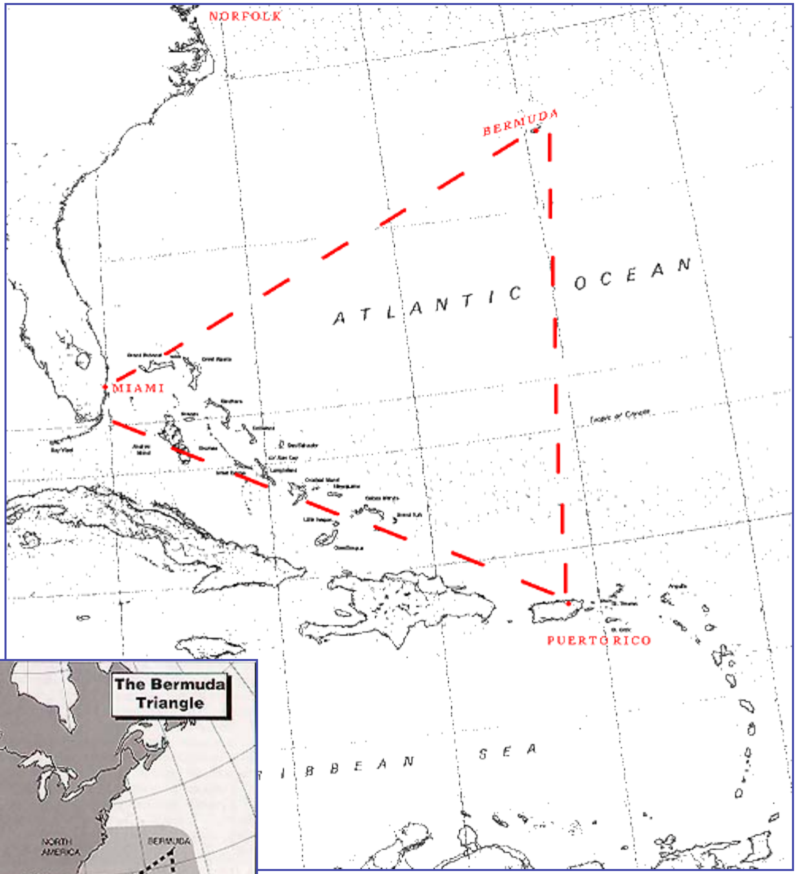


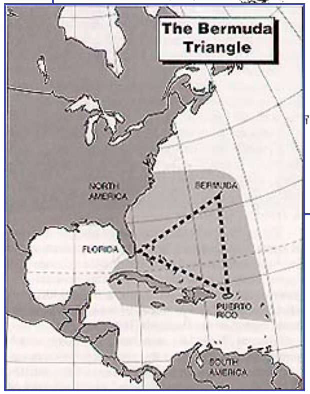


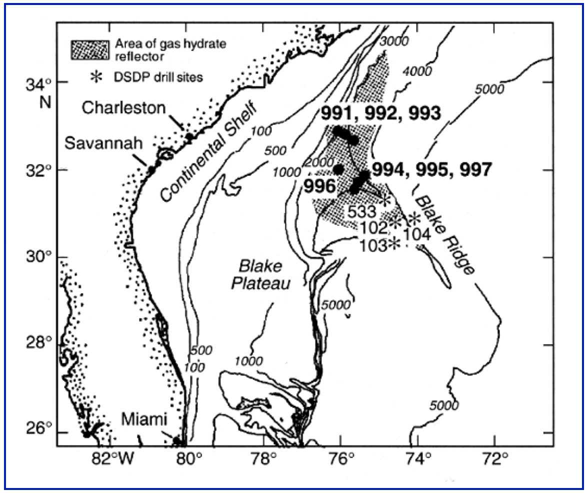


(Dillon et al., 1998)

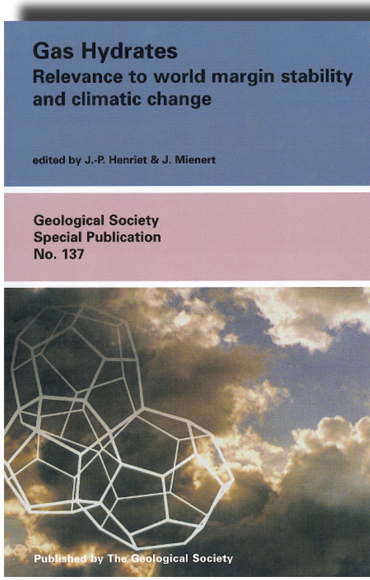
AT THE EDGE OF SCIENCE



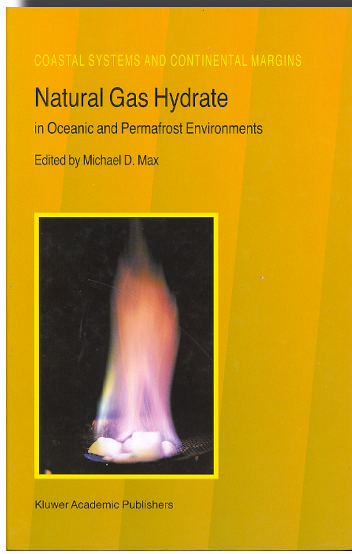




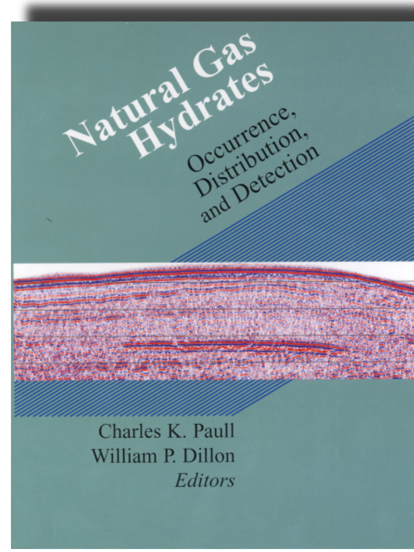
4 scientific books



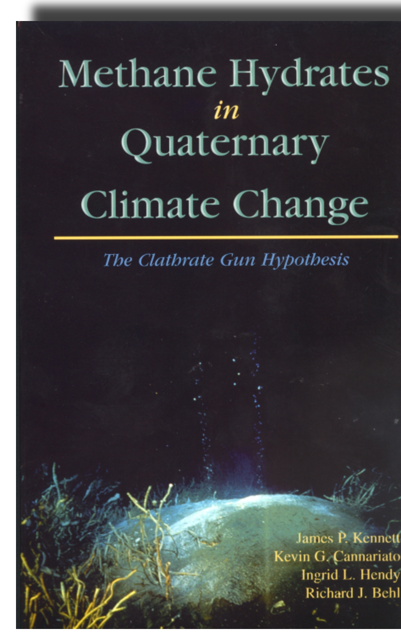
1998



2000



2001



2003

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